On Cl_b Type Alloys in the Rh–Mn–Sb System*

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Crystal structures and magnetic properties of Rh–Mn–Sb alloys have been investigated by means of X-ray and magnetic analysis. It is shown that Cl_b type alloys exist near the stoichiometric composition in the Rh–Mn–Sb system. $\text{Rh}_{0.90}\text{Mn}_{1.20}\text{Sb}_{0.90}$ and $\text{Rh}_{1.10}\text{Mn}_{1.10}\text{Sb}_{0.80}$ alloys with the crystal structure of the Cl_b type have lattice parameters of about 6.145 and 6.170 Å at room temperature, saturation magnetizations of 79.5 and 75.0 emu/g at absolute zero, saturation magnetic moments of 3.19 and 3.29 μ_B per Mn atom at absolute zero, and Curie temperatures of 325 and 350°K, respectively. Moreover, the reciprocal magnetic susceptibility of these alloys has been found to satisfy the Curie-Weiss law above the Curie temperature.

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I. Introduction

Studies of ferromagnetic or antiferromagnetic Cl_b type compounds have heretofore been reported for $\text{NiMnSb}^{(1)}$, $\text{PdMnSb}^{(2)}$ and $\text{CuMnSb}^{(3)}$, including those on PtMnSb , PtMnSn and AuMnSb by the present authors^{(4)~(6)}. For Heusler(L_2)-type alloys in which the atomic proportion of the first element, e.g. Cu and Pd, is greater than the equi-atomic composition, there have been reports on Cu_2MnX ($\text{X} = \text{Al, In, Sn or Ga}$) compounds⁽⁷⁾ and Pd_2MnX ($\text{X} = \text{Al, In, Sn or Sb}$) compounds⁽⁸⁾ have been reported. These Cl_b and L_2 type compounds are considered to provide very useful information on the origin of their magnetic properties which may be elucidated in terms of the coordination number of atoms adjacent to Mn atoms, the kind of the neighboring atoms and the inter-atomic distance of Mn–Mn. However, it is very difficult to make clear the origin of the magnetic properties by the above factors because of the scarcity of kinds of the first elements in the already known Cl_b compound. Since the electronic structure of Rh bears a resemblance to Pd or Ni as the first element in other compounds of the Cl_b type, Rh was chosen in the present research of Rh–Mn–Sb alloys.

II. Experimental Procedure

The alloys were prepared from 99.99% Rh and Mn and Sb of the same purities as reported previously^{(4)~(6)}. For the specimen preparation, Rh and

Mn were weighed out in appropriate proportions. After vacuum sealing in a silica tube of 6 ~ 7 mm in inner diameter and 50 ~ 60 mm long, the powders were melted at 1200 ~ 1350°C for 1 hr with an electric furnace and then plunged into iced water. For further homogenization, the alloys were again reduced to powder, resealed in an evacuated silica tube and plunged into iced water. The alloys thus obtained were examined by means of X-ray diffraction, and the above-mentioned operation was repeated for sufficient homogenization. Finally, the alloys were reduced into a powdered or bulk state, homogenized at 500 ~ 1100°C for 15 ~ 200 hr and then quenched into water or cooled slowly at a rate of 50°C/hr. In the present investigation 42 specimens of different compositions were employed.

The X-ray analyses of the crystal structures, and the lattice constant and magnetic measurements were entirely the same as those described in previous papers^{(4)~(6)}.

III. Results and Discussion

1. Crystal structure

Crystal structure analyses of Rh–Mn–Sb alloys were performed on 42 kinds of the ternary alloys whose compositions are denoted by solid circles in Fig. 1. Figure 2 shows X-ray diffraction data on alloy No. 23 ($\text{Rh}_{1.00}\text{Mn}_{1.00}\text{Sb}_{1.00}$) as a representative alloy of stoichiometric composition and on alloys No. 30 ($\text{Rh}_{1.075}\text{Mn}_{0.85}\text{Sb}_{1.075}$), No. 14 ($\text{Rh}_{0.90}\text{Mn}_{1.20}\text{Sb}_{0.90}$) and No. 6 ($\text{Rh}_{0.75}\text{Mn}_{1.50}\text{Sb}_{0.75}$) in which the atomic ratios of Rh and Sb are equalized and the atomic ratio of Mn is variant. Figure 3 shows alloys No. 16 ($\text{Rh}_{0.90}\text{Mn}_{0.90}\text{Sb}_{1.20}$), No. 29 ($\text{Rh}_{1.10}\text{Mn}_{1.10}\text{Sb}_{0.80}$), No. 36 ($\text{Rh}_{1.275}\text{Mn}_{1.275}\text{Sb}_{0.45}$) and No. 39 ($\text{Rh}_{1.425}\text{Mn}_{1.425}\text{Sb}_{0.15}$) in which the atomic ratios of Rh

