Electrical and Magnetic Properties, and Electronic Structures of Pseudo-Gap-Type Antiferromagnetic $L1_0$ -Type MnPt Alloys

Rie Y. Umetsu^{1,*1}, Kazuaki Fukamichi^{1,*2} and Akimasa Sakuma²

¹Department of Materials Science, Graduate School of Engineering, Tohoku University, Sendai 980-8579, Japan

²Department of Applied Physics, Graduate School of Engineering, Tohoku University, Sendai 980-8579, Japan

The electrical resistivity ρ , magnetic susceptibility χ , electronic specific heat coefficient γ_e , the Néel temperature T_N and the electronic structure and the magnetocrystalline anisotropy energy (MAE) have been investigated for $L1_0$ -type MnPt alloy system. This alloy system exhibits the characteristic behaviors of pseudo-gap type antiferromagnets, presenting with the highest T_N , the smallest values of ρ , χ and γ_e in the vicinity of the equiatomic composition. The values of ρ , χ and γ_e increase with deviating from the equiatomic composition.

From the linear muffin-tin orbital (LMTO) band calculations, the $L1_0$ -type MnPt alloy system has a pseudo-gap in the electronic structure and the density of states (DOS) at the Fermi energy (E_F) is lowest at the equiatomic composition in accord with the experimental results. Furthermore, the results of the LMTO band calculations including the spin-orbit interaction make it clear that the direction of the magnetic moment of Mn in the equiatomic composition is parallel to the c -axis, consistent with the reported spin structure determined by neutron diffractions. The magnetocrystalline anisotropy constant K is about $1.39 \times 10^6 \text{ J m}^{-3}$ which is larger in magnitude than that of $L1_0$ -type MnNi equiatomic alloy, though the signs are different.

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1. Introduction

In the vicinity of the equiatomic concentration, Mn forms alloys with Ni, Pd, Pt, Rh and Ir in a wide range of concentration.¹⁻⁴⁾ The crystal structure of these alloys is a $B2$ (CsCl)-type cubic phase at high temperatures and transforms into an $L1_0$ (CuAu-I)-type tetragonal phase with a diffusionless martensitic transformation process at low temperatures. From neutron diffractions and magnetic data,⁵⁻¹⁰⁾ it has been reported that the $L1_0$ -type phase exhibits a collinear antiferromagnetic structure and MnNi, MnPd and MnPt equiatomic alloys have a very high Néel temperature T_N of about 1100, 780 and 970 K, respectively.

Due to such a high stability of antiferromagnetism, especially, MnPt alloy has been investigated intensively from the viewpoint of practical applications as antiferromagnetic pinning layers of giant magnetoresistance (GMR)¹¹⁻¹⁴⁾ and tunnel magnetoresistance (TMR) devices.¹⁵⁻¹⁸⁾ In order to develop the excellent properties for GMR and TMR devices, however, the investigations on fundamental magnetic properties for these practical antiferromagnets have been highly desired, because the exchange biasing characteristics are closely related to the spin structures, magnetocrystalline anisotropy energy (MAE) and the magnitude of T_N of the antiferromagnetic materials.¹⁹⁻²¹⁾ In addition, recent interest is how to design the devices with a low electrical resistance at room temperature,^{22,23)} especially in the current perpendicular to the plane (CPP)-type spin valves.²⁴⁻²⁷⁾ Because the antiferromagnetic layer is relatively thick, compared with other magnetic layer in the GMR and TMR devices, the reduction of its electrical

resistivity is important for such devices. Accordingly, it is meaningful to investigate the electrical properties of antiferromagnetic Mn alloys.

Recently, it has been pointed out from the theoretical calculations that the density of states (DOS) of the $L1_0$ -type MnPt equiatomic alloy exhibit a pseudo-gap around the Fermi energy E_F .²⁸⁾ Such a characteristic electronic structure is common to the $L1_0$ -type MnNi,²⁹⁾ MnPd³⁰⁾ and MnIr^{31,32)} equiatomic alloys with the same crystal structure. The pseudo-gap is attributed to the antiferromagnetic staggered field due to the antiferromagnetic spin arrangements because no pseudo-gap is formed in the paramagnetic state as well as the ferromagnetic state.²⁹⁾ Therefore, the high stability of the antiferromagnetism for these alloys is closely correlated to their characteristic electronic structure.

