

# $T(z)$ Diagram and Optical Energy Gap Values of $Zn_{1-z}Mn_zGa_2Se_4$ Alloys

M. Morocoima, M. Quintero, and J. C. Woolley<sup>1</sup>

*Centro de Estudios de Semiconductores, Departamento de Física, Facultad de Ciencias, Universidad de Los Andes, Mérida, Venezuela*

Received April 12, 1994; in revised form August 29, 1994; accepted August 30, 1994

The  $T(z)$  diagram of the system  $Zn_{1-z}Mn_zGa_2Se_4$  was obtained from X-ray diffraction and differential thermal analysis measurements. It was found that at lower temperatures, a single phase solid solution occurs across the whole composition range and values of the lattice parameters were determined as a function of  $z$ . At higher temperatures, an order-disorder transition occurs to what is probably a partially ordered tetragonal structure when  $0 < z < 0.83$ , and to a disordered defect zinc-blende structure when  $0.83 < z < 1.0$ . In the  $T(z)$  diagram, it is found that all of the phase boundaries show discontinuities at  $z \approx 0.83$ . Although the two terminal compounds have very similar tetragonal structures, they have different space group symmetries, and hence the discontinuities at  $z \approx 0.83$  are attributed to an abrupt change in space group symmetry at this composition. The values of the optical energy gap are found to show a similar discontinuity at the same composition. Two other similar alloy systems have recently been found to show similar behavior, and the results for the three systems are compared. © 1995 Academic Press, Inc.

## INTRODUCTION

Semiconductor materials containing manganese are of interest because of the manner in which the magnetic behavior associated with the manganese can modify and complement the semiconductor properties (1, 2). It has been found that adamantine compounds with tetrahedral coordination can accept a large amount of manganese in cation substitutional solid solution. Well-known examples of such materials are the alloys based on the II-VI compounds, e.g.,  $Cd_{1-z}Mn_zTe$  (1). Similar alloys can be obtained by introducing manganese into the equivalent ternary compounds, the tetrahedrally coordinated I-III-VI<sub>2</sub> chalcopyrites, e.g.,  $(CuIn)_{1-z}Mn_zTe_2$  (3). Other compounds that show the tetrahedrally bonded form are some of the II-III<sub>2</sub>-VI<sub>4</sub> compounds, e.g.,  $CdGa_2Te_4$  and  $CdIn_2Te_4$ . In these materials, Mn can be made to replace the divalent elements Cd, Zn, etc. Complete replacement gives the compounds  $MnGa_2Se_4$ ,  $MnIn_2Te_4$ , etc., and it

has been shown that complete solid solution occurs between corresponding Cd and Mn compounds, i.e., in the systems  $Cd_{1-z}Mn_zGa_2Se_4$  (4) and  $Cd_{1-z}Mn_zIn_2Te_4$  (5). All four of the compounds involved in these alloy systems have a defect tetragonal structure, the two Cd compounds having  $I\bar{4}$  symmetry (6, 7) and the Mn compounds  $I\bar{4}2m$  symmetry (8). For the cases of the two Cd compounds and  $MnGa_2Se_4$ , the lattice vacancies and the Ga/In and Cd/Mn atoms are all ordered on the cation sublattice, but for  $MnIn_2Te_4$ , while the lattice vacancies are ordered, the Mn and In atoms are disordered on the occupied cation sites. In both alloy systems, the change in space group is observed as a discontinuity in various phase boundaries in the  $T(z)$  diagram, but for the optical energy gap  $E_0$ , a discontinuity in the  $E_0$  vs  $T$  curve was observed in the Se system, but the Te alloys showed a linear variation of  $E_0$  with  $T$  with no discontinuity. The effects of ordering of the Cd and Mn atoms on the cation sublattice is seen from the magnetic properties (9), the magnetic behavior of  $MnGa_2Se_4$  and  $MnIn_2Te_4$  being very different.

At room temperature, the compound  $ZnGa_2Se_4$  has the same defect tetragonal structure as  $CdGa_2Se_4$ , with  $I\bar{4}$  symmetry and with all the cations ordered (7). In the present work, the  $T(z)$  and  $E_0$  data have been obtained for the  $Zn_{1-z}Mn_zGa_2Se_4$  alloy system, and its behavior compared with that of the systems described above.

