New magnetic compounds with Heusler and Heusler-related structures

James C. Suits

IBM Research Laboratory, San Jose, California 95193

Magnetic and structural properties are presented for new ferromagnetic compounds of the form Rh_2MnX where X is Al, Ga, In, Tl, Sn, Pb, and Sb. The exchange is described in terms of competing ferromagnetic Mn-Rh-Mn interactions and antiferromagnetic Mn-Mn interactions.

INTRODUCTION

A number of new magnetic compounds and alloys have been originated from the Mn-Bi-Rh ternary system. Small amounts of Rh in the compound MnBi were reported earlier to be effective in stabilizing the high-temperature phase of MnBi and thus to have application to optically address-able memory.[1] A new group of ferromagnetic compounds of the form $Mn_5Rh_2Bi_4$ with a new crys-tal structure was reported to exist in the central region of this ternary[2]; detailed calculations of the magnetic properties were made by Goodenough.[3]

Further exploration of this ternary system, using magnetic separation as a tool for isolating magnetic compositions, revealed that $Mn_{0.8}Bi_{0.2}Rh$ was a single-phase ferromagnetic compound.[4] The structure of this compound is CsCl with $Mn_{0.8}Bi_{0.2}$ on one simple cubic sublattice and Rh on the other sublattice. This structure is that of the well-known compound MnRh where the Bi par-tially substitutes on the Mn sublattice. MnRh is antiferromagnetic,[4] whereas addition of the Bi in-duces ferromagnetism.

The maximum solubility of Bi in the MnRh lat-tice is $Mn_{0.8}Bi_{0.2}Rh$. This formula can also be written $Rh_2Mn_{1.6}Bi_{0.4}$. Both the structure and the composition of this Bi compound bring to mind the Heusler compounds. If another atom could be found with greater solubility than Bi in this lattice then perhaps new Heusler compounds could be generated of the form Rh_2TX, where T is a $3d$ transition-metal atom and X is a group-B atom. One example of this which has already been re-ported in Rh_2MnGe.[5]

We have found and reported earlier that letting X = Sn allows variation of the T atom across the entire $3d$ series including Cu. Some of these Rh_2-TSn compounds have the Heusler structure and some exhibit a curious tetragonal modification of the Heusler structure.[6] In the present paper we will describe the magnetic and crystallographic properties of the Heusler and Heusler-related compounds generated by variation of atom X in the manganese compound series Rh_2MnX.

SAMPLE PREPARATION AND STRUCTURE

The compounds made were of the formula Rh_2MnX, where X is a group-IIIB, IVB, VB, or VIB element. The compounds were made by mixing together powders of the elements, sealing this mix-ture in evacuated quartz ampoules and annealing at 250 °C for 7 h, followed by 700 °C for 6 days. The samples were then pulverized and reannealed in vacuum for 5 days at 700 °C. The upper part of Fig. 1 shows an experimental x-ray diffraction pattern taken on a powder sample of Rh_2MnPb (X = Pb). A calculated pattern is shown in the lower part of Fig. 1. This pattern was calculated for the Heusler structure with the aid of the Smith program.[7]

The good agreement between these patterns shows the sample to be of single phase quality and also shows that the Heusler structure is a good representation of the actual structure.

Figure 2 shows the Heusler structure for Rh_2MnX. The Rh atoms occupy the corners of a sim-ple cubic sublattice. The atoms of the second simple cubic sublattice occupy the body-center positions of the first sublattice. In the fully or-
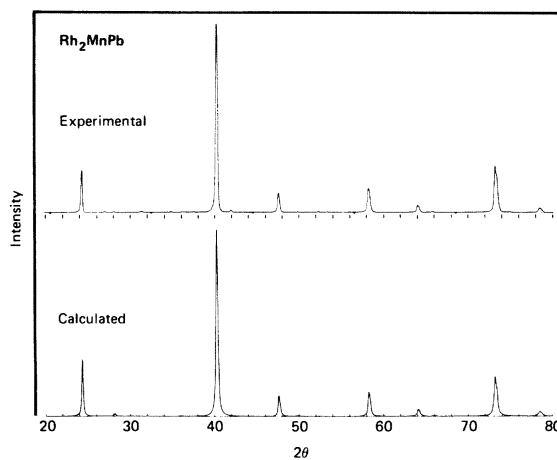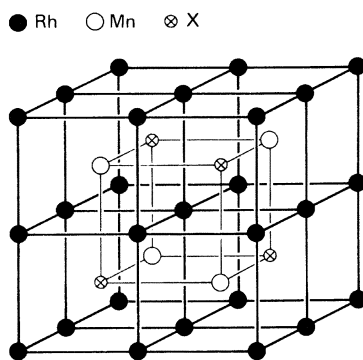

FIG. 1. Experimental and calculated x-ray diffrac-tometer pattern for a powder sample of Rh_2MnPb.

