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Magnetic Behaviour for the $MnIn_{2(1-z)}Ga_{2z}Se_4$ Alloys

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Polycrystalline samples of $MnIn_{2(1-z)}Ga_{2z}Se_4$ system were prepared by the melt and anneal technique. Low-field measurements of magnetic susceptibility χ were made as a function of temperature in the range 2 to 300 K. Values of T_N, the Néel temperature, were obtained from the cusp in the χ versus T curves. The $1/\chi$ versus T curves indicated that for $0 < z < 0.30$, the Mn is randomly distributed over the cation sublattice and the compound $MnIn_2Se_4$ ($z = 0$) was found to be spin-glass, with $T_g = 2.75$ K and $\theta = -94$ K. The samples in the composition range $0.75 < z < 1.0$ all showed an ordered distribution of Mn^{2+} ions on the cation sublattice and were antiferromagnetic showing ideal Curie-Weiss behaviour, $T_N = 8$ K and $\theta = -24$ K.

Introduction Magnetic semiconducting compounds and alloys in which manganese is one of the component elements are of interest because they show both magnetic and semiconductor behaviour [1]. The $MnB_2^{III}C_4^{VI}$ compounds fall into this category and in recent works [2, 3], the magnetic behaviour was studied for the $MnGa_2Se_4$, $MnIn_2Se_4$ and $MnIn_2Te_4$ compounds and for some alloy systems of which they are components. It was found that when the Mn and Ga/In atoms are ordered on the cation sublattice, as in the case for $MnGa_2Se_4$, the compound shows almost ideal antiferromagnetic behaviour. However, when the Mn and Ga/In atoms are randomly mixed on the cation sublattice, as in the case for $MnIn_2Te_4$, the compound shows spin-glass behaviour. It was found that these conditions apply also in the various alloy systems and it was shown [2, 3] that values of the Curie-Weiss constant θ, determined from magnetic susceptibility measurements, gave a very good indication of the ordered arrangement of the Mn atoms in the various materials.

In the present work, the alloy system $MnIn_{2(1-z)}Ga_{2z}Se_4$ was investigated. The crystal structure of the terminal compounds has been studied by several workers [3 to 6], and it has been found that the $MnGa_2Se_4$ has a defect tetragonal structure (η-phase) with lattice parameter values $a = 5.674$ Å and $c = 10.757$ Å, isomorphous with $CdGa_2S_4$, space group $I\bar{4}$ [3]. While in the case of the $MnIn_2Se_4$, the structure has been shown to be trigonal (δ-phase), with lattice parameter values $a = 4.051$ Å and $c = 39.46$ Å, and space group $R\bar{3}m$ [6].

Here, for the alloy system $MnIn_{2(1-z)}Ga_{2z}Se_4$, the behaviour of the magnetic susceptibility χ as a function of temperature T has been investigated for a wide range of z values. From the resulting data, the values of the Curie-Weiss θ temperature were used to indicate the ordering of the Mn^{+2} ions in the single-phase fields.

Sample Preparation and Experimental Techniques The polycrystalline samples of $MnIn_{2(1-z)}Ga_{2z}Se_4$ used in this study were prepared by the melt and anneal technique, the description of the preparation having been published previously [7]. In each case, a Guinier X-ray powder photograph was taken of the prepared sample to check the equilibrium conditions as well as the presence of secondary phases in the alloy. After the equilibrium condition of the material was checked, on all single-phase samples, magnetic susceptibility χ measurements as a function of the temperature T from 2 to 300 K were made using a Quantum Design MPMS-5 SQUID magnetometer with an external magnetic field of 1×10^{-2} T. The resulting $1/\chi$ versus T curves were analysed to give various magnetic parameters, as discussed below.

Experimental Results Measurements of magnetic susceptibility χ were made as a function of temperature on samples shown by the X-ray photographs to be single phase. The resulting graphs of $1/\chi$ versus T were found to be very similar in form to those reported previously for $MnB_2^{III}C_4^{VI}$ and for some alloys systems of which they are components [2, 3], and typical curves for two different single phase fields are shown in Figs. 1a and b. In the range $0.75 < z < 1.0$ (η field), Fig. 1a, the samples showed ideal antiferromagnetic behaviour, giving a linear $1/\chi$ versus T form down to the Néel temperature T_N, which was observed as a sharp cusp in the graph. However, alloys in the range $0 < z < 0.30$ (δ field), Fig. 1b, showed deviations from the linear Curie-Weiss behaviour at lower temperatures, indicating either spin-glass behaviour or a mixture of part spin-glass and part antiferromagnetic form. In all cases, the linear regions of the $1/\chi$ versus T graphs were extrapolated to obtain values of the Curie-Weiss temperature θ.

