High Field Magnetization in Manganese Intermetallic Compounds(Magnetism)

High Field Magnetization in Manganese Intermetallic Compounds*

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Synopsis

Magnetization measurements were carried out on manganese intermetallic compounds Mn_3MC(M=Ga,Zn), $Mn_{2-x}Co_xSb$(x=0.09 and 0.15) and MnMX(M=Ru,Rh,Pd;X=As,P) in magnetic fields up to 150 or 320 kOe. Antiferromagnetic(AF)-ferromagnetic(F) field-induced transitions and (AF+F)-(F) one were observed for Mn_3GaC and Mn_3ZnC, respectively. For $Mn_{1.91}Co_{0.09}Sb$, intermediate(I)- ferrimagnetic (Fr) field-induced transitions were observed. For $Mn_{1.85}Co_{0.15}Sb$, AF-Fr field -induced transitions were observed. These transitions were of the first order except one of Mn_3ZnC. The magnetic properties of MnMX (M=Ru,Rh,Pd;X=As,P) were discussed on the basis of the values of magnetization and high-field magnetic susceptibility.

I. Introduction

Ternary manganese compounds Mn_3MX(M=Ga,Zn,Al,Sn and In;X=C and N) have the cubic perovskite structure. Their magnetic properties have been extensively studied because they show magnetic moments,magnetic structures and magnetic transitions characteristic of itinerant electron magnets in great variety.[1,2] The magnetic properties of Mn_3GaC are characterized by an AF-F first-order transition at the transition temperature(T_t) which is approximately 170 K at zero field. The AF state below T_t has the magnetic structure of a (π π π)-type. The magnetic moment of Mn is μ_{Mn}=1.8μ_B at 4.2 K. The Curie temperature(T_c) of the F state is about 255 K. Mn_3ZnC also shows the transition between magnetically ordered states at T_t ~230K. Neutron diffraction studies show that both AF and F state coexist below T_t. The magnetic structure is tetragonal noncollinear with a F component along the tetragonal [001] axis and an AF component in the (001) plane. It is noticed that the magnetic moment on the AF sublattice is 2.7 μ_B and much larger than 1.6 μ_B on the F sublattice at 4.2 K. The transition from an (AF+F) to F state at T_t is of the second order.

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The intermetallic compounds $Mn_{2-x}Co_xSb$ ($x<0.37$) crystallize in the tetragonal Cu_2Sb-type structure. Mn_2Sb is a ferrimagnet with a Neel temperature of 550 K. The spin ordering of the Fr state for Mn_2Sb is an antiparallel arrangement of unequal magnetic moments associated with two kinds of manganese atoms (Mn_I and Mn_{II}), where the Mn_I and Mn_{II} atoms have magnetic moments of 2.1 μ_B and 3.9 μ_B at 0 K, respectively. The magnetic moments are perpendicular to the c axis below 240 K and parallel to that axis above 240 K. Bither et al,[3] and Kanomata and Ido[4] observed that substitution of Co in Mn_2Sb results in a magnetic transition from a Fr to an AF state with decreasing temperature. According to the results of the magnetic measurements for $Mn_{2-x}Co_xSb$, the compounds with $0.10<x<0.35$ exhibits a first-order AR-Fr phase transition at T_t which accompanies the discontinuous change of lattice constants a and c. For the compounds with $0.06<x<0.10$, an I phase appears at low temperatures and the first order phase transitions from the I state to the Fr one have been observed with increasing temperature.

The ternary intermetallic cmpounds MnMX(M=Ru,Rh,Pd:X=As,P) crystallize into the hexagonal Fe_2P-type structure. In the Fe_2P-type structure, the non-metal atoms form tetrahedra and square-based pyramids both stacked in triangular channels along the hexagonal c axis. The 4d atoms are located on the tetrahedral sites of one channels and Mn atoms on the pyramidal sites of adjacent channels. The compounds MnRhAs and MnRuP have been extensively investigated because of their interesting magnetic properties[5,6] which have magnetic order-order transition from the AF state to the AF+F coexistent one of the antiferromagnetic and ferromagnetic components of magnetic moment(canted state) for MnRhAs and from the AF1 state to the AF2 one for MnRuP. The compounds MnRuAs and MnRhP are ferromagnets. Recently, the magnetic and electrical properties of the compounds MnMX(M=Ru,Rh,Pd;X=As,P) have been studied by Kanomata et al[7] and Harada et al.[8] Their magnetic properties are summarized in Table 1.

