Cl_b-Type Intermetallic Compound in the Ir–Mn–Sb System and Its Magnetic Properties*

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Crystal structures and magnetic properties of Ir–Mn–Sb alloys were studied through X-ray and magnetic analyses. Intermetallic compounds of the Cl_b-type structure are found in IrMn_{1+x}Sb alloys with $x=0.5\sim0.8$.

IrMn_{1.5}Sb and IrMn_{1.8}Sb have lattice parameters of 0.6154 and 0.6141 nm at room temperature, magnetic moments n_B of 2.6 and 2.1 μ_B per Mn atom at absolute zero, and Curie temperatures T_c of 278 and 258 K, respectively. From the temperature dependence of reciprocal magnetic susceptibility, these Cl_b-type alloys with excess Mn are expected to be ferrimagnetic.

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I. Introduction

The existence of ferromagnetic or antiferromagnetic Mn-base intermetallic compounds with the Cl_b structure including PtMnSb⁽¹⁾⁽²⁾, PtMnSn⁽²⁾⁽³⁾, AuMnSb⁽⁴⁾, RhMnSb⁽⁵⁾⁽⁶⁾, PdMnTe⁽⁷⁾⁽⁸⁾ and others^{(6)(8)~(11)}, has been reported in the literature. All of these compounds have Mn–Mn interatomic distances of approximately 0.42~0.45 nm, and magnetic moments of approximately 4 μ_B per Mn atom. The crystal structures and magnetic properties of these compounds are very similar to those of the Heusler, L2₁-type alloys with compositions X₂MnY where X is Cu, Ni, Co or Pd, and Y is Al, Ga, In or Sn⁽¹²⁾⁽¹³⁾.

We have investigated the relations of the magnetic properties to the valence electron number and the interatomic distance for those alloys with the Cl_b- or the Heusler-type structures. It has been found that the Curie temperatures of ferromagnetic Cl_b-type NiMnSb,

PtMnSb and PdMnSb compounds with six valence electrons per chemical formula [cf. Ref. (14)] decreased gradually with increasing Mn–Mn distance, and the CuMnSb, PdMnTe and AuMnSb compounds with seven valence electrons per chemical formula, the transition from antiferromagnetism to weakly ferromagnetism takes place with increase in Mn–Mn distance⁽¹⁴⁾. The present work is concerned with the confirmation of the Cl_b-type compound in Ir–Mn–Sb alloys⁽⁸⁾.

II. Experimental

The starting materials were 99.9% pure Ir, 99.999% pure Mn and 99.99% pure Sb. Appropriate quantities of the constituent elements were filled in an alumina crucible 6~7 mm in inner diameter and 30~40 mm in length and sealed in evacuated silica tubes, followed by melting in an electric furnace at 1200~1300°C for 2~10 h and furnace cooling. The alloys thus prepared were further heated at 500~900°C for 15~200 h for homogenization. X-ray crystal structure and magnetic analyses were carried out in the same way as reported previously^{(1)~(7)}. Density measurements were made in carbon tetrachloride by using a pycnometer.

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Fig. 3 Cl_b-type crystal structure of IrMnSb compound.

composition with an atomic ratio of 1:1:1, the structure factors F are given as follows:
 h, k, l all odd

$$|F|^2 = 16f_{\text{Ir}}^2 + 16|f_{\text{Mn}} - f_{\text{Sb}}|^2$$

h, k, l all even and $(h+k+l)/2 = 2n+1$

$$|F|^2 = 16|f_{\text{Ir}} - f_{\text{Mn}} - f_{\text{Sb}}|^2$$

h, k, l all even and $(h+k+l)/2 = 2n$

$$|F|^2 = 16|f_{\text{Ir}} + f_{\text{Mn}} + f_{\text{Sb}}|^2$$

On the other hand, if this alloy is the Cl structure, in which Mn and Sb sites are disordered, $|F|^2$ for all odd h, k, l becomes $16f_{\text{Ir}}^2$ only.

