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CRYSTALLOGRAPHIC AND MAGNETIC PROPERTIES OF THE SYSTEM $(AgInCd_2)_x(CuIn)_{2y}Mn_{4z}Te_4(x+y+z=1)$ WITH $x=3y$

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Samples of the alloy system $(AgInCd_2)_x(CuIn)_{2y}Mn_{4z}Te_4(x+y+z=1)$ with $x=3y$ were prepared by a melt and anneal technique. Lattice parameter values are measured and the limit of single phase behaviour determined. Magnetic susceptibility measurements are made in the temperature range between 80 and 300 K. Values of the Curie-Weiss temperature θ and Curie constant C are obtained from the susceptibility results.

1. Introduction

There has been considerable interest in semimagnetic semiconductor alloy systems involving manganese, partly because the presence of paramagnetic Mn ion causes differences in the semiconducting properties from that of a normal semiconductor, particularly in a magnetic field. In addition, these systems display interesting magnetic behaviour at low temperature, i.e. spin glass transition, etc.

Most of the work on these alloys has been carried out on alloy systems involving the II-VI compounds and MnVI, i.e. $Cd_xZn_yMn_zTe$ (1), $Cd_xZn_yMn_zSe$(2), etc. Recently, this work has been extended to materials involving the $(I\text{-}III\text{-}VI_2)$-2(II-VI) alloys and the paramagnetic Mn ion. In this case, in order to retain the electron to atom ratio, it is necessary to replace one I and one III cation simultaneously by two Mn or two II atoms. The crystallographic and optical energy gap values for the $Cd_{2x}(CuIn)_yMn_{2z}Te_2$ and $Cd_{2x}(AgIn)_yMn_{2z}Te_2(x+y+z=1)$ pseudoternary systems have been discussed previously (3,4). More recently, Aresti *et al.* have obtained the phase diagram of the pseudobinary section $(CuIn)_{1-z}Mn_{2z}Te_2$ (5). Woolley *et al.* (6) investigated the crystallographic and magnetic properties of the $(I\text{-}III)_{1-z}Mn_{2z}Te_2$(I=Cu,Ag III=In,Ga) alloys, and reported the range of solid solubility as well as values of the spin-glass transition temperature Tg for these systems.

In the present work, the properties of alloys of the system $(AgInCd_2)_x(CuIn)_{2y}Mn_{4z}Te_4$ are being studied. The aim of this paper is to show some results of the initial work on the crystallographic and magnetic properties of this alloy system. Here, results are presented for the line $x=3y$ of the pseudoternary system $(AgInCd_2)_x(CuIn)_{2y}Mn_{4z}Te_4(x+y+z=1)$.

2. Experimental method

Polycrystalline samples were produced by the standard melt and anneal technique. In each case, 1.5 g were made from the appropriate amounts of the elements and were sealed under vacuum in quartz ampoules which had previously been carbonized to prevent interaction of the components with the quartz. The equilibrium condition of each sample was determined from Guinier x-ray powder photograph. It was found that an annealing period from twenty to thirty days produces good equilibrium conditions.

The magnetic susceptibility measurements were made using a Faraday magnometer with a constant field gradient of 343 Oe/cm, and external magnetic field up to 0.6 T. The magnetic susceptibility data were calibrated using a N.B.S. Platinum sample. The temperature was controlled by a precalibrated Si diode sensor.

3. X-ray results and analysis

Samples of composition z=0, 0.1, 0.2, 0.4, 0.5 and 0.6 of the line x=3y, i.e. $(AgInCd_2)_{3y}(CuIn)_{2y}Mn_{4z}Te_4$ with $y=(1-z)/4$ and $x=1-y-z$, were investigated. It was found that the single phase samples gave x-ray photographs which showed the zinc-blende structure typical of $AgInCd_2Te_4$ (4). For the case z=0.6, lines of the nickel arsenide structure of MnTe were observed in addition to the apparent zinc-blende lines. In each case the value of the lattice parameter a was determined using Ge as internal standard. The variation of a with z is shown in Fig. 1. It is seen that, within the limits of experimental error, this variation appears to be linear and that this line extrapolated to 6.333 Å at z=1, representing the lattice parameter value

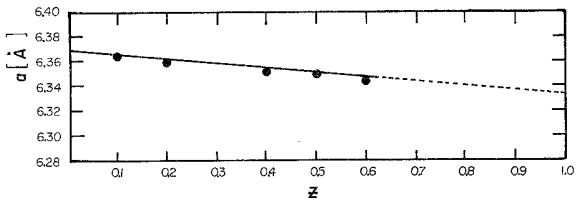

Figure 1. Variation of lattice parameter a with z.

that MnTe would have in the zinc-blende structure. Using this value and the Phillips radii for the Te atom, a value of 1.33 Å is found for the normal tetrahedral covalent radii of manganese. This is in good agreement with the equivalent value obtained for alloys of this type (1, 3,4).

For interpolation purposes, the linear variation of a vs z was fitted to a linear equation in z, giving

$$a = 0.6368 - 0.00374z \text{ (nm)}$$

with standard deviation of the fitted points of 2.7×10^{-4} nm.