As mentioned above the curve in Fig. 1a, for a sample with $z = 0.9$, shows a linear $1/\chi$ variation with T over the complete range investigated, with a Curie-Weiss θ value of -24 K. The curve in Fig. 1b, for the $z = 0.2$ sample, is linear down to approximately 50 K, but below this temperature deviates appreciably from the Curie-Weiss behaviour. In this case extrapolation of the linear region of the curve gave a value of θ of about -100 K.

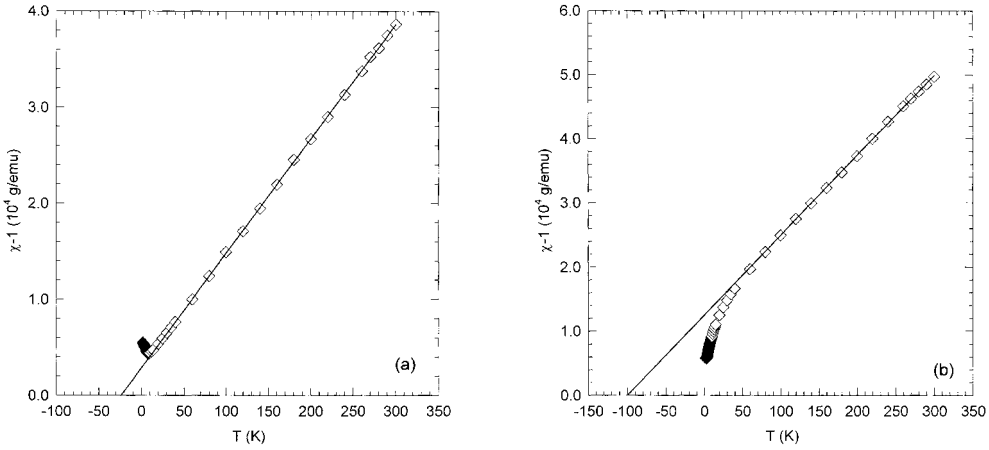

Fig. 1. Variation of $1/\chi$ with T for typical $MnIn_{2(1-z)}Ga_{2z}Se_4$ alloys. a) Sample with $z = 0.9$, b) sample with $z = 0.2$

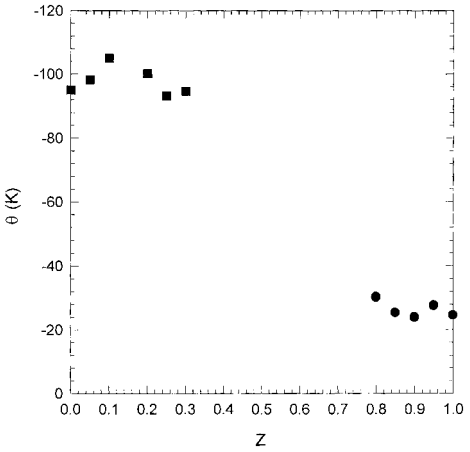

Fig. 2. Variation of Curie-Weiss constant θ with composition z for the $MnIn_{2(1-z)}Ga_{2z}Se_4$ alloys. ● samples showing linear Curie-Weiss form (Fig. 1a). ■ samples showing significant deviation from linearity in Curie-Weiss plot (Fig. 1b)

As was shown previously [2], the antiferromagnetic behaviour occurs when the Mn atoms are ordered on the cation sublattice, while disordered, random distribution of the Mn results in the spin-glass form. Thus the values of θ obtained from the magnetic susceptibility measurements give a very good indication of the degree of order of the Mn on the cation sublattice. The resulting values of θ as a function of z are shown in Fig. 2.

Analysis and Discussion As indicated above, at low temperatures two single-phase solid fields occur. The first one (δ) has a trigonal form based on a close-packed Se sublattice with the Mn and In atoms occupying both tetrahedral and octahedral interstices of the Se sublattice, and the second one (η) having body-centered tetragonal form based on some cation ordering in the zincblende sublattice. With the polycrystalline samples used in the present work, it is quite difficult to make any estimate from the powder X-ray data of the arrangement of the Mn in each lattice. However, as was shown previously [4, 8, 9] for alloys of similar phase diagrams, the values of the Curie-Weiss constant θ determined from magnetic measurements give a good indication of the ordering of the Mn atoms in the lattice. Thus, in the present work, the values of θ shown in Fig. 2 can be used to give information on the form of the δ and η phases.

