

Mössbauer Spectroscopy and Magnetic Studies of EuPdGe_3 , $\text{Al}_{13}\text{Fe}_4$, and FeNiSn .

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Abstract

In this thesis the result x-ray diffraction, magnetic susceptibility, magnetization, and Mössbauer spectroscopy measurements of EuPdGe_3 , $\text{Al}_{13}\text{Fe}_4$, and FeNiSn are reported.

The compound EuPdGe_3 crystallizes in the BaNiSn_3 -type tetragonal structure (space group $I4mm$) with the lattice constants $a = 4.4457(1) \text{ \AA}$ and $c = 10.1703(2) \text{ \AA}$. The results are consistent with EuPdGe_3 being an antiferromagnet with the Néel temperature $T_N = 12.16(1) \text{ K}$ and with the Eu spins $S = 7/2$ in the ab plane. The temperature dependence of the magnetic susceptibility above T_N follows the modified Curie-Weiss law with the effective magnetic moment of $7.82(1) \mu_B$ per Eu atom and the paramagnetic Curie temperature of $-5.3(1) \text{ K}$ indicative of dominant antiferromagnetic interactions. The $M(H)$ isotherms for temperatures approaching T_N from above are indicative of dynamical short-range antiferromagnetic ordering in the sample. The temperature dependence of the hyperfine magnetic field follows a $S = 7/2$ Brillouin function. The principal component of the electric field gradient tensor is shown to increase with decreasing temperature and is well described by a $T^{3/2}$ power-law relation. The Debye temperature of EuPdGe_3 determined from the Mössbauer data is $199(2) \text{ K}$.

The compound $\text{Al}_{13}\text{Fe}_4$ crystallizes in the monoclinic space group $C2/m$, in which Fe atoms are located at five inequivalent crystallographic sites, with the lattice parameters $a = 15.503(2) \text{ \AA}$, $b = 8.063(2) \text{ \AA}$, $c = 12.464(2) \text{ \AA}$, and $\beta = 107.71(2)^\circ$. It is demonstrated that zero-field Mössbauer spectra can be decomposed into three quadrupole doublets. With the aid of the calculated electric field gradient (EFG) parameters we show that the first doublet results from one Fe site, the second doublet is due to two other Fe sites, and the third doublet originates from the last two Fe sites. We find that the shape of the Mössbauer spectrum of $\text{Al}_{13}\text{Fe}_4$ measured in an external magnetic field of 90 kOe can be accounted for with five component subspectra generated using the calculated

EFG parameters at five inequivalent Fe sites. The quadrupole splittings corresponding to three component doublets are shown to increase with decreasing temperature and are well described by a $T^{3/2}$ power-law relation. The Debye temperature of $\text{Al}_{13}\text{Fe}_4$ is found to be 383(3) K. We find a pseudogap in the density of states (DOS), with a width of ~ 0.2 eV, that is centered 0.1 eV above the Fermi energy. The finite DOS at the Fermi energy confirms good metallicity of $\text{Al}_{13}\text{Fe}_4$. The $1/T$ -like dependence of the magnetic susceptibility shows that $\text{Al}_{13}\text{Fe}_4$ is a paramagnet.

The compound FeNiSn crystallizes in the ZrBeSi -type crystal structure (space group $P6_3/mmc$) with the lattice constants $a = 4.1329(1)$ Å and $c = 5.1912(2)$ Å. It is a ferromagnet with the Curie temperature $T_C = 1024(10)$ K. Evidence is provided for a possible phase separation in the studied compound, into a majority magnetic phase and a minority, nanoscale, disordered phase with the corresponding iron magnetic moments at 4.6 K of 2.39(1) and 1.17(1) μ_B . It is demonstrated that FeNiSn decomposes at a temperature significantly below T_C when it is annealed in vacuum for about 30 hours. The Debye temperature of FeNiSn is found to be 445(6) K.

Statement of originality and contributions of co-authors

To the best of his knowledge, the author states that the three research projects on EuPdGe_3 , $\text{Al}_{13}\text{Fe}_4$, and FeNiSn compounds described in this Master's thesis constitute original research in the field of condensed-matter physics. In the following paragraphs, I provide detailed information on contributions of each participant in these projects.

Chapter 5. a) I synthesized the EuPdGe_3 compound, carried out all X-ray diffraction (XRD) and ^{151}Eu Mössbauer experiments, fitted all the XRD, Mössbauer, and magnetic data to appropriate models, and wrote the first draft of the paper. b) K. Al-Qadi participated in the sample synthesis. c) Z.M. Stadnik suggested the project and wrote the final draft of the paper. d) J. Przewoźnik collected magnetic susceptibility and magnetization data.

Chapter 6. a) I conducted all XRD and ^{57}Fe Mössbauer experiments, evaluated XRD, Mössbauer, and magnetic data, and wrote the first draft of the paper. b) F. Nejdassattari carried out calculations of the density of states and of the electric field gradient at the Fe and Al sites. c) Z.M. Stadnik designed the project and wrote the final version of the paper. d) J. Przewoźnik measured magnetization and magnetic susceptibility data.

Chapter 7. a) I conducted all XRD and ^{57}Fe Mössbauer experiments, evaluated XRD, Mössbauer, and magnetic data, and wrote the first draft of the manuscript. b) Z.M. Stadnik suggested the project and wrote the final version of the manuscript. c) J. Przewoźnik made magnetization and magnetic susceptibility measurements.

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Chapter 1: Introduction

1.1: Motivation

The long history of condensed-matter physics is marked with numerous discoveries and developments of new materials and their novel applications. One class of new materials that has exhibited a wide range of physical properties and large application potential is that of intermetallic compounds. These are solid phases that contain two or more metallic elements. Their physical properties often differ markedly from those of their constituents. A large number of binary, ternary, and even quaternary intermetallic compounds have been investigated and the results of some of these investigations have been applied to our daily lives.

This thesis is an experimental study of structural, hyperfine interaction, and magnetic properties of three intermetallic compounds: EuPdGe_3 , $\text{Al}_{13}\text{Fe}_4$, and FeNiSn . The choice of these compounds was dictated either by their novelty (The compound EuPdGe_3 was synthesized only two years ago and most of its physical properties have not been investigated; the compound FeNiSn was synthesized a long time ago but most of its physical properties were never studied) or the existence of a long-standing controversy concerning the interpretation of Mössbauer spectra ($\text{Al}_{13}\text{Fe}_4$).

The newly synthesized EuPdGe_3 contains an Eu constituent. It is known that Eu carries a well-localized magnetic moment in many Eu-containing compounds. The question then arises as to the type of magnetic ordering of the Eu magnetic moments (ferromagnetic, antiferromagnetic, or ferrimagnetic) in this compound. If EuPdGe_3 exhibits long-range magnetic ordering, what is the magnetic ordering temperature, that is, the temperature below which the magnetic order sets in? Eu atoms in a Eu-containing compound are generally either in a divalent or trivalent oxidation state; they may also exhibit valence fluctuations with changing temperature. The question to be addressed then is what is the oxidation state of Eu atoms in EuPdGe_3 in the temperature range 2–297 K. Hyperfine-interaction parameters (isomer shift, electric field gradient, hyperfine magnetic field) determined from local probe measurements (here, from Mössbauer spectroscopy measurements) usually change with temperature. What is the nature of the temperature dependences of these parameters? And finally, a prerequisite to study physical properties of any

compound is the knowledge of its precise crystal structure. All the questions mentioned above will be answered by analyzing and interpreting the data obtained from X-ray diffraction, ^{151}Eu Mössbauer spectroscopy, and magnetic measurements.

The Al-rich Fe aluminide $\text{Al}_{13}\text{Fe}_4$ has a complex atomic structure. Iron atoms are located in this compound at five inequivalent crystallographic sites. As the point symmetries of these five sites are lower than cubic, one could expect that the ^{57}Fe Mössbauer spectrum of $\text{Al}_{13}\text{Fe}_4$ should be a superposition of five quadrupole doublets. The experimental ^{57}Fe Mössbauer spectrum of $\text{Al}_{13}\text{Fe}_4$ exhibits a three-valley structure and has been interpreted in the literature in two qualitative, controversial ways. The first interpretation involves the assumption that the ^{57}Fe Mössbauer spectrum of $\text{Al}_{13}\text{Fe}_4$ is a superposition of three single-line components. Clearly, such an interpretation has no justification (component spectra should be in a form of quadrupole doublets and there should be five such components). The second interpretation is based upon fitting the experimental spectrum with two quadrupole doublets. The justification of such a fit is based upon a purely qualitative argument, which is shown in this thesis to be false, that the first doublet component originates from Fe atoms located at four crystallographic sites and the second doublet component originates from Fe atoms at the fifth site. One of the objectives of this thesis is to resolve the controversy just described. This has been achieved through measuring ^{57}Fe Mössbauer spectra of $\text{Al}_{13}\text{Fe}_4$ at different temperatures (in the temperature range 4–295 K) and the spectrum at helium temperature in an external magnetic field of 90 kOe, and interpreting these spectra with the aid of *ab initio* electric field gradient calculations. The temperature dependences of the electric field gradient and the absorption spectra were determined and explained within the existing theories. In addition, the magnetic ordering in $\text{Al}_{13}\text{Fe}_4$ was studied through the magnetization and magnetic susceptibility measurements. And finally, the issue of the electronic structure of $\text{Al}_{13}\text{Fe}_4$ was investigated by calculating the energy band structure and the total density of states.

The intermetallic compound FeNiSn contains two magnetic elements, Fe and Ni, and therefore is expected to be magnetically ordered. The problem addressed in this thesis is the nature of this magnetic ordering. What is the magnetic moment carried by Fe atoms? This important question is answered by measuring and analyzing ^{57}Fe Mössbauer spectra of FeNiSn . What is the magnetic ordering temperature of the compound? This question is addressed by carrying out measurements with two different experimental techniques in a very wide temperature range

5–1024 K. And finally, the problem of lattice vibrations in this compound is addressed by studying the temperature dependence of the isomer shift.

1.2: Thesis outline

The remainder of this thesis includes six chapters. Prior to describing the results and conclusions, the theoretical background relevant to the physical problems addressed in this thesis is described in chapter two. In chapter three, experimental details are presented. Chapter four contains general discussion and conclusions, which integrates the material presented in chapters five, six, and seven. Chapter five is an article on EuPdGe_3 that was published in *J. Alloys Comp.* **613**, 344 (2014). Chapter six is an article on $\text{Al}_{13}\text{Fe}_4$ that was published in *J. Alloys Comp.* **619**, 839 (2015). And chapter seven is a manuscript of an article on FeNiSn that will be published.

Chapter 2: Theoretical background

2.1: X-ray powder diffraction and Rietveld refinement

2.1.1: X-ray powder diffraction

X-ray powder diffraction is mainly used to identify the structure of compounds based on their diffraction pattern. X-ray radiation can be identified in the short-wavelength and (high-energy) range of the electromagnetic spectrum. The energy of x-rays is in the range of 0.1-100 keV, and the wavelength is in the range of 0.1-100 Å as is shown in Fig. 2-1.

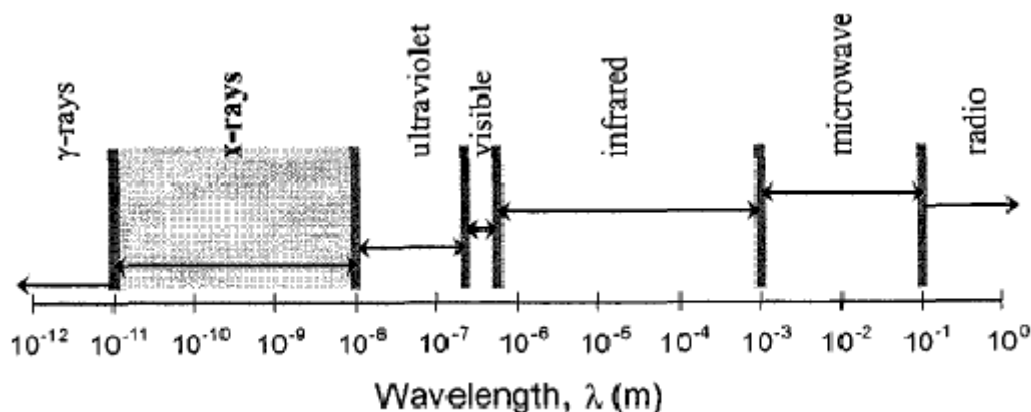


Fig. 2-1: The spectrum of the electromagnetic waves. The range of typical x-ray wavelengths is shaded; reproduced from reference [1].

Diffraction happens when coherent radiation is scattered from a periodic array of objects, and constructive interference at specific angles is created.

The mechanism of diffraction can be described as follows. When there are many crystallographic planes which can be described by Miller indices (hkl) (Fig. 2-2), the x-ray beams will reflect from each of the planes in the family. The initial waves are considered to be in phase with one another, and the angle of incidence must be equal to the reflection angle. Fig. 2-2 shows that the reflection of the incident wave from plane 2 travels a longer distance (ABC) than from the first plane. Also, the wave that is reflected from plane 3 travels a farther distance (DEF) than the one reflected from plane 2. As a result, there would be interference on all these waves which are phase retarded with respect to the first wave. It is already known from plane geometry that when

the distance of ABC is equivalent to the wavelength λ then the distance of DEF will be equal to 2λ , and there will be constructive interference as the reflection from all the planes are in phase. The previous process is called diffraction. Here the Bragg equation is valid and can be easily calculated as is shown in Fig. 2-2 [2]:

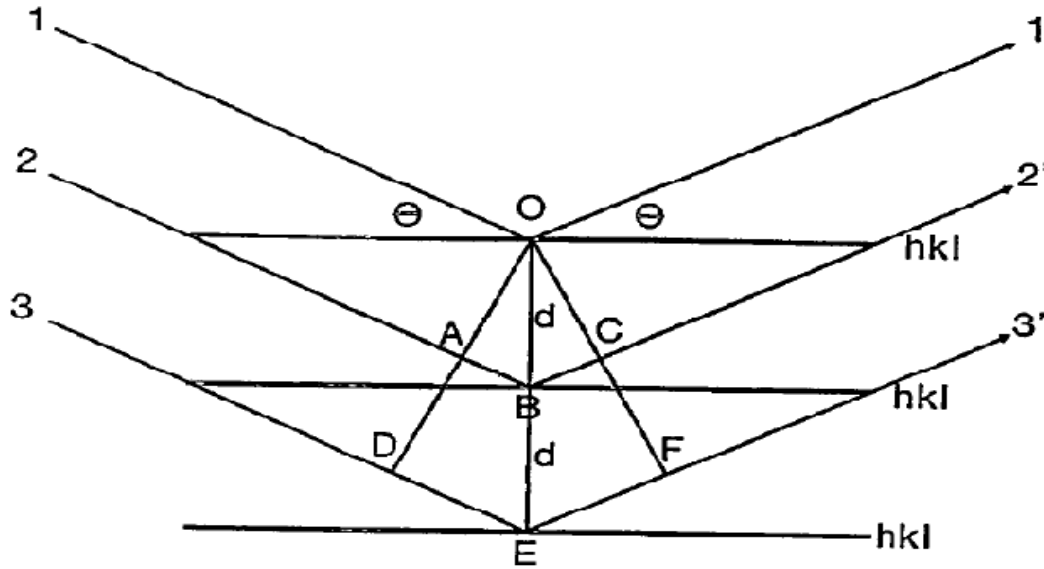


Fig. 2-2: Three incident x-rays are reflected from three successive planes of the family hkl . The path difference of each ray is an essential parameter for the resulting interference; reproduced from reference [2].

$$2d_{hkl} \sin \theta_{hkl} = n\lambda, \quad (2 - 1)$$

where n is an integer known as the order of diffraction, d_{hkl} is the distance between planes (hkl) and θ_{hkl} is the incident angle.

Diffraction is explained well by understanding the Ewald's sphere construction. If an incident wave has a certain propagation vector $\mathbf{k}_0$ and a wavelength λ , the magnitude of $\mathbf{k}_0$ is $|\mathbf{k}_0| = 1/\lambda$. When the primary wave scatters elastically, the magnitude of the wavelength remains constant. Therefore, the scattered wave is described by a different wave vector $\mathbf{k}_1$, which has the same length as $\mathbf{k}_0$, so $|\mathbf{k}_0| = |\mathbf{k}_1| = 1/\lambda$.

In reciprocal space, the end of $\mathbf{k}_0$ overlaps with the origin of the reciprocal lattice. When the end of $\mathbf{k}_1$ overlaps with a point on the reciprocal lattice, the condition of constructive interference is satisfied. As $\mathbf{k}_0$ and $\mathbf{k}_1$ have identical length, and their ends are equal distances from a common reciprocal space point, so they will span a sphere in three dimensions in k space. The sphere is called Ewald's sphere, and the radius of the sphere is $1/\lambda$. Fig. 2-3 shows that diffraction can happen when a reciprocal lattice point interconnects with the surface of the Ewald's sphere.

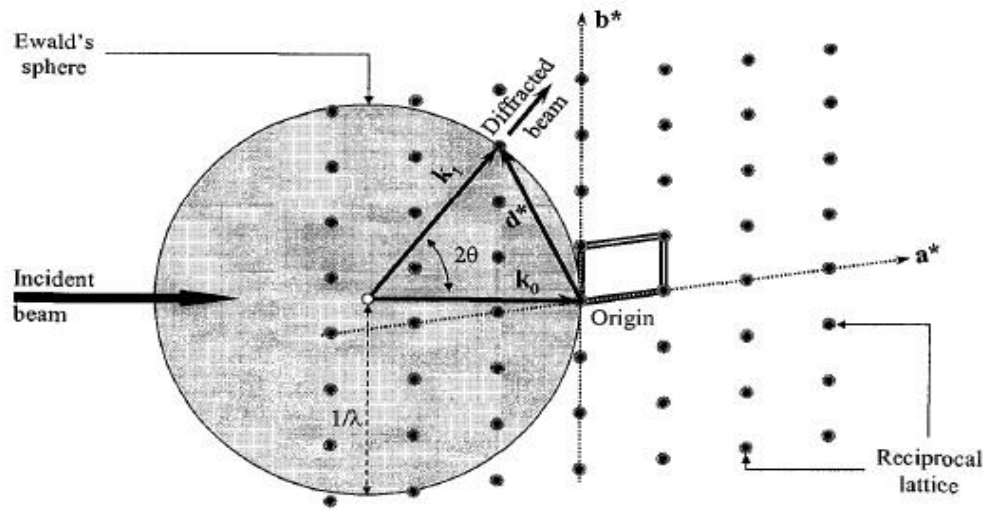


Fig. 2-3: The visualization of diffraction using the Ewald's sphere with radius $1/\lambda$ and the two-dimensional reciprocal lattice with unit vectors $\mathbf{a}^*$ and $\mathbf{b}^*$; reproduced from reference [1].

In the case of powder diffraction, as is shown in Fig. 2-4, there will be many grains, oriented randomly, that are irradiated with a monochromatic beam. In order to have constructive interference in a particular direction the incident wavevector $\mathbf{k}_0$ should be perpendicular to the family of planes separated by distance d_{hkl} , and the diffracted wavevector $\mathbf{k}_1$ will end up at the surface of the Ewald's sphere centered at the head of the cone (shaped by $\mathbf{k}_0$ and $\mathbf{k}_1$).

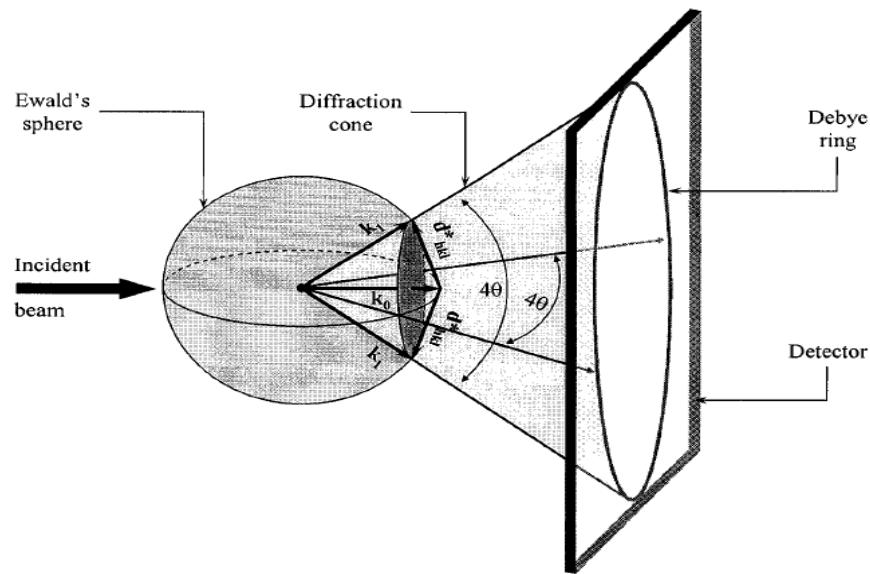


Fig. 2-4: The origin of the powder diffraction comes as a result of the infinite number of the completely randomly oriented reciprocal lattice vectors d^*_{hkl} forming a circle with their ends on the surface of the Ewald's sphere, thus producing the powder diffraction cone and the corresponding Debye ring on the detector; reproduced from reference [1].

In the case in which thousands of randomly oriented crystallites exist, many rings that are formed by the intersections of the cones with the planes of the detector with different intensities and diameters will be observed. These rings are known as Debye rings, as is shown in Fig. 2-5.

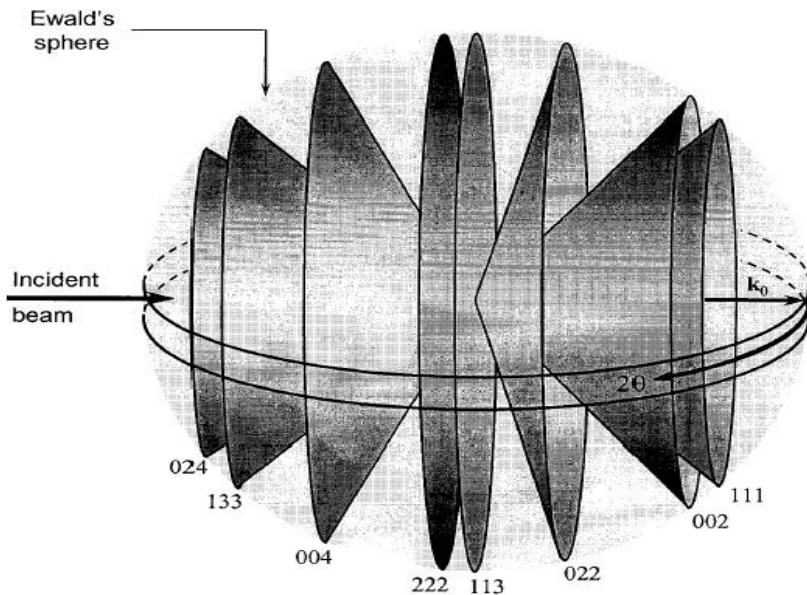


Fig. 2-5: The schematic of the powder diffraction cones produced by a polycrystalline sample. The difference in the relative intensities of various Bragg peaks (different cones) are not discriminated. Each cone is marked with the corresponding triplet of Miller indices; reproduced from reference [1].

Finally, a typical plot of the relative intensities against the scattering angle at different planes of a powder sample of copper is shown Fig. 2-6.

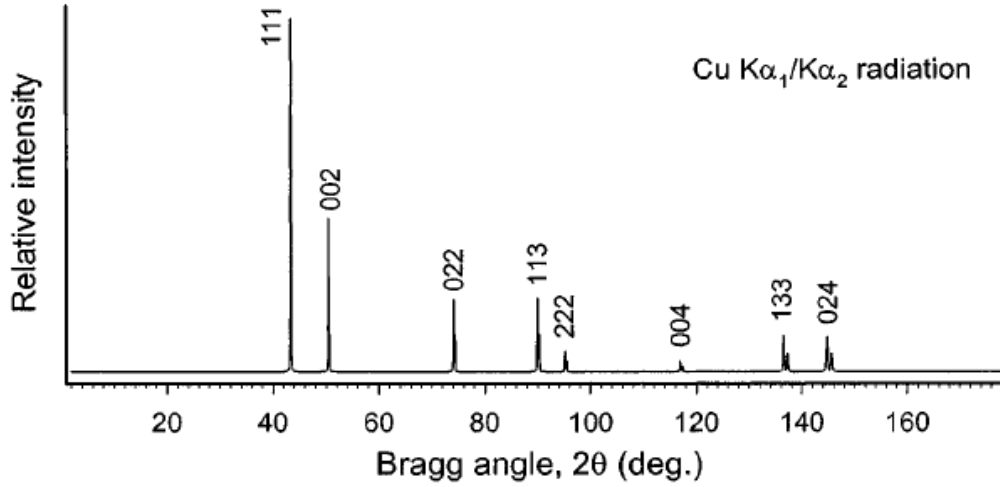


Fig. 2-6: The simulated powder diffraction pattern of copper; reproduced from reference [1].

2.1.2: Rietveld refinement

The Rietveld method, also known as the whole-profile method, is used as a data analysis technique to refine and confirm the structural information of the crystalline sample and to enhance the x-ray powder diffraction spectrum by eliminating device related errors from it. The fitting begins when the program generates the crystal structure peak intensities and profiles. Then the basic refinement is done by calculating the least squares refinement residual S_y defined by [2]:

$$R = \sum_j w_i (I_{j(o)} - I_{j(c)})^2, \quad (2-2)$$

where w_i is the reciprocal of I_j , $I_{j(o)}$ is the observed intensity, $I_{j(c)}$ is the calculated intensity. It should be noted that in the formula above, the sum runs over all data points j . As the value of R gets smaller, the data resembles the theoretical pattern better.

The Rietveld refinement analysis proceeds in a few steps [2]: data collection, background determination, peak-shape selection, profile parameters refinement and structural parameters refinement. We take a look at each of these stages separately.

2.1.2.1: Data collection

The most used device to collect x-ray spectra for further analyses is the x-ray powder diffractometer based on Bragg-Brentano geometry. To achieve data accuracy, some factors must be controlled. These are:

- a) The mechanical precision of the 2θ values of the diffractometer is a critical parameter to get high quality raw spectra. Although the precision of 2θ is determined by the manufacturer, the precision of the 2θ values can be improved by using mathematical techniques aimed to improve the quality of the intensity spectrum.
- b) Signal-to-noise-ratio (SNR). Automatic divergence slits are used in modern labs to improve the SNR.
- c) Thickness of the pulverized sample. Because x-ray penetration depths are different from sample to sample, in order to ensure the exact 2θ geometry, the thickness of the pulverized sample must be calculated carefully. Experimental problems, such as orientation of a sample grain which so often lead to incorrect intensity measurements are solved, or corrected, by rotating the sample while taking the measurement.

2.1.2.2: Background determination

The spectrum background results from different causes such as x-ray sources, the sample tray or environmental interferences. A fitted empirical function for the specific background can be used to remove the background from the raw spectrum.

2.1.2.3: Peak-shape selection

Peak shapes vary with of the structure of the sample, the type of lab instrument used (radiation source, slits sizes) and the 2θ geometry. The pseudo-Voigt approximation of a Voigt function is the commonly used peak-shape for x-ray analysis. In the Rietveld refinement technique, the researcher freely chooses the peak shape function. In order to attain the right desired shape and relevant parameters, a trial and error method can be used on the pool of available peak functions.

2.1.2.4: Profile parameters refinement

In the case of incompleteness of the structural model, the difference between observed intensities and theoretical intensities could be arbitrarily large. To deal with this potential problem, one can employ the so-called structure-free approach [2]. The improvement process involves a

refinement of the unit cell parameters and the 2θ correction factors. When the lattice parameters and 2θ are in accordance, the full width at half maximum (FWHM) of the Gaussian component is determined by an equation proposed by Caglioti *et al.* [2], [3]:

$$\text{FWHM}^2 = U \tan^2 \theta + V \tan \theta + W. \quad (2 - 3)$$

The Lorentzian component is written as:

$$\text{FWHM} = X \tan \theta + Y / \cos \theta. \quad (2 - 4)$$

where X and Y are the Lorentzian half width parameters. It should be noted that the Gaussian parameters U, V, and W are subjected to constraints under some circumstances in order to avoid nonphysical results.

2.1.2.5: Structural parameters refinement

Structural parameters refinement is performed by generating a difference Fourier map which represents a difference electron density. This is useful in the case of an incomplete structural model and missing atomic positions. The difference electron density is obtained by subtracting the electron density generated from the initial model from the one obtained from observed experimental spectrum. The process of refinement compares the generated profiles with the experimental ones using the least-squares residual functions. The least-squares residual functions are used to refine the specified parameters by minimizing the difference between the generated profiles and the experimental spectrum. The factor used to determine the quality of the refinement is GOF (goodness of the fit). The process of refinement converges at each step, and the GOF is smaller than the one obtained at the previous stage. The range of parameters is determined by a set of constraints on the possible values that may affect relative peak intensities. One example is the thermal value (changes in T will result of different intensities). Keeping the previous parameters under control prevents unrealistic results such as a negative value for the square of a real variable.

2.2: Magnetic properties of solids

2.2.1: Introduction

The solutions for Schrodinger's equation provide valuable information regarding the atomic energy levels. These states can be characterized by four quantum numbers:

1. Principal quantum numbers n : It gives the energy of the shell. Electrons in shells with total quantum numbers of $n = 1, 2$ and 3 are referred to as occupying K, L and M shells, respectively.
2. The orbital angular momentum quantum number l : It describes the magnitude of angular momentum of the orbital motion. The angular momentum $|\vec{l}|$ can take values equal to $\hbar\sqrt{l(l+1)}$. Here $\hbar = h/2\pi$, where h is Planck's constant and l can take different values depending on the shape of the orbit. The electrons with $l = 0, 1, 2, 3$ and 4 are referred to as s, p, d, f and g electrons, respectively.
3. The magnetic quantum number m_l : It describes the component of the orbital angular momentum $\vec{l}$ along a particular direction. The number m_l can take values equal to $m_l = -l, -l+1, \dots, l-1, l$.
4. The spin quantum number m_s : It describes the component of electron spin along a particular direction namely the z direction. m_s only has two possible values, either $\frac{1}{2}$ or $-\frac{1}{2}$.

It is important here to take care of Pauli's exclusion principle which states that no more than one electron can occupy the same quantum state. Also, it should be understood that an electron with orbital angular momentum $\vec{l}$ has a magnetic moment [4]:

$$\vec{\mu}_l = -\frac{|e|\hbar}{2m}\vec{l} = -\mu_B\vec{l}, \quad (2-5)$$

where μ_B is the Bohr magneton, e is the electron charge, and m is the electron mass. Similarly, the associated magnetic moment that comes with spin angular momentum is [4]:

$$\vec{\mu}_s = -g_e\mu_B\vec{s}, \quad (2-6)$$

where g_e is the spectroscopic splitting factor.

The energy (Hamiltonian) of the magnetic moment $\vec{\mu}$ in magnetic field $\vec{B}$ is [4]:

$$H = -\vec{\mu} \cdot \vec{B}. \quad (2-7)$$

Furthermore, in the absence of a magnetic field the states are equal in energy. The study of the electrons' orbital angular momenta together with the spin angular momenta and their interaction with each other plays an important role in understanding the atomic origin of magnetism. The orbital angular momentum of an atom is given by [4]:

$$\vec{L} = \sum_i \vec{l}_i, \quad (2-8)$$

where $\vec{L}$ represents the atomic orbital angular momentum, and i sums over individual electrons in the atom. The spin angular momentum for all electrons is given by [4]:

$$\vec{S} = \sum_i \vec{s}_i, \quad (2-9)$$

where $\vec{S}$ is the spin angular momentum of the atom.

The resultants $\vec{S}$ and $\vec{L}$ can be coupled to obtain the angular momentum of an atom. One such method to combine $\vec{S}$ and $\vec{L}$ is known as Russell-Saunders coupling. The total angular momentum of an atom, $\vec{J}$, is defined as [4]:

$$\vec{J} = \vec{L} + \vec{S} \quad (2-10)$$

The range of values of $\vec{J}$ is:

$$|\vec{L} - \vec{S}| \leq \vec{J} \leq |\vec{L} + \vec{S}|$$

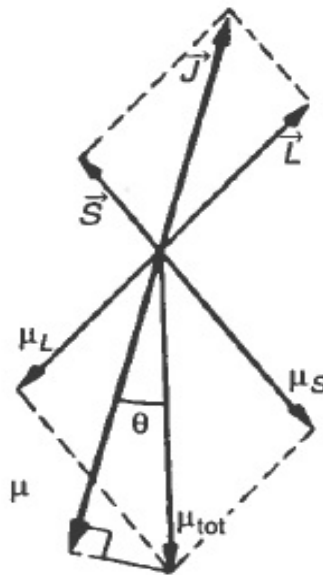


Fig. 2-7: Spin orbital interaction between the angular momenta $\vec{S}$ and $\vec{L}$; reproduced from reference [4].

Fig. 2-7 depicts the interaction between $\vec{S}$ and $\vec{L}$, where μ_s is the magnetic moment due to the spin angular momentum, μ_L is the magnetic moment for the orbital angular momentum, $\vec{\mu}_{tot} = \vec{\mu}_L + \vec{\mu}_S$, and the magnetic moment $\mu = \mu_{tot} \cos \theta = -\mu_B g J$ [4]. Here θ is the angle between $\vec{\mu}$ and $\vec{\mu}_{tot}$, and g is Landé's spectroscopic factor given by [4]:

$$g = \frac{1 + J(J + 1) + S(S + 1) - L(L + 1)}{2J(J + 1)}. \quad (2 - 11)$$

There are two types of magnetic moments: permanent and temporary (induced by an external field). When an external magnetic field is applied to an atom, magnetic dipole moments can be induced. In the presence of a magnetic field, the elementary magnetic dipoles will align themselves in the direction of the original field. Magnetic dipole moments are therefore a source of magnetic induction $\vec{B}$, given by [5]:

$$\vec{B} = \mu_0 \vec{H} + \mu_0 \vec{M} = \mu \vec{H}, \quad (2 - 12)$$

where μ_0 is the permeability of free space, the magnetization is $\vec{M} = \frac{d\vec{\mu}}{dV}$, dV is a microscopic volume element of the material, and H is the magnetic field. For linear materials, the magnetization is defined as $\vec{M} = \chi \vec{H}$, where χ is the magnetic susceptibility [5].

2.2.2: Diamagnetism

Lenz's law can give a good explanation of the interaction between external magnetic fields and the electrons in orbitals of atoms. According to Lenz's law, when the magnetic flux enclosed by a current loop is changed, a current is induced in such a direction that its magnetic field opposes the original field. Hence, the electronic orbital motion in the atoms will change in a manner such that a magnetic moment will be induced in the opposite direction of the applied field.

