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THIS DISSERTATION HAS BEEN MICROFILMED EXACTLY AS RECEIVED
CRYSTALLOGRAPHY AND OPTICAL PROPERTIES OF SOME CHALCOPYRITE MATERIALS

by

ROBERT GERALD GOODCHILD

A thesis
presented to the School of Graduate Studies and Research
of the University of Ottawa
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy
in Physics

Ottawa, Canada, 1982

to my wife Joanne . . . . .
ABSTRACT

This thesis investigates the crystallography and optical properties of some quaternary compounds as well as the behaviour of the \( \Gamma \) point energy gaps as a function of temperature for several compositions of the alloy system \( \text{CuGa(Se}_{1-x}\text{S}_x)\text{Se}_2 \).

Polycrystalline samples, of the general chemical formula I-\([\text{I-III-IV-}\text{Se}_4]\), where \([\text{I-III-IV-}]\) indicates a vacancy in the lattice structure, were produced by direct synthesis, and used for both crystallographic investigations and transmission measurements.

Debye-Scherrer X-ray powder photographs were obtained for the compounds. An analysis of the films showed that the lattice structure is tetragonal with \( c/a \) ratios ranging from 1.73 to 2.00. Calculations involving relative diffraction line intensities showed that this structure is chalcopyrite and further, that the vacancy is associated with the Group I cations.

Transmission measurements were made on the polycrystalline quaternary samples and the nature and value of the lowest band-gap \( E_g \) for the materials were determined. The lowest band-gap would appear to be a direct transition.

A study of the behaviour of the lowest band-gap as a function of temperature for two quaternary compounds \( \text{AgGaSnSe}_4 \) and \( \text{AgGaGeSe}_4 \) was undertaken, the value of \( E_g \) being determined from transmission measurements. As this variation of \( E_g \) with temperature could not be fitted to the Varshni equation (67V1),
\[ E = E_0 - \frac{\gamma T^2}{(8+T)} \]

the Manoogian-Leclerc equation (79M1) was used:
\[ E = E_0 - UT^d \sqrt{\frac{\theta}{2T}} (\coth \frac{\theta}{2T} - 1) \]

Measurements of reflectance as a function of temperature from 4 K to 300 K were made on a single crystal sample of CuGaSnSe\(_4\), using light polarised (a) perpendicular to and (b) parallel to the c axis of the crystal. Values of the energy gaps \( E_A, E_B \) and \( E_C \) between the three valence bands and the conduction band were thus determined as a function of temperature. These values were fitted to the Manoogian-Leclerc equation. Values of spin-orbit splitting \( \Delta_{SO} \) and crystal field splitting \( \Delta_{CF} \) were determined and the temperature variation of these quantities explained in terms of contributions from d orbitals to the valence band. Values of the various spin-orbit splittings and deformation potentials are discussed in the text.

Measurements of reflectance as a function of temperature from 4 K to 300 K were made on single crystal samples and one polycrystalline sample of the alloy system CuGa(Se\(_{1-x}\)\(S_x\))\(_2\). Values of the energy gaps \( E_A \) and \( E_B \) only were thus determined as a function of temperature. The variations of these gaps were again fitted to the Manoogian-Leclerc equation. The values of the various parameters as a function of alloy composition are discussed in the text. The crystal field splitting of CuGaS\(_2\) as a function of temperature was determined and explained in terms of contributions to the valence band from the d orbitals. Values of the deformation potentials used in the analysis are discussed.
STATEMENT OF ORIGINALITY

The work described in the thesis has been carried out in collaboration with workers at University of Nottingham, University of Bath and Universidad de los Andes. The parts of the work which the author has contributed are indicated below.

Chapter 2

This work was carried out jointly with Dr. O. H. Hughes of Nottingham while he was on sabbatical at University of Ottawa. The author was involved in the preparation of some of the compounds and only the X-ray photographs of the samples. The analysis of the intensity values and the determination of the ordered structure was the work of the author.

Chapter 3

The author made about half of the experimental measurements described in the section and was responsible for most of the analysis.

Chapter 4

All of the work described here was carried out by the author.

Chapter 5

The single crystal sample was produced by Adan Lopez who aided in the experimental measurements. Most of the experimental work and all of the analysis in this section was done by the author.

Chapter 6

The single crystal samples were prepared by Jesus Gonzales who helped with the experimental measurements. Again most of the experimental work and all of the analysis was carried out by the author.
ACKNOWLEDGEMENTS

The author would like to thank Dr. J. C. Woolley for the opportunity to work on this problem and for his assistance, encouragement and patience throughout the course of this work.

Many thanks are also due to Dr. Q. H. Hughes for his collaboration in some of the measurements and analysis. The author has benefited greatly from his friendship and the many discussions with him.

The author would also like to thank at this time Dr. A. Lopez-Rivera for growing the single crystals of CuGaSnSe$_4$ and for his assistance in the reflection measurements. In addition he would also like to thank Dr. J. Gonzales for providing the samples of the CuGa(Se$_{1-x}$S$_x$)$_2$ alloy system and for his assistance in the reflection measurements. Thanks are also due to L. Bourbonais, for his assistance in the growth of some of the quaternaries and to S. Lee for his assistance in the analysis of some of the absorption data.

The author also wishes to express his thanks to Dr. A. Manoogian for the many helpful discussions on the Manoogian-Leclerc equation. As well Dr. K. S. Song's interest in the analysis of the crystal field and spin-orbit splitting of the valence bands of CuGaSnSe$_4$ is greatly appreciated.

The financial support provided by Dr. J. C. Woolley from his NSERC grant is gratefully acknowledged. Finally the author would like to thank Mrs. L. Leroux for typing some of the thesis.
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1.1 PREFACE

In recent years, it has been argued that applied research is more worthy of public funding than pure research. While it is an undeniable fact that applied research yields fairly immediate and lucrative dividends, such investigations would not in many cases have been possible without the 'pure' research that came before. This is certainly the case in the field of semiconductor physics.

Semiconductivity was first discovered by Faraday in 1883 when the temperature coefficient of resistance of silver sulphide was observed to be negative. Earlier in 1874 F. Braun and A. Schuster had been the first to investigate rectifying systems using for the most part natural crystals of lead sulphide and copper oxide. Definitely, at that time, such studies had little application outside the laboratory and were but curiosities to occupy the minds of learned men. This was the case for almost seventy years as experimentalists and theorists continued to expand the body of knowledge. However, the invention of the semiconducting transistor in 1949 (49B1), touched off a technological revolution, which not only drew upon this knowledge, but simultaneously stimulated expanded research into new semiconducting materials and properties.
In a mere thirty years, knowledge which at one time was of little sociological relevance, has become the focal point of much of today's high technology from which much benefit accrues.

1.2 BRIEF HISTORY

Essentially this thesis is concerned with the investigation of new semiconducting materials with respect to their optical and physical properties.

Early researchers concentrated on the elemental semiconductors silicon and germanium, which form in the diamond lattice structure. In 1952 it was reasoned that those compounds which were iso-electronic, i.e. tetrahedrally bonded, with the elemental semiconductors might also share their properties (52Wl). This led to the investigation of the III-V compounds. These compounds have the zinc-blende structure, which is derived from diamond structure and consists of two ordered interpenetrating sub-lattices. InSb was the first of these to be extensively studied; also of interest was GaAs, the structural and electronic analog of germanium.

As the possible III-V compounds were being investigated, the obviously advantageous possibility of alloying the binary compounds was considered as one possible way of extending various semiconducting parameters. In the mid 1950's work was begun on the mixed III-V ternary systems by such workers as Goryunova, Ivanov-Omskii and Woolley, and is still continuing today (78G1, 79G1, 80G1). This way, instead of discrete values of such parameters as band-gap or effective mass,
continuous ranges could be made available to the technologists for device applications. With the advent of vapour and liquid phase thin film single crystal techniques, researchers began to study III-V quaternary alloy systems. Such alloys would provide a range of not only the previously mentioned parameters, but also a wider variation of lattice constants. Thus, materials with the desired optical and electrical characteristics could be grown on a substrate of quite different composition, facilitating device production.

Another path which was followed was the study of the II-VI compounds and the ternary II-VI alloys of zinc-blende structure. Following from this, interest grew in the ternary chalcopyrite structured compounds derived from either the II-VI's, i.e. the I-III-VI$_2$'s, or from the III-V's, i.e. the II-IV-V$_2$'s (53H1, 54D1, 57G1). Typical examples are CuGaS$_2$ for the former and ZnGeAs$_2$ for the latter case.

Previous interest in chalcopyrite structure materials was directed toward the production of thermoelectric devices. Presently the interest in these materials is for possible applications in the fields of solar, luminescent, and non-linear devices. While much has been, and still remains to be done on ternary chalcopyrites, researchers are beginning to shift to the derived quaternary and pentenary compounds and alloys of the ternaries.

With this in mind, some thirty polycrystalline quaternary compounds of the general chemical formula I-III-IV-$[I]-VI_4 ([I] - vacancy)$, were prepared and various parameters studied.
This thesis can be divided into two main topics: (1) characterization of the materials with respect to their crystallographic properties and (2) the variation of the band-gap values of these materials as a function of composition and temperature.

The first topic is dealt with in Chapter 2. The preparation of these quaternary compounds and their crystallographic structure and ordering condition, as determined from an analysis of Debye-Scherrer powder X-ray films is discussed. A comparison of several adamantine structures will also be presented. Chapters 3 to 6 deal with the second topic. In Chapter 3 the basic theoretical and experimental aspects of the determination of a principal band-gap value from an analysis of transmission measurements will be discussed. As well, the results of room temperature transmission measurements on these compounds will be presented with particular emphasis on the variation of the principal band-gap as a function of composition. The behaviour, as a function of temperature, of the lowest direct band-gap, \( E_g \), of two of the quaternary compounds, \( \text{AgGaSnSe}_4 \) and \( \text{AgGaGeSe}_4 \), is dealt with in the fourth chapter. This behaviour is analysed using the semi-empirical equations suggested by Manoogian and Leclerc (79Ml) and Varshni (67V1). Chapters 5 and 6 discuss reflectance measurements made on single crystal samples of the quaternary compound \( \text{CuGaSnSe}_4 \), and the ternary alloy system \( \text{CuGa(Se}_{1-x}\text{S}_x)_{2} \) respectively. The behaviour of the \( \Gamma \) point band-gaps, as a function of temperature, for the above mentioned materials, is discussed with respect to the Manoogian and Leclerc equation. In Chapter 5, the values of the crystal field and spin-orbit splittings of the valence bands for \( \text{CuGaSnSe}_4 \) are calculated using the Hopfield
relation and their variation with temperature is discussed. Similarly, the behaviour of the crystal field splitting of CuGaS$_2$ as a function of temperature, is discussed in Chapter 6.
Chapter II
STRUCTURAL ANALYSIS

2.1 INTRODUCTION

Any material with a crystallographic structure derived from the tetrhedral bonded diamond structure can be called adamantine. Typical examples are the Group IV elements which crystallize in the diamond structure, the III-V compounds which have the zinc-blende structure and various ternary compounds which crystallize in the chalcopyrite lattice structure. Two basic requirements for these structures to be adamantine are a; an average of four valence electrons per lattice site (79Pl) and b; equal numbers of anions and cation sites. The I-III-IV-VI₄ compounds satisfy this condition by having one cation site in four vacant - thus being examples of defect adamantine compounds. The assumption that the vacancy acts effectively as a cation is valid in as much as in all known examples of defect adamantine compounds, the lattice vacancies only occur on the cation sites.

As the main aim of this Chapter is to establish the crystallographic structure and the ordering condition of these compounds, it would be instructive at this point to review the previously mentioned adamantine structures.
Fig. 2.1 Perspective drawing of the diamond structure. 
Shaded atoms differentiate the two interpenetrating sub-lattices.
(a) $F^{x+3} \frac{2}{m}$ (one octant of the cell).

Fig. 2.2 Diamond structure:

(a) Space and point group symmetry.

(b) Projection of atomic positions on cube face.
Figure 2.1 shows a perspective drawing of the diamond structure. The tapered arrows indicate the tetrahedral bonding to the four nearest neighbours. Figure 2.2b is a projection on a cube face of the atomic positions in the unit cell. The shaded circles at 0 and 1/2 are on one face centered cubic lattice and those at 1/4 and 3/4 are on a similar lattice displaced along the body diagonal by a quarter of its length. As can be seen there are eight atoms per unit cell.

The point and space group symmetry of the structure is shown in Figure 2.2a. As indicated, there is an inversion centre at the mid-point of each line connecting nearest neighbours.

The III–V compounds with one cation (III) and one anion (V) and an average of four valence electrons per site are adamantane compounds which crystallize in the zinc–blende structure. Examining Figure 2.3, it is evident that this structure results from the diamond structure when Group III atoms are placed on one fcc lattice and Group V atoms on the other. The bonding is slightly different in that a degree of ionicity is introduced. The planar map, Figure 2.4b, showing the atomic positions of this structure is seen to be similar to that depicted in Figure 2.2b. The only difference is that the shaded circles now differentiate between the two atoms as well as the two sub-lattices. The ordering of the atoms reduces the symmetry to that indicated in Figure 2.4a. It is evident that there is no longer an inversion centre between nearest neighbours and that the diamond glide symmetry is also lost. As well the screw tetrads of the diamond structure are reduced to screw diads.
Fig. 2.3 Perspective drawing of zinc-blende structure (Sphalerite).
Fig. 2.4 Zinc-blende structure:
(a) Space and point group symmetry.
(b) Projection of atomic positions on cube face.
When one alloys these compounds together, the structure remains zinc-blende but now the constituent cations (or anions, depending on the case) are randomly arranged on the appropriate sub-lattice. Ga$_x$In$_{1-x}$As is an example of such an alloy system. On an average taken over many atoms, it will appear as if the cation sub-lattice is occupied by identical atoms of the form (Ga$_x$In$_{1-x}$).

The compounds and alloys formed from the combinations of Groups I, III and VI atoms are also adamantane. However, because of the ordering of the constituent atoms, the unit cell symmetry is no longer cubic as in the above cases. These compounds have a tetragonal structure with c/a ratios equal to or slightly less than 2. One example is CuGaSe$_2$ with a c/a ratio equal to 1.962 (75S1). The structure involved is identical with the CuFeS$_2$ structure, commonly known as chalcopyrite. The unit cell of this structure contains sixteen atoms as compared to eight atoms for the previously discussed structures.

In the chalcopyrite structure there are two cation sub-lattices each occupied by one type of cation and one anion sub-lattice. The planar maps of the lattice sites projected on the c and b faces, shown in Figures 2.5b and 2.5c, clearly show the three sub-lattices involved. The shaded and open circles represent the two cation sub-lattices and the crosses the anion sub-lattice. Due to the difference in bond strengths, the anion positions will be shifted by a small amount from the ideal positions towards one of the pairs of cations. One can see this in Figure 2.6 where the tetrahedral bonding is indicated by the tapered arrows.
Fig. 2.5 Chalcopyrite structure:
(a) Space and point group symmetry.
(b) Projection of atomic positions on c face.
(c) Projection of atomic positions on b face.
Fig. 2.6 Perspective drawing of chalcopyrite structure (I-III-VI$_2$)
It is immediately obvious from Figures 2.5b and 2.5c that the 'doubled cube' ordering of the elements gives rise to a considerable lowering of the symmetry of the crystal. For example, in Figure 2.5a it can be seen that the previously mentioned screw diads of zinc-blende are lost altogether. Also eliminated are the inclined triads of the cubic structures. As well, the inversion tetrads positioned at the centres of the octants for both diamond and zinc-blende structures are reduced to screw diads.

Alloys of these ternary compounds have a random arrangement of atoms on the appropriate sub-lattices as is also the case with the zinc-blende compounds. For example, in the CuGa(Se$_1$-xS$_x$)$_2$ system the cations are located as before but now there is a random arrangement of the sulphur and selenium atoms on the anion sub-lattice. Similarly alloying AgGaSe$_2$ with CuGaSe$_2$ will result in a random arrangement of Ag and Cu on the Group I sub-lattice.

The crystallographic structure of the binary and ternary compounds having been discussed, the question of what structure these quaternaries compounds will favour, if in fact they form, arises.

