Crystal Structures and Magnetic Properties of the System Rh$_{1}$Mn$_{1-x}$Sb$_{x}$

By Hakaru Masumoto** and Kiyoshi Watanabe**

Crystal structures and magnetic properties of Rh-Mn-Sb alloys have been investigated by means of X-ray diffraction and magnetic measurements. It has been found that alloys in the composition range of Rh$_{1.00}$Mn$_{0.66}$Sb$_{0.34}$—Rh$_{1.00}$Mn$_{0.55}$Sb$_{0.45}$ are a solid solution of the face-centered tetragonal L1$_0$-type with lattice parameters of 4.200—4.182 Å and axial ratios of 0.806—0.829. The typical Rh$_{1.00}$Mn$_{0.55}$Sb$_{0.45}$ alloy has a saturation magnetization of 52.3 emu/g at absolute zero, a magnetic moment of 3.20 µB per Mn atom, a Curie point of 330°C and a paramagnetic Curie point of 286°C. The observed relationship between reciprocal susceptibility and temperature indicates weak ferrimagnetic behavior of this alloy.

(Received May 23, 1975)

I. Introduction

Previous work on the crystal structures and magnetic properties of the intermetallic compounds in a series of Rh–Mn–Sb alloys(1) has shown that Cl$_5$-type compounds are formed near the composition Rh$_1$Mn$_1$Sb$_1$, whereas at higher Rh concentrations the alloys indicate the X-ray diffraction patterns indicative of the presence of a new crystal structure type in addition to the Cl$_5$-type. A feature of interest also is the strong magnetization of these alloys.

The present work is concerned with the experimental results on alloys of the new crystal structure type.

II. Experimental Procedure

The alloy specimens were prepared from 99.99% Rh and Mn and Sb of the same purities as reported previously(1). Carefully weighed quantities of Rh, Mn and Sb were sealed in evacuated silica tubes 6—7 mm in inner diameter and 50—70 mm long, melted at 1150—1350°C for 1 hr in an electric furnace and then quenched in iced water. For the purpose of further homogenization, the alloys were pulverized, resealed in evacuated silica tubes and quenched in iced water again. The alloys thus obtained were examined by means of X-ray diffraction, and the above-mentioned operation was repeated until sufficient homogenization was realized. Finally, the alloys were prepared in the form of powder, bulk matter or rods, then homogenized at 700—1000°C for 40—100 hr and cooled slowly at a rate of 100°C/hr.

The X-ray analysis of the crystal structures, and the lattice constant and magnetic measurements were entirely the same as described in a previous paper(1).

III. Results and Discussion

1. Crystal structure

X-ray diffraction studies on crystal structures of Rh–Mn–Sb alloys were performed using 29 alloys whose compositions are shown in Fig. 1. Figure 2 shows the diffraction patterns of the typical alloys Rh$_{1.00}$Mn$_{0.30}$Sb$_{0.50}$ (No. 19), Rh$_{1.00}$Mn$_{0.55}$Sb$_{0.45}$ (No. 18), Rh$_{1.00}$Mn$_{0.66}$ Sb$_{0.34}$ (No. 13) and Rh$_{1.00}$Mn$_{0.70}$Sb$_{0.30}$ (No. 11) which were held at 1000°C for 98 hr and then slowly cooled. These alloys have compositions indicated by the open circles in the figure. Alloys No. 18 and No. 13 exhibit a single phase of the fct lattice type, while alloy No. 19 with a higher Sb concentration than alloy No. 18 shows the fct

* This paper was presented at the Autumn Meeting of the Japan Institute of Metals, October, 1971, Kanazawa, Japan. Published originally in Japanese in J. Japan Inst. Metals, 39 (1975), 1065. The 85th report from the Research Institute of Electric and Magnetic Alloys.

