

Theoretical and experimental studies of electronic structure, magnetic, and hyperfine interaction properties of novel compounds

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Abstract

This thesis consists of the results of theoretical and experimental studies on the electronic structure, magnetic properties and hyperfine-interaction parameters of five compounds. The theoretical studies are based on *ab-initio* calculations, and the experimental studies are based on Mössbauer spectroscopy, magnetic measurements, and X-ray powder diffraction measurements. The calculated hyperfine-interaction parameters are shown to be in good agreement with the corresponding experimental parameters for all studied compounds.

$\text{Al}_{13}\text{Fe}_4$ crystallizes in the monoclinic space group $C2/m$, in which Fe atoms are located at five inequivalent crystallographic sites. It is shown that the zero-field Mössbauer spectra can be decomposed into three quadrupole doublets. It is found that the shape of the Mössbauer spectrum measured in an external magnetic field can be accounted for with five component subspectra generated using the calculated EFG parameters at five inequivalent Fe sites. A pseudogap is observed in the density of states (DOS) in the vicinity of the Fermi level.

The recently discovered layered iron oxyselenide $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$ is confirmed to be a Mott insulator. It is demonstrated that $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$ orders antiferromagnetically. The Debye temperature of $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$ is found to be 274(3) K.

The Fe_2NiGa compound crystallizes in the cubic space group $F\bar{4}3m$ and is predicted to be half-metallic with covalent chemical bonding. It orders ferromagnetically. The saturation magnetization per formula unit and the estimated Fe magnetic moments at the A and B sites are given. It is observed that the magnetic properties of Fe_2NiGa are very strongly dependent on their heat treatment.

The presence of a mixture of strong covalent and weak ionic chemical bonding and of metallic characteristics for the $(\text{Li}_{0.8}\text{Fe}_{0.2})\text{OHFeSe}$ superconductor is shown. The Mössbauer spectra consist of two quadrupole-doublet patterns. It is demonstrated that there is no magnetic ordering of the $2a$ -site Fe magnetic moments down to 2.0 K.

The final compound is the $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ approximant. The existence of a pseudogap in the calculated electronic density of states slightly above the Fermi level suggests electronic stabilization according to the Hume-Rothery-type mechanism. High metallicity is predicted. Both the Mössbauer spectra and magnetic susceptibility data indicate that $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ is a paramagnet down to 2.0 K.

Statement of originality

To the best of his knowledge, the author states that the five projects on the compounds $\text{Al}_{13}\text{Fe}_4$, $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$, Fe_2NiGa , $(\text{Li}_{0.8}\text{Fe}_{0.2})\text{OHFeSe}$, and $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ described in this PhD thesis constitute original research in the field of condensed-matter physics. The author has performed all of the theoretical calculations on all five compounds and has participated in conducting the experimental measurements in this thesis. Except where acknowledged otherwise, the work in this thesis is of the author's own.

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Table of Contents

Abstract	ii
Statement of originality.....	iii
Acknowledgments.....	iv
List of Figures	xiii
List of Tables	xx
Chapter one	1
Introduction	1
1.1 Directions and main schemes of research in solid state physics	1
1.2 Proposed problems and motivations of research.....	2
1.3 Thesis Outline	5
1.4 List of Publications based on the thesis results	6
Chapter two	7
The theory of magnetism and superconductivity	7
2.1 Introduction.	7
2.2 Diamagnetism.....	9
2.2.1 The diamagnetic susceptibility	9
2.2.2 The diamagnetic susceptibility of atoms, ions, and molecules.....	9
2.3 Paramagnetism	11
2.3.1 Curie's law of paramagnetic susceptibility	11
2.3.1.1 The semi-classical approach	12
2.3.1.2 The quantum mechanical approach	14
2.3.2 The effects of the internal electromagnetic fields on the paramagnetic susceptibility of solids.....	17
2.3.3 Paramagnetic susceptibilities of molecules and nuclei.....	18
2.3.4 Paramagnetic saturation.....	19
2.4 Ferromagnetism.....	20
2.4.1 Introduction	20
2.4.2. The molecular field theory of ferromagnetism.....	20
2.4.2.1 The classical molecular field theory	21
2.4.2.1.1 Spontaneous magnetization region, $T < T_f$	21

2.4.2.1.2 The paramagnetic region	24
2.4.2.2 The quantum mechanical approach to ferromagnetism	25
2.4.2.2.1 The Heisenberg model(s) of ferromagnetism.....	25
2.4.2.2.2 Band model theories of ferromagnetism	28
2.4.2.2.2.1 Collective electron ferromagnetism; Stoner's theory	28
2.4.2.2.2.2 The theory of Vonsovsky and Zener	29
2.5 Antiferromagnetism	31
2.5.1 Introduction	31
2.5.2 The molecular field theory of antiferromagnetism.....	31
2.5.2.1 The paramagnetic region, $T > T_N$	32
2.5.2.2 At the Néel temperature, $T = T_N$	33
2.5.2.3 Susceptibility below the Néel temperature, $T < T_N$	33
2.5.2.4 The paramagnetic-antiferromagnetic transition in the presence of an applied magnetic field.....	34
2.5.3 The super-exchange interaction.....	35
2.6 Superconductivity.....	36
2.6.1 Introduction	36
2.6.2 The transition (critical) temperature	37
2.6.3 The magnetic properties of superconductors.....	37
2.6.3.1 Perfect diamagnetism in superconductors	37
2.6.3.2 The critical field in superconductors.....	37
References.....	40
Chapter three	43
Mössbauer spectroscopy and X-ray diffractometry	43
3.1 Mössbauer spectroscopy	43
3.1.1 Introduction	43
3.1.2 Hyperfine interactions	47
3.1.2.1 The Classical approach	47
3.1.2.2 The Quantum mechanical treatment	50
3.1.3 The Isomer Shift	51
3.1.4 Electric quadrupole interaction.....	53
3.1.5 The Electric Field Gradient (EFG)	53
3.1.6 The quadrupole splitting.....	54

3.1.7 Magnetic dipole interaction and magnetic splitting	55
3.1.8 The combined electric and magnetic interactions	57
3.2 Experimental setup in Mössbauer spectroscopy	57
3.2.1 Transmission Mössbauer spectrometer setup	57
3.2.2 Sample preparation	58
3.2.3 The Mössbauer set up	59
3.2.3.1 Low and High temperature spectrometers	59
3.2.3.2 The 90 kOe Mössbauer spectrometer	59
3.2.4 The Mössbauer spectrum.....	60
3.3 X-ray powder diffractometry	61
3.3.1 Crystal structures	61
3.3.1.1 Symmetries of Bravais lattices.....	61
3.3.1.2 The seven crystal systems.....	61
3.3.1.3 The fourteen Bravais lattices	62
3.3.1.4 The 230 space groups.....	64
3.3.2 X-ray diffraction	64
3.3.2.1. The Bragg formulation.....	64
3.3.2.2 The Von Laue formulation.....	65
3.3.2.3 Experimental methods for X-ray diffraction.....	65
3.3.3 The Rietveld refinement method	67
3.3.3.1 Data collection	67
3.3.3.2 Background determination.....	68
3.3.3.3 Peak shape.....	68
3.3.3.4 Peak width.....	68
3.3.3.5 Refinement of the structural parameters	68
References.....	69
Chapter four	70
Density functional theory and the LAPW methods; a basis for the theoretical calculations	70
4.1 Introduction	70
4.2 The quantum many body problem	70
4.2.1 The Born-Oppenheimer approximation.....	70
4.2.2 Density functional theory	71

4.2.2.1 The theorems of Hönenberg and Kohn	71
4.2.2.2 The Kohn-Sham equations.....	72
4.2.2.2.1 The exchange and correlation energies	72
4.2.2.2.2 The theorems of Kohn and Sham	73
4.2.2.2.3 The self-consistency problem.....	73
4.2.2.3 The exchange correlation functional.....	75
4.2.2.3.1 The local density approximation (LDA)	75
4.2.2.3.2 The generalized gradient approximation (GGA)	75
4.2.3 Solving the equations.....	76
4.2.3.1 Efficient basis sets.....	76
4.2.3.2 Biased basis set	76
4.3 The pseudopotential method	77
4.4 The Augmented plane wave (APW) method	78
4.5 The LAPW method	81
4.5.1 The regular LAPW method	81
4.5.2 LAPW with local orbitals (LAPW+LO)	82
4.6 The APW+lo method	83
4.6.1 The APW+lo basis set	83
4.6.2 Mixed LAPW/APW+lo basis sets	83
4.6.3 APW+lo with local orbitals (APW+lo+LO).....	84
4.7 Electronic density distributions	84
References	85
Chapter five	86
Studied alloys and compounds	86
5.1 Al ₁₃ Fe ₄	86
5.1.1 Introduction	86
5.1.2 General considerations and structural parameters	87
5.1.3 Theoretical calculations and results.....	88
5.1.3.1 Theoretical methodology	88
5.1.3.2 Theoretical results.....	88
5.1.3.2.1 Density of states	88
5.1.3.2.2 Electronic band structure.....	89

5.1.3.2.3 Electric field gradient	89
5.1.4 Experimental methods and results	90
5.1.4.1 Sample preparation	90
5.1.4.2 X-ray diffraction measurements	90
5.1.4.3 Magnetic measurements.....	91
5.1.4.3.1 Magnetization curves	91
5.1.4.3.2 Magnetic susceptibility	92
5.1.4.4 Mössbauer spectroscopy	93
5.1.4.4.1 Experimental set up	93
5.1.4.4.2 Mössbauer spectroscopy	94
5.1.5 Summary and conclusions	100
5.2 Na ₂ Fe ₂ Se ₂ O	101
5.2.1 Introduction	101
5.2.2 General considerations and structural parameters	101
5.2.3 Theoretical calculations and interpretations	102
5.2.3.1 Theoretical methodology	103
5.2.3.2 Theoretical results.....	103
5.2.3.2.1 Electronic charge density distribution.....	103
5.2.3.2.2 The nonmagnetic and magnetic states.....	104
5.2.3.2.2.1 The electronic density of states	104
5.2.3.2.2.2 The electronic band structure	107
5.2.3.2.2.3 Magnetic orderings	109
5.2.3.2.3 The hyperfine interaction parameters.....	110
5.2.3.2.3.1 The isomer shift calculations.....	111
5.2.3.2.3.2 The calculated magnetic dipole moments	111
5.2.3.2.3.3 The hyperfine magnetic field.....	111
5.2.3.2.3.4 The calculated electric field gradient tensor.....	111
5.2.4 The experimental measurements and results	112
5.2.4.1 Mössbauer spectroscopy	112
5.2.4.1.1 Experimental set up for the Mössbauer measurements.....	112
5.2.4.1.2 The Mössbauer spectra and interpretations	113
5.2.4 Summary and conclusions	122

5.3 Fe ₂ NiGa.....	123
5.3.1 Introduction	123
5.3.2 General considerations and structural parameters	123
5.3.3 Theoretical calculations and interpretations	123
5.3.3.1 Theoretical methodology	124
5.3.3.2 Theoretical results.....	125
5.3.3.2.1 Charge density distribution	125
5.3.3.2.2 The nonmagnetic and ferromagnetic states.....	126
5.3.3.2.2.1 The electronic density of states	126
5.3.3.2.2.2 The electronic band structure	129
5.3.3.2.3 The calculated magnetic moments	130
5.3.3.2.4 The hyperfine interaction parameters.....	131
5.3.3.2.4.1 The isomer shift calculations.....	131
5.3.3.2.4.2 The calculated hyperfine magnetic field	131
5.3.3.2.5 The elastic parameters	131
5.3.4 The experimental measurements and results	133
5.3.4.1 Sample preparation	133
5.3.4.2 X-ray diffraction pattern	133
5.3.4.3 Mössbauer spectroscopy	134
5.3.4.3.1 Experimental set up for the Mössbauer measurements.....	134
5.3.4.3.2 Mössbauer spectra	134
5.3.4.3.3 The experimental values for the hyperfine interaction parameters	136
5.3.4.4 Magnetic measurements.....	140
5.3.4.4.1 measured magnetic moments	140
5.3.4.4.2 The magnetization curves.....	140
5.3.4.4.3 The magnetic susceptibility.....	141
5.3.5 Summary and conclusions	142
5.4 (Li _{0.8} Fe _{0.2})OHFeSe.....	143
5.4.1 Introduction and motivations.....	143
5.4.2 The structural parameters and general considerations.....	143
5.4.3 Theoretical calculations and interpretations	144
5.4.3.1 Theoretical methodology	144

5.4.3.2 Theoretical results	146
5.4.3.2.1 Charge density distribution	146
5.4.3.2.2 Density of states	147
5.4.3.2.3 Electronic band structure	148
5.4.3.2.4 The hyperfine-interaction parameters	150
5.4.3.2.4.1 Isomer shift calculations	150
5.4.3.2.4.2 Electric field gradient calculations	150
5.4.4 Experimental methods and results	151
5.4.4.1 X-ray diffraction measurements	151
5.4.4.2 Mössbauer spectroscopy	152
5.4.4.2.1 Experimental set up	152
5.4.4.2.2 Mössbauer spectra	152
5.4.4.2.3 Experimental values of the isomer shift and electric quadrupole splitting parameter	155
5.4.5 Comparison between experiment and theory	159
5.4.6 Summary and conclusions	160
5.5 $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$	161
5.5.1 Introduction and motivations	161
5.5.2 General considerations and structural parameters	161
5.5.3 Theoretical calculations and interpretations	163
5.5.3.1 Theoretical methodology	163
5.5.3.2 Theoretical results	164
5.5.3.2.1 Electronic density of states	164
5.5.3.2.2 Electronic band structure	165
5.5.3.2.3 Charge density distribution	166
5.5.3.2.4 The hyperfine interaction parameters	168
5.5.3.2.4.1 Isomer shift calculations	168
5.5.3.2.4.2 Electric field gradient calculations	168
5.5.4 Experimental methods and results	168
5.5.4.1 Sample preparation	169
5.5.4.2 X-ray diffraction measurements	169
5.5.4.3 Mössbauer spectroscopy	170
5.5.4.3.1 The experimental set up for Mössbauer measurements	170

5.5.4.3.2 The Mössbauer spectra and interpretations	170
5.5.4.3.3 Hyperfine interaction parameters; a comparison between theory and experiment.....	176
5.5.4.4 Magnetic measurements.....	176
5.5.4.4.1 Magnetization curves	178
5.5.4.4.2 Magnetic susceptibility	178
5.5.5 Summary and conclusions	181
References	182
Chapter six	191
Summary and Conclusions	191
Appendix	194
The WIEN2k code	194
A.1 Initialization.....	194
A.1.1 NN.....	194
A.1.2 SGROUP.....	195
A.1.3 SYMMETRY.....	195
A.1.4 LSTART	195
A.1.5 KGEN	197
A.1.6 DSTART.....	198
A.2 The SCF cycle	198
A.2.1 LAPW0	200
A.2.2 ORB	202
A.2.3 LAPW1	203
A.2.4 LAPWSO.....	205
A.2.5 LAPW2	207
A.2.6 LAPWDM.....	208
A.2.7 LCORE	209
A.2.8 MIXER	210
A.3 Access to the calculated quantities	211
References	212

List of Figures

Figure 2.1 χ versus T curves for Sm^{3+} and Eu^{3+} ions [17].	17
Figure 2.2 Saturation effects for the magnetization of gadolinium, iron, and chromium ions at low temperatures compared to the theoretical Brillouin functions [17].	19
Figure 2.3 Graphical method of determining the spontaneous magnetization at a temperature T , $M(T)$. Spontaneous magnetization in temperatures above and below the critical temperature, T_f , is given by the intersection of the straight lines and the Brillouin function [17].	22
Figure 2.4 The spontaneous magnetization as a function of temperature. The solid lines are obtained from theory, while the points represent experimental data [22].	23
Figure 2.5 Spontaneous magnetization near absolute zero. The power 3/2 law fits better than the power 2 law predicted from Weiss theory [17].	24
Figure 2.6 The reciprocal of the susceptibility in terms of temperature above the ferromagnetic ordering point, T_f . θ is the paramagnetic Curie point. For temperatures a few degrees above the ordering temperature, the Curie-Weiss law of paramagnetism is realized [17].	25
Figure 2.7 Schematic variation of the exchange integral as a function of the interatomic distance, r_{ab} .	27
Figure 2.8 The magnetization and reciprocal of the susceptibility as a function of temperature calculated from the theory of collective electron ferromagnetism [17].	29
Figure 2.9 The Vonsovsky-Zener model.	30
Figure 2.10 Plot of $\frac{1}{\chi}$ versus temperature. Curve (1), $\chi = \frac{C}{T-\theta}$ (Curie-Weiss law); curve (2), $\chi = \frac{C}{T}$ (Curie's law), and curve (3), $\chi = \frac{C}{T+\theta}$ [17].	33
Figure 2.11 The susceptibility of an antiferromagnetic material as a function of temperature in reduced units [34].	34
Figure 2.12 The super-exchange interaction in MnO [17].	35
Figure 2.13 The nearest neighbor interaction in MnO [17].	36
Figure 2.14 (a) The phase boundary diagram in type I superconductors [40]. (b) Magnetization in terms of applied magnetic field for type I and type II superconductors [39].	38
Figure 3.1 Nuclear resonant absorption and emission of gamma radiation known as the Mössbauer effect [1].	43
Figure 3.2 The natural linewidth of the nuclear gamma transition energy between the excited state and ground state [1].	44

Figure 3.3 The electric monopole interaction between the nuclear charge and the electron density at the nucleus. This interaction results in the shift of the nuclear state energy levels [1].	51
Figure 3.4 Quadrupole splitting of the $^{57}\text{Fe} \left I = 3/2, m_{3/2} \right\rangle$ state and the related Mössbauer spectrum [1].	55
Figure 3.5 Magnetic dipole interaction splitting in ^{57}Fe and the resultant spectrum [1].	56
Figure 3.6 The experimental set-up of transmission Mössbauer spectroscopy [15].	58
Figure 3.7 A schematic view of the low temperature Mössbauer spectrometer [14].	59
Figure 3.8 The Michelson interferometer geometry used in the 90 kOe Mössbauer spectrometer.	60
Figure 3.9 The seven crystal systems: (a) cubic, (b) tetragonal, (c) orthorhombic, (d) monoclinic, (e) triclinic, (f) trigonal, and (g) hexagonal.	62
Figure 3.10 The fourteen Bravais lattices	63
Figure 3.11 A Bragg reflection from a particular family of lattice planes, separated by a distance d .	64
Figure 3.12 The Laue condition [5].	65
Figure 3.13 The Ewald construction [5]	66
Figure 3.14 The X-ray powder diffraction pattern of copper [18].	67
Figure 4.1 The flow chart describing the self-consistent cycles in solving the Kohn-Sham Hamiltonian eigenvalue equation.	74
Figure 4.2 The partitioning of the unit cell into muffin-tin spheres and the interstitial region, for a case with two atoms. The center of the left atom is the center of the coordinate system [3].	79
Figure 4.3 Flowchart of the APW method [3].	80
Figure 5.1 The unit cell of $\text{Al}_{13}\text{Fe}_4$.	87
Figure 5.2 Total and atom resolved electronic density of states (DOS) of $\text{Al}_{13}\text{Fe}_4$.	89
Figure 5.3 The electronic band structure of $\text{Al}_{13}\text{Fe}_4$.	90
Figure 5.4 Powder X-ray diffraction pattern of $\text{Al}_{13}\text{Fe}_4$. 298 K. The experimental data are denoted by open circles while the line through the circles represent the results of the Rietveld refinement. The row of vertical bars shows the Bragg peak positions for the $C2/m$ space group. The lower solid line represents the difference curve between the calculated and experimental patterns.	91
Figure 5.5 Magnetization (M) vs. external field (H) in various temperatures in intervals of (a) -90 to 90 kOe and (b) -4.5 to 4.5 kOe.	92
Figure 5.6 The temperature dependence of the magnetic susceptibility of $\text{Al}_{13}\text{Fe}_4$ in an external field of 10 kOe.	93

Figure 5.7 The room temperature (above) and the liquid-nitrogen temperature (below) of the ^{57}Fe Mössbauer spectra of $\text{Al}_{13}\text{Fe}_4$. fitted with three quadrupole doublets (dark grey, dark green, and dark red solid lines).	94
Figure 5.8 The ^{57}Fe Mössbauer spectrum of $\text{Al}_{13}\text{Fe}_4$. at 5.7 K (blue solid line) fitted with three quadrupole doublets (dark grey, dark green, and dark red solid lines). The zero-velocity origin is relative to the source at 5.7 K.	95
Figure 5.9 (a) ^{57}Fe Mössbauer spectrum of $\text{Al}_{13}\text{Fe}_4$. at 5.7 K and simulated spectrum (blue solid line) resulting from the superposition of quadrupole doublets due to the iron atoms at the Fe(1) site (pink solid line), Fe(2) site (dark blue solid line), Fe(3) site (green solid line), Fe(4) site (black short-dash line), and Fe(5) site (red short-dash line) (b) the same as in (a) but with Δ values increased by 14.0%.	96
Figure 5.10 The ^{57}Fe Mössbauer spectrum measured in an external magnetic field of 90 kOe at 5.7 K (red open circles) in comparison with the simulated spectrum (increased by 14%) resulting from the theoretical values of V_{zz} and η from table 5.1 (solid blue line). The simulated spectrum is a superposition of iron atom contributions from five inequivalent sites: Fe(1) (pink solid line), Fe(2) (dark blue solid line), Fe(3) (green solid line), Fe(4) (black short-dash line), and Fe(5) (red short-dash line).	97
Figure 5.11 ^{57}Fe Mössbauer spectra of $\text{Al}_{13}\text{Fe}_4$ in various temperatures fitted (the blue solid lines) with three quadrupole doublets (dark grey, dark green, and dark red solid lines).	98
Figure 5.12 Temperature dependence of the quadrupole splittings and the absorption spectral area A of $\text{Al}_{13}\text{Fe}_4$	99
Figure 5.13 (a) The unit cell of the $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$ compound. (b) The $\text{Fe}_2\text{Se}_2\text{O}$ block consisting of Fe-O square planar structure capped with two Se atoms.	102
Figure 5.14 Electron valence charge density distribution in (a) (001) plane and (b) (100) plane.	104
Figure 5.15 The atomic orbital-resolved partial density of states of $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$ in the nonmagnetic state.	105
Figure 5.16 atom- and orbital-resolved density of states of $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$ in the ferromagnetic state.	106
Figure 5.17 Total and atom-resolve density of states of $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$ in (a) the ferromagnetic state and (b) the nonmagnetic state.	107
Figure 5.18 Energy band structure of $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$ in various states: (a) spin up and (b) spin down ferromagnetic state, (c) nonmagnetic state, and (d) blocked checkerboard antiferromagnetic state.	108
Figure 5.19 In-plane arrangement of Fe magnetic moments for $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$ in the (a) ferromagnetic state, (b) striped antiferromagnetic state, (c) checkerboard antiferromagnetic state, and (d) blocked checkerboard antiferromagnetic state.	110

Figure 5.20	^{57}Fe Mössbauer spectrum of $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$ at 296.8 K fitted (black solid line) with an asymmetric quadrupole doublet (blue solid line) due to main phase, an asymmetric quadrupole doublet (dark green solid line) due to air-environment induced impurity, and a Zeeman pattern (pink solid line) originating from Fe impurity. The left inset shows the spectrum with an enlarged vertical scale and the right inset shows the spectrum measured at the magic angle, as described in the text. The zero-velocity origin is relative to α -Fe at room temperature.	113
Figure 5.21	^{57}Fe Mössbauer spectra of $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$ at the indicated temperatures fitted (black solid lines) with an asymmetric quadrupole doublet (blue solid line) due to main phase, and asymmetric quadrupole doublet (dark green solid lines) due to air-environment induced impurity, and a Zeeman pattern (pink solid line) originating from Fe impurity. The zero-velocity origin is relative to α -Fe at room temperature.	115
Figure 5.22	^{57}Fe Mössbauer spectra of $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$ at 5.8 K in zero and 90 kOe external magnetic field H_{ext} applied parallel to the direction of the γ -rays. The $H_{\text{ext}} = 0$ kOe spectrum is fitted (blue solid line) to a Zeeman pattern. The inset shows a $H_{\text{ext}} = 90.0$ kOe simulated spectrum. The zero-velocity origin is relative to the source. ...	116
Figure 5.23	The ^{57}Fe Mössbauer spectra of $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$ at the indicated temperatures fitted (black solid lines) with a Zeeman pattern. The spectra at 72.2, 73.2, and 74.4 K are fitted with three components – a Zeeman pattern (blue solid lines) due to the main phase, an asymmetric quadrupole doublet (pink solid lines) due to the main phase, and an asymmetric quadrupole doublet (dark green solid lines) due to air-environment induced impurity. The zero-velocity origin is relative to α -Fe at room temperature.	118
Figure 5.24	Temperature dependence of (a) the absorption spectral area A , (b) the center shift δ , and (c) the quadrupole splitting Δ . The solid lines are the fits to equation (5 – 4) in (a) and to equation (5 – 7) in (b).	119
Figure 5.25	Temperature dependence of (a) the hyperfine magnetic field H and (b) the angle α between V_{zz} and H . The blue and green solid lines in (a) are the fits to equation (5 – 9) and to the power-law, respectively.	121
Figure 5.26	The unit cell of the Fe_2NiGa compound in the space group $F\bar{4}3m$ (No. 216).	124
Figure 5.27	Electronic charge density distribution of Fe_2NiGa (in units of $\frac{e}{\text{\AA}^3}$) along the (a) (110) plane, and (b) (100), plane.	125
Figure 5.28	The total, atomic, and orbital resolved density of states of Fe_2NiGa in the nonmagnetic state.	127
Figure 5.29	The spin-polarized total, atomic, and orbital resolved density of states of ferromagnetic Fe_2NiGa	129
Figure 5.30	The energy band structure of Fe_2NiGa in the (a) nonmagnetic state, and in the (b) spin up and (c) spin down configurations in the ferromagnetic state.	130

Figure 5.31 Total energy as a function of primitive cell volume in the <i>fcc</i> structure of Fe ₂ NiGa	132
Figure 5.32 X-ray diffraction pattern of Fe ₂ NiGa at 298 K. The experimental data are denoted by open circles, while the line through the circles represents the results of Rietveld refinement. The row of vertical bars shows the indexed Bragg peak positions for the <i>Fm</i> $\bar{3}$ <i>m</i> space group. The * symbol indicates the Bragg peak position corresponding to an unidentified impurity phase. The lower solid line represents the difference curve between experimental and calculated patterns.....	133
Figure 5.33 ⁵⁷ Fe Mössbauer spectra of the Fe ₂ NiGa Mössbauer absorber ($\sigma_{\text{exp}} = 21.9$ mg/cm ²) at the indicated temperatures fitted (blue solid lines) (left panel) with the A site and B site (dark red and dark green solid lines) Zeeman patterns resulting from the hyperfine magnetic field distributions $P(H_{\text{hf}})$ (right panel). The zero velocity origin is relative to α -Fe at room temperature.	135
Figure 5.34 ⁵⁷ Fe Mössbauer spectra of the Fe ₂ NiGa Mössbauer absorber ($\sigma_{\text{exp}} = 21.6$ mg/cm ²) at the indicated temperatures fitted (blue solid lines) (left panel) with the A site and B site (dark red and dark green solid lines) Zeeman patterns resulting from the hyperfine magnetic field distributions $P(H_{\text{hf}})$ (right panel). The spectra were measured consecutively starting with the spectrum at 300.2 K (top left column) down to the spectrum at 300.2 K (bottom left column). The zero velocity origin is relative to α -Fe at room temperature.	136
Figure 5.35 ⁵⁷ Fe Mössbauer spectra of the Fe ₂ NiGa Mössbauer absorber ($\sigma_{\text{exp}} = 33.0$ mg/cm ²) at the indicated temperatures fitted (blue solid lines) (left panel) with the A site and B site (dark red and dark green solid lines) Zeeman patterns resulting from the hyperfine magnetic field distributions $P(H_{\text{hf}})$ (right panel). The spectra were measured consecutively starting with the spectrum at 300.2 K (top left column) down to the spectrum at 300.2 K (bottom left column). The zero velocity origin is relative to α -Fe at room temperature.	137
Figure 5.36 Temperature dependence of the average hyperfine magnetic fields $\bar{H}_{\text{hf,A}}$ and $\bar{H}_{\text{hf,B}}$	138
Figure 5.37 Temperature dependence of (a) the average center shifts $\bar{\delta}_{\text{A}}$ and $\bar{\delta}_{\text{B}}$ and (b) the absorption spectral area A. The solid lines are fits to the theoretical relations explained in the text.	139
Figure 5.38 Hysteresis curves of Fe ₂ NiGa at selected temperatures in the magnetic field range - 90 to +90 kOe.	141
Figure 5.39 Temperature dependence of the magnetic susceptibility of Fe ₂ NiGa measured in external magnetic fields of 10 and 100 Oe.	141
Figure 5.40 The unit cell (a) and the layered structure (b) of (Li _{0.8} Fe _{0.2})OHFeSe.....	145

Figure 5.41 Electron charge density distribution of $(\text{Li}_{0.8}\text{Fe}_{0.2})\text{OHFeSe}$ (in units of $\frac{e}{\text{\AA}^3}$) in the (a) (100), (b) (001), and (c) (110) planes.	147
Figure 5.42 Total and atom-resolved density of states of the $(\text{Li}_{0.8}\text{Fe}_{0.2})\text{OHFeSe}$ system.	148
Figure 5.43 The electronic energy band structure of $(\text{Li}_{0.8}\text{Fe}_{0.2})\text{OHFeSe}$	149
Figure 5.44 Powder X-ray diffraction pattern of $(\text{Li}_{0.8}\text{Fe}_{0.2})\text{OHFeSe}$ at 298 K. The experimental data are denoted by the red circles, while the line through the circles represent the results of the Rietveld refinement. The row of vertical bars show the Bragg peak positions for the $P4/nmm$ space group. The lower solid line represents the difference curve between experimental and calculated patterns. The ∇ symbol indicates the position of the Bragg peak related to the unidentified impurity phase.	151
Figure 5.45 ^{57}Fe Mössbauer spectra of $(\text{Li}_{0.8}\text{Fe}_{0.2})\text{OHFeSe}$ at indicated temperatures fitted (black solid lines) with two quadrupole doublets (blue and dark green solid lines) due to Fe_1 and Fe_2 atoms of the main phase, and a quadrupole doublet, (pink solid lines) originating from the impurity phase. The inset shows the 295.2 K spectrum with enlarged vertical and horizontal scales. The zero-velocity origin is relative to $\alpha\text{-Fe}$ at room temperature.	153
Figure 5.46 The ^{57}Fe Mössbauer spectra of $(\text{Li}_{0.8}\text{Fe}_{0.2})\text{OHFeSe}$ at indicated temperatures fitted (black solid lines) with two quadrupole doublets (blue and dark green solid lines) due to Fe_1 and Fe_2 atoms of the main phase, and a Zeeman pattern, (pink solid lines) originating from the impurity phase. The inset shows the 49.5 K spectrum with enlarged vertical and horizontal scales. The zero-velocity origin is relative to $\alpha\text{-Fe}$ at room temperature.	154
Figure 5.47 ^{57}Fe Mössbauer spectra of $(\text{Li}_{0.8}\text{Fe}_{0.2})\text{OHFeSe}$ at indicated temperatures fitted (black solid lines) with two quadrupole doublets (blue and dark green solid lines) due to Fe_1 and Fe_2 atoms of the main phase, and a quadrupole doublet, (pink solid lines) originating from the impurity phase. The zero-velocity origin is relative to $\alpha\text{-Fe}$ at room temperature.	156
Figure 5.48 ^{57}Fe Mössbauer spectra of $(\text{Li}_{0.8}\text{Fe}_{0.2})\text{OHFeSe}$ at indicated temperatures fitted (black solid lines) with two quadrupole doublets (blue and dark green solid lines) due to Fe_1 and Fe_2 atoms of the main phase, and a Zeeman pattern, (pink solid lines) originating from the impurity phase. The zero-velocity origin is relative to $\alpha\text{-Fe}$ at room temperature.	157
Figure 5.49 Temperature dependence of the quadrupole splitting parameters, Δ , and their related absorber line widths, Γ , corresponding to iron at sites Fe_1 and Fe_2	158
Figure 5.50 Temperature dependence of isomer shift, δ of the Fe_1 and Fe_2 site quadrupole doublets in $(\text{Li}_{0.8}\text{Fe}_{0.2})\text{OHFeSe}$. The solid lines are fitted to equation (5 – 5).	159
Figure 5.51 The unit cell of the $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ compound.	162
Figure 5.52 The total and atom-resolved density of states of $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$	164

Figure 5.53 The electronic energy band structure of $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$.	166
Figure 5.54 The electronic charge density distributions (in units of $\frac{e}{\text{\AA}^3}$) along the (a) $z = 0.726$ plane and (b) $z = 0.5$ plane	167
Figure 5.55 The X-ray powder diffraction pattern of $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ at 298 K. The red open circles represent the experimental data, while the solid blue line through the circles is the results of Rietveld refinement. The row of vertical bars shows the Bragg peak positions for the space group $C2/m$. The lower solid line represents the difference between experimental and calculated patterns.	169
Figure 5.56 Room and liquid nitrogen temperature ^{57}Fe Mössbauer spectra of $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ measured in a large velocity range fitted (blue solid line) with a distribution of quadrupole splittings. The zero-velocity origin is relative to $\alpha\text{-Fe}$ at room temperature.	171
Figure 5.57 ^{57}Fe Mössbauer spectra of $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ at indicated temperatures and fitted (blue solid lines) with the quadrupole splitting distributions $P(\Delta)$ shown in figure 5.58. The zero-velocity origin is relative to $\alpha\text{-Fe}$ at room temperature.	172
Figure 5.58 The quadrupole splitting distributions, $P(\Delta)$ which optimally fit the ^{57}Fe Mössbauer spectra of the $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ approximant.	173
Figure 5.59 The temperature dependence of the average quadrupole splitting parameter for $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ fitted with the empirical equation (5 – 8).	174
Figure 5.60 Temperature dependence of (a) the average isomer shift, $\bar{\delta}$, and (b) the absorption spectral area. The solid lines represent the fits of the experimental data with equations (5 – 15) and (5 – 4).	175
Figure 5.61 (a) The ^{57}Fe Mössbauer spectrum of $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ at 4.5 K and the simulated spectrum (blue solid line) resulting from the superposition of five quadrupole doublets (with the calculated δ_0 and Δ values) due to the iron atoms at the Fe(1) site (pink solid line), Fe(2) site (black solid line), Fe(3) site (green solid line), Fe(4) site (dark grey solid line), and Fe(5) site (red solid line) (b) the same as in (a) but with fitted δ_0 values.	177
Figure 5.62 Magnetization of the $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ specimen in indicated temperatures and in magnetic fields ranging from -90 kOe to 90 kOe.	178
Figure 5.63 (a) Temperature dependence of the magnetic susceptibility of $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ measured in an external magnetic field of 10 kOe. The solid line is fitted to equation (5 – 16) in the temperature range 250 to 390 K. (b) Temperature dependence of the inverse magnetic susceptibility, $(\chi - \chi_0)^{-1}$ corrected for the contribution χ_0 . The solid line is fit to equation (5 -16).	179
Figure A.1 Schematic dependence of DOS and $u_l(r, E_l)$ on energy [1].	205

List of Tables

Table 3.1 The seven crystal systems in three dimensions.	62
Table 5.1 Crystallographic data [4] for $\text{Al}_{13}\text{Fe}_4$ and calculated V_{zz} (in units of 10^{21} V/m^2) and η	87
Table 5.2 The magnetic moments, μ of Na, Fe, Se, and O atoms in the ferromagnetic and blocked checkerboard anti ferromagnetic states of $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$ and the total-energy difference, ΔE (with respect to the nonmagnetic state).	110
Table 5.3 The atomic positions for tetragonal $(\text{Li}_{0.8}\text{Fe}_{0.2})\text{OHFeSe}$ compound obtained through Rietveld analysis.	144
Table 5.4 The atomic positions for monoclinic $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ (space group $C2/m$) and calculated V_{zz} (in units of 10^{21} V/m^2) and η	162
Table A.1 Relativistic quantum numbers [1].	197
Table A.2 Input and output files of main programs in an SCF cycle [1].	199
Table A.3 LM combinations of the cubic groups [1].	207
Table A.4 LM combinations and the local coordinate system of non-cubic groups [1].	208

Chapter one

Introduction

In this chapter, the general framework on which this thesis is based is introduced. The areas and topics subject to modern research in condensed matter physics, and particularly solid state physics, are briefly stated. The motivations and the various research topics covered in the thesis are briefly discussed and the overall structure of the thesis is presented.

1.1 Directions and main schemes of research in solid state physics

Modern solid state physics can be considered to form the theoretical basis of material science. Many wide areas of scientific research in solid state physics involve the study of the large scale properties of solid materials as a result of their atomic scale properties. The techniques of modern statistical mechanics and quantum mechanics serve as the theoretical platform for research in solid state physics. As the largest branch of condensed matter physics, the majority of current research topics in solid state physics include theoretical and experimental studies of strongly correlated materials, quasicrystals, spin glasses, high-temperature superconductivity, etc. The complementary methods of theoretical analysis combined with experimental techniques serve as the main (and only) available tools to investigate the diverse phenomenon arising from the physical properties of matter in the solid state.

Among various experimental techniques applied in research to probe the physical properties of the solid state, the method of spectroscopy is considered to be one of the most efficient and adequate scientific tools used in modern research facilities worldwide. From a theoretical point of view, modern research in solid state physics invokes computer modelling and simulations to understand the physical properties of solid materials. In recent years the development and improvement of a wide variety of computer codes designed to calculate the electronic and magnetic properties of materials, both in the bulk form and in the nanoscale, indicates the demanding need of modern theoretical techniques in solid state research. The theoretical platform for our modern understanding of the physics of the solid state can be categorized into two major approaches: *many body theory* (MBT) which invokes electron correlations and is useful for a qualitative understanding of the nature of interactions based on a model Hamiltonian and *density functional theory* (DFT) which is more material specific and applies *ab initio* methods. The techniques of DFT which are based on effective one-particle approaches allow solid state theorists to obtain a somewhat quantitative picture and are often more successful than the many-body treatment. In order to understand the physical properties of solid state materials in a relatively efficient way, both theoretical and experimental techniques are applied as complementary schemes. The theoretical calculations support the experimental results, while at the same time experiment directs the theoretical research.

In the recent years the study and synthesis of novel compounds with a variety of physical and chemical properties has been an ever growing subject of interest among material scientists. The promising progress in many diverse fields of condensed matter, such as search for high-temperature superconductivity, the development of spin-based electronics, nanotechnology,

growth and applications of thin layers, developments in high performance computing systems based on q-bits and quantum computation, the physical properties of graphene and many other similar examples indicate the impact that research in solid state physics has on our understanding of the ways nature operates and how it can revolutionize our technological methods. The appearance of such a vast region of research topics in solid state physics might in fact cause one to draw a conclusion that developing an understanding of the fundamental basics of all of the mentioned examples is a hopeless task. However, the atomic theory of matter and the current understanding of electromagnetic interactions between charged particles in a solid suffice to account for the many of the phenomena observed in the solid state. Electronic transport properties, magnetic properties, mechanical, thermal, and acoustic properties, along with optical properties of materials can all be traced down to the interactions between the valence electrons of the atoms composing the system with its environment.

There are areas of research in solid state physics that consider the structure of matter on a scale of a nucleus. In particular, some emergent properties of solids originate from the nuclei of their constituent atoms. The techniques of *nuclear magnetic resonance* (NMR) and *Mössbauer spectroscopy* (MS) are among two of the major experimental methods. NMR spectroscopy is mostly used to probe the electronic structure of molecules providing detailed information on the structure, dynamics, reaction state, and chemical environment of molecules. MS has been used in many areas of physics and chemistry, for example in the determination of life-times of excited nuclear states, in the measurement of nuclear magnetic moments, in the study of electric and magnetic fields in atoms and crystals, and in the testing of special relativity and the equivalence principle.

In this thesis the experimental techniques of MS are combined with the theoretical methods of DFT to investigate various physical properties of a wide range of novel compounds and alloys.

1.2 Proposed problems and motivations of research

Historically, condensed matter physics and especially solid-state physics were among the first branches of science and in particular physics that came to humankind's attention and curiosity. This of course is of no surprises since the world around us is full of what can be counted as condensed matter, rocks, stones, mountains, rivers, grains of sand, minerals, and etc. In fact, the role that (what is now known as) condensed matter has played in shaping our civilization is undeniable. From the dawn of civilization the application of material in condensed form has been both necessary and advantageous to the use and survival of humans. From the shaping of metals and rigid material to form simple weapons to protect against wild predators to the discovery of magnetism and its properties in navigation, throughout the bronze and iron ages, and well into the industrial revolution, if not all, but certainly most of our life style, culture and etc. owes its existence to the science and engineering of condensed matter. Today, more than any other time in the history of humankind have we seen the applications of condensed matter physics around us. From all old fashion electronic systems such as radios, TVs, computers and cellphones, to novel devices such as smart phones, modern display screens, LCDs, LEDs, OLEDs,

supercomputers, high storage capacity devices that can store thousands of terabytes on a fingertip sized chip, one can trace material science and engineering. Even a few decades ago some of the practical consequences of condensed matter physics were unimaginable. Progress in nanotechnology, semiconductors, superconductors and etc. has been tremendous in scale in the recent years. One can imagine what potentially practical applications may the synthesis and characteristic determination of novel materials reveal in the future.

The frontiers of progress in solid state physics in modern days lies in the laboratories and research facilities. Research in particular areas in solid state physics aim towards understanding the underlying physical properties of materials. As pointed out earlier, Mössbauer spectroscopy up to some extent provides the means to this purpose.

This thesis is a theoretical and experimental study of the structural, hyperfine interaction, and magnetic properties of five compounds, that have been chosen based either on their novelty or due to their interesting features which require further study.

$\text{Al}_{13}\text{Fe}_4$ has a complex atomic structure. The iron atoms in this compound are located at five inequivalent crystallographic sites. Due to the fact that the point group symmetries of the five sites is lower than cubic, one expects that the low temperature ^{57}Fe Mössbauer spectrum of $\text{Al}_{13}\text{Fe}_4$ to be a superposition of five quadrupole doublets. The experimental ^{57}Fe Mössbauer spectrum of $\text{Al}_{13}\text{Fe}_4$ shows a three-valley structure, and has been interpreted in the literature in two qualitative ways. The first interpretation, assumes that the spectra is a superposition of three single-line components. Clearly, this interpretation would not be correct, since the spectra should be in a form of five quadrupole doublets. The second interpretation, is based on fitting the experimental spectrum with two quadrupole doublets, one from the Fe atoms at four crystallographic sites and the other, from the fifth Fe atom. But this justification turns out to be false. The controversy has been resolved by the ^{57}Fe Mössbauer measurements of the system in different temperatures, and also the Mössbauer spectrum in an external magnetic field of 90 kOe in liquid helium temperatures. These spectra have been compared and interpreted with the aid of *ab initio* calculations of the electric field gradient at the five iron nuclei sites. The temperature dependencies of the electric field gradient and the absorption spectra were determined and explained within the existing theories. The magnetic ordering in $\text{Al}_{13}\text{Fe}_4$ was studied through magnetization and magnetic susceptibility measurements. The electronic structure of $\text{Al}_{13}\text{Fe}_4$ has been investigated by *ab initio* calculations of the energy band structure and the total and atom resolved density of states.

The new layered $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$ oxyarsenide was synthesized very recently. It is a new member of the iron based oxyarsenides with similar physical properties of layered *d*-metal pnictide oxides $\text{Na}_2\text{Ti}_2\text{Pn}_2\text{O}$. Many of the physical properties of interest in this system regarding electronic structure and magnetic ordering have been calculated and experimentally determined via Mössbauer spectroscopy. The hyperfine-interaction parameters, electric field gradient, hyperfine magnetic field and the isomer shift for the Fe sites have never been performed on this system. The electronic energy band structure of $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$ has not been investigated. Though its electronic structure has been studied before for certain types of magnetic orderings, a complete *ab initio* based calculation regarding the possible magnetic orderings in this system and its

avored ground state has not been done. Therefore, $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$ is a good candidate for exploring its hidden physical properties. The agreements between the *ab initio* calculations and the results from the Mössbauer spectra are strong motivations to carry on research on future compounds.

Fe_2NiGa is an intermetallic Heusler compound. These compounds exhibit a rich variety of physical properties. They can appear as superconductor, insulators, semiconductors, and metals. These characteristics make Heusler compounds good candidates for practical applications such as spintronics and etc. In recent years, a subset of Heusler compounds, Fe_2NiZ , has been of interest. Few experimental studies on these compounds have been performed. An experimental ^{57}Fe Mössbauer spectroscopy study completed by *ab initio* calculations reveals many physical properties of the Fe_2NiGa Heusler compound. The electronic structure, magnetic moments, elastic constants, X-ray diffraction pattern and ^{57}Fe Mössbauer spectroscopy study of this compound completes some of the previous studies reported in the scientific literature.

The 40 K $(\text{Li}_{0.8}\text{Fe}_{0.2})\text{OHFeSe}$ superconductor was recently synthesized. An interesting feature about this system is the claims made in literature on the existence of long range ^{57}Fe magnetic ordering in this system (both ferromagnetism and antiferromagnetism) at very low temperatures. The measured ^{57}Fe Mössbauer spectra show no existence of magnetic ordering down to 2.0 K. This debate is potentially settled by support from *ab initio* calculations performed at 0.0 K. Hyperfine interaction calculations have not been performed on this system before and this can be a good reason for research on this system. Via Mössbauer spectroscopy and *ab initio* calculations, the physical properties of the $(\text{Li}_{0.8}\text{Fe}_{0.2})\text{OHFeSe}$ system are extracted. The electronic structure and electronic charge density distribution and also the type of chemical bonding in this compound have never been studied previously. Many of the physical properties of $(\text{Li}_{0.8}\text{Fe}_{0.2})\text{OHFeSe}$ have not been determined especially from the theoretical point of view and this makes it an interesting topic to consider as a project.

Many of the structural, magnetic, and Mössbauer spectral properties of the approximant $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ have not been studied and its electronic structure and hyperfine-interaction parameters have never been studied theoretically. The $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ can be regarded as an approximant to a decagonal Al-Ni-Fe quasicrystal. Many undiscovered physical properties of this system both from a theoretical and experimental point of view are the main motivations to consider the $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ as a research topic.

In defying Einstein's romantic quote as an iconic physicist which states "I am not interested in this or that phenomenon, or in the spectrum of this or that element, I want to know his thoughts", many of the advances in science in the 21st century would not have occurred if it were not for the interests of physicists in exactly *the spectrum of this or that material*.

Apart from what was mentioned, observing density functional theory and in a wider context quantum mechanics at work and agreement within the experimental facts obtained from the Mössbauer spectra of the mentioned compounds, is the best motivation for a physicist.

1.3 Thesis Outline

Apart from the introductory chapter, this thesis includes six chapters. In chapter two a brief overview of the theory of magnetism and superconductivity is introduced. Various magnetic phases and orderings are discussed via a semi-classical treatment and within the framework of the molecular mean field theory. The different compounds studied in this research are investigated in a wide variety of magnetic phases and orderings and under different thermal conditions and chapter two develops a theoretical model for understanding the magnetic properties of the studied compounds. Magnetization, magnetic susceptibility, phase change, and ordering temperatures for various solids exhibiting diamagnetism, paramagnetism, ferromagnetism, antiferromagnetism, and superconductivity are discussed in this chapter.

Chapter three provides the theoretical and experimental backgrounds of the research introduced in this thesis. An introduction to the Mössbauer effect is given followed by a discussion on the nature of hyperfine interactions. The three dominant hyperfine interactions in a typical Mössbauer spectrum are introduced and discussed from both a theoretical and an experimental point of view. The theoretical part covers the isomer shift, magnetic dipole interaction and electric quadrupole interaction, including a review on the electric field gradient. The second part of chapter three introduces the experimental techniques and instrumentation used in MS. This part covers the individual steps in carrying a Mössbauer measurement, including sample preparation, installation of the absorber and the radioactive source, pressure and temperature controls, and interpreting the Mössbauer spectrum. The third part of chapter three is mainly on X-ray diffraction and it starts with an introduction to crystal structures. The technique of X-ray diffractometry in determining the crystal structure of a sample either in a powder or a single-crystal form is discussed. The chapter is concluded by the Rietveld refinement technique which is introduced as an approach to refine a theoretical line profile of intensity versus scattering angle until it matches the experimental profile. In this process possible impurities of the sample can be identified.

Chapter four provides the theoretical basis for the computational calculations that have been performed for the compounds studied in this thesis. This chapter is on DFT and the linearized augmented plane wave (LAPW) methods which are used for the theoretical calculations. The chapter begins with introducing two main approaches to solid state problems. The main elements of density functional theory are introduced. The many-body problem is treated with local density approximations. The theorems of Hönenberg and Sham are briefly introduced and the resulting Kohn-Sham equations are discussed. The various forms of the exchange-correlation functional are treated. The main core of this chapter includes three sections. The first section is on the rather “old” *augmented plane wave* method (APW). The second section describes the *linearized augmented plane wave* methods (LAPW) and the third section discussing the *augmented plane wave plus local orbital* methods (APW+lo). These methods have been extensively used in all of the theoretical calculations in this research.

Chapter five is the central part of this thesis and consists of all the experimental and theoretical research in which the author has participated. This chapter contains five sections. Each section focuses on a particular compound that has been studied experimentally and

theoretically. The experimental data are presented and the results of theoretical calculations are presented and analyzed. Each section contains a discussion on the results of the study and also the conclusions. The theoretical studies consider possible magnetic orderings of the compounds, their electronic charge density distributions, the individual magnetic moments of the atoms within the unit cells, and their hyperfine interaction parameters. The electronic band structures and also density of states of the studied materials are discussed in detail and possible explanations on the electronic and magnetic properties are offered based on theoretical and experimental results. The experimental studies contain the Mössbauer transmission spectra at different temperatures and the measured magnetic susceptibilities.

Chapter six contains the summary and main conclusions of this thesis, it is concluded by a number of suggestions for future research.

The appendix at the end of the thesis, describes the “WIEN2k” package. This part contains the steps in initializing a calculation, running the various commands, and finally analyzing the results of the calculations. The WIEN2k package is widely used for different areas of research in physics, chemistry, and material science. In this chapter however we only emphasize parts of the program which were used in performing the calculations for the studied compounds in this research.

1.4 List of Publications based on the thesis results

In what follows the list of publications in which the results of the thesis has been presented is given. These publications are listed in order of their publication dates.

- M. A. Albedah, F. Nejadstari, Z. M. Stadnik, J. Przewoźnik, J. Alloys Compd. 619 (2015) 839.
- F. Nejadstari, Z. M. Stadnik, J. Żukrowski, J. Alloys Compd. 639 (2015) 547.
- F. Nejadstari, Z. M. Stadnik, J. Przewoźnik, K. H. J. Buschow, Physica B 477 (2015) 113.
- F. Nejadstari, Z. M. Stadnik, J. Alloys Compd. 652 (2015) 470.
- F. Nejadstari, Z. M. Stadnik, J. Przewoźnik, B. Grushko, J. Alloys Compd. 662 (2016) 612.

Chapter two

The theory of magnetism and superconductivity

In this chapter we briefly introduce the theoretical background which describes the magnetic properties of materials in the bulk state. The samples studied throughout this research possess various magnetic phases and are examined under different temperature regimes. The experimental and calculated magnetic properties of the studied compounds, including magnetic moments, magnetic susceptibilities, and ordering temperatures, can only be understood by the existing theories of magnetism. This chapter is concluded by a short review on the topic of superconductivity

2.1 Introduction.

The fundamental constituent of all magnetic materials and of the emerging properties associated with magnetic phenomena is the so-called *magnetic dipole moment* μ . The collective behavior of these magnetic moments gives rise to the magnetic characteristics of materials. Modern theories based on quantum mechanics suggest that the magnetic dipole moments observed in bulk material originate from two dominant sources. The orbital angular momentum and the spin angular momentum of electrons within the atom have the main contribution to the magnetic moments of matter. There is also a magnetic dipole moment corresponding to the nuclei which, in most cases, can be neglected due to its relatively small magnitude. The orbital motion of the electrons about the atomic nucleus can be considered to form a minute current loop which generates a magnetic dipole moment. In addition, electrons possess intrinsic magnetic dipole moment which is proportional to their intrinsic spin degree of freedom. One can consider the electrons to be ideal magnetic dipoles.

It is well known that a magnetic induction field $\mathbf{B}$ interacts with the electrons of an atom resulting in an *induced* magnetic dipole moment. This phenomenon, known as *diamagnetism* occurs in all substances since essentially all materials consist of electrons in orbital motion.

The electronic structure of the atoms in many substances can be such that it allows *permanent* magnetic moments to exist. All the magnetic effects other than diamagnetism are a consequence of the existence of permanent dipole moments. The permanent moments of different atoms interact with each other resulting in the coupling of the magnetic dipole moments. Depending on the strength of the couplings of the magnetic moments, materials can be classified based on their magnetic behavior. When the coupling is weak or essentially zero, the substance is considered to be *paramagnetic*. Paramagnetic materials show magnetic effects only when they are subject to external magnetic fields. Upon the removal of the external magnetic field, the net magnetic moment of paramagnetic materials vanishes. If the coupling between the dipole moments is strong, then the phenomena of *ferromagnetism* and *antiferromagnetism* can occur in a substance. If the magnetic moments of the atoms are aligned parallel, the substance is called *ferromagnetic*, resulting in a relatively strong net magnetic moment. If, however, the individual pairs of dipole moments (or groups of dipole moments) align themselves in antiparallel configuration, the

resulting net magnetic moment will be zero due to the cancelations of the adjacent dipoles (or group of dipoles). The substance in this magnetic phase is known to be *antiferromagnetic*¹.

For substances possessing a net magnetic moment one defines a field vector called *magnetization*, $\mathbf{M}(\mathbf{x}, t)$, which generally is a function of space and time (and also temperature). Magnetization of a substance, which is considered a bulk property of matter, is defined as the magnetic moments per unit volume of the material:

$$\mathbf{M} = \frac{d\boldsymbol{\mu}}{d\mathbf{x}}, \quad (2-1)$$

where $d\mathbf{x}$ is a small element of volume and $d\boldsymbol{\mu}$ is the magnetic moment within the volume element. For linear media, the magnetization is proportional to the magnitude of the applied magnetic field $\mathbf{H}$. The proportionality factor is known as the *magnetic susceptibility*, χ :

$$\mathbf{M} = \chi \mathbf{H}. \quad (2-2)$$

The magnetic susceptibility can be expressed in different units, depending on the type of substance and the measurement. One can define the susceptibility per unit mass χ_ρ as $\frac{\chi}{\rho}$, where ρ is the density. Likewise, atomic susceptibility χ_a and molar susceptibility χ_m are defined by multiplying χ_ρ by the atomic or molecular mass. The magnetization and magnetic susceptibilities of different substances can be measured against external magnetic field and temperature variations.

In the present research, five different compounds have been studied theoretically and have been subject to experiments including magnetic measurements. The different types of magnetic ordering, paramagnetism, ferromagnetism, and antiferromagnetism, have been observed depending on the material and the temperature ranges involved in the measurements. The *ab initio* calculations performed, compare the ground state energies of different possible orderings of a particular compound and the resulting preferred magnetic orientations are determined by the state of minimum energy, which is later compared with experiment. These results are extensively presented and discussed in chapter five.

After an introduction to diamagnetism, in the following sections of the present chapter the three magnetic orderings (paramagnetism, ferromagnetism, and antiferromagnetism) are discussed on the basis of the molecular field theory and their susceptibility profiles are introduced. The chapter is concluded by a brief review of the phenomenon of superconductivity.

¹ A third type of phenomenon known as *ferrimagnetism* occurs when magnetic moments (or groups of magnetic moments) not equal in magnitude are aligned in an antiparallel configuration such that a nonzero net magnetic moment arises. However, this phenomenon can be regarded as a special case of antiferromagnetism.

2.2 Diamagnetism

2.2.1 The diamagnetic susceptibility

As mentioned earlier, all materials exhibit diamagnetism. The phenomenon of diamagnetism is a direct result of Faraday's induction law and Lenz's sign correction to it: the change in the magnetic flux in a current loop induces a current in such a direction that opposes the original field. Electrons in orbital motion about the nucleus can represent miniature currents. Therefore when the material is subject to an external magnetic field, a magnetic moment is induced in a direction to reduce the field. This induced diamagnetic moment lasts as long as the substance is inside the external field. As a result of the interaction between the magnetic dipole moment and the external field, the delivered torque results in the electrons orbital angular momentum precession about the direction of the applied field. This precession occurs with a frequency known as *Larmor's frequency*, ω_L :

$$\omega_L = \frac{|e|\hbar}{2mc} H, \quad (2-3)$$

where e is the electrons charge, m the electron's mass, and c is the speed of light. The induced magnetic dipole moment can be shown to be:

$$\mu = -\frac{e^2}{6mc^2} \langle x^2 \rangle H. \quad (2-4)$$

In this equation $\langle x^2 \rangle$ is the average square distance of the electron from the nucleus. Considering Z electrons in an atom and a number density of n atoms per unit volume of the substance, Langevin (along a correction made by Wolfgang Pauli) expressed the diamagnetic susceptibility as [1]:

$$\chi_{\text{diamagnetic}} = -n \frac{e^2}{6mc^2} \sum_{i=1}^Z \langle x_i^2 \rangle. \quad (2-5)$$

Experimentally the order of magnitude of the diamagnetic susceptibility is 10^{-6} . It is understood that the diamagnetic susceptibility is a relatively small quantity, in other words, induced diamagnetism can only be accurately measured if the other types of magnetism are absent. On the other hand, the paramagnetic susceptibility is usually two to four orders of magnitude larger, making it to be the dominant part of the overall susceptibility (*vide infra*). Important facts about the diamagnetic susceptibility follows (2 – 5): diamagnetism is always negative, it is relatively small, it is temperature independent (temperature doesn't explicitly appear in Langevin's formula), and it is also field independent. The last two conclusions were experimentally established by P. Curie [2].

2.2.2 The diamagnetic susceptibility of atoms, ions, and molecules

Langevin's formula is considered valid only in the case of monatomic molecules (noble gases) since it only considers one single center of force in the atom. In order to detect the diamagnetic susceptibility it is convenient to consider only atoms and ions that lack orbital and spin angular momentum, otherwise the contribution from the paramagnetic susceptibility will

dominate. From a theoretical point of view the electronic charge distribution of the atom determines the diamagnetic susceptibility via the average square distance to the center of force. Exact solutions can be obtained only for hydrogen-like atoms:

$$\langle x^2 \rangle = \frac{a_0^2 n^2}{Z^2} \left[\frac{5}{2} n^2 - \frac{3l(l+1)-1}{2} \right]. \quad (2-6)$$

In this relation n represents the principle quantum number indicating the energy level, a_0 is the Bohr radius, and l is the orbital angular momentum quantum number of the electron.

In principle, quantum mechanics adequately allows the calculations of the charge distribution. However, in practice, numerical methods and simulations are required to perform the task and one cannot proceed analytically. One can consider the screening effects of other electrons on the nucleus to introduce an “effective” Z . Other approximation methods such as *self-consistent field* theories invoke the Hartree-Fock wave functions [3]. The Thomas-Fermi statistical analysis of the atom also yields adequate expressions for the diamagnetic susceptibility [4].

In ionic solids, such as NaCl, and also in their solutions, the diamagnetic susceptibility can be assumed to be the sum of the contribution from the cation and that of the anion:

$$\chi_{\text{diamagnetic}} = \chi_{\text{anion}} + \chi_{\text{cation}}. \quad (2-7)$$

However, experimentally it is found that the measured value for solids is less than the above equation predicts [5-8]. One can explain this fact by considering the limited region in solids which confines the electron cloud causing their average distances to the nuclei to be reduced. For liquid solutions the electronic charge distributions are on average at larger distances with respect to the nuclei.

Concerning molecules, Van Vleck’s work based on quantum mechanical treatment led to a general expression for the diamagnetic susceptibility of molecules [9]:

$$\chi_M = -\frac{e^2 n}{6mc^2} \sum \langle x^2 \rangle + \frac{2}{3} n \left(\frac{e}{2mc} \right)^2 \sum_k \frac{|\langle k | \hat{J} | g \rangle|^2}{E_k - E_g} = -\frac{e^2 n}{6mc^2} \sum \langle x^2 \rangle + n\alpha(g). \quad (2-8)$$

In the equation above, $\langle k | \hat{J} | g \rangle$ is the matrix element of the angular momentum operator $\hat{J}$ between the excited states (represented by the index k and associated with the energy E_k) and the ground state (represented by the index g and associated with the energy E_g). The second term is called the *Van Vleck temperature independent paramagnetism* and it is a positive quantity. Its absolute value is considerably smaller than the first term, causing the molecular susceptibility to remain negative. Other theoretical methods of calculating the diamagnetic susceptibility based on the linear combination of atomic orbitals (LCAO) and the Hartree-Fock wave functions, combined with approximation methods such as variational techniques and perturbation theory, are listed in the references at the end of the chapter [10-14]. Based on experimental measurements, Pascal and others have fitted the molecular susceptibility with a simple relation [15]:

$$\chi_M = \sum N_A \chi_A + \lambda, \quad (2-9)$$

where N_A is the number of atoms in the molecule and χ_A is the corresponding susceptibility. λ is a constant that is determined by the chemical bonding of the molecule's atoms. The value of this constant has been derived by means of theoretical calculations [16].

In general, one observes that the diamagnetic susceptibility of a molecule is less than the sum of the susceptibilities of each of its individual atoms. This fact can be accounted to be a result of two important properties of the molecule and of its constituent atoms. As for the molecule part, the outer-most electrons in a molecule experience a force center with a larger effective charge. Considering the atoms, the outermost electrons in the atom make the largest contribution to the susceptibility since their average distances from the nuclei are largest.

2.3 Paramagnetism

As mentioned earlier, the phenomenon of paramagnetism is related to the existence of permanent magnetic dipole moments within a material which tend to align themselves with the direction of an applied external magnetic field. Paramagnetism, therefore can be considered to be a collective emerging property of bulk material.

2.3.1 Curie's law of paramagnetic susceptibility

In substances that (due to their physical and chemical structures) contain permanent magnetic dipole moments, the phenomenon of paramagnetism is observed. Based on the earlier experimental works of Curie and Weiss, one can categorize the paramagnetic materials into two major types. The susceptibility of a certain type of materials which are known as *normal paramagnets*, is shown to follow a simple pattern with changing temperature in such a way that the product of the susceptibility and the temperature remains constant. This relation, which is known as *Curie's law*, applies also to ferromagnets and antiferromagnets above a (material specific) temperature known as the *Curie temperature* (ordering temperature):

$$\chi_{\text{paramagnetic}} = \frac{C}{T}. \quad (2 - 10)$$

The other type of paramagnetic material show susceptibilities which deviate from Curie's law. The deviation is such that the susceptibility approaches a finite value related to what is known as the *paramagnetic Curie point*, θ as the temperature of the substances approaches absolute zero. The modified Curie law, known as the *Curie-Weiss law*, is described by the following equation:

$$\chi_{\text{paramagnetic}} = \frac{C}{T - \theta}. \quad (2 - 11)$$

By means of the molecular field theory, the Curie-Weiss law is understood by taking into account the effects of neighboring atoms, molecules, or ions to contribute a magnetic field of magnitude $N_W M$ to the external field. Therefore the total field is considered to be $H + N_W M$. The resulting magnetization, combined with Curies law, leads to:

$$M = \chi(H + N_W M) \xrightarrow{\chi = \frac{C}{T}} M = \frac{CH}{T - CN_W} = \frac{CH}{T - \theta} \xrightarrow{\chi = \frac{M}{H}} \chi = \frac{C}{T - \theta}. \quad (2 - 11a)$$

Due to the unfilled inner shells of transition group elements, the atoms and ions belonging to this group in the periodic table of elements have permanent moments. Atoms and molecules with odd number of electrons also have permanent moments. In addition, free atoms of alkali metals (which occur in vapor form) have permanent moments. Although in general, metals are paramagnetic, they do not obey Curie's law [17]. For the more complicated systems, including compounds studied in this thesis, paramagnetism occurs always above the ordering temperature.

Curie's law is theoretically derived by applying Maxwell-Boltzmann's statistics using a semi-classical approach to a gaseous state of paramagnetic atoms. Due to thermal agitations, this classical gas consists of an ensemble of magnetic dipole moments in all random directions distributed according to Maxwell-Boltzmann statistics. When an external magnetic field is applied, the random dipoles tend to align themselves along the field, whereas the thermal agitations tend to randomize their directions. In the limit of extremely low temperatures, all dipoles are completely aligned with the external field. So one understands that when the external magnetic field is switched off the net magnetization vanishes due to the thermal randomizing effects. In what follows, we examine the paramagnetic susceptibilities, both from a semi-classical point of view and later from the more accurate quantum mechanical treatment.

2.3.1.1 The semi-classical approach

The classical kinetic theory of gases considers the (average) energy of particles in an equilibrium state at (an absolute) temperature T to be of the order of $k_B T$, where k_B is Boltzmann's constant. The energy eigenstates of the particles in the system are degenerate according to the quantum mechanical total angular momentum, J . Upon the application of an external magnetic field, the degeneracy is removed and the degenerate states form multiplets of energy. A state with a total angular momentum quantum number J forms $2J + 1$ multiplets. Each state in a particular multiplet may or may not be occupied according to the classical probability distribution. In what follows, three different regimes are examined regarding the spacings of the multiplets in energy in comparison to $k_B T$.

i) Wide multiplets compared to $k_B T$

In the regime $E_e - E_g \gg k_B T$, where the energy levels are widely separated, the excited states are unoccupied (or at least their populations are negligible compared to the ground state). Under the application of an external (static) magnetic field the degeneracy of the ground state (characterized by the angular momentum quantum number J) is removed. The interaction results in magnetic moments with components $m_J g \mu_B$ along the field direction. Here m_J takes integer values between $+J$ and $-J$. g is the so-called *gyromagnetic ratio*, and μ_B is *Bohr's magneton*. The energy of the dipoles are therefore $-m_J g \mu_B H$, where H is the applied field. The (average) magnetization according to Boltzmann's statistics is:

$$M = n \frac{\sum_{-J}^J m_J g \mu_B e^{\frac{m_J g \mu_B H}{k_B T}}}{\sum_{-J}^J e^{\frac{m_J g \mu_B H}{k_B T}}} . \quad (2 - 12)$$

For small values of the interaction energy compared to $k_B T$, one can expand the exponents keeping only the first two leading terms:

$$e^x = \sum_{n=0}^{\infty} \frac{x^n}{n!} = 1 + x + \frac{x^2}{2!} + \dots \xrightarrow{x \ll 1} e^x \approx 1 + x. \quad (2-13)$$

Here $x \equiv \frac{m_J g \mu_B H}{k_B T}$. The magnetization thus reads:

$$M = n \frac{\sum_{-J}^J m_J g \mu_B e^{\frac{m_J g \mu_B H}{k_B T}}}{\sum_{-J}^J e^{\frac{m_J g \mu_B H}{k_B T}}} = n \frac{\sum_{-J}^J m_J g \mu_B (1 + \frac{m_J g \mu_B H}{k_B T})}{\sum_{-J}^J (1 + \frac{m_J g \mu_B H}{k_B T})} = n \frac{g \mu_B \sum_{-J}^J m_J + \frac{g^2 \mu_B^2 H}{k_B T} \sum_{-J}^J m_J^2}{\sum_{-J}^J 1 + \frac{g \mu_B H}{k_B T} \sum_{-J}^J m_J}. \quad (2-14)$$

The summations can be carried out accordingly:

$$\sum_{-J}^J m_J = -J + (-J) + 1 + (-J) + 2 + \dots + J - 2 + J - 1 + J = 0,$$

$$\sum_{-J}^J 1 = 2J + 1,$$

$$\sum_{-J}^J m_J^2 = 2[J^2 + (J-1)^2 + (J-2)^2 + \dots] = \frac{J(J+1)(2J+1)}{3}.$$

By substituting these results into (2-14), one finds an expression for the magnetization and hence the paramagnetic susceptibility confirming Curie's law:

$$M = \frac{n g^2 J(J+1) \mu_B^2 H}{3 k_B T} \xrightarrow{M = \chi H} \chi_{\text{paramagnetic}} = \frac{n g^2 J(J+1) \mu_B^2}{3 k_B T}. \quad (2-15)$$

A quantum mechanical approach leads to a complete expression for the susceptibility [9]:

$$\chi_{\text{paramagnetic}} = \frac{n g^2 J(J+1) \mu_B^2}{3 k_B T} + \frac{n \mu_B^2}{6(2J+1)} \left[\frac{F(J+1)}{E_{J+1} - E_J} - \frac{F(J)}{E_J - E_{J-1}} \right], \quad (2-16)$$

where $F(J) = \frac{[(S+L+1)^2 - J^2][J^2 - (S-L)^2]}{J}$, and S and L refer to the total spin quantum number and the total orbital angular momentum quantum number, respectively. The second term of (2-16), is a temperature independent term that contributes to the paramagnetic susceptibility. This term can be written as $n\alpha(J)$, where $\alpha(J) = \frac{\mu_B^2}{6(2J+1)} \left[\frac{F(J+1)}{E_{J+1} - E_J} - \frac{F(J)}{E_J - E_{J-1}} \right]$.

ii) Multiplet widths comparable to $k_B T$

In contrast to the first case, in multiplets with energies comparable to $k_B T$ the excited states, in addition to ground states, are also occupied with a certain probability distribution. In this case the total magnetization will consist of contributions arising from the sum of all atoms in different states. The number of atoms with a given angular momentum quantum number J will be

proportional to the Boltzmann factor $e^{\frac{m_J g \mu_B H}{k_B T}}$ and its degree of degeneracy is $2J + 1$. Thus the paramagnetic susceptibility can be evaluated by the same method as for the case of wide multiplets. The result is [17]:

$$\chi_{\text{paramagnetic}} = n \frac{\sum_{J=|L-S|}^{L+S} \left\{ \left[\frac{g_J^2 \mu_B^2 J(J+1)}{3k_B T} \right] + \alpha(J) \right\} (2J+1) e^{-E(J)/k_B T}}{\sum (2J+1) e^{-E(J)/k_B T}}. \quad (2-17)$$

iii) Narrow multiplets compared to $k_B T$

In the case in which the multiplets are separated in energies much smaller than $k_B T$, one can consider the orbital angular momenta and spin angular momenta to be decoupled such that each term contributes to the susceptibility independently. In this case, the magnetization (in an external applied field H), and thus the resulting paramagnetic susceptibility, are found to be:

$$M = n \left(\frac{\sum_{-L}^L M_L g_L \mu_B e^{\frac{M_L g_L \mu_B H}{k_B T}}}{\sum e^{\frac{M_L g_L \mu_B H}{k_B T}}} + \frac{\sum_{-S}^S M_S g_S \mu_B e^{\frac{M_S g_S \mu_B H}{k_B T}}}{\sum e^{\frac{M_S g_S \mu_B H}{k_B T}}} \right) \\ \xrightarrow{M=\chi H} \chi_{\text{paramagnetic}} = \frac{N \mu_B^2}{3k_B T} [L(L+1) + 4S(S+1)] \quad (2-18)$$

The summations leading to the above result are carried out similarly to the ones leading to (2-15). In addition, the gyromagnetic ratios related to the orbital angular momentum, g_L , and spin angular momentum, g_S , are taken as 1 and 2, respectively (this is due to relativistic effects).

2.3.1.2 The quantum mechanical approach

A more accurate description of the paramagnetic susceptibility can be obtained by a full quantum mechanical treatment. The accuracy is related to the fact that the external field not only tends to orient the magnetic dipoles but it also alters their energy states. One can apply perturbation theory to obtain an expression for the paramagnetic susceptibility:

$$\mathcal{H} = \mathcal{H}_0 + H\mathcal{H}_1 + H^2\mathcal{H}_2 + \dots \quad (2-19)$$

$$E = E_0 + HE_1 + H^2E_2 + \dots \quad (2-20)$$

The full Hamiltonian $\mathcal{H}$ in (2-19) is expanded in a power series with the external field H treated as the perturbation parameter. In the absence of the external field, the full Hamiltonian is equal to the atomic Hamiltonian, $\mathcal{H}_0$. The energy eigenvalue of the full Hamiltonian is also expanded in a power series of the external field, where E_0 is the energy of the system in zero field. The first and second order corrections to the energy are given by E_1 and E_2 [9 or 18]:

$$E_1 = \langle j | \mathcal{H}_1 | j \rangle, \quad E_2 = \sum_{j' \neq j} \frac{|\langle j' | \mathcal{H}_1 | j \rangle|^2}{E_{j'} - E_j} + \langle j | \mathcal{H}_2 | j \rangle. \quad (2-21)$$

The ket states in Dirac's notation represent the unperturbed eigenkets of the Hamiltonian. On the other hand, the Hamiltonian of an atomic or molecular system subject to an external magnetic field can be represented by:

$$\mathcal{H} = \sum_i \frac{1}{2m_i} \left(\mathbf{p}_i - \frac{e_i}{c} \mathbf{A}_i \right)^2 + V. \quad (2-22)$$

Here the summation runs over all the (charged) particles in the system. $\mathbf{A}_i$ is the vector potential associated the i -th particle. The term in the brackets can be expanded as follows:

$$\left(\mathbf{p}_i - \frac{e_i}{c} \mathbf{A}_i \right)^2 = \left(\mathbf{p}_i - \frac{e_i}{c} \mathbf{A}_i \right) \cdot \left(\mathbf{p}_i - \frac{e_i}{c} \mathbf{A}_i \right) = p_i^2 - \frac{e_i}{c} (\mathbf{p}_i \cdot \mathbf{A}_i + \mathbf{A}_i \cdot \mathbf{p}_i) + \frac{e_i^2}{c^2} A_i^2. \quad (2-23)$$

There is a gauge freedom in choosing the vector potential such that the magnetic induction, $\mathbf{B}$ satisfies the condition: $\mathbf{B} = \nabla \times \mathbf{A}$. If the applied field is chosen to be along the z axis, that is if $\mathbf{H} = H\hat{z}$, then a possible choice for the vector potential (apart from a factor of μ_0) is:

$$\mathbf{A}_i = -\frac{1}{2} (y_i \hat{x} - x_i \hat{y}) H. \quad (2-24)$$

In calculating the inner products between the vector potential and the momentum one must consider the noncommutativity of the similar components of the position and momentum operators of the same particle:

$$[x_i, p_j] = i\hbar \delta_{ij}. \quad (2-25)$$

Therefore:

$$\mathbf{p} \cdot \mathbf{A} + \mathbf{A} \cdot \mathbf{p} = -\frac{1}{2} H (p_x y - p_y x + y p_x - x p_y) = H (x p_y - y p_x). \quad (2-26)$$

$$A^2 = \frac{1}{4} (x^2 + y^2) H^2. \quad (2-27)$$

Substituting equations (2-23) - (2-27) into (2-22) leads to:

$$\mathcal{H} = \sum_i \left[\frac{p_i^2}{2m_i} - \frac{e_i}{2m_i c} H (x_i p_{y_i} - y_i p_{x_i}) + \frac{e_i^2}{8m_i c^2} H^2 (x_i^2 + y_i^2) \right] + V. \quad (2-28)$$

By rearranging and grouping the terms we have:

$$\mathcal{H} = \left\{ \sum_i \frac{p_i^2}{2m_i} + V \right\} + \left\{ - \sum_i \frac{e_i \hbar}{2m_i c} \right\} H + \left\{ \sum_i \frac{e_i^2 \hbar^2}{8m_i c^2} (x_i^2 + y_i^2) \right\} H^2. \quad (2-29)$$

The first of the curly brackets represents the unperturbed Hamiltonian, $\mathcal{H}_0$. The second curly bracket represents $\mathcal{H}_1$ which is the component of the permanent magnetic moment in the z direction and the third curly bracket represents $\mathcal{H}_2$. The expectation value for the magnetic moment in the field direction for a particular energy state is found accordingly:

$$\mu_z = -\frac{\partial E}{\partial H} = -E_1 - 2HE_2 - \dots. \quad (2-30)$$

(2-21), (2-29), and (2-30) lead to:

$$\mu_z = \langle j | \mu_0 | j \rangle + 2H \sum_{j'} \frac{|\langle j' | \mu_0 | j \rangle|^2}{E_{j'} - E_j} - H \left\langle j \left| \sum_i \frac{e_i^2}{4m_i c^2} (x_i^2 + y_i^2) \right| j \right\rangle. \quad (2-31)$$

The first term in (2-31) is the permanent moment and is field independent, whereas the second and third terms vanish in the absence of the field; therefore they are induced moments. The second term, which is positive, is the paramagnetic moment. The third term, which is negative, is the diamagnetic moment. The magnetic susceptibility thus follows applying Maxwell-Boltzmann statistics by summing over all the states of the system:

$$\chi = \frac{n \langle \mu_z \rangle}{H} = \frac{n \sum \mu_z e^{-\frac{E}{k_B T}}}{\sum e^{-\frac{E}{k_B T}}}. \quad (2-32)$$

One can expand the energy in the exponent as $E = E_0 + E_1 H + E_2 H^2 + \dots$. The result is:

$$\begin{aligned} \chi &= \frac{n \sum \mu_z e^{-\frac{1}{k_B T}(E_0 + E_1 H + \dots)}}{\sum e^{-\frac{1}{k_B T}(E_0 + E_1 H + \dots)}} = \frac{n \sum \mu_z e^{-\frac{E_0}{k_B T}} e^{-\left(\frac{E_1 H}{k_B T} + \dots\right)}}{\sum e^{-\frac{E_0}{k_B T}} e^{-\left(\frac{E_1 H}{k_B T} + \dots\right)}} \approx \frac{n \sum \mu_z e^{-\frac{E_0}{k_B T}} \left(1 - \frac{E_1 H}{k_B T}\right)}{\sum e^{-\frac{E_0}{k_B T}}} \\ &\xrightarrow{\mu_z = -E_1 - 2HE_2 - \dots} = \frac{n \sum (-E_1 - 2HE_2 - \dots) \left(1 - \frac{E_1 H}{k_B T}\right) e^{-\frac{E_0}{k_B T}}}{\sum e^{-\frac{E_0}{k_B T}}} = \frac{n}{H} \left(-\frac{\sum E_1 e^{-\frac{E_0}{k_B T}}}{\sum e^{-\frac{E_0}{k_B T}}} + \frac{H \sum \left[\frac{E_1^2}{k_B T} - 2E_2 \right] e^{-\frac{E_0}{k_B T}}}{\sum e^{-\frac{E_0}{k_B T}}} \right). \end{aligned} \quad (2-33)$$

The first term in the parentheses vanishes since it refers to the average magnetic moment in the absence of the field (there is no preferred direction for the moments due to thermal agitations). The susceptibility then takes the form:

$$\chi = n \frac{\sum \left(\frac{E_1^2}{k_B T} - 2E_2 \right) e^{-\frac{E_0}{k_B T}}}{\sum e^{-\frac{E_0}{k_B T}}}. \quad (2-34)$$

By substituting the expressions $E_1 = \langle j | \mu_0 | j \rangle$ and $E_2 = -\sum_{j'} \frac{|\langle j' | \mu_0 | j \rangle|^2}{E_{j'} - E_j}$ into (2-34) one arrives at:

$$\chi = \frac{n}{\sum e^{-\frac{E_0}{k_B T}}} \sum_j \left(\frac{|\langle j | \mu_0 | j \rangle|^2}{k_B T} + 2 \sum_{j'} \frac{|\langle j' | \mu_0 | j \rangle|^2}{E_{j'} - E_j} \right) e^{-\frac{E_0}{k_B T}}. \quad (2-35)$$

The results of section 2.3.1.1 follow by specifying the quantum number j for this atomic model [9].

