

The Magnetic Properties of the Manganese-Gallium-Aluminum-Germanium System

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The properties of solid solutions of composition $\text{MnGa}_{1-x}\text{Al}_x\text{Ge}$ formed from ferromagnetic MnGaGe ($T_c = 185^\circ\text{C}$) and MnAlGe ($T_c = 245^\circ\text{C}$) have been examined. In the range, $0 < x < 0.1$, the Curie temperature and saturation magnetization are not a monotonic function of x as might be expected for a solid solution of two ferromagnets. Instead, for $x = 0.025$, the Curie temperature is actually $\sim 77^\circ\text{C}$ lower than that of MnGaGe . Despite the similarity in the structure and lattice constants of MnGaGe and MnAlGe , aluminum rich compositions, e.g., $x = 0.95$ show no solid solution. Attempts to prepare other ferromagnetic ternary Mn (IIIA) (IVA) compounds have not been successful.

Introduction

The ferromagnetic, ternary, intermetallic Mn (IIIA) (IVA) compounds are of current interest (1, 2) because of their magneto-optic properties. The first member of this series MnAlGe (3-5) has been known for some time and the second member MnGaGe (1, 6, 7) was synthesized more recently. Both these compounds are isostructural with Mn_2Sb . Attempts to prepare other members of this series illustrated in Fig. 1 have not been successful. No new tetragonal phases were identified in any of the other seven ternary compositions, although some of these compositions did contain unidentified ferromagnetic phases.

Both MnGaGe and MnAlGe show strong magneto-crystalline anisotropy along the tetragonal c axis. The magnetic anisotropy indicates

strong coupling between the ferromagnetically aligned planes of manganese atoms. This magnetic coupling along the c axis is via two layers of nonmagnetic atoms. However, comparison of the magnetic properties of MnGaGe and MnAlGe (Table I), shows that the nature of the group (IIIA) metal is more important in determining the strength of this interaction than the separation of the ferromagnetic planes of manganese atoms.

From the small difference in lattice constants between MnGaGe and MnAlGe ($< 1.5\%$) an extensive range of mutual solid solutions would be expected. We report here on the structure and magnetic properties of such solid solutions in the manganese-gallium-aluminum-germanium system over the limited composition range, $\text{MnGa}_{1-x}\text{Al}_x\text{Ge}$ ($0 < x < 0.1$).

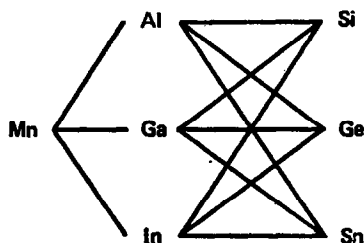


FIG. 1. Potential Mn (IIIA) (IVA) compounds.

TABLE I

COMPARISON OF THE LATTICE CONSTANTS AND MAGNETIC PROPERTIES OF MnAlGe AND MnGaGe

	T_c ($^\circ\text{C}$)	σ_{sat} (emu/g)	a_0 (\AA)	c_0 (\AA)
MnAlGe	245	57.8	3.916	5.950
MnGaGe	185	47.1	3.966	5.885

Preparation of Materials

Samples of $\text{MnGa}_{1-x}\text{Al}_x\text{Ge}$ ($0 < x < 0.1$) were prepared by heating a melt of the components to 1000°C and quenching to room temperature, followed by a solid state anneal of the powdered reaction product at 575°C for 21 days.

Attempts to prepare MnAlGe by the methods described in the literature were not entirely satisfactory. Quartz reaction tubes (3) were attacked and this frequently led to explosion on slow cooling after the reaction. Use of magnesia crucibles (5) gave a contaminated product. In view of these difficulties, we used the technique described earlier for MnGaGe (1) because this allowed the exposure of the melt to the quartz tube to be reduced to less than 30 min. For each preparation, the manganese (99.9%) and germanium (99.999%) were reduced in hydrogen immediately prior to use. The gallium shot (99.999%) and the aluminum ingot (99.995%) were not powdered before use in order to avoid oxidation.