In diamagnetic atoms, the electronic shells are completely filled, therefore the sum of the orbital angular momenta is equal to zero if $\vec{H} = 0$. When an external magnetic field is applied, the electrons' orbital angular momentum will interact with the field. This results in a change in the energy of the ground state due to the interaction with the induced field. This change is given by [4, 6]:

$$\Delta E = \frac{e^2}{12 mc^2} B^2 Z \overline{r^2}, \quad (2 - 13)$$

where Z is the atomic number of the atom, $\overline{r^2}$ is the mean square distance of electrons from the nucleus, and c is the speed of light. The susceptibility can be given from the Langevin's diamagnetic susceptibility as [4, 6]:

$$\chi = -N \frac{e^2}{6mc^2} \sum_{i=1}^Z \overline{r_i^2}, \quad (2 - 14)$$

where N denotes the number of atoms. It is also clear from equation (2 - 14) that the temperature T does not affect susceptibility. The magnetic susceptibility of diamagnetic materials is in order of 10^{-6} .

2.2.2.1: Susceptibility of atoms and ions

To consider the susceptibility of atoms let us consider an atom or an ion that has no orbital or spin moment. The theoretical problem of calculating the diamagnetic susceptibility requires only the calculation of $\overline{r^2}$. If we consider hydrogen-like atoms, an electron under the influence of a nucleus of charge $+Ze$ has a mean square distance from the nucleus, which is given by [6]:

$$\overline{r^2} = a_o^2 \frac{n^2}{Z^2} \left[\frac{5}{2} n^2 - \frac{3l(l+1)-1}{2} \right], \quad (2 - 15)$$

where a_o is Bohr radius.

2.2.2.2: Susceptibility of molecules

It has been shown by experiment that almost all organic and many inorganic molecules are diamagnetic. Because the number of electrons in a molecule is even, the spins of the electrons balance in pairs, i.e., one electron cancels the effect of the spin of the other electron. Therefore, we can say that the sum of the individual atoms that make up a molecule when treated independently from one another will exceed the susceptibility of the molecule they form. In the quantum mechanical treatment Van Vleck [7] has shown that the molecular susceptibility is given by [6]:

$$\chi_M = - \frac{e^2 N}{6mc^2} \sum \overline{r^2} + N \alpha(n), \quad (2 - 16)$$

where $\alpha(n) = \left(\frac{e}{2mc}\right)^2 \sum_{n'} \frac{|\langle n' | J | n \rangle|^2}{(E_{n'} - E_n)}$, where $\langle n' | J | n \rangle$ is the matrix element of the angular momentum.

2.2.3: Paramagnetism

2.2.3.1: Curie's law

Materials that have permanent magnetic dipoles may obey a special kind of susceptibility relationship that has been given by Curie [6]:

$$\chi = \frac{C}{T}, \quad (2-17)$$

where T measured in kelvins is the absolute temperature and C is called Curie's constant. Nevertheless, not all paramagnetic materials obey Curie's law. Weiss modified Curie's law in a way considering the interaction between the magnetic ions [8]. If the field due to neighboring atoms is $N_W M$, where N_W is a constant, Weiss obtained the following result for susceptibility of some paramagnetic materials [6]:

$$\chi = \frac{C}{T - \theta}, \quad (2-18)$$

where θ is constant. This relationship is called Curie –Weiss law. Many elements have a permanent moment, such as transition metal elements and isoelectronic ions. Atoms and molecules of these elements that have an odd number of electrons obey the Curie –Weiss law. Experimentally it turns out that the paramagnetic contribution is about $10^{-2} - 10^{-4} \frac{\text{emu}}{\text{mol}}$ [6].

In a volume of gas containing N paramagnetic atoms per unit volume with a permanent moment per atom of magnitude μ , the moments are distributed randomly because of thermal agitation, in the absence of an applied field. As a result, there should be no net magnetization M . When an external field is applied, the dipoles will partially align themselves in the direction of the field, and the complete alignment would occur at a temperature of absolute zero. It is also assumed that there is no interaction between the atomic dipoles. Temperature and level spacing between multiplets gives rise to three special cases:

1. Wide multiplets compared to kT where k is Boltzmann constant. If all atoms are in their ground state, the susceptibility is [6]:

$$\chi = \frac{N g^2 J(J+1) \mu_B^2}{3kT} \quad (2-19)$$

$$= \frac{N \mu^2}{3kT}. \quad (2-20)$$

In other words, the constant C in Curie's law has value equal to $C = \frac{N \mu^2}{3k}$. The quantum mechanical treatment shows that the complete expression for the susceptibility is [7]:

$$\chi = \frac{N g^2 J(J+1) \mu_B^2}{3kT} + \frac{N \mu_B^2}{6(2J+1)} \left[\frac{F(J+1)}{E_{J+1}} - \frac{F(J)}{E_J - E_{J-1}} \right], \quad (2-21)$$

where $F(J) = (1/J)[(S+L+1)^2 - J^2][J^2 - (S-L)^2]$.

2. Multiplet widths comparable to kT . The susceptibility can be obtained if we sum over all the atoms in different states. The number of atoms with a given J value will be proportional to the Boltzmann factor and the degree of degeneracy of the level, which is $(2J+1)$. It can be shown that [8]:

$$\chi = N \frac{\sum_{J=|L-S|}^{L+S} \{ [g^2 \mu_B^2 J(J+1)/3kT] + \alpha(J) \} (2J+1) e^{-E(J)/kT}}{\sum (2J+1) e^{-E(J)/kT}}. \quad (2-22)$$

3. Narrow multiplets with respect to kT . If the multiples are very narrow when compared to kT , the susceptibility is [6]:

$$\chi = \frac{N \mu_B^2}{3kT} [L(L+1) + 4S(S+1)]. \quad (2-23)$$

All three cases lead to Curie's law for the magnetic susceptibility.

2.2.3.2: Saturation in paramagnetic substances

At low temperatures and high fields the magnetization in a paramagnetic substance would take the value [6]:

$$M = N g \mu_B J B_{J(y)}, \quad (2-24)$$

where $y = \frac{Jg\mu_B H}{kT}$ and $B(y)$ is called the Brillouin function [9]. When $J \rightarrow \infty$, that is, when all orientations of the moment become possible on application of an external magnetic field, we obtain [6]:

$$B_{J \rightarrow \infty}(y) = \coth y - \frac{1}{y} = L(y), \quad (2 - 25)$$

where $L(y)$ is the classical Langevin function. Since $B(y)$ and $L(y)$ approach unity as $y \rightarrow \infty$, in large fields the dipoles will be directed such that the magnetization along H reaches the maximum possible value. Thus there will be saturation, as shown in Fig. 2-8.

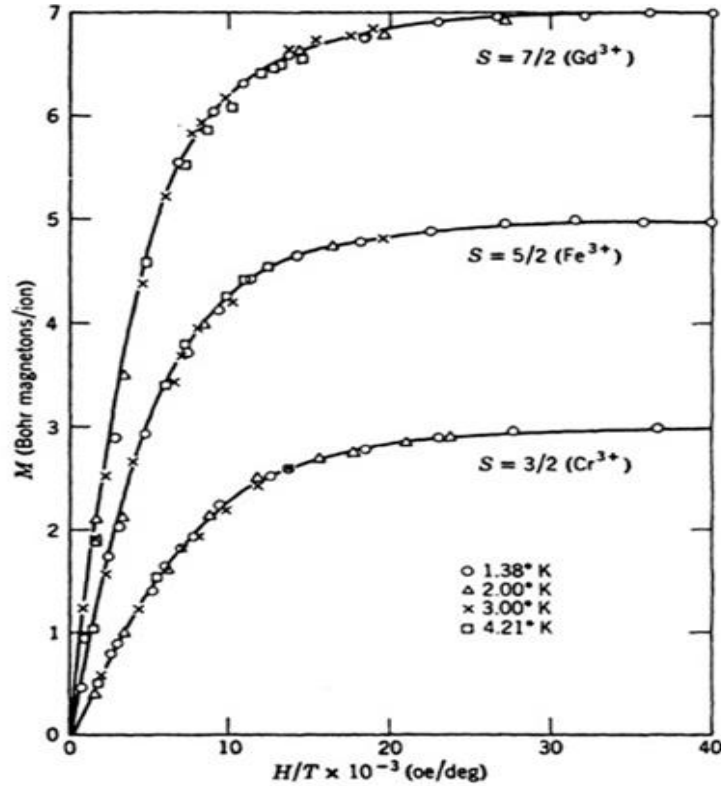


Fig. 2-8: Saturation effects in high fields and at low temperatures for various paramagnetic ions; reproduced from reference [6].

2.2.3.3: Paramagnetic molecules

Paramagnetism might occur in some molecules due to an odd number of electrons. The paramagnetism in molecules is usually caused by the spin. When the multiplets are widely separated in energy compared to kT , the multiplet states are occupied by electrons. The component of the magnetic moment along the nuclear axis is given by [6]:

$$\mu_{\parallel} = \mu_B(\Lambda + 2\Sigma), \quad (2 - 26)$$

where Λ is the orbital angular momentum of the molecules and Σ is the spin momentum component of a molecule. This results in a susceptibility given by [6]:

$$\chi = \frac{\mu_B^2}{3kT}(\Lambda + 2\Sigma)^2. \quad (2 - 27)$$

2.2.3.4: Paramagnetic susceptibility of the nucleus

The spin of the nucleus I will result in a magnetic moment that can be shown to be [6]:

$$\mu_n = g_n \frac{e\hbar}{2M_p c} [I(I + 1)]^{1/2}, \quad (2 - 28)$$

where M_p is the mass of the proton and g_n is a nuclear gyromagnetic ratio. There is a hyperfine structure which is a result of the combination of I with J to form a resultant F (total angular momentum of the atom). The spacing of these hyperfine levels is small when compared with kT , except at extremely low temperatures. Moreover, as the coupling of I and J is small there will be a decoupling for the vectors even in a small magnetic field; hence they contribute to susceptibility independently. The susceptibility of the nucleus is given by [6]:

$$\chi_{nuc} = \frac{N g_n^2 I(I + 1)}{3kT} \mu_{Bn}^2, \quad (2 - 29)$$

where g_n is the nuclear gyromagnetic ratio and μ_{Bn} is the nuclear Bohr magnetron.

2.2.4: Ferromagnetism

Strongly coupled atomic dipole moments which are aligned parallel to each other result in a strong spontaneous magnetization. Therefore, there will be a magnetic moment even in the absence of the external magnetic field. Above a critical temperature T_f , called the ferromagnetic Curie temperature, the spontaneous magnetization vanishes and the material turns to a paramagnet. There are a few materials that exhibit ferromagnetism, such as Fe, Ni, Co, and Gd.

Weiss [10] stated that ferromagnetic materials consist of small regions called domains. Each of these domains is spontaneously magnetized. Hence, the vector sum of the magnetic moments of each individual domain is equal to the magnetic moment of the entire specimen. However, for certain domains there is a possibility that the net moment will equal zero even if the

direction of the magnetizations within the domain are not aligned. The application of a relatively small field changes the domain arrangement of magnetic moment, and hence leads to an appreciable net magnetization.

2.2.4.1: Classical molecular field theory

The interactions that tend to align the atomic dipoles parallel to each other in ferromagnetic materials may be considered equivalent to some internal magnetic field H_m . The thermal agitation of the atoms be in opposition to the orientation effect of H_m . At a certain temperature, called the Curie point, the thermal agitation energy destroys the spontaneous magnetization for atoms with dipole moments. For atoms with dipole moments of one Bohr magneton, we can say that [6]:

$$\mu_B H_m = kT_f. \quad (2 - 30)$$

Weiss assumed that H_m equals [6]:

$$H_m = N_w M, \quad (2 - 31)$$

where N_w is a constant called molecular field constant. The field H_m is usually called the molecular field. In the presence of any applied magnetic field H the actual field acting on a given dipole is [6]:

$$H_T = H + N_w M. \quad (2 - 32)$$

2.2.4.2: Spontaneous magnetization region

The atoms in solids have an angular momentum quantum number J . The magnetization of the specimen is given by [6]:

$$M = Ng\mu_B J B_J(x), \quad (2 - 33)$$

where

$$x = \frac{g\mu_B J H}{kT} \quad (2 - 34)$$

$$B_J = \frac{2J+1}{2J} \coth \frac{2J+1}{2J} x - \frac{1}{2J} \coth \frac{x}{2J} \quad (2 - 35)$$

and N is the number of atoms per unit volume. The field of the ferromagnetic material is replaced by equation (2 - 32) so [6]:

$$x = \frac{g\mu_B J}{kT} (H + N_w M) \quad (2 - 36)$$

When $H = 0$, the spontaneous magnetization can be described by rewriting equation (2 - 33) and (2 - 36) [6]:

$$\frac{M(T)}{M(0)} = B_J(x), \quad (2 - 37)$$

and

$$\frac{M(T)}{M(0)} = \frac{kT}{N N_w g^2 \mu_B^2 J^2} x, \quad (2 - 38)$$

where

$$M(0) = N g \mu_B J. \quad (2 - 39)$$

It is clearly seen from equation (2 - 38) that magnetization depends on temperature. There is a relationship between T_f and N_w . For small values of x , the Brillouin function is given by [6]:

$$B_J(x) \cong \frac{J+1}{3J} x - \frac{J+1}{3J} \frac{2J^2+2J+1}{30J^2} x^3 \quad (x \ll 1). \quad (2 - 40)$$

Similarly, for $x \rightarrow 0$, the slope of the tangent is given by $(J + 1)/3J$. When this equals to the slope of the straight line in equation (2 - 38) for $T = T_f$, then we obtain [6]:

$$T_f = \frac{N g^2 \mu_B^2 J(J + 1)}{3k} N_w. \quad (2 - 41)$$

By combining equation (2 - 41) with equation (2 - 38) we obtain [6]:

$$\frac{M(T)}{M(0)} = \frac{J + 1}{3J} \left(\frac{T}{T_f} \right) x. \quad (2 - 42)$$

Fig. 2-9 shows the relation between $\frac{M(T)}{M(0)}$ and $\left(\frac{T}{T_f}\right)$ for three different J values.

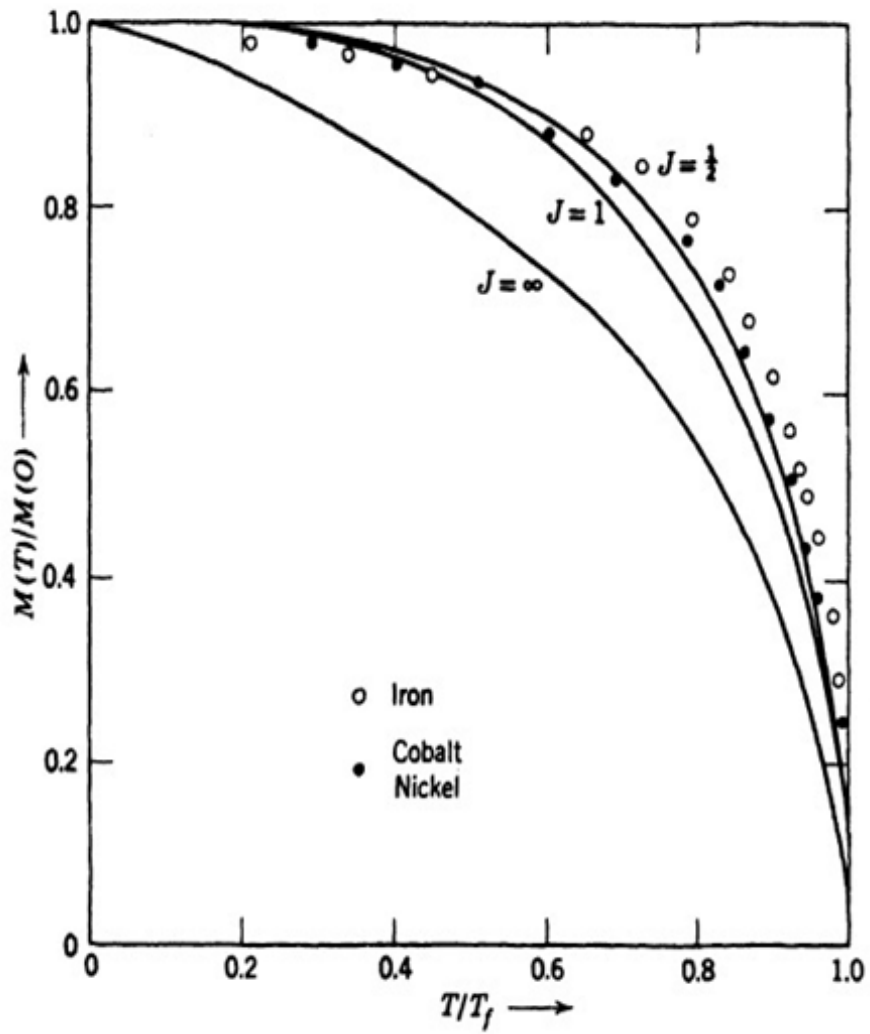


Fig. 2-9: The spontaneous magnetization as a function of temperature. The curves are obtained from theory; the points represent experimental data where the open circles stand for iron and black circles stand for nickel and cobalt; reproduced from reference [6].

2.2.4.3: The paramagnetic region

It is known that spontaneous magnetization is zero above the ferromagnetic Curie point T_f . The application of an external magnetic field H will produce a magnetization given by [6]:

$$M = \frac{Ng\mu_B(J+1)}{3} x, \quad (2-43)$$

where x is:

$$x = \frac{Jg\mu_B}{kT} (H + N_w M). \quad (2-44)$$

So the susceptibility which results from Curie-Weiss law is [6]:

$$\chi = \frac{M}{H} = \frac{C}{T - \theta}, \quad (2-45)$$

where

$$C = \frac{Ng^2\mu_B^2 J(J+1)}{3k}, \quad (2-46)$$

and

$$\theta = N_w \frac{Ng^2\mu_B^2 J(J+1)}{3k} = N_w C. \quad (2-47)$$

If we compare equation (2 - 47) with (2 - 41), it is observed that Weiss predicted $\theta = T_f$. The figure below shows the susceptibility of a ferromagnetic metal above the Curie point.

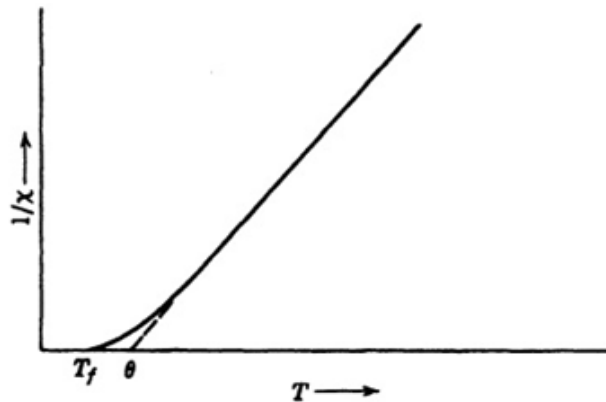


Fig. 2-10: Illustration of the susceptibility of a ferromagnetic metal above the Curie point. T_f is the ferromagnetic Curie point; θ is the paramagnetic Curie point; reproduced from reference [6]. Below T_f the susceptibility is infinite, and above θ the inverse of susceptibility will increase with the temperature.

2.2.5: Antiferromagnetism

An antiferromagnetic material is defined as a material that consists of antiparallel arrangements of strongly coupled atomic dipoles. Néel proposed that an antiferromagnetic substance is composed of a pair of sublattices that share the same magnetic structure but their spins are aligned anti-parallel to each other [6, 11]. Examples of such magnetic sublattices are: the simple cubic sublattice, which can be seen as two interpenetrating face-centered cubic lattices, and the body-centered cubic lattice, as shown in the Fig. 2-11 below.

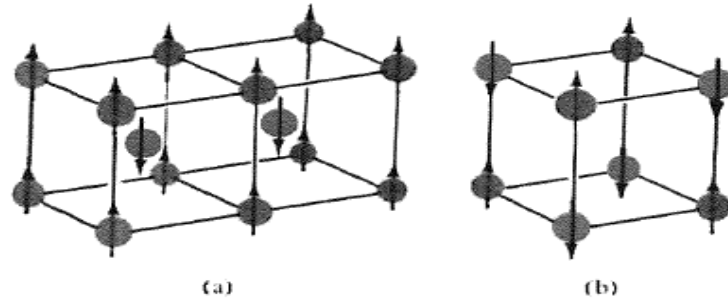


Fig. 2-11: Two simple antiferromagnetic spin arrangements for (a) body-centre cubic lattice, and (b) simple cubic lattice; reproduced from reference [14].

The net moment of an antiferromagnetic material is zero as the magnetic moments of the two sublattices are equal and opposite to each other, hence canceling out the overall effect. It is important here to introduce the Néel temperature T_N which is defined as the temperature above which the ordered antiparallel arrangement of the dipoles disappears.

2.2.5.1: Molecular field theory of antiferromagnetism

The simple case for an antiferromagnetic material is of one consisting of two sublattices A and B [12]. In case of the body-centered cubic lattice, the sublattice A consists of the corner positions and the sublattice B takes the body-centered positions. Considered an A atom, the nearest neighbors to it are atoms of type B and the next nearest neighbors are atoms of type A . The molecular field H_{mA} acting on an atom at site A is given by [6]:

$$H_{mA} = -N_{AA}M_A - N_{AB}M_B, \quad (2 - 48)$$

where M_A and M_B are the magnetization of the A and B sublattices, N_{AB} is molecular field constant for nearest neighbor interaction, and N_{AA} is molecular field constant for second-nearest neighbor interaction. Similarly, the molecular field H_{mB} acting on an atom at site B is given by [6]:

$$H_{mB} = -N_{BA}M_A - N_{BB}M_B. \quad (2-49)$$

As long as the same type of atom occupies the A and B lattice sites $N_{AA} = N_{BB} = N_{ii}$, and therefore $N_{AB} = N_{BA}$. If a field H is applied, the fields H_A and H_B at an atom on the A and B lattices are given by [6]:

$$H_A = H - N_{ii}M_A - N_{AB}M_B \quad (2-50)$$

$$H_B = H - N_{AB}M_A - N_{ii}M_B. \quad (2-51)$$

The molecular field constant N_{AB} is positive because the interaction between the nearest neighbors is antiferromagnetic in this case.

In thermal equilibrium the magnetization of the sublattice is given by [6]:

$$M_A = \frac{1}{2}Ng\mu_B S B_S(x_A), \quad (2-52)$$

where

$$x_A = \frac{Sg\mu_B}{kT} H_A, \quad (2-53)$$

$$B_S(x_A) = \frac{2S+1}{2S} \coth \frac{2S+1}{2S} x_A - \frac{1}{2S} \coth \frac{x_A}{2S}, \quad (2-54)$$

and

$$M_B = \frac{1}{2}Ng\mu_B S B_S(x_B), \quad (2-55)$$

where

$$x_B = \frac{Sg\mu_B}{kT} H_B, \quad (2-56)$$

$$B_S(x_A) = \frac{2S+1}{2S} \coth \frac{2S+1}{2S} x_B - \frac{1}{2S} \coth \frac{x_B}{2S}. \quad (2-57)$$

Here N is the total number of atoms (or ions) with a permanent dipole moment per unit volume, and the total angular momentum is equal to S (there is no orbital angular momentum).

2.2.5.2: Above the Néel temperature

If an external field is applied for an antiferromagnetic material above Néel temperature, a small magnetization still exists. The magnetization of each sublattice can be written as [6]:

$$M_A = \frac{Ng^2\mu_B^2S(S+1)}{6kT}(H - N_{ii}M_A - N_{AB}M_B), \quad (2-58)$$

and

$$M_B = \frac{Ng^2\mu_B^2S(S+1)}{6kT}(H - N_{AB}M_A - N_{ii}M_B). \quad (2-59)$$

Now the susceptibility is [6]:

$$\chi = \frac{M}{H} = \frac{C}{T + \theta}, \quad (2-60)$$

where

$$C = \frac{Ng^2\mu_B^2S(S+1)}{3k}, \quad (2-61)$$

and

$$\theta = \frac{1}{2}C(N_{ii} + N_{AB}). \quad (2-62)$$

Since, in general, $N_{AB} > N_{ii}$, θ is positive. A comparison between three results of susceptibility versus temperature is shown in Fig. 2-12.

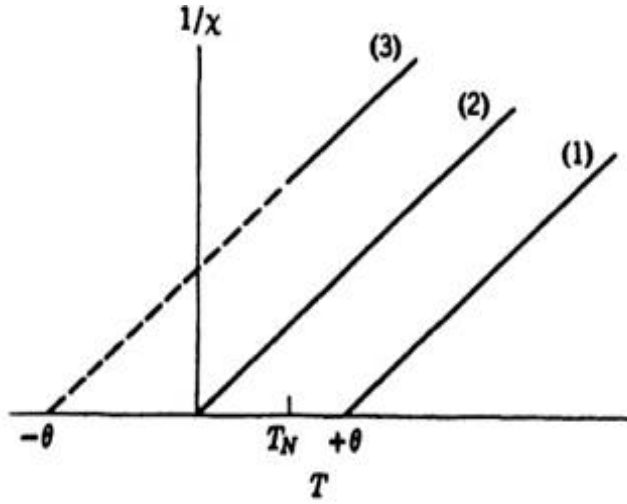


Fig. 2-12: Plot of $1/\chi$ versus temperature T . Curve 1, $\chi = C/(T - \theta)$ (Curie-Weiss law); curve 2, $\chi = C/T$ (Curie's law), and curve 3, $\chi = C/(T + \theta)$; reproduced from reference [6].

2.2.5.3: The Néel temperature

Below the Néel temperature both sublattices possess a spontaneous magnetization (for $H = 0$) of equal magnitude and opposite direction. In this situation the Néel temperature T_N is given by [6]:

$$T_N = \frac{1}{2}C(N_{AB} - N_{ii}). \quad (2 - 63)$$

It is clear that T_N will be high if the interaction of AB is strong while AA and BB interactions are weak. Substituting C in equation (2 - 62), gives [6]:

$$\frac{\theta}{T_N} = \frac{N_{AB} + N_{ii}}{N_{AB} - N_{ii}}. \quad (2 - 64)$$

If $N_{ii} = 0$ then $T_N = \theta$, whereas if $N_{ii} > 0$ then $\theta > T_N$.

2.2.5.4: Susceptibility below the Néel temperature

In the absence of an external field and below the Néel temperature, the sublattice magnetizations M_A and M_B are antiparallel to one another. We can assume the applied field H is

parallel to H_{mA} and antiparallel to H_{mB} . When the magnetic field is applied parallel to easy axes $\chi_{\parallel}$, then the susceptibility can be written as [6]:

$$\chi_{\parallel} = \frac{Ng^2\mu_B^2 S^2 B'_s(x_0)}{kT + \frac{1}{2}(N_{ii} + N_{AB})Ng^2\mu_B^2 S^2 B_s(x_0)}, \quad (2 - 65)$$

where $B'_s(x_0)$ is the derivative of the Brillouin function with respect to its argument.

At absolute zero, this equation predicts $\chi_{\parallel} = 0$. This can be explained by the fact that all the atomic moments are either parallel or antiparallel to the applied field at $T = 0$ K. When T increases, $\chi_{\parallel}$ also increases until at the Néel temperature; $\chi_{\parallel}(T_N)$ becomes equal to the susceptibility $\chi(T)$ in equation (2 - 60). Also when the temperature further increases, i.e., at $T > T_N$ the susceptibility is reduced to equation (2 - 60). A plot of $\chi_{\parallel}$ as a function of T/T_N , for $N_{ii} = 0$ is illustrated in Fig. 2-13 [6].

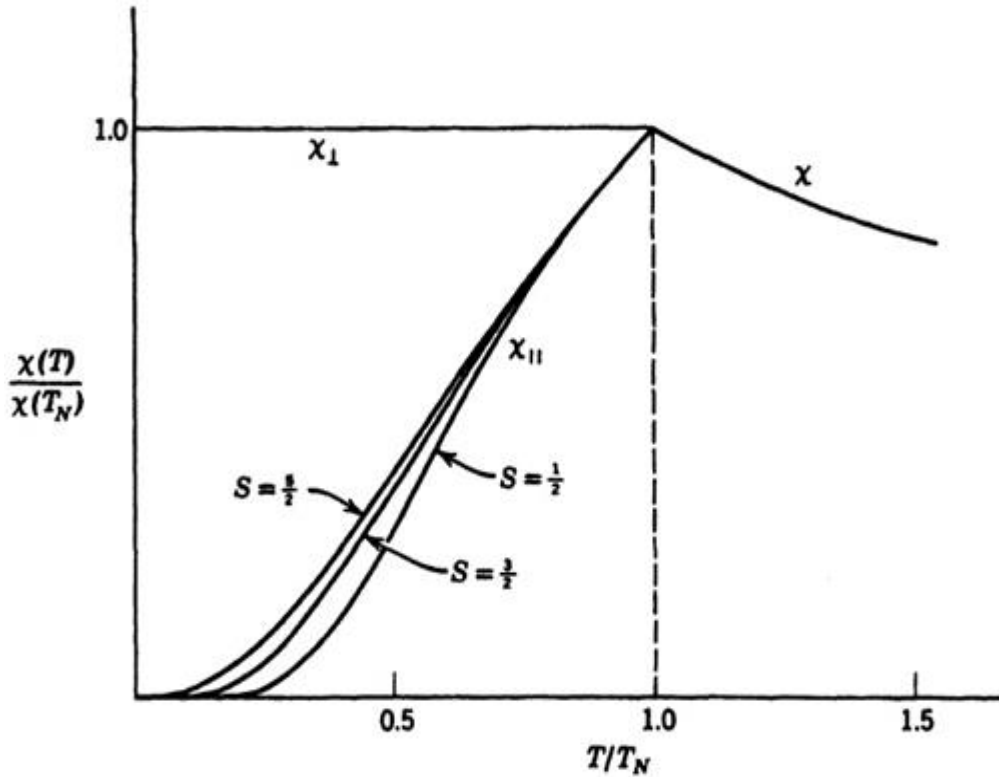


Fig. 2-13: The susceptibility of an antiferromagnetic material as a function of temperature; reproduced from reference [6].

2.2.5.5: Susceptibility of single crystal when applied field is perpendicular to the easy axis

When a magnetic field is applied in a perpendicular direction to the easy axis, the sublattice magnetization will rotate, as shown in Fig. 2-14 [6]:

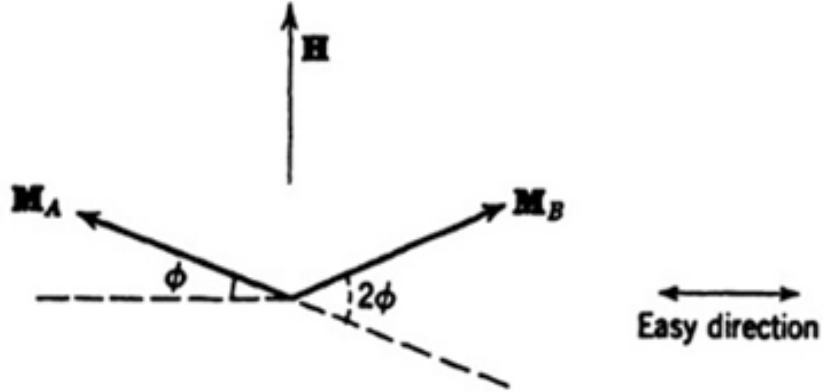


Fig. 2-14: illustration of the calculation of the susceptibility $\chi_{\perp}$; reproduced from reference [6].

The molecular field will be set up in a manner that opposes the rotation of the sublattices. The susceptibility is [6] $\chi = \frac{M}{H}$, where $M = 2M_B \sin \phi$ and $H = 2M_B N_{AB} \sin \phi$, so the susceptibility can be expressed as [6]:

$$\chi_{\perp} = \frac{1}{N_{AB}}, \quad (2-66)$$

where $\chi_{\perp}$ is constant. The susceptibility $\chi = \frac{C}{T+\theta}$ for $T \geq T_N$ also reduces to $\chi = \frac{1}{N_{AB}}$ at $T = T_N$, as shown in Fig. 2-13.

2.2.5.6: Susceptibility of polycrystalline materials

For antiferromagnetic materials in the form of a powder, the susceptibility is calculated by considering the two components of the field that are parallel and perpendicular to the easy direction. The susceptibility is given by the following equation [6]:

$$\chi_p = \frac{1}{3} \chi_{\parallel} + \frac{2}{3} \chi_{\perp}, \quad \text{for } 0 < T < T_N, \quad (2-67)$$

$$\chi_p = \chi_{\parallel} = \chi_{\perp}, \quad \text{for } T = T_N, \quad (2-68)$$

and

$$\chi_p = \frac{2}{3} \chi_{\perp} \quad \text{for } T = 0 \quad (2-69)$$

2.2.6: Ferrimagnetism

Ferrimagnetic materials can be defined as the materials which have spontaneous magnetization at certain temperatures [13]. In ferrimagnetic materials, the magnetic moments are aligned parallel within sublattices (usually two). If pairs of sublattices are aligned antiparallel with respect to each other, and the atomic moments within each sublattice are not of equal strength there will be a magnetic moment as illustrated in the Fig. 2-15 [6]:

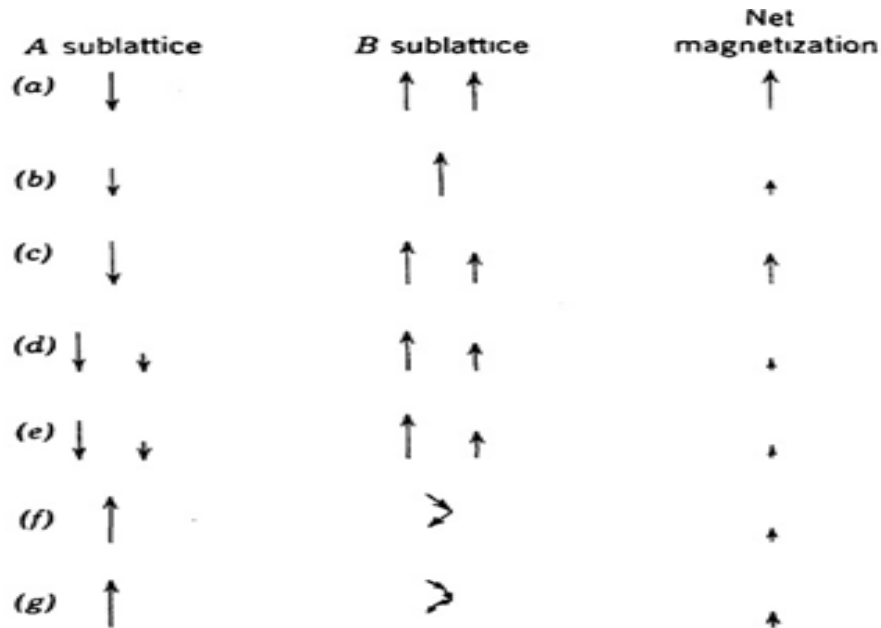


Fig. 2-15: Various possible ferrimagnetic arrangements for two sublattices. The magnitudes of the vectors may represent either the magnetic moments of the individual ions or the moment per chemical formula unit for each type of ion; reproduced from reference [6].