## SAMPLE PREPARATION AND EXPERIMENTAL MEASUREMENTS

Alloy samples of  $Zn_{1-z}Mn_zGa_2Se_4$  with various values of  $z$  were prepared by the usual melt and anneal technique. The components of each 1.0-g sample were sealed under vacuum in a quartz capsule, melted together at 1150°C, annealed to equilibrium at 500°C, and slowly cooled to room temperature. Previous experience indicates that for this type of alloy, this procedure gives samples showing conditions corresponding to equilibrium at 200–300°C. Guinier X-ray powder photographs were used to check the conditions of each of the resulting sam-

<sup>1</sup> Permanent address: Physics Department, University of Ottawa, Ottawa, Ontario, Canada K1N 6N5.

ples and to determine values of lattice parameters as a function of  $z$ , germanium being used as an internal standard.

Transition temperatures were determined from differential thermal analysis (DTA) measurements with silver used as a reference material. The charge was of powdered alloy of typical weight 50 to 100 mg. The temperatures of the sample and the reference were determined with Chromel–Alumel thermocouples, the difference signal between the sample and the reference and the temperature signal being continuously recorded. For each peak in the difference signal, a phase transition temperature was determined from the baseline intercept of the tangent to the leading edge of the peak (10). Both heating and cooling runs were made, the average rates of heating and cooling being approximately  $15^\circ\text{C}/\text{min}$ .

Slices of each sample were cut and thinned by the usual method (11) to give specimens for optical absorption measurements. Values of  $\ln(I_0/I)$ , where  $I_0$  and  $I$  are respectively the incident and transmitted intensities, were determined as a function of photon energy  $h\nu$  and corrected by subtracting a background value to give the absorption coefficient  $\alpha$ . Graphs of  $(\alpha h\nu)^2$  vs  $h\nu$  were then used to give values of the optical energy gap  $E_0$ .

## RESULTS AND ANALYSIS

In all cases, the X-ray photographs for the samples prepared as described above showed single phase behavior. Analysis of these data indicated tetragonal structure with lattice parameter  $c/a$  ratios of a little less than 2, consistent with the earlier results for the compounds. Faint ordering lines were observed, consistent with the space groups  $I\bar{4}$  and  $I\bar{4}2m$  reported previously. It is found that, within the limits of experimental error, both  $a$  and  $c$  vary linearly with  $z$ , no discontinuity being observed in either case. A least-squares fit to these data gave values of  $a = 0.5531 + 0.0146z$  (nm) with  $R = 0.999$ ,  $c = 1.0948 - 0.0182z$  (nm) with  $R = 0.999$ , and  $c/a = 1.980 - 0.083z$  with  $R = 0.999$ . The experimental variations of the parameters  $a$  and  $c/a$  with composition  $z$  are shown in Fig. 1, together with the fitted lines. As seen from these values, while  $a$  increases with increasing  $z$ ,  $c$  decreases. The data show that the volume of the unit cell increases from  $0.3349 \text{ nm}^3$  at  $z = 0$  to  $0.3465 \text{ nm}^3$  at  $z = 1$ , but that in the same range the X-ray density decreases from  $5.160$  to  $4.886 \text{ g}/\text{cm}^3$ . The lattice distortion  $\delta$ , given by  $\delta = 2 - c/a$ , correspondingly increases from  $2.0 \times 10^{-2}$  to  $10.5 \times 10^{-2}$ .

The  $T(z)$  phase diagram obtained from the DTA data is shown in Fig. 2, where the estimated relative accuracy of the points is  $\pm 15^\circ\text{C}$ . For  $z = 1$ , i.e.,  $\text{MnGa}_2\text{Se}_4$ , it is seen that three transitions are observed, corresponding to the behavior observed in the  $\text{Ga}_{2(1-z)}\text{Mn}_{3z}\text{Se}_3$  diagram (12) at

