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**Crystallographic, Magnetic and Optical
Properties of $I_2\text{Mn.IV.VI}_4$ Compounds with
 $I = \text{Cu, Ag, IV} = \text{Si, Ge, Sn}$ and $\text{VI} = \text{S, Se, Te}$**

by

X. Luna Chen

Thesis
presented to the University of Ottawa
in partial fulfillment of the
requirements for the degree of Master of Science

Ottawa-Carleton Institute for Physics
University of Ottawa



Xuejun Luna Chen, Ottawa, Canada, 1993



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Abstract

For the first time, a systematic study was performed on the structural, magnetic and optical properties of polycrystalline $I_2.Mn.IV.VI_4$ compounds with $I = Ag$ or Cu , $IV = Si, Ge, Sn$, $VI = S, Se$ and Te . X-ray diffractometry, SQUID magnetometry and optical absorption techniques were used to characterize these compounds.

In the X-ray work, three different crystal structures were observed, two corresponding to the tetragonal stannite and orthorhombic wurtzstannite structures reported previously, and thirdly a cubic rock salt-like structure. While the Cu, S and Cu, Se compounds each showed only one structure independent of temperature, most of the Ag and Te compounds showed either of two phases depending upon the temperature of preparation, and all the Te compounds were found to be two or three-phase when in room temperature equilibrium. Lattice parameter values were obtained for all observed single phases and values were determined for the effective lattice parameter $a_e (= (V/N)^{1/3})$ where V is the unit cell volume and N the number of molecules per unit cell).

Magnetic susceptibility (χ) measurements showed that most of the selenide phases were ferrimagnetic. From the $1/\chi$ vs. T data, values were determined in each case for the magnetic parameters T_N , the Néel temperature, and θ_a , the Curie-Weiss temperature.

Optical absorption measurements were made to determine values of

optical energy gap E_0 for a number of the single phase samples, and in five cases the variation of E_0 with temperature in the range 10K to 300K was determined.

When the values of these various parameters (a_e , T_N , θ_a and E_0) were compared for the various phases, it was found that the phases could be classified into five different sets, viz.

1) tetrahedrally bonded (orthorhombic or tetragonal structure)
with I = Cu,

2) tetrahedrally bonded (orthorhombic or tetragonal structure)
with I = Ag and antiferromagnetic behaviour,

3) tetrahedrally bonded (orthorhombic or tetragonal structure)
with I = Ag and ferrimagnetic behaviour,

4) octahedrally bonded cubic structure with I = Cu,

5) octahedrally bonded cubic structure with I = Ag.

It was found that within a given set, the parameter a_e varied linearly with molecular weight, and the parameters T_N , θ_a and E_0 in almost all cases varied linearly with a_e . For any given parameter, the lines were quite different from one set to another. It is suggested that these differences in behaviour are due to different types of ordering of the Mn atoms on the particular crystal lattice.

In each case investigated, the variation of E_0 with temperature was found to agree well with the theoretical predictions of Alexander et al.(76A1). The change in band gap E_0 in the vicinity of T_N , caused by

magnetic effects, was found to be positive for the antiferromagnetic samples and negative for the ferrimagnetic samples. The critical exponent μ appearing in the equation of Alexander et al. was found to have a value of - 0.5 in the critical temperature range in all cases.

Acknowledgement

I wish to express deep thanks to my supervisor, professor John C. Woolley for the opportunity to work on this project and for his patient guidance and encouragement throughout the course of this work.

Many thanks to professor Gilles Lamarche for his excellent guidance and assistance in the measurements of magnetic susceptibility and in the cryogenic energy gap measurements.

Thanks to Anne-Marie Lamarche for helping in the preparation of the samples, the analysis of crystal structures, and for the measurements of magnetic susceptibilities.

Finally, I wish to thank all members of the physics department at the University of Ottawa for the great help and support during the past two years.

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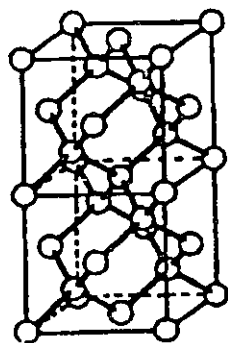
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Chapter 1 Introduction

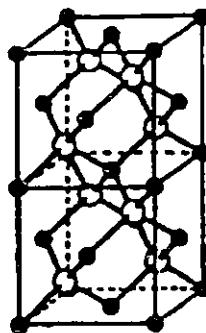
Since the invention of the transistor in 1949, research into new semiconducting materials and their properties has become one of the focal points of today's high technology. Such research is the essential concern of this thesis, which describes an investigation of a group of new magnetic semiconductor compounds in terms of their crystallographic, magnetic and optical properties.

The elements Si and Ge are the semiconductor materials on which all of the original technological applications were based. Both elements are tetravalent, which is the ideal condition for covalently-bonded solids, and in the solid phase these elements show sp^3 hybridization giving tetrahedral bonding. This bonding form results in the diamond structure shown in Fig.1.1a, which is called the diamond structure. The four valence electrons just fill the bonding orbitals of the solid or, in different terms, just fill the valence band, and this gives the semiconductor behaviour which is technologically so important.

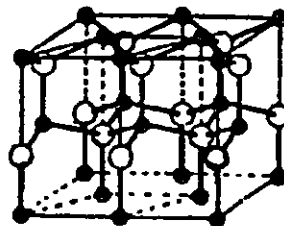
It was soon realized that this behaviour was not limited to the group IV elements, but that various compounds could be derived which would show similar electronic form. The essential requirement was an average of four valence electrons per lattice site (69P1). Thus, it was shown (41I1) that the III-V compounds, which satisfied this condition, showed a very similar crystal structure, the zinc-blende structure (Fig.1.1b). However, since there are now two different types of atoms in the lattice, ordering of



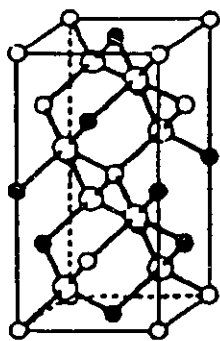
a. diamond



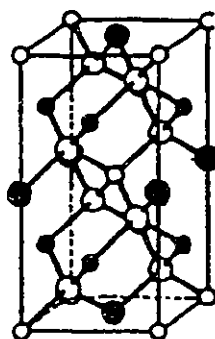
b. zincblende



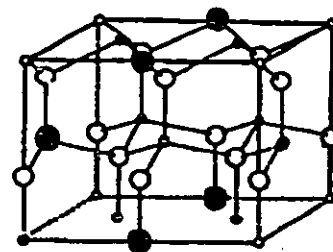
c. wurtzite



d. chalcopyrite



e. stannite



f. wurtz-stannite

Fig.1.1 Tetrahedral structure types.

these atoms occurs, resulting in a reduction in crystal symmetry. In the III-V compounds, the overall atomic positions are identical with those of the diamond structure but each III is coordinated by four V's and each V by four III atoms.

A similar set of compounds which satisfy the four electrons per site rule are the II-VI compounds and these again show the sp^3 hybridized tetrahedral bonding. Some of these compounds again have the standard zinc-blende structure, but a second structure which can be developed with this tetrahedral bonding is the hexagonal wurtzite structure (Fig. 1.1c) and some of the II-VI compounds show this alternative form. Again, each II is coordinated by four VI's and each VI by four II atoms. One important difference between these II-VI compounds and Ge and Si is that the II elements have quite different electronegativities from the VI elements and, as a result, the bonds are no longer purely covalent when the physical properties of the materials are being considered.

This development of progressively more complex tetrahedrally coordinated semiconductor compounds is illustrated in Fig.1.2. The next step after the binary compounds involves ternary compounds such as the I-III-VI₂ and II-IV-V₂ materials. In these compounds, where there are two different cations, further ordering and resulting reduction in crystal symmetry occur, and most of these compounds show the tetragonal chalcopyrite structure, illustrated in Fig. 1.1d. Again four cations are tetrahedrally arranged around each anion, the tetrahedra being charge-balanced, consisting of two I (II) and two VI (IV) cations.

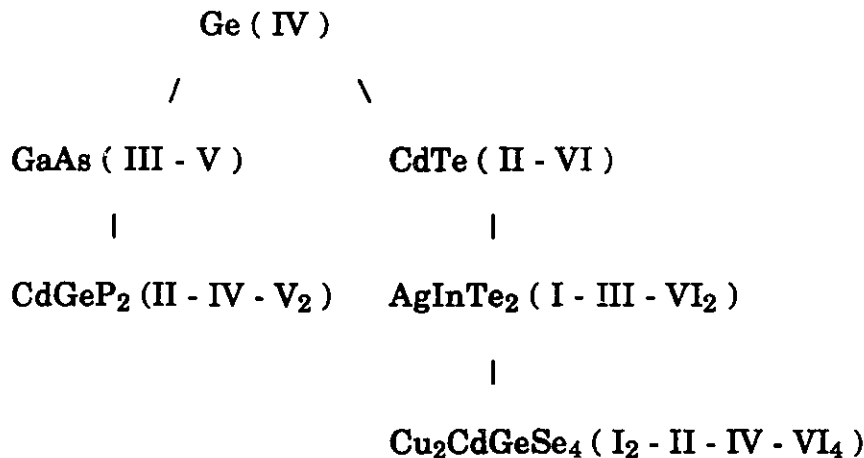


Fig. 1.2 The development of tetrahedrally coordinated semiconductor compounds.

Beyond these ternaries, various quaternary compounds can be postulated. One set of such compounds are the subject of this thesis, viz. the I₂-II-IV-VI₄ compounds. The crystallographic structures of the Cu-S and Cu-Se compounds of this type have been investigated in some detail (69P1, 74S1) and it was shown that they have either the tetragonal stannite structure shown in Fig.1.1e, which is derived from the zinc-blende form, or an orthorhombic structure derived from the ordering in the wurtzite structure, and which has been labelled wurtz-stannite. From detailed analysis of the X-ray diffraction data for Cu₂CdGeS₄ and associated compounds, Parthe et al. showed that the ordered structure of wurtz-stannite was as shown in Fig.1.1f. However, other related compounds,

such as $\text{Na}_2\text{ZnSiO}_4$, $\text{Ag}_2\text{CdSnS}_4$, $\text{Ag}_2\text{CdSnSe}_4$ etc., were shown to have similar orthorhombic structures, based on the wurtzite form but with the cations showing a different ordered arrangement, the X-ray diffraction data for the various cases differing only in the relative intensities of the weak ordering reflections.

All of the above semiconductors are essentially diamagnetic because of the complete balance of the valence electrons. However, this condition can be changed by replacing some of the cations by atoms which have the appropriate valency to maintain the four electrons-per-site condition, but which have an incomplete inner electron shell, e.g. Mn, Fe, Cr, etc.. The presence of these atoms in the compounds produces interesting magnetic properties which complement and / or modify the normal semiconductor properties. Some of the more interesting of these effects, and ones with possible technological application, are the magneto-optical effects, and these will be discussed in more detail below.

Almost all of the previously reported works on materials of this type have used Mn as the introduced paramagnetic atom, and much of this work has been concerned with alloys of the form $\text{II}_{1-z}\text{Mn}_z\text{VI}$, in which a fraction z of the II atoms are replaced by Mn while still retaining the zinc-blende structure (88F1). These alloys have been labelled diluted magnetic semiconductors (DMS) or semimagnetic semiconductors (SMSC) and are of interest because, in some cases, values of z of up to 0.7 or 0.8 can be used before the single phase zinc-blende structure is lost (88F1). In these

materials, the Mn atoms occur at random in the cation sub-lattice, i.e., no further ordering occur, and the resulting magnetic properties of the alloy is that of a spin-glass (88F1). Similar alloys can be produced based on the chalcopyrite compounds, e.g. (I.III)_{1-z}Mn_{2z}VI₂, and for these the Mn atoms can be either at random or ordered on the cation sublattice, depending upon the heat treatment used in their production (91L1).

Another way in which Mn can be introduced into semiconductors of this type is shown by the compounds I₂.II.IV.VI₄ in which the II can be Mn, i.e. I₂.Mn.IV.VI₄. (In this thesis, every compound discussed contains Mn as shown and so, for convenience, these compounds will be labelled I.IV.VI). In these cases, the Mn makes up a fixed fraction (0.25) of the cations and, as opposed to the random form in most of the alloys, the Mn will be ordered on the cation lattice, which can have significant effect on the magnetic behaviour of the material.

Guen and Glaunsinger (80G1) investigated the magnetic behaviour of five cases, CuSiS, CuGeS, CuSnS, CuGeSe and CuSnSe, and showed the first four to be antiferromagnetic with Curie-Weiss θ_a values in the range of 20 to 0K and Néel temperatures T_N in the range 0 to 20K . From their results for CuSnSe, they concluded that this was ferromagnetic with $T_c = 27K$. They also showed that the magnetic ordering temperature T_N (T_c) had an almost linear variation with $(V / N)^{1/3}$ where V is the volume of the unit cell and N the number of molecules per cell. In the present work, the parameter $(V / N)^{1/3}$ will be written as a_e , the effective lattice parameter.

Measurements of the optical energy gap values for various $\text{I}_2\text{II.IV.VI}_4$ compounds have been made by a number of workers (67N1, 69P1, 70A1, 74S1 and 80G1) and the values obtained lie in the range of 1.0 to 2.5eV. However no systematic investigation of the variation of this parameter with composition, ordering of the cations etc. appears to have been carried out.

Recently, interest has increased in quaternary semiconductors containing Mn, because of possible technological applications. It has been pointed out that the magnitude of the magneto-optical effects observed depends upon the magnetization that can be produced in the material by typical laboratory magnetic fields (76A1). Work on SMSC alloys such as $\text{Cd}_{1-z}\text{Mn}_z\text{Te}$ has shown (88S1) that, in these materials, only modest magnetization can be obtained because of the appreciable antiferromagnetic interaction between the Mn ions, and this interaction becomes more pronounced with increase of the Mn concentration. To increase the magnitude of the magneto-optical effects, materials are needed in which the exchange interactions between the Mn ions are smaller. It has been suggested recently (87W1, 2) that the $\text{I}_2\text{Mn.IV.VI}_4$ compounds could be suitable in this case. As can be seen from Fig.1.1, in the case of the stannite and wurtz-stannite structures, the ordering is such that no two Mn ions are bonded to a common anion. Thus the antiferromagnetic interactions between any two Mn ions would be expected to be much weaker in these quaternary compounds than in the II-VI SMSC alloys.

Until the present program, no data were published for $I_2.Mn.IV.VI_4$ compounds with $I = Ag$ and $VI = Te$. In this thesis, all 18 compounds given by $I = Cu, Ag, IV = Si, Ge, Sn$ and $VI = S, Se, Te$ have been investigated with reference to their crystallographic, magnetic and optical energy gap behaviour.

This investigation is part of a research program involving magnetic semiconductors carried out by a research group of Dr. J. C. Woolley, Dr. G. Lamarche and Mrs. A. M. Lamarche and the author. Thus preparation, measurement and analysis are all shared by the various members of the group. In the work described in this thesis, the author was responsible for almost all of the optical measurements and analysis, and for a large percentage of the magnetic analysis. The author also contributed to a lesser extent (about 15%) to the preparation of samples, crystallographic measurements, analysis and magnetic measurements.

Chapter 2 Sample Preparation and Measurement

§ 2.1 Sample preparation

The materials to be investigated in this thesis were prepared from the elements by the melt and anneal technique (83B1). The components of each 1.0 gram sample, weighted to $\pm 0.0004\text{g}$ precision, were placed in a quartz capsule, and sealed with an oxy-acetylene torch under 10^{-4} - 10^{-5} Torr vacuum. The capsule was then raised to a temperature of 1150°C , in the case of the Se and Te compounds, in approximately an hour. For S compounds, it was kept at 600°C for 24 hours, then raised to 800°C and held for 3 days before being heated up to 1150°C for half an hour. This slow rate of heating of the S compounds allows some reaction to occur and avoids the chance of blow-ups. The samples were then cooled by switching off the power to the furnace and leaving this to cool overnight.

The samples were then annealed at various temperatures for a week. The annealing temperatures were chosen, when possible, according to the differential thermal analysis results (90W1, 91L1). Samples were then either brine quenched, in an attempt to retain the equilibrium condition at the temperature of anneal, or were slowly cooled to room temperature to give as near as possible the room temperature equilibrium condition. Details of the individual heat-treatments will be discussed in another section.

It was necessary when producing these Mn-based materials to

'carbonize' the interior of the quartz capsule to prevent the reaction of the quartz tubing with Mn at high temperature. The carbonizing was done by depositing a light film of acetone on the tube wall and turning in a Bunsen flame. The procedure was repeated once and the tube was cleaned thoroughly with an acetone rinse.

The amount of handling of the finished samples was kept to a minimum in order to decrease the chance of surface contamination. Samples were powdered or sliced for the purpose of various measurements which will be described in the following sections.

§ 2.2 X-ray Measurements and Crystal Analysis

2.2.1 Introduction

X-ray diffraction is a common tool to investigate crystal structures. When an X-ray beam is incident on a set of lattice planes (hkl), if the Bragg law, $n\lambda = 2d\sin\theta$, is satisfied, diffraction can occur. Here λ is the wavelength of incident beam, θ is the angle between the incident beam and the lattice plane, and d the distance between adjacent planes.

In the powder diffraction method, which was used in the present experiment, the sample to be examined is reduced to a very fine powder, and is placed in a beam of monochromatic X-rays. Each particle of the powder is a tiny crystalline fragment oriented at random with respect to the incident beam. Consider one particular hkl plane reflection, one or more particles of powder will, by chance, be so oriented that their { hkl } planes

make the correct Bragg angle for reflection.

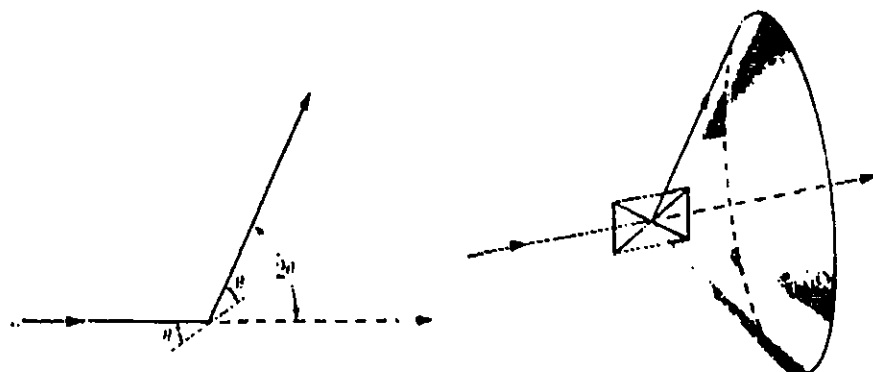


Fig. 2.2.1 Formation of a diffracted cone of radiation
in the powder method

Fig. 2.2.1a shows one plane in this set and the diffracted beam formed. If this plane is now rotated about the incident beam as axis in such a way that θ is kept constant, then the reflected beam will travel over the surface of a cone as shown in Fig.2.2.1b. This rotation does not actually occur in the powder method, but the presence of a large number of crystal particles having all possible orientations is equivalent to this rotation, since among these particles there will be a certain fraction whose $\{ hkl \}$ planes make the right Bragg angle with the incident beam and which at the same time lie in all possible rotational positions about the axis of the incident beam. The hkl reflection from a stationary mass of powder thus has the form of a cone of diffracted radiation, and a separate cone is formed for each set of

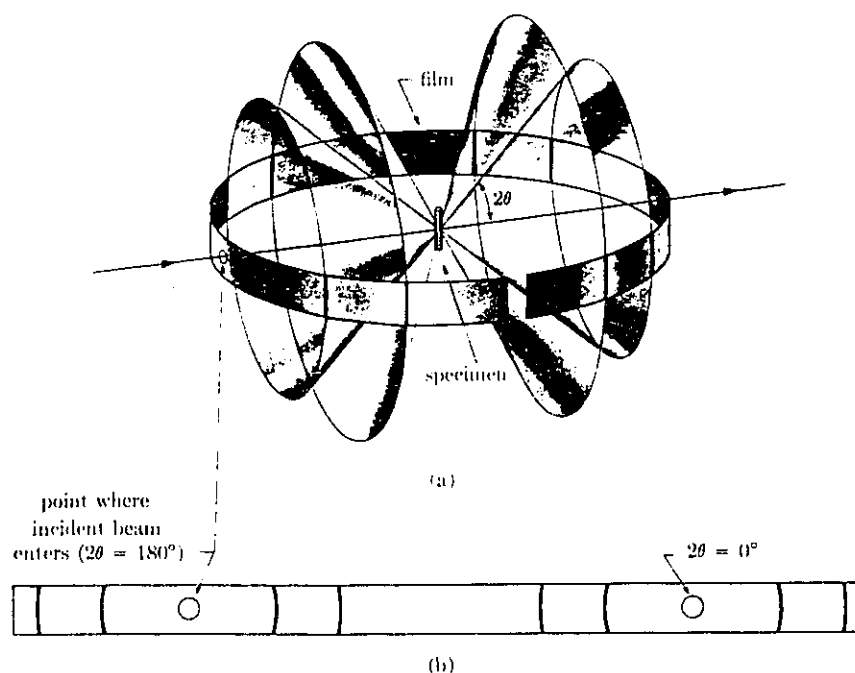


Fig. 2.2.2 Debye-Scherrer powder method : (a) relation of film to specimen and incident beam; (b) appearance of film when laid out flat.

illustrates the most common powder diffraction method. In this, the Debye - Scherrer method, a narrow strip of film is curved into a short cylinder with the specimen placed on its axis and the incident beam directed at right angle to this axis. The cones of diffracted radiation intersect the cylindrical strip of film in lines and, when the strip is unrolled and laid out flat, the resulting pattern has the appearance of the one illustrated in Fig.2.2.2b. From the measured position of a given diffraction line on the film, θ can be determined, and knowing λ , we can calculate the spacing d of the reflecting planes which produced the line.

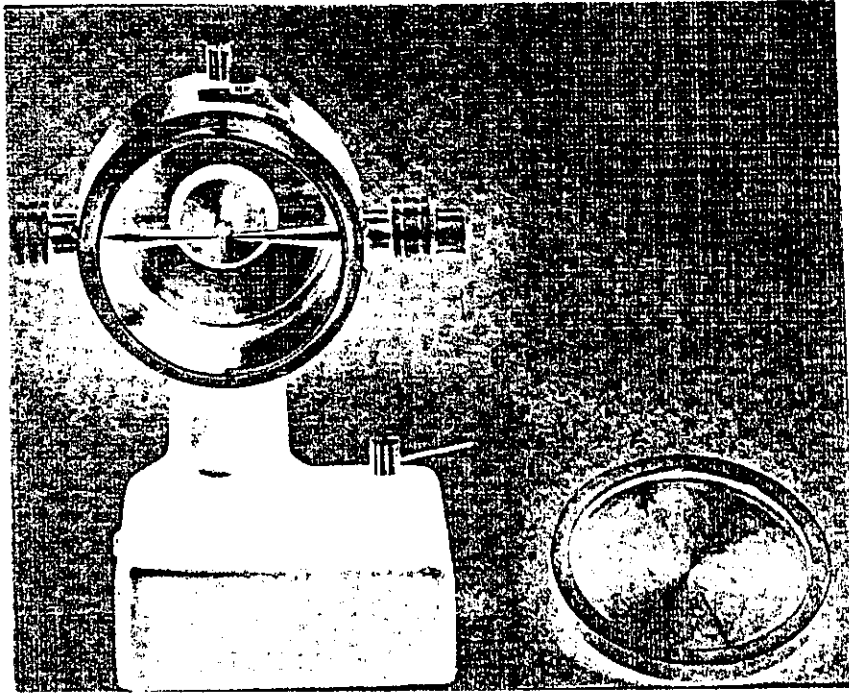


Fig. 2.2.3. Debye-Scherrer camera, with cover removed.

2.2.2 Experiment

A 180 mm Debye-Scherrer camera is employed in this measurement, as shown in Fig. 2.2.3. It consists essentially of a cylindrical chamber with a light-tight cover, a collimator to admit and define the incident beam, a beam stop to confine and stop the transmitted beam, a means for holding the film tightly against the inside circumference of the camera, and a specimen holder that can be rotated.

The specimen holder is a fine glass fibre, coated on its surface with

The specimen holder is a fine glass fibre, coated on its surface with the sample powder held by a small amount of glue or petroleum jelly. Rotation about the fibre axis of the specimen during the exposure would produce continuous diffraction lines.

K_{α} radiation from a Cu target was used as the X-ray source, giving a wavelength equal to $1.543 \text{ \AA}$. Samples were exposed to radiation for four hours. The films were then developed in the laboratory dark room.

2.2.3 Film Analysis

X-ray diffraction films were obtained as shown in Fig.2.2.2b, with a 180 mm camera, and θ (in degrees) was determined by measuring the positions of diffraction lines represented by D (in mm).

In X-ray diffraction, the Bragg condition is written as

$$n \lambda = 2d \sin \theta \quad (2.2 - 1)$$

For an orthogonal crystal system, i.e.. $\alpha = \beta = \gamma = 90^\circ$, this gives

$$Q = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \quad (2.2 - 2)$$

where Q is defined by $Q = 4 \sin^2 \theta / \lambda^2$, where a b c are lattice parameters, and h k l are Miller indices (56C1).

Or for convenience, this may be written as

$$Q = AN_1 + BN_2 + CN_3 \quad (2.2 - 3)$$

where N_1, N_2, N_3 are squares of integers, and A, B and C are $1/a^2, 1/b^2$

and $1/c^2$ respectively.

In the cubic case, $a = b = c$, and the formula above can be written as

$$Q = (h^2 + k^2 + l^2) / a^2 = NA \quad (2.2 - 4)$$

For the tetragonal case, $a = b \neq c$, and the equation becomes:

$$Q = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} = N_1A + N_2C \quad (2.2 - 5)$$

For the orthorhombic case, $a \neq b \neq c$, therefore the equation remains as equn.(2.2-2), and can be written as

$$Q = N_1A + N_2B + N_3C \quad (2.2 - 6)$$

If values of hkl are known or can be determined, the lattice parameters a, b, c can then be found.

In order to obtain lattice parameter values, it is necessary to know the hkl for each line. All the cubic samples investigated here have the rock-salt type structure, where the condition for strong intensity lines was found to be $h^2 + k^2 + l^2 = 4S$, where S is an integer(56C1). Thus it is very simple to determine the hkl values.

In the tetragonal case, previous work(74S1) showed that these materials have stannite structure and the present photographs agree with this. Therefore the required values of hkl are known.

The orthorhombic analysis is in principle much more difficult because three lattice parameters need to be found. However the results of Schafer and Nitsche (74S1) for various $I_2.II.IV.VI_4$ compounds give a very good guide to the particular hkl values which are to be expected in these

orthorhombic materials. With a little trial and error, it was possible to find values of hkl which fitted the first 10 or so of the orthorhombic lines and this was sufficient to give the values of a , b , and c .

One practical problem that needs to be allowed for is the absorption effect. In fact, only for a sample in which absorption is negligible can the centers of the powder lines be taken as the correct positions. This is due to a factor which affects the intensities of the diffracted rays, that is the absorption which takes place in the sample itself. It was shown that the relative absorption increases as θ decreases (56C1). Therefore, back-reflected rays come almost entirely from that side of the sample which faces the collimator, instead of coming from the center of the sample. The exact form of the error has not yet been found. However, in the cubic case, where only one lattice parameter a is to be found, it was suggested (51H1), this can be allowed for by plotting a vs. $f(\theta)$, where

$$f(\theta) = \frac{1}{2} \left(\frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta} \right) \quad (2.2-7)$$

and extrapolating a to $f(\theta) = 0$.

However for tetragonal and orthorhombic materials, this method is not suitable and so in these cases, values must be corrected by including a standard substance such as Si or Ge in the sample to be X-rayed. Corrections to the Q value for each line can then be determined (see § 3.1).

§ 2.3 Magnetic Susceptibility Measurements

2.3.1 Introduction

An electron bound to a nucleus possesses a magnetic moment due to its spin and orbital angular momenta, and the total magnetic moment for a free atom is

$$\mu = -g \mu_B J \quad (2.3 - 1)$$

The g factor is given by the Landé equation (66S1):

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \quad (2.3 - 2)$$

where μ_B is the Bohr magneton, S and L are spin and orbital angular momenta, and J is the total angular momentum.

The vector addition of the quantum numbers results in only the partially filled electronic levels possessing a non-zero resultant momentum. Since in a solid, the valence electron are used for bonding etc., only atoms such as Mn, which have an partially filled inner shell, can show a net magnetic moment. The five unpaired 3d electrons of Mn results in a value of spin momentum, S, equal to 5 / 2. In a solid, the angular momentum, L, may be quenched by the crystal field (66S1). Consequently it may not contribute to the total magnetic moment. Substituting $S = J = 5 / 2$ and $L = 0$ into eq.2.3-2 gives $g = 2$ for Mn.

According to their magnetic properties, materials may be classified into three general categories: diamagnetic and paramagnetic, with no coupling between individual atom and exchange coupled magnetic systems.

The response of these materials to an applied magnetic field, especially as a function of temperature, provides one method of distinguishing them.

The magnetic susceptibility χ is defined as

$$\chi = M / H \quad (2.3 - 3)$$

For diamagnetic materials, M is negative and independent of temperature. Paramagnetic systems have a positive susceptibility and in small magnetic fields follow the Curie law (66S1):

$$\chi = \frac{N g^2 \mu_B^2 J(J+1)}{3 k_B T} = \frac{C}{T} \quad (2.3 - 4)$$

where C is the Curie constant, N is the number of magnetic atoms, k_B is the Boltzman constant, T is the temperature in Kelvin, and the spectroscopic splitting factor g is given by equation 2.3-2.

Exchange coupled systems possess the common feature of having interactions between the atomic magnetic moments that result in some kind of alignment or correlation among these various moments or spins in the lattice. This category includes such substances as ferromagnetic, antiferromagnetic and ferrimagnetic materials.

The exchange interaction tends to orient a pair of spins in a particular manner and competes with thermal processes which tend to disrupt the correlation. For a ferromagnet, the interaction is positive, so all spins are arranged in a parallel manner. Above a certain characteristic temperature, the thermal agitation overcomes the exchange forces and the alignment is lost. In this range, the material behaves in a similar way to a paramagnet. At temperatures well above this point and in small magnetic

fields, the susceptibility may be described by the Curie-Weiss law (66S1):

$$\chi = \frac{C}{T - \theta_f} \quad (2.3 - 5)$$

where θ_f is the ferromagnetic ordering temperature and is positive, C is the Curie constant as defined in eq. 2.3-4.

In materials for which interaction is negative, spins tend to be antiparallel. Because of this, the spins break up into two or more sublattices, the spins in each sublattice being parallel to each other. In the simplest case of two sub-lattices, the spin directions tend to be antiparallel. Again the alignment is lost above a characteristic temperature, known as the Néel point, T_N , and the material assumes a paramagnetic-like state. At high temperatures above T_N and in a small magnetic field, the susceptibility is also described by equation 2.3-5, but with the Curie-Weiss temperature, θ , is negative. Materials with this type of interaction fall into two classes. When the spins are equal in magnitude and there are equal numbers on each sublattice, the material is antiferromagnetic. In this case, below T_N the total spin vectors for the sub-lattices are equal and hence in a magnetic field, the resultant magnetization is small, comparable with that of a paramagnet.

Ferrimagnetic material have non-equivalent sublattices, say A and B. The difference can be due to different spin magnitudes on the different magnetic atoms and / or different numbers of atoms on each sub-lattice. In the case when the spin magnitudes are different for different atoms or

different lattice sites, the concept of two sub-lattices still applies even with positive interaction.

The relations were given (66S1) for the two sub-lattices case and showed that the $1 / \chi$ vs. T curve for ferrimagnetic interaction is a hyperbolic curve with the form

$$\frac{1}{\chi} = \frac{T - \theta_a}{C} - \frac{\xi}{T - \theta} \quad (2.3 - 6)$$

where only the behaviour above the critical point T_N is observed. The values of θ_a , θ and ξ can be related to the various exchange parameters, ie.

$$\begin{aligned} \theta_a &= C \gamma_{ab} \lambda \mu (2 + \lambda \alpha / \mu + \mu \beta / \lambda) \\ \theta &= - C \gamma_{ab} \lambda \mu (2 - \alpha - \beta) \\ \xi &= C \gamma_{ab}^2 \lambda \mu [\lambda (1 - \alpha) - \mu (1 - \beta)]^2 \end{aligned} \quad (2.3 - 7)$$

where λ is the fraction of magnetic atoms on A sites and $\mu = 1 - \lambda$ is that on B. The Weiss molecular field coefficients γ_{ab} , $\gamma_{aa} (= \alpha \gamma_{ab})$, $\gamma_{bb} (= \beta \gamma_{ab})$ are defined in terms of the molecular field.

2.3.2 Measurement of Susceptibility

The susceptibility of a magnetic material was found by measuring its magnetization caused by an applied magnetic field. This was accomplished by using a niobium SQUID magnetometer. The apparatus has been described in other work (86D1), it consists of a reverse dewar setup whereby the niobium SQUID can be kept at 4 K while the movable

sample chambers within the dewar may be heated to approximately 300 K. The measurements can usually be made through the range of 4 K to 250 K. The upper limit is set by the large amount of liquid helium which would be boiled off to retain that temperature.

The measuring system used in the present work had been calibrated by Dr. Gilles Lamarche, and the relation obtained is

$$\chi = \frac{(1.8 \times 10^{-4}) V}{(0.5 I + 0.23) m} \quad (\text{emu} / \text{g}) \quad (2.3 - 8)$$

The units of this equation are electron magnetic units per gram of the sample. The SQUID voltage is represented by V in volts, and the mass of the sample in grams, by m. I represents the current through the solenoid which provides the required magnetic fields, usually in the range 1 to 2.5 mT. χ has the precision of $\pm 0.005 \times 10^{-4}$ emu/g.

2.3.3 Evaluation of Curie - Weiss Parameters

As mentioned previously, a paramagnetic system follows the Curie law $1/\chi = T/C$, and so the Curie constant can be determined by simply plotting $1/\chi$ against temperature.

For antiferromagnetic behaviour of this type, the variation of $1/\chi$ with T well above the Néel temperature is given (66S1) by the Curie-Weiss relation

$$\frac{1}{\chi} = \frac{T - \theta_a}{C} \quad (2.3 - 9)$$

where θ_a is the Curie-Weiss temperature and C the Curie constant, while a minimum in $1/\chi$ at lower temperatures gives the Néel temperature T_N . Thus when experimental data of $1/\chi$ are fitted to the equation 2.3-9, values of the Néel temperature T_N , Curie-Weiss temperature θ_a , and Curie constant C can easily be obtained.

For samples containing one Mn atom per molecule, which applies to all the samples investigated here, the theoretical value of C is given by Smart (66S1):

$$C = \frac{N_a g^2 \mu_B S (S + 1)}{3k_B W} \quad (2.3 - 10)$$

where N_a is Avogadro's number, μ_B the Bohr magneton and W the molecular weight giving C in emu.K/gram. Assuming for Mn that $g = 2$ and $S = 5/2$, C can be separately determined for each material, this can be used either in the fitting of an experimental curve or for comparison with experimental values.

For ferrimagnetic behaviour, the variation of the magnetic susceptibility χ with temperature T in the range $T > T_N$ is given by the relation 2.3-6. Here θ_a is the asymptotic Curie-Weiss temperature, C is the Curie constant and ξ and θ are parameters which depend upon magnetic ion concentration, exchange interaction, etc.. Thus if the experimental curves are fitted to equation 2.3-6, the parameters to be determined are θ_a , θ

and T_N , since the value of C can be determined from formula 2.3-10. This analysis will be considered in detail below (see page 68).

Due to the fact that the high temperature measurements from which the Curie-Weiss parameters are derived involve the weakest susceptibility signal, the relative importance of the temperature-independent diamagnetic correction also increases with temperature. This could in principle, lead to errors in resulted Curie-Weiss parameter values. In fact, it was estimated(91B1) that the total diamagnetic susceptibilities for the samples investigated in this course are two or three orders of magnitude smaller than the observed susceptibilities of the materials, thus it can generally be neglected in the analysis of the experimental susceptibility data.