In the present paper, we have carried out systematic investigations for electrical resistivity, magnetic susceptibility and electronic specific heat coefficient. Especially, we added new data for low temperature region to the preliminary results³³⁾ in order to discuss the electrical and magnetic properties as well as the theoretical results for the present alloy system. For detailed discussion of the correlation between the antiferromagnetic stability and the electronic state for the $L1_0$ type MnPt alloy system and their variation with the Pt composition, the electronic structures have been calculated by using the tight-binding linear muffin-tin orbital (LMTO) method with the coherent potential approximation (CPA) in the off-equiatomic composition. Furthermore, the LMTO band calculations including the spin-orbit interaction were performed in order to investigate the magnetocrystalline anisotropy energy (MAE) because the MAE in the antiferromagnetic materials plays an important role in the exchange biasing-field in spin valves.²¹⁾ Furthermore, the theoretical calculations of the MAE give the reason why the magnetic phase diagram of the MnPt alloy system is rather complicated, compared with that of other $L1_0$ -type Mn alloy

*¹Present address: CREST-Japan Science and Technology Agency, Tokyo 105-6218, Japan

*²Present address: Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan

systems, changing the magnetocrystalline anisotropy with the temperature or the composition.

2. Experiments

Several kinds of the specimens were prepared by arc-melting in an argon gas atmosphere and annealed at 1073 K for 72 h in vacuum sealed quartz tubes and slowly cooled down to room temperature. Their crystal structure was identified as an $L1_0$ -type single phase by X-ray powder diffraction and the room temperature lattice constants were in agreement with the data in literatures.⁵⁻⁷⁾ The mass density of the specimens was examined by using toluene as a working liquid. The alloy compositions were confirmed by an inductively coupled plasma (ICP) analysis and also decided from the density derived from the lattice constants. The electrical resistivity was measured by a conventional four-probe method from 6 to 1100 K. The magnetic measurements were carried out with a superconducting quantum interference device (SQUID) magnetometer below room temperature and with a vibrating sample magnetometer (VSM) from room temperature up to 1100 K. The low-temperature specific heat capacity measurements from 2 to 10 K were made by a thermal relaxation method.

3. Outline of Theoretical Calculation Method

For the electronic structure calculations, the linear muffin-tin orbital (LMTO) method³⁴⁾ is employed within the framework of the local spin density approximation (LSDA). The exchange constant term follows the Barth and Hedin form³⁵⁾ with parameters given by Janak.³⁶⁾ After the self-consistent calculations, we evaluate the Néel temperature T_N by using the effective exchange constant J_0 given by the following equation.^{28,37)}

$$J_0 = -\frac{1}{4\pi} \text{Im} \int_{E_F} d\omega \text{Tr}_{lm} \left[\Omega_0(\omega) \{ g^{\uparrow\uparrow}_{00}(\omega) - g^{\downarrow\downarrow}_{00}(\omega) \} + \Omega_0(\omega) g^{\uparrow\downarrow}_{00}(\omega) \Omega_0(\omega) g^{\downarrow\uparrow}_{00}(\omega) \right]. \quad (1)$$

The quantity J_0 can be regarded as the sum of the effective exchange field of an atom in 0 site acted by surrounding moments. In the above equation,

$$\Omega_0(\omega) \equiv \{ p^{\uparrow}_0(\omega) - p^{\downarrow}_0(\omega) \}, \quad (2)$$

where $p^\gamma(\omega)$ is the potential function as a function of the energy ω of the electrons and given by $p^\gamma(\omega) = \{ (\omega - C) / \Delta \} \delta_{L,L} \delta_{\sigma',\sigma}$. In eq. (1), $g^{\sigma\sigma'}_{00}(\omega) = [(p^\gamma(\omega) - S^\gamma)^{-1}]_{00}^{\sigma\sigma'}$ is the so-called auxiliary Green function in the tight-binding LMTO scheme³⁸⁾ and the screened structure constant S^γ is given by $S^\gamma = S(1 - \gamma S)^{-1}$. Here, we define $L = (i, l, m)$ (i denotes the site, l and m are orbital indices) and σ as the spin state, the quantities C , Δ and γ are the potential parameters determined within each atomic sphere by using the LSDA. In fact, J_0 corresponds to the exchange energy J in the Heisenberg model. Using J_0 , therefore, the Néel temperature T_N is estimated by the following expression based on the generalized molecular field theory by Liechtenstein *et al.*:³⁷⁾

$$T_N = \frac{2J_0}{3k_B} \quad (3)$$

where k_B is the Boltzmann constant.