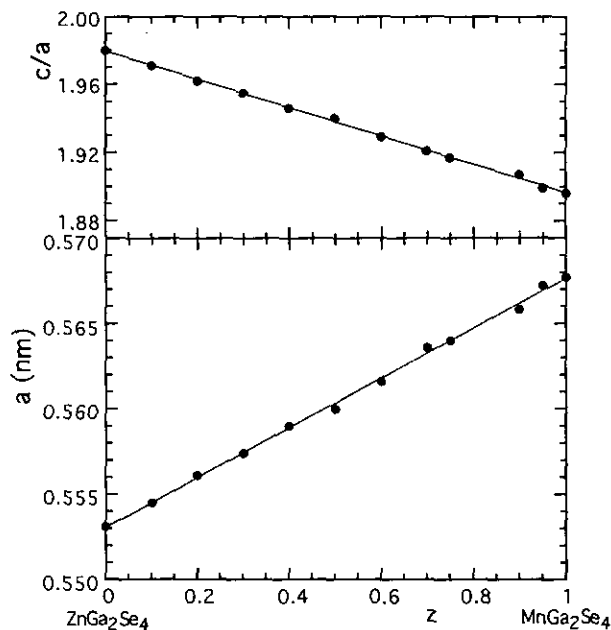


FIG. 1. The variation of lattice parameters  $a$  and  $c/a$  with  $z$  for  $\text{Zn}_{1-z}\text{Mn}_z\text{Ga}_2\text{Se}_4$  alloys; (●) experimental values, (—) lines fitted to the linear equation.

$z = 0.25$ . Thus at room temperature, this  $\gamma$  phase occurs with  $I\bar{4}2m$  symmetry, but it disorders at  $660^\circ\text{C}$  to a defect zinc-blende form  $\beta$ , in which the cations and lattice vacancies are arranged at random on the cation sublattice. At  $z = 0$ , i.e.,  $\text{ZnGa}_2\text{Se}_4$ , the room temperature phase  $\alpha$  is again tetragonal, with the  $c/a$  ratio a little below 2.0, and reported by Hahn *et al.* (7) to have  $I\bar{4}$  symmetry. Phase transitions are observed at  $455$  and  $940^\circ\text{C}$ , with the melting point  $1138^\circ\text{C}$ . From comparison with the results for  $\text{CdGa}_2\text{Se}_4$  (6), it is suggested that between  $455$  and  $940^\circ\text{C}$

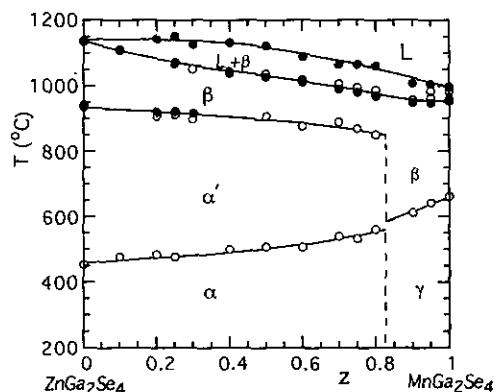


FIG. 2. The  $T(z)$  diagram for  $\text{Zn}_{1-z}\text{Mn}_z\text{Ga}_2\text{Se}_4$  alloys; (○) DTA heating run, (●) DTA cooling run;  $\alpha$ , ordered  $I\bar{4}$  structure,  $\alpha'$ , partially disordered tetragonal structure,  $\gamma$ , ordered  $I\bar{4}2m$  structure,  $\beta$ , disordered defect zinc-blende structure.

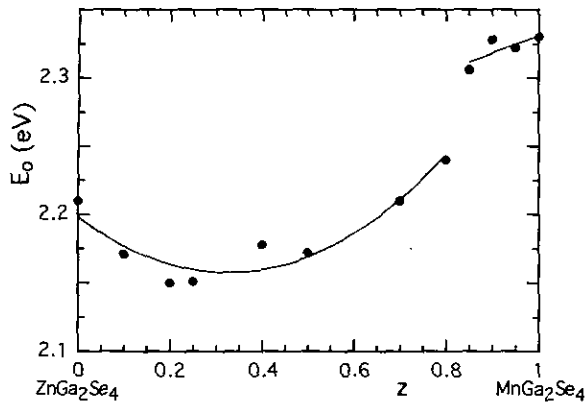


FIG. 3. Variation of optical energy gap  $E_0$  with  $z$  for  $\text{Zn}_{1-z}\text{Mn}_z\text{Ga}_2\text{Se}_4$  alloys; (●) experimental values, (—) fitted curves.

the compound has the partially disordered tetragonal structure, described previously for  $\text{CdGa}_2\text{Se}_4$ , labeled here  $\alpha'$ , and that above  $940^\circ\text{C}$  the structure is the disordered zinc-blende  $\beta$  observed in most of these compounds at higher temperatures.

