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Crystal Symmetry of $Ag_2MnGeTe_4$ Phases

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Room-temperature neutron diffraction measurements were made on a polycrystalline sample of $Ag_2MnGeTe_4$, prepared by the melt and anneal technique. The results showed that both the ordered rock-salt form and the ordered zinc-blende form were present in the sample obtained and also three phases corresponding to the three-phase equilibrium condition at room temperature. Analysis of the diffraction data showed that both of the $Ag_2MnGeTe_4$ phases have orthorhombic *Imm*2 symmetry. It was also shown that the three room-temperature phases are $MnTe_2$, Ag_8GeTe_6, and $MnGe_3Te_4$. © 1995 Academic Press, Inc.

INTRODUCTION

Semiconductor compounds which contain manganese are of interest because of the influence of the magnetic behavior of the manganese on the semiconductor properties. A wide range of such compounds has been investigated (1, 2), and in recent work the present authors have carried out an investigation of the crystallographic, magnetic, and optical properties of the $I_2 \cdot Mn \cdot IV \cdot VI_4$ compounds (3–5). Previous investigation (6, 7) of $I_2 \cdot II \cdot IV \cdot VI_4$ sulfide and selenide compounds indicated that they had one of two ordered structures, one based on the zinc-blende form and the other an orthorhombic structure based on the wurtzite form and labeled wurtz-stannite. However, the present program has shown that in the case of all of the tellurides and a number of the selenides, in addition to the ordered zinc-blende form, the compounds can also show an ordered structure based on the rock-salt form. In each case the structure observed depends on the heat treatment used in the preparation of the material. In addition, it was shown that all of the tellurides are unstable at room temperature, decomposing into three phases. However, the single-phase form obtained at higher temperatures can be retained at room temperature by rapid quenching, and these single phases are quasi-stable under these conditions.

Measurements of magnetic susceptibility (4) indicated that the tellurides and some selenides showed weak ferromagnetic behavior at low temperatures, with critical temperatures T_C in the range 50–250 K. The magnetic parameters were found to be quite different for the rock-salt- and zinc-blende-based phases of each compound. It is to be expected that for magnetic behavior of this type, the magnetic symmetry of the phase will be relatively low, orthorhombic or less. Thus in the present compounds, both phases can be expected to show ordering which reduces the symmetry from the face-centered cubic form. The initial X-ray investigation (3) was insufficient to allow the symmetry groups of the ordered phases to be determined, partly because the X-ray scattering parameters of the various metallic atoms involved were all similar in magnitude so that any ordering lines were so weak as to be lost in the background. In the present work, neutron diffraction has been used since the differences in the neutron scattering lengths of the elements concerned give a better chance for ordering lines to be observed and hence for the symmetries of the ordered phases to be determined. Here, measurements have been made on a sample of $Ag_2MnGeTe_4$ which contained both the ordered zinc-blende and the ordered rock-salt phases, and analyses were carried out to give information on the symmetry of both structures. In addition, all three decomposition phases were present, so that useful information about these could also be obtained.

SAMPLE PREPARATION AND EXPERIMENTAL MEASUREMENTS

The sample used in this work was prepared from the elements by the melt and anneal technique, and in order that fairly rapid quenching could be used in the preparation, the 6 g of sample required for the neutron powder diffraction study was made up from separate 1-g samples. In each case, the appropriate weights of the elements were

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sealed under vacuum in small quartz ampoules which had previously been carbonized to prevent interaction of the charge with the quartz. Each sample was melted at 1150°C and then slowly cooled to room temperature. The samples were then annealed for several days at 525°C to homogenize, this temperature having been previously established as that at which the ordered rock-salt structure was formed (3). The samples were then quenched to room temperature in an attempt to retain this phase.

A room-temperature neutron diffraction pattern for a wavelength of 0.15055 nm was obtained on the DUAL SPEC C2 powder diffractometer at the Chalk River Laboratories of AECL. Observations were made in the range $5° < 2\theta < 120°$ in steps of 0.05°.