2.2.6.1: Paramagnetic region

The temperature at which the spontaneous magnetizations of ferrimagnetic materials disappear is called the Néel temperature and it takes the symbol T_{FN} . Above T_{FN} the sublattice magnetizations are [6]:

$$M_A = \frac{C_A}{T} H_A \text{ and } M_B = \frac{C_B}{T} H_B, \quad (2 - 70)$$

where

$$C_A = \sum_i \frac{N_i g^2 \mu_B^2 S_i (S_i + 1)}{3k}, \quad (2 - 71)$$

and

$$C_B = \sum_j \frac{N_j g^2 \mu_B^2 S_j (S_j + 1)}{3k}. \quad (2 - 72)$$

After applying the magnetic field H the magnetization can be described as [6]:

$$M_A = \frac{C_A(T + C_B N_{BB}) - C_A C_B N_{AB}}{(T + C_A N_{AA})(T + C_B N_{BB}) - C_A C_B N_{AB}^2} H \quad (2 - 73)$$

and

$$M_B = \frac{C_B(T + C_A N_{AA}) - C_A C_B N_{AB}}{(T + C_A N_{AA})(T + C_B N_{BB}) - C_A C_B N_{AB}^2} H. \quad (2 - 74)$$

The susceptibility is now given by:

$$\chi = [(M_A + M_B)/H], \quad (2 - 75)$$

where the inverse of the susceptibility is [6]:

$$\frac{1}{\chi} = \frac{T}{C} - \frac{1}{\chi_0} - \frac{\sigma}{T - \theta'}, \quad (2 - 76)$$

where C is defined as

$$C = C_A + C_B, \quad (2 - 77)$$

and

$$\frac{1}{\chi_0} = -\frac{1}{C^2} (C_A^2 N_{AA} + C_B^2 N_{BB} + 2C_A C_B N_{AB}), \quad (2 - 78)$$

$$\begin{aligned} \sigma = \frac{C_A C_B}{C^3} \{ & C_A^2 (N_{AA} - N_{AB})^2 + C_B^2 (N_{BB} - N_{AB})^2 \\ & - 2C_A C_B [N_{AB}^2 - (N_{AA} - N_{BB})N_{AB} + N_{AA}N_{BB}] \}, \end{aligned} \quad (2 - 79)$$

$$\theta' = -\frac{C_A C_B}{C} (N_{AA} - N_{BB} - 2N_{AB}). \quad (2 - 80)$$

For very high temperatures equation (2 - 76) becomes [6]:

$$\frac{1}{\chi} = \frac{T}{C} - \frac{1}{\chi_0}. \quad (2 - 81)$$

If θ is defined at the T-intercept by extrapolation of the line then,

$$\theta = -\frac{C}{\chi_0}, \quad (2 - 82)$$

and the equation may be written as:

$$\chi = \frac{C}{T + \theta}. \quad (2 - 83)$$

Since $T_{FN} > 0$ and the susceptibility is infinite at this point, as shown in Fig. 2-16 the $1/\chi$ versus T curve must have a reasonable curvature just above the ferrimagnetic Néel temperature.

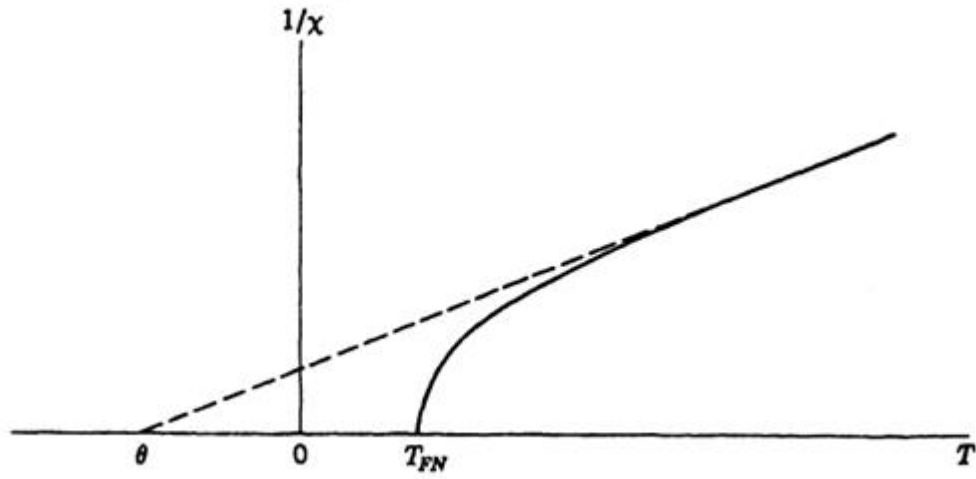


Fig. 2-16: Inverse susceptibility of a ferrimagnet above the Néel temperature T_{FN} according to the molecular field theory; reproduced from reference [6].

2.2.6.2: Néel temperature

When magnetic field $H = 0$, the Néel temperature can be written as [6]:

$$T_{FN} = -\frac{1}{2}(C_A N_{AA} + C_B N_{BB}) + \frac{1}{2}[(C_A N_{AA} - C_B N_{BB})^2 + 4C_A C_B N_{AB}^2]^{1/2}. \quad (2-84)$$

2.3: Mössbauer spectroscopy

Mössbauer spectroscopy is an efficient technique to study magnetic, chemical, and structural information of solid materials. The technique is based on the effect of recoilless gamma ray emission and absorption. Mössbauer spectroscopy is highly sensitive to energy changes of the order 10^{-8} eV. The setup, as is shown in Fig. 2-17, consists of a radioactive isotope that is attached in front of a velocity transducer. The transducer moves, and it is controlled by a function generator. The oscillation 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 amplifier. The signal which comes from the amplifier goes into a single channel analyser (SCA) and then to a multi-channel analyser (MCA). The synchronization is achieved between the transducer and MCA, and it is under the control of the function generator that send start and delay pulses to the MCA and proper timescale voltage pulses to the transducer. There are more than 100 isotopes that can be used in Mössbauer spectroscopy.

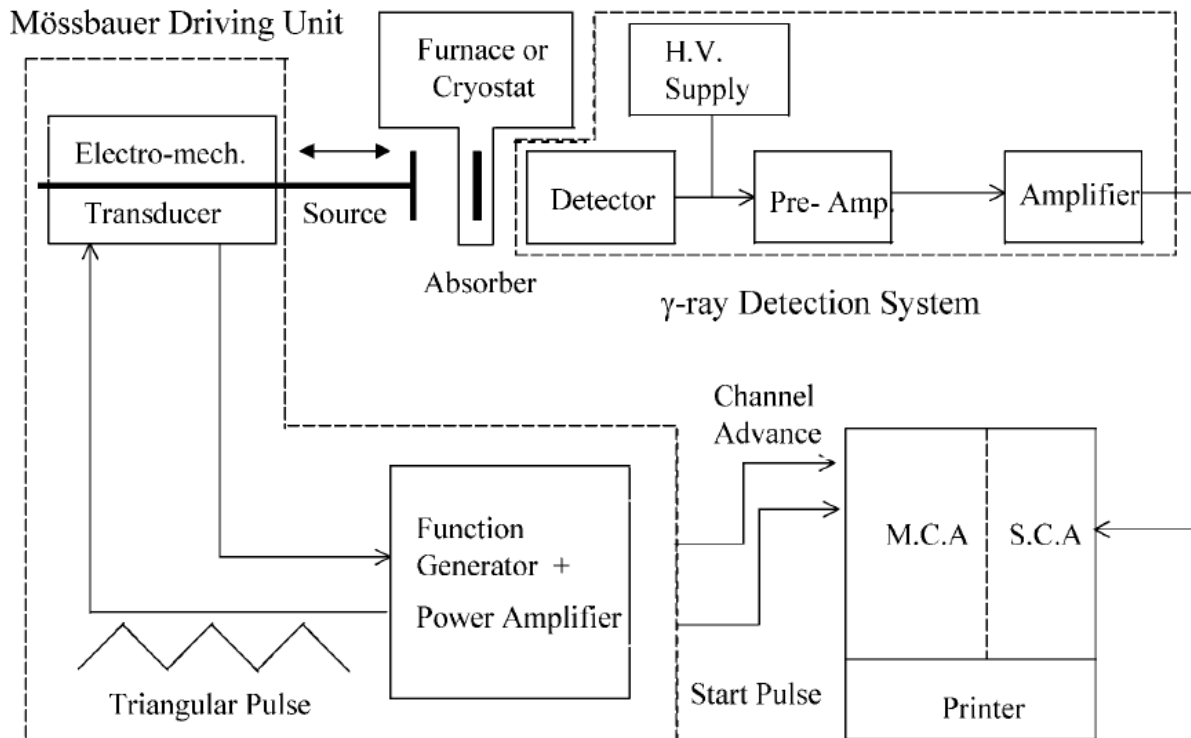


Fig. 2-17: Experimental set-up of transmission Mössbauer spectroscopy; reproduced from reference [15].

2.3.1: Mössbauer effect theory

In order to observe the Mössbauer effect, two main conditions must be satisfied. The first condition is recoilless emission of photons. The second one is recoilless resonant absorption of photons. When the atom emits a photon due to energy and momentum conservation, the nucleus will suffer recoil given by equation [16]:

$$E_R = \frac{E_\gamma^2}{2Mc^2}, \quad (2 - 85)$$

where E_γ is the gamma rays energy, M is the mass of the nucleus, and c is the speed of light.

If the process happens in solid materials, the effective mass of the nucleus will be very large because the recoil energy will be transferred to the entire crystal; then E_R will be highly reduced. In this way the first condition will be satisfied. But this not enough to observe the Mössbauer effect till the second condition is applied. For the second condition there should not be any shift in the photon energy. The source of hyperfine interactions are divided into two; the first source is the magnetic and electric fields originating from the atoms' electrons, and the second source originates from the fields of neighboring atoms. In order to obtain resonance (resonant absorption) there must be a shift in the energy of the emitted photons. Moreover, this can be achieved by adding a Doppler shift. The whole process occurs when moving the source back and forth in a small velocity range. The energy of the γ -ray emitted from a moving atom is shifted by [16]:

$$E_D = vE_0/c, \quad (2 - 86)$$

where v is the velocity of the atom, and E_0 is the energy difference between the excited state and the ground state of the nucleus. By adding the Doppler shift, the energy relation of the emission process is [16]:

$$E_\gamma = E_0 - E_R + E_D. \quad (2 - 87)$$

The absorption is given by [16]:

$$E_\gamma = E_0 + E_R + E_D. \quad (2 - 88)$$

The recoil energy of a single-phonon process can be written in a quantum mechanical treatment as [16]:

$$E_R = (1 - f)\hbar\omega_E, \quad (2 - 89)$$

where f is the recoil-free fraction, ω_E is angular frequency. The recoil-free fraction in the Debye model is [16]:

$$f = \exp\left(-\frac{3E_R}{2k_B\theta_D}\right); \quad T \ll \theta_D, \quad (2 - 90)$$

$$f = \exp\left(-\frac{6E_RT}{2k_B\theta_D^2}\right); \quad T > \theta_D, \quad (2 - 91)$$

where f is also known as a Debye –Waller factor.

The uncertainty in time of the γ -ray emission and absorption can be described by Heisenberg's uncertainty principle which is also used in describing the spectral line width. The Heisenberg uncertainty principle is [16]:

$$\Delta E \Delta t \geq \hbar. \quad (2 - 92)$$

A ground state with infinite lifetime leads to zero uncertainty in energy. The mean lifetime τ of the excited state controls the width of the energy uncertainty [16]:

$$\Gamma\tau \approx \hbar, \quad (2 - 93)$$

where Γ is the full width at half maximum of the transition spectral line, as is shown in Fig. 2-18. The life time of the excited nuclear states suitable for Mössbauer spectroscopy is in the range of 10^{-6} s to 10^{-11} s.

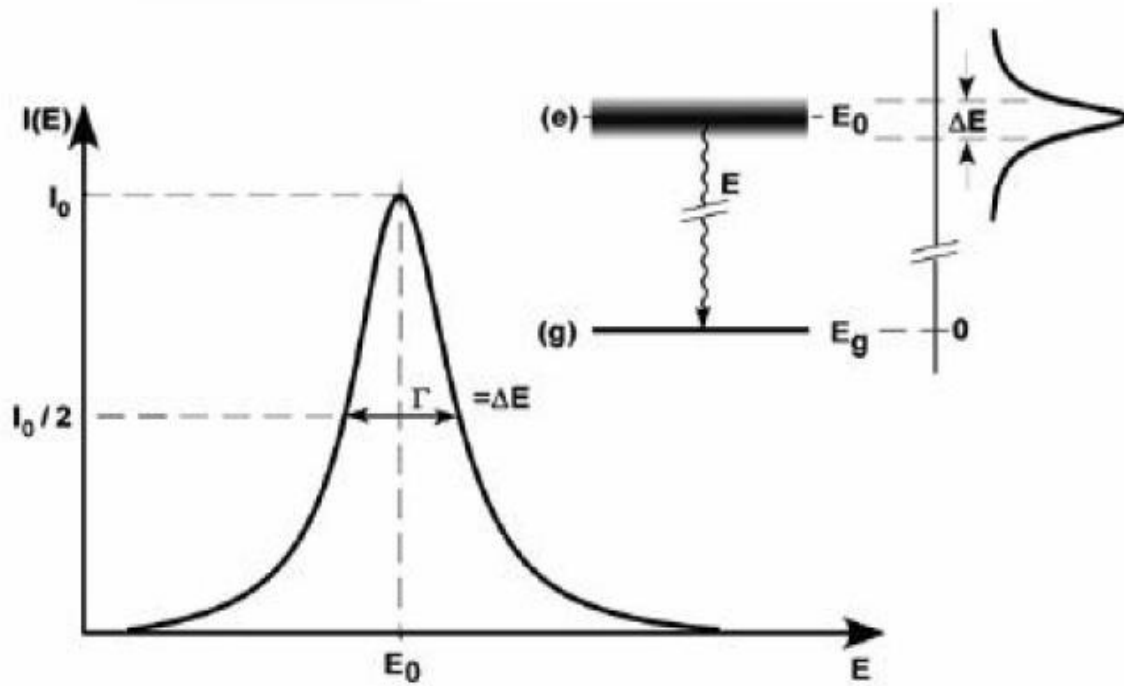


Fig. 2- 18: Intensity distribution $I(E)$ for the emission of γ -ray with mean transition energy E_0 . The Heisenberg natural line width of the distribution, $\Gamma = \hbar/\tau$, is determined by the mean lifetime τ of the excited state (e); reproduced from reference [17].

The intensity as a function of transition energy is [17]:

$$I(E) \sim \frac{\Gamma/2\pi}{(E - E_0)^2 + (\Gamma/2)^2}. \quad (2 - 94)$$

The condition for resonant absorption only occurs if the spectral line for the emission and absorption process appear at the same energy position.

2.3.2: Hyperfine interactions

Hyperfine interactions are a result of the interactions between the nuclear moments and the electromagnetic fields. There are three main hyperfine interactions: isomer shift (electric monopole interaction), nuclear Zeeman effect (magnetic dipole interaction), and quadrupole splitting (electric quadrupole interaction) [16].

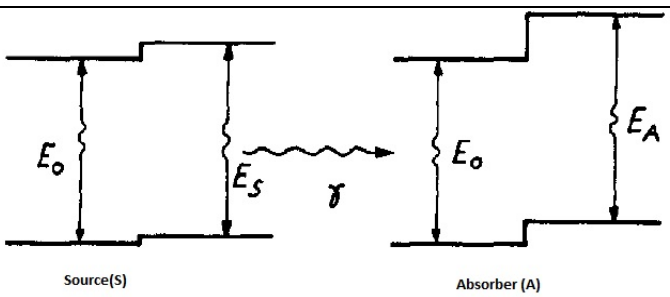
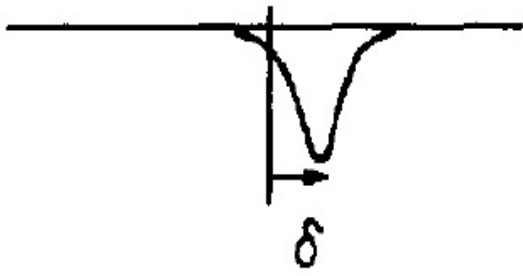
2.3.2.1: Isomer shift

If the chemical environment of the absorber and the source are the same, the absorption of gamma photons will occur at 0 mm/s speed. On the other hand, if the chemical environment is different, the densities of the electrons at the nuclear sites in the absorber and in the source will differ. So, in order for the gamma photons to be absorbed there should be a slight shift in the gamma photon energy. This process would lead to a slight shift of the spectrum. The chemical shift, δ , can be negative or positive depending on the electron charge density at the nucleus in the source and the absorber, as it is shown in equation (2 - 95) [16]:

$$\delta = C \frac{\delta R}{R} [|\psi_A(0)|^2 - |\psi_S(0)|^2], \quad (2 - 95)$$

where C is a constant for a given isotope, $\frac{\delta R}{R}$ is the relative change of nuclear radius between excited state and ground state, and the term in parenthesis represents the difference in the total electron density evaluated at the nucleus $|\psi(0)|^2$, between absorber (A) and source (S) isotopes. For example, δR for ^{57}Fe isotope is negative. Table. 2-1 represents the allowed transitions, and the resulted spectrum.

Table. 2-1: Demonstration of ^{57}Fe energy level diagram with allowed transitions and schematic representation of observation (resonance absorption vs. velocity); reproduced from reference [16].

^{57}Fe energy level diagram with allowed transitions	Schematic representation of observation (resonance absorption vs. velocity)
 The diagram shows two sets of energy levels. On the left, labeled 'Source (S)', there are two levels with a gap E_0 between them. On the right, labeled 'Absorber (A)', there are two levels with a gap E_A between them. A wavy arrow labeled γ points from the lower level of Source (S) to the lower level of Absorber (A). Another wavy arrow labeled E_S points from the lower level of Source (S) to its upper level. A third wavy arrow labeled E_0 points from the lower level of Absorber (A) to its upper level.	 The schematic shows a horizontal line representing a baseline. A vertical line intersects it. A curve dips below the baseline, forming a resonance shape. A horizontal arrow labeled δ indicates the shift of the minimum of the dip from the vertical line.

2.3.2.2: Nuclear Zeeman effect

A magnetic dipole moment μ will be present if the spin quantum number I of the nucleus is higher than zero. The value of μ is given by [16]:

$$\mu = g_n \mu_{Bn} I, \quad (2 - 96)$$

where g_n is the nuclear Landé splitting factor.

When there is a magnetic field at the site of the nucleus, the magnetic dipole moment will split into $(2I + 1)$ sublevels with the eigenvalues [16]:

$$E_m = -\frac{\mu H m_I}{I} = -g_n \mu_{Bn} H m_I, \quad (2 - 97)$$

where m_I is the nuclear magnetic quantum number with the values $m_I = I, I - 1, \dots, -I$.

When applied to ^{57}Fe considering the selection rules $\Delta m = 0, \pm 1$, there will be six allowed transitions, as is shown in the table below.

Table. 2-2: Demonstration of ^{57}Fe energy level diagram with allowed transitions and schematic representation of observation (resonance absorption vs. velocity); reproduced from reference [16].

^{57}Fe energy level diagram with allowed transitions	Schematic representation of observation (resonance absorption vs. velocity)

2.3.2.3: Quadrupole splitting

If I is larger than $1/2$, the nucleus will have an electric nuclear quadrupole moment. Another sublevel splitting in the nuclear energy will occur as a result of the interaction between the nuclear quadrupole moment eQ with the principal component of the diagonalized electric field gradient (EFG) tensor V_{zz} [16]:

$$E_Q = \frac{eQV_{zz}}{4I(2I-1)} [3m_I^2 - I(I+1)] \left(1 + \frac{\eta^2}{3}\right)^{1/2}, \quad (2-98)$$

where, $\eta = \frac{V_{xx}-V_{yy}}{V_{zz}}$. The value of m_I can be $m_I = I, I-1, \dots, -I$.

For the example of ^{57}Fe , the spectrum will be separated into two levels which are $m_I = \pm 1/2$, and $m_I = \pm 3/2$, as is shown in Table. 2-3.

Table. 2-3: Demonstration of ^{57}Fe energy level diagram with allowed transitions and schematic representation of observation (resonance absorption vs. velocity); reproduced from reference [16].

^{57}Fe energy level diagram with allowed transitions	Schematic representation of observation (resonance absorption vs. velocity)

2.3.2.4: Combined hyperfine interaction

All three kinds of hyperfine interactions might occur at the same time. For ^{57}Fe the Mössbauer spectrum is shown in Fig. 2-19.

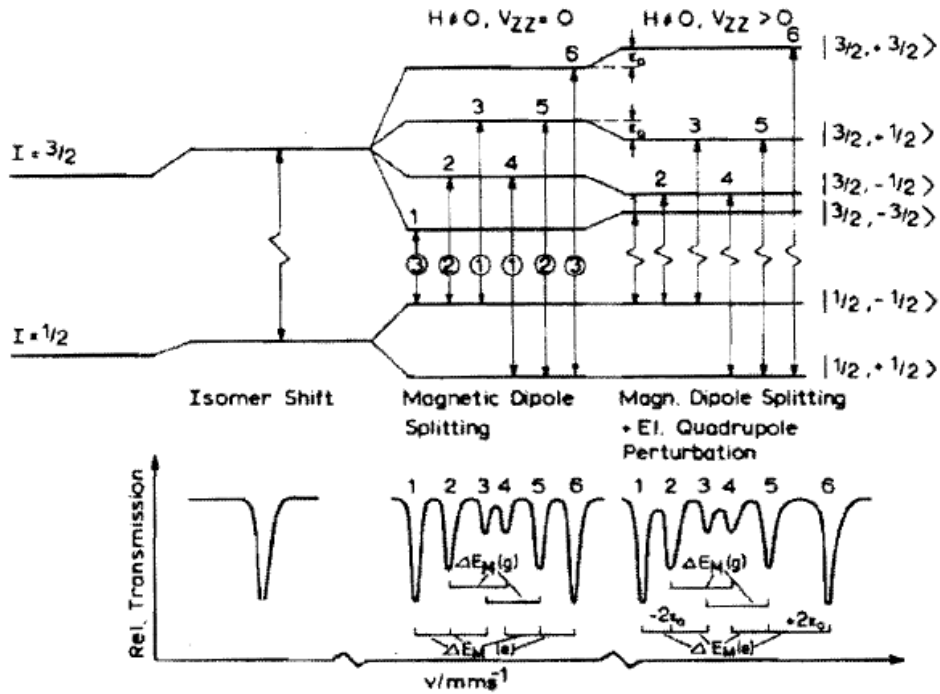


Fig. 2-19: Mössbauer spectra for ^{57}Fe ; reproduced from reference [17].

2.3.3: ^{151}Eu Mössbauer spectroscopy

^{151}Eu is one of the most studied Mössbauer isotopes. Europium exists in two valance states, the magnetic europium (II) ion, with the $^8\text{S}_{7/2}$ ground state, and the nonmagnetic europium (III) ion, with the $^7\text{F}_0$ ground state. The Mössbauer transition energy for ^{151}Eu between the excited state of the nuclear spin $\frac{7}{2} +$ and the ground state the nuclear spin $\frac{5}{2} +$ is 21.54 keV. The usual way to get the ^{151}Eu Mössbauer excited state is to use the nuclear decay of ^{151}Sm , as is shown in Fig. 2-20.

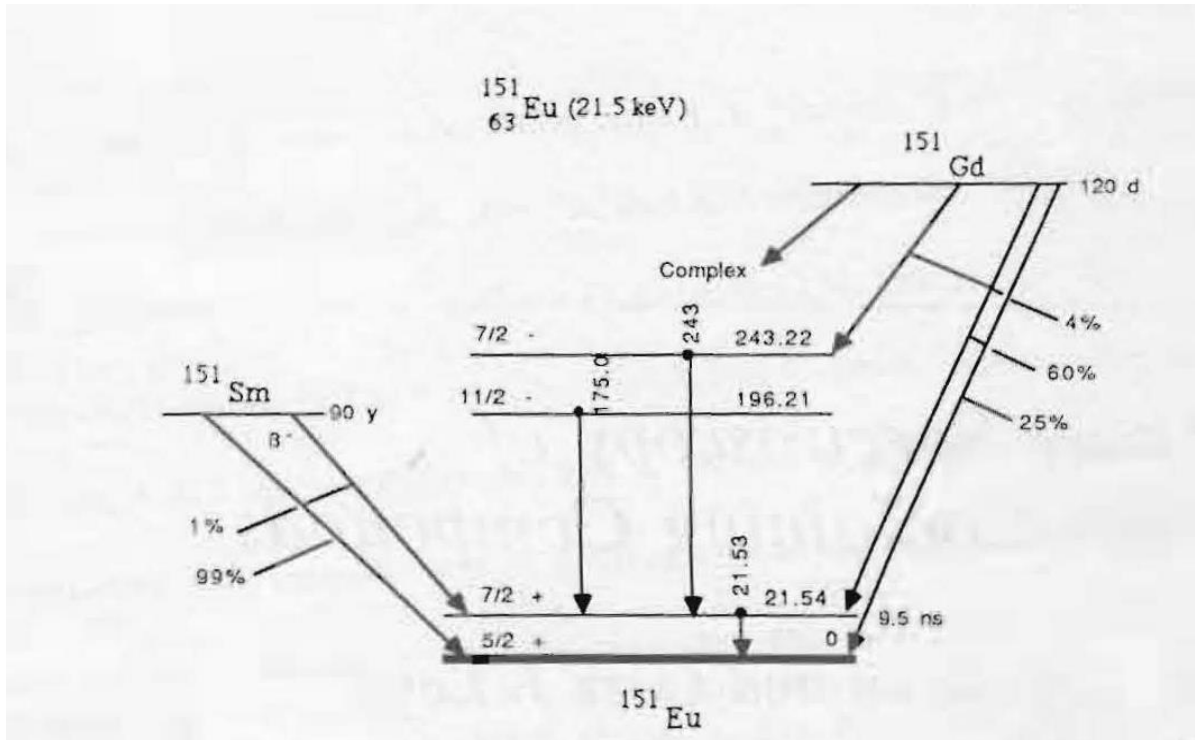


Fig. 2-20: The nuclear decay scheme for ^{151}Eu Mössbauer excited state; reproduced from reference [18].

2.3.3.1: Hyperfine interactions in ^{151}Eu

2.3.3.1.1 Isomer shift

The isomer shift of non-metallic europium (III) compounds are in the range of 1 mm/s centered at 0.5 mm/s, and for non-metallic europium (II) compounds the isomer shifts are about 2 mm/s centered at -13.5 mm/s, as is shown in Fig. 2-21. The isomer shift for europium (II) and europium (III) metallic compounds are more positive than for the non-metallic compounds. The relatively high value of $\frac{\delta R}{R}$ for ^{151}Eu represents a large nuclear radius for the excited state compared to the ground state.

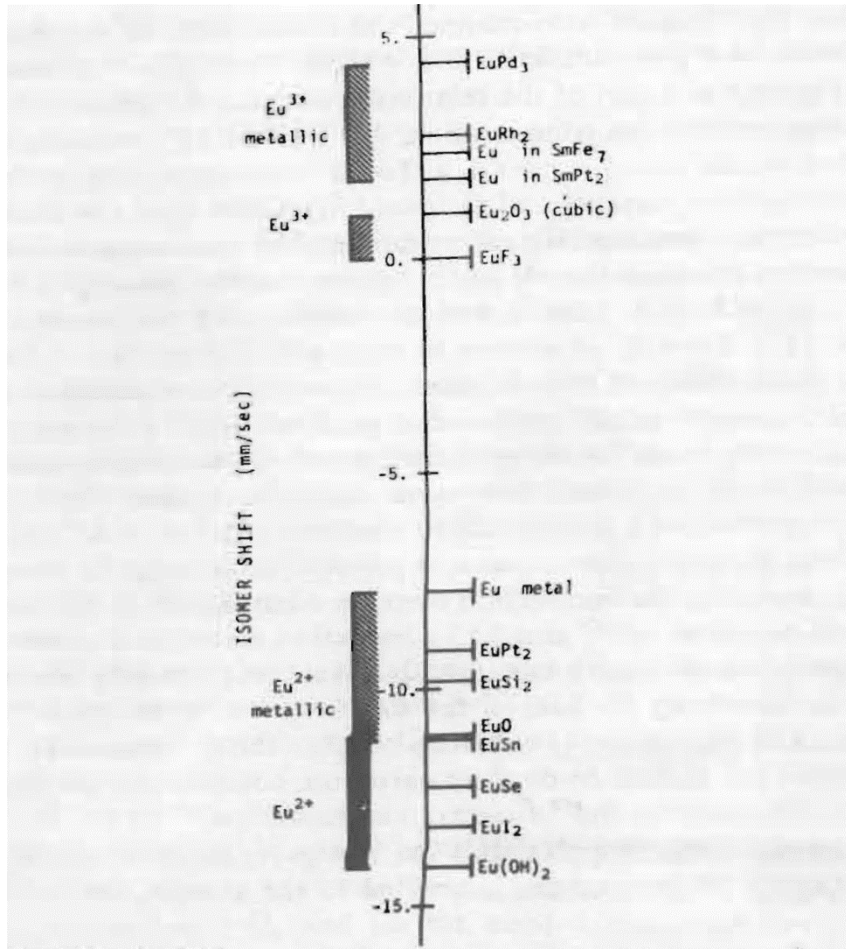


Fig. 2-21: ^{151}Eu Mössbauer effect shift scale δ ; reproduced from reference [18].

2.3.3.1.2: Quadrupole interaction

Due to quadrupole interaction the degeneracy of ground state and excited state will no longer occur, and the ground state will split into three sublevels and the excited state will split into four sublevels, as is shown in Fig. 2-22. There will be eight magnetic dipole transitions that are allowed. The value of quadrupole interaction is given by [16]:

$$E_Q = eQV_{zz} \quad (2 - 99)$$

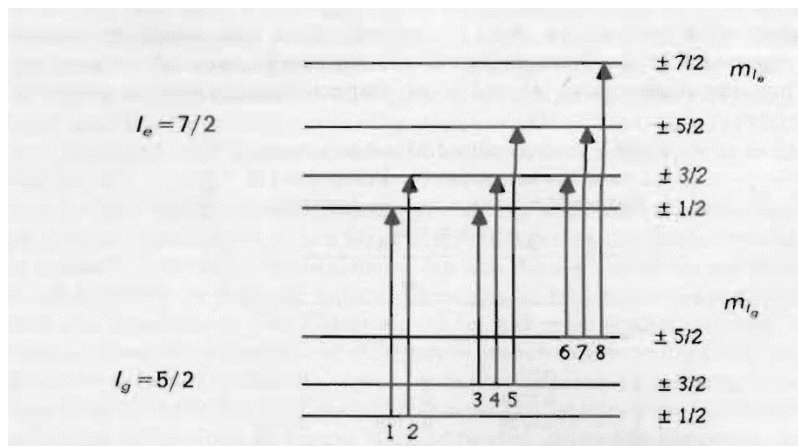


Fig. 2-22: Nuclear energy levels of ^{151}Eu in presence of a quadrupole interaction; reproduced from reference [18].

The Mössbauer spectrum for ^{151}Eu is shown in Fig. 2-23 for different values of η with quadrupole interaction $eV_{zz}Q_g = 20 \text{ mm/s}$ and Lorentzian full line width of 2.3 mm/s .

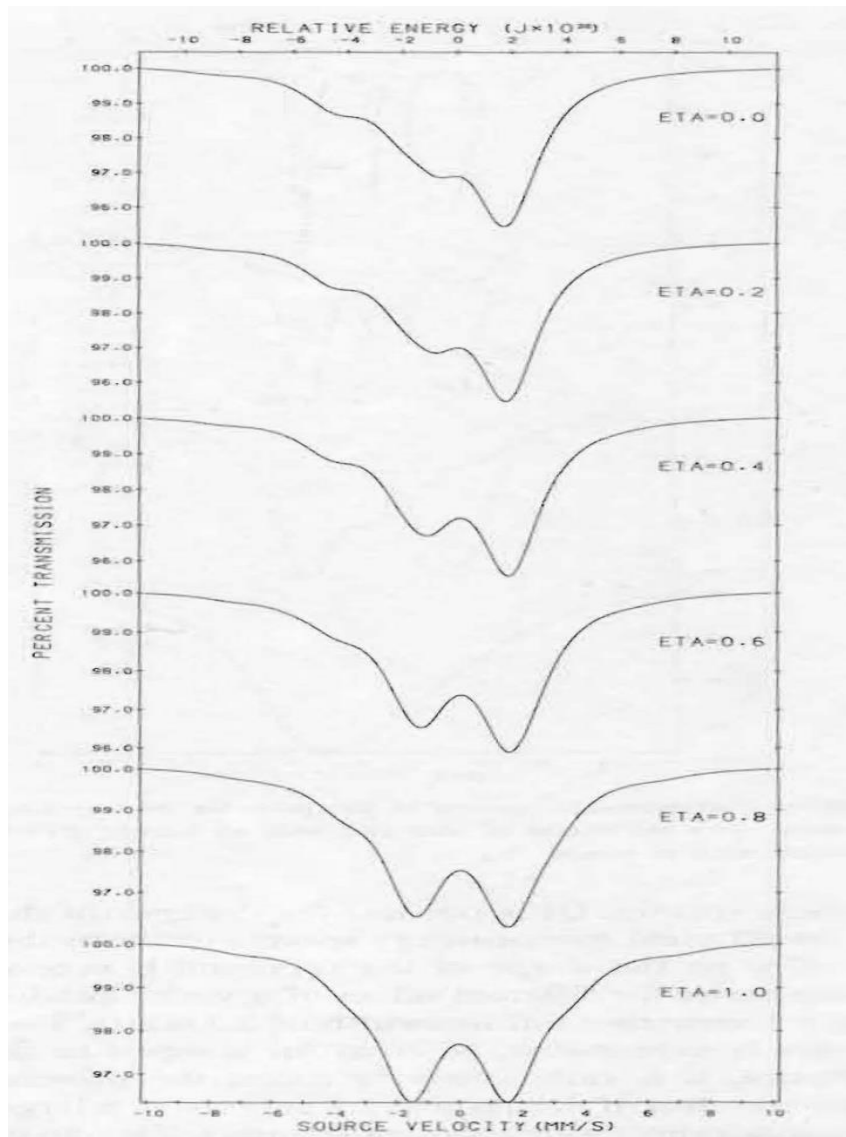


Fig. 2-23: Theoretical ^{151}Eu Mössbauer spectra in the presence of a quadrupole interaction of 20 mm/s , with an isomer shift of 0.0 mm/s , a line width of 2.3 mm/s , and different asymmetry parameters; reproduced from reference [18].

