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Journal of Magnetism and Magnetic Materials 187 (1998) 105–112

Journal of magnetism and magnetic materials

Electronic structures and magnetism of CuAu-type MnNi and MnGa

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Received 24 June 1997; received in revised form 28 October 1997

Abstract

Electronic and magnetic structures of CuAu-type MnNi and MnGa have been studied by LMTO-ASA including the spin–orbit interaction in the frame of the LSD. In MnNi, the anti-parallel arrangement of the Mn moments lowers the electronic energy by forming a pseudo-gap in the energy bands. The Mn moment lies in the *c*-plane with a value of 3.29 μ_B. The magnetocrystalline anisotropy constant, K_u is found to be -9.7×10^5 J/m^3. In MnGa, the hybridization between the Mn d electrons and the delocalized Ga p electrons promotes an itineracy of the Mn d electrons. This reduces the Mn moment to 2.51 μ_B but aligns the moments ferromagnetically along the *c*-axis with K_u of 2.6×10^6 J/m^3. Based on these two results, we have discussed the condition of metallic ferromagnetism of the Mn alloys.

Keywords: Manganese alloys; Ferromagnetism; Anti-ferromagnetism; LMTO-ASA; Magnetocrystalline anisotropy

1. Introduction

Recent progress of the (thin film) fabrication technique of transition metal alloys makes it possible to prepare the high-quality samples of ordered alloys with stoichiometric composition. Especially, the films of Mn ordered alloys have attracted much concern for use in a value-added device. Recently, CuAu-type MnAl [1] and MnGa [2] ferromagnetic metals with uniaxial anisotropy have been grown on semiconductor substrates for laying the technological foundation and developing hybrid devices. On the other hand, MnNi, the same crystal structure as MnGa, is an anti-ferromagnetic metal with planar magnetic anisotropy. Although, up to the present, anti-ferromagnetic materials have not been employed for practical use, some anti-ferromagnetic Mn alloys including MnNi are recently expected to have a potential application for the use in the magneto-resistance (MR) heads and spin-valve heads for the magnetic recording.

In these Mn alloys, not only the magnetic moments but also the magnetic anisotropy plays an important role in the industrial use. However, the intrinsic properties of these alloys have not yet been established because of the difficulty of both the preparation of high-quality samples and the direct

0304-8853/98/$19.00
PII: S0304-8853(98)00115-2

measurements of the magnetic properties. In addition, we consider that these materials provide a good stage for the study of magnetism of the transition metal system.

Previously, we investigated the magnetic structure of MnAl based on the band calculation [3]. As for MnNi, Yamashita et al. [4] showed the electronic structure, and discussed the magnetism except for the magnetic anisotropy. In the present work, we study the electronic and magnetic structures including magnetic anisotropy of MnNi and MnGa using the linearized muffin-tin orbital method combined with atomic sphere approximation (LMTO-ASA) based on the local spin density functional theory, and discuss the mechanism of metallic ferromagnetism of Mn alloys.

2. Method of calculation

The LMTO-ASA [5,6] was employed to perform a semi-relativistic band calculation in the frame of local spin density (LSD) functional method. The exchange-correlation term was adopted as the form of Barth and Hedin [7] with parameters given by Janak [8]. The core charge density was used as a so-called frozen core. For valence states, we adopted the s-, p- and d-basis functions for Mn, Ni atoms and s- and p-basis functions for Ga. For the calculation of the orbital moment and the magnetocrystalline anisotropy energy (MAE), the spin–orbit interaction is introduced in the LMTO Hamiltonian. We followed the manner given by Andersen [5] for evaluating the spin–orbit coupling and constructing the spin–orbit matrix in the LMTO Hamiltonian. The MAE was obtained from $\Delta E = E[1\,0\,0] - E[0\,0\,1]$ where $E[n]$ is sum of eigenvalues of the Kohn–Sham equation over occupied states when the magnetic moment is parallel to $[n]$ defined in the crystal axis of CuAu($L1_0$)-type structure in Fig. 1a. The details of the method can be seen in our previous paper [3].