Table 2.1 shows that there are many combinations of the form I-III-IV-VI$_4$ which can be postulated. However, combinations involving the row 5 atoms may be ruled out as they do not form tetrahedrally coordinated compounds. Quaternary compounds involving row 1 atoms are ruled out for technical reasons, but are still feasible. There remain, therefore, fifty four possible compounds.
TABLE 2.1  SECTION OF PERIODIC TABLE

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</tr>
<tr>
<td>29</td>
<td>Cu</td>
<td>Ga</td>
<td>Ge</td>
<td>Se</td>
</tr>
<tr>
<td>47</td>
<td>Ag</td>
<td>In</td>
<td>Sn</td>
<td>Te</td>
</tr>
<tr>
<td>79</td>
<td>Au</td>
<td>Tl</td>
<td>Pb</td>
<td>Po</td>
</tr>
</tbody>
</table>

Initial investigation of copper compounds of this type were carried out by Hahn and Strick (67H1). These authors determined lattice parameter values, demonstrating that the compounds are tetragonal but did not establish the cation ordering condition. Pamplin et al. (77P1) and most recently Hughes et al. (80H1) have reported further preliminary work on both the copper and silver quaternary compounds.

In the present work, fifteen selenium compounds have been investigated. These involve all the possible combinations of Cu or Ag, Al, Ga or In, and Ge or Sn as the cations with selenium as the anion, as well as three compounds involving Si, AgGaSiSe$_4$, CuGaSiSe$_4$ and
CuAlSiSe₄. In addition, eight possible tellurium compounds and five sulphides have been considered, no aluminum compounds being investigated in this case.

2.2 PREPARATION

The method of preparation by direct synthesis used previously by Hahn and Strick (67H1) has been followed in the present work, i.e. melting together the component elements followed by slow cooling and annealing at a lower temperature. The required masses of the elements were sealed in an evacuated quartz ampoule. The ampoule was slowly heated (20–40°C per hour) up to 1050–1100°C, left at that temperature for 5–10 hours, slowly cooled (10–20°C per hour) down to approximately 500°C and then annealed at that temperature for 10–100 hours before cooling to room temperature. The heating was carried out in a furnace mounted on a platform which was slowly oscillated through an arc of 60° either side of the horizontal. This ensured good mixing of the components. During the cooling of the ampoules and subsequent annealing of the ingots, the furnace was positioned as near vertical as possible. The resulting ingot was cut up to provide specimens for powder X-ray photographs and for optical work.

It was found for all of the selenides that the quaternary compound formed and hence lattice parameter values could be determined. However in no instance was a telluride quaternary produced; in each case a mixture of the ternary I-III-Te₂ plus IV-Te and free tellurium being
obtained. In the case of the sulphide quaternaries, X-ray photographs revealed that some of the samples produced by the above method showed a range of structures. One compound, AgGaGe[II]S₄, was found to have an orthorhombic structure, while two others, CuInSn[II]S₄ and AgInSn[II]S₄, crystallized in the spinel structure. The remaining two compounds, CuGaGe[II]S₄ and CuGaSn[II]S₄, gave the same tetragonal structure as the selenides. As the work on the sulphides is not completed, these compounds will not be discussed further.

In the case of the selenides, the X-ray results showed the presence to a greater or lesser extent, of small amounts of the ternary I-III-Se₂ and binary IV-Se₂ compounds. In some cases the diselenide was barely discernible and the ternary undetectable. Whether the existence of the three phases indicated the breakdown of the quaternary into ternary and diselenide or to incomplete reaction despite the long annealing and slow cooling rates was not established in this work. In some cases, it was found that the ratio of quaternary to ternary could be increased by adding up to 20% excess IV-Se₂ to the ampoule charge. This increase could be determined qualitatively by comparing the relative intensities of the X-ray lines belonging to the two phases. However, it was found that the ratio changed only to a small extent. Longer annealing of the stoichiometric charges at 500°C also increased the quaternary content but some trace of IV-Se₂ could always be detected in the powder photographs.

In the case of CoGaSn[II]Se₄, growth of single crystals has been carried out using the iodine transport temperature oscillation method of
Pendelofen (77Al). This work has been done by Adan Lopez-Rivera at the University of Bath in England in collaboration with this group. The process was carried out in a two zone furnace - the deposition zone being subjected to a periodic upward fluctuation of temperature during the growth period. This fluctuation was controlled in five steps by a microprocessor. The source zone was heated up in two stages; the first stage was relatively fast (though always keeping the temperature lower than that of the deposition zone) and the second stage was very slow - this being the nucleation period. The source zone was finally held at constant temperature, while the crystals grew.

Needle shaped crystals of approximate dimensions 1 x 13 mm were obtained. The vapour transport technique also gave, in some cases, single crystal platelets of SnSe₂. The optimum conditions for the growth of single crystals of the quaternary compounds have still to be determined.

2.3 STRUCTURE AND LATTICE PARAMETERS

A set of Debye-Scherrer powder X-ray photographs for the fifteen compounds was obtained using 114.6 mm diameter cameras and Cu Kα radiation. The positions of the diffraction lines were determined and from the subsequent analysis, the Miller indices involved for each line were established. The structure was found to be tetragonal and the lattice parameter values are summarized in Table 2.2. The values listed for the quaternaries are for c and a parameters extrapolated to 90° Bragg angle. An examination of the low angle lines showed that there
was a consistent set of ordering lines present in each film. These were the \((101),(103),(105),(211)\), and \((301)\) lines. The position of these ordering lines showed that the \(c/a\) ratios of interest here range from a low of 1.730 for \(\text{AgGaSiSe}_4\) to a maximum of 2.000 in the case of \(\text{CuInSnSe}_4\).

### Table 2.2

**Summary of Lattice Parameters for Ternary and Quaternary Compounds**

<table>
<thead>
<tr>
<th>Ternary</th>
<th>(a (\text{nm}))</th>
<th>(c/a)</th>
<th>(V \times 10^{-30} \text{m}^3)</th>
<th>Quaternary</th>
<th>(a (\text{nm}))</th>
<th>(c/a)</th>
<th>(V \times 10^{-30} \text{m}^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{AgAlSe}_2)</td>
<td>0.5968</td>
<td>1.800</td>
<td>383</td>
<td>(\text{AgAlGeSe}_4)</td>
<td>0.5871</td>
<td>1.755</td>
<td>355</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(\text{AgAlSnSe}_4)</td>
<td>0.5882</td>
<td>1.821</td>
<td>371</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(\text{AgGaSiSe}_4)</td>
<td>0.5470</td>
<td>1.73</td>
<td>283</td>
</tr>
<tr>
<td>(\text{AgGaSe}_2)</td>
<td>0.5992</td>
<td>1.817</td>
<td>391</td>
<td>(\text{AgGaGeSe}_4)</td>
<td>0.5826</td>
<td>1.782</td>
<td>352</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(\text{AgGaSnSe}_4)</td>
<td>0.5869</td>
<td>1.843</td>
<td>373</td>
</tr>
<tr>
<td>(\text{AgInSe}_2)</td>
<td>0.6102</td>
<td>1.910</td>
<td>434</td>
<td>(\text{AgInGeSe}_4)</td>
<td>0.5759</td>
<td>1.877</td>
<td>359</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(\text{AgInSnSe}_4)</td>
<td>0.5877</td>
<td>1.920</td>
<td>390</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(\text{CuAlSe}_4)</td>
<td>0.5584</td>
<td>1.925</td>
<td>335</td>
</tr>
<tr>
<td>(\text{CuAlSe}_2)</td>
<td>0.5617</td>
<td>1.940</td>
<td>344</td>
<td>(\text{CuAlGeSe}_4)</td>
<td>0.5575</td>
<td>1.916</td>
<td>332</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(\text{CuAlSnSe}_4)</td>
<td>0.5604</td>
<td>1.954</td>
<td>344</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(\text{CuGaSiSe}_4)</td>
<td>0.5571</td>
<td>1.918</td>
<td>332</td>
</tr>
<tr>
<td>(\text{CuGaSe}_2)</td>
<td>0.5616</td>
<td>1.962</td>
<td>348</td>
<td>(\text{CuGaGeSe}_4)</td>
<td>0.5568</td>
<td>1.947</td>
<td>336</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(\text{CuGaSnSe}_4)</td>
<td>0.5611</td>
<td>1.958</td>
<td>346</td>
</tr>
<tr>
<td>(\text{CuInSe}_2)</td>
<td>0.5782</td>
<td>2.000</td>
<td>387</td>
<td>(\text{CuInGeSe}_4)</td>
<td>0.5640</td>
<td>1.980</td>
<td>355</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(\text{CuInSnSe}_4)</td>
<td>0.5700</td>
<td>2.000</td>
<td>370</td>
</tr>
</tbody>
</table>
To establish which tetragonal structure was involved, a computer program was written to enable the calculation of the approximate intensities of the powder x-ray diffraction lines which would be expected from a particular ordering. Implied in this statement is the fact that there would be lines with intensities identically equal to zero. These lines which henceforth will be called absence lines, will, along with the consistent set of indexed lines mentioned previously, establish the general ordering of the cations.

For the purpose of calculation, it was assumed that the intensity of the lines on a Debye-Scherrer powder photograph would be proportional to the expression given by equation 2.1 (5lH1). This expression will not only allow the determination of the Miller indices of diffraction lines of zero and non-zero intensities, but also the relative intensities of the low angle ordering lines as compared with nearby structure lines.

$$I \propto \frac{(1+\cos^2 \theta)/\sin^2 \theta \cos \theta)P \epsilon F^2}{(2.1)}$$

In equation 2.1, I is the integrated intensity of the diffraction line, and $\theta$ is the Bragg angle. The trigonometric expression takes into account the probability that a particular set of planes will pass through a reflecting position and that the total intensity of a reflection is spread out along a curved line. This is a slowly varying function which may be ignored in the low Bragg angle region of interest. $A_p$ is the absorption factor for the powder sample and will depend upon the linear absorption coefficient $\mu$ of the material. For all intents and purposes, $A_p$ can be assumed to be essentially constant over the
region of interest and of the same magnitude for all the samples considered. Thus this factor will also be ignored.

The factor $p$, takes into account the possible number of different sets of planes which can be generated from a single set by the operation of all symmetry elements in the appropriate point group. This multiplicity factor depends upon the Miller indices of the reflecting planes and on the crystal symmetry. For the tetragonal symmetry seen here $p$ has the following values:

<table>
<thead>
<tr>
<th>hkl</th>
<th>p</th>
</tr>
</thead>
<tbody>
<tr>
<td>h00</td>
<td>4</td>
</tr>
<tr>
<td>001</td>
<td>2</td>
</tr>
<tr>
<td>h01</td>
<td>8</td>
</tr>
<tr>
<td>h00</td>
<td>8</td>
</tr>
<tr>
<td>hh0</td>
<td>4</td>
</tr>
<tr>
<td>hh1</td>
<td>8</td>
</tr>
<tr>
<td>hkl</td>
<td>16</td>
</tr>
</tbody>
</table>

$F^2$, the geometrical structure factor, depends upon the type of atoms present in the unit cell and upon their relative positions. This term is essentially given by

$$F^2 = \left( \frac{2}{n} \right) \cos 2\pi \left( \frac{hx_n + ky_n + lz_n}{n} \right)^2 + \left( \frac{2}{n} \sin 2\pi \left( \frac{hx_n + ky_n + lz_n}{n} \right)^2 \right)$$  (2.2)
where the summation is taken over all the atoms in the unit cell. It is this term which can become identically zero for the absence lines. The atomic scattering factor $f_n$ was assumed to be proportional to the average atomic number of the cation row of the particular atom concerned and constant over all $\theta$. Thus recalling Table 2.1 it can be seen that for the row 2 atoms a value of 13.5 was assumed for $f_n$. Similarly, values of 30.7 and 48.7 were assigned to $f_n$ for row 3 atoms and row 4 atoms respectively. The atomic number of selenium, 34.0, was assumed for the value of the scattering factor for the anions.

Obviously, $h$, $k$ and $l$ are the Miller indices and $x_n$, $y_n$ and $z_n$ are the coordinates, expressed as fractional values of the cell dimensions, of the various atoms involved in scattering the X-rays. In Figure 2.7 the cation sites are labelled by the letters A-H and have the coordinates indicated. The anion sites, not shown, have been assumed to be in the ideal positions mentioned previously.

This approach is of course simplified since apart from the above approximations, $f_n$ has been assumed to be independent of the Bragg angle $\theta$ and the wavelength of radiation used. However since the Miller indices of lines of zero and non-zero intensity and the relative intensities of certain ordering lines to adjacent structure lines are required, the simplifications mentioned will not pose any problems.

The first possibility investigated was that the quaternaries formed a tetragonal structure in which the two vacancies of the compounds are ordered on their own sub-lattice. In order that the differences in intensity can be attributed to the vacancies only, it was assumed that the cations were all row 3 atoms i.e. Cu, Ga and Ge.
Fig. 2.7  General tetragonal diagram (cation positions).
To this end the calculations involved placing vacancies on the corners of the general lattice (Figure 2.7) and pairing these sites with all other possible sites i.e. AB, AD, AE etc.

All feasible combinations predicted either lines of non-zero intensity which experimentally did not occur, or indicated that the experimentally observed ordering lines should not occur. Thus it must be concluded that the vacancies do not occupy a separate sub-lattice.

The next possibility to be considered is that the vacancies are randomly distributed on a cation sub-lattice together with one of the three cations.

Several possible tetragonal structures could accommodate such a random arrangement of the vacancies. The possible candidates considered here are thiogallate, stannite and chalcopryte.

The thiogallate structure is named for the compound CdGa$_2$(I$_2$S$_4$). The open circles of Figure 2.8 are the cadmium atoms and the shaded circles are the gallium atoms. The vacancies are located at the E and H sites of the general tetragonal diagram shown previously. The cadmium atoms sit on the AB sub-lattice and the gallium atoms on the CDFG sites. As before, the anions are located at the ideal positions.

Figure 2.8 can be redrawn such that the corners of the structure are occupied by the vacancies. Thus the B site of the new representation is occupied by a vacancy as well. This is accomplished by translating all sites by $-1/2$ a $+$ $1/4$ c $+$ $1/4$ a. Referring to the quaternary compounds, it can be seen that this arrangement was covered by the first analysis.
Fig. 2.8  Perspective drawing of Thio gallate (CoGa₂[SS₄]).
Fig. 2.9 Perspective drawing of Stannite (Cu₂FeSnS₄).
The next analysis assumed that the cations of these compounds are arranged such that one type is on the AB sub-lattice another on the EH sub-lattice with the remaining atom arranged randomly with the vacancy on the CDPG sites. This analysis predicts a set of ordering lines that contains not only the observed set but in addition, lines which are not seen experimentally. Therefore it must be concluded that the compounds do not have this ordering.

The next possibility considered is Stannite. This structure is named for Cu$_2$FeSnS$_4$. We can see in Figure 2.9 that there are again three cation sub-lattices; the AB sub-lattice is occupied by the iron atoms (open circles), the CD sub-lattice is occupied by the tin atoms (black dots) and finally the copper atoms are situated on the EFGH sites. There are two possible Stannite orderings which could accommodate the quaternary compounds. These are referred to as Stannite A and Stannite B.

Stannite A would have the AB or CD sub-lattice occupied by vacancies. This also has been ruled out by the first analysis.

Stannite B on the other hand would have separate cations on the AB and CD sub-lattices with the vacancies randomly arranged with the remaining cation on the sub-lattice formed by the EFG and H sites.

This structure is also an unsatisfactory choice as the calculations predict that the observed ordering lines should be missing and that the experimentally determined absent spectra are present.
Finally, there remains the previously discussed chalcopyrite structure. With reference to Figure 2.7, it can be seen that the two cation sub-lattices are formed by the ABEH sites for one and the CDFG sites for the other. With the different effective cations, the only probable structure is one in which the the vacancies are randomly distributed with one cation on one sub-lattice and the remaining two cations randomly distributed on the other. For all the compounds investigated it was found that this arrangement predicted the correct absence and ordering lines. Hence the quaternary compounds have the same general structure as the ternary I-III-VI$_2$ compounds.