Over most of the diagram, the behavior is similar to that for  $\text{ZnGa}_2\text{Se}_4$ , showing the  $\alpha$ ,  $\alpha'$ , and  $\beta$  phases, with the  $\alpha$ - $\alpha'$  boundary increasing in temperature with increasing  $z$  and the  $\alpha'$ - $\beta$  boundary decreasing. However, a change in form occurs close to  $z = 0.8$  and at  $z$  values greater than this, the behavior is similar to that of  $\text{MnGa}_2\text{Se}_4$ , showing the  $\gamma$  and  $\beta$  phases. Thus the  $\alpha'$ - $\beta$  boundary terminates at  $z = 0.8$ , while there is a discontinuity between the  $\alpha'$ - $\alpha$  and  $\gamma$ - $\beta$  boundaries. This indicates that in this system, the space group transition from  $I\bar{4}$  to  $I\bar{4}2m$  occurs near  $z = 0.8$ .

The variation of the optical energy gap  $E_0$  with  $z$  is shown in Fig. 3. In this case, a discontinuity is clearly seen between the  $z$  values of 0.8 and 0.85. For the  $\alpha$  phase,  $0 < z < 0.8$ , the variation of  $E_0$  with  $T$  can be well fitted with a quadratic form giving

$$E_{0\alpha} = 2.198 - 0.249z + 0.382z^2 \text{ eV} \quad \text{with } R = 0.942.$$

This form of variation has been observed previously for a wide range of semiconductor alloys (13–15). In the range of the  $\gamma$  phase,  $0.85 < z < 1.0$ , there are insufficient data to say whether a quadratic variation occurs. However, a linear fit to the available values shows clearly the discontinuity between  $z = 0.8$  and  $z = 0.85$ .

## DISCUSSION

As with the alloy systems  $\text{Cd}_{1-z}\text{Mn}_z\text{Ga}_2\text{Se}_4$  and  $\text{Cd}_{1-z}\text{Mn}_z\text{In}_2\text{Te}_4$  discussed previously (4, 5), the  $\text{Zn}_{1-z}\text{Mn}_z\text{Ga}_2\text{Se}_4$  alloys show single phase solid solution across the complete range of composition, but the space

group symmetries of the two end compounds are different, so that there must be a change in symmetry somewhere in the composition range. This symmetry change involves only the change in site of some of the III atoms. Thus, if a II/Mn site is taken as the origin, the change involves the movement of III atoms from  $\frac{1}{2}, \frac{1}{2}, 0$  and  $0, 0, \frac{1}{2}$  sites in the  $I\bar{4}$  case to  $0, \frac{1}{2}, \frac{3}{4}$  and  $\frac{1}{2}, 0, \frac{1}{4}$  sites in the  $I\bar{4}2m$  case. Experimentally, this change is observed in all cases as a discontinuity in some of the phase boundaries in the  $T(z)$  diagram, and the form of these discontinuities indicates that the symmetry change occurs abruptly at some composition in each system and not gradually over a range of alloy compositions. For the  $\text{Cd}_{1-z}\text{Mn}_z\text{Ga}_2\text{Se}_4$  alloys, the discontinuity is most clearly observed in solid–solid phase boundaries, the discontinuity in the boundaries involving a liquid phase being relatively small. For the present  $\text{Zn}_{1-z}\text{Mn}_z\text{Ga}_2\text{Se}_4$  case, discontinuities can be seen in the phase boundaries involving only solid phases. In the previous systems, the change in symmetry has occurred close to the center of the system, being at  $z = 0.5$  for  $\text{Cd}_{1-z}\text{Mn}_z\text{In}_2\text{Te}_4$  and at  $z = 0.6$  for  $\text{Cd}_{1-z}\text{Mn}_z\text{Ga}_2\text{Se}_4$ . For the present system, the symmetry change occurs closer to  $\text{MnGa}_2\text{Se}_4$ , i.e., at a  $z$  value in the range 0.80–0.85, possibly indicating the higher stability of the  $\text{ZnGa}_2\text{Se}_4$  structure.