Table 1 Magetic data of ternary compounds MnMX(M=Ru,Rh,Pd;X=As,P) from refs.(6) and (7).

Compound	Magnetic order	T_c, T_N, T_f or T_t (K)
MnRuAs	F	496K(T_c)
MnRhAs	AF1/Cant/AF2?	160(T_t), 200(T_c)
MnPdAs	Cant?	210(T_c)
MnRuP	AF1/AF2/AF3	116(T_t), 176(T_t), 296(T_N)
MnRhP	F	401(T_c)
MnPdP	Spin-glass?	26(T_f)

As stated above, the magnetic moments of the Mn atoms in Mn_3MC(M=Ga,Zn) and $Mn_{2-x}Co_xSb$ are much smaller than about 4 μ_B observed in other ordered manganese alloys, in which the magnetic moment of Mn is considered to be localized, and their magnitude depend strongly on the magnetic states. Therefore, the magnetic properties of these compounds are considered to be interpreted in terms of an itinerant-electron magnetism. This is also supported by the band calculations[9-12] for these compounds. The band structures calculated for MnCoP show that the 3d bandwidth is fairly wide.[13] This means that the d electrons for MnCoP should be treated as itinerant electrons. So, it is considered that the magnetic properties of the compounds MnMX(M=Ru,Rh,Pd;X=As,P) should be also interpreted in terms of the itinerant-electron magnetism. We have studied the magnetic properties of Mn_3MC(M=Ga,Zn),[2,14] $Mn_{2-x}Co_xSb$[15] and MnMX(M=Ru,Rh,Pd;X=As,P)[16,17] under high field. Our results are reviewed here from the viewpoint of itinerant electron magnetism.

II. Experimental Results and Discussions

1. Mn_3MC(M=Ga,Zn)

Figure 1 shows the temperature dependence of specific magnetization (σ_g) and reciprocal magnetic susceptibility per mole ($1/\chi_{mol}$) for Mn_3MC(M=Ga,Zn). As seen in the figure, the magnetic order-order transitions occur at 165 K and 215 K for Mn_3GaC and Mn_3ZnC, respectively. The field-induced transitions were examined at various temperatures below these transition temperatures.[14] As an example the magnetization curve at Mn_3GaC at 4.2 K is shown in Fig.2, in which a field-induced transition from an AF to F state takes place around 200 kOe with increasing field. There is observed a large hysteresis and ($H_c - H_c$) is 50 kOe. The magnetization in the F state is σ_g=70 emu/g, which gives μ_{Mn}= 1.0 μ_B. It should be noted that the value of μ_{Mn} in the F state is much smaller than 1.8 μ_B in the AF state. This reduction of magnetic moment is ascribed to the volume contraction caused by the field-induced AF - F transition. All the field-induced transitions from the AF to F state below T_t were found to be of the first order. The temperature variations of the transition fields are shown in Fig.3(b). The value of dH_c/dT just below T_t is estimated to be -2.3 kOe/K. The entropy change at T_t, ΔS, can be deduced from the Clausius-Clapeyron equation, $\Delta S = -(dH_c/dT)\,\Delta\sigma$. ΔS is estimated to be 0.42R(R is the gas constant) which is consistent with 0.5R obtained from the specific heat measurement.[18] For Mn_3ZnC, no abrupt change of magnetization was observed at the field-induced transition from an (AF+F) to F state and the field-induced transition is of the second order. The H_c versus T curve is shown in Fig.3(d).