2.3.3.1.3: Magnetic hyperfine interaction

The europium (II) has an effective magnetic moment, whereas the value for effective magnetic moment for europium (III) is zero. So the magnetic hyperfine fields occur because of the neighboring magnetic ions. On the other hand, the origins of magnetic hyperfine fields of europium (II) ions in intermetallic systems are divided into three equally important contributions:

$$H_{hf} = H_c + H_{op} + H_n, \quad (2 - 100)$$

where H_c is the core-polarization field, H_{op} is due to conduction electron polarization by the ion itself, and H_n includes all contributions from neighboring magnetic ions. It is clear from Fig. 2-24 that there will be eighteen allowed transitions, and the spectra for a variety of widths are shown in Fig. 2-25.

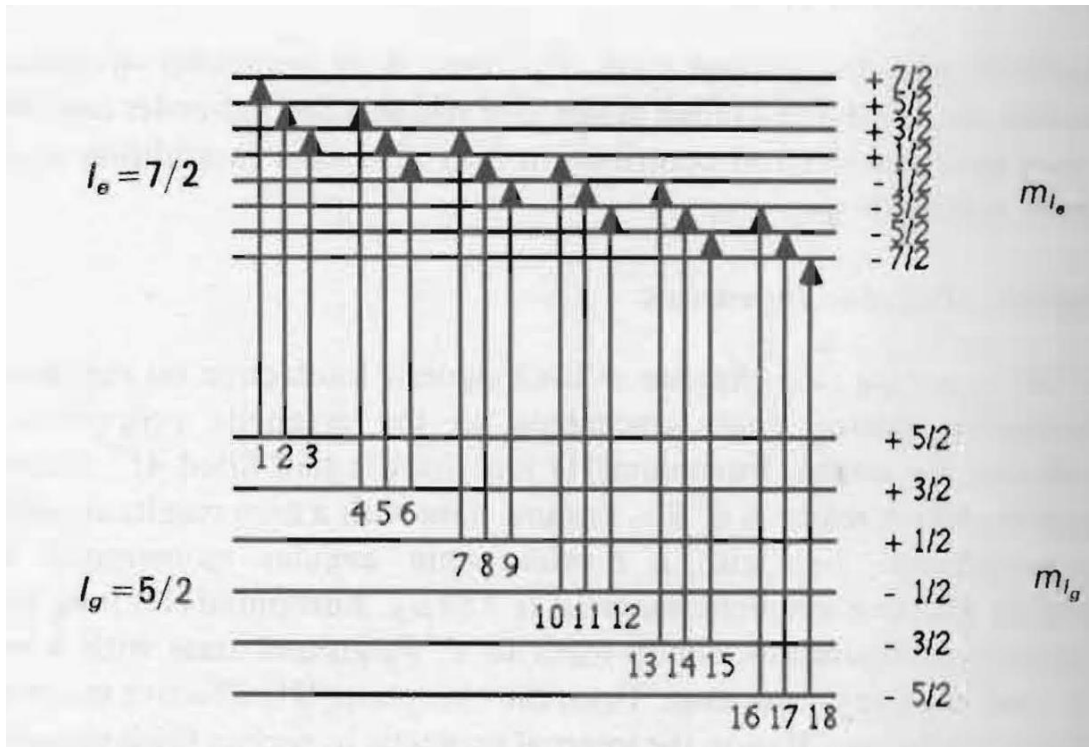


Fig. 2-24: Nuclear energy levels for ^{151}Eu in the presence of a magnetic hyperfine interaction; reproduced from reference [18].

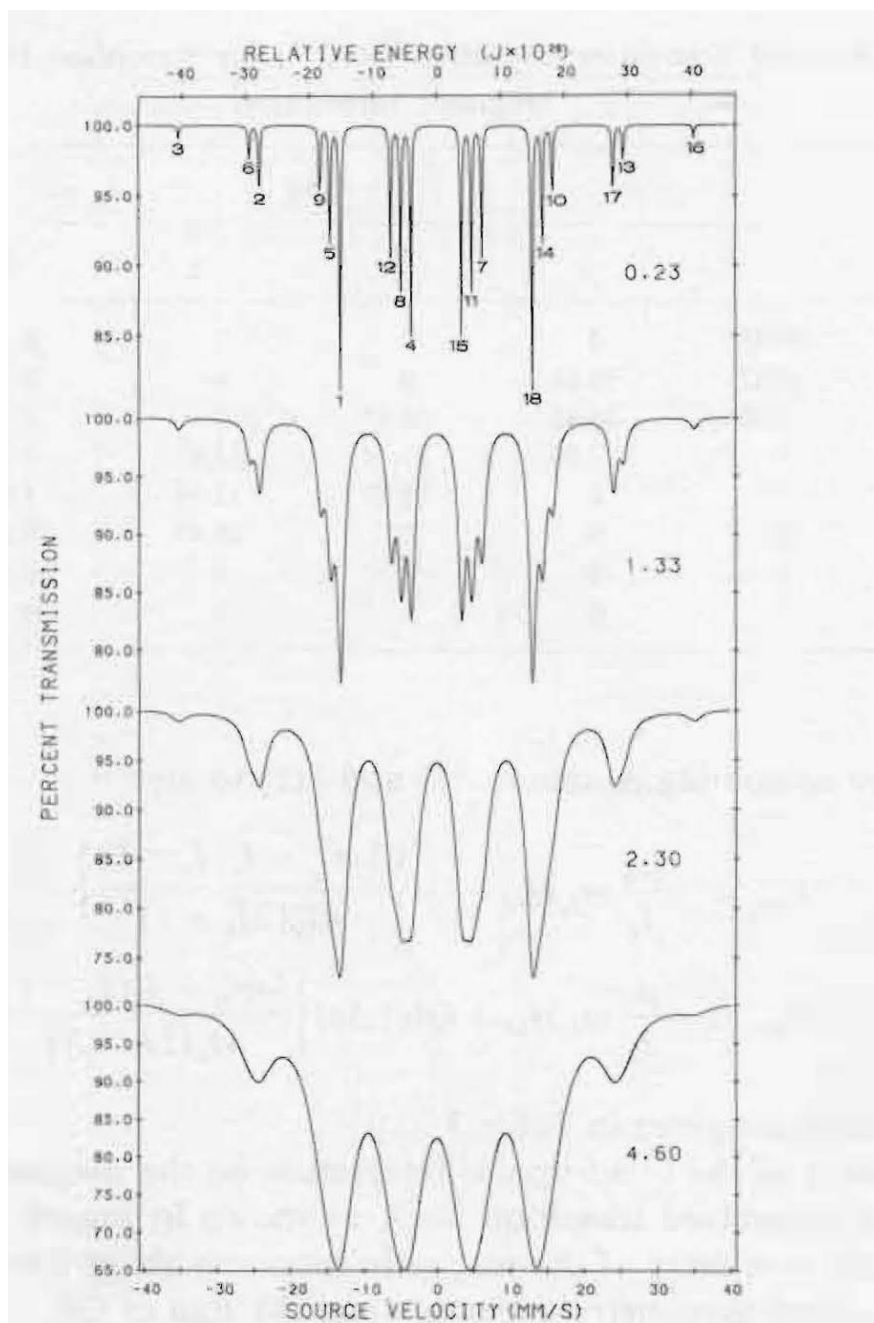


Fig. 2-25: Theoretical ^{151}Eu Mössbauer spectra in the presence of a magnetic hyperfine field of -340 kOe, with isomer shift of 0.0 mm/s and for different linewidths given in mm/s; reproduced from reference [18].

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Chapter 3: Experimental details

In this section there is information about the sample preparation, the instrument set-ups, and the measurement techniques.

3.1: Sample preparation

There are three main topics that will be discussed in this section: weighing the sample, using the arc furnace, and using the electric furnace.

3.1.1: Sample weighing

Weighing the sample plays an important role in the quality of the sample produced. Many precautions must be taken in the process of weighing the sample, such as working in a very clean environment, avoiding the use of powder form of the sample, and using a very precise scale. It is preferable for the sample to be taken in chunk form to minimize sample loss. The scale is shown in Fig. 3-1.



Fig. 3-1: The scale which is used for weighing the sample.

3.1.2: Arc furnace

The arc furnace can be used in many important ways, such as melting the sample and sealing the metallic crucibles.

The arc furnace makes it possible to reach a temperature greater than 3500°C, which is high enough to melt and mix the chosen elements.

The arc furnace is used to seal crucibles made of tantalum, which are good for use at high temperatures. The tantalum does not react with other elements even at high temperatures.

The arc furnace, as is shown in Fig. 3-2, consists of a wooden handle which is attached to copper rod, which can be moved freely by a swivel ball. At the end of the copper rod there is a tungsten pin that acts as an electrode. A transparent quartz window is located between the upper copper section and the lower copper section, and the copper hearth in the bottom is chilled by cold water. There are several openings in the device: the opening for the gas inlet and outlet, and the opening for the rotary pump. The air will be evacuated by opening the rotary pump valve. Then the chamber is filled with argon gas to atmospheric pressure. The pressure of the filled argon gas

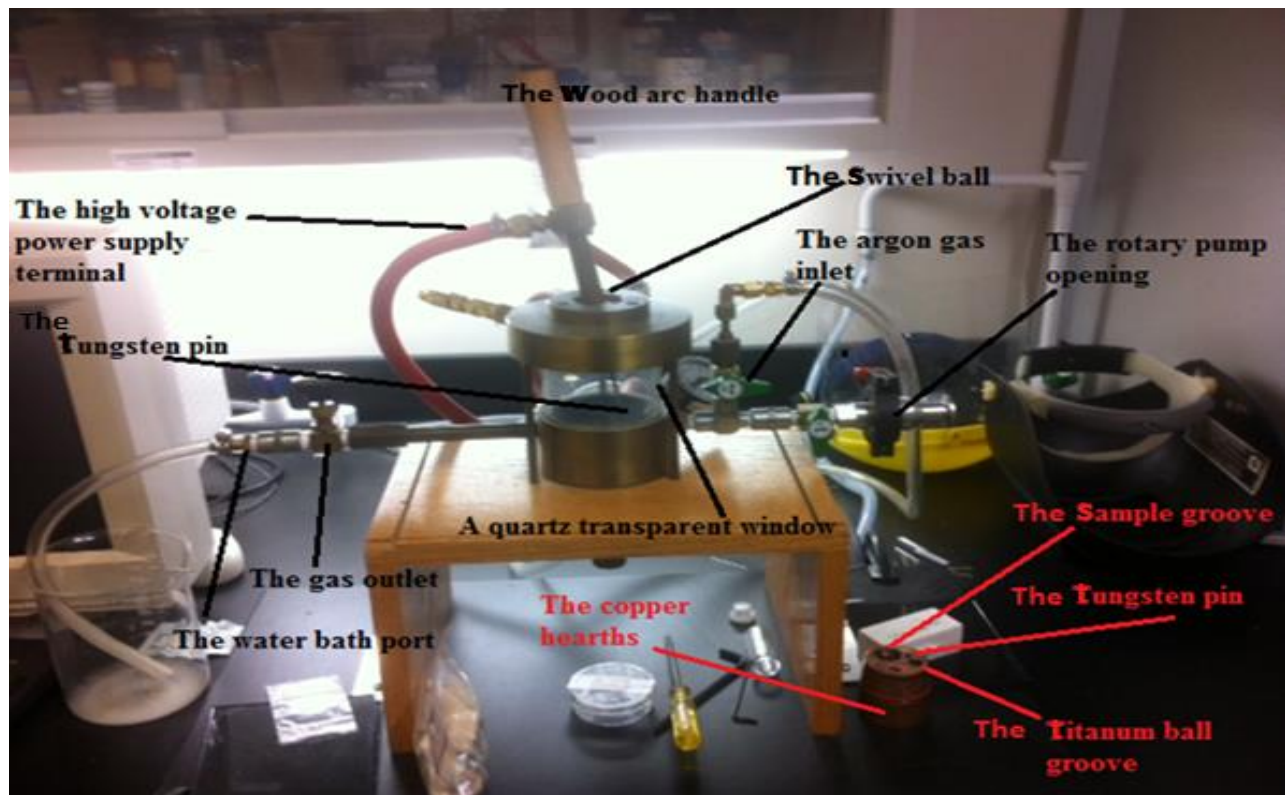


Fig. 3-2: Arc furnace set-up.

can be adjusted by using the outlet valve which lets the argon seep into a water bath to prevent air from flowing back to the chamber.

The process of making an ingot, where the sample is formed in a bulk form, is described as follows. The sample should be placed in the sample groove, and the gas inside the chamber should be evacuated. Then the argon gas should be filled into the chamber. The process of filling the chamber with the argon gas and evacuating it should be repeated at least three times. Then the arc is started by touching the two tungsten pins. Pointing the handle at the titanium ball helps to create a uniform arc flame and remove any gas impurities. Then the tungsten pin should be moved around the elements many times, so the molten mixture will be more uniform.

Sealing the tantalum crucible, which is the container that holds the sample, can be described as follows. The tantalum crucible that is shown in Fig. 3-3, is attached to the copper hearth by tightening four stainless steel screws. After the elements are put in, in a predetermined order, the cap is put on the crucible. Then the air inside the chamber should be evacuated and the argon gas should be filled. One should avoid concentrating the flame on the cap for a long time to prevent the heat from reaching the sample. Then the tantalum crucible is sealed into an evacuated or inert-gas filled quartz capsule, as is shown in Fig. 3-4. This prevents the tantalum crucible reacting with air above 600°C.



Fig. 3-3: The tantalum crucible with its cap at the bottom.

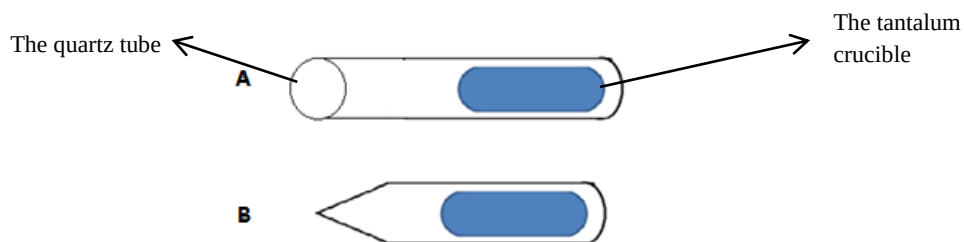


Fig. 3-4: The set-up of sealing the tantalum crucible inside the quartz tube. A) the tantalum crucible is inside the quartz tube. B) the quartz tube is sealed and partially filled with argon gas.

3.1.3: Electric furnace

The electric furnace shown in Fig. 3-5 is an important instrument in preparing samples. The electric furnace is used to anneal and melt the elements. The temperature of the furnace can reach up to 1400°C, and the heating elements of the furnace consist of nickel- chromium alloy. The temperature inside the furnace can be measured by using a thermocouple sensor. After setting the furnace to the required temperature, the quartz tube which is attached to the thermocouple, as is shown in Fig. 3-6, is gently placed inside the furnace. The oven maintains its temperature with ± 1 K accuracy. After annealing the sample, it should be cooled in icy water, so that the sample can maintain the required crystalline structure.



Fig. 3-5: The electric furnace where the sample is placed.

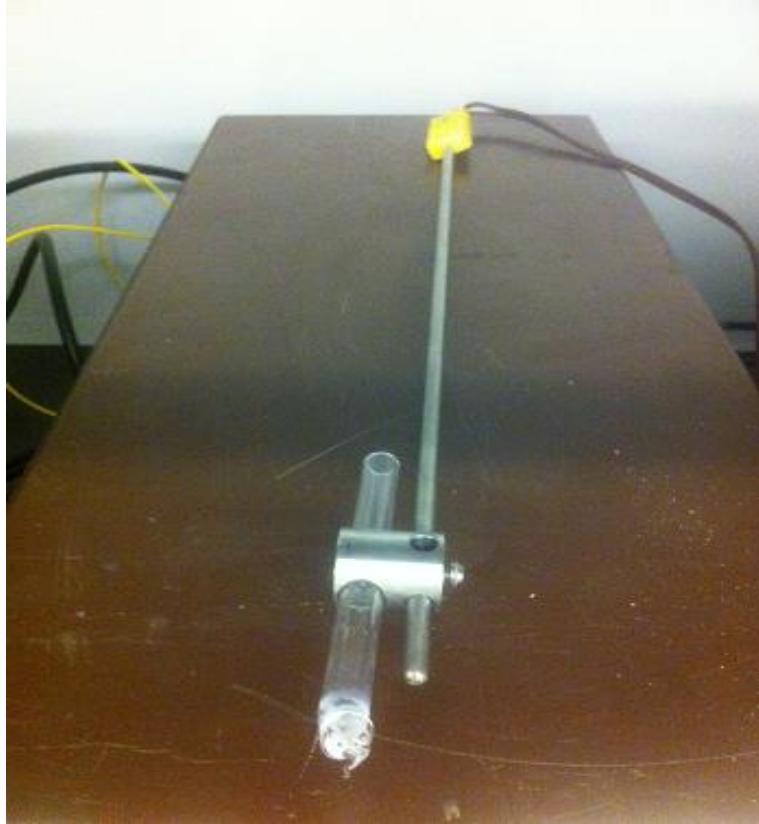


Fig. 3-6: The thermocouple and the attached quartz tube.

3.2: Mössbauer set-up

The whole set-up of the Mössbauer spectrometer consists of a radioactive source, transducer, absorber, and detector. The radioactive source is kept at room temperature. There are three main Mössbauer spectrometer set-ups used in this research. The first one is for low-temperature measurements below room temperature, the second one is for high-temperature measurements above room temperature, and the third one is a Mössbauer spectrometer with a 9 T superconducting magnet.

A convenient source which provides the resonant gamma radiation should be used. The transducer is a mechanical movement generator for the source. The detector is a proportional counter.

For low-temperature Mössbauer measurements, the absorber is made by mixing the powder material with boron nitride and putting the pressed mixture pellet into a high-purity, $8\mu\text{m}$ thick Al disk container to ensure a uniform temperature over the whole absorber. The sample is placed in a cryostat which has a static exchange gas atmosphere at the pressure of

$\sim 7 \times 10^{-3}$ mbar. The temperature in the cryostat can reach about 2 K by pumping liquid helium. The schematic figure of the low-temperature Mössbauer spectrometer is shown in Fig. 3-7.

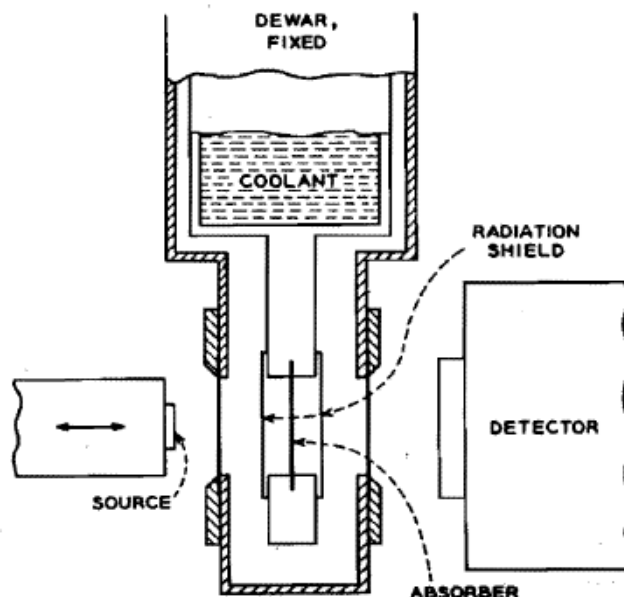


Fig. 3-7: A schematic of the low temperature Mössbauer spectrometer; reproduced from reference [1].

For the high-temperature Mössbauer measurement, the absorber is made of a mixture of the pure sample and boron nitride which is put in a boron-nitride container. The absorber is put inside a Mössbauer oven in which it is kept in a dynamic vacuum of $\sim 2 \times 10^{-5}$ mbar. The oven is shown in Fig. 3-8.

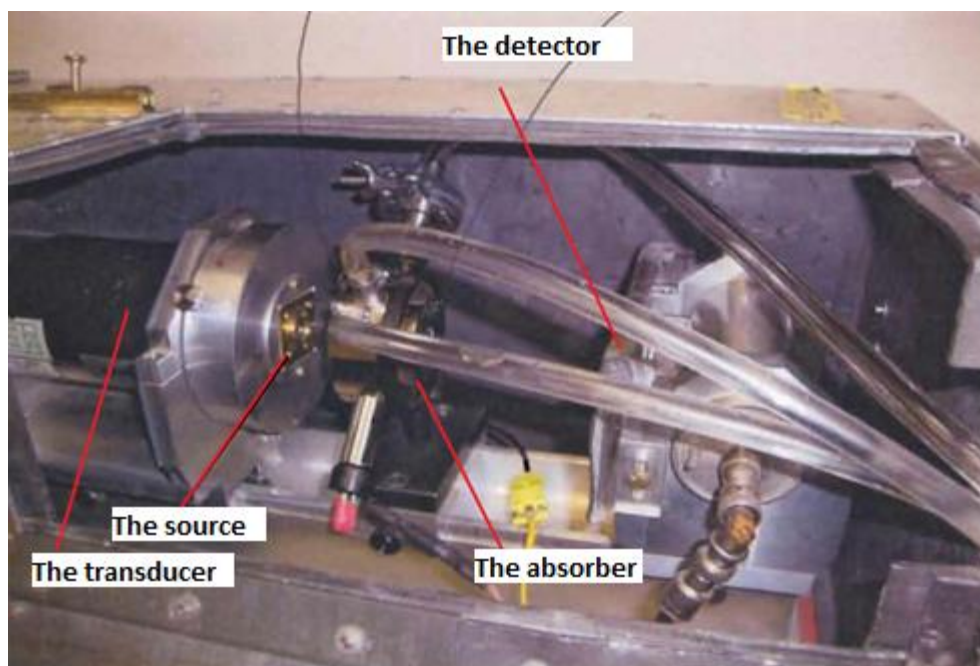


Fig. 3-8: The high-temperature Mössbauer spectrometer.

In the Mössbauer spectrometer a 9 T magnetic field is produced by using a superconducting magnet which is located in the bottom of the cryostat. The helium vapor is used to cool the absorber and the source. The sample chamber is filled with liquid helium through a needle valve. There is a valve and a vacuum pump combination that can be used to control the pressure inside the sample chamber. The heat that reaches the absorber and the source is regulated by using the heater and vaporizer that are located in the bottom of the sample chamber. The accuracy of the temperature which is reached by the source and the absorber is about ± 0.1 K around the set value. At the bottom of the cryostat there is a Mylar window which allows the radiation to travel to the Mössbauer detector. The source is attached to a transducer, and its velocity can be measured by using a Michelson interferometer, as shown in the Fig. 3-9.

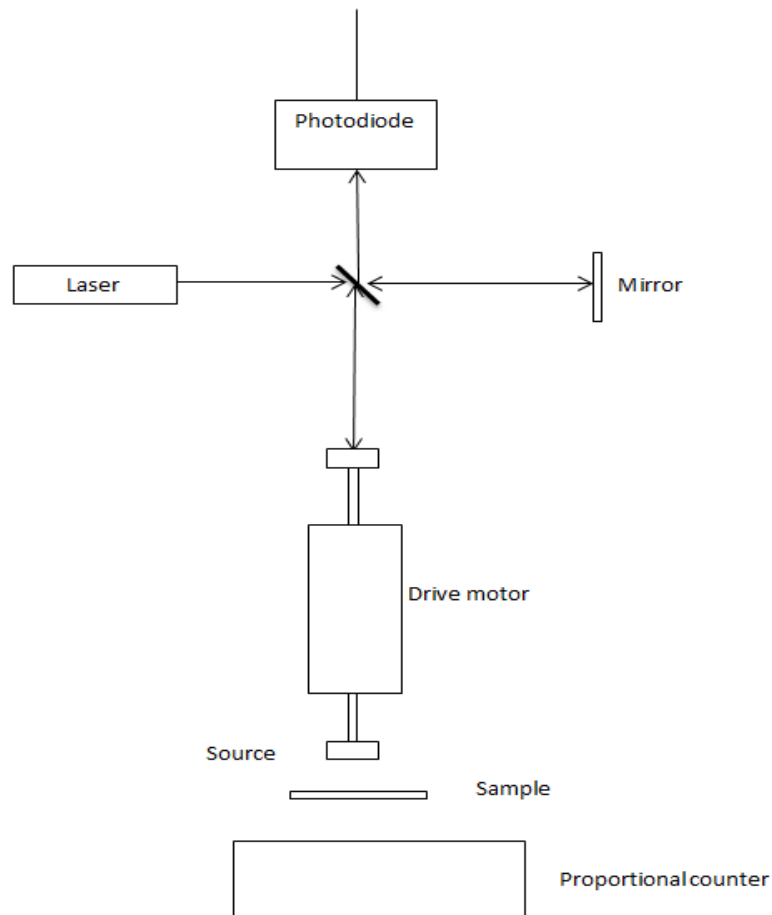


Fig. 3-9: Michelson Interferometer geometry which is used in the 9 T Mössbauer spectrometer.

3.3: X-ray diffractometer

The x-ray diffraction pattern (XRD) can be obtained by the means of the x-ray diffractometer which is very useful in determining the crystal structure of the specimen. The diffractometer consists of x-ray tube, sample stage, variable slits, goniometer, and the detectors.

A PANanalytical X'Pert scanning diffractometer is used to measure the x-ray diffraction spectra. This device uses the Bragg Brentano geometry as is shown in Fig. 3-10. In order to reduce experimental errors, the sample should be carefully prepared before the XRD measurement. First, the size of the collected grains should be in a certain range, and then should be ground lightly until a homogenous fine powder of the sample is created. Then the sample is put on a Si holder as is shown in Fig. 3-11, and drops of methanol are added to it. Next, the mixture is spread evenly all over the holder by moving it horizontally. After the methanol dries, the holder contents are put inside the x-ray diffractometer. The process of producing the x-ray radiation in the x-ray diffractometer is started when the copper anode is hit by accelerated electrons in the x-ray tube. The copper anode should be chilled by cold water to avoid any extra heat, which would cause major damage. It is known that many lines are present in the x-ray spectrum due to many effects due to many possible transitions. Therefore, a suitable filter should be used in order to get the proper lines which are $K\alpha_1$ and $K\alpha_2$. As the detector moves in a circle around the sample, it records the number of x-rays (as counts per second) observed at each angle 2θ . Each solid crystal structure has its own spectrum which is a consequence of the atomic arrangement of the material. This makes it easy to determine what and how many crystalline phases are present in a sample.

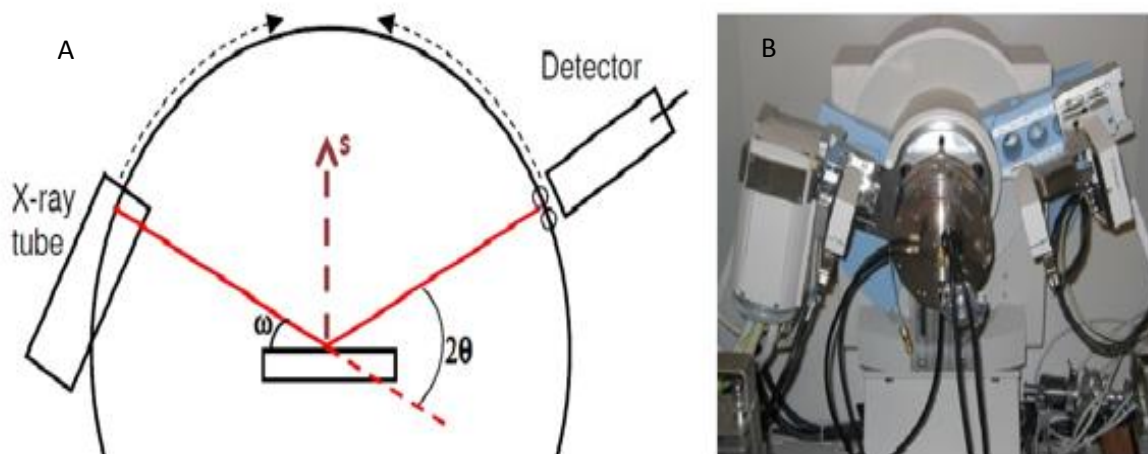


Fig. 3-10: Powder diffractometers typically use the Bragg-Brentano geometry. A) The X-ray geometry, B) the real X-ray diffractometer device; reproduced from reference [2].



Fig. 3-11: Silicon holder for the XRD.

References

[1] K. Wertheim, *Mössbauer Effect Principles and Applications* (Academic Press , New Jersey, 1964).

[2] Scott A Speekman, “Introduction to X-ray powder Diffraction Data Analysis”, MIT Center for Materials Science and Engineering (January 12, 2008, <http://prism.mit.edu/xray>).

Chapter 4: Discussion and conclusions

In the following pages, I will discuss the results presented in chapters five, six, and seven, and draw conclusions.

The Rietveld analysis of the X-ray diffraction (XRD) spectrum of EuPdGe_3 shows that the studied material crystallizes in the BaNiSn_3 -type crystal structure with the tetragonal space group $I4mm$. The unit cell parameters determined from this analysis are $a = 4.4457(1) \text{ \AA}$ and $c = 10.1703(2) \text{ \AA}$.

The temperature dependence of the dc (direct current) magnetic susceptibility of EuPdGe_3 , $\chi_{\text{dc}}(T)$, exhibits the shape characteristic of an antiferromagnet. This, however, does not prove that EuPdGe_3 is an antiferromagnet because the same shape of $\chi_{\text{dc}}(T)$ is observed for a spin-glass compound. By measuring the temperature dependence of the ac (alternating current) magnetic susceptibility, $\chi_{\text{ac}}(T)$, for different frequencies of a 10 Oe ac magnetic field, it is observed that the position of a sharp peak in the $\chi_{\text{ac}}(T)$ data is frequency independent. This constitutes proof of an antiferromagnetic ordering of the Eu magnetic moments in EuPdGe_3 because, for a spin-glass compound, the position of a sharp peak in the $\chi_{\text{ac}}(T)$ data does depend on frequency. The position of the peak in the $\chi_{\text{dc}}(T)$ data defines the magnetic ordering temperature (called Néel temperature) $T_N = 12.27(10) \text{ K}$. Additional evidence for the existence of antiferromagnetic ordering in EuPdGe_3 comes from the observed linear dependence of the magnetization M on the applied magnetic field H . For large H , $M(H)$ curves at very low temperatures have a downward curvature. This is interpreted as evidence for a series of magnetic field-induced first-order spin-flop transitions where the Eu magnetic moments flop to a perpendicular orientation with respect to H .

The temperature dependence $\chi_{\text{dc}}(T)$ above 50 K is shown to be well described by a theoretical Curie-Weiss law. The fit of the $\chi_{\text{dc}}(T)$ data to this law yields the effective Eu magnetic moment of $7.82(1) \mu_B$ that is very close to the theoretical value of $7.92 \mu_B$ expected for a free divalent Eu atom. One can thus conclude that Eu atoms in EuPdGe_3 are in a divalent oxidation state.

The fits of the ^{151}Eu Mössbauer spectra of EuPdGe_3 in the paramagnetic region, that is, at temperatures above T_N , yield the values of the following hyperfine-interaction parameters: the isomer shift δ , the principal component of the electric field gradient tensor V_{zz} , and the absorption spectral area A . The values of δ of ~ -11.2 mm/s prove that the Eu atoms are in a divalent oxidation state [for Eu atoms in a trivalent oxidation state, the values of δ are in the range $+(1-5)$ mm/s]. The temperature dependence of V_{zz} is demonstrated to obey a $T^{3/2}$ power-law relation. It is shown that the temperature dependence of A can be well described by the Debye model of lattice vibrations, with the Debye temperature of 199(2) K.

The values of the hyperfine-interaction parameters δ , V_{zz} , the hyperfine magnetic field H_{hf} , and the angle θ between the direction of H_{hf} and V_{zz} , are obtained from the fits of the ^{151}Eu Mössbauer spectra of EuPdGe_3 at temperatures below T_N . From the value of $\theta = 92(5)^\circ$ one concludes that the Eu magnetic moments in EuPdGe_3 lie in the ab plane (as the V_{zz} -axis is along the tetragonal c -axis). It is demonstrated that the temperature dependence of H_{hf} can be perfectly accounted for in terms of the molecular field model of antiferromagnetism. The fit of the $H_{\text{hf}}(T)$ dependence to a spin $S = 7/2$ Brillouin function yields the precise Néel temperature $T_N = 12.16(1)$ K.

The measured XRD spectrum of $\text{Al}_{13}\text{Fe}_4$ shows that the studied specimen is a single-phase compound, that is, it does not contain any impurity second phases (at a level larger than ~ 1 wt%). Its Rietveld analysis demonstrates that $\text{Al}_{13}\text{Fe}_4$ crystallizes in the monoclinic space group $C2/m$ with the unit cell parameters $a = 15.302(2)$ Å, $b = 8.063(2)$ Å, $c = 12.464(2)$ Å, and $\beta = 107.71(2)^\circ$.

The $M(H)$ curves of $\text{Al}_{13}\text{Fe}_4$ clearly demonstrate the presence in the studied specimen of a tiny amount of ferromagnetic impurity (at the level smaller than ~ 1 wt%) that could not be detected in XRD and ^{57}Fe Mössbauer spectra. The presence of this impurity was taken into account when fitting the $\chi_{\text{dc}}(T)$ data. The $\chi_{\text{dc}}(T)$ data could be fitted to the Curie-Weiss law, which proves that $\text{Al}_{13}\text{Fe}_4$ is not magnetically ordered down to 2 K, and thus it is concluded that $\text{Al}_{13}\text{Fe}_4$ is a paramagnet.

The ^{57}Fe Mössbauer spectrum of $\text{Al}_{13}\text{Fe}_4$ has a three-valley structure. It is shown that this three-valley structure allows this spectrum to be fitted with the maximum, practically possible, three component quadrupole doublets. With the aid of *ab initio* electric field gradient calculations,

it is demonstrated that the first component doublet results from one (out of five inequivalent crystallographic Fe sites) Fe site, the second component doublet is due to two overlapping quadrupole doublets originating from two other Fe sites, and the third component doublet arises from two overlapping quadrupole doublets originating from the last two Fe sites. The assignment of the three component doublets to specific Fe sites is additionally proved by simulating zero-field and in-field theoretical Mössbauer spectra whose shapes agree very well with those of the experimental spectra. One can thus conclude that the controversy regarding the interpretation of the ^{57}Fe Mössbauer spectrum of $\text{Al}_{13}\text{Fe}_4$ has been resolved. It is also demonstrated that the assumption used in the previous interpretation of the Mössbauer spectrum of $\text{Al}_{13}\text{Fe}_4$ is false.

It is found that the quadrupole splitting corresponding to three component quadrupole doublets increases with decreasing temperature. It is demonstrated that this temperature dependence of the quadrupole splitting can be well accounted for by a $T^{3/2}$ power-law relation.

Analysis of the temperature dependence of the area of the Mössbauer spectra of $\text{Al}_{13}\text{Fe}_4$ shows that the lattice vibrations in $\text{Al}_{13}\text{Fe}_4$ can be well described by the Debye model. The Debye temperature of $\text{Al}_{13}\text{Fe}_4$ is found to be 383(3) K.