Now that the general ordering of these compounds has been established as chalcopyrite, there remains the problem of determining which cation is associated with the vacancies. The three possibilities are:

\[(I-I) (III-IV) Se_4\]
\[(I-III) (IV-I) Se_4\]
\[(I-IV) (III-I) Se_4\]

For all the compounds, the sum of the ratios of the intensities of the 103 to the 112 and the 211 to the 220 diffraction lines were determined from the calculated values, for each of the three arrangements mentioned above. The sum calculated for Cu[InSnSe$_4$] (vacancy associated with the copper atoms) was further rationalized by assigning a value of 10 to this arrangement. All other calculated sums were then adjusted relative to this value.
Experimentally, the 103 and 211 ordering lines were identified and the intensity of each relative to the nearest structure line i.e. 112 and 220 was visually determined by two independent observers. An average of the four values so obtained was calculated and used to characterize the intensity of the ordering lines. It was found that the powder X-ray film of CuInSn[II]Se₄ had the most intense ordering lines. Thus this film was assigned a value of 10. The other films were subsequently ranked relative to this film and assigned a value of relative intensity from 0 to 10.

Table 2.3 summarizes the experimental and theoretical results. Column one shows the ranking and relative intensities determined from the films. The second, third and fourth columns list the calculated relative intensities. The good agreement of the magnitudes of columns 1 and 2 show that the random arrangement of I-[II] on one sub-lattice and III-IV on the other is the actual cation ordering. As well, examining lines 2,5,8,9,10 and 12 of Table 2.3, it can be seen that the vacancies cannot be associated with the Group III cations as the relative intensities of the lines are predicted to be other than actually observed. Similarly an examination of lines 1,5,6,11 and 13 rules out the possibility of the arrangement being I-[II]-IV.

Thus these quaternaries have the chalcopyrite structure and should be written as

\[(\text{I-[II]})(\text{III-IV})\text{Se}_4\]
TABLE 2.3

CALCULATED AND EXPERIMENTAL INTENSITY RATIOS OF QUATERNARY COMPOUNDS

<table>
<thead>
<tr>
<th>Exp</th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>I [-]</td>
</tr>
<tr>
<td>Cu[InSnSe]_4</td>
<td>10.0</td>
</tr>
<tr>
<td>Cu[InGeSe]_4</td>
<td>7.0</td>
</tr>
<tr>
<td>Ag[InSnSe]_4</td>
<td>7.0</td>
</tr>
<tr>
<td>Cu[GaSnSe]_4</td>
<td>6.0</td>
</tr>
<tr>
<td>Cu[AlSnSe]_4</td>
<td>3.0</td>
</tr>
<tr>
<td>Ag[InGeSe]_4</td>
<td>3.0</td>
</tr>
<tr>
<td>Cu[GaGeSe]_4</td>
<td>2.0</td>
</tr>
<tr>
<td>Ag[GaSnSe]_4</td>
<td>2.0</td>
</tr>
<tr>
<td>Cu[AlGeSe]_4</td>
<td>0.5</td>
</tr>
<tr>
<td>Ag[AlSnSe]_4</td>
<td>0.5</td>
</tr>
<tr>
<td>Ag[GaGeSe]_4</td>
<td>0.5</td>
</tr>
<tr>
<td>Ag[AlGeSe]_4</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>Ag[GaSiSe]_4</td>
<td>&lt;0.5</td>
</tr>
</tbody>
</table>

2.4 OTHER STRUCTURES

Different structures were obtained in one or two cases which indicated a more complicated form of phase diagram. Thus in the case of CuInSnSe_4, when the ampoule was slowly cooled to room temperature from 1000 °C without annealing at 500 °C, in addition to the quaternary compound, strong lines of a cubic phase (probably with an NaCl structure of lattice parameter 0.544 nm) were obtained. When the same sample was
annealed at 500°C, this cubic phase disappeared. However, if the annealing time at this temperature was relatively short (e.g. 1 day), lines of both the quaternary and the ternary CuInSe₂ were obtained. The lattice parameters of these phases are not greatly different and hence corresponding h k l lines were close together in the powder photograph. A qualitative study of the intensities of such pairs of lines indicated that the intensity at points between the lines did not fall to the background level, indicating the possibility that solid solution can occur between the ternary and quaternary compounds. Longer annealing of such samples with the stoichiometric quaternary composition gave good quaternary lines with no ternary lines visible, although as mentioned above, some small traces of SnSe₂ could still be detected.

In the case of AgAlGeSe₄, one of the materials for which the effect of addition of excess GeSe₂ was investigated, it was found that when 40 mole% excess GeSe₂ was added, a new compound with orthorhombic structure was obtained.

2.5 DISCUSSION

Hughes et al. (80H1) have demonstrated that there is a systematic relation between the ternaries and the Ge and Sn substituted quaternaries. For example if one plots the difference between the ternary and quaternary unit cell volumes \( \Delta V = V_T - V_Q \) against the ternary unit cell volume \( V_T \) Figure 2.10 is obtained. The lattice parameter values for the ternary compounds have been taken from the literature (75S1) and the volumes used are listed in Table 2.2. In all
cases except CuAlSnSe₄ the quaternary unit cell is smaller than the related ternary, i.e. ΔV is positive, and the change in volume ΔV due to the inclusion of either Sn or Ge is greater the larger the volume of the corresponding ternary unit cell. To a good approximation the data can be represented by straight line equations. The slope of the line passing through the points for the Ge substituted compounds is 1.47 times that for the Sn substituted compounds. This larger slope can be attributed to the relatively smaller size of the Ge atom compared with the Sn atom. Taking the volume of an atom to be proportional to the cube of its atomic radius (52E1), one finds that the ratio of volumes of Sn to Ge is 1.50. This agreement strongly indicates that the compounds all have the same structure and that the change from ternary to quaternary is due to a consistent substitution of a combination of atoms and vacancies which require less volume.

In Figure 2.11 the difference between the ternary and quaternary c/a ratios \( \Delta(c/a) = (c/a)_T - (c/a)_Q \) is plotted against the related ternary ratio \( (c/a)_T \). \( \Delta(c/a) \) is positive for the Ge substituted compounds (the ternary c/a ratio is larger than that of the quaternary) but is negative for the Sn substituted compounds. The values of \( \Delta(c/a) \) are relatively small and hence less accurate but again, within the limits of the experimental error, for each case the variation of \( \Delta(c/a) \) with \( (c/a)_T \) be taken as a straight line, the line having positive slope for the Sn substituted compounds and negative slope for the Ge substituted compounds. The magnitudes are, within the limits of experimental error, equal.
Fig. 2.10 Variation of the difference between the ternary and quaternary unit cell $\Delta V = V_T - V_0$ with the ternary unit cell volume $V_T$ for Ge and Sn substituted quaternary compounds.
Fig. 2.11 Variation of the difference between the ternary and quaternary c/a ratios \( \Delta(c/a) = \langle c/a \rangle_T - \langle c/a \rangle_o \) with the ternary ratio \( \langle c/a \rangle_T \) for Ge and Sn substituted quaternary compounds.
2.6 SUMMARY

This Chapter has established that the selenide quaternary compounds of the form I-[]-III-IV-Se$_4$ have the same crystallographic structure as the compound chalcopyrite. Further, the vacancy [] has been shown to be associated with the Group I atoms. The lattice parameters determined for these compounds are listed in Table 2.2.
Chapter III

ENERGY GAP VALUES AS A FUNCTION OF QUATERNARY COMPOSITION

3.1 INTRODUCTION

A material is characterized by more than just its crystallographic structure. In addition, the optical and electrical properties of the material are of great importance. Due to technical difficulties in obtaining reliable ohmic contacts to these compounds, no detailed electrical measurements were performed. For this same reason, such methods as Photovoltaic effect, Photo-Conductivity and Electroreflectance, were ruled out as methods to determine the principal band-gap, $E_g$.

In this Chapter, the values of the principal band-gap of the quaternary selenides, as determined from the analysis of optical transmission measurements, are reported. Further, the relation of these values to the band-gap values of the ternary compounds from which the quaternaries are derived is investigated.

The principal band-gap of a material involves a transition from the highest valence band to the lowest conduction band. This transition is
either of a direct or indirect nature. However, with the chalcopyrite structure, the direct transition is divided into two sub-classes - direct and pseudodirect.

Thalyshev and Pokrovski (60C1, 63C1), Karavaev and Poplavnoi (66K1) and Karavaev et al. (68K1), have shown that since there is a 'doubling' of the lattice in the z direction, there is a subsequent folding of an X point of the zinc-blende Brillouin zone into the Γ point of the chalcopyrite zone. If this process results in the lowest conduction band, the transition will be direct but to a band which in a zinc-blende material would have resulted in an indirect transition. This is hence referred to as pseudodirect.

Due to the tetragonal compression along the z axis (c < 2a) and the interaction of the four kinds of cations, (Cu, Ga, Sn, []), which shifts the anion sites away from the ideal (1/4, 1/4, 1/4) and symmetrically related positions, there is a noncubic crystalline field of tetragonal symmetry.

When, in the absence of spin-orbit splitting, this tetragonal field is applied to the triply degenerate Γ15 valence band, the result is a non-degenerate band of Γ4 symmetry and a doubly degenerate band of Γ5 symmetry. The inclusion of spin-orbit effects changes the symmetry of the Γ4 band to one of Γ7 and lifts the degeneracy of the Γ5, resulting in bands of Γ6 and Γ7 symmetry.
The $\Gamma_6$ conduction band of chalcopyrite corresponds to the $\Gamma_6$ band of zinc-blende. As indicated above an $X$ point of zinc-blende is folded into the $\Gamma$ point of chalcopyrite and this results in a conduction band of $\Gamma_7$ symmetry when the crystal field and spin-orbit effects are included.

If the lowest conduction band is of $\Gamma_6$ symmetry, the principal band-gap will be direct. However if the $\Gamma_7$ conduction band is lower than the $\Gamma_6$ band then the principal band-gap is pseudodirect. The two cases are summarized in Figures 3.1 a and b.
Fig. 3.1  (a) Band structure for the direct transitions in a chalcopyrite crystal derived from the $\Gamma_{15} + \Gamma_1$ band-gap in a zinc-blende crystal.

(b) Band structure for the pseudodirect transitions in a chalcopyrite crystal derived from the $\Gamma_{15} + X_1$ indirect transitions in a zinc-blende crystal.
Due to the mechanical properties of the polycrystalline materials (to be discussed below) and as no contacts were required, transmission measurements were decided upon as a method which was applicable for all of the materials under investigation. Such measurements have long been used to study the fundamental absorption edge. A very good review of the subject can be found in Volume 3 of Semiconductors and Semimetals (67W1).

This edge arises from a process called interband absorption in which photons excite electrons from the valence band to the conduction band. The process has a threshold at an energy corresponding to the band-gap energy and results in a rise in the value of the absorption coefficient above the background as the energy of the incident radiation increases.

Two possible cases must be considered for interband absorption. The first case arises when the transition occurs between band extrema situated at the same point in the Brillouin zone and as a result is called a direct or pseudodirect transition (depending upon the conduction band symmetry as discussed above). The absorption curve for a direct transition is characterized by a steep rise in the value of the absorption coefficient over several tens of milli electron-volts, while the curve for a pseudodirect transition is considerably less steep (72B1). If the transition is between band extrema located at different points in the zone, then phonons must be involved to provide the required change of momentum. This case is appropriately referred to as an indirect transition. The absorption curve in this case is shallow and spread over several hundred milli electron-volts.
If the above process is approached from a quantum mechanical viewpoint, the absorption coefficient is seen to depend on the probability of an electron being promoted from the valence band to the conduction band. Thus the absorption coefficient $\alpha$ is the number of quanta absorbed per unit time per unit volume divided by the flux density. For simple parabolic bands, the absorption coefficient due to direct transitions has been shown (67W1) to satisfy the equation

$$(ahv) = \frac{2\pi h}{n} \frac{(2\pi^{3/2}|H_{cv}(0)|^2 (h\nu - E_g)^{1/2}}{(3.1)}$$

i.e.

$$(ahv)^2 = A(h\nu - E_g)$$

(3.2)

where $\mu$ is the reduced mass of the electron hole pair, $|H_{cv}(0)|$ is the optical matrix element between the initial and final band states and $\nu$ is the photon energy.

If however the transition is indirect then it may be shown that the absorption coefficient satisfies the form given by (67W1)

$$(ahv) = B(h\nu - E_g)^2$$

(3.3)
3.2 EXPERIMENTAL METHOD

The fundamental edge may be determined from transmission measurements by observing the change in the absorption as a function of incident energy. In general, measurements are made at near normal incidence with both the transmitted and reflected intensities being recorded. However, as will be shown presently, the reflected portion of the incident radiation need not be considered here.

Consider a dielectric medium with a complex index of refraction given by \( N = n + ik \). At normal incidence, the complete formulae for the transmitted and reflected intensities \( I_T \) and \( I_R \), respectively normalized to \( I_0 \), are given by Stratton (41S1) as

\[
I_T = \frac{e^{-ad} [(1 - R)^2 + 4R \sin^2 \theta]}{(1 - Re^{-ad})^2 + 4 Re^{-ad} \sin^2 (\theta + \delta)} \tag{3.4}
\]

\[
I_R = \frac{R [(1 - e^{-ad})^2 + 4e^{-ad} \sin^2 \delta]}{(1 - Re^{-ad})^2 + 4 Re^{-ad} \sin^2 (\theta + \delta)} \tag{3.5}
\]

The nomenclature adopted by Greenway and Harbeke (66G1) has been used here. Thus \( \alpha \) is the absorption coefficient and is given by

\[
\alpha = 4\pi k / \lambda \tag{3.6}
\]

\( \lambda \) being the wavelength in vacuum. Equations 3.7 and 3.8 give \( R \) and \( \theta \) in terms of \( n \), the refractive index, and \( k \), the extinction coefficient.

\[
R = \frac{[(n - 1)^2 + k^2]}{[(n + 1)^2 + k^2]} \tag{3.7}
\]
\[ \tan \theta = \frac{2k}{n^2 + k^2 - 1} \]  

(3.8)

The quantity \( \delta = 2\pi nd/\lambda \) indicates the phase change on one traverse of the radiation through a dielectric sheet of thickness \( d \). The second term in the denominator of equations 3.1 and 3.2 is an interference term which becomes important only when \( \alpha \) is small enough to allow multiple traverses of the material by the incident radiation. If the sample is too thick or too large, or the surface of the material is rough, no interference fringes will be observed. In this case the interference term must be averaged, resulting in the reduction of equations 3.1 and 3.2 to

\[ I_t = \frac{(1 - R)^2 e^{-\alpha d}}{1 - R^2 e^{-2\alpha d}} \left( 1 + \frac{k^2}{n^2} \right) \]  

(3.9)

and

\[ I_r = \frac{R (1 - e^{-2\alpha d})}{1 - R^2 e^{-2\alpha d}} \]  

(3.10)

For energies near the absorption edge, \( k \) is very much less than \( n \). If in addition \( d \) is large enough to ensure that \( R^2 e^{-2\alpha d} \) is much less than 1, equation 3.6 further reduces to the simple form

\[ I_t = \frac{(1 - R)^2 e^{-\alpha d}}{1 - R} \]  

(3.11)

Generally \( R \) is a slowly varying function of photon energy and its maximum possible value is one. Thus the \((1-R)^2\) term may be treated to a good approximation as a constant. Taking the natural log of both sides of equation 3.11 one obtains (writing \( I_t \) as \( I_t/I_0 \))

\[ \ln \left( \frac{I_t}{I_0} \right) = \alpha d - \ln (C) \]  

(3.12)
In the experimental work the value of \( \frac{1}{d} \ln \frac{I_0}{I_m}(\xi) \) has been determined as a function of photon energy \( \nu \). In order to determine \( \alpha \) from \( \xi \) it is necessary to find a value for \( \ln(c) \). This \( \ln(c) \) gives rise to a 'background' that must be subtracted from the measured values of \( \xi \) before proceeding with any further analysis. The criterion used in deciding the value of this background is dealt with in section 1.4 of this Chapter.

