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## Phase Relations and the Effects of Ordering in $(\text{AgIn})_{1-z}\text{Mn}_z\text{Te}_2$ and $(\text{CuIn})_{1-z}\text{Mn}_z\text{Te}_2$ Alloys

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Polycrystalline samples of the semimagnetic semiconductor alloys  $(\text{AgIn})_{1-z}\text{Mn}_z\text{Te}_2$  and  $(\text{CuIn})_{1-z}\text{Mn}_z\text{Te}_2$  are used in lattice parameter, optical energy gap  $E_0$ , and differential thermal analysis (DTA) measurements. The results indicate that in both, the zinc blende and chalcopyrite ranges of composition, ordering of the manganese can occur at lower temperatures, and a combination of the results is used to delineate the composition and temperature ranges in which disordered  $\alpha$  and ordered  $\alpha'$  chalcopyrite and disordered  $\beta$  and ordered  $\beta'$  zinc blende is the equilibrium structure. It is shown that while the manganese ordering has little effect on the lattice parameter, it has appreciable effect on the values of  $E_0$ . This is demonstrated by the different aiming points at  $z = 1.0$  for the  $E_0$  vs.  $z$  lines in the different fields, the values being 2.8 eV for  $\beta$ , 1.95 eV for  $\beta'$ , and 1.35 eV for  $\alpha'$ .

Polykristalline Proben der semimagnetischen Halbleiterlegierungen  $(\text{AgIn})_{1-z}\text{Mn}_z\text{Te}_2$  und  $(\text{CuIn})_{1-z}\text{Mn}_z\text{Te}_2$  werden für Messungen der Gitterparameter, optischen Bandlücken  $E_0$  und differentiellen Thermoanalyse (DTA) benutzt. Die Ergebnisse zeigen, daß sowohl im Zinkblende- als auch im Chalkopyrit-Bereich der Zusammensetzung die Ordnung des Mangans bei tieferen Temperaturen auftritt, und eine Kombination der Ergebnisse wird benutzt, die Zusammensetzungs- und Temperaturbereiche zu zeichnen, in denen fehlgeordnetes  $\alpha$ - und geordnetes  $\alpha'$ -Chalkopyrit und fehlgeordnete  $\beta$ - und geordnete  $\beta'$ -Zinkblende die Gleichgewichtsstrukturen sind. Während der Manganordnungsprozeß nur einen geringen Einfluß auf den Gitterparameter hat, wird gezeigt, daß er einen wesentlichen Einfluß auf die Werte von  $E_0$  hat. Dies wird durch die verschiedenen Zielpunkte bei  $z = 1,0$  für die  $E_0$ - $z$ -Linien in den verschiedenen Feldern demonstriert, wobei die Werte 2,8 eV für  $\beta$ , 1,95 eV für  $\beta'$  und 1,35 eV für  $\alpha'$  betragen.

### 1. Introduction

Semiconductor alloys containing paramagnetic manganese ions are of interest because of their magnetic as well as semiconductor properties. Pseudobinary alloys of the form  $\text{II}_{1-z}\text{Mn}_z\text{VI}$ , such as  $\text{Cd}_{1-z}\text{Mn}_z\text{Te}$ , have been investigated in much detail [1 to 4] and the work has been extended to pseudo-ternary alloys such as  $\text{Cd}_x\text{Zn}_y\text{Mn}_z\text{Te}$  ( $x + y + z = 1$ ) (e.g. [5, 6]). In all of these alloys, the manganese ions are arranged at random on the cation sublattice and as a result the alloys show spin-glass behaviour at low temperatures. These alloys have been given the names semimagnetic semiconductors or diluted magnetic semiconductors. Other possible semimagnetic alloys can be derived from the chalcopyrite I-III-VI<sub>2</sub> compounds, the ternary analogs of the II-VI compounds. To retain the electron to atom ratio and hence the semiconductor properties, it is necessary to replace one I and one III cation simultaneously by two manganese

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atoms, so that the alloys of interest have the form  $(\text{I-III})_{1-z}\text{Mn}_{2z}\text{Te}_2$  or in the more general pseudo-ternary case  $\text{II}_{2z}(\text{I-III})_y\text{Mn}_{2z}\text{Te}_2$  ( $x + y + z = 1$ ).