Characterization of Materials

X-Ray Data

The X-ray data were obtained using $\text{CuK}\alpha$ radiation and vacuum-path diffractometers (8) with a focusing graphite monochromator in the diffracted beam. The powder was mounted on a single crystal plate of silicon cut parallel to (510) and rotated continuously in its own plane during the scans. In the preparation of MnGaGe reported previously, some unreacted Ge remains even after long periods of annealing. It was rather surprising, therefore, that for the composition $x = 0.025$ no unreacted Ge was detected in the X-ray scans. However, as the amount of Al increased to $x = 0.05, 0.075,$ and 0.1 , the amount of unreacted germanium observed in the X-ray scans also increased. No other phases were observed except for a trace of MnO in some samples.

The unreacted germanium can be made to react in each of these $\text{MnGa}_{1-x}\text{Al}_x\text{Ge}$ samples by heating with $\sim 1\%$ by weight of iodine at 500°C for 7 days. The iodine forms volatile iodides which facilitate completion of the reaction, leading to a highly crystalline product with no free germanium. However, in the process, about 1 atomic% of manganese is extracted as MnI_2 . As will be discussed later, removal of this amount of manganese does not seem to influence the

Curie temperature, though it may affect the saturation magnetization. The lattice constants of each sample did not change significantly after treatment with iodine.

The MnAlGe prepared by this quenching technique, and annealed at 500°C for 14 days also contained a small amount of unreacted germanium. No unreacted germanium was reported in the MnAlGe prepared by Wernick et al. (3). However, it is interesting to note that

TABLE II

OBSERVED AND CALCULATED INTERPLANAR SPACINGS AND POWDER INTENSITIES FOR MnAlGe. $\text{CuK}\alpha$ RADIATION

hkl	d_{calc}	d_{obs}	I/I_1 (calc)	I/I (obs)
0 0 1	5.951	5.988	42	20
1 0 1	3.271	3.278	48	41
0 0 2	2.975	2.981	6	6
1 1 0	2.769	2.773	14	14
1 1 1	2.511	2.513	54	58
1 0 2	2.369	2.372	2	<1
1 1 2	2.027	2.026	100	100
0 0 3	1.983	1.984	13	17
2 0 0	1.958	1.959	49	52
2 0 1	1.860	1.861	4	4
1 0 3	1.769	1.770	4	7
2 1 1	1.680	1.681	10	3
2 0 2	1.6356	1.6353	3	4
2 1 2	1.5091	1.5091	1	<1
0 0 4	1.4875	1.4875	5	5
2 0 3	1.3934	1.3933	12	17
1 0 4	1.3906	1.3904	9	10
2 2 0	1.3846	1.3846	12	15
2 2 1	1.3485	1.3489	1	1
2 1 3	1.3128	1.3131	3	5
1 1 4	1.3104	NR	2	NR
3 0 1	1.2751	1.2752	2	2
2 2 2	1.2553	1.2553	1	2
3 1 0	1.2384	1.2384	2	2
3 1 1	1.2124	1.2127	5	7
3 0 2	1.1953	NR	<1	<1
0 0 5	1.1900	NR	<1	<1
2 0 4	1.1845	1.1848	7	8
3 1 2	1.1433	1.1428	16	19
1 0 5	1.1386	NR	10	NR
2 2 3	1.1353	1.1352	5	8
2 1 4	1.1337	NR	5	8
1 1 5	1.0933	1.0931	5	NR
3 0 3	1.0904	1.0906	4	6
3 2 1	1.0685	1.0681	1	2
2 0 5	1.0169	NR	1	1
2 2 4	1.0135	1.0132	3	6

N.R., Not resolved.