§ 2.4 Optical Measurements

2.4.1 Introduction

In addition to the crystallographic structure and magnetic susceptibility, a SCSM material is also characterized by its optical properties. Optical absorption with electronic transitions from the valence band to states in the conduction band take place when photon energy $h\nu \geq E_0$, where the energy gap E_0 is the minimum energy between the valence and conduction bands. For the case when the absorption corresponds to a direct band-gap transition, i.e. when no change in the electron k vector occurs in the transition, (67J1), the absorption coefficient α has been shown

to satisfy the equation

$$(\alpha h\nu)^2 = A (h\nu - E_o) \quad (2.4 - 1)$$

However for the indirect gap case, ie. when the transition involves a change in electron momentum as well as electron energy, it is necessary to have a phonon also involved in the process to provide the necessary momentum change. Such a "three-particle collision process" (electron, photon and phonon) has a resulting small probability, so that the absorption coefficient is smaller in this case, and is related to the photon energy by the relation (67J1)

$$(\alpha h\nu)^{1/2} = B (h\nu + h\omega - E_o) \quad (2.4 - 2)$$

However in almost all cases, $h\omega$, the phonon energy is small and can be neglected in the analysis, and the relation

$$(\alpha h\nu)^{1/2} = B (h\nu - E_o) \quad (2.4 - 3)$$

can be used.

2.4.2 Experimental Method

The energy band gap may be determined from transmission measurements by observing the change in the absorption as a function of incident photon energy. At an energy corresponding to the band-gap energy, the absorption coefficient curve has a rise above the background as the energy of the incident radiation increases.

From classical electromagnetic theory (67J1), when the light of

intensity I_0 is incident normally on the surface of a sample with thickness d , because of the absorption, the intensity of the transmitted light is reduced to

$$I = \frac{I_0 (1 - R)^2 (1 + k^2 / n^2) \exp(-\alpha d)}{1 - R^2 \exp(-2\alpha d)} \quad (2.4 - 3)$$

where R is the reflection coefficient, α is the absorption coefficient, given by $\alpha = 4\pi k / \lambda$, n , the refractive index, and k , the extinction coefficient of the material. R is given by

$$R = [(n - 1)^2 + k^2] / [(n + 1)^2 + k^2] \quad (2.4 - 4)$$

For energies near the absorption edge, where α is very small, k is much less than n . If, in addition, d is large enough to ensure that $R^2 \exp(-2\alpha d)$ is much less than 1 (this is the case in the present measurements, where d is about $30 \mu\text{m}$), equation 2.4-3 can then be simplified to

$$I = I_0 (1 - R^2) \exp(-\alpha d) \quad (2.4 - 5)$$

According to Wooten (72W1), n is approximately constant, and k is relatively much smaller than n . It is then obvious from equation 2.4-4, that R is a slow varying function of photon energy and its maximum possible value is 1. Thus $(1 - R^2)$ term may be treated as a constant. By taking $\ln$ of both sides of equation 2.4-5, we have

$$\ln \left| \frac{I_0}{I} \right| = \alpha d - \text{constant} \quad (2.4 - 6)$$

In the experimental measurements, the value of $(1/d) \ln(I_0/I)$ has been determined as a function of photon energy $h\nu$. By subtracting a background value, which can usually be taken as constant, values of α are

obtained. From equation 2.4-1, we have

$$(\alpha h\nu)^2 = A (h\nu - E_0) \quad (2.4 - 7)$$

Therefore a plot of $(\alpha h\nu)^2$ against $h\nu$ should be a straight line, and the value of E_0 is given by the intercept on the $h\nu$ axis.

For indirect absorption, it is necessary to take the $h\nu$ intercept from a plot of $(\alpha h\nu)^{1/2}$ against $h\nu$.

The experimental set up used to determine the absorption edge is shown in Fig. 2.4.1. The light source used in the present work was a 30 Watt tungsten filament light bulb. The light was focused on to the entrance slit of a Spex 1702 spectrometer by a concave mirror. The monochromatic light from the output slit of the spectrometer was focused by another concave mirror on to the sample which was supported directly in front of the detector. The light beam was amplitude modulated by a Rofin model 7500 light chopper placed in front of the entrance slit of the spectrometer.

Depending upon the photon 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 preamplifier. The output of the lock-in was registered on a strip chart recorder.

In order to minimize errors in reading data from the charts, the sensitivity of the lock-in and the chart recorder were adjusted to maintain as close to full scale deflection as possible on the chart. If at the maximum

response the signal was still not large enough, the pre-amplifier (maximum amplification of $1000 \times$) was used.

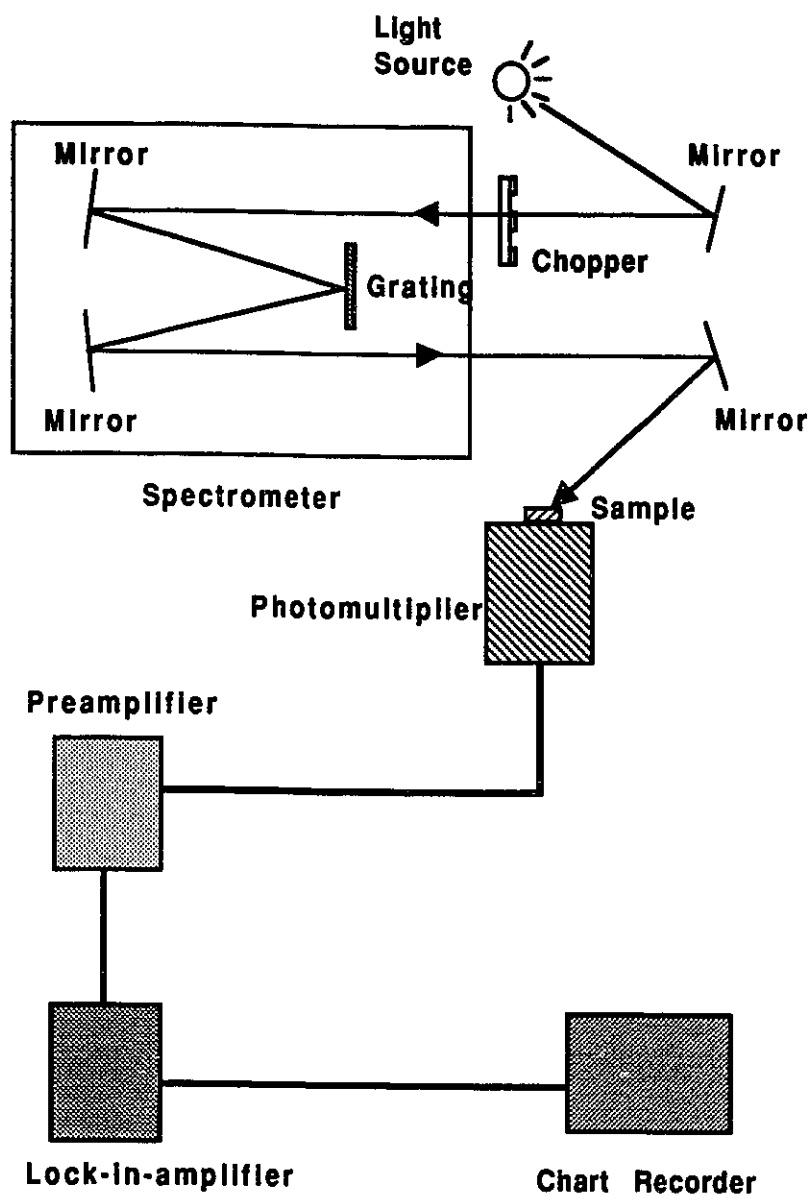


Fig. 2.4.1 Optical transmission measurement apparatus

One typical problem was that in many cases the spectrum signal of the light transmitted through the sample was so small that it could hardly be distinguished from the background noise. To obtain a good signal, the alignment of the optical system had to be very carefully adjusted. When the optical system was aligned for a specific light source and grating, a spectrum of the incident light I_0 without any absorption by a sample was obtained for calibration purposes. To keep this signal within a measurable range, light was passed through a small pinhole in front of the detector. Once I_0 was obtained, the alignment of the optical system must not be changed and the same power was always supplied to the light source, so that the effective I_0 spectrum remained the same. As the transmission measurements were made using different amplifications and different detector voltages than were used for the I_0 curves, there was 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. However this scaling factor is not very important because when $\ln(I_0 / I)$ is determined, it appears as an added constant and this effectively forms part of the subtracted background value.

2.4.3 Sample Preparation

After the samples were removed from their quartz capsules, they were then 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. Sliced sample were mounted on a polishing rod (shown in Fig.2.4.2) with small amount of wax, then reduced in thickness as much as was feasible by lapping on a piece of sandpaper (size #3) covered with water. Both sides of the sample needed to be ground down. The sample could be removed from the rod by simply melting the wax with a heater, and then using the sharp edges of a piece of paper to carefully remove the sample. The lapped slices were typically 20 to 80 microns in thickness. The samples were not polished to a high reflectivity as the thinned slices tended to be quite fragile, also, it would decrease the intensity of light.

Each sample was next mounted on a brass disc, the centre 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 applied to the edge of the sample as observed under a microscope. Before use, the silver print was allowed to thicken slightly to ensure that the solvent did not penetrate into the slice and also that the fluid silver print did not spread on to the surface of the slice. The presence of any small pinholes in the sample was detected by placing an intense light behind the disc. If present, these pinholes were plugged with small droplets of the silver print, which is opaque. The disc was then mounted on the appropriate detector for the wavelength range of interest.

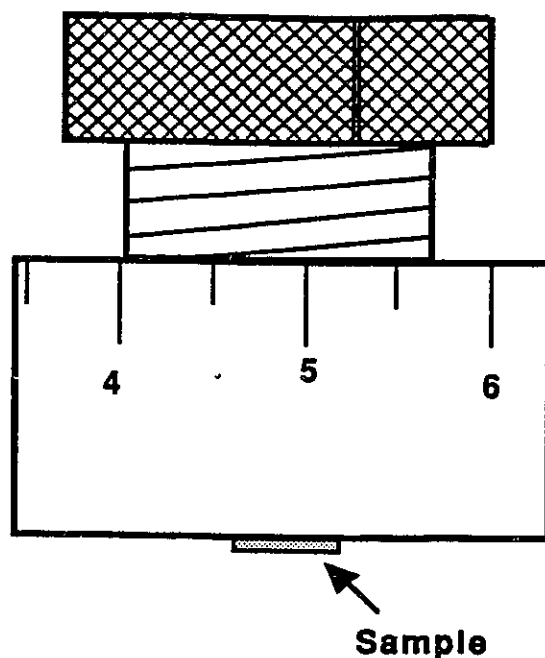


Fig.2.4.2 The screw rod for sample polishing

2.4.4 Cryogenic Measurements

The behaviour of the energy gap with temperature was investigated for three quaternary compounds, $\text{Cu}_2\text{MnGeS}_4$, $\text{Ag}_2\text{MnSiTe}_4$ and $\text{Cu}_2\text{MnSiSe}_4$. For temperatures below 300 K, a CTI-CRYOGENICS model 21SC CRYODYNE cryocooler was used. The system is based on the Joule Thompson expansion of He gas to cool down to just below 10K. A schematic diagram of the entire system is presented in Fig. 2.4.3. The compressor is connected to the cold head by He supply and return lines, to compress and expand the gas and so provide cooling for the cold station below the cold head.

To control the temperature, a LAKE SHORE CRYOTRONICS model

drc-80C digital cryogenic thermometer / controller was used. The temperature could be set for a resolution of 0.1K above 100K and for 0.01K below. The photomultiplier was mounted on the cold station to which the sample holder was firmly attached. This sample holder was made of copper with a hole in its center, and was designed to attach to the bottom of the cold head in such a way as to provide the maximum possible surface contact. The sample disc was attached to sample holder with heat sink grease, which has a high thermal conductivity. It is worth mentioning that the use of too much grease would affect the thermal conduction and the cooling of the sample. The grease was allowed to dry up to some extent before being applied, in order to ensure that the sample disk was well attached to the holder. The temperature indicated by the sensor was assured to be that of the sample. However it was possible that some difference in temperature would occur between the sensor and the sample. This would occur when thermal equilibrium was not reached at the time of the measurement. The temperature difference in such a case would be affected by the distance between the sensor and the sample, the grease used, and would be more important if insufficient time was allowed between readings at different temperatures.

The entire cold station was enclosed in a vacuum chamber of an OXFORD CF 204 cryostat, which was maintained at a pressure of 10^{-4} mm of Hg during operation to provide thermal isolation. The chamber possessed four windows for optical measurements of the enclosed sample.

The detector was placed behind the chamber. The transmission

measurements were made at some 20 different temperatures from 10 K up to room temperature 300K, following the procedure described in the previous section. The curve of band-gap E_0 vs. temperature T was fitted to a Varshni-Leclerc equation, and this will be discussed in detail later in chapter five.

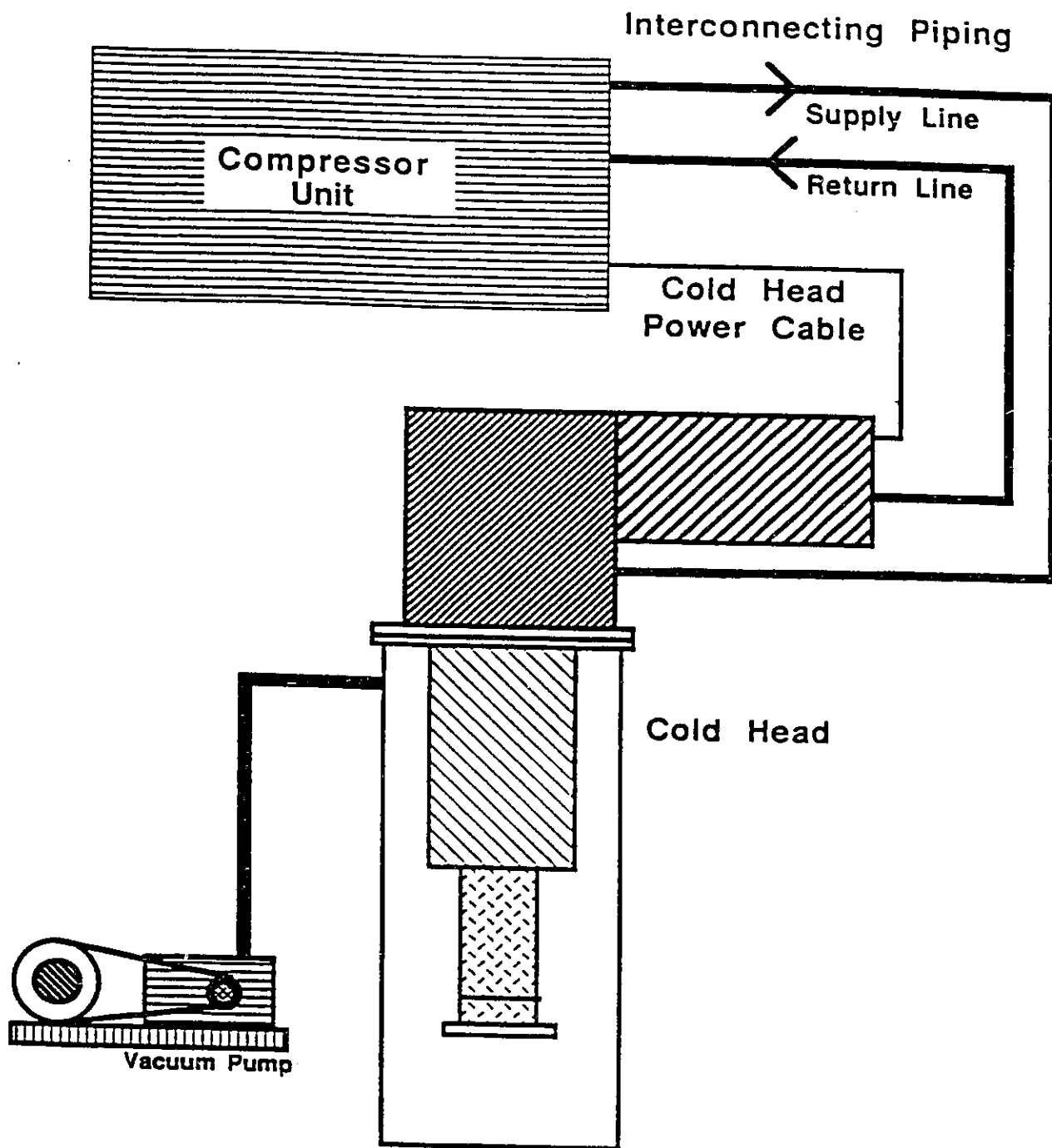


Fig. 2.4.3 Schematic of the cryogenic apparatus for measuring the energy gap at low temperatures.

Chapter 3. X-ray Results and Crystallographic Analysis

§ 3.1 Results and Analysis

As indicated below, when the samples investigated showed single phase form, they all had one of these different structures, i. orthorhombic, apparently corresponding to the wurtz-stannite form mentioned previously (Fig. 1.1f), ii. tetragonal, similarly corresponding to the stannite form (Fig. 1.1e), iii. a cubic form with an X-ray line distribution corresponding to the rock-salt structure. The X-ray photographs of each of these three forms can easily be distinguished one from another and so in the initial work the structure produced by any particular heat treatment could be determined. Thus the first part of the work was to investigate the results of various heat treatments on all of the compounds investigated.

Polycrystalline samples of eighteen quaternary compounds of the form $I_2.Mn.IV.VI_4$ with $I = Cu, Ag$, $IV = Si, Ge, Sn$ and $VI = S, Se, Te$ were made from the elements using the melt and anneal technique as described in chapter 2. The compounds containing Cu and S or Se were annealed at 625 °C and then quenched to room temperature. The resulting X-ray photographs showed crystal structures in good agreement with the results of Schafer and Nitsche (74S1). Samples annealed at lower temperatures showed no difference from that obtained at higher temperatures, indicating that the structures observed were stable from

temperatures above 625 °C down to room temperature. Differential thermal analysis (DTA) data for the $(\text{Cu}_2\text{Ge})_{1-z}\text{Mn}_{3z}\text{Se}_3$ diagram made by other group members (90W1, 91L1) confirmed this for the case of $\text{Cu}_2\text{MnGeSe}_4$, which corresponds to the $z = 0.25$ point of that diagram.

In the case of many of the compounds containing Te and / or Ag, a very different behaviour was observed: with the phase conditions determined from the X-ray photographs differing with different annealing temperatures. Only in the cases of AgGeS, AgSiSe and AgGeSe were the results similar to those observed for the Cu-S and Cu-Se compounds, with the three compounds showing the ordered orthorhombic structure only. For AgSiS, no clear single phase condition was obtained, even though annealing was carried out at some seven different temperatures in the range 400-750 °C. In all other cases, more than one structure were observed for the each compound, depending on the temperature of annealing.

In addition, for all of the Te compounds, annealing at 400 °C or below produced lines corresponding to MnTe_2 , indicating that the compound was unstable in this lower temperature range, and split up into two or three phases. This was confirmed in two cases (CuGeTe and CuSnTe) by DTA data (90W1, 91L1). One problem arising from this two- or multi-phase behaviour, was that in order to obtain reasonably single phase samples of a compound in any structure, the sample had to be very rapidly quenched from the annealing temperature. Thus it was found that

even in the best cases, the Te compounds contained slight traces of MnTe_2 . While this was no problem in the crystallographic work, it had to be considered in the magnetic measurements. However, the single phase samples produced in this way were certainly meta-stable at room temperature. Thus it was found that for all three single phase structures, samples measured at up to eighteen months after production showed the same crystallographic and magnetic behaviour as had been observed in the initial measurements.

As indicated above, the phase condition of many of the samples depended upon the details of the heat-treatment used. The phase behaviour of each of the materials investigated can be summarized as follows.

i) CuSiS , CuGeS , CuSnS , CuSiSe , CuGeSe , CuSnSe , AgSiSe and AgGeSe . In all cases, samples were annealed at 625 or 600 °C and in each case showed the single phase structure listed in Table 3.1.3, regardless of whether the sample was brine-quenched to room temperature or cooled more slowly. This indicated that in each case, the single phase condition was stable from the annealing temperature down to room temperature. The DTA(Differential Thermal Analysis) results for the compounds carried out by other members of the group (90W1, 91L1) confirmed this for the case of CuGeSe .

ii) AgSiS . Samples were annealed at some seven temperatures in the range 400 - 750 °C and then quenched. The resulting X-ray photographs were all very similar, but no set of lines corresponding to any of the expected phases could be observed. It appears possible that in all cases

investigated, the sample was in a multi-phase condition. DTA measurements on a typical sample gave no useful indication of a suitable annealing temperature.

iii) AgGeS. A sample annealed at 625 °C and then quenched to room temperature gave an X-ray photograph very similar to the ones mentioned in section ii. However a sample annealed at 500 °C and quenched showed a orthorhombic single phase. In this case, DTA data for this compound gave a good guide to the choice of 500 °C as an annealing temperature.

iv) AgSnS. In this case, annealing at 625 °C and brine-quenching gave a sample that showed the cubic structure plus very faint extra lines corresponding to the orthorhombic phase. Guided by DTA data, annealing at 550 °C and quenching provided a sample showing single phase orthorhombic form.

v) AgSnSe. A sample annealed at 600 °C and then brine - quenched showed the orthorhombic structure with faint cubic lines. However, a similar sample annealed at 600 °C and then air-cooled to room temperature was cubic with only faint orthorhombic lines.

vi) CuSiTe. Samples were annealed at 700 and 650 °C and then brine-quenched. Each showed the tetragonal phase plus faint lines corresponding to the cubic phase and faint MnTe₂ lines. A sample annealed at 400 °C and brine-quenched showed the tetragonal phase with no cubic phase but again very faint MnTe₂ lines.

vii) CuGeTe. A sample annealed at 700 °C and then brine-quenched

showed only tetragonal plus very faint MnTe_2 lines. A sample similarly annealed at 700 °C and then slowly cooled to room temperature (in approximately 24 hours) showed the tetragonal phase plus several other undetermined phases and MnTe_2 . However, a sample annealed at 600 °C and air - quenched to room temperature had mainly tetragonal lines plus faint cubic and very faint MnTe_2 lines.

viii) CuSnTe . In this case, the annealing temperatures were chosen from study of the DTA. A sample annealed at 525 °C and then brine-quenched was tetragonal with faint cubic and MnTe_2 lines. However, when annealed at 450 °C and brine-quenched, the sample showed strong cubic lines, very faint MnTe_2 lines and no tetragonal lines.

ix) AgSiTe . Samples were annealed and quenched from various temperatures in the range 400-750 °C. All showed mainly orthorhombic structure plus a little cubic and MnTe_2 , the amounts of the last two varying somewhat with the different samples.

x) AgGeTe . When samples were annealed at 600 °C and either brine-quenched or air-quenched to room temperature, they showed mainly cubic lines plus other extra lines including MnTe_2 , the intensity of the extra lines varying from very faint to medium in the different samples. Annealing at 550 and 440 °C and quenching showed similar results. However a sample annealed at 400 °C and quenched was tetragonal plus a little MnTe_2 .

xi) AgSnTe . A sample annealed at 600 °C and air-quenched was cubic

with very faint tetragonal and MnTe_2 lines present. When annealed at 400 °C and brine-quenched, the sample showed both tetragonal and cubic lines and fainter MnTe_2 lines.

The actual X-ray films taken for the phases discussed above and being analyzed are shown in Figs.3.1.3-24.

As indicated by the above notes, for many of the compounds, X-ray patterns of both the orthorhombic or tetragonal and the cubic phases were observed so that lattice parameter data could be obtained for each (Figs. 3.1. 11, 21 and 24). In some cases, when the intensity of a particular set of lines was rather weak, the accuracy of the analysis was lower, but in all cases reasonable values could be obtained.

To show how lattice parameters were obtained, examples for each structure case are described as below.

1) Cubic case: CuSnTe

As mentioned in § 2.2, for cubic structure, $Q = NA$. It is known (74M1) for rock salt structure that the strong lines have $N = 4S$, where S is an integer. So for each measured Q, the corresponding A value could be obtained. But because of the absorption effect, there is a variation in the apparent value of a with θ . By plotting a vs. $f(\theta)$ as in Fig.3.1.1, where

$$f(\theta) = \frac{1}{2} \left(\frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta} \right) \quad (3.1 - 1)$$

by extrapolating a to $f(\theta) = 0$, the lattice parameter a is then obtained (56C1).

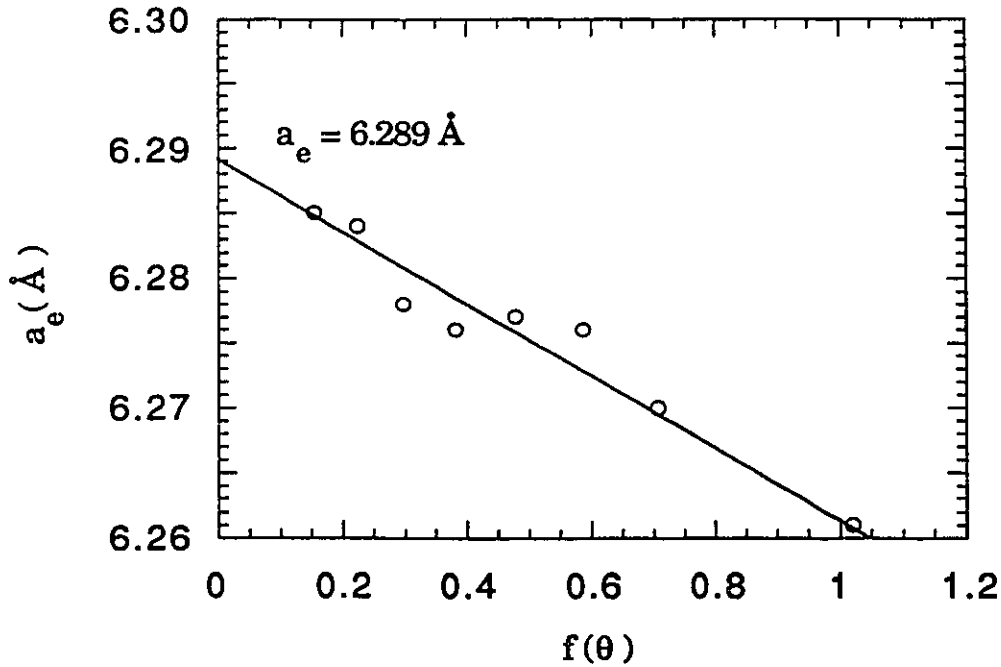


Fig.3.1.1 Extrapolation of measured lattice parameters against $f(\theta)$.

2) Tetragonal case: CuSnS

As is known for a tetragonal system $Q = N_1A + N_2C$ (equn.2.2-5)

Because all tetragonal samples investigated here have the stannite structure(74S1), hkl are known. For all the lines with known hkl values, a program was written to solve the equations below for A and C:

$$\begin{aligned} \sum Q &= A \sum N_1 + C \sum N_2 \\ \sum Q N_1 &= A \sum N_1^2 + C \sum N_1 N_2 \end{aligned} \quad (3.1 - 2)$$

With regard to the absorption effect, because it is necessary to solve for two parameters, the method used for the cubic case is difficult to apply. So while doing the X-ray diffraction, a standard substance such as Ge, Si

was included in the specimen. From the X-ray lines of the standard substance, a calibration curve of ΔQ ($= Q_m - Q_e$) was determined as a function of Q_m , as is shown in Fig.3.1.2. Here Q_m is the measured value and Q_e is the expected value given by the handbook. These corrections were then applied to the Q_m values for the sample to give the corrected values of Q for the sample. These values were then used as Q in the equations 3.1-2 to solve for A and C , once the values of A and C were obtained, they were submitted into equation 2.2-5, to produce the calculated values, indicated as Q_c , in order to compare with corrected Q values, the difference between these two values is calculated and indicated by δQ .

The calculated results of CuSnS are listed in table 3.1. 1.

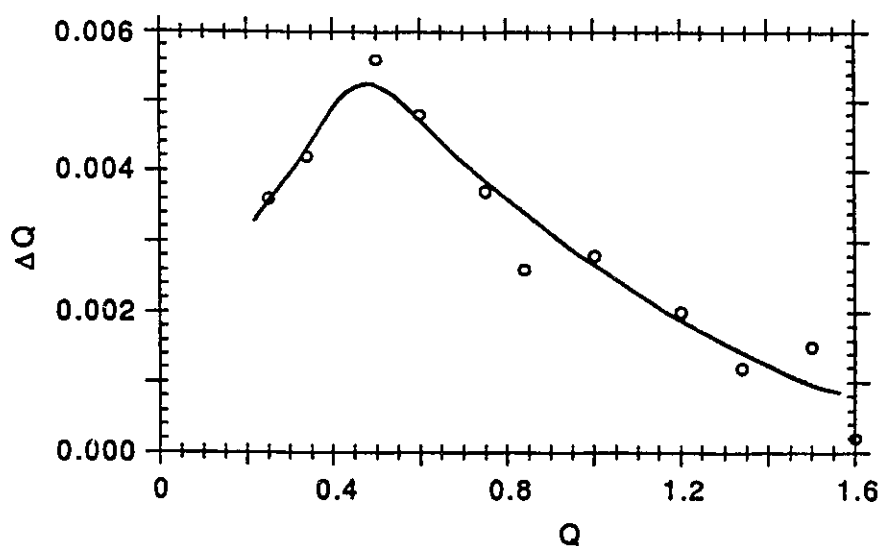


Fig. 3.1.2 Calibration curve of ΔQ against Q_m for the standard substance Ge.

3) Orthorhombic case: AgSiSe

In this case, equation 2.2 - 3 gives

$$Q = AN_1 + BN_2 + CN_3$$

From the results of Schafer and Nitsche, the first few strong lines for this case should have hkl values belonging to the set 210, 020, 002, 211, 021. Thus first few lines in the present work were fitted, where possible, to these hkl values, the rough values of A, B, C could be obtained. With the A, B, C values thus obtained above, different combinations of hkl were then tried in order to find the best fitting hkl values for higher angle lines. After h, k, l were found for all the structure lines which were well observed, a program was used to solve equations for A, B, C:

$$\begin{aligned}\sum Q &= A \sum N_1 + B \sum N_2 + C \sum N_3 \\ \sum QN_1 &= A \sum N_1^2 + B \sum N_1N_2 + C \sum N_1N_3 \\ \sum QN_3 &= A \sum N_1N_3 + B \sum N_2N_3 + C \sum N_3^2\end{aligned}\quad (3.1 - 3)$$

where values of Q were obtained in the same way as for the tetragonal case. The lattice parameters can then be found. With these values, the Q values were recalculated from equation 2.2-3, indicated as Q_c .

The results for AgSiSe are listed in table 3.1.2.

Line Posi.(mm)	N ₁	N ₂	Q	Q _c	δQ
28.12	2	4	0.0995	0.1001	-0.0006
46.57	8	0	0.2634	0.2633	0.0001
47.10	4	16	0.2691	0.2686	0.0005
55.31	10	4	0.3631	0.3634	-0.0003
56.23	2	36	0.3743	0.3738	0.0005
67.99	16	0	0.5269	0.5267	0.0002
69.52	0	64	0.5479	0.5476	0.0003
75.15	18	4	0.6268	0.6267	0.0001
75.89	10	36	0.6373	0.6372	0.0001
86.77	20	16	0.7953	0.7952	0.0001
87.93	8	64	0.8123	0.8109	0.0014
93.14	26	4	0.8889	0.8901	-0.0012
93.84	18	36	0.8992	0.9005	-0.0013
111.59	34	4	1.1529	1.1534	-0.0005
112.43	26	36	1.1643	1.1639	0.0004
114.10	36	0	1.1868	1.1850	0.0018
124.44	40	0	1.3194	1.3167	0.0027
133.94	34	36	1.4275	1.4272	0.0003
136.08	40	16	1.4498	1.4536	-0.0038
153.99	32	64	1.6001	1.6009	-0.0008

Table 3.1.1 X-ray film analysis for CuSnS(t).

h	k	l	Q	Q _c	δQ
0	2	0	0.9080	0.9096	0.0002
0	0	2	0.1015	0.1020	-0.0005
2	1	1	0.1144	0.1145	-0.0001
0	2	1	0.1156	0.1161	-0.0005
2	0	2	0.1689	0.1684	0.0005
2	3	0	0.2703	0.2703	0.0000
0	2	3	0.3205	0.3202	0.0003
2	3	2	0.3722	0.3723	-0.0001
4	2	1	0.3823	0.3816	0.0007
0	0	4	0.4083	0.4081	0.0002
2	4	0	0.4285	0.4289	-0.0004
4	2	2	0.4575	0.4581	-0.0006
4	2	3	0.5852	0.5856	-0.0004
2	3	4	0.6790	0.6784	0.0006
4	4	2	0.7301	0.7300	0.0001

Table 3.1.2 X-ray film analysis for AgSiSe(o).

Using the above methods of analysis, values of lattice parameters were obtained for all of the different phases listed above. Values are summarized in table 3.1.3. The lattice parameters listed in the table have the precision of $\pm 0.0005\text{nm}$. As shown by Guen and Glaunsinger (80G1), one convenient parameter for characterizing these compounds is the effective lattice parameter a_e ,

$$a_e = (V / N)^{1/3} \quad (3.1 - 4)$$

where V is the volume of the unit cell and N, the number of molecules per cell. The values of a_e for all the structures investigated here are given in table 3.1.3.

In order to look at the variation of the a_e values shown in table 3.1.3, it has been found useful to plot them against the values of the molecular weight W of the compound concerned, and the results are shown in Fig. 3.1.29. It is seen that for given groups of compounds, the variation of a_e with W is linear. Thus it is seen that for the Cu compounds, all of the phases with a tetrahedrally bonded structure, whether tetragonal or orthorhombic, lie on the same straight line. However, in the case of the corresponding tetrahedrally bonded Ag structures, two straight lines are observed. If these Ag values are compared with the magnetic data (see chapter 4), it is found that the three phases lying on the higher line (AgGeS, AgSnS and AgSnSe-all orthorhombic) are antiferromagnetic, while the phases lying on the lower line (AgSiSe, AgGeSe, and AgSiTe - orthorhombic , and AgGeTe and AgSnTe -tetragonal) are all ferrimagnetic.

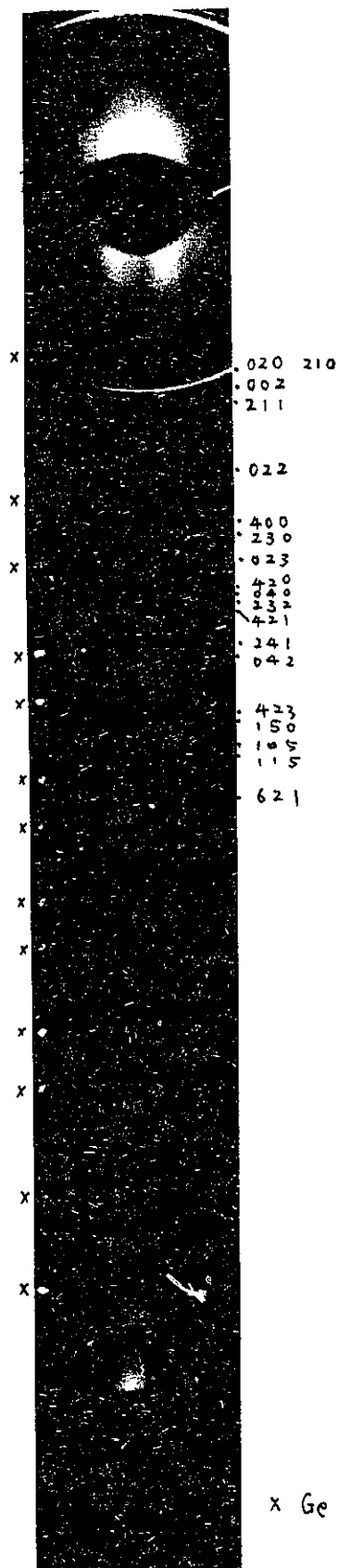
	Compound	Symm.	a (nm)	b (nm)	c (nm)	a _o (nm)	W
1	CuSiSe	o	0.7914	0.6784	0.6502	0.5589	526.0
2	CuGeSe	o	0.7981	0.6874	0.6550	0.5642	570.5
3	CuSnSe	t	0.5774		1.1423	0.5753	616.6
4	CuSiTe	t	0.5983		1.1724	0.5942	720.6
5		c	0.6050			0.6050	
6	CuGeTe	t	0.5989		1.1978	0.5989	765.1
7		c	0.6150			0.6150	
8	CuSnTe	t	0.6049		1.2098	0.6049	811.2
9		c	0.6289			0.6289	
10	AgSiSe	o	0.7764	0.6644	0.6261	0.5445	614.6
11	AgGeSe	o	0.7830	0.6721	0.6417	0.5527	659.1
12	AgSnSe	o	0.8424	0.7348	0.6986	0.6002	705.2
13		c	0.5490			0.5490	
14	AgSiTe	o	0.8120	0.6876	0.6689	0.5717	809.2
15		c	0.5750			0.5750	
16	AgGeTe	t	0.5790		1.1580	0.5790	853.7
17		c	0.5882			0.5882	
18	AgSnTe	c	0.6005		0.6005		
19		t	0.5850		1.1700	0.5850	899.8
20	CuSiS	o	0.7534	0.6330	0.6205	0.5320	338.4
21	CuGeS	o	0.7629	0.6514	0.6265	0.5380	382.9
22	CuSnS	t	0.5511		1.0820	0.5474	429.0
23	AgGeS	o	0.7947	0.6892	0.6527	0.5632	471.0
24	AgSnS	o	0.8019	0.6964	0.6527	0.5705	517.7
25		c	0.5235			0.5235	
26	AgSiS	-					427.1

Table. 3.1.3 Symmetry and lattice parameter values for each compound.

o = orthorhombic, t = tetragonal, c = cubic.