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Fig. 1 Compositions of alloys in the Rh-Mn-Sb system. (○: Solid solution of Cl_b type)

Fig. 2 X-ray diffraction pattern obtained with Cu- K_α radiation on Rh-Mn-Sb alloys cooled at a rate of 50°C/hr after heating at 800°C for 100 hr. (Weak lines shown by the arrow are obtained from monoclinic RhSb_2)

and Mn are equalized and that of Sb is variant, and Fig. 4 shows alloy No. 15 ($\text{Rh}_{0.90}\text{Mn}_{1.05}\text{Sb}_{1.05}$) and No. 31 ($\text{Rh}_{1.08}\text{Mn}_{0.96}\text{Sb}_{0.96}$) with equal atomic ratios of Mn and Sb and variant atomic ratios of Rh. These alloys were homogenized at 800°C for 100 hr and then slowly cooled at a rate of 50°C/hr prior to X-ray diffraction.

As shown in Fig. 2, alloy No. 23 with stoichiometric composition shows strong diffraction lines of the face-centered cubic lattice type and, in addition, there appear very weak diffraction lines of a RhSb_2 compound as indicated by arrows in the figure. Although these diffraction lines of the RhSb_2 compound do not appear in alloys No. 14 and No. 6 of higher Mn content, they can clearly be observed in alloy No. 30 of lower Mn content. As shown in Fig. 3, alloy No. 29 which is lower in Sb content than the stoichiometric composition exhibits only diffraction lines of the *fcc* lattice type. However, with further decrease in Sb content, the intensity of the (111) diffraction lines is

Fig. 3 X-ray diffraction pattern obtained with Cu- K_α radiation on Rh-Mn-Sb alloys cooled at a rate of 50°C/hr after heating at 800°C for 100 hr. (Weak lines shown by the arrow are obtained from monoclinic RhSb_2)

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greatly reduced in similar behavior to alloy No. 36 and disappears completely, replaced by the (100) diffraction lines of the B2 type. With increase in Sb content beyond that in alloy No. 23 of stoichiometric composition, the diffraction lines of the RhSb_2 compound are clearly observed. As indicated by Fig. 4, alloys No. 15 and No. 31 whose compositions are near the stoichiometric ratio with an identical ratio between Mn and Sb against a variance of the Rh atomic ratio exhibit diffraction lines of the RhSb_2 compound in addition to those of the *fcc* lattice type. Detailed X-ray analyses of the other alloys of nearly stoichiometric compositions in the range from room

Table 1 Lattice parameter and density of Rh-Mn-Sb alloy.

Alloy	Heat treatment	Lattice parameter (Å)	Density (g/cc)	
			Calculated	Measured
Rh _{0.90} Mn _{1.20} Sb _{0.90}	Cooled at a rate of 50°/hr after heating at 800°C/100 hr	6.145±0.001	7.673±0.004	7.70±0.03

temperature to about 800°C have not revealed any different diffraction lines from those mentioned above. Despite a thorough homogenizing treatment of the specimens as mentioned already, simple diffraction lines of the *fcc* lattice type have not been observed for the stoichiometric composition. According to the recent extensive studies, it has been established that compounds Mn₂Sb, Co₂MnSb and CuMnSb which have so far been considered as possessing simple integral atomic ratios are stable in cases where these compounds have atomic ratios of Mn_{1.77}Sn⁽⁹⁾, Co_{1.5}MnSb⁽¹⁰⁾ and CuMnSb_{1.03}⁽³⁾ respectively. Accordingly, it is not exceptional that the compounds in the Rh-Mn-Sb system whose compositions deviate from the stoichiometric ratio are stable.

In order to analyze the crystal structures of Rh-Mn-Sb alloys, results of X-ray diffraction lines for the Rh_{0.90}Mn_{1.20}Sb_{0.90} alloy have been examined. The diffraction lines of this alloy consists of the odd numbers of indices such as (111), (311), (331)... , the even numbers of $(h+k+l)/2 = 2n+1$ such as (200), (222), (420)... , and the even numbers of $(h+k+l)/2 = 2n$ such as (220), (400), (422)... , its crystal lattice type being face-centered cubic. Then, assuming that the crystal structure is of the Cl or Cl_b type, a unit cell of which contains 12 atoms, the density of the alloy was calculated from the lattice parameter obtained from the diffraction lines. Table 1 shows a comparison between the measured and calculated values of density, an excellent agreement between the two values is observed.