The transmission measurements were made using the experimental set-up depicted in Figure 3.2. Light from either a nominal 47 Watt quartz-iodine bulb or a 30 Watt tungsten filament light bulb was collected by a mirror and focused at the entrance slit of a Spex 1702 monochromator. The light beam was amplitude modulated by a Rofin model 755W light chopper positioned before the entrance slit.

The diverging monochromatic output was refocused on to the sample under investigation by means of a mirror. The sample was mounted directly on to the front of a detector appropriate to that energy range. The detectors used were a DUMONT 6911, an EMI 6255S photomultiplier or a PbS cell biased at 67.5 volts. The square wave output signal of the detector was sent to a P.A.R. 186A lock-in amplifier either directly or through a P.A.R. model 113 roll-off amplifier.
Fig. 3.2 Block diagram of optical experimental set-up.

S light source
C copper
G grating
M mirror
D detector
Sa sample
P.A. pre-amplifier
L.A. lock-in amplifier
C.R. chart recorder
In practice when the detector was either of the photomultipliers, the anode voltage was increased, within the limits allowed by the maximum rating of the tube, so that at the wavelength of maximum transmission, the signal could just be accommodated on the largest scale of the lock-in. If however at the maximum rating of the tube the signal was still not large enough the roll-off was used. When the detector was the PbS cell, the signal was amplified, if necessary, using the roll-off (maximum amplification of 10000 x). The output of the lock-in was registered on a strip chart recorder. In order to minimize the error in reading data from these charts, the sensitivity of the lock-in and/or the chart recorder were adjusted to maintain as close to full scale deflection as possible on the chart.

When the optical system was aligned for a specific light source and grating, a spectrum of the detector response was obtained for calibration purposes, with the appropriate voltages and amplifications being noted. It was assumed that since, from one occasion to another, the alignment of the optical system was not disturbed and that the same power was always supplied to the light source, this spectrum would represent $I^0$. As the transmission measurements were made using different amplifications and/or different detector voltages than were used for the various possible $I^0$ curves, it was necessary to determine a scaling factor for each run. This scaling factor represents the difference in magnitude between the measured $I^0$ spectra and what the magnitude would be if the $I^0$ spectra were determined under the same experimental conditions as the transmission measurements. For the calculation of $\alpha$ it was thus necessary to multiply the $I^0$ curves by this.
factor to obtain the proper normalization of the transmission spectra. For reasons which will be discussed below, this scaling factor will not be very important.

3.3 SAMPLE PREPARATION

The sample preparation was undertaken as soon as possible after the ingots were removed from their quartz ampoules and immediately prior to the transmission measurements. It was found that most of the polycrystalline materials were coarse grained and that, in addition, in some instances tiny voids were distributed at random through the ingots. These voids were probably due to the occurrence of small pockets of unreacted selenium gas as the molten charge froze.

All samples were sliced to a thickness of 0.5 mm to 1 mm on a tungsten wire saw which used a mixture of oil and silicon carbide grit (320 mesh size) as the cutting slurry. The slices were reduced in thickness as much as was feasible by lapping on a glass plate covered with a slurry of methanol and alumina powder (1 micron mesh size). When lapped the slices were typically two hundred microns in thickness. The samples were not polished to a high reflectivity as the thinned slices tended to be quite fragile.

Methanol was chosen instead of water for two reasons. Firstly, it evaporates rapidly and completely from the slices, unlike water which
would have to be removed before any transmission measurements. The further handling that this would entail would only increase the probability of damaging the thinned slice. Secondly, the uncertainty of whether or not the quaternary compounds would react with water had to be considered. It was certainly felt that this might be a problem for the quaternary and ternary selenide compounds which contained aluminum.

The samples were next mounted on brass discs, the centres of which had been drilled out to as large an aperture as could be covered by the prepared slice. The sample was affixed to the disc by a small amount of silver print (G.C. Electronics cat. no. 21-1) applied to the edge of the aperture. The silver print was allowed to thicken slightly to ensure that the solvent (n-Butyl Acetate) did not penetrate into the slice and also that the fluid did not flow onto the slice.

An intense light was placed behind the disc in order to detect the presence of any small pinholes. If present, these were plugged with small droplets of the silver print which is opaque. At this point the disc would be mounted on the appropriate detector for the wavelength range of interest.

After the transmission measurements were made, the disc was placed in n-Butyl Acetate to dissolve the silver print. The sample once free, was carefully removed and its thickness determined using a micrometer capable of reading to within one micron.
3.4 ANALYSIS AND DISCUSSION

Transmission measurements on fifteen quaternary selenide compounds and one ternary selenide compound (AgAlSe$_2$), have been performed using the method described above.

The $\xi$ vs. $h\nu$ curves for the quaternary compounds are observed to be similar. For all polycrystalline samples, these curves resemble region B of the $\xi$ vs. $h\nu$ curve of AgGaSnSe$_4$ depicted in Figure 3.3; i.e. there is a straight line ramp below the absorption edge. However, in the cases of CuInGeSe$_4$, CuAlSnSe$_4$ and CuAlGeSe$_4$ the slope of the edge is quite shallow compared to the slope of the edge depicted in Figure 3.3. As seen from equations 3.11 and 3.12, the reflected portion of the incident radiation adds a constant term to the value of $\xi$. Thus, it would be expected that below the absorption edge, $\xi$ would tend to a constant value. As can be seen in Figure 3.3 the $\xi$ vs. $h\nu$ curve does not have an extended region of constant $\xi$ below the edge. However, the $\xi$ curves of a single crystal sample of CuGaSnSe$_4$ and polycrystalline samples of GaAs and AgInGeSe$_4$ did show such an extended region. For some of the samples, in addition to region-B, behaviour similar to that of region A is observed. It is found that this region can be very well fitted to a power law relation of the form $\xi = \xi_1 E^{-m}$, where $\xi_1$ is the value of $\xi$ at 1 eV.
Fig. 3.3 $\xi$ vs. $h\nu$ for $\text{AsGaSnSe}_4$. 
It is well known that effects other than that of reflectance can contribute to the background value of $\xi$ of a sample (67W). One effect which can explain the behaviour of $\xi$ in region A is that of scattering of the incident radiation which increases the value of $\xi$ below the absorption edge as the energy of the incident radiation decreases. This scattering can be due to the grains of the polycrystalline sample, to the presence of a finely distributed impurity, or to free carrier effects. A second effect is absorption in an impurity which has a lower band-gap than the sample. This effect, which increases the value of $\xi$ as the energy of the incident radiation increases, could explain the linear ramp below the edge. Both mechanisms may be present to some extent for any particular sample and hence the variation of $\xi$ with photon energy below the edge will have no simple mathematical form. Indeed, for those cases where region A was observed, the exponent, $m$, was found to vary over a range of values from $-0.5$ to $-6.0$ indicating a variety of scattering processes.

Whatever the origin of the dominant background feature close to the absorption edge, it must be subtracted from the values of $\xi$ to obtain values of $\alpha$. If scattering is the dominant feature, then a power law fit to the background is subtracted. On the other hand, if impurity absorption or the $(1-R)^2$ term of equation 3.41 is the dominant feature, a straight line extrapolation can be used. The values of $\alpha$ are subsequently used in the analysis involving either equation 3.2 or 3.3.
Fig. 3.4 Absorption coefficient $\alpha$ vs. $h\nu$ for $\text{AgGaSnSe}_4$:

(a) power law fitted background removed, (b) ramp background removed.
Fig. 3.5 $(ahv)^2$ vs. $hv$ curves for AgGaSnSe$_4$:
(a) power law fitted background removed; (b) ramp background removed.
To demonstrate the methods used to allow for the background effects, the analysis of several samples will be considered in some detail.

The results for \( \text{AgGaSnSe}_4 \) depicted in Figure 3.3 show the presence of both scattering and impurity absorption effects. It can be shown that the method chosen for background subtraction makes very little difference to the final value of \( E_g \) obtained.

Figure 3.4a shows the effect of removing a power law fitted background from the \( \xi \) values. The power law was fitted to the region of Figure 3.3 below 1.2 eV and subtracted from the value of \( \xi \) determined from the transmission data. It is seen that the maximum value of the \( \alpha \) curve is 550 cm\(^{-1}\). In Figure 3.4b, a ramp, representing a straight line fit to the values of \( \xi \) between 1.2 eV and 1.5 eV has been subtracted from Figure 3.3, the variation of \( \xi \) with \( h\nu \) below 1.2 eV having been ignored. In this case, the maximum value of \( \alpha \) is 450 cm\(^{-1}\). It is to be noted that though the energy scale of Figure 3.4b is expanded by a factor of 2.5, compared to Figure 3.34, the two absorption curves are essentially the same. Indeed, as illustrated in Figures 3.5a and b, when the data is analysed according to equation 3.2, a good straight line is obtained and it is seen that the shift in the band-gap value is quite small, being only 4 meV. This shift is within the experimental uncertainty estimated at \( \pm 10 \) meV.

Curves a and b of Figures 3.6 show the variation of \( \xi \) with energy for a polycrystalline sample of CuGaSnSe\(_4\) (a) and a single crystal of the same compound (b).
Fig. 3.6 $\xi$ vs. $h\nu$ curves for:

(a) polycrystalline CuGaSnSe$_4$  (b) single crystal CuGaSnSe$_4$

(c) polycrystalline AgInGeSe$_4$. 
Curve a is quite similar to that depicted in Figure 3.3. In both cases the low energy rise of $\xi$ below the absorption edge can be attributed to scattering processes. When this region is fitted to a power law and subtracted from the $\xi$ values, a ramp remains below the edge. As indicated above the $\xi$ values in this ramp are due to absorption by an impurity. If these particular values of $\xi$ are analysed in accordance with the work of Domingo et al. (66D1), the extrapolated curve yields the value of the indirect forbidden band-gap of SnSe$_2$. This impurity has been shown by powder X-ray photographs to be present in an appreciable amount in this particular sample.

In the case of curve b for the single crystal sample there is a constant value of $\xi$ lower than that due to SnSe$_2$ absorption below the observed edge. This is to be expected since no trace of SnSe$_2$ was observed in the X-ray photographs of this sample. Recalling equation 3.11, this constant value can be attributed to the effect of the $(1-R)^2$ term. For the thickness of sample used, a value of the order of 68% reflectivity is obtained. This is consistent with the fact that the sample was not highly polished.

For both curves of Figure 3.6 a and b, the background values discussed above have been subtracted from $\xi$ to give values of $\alpha$. Plots of $(\alpha h\nu)^2$ against $h\nu$ (Figure 3.7) in accordance with equation 3.2, in each case give good straight lines indicating a direct gap. The energy gap values obtained agree within the limits of experimental error giving a value of 1.42 eV.
Fig. 3.7 \((\alpha h\nu)^2\) vs. \(h\nu\) curves for:
(a) polycrystalline CuGaSnSe₄,  (b) single crystal, CuGaSnSe₄
(c) polycrystalline AgInGeSe₄.
Figure 3.6 shows the variation of $\xi$ with $h\nu$ for a polycrystalline sample of AgInGeSe$_4$. In this case even though the X-ray results show the presence of some GeSe$_2$, impurity absorption is not observed because the band-gap of GeSe$_2$ is well above 2.0 eV. Once again the background is constant below the absorption edge and can be attributed to the $(1-R)^2$ term of equation 3.11. With the thickness of sample used, this corresponds to a reflectivity of the order of 53%, which again is not unreasonable for the sample surface used. The subtraction of this background from the $\xi$ data gave values and the analysis according to equation 3.2 (Figure 3.7) indicated a direct band-gap with a value of 1.58 eV.

Since the background in each case can be explained by one of these three effects and its removal gives consistent results, the curves for the remaining compounds are presented with the background suitably removed.

It was found that for all the quaternary materials investigated, the observed edge was best fitted by equation 3.2. Thus for all compounds, the observed absorption edge is of a direct nature. In the cases of CuAlGeSe$_4$, CuAlSnSe$_4$ and CuInGeSe$_4$ where the slope of the observed edge is shallow compared to the others, the transition is probably pseudodirect.
Fig. 3.8 Absorption coefficient $\alpha$ vs. $h\nu$ curves for:
(a) $\text{AgGaGeSe}_4$, (b) $\text{CuGaGeSe}_4$, (c) $\text{CuAgGeSe}_4$.
Fig. 3.9 $(a h v)^2$ vs. $h v$ curves for (a) CuGaGeSe$_4$ and (b) AgGaGeSe$_4$.
Fig. 3.10 Absorption coefficient $\alpha$ vs. $h\nu$ curves for:
(a) $\text{CuInSnSe}_4$, (b) $\text{AgInSnSe}_4$
Figures 3.8 through 3.18 show the curves of absorption coefficient $(a)$ plotted against energy as well as the $(ahv)^2$ vs. energy curves used to determine the band-gaps of the remaining quaternary compounds. The absorption coefficients are of the same magnitude in most cases, the only exceptions being curves a and b of Figure 3.10, where the values of $\alpha$ are an order of magnitude smaller.

Curves a and b of Figure 3.8 show the variation of $\alpha$ with $hv$ for polycrystalline samples of AgGaGeSe$_4$ and CuGaGeSe$_4$, respectively. The corresponding $(ahv)^2$ vs. $hv$ curves of Figure 3.9 give values of 1.845 eV and 1.855 eV for AgGaGeSe$_4$ and CuGaGeSe$_4$, respectively.

The absorption curves of Figure 3.10 show the results obtained from measurements on samples of the two quaternary compounds CuInSnSe$_4$ and AgInSnSe$_4$. As mentioned above, the $\alpha$ values in these cases are an order of magnitude smaller than the values obtained for the other compounds. It was observed that the $\epsilon$ curves for both of these compounds showed the presence of two edges. From the X-ray work it is known that both the ternary and quaternary compounds are present in both of these samples. If the quaternary band-gap is below the ternary band-gap value in energy, it should be possible to determine a value of $E_q$ for the quaternary compound. In both cases the higher energy edge was seen to occur in the vicinity of that expected for the associated ternary compound and when this edge was analysed according to equation 3.2 the appropriate ternary band-gap was obtained.
An examination of X-ray films of the samples of both compounds used in the absorption work revealed that a greater amount of the ternary compound was present in the material than was found in any of the other samples investigated. In view of this, the fact that the absorption edge of the ternary proved to be the dominant feature of the total absorption curve for these particular samples is not in the least surprising.

The curves depicted in Figure 3.10 are those for the lower energy edge and are due to the quaternary band-gap. From these data curves of \((ahv)^2\) vs. \(hv\) were obtained as in Figure 3.11 and these showed conclusively that the band-gap is direct in each case. Thus values of 0.71 eV and 0.94 eV are found for \(E_g\) for the compounds CuInSnSe\(_4\) and AgInSnSe\(_4\) respectively.

The absorption curves of Figure 3.12 are for AgAlSnSe\(_4\) and AgAlGeSe\(_4\) and the corresponding curves of \((ahv)^2\) vs. \(hv\) are shown in Figure 3.13. The values of direct band-gap determined for AgAlSnSe\(_4\) and AgAlGeSe\(_4\) are 1.87 eV and 2.02 eV respectively.

The absorption curves of CuAlSnSe\(_4\) and CuAlGeSe\(_4\) are shown in Figure 3.14 while Figure 3.15 shows the absorption curve obtained for CuInGeSe\(_4\). It is immediately obvious that the slope of all three of these curves is shallow when compared to the previous absorption curves. Such shallow curves must be attributed to either pseudodirect or indirect band-gaps. However in each case, the data were best fitted by equation 3.2 (Figures 3.15 b and c, d). Thus the principal band-gaps of these materials are of direct nature and probably correspond to a pseudodirect transition. The energy gap values determined in these cases were CuAlSnSe\(_4\) 1.90 eV, CuAlGeSe\(_4\) 2.25 eV and CuInGeSe\(_4\) 1.26 eV.
Fig. 3.11 \((ahv)^2\) vs. \(hv\) for CuInSnSe\(_4\) and AgInSnSe\(_4\).
Fig. 3.12 Absorption coefficient $a$ vs. $h\nu$ curves for:
(a) $\text{AgAlSnSe}_4$,
(b) $\text{AgAlGeSe}_4$. 
Fig. 3.13 $(a h \nu)^2$ vs. $h \nu$ curves for (a) $\text{AgAlSnSe}_4$ and (b) $\text{AgAlGeSe}_4$. 