Lattice parameter and optical energy gap data have been obtained for the systems  $\text{Cd}_{2x}(\text{CuIn})_y\text{Mn}_{2z}\text{Te}_2$  [7] and  $\text{Cd}_{2x}(\text{AgIn})_y\text{Mn}_{2z}\text{Te}_2$  [8] and magnetic measurements made on various  $(\text{I-III})_{1-z}\text{Mn}_{2z}\text{Te}_2$  alloys [9]. The results indicate that ordering of the manganese ions on the cation sublattice occurs in these alloys and that this has a significant effect on the magnetic behaviour and on the optical energy gap value. In order to examine these effects in more detail, it is necessary to have information concerning the phase diagram and the ordered structure of those alloys. Aresti et al. [10] have used DTA measurements to give a  $T(z)$  phase diagram of the  $(\text{CuIn})_{1-z}\text{Mn}_{2z}\text{Te}_2$  system, but did not obtain any indication of ordering temperatures etc. They suggest that in the range of chalcopyrite behaviour, the manganese tends to order on a stannite type of arrangement.

In the present work, the phase diagram of  $(\text{AgIn})_{1-z}\text{Mn}_{2z}\text{Te}_2$  is given and that of  $(\text{CuIn})_{1-z}\text{Mn}_{2z}\text{Te}_2$  extended to include ordering temperatures, etc. The effect of the ordering on crystallographic and optical properties is discussed.

## 2. Experimental Methods

The preparation of polycrystalline samples by the melt and anneal technique, the determination of lattice parameter values using Debye-Scherrer and Guinier powder X-ray photographs, and the measurements of the room temperature optical energy gap by the standard transmission method have been described in detail elsewhere [5, 11]. Standard differential thermal analysis (DTA) measurements [12] were made using chromel-alumel thermocouples and with either silver or gold for the reference material. Heating and then cooling runs were carried out on each sample investigated.

## 3. Phase and Crystallographic Results

The results of the DTA measurements on the two systems are shown in Fig. 1. In each case, since the work was part of a programme for the investigation of semimagnetic semiconductors, the range of composition investigated was limited to  $0 \leq z \leq 0.8$  and the behaviour of the MnTe-rich phases was not considered. The results shown in Fig. 1a for the  $(\text{CuIn})_{1-z}\text{Mn}_{2z}\text{Te}_2$  alloys are in good agreement with those given by Aresti et al. [10] and with the results for  $\text{CuInTe}_2$  given by Palatnik and Rogacheva [13]. The labelling of the various phase fields follows that of Aresti et al. Here  $\alpha$  is the chalcopyrite structure,  $\beta$  the zincblende structure, and  $\gamma$  the NiAs structure of MnTe. The  $\delta$  phase has the rocksalt structure [10] shown by MnTe above 1050 °C but which exists at lower temperatures elsewhere in the general diagram — the section shown is clearly not pseudobinary. In order to determine the ordering temperatures, i.e. the  $\alpha$ - $\alpha'$  and  $\beta$ - $\beta'$  boundaries, not given by Aresti et al., samples were annealed until magnetic and optical energy gap values indicated that the ordered condition was present. In the initial heating curves for these samples, the transitions shown in Fig. 1 were observed. However, the ordered condition was then lost and so no such transitions could be observed in the cooling or subsequent heating curves without further annealing to the ordered state.