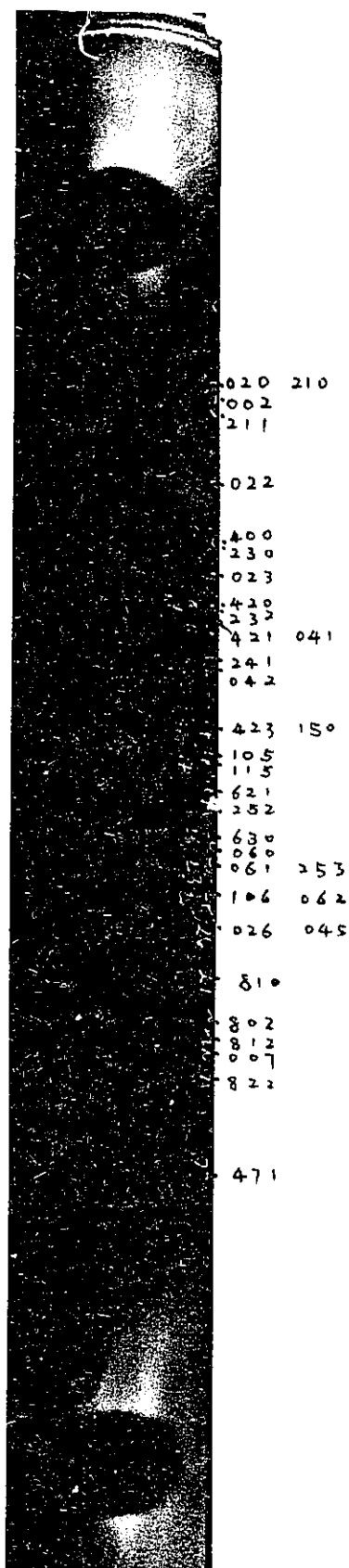
These three lines corresponding to the tetrahedrally bonded structure have very similar slopes. Turning to the presumed octahedrally bonded cubic structures, it is seen that again the three Cu cases appear to lie on a straight line, while the four ferrimagnetic Ag phases of this form lie on a second line of very similar slope. Finally there is one cubic Ag compound which is antiferromagnetic (AgSiS), and this lies on none of the above lines, thus is not shown in the graph.

The question arises as to why there are two distinct lines for the Ag tetrahedrally coordinated phases, while all of the corresponding Cu phases lie on a single line. One possibility is that the behaviour is due to differences in structure. Parthé et al. (69Pi) carried out a detailed investigation of the crystal structure of $\text{Cu}_2\text{CdGeS}_4$, which has the orthorhombic symmetry, and other related compounds. In addition to the wurtz-stannite structure with space group $\text{Pmn}2_1$, they also considered the $\text{Na}_2\text{ZnSiO}_4$ structure with pseudo-orthorhombic Pn symmetry and other possible structures. It was shown that for $\text{Cu}_2\text{CdGeS}_4$, the wurtz-stannite and $\text{Na}_2\text{ZnSiO}_4$ structures would give very similar X-ray photographs, differing only in the intensity of the weak ordering lines. In the present work, the Debye-Scherrer powder method used are not able to distinguish between different structures of this type, and hence it is not possible to say from the X-ray data what the details of the orthorhombic structure are. Thus it is quite possible that the two different lines for the tetrahedrally coordinated Ag compounds represent different ordered structures.



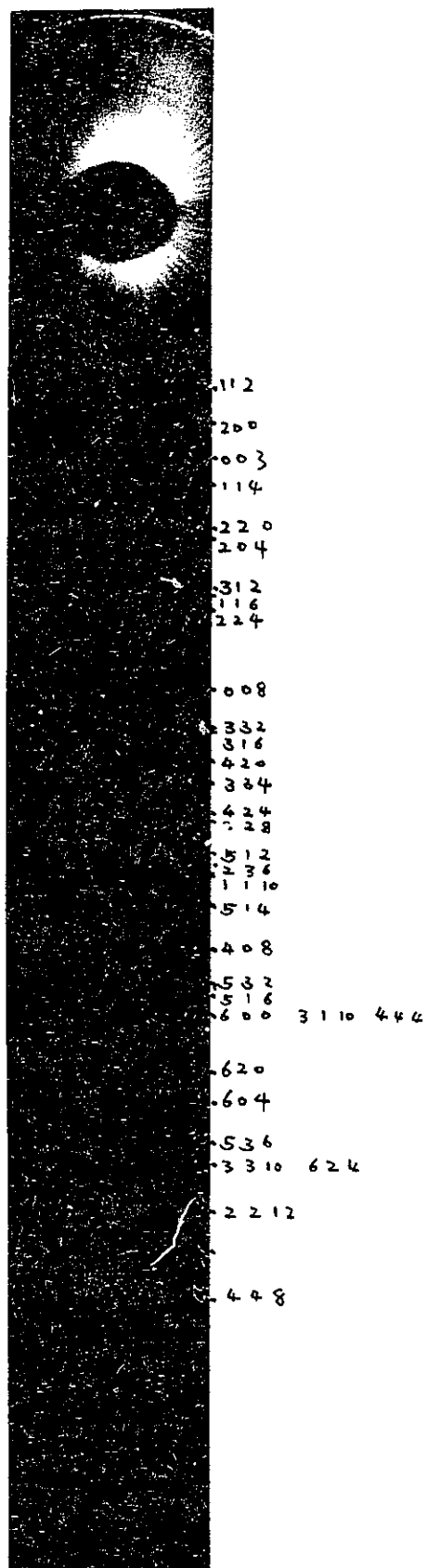
1. CuSiS (0)
+ Ge

Fig. 3.1.3



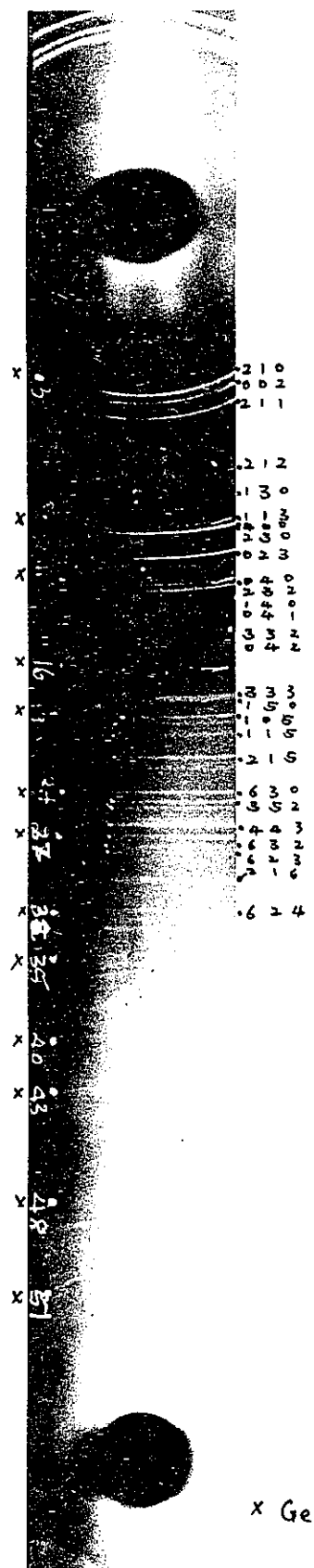
2. CuGeS (0)