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Fig 23.14 Absorption coefficient $\alpha$ vs. $hv$ curves for (a) CuAlSnSe$_4$ and (b) CuAlGeSe$_4$. 
Fig. 3.15  (a) Absorption coefficient $\alpha$, and 
(b) $(\alpha h\nu)^2$ vs. $h\nu$ curves for CuInGeSe$_4$. 
Fig. 3.16  $(ahv)^2$ vs. $hv$ curves for (a) CuAlS$_2$Se$_4$ and (b) CuAlGeSe$_4$. 

(a) CuAlS$_2$Se$_4$

(b) CuAlGeSe$_4$
Fig. 3.17 (a) Absorption coefficient $\alpha$, and  
(b) $(\alpha h\nu)^2$ vs. $h\nu$ curves for CuGaSiSe$_4$. 

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Fig. 3.18 (a) Absorption coefficient $\alpha$, and
(b) $(\alpha h\nu)^2$ vs. $h\nu$ curves for CuAlSiSe$_4$.
Several quaternary compounds containing silicon have also been investigated. It was found that some of these materials had the same structure as the other quaternaries discussed above. These compounds were AgGaSiSe$_4$, CuGaSiSe$_4$, and CuAlSiSe$_4$.

X-ray powder photographs of samples of the first compound revealed the presence of an amount of the associated ternary (AgGaSe$_2$), as in the case of the specimens of CuInSnS$_2$ and AgInSnSe$_4$ that were discussed above. The band-gap values discussed above indicate that the smaller the Group IV atom substituted into the ternary compound the larger the value of $E_g$ for the quaternary. Therefore, it is expected that AgGaSiSe$_4$ should have a band-gap value above that found for AgGaGeSe$_4$. The $E_g$ value for this material is 50 meV above the band-gap value of 1.80 eV quoted in the literature (7551) for AgGaSe$_2$. An analysis of the transmission measurements made on samples of AgGaSiSe$_4$ found a value of 1.80 eV for the observed edge in agreement with the value quoted for AgGaSe$_2$. Unlike the case of CuInSnS$_2$ or AgInSnSe$_4$, absorption by the associated ternary totally obscured the band edge of the quaternary.

The other two samples containing silicon did not show a significant presence of the associated ternary. Therefore only one band edge was observed in the measurements and this was assigned to the quaternary compound. For CuGaSiSe$_4$ and CuAlSiSe$_4$, the $\alpha$ vs. $hv$ and the $(\alpha hv)^2$ vs. $hv$ curves are shown together in Figures 3.17 and 3.18. The value of the lowest band-gap of CuGaSiSe$_4$ is 1.88 eV and that of CuAlSiSe$_4$ is 2.3 eV.

The results obtained for the lowest band-gap of the quaternary compounds as determined from the above analysis of the transmission...
data, are summarized in Table 3.1. Except for the case of AgAlSe₂, the value listed for the lowest band-gap of the associated ternary is taken from the literature (75S1). The value quoted in the table for AgAlSe₂ has been determined in the present work from an analysis of transmission measurements made on a polycrystalline sample. This ternary compound was produced by direct synthesis in the same manner as the quaternary compounds.

<table>
<thead>
<tr>
<th></th>
<th>Eₜ (eV)</th>
<th>E₀ (eV)</th>
<th>ΔE₀-T</th>
<th>ΔEₜ/ΔEₜSn</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgAlSe₂</td>
<td>2.54</td>
<td>2.02</td>
<td>-0.52</td>
<td>-0.77</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.87</td>
<td>-0.67</td>
<td></td>
</tr>
<tr>
<td>AgGaSe₂</td>
<td>1.80</td>
<td>1.85</td>
<td>+0.05</td>
<td>0.50</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.70</td>
<td>-0.10</td>
<td></td>
</tr>
<tr>
<td>AgInSe₂</td>
<td>1.24</td>
<td>1.58</td>
<td>-0.34</td>
<td>1.13</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.94</td>
<td>-0.30</td>
<td></td>
</tr>
<tr>
<td>CuAlSe₂</td>
<td>2.50</td>
<td>2.30</td>
<td>-0.20</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.25</td>
<td>-0.27</td>
<td>-0.45</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.90</td>
<td>-0.60</td>
<td></td>
</tr>
<tr>
<td>CuGaSe₂</td>
<td>1.71</td>
<td>1.89</td>
<td>+0.17</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.85</td>
<td>+0.14</td>
<td>0.58</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.42</td>
<td>-0.24</td>
<td></td>
</tr>
<tr>
<td>CuInSe₂</td>
<td>0.95</td>
<td>1.26</td>
<td>0.31</td>
<td>1.30</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.71</td>
<td>-0.24</td>
<td></td>
</tr>
</tbody>
</table>
As was indicated in the previous Chapter, there is a strong relationship between the quaternary germanium and tin substituted compounds and the ternaries from which they are derived. The entries in column 5 of Table 3.1 show the change in the value of the band-gap as either germanium or tin is substituted into the structure of the ternary compound. The change is considered to be negative for a reduction of the band-gap and positive if the value is increased. The negative ratio of the change in the band-gap for the compound containing germanium to that containing tin is listed in column 6 of Table 3.1.

Figure 3.19 is a plot of column 6 of Table 3.1 against the associated ternary band-gap value. It is observed that within the experimental error the points are represented by a straight line.

---

**Fig. 3.19** Variation of $-\Delta E_{Ge}/\Delta E_{Sn}$ vs. $E_T$ (ternary band-gap).
3.5 SUMMARY

The analysis of the absorption curves has shown that for all of the quaternary compounds considered the band-gap is direct probably being pseudodirect in the cases of CuAlSnSe$_4$, CuAlGeSe$_4$ and CuInGeSe$_4$. The energy gap values of the quaternaries are found to be related to those of the corresponding ternary compounds and the straight line character of the graph of $\frac{\Delta E_{Ge}}{\Delta E_{Sn}}$ vs. $E_T$ confirms that in all cases the same type of band-gap is present.

In all of the measurements a background value of $\xi$ was observed and it has been shown that this can be attributed to one or more of three different effects, viz; i) scattering by small impurity particles or by free electrons, ii) absorption due to impurities and iii) the presence of the term $(1-R)^2$ in equation 3.11. In the case of effects (ii) and (iii) analysis of relevant data gave satisfactory values for the energy gap of SnSe$_2$ impurity and for reflectance coefficients.
Chapter IV

TEMPERATURE VARIATION OF $E_f$ FOR $\text{AgGaSnSe}_4$ AND $\text{AgGaGeSe}_4$

4.1 INTRODUCTION

The behaviour of the lowest energy band-gap with temperature was investigated for two quaternary compounds, $\text{AgGaSnSe}_4$ and $\text{AgGaGeSe}_4$. The temperature was varied from the ambient room temperature of 300 K down to 4.2 K in steps of 25 K using a continuous flow helium cryostat which will be described below. Transmission measurements were made at each temperature and a value of the lowest band-gap was determined from an analysis of the data in the manner described in the previous Chapter. The resulting energy versus temperature data was fitted using a form of the equation proposed by Manoogian and Leclerc (79M1).

4.2 EXPERIMENTAL PROCEDURE

The transmission measurements were made with the specimen positioned at the centre of the experimental chamber of an OXFORD CF 204 cryostat. Apart from this difference in the positioning of the sample, the procedure described in the previous Chapter was followed.

The CF 204 system (cryostat and digital temperature controller) operates on the principle of a controlled continuous transfer of either
liquid nitrogen or helium from a storage dewar to the cooling coil situated on the exterior of the sample chamber. This chamber is vacuum insulated and thermally shielded. Thermal contact between the sample and the chamber is established by means of an exchange gas, usually helium, which is introduced into the chamber at the beginning of the experiment. In practice it was found that the temperature of the system could be regulated to within 0.1 K.

From the schematic diagram shown in Figure 4.1, it can be seen that the sample is introduced into the chamber from the top of the cryostat. Thus the sample must be mounted on a rigid support suspended from the top flange. A stainless-steel tube, soldered at one end to a threaded brass cylinder and at the other end to a stainless-steel flat positioned parallel to the tube axis was used for this purpose. The cylinder threads into a brass ring which sits on the top flange. This arrangement permits vertical adjustment of the sample position. Thus the contraction of the length of the tube as the temperature is lowered may be compensated for. A brass disc, on which a sample has been mounted in the manner described in the previous Chapter, is secured with GC Electronics Type 29 Silicone, a heat sink compound, over an aperture drilled in the stainless-steel flat. The tube is rotated such that the sample is positioned perpendicular to and at the focus of the incident monochromatic light. The diverging transmitted light, upon exiting the cryostat, was directed by a flat mirror onto a spherical mirror which refocussed the light at the detector (a DUMONT 6911 pmt).
Sample access port

Combined evacuation and safety valve

Also—inner evacuation valve

- 10 pin electrical connection

Exchange gas space

Windows

Helium inlet

Fig. 4.1 Schematic diagram of CF 204 cryostat.
4.3 ANALYSIS AND DISCUSSION

The transmission data was analysed in the same manner as described in the previous Chapter. For both materials investigated the absorption coefficients ($\alpha$) were obtained by subtracting a ramp fitted to the values of $\xi$ below the edge. The curves of $(\alpha \nu)^2$ vs. $\nu$ for various temperatures for a specimen of AgGaSnSe$_4$ are presented in Figures 4.2 and 4.3. The variation of the band-gap with temperature as determined from these curves is shown in Figure 4.4.

Similarly, Figures 4.5 and 4.6 show the $(\alpha \nu)^2$ vs. $\nu$ curves at several temperatures for a sample of AgGaGeSe$_4$. Figure 4.7 indicates the band-gap variation as a function of temperature for this material.

Table 4.1 summarizes the results obtained from the analysis of the transmission data at the temperatures indicated, for the two materials investigated. A cursory examination of this table reveals that in the case of AgGaSnSe$_4$, the band-gap variation is 86 meV over the temperature range investigated. For the same range, the band-gap for AgGaGeSe$_4$ changes by 157 meV from the room temperature value to that found at 4.2 K.

Since the transmission measurements as a function of temperature were performed in one continuous run, it was estimated that although the absolute accuracy in $E_g$ is no better than 10 meV as indicated above, the relative accuracy for $E_g$ at different temperatures is considerably better. The estimated relative accuracy is of the order of 1 meV as is shown by the small value of standard deviation obtained with the least-squares fit to the experimental points.
Fig. 4.2 $(\alpha h \nu)^2$ vs. $h \nu$ for AgGaSnSe$_4$ at $T = 300$ K, 250 K and 200 K
Fig. 4.3 $(ahv)^2$ vs. $hv$ for AgGaSnSe$_4$ at $T = 175$ K, 125 K, 100 K and 4.2 K.
Fig. 4.4 Variation of the band-gap $E_g$ with temperature $T$ for $\text{AgGaSnSe}_4$. 
Fig. 4.5 \((ahv)^2\) vs. \(hv\) for \(\text{AgGaGeSe}_4\) at \(T = 300\) K, 250 K and 175 K.
Fig. 4.6 \((a h v)^2\) vs. \(h v\) for AgGaGeSe$_4$ at 125 K and 50 K.
Fig. 4.7 Variation of the band-gap $E_g$ with temperature $T$ for AgGaGeSe$_4$. 

$E_g$ (ev)

TEMPERATURE (K)

0  100  200  300

1.85  1.90  1.95
For temperatures above 150 K, it can be seen from Figures 4.4 and 4.7 that the change in the band-gap may be approximated by a straight line. The slope of such a line, $-\text{dE/dT}$, is found to be $-4.4 \times 10^{-4}$ ev/K for AgGaSnSe$_4$ and $-8.0 \times 10^{-4}$ ev/K in the case of AgGaGeSe$_4$.

**TABLE 4.1**

VARIATION OF BAND-GAP WITH TEMPERATURE FOR AgGaSnSe$_4$ AND AgGaGeSe$_4$

<table>
<thead>
<tr>
<th>TEMPERATURE (K)</th>
<th>AgGaSnSe$_4$ (ev)</th>
<th>AgGaGeSe$_4$ (ev)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298.0</td>
<td>1.698</td>
<td>1.845</td>
</tr>
<tr>
<td>275.0</td>
<td></td>
<td>1.867</td>
</tr>
<tr>
<td>250.0</td>
<td>1.721</td>
<td>1.888</td>
</tr>
<tr>
<td>225.0</td>
<td></td>
<td>1.907</td>
</tr>
<tr>
<td>200.0</td>
<td>1.744</td>
<td>1.928</td>
</tr>
<tr>
<td>175.0</td>
<td>1.755</td>
<td>1.948</td>
</tr>
<tr>
<td>150.0</td>
<td>1.764</td>
<td>1.966</td>
</tr>
<tr>
<td>125.0</td>
<td>1.773</td>
<td>1.978</td>
</tr>
<tr>
<td>100.0</td>
<td>1.778</td>
<td>1.989</td>
</tr>
<tr>
<td>75.0</td>
<td>1.782</td>
<td>1.995</td>
</tr>
<tr>
<td>50.0</td>
<td>1.783</td>
<td>2.000</td>
</tr>
<tr>
<td>25.0</td>
<td>1.784</td>
<td>2.002</td>
</tr>
</tbody>
</table>
The variations of the band-gap with temperature of various materials have previously been described by the semi-empirical equation proposed by Varshni (67V1). This equation is generally written as:

\[ E_g = E_0 - \gamma T^2 / (\beta + T) \]  

(4.1)

where \( E_0 \), \( \gamma \) and \( \beta \) are constants to be determined, \( \beta \) being closely related to the Debye temperature. Varshni (67V1) has shown that a good fit to the experimental data is obtained for the Group IV elements, III-V and II-VI compounds and that there is a fair correlation between the value of \( \beta \) determined and the Debye temperature.

It was found that the data in Table 4.1 could not be fitted satisfactorily by this equation for any reasonable combination of \( E_0 \), \( \gamma \) and \( \beta \). Even when all three parameters were allowed to assume any value, the best fit gave a very poor value of standard deviation \( \sigma \) and the value of \( \beta \) obtained was of the order of several thousand Kelvin which is clearly inconsistent with the assumed correlation with the Debye temperature.

Varshni (80V1) has indicated that it is quite possible that this simple form of equation need not be valid for these more complicated multi-component compounds.

Manoogian and Leclerc (79M1, 79M2) have proposed an equation, again semi-empirical, to describe the variation of the band-gap with temperature which is very different from the Varshni equation. This equation has been applied to band-gap vs. temperature data for the Group IV semiconductors and several compounds, GaAs, CdS and it is found that
the expression fits very well. The Manoogian-Leclerc expression is usually written in the following form:

$$E_g = E_D (1 + AT^2) + B \left[ \theta_1 \coth(\theta_1/2T) + \theta_2 \coth(\theta_2/2T) \right]$$ \hspace{1cm} (4.2)

where $E_D$, $A$, $B$, $\theta_1$, and $\theta_2$ are parameters determined from a fit to the experimental data. The first term in equation 4.2 represents the effect of lattice dilatation. The second term represents contributions due to two vibration frequencies, namely that of the average acoustic and optical phonon modes. These frequencies are expressed in terms of absolute temperature by using the relation $10^{12}$ Hz = 47.977 K. It has been found that the values of $\theta_1$ and $\theta_2$ predicted from the fit to the data for the various materials mentioned above are indeed those of the average acoustic and optical phonon modes. The second term of equation 4.2 may for simplicity be written in terms of only one theta. Thus Manoogian and Leclerc have found that when the data is fitted by this form of their equation, the resulting value of $\theta$, within experimental error, corresponds to the average phonon frequency.

