

Crystal Structures of $I_2 \cdot Mn \cdot IV \cdot VI_4$ Compounds

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Polycrystalline samples of 18 quaternary compounds of the form $I_2 \cdot Mn \cdot IV \cdot VI_4$ with $I = Cu, Ag$, $IV = Si, Ge, Sn$, and $VI = S, Se, Te$ were made from the elements using the melt and anneal technique. By using various annealing temperatures, it was shown that while the compounds involving $I = Cu$, $IV = Si$ and Ge , and $VI = S$ and Se showed only one structure which was stable down to room temperature, for most of the other compounds, two different structures could be found, depending upon the annealing temperatures used. Also for all of the Te compounds, annealing or slow cooling below $400^\circ C$ produced a two- or multiphase condition. However, single-phase conditions produced by rapid quenching from higher temperatures were quasistable at room temperature. Lattice parameter values were determined for all of the single-phase forms and values were calculated for the effective lattice parameter $a_e (= (V/N)^{1/3})$. It was found that with a_e plotted against the molecular weight W , five straight lines were obtained, each characteristic of a particular structure and magnetic behavior.

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Introduction

Semimagnetic compounds and alloys in which manganese is one of the component elements are of interest because of the large magneto-optical effects which can occur in these materials. Most work has so far been concerned with the semimagnetic semiconductor alloys obtained from the $II \cdot VI$ compounds by replacing a fraction of the group II cations with manganese, producing an alloy which shows spin-glass behavior (1). It was recently suggested (2–4) that magneto-optical effects larger than those for the $II \cdot VI$ -derived alloys could be obtained in materials in which the antiferromagnetic interaction between nearest-neighbor manganese ions was smaller, and the interaction between ions on the same magnetic sublattice was greater. It was suggested that one

set of materials which could satisfy these conditions were the $I_2 \cdot Mn \cdot IV \cdot VI_4$ compounds.

These compounds are a set of the $I_2 \cdot II \cdot IV \cdot VI_4$ compounds, which have been investigated by a number of workers (5–9), the work being almost completely concerned with the compounds with $I = Cu$ and $VI = S$ or Se . It was shown that in almost all cases, the compounds investigated showed an ordered structure based on either the zinc-blende or wurtzite form and were either tetragonal, with the stannite structure, or orthorhombic, with the wurtz-stannite structure (6, 8). For the $I_2 \cdot Mn \cdot IV \cdot VI_4$ compounds (hereafter labeled $I \cdot IV \cdot VI$ for convenience), Guen and Glaunsinger (9) investigated the magnetic behavior of five cases, $CuSiS$, $CuGeS$, $CuSnS$, $CuGeSe$, and $CuSnSe$, and showed the first four to be

antiferromagnetic with Curie–Weiss θ values in the range -20 – 0 K and Néel temperatures T_N in the range 0 – 20 K. From their results on CuSnSe, they concluded that this was ferromagnetic with $T_C = 27$ K. 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. Here the parameter $(V/N)^{1/3}$ will be written as a_e , the effective lattice parameter.

No data appears to have been published for $I_2 \cdot Mn \cdot IV \cdot VI_4$ compounds with $I = Ag$ or with $VI = Te$. In the present work, all 18 compounds given by $I = Cu, Ag, IV = Si, Ge, Sn$, and $VI = S, Se$, Te have been investigated and correlations found between the values of effective parameters a_e .

Sample Preparation and Experimental Measurements

All of the samples were prepared from the elements by the melt and anneal technique. The components of each 1.0-g sample were sealed under vacuum in a quartz capsule which had previously been coated with carbon in order to prevent reaction of the charge with the quartz. The capsule was then raised to a temperature of 1150°C , in the case of the Se and Te compounds in approximately an hour, but at a much slower rate for the S compounds with stops at intermediate temperatures to allow some reaction to occur. The samples were held at 1150°C for a time of $\frac{1}{2}$ to 1 hr and then cooled to room temperature. Samples were then annealed at various temperatures for a week and then, in most cases, quenched to room temperature. Details of the individual heat treatments will be discussed further below.

After annealing, Debye–Scherrer X-ray powder photographs, with a 114.6-mm radius camera, were used to check the condi-

tion of the samples and, where appropriate, to determine lattice parameter values.