Fig. 3.1.4



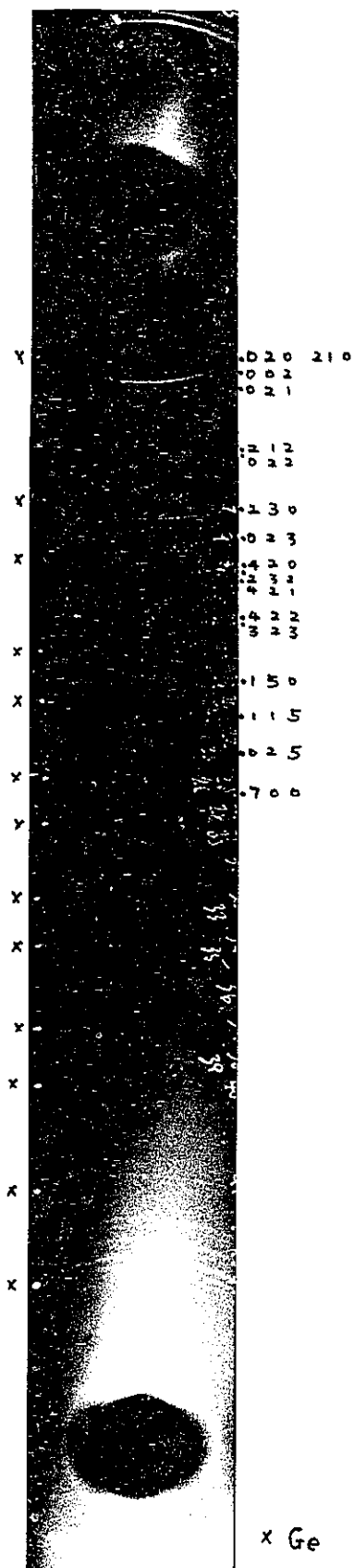
3. CuSnS_2

Fig. 3.1.5



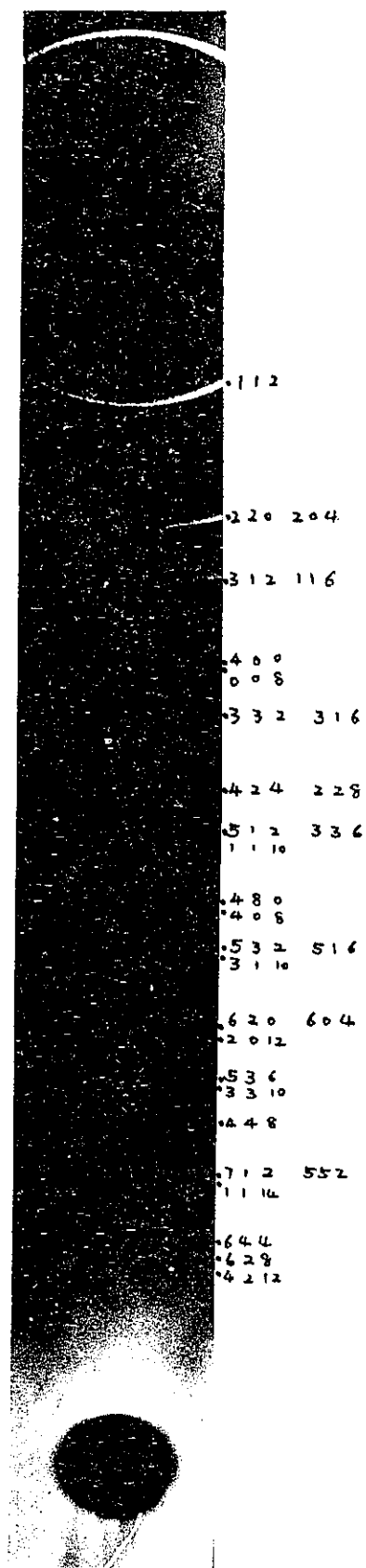
4. $\text{CuSiSeO} + \text{Ge}$

Fig. 3.1.6



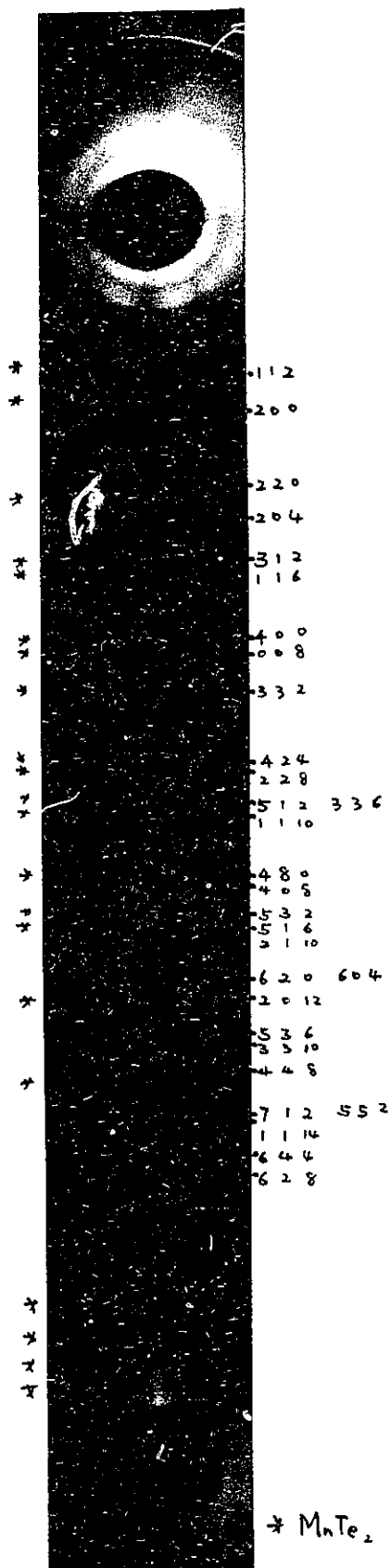
5. CuGeSe. 0 + Ge

Fig. 3.1.7



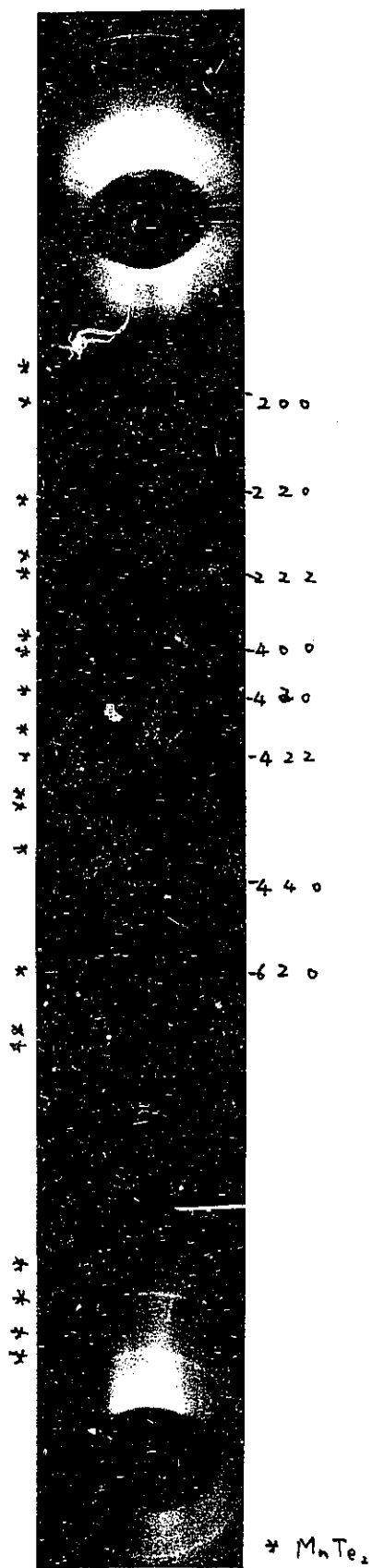
6. CuSnSe. *

Fig. 3.1.8



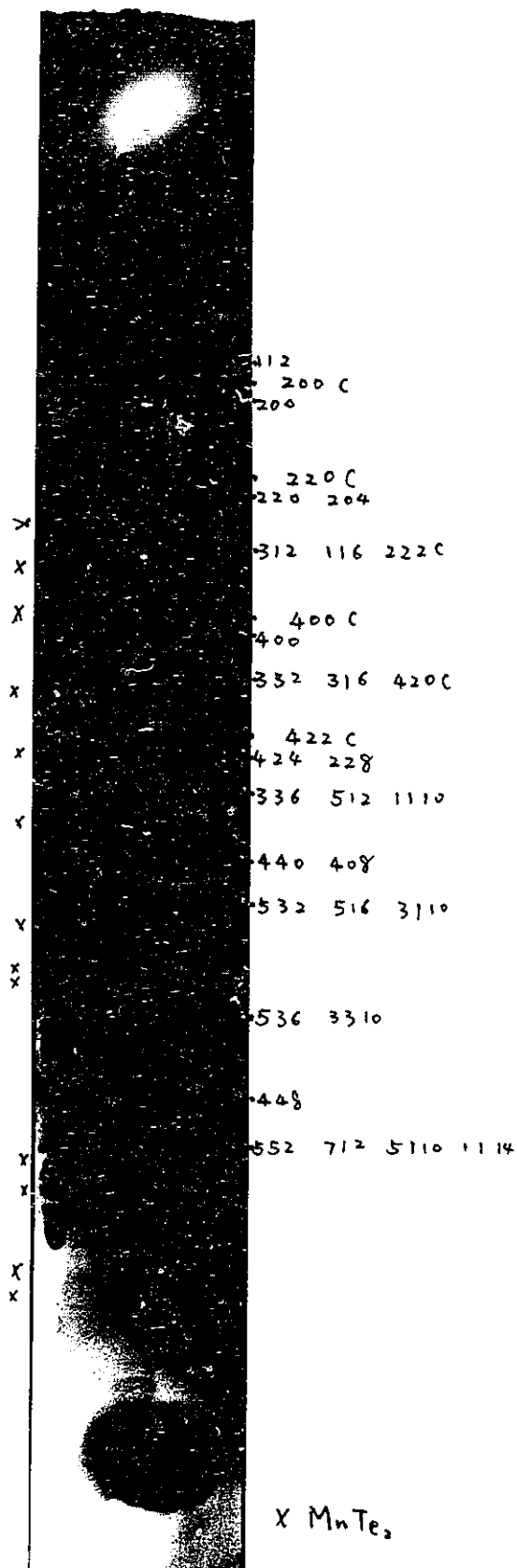
7. CuSiTe₂ t

Fig.3.1.9



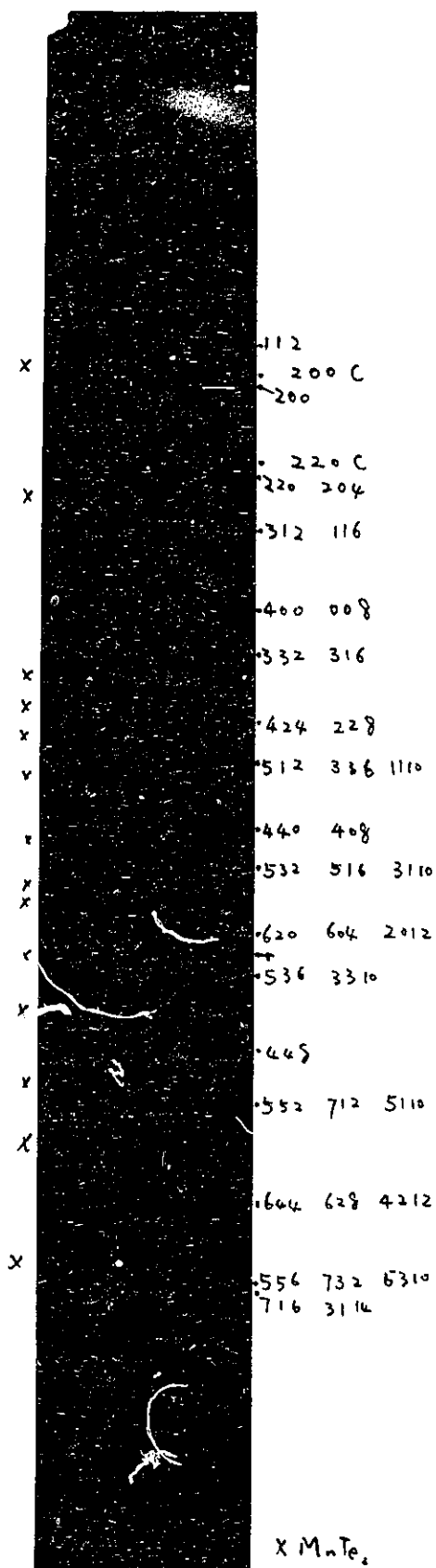
8. CuSiTe₂ c

Fig.3.1.10



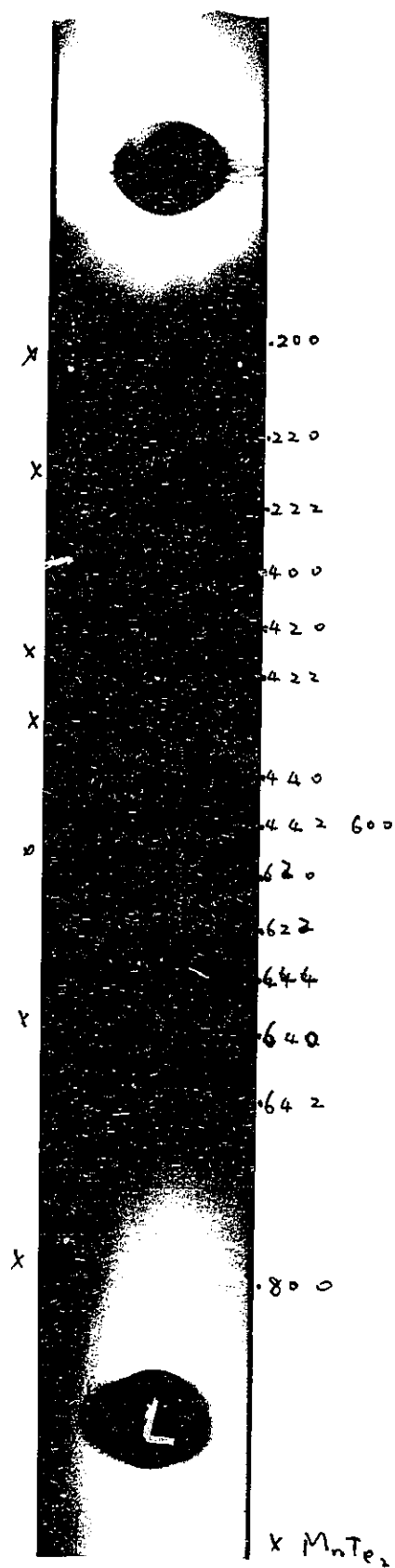
9.10. CuGeTe. C + t

Fig. 3.1-11



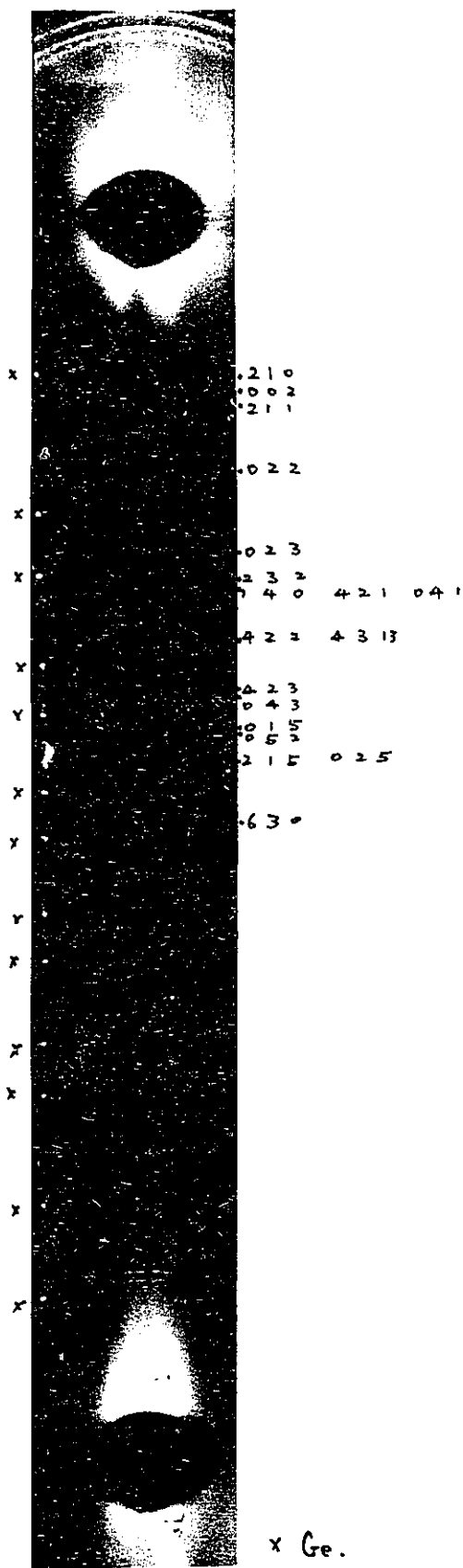
11. CuSnTe. x

Fig. 3.1.12



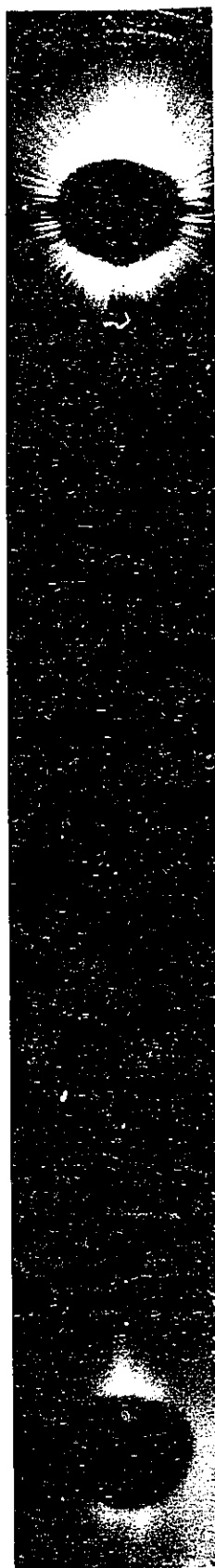
12. CuSnTe. c

Fig. 3.1.13



14. AgGeS.0 + Ge

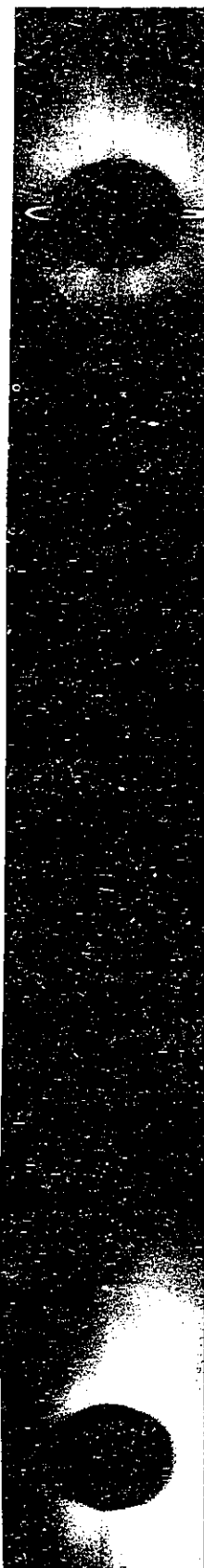
Fig-3.1.14



210 020
 002
 211
 022
 400 230
 023
 232
 421
 241
 042
 423 150
 105
 115

15. AgSnS.0

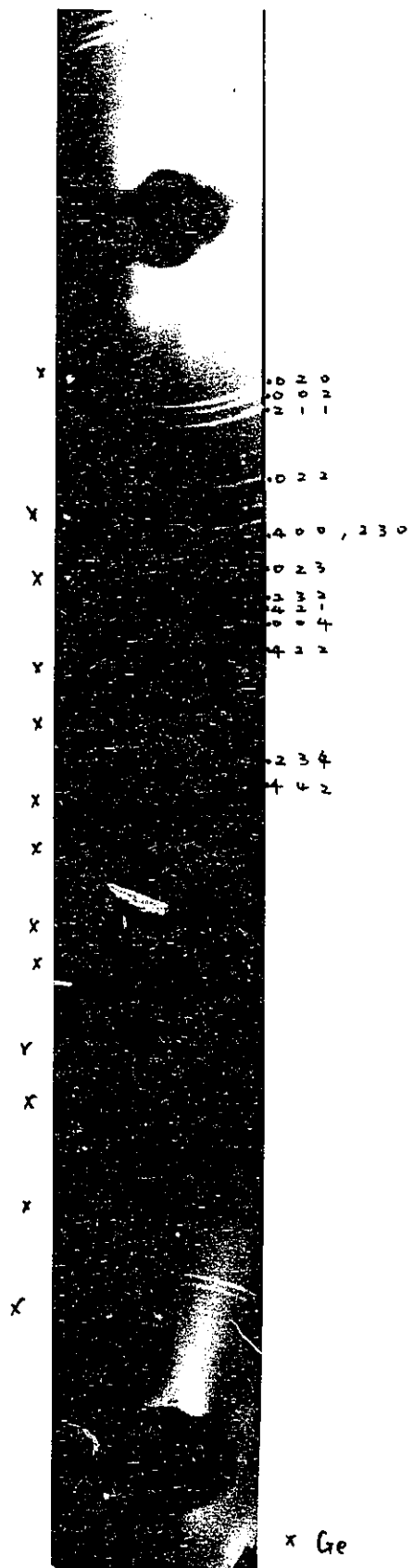
Fig. 3.1.15



111
 200
 220
 311
 222
 400
 420
 422
 440
 442 600
 620
 622

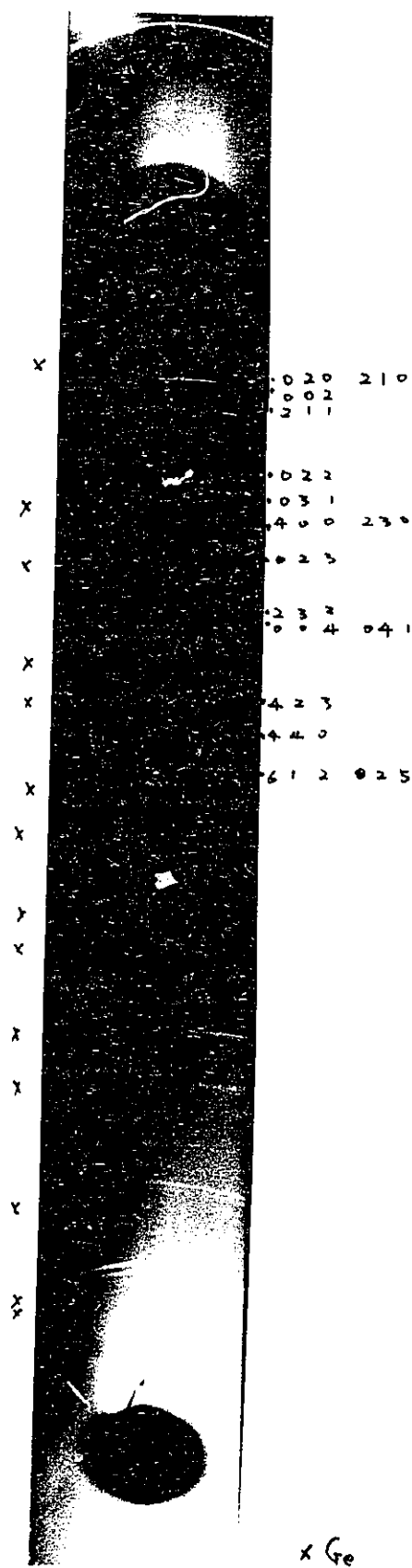
16. AgSnS.c

Fig. 3.1.16



17. AgSiSe.0 + Ge

Fig. 3.1.17



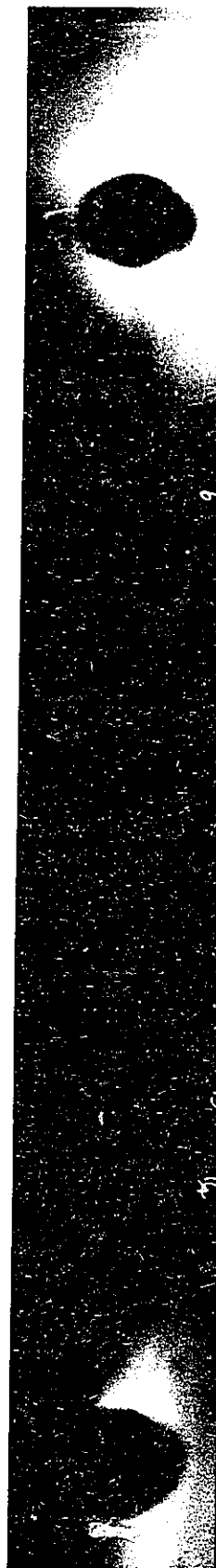
18. AgGeSe.0 + Ge

Fig. 3.1.18



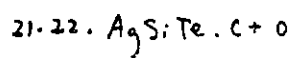
19. AgSnSe.0

Fig. 3.1.19

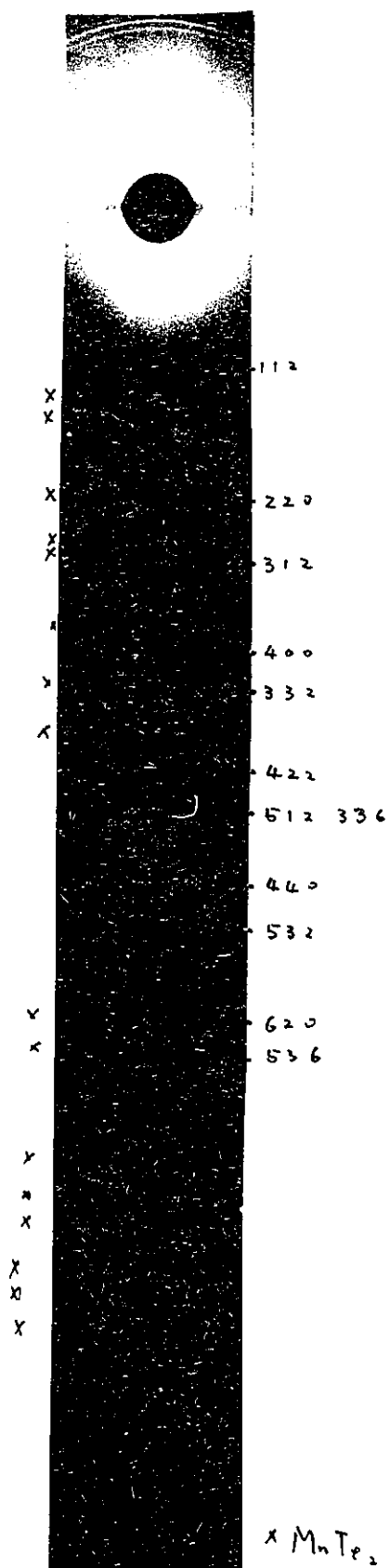


20. AgSnSe.C

Fig. 3.1.20

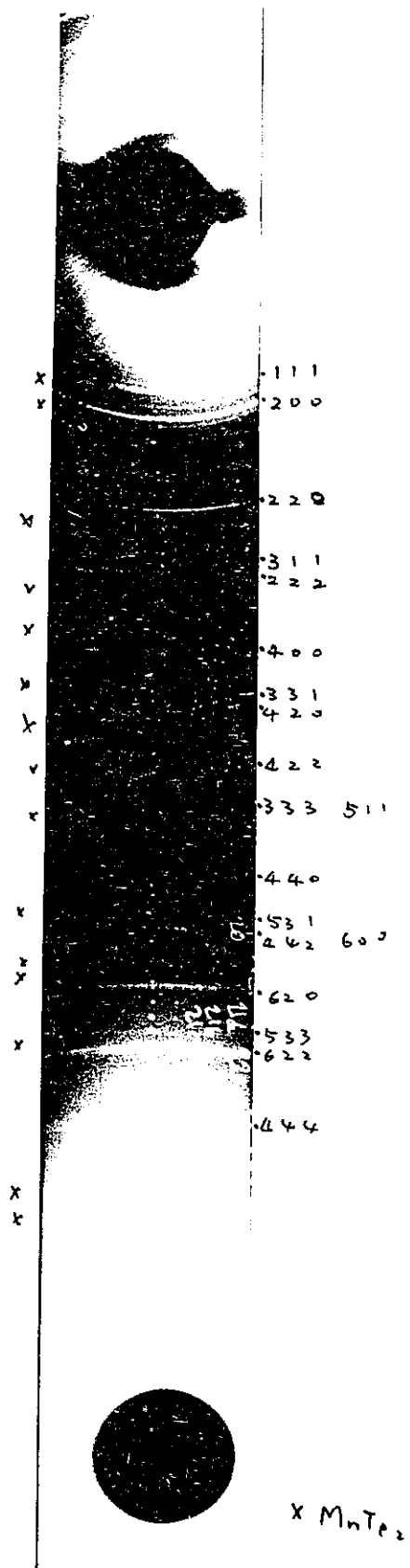


58



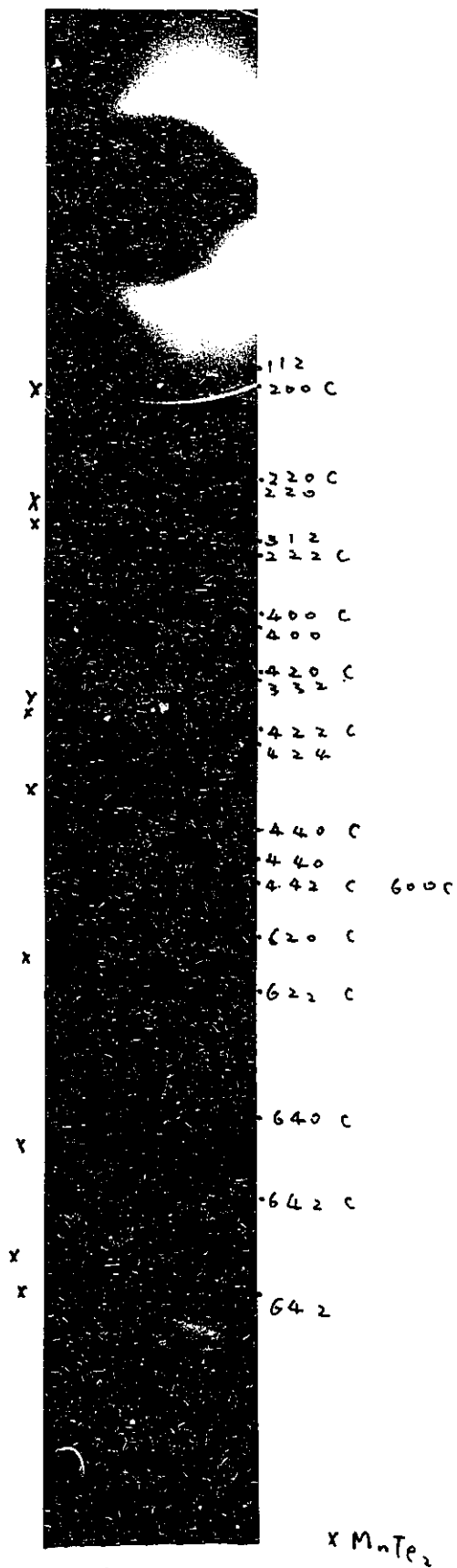
23. $\text{AgGeTe} \cdot x$

Fig. 3.1.22



24. $\text{AgGeTe} \cdot \text{C}$

Fig. 3.1.23



25.26. AgSnTe. $\lambda + c$

Fig. 3.1.24

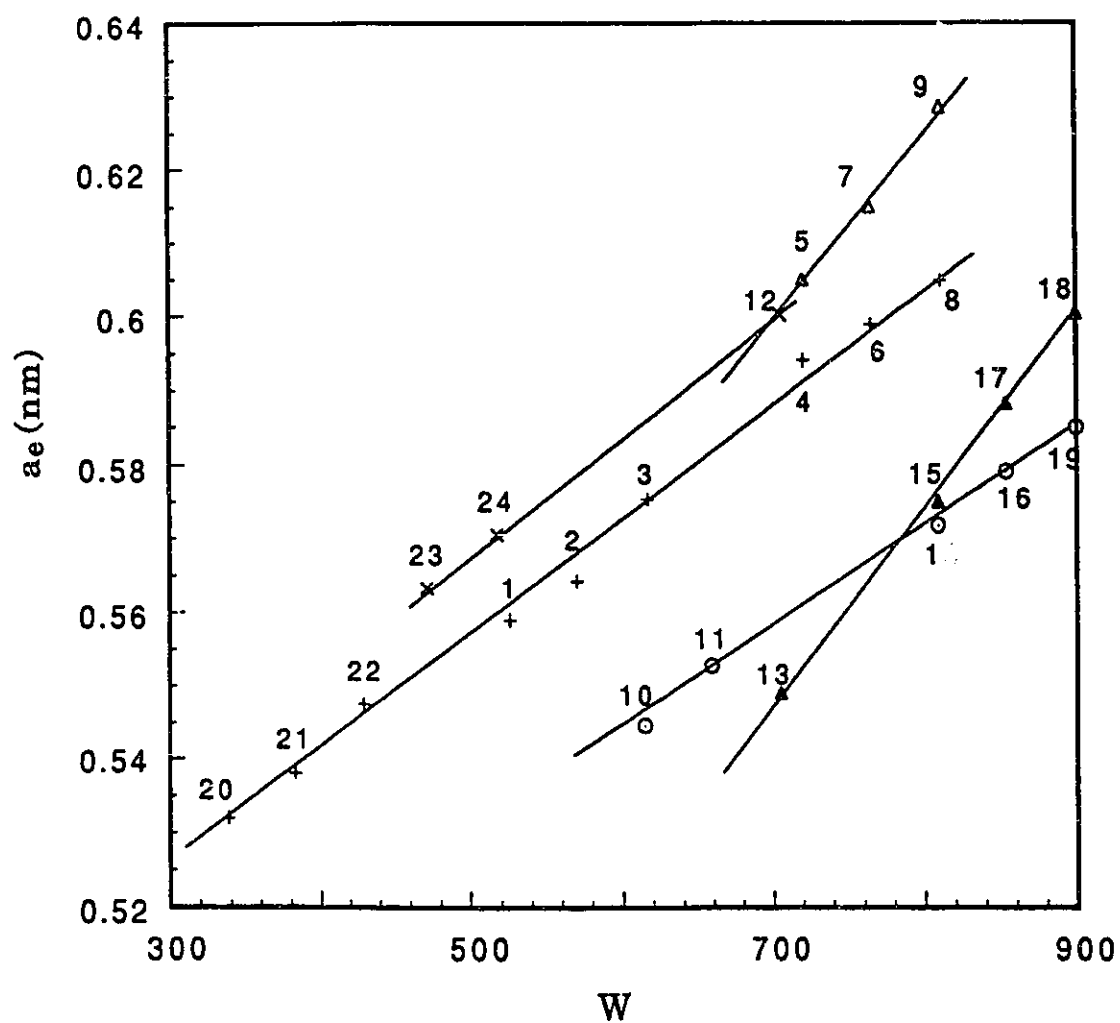


Fig. 3.1.25 Variation of effective lattice parameter a_e with molecular weight W .

Composition numbers as in table 3.1.3.

+ set I × set II o set III Δ set IV ▲ set V

§ 3.2 Summary

The $I_2.Mn.IV.VI_4$ compounds which contain neither Ag or Te show only one structure for each compound and these are stable down to room temperature, the structure in each case appearing to be one of the ordered tetrahedrally-bonded tetragonal stannite or orthorhombic wurtz-stannite structures previously described (Chapter 1). However, for all the Te compounds plus AgSnS and AgSnSe, two different structures are observed for each compound, depending on the heat-treatment given. In addition, all of the Te compounds break up into two or more phases when slowly cooled to room temperature, one of these phase being $MnTe_2$. For each of these latter compounds, in addition to tetragonal or orthorhombic ordered structures mentioned above, a cubic structure is observed with X-ray line pattern indicating the rock-salt structure. In the case of the Te compounds, these structures are meta-stable when brine-quenched to room temperature, samples retaining their crystallographic and magnetic behaviour for at least eighteen months of shelf-life. If the values of the parameter $a_0 (= (V / N)^{1/3})$ for each phase observed are plotted against values of the molecular weight of the compound, it is found that the points line on five different straight lines, each line being characteristic of a particular structure and magnetic behaviour. On this basis, it is suggested that the Ag compounds with orthorhombic symmetry show two different, but very similar, structures.

Chapter 4 Magnetic Behaviour

§ 4.1 Results and Analysis

Measurements of magnetic susceptibility were made as a function of temperature on 18 different samples. In all case sample was initially zero field cooled(ZFC) and then the field applied. Measurements were then made when the temperature of the samples was increased(FW). Seven of these samples showed antiferromagnetic behaviour, viz. CuSiSe(o), CuGeSe(o), CuSnSe(t), CuSiTe(t), CuSiTe(c), CuGeTe(t) and AgSnSe(o) where (o), (t) and (c) indicate respectively orthorhombic, tetragonal and cubic symmetry. The curves of $1/\chi$ vs. T for AgSnSe(o) and CuSiSe(o) are shown in Figs. 4.1.1a & b, and are similar to the previously reported antiferromagnetic behaviour of various Cu compounds (80G1, 88S1). The curves for the CuGeSe(o) and CuSnSe(t) samples showed very similar forms as in Fig. 4.1.1c & d. For antiferromagnetic behaviour of this type, as discussed in § 2.3, the variation of $1/\chi$ with T well above the Néel temperature T_N is given by the relation

$$\frac{1}{\chi} = \frac{T - \theta_a}{C} \quad (4.1-1)$$

where θ_a is the Curie-Weiss temperature and C the Curie constant, while the minimum in $1/\chi$ at lower temperatures gives the Néel temperature T_N . Thus experimental values of the Néel temperature T_N , Curie-Weiss θ_a and Curie constant C were obtained for these latter four samples. For

materials of this type, with one Mn atom per molecule, the theoretical values of C is given by (66S1)

$$C = \frac{N_A g^2 \mu_B^2 S (S + 1)}{3 k W} \quad (4.1 - 2)$$

where N_A is Avogadro's number, μ_B the Bohr magneton and W the molecular weight . Assuming for Mn that $g = 2$ and $S = 5/2$, C can be separately determined for each material by

$$C = 4.375 / W \text{ (emu K / g)} \quad (4.1 - 3)$$

It was found that the experimental values obtained for C for the above four cases (i.e. CuSiSe (o), CuGeSe (o), CuSnSe (t) and AgSnSe (o)) agree with the theoretical values within the error of $\pm 10\%$ expected for the present measurements as discussed below. The values obtained for T_N and θ_a in these cases are given in Table 4.1.1(page 75).

However, for the cases of compounds showing two different structures, it was not always possible to obtain a sample of a given structure without any amount of the other phase being present and contributing some effect to the $1/\chi$ vs. T curve. This occurred for the samples CuSiTe(t), CuSiTe(c) and CuGeTe(t) as shown in Figs. 4.1.1e & f. While it was still possible to determine separate values of T_N for each structure, no accurate value of θ_a or C could be found in these cases. An extreme case of this shown in Fig. 4.1.1e for CuSiTe, where similar amount of the t and c phases were present, and the $1/\chi$ vs. T curve shows the two separate peaks corresponding to the T_N values. The values of T_N obtained

for these cases are again given in Table 4.4.1(page 75).

For the other 11 samples, the $1/\chi$ vs. T curves showed in each case a form usually ascribed to ferrimagnetic behaviour. At this stage, it is not possible to rule out other effects such as the canted antiferromagnetism (weak ferromagnetism) forms proposed by Dzialoshinsky (58D1) and Moriya (60M1). However, the present $1/\chi$ vs. T curves seemed to have a form closer to that of Néel ferrimagnetism than to these latter cases, and, as will be discussed below, the analysis in terms of a Néel equation gave parameters which were consistent with conclusions from the crystallographic data. For convenience, the term ferrimagnetic will be used here to refer to the magnetic materials. As indicated above and also in the crystallographic work (Chapter 3), in the majority of cases the condition of a sample was critically dependent upon the exact heat-treatment used, particularly in the case of the Te materials for which the equilibrium state at lower temperatures is two- or three-phase. Thus after the appropriate anneal and quench treatment, samples for magnetic measurements were chosen to have a minimum of unwanted phases, as seen from the X-ray photographs. Of the 12 ferrimagnetic samples, 7 were found to show only very small traces of other phases. These were CuGeTe(c) , AgSiSe(o) , AgGeSe(o) , AgSiTe(o) , AgGeTe(t) , AgGeTe(c) and AgSnTe(c) , and the resulting curves of $1/\chi$ vs. T are shown in Figs. 4.1.2a, b, c, d and 4.1.3a, b, c. For the other 4 samples, although the ferrimagnetic behaviour of the main phase could be clearly observed, this was superimposed on the contribution of another phase. These are shown

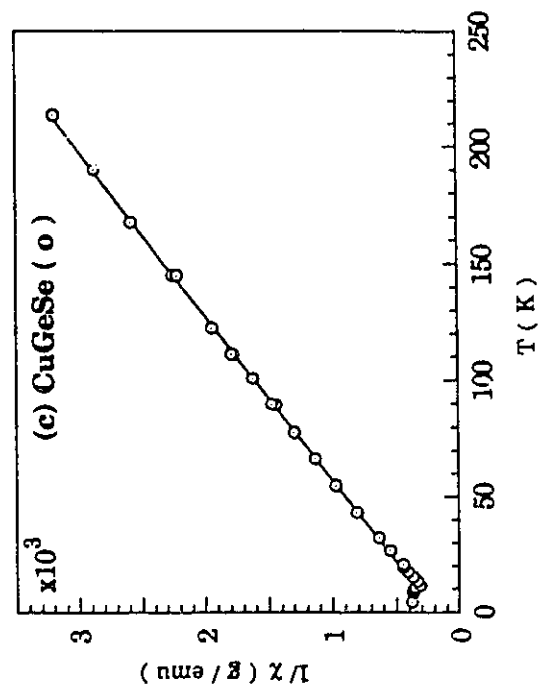
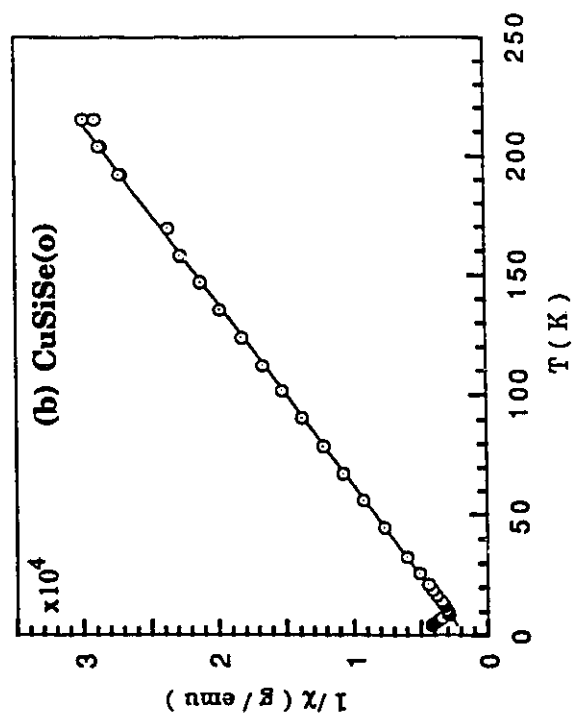
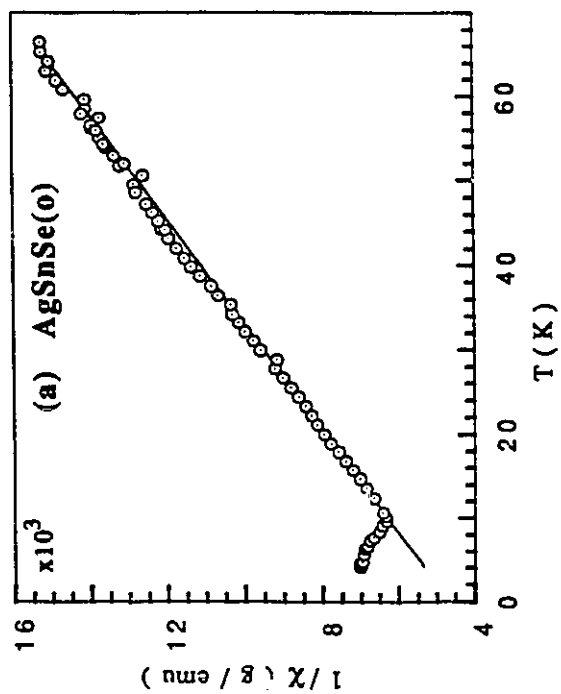


Fig. 4.1.1 Variation of $1/\chi$ with T for typical antiferromagnetic Mn quaternaries.
 • experimental values
 — fit to eqn. 4.1-1

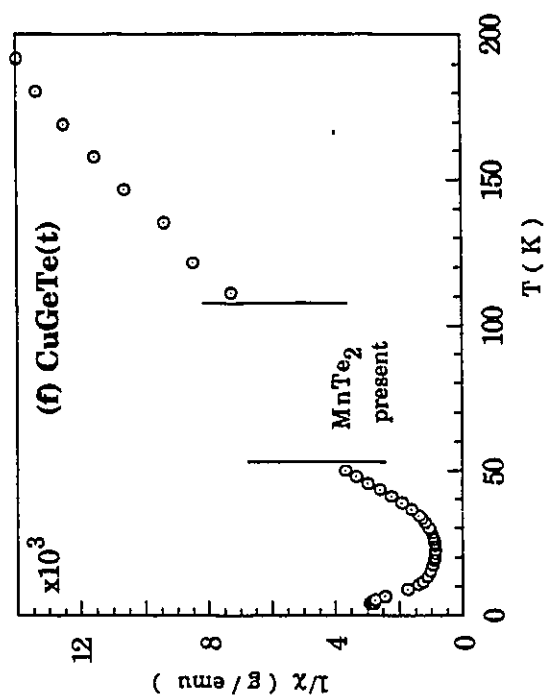
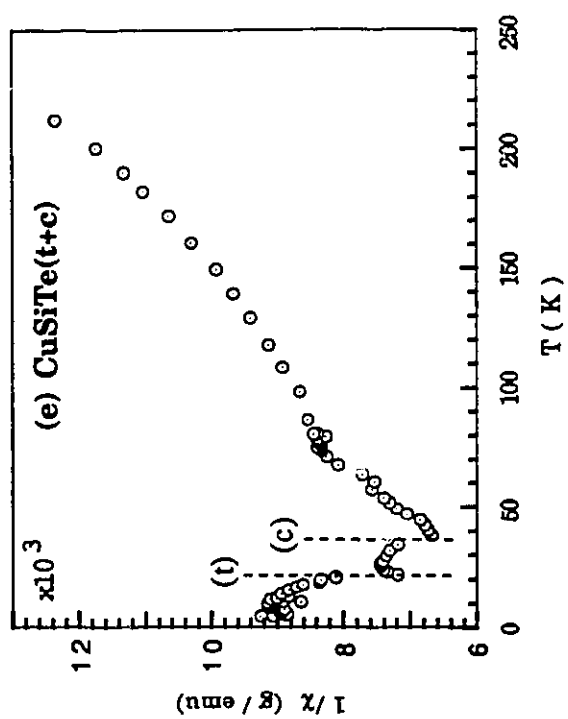
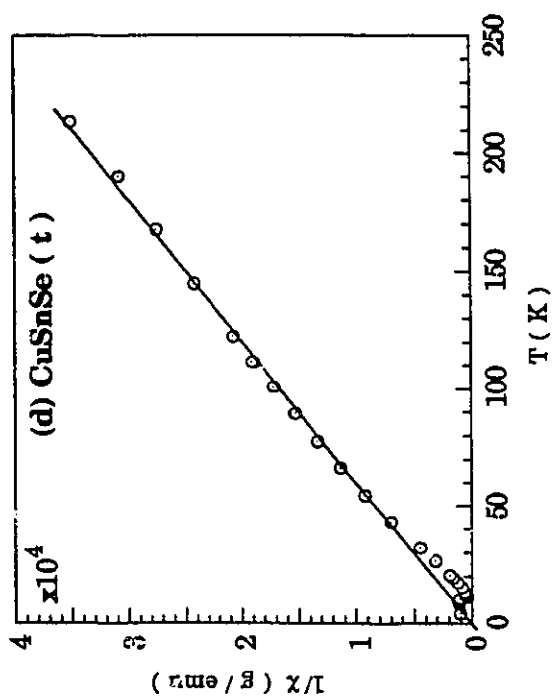


Fig. 4.1.1 continued

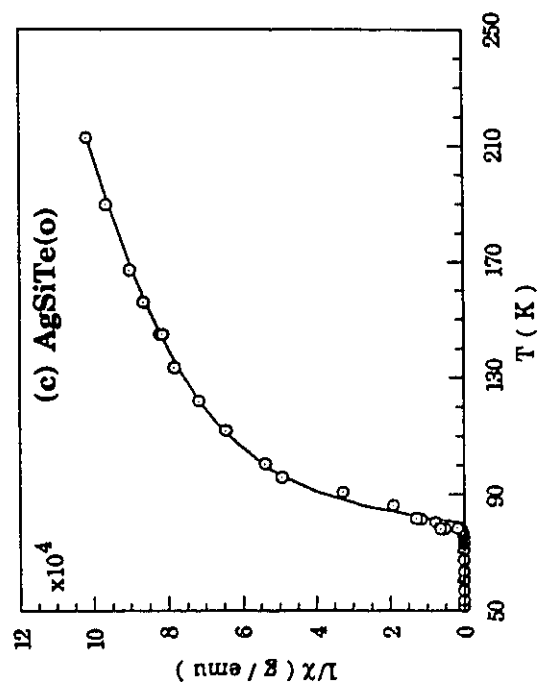
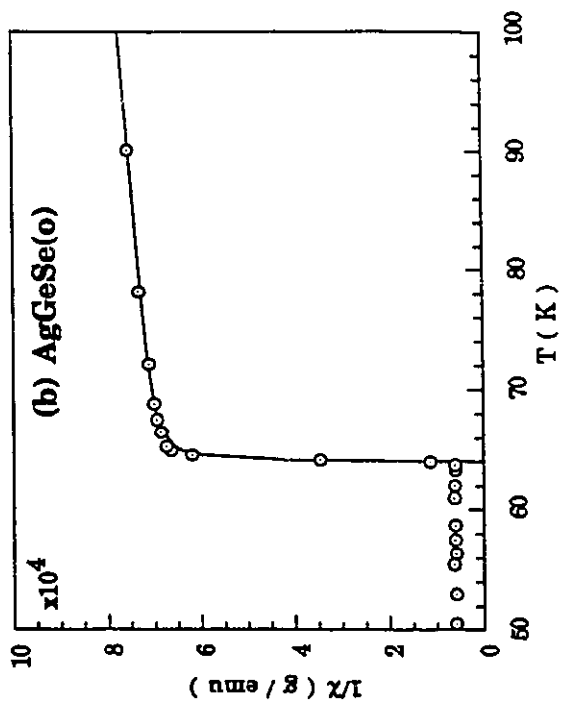
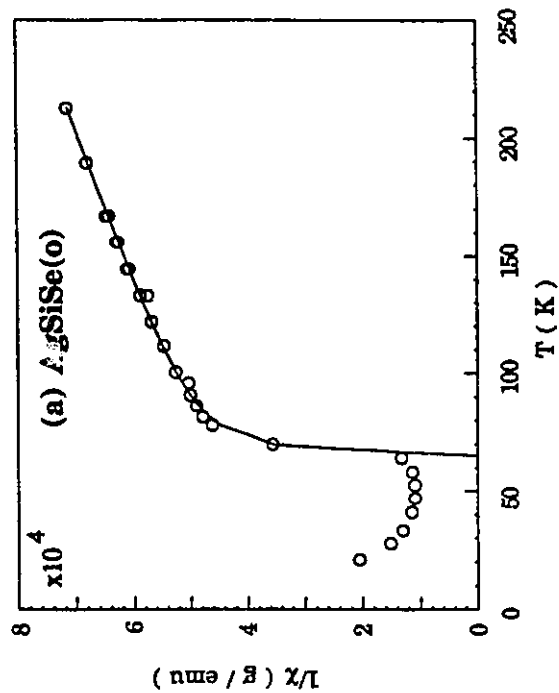


Fig. 4.1.2 Variation of $1/\chi$ with T for typical ferrimagnetic tetrahedrally-coordinated quaternaries.
 ○ experimental values
 — fit to equn. 4.1-5

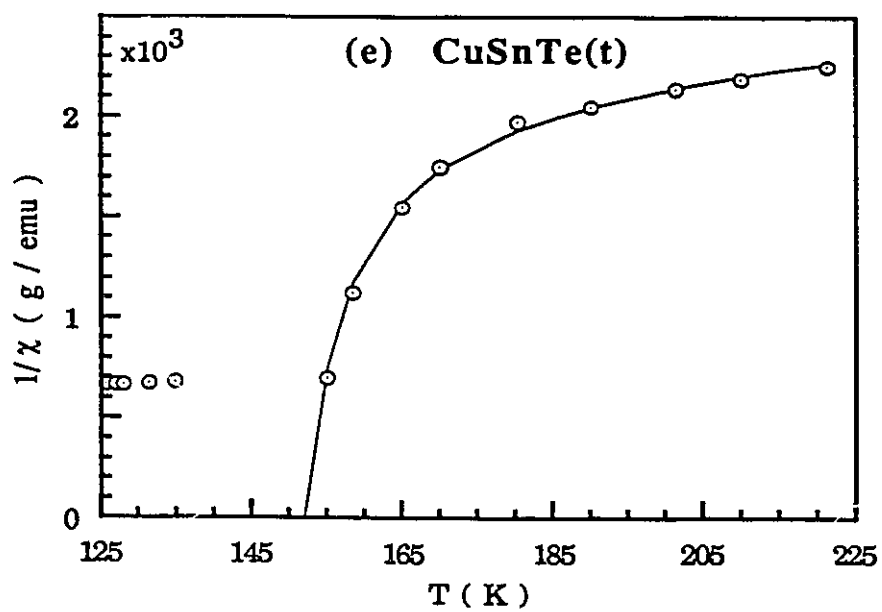
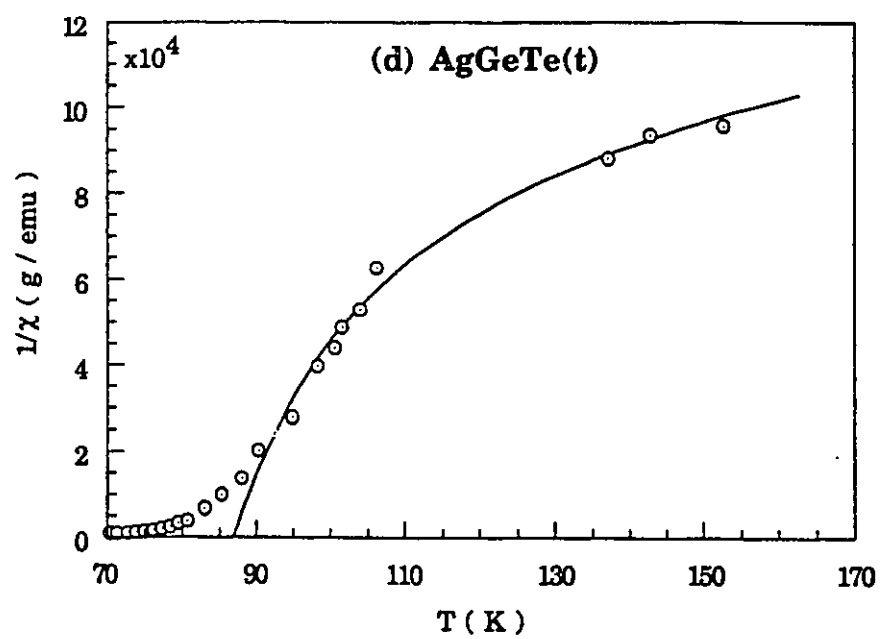


Fig. 4.1.2 continued

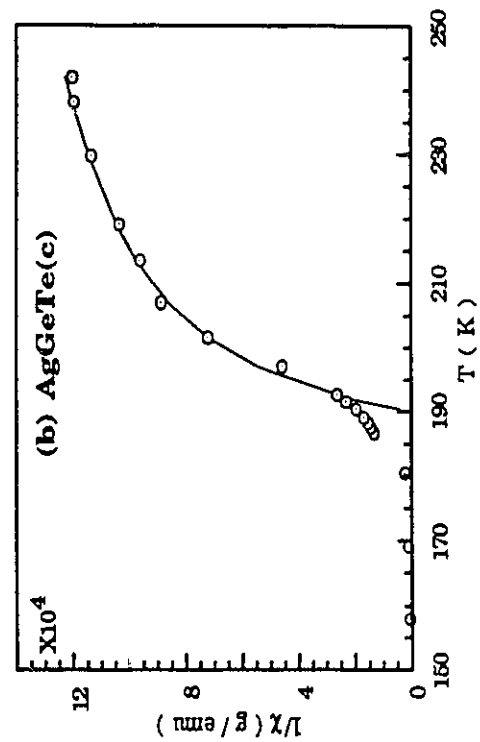
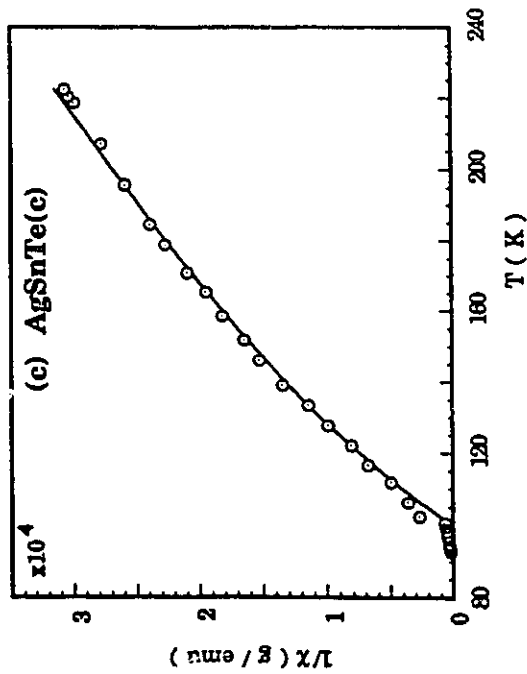
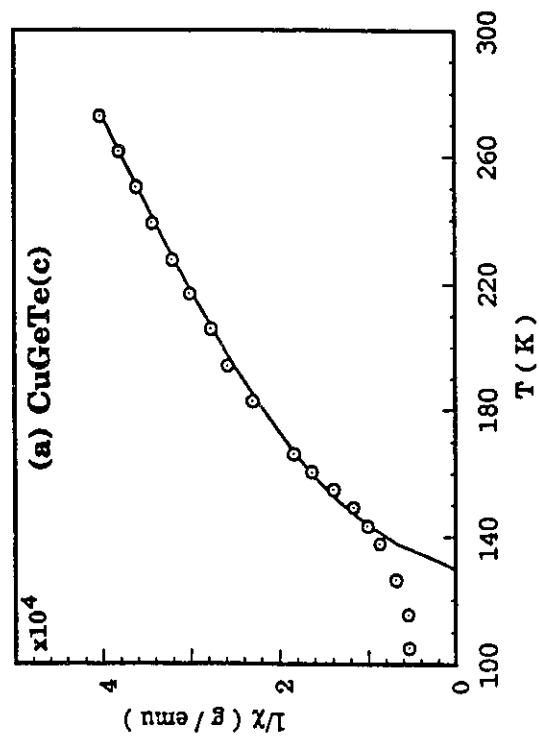


Fig. 4.1.3 Variation of $1/\chi$ with T for ferrimagnetic 'cubic' Mn quaternaries.
 • experimental values
 — fit to eqn. 4.1-5

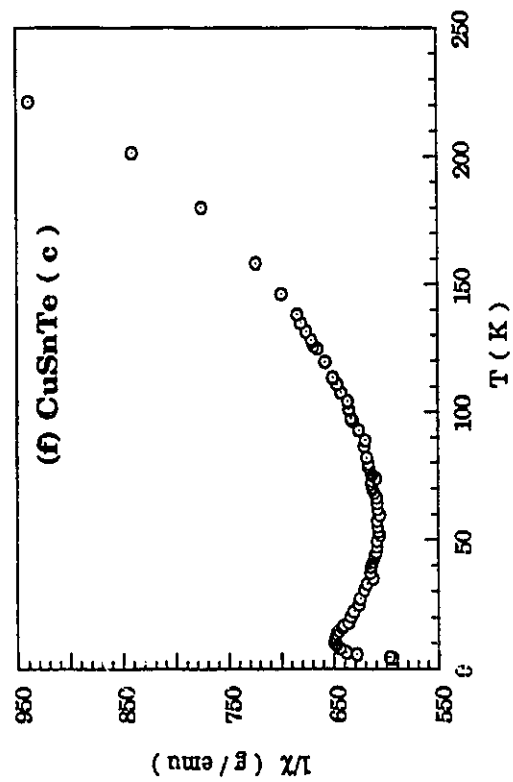
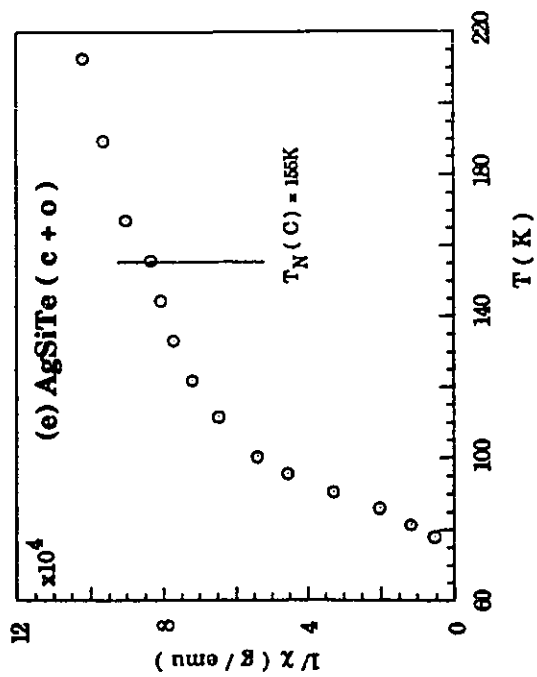
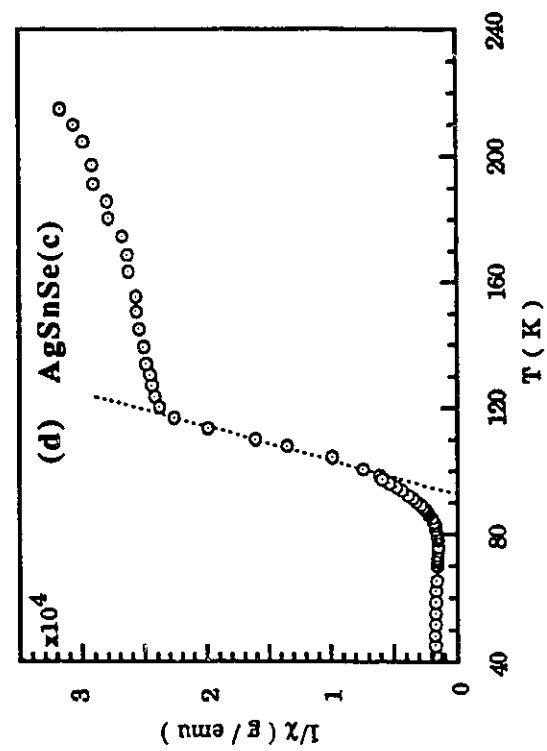


Fig. 4.1.3 continued

in Figs. 4.1.2e and 4.1.3d, e, f for the cases of CuSnTe(t) and AgSnSe(c), AgSiTe(c + o), CuSnTe(c) which are discussed further below. Hence, for these four samples, a reasonable value could be estimated for T_N , but other ferrimagnetic parameters could not be determined.

With regard to the magnitude of the $1/\chi$ values, the experimental system was calibrated using superconducting lead spheres as a standard so as to give χ in units of e.m.u. /g. However, two factors can affect the values obtained for χ . Firstly, the value determined for χ depends upon the mass m of material measured. Thus if an amount of a second phase were present, the weighed value of the sample would not be accurate for m . However the amount of second phase present was never more than a few percent, so that at this stage the effect is quite small, as shown below in the analysis. Because the masses of the samples used in the measurements were usually in the range 1 to 20 mg, the absolute accuracy of the susceptibility values is probably not better than $\pm 10\%$ when in the absence of any impurity, although, as seen from the curves, the relative accuracy of the points on a given curve was much better than this. If further measurements are made on these materials, the accuracy in χ could be improved by using larger masses and correspondingly smaller fields. Secondly, if the second phase contributed to the value of χ , again the value determined would not accurately represent the phase being investigated. Usually, if the small amount of second phase were antiferromagnetic, this would have very little effect on the analysis because of the very small

contribution to the measured value of χ , so that the main problem to be considered is the presence of a ferrimagnetic (or ferromagnetic) second phase. This is discussed further below.