One can well appreciate that with six adjustable parameters to be determined the uncertainty in the experimental values of both the temperature or the band-gap must be small and that there must be appreciable data. Since in the present work at most only thirteen points were obtained, it was felt that a fit to two $\theta$'s was not justified. Thus the equation was rewritten so that only one $\theta$ was used which, following the arguments of Manoogian and Leclerc (79M1, 79M2), would correspond to the average phonon frequency. From the work on the Group IV semiconductors (79M2) a value of 0.7 for $s$ was found. An
analysis of the variation of the three Γ-point transitions of CuGaSe₂, reported in Chapter 6, gave a value of 0.65 for s. Hence for the work reported here a value of 2/3 was assumed. The effect of the first term is small compared to that of the second and thus an approximate value of this parameter is sufficient. Thus equation 4.2 is reduced to the following form;

$$E_g = E_0 - U_1^{2/3} - V_0 [\coth(\theta/2T) - 1]$$

(4.3)

where $E_0$ is the value of $E_g$ at $T = 0$ K and $U$, $V$ and $\theta$ are constants independent of $T$, and are determined from a fit to the experimental data.

This equation was used then to fit the data obtained for the two quaternary compounds investigated. The solid line of Figures 4.4 and 4.7 represents the fit obtained in each case. It can readily be seen that the fit is very good. The maximum deviation of any data point from the line is 0.3 meV for the AgGaSnSe₄ curve and 1.0 meV for the AgGaGeSe₄ curve. The parameters obtained for the two materials are summarized in Table 4.2.

<table>
<thead>
<tr>
<th>TABLE 4.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>MANOOGIAN FIT PARAMETERS FOR AgGaSnSe₄ and AgGaGeSe₄</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>AgGaSnSe₄</td>
</tr>
<tr>
<td>AgGaGeSe₄</td>
</tr>
</tbody>
</table>
4.4 CONCLUSION

In this chapter the values of band-gap $E_g$ have been determined as a function of temperature in the range 4.2 - 300 K for the two compounds $\text{AgGaSnSe}_4$ and $\text{AgGaGeSe}_4$. It is found that the Varshni equation will give only a poor fit to the experimental data while the Manoogian equation gives a good fit. Notwithstanding the fact that the Manoogian equation has more adjustable parameters and hence for this reason could give a better fit, it is considered that for these materials this equation is very useful in describing the temperature variation. However a fuller test of this equation is not possible at this stage since the phonon distribution curves for these materials are not known and hence no comment can be made on the accuracy of the values of $\theta$ determined in the two cases. The values for the different parameters determined for all of the various materials investigated in this work will be discussed later.
Chapter V

TEMPERATURE VARIATION OF ENERGY GAP VALUES IN CuGaSnSe$_4$

5.1 INTRODUCTION

It has been shown that the compound Cu[]GaSnSe$_4$ has a disordered defect chalcopyrite structure with the vacancies ([]) associated with the copper atoms and randomly arranged on one cation sub-lattice (Chapter 2, 81G2).

As was previously discussed in Chapter 3 the combined effects of the resulting tetragonal crystalline field and the spin-orbit interaction completely remove the triple degeneracy of the p-like valence bands. This gives rise to three valence to conduction band transitions $E_A$, $E_B$, and $E_C$.

Since it has been established that the lowest band-gap $E_A$ is a direct transition (Chapter 3, 82G1), it was deduced from the shape of the absorption curve of this material, that the lowest $\Gamma$ point conduction band has $\Gamma_6$ symmetry as opposed to $\Gamma_7$ symmetry. However, the symmetry of the highest valence band (A) was not established.

In this Chapter, the results of reflectance measurements that have been made on a single crystal sample of CuGaSnSe$_4$ to determine the polarization dependence of these $\Gamma$ point energy gaps and hence the symmetry of the three valence bands are presented. In addition the
variation of these gaps with temperature is reported. Previously in Chapter 4 it was shown that for certain quaternary compounds a very good fit to the variation of the lowest band-gap with temperature could be obtained using the equation suggested by Manogian and Leclerc (79M1, 79M2). That equation has been used in the present case also. Utilizing the curves generated by the best fits to the experimental data, values of the crystal field \( \Delta_{cf} \) and spin-orbit splitting \( \Delta_{SO} \) have been determined from the Hopfield relation (60H1). Thus the behaviour of \( \Delta_{cf} \) and \( \Delta_{SO} \) as a function of temperature has been obtained.

5.2 PREPARATION OF SAMPLES

The single crystal samples were grown by iodine vapour transport, details of the method used having been discussed in Chapter 2. Crystal plates of various sizes were produced, the sample used in the reflectance work being of approximate dimensions 3 \( \times \) 5 \( \times \) 2 mm. An analysis of a back reflection Laue X-ray photograph showed that the plane of the sample was the (112) and hence the c axis was inclined at 35.7° to this plane. This result is not surprising in that the ternary chalcopyrite single crystals also have this growth habit. The surface of the crystal was very good and no polishing was deemed necessary. Just prior to making reflectance measurements, the surface was lightly etched in warm HCl (50°C) to remove any oxides or other contaminants.
5.3 OPTICAL MEASUREMENTS AND RESULTS

The SPEX 1702 monochromator was again used to give radiation in a wavelength range of 0.95 to 7.65 µm, which would cover the required range for the various band gap energies. The light source was a tungsten filament lamp (30 watts) powered by a stabilized D.C. supply and the light was chopped at the input of the monochromator. The output from the monochromator was focused on the reflecting surface at almost normal incidence and the reflected light refocused on to a Dumont 6911 photomultiplier. The output from the photomultiplier was applied to a P.A.R. 186-A lock-in amplifier and the output of this registered by an Electronik Model 19 strip chart recorder. Thus a spectrum of the reflected sample signal as a function of wavelength was obtained at each temperature. A spectrum of the reflected signal of an aluminum surface, prepared by flash evaporation of aluminum on to a glass substrate, was obtained at room temperature. This spectrum was taken to be a measure of \( I_o \), and thus the ratio of the reflectance signals from the sample and the aluminum standard was taken as the reflectance value \( R \) of the sample.

All reflectance measurements were made with the sample or standard positioned at the centre of the same OXFORD CF 204 cryostat described in Chapter 4 and held in place on the sample holder by a small amount of 'heat sink'. The quartz windows of the cryostat were replaced by CaF\(_2\) windows to permit reflectance measurements using polarized incident light.
The use of the two polarization orientations can give useful information since, as has been indicated by Shay and Wernick (75S1) for these non-cubic materials, the three reflectance peaks are polarization dependent. Therefore an HR polarizer was placed in the beam between the monochromator and the sample so that the reflectance spectrum could be determined for different polarizations. Owing to the orientation of the sample face, spectra with polarization perpendicular to the c axis could be obtained, but it was not possible with normal incidence to obtain spectra with the polarization completely parallel to the c axis. However, spectra were taken with the polarization having a maximum component parallel to c (i.e. at \(75.7^\circ\) to the c axis).

In the present work, while the wavelength of the peaks corresponding to the transitions (\(E_B\) and \(E_C\)) from the second and third valence bands could be determined satisfactorily from the curve using unpolarized light, it was not possible to obtain \(E_A\), the transition from the highest valence band, with any reasonable accuracy as is shown by the curve in Figure 5.1. As indicated in this diagram, the shoulder on the curve below 1.5 eV could be \(E_A\). Certainly \(E_B\) and \(E_C\) are much more pronounced than this and can be determined more accurately. Figures 5.2 and 5.3 show the reflectance curves for room temperature (295 K) and 4 K with the two polarization arrangements respectively. In both figures it is obvious that the transitions \(E_B\) and \(E_C\) are more clearly defined than in Figure 5.1 and thus the uncertainty in the positions of the gaps is somewhat reduced.
Fig. 5.1 CuGaSnSe$_4$ room temperature variation of reflectance $R$ with photon energy $h\nu$ for unpolarized light. A, B and C indicate $\Gamma$ point valence band to conduction band transitions.
Fig. 5.2 Room temperature variation of reflectance $R$ with photon energy $h\nu$ for light polarized parallel and perpendicular to the $c$ axis of CuGaSnSe$_4$. B and C indicate $\Gamma$ point valence band to conduction band transitions.
Fig. 5.3 Variation of reflectance $R$ with photon energy $h\nu$ at 4.2 K for light polarized parallel and perpendicular to the c axis of CuGaSnSe$_4$. B and C indicate $\Gamma$ point valence band to conduction band transitions.
To determine the value of $E_A$, graphs of $\Delta R = R_+ - R_-$ were plotted as a function of $h\nu$ and the curves, corresponding to temperatures of 295 K, 200 K and 4.2 K, are shown in Figure 5.4. As one can see, the transition becomes better defined as the temperature is reduced and in all cases it was possible to determine $E_A$ with the same degree of certainty as for the other two transitions.

The resulting variations of $E_A$, $E_B$ and $E_C$ with temperature are shown in Figure 5.5, the error bars indicating the error which it was estimated could occur in the determination of the energy peak, due to the broadness of the peak.

### 5.4 ANALYSIS AND DISCUSSION

As was found in Chapter 4, a good fit to the experimental data could be obtained using the equation proposed by Manoogian and Leclerc (79M1, 79M2) (see equation 4.3). The parameter $s$ was taken to be $2/3$ for the same reasons indicated previously and, as before, the remaining constants determined by a least squares fit, subject however to one further constraint. Manoogian and Leclerc indicated from the values of $\theta$ obtained in their experimental analysis that $k_B \theta$ agrees very well with the known value of the mean phonon energy for the material concerned and so in the present analysis, the condition has been imposed that $\theta$ has the same value for all three curves, i.e., the best fit to the three curves has been obtained with seven parameters viz, $\theta$, $U_A$, $U_B$, $U_C$, $V_A$, $V_B$, $V_C$. Using the condition of minimum mean square deviation, good fits were obtained to all three curves as is shown by the full lines in
Fig. 5.4 Variation of the difference of perpendicular and parallel reflectance $R_\perp - R_\parallel$ with photon energy $h\nu$ for CuGaSnSe$_4$ at the indicated temperatures.
Fig. 5.5 Variation of Γ point band-gaps $E_A$, $E_B$, and $E_C$ of CuGaSnSe$_4$ with temperature. The solid lines are the fitted curves.
Figure 5.5. The values of the parameters determined by the fit to the data of each curve are listed in Table 5.1.

TABLE 5.1 MANOOGIAN FIT PARAMETERS FOR CuGaSnSe$_4$

<table>
<thead>
<tr>
<th></th>
<th>( E_A ) (eV)</th>
<th>( E_{0A} ) (x ( 10^{-4} ) eV/K)</th>
<th>( V_A ) (x ( 10^{-5} ) eV/K$^{2/3}$)</th>
<th>( U_A )</th>
<th>( E_B ) (eV)</th>
<th>( E_{0B} ) (x ( 10^{-4} ) eV/K)</th>
<th>( V_B ) (x ( 10^{-5} ) eV/K$^{2/3}$)</th>
<th>( U_B )</th>
<th>( E_C ) (eV)</th>
<th>( E_{0C} ) (x ( 10^{-4} ) eV/K)</th>
<th>( V_C ) (x ( 10^{-5} ) eV/K$^{2/3}$)</th>
<th>( U_C )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \theta )</td>
<td>459 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

As was indicated in Chapter 4 for the other quaternary compounds, the value of \( \theta \) listed above is the one given by the condition of minimum mean square deviation of the fit from the experimental points. However, within the range of the error bars indicated in Figure 5.5, a considerable range of \( \theta \) can be used and curves obtained which satisfy the experimental values. The present parameters may be compared with the parameters determined using the same criterion from the data for the CuGa(Se$_{1-x}$S$_x$)$_2$ alloys, which will be presented in Chapter 6. It will be seen that the values of \( \theta \), in that case, lie in the range 550-800 K. If \( k_B \theta \) is the mean phonon energy, then \( \theta \) can be looked upon as a measure of the average bond strength in the material, so that a lower value of \( \theta \) in CuGaSnSe$_4$ is not unreasonable since it is a defect structure with, on the average, one cation site in four vacant.

As was mentioned previously, the third term in equation 4.3 is the dynamic contribution due to phonon interaction. The values of the \( V \) parameter listed in Table 5.1 are roughly the same size as those found for AgGaSnSe$_4$ and AgGaGeSe$_4$ (Chapter 4) and the CuGa(Se$_{1-x}$S$_x$)$_2$ alloys.
(Chapter 6). As in the latter case, the value of V is found to increase somewhat as one proceeds from A to B to C. Assuming that the value of V is a measure of the effect of the phonon interaction with the bands concerned, this variation in V would seem to indicate that, for a given material, the lower the valence band in energy the larger the effect of the phonon interaction.

Again, as has been shown for the compounds in Chapter 4 and as will be seen with the alloys in Chapter 6, the $V^S$ term, which is the static or dilatation term, is very much smaller than the dynamic term. Thus it is felt that this term can not be determined with any great accuracy using the present data and hence no comment can be made here.

From the values of $E_A$, $E_B$ and $E_C$ as fitted above, values of spin-orbit splitting $\Delta_{so}$ and crystal field splitting $\Delta_{cf}$ can be calculated using Hopfield's quasi-cubic model (60H1).

The quasi-cubic model was originally proposed by Hopfield to explain the observed exciton fine structure in ZnO and CdS. The model suggests that the observed splitting of the valence band is a result of two contributions. The first is a small amount of spin-orbit coupling ($\Delta_{so}$) which mixes the $P$ valence bands. The second, arising from a strain applied along the $z$ axis of the crystal, is a second order energy shift of the $P_z$ states ($\Delta_{cf}$). The eigenvalues of the resulting Hamiltonian, thus yield the Hopfield relation:

$$ E_{1,2} = -\frac{1}{2}(\Delta_{so} + \Delta_{cf}) + \frac{i}{3}[(\Delta_{so} + \Delta_{cf})^2 - 8/3 \Delta_{so}\Delta_{cf}]^{1/2} $$

(5.1)
where the sign convention differs from the original paper in that the positive energy direction is now the same for both the conduction and valence bands. For materials having wurtzite structure $E_1$ and $E_2$ are the energies of the $\Gamma_7$ valence bands relative to the $\Gamma_9$ valence band. In the case of Cds excellent agreement was found between the predictions of the model and experimental fact. However the model was only qualitatively successful in the case of ZnO.

Rowe and Shay (71R1) extended the quasi-cubic model to ternary chalcopyrite crystals. The authors noted that the strain Hamiltonian is formally the same for both the trigonal distortion appropriate for wurtzite and the tetragonal distortion appropriate to chalcopyrite. The model quantitatively explained the observed polarization dependences for both ZnSiAs$_2$ and CdSn$_2$.

Since CuGaSnSe$_4$ also has a chalcopyrite structure, Hopfield's relation is applicable and has therefore been used here. In this case, $E_1$ and $E_2$ of the above equation are the energies of the $\Gamma_7$ valence bands relative to the $\Gamma_6$ valence bands.

Therefore, before the Hopfield relation can be applied, it is necessary to determine the valence band symmetry arrangement.

Figure 5.6a and 6b show two possible valence band orderings. In both diagrams the tetragonal crystalline field splits the $\Gamma_{15}$ band into two valence bands, a singlet $\Gamma_4$ and a doublet $\Gamma_5$. From group theory it can be shown that the $\Gamma_4-\Gamma_1$ transition is allowed for light polarized parallel to the $c$ axis and that the $\Gamma_5-\Gamma_1$ transition is seen only for light polarized perpendicular to the $c$ axis.
Fig. 5.6 Two possible \( \Gamma \) point valence band orderings for CuGaSe\(_2\):
(a) \( \Gamma_7', \Gamma_6', \Gamma_7' \) after interaction of spin-orbit and negative crystal field splittings; (b) \( \Gamma_6', \Gamma_7', \Gamma_7' \) after interaction of spin-orbit and positive crystal field splittings.
In Figure 5.6a, the $\Gamma_4$ band lies above the $\Gamma_5$ valence band and by convention (70S1) the crystal field is negative. The spin-orbit interaction lifts the degeneracy of the $\Gamma_5$ band yielding two valence bands of $\Gamma_6$ and $\Gamma_7$ symmetry as depicted. The selection rules mentioned above are now somewhat relaxed in that $E_A$ is weakly visible for perpendicular polarization and $E_C$ for parallel polarization. With this valence band arrangement, $\Gamma_7', \Gamma_6', \Gamma_7$, the theoretical values of the relative intensities of the transitions should be as follows: for $\perp$ polarization $E_A$ weak and $E_B$ and $E_C$ strong, for $\parallel$ polarization $E_C$ weak and $E_A$ strong with no $E_B$.