Fig. 1a shows CuAu-type crystal structure where the open circles denote Mn atoms and closed circles Ga or Ni atoms. In this work, we adopt the super cell structure shown in Fig. 1b as a unit cell in order to perform the systematic calculation both for ferromagnetic and anti-ferromagnetic structures on the same footing. Here we account for two types of anti-ferromagnetic structures denoted by AF-I and AF-II whose magnetic structures are indicated in the caption for Fig. 1a. Lattice constants defined in the $L1_0$ cell (Fig. 1a) for MnNi and MnGa are set as $a = 3.74$ Å, $c = 3.52$ Å [9] and $a = 3.897$ Å, $c = 3.625$ Å [10], respectively, from the experimental measurements. The atomic sphere radii are set at $r_{Mn} = r_{Ni} = 2.70673$ a.u. for MnNi and $r_{Mn} = r_{Ga} = 2.74245$ a.u. for MnGa.

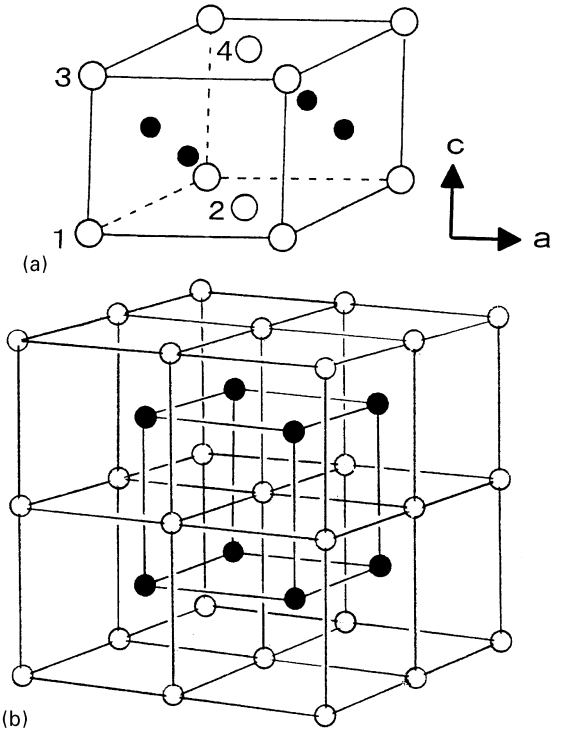

Fig. 1. (a) Crystal structure of CuAu ($L1_0$)-type Mn alloy. The open circles denote Mn atoms and the closed circles Ni or Ga atoms. The anti-ferromagnetic structure defined by AF-I has a relation $M_1 = -M_2 = M_3 = -M_4$, where M_i denotes the Mn moment on the i site labeled in the figure, and AF-II type is defined by $M_1 = -M_2 = -M_3 = M_4$. (b) Super cell structure adopted in the present calculation.

3. Results and discussion

3.1. MnNi

Fig. 2 shows the density of states (DOSs) of MnNi for several magnetic states. The local DOS of

Mn at the Fermi level, ρ_F for the NM (non-magnetic) state is around 24/(Ry spin atom). The product of ρ_F with the Stoner parameter I for the Mn atom ($\fallingdotseq$ 0.066 Ry) reaches 1.6. Though the value narrowly satisfies the Stoner condition of the ferromagnetism, the total energy calculations indicate that the ground state is the AF-I state at the lattice constants given here. The energy differences from the FM (ferromagnetic) state and the AF-II state are about 200 and 54 meV/atom, respectively. It is remarkable to observe that the ρ_F of the AF-I state is quite low for both spin states, that is, the pseudogap is formed at the Fermi level, E_F. The magnetic moment of the Mn atom estimated within the atomic sphere is 3.29 μ_B and one of the Ni atom is non-magnetic. The calculated Mn moment is considerably smaller than that of neutron data measured by Kasper et al. [9] which suggested around 4 μ_B.