RESULTS AND ANALYSIS

The diffraction spectrum obtained showed a large number of peaks, and the initial analysis indicated that several different phases were present in the sample used. The previous X-ray work (3) had shown that three of the phases which could be present in the sample were the ordered phases of $Ag_2MnGeTe_4$, rock-salt and zinc-blende based, and $MnTe_2$, which had been found to occur when the single-phase material decomposed at low temperatures. However, no information concerning the other phases which occurred in this lower temperature range was available. The lattice parameters of the cubic subcells of the rock-salt and zinc-blende phases of $Ag_2MnGeTe_4$ had been determined previously (3) and the data for the structure of $MnTe_2$ are available in standard tables (e.g., 8). Hence, on this basis, the separation of the various structure lines (i.e., the lines corresponding to the subcell) into the different phases could be started, since the resolution of the lines was such that only a small amount of overlap occurred in the structure lines. This is illustrated in Figs. 1, 2, and 3 where three typical sections of the total diffraction pattern are shown.

(i) $Ag_2MnGeTe_4$

Considering first the $Ag_2MnGeTe_4$ phases, when the structure lines were studied, it was found that in both cases the ordering had produced distortion in the unit cell, so that the structure lines were split. At low scattering angles (2θ), this resulted only in an obvious broadening of the line as seen in Fig. 1, but at higher values of 2θ, the structure line was split into two or more distinct parts as seen in Figs. 2 and 3, e.g., in the ranges of 2θ of 76°–78°, 79°–80°, and 115°–117°. This type of splitting has previously been interpreted as showing tetragonal distortion with c/a different from an integral value, which could account for the previous reports that the ordered zinc-blende structures had the stannite structure (7). However, initial work on various $(I_2 \cdot IV \cdot Te_3)_{1-z}$–$(Mn\text{-}Te)_{3z}$ systems (9), for which $z = 0.25$ gives the composition $I_2 \cdot Mn \cdot IV \cdot VI_4$, indicates that single-phase solid solution fields extend from $z = 0$ to $z \sim 0.4$, thus including the $I_2 \cdot Mn \cdot IV \cdot Te_4$ phases. Parthé (10) has indicated that some of these $I_2 \cdot IV \cdot VI_3$ compounds have orthorhombic $Imm2$ symmetry, so it is likely that the $I_2 \cdot Mn \cdot IV \cdot Te_4$ phases also have this form. Also, as indicated above, the magnetic data for both $Ag_2MnGeTe_4$ phases would indicate a low symmetry, such as orthorhombic.

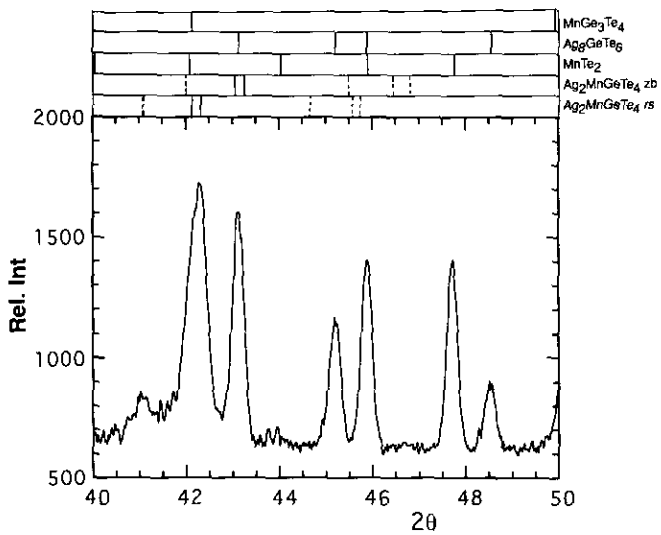

FIG. 1. Neutron diffraction spectrum in the range $40° < 2\theta < 50°$. (|) Structure lines and (:) ordering lines of phases are indicated.

As shown by Parthé, when compounds of the form $I_2 \cdot IV \cdot VI_3$ order on a zinc-blende-type subcell to $Imm2$, in the ideal case the orthorhombic lattice parameters are given by $a = 3a_c/\sqrt{2}$, $b = a_c/\sqrt{2}$ and $c = a_c$, where a_c is the original cubic parameter. This combination would leave the structure lines unsplit. However, if a and b retain the relation $a = 3b$, but c is changed, then the structure line distribution for this orthorhombic case would be identical with that for tetragonal. As indicated above, most of the structure lines for both the rock-salt- and zinc-blende-derived phases showed this form.