2.3.2 The effects of the internal electromagnetic fields on the paramagnetic susceptibility of solids

At ordinary temperatures the effects due to the inhomogeneous electromagnetic fields of the neighboring atoms in a solid on paramagnetic ions (mainly rare earth elements) are negligibly small. The reason lies in the electronic configuration of rare earth elements. The paramagnetism of rare earth elements is a result of the unfilled $4f$ shells. The electrons of the $4f$ orbitals being localized in the interior of the atom are surrounded by $5s$ and $5p$ electrons and therefore they are shielded from the effects of neighboring atoms. Figure 2.1 shows the paramagnetic susceptibility plotted against temperature for two rare earth ions Sm^{3+} and Eu^{3+} .

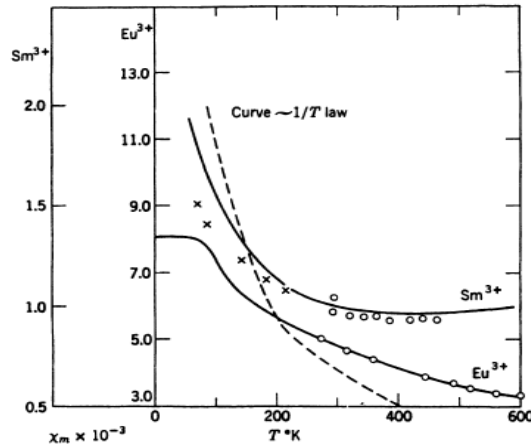


Figure 2.1 χ versus T curves for Sm^{3+} and Eu^{3+} ions [17].

The temperature dependence of the susceptibility for these ions is given by (2 – 17), and therefore deviates from Curie's law. In case of Sm^{3+} there is a minimum at about 385K. The increase in χ at higher temperatures is due to the fact that the occupation number of ions in higher energy levels increases leading to an increase in the magnetic moment. The flat χ for Eu^{3+} at very low temperatures is due to $\alpha(J)$ term in (2 – 17) for the ground state, $J = 0$.

The effects of the electromagnetic fields of neighboring atoms on the paramagnetic susceptibility of iron group ions are much higher than that of the rare earths. This effect can be explained by the fact that the $3d$ shell electrons are not screened by outer electrons and, in addition, the $3d$ shell is more extended towards the outer regions of the atom compared to the $4f$ shell. The general effect of the neighboring fields results in the degeneracy removal of the energy levels leading to a further deviation of the susceptibility from Curie's law.

The breaking of the degenerate atomic energy levels in a solid due to the electromagnetic fields of neighboring atoms results from several factors. The space group symmetries, the oddness or evenness of the number of electrons in the system, and the spontaneous distortion of nonlinear complexes with degenerate ground states determine the nature of the splitting [19,20].

In solids, depending on the type of chemical bonding between atoms, the paramagnetic susceptibility varies. In the case of ionic bonding, for example iron group salts, due to the strong electrostatic crystalline fields, the splitting of the energy levels are much larger than those produced by the spin-orbit coupling. On the other hand, in covalent bond solids there is a high degree of overlap between the atomic orbitals which results in an effective crystalline field. This effective field is larger than the $l-l$ and $s-s$ coupling between the electrons; the result is that the susceptibilities are often quite different from those for ionic bound solids. An extensive treatment of the effects of crystalline electromagnetic fields on the paramagnetic susceptibility can be found in [17].

2.3.3 Paramagnetic susceptibilities of molecules and nuclei

Molecules with odd number of electrons exhibit paramagnetism. The paramagnetism is mainly due to the spin of the electrons. Most molecules, however, have an even number of electrons and therefore are diamagnetic. In a molecule, in addition to the total orbital angular momentum of the electrons, $\mathbf{L}$ and the total spin angular momentum of the electrons, $\mathbf{S}$, one must consider the contributions arising from the rotational angular momentum of the molecule, $\mathbf{K}$.

Here we consider two cases of interest:

i) Wide multiplets compared to $k_B T$:

In this case, only the lowest molecular energy state is occupied. The components of the magnetic moment along the quantization axis (namely the nuclear axis) are [17]:

$$\mu = \mu_B (\Lambda + 2\Sigma), \quad (2-36)$$

where μ_B is the Bohr magneton and Λ takes values $0, 1, 2, \dots, L$ and for a certain Λ , the spin components are denoted by the quantum number Σ . The susceptibility therefore becomes:

$$\chi = \frac{\mu_B^2}{3k_B T} (\Lambda + 2\Sigma)^2. \quad (2-37)$$

ii) Narrow multiplets compared to $k_B T$:

In the case of narrow multiplets, all states with different Σ 's are occupied and must be considered. Taking the average of (2-37), one obtains:

$$\chi = \frac{\mu_B^2}{3k_B T} \langle (\Lambda + 2\Sigma)^2 \rangle = \frac{\mu_B^2}{3k_B T} \langle \Lambda^2 + 4\Sigma^2 + 4\Sigma\Lambda \rangle = \frac{\mu_B^2}{3k_B T} (\langle \Lambda^2 \rangle + 4\langle \Sigma^2 \rangle + 4\langle \Sigma \rangle \langle \Lambda \rangle). \quad (2-38)$$

Since $\langle \Sigma \rangle = 0$, $\langle \Lambda^2 \rangle = \Lambda^2$, $\langle \Lambda \rangle = \Lambda$ and $\langle \Sigma^2 \rangle = S(S+1)$, one is led to the expression for the susceptibility :

$$\chi = \frac{\mu_B^2}{3k_B T} [\Lambda^2 + 4S(S+1)]. \quad (2-39)$$

In the case of atomic nuclei, the spin angular momentum is $\mathbf{I}$. The coupling of the nuclear angular momentum with the electronic angular momentum $\mathbf{J}$ leads to a hyperfine term in the energy states. Therefore the spacing of the nuclear multiplets is extremely narrow compared to $k_B T$ at ordinary temperatures. The susceptibility of the nucleus is found to be [17]:

$$\chi = n \frac{g_N^2 I(I+1)}{3k_B T} \mu_{B_N}^2, \quad (2-40)$$

where g_N is the nuclear Bohr magneton. Numerically the nuclear susceptibility is six orders of magnitude smaller than the electronic susceptibility. Therefore, in most cases, one can easily neglect the contributions arising from the nuclei to the susceptibility.

2.3.4 Paramagnetic saturation

The final section on paramagnetism considers saturation in paramagnetic substances. In the limit of low temperatures and high magnetic fields, Curie's law is not valid. It is shown that in this regime the magnetization of a paramagnetic substance can be described by the following equation [17]:

$$M = ng\mu_B J B_J(x), \quad (2-41)$$

where $x = \frac{Jg\mu_B H}{k_B T}$ and $B_J(x)$ is the *Brillouin function* defined as [21]:

$$B_J(x) = \left[\frac{2J+1}{2J} \coth\left(\frac{2J+1}{2J}x\right) - \frac{1}{2J} \coth\frac{x}{2J} \right]. \quad (2-42)$$

In the classical limit of $J \rightarrow \infty$, which corresponds to the possibility of all directional orientations for the magnetic dipoles, the Brillouin function becomes the classical *Langevin function*:

$$\lim_{J \rightarrow \infty} B_J(x) = \coth x - \frac{1}{x} = L(x). \quad (2-43)$$

In the limit of large applied magnetic fields (large x), the Brillouin and Langevin functions approach unity. In these extreme conditions all magnetic dipole moments align themselves with the direction of the applied field and the magnetization obtains its maximum value. In this case, the substance is said to be magnetically saturated. In figure 2.1, the graph of the theoretical and experimental results of magnetization against the applied magnetic field is shown.

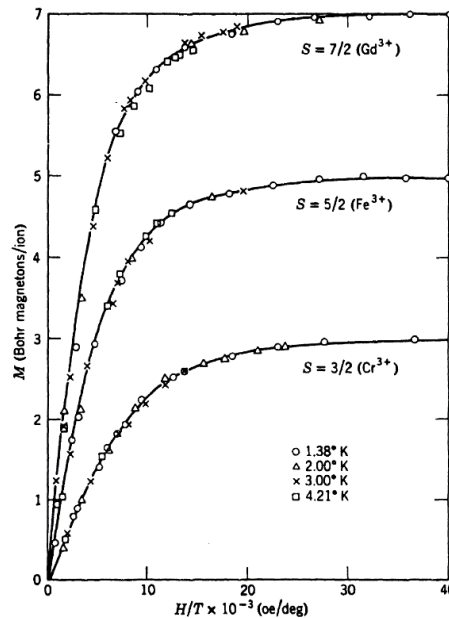


Figure 2.2 Saturation effects for the magnetization of gadolinium, iron, and chromium ions at low temperatures compared to the theoretical Brillouin functions [17].

2.4 Ferromagnetism

2.4.1 Introduction

In this section, the phenomenon of *ferromagnetism*, (FM) is presented. Among the studied compounds, Fe_2NiGa appears to favor the ferromagnetic ordering to be as its predominant magnetic phase (in low temperatures). Therefore a brief theoretical review of the ferromagnetic phase seems necessary in order to understand the physics of ferromagnetism.

Ferromagnetism in a substance occurs when the coupling of the magnetic moments of individual constituents (whether atoms or molecules) strongly favors parallel alignment. Therefore, even in the absence of an external applied magnetic field a non-zero magnetization exists. This *spontaneous* magnetization is observed below a certain temperature, namely the *ferromagnetic Curie temperature*, T_f , which is material dependent. At temperatures exceeding T_f , the couplings between the dipole moments *break* and the material becomes paramagnetic.

Iron, nickel, and cobalt are the most recognized ferromagnetic elements. In addition, gadolinium and dysprosium also are ferromagnetic. These five elements happen to be the only elements exhibiting ferromagnetism². On the contrary, a wide majority of ferromagnetic materials are metals or alloys. In the bulk form, many materials are ferromagnetic such that in the absence of an applied field they show no net magnetization. However upon an external magnetic field no matter how weak, strong magnetic couplings between the magnetic dipole moments occurs. This phenomenon can be explained by means of the existence of the so-called *magnetic domains*. In each magnetic domain, the individual magnetic moments are aligned parallel resulting in net a magnetization vector. However, in neighboring domains the magnetization vectors are randomly oriented, thus leading to a zero net magnetization for the bulk material. When an external field is applied, the magnetic domains change their volume. The ones possessing magnetization vectors directed along the external field *grow* in size, whereas magnetic domains with magnetization vectors opposing the magnetic field *shrink*. The result is the observed field dependent magnetization, which increases upon increasing field up to a saturating value. In many cases this *field induced* magnetization exists even after the field is off and it may or may not (depending on the particular substance) become a permanent property of the material. The dynamics and time evolution of possible magnetic domains and also the structural analysis of *Hysteresis loops* are not of interest for the ferromagnetic compound studied in this thesis³.

2.4.2. The molecular field theory of ferromagnetism

In this section, we present a theory that enables us a firm understanding of ferromagnetism without introducing rigorous methods and analysis. Our approach to the subject of ferromagnetism is based on two different treatments, the *classical* approach and the *quantum mechanical* approach.

² The elements Tb, Ho, Er, and Tm are also ferromagnetic but only in low temperatures [17].

³ As proposed by the author, these properties of the studied compounds can potentially remain a subject for future research and investigation.

2.4.2.1 The classical molecular field theory

In this approach, the source of the strong interaction that tends to align the magnetic dipole moments in a ferromagnetic substance is represented by an internal magnetic field, $\mathbf{H}_m$, called the molecular field. The strength of the molecular field is assumed to be proportional to the spontaneous magnetization of the ferromagnetic substance:

$$H_m = N_W M. \quad (2 - 44)$$

In (2 – 44), N_W is the molecular field constant otherwise known as the Weiss constant. In the presence of an external magnetic field, the total field is:

$$\mathbf{H} = \mathbf{H}_{\text{ext}} + \mathbf{H}_m = \mathbf{H}_{\text{ext}} + N_W \mathbf{M}. \quad (2 - 45)$$

For simplicity and without any loss of generality we ignore the vectorial nature of the fields and consider the fields within a ferromagnetic material in 1D. The magnetization, M of a ferromagnetic specimen is now given by

$$M = ng\mu_B J B_J(x), \quad (2 - 46)$$

where n is the number density of atoms, g is the gyromagnetic ratio, μ_B is the Bohr magneton, J is the total angular momentum of the atoms in the solid, $B_J(x)$ is the classical Brillouin function (defined by $B_J = \frac{2J+1}{2J} \coth \frac{2J+1}{2J} x - \frac{1}{2J} \coth \frac{x}{2J}$), and x is a parameter defined below

$$x = \frac{Jg\mu_B H}{k_B T}. \quad (2 - 47)$$

H in (2 – 47) is given by (2 – 45) for a ferromagnetic material, thus

$$x = \frac{Jg\mu_B}{k_B T} (H_{\text{ext}} + N_W M). \quad (2 - 48)$$

2.4.2.1.1 Spontaneous magnetization region, $T < T_f$

The spontaneous magnetization of a specimen is found by setting H_{ext} equal to zero in (2 – 48) and considering the properties of the Brillouin function at very low temperatures, one arrives at [17]

$$\frac{M(T)}{M(0)} = \frac{k_B T}{n N_W g^2 \mu_B^2 J^2} x, \quad \frac{M(T)}{M(0)} = B_J(x) \quad (2 - 49)$$

where $M(0) = ng\mu_B J$. One can solve the equations in (2 – 49) simultaneously via a graphical method. In figure 2.3, the graphical method for determining the spontaneous magnetization as a function of temperature is shown. The critical temperature, T_f corresponds to a case in which the straight line is tangent to the Brillouin function at the origin. Below this temperature, the curve and the straight line intersect at two points, one at a non-zero value of $\frac{M(T)}{M(0)}$ and one at a zero value. A stable situation is represented by the former [17]. Thus, at temperatures below the critical temperature, T_f , spontaneous magnetization is realized. Above the critical temperature based on what mentioned above, the spontaneous magnetization vanishes.

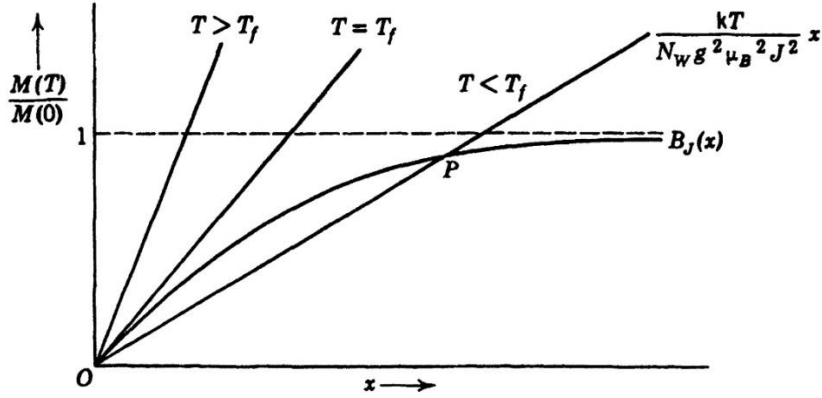


Figure 2.3 Graphical method of determining the spontaneous magnetization at a temperature T , $M(T)$. Spontaneous magnetization in temperatures above and below the critical temperature, T_f , is given by the intersection of the straight lines and the Brillouin function [17].

For small values of x the classical Brillouin function can be approximated by

$$B_J(x) \approx \frac{J+1}{3J} x - \frac{J+1}{3J} \frac{2J^2+2J+1}{30J^2} x^3. \quad (2-50)$$

In (2-50), as x approaches zero, the slope of the tangent line approaches $\frac{J+1}{3J}$. On the other hand, the slope of the straight line is $\frac{k_B T}{n N_W g^2 \mu_B^2 J^2}$. Thus, at the critical temperature, $T = T_f$, one arrives at

$$T_f = \frac{n g^2 \mu_B^2 J(J+1)}{3 k_B} N_W. \quad (2-51)$$

According to equations (2-49) and (2-51), the spontaneous magnetization at temperature T can be written as

$$\frac{M(T)}{M(0)} = \frac{J+1}{3J} \left(\frac{T}{T_f} \right) x. \quad (2-52)$$

It should be noted here that for a given J , the curve $\frac{M(T)}{M(0)}$ as a function of $\left(\frac{T}{T_f} \right)$ yields a universal curve [17]. Such curves for $J = \frac{1}{2}$, $J = 1$, and $J = \infty$ are shown in figure 2.4.

Two specific temperatures of interest are absolute zero and the Curie point. For temperatures very close to absolute zero, x approaches very large values and upon expansion of the Brillouin function one arrives at

$$\frac{M(T)}{M(0)} = 1 - \frac{e^{-\left[\frac{3}{J+1} \right] \left(\frac{T_f}{T} \right)}}{J}. \quad (2-53)$$

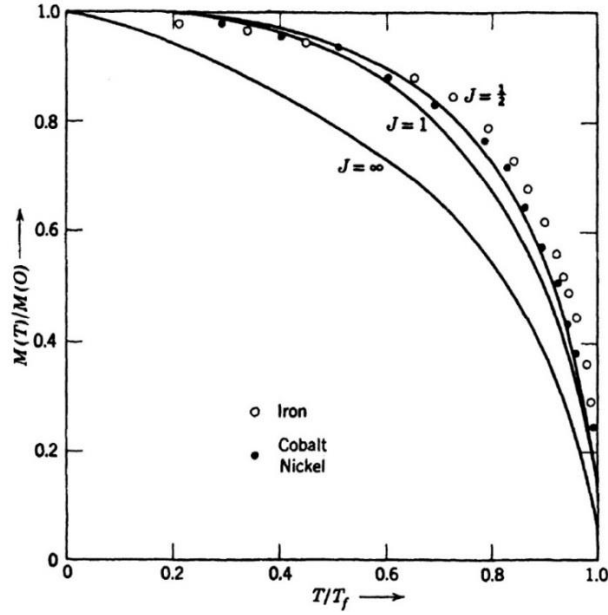


Figure 2.4 The spontaneous magnetization as a function of temperature. The solid lines are obtained from theory, while the points represent experimental data [22].

For temperatures close to the ferromagnetic Curie point, one finds the following expression

$$\left(\frac{M(T)}{M(0)}\right)^2 = \frac{10}{3} \frac{(J+1)^2}{J^2 + (J+1)^2} \left(1 - \frac{T}{T_f}\right). \quad (2-54)$$

According to this equation, the magnetization disappears continuously but has an infinite slope at the Curie temperature.

From an experimental point of view, due to the various magnetic domains of a ferromagnetic specimen, it is not feasible to measure the spontaneous magnetization of a single domain. Thus experimentally one applies external magnetic fields powerful enough to remove the domain structure and orient the magnetization vector along the direction of the field. Magnetic fields above 1 kOe are usually sufficient for many ferromagnetic materials to fulfill this purpose. For fields up to 30 kOe the magnetization is found to follow the empirical relationship [17]

$$M_H = M_s(T) \left(1 - \frac{a}{H} - \frac{b}{H^2}\right) + cH. \quad (2-55)$$

In (2-55), M_H is the magnetization component along the field direction and $M_s(T)$ is the saturation magnetization. a , b , and c are small constants. At very small temperatures and very high dc magnetic fields, the magnetization reaches a limit called the absolute saturation magnetization, $M_s(0)$. For temperatures below $\sim 0.8 T_f$ the difference between saturation and spontaneous magnetization is negligible. Near the ordering temperature (Curie point), the difference is around 1% which is predicted in the Weiss theory [17]. In figure 2.5, the spontaneous magnetization curves of the important transition metal elements, iron and nickel are shown. The fit to the experimental data suggests that the magnetism in these elements originate

mainly from their spin angular momentum rather than their orbital angular momentum. The Weiss theory leads to a power 2 law governing the spontaneous magnetization [17], whereas the fit with experimental data shows a power 3/2 law relation between spontaneous magnetization and the temperature given below

$$\frac{M(T)}{M(0)} = (1 - A_{\text{exp}} T^{3/2}), \quad (2-56)$$

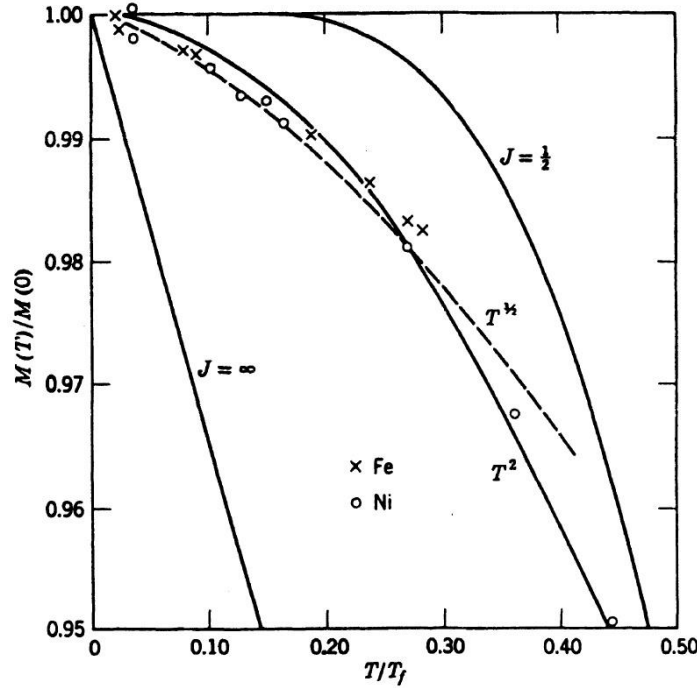


Figure 2.5 Spontaneous magnetization near absolute zero. The power 3/2 law fits better than the power 2 law predicted from Weiss theory [17].

2.4.2.1.2 The paramagnetic region

For temperatures above the ferromagnetic ordering temperature, T_f , the spontaneous magnetization vanishes. However, if one applies an external magnetic field, magnetization is produced. Assuming that the external magnetic field is not strong enough to produce saturation effects, the magnetization can be expressed by

$$M = \frac{ng\mu_B(J+1)}{3} x, \quad (2-57)$$

where $x = \frac{Jg\mu_B}{k_B T} (H_{\text{ext}} + N_W M)$. Upon substituting x into (2-57), one obtains an expression for the magnetic susceptibility as

$$\chi = \frac{M}{H_{\text{ext}}} = \frac{C}{T - \theta}, \quad (2-58)$$

where the constant $C = \frac{ng^2\mu_B^2J(J+1)}{3k_B}$ and $\theta = N_W \frac{Ng^2\mu_B^2J(J+1)}{3k_B} = N_W C$. In figure 2.6, the reciprocal of ferromagnetic susceptibility above the ordering temperature is plotted against temperature.

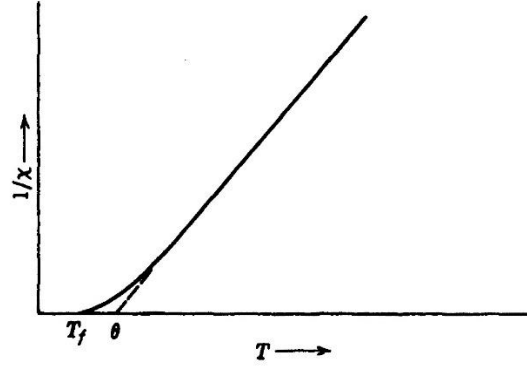


Figure 2.6 The reciprocal of the susceptibility in terms of temperature above the ferromagnetic ordering point, T_f . θ is the paramagnetic Curie point. For temperatures a few degrees above the ordering temperature, the Curie-Weiss law of paramagnetism is realized [17].

2.4.2.2 The quantum mechanical approach to ferromagnetism

The origins of the molecular field theory lie in quantum mechanics. In what follows, two main approaches based on the quantum mechanical theory of ferromagnetism are presented. The first of these approaches considers the models developed by Werner Heisenberg, and the second one is based on band theories of ferromagnetism.

2.4.2.2.1 The Heisenberg model(s) of ferromagnetism

Werner Heisenberg explained the molecular fields as the result of quantum mechanical exchange interaction [23] with no classical analog. The details of Heisenberg's theory on ferromagnetism can be found in advanced text books on quantum mechanics.

Heisenberg's theory is based on the Heitler-London method developed for the hydrogen molecule and is discussed briefly here.

According to fermion statistics, the state describing a many-particle fermion system should be anti-symmetric upon exchange of any two particles. For the (pair of) electrons in a hydrogen atom the possible configuration of the wave functions are:

$$\varphi_{\text{sym}}(1,2)\chi_{\text{anti}}(1,2), \quad (2-59)$$

or

$$\varphi_{\text{anti}}(1,2)\chi_{\text{sym}}(1,2), \quad (2-60)$$

where $\varphi_{\text{sym}}(1,2)$ and $\varphi_{\text{anti}}(1,2)$ are the symmetrical and anti-symmetrical spatial wave functions respectively, whereas $\chi_{\text{anti}}(1,2)$ and $\chi_{\text{sym}}(1,2)$ are the anti-symmetrical and

symmetrical spin wave functions, respectively. In explicit form, the wave functions of (2 -59) and (2 - 60) are written in terms of single-electron wave functions as

$$\psi_I = A[\varphi_a(1)\varphi_b(2) + \varphi_a(2)\varphi_b(1)][\chi_+(1)\chi_-(2) - \chi_+(2)\chi_-(1)], \quad (2 - 61)$$

and

$$\psi_{II} = B[\varphi_a(1)\varphi_b(2) - \varphi_a(2)\varphi_b(1)] \begin{cases} \chi_+(1)\chi_+(2) \\ [\chi_+(1)\chi_-(2) + \chi_+(2)\chi_-(1)], \\ \chi_-(1)\chi_-(2) \end{cases} \quad (2 - 62)$$

In (2 - 61) and (2 - 62), the $\varphi_i(j)$ represent the one-electron wave functions when electron j ($j = 1,2$) is in state i ($i = a, b$), and χ_+ and χ_- are the spin eigenstates for spin-up and spin-down configurations respectively. The coefficients A and B are normalization factors. Now if the electrons interact with a known Hamiltonian H_{12} , such as a Coulomb potential, the energies of the electronic states are increased (or decreased) by $E = \int \psi^* H_{12} \psi d\tau$ where $d\tau$ is an infinitesimal element of volume. The corresponding interaction energies for ψ_I and ψ_{II} in (2 - 61) and (2 - 62) are, respectively,

$$E_I = A^2(K_{12} + J_{12}), \quad (2 - 63)$$

and

$$E_{II} = B^2(K_{12} - J_{12}), \quad (2 - 64)$$

where K_{12} and J_{12} are defined below

$$K_{12} = \int \varphi_a^*(1)\varphi_b^*(2)H_{12}\varphi_a(1)\varphi_b(2)d\tau_1d\tau_2, \quad (2 - 65)$$

and

$$J_{12} = \int \varphi_a^*(1)\varphi_b^*(2)H_{12}\varphi_a(2)\varphi_b(1)d\tau_1d\tau_2, \quad (2 - 66)$$

K_{12} is the average Coulomb interaction energy and J_{12} is the so-called exchange integral and is a direct result of the indistinguishability of electrons.

For the hydrogen molecule, J_{12} is negative, hence in the ground state the spins are anti-parallel [equation (2 - 61)]. In ferromagnetism, the spin are parallel, thus J_{12} must be positive.

In figure 2.7, the typical variations of the exchange integral in terms of interatomic distance is shown. This diagram best describes situations in which the interatomic spacing is large compared to radii of the orbitals [17]. Hence, J_{12} is most likely to be positive for d and f wave functions for atoms of some transition metal and rare earth elements. J_{12} is positive for Fe, Ni, Co, and Gd. For Mn and Cr, although it is negative, in some of their compounds and alloys it is positive. The possible explanation is that, there is a change in the interatomic spacing in alloys that favor ferromagnetism [17].

The energy of the two states of the two-electron system in terms of the electron spins is given by [17]

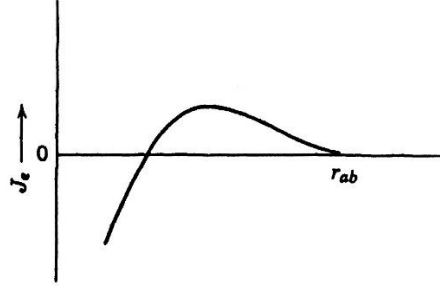


Figure 2.7 Schematic variation of the exchange integral as a function of the interatomic distance, r_{ab} .

$$E = K_{12} - \frac{1}{2}J_{12} - 2J_{12}\mathbf{s}_1 \cdot \mathbf{s}_2. \quad (2 - 67)$$

In problems concerning ferromagnetism, it is the spin coupling term (third term in (2 – 67)) that is of interest. In the quantum mechanical operator form, this term is known as the exchange Hamiltonian, $\mathcal{H}$. Extending this concept to a solid and assuming that the exchange integral in a solid is negligible except for nearest neighbors, the exchange Hamiltonian for a given atom, i , is given as

$$\mathcal{H} = -2 \sum_j J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j, \quad (2 - 67)$$

where the summation runs over all nearest neighbors of atom i . In (2 – 67), the total atomic spins are defined as the vector sum of the individual spins, in other words, the total spin of atom k , for instance is given by $\mathbf{S}_k = \sum \mathbf{s}_k$. If the exchange integral, J_{ij} , in (2 – 67) is isotropic, that is if it is the same for any pair of particles, then (2 – 67) becomes

$$\mathcal{H} = -2J_e \sum_j \mathbf{S}_i \cdot \mathbf{S}_j, \quad (2 - 68)$$

where J_e is the isotropic exchange integral. The exchange Hamiltonian of the entire crystal is given by summing over all atoms which is given below

$$\mathcal{H} = -2J_e \sum_{i \neq j} \sum_j \mathbf{S}_i \cdot \mathbf{S}_j. \quad (2 - 69)$$

The quantum mechanical theory of ferromagnetism is followed by solving Schrödinger's equation for the above Hamiltonian. A number of methods for solving the Hamiltonian above are developed which are briefly stated below but not solved. For further reading, the reader is referred to the citations in the bibliography.

The problem of solving for the Hamiltonian (2 – 69) is that only for very low or very high temperatures an exact solution exists. For moderate temperatures further approximations must be made.

In the method developed by Ising, which is known as the *Ising model*, the exchange Hamiltonian of (2 – 69) is solved by assuming that the instantaneous values of neighboring spins may be replaced by their time averages. For a comprehensive review of the Ising model, the reader is referred to the Ising's original article [24].

Another model for solving the exchange Hamiltonian of (2 – 69) which applies in magnetic domain theory, is to consider the spin matrix operators of (2 – 69) to be classical vectors, this approximation is valid when neighboring spins make small angles with one another. In this case (2 – 68) can be written as $\mathcal{H} = -2J_e S^2 \sum_j \cos\varphi_{ij}$ where φ_{ij} is the angle between directions of the classical spin angular momentum vectors. The solutions to this Hamiltonian is found in Ref. [17].

Other methods are based on series expansions [25]⁴ and approximations involving short-range-order theories [26-28] applied to certain alloys also exist.

2.4.2.2.2 Band model theories of ferromagnetism

In the Heisenberg model based theories of ferromagnetism, the electrons were assumed to be localized in the atoms. However, ferromagnetic materials are mainly metals or alloys, which due to their conduction properties, the assumption of localized electrons is not a reasonable assumption. In this section, two theories based on mobile electrons and holes in unfilled energy bands are briefly discussed.

2.4.2.2.2.1 Collective electron ferromagnetism; Stoner's theory

Collective electron theories are those in which the interactions between the electrons of an electron gas have been considered. The collective electron theory of ferromagnetism was first developed by Stoner [29]. Stoner's theory is based on three simple assumptions:

- 1- The 3d band in the vicinity of the Fermi level is parabolic; in other words the electronic energies are given by $E(k) = \frac{\hbar^2 k^2}{2m^*}$ where m^* is the effective mass of the electrons and k is their related wave vector.
- 2- The exchange energy interaction between the electrons is represented by a molecular field. Thus the interaction energy of an electron with spin parallel or anti-parallel to the magnetization is given by $E_I = \pm N_W M \mu_B$ (the + and – are representatives of anti-parallel and parallel orientations of the electronic spins).
- 3- The electrons and holes obey the Fermi-Dirac statistics

Thus in the presence of an external applied field H_{ext} , the total energy in Stoner's theory will have the following form

$$E = \frac{\hbar^2 k^2}{2m^*} \pm N_W M \mu_B \pm \mu_B H_{\text{ext}}. \quad (2 - 70)$$

The magnetization, M , can be calculated by the product of Bohr's magneton, μ_B , and the difference between the number of electrons with spin parallel, $N_{\uparrow\uparrow}$, and anti-parallel, $N_{\uparrow\downarrow}$, as follows

⁴ The series expansion method considers the ferromagnetic susceptibility to be written in a form of a series $\chi = \frac{ng^2\mu_B^2 S(S+1)}{3k_B T} \sum \frac{a_n}{t^n}$ where $t = \frac{k_B T}{J_e}$.

$$M = \mu_B(N_{\uparrow\uparrow} - N_{\uparrow\downarrow}) = \mu_B \int \{f_{FD}[E(k) - N_W n \mu_B^2] - f_{FD}[E(k) + N_W n \mu_B^2]\} \frac{D(E)}{2V} dE, \quad (2-71)$$

where f_{FD} is the Fermi-Dirac distribution function, $D(E)dE$ is the density of states, and V is the magnetic specimen's volume.

At absolute zero, (2-71) in Stoner's theory becomes [17]

$$M = \frac{\mu_B}{6\pi^2} \left(\frac{2m^*}{\hbar^2} \right)^{3/2} [(E_F + N_W n \mu_B^2)^{3/2} - (E_F - N_W n \mu_B^2)^{3/2}], \quad (2-72)$$

where E_F is the Fermi energy.

The relative magnetization defined as $\zeta(0) = \frac{M(0)}{n\mu_B}$ depends on the magnitude of the exchange energies compared to the Fermi energy and its value lies between 0 and 1.

At finite temperatures, the magnetization is found via numerical methods [29] and details are not given here, only the results are plotted in figure 2.8. In this figure the (relative) magnetization and the reciprocal of susceptibility in Stoner's theory are plotted as functions of $\frac{T}{T_f}$. In figure 2.8 the left ordinate represents the relative magnetization at temperature T to that of absolute zero, and the right ordinate is proportional to the reciprocal of susceptibility as [17]

$$\frac{\zeta(T)}{\zeta(0)} \frac{\mu_B H}{k_B T_f} = \frac{\mu_B M(0)}{k_B T_f} \frac{1}{\chi}. \quad (2-73)$$

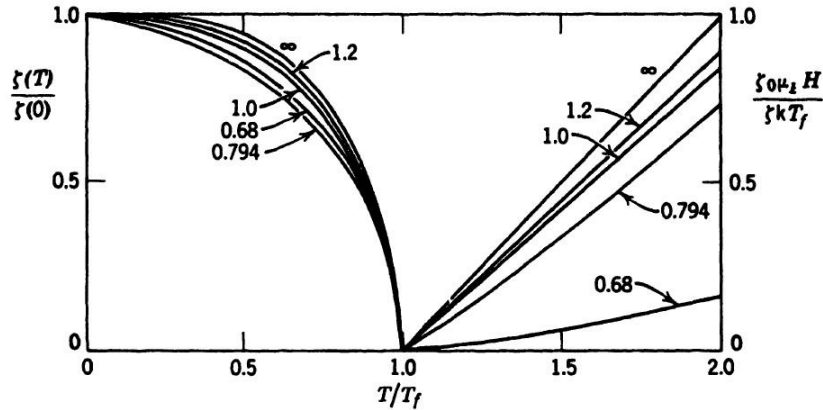


Figure 2.8 The magnetization and reciprocal of the susceptibility as a function of temperature calculated from the theory of collective electron ferromagnetism [17].

2.4.2.2.2 The theory of Vonsovsky and Zener

In this section, the theory proposed by Vonsovsky and Zener [30,31] which is the second of the mobile electron theories of ferromagnetism, is presented. This theory is an intermediate situation between the theories based on Heisenberg's model and that of Stoner in a sense that here the 3d electrons are considered to be localized at the atoms. In this theory, the mobile

electrons are the 4s conduction electrons which interact with the 3d electrons via the exchange interaction.

In Vonsovsky's theory, the exchange interaction between the 3d shells of neighboring atoms aligns the spins of the 3d shells. This forms an internal field that interacts with the conduction electrons. As a result more conduction electrons will have their spins parallel than anti-parallel to the spin direction of the ion cores. This effect corresponds to an effective number of about 0.15 μ_B per atom.

In Zener's theory, the spin energy per atom is given by

$$E_{\text{spin}} = \frac{1}{2}\alpha S_d^2 - \kappa S_d S_s + \frac{1}{2}\gamma_s S_s^2, \quad (2-74)$$

where S_d and S_s are the average values per atom of the spin components along the magnetization direction of the 3d and 4s electrons, respectively. In (2-74), α , κ , and γ_s are material dependent parameters which are found experimentally. The first term represents the exchange energy of the *d-d* shell interaction, the second term, the exchange energy of the *s-d* interaction, and the last term is the increase in kinetic energy of the conduction electrons due to their polarization. For $S_s = \frac{\kappa}{\gamma_s} S_d$, the spin energy is minimized to $\frac{1}{2}\left(\alpha - \frac{\kappa^2}{\gamma_s}\right)$ and this leads to a Heisenberg exchange energy of $J_e = \frac{1}{4}\left(\alpha - \frac{\kappa^2}{\gamma_s}\right)$.

Figure 2.9 illustrates schematically the theory of Vonsovsky and Zener.

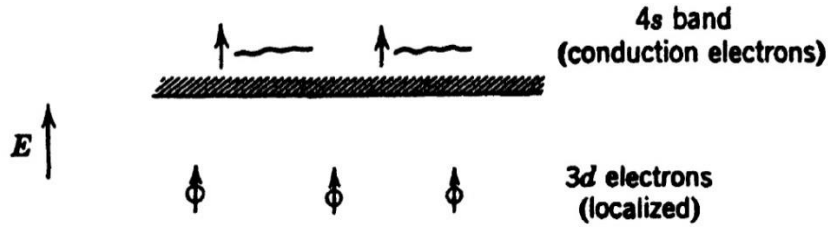


Figure 2.9 The Vonsovsky-Zener model.

The theory of ferromagnetism and its applications extend well beyond what was introduced here. The objective of this section was a basic and formal understanding of the phenomena of ferromagnetism in matter which is sufficient to understand and interpret the relevant results in chapter 5.

2.5 Antiferromagnetism

2.5.1 Introduction

In this section, the phenomenon of *antiferromagnetism*, (AFM) is presented. Among the studied compounds in this thesis, $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$ was found to favor antiferromagnetic ordering as its predominant magnetic phase (in low temperatures). The appearance of iron in this compound alone, suggests the existence of some kind of magnetic ordering in this material. Therefore a brief theoretical review of the antiferromagnetic phase seems necessary in order to understand the physics of antiferromagnetism in $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$.

Antiferromagnetism in a substance occurs when the coupling of the magnetic moments of the individual constituents (whether atoms or molecules) strongly favors the anti-parallel orientation. It was proposed by Néel that an antiferromagnetic solid can be pictured as if it was composed of two sub-lattices, one of whose spins tend to align anti-parallel to those of the other [32]. Thus the net magnetic moment of the antiferromagnetic material is zero. By means of neutron diffraction techniques one can experimentally study Néel's hypothesis to uncover the arrangements of the magnetic dipole moments in a material. It turns out that the variety of different antiferromagnetic orderings is much richer than Néel's simple model suggests. In fact, in nature many different arrangements of antiferromagnetic orderings appear; from different types of 2D antiferromagnetic orderings such as striped, checkerboard, and blocked checkerboard antiferromagnetic ordering to more complicated arrangements such as spiral and triangular orderings.

In what follows, is a brief introduction to some of the most important physical theories of antiferromagnetism.

2.5.2 The molecular field theory of antiferromagnetism

The molecular field theory of antiferromagnetism is presented here for one of the simplest antiferromagnetic orderings. A body-centered cubic structure can be considered to be composed of two interpenetrating cubic cells along the diagonal direction, such that the corners of one cell are at the centers of the other cell. In this picture the two cubic sub-lattices named *A* and *B*, have their dipole moments aligned anti-parallel with one another [33]. In other words an atom at an *A* site is in anti-parallel spin configuration with its 6 nearest neighbors which are atoms on *B* sites and vice versa.

In this model, if one only considers the interactions of a dipole moment with dipole moments of its nearest and next nearest neighbors, the molecular fields on the atomic sites of *A* and *B* will have the following form:

$$\mathbf{H}_{mA} = -N_{AA}\mathbf{M}_A - N_{AB}\mathbf{M}_B \quad , \quad \mathbf{H}_{mB} = -N_{BA}\mathbf{M}_A - N_{BB}\mathbf{M}_B \quad (2 - 75)$$

In (2 – 75), N_{ij} is the molecular field constant for nearest neighbor interactions if $i \neq j$, and for next nearest neighbor interactions if $i = j$. $\mathbf{M}_A$ and $\mathbf{M}_B$ are the magnetizations of the sub-lattices *A* and *B*, respectively. If one assumes that the lattice basis is monatomic, then the same type of

atoms occupy the A and B sites, and thus $N_{AA} = N_{BB} = N_{ii}$, and $N_{AB} = N_{BA}$. If an external magnetic field, $\mathbf{H}_{\text{ext}}$ is applied to the system of sub-lattices, the fields at sites A and B can be expressed by

$$\mathbf{H}_A = \mathbf{H}_{\text{ext}} - N_{ii}\mathbf{M}_A - N_{AB}\mathbf{M}_B \quad , \quad \mathbf{H}_B = \mathbf{H}_{\text{ext}} - N_{AB}\mathbf{M}_A - N_{ii}\mathbf{M}_B \quad (2-76)$$

Similar to the sections on paramagnetism and ferromagnetism, the magnetizations and Brillouin functions for the sublattices A and B are given by

$$M_A = \frac{1}{2}ng\mu_B SB_S(x_A) \quad , \quad M_B = \frac{1}{2}ng\mu_B SB_S(x_B) \quad (2-77)$$

where $x_A = \frac{Sg\mu_B}{k_B T} H_A$, $x_B = \frac{Sg\mu_B}{k_B T} H_B$, $B_S(x_A) = \frac{2S+1}{2S} \coth \frac{2S+1}{2S} x_A - \frac{1}{2S} \coth \frac{x_A}{2S}$, and $B_S(x_B) = \frac{2S+1}{2S} \coth \frac{2S+1}{2S} x_B - \frac{1}{2S} \coth \frac{x_B}{2S}$.

The ordering (Néel) temperature in an antiferromagnetic substance indicated by T_N is defined as the temperature above which the ordered anti-parallel arrangements of the dipoles disappear. In what follows, the behavior of the antiferromagnetic model developed above, is presented at temperatures above and below the ordering temperature. A brief discussion on the transition between paramagnetism and antiferromagnetism under an external applied field and its effect on the Néel temperature is given.

2.5.2.1 The paramagnetic region, $T > T_N$

Above the Néel temperature, there is no magnetic ordering in an antiferromagnetic substance. From a classical point of view, due to thermal agitations, the dipole moments orient themselves in random directions which results in a net zero magnetization. However, subject to an external magnetic field, a small magnetization is induced. If the applied field is not strong enough to consider saturation effects, one can replace the Brillouin function by the first term in (2-50), $B_S(x) \approx \frac{S+1}{3S} x$. In this case the magnetization of the sub-lattices A and B become

$$M_A = \frac{ng^2\mu_B^2 S(S+1)}{6k_B T} H_A \quad , \quad M_B = \frac{ng^2\mu_B^2 S(S+1)}{6k_B T} H_B. \quad (2-78)$$

Substituting the magnitude of the fields in equations (2-76) into their corresponding equations in (2-78), and regarding the total magnetization as $M = M_A + M_B$, one arrives at

$$M = \frac{ng^2\mu_B^2 S(S+1)}{6k_B T} [2H_{\text{ext}} - (N_{ii} + N_{AB})M]. \quad (2-79)$$

Rearranging the terms to solve for M , the antiferromagnetic susceptibility, $\chi_{\text{afm}} = \frac{M}{H}$, becomes

$$\chi_{\text{afm}} = \frac{C}{T+\theta}, \quad (2-80)$$

where $C = \frac{ng^2\mu_B^2 S(S+1)}{6k_B T}$, and $\theta = \frac{1}{2}C(N_{ii} + N_{AB})$. In general since the molecular field constant for nearest neighbor interactions is larger than that of next nearest neighbor interactions, θ is positive. In figure 2.10, the reciprocal of the magnetic susceptibility is plotted against

temperature for three cases: The Curie law of (2 – 10), the Curie-Weiss law of (2 – 11), and (2 – 80).

2.5.2.2 At the Néel temperature, $T = T_N$

The equations of (2 – 78) combined with (2 – 76) and in the absence of an external applied field yield

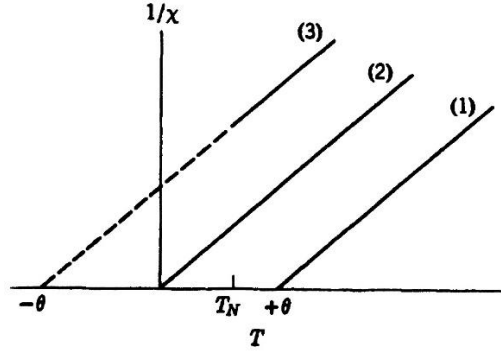


Figure 2.10 Plot of $\frac{1}{\chi}$ versus temperature. Curve (1), $\chi = \frac{C}{T-\theta}$ (Curie-Weiss law); curve (2), $\chi = \frac{C}{T}$ (Curie's law), and curve (3), $\chi = \frac{C}{T+\theta}$ [17].

$$M_A = \frac{C}{2T}(-N_{ii}M_A - N_{AB}M_B) \quad , \quad M_B = \frac{C}{2T}(-N_{AB}M_A - N_{ii}M_B). \quad (2-81)$$

Upon solving the pair of equations in (2 – 81) for nonzero magnetizations, one arrives at an expression for the Néel temperature

$$T_N = \frac{1}{2}C(N_{AB} - N_{ii}). \quad (2-82)$$

Substituting C from (2 – 80) gives the ratio of the paramagnetic temperature, θ , to the Néel temperature, T_N as below

$$\frac{\theta}{T_N} = \frac{N_{AB} + N_{ii}}{N_{AB} - N_{ii}}. \quad (2-83)$$

2.5.2.3 Susceptibility below the Néel temperature, $T < T_N$

In figure 2.11, the susceptibility of an antiferromagnetic substance is given in terms of temperature. As one can observe from this figure, the Susceptibility below the ordering temperature for a given spin, splits into two branches; a constant function, $\chi_{\perp}$ which is the susceptibility perpendicular to the applied external field, and $\chi_{\parallel}$, which is the susceptibility in the direction parallel to the applied field. Here, the functional form of the susceptibilities below the Néel temperature are stated without proof. A complete derivation for $\chi_{\perp}$ and $\chi_{\parallel}$ is given in the case of a uniaxial crystal in Ref. [17].

$$\chi_{\parallel} = \frac{n\mu_B^2 g^2 S^2 \left(\frac{\partial B_S}{\partial x}\right)_{x_0}}{k_B T + \frac{1}{2}(N_{ii} + N_{AB})\mu_B^2 g^2 S^2 N \left(\frac{\partial B_S}{\partial x}\right)_{x_0}}, \quad \chi_{\perp} = \frac{1}{N_{AB}} \quad (2-84)$$

In the equations above, $x_0 = \frac{g\mu_B S}{k_B T} [(N_{AB} - N_{ii})M_0]$, where M_0 is the magnetization of sub-lattice A in the absence of the external magnetic field.

In general, the applied magnetic field will make an angle, α , with the easy direction of the uniaxial crystal, in this case the antiferromagnetic susceptibility is expressed as

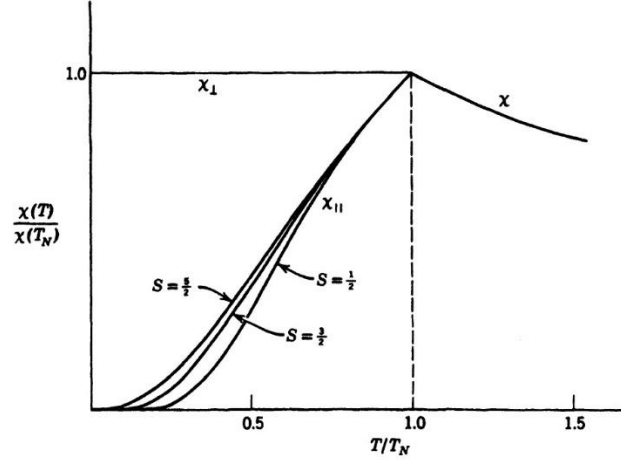


Figure 2.11 The susceptibility of an antiferromagnetic material as a function of temperature in reduced units [34].

$$\chi_{\text{afm-sc}} = \chi_{\parallel} \cos^2 \alpha + \chi_{\perp} \sin^2 \alpha. \quad (2-85)$$

For a powdered or polycrystalline material, one takes the average of (2-85) over the unit sphere to obtain

$$\chi_{\text{afm-pc}} = \chi_{\parallel} \langle \cos^2 \alpha \rangle + \chi_{\perp} \langle \sin^2 \alpha \rangle = \frac{1}{3} \chi_{\parallel} + \frac{2}{3} \chi_{\perp}. \quad (2-86)$$

2.5.2.4 The paramagnetic-antiferromagnetic transition in the presence of an applied magnetic field

Under the application of an external magnetic field, the Néel temperature will be shifted to lower values. This fact is justified if one considers an antiferromagnetic material at a temperature just below the Néel temperature when no external field is applied. Now if the field is turned on, (and for simplicity assuming the field is parallel to the magnetization of sub-lattice A), as it increases, the magnetization of the sub-lattice B decreases until eventually becomes zero. Further increase in the field and the magnetization of sub-lattice B increases in parallel direction to that of sub-lattice A until it's magnitude coincides with the magnetization of sub-lattice A . It is clear

that a larger field would have been needed for this coincidence if the sample was at a lower temperature.

2.5.3 The super-exchange interaction

At this point, the origins of the molecular field theory in the case of antiferromagnetism are presented based on the quantum mechanical exchange interactions of Heisenberg. In the Heisenberg theory, the sign of the exchange integral in the Hamiltonian given by (2 – 68) for ferromagnetism has to be changed for the antiferromagnetic case. In other words, J_e is negative in the case of antiferromagnetism, thus the corresponding Hamiltonian in (2 – 68) changes to

$$\mathcal{H} = 2|J_e| \sum_j \mathbf{S}_i \cdot \mathbf{S}_j. \quad (2 - 87)$$

It turns out that due to its strength, the exchange interaction is not the only source of antiferromagnetic coupling [17] in antiferromagnetic compounds. In fact, the next nearest neighbor interactions in some antiferromagnetic compounds such as MnO is stronger than the nearest neighbor interactions. Kramers [17] proposed a super-exchange mechanism for the exchange interaction in some paramagnetic salts. Anderson and others have improved the super-exchange theory of Kramers [17].

In figure 2.12, the idea of super-exchange interaction is shown for the well-known MnO antiferromagnet in which the ions Mn^{2+} and O^{2-} are aligned collinearly. Four electrons are considered. In the ground state configuration, (figure 2.12(a)), two p electrons of the O^{2-} ion are aligned anti-parallel to each other and one d in each of the Mn^{2+} ions are shown in anti-parallel configuration. Due to the elongated shape of the p orbital there is a good chance that one of the p electrons of the oxygen ion transfers to the d orbital of a manganese ion, (figure 2.12(b)). In this excited state, there will be a coupling between electrons in d_1 and d'_1 states and also between the remaining oxygen's electron and the one electron from the other manganese ion. The complete exchange of the electrons on the magnetic ions are illustrated in figures 2.12(c) and 2.12(d).

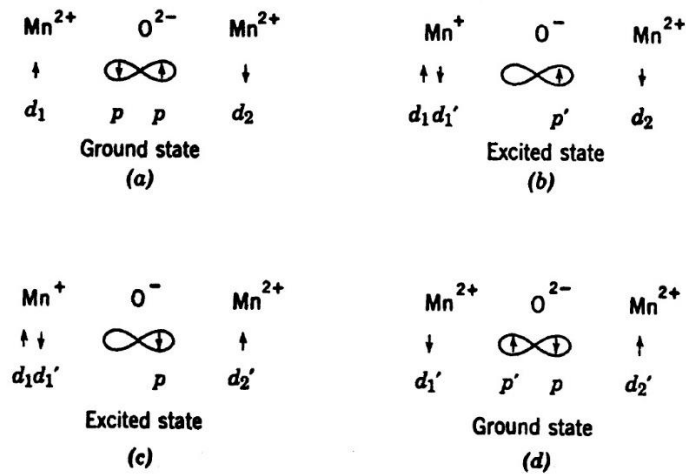


Figure 2.12 The super-exchange interaction in MnO [17].

The bond joining two neighboring manganese ions with the intervening oxygen ion are at right angles (figure 2.13). Thus the dumbbell-shaped p orbital of the oxygen atom overlaps appreciably only with one of the neighboring magnetic ions making the nearest neighbor interaction to be rather weak compared to the next nearest neighbor interaction.

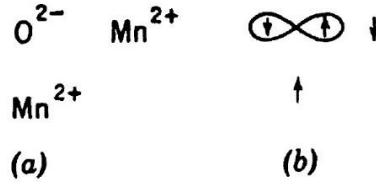


Figure 2.13 The nearest neighbor interaction in MnO [17].

The molecular field theory successfully predicts many of the main features from experimental data, however there are some deficiencies in the theory which are not discussed here. Other theories such as the series expansion method, the Bethe-Peierls-Weiss method, and spin waves have been developed to overcome the discrepancies. A comprehensive study on these theories is found in Ref. [17].

2.6 Superconductivity

In this section, a brief survey on the topic of superconductivity is introduced. Among the alloys and compounds studied in this research, $(Li_{0.8}Fe_{0.2})OHFeSe$ is found to be a superconductor below 40 K [35,36]. Therefore, in this stage a somewhat elementary review on superconductors is presented. However, this introduction is mainly concentrated on the magnetism of superconductivity, so other aspects such as thermoelectric properties, specific heat, and acoustic properties are not discussed. An elementary and qualitative introduction to these features can be found in [37].

2.6.1 Introduction

In many metals without any magnetic ordering, still a spectacular feature exists at very low temperatures; another form of an electronically ordered state, known as the superconducting state is established. Historically, superconductivity was discovered in 1911 by H. Kammerlingh Onnes. While working on a sample of mercury, Onnes realized that below 4.2 K the resistance of mercury abruptly disappears and persistent currents flow through it. It has been found that more than 20 metallic elements can become superconductors and certain semiconductors under convenient conditions can become superconducting [37]. Among alloys, thousands show superconducting properties [38] and various measurements have been conducted on them.

In what follows, the most important properties of superconductors are stated:

1. The most remarkable characteristic of a superconductor is the lack of DC electrical resistivity. Even in the absence of a driving field, electrical currents in a superconductor persist without any discernible decay.

2. A superconductor can behave as a perfect diamagnet. A typical superconducting material embedded in an external magnetic field carries surface currents. These surface currents produce an additional magnetic field that exactly cancels the external field within the superconductor.
3. The band-structure of a superconductor is such that a band gap centered at the Fermi energy is present. One can therefore extract from or add an electron to the set of allowed single-electron levels. This is obtained only if the absolute value of the difference between the fermi energy and the single-electron energy exceeds half of the bandgap mentioned above. The energy gap increases as temperatures drop and approach a maximum value at very low temperatures.

2.6.2 The transition (critical) temperature

The transition, or critical, temperature, T_C , is the temperature at which the transition between the normal state and the superconducting state takes place. This temperature is material dependent and varies (lowers) in the presence of an external magnetic field. Above T_C the material is in a normal state, below T_C the superconducting state is established. The critical temperature can also depend on the chemical purity and crystalline perfection of the sample. In fact, inhomogeneities in the purity and strain of the sample generally tend to broaden the temperature range of the transition between the normal and superconducting states. In particular, for a pure well-annealed sample, the transition temperature range can be as small as 1 mK [39].

2.6.3 The magnetic properties of superconductors

In this section, perfect diamagnetism and the critical magnetic field in superconductors are presented and discussed.

2.6.3.1 Perfect diamagnetism in superconductors

In the ordinary state of a metal, external magnetic fields can penetrate within the interior of the metal. As mentioned in sections 2.2 and 2.3, a normal metal is diamagnetic or weakly paramagnetic. In its superconducting state however, the metal does not allow the external magnetic fields to penetrate into its interior. This phenomena is known as *the Meissner-Ochsenfeld effect* which states that if a metal is cooled to its superconducting state, the magnetic flux is abruptly expelled from it. In this process, surface currents appear such that their magnetic fields cancel those of the interior⁵.

2.6.3.2 The critical field in superconductors

At temperatures T , below the transition temperature T_C of a superconductor, if one applies a magnetic field, H , a certain amount of energy is used in order to create the surface currents

⁵ It should be noticed that perfect conductivity implies a time-independent magnetic field in the interior. However, in a superconductor the magnetic field is not only time-independent, but also zero.

needed to cancel the interior magnetic field. At high enough magnetic fields, the superconductor will change back to its normal state, allowing the external field to penetrate through it. In general, the way in which the penetration of the field occurs upon increasing magnetic field strengths, depends on the geometry of the specimen. In the case of long, thin cylindrical shaped superconductors with their axes parallel to the applied magnetic field, two distinct types of behavior are observed:

Type I superconductors

In figure 2.14(a), the phase boundary between the normal state and the superconducting state for what is known as type I superconductors is depicted. To a good approximation, the shape of this curve can be given by the following equation:

$$H_c(T) = H_c(0) \left[1 - \left(\frac{T}{T_c} \right)^2 \right], \quad (2 - 88)$$

In (2 – 88), $H_c(T)$ is the critical field (defined below) at temperature T and $H_c(0)$ is the critical field at absolute zero. At any given temperature (below the transition temperature) the maximum magnetic field for which under the superconducting state is established is known as the critical field, $H_c(T)$. As the temperature drops the critical magnetic field increases and at absolute zero it reaches a maximum. For fields above the critical field the magnetic field penetrates the specimen and superconductivity diminishes.

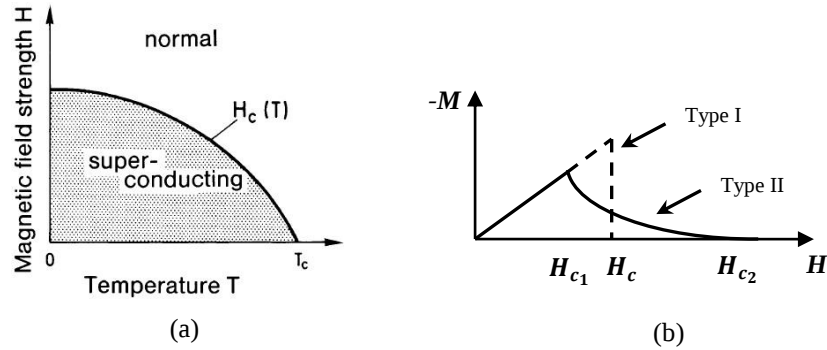


Figure 2.14 (a) The phase boundary diagram in type I superconductors [40]. (b) Magnetization in terms of applied magnetic field for type I and type II superconductors [39].

Type II superconductors

In type II superconductors two critical fields are present, $H_{c1}(T)$ and $H_{c2}(T)$. Assuming $H_{c2}(T)$ to be greater than $H_{c1}(T)$, for external fields below $H_{c1}(T)$ there is no penetration of the flux into the specimen. If the external field is greater than $H_{c2}(T)$, then the specimen reverts to the normal state and the magnetic flux penetrates perfectly. For external fields between $H_{c1}(T)$ and $H_{c2}(T)$, the flux penetrates partially and the sample is in a so-called *mixed state* which is a microscopic structure of both normal and superconducting states. In figure 2.14(b) schematic

representation of magnetization versus applied field for type I and type II superconductors is given.

Typical critical fields in type I superconductors are about 10^2 Ga well below the transition temperature. However, In so-called “hard” type II superconductors the upper critical field can be as high as 10^5 gauss, which makes type II materials of considerable practical importance in the design of high-field magnets [37].

Superconductivity is much richer in context that was introduced here, and has always been among the active areas of research in solid state physics. For the purpose of this thesis however, what was introduced, is sufficient.

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Chapter three

Mössbauer spectroscopy and X-ray diffractometry

3.1 Mössbauer spectroscopy

3.1.1 Introduction

In 1958, Rudolf Mössbauer discovered the recoilless resonant absorption and emission of gamma rays by atomic nuclei which was later named after him, the *Mössbauer effect*. In figure 3.1, the physical mechanisms leading to the Mössbauer effect is schematically shown.

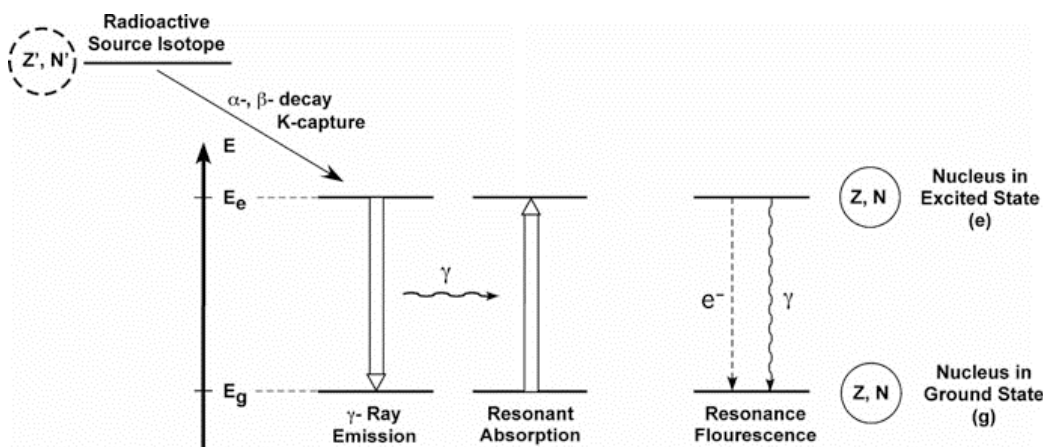


Figure 3.1 Nuclear resonant absorption and emission of gamma radiation known as the Mössbauer effect [1].

According to Figure 3.1, the nucleus of a radioactive isotope, which is generally characterized by its atomic number, Z' , and neutron number, N' , undergoes radioactive decay⁶ (via α decay or β decay or through electron capture). The daughter nucleus, characterized by Z and N , is created to be in one of its excited states, E_e , and later on decays to its ground state, E_g , resulting in the emission of a gamma photon. The generated gamma photon is then (re)absorbed by a nucleus of the same type in its ground state causing it to excite to an excited state (resonant absorption). The excited nucleus reemits the gamma photon and decays back to its ground state⁷ (resonant fluorescence). This process is the underlying mechanism of what is known as the Mössbauer effect.

In Figure 3.2, the natural linewidth of the transition energy between the excited nuclear state and the ground state is shown (the plot is considered at extremely low temperatures where the effects of thermal broadening are minimized).

⁶ For all of the compounds studied in this research, the radioisotope ^{57}Co was used as the parent nucleus for ^{57}Fe Mössbauer spectroscopy measurements.

⁷ Some fraction of the nuclei undergo electron ejection.

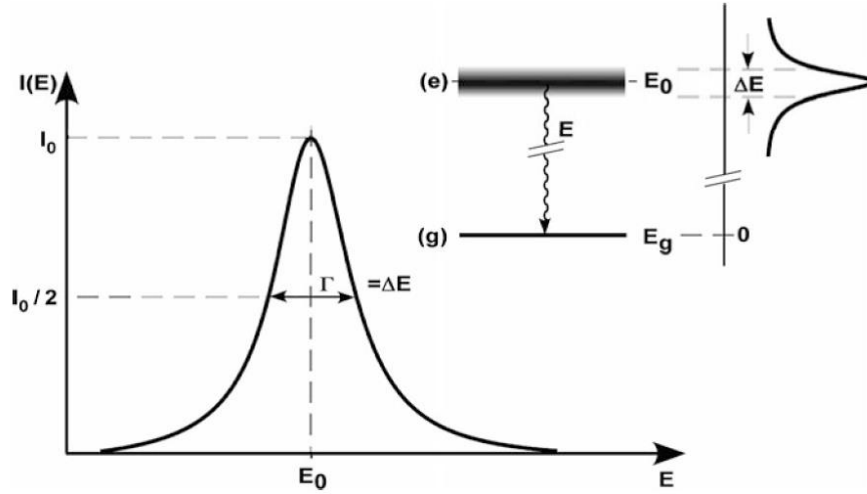


Figure 3.2 The natural linewidth of the nuclear gamma transition energy between the excited state and ground state [1].

The mean lifetime of the excited nuclear state is typically between 10^{-11}s and 10^{-6}s (the lifetime of the first excited state of ^{57}Fe is $1.43 \times 10^{-7}\text{s}$). The transition energy of the γ radiation used for Mössbauer spectroscopy is usually between 10 to 100 keV (for ^{57}Fe Mössbauer spectroscopy, the transition energy is 14.4 keV). The relative widths of nuclear levels are extremely small, typically 13 orders of magnitude smaller than the transition energies ($\frac{\Delta E}{E_0} \approx 10^{-13}$). The full width at half maximum of the natural linewidth (the so-called *Lorentzian profile*), Γ , is a measure of the uncertainty in the energy of the excited nuclear state (for ^{57}Fe , $\Gamma = 4.55 \times 10^{-9}\text{ eV}$).

Prior to Mössbauer's discovery, scientists believed it to be impossible to have resonant emission and absorption of gamma radiation. Their reasoning was based on arguments related to the energy and linear momentum transferred to (or in the case of absorption, delivered by) the nucleus upon gamma radiation. The conservation of momentum and the recoil energy demands the centers of the emission and absorption lines to shift and become widely separated such that essentially no overlap between the emission and absorption lines is possible, thus preventing nuclear resonance. Attempts to increase the degree of overlap were focused on broadening the emission lines via the relativistic Doppler effect. This was done by mounting the source and/or the absorber on transducers to keep them in constant relative motion. As a result, the emission and absorption lines broaden and there exists a chance of some degree of overlap between them.

According to Maxwell-Boltzmann statistics (particularly in gaseous systems), there is a temperature dependent velocity distribution of the particles constituting the system. Various particles in the system can be found to have a wide range (normal distribution) of speeds. Therefore, the energy of the γ rays emitted resulting from transitions of nuclei states will undergo Doppler shifts. On a statistical basis, the profile due to the Doppler shifts related to emission and absorption lines resulting from the recoil of nuclei for sufficiently high γ energies and fast kinetic

motion is Gaussian in shape (on the contrary to the natural linewidth which has a Lorentzian profile).

The Doppler broadening in energy associated with a gas of particles (atoms, and in particular, their nuclei) at a temperature T is given by [1]

$$\Gamma_D = 2\sqrt{E_R k_B T}, \quad (3-1)$$

where E_R is the recoil energy of the nucleus in transitions between ground and excited states. Based on (3-1), one expects that the Doppler broadening would be of the order of the recoil energy. For the 14.4 keV transition energy of ^{57}Fe and a recoil energy of $1.95 \times 10^{-3} \text{ eV}$ at room temperature Γ_D is about 10^{-2} eV . Therefore, there exists a certain probability that nuclei in gases and liquids can compensate the loss due to recoil energy by the Doppler shift. However, the overlap of the absorption and emission lines remains so small that detecting the resonant effect experimentally for gases and liquids is almost impracticable.

From equation (3-1), one might expect that as the temperature decreases the Doppler broadening decreases such that even the small amount of overlap between emission and absorption lines decreases further leading to no resonant effect. However, it turns out that in solids the lower the temperature the more efficient is the nuclear resonant effect. In other words, the Mössbauer effect is best observed at lower temperatures. This phenomenon can be only understood by means of the quantum theory of solids [2]. In what follows, a brief explanation of this phenomenon is given.

In the solid state, it is assumed that the nuclei are physically bound in certain spatial positions (lattice points) and vibrate about these so-called equilibrium points. The amplitudes of these vibrations generally depend on temperature. The order of the vibrational frequencies is $\sim 10^{13} \text{ Hz}$ [3]. On the other hand, the mean transition time of the nuclei is approximately six orders of magnitude longer than the vibration periods. Therefore, one can consider an average of zero displacement of the nuclei during transition times leading to no Doppler shift in the emission profile. One also assumes that the recoil momentum during the nuclear transition will be transferred to the crystal as a whole and, because of the very large mass of the crystal, the impart velocity on the emitting nuclei are almost completely negligible, leading to a vanishing recoil energy:

$$P = M_{\text{crystal}} v_n, \quad v_n \ll 1 \Rightarrow E_R = \frac{1}{2} M_{\text{crystal}} v_n^2 \approx 0. \quad (3-2)$$

(Due to the large mass of the crystal and its vanishing speed, a nonrelativistic description of its kinetic energy is justified).

In the solid state, when the nuclear transition occurs, part of the transition energy may be transferred to the system in a form of lattice vibration excitations, otherwise known as phonons. It has been demonstrated that in these phonon creation (and in the case of absorption, annihilation) processes, the energy transfer is typically of several orders of magnitude larger than the natural linewidth of the nuclear levels, causing resonant effects to become impossible [1]. However, there exists a finite probability of nuclear transitions in a solid without phonon creations or annihilations, known as zero-phonon processes. It is this non-zero probability that corresponds to a fraction of nuclei within a solid that undergo recoil-free emission and absorption of γ rays, leading to the resonant effects. This fraction of nuclei that undergoes zero-

phonon processes is known as the Mössbauer-Lamb factor, f , and it is very much similar to the Debye-Waller factor in X-ray diffraction from solids. A typical f factor of 0.91 is associated with iron at room temperature corresponding to the 14.4 keV nuclear transition [1]. One can consider the recoil-free factor, f , to be related to the local displacement of the nucleus from its equilibrium position x via the following equation [4]

$$f = e^{-\frac{\langle x^2 \rangle E_\gamma}{(hc)^2}}, \quad (3-3)$$

where $\langle x^2 \rangle$ is the mean square displacement or the square of the vibrational amplitude of the nucleus and E_γ is the emitted (absorbed) photon energy. In order to account for the temperature dependence of f for most practical cases one can use the simple Debye model for the phonon frequency distributions. According to the Debye model the phonon frequencies are distributed continuously from 0 up to the so called Debye frequency ν_D and the density of states is proportional to ν^2 [5]. The Debye temperature (of the solid material) is related to the highest phonon energy, $h\nu_D$ and is defined as follows

$$T_D = \frac{h\nu_D}{k_B}. \quad (3-4)$$

The temperature dependence of the recoil-free factor is given by [1]

$$f(T) = e^{\left\{ -\frac{3E_\lambda^2}{k_B T_D M c^2} \left[\frac{1}{4} + \left(\frac{T}{T_D} \right)^2 \int_0^{\frac{T_D}{T}} \frac{x}{e^x - 1} dx \right] \right\}}. \quad (3-5)$$

This expression can be examined in the high- and low-temperature regimes. At extremely low temperatures ($T \ll T_D$) the upper limit of the integral in the exponent approaches infinity

$$\int_0^\infty \frac{x}{e^x - 1} dx = \frac{\pi^2}{6} \Rightarrow f(T) \approx e^{\left\{ -\frac{3E_\lambda^2}{k_B T_D M c^2} \left[\frac{1}{4} + \left(\frac{T}{T_D} \right)^2 \frac{\pi^2}{6} \right] \right\}} = e^{-\frac{E_\lambda^2}{2k_B T_D M c^2} \left(\frac{3}{2} + \frac{\pi^2 T^2}{T_D^2} \right)}. \quad (3-6)$$

As one can observe the exponent varies with temperature in a quadratic fashion. However, in the high-temperature regime, ($T \gtrsim T_D$), a linear behavior in the exponent is observed. One can approximate e^x in the integral in the exponent by $1 + x$ (since x is of the order of $\frac{T}{T_D}$):

$$\int_0^{\frac{T_D}{T}} \frac{x}{e^x - 1} dx \approx \int_0^{\frac{T_D}{T}} dx = \frac{T}{T_D} \Rightarrow f(T) \approx e^{-\frac{3E_\lambda^2 T}{k_B T_D^2 M c^2}}. \quad (3-7)$$

The intensity of the Mössbauer spectrum depends on the recoil-free factor and since the time necessary to obtain a good signal to noise ratio depends on the square of the intensity [1], one can improve the quality of the Mössbauer spectra substantially by cooling the samples down to liquid nitrogen and liquid helium temperatures.

As mentioned earlier, the recoilless emission and absorption of γ rays by nuclei in the solid state, otherwise known as the Mössbauer effect, is a result of zero-phonon processes. The recoil free factor f is the probability of the occurrence of such processes and therefore it is of experimental interest to obtain a larger value for it.

In general, one realizes that the recoil-free factor increases by decreasing the temperature of the system. In general considering different compounds, the higher the Debye temperature, the

larger the recoil-free factor. The recoil-free factor also depends on the transition energies of the Mössbauer nuclei, being larger for smaller transition energies.

3.1.2 Hyperfine interactions

In Mössbauer spectroscopy, hyperfine-interactions refer to the influence of internal electromagnetic fields within the material upon the Mössbauer nucleus. These electromagnetic fields originate mainly from the electrons of the Mössbauer atom and of the neighboring atoms. The fields interact with the electronic charge distribution and magnetic dipole moments of the nucleus, causing a perturbation of its energy levels. In a typical Mössbauer spectrum, the effects of three of the most dominant of these interactions can be detected (*vide infra*). The theory predicts that the perturbations of the energy levels are a consequence of more than three distinct interactions. However, the effects resulting from them cannot be detected in a Mössbauer spectrum for practical reasons.

The three different nuclear hyperfine-interactions will perturb the energy levels of the nucleus in two ways: these interactions result either in a shift in the nuclear energy levels or the degeneracy removal of the nuclear energy states.

The shift in the energy of the nuclear levels is the result of the electric monopole interaction and in scientific literature is technically named the *isomer shift* or the *chemical shift*. This effect is related only to the total charge of the Mössbauer nucleus, regardless of how this charge is spatially distributed. In other words, it is independent of the “shape” of the nucleus.

The degeneracy removal of the nuclear states is a result of two different types of interactions. The *magnetic dipole interaction* is a result of the interaction between the magnetic field and the non-zero magnetic dipole moment of the Mössbauer nucleus. Magnetic fields generated by the electrons of the Mössbauer atom and of the ligands interact with the nucleus’s magnetic dipole moment causing the degenerate nuclear energy states to “split”. This phenomenon is known as the nuclear Zeeman effect. The *electric quadrupole dipole interaction* is a result of the interaction of the electric fields and the “spatial” charge distribution of the Mössbauer nucleus. Since this type of interaction depends on the “shape” of the nucleus, the spatial change in the electric field along the nucleus will introduce splitting in the resonance transition lines between ground and excited levels. The interaction thus, is a result of the existence of a non-zero *electric field gradient* within the Mössbauer nucleus.

These interactions can be understood both from a classical treatment and a quantum mechanical point of view based on a Taylor expansion of the electrostatic potential about the equilibrium position of the Mössbauer nucleus.

3.1.2.1 The Classical approach

For simplicity and with no loss of generality, we shall assume that the nucleus under study is located at the origin of a frame of reference. We will use the Cartesian coordinate system as our frame of reference. In the computational calculations, a spherical system of coordinates is used for the potential expansion (see chapters 4 and 6). One can describe the interaction energy

between the nucleus and the electrostatic potential accordingly (working in the c-g-s system of units where $\frac{1}{4\pi\epsilon_0} = 1$):

$$E_{\text{el}} = \int \rho_{\text{N}}(\mathbf{x}) V(\mathbf{x}) d\mathbf{x}, \quad (3-8)$$

where $\rho_{\text{N}}(\mathbf{x})$ describes the nuclear charge density at $\mathbf{x} = (x_1, x_2, x_3)$ and $V(\mathbf{x})$ is the electrostatic potential due to all other charges at $\mathbf{x}$. The integral is taken over all space with the volume elements defined as $d\mathbf{x} = dx_1 dx_2 dx_3$. Using the general relation $f(\mathbf{x} + \mathbf{a}) = e^{\mathbf{x} \cdot \nabla} f(\mathbf{a})$, one can expand the potential about the position of the nucleus, $\mathbf{x} = \mathbf{0}$:

$$\begin{aligned} V(\mathbf{x}) &= e^{\mathbf{x} \cdot \nabla} V(\mathbf{0}) = \sum_{n=1} \frac{(\mathbf{x} \cdot \nabla)^n}{n!} V(\mathbf{0}) \\ &= V(\mathbf{0}) + \sum_{i=1}^3 x_i \left(\frac{\partial V}{\partial x_i} \right)_0 + \frac{1}{2} \sum_{i,j=1}^3 x_i x_j \left(\frac{\partial^2 V}{\partial x_i \partial x_j} \right)_0 + \dots \end{aligned} \quad (3-9)$$

The first derivatives of the potential with respect to spatial coordinates (with a negative sign) represent the electric field $\mathbf{E}$ and the second derivatives of potential represent the electric field gradient tensor $\vec{V}$ evaluated at the origin:

$$E_i \equiv -\left(\frac{\partial V}{\partial x_i} \right)_0 \quad \text{and} \quad V_{ij} \equiv \left(\frac{\partial^2 V}{\partial x_i \partial x_j} \right)_0. \quad (3-10)$$

Substituting (3-9) into (3-8) and using the simplified notations of (3-10), the electrostatic interaction energy takes the following form:

$$E_{\text{el}} = V(\mathbf{0}) \int \rho_{\text{N}} d\mathbf{x} - \sum_{i=1}^3 E_i \int \rho_{\text{N}} x_i d\mathbf{x} + \frac{1}{2} \sum_{i,j=1}^3 V_{ij} \int \rho_{\text{N}} x_i x_j d\mathbf{x} + \dots \quad (3-11)$$

The first term in this expression represents a constant shift of the interaction energy. The second term represents the electric dipole interaction and based on parity arguments this term vanishes. The terms of higher order than the third term can be considered negligible due to the vanishingly small nuclear moments and interaction energies. Thus, the only relevant term is the second order term. The integral in this term can be written as:

$$\int \rho_{\text{N}} x_i x_j d\mathbf{x} = \frac{1}{3} \int \rho_{\text{N}}(\mathbf{x}) x^2 d\mathbf{x} + \frac{1}{3} \int \rho_{\text{N}}(\mathbf{x}) (3x_i x_j - \delta_{ij} x^2) d\mathbf{x}, \quad (3-12)$$

where $x^2 = x_1^2 + x_2^2 + x_3^2$ and δ_{ij} is the Kronecker delta symbol. The first term is spherically symmetric and (along with the first term in (3-11)) represents the *nuclear monopole moment*. The second term, which is anisotropic and is highly sensitive to the orientation (or shape) of the nucleus, represents the *nuclear quadrupole moment* $\vec{Q}$. One can clearly see that this term is an irreducible second ranked tensor. The first integral in (3-12) can be evaluated by considering the nucleus to have an average mean radius R and a uniform charge distribution with the total charge of $+Ze$. R can be given in terms of the experimental value of the root mean square of the nuclear radius as $R = \sqrt{\frac{5}{3}} \langle x^2 \rangle^{\frac{1}{2}}$ [6]. Therefore, we have

$$\int \rho_N(\mathbf{x}) x^2 d\mathbf{x} = \frac{1}{\frac{4}{3}\pi R^3} Ze \int x^2 d\mathbf{x} = ZeR^2. \quad (3-13)$$

Substituting this result into the second-order term of (3-11) leads to

$$\frac{1}{6} \sum_{i,j=1}^3 V_{ij} ZeR^2 = \frac{ZeR^2}{6} \sum_{i,j=1}^3 V_{ij}. \quad (3-14)$$

In the principle axis system, the electric field gradient tensor is symmetric and the above summation becomes $V_{xx} + V_{yy} + V_{zz}$. According to Poisson's equation, this gives the electronic charge density at the nucleus (apart from a factor of 4π). The electronic charge density can be given as the probability of finding the electron times its charge

$$\begin{aligned} \sum_{i,j=1}^3 V_{ij} &\xrightarrow{\text{principal axis system}} \sum_{i,j=1}^3 V_{ij} \delta_{ij} = \sum_{i=1}^3 V_{ii} = -4\pi\rho(0), \rho(0) = -e|\psi(0)|^2 \\ &\Rightarrow \sum_{i=1}^3 V_{ii} = 4\pi e|\psi(0)|^2. \end{aligned} \quad (3-15)$$

This result primarily assumes that the electronic wave function is normalized to unity

$$-e = \int \rho(0) d\mathbf{x} = -e \int |\psi(0)|^2 d\mathbf{x} \Leftrightarrow \rho(0) = -e|\psi(0)|^2. \quad (3-16)$$

The non-zero electronic charge density on the nuclear site is due to the non-zero probability of the penetration of s shell electrons in the nucleus. By taking into account relativistic effects there is also a non-zero probability of finding $p_{1/2}$ electrons within the nucleus (these non-zero probability densities have been considered when calculating the isomer shift in the calculations).