The tight-binding LMTO method is also useful for the treatments of substitutional disordered systems in which we can apply the coherent potential approximation (CPA).^{39,40)} In the present work, the CPA calculations have been carried out for the partial substitutional system in which the Mn (Pt) atoms are randomly distributed in the Pt (Mn) sublattice when the excess Mn (Pt) atoms are substituted in the $L1_0$ ordered MnPt alloy in the off-equiatomic composition. For the calculations of the magnetocrystalline anisotropy energy (MAE), the spin-orbit interaction is introduced in the LMTO Hamiltonian, following the method given by Andersen³⁴⁾ for the spin-orbit coupling and the spin-orbit matrix in the LMTO Hamiltonian. By using the force theorem,⁴¹⁾ the MAE is obtained from the following expression.

$$\Delta E = E[100] - E[001], \quad (4)$$

where $E[n]$ is the sum of the eigenvalues of the Kohn-Sham equation⁴²⁾ when the magnetic moment is parallel to the crystal axis $[n]$ in the $L1_0$ -type structure. The details have been described elsewhere.^{43,44)} In the present calculations for the MAE, we settle the number of k -points of 11616.

4. Results and Discussion

4.1 Electrical and magnetic properties, and electronic structure

Figures 1(a) and (b) show the temperature T dependence of electrical resistivity ρ of the $L1_0$ -type MnPt alloys with (a) the concentrations less or equal and (b) more than 50% Pt, respectively. The resistivity-temperature (ρ - T) curves of all the specimens exhibit a hump, showing a characteristic behavior of pseudo-gap-type antiferromagnets.³⁰⁻³³⁾ The arrows in the figures indicate T_N defined from the minimum point in the $d\rho/dT$ - T curves. The feature of ρ in antiferromagnets at T_N depends on the periodicity of their magnetic structure. Using the scaling of the critical exponents, α_c , β_c and γ_c with $\alpha_c + 2\beta_c + \gamma_c = 2$, $d\rho/dT$ is expressed as^{45,46)}

$$d\rho/dT = -A\varepsilon^{-(\alpha_c+\gamma_c)/2} + B\varepsilon^{-(\alpha_c+\gamma_c-1)} \quad (T < T_N). \quad (5)$$

$$\text{with } \varepsilon = \left| \frac{T - T_N}{T_N} \right|$$

The sign of $d\rho/dT$ at T_N depends on the magnitudes of the coefficients A and B . The first term is dominant below T_N . As a result, $d\rho/dT$ exhibits a minimum at T_N , accompanied by a hump just below T_N in the ρ - T curve. From the figures, the value of T_N is highest in the vicinity of the equiatomic composition and decreases with deviating from the equiatomic composition. For more detail, the variation of T_N in the concentration range less than 50% Pt is more significant, compared with more than 50% Pt.

The low-temperature specific heat capacity C_p in the form of $C_p T - T^2$ is given in Figs. 2(a) and (b) for the MnPt alloys with the concentrations less or equal and more than 50% Pt, respectively. The data are well fitted by a straight line as shown in the figures. The intercepting point of the ordinate

Fig. 1 Temperature dependence of the electrical resistivity ρ of $L1_0$ -type MnPt alloys with (a) the concentrations less or equal and (b) more than 50% Pt. The arrows indicate the Néel temperature T_N defined from the minimum point in the temperature derivative curves of ρ .

Fig. 2 The low-temperature specific heat capacity C_p in the form of C_p/T^2 for $L1_0$ -type MnPt alloys. (a) and (b) are the data for the concentrations less or equal and more than 50% Pt, respectively.

Fig. 3 The density of states (DOS) of $L1_0$ -type MnPt alloys in the collinear antiferromagnetic state calculated by the tight-binding linear muffin-tin orbital (LMTO) method with the coherent potential approximation (CPA). The upper, middle and lower panels are the DOSs for the alloys with 35, 40 and 45% Pt, respectively. The left and right panels are the DOSs at the Mn and Pt sites, respectively. The upper and lower curves in each figure refer to the majority and the minority spin states, respectively.

obtained from the linear extrapolation corresponds to the electronic specific heat coefficient γ_e . By neglecting the electron-phonon coupling term, the value of γ_e is expressed by the following expression:

$$\gamma_e = \frac{1}{3} \pi^2 k_B^2 N(E_F), \quad (6)$$

where $N(E_F)$ is the density of states (DOS) at the Fermi energy E_F . The value of γ_e for the equiatomic composition is significantly small, indicating a very low DOS at E_F , in good agreement with the calculated electronic structure with a pseudo-gap around E_F as seen from the upper panel in Fig. 4.