Fig. 1b shows the corresponding data for  $(\text{AgIn})_{1-z}\text{Mn}_{2z}\text{Te}_2$  alloys. The diagram is a little more complicated in this case due to the occurrence of two different zincblende phases in the  $\text{Ag}_2\text{Te-In}_2\text{Te}_3$  diagram as shown by Palatnik and Rogacheva [13] and by Chiang et al. [14]. The present results for  $\text{AgInTe}_2$  agree with those of Chiang et al. rather than those of Palatnik and Rogacheva. In other respects this diagram is very

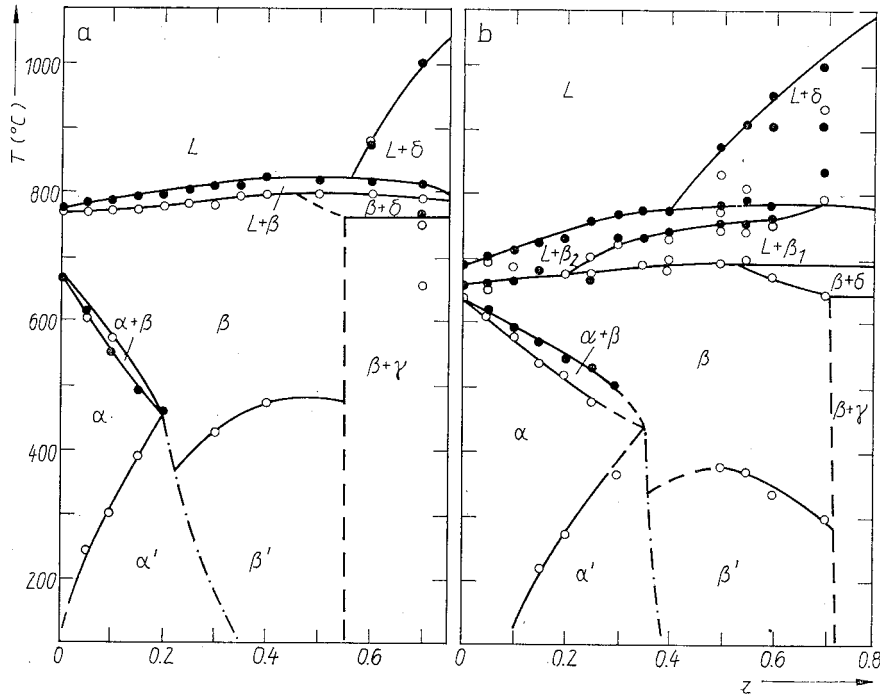


Fig. 1.  $T(z)$  diagram for a)  $(\text{CuIn})_{1-z}\text{Mn}_{2z}\text{Te}_2$  and b)  $(\text{AgIn})_{1-z}\text{Mn}_{2z}\text{Te}_2$  alloys;  $\circ$  heating run;  $\bullet$  cooling run

similar to that of the CuIn alloys. Again the transitions  $\alpha'$ - $\alpha$  and  $\beta'$ - $\beta$  were observed only in the initial heating run for alloys annealed to the ordered condition.

The X-ray photographs taken for samples annealed in the range 500 to 600 °C and then slowly cooled to room temperature justify the field labelling of Fig. 1. Thus for the CuIn case, all alloys in the range  $0 \leq z \leq 0.55$  appeared to be zincblende phase. However, at the lower values of  $z$ , faint chalcopyrite ordering lines could be observed, but no splitting of the structure lines was seen because  $c/a = 2.0$  in these materials. The variation of the lattice parameter  $a$  with  $z$  is shown in Fig. 2. This indicates that the limit of single phase behaviour occurs at  $z = 0.55$  while the change in slope at

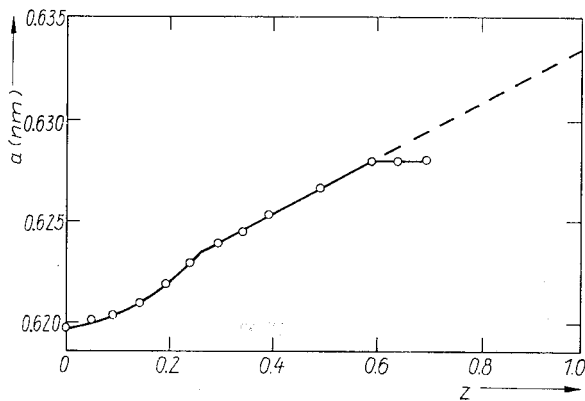


Fig. 2. Variation of lattice parameter  $a$  with  $z$  for  $(\text{CuIn})_{1-z}\text{Mn}_{2z}\text{Te}_2$  alloys