FIG. 2. Fully ordered Heusler structure, Rh_2TX.

dered Heusler structure the second sublattice is occupied by Mn and X atoms (e.g., X = Pb) ordered as shown.

Three variations of the fully ordered Heusler structure have been observed. The first, already mentioned, is with Mn and Bi on the second sub-lattice as in $Mn_{0.8}Bi_{0.2}Rh$. Another variation is where the Mn and X atoms of the second sublattice are completely disordered on this second sublat-tice (e.g., Rh_2MnAl). A third variation is where the unit cell of Fig. 2 is stretched along a cube edge, say the c direction, to produce a unit cell which is tetragonal.[6] The cell shrinks along the a and b directions to maintain a nearly constant volume. The tetragonal distortion is large $(c/a \sim 1.2)$. Rh_2MnSb is the only known example of this structure among the Mn compounds but the structure is seen often when Mn is replaced by other $3d$ transition metal elements.[6]

MAGNETIC MEASUREMENTS

Magnetization measurements taken at 4.2 °K on powder samples are shown in Fig. 3. These data were taken with a vibrating sample magnetometer, using a superconducting solenoid with a maximum field of about 70 kOe. In the compounds shown in Fig. 3, X belongs to group IIIB (Al, Ga, In, Tl) or group IVB (Pb, Sn). Not only is the magnetiza-tion lower for the group-IIIB compounds, but the approach to saturation is more gradual. The group-IIIB compounds are not really saturated even at 65 kOe.

Figure 4 shows inverse susceptibility versus temperature data taken on the same samples. These data are taken also with a vibrating-sample magnetometer but the field is provided by a 12-in. electromagnet. The system calibrations were checked by making measurements of the suscep-tibility and Curie temperature of pure nickel. The paramagnetic Curie temperatures Θ given by the horizontal axis intercepts in Fig. 4 are much low-
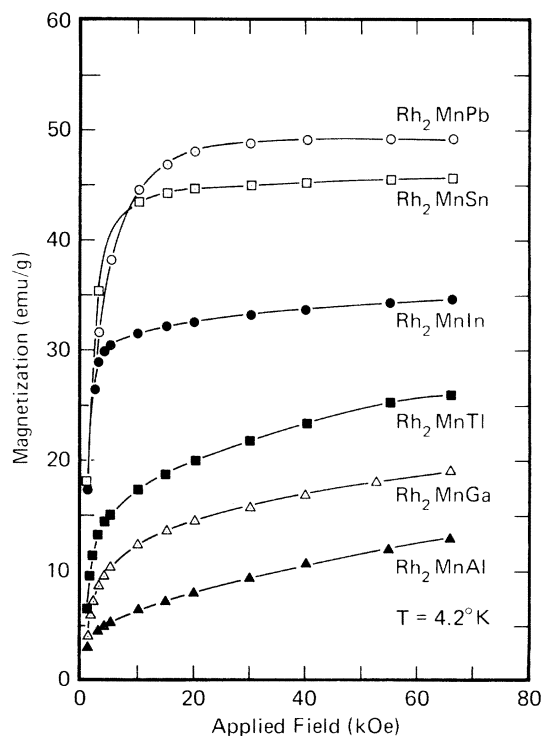
FIG. 3. Magnetization vs applied magnetic field at 4.2 °K for Rh_2MnX compounds.

er for the group IIIB compounds. The Rh_2MnAl compound shows significant curvature in its $1/\chi$-T curve.

Table I gives crystallographic data and Curie temperatures for the Rh_2MnX compounds. For the fully ordered Heusler structure the lattice con-stant a is given, whereas for the disordered Heus-ler structure $B2$, the double lattice constant is given to facilitate direct comparison with the $L2_1$ compounds. The paramagnetic Curie tempera-ture Θ was taken from $1/\chi$-T plots, and the fer-romagnetic Curie temperature T_C was measured as the temperature of the abrupt decrease in mag-netization with increasing temperature while the sample is maintained in a small constant field. Data shown for X = Bi and Te are actually for the compositions $Rh_2Mn_{1.6}Bi_{0.4}$ and $Rh_2Mn_{1.6}Te_{0.4}$.