Assuming the crystal structure of this alloy to be the Cl_b type, the sites of Rh, Mn and Sb atoms will be 4a: (000, 0½½, ½2½, ½½0), 4b: (¼¼¼, ¼¼¾, ¾¼¼, ¾¾¼) and 4d: (¾¾¾, ¾¼¼, ¼¾¼, ¼¼¾), respectively. Then the square of the structure factor $|F|^2$ can be expressed as

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

in case h, k and l are all odd numbers. For even numbers of h, k and l and $(h+k+l)/2 = 2n+1$,

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

In case h, k and l are all even numbers and $(h+k+l)/2 = 2n$,

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

Here f are the atomic scattering factors. If this alloy is assumed to be of the Cl type, $|F|^2$ for the odd number of h, k and l becomes $16f_{\text{Rh}}^2$ which differs from the case of the Cl_b type.

Table 2 Comparisons of observed and calculated data of X-ray (Cu-Kα) diffraction lines of Rh_{0.90}Mn_{1.20}Sb_{0.90} slow-cooled from 800°C.

h k l	sin ² θ		I _(hkl) /I ₍₂₂₀₎ (%)		
	obs.	calc.	obs. (±3%)	calc.	
				Cl type	Cl _b type
(111)	0.047	0.047	50	36	48
(200)	0.063	0.063	10	9	9
(220)	0.126	0.126	100	100	100
(311)	0.173	0.173	24	17	23
(222)	0.189	0.189	3	2	2
(400)	0.252	0.252	18	16	16
(331)	0.299	0.299	9	7	9
(420)	0.314(Kα ₁) 0.316(Kα ₂)	0.314 0.316	3	3	3
(422)	0.377(Kα ₁) 0.379(Kα ₂)	0.377 0.379	33	33	33
(511, 333)	0.424(Kα ₁) 0.426(Kα ₂)	0.424 0.426	8	5	7
(440)	0.502(Kα ₁) 0.505(Kα ₂)	0.502 0.505	10	11	11
(531)	0.549(Kα ₁) 0.552(Kα ₂)	0.549 0.552	7	6	8
(600, 442)	0.564(Kα ₁) 0.567(Kα ₂)	0.564 0.567	1	1	1
(620)	0.627(Kα ₁) 0.631(Kα ₂)	0.627 0.631	17	18	18

Fig. 5 Cl_b-type crystal structure of RhMnSb compound.

Table 2 shows a comparison between the experimental and calculated values of diffraction line indices and the corresponding sin²θ and relative values of diffraction line intensity, $I_{(hkl)}/I_{(220)}$. The experimental values of sin²θ are in excellent agreement with the calculated values and the experimental values of $I_{(hkl)}/I_{(220)}$ for the Cl_b type shows a better agreement than those for the Cl type with the calculated values, indicating that this alloy has a crystal structure of the Cl_b type. Figure 5 shows a Cl_b type crystal structure of the ideal compound RhMnSb.

Figure 6 shows the composition dependence of lattice parameters for the ternary alloys in the com-

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Fig. 6 Lattice parameters of $Rh_{1+x/2}Mn_{1+x/2}Sb_{1-x}$ alloys.

Fig. 7 Lattice parameters of Cl_b type $Rh_{1-x/2}Mn_{1+x}Sb_{1-x/2}$ alloys.

position range from the compound $RhMn$ to the stoichiometric composition in the Rh-Mn-Sb system. The lattice parameter begins to increase rapidly by the addition of Sb to the $RhMn$ compound of the bcc type (B2) and the rate of increase decreases to within a range of 0.30 ~ 0.80 Sb where the diffraction line of the Cl_b type appears. With a further increase in Sb content, the lattice parameter decreases suddenly up to the atomic ratio of 0.85 and then becomes almost constant, revealing a mixed phase. Figure 7 shows the composition dependence of lattice parameters of the Cl_b type crystals with equal atomic ratios of Rh and Sb and variant atomic ratio of Mn. As shown in the figure, the lattice parameters of the Cl_b type crystals whose atomic ratio of Mn is higher than the stoichiometric composition are nearly constant up to the Mn atomic ratio of 1.16 at which a mixed phase of a Cl_b type alloy and the $RhSb_2$ compound is shown. However, with a further increase in Mn content, the mixed phase becomes a single phase and the lattice parameters increase linearly. Therefore, it can be predicted that Rh-Mn-Sb alloys have a very wide composition range in which the Cl_b type crystal structure is revealed. The lattice parameters of $Rh_{0.90}Mn_{1.20}Sb_{0.90}$ and $Rh_{1.10}Mn_{1.10}Sb_{0.80}$ alloys consisting of a single phase are 6.145 and 6.170 Å, respectively.