the (114) line reported for MnAlGe by Wernick et al. (3) is in error by more than the expected experimental error but is in good agreement with the (331) line of germanium. However, Wernick et al. (3) report no other X-ray spacings which could be ascribed to germanium. The experimentally observed interplanar spacings and relative intensities observed for our sample of MnAlGe (omitting the peaks for Ge), are shown in Table II. These data compare very well with those obtained from the pattern computed by Smith's (9) method. The relatively poor agreement between the calculated and observed intensities of the (001) peak probably results from surface roughness effects which are important at low angles. The agreement between the calculated and computed interplanar spacings is somewhat better at higher d spacings than that reported by Wernick et al. (3). However, the lattice constants from the two sets of data agree. Attempts to prepare solid solutions by partial replacement of the aluminum in MnAlGe by Ga were not successful. For instance when $x = 0.95$ a two phase mixture of MnGaGe and MnAlGe was obtained.

Thermal Analysis Data

The thermal analysis data for MnGa_{1-x}Al_xGe samples ($0 < x < 0.1$), obtained using DuPont thermal analysis apparatus, was essentially the same as that reported for MnGaGe. The data for MnAlGe is similar to that of Wernick et al. (3) except that in agreement with Velge and DeVos (4), no peak at 584°C was detected. However, from the shape of the peak at 800°C shown in Fig. 2 and from the observation of the

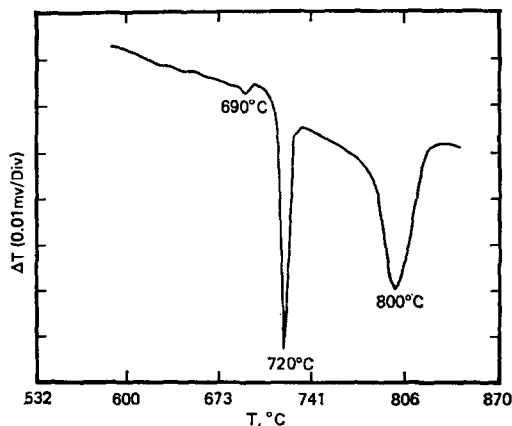


FIG. 2. Thermal analysis data for MnAlGe.

sample on cooling, we do not believe that this peak is due to eutectic melting. The peritectic nature of this melting was confirmed by X-ray analysis, which showed that considerable decomposition had taken place on melting.

The specific heat of MnAlGe measured using a DuPont differential scanning calorimeter was 0.15 cal/g°C at 140°C which compares with the value of 0.11 cal/g°C for MnGaGe (1) at the same temperature.

Magnetic Measurements

Curie temperatures of the specimens were measured using a DuPont thermogravimetric balance, modified to provide a magnetic field gradient at the sample. Magnetization measurements were made using a vibrating sample magnetometer. The results are shown in Figs. 3 and 4. Instead of the monotonic rise in T_c and σ_{sat} expected for a solid solution of MnGaGe and MnAlGe, T_c and σ_{sat} initially fall appreciably with the addition of small amounts of aluminum. Treatment of the MnGa_{1-x}Al_xGe samples ($0 < x < 0.1$) with iodine, to achieve a more completely reacted product, with no unreacted germanium, causes T_c to decrease except for $x = 0.025$. In this latter case, the sample is already completely reacted prior to iodine treatment and, therefore, contains no unreacted germanium. The value of the saturation magnetization for MnAlGe in Table I is somewhat higher than that reported by Wernick et al. (3) and is in better agreement with some of the values reported by Velge and DeVos (4). This value of

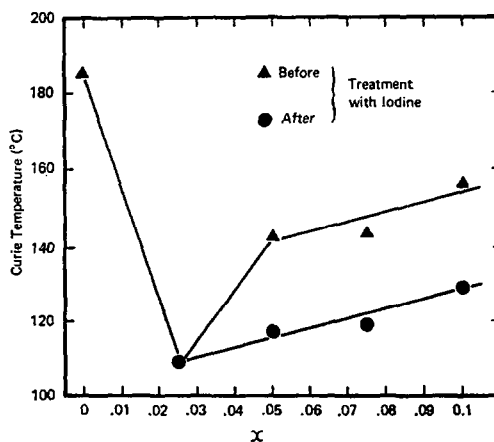


FIG. 3. Curie temperature as a function of composition for MnGa_{1-x}Al_xGe.