Ab initio calculations of the electronic density of states (DOS) in $\text{Al}_{13}\text{Fe}_4$, which is an approximant to a decagonal quasicrystal, predict the presence of a narrow pseudogap located slightly above the Fermi energy E_F . The existence of such a pseudogap has been observed experimentally in literature in various decagonal/icosahedral quasicrystals and their crystalline approximants. The calculated finite DOS at E_F confirms good metallicity of $\text{Al}_{13}\text{Fe}_4$.

It is shown from Rietveld analysis of the XRD spectrum of FeNiSn that this compound crystallizes in the ZrBeSi -type crystal structure with the hexagonal space group $P6_3/mmc$. The unit cell parameters are found to be $a = 4.1329(1)$ Å and $c = 5.1912(2)$ Å.

The $M(H)$ curves of FeNiSn prove that the studied compound is a ferromagnet. Its magnetic ordering temperature, called the Curie temperature T_C , is determined from the temperature dependence of magnetization. It is found that $T_C = 1024(10)$ K. This high value of T_C is confirmed by the analysis of the temperature dependence of H_{hf} determined from the ^{57}Fe Mössbauer spectra of FeNiSn .

Analysis of the ^{57}Fe Mössbauer spectra of FeNiSn shows the presence in the studied compound of a nanoscale, disordered FeNiSn phase, in addition to the main FeNiSn phase. The magnetic moments at 4.6 K carried by Fe atoms in the main and nanoscale phases are found to be $2.39(1) \mu_{\text{B}}$ and $1.17(1) \mu_{\text{B}}$, respectively.

It is found that the FeNiSn compound decomposes at temperatures much below T_{C} , when it is annealed in vacuum for a few tens of hours. This required fresh samples to be used for each high-temperature Mössbauer measurement.

It is demonstrated from the analysis of the temperature dependence of δ , that the Debye model of lattice vibrations describes reasonably well the vibrations in FeNiSn. The Debye temperature determined from this analysis is $445(6) \text{ K}$.

Chapter 5: Antiferromagnetism in EuPdGe₃

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Antiferromagnetism in EuPdGe₃



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ABSTRACT

The results of X-ray diffraction, magnetic susceptibility and magnetization, and ¹⁵¹Eu Mössbauer spectroscopy measurements of polycrystalline EuPdGe₃ are reported. EuPdGe₃ crystallizes in the BaNiSn₃-type tetragonal structure (space group *I4mm*) with the lattice constants $a = 4.4457(1)$ Å and $c = 10.1703(2)$ Å. The results are consistent with EuPdGe₃ being an antiferromagnet with the Néel temperature $T_N = 12.16(1)$ K and with the Eu spins $S = 7/2$ in the *ab* plane. The temperature dependence of the magnetic susceptibility above T_N follows the modified Curie-Weiss law with the effective magnetic moment of $7.82(1) \mu_B$ per Eu atom and the paramagnetic Curie temperature of $-5.3(1)$ K indicative of dominant antiferromagnetic interactions. The $M(H)$ isotherms for temperatures approaching T_N from above are indicative of dynamical short-range antiferromagnetic ordering in the sample. The temperature dependence of the hyperfine magnetic field follows a $S = 7/2$ Brillouin function. The principal component of the electric field gradient tensor is shown to increase with decreasing temperature and is well described by a $T^{3/2}$ power-law relation. The Debye temperature of EuPdGe₃ determined from the Mössbauer data is 199(2) K.

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1. Introduction

There are more than 100 ternary compounds of the general chemical formula XYZ₃ that crystallize in different crystal structure types [1,2]. The largest number of XYZ₃ compounds crystallizes in the BaNiSn₃-type crystal structure [3], which belongs to the tetragonal space group *I4mm* (No. 107). Among the BaNiSn₃-type compounds, the most intensively studied are those exhibiting superconductivity, heavy-fermion or Kondo lattice characteristics: LaIrSi₃ [4–8], LaRhSi₃ [5–7,10–13], LaPdSi₃ [14,15], LaPtSi₃ [15], CeIrSi₃ [7,8,16–21,9,22–33], CeRhSi₃ [7,16,11,17,18,21,34–49], CeCoSi₃ [6,21,50–57], CeIrGe₃ [16,21,9,57–62], CeRhGe₃ [16,21,60,58,63], CeCoGe₃ [58,57,64–72], CeFeGe₃ [73–75], BaPtSi₃ [76,77], CaYSi₃ (Y = Ir, Pt) [78], SrYGe₃ (Y = Pd, Pt) [77] and SrAuSi₃ [79]. Other compounds of the BaNiSn₃ structure type, such as CeCuZ₃ (Z = Al, Ga) [80], XIrSi₃ (X = Gd, Tb, Dy) [81,82], GdCoSi₃ [54,83], GdYGa₃ (Y = Ni, Cu) [83], GdCuAl₃ [83], XCoGe₃ (X = Pr, Nd) [84], EuPtZ₃ (Z = Si, Ge) [85,86], XPdGe₃ (X = La, Eu) [87,88], EuNiGe₃ [90,89] and LaOsSi₃ [91], are also reported and studied for their interesting physical properties. The presence of a very

wide range of elements in the selected BaNiSn₃-type compounds indicated above point to the possibility of discovering new isostructural compounds of this type.

In this paper, we report on the synthesis and the results of crystallographic, magnetic, and ¹⁵¹Eu Mössbauer spectroscopy investigations of a polycrystalline EuPdGe₃ compound. We demonstrate that this compound exhibits a long-range antiferromagnetic order below $T_N = 12.16(1)$ K with the Eu magnetic moments lying in the *ab* plane. We provide evidence for the presence of short-range antiferromagnetic correlations above T_N . We show that magnetic and Mössbauer data are consistent with the Eu atoms having spin 7/2. We find that the Debye temperature of EuPdGe₃ is 199(2) K.

2. Experimental methods

The polycrystalline sample of EuPdGe₃ was prepared using the constituent elements of Eu (purity 99.9%), Pd (purity 99.99%), and Ge (purity 99.999%) in stoichiometric ratio. Appropriate amounts of these elements were weld sealed under a purified argon atmosphere into a tantalum container. The container in turn was held within an evacuated fused silica jacket to avoid its air oxidation. The mixture was melted at 1050 °C for 4 h, followed by annealing at 600 °C for 190 h, and then quenching into cold water.

X-ray diffraction measurements were performed at 298 K in Bragg–Brentano geometry on the PANalytical X'Pert scanning diffractometer using Cu Kα radiation in the 2θ range 15–111.5° in steps of 0.02°. The Kβ line was eliminated by using a Kevex PSi2 Peltier-cooled solid-state Si detector.

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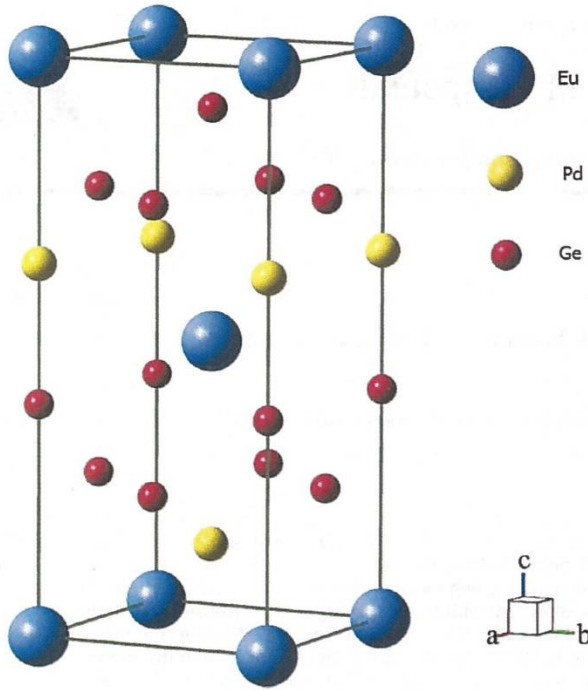


Fig. 1. The unit cell of the EuPdGe_3 compound.

Table 1

Atomic positions for the tetragonal EuPdGe_3 obtained through Rietveld analysis.

Atom	Site	Point symmetry (mm)	Occupancy	x	y	z
Eu	2a	4	1.0	0	0	0
Pd	2a	4	1.0	0	0	0.645(2)
Ge	4b	2	1.0	0	$\frac{1}{2}$	0.257(2)
Ge	2a	4	1.0	0	0	0.403(2)

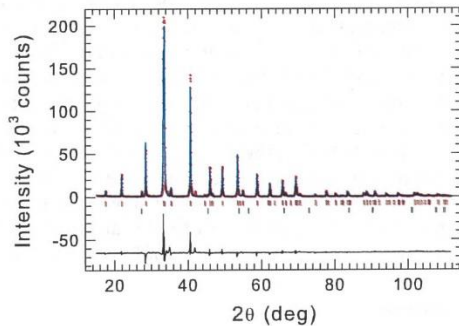


Fig. 2. The X-ray diffraction spectrum of the compound EuPdGe_3 at 298 K. The experimental data are denoted by open circles, while the line through the circles represents the results of the Rietveld refinement. The upper set of vertical bars represents the Bragg peak positions corresponding to the EuPdGe_3 phase, while the lower set refers to the positions of the impurity phase of Ge (space group $Fd\bar{3}m$). The lower solid line represents the difference curve between experimental and calculated spectra.

The dc magnetization was measured in the temperature range 2–300 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 was measured using PPMS in magnetic fields of 100 and 1000 Oe in the temperature range of 2–300 K. The ac magnetic

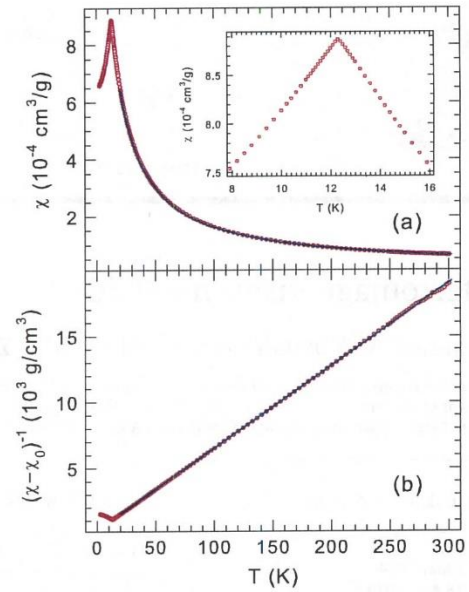


Fig. 3. (a) The temperature dependence of the magnetic susceptibility of EuPdGe_3 , measured in an external magnetic field of 1000 Oe. The solid line is the fit to Eq. (1) in the temperature range 50–300 K, as explained in the text. The inset shows the magnetic susceptibility data in the low-temperature range. (b) The inverse magnetic susceptibility corrected for the contribution χ_0 , $(\chi - \chi_0)^{-1}$ versus temperature T . The solid line is the fit to Eq. (1).

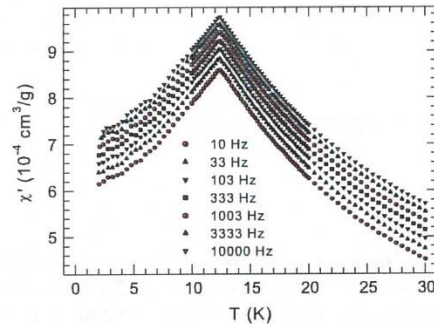


Fig. 4. Temperature dependence of the in-phase component χ' of the ac magnetic susceptibility of EuPdGe_3 for different applied frequencies from 10 to 10,000 Hz. As all these $\chi'(T)$ curves overlap, they are shifted upward with respect to each other by $2 \times 10^{-5} \text{ cm}^3/\text{g}$.

susceptibility data were collected using PPMS between 2.0 and 30 K in a 10 Oe ac magnetic field and zero external dc magnetic field for frequencies varying from 10 Hz to 10 kHz.

The ^{151}Eu Mössbauer measurements were conducted using a standard, constant acceleration Mössbauer spectrometer operating in sine mode and a $^{151}\text{Sm}(\text{SmF}_3)$ source at room temperature. The 21.5 keV γ -rays were detected with a proportional counter. The spectrometer was calibrated with a Michelson interferometer [92], and the spectra were folded. The Mössbauer absorber consisted of a mixture of powder EuPdGe_3 and boron nitride, which was pressed into a pellet that was put into an Al disk container of thickness 0.008 mm to ensure a uniform temperature over the whole sample. The surface density of the Mössbauer absorber was $28.5 \text{ mg}/\text{cm}^2$. This corresponds to an effective thickness parameter [93] $T = 4.1f_a$, where f_a is the Debye–Waller factor of the absorber. Since $T > 1$, the resonance line shape of the Mössbauer spectra was described using a transmission integral formula [94].

The Mössbauer source $^{151}\text{Sm}(\text{SmF}_3)$ used is not a monochromatic source as ^{151}Sm nuclei are located in the SmF_3 matrix at a site of noncubic symmetry. By measuring the ^{151}Eu Mössbauer spectra of a cubic EuSe compound we determined that the electric quadrupole coupling constant [93] $eQ_q V_{zz}$ (here e is the proton charge, $Q_q = 0.903 \text{ b}$ (Ref. [95]) is the ground-state electric quadrupole moment of the ^{151}Eu nucleus, and V_{zz} is the principal component of the electric field gradient (EFG)

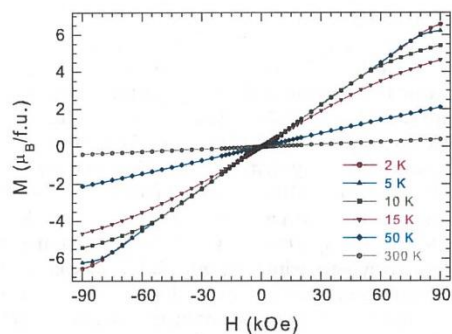


Fig. 5. Magnetization M versus applied magnetic field H isotherms of EuPdGe_3 measured at the indicated temperatures.

tensor) in our source is $-3.69(13)$ mm/s, which is close to the value of -3.6 mm/s found in Ref. [96]. The precise shape of the source emission line was taken into account in the fits of the ^{151}Eu Mössbauer spectra. The isomer shift δ of the ^{151}Eu Mössbauer spectra is given here relative to the $^{151}\text{Sm}(\text{SmF}_3)$ source at room temperature.

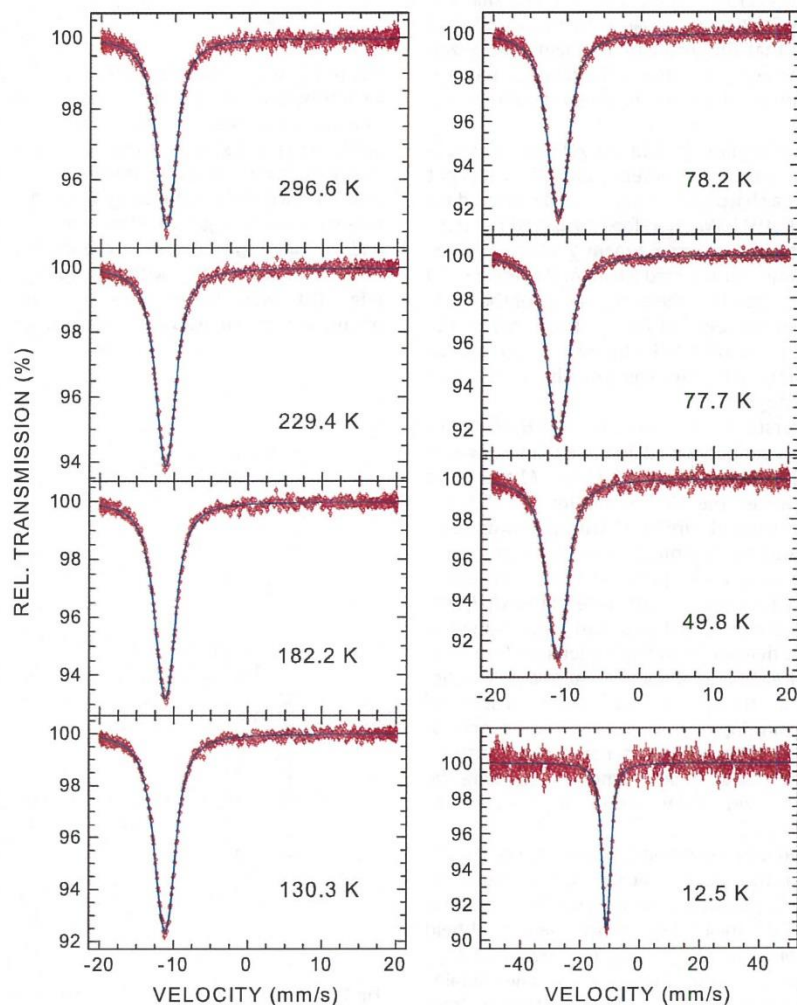


Fig. 6. ^{151}Eu Mössbauer spectra of EuPdGe_3 obtained at the indicated temperatures, fitted (solid lines) with an electric quadrupole hyperfine interaction, as described in the text. The zero-velocity origin is relative to the source.

3. Experimental results and discussion

3.1. Structural characterization

The ternary compound EuPdGe_3 crystallizes in the BaNiSn_3 -type crystal structure with the tetragonal space group $I4mm$ (No. 107) [97]. There are two formula units of EuPdGe_3 per unit cell. The crystal structure of EuPdGe_3 is shown in Fig. 1, with the crystallographic data for the Eu, Pd, and Ge sites listed in Table 1.

The room-temperature X-ray diffraction pattern of EuPdGe_3 is shown in Fig. 2. A Rietveld refinement [98] of the spectrum in Fig. 2 yields the lattice constants $a = 4.4457(1)$ Å and $c = 10.1703(2)$ Å. The values of these lattice parameters compare well with the corresponding values reported earlier [88,97]. As determined from the Rietveld refinement (Fig. 2), the EuPdGe_3 specimen contains a second phase of Ge (space group $Fd\bar{3}m$) in the amount of 1.0(2) wt%.

3.2. Magnetic measurements

The temperature dependence of the magnetic susceptibility χ of EuPdGe_3 measured in an applied magnetic field of 1000 Oe is

shown in Fig. 3(a) (the identical $\chi(T)$ data were also obtained in an applied magnetic field of 100 Oe). The sharp peak at $T_N = 12.27(10)$ K in the $\chi(T)$ data is indicative of antiferromagnetic ordering occurring at this temperature.

The $\chi(T)$ data above 50 K (Fig. 3(a)) could be fitted to a modified Curie–Weiss law

$$\chi = \chi_0 + \frac{C}{T - \Theta_p}, \quad (1)$$

where χ_0 is the temperature-independent term that includes 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. The Curie constant can be expressed as $C = \frac{N\mu_{\text{eff}}^2}{3k_B}$, where N is the number of Eu ions per formula unit, μ_{eff} is the effective magnetic moment, and k_B is the Boltzmann constant. Fig. 3(b) shows the inverse magnetic susceptibility corrected for the contribution χ_0 as $(\chi - \chi_0)^{-1}$ versus temperature; the validity of the modified Curie–Weiss law is evident. The values of χ_0 , C , and Θ_p obtained from the fit are, respectively, $1.06(1) \times 10^{-5} \text{ cm}^3/\text{g}$, $16.04(3) \times 10^{-3} \text{ cm}^3 \text{ K/g}$, and $-5.3(1)$ K. The value of C corresponds to $\mu_{\text{eff}} = 7.82(1) \mu_B$ per Eu atom.

For a free Eu^{2+} ion (electronic configuration $8S_{7/2}$), the theoretical value of $\mu_{\text{eff}}^{\text{th}} = g\mu_B\sqrt{J(J+1)}$ is $7.94 \mu_B$ [99]. The fact that the experimental value $\mu_{\text{eff}} = 7.82(1) \mu_B$ is close to the theoretical value of $7.94 \mu_B$ confirms that the magnetic moment is localized on the divalent Eu ions. The negative value of Θ_p indicates the predominantly antiferromagnetic interaction between the Eu^{2+} magnetic moments.

Although the presence of a sharp peak in the $\chi(T)$ data is a necessary condition for the occurrence of antiferromagnetism, it is not a sufficient condition since a sharp peak in $\chi(T)$ is also observed for spin-glass compounds [100,101]. We therefore measured the temperature dependence of the in-phase component χ' of the ac magnetic susceptibility of EuPdGe_3 for selected frequencies between 10 and 10,000 Hz (Fig. 4). It is clear that the temperature of the maximum in $\chi'(T)$ curves does not depend on the frequency of the applied ac magnetic field, in contrast to its frequency dependence observed for spin glasses [100,101]. This confirms that the studied compound is an antiferromagnet.

The magnetization M versus applied magnetic field H isotherms of EuPdGe_3 at six temperatures between 2 and 300 K are shown in Fig. 5. It is seen from Fig. 5 that at 300 and 50 K the M exhibits a linear H dependence. However, the $M(H)$ curve for $T = 15$ K, i.e. slightly above T_N , has a downward curvature. This downward curvature is most probably due to dynamical short-range antiferromagnetic ordering in the sample on approaching T_N from above [90]. The presence of such a downward curvature in the $M(H)$ isotherms below T_N at $T = 2, 5$ and 10 K (Fig. 5) can be explained as being caused by a series of field-induced first-order spin-flop transitions where the ordered magnetic moments flop to a perpendicular orientation with respect the applied field [90]. It is a series of field-induced first-order spin-flop transitions occurring at increasing magnetic fields, rather than one first-order spin-flop transition in a single crystal occurring at a single magnetic field along the easy axis, because of the random orientation of the crystallites in the polycrystalline sample [90].

The maximum observed magnetization of $6.56 \mu_B/\text{Eu}$ at $T = 2$ K and $H = 90$ kOe (Fig. 5) is rather close to the saturation magnetization ($M_{\text{sat}} = gS\mu_B$) of $7 \mu_B/\text{Eu}$ expected for the free Eu^{2+} ion with $S = 5/2$ and $g = 2$. Within the mean-field theory, the critical field H_c at which M reaches M_{sat} with increasing H is equal to $M_{\text{sat}}/\chi(T_N)$. By taking the $\chi(T_N)$ value from Fig. 3, one obtains $H_c = 93$ kOe. This is close to the value of ~ 100 kOe estimated from an extrapolation of the $T = 2$ K isotherm (Fig. 5) to the value $M_{\text{sat}} = 7\mu_B$.

3.3. Mössbauer spectroscopy

The ^{151}Eu Mössbauer spectra of EuPdGe_3 recorded at temperatures at which no magnetic dipole hyperfine interaction [93] is present are shown in Fig. 6. These spectra are in a form of a broadened single line. The Eu atoms in EuPdGe_3 are located at the 2a site with the point symmetry $4/\text{mm}$ (Table 1), which ensures a non-zero, axially symmetric (the asymmetry parameter $\eta = 0$) EFG tensor at this site, and hence a non-zero electric quadrupole hyperfine interaction [93]. The spectra in Fig. 6 thus result from a pure electric quadrupole hyperfine interaction [102]. They 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 [93]. The fit of the 296.6 K Mössbauer spectrum yields $eQ_qV_{zz} = 3.65(23) \text{ mm/s}$ and $\delta = -11.23(1) \text{ mm/s}$. The value of δ proves that Eu is divalent in the studied compound [102].

The principal component of the EFG tensor V_{zz} derived from the fits of the spectra in Fig. 6 clearly increases with decreasing temperature [Fig. 7(a)]. In the traditional [103], i.e., not based on a first-principles method [104], interpretation of V_{zz} one uses the formula

$$V_{zz} = (1 - \gamma_{\infty})V_{zz}^{\text{ext}} + (1 - R)V_{zz}^{\text{local}}, \quad (2)$$

where V_{zz}^{ext} is a contribution due to external (point) charges, V_{zz}^{local} is a contribution due to local charges (caused by valence and conduction electrons near the probe site), γ_{∞} and R are, respectively, Steinhilber antishielding and shielding factors that account for the amplification or attenuation of V_{zz} resulting from the deformation of closed shells induced by V_{zz}^{ext} and V_{zz}^{local} , respectively. For Eu^{2+} ions with the $8S_{7/2}$ ground state, the V_{zz}^{local} contribution is negligible and thus any V_{zz} must arise from the V_{zz}^{ext} contribution [105].

An increase of V_{zz} with decreasing temperature found here [Fig. 7(a)], was also observed in many other crystalline, amorphous, and quasicrystalline compounds [103,106–109]. Although

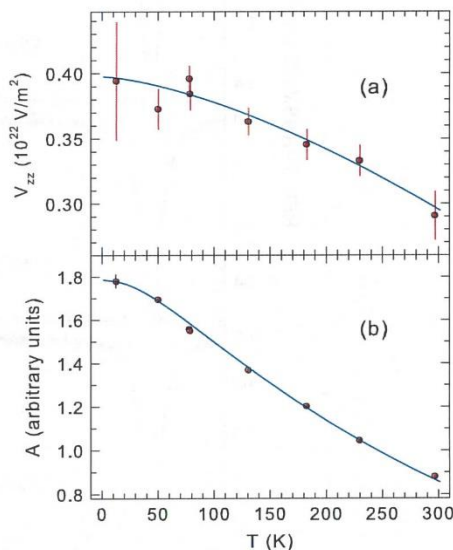


Fig. 7. Temperature dependence of (a) the principal component of the electric field gradient tensor V_{zz} and (b) the absorption spectral area A derived from the fits of the spectra in Fig. 6. The solid lines are the fits to Eq. (3) in (a) and to Eq. (4) in (b), as explained in the text.

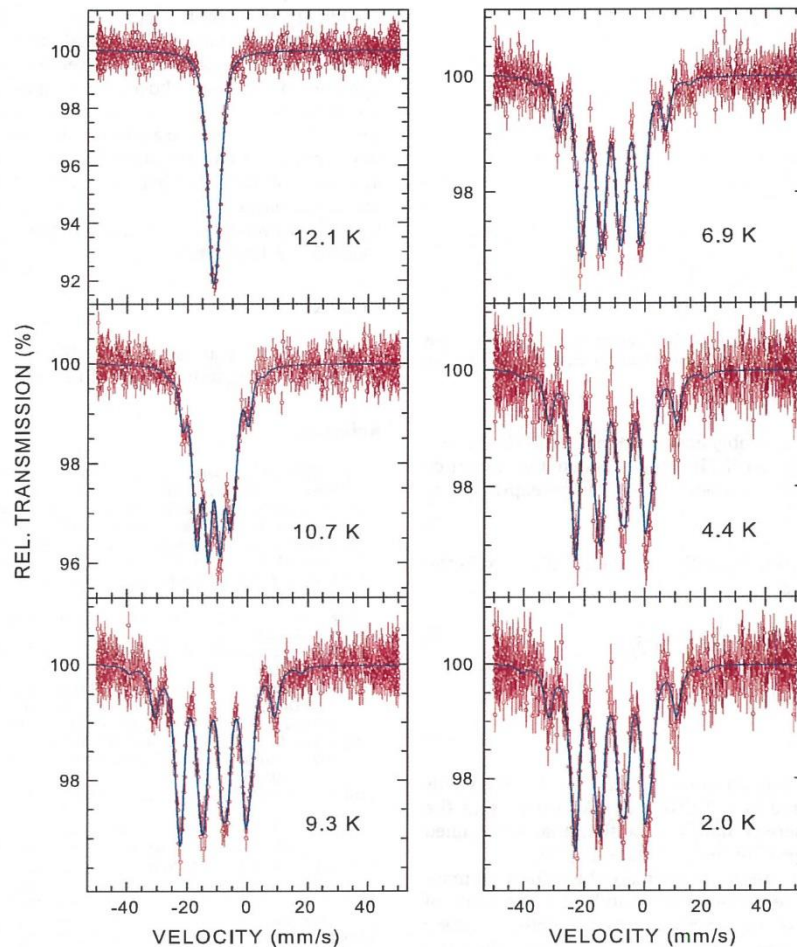


Fig. 8. ^{151}Eu Mössbauer spectra of EuPdGe_3 obtained at the indicated temperatures, fitted (solid lines) with combined magnetic dipole and electric quadrupole hyperfine interactions, as described in the text. The zero-velocity origin is relative to the source.

its mechanism is not well understood, it is surprisingly well described by the empirical relation [103]

$$V_{zz}(T) = V_{zz}(0) \left(1 - BT^{3/2}\right), \quad (3)$$

where $V_{zz}(0)$ is the value of V_{zz} at 0 K and B is a constant. The fit of the $V_{zz}(T)$ data [Fig. 7(a)] to Eq. (3) yields $V_{zz}(0) = 0.398(6) \times 10^{22} \text{ V/m}^2$ and $B = 4.97(70) \times 10^{-5} \text{ K}^{-3/2}$. We note that our value of $V_{zz}(0) = 0.398(6) \times 10^{22} \text{ V/m}^2$ is almost identical to the value of $V_{zz}(4.2 \text{ K}) = 0.39 \times 10^{22} \text{ V/m}^2$ at the Gd site in the isostructural GdCoSi_3 as determined from ^{155}Gd Mössbauer spectroscopy [83]. The value of B found here is similar to that found for other systems [103,107].

Fig. 7(b) displays the temperature dependence of the absorption spectral area A derived from the fits of the Mössbauer spectra in Fig. 6. This area is proportional to the absorber Debye–Waller factor f_a given [93] by

$$f_a(T) = \exp \left\{ -\frac{3}{4} \frac{E_\gamma^2}{Mc^2 k_B \Theta_D} \left[1 + 4 \left(\frac{T}{\Theta_D} \right)^2 \int_0^{\Theta_D/T} \frac{x dx}{e^x - 1} \right] \right\}, \quad (4)$$

where M is the mass of the Mössbauer nucleus, c is the speed of light, E_γ is the energy of the Mössbauer transition, and Θ_D is the

Debye temperature. The fit of the $A(T)$ data [Fig. 7(b)] to Eq. (4) gives $\Theta_D = 199(2) \text{ K}$. The value of Θ_D found here should be compared with the value of $268(2) \text{ K}$ derived from the specific heat data for the isostructural EuNiGe_3 [90].

The ^{151}Eu Mössbauer spectra of EuPdGe_3 measured at temperatures at which both magnetic dipole and electric quadrupole hyperfine interactions are present are shown in (Fig. 8). The fit of the 2.0 K Mössbauer spectrum yields the following values of the hyperfine parameters: $\delta = -11.15(5) \text{ mm/s}$, the hyperfine magnetic field $H_{\text{hf}} = 293.4(1.3) \text{ kOe}$, $eQ_{\text{g}}V_{zz} = 4.98(87) \text{ mm/s}$, and the angle between the direction of H_{hf} and the V_{zz} -axis $\theta = 92(5)^\circ$. As the principal axis of the EFG tensor (V_{zz} -axis) is along the tetragonal c -axis, the value $\theta = 92(5)^\circ$ implies that the Eu magnetic moments in EuPdGe_3 must lie in the ab plane. We note here that it was suggested [90] that the Eu magnetic moments are also aligned in the ab plane in the isostructural EuNiGe_3 . Similarly, in the isostructural GdCoSi_3 the Gd magnetic moments were shown with ^{155}Gd Mössbauer spectroscopy to be perpendicular to the crystallographic c axis [83].

The temperature dependence of H_{hf} determined from the fits to the Mössbauer spectra in Fig. 8 is shown in Fig. 9. It is usually assumed that the temperature variation of H_{hf} in an

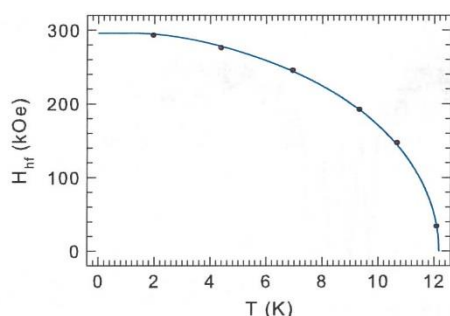


Fig. 9. Temperature dependence of the hyperfine magnetic field H_{hf} determined from the fits of the spectra in Fig. 8. The solid line is the fit to Eq. (5), as explained in the text.

antiferromagnet can be reasonably explained in term of the molecular field model, assuming that H_{hf} is proportional to the sublattice magnetization. In terms of this model, $H_{\text{hf}}(T)$ can be expressed as

$$H_{\text{hf}}(T) = H_{\text{hf}}(0)B_J(x), \quad (5)$$

where $H_{\text{hf}}(0)$ is the saturation hyperfine magnetic field, $B_J(x)$ is the Brillouin function defined as

$$B_J(x) = \frac{2J+1}{2J} \coth\left(\frac{2J+1}{2J}x\right) - \frac{1}{2J} \coth\left(\frac{x}{2J}\right) \quad (6)$$

and

$$x = \frac{3J}{J+1} \frac{H_{\text{hf}}(T)}{H_{\text{hf}}(0)} \frac{T_N}{T}. \quad (7)$$

The fit of the $H_{\text{hf}}(T)$ data (Fig. 9) to Eq. (5) with $J = S = 7/2$ yields $H_{\text{hf}}(0) = 296.4(1.1)$ kOe and $T_N = 12.16(1)$ K. We believe that the value of T_N determined here is more precise than that determined from the position of the peak in the $\chi(T)$ data (Fig. 3).

In principle, one could attempt to estimate the saturation magnetic moment of Eu in the studied compound from the value of $H_{\text{hf}}(0)$ found here, based on the expected proportionality between the latter and the former. The hyperfine magnetic field at the ^{151}Eu nucleus in a metallic system can be written as the sum of three contributions [110]

$$H_{\text{hf}} = H_{\text{core}} + H_{\text{cep}} + H_n, \quad (8)$$

where H_{core} is the core-polarization field, H_{cep} is the contribution of the valence and conduction band electrons, and H_n includes all contributions from neighboring magnetic moments. It is only the H_{core} contribution that is truly proportional to the Eu magnetic moment. However, since all these three contributions are approximately of a similar magnitude [102], one is unable to determine the magnitude of the Eu magnetic moment from the measured value of H_{hf} .

4. Conclusions

We have reported the results of X-ray diffraction, magnetic susceptibility and magnetization, and ^{151}Eu Mössbauer spectroscopy measurements of the EuPdGe_3 compound. The studied compound crystallizes in the BaNiSn_3 -type crystal structure with the lattice constants $a = 4.4457(1)$ Å and $c = 10.1703(2)$ Å. The high-temperature $\chi(T)$ data follow the modified Curie–Weiss law with a Curie constant consistent with Eu^{2+} spins $S = 7/2$ and Weiss temperature $\Theta_p = -5.3(1)$ K indicative of dominant antiferromagnetic interactions. We find that EuPdGe_3 is an antiferromagnet with the Néel temperature $T_N = 12.16(1)$ K and the Eu ordered magnetic moments in the ab plane. The temperature dependence of

the hyperfine magnetic field is well described by a $S = 7/2$ Brillouin function. Evidence of dynamical short-range antiferromagnetic ordering in the sample is observed in the $M(H)$ curves on approaching T_N from above. The shape of the $M(H)$ isotherms at temperatures below T_N is indicative of a series of field-induced first-order spin-flop transitions where the ordered magnetic moments flop to a perpendicular orientation with respect to the applied field. The principal component of the electric field gradient tensor increases with decreasing temperature and is well described by a $T^{-3/2}$ power-law relation. The Debye temperature of EuPdGe_3 is found to be 199(2) K.