2. Magnetic properties

In order to obtain a better understanding of magnetic properties of Rh-Mn-Sb alloys of the Cl_b type subjected to slow cooling after heating at high temperature, experiments have been performed

Fig. 8 Temperature dependence of saturation magnetization of $Rh_{1+x/2}Mn_{1+x/2}Sb_{1-x}$ alloys cooled at a rate of 50°C/hr after heating at 800°C for 100 hr.

Fig. 9 Temperature dependence of saturation magnetization of $Rh_{1-x/2}Mn_{1+x}Sb_{1-x/2}$ alloys cooled at a rate of 50°C/hr after heating at 800°C for 100 hr.

on 14 kinds of the ternary alloys of different compositions. In these $Rh_{1+x/2}Mn_{1+x/2}Sb_{1-x}$ and $Rh_{1-x/2}Mn_{1+x}Sb_{1-x/2}$ alloys, the compositions are changed for the atomic ratio of Sb_{1-x} and Mn_{1+x} . The temperature dependence of saturation magnetization σ_s in both cases is shown in Figs. 8 and 9, respectively. The values of σ_s at the measuring temperatures are those obtained by the law of saturation approach.

As shown in Fig. 8, when the atomic ratios of Rh and Mn are equalized while changing the atomic ratio of Sb, σ_s at each temperature increases gradually with increase in Sb content and decreases after passing through a maximum. The decrease in σ_s seems to be attributable to the composition of the ternary alloys which consist of a ferromagnetic Cl_b type phase and

the nonmagnetic RhSb_2 compound. The value of $\sigma_{s,0}$ obtained by extrapolation to 0°K shows a maximum value of 75.0 emu/g for the $\text{Rh}_{1.10}\text{Mn}_{1.10}\text{Sb}_{0.80}$ alloy and 59.5 emu/g for the stoichiometric alloy. When the atomic ratios of Rh and Sb are equalized against a variant atomic ratio of Mn (Fig. 9), the alloys of a mixed phase with Mn atomic ratios of 1.05 and 1.16 exhibit a nearly equal value of $\sigma_{s,0}$ while the $\text{Rh}_{0.90}\text{Mn}_{1.20}\text{Sb}_{0.90}$ alloy of the single Cl_b type phase shows a maximum value of 79.5 emu/g and the value of $\sigma_{s,0}$ decreases gradually with further increase in Mn content.

Figures 10 and 11 show the Curie temperatures, T_c , for the alloys of the Cl_b type and near its composition and the composition dependence of the saturation magnetic moment per Mn atom, n_B , for solid solution alloys of the Cl_b type. As shown in Fig. 10, in the ternary alloys the atomic ratios of Rh and Mn are equalized and the atomic ratio of Sb is changed. In this case, with increase in Sb content, T_c of the alloys increases gradually and reaches a maximum value of

Fig. 10 Curie temperature and saturation magnetic moment of $\text{Rh}_{1+x/2}\text{Mn}_{1+x/2}\text{Sb}_{1-x}$ alloys.

Fig. 11 Curie temperature and saturation magnetic moment in $\text{Rh}_{1-x/2}\text{Mn}_{1+x}\text{Sb}_{1-x/2}$ alloys.

Fig. 12 Temperature dependence of magnetic susceptibility of the $\text{Rh}_{0.90}\text{Mn}_{1.20}\text{Sb}_{0.90}$ and $\text{Rh}_{1.10}\text{Mn}_{1.10}\text{Sb}_{0.80}$ alloys cooled at a rate of 50°C/hr after heating at 800°C for 100 hr.