$z = 0.27$  is taken to be the point where the change from chalcopyrite to zincblende occurs. These values have been used to give the phase boundaries at 250 °C in Fig. 1a since previous experience has indicated that in materials of this type, furnace cooled samples tend to show the equilibrium conditions at approximately this range of temperature. It is to be noted that the form of the  $a$  versus  $z$  curve in Fig. 2 appears to be appreciably different from that given by Aresti et al. This is partly due to the fact that their value of  $a$  for  $\text{CuInTe}_2$  is 0.6189 nm while the value in the present work is 0.6200 nm. This difference in value of  $a$  for different samples of the same chalcopyrite compound has been attributed to non-stoichiometry differences due to different preparation techniques [15].

Fig. 3 gives the variation of  $a$  and  $c/a$  with  $z$  for the  $\text{AgIn}$  alloys. Again the limits of chalcopyrite and zincblende single phase condition can be taken as  $z = 0.38$  and  $z = 0.72$ , respectively, and these are taken as the values at 250 °C in Fig. 1b.

Turning to the question of the  $\alpha'$  and  $\beta'$  fields, it was found that for a given composition, samples quenched from 500 °C and samples slow-cooled to room temperature gave essentially the same X-ray photographs even though the magnetic behaviour was very different. For this reason, it was assumed that the difference between  $\alpha$  and  $\alpha'$  and between  $\beta$  and  $\beta'$  was the ordering of manganese on the cation sublattice. Careful inspection for ordering lines indicated very weak lines in some cases, but only for two samples, viz.  $\text{CuIn}$  with  $z = 0.5$  and  $\text{AgIn}$  with  $z = 0.6$ , were sufficiently clear lines observed to justify any attempt at analysis. Aresti et al. suggested in the case of  $\text{CuIn}$  in the chalcopyrite  $\alpha$  range that the structure of the  $\alpha$  phase would change from chalcopyrite to stannite as  $z$  increased from 0 to 0.5, so that at  $z = 0.5$  the Cu and In atoms at the  $0\frac{1}{2}\frac{1}{4}$ ,  $0\frac{1}{2}\frac{3}{4}$ ,  $\frac{1}{2}0\frac{1}{4}$ , and  $\frac{1}{2}0\frac{3}{4}$  sites would be systematically replaced by Mn. In the present case, the alloys of interest are in the cubic  $\beta$  field, but ESR results [16] indicate that the ordered  $\alpha'$  and  $\beta'$  phases have very similar behaviour. Hence an analysis was carried out assuming a  $\beta'$  phase which was tetragonal with Mn atoms at  $0\frac{1}{2}\frac{1}{4}$ ,  $0\frac{1}{2}\frac{3}{4}$ ,  $\frac{1}{2}0\frac{1}{4}$ , and  $\frac{1}{2}0\frac{3}{4}$  sites and with the other cation sites randomly occupied by Cu and In or by Ag and In. (This structure actually has a unit cell with  $c/a = 1$  but the double size unit cell was used to facilitate comparison with the results for stannite). The analysis predicted two sets of ordering lines with  $hkl$  values satisfying the conditions (i)  $h$  and  $k$  even and  $l$  single even, (ii)  $h$  and  $k$  odd and  $l$  doubly even, with essentially the same intensities. However, in practice in the present work,