Illustrated in Fig. 3 is a series of the calculated density of states (DOS) of Mn and Pt of the $L1_0$ -type MnPt alloys in the collinear antiferromagnetic state. The upper, middle and lower panels are the DOS of the alloys with the composition of 35, 40 and 45% Pt, respectively. Figure 4 also shows a series of the calculated results for the alloys with 50, 55 and 60% Pt. The left and right panels in Figs. 3 and 4 are the DOS at the Mn and Pt sites, respectively. The upper and lower curves in each figure refer to the majority and minority spin states, respectively. It is clear that a pseudo-gap formed around E_F is most distinct in the equiatomic composition and becomes sluggish in the off-equiatomic composition. These calculated results are in good conformity with the concentration dependence of γ_e , that is, the smallest value of γ_e is observed in the vicinity of the equiatomic composition. The DOS of the equiatomic composition (50 at% Pt) is about 1.9 states $\text{Ry}^{-1} \text{ atom}^{-1} \text{ spin}^{-1}$, corresponding to $0.3 \text{ mJ mol}^{-1} \text{ K}^{-2}$ in γ_e from eq. (6). In detail, the excess Mn or Pt atoms substituted in the opponent sites increase the DOS at E_F ,

Fig. 4 The density of states (DOS) of $L1_0$ -type MnPt alloys in the collinear antiferromagnetic state calculated by the tight-binding linear muffin-tin orbital (LMTO) method with the coherent potential approximation (CPA). The upper, middle and lower panels are the DOS for the alloys with 50, 55 and 60% Pt, respectively. The left and right panels are the DOSs at the Mn and Pt sites, respectively.

Fig. 5 Concentration dependence of the experimental electronic specific heat coefficient γ_e and the calculated electronic specific heat coefficient γ_e^{cal} of $L1_0$ -type MnPt alloy system.

especially, the DOS of Mn at the Pt site for the compositions with 35, 40 and 45% Pt is relatively high.

Shown in Fig. 5 is the concentration dependence of the observed electronic specific heat coefficient γ_e obtained from Figs. 2(a) and (b), together with the calculated electronic specific heat coefficient γ_e^{cal} given from the results of the DOS and eq. (6). As shown in the figure, the concentration dependences of γ_e and γ_e^{cal} accord with each other, however, γ_e deviates from γ_e^{cal} in the concentration range less than 50% Pt. That is, the concentration dependence of the experimental γ_e is sensitive in the concentration range less than 50% Pt, compared with that in the more than 50% Pt, in

analogy with the concentration dependence of T_N . Geometrically frustrated systems Y(Sc)Mn_2 ⁴⁷⁾ compounds and $\beta\text{-Mn}$ ⁴⁸⁾ also exhibit a large value of γ_e . The theoretical calculations indicate that the spin magnetic moments of Mn atoms substituted at the Pt site exhibit large values of about $2.5 \mu_B$ in the $L1_0$ -type MnPt off-equiatomic alloys (see Fig. 8). This situation implies that a certain level of magnetic frustration results in the enhancement of γ_e value in the concentration range less than 50% Pt.

From the results of the electrical resistivity and low-temperature specific heat capacity measurements and the band calculations, the $L1_0$ -type MnPt alloy system is identified as a characteristic pseudo-gap type antiferromagnet in analogy with the $L1_0$ -type MnNi,²⁹⁾ MnPd³⁰⁾ and MnIr^{31,32)} alloy systems. The formation of the pseudo-gap is attributed to the antiferromagnetic staggered field due to the antiferromagnetic spin arrangements because no pseudo-gap is formed in the paramagnetic state as well as the ferromagnetic state.²⁹⁾ Accordingly, the high stability of the antiferromagnetism of the MnPt alloy system is considered to be closely connected with the peculiar electronic structure. The d electrons in Mn atoms are relatively localized, having a large spin polarization within each Mn atom. These magnetic moments of Mn atoms are forced to be arranged antiferromagnetically, and thus, the antiferromagnetic arrangement of the magnetic moments lowers the electronic energy by forming a pseudo-gap in the energy bands.²⁹⁾ In the case of $L1_0$ -type MnNi equiatomic alloy, the calculated energy in the ferromagnetic state is about 200 meV/atom higher than that in the collinear antiferromagnetic state.²⁸⁾ These facts imply that the more clear pseudo-gap their electronic structure shows, the higher T_N the antiferromagnetic alloy exhibits. However, this effect goes down in the $L1_0$ -type MnIr alloy system in which T_N is highest among the Mn alloy systems, nevertheless the DOS at E_F is not so low compared to the present $L1_0$ -type MnPt alloy system.^{31,32)} In the MnIr alloy system, the high T_N is explained from the calculated results of the effective exchange constant J_0 as a function of the Fermi energy E_F . The large value of J_0 is due to the fact that the origin of the abscissa is close to the peak of the J_0 curve. Therefore, the magnetic stability would be correlated to the location of E_F in the pseudo-gap of the electronic structure.