Since the composition of IrMn_{1.7}Sb deviates considerably from the 1:1:1 composition of the Cl_b structure, we investigate how the excess Mn atoms are distributed. In Fig. 4 relative intensities $I_{(111)}/I_{(220)}$ for IrMn_{1+x}Sb are plotted as a function of x , calculated from $|F|^2$ on various assumptions for the atomic distribution. Solid line I (type I) indicates the case where 4a sites and 4d sites are occupied by $(3\text{Ir} + x\text{Mn})/(3+x)$ and $(3\text{Sb} + x\text{Mn})/(3+x)$, respectively. Solid line II (type II) represents the Cl type structure in which the Ir and Sb atoms are equally replaced by excess Mn atoms. Solid line III (type III) shows the case of the transition from the Cl_b to the L2₁ structure, where the excess Mn atoms go onto the 4c site (cf. Fig. 3). The open circles in Fig. 4 show the measured values of the relative intensities, which are in excellent agreement with the solid line I.

Fig. 4 Relative intensity $I_{(111)}/I_{(220)}$ of IrMn_{1+x}Sb, assuming the configuration of atoms:

Type I: $\frac{3\text{Ir} + x\text{Mn}}{3+x}$, Mn, $\frac{3\text{Sb} + x\text{Mn}}{3+x}$,

Type II: Cl → Disorder, Type III: Cl_b → L2₁.

Table 1 shows that the experimental values $I_{(hkl)}/I_{(220)}$ are in good agreement with the calculated values for type I i.e. the Cl_b structure. Figure 5 shows a comparison between the density data calculated using the lattice parameters in these models and their observed values. Good agreement is seen for types I and II. The above results lead to the conclusion that the crystal structure of IrMn_{1+x}Sb is undoubtedly of the Cl_b type.

Figure 6 shows the composition dependence of lattice parameter. The alloys with $x \leq 0.4$ and $x \geq 0.9$ have nearly constant lattice para-

Fig. 5 Densities of IrMn_{1+x}Sb, assuming the configuration of atoms to be types I, II and III.

Fig. 6 Lattice parameters of the Cl_b -type $\text{IrMn}_{1+x}\text{Sb}$ alloys cooled at a rate of 50°C/h after heating at 850°C for 100 h.

Fig. 7 Temperature dependence of saturation magnetization of $\text{IrMn}_{1+x}\text{Sb}$ alloys cooled at a rate of 50°C/h after heating at 850°C for 100 h.

meters, respectively, being in the range where two or three phases coexist. The lattice parameters of the single-phase alloys with $x=0.5\sim 0.8$ are $0.6154\sim 0.6141$ nm, thus decreasing with increase in Mn concentration.

2. Magnetic properties

The temperature dependence of the magnetization σ_s per gram unit as measured by the application of a nearly saturating magnetic field of about 0.8 MA/m is shown in Fig. 7 for four alloys of the system $\text{IrMn}_{1+x}\text{Sb}$ at $x=0.2, 0.5, 0.8$ and 0.9 which were slowly cooled at a rate of 50°C/h after heating at 850°C for 100 h. From the figure it is apparent that the 0 K values of $\sigma_{g(0)}$ for the Cl_b -type

Fig. 8 Curie temperature, magnetization and magnetic moment of $\text{IrMn}_{1+x}\text{Sb}$ alloys cooled at a rate of 50°C/h after heating at 850°C for 100 h.

single phase alloys with $x=0.5$ and 0.8 are greater than 60×10^{-6} Wb-m/kg, but those obtained for the two-phase alloy with $x=0.2$ is smaller than 50×10^{-6} Wb-m/kg.

Figure 8 shows the composition dependences of the Curie temperature T_c , $\sigma_{g(0)}$ and the magnetic moment per Mn atom n_B as obtained from magnetic analysis of $\text{IrMn}_{1+x}\text{Sb}$. As can be seen from the figure, the values of T_c for the three-phase alloys with $x=0.2$ and 0.4 are nearly constant regardless of the composition. On the other hand, the Cl_b -type single phase alloys with $x=0.5\sim 0.8$ show a decrease in T_c with increase in x , while the two-phase alloys with $x=0.9$ and 1.0 have nearly constant values of T_c . The values of $\sigma_{g(0)}$ in the alloys with $x=0.2$ and 0.4 are both small. As x increases, however, the Cl_b -type single phase alloy with $x=0.5$ exhibits a sharp increase in $\sigma_{g(0)}$ at the early stage, followed by a gradual decrease. This decrease in $\sigma_{g(0)}$ becomes pronounced when the alloy orders to form two phases. The single phase alloys show a change in n_B similar to that in $\sigma_{g(0)}$ with increase in x . The value of n_B for the $x=0$ alloy (1:1:1 composition) obtained by linear extrapolation is $3.35 \mu_B$, which is a