As a reference, we have further performed band calculation for the same structure as MnNi by setting empty spheres at the Ni sites. Let us call this structure nominally MnE, hereafter. Fig. 3 shows the calculated results. The ground state of MnE is also found to be anti-ferromagnetic, although, contrary to MnNi, the AF-II state has the lowest

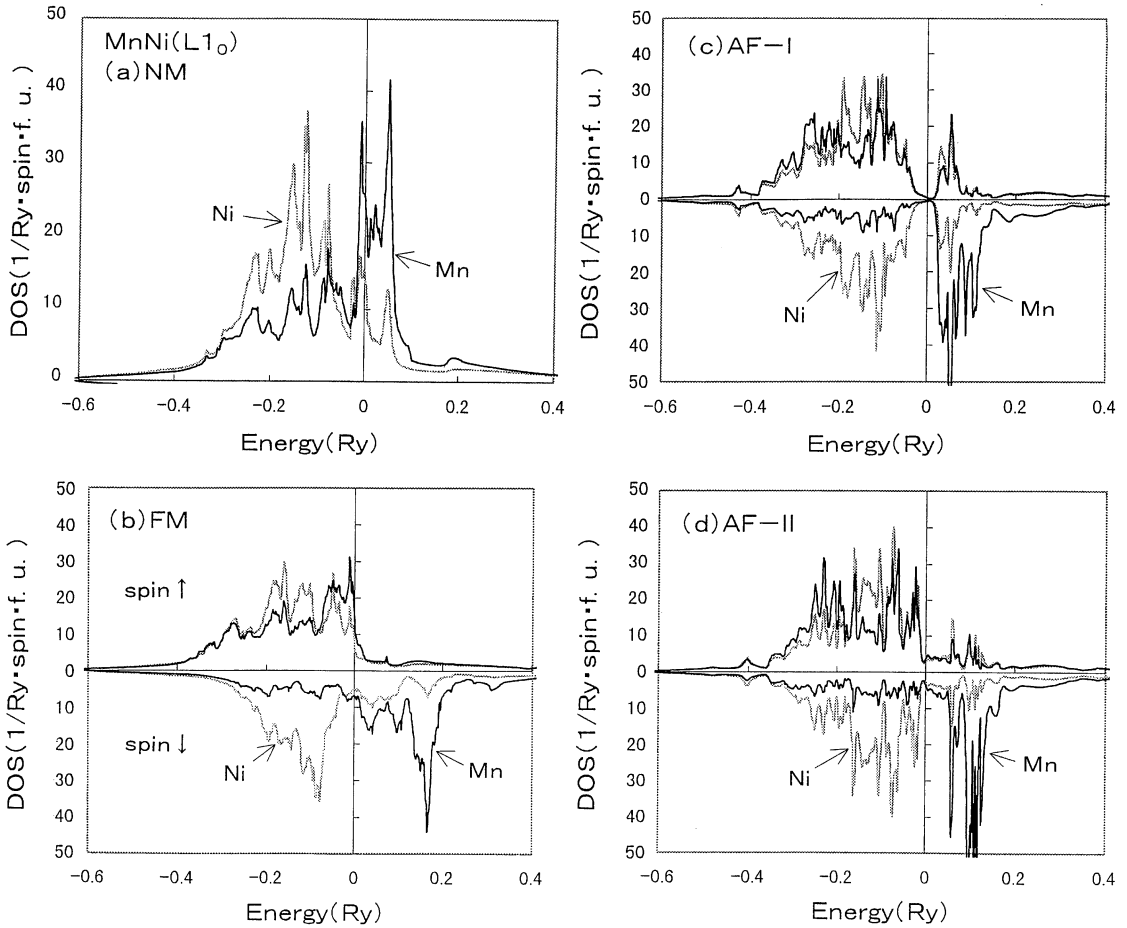

Fig. 2. Local density of states of Mn and Ni sites in MnNi for (a) non-magnetic (NM), (b) ferromagnetic (FM), (c) AF-I type and (d) AF-II type states. The energy is measured with respect to the Fermi energy, E_F.