4. Magnetic susceptibility results and analysis

Magnetic susceptibility measurements were carried out on each sample in the temperature range between 80 and 300 K. The experimental values were corrected by substracting the diamagnetic contributions from the $AgInCd_2Te_4$ and $CuInTe_2$ using the following relation,

$$\chi = \chi_e - (x\chi_1 + 2y\chi_2)$$

where χ_e is the experimental value, χ_1 and χ_2 are de diamagnetic susceptibilities of $AgInCd_2Te_4$ and $CuInTe_2$ respectively which were measured in this work, and χ represents the corrected values. These results are shown in Fig. 2 where $1/\chi$ is plotted as a function of temperature for all the samples. It is seen from this figure that the $1/\chi$ vs T results have, within the experimental limits of error, the linear Curie-Weiss behaviour in the temperature range investigated here and can be extrapolated to give the Curie-Weiss temperature θ. The obtained values of θ are shown in Fig. 3 together with the values for the $Cd_{1-z}Mn_zTe$ (7) alloys. For all compositions the Curie-Weiss temperature appears to be negative indicating the presence of an antiferromagnetic interaction between the Mn atoms. The values of θ were fitted to a linear equation in z, giving

$$\theta = -1.7 + 623.4z \text{ K}$$

the standard deviation in this case is 6.1 K.

For each value of z, the Curie constant C is determined by the slope of curve ($1/\chi$ vs T); these results are shown in Fig. 4. It was found that the value of the effective magnetic moment varied from 5.98 for z=0.1 to 6.09 for z=0.6. The magnetic composition for all samples was determined from the value of the Curie constant. These compositions were found to be within 1%

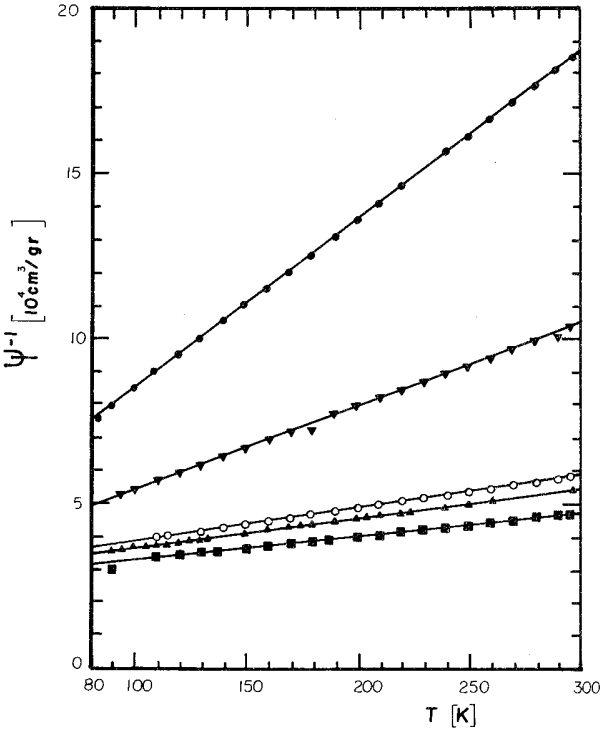

Figure 2. Reciprocal magnetic susceptibility versus temperature for different concentration of Mn. ● Z = 0.1, ▼ Z = 0.2, ○ Z = 0.4, ▲ Z = 0.5 and ■ Z = 0.6.

with respect to the nominal values. Hence, it is possible to determine the composition z of an unknown alloy of this system with good accuracy by determining its value of C. This is of interest since the composition of an alloy grown by a directional freeze technique can then be obtained from its corresponding value of the parameter a and C.

5. Discussion

Regarding the magnetic properties of the present alloys, one point of interest is the exchange mechanisms between the Mn ions. It has been assumed that the exchange interaction between two manganese ions depends on the cation nearest neighbour distance (d) (2,7). An exchange mecanism, proposed by Geertsma *et al.* (8) has the exponential form

$$J(r) = J_o \exp(-\alpha r) r^2 \qquad (1)$$

where r is related to the spacing d and to the Mn composition by $r=dz^{-1/3}$, and α is a measure of the range of the interaction between the paramagnetic ions. If it is assumed that $kTg=-AJ$, where A is a constant independent of z, equation 1 gives

$$\ln(d^2 Tg z^{-2/3}) = \ln(-\frac{AJ_o}{K}) - \alpha d z^{-1/3} \qquad (2)$$

In order to continue this analysis, a set of data for the spin-glass transition temperature is needed. Hence, here the experimental results of the spin-glass transtion temperature Tg reported