If the symmetry is actually orthorhombic, the question arises as to whether the a and b parameters show any deviation from the ideal ratio of $a/c = 3.0$. If such an effect can be observed, it should be seen in the lines of highest observed 2θ value, i.e., the lines at ~115.5° for the rock-salt case and at ~117.0 for the zinc-blende case (Fig. 3). These lines correspond to the reflections 642 and 12,2,2 for the rock-salt case and 343 and 12,1,3 for the zinc-blende case. Unfortunately, an $MnTe_2$ line coincides with each of these $Ag_2MnGeTe_4$ lines. However, the form of the lines appears to indicate that in both cases more than two lines are present, and thus an estimate of the separation of the $Ag_2MnGeTe_4$ lines can be made in each

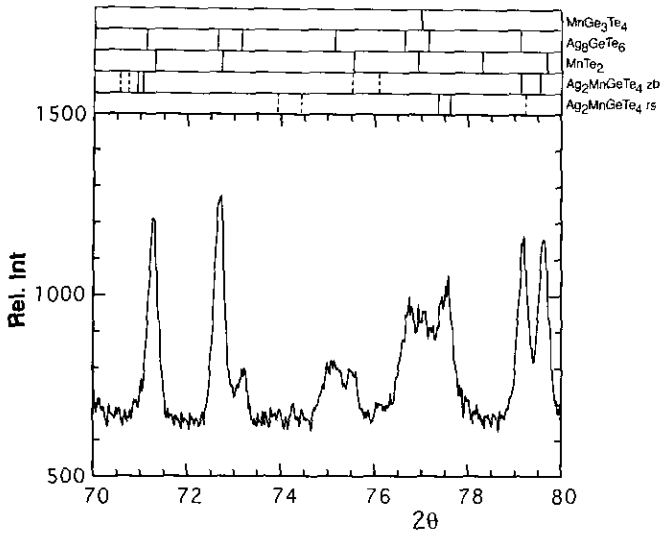

FIG. 2. Neutron diffraction spectrum in the range $70° < 2\theta < 80°$. (|) Structure lines and (¡) ordering lines of phases are indicated.

case. From this, it is found that for the rock-salt form a/b has a value of either 2.994 or 3.006 and the zinc-blende form either 2.996 or 3.004, and here it has been assumed, as in the case of Cu_2GeSe_3 with the same $Imm2$ symmetry (10), that a/b is less than 3.0. Analysis of the 2θ values of the structure lines then gave lattice parameter values for the two phases as

rock salt: $a = 1.2520$ nm, $b = 0.4182$ nm, $c = 0.5987$ nm;

zinc blende: $a = 1.2307$ nm, $b = 0.4107$ nm, $c = 0.5752$ nm.

Using these parameters, the expected values of 2θ for all of the structure lines of the two phases were calculated and are shown in Figs. 1, 2, and 3.

To complete this analysis, 2θ values for all ordering lines with 2θ less than 80° were calculated for both phases, and these are also shown in the figures. In the experimental data, the ordering lines were found to be fairly weak, and when the calculated values were checked, a large percentage of them overlapped with stronger structure lines of the various phases present. However, where ordering lines could be observed, they appeared to fit the predictions of the orthorhombic structure, as seen in Figs. 1 and 2. Although insufficient ordering lines could be observed to be conclusive, these results combined with the additional factors of the structure similarity with the $I_2 \cdot IV \cdot VI_3$ compounds and the magnetic behavior, mentioned above, would indicate that for both the rock-salt and the zinc-blende ordered forms the symmetry is orthorhombic with space group $Imm2$.

(ii) Decomposition Phases

As was indicated previously (3), $Ag_2MnGeTe_4$ is unstable and decomposes below approximately 400°C, although both ordered phases, if quenched to room temperature, can be retained in a single-phase metastable state. One of the decomposition phases which was determined previously (3) in $MnTe_2$. The database (8) gives this as primitive cubic with $a = 0.6950$ nm. Using these data, values of 2θ for $MnTe_2$ in the present case were calculated, and these are indicated in Figs. 1, 2, and 3.

With the structure lines of three phases thus obtained, a considerable number of lines in the diffraction spectrum were left undetermined. Study of the $\sin^2\theta$ values for these lines showed that a further face-centered cubic phase was present, and a least-squares fit to these values gave a lattice parameter of $a = 1.1580$ nm. The database (8) indicated that this phase must be the compound Ag_8GeTe_6. Again, the relevant values of 2θ were calculated and these are shown in Figs. 1, 2, and 3.