energy. The magnetic moment of the Mn atom of the AF-II state reaches 4.02 μ_B which results from nearly full polarization within the Mn atom. Judging from the number of d electrons in MnE (about 5.2) which is nearly equal to that of the isolated Mn atom, the magnetic moment of 4.02 μ_B may be a reasonable value for this layered structure each of which is separated by an empty layer. Once this value is accepted, the moment of 4 μ_B for MnNi suggested from neutron measurement may be too large since Ni atoms may bring a delocalization to Mn d electrons, at least than the empty spheres do.

As for the ferromagnetic case of MnNi (Fig. 2b), the pseudo-gap vanishes and the itineracy seems to be fulfilled. This may indicate that the pseudo-gap in the anti-ferromagnetic state is attributed to the staggered field due to the anti-ferromagnetic arrangement of spins. Though the magnetic moment of the Mn atom is nearly the same as that in the AF-I state, 3.2 μ_B, the magnetic moment of the Ni atom is quite larger, that is 0.6 μ_B, and parallel to that of the Mn atom. This can be interpreted as follows. When the magnetic moments of the Mn atoms are arranged ferromagnetically, the spin polarized Ni atoms with the same direction as the Mn

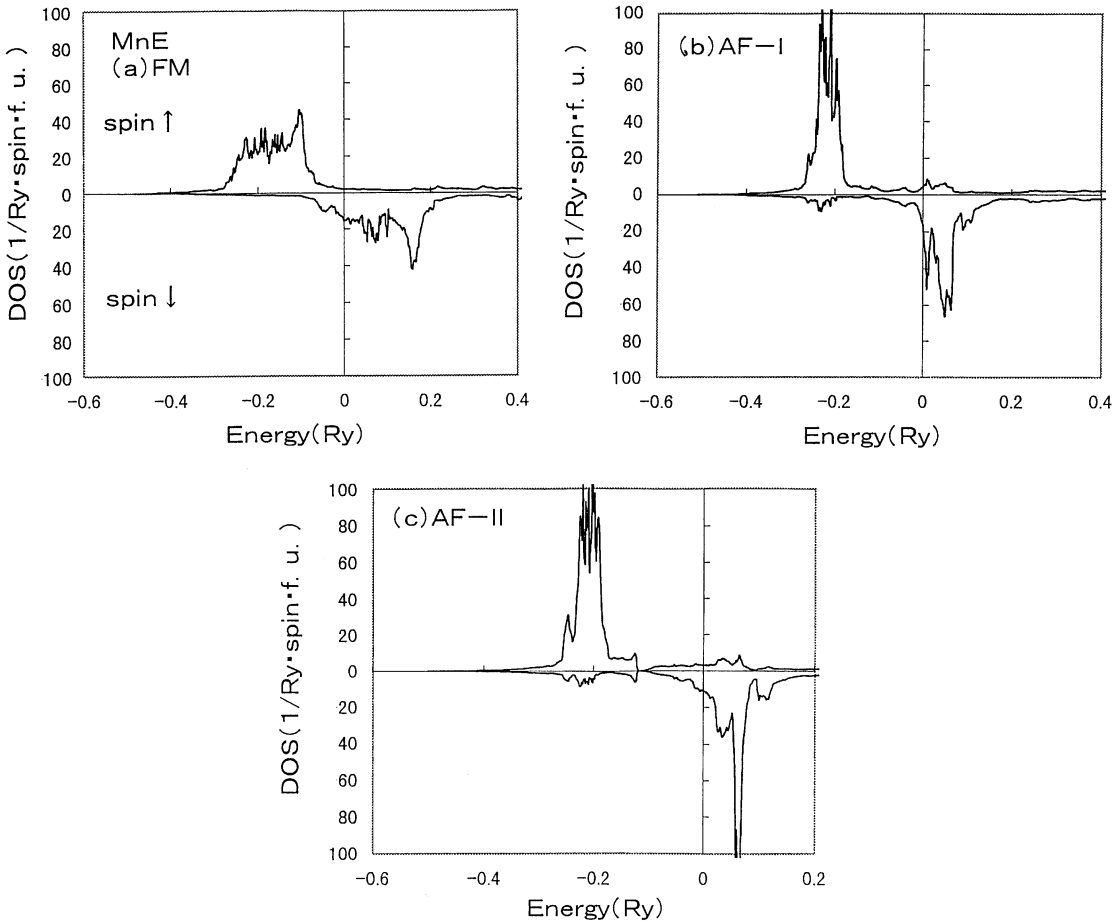

Fig. 3. The density of states of MnE in which the empty spheres denoted by E are located at the Ni sites for (a) ferromagnetic (FM), (b) AF-I type and (c) AF-II type states. The energy is measured with respect to the Fermi energy, E_F.

atoms may provide a more flat potential for electrons and save kinetic energy by spreading the bandwidth.