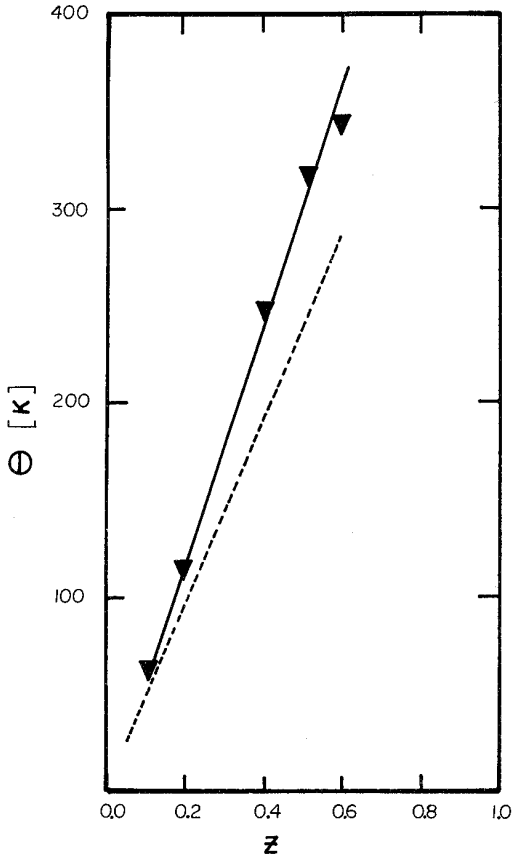

Figure 3. Plot of the Curie-Weiss temperature versus the Mn concentration.

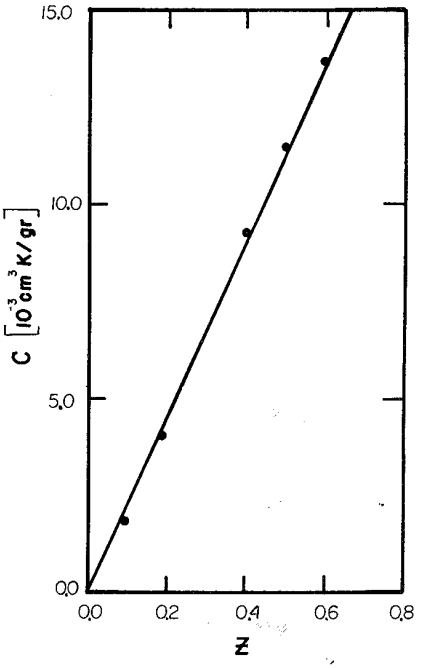

Figure 4. Plot of the Curie-Weiss constant C versus the Mn concentration.

in ref. 6 for the pseudobinary lines $(CuIn)_{1-z}Mn_{2z}Te_2$ and $(AgIn)_{1-z}Mn_{2z}Te_2$ have been used to determine values of α and AJo/k. Also it is assumed that the cation-cation distance is related to the lattice parameter by $d=a/\sqrt{2}$ and that the constant A can be written as $S(S+1)$ since the interaction in the present case is antiferromagnetic. These resulting values are as follow,

$$\alpha = 5.9 \text{ nm}^{-1}$$

$$J_o/k = -22 \text{ K nm}^2, \text{ with } A = 35/4$$

The value of α and that of J_o/k are to be compared with the values of 6.1 nm^{-1} and -23 K nm^2 obtained for the zinc-blende materials (9). This indicated that the exchange interaction and the range of the interaction of the present alloys are very similar to those of the zinc-blende materials. In the present case, the value of the interaction range is found to be 0.17 nm and the mean cation-cation distance d is of about 0.45 nm, so that the interaction is short range.

Equation 1 together with the value of α and J_o/k obtained above can be used to predict values of θ, the standard mean field theory gives

$$\theta = \frac{2S(S+1)}{3K} \sum_i n_i J_i \qquad (3)$$

where the summation is over consecutive sets of neighbours. Substituting Eq. 1 into 3 and replacing n_i by zn_i, then

$$\theta = \frac{2S(S+1)}{3K} J_o z \sum \frac{n_i \exp(-\alpha r_i)}{r_i^2} \qquad (4)$$

where α and J_o/k are given as above.

Values of n_i and r_i up to the seventh nearest neighbours were considered and values of θ were calculated using Eq. 4 and compared with the experimental values. These values are shown in Fig. 3, where the solid line represents the calculated values for the present system and the dashed line gives the predicted values for the $Cd_{1-z}Mn_zTe$ alloys obtained from Eq. 4. It is seen that a good agreement between experimental and predicted values is obtained using this simple method.

The variation of the Curie constant is linear and within experimental error extrapolates to the origin of coordinates. This result is to be expected since C depends upon the concentration of Mn atoms.

The magnetic susceptibility was calculated for each sample using a cluster model as was made by Sagredo *et al.* in $Zn_{1-z}Mn_zS$ (10) and $Cd_{1-z}Mn_zSe$ (11) in the same temperature range. It was found in the present work that for the sample z=0.1 the agreement between calculated and experimental data is no very good when J is assumed to be constant throughout the temperature range. For samples with z>0.1 the agreement is poorer. One possibility is that in the composition range investigated here the amount of Mn ions is very high so that the probability of formation of quadruplet clusters needs to be considered in the equation for susceptibility. Another factor would be that the temperature range of the present results is well above Tg, where Mn spins interact weakly and the effective number of inter-

acting Mn ions which will form the clusters at that temperature is small. On the other hand, the values of the concentration of clusters of a specific type, N_1, N_2 and N_3, used to determine the predicted susceptibility data could not represent their real values, so that a better set of these values needs to be considered, possibly of the modified form suggested by Lyapilin *et al.* (12).

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