As described in 2.3, from the Néel theory of ferrimagnetism, the variation of the magnetic susceptibility χ with temperature T in the range T greater than T_N is given by the relation (66S1)

$$\frac{1}{\chi} = \frac{T - \theta_a}{C} - \frac{\xi}{T - \theta} \quad (4.1-4)$$

where θ_a is the asymptotic Curie-Weiss temperature, C is the Curie constant and ξ and θ are parameters which depend upon magnetic ion concentration, exchange interactions, etc.. From the usual form of the $1/\chi$ vs. T curve given by equn.4.1-4, $1/\chi$ is effectively zero at $T = T_N$, the Néel temperature. With this result, equn.4.1-4 can be rewritten as

$$\frac{C}{\chi} = T - \theta_a - \frac{(T_N - \theta_a)(T_N - \theta)}{T - \theta} \quad (4.1-5)$$

thus when the experimental curves in Fig.4.1.4 are fitted to equn. 4.1-5, the parameters to be fitted are θ_a , θ and T_N , since C can be determined from equn. 4.1-3. As indicated above, a close estimate of T_N can be obtained from inspection of the curves, while for $1/\chi$ to remain positive throughout, θ must have a value less than T_N . In equn.4.1-5, the term $\xi/(T - \theta)$ becomes negligible for T values appreciably larger than T_N , so that from this range a good estimate of θ_a could be obtained from the usual extrapolation to zero $1/\chi$. However, because of the upper limit of $T = 250$ K available in the

present measurements, it was found that in most cases the $\xi / (T - \theta)$ term still contributed to some extent to $1/\chi$ even at the highest temperature of observation, so that only an approximate estimate of θ_a could be made by extrapolation, which gave an upper limit value. Thus in fitting the experimental data to equn. 4.1-5, the parameters θ_a , θ and T_N were allowed to vary within these limits and the final values obtained from the best fit.

When the experimental data were fitted to equn. 4.1-5, it was found that good fits could be obtained for all seven cases listed above, as indicated by the fitted graphs. These fitted values of T_N , θ_a and θ , together with the values of C from equn. 4.1-2, are shown in Table 4.1.1(page 75).

The problem with the other five ferrimagnetic materials can be attributed to the presence of small amount of a second phase in addition to that being investigated. This is illustrated by the results for the $\text{CuSnTe}(t)$ and $\text{AgSnSe}(c)$ samples shown in Figs. 4.1.2e and 4.1.3d. As indicated above, when only small amount of the second phase is present, as indicated by the X-ray photograph, if this phase is antiferromagnetic, e.g. $\text{MnTe}_2(59\text{H1})$, then in the majority of cases the effect is negligible in the present analysis. The only exception observed was for MnSe , as discussed below. Thus most of the problems considered in this section are due to the presence of small amounts of a ferrimagnetic second phase. The results for these samples are discussed here, because in all cases a good value of T_N can be obtained for the sample investigated. The effects of the second phases are considered in order to justify the forms of the experimental

#	Sample	Field (mT)	Mass (mg)	Sym	A/F	Set	T _N (K)	θ_a (K)	θ (K)	C x10 ⁻³	a _c (nm)
1	CuSiSe	1.805	35.5	o	A	I	9	-13	/	8.31	.5589
2	CuGeSe	1.500	8.0	o	A	I	11	-14	/	7.66	.5642
3	CuSnSe	1.500	7.7	t	A	I	13	0	/	7.09	.5753
4	CuSiTe	1.240	16.7	t	A	I	22	/	/	6.07	.594
5	CuSiTe	1.240	16.7	c	A	IV	36	/	/	6.07	.605
6	CuGeTe	1.570	12.2	t	A	I	33	/	/	5.71	.5989
7	CuGeTe	1.035	18.3	c	F	IV	130	10	110	5.71	.615
8	CuSnTe	1.145	3.4	t	F	I	148	/	/	5.39	.6049
9	CuSnTe	1.145	9.8	c	F	IV	>250	/	/	5.39	.6286
10	AgSiSe	1.525	16.7	o	F	III	65	-285	60	7.11	.5445
11	AgGeSe	5.065	40.8	o	F	III	64	-300	63.9	6.63	.5527
12	AgSnSe	2.600	11.7	o	A	II	10	-27	/	6.20	.6002
13	AgSnSe	2.790	6.5	c	F	V	92	/	/	6.20	.549
14	AgSiTe	1.240	3.8	o	F	III	80	-395	67	5.40	.5717
15	AgSiTe	3.045	3.9	c	F	V	155	/	/	5.40	.575
16	AgGeTe	3.585	23.3	t	F	III	90	-470	66	5.12	.579
17	AgGeTe	9.540	32.9	c	F	V	191	-510	179	5.12	.5882
18	AgSnTe	1.495	0.9	c	F	V	99	20	50	4.86	.6005

Table.4.1.1 Summary of magnetic and crystallographic results.

curves and to show why, although T_N can be determined, the parameters θ_a and θ cannot be obtained. The curves in Figs. 4.1.2e and 4.1.3d are similar to those for the good samples discussed above, and it is very easy in

each case to obtain a reasonable estimate of the values for T_N . However, for the case of $\text{CuSnTe}(t)$ in Fig. 4.1.2e, the values of $1/\chi$ are very small compare with those for the previous cases. If this $1/\chi$ vs. T curve is fitted to equn. 4.1-5, it is found that the value of C obtained is too small by a factor of the order of 50 when compared with the value from equn. 4.1-2. It can be seen from the X-ray results that for this sample, some amount of the $\text{CuSnTe}(c)$ phase is present and, as is shown below, this phase is ferrimagnetic with a Néel temperature of $>250\text{K}$, i.e. considerably higher than that for the $\text{CuSnTe}(t)$ phase. Thus in the temperature range considered in Fig. 4.1.2e, when the tetragonal phase is in its paramagnetic range, the cubic phase is below its Néel temperature and is thus making a dominant contribution to the value of χ . Thus the measured value of χ is far too large for the tetragonal phase and the value of $1/\chi$ correspondingly very low. As a result, values of θ_a and θ obtained from these data have little significance, but a value of T_N for the tetragonal phase can be obtained.

For the case of the $\text{CuSnTe}(c)$ sample, a small amount of $\text{CuSnTe}(t)$ phase was present and its effects could be detected in the temperature range around 150K , as indicated earlier. However, the problem in this case was that the effects of the cubic phase were seen at considerably higher temperature, and because of the temperature limit of the equipment, it was possible only to say that in this case T_N is greater than 250K (Fig. 4.1.3f).

With regard to the data for $\text{AgSnSe}(c)$ in Fig. 4.1.3d, the shape of the curve in the temperature range where the $(T - \theta_a)/C$ term should dominate

is unusual, being almost flat from 130 to 180K and then beginning to rise at T about 180K. This cannot be attributed to the presence of the orthorhombic phase of the compound since the X-ray photograph in this case showed no sign of this phase, which moreover is antiferromagnetic with $T_N = 10$ K, (as seen in Fig. 4.1.1a). However, one other possible impurity phase is MnSe, for which the χ vs. T curve shows peaks with unusually large χ values in a broad range around 180 K (58D1). This phase could not be detected in the X-ray photographs of AgSnSe(c), since the two compounds both have rock-salt structure and the lattice parameters are very similar (85C1). However, the X-ray photograph of CuSnSe(t) shows faint lines corresponding to MnSe and its $1/\chi$ vs. T curve shows a broad minimum around 180K, similar to that described above for AgSnSe(c). A line corresponding to MnSe also was observed in the ESR data (92L1) for the CuSnSe(t) sample. In the case of AgSnSe(o), faint cubic lines were observed in the X-ray photograph, which could be due to either AgSnSe(c) or the antiferromagnetic MnSe (80H1). However, the $1/\chi$ vs. T curve again showed the broad minimum around 180K and the MnSe line was again observed in the ESR data. In the cases of AgSnSe(c), its ESR line is much closer in width to that of MnSe and so the MnSe line was much more difficult to detect, but analysis of the AgSnSe(c) data indicated that a little MnSe was probably present. Thus it seems reasonable to conclude that the phase which affects the AgSnSe(c) $1/\chi$ vs. T curve and prevents the determination of θ_a and θ in that case is MnSe. In fig. 4.1.3d, T_N obtained

for $\text{AgSnSe}(c)$ is indicated by a dashed line.

In the case of AgSiTe shown in Fig. 4.1.3e, the dominated phase was the orthorhombic which showed a T_N about 80K. An obvious rise in the $1/\chi$ curve was observed at $T = 155\text{K}$, this is due to the small amount of cubic phase present. Hence a estimate of T_N of $\text{AgSiTe}(c)$ was obtained.

Values of T_N obtained for the last four ferrimagnetic samples are listed in table 4.1.1(page 75).

§ 4.2 Discussion

It has been shown previously (§ 2.2) that the various parameters of these compounds vary smoothly with the quantity $(V / N)^{1/3}$, written here as a_e , where V is the volume of the unit cell and N the number of molecules per cell. Values of a_e , determined previously (Chapter 3), are given in table 4.1.1. In the crystallographic work, it was found that the various phases divided into different sets, each of which showed a different linear variation of a_e with the molecular weight W , as shown in Fig. 3.1.3. Figs. 4.1.4 and 4.1.5 show respectively the variations of T_N and θ_a with a_e for all of the phases for which values were obtained, plus values for three antiferromagnetic Cu sulphides, ($\text{CuSiS}(o)$, $\text{CuGeS}(o)$ and $\text{CuSnS}(t)$), taken from the literature (80G1, 88S1) and for two antiferromagnetic Ag sulphides, ($\text{AgGeS}(o)$ and $\text{AgSnS}(o)$), from preliminary work of other members of the research group(92L1). It is seen from Fig.4.1.4, that the

variation of T_N with a_c shows the same grouping as in the crystallographic case and the lines labelled I to V again show a linear variation within each set. Only two phases appear to show anomalous behaviour, viz. $\text{CuSnTe}(t)$ and $\text{AgSnTe}(c)$. $\text{CuSnTe}(t)$ fitted with set I in the crystallographic data, but is the only one of that set to show ferrimagnetic behaviour and so gives an isolated point in the T_N vs. a_c plot. Such behaviour is perhaps to be expected since, as indicated above, the Ag phases divide into two sets, one being antiferromagnetic and one ferrimagnetic. In the case of $\text{AgSnTe}(c)$, this phase was expected to belong to set V, all of which are ferrimagnetic, but its ferrimagnetic parameters are found to be quite different from those of the other set V phases.

In the case of the θ_a values shown in Fig.4.1.4, the distribution is similar to that for T_N , but with fewer points available, the distribution into sets is less clear. Straight lines have been drawn to show the positions of sets I, II and III. For set IV, only one point was found, ($\text{CuGeTe}(c)$). Values were obtained for two set V phases, but again the phase $\text{AgSnTe}(c)$ is very different from the other set V point, ($\text{AgGeTe}(c)$), being similar in value to $\text{CuGeTe}(c)$.

It was suggested in the investigation of the crystallography of these samples (Chapter 3), that the occurrence of different lines in these plots indicates that each line corresponds to a different crystal structure. Since the data for tetragonal and orthorhombic samples in many cases fall on the same line, it would be better to say that the different lines are due to

differences in the symmetry of the local environment of the Mn atoms, which can result in different crystal structures. However, in many cases the differences in structure may not be observed in routine polycrystalline X-ray photographs.

As indicated above, the magnetic behaviour of these materials can be fitted well with the simple Néel equation for ferrimagnetism, and the values of T_N and θ_a are quite consistent with the proposal made from the crystallographic data, that the different behaviour of the various phases can be attributed to different types of ordering of the cations on their sublattice. However, other mechanisms can produce similar χ vs. T behaviour, such as the canted antiferromagnetic (weak ferromagnetism) discussed by Moriya (60M1) and by Dzialoshinsky (58D1), which are attributed to effects such as single ion anisotropy and antisymmetric spin interactions (66S1). These effects can occur in low symmetry crystalline systems, which could be the case for the present materials. The essential difference between the ferrimagnetic and canted antiferromagnetic cases appears to be that in the former, magnetic ions need to be present on crystallographically non-equivalent sites, while for the latter case crystallographically equivalent sites are postulated.

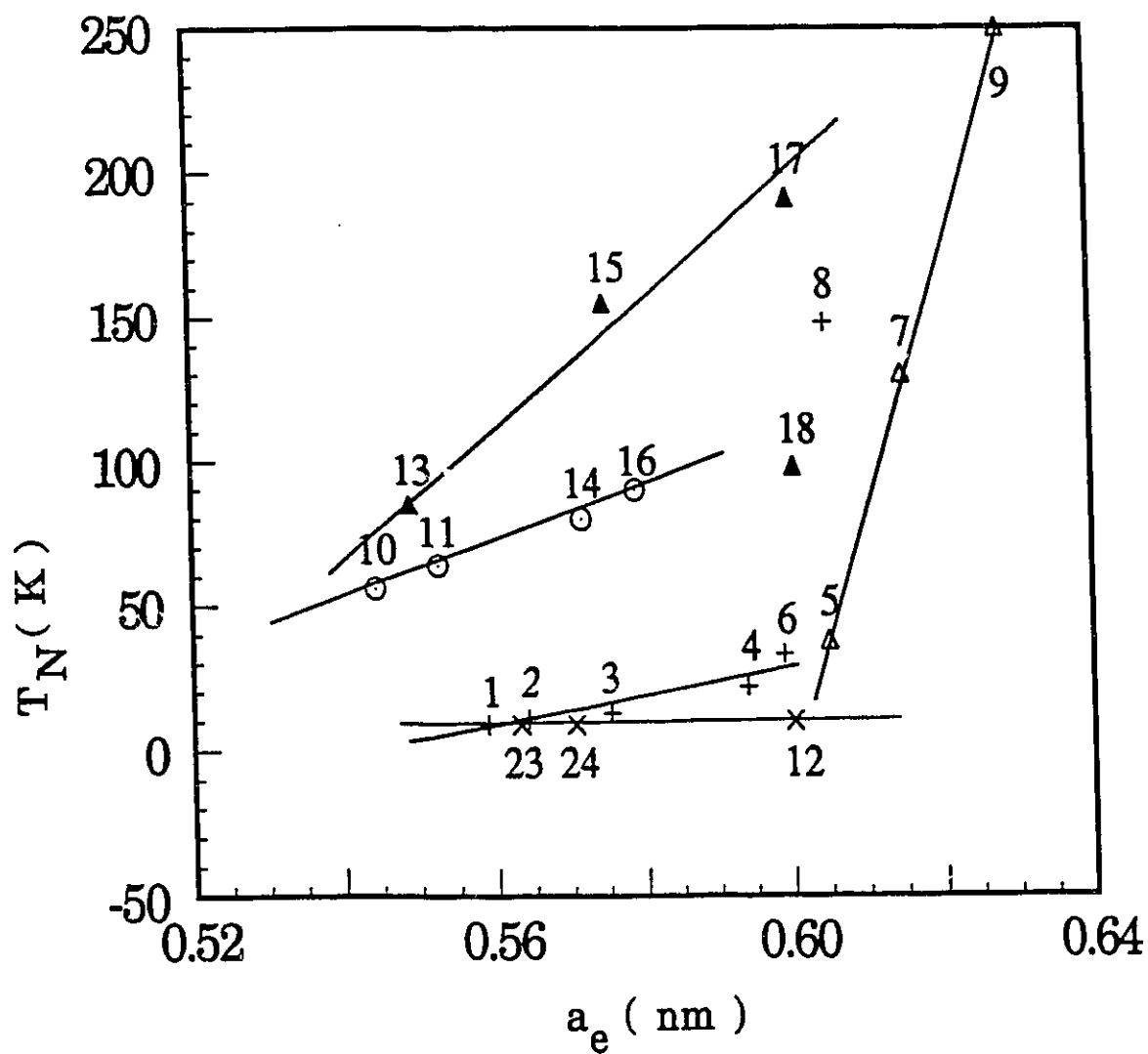


Fig. 4.1.4 Variation of Néel temperature T_N with effective lattice parameter a_e .

+ set I x set II o set III Δ set IV $\blacktriangle$ set V
Composition numbers as in table 4.1.1 plus:
23 AgGeS(o) 24 AgSnS(o)

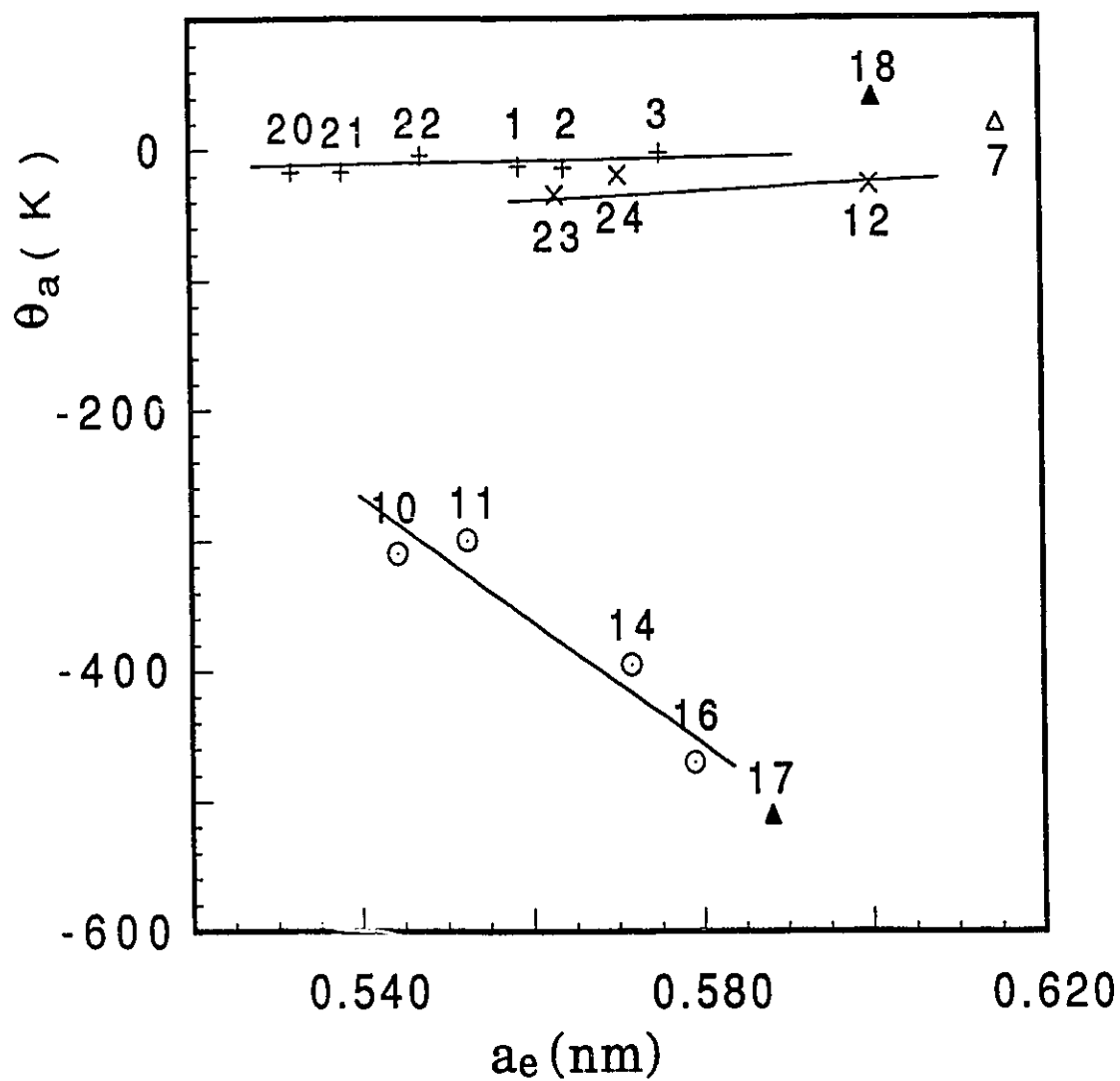


Fig. 4.1.5 Variation of Curie-Weiss temperature θ_a with effective lattice parameter a_e .

+ set I x set II o set III Δ set IV $\blacktriangle$ set V
Composition numbers as in table 4.1.1 plus:
20 CuSiS(o) 21 CuGeS(o) 22 CuSnS(t)
23 AgGeS(o) 24 AgSnS(o)

Chapter 5 Investigation of Optical Energy Gap

§ 5.1 Room Temperature Results

5.1.1 Introduction

Optical transmission measurements at 300 K were made on 13 different quaternary compound phases: CuGeS(o), CuSnSe(t), CuGeSe(o), CuSiSe(t), CuSiTe(t), AgSiTe(c), AgSiTe(o), AgGeS(o), AgSiSe(o), AgGeTe(c), AgSnTe(c), AgSnS(o), AgSnSe(o), using the method described in § 2.4. As is known from previous discussion, in order to obtain a good optical transmission signal, it is necessary to have a sample which: (a) has been treated at right temperature to obtain the correct single phase structure, and (b) needs to be big enough to be ground to a small enough thickness, with no cracks on its surface. All of the above needs extreme patience and cautious treatment, and these factors limited the number of samples for which optical band-gap values could be obtained. In addition to the room temperature results, the energy gap measurements as a function of temperature were made on 3 samples: CuGeS(o), AgSiTe(o + c) and CuSiSe(o). These three samples were chosen from those which gave good response signals in room temperature measurements, and measurements on both ferrimagnetic and antiferromagnetic types of samples needed to be investigated. The results and analysis for temperature variation will be discussed in detail in the

next section. However, when that temperature analysis had been carried out, it was found that the data in the case of CuSiSe(o) showed an indirect gap form as will be shown in § 5.1.3, thus the choice of CuSiSe(o) was unsatisfactory in this respect.

5.1.2 Results and Analysis

As described previously in § 2.4, from the variations of I_o , the incident intensity, and I_t , the transmitted intensity as a function of wavelength λ , which were recorded on a chart recorder, the values of the ratio I_o / I_t were determined as a function of $h\nu$. The values of $\ln (I_o / I_t)$ were corrected by subtracting a background value, so as to give values of αd where α is the absorption coefficient and d is the thickness of the sample. The relation 2.4-1 was then used to give a value for the direct optical energy gap, while the relation 2.4-3 would give a value for an indirect gap if present.

A typical curve of $\ln (I_o / I)$ vs. $h\nu$, taken at room temperature for the case of CuGeS(o) is shown in Fig. 5.1.1a. It was assumed that the background value could be linearly extrapolated as shown by the dashed line and the difference between the experimental curve and the dashed line taken to be proportional to the absorption coefficient α . Hence, Fig 5.1.1b shows the variation of α vs. $h\nu$, and 5.1.1c shows the variation of $(\alpha h\nu)^2$ as a function of $h\nu$.

It is observed that within the limits of experimental error, the variation of $(\alpha h\nu)^2$ with $h\nu$ is linear, justifying the use of the relation 2.4-1 which applies for the direct gap case. Extrapolation to $(\alpha h\nu)^2 = 0$ gives a value of $E_0 = 2.020 \pm 0.003$ eV in this case, as indicated by a solid line in the graph. It was found that for all samples except one (CuSiSe (o), see below), the graph of $(\alpha h\nu)^2$ vs. $h\nu$ indicated that the observed gap was direct and this standard extrapolation method was used in all cases.

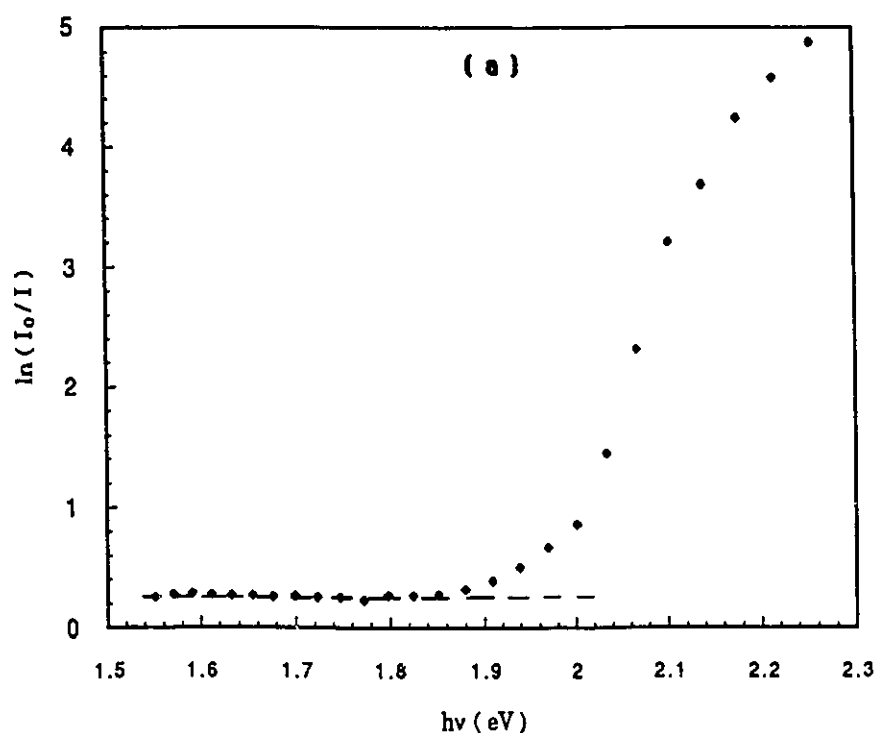


Fig. 5.1.1a Variation of $\ln(I_0/I)$ with photon energy $h\nu$ at 300 K for CuGeS(o).

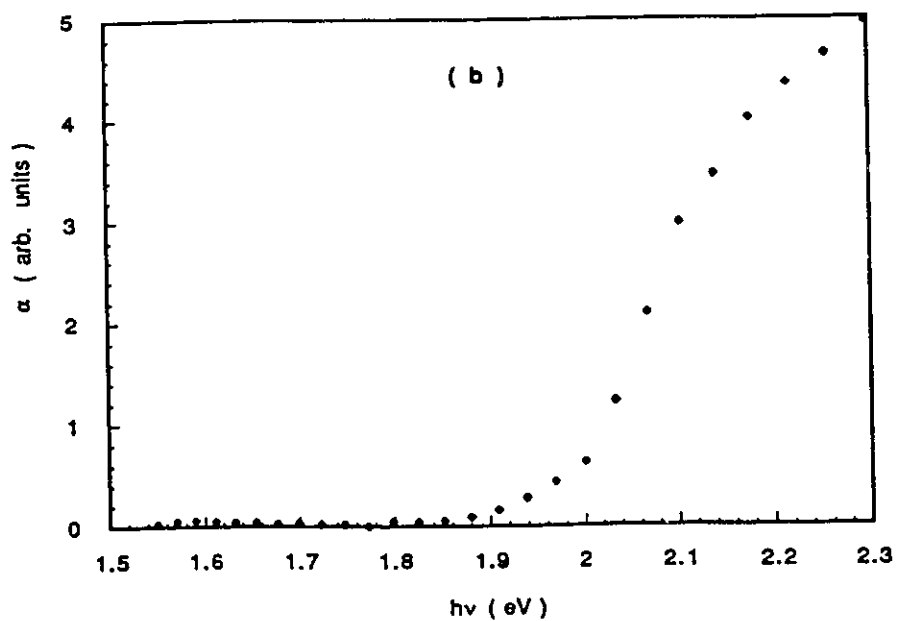


Fig. 5.1.1b Variation of α with photon energy $h\nu$ at 300 K for CuGeS(o).

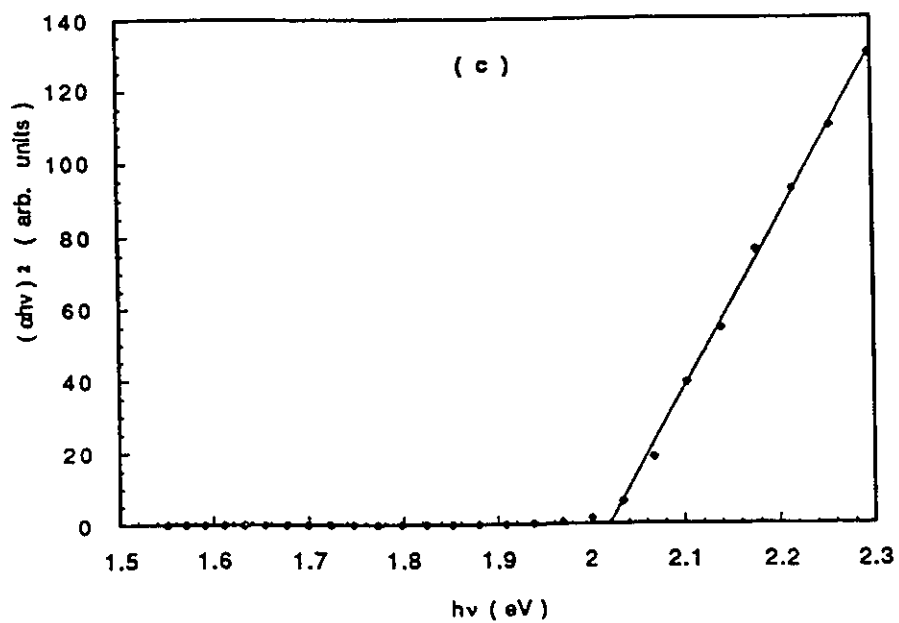


Fig. 5.1.1c Variation of $(\alpha h\nu)^2$ with photon energy $h\nu$ at 300 K for CuGeS(o).

It is worth mentioning that the thickness, 40 μm in this case, the value of which was needed in order to obtain the values of α in Fig 5.1.1b, was measured using a microscope. Because of the variation in the thickness at different points of sample, this measured values of d will be only a mean value, hence there could be a systematic error in the α values. However, this does not affect the E_0 values since the values of d does not affect the extrapolation of $(\alpha h\nu)^2$ to zero. In most cases, therefore, the value of d was not determined and the background corrected $\ln(I_0/I)$ was used instead of α .

There are three major effects which contribute to the background value of $\ln(I_0/I)$. First of all, it is well known that reflectance will contribute an effective background (67J1). However, in the wavelength range close to the absorption edge, this effect can be treated as constant (67J1). A second effect is absorption in an impurity or second phase which has a lower band-gap than the phase being investigated. This effect, which increases the value of $\ln(I_0/I)$ as the energy of the incident radiation increases, could explain the linear ramp below the edge, observed in some cases. If this is the dominant feature, a straight line extrapolation can be used. The third effect is that of scattering of the incident radiation which increases the value of $\ln(I_0/I)$ below the absorption edge as the energy of the incident radiation decreases. This scattering can be due to the grains of the polycrystalline sample, or to the presence of a finely distributed impurity. If this effect is clearly present, then a power law fit to the

background can be used (82G1). However, it has been shown (82G1) that, for most normal cases the method chosen for background subtraction makes little difference to the final value of E_0 obtained. In addition, for the samples investigated in present work, the effect of scattering did not appear to be of significance.

For most of the measurements, the lock-in amplifier was used at different gain settings in the measurements of I_0 and I . However, since as indicated above, an arbitrary scale for α was used, again a setting conversion factor was not included in the calculations.

The X-ray power photographs showed that in several of these samples, a small amount of impurity or second phase was present. Since these amounts were small in most cases, the effects on the optical energy gap measurements were negligible. If the second phase had an energy gap larger than the phase being investigated, its absorption edge would occur at higher $h\nu$ than the one being investigated, and so would not be observed. Even when the second phase energy gap was lower than that of the major phase, since only small amounts were present, its absorption formed part of the background discussed above, and so did not need to be considered separately. One exception to this was the case of AgSiTe where the main phase was AgSiTe(o) but a small amount, probably not exceeding 5 %, of AgSiTe(c) was present. This was one of the samples investigated as a function of temperature and so it received more detailed study than some of the other samples. It was found during this work that careful study of the

apparent background showed that the energy gap of the AgSiTe(c) could be determined at lower values, so that in this case E_0 values were observed for both the orthorhombic and cubic phases from the single set of data.

One other sample which showed different behaviour from the others was CuSiSe(o), which again was one of the samples chosen for detailed study as a function of temperature. In this case, the plot of $(\alpha h\nu)^2$ vs. $h\nu$ did not appear to be linear. Thus a graph of $(\alpha h\nu)^{1/2}$ vs. $h\nu$ was plotted, (Fig.5.1.2), and was found to be reasonably linear. This would indicate that the lower energy gap in this case is indirect. The indirect gap observed is 2.030 ± 0.003 eV. However, in the $(\alpha h\nu)^{1/2}$ vs. $h\nu$ curve, it was seen that at a higher energy there was a fairly abrupt increase in α . This was attributed to the direct gap contribution to α . Because of the limited range of $h\nu$ in which the direct gap could be observed, only an approximate estimate of the direct gap could be made.

Fig. 5.1.3a and 5.1.3b show the absorption curve and corresponding curve of $(\alpha h\nu)^2$ vs. $h\nu$ for CuSiSe(t). The values of direct band-gap determined in this case is 2.27 ± 0.01 eV. Similar diagrams showing graphs of α and $(\alpha h\nu)^2$ vs. $h\nu$ for other eleven samples are illustrated in Figs. 5.1.4-14.

The figure and values for AgGeSe(o) were taken from the literature (90Q1). The $(\alpha h\nu)^2$ vs. $h\nu$ curve is shown in Fig. 5.1.15 for this case, and the energy gap value obtained for room temperature is $E_0 = 1.472 \pm 0.005$ eV.

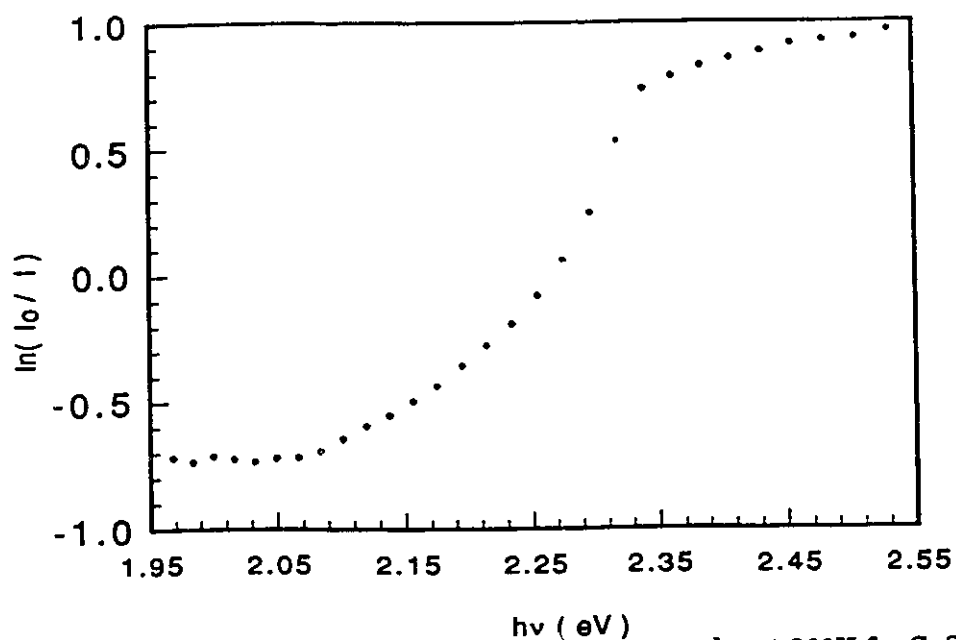


Fig. 5.1.2a Variation of $\ln(I_0/I)$ with photon energy $h\nu$ at 300K for CuSiSe(o).

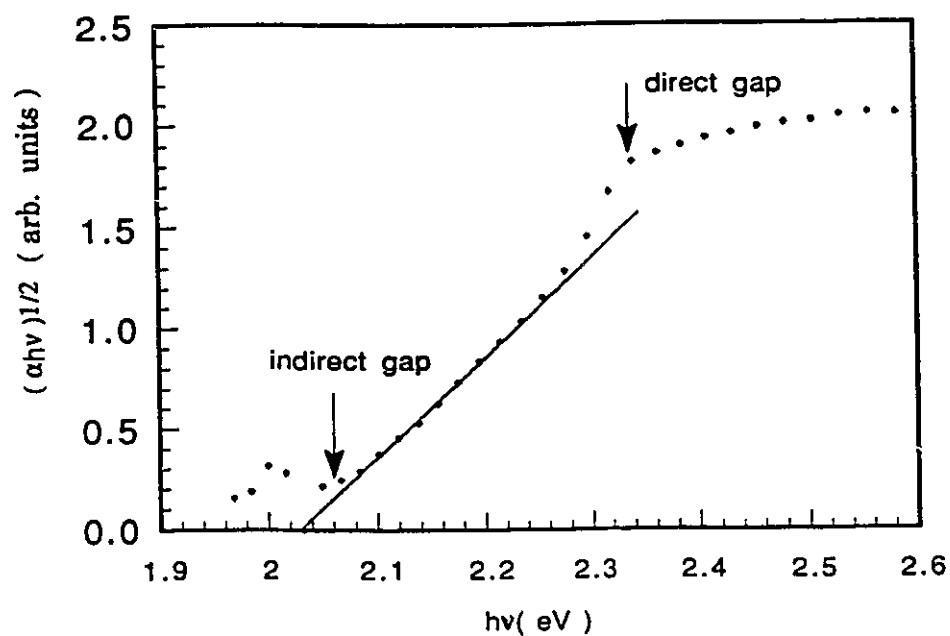


Fig. 5.1.2b Variation of $(\alpha h\nu)^{1/2}$ with photon energy $h\nu$ at 300K for CuSiSe(o).