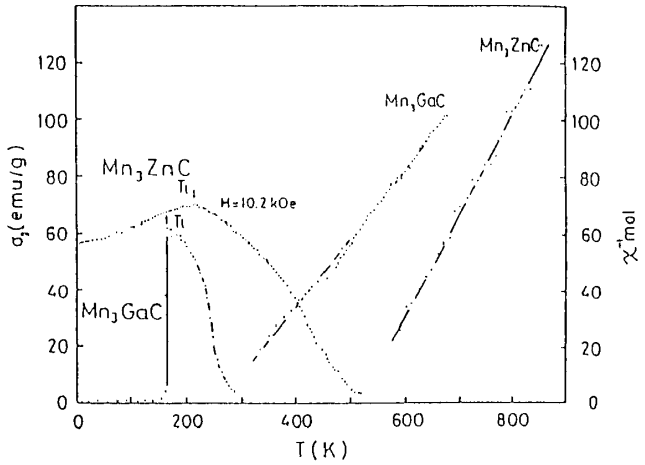


Fig.1 Thermomagnetic curves for Mn_3MC (M=Ga and Zn)[2)]

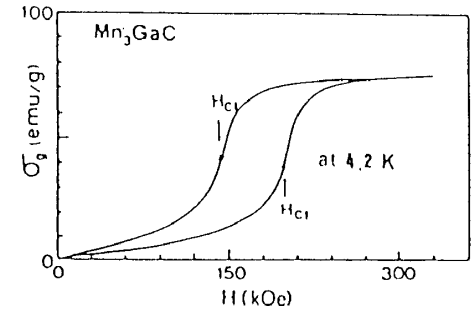
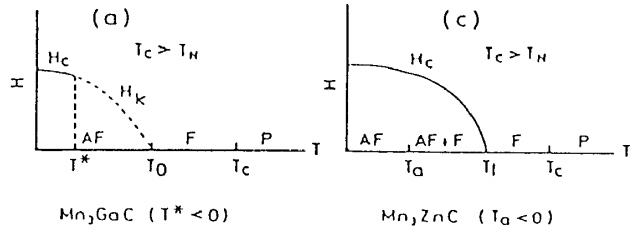


Fig.2 Magnetization curves for Mn_3GaC[14)]



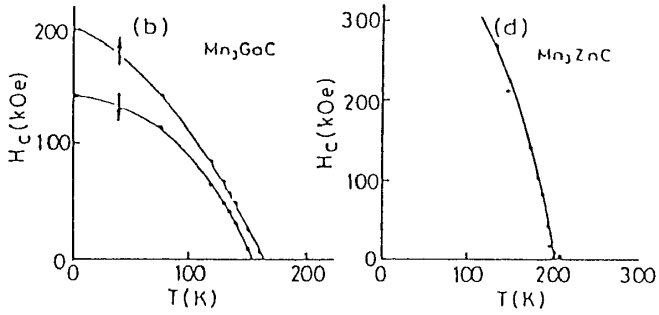


Fig.3 Temperature dependence of critical field for Mn_3GaC and Mn_3ZnC.[2)]

As stated in the section I, in the present compounds the amplitude of local spin density at Mn atoms is variable. There occur the coexistence of ferromagnetism and antiferromagnetism, and also a transition between them. Moriya and Usami showed that a coexistence of ferro-and antiferromagnetism and a phase transition between magnetically ordered states takes place in itinerant electron system on the basis of SCR theory of spin fluctuation.[19)] According to the theory, in the itinerant electron system without magnetically anisotropy the free energy F as a function of uniform (M_0) and staggered (M_Q) components of magnetization is expressed as follows,

$$F=(1/2\chi_0)M_0^2+(1/2\chi_Q)M_Q^2+(1/4)\gamma_u M_0^4+(1/4)\gamma_s M_Q^4+(1/2)\gamma_{us}M_0^2M_Q^2-HM$$

where H is the uniform external field, χ_0 and χ_Q are the uniform and staggered susceptibility, respectively, and γ's are coeffecients of 4th power of magnetization. The temperature dependence of $1/\chi_0$ and $1/\chi_Q$ are dominated by the effect of correlated spin fluctuations. In the F(AF) system $1/\chi_0$ and $1/\chi_Q$ pass through zero as T is changed. T_c and T_N are defined as $1/\chi_0(T_c)=0$ and $1/\chi_Q(T_N)=0$. When the temperature dependence of γ's is neglected, four different phase diagrams are derived by minimizing the free energy. Two of them are shown in Fig.3(a) and (c). The diagram(a) appears when the mode-mode coupling is strong($\gamma_{us}^2>\gamma_u\gamma_s$) and (c) when the coupling is weak ($\gamma_{us}^2<\gamma_u\gamma_s$). T_0, T_a and T_f are defined by $\chi_Q/\chi_0(T_0)=(\gamma_u/\gamma_s)^{1/2}$, $\chi_Q/\chi_0(T_a)=\gamma_{us}/\gamma_s$ and $\chi_Q/\chi_0(T_f)=\gamma_u/\gamma_{us}$, respectively. H_c and H_k are the critical fields, at which the second order and the first order phase transitions take place, respectively. It is thought that the phase diagram (b) for Mn_3GaC corresponds to the diagram (a) with $T^*<0$ and the phase diagram(d) for Mn_3ZnC to the diagram(c) with $T_a<0$. The magnetic moment in the field-induced F state in Mn_3GaC is much smaller than that in the AF state at 4.2 K. This can be understood in terms of itinerant electron magnetism, because the large volume contraction caused by the field-induced AF-F transition broadens the electronic band and consequently reduces the moment. A study of magnetostriction under high field for Mn_3GaC is in progress.