Concentration dependence of the electrical resistivity at 4.2 K, $\rho_{4.2}$, of the $L1_0$ -type MnPt alloy system is shown in Fig. 6. The important point to note is that the value of $\rho_{4.2}$ is quite different, depending on the composition. That is, the value of $\rho_{4.2}$ is smallest in the vicinity of the equiatomic composition and increases by about one order of magnitude for the composition of 40.7% Pt.

Within the Drude scheme, resistivity ρ_0 is related as

$$\rho_0 \propto \left\{ \sum_{\sigma} (N_{\sigma}(E_F) \tau_{\sigma}) \right\}^{-1} \propto \left\{ \sum_{\sigma} -N_{\sigma}(E_F) / \text{Im } \Sigma_{\sigma}(E_F) \right\}^{-1} \quad (7)$$

where τ is the relaxation time. Here, $\Sigma_{\sigma}(E_F)$ is the coherent potential at E_F . Consequently, the steep increase in ρ_0 in the off-equiatomic composition ranges can be connected with the

Fig. 6 Concentration dependence of the electrical resistivity at 4.2 K, $\rho_{4.2}$, of $L1_0$ -type MnPt alloy system.

decrease in $N_\sigma(E_F)$ and/or τ_σ with deviating from the equiatomic composition. Judging from both the experimental data and theoretical results in Fig. 5, the value of $N_\sigma(E_F)$ increases with deviating from the equiatomic composition. This leads us to infer that the increase of ρ_0 is mainly attributed to a significant decrease of τ_σ . Theoretically, $-\text{Im } \Sigma_\sigma(E_F)$ is proportional to $(\tau_\sigma)^{-1}$ as given in eq. (7), and hence it is also proportional to ρ_0 . Although it is not so easy to calculate the absolute value of ρ_0 , $-\text{Im } \Sigma_\sigma(\omega)$ is obtainable from the CPA calculations, providing us the understanding of the qualitative concentration dependence of $\rho_{4.2}$. Strictly speaking, when we define the coherent potential function as $p^{\text{CPA}}(\omega) = (\omega - \Sigma(\omega))/\Delta$ under the CPA calculations, the imaginary part of $p^{\text{CPA}}(\omega)$ is given by the following expression:

$$-\text{Im} \frac{\Sigma(\omega)}{\Delta} \approx \text{Im } p^{\text{CPA}}(\omega). \quad (8)$$

Figures 7(a) and (b) show the representative results of the CPA calculations of $\text{Im } p^{\text{CPA}}(\omega)$ for the magnetic quantum number $m = -1$ in the Mn d -state, for the compositions with 55 and 60% Pt, respectively. In these figures, the solid and dotted lines represent the results for the down spin and the up spin states, respectively. The ordinate is dimensionless, and then $\text{Im } p^{\text{CPA}}(\omega)$ gives the relative magnitude. It is clear that $\text{Im } p^{\text{CPA}}(\omega)$ at E_F increases with deviating from the equiatomic composition. The CPA calculations for the magnetic quantum number $m = 0$ and -2 in the Mn d -state, and for the compositions with 40 and 45% Pt have revealed a similar trend. In other words, the value of ρ_0 relative to that of the equiatomic alloy of MnPt increases with deviating from the equiatomic composition. It is well-known that the electrical resistivity of CuAu alloy system depends on the concentration and the degree of atomic order.⁴⁵⁾ In the disordered alloy system, the residual electronic resistivity exhibits a broad maximum at the equiatomic composition. On the other hand, it takes a minimum at the Au concentration of 25 and 50 at% in the ordered alloy system.⁴⁵⁾ In the present $L1_0$ -type MnPt alloy system, the concentration dependence of ρ is similar to that for CuAu ordered alloy system, although the variation of ρ_0 against to the Pt concentration for the $L1_0$ -type

Fig. 7 The imaginary part of the potential function from the CPA calculations $\text{Im } p^{\text{CPA}}$ as a function of energy ω for the magnetic quantum number $m = -1$ in the Mn d -state. (a) and (b) are the results for the alloys with 55 and 60% Pt, respectively.

Fig. 8 Concentration dependence of the calculated spin magnetic moments of Mn and Pt in $L1_0$ -type MnPt alloy system.

MnPt alloy system is significantly large. The substituted effect of Mn element on the electronic scattering would be more significant. To be exact, the effects on the electronic scattering of s - and p -states and s - d exchange interactions should be taken into the consideration in order to discuss the absolute value of ρ_0 for this alloy system, for example.

4.2 Magnetic moment and magnetic phase diagram

Shown in Fig. 8 is the concentration dependence of calculated spin magnetic moments of Mn and Pt for the

Fig. 9 Temperature dependence of the magnetic susceptibility χ of $L1_0$ -type MnPt alloys. (a) and (b) are the data for the concentration less or equal and more than 50% Pt, respectively. The arrows indicate the Néel temperature T_N defined from Figs. 1(a) and (b).