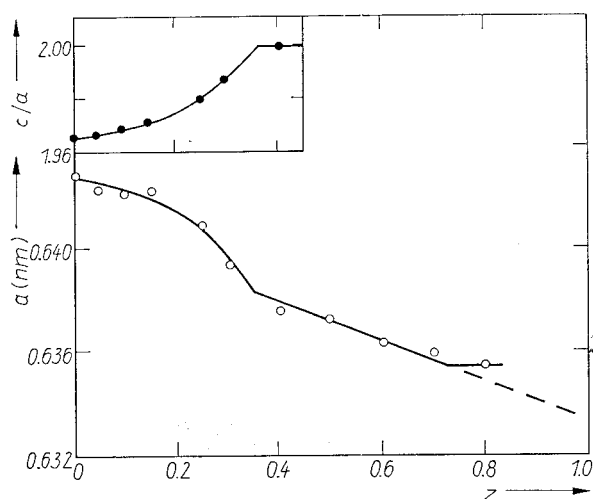


Fig. 3. Variation of lattice parameter  $a$  and  $c/a$  with  $z$  for  $(\text{AgIn})_{1-z}\text{Mn}_{2z}\text{Te}_2$  alloys

the lines observed had  $hkl$  values of 002, 110, 202, 006, 206, 222, and 402, i.e. only 110 was from set (ii) and all the others from set (i). The analysis was extended to the case when the Mn atoms were displaced along the  $z$  direction by amounts  $\delta$  up to  $c/8$ . It was found that this had little effect on the predicted intensities for set (i), but that depending upon the value of  $\delta$ , intensities of various reflections in set (ii) were appreciably reduced. This indicates that the ordered structure around  $z = 0.5$  may be the above tetragonal structure related to stannite, but with some systematic displacement of the Mn atoms. The observed intensities of these ordered X-ray reflections did not justify taking this analysis further, but neutron diffraction measurements are planned, since these should give very enhanced intensities to the ordering lines.

One further point concerning both phase diagrams was the position of the  $\alpha - \alpha'$  boundary relative to the  $\alpha + \beta$  two-phase region. Aresti et al. proposed that in the range of the  $\alpha + \beta$  field, the  $\beta \rightarrow \alpha$  transition was first order, but at higher  $z$  values (in the range shown as a dash-dotted line in Fig. 1) the transition was a second-order one. This was attributed to the gradual change in the  $\alpha$  phase from chalcopyrite to stannite form. Here, it is suggested that the  $\alpha - \alpha'$  boundary must touch the end point of the  $\alpha + \beta$  two-phase field, this being the point where the change from first-order to second-order transition occurs, as shown in Fig. 1. Then the  $\beta \rightarrow \alpha$  transition would be first order and the  $\beta \rightarrow \alpha'$  (and  $\beta' \rightarrow \alpha'$ ) transition would be second order.

#### 4. Effects of Ordering on Other Properties

It is found that if lattice parameter values are determined for samples quenched from the disordered field and for samples annealed to the ordered state, negligible difference

is observed, indicating that ordering has very little effect on the lattice parameter value. However, in the case of the optical energy gap  $E_0$  very different results can be observed. The variation of the measured room temperature optical energy gap with  $z$  for the AgIn alloys is shown in Fig. 4a for the case of slowly cooled samples. It is seen that the line can be considered in three parts,

- (i)  $0 \leq z \leq \approx 0.1$ ,
- (ii)  $0.1 \leq z \leq 0.35$ ,
- (iii)  $0.35 \leq z \leq 0.65$ .