Table II gives the results of magnetization mea-surements on the Rh_2MnX compounds. The mo-ment data are in terms of a formula unit rather than per Mn atom, since some moment will probably reside on the Rh atoms as in the case of FeRh. The determination of the Mn moment must await neutron diffraction measurements.

DISCUSSION

The data on X = Bi and X = Te (Table I) were re-ported earlier[4] and are included for completeness.
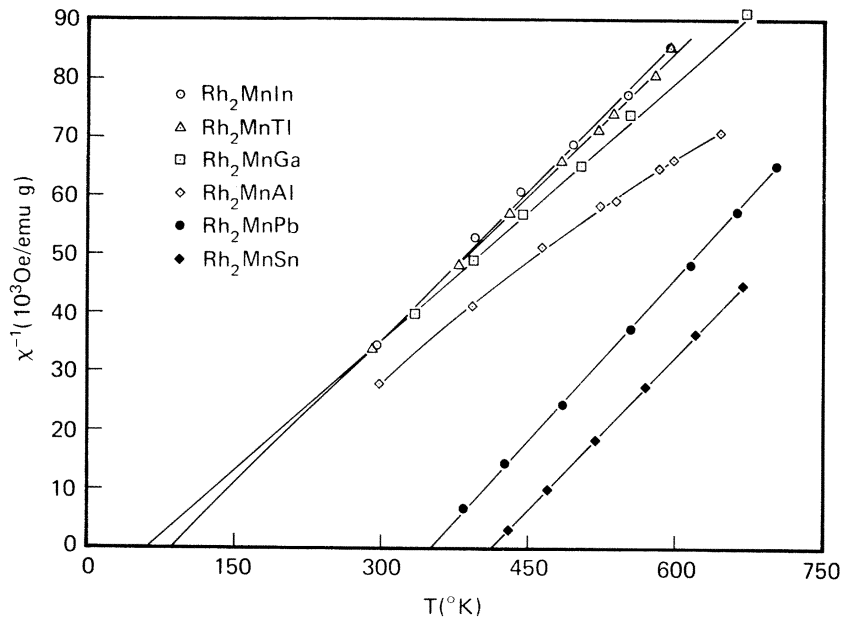
FIG. 4. Inverse susceptibility vs temperature for Rh_2MnX compounds.

Rh_2MnGe reported earlier by Hames and Crangle[5] and our data (Tables I and II) are in substantial agreement. The remaining compounds are believed to be reported here for the first time. For $X =$ Sb the structure is the same tetragonal modification of the fully ordered Heusler structure exhibited by and reported earlier for some of the Rh_2TSn compounds.[6] Table I shows that for X in group

IVB (Rh_2MnPb, Rh_2MnSn, and Rh_2MnGe) the structure is the fully ordered Heusler structure $L2_1$ (Figure 2), whereas for X in group $IIIB$ (Rh_2MnTl, Rh_2MnIn, Rh_2MnGa, and Rh_2MnAl) the structure is the disordered Heusler structure $B2$ where the Mn and X atoms are disordered. The driving force for ordering in this system is a strong function of the valence of element X. The

TABLE I. Crystal structure and Curie temperature for Rh_2MnX compounds.

$IIIB$ (s^2p)	IVB (s^2p^2)	VB (s^2p^3)	VIB (s^2p^4)
Al $B2$ $2a = 6.005$ Å $\Theta =$ nonlinear $T_C = 85-105$ °K	Si multiphase	P	S
Ga $B2$ $2a = 6.056$ Å $\Theta = 60$ °K $T_C = 75-85$ °K	Ge $L2_1$ $a = 6.030$ Å $\Theta = 460$ °K $T_C = 450$ °K	As multiphase	Se
In $B2$ $2a = 6.287$ Å $\Theta = 81$ °K $T_C = 100-110$ °K	Sn $L2_1$ $a = 6.252$ Å $\Theta = 413$ °K $T_C = 412$ °K	Sb tetragonal (new) $a = 5.898$ Å $c = 6.987$ Å $\Theta = 312$ °K $T_C = 304$ °K	Te limited solubility $a = 6.184$ Å $\Theta = 150$ °K $T_C = -$
Tl $B2$ $2a = 6.324$ Å $\Theta = 90$ °K $T_C = -$	Pb $L2_1$ $a = 6.332$ Å $\Theta = 348$ °K $T_C = 338$ °K	Bi limited solubility $a = 6.220$ Å $\Theta = 185$ °K $T_C = -$	Po