From (3-15) and (3-13), one deduces a relation for the first term of (3-12), and together with (3-11), the shift in energy due to the electric monopole interaction is

$$E_{\text{I.S.}} = \delta E_{\text{el}} = -\frac{2\pi}{5} Ze^2 R^2 |\psi(0)|^2. \quad (3-17)$$

This gives rise to the so-called *isomer shift* in the Mössbauer spectrum. It is an extremely small shift in energy (of the order of 10^{-8} eV).

The second term of (3-12) represents the nuclear quadrupole moment, $\vec{Q}$. The nuclear quadrupole moment is a second ranked tensor. Out of the nine elements of this tensor, five are independent. This fact is due to the symmetrical nature of the nuclear quadrupole moment and its traceless character

$$Q_{ij} = \int \rho_N(\mathbf{x}) (3x_i x_j - \delta_{ij} x^2) d\mathbf{x} \Rightarrow Q_{ij} = Q_{ji}, i, j = 1, 2, 3. \quad (3-18a)$$

$$\begin{aligned} \text{tr}(\vec{Q}) &= \sum_{i=1}^3 Q_{ii} = \sum_{i=1}^3 \int \rho_N(\mathbf{x}) (3x_i^2 - x^2) d\mathbf{x} \\ &= 3 \int \rho_N(\mathbf{x}) \sum_{i=1}^3 x_i^2 d\mathbf{x} - (\sum_{i=1}^3 1) \int \rho_N(\mathbf{x}) x^2 d\mathbf{x}, \\ \sum_{i=1}^3 x_i^2 &= x^2, \sum_{i=1}^3 1 = 3 \Rightarrow \text{tr}(\vec{Q}) = 0. \end{aligned} \quad (3-18b)$$

Invoking the Q_{ij} notation in the second term in (3 – 12) and substituting the result into the second order term of (3 – 4) leads to an expression for the electric quadrupole interaction energy, E_Q , in terms of the nuclear quadrupole moment

$$E_Q = \frac{1}{6} \sum_{i,j=1}^3 Q_{ij} V_{ij} . \quad (3 - 19)$$

Therefore, one notices that the quadrupole interaction energy is described by a tensor product of the nuclear quadrupole moment and the electric field gradient evaluated on the nuclear sites

$$E_Q \propto \vec{Q} \vec{V} . \quad (3 - 20)$$

3.1.2.2 The Quantum mechanical treatment

A more accurate description of the quadrupole interaction can be achieved by means of a quantum mechanical approach. In this formalism one replaces the nuclear charge density $\rho_N(\mathbf{x})$ by a density operator, $\hat{\rho}_N(\mathbf{x})$, defined as

$$\hat{\rho}_N(\mathbf{x}) = \sum_k e(\mathbf{x} - \mathbf{x}_k) = e \sum_k \delta(\mathbf{x} - \mathbf{x}_k) . \quad (3 - 21)$$

Here the sum runs over all the protons within the Mössbauer nucleus. In (3 – 21), the positions of each proton within the nucleus is given by $\mathbf{x}_k$.

The nuclear quadrupole moment operator is thus defined as

$$\begin{aligned} \hat{Q}_{ij} &= \int \hat{\rho}_N(\mathbf{x}) (3x_i x_j - x^2 \delta_{ij}) d\mathbf{x} = e \sum_k \int \delta(\mathbf{x} - \mathbf{x}_k) (3x_i x_j - x^2 \delta_{ij}) d\mathbf{x} \\ &= e \sum_k (3x_{ik} x_{jk} - x_k^2 \delta_{ij}) . \end{aligned} \quad (3 - 22)$$

Hence the Hamiltonian operator for the quadrupole interaction can be written as:

$$\hat{H}_Q = \frac{1}{6} \sum_{i,j=1}^3 V_{ij} \hat{Q}_{ij} . \quad (3 - 23)$$

The energy eigenstates of the nuclei in Mössbauer spectroscopy are fully characterized by the spin angular momentum quantum number of the nuclei, I . It is shown that Hamiltonian for the quadrupole interaction can be written in terms of the nuclear spin angular momentum operators, $\hat{I}$ and $\hat{I}_i$, where i represents the x, y and z components [7]

$$\hat{H}_Q = \frac{eQ}{6I(2I+1)} \sum_{i,j=1}^3 V_{ij} \left[\frac{3}{2} (\hat{I}_i \hat{I}_j + \hat{I}_j \hat{I}_i) + \delta_{ij} \hat{I}^2 \right] . \quad (3 - 24)$$

In (3 – 24), the axis of symmetry of the nucleus has been taken to be along the z direction. It has been assumed that the nucleus itself has a cylindrical charge distribution. The electric quadrupole moment tensor is then diagonal and the interaction energy will remain constant unless the charge distribution is rotated to another direction such as x or y . Thus, the nuclear quadrupole moment can be treated as a constant, Q [1]. The nuclear quadrupole constant is positive for cigar shaped nuclei, negative for disk shaped nuclei, and zero for spherical nuclei. Therefore, the nuclear quadrupole interaction can be considered to be dependent on the physical shape of the

Mössbauer nucleus. Moreover, the quadrupole moment is nonzero only for nuclear states with a nuclear spin quantum number I greater than $\frac{1}{2}$.

In what follows, we briefly introduce the nuclear hyperfine interactions which have been studied in the different materials used in this research.

3.1.3 The Isomer Shift

In Mössbauer spectroscopy, the term *isomer* is referred to nuclei with the same charge and mass but different states of energy. The electric monopole interaction energy given by (3 – 17) depends on the square of the nucleus' average radius and, since identical nuclei in different states of energy have different radii ($R_g \neq R_e$), the monopole interaction energy is different for nuclei in their ground states compared to that for nuclei in their excited states. As a result, the shift in the nuclear energy level for the ground state, $(\delta E)_g$ is not the same as the shift in energy of the excited state, $(\delta E)_e$. This effect gives rise to the Mössbauer *isomer shift* (IS). In figure 3.3, the isomer shift is depicted schematically for the source and absorber nuclei by means of energy level diagrams and the resulting shift in the Mössbauer spectrum is shown.

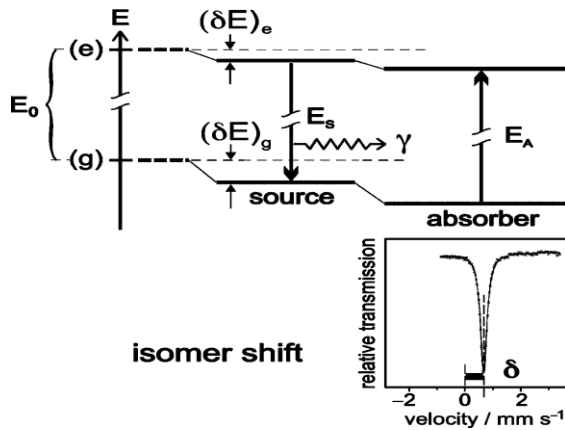


Figure 3.3 The electric monopole interaction between the nuclear charge and the electron density at the nucleus. This interaction results in the shift of the nuclear state energy levels [1].

If one takes E_0 to be the transition energy of a bare nucleus, then the energy of a γ photon emitted by the excited state of the source nucleus is

$$E_S = E_0 - [(\delta E)_e - (\delta E)_g] = E_0 + \frac{2\pi}{5} Z e^2 |\psi(0)|_S^2 (R_e^2 - R_g^2). \quad (3 - 25)$$

The corresponding relation for the absorbing nucleus is

$$E_A = E_0 - [(\delta E)_e - (\delta E)_g] = E_0 + \frac{2\pi}{5} Z e^2 |\psi(0)|_A^2 (R_e^2 - R_g^2). \quad (3 - 26)$$

The letters “S” and “A” stand for source and absorber, respectively. The electronic charge density at the location of the nucleus is different for the source and the absorber. As a result, the energies E_S and E_A are not equal. Hence, there is a shift in the resonance energy in the Mössbauer spectrum, which is known as the isomer shift, δ

$$\delta = E_A - E_S = \frac{2\pi}{5} Z e^2 [|\psi(0)|_A^2 - |\psi(0)|_S^2] (R_e^2 - R_g^2). \quad (3 - 27)$$

The difference between the squares of the nucleus's radius can be written as

$$R_e^2 - R_g^2 = (R_e - R_g)(R_e + R_g) = 2(\Delta R)R, \quad (3-28)$$

where the difference in the radii is represented by ΔR and the sum of the radii can be approximated by $2R$ since R is the average radius between the excited state and the ground state. Since ^{57}Fe is the source nucleus in the study of the compounds and alloys in this research, $|\psi(0)|_s^2$ would be the same in all cases, therefore it can be considered a constant, C . The reference compound in the Mössbauer study used in this research was the α phase of iron which has a body centered cubic structure with a lattice constant of 2.8665 Å. By substituting (3-28) into (3-27), and considering the arguments on the reference compound, the isomer shift can be written as

$$\delta = \alpha(|\psi(0)|_A^2 - C), \quad (3-29)$$

where $\alpha = \frac{4\pi}{5}Ze^2(\Delta R)R$ is known as the *isomer shift calibration constant*. In this research, the calibration constant $\alpha = -0.291 \text{ a.u.}^3 \text{ mms}^{-1}$ was used in evaluating the isomer shift of iron-based compounds [8]. The negative sign in α shows that a positive isomer shift of a compound relative to a certain reference material indicates a lower charge density at the nucleus of the compound relative to that of the reference material.

An important factor to be considered in the context of isomer shifts, is the impact that *relativistic effects* have on the isomer shift. As relativistic effects vary with the fourth power of the number of protons in the nucleus, these effects can be neglected in lighter atoms but must be considered in heavier elements. For iron, the error arising from neglecting relativistic effects will change the electronic charge density at the nucleus site by about 30%. Therefore, one must always consider relativistic effects, especially in comparing the results of theoretical calculations with the experimental spectra.

Another important effect due to relativity is the so-called *second order Doppler shift* (SOD). When one encounters the experimental isomer shift, δ_{exp} , a difference from the genuine isomer shift, δ , is noticed. This term, shown by δ_{SOD} , is a result of the relativistic shift in energy of the γ photons due to the thermal motion of the emitting and absorbing nuclei

$$\delta_{\text{SOD}} = -E_\gamma \frac{\langle v^2 \rangle}{2c^2}, \quad \delta_{\text{exp}} = \delta + \delta_{\text{SOD}}, \quad (3-30)$$

where E_γ is the photon energy, c is the speed of light in vacuum, and $\langle v^2 \rangle$ is the mean square velocity of the Mössbauer nuclei. It is clear that the second order Doppler shift is expected to vanish as temperatures approach absolute zero. Using the Debye model of phonon energy distributions in a solid, the temperature dependence of the second order Doppler shift is [9]

$$\delta_{\text{SOD}} = -\frac{9k_B E_\gamma}{16M_{\text{eff}}c^2} \left(T_M + 8T \left(\frac{T}{T_M} \right)^3 \int_0^{\frac{T}{T_M}} \frac{x^3}{e^x - 1} dx \right). \quad (3-31)$$

where T_M is the *Mössbauer temperature*, which is specific for the environment which is “sensed” by the Mössbauer nucleus [10]. M_{eff} is the effective mass which accounts for the Mössbauer atoms taking part in collective motions together with the surrounding ligands. Thus, the measured isomer shift will be temperature dependent:

$$\delta_{\text{exp}}(T) = \delta + \delta_{\text{SOD}}(T). \quad (3 - 32)$$

All of the compounds studied in this research are iron- based. In general, the Mössbauer isomer shifts of iron-containing compounds can be explained as a result of two effects. The first effect is due to the shielding of the s electrons by the $3d$ electrons, thus reducing the nuclear potential sensed by the s electrons. The second effect is due to the $4s$ electrons in their participation in bond formations.

3.1.4 Electric quadrupole interaction

The electric quadrupole interaction relates to the possible shapes and structures that non-spherical nuclei can take, subject to a non-homogeneous electric field. The non-homogeneous electric field is generated by a non-cubic arrangement of the nucleus’s surrounding electronic charge distributions.

The shape of the nucleus is described by a power series and the dominant term yields the nuclear quadrupole moment. In Cartesian coordinates, the quadrupole moment integrals are of the type $\int \rho_n(r)(3x_i x_j - \delta_{ij} r^2) d\tau$ where $x_i = x, y, z$ and $\rho_n(r)$ is the nuclear charge distribution. Calculating the nuclear charge density is often challenging.

Quantum mechanically the quadrupole interaction is described by the Hamiltonian [7]

$$\hat{H}_Q = \frac{eQV_{zz}}{4I(2I-1)} \left[3\hat{I}_z^2 - I(I+1) + \frac{\eta}{2} (\hat{I}_+^2 + \hat{I}_-^2) \right], \quad (3 - 33)$$

where I is the nuclear spin quantum number, $\hat{I}_{\pm} = \hat{I}_x \pm i\hat{I}_y$ are the shift operators, and $\hat{I}_x$, $\hat{I}_y$, and $\hat{I}_z$ are the spin projection operators onto the principle axis. Q is the quadrupole moment of the nucleus, and V_{zz} and η represent the main component and the asymmetry parameter of the electric field gradient (EFG) tensor (*vide infra*). The nuclear charge distribution has cylindrical symmetry due to its well defined angular momenta [11]. If one takes the z direction to be the axis of quantization, then a positive quadrupole moment, $Q > 0$ describes an elongated (cigar shaped) nucleus, whereas a negative quadrupole moment, $Q < 0$ relates to an oblate shaped, (flattened) nucleus. Only nuclei with $I > 1/2$ exhibit non-zero quadrupole moments. For a detailed review of nuclear quadrupole moments, the reader is referred to [12].

3.1.5 The Electric Field Gradient (EFG)

Due to the electric charge distribution of the electrons of a Mössbauer atom, and that of the neighboring ligands, a net electric potential, $V(0)$, exists at the site of the Mössbauer nucleus. The electric field gradient (EFG) at the site of a Mössbauer nucleus, is a second ranked tensor in which the elements are the second spatial derivatives of the electric potential, $V(0)$, in Cartesian coordinates

$$EFG \Rightarrow -\nabla E = \nabla \nabla V \doteq \begin{bmatrix} V_{xx} & V_{xy} & V_{xz} \\ V_{yx} & V_{yy} & V_{yz} \\ V_{zx} & V_{zy} & V_{zz} \end{bmatrix}, \quad (3-34)$$

where $V_{ij} = \left(\frac{\partial^2 V}{\partial x_i \partial x_j} \right)_0$ are the nine components of the electric field gradient tensor at the nuclear site. Due to symmetry arguments, ($V_{ij} = V_{ji}$), only five of these components are independent. Moreover, Laplace's equation demands that EFG be a traceless tensor. The reason is based on the fact that only p and d electrons contribute to the EFG tensor and the probability of their appearance inside the nucleus is zero (Thus Laplace's equation applies as opposed to Poisson's equation). Therefore

$$\sum_{i=1}^3 V_{ii} = 0 \quad (3-35)$$

Due to its symmetry, one can diagonalize the EFG matrix to the so-called *principle axis system* (PAS) in which the off-diagonal components of the EFG tensor vanish. By convention, the principle axes are chosen such that⁸ $|V_{zz}| \geq |V_{xx}| \geq |V_{yy}|$. The asymmetry parameter, η , is defined as

$$\eta = \frac{V_{xx} - V_{yy}}{V_{zz}}, \quad (3-36)$$

From (3-35) and (3-36), it is clear that a complete description of the electric field gradient is obtained only if two independent parameters, V_{zz} and η , are determined.

For a three-fold or four-fold axis of symmetry passing through the Mössbauer nucleus, as the center of symmetry, one can show that the asymmetry parameter vanishes, ($\eta = 0$), and therefore the only non-zero component of the EFG tensor is V_{zz} . In a system with two mutually perpendicular axes of three-fold or higher symmetry, the EFG must be zero [1]. The mentioned features are realized for some of the compounds studied in chapter 5.

3.1.6 The quadrupole splitting

The quadrupole Hamiltonian of equation (3-33) for the simple case of an axial symmetric EFG, ($\eta = 0$), can be used in Schrödinger's equation to find the possible eigenvalues of the quadrupole interaction energies. The convenient basis in which one solves the Schrödinger equation is the nuclear spin basis set, $\{|I, m_I\rangle\}$. The quadrupole interaction energy eigenvalues are

$$E_Q(m_I) = \frac{eQV_{zz}}{4I(2I-1)} [3m_I^2 - I(I+1)]. \quad (3-37)$$

The electric quadrupole interaction removes the $2I + 1$ fold degeneracy of the $|I, m_I\rangle$ states without shifting the energy levels. States with the same absolute value of m_I remain degenerate (in general this will not be the case for $\eta \neq 0$).

⁸ The V_{ii} 's are often referred to as *the main components* of the EFG tensor.

In figure 3.4, the quadrupole splitting is shown in the case of ^{57}Fe Mössbauer nuclei. The nuclear spin quantum number of the ground state of iron is $1/2$ thus no splitting is expected. However, the first nuclear excited state which is characterized by the nuclear spin number $3/2$, is split into a (symmetric) doublet. The quadrupole interaction energy for the two states are given by $E_Q(\pm 3/2) = 3eQV_{zz}/12$ and $E_Q(\pm 1/2) = -3eQV_{zz}/12$, according to (3 – 37). The energy difference between the two sub-states is thus

$$\Delta E_Q = eQV_{zz}/2. \quad (3 - 38)$$

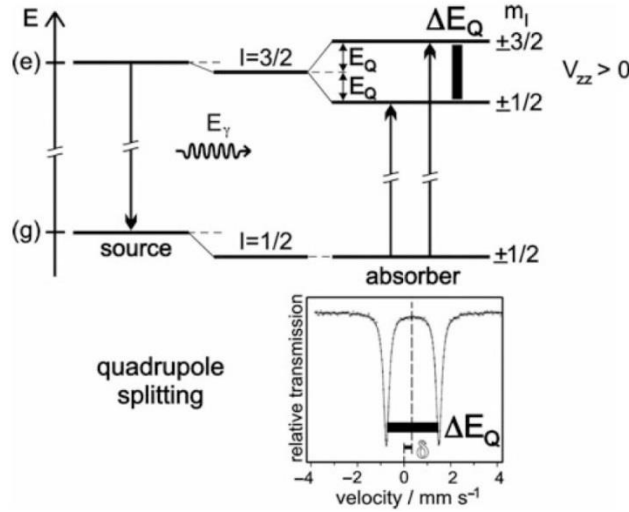


Figure 3.4 Quadrupole splitting of the $^{57}\text{Fe} \left| I = 3/2, m_{3/2} \right\rangle$ state and the related Mössbauer spectrum [1].

In the case in which the EFG tensor does not possess axial symmetry, ($\eta \neq 0$), the energy eigenvalues for the $^{57}\text{Fe} \ I = 3/2$ excited state are given by [1]

$$E_Q(m_I) = \frac{eQV_{zz}}{4I(2I-1)} [3m_I^2 - I(I+1)] \sqrt{1 + \frac{\eta^2}{3}}. \quad (3 - 39)$$

There is much more to the quadrupole interaction which is beyond the scope of this thesis. The interested reader is referred to the references listed at the end of this chapter.

3.1.7 Magnetic dipole interaction and magnetic splitting

Due to its spin angular momentum, the Mössbauer nucleus has a magnetic dipole moment, μ . The nuclear magnetic dipole moments interacts with the magnetic field induction, $\mathbf{B}$, at the site of the Mössbauer nucleus. This interaction is described by the following Hamiltonian

$$\hat{H}_m = -\hat{\mu} \cdot \hat{\mathbf{B}} = -g_N \mu_N \hat{\mathbf{I}} \cdot \hat{\mathbf{B}}, \quad (3 - 40)$$

where g_N is the nuclear Landé factor and μ_N is the nuclear Bohr magneton. The energy eigenvalues related to the Hamiltonian above are given by

$$E_M(m_I) = -\frac{\mu_B m_I}{I} = -g_N \mu_N B m_I. \quad (3-41)$$

Thus, the magnetic dipole interaction splits the degenerate nuclear spin states, $|I, m_I\rangle$, to $2I + 1$ sub-states. In figure 3.5, the magnetic dipole interaction in the case of ^{57}Fe nuclear states characterized by $I = 1/2$ (ground state), and $I = 3/2$ (first excited state) is given. From (3-41), it can be seen that the $I = 3/2$ state splits into four subsets, and the $I = 1/2$ state splits into two equal subsets.

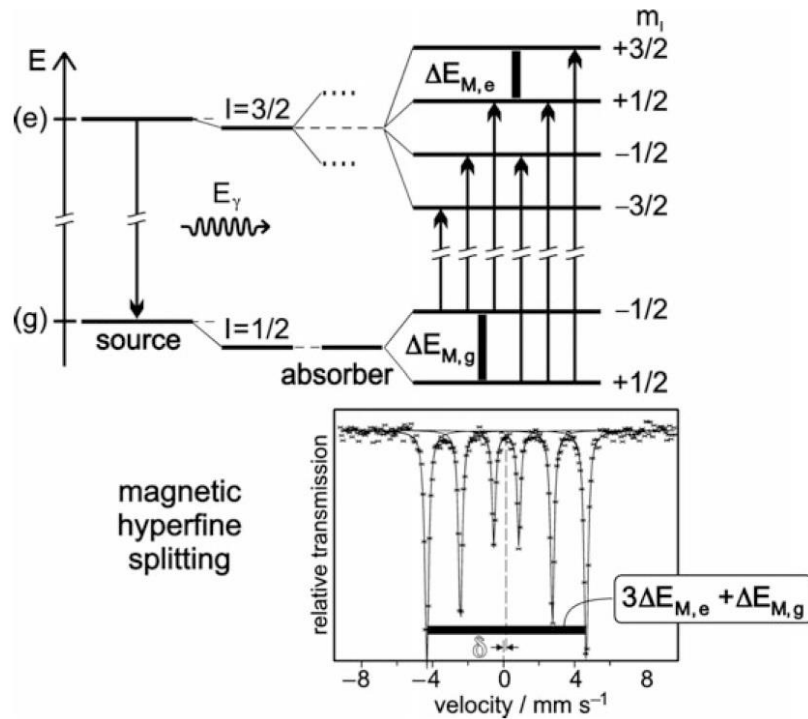


Figure 3.5 Magnetic dipole interaction splitting in ^{57}Fe and the resultant spectrum [1].

The transitions pictured in figure 3.5 are determined by the quantum mechanical selection rules of $\Delta m_I = 0, \pm 1$. The intensities of the allowed transitions are given by the squares of the Clebsch-Gordan coefficients and their relative intensities are 3:2:1:1:2:3 [1].

The magnetic hyper-fine field at the site of the nucleus is in general the result of the superposition of five terms as listed below

- 1- The external magnetic field, H_{ext} . In the case of an applied external magnetic field, the net magnetic field at the nuclear site is modified and results in a change in the intensities and even the appearances of the Zeeman patterns.
- 2- The Fermi contact term, H_c which is due to the differences in the spin up and down densities of the s electrons at the nuclear sites.

- 3- The orbital term, H_{orb} , arising from the orbital angular momentum of the electrons about the nucleus.
- 4- The dipolar term, H_{dip} , which arises from the magnetic dipole-dipole interaction between the electrons and that of the nucleus
- 5- The lattice contribution, H_{lat} . This term arises from the interactions between the Mössbauer nucleus and the fields of neighboring atoms and ligands in the solid.

Among the five terms listed, the Fermi contact term is in general, the dominant term while the lattice term is the weakest. In most cases, the lattice contribution does not affect the Mössbauer spectrum in a noticeable way.

3.1.8 The combined electric and magnetic interactions

In a typical Mössbauer spectrum, all three interactions appear. The total hyper-fine Hamiltonian is thus given by $\hat{H} = \delta E + \hat{H}_Q + \hat{H}_M$. For the isomer shift contribution, all the spectrum including transmission lines are shifted with the same amount, without any change in their relative positions. However, for the combined magnetic dipole and electric quadrupole interactions, the spectrum is hard to evaluate. There are, however, special cases in which the problem of determining which feature of the Mössbauer spectrum corresponds to which hyperfine interaction is resolved [13,14].

3.2 Experimental setup in Mössbauer spectroscopy

The essential experimental backgrounds in Mössbauer measurements are stated in this section.

3.2.1 Transmission Mössbauer spectrometer setup

Figure 3.6 shows a Mössbauer setup which consists of a Radioisotope attached to the front a velocity transducer. The transducer moves back and forth, controlled by a function generator. The oscillations of the transducer can be controlled and improved by the voltage waveform from the function generator. The detector is a proportional counter join up with a preamplifier and an amplifier. The signal from the amplifier is guided into a single channel analyzer (SCA) and then to a multi-channel analyzer (MCA). The transducer and MCA are synchronized, under the control of the function generator that sends start and delay pulses to the MCA and proper timescale voltage pulses to the transducer.

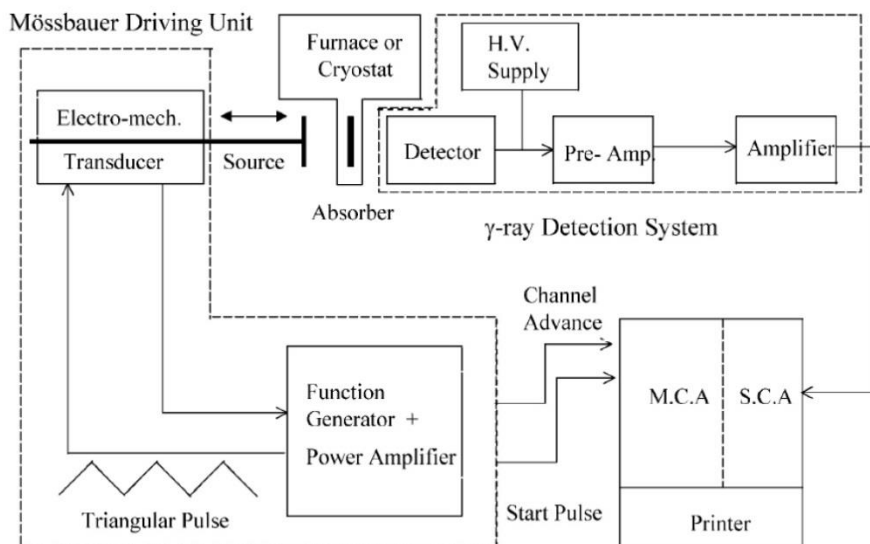


Figure 3.6 The experimental set-up of transmission Mössbauer spectroscopy [15].

In order to achieve optimal results in a Mössbauer measurement, one must consider extreme care in carrying all the steps included in the experiment. The use of high-quality and standard equipment alone is not enough to obtain useful Mössbauer spectra. In this context, the setup of a Mössbauer measurement especially in the process of sample preparation is a delicate procedure. In this section, the steps necessary to prepare a Mössbauer absorber are introduced.

3.2.2 Sample preparation

Before installing the sample into the absorber, a number of steps has to be taken. These preparation stages include grinding the sample to produce fine grains which will later be combined with boron nitride powder to form the absorbing environment. The ratio of the amount of boron nitride to the sample in the mixture depends mainly on the specific compound used for the experimental study, this stage is followed by uniformly mixing the sample with boron nitride powder and using a scale to measure the mass of the mixture. The mixture would then be placed in the absorber. The exact amount of the sample required for a particular absorber is given in [16].

To synthesize the samples, an arc furnace is used. In the arc furnace used for the measurements, temperatures as high as 3700 K are obtained which is higher than the melting points of many elements, therefore it is a convenient instrument to combine the elements.

The synthesized sample is placed in a sample groove, and the gas within the chamber is evacuated, and later filled with argon gas. The process of filling the chamber with argon gas and evacuating it should be done several times. Afterwards via the arc furnace a uniform arc flame is produced and any gas impurities are removed.

Another element used in sample preparation is the electric furnace, which is used to melt and anneal the elements. The temperatures in a typical electric furnace can reach up to 1700 K and uniform temperatures up to ± 1 K are typically achieved. After the sample is annealed, it is placed in cooled water (preferably icy water) to maintain the crystalline structure.

3.2.3 The Mössbauer set up

The Mössbauer spectroscopy of the studied compounds has been carried out in three physical conditions: low-temperature measurements, high-temperature measurements, and within external magnetic fields up to 90 kOe. The setups for these three regimes are provided in the experimental methodology section in detail and compound specific for all five compounds studied in this research.

3.2.3.1 Low and High temperature spectrometers

For low-temperature measurements, the prepared absorber is placed in a Mössbauer cryostat that via pumping liquid nitrogen or liquid helium can maintain the sample in liquid nitrogen and liquid helium temperatures. The cryostat has a static exchange gas atmosphere at an approximate pressure of 7×10^{-3} mbar. In figure 3.7, the low-temperature Mössbauer spectrometer is shown schematically.

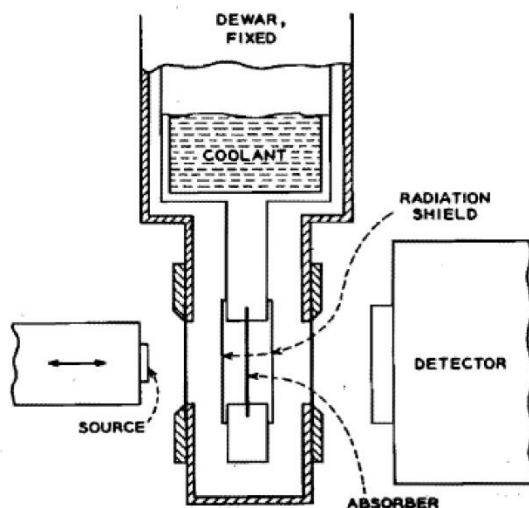


Figure 3.7 A schematic view of the low temperature Mössbauer spectrometer [14].

The high-temperature measurements are conducted by installing the prepared absorber in a Mössbauer oven which is kept in a dynamic vacuum of $\sim 2 \times 10^{-3}$ mbar.

3.2.3.2 The 90 kOe Mössbauer spectrometer

For Mössbauer measurements in an external applied magnetic field, a Mössbauer spectrometer which produces a dc magnetic field up to 90 kOe is used. The field is obtained by a superconductor magnet which is placed at the bottom of the cryostat. Helium vapor is used to

cool the absorber and the source. The sample chamber is filled with liquid helium via a needle valve. The pressure inside the chamber is controlled by a valve and a vacuum pump. The accuracy of the temperature at the source and device is about ± 0.1 K. At the bottom of the cryostat, a Myler window allows the radiation to travel to the Mössbauer detector. The velocity of the source, which is attached to a transducer, is measured by using a Michelson interferometer, shown in figure 3.8.

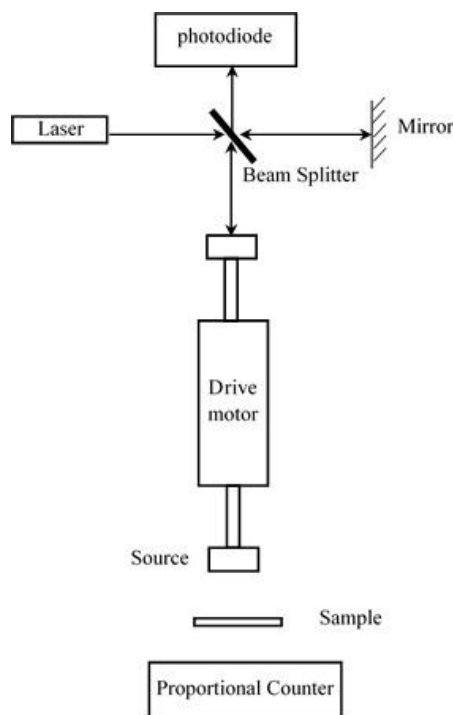


Figure 3.8 The Michelson interferometer geometry used in the 90 kOe Mössbauer spectrometer.

3.2.4 The Mössbauer spectrum

In the Mössbauer experiment, the radioactive source is mounted on a transducer and moves back and forth with respect to the fixed absorber with a certain velocity profile v . As a result of the Doppler effect, the γ ray energies are modulated⁹ upon arrival to the absorber. The transmitted γ rays reach a detector that registers the γ photons and the transmission intensity is graphed as a function of the Doppler velocity v . The overlap between the emission lines and absorption lines will result in reduced intensity of the transmission spectrum and upon maximum overlap a minimum occurs in the registered transmission intensity spectrum.

In chapter five, the Mössbauer spectra for the studied compounds and in different temperature ranges are provided. They are typical examples of an experimental spectrum in comparison to the theoretical ones discussed earlier in this chapter.

⁹ Statistically speaking, the distribution profile of the γ photons in energy will broaden due to the Doppler effect.

3.3 X-ray powder diffractometry

In this section, the methods and techniques used in order to determine the structural properties of the material studied in this thesis is presented. The background theory of X-ray diffraction is briefly reviewed.

3.3.1 Crystal structures

Among the compounds studied in this work, Fe_2NiGa crystallizes in a cubic structure, $\text{Al}_{13}\text{Fe}_4$ and $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ crystallize in a monoclinic structure, and $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$ and $(\text{Li}_{0.8}\text{Fe}_{0.2})\text{OHFeSe}$ crystallize in tetragonal structures. In what follows, crystal structures are introduced and their properties are discussed with emphasize on their symmetry properties. Typically, the introduction is narrowed down to Bravais lattices without considering a particular atomic basis. The material introduced in this section is comprehensively discussed in Ref. [5,17].

3.3.1.1 Symmetries of Bravais lattices

In general, a 3D *Bravais lattice* is a set of geometrical points with position vectors $\mathbf{R}$ of the form

$$\mathbf{R} = \sum_{i=1}^3 n_i \mathbf{a}_i, \quad (3 - 42)$$

where n_i are integers ranging through all integral numbers and $\mathbf{a}_i$ are any three vectors not all in the same plane, known as primitive vectors. The primitive vectors generate the lattice. Thus, inherent in the definition (3 – 42), the translational symmetry of a Bravais lattice is realized. This translational symmetry property allows the existence of 14 different Bravais lattices in three dimensional space in which all belong to 7 types of crystal structures.

From a symmetry point of view, a Bravais lattice is characterized by all rigid operations that take the lattice into itself. In the language of group theory, the set of these operations is known as the *symmetry group* or *space group* of the Bravais lattice. The operations in the space group of a Bravais lattice include all *translations* through primitive vectors, and in addition there will be in general *rotations*, *reflections*, and *inversions* that take the lattice into itself.

Any symmetry operation of a Bravais lattice can be compounded out of a translation $T_{\mathbf{R}}$ through a lattice vector $\mathbf{R}$ and a rigid operation leaving at least one lattice point fixed.

The full symmetry group of a Bravais lattice contains operations only of the following forms:

1. Translations through Bravais lattice vectors, $T_{\mathbf{R}}$;
2. Operations that leave a particular point of a lattice fixed;
3. Operations that are constructed by successive applications of the above two operations

3.3.1.2 The seven crystal systems

The subset of the full symmetry group operations, that leave a particular point of a lattice fixed, are known as *point group symmetry operations*. A Bravais lattice can at most have 7 distinct point group symmetries. In other words, any crystal structure belongs to one of the seven

crystal systems, depending on which of these seven point groups is the point group of its underlying Bravais lattice. In figure 3.9, the seven crystal systems are shown schematically and in table 3.1, the geometrical characteristics of the seven crystal structures are given.

3.3.1.3 The fourteen Bravais lattices

Combining the point symmetry operations with the translational symmetry, one arrives at fourteen distinct space groups for a Bravais lattices described below (figure 3.10).

Cubic The cubic system contains those Bravais lattices whose point group is that of a cube. The simple cubic (*c*), body-centered cubic (*bcc*), and face-centered cubic (*fcc*) are the three Bravais lattices of the cubic system.

Crystal system	Axial lengths	Axial angles	Number of Bravais lattices
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	3
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	2
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	4
Monoclinic	$a \neq b \neq c$	$\alpha = \beta = 90^\circ \neq \gamma$	2
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	1
Trigonal	$a = b = c$	$\alpha = \beta = \gamma < 120^\circ, \neq 90^\circ$	1
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$	1

Table 3.1 The seven crystal systems in three dimensions.

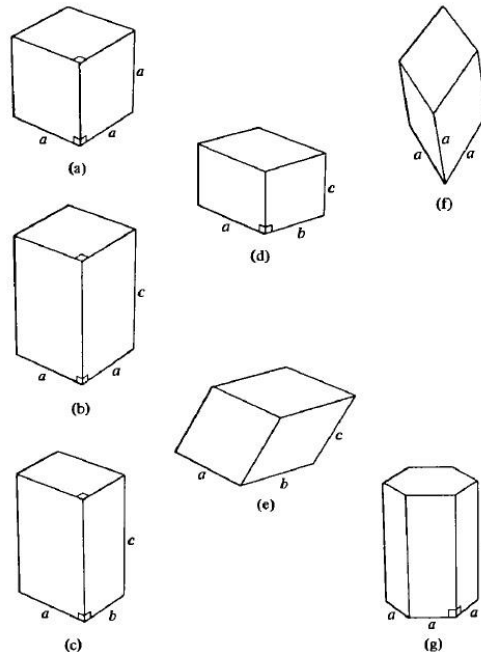


Figure 3.9 The seven crystal systems: (a) cubic, (b) tetragonal, (c) orthorhombic, (d) monoclinic, (e) triclinic, (f) trigonal, and (g) hexagonal [5].

Tetragonal Two Bravais lattices belong to the tetragonal system: the *simple tetragonal* Bravais lattice, which is in the form of a rectangular prism with a square base, and the *centered tetragonal* which is a simple tetragonal with a lattice point at its center.

Orthorhombic four Bravais lattices constitute the Orthorhombic crystal system: *simple orthorhombic* which takes the form of a rectangular cube with nonequivalent edges; *base-centered orthorhombic*, which is the simple orthorhombic but with two additional lattice points on the center of the two bases of its elongated side. *body-centered orthorhombic* and *face-centered orthorhombic* are the other two Bravais lattices in this system

Monoclinic The monoclinic system contains two Bravais lattices, the *simple monoclinic*, and the *centered monoclinic*

Trigonal The trigonal point group contains one Bravais lattice which is generated by three primitive vectors of equal length that make equal angles with one another.

Hexagonal The hexagonal point group is the symmetry group of a right prism with a regular hexagon as its base. The simple hexagonal Bravais lattice is the only Bravais lattice in the Hexagonal system.

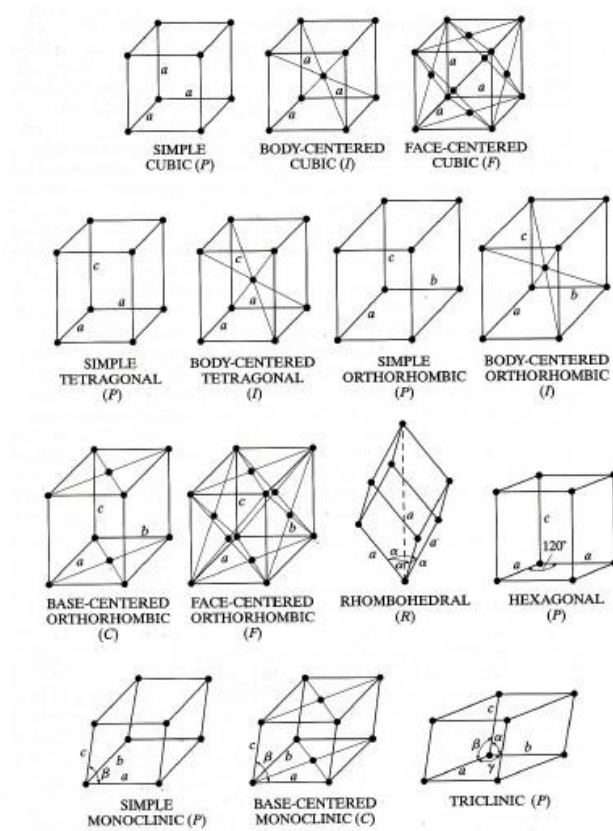


Figure 3.10 The fourteen Bravais lattices.

3.3.1.4 The 230 space groups

If one adds to the lattice points of the 14 Bravais lattices a basis, which need not to have complete symmetry (as a geometrical dot has), then the total number of the possible symmetry groups that a lattice with a basis can have is 230, known as the 230 *space groups*.

The 230 space groups with their complete symmetry operations are found at the following website: www.cryst.ehu.es/cgi-bin/cryst/programs/nph-getgen.

3.3.2 X-ray diffraction

The crystal structures discussed above, along with their atomic basis, can only be visualized by means of X-ray diffraction or neutron diffraction. In this section, we briefly encounter the X-ray diffraction technique in determining the crystal structure.

3.3.2.1. The Bragg formulation

Theoretically parallel X-rays incident upon a single crystal solid reflect at different families of planes and scatter off the specimen. The parallel rays incident on one set of family planes, reflect and their interferences will form the X-ray pattern of the set of the lattice planes. Mathematically, the X-ray Image of a crystal is in fact an image of its reciprocal lattice. This is understood based on the Fourier transformations between k-space and real space.

In the simple case of incident plane waves, the condition of constructive interference leads to the following set of reflection angles in which the intensity of the X-rays is maximum. This is the so-called Bragg condition of X-ray diffraction and is depicted schematically in figure 3.11

$$n\lambda = 2d\sin\theta, \quad (3 - 43)$$

where n is the order of reflection, θ is the angle of reflection, d is the distance between two successive planes in the crystal, and λ is the wavelength of the incident X-ray beam.

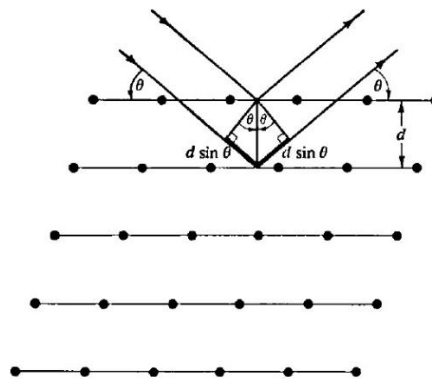


Figure 3.11 A Bragg reflection from a particular family of lattice planes, separated by a distance d [5].

3.3.2.2 The Von Laue formulation

Von Laue's method is equivalent to Bragg's formalism, but it is more abstract and involves the reciprocal space. According to Laue's theory, the condition for constructive interference of the X-rays is

$$\mathbf{k} \cdot \hat{\mathbf{K}} = \frac{1}{2}K, \quad (3-44)$$

where $\mathbf{k}$ is the wave vector of the incident X-ray, $\mathbf{K}$ is a reciprocal lattice vector with magnitude K and pointing along the $\hat{\mathbf{K}}$ direction. In figure 3.12, the Laue condition for X-ray diffraction is depicted. According to this formulation, an incident wave vector $\mathbf{k}$ will satisfy the Laue condition if and only if the tip of the wave vector lies in a plane that is perpendicular to the bisector of a line joining the origin of $\mathbf{k}$ -space to a reciprocal lattice point $\mathbf{K}$.

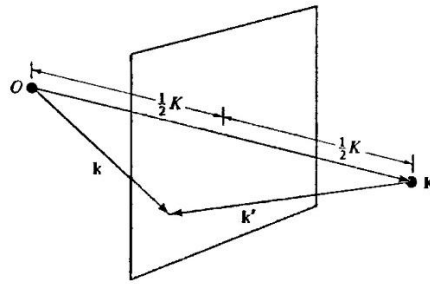


Figure 3.12 The Laue condition [5].

3.3.2.3 Experimental methods for X-ray diffraction

If one is to experimentally determine the Bragg peaks, the constraint mentioned in the previous section on $\mathbf{k}$ must be relaxed. One can either vary the wave length of the incident beam (for instance using white X-rays rather than narrow wavelengths such as $K\alpha$ or $K\beta$ radiation) or vary the directions of the incident beam (by varying the orientation of the crystal with respect to the incident direction).

In figure 3.13, the so-called *Ewald construction* is shown. The Ewald sphere is constructed in reciprocal space and is centered at the incident wave vector, $\mathbf{k}$. The condition for Bragg peaks is that reciprocal points must lie on the surface of the Ewald sphere (figure 3.13).

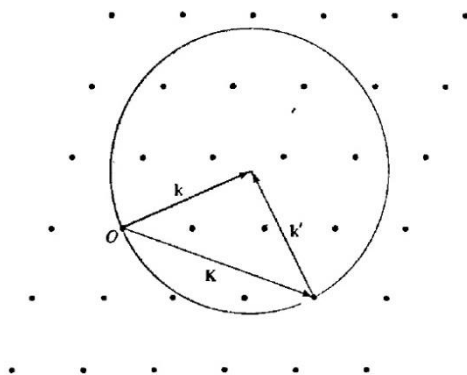


Figure 3.13 The Ewald construction [5].

Theoretically the reciprocal lattice points can lie on the surface of the sphere, however, experimentally this is not the case. The reason is that the beams are never absolutely monochromatic and the Ewald sphere has a sharp surface. There are three methods to overcome this problem.¹⁰

1-The Laue method: in this method, one uses a polychromatic beam within a certain wavelength window. As a result, the Ewald sphere expands and in the region between the largest and smallest incident wave vector, the reciprocal points satisfy the Laue condition and Bragg peaks appear.

2-The rotating crystal method: in this method, a monochromatic X-ray is used, however the angle of incidence is varied. In many case, this is achieved by fixing the direction of the X-ray incident beams and rotating the crystal. In this situation, the Ewald sphere is fixed in space, whereas the entire reciprocal lattice rotates about the axis of the rotation of the crystal. During the rotation, each reciprocal lattice point traverses a circle about the rotation axis. A Bragg reflection occurs whenever this circle intersects the Ewald sphere.

3-The Powder method: this method is the same as the rotating crystal method but in addition the fixed rotating axis now is free to rotate over all possible orientations. This is justified by the fact that a powdered crystal is composed of numerous crystallites and grains in random directions. In this geometry, each reciprocal lattice vector of length less than $2k$ generates a cone of scattered radiation at an angle ϕ to the forward radiation such that $K = 2k \sin \frac{\phi}{2}$.

It turns out that each crystallographic plane reflects 10^{-3} to 10^{-5} of the incident radiation [17]. Thus, the 10^3 to 10^5 planes contribute to the formation of a Bragg-reflected beam in a single crystallite. In the powdered form, which contains innumerable crystallites all randomly oriented, the intersections of reciprocal lattice vectors for a certain family of planes with the Ewald sphere as mentioned above, forms a circle, a so-called Debye ring. In the case of thousands of randomly oriented crystallites, a set of Debye rings each related to the intersections

¹⁰ For a detailed and illustrative discussion on the methods based on Ewald's sphere the reader is referred to [5,17,18].

of the reciprocal lattice vectors with the Ewald sphere is formed. In the X-ray spectrum, each ring is related to an intensity peak at a scattering angle in which Bragg's condition is met. A typical powder diffraction pattern for Copper is shown in figure 3.14.

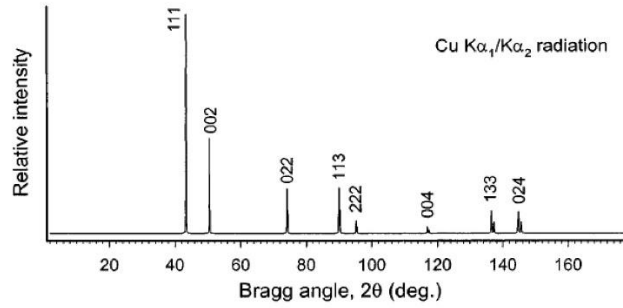


Figure 3.14 The X-ray powder diffraction pattern of copper [18].

3.3.3 The Rietveld refinement method

The Rietveld refinement method is a technique that is designed to refine and confirm the structural information of the crystalline samples and to fit the X-ray powder diffraction spectrum by eliminating device related errors from it. The fitting starts by generating the crystal structure peak intensities and profiles from the related data base. The refinement is done by calculating the least squares refinement residual, R defined as [19]

$$R = \sum_j w_j (I_{j(o)} - I_{j(c)})^2 \quad (3 - 45)$$

where w_j is the reciprocal of the intensity, I_j . $I_{j(o)}$ and $I_{j(c)}$ are the observed and calculated intensities respectively. j in (3 – 45) represent the data points. The smaller R , the closer is the data to the actual theoretical pattern. With the least squares approach, the theoretical line profile is refined until it matches the measured profile.

The Rietveld analysis is performed in several successive stages [19] namely: data collection, background determination, peak-shape selection, profile parameters refinement, and structural parameters refinement. In what follows, a brief description of these steps is given.

3.3.3.1 Data collection

The Bragg-Brentano geometry based X-ray powder diffractometer is among the most popular devices used for X-ray spectra data collection. Three of the most crucial parameters that must be controlled in gathering the data are the scattering angle (2θ) precision, the signal to noise ratio (SNR), and the thickness of the prepared sample. Mechanical vibrations of the device must be controlled and decreased as much as possible in order to obtain a high quality raw spectra. In general, X-rays penetration depths vary from sample to sample, thus the thickness of the pulverized sample must be calculated carefully in order to ensure an exact 2θ geometry.

Experimental problems, such as accidentally pre-orientations of a sample grain usually lead to incorrect intensity measurements. One can improve the results by rotating the sample while conducting the measurement.

3.3.3.2 Background determination

Due to the environment and X-ray scattering from nearby objects, there is always an unavoidable background noise which must be considered and removed during the refinement procedure.

3.3.3.3 Peak shape

The shape of a powder diffraction pattern depends strongly on the characteristics of the incident beam, the experimental set up, and the size and shape of the sample. The pseudo-Voigt approximation of a Voigt function is the commonly used peak-shape for X-ray analysis¹¹.

3.3.3.4 Peak width

The width of the diffraction peaks broadens as the Bragg angle θ , increases. The full width at half-maximum is given by $U \tan^2 \theta + V \tan \theta + W$ for the Gaussian component of the beam and by $X \tan \theta + \frac{Y}{\cos \theta}$ for the Lorentzian component of the beam. In these relations, U, V, and W are the Gaussian half-width parameters and X and Y are the Lorentzian half-width parameters.

3.3.3.5 Refinement of the structural parameters

The refinement of the structural parameters is established by the generation of a difference Fourier map which represents a difference electron density. The difference electron density is obtained by subtracting the electron density generated from the initial model from the one obtained from the experimental spectrum. Using the least square-residual functions, the difference between the generated profiles and that of the experimental spectrum is minimized for each of the specified parameters. The factor used in order to determine the quality of the fit is called *the goodness of fit* (GOF). After each refinement process, the value of GOF must become smaller than that of its previous stage to indicate the convergence of the refinement procedure. The range of the parameters is determined by a number of constraints that may affect the relative peak intensities. For instance, changes in temperature will result in different intensities. Controlling the fore mentioned parameters prevents unrealistic results.

For four of the studied compounds, a Rietveld refinement of the X-ray powder diffraction data is presented in chapter 5. Compound specific examples of the X-ray powder diffraction patterns are found in chapter five regarding the materials studied in this research.

¹¹ In the case of monochromatic neutron sources used in neutron diffraction, the convolution of the various parameters involved has been found to result in a reflection almost exactly Gaussian in shape.

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Chapter four

Density functional theory and the LAPW methods; a basis for the theoretical calculations

4.1 Introduction

A proper understanding of the solid state requires a quantum mechanical treatment of a solid as a system of many interacting particles; namely, the problem of a solid is a *many-body problem*. The interaction of particles constituting a solid is described by a model Hamiltonian of the many body system. In this model, one considers the system to be composed of N nuclei (N is a very large number, typically 10^{23} nuclei per cubic centimeter), each with an electrical charge of $+Ze$ interacting with ZN electrons. The nuclei are considered to be positioned at locations specified by $\mathbf{R}_i$ and with mass M_i , where $i=1, 2, 3, \dots, N$. Due to constant thermal vibrations, one can consider the $\mathbf{R}_i$'s to be the average positions of the nuclei, that is, their equilibrium coordinates. The electrons with mass m interact with each other and with the nuclei electrostatically described by the Coulomb interaction. The positions of the electrons in the system are specified by $\mathbf{r}_i$. The Hamiltonian of the system is thus described by

$$\hat{H} = -\frac{\hbar^2}{2m} \sum_i \nabla_{\mathbf{r}_i}^2 - \frac{\hbar^2}{2} \sum_i \frac{\nabla_{\mathbf{R}_i}^2}{M_i} - \frac{1}{4\pi\epsilon_0} \sum_{i,j} \frac{Z_i Z_j e^2}{|\mathbf{r}_i - \mathbf{R}_j|} + \frac{1}{8\pi\epsilon_0} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{1}{8\pi\epsilon_0} \sum_{i \neq j} \frac{Z_i Z_j e^2}{|\mathbf{R}_i - \mathbf{R}_j|}. \quad (4-1)$$

The first term in (4-1) describes the total kinetic energy of the electrons, the second term is the total kinetic energy of the nuclei, the third term is the total attractive interaction energy between the electrons and the nuclei, the fourth term describes the total repulsive interaction energy between electrons, and the fifth term is the total repulsive interaction energy between nuclei. Due to the very large number of particles involved, it is practically impossible to find exact solutions for a system described by this Hamiltonian. Therefore one must seek approximate methods. There are generally three layers of approximations used to solve this many-body problem. In what follows, we briefly discuss these approximations.

4.2 The quantum many body problem

4.2.1 The Born-Oppenheimer approximation

Due to the large mass of the nuclei, one neglects the motion of the nuclei compared to that of the electrons in the so-called *Born-Oppenheimer approximation*. The accuracy of this level of approximation increases with decreasing temperature¹². The nuclei are then considered immobile and fixed at their equilibrium positions. Thus, the second term in (4-1) is omitted and the nuclei are considered only to interact with the electrons via producing an external electrostatic field. Furthermore, the last term of (4-1) which only depends on the relative positions of the nuclei

¹² The theoretical calculations are performed *without* considering lattice vibrations and phonon interactions. In the low-temperature regime, the significance of thermal agitations can be neglected with a high degree of accuracy.

becomes a constant in this level of approximation. Therefore, the Hamiltonian will only contain contributions from the first, third, and fourth terms and is written as

$$\hat{H} = \hat{K} + \hat{V} + \hat{V}_{\text{ext}}, \quad (4-2)$$

where $\hat{K} \equiv -\frac{\hbar^2}{2m} \sum_i \nabla_{\mathbf{r}_i}^2$, $\hat{V} \equiv \frac{1}{8\pi\epsilon_0} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$, and $\hat{V}_{\text{ext}} \equiv -\frac{1}{4\pi\epsilon_0} \sum_{i,j} \frac{Z_j e^2}{|\mathbf{r}_i - \mathbf{R}_j|}$. The external potential due to the positive charge of the nuclei is given by $\hat{V}_{\text{ext}}$.

4.2.2 Density functional theory

The many-body problem in the Born-Oppenheimer approximation can still be further simplified and several theoretical methods of solving the many-body problem exist. Among the most important of these approaches is the Hartree-Fock method (HF) which is found in many condensed matter text books. The HF method is very accurate in describing systems of atoms and molecules. However, it is not very accurate in describing solids. There exists a very powerful and useful method as an alternative theoretical tool in treating the many-body problem in solids which is known as *density functional theory*, (DFT). As mentioned before, all of the theoretical calculations in this research are based on DFT methods. In what follows the general scheme of DFT is presented in further detail.

4.2.2.1 The theorems of Hönenberg and Kohn

Historically, DFT was developed formally by two theorems due to Hönenberg and Kohn in 1964 [1]. Here the two theorems are presented without proof.

Theorem 1: There is a one-to-one correspondence between the ground state density, $\rho(\mathbf{r})$, of a many-body electron system (atom, molecule, solid) and the external potential V_{ext} . As an immediate consequence, the ground state expectation value of any observable $\hat{O}$ is a unique functional of the exact ground state electron density

$$\langle \Psi | \hat{O} | \Psi \rangle = O[\rho(\mathbf{r})]. \quad (4-3)$$

Theorem 2: In the case of the Hamiltonian, $\hat{H}$, the ground state total energy functional, $H[\rho] \equiv E_{V_{\text{ext}}}[\rho]$, is of the form

$$E_{V_{\text{ext}}}[\rho] = \langle \Psi | \hat{K} + \hat{V} | \Psi \rangle + \langle \Psi | \hat{V}_{\text{ext}} | \Psi \rangle = F_{\text{HK}}[\rho] + \int \rho(\mathbf{r}) V_{\text{ext}}(\mathbf{r}) d\mathbf{r}, \quad (4-4)$$

where the Hönenberg-Kohn density functional $F_{\text{HK}}[\rho]$ is *universal* for any many-electron system. $E_{V_{\text{ext}}}[\rho]$ reaches its minimal value (equal to the ground state total energy) for the ground state density corresponding to V_{ext} .

A few remarks on these theorems can be made. First, the density contains as much information as the wave function itself. All observables can be considered as functionals of density. Second, is the universality of the Hönenberg-Kohn functional. Although there is no known explicit expression for the Hönenberg-Kohn functional, it can be regarded as a universal function for any many-electron system. This is because the Hönenberg-Kohn functional does not

contain information on the nuclei and their positions. Third, the second theorem makes it possible to use the variational principle of Rayleigh-Reitz to find the ground state energy.

4.2.2.2 The Kohn-Sham equations

The equations of Kohn-Sham provide a practical method in obtaining the ground state density. Before introducing these equations, a brief review of the exchange and correlation energies are presented.

4.2.2.2.1 The exchange and correlation energies

The total (exact) energy functionals, $E_e[\rho]$ and $E_{\text{HF}}[\rho]$ related to the exact and Hartree-Fock Hamiltonians are given by

$$E_e = K + V, E_{\text{HF}} = K_0 + V. \quad (4-5)$$

V , which is the electron-electron interaction functional, can be expressed as the sum of two terms: the Hartree contribution, V_H , and the exchange contribution, V_x . Thus,

$$V = V_x + V_H. \quad (4-6)$$

K is the exact kinetic energy of the system and K_0 is the kinetic energy of the non-interacting electron gas. The *correlation energy* is defined as part of the total energy which is present in the exact solution, but absent in the Hartree-Fock solution. The correlation potential is given by

$$V_c = K - K_0. \quad (4-7)$$

The exchange contribution to the total energy, is defined as the part which is present in the Hartree-Fock solution but absent in the Hartree solution. If one considers the Hartree energy functional to be written as the sum of the total kinetic energy of the non-interacting electron gas, K_0 , and the Hartree potential, V_H , $E_H = K_0 + V_H$, then the exchange potential can be defined as:

$$V_x = V - V_H. \quad (4-8)$$

The Hönenberg-Kohn functional can now be written as

$$F_{\text{HK}} = K + V = K + V + K_0 - K_0 + V_H - V_H = K_0 + V_H + (K - K_0) + (V - V_H). \quad (4-9)$$

In (4-9), the term in the first parentheses according to (4-7) is the correlation potential, V_c , and the term in the second parentheses is the exchange potential, V_x , defined in (4-8). Therefore, (4-9) can be written as

$$F_{\text{HK}} = K_0 + V_H + V_c + V_x. \quad (4-10)$$

The *exchange correlation potential functional*, V_{xc} , is defined as the sum of the correlation potential and the exchange potential, that is the sum of the last two terms in (4-10). Thus,

$$V_{\text{xc}} \equiv V_x + V_c. \quad (4-11)$$

Therefore, the Hönenberg-Kohn functional can be summarized as the sum of two terms, the Hartree energy and the exchange-correlation potential

$$F_{\text{HK}} = E_{\text{H}} + V_{\text{xc}}. \quad (4 - 12)$$

The energy functional can take the explicit form as

$$E_{V_{\text{ext}}}[\rho] = K_0[\rho] + V_{\text{H}}[\rho] + V_{\text{xc}}[\rho] + V_{\text{ext}}[\rho]. \quad (4 - 13)$$

The expression above can be interpreted as the energy functional of a non-interacting electron gas subject to two external potentials: one due to the nuclei and the other due to exchange-correlation effects. The corresponding Hamiltonian is known as the *Kohn-Sham Hamiltonian*, $\hat{H}_{\text{KS}}$ and is written as

$$\hat{H}_{\text{KS}} = \hat{K}_0 + \hat{V}_{\text{H}} + \hat{V}_{\text{xc}} + \hat{V}_{\text{ext}} = -\frac{\hbar^2}{2m} \sum_i \nabla_{\mathbf{r}_i}^2 + \frac{e^2}{4\pi\epsilon_0} \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + V_{\text{xc}} + V_{\text{ext}}. \quad (4 - 14)$$

The exchange-correlation potential is given by the functional derivative

$$\hat{V}_{\text{xc}} = \frac{\delta V_{\text{xc}}[\rho]}{\delta \rho}. \quad (4 - 15)$$

4.2.2.2.2 The theorems of Kohn and Sham

Below the theorem of Kohn and Sham is presented without proof.

Theorem 3: The exact ground state density $\rho(\mathbf{r})$ of a system consisting of N electrons is

$$\rho(\mathbf{r}) = \sum_{i=1}^N \psi_i(\mathbf{r})^* \psi_i(\mathbf{r}), \quad (4 - 16)$$

where the single-particle wave functions $\psi_i(\mathbf{r})$ are the N lowest-energy solutions of the Kohn-Sham equation:

$$\hat{H}_{\text{KS}} \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}). \quad (4 - 17)$$

One must realize the fact that the single particle wave functions ψ_i are *not* electronic wave functions, but rather they describe mathematical quasi-particles. Only the overall density of these quasi-particles is to be equal to the true electron density. The energy eigenvalues of ε_i are also *not* single-electron energies.

4.2.2.2.3 The self-consistency problem

In (4 - 14), the Hartree operator $\hat{V}_{\text{H}}$ and the exchange-correlation operator $\hat{V}_{\text{xc}}$ depend on the density $\rho(\mathbf{r})$. The density itself depends on the wave functions $\psi_i(\mathbf{r})$ which are the solutions to Kohn-Sham Hamiltonian. Therefore, the problem of solving equation (4 - 17) is a self-consistency problem. The solutions, $\psi_i(\mathbf{r})$, determine the original equation through $\hat{V}_{\text{H}}$ and $\hat{V}_{\text{xc}}$ in $\hat{H}_{\text{KS}}$, and the equation cannot be solved before its solution is known.

In order to deal with this problem, one starts by *guessing* a starting density, ρ_0 . With the starting density one constructs a Hamiltonian $H_{\text{KS}1}$ and then attempts to solve the eigenvalue problem. The results are a set of wave functions, ψ_1 , which are used to form the density, ρ_1 . It will turn out in most cases that ρ_1 is different than ρ_0 . The density ρ_1 , is now used to construct the Hamiltonian $H_{\text{KS}2}$, which yields ρ_2 and the procedure is continued until a density ρ_f is

reached such that it generates a $H_{\text{KS}f}$ for which the solution is again ρ_f . In this case the final density is said to be *consistent* with the Hamiltonian. The self-consistent cycle is shown schematically by the flow chart below.

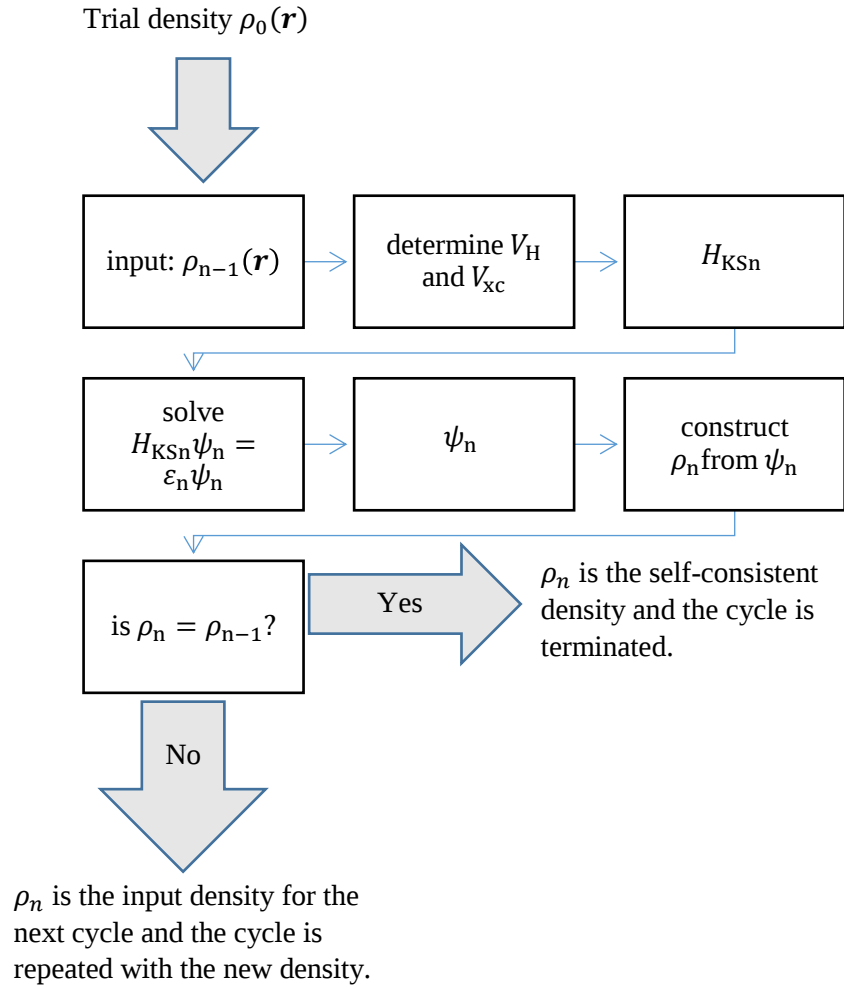


Figure 4.1 The flow chart describing the self-consistent cycles in solving the Kohn-Sham Hamiltonian eigenvalue equation.

4.2.2.3 The exchange correlation functional

Apart from the Born-Oppenheimer approximation made earlier, the Kohn-Sham scheme is exact. Now the problem reduces to finding the form of the exchange correlation functional. At this stage, approximations enter the theory. In what follows, a brief description of the known approximations used for the exchange correlation functional is presented.

4.2.2.3.1 The local density approximation (LDA)

In the so-called *local density approximation* (LDA), it is postulated that the exchange-correlation functional takes the following form

$$E_{xc}^{LDA} = \int \rho(\mathbf{r}) \varepsilon_{xc}(\rho(\mathbf{r})) d\mathbf{r}. \quad (4 - 18)$$

The exchange correlation energy, ε_{xc} , is a known function of density. It is derived numerically from the interacting homogeneous electron gas model via the quantum Monte Carlo calculations. Subtracting the non-interacting kinetic energy from the Hartree energy gives a numerical result for ε_{xc} . In LDA the exchange-correlation energy due to a particular density, $\rho(\mathbf{r})$ could be found by dividing the material into infinitesimally small volumes with a constant density. Each volume element contributes to the total exchange-correlation energy by an amount equal to the exchange correlation energy of an identical volume filled with a homogeneous electron gas with the same density as of the original material. Therefore, one expects LDA to be quite accurate for systems of slowly varying densities. LDA is also applicable for other cases including realistic ones as well.

4.2.2.3.2 The generalized gradient approximation (GGA)

One can improve the LDA approximation one step further by considering the exchange-correlation contribution of every infinitesimal volume not only dependent on the local density in that volume, but also on the density in the neighboring volumes. Therefore, the *gradient* of the density is taken into account. This approximation is called the *generalized gradient approximation*, (GGA)¹³ [2]. The exchange correlation functional for the GGA has the following form

$$E_{xc}^{GGA} = \int \rho(\mathbf{r}) \varepsilon_{xc}(\rho(\mathbf{r}), \nabla \rho(\mathbf{r})) d\mathbf{r}. \quad (4 - 19)$$

In the equation above, the exchange correlation energy, ε_{xc} , is a known function of density, $\rho(\mathbf{r})$, and its spatial gradient, $\nabla \rho(\mathbf{r})$. There are improved and extended versions of GGA which are known as meta-GGA schemes. The meta-GGA, however has not been studied and applied in this research.

¹³ It should be noted that the generalized gradient approximation scheme of Perdew, Ernzerhof, and Burke, is used for the exchange correlation potential in all the calculations for the various compounds in this research.

4.2.3 Solving the equations

Using either the Hartree-Fock method or DFT, one must solve the infinite set of single-electron equations given below:

$$\left(-\frac{\hbar^2}{2m}\nabla_1^2 + \frac{e^2}{4\pi\epsilon_0}\int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' + V_\alpha + V_{\text{ext}}\right)\phi_m(\mathbf{r}) = \hat{H}_{\text{sp}}\phi_m(\mathbf{r}) = \epsilon_m\phi_m(\mathbf{r}). \quad (4-20)$$

Here $\hat{H}_{\text{sp}}$ is the single-particle Hamiltonian. In the case of Hartree-Fock method, V_α is the *exchange* operator and $\phi_m(\mathbf{r})$ are the true one-electron wave functions. In DFT, V_α is the *exchange-correlation* operator in the LDA, GGA or other approximations. In this case, $\phi_m(\mathbf{r})$ is the mathematical single-particle function.

In order to solve (4-20), one expands the ϕ_m 's in terms of a known basis set, ϕ_p^b

$$\phi_m = \sum_{p=1}^P c_p^m \phi_p^b. \quad (4-21)$$

In principle, the functions ϕ_m belong to a function space of infinite dimensionality, thus P is infinite. Practically one considers a finite set of base functions in order to solve (4-20). The solutions, however, are not exact but can be very close to the actual wave functions. By substituting (4-21) into (4-20) and left-multiplying by $\langle \phi_i^b |$, where $i=1,\dots,P$ one finds [3]

$$\begin{bmatrix} \dots & \dots & \dots \\ \vdots & \langle \phi_i^b | \hat{H}_{\text{sp}} | \phi_j^b \rangle - \epsilon_m \langle \phi_i^b | \phi_j^b \rangle & \vdots \\ \dots & \dots & \dots \end{bmatrix} \begin{bmatrix} c_1^m \\ \vdots \\ c_P^m \end{bmatrix} = \begin{bmatrix} 0 \\ \vdots \\ 0 \end{bmatrix} \quad (4-22)$$

Diagonalization of the Hamiltonian matrix leads to P eigenvalues with P sets of coefficients which describe each of the P eigen-states in a given basis set. The larger the number of eigen-functions, the larger the P and the more computational time required.

4.2.3.1 Efficient basis sets

An efficient basis set is a basis set such that it resembles ϕ_m as much as possible. In other words, a basis set which is very similar to ϕ_m . In this case, only a few limited numbers of such states are needed to describe the system and thus the size of the matrix is reduced resulting in less computational time.

4.2.3.2 Biased basis set

An efficient choice for the basis set however, assumes that one knows the solutions before solving the problem. Therefore, such a basis set is never very general; for some cases it quickly leads to the solutions while for the majority of cases it poorly describes the eigenfunctions. In the latter case, the required P is much higher than what is affordable, while limiting P leads to approximate eigen-functions that are not acceptable. These basis sets are called biased.

The task of theoretical condensed matter physics in this case is to find a basis set that is both efficient and unbiased. In the remainder of this chapter, two families of such basis sets are presented; the plane waves and the augmented plane waves.

4.3 The pseudopotential method

The eigenstates of the solid state Hamiltonian are expanded in a basis set which is desired to be both mathematically simple and also efficient in a way that the number of bases functions remain relatively low. These criterion make the theoretical development and the programming simpler. The simplest of the basis sets is the *plane wave* (PW) basis set.

According to Bloch's theorem any, eigenfunction of a periodic Hamiltonian (that is, the Hamiltonian describing a perfect crystal), $\psi_{\mathbf{k}}^n$, can be expanded in plane waves as

$$\psi_{\mathbf{k}}^n = \sum_{\mathbf{K}} c_{\mathbf{K}}^{n,\mathbf{k}} e^{i(\mathbf{k}+\mathbf{K})\cdot\mathbf{r}}. \quad (4-23)$$

By comparing (4-23) with (4-21), one can write the basis function for $\psi_{\mathbf{k}}^n(\mathbf{r})$ as crystal momentum eigenstates

$$\phi_{\mathbf{K}}^{\mathbf{k}} \rightarrow |\mathbf{K}\rangle = e^{i(\mathbf{k}+\mathbf{K})\cdot\mathbf{r}}. \quad (4-24)$$

These eigen-states satisfy the orthogonality relation

$$\langle \mathbf{K}_2 | \mathbf{K}_1 \rangle = \int e^{i(\mathbf{K}_1 - \mathbf{K}_2)\cdot\mathbf{r}} d\mathbf{r} = \delta(\mathbf{K}_1 - \mathbf{K}_2). \quad (4-25)$$

Working with an infinite basis set is not practically convenient, especially regarding numerical calculations. Therefore, the expansion (4-23) should be chosen to terminate after a certain value of $\mathbf{K}$, namely $\mathbf{K}_{\max}$. For the plane wave expansion, this corresponds to a sphere of radius $K_{\max}$ centered at the origin of the reciprocal space. All the reciprocal lattice vectors inside this sphere are taken into the basis set. The energy related to $\mathbf{K}_{\max}$ is often named the *cutoff energy*, E_c

$$E_c = \frac{\hbar^2 K_{\max}^2}{2m}. \quad (4-26)$$

The matrix elements of the Kohn-Sham Hamiltonian are calculated in the plane wave basis and the resulting matrix is diagonalized. For each eigenvalue $\epsilon^{n,\mathbf{k}}$ an eigenvector $[c_{\mathbf{K}}^{n,\mathbf{k}}]_{P \times 1}$ of P values corresponds. In other words, P different eigenfunctions with the same $\mathbf{k}$ but a different band index is found. This process is should be repeated for as many $\mathbf{k}$ -points required for a dense enough sampling of the first Brillouin zone.

In order to justify the efficiency of the plane wave basis set, it is noted that the most oscillating part of the wave functions are the tails which extend out into the region close to the nucleus. In solids, this region however, is mostly shielded from the more outer regions of the atoms where chemistry takes place. In these inner regions of the atoms, electrons behave almost as if they were in free atoms. Thus, it is reasonable to replace the potential in the inner regions of the atoms by a *pseudopotential* which leads to wave functions with very smooth tails inside the atoms and therefore only a few plane waves are needed. Into the outer regions of the atoms, the

pseudopotential continuously evolves into the true potential, such that in these regions the crystal behaves as if nothing has changed.

There is no unique procedure to construct a pseudopotential for a particular system. However, two criteria should be considered in constructing the pseudopotential. First is a choice in which only few plane waves are needed, in this case the pseudopotential is often referred to as a *soft* pseudopotential. Secondly, is a choice that can apply for systems in different environments such as molecules, clusters, solids, surfaces, and etc. Such a pseudopotential is known as a *transferrable* pseudopotential.

4.4 The Augmented plane wave (APW) method

The pseudopotential method lacks efficiency when one considers the region near the nucleus, for instance, in the case of studying the hyperfine fields. Due to the strong nuclear potential, an expansion based on plane waves is not accurate enough, therefore one must seek alternative approaches to the problem. The first of these alternatives is the so-called *Augmented Plane Wave* (APW) basis set which is briefly discussed in this section.

Regarding the unit cell in the crystal structure of typical solids, one can consider the electrons to be almost *free* in regions relatively far from the atomic nuclei. In these areas, one can describe the electronic wave function by *plane waves*. This is justified by the fact that in regions far from the atomic nucleus, the attractive electrostatic potential is weak. One can understand this based on two major arguments. The first is due to the fact that the outermost electrons (which are responsible for almost all the physical and chemical properties of a solid) are further apart from the nucleus and thus are weakly bound to it. The second is due the screening effect of core electrons, which even further weaken the electrostatic potential of the nucleus experienced by the outer electrons. As a result, one can neglect the potential of the nucleus all together and the Hamiltonian describing the energy of these electrons will only contain a kinetic energy part. The solutions of the Schrödinger equation in this case are well known to be plane waves. On the other hand, in regions close to the nuclei, electrons can be considered to behave as if they were in *free atoms*. Therefore, in these regions one expects that a different basis set is convenient in order to describe the electrons, namely the atomic wave functions.

The APW method therefore, deals with two set of basis: the plane waves and the atomic wave functions. This is possible only if one partitions the volume of the unit cell into two distinct regions. The region away from the atomic nuclei is known as the *interstitial* region. The region in the vicinity of the center of atoms (or more specifically around the lattice points) is known as the *muffin-tin* (MT) *region*. One can geometrically picture these regions by a sphere centered at the lattice point. These spheres are known as *muffin-tin* (MT) *spheres* and are identified by a *muffin-tin radius*. In figure 4.2, these two regions are shown schematically for a unit cell consisting of two atoms.

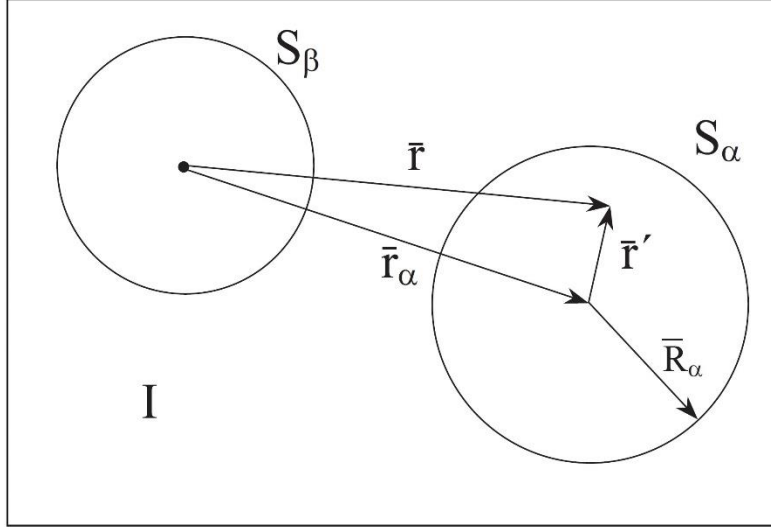


Figure 4.2 The partitioning of the unit cell into muffin-tin spheres and the interstitial region, for a case with two atoms. The center of the left atom is the center of the coordinate system [3].