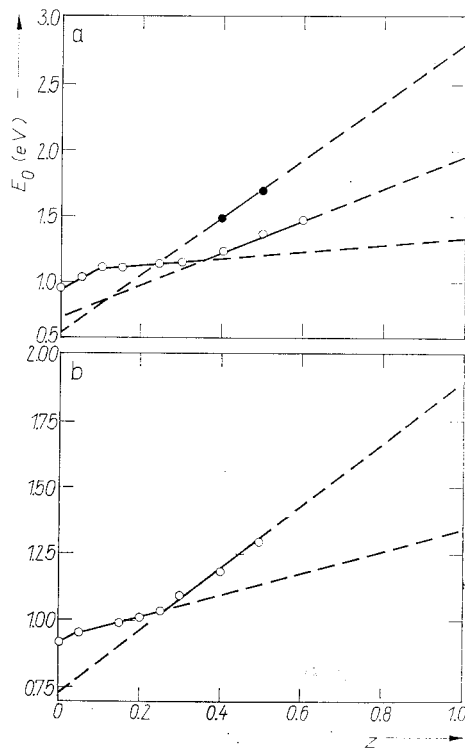


Fig. 4. Variation of room temperature optical energy gap  $E_0$  with  $z$  for a)  $(\text{AgIn})_{1-z}\text{Mn}_{2z}\text{Te}_2$  alloys;  $\circ$  samples slowly cooled to room temperature;  $\bullet$  samples rapidly quenched from  $500^\circ\text{C}$  and b)  $(\text{CuIn})_{1-z}\text{Mn}_{2z}\text{Te}_2$  alloys

From Fig. 1b these can be attributed to the  $\alpha$ ,  $\alpha'$ , and  $\beta'$  phases, respectively. As has been indicated previously [8], the aiming point at  $z = 1$  is characteristic of these ranges, the ordered  $\beta'$  phase having an aiming point of 1.95 eV, and the ordered  $\alpha'$  phase one of 1.35 eV. There is insufficient  $\alpha$  phase data to give any accurate estimate of the aiming point in this case. However, the data for the  $(\text{AgGa})_{1-z}\text{Mn}_{2z}\text{Te}_2$  alloys give an aiming point of  $\approx 2.2$  eV for the disordered chalcopyrite  $\alpha$  field, and the present results are not inconsistent with this value. The results for the CuIn alloys, shown in Fig. 4b, are very similar to those shown in Fig. 4a.

When attempting to find the  $E_0$  values for the disordered phase at higher values of  $z$ , it must be noted that when two phases are present in a sample, the lower energy gap absorption edge is the one easily observed and if any appreciable amount of that phase is present, the higher edge is masked. Thus, since in these materials it is found that the disordered  $E_0$  is higher than the ordered  $E_0$ , in order to observe the edge corresponding to the disordered phase, the sample must contain very little of the ordered phase or must be polished down to a very small thickness, say  $\leq 25$   $\mu\text{m}$ . With the polycrystalline samples used in the present work, this second condition is not possible since the samples crumble and disintegrate on polishing. Thus attempts were made to quench samples as rapidly as possible to prevent the occurrence of ordering. For the AgIn alloys, two samples were produced (with  $z = 0.5$  and  $0.6$ ) which satisfied this condition to a sufficient extent that measurements of the higher absorption edge could be made. The resulting  $E_0$  values, corresponding to the  $\beta$  phase, are shown in Fig. 4a. It was not found possible to quench samples in the range  $0.1 \leq z \leq 0.4$  sufficiently rapidly that the higher absorption edge could be observed. It is seen that for the  $\beta$  phase, the aiming point at  $z = 1$  is  $\approx 2.8$  eV in good agreement with the value obtained for disordered cubic (i.e. zincblende) samples in the  $\text{Cd}_x\text{Zn}_y\text{Mn}_z\text{Te}$  alloy system [5]. One other extrapolation of interest is for both  $\beta$  and  $\beta'$  results to  $z = 0$ . For both CuIn and AgIn alloys, the lines extrapolate at  $z = 0$  to a value in the range 0.6 to 0.8 eV which can be interpreted as the energy gap that CuInTe<sub>2</sub> and AgInTe<sub>2</sub> would have in the disordered zincblende form. Similar extrapolations for the  $(\text{CuIn})_x(\text{AgIn})_y\text{Cd}_{2z}\text{Te}_2$  alloys [17] gave values  $\approx 0.6$  eV.

Even more pronounced effects of ordering are found in the magnetic susceptibility and ESR results. These have been discussed elsewhere [9].

