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Ferromagnetism in Bi- and Te-substituted MnRh

Abstract: A series of experiments shows that substitution of Bi into antiferromagnetic MnRh causes this alloy to become ferromagnetic. The Curie temperature of $(Mn_{0.8}Bi_{0.2})$ Rh is 185°K and the moment is $3.5\mu_B$ per formula unit. Substitution of Te instead of Bi gives similar results. This effect is consistent with a model of competitive ferromagnetic and antiferromagnetic exchange in MnRh-type compounds.

Above 170 K MnRh is an ordered alloy with the B2 (CsCl) crystal structure [1]. The susceptibility obeys a Curie-Weiss relation, $\chi^{-1} = C^{-1}(T - \theta)$ where $\theta = -260$ K [2], indicating antiferromagnetic behavior. (Below 170 K MnRh transforms to a tetragonal CuAu structure [2].) This note reports that Bi or Te may be substituted for Mn in the MnRh lattice, and that this substitution induces ferromagnetism. This effect suggests the presence of ferromagnetic and antiferromagnetic exchange of similar magnitude in MnRh.

Samples were prepared by mixing Mn, Rh, and Bi (or Te) powders, sealing them in evacuated quartz tubes, heating to 1323 K for 30 minutes, and annealing at 673 K for nine days. The following series was made: $Mn_{1-x}Bi_x$-Rh, where $x = 0.1$, 0.2, 0.3, and 0.4. These compositions are starting compositions. For $x = 0.1$ and 0.2, x-ray diffraction showed single-phase material with the B2 structure. The lines were broad for $x = 0.1$ (full width at half maximum of the (220) line: $\Delta 2\theta = 0.8°$), and relatively sharp for $x = 0.2$ ($\Delta 2\theta = 0.3°$). For higher Bi content, RhBi was observed as a second phase, showing that the solubility limit had been exceeded. For all samples a few percent of MnO is present. For $x = 0.2$, the lattice constant a is 3.110 Å (for MnRh, $a = 3.045$ Å) [1].

Figure 1 shows the results of measurements of magnetization and susceptibility for $Mn_{0.8}Bi_{0.2}Rh$ and $Mn_{0.8}Te_{0.2}Rh$. For both materials the field dependence of the magnetization at 4.2 K is characteristic of a ferromagnet rather than an antiferromagnet. For $Mn_{0.8}Bi_{0.2}Rh$ the reciprocal susceptibility shows a linear relation with temperature with a paramagnetic Curie temperature $\theta = 185$ K and a Curie-Weiss constant $C_{mol} = 3.85$ cm^3 deg/mole. The effective moment per Mn atom calculated from C_{mol}, assuming no moment on the Rh, is $4.39\mu_B$, which corresponds to a spin-only moment of $2S = 3.5\mu_B$. The low temperature moment at 4.2 K and 66 kOe (5.5×10^6 A/m) (Fig. 1b) is $3.1\mu_B$ per Mn atom (again assuming no moment on the Rh).

Substitution of Te instead of Bi into MnRh produces very similar results. The solubility limit is about the same ($0.2 \lesssim x < 0.3$). The reciprocal susceptibility gives the paramagnetic Curie temperature as 150 K, and the Curie constant as $C_{mol} = 3.62$ cm^{3}deg/mole. The effective moment per Mn atom calculated from C_{mol}, assuming no moment on the Rh, is $4.25\mu_B$, which corresponds to a spin-only moment of $2S = 3.4\mu_B$. The low temperature moment at 4.2°K and 5.25×10^4A/m (Fig. 1b) is $3.7\mu_B$. Thus, for both materials the moments calculated from high temperature susceptibility are in reasonable agreement with the moments measured at 4.2 K. These moments are also in approximate agreement with the moment of MnRh (the effective moment of MnRh per Mn atom calculated from C_{mol}, assuming no moment on the Rh, is $4.74\mu_B$) [2].

To interpret the appearance of ferromagnetism with Bi addition, we first consider the x-ray diffraction line intensities. In the ordered B2 structure the (100) line intensity is due to 180° out-of-phase scattering from the 0, 0.0 and ½,½,½ atom positions. Because the atomic scattering factor of Mn is smaller than Rh, the (100) x-ray intensity in MnRh is predominantly due to Rh. Addition of Bi to the Mn sublattice will decrease the (100) intensity and addition of Bi to the Rh sublattice will increase the (100) intensity. Table 1 shows experimental and calculated (100) (peak) intensities relative to the (200) line intensity. The calculated values were determined with the aid of the Smith program [3].