One such APW used for the expansion of the wave function $\psi_{\mathbf{k}}^n$ is defined as:

$$\phi_{\mathbf{k}}^{\mathbf{k}}(\mathbf{r}, E) = \begin{cases} \frac{1}{\sqrt{V}} e^{i(\mathbf{k}+\mathbf{K}) \cdot \mathbf{r}}, & \mathbf{r} \in I \\ \sum_{l,m} A_{lm}^{\alpha, \mathbf{k}+\mathbf{K}} u_l^{\alpha}(r', E) Y_m^l(\hat{\mathbf{r}}'), & \mathbf{r} \in S_{\alpha} \end{cases} \quad (4-27),$$

where V is the volume of the unit cell. From (4-27), one realizes that the APW basis set is $\mathbf{k}$ -dependent. The Y_m^l are the spherical harmonics. $A_{lm}^{\alpha, \mathbf{k}+\mathbf{K}}$ and E are yet undetermined parameters, and $\hat{\mathbf{r}}'$ describes the direction of $\mathbf{r}'$ in terms of the spherical angles θ' and ϕ' . The u_l^{α} are the radial wave functions for a free atom α and energy E . It must be mentioned that u_l^{α} are part of the basis set and not the eigen-functions themselves since the atoms in a solid are not free. The boundary condition requires that the plane waves in the interstitial region match the wave functions in the muffin-tin spheres at the muffin-tin boundaries. This is done via expanding the plane waves in terms of the spherical harmonics about the center of the muffin-tin spheres. For atom α such an expansion is given by

$$\frac{1}{\sqrt{V}} e^{i(\mathbf{k}+\mathbf{K}) \cdot \mathbf{r}} = \frac{4\pi}{\sqrt{V}} e^{i(\mathbf{k}+\mathbf{K}) \cdot \mathbf{r}_{\alpha}} \sum_{l,m} i^l j_l(|\mathbf{k} + \mathbf{K}| |\mathbf{r}'|) Y_m^l \left(\frac{\mathbf{k}+\mathbf{K}}{|\mathbf{k}+\mathbf{K}|} \right) Y_m^l(\mathbf{r}'). \quad (4-28)$$

In (4-28), j_l is the l -th order Bessel function. Matching (4-27) and (4-28) at the boundary of the sphere ($\mathbf{r}' = \mathbf{R}_{\alpha}$) yields

$$A_{lm}^{\alpha, \mathbf{k}+\mathbf{K}} = \frac{4\pi i^l e^{i(\mathbf{k}+\mathbf{K}) \cdot \mathbf{r}_{\alpha}}}{\sqrt{V} u_l^{\alpha}(\mathbf{R}_{\alpha}, E)} j_l(|\mathbf{k} + \mathbf{K}| |\mathbf{r}'|) Y_m^l \left(\frac{\mathbf{k}+\mathbf{K}}{|\mathbf{k}+\mathbf{K}|} \right). \quad (4-29)$$

This uniquely defines the $A_{lm}^{\alpha, \mathbf{k}+\mathbf{K}}$. Since there are an infinite number of terms in (4-28), there will be an infinite number of corresponding $A_{lm}^{\alpha, \mathbf{k}+\mathbf{K}}$ to achieve the matching which is

computationally impractical. In practice, one should choose an $l_{\max}$ such that the infinite series in (4 – 28) truncates for $l > l_{\max}$. A reasonable choice for $l_{\max}$ is given by the condition $R_{\alpha}K_{\max} = l_{\max}$ [3], where $K_{\max}$ is the cut-off for the plane waves. The finite value for $l_{\max}$ indicates that for each APW, the matching at the boundaries will not be exact, however it yields reasonable solutions. If one chooses a higher value for $l_{\max}$ than conditioned by $R_{\alpha}K_{\max} = l_{\max}$, the behavior of the solutions at the boundaries will become unstable.

The only problem with the APW method is the undetermined value of E . The procedure is as follows: one starts off with a trial value for E , say $\varepsilon_{\mathbf{k}}^n$ and constructs the related APW's. Next the Hamiltonian matrix is constructed and the secular equation is solved. If $\varepsilon_{\mathbf{k}}^n$ turns out to be a root of the secular equation, the trial value for E is correct. However, usually this is not the case and one should use another trial value, and the procedure is repeated. With the help of root determination algorithms, the cycles continue until a root such as $\varepsilon_{\mathbf{k}}^{n=1}$ is found. The whole procedure now starts over for $\varepsilon_{\mathbf{k}}^{n=2}$ and etc.

Considering the computational time for the APW method, it is inherently slow, much slower than the pseudopotential method. The reason lies in the fact that with a plane wave basis set, all eigenvalues are found by single diagonalization, while in the APW method, one diagonalization is needed for every eigenvalue.

In figure 4.3, a schematic representation of the flowchart algorithm for the APW method is shown.

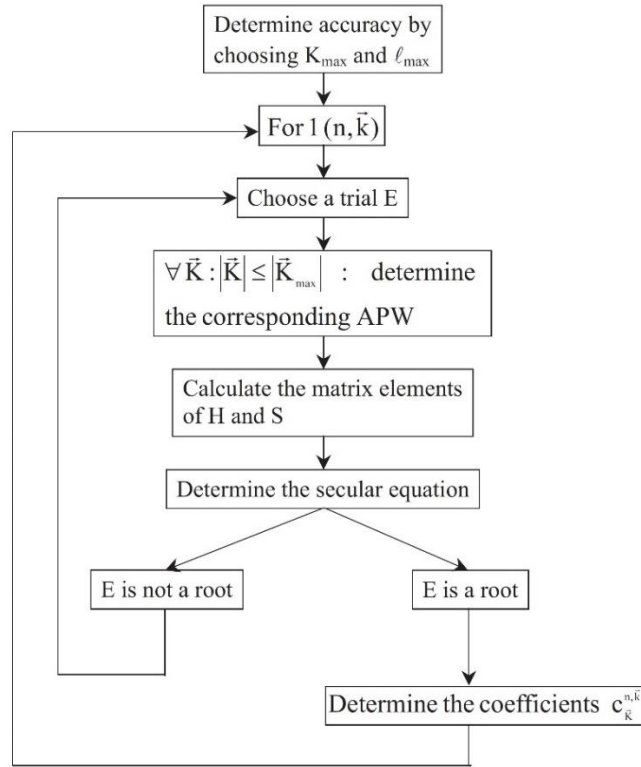


Figure 4.3 Flowchart of the APW method [3].

4.5 The LAPW method

In this section, a brief review of the linearized augmented plane wave (LAPW) method is presented. First the regular LAPW method is introduced and later the LAPW with local orbitals (LAPW+LO) method is discussed.

4.5.1 The regular LAPW method

The LAPW method is just an extension and manipulation of the regular APW method in the following way: If one knows (or has calculated) the atomic radial wave functions, $u_l^\alpha(r', E)$, (where $E = \epsilon_k^n$ are the yet unknown eigenenergies) at a particular energy, E_0 , a Taylor expansion can be constructed in order to find the $u_l^\alpha(r', E)$'s at energies not far away from it

$$u_l^\alpha(r', \epsilon_k^n) = u_l^\alpha(r', E_0) + (E_0 - \epsilon_k^n) \left(\frac{\partial u_l^\alpha(r', E)}{\partial E} \right)_{E=E_0} + \dots \quad (4-30)$$

Upon substitution of the first two terms of (4-30) in the APW for a fixed E_0 , an LAPW is defined. However, the energy difference $E_0 - \epsilon_k^n$ is unknown and therefore an undetermined coefficient, $B_{lm}^{\alpha, k+K}$, must be introduced

$$\phi_{\mathbf{k}}^{\mathbf{k}}(\mathbf{r}) = \begin{cases} \frac{1}{\sqrt{V}} e^{i(\mathbf{k}+\mathbf{K}) \cdot \mathbf{r}} & \mathbf{r} \in I \\ \sum_{l,m} \left(A_{lm}^{\alpha, k+K} u_l^\alpha(r', E_0) + B_{lm}^{\alpha, k+K} \left(\frac{\partial u_l^\alpha(r', E)}{\partial E} \right)_{E=E_0} \right) Y_m^l(\hat{\mathbf{r}}') & \mathbf{r} \in S_\alpha \end{cases} \quad (4-31)$$

The coefficients $A_{lm}^{\alpha, k+K}$ and $B_{lm}^{\alpha, k+K}$ are determined via the boundary conditions, that is at the sphere boundary, the function should match the plane wave both in magnitude and in slope. This is done by an expansion similar to (4-28) and its radial derivatives. The result is a 2×2 system for which both coefficients are determined.

The equation (4-27) is not the final definition of LAPW yet. For instance, if one considers an eigenstate ψ_k^n that has a pre-dominantly p-character ($l = 1$) for atom α , this indicates that the $A_{(l=1)m}^{\alpha, k+K}$ are large in the LAPW expansion. Thus it is reasonable to choose E_0 near the center of the p-band, in this case only the first two terms in the Taylor expansion (4-30) can be considered and one can terminate the expansion after the linear term. This procedure can be repeated for every physically important l (s, p, d , and f states) and for every atom. Therefore a set of well-chosen $E_{1,l}^\alpha$ up to $l = 3$ should be considered. The ultimate definition of an LAPW is thus,

$$\phi_{\mathbf{k}}^{\mathbf{k}}(\mathbf{r}) = \begin{cases} \frac{1}{\sqrt{V}} e^{i(\mathbf{k}+\mathbf{K}) \cdot \mathbf{r}} & \mathbf{r} \in I \\ \sum_{l,m} \left(A_{lm}^{\alpha, k+K} u_l^\alpha(r', E_{1,l}^\alpha) + B_{lm}^{\alpha, k+K} \left(\frac{\partial u_l^\alpha(r', E)}{\partial E} \right)_{E=E_{1,l}^\alpha} \right) Y_m^l(\hat{\mathbf{r}}') & \mathbf{r} \in S_\alpha \end{cases} \quad (4-32)$$

With the fixed values of $E_{1,l}^\alpha$, the basis functions can be calculated once and for all.

In order to consider the accuracy of the LAPW basis set, the product of the smallest muffin-tin radius, $R_\alpha^{\min}$ and the maximum wave vector $K_{\max}$, in the plane wave expansion, is to be determined: $R_\alpha^{\min} \times K_{\max}$. This is reasoned by the following argument: if the smallest muffin-tin radius is increased, the closest point a plane wave can come to a nucleus is moved further away from it, and less plane waves are needed in order to describe the behavior of the wave function in the interstitial region, therefore $K_{\max}$ can be reduced, in other words a reasonable criterion would be such that $R_\alpha^{\min} \times K_{\max}$ remains constant. From the computational point of view the smaller $K_{\max}$, the smaller the size of the matrices and thus the less computational time needed, however, one must consider the fact that increasing $R_\alpha^{\min}$ too much does come with a price; the spherical harmonics become practically less convenient to describe wave functions in regions far from the nucleus and thus the precision of the computations will be less.

4.5.2 LAPW with local orbitals (LAPW+LO)

In the LAPW method, one should distinguish between the *core states* and the *valence states*. Core states are those electronic states that are strongly bound to the nucleus and large negative energy values. Electrons in these states behave such as if they were in a free atom. The criterion for a core state is that it does not participate directly in the chemical bonding with other atoms, thus they must be entirely contained inside the muffin-tin spheres. States that leak out of the muffin-tin spheres are the so-called valence states. These states participate in chemical bonds and are treated by LAPW. One must realize that although the core states are treated as in free atoms, but they are subject to the potential due to the valence states as well as they are subject to the potential of the nucleus.

Regarding this classification of states, it might happen that states with the same orbital angular momentum quantum l but with different principal quantum numbers n are both considered valence states (for instance two valence states with energies $E_{1,l}^\alpha$ and $E_{2,l}^\alpha$). In such cases, some of these states (with known energies $E_{2,l}^\alpha$) will lie deeply below the Fermi level but also not entirely confined to the core, such states are called *semi-core* states, whereas the other states (with different energies, i.e. $E_{1,l}^\alpha$) are much closer in energy to the Fermi level. In such cases, it is not clear how to choose $E_{1,l}^\alpha$. The dilemma is solved by adding another basis function to the LAPW basis set, called a *local orbital* (LO). The definition of a local orbital is as follows

$$\phi_{\alpha,LO}^{lm}(\mathbf{r}) = \begin{cases} 0 & \mathbf{r} \notin S_\alpha \\ \left(A_{lm}^{\alpha,LO} u_l^\alpha(r', E_{1,l}^\alpha) + B_{lm}^{\alpha,LO} \left(\frac{\partial u_l^\alpha(r', E)}{\partial E} \right)_{E=E_{1,l}^\alpha} + C_{lm}^{\alpha,LO} u_l^\alpha(r', E_{2,l}^\alpha) \right) Y_m^l(\hat{\mathbf{r}}') & \mathbf{r} \in S_\alpha \end{cases} \quad (4-33)$$

In the equation above, $E_{1,l}^\alpha$ is related to the valence state(s) which is or are close to the Fermi level and an ordinary LAPW basis set is used with radial functions and their first derivatives at $E_{1,l}^\alpha$. On the other hand, valence state(s) lower in energy are sharply peaked at $E_{2,l}^\alpha$ (since they are atomic like states). A local orbital is defined for a particular l , m , and atom α . In the interstitial region and within the muffin-tin spheres of other atoms, the local orbital is zero. Local orbitals

are not connected to plane waves in the interstitial region, therefore the coefficients $A_{lm}^{\alpha,LO}$, $B_{lm}^{\alpha,LO}$, and $C_{lm}^{\alpha,LO}$ have no $\mathbf{k}$ and $\mathbf{K}$ dependence. These three coefficients are determined by boundary conditions and the condition that the local orbitals are normalized. The boundary conditions require the coefficients and their slopes to be zero at the muffin-tin boundary.

The addition of local orbitals increases the size of the basis set; for instance adding local orbitals to p , d , and f states increases the basis set by $3+5+7=15$ function per atom in the unit cell. This increases the computational time but in exchange a better accuracy for the results are obtained.

4.6 The APW+lo method

4.6.1 The APW+lo basis set

As mentioned in section 4.4, in the APW method, the basis set is energy dependent. This energy dependence is removed in the LAPW+LO method as discussed in section 4.5, although it increases the computational time due to the increase in the size of the basis set. The APW+lo method invokes the advantages of both APW and LAPW+LO methods without their deficiencies. In other words, in this method the basis set is energy independent and it has the same size as in the APW method.

The APW+lo basis set contains two kinds of basis functions. The first kind are the regular APW basis set but at fixed energies, $E_{1,l}^\alpha$ defined below:

$$\phi_{\mathbf{K}}^{\mathbf{k}}(\mathbf{r}) = \begin{cases} \frac{1}{\sqrt{V}} e^{i(\mathbf{k}+\mathbf{K})\cdot\mathbf{r}} & \mathbf{r} \in I \\ \sum_{l,m} A_{lm}^{\alpha,\mathbf{k}+\mathbf{K}} u_l^\alpha(r', E_{1,l}^\alpha) Y_m^l(\hat{\mathbf{r}}') & \mathbf{r} \in S_\alpha \end{cases} \quad (4-34)$$

The second kind of functions augment the first kind by so-called *local orbitals*. One must consider the fact that these are not the same as the local orbitals used in the LAPW method. The local orbitals are defined as:

$$\phi_{\alpha,lo}^{lm}(\mathbf{r}) = \begin{cases} 0 & \mathbf{r} \notin S_\alpha \\ \left(A_{lm}^{\alpha,lo} u_l^\alpha(r', E_{1,l}^\alpha) + B_{lm}^{\alpha,lo} \left(\frac{\partial u_l^\alpha(r', E)}{\partial E} \right)_{E=E_{1,l}^\alpha} \right) Y_m^l(\hat{\mathbf{r}}') & \mathbf{r} \in S_\alpha \end{cases} \quad (4-35)$$

The coefficients $A_{lm}^{\alpha,lo}$ and $B_{lm}^{\alpha,lo}$ are determined by the normalizing the local orbitals and the boundary conditions which implies the local orbitals to have zero value at the muffin-tin boundary.

4.6.2 Mixed LAPW/APW+lo basis sets

The LAPW method requires a higher K_{max} than the APW+lo method. The reason is that, states with higher orbital angular momentum quantum number, l such as d and f states are difficult for LAPW. Also in cases in which the unit cell contains atoms with states such that their associated muffin-tin spheres are much smaller than the other spheres the LAPW method becomes computationally expensive. In these cases, one can treat such states with the APW+lo

method while for the other states a LAPW basis set can be used. Such an approach leads to a mixed LAPW/APW+lo basis set¹⁴.

4.6.3 APW+lo with local orbitals (APW+lo+LO)

Just as in the case discussed in section 4.5.2, the problem of semi-core states may appear within the APW+lo basis set. In such a case one adds local orbitals (LO). In the equation below, LO is defined for the APW+lo method:

$$\phi_{\alpha,LO}^{lm}(\mathbf{r}) = \begin{cases} 0 & \mathbf{r} \notin S_{\alpha} \\ \left(A_{lm}^{\alpha,LO} u_l^{\alpha}(\mathbf{r}', E_{1,l}^{\alpha}) + C_{lm}^{\alpha,LO} u_l^{\alpha}(\mathbf{r}', E_{2,l}^{\alpha}) \right) Y_m^l(\hat{\mathbf{r}}') & \mathbf{r} \in S_{\alpha} \end{cases} \quad (4-36)$$

As seen from (4 – 31) there is no derivative of the radial functions. In this way the APW+lo+LO basis set differs from the LAPW+LO set discussed in section 4.5.2. The coefficients $A_{lm}^{\alpha,LO}$ and $C_{lm}^{\alpha,LO}$ are determined by normalizing the local orbitals (LOs) and considering the boundary condition; the local orbitals are zero at the boundary of the muffin-tin spheres.

4.7 Electronic density distributions

Regarding the formation of chemical bonds in solids, one must distinguish the so-called *bonding charge densities* from *total charge densities*. In a given solid, an increase in charge density implies that the number of electrons per atom is increased, therefore the bond strength is altered. However, not always the increase in charge density strengthens the bonds. For energy bands that are more than half filled, an increase in the number of electrons per atom results in a smaller bond charge density contribution to the total charge density, thus localizing the valence electrons further (this situation is fully realized in a completely filled band leading to an insulating state). On the other hand, for energy bands that are less than half filled an increase in charge density leads to the formation of stronger covalent bonds leading to delocalized electrons. Thus, bond charge density differs from total charge density due to the energy band structure and available electronic Bloch states. The physical and chemical properties of solids are almost entirely due to the bond charge density distributions. The semi-core and core states, as mentioned before, have negligible effect on bond formation.

Valence charge density distributions of four out of the five compounds studied in this thesis have been calculated. Based on the brief discussion above one can analyze the role of bond charge density in formation of the chemical bonds in these systems (see chapter five).

Most of the material regarding the APW methods have been taken from Ref.[3]. For computational examples regarding these methods, the reader is referred to Ref.[3].

¹⁴ This mixed basis set, is the basis set used for the theoretical calculations for the various compounds in this research.

References

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- [2] J. P. Perdew, K. Burke, and Y. Wang, Phys. Rev. B, 54 (1996) 23.
- [3] S. Cottenier, Density Functional Theory and the family of (L) APW-methods: a step-by-step introduction, 2002-2013 (2nd edition), ISBN 978-90-807215-1-7 (freely available at http://www.WIEN2k.at/reg_user/textbooks).

Chapter five

Studied alloys and compounds

In this chapter, the compounds $\text{Al}_{13}\text{Fe}_4$, $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$, Fe_2NiGa , $(\text{Li}_{0.8}\text{Fe}_{0.2})\text{OHFeSe}$, and $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ studied in this thesis, are presented. This chapter contains five sections, each on a particular studied compound. The general format of each section is such that it starts with an introduction, followed by the theoretical methods of calculations, and discussion on their interpretations. Next, the experimental results are introduced and discussed. Each section ends with a short summary and conclusions.

5.1 $\text{Al}_{13}\text{Fe}_4$

5.1.1 Introduction

Al-rich aluminides form complex atomic structures. Examples of such structures are those of Al_2Fe [1], Al_5Fe_2 [2], and $\text{Al}_{13}\text{Fe}_4$ [3,4]. $\text{Al}_{13}\text{Fe}_4$ has been identified [5] as an approximant [6] to the decagonal quasicrystal [7]. The experimental studies of the magnetic properties of these three compounds show no long range magnetic ordering. The difficulty in studies of magnetic properties of these compounds lies in the fact that in both polycrystalline and single-crystal specimens a tiny fraction of a ferromagnetic second phase is unavoidably present. Al_2Fe (Ref. [8-10]) and Al_5Fe_2 (Refs. [10,11]) were shown to be spin glasses whereas $\text{Al}_{13}\text{Fe}_4$ was found to be a paramagnet [12,13].

Iron atoms are located at five inequivalent crystallographic sites in the monoclinic structure of $\text{Al}_{13}\text{Fe}_4$ [3,4]. Since the point symmetries of these sites are lower than the cubic (table 5.1), one could thus expect that the ^{57}Fe Mössbauer spectrum of $\text{Al}_{13}\text{Fe}_4$ should be a superposition of five quadrupole doublets [14]. In some Mössbauer studies [15-17], the spectra of $\text{Al}_{13}\text{Fe}_4$ were fitted with three single-Lorentzian-lineshape components, with no justification for the origins of these components. In other Mössbauer studies [12,18,19] the spectra at room temperature were fitted with two quadrupole-doublet components based on the following qualitative justification: Fe atoms in four $4i$ sites (table 5-1) have similar asymmetric atomic environments and thus contribute to one quadrupole-doublet component, and Fe atoms in the $8j$ site have a less asymmetric atomic environment and thus contribute to another quadrupole-doublet component with a smaller quadrupole splitting [14]. As shown from *ab initio* EFG calculations, this justification is incorrect (*vide infra*).

The situation described above, provides strong motivation to revisit the ^{57}Fe Mössbauer spectra of $\text{Al}_{13}\text{Fe}_4$. With the aid of *ab initio* EFG calculations, it is demonstrated that the shape of the ^{57}Fe Mössbauer spectra of $\text{Al}_{13}\text{Fe}_4$ can be accounted for with three quadrupole-doublet components resulting from Fe atoms at five inequivalent crystallographic sites. It is found that the quadrupole splittings corresponding to three quadrupole-doublets increase with decreasing temperature and that their temperature dependence is well described by a $T^{3/2}$ power-law relation. The Debye temperature of $\text{Al}_{13}\text{Fe}_4$ is determined and it is shown that the studied

compound is paramagnet down to 2.0 K. The presence of a pseudogap is around the Fermi energy in the electronic DOS of $\text{Al}_{13}\text{Fe}_4$ is found via theoretical calculations.

5.1.2 General considerations and structural parameters

$\text{Al}_{13}\text{Fe}_4$ crystallizes in the monoclinic space group $C2/m$ (No.12) [4]. The formula unit contains 13 Al atoms and 4 Fe atoms adding to a total of 17 atoms. The unit cell consists of 6 formula units, therefore a total number of 102 atoms are present in the unit cell of $\text{Al}_{13}\text{Fe}_4$. In table 5.1, the atomic coordinates, point symmetries, and multiplicities of the Al and Fe atoms within the unit cell is given. The crystallographic data used is taken from [4]. In figure 5-1, the unit cell of $\text{Al}_{13}\text{Fe}_4$ is shown.

Atom	Site	Point symmetry	x	y	z	V_{zz}	η
Fe(1)	4i	m	0.0851	0.0	0.3821	2.189	0.103
Fe(2)	4i	m	0.4018	0.0	0.6234	-2.308	0.532
Fe(3)	4i	m	0.0906	0.0	0.9889	-0.272	0.989
Fe(4)	4i	m	0.4031	0.0	0.9859	0.413	0.007
Fe(5)	8j	1	0.3195	0.2938	0.2777	2.337	0.399
Al(1)	4i	m	0.0649	0.0	0.1743	3.613	0.999
Al(2)	4i	m	0.3232	0.0	0.2819	-6.783	0.131
Al(3)	4i	m	0.2377	0.0	0.5349	-4.332	0.448
Al(4)	4i	m	0.0736	0.0	0.5803	1.723	0.832
Al(5)	4i	m	0.2406	0.0	0.9608	-4.972	0.377
Al(6)	4i	m	0.4792	0.0	0.8288	-3.707	0.924
Al(7)	2d	2/m	$\frac{1}{2}$	0.0	$\frac{1}{2}$	-4.742	0.868
Al(8)	4i	m	0.3057	0.0	0.7728	-1.495	0.059
Al(9)	4i	m	0.0870	0.0	0.7885	-2.498	0.160
Al(10)	8j	1	0.1850	0.2168	0.1106	-3.086	0.368
Al(11)	8j	1	0.3677	0.2113	0.1097	-3.389	0.152
Al(12)	8j	1	0.8217	0.7790	0.6654	-3.163	0.802
Al(13)	8j	1	0.4916	0.2334	0.3296	3.472	0.692
Al(14)	8j	1	0.3634	0.2188	0.4786	-3.584	0.444
Al(15)	4g	2	0.0	0.2496	0.0	4.690	0.739

Table 5.1 Crystallographic data [4] for $\text{Al}_{13}\text{Fe}_4$ and calculated V_{zz} (in units of $10^{21} \frac{\text{V}}{\text{m}^2}$) and η .

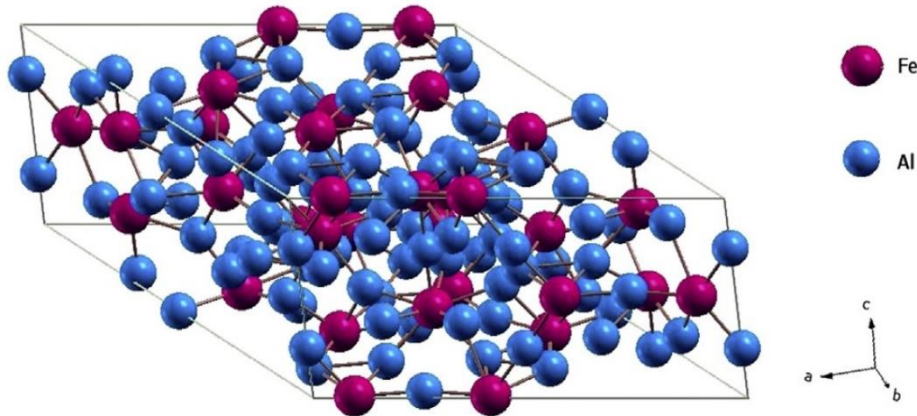


Figure 5.1 The unit cell of $\text{Al}_{13}\text{Fe}_4$.

In figure 5.1, the monoclinic unit cell of $\text{Al}_{13}\text{Fe}_4$ is characterized by the following lattice parameters which are obtained by the X-ray diffraction pattern of the sample in powdered form, $a = 15.503(2) \text{ \AA}$, $b = 8.063(2) \text{ \AA}$, $c = 12.464(2) \text{ \AA}$, and $\beta = 107.71(2)^\circ$.

5.1.3 Theoretical calculations and results

In this section, the theoretical methodology used in the calculations is presented and the following results are discussed.

5.1.3.1 Theoretical methodology

The theoretical calculations are performed within the WIEN2k package [20]. In carrying out the calculations the full potential linearized augmented plane wave plus local orbital (FP-LAPW+lo) method is used. In this method, the unit cell of the compound is partitioned into two regions; the non-overlapping muffin-tin (MT) spheres which are centered at the atomic nuclei, and the interstitial region in between the MT spheres. The wave functions within the interstitial region are expanded in terms of plane waves whereas inside the MT spheres they are expanded in basis of atomic radial functions times spherical harmonics. As in the case of all the alloys and compounds studied in this thesis, the form of the exchange-correlation potential used in the calculations is the so-called generalized gradient approximation (GGA) scheme developed by Perdew, Burke, and Ernzerhof [21]. The spherical harmonic basis used for the expansion of the wave function inside the MT spheres were cut off at a maximum orbital angular momentum quantum number of $l_{\text{max}} = 10$. A total number of 115 nonequivalent k -points in the irreducible wedge of the Brillouin zone was used in order to carry out the integrations of the self-consistency cycles. A cut-off criterion of $R_{\text{MT}} \times K_{\text{MAX}} = 7$ was used in the initialization of the calculations, where R_{MT} represents the smallest spherical muffin-tin radius present in the system and K_{MAX} is the maximum modulus of the reciprocal lattice vector used in the expansion of the wavefunction in the interstitial region (see chapters 4 and 6). The values used for the muffin-tin radii of aluminum and iron atoms were $2.00 \text{ \AA}$ and $2.33 \text{ \AA}$ respectively. The convergence criterion used for charge and energy in the successive iterations of the self-consistency cycles (see Appendix) were $10^{-3} e$ and 10^{-3} Ry respectively.

5.1.3.2 Theoretical results

In this section the results of the theoretical calculations regarding the electronic structure of the $\text{Al}_{13}\text{Fe}_4$ system along with the electric field gradient at the atomic nuclei are given.

5.1.3.2.1 Density of states

The total and atomic density of states (DOS) for paramagnetic $\text{Al}_{13}\text{Fe}_4$ is given in figure 5.2. In this figure, the total contribution arising from the aluminum atoms and the total contribution arising from iron atoms is given in comparison with each other. The highly peaked DOS near the Fermi region, below the fermi energy, E_F , is mainly due to iron states which arise from the contributions originating from Fe $3d$ orbitals. However, the DOS arising from the numerous Al atoms in this system appear to be widely spread across the Fermi region with a rather uniform

distribution along with a relatively small minimum at the Fermi level. The Al 3s and 3p states are the main contributions of Al atoms to the DOS in this system.

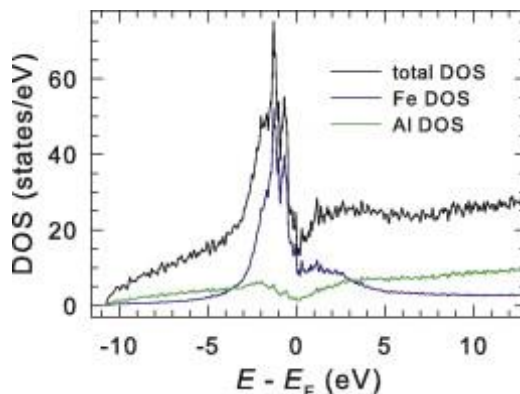


Figure 5.2 Total and atom resolved electronic density of states (DOS) of $\text{Al}_{13}\text{Fe}_4$.

Considering the total density of states, one observes the presence of a narrow pseudogap with a width of ~ 0.2 eV located at 0.1 eV above the Fermi energy in figure 5.2. The existence of such a pseudogap is a characteristic feature of quasicrystals along with their crystalline approximants. The origins of this pseudogap might be due to the strong hybridization between Fe 3d states and Al 3s and 3p states [27,28]. Another remarkable feature which is deduced from figure 5.2 is the finite (non-zero) DOS at the Fermi level. This fact can count for the metallicity of this system. The large degree of overlap between Fe 3d states and Al 3s and 3p states along a wide energy interval indicates metallic bonding to be the dominant type of bonding in this system verifying its metallic nature.

5.1.3.2.2 Electronic band structure

In figure 5.3, the result of the electronic band structure calculations along the various directions in the first Brillouin zone of $\text{Al}_{13}\text{Fe}_4$ is presented. The existence of such compact and high energy bands and the high degree of overlap between valence and conduction states around the Fermi energy indicates that the nature of the studied compound is metallic. Due to the large number of atoms present in the unit cell, the calculated bandstructure of this system results in the presence of numerous energy bands.

5.1.3.2.3 Electric field gradient

Due to the noncubic form of the unit cell, one expects non-zero electric field gradients at the atomic nuclei in $\text{Al}_{13}\text{Fe}_4$. In table 5.1, the calculated values for the principle component of the electric field gradient tensor, V_{zz} , and the asymmetry parameter, η , are given at all Fe and Al sites. After considering the experimental methods, the comparison between the calculated and measured EFG components is analyzed and discussed.

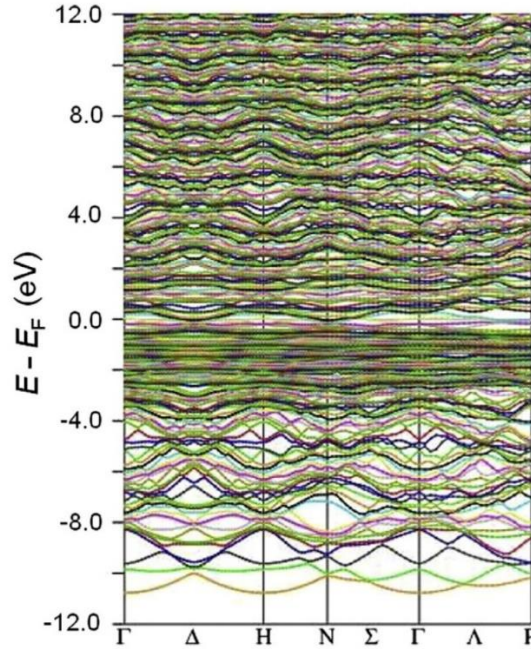


Figure 5.3 The electronic band structure of $\text{Al}_{13}\text{Fe}_4$.

5.1.4 Experimental methods and results

In this section, the experimental methodology used in the preparation of the $\text{Al}_{13}\text{Fe}_4$ sample is presented. The experimental results are briefly discussed and compared with the theoretical calculations.

5.1.4.1 Sample preparation

An ingot of nominal composition $\text{Al}_{13}\text{Fe}_4$ was prepared by inductive melting constituent elements in water-cooled copper crucible under an argon atmosphere [24]. It was then annealed at 1223 K for 400 h and at 853 K for 24 h, followed by a slow cooling to room temperature.

5.1.4.2 X-ray diffraction measurements

In order to determine the structural parameters of $\text{Al}_{13}\text{Fe}_4$, X-ray diffraction measurements were performed at 298 K in Bragg-Brentano geometry on a PANalytical X'Pert scanning diffractometer using $\text{Cu K}\alpha$ radiation in the 2θ range in steps of 0.02° . The $\text{K}\beta$ line was eliminated by using a Kevex PSi2 Peltier-cooled solid-state Si detector.

In figure 5.4, the X-ray powder diffraction pattern for $\text{Al}_{13}\text{Fe}_4$ is given. A Rietveld refinement [25] of the X-ray powder diffraction data was performed using the atomic coordinates in table 5.1 which yield to the lattice parameters used in the theoretical calculations. There is good agreement between the measured values for the lattice parameters and those of the earlier reports [4].

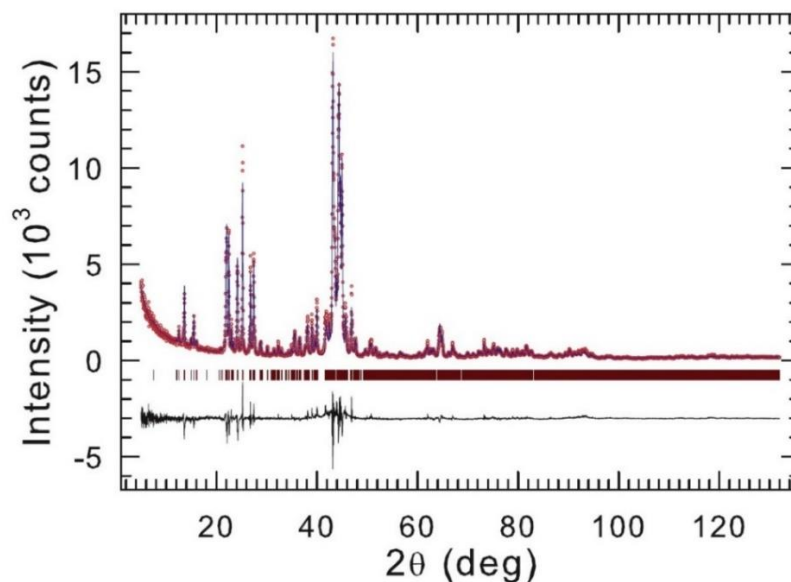


Figure 5.4 Powder X-ray diffraction pattern of $\text{Al}_{13}\text{Fe}_4$ at 298 K. The experimental data are denoted by open circles while the line through the circles represent the results of the Rietveld refinement. The row of vertical bars shows the Bragg peak positions for the $C2/m$ space group. The lower solid line represents the difference curve between the calculated and experimental patterns.

5.1.4.3 Magnetic measurements

In this section, the magnetic properties of $\text{Al}_{13}\text{Fe}_4$ are presented. In particular the results of magnetization and susceptibility measurements are introduced.

5.1.4.3.1 Magnetization curves

The dc magnetization of the $\text{Al}_{13}\text{Fe}_4$ sample was measured in the temperature range between 2.0 to 350 K and in external magnetic fields up to 90 kOe. These measurements were performed using the vibrating sample magnetometer (VSM) option of the quantum design physical property measurement system (PPMS).

In figure 5.5, the magnetization curves of $\text{Al}_{13}\text{Fe}_4$ measured in various temperatures and in two external magnetic field intervals of -90 to 90 kOe and -4.5 to 4.5 kOe are presented. Even at field strengths of 90 kOe the magnetization does not reach saturation and also the magnetization pattern resembles that of a ferromagnet. This can only be explained by the existence of a ferromagnetic impurity in the sample as $\text{Al}_{13}\text{Fe}_4$ is in its pure form a paramagnetic compound.

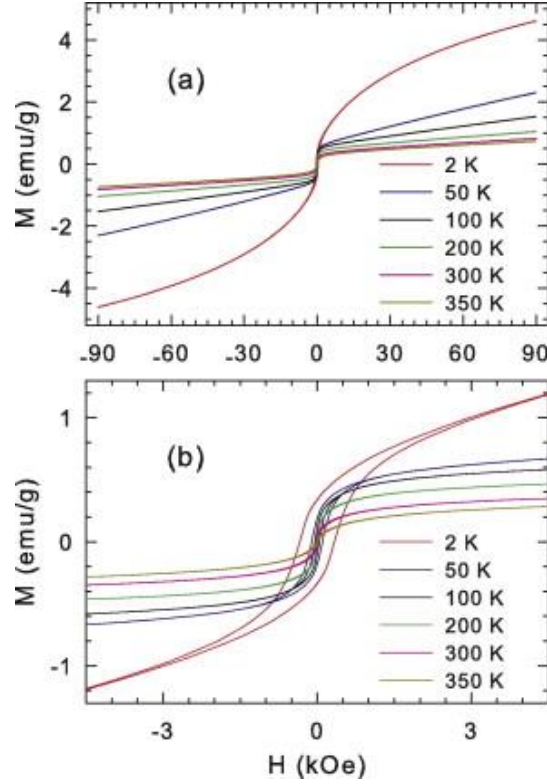


Figure 5.5 Magnetization (M) vs. external field (H) in various temperatures in intervals of (a) -90 to 90 kOe and (b) -4.5 to 4.5 kOe.

5.1.4.3.2 Magnetic susceptibility

The magnetic susceptibility of the $\text{Al}_{13}\text{Fe}_4$ sample was measured in an external dc magnetic field of 10 kOe and within temperature ranges between 2 to 390 K. The susceptibility measurements were also conducted by PPMS (*vide supra*).

In figure 5.6, the temperature dependence of the measured magnetic susceptibility in an external magnetic field of 10 kOe is shown. The temperature dependence of the magnetic susceptibility resembles the Curie-Weiss law. The presence of the ferromagnetic impurity in the specimen contributes an additional $T^{3/2}$ dependent term to the magnetic susceptibility [12,26], along with the temperature independent diamagnetic susceptibility, χ_0 , the total susceptibility can be written as

$$\chi = \chi_0 + \frac{C}{T - \theta_p} + \frac{M_0}{H} (1 - a_{3/2} T^{3/2}). \quad (5 - 1)$$

where M_0 is the saturated magnetization of the ferromagnetic impurity, H is the external magnetic field, θ_p is the paramagnetic Curie temperature, and $C = \frac{N\mu_{\text{eff}}^2}{3k_B}$ is Curie's constant. In Curie's constant, N is the number of iron atoms per formula unit, μ_{eff} is the effective magnetic moment, and k_B is Boltzmann's constant. In figure 5.6, the solid line is fitted to equation (5 - 1).

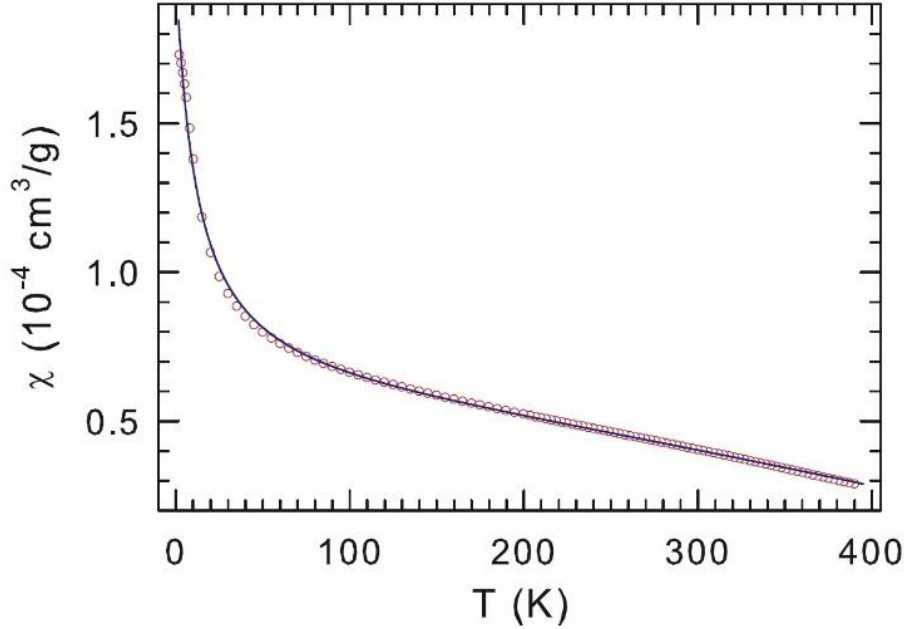


Figure 5.6 The temperature dependence of the magnetic susceptibility of $\text{Al}_{13}\text{Fe}_4$ in an external field of 10 kOe.

5.1.4.4 Mössbauer spectroscopy

In this section the experimental procedure involving the set up for the Mössbauer measurements is introduced and the results of the ^{57}Fe Mössbauer spectroscopy on $\text{Al}_{13}\text{Fe}_4$ is presented and discussed.

5.1.4.4.1 Experimental set up

^{57}Fe Mössbauer measurements on $\text{Al}_{13}\text{Fe}_4$ were conducted using standard Mössbauer spectrometers operating in sine mode. A 50-mCi ^{57}Co source kept at room temperature for zero-field measurements and at the same temperature as the $\text{Al}_{13}\text{Fe}_4$ sample for in-field measurements was used. The spectrometers used for zero-field and in-field measurements were calibrated respectively with a 6.35- μm -thick α -Fe foil [27] and a Michelson interferometer [28], and the spectra were folded.

The Mössbauer absorber consists of a mixture of powdered $\text{Al}_{13}\text{Fe}_4$ and powdered boron nitride. The mixture is pressed into a pellet and put into a high purity, 8- μm -thick aluminum container to ensure temperature uniformity over the sample. The absorber is then placed into a cryostat and kept at a static exchange gas atmosphere with a constant pressure of $\sim 7 \times 10^{-3}$ mbar. The Mössbauer absorber's surface mass density was $9.8 \frac{\text{mg}}{\text{cm}^2}$ which corresponds to an effective thickness parameter [14] of $t_a = 2.2f_a$, where f_a is the Debye-Waller factor of the absorber. Since $t_a > 1$, the resonance line shape of the Mössbauer spectra is described using a transmission integral formula [29].

The ^{57}Fe Mössbauer spectra was analyzed by means of a least-squares fitting procedure which entailed calculations of the positions and the relative intensities of the absorption lines by numerical diagonalization of the full hyperfine interaction Hamiltonian [14].

5.1.4.4.2 Mössbauer spectroscopy

In figure 5.7, the Mössbauer transmission spectra of the $\text{Al}_{13}\text{Fe}_4$ sample is given in room and liquid-nitrogen temperatures and in the velocity range between -10 to 10 $\frac{\text{mm}}{\text{s}}$.

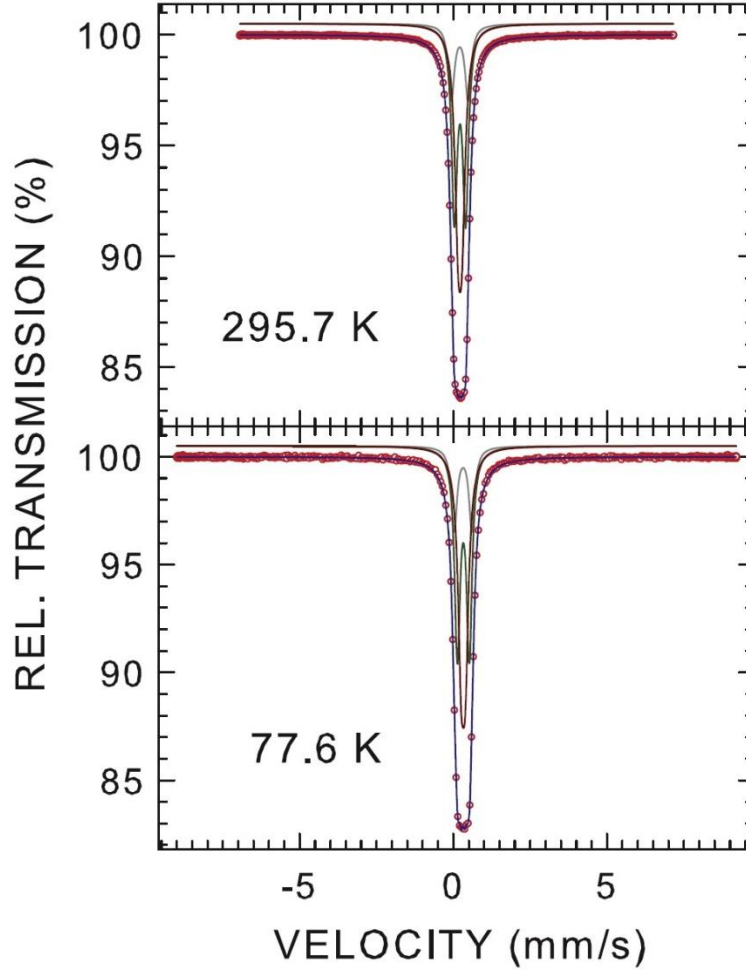


Figure 5.7 The room temperature (above) and the liquid-nitrogen temperature (below) of the ^{57}Fe Mössbauer spectra of $\text{Al}_{13}\text{Fe}_4$ fitted with three quadrupole doublets (dark grey, dark green, and dark red solid lines).

The spectra shows three quadrupole doublets and no Zeeman pattern originating from possible magnetic impurities in the specimen. In a ^{57}Fe Mössbauer spectrum, a quadrupole splitting, which is the separation distance between two resonance lines is given by [14]

$$\Delta = \frac{1}{2} eQ |V_{zz}| \sqrt{1 + \frac{\eta^2}{3}}. \quad (5 - 2)$$

In equation (5 – 2), e is the proton charge and Q is the electric quadrupole moment of the ^{57}Fe nucleus [30].

In Figure 5.8, the ^{57}Fe Mössbauer spectrum of $\text{Al}_{13}\text{Fe}_4$ is shown in detail at the temperature of 5.7 K. One clearly observes a three-valley structure in the spectrum, yet Fe resides in five inequivalent crystallographic sites in $\text{Al}_{13}\text{Fe}_4$ (see table 5.1), therefore one would expect to see five quadrupole lines in the spectrum. However, it is not practically possible to fit the spectrum with five quadrupole doublets.

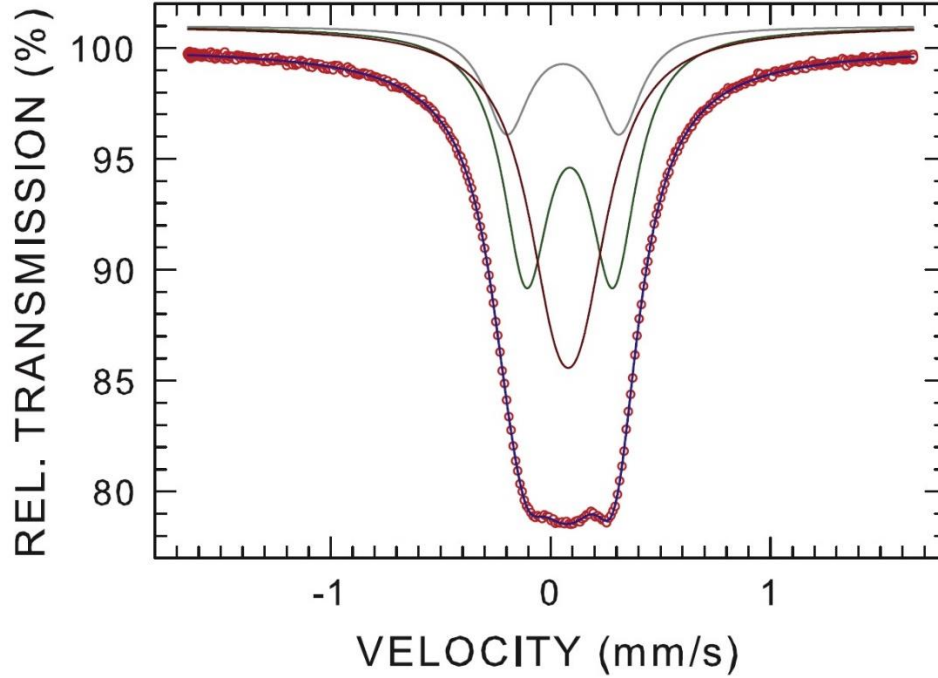


Figure 5.8 The ^{57}Fe Mössbauer spectrum of $\text{Al}_{13}\text{Fe}_4$ at 5.7 K (blue solid line) fitted with three quadrupole doublets (dark grey, dark green, and dark red solid lines). The zero-velocity origin is relative to the source at 5.7 K.

In fact, the spectrum can be fitted with maximum three quadrupole doublets. The spectral weights of these three component doublets in order of decreasing Δ (Δ_a , Δ_b , Δ_c), are 15.7(1)%, 40.9(1)%, and 43.4(1)%. In what follows a discussion based on the ab-initio calculations of the EFG tensors on the five inequivalent iron sites is given to justify the apparent discrepancy.

From the calculated values of V_{zz} and η (table 5.1), one expects the Mössbauer spectrum of $\text{Al}_{13}\text{Fe}_4$ to be a superposition of five quadrupole doublet components with $\Delta_1 = 0.342$, $\Delta_2 = 0.377$, $\Delta_3 = 0.049$, $\Delta_4 = 0.064$, and $\Delta_5 = 0.374 \frac{\text{mm}}{\text{s}}$. It is seen that $\Delta_3 \approx \Delta_4 \ll \Delta_1 \leq \Delta_2 \approx \Delta_5$. Therefore, the three component doublets Δ_a , Δ_b , and Δ_c are associated with iron atoms at sites Fe(1), Fe(2) and Fe(5), and Fe(3) and Fe(4), respectively.

In figure 5.9, the simulated Mössbauer spectrum resulting from the superposition of the five calculated quadrupole doublets above is given. The simulated spectrum clearly shows a three valley structure, though the numerical values are smaller than the experimental ones.

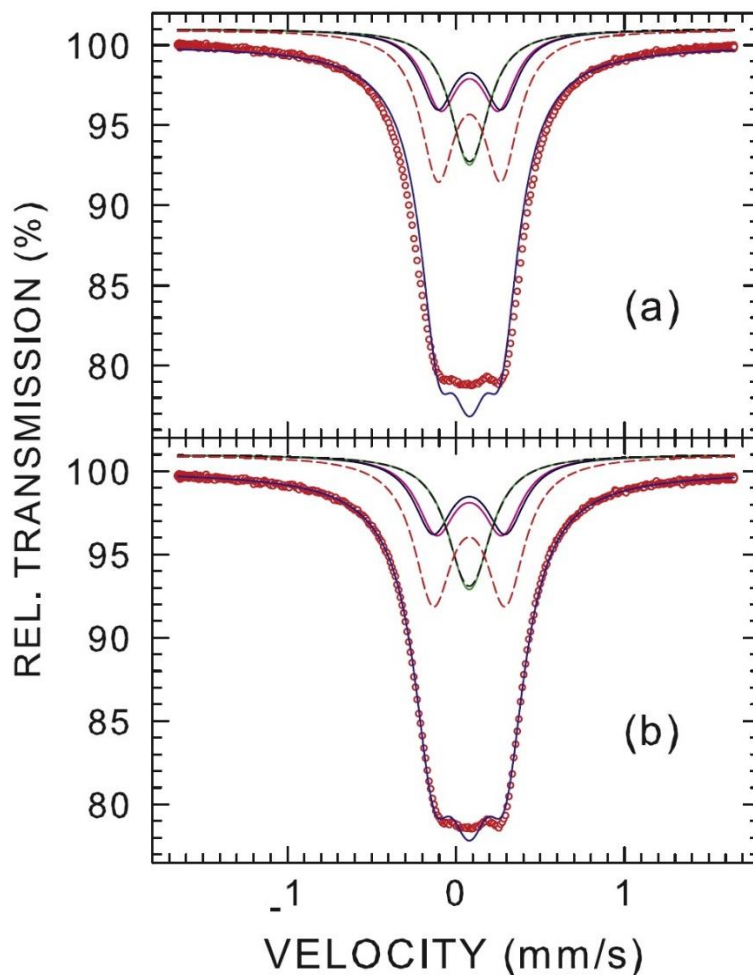


Figure 5.9 (a) ^{57}Fe Mössbauer spectrum of $\text{Al}_{13}\text{Fe}_4$ at 5.7 K and simulated spectrum (blue solid line) resulting from the superposition of quadrupole doublets due to the iron atoms at the Fe(1) site (pink solid line), Fe(2) site (dark blue solid line), Fe(3) site (green solid line), Fe(4) site (black short-dash line), and Fe(5) site (red short-dash line) (b) the same as in (a) but with Δ values increased by 14.0%.

This disagreement is justified by realizing the fact that the precision of the calculated doublets is dictated by the accuracy of the Q value which is 13.3% [30]. The simulated spectrum generated by the five calculated quadrupole doublets with a 14% increase in their values is in good agreement with the experimental spectrum as seen in figure 5.9 (b).

The Mössbauer spectra of nonmagnetic polycrystalline compounds in the absence of an external magnetic field provide information only on the *absolute* value of the EFG components and *not* their signs. However, the orientation of the EFG components can be determined, if an external magnetic field is exposed to the system [31]. In figure 5.10, the ^{57}Fe Mössbauer spectra

of $\text{Al}_{13}\text{Fe}_4$ at 5.7 K measured in an external magnetic field of 90 kOe is given in comparison from the generated spectrum using the values of V_{zz} and η from table 5.1.

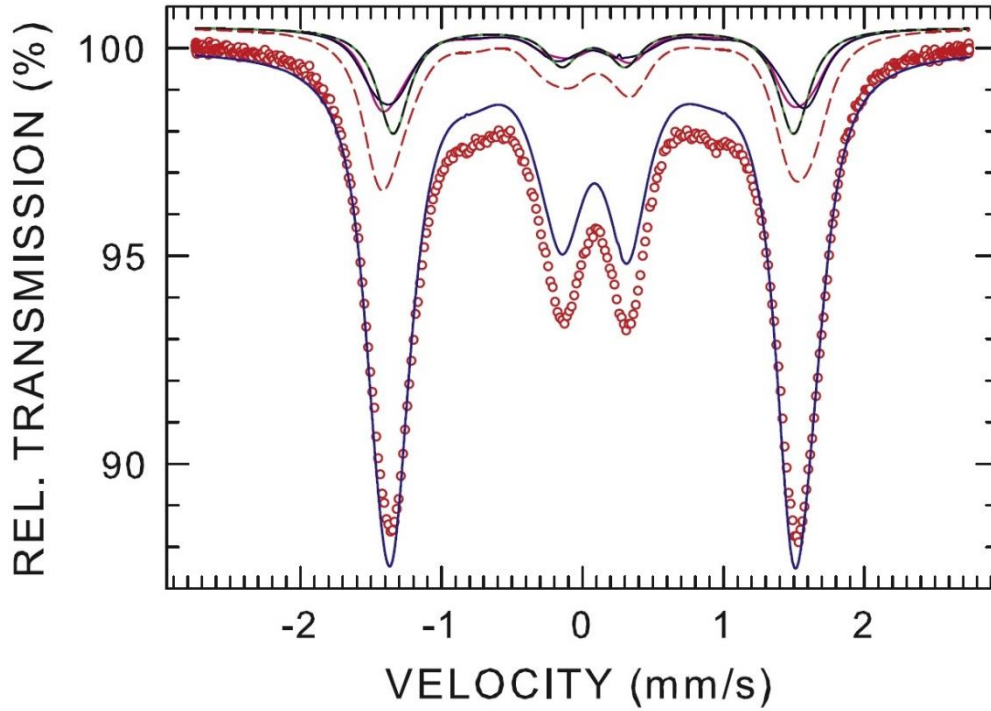


Figure 5.10 The ^{57}Fe Mössbauer spectrum measured in an external magnetic field of 90 kOe at 5.7 K (red open circles) in comparison with the simulated spectrum (increased by 14%) resulting from the theoretical values of V_{zz} and η from table 5.1 (solid blue line). The simulated spectrum is a superposition of iron atom contributions from five inequivalent sites: Fe(1) (pink solid line), Fe(2) (dark blue solid line), Fe(3) (green solid line), Fe(4) (black short-dash line), and Fe(5) (red short-dash line).

Neglecting texture effects, the EFG axes can be assumed to be randomly oriented with respect to the external magnetic field direction. The method used for calculating the spectrum in this case is given in Ref. [33]. The agreement between the simulated spectrum and the measured spectrum in figure 5.10 confirms the validity of the theoretical calculations of the EFG.

In figure 5.11, the results of the Mössbauer spectra of $\text{Al}_{13}\text{Fe}_4$ measured in the temperature range between 4.4 K and 295.4 K and in the absence of the external field are given. As one can clearly see, with increasing temperature the quadrupole doublets decrease which is a common behavior observed in many crystalline [33], quasi-crystalline [34], and amorphous [35] compounds. A possible explanation is that with the increase in temperature, thermal agitations of the atoms within the unit cell amplify resulting in a decrease in the average values of η and Q thus decreasing the value of Δ . It is noticed that the temperature dependence of Δ follows the empirical relation:

$$\Delta(T) = \Delta(0) \left(1 - BT^{\frac{3}{2}}\right). \quad (5-3)$$

In (5 – 3), $\Delta(0)$ is the value of Δ at 0 K and B is a constant.

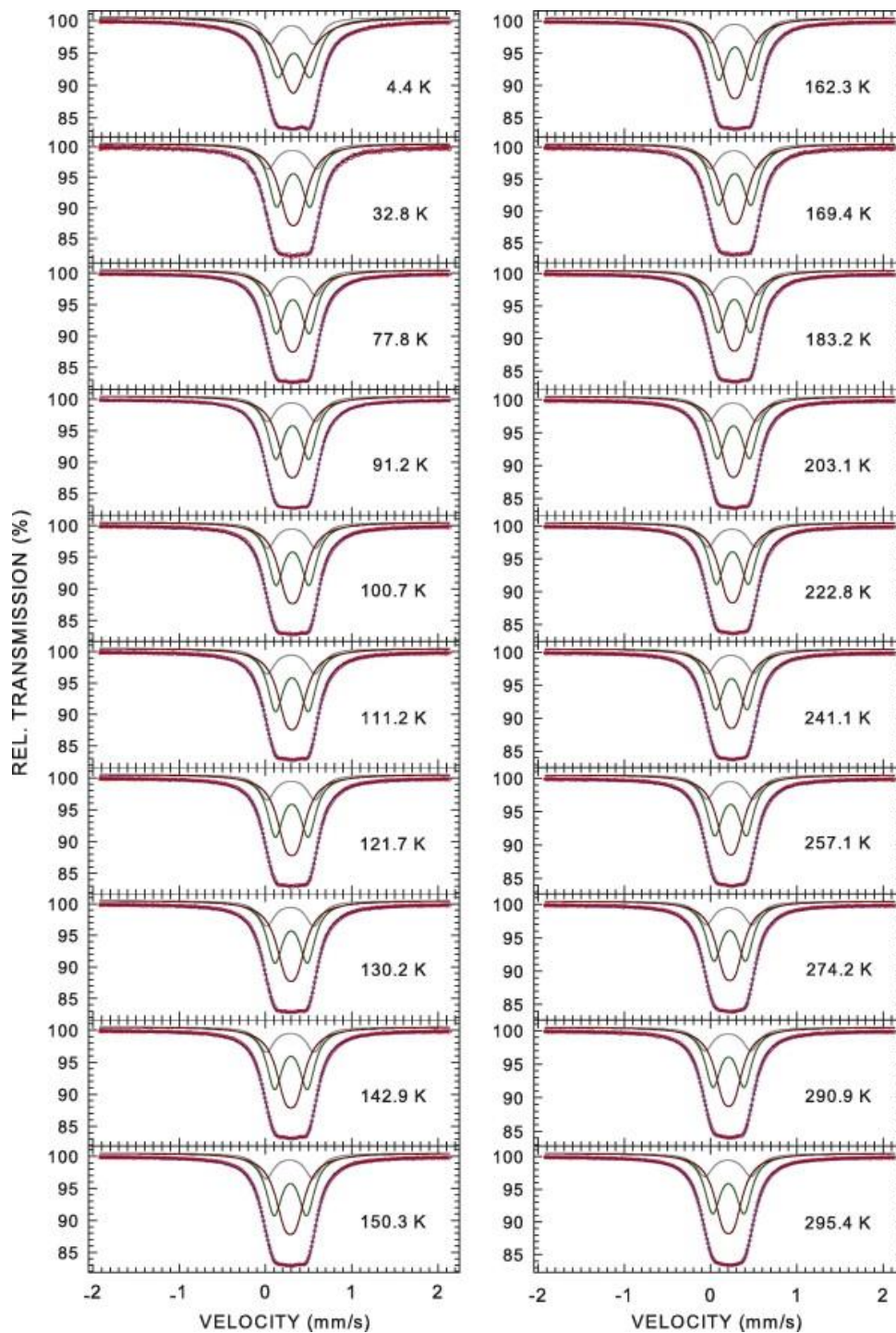


Figure 5.11 ^{57}Fe Mössbauer spectra of $\text{Al}_{13}\text{Fe}_4$ in various temperatures fitted (the blue solid lines) with three quadrupole doublets (dark grey, dark green, and dark red solid lines).

In figures 5.12 (a) and 5.12(c), the fitted values of the $\Delta_i(T)$ data gives $\Delta_a(0) = 0.564(3) \frac{\text{mm}}{\text{s}}$, $B_a = 1.23(13) \times 10^{-5} K^{-\frac{3}{2}}$, $\Delta_b(0) = 0.386(1) \frac{\text{mm}}{\text{s}}$, $B_b = 1.20(7) \times 10^{-5} K^{-\frac{3}{2}}$, and $\Delta_c(0) = 0.129(6) \frac{\text{mm}}{\text{s}}$, $B_c = 1.11(15) \times 10^{-5} K^{-\frac{3}{2}}$. These values for the constant B are similar to those found for other compounds [33 – 35].

Finally in figure 5.12(d), the temperature dependence of the absorption spectral area of the Mössbauer spectrum derived from the fits of the Mössbauer spectra in figure 5.11 is given. The absorption spectral area is proportional to the Debye-Waller factor, f_a given in the Debye theory of solids [14]

$$f_a(T) = e^{\left\{ \frac{3}{4Mc^2k_B T_D} \left[1 + 4 \left(\frac{T}{T_D} \right)^2 \int_0^{\frac{T_D}{T}} \frac{x dx}{e^x - 1} \right] \right\}} \quad (5 - 4)$$

In (5 – 4), M is the mass of the Mössbauer nucleus, c is the speed of light, E_γ is the γ photon energy, and T_D is the Debye temperature. The Debye temperature derived from the fit of the absorption spectral area with equation (5 – 4) is $T_D = 383(3)$ K. The obtained value for T_D is relatively close to the value 419(5) K found in a previous study of $\text{Al}_{13}\text{Fe}_4$ [17, 19], but significantly smaller from the value of 544 K obtained from specific-heat measurements [13].

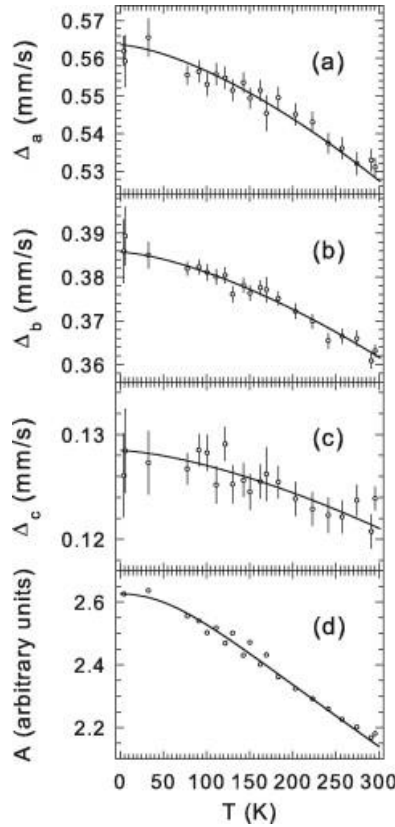


Figure 5.12 Temperature dependence of the quadrupole splittings and the absorption spectral area A of $\text{Al}_{13}\text{Fe}_4$.

5.1.5 Summary and conclusions

In summary, the results of *ab-initio* electronic structure and electric field gradient calculations, X-ray diffraction measurements, ^{57}Fe Mössbauer spectroscopy, and magnetic measurements of the $\text{Al}_{13}\text{Fe}_4$ compound are presented. The studied compound is shown to crystallize in the monoclinic space group $C2/m$ with the lattice parameters $a = 15.503(2) \text{ \AA}$, $b = 8.063(2) \text{ \AA}$, $c = 12.464(2) \text{ \AA}$, and $\beta = 107.71(2)^\circ$. Excellent fits of the zero-field Mössbauer spectra are obtained with three component quadrupole doublets which are shown to result from iron atoms located at five inequivalent crystallographic sites. It is found that the quadrupole splittings corresponding to three component doublets increase with decreasing temperature and are well described by a $T^{3/2}$ power-law relation. The shape of the Mössbauer spectrum of $\text{Al}_{13}\text{Fe}_4$ measured in an external magnetic field of 90 kOe is well accounted for with five component subspectra generated using the calculated electric field gradient parameters at five inequivalent iron sites. It is found that the Debye temperature of $\text{Al}_{13}\text{Fe}_4$ is 383(3) K. The density of states calculations predict the presence of a pseudogap located at 0.1 eV above the Fermi energy and with a width of ~ 0.2 eV. Good metallicity of $\text{Al}_{13}\text{Fe}_4$ is confirmed by the calculated finite density of states at the Fermi level. The studied compound is shown to be paramagnetic down to 2.0 K.

5.2 Na₂Fe₂Se₂O

5.2.1 Introduction

The recent discovery of high- T_C superconductivity in iron-based compounds [36-39] has led to a renewed interest in studies of complex oxides with layered structures [40]. This interest has been precipitated by the observation that the crystal structure of the Fe-based superconductors is very similar, or the same, as that of some complex oxide compounds.

Layered d -metal pnictide oxides Na₂Ti₂Pn₂O, with pnictide Pn = Sb and As, that were synthesized for the first time by Adam and Schuster [41], have layered structure (a tetragonal unit cell with $I4/mmm$ space group) resembling the structure of cuprate high- T_C superconductors such as La_{2- x} Ba _{x} CuO_{4- δ} [42]. This structure consists of an alternation of the Ti₂Pn₂O²⁻ layer and the Na⁺ double layer [41,43,44]. The anomalous temperature dependences of the electrical resistivity, magnetic susceptibility [43-46], and other physical quantities [47] in Na₂Ti₂Pn₂O were taken as evidence for the occurrence of a charge- or spin-density wave instability [48,49]. These anomalous temperature dependences suggest the possibility of antiferromagnetic order in the Na₂Ti₂Pn₂O compounds, but no such order has been yet detected [45]. Theoretical calculations by Picket [48] show that Ti ions in Na₂Ti₂Pn₂O show no inclination to carry a magnetic moment, whereas the recent calculations by Yan and Lu [50] predict that Na₂Ti₂As₂O is a novel blocked checker-board antiferromagnetic semiconductor and that Na₂Ti₂Sb₂O is a bi-collinear antiferromagnetic semimetal. The experimentally observed anomalous dependences of various physical quantities in the Na₂Ti₂Pn₂O compounds [43-47] are quite similar to those observed in some oxypnictide parent compounds of high- T_C iron-based superconductors. One could thus even consider pnictide oxides Na₂Ti₂Pn₂O as possible superconductor parent compounds.

Very recently, a new layered oxyselenide Na₂Fe₂Se₂O was successfully synthesized [51]. It has the same structure as that of Na₂Ti₂Pn₂O, that is, it is built by alternately stacking along the c axis the edge-shared [Fe₂Se₂O]²⁻ layers and the double layers of Na⁺ [51]. The recent *ab-initio* study of Na₂Fe₂Se₂O predicts [52] that this compound is a Mott insulator with the Fe magnetic moments antiferromagnetically coupled in a blocked checkerboard configuration. In the present work, ⁵⁷Fe Mössbauer spectroscopy has been used to determine experimentally the type of magnetic ordering and several hyperfine-interaction properties in this new oxyselenide. In addition, *ab-initio* calculations of the energy band structure and of hyperfine-interaction parameters of this compound have been carried out.

5.2.2 General considerations and structural parameters

Polycrystalline samples of nominal composition Na₂Fe₂Se₂O are synthesized by solid-state reaction as described earlier [51]. The Na₂Fe₂Se₂O compound crystallizes in the anti-K₂NiF₄ structure type [space group $I4/mmm$ (No.139)] with the room temperature lattice constants $a = 4.107(8)$ Å and $c = 14.641(8)$ Å [51]. The studied Na₂Fe₂Se₂O compound is a single-phase compound because no impurities could be detected in its X-ray diffraction spectrum [51].

In figure 5.13(a), the crystal structure and the relative atomic positions of the $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$ is presented. Each block of $\text{Fe}_2\text{Se}_2\text{O}$ consists of a square planar layer of Fe_2O [figure 25.13(b)], which is an anti-configuration to the Cu_2O layer observed in high- T_C cuprate superconductors with the Se atoms located above and below the center of the square layer.

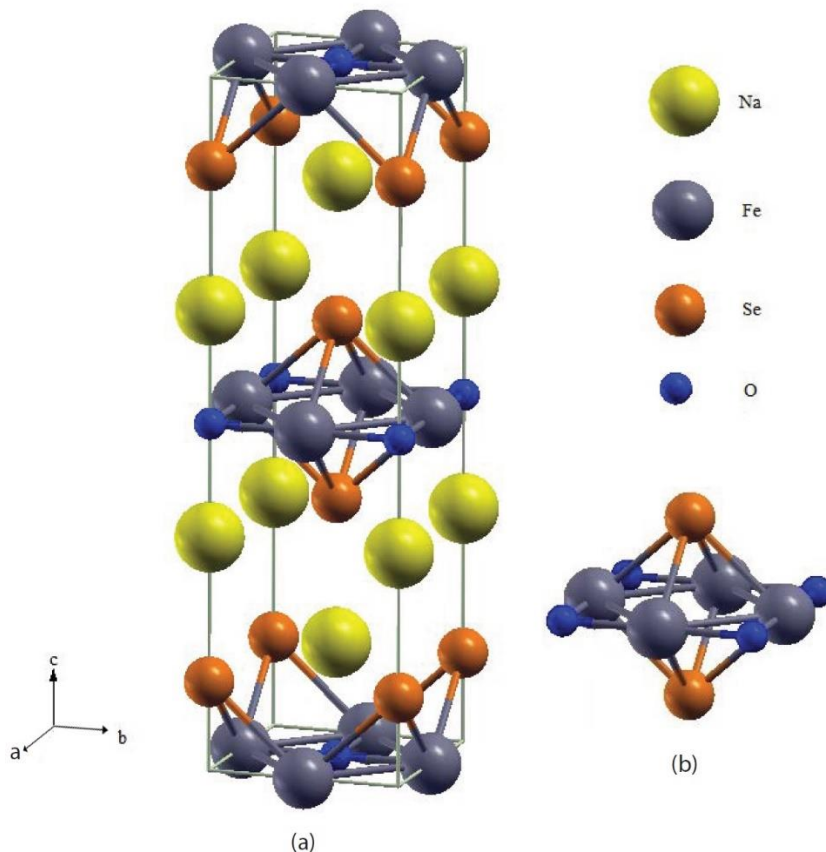


Figure 5.13 (a) The unit cell of the $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$ compound. (b) The $\text{Fe}_2\text{Se}_2\text{O}$ block consisting of Fe-O square planar structure capped with two Se atoms.

In the remainder of this section, the results of comprehensive studies on the $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$ compound from both theoretical and experimental viewpoints are presented.

5.2.3 Theoretical calculations and interpretations

In what follows, the theoretical methods involved in the calculations of the various physical properties of the $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$ system are introduced. A detailed analysis and discussion of the results of the theoretical calculations is presented later on.

5.2.3.1 Theoretical methodology

Ab-initio calculations of several physical properties of $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$ have been performed within the framework of density functional theory using the full-potential linearized augmented plane wave plus local orbitals (FP-LAPW+lo) method as implemented in the WIEN2k package [20]. In this method, the unit cell is partitioned into two regions: a region of non-overlapping muffin-tin (MT) spheres centered at the atomic nuclei and an interstitial region. The electronic states in the interstitial region are expanded in plane waves, whereas in the MT region the states are expanded in terms of spherical harmonics. All calculations are carried out for the lattice constants and the atomic coordinates determined from the Rietveld analysis of the X-ray diffraction spectrum of $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$ [51]. The exchange-correlation potential used in the calculations follows the generalized gradient approximation (GGA) scheme developed by Perdew et al [21].

In the calculations, a separation energy of -8.0 Ry between the valence and core states of the individual atoms in the unit cell is applied. The radii of the MT spheres used in the calculations are 2.00 a.u. for Na, 1.80 a.u. for Fe, 2.10 a.u. for Se, and 1.90 a.u. for O. The plane wave cut-off parameter $R_{\text{MT}} \times K_{\text{MAX}}$ (R_{MT} is the radius of the smallest sphere in the unit cell and K_{MAX} is the maximum K vector used in the Fourier expansion of the plane waves in the interstitial region) value of 6.5 is used. The wave functions in the core regions are expanded to a maximum of $l = 12$ harmonics whereas the valence wave functions are expanded in spherical harmonics up to $l = 4$. A total number of 726 k -points is generated on a $21 \times 21 \times 21$ k -mesh in the irreducible wedge of the first Brillouin zone. An energy convergence criterion of 10^{-4} Ry for successive iterations in the self-consistent field (SCF) cycles is chosen. Calculations for the antiferromagnetic state are carried out using a supercell of dimensions $2a \times 2a \times c$.

5.2.3.2 Theoretical results

In this section, the theoretical results regarding electronic structure, charge density distributions, and hyperfine interaction parameters of the $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$ compound are presented and discussed. The electronic density of states and also the electronic energy band structure of the nonmagnetic and magnetic phases of the $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$ system are discussed in detail.

5.2.3.2.1 Electronic charge density distribution

Figure 5.14 shows the qualitative electronic valence charge density distribution in the (001) and (100) planes in $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$. The chemical bonding between the $\text{Fe}_2\text{Se}_2\text{O}$ blocks and the Na sheets is of ionic character, resulting in a localized charge density distribution. The valence charge transfer from the Na atoms to the $\text{Fe}_2\text{Se}_2\text{O}$ blocks is reflected in a relatively low charge density around Na atoms and a large charge density within the $\text{Fe}_2\text{Se}_2\text{O}$ blocks (figure 5.14). The ionic character of the chemical bonding between Na sheets and the $\text{Fe}_2\text{Se}_2\text{O}$ blocks is also reflected in the electronic density of states (DOS) (*vide infra*). It is also seen from Figure 5.13(a) that no rods connect the Na atoms to the $\text{Fe}_2\text{Se}_2\text{O}$ blocks, this is indicative of complete charge transfer resulting in insulating layers that separate the $\text{Fe}_2\text{Se}_2\text{O}$ blocks in the c direction. However, the atoms of the $\text{Fe}_2\text{Se}_2\text{O}$ blocks are connected to each other shown schematically by

rods in figure 5.13. In fact the connecting “rods” represent covalent chemical bonding. From the charge density distribution shown in figure 5.14, the high charge density region across the $\text{Fe}_2\text{Se}_2\text{O}$ blocks indicates the sharing of electronic charge between atoms present in these blocks leading to covalent bonding.

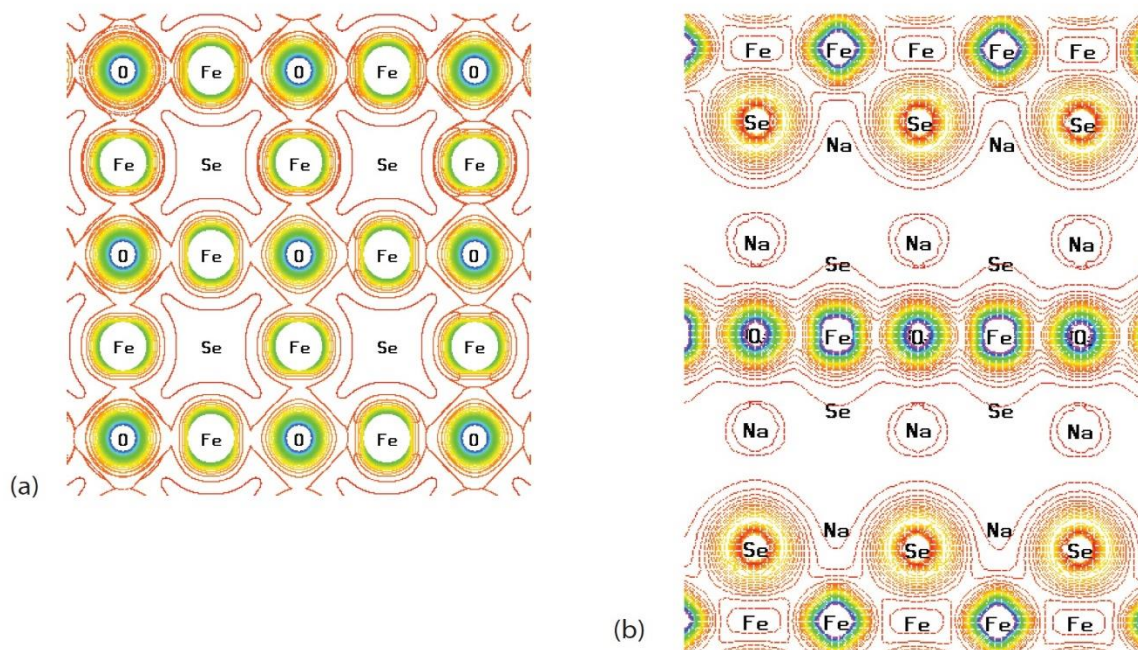


Figure 5.14 Electron valence charge density distribution in (a) (001) plane and (b) (100) plane.

5.2.3.2.2 The nonmagnetic and magnetic states

In this section, the calculated properties of the nonmagnetic or paramagnetic phase, ferromagnetic phase, and antiferromagnetic phase(s) of $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$ is presented. The nonmagnetic phase of this system occurs above the ordering temperature and thus it is the high temperature regime phase of the system. The antiferromagnetic state(s), however, is (are) the low temperature phase(s) or state(s) of the $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$ system in which magnetic ordering between the dipole moments is observed. The ferromagnetic phase is a hypothetical possible phase in which the iron magnetic moments align parallel with one another. The existence of this phase has not yet been experimentally determined.

5.2.3.2.2.1 The electronic density of states

As mentioned above, the nonmagnetic state of the $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$ compound describes the high-temperature phase of this system. The atomic and orbital-resolved partial density of states (DOS) of the nonmagnetic state of $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$ is shown in figure 5.15. Near the Fermi level, the DOS is dominated by the Fe 3d states, whereas the 4p and 4s electrons do not contribute significantly to the DOS in this energy region. One can clearly notice the nesting of the five 3d states, each at a slightly different energy.