2. $Mn_{2-x}Co_xSb$

Figure 4 and 5 show the magnetization σ versus field at various temperatures for $Mn_{1.91}Co_{0.09}Sb$ and $Mn_{1.85}Co_{0.15}Sb$, respectively.[15] The field-induced metamagnetic phase transitions from the I to the Fr state and from the AF to the Fr state were observed for $Mn_{1.91}Co_{0.09}Sb$ and $Mn_{1.85}Co_{0.15}Sb$, respectively. The field-induced transition fields, $H_{c\uparrow}$ and $H_{c\downarrow}$, are defined as shown with arrows in the figure. The first order magnetic transition of $Mn_{1.85}Co_{0.15}Sb$ takes place between the spin structures of the Mn_2As- and Mn_2Sb-types. Figures 6 and 7 show the temperature dependence of magnetization for $Mn_{1.91}Co_{0.09}Sb$ and $Mn_{1.85}Co_{0.15}Sb$, respectively. For $Mn_{1.85}Co_{0.15}Sb$, the magnetization in the temperature range from 120 to 200 K in a field of 150 kOe is $\sim$20 % higher than the saturation magnetization of Mn_2Sb in the same temperature range. In the temperature range from 5.9 to 135 K in a field of 150 kOe, the magnetizations of $Mn_{1.91}Co_{0.09}Sb$ are $\sim$30 % higher than the saturation magnetization of Mn_2Sb in the same temperature range. By extrapolating the magnetization versus temperature curves at 150 kOe in the Fr state to 0 K in Figs.6 and 7, averaged magnetic moments are defined to be 2.2 μ_B and $\sim$2.2 μ_B for $Mn_{1.91}Co_{0.09}Sb$ and $Mn_{1.85}Co_{0.15}Sb$, respectively. The

increase of moment by substitution of Mn for Co is explained by assuming that nonmagnetic Co atoms occupy siteI and the magnetic moments of Mn_I and Mn_{II} atoms have value equal to those of Mn_2Sb in the pseudobinary syatem $Mn_{2-x}Co_xSb$. The temperature variations of the observed transition fields are

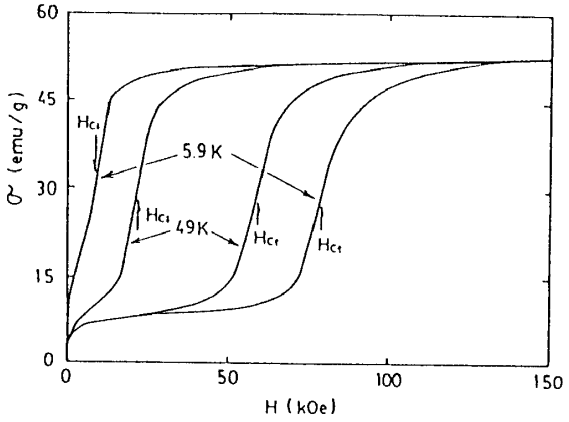


Fig.4 Magnetization curves at various temperatures for $Mn_{1.91}Co_{0.09}Sb$.[15]