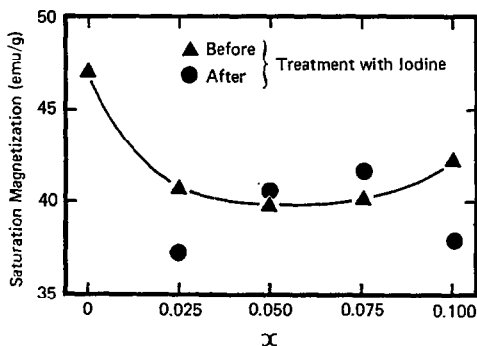


FIG. 4. Saturation magnetization as a function of composition for $\text{MnGa}_{1-x}\text{Al}_x\text{Ge}$.

57.8 emu/g for the saturation magnetization of MnAlGe corresponds to $1.57 \mu_{\text{B}}/\text{Mn}$ atom. By comparison, the saturation magnetization of MnGaGe is 47.1 emu/g which corresponds to $1.66 \mu_{\text{B}}/\text{Mn}$ atom.

Discussion

Only two ferromagnetic compounds of the series Mn (IIIA) (IVA) have been prepared, MnGaGe and MnAlGe . Both appear to decompose partially on melting. Despite the similarity in the structure and lattice constants of these two materials, they do not form a complete range of solid solutions. For compositions for which $0 < x < 0.1$, single phase solid solutions were observed, except for the presence of some unreacted germanium. This unreacted germanium could be removed by iodine treatment which causes the reaction to proceed to completion. However, at the aluminum rich end of the composition range, e.g., $x = 0.95$, a two-phase system of MnGaGe and MnAlGe was obtained. This difficulty in substituting gallium for aluminum in MnAlGe may be due to the fact that above 720°C MnAlGe has a different crystal structure from MnGaGe as can be seen from the thermal analysis data in Fig. 2.

In the region of solid solution investigated, the observed magnetic properties (Figs. 3 and 4) were somewhat unexpected. At low values of x , the Curie temperature and saturation magnetization rapidly decrease with x , instead of slowly increasing with x , as would be expected for a solid solution of MnGaGe and MnAlGe . This rapid fall in T_c and σ_{sat} is not accompanied by any significant change in lattice constants ($< 0.33\%$), and cannot be readily explained if the

aluminum is simply occupying the vacant gallium sites. If, however, some of the aluminum occupies manganese sites and a corresponding amount of the manganese occupies the non-magnetic atom sites, the decrease in T_c and σ_{sat} can be explained in terms of antiferromagnetic coupling between the manganese atoms on the two different kinds of lattice sites. Such antiferromagnetic coupling between the manganese in these two sites is observed for the isostructural compound Mn_2Sb (10). At higher aluminum concentration ($x > 0.025$), T_c and σ_{sat} begin to increase slowly as would be expected for a solid solution. Prior to treatment with iodine samples with $x = 0.05, 0.075$, and 0.1 , all contain unreacted germanium and are, therefore, deficient in germanium. Figure 3 shows that these samples have higher Curie temperatures than the corresponding iodine completely reacted, stoichiometric samples. This suggests that a truly stoichiometric sample of MnGaGe would have a Curie temperature somewhat lower than the reported 185°C . As shown in Fig. 4, the magnetization data for the iodine treated samples shows some scatter about the data for the samples prior to iodine treatment. The reason for this is not understood. In a ternary intermetallic compound of this kind, there are several possible forms of lattice disorder in addition to non-stoichiometry. Such lattice disorder can influence the magnetic properties. Thus, it is apparent that without a full knowledge of the actual location of each of the three elements within the lattice, any explanation of the resultant magnetic properties is somewhat speculative.

Acknowledgments

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