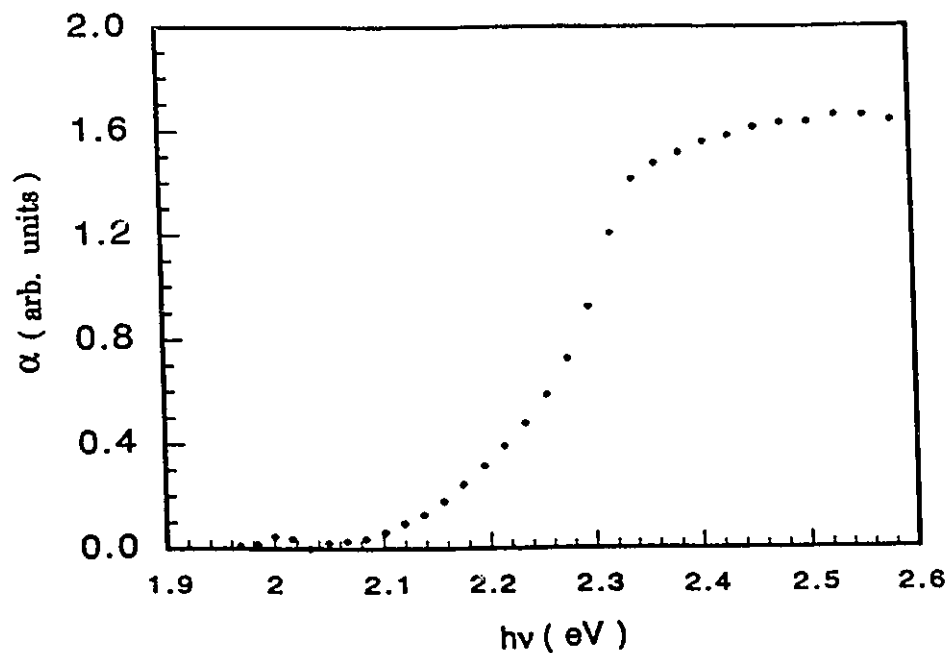


Fig. 5.1.3a Variation of α with photon energy $h\nu$ at 300K for CuSiSe(0).

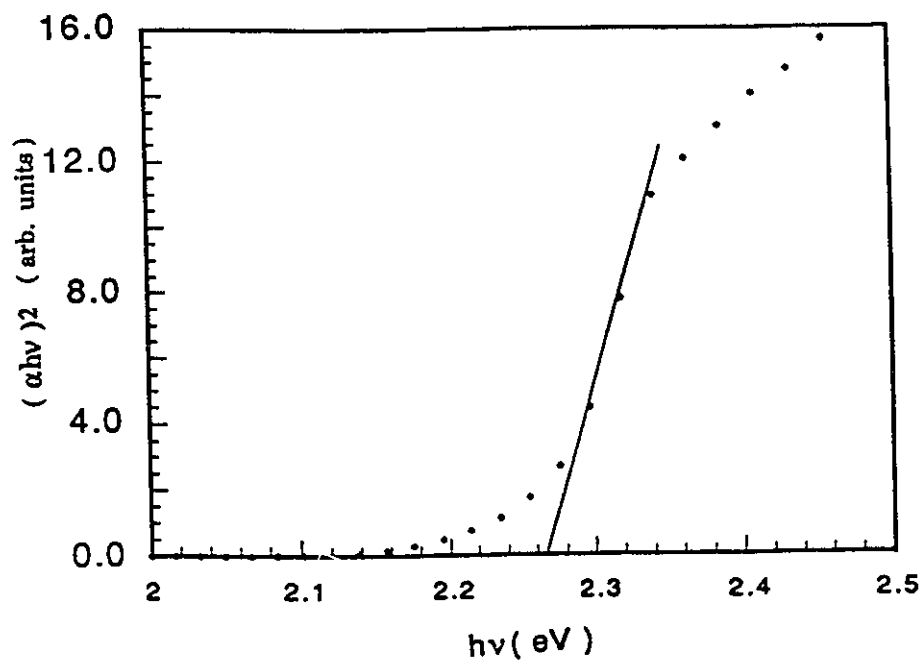


Fig. 5.1.3b Variation of $(\alpha h\nu)^2$ with photon energy $h\nu$ at 300K for CuSiSe(0).

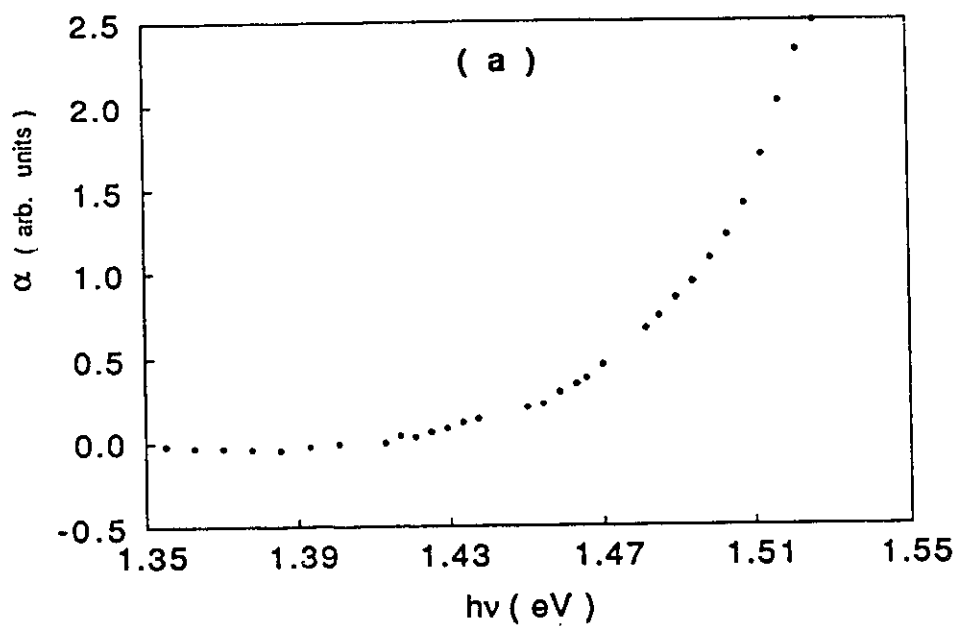


Fig. 5.1.4a Variation of α with photon energy $h\nu$ at 300K for CuGeSe (o).

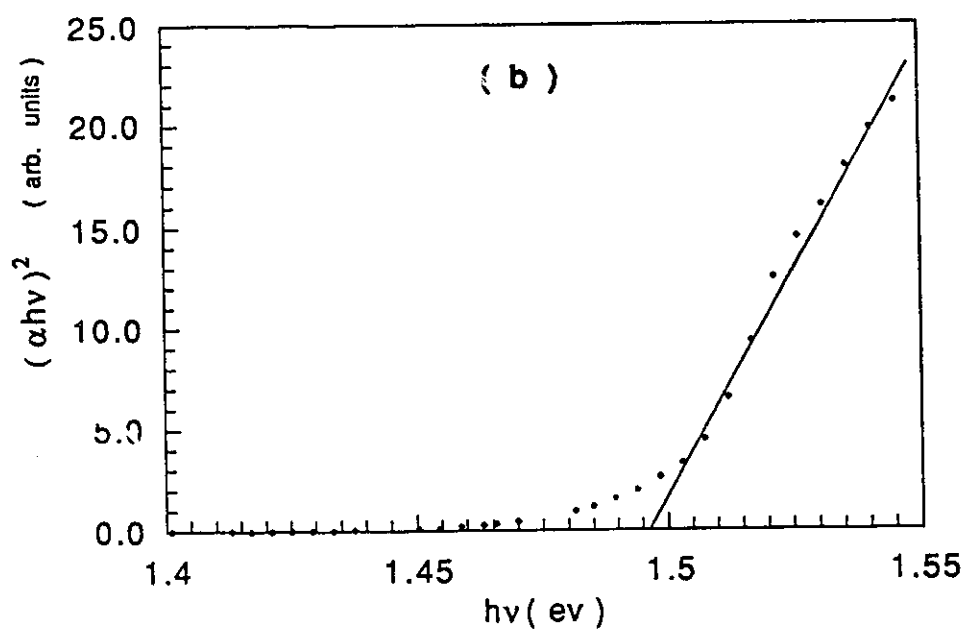


Fig. 5.1.4b Variation of $(\alpha h\nu)^2$ with photon energy $h\nu$ at 300K for CuGeSe (o).

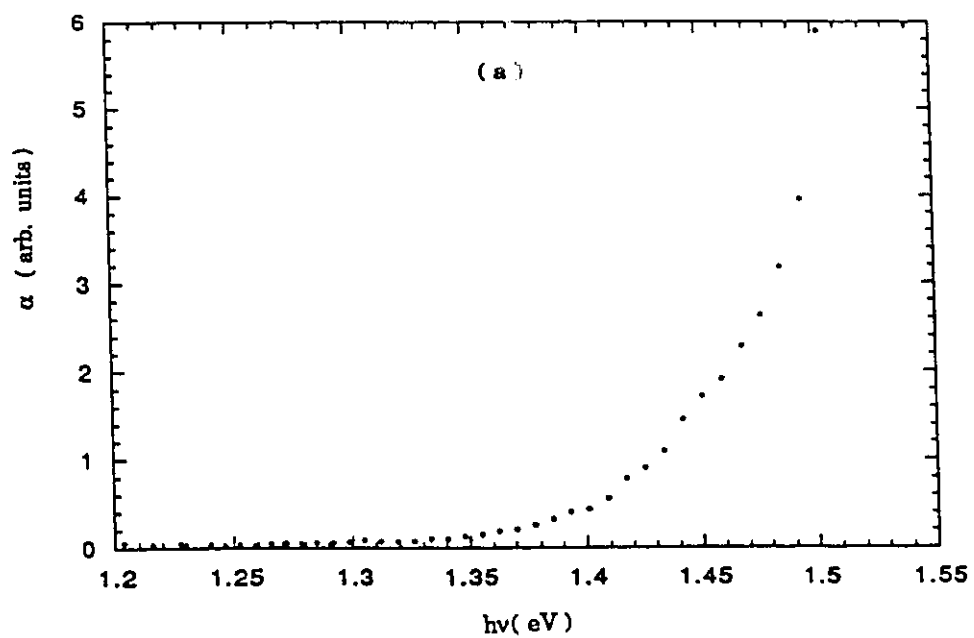


Fig. 5.1.5a Variation of α with photon energy $h\nu$ at 300K for CuSiTe(t).

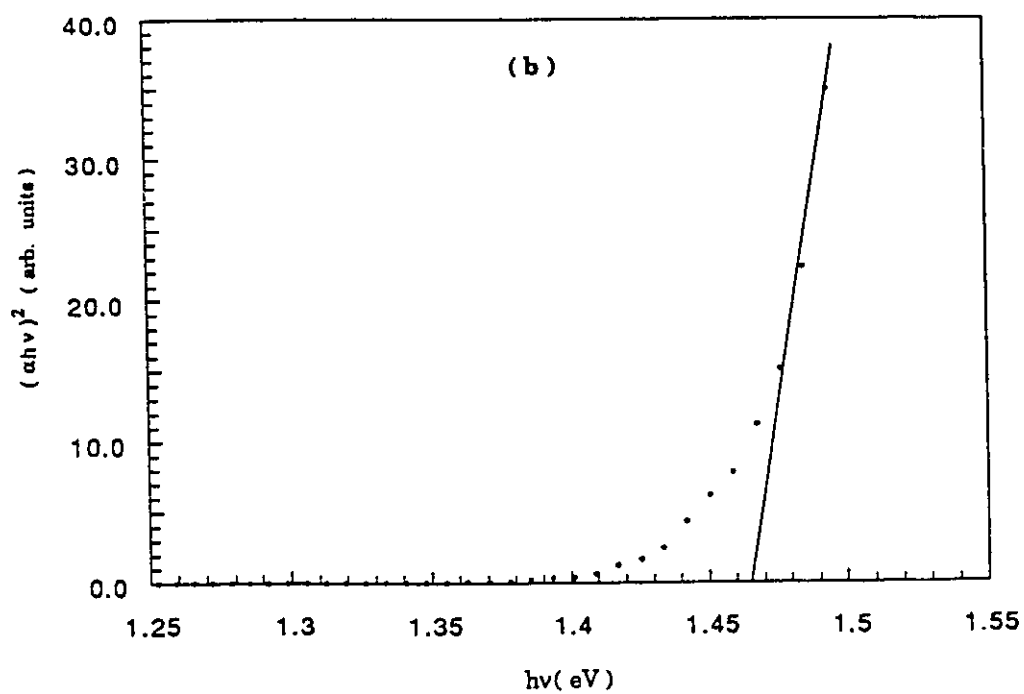


Fig. 5.1.5b Variation of $(\alpha h\nu)^2$ with photon energy $h\nu$ at 300K for CuSiTe(t).

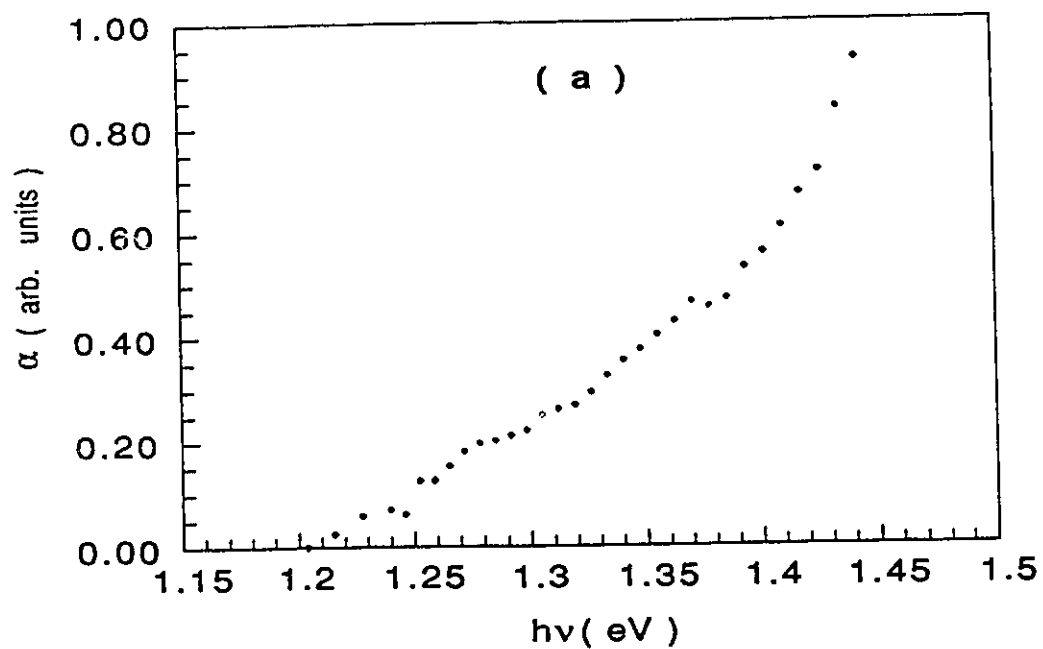


Fig. 5.1.6a Variation of α with photon energy $h\nu$ at 300K for AgSiTe(c).

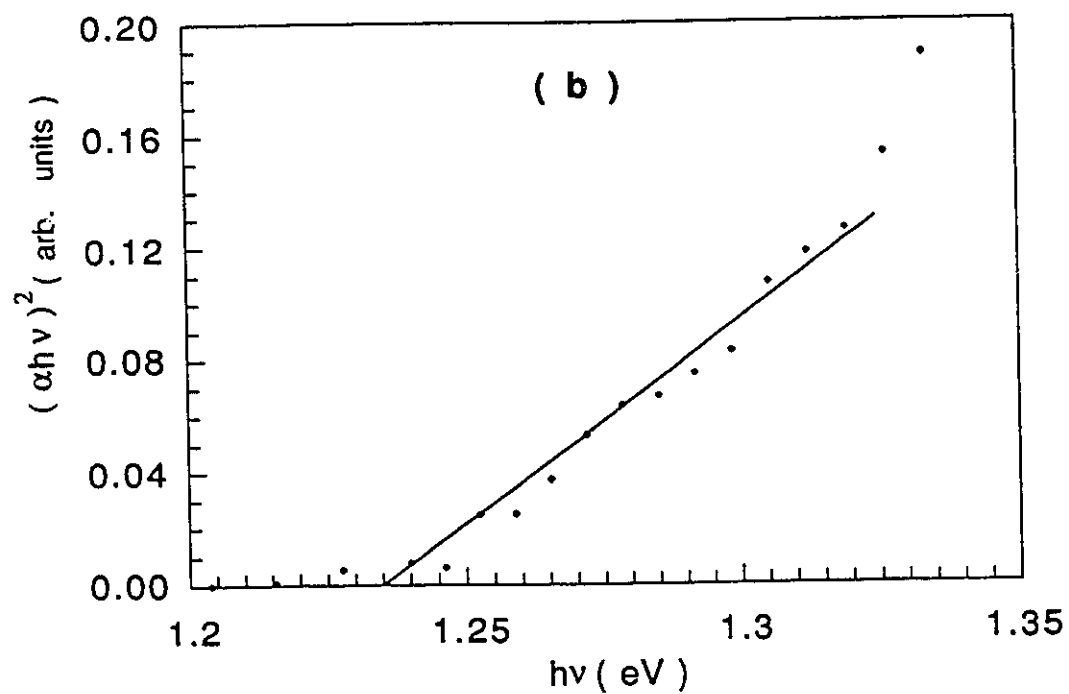


Fig. 5.1.6b Variation of $(\alpha h\nu)^2$ with photon energy $h\nu$ at 300K for AgSiTe(c).

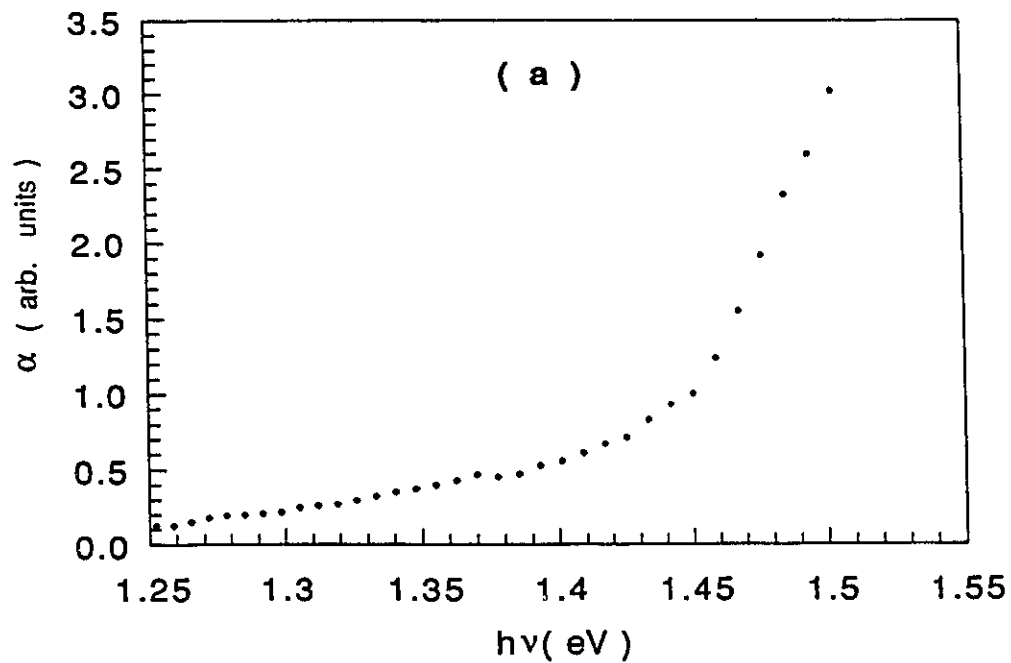


Fig. 5.1.7a Variation of α with photon energy $h\nu$ at 300K for AgSiTe(o).

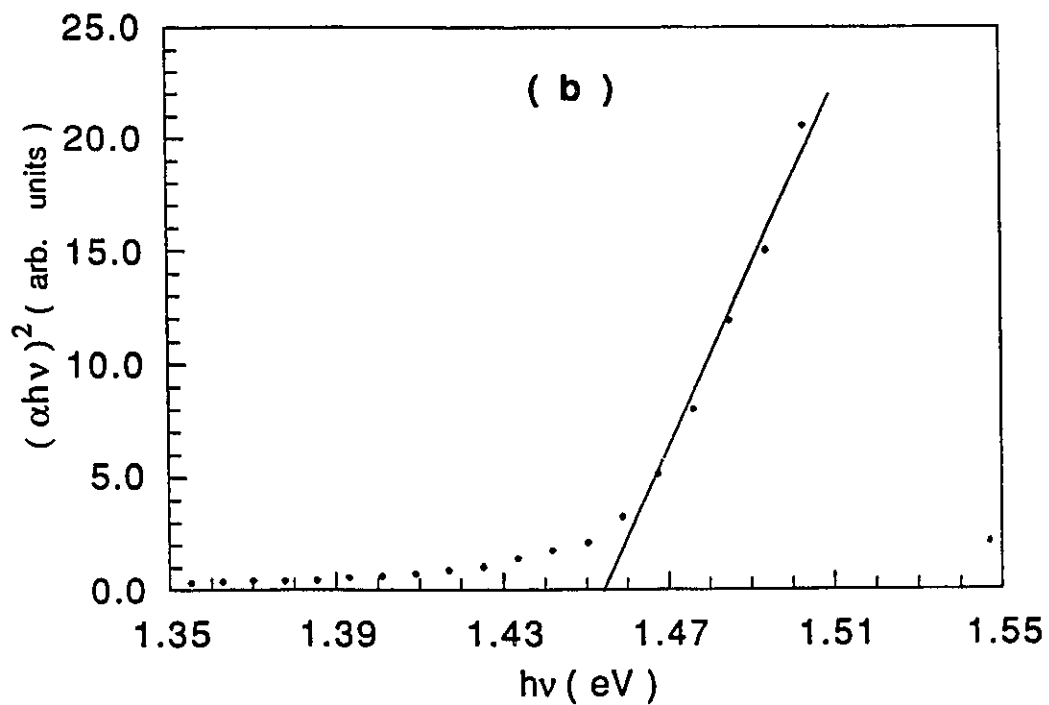


Fig. 5.1.7b Variation of $(\alpha h\nu)^2$ with photon energy $h\nu$ at 300K for AgSiTe(o).

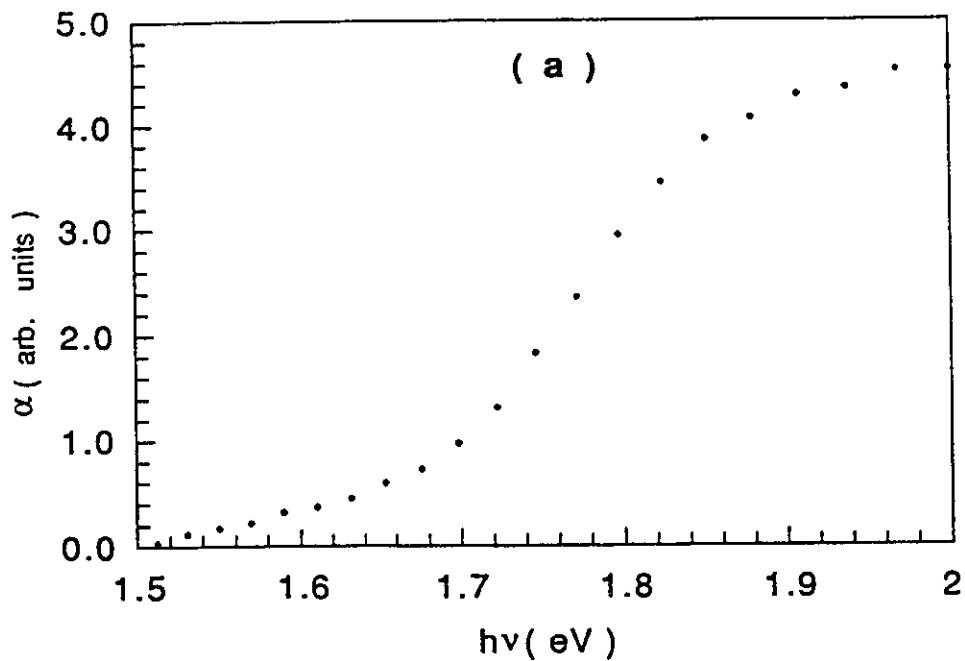


Fig. 5.1.8a Variation of α with photon energy $h\nu$ at 300K for AgGeS (o).

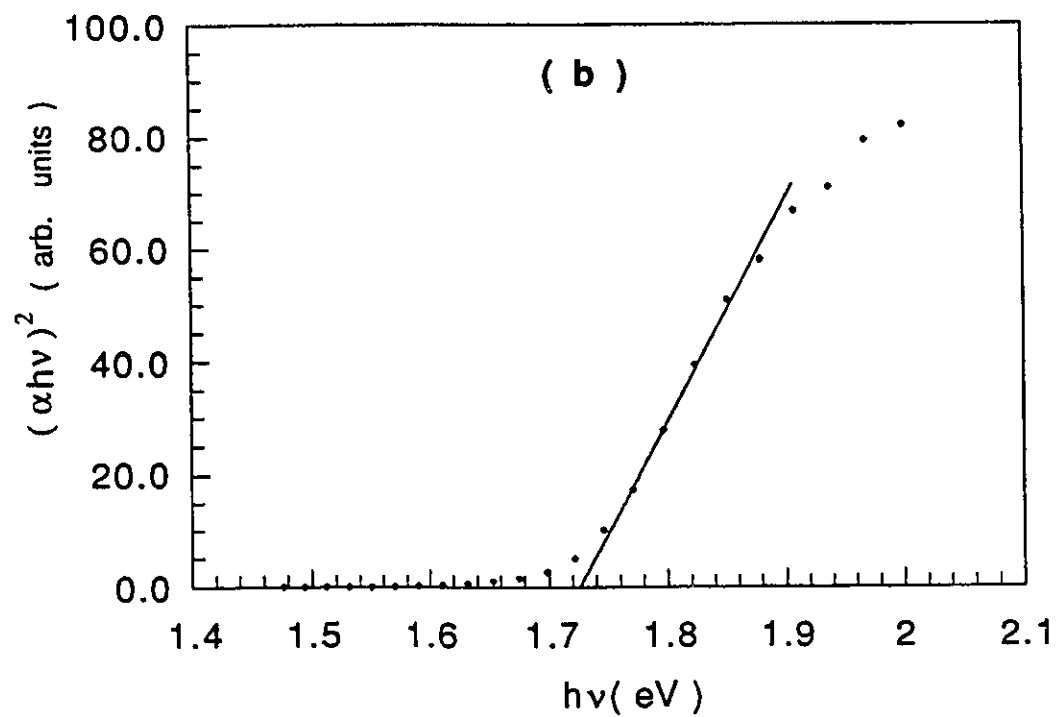


Fig. 5.1.8b Variation of $(\alpha h\nu)^2$ with photon energy $h\nu$ at 300K for AgGeS (o).

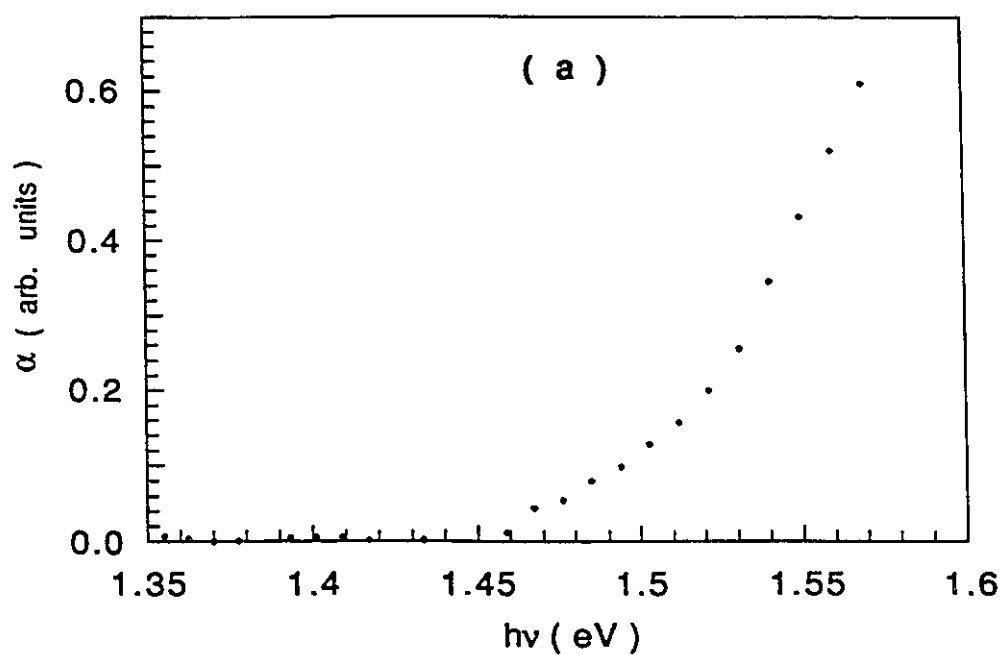


Fig. 5.1.9a Variation of α with photon energy $h\nu$ at 300K for AgSiSe (o).

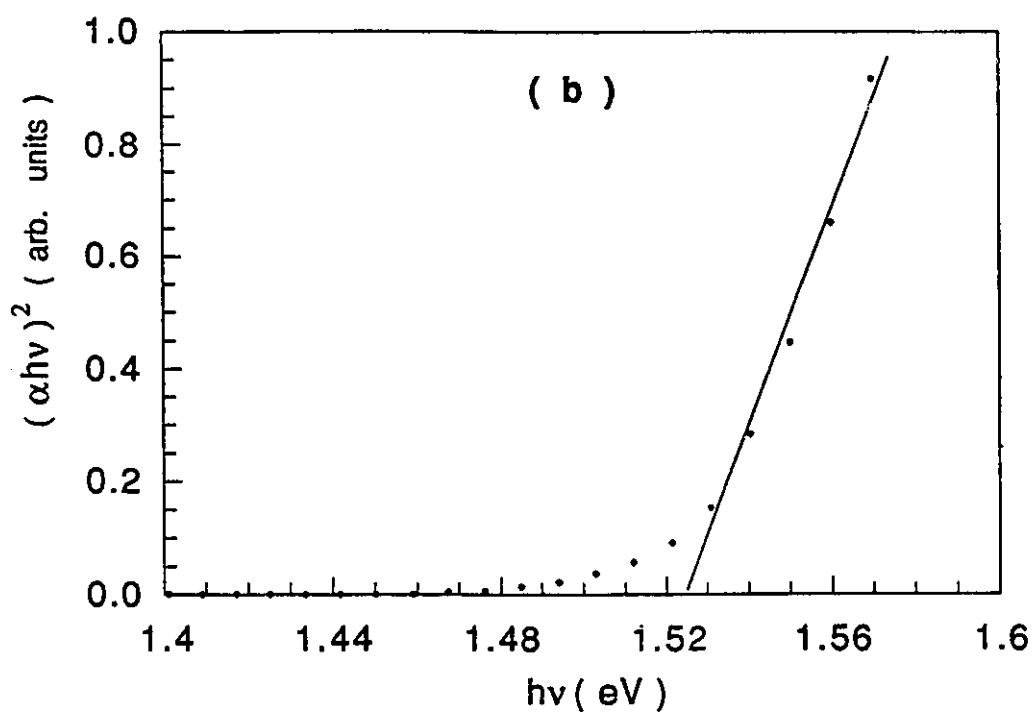


Fig. 5.1.9b Variation of $(\alpha h\nu)^2$ with photon energy $h\nu$ at 300K for AgSiSe (o).

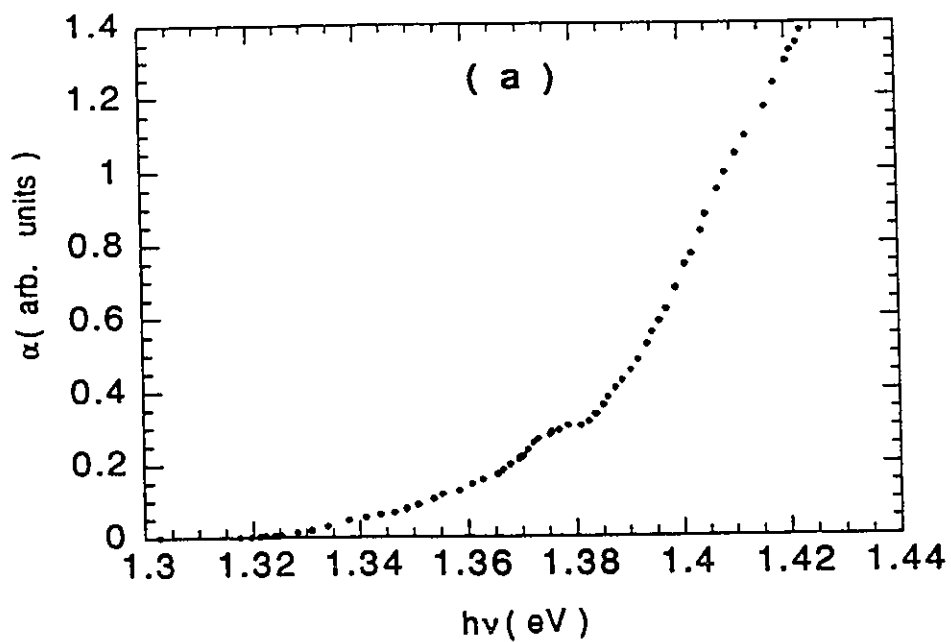


Fig. 5.1.10a Variation of α with photon energy $h\nu$ at 300K for AgGeTe(c).

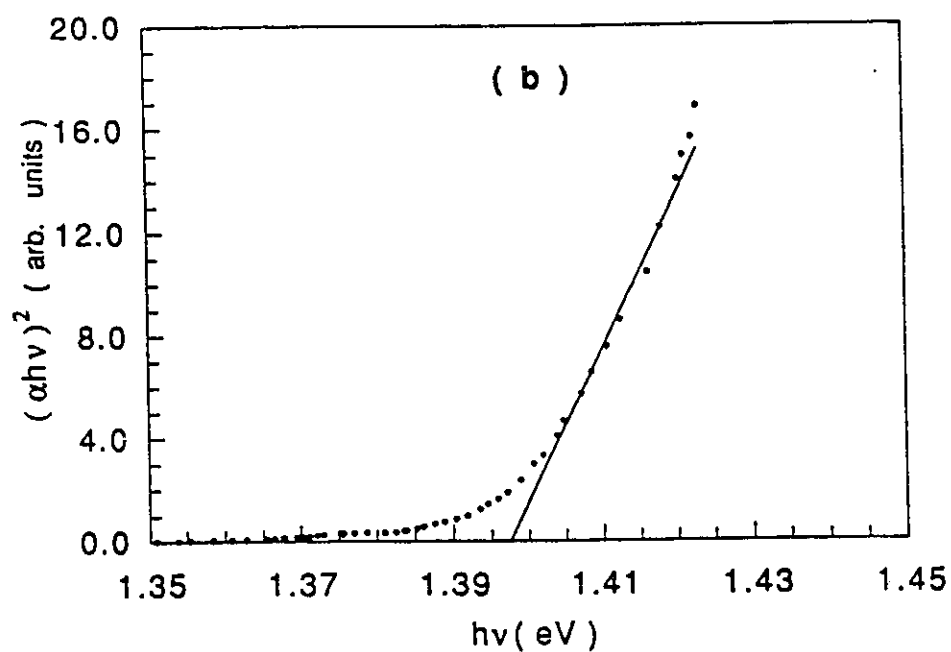


Fig. 5.1.10b Variation of $(\alpha h\nu)^2$ with photon energy $h\nu$ at 300K for AgGeTe(c).

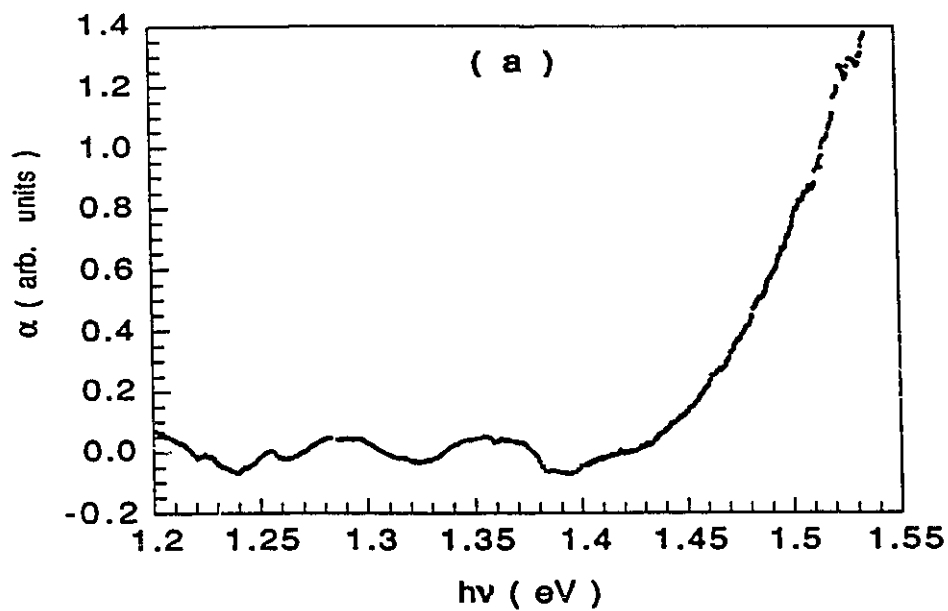


Fig. 5.1.11a Variation of α with photon energy $h\nu$ at 300K for AgSnTe(c).