Results and Discussion

The compounds containing Cu and S or Se were annealed at 625°C and then quenched to room temperature. The resulting X-ray photographs were in good agreement with the results of Schafer and Nitsche (8) and the structures, lattice data, and values of a_e are given in Table I. Samples annealed at lower temperatures showed no difference from those above, indicating that the structures observed were stable from temperatures above 625°C down to room temperature. Differential thermal analysis (DTA) data for the $(Cu_2Ge)_{1-z}Mn_{3z}Se_3$ diagram (10, 11) confirmed this for the case of $Cu_2MnGeSe_4$, which corresponds to the $z = 0.25$ point of that diagram.

In the cases of many of the compounds containing Te and/or Ag , very different behavior 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. The lattice parameters found for these phases are shown in Table I. For $AgSiS$, no clearly 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 was observed for each compound, depending on the temperature of annealing. In addition to the tetragonal and orthorhombic structures, apparently corresponding to the stannite and wurtz–stannite forms previously reported (6, 8), a cubic form with X-ray line distribution

TABLE I
SYMMETRY AND LATTICE PARAMETER VALUES IN NANOMETERS FOR EACH COMPOUND

Compound	Symmetry	<i>a</i>	<i>b</i>	<i>c</i>	<i>a_c</i>	W
CuSiS	o	0.7534	0.6330	0.6205	0.5320	338.4
CuGeS	o	0.7629	0.6514	0.6265	0.5380	382.9
CuSnS	t	0.5511	—	1.0820	0.5474	429.0
CuSiSe	o	0.7914	0.6784	0.6502	0.5589	526.0
CuGeSe	o	0.7981	0.6874	0.6550	0.5642	570.5
CuSnSe	t	0.5774	—	1.1423	0.5753	616.6
CuSiTe	t	0.5983	—	1.1724	0.5942	720.6
	c	0.605	—	—	0.605	
CuGeTe	t	0.5989	—	1.1978	0.5989	765.1
	c	0.615	—	—	0.615	
CuSnTe	t	0.6049	—	1.2098	0.6049	811.2
	c	0.6286	—	—	0.6286	
AgSiS	—	—	—	—	—	427.1
AgGeS	o	0.7947	0.6892	0.6527	0.5632	471.6
AgSnS	o	0.8019	0.6964	0.6527	0.5705	517.7
	c	0.5235	—	—	0.5235	
AgSiSe	o	0.7764	0.6644	0.6261	0.5445	614.6
AgGeSe	o	0.7830	0.6721	0.6417	0.5527	659.1
AgSnSe	o	0.8424	0.7348	0.6986	0.6002	705.2
	c	0.549	—	—	0.549	
AgSiTe	o	0.8120	0.6876	0.6689	0.5717	809.2
	c	0.575	—	—	0.575	
AgGeTe	t	0.579	—	1.158	0.579	853.7
	c	0.5882	—	—	0.5882	
AgSnTe	t	0.585	—	1.170	0.585	899.8
	c	0.6005	—	—	0.6005	

Note. o, orthorhombic; t, tetragonal; c, cubic.

corresponding to the rock-salt structure was observed in many cases.

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 (10, 11). One problem arising from this two- or multiphase behavior 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 present crystallographic work, it had to be considered in the magnetic measurements (12). However, the single-phase samples produced in this way were certainly metastable at room temperature. Thus it was found that for all three single-phase structures, samples measured at up to 18 months after production showed the same crystallographic and magnetic behavior 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 behavior 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 I, 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 results for the $(\text{Cu}_2\text{Ge})_{1-z}\text{Mn}_{3z}\text{Se}_3$ diagram 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 multiphase 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 above in Section ii. However, a sample annealed at 500°C and quenched showed a single-phase orthorhombic condition, with parameters as listed in Table I. In this case, DTA data for the 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 a 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 MnTe_2 lines. A sample annealed at 400°C and brine-quenched showed the tetragonal phase with no cubic phase but again very faint MnTe_2 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 (approximately 24 hr) showed the tetragonal phase plus several other undetermined phases and MnTe_2 . However, a sample annealed at 600°C and air-cooled 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 by reference to the phase diagram data for the $(\text{Cu}_2\text{Sn})_{1-z}\text{Mn}_{3z}\text{Te}_3$ system (10, 11). 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-cooled 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 with a little MnTe_2 .