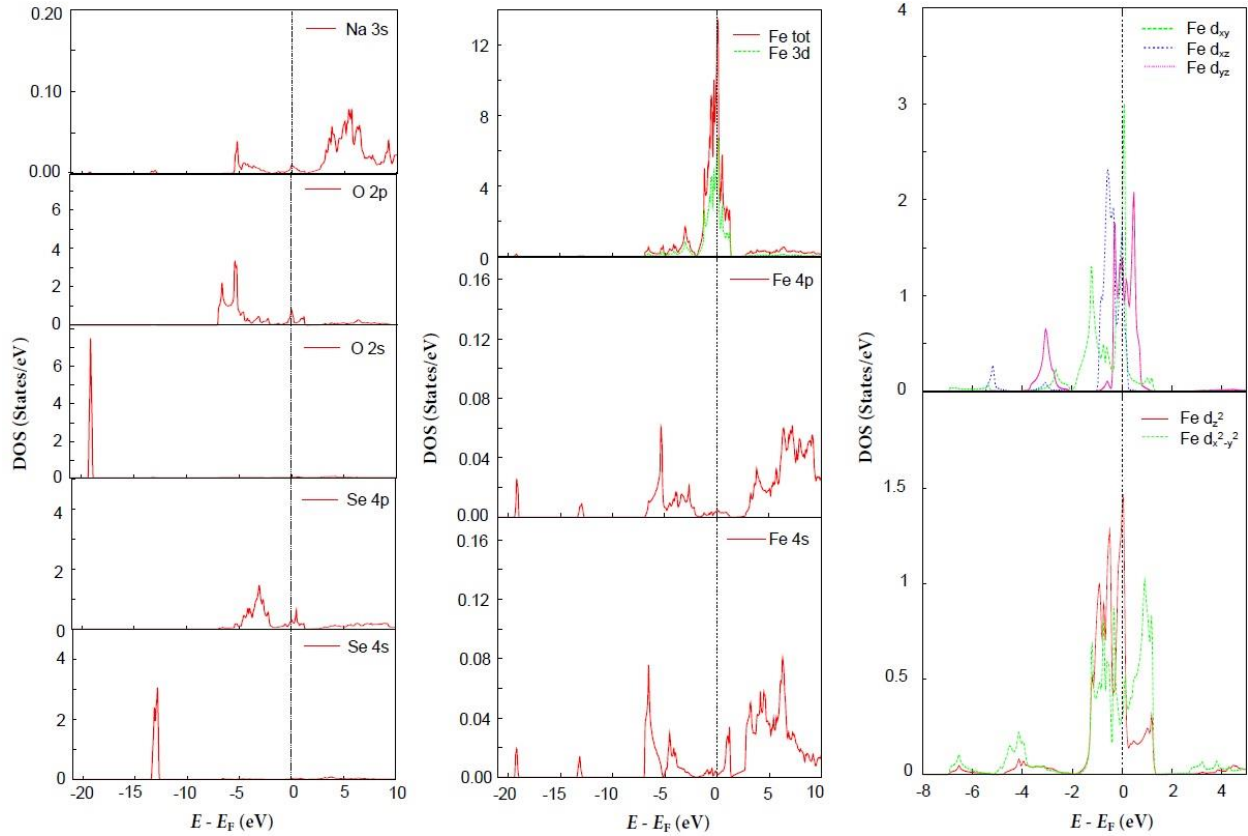


Figure 5.15 The atomic and orbital-resolved partial density of states of $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$ in the nonmagnetic state.

The contributions from the s electrons of Se and O are almost zero at the Fermi level, whereas the p states of these elements have non-zero DOS at the Fermi level. The DOS due to Na, Se, and O atoms occur at specific, non-overlapping energy intervals (figure 5.15) that are indicative of strong ionic bonding between these elements (these characteristics also occur for ferromagnetic and antiferromagnetic states discussed below). On the contrary, the Fe and Se atoms form covalent bonds as their DOS strongly overlap. These bonds, as mentioned earlier, are represented by rods joining the Fe and Se atoms in figure 5.13. The calculations show that (table 5.2), as expected, the magnetic moments of all atoms in this nonmagnetic state are zero.

In figure 5.16, the spin polarized DOS and partial DOS for the various atoms and orbitals in the ferromagnetic phase of $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$ is presented. As can be seen from this figure, the Fe $3d$ states in the spin-up configuration are distributed mainly from 6 eV below the Fermi level to the immediate vicinity of the Fermi level, highly peaked and localized between -4 to -2 eV with respect to the Fermi energy. On the contrary the spin-down Fe $3d$ states spread well beyond the Fermi level and up to ~2.2 eV above the Fermi energy. The relative contributions of each of the five iron d orbitals to the total spin-up and spin-down DOS is also observed from the figure. If one compares the Fe DOS arising from their d states, with DOS of O, Se, and Na in figure 5.16, the significant polarization between the peaks of the maxima and minima of the Fe d states in the spin polarized system is realized. This fact explains the high magnetic moments of Fe atoms

compared to the almost zero magnetic moments of the rest of the elements present in the $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$ system (*vide infra*).

In figure 5.17, the total and atom resolved DOS for the ferromagnetic and nonmagnetic phases are introduced for comparison. In both cases, despite their major differences, the Fe d states are the main contributors to the total DOS in the Fermi region. The portion of the DOS arising from Na atoms in both cases is extremely small and negligible, and the atom resolved DOS of Se and O are peaked at energies much smaller than the Fermi level. In the case of O, the DOS is peaked at ~ -13 eV with respect to the Fermi level and for Se the DOS is highly peaked at ~ -19 eV. In both nonmagnetic and ferromagnetic orientations, the DOS for Se and O remain at the same energies. The magnetic ordering thus only affects the Fe DOS as expected.

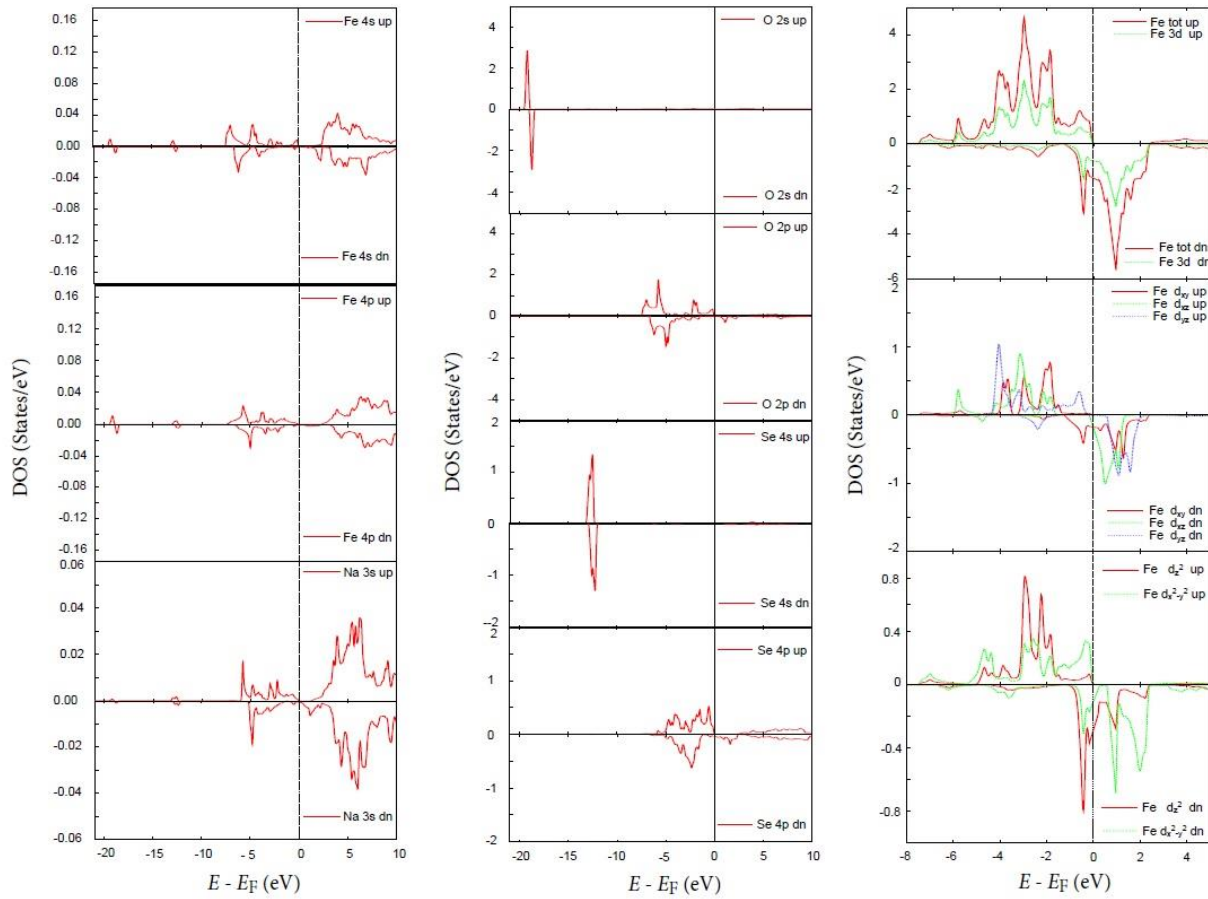


Figure 5.16 Atom- and orbital-resolved density of states of $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$ in the ferromagnetic state.

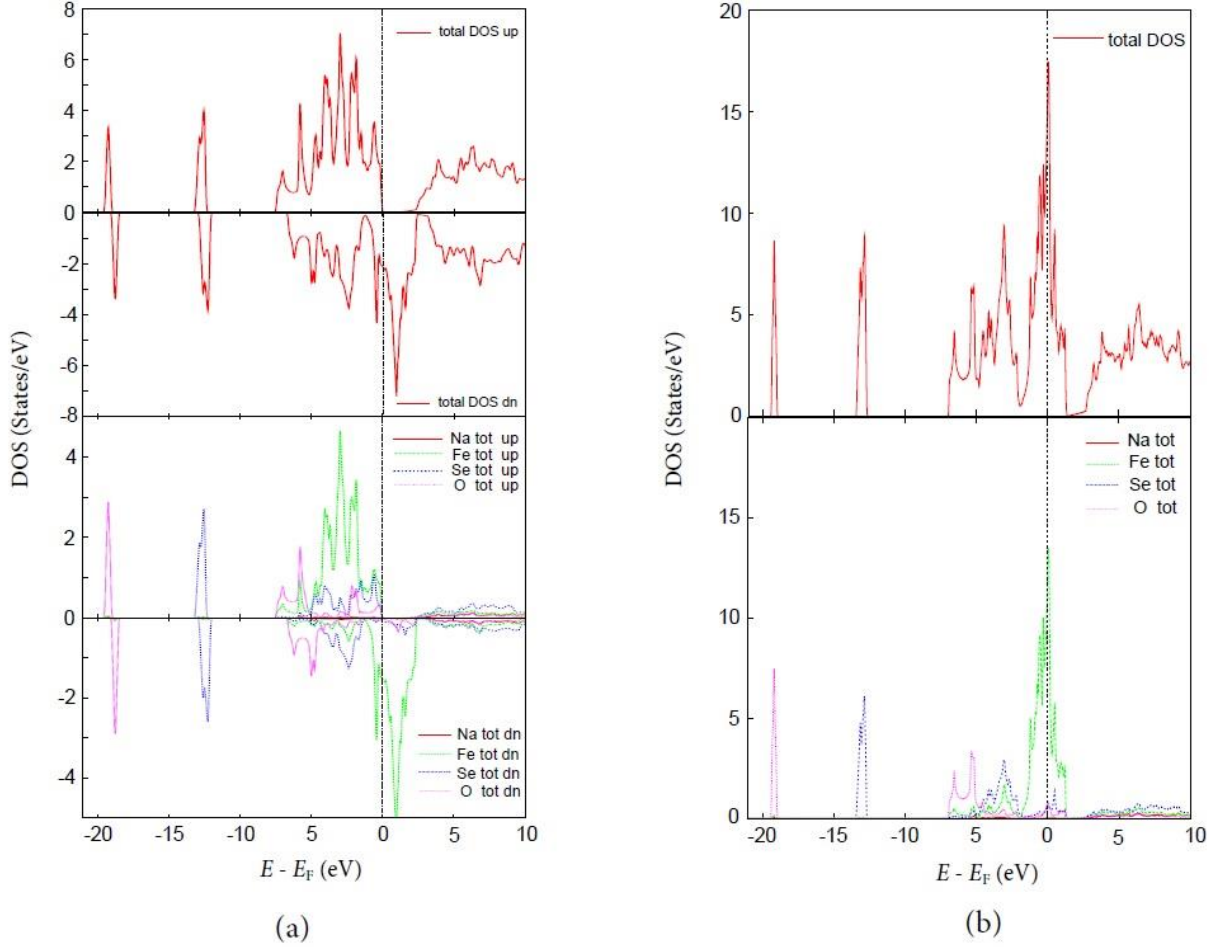


Figure 5.17 Total and atom-resolve density of states of $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$ in (a) the ferromagnetic state and (b) the nonmagnetic state.

5.2.3.2.2 The electronic band structure

The electronic band structure of the nonmagnetic, ferromagnetic, and antiferromagnetic states has been determined and is discussed below.

The electronic band structure of the nonmagnetic state (the high temperature regime) of the $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$ compound is shown in figure 5.18(c). The absence of an energy gap across the Fermi level points to the metallic-like character of the studied system at high temperatures. In the vicinity of the Fermi level, one observes [figure 5.18(c)] a number of energy bands in different directions in the Brillouin zone. This leads to a high electrical conductivity in this state. The calculations show that, as mentioned before, the magnetic moments of all atoms in this nonmagnetic state is zero.

The spin-up and spin-down energy bands in the ferromagnetic state of $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$ is shown in figures 5.18(a) and 5.18(b). One can notice the formation of a spin dependent energy band gap. The maximum of the valence band lies about 0.1 eV below the Fermi level, whereas the

minimum of the conduction band is located at about 1.3 eV above the Fermi level. This allows indirect inter-band transitions of energies larger than about 1.4 eV along the $N - \Gamma$ direction. As can be seen from figures 5.18(a) and 5.18(b), the strong ferromagnetic coupling of the Fe magnetic moments is responsible for the localization of the Fe 3d states in the spin-up configuration.

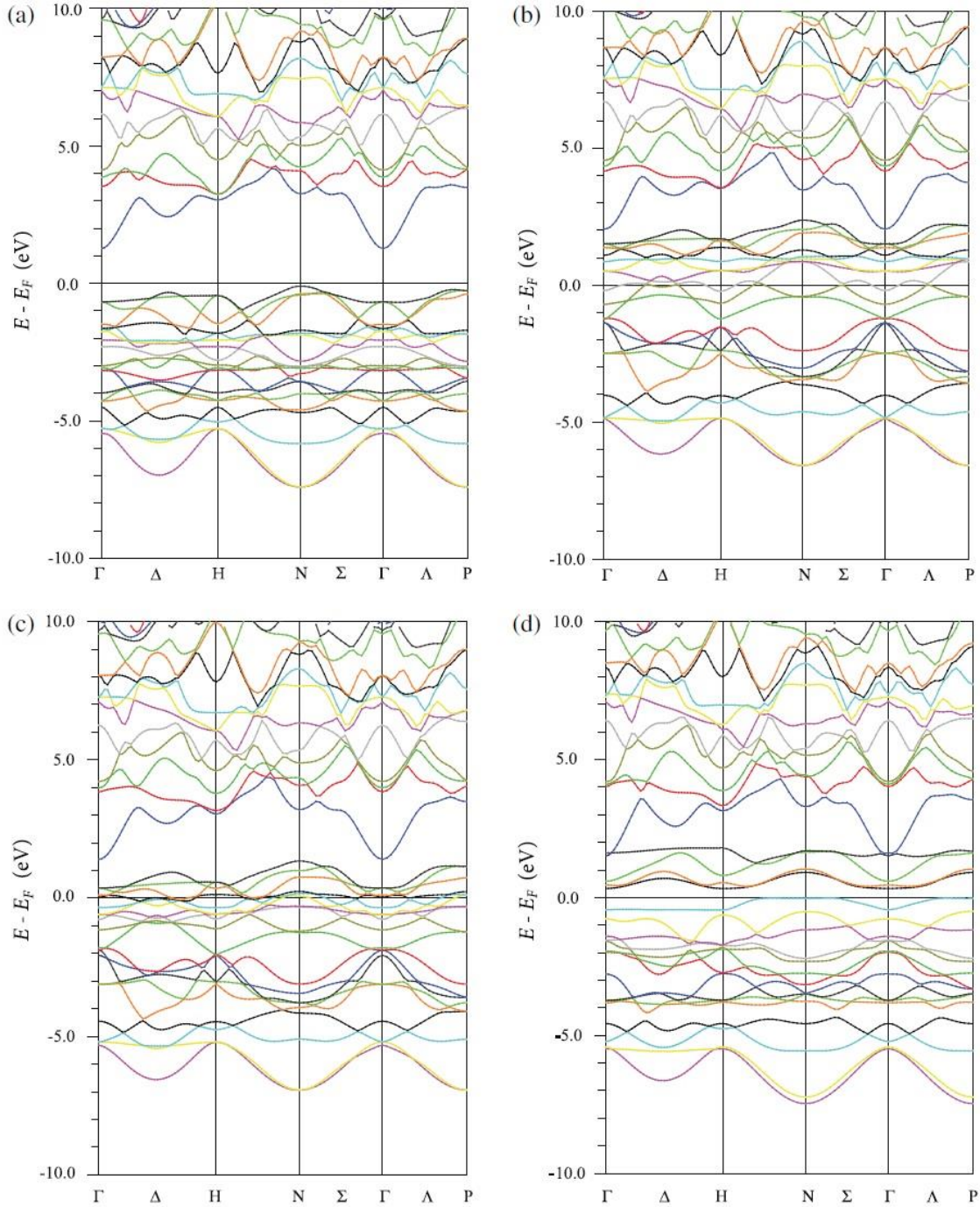


Figure 5.18 Energy band structure of $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$ in various states: (a) spin up and (b) spin down ferromagnetic state, (c) nonmagnetic state, and (d) blocked checkerboard antiferromagnetic state.

This prevents the existence of electronic states above the Fermi level and creates a band gap of ~ 2.2 eV. On the contrary, for the spin-down configuration one can clearly observe the metallic behavior (figure 5.18(b)). This clear spin-dependent distinction in the electronic properties of the Fe 3d states can be potentially useful in spintronics applications where one can open a channel for the spin-down currents which feel no potential barrier on their way, whereas the spin-up currents are blocked. This leads to a spin-polarized current that can be of important use in quantum computation (for instance, the spin-polarized current can lead to distinct bits of information, very much similar to the traditional “0” and “1” bits used in ordinary binary-based computation systems).

An inspection of the band structure of the so-called blocked checkerboard antiferromagnetism configuration (described in the next section) in figure 5.18(d) shows that the bands which are not in the vicinity of the Fermi level are unaltered and remain at the same energy as the bands corresponding to the nonmagnetic state [figure 5.18(c)]. The band structure in the vicinity of the Fermi level shows a small energy gap [figure 1(d)] that implies the existence of a Mott insulating state [54].

5.2.3.2.2.3 Magnetic orderings

Three different in-plane antiferromagnetic spin configurations, that are often realized in layered parent compounds of Fe-based superconductors [37,39,53] were considered in the previous *ab-initio* study of $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$ [52]. The antiferromagnetically coupled Fe magnetic moments were assumed to lie in the *a-b* plane along the [110] direction, hence creating a 2D magnetic system. A similar antiferromagnetic order was reported [50] to exist in the $\text{Na}_2\text{Ti}_2\text{Pn}_2\text{O}$ (Pn = Sb, As) pnictide oxides. The three antiferromagnetic spin configurations that could occur in $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$ are shown in figures 5.19(b), 5.19(c), and 5.19(d). In the stripe like antiferromagnetic spin configuration [figure 5.19(b)], the chains of Fe magnetic moments are coupled ferromagnetically with an antiferromagnetic coupling between the adjacent chains. The checkerboard antiferromagnetic configuration [figure 5.19(c)], has an Fe magnetic moment coupled antiferromagnetically with its nearest-neighbor Fe magnetic moments. In the blocked checkerboard antiferromagnetic configuration [figure 5.19(d)], four adjacent Fe atoms form a $\sqrt{2}a \times \sqrt{2}a$ block in which all Fe magnetic moments are coupled ferromagnetically, whereas the block is antiferromagnetically coupled to the adjacent blocks in a checkerboard fashion. Energy considerations show [52] that the lowest total energy is for the blocked checkerboard antiferromagnetic configuration, and therefore this configuration appears to be the most probable.

The in-plane ferromagnetic ordering of $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$ is displayed in figure 5.19(a). It is found that the total energy calculated for the ferromagnetic state of $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$ is larger than the total energy calculated for the blocked checkerboard antiferromagnetic state (table 5.2). Therefore, it is confirmed that the antiferromagnetic spin configuration is the preferred spin configuration of the $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$ system.

5.2.3.2.3 The hyperfine interaction parameters

In this section the results of the calculations of the isomer shift, δ , and the principle component of the electric field gradient (EFG) tensor, V_{zz} , and the asymmetry parameter, η , of $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$ are presented and discussed. The hyperfine magnetic field is also calculated and presented.

State	μ_{Na} (μ_{B})	μ_{Fe} (μ_{B})	μ_{Se} (μ_{B})	μ_{O} (μ_{B})	ΔE (eV)
Ferromagnetic	0	3.23	0.18	0.29	−0.2584
Antiferromagnetic	0	3.19	0	0	−0.2739

Table 5.2 The magnetic moments, μ of Na, Fe, Se, and O atoms in the ferromagnetic and blocked checkerboard antiferromagnetic states of $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$ and the total-energy difference, ΔE (with respect to the nonmagnetic state).

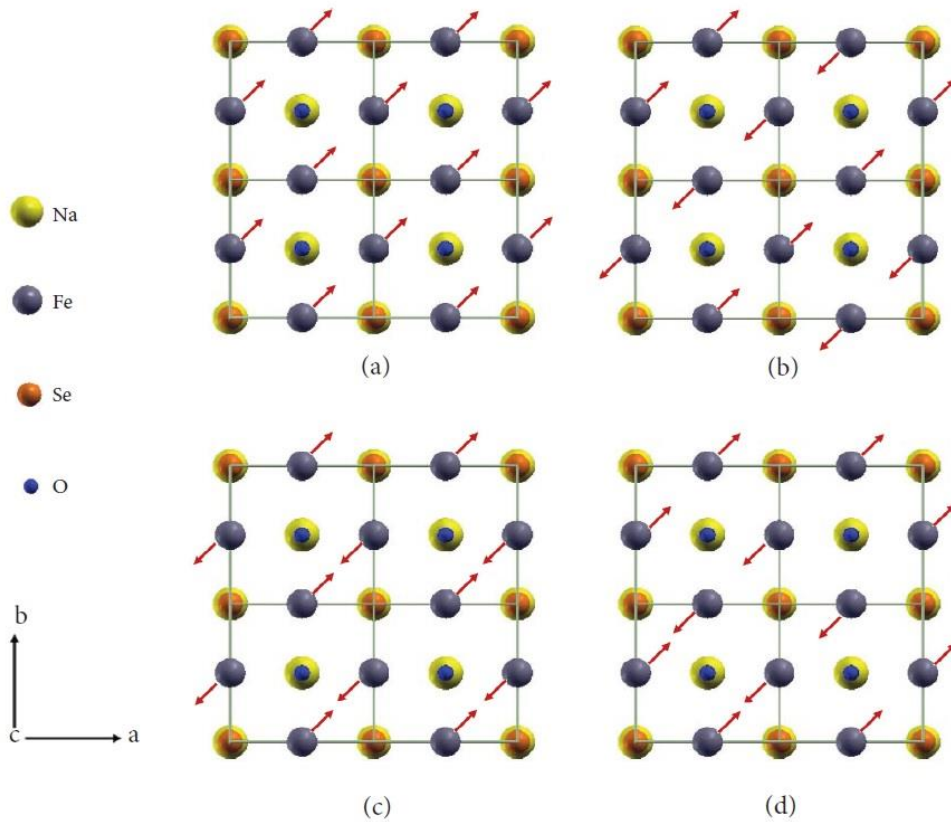


Figure 5.19 In-plane arrangement of Fe magnetic moments for $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$ in the (a) ferromagnetic state, (b) striped antiferromagnetic state, (c) checkerboard antiferromagnetic state, and (d) blocked checkerboard antiferromagnetic state.

5.2.3.2.3.1 The isomer shift calculations

The isomer shift is proportional to the total electron density at the Mössbauer nucleus, $\rho(0)$ as follows

$$\delta_0 = \alpha(\rho(0) - \rho_{\text{ref}}(0)), \quad (5 - 5)$$

where $\rho_{\text{ref}}(0)$ is the electron density in a reference compound and α is a calibration constant. In calculating $\rho(0)$, relativistic spin-orbit effects were involved in order to account for the possibility of the penetration of the $p_{1/2}$ electrons into the ^{57}Fe nuclei. As a reference compound, an α -Fe (with *bcc* structure and the lattice constant of 2.8665 Å) was chosen. The calculated values of $\rho(0)$ and $\rho_{\text{ref}}(0)$ are, respectively, 15306.521 and 15309.918 a.u.⁻³. Using the calibration constant $\alpha = -0.291 \text{ a.u.}^3 \text{ mms}^{-1}$ (Ref. [55]), equation (5 - 5) yields $\delta_0 = 0.988 \text{ mms}^{-1}$.

5.2.3.2.3.2 The calculated magnetic dipole moments

The values of the calculated magnetic moments for the ferromagnetic state of $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$ are listed in table 5.2. A strong magnetic coupling of the large Fe magnetic moment ($3.23\mu_B$) may lead to the induced magnetic moments on the Se and O atoms.

The calculations yield the value of $3.186\mu_B$ for the Fe magnetic moment (table 5.2) in the blocked checker board antiferromagnetic configuration. There are no induced magnetic moments on the Na, Se, and O atoms in contrast to the ferromagnetic state. This can possibly be due to the fact the magnetic fields from the anti-spin alignments of Fe atoms in the antiferromagnetic state cancel each other on the Na, Se, and O sites thus no net magnetic fields on these atomic sites exist which in turn results in no magnetic induction.

5.2.3.2.3.3 The hyperfine magnetic field

The hyperfine magnetic field in a magnetic material consists of four distinct contributions: The Fermi contact term H_C , the magnetic dipolar term, H_{dip} , the orbital moment term, H_{orb} [14], and the term arising from the fields of neighboring atoms in the crystal, the lattice term, H_{lat} . The Fermi contact term is given by

$$H_C = \frac{8\pi}{3} \mu_B^2 (\rho_{\uparrow}(0) - \rho_{\downarrow}(0)), \quad (5 - 6)$$

where $\rho_{\uparrow}(0)$ and $\rho_{\downarrow}(0)$ are the spin-up and spin-down densities at the Mössbauer nucleus, respectively. The magnitude of H_C in $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$ calculated from equation (5 - 6) is 215 kOe.

5.2.3.2.3.4 The calculated electric field gradient tensor

The calculations of V_{zz} and η yields the values $11.113 \times 10^{21} \frac{\text{V}}{\text{m}^2}$ and 0.0 respectively. The zero value for the asymmetry parameter is expected from the tetragonal structure of the unit cell of $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$. The dominant contribution to V_{zz} ($\sim 8 \times 10^{21} \frac{\text{V}}{\text{m}^2}$) comes from the electrons

with a strong d character, and the remaining contribution ($\sim 3 \times 10^{21} \frac{\text{V}}{\text{m}^2}$) is the result of s - d orbital hybridization. V_{zz} is dominated by the contribution from a region very close to the Mössbauer nucleus: the contribution from the region within 20% of the muffin-tin radius ($10.784 \times 10^{21} \frac{\text{V}}{\text{m}^2}$) almost reaches the saturation value of V_{zz} .

5.2.4 The experimental measurements and results

In this section, the results of the experimental studies on the $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$ system including ^{57}Fe Mössbauer measurements are presented and compared with the results of ab-initio calculations.

5.2.4.1 Mössbauer spectroscopy

In what follows, a comprehensive study of the $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$ system via Mössbauer spectroscopy is presented. The physical quantities of interest including hyperfine-interaction parameters are derived from careful analysis of the Mössbauer spectra at various temperatures.

5.2.4.1.1 Experimental set up for the Mössbauer measurements

The ^{57}Fe Mössbauer measurements were conducted using standard Mössbauer spectrometers [14] operating in sine mode and a ^{57}Co source, which was kept at room temperature for zero-field measurements and at the same temperature as that of the absorber for an in-field measurement. The spectrometers used for zero-field and in-field measurements were calibrated, respectively with a $6.35\text{-}\mu\text{m}$ -thick $\alpha\text{-Fe}$ foil [27] with a Michelson interferometer [28], and the spectra were folded. The Mössbauer absorber was made in a glove box. The powder material was mixed with boron nitride and was put into a high purity $8\text{-}\mu\text{m}$ -thick aluminum disk container to ensure a uniform temperature over the whole absorber. The Mössbauer absorber was exposed to air for about 100 s when it was transported from the glove box to the Mössbauer cryostat in which it was kept in a static exchange gas atmosphere at the pressure of $\sim 7 \times 10^{-3}$ mbar. The surface density of the prepared Mössbauer absorber of $26.5 \frac{\text{mg}}{\text{cm}^2}$ corresponds to an effective thickness parameter [14] $t_a = 5.2f_a$, where f_a is the Debye-Waller factor of the absorber. Since $t_a > 1$, the resonance line shape of the Mössbauer spectrum was described using a transmission integral formula [29]. The source linewidth $\Gamma_s = 0.13 \frac{\text{mm}}{\text{s}}$ and the background-corrected Debye-Waller factor of the source $f_s^* = 0.50$ were used in the fits of the Mössbauer spectra [29]. As the magnitude of the electric quadrupole interaction is comparable to that of the magnetic dipole interaction in the studied compound at temperatures below T_N , the ^{57}Fe Zeeman spectra were analyzed by means of a least-squares fitting procedure which entailed calculations of the positions and relative intensities of the absorption lines by numerical diagonalization of the full hyperfine interaction Hamiltonian [14].

5.2.4.1.2 The Mössbauer spectra and interpretations

In figure 5.20, the room-temperature ^{57}Fe Mössbauer spectrum of $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$ is presented. The spectrum consists of two asymmetric quadrupole doublets and a Zeeman sextet. The asymmetry of the two quadrupole doublets is caused by preferred orientation (texture) in the polycrystalline Mössbauer absorber (the tendency of the polycrystalline grains of a layer-structure compound to align themselves predominantly with the c -axis perpendicular to the plane of the absorber). This is confirmed by the observation that this asymmetry almost disappears (the right inset of figure 5.20) if the spectrum is measured at the so-called *magic angle*; in such a measurement the normal to the Mössbauer absorber plane and the direction of the γ -rays form an angle of 54.7° [56]. The major quadrupole doublet originates from the compound studied. The minor quadrupole doublet is due to the impurity in the absorber that was produced during its short exposure to air. This is corroborated by the fact that the spectral weight of this minor quadrupole doublet significantly increased in the magic-angle spectrum (the right inset in figure 5.20) that was measured for 15 hours with the Mössbauer absorber accidentally exposed to air at the pressure of ~ 1.5 mbar. The Zeeman sextet component originates from a trace amount of Fe metal impurity.

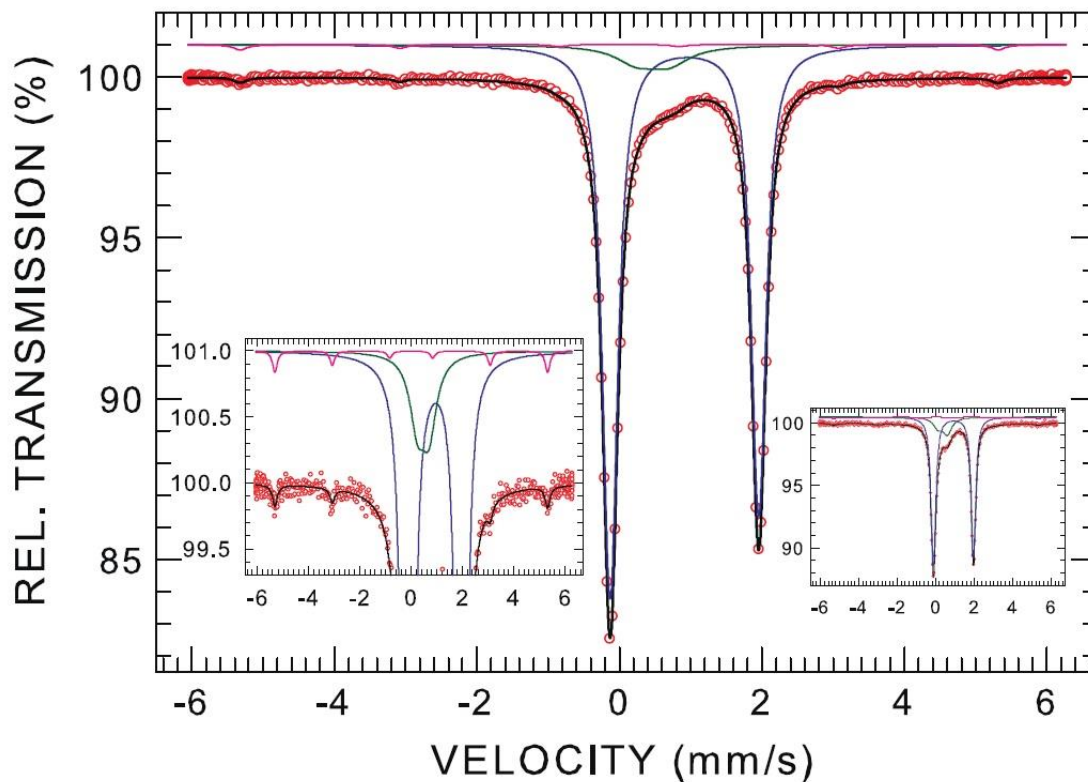


Figure 5.20 ^{57}Fe Mössbauer spectrum of $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$ at 296.8 K fitted (black solid line) with an asymmetric quadrupole doublet (blue solid line) due to main phase, an asymmetric quadrupole doublet (dark green solid line) due to air-environment induced impurity, and a Zeeman pattern (pink solid line) originating from Fe impurity. The left inset shows the spectrum with an enlarged vertical scale and the right inset shows the spectrum measured at the magic angle, as described in the text. The zero-velocity origin is relative to α -Fe at room temperature.

The fit of the room-temperature spectrum in figure 5.20 with these three components yields the following parameters: the absorber linewidth Γ_a , the center shift δ (relative to α -Fe at 298 K), the effective quadrupole splitting, $\tilde{\Delta} = \frac{1}{2}eQ|V_{zz}|\sqrt{1 + \frac{\eta^2}{3}}$ (where e is the proton charge and Q is the electric quadrupole moment of the ^{57}Fe nucleus [30]), the hyperfine magnetic field H , and the spectral area A [14]. The values of these parameters corresponding to these three components are $\Gamma_{a1} = 0.132(2) \frac{\text{mm}}{\text{s}}$, $\delta_1 = 0.919(1) \frac{\text{mm}}{\text{s}}$, $\tilde{\Delta}_1 = 2.083(1) \frac{\text{mm}}{\text{s}}$, $A_1 = 91.6(1)\%$, $\Gamma_{a2} = 0.579(49) \frac{\text{mm}}{\text{s}}$, $\delta_2 = 0.465(29) \frac{\text{mm}}{\text{s}}$, $\tilde{\Delta}_2 = 0.449(28) \frac{\text{mm}}{\text{s}}$, $A_2 = 7.0(4)\%$, and $\Gamma_{a3} = 0.089(6) \frac{\text{mm}}{\text{s}}$, $\delta_3 = 0.002(3) \frac{\text{mm}}{\text{s}}$, $H_3 = 329.6(8) \text{ kOe}$, $A_3 = 1.3(2)\%$.

The values of δ_1 and Δ_1 are typical of high-spin Fe^{2+} ions [14]. The ferrous state of Fe atoms can be expected from the ionic formula $\text{Na}_2^{1+}\text{Fe}_2^{2+}\text{Se}_2^{2-}\text{O}_{2-}$ in which the usual oxidation numbers are assigned to Na, Se, and O atoms. ^{57}Fe Mössbauer spectra similar to the room-temperature spectrum (figure 5.20) were recorded at other temperatures down to 75.4 K. these spectra are shown in figure 5.21. The presence of the major asymmetry quadrupole doublet down to 75.4 K indicates that the magnetic ordering temperature of $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$ must be below 75.4 K. The temperature dependence of hyperfine parameters derived from the fits of the spectra in figures 5.20 and 5.21 is discussed later.

The ^{57}Fe Mössbauer spectra of $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$ at 5.8 K, i.e., at the temperature much below the magnetic ordering temperature, measured in the external magnetic fields $H_{\text{ext}} = 0$ and 90 kOe applied parallel to the γ -ray propagation direction are shown in figure 5.22. The zero-field spectrum can be fitted well with one Zeeman pattern originating from the compound studied (a Zeeman pattern due to an Fe impurity is not included in the fit due to its negligible spectral weight; a possible Zeeman pattern with a small spectral weight due to the impurity caused by the sample's short exposure to air is also not included in the fit as it overlaps with, and is completely overwhelmed by, the Zeeman pattern due to the main phase). The values of the parameters obtained from the fit are $\Gamma_a = 0.045(3) \frac{\text{mm}}{\text{s}}$, $H = 190.4(2) \text{ kOe}$, the quadrupole splitting $\Delta = 2.039(3) \frac{\text{mm}}{\text{s}}$ ($\Delta = \frac{1}{2}eQV_{zz}$), $\eta = 0.0(1)$, and the angle between V_{zz} and H , $\alpha = 5.0(7)^\circ$. The value $\Delta = 2.039(3) \frac{\text{mm}}{\text{s}}$ implies [30] that $V_{zz} = 13.070(19) \times 10^{21} \frac{\text{V}}{\text{m}^2}$. Whereas the experimental value of V_{zz} is 17.6% larger than the calculated value of $11.113 \times 10^{21} \frac{\text{V}}{\text{m}^2}$. This, however, does not mean that the calculated V_{zz} is imprecise as the precision of the experimentally determined V_{zz} is dictated by the accuracy of the Q value which is 13.3% [30].

The ^{57}Fe Mössbauer spectra of a magnetically ordered compound measured in zero external magnetic field give information on the magnitude and direction of the hyperfine magnetic field, and thus of the Fe magnetic moment, but not on the type of magnetic ordering of these moments. The type of magnetic ordering can be inferred from Mössbauer spectra measured in a strong enough external magnetic field [57]. The most striking feature of the $H_{\text{ext}} = 90 \text{ kOe}$ spectrum (figure 5.22) is its dramatic broadening as compared to the $H_{\text{ext}} = 0 \text{ kOe}$ spectrum. As is

explained below, this broadened spectrum constitutes experimental proof of the antiferromagnetic ordering of the Fe magnetic moments in the compound studied.

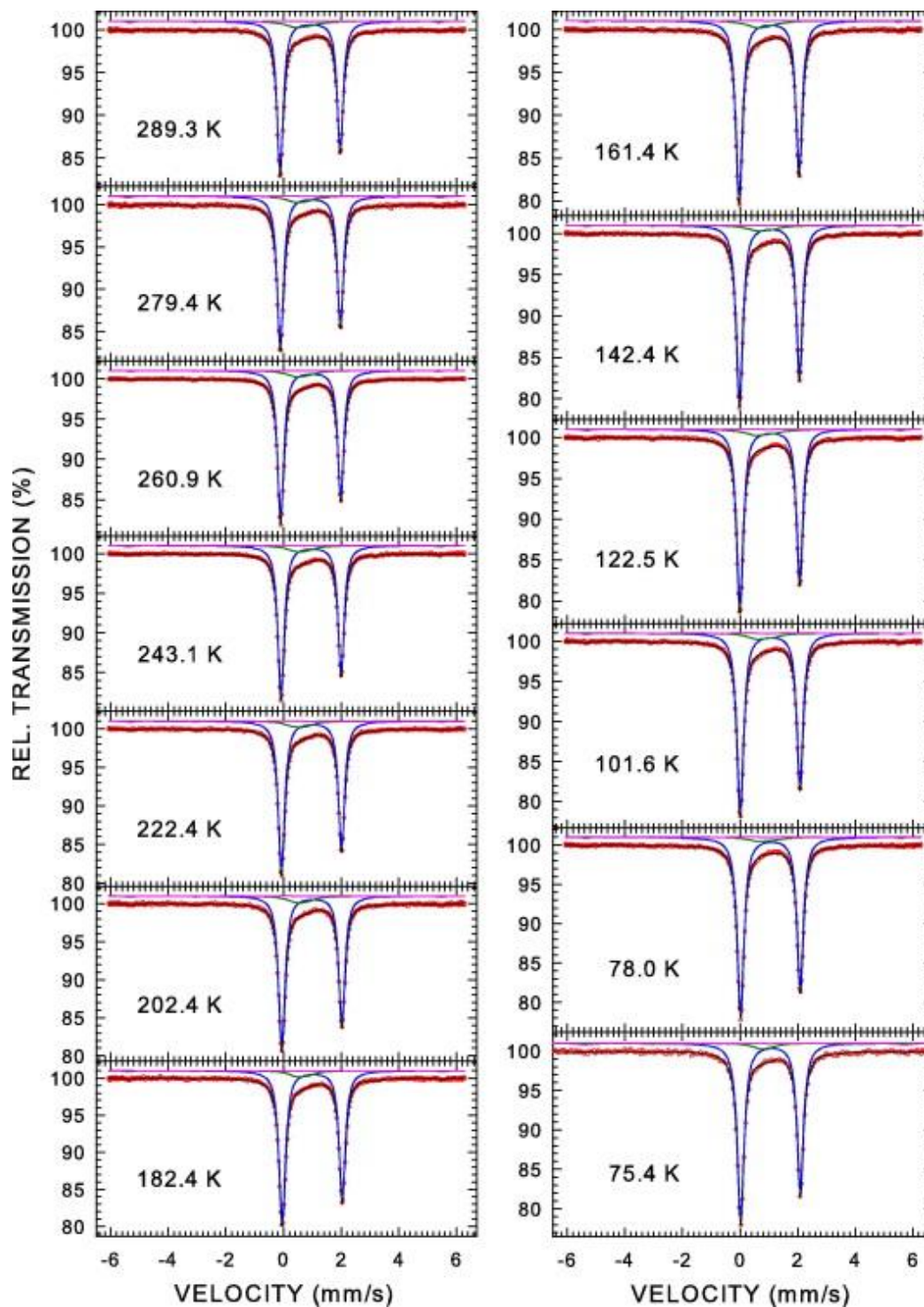


Figure 5.21 ^{57}Fe Mössbauer spectra of $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$ at the indicated temperatures fitted (black solid lines) with an asymmetric quadrupole doublet (blue solid line) due to main phase, and asymmetric quadrupole doublet (dark green solid lines) due to air-environment induced impurity, and a Zeeman pattern (pink solid line) originating from Fe impurity. The zero-velocity origin is relative to $\alpha\text{-Fe}$ at room temperature.

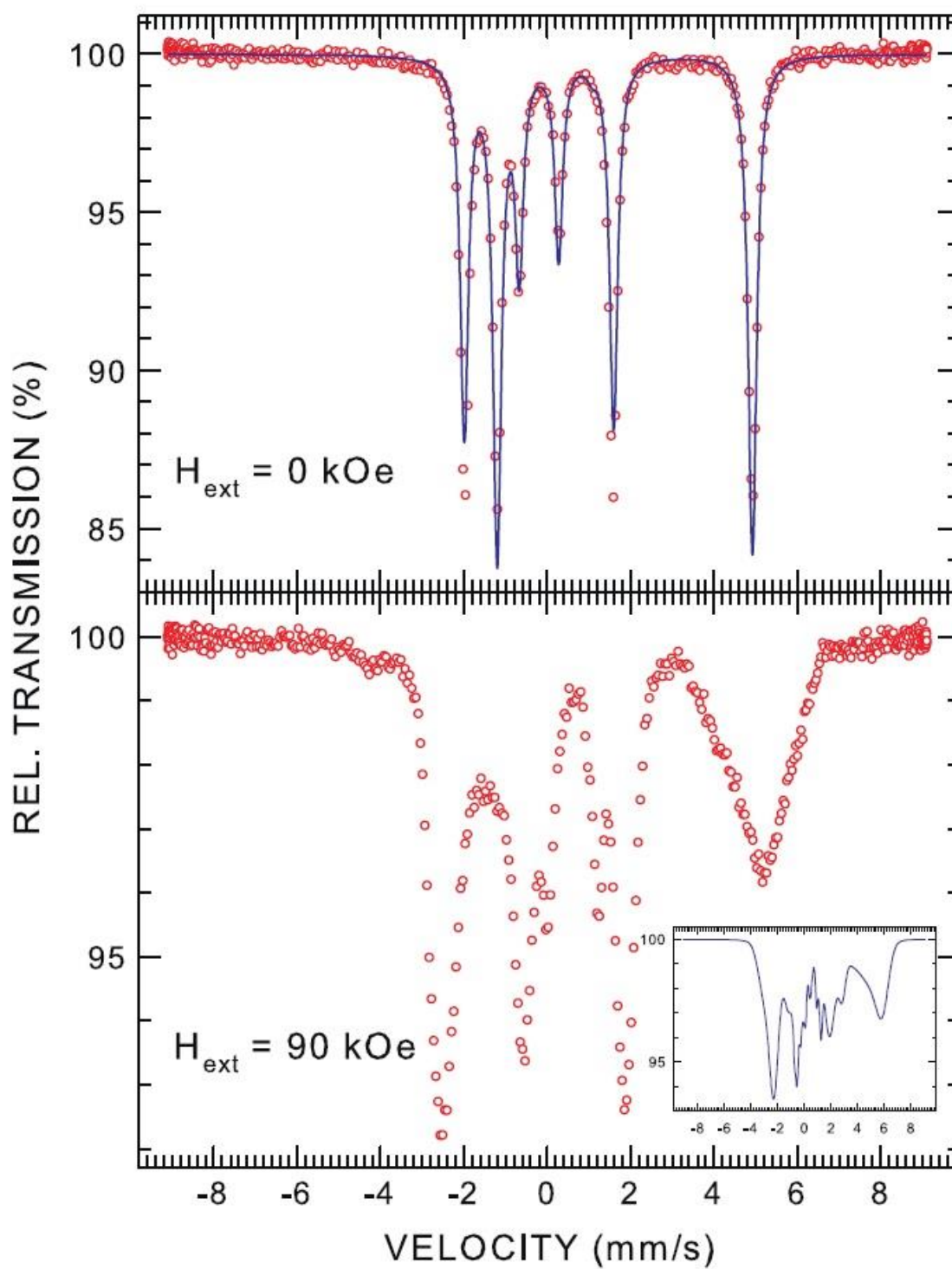


Figure 5.22 ^{57}Fe Mössbauer spectra of $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$ at 5.8 K in zero and 90 kOe external magnetic field H_{ext} applied parallel to the direction of the γ -rays. The $H_{\text{ext}} = 0$ kOe spectrum is fitted (blue solid line) to a Zeeman pattern. The inset shows a $H_{\text{ext}} = 90.0$ kOe simulated spectrum. The zero-velocity origin is relative to the source.

There are two types of behavior of a polycrystalline uniaxial antiferromagnet in H_{ext} [58]. When the magneto-crystalline anisotropy energy is small, the antiferromagnetic spin-system will flop, i.e., the spin-system will rotate perpendicular to H_{ext} . In this case, H_{ext} will add in quadrature to H and all ^{57}Fe nuclei will experience the same effective field $H_{\text{eff}} = \sqrt{H^2 + H_{\text{ext}}^2}$, and consequently no broadening is produced. Clearly, this is not the case here. In the second case, for a high magneto-crystalline anisotropy energy, the effective field $H_{\text{eff}} = \sqrt{H_{\text{ext}}^2 + H^2 + 2H_{\text{ext}}H\cos\theta}$ (θ is the angle between H_{ext} and H_{eff}) will range from $|H - H_{\text{ext}}|$ to $|H + H_{\text{ext}}|$ with the probability of the occurrence of a particular H_{eff} value $p(H_{\text{eff}}) = \frac{H_{\text{eff}}}{2HH_{\text{ext}}}$ [59]. This distribution of the effective fields will lead qualitatively to the broadening observed in figure 5.22. To be more quantitative, an expected $H_{\text{ext}} = 90$ kOe spectrum has been simulated (the quadrupole interaction could not be rigorously included in the simulation for reasons elaborated in Ref. [59]) as a superposition of the six $p(H_{\text{eff}})$ -weighted Zeeman patterns with H_{eff} values of 100.4, 136.4, 172.4, 208.4, 244.4, and 280.4 kOe (inset in figure 5.22). The simulated spectrum reflects the shape of the experimental spectrum reasonably well, thus validating the claim of antiferromagnetic coupling of the Fe magnetic moments in the compound studied.

The ^{57}Fe Mössbauer spectrum of $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$ measured at temperatures below the Néel temperature, T_N are shown in figure 5.22. They can be fitted well with a Zeeman pattern originating from the main phase. The spectra measured at 72.2, 73.2 and 74.4 K, i.e., at temperatures in the vicinity of T_N , show that magnetically ordered (a Zeeman pattern) and paramagnetic (an asymmetric quadrupole doublet pattern) material coexist, with the spectral weight of the doublet pattern increasing at the expense of the spectral weight of the Zeeman pattern as the temperature approaches T_N . Such a coexistence may be attributable to a small spreading out of T_N resulting from some inhomogeneity of the sample's composition.

Figure 5.23 shows the ^{57}Fe Mössbauer spectra of $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$ measured in selective temperatures below 75 K. In figure 5.24(a), the temperature dependence of the absorption spectral area A of $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$ derived from the fits of the Mössbauer spectra in figures 5.20, 5.21, and 5.23, is displayed. This area is proportional to the absorber Debye-Waller factor f_a , which is given in the Debye theory by [14] (5 – 4). The fit of the experimental dependence $A(T)$ [figure 5.24(a)] to equation (5 – 4) yields $T_D = 260(4)$ K.

The temperature dependence of $\delta(T)$, determined from the fits of the Mössbauer spectra in figures 5.20, 5.21, and 5.23, is shown in figure 5.24(b). $\delta(T)$ is given by

$$\delta(T) = \delta_0 + \delta_{\text{SOD}}(T), \quad (5 - 7)$$

where δ_0 is the intrinsic isomer shift and $\delta_{\text{SOD}}(T)$ is the second order Doppler shift (SOD) which depends on the lattice vibrations of the iron atoms [14]. In terms of the Debye approximation of the lattice vibrations, $\delta_{\text{SOD}}(T)$ is expressed in terms of the Debye temperature, T_D as

$$\delta_{\text{SOD}}(T) = -\frac{9}{2} \frac{k_B T}{Mc} \left(\frac{T}{T_D} \right)^3 \int_0^{\frac{T_D}{T}} \frac{x^3 dx}{e^x - 1}, \quad (5 - 8)$$

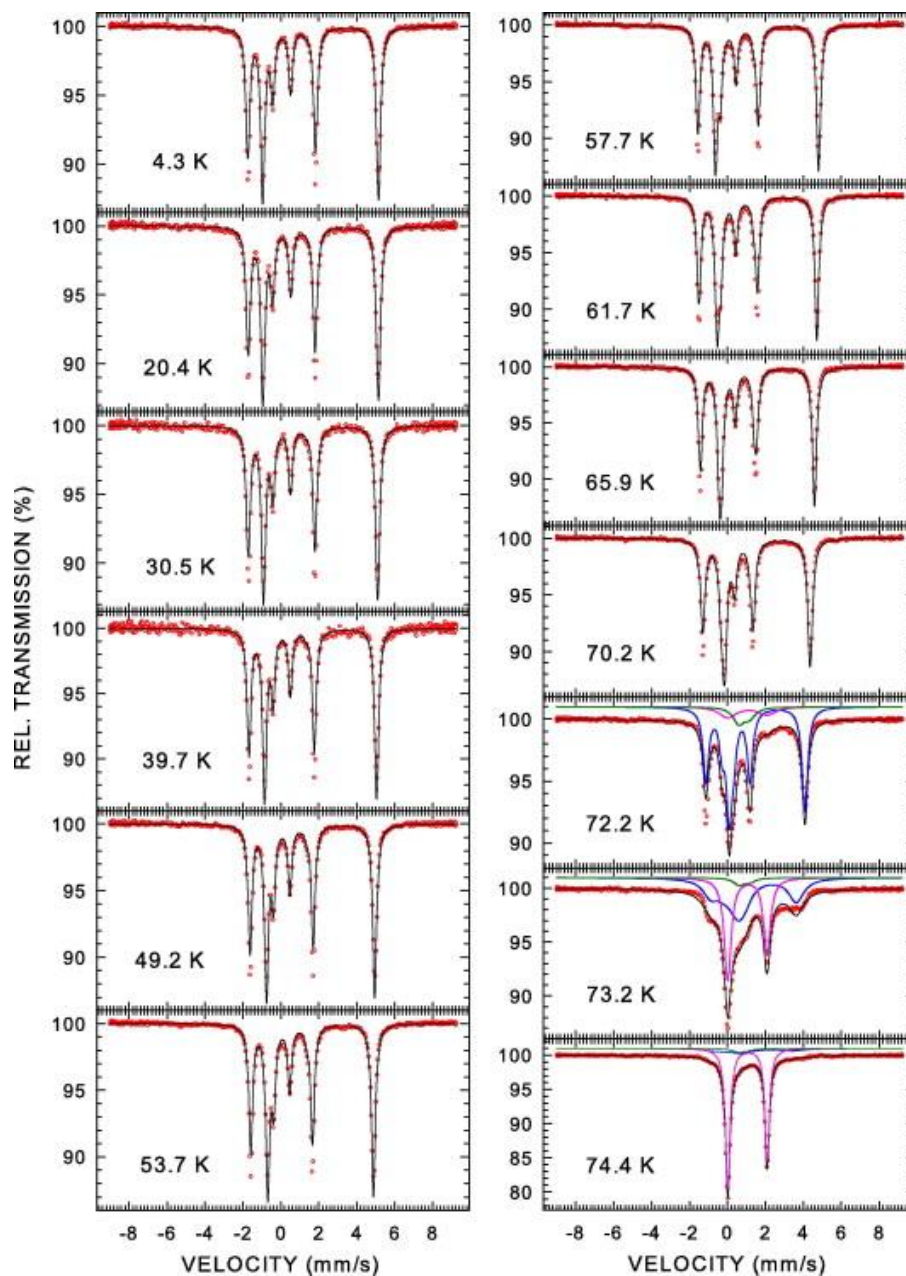


Figure 5.23 The ^{57}Fe Mössbauer spectra of $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$ at the indicated temperatures fitted (black solid lines) with a Zeeman pattern. The spectra at 72.2, 73.2, and 74.4 K are fitted with three components – a Zeeman pattern (blue solid lines) due to the main phase, an asymmetric quadrupole doublet (pink solid lines) due to the main phase, and an asymmetric quadrupole doublet (dark green solid lines) due to air-environment induced impurity. The zero-velocity origin is relative to $\alpha\text{-Fe}$ at room temperature.

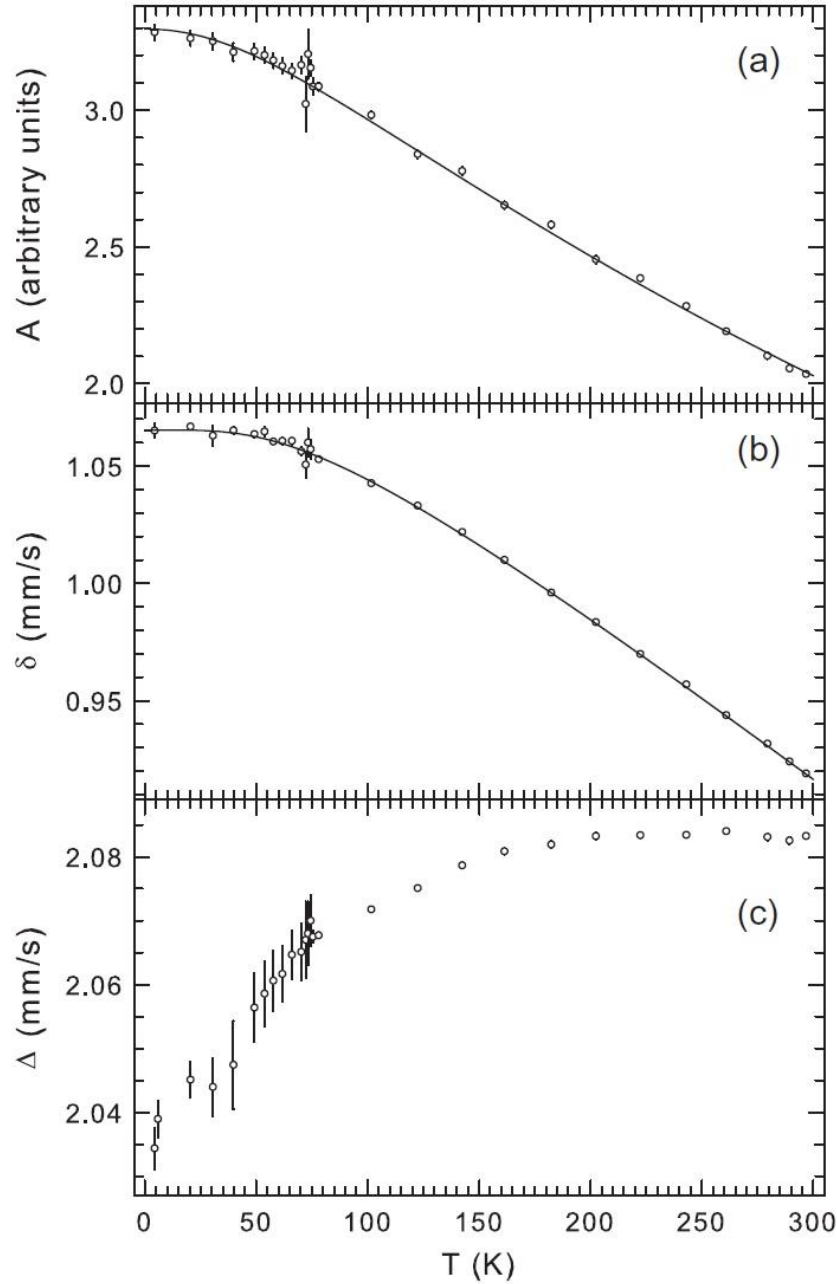


Figure 5.24 Temperature dependence of (a) the absorption spectral area A , (b) the center shift δ , and (c) the quadrupole splitting Δ . The solid lines are the fits to equation (5 – 4) in (a) and to equation (5 – 7) in (b).

By fitting the experimental data $\delta(T)$ [figure 5.24(b)] to equation (5 – 7), the quantities δ_0 and T_D were found to be $1.065(3) \frac{\text{mm}}{\text{s}}$ and 295(5) K, respectively. It should be note here that the calculated $\delta_0 = 0.998 \frac{\text{mm}}{\text{s}}$ is very close to the experimental value of $1.065(3) \frac{\text{mm}}{\text{s}}$, which gives credence to the reliability of the *ab-initio* calculations of the hyperfine-interaction parameters.

The value of T_D determined from the $A(T)$ data is clearly smaller than the one derived from the $\delta(T)$ data. In fact, the T_D values determined from the $A(T)$ data are always smaller than the ones obtained from the $\delta(T)$ data. This results from the way in which T_D is calculated. It is known that f_a and δ_{SOD} are related to the mean-square vibrational displacement $\langle x^2 \rangle$ and the mean-square velocity $\langle v^2 \rangle$ of the Mössbauer nucleus, respectively [14]. Because $\langle x^2 \rangle$ weights the phonon frequency distribution by ω^{-1} while $\langle v^2 \rangle$ weights it by ω^{+1} [60], the T_D values derived from the $A(T)$ data are necessarily lower than those determined from the $\delta(T)$ data. The weighted average of these two T_D values is 274(3) K. It is in excellent agreement with the value of 277 K determined from specific heat measurements [51].

Figure 5.24(c) shows the temperature dependence of the quadrupole splitting Δ derived from the fits of the Mössbauer spectra in figures 5.20 – 5.23. One observes that Δ is approximately constant at high temperatures above ~ 150 K and then clearly decreases at lower temperatures. It is suggested that this decrease is probably caused by a possible subtle structural transition below ~ 150 K, as observed in the structurally similar compound $\text{La}_2\text{Fe}_2\text{Se}_2\text{O}_3$ [61].

The temperature dependences of H and α determined from the fits of the Mössbauer spectra in figures 5.22 and 5.23 are displayed in figure 5.25. The $H(T)$ dependence in figure 5.25(a) was fitted in terms of the Bean-Rodbell exchange model [62] in which the reduced magnetization $\sigma = \frac{M(T)}{M(0)}$, and hence (assuming proportionality between M and H) the reduced hyperfine magnetic field $\sigma = \frac{H(T)}{H(0)}$, is given by

$$\sigma = B_S \left[\frac{3S}{S+1} \frac{\sigma}{\Theta} \left(1 + \frac{3}{80} \frac{(2S+1)^4 - 1}{S(S+1)^3} \zeta \sigma^2 \right) \right], \quad (5-9)$$

where B_S is the Brillouin function for spin S , $\Theta = \frac{T}{T_N}$, and ζ is the order parameter of the transition. For an ideal second-order transition $\zeta = 0$ and for the first-order transition $\zeta > 1$. The ζ values between 0 and 1 correspond to intermediate-order transitions [62]. As the δ and Δ values indicate that Fe^{2+} ions in the compound studied are in a high-spin configuration, $S = 2$ was used in fitting the $H(T)$ data to equation (5 – 9). The fit [fig 5.25(a)] yields $H(0) = 189.6(1.8)$ kOe, $T_N = 74.7(5)$ K, and $\zeta = 1.22(19)$. It should be stated that the experimental value of $H(0)$ is quite close to the calculated H_C contribution of 215 kOe. This seems to confirm the general observation that the $|H_{\text{dip}} + H_{\text{orb}} + H_{\text{lat}}|$ contribution (about 25 kOe in our case) is about an order of magnitude smaller than the H_C contribution. The value of ζ indicates that the nature of the antiferromagnetic transition is first order. Since H is, to a first approximation, proportional to the on-site magnetic moment of iron atoms μ_{Fe} through the relation $H = a\mu_{\text{Fe}}$, where the value of the proportionality constant a is compound specific [63], one can estimate μ_{Fe} from the measured H . In converting $H(0)$ to $\mu_{\text{Fe}}(0)$, $a = 62.6(1.9) \frac{\text{kOe}}{\mu_B}$, which results from $H(4.2 \text{ K}) = 206(5)$ kOe and $\mu_{\text{Fe}}(16 \text{ K}) = 3.1(1)\mu_B$ determined from a Mössbauer and a neutron diffraction study of a structurally similar compound $\text{Sr}_2\text{Fe}_2\text{S}_2\text{F}_2\text{O}$ [64,65] was used. Thus, the value of $\mu_{\text{Fe}}(0)$ in $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$ is $3.0(1)\mu_B$. The value of $\mu_{\text{Fe}}(0)$ is in rather good agreement with the calculated value of $3.19\mu_B$ (table 5.2).

The $H(T)$ data was also fitted for temperatures above $0.66T_N$ to power-law function, $H(T) \propto \left(1 - \frac{T}{T_N}\right)^\beta$. Such a fit [figure 5.25(a)] yields $T_N = 74.8(2)$ K and $\beta = 0.159(12)$. The β value is close to the theoretical value of 0.125 expected for a 2D square planar Ising system [66]. The angle α does not change with temperature [figure 5.25(b)] and its average value is $4.7(1)^\circ$.

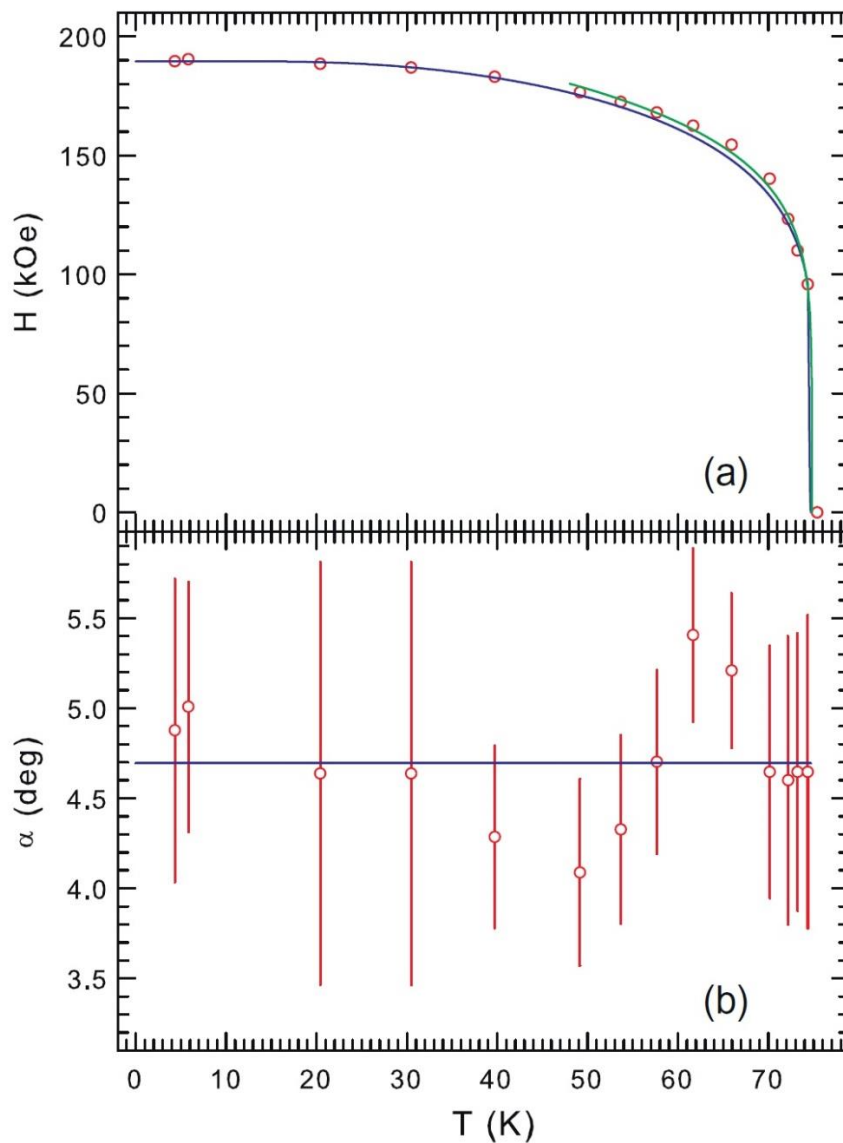


Figure 5.25 Temperature dependence of (a) the hyperfine magnetic field H and (b) the angle α between V_{zz} and H . The blue and green solid lines in (a) are the fits to equation (5-9) and to the power-law, respectively.

5.2.4 Summary and conclusions

In summary, the results of Mössbauer spectroscopy measurements and of *ab-initio* calculations of the electronic energy bands and hyperfine-interaction properties of the $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$ compound have been presented. It has been confirmed that $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$ is a Mott insulator. It has been found that in its ground state, $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$ is an antiferromagnet with the Néel temperature $T_N = 74.8(2)$ K and with the iron magnetic moment of $3.0(1)\mu_B$. Good agreement is observed between the calculated hyperfine-interaction and magnetic parameters and the corresponding measured ones. It is also found that the Debye temperature of $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$ is $274(3)$ K.

5.3 Fe₂NiGa

5.3.1 Introduction

Heusler compounds are a class of more than 1000 ternary intermetallic materials with composition X_2YZ or XYZ , where X and Y are transition metals and Z is a main group element [67]. They exhibit a rich variety of physical properties [68]. They occur as metals, semiconductors, or superconductors. These are compounds with different magnetic orderings. They possess shape-memory characteristics, exhibit heavy-fermion behavior, have giant magneto resistance and enhanced thermoelectric properties. Some of them are topological insulators. Some of these properties have great potential for practical applications in, for example, spintronics or magnetocaloric technology.

Heusler compounds crystallize in the cubic space groups $Fm\bar{3}m$ or $F\bar{4}3m$. Within these two space groups, different types of atomic disorder, i.e., various possible distributions of the X , Y , and Z elements among the specific crystallographic sites, are possible [69]. It is this disorder upon which the physical properties of the Heusler compounds are strongly dependent [68].

A subset of the Heusler compounds, Fe_2NiZ , is of current interest, especially from a theoretical point of view [70-76]. A few experimental studies of the Fe_2NiZ compounds have also been carried out [71,73,77-80]. In what follows the results of X-ray diffraction, ^{57}Fe Mössbauer spectroscopy, magnetic study, complemented by first principle electronic structure and hyperfine interaction parameters calculations of Fe_2NiGa is presented.

5.3.2 General considerations and structural parameters

The Heusler compound Fe_2NiGa crystallizes in the $F\bar{4}3m$ (No. 216) space group according to Burch's rule [25]. The Fe atoms occupy two sites denoted by A and B with positional coordinates (0,0,0) and (0.25,0.25,0.25) respectively, while the Ni atoms occupy the (0.5,0.5,0.5) site represented by the symbol C and the Ga atoms occupy the (0.75,0.75,0.75) site denoted by D. In figure 5.26, the unit cell of the Fe_2NiGa compound is schematically shown. As discussed later the rods connecting the atoms in the unit cell shows the chemical bonding between them.

The cubic unit cell of the Fe_2NiGa compound has a lattice constant $a = 5.7961(4)$ Å which is obtained through the X-ray powder measurements of the sample and with a Rietveld refinement analysis. (*vide infra*).

5.3.3 Theoretical calculations and interpretations

In what follows, the theoretical methods involved in the calculations of the various physical properties of the Fe_2NiGa system are introduced. A detailed analysis and discussion of the results of the theoretical calculations is presented later on.

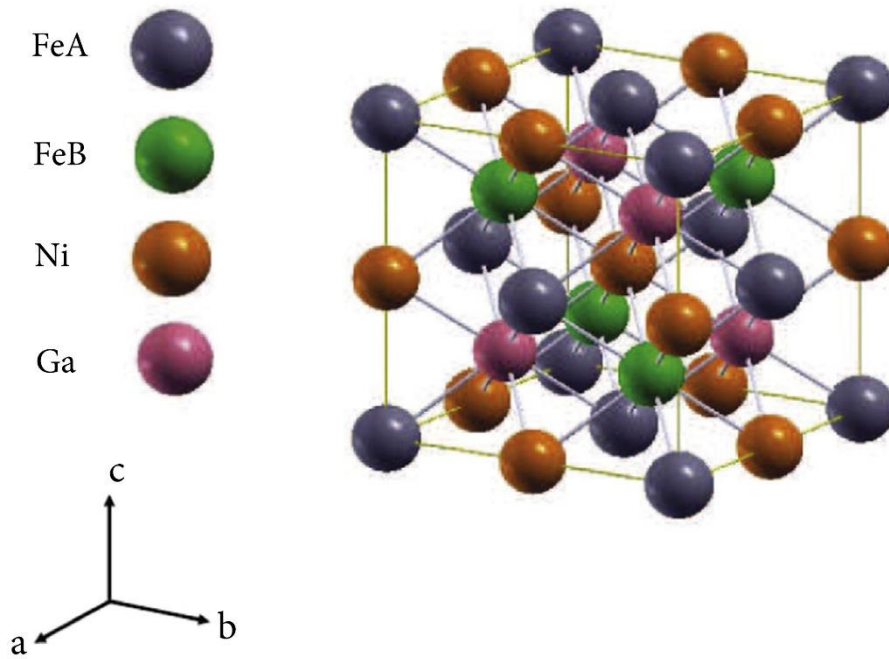


Figure 5.26 The unit cell of the Fe_2NiGa compound in the space group $F\bar{4}3m$ (No. 216).

5.3.3.1 Theoretical methodology

In what follows the specific computational details used in the theoretical calculations for the Fe_2NiGa compound is presented.

First principle (*ab-initio*) electronic structure and Mössbauer hyperfine interaction parameter calculations have been carried out using the full potential linearized augmented plane wave plus local orbital (FP-LAPW+lo) method implemented in the WIEN2k package [20]. The FP-LAPW+lo method falls within the framework of density functional theory discussed in chapter four. In this method, one partitions the unit cell into two distinct regions. The first regions are the so-called muffin-tin (MT) spheres centered at the locations of the atomic nuclei. These spheres are sometimes denoted as the atomic spheres or atomic regions. The second regions are the interstitial regions between the muffin-tin spheres. The electronic wave functions in the interstitial regions are expanded in plane wave bases whereas in the muffin-tin spheres they are expanded in terms of spherical harmonics times atomic radial functions.

The basis set inside each muffin-tin sphere is split into a core and valence subset. The core states are treated within the spherical part of the atomic potential only and their charge density distributions inside the muffin-tin spheres are assumed to be spherically symmetric. However, the valence wave functions are expanded in spherical harmonics to a maximum orbital angular momentum quantum number of $l = 12$, whereas within the interstitial region they are expanded up to $l = 4$. For the exchange-correlation potential, the generalized gradient approximation

(GGA) scheme of Perdew, Burke, and Ernzerhof [21] is used. A separation energy of -6.0 Ry is used in order to distinct valence states from core states for individual atoms in the unit cell.

As for the muffin-tin radii, the values 2.36 a.u., 2.36 a.u., and 2.30 a.u. are chosen for iron, nickel and gallium atoms respectively. The plane wave cut-off parameter used is such that $R_{MT} \times K_{MAX} = 7$, where R_{MT} is the smallest muffin-tin radius in the unit cell and K_{MAX} is the maximum k-vector used in the plane wave expansion of the wave functions in the interstitial region. For electronic band structure calculations a total number of 286 k-points is used within a $21 \times 21 \times 21$ k-mesh in the irreducible wedge of the first Brillouin zone. For the self-consistency cycles, a convergence criterion used for energy is chosen such that the differences in energy between two successive iterations does not exceed 10^{-4} Ry. As mentioned earlier, experimental values obtained from X-ray diffraction measurements are used for the lattice parameters in the calculations. The experimental lattice constant a in the space group $F\bar{4}3m$ obtained by X-ray diffraction measurements is used as the input for the calculations.

5.3.3.2 Theoretical results

In this section the theoretical results regarding electronic structure, charge density distributions, hyperfine interaction parameters, and elastic properties of the Fe_2NiGa compound are presented and discussed. The electronic density of states and also the electronic energy band structure of the nonmagnetic and magnetic phases of the Fe_2NiGa system are discussed in detail.

5.3.3.2.1 Charge density distribution

In figure 5.27, the calculated electronic charge distribution of Fe_2NiGa along the two crystallographic planes (110) and (100) is presented.

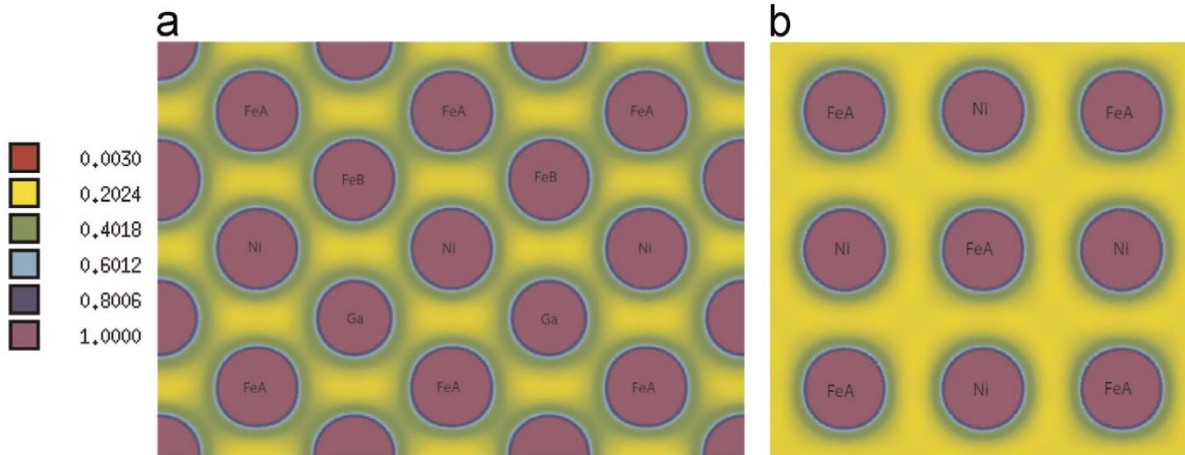


Figure 5.27 Electronic charge density distribution of Fe_2NiGa (in units of $\frac{e}{\text{\AA}^3}$) along the (a) (110) plane, and (b) (100), plane.

By examining figure 5.27, one concludes qualitative information on charge distribution, localization, and chemical bonding in the Fe_2NiGa system. The charge density distribution in the

(100) plane shows a high degree of electron charge localization around Ni atoms and also Fe atoms at the A sites, these areas of high charge concentration are represented by the blue-green colors around the atomic sites (Fig 2.27(b)). In between these atoms the charge density is relatively low and it is indicated by the yellow-red region. As a result, there would be a rather weak covalent bonding between the nickel atoms and the iron atoms at sites A. For the charge density distribution in the (110) plane, the electron charge distribution is less localized and thus the low density regions are smaller in volume (Fig 5.27(a)). Consequently, directional covalent bonding between neighboring Fe and Ga atoms, and also Fe and Ni atoms is formed. The nature of the covalent bonding between Fe and Ga atoms is due to p - d hybridization.

Considering the valence electron configurations of Ga, Fe and Ni atoms, one expects the formation of p - d covalent bonds in which two electrons (from each of the two Fe atoms) from $3d$ states along with three electrons from the Ni $3d$ states join the $4p$ states of Ga, forming relatively strong covalent bonds.

Another possible explanation is based on the fact that on average, the neighboring atoms on the (100) plane are further apart from each other than the atoms on the (110) plane. Thus, the electrons in the (100) plane are less likely to participate in forming bonds. This is because of the Coulomb interaction between neighboring atoms. In other words, Due to their relatively large separation distance, the interaction energy between the neighboring atoms in the (100) plane is not strong enough to overcome the atomic binding of the electrons to their parent atoms. This results in the localization of the electrons around their parent atoms. But the situation along the (110) plane is completely different. In the (110) plane, the separation distance between neighboring atoms is relatively small, thus the Coulomb interaction energy between the electrons of one atom and the nuclei of its neighboring atoms, is large enough to form strong covalent bonds.

5.3.3.2.2 The nonmagnetic and ferromagnetic states

In this section, the calculated properties of the nonmagnetic or paramagnetic phase and the ferromagnetic phase of Fe_2NiGa are presented. The nonmagnetic phase of this system occurs above the ferromagnetic ordering temperature and thus it is the high temperature regime phase of the system. The ferromagnetic state, however, is the low temperature phase or state of the Fe_2NiGa system in which magnetic ordering between the dipole moments is observed.

5.3.3.2.2.1 The electronic density of states

In the nonmagnetic state of Fe_2NiGa , thermal agitations are strong enough to overcome any preferred magnetic ordering of the system. In figure 5.28, the results of the electronic density of state calculations for the nonmagnetic state of Fe_2NiGa are presented. The large concentration of electronic states observed around the Fermi energy, E_F , can lead to high electrical and thermal conductivities in the high temperature regime of the Fe_2NiGa system. The high degree of overlap between electronic states around the Fermi level explains the covalent nature of the chemical bonding between atoms in the Fe_2NiGa compound. This conclusion confirms the earlier discussions based on electronic charge distributions in the Fe_2NiGa system. The dominant

contributions to the density of states originate from the 3d states of Fe atoms of type B and nickel states. The Ga states *s* and *p* which are peaked at around 7 and 3.5 eV below the Fermi energy, contribute only a tiny amount to the density of states of the Fe₂NiGa compound.