Fig. 9 Temperature dependence of magnetic susceptibility and reciprocal magnetic susceptibility of the $\text{IrMn}_{1+x}\text{Sb}$ ($x=0.5$ and 0.7) alloys cooled at a rate of $50^\circ\text{C}/\text{h}$ after heating at 850°C for 100 h.

Fig. 10 Composition dependence of the paramagnetic effective Bohr magneton number for $\text{IrMn}_{1+x}\text{Sb}$ alloy cooled at a rate of $50^\circ\text{C}/\text{h}$ after heating at 850°C for 100 h.

little smaller than the values of the ordinary Cl_b-type compounds. The values of T_c and n_B for alloys $\text{IrMn}_{1.5}\text{Sb}$ and $\text{IrMn}_{1.8}\text{Sb}$ are 278 and 258 K and 2.6 and $2.1 \mu_B$, respectively.

Figure 9 shows the temperature dependence of the magnetic susceptibility χ_g and the reciprocal magnetic susceptibility $1/\chi_g$ for alloys $\text{IrMn}_{1.5}\text{Sb}$ (alloy (B)) and $\text{IrMn}_{1.7}\text{Sb}$. As shown in the figure, the linear decrease in $1/\chi_g$ with descending temperature shows Curie-Weiss behavior, but the rate of decrease becomes very rapid from about 650 K showing a deviation from the behavior. This is indicative of the existence of the ferrimagnetic property in those alloys. Figure 10 shows the com-

position dependence of the paramagnetic effective Bohr magneton number per Mn atom, P_{eff} , for $\text{IrMn}_{1+x}\text{Sb}$ as obtained from the $1/\chi_g$ vs T curves at high temperatures.

The aforementioned results suggest that in Cl_b-type $\text{IrMn}_{1+x}\text{Sb}$ alloys, as with other Cl_b- and L2₁-type compounds⁽¹³⁾, Mn atoms at the *b* lattice points exhibit strong ferromagnetism mainly due to the *s-d* interaction^{(15)~(18)} based on the free electron model. However, in this alloy system the Cl_b-type single phase exists at compositions of fairly high Mn concentrations, and consequently Mn atoms are localized at the *a* and *d* lattice points in addition to the *b* lattice points. For this reason, the interactions between Mn atoms at each pair of *a* and *b*, *a* and *d* ($d=0.266$ nm), and *b* and *d* ($d=0.308$ nm) should also be taken into consideration. Thus the ferrimagnetic property observed in the Cl_b-type alloys appears to be due to the fact that the excess Mn of *a* or *d* sites has the magnetic moment antiparallel to the Mn of *b* sites.

IV. Conclusions

X-ray crystal structure analysis and magnetic measurements were performed on the system $\text{IrMn}_{1+x}\text{Sb}$. The results obtained are as follows.

(1) Solid solutions with a Cl_b-type crystal structure exist over a composition range with $x=0.5\sim 0.8$ in the alloy system and their lattice parameters are found to vary from approximately 0.6154 to 0.6141 nm.

(2) The magnetic moment n_B per Mn atom and the Curie point T_c for $\text{IrMn}_{1.5}\text{Sb}$ are $2.6 \mu_B$ and 278 K, respectively. Both values decrease gradually with increase in Mn concentration, and $\text{IrMn}_{1.8}\text{Sb}$ shows $n_B=2.1 \mu_B$ and $T_c=258$ K.

(3) The Cl_b-type $\text{IrMn}_{1+x}\text{Sb}$ alloys indicate the ferrimagnetic property, and the property is enhanced with increase in Mn concentration.

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