$L1_0$ -type MnPt alloy system. The calculated spin magnetic moment of Mn for the equiatomic composition is about $3.6 \mu_B$, smaller than the reported experimental value of about $4.3 \mu_B$ from neutron diffraction studies.^{5,6} In the off-equiatomic compositions, the Mn atoms substituted at the Pt site carry a large spin magnetic moment of about $2.5 \mu_B$, whereas the spin magnetic moment of Pt atoms substituted at the Mn site is very small less than $0.3 \mu_B$. This causes a difference between susceptibility of two antiferromagnetic sub-lattices.

Figures 9(a) and (b) show the temperature dependence of magnetic susceptibility χ measured in a magnetic field of 1 T for the $L1_0$ -type MnPt alloys with the concentrations less or equal and more than 50% Pt, respectively. The arrows in the figures indicate the Néel temperature T_N defined from the ρ - T curves in Figs. 1(a) and (b), and a clear anomaly associated with T_N is confirmed. The magnetic susceptibility χ exhibits an up-turn at low temperatures in the concentration range less than 50% Pt. Such behavior has been observed in the data of the $L1_0$ -type MnIr⁸) and MnNi⁹) alloy systems and also in our data of MnPd alloy system.³⁰ From neutron diffractions, their antiferromagnetic spin structure does order collinearly, and hence such an up-turn is thought to be caused by a slight canting of the magnetic moments.^{8,9} Furthermore, the magnitude of magnetic susceptibility at lower temperatures becomes larger with deviating from the equiatomic composition. The latter behavior would be attributed to the difference in the magnetic moment between two antiferro-

Fig. 10 Concentration dependence of the magnetic susceptibility at 4.2 K, $\chi_{4.2}$, for $L1_0$ -type MnPt alloy system.

magnetic sub-lattices in the off-equiatomic composition. That is, the excess Mn or Pt atom substituted at the opponent sites in the off-equiatomic composition has a spin magnetic moment. The value of the excess Mn substituted at the Pt site is much larger than that of the excess Pt substituted at the Mn site (see Fig. 8). Figure 10 shows the concentration dependence of magnetic susceptibility χ at 4.2 K $\chi_{4.2}$ for the $L1_0$ -type MnPt alloy system obtained from Figs. 9(a) and (b). The magnitude of $\chi_{4.2}$ becomes larger with deviating from the equiatomic composition. This behavior is more significant in the concentration range less than 50% Pt, reflecting the difference in the magnitude of the spin magnetic moments mentioned above.

The effective exchange constant J_0 curves as a function of the Fermi energy E_F of the $L1_0$ -type MnPt alloys in the collinear antiferromagnetic state in the concentrations less and more than 50% Pt is illustrated in Figs. 11(a) and (b), respectively, together with the result of 50% Pt. The abscissa is the upper value of the integral of eq. (1) and the actual E_F is located at the origin of the abscissa ($E_F = 0$). Therefore, these figures represent the variation of J_0 as a function of band-filling, number of the electrons, in the rigid band scheme. The value of J_0 gives an estimation of the Néel temperature T_N from eq. (3) in the molecular field approximation scheme. From these figures, it is evident that the value of J_0 for the composition with 50% Pt is largest and becomes smaller with deviating from the equiatomic composition. This behavior is in harmony with the experimental results of the concentration dependence of T_N . Although, the feature of the J_0 curve as a function of E_F does not so different in the off-equiatomic composition, the substitution mainly results in the decrease of the magnitude of J_0 . The value of J_0 for the alloy with 50% Pt is about 126 meV, corresponding to $T_N = 953$ K. This calculated T_N is in good agreement with the experimental values obtained from the present work and also the reported neutron diffraction data.^{5,6}

Plotted in Fig. 12 is the concentration dependence of the Néel temperature T_N obtained from the experiments and calculations. The solid circles and squares indicate T_N defined from the $d\rho/dT$ - T curves and estimated one from

Fig. 11 The effective exchange constant J_0 of $L1_0$ -type MnPt alloys as a function of the Fermi energy E_F . (a) and (b) are the results for the concentrations less or equal and more than 50% Pt, respectively.