Table 1 indicates that Bi is going principally on the Mn rather than the Rh sublattice. This is supported by the chemistry of the system: experimentally, $(Mn_{0.8}Bi_{0.2})Rh$ is single phase with the B2 structure, whereas $Mn(Rh_{0.8}Bi_{0.2})$ does not give the B2 structure but instead consists of two phases – $Mn_5Rh_2Bi_4$ [4] and a second unidentified phase. This result is somewhat surprising since Bi is a large atom ($r = 1.70$ for CN12), and it is substituting into the lattice for the smaller of the two atoms ($r = 1.26$ Å for Mn and 1.34 Å for Rh). However, comparison of the melting points of MnBi (718 K) and RhBi (1270 K) suggests that Bi-Mn bonding is considerably weaker than Bi-Rh bonding, and

Table 1 Ratio of (100) to (200) x-ray line intensities

Calculated	
MnRh	1.20
$(Mn_{0.8}Bi_{0.2})Rh$	0.10
$Mn(Rh_{0.8}Bi_{0.2})$	1.80
Experimental	
$(Mn_{0.8}Bi_{0.2})Rh$	0.30

therefore it is reasonable that Bi would prefer Rh nearest neighbors, i.e., Mn sites.

In MnRh, nearest-neighbor Mn atoms are separated along a ⟨100⟩ direction by 3.04 Å. Next-nearest-neighbor Mn atoms are separated along a ⟨110⟩ direction by 4.4 Å and can interact via intermediate Rh atoms. It is suggested that the Mn-Mn nearest-neighbor exchange is antiferromagnetic via e_g-e_g $3d$ orbital overlap [5], and the Mn-Rh-Mn next-nearest-neighbor superexchange is ferromagnetic. The result is a competition between ferromagnetic and antiferromagnetic exchanges. The Mn-Mn interaction dominates in MnRh and the compound is antiferromagnetic. Placing Bi or Te on the Mn sites reduces the number of nearest-neighbor Mn-Mn pairs, allowing the ferromagnetic Mn-Rh-Mn to dominate. An additional contribution to exchange will come from 180° Mn-Bi-Mn superexchange; however, because of the high electronegativity of Bi, this interaction is likely to be antiferromagnetic as in Cu_2MnSb [5]. The situation is similar to that in Ni_3Mn, where ordering of Ni and Mn reduces the number of antiferromagnetic Mn-Mn nearest neighbors, allowing the ferromagnetic Ni-Ni and Ni-Mn interactions to dominate [6]. This treatment is in apparent conflict with estimates by Forrer that Mn-Mn exchange is ferromagnetic for atomic separation greater than 2.8 Å [7, 8].

If the formula $(Mn_{1-x}Bi_x)Rh$ is generalized to $(Mn_{1-x}X_x)Rh$, where X represents a group IIIB-VIB element, then $x = 0.5$ represents the Heusler alloy composition. One rhodium-based Heusler alloy ($L2_1$ structure) has been reported: Rh_2MnGe [9]. As expected from the above argument, this compound is strongly ferromagnetic (T_c = 450 K). We note that this general effect. i.e., inducing ferromagnetism in MnRh, is relatively independent of the type of substituted X atom, since Bi, Te, and Ge are all from different rows and columns of the periodic table.

We conclude that the present family of MnRh-based compounds—MnRh, $(Mn_{0.8}Bi_{0.2})Rh$, $(Mn_{0.8}Te_{0.2})Rh$, and Rh_2MnGe—can be described consistently with a simple model of competitive ferromagnetic and antiferromagnetic exchange.

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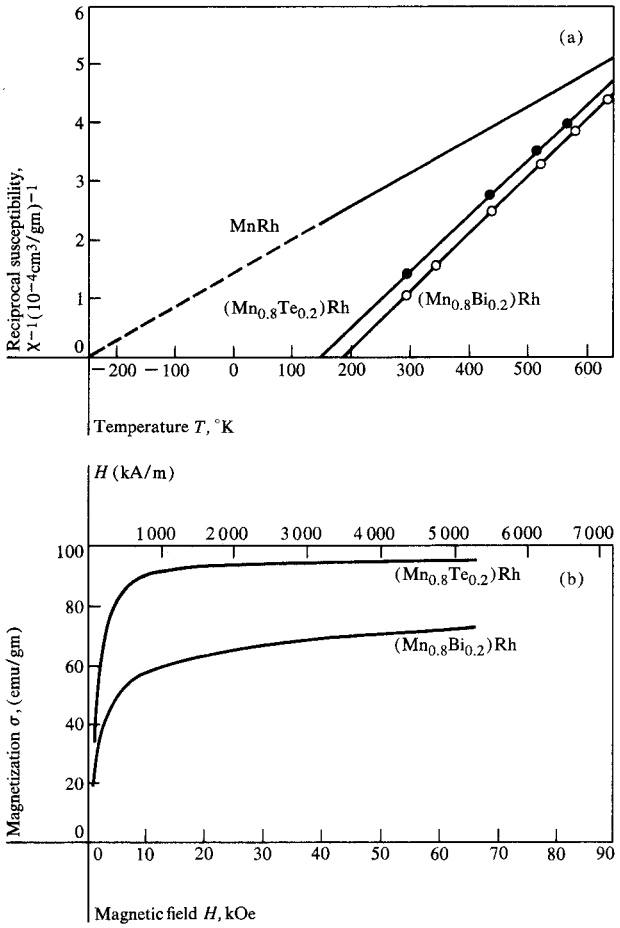

Figure 1 Measured magnetic properties of the Rh compounds. (a) Reciprocal susceptibility vs temperature. The data for MnRh are taken from Ref. [2]. (b) Magnetization versus applied magnetic field at 4.2 K.

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