With regard to the lattice parameter values, these are less affected by the symmetry change. Thus, for the  $\text{Cd}_{1-z}\text{Mn}_z\text{Ga}_2\text{Se}_4$  alloys the parameters  $a$  and  $c$  vary linearly across the complete composition range with no discontinuity, while with the present  $\text{Zn}_{1-z}\text{Mn}_z\text{Ga}_2\text{Se}_4$  alloys, any discontinuity in the  $a$  or  $c$  values is comparable with the experimental error. However, for the  $\text{Cd}_{1-z}\text{Mn}_z\text{In}_2\text{Te}_4$  case, there is a discontinuity in the value for  $a$  at the symmetry change and also the slope of  $a$  vs  $z$  changes from positive below the transition to negative above. In the case of the optical energy gap  $E_0$  values, a discontinuity is observed in both the  $\text{Cd}_{1-z}\text{Mn}_z\text{Ga}_2\text{Se}_4$  and  $\text{Zn}_{1-z}\text{Mn}_z\text{Ga}_2\text{Se}_4$  cases but not for the  $\text{Cd}_{1-z}\text{Mn}_z\text{In}_2\text{Te}_4$  alloys.

In all cases, the lattice parameter values vary linearly with  $z$ , but the variation of the energy gap  $E_0$  with  $z$  is different in the three systems. For the  $\text{Cd}_{1-z}\text{Mn}_z\text{In}_2\text{Te}_4$  alloys, the variation of  $E_0$  with  $z$  is linear, but for the other two systems shows quadratic form. However, the bowing parameter  $C$  (i.e., the coefficient of the  $z^2$  term) is negative for the  $\text{Cd}_{1-z}\text{Mn}_z\text{Ga}_2\text{Se}_4$  alloys and positive for the  $\text{Zn}_{1-z}\text{Mn}_z\text{Ga}_2\text{Se}_4$  case. The latter form is the far more common one in semiconductor alloys, and the value of  $C = 0.382$  is very similar to that for many alloy systems (13, 14).

## ACKNOWLEDGMENTS

The authors are grateful to BID-CONICIT (Project MN-09) and CDCH-ULA Venezuela for financial support.

## REFERENCES

1. J. K. Furdyna and J. Kossut, "Diluted Magnetic Semiconductors, Semiconductors and Semimetals" Chap. 1. Academic Press, New York, 1989.
2. Y. Shapira, E. J. McNiff, Jr., N. F. Oliveira, Jr., E. D. Honig, K. Dwight, and A. Wold, *Phys. Rev. B* **37**, 411 (1988).
3. M. Quintero, P. Grima, R. Tovar, C. S. Pérez, and J. C. Woolley, *Phys. Status Solidi A* **107**, 205 (1988).
4. E. Guerrero, M. Quintero, R. Tovar, T. Tinoco, J. Gonzalez, J. C. Woolley, and P. Conflant, *J. Electron. Mat.* **22**, 297 (1993).
5. E. Guerrero, M. Quintero, M. Delgado, and J. C. Woolley, *Phys. Status Solidi A* **129**, K83 (1992).
6. A. M. Loireau-Lozac'h, M. Guittard, and J. Flahaut, *Mater. Res. Bull.* **20**, 443 (1985).
7. H. Hahn, G. Frank, W. Klingler, A. Störger, and G. Störger, *Z. Anorg. Allg. Chem.* **279**, 241 (1955).
8. K.-J. Range and H.-J. Hubner, *Z. Naturforsch. B* **31**, 886 (1976).
9. J. C. Woolley, S. Bass, A.-M. Lamarche, and G. Lamarche, *J. Magn. Magn. Mat.* **131**, 199 (1994).
10. R. Chen and D. Y. Kirsh, "Analysis of Thermally Stimulated Processes," Int. Series in Solid State Physics, Vol. 15, p. 96. Pergamon, Elmsford, NJ, 1981.
11. R. G. Goodchild, O. H. Hughes, S. A. López-Rivera, and J. C. Woolley, *Can. J. Phys.* **60**, 1096 (1982).
12. M. Morocoima, M. Quintero, and J. C. Woolley, *Phys. Status Solidi A* **141**, 53 (1994).
13. J. A. Van Vechten and T. K. Bergstresser, *Phys. Rev. B* **1**, 3351 (1970).
14. J. Avon, K. Yoodee, and J. C. Woolley, *Nuovo Cimento D* **2** 1858 (1983).
15. S. Chatraphorn, T. Panmatarite, S. Pramatus, A. Prichavudhi, R. Kritayakirana, J.-O. Berananda, V. Sa-yakanit, and J. C. Woolley, *J. Appl. Phys.* **57**, 1791 (1985).