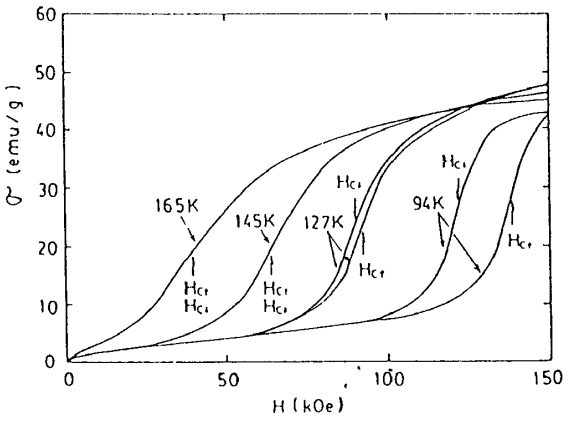


Fig.5 Magnetization curves at various temperatures for $Mn_{1.85}Co_{0.15}Sb$.[15]

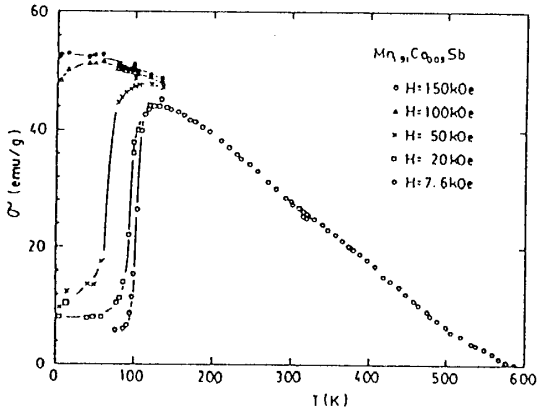


Fig.6 Thermomagnetic curves in various fields for $Mn_{1.91}Co_{0.09}Sb$.[15]

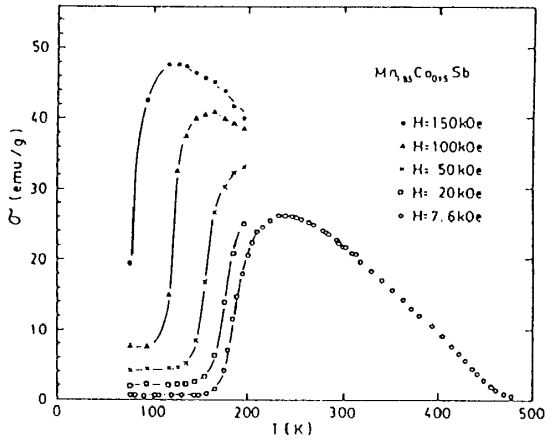


Fig.7 Thermomagnetic curves in various fields for $Mn_{1.85}Co_{0.15}Sb$.[15]

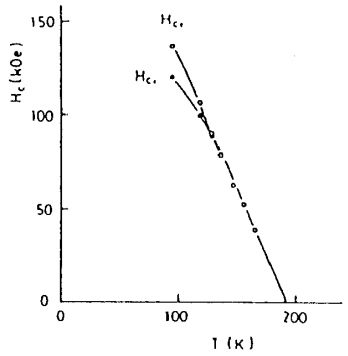


Fig.8 Transition field versus temperature for $Mn_{1.85}Co_{0.15}Sb$.[15]

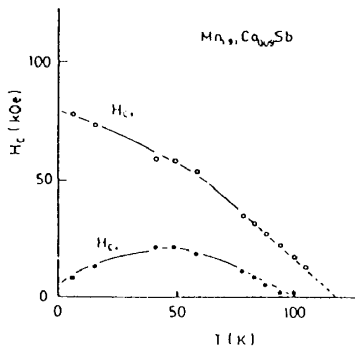


Fig.9 Transition field versus temperature for $Mn_{1.91}Co_{0.09}Sb$.[15]

shown in Figs. 8 and 9 for $Mn_{1.85}Co_{0.15}Sb$ and $Mn_{1.91}Co_{0.09}Sb$, respectively. The values of dH_c/dT just below T_t are estimated to be -0.86 kOe/K and -1.42 kOe/K for $Mn_{1.91}Co_{0.09}Sb$ and $Mn_{1.85}Co_{0.15}Sb$ from the temperature variations of the observed transition fields, respectively. Using Clausius-Clapeyron's equation, the total entropy change ΔS at T_t of $Mn_{1.91}Co_{0.09}Sb$ and $Mn_{1.85}Co_{0.15}Sb$ are estimated to be 0.11R and 0.17R, using the values of dH_c/dT and $\Delta\sigma$, respectively. The main sources of these large entropy change at T_t was considered to be ascribed to the magnetic contribution at the Mn_{II} site. In fact, the AF-Fr phase transition is accompanied by a change in the magnetic moment of the Mn atoms according to the results of neutron diffraction for $Mn_{1.80}Co_{0.20}Sb$.[20] In particular, the magnetic moment on the Mn_{II} atoms is found to be $\sim 3.4\ \mu_B$ just below T_t and $\sim 2.4\ \mu_B$ just above T_t.