Acknowledgment

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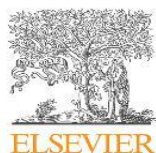
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Chapter 6: ^{57}Fe Mössbauer spectroscopy and magnetic study of $\text{Al}_{13}\text{Fe}_4$

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^{57}Fe Mössbauer spectroscopy and magnetic study of $\text{Al}_{13}\text{Fe}_4$



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ABSTRACT

The results of *ab initio* electronic structure and electric field gradient (EFG) calculations, and of X-ray diffraction, ^{57}Fe Mössbauer spectroscopy, and magnetic studies of $\text{Al}_{13}\text{Fe}_4$ are reported. It is shown that $\text{Al}_{13}\text{Fe}_4$ crystallizes in the monoclinic space group $C2/m$, in which Fe atoms are located at five inequivalent crystallographic sites, with the lattice parameters $a = 15.503(2)$ Å, $b = 8.063(2)$ Å, $c = 12.464(2)$ Å, and $\beta = 107.71(2)^\circ$. We demonstrate that zero-field Mössbauer spectra can be decomposed into three quadrupole doublets. With the aid of the calculated EFG parameters we show that the first doublet results from one Fe site, the second doublet is due to two other Fe sites, and the third doublet originates from the last two Fe sites. We find that the shape of the Mössbauer spectrum of $\text{Al}_{13}\text{Fe}_4$ measured in an external magnetic field of 90 kOe can be accounted for with five component subspectra generated using the calculated EFG parameters at five inequivalent Fe sites. The quadrupole splittings corresponding to three component doublets are shown to increase with decreasing temperature and are well described by a $T^{3/2}$ power-law relation. The Debye temperature of $\text{Al}_{13}\text{Fe}_4$ is found to be 383(3) K. We find a pseudogap in the density of states (DOS), with a width of ~ 0.2 eV, that is centered 0.1 eV above the Fermi energy. The finite DOS at the Fermi energy confirms good metallicity of $\text{Al}_{13}\text{Fe}_4$. The $1/T$ -like dependence of the magnetic susceptibility shows that $\text{Al}_{13}\text{Fe}_4$ is a paramagnet.

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1. Introduction

Al-rich Fe 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 magnetic properties of these three compounds indicate that in none of them is a long-range magnetic order developed. 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 (Refs. [8–10]) and Al_5Fe_2 (Refs. [11,10]) 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 cubic (Table 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

origin 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 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 will be shown below from *ab initio* EFG calculations, this justification is incorrect.

The situation described above provides a strong motivation to revisit the ^{57}Fe Mössbauer spectra of $\text{Al}_{13}\text{Fe}_4$. With the aid of *ab initio* EFG calculations, we demonstrate that the shape of ^{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. We find that the quadrupole splittings corresponding to three component doublets increases with decreasing temperature and that their temperature dependence is well described by a $T^{3/2}$ power-law relation. We also determine the Debye temperature of $\text{Al}_{13}\text{Fe}_4$ and show that the studied compound is a paramagnet down to 2.0 K. We demonstrate the presence of a pseudogap around the Fermi energy in the electronic DOS of $\text{Al}_{13}\text{Fe}_4$.

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Table 1Crystallographic data [4] for $\text{Al}_{13}\text{Fe}_4$ and calculated V_{zz} (in units of 10^{21} V/m^2) and η .

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

2. Experimental methods

An ingot of nominal composition $\text{Al}_{13}\text{Fe}_4$ was prepared by inductive melting constituent elements in a water-cooled copper crucible under an argon atmosphere [20]. 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.

X-ray diffraction measurements were carried out at 298 K in Bragg–Brentano geometry on a PANalytical X'Pert scanning diffractometer using $\text{Cu K}\alpha$ radiation in the 2θ range 5–132° in steps of 0.02°. The $K\beta$ line was eliminated by using a Kevex PSi2 Peltier-cooled solid-state Si detector.

The dc magnetization was measured in 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 was measured using PPMS in a magnetic field of 10 kOe in the temperature range of 2–390 K.

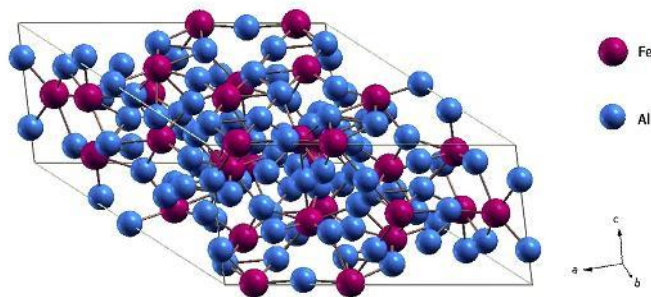
The ^{57}Fe Mössbauer measurements were conducted using standard Mössbauer spectrometers operating in sine mode and a 50-mCi $^{57}\text{Co(Rh)}$ source, which was kept at room temperature for zero-field measurements and at the same temperature as that of the absorber for an in-field measurement. The spectrometers used for zero-field and in-field measurements were calibrated, respectively, with a 6.35- μm -thick $\alpha\text{-Fe}$ foil [21] and a Michelson interferometer [22], and the spectra were folded. The Mössbauer absorber consisted of a mixture of powdered $\text{Al}_{13}\text{Fe}_4$, and powdered boron nitride, which was pressed into a pellet and put into a high-purity, 8- μm -thick Al disk container to ensure a uniform temperature over the whole absorber. The Mössbauer absorber was put into a Mössbauer cryostat in which it was kept in a static exchange gas atmosphere at a pressure of $\sim 7 \times 10^{-3}$ mbar. The surface density of the Mössbauer absorber was 9.8 mg/cm^2 . This corresponds to an effective thickness parameter [14] $t_a = 2.2f_a$, where f_a is the Debye–Waller factor of the absorber. Since $t_a > 1$, the resonance line shape of the Mössbauer spectra was described using a transmission integral formula [23]. The ^{57}Fe Mössbauer 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].

Ab initio electronic structure and EFG calculations 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 [24].

3. Results and discussion

3.1. Structural characterization

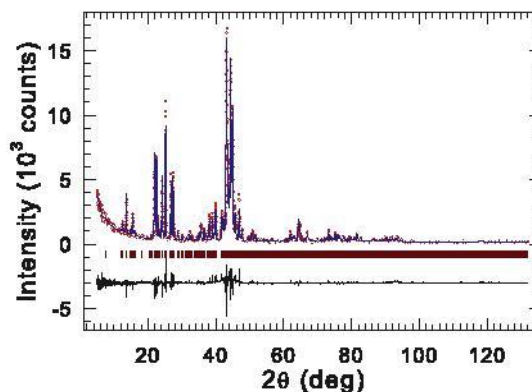
The studied compound $\text{Al}_{13}\text{Fe}_4$ crystallizes in the monoclinic space group $C2/m$ (No. 12) [4]. There are 6 formula units of $\text{Al}_{13}\text{Fe}_4$ per unit cell, i.e., there are 102 atoms in a unit cell. Fig. 1 shows the crystal structure of $\text{Al}_{13}\text{Fe}_4$, and the atomic coordinates of the Al and Fe sites, taken from Ref. [4], are given in Table 1.

**Fig. 1.** The unit cell of the $\text{Al}_{13}\text{Fe}_4$ compound.

The X-ray powder diffraction pattern of $\text{Al}_{13}\text{Fe}_4$ is shown in Fig. 2. A Rietveld refinement [25] of the X-ray powder diffraction data was carried out using the atomic coordinates in Table 1, yielding the lattice parameters $a = 15.503(2) \text{ \AA}$, $b = 8.063(2) \text{ \AA}$, $c = 12.464(2) \text{ \AA}$, and $\beta = 107.71(2)^\circ$. The values of these lattice parameters compare well with the corresponding values reported earlier [4]. No second phases could be detected in the X-ray powder diffraction pattern of $\text{Al}_{13}\text{Fe}_4$ (Fig. 2).

3.2. Electronic structure and EFG calculations

In the FP-LAPW+lo method used for the calculations, the unit cell is divided into non-overlapping muffin-tin (MT) spheres centered at nuclei, and an interstitial region. The wave functions in the interstitial regions are expanded in plane waves and the wave functions inside the MT spheres are linear combinations of radial functions times spherical harmonics. The exchange-correlation potential is calculated by the generalized gradient approximation, using the scheme developed by Perdew, Burke, and Ernzerhof [26]. The maximum orbital angular momentum for the expansion of the wave function in spherical harmonics inside the MT spheres was taken to be $l_{\text{max}} = 10$. The Brillouin zone integrations within the self-consistency cycles were performed via a tetrahedron method, using 115 k -points in the irreducible wedge of the Brillouin zone. To obtain as precise results as possible, we expanded the basis function up to $R_{\text{MT}} \times K_{\text{MAX}} = 7$, where R_{MT} is the smallest spherical muffin-tin radius present in the system and K_{MAX} is the maximum modulus of the reciprocal lattice vector. We adopted the values of 2.00 and 2.33 $\text{\AA}$ for Al and Fe, respectively, as the R_{MT} radii. In the calculations self-consistency was achieved by demanding the convergence of the integrated charge and energy difference between succeeding iterations to be smaller than $10^{-3} e$ and 10^{-3} Ry .

**Fig. 2.** 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 represents 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 experimental and calculated patterns.

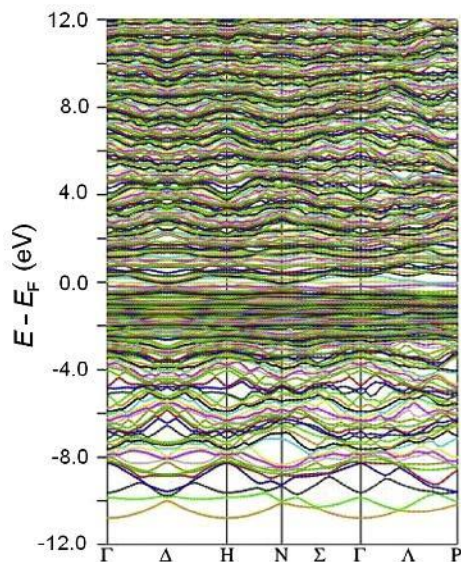


Fig. 3. Energy band structure of $\text{Al}_{13}\text{Fe}_4$.

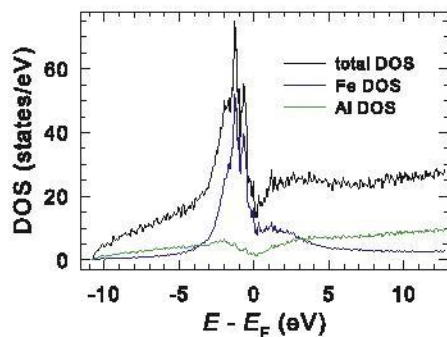


Fig. 4. Total electronic density of states (DOS) of $\text{Al}_{13}\text{Fe}_4$, and Fe and Al DOS.

respectively. The experimental lattice parameters (a, b, c , and β) and atomic coordinates (Table 1) were used.

The calculated electronic band structure of $\text{Al}_{13}\text{Fe}_4$ is shown in Fig. 3. It shows that the nature of the compound studied is metallic as the valence and conduction bands overlap around the Fermi energy. To the best of our knowledge, there are no experimental data on the band structure of this compound to be compared with our results.

Fig. 4 shows the total electronic DOS of $\text{Al}_{13}\text{Fe}_4$. The presence of a narrow pseudogap, with a width of ~ 0.2 eV, located at 0.1 eV above the Fermi energy E_F , is clearly visible. The existence of such a pseudogap in the DOS at or around E_F is a characteristic feature of the DOS of quasicrystals and their crystalline approximants. This pseudogap results either from Fermi surface – Brillouin zone interactions or from the strong hybridization of Fe d states with the Al s and p states [27,28]. Fig. 4 implies good metallicity of $\text{Al}_{13}\text{Fe}_4$ due to a finite DOS at E_F .

We calculated V_{zz} and the asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$ ($0 \leq \eta \leq 1$), where V_{yy}, V_{xx} , and V_{zz} are the eigenvalues of the EFG tensor in order of increasing magnitude [14], at all Fe and Al crystallographic sites. The calculated V_{zz} and η values are displayed in Table 1 and their comparison with experiment will be discussed below.

3.3. Mössbauer spectroscopy

The room- and liquid-nitrogen temperature ^{57}Fe Mössbauer spectra of $\text{Al}_{13}\text{Fe}_4$ measured in a large velocity range are shown

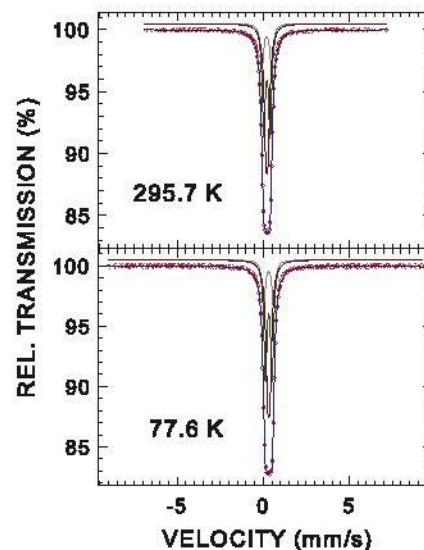


Fig. 5. Room- and liquid-nitrogen ^{57}Fe Mössbauer spectra of $\text{Al}_{13}\text{Fe}_4$ measured in a large velocity range fitted (blue solid line) with three quadrupole doublets (dark grey, dark green, and dark red solid lines), as described in the text. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

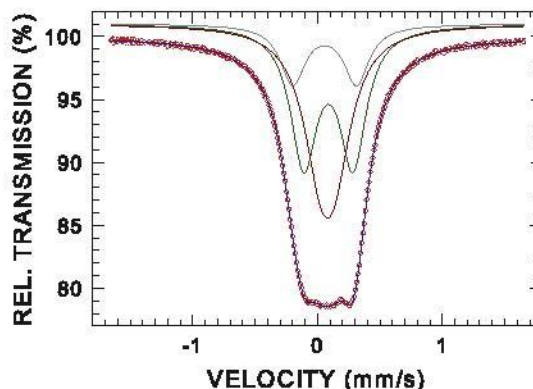


Fig. 6. ^{57}Fe Mössbauer spectrum of $\text{Al}_{13}\text{Fe}_4$ at 5.7 K fitted (blue solid line) with three quadrupole doublets (dark grey, dark green, and dark red solid lines), as described in the text. The zero-velocity origin is relative to the source at 5.7 K. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

in Fig. 5. The spectra can be fitted well with three component quadrupole doublets (*vide infra*) and no Zeeman pattern originating from a possible magnetic impurity phase present in the studied specimen can be discerned in them.

A quadrupole splitting, i.e., the distance between two resonance lines in a ^{57}Fe Mössbauer quadrupole doublet, is given by [14]

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

where e is the proton charge and Q is the electric quadrupole moment of the ^{57}Fe nucleus (0.15 b) [29].

A visual inspection of the Mössbauer spectrum of $\text{Al}_{13}\text{Fe}_4$ (Fig. 6) shows that it exhibits a three-valley structure. As there are five inequivalent Fe sites in the crystal structure of $\text{Al}_{13}\text{Fe}_4$ (Table 1), one could attempt to fit this spectrum with five quadrupole doublets. This, however, is impossible in practice as the structure of the spectrum is not rich enough to allow for a fit with the number of free parameters corresponding to five component quadrupole doublets. This spectrum can be very well fitted with the maximum,

practically possible, three component quadrupole doublets (Fig. 5(a)). The spectral weights of these three component doublets, in the order of decreasing Δ ($\Delta_a, \Delta_b, \Delta_c$), are 15.7(1)%, 40.9(1)%, and 43.4(1)%. In what way are these three component doublets related to the five Fe sites, if they are related in any way at all?

A convincing indication of such a relation comes from the calculations of the EFG tensor at the five Fe sites. Using the calculated values of V_{zz} and η (Table 1), one would expect the Mössbauer spectrum of $\text{Al}_{13}\text{Fe}_4$ to be a superposition of five component quadrupole doublets with $\Delta_1 = 0.342$, $\Delta_2 = 0.377$, $\Delta_3 = 0.049$, $\Delta_4 = 0.064$, and $\Delta_5 = 0.374$ mm/s. One can see that $\Delta_3 \approx \Delta_4 \ll \Delta_1 \leq \Delta_2 \approx \Delta_5$. Thus, the component doublets Δ_a, Δ_b , and Δ_c can be associated with the Fe atoms at sites (Table 1) Fe(1), Fe(2) and Fe(5), and Fe(3) and Fe(4), respectively.

Fig. 7(a) shows a simulated Mössbauer spectrum resulting from a superposition of five quadrupole-doublet components with Δ_i values ($i = 1, 2, 3, 4, 5$) calculated above and with the same value of δ . One can observe that the simulated spectrum has a three-valley structure, although the experimental Δ_i values are larger than the calculated ones. However, this does not mean that the calculated Δ_i are imprecise; their precision is dictated by the accuracy of the Q value which is 13.3% [29]. The simulated spectrum generated with the Δ_i values larger by 14.0% than the theoretical ones (Fig. 7(b)) almost fits the experimental spectrum well.

Zero-field ^{57}Fe Mössbauer spectra of nonmagnetic polycrystalline compounds provide information only on the absolute value of the EFG (Eq. (1)). The sign of the EFG can be determined from ^{57}Fe Mössbauer spectra measured in external magnetic fields [30]. Fig. 8 shows a comparison between the ^{57}Fe Mössbauer spectrum of $\text{Al}_{13}\text{Fe}_4$ at 5.7 K measured in an external magnetic field of 90.0 kOe and the spectrum generated for the V_{zz} and η values in Table 1. Similarly to what has been done for calculating the simulated spectrum in Fig. 7(b), the values of V_{zz} were increased by 13.3%. If texture effects are negligible, one can assume that the principal axes of the EFG tensor are randomly oriented with respect to the external magnetic field. The algorithm for calculating the spectrum in such a case was given in Ref. [31] and was used here. We also assumed the same δ value for each of five component

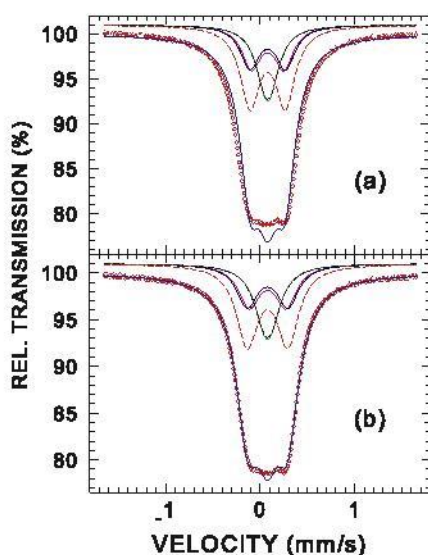


Fig. 7. (a) ^{57}Fe Mössbauer spectrum of $\text{Al}_{13}\text{Fe}_4$ at 5.7 K and simulated spectrum (blue solid line) resulting from the superposition of quadrupole doublets (with Δ values calculated from the data in Table 1) due to the Fe atoms at the Fe(1) site (pink solid line), Fe(2) site (dark 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%. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

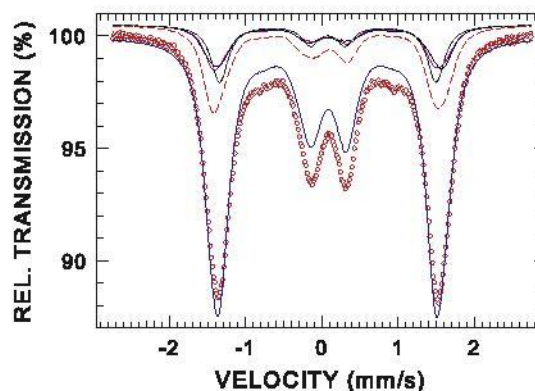


Fig. 8. Comparison of the ^{57}Fe Mössbauer spectrum of $\text{Al}_{13}\text{Fe}_4$ at 5.7 K measured in an external magnetic field of 90.0 kOe parallel to the direction of the γ rays (red open circles) with the simulated spectrum (blue solid line) resulting from the superposition of five component spectra, that were generated for the values of V_{zz} (multiplied by 1.14) and η in Table 1, due to the Fe 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). The zero-velocity origin is relative to the source at 5.7 K. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

spectra. The structure of the in-field Mössbauer spectrum is relatively well accounted for by the simulated spectrum (Fig. 8). This provides additional support for the correctness of the calculated values of V_{zz} (magnitude and sign) and η at five Fe sites.

We note here in passing that a qualitative reasoning, used in previous Mössbauer studies of $\text{Al}_{13}\text{Fe}_4$ [12,18,19], affirming that, since the Fe atoms in four $4i$ sites have similar asymmetric atomic environments, they must therefore contribute to one quadrupole-doublet component, is unjustified. As one can see in Table 1, the values of V_{zz} at these four Fe sites are widely different.

Fig. 9 shows the ^{57}Fe Mössbauer spectra of $\text{Al}_{13}\text{Fe}_4$ measured in the temperature range 4.4–295.4 K. Excellent fits of these spectra are obtained with the three-quadrupole-doublet model discussed above. The values of Δ_i ($i = a, b, c$) derived from the fits of these spectra and of the spectrum in Fig. 6 are shown in Fig. 10(a)–(c). A clear increase of Δ_i with decreasing temperature is observed. Such a temperature dependence of Δ has been observed in many crystalline [32], quasicrystalline [33], and amorphous [34] compounds. It is well described by the empirical equation

$$\Delta(T) = \Delta(0) \left(1 - BT^{3/2} \right), \quad (2)$$

where $\Delta(0)$ is the value of Δ at 0 K and B is a constant. The fit of the $\Delta_i(T)$ data (Fig. 10(a)–(c)) to Eq. (1) gives $\Delta_a(0) = 0.564(3)$ mm/s, $B_a = 1.23(13) \times 10^{-5} \text{ K}^{-3/2}$, $\Delta_b(0) = 0.386(1)$ mm/s, $B_b = 1.20(7) \times 10^{-5} \text{ K}^{-3/2}$, and $\Delta_c(0) = 0.129(6)$ mm/s, $B_c = 1.11(15) \times 10^{-5} \text{ K}^{-3/2}$. The values of B_i are similar to those found for other compounds [32–34].

The absorption spectral area A of a Mössbauer spectrum is proportional to f_a , which is given in the Debye theory by [14]

$$f_a(T) = \exp \left\{ -\frac{3}{4} \frac{E_\gamma^2}{Mc^2 k_B \Theta_D} \left[1 + 4 \left(\frac{T}{\Theta_D} \right)^2 \int_0^{\Theta_D/T} \frac{x dx}{e^x - 1} \right] \right\}, \quad (3)$$

where M is the mass of the Mössbauer nucleus, c is the speed of light, E_γ is the energy of the Mössbauer transition, and Θ_D is the Debye temperature. Fig. 10(d) shows the temperature dependence of the spectral area A derived from the fits of the Mössbauer spectra in Fig. 9. The fit of the $A(T)$ data (Fig. 10(d)) to Eq. (3) yields $\Theta_D = 383(3)$ K. The value of Θ_D found here is close to the value of 419(5) K found in another Mössbauer study of $\text{Al}_{13}\text{Fe}_4$ [17,19], but is significantly smaller than the value of 544 K derived from specific-heat measurements [13].

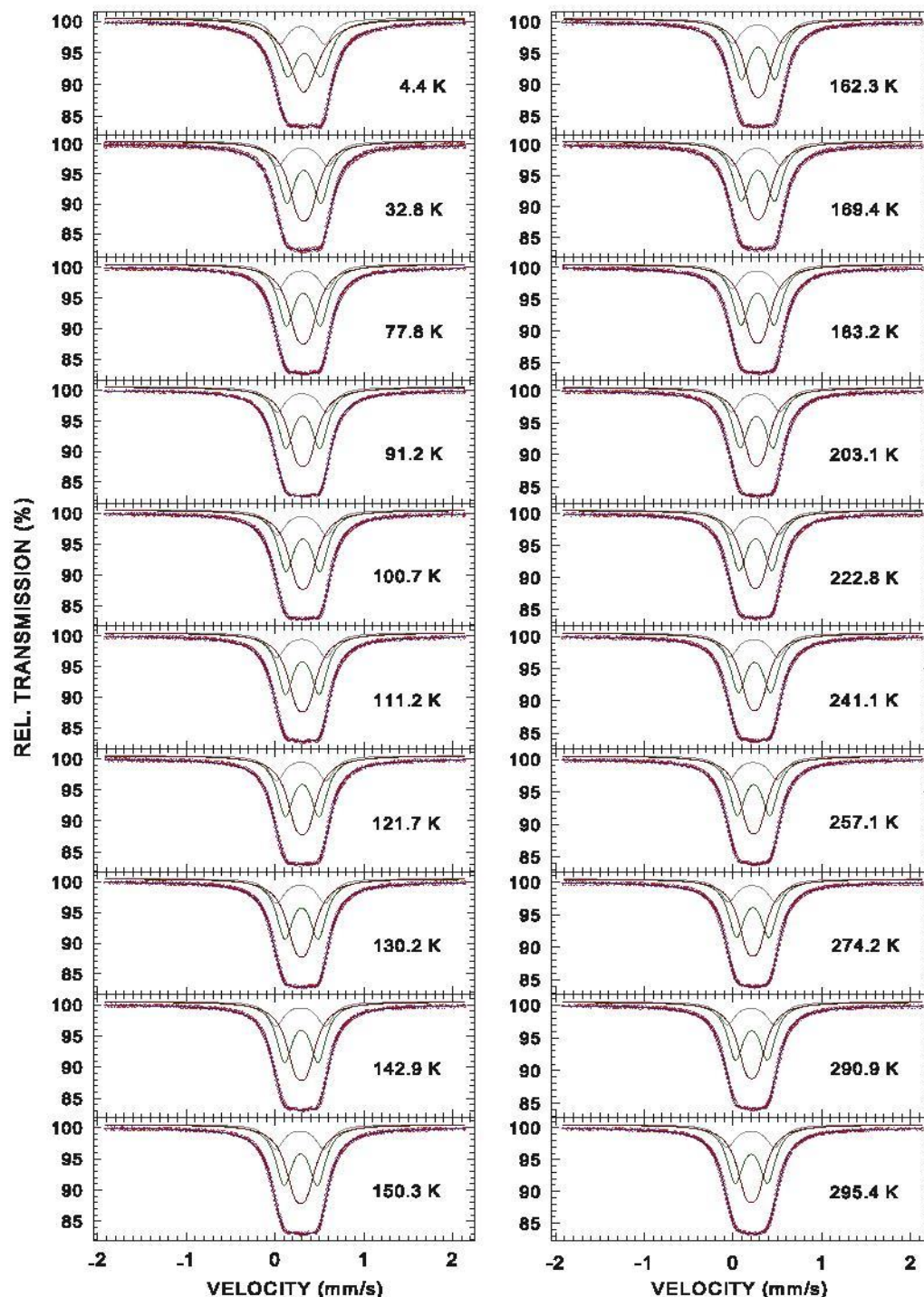


Fig. 9. ^{57}Fe Mössbauer spectra of $\text{Al}_{13}\text{Fe}_4$ at the indicated temperatures fitted (blue solid line) with three quadrupole doublets (dark grey, dark green, and dark red solid lines), as described in the text. The zero-velocity origin is relative to $\alpha\text{-Fe}$ at room temperature. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3.4. Magnetic measurements

Although the Mössbauer spectra in Fig. 3 show no presence of a possible magnetic impurity in the specimen studied (at the level of ~ 1 wt%), the magnetic field dependence of magnetization curves $M(H)$ measured at selected temperatures (Fig. 11) are typical for a ferromagnet. They show that M does not saturate in the highest

field available of 90 kOe. Clearly, the studied specimen does contain a ferromagnetic impurity (at the ppm concentration level), probably in the form of an iron-oxide phase at the sample's surfaces or precipitated iron superparamagnetic clusters.

The temperature dependence of the magnetic susceptibility χ of $\text{Al}_{13}\text{Fe}_4$ measured in an applied magnetic field of 10 kOe is shown in Fig. 12. It follows approximately a $1/T$ -like dependence

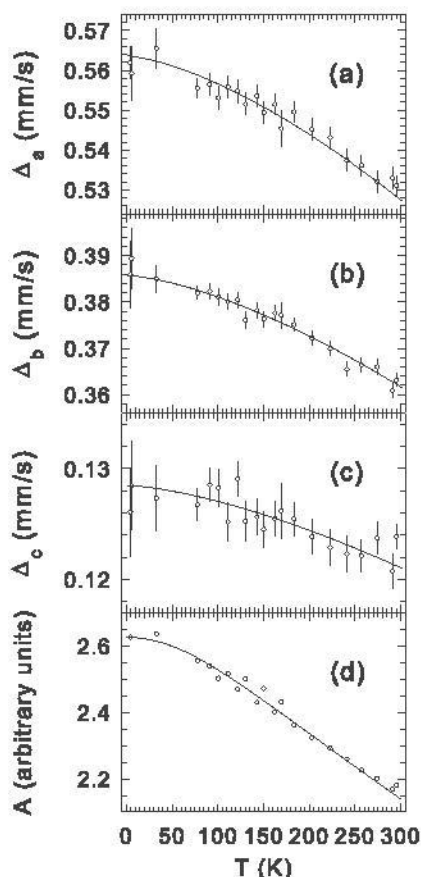


Fig. 10. Temperature dependence of (a) the quadrupole splittings Δ_i ($i = a, b, c$) and (b) the absorption spectral area A of $\text{Al}_{13}\text{Fe}_4$. The solid lines are the fits to Eq. (2) in (a) and to Eq. (3) in (b), as explained in the text.

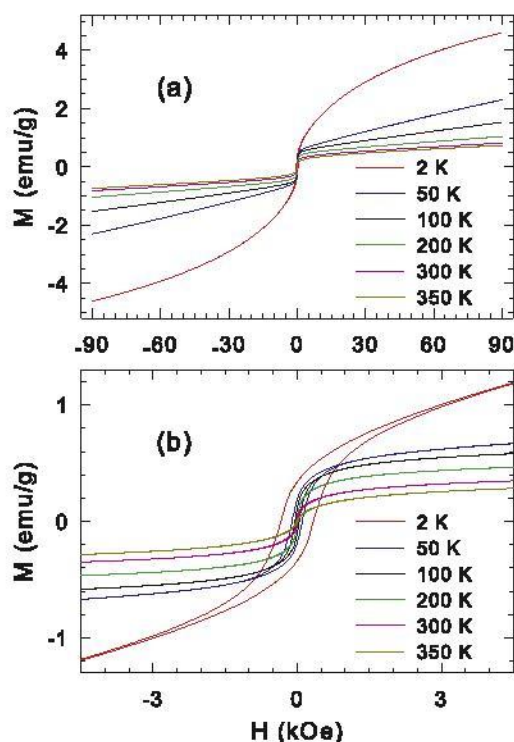


Fig. 11. $M(H)$ curves of $\text{Al}_{13}\text{Fe}_4$ at selected temperatures in the magnetic field range -90 – $+90$ kOe (a) and -4.5 – $+4.5$ kOe (b).

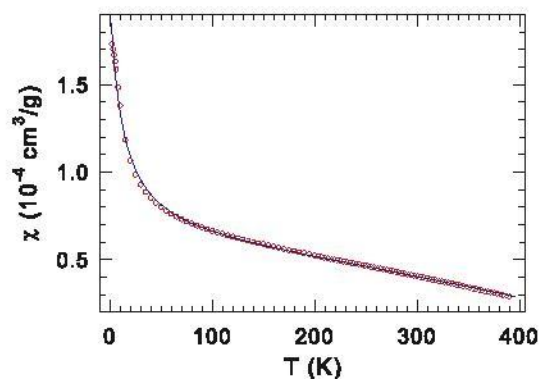


Fig. 12. Temperature dependence of the magnetic susceptibility of $\text{Al}_{13}\text{Fe}_4$ measured in an external magnetic field of 10 kOe. The solid line is the fit to Eq. (4), as explained in the text.

characteristic of the Curie–Weiss law. To allow for the presence in the studied specimen of a small amount of ferromagnetic impurity with the saturation magnetization M_0 , the $\chi(T)$ data were fitted to the equation containing an additional $T^{3/2}$ term associated with Bloch spin-waves [12,35]

$$\chi = \chi_0 + \frac{C}{T - \Theta_p} + \frac{M_0}{H} (1 - a_{3/2} T^{3/2}), \quad (4)$$

where χ_0 is the temperature-independent term that includes 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. The Curie constant can be expressed as $C = \frac{N\mu_{\text{eff}}^2}{3k_B}$, where N is the number of Fe atoms per formula unit, μ_{eff} is the effective magnetic moment, and k_B is the Boltzmann constant. The value of $M_0 = 2.53$ emu/g used in the fit was estimated from a linear extrapolation of the 2 K $M(H)$ curve (Fig. 11(a)) to $H = 0$. The fit of the $\chi(T)$ data (Fig. 12)) to Eq. (4) gives $\chi_0 = 2.62(3) \times 10^{-5} \text{ cm}^3/\text{g}$, $C = 1.77(6) \times 10^{-3} \text{ cm}^3 \text{ K/g}$, and $\Theta_p = -12.0(5) \text{ K}$. The value of C corresponds to $\mu_{\text{eff}} = 1.42(1) \mu_B$ per Fe atom.

4. Summary

We report the results of *ab initio* electronic structure and EFG calculations, and of X-ray diffraction, magnetic and ^{57}Fe Mössbauer spectroscopy studies of $\text{Al}_{13}\text{Fe}_4$. The studied alloy 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 Fe atoms located at five inequivalent crystallographic sites. We find 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 EFG parameters at five inequivalent Fe sites. We find that the Debye temperature of $\text{Al}_{13}\text{Fe}_4$ is 383(3) K. The DOS calculations predict the presence of a pseudogap located at 0.1 eV above E_F and with a width of ~ 0.2 eV. Good metallicity of $\text{Al}_{13}\text{Fe}_4$ is confirmed by the calculated finite DOS at E_F . The studied compound is shown to be a paramagnet down to 2.0 K.