Fig. 4 shows the calculated results of MAE (defined by ΔE) as a function of band filling q (valence electron number) for the AF-I type MnNi. Because the MAE is quite sensitive to the calculation condition, the ΔE versus q plot is useful when one makes a comparison of his/her calculated results with the present one. At an actual value of q ($=17$), MAE has a negative value. This means that the magnetic moments lie in the c-plane, which is consistent with the result of neutron-diffraction measurement by Kasper et al. They concluded that the magnetic easy direction is either [1 0 0] or [1 1 0]. The calculated energy difference between E[1 0 0] and E[1 1 0] has been found to be less than 10^{-9} Ry/atom. This is too small for us to determine the magnetic easy direction in the c-plane within an accuracy of the present calculation. From ΔE, the magnetocrystalline anisotropy constant is estimated as $K_u = -9.7 \times 10^5$ J/m^3.

In addition, we have calculated the MAE for MnE of the AF-II state. The absolute value of ΔE was less than 10^{-7} Ry/atom, which means that the magnetic moment of MnE is almost isotropic, in spite of its structural anisotropy. Thus the Ni atoms in MnNi, although non-magnetic, are confirmed to have a considerable influence on the magnetic anisotropy.

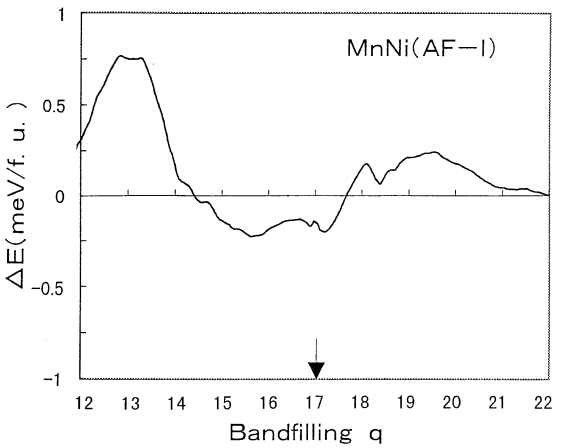

Fig. 4. Magnetocrystalline anisotropy energy (MAE) defined by $\Delta E = E$[1 0 0] $- E$[0 0 1] of MnNi as a function of band filling q. The arrow indicates the actual valence electron number in the formula unit.