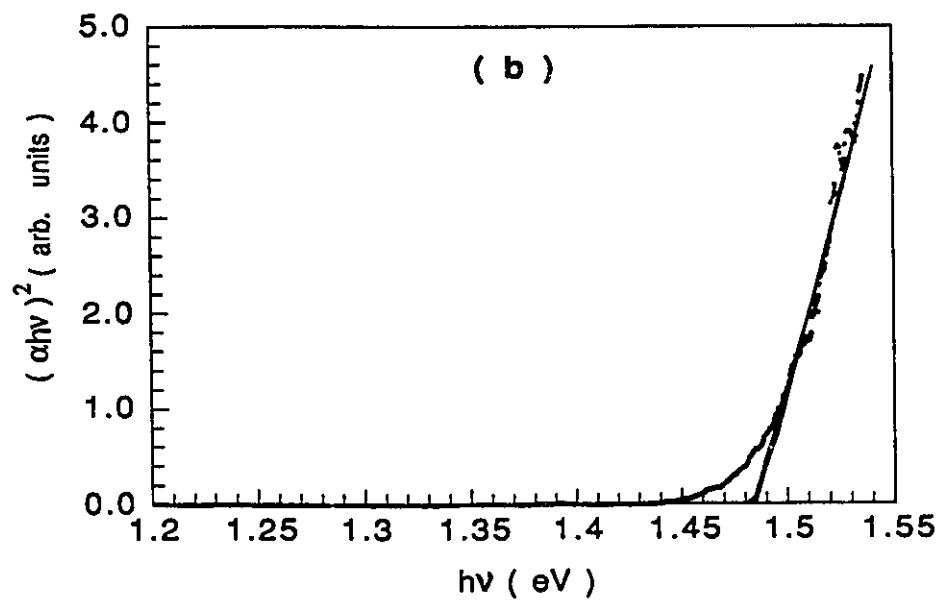


Fig. 5.1.11b Variation of $(\alpha h\nu)^2$ with photon energy $h\nu$ at 300K for AgSnTe(c).

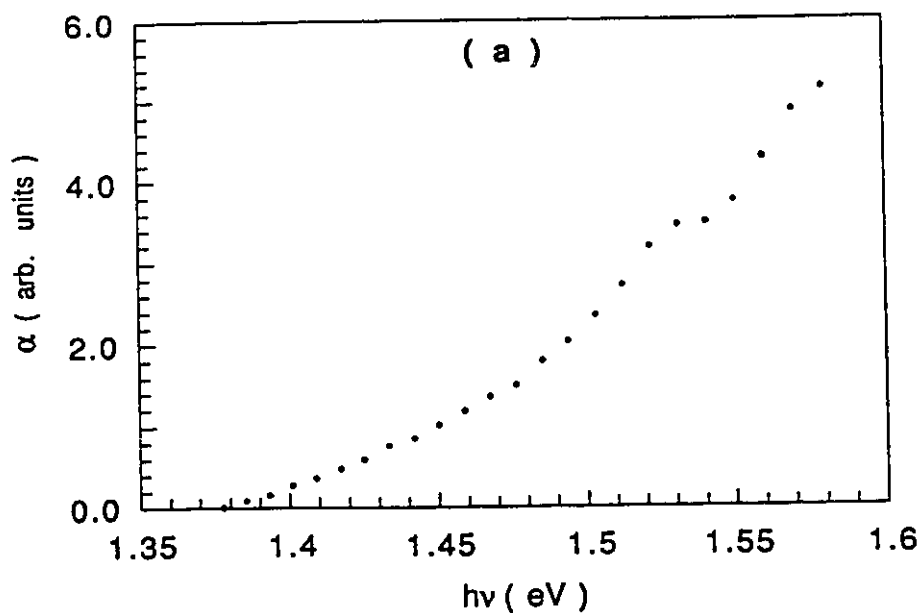


Fig. 5.1.12a Variation of α with photon energy $h\nu$ at 300K for AgSnS(o).

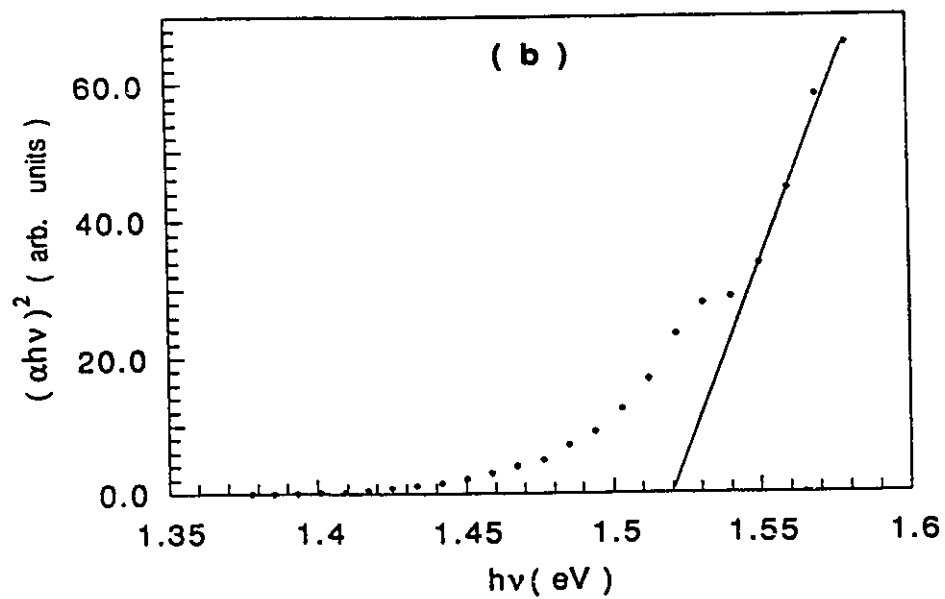


Fig. 5.1.12b Variation of $(\alpha h\nu)^2$ with photon energy $h\nu$ at 300K for AgSnS(o).

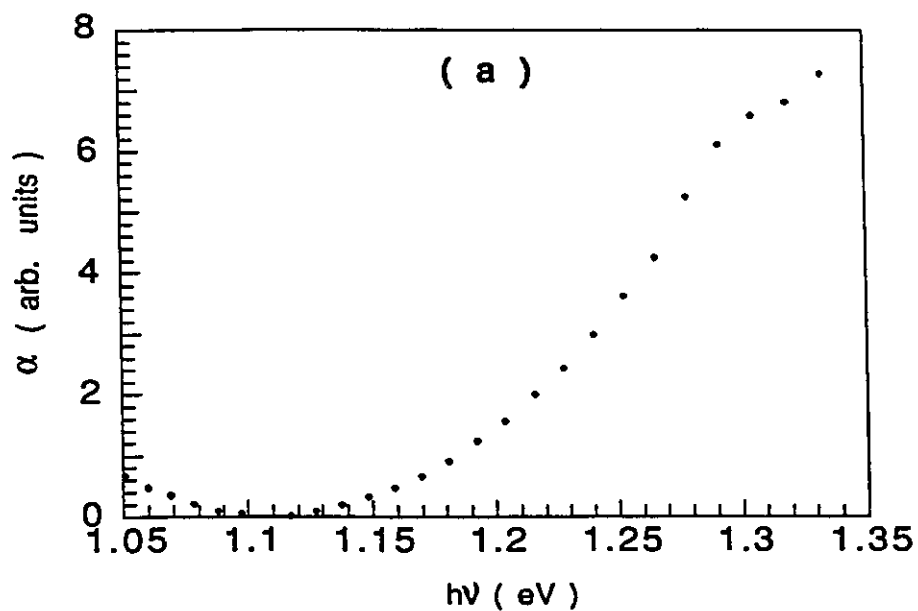


Fig. 5.1.13a Variation of α with photon energy $h\nu$ at 300K for AgSnSe(o).

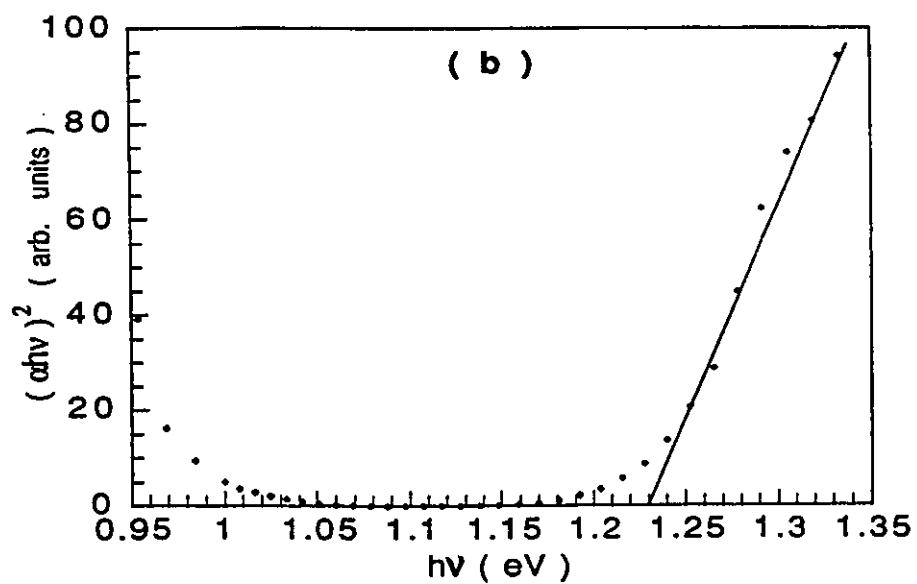


Fig. 5.1.13b Variation of $(\alpha h\nu)^2$ with photon energy $h\nu$ at 300K for AgSnSe(o).

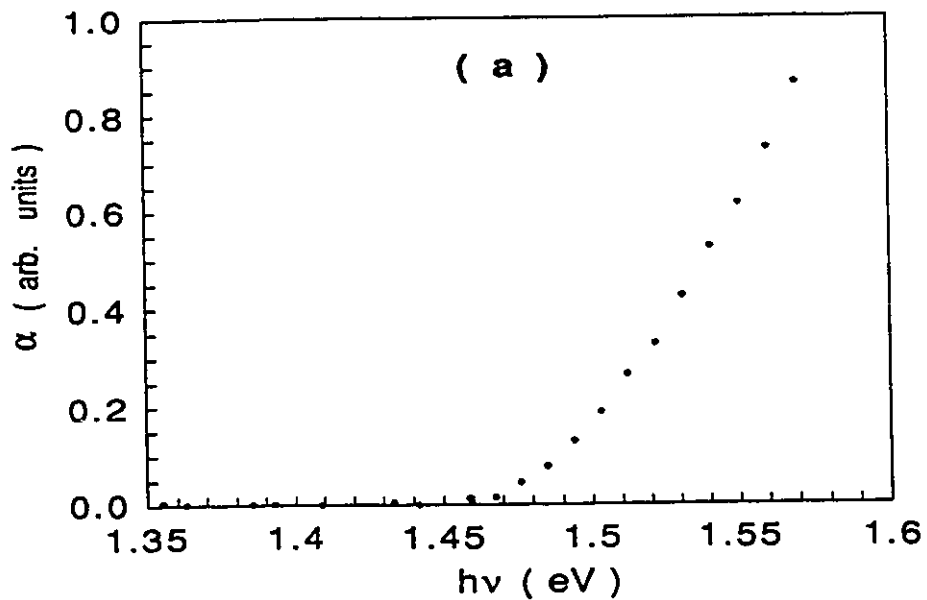


Fig. 5.1.14a Variation of α with photon energy $h\nu$ at 300K for CuSnSe (o).

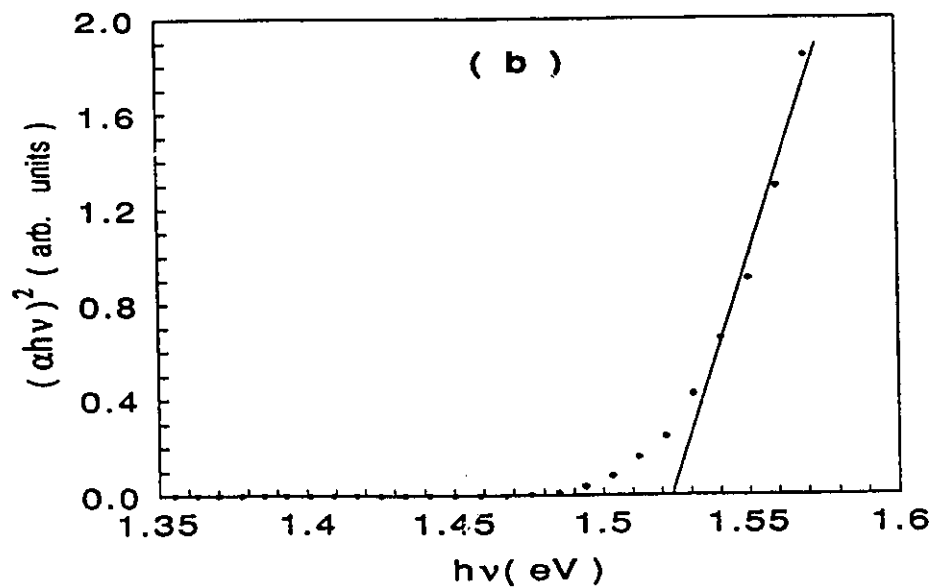


Fig. 5.1.14b Variation of $(\alpha h\nu)^2$ with photon energy $h\nu$ at 300K for CuSnSe (o).

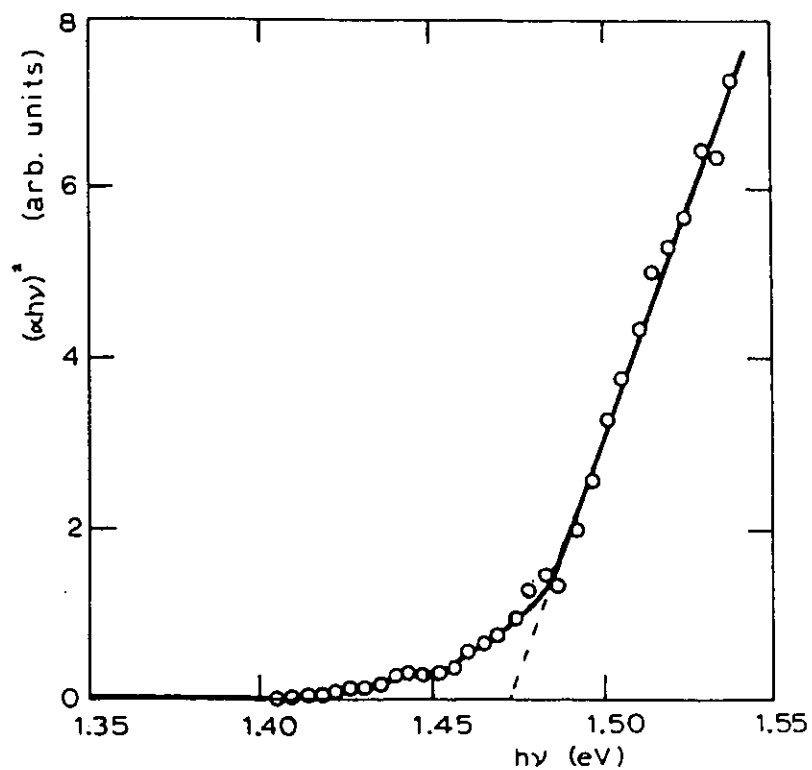


Fig. 5.1.15 Variation of $(\alpha h\nu)^2$ with photon energy $h\nu$ at 300 K for AgGeSe(o), taken from the literature (90Q1).

The energy gap values obtained at room temperature for these 14 phases together with their lattice symmetry and lattice parameter values are listed in table 5.1.1.

	Compound	Symmetry	a_e (nm)	Direct E_0 (eV)	h ν range fitted(eV)
1	CuGeS	o	0.5380	2.020 ± 0.003	2.030 - 2.300
2	CuSiSe	o	0.5589	2.27 ± 0.01	2.280 - 2.330
3	CuGeSe	o	0.5642	1.490 ± 0.003	1.500 - 1.550
4	CuSnSe	t	0.5753	1.520 ± 0.003	1.530 - 1.570
5	CuSiTe	t	0.5942	1.465 ± 0.005	1.470 - 1.490
6	AgGeS	o	0.5632	1.730 ± 0.005	1.740 - 1.880
7	AgSnS	o	0.5705	1.520 ± 0.005	1.540 - 1.580
8	AgSiSe	o	0.5445	1.525 ± 0.005	1.530 - 1.570
9	AgGeSe	o	0.5527	1.472 ± 0.005	1.480 - 1.540
10	AgSnSe	o	0.6002	1.230 ± 0.005	1.240 - 1.330
11	AgSiTe	c	0.5750	1.244 ± 0.005	1.240 - 1.320
12	AgSiTe	o	0.5717	1.454 ± 0.003	1.460 - 1.500
13	AgGeTe	c	0.5882	1.397 ± 0.003	1.402 - 1.422
14	AgSnTe	c	0.6005	1.490 ± 0.005	1.490 - 1.530

Table 5.1.1 Optical energy gap E_0 at 300 K and effective lattice parameter a_e for various Mn - quaternary compound phases.

5.1.3 Indirect Gap Contribution

As mentioned above, in the case of CuSiSe(o), the plot of $(\alpha h\nu)^2$ vs. $h\nu$ did not appear to be linear(Fig.5.1.3b). However, from the graph of $(\alpha h\nu)^{1/2}$ vs. $h\nu$ shown in Fig.5.1.2b, at lower temperature range, a better

straight line was observed. According to equn.2.4 - 3, this is due to an indirect gap contribution. After subtracting the background as in the direct gap analysis, the intercept of this straight line part results an indirect gap $E_0 = 2.05\text{eV}$. From the analysis of the energy gap variation with temperature, which will be described in the next section, it was found that within the limits of experimental error, this indirect gap seemed to be almost constant independent of temperature, as compared with the direct gap variations (shown in Fig.5.2.1). Therefore, in next section where energy gap variation with temperature is discussed, the indirect gap of $\text{CuSiSe}(\text{o})$ will not be further considered.

5.1.4 Discussion:

In previous chapters, it has been shown that the various parameters of these compounds vary smoothly with the effective lattice parameter $a_e (= (V / N)^{1/3})$. In the crystallographic work, it was found that the various phases divided into different sets, each of which showed a linear variation of a_e with the molecular weight W (Fig. 3.1.3). Essentially, five sets of points were observed. It was then suggested that the occurrence of different lines in these plots indicates that each line corresponds to a different crystal structure. The Figs. 4.1.4 & 5 in magnetic work showed that the values of T_N and θ_a are quite consistent with the proposal made from the crystallographic data.

In the optical energy gap measurements, the energy gap values obtained for 14 quaternary compound phases at room temperature were plotted against their effective lattice parameters. These results are shown in Figs. 5.1.16a, b, c and d. The E_o values obtained here for II, III and V are shown in Figs. 5.20 b, c and d. No data was obtained for any sample of set IV. It is seen that in each case the variation of E_o with a_e is practically linear. However in the case of set I, shown in Fig. 5.1.16a, E_o values are given for the present samples plus values for $\text{Cu}_2\text{ZnSiS}_4(o)$, $\text{Cu}_2\text{ZnSiSe}_4(o)$, $\text{Cu}_2\text{ZnGeS}_4$ and $\text{Cu}_2\text{ZnGeSe}_4(o)$ taken from the literature (77S1). It is seen that in this case the values appear to divide into 3 subsets, labelled I_a , I_b , and I_c in Fig. 5.20a. Subset I_a has only one value, but again the 4 points in I_b show a linear variation with a_e . In I_c , the three points obtained in the present work again vary linearly with a_e , but the fourth point, taken from the literature, lies at a slightly lower value.

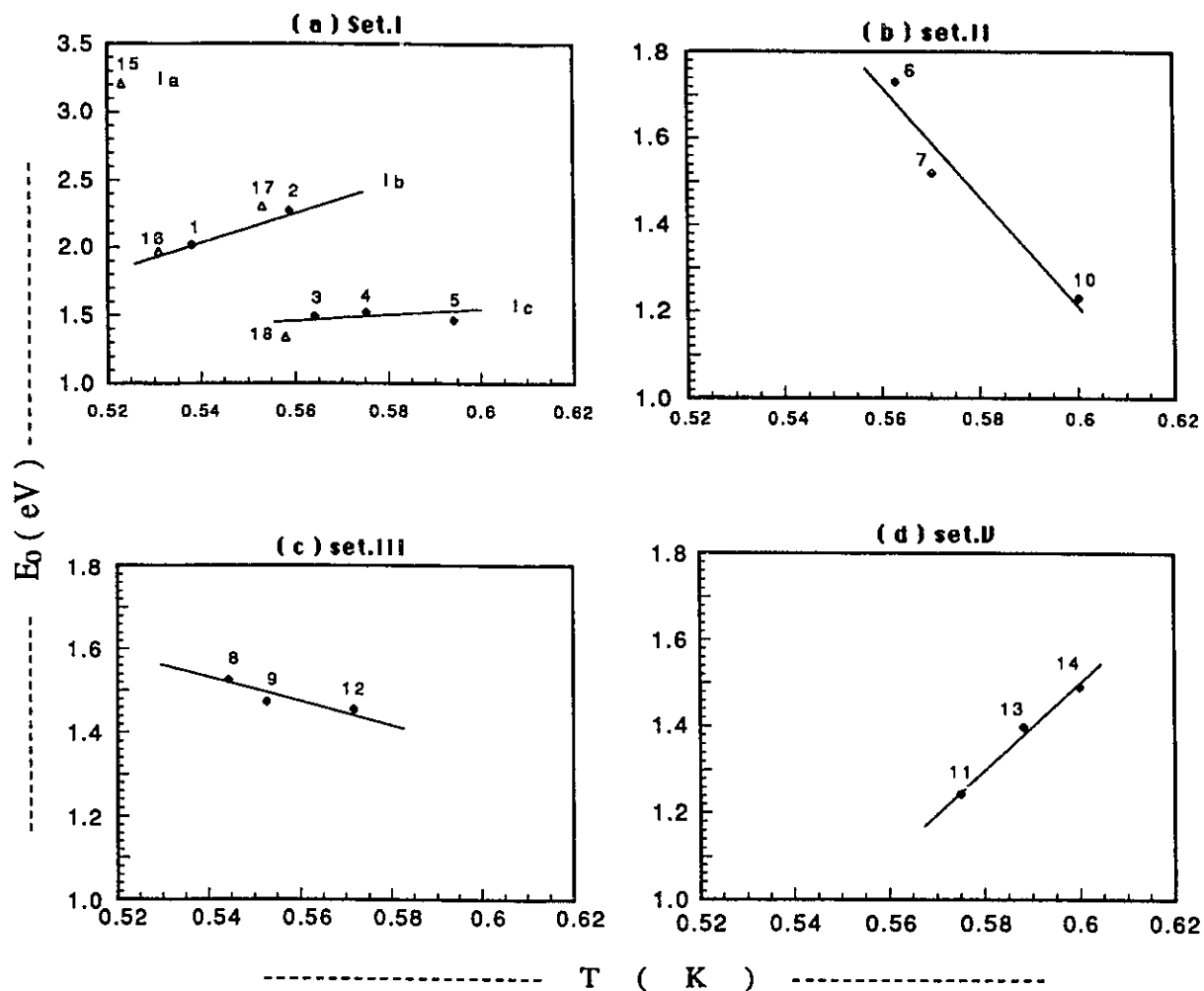


Fig. 5.1.16 Variation of optical energy gap E_0 with effective lattice parameter a_0 at 300K.

measured results, taken from literature(77S1).
Composition numbers as in table 5.1.1 plus:
15. CuZnSiS. 16. CuZnGeS.
17. CuZnSiSe. 18. CuZnGeSe.

§ 5.2 Temperature Variation of Energy Gap

5.2.1 Results and Analysis

One semiconductor property which is affected by the magnetic behaviour of materials containing manganese is band-gap. Theoretical analysis by Alexander et al. (76A1) has shown that around a magnetic critical point, in addition to the normal semiconductor effects, there will be a magnetic contribution to the variation of band-gap with temperature. They indicated that for an antiferromagnetic exchange interaction, the effects should cause an increase in the band-gap of the semiconductor, while a decrease in the band - gap should be observed for a ferromagnetic exchange. It has been shown by Donofrio et al.(85D1), that the spin glass case of antiferromagnetic exchange interaction type for $\text{Cd}_x\text{Zn}_y\text{MnTe}$ alloys, showed good agreement with Alexander et al's theory. It has also been shown by Quintero et al. (90Q1), for the ferrimagnetic case of AgGeSe (o), that band-gap variation with temperature for that case also is in reasonable agreement with the prediction of Alexander et al.. This latter case is the only investigation involving the present types of quaternary compound and so there is no previous investigations of antiferromagnetic compounds of this type. Here in the present work, further examples of both antiferromagnetic and ferrimagnetic phases are investigated.

The variation of the optical energy gap E_o was determined as a function of temperature in the range of $10 \text{ K} \leq T \leq 300 \text{ K}$ for three

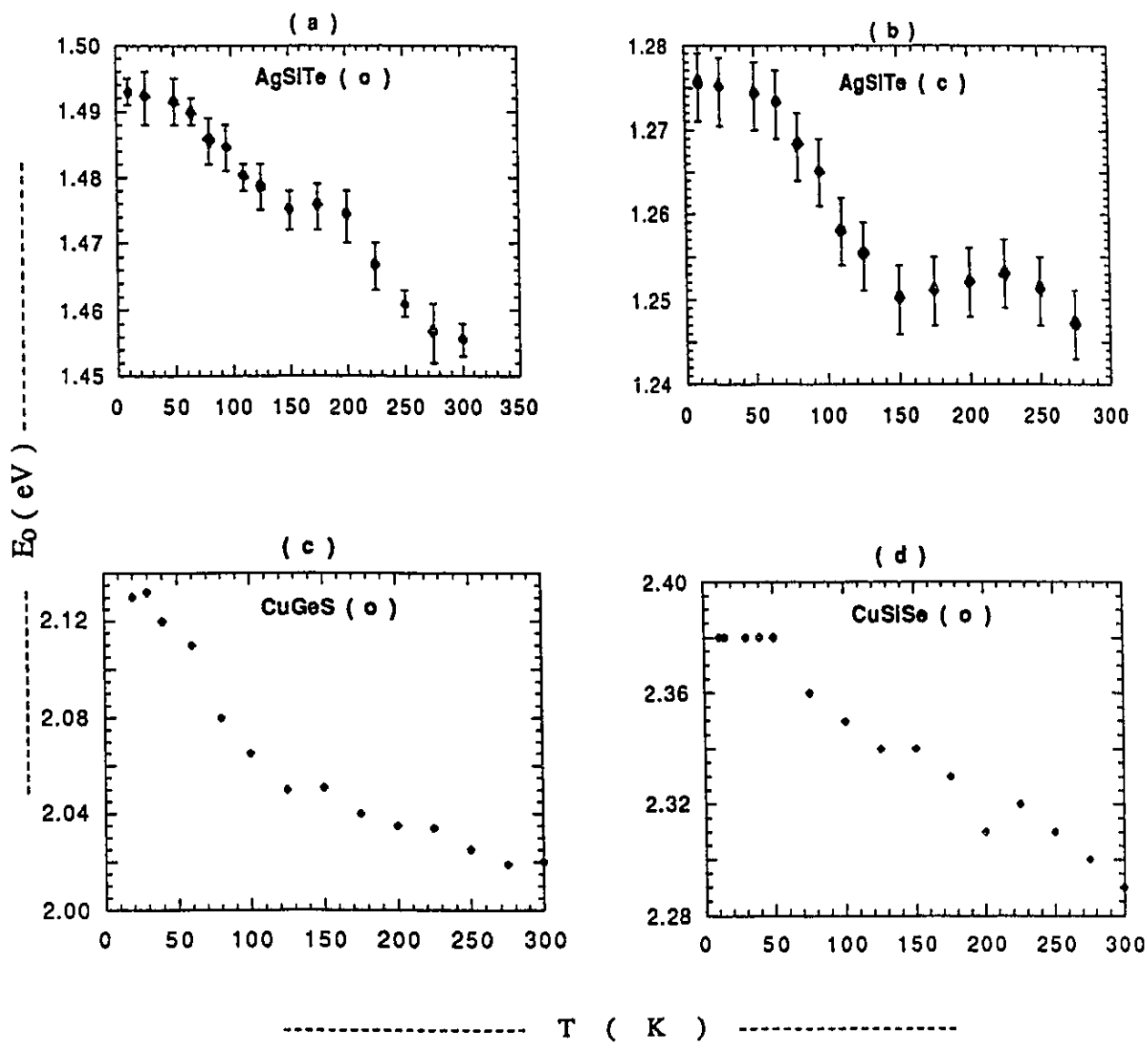


Fig. 5.2.1 Variation of optical energy gap E_0 with temperature T .

Error bars are shown in a & b for AgSiTe (o) & (c).

I₂.Mn.IV.VI₄ compounds: AgSiTe(o + c), CuGeS(o), CuSiSe(o). Both AgSiTe phases are ferrimagnetic with T_N of 155 K for cubic phase, and 90 K for orthorhombic phase, while the latter two are antiferromagnetic with T_N = 10 K and 9 K respectively.

As described in § 2.4, the optical samples were mounted in an OXFORD 204 Cryostat so that the temperature could be controlled at any point in the range 10-300K, and values of E_o were determined at various temperature in that range. The same method of optical absorption measurements and analysis as was used in the room temperature was applied at each lower temperature to obtain the energy gap at that temperature. The resulting curves of E_o vs.T for AgSiTe(o), AgSiTe(c), CuGeS(o), and CuSiSe(o) are shown in Fig.5.2.1a, b, c, d. As is seen from Fig.5.2.1a & b, in the case of AgSiTe, energy gap values were determined for both the cubic phase and the orthorhombic phase, and this will be discussed further below.

The theoretical predictions of Alexander et al.(76A1), based on an analysis of the effects of spin fluctuations around a magnetic critical point T_c on the energy value of band extrema indicated that the variation of the magnetic contribution to the band gap satisfies a relation of the form

$$\frac{d}{dt} \Delta E = - P t^{-\mu} \quad (5.2-1)$$

where ΔE represents the extra contribution to the energy gap due to the magnetic behaviour, i.e.

$$\Delta E = E_o - E_{on} \quad (5.2 - 2)$$

where E_o is the observed energy gap, and E_{on} the value the energy gap would have if no magnetic effect occurred, while t is the reduced temperature difference $|T - T_c| / T_c$ and the exponent μ depends upon the particular conditions being considered, P is a constant independent with t and μ . Alexander et al.(76A1) considered two different temperature regions, the critical one, close to T_c , and the noncritical region outside this critical range. For the noncritical region, Alexander et al. showed that μ should have a value of 0.5, while Kasuya and Kondo (74K1) indicated that in the critical range μ should have a value close to zero. Integration of eq. 5.2-1 gives

$$\Delta E = - P t^{1-\mu} / (1 - \mu) + K \quad (5.2 - 3)$$

The value of ΔE at T_c is written as ΔE_c and hence

$$\Delta E = - P t^{1-\mu} / (1 - \mu) + \Delta E_c \quad (5.2 - 4)$$

Thus if values of ΔE are determined from the experimental data, P and μ values can then be determined from analysis in terms of eq. 5.2-4. It is easily seen that in an antiferromagnetic case, $\Delta E_c \geq \Delta E \geq 0$, this gives a P value with a positive sign, and for a ferrimagnetic case, $\Delta E_c \leq \Delta E \leq 0$, and this gives a P value with a negative sign.

In order to determine ΔE values, it is necessary to know $E_{on}(T)$, the values that the energy gap would have in the absence of any magnetic effects. These can be determined by extrapolating the E_o vs. T curve from

the region where the magnetic contribution are negligible, i.e. regions well different in temperature from T_c , to the temperature region where magnetic effects occur. In the nonmagnetic regions $E_{on} = E_o$, and the extrapolation can be made by using a simple Manoogian-Leclerc equation(79M1)

$$E_{on}(0) - E_{on}(T) = UT^{2/3} + V\phi(\coth(\phi/2T) - 1) \quad (5.2 - 5)$$

where U, V and ϕ are constants independent of T.

Because of the limited temperature range over which equn 5.2 - 5 can be used in the present cases, it is not possible to determine all of the unknown parameters, i.e. $E_{on}(0)$, U, V and ϕ by least squares fitting. However certain assumptions can be made about the values of the parameters. As pointed out by Manoogian and Leclerc (79M1), over most of the temperature range the term in U is appreciably smaller than that in V so that the value of U is less critical. From previous analysis (85D1, 87C1, 90G1 , 89Q1), it appears that in magnitude $2U = V$ is a reasonable estimate in many cases. This leaves the parameters $E_{on}(0)$, V and ϕ to be determined. When T_c is in the approximate range 80 - 220K, which is the case for AgSiTe(o) and AgSiTe(c), data from both the low temperature and the high temperature ends of the measured range can be used in the Manoogian fit, and as a result accurate values can be determined for all three parameters, as shown below. However when only the high temperature data can be fitted, e.g. cases of CuGeS(o) and CuSiSe(o), it is found necessary to assume a value for ϕ . From the cases above and also

from previous work (89Q1, 85D1), it is found that a good estimate of ϕ in these particular materials is about 220 K. Values of $E_o(0)$ and V can be obtained by a least squares fit to the relevant data.

The values of μ and P can usually be obtained by plotting $\ln|\Delta E_c - \Delta E|$ against $\ln t$. By taking $\ln$ values, equn. 5.2 - 4 gives

$$\ln|\Delta E_c - \Delta E| = \ln \frac{|P|}{1 - \mu} + (1 - \mu) \ln t \quad (5.2 - 6)$$

If $\ln|\Delta E_c - \Delta E|$ is plotted against $\ln t$, it is obvious that

$$\mu = 1 - s \quad (5.2 - 7)$$

$$|P| = (1 - \mu) \exp I \quad (5.2 - 8)$$

where s is the slope and I the intercept on the $\ln|\Delta E_c - \Delta E|$ axis. This method was used to determine the values of μ and P for the cases of $\text{AgSiTe}(o)$, $\text{AgSiTe}(c)$ and $\text{CuGeS}(o)$, as will be discussed in more detail below.

As indicated above, for AgSiTe compound, X-ray data showed that in addition to the main orthorhombic phase, a small amount of the cubic phase was also present. In the curves of α vs. $h\nu$ for various temperatures, the effects of the two band-gap were both observed at each temperature. From the curves of α vs. $h\nu$, it is seen that the phase with lower energy gap has a much smaller α value and hence since both gaps are direct, the smaller α values must be due to a much smaller amount of that phase. Thus the lower energy gap must be associated with the cubic phase, and the higher gap is due to the dominant orthorhombic phase.

Figs. 5.2.1a & b (page 109) show the variation of E_o with T for the two

cases, and the error bars shown in each case indicate the estimated experimental uncertainty from the $(\alpha h\nu)^2$ vs. $h\nu$ curves. When this data was fitted to the Manoogian equation, the value corresponding to the centre of each error bar was used.