With a positive crystal field, the $\Gamma_5$ valence band lies above the $\Gamma_4$ valence band as depicted in Figure 5.6b. The spin-orbit interaction yields a valence band ordering of $\Gamma_6', \Gamma_7$, and $\Gamma_7'$. As before, the selection rules are relaxed and the theoretical relative intensities will be as follows: for $\perp$ polarization $E_C$ weak, $E_A$ and $E_B$ strong, for $\parallel$ polarization $E_B$ weak, $E_C$ strong and no $E_A$.

An examination of the experimental values in Figures 5.2 and 5.3 reveals that while $E_B$ and $E_C$ are seen for both the $\parallel$ and $\perp$ polarizations, $E_A$ is observed only for the $\perp$ case and even then is weak compared with $E_B$ and $E_C$. Since the background values in Figures 5.2 and 5.3 show a peak close to the value corresponding to $E_B$, it is not possible to comment on the relative intensities of $E_B$ and $E_C$ for the two different polarizations.

Comparing these values with the theoretical predictions given above, it is seen that the $\Gamma_6', \Gamma_7'$ case gives a closer resemblance to the experimental data but even in this case the agreement is not
excellent. If other possible valence band arrangements are postulated, no better agreement is obtained.

One important experimental fact that must be taken into account is that the parallel configuration is only nominal and in this case some 33% of the incident intensity is in fact polarized \( \perp \) to the \( c \) axis. Thus all values for the nominal parallel case will include some \( \perp \) contribution. When this condition is included in the considerations of the data, it is found that it is not possible to make any definite conclusion about the band ordering; i.e. while \( \Gamma_6 \Gamma_7 \) appears more probable the \( \Gamma_7 \Gamma_6 \) arrangement cannot be ruled out. Since the chalcopyrite ternary compounds are known to show the \( \Gamma_7 \Gamma_6 \Gamma_7 \) ordering of valence bands (75Sl) and since the quaternaries have the same chalcopyrite structure (80H1) it was felt that the \( \Gamma_7 \Gamma_6 \Gamma_7 \) case could not, in light of the above discussion, be ignored. Hence below, the analysis is made for both cases and both sets of results are considered.

The first case is of a valence band ordering of \( \Gamma_6 \Gamma_7 \Gamma_7 \). This ordering, suggested by the experimental results, would mean that the \( E_A \) peak corresponds to a transition from a \( \Gamma_6 \) valence band to a \( \Gamma_6 \) conduction band and that \( E_B \) and \( E_C \) correspond to transitions from valence bands of \( \Gamma_7 \) symmetry to the same conduction band. Analysis on this basis (case 677) gives the values of \( \Delta_{SO} \) and \( \Delta_{CF} \) shown in Figure 5.7. It is to be noted that \( \Delta_{SO} \) and \( \Delta_{CF} \) are positive and that the magnitude of each increases as the temperature is reduced.
Fig. 5.7 Variation of spin orbit splitting $\Delta_{so}$ and crystal field splitting $\Delta_{cf}$ as a function of temperature: points calculated from the fitted curves in Fig. 5.5 using the $\Gamma_6\Gamma_7$ valence band ordering.
Fig. 5.8 Variation of spin orbit splitting $\Delta_{so}$ and crystal field splitting $\Delta_{cf}$ as a function of temperature: points calculated from the fitted curves in Fig. 5.5 using the $\Gamma_7\Gamma_6\Gamma_7$ valence band ordering.
The second possibility is of a valence band ordering of \( \Gamma_7 \Gamma_6 \Gamma_7 \). The resulting values of \( \Delta_{SO} \) and \( \Delta_{cf} \) calculated from the present fitted data in this case (767) are shown in Figure 5.8. It is to be noted that this gives \( \Delta_{SO} \) as positive and \( \Delta_{cf} \) as negative and that the magnitudes of both splittings increase as the temperature is reduced.

In both cases, the variation of the \( \Delta_{SO} \) and \( \Delta_{cf} \) values with temperature can be attributed to a change in the contribution of d orbitals to the valence band form (75S1, 79Y1). Thus as has been indicated previously (75S1, 79Y1), if the fractional p character in the valence band is \( \phi \), and hence \( (1 - \phi) \) the fractional d character, the values of \( \Delta_{SO} \) and \( \Delta_{cf} \) can be written as

\[
\Delta_{SO} = \phi \Delta_{SO}^p + (1 - \phi) \Delta_{SO}^d \quad (5.2)
\]

\[
\Delta_{cf} = \phi \Delta_{cf}^p + (1 - \phi) \Delta_{cf}^d \quad (5.3)
\]

where \( \Delta_{SO}^p \) and \( \Delta_{SO}^d \) are the spin-orbit splitting due to the p and d levels respectively and \( \Delta_{cf}^p \) and \( \Delta_{cf}^d \) are the corresponding crystal field splittings which may be expressed as

\[
\Delta_{cf}^p = \frac{3}{2} b_p (2 - \frac{c}{a}) \quad (5.4)
\]

\[
\Delta_{cf}^d = \frac{3}{2} b_d (2 - \frac{c}{a}) \quad (5.5)
\]

where \( \frac{c}{a} \) is the crystallographic axial ratio of the compound and \( b_p \) and \( b_d \) are the deformation potentials associated with the p and d orbitals respectively.
To apply these equations to the present results, it is assumed that $\Delta^{P}_{SO}$, $\Delta^{d}_{SO}$, $b_p$ and $b_d$ are temperature independent and that the variation of $\Delta^{P}_{SO}$ and $\Delta_{CF}$ with temperature is due to variations in $\phi$ and $\frac{C}{a}$. It has been assumed that the variation of $\frac{C}{a}$ may be taken as linear with temperature, the value at 300 K being known to be 1.058 (80H1). Thus it is convenient to write that

$$
\frac{3}{2} \left( 2 - \frac{C}{a} \right) = 0.963 + \epsilon(T - 300)
$$

(5.6)

where $\epsilon$ is a temperature coefficient not as yet determined crystallographically but which may be treated as an adjustable parameter in the fit to $\Delta^{P}_{SO}$ and $\Delta_{CF}$. Substituting into equation 5.3 one finds

$$
\Delta_{CF} = [\phi b_p + (1 - \phi) b_d] \left[ 0.963 + \epsilon(T - 300) \right]
$$

(5.7)

In order to carry out any analysis based on equations 5.2-5.7, it is necessary to assume values for some of the various parameters. Following the analysis of Braunstein and Kane (62B1) and that of Poplavnoi and Polyakov (71P1) it will be assumed that

$$
\Delta^{P}_{SO} = G \left( \frac{1}{32} \Delta^{P}_{Cu} + \frac{3}{32} \Delta^{P}_{Ca} + \frac{1}{8} \Delta^{P}_{Sn} + \frac{3}{4} \Delta^{P}_{Se} \right)
$$

(5.8)

where $\Delta^{P}_{Cu}$, etc. are atomic p spin-orbit splittings of the elements and $G_p$ is an enhancement factor for the solid. For both zinc-blende (62B1, 69C1) and ternary chalcopyrite structures (71P1), $G_p$ has been taken as $\frac{29}{20}$ and so that value will be used here. Previous workers (62B1, 71P1, 63Y1) give the values of the atomic splittings as

$$
\Delta^{P}_{Cu} = 0.031 \text{ eV} \quad \Delta^{P}_{Ca} = 0.102 \text{ eV}
$$

$$
\Delta^{P}_{Sn} = 0.458 \text{ eV} \quad \Delta^{P}_{Se} = 0.370 \text{ eV}
$$
Hence from equation 5.8, for CuGaSnSe₄, \[ \Delta_{SO}^{P} = 0.50 \text{ eV.} \]

It is assumed that the d contribution in \[ \Delta_{SO}^{d} \] is due to the copper atoms only, the other d levels being much too deep (63Y1) to contribute. Thus \[ \Delta_{SO}^{d} = G_{d}(\Delta_{CU}^{d}). \] For copper in a cubic environment \[ \Delta_{CU}^{d} = \frac{3}{2} \varepsilon_{d} \] (67S1), where \( \varepsilon_{d} \) is the Condon-Shortley one-electron parameter (62B1). For copper \( \varepsilon_{d} = -0.101 \) eV, i.e. \[ \Delta_{CU}^{d} = -0.152 \text{ eV} \ (69C1). \] Under these conditions the d level triplet acts like the p levels (67S1) and so it will be assumed that \( G_{d} = \frac{29}{20} \) also. Thus \[ \Delta_{SO}^{d} = -0.22 \text{ eV.} \] With these values of \[ \Delta_{SO}^{P} \text{ and } \Delta_{SO}^{d} \] and the experimental values of \[ \Delta_{SO} \text{, values of } \phi \text{ as a function of temperature can be determined from equation 5.2.} \]

In equation 5.7, there still remain three parameters to be determined. However, it has been shown for the ternary chalcopyrites that \( b_{p} \) may be taken as \(-1.0 \) eV (75S1). This magnitude will therefore be used in the present analysis. However, because of the different sign for \( \Delta_{cf} \) in the two cases, it is necessary to assume that \( b_{p} = +1.0 \) eV for the 677 case and \( b_{p} = -1.0 \) eV for the 767 case.

With these parameter values, equation 5.7 has been fitted by a least squares analysis to give values for \( b_{d} \) and \( \varepsilon \) from the experimental values of \( \Delta_{cf} \). The results thus obtained are summarized in Table 5.2 below.
TABLE 5.2

677 case

\[ \Delta_{SO}^p = 0.50 \text{ eV} \quad \Delta_{SO}^d = -0.22 \text{ eV} \quad b_p = +1.0 \text{ eV} \]

\[ b_d = +2.02 \text{ eV} \quad \epsilon = -8.00 \times 10^{-5} / \text{K} \]

and \( \phi \) varies from 0.63 to 0.62 with temperature.

767 case

\[ \Delta_{SO}^p = 0.50 \text{ eV} \quad \Delta_{SO}^d = -0.22 \text{ eV} \quad b_p = -1.0 \text{ eV} \]

\[ b_d = -1.26 \text{ eV} \quad \epsilon = -6.60 \times 10^{-5} / \text{K} \]

and \( \phi \) varies from 0.65 to 0.625 with temperature.

In these two sets of results the values of \( \phi \) are practically the same and very similar to the values of \( \phi \) quoted for the various ternary I-III-VI\(_2\) chalcopyrite compounds (75SI). Yamamoto et al. (79Y1) obtained a value of \( \epsilon = +2.80 \times 10^{-5} / \text{K} \) for CuGaS\(_2\) and found that a value of \( b_d = -4.9 \) was required to explain their data. In a further analysis of reflectance measurements on CuGaS\(_2\), Goodchild et al. (81G1) showed that their data required that \(-2.2 \text{ eV} > b_p > -\infty\). Thus by comparison with the CuGaS\(_2\) results, the value of \(|b_d| = 2.0 \text{ eV}\) in the 677 case appears more probable. However, the value of \( \epsilon \) in this case is large, indicating a variation of the \( \frac{c}{a} \) value of \( \frac{c}{a} = 1.958 + 5.9 \times 10^{-5} (T - 300) \). No experimental value of the temperature coefficient is available at the present time.
5.5 CONCLUSIONS

The results show that the behaviour of this quaternary defect chalcopyrite compound is in general form similar to that of the ternary chalcopyrite compound to which it is analogous. The temperature variation of the three Γ point band gaps can be fitted well by the equation of Manoogian and Leclerc, but as will be seen in the case of the CuGa(Se$_{1-x}$S$_x$)$_2$ alloys, the range of temperature used (θ = 300 K) is not sufficient to allow an accurate determination of the parameter θ. However, the θ value is lower than those of the alloys, demonstrating the softening of the structure due to the presence of lattice vacancies.

The variation with temperature of the values of spin-orbit splitting and 'crystal field splitting from the measured data can be explained by admixture of d orbitals with the normal p orbitals forming the valence bands of the compound.

An analysis has been carried out for two different orderings of the valence bands. Values for the spin-orbit splittings of the p and d orbitals have been calculated from atomic values and hence values determined for the deformation potential associated with the d orbitals of copper and for the temperature coefficient of the $\frac{C}{a}$ ratio of the crystal. These values may be compared with the corresponding values quoted for the ternary chalcopyrite compound CuGaS$_2$. The values of the deformation potential for the copper d orbitals seem to give some support for the proposed $\Gamma_{6'7'}^7$ valence band ordering.
Chapter VI

TEMPERATURE VARIATION OF ENERGY GAP VALUES IN CuGa(Se$_{1-x}$S$_x$)$_2$

6.1 INTRODUCTION

It is well established that in the alloy system CuGa(Se$_{1-x}$S$_x$)$_2$ single phase solid solution occurs at all values of x and that the lattice parameter values of the chalcopyrite structure vary linearly with x (75S1). Measurements of the energy gap values have been made for the compounds by various techniques (75S1, 75S2), but no systematic investigation of the temperature variation of the energy gaps has been made.

Reflectance measurements on single crystal samples have a clear advantage over absorption since in the former case all three valence-conduction band transitions at the $\Gamma$ point $E_A$, $E_B$ and $E_C$ may be investigated while in the latter case only $E_A$ can be observed. Here, reflectance measurements have been used to determine energy gap values in the temperature range from liquid helium to room temperature.

The application of the Manoogian and Leclerc equation to the temperature variation of energy gaps has been shown in previous chapters to be quite successful in describing the variation of a band-gap with temperature. This equation will be used here also.
6.2 PREPARATION OF SAMPLES

For each sample, the appropriate amounts of the required elements were melted together in an evacuated quartz capsule, a rocking furnace being used to give good mixing. The charge was heated slowly (approximately 20°/hour) and after being held in a molten state was slowly cooled. In all cases except x = 0.25 the resulting material was then resealed and crystals grown by the iodine vapour transport method described in Chapter 2. The growth of the single crystal samples was undertaken by Jesus Gonzales at Universidad de Los Andes in Venezuela in collaboration with this group. The source material was sealed in a quartz tube of diameter 16 mm and length 120 mm with approximately 10 mg/cm of iodine added as the transport medium. The tube was placed in a horizontal furnace with a temperature gradient producing a hot zone of 750°C and a cold zone of 700°C. The time of growth for the crystals was of the order of 7 days and the resulting crystals had good reflecting surfaces and were of typical dimensions 10 x 4 x 1 mm.

Small pieces of the final crystals were powdered and lattice parameter data obtained from Debye-Scherrer X-ray powder photographs. These data showed that the required composition values were obtained to within ±0.01 in x.

The optical specimens (except for x = 0.25) were the as-grown crystals which were carefully cleaned in boiling acetone, methanol...
vapour and then lightly etched in warm HCl \((50^\circ C)\). The sample of composition \(x = 0.25\) was cut and one surface carefully lapped with alumina powder down to \(0.3\ \mu m\) size to give a good reflecting surface. This was then treated in the same manner as the single crystal samples above.

6.3 **OPTICAL MEASUREMENTS AND RESULTS**

Essentially, the same set up as described in the previous Chapter was used to obtain the reflectance data. The only difference was the use of the EMI 6255S pmt or of an EG&G SFD 160 flat response silicon diode rather than the Dumont 6911 pmt as the detector in the visible wavelength region for some of the measurements. As before, the ratio of the reflectance signals from the sample and an aluminum standard was taken as the reflectance value \(R\) of the sample. The variation of \(R\) with photon energy \(h\) at certain temperatures for the case of \(\text{CuGaSe}_2\) is shown in Figure 6.1. Two peaks are observed corresponding to the transitions from the higher valence bands \((A \& B)\) to the conduction band. The estimated accuracy in the determination of each peak was \(\pm 2\) meV. The transition from the lowest valence band \((C)\) could not be detected with any accuracy and has not been considered further here.
Fig. 6.1 Variation of reflectance $R$ with photon energy $h\nu$ at various temperatures for CuGaSe$_2$. 
Fig. 6.2 Variation of band gaps $E_A$ and $E_B$ with temperature $T$ for CuGaSe$_2$. 
Fig. 6.3  Variation of band-gaps $E_A$ and $E_B$ with temperature $T$ for $\text{CuGe}(\text{Se}_{0.75}\text{S}_{0.25})_2$. 
Fig. 6.4  Variation of band-gaps $E_A$ and $E_B$ with temperature $T$ for
$\text{CuGa(Se}_{0.5}\text{S}_{0.5})_2$. 