3.2. MnGa

In Fig. 5, we show the calculated DOS for several magnetic states. The DOS of the NM state has a sharp peak just at the E_F, which leads us to expect that MnGa is ferromagnetic. In fact, the product of ρ_F with the Stoner parameter I gives 2.3 which overcomes far beyond the Stoner criteria, and comparison of the total energies of these states shows that the ground state is a ferromagnetic state at the given lattice constants. The energy difference between the FM and AF-I states is around 33 meV/atom. Besides, the DOS has a sharp peak at the E_F, the bandwidth including the low-energy tail below the E_F is quite larger than that of MnNi. This is mainly attributed to the delocalization of the p orbitals of Ga atoms, contrary to the case of Ni atoms in MnNi. There is less remarkable distinction between the DOSs of FM and AF states than in MnNi. This may reflect a situation given below. The hopping strength of Mn d electrons is enhanced by the hybridization with the p electrons of Ga atoms and overcomes the exchange splitting of the Mn atoms. This diminishes the difference of the DOSs of different arrangements of the magnetic moments. Actually, the magnetic moments of the Mn atom estimated within the atomic sphere (2.51 μ_B for the FM state and 2.61 μ_B for the AF state) are considerably smaller than that of MnNi. However, the value of 2.51 μ_B for the FM state is still larger than that obtained experimentally by Hasegawa and Tsuboya [11], that is 1.7 μ_B. The discrepancy from the present result may be associated with the excess Mn atoms over 50 at% of the sample, whereas they accounted for the deviation of the Mn content to derive the moment. The excess Mn atoms not only have an anti-parallel moment to the rest but also cause a change of the lattice constant. The calculated moment of the Ga atom is -0.09 μ_B, that is anti-parallel to the Mn moment. In Table 1, we summarize the calculated results of MnNi (AF-I), MnGa (FM) and MnE (AF-II).

From the above results and the comparison with one for MnNi and MnAl of our previous work, occurrence of the ferromagnetism of CuAu-type