For ordered structures which have a body-centered tetragonal lattice with $c/a \approx 2$, based on a cubic zincblende type subcell, the anions form a cubic close-packet lattice. The cation sites form four different pairs, the sites in each pair being identical because of the body-centered symmetry, and these can be conveniently labelled:

(i) 0, 0, 0 and 1/2, 1/2, 1/2; (ii) 1/2, 1/2, 0 and 0, 0, 1/2;

(iii) 0, 1/2, 1/4 and 1/2, 0, 3/4; (iv) 1/2, 0, 1/4 and 0, 1/2, 3/4.

These positions can also be labelled according to the standard crystallographic nomenclature, viz.

$I\bar{4}$: (i) −2a, (ii) −2b, (iii) −2c and (iv) −2d;

$I\bar{4}2m$: (i) −2a, (ii) −2b, (iii) and (iv) −2d;

i.e. (iii) and (iv) must be identical.

$$I\bar{4}2d : (i) \quad \text{and} \quad (iii) -4a, \qquad (ii) \quad \text{and} \quad (iv) -4b;$$

i.e. (i) and (iii) are identical, (ii) and (iv) are identical.

In a previous work [8], it was shown that if the Mn atoms are present (a) on only one of the four different sites (resulting in $I\bar{4}$ or $I\bar{4}2m$ symmetry) or (b) on two of the four different sites (as is required for $I\bar{4}2d$), with antiferromagnetic exchange between the Mn atoms, no frustration occurs, the material shows the ideal Curie-Weiss behaviour described above, and it shows antiferromagnetic behaviour below T_N.

For the cases when the Mn atoms are randomly distributed over (c) three different sites or (d) over all of the available sites, with antiferromagnetic interaction between the Mn atoms, frustration will always occur, the geometry of the occupied sites being identical with that for face-centered cubic case.

When the alloy system is produced by substituting a fraction of non-magnetic cations by Mn atoms the values of θ are found to vary linearly with the Mn concentration, for a given Mn concentration, a change in the ordering of the non-magnetic cations causes only a small change in the value of θ [8].

Returning to the magnetic data, it is seen from Fig. 2 that the θ values fall into two groups. For all of the $MnGa_2Se_4$-rich samples ($z > 0.75$), the $1/\chi$ versus T curves are of type shown in Fig. 1a, and the values of θ are relatively low and, within experimental limits, remain constant with z, the value being ≈ -28 K, in good agreement with the value obtained previously for the $MnGa_2Se_4$. This indicates that, for samples showing this antiferromagnetic form, the Mn atoms are ordered on the cation sublattice in such a way that magnetic frustration does not occur below the magnetic ordering temperature T_N. Thus the Mn atoms are situated either on one type of site, e.g. on site (i), or on two sites, e.g. on (i) and (iii) sites, but not on three or four types of site since this would result in frustration. For the space group $I\bar{4}$, which is the only tetragonal form in the present system, the occupation of two sites, e.g. (i) and (iii), is ruled out. Thus, for this $I\bar{4}$ symmetry sites are occupied as (i) Mn, (ii) Ga or In, (iii) Ga or In and (iv) vacancy.

For the $MnIn_2Se_4$-rich alloys with trigonal symmetry ($0 < z < 0.30$), the $1/\chi$ versus T curves are of type shown in Fig. 1b giving high values of θ (≈ -100 K), which also remain constant with z as it is seen in Fig. 2. These high values of θ and the large deviations from Curie-Weiss behaviour confirm that the Mn atoms are distributed at random on the cation sublattice, resulting in a spin-glass behaviour.

For the case of $MnIn_2Se_4$ ($z = 0$), Döll et al. [6] reported a value for θ of -60 K and found no indication of a magnetic transition above 2 K. However, the present data indicate that $MnIn_2Se_4$ has $\theta = -95$ K and shows a spin-glass transition at $T_g = 2.75$ K. Because, as indicated above, the magnetic behaviour of these materials is sensitive to the detail of Mn positioning in the cation sublattice, it is possible that the differences between the present results and those of Döll et al. are due to differences in the methods of preparation of the $MnIn_2Se_4$ samples.

Conclusions It is seen that the values of Curie-Weiss constant θ, determined from the measured variation of magnetic susceptibility with temperature, are very useful in determining the positions of the Mn atoms in the cation sublattice.

The present results confirm the positions of the Mn atoms in the trigonal structure of $MnIn_2Se_4$ [6], but indicate that the compound shows spin-glass behaviour with a transi-

tion temperature T_g of about 2.75 K. While the magnetic behaviour of $MnGa_2Se_4$ is quite different. $MnGa_2Se_4$ shows practically ideal antiferromagnetic form, with the graph of $1/\chi$ versus T being a straight line down to the Néel temperature T_N, with T_N = 8 K and the Curie-Weiss temperature $\theta = -24$ K.

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