(xi) *AgSnTe*. A sample annealed at 600°C

and air-cooled was cubic with very faint tetragonal and $MnTe_2$ lines present. When annealed at $400^\circ C$ and brine-quenched, the sample showed both tetragonal and cubic lines and fainter $MnTe_2$ lines.

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. 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. These values are all summarized in Table I. The problem of obtaining single-phase samples of each structure requires more detailed information of the relevant phase diagrams. DTA measurements were made on representative samples of most of the compounds, but interpretation of the data for a single composition was difficult and, as indicated above, in some cases did not help in the selection of annealing temperatures. Thus the $T(z)$ diagrams of the $(I_2IV)_{1-z}Mn_{3z}VI_3$ systems, for which the $I \cdot IV \cdot VI$ compound occurs at $z = 0.25$, are of interest. Three of these diagrams have been investigated (10, 11) and it is planned to continue with DTA measurements on others.

As shown by Guen and Glaunsinger (9), one convenient parameter for characterizing these compounds is the effective lattice parameter a_e ; values of a_e for all structures investigated here are given in Table I. In order to look at the variation of these values, it has been found useful to plot them against the values of the molecular weight W of the compound concerned; the results are shown in Fig. 1. It is seen that for given groups of compounds, the variation of a_e with W is linear. Thus it is seen that for all of the Cu compounds, 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

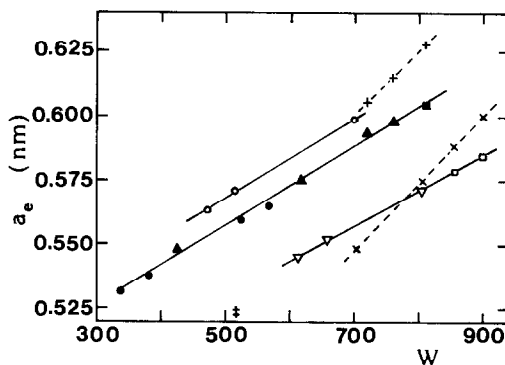


FIG. 1. Variation of effective lattice parameter a_e with molecular weight W . Cu compounds: ●, o a; ▲, t a; ■, t f; +, c f. Ag compounds: ○, o a; ‡, c a; ▽, o f; □, t f; ×, c f; o = orthorhombic, t = tetragonal, c = cubic, a = antiferromagnetic, and f = ferrimagnetic.

straight lines are observed. If these Ag values are compared with the magnetic data (12), 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. These three lines corresponding to the tetrahedrally bonded structures have very similar slopes. Turning to the presumed octahedrally bonded cubic structures, it is seen that again the three Cu cases (all of which are ferrimagnetic (12)) 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 (AgSnS), and this lies on none of the above lines.

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 behavior is due to differences in structure. Parthé *et al.* (6) carried out a detailed investigation of the crys-

tal structure of $\text{Cu}_2\text{CdGeS}_4$, which has orthorhombic symmetry, and other related compounds. In addition to the wurtz-stannite structure with space group $Pmn2_1$, they also considered the $\text{Na}_2\text{ZnSiO}_4$ structure with pseudoorthorhombic 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 photographs used would not be good enough to distinguish between different structures of this type, and hence it is not possible to say from X-ray data what the details of the orthorhombic structures are. Thus it is quite possible that the two different lines for the tetrahedrally coordinated Ag compounds represent different ordered structures. It is hoped that more detailed single crystal work on some of these materials will be carried out in the near future.

Conclusions

The $\text{I}_2 \cdot \text{Mn} \cdot \text{IV} \cdot \text{VI}_4$ compounds which contain neither Sn nor Te all 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 reported (6, 8). 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 phases being MnTe_2 . For each of these latter compounds, in addition to the tetragonal or orthorhombic ordered structures mentioned above, a cubic structure is observed with an X-ray line pattern indicating the rock-salt structure. In the case of the Te compounds, these struc-

tures are metastable when brine-quenched to room temperature, the samples retaining their crystallographic and magnetic behavior for at least 18 months of shelf-life. If the values of the parameter $a_c (= (V/N)^{1/3})$ for each phase observed are plotted against values of the molecular weight of the compound, it is found that the points lie on five different straight lines, each line being characteristic of a particular structure and magnetic behavior. On this basis, it is suggested that the Ag compounds with orthorhombic symmetry show two different, but very similar, structures.

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