Acknowledgements

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Chapter 7: Magnetic and ^{57}Fe Mössbauer spectroscopy study of the intermetallic compound FeNiSn

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Abstract

The results of x-ray diffraction, magnetic and ^{57}Fe Mössbauer spectroscopy studies of intermetallic compound FeNiSn are reported. It is shown that FeNiSn crystallizes in the ZrBeSi-type crystal structure (space group $P6_3/mmc$) with the lattice constants $a = 4.1329(1)$ Å and $c = 5.1912(2)$ Å. It is a ferromagnet with the Curie temperature $T_C = 1024(10)$ K. Evidence is provided for a possible phase separation in the studied compound, into a majority magnetic phase and a minority, nanoscale, disordered phase with the corresponding iron magnetic moments at 4.6 K of $2.39(1)$ and $1.17(1)$ μ_B . It is demonstrated that FeNiSn decomposes at temperature significantly below T_C when it is annealed in vacuum for about 30 h. The Debye temperature of FeNiSn is found to be $445(6)$ K.

7.1: Introduction

Thousands of the equiatomic ternary compounds XY Z crystallize in many different structures. A limited number of them crystallizes in the ZrBeSi-type crystal structure [1,2], with the hexagonal space group $P6_3/mmc$ (No. 194). These compounds are SrCuZ ($Z = \text{Sb, Bi}$) and CaCuZ ($Z = \text{Sb, Bi}$) [3], SrAgZ ($Z = \text{P, As}$), SrCuZ ($Z = \text{P, As}$), and CaCuZ ($Z = \text{P, As}$) [4], SrPdZ ($Z = \text{P, As}$) [5], SrAuZ ($Z = \text{P, As}$) [5], EuCuZ ($Z = \text{As, Sb, Bi}$) [4,6-9], EuAgZ ($Z = \text{As, Bi, Sb}$) and EuAuZ ($Z = \text{As, Sb, Bi}$) [6,7], EuY P ($Y = \text{Cu, Ag, Au}$) [6-8], EuPtP [10-12], XPdAs ($X = \text{La, Ce, Pr, Nd}$) [13-16], CePdP [15,16], LaPdSb [17], XNiSb ($X = \text{La, Ce, Pr, Nd, Sm}$) [18-21], SrPtAs [22], KZnZ ($Z = \text{P, Sb}$) and KCuZ ($Z = \text{Se, Te}$) [23], KHgZ ($Z = \text{As, Sb}$) and KZnAs [24], BaHgSn,

CaHgPb, and YbHgPb [25], SrZnSi [26], PtMnAl, PtMnGa, FeNiIn, FeMnIn, FeNiGe, FeCoGe, FeMnGe, CoNiSn, FeNiSn, FeCoSn, and MnCoSn [27], CaZnZ (Z = Si, Ge) [28], CaAuZ (Z = P, As) [5,28], BaZnZ (Z = Si, Ge, Sn), EuZnSi, SrY₂Sn (Y = Zn, Pb), BaPbSn, and BaCdGe [29], EuZnGe [29,30], YbCuSb [31], LiBaSb [32], BaAuSb [33], BaAuZ (Z = P, As) [5,34], LiAuSn [35], TiAuAl [36], TiPdGa [37], TiAuGa and TiPtGa [38], TiPtAl [39], LaCuSn [40,41], and XCuSi (X = La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y) [42-44]. Physical properties of only a small number of these compounds were investigated. From the magnetic point of view, these compounds occur as ferromagnets [7,16,20,27], antiferromagnets [7,9,30], or paramagnets [31].

Here we report on x-ray diffraction, magnetic and ^{57}Fe Mössbauer spectroscopy measurements of the intermetallic compound FeNiSn. We confirm that it crystallizes in the space group $P6_3/mmc$. We show that FeNiSn is a ferromagnet with the saturation magnetization at 3.0 K and in 9.0 T of $1.62 \mu_B$ per formula unit and the Curie temperature $T_C = 1024(10)$ K. We provide evidence for a possible phase separation into a majority magnetic phase and a minority, nanoscale, disordered phase. We show that the studied compound decomposes during the high-temperature Mössbauer measurements at temperatures much below T_C .

7.2: Experimental methods

An ingot of nominal composition FeNiSn was prepared by arc melting constituent elements in an atmosphere of purified argon gas. Purities of the starting elements were at least 99.9%. The ingot was then wrapped into a tantalum foil and placed into an evacuated quartz tube where it was annealed at 973 K for 30 days [27].

X-ray diffraction measurements were carried out at 298 K in Bragg-Brentano geometry on a PANalytical X'Pert scanning diffractometer using Cu $K\alpha$ radiation in the 2θ range 20-120° in steps of 0.02°. The $K\beta$ line was eliminated by using a Kevex PSi2 Peltier-cooled solid-state Si detector.

The dc magnetization was measured in the temperature range from 3.0 to 1050 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 was used

for dc magnetization measurement at temperatures higher than 400 K. The magnetic measurements were done on a solid FeNiSn specimen in a form of a parallelepiped.

The ^{57}Fe Mössbauer measurements were conducted using standard Mössbauer spectrometers operating in sine mode and 50-mCi and 100-mCi $^{57}\text{Co}(\text{Rh})$ sources, which were kept at room temperature, for low-temperature (< 300 K) and high-temperature (> 300 K) measurements, respectively. The spectrometers were calibrated with a $6.35\text{-}\mu\text{m}$ -thick $\alpha\text{-Fe}$ foil [45].

The Mössbauer absorber for low-temperature measurements was made by mixing the powder material with boron nitride and putting the pressed mixture pellet into a high-purity, $8\text{-}\mu\text{m}$ -thick Al disk container to ensure a uniform temperature over the whole absorber. The Mössbauer absorber for high-temperature measurements was made by mixing the powder material with boron nitride and placing the mixture into a boron-nitride container. The Mössbauer absorber for low-temperature measurements was put into a Mössbauer cryostat in which it was kept in a static exchange gas atmosphere at the pressure of $\sim 7 \times 10^{-3}$ mbar. The Mössbauer absorber for high-temperature measurements was placed in a Mössbauer oven in which it was kept in a dynamic vacuum of $\sim 2 \times 10^{-5}$ mbar. The surface density s of the prepared Mössbauer absorbers (there were several absorbers used for high-temperature measurements, vide infra) was in the range $19.3\text{--}32.6$ mg/cm^2 ; this corresponds to an effective thickness parameter [46] T in the range $(2.7\text{--}4.6)f_a$, where f_a is the Debye-Waller factor of the absorber. Since $T > 1$, the resonance line shape of the Mössbauer spectrum was described using a transmission integral formula [47]. The source linewidth $\Gamma_s = 0.12(0.14)$ mm/s and the background-corrected Debye-Waller factor of the source $f_s^* = 0.50(0.40)$ were used in the fits of low-temperature (high-temperature) Mössbauer spectra [47]. As the electric quadrupole interaction is significantly smaller than the magnetic dipole interaction in the studied compound, the ^{57}Fe Zeeman spectra at temperatures below T_C were analyzed using a first-order perturbation treatment [46]. The values of the centre shift δ (Ref. 46) are given here relative to $\alpha\text{-Fe}$ at 298 K and the electric quadrupole splitting Δ is defined as [46] $\Delta = \frac{1}{2}eQV_{zz}$ (where e is the proton charge, Q is the electric quadrupole moment of the ^{57}Fe nucleus [48], and V_{zz} is the principal component of the electric field gradient tensor).

7.3: Result and discussion

7.3.1: Structural characterization

The studied compound FeNiSn crystallizes in the ZrBeSi-type crystal structure with the space group $P6_3/mmc$ (No. 194) [PDF4+, card No. 04-005-7675]. There are 2 formula units of FeNiSn per unit cell. Fig. 1 shows the crystal structure of FeNiSn and the crystallographic data for the Fe, Ni, and Sn sites are given in Table I.

The x-ray powder diffraction pattern of FeNiSn is shown in Fig. 2. A Rietveld refinement [49] of the x-ray powder diffraction data was carried out, yielding the lattice constants $a = 4.1329(1) \text{ \AA}$ and $c = 5.1912(2) \text{ \AA}$. The values of these lattice parameters compare well with the corresponding values reported earlier [27]. As determined from the Rietveld refinement (Fig. 2), the FeNiSn specimen contains a second phase of $\text{Fe}_{0.8}\text{Ni}_{0.2}$ (space group $Im\bar{3}m$, Ref. 50) in the amount of 12.5(6) wt%.

7.3.2: Magnetic measurements

The magnetic field dependence of magnetization curves $M(H)$ measured at 3 and 300 K (Fig. 3) are typical for a ferromagnet. They show that M does not saturate in the highest field available of 90 kOe. The values of M in that field at 3 and 300 K are, respectively, 38.80 emu/g ($1.62 \mu_B/\text{f.u.}$) and 31.49 emu/g ($1.32 \mu_B/\text{f.u.}$).

In an attempt to determine the Curie temperature T_C of the FeNiSn ferromagnet, the temperature dependence of the magnetic susceptibility χ in an external magnetic field of 100 Oe was measured. Because it was found from high-temperature Mössbauer spectra that the studied compound decomposes at temperatures much below T_C (*vide infra*), we first measured three consecutive $\chi(T)$ dependencies in temperatures up to 923 K (Fig. 4). The χ values in the first measurement decrease, as expected, with increasing temperature up to 819 K, but then start to increase with increasing temperature up to 874 K, and then decrease with increasing temperature up to 892 K. The increase of χ above 819 K might be indicative of the specimen partial decomposition that occurred at lower temperatures.

In the following second measurement (Fig. 4), the χ values decrease monotonically with increasing temperature from 693 to 923 K, but the $\chi(T)$ values are larger than the corresponding

values in the first measurement. This seems to confirm the partial specimen decomposition because, in the absence of such a decomposition, the $\chi(T)$ curves in the first and second measurements should be the same.

The χ values in the following third measurement (Fig. 4) decrease monotonically with temperature decreasing from 923 to 293 K, with the $\chi(T)$ values that are different from the corresponding values in the first and second measurement. It is reasonable to conclude that the measured specimen experienced a partial decomposition in each of these three measurements. However, this conclusion is at variance with the fact (*vide infra*) that the x-ray diffraction pattern of the specimen from these three (and following next seven, described below) experiments is identical to that in Fig. 1, with the lattice constants a and c that are larger only by 0.09 and 0.06% than the corresponding constants of the virgin sample.

In the following fourth measurement, a hysteresis curve $M(H)$ at 300 K of the oven sample after the preceding third measurement was measured and is compared with the corresponding curve of the virgin sample in Fig. 5. One can notice a small increase of M (by 4.08% at the field of 90 kOe) with respect to M of the virgin sample. This small increase could be interpreted as evidence of a partial decomposition of the studied compound into another magnetically ordered phase. In subsequent three $M(H)$ measurements at 500, 700, and 800 K (Fig. 5), one observes an expected decrease of M . In the following $M(H)$ measurement at 300 K the $M(H)$ hysteresis curve virtually coincides (Fig. 5) with the corresponding curve of the fourth measurement, which seems to indicate that at 500, 700, and 800 K no further decomposition has occurred.

In the following ninth measurement, the temperature dependence of magnetization was measured in an external magnetic field of 10 kOe and in the temperature range 2–1058 K (Fig. 6). If one uses the definition of the Curie temperature as the temperature where the $M(T)$ curve has an inflection point (Fig. 6), then $T_C = 1024(10)$ K. This is a surprisingly large value of T_C . In the last measurement a hysteresis curve $M(H)$ at 300 K was measured. It turned out to coincide with the corresponding curve of the virgin sample. As mentioned above, the x-ray diffraction spectrum of the sample after the above 10 measurements is virtually identical to that shown in Fig. 1. Furthermore, the room-temperature Mössbauer spectrum of the sample after the above 10 measurements is essentially the same as the spectrum of the virgin sample (Fig. 7), with the hyperfine magnetic field smaller only by 0.76% than the corresponding field of the virgin sample.

This seems to indicate that no appreciable decomposition of the studied specimen had occurred after the above 10 measurements. It should be indicated here that the time of each of the above high-temperature magnetic measurements was of the order of a few hours, whereas the time of a high-temperature Mössbauer measurement was of the order of a few tens of hours (*vide infra*). In addition, magnetic measurements were carried out on the bulk specimen, whereas the Mössbauer high-temperature measurements were done on pulverized specimens.

7.3.3: Mössbauer spectroscopy

The room-temperature ^{57}Fe Mössbauer spectrum of FeNiSn is shown in Fig. 7. It is evident from a visual inspection that this spectrum can be decomposed into three components: a major Zeeman pattern ($\delta = 0.014(1)$ mm/s, the hyperfine magnetic field $H_{\text{hf}} = 330.7(1)$ kOe, the electric quadrupole shift (Ref. 46) $\varepsilon = 0.001(1)$ mm/s), a minor Zeeman pattern ($\delta = 0.089(8)$ mm/s, $H_{\text{hf}} = 309.9(8)$ kOe, $\varepsilon = 0.009(8)$ mm/s), and a quadrupole doublet pattern ($\delta = 0.359(2)$ mm/s, $\Delta = 0.657(3)$ mm/s). The major Zeeman component must be due to Fe atoms located at the 2d sites (Table I) in the structure of FeNiSn. The minor Zeeman pattern can be associated with Fe atoms in the second phase of $\text{Fe}_{0.8}\text{Ni}_{0.2}$ present (Fig. 1) in the studied compound. The presence of the quadrupole doublet pattern, however, is entirely unexpected. It cannot originate from another Fe-containing second phase as no such phase can be detected in the x-ray diffraction pattern (Fig. 1). We suggest that it most likely arises from a separated nanoscale disordered FeNiSn phase. Such a nanoscale phase separation has been observed in a variety of compounds [51-53].

The low-temperature ^{57}Fe Mössbauer spectra of FeNiSn are displayed in Fig. 8. They could be fitted well in a similar way as the spectrum in Fig. 7, with the component (in the spectrum at 4.6 K) corresponding to the nanoscale disordered FeNiSn phase in a form of a Zeeman pattern (Fig. 8). The presence of this third Zeeman pattern means that the nanoscale disordered FeNiSn phase is magnetically ordered at 4.6 K. The values of H_{hf} corresponding to the main FeNiSn phase and the nanoscale disordered FeNiSn phase in the spectrum at 4.6 K are 339.5(2) and 166.1(3) kOe, respectively. This allows one to estimate the magnitude of the magnetic moment μ_{Fe} carried out by Fe atoms in the FeNiSn compound and its nanoscale disordered phase based of the relation $H_{\text{hf}} = a\mu_{\text{Fe}}$, where the value of the proportionality constant $a = 142 \text{ kOe}/\mu_B$ [54]. The

values of μ_{Fe} at 4.6 K for these two phases are 2.39(1) and 1.17(1) μ_B , respectively.

Figure 9 shows the first series of consecutively measured high-temperature ^{57}Fe Mössbauer spectra of FeNiSn. One can observe that the spectra up to 603.2 K preserve a three-component structure. However, the following spectra at 703.2 and 803.2 K contain two additional Zeeman components which clearly must originate from two new phases into which the studied specimen was decomposed at ~ 700 K. The following two spectra at 903.2 and 853.2 K are in a form of a quadrupole doublet (with the values of δ and Δ equal, respectively, to 0.127(3) mm/s, 0.214(12) mm/s, and 0.149(6) mm/s, 0.194(4) mm/s). The occurrence of a quadrupole doublet spectrum at 853.2 K (Fig. 9) does not imply that T_C of FeNiSn must be smaller than 853.2 K because this is a paramagnetic spectrum of the previously precipitated two (or more) new phases and not of FeNiSn. This is confirmed by the fact that the δ value corresponding to the spectrum at 853.2 K is positive whereas the δ values corresponding to the FeNiSn compound and its nanoscale disordered phase at a slightly lower temperature of 803.2 K are negative.

The spectra following the 853.2 K spectrum (Fig. 9), which were not fitted, consist of at least three new components which must originate from three new phases into which the studied sample has been decomposed in previous measurements. It is reasonable to assume that the decomposition has been occurring during each high-temperature Mössbauer measurement, which lasted a few tens of hours, at temperatures above ~ 700 K. The last spectrum in this series at 300.2 K (Fig. 9) is in a form of a single Zeeman pattern. This means that the studied sample was decomposed into a single phase through the annealing scheme corresponding to the order in which the high-temperature Mössbauer spectra were measured in Fig. 9.

In the second series of consecutively measured high-temperature ^{57}Fe Mössbauer spectra of FeNiSn, an attempt was made to start the measurements at temperatures above ~ 700 K in order to postpone the decomposition process (Fig. 10). The first in this series 300.2 K spectrum (Fig. 10) can be fitted, as before (Fig. 7), with three components. The first in this series high-temperature spectrum at 813.2 K is fitted with two components as the Zeeman sextet originating from the $\text{Fe}_{0.8}\text{Ni}_{0.2}$ impurity phase is not visible in the spectrum [most probably due to the fact that the temperature of 813.2 K is around the T_C of $\text{Fe}_{0.8}\text{Ni}_{0.2}$ (Ref. 50)].

In the following 833.2 K spectrum, one can notice (Fig. 10) that the spectral area of the

Zeeman pattern decreases and the spectral area of the quadrupole doublet pattern increases. This must be due to the decomposition of the FeNiSn main phase into a new nonmagnetic (at 833.2 K) phase. This process of decreasing of the spectral area of the Zeeman pattern and increasing of the spectral area of the quadrupole doublet pattern is continued (Fig. 10) in the following spectra at 843.2, 848.2, and 853.2 K. In the next spectrum at 863.2 K, the value of H_{hf} corresponding to a Zeeman pattern is much larger than the corresponding value in the previous 853.2 K spectrum. This must mean that at 863.2 K a complete decomposition of the FeNiSn main phase, that was subjected to a high-temperature annealing scheme of Fig. 10, has occurred with a new magnetically ordered (at 863.2 K) precipitated phase. The same new Zeeman pattern, but with a slightly smaller value of H_{hf} , is observed in the following spectrum at 873.2 K. And finally, the last spectrum in this series at 300.2 K (Fig. 10), which was not fitted, consists of at least three component patterns. This indicates that the FeNiSn main phase subjected to the annealing scheme of Fig. 10 has decomposed into at least three distinct phases.

The temperature dependence of the hyperfine magnetic field corresponding to the FeNiSn main phase derived from the fits of the spectra in Figs. 7–10 is displayed in Fig. 11. This dependence was fitted in terms of the Bean-Rodbell exchange model [55] in which the reduced magnetization $\sigma = M(T)/M(0)$, and hence (assuming proportionality between M and H_{hf}) the reduced hyperfine magnetic field $\sigma = H_{\text{hf}}(T)/H_{\text{hf}}(0)$, is given by

$$\sigma = B_S \left[\frac{3S}{S+1} \frac{\sigma}{\Theta} \left(1 + \frac{3}{80} \frac{(2S+1)^4 - 1}{S(S+1)^3} \eta \sigma^2 \right) \right], \quad (1)$$

where B_S is the Brillouin function for spin S , $\Theta = T/T_C$, and η is the order parameter of the transition. For an ideal second-order transition $\eta = 0$ and for the first order transition $\eta > 1$. The η values between 0 and 1 correspond to intermediate-order transitions [55]. The fits of the $H_{\text{hf}}(T)$ data to Eq. (1) for S values of 1/2, 3/2, and 5/2 (Fig. 11) yield the T_C values of 1120(130), 1170(80), and 1220(50) K, respectively, and the same η value of 0.0(2) for the three fits. These values of T_C are larger than the value of 1024(10) K deduced from the $M(T)$ data (Fig. 6). The overestimation of T_C from the $H_{\text{hf}}(T)$ data is most probably the consequence of the paucity of the $H_{\text{hf}}(T)$ data for $T > 860$ K. Notwithstanding this overestimation, the large T_C values estimated from the $H_{\text{hf}}(T)$ data give credence to the value of 1024(10) K determined from the $M(T)$ data.

Figure 12 displays the temperature dependence of the center shift corresponding to the

FeNiSn main phase determined from the fits of the spectra in Figs. 7–10. The center shift at a given temperature, $\delta(T)$, is given by

$$\delta(T) = \delta_0 + \delta_{\text{SOD}}(T), \quad (2)$$

where 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 Fe atoms [46]. In terms of the Debye approximation of the lattice vibrations, $\delta_{\text{SOD}}(T)$ is expressed [46] in terms of the Debye temperature, Θ_D

$$\delta_{\text{SOD}}(T) = -\frac{9}{2} \frac{k_B T}{Mc} \left(\frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} \frac{x^3 dx}{e^x - 1}, \quad (3)$$

where M is the mass of the Mössbauer nucleus and c is the speed of light. By fitting the experimental data in Fig. 12 to Eq. (2), the quantities δ_0 and Θ_D were found to be 0.131(1) mm/s and 445(6) K, respectively.

7.4: Summary

We report the results of x-ray diffraction, magnetic and ^{57}Fe Mössbauer spectroscopy studies of intermetallic compound FeNiSn. We find that FeNiSn crystallizes in the hexagonal space group $P6_3/mmc$ with the lattice constants $a = 4.1329(1) \text{ \AA}$ and $c = 5.1912(2) \text{ \AA}$. We show that the studied compound is a ferromagnet with the Curie temperature $T_C = 1024(10) \text{ K}$. We provide evidence for a possible phase separation into the majority magnetic phase and a minority, nanoscale, disordered phase. We find that the Fe magnetic moments at 4.6 K corresponding to these phases are 2.39(1) and 1.17(1) μ_B . We show that FeNiSn decomposes when annealed in vacuum for about 30 h. We find that the Debye temperature of FeNiSn is 445(6) K.

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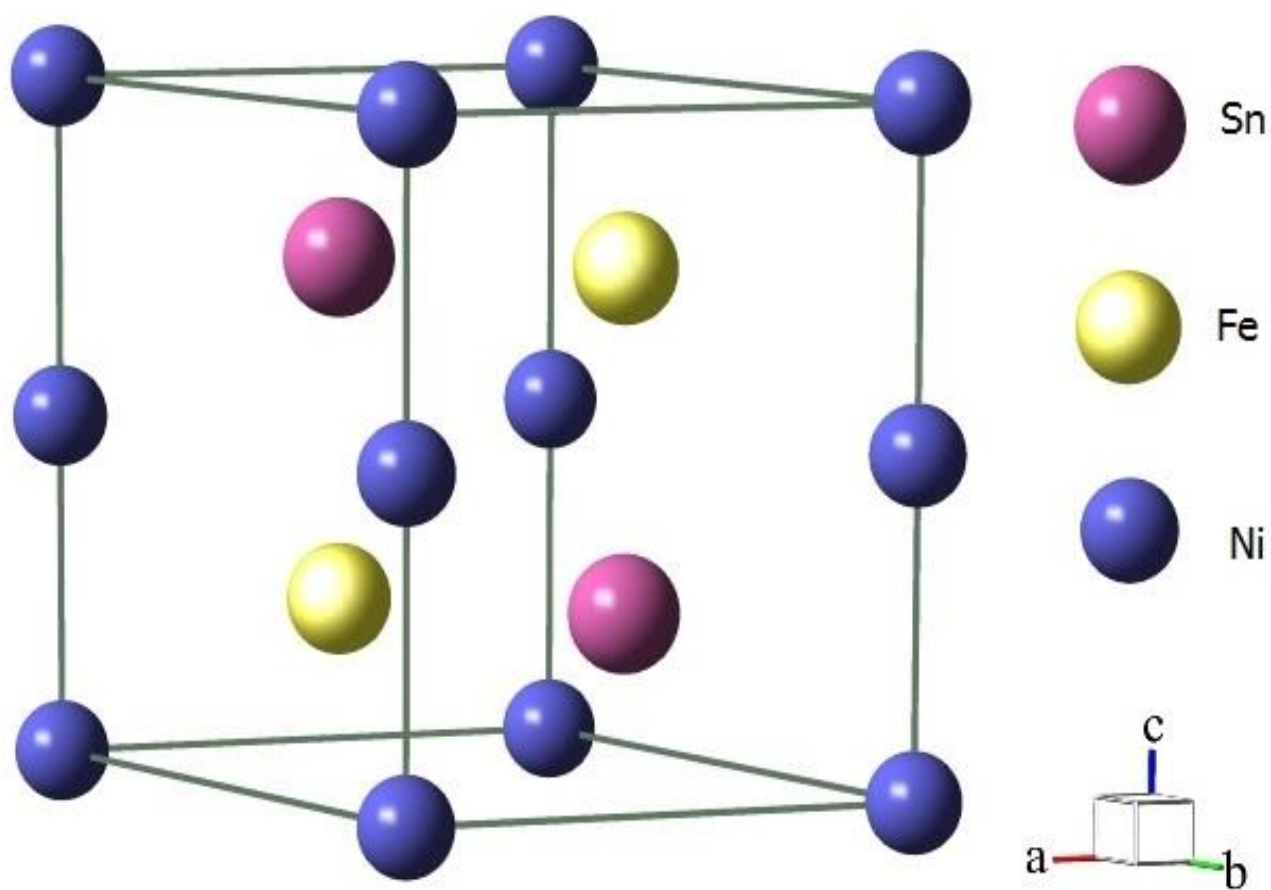


FIG. 1. The unit cell of the FeNiSn compound.

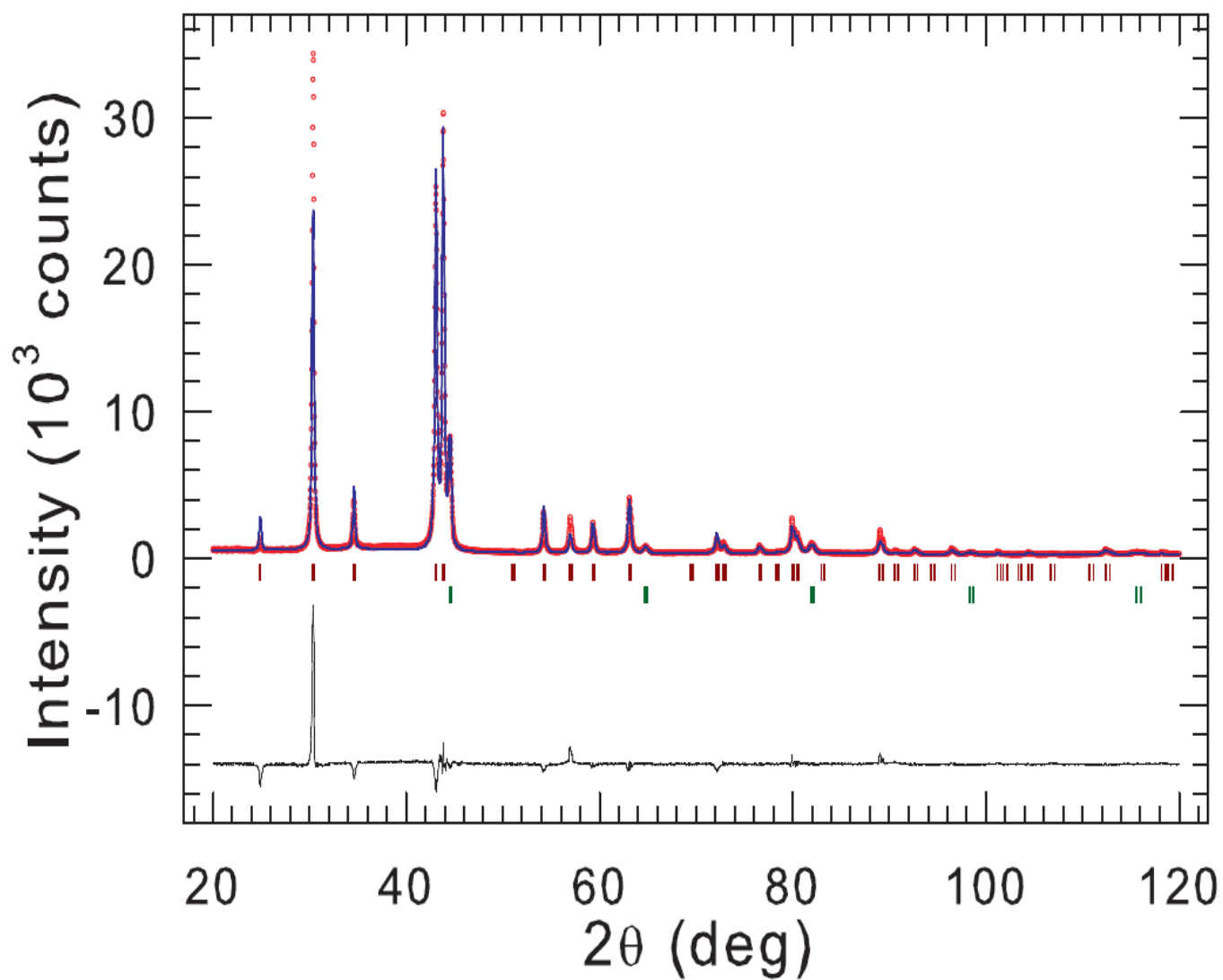


FIG. 2. Powder x-ray diffraction pattern of FeNiSn 298 K. The experimental data are denoted by open circles, while the line through the circles represents the results of the Rietveld refinement. The upper set of vertical bars represents the Bragg peak positions corresponding to the principal FeNiSn phase, while the lower set refers to the positions of the impurity phase of $\text{Fe}_{0.8}\text{Ni}_{0.2}$. The lower solid line represents the difference curve between experimental and calculated patterns.

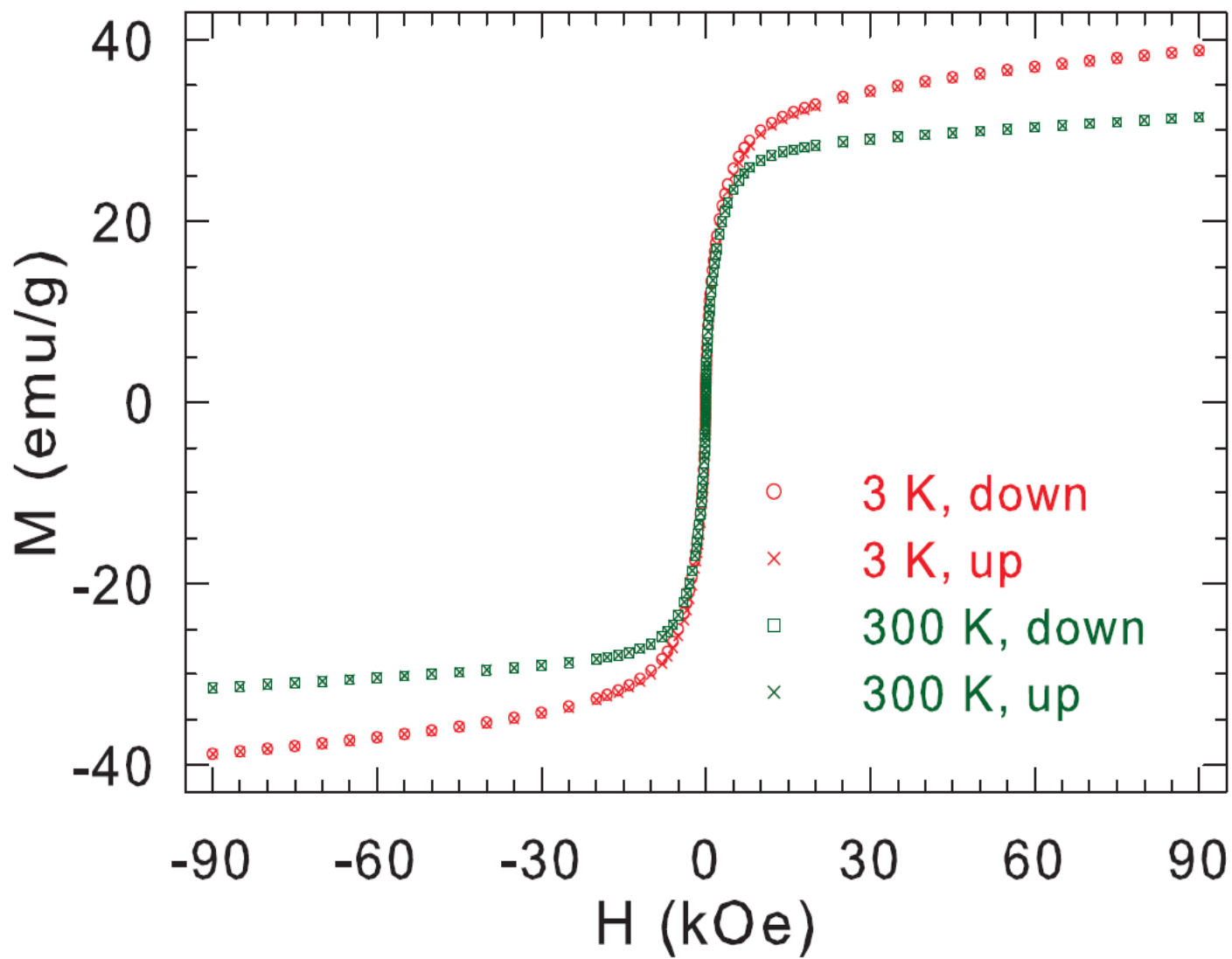


FIG. 3. Hysteresis curves of FeNiSn at 3 and 300 K in the magnetic field range -90 – $+90$ kOe for the decreasing (down) and increasing (up) magnetic field.