350°C with the Sb atomic ratio of 0.80. Then the value decreases slightly and becomes constant. With increase in Sb content, n_B increases gradually and attains a maximum value of $3.29 \mu_B$ for the composition of $\text{Rh}_{1.10}\text{Mn}_{1.10}\text{Sb}_{0.80}$. When equalizing the atomic ratios of Rh and Sb and changing the atomic ratio of Mn, T_c remains nearly constant at Mn atomic ratios of $1.00 \sim 1.20$, but the value decreases gradually with further increase in atomic ratio of Mn (Fig. 11). With increasing Mn content, n_B of the alloys with the Cl_b type crystal structure decreases linearly, and that of the $\text{Rh}_{0.90}\text{Mn}_{1.20}\text{Sb}_{0.90}$ alloy near in composition to the stoichiometric ratio shows the highest value of 3.19. For the stoichiometric alloy which is assumed to consist of an ideal Cl_b type single phase, the value of n_B obtained by extrapolation is about $4.2 \mu_B$.

Figure 12 shows the temperature dependences of susceptibility χ_g and $1/\chi_g$ for the $\text{Rh}_{1.10}\text{Mn}_{1.10}\text{Sb}_{0.80}$ and $\text{Rh}_{0.90}\text{Mn}_{1.20}\text{Sb}_{0.90}$ alloys which consist of a single phase of Cl_b type and are nearest in composition to the stoichiometric composition. As is evident from this figure, $1/\chi_g$ of both alloys changes linearly with temperature and satisfies the Curie-Weiss law. The paramagnetic Curie temperatures of both alloys, θ_p , are 330 and 377°C , respectively, which are somewhat higher than the values of T_c , indicating the alloys to be ordinary ferromagnetic substances. The numbers of paramagnetic effective magnetons per Mn atom, P_{eff} , derived from a straight line in Fig. 12 for the two alloys are 3.47 and $3.48 \mu_B$, respectively.

IV. Conclusions

X-ray crystal structure analyses and magnetic measurements have been carried out for 42 kinds of Rh-Mn-Sb ternary alloys subjected to slow cooling after a thorough homogenizing treatment at high

temperature. The obtained results are summarized as follows:

(1) The $\text{Rh}_{0.90}\text{Mn}_{1.20}\text{Sb}_{0.90}$ alloy of nearly stoichiometric composition possesses basically a crystal structure of the Cl_b type, in which the sites of Rh, Mn and Sb atoms are $(000, 0\frac{1}{2}\frac{1}{2}, \frac{1}{2}0\frac{1}{2}, \frac{1}{2}\frac{1}{2}0)$, $(\frac{1}{4}\frac{1}{4}\frac{1}{4}, \frac{1}{4}\frac{3}{4}\frac{3}{4}, \frac{3}{4}\frac{1}{4}\frac{3}{4}, \frac{3}{4}\frac{3}{4}\frac{1}{4})$, $(\frac{3}{4}\frac{3}{4}\frac{3}{4}, \frac{3}{4}\frac{1}{4}\frac{1}{4}, \frac{1}{4}\frac{3}{4}\frac{1}{4}, \frac{1}{4}\frac{1}{4}\frac{3}{4})$, respectively.

(2) The lattice parameters of the $\text{Rh}_{0.90}\text{Mn}_{1.20}\text{Sb}_{0.90}$ and $\text{Rh}_{1.10}\text{Mn}_{1.10}\text{Sb}_{0.80}$ alloys, nearest to the stoichiometric composition, show nearly equal values of 6.145 and 6.170 Å, respectively. The $\text{Rh}_{1.00}\text{Mn}_{1.00}\text{Sb}_{1.00}$ alloy of stoichiometric composition consists of a phase of the Cl_b type crystal structure and a very small amount of the RhSb_2 compound.

(3) The saturation magnetic moment per Mn atom, n_B , and the Curie temperature, T_c , for the $\text{Rh}_{0.90}\text{Mn}_{1.20}\text{Sb}_{0.90}$ alloy of the Cl_b type are 3.19 μ_B and 325°K respectively. n_B and T_c for the $\text{Rh}_{1.10}\text{Mn}_{1.10}\text{Sb}_{0.80}$ alloy of the Cl_b type are 3.29 μ_B and 350°K respectively.

(4) The lattice parameters, Curie temperatures and saturation magnetic moments show a gradual increase with increasing ratio of Sb in $\text{Rh}_{1+x/2}\text{Mn}_{1+x/2}\text{Sb}_{1-x}$ alloys. In the case of $\text{Rh}_{1-x/2}\text{Mn}_{1+x}\text{Sb}_{1-x/2}$ alloys, the lattice parameters increase gradually with increasing ratio of Mn, but T_c and n_B decrease. These magnetic values become maximum near the stoichiometric composition.