** The Research Institute of Electric and Magnetic Alloys, 2, Yagiyama-Minami, Sendai 982, Japan.
phase together with a weak second phase corresponding to the RhSb compound\(^2\). This second phase cannot be removed by any heat treatment. Alloy No. 11 exhibits fairly strong diffraction lines of the B2-type that correspond to those of the RhMn compound\(^{3-5}\). Next, the crystal structure in alloy No. 18 with the typical fct single phase has been analyzed. Table 1 shows a comparison between the calculated and experimental values of the interplanar spacing \(d\) and the observed intensity of each diffraction line. There is excellent agreement between the calculated and observed values of the interplanar spacings. Assuming that the crystal structure of the alloy is of the fct \(L_{10}\) type (CuAu type) and that the Rh atom and the Mn and Sb atoms occupy the sites, \((000, 1/2, 1/2, 0)\) and \((01/2, 1, 01/2)\), respectively, the crystal structure factor \(F\) of this alloy can be given as follows:

\[
F = \begin{cases} 
2f_{Rh} + f_{Mn + Sb}/2 & \text{when } h+K \text{ is even with } \{h=2n, l=2n+1\}
\end{cases}
\]

In the case of \(h=2n\) and \(l=2n+1\):

\[
F = 2f_{Rh} - f_{(Mn+Sb)/2}. \]

Here \(f\) is the atomic scattering factor. The integral intensity of each diffraction line calculated from the \(F\), the results are in excellent agreement with the observed intensity. Therefore, the crystal structure of this alloy is determined to be of the fct \(L_{10}\)-lattice type as shown in Fig. 3.

Figure 4 shows the lattice parameter for \(\text{Rh}_{1-x}\text{Mn}_x\text{Sb}\) alloys where \(x\) is varied from 0.3 to 0.6. As can be seen from the figure, the crystal
Crystal Structures and Magnetic Properties of the System Rh$_1$Mn$_{1-x}$Sb$_x$

Fig. 3 Crystal structure of L1$_0$-type. Structures of alloys with $x = 0.30 \sim 0.33$ show the coexistence of the two phases of the L1$_0$- and B2-types. The lattice parameter of the L1$_0$-type is $a = 4.200$ Å, which is nearly constant against composition. On the other hand, higher Sb-concentration alloys with $x = 0.50 \sim 0.60$ show the coexistence of the two phases of the L1$_0$- and B31-types, and the lattice parameter of L1$_0$-type is almost constant at $a = 4.182$ Å. The crystal structures of intermediate alloys with $x = 0.34 \sim 0.45$ alloys out of the range of coexistence of the two phases are in the single phase state of the L1$_0$-type. The values of the lattice parameter $a$ in these alloys decreased linearly with increase in $x$, and both the lattice parameter $c$ and the atomic ratio $c/a$ increased appreciably with increase in $x$. The single-phase alloy No. 18 of the L1$_0$-type which is nearest to the stoichiometric composition has $a = 4.182$ Å, $c = 3.467$ Å, and $a, c/a$ ratio of 0.829.

Figure 1 shows the relation between the alloy phase and composition, where ○ indicates the single phase of the L1$_0$-type, ● the coexisting state of the L1$_0$-type with an additional crystal structure type phase, and □ the single phase of the B2-type.

2. Magnetic properties

Figure 5 shows the relation between the saturation magnetization $\sigma_s$ in a field of about 10.6 kOe and the temperature $T$ for seven Rh$_1$Mn$_{1-x}$Sb$_x$ alloys cooled at a rate of 50°C/hr after heating at 1000°C for 98 hr. The saturation magnetization of these alloys is a low as about 3 emu/g for the composition at $x = 0.34$, whereas the value of $\sigma_s$ for the alloys with the compositions $x = 0.36$ increases to about 10 emu/g at low temperature. Further, the alloy with the composition $x = 0.37$ increases $\sigma_s$ up to about 27 emu/g, and all the alloys with more than $x = 0.40$ have constant $\sigma_s$ values of about 50 emu/g at low temperature. The Curie points $T_c$ in these alloys increase gradually with increase in $x$. The alloy with $x = 0.45$ which is in the single phase of the L1$_4$-type and is nearest to the stoichiometric composition shows the highest temperature of 330°C.