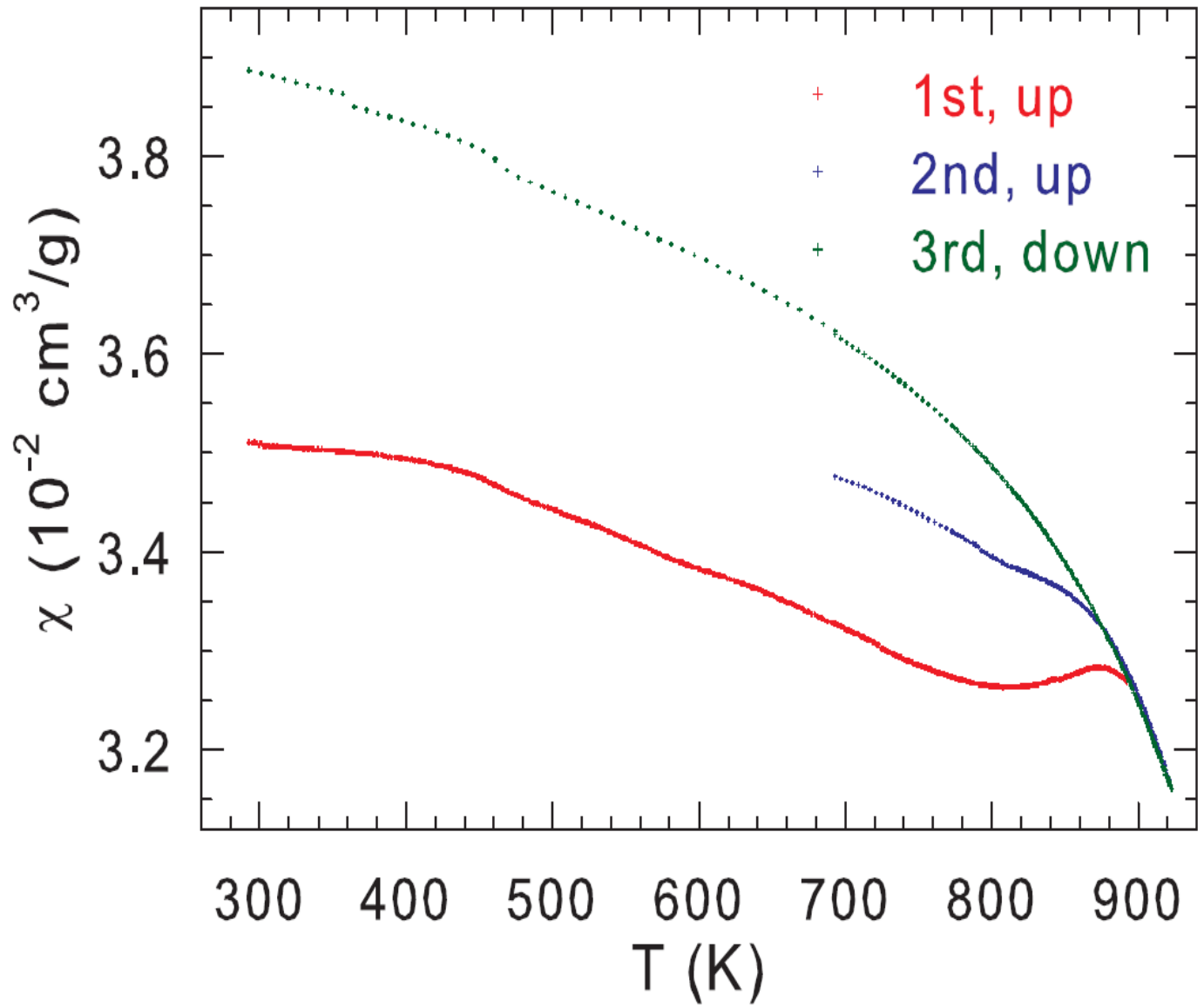


FIG. 4. Temperature dependence of the magnetic susceptibility of FeNiSn measured in an external magnetic field of 100 Oe for three consecutive measurements. In the first measurement the temperature was increasing from 293 to 892 K. Then the temperature was lowered to 693 K and was increasing in the second measurement up to 923 K. In the following third measurement, the temperature was decreasing from 923 to 293 K.

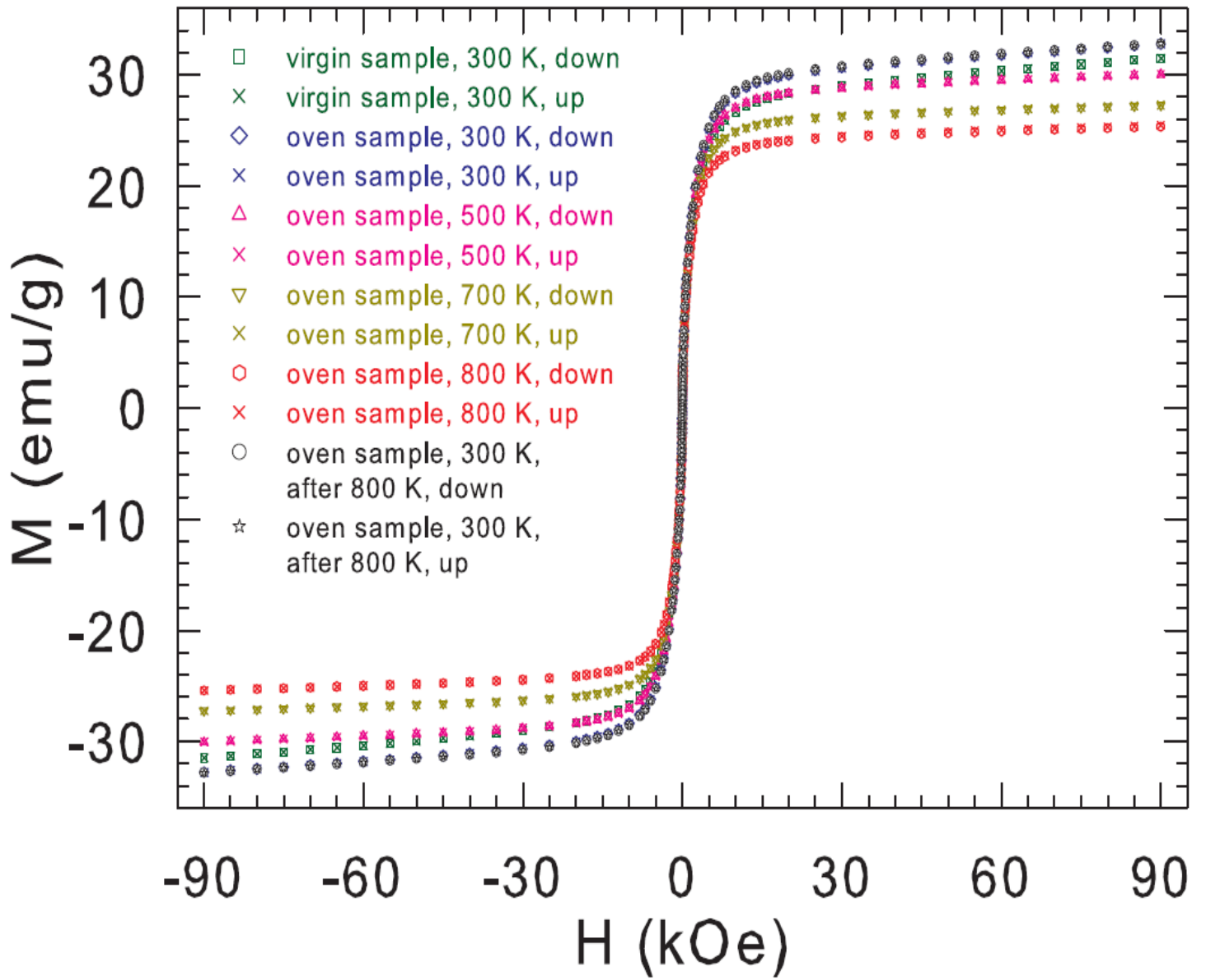


FIG. 5. Hysteresis curve at 300 K of the virgin FeNiSn sample compared with hysteresis curves measured in a consecutive order a) at 300 K of the oven sample after the third measurement (Fig. 4), b) at 500, 700, and 800 K of the oven sample, and c) at 300 K of the sample after the preceding 800 K $M(H)$ measurement.

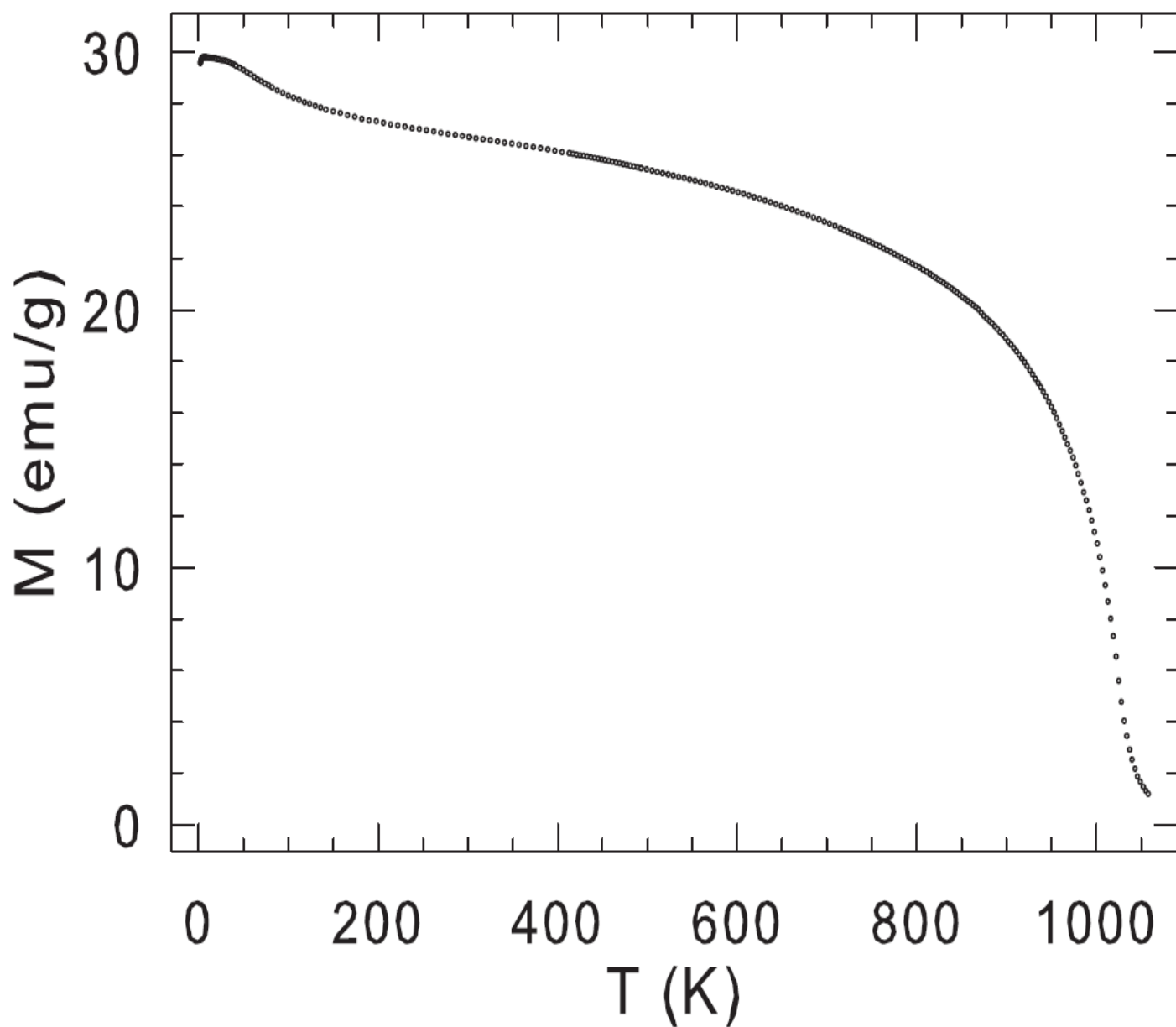


FIG. 6. Temperature dependence of the magnetization of the oven FeNiSn sample (after the last measurement in Fig. 5) measured in an external magnetic field of 10 kOe.

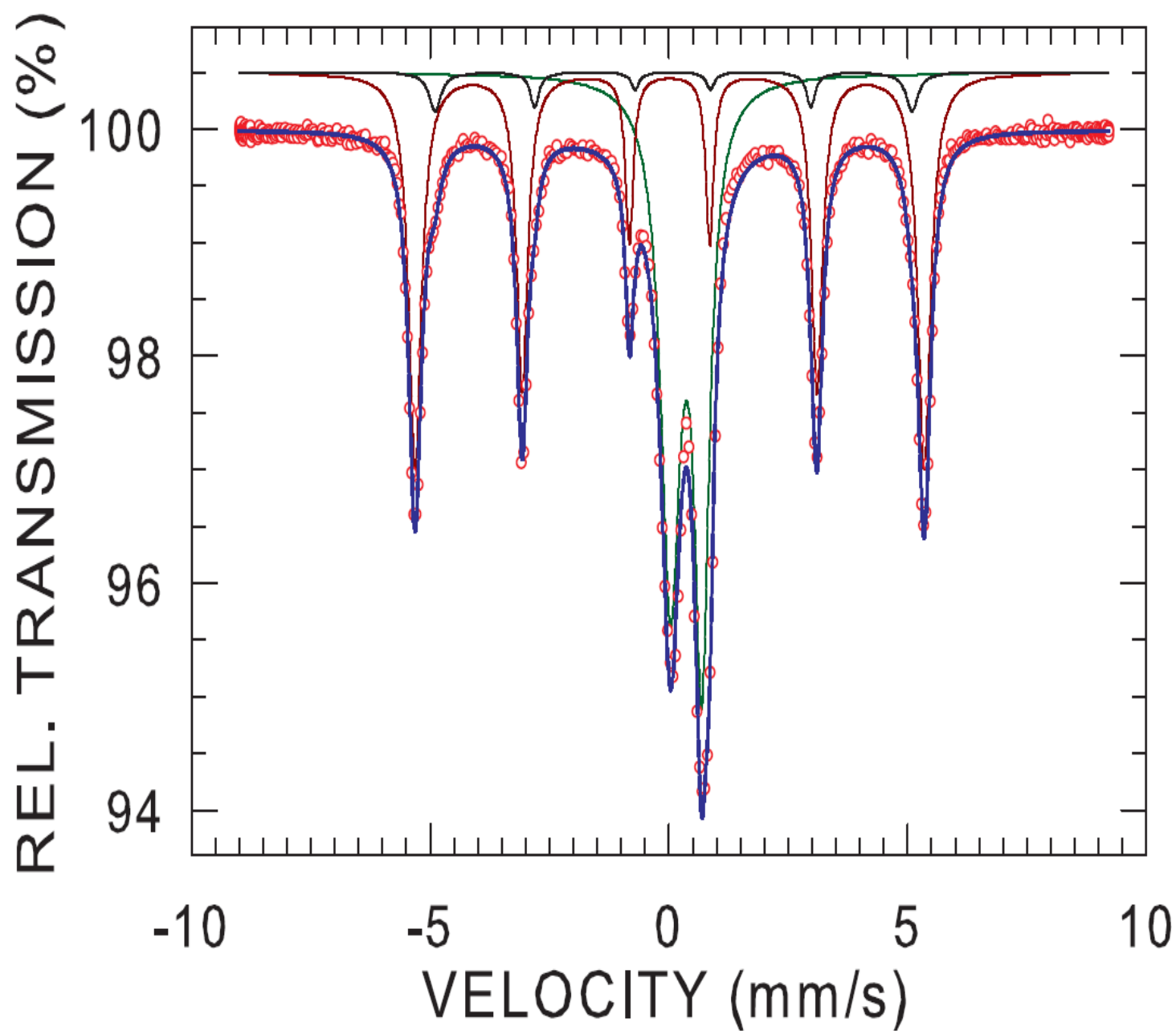


FIG. 7. ^{57}Fe Mössbauer spectrum of FeNiSn ($\sigma = 19.3 \text{ mg/cm}^2$) at 297.2 K fitted (blue solid line) with two Zeeman patterns (dark red and black solid lines) and a quadrupole doublet pattern (dark green solid line). The zero-velocity origin is relative to $\alpha\text{-Fe}$ at room temperature.

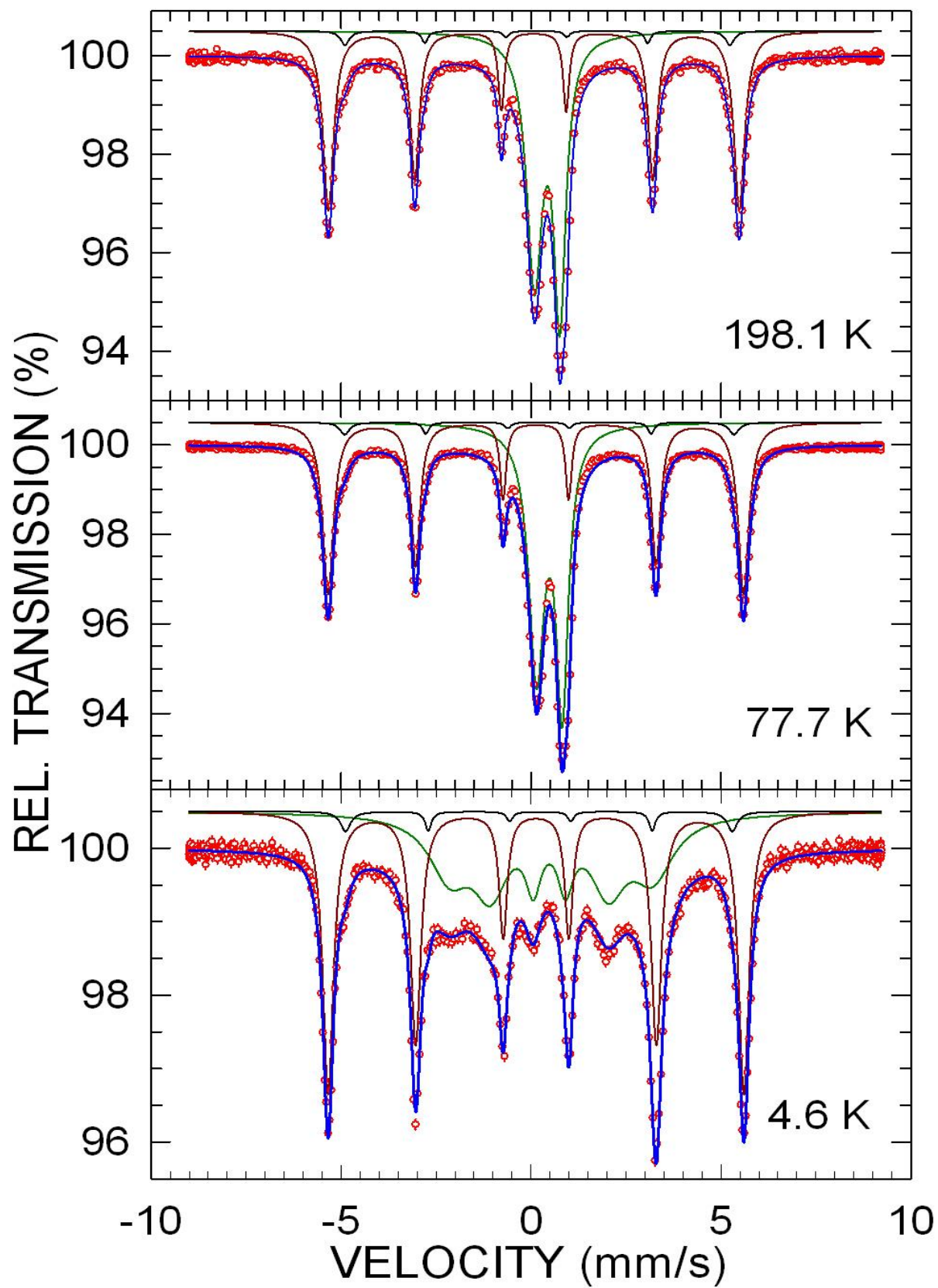


FIG. 8. Low-temperature ^{57}Fe Mössbauer spectra of FeNiSn ($\sigma = 19.3 \text{ mg/cm}^2$) fitted with three component patterns, as explained in the text. The zero-velocity origin is relative to $\alpha\text{-Fe}$ at room temperature.

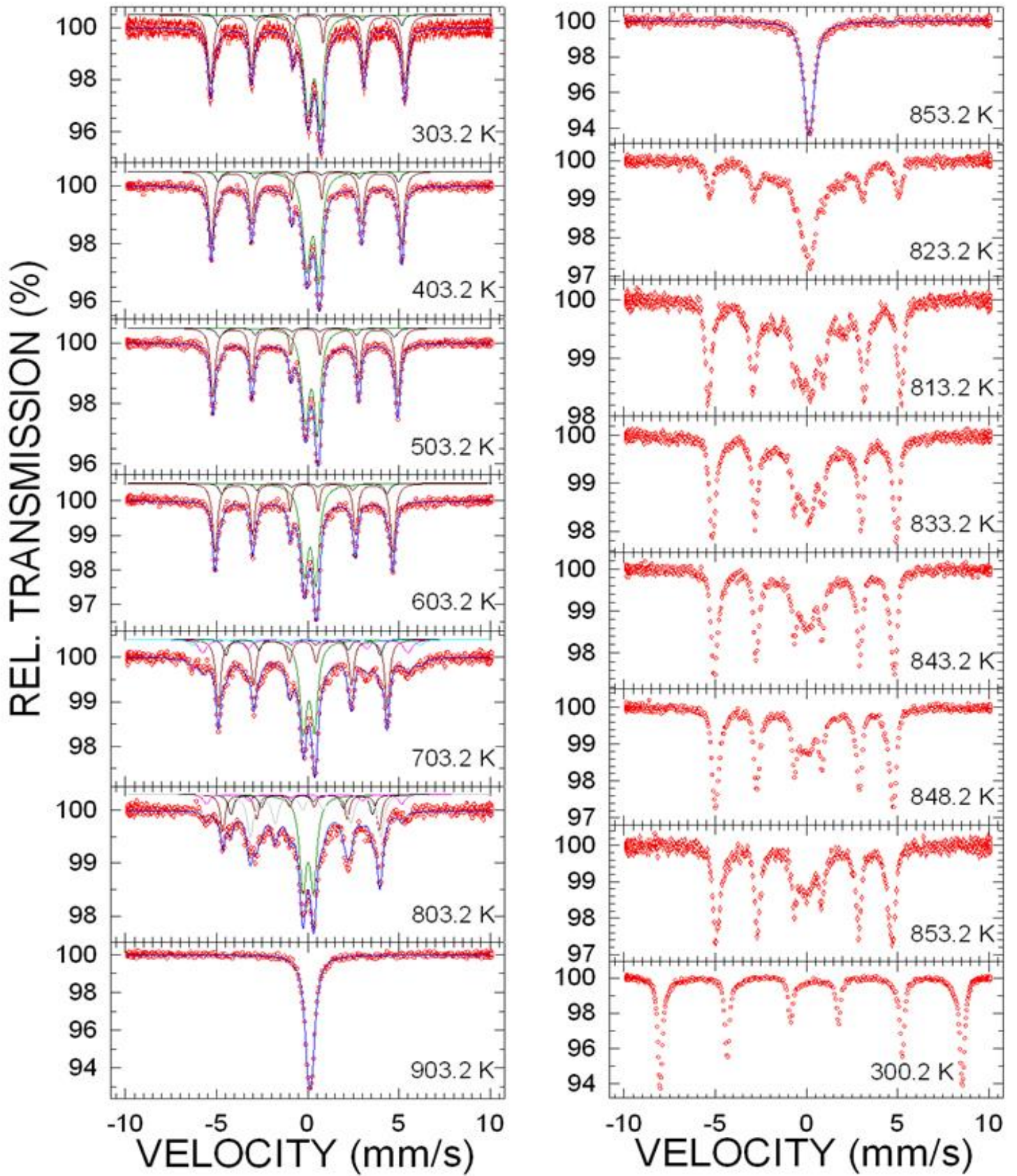


FIG. 9. High-temperature ^{57}Fe Mössbauer spectra of FeNiSn ($\sigma = 20:8 \text{ mg/cm}^2$) fitted with several component patterns, as explained in the text. The spectra were measured consecutively starting with the spectrum at 300.2 K down to the spectrum at 903.2 K (left panel), followed by the spectrum at 853.2 K down to the spectrum at 300.2 K (right panel). The zero-velocity origin is relative to $\alpha\text{-Fe}$ at room temperature.

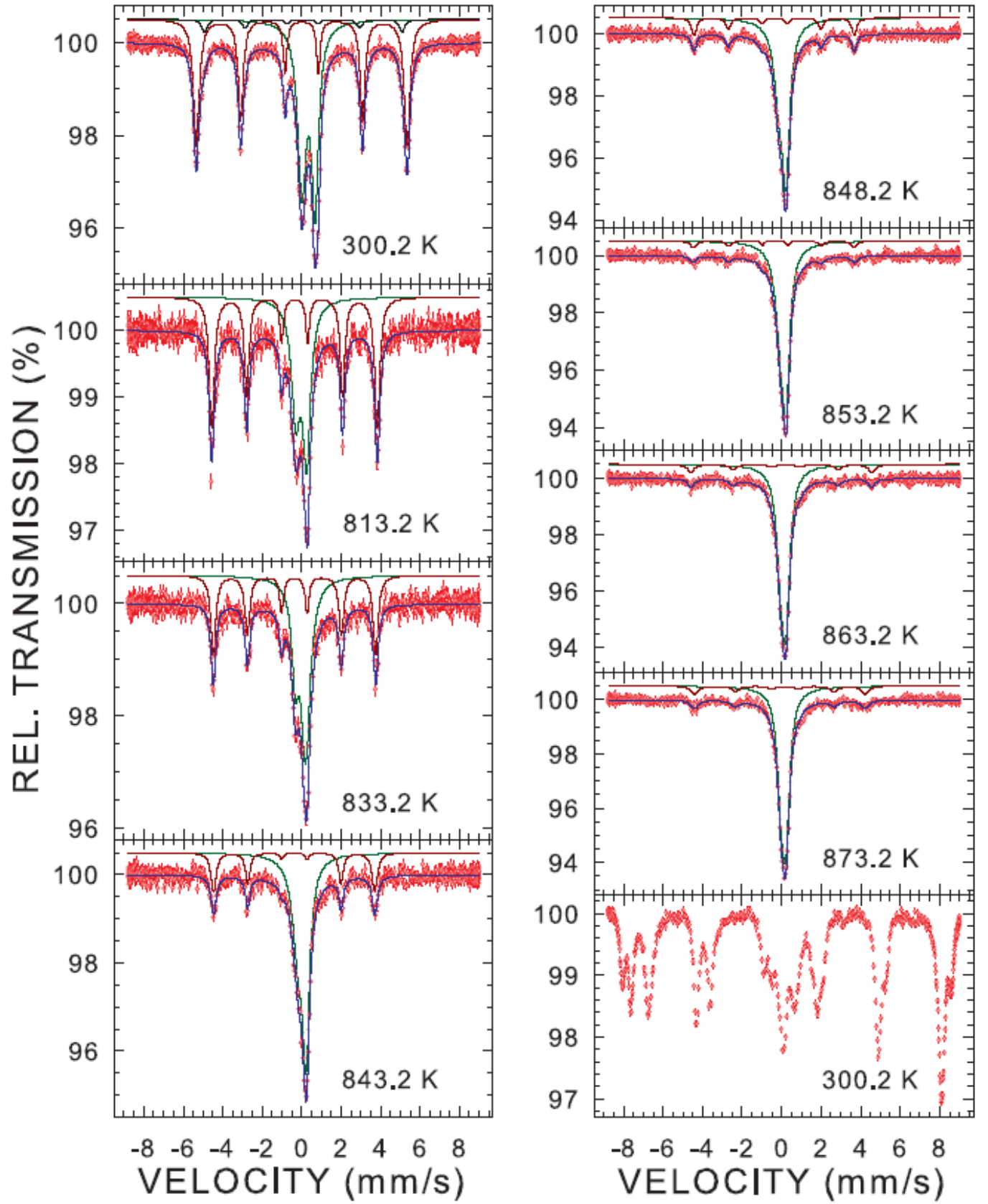


FIG. 10. High-temperature ^{57}Fe Mössbauer spectra of FeNiSn ($\sigma = 32.6 \text{ mg/cm}^2$) fitted with several component patterns, as explained in the text. The spectra were measured consecutively starting with the spectrum at 300.2 K down to the spectrum at 843.2 K (left panel), followed by the spectrum at 848.2 K down to the spectrum at 300.2 K (right panel). The zero-velocity origin is relative to $\alpha\text{-Fe}$ at room temperature.

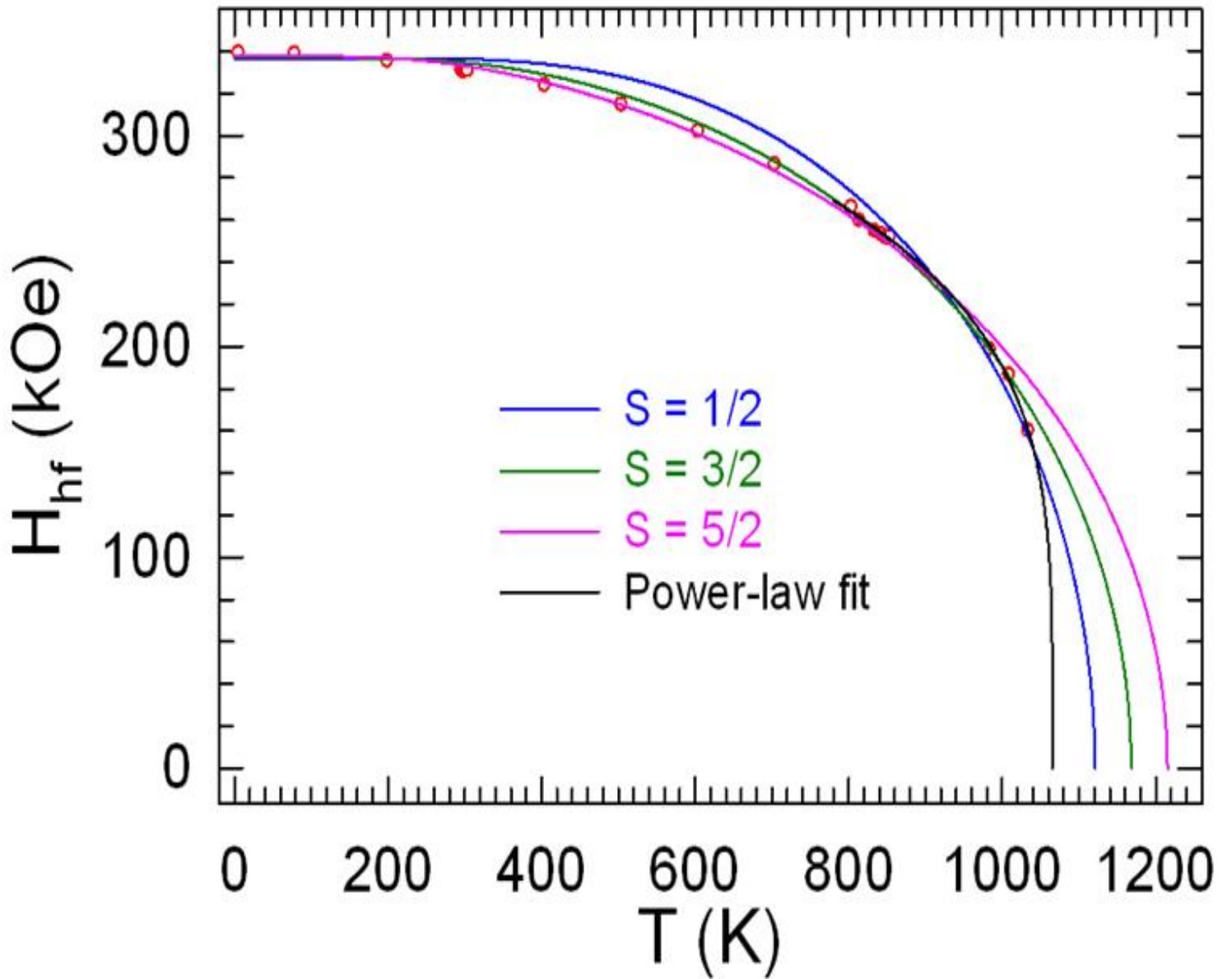


FIG. 11. Temperature dependence of the hyperfine magnetic field H_{hf} determined from the fits of the spectra in Figs. 7–10. The solid lines are the fits to Eq. (1), as explained in the text. The size of the error bars is smaller than the size of the experimental points.

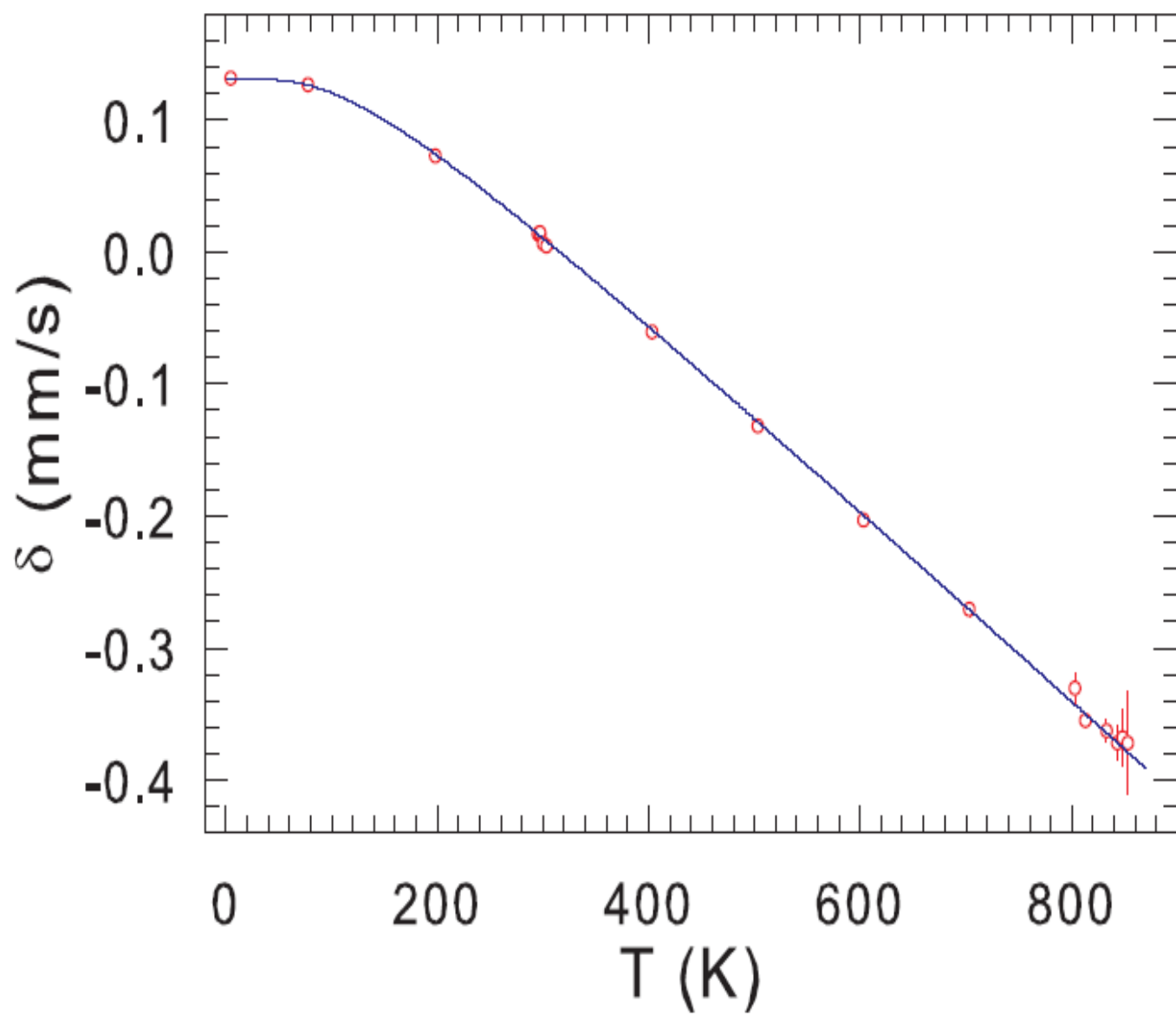


FIG. 12. Temperature dependence of the center shift δ determined from the fits of the spectra in Figs. 7–10. The solid line is the fit to Eq. (2), as explained in the text.

TABLE I. Crystallographic data for FeNiSn.

Atom	Site	Point symmetry	Occupancy	x	y	z
Fe	$2d$	$\bar{6}m2$	1.0	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{3}{4}$
Ni	$2a$	$\bar{3}m$	1.0	0	0	0
Sn	$2c$	$\bar{6}m2$	1.0	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$