Recently, Chonan et al[11] and Suzuki et al[12] calculated the band structure of Mn_2Sb by a self-consistent augmented plane wave method. According to their calculation, the density of states consists of three parts:bonding and antibonding d-p bands and a nonbonding d-band with the Fermi level lying in the nonbonding band. The non-bonding d band width is about 3-4 eV, which is fairly wide. Therefore, these authors concluded that the d electrons of Mn atoms should be treated not as localized electrons, but as itinerant electrons. Thus, it is considered that the magnetic properties of $Mn_{2-x}Co_xSb$ should be discussed in terms of the itinerant-electron magnetism. General theories of magnetic transitions in an itinerant-electron system were proposed by Moriya and Usami[19] and Isoda[21] on the basis of spin fluctuation. However, the transitions from the I to the Fr state and the AF to the Fr state observed for $Mn_{2-x}Co_xSb$ do not occur in both the theories mentioned above. A further experimental and theoretical investigation of the magnetic order-order transition will be necessary.

3. MnMX(M=Ru,Rh,Pd;X=As,P)

Figure 10 shows the magnetization curves of MnRuAs(T=5.5 K) and MnPdAs(T=8 K) together with that of MnRhAs(T=4.2 K). Figure 11 shows the magnetization curve of MnRhP. The magnetization of the ferromagnet MnRuAs was saturated at magnetic fields above 50 kOe and the spontaneous magnetization(σ_s) was found to be 21.5×10^3 emu/mol giving the magnetic moment per Mn atom of $\mu_{Mn}=3.9\ \mu_B$ provided the moments are located at Mn atoms only. The high field susceptibility was found to be $\chi_{hf}=1.7\times10^{-3}$ emu/mol. The magnetization of the ferromagnet MnRhP was saturated above 25 kOe and the spontaneous magnetization was found to be 17×10^3 emu/mol giving $\mu_{Mn}=3\ \mu_B$. Thus, the value of the magnetic moment per Mn atom in MnRhP, 3 μ_B, is smaller by about 1 μ_B compared with 3.9 μ_B in MnRuAs. The previous results show that the

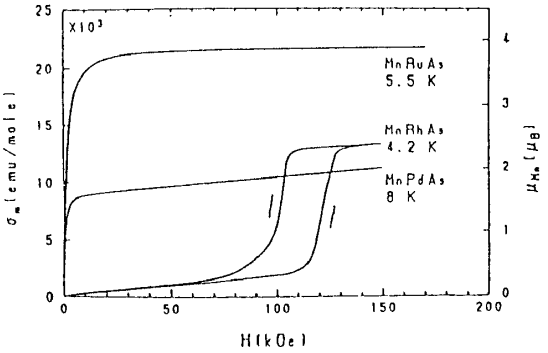


Fig.10 Magnetization curves of MnRuAs, MnRhAs and MnPdAs.[16]

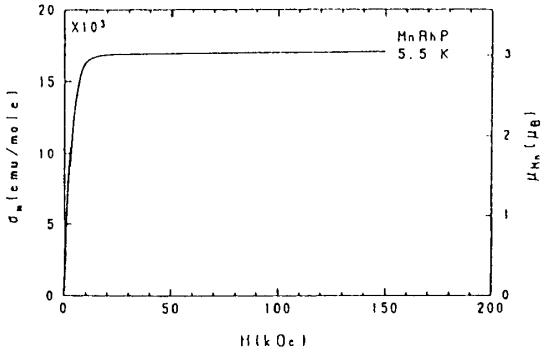


Fig.11 Magnetization curve of MnRhP.[16]