## 5. Conclusions

The DTA and X-ray results for both the  $(\text{AgIn})_{1-z}\text{Mn}_{2z}\text{Te}_2$  and  $(\text{CuIn})_{1-z}\text{Mn}_{2z}\text{Te}_2$  alloys show that a wide range of solid solution occurs for both the chalcopyrite and zincblende structures and that for both structures an ordered form, attributed to the manganese ions ordering on the cation sublattice occurs at approximately 400 °C. A preliminary analysis of ordering lines in the zincblende case indicates that the Mn atoms probably order in planes perpendicular to the  $z$  axis in a structure analogous to stannite, but that the Mn planes may be displaced along the  $z$  axis from the ideal position.

This ordering has little effect on lattice parameter values but greatly affects the optical energy gap  $E_0$  and the magnetic behaviour. Measurements of  $E_0$  show that the extrapolation of the results to  $z = 1$  gives  $E_0$  values characteristic of the particular structure, viz. 1.35 eV for the ordered chalcopyrite  $\alpha'$  structure, 1.95 eV for the ordered zincblende  $\beta$  cases and possibly  $\approx 2.2$  eV for the disordered chalcopyrite  $\alpha$  case. For both  $\beta$  and  $\beta'$  structures, extrapolation to  $z = 0$  gives values of  $E_0$  in the range 0.6 to 0.8 eV corresponding to CuInTe<sub>2</sub> and AgInTe<sub>2</sub> in the disordered zincblende form.

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**References**

- [1] J. K. FURDYNA, *J. appl. Phys.* **53**, 7637 (1982).
- [2] J. A. GAJ, *J. Phys. Soc. Japan* **49**, 797 (1980).
- [3] R. R. GALAZKA, *Inst. Phys. Conf. Ser. No. 43*, 133 (1979).
- [4] J. MYCIELSKI, *Prog. Crystal Growth Charact.* **10**, 101 (1985).
- [5] R. BRUN DEL RE, T. DONOFRIO, J. E. AVON, J. MAJID, and J. C. WOOLLEY, *Nuovo Cimento* **2D**, 1911 (1983).
- [6] T. DONOFRIO, G. LAMARCHE, and J. C. WOOLLEY, *J. appl. Phys.* **57**, 1932 (1985).
- [7] M. QUINTERO, L. DIERKER, and J. C. WOOLLEY, *J. Solid State Chem.* **63**, 110 (1986).
- [8] M. QUINTERO and J. C. WOOLLEY, *phys. stat. sol. (a)* **92**, 449 (1985).
- [9] J. C. WOOLLEY, G. LAMARCHE, A. MANOOGIAN, M. QUINTERO, L. DIERKER, M. AL-NAJJAR, D. PROULX, C. NEAL, and R. GOUDREAU, *Proc. 7th Internat. Conf. Ternary and Multinary Compounds*, Colorado Materials Research Society, 1987 (p. 479).
- [10] A. ARESTI, L. GARBATO, A. GEDDO-LEHMANN, and P. MANCA, *ibid.* (p. 497).
- [11] R. G. GOODCHILD, O. H. HUGHES, S. A. LOPEZ-RIVERA, and J. C. WOOLLEY, *Canad. J. Phys.* **60**, 1096 (1982).
- [12] R. CHEN and Y. KIRSH, *Analysis of Thermally Stimulated Processes*, Internat. Series on Sci. Solid State, Vol. 15 Pergamon Press, 1981 (p. 97).
- [13] L. S. PALATNIK and E. I. ROGACHEVA, *Soviet Phys. — Doklady* **12**, 503 (1967).
- [14] R. W. CHIANG, D. F. O'KANE, and D. R. MASON, *J. Electrochem. Soc.* **114**, 759 (1967).
- [15] J. P. SHAY and G. H. WERNICK, *Ternary Chalcopyrite Semiconductors*, Pergamon Press, New York 1975 (p. 4).
- [16] J. C. WOOLLEY, R. BRUN DELRE, and A. MANOOGIAN, to be published.
- [17] E. GUERRERO, M. QUINTERO, and J. C. WOOLLEY, *J. appl. Phys.* in the press.

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