The positions of the three compounds $Ag_2MnGeTe_4$, $MnTe_2$, and Ag_8GeTe_6 in the general quaternary diagram Ag–Mn–Ge–Te are shown in Fig. 4. Since, as can be seen, the points $Ag_2MnGeTe_4$, $MnTe_2$, and Ag_8GeTe_6 are not collinear, there must be a third low-temperature phase present, and it must lie on the plane through the three other points and form with the points $MnTe_2$ and Ag_8GeTe_6 a triangle which contains the point $Ag_2MnGeTe_4$, as indicated in Fig. 4. Several postulated points representing relatively simple formulas were looked for in the database, but none were found. However, one obvious possibility was the point where the plane in question cuts the

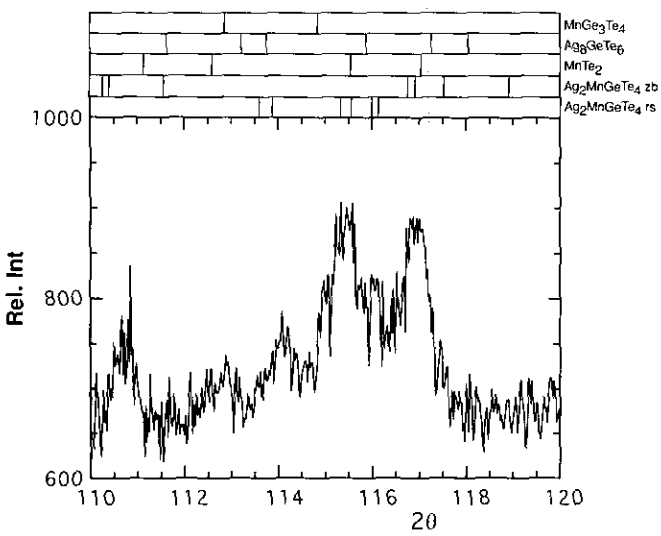

FIG. 3. Neutron diffraction spectrum in the range $110° < 2\theta < 120°$. (|) Structure lines and (¡) ordering lines of phases are indicated.

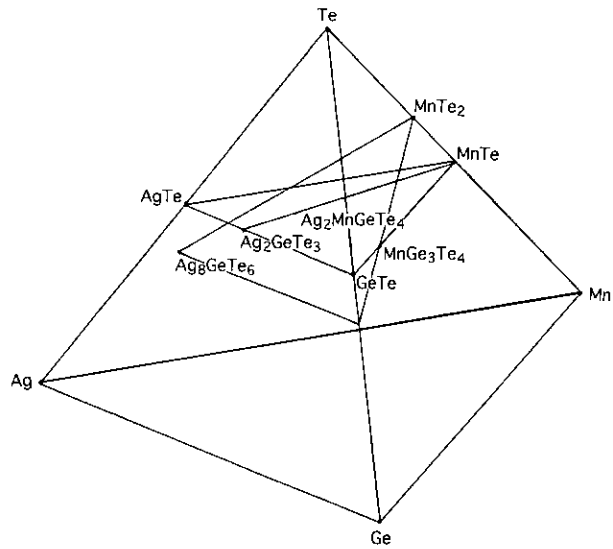

FIG. 4. Phase decomposition diagram for the Ag–Ge–Mn–Te system showing the positions of the various phases involved in the present analysis.

GeTe–MnTe line. Calculation shows that the composition of this point is $MnGe_3Te_4$. The alloy system $Ge_{1-z}Mn_zTe$ was investigated previously (11), and it was shown that the point $z = 0.25$ ($MnGe_3Te_4$) lies in a range of single-phase solid solution with rock-salt structure, with the lattice parameter $a = 0.5924$ nm. Calculation of the 2θ values in this case showed that a large fraction of the structure lines in this case would almost coincide with lines of the previously described phases. However, sufficient lines could be observed to indicate that this was the third dissociation phase. Again, the calculated values of 2θ for this phase are shown in Figs. 1, 2, and 3.