magnetic moment of the Mn atom at the pyramidal site in manganese compounds with the crystal structure of Fe_2P-, Co_2P- and Cu_2Sb-type is usually about 3 μ_B in the phosphide and about 4 μ_B in the arsenides. The values of μ_{Mn} in MnRuAs and MnRhP obtained in this experiment agree well with those expected for the arsenides and phosphides, respectively. The magnetization of MnRhAs shows an abrupt increase around 80 kOe.[17] This discontinuous increase of σ corresponds to the field-induced transition from the AF state to the canted (AF+F) state. The extrapolation of the magnetization curve after the transition to H=0 intersects the σ axis at 11×10^{3} emu/mol, which gives μ_{Mn} $=2.0\mu_B$. χ_{hf} was estimated to be 15×10^{-3} emu/mol. The magnetization of MnPdAs appears to be saturated above about 15 kOe with large high field susceptibility. The spontaneous magnetization was found to be 9×10^{3} emu/mol giving μ_{Mn}=1.6 μ_B. χ_{hf} was estimated to be 15×10^{-3} emu/mol. Thus, the values of μ_{Mn} obtained for MnRhAs and MnPdAs are almost the same, but much smaller than those for the ferromagnets MnRuAs and MnRhP. Furthermore, the values of χ_{hf} for MnRhAs and MnPdAs are the same, but much larger than those for MnRuAs and MnRhP. The values of μ_{Mn} and χ_{hf} for MnRhAs were obtained from the magnetization of the field-induced canted state. The similar values of μ_{Mn} and χ_{hf} obtained for MnRhAs and MnPdAs suggest that MnPdAs is also in the canted state. The large values of χ_{hf} for MnRhAs and MnPdAs can be ascribed to the existence of canted magnetic moments. Figure 12 shows the magnetization curves for the antiferromagnet MnRuP. The magnetization curves below 77 K did not show any field dependence of magnetic susceptibility. The magnetization curve at 150 K just below T_t showed the existence of a field-induced transition at fields between 70 and 100 kOe, where the magnetization curves have hysteresis. At 227 K, between T_t and T_N, the magnetization increases almost linearly with the field. Figure 13 shows the magnetization curves for MnPdP. In the magnetization process for MnPdP, the remanent magnetization was observed at 8 K but not at 41.5 K. According to Kanomata et al[17], MnPdP shows spin-glass-like freezing with the freezing

temperature (T_t) of 26 K. The remanent magnetization was observed in the magnetization curve at low temperature and found to disappear around T_t. This result is consistent with an occurence of spin-glass freezing below T_t in ref.7.

The transition from the AF state to the AF+F one observed for MnRhAs does not occur in the theories[19,21] on the basis of the itinerant-electron magnetism. A further investigation of magnetic transitions will be also necessary experimentally and theoretically for MnMX (M=Ru,Rh,Pd;X=As,P) systems.

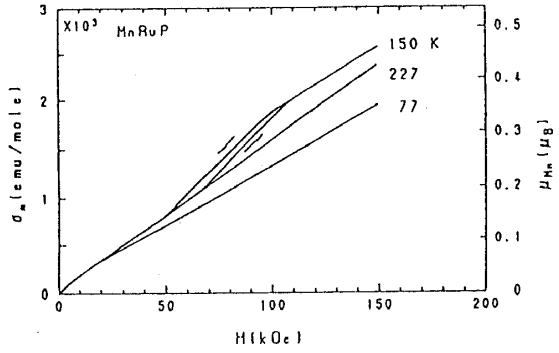


Fig.12 Magnetization curves of MnRuP.[16]

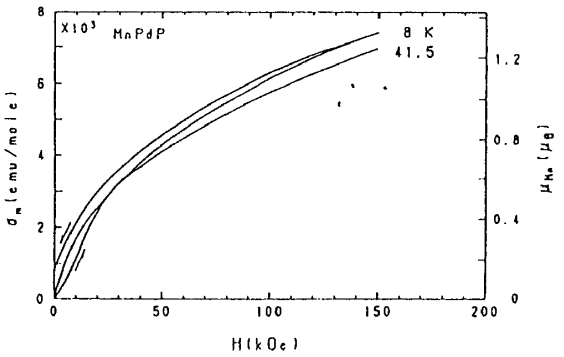


Fig.13 Magnetization curves of MnPdP.[16]

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