Fig. 12 Concentration dependence of the Néel temperature T_N determined from the experiments and the calculations for $L1_0$ -type MnPt alloy system, together with the results reported by Krén *et al.*⁵⁾ The solid circles and squares stand for T_N defined from $d\rho/dT$ - T curves and estimated from the effective exchange constant J_0 , respectively. The open circles and triangles are the experimental Néel temperature T_N and the magnetic transition temperature T_m , respectively.⁵⁾

the effective exchange constant J_0 in Figs. 11(a) and (b), and eq. (3), respectively. The open circles stand for the experimental T_N reported by Krén *et al.*⁵⁾ From neutron diffractions,⁵⁾ it has been reported that additional magnetic transition below T_N can be observed only in the $L1_0$ -type MnPt alloy system among the MnTM (TM = Ni, Pd and Pt)

Fig. 13 Magnetic structures of II and III-type of $L1_0$ -type MnPt alloy system defined from neutron diffractions.^{5,6)}

alloy systems with the same crystal structure.⁶⁾ Krén *et al.* discussed possible four kinds of magnetic structures; I, II, III and VI in the $L1_0$ -type lattice,⁵⁾ and the magnetic structures II and III sketched in Fig. 13 have been considered to be established in the MnPt alloy system. As shown in the figure, below and above the magnetic transition temperature T_m , the direction of the magnetic moment changes from parallel (II) to perpendicular (III) to the c -axis, in other words, the magnetocrystalline anisotropy changes with the temperature and/or the Pt concentration. The magnetic structure changes in the sequence of the III $\rightarrow$ II $\rightarrow$ III-type with increasing Pt concentration. In addition, the magnetic structure change occurs from the II to III-type in different two concentration ranges. The magnetic transition has been observed from the 100 and 101 magnetic peaks in neutron diffractions, although no anomalous changes in the temperature dependences of magnetic susceptibility and the lattice constants have been confirmed.⁵⁾ In the present study, the temperature dependences of electrical resistivity ρ and magnetic susceptibility χ have also been measured in wide temperature regions. However, no clear anomalies associated with the magnetic transition have been confirmed (see Figs. 1 and 9). On the other hand, recently, neutron diffraction study using a single crystal of the $L1_0$ -type MnPt equiatomic alloy has been carried out and the existence of the magnetic transition around 750 K have been reconfirmed.⁴⁹⁾ Although the precise direction of the magnetic moment of Mn above T_m was not confirmed in the c -plane from powder neutron diffractions, it has become clear that the direction of the magnetic moment of Mn lies in the c -plane pointing to the $[010]$ direction.⁴⁹⁾ Krén *et al.*⁵⁾ examined the magnetic moments of Pt in the magnetic structure III. However, their analyses revealed that a good agreement between the calculated and experimental neutron diffractions was obtained by assuming zero magnetic moment of the Pt atoms.

4.3 Magnetocrystalline anisotropy energy

Figure 14 shows the calculated results of magnetocrystalline anisotropy energy (MAE) defined by eq. (4) as a function of electron number q/cell of the $L1_0$ -type MnPt equiatomic alloy, together with that of the $L1_0$ -type MnNi equiatomic alloy reported previously.²⁹⁾ The solid and dotted lines stand for the results of MnPt and MnNi with the equiatomic

Fig. 14 The magnetocrystalline anisotropy energy (MAE) defined by $\Delta E = E[100] - E[001]$ of $L1_0$ -type MnPt equiatomic alloy as a function of electron number of q , together with that of the $L1_0$ -type MnNi equiatomic alloy.²⁹⁾ The dashed vertical line stands for the actual valence electron number in the formula unit.

composition, respectively. The dashed vertical line stands for the actual valence electron number in the cell. Because the MAE is quite sensitive to the calculation condition, the MAE curves as a function of q are meaningful for the comparison with other calculated results. At the actual value of q ($= 34$), the MAE in the MnPt equiatomic alloy exhibits a positive value, revealing that the direction of the magnetic moments of Mn is parallel to the c -axis of the $L1_0$ -type structure. On the contrary, the MAE of the MnNi equiatomic alloy shows a negative value, indicating that the magnetic moments of Mn lie in the c -plane.²⁹⁾ These results are consistent with the magnetic structure determined by neutron diffractions.^{6,50)} Furthermore, the important point to note is that the variations of the MAE against q for the former alloy is more sensitive than that for the latter alloy. Especially, in the vicinity of the actual value of q ($= 34$), the MAE sets off the change of the sign from negative to positive. This fact implies that the sign of the MAE, in other words, the direction of the magnetic moment can be easily changed, depending upon the temperature and/or the concentration. Note that the spin structure in Figs. 12 and 13 is in accord with the present calculations for the $L1_0$ -type MnPt alloy system. Furthermore, our recent systematic theoretical calculations of the MAE for several kinds of $L1_0$ -type Mn alloy systems⁵¹⁾ are also consistent with the spin structure determined by neutron diffractions.^{5,6,10,50)}