TABLE II. Magnetization data for Rh_2MnX compounds. p is the effective moment per formula unit calculated from the slope of $1/\chi$ vs T; μ_1 is the moment calculated from $p = 2[\frac{1}{2}\mu_1 + (1 + \frac{1}{2}\mu_1]^{1/2}$; σ is the magnetization; H_c is the coercive force; and μ is the moment per formula unit calculated from σ.

X	Al	Ga	In	Tl	Ge	Sn	Pb
$p\,(\mu_B)$	~4.1	4.23	4.28	4.75	4.64	4.19	4.49
$\mu_1\,(\mu_B)$	~3.3	3.35	3.40	3.86	3.75	3.30	3.60
σ(emu/g), 5 °K, 6 kOe	13.1 [a]	19.8 [a]	34.5 [a]	26.6	77.5	45.6	49.2
$\mu\,(\mu_B)$, 5 °K, 66 kOe	>0.7	>1.2	>2.3	>2.2	4.62	3.10	4.12
σ(emu/g), 300 °K, 19 kOe	•••	•••	•••	•••	64.2	33.6	28.2
H_c(Oe), 300 °K	•••	•••	•••	•••	70	38	•••

[a]Not saturated.

ordering is not a function of lattice parameter since the lattice constants shown in Table I overlap between the X group-IIIB and X group-IVB columns. Therefore we infer that the valence of element X influences the atomic ordering primarily by variation of electron concentration. The ordering does not depend much on cooling rate since X group-IIIB samples were very slowly cooled without inducing $L2_1$ order, and X group-IVB samples were quenched without inducing $B2$-type disorder.

Also a strong function of the valence of element X are the magnetic properties. For X in group IVB the compounds are all ferromagnetic with relatively high Curie temperatures. The Curie temperatures decrease with increasing lattice constant (Table I). For X in group IIIB the Curie temperatures are a factor of 4 to 5 smaller, and the Curie temperatures increase with increasing lattice constant.

It is believed that the principal exchange interaction in these compounds is a ferromagnetic Mn-Rh-Mn exchange. A second exchange mechansim which may occur is an antiferromagnetic Mn-Mn exchange between nearest-neighbor Mn. For X in group IVB there are no nearest-neighbor Mn and the compounds exhibit a high Curie temperature and rapid magnetic saturation (Fig. 3). For X in group IIIB there are many antiferromagnetic Mn-Mn interactions present due to atomic disorder and therefore the Curie temperature is reduced. This may explain the slow approach to saturation of the X group-IIIB compounds.

The Mn-Mn exchange will fall off more rapidly with distance than the Mn-Rh-Mn exchange due to the larger d orbitals of the Rh. This causes the Curie temperature to increase with increasing separation for X in group IIIB (rapid reduction

in Mn-Mn exchange) and to decrease with increasing distance for X in group IVB (slow reduction in Mn-Rh-Mn exchange).

One consequence of this model is that the magnetic moment at low temperatures should be low for the X group-IIIB compounds due to the presence of antiparallel spins, and Fig. 3 shows that this is the case. For the X group-IVB compounds the low-temperature moments are comparable to the moments calculated from high-temperature susceptibility.

CONCLUSION

A number of new magnetic compounds have been found. These compounds have the formula Rh_2MnX where X = Al, Ga, In, Tl, Sn, Pb, and Sb. For X in group IVB the compounds are ferromagnetic with Curie temperatures above room temperature and exhibit large magnetic moments at low temperature and large effective moments above the Curie temperature. For X in group IIIB the compounds predominantly are ferromagnetic with low Curie temperatures and low moments at low temperature. The difference in atomic order between X group-IIIB and X group-IVB compounds is attributed to the variation of electron concentration by atom X, and the difference in magnetic behavior between X group IIIB and X group-IVB compounds is ascribed to the presence of antiferromagnetic Mn-Mn exchange interactions due to variation of this atomic order.

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