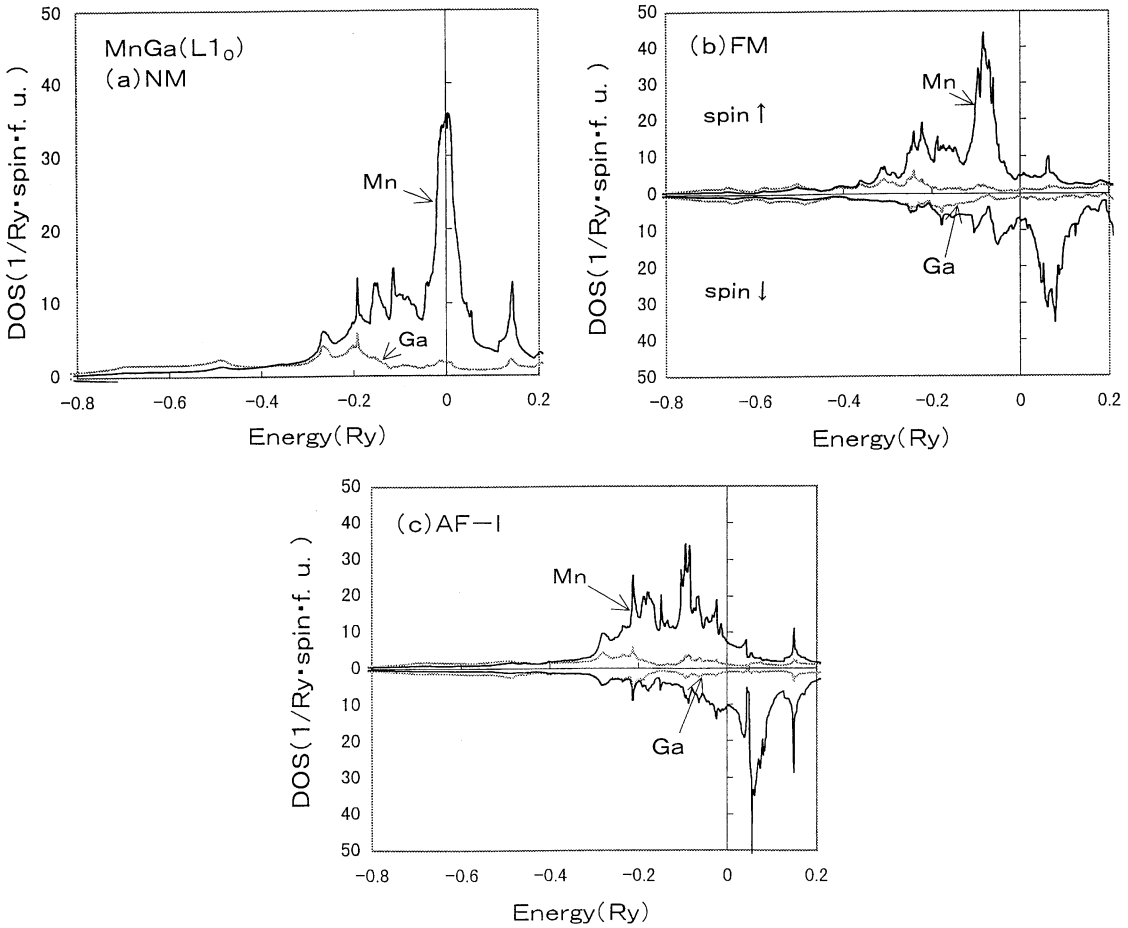

Fig. 5. Local density of states of Mn and Ga sites in MnGa for (a) non-magnetic (NM), (b) ferromagnetic (FM), (c) AF-I type and (d) AF-II type states. The energy is measured with respect to the Fermi energy, E_F.

Table 1
Number of d electrons ($n_{(Mn)\ d}$) on Mn site, the spin (S) and orbital (L) magnetic moments (in μ_B) on Mn and Ni or Ga sites, and the magnetocrystalline anisotropy constant (K_u) of MnNi (AF-I), MnGa (FM) and MnE (AF-II)

	$n_{(Mn)\ d\uparrow}$	$n_{(Mn)\ d\downarrow}$	S_{Mn}	L_{Mn}	$S_{Ni,Ga}$	$L_{Ni,Ga}$	K_u (10^5 J/m^3)
MnNi (AF-I)	4.33	1.18	3.255	0.028	–	–	− 9.69
MnGa (FM)	4.07	1.66	2.449	0.056	− 0.088	0.005	26.14
MnE (AF-II)	4.53	0.65	4.02	0.000	–	–	–

Mn alloys can be interpreted as follows. In MnGa and MnAl, p electrons of Ga and Al atoms give an adequate itineracy to the d electrons of Mn atoms through their hybridization. In a single-particle scheme, in this case, the ferromagnetic arrangement stabilizes the band energy because it provides a flat potential for the electrons of each spin. The key feature in this case is that the hybridization

between the p and d orbitals does not give rise to multiple minima in the d bands which can be seen in the case of MnNi, but maintains the sharp peak of the d bands. Due to this highly degenerate (sharp) d bands, which are located at the E_F in the NM state, the ferromagnetic arrangement does not consume the kinetic energy so much under the restraint of the Pauli principle in the many electron system. To realize this situation, it is also necessary for these moving electrons to have a strong intra-atomic Coulomb interaction. In this sense, the five d orbitals of different degrees of localization take great advantage of the ferromagnetism.

Finally, we show the calculated results of MAE of MnGa in Fig. 6. At around $q = 8$ it takes a prominent negative value and recovers to be positive at an actual value of $q = 10$. This behavior of ΔE versus q is quite similar to that of MnAl which was reported previously by the present author [3]. The value of ΔE at $q = 10$ is 0.42 meV/f.u. for MnGa, while that for MnAl was 0.26 meV/f.u. From this we obtain the magnetocrystalline anisotropy constant as $K_u = 2.6 \times 10^6$ J/m^3, which is about twice the measured value of MnAl. As for MnGa, unfortunately, an information about the measured value has not yet been given.