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Fig. 6.5 Variation of band-gaps $E_A$ and $E_B$ with temperature $T$ for CuGa(Se$_{0.25}$S$_{0.75}$)$_2$. 
Fig. 6.6 Variation of band-gaps $E_A$ and $E_B$ with temperature $T$ for CuGaS$_2$. 
The spectra obtained for the alloys and for CuGaS$_2$ showed a little more noise than for CuGaSe$_2$. The estimated error in the position of both peaks in these cases was 4 meV. In the case of the polycrystalline sample of composition $x = 0.25$, the spectrum was appreciably noisier and though the error in the position of the A peak was the same, the position of the higher energy B peaks could not be determined with any great accuracy. The estimated error in this case was 10 meV.

For each value of $x$, the energy value of each peak was plotted as a function of temperature and the results, at increments of $x = 0.25$, are shown in Figures 6.2 through 6.6.

6.4 ANALYSIS AND DISCUSSION

As discussed before, a good fit to the temperature variation data of the chalcopyrite materials could not be obtained using the Varshni equation (equation 4.1). Although the Debye temperatures of CuGaSe$_2$ and CuGaS$_2$ are estimated to be 239 K and 320 K respectively (7601), to obtain any fit at all it was found, as for the quaternary compounds, that $\theta$ needed to be greater than 2000 K so that the temperature term in equation 4.1 effectively takes an $T^2$ form. Even with these values, the fit was poor and values fitted to the intermediate temperature range used here would clearly show deviation from experiment at higher temperatures. Hence a fit to the experimental data was attempted using the Manoogian and Leclerc expression in the same form as used in the previous Chapters,
\[ E = E_0 - UT^S + V\theta (\coth \theta / 2T - 1) \quad (6.1) \]

where \( s, U, V \) and \( \theta \) are constant and independent of \( T \).

In the present analysis, \( s \) was first treated as an unknown parameter and determined, together with the other parameters, by a least squares fit to the CuGaSe\(_2\) data and a value of \( s = 0.65 \) was obtained. The CuGaSe\(_2\) data were used as they were considered the best experimental values of the present set. However, it was found in the analysis of the present results that the \( UT^s \) term is considerably smaller than the second term on the RHS of equation 6.1, so that the fit to the experimental data was not very dependent on the exact value of \( s \) used. Hence to simplify the fitting process, it was assumed in the analysis of all curves that \( s \) had a value of 2/3.

As has been previously indicated, \( k_B\theta \) is the mean phonon energy for the material and as in the previous Chapter, the condition has been imposed that \( \theta \) has the same value for both the \( E_A \) and \( E_B \) curves. Thus the best fit to the two curves has been obtained with five variables, viz. \( \theta, U_A, U_B, V_A, V_B \), the normal criterion of minimum mean square deviation of the experimental points being used. Under these conditions, good fits were obtained to all curves both for \( E_A \) and \( E_B \) as can be seen in Figures 6.2 to 6.6 where the full line represents the curve fitted in this manner.
Fig. 6.7  Variation of the value of $\theta$ determined from best fit to $E$ vs. $T$ curves with composition $x$ of CuGa(Se$_{1-x}$S$_x$)$_2$.  

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Figure 6.7 shows the value of $\Theta$ determined in this way as a function of $x$, the values lying in the range 520 - 820 K and the variation being obviously non-linear. In an attempt to find a relation between $\Theta$ and $x$, the next approximation of a parabolic form was considered. Excluding the value at $x = 0.25$, the points gave a very good fit to an equation of the form

$$\Theta = 588 - 163x + 391x^2$$

(6.2)
as is shown by the full line in Figure 6.7. Since the sample with $x = 0.25$ was the only one which was not single crystal, it was considered likely that any discrepancy between the various samples could probably be attributed to problems with this sample.

However, if the proposals of Manoogian and Léclerc apply in the case of these materials, these values of $\Theta$ should give mean phonon frequencies for the alloys. The values of the various optical phonon frequencies for these alloys has been given by Bodnar et al. (77B1). It is found that the values of $\Theta$ determined above are all higher than the values to be expected from the phonon frequencies. In order to check this disagreement further, an attempt has been made to calculate mean phonon energies and hence $\Theta$ values from the data of Bodnar et al. The phonons divide into two sections, one being CuGaSe$_2$-like and the other CuGaS$_2$-like, as has been found to be the case with III-V alloys also (70L1). Since Bodnar et al. do not give intensity values, for each alloy in the CuGa(Se$_{1-x}$S$_x$)$_2$ system, a weighted mean has been used giving the CuGaSe$_2$-like phonons a weight of $1 - x$ and the CuGaS$_2$-like phonons a weight of $x$. The resulting values of $\Theta$ obtained in this way are shown in Figure 6.8 and are fitted to the equation
\[ \theta = 301 + 97x + 50x \]  \hfill (6.3)

(Fig. 6.8) Variation of the value of \( \theta \) determined from photon spectra with composition \( x \) of CuGa(Se\(_{1-x}\)S\(_x\))\(_2\).

With these values of \( \theta \), the experimental values of \( E_A \) and \( E_B \) vs. \( T \) have been fitted using the \( U \) and \( V \) parameters as adjustable and the resulting fitted curves are shown as the dashed lines in Figures 6.2 through 6.6. While these curves do not fit quite as well as the best-fitted curves given previously, the minimum mean square deviation being 2 to 3 times greater in this case, it is seen that the fit can still be considered to be well within the limits of experimental error quoted above for the various samples investigated.
It is apparent that although a good fit to the experimental data can be obtained with the equation of Manoogian and Leclerc, an accurate determination of the value of $\theta$ requires measurements at many more temperatures—particularly in an extended range of temperature—or very accurate determination of the values of $E_A$ and $E_B$.

In fitting the experimental data to equation 6.1, the values obtained for $V$, and to some extent those for $U$, depend appreciably on the value of $\theta$ used. But which ever of the two fitted results from above is used, the values determined for the $V$ and $U$ parameters show similar general form. In all cases, the values of $U$ determined are very small, the values lying in the range of experimental fluctuations and so no effective comment can be made on these. However, the values of $V$ are larger and can be determined with reasonable relative accuracy. In each case, both the A and B curves, it is found that the values of $V$ can be fairly well fitted to a parabolic form of $V = a_V + b_V x + c_V x^2$ and the values of $V$ show a minimum at about $x = 0.4$. As an example, the values of $V$ using the phonon 0 curve are shown in Figure 6.9 for both $E_A$ and $E_B$ values. The lines fitted to these points are given by

\[ V_A = 1.66 - 1.74x + 2.26x^2 \]
\[ V_B = 1.82 - 1.57x + 2.01x^2 \]
Thus the value of $V_B$ is somewhat larger than that of $V_A$, which is found to be the case also for the results on the quaternary chalcopyrite type compound CuGaSnSe$_4$ (82L1) discussed in Chapter 5. However, the variation of the two curves with alloying is very similar, as indicated by the similarity of the values of the bowing parameter $c_V$. If the values of $\theta$ determined from the best fit condition are used, different values of $V$ are of course obtained, but the variation with $x$ is of a very similar form to that mentioned above i.e.
\[ V_A = 2.25 - 3.76x + 5.02x^2 \times 10^{-4}\text{eV/K} \] (6.6)

\[ V_B = 2.55 - 3.96x + 5.17x^2 \]

It has been indicated by Manoogian and Leclerc that the \( V \) term in equation 6.1 represents dynamic or phonon interaction effects. Thus it is seen that the effects of phonon interaction are very similar for the two valence bands investigated here, as are also the effects of alloying.

It is observed that the two methods of fitting described above yield very similar values both for \( E_A \) and for \( E_B \) at absolute zero, i.e. \( E_{0A} \) and \( E_{0B} \). Figure 6.10 shows the variation with composition of \( E_{0A} \) and \( E_{0B} \). It is found that within the limits of experimental error both values vary linearly with \( x \), the values from least squares fitting being

\[ E_{0A} = 1.729 + 0.783x \text{ eV} \] (6.7)

\[ E_{0B} = 1.804 + 0.819x \]

Since the third transition \( E_C \) could not be observed, it is not possible to calculate values of spin-orbit \( \Delta_{SO} \) and crystal field \( \Delta_{CF} \) splittings for the alloys. However, if a linear variation of both \( \Delta_{SO} \) and \( \Delta_{CF} \) between the quoted room temperature values for the compounds (77Y1) is assumed, the predicted room temperature values of \( E_A \) and \( E_B \) agree with the values determined experimentally to within 4%. This assumption is reasonable since as, mentioned above, the band-gap variation of both \( E_A \) and \( E_B \) with composition is linear.
Fig. 6.10 Variation of zero temperature values $E_{0A}$ and $E_{0B}$ with composition $x$ of CuGa(Se$_{1-x}$S$_x$)$_2$.

In the special case of CuGaS$_2$, the spin-orbit splitting is given as zero (75S1) and hence the difference $E_A - E_B$ gives the value of $\Delta_{cf}$ in this case. These values are found to vary smoothly between 122 meV at 0 K and 177 meV at 300 K. This decrease in $\Delta_{cf}$ with temperature has been attributed (75S1) to the variation with temperature of the contribution of d orbitals to the valence band form. Thus as previously...
stated in Chapter 5, if the fraction of $p$ character in the valence band is $\phi$, and hence that of $d$ character $(1 - \phi)$, as indicted by Yamamoto et al. (77Y1, 79Y1), the crystal field splitting should be given by

$$\Delta_{cf} = \phi \Delta^p_{cf} + (1 - \phi) \Delta^d_{cf}$$  \hspace{1cm} (6.8)$$

with

$$\Delta^p_{cf} = \frac{3}{2} b_p \left(2 - \frac{C}{a}\right)$$  \hspace{1cm} (6.9)$$

and

$$\Delta^d_{cf} = \frac{3}{2} b_d \left(2 - \frac{C}{a}\right)$$  \hspace{1cm} (6.10)$$

where $\frac{C}{a}$ is the crystallographic axial ratio for CuGaS$_2$ and $b_p$ and $b_d$ are the deformation potentials of the $p$ and $d$ orbitals respectively.

Yamamoto et al. determined $\frac{C}{a}$ as a function of temperature in this case and their results can be expressed as;

$$\frac{3}{2} \left(2 - \frac{C}{a}\right) = 0.0495 + 2.88 \times 10^{-5} T.$$  \hspace{1cm} (6.11)$$

For the II-IV-V$_2$ chalcopyrite materials, it has been shown that the coefficient $b_p$ has a value of $-1.2$ eV. For the I-III-VI$_2$ chalcopyrite materials, a value of $-1.0$ eV has been used although this may be suspect since in its estimate the effects of $d$ contributions were not allowed for. From their measurements on CuGaS$_2$, Yamamoto et al. estimate that $b_d = -4.9$ eV. Using these values, the variation of $\phi$ with temperature can be determined from the present data. Using $b_p = -1.0$ eV and $b_d = -4.9$ eV the values of $\phi$ obtained vary almost linearly with temperature from 0.63 at 0 K to 0.74 at 300 K. Values of $\phi$ about 5% larger are obtained if $b$ is taken as $-1.2$ eV. Yamamoto et al.
estimated a value of $\phi$ of 0.61 at 300 K while values of $\phi$ in the range 0.55 to 0.87 have been determined for other I III VI$_2$ compounds from values of spin-orbit splitting (75SL).

In work on the chalcopyrite-like quaternary compound CuGaS$_2$Se$_4$ (82L1) it has been found necessary to assume a positive value for $b_d$ in that case to give any fit to the experimental data. It seemed of interest therefore to determine the range of $b_d$ possible in the interpretation of the present results for CuGaS$_2$, applying the obvious condition that $0 < \phi < 1$ at all temperatures. With a value of $b_p = -1.2$ eV, this condition requires that $b_d$ must lie in the range from -2.0 eV to $-\infty$. With $b_p = -1.0$ eV, the corresponding limit to $b_d$ was -2.2 eV. Thus the positive value of $b_d$ required for the interpretation of the results on the quaternary compound cannot apply in this case.

6.5 CONCLUSIÓN

For these chalcopyrite type alloys, the variation with temperature of the band gap values $E_A$ and $E_B$ cannot be fitted satisfactorily to the Varshni-type equation which applies well in the case of Group IV elements and the III-V and II-VI compounds and their alloys. The Manoogian-Leclerc type of equation can give a satisfactory fit to all of the $E_A$ and $E_B$ vs. $T$ curves, but unless a very wide range of temperatures is covered or very accurate values of energy are known, it is not possible to make an accurate determination of the $\theta$ parameter. Thus the present results do not contradict the statement of Manoogian
and Leclerc that the value of $k_B\theta$ is that of the mean phonon energy of the material. The parameters determined in the analysis indicate that the effects of phonon interaction and of the alloying are very similar on both the A and B valence bands.

The variations of the absolute zero values of $E_{0A}$ and $E_{0B}$ with composition are found to be linear with no measurable bowing due to alloying effects in this case.

An analysis of the crystal field splitting for CuGaS$_2$ shows that the value of the d orbital parameter $b_d$ must for these results be in the range $-2.0 \text{ eV}$ to $-5.0$. Use of the value of $-4.9 \text{ eV}$ proposed by Yamamoto et al. gives a value for $\phi$, the fractional contribution of p character to the valence bands, which is somewhat larger than that estimated by Yamamoto et al.
Chapter VII

RECOMMENDATIONS FOR FUTURE WORK

7.1 INTRODUCTION

Recent work (81L1) has shown that these compounds can be synthesized in a much purer form than the materials used in the work described above and this has been confirmed by the latest work in the laboratory at the University of Ottawa. This is accomplished by simply annealing for a few days at temperatures much nearer the melting point of the compound. For example, the two materials which proved to be the most difficult, CuInSnSe$_4$ and AgInSnSe$_4$, have now been grown here with no ternary or SnSe$_2$ dissolved in the ingot. However, measurements of optical absorption on this sample of AgInSnSe$_4$ gave the same value of energy gap as was obtained with the previous sample, indicating that the analysis described above is not affected by the presence of impurities. This material is of interest for possible application in the optical communication field as the value of the lowest band-gap is quite near to the lowest minimum in the absorption vs. energy curve of the material currently used for optical fibers.

With the availability of better polycrystalline materials, work is progressing towards the growth of single crystal samples by the iodine transport method.
More detailed measurements of optical absorption would give information as to which compounds show direct and which pseudodirect band-gaps. Comparissoon of these results with similar ones for the corresponding ternary compounds would allow a further comparison of the band structures of the two types of compound to be made.

Measurements, either by direct or modulated reflectance, would yield detailed information about the band structure of these quaternary compounds. For example, the crystal field and spin-orbit splittings of these materials can be determined from the values of the three $\Gamma$ point band-gaps. From these values, an analysis similar to that of Chapter 5 could be undertaken to determine the values of the deformation potentials $b_p$ and $b_d$. Detailed X-ray work could also be done to investigate the variation of $\frac{C}{a}$ with temperature, thus eliminating $\epsilon$ as an adjustable parameter in equation 5.7.

For the Manoogian-Leclerc equation to be tested more thoroughly, it would be necessary to investigate these compounds in much greater detail. Thus more accurate values of energy gaps over a wider range of temperature and some information on the phonon dispersion curves would be required. However, material for which more information is already available would be a better candidate than these new quaternaries for which so little data has as yet been obtained. Detailed studies would no doubt establish values for the $s$ parameter which could either be the same for all materials or more likely for materials of the same form.

Good quality polycrystalline materials, if not single crystals, are required for a study of ohmic contacts. Once this work is done detailed investigations into the transport properties of these compounds may be
undertaken. Such investigations would determine mobility and carrier concentration values and the effect of doping.

It is quite evident that there remains a great deal more work to be done on these quaternary chalcopyrite structured materials.
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