For AgSiTe(o), the magnetic results give $T_c = 90K$, therefore both low temperature and high temperature ends can be fitted with Manoogian equation. From the lower T end, the $E_o(T)$ vs. T curve (Fig. 5.2.1a) shows that $E_{on}(0) = 1.491eV$. Assuming that in magnitude $2U = V$, as mentioned above, the Manoogian equation 5.2.5 becomes

$$E_{on}(0) - E_{on}(T) = (V/2) \{ T^{2/3} + 2\phi [\coth(\phi/2T) - 1] \} \quad (5.2-9)$$

let

$$x = \{ T^{2/3} + 2\phi [\coth(\phi/2T) - 1] \} \quad (5.2-10)$$

equation above can be simplified as

$$E_{on}(0) - E_{on}(T) = (V/2) x \quad (5.2-11)$$

this leaves V and ϕ to be determined. To determine these two parameters, $E_o(m)$ against x in the range $T \geq 150K$ were plotted as shown in Fig.5.2.2a (page 103) and it was found that the values of $\phi = 220K$ and $V/2 = 4.325 \times 10^{-5} eV / K$ gave the best fit, as shown in Fig. 5.2.2b. The fitted curve was then extrapolated to the temperature range below 150K, and ΔE values could then be obtained (Fig. 5.2.2c). Thus a graph of $\ln|\Delta E_c - \Delta E|$ vs. $\ln t$ could be plotted, t being the value $|T - T_c|/T_c$. When T_c was taken to be 90K, as determined from the magnetic data, the resulting graph splits into two

parallel lines, corresponding to the values above and below T_c , which appeared inconsistent with the theoretical development. However, this splitting was clearly dependent on the value taken for T_c and when T_c was taken as 92K, the plot of ΔE vs. T showed good symmetrical form(Fig. 5.2.2c) and the plot of $\ln|\Delta E_c - \Delta E|$ vs. $\ln t$ became a single straight line (Fig. 5.2.2). The small difference between T_c of 92K and 90K is well within the experimental error for temperatures measured on two completely different pieces of equipment. The $\ln|\Delta E_c - \Delta E|$ vs. $\ln t$ line gave values of $s = 1.52$ and intercept $I = -4.21$, and hence from equations 5.2-7 & 8, the values of $\mu = -0.52 \pm 0.05$ and $P = -0.023 \pm 0.003$ eV were obtained.

In the case of AgSiTe(c), magnetic results showed that $T_c = 155K$, therefore both low temperature and high temperature ends can again be used in Manoogian fitting. From the curve of $E_o(t)$ vs. T shown in Fig. 5.2.1b, $E_o(0) = 1.275\text{eV}$ was taken and the Manoogian equation was fitted to the ranges of both T below 80K and T above 200K. A reasonable fit (Fig. 5.2.3a) was obtained with $\phi = 220K$ and $V/2 = 3.80 \times 10^{-5}$ eV/ K. In order to obtain a single line for the plots $\ln|\Delta E_c - \Delta E|$ vs. $\ln t$, T_c was taken to be 145 K, so that the curve of ΔE vs. T showed a good symmetry (Fig. 5.2.3b), and the graph of $\ln|\Delta E - \Delta E_c|$ vs. $\ln t$, shown in Fig. 5.2.3c, was a reasonable straight line. From this line, the resulting values of $\mu = -0.52 \pm 0.05$ and $P = -0.053 \pm 0.003\text{eV}$ were again obtained. As indicated above, the value of T_c obtained is within the limits of experimental error when

compared with the magnetic results obtained in § 4.1.

In the case of CuGeS(o), the variation of E_o with T is shown in Fig. 5.2.1c. In this case, the experimental values of E_o could be determined to $\pm 0.003\text{eV}$, so no error bars are shown in the graph. From the magnetic results (see § 4.1), $T_c = 10\text{K}$, so the low temperature end of the E_o vs. T graph could no longer be used to fit with the Manoogian equation. It was therefore necessary to assume the value of ϕ to be 220K , as found in the previous analysis. By plotting E_o vs. x in the range $T \geq 150\text{K}$, as is shown in Fig. 5.2.4a, the slope $= 1.10 \times 10^{-4} = V$ and the intercept $= 2.064\text{eV} = E_o(0)$ were found. The resulting fit to the Manoogian equation in the range $150 - 300\text{K}$ is shown in Fig. 5.2.4b. Values of ΔE are determined as before and the plot of $\ln |\Delta E - \Delta E_c|$ vs. $\ln t$ for $T_c = 10\text{K}$, is shown in Fig. 5.2.4c. From this graph values of $\mu = -0.42 \pm 0.05$ and $P = 0.0051 \pm 0.0005\text{eV}$ were obtained. In the case of CuSiSe(o), as indicated above, the value of the direct gap could be determined only to the nearest 0.01eV , as shown in Fig. 5.2.1d. Because of this, it is not feasible to carry out a direct analysis of the data to give values of the parameters occurring in equns. 5.2-4 & 5 using the same method as was used for the three cases discussed above. However, an alternative approach is to assume that the value of μ is -0.5 and to show that with an appropriate value for P , equns. 5.2-4 & 5 can give a good fit to the experimental data. Again the Manoogian equation was fitted to the experimental data in the range $T \geq 125\text{K}$ assuming $\phi = 220\text{K}$. This gave the

resulting curve of E_{on} shown in Fig. 5.2.5a. For $T_c = 10K$ in this case, from the curve in Fig. 5.2.5a, ΔE_c was taken as 0.025eV. The variation of ΔE and hence E_o with T was then calculated from equn. 5.2-4 for various values of P , and it was found that $P = 0.0025 \pm 0.0002eV$ gave a good fit to the experimental data as shown in Fig. 5.2.5b.

The above method of analysis for $CuSiSe(o)$, is very similar to that used by Quintero et al.(90Q1) in the case of $AgGeSe(o)$. In that case, the Manoogian equation with $\phi = 220K$ was fitted in the range 125 - 300K. The resulting curve is shown in Fig. 5.2.6a. Since Kasuya and Kondo (74K1) had indicated that the value of μ should be close to zero in the critical region, a value of $\mu = 0$ was assumed in that case (90Q1) and a good fit to the experimental data with $E_o(0) = 1.5082eV$ was obtained as shown in Fig. 5.2.6a. However, in the present work, the measured E_o against x was plotted in the range $T \geq 150 K$ with assuming value $\phi = 220K$ (shown in Fig. 5.2.6b), it was found that the slope $= 8.9 \times 10^{-5} = V$ and the intercept $= 1.51eV = E_o(0)$, this gives a Manoogian fit shown in Fig. 5.2.6c. According to the analysis of all the above cases, in the critical region μ tends to have a value close to - 0.5. Thus, in the present work, the experimental data of $AgGeSe(o)$ was refitted with $\mu = - 0.5$ and using various values of P as described for $CuSiSe(o)$. In this case, a good fit was obtained, with $P = 0.004 \pm 0.005eV$, and the resulting curve is again shown in Fig. 5.2.6c.

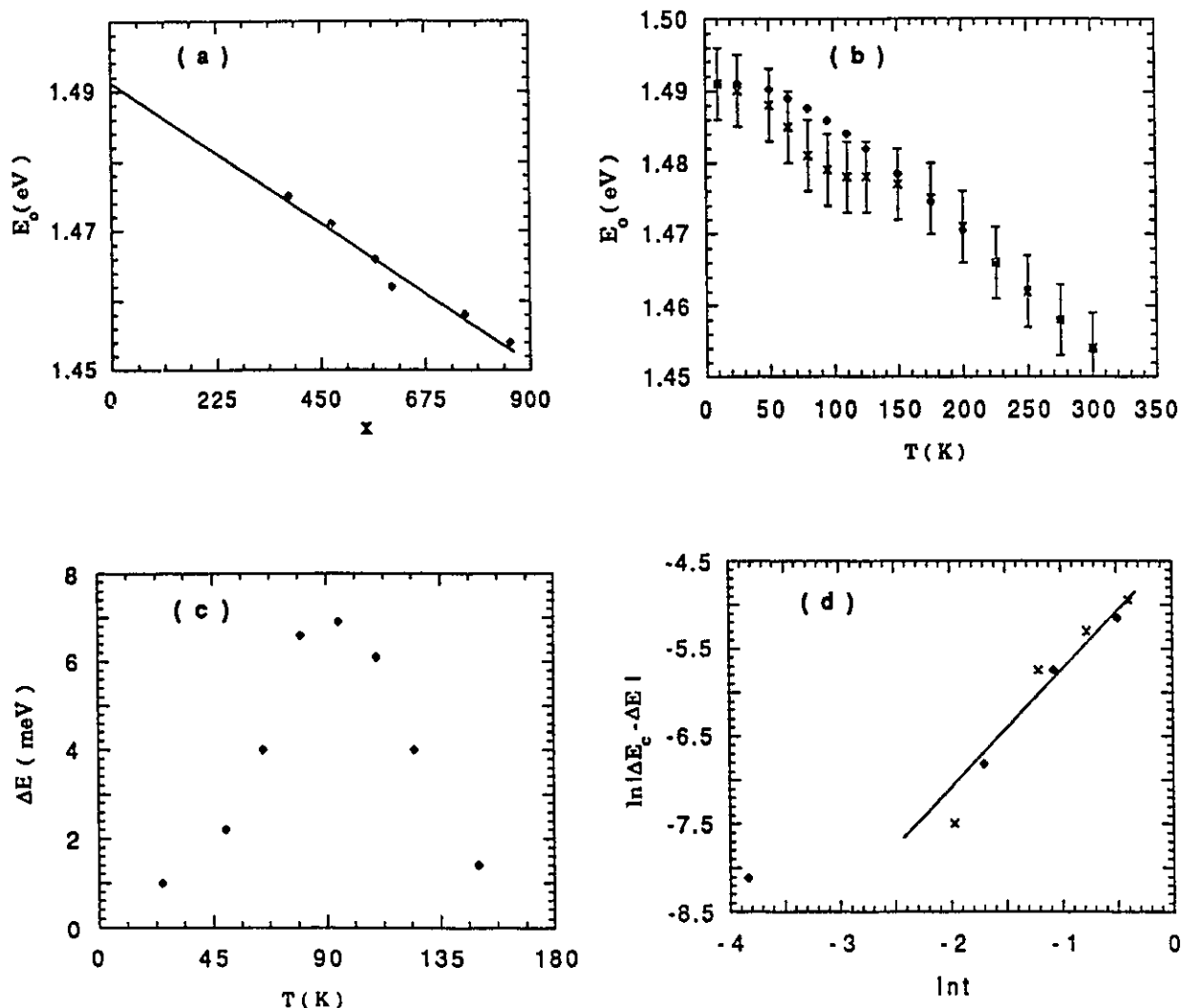


Fig. 5.2.2 Analysis for energy gap E_0 variation with temperature T for AgSiTe (o).

a. Extrapolation of measured energy gap with x (x is defined in eq. 5.2-9).

b. Variation of optical energy gap E_0 with temperature T .

—x— experimental values

◆ fit of Manogian - Leclerc equation to range 150 - 300 K

c. The symmetrical curve of ΔE against T .

d. Variation of $\ln|\Delta E_c - \Delta E|$ with $\ln t$.

◆ points above T_c

x points below T_c

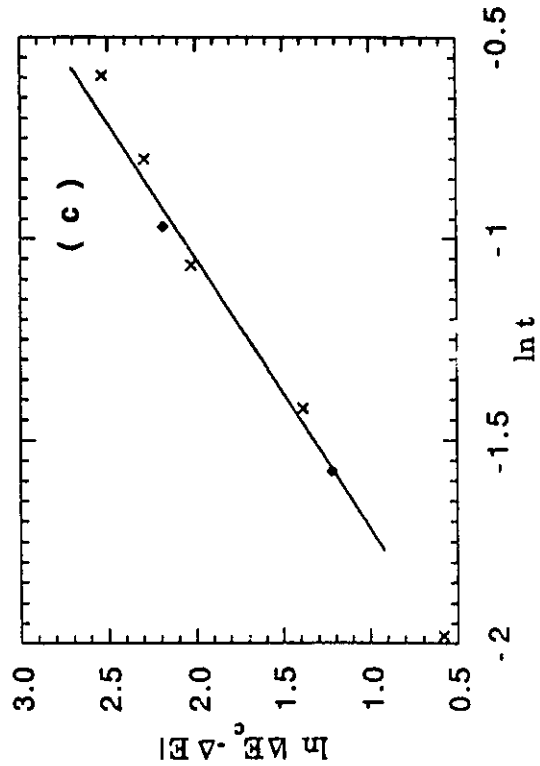
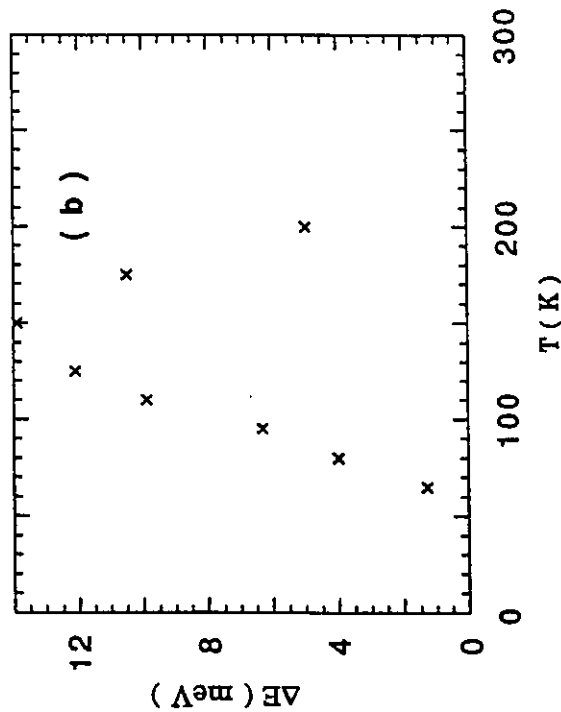
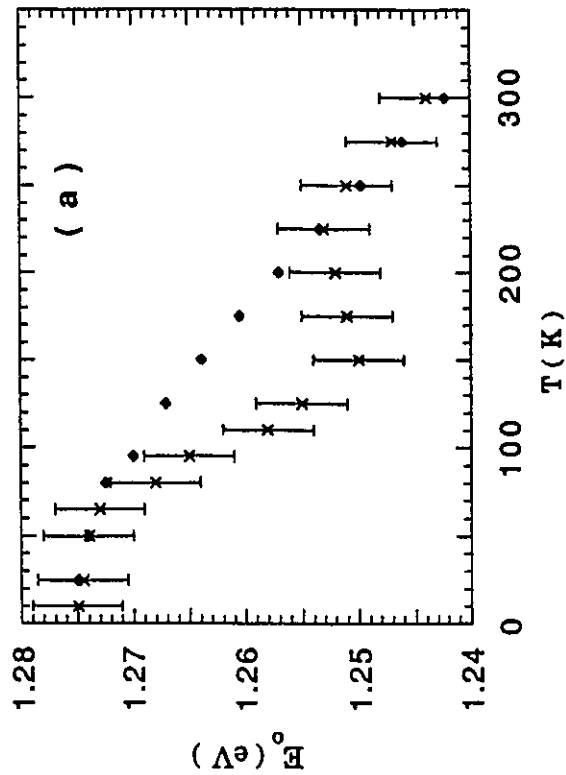


Fig. 5.2.3 Analysis for energy gap E_o variation with temperature T for AgSiTe (c).

- a. Variation of optical energy gap E_o with temperature T .
 $\times$ experimental values
 $\diamond$ fit of Manoogian - Leclerc equn. for T below 80K and T above 200K
- b. The symmetrical curve of ΔE against T .
 $\diamond$ Variation of $\ln |\Delta E_c - \Delta E|$ with $\ln t$.
 $\times$ points above T_c
 $\times$ points below T_c

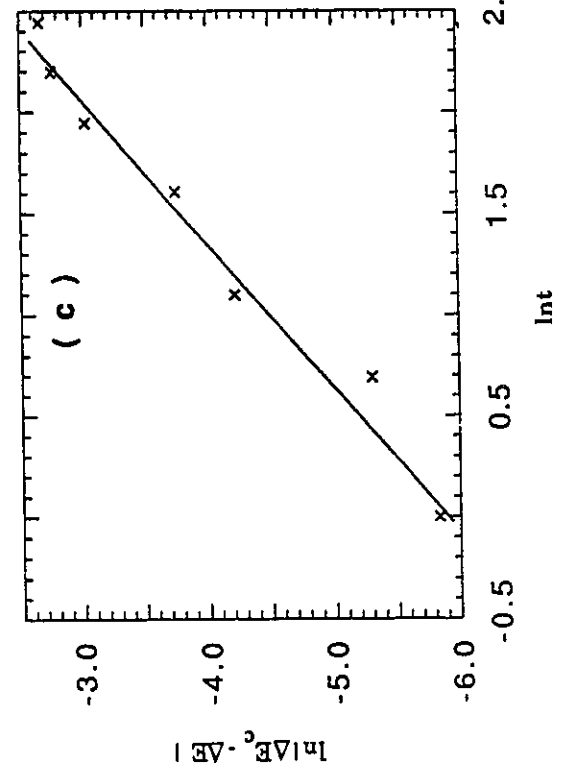
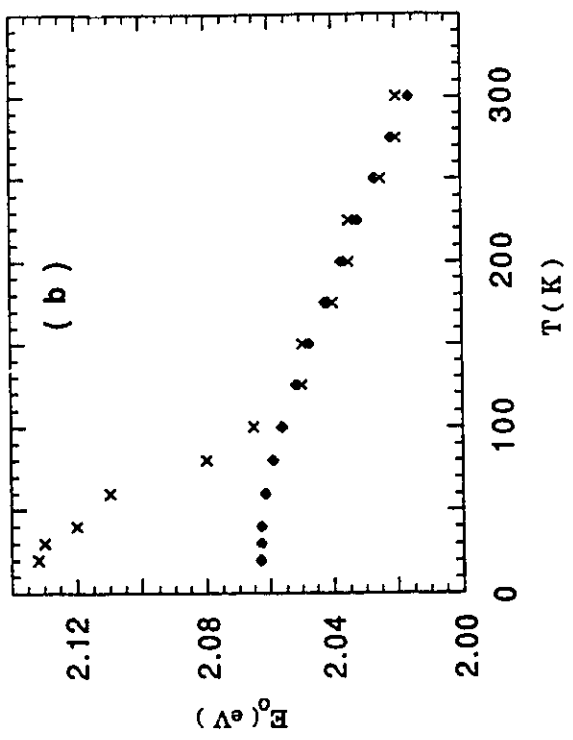
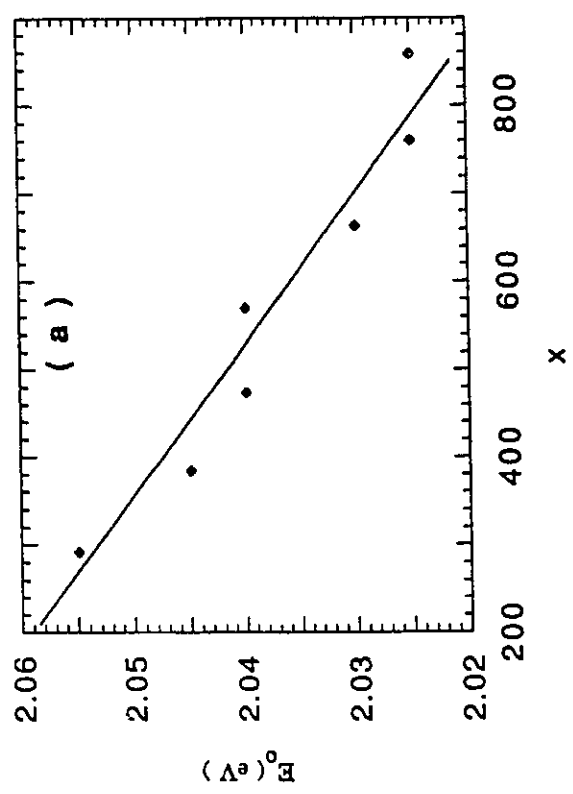


Fig. 5.2.4 Analysis for energy gap E_o variation with temperature T for CuGeS (o).

a. Extrapolation of measured energy gap E_o with x .

b. Variation of optical energy gap E_o with temperature T .

c. Variation of $\ln|\Delta E_c - \Delta E|$ with $\ln t$.

x experimental values
 $\diamond$ fit of Manogian; - Leclerc eqn. for T above 150K

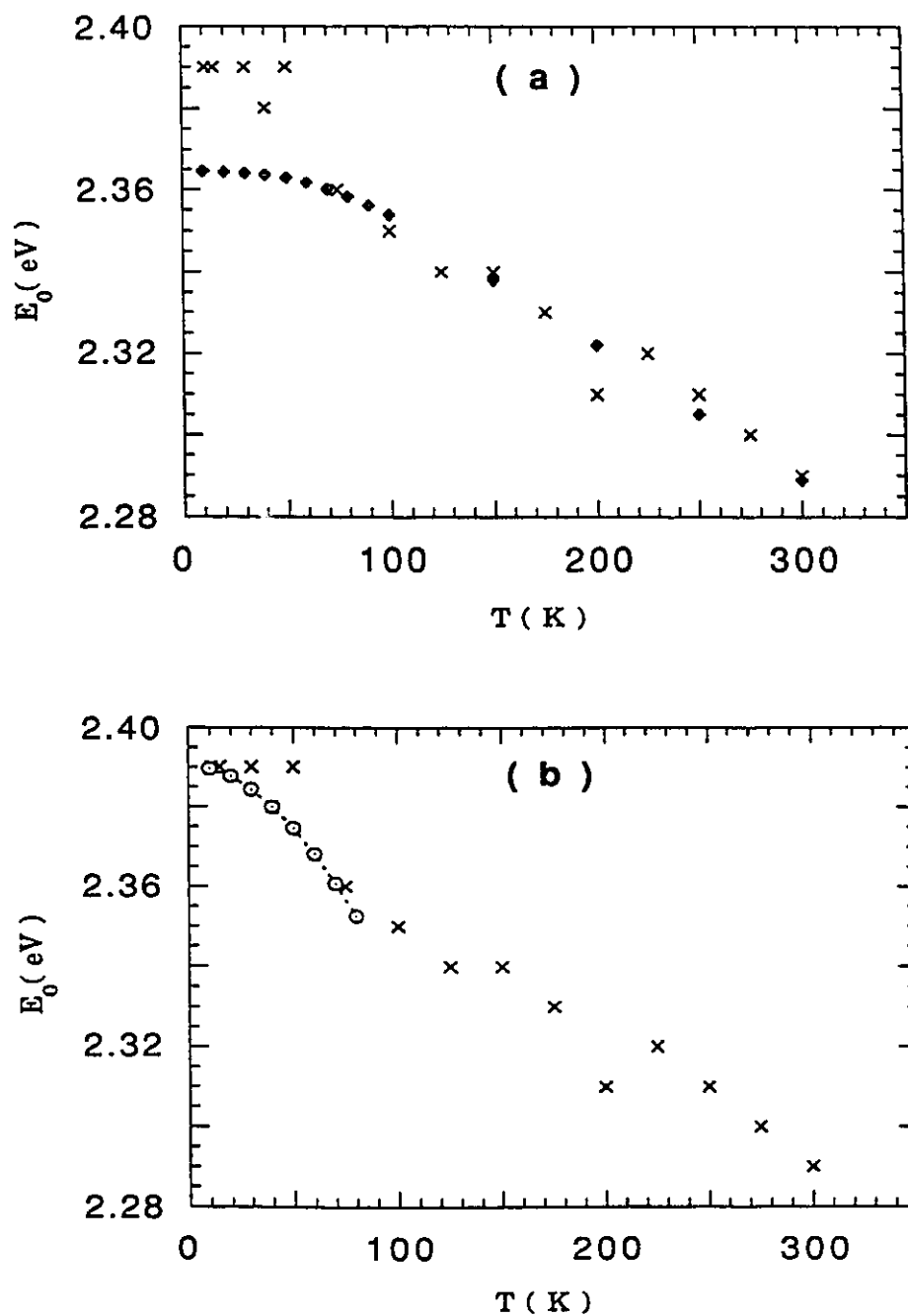


Fig. 5.2.5 Variation of optical energy gap E_0 with temperature T for CuSiSe .
 × experimental values
 ◆ fit of Manogian-Leclerc equation for T above 125K
 ---○--- predicted values of E_0 from analysis of Alexander et al.

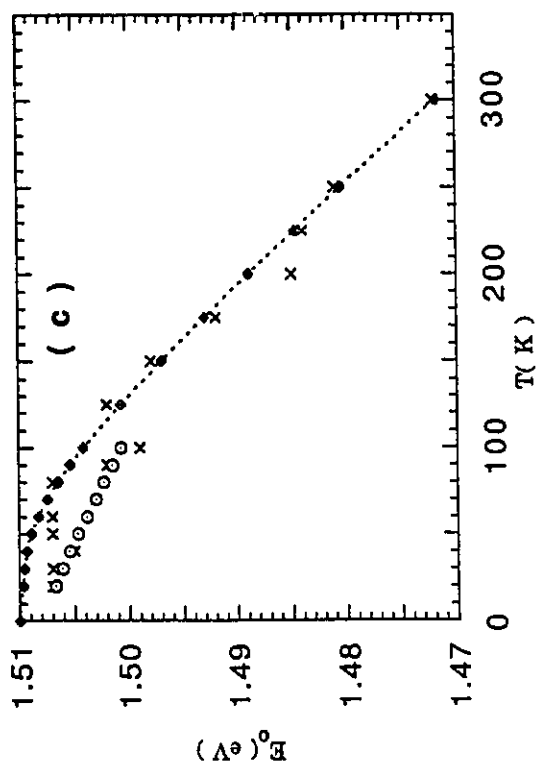
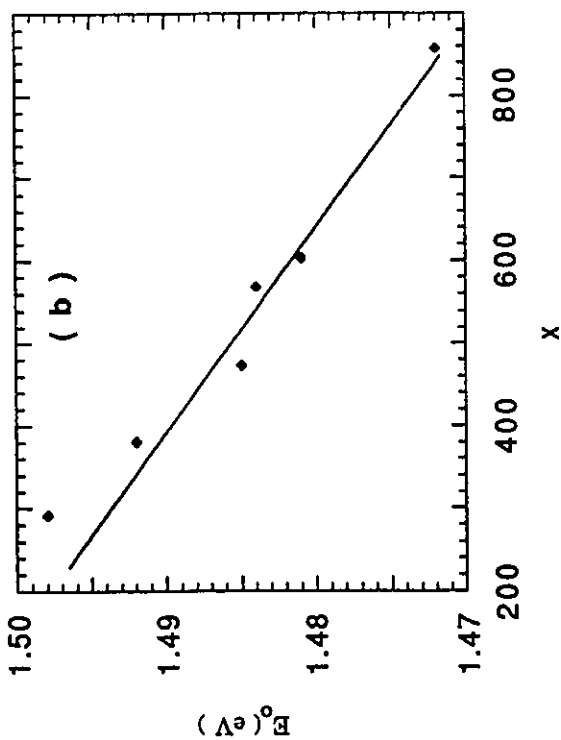
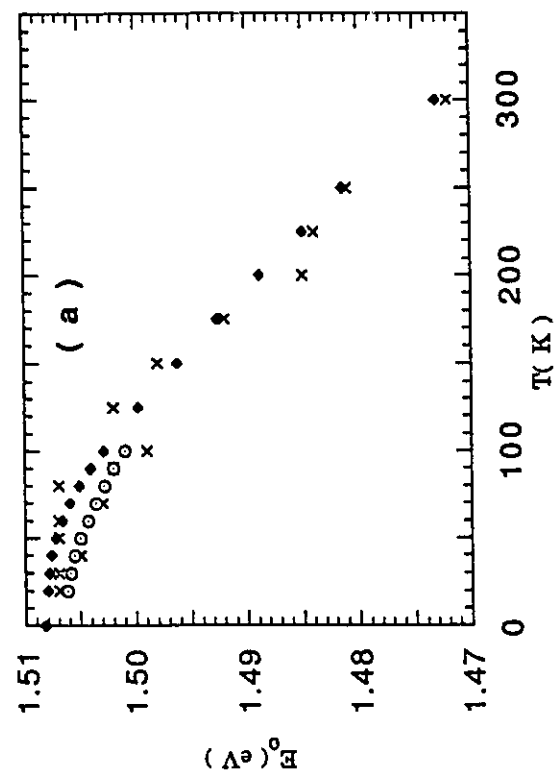


Fig. 5.2.6 Analysis for energy gap E_0 variation with temperature T for AgGeSe (o).

- a. Variation of E_0 with T taken from literature(90Q1).
- x experimental values
 - ◆ Manooogian fit with $E_{on}(0) = 1.5082\text{eV}$.
 - predicted values assuming $\mu = 0$.
- b. Extrapolation of measured energy gap $E_0(m)$ with x .
- c. Variation of energy gap E_0 with T .
- x experimental values
 - ◆ Manooogian fit with $E_{on}(0) = 1.51\text{eV}$.
 - predicted values assuming $\mu = -0.5$.

5.2.2 Discussion:

Here measurements were made on the variation of E_o with T for four different $I_2.Mn.IV.VI_4$ quaternary compound phases. In previous work (90Q1) on one example of this type of compound with ferromagnetic behaviour, it was shown that the predictions of Alexander et al. fitted well the experimental data, with regard to the contributions due to the magnetic behaviour acting to decrease the observed energy gap. In the present work, different samples showing either antiferromagnetic or ferromagnetic behaviour were investigated. It was shown that the theoretical predictions of Alexander et al., when applied to a Manogian-Leclerc equation, give a good fit to these experimental data, where in the antiferromagnetic cases of $CuGeS(o)$ and $CuSiSe(o)$, the magnetic contribution acts to increase the value of the energy gap, while for the ferromagnetic cases of $AgSiTe(o)$, $AgSiTe(c)$, and $AgGeSe(o)$, the magnetic contribution tends to decrease the value of the energy gap. The values of μ and P obtained from this analysis are summarized in table 5.2.1. Previous theoretical analysis of Kasuya and Kondo (74K1) indicated that in the critical region, μ should have a value close to zero, and previously, experimental investigation of the spin-glass alloys (86D1) gave values of μ in good agreement with this. However, in the present work the values of μ for the $I_2.Mn.IV.VI_4$ phases in the critical regions are found to be close to -0.5. The reasons for this difference in μ has not as yet been determined.

	Compound	Symmetry	A/F	T _c (K)	μ	P(eV)
1	CuGeS	o	A	10	- 0.42 ± 0.05	0.0051 ± 0.0005
2	CuSiSe	o	A	10	- 0.5	0.0025 ± 0.0002
3	AgGeSe	o	F	64	- 0.5	0.0040 ± 0.0005
4	AgSiTe	c	F	145	- 0.52 ± 0.05	- 0.053 ± 0.003
5	AgSiTe	o	F	92	- 0.52 ± 0.05	- 0.023 ± 0.003

Table 5.2.1 Parameters obtained from analysis of Alexander et al.'s theory.

Chapter 6 Summary of Results

§ 6.1 Summary of Present Results

Polycrystalline semimagnetic semiconductor compounds of the form $I_2\text{Mn.IV.VI}_4$ with $I = \text{Ag or Cu}$, $\text{IV} = \text{Si, Ge, Sn}$ and $\text{VI} = \text{S, Se, Te}$ were prepared by melt and anneal technique. X-ray diffraction, SQUID and optical absorption measurements were performed to characterize the various compound phases obtained.

From the Debye-Scherrer X-ray powder photographs it was found that three different crystal structures occurred in these compounds. Two of these corresponded to the tetragonal stannite and orthorhombic wurtz-stannite structures reported previously but, as indicated below, the ordering of the Mn atoms in some of these compounds may be different from the stannite and wurtz-stannite structures. The third structure observed showed the lines corresponding to the cubic rock-salt form but showed also various ordering lines, indicating again that ordering of the cations is present and that the crystal symmetry is lower than cubic.

The Cu, S and Cu, Se compounds each showed only one structure, either the tetragonal or orthorhombic form, independent of temperature. However most of the Ag and Te compounds showed two different structures, either the tetragonal or orthorhombic but also the cubic form, depending upon the temperature of annealing and the method of cooling to room temperature. Also all of the Te compounds were found to be two or

three-phases in room temperature equilibrium, but quasi-stable single phase samples could be obtained at room temperature by rapid quenching. Lattice parameter values were obtained for all single phases observed and hence values determined for the effective lattice parameter $a_e (= (V/N)^{1/3}$, where V is the unit cell volume and N the number of molecules per unit cell).

Magnetic susceptibility measurements were made as a function of temperature on all available phases of the Se and Te compounds, and it was found that some seven phases were antiferromagnetic (mainly Se phases) but that twelve phases (almost all Te phases) were ferrimagnetic. From the $1/\chi$ vs. T data, values were determined for the Néel temperature T_N and, where possible, for the Curie-Weiss temperature θ_a .

Standard optical absorption measurements were made to determine values of optical energy gap E_o for a number of the single-phase samples. However for a number of cases, the materials crumbled when polishing was attempted and so samples thin enough for optical absorption measurements could not be obtained. For four phases, the variation of E_o with T in the range 10 - 300K was determined. The results for $\text{AgGeSe}(o)$ taken from the literature(90 Q1) were reanalyzed.

When the values of the parameter a_e were plotted as a function of molecular weight W , it was found that the values lie on five separate straight lines, effectively defining five different sets of phases. The values of the parameters T_N , θ_a and E_o were then plotted against a_e and again

different lines corresponding to the different sets were observed. For any given parameters, the lines were clearly different from one set to another.

The five sets of phases can be listed as follows:

1) tetrahedrally bonded (orthorhombic or tetragonal structure)
with $I = \text{Cu}$,

2) tetrahedrally bonded (orthorhombic or tetragonal structure)
with $I = \text{Ag}$ and antiferromagnetic behaviour,

3) tetrahedrally bonded (orthorhombic or tetragonal structure)
with $I = \text{Ag}$ and ferrimagnetic behaviour ,

4) Octahedrally bonded cubic structure with $I = \text{Cu}$,

5) Octahedrally bonded cubic structure with $I = \text{Ag}$.

The structures of sets 1, 2 and 3 must all be very similar from the present X-ray work, but differ in the detailed ordering on the cation sub-lattice, a detail which the present Debye-Scherrer photographs can not resolve. A similar story may apply in the case of sets 4 & 5, where ordering on a basic rock-salt type cubic sub-lattice occurs. For any further analysis of the behaviour of these phases, it would be necessary to obtain more detailed information on the various structures (see below).

For phases showing magnetic behaviour of the type described above, in a range of temperature around the critical temperature T_N , the value and temperature dependence of the optical energy gap E_o are affected by the magnetic interactions. This has been analyzed theoretically by Alexander et al.(76A1) who showed that there is a magnetic contribution

ΔE_0 to the band gap and that the magnitude of ΔE_0 is maximum at T_N , with ΔE_0 being positive for antiferromagnetic interaction and negative for ferromagnetic interaction. In the present work, it has been found that the variations of E_0 with T for five different phases are in very good agreement with the predictions of Alexander et al.. For two antiferromagnetic phases, positive values of ΔE_0 have been obtained, with maximum values at T_N , these maximum values being 72 meV for CuGeS(o) and 25 meV for CuSiSe(o). In the case of the three ferrimagnetic phases, the values of ΔE_0 were negative, again having maximum magnitude close to T_N , but these maximum were of the order 10 meV. The lower values of ΔE_0 in the case of the ferrimagnetic samples may be due to the fact that in those materials both ferromagnetic and antiferromagnetic exchange occur, so that the two effects could tend to cancel one another. In both the ferrimagnetic and antiferromagnetic cases, a value could be estimated for the critical parameter μ which appears in the equation of Alexander et al.. In all cases, for the critical temperature region, a value of $\mu = -0.5$ gave a good fit to the experimental data. This is in contrast to the value of $\mu = 0$ predicted by Kasuyi and Kondo (74K1) and observed for the zinc-blende type $Cd_xZn_yMn_zTe$ alloys (86D1), which show spin - glass behaviour. It is not known at the moment why these quaternary compounds show a different value for this parameter.

§ 6.2 Suggestions for Future Work

For many samples, the crystal structure analysis, the magnetic susceptibility fitting and the determination of optical energy gaps were limited by the crystalline condition of the samples being used. Thus to carry out further work on these materials, it is necessary to improve the production techniques used so as to obtain good single phase samples of the various phases of all of the compounds. If possible, single crystal samples should be obtained.

As indicated above, it is probable that the differences in behaviour of the various sets of phases are due to detailed differences in the ordered crystallographic structures. However the present X-ray powder photographs are insufficient to detect such differences in the Mn ordering in the phases. If single crystal samples were obtained, more detailed X-ray diffraction techniques could give useful information. However, a better technique to show the positions of the Mn atoms in the crystal lattice would be neutron diffraction measurements, which could be carried out on polycrystalline single-phase samples. With such measurements, the ordered arrangement of Mn on each crystal lattice could be obtained.

The values of T_N , θ_a and θ obtained from the magnetic susceptibility data are related to the values of the various exchange interaction parameters, γ_{ab} , α and β as indicated by the equns. 2.3 - 6 & 7. But in order to analyze the magnetic data in this way, details of the ordered

crystallographic structure are required. If this were obtained from neutron diffraction work, as indicated above, values of the exchange interaction parameters of the various structures could be determined. As indicated in the introduction, such information could be very useful in considering the possible technological applications of these materials.

The study of optical energy gap values, their variation with crystallographic structure and their temperature variation and correlation with magnetic behaviour has been limited by the physical condition of the materials. Thus in many cases, sufficiently thin samples for optical transmission could not be obtained, since even with very careful treatment the samples tended to crumble to a powder. Samples with better crystallographic and physical conditions would allow more detailed measurements of optical energy gap behaviour to be carried out.

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