Figure 6 shows the composition dependence of the Curie point for the ten alloys containing those
in the two-phase state (a) and of the magnetic moment $n_B$ per Mn atom, obtained by extrapolating the saturation magnetization to 0°K, for the alloys in the single phase of the L1$_0$-type (b). As regards the relation between the Curie points and composition in (a), the Curie points of the alloys with the compositions $x = 0.30$ and $0.33$ are about 210°K and those of the alloys with $x = 0.50$ and $0.45$ have the temperature of 330°K. Next, the magnetic moments of the alloys with $x = 0.36$ are as low as $1.4\,\mu_B$, but a large increase in a moment with increase in Sb concentration is observed indicating the highest value of $3.20\,\mu_B$ in alloy No. 18 of the nearest stoichiometric composition. Since Mn and Sb atoms in alloy No. 18 of the L1$_0$-type are arranged in a disorder state at the sites $0\frac{1}{2}\frac{1}{2}$ and $\frac{1}{2}0\frac{1}{2}$, the Mn–Mn pair is considered to possess three different Mn–Mn pairs as shown in Fig. 7. However, according to the studies on ferromagnetic and antiferromagnetic Mn base compounds, flourite-type compounds or Heusler-type compounds, the interatomic distances of these ferromagnetic and antiferromagnetic Mn–Mn pairs are experimentally assigned generally to be of the order of 2.89 and 4.18 Å as shown in Fig. 7. Consequently, if the two kinds of the Mn–Mn pairs in the alloys of the L1$_0$-type have different magnetic moments and the directions of the spins in the Mn atom are antiparallel to each other, the alloys exhibit ferrimagnetic properties. Further, if one of the two Mn–Mn pairs is non-magnetic, these alloys appear to have ferromagnetic properties due to the spin of another pair.

In Fig. 8 is shown the relation between the magnetic susceptibility $\chi_g$ and the reciprocal susceptibility $1/\chi_g$ above the Curie temperature, and temperature for alloy No. 18 which is a representative fct alloy in the system Rh$_1$–Mn$_{1-x}$Sb$_x$. As can be seen from the figure, the values of $1/\chi_g$ between 550 and 800°C are varied linearly with temperature obeying a Curie-Weiss law, but at lower temperatures it decreases along the concave curve against transverse axis with decreasing temperature. Therefore, the paramagnetic Curie point $\theta_p$ of this alloy show

![Fig. 6 Curie points and magnetic moments in Rh$_{1.00}$Mn$_{0.55}$Sb$_{0.45}$ alloys.](image)

![Fig. 7 Distances of pair of Mn–Mn in L1$_0$-type alloy Rh$_{1.00}$Mn$_{0.55}$Sb$_{0.45}$.](image)

![Fig. 8 Temperature dependence of magnetic susceptibility and reciprocal magnetic susceptibility of the alloy Rh$_{1.00}$Mn$_{0.55}$Sb$_{0.45}$.](image)
the low 286 ± 3°K, rather than the Curie point $T_c = 330°K$. This result shows that this alloy may have some ferrimagnetic properties.

**IV. Conclusions**

X-ray diffraction and magnetic measurements have been performed on 29 Rh–Mn–Sb ternary alloys after sufficient homogenizing treatment at high temperatures. The obtained results are summarized as follows.

1. The Rh$_{1.00}$Mn$_{0.55}$Sb$_{0.45}$ alloy have the crystal structure of the face-centered tetragonal L1$_0$-type, in which the Rh sites are (000, 1/2 1/2 0) and the Mn and Sb sites are (0 1/2 1/2, 1/2 0 1/2). This alloy has a lattice parameter of 4.182 Å, its axial ratio $c/a$ being 0.829.

2. The lattice parameters of Rh$_1$Mn$_{1-x}$Sb$_x$ with $x = 0.34$ to $x = 0.45$ in the single phase of the solid solution of the L1$_0$-type range from 4.200 to 4.182 Å. In the lower composition region $x = 0.34$ the alloys show the coexistence of the two phases of the L1$_0$-type and the B2-type (RhMn), whereas in the higher composition region than $x = 0.45$ the alloys show the coexistence of the two phases of the L1$_0$-type and B31-type (RhSb).

3. The saturation magnetic moment per Mn atom and the Curie point of the Rh$_{1.00}$Mn$_{0.55}$Sb$_{0.45}$ alloy are found to be 3.2 $\mu_B$ and 330°K, respectively, this alloy has been assumed to have some ferrimagnetic properties from the relation between $1/\chi_g$ and temperature.

**Acknowledgment**

The authors wish to thank Mr. Y. Kobayashi, a technical staff at our Institute, for his cooperation in making the alloys.

**REFERENCES**