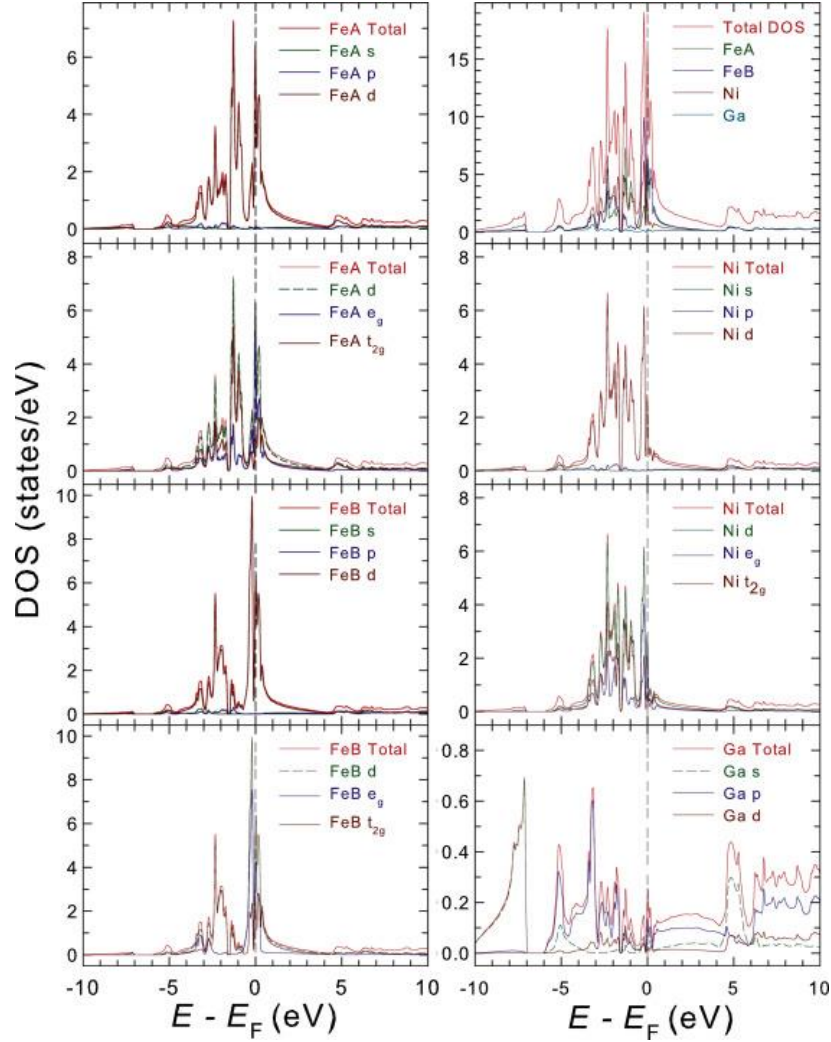


Figure 5.28 The total, atomic, and orbital resolved density of states of Fe₂NiGa in the nonmagnetic state.

The density of states for the *e_g* and *t_{2g}* states of Fe atoms at sites A and B, and also nickel atoms is calculated and displayed in figure 5.28. As one can observe from these figures, the *e_g* states lie higher in energy than the *t_{2g}* states which is expected. In the case of nickel, the *e_g* states are distributed from about 3.5 eV below to the immediate vicinity the Fermi energy, and are peaked at about -0.5 eV with respect to the Fermi level. The *t_{2g}* states of Ni however, are peaked around 2.5 eV below the Fermi energy. The location of these states for Fe atoms at B sites is relatively similar. Therefore, the *e_g* and *t_{2g}* states are not localized and are spread in energies below the Fermi level.

In figure 5.29, the calculated spin polarized density of states for the ferromagnetic phase of Fe_2NiGa is displayed. For each of the two possible spin configurations shown in figure 5.29, the dominant contributions to the total density of states are due to Fe and Ni d states.

In the spin up configuration of figure 5.29, the density of states are spread in an energy range between -4.5 to -1 eV with respect to the Fermi energy and are almost absent in the vicinity of the Fermi level. This leads to the formation of an energy gap above the Fermi level. However, for the spin down configuration in figure 5.29, the density of states are spread in a wider region; typically between -4 to 2 eV with respect to the Fermi energy. Therefore there exists a rather high concentration of accessible spin down states at the Fermi level.

These spin dependent characteristics are reminiscent of half metallic behavior, a behavior that can have important implications in fields such as spintronics where one considers spin-dependent currents. In the present case for instance, spin up electrons face a potential barrier and are blocked whereas the spin down electrons can freely flow and participate in the current. This creates a spin filter, or a spin switch which can be practically used in quantum computation whereby the traditional bits “0” and “1” are replaced by spin dependent currents.

For both spin configurations, the Fe d states at both sites are the main contributions to density of states (figure 5.29). In the case of Fe atoms at site A, the d states are widely distributed between -1 to -4 eV with respect to the Fermi energy, and are highly peaked around -1 to -1.5 eV. The Fe states at site B however, are strongly peaked at -1.5 and -3.3 eV. In the case of spin down configuration, the Fe d states at A sites occupy a region from -2 to 2 eV in energy with respect to the Fermi level and are strongly peaked at -1 to 1 eV. A similar pattern is observed for Fe B d states but with a lower concentration of density of states below the Fermi energy.

As was discussed in the case of the nonmagnetic phase, within the Fe d states of the ferromagnetic phase of Fe_2NiGa , the e_g states are peaked in energies closer to the Fermi energy, whereas the t_{2g} states are distributed over lower energies. The contributions to the density of states arising from e_g and t_{2g} states for both spin configurations are of almost identical weight. The density of states arising from the Ni d states is different from that of the Fe d states in the sense that the main contribution of the d states for the spin up configuration is mainly of the e_g type and is concentrated between about 1 and 1.8 eV below the Fermi energy. However, for the spin down configuration the dominant contribution of the Ni d states is peaked at about 2 eV below the Fermi energy and is mainly of the t_{2g} type.

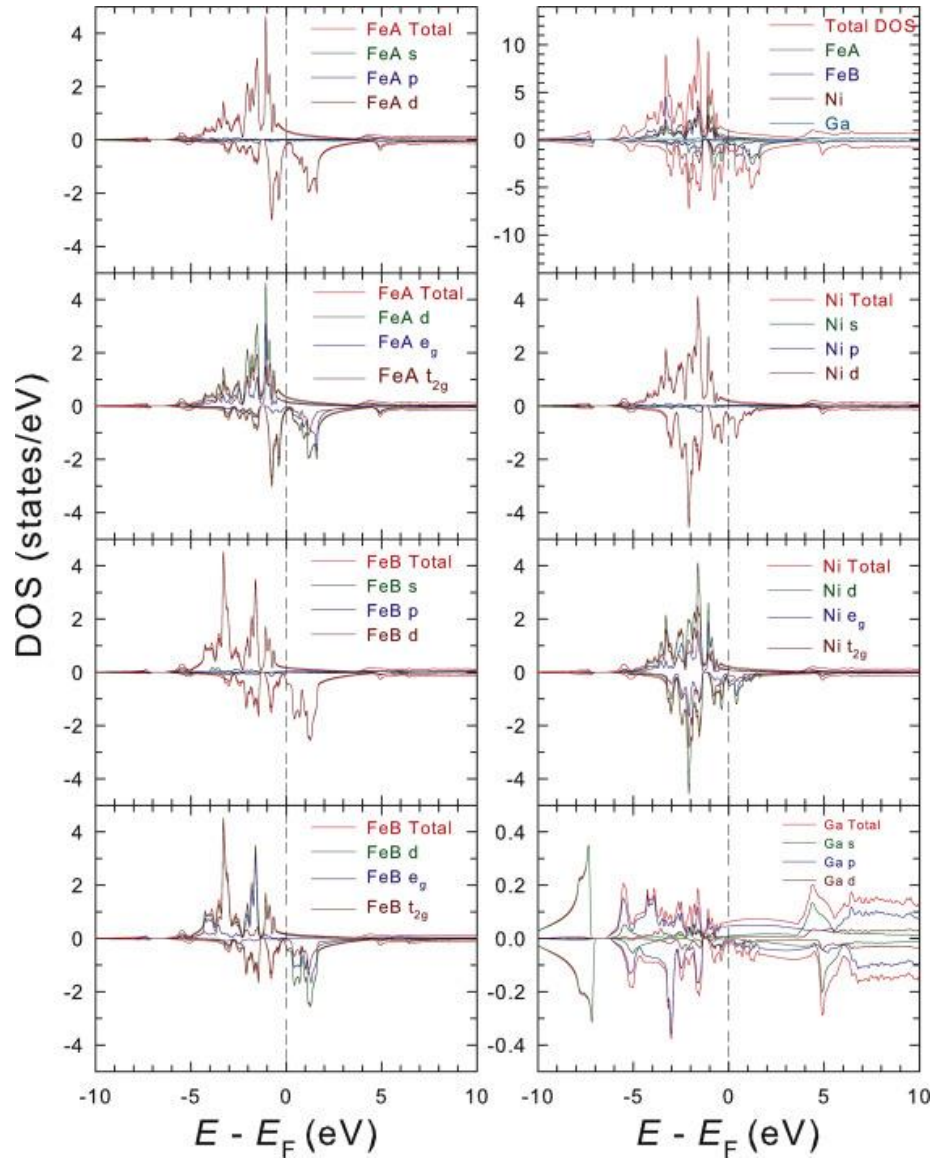


Figure 5.29 The spin-polarized total, atomic, and orbital resolved density of states of ferromagnetic Fe_2NiGa .

5.3.3.2.2 The electronic band structure

The electronic energy band structure of the Fe_2NiGa in both nonmagnetic and ferromagnetic states is presented in figure 5.30. For the nonmagnetic phase of Fe_2NiGa (figure 5.30(a)) a large number of accessible states are observed at and below the Fermi level. These states fall into a rather narrow range in energy as compared to the other states lower in energy. In other words, these states are localized in energy and in all directions of the Brillouin zone, and are dominated by Fe and Ni d states. There is also a region of high density of conduction bands in the energy interval between 4 and 7 eV above the Fermi level.

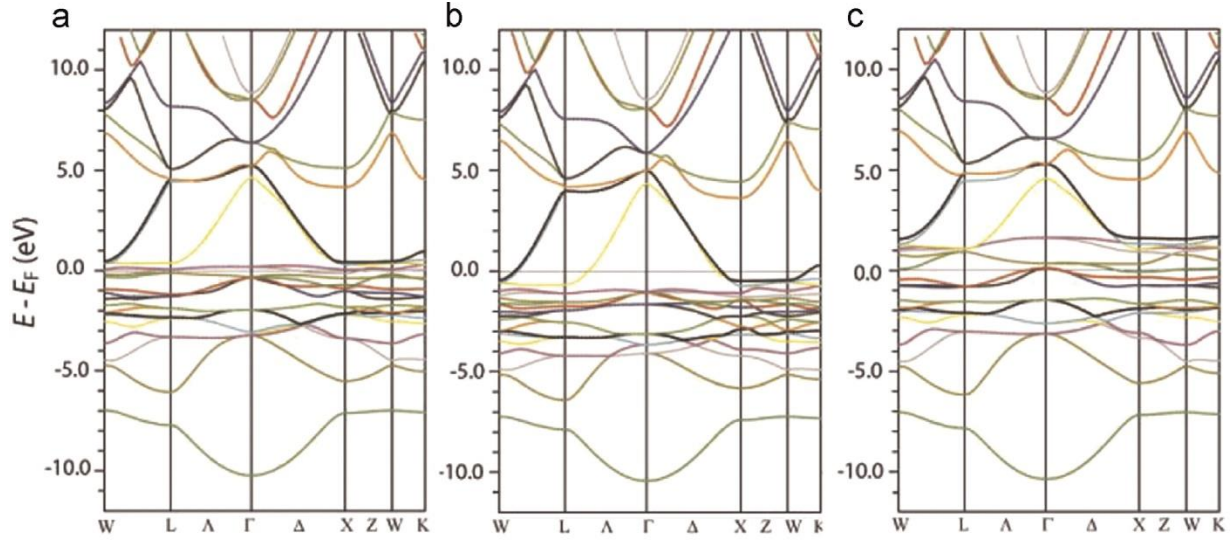


Figure 5.30 The energy band structure of Fe_2NiGa in the (a) nonmagnetic state, and in the (b) spin up and (c) spin down configurations in the ferromagnetic state.

In figure 5.30(b) and 5.30(c), the spin polarized electronic band structure of Fe_2NiGa is shown. One observes an energy gap below the Fermi level for the spin up configuration, whereas the spin down configuration does not show any band gap across the Fermi level. Instead, a rather large number of energy bands are seen around the Fermi level in the spin down configuration. This difference in the energy band structure around the Fermi level and between spin up and spin down configurations, gives rise to the nearly half-metallic nature of the Fe_2NiGa system. This confirms the previous discussion based on the density of states in the spin polarized system.

5.3.3.2.3 The calculated magnetic moments

The separation of spin up and spin down density of states for Fe and Ni leads to non-zero Fe and Ni magnetic moments. This is a direct result of the unfilled $3d$ shells in both atoms. As one can see from the bottom graph of figure 5.29, the total contribution of Ga to the overall density of states is negligibly small. More importantly, the states in both spin up and spin down configurations are distributed in a similar way. This accounts for the fact that the value of the Ga magnetic moment is close to zero. The calculated magnetic moments $\mu_{\text{Fe,A}}$, $\mu_{\text{Fe,B}}$, μ_{Ni} , and μ_{Ga} in the ferromagnetic state of Fe_2NiGa are 1.941, 2.680, 0.492, and $-0.054\mu_B$, respectively. The fact that $\mu_{\text{Fe,B}}$ is larger than $\mu_{\text{Fe,A}}$ can be deduced by inspecting figure 5.29. One observes that the difference in the distribution of the d states of Fe at B sites, between spin up and spin down configurations is larger than that of the d states of Fe at A sites. The calculated magnetic moment per formula unit, $\mu_{\text{f.u.}}$ is $4.958\mu_B$ [81].

5.3.3.2.4 The hyperfine interaction parameters

In this section, the results of the first principle calculations leading to the hyperfine interaction parameters in Fe_2NiGa are presented. Ab-initio calculations on the non-magnetic phase of the Fe_2NiGa system, yields two important hyperfine-interaction parameters which later on are compared with the experimental results based on the ^{57}Fe Mössbauer spectroscopy of this compound. The first of these is the so-called isomer shift, δ_0 , and the second one is the magnetic hyperfine field, H_{hf} [14]. Due to the cubical crystal structure of the Fe_2NiGa compound, i.e. the iron atoms are located at sites with point symmetry $\bar{4}3m$, a vanishing electric field gradient (EFG) tensor is guaranteed.

5.3.3.2.4.1 The isomer shift calculations

The isomer shift is a result of the difference between the total electron density at the Mössbauer nucleus in Fe_2NiGa , denoted by $\rho(0)$, and the electron density at nucleus of the reference compound, $\rho_{\text{ref}}(0)$ (equation (5 – 5)). For the reference element, an $\alpha - \text{Fe}$ (iron in a *bcc* structure) with lattice constant $2.8665 \text{ \AA}$ was chosen. The calculated values for the electronic charge density at the Mössbauer nuclei for Fe at the A and B sites in the Fe_2NiGa system are 15308.677 and $15309.300 \text{ a.u.}^{-3}$ respectively. The corresponding calculated value for the reference element is $15309.918 \text{ a.u.}^{-3}$. Using the isomer shift calibration constant of $\alpha = -0.291 \text{ a.u.}^3 \text{ mms}^{-1}$ from Ref. [55] in equation (5 – 5), the isomer shift values of $\delta_{0,A} = 0.361 \text{ mms}^{-1}$ and $\delta_{0,B} = 0.180 \text{ mms}^{-1}$ are obtained for Fe atoms at sites A and B respectively in the compound Fe_2NiGa .

5.3.3.2.4.2 The calculated hyperfine magnetic field

The hyperfine magnetic field at the Mössbauer nucleus in a magnetically ordered material consists of four main contributions, The Fermi contact term, H_c , the magnetic dipolar term, H_{dip} , the orbital moment term, H_{orb} , and the term arising from the magnetic fields due to neighboring atoms in the lattice, the lattice term, H_{lat} [14]. Of these terms, the Fermi contact term is usually significantly larger in magnitude than the other three terms. The Fermi contact term is given by equation (5 – 6). The magnitudes of H_c at the A and B sites in the Fe_2NiGa system calculated from (5 – 6) are $H_{c,A} = 166 \text{ kOe}$ and $H_{c,B} = 260 \text{ kOe}$ respectively.

5.3.3.2.5 The elastic parameters

The elastic parameters discussed here are calculated for the optimized lattice constant of $5.7646 \text{ \AA}$ derived from the structural optimization of the Fe_2NiGa system. In figure 5.31, the volume optimization of the Fe_2NiGa unit cell is given. The calculated density ρ of the Fe_2NiGa compound is $8.1903 \frac{\text{g}}{\text{cm}^3}$. For the cubic structure of Fe_2NiGa , the calculated second order elastic constants [82] C_{11} , C_{12} , and C_{44} are 233.04 , 196.20 , and 175.40 GPa , respectively.

Using the calculated values of ρ and the elastic constants, one finds the longitudinal and transverse sound velocities within Fe_2NiGa which are given by the following relations,

$$v_l = [(C_{11} + 0.4(2C_{44} + C_{12} - C_{11}))/\rho]^{1/2}, v_t = [(C_{44} - 0.2(2C_{44} + C_{12} - C_{11}))/\rho]^{1/2} \quad (5-10)$$

to be 6624.5 and 3712.1 ms^{-1} respectively.

The Debye temperature is given by [82]

$$\Theta_D = h/k_B(3nN_A\rho/4\pi M)^{1/3}v_m, \quad (5-11)$$

where h is Planck's constant, k_B is Boltzmann's constant, n is the number of atoms per formula unit, N_A is Avogadro's constant, M is the molecular weight of the compound, and v_m is the average sound velocity

$$v_m = \left[\frac{1}{3} \left(\frac{2}{v_t^3} + \frac{1}{v_l^3} \right) \right]^{-1/3}. \quad (5-12)$$

The calculated Θ_D is 427 K. The equilibrium bulk modulus, B_0 , is also calculated $B_0 = 204.2$ GPa.

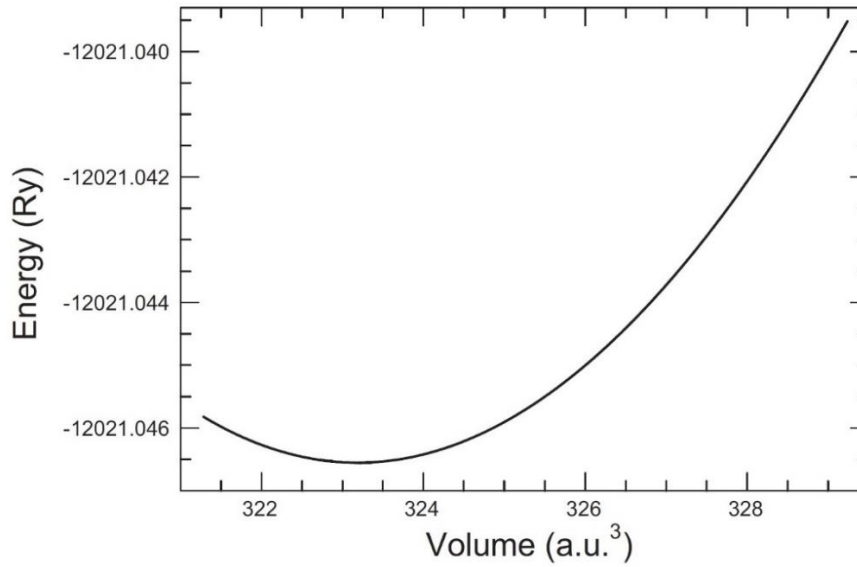


Figure 5.31 Total energy as a function of primitive cell volume in the *fcc* structure of Fe_2NiGa .

5.3.4 The experimental measurements and results

In this section, the results of the experimental studies on the Fe_2NiGa system, including X-ray powder diffractometry, magnetic measurements, and Mössbauer measurements are presented and compared with the results of *ab-initio* calculations.

5.3.4.1 Sample preparation

An ingot of nominal composition Fe_2NiGa is prepared by arc melting the constituent elements of purity 99.9% in an atmosphere of purified argon. The ingot is then wrapped in a tantalum foil and vacuum-annealed at 1073 K for two weeks [80].

5.3.4.2 X-ray diffraction pattern

The X-ray diffraction (XRD) spectrum of Fe_2NiGa , was measured at 298 K in Bragg-Brentano geometry on a PANalytical X'Pert scanning diffractometer using $\text{Cu K}\alpha$ radiation in the 2θ range $20 - 120^\circ$ in steps of 0.02° . The $\text{K}\beta$ line was eliminated by using a Kevex Psi2 Peltier-cooled solid-state Si detector.

In figure 5.32, the room temperature powder X-ray diffraction pattern of the Fe_2NiGa sample is shown. As mentioned earlier, the studied compound crystallizes in the cubic space group $Fm\bar{3}m$ (No. 216) [25]. A Rietveld refinement of the X-ray diffraction pattern in figure 5.32 yields the lattice parameter $a = 5.7961(4) \text{ \AA}$, and also the atomic positional parameters mentioned earlier in section 5.3.2 which are used in the theoretical calculations discussed above.

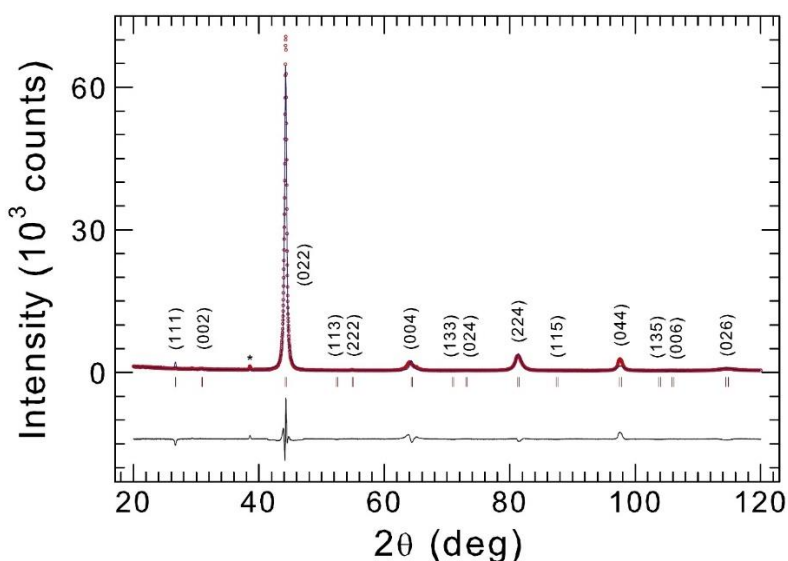


Figure 5.32 X-ray diffraction pattern of Fe_2NiGa at 298 K. The experimental data are denoted by open circles, while the line through the circles represents the results of Rietveld refinement. The row of vertical bars shows the indexed Bragg peak positions for the $Fm\bar{3}m$ space group. The * symbol indicates the Bragg peak position corresponding to an unidentified impurity phase. The lower solid line represents the difference curve between experimental and calculated patterns.

The absence of the (111) and (002) *fcc* superstructure Bragg peaks in the experimental pattern indicates that the studied Heusler compound is poorly ordered. In other words, some structural disorder (possible random occupation of the constituent elements in the available crystallographic sites) must exist in the compound.

5.3.4.3 Mössbauer spectroscopy

In this section, the results of the ^{57}Fe Mössbauer spectroscopy measurements on the Fe_2NiGa compound is presented and discussed. The results of the measurements are then compared with those of first principle calculations.

5.3.4.3.1 Experimental set up for the Mössbauer measurements

The ^{57}Fe Mössbauer measurements are carried out using a standard Mössbauer spectrometer operating in sine mode and a ^{57}Co source at room temperature. The spectrometer is calibrated with a $6.35\ \mu\text{m}$ thick $\alpha\text{-Fe}$ foil [27]. The spectra is then folded. The Mössbauer absorber for low temperature ($< 300\ \text{K}$) measurements consists of a mixture of powdered Fe_2NiGa , and powdered boron nitride, which is pressed into a pellet and put into a high purity, $8\ \mu\text{m}$ thick aluminum disk container to ensure a uniform temperature over the whole absorber. The Mössbauer absorbers for two series of high-temperature ($> 300\ \text{K}$) measurements are mixtures of powdered Fe_2NiGa and powdered boron nitride, which are placed into the solid boron nitride containers.

The low-temperature Mössbauer absorber is put into a Mössbauer cryostat in which it is kept in a static exchange atmosphere at a pressure $\sim 7 \times 10^{-3}$ mbar. The high temperature Mössbauer absorbers are put into a Mössbauer oven in which the dynamic pressure is kept at $\sim 2 \times 10^{-5}$ mbar. The surface densities, σ_{exp} , of the prepared low-temperature/high-temperature Mössbauer absorbers are, respectively 21.9, and 21.6, $33.0\ \frac{\text{mg}}{\text{cm}^2}$. These surface densities correspond to an effective thickness parameter [14] t_a in the range $(5.9\text{-}9.0)f_a$, where f_a is the Debye-Waller factor of the absorber. Since $t_a > 1$, the resonance line shape of the Mössbauer spectrum is described using a transmission integral formula [29].

5.3.4.3.2 Mössbauer spectra

The room and low-temperature ^{57}Fe Mössbauer spectra of the Fe_2NiGa compound are shown in figure 5.33. As one can clearly observe, these spectra are in a form of significantly broadened Zeeman patterns that are very much similar to patterns observed for Fe containing amorphous alloys [24]. These spectra clearly must result from the presence of a distribution $P(H_{\text{hf}})$ of the hyperfine magnetic fields H_{hf} at Fe A and Fe B sites. This distribution originates from significant structural disorder present in the Fe_2NiGa specimen. Reasonable fits of these spectra (left panel of figure 5.33) are obtained with the distributions [25] $P(H_{\text{hf}})$ at the Fe A and Fe B sites shown in the right panel of figure 5.33.

In figure 5.34, the first series of consecutively measured high-temperature ^{57}Fe Mössbauer spectra of Fe_2NiGa is shown. One observes that the last spectrum of this series measured at $300.2\ \text{K}$ and its corresponding distributions $P(H_{\text{hf}})$ distributions are very different from the

300.2 K spectrum and the corresponding distributions measured at the beginning of this series. This indicates that the specimen studied must have decomposed at ~ 500 K.

In the second series of consecutively measured high-temperature ^{57}Fe Mössbauer spectra shown in figure 5.35, the first high-temperature spectrum is measured at 600.2 K. It is in the form of a single line which indicates that the Curie temperature, T_C of Fe_2NiGa must be smaller than 600.2 K. Similar to the first series, the last 300.2 K spectrum and the corresponding distributions $P(H_{\text{hf}})$ are very different from the 300.2 K spectrum and its distributions measured at the beginning of the second series. This observation confirms that the studied compound decomposes when heated above ~ 500 K.

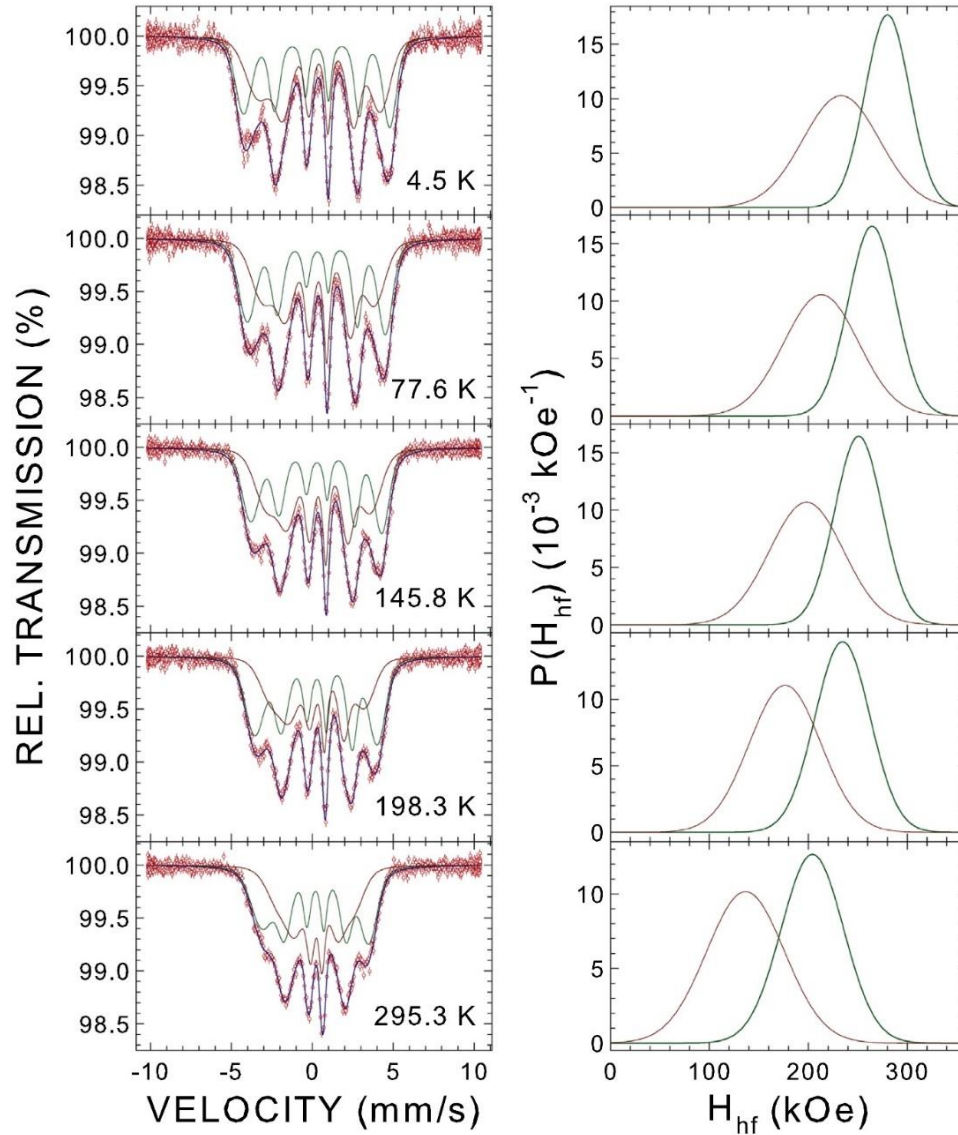


Figure 5.33 ^{57}Fe Mössbauer spectra of the Fe_2NiGa Mössbauer absorber ($\sigma_{\text{exp}} = 21.9 \text{ mg/cm}^2$) at the indicated temperatures fitted (blue solid lines) (left panel) with the A site and B site (dark red and dark green solid lines) Zeeman patterns resulting from the hyperfine magnetic field distributions $P(H_{\text{hf}})$ (right panel). The zero velocity origin is relative to $\alpha\text{-Fe}$ at room temperature.

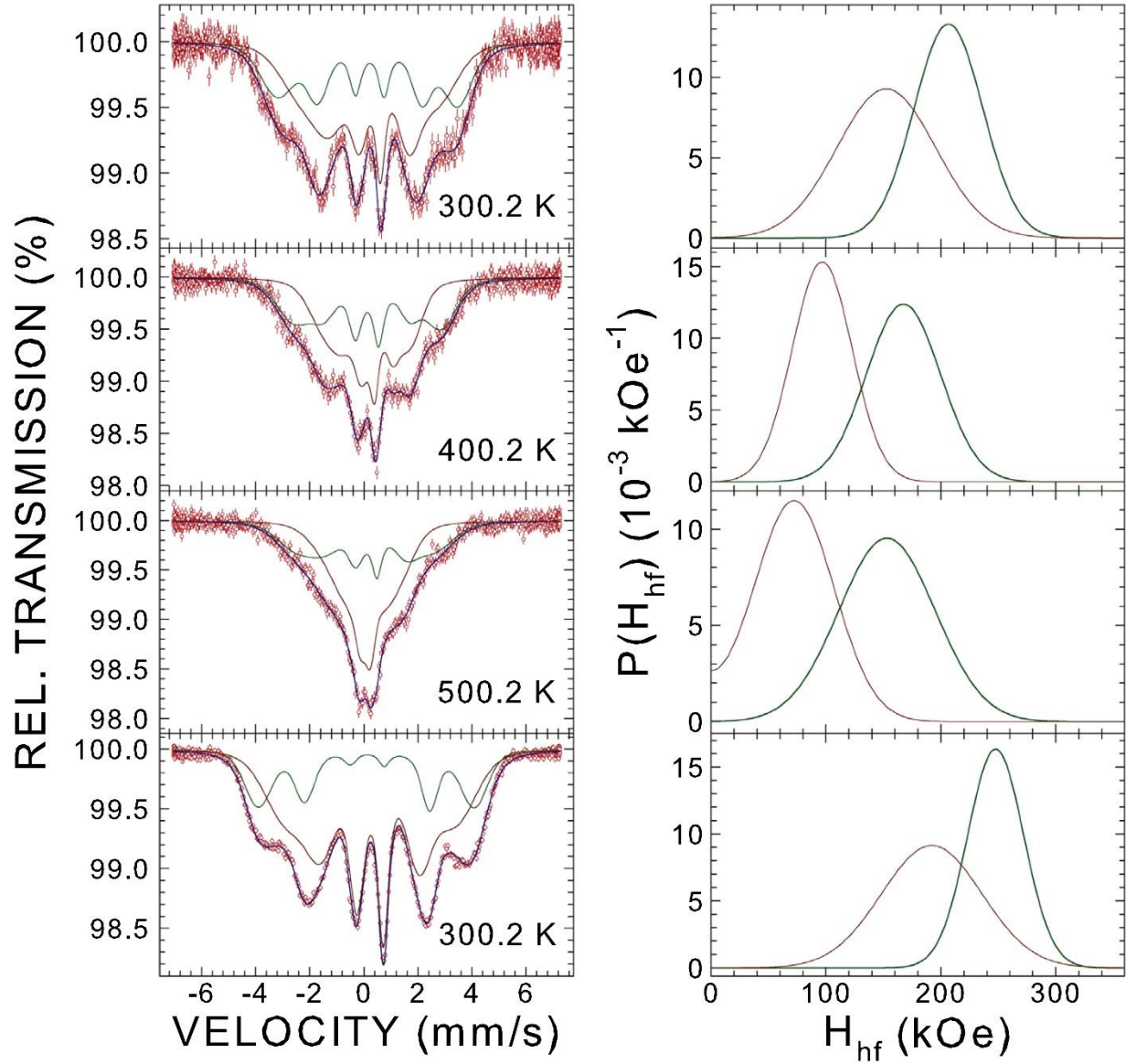


Figure 5.34 ^{57}Fe Mössbauer spectra of the Fe_2NiGa Mössbauer absorber ($\sigma_{\text{exp}} = 21.6 \text{ mg/cm}^2$) at the indicated temperatures fitted (blue solid lines) (left panel) with the A site and B site (dark red and dark green solid lines) Zeeman patterns resulting from the hyperfine magnetic field distributions $P(H_{\text{hf}})$ (right panel). The spectra were measured consecutively starting with the spectrum at 300.2 K (top left column) down to the spectrum at 300.2 K (bottom left column). The zero velocity origin is relative to $\alpha\text{-Fe}$ at room temperature.

5.3.4.3.3 The experimental values for the hyperfine interaction parameters

The average values of the hyperfine magnetic field at the A and B sites, $\bar{H}_{\text{hf,A}}$ and $\bar{H}_{\text{hf,B}}$, at a given temperature are calculated from the corresponding $P(H_{\text{hf}})$ distributions at that temperature (figures 5.33 – 5.35). The temperature dependence of $\bar{H}_{\text{hf,A}}$ and $\bar{H}_{\text{hf,B}}$ is shown in figure 5.36. One notices a strong, almost linear decrease of $\bar{H}_{\text{hf,A}}$ and $\bar{H}_{\text{hf,B}}$ with increasing temperature and a

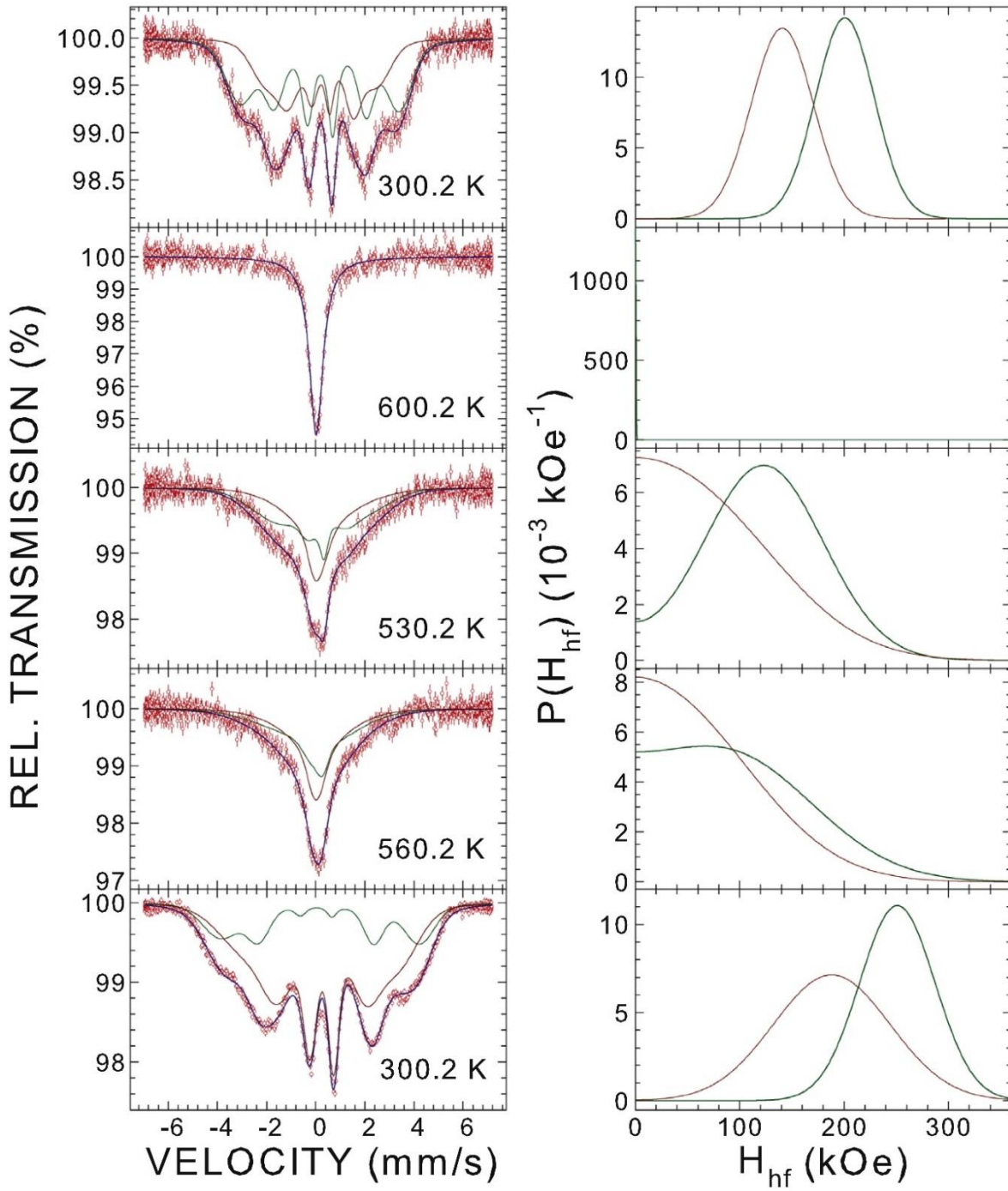


Figure 5.35 ^{57}Fe Mössbauer spectra of the Fe_2NiGa Mössbauer absorber ($\sigma_{\text{exp}} = 33.0 \text{ mg}/\text{cm}^2$) at the indicated temperatures fitted (blue solid lines) (left panel) with the A site and B site (dark red and dark green solid lines) Zeeman patterns resulting from the hyperfine magnetic field distributions $P(H_{\text{hf}})$ (right panel). The spectra were measured consecutively starting with the spectrum at 300.2 K (top left column) down to the spectrum at 300.2 K (bottom left column). The zero velocity origin is relative to $\alpha\text{-Fe}$ at room temperature.

sudden disappearance of $\bar{H}_{\text{hf,A}}$ and $\bar{H}_{\text{hf,B}}$ above ~ 560 K. This unusual temperature dependence of $\bar{H}_{\text{hf,A}}$ and $\bar{H}_{\text{hf,B}}$ could be fitted neither to a Brillouin function [85] nor a Bean-Rodbell function [86]. The Curie temperature $T_C = 580.2(20.0)$ K is estimated from the observation (figure 5.36) that $\bar{H}_{\text{hf,A}} \neq 0$ and $\bar{H}_{\text{hf,B}} \neq 0$ at 560.2 K, but $\bar{H}_{\text{hf,A}} = \bar{H}_{\text{hf,B}} = 0$ at 600.2 K.

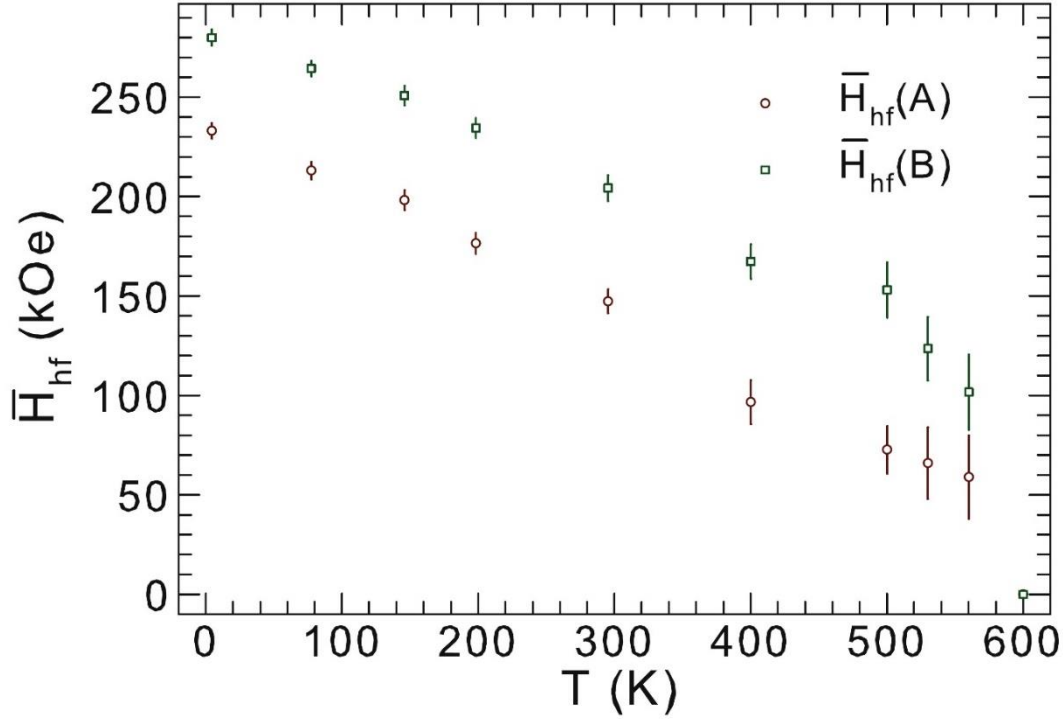


Figure 5.36 Temperature dependence of the average hyperfine magnetic fields $\bar{H}_{\text{hf,A}}$ and $\bar{H}_{\text{hf,B}}$.

The saturation values of the hyperfine magnetic fields $\bar{H}_{\text{hf,A},0} = 234.3(2.2) \text{ kOe}$ and $\bar{H}_{\text{hf,B},0} = 280.9(2.1) \text{ kOe}$ are obtained from a linear extrapolation of the $\bar{H}_{\text{hf,A}}$ and $\bar{H}_{\text{hf,B}}$ data to 0 K (figure 5.34). The experimental values of $\bar{H}_{\text{hf,A},0}$ and $\bar{H}_{\text{hf,B},0}$ found here are higher, by 41% and 8.0% than the calculated Fermi contact field contributions, $H_{\text{c,A}}$ and $H_{\text{c,B}}$. This confirms a general observation of the $|H_{\text{dip}} + H_{\text{orb}} + H_{\text{lat}}|$ contribution being smaller in magnitude than the H_{c} contribution.

In figure 5.37(a), the temperature dependence of the average values of the isomer shift at the A and B sites and relative to $\alpha\text{-Fe}$ at 298 K is shown. The average values are denoted by $\bar{\delta}_{\text{A}}$ and $\bar{\delta}_{\text{B}}$ respectively and are determined from the fits of the Mössbauer spectra in figures 5.33 to 5.35. The temperature dependence of the isomer shift is given by (5 – 7). In terms of the Debye approximation of the lattice vibrations, $\delta_{\text{SOD}}(T)$ is expressed in terms of the Debye temperature, T_{D} , as in equation (5 – 8). By fitting the temperature dependence of $\bar{\delta}_{\text{A}}$ and $\bar{\delta}_{\text{B}}$ to equation (5 – 7), the quantities $\bar{\delta}_{\text{A},0} = 0.391(9) \text{ mms}^{-1}$ and $\bar{\delta}_{\text{B},0} = 0.305(8) \text{ mms}^{-1}$, and also $T_{\text{D,A}} = 256(15) \text{ K}$ and $T_{\text{D,B}} = 498(14) \text{ K}$ are determined.

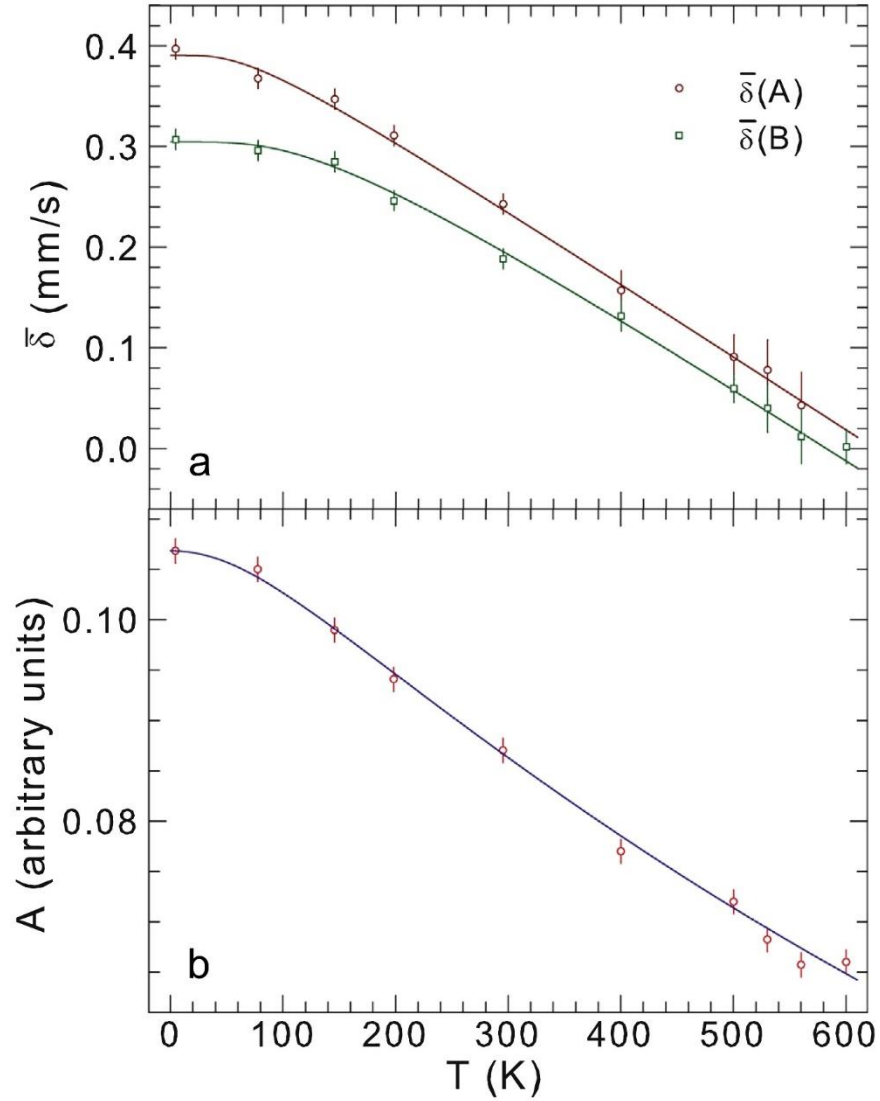


Figure 5.37 Temperature dependence of (a) the average center shifts $\bar{\delta}_A$ and $\bar{\delta}_B$ and (b) the absorption spectral area A . The solid lines are fits to the theoretical relations explained in the text.

The experimental value of $\delta_{0,A}$ determined here is quite close to the calculated value of 0.361 mms^{-1} . However, the experimental value of $\delta_{0,B}$ is significantly larger than the calculated value of 0.180 mms^{-1} . The observed inequality $T_{D,A} < T_{D,B}$ is indicative of a much larger bonding strength of the Fe atoms at the B sites than the A sites. This conclusion can also be deduced from 5.28 where one can observe a higher degree of overlap between the states of Fe atoms at the B sites and Ni states in comparison to that of Fe A and Ni states. The calculated Debye temperature of Fe_2NiGa as the weighted average of $T_{D,A}$ and $T_{D,B}$ is $385(10) \text{ K}$.

There is a second method of determining the Debye temperature from Mössbauer spectroscopy data. In figure 5.37(b), the temperature dependence of the normalized absorption spectra area A derived from fits of the Mössbauer spectra in figures 5.33 to 5.35, is displayed.

This area is proportional to the absorber Debye-Waller factor f_a , which is given in the Debye theory by [14] equation (5 – 4). The fit of the experimental dependence $A(T)$ in figure 5.37(b) to equation (5 – 4) yields $T_D = 374(6)$ K. The weighted average of the above two T_D values determined from the temperature dependence of two different physical parameters is $378(5)$ K. This value is 11% lower than the calculated $T_D = 427$ K.

5.3.4.4 Magnetic measurements

In this section, the results of magnetic measurements on the Fe_2NiGa compound are presented. In particular the magnetic moments, magnetization curves, and the magnetic susceptibility of the Fe_2NiGa system are investigated.

The dc magnetization of the Fe_2NiGa system is measured within the temperature range from 3.0 to 720 K and in magnetic fields up to 90 kOe using the vibrating sample magnetometer (VSM) option of the Quantum Design physical property measurement system (PPMS). The VSM oven option is used for dc magnetization measurements at temperatures higher than 400 K. The magnetic measurements are performed on a solid Fe_2NiGa specimen in the form of a parallelepiped.

5.3.4.4.1 measured magnetic moments

To a first approximation, H_{hf} is proportional to the on-site magnetic moment of Fe atoms, μ_{Fe} through the relation

$$H_{\text{hf}} = a\mu_{\text{Fe}}, \quad (5 - 13)$$

where the value of the proportionality constant, a is compound specific [87]. In converting H_{hf} to μ_{Fe} , the value $a = 125 \text{ kOe}/\mu_B$ was used [73]. Thus, the experimental $\bar{H}_{\text{hf,A},0}$ and $\bar{H}_{\text{hf,B},0}$ values correspond to $\bar{\mu}_{\text{Fe,A},0} = 1.87(2)\mu_B$ and $\bar{\mu}_{\text{Fe,B},0} = 2.25(2)\mu_B$, respectively. These values of $\bar{\mu}_{\text{Fe,A},0}$ and $\bar{\mu}_{\text{Fe,B},0}$ are only 4% and 16% lower than the calculated $\mu_{\text{Fe,A}} = 1.941\mu_B$ and $\mu_{\text{Fe,B}} = 2.680\mu_B$, respectively. It would be useful to estimate the experimental value of μ_{Ni} in Fe_2NiGa from the ^{61}Ni Mössbauer measurements [88] and compare it with the calculated value of $0.492\mu_B$.

5.3.4.4.2 The magnetization curves

The magnetic field dependence of magnetization curves $M(H)$ measured at selected temperatures is shown in figure 5.38. These curves are typical for a ferromagnet. They show that the magnetization at 3 K saturates at the highest available field of 90 kOe. The value of the magnetization, M at 3 K in that field is 69.86 emu/g ($3.00\frac{\mu_B}{\text{f.u.}}$). The value of $3.00\frac{\mu_B}{\text{f.u.}}$ is significantly lower than the calculated $\mu_{\text{f.u.}} = 4.958\mu_B$ and the experimental values of $4.89\frac{\mu_B}{\text{f.u.}}$ reported in Ref. [71] and $4.20\frac{\mu_B}{\text{f.u.}}$ reported in Ref. [73].

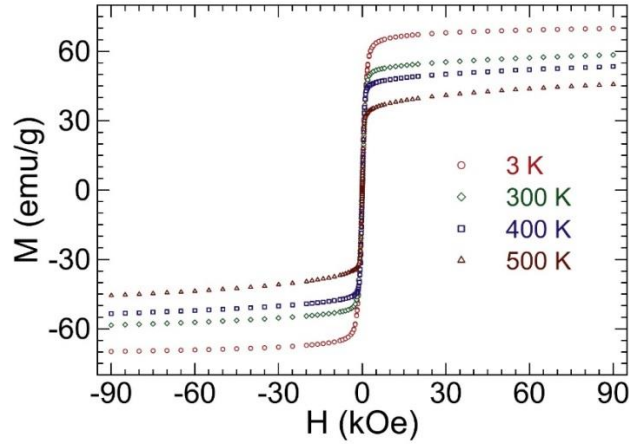


Figure 5.38 Hysteresis curves of Fe_2NiGa at selected temperatures in the magnetic field range -90 to +90 kOe.

5.3.4.4.3 The magnetic susceptibility

In order to determine the Curie temperature T_C of the Fe_2NiGa system, the temperature dependence of the magnetic susceptibility χ in external fields of 10 and 100 Oe is measured and the results are displayed in figure 5.39.

If one uses the definition of T_C as the temperature where the $\chi(T)$ has an inflection point, then from figure 5.39 T_C is 587(1) K [585(1) K] as determined from the 10 Oe [100 Oe] $\chi(T)$ curves. It is thus concluded that the $\chi(T)$ data indicate that $T_C = 586.0(7)$ K. This value of T_C is close to the less precise value of 580.2(20.0) K estimated from the $\bar{H}_{\text{hf}}(T)$ data. It should be noted that the $T_C = 586.0(7)$ K is significantly smaller than $T_C = 785$ K reported in Ref. [71] (specimen annealed at 925 K for three days) or $T_C = 845$ K reported in Ref. [73] (specimen annealed at 673 K for two weeks). As the specimen studied here was annealed at 1073 K for two weeks, this wide spread of T_C and $\mu_{\text{f.u.}}$ is indicative of a dramatic influence of heat treatment on magnetism of the Heusler compound Fe_2NiGa .

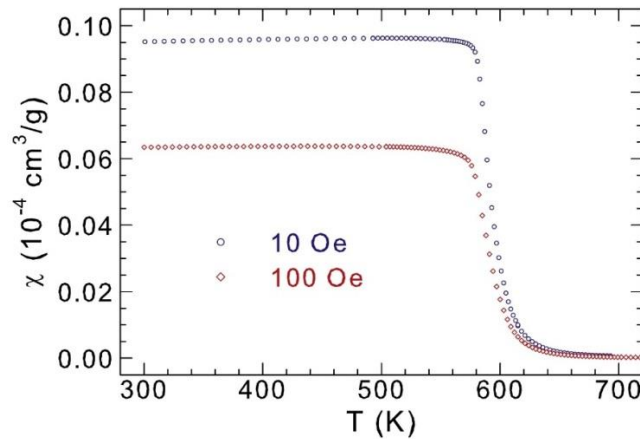


Figure 5.39 Temperature dependence of the magnetic susceptibility of Fe_2NiGa measured in external magnetic fields of 10 and 100 Oe.

5.3.5 Summary and conclusions

In summary, the results of *ab-initio* electronic structure and the hyperfine-interaction parameters calculations, X-ray diffraction measurements, ^{57}Fe Mössbauer spectroscopy, and magnetic measurements of the Heusler compound Fe_2NiGa is presented. Both the X-ray diffraction spectrum and the Mössbauer spectra indicate the presence of significant structural disorder in the compound studied. It is predicted that Fe_2NiGa is half-metallic with covalent chemical bonding. It is demonstrated that Fe_2NiGa is a ferromagnet with the Curie temperature $T_C = 586.0(7)$ K. The Fe magnetic moments at the A and B sites estimated at 0 K and the saturation magnetization per formula unit are, respectively, 1.87(2), 2.25(2), and $3.00\mu_B$. It is found that *ab-initio* calculations overestimate the Fe magnetic moments. It is observed that different heat treatments of Fe_2NiGa result in its dramatically different magnetic properties. There is a reasonable agreement between the calculated and measured hyperfine-interaction parameters. It is found that the Debye temperature of Fe_2NiGa is 378(5) K. It is observed that the compound studied decomposes when heated and kept at temperatures above around 500 K.

5.4 (Li_{0.8}Fe_{0.2})OHFeSe

5.4.1 Introduction and motivations

The tetragonal binary phase β - Fe_{1.01}Se exhibits superconductivity below the critical temperature $T_C \approx 8.5$ K [89,90]. Intercalation of alkali metals, alkali earths, rare earths (A) or small molecules into the adjacent FeSe layers increases the T_C value of the derived superconductors $A_x\text{Fe}_{2-y}\text{Se}_2$ [91,92], $\text{Li}_x(\text{C}_5\text{H}_5\text{N})_y\text{Fe}_{2-z}\text{Se}_2$ [93], and $\text{Li}_x(\text{NH}_2)_y(\text{NH}_3)_{1-y}\text{Fe}_2\text{Se}_2$ (Ref. [94]) up to ~ 46 K. Films of FeSe one unit cell thick grown on SrTiO₃ substrates become superconducting [95-98] below ~ 65 K – the highest T_C in the Fe-based superconductors.

Very recently, new FeSe-derived superconductors (Li_{0.8}Fe_{0.2})OHFeSe (Ref. [99,100]) with $T_C \approx 40$ K, (Li_{0.8}Fe_{0.2})OH(Fe_{0.92}Li_{0.08})Se (Ref. [101]) with $T_C = 43$ K, and the series (Li_{1-x}Fe_x)OHFeSe [102], (Li_{1-x}Fe_x)OHFe_{1-y}Se [103], and (Li_{0.8}Fe_{0.2})OHFe(S_{1-x}Se_x) (Ref. [104]) with T_C values up to 40 K, were discovered. What is particularly interesting about these new superconductors is the claim of the existence in them of long-range, 3d magnetic ordering with ordering temperatures much lower than T_C . In particular, canted antiferromagnetism at ~ 8.5 K (Ref. [99]) or field-induced ferromagnetism [100] were suggested to exist in the (Li_{0.8}Fe_{0.2})OHFeSe superconductor. In a superconductor of a similar composition, (Li_{0.8}Fe_{0.2})OH(Fe_{0.92}Li_{0.08})Se, ferromagnetism with Curie temperature $T_C \approx 10$ K was suggested [101]. In both superconductors, the magnetic ordering was suggested to be associated with Fe atoms located at a site in the hydroxide layer [99-101].

Whereas the coexistence of the commonly believed antagonistic phenomena of superconductivity and long-range, 3d magnetic order in the bulk is not impossible, it is nevertheless surprising. Since the putative magnetic order is associated with Fe atoms, the best way to assess whether it is intrinsic to the superconducting phase, or is due to extrinsic effects (such as magnetic secondary phases or grain boundaries), is to use an Fe-sensitive local probe. Here ⁵⁷Fe Mössbauer spectroscopy [14] is used to demonstrate unequivocally that the Fe magnetic moments in the 40 K superconductor (Li_{0.8}Fe_{0.2})OHFeSe do not order magnetically down to 2.0 K.

5.4.2 The structural parameters and general considerations

The compound (Li_{0.8}Fe_{0.2})OHFeSe crystallizes in a tetragonal structure and belongs to the space group $P4/nmm$, origin choice 2 (No. 129). In table 5.4 the atomic coordinates, Wyckoff positions and point symmetries of (Li_{0.8}Fe_{0.2})OHFeSe is given. These coordinates are obtained via a Rietveld analysis of the (Li_{0.8}Fe_{0.2})OHFeSe specimen (*vide infra*).

Atom	Site	Point symmetry	Occupancy	x	y	z
Li	2a	$\bar{4}$ m2	0.82(1)	$\frac{3}{4}$	$\frac{1}{4}$	0
Fe ₁	2a	$\bar{4}$ m2	0.18(1)	$\frac{3}{4}$	$\frac{1}{4}$	0
O	2c	4 mm	1.0	$\frac{1}{4}$	$\frac{1}{4}$	-0.074(2)
H	2c	4 mm	1.0	$\frac{1}{4}$	$\frac{1}{4}$	0.174(2)
Fe ₂	2b	$\bar{4}$ m2	1.00	$\frac{3}{4}$	$\frac{1}{4}$	$\frac{1}{2}$
Se	2c	4 mm	1.0	$\frac{1}{4}$	$\frac{1}{4}$	0.338(2)

Table 5.3 The atomic positions for tetragonal (Li_{0.8}Fe_{0.2})OHFeSe compound obtained through Rietveld analysis.

In figure 5.40, the unit cell of (Li_{0.8}Fe_{0.2})OHFeSe and its layered structure is presented. From the layered structure it is clear that this compound is elongated along the c crystallographic direction and alternating layers of Fe₂, Se separate the layered structures consisting of Li/Fe₁, O, and H. The lattice parameters of (Li_{0.8}Fe_{0.2})OHFeSe derived from the X-ray powder diffraction method under Rietveld refinement analysis are $a=3.7865(2)$ Å and $c=9.2802(6)$ Å. The presence of covalent bonding (*vide infra*) is indicated pictorially by rods in the unit cell (figure 5.40).

5.4.3 Theoretical calculations and interpretations

The (Li_{0.8}Fe_{0.2})OHFeSe compound is studied both experimentally and theoretically. In this section the theoretical methodology used in calculating various properties of this system is presented, analyzed and the results are discussed.

5.4.3.1 Theoretical methodology

Ab-initio calculations regarding the electronic structure and hyperfine-interaction parameters were carried out within the framework of density functional theory. In these calculations, the full-potential linearized augmented plane wave plus local orbitals method known in brief as FP-LAPW+lo is used which is provided within the WIEN2k package [20]. In this method, as described in chapter 4, the unit cell is partitioned into two distinct regions; the so-called muffin-tin (MT) spheres located at atomic sites and centered on atomic nuclei, and the so-called interstitial region between the atomic spheres. The wave functions in the interstitial region are expanded in terms of plane waves, whereas in the muffin-tin spheres they are expanded in spherical harmonics times atomic wave functions. The basis set within each muffin-tin sphere itself is split into a core and valence subset. The core states are treated within the spherical part of the potential only (they are strongly influenced by the atomic nuclei therefore one can consider them as bound in a spherical potential set by the nucleus). However, the valence states are expanded in spherical harmonics, within the interstitial region up to a maximum orbital angular momentum quantum number of $l = 4$, and within the muffin-tin spheres up to a maximum of $l = 12$.

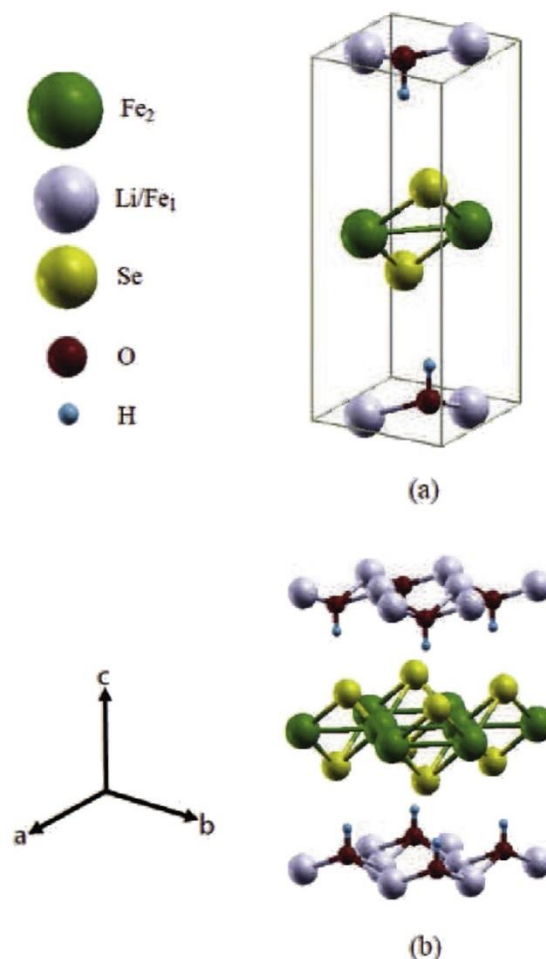


Figure 5.40 The unit cell (a) and the layered structure (b) of $(\text{Li}_{0.8}\text{Fe}_{0.2})\text{OHFeSe}$.

As for the exchange-correlation potential used for this system, the generalized gradient approximation (GGA) scheme of Perdew, Burke, and Ernzerhof [21] is invoked. A separation energy of -6.0 Ry between valence and core states of the atoms in the unit cell is considered. In order to account for the partial occupation of the 2a sites by lithium and iron atoms, the calculations are conducted using a $2a \times 2b \times c$ supercell.

The muffin-tin radii used for H, O, Fe, Li, and Se are 0.59 a.u., 1.09 a.u., 2.30 a.u., 1.69 a.u., and 2.19 a.u. respectively. As for the plane wave cut-off parameter used in the calculations, $R_{\text{MT}} \times K_{\text{MAX}} = 3$, where R_{MT} is the smallest muffin-tin radius in the unit cell and K_{MAX} is the largest modulus of the K vector used in the expansion of the plane-waves in the interstitial region. For band structure calculations a total number of 100 inequivalent k-points is used in the first Brillouin zone within a $10 \times 10 \times 10$ k space mesh. The energy convergence criterion for the self-consistency cycles is chosen such that the difference in energy between two successive iterations does not exceed 10^{-4} Ry. The values chosen for the lattice parameters as input data for

the calculations are chosen from the results of the X-ray structural characterization of the $(\text{Li}_{0.8}\text{Fe}_{0.2})\text{OHFeSe}$ specimen (table 5.3).

5.4.3.2 Theoretical results

In this section, we present and discuss the theoretical results from *ab-initio* calculations on $(\text{Li}_{0.8}\text{Fe}_{0.2})\text{OHFeSe}$. These results include charge density distributions, electronic band structure calculations, and hyperfine-interaction parameters.

5.4.3.2.1 Charge density distribution

The charge density distribution along the three crystallographic planes (100), (001), and (110) is presented in figure 5.41.

From figure 5.41(a), it is seen that the electronic charge is mainly concentrated along three structural layers, this is shown by the green regions in the figure. The top and bottom layers consist of O, H and Fe atoms and the middle layer is structured by Fe and Se atoms. The distribution of electronic charge density along the three layers indicates the existence of a covalent bonding within each layer. The existence of such covalent bonds is also shown schematically by rods connecting the atoms within these layers (figure 5.40(b)). The red regions in figure 5.41(a) are associated with negligible charge density concentration in the interlayer space. Thus, one can deduct the presence of relatively strong ionic bonds between these layers.

In figure 5.41(b), the charge distribution along the (001) plane is shown. An inspection of this figure shows the existence directional covalent bonds between Fe and four neighboring O atoms (green regions). However, there is negligible charge density in the vicinity of Li atoms which suggest that these atoms participate in ionic bonds.

In figure 5.41(c), the electronic charge density distribution is shown along the (110) plane. One can indicate relatively weak covalent bonds (yellow regions) between neighboring Fe atoms and also between Fe and Se atoms.

The electronic charge density distribution in the three crystallographic planes discussed above leads to the conclusion that relatively good electrical transport is expected to exist in this compound. The relatively good electrical conductivity may be attributed to the iron-selenium layers. However, because of the existence of ionic bonds along the c direction, one arrives at a conclusion that this system weakly conducts electricity in the direction perpendicular to the three structural layers discussed above.

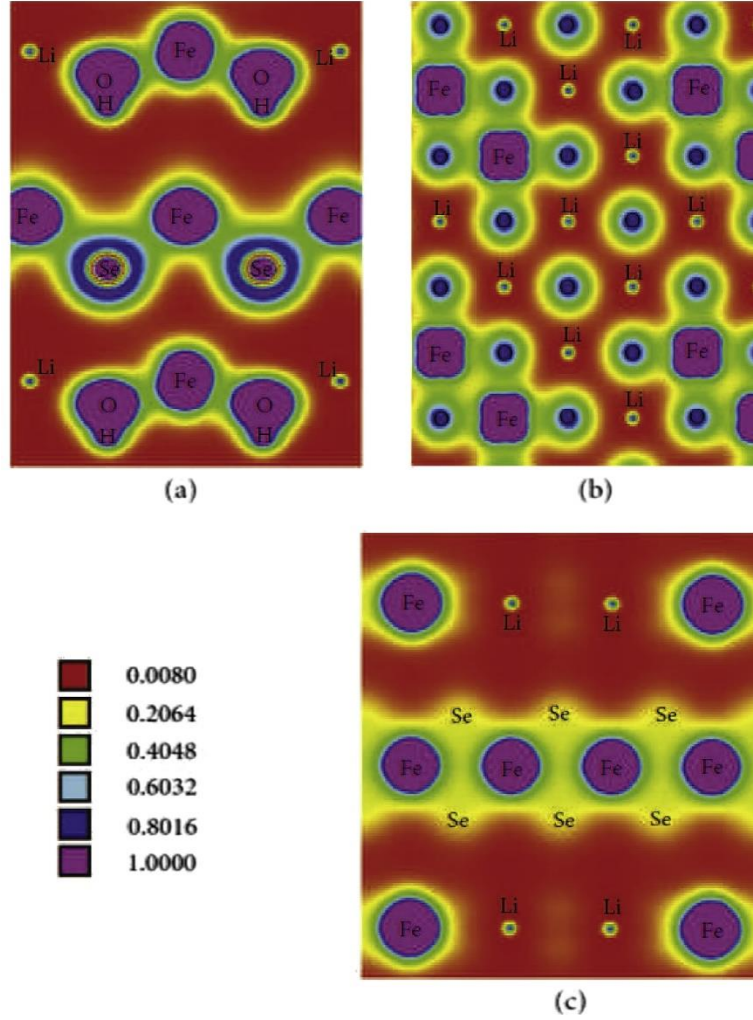


Figure 5.41 Electron charge density distribution of $(\text{Li}_{0.8}\text{Fe}_{0.2})\text{OHFeSe}$ (in units of $\frac{e}{\text{\AA}^3}$) in the (a) (100), (b) (001), and (c) (110) planes.

5.4.3.2.2 Density of states

The total and atom-resolved density of states of the $(\text{Li}_{0.8}\text{Fe}_{0.2})\text{OHFeSe}$ system is calculated and presented in figure 5.42. A quick inspection of this figure clearly indicates two distinct energy regions containing a large number of electronic states. The first region is roughly between -2.75 to -6 eV with respect to the Fermi level, E_F , and the second region lies in between -2 to 1.5 eV with respect to the Fermi energy. The density of states in the first energy region originates mainly from Fe_2 , Se, and O atoms. However, in the second region which contains the Fermi level, the density of states is almost completely dominated by Fe_1 and Fe_2 atoms. In the immediate vicinity of the Fermi energy, Fe_1 states are the dominant contributors to the total density of states. This result has not been observed in the idealized (the approximate of the real compound) compound LiOHFeSe in Ref. [105].

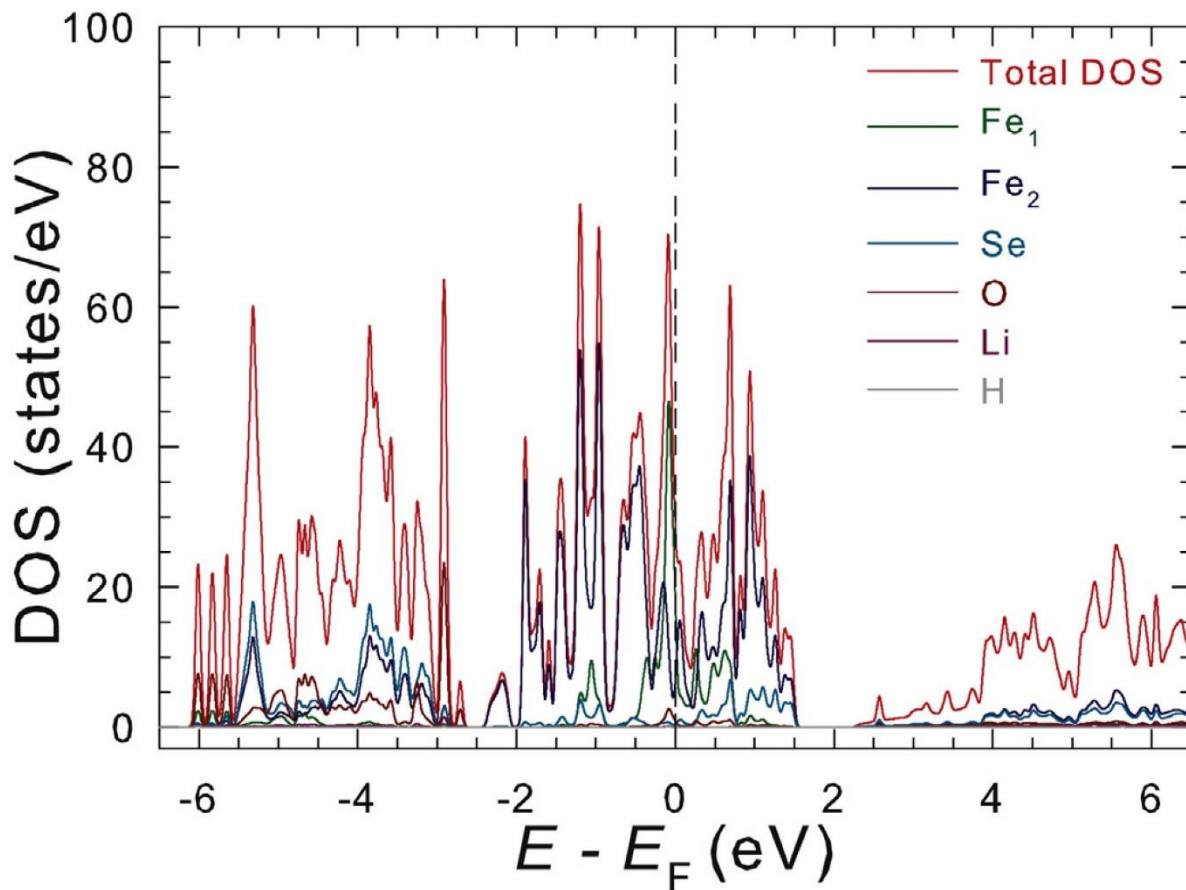


Figure 5.42 Total and atom-resolved density of states of the $(\text{Li}_{0.8}\text{Fe}_{0.2})\text{OHFeSe}$ system.

As one can observe from figure 5.42, the Fe_1 states are highly peaked around the Fermi energy. However, the Fe_2 states are more or less continuously distributed across the Fermi region, with relatively high peaks above and below the Fermi energy. H atoms contribute almost nothing to the density of states in this system. In the lower energy region, typically from -2.75 to -6 eV with respect to the Fermi energy, O and Se states significantly contribute to the density of states in this system.

Careful examination of the density of states in figure 5.42 provides information on the type of the chemical bonding between the various atoms in $(\text{Li}_{0.8}\text{Fe}_{0.2})\text{OHFeSe}$. The high degree of overlap between Fe_2 , Se, and O states indicates the covalent nature of the chemical bonding between these elements. This conclusion agrees with the arguments based on charge density distribution mentioned earlier in section 5.4.3.2.1.

5.4.3.2.3 Electronic band structure

The electronic band structure of the $(\text{Li}_{0.8}\text{Fe}_{0.2})\text{OHFeSe}$ system has been calculated and the result is plotted in figure 5.43. A high density of electronic bands is observed within the energy

region between -1.4 to 1.2 eV with respect to the Fermi energy. This points towards good electrical conductivity of this system. As previously discussed, these energy bands are mainly due to iron states. Another conclusion that is made by careful inspection of figure 5.43, is the relatively small variations in energy of the bands along various symmetry directions in the Brillouin zone. In other words, the electronic bands are relatively flat. This can indicate a relatively small effective mass within this energy region and hence, leading to high electron mobility and as a result, good electrical conductivity of the $(\text{Li}_{0.8}\text{Fe}_{0.2})\text{OHFeSe}$ system.

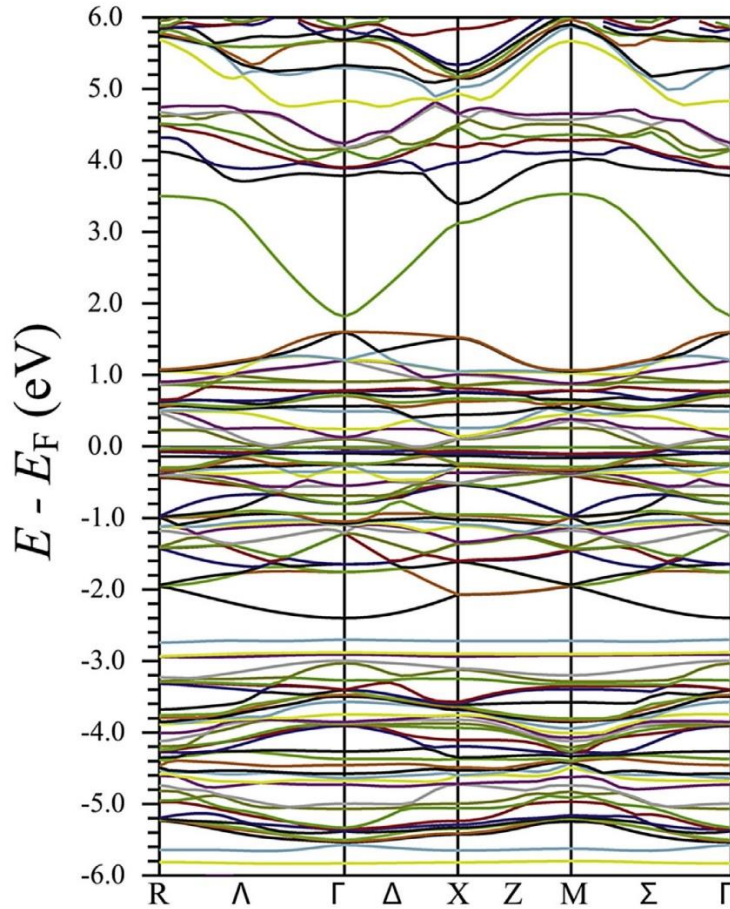


Figure 5.43 The electronic energy band structure of $(\text{Li}_{0.8}\text{Fe}_{0.2})\text{OHFeSe}$.

As one expects from the highest symmetry point in the Brillouin zone, a high degree of degeneracy of the electronic states is observed along the Γ direction in figure 5.43. The X and M symmetry points also show relatively high degeneracy of electronic states. As one moves away from these high-symmetry points, the degeneracy of the electronic states is partially removed. The electronic states remain confined to a relatively narrow energy region between high symmetry points, this can account for the metallic behavior of the studied compound. In figure 5.43 one can also observe a highly packed band region about 3 eV below the fermi energy. These energy bands are related to the semi-core states of the various atoms in the $(\text{Li}_{0.8}\text{Fe}_{0.2})\text{OHFeSe}$ system and do not play a significant role in the electronic transport properties of this compound.