In the tetragonal symmetry, the angular dependence of the MAE $E(\theta)$ is expanded as follows;

$$E(\theta) = K_0 + K_1 \sin^2 \theta + K_2 \sin^4 \theta \cdots, \quad (9)$$

where θ is the angle between the direction of magnetic moment and the c -axis, and K_1 and K_2 are the magnetocrystalline anisotropy constants. Combining eq. (4) with (9), ΔE is represented,

$$\Delta E = E(\theta = 90^\circ) - E(\theta = 0^\circ) = K_1 + K_2 = K. \quad (10)$$

The value of MAE at the actual value of q ($= 34$) is estimated to be about 0.51 meV/cell from Fig. 14. This leads the magnetocrystalline anisotropy constant K to be about

$1.39 \times 10^6 \text{ J m}^{-3}$, being larger in magnitude with the positive sign than that with the negative sign of about $-0.97 \times 10^6 \text{ J m}^{-3}$ for MnNi.²⁹⁾ The difference between the magnitude of MAE as a function of q for MnPt and MnNi would originate from the large spin-orbit coupling of the Pt atom.

It is useful to investigate the MAE of antiferromagnetic materials for spintronic devices. The exchange-bias field which is one of the characteristic properties of the spin-valve-type multilayers is considered to be closely correlated to the MAE of the antiferromagnetic layer, although the mechanism of the exchange coupling between the ferromagnetic and the antiferromagnetic layer is controversial. Several models for the exchange-bias H_E give the following expression^{52–55)}

$$H_E \propto \sqrt{KA}, \quad (11)$$

where K and A are the magnetocrystalline anisotropy constant and the exchange stiffness of the antiferromagnets, respectively. Consequently, we should notice that the antiferromagnets with a large magnetocrystalline anisotropy bring about a large value of H_E . Actually, the experimental result of the unidirectional anisotropy field for MnPt¹²⁾ is larger than that for MnNi,¹¹⁾ reflecting the difference in magnitude of the magnetocrystalline anisotropy constant mentioned above.

5. Conclusion

The relation between the antiferromagnetic stability and the electronic structure for $L1_0$ -type MnPt alloy system has been investigated. The measurements of electrical resistivity, magnetic and low-temperature specific heat capacity have been carried out. Furthermore, the band calculations by using the tight-binding linear muffin-tin orbital (LMTO) method based on the local spin density approximation (LSDA) with the coherent potential approximation (CPA) have been performed. In addition, the LMTO band calculations including the spin-orbit interaction have been carried out in order to discuss the relation between the magnetocrystalline anisotropy energy and the spin structure. Characteristic antiferromagnetic properties associated with a pseudo-gap in the electronic structure emerge in the present study. The main results are summarized as follows:

- (1) The temperature dependence of electrical resistivity ρ exhibits a hump just below the Néel temperature T_N , being characteristic to pseudo-gap-type antiferromagnets.
- (2) From the LMTO band calculations, it is evident that the density of states (DOS) at the Fermi energy E_F of the equiatomic composition is lowest and the pseudo-gap becomes sluggish with deviating from the equiatomic composition. These results are in accord with the concentration dependence of the experimental electronic specific heat coefficient γ_e , especially, in the concentration range more than 50% Pt.
- (3) The magnitude of electrical resistivity at 4.2 K $\rho_{4.2}$ is lowest in the vicinity of the equiatomic composition and increases with deviating from the equiatomic composition. The increase of resistivity would be mainly attributed to a significant decrease of the relaxation time.

- (4) The magnitude of magnetic susceptibility χ becomes larger with deviating from the equiatomic composition. This is caused by the magnetic moment of excess Mn and Pt substituted at the opponent sites in the off-equiatomic compositions, that is, the difference in susceptibility between two antiferromagnetic sub-lattices.
- (5) The concentration dependence of the Néel temperature T_N estimated from the effective exchange constant J_0 is in accord with the experimental values defined from the resistivity-temperature curves. The substitution results in the decrease of the magnitude of J_0 , although the feature of the J_0 curve scarcely depends on the composition.
- (6) The LMTO band calculations including the spin-orbit interaction bring out that the direction of the magnetic moment of Mn is parallel to the c -axis in the $L1_0$ -type structure, in contrast to MnNi equiatomic alloy in which the magnetic moments of Mn lie in the c -plane.
- (7) The magnetocrystalline anisotropy of the $L1_0$ -type MnPt alloy is significantly sensitive to the electron number q , associated with the fact that the $L1_0$ -type MnPt alloy system exhibits a complicated magnetic phase diagram.
- (8) The magnetocrystalline anisotropy constant K of the MnPt equiatomic alloy is calculated to be about $1.39 \times 10^6 \text{ J m}^{-3}$, larger in magnitude with the positive sign than that with the negative sign of the MnNi equiatomic alloy.

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