DISCUSSION

The analysis of the diffraction data, together with the magnetic results (4) and the lattice parameter data for some $(I_2 \cdot IV \cdot VI_3)_{1-z}$–$(MnTe)_{3z}$ diagrams, indicates that both ordered phases of $Ag_2MnGeTe_4$ have orthorhombic symmetry, with probable space group *Imm*2. The difference between these two *Imm*2 structures can be seen in the form of the two subcells, i.e., rock-salt and zinc-blende types. Thus in each case, the Te anions form a close-packed cubic array, with the cations systematically occupying a set of interstitial positions in this array, being octahedrally coordinated by the anions in the rock-salt case and tetrahedrally coordinated in the zinc-blende case.

In the structure for the *Imm*2 ordered cell given by Parthé, based on a zinc-blende subcell, the two different cations occupy the following sites:

$$\text{IV: } 000,\ \tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2} \qquad [1]$$

$$\text{I: } \tfrac{1}{3}00,\ \tfrac{2}{3}00,\ \tfrac{1}{6}\tfrac{1}{2}\tfrac{1}{2},\ \tfrac{5}{6}\tfrac{1}{2}\tfrac{1}{2}. \qquad [2]$$

Using this convention of a cation as the reference origin for the present two *Imm*2 phases, the same cation positions can be assumed for both; the difference between the zinc-blende and rock-salt forms is then in the positions of the anions. In the cases of the alloys $(Cu_2Ge)_{1-z}Mn_{3z}Te_3$ and $(Cu_2Sn)_{1-z}Mn_{3z}Te_3$, it has been found (9) that for both ordered structures the lattice parameters vary almost linearly with z over the solid solution range ($0 < z < \sim 0.4$), and the initial work on the phase diagram of $(Ag_2Ge)_{1-z}Mn_{3z}Te_3$ indicates that this has similar form. This linear variation of the lattice parameters has been taken to indicate that the Mn atoms enter one or both of the cation sublattices at random. In each of these systems, the $z = 0.25$ point represents the quaternary similar to the one discussed here, $Ag_2MnGeTe_4$. Thus, it would appear that, in the present case, it must be assumed that the Mn atoms are at random on the IV(Ge) or I(Ag) sublattice or on the whole cation sublattice. Simple intensity calculations showed that if the Mn atoms were distributed over all sites on the cation sublattice, the intensities of the ordering lines would be too small for them to be observed. These intensities are greatly increased when the Mn is distributed at random on either the Ge or the Ag sublattices, and either case would allow the ordering lines to be observed.

The symmetry of the cation sites is of importance when the magnetic data are considered. From [1], the IV sites are high symmetry points, with two axial reflection planes intersecting to give a diad axis parallel to the c axis. In this case, any magnetic spin could be oriented only along one of the crystallographic axes, and, as a result, under the magnetized condition all such spins would be parallel or antiparallel; i.e., the magnetic condition would be full ferromagnetism or antiferromagnetism. However, any spins on the I sites, [2], would be on single reflection planes and so could take any orientation in the plane, provided the reflection operation involves a magnetic inversion. This would allow canting of the spins to occur and the resultant magnetic behavior could be canted antiferromagnetism (weak ferromagnetism). The experimental magnetic data (4) clearly indicate the presence of weak ferromagnetism in both ordered phases, so that in each case it is likely that the majority, if not all, of the Mn atoms are randomly distributed on the I sites.

To confirm these results, it is planned to produce single-phase samples of both of the ordered $Ag_2MnGeTe_4$ phases for more detailed neutron diffraction analysis. It is clear from the present work that the main problem in this preparation is to obtain sufficiently rapid quenching of each sample from its annealing temperature. Thus the quenching of 1-g samples in brine is insufficient to prevent decom-

position, etc., and it appears that samples must be prepared in amounts of 1/4 g or less in very thin quartz tubes.

CONCLUSIONS

The study of the neutron diffraction spectra, together with the results of previous measurements of magnetic susceptibility as a function of temperature and with X-ray data on corresponding copper compounds and alloys, shows that for both the rock-salt-derived and the zinc-blende-derived phases of $Ag_2MnGeTe_4$, the cations order to give an orthorhombic structure, with probable space group *Imm*2. The above range of data also indicates that the Mn atoms probably replace Ag atoms in the I cation sites listed above. The present results also show that below approximately 350°C, the compound is unstable and that the equilibrium condition is three phase, the three phases being $MnTe_2$, Ag_8GeTe_6, and $MnGe_3Te_4$.

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