5.4.3.2.4 The hyperfine-interaction parameters

Ab-initio calculations on the non-magnetic phase of the $(\text{Li}_{0.8}\text{Fe}_{0.2})\text{OHFeSe}$ system, yields two important hyperfine-interaction parameters which later on are compared with the experimental results based on the ^{57}Fe Mössbauer spectroscopy of this compound. The first of these is the so-called isomer shift, δ_0 , and the second one is the principle component of the electric field gradient (EFG) tensor, V_{zz} along with the asymmetry parameter, η [14]. Due to the lack of magnetic interactions in this system, the magnetic hyperfine interaction parameters are absent in this compound.

5.4.3.2.4.1 Isomer shift calculations

The isomer shift is a result of the difference between the total electron density at the Mössbauer nucleus in $(\text{Li}_{0.8}\text{Fe}_{0.2})\text{OHFeSe}$, $\rho(0)$, and the reference compound, $\rho_{\text{ref}}(0)$ (equation (5 – 5)). For the reference element, an α – Fe (iron in a *bcc* structure) with lattice constant $2.8665 \text{ \AA}$ was chosen. The calculated values for the electronic charge density at the Mössbauer nuclei for Fe_1 and Fe_2 in the $(\text{Li}_{0.8}\text{Fe}_{0.2})\text{OHFeSe}$ system are 15307.058 and $15308.059 \text{ a.u.}^{-3}$ respectively. The corresponding calculated value for the reference element is $15309.918 \text{ a.u.}^{-3}$. Using the isomer shift calibration constant of $\alpha = -0.291 \text{ a.u.}^3 \text{ mms}^{-1}$ from Ref. [55] in equation (5 – 5), leads to the isomer shift values of $\delta_{0,1} = 0.832 \text{ mms}^{-1}$ and $\delta_{0,2} = 0.541 \text{ mms}^{-1}$ for Fe_1 and Fe_2 respectively in the compound $(\text{Li}_{0.8}\text{Fe}_{0.2})\text{OHFeSe}$.

5.4.3.2.4.2 Electric field gradient calculations

Ab-initio calculations of the principle component of the electric field gradient tensor, V_{zz} at Fe_1 and Fe_2 sites in $(\text{Li}_{0.8}\text{Fe}_{0.2})\text{OHFeSe}$ lead to the values -6.762×10^{21} and $0.505 \times 10^{21} \frac{\text{V}}{\text{m}^2}$, respectively. The quadrupole splitting, which is the distance between two resonant lines in a quadrupole doublet, is defined in (5 – 2). In the case of $(\text{Li}_{0.8}\text{Fe}_{0.2})\text{OHFeSe}$ and from table 5.3 the iron atoms are located at sites with point symmetries of $\bar{4}m2$, which ensures $\eta=0$ at these sites¹⁵. Therefore $\Delta = \frac{1}{2}eQ|V_{zz}|$, where e is the proton charge and Q is the electric quadrupole moment of the ^{57}Fe nucleus [30]. The calculated values of V_{zz} at the Fe_1 and Fe_2 sites therefore result in $\Delta_1 = 1.055 \text{ mms}^{-1}$ and $\Delta_2 = 0.079 \text{ mms}^{-1}$ respectively. The theoretical calculations predict that the quadrupole doublet due to iron atoms at the Fe_1 site should have larger values for Δ and δ_0 than their corresponding quantities for iron atoms at the Fe_2 sites. This conclusion turns out to be verified via experiment (*vide infra*).

¹⁵ This is justified from the fact that the asymmetry parameter is defined as $\eta = \frac{V_{xx}-V_{yy}}{V_{zz}}$. Due to the tetragonal symmetry of $(\text{Li}_{0.8}\text{Fe}_{0.2})\text{OHFeSe}$ (figure 5.40) and the point symmetry of the iron atoms in this system, $V_{xx} = V_{yy}$ and therefore $\eta = 0$.

5.4.4 Experimental methods and results

In this section, the results of the experimental studies on the $(\text{Li}_{0.8}\text{Fe}_{0.2})\text{OHFeSe}$ system including X-ray powder diffractometry and Mössbauer measurements are presented and compared with the results of ab-initio calculations.

5.4.4.1 X-ray diffraction measurements

An X-ray diffraction measurement on the polycrystalline sample, $(\text{Li}_{0.8}\text{Fe}_{0.2})\text{OHFeSe}$, was performed at 298 K in Bragg-Brentano geometry on a PANalytical X'Pert scanning diffractometer using Cu $K\alpha$ radiation in the 2θ range $5 - 80^\circ$ in steps of 0.02° . The $K\beta$ line was eliminated by using a Kevex Psi2 Peltier-cooled solid-state Si detector.

In figure 5.44, the room temperature powder X-ray diffraction pattern of the $(\text{Li}_{0.8}\text{Fe}_{0.2})\text{OHFeSe}$ sample is shown. As mentioned earlier, the studied compound crystallizes in the tetragonal space group $P4/nmm$ (No. 129) [99].

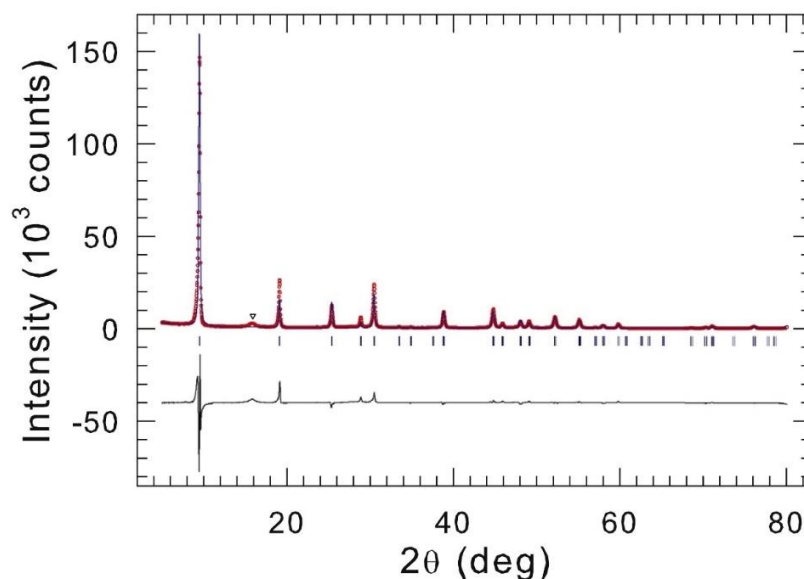


Figure 5.44 Powder X-ray diffraction pattern of $(\text{Li}_{0.8}\text{Fe}_{0.2})\text{OHFeSe}$ at 298 K. The experimental data are denoted by the red circles, while the line through the circles represent the results of the Rietveld refinement. The row of vertical bars show the Bragg peak positions for the $P4/nmm$ space group. The lower solid line represents the difference curve between experimental and calculated patterns. The ∇ symbol indicates the position of the Bragg peak related to the unidentified impurity phase.

A Rietveld refinement of the X-ray diffraction pattern in figure 5.44 yields the lattice parameters $a = 3.7865(2) \text{ \AA}$ and $c = 9.2802(6) \text{ \AA}$, and also the atomic positional parameters listed in table 5.3 which are used in the theoretical calculations discussed earlier. These values compare well with the corresponding values reported in previous studies [99,101]. The Bragg peak at $2\theta \approx 15.9^\circ$ in figure 5.44 probably originates from a small amount of an unidentified second phase present in the studied sample.

5.4.4.2 Mössbauer spectroscopy

In this section, the results of the ^{57}Fe Mössbauer spectroscopy measurements on the $(\text{Li}_{0.8}\text{Fe}_{0.2})\text{OHFeSe}$ sample is presented and discussed. The results of the measurements are then compared with those of *ab-initio* calculations.

5.4.4.2.1 Experimental set up

The ^{57}Fe Mössbauer measurements on the $(\text{Li}_{0.8}\text{Fe}_{0.2})\text{OHFeSe}$ specimen were performed using a standard Mössbauer spectrometer operating in sine mode and a ^{57}Co source kept at room temperature. The spectrometer is calibrated with a $6.35\text{ }\mu\text{m}$ thick $\alpha\text{-Fe}$ foil and the spectra were folded [27]. The Mössbauer absorber was made in a glove box. The powdered $(\text{Li}_{0.8}\text{Fe}_{0.2})\text{OHFeSe}$ specimen was then combined with boron nitride in powdered form. The mixture was put into a high-purity, $8\text{ }\mu\text{m}$ thick Al disk container to ensure uniform temperature over the entire absorber. During the transfer from the glove box to the cryostat, the Mössbauer absorber was exposed to air for approximately 50 seconds. In the Mössbauer cryostat, the absorber was kept at a static exchange gas atmosphere at the pressure of $\sim 5 \times 10^{-3}$ mbar. The surface mass density of the absorber was $17.3\text{ }\frac{\text{mg}}{\text{cm}^2}$. This value corresponds to an effective thickness parameter [14] $t_a = 4.0f_a$, where f_a is the Debye-Waller factor of the absorber. Since $t_a > 1$, the resonance line shape of the Mössbauer spectrum was described using a transmission integral formula [29].

5.4.4.2.2 Mössbauer spectra

In figures 5.45 and 5.46, the ^{57}Fe Mössbauer spectra of the $(\text{Li}_{0.8}\text{Fe}_{0.2})\text{OHFeSe}$ sample over a wide velocity range (namely between -8 and 8 mms^{-1}) and at various temperatures are presented. It is clearly seen from figure 5.47 that down to approximately 77 K a quadrupole doublet appears in addition to the quadrupole doublets corresponding to the main phase. The main phase quadrupole doublets are due to iron atoms at sites Fe_1 and Fe_2 (see table 5.3). The quadrupole doublet corresponding to Fe_2 is more intense than that of Fe_1 which is caused by the preferred orientation of the texture in the polycrystalline Mössbauer absorber.

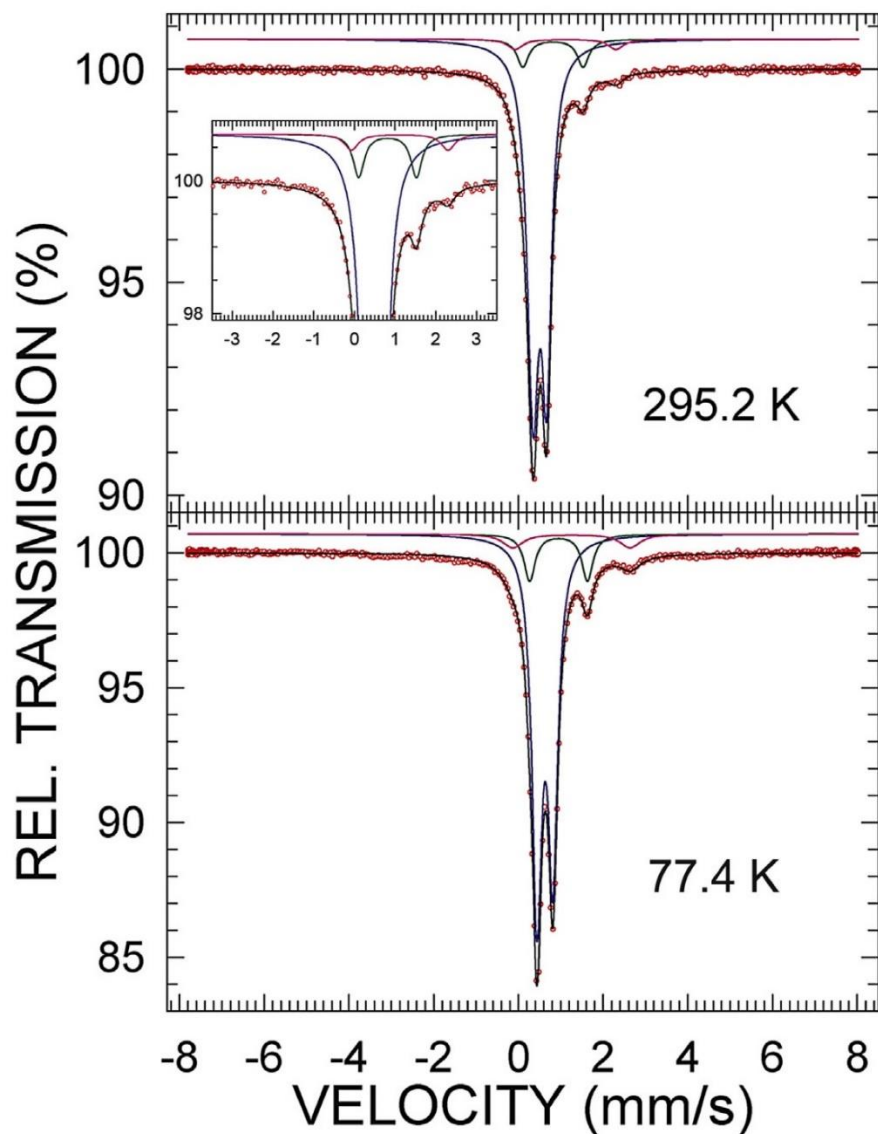


Figure 5.45 ^{57}Fe Mössbauer spectra of $(\text{Li}_{0.8}\text{Fe}_{0.2})\text{OHFeSe}$ at indicated temperatures fitted (black solid lines) with two quadrupole doublets (blue and dark green solid lines) due to Fe_1 and Fe_2 atoms of the main phase, and a quadrupole doublet, (pink solid lines) originating from the impurity phase. The inset shows the 295.2 K spectrum with enlarged vertical and horizontal scales. The zero-velocity origin is relative to $\alpha\text{-Fe}$ at room temperature.

As seen from figure 5.46, below 50 K the two quadrupole doublets corresponding to Fe_1 and Fe_2 sites persist, and the impurity phase shows structure. In other words the impurity phase becomes magnetically ordered. This indicates that the transition temperature for the impurity phase must lie between 50 and 77 K. Figure 5.46 also shows that the main phase doublets persist down to 4.8 K. This is an evidence that the main phase has no magnetic ordering down to 4.8 K.

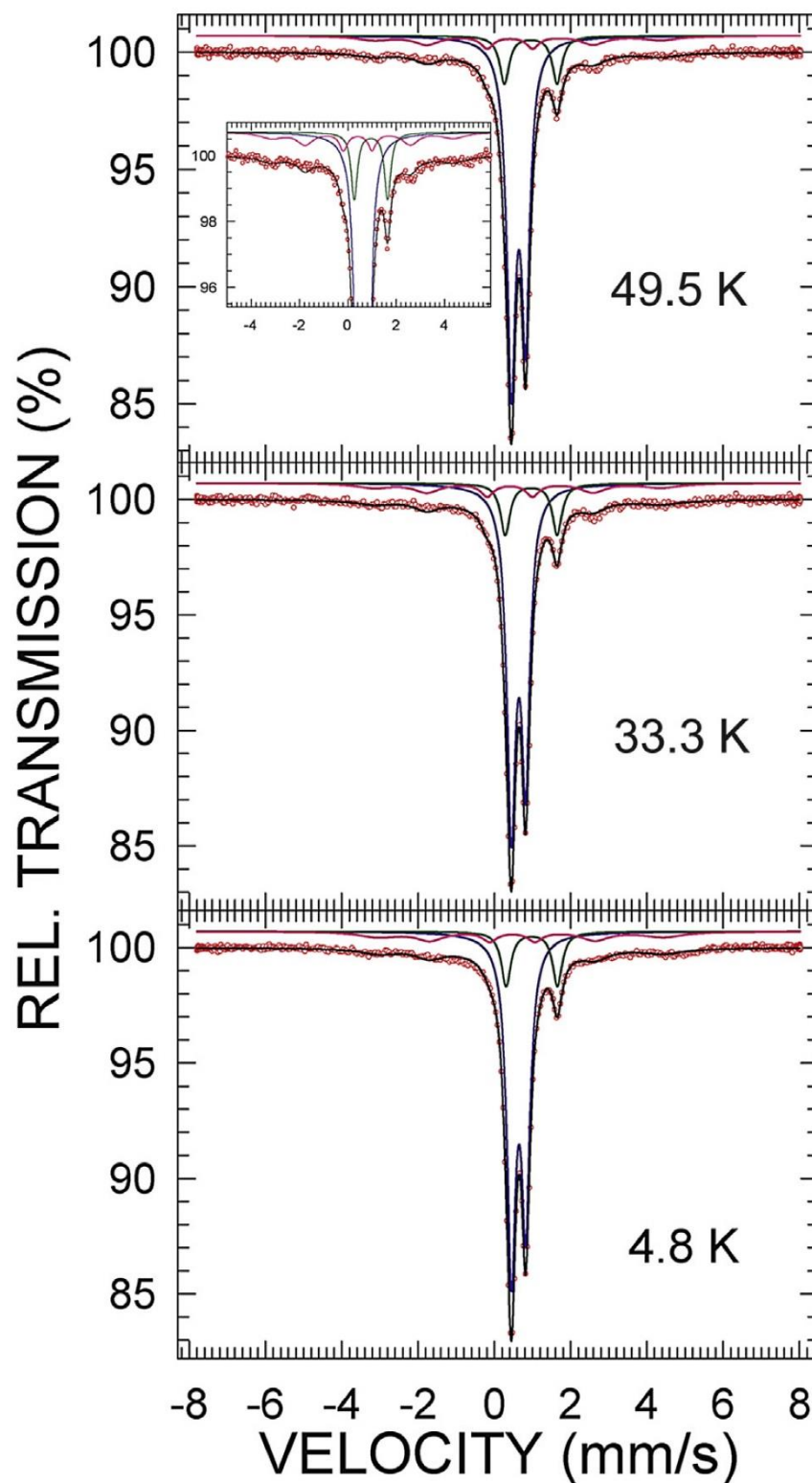


Figure 5.46 The ^{57}Fe Mössbauer spectra of $(\text{Li}_{0.8}\text{Fe}_{0.2})\text{OHFeSe}$ at indicated temperatures fitted (black solid lines) with two quadrupole doublets (blue and dark green solid lines) due to Fe_1 and Fe_2 atoms of the main phase, and a Zeeman pattern, (pink solid lines) originating from the impurity phase. The inset shows the 49.5 K spectrum with enlarged vertical and horizontal scales. The zero-velocity origin is relative to $\alpha\text{-Fe}$ at room temperature.

In figures 5.47 and 5.48, the results of Mössbauer measurements of $(\text{Li}_{0.8}\text{Fe}_{0.2})\text{OHFeSe}$ over a narrower velocity range (typically between -3 to 3 mms^{-1}) and in various temperatures between 294.9 K and 2.0 K is introduced. The presence of the two quadrupole doublets down to 2.0 K with no sign of Zeeman patterns, proves that there is absolutely no magnetic ordering in the $(\text{Li}_{0.8}\text{Fe}_{0.2})\text{OHFeSe}$ specimen at temperatures above 2.0 K , thus the superconductor can be regarded as a paramagnet.

5.4.4.2.3 Experimental values of the isomer shift and electric quadrupole splitting parameter

The Mössbauer spectra in figures 5.47 and 5.48, are fitted to provide experimental values for the quadrupole splitting parameter, Δ , and the isomer shift, δ (relative to the α phase of iron at 298 K). The absorber line width, Γ , has also been fitted. In these fits the source line width of 0.12 mms^{-1} and the background-corrected Debye-Waller factor of the source of 0.60 is used [29].

In figure 5.49, the temperature dependences of Δ_1 , Δ_2 , Γ_1 , and Γ_2 are shown. The experimental data for the quadrupole splitting parameters have been extrapolated to estimate the values of these quantities at 0 K . The results are $1.351(12)$ and $0.380(1) \text{ mms}^{-1}$ for Δ_1 and Δ_2 respectively which are larger than the values obtained from theoretical calculations.

Careful inspection of figure 5.49 shows that Δ_1 increases with temperature and remains almost constant above 150 K , whereas Δ_2 is constant below 150 K and decreases at temperatures above 150 K . Although this behavior can be accounted to be results of the crystal field effects on the electronic states of ferrous iron [14, 106], there is still not any convincing argument of why this sudden transition occurs at this particular temperature¹⁶.

The absorption line widths Γ_1 and Γ_2 remain almost constant in the temperature range between 0 and 300 K . This result also indicates that no sudden (magnetic) phase transition occurs throughout the mentioned temperature range.

As explained before, the isomer shift can be expressed as the sum of two terms, a temperature independent term, δ_0 , and a temperature dependent term, $\delta_{\text{SOD}}(T)$ given by (5 – 7). Furthermore, the second order Doppler shift can be expressed in the Debye theory of lattice vibrations as (5 – 8).

The experimental values obtained for $\delta_{0,1}$ and $\delta_{0,2}$ by fitting the experimental data in figure 5.50 are $0.974(5) \text{ mms}^{-1}$ and $0.636(1) \text{ mms}^{-1}$ respectively. These experimental values turn out to be relatively close to the values obtained based on ab-initio calculations ($\delta_{0,1} = 0.832 \text{ mms}^{-1}$ and $\delta_{0,2} = 0.541 \text{ mms}^{-1}$).

¹⁶ Observations of these kind can be proposed as interesting topics of research for future studies.

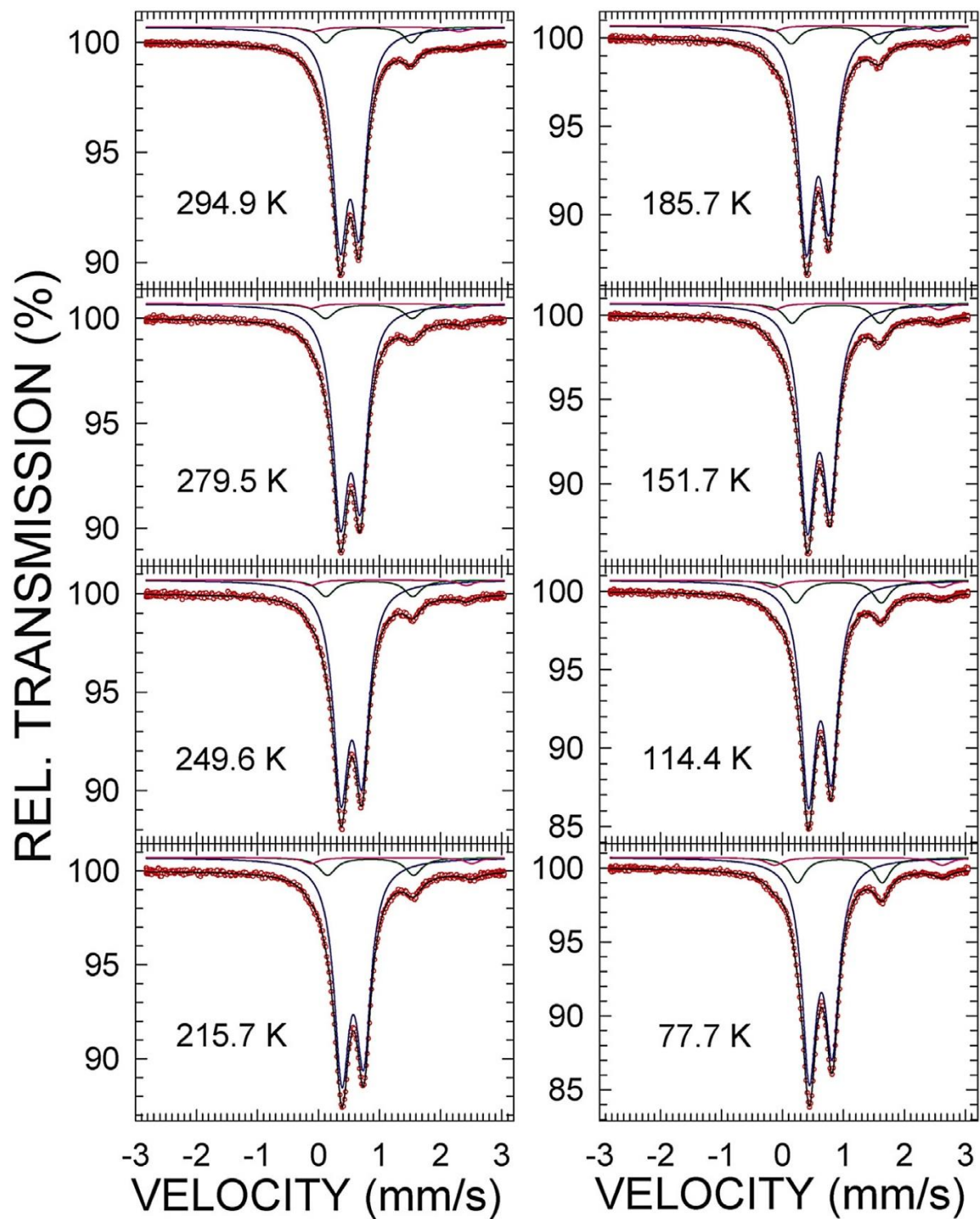


Figure 5.47 ^{57}Fe Mössbauer spectra of $(\text{Li}_{0.8}\text{Fe}_{0.2})\text{OHFeSe}$ at indicated temperatures fitted (black solid lines) with two quadrupole doublets (blue and dark green solid lines) due to Fe_1 and Fe_2 atoms of the main phase, and a quadrupole doublet, (pink solid lines) originating from the impurity phase. The zero-velocity origin is relative to α -Fe at room temperature.

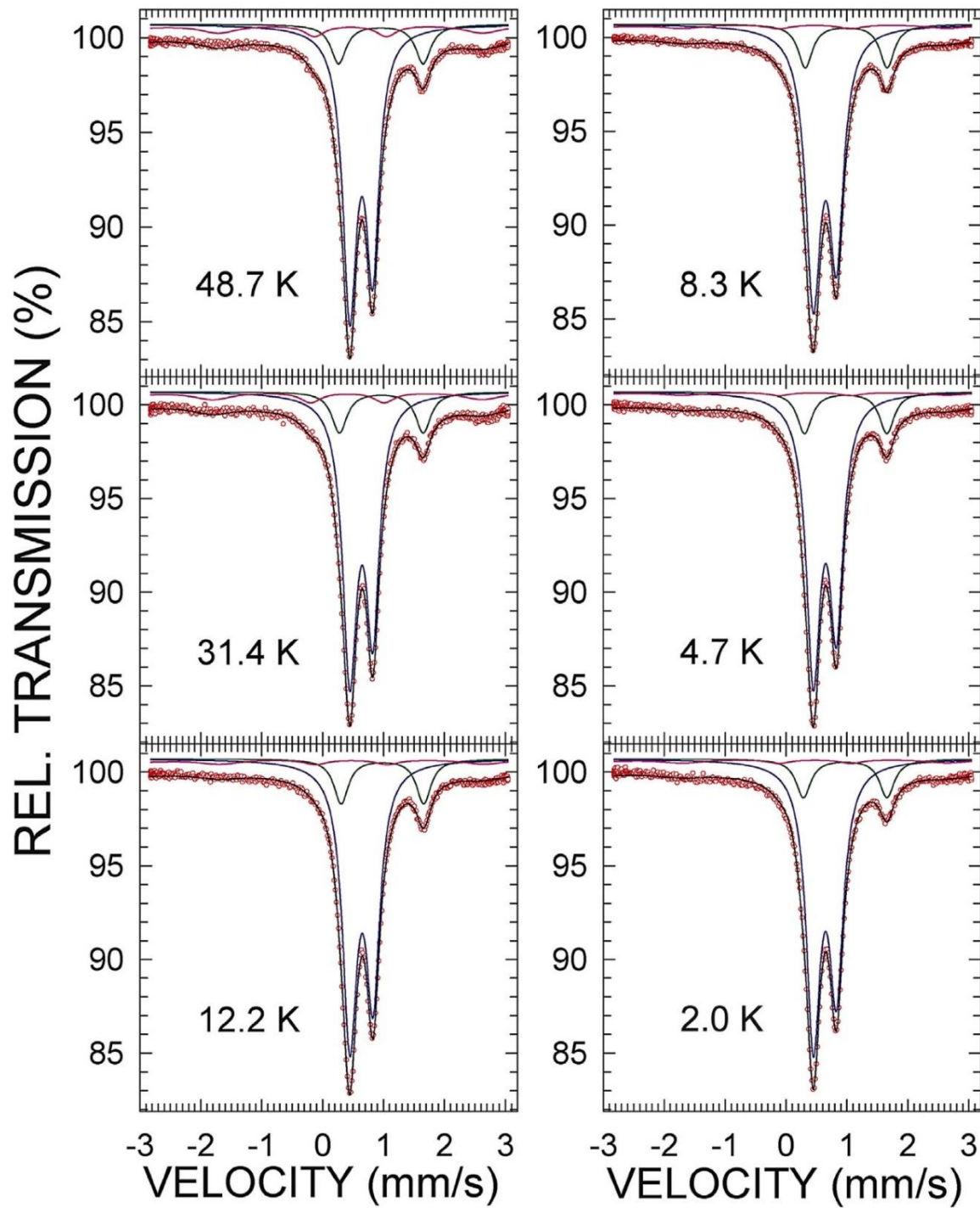


Figure 5.48 ^{57}Fe Mössbauer spectra of $(\text{Li}_{0.8}\text{Fe}_{0.2})\text{OHFeSe}$ at indicated temperatures fitted (black solid lines) with two quadrupole doublets (blue and dark green solid lines) due to Fe_1 and Fe_2 atoms of the main phase, and a Zeeman pattern, (pink solid lines) originating from the impurity phase. The zero-velocity origin is relative to $\alpha\text{-Fe}$ at room temperature.

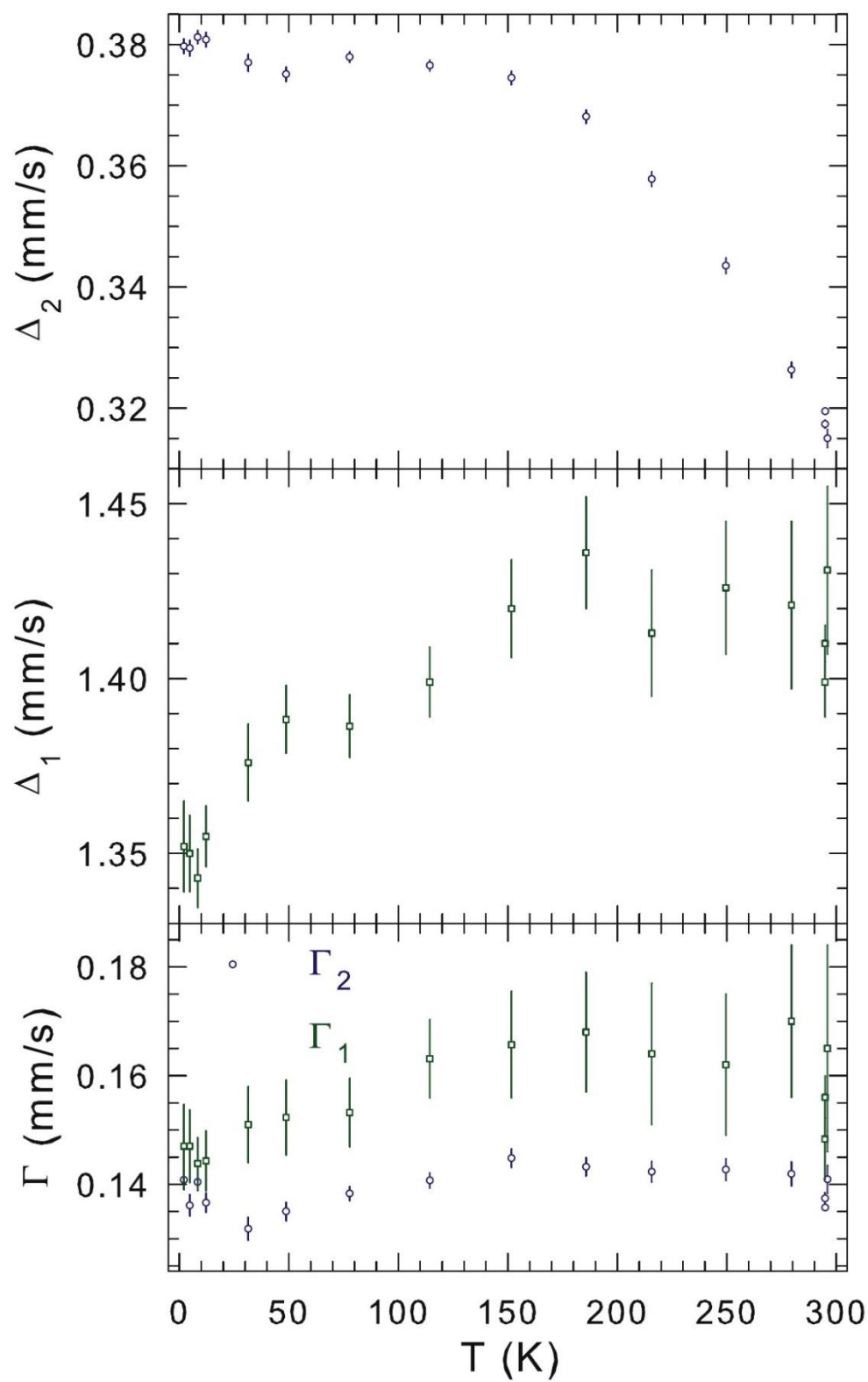


Figure 5.49 Temperature dependence of the quadrupole splitting parameters, Δ , and their related absorber line widths, Γ , corresponding to iron at sites Fe_1 and Fe_2 .

In figure 5.50, the temperature dependence of the isomer shifts related to the two iron sites in $(\text{Li}_{0.8}\text{Fe}_{0.2})\text{OHFeSe}$ is given.

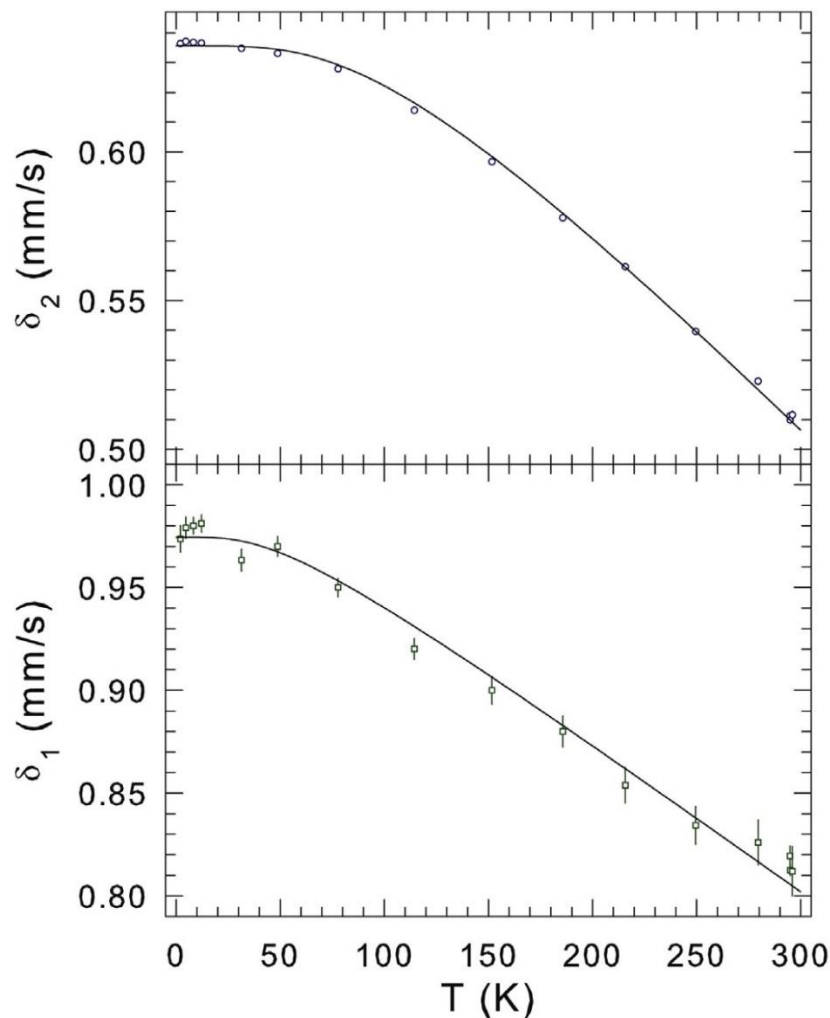


Figure 5.50 Temperature dependence of isomer shift, δ of the Fe_1 and Fe_2 site quadrupole doublets in $(\text{Li}_{0.8}\text{Fe}_{0.2})\text{OHFeSe}$. The solid lines are fitted to equation (5 – 5).

5.4.5 Comparison between experiment and theory

Regarding the hyperfine-interaction parameters in $(\text{Li}_{0.8}\text{Fe}_{0.2})\text{OHFeSe}$ the theoretical and experimental results discussed in the previous sections have general agreement. In particular, the experimental values of the isomer shifts $\delta_{0,1}$ and $\delta_{0,2}$, and the quadrupole splitting parameters Δ_1 and Δ_2 fulfill the theoretically predicted inequalities $\delta_{0,1} > \delta_{0,2}$ and $\Delta_1 > \Delta_2$.

5.4.6 Summary and conclusions

In summary, the results of *ab-initio* electronic structure and the hyperfine-interaction parameters calculations, X-ray diffraction, and ^{57}Fe Mössbauer spectroscopy measurements of the recently discovered 40 K superconductor $(\text{Li}_{0.8}\text{Fe}_{0.2})\text{OHFeSe}$ is introduced. The superconductor studied is shown to crystallize in the tetragonal space group $P4/nmm$ with lattice constants $a = 3.7865(2) \text{ \AA}$ and $c = 9.2802(6) \text{ \AA}$. It exhibits a mixture of strong covalent and weak ionic chemical bonding and has metallic characteristics. The Mössbauer spectra measured in the temperature range 2.0-294.9 K are the superposition of two quadrupole-doublet components originating from Fe atoms located at the $2a$ and $2b$ sites. It is shown that there is no magnetic ordering of the $2a$ -site iron magnetic moments down to 2.0 K. General agreement between the calculated hyperfine-interaction parameters at the two iron sites and the experimental one is observed. The Debye temperatures for the $2a$ and $2b$ sites are 186(21) and 397(4) K, respectively. The Fe concentration ratio at the $2a$ and $2b$ sites determined from Rietveld analysis is in excellent agreement with that derived from Mössbauer spectroscopy.

5.5 Al₇₆Ni₉Fe₁₅

5.5.1 Introduction and motivations

The most numerous class of quasicrystals (QCs) is that of icosahedral QCs [107]. The second, less numerous class of axial QCs [108] includes the decagonal QCs. The latter can be considered as being quasiperiodic in two dimensions and periodic in the third one, whereas the former have no periodicity along any direction.

The first observation of a metastable decagonal quasicrystalline phase Al₇₅Ni₁₀Fe₁₅ obtained by rapid solidification in the Al-Ni-Fe alloy system was reported by Tsai, Inoue and Masumoto [109]. This particular metastable decagonal phase was subsequently studied, mainly from structural point of view, in several publications [110-112]. It was shown [112-118] that other metastable decagonal QCs in the compositional range Al₇₀₋₇₅Ni₃₋₂₀Fe₁₀₋₂₂ could also be rapidly solidified. It was Lemmerz *et al.* [119] who discovered thermodynamically stable decagonal QCs in a narrow compositional range around Al₇₁Ni₂₄Fe₅. Structural and some physical properties of these high-quality decagonal Al-Ni-Fe QCs were studied in Al_{71.5}Ni_{23.1}Fe_{5.4} [120], Al₇₁Ni₂₄Fe₅ [116,121-124], Al_{71.6}Ni_{23.7}Fe_{4.7} [125], single-grain Al_{70.1}Ni_{24.2}Fe_{5.7} [126,127], Al_{71.5}Ni_{23.5}Fe₅ [128-130], Al_{71.6}Ni_{23.7}Fe_{4.7} [131], Al₇₃Ni₂₂Fe₅ [132], single-grain Al₇₂Ni₁₈Fe₁₀ [133,134], and Al_{71.3}Ni₂₄Fe_{4.7} [135-138]. Very recently, the first natural decagonal QC with composition Al₇₁Ni₂₄Fe₅ has been discovered [139].

Studies of crystalline compounds, called approximants, play an important role in elucidating the local atomic structure of QCs and their corresponding physical properties. An approximant to a QC is a structurally complex crystalline compound, usually close in composition to the QC, that contains the arrangements of atoms in its large unit cell that closely approximate the local atomic structures in the QC [6,140,141]. Al₁₃Fe₄ has been identified [5] as an approximant to the metastable decagonal Al-Fe QC. As the crystal structure of Al₇₆Ni₉Fe₁₅ studied here is the same as that of Al₁₃Fe₄ [120], this compound can be regarded as an approximant to a decagonal Al-Ni-Fe QC. Here the results of X-ray diffraction, ⁵⁷Fe Mössbauer spectroscopy, and magnetic study of Al₇₆Ni₉Fe₁₅, complemented by first principles electronic structure and hyperfine-interaction parameters calculations are presented.

5.5.2 General considerations and structural parameters

The Al₇₆Ni₉Fe₁₅ compound crystallizes in a monoclinic structure belonging to the space group *C2/m* (No.12) [4]. In fact, the structural characteristics of Al₇₆Ni₉Fe₁₅ are similar to the Al₁₃Fe₄ compound studied earlier (see section 5.1). The only difference between Al₇₆Ni₉Fe₁₅ and Al₁₃Fe₄ is in the atomic bases of their crystal structures; in Al₁₃Fe₄, a fraction (about 37.5%) of the Fe atoms in each of the crystallographic sites is replaced by Ni atoms resulting in a compound with a chemical formula Al₇₆Ni₉Fe₁₅. The unit cell of Al₇₆Ni₉Fe₁₅ consists of 102 atoms with a single formula unit. In table 5.4 the atomic positions point symmetries of the Al, Ni, and Fe atoms in the Al₇₆Ni₉Fe₁₅ compound is given. These values are obtained via the Rietveld refinement method on the results of the X-ray powder diffraction measurements which will be described later in this section.

Atom	Site	Point symmetry	x	y	z	V_{zz}	η
0.625Fe(1)+0.375Ni(1)	4i	m	0.0825	0.0	0.3843	1.639	0.465
0.625Fe(2)+0.375Ni(2)	4i	m	0.3917	0.0	0.6306	3.803	0.531
0.625Fe(3)+0.375Ni(3)	4i	m	0.0897	0.0	0.9829	-0.148	0.781
0.625Fe(4)+0.375Ni(4)	4i	m	0.4019	0.0	0.9820	-0.065	0.366
0.625Fe(5)+0.375Ni(5)	8j	1	0.3172	0.2910	0.2762	-1.289	0.636
Al(1)	4i	m	0.0622	0.0	0.1795	1.714	0.789
Al(2)	4i	m	0.3270	0.0	0.2870	-0.752	0.192
Al(3)	4i	m	0.2419	0.0	0.5381	-3.724	0.408
Al(4)	4i	m	0.0721	0.0	0.5628	1.356	0.741
Al(5)	4i	m	0.2410	0.0	0.9600	-5.266	0.280
Al(6)	4i	m	0.4797	0.0	0.8320	-1.205	0.819
Al(7)	2d	2/m	$\frac{1}{2}$	0.0	$\frac{1}{2}$	-0.794	0.273
Al(8)	4i	m	0.2971	0.0	0.7727	-0.389	0.394
Al(9)	4i	m	0.0935	0.0	0.7982	-3.009	0.337
Al(10)	8j	1	0.1828	0.2205	0.1088	-0.421	0.423
Al(11)	8j	1	0.3697	0.2081	0.1141	-1.536	0.272
Al(12)	8j	1	0.8135	0.7899	0.6605	-3.411	0.553
Al(13)	8j	1	0.4862	0.2245	0.3324	3.736	0.733
Al(14)	8j	1	0.3683	0.2009	0.4781	-1.123	0.576
Al(15)	4g	2	0.0	0.2474	0.0	4.382	0.796

Table 5.4 The atomic positions for monoclinic $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ (space group $C2/m$) and calculated V_{zz} (in units of $10^{21} \frac{\text{V}}{\text{m}^2}$) and η .

Figure 5.51 represents the unit cell of the $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ compound. At first glance, one clearly observes the numerous atoms within the unit cell and the chemical bonds which connect them throughout the unit cell. The similarity between the structures of $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ and $\text{Al}_{13}\text{Fe}_4$ is best observed by comparing figures 5.51 and 5.1. The input data in producing the graphical representation of the unit cell are the space group parameters along with the lattice constants of $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ which are determined from the powdered X-ray diffraction pattern of the specimen. The results of X-ray diffraction measurements and the values for the lattice parameters of $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ are discussed in detail in section 5.5.4.1.

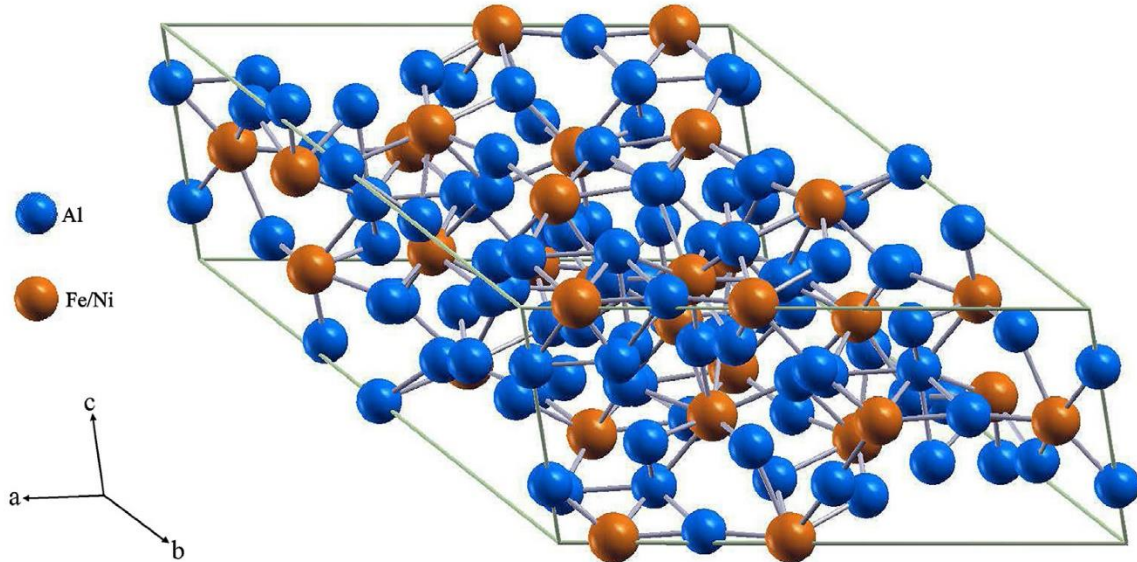


Figure 5.51 The unit cell of the $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ compound.

5.5.3 Theoretical calculations and interpretations

In this section, the results of first principle calculations on the $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ compound are presented following with their related physical interpretations. The results are introduced after a brief introduction to the computational details used in these theoretical calculations.

5.5.3.1 Theoretical methodology

In what follows, the specific computational details used in the theoretical calculations for the $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ compound are given.

First principle (*ab-initio*) electronic structure and Mössbauer hyperfine interaction parameter calculations have been carried out using the full potential linearized augmented plane wave plus local orbital (FP-LAPW+lo) method embedded in the WIEN2k package [20]. The FP-LAPW+lo method falls within the framework of density functional theory discussed in chapter four. In this method one partitions the unit cell into two distinct regions. The first regions are the so-called muffin-tin (MT) spheres centered at the locations of the atomic nuclei. These spheres are sometimes denoted as the atomic spheres or atomic regions. The second regions are the interstitial regions between the muffin-tin spheres. The electronic wave functions in the interstitial regions are expanded in plane wave bases whereas in the muffin-tin spheres they are expanded in terms of spherical harmonics times atomic radial functions.

The basis set inside each muffin-tin sphere is split into a core and valence subset. The core states are treated within the spherical part of the atomic potential only and their charge density distributions inside the muffin-tin spheres are assumed to be spherically symmetric. However, the valence wave functions are expanded in spherical harmonics to a maximum orbital angular momentum quantum number of $l = 12$, whereas within the interstitial region they are expanded up to $l = 4$. For the exchange-correlation potential, the generalized gradient approximation (GGA) scheme of Perdew, Burke, and Ernzerhof [21] is used. A separation energy of -8.5 Ry is used in order to distinct valence states from core states for individual atoms in the unit cell.

As for the muffin-tin radii, the values 2.07, 1.20, and 1.03 a.u. are chosen for Fe, Ni and Al atoms respectively. The plane wave cut-off parameter used is such that $R_{\text{MT}} \times K_{\text{MAX}} = 6.5$, where R_{MT} is the smallest muffin-tin radius in the unit cell and K_{MAX} is the maximum k-vector used in the plane wave expansion of the wave functions in the interstitial region. For electronic band structure calculations a total number of 432 k-points is used within a $9 \times 8 \times 12$ k-mesh in the irreducible wedge of the first Brillouin zone. For the self-consistency cycles, a convergence criterion used for energy is chosen such that the differences in energy between two successive iterations do not exceed 10^{-4} Ry. As mentioned earlier, experimental values obtained from X-ray diffraction measurements are used for the lattice parameters in the calculations. For the numerical values of the lattice parameters and the input data for the calculations the reader is referred to table 5.4 and section 5.5.4.1.

5.5.3.2 Theoretical results

In this section, the theoretical results regarding electronic structure, charge density distributions, and hyperfine interaction parameters for the $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ compound are presented and discussed.

5.5.3.2.1 Electronic density of states

In figure 5.52, the results of the electronic density of states (DOS) calculations on $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ are presented. Only the total density of states and the collective atom resolved partial density of states has been given in this figure. A quick observation of figure 5.52 reminds us of the density of states of the similar compound $\text{Al}_{13}\text{Fe}_4$ shown in figure 5.2. Since the space group and the atomic site occupancies in the two compounds are identical, the similarities in the electronic structure and density of states of the two compounds, regarding the relative positions of their maxima and minima in terms of energy, can be easily understood. The slight (and important) differences arise from the fact that the role of 37.5% of the iron atoms in $\text{Al}_{13}\text{Fe}_4$ is given to nickel atoms in $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$. Thus the total number of iron electronic states is fewer in $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ compared to that of $\text{Al}_{13}\text{Fe}_4$. Instead, a relatively small contribution due to the small number of nickel atoms present in $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ is observed in figure 5.52.

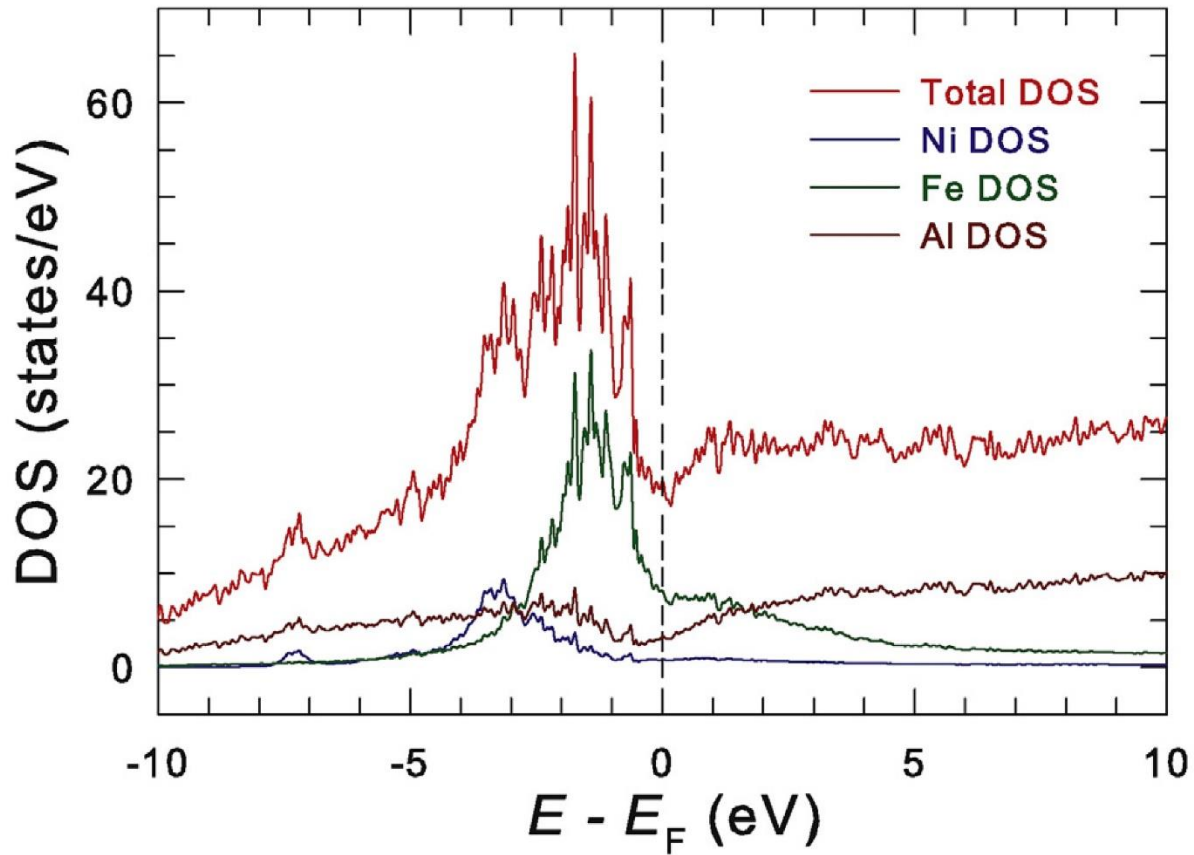


Figure 5.52 The total and atom-resolved density of states of $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$.

From figure 5.52, it is seen that a non-zero density of states exist across a wide energy range from -10 to 10 eV with respect to the Fermi energy, E_F . In other words, no energy gaps within or outside the Fermi region is observed. Considering the distribution of the Al and Fe states in figure 5.52, one clearly realizes the high degree of overlap between them which can be accounted for the existence of metallic bonding between these atoms. This long-range and non-directional bonding is shown schematically in figure 5.51 with rods connecting the atoms in the unit cell. In this figure, one also observes that every atom is connected to other atoms, either of the same or different type, in its surrounding environment and in all directions. This pattern is spread over the entire unit cell.

A possible explanation of the metallic bonds can be offered based on simple arguments regarding the electronic structure of the individual atoms within the $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ compound. Each of the 78 atoms of Al in the unit cell contribute three electrons from their 3s and 3p orbitals, which gives rise to the metallic bonding and allows the wave functions of these electrons to spread over large distances as compared to the atomic separations in the compound.

The relatively large number of conduction electrons present in $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ predicts good electrical and thermal conductivity for this system. Other mechanisms, such as scattering of free electrons by lattice vibrations at high temperatures, also contribute to the conductivity of $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$.

A more careful inspection of figure 5.52, shows a highly peaked region of density of states between -3.5 to -0.5 eV with respect to the Fermi energy ($E_F = 0$ eV). This region is dominated by mainly iron *d* states. In addition, a much smaller contribution from nickel *d* states adds to the contributions from iron states in forming the density of states in this energy region. However, the most intense nickel states are peaked at lower energies than the corresponding iron states. As stated earlier, a relatively high density of states above the Fermi energy can be assumed to originate from the numerous aluminum conduction electrons.

In figure 5.52, one can also observe a pseudogap at approximately 0.16 eV above the Fermi energy. This pseudogap is induced only by the Fe states. The existence of such a minimum in the density of states close to the Fermi level is interpreted as an electronic stabilization in terms of the Hume-Rothery mechanism [142]. However, the existence of a pseudogap in the vicinity of the Fermi energy is an intrinsic feature of icosahedral quasicrystals and their approximants [143-152]. The presence of such pseudogaps was observed only in Al-Ni-Co and Al-Fe decagonal quasicrystals and their approximants [85,153-156]. The presence of the pseudogap studied in the $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ approximant suggests that the pseudo gap should also exist in the Al-Ni-Fe decagonal quasicrystals.

5.5.3.2.2 Electronic band structure

In figure 5.53, the electronic energy band structure of the $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ approximant is shown. As the calculations show, the presence of numerous and dense electronic bands all tightly packed leads towards the existence of numerous accessible electronic states in this system. It is seen that the electronic bands are even denser in the Fermi region which in turn accounts for the high metallicity of the $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ system (there is no energy band gap across the Fermi level).

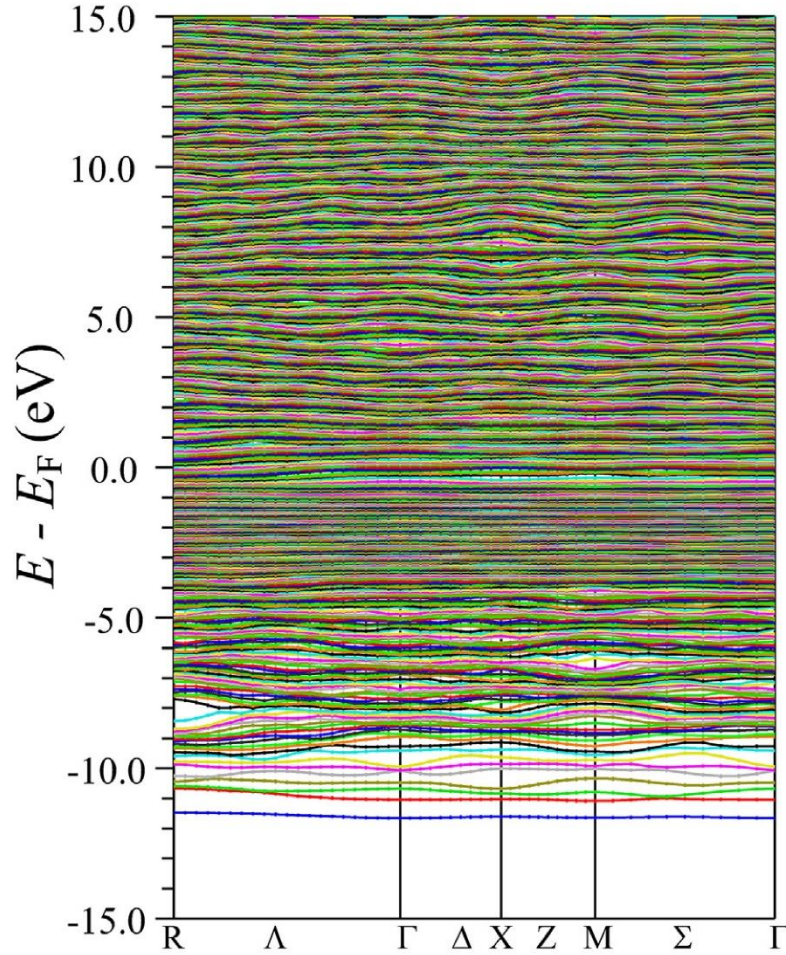


Figure 5.53 The electronic energy band structure of $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$.

5.5.3.2.3 Charge density distribution

The results of first principle electronic charge density distributions for $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ is shown figure 5.54. These charge densities have been calculated along two planes parallel to the ab plane. As one can clearly observe, regions with high charge densities are present throughout the system. Especially, the inter-atomic regions are teamed with electronic charge densities (the green regions in figure 5.54). This high presence of charge density suggests the existence of relatively good charge transport properties in the $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ system.

In what follows, possible explanations of the charge density patterns observed in figure 5.54 is given. The primitive unit cell of the $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ system contains 102 atoms which are distributed within a region of volume $1470.3 \text{ \AA}^3$. From the unit cell representation in figure 5.51 one notices that the atoms within the cell are on average, evenly distributed, with a slight preference of occupying the volume between $z = 0.247$ and $z = 0.753$ planes. Thus on average,

the volume occupied by each atom is $14.4 \text{ \AA}^3$, that is, the average separation between the atoms is about $2.43 \text{ \AA}$ which is a relatively small distance.

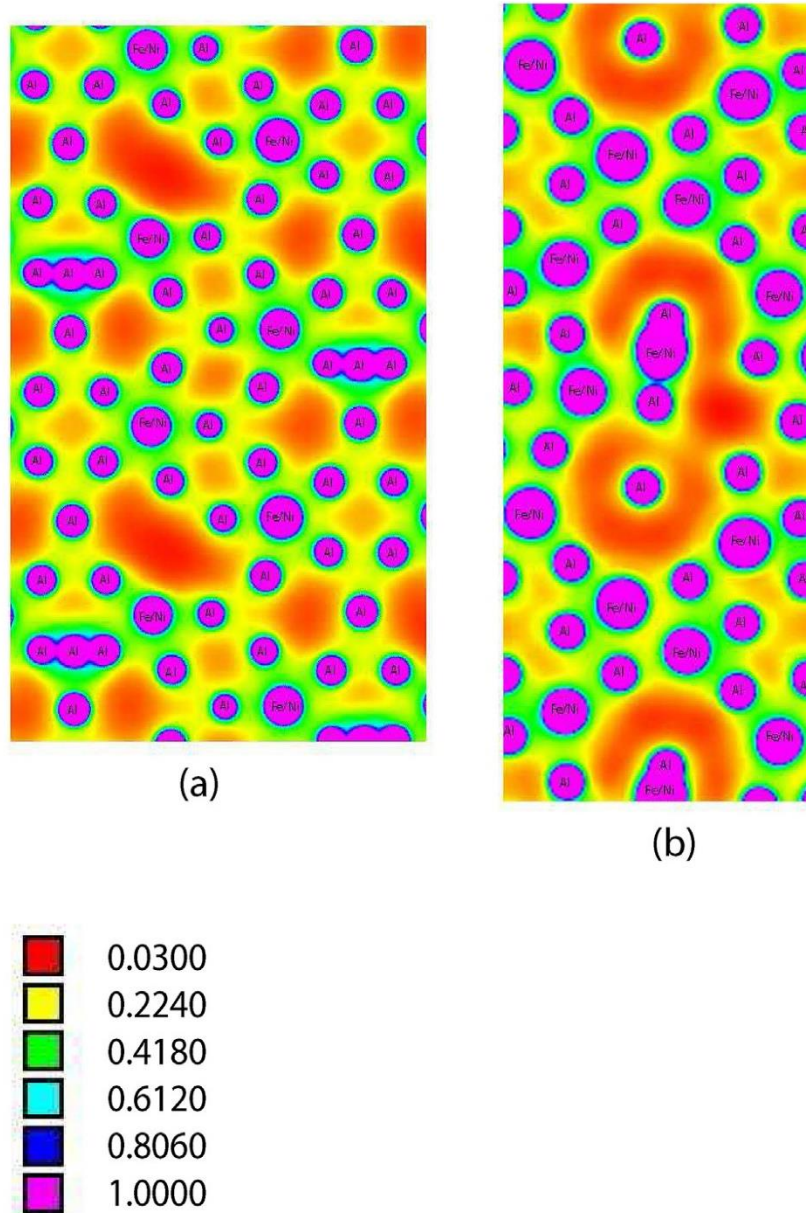


Figure 5.54 The electronic charge density distributions (in units of $\frac{e}{\text{\AA}^3}$) along the (a) $z = 0.726$ plane and (b) $z = 0.5$ plane

The small separation distance between the atoms in $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ leads to a strong Coulomb interaction between them, which results in the formation of regions with high charge concentration. The hybridization between Fe/Ni and Al states can also lead to the high charge

density regions observed in figure 5.54. These explanations are generally in agreement with the earlier discussions made, based on the results obtained from the density of states calculations.

5.5.3.2.4 The hyperfine interaction parameters

It should be mentioned at this point that the $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ approximant shows no magnetic ordering (*vide infra*) and thus among the three hyperfine interaction parameters, the term related to the magnetic dipole interaction is absent. Thus the isomer shift and the quadrupole splitting are the two hyperfine interaction parameters observed in the Mössbauer spectrum of this system. This is true for all paramagnetic compounds. In what follows, the results of first principle calculations on the hyperfine-interaction parameters for the $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ approximant are presented. The calculated values for the isomer shift, δ , principle component of the electric field gradient, V_{zz} , and the asymmetry parameter, η are given and discussed.

5.5.3.2.4.1 Isomer shift calculations

The isomer shift, δ_0 , as given in equation (5 – 5) is a result of the differences in the electronic charge densities at the Mössbauer nuclei of the studied compound, $\rho(0)$, and that of the reference compound, $\rho_{\text{ref}}(0)$. In the case of ^{57}Fe Mössbauer spectroscopy of $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$, the Mössbauer nuclei are the Fe atoms present at the five crystallographic sites listed in table 5.4 and the reference compound is the α phase of Fe (iron in the *bcc* structure) with a lattice constant of 2.8665 Å. As for the case of the previous compounds, the same value for the isomer shift calibration constant is chosen for the calculations ($\alpha = -0.291 \text{ a.u.}^3 \text{ mms}^{-1}$ from Ref. [131]). In order to account for the non-zero probability of the penetration of $p_{1/2}$ electrons inside the Mössbauer nucleus, relativistic spin-orbit effects have been considered in performing the calculations. The results of the calculations for the electronic charge density at the nuclei sites are as follows: 15309.918 a.u. $^{-3}$ for $\rho_{\text{ref}}(0)$ and 15308.901, 15309.231, 15309.092, 15308.996, and 15309.068 a.u. $^{-3}$ for $\rho(0)$ at the first five crystallographic sites in table 5.4.

5.5.3.2.4.2 Electric field gradient calculations

In table 5.4, the results of the theoretical first principle calculations [157] of the principle component of the electric field gradient (EFG) tensor, V_{zz} at all twenty crystallographic sites of the $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ system is given. The values of the calculated asymmetry parameter η , defined as $\eta = \frac{V_{xx} - V_{yy}}{V_{zz}}$ are also presented in table 5.4. The comparison of these calculated values with experiment is discussed in section 5.5.4.2.3.

5.5.4 Experimental methods and results

In this section, the results of the experimental studies on the $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ system including X-ray powder diffractometry and Mössbauer measurements are presented and compared with the results of first principle calculations.

5.5.4.1 Sample preparation

An ingot of nominal composition $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ is prepared via inductive melting constituent elements in a water-cooled copper crucible under argon atmosphere [120]. It is then annealed at 1073 K for 550 hours and then water quenched.

5.5.4.2 X-ray diffraction measurements

X-ray powder diffraction measurements are conducted on $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ in order to determine its crystal structural properties. These measurements take place at an environmental temperature of 298 K in Bragg-Brentano geometry on a PANalytical X'Pert scanning diffractometer using copper $K\alpha$ radiation. The diffraction peaks are measured in a scattering angle range of 2θ from 2 to 120° in steps of 0.02° . The $K\beta$ line is eliminated using a Kevex PSi2 Peltier-cooled solid-state silicon detector.

In figure 5.55, the result of the X-ray powder diffraction measurements on $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ is presented. Using the Rietveld refinement method [144], the lattice parameters of the unit cell are found to be: $a = 15.3898(3) \text{ \AA}$, $b = 8.0840(2) \text{ \AA}$, $c = 12.4169(3) \text{ \AA}$, and $\beta = 107.870(2)^\circ$. The atomic positional parameters from the Rietveld refinement of the X-ray diffraction data are listed in table 5.4. It is noted that the values of the lattice parameters and atomic positions are similar to the corresponding values for $\text{Al}_{13}\text{Fe}_4$ [4,13].

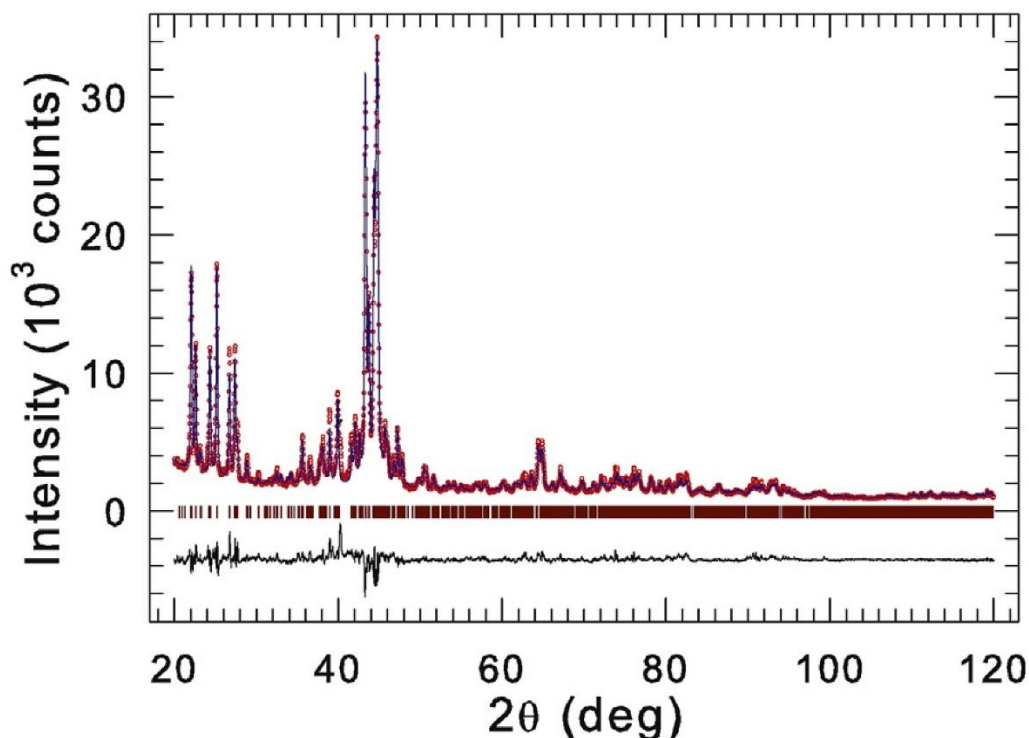


Figure 5.55 The X-ray powder diffraction pattern of $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ at 298 K. The red open circles represent the experimental data, while the solid blue line through the circles is the results of Rietveld refinement. The row of vertical bars shows the Bragg peak positions for the space group $C2/m$. The lower solid line represents the difference between experimental and calculated patterns.

5.5.4.3 Mössbauer spectroscopy

In this section, the results of the ^{57}Fe Mössbauer spectroscopy measurements on the $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ specimen is presented and discussed. The results of the measurements are then compared with those of first principle calculations.

5.5.4.3.1 The experimental set up for Mössbauer measurements

The ^{57}Fe Mössbauer measurements [14] on the $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ specimen are performed using a standard Mössbauer spectrometer operating in sine mode and a ^{57}Co source kept at room temperature. The spectrometer is calibrated with a $6.35\text{ }\mu\text{m}$ thick $\alpha\text{-Fe}$ foil and the spectra are folded [27]. The powdered $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ specimen is then combined with boron nitride in powdered form. The mixture is pressed into a pellet and put into a high-purity, $8\text{ }\mu\text{m}$ thick aluminum disk container to ensure uniform temperature over the entire absorber. The Mössbauer absorber is then placed into a cryostat. In the Mössbauer cryostat, the absorber is kept at a static exchange gas atmosphere at the pressure of $\sim 6 \times 10^{-3}$ mbar.

5.5.4.3.2 The Mössbauer spectra and interpretations

In figure 5.56, the ^{57}Fe Mössbauer spectra of $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ are presented at room and liquid-nitrogen temperatures. The spectra is taken over a large velocity range (typically between -8 and 8 mms^{-1}). As it is seen from this figure, a single quadrupole doublet pattern is present in the spectra which corresponds to a single (main) phase of the $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ specimen. In other words, no second phase quadrupole doublet is present within the velocity range mentioned above, thus if there is a possible second phase from a magnetic impurity, it should be beyond the detector range.

The Mössbauer spectra of the $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ system at various temperatures between 4.5 and 296.1 K are shown in figure 5.57. A quick comparison between this figure and that of the similar compound, $\text{Al}_{13}\text{Fe}_4$ shown in figures 5.8 and 5.11, shows that the three valley structure observed in the $\text{Al}_{13}\text{Fe}_4$ Mössbauer spectra, is not seen in the spectra of the corresponding system, $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$. In fact all the spectra in figure 5.57 are in the form of a *broadened* quadrupole doublet which is a result of the presence of a distribution, $P(\Delta)$ of quadrupole splittings rather than a single quadrupole splitting, Δ [159].

The Mössbauer spectra of figure 5.57 are fitted with the Voigt-based quadrupole distribution method of Rancourt and Ping [34]. To account for the small asymmetry of the spectra a linear coupling between the chemical shift (center shift), δ , and Δ is assumed for the doublets [84, 160].

In figure 5.58, the quadrupole splitting distributions, $P(\Delta)$ which fit the ^{57}Fe Mössbauer spectra of figure 5.57 are shown at corresponding temperatures. From these distributions one can calculate the average quadrupole splitting, $\bar{\Delta}$, at a given temperature. The average quadrupole splitting at the indicated temperatures of figure 5.58 is calculated and plotted in figure 5.59. The experimental data are shown to be well fitted with the empirical equation below

$$\bar{\Delta}(T) = \bar{\Delta}(0)(1 - BT^{3/2}). \quad (5 - 14)$$

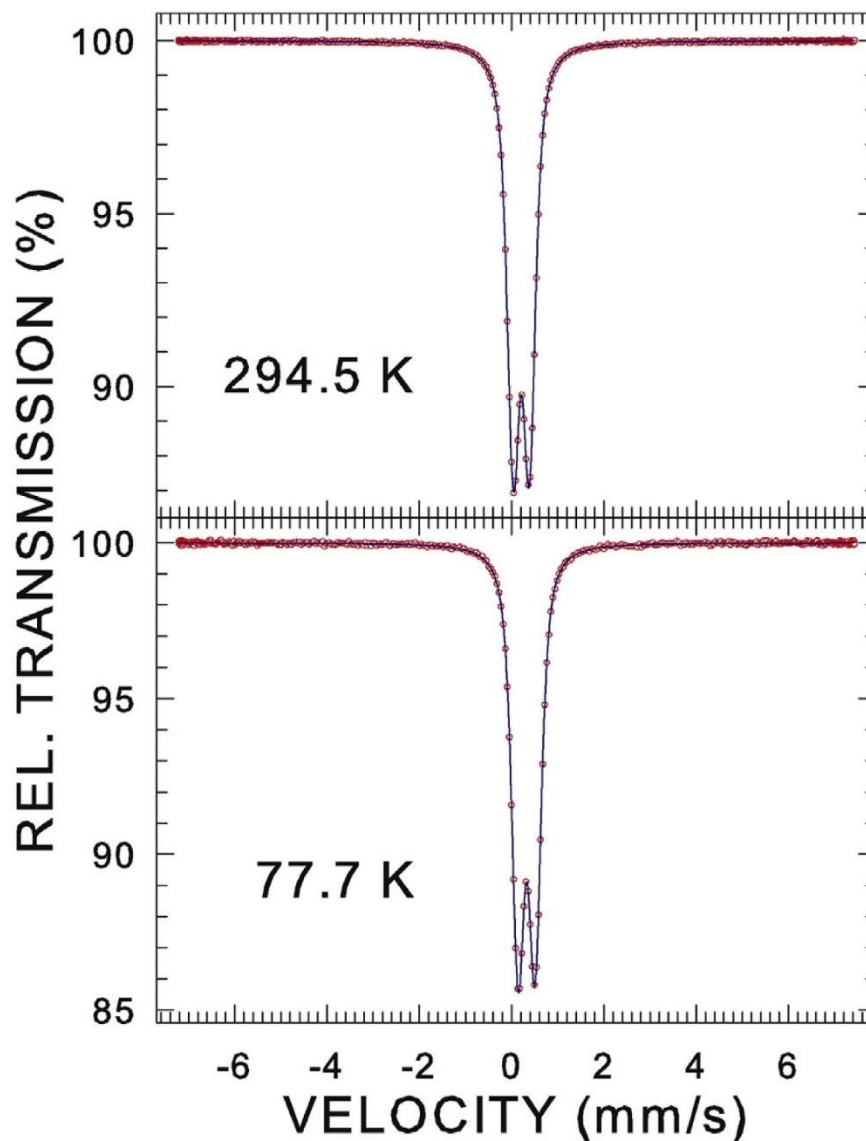


Figure 5.56 Room and liquid nitrogen temperature ^{57}Fe Mössbauer spectra of $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ measured in a large velocity range fitted (blue solid line) with a distribution of quadrupole splittings. The zero-velocity origin is relative to $\alpha\text{-Fe}$ at room temperature.

In equation (5 – 14), $\bar{\Delta}(T)$ is the average quadrupole splitting at temperature T , $\bar{\Delta}(0)$ is the average quadrupole splitting at 0 K, and B is a constant. The fit of the experimental $\bar{\Delta}(T)$ data in figure 5.59 with (5 – 14) leads to the values $0.379(3) \text{ mms}^{-1}$ and $1.24(3) \times 10^{-5} \text{ K}^{-3/2}$ for $\bar{\Delta}(0)$ and B respectively.

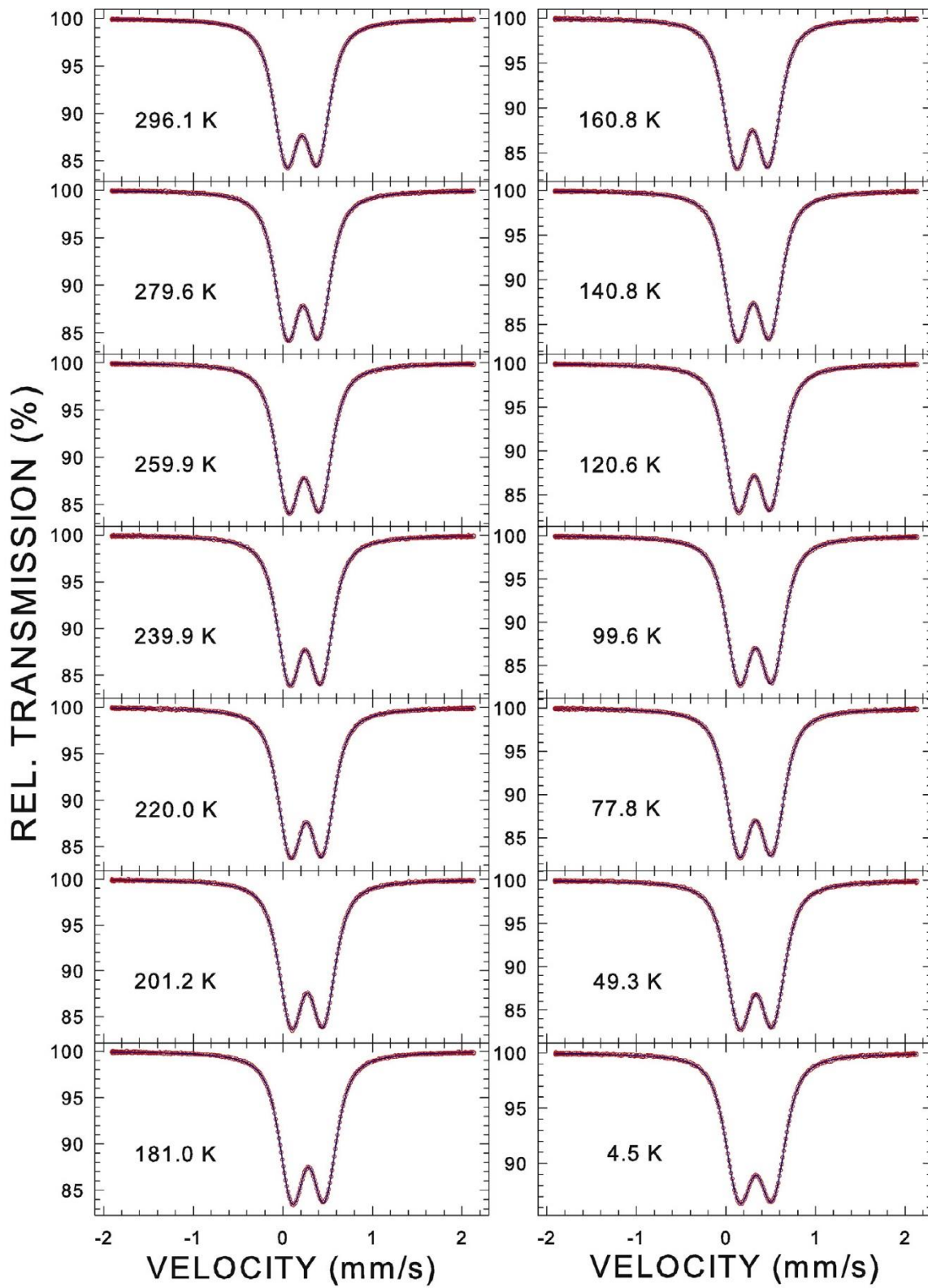


Figure 5.57 ^{57}Fe Mössbauer spectra of $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ at indicated temperatures and fitted (blue solid lines) with the quadrupole splitting distributions $P(\Delta)$ shown in figure 5.58. The zero-velocity origin is relative to $\alpha\text{-Fe}$ at room temperature.

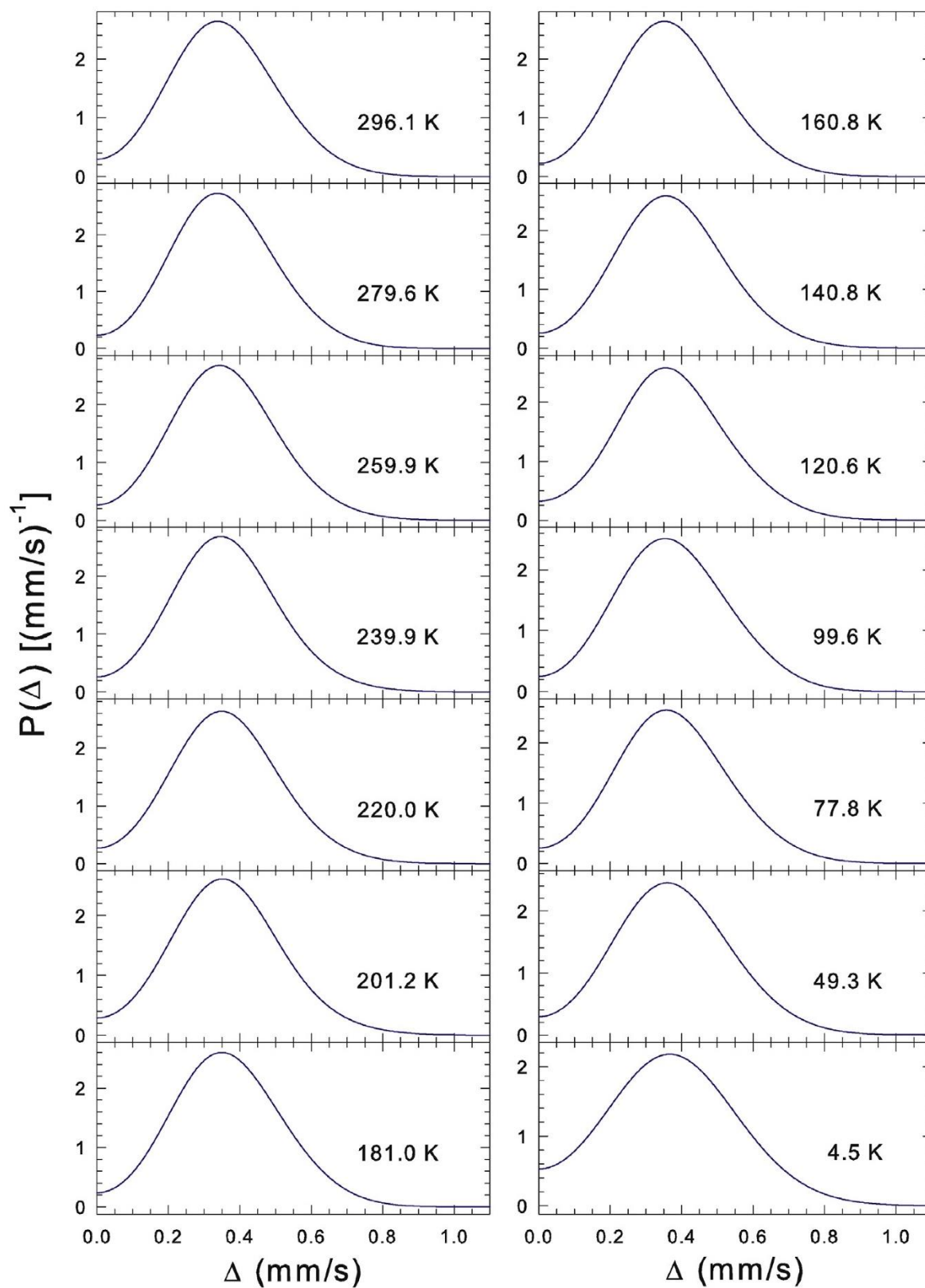


Figure 5.58 The quadrupole splitting distributions, $P(\Delta)$ which optimally fit the ^{57}Fe Mössbauer spectra of the $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ approximant.

The $T^{3/2}$ behavior given in equation (5 – 14) is observed in various crystalline, quasi-crystalline, and amorphous compounds [34,35,158,161] and it is yet not fully understood. A possible explanation is that this observed temperature dependence of the (average) quadrupole splitting parameter may originate from the strong temperature related mean-square lattice displacements or even the temperature dependence of the lattice parameters [162].

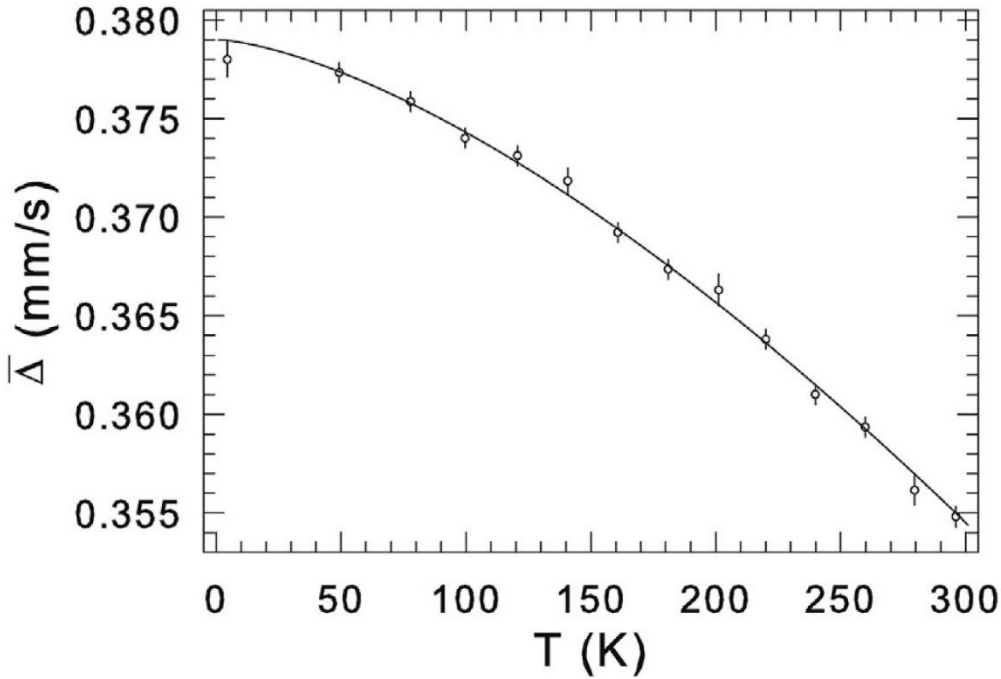


Figure 5.59 The temperature dependence of the average quadrupole splitting parameter for $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ fitted with the empirical equation (5 – 8).

As discussed before, in chapter three and in considering the different compounds in the current chapter, a general relation holds for the temperature dependence of the isomer shift. This relation is given in equation (5 – 7). In figure 5.60(a), the temperature dependence of the *average* isomer shifts, $\bar{\delta}$ (relative to α -Fe at 298 K), defined below is shown

$$\bar{\delta}(T) = \delta_0 + \delta_{\text{SOD}}(T). \quad (5 - 15)$$

In (5 – 15), δ_0 is the intrinsic isomer shift and $\delta_{\text{SOD}}(T)$ is the second order Doppler (SOD) shift which depends on the lattice vibrations of the iron atoms [4]. $\delta_{\text{SOD}}(T)$ is expressed in terms of the Debye temperature, T_D , in the Debye approximation of lattice vibrations (eq. (5 – 8)). The values for δ_0 and T_D from the fitting of the experimental data are $0.333(1) \text{ mms}^{-1}$ and $430(5) \text{ K}$ respectively.

In figure 5.60(b), the temperature dependence of the absorption spectral area, A , which are derived from the fits of the Mössbauer spectra in figure 5.57 is given.

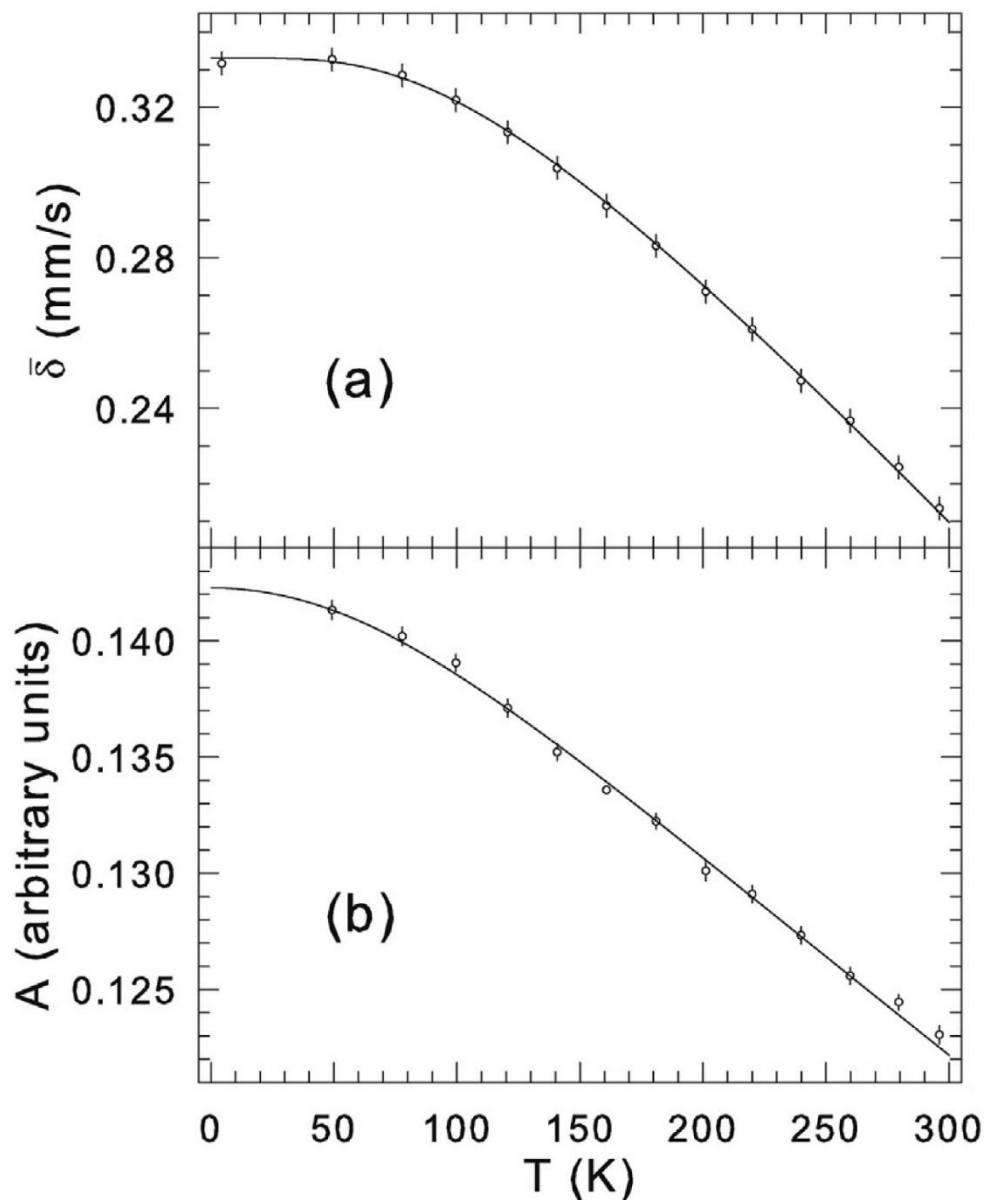


Figure 5.60 Temperature dependence of (a) the average isomer shift, $\bar{\delta}$, and (b) the absorption spectral area. The solid lines represent the fits of the experimental data with equations (5 – 15) and (5 – 4).

The spectral absorption area is proportional to the Debye-Waller factor, f_a , which is given by equation (5 – 4). From the fit of the experimental data for the absorption spectral area in figure 5.60(b) with equation (5 – 4), the value of 432(3) K is derived for the Debye temperature. This value for the Debye temperature of $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ is close to the corresponding Debye temperature 383(3) of the structurally similar compound $\text{Al}_{13}\text{Fe}_4$ studied earlier in section 5.1.

5.5.4.3.3 Hyperfine interaction parameters; a comparison between theory and experiment

As mentioned earlier, numerical analysis of the Mössbauer spectra of a non-magnetic compound yields two important hyperfine interaction parameters: the quadrupole splitting (the separation between two resonance lines in an ^{57}Fe Mössbauer quadrupole doublet), Δ , defined in (5 – 2), and the isomer shift, δ_0 . In order to compare these Mössbauer parameters of $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ with the calculated ones, a theoretical 0.0 K Mössbauer spectrum is generated. From equation (5 – 2) and the calculated values of V_{zz} and η in table 5.4, the quadrupole splitting parameter for the first five crystallographic sites in table 5.4 are $\Delta = 0.265, 0.621, 0.025, 0.010$, and 0.225 mms^{-1} respectively. The numerical values for the isomer shift using the calculated parameters of $\rho(0)$ and $\rho_{\text{ref}}(0)$ in section 5.5.3.2.4.1 for the first five crystallographic sites in table 5.5 are $\delta_0 = 0.296, 0.200, 0.240, 0.268$, and 0.247 mms^{-1} respectively. The generated Mössbauer spectrum is compared with the experimental spectrum at 4.5 K and shown in figure 5.61(a). As seen from figure 5.61 there is a significant disagreement between the experimental spectrum and the calculated spectrum. As seen from figure 5.61(a), the theoretical calculated isomer shift is much lower than the experimental one. In figure 5.61(b) however, the isomer shift has been set as a free parameter and fitted, in this case a reasonable between the two spectra is achieved.

A possible explanation for the difference between the calculated and measured parameters, Δ and δ_0 , arises from the fact that the first principle calculations have been performed for an *ordered* system, whereas in the actual $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ system studied experimentally, the iron and nickel atoms are randomly distributed at the first five crystallographic sites in table 5.4. This random and statistical distribution leads to a distribution for the values of the isomer shift and the quadrupole splitting (*vide supra*) rather than to a single value for each of the two parameters.

5.5.4.4 Magnetic measurements

In the Mössbauer spectra of $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$, shown in figure 5.57, other than the quadrupole doublet there is no sign of any particular structure. The absence of the magnetic dipole hyperfine-interaction [14] in these spectra leads to the conclusion that the $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ must be nonmagnetic down to 4.5 K. In this section, the results of magnetic measurements on the $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ compound are presented and via these results the paramagnetic nature of this compound is verified. In particular, the magnetization curves and the magnetic susceptibility of the $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ system are investigated.

The dc magnetization of the $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ system is measured within the temperature range from 2.0 to 350 K and in magnetic fields up to 90 kOe using the vibrating sample magnetometer (VSM) option of the Quantum Design physical property measurement system (PPMS). The dc magnetic susceptibility is measured using the PPMS in the magnetic field of 10 kOe in the temperature range of 2.0 to 390 K.

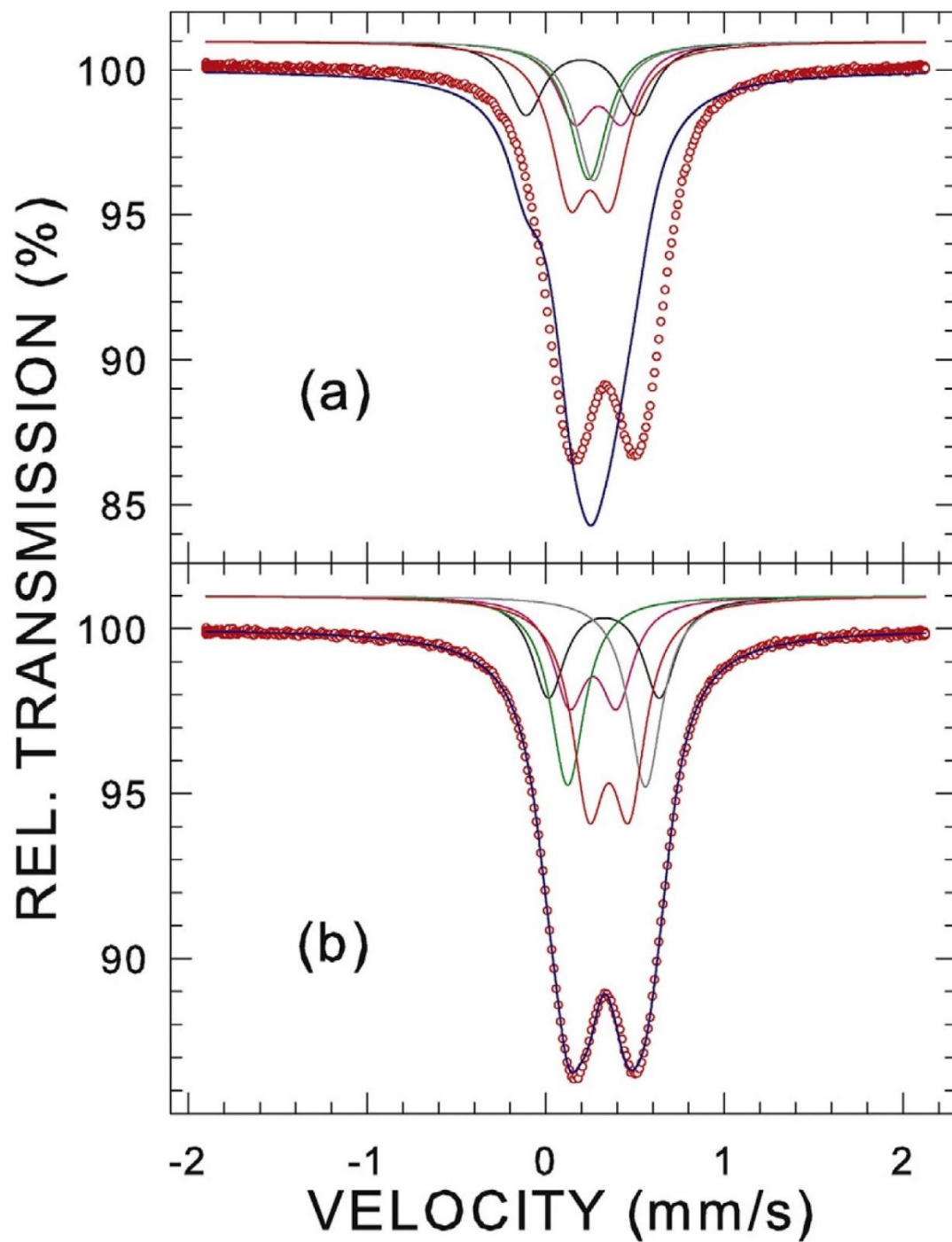


Figure 5.61 (a) The ^{57}Fe Mössbauer spectrum of $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ at 4.5 K and the simulated spectrum (blue solid line) resulting from the superposition of five quadrupole doublets (with the calculated δ_0 and Δ values) due to the iron atoms at the Fe(1) site (pink solid line), Fe(2) site (black solid line), Fe(3) site (green solid line), Fe(4) site (dark grey solid line), and Fe(5) site (red solid line) (b) the same as in (a) but with fitted δ_0 values.

5.5.4.4.1 Magnetization curves

In figure 5.62, the measured magnetization of the $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ system in various temperatures and in a magnetic field range between -90 kOe and 90 kOe is shown. The magnetization dependence on the external magnetic field, $M(H)$ observed in this figure resembles hysteresis curves of a ferromagnetic material. The magnetization curves do not saturate in the highest measured fields of 90 kOe. This shows that the $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ specimen must contain a form of ferromagnetic impurity.

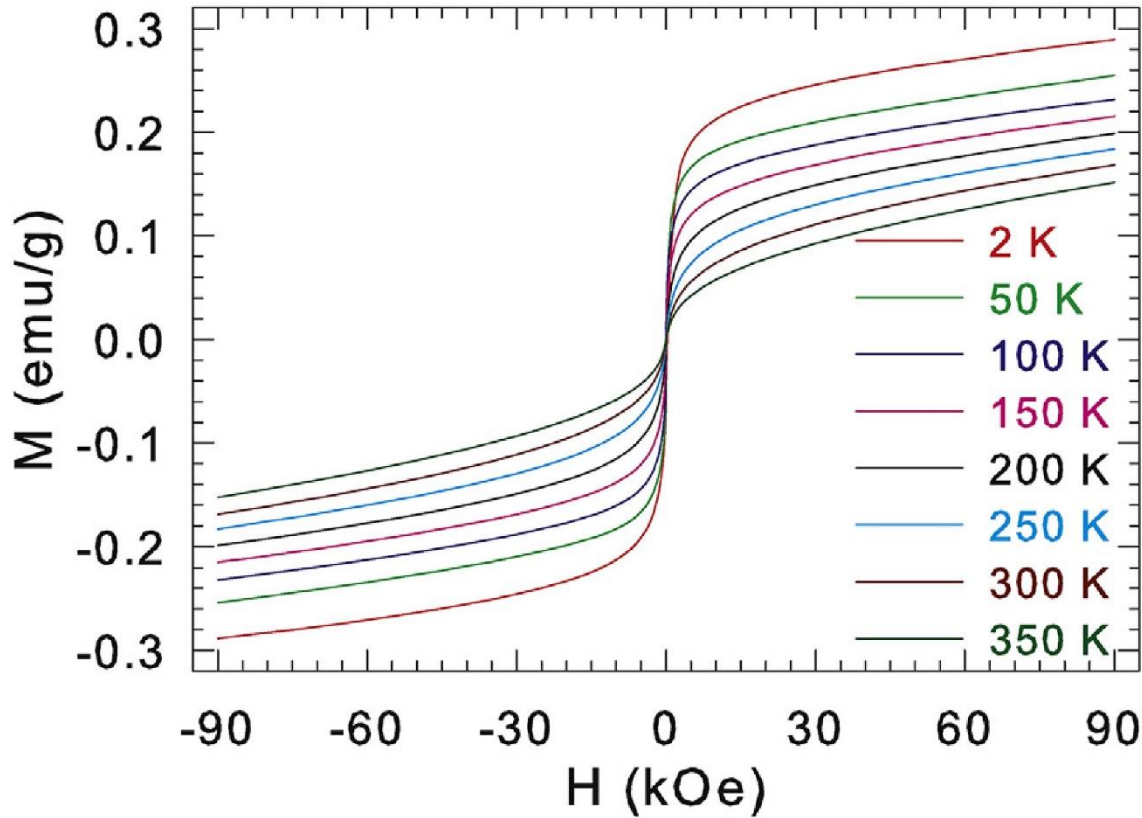


Figure 5.62 Magnetization of the $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ specimen in indicated temperatures and in magnetic fields ranging from -90 kOe to 90 kOe.

5.5.4.4.2 Magnetic susceptibility

In figure 5.63(a), the temperature dependence of the magnetic susceptibility, χ of $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ in an applied magnetic field of 10 kOe is presented. The susceptibility curve shows approximately (because of the presence of a small amount of ferromagnetic impurity) an inverse temperature dependence behavior. The $\chi(T)$ data above 250 K is fitted to a modified Curie-Weiss law

$$\chi = \chi_0 + \frac{C}{T - \Theta_p}. \quad (5 - 16)$$

In (5 – 16), χ_0 is the temperature independent term which includes the contributions from Pauli and Van Vleck paramagnetism as well as core and Landau diamagnetism, C is the Curie constant, and Θ_p is the paramagnetic Curie temperature.

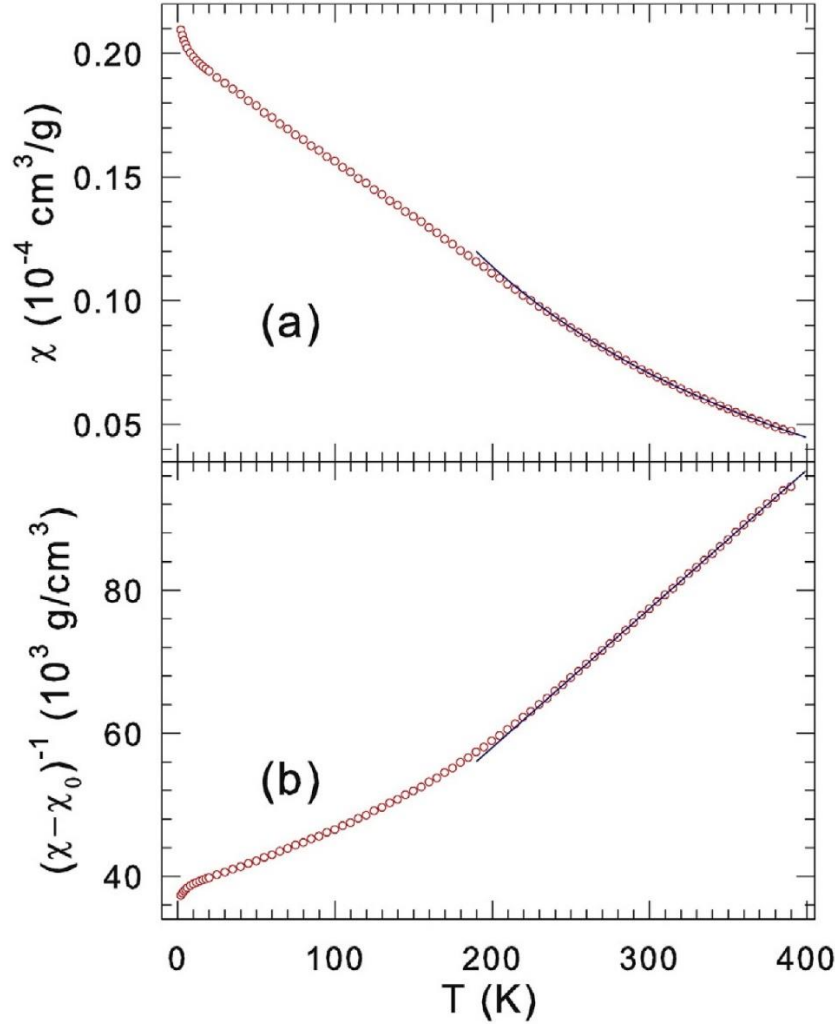


Figure 5.63 (a) Temperature dependence of the magnetic susceptibility of $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ measured in an external magnetic field of 10 kOe. The solid line is fitted to equation (5 – 16) in the temperature range 250 to 390 K. (b) Temperature dependence of the inverse magnetic susceptibility, $(\chi - \chi_0)^{-1}$ corrected for the contribution χ_0 . The solid line is fit to equation (5 -16).

The Curie constant is given by $C = \frac{N\mu_{\text{eff}}^2}{3k_B}$, where N is the number of transition metal atoms per formula unit, and μ_{eff} is the effective magnetic moment. The fit of the experimental data of $\chi(T)$ to equation (5 – 16) yields the values $\chi_0 = -5.85(31) \times 10^{-6} \frac{\text{cm}^3}{\text{g}}$, $C = 5.15(25) \times$

$10^{-3} \frac{\text{cm}^3\text{K}}{\text{g}}$, and $\Theta_p = -99(10)$ K. In figure 5.63(b) the inverse magnetic susceptibility corrected for the contribution χ_0 as $(\chi - \chi_0)^{-1}$ versus temperature. The value of C corresponds to a $\mu_{\text{eff}} = 2.42(6)\mu_B$ per transition metal atom. The unusually small value of Θ_p indicates the antiferromagnetic interaction between the transition metal atoms.

5.5.5 Summary and conclusions

In summary, the results of *ab-initio* electronic structure and the hyperfine-interaction parameters calculations, X-ray diffraction measurements, ^{57}Fe Mössbauer spectroscopy, and magnetic measurements of the approximant $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ to a decagonal Al-Ni-Fe quasicrystal is presented. The studied compound is shown to crystallize in the monoclinic space group $C2/m$ with the lattice parameters $a = 15.3898(3) \text{ \AA}$, $b = 8.0840(2) \text{ \AA}$, $c = 12.4169(2) \text{ \AA}$, and $\beta = 107.870(2)^\circ$. The calculated density of states reveals the existence of a pseudogap slightly above the Fermi energy, which points to a possible contribution of the Hume-Rothery mechanism to the stabilization of the structure. Good metallicity of $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ is predicted. The Mössbauer spectra measured in the temperature range 4.5 – 296.1 K reveal the presence of a distribution of the electric quadrupole splitting. The decrease of the average quadrupole splitting with temperature is well accounted for by a $T^{3/2}$ power-law relation. The compound studied is shown to be paramagnet down to 2.0 K. The Debye temperature of $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ is found to be 431(3) K.

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($-0.101\mu_B$) which results from the leakage of a small amount of valence charge from the MT region into the interstitial region. This presence of charge in the interstitial region can also be taken as evidence for covalent nature of chemical bonding.

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Chapter six

Summary and Conclusions

In summary, the results of theoretical and experimental studies on five compounds, $\text{Al}_{13}\text{Fe}_4$, $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$, Fe_2NiGa , $(\text{Li}_{0.8}\text{Fe}_{0.2})\text{OHFeSe}$, and $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ are presented in this thesis. The ^{57}Fe Mössbauer spectra of all five compounds has been measured at various temperatures. From the analysis of these spectra, hyperfine-interaction parameters have been extracted. The results of magnetic measurements are also given and discussed. X-ray powder diffraction measurements and Rietveld refinements on the compounds are presented and the resulting structural and lattice parameters are used for the theoretical calculations. First principle theoretical calculations based on density functional theory have been performed for all of the studied compounds. These calculations were carried out by using the WIEN2k package. For each of the studied compounds, various physical properties have been examined both theoretically and experimentally.

Main conclusions

Based on the results from X-ray diffraction measurements and Rietveld refinements on the diffraction data, it is shown that:

- 1) $\text{Al}_{13}\text{Fe}_4$ crystallizes in the monoclinic space group $C2/m$ with the lattice parameters $a = 15.503(2) \text{ \AA}$, $b = 8.063(2) \text{ \AA}$, $c = 12.464(2) \text{ \AA}$, and $\beta = 107.71(2)^\circ$.
- 2) The Heusler compound Fe_2NiGa crystallizes in the cubic space group $Fm\bar{3}m$ with the lattice parameter $a = 5.7961(4) \text{ \AA}$. The X-ray diffraction spectrum indicates the presence of significant structural disorder in this compound.
- 3) The 40K superconductor $(\text{Li}_{0.8}\text{Fe}_{0.2})\text{OHFeSe}$ crystallizes in the tetragonal space group $P4/nmm$ with the lattice constants $a = 3.7865(2) \text{ \AA}$ and $c = 9.2802(6) \text{ \AA}$.
- 4) The $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ compound crystallizes in the monoclinic space group $C2/m$ with the lattice parameters $a = 15.3898(3) \text{ \AA}$, $b = 8.0840(2) \text{ \AA}$, $c = 12.4169(2) \text{ \AA}$, and $\beta = 107.870(2)^\circ$.

Based on ^{57}Fe Mössbauer spectroscopy and dc magnetic measurements, it has been demonstrated that:

- 1) $\text{Al}_{13}\text{Fe}_4$ shows a three component quadrupole doublet structure in zero-field. The corresponding quadrupole splittings increase with decreasing temperature and are well described by a $T^{3/2}$ power-law relation. The shape of the Mössbauer spectrum of $\text{Al}_{13}\text{Fe}_4$ measured in an external magnetic field of 90 kOe is well accounted for with five component subspectra generated using the calculated electric field gradient parameters at five inequivalent iron sites. The Debye temperature of $\text{Al}_{13}\text{Fe}_4$ is 383(3) K.

2) The ground state of $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$ favors the antiferromagnetic ordering. The Néel temperature of this system is $T_N = 74.8(2)$ K. The measured Fe magnetic moment is $3.0(1)\mu_B$. The Debye temperature of $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$ is $274(3)$ K.

3) Fe_2NiGa is a ferromagnet with the Curie temperature $T_C = 586.0(7)$ K. A significant structural disorder is present in Fe_2NiGa . The Fe magnetic moments at the A and B sites estimated at 0 K and the saturation magnetization per formula unit are, respectively, $1.87(2)$, $2.25(2)$, and $3.00\mu_B$. Different heat treatments of Fe_2NiGa result in its dramatically different magnetic properties. The Debye temperature of Fe_2NiGa is $378(5)$ K. The compound studied decomposes when heated and kept at temperatures above around 500 K.

4) A superposition of two quadrupole-doublet components originating from iron atoms located at the $2a$ and $2b$ sites in $(\text{Li}_{0.8}\text{Fe}_{0.2})\text{OHFeSe}$ is observed in the temperature range 2.0–294.9 K. No magnetic ordering of the $2a$ -site Fe magnetic moments exists down to 2.0 K. The Debye temperatures for the $2a$ and $2b$ sites are $186(21)$ and $397(4)$ K, respectively.

5) $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ is paramagnet down to 2.0 K. A distribution of the electric quadrupole splitting is present in the temperature range 4.5 – 296.1 K. The decrease of the average quadrupole splitting with temperature is well accounted for by a $T^{3/2}$ power-law relation. The Debye temperature of $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ is $431(3)$ K.

Based on the results from first principle density functional theory calculations:

1) The presence of a pseudogap located at 0.1 eV above the Fermi energy and with a width of ~ 0.2 eV is predicted in the $\text{Al}_{13}\text{Fe}_4$ system. Good metallicity of $\text{Al}_{13}\text{Fe}_4$ is confirmed by the calculated finite density of states at the Fermi level. The results of electric field gradient calculations for the five inequivalent Fe sites agree very well with the measured electric field gradients.

2) It is shown that the blocked checkerboard antiferromagnetic ordering of $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$ is energetically favored over other magnetic orderings. It has been demonstrated that $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$ is a Mott insulator. Very good agreement between the measured hyperfine-interaction parameters and the calculated ones is observed for this system. The covalent nature of the chemical bonds between the atoms along the Fe-Se-O layers is predicted and strong ionic bonds between these layers and the double layers of Na is observed.

3) It is predicted that the Heusler compound Fe_2NiGa is half-metallic with covalent chemical bonding. The calculated magnetic moments of Fe on A and B sites are generally greater than the measured ones. However, the calculated hyperfine-interaction parameters are in general agreement with the experimental ones. The Debye temperature of this system is calculated and is about 11% higher than the measured value. The calculated cubic lattice constant by the unit cell relaxation method is found to be very close to the experimental value.

4) It is shown that a mixture of strong covalent bonds and weak ionic bonds exist in the $(\text{Li}_{0.8}\text{Fe}_{0.2})\text{OHFeSe}$ system. The calculated electric field gradient and isomer shifts for the two Fe sites show general agreement with the measured values. This supports the argument that no

long range magnetic ordering exists within this system. The calculated density of states shows the different contributions from the two Fe sites in the electronic structure of this system.

5) The calculated hyperfine-interaction parameters when compared to the measured ones show that the $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$ compound is a statistically disordered system. The calculated density of states reveals the existence of a pseudogap slightly above the Fermi energy, which points to a possible contribution of the Hume-Rothery mechanism to the stabilization of the structure. Lack of magnetic ordering and long range overlap between various Al and Fe-Ni states indicate the metallic bonding in this compound. Electronic energy band structure calculations lead to a good metallicity for $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$.

Suggestions for future research

There are a number of suggestions to further extend the investigation for these and other compounds.

1. Regarding theoretical calculations, one can consider the role of temperature by introducing the contributions due to lattice vibrations (phonons) in our model and investigate how effective and reliable the results turn out.

2. It is suggested that the elastic properties of the other compounds, ($\text{Al}_{13}\text{Fe}_4$, $\text{Al}_{76}\text{Ni}_9\text{Fe}_{15}$, $\text{Na}_2\text{Fe}_2\text{Se}_2\text{O}$, and $(\text{Li}_{0.8}\text{Fe}_{0.2})\text{OHFeSe}$) are investigated as it was done for the Heusler compound.

3. The effects of the external applied magnetic field on the hyperfine-interaction parameters can also be a starting point for theoretical studies.

4. Research on the optical properties of these compounds, such as the dielectric function, is suggested.

5. One can use methods other than the augmented plane wave method to investigate the physical properties of the various systems studied in this thesis and compare them with the results presented here. More efficient computational codes can be developed based on field theories of quantum mechanics and statistical mechanics to probe the solid state.

6. From the experimental side, it is suggested that research on very similar compounds to be continued in the future. Careful measurements can be performed with the aid of advanced technological equipment capable of producing higher magnetic fields and reaching lower temperatures. This will allow access to high quality data which, upon comparison with structurally and chemically similar compounds and alloys, would allow deeper insight into the physics of solid materials.

7. Research on similar class of materials is encouraged to broaden our scientific data on the magnetic and electronic properties of solids. This would allow one to improve our understanding of existing theoretical models.

Appendix

The WIEN2k code

In this chapter, the software program which was used to run the computational calculations for the studied compounds is introduced. This software, known as the WIEN2k code, is used by approximately two thousand research groups in physics, material science, and chemistry in universities and research facilities worldwide. The WIEN2k code is capable of calculating numerous physical properties of materials up to a high degree of precision. The WIEN2k program is based on the linearized augmented plane wave plus local orbital methods which was introduced in chapter 4. All the relevant concepts in understanding the physics behind the calculations using this code, have been presented in chapter 4, therefore it is suggested that the reader should review chapter 4 before reading this chapter. In what follows part of the code that was used in this research is introduced. This chapter covers only the essential parts of setting up, performing, and interpreting the calculations. An extensive introduction to the WIEN2k package can be found in WIEN2k's official website [1].

A.1 Initialization

In what follows, we briefly describe the steps to set up a calculation in WIEN2k, otherwise known as the initialization procedure. The initialization process is performed by running a set of successive programs. The outputs generated by these programs are necessary in order to start the self-consistent field (SCF) cycles. In order to start the initialization procedure, one must create a master input file for the program. This file contains all the structural information of the system and we refer to it as “**case.struct**” where “**case**” is replaced by the title of the compound studied [1]. For instance **Al13Fe4.struct** will represent the file involving the structural information for the compound $\text{Al}_{13}\text{Fe}_4$.

The initialization procedure consists of several successive steps. These programs must be executed in the order which is discussed below.

A.1.1 NN

The first program to be executed once a proper structure file has been created is the NN program. The structure file contains information on the lattice parameters, atomic positions within the unit cell, and the space group to which the compound belongs. The unit cell parameters are determined by X-ray diffractometry and the Rietveld refinement method.

The NN program calculates the nearest-neighbor distances for the atoms in the unit cell and also checks whether the atomic spheres overlap or not. If an overlap is found then an error occurs and one must re-define the muffin-tin radii and rerun the program. The next nearest neighbor distances are also calculated by this program up to an arbitrary distance (namely f times the nearest-neighbor distance).

The NN program also checks the master input structure file to see if equivalent atoms in the structure really do have equivalent environments, otherwise an error message will appear in the output file indicating that one must modify the structure file.

The execution of this program is by typing “**x nn**” in the command line.

A.1.2 SGROUP

This program uses the information on the lattice type, lattice parameters, and the atomic positions provided in the structure file to produce the space group and the point groups of all nonequivalent sites in the unit cell. This program is particularly useful for handmade structures since it has the capability to offer smaller unit cells or to shift the origin of the cell and to produce a new structure file.

This program is executed by typing “**x sgroup**” in the command line.

A.1.3 SYMMETRY

The program SYMMETRY uses information in the original structure file, such as lattice type, atomic positions, etc. Once executed, this program will produce three sets of data.

1. Symmetry operations

If NSYM (number of symmetry operations) is set to be 0, then the program will generate the symmetry operations. On the other hand, if NSYM is nonzero then the generated symmetry operations will be compared with the existing one(s) and if they disagree, a warning message is sent.

2. LM values

The point group of each atomic site is determined and the LM values for the lattice harmonics representations are produced.

3. The local rotation matrix

The program also generates the local rotation matrix on each atomic site in the unit cell. The execution of this program is performed via typing “**x symmetry**” in the command line.

A.1.4 LSTART

The program LSTART is among the most important programs in the initialization procedure. This program is an atomic LSDA (local spin density approximation) code which generates the following information.

1. The atomic densities

These densities will later be used as input data for the DSTART program to generate the starting densities required for the SCF calculations.

2. The atomic potentials

The atomic potentials produced by LSTART are truncated at their corresponding atomic radii. The atomic potentials will be used later to run the LAPW1 program.

3. The atomic valence densities

Optional atomic valence densities are also produced by executing this program. The data will later be used to run LAPW5 to produce electron density plots.

4. The atomic total energies

The execution of this program is via invoking “**x lstart**” in the command line.

Some parameters appear in the input files, which will need to be defined:

NPT - the total number of radial mesh points

NPT00 - the maximum number of mesh points beyond the specified muffin-tin radii

NRAD - the number of mesh points up to the specified muffin tin radii

RMAX0 - maximum distance of radial mesh points

One must consider that NPT should be greater than $NPT00 + NRAD$

In order to generate the input file, LSTART asks one to provide the exchange correlation potential scheme. There are a number of different methods available within the WIEN2k code. The one used for studying all the compounds in this research is the generalized gradient approximation scheme of Perdew, Bruke, and Ernzerhof [2]. This choice of the exchange correlation potential is more efficient than other forms of the exchange correlation potential and has advantage over other methods of approximation concerning the materials studied in this research.

LSTART also requires the so-called *separation energy*. The value chosen for this energy will mark the boundary between core and valence states in terms of energy. In other words, it is the separation energy between core states and valence states. In choosing the numerical value for this energy one must be careful to consider the charge leakage of core states out of the muffin-tin radii, preferably by minimizing it as much as possible. This can be done by choosing lower values for the separation energy and by this one includes more states to be treated as valence states.

The input file for LSTART is **case.inst**. The example below shows the input file for LSTART in the case of Zn.

```

----- top of file: case.inst -----
ZINC
Ne 6          (inert gas, # OF VALENCE ORBITALS not counting spin)
3,-1,1.0  N      ( N,KAPPA,OCCUP; = 3S UP, 1 ELECTRON)
3,-1,1.0  N      3S DN
3,-2,2.0  N      3P UP
3,-2,2.0  N      3P DN
3, 1,1.0  N      3P*UP
3, 1,1.0  N      3P*DN
3,-3,3.0  P      3D UP
3,-3,3.0  P      3D DN
3, 2,2.0  P      3D*UP
3, 2,2.0  P      3D*DN
4,-1,1.0  P      4S UP
4,-1,1.0  P      4S DN
****          END OF Input
****          END OF Input
----- bottom of file -----

```

The first line is the given title of the compound.

The second line gives the core state configuration in terms of an inert gas (in this case Ne) and the number of valence orbitals without considering spin.

In line three the principle quantum number (n), the relativistic quantum number (κ) and the occupation number (per spin) is given. This line is repeated for the other spin and all other orbitals.

The spin quantum number (s) can take numbers +1 or -1, the orbital quantum number (j) is defined as $j = l + \frac{s}{2}$, and the relativistic quantum number (κ) is given as $\kappa = -s(j + \frac{1}{2})$. In the table below possible values for these quantum numbers concerning s, p, d and f orbitals is given.

		$j = l + s/2$		κ		max. occupation	
	l	$s = -1$	$s = +1$	$s = -1$	$s = +1$	$s = -1$	$s = +1$
s	0		1/2		-1		2
p	1	1/2	3/2	1	-2	2	4
d	2	3/2	5/2	2	-3	4	6
f	3	5/2	7/2	3	-4	6	8

Table A.1 Relativistic quantum numbers [1].

A.1.5 KGEN

The program KGEN generates the k-mesh in the irreducible wedge of the Brillouin zone (IBZ). As an input for this program, one must provide the total number of k points in the Brillouin zone. The choice for the number of k points differs from system to system. The larger

the number, the more cpu time is spent for the calculations. In entering the number of k points one should also account for the fact that this program generates a grid in reciprocal space. For example, a large unit cell containing a large number of atoms will require a smaller number of k points compared to a simpler system.

The k points generated using this program will later be used in the LAPW1 program in the SCF cycles. In addition, if one is interested in electronic band structure calculations and the electronic density of states, the k point files generated by KGEN will be used as inputs for the programs TETRA and LAPW2.

The execution of this program is started by typing “**x kgen**” in the command line. In case of working on a system lacking inversion symmetry, one can activate the “so” switch. This switch is particularly useful for magnetic systems. The execution is done by typing “**x kgen –so**”. One can also choose to run the program considering the full Brillouin zone. In this case the execution is done by typing “**x kgen –fbz**” in the command line. The “fbz” switch stands for a full Brillouin zone and generates a k mesh in the full Brillouin zone (no symmetry).

A.1.6 DSTART

The final step in the initialization procedure involves running the program DSTART. This program uses the atomic charge densities generated by the program LSTART. It generates a crystalline density by the superposition of the atomic charge densities. The LM values for the lattice harmonics and the Fourier coefficients for the plane wave expansion in the interstitial region are taken from the files produced by LSTART. The files generated by DSTART are used as input data for the SCF programs. The execution of DSTART is done by typing “**x dstart**” in the command line. Three important parameters for the running DSTART program are labeled as NPT (number of radial mesh points), LMAX2 (maximum l in LM expansion), and NCOM (number of LM terms in density).

A.2 The SCF cycle

Upon completion of the initialization procedure, one can run the SCF cycles. Within each SCF cycle a successive series of programs are executed. Some of these programs are common and necessary for all cases, whereas some others depend on the type of the specific problem studied. In this section, we introduce in detail only those programs of the SCF cycle which were used in studying the materials in this research. It is essential that the SCF programs are executed in order. The main SCF cycles consist of the following programs: LAPW0 (generates the potential from the charge density), LAPW1 (calculates valence bands, eigenvalues, and eigenstates), LAPW2 (computes valence densities from eigenvectors), LCORE (computes core states and densities), and MIXER (mixes input and output densities). In addition to these necessary programs, depending on the properties of the system under study additional programs are added to the SCF cycles. Table 6.2, gives the input and output files required and generated by the SCF cycle. With the exception of SUMPARA, all these programs consisted the SCF cycle for the materials studied in this thesis. These programs are introduced in order of execution.

program	Needs		generates	
	necessary	Optional	necessary	optional
LAPW0	lapw0.def case.struct case.in0 case.clmsum	case.clmup/dn case.vrespsum/up/dn case.inm	case.output0 case.scf0 case.vsp(up/dn) case.vns(up/dn)	case.r2v case.vcoul case.vtotal
ORB	orb.def case.struct case.inorb case.dmat case.vsp	case.energy case.vorb-old	case.outputorb case.scforb case.vorb orb.error	case.br1orb case.br2orb
LAPW1	lapw1.def case.struct case.in1 case.vsp case.klist	case.vns case.vorb case.vector.old	case.output1 case.scf1 case.vector case.energy	case.nsh(s) case.nmat-only
LAPWSO	lapwso.def case.struct case.inso case.in1 case.vector case.vsp case.vns case.energy	case.vorb case.normso	case.vectorso case.outputso case.scfso case.energyso	
LAPW2	lapw2.def case.struct case.in2 case.vector case.vsp case.energy	case.kgen case.nsh case.weight case.weigh case.recprlist	case.output2 case.scf2 case.clmval	case.qtl case.weight case.weigh case.help03* case.vrespval case.almb1m case.radwf case.dmat
LAPWDM	lapwdm.def case.struct case.indm case.vector case.vsp case.weigh case.energy	case.inso	case.outputdm case.scfdm case.dmat lapwdm.error	
SUMPARA	case.struct case.clmval	case.scf2p	case.outputsum case.clmval case.scf2	
LCORE	lcore.def case.struct case.inc case.vsp	case.vns	case.outputc case.scfc case.clmcor lcore.error	case.corewf
After LCORE the case.scfX files are appended to case.scf and the case.clmsum file is renamed to case.clmsum-old (see run-lapw)				
MIXER	mixer.def case.struct case.inm case.clmval	case.clmsum old case.clmsc case.clmcor case.scf case.broyd1 case.broyd2 case.dmat	case.outputm case.scfm case.clmsum mixer.error	case.broyd*
After MIXER the file case.scfm is appended to case.scf , so that after an iteration is completed, the two essential files are case.clmsum and case.scf .				

Table A.2 Input and output files of main programs in an SCF cycle [1].

A.2.1 LAPW0

The LAPW0 program generates the total potential (energy) functional by using the electron (spin) densities of the specific material under study as input data. The total potential (energy) functional, V_{tot} , consists of two parts: the Coulomb interaction energy, V_C , and the exchange correlation potential, V_{xc} . These potentials are expanded by two sets of basis functions in the spherical regions (atomic spheres) and the interstitial region. In the atomic region the total potential is expanded in spherical harmonics, whereas in the interstitial region a plane wave expansion (a Fourier series expansion) of the total potential is used.

The generated spherical part of the potential ($L = 0$) and the non-spherical part are stored in two separate files (in the case of spin-polarized calculations the potentials for each part are produced in a pair of files, one for each spin configuration).

The Coulomb potential is calculated by a multipolar Fourier expansion [1]. In this method, the multipole moments inside the muffin-tin spheres are calculated (Q-sp). In the interstitial region, the multipole moments from the Fourier series expansion of the charge density, which *artificially* represent *some* charge inside the muffin-tin spheres are calculated (Q-pw). The pseudo-multipole moments, Q , are obtained as the difference between Q-sp and Q-pw. Afterwards a plane wave series is generated based on two properties: having zero density in the interstitial region and a charge distribution inside the muffin-tin spheres that reproduces the pseudo-multipole moments, Q . This generated series is then added to the original interstitial Fourier series for the density to form a new density. This new density simultaneously represents the interstitial charge density and it has the same multipole moments inside the spheres as the actual density. The Fourier coefficients (up to a constant) represent the interstitial Coulomb potential.

Within the muffin-tin spheres a boundary value problem is solved using the Green's function method [1].

The exchange-correlation potential is computed numerically on a grid. Inside the muffin-tin spheres a Gauss-Legendre integration is used to produce the potential in terms of lattice harmonics, whereas in the interstitial region a 3-dimensional fast Fourier transformation (FFT) is used [1].

As mentioned earlier, the total potential, V , is obtained via summing the Coulomb potential V_C , and the exchange-correlation potential, V_{xc} .

The electric field gradient (EFG), which is of interest in the compounds studied in this research, is evaluated in this stage of the SCF cycle. As described in chapter four, because the electric field gradient is a second ranked tensor, it is calculated only if an $L=2$ term (in spherical harmonics) exists in the density expansion. The electric field gradient is given both in local and global coordinate systems.

The execution of LAPW0 is done by typing “**x lapw0**” in the command line.

Four parameters are used in LAPW0 which are collected in the file, “**param.inc**”. These parameters are described below

NCOM: number of lm components in charge density and potential representation. This number should be such that:

$$NCOM + 3 > \{[\text{number of } l, m \text{ with } m = 0] + [2 \times \text{number of } l, m \text{ with } m > 0]\}$$

NRAD: number of radial mesh points

LMAX2: highest L in the LM expansion of charge and potential

LMAX2X: highest L for the g-point-grid in the exchange-correlation potential expansion

The input file for LAPW0 is generated in the initialization stage. One can use this generated file for LAPW0 and it needs modification only if a different exchange correlation potential is to be used. The general form of a typical input file for LAPW0 is given below

```
----- top of file: case.in0 -----
TOT   XC_PBE                               ! MULT/COUL/EXCH/POT /TOT ;   VXC-SWITCH
NR2V   IFFT  8                               ! R2V  EECE/HYBR IFFT  LUSE
  30  30 108  4.00  1 ! min IFFT-parameters, enhancement factor, iprint
  0 0.0      (#of FK in E-field expansion, EFELD (Ry))

----- bottom of file -----
```

In the file above, “case.in0” is a naming convention standing for the input file for LAPW0 of a particular compound, for instance in the case of $\text{Al}_{13}\text{Fe}_4$, it will appear as “ $\text{Al}_{13}\text{Fe}_4.\text{in0}$ ”.

The first line of the file above includes two parts in the following order: switch, indx

switch

TOT: total energy contributions and total potential calculated.

KXC: total energy contributions and total potential calculated. In addition the kinetic energy contribution as well as the XC-energy will be printed.

POT: total potential is calculated, but not the total energy.

MULT: multipole moments calculated only.

COUL: Coulomb potential calculated only.

EXCH: exchange correlation potential calculated only.

Indxc

This keyword specifies the type of the exchange and correlation potential. The most common options are listed below [1]:

XC_LDA: Perdew and Wang 92, parameterization of Ceperly-Alder data, which is the recommended option for LDA calculations.

XC_PBE: Generalized Gradient approximation PBE by Perdew-Burke-Ernzerhof 96¹⁷.

XC_WC: Generalized Gradient approximation by Wu-Cohen 2006, Tran *et al.* 2007.

XC_PBESOL: Generalized Gradient approximation (PBEsol, Perdew 2008).

XC_MGGA_MS: Meta Generalized Gradient approximation (Sun *et al.* 2013).

XC_MBJ modified Becke-Johnson (mBJ-LDA) potential (Tran and Blaha 2009).

There are a few more options for the exchange-correlation potential which can be found in [1].

A.2.2 ORB

The program ORB calculates the orbital dependent potentials otherwise known as the orbital potentials. The orbital potentials are those which are non-zero only within the muffin-tin spheres and depend on the quantum numbers l and m_l . In order to run this program, the density matrix is required. To generate the density matrix one must run the following commands separately: “**x lapwdm_up**” and “**x lapwdm_dn**”.

The input files for ORB are **case.struct**, **case.inorb**, **casedmat**, and **case.vsp**. The output files are **case.outputorb**, **case.scforb**, and **case.vorb**.

The format of the input file case.inorb is given for the case of NiO [1].

```
----- top of file: case.inorb -----
1  2  0          nmod, natorb, ipr
PRATT,1.0        mixmod, amix
1  1  2          iatom nlorb, lorb
2  1  2          iatom nlorb, lorb
1                nsic (LDA+U(SIC) used)
0.52 0.0         U J
0.52 0.0         U J
----- bottom of file: -----
```

In the file above, the effective onsite potential is given by the difference $U - J$, where U and J are the Coulomb and exchange parameters respectively. The effective potential is given in Ry units.

¹⁷ This is the option used for all the theoretical calculations throughout this research.

A.2.3 LAPW1

The program LAPW1 sets up the Hamiltonian and the overlap matrix and via diagonalization finds the eigenvalues and eigenvectors. In addition to the traditional LAPW method, one can also use the APW+lo method for maximizing the efficiency (see chapter 4).

For structures lacking inversion symmetry, in which the elements in the Hamiltonian and overlap matrix are complex numbers, one must use the complex version of this program, **lapw1c** (This program is executed by invoking “**x lapw1 -c -up/dn**” in the command line). The computational time for LAPW1 depends on the size of the Hamiltonian matrix. If a large number of k-points are used, the computational time increases dramatically¹⁸.

An alternative way to reduce the calculation time is via parallel execution. In this way, the k-points are distributed among several computers and LAPW1 uses the combined cpu power of these computers to perform the calculations. This can be done by executing “**x lapw1 -p -c -up/dn**” in the command line. In addition, in recent versions of WIEN2k the standard routines LAPCK have been optimized. These new routines are often referred to as full diagonalization routines. In practice full diagonalization is never achieved, nevertheless the diagonalization is performed in a gradual and step by step fashion known as the block-Davidson scheme [1]. This method, however approximate, is advantageous over the standard LAPCK method due to its high calculation speed, especially when the size of the Hamiltonian matrix is large. The deficiency of this method is that it requires a large RAM memory. This is because the data produced in previous stages, such as the generated eigenvectors in the previous SCF cycle, are needed for the calculation of new eigenvectors. In other word, the old and new eigenvectors must be accessible at the same time and this requires a larger RAM memory.

The necessary input files in order to run the LAPW1 program are **case.struct**, **case.in1**, **case.klist**, and **case.vsp** and the generated output files are **case.output1**, **case.scf1**, **case.vector**, and **case.energy** (table 6.2). LAPW1 also accepts **case.vnsp** as an input file which was described earlier in LAPW0, in this case the full potential is used. In cases without inversion symmetry, the input file **case.in1** should be replaced by **case.in1c**.

Below a sample input is shown for TiO₂ (rutile), one of the test cases which is provided in the WIEN2k package. The input file is written automatically by LSTART, but was modified to set APW only for Ti-3d and O-2p orbitals.

¹⁸ For example, in the first attempt to calculate the physical properties of the Al₇₆Ni₉Fe₁₅ system, the cpu time for nonstop lapw1 calculations was 40 days.

```

----- top of file: case.in1 -----
WFFIL EF=0.5000 (WFPRI,WFFIL,SUPWF ; wave fct. print,file,suppress
7.500 10 4 (R-mt*K-max; MAX 1, max 1 for hns )
0.30 5 0 (global energy parameter E(1), with 5 other choices, LAPW)
0 -3.00 0.020 CONT 0 ENERGY PARAMETER for s, LAPW
0 0.30 0.000 CONT 0 ENERGY PARAMETER for s-local orbital, LAPW-LO
1 -1.90 0.020 CONT 0 ENERGY PARAMETER for p LAPW
1 0.30 0.000 CONT 0 ENERGY PARAMETER for p-local orbitals LAPW-LO
2 0.20 0.020 CONT 1 APW
0.20 3 0 (global energy parameter E(1), with 1 other choice, LAPW)
0 -0.90 0.020 STOP 0 LAPW
0 0.30 0.000 CONT 0 LAPW-LO
1 0.30 0.000 CONT 1 APW
K-VECTORS FROM UNIT:4 -9.0 2.0 69 emin/emax/nband
1.d-15 0.0 spro_limit for it.diag., lambda for it.diag
----- bottom of file -----

```

In **case.in1**, the $R_{\text{mt}} * K_{\text{max}} = 7.5$ is a parameter that determines the speed and precision of the calculations. R_{mt} is the smallest muffin-tin radius and K_{max} is the maximum (largest) wave vector used in the plane wave expansion of the wave-functions outside the muffin-tin spheres (In the expansion of the wave-function in terms of plane waves, in other words pseudopotential calculations, K_{max}^2 determines the cut-off energy in Ry, [see chapter 4]). The numerical values used for $R_{\text{mt}} * K_{\text{max}}$ (which is sometimes written as RK_{max}), depending on the basis set and the required precision, varies. In the APW+lo method, it is usually between 5 and 9. In the LAPW+LO method, it is chosen to be between 6 and 10. The units used for $R_{\text{mt}} * K_{\text{max}}$ are bohr * $\sqrt{\text{Ry}}$. The computational time of LAPW1 and the precision of the calculations increases with increasing the $R_{\text{mt}} * K_{\text{max}}$ parameter. The larger the value of $R_{\text{mt}} * K_{\text{max}}$, the higher the cut-off energy. The accuracy achieved by an $R_{\text{mt}} * K_{\text{max}} = 8$ in the LAPW method is equivalent to the same accuracy when $R_{\text{mt}} * K_{\text{max}} = 6.5$ or 7 in the APW+lo method.

The 0's and 1's in the fifth column from the left in **case.in1** are representative of the LAPW and APW basis sets respectively, in other words the manifestation of the mixed basis sets discussed in chapter 4 is realized in the **case.in1** input file. The numbers in the first column from the left represent the orbital angular momentum quantum number, l . The second column represents the average energies of the electrons within the related orbitals. In other words, one expects the average energies of the electrons within a particular orbital in a crystal to be around these values. The numbers in the third column represent energy increments, if it is set to 0, the default trial energy of line three in **case.in1** is used, for values other than zero a search for a resonance energy using this value is done. The radial function $u_l(r, E_l)$ up to the muffin-tin radius, R_{MT} varies with the energy. A typical case is schematically shown in figure 6.1.

At the bottom of the energy bands $u_l(r, E_l)$ has a zero slope which refers to a bonding state and a zero value at the top of the bands, which refers to an anti-bonding state. One can use E_l and search up and down in energy with increment de to find where $u_l(R_{\text{MT}}, E_l)$ will change sign. This value determines E_{top} . The same searching procedure can be done with slope to find E_{bottom} . The average of E_{top} and E_{bottom} determines E_l .

The 0 and 1 in the fifth column represent the LAPW and APW basis respectively. The choice depends on the specific l state of the atom and the radius of the corresponding atomic sphere compared to other atoms in the unit cell [1].

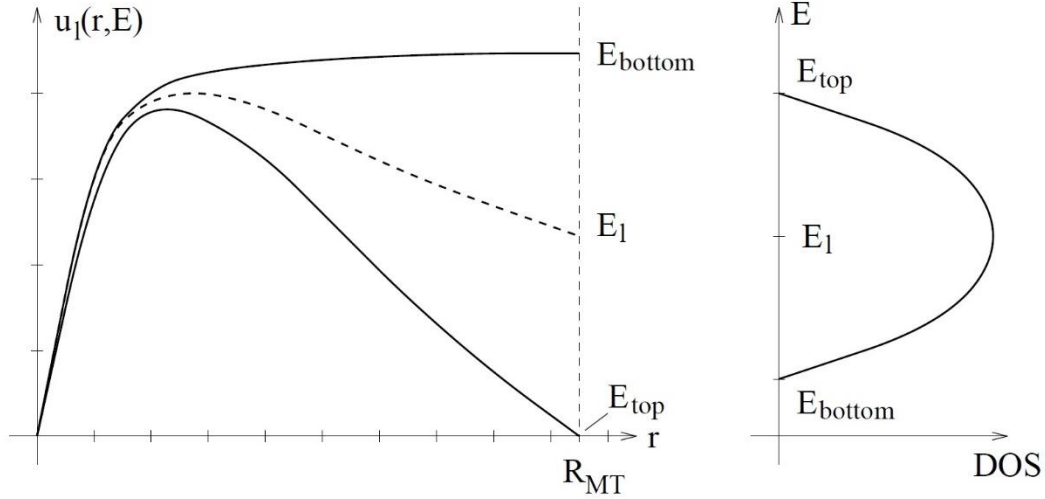


Figure A.1 Schematic dependence of DOS and $u_l(r, E_l)$ on energy [1].

A.2.4 LAPWSO

The LAPSWO program, evaluates the spin-orbit interaction in a second order variational method for the valence electrons within the muffin-tin spheres. This program uses the eigenvectors generated from LAPW1 in a scalar-relativistic scheme for the electrons within the muffin-tin spheres, while a non-relativistic method is used for the electrons in the interstitial region.

The inputs for the LAPWSO program are **case.struct**, **case.iso**, **case.energy**, **case.vsp**, and **case.vector** and the output files are **case.outputso**, **case.scfso**, and **case.vectorso** [Table 6.2].

This program adds the spin-orbit interaction as a perturbation term to the Hamiltonian. The resulting eigenvectors are stored in **case.vectorso**. The advantage of this method is that it decreases the cpu time for the calculations. The spin-orbit coupling results in non-zero matrix elements between spin-up and spin-down basis functions [1]. This means that in the case of spin-orbit interactions, the spin-up and spin-down are not independent. Thus, it is natural to consider both spin-up and spin-down by doubling the size of the Hamiltonian matrix. For large systems this option may be difficult. Therefore it is more convenient to use the perturbation method. In this method, LAPW1 solves the scalar-relativistic equations for spin-up and spin-down electrons separately without taking the spin-orbit interactions into account and stores the eigenvectors in the file **case.vector**. In the second stage, LAPWSO uses these generated eigenvectors as basis for the total Hamiltonian.

In order to consider spin-orbit interactions, it suffices to diagonalize the perturbation spin-orbit Hamiltonian matrix. The eigenvectors generated from LAPWSO are stored in the **case.vectorso** file. The elements of the diagonalized spin-orbit coupling matrix are smaller for lighter atoms but considerable for larger atoms. In principle, the number of these elements cannot be large due to the fact that the diagonalization is performed in the space of eigenvectors that result from the scalar-relativistic equation. This indicates that part of the relativistic effects such as the mass-correction and the Darwin term has already been considered in the relativistic equation. In order to complete the relativistic scalar space, one has to generate more eigenvectors from LAPW1. To do so, one must expand the energy window $E_{\max}$ sometimes as wide as 10 Ry. This increase in $E_{\max}$ would increase the cpu time. On the other hand, one must consider the energy convergence as well. Adding the $p_{1/2}$ basis to the radial wave-function in the semi-core region improves the expansion basis such that even with a smaller $E_{\max}$, an acceptable result is obtained. The reason why the cut-off energy decreases after adding the $p_{1/2}$ basis is that p wave-functions are almost zero near the nucleus. Thus attempts to complete the basis set in the scalar-relativistic space are usually made to generate these $p_{1/2}$ wave-functions. Therefore, if these wave-functions were generated earlier, there is no need to increase the cut-off energy.

The relativistic calculations apply only to the electrons inside the muffin-tin spheres. As a consequence, the results of the calculations will be highly dependent on the muffin-tin radii. Adding the $p_{1/2}$ basis improves the calculations by decreasing the dependence of the results to the muffin-tin radii.

Below an example for the **case.inso** input file is given.

```
----- top of file: case.inso -----
WFFIL
 4  0  0                      llmax, ipr, kpot
-10.0000  1.5000              Emin, Emax
  0  0  1                      h, k, l (direction of magnetization)
  2                      number of atoms with RLO
 1  -3.5      0.005 STOP      atom-number, E-param for RLO
 3  -4.5      0.005 STOP      atom-number, E-param for RLO
 1  2                      number of atoms without SO, atomnumbers
----- bottom of file -----
```

The full interpretation of the file is given in the WIEN2k user guide [1], and it is very similar to **case.in1**. The only main difference is in the fourth line, which determines the direction of the magnetic axis (in the file above, the magnetization is in the z direction). If the system is magnetic, the spin-orbit interaction along the magnetization direction is larger than the other directions. This reduces the point symmetry. For instance, from 48 in a cubic system to 16 in an orthorhombic system. The reduction of the symmetry should be done in the **case.struct** master file. This modification influences all of the calculations specifically the **case.klist**, **case.in2c**, **case.in1**, and **case.kgen**. The **case.in2** file is the input file for LAPW2 which will be discussed shortly (if one considers spin-orbit interactions, then the input file for LAPW2 should be **case.in2c**). The execution of LAPWSO is done by typing “**x lapwso**” in the command line.

A.2.5 LAPW2

The LAPW2 program uses the generated eigenvalues from LAPW1 and/or LAPWSO. The LAPW2 program uses these eigenvalues to generate the Fermi energy and the electronic charge density expansions. These electronic charge densities are expanded in terms of plane waves in the interstitial region and in terms of spherical harmonics in the muffin-tin spheres.

The input files for LAPW2 are **case.struct**, **case.vector**, **case.vsp**, and **case.energy**. The output files for LAPW2 are **case.output2**, **case.scf2**, **case.clmval**, **case.clmsc**, and **case.qtl** [Table 6.2].

This program also calculates the Pauli force correction and adds it to the forces that were evaluated previously on the site of the atomic nuclei. As in similar cases before, if the studied system lacks inversion symmetry, the program LAPW2C must be executed (of course, in order to run this program, one must have the input file **case.in2c**). Sometimes even if the system has inversion symmetry, one must run LAPW2C. The reason is that the eigenvectors generated from LAPWSO are always complex.

An example for the LAPW2 input file is given below.

```

----- top of file: case.in2 -----
TOT                               (TOT, FOR, QTL, EFG)
-1.2      32.000    0.5  0.05 1 (EMIN, # of electrons, ESEPERMIN, ESEPER0, iqtlsave)
TETRA      0.0      (EF-method (ROOT, TEMP, GAUSS, TETRA, ALL), value)
  0 0  2 0  2 2  4 0  4 2  4 4
  0 0  1 0  2 0  2 2  3 0  3 2  4 0  4 2  4 4
14.0      (GMAX)
FILE      (NOFILE, optional)
----- bottom of file -----

```

The parameter $G_{\max}$ determines the cut-off energy in terms of $(\text{Ry})^{1/2}$ for the potential and density expansions, outside the muffin-tin regions. $G_{\max}$ lies between 9 and 25. A full description of this parameter is given in [1].

The series of numbers in lines four and five of the file above represent the LM combinations for the expansions of potential and density of the two inequivalent atoms in the system. The choice of the LM combinations depends on the symmetry group of the system. Possible LM combinations for the cubic groups and for the non-cubic groups are given in tables 6.3 and 6.4.

Symmetry	LM combinations
23	0 0, 4 0, 4 4, 6 0, 6 4, -3 2, 6 2, 6 6, -7 2, -7 6, 8 0, 8 4, 8 8, -9 2, -9 6, -9 4, -9 8, 10 0, 10 4, 10 8, 10 2, 10 6, 10 10
M3	0 0, 4 0, 4 4, 6 0, 6 4, 6 2, 6 6, 8 0, 8 4, 8 8, 10 0, 10 4, 10 8, 10 2, 10 6, 10 10
432	0 0, 4 0, 4 4, 6 0, 6 4, 8 0, 8 4, 8 8, -9 4, -9 8, 10 0, 10 4, 10 8
-43M	0 0, 4 0, 4 4, 6 0, 6 4, -3 2, -7 2, -7 6, 8 0, 8 4, 8 8, -9 2, -9 6, 10 0, 10 4, 10 8
M3M	0 0, 4 0, 4 4, 6 0, 6 4, 8 0, 8 4, 8 8, 10 0, 10 4, 10 8

Table A.3 LM combinations of the cubic groups [1].

Symmetry	Coordinate axes	Indices of $Y_{\pm LM}$	crystal system
1	any	ALL ($\pm l, m$)	triclinic
-1	any	($\pm 2l, m$)	
2	$2 \parallel z$	($\pm 1, 2m$)	monoclinic
M	$m \perp z$	($\pm 1, l-2m$)	
2/M	$2 \parallel z, m \perp z$	($\pm 2l, 2m$)	
222	$2 \parallel z, 2 \parallel y, (2 \parallel x)$	($+2l, 2m$), ($-2l+1, 2m$)	orthorhombic
MM2	$2 \parallel z, m \perp y, (2 \perp x)$	($+1, 2m$)	
MMM	$2 \perp z, m \perp y, 2 \perp x$	($+2l, 2m$)	
4	$4 \parallel z$	($\pm 1, 4m$)	tetragonal
-4	$-4 \parallel z$	($\pm 2l, 4m$), ($\pm 2l+1, 4m+2$)	
4/M	$4 \parallel z, m \perp z$	($\pm 2l, 4m$)	
422	$4 \parallel z, 2 \parallel y, (2 \parallel x)$	($+2l, 4m$), ($-2l+1, 4m$)	
4MM	$4 \parallel z, m \perp y, (2 \perp x)$	($+1, 4m$)	
-42M	$-4 \parallel z, 2 \parallel x (m=xy \rightarrow yx)$	($+2l, 4m$), ($-2l+1, 4m+2$)	
4MMM	$4 \parallel z, m \perp z, m \perp x$	($+2l, 4m$)	
3	$3 \parallel z$	($\pm 1, 3m$)	rhombohedral
-3	$-3 \parallel z$	($\pm 2l, 3m$)	
32	$3 \parallel z, 2 \parallel y$	($+2l, 3m$), ($-2l+1, 3m$)	
3M	$3 \parallel z, m \perp y$	($+1, 3m$)	
-3M	$-3 \parallel z, m \perp y$	($+2l, 3m$)	
6	$6 \parallel z$	($\pm 1, 6m$)	hexagonal
-6	$-6 \parallel z$	($+2l, 6m$), ($\pm 2l+1, 6m+3$)	
6/M	$6 \parallel z, m \perp z$	($\pm 2l, 6m$)	
622	$6 \parallel z, 2 \parallel y, (2 \parallel x)$	($+2l, 6m$), ($-2l+1, 6m$)	
6MM	$6 \parallel z, m \parallel y, (m \perp x)$	($+1, 6m$)	
-62M	$-6 \parallel z, m \perp y, (2 \parallel x)$	($+2l, 6m$), ($+2l+1, 6m+3$)	
6MMM	$6 \parallel z, m \perp z, m \perp y, (m \perp x)$	($+2l, 6m$)	

Table A.4 LM combinations and the local coordinate system of non-cubic groups [1].

The execution of LAPW2 is done by invoking “**x lapw2**” in the command line.

A.2.6 LAPWDM

The LAPWDM program generates the density matrix for the orbital dependent potentials. The ORB program calculates the orbital potentials from the density matrices. However, the ORB program runs before the LAPWDM program. Thus, in the first cycle of the self-consistent cycles, the density matrix has not been generated yet. To overcome this problem, one can produce the density matrix before the SCF cycles by invoking “**x lapwdm (-up/dn)**” in the command line. In the next cycles, the density matrix is re-generated until convergence is achieved.

The LAPWDM program can evaluate the orbital and dipolar hyperfine fields. This program can also calculate the average value of the operator X . The operator X must have non-zero values inside the muffin-tin spheres and its angular and radial parts can be separated in the form of $X = X_r(r)X_{ls}(l, s)$.

The input files for LAPWDM are **case.struct**, **case.indm**, **case.vsp**, **case.vector(so)**, **case.inso**, **case.energy**, and **case.weight**. The output files of LAPWDM are **case.outputdm**, **case.scfdm**, and **case.dmat** [Table 6.2]. The output file, **case.dmat** contains the density matrix. The sum of the diagonal elements of the density matrix gives the number of electrons in the orbitals.

An example for the LAPWDM input file is given below

```

----- top of file: case.indm -----
-9.          Emin cutoff energy
 1          number of atoms for which density matrix is calculated
 1  1  2          index of 1st atom, number of L's, L1
 0  0          r-index, (l,s)-index
----- bottom of file -----

```

which shows that for the d orbital of the first atom, the density matrix must be calculated. In the fourth line of the file above, the radial, angular, and the average value of the X operator are defined as below.

- RINDEX=0 LSINDEX=0: the density matrix is calculated (this is needed for LDA+U calculations)
- RINDEX=1 LSINDEX=1: $\langle X \rangle$ is number of electrons inside the atomic sphere (for test)
- RINDEX=2 LSINDEX=1: $\langle X \rangle$ is the $\langle 1/r^3 \rangle$ expectation value inside the atomic sphere
- RINDEX=1 LSINDEX=2: $\langle X \rangle$ is the projection of the electronic spin inside the atomic sphere (must be multiplied by $g=2$ to get the spin moment)
- RINDEX=1 LSINDEX=3: $\langle X \rangle$ is the projection of the orbital moment inside the atomic sphere (in case of SO-calculations WITHOUT LDA+U)
- RINDEX=3 LSINDEX=3: $\langle X \rangle$ is the orbital part of the hyperfine field at the nucleus (for a converged calculation at the very end)
- RINDEX=3 LSINDEX=5: $\langle X \rangle$ is the spin dipolar part of the hyperfine field at the nucleus (for a converged calculation at the very end)

For further examples on the LAPWDM, the reader is referred to [1].

A.2.7 LCORE

The LCORE program is a modified version of an atomic code. This code uses the LSDA approximation in Dirac's equation to solve for the core electrons relativistically (considering the spin-orbit interaction) or non-relativistically, if it is chosen in the **case.struct** file.

The input files for the LCORE are **case.struct**, **case.inc**, and **case.vsp**. The output files for LCORE are **case.outputc**, **case.scfc**, and **case.clmcore**. The spherical part of the potential generated by LAPW0 in **case.vsp** in each cycle, is the input for LCORE. LCORE produces the eigenvalues, **case.clmcore**, densities related to the core electrons, and the contribution of core electrons to the atomic forces.

An example for the LCORE input file is given below.

```

----- top of file: case.inc -----
 4 0.0 0      # of orbitals,  shift of potential, print switch
 1,-1,2      n (principal quantum number), kappa, occup. number
 2,-1,2      2s
 2,-2,4      2p
 2, 1,2      2p*
 1  0.0      # of orbital of second atom
 1,-1,2      1s
 0           end switch
----- bottom of file -----

```

The structure of the input file `case.inc` is similar to the main input file for the LSTART program, **case.inst**. The LCORE and LSTART have the same atomic origins and are very similar to each other. Here, we only state the difference between the input for LSTART and LCORE. The shift of the potential energy in the first line (0.0) is considered for the appliance of the open-core method. If one uses the open-core method, a non-zero value for this shift is obtained. Apart from this, the rest of the input file is exactly the same as the input file for LSTART (in **case.inst** the electrons with opposite spins were distinguished from one another, whereas in **case.inc** the spins are not resolved).

For further reading, the reader is referred to the user guide [1].

A.2.8 MIXER

The MIXER program combines the electron densities of the core, semi-core, and valence states. These electron densities are summed and a new total density is obtained. Other than the hydrogen atom which has only a single valence electron, other atoms depending on the choice of the separation energy may or may not have core electrons. This program checks that the densities are normalized and if not, by adding a constant density to the interstitial region, normalizes them.

Using new densities in a cyclic process, such as self-consistent cycles, may result either in very long convergence times or no convergence at all. In WIEN2k, the stabilization of the self-consistent cycles is obtained by mixing the input and output densities to generate a new input density. Two methods of mixing are available in WIEN2k: the Pratt method and the Broyd method. The Broyd method is recommended for magnetic systems.

A comparison between the input files **case.inorb** and **case.inm** shows that in systems with orbital potentials, the mixing process happens twice. Once, by the ORB program and once by the MIXER program.

For further information on the mixing schemes the reader is referred to the user guide [1].

A.3 Access to the calculated quantities

After the successful convergence of the SCF cycles all relevant physical quantities that have been calculated are stored in the file **case.scf**. The physical quantities and parameters that were of interest in this thesis were mainly the hyperfine-interaction parameters, the magnetic moments, and the total ground state energy of the studied systems.

The (numerical values) of the calculated physical quantities of interest in the **case.scf** file are labeled, and one can access them by using the following abbreviations:

ENE: The total energy in Rydberg units

DIS: Charge distance between last two iterations

FER: The Fermi energy

GAP: The energy gap (only for insulators)

FORXX: Force on atom XX in $\frac{\text{mRy}}{\text{Bohr}}$ units (XX indicates the number related to the inequivalent atoms which is given in the **case.struct** file, for instance 02 is the 2nd, and 16 is the 16th atom and so forth).

EFGXX: Electric field gradient (V_{zz}) for atom labeled XX

ETAXX: The asymmetry parameter (η) for atom labeled XX

RTOXX: Electronic charge density at the nucleus of atom XX (The numerical value of this quantity is used to calculate the isomer shift).

MMTOT: The magnitude of the net magnetic moment in the unit cell

MMIXX: The magnetic moment of atom labeled XX

MMINT: The total magnetic moment in the interstitial region

ORBXX: Orbital magnetic moment of atom labeled XX

HFF: Hyperfine magnetic field (The core contribution) of atom XX in kOe.

The rather compact introduction to the WIEN2k code presented here is only a short review of the important concepts embedded in this rich code. It is recommended for the interested reader to refer to the user guide [1] to understand and develop the techniques for calculating the physical properties of solids.

References

- [1] P. Blaha, K. Schwarz, G. Madsen, D. Kvasnicka and J. Luitz, WIEN2k An Augmented PlaneWave Plus Local Orbitals Program for Calculating Crystal Properties (2014).
- [2] J. P. Perdew, K. Burke, and Y. Wang, Phys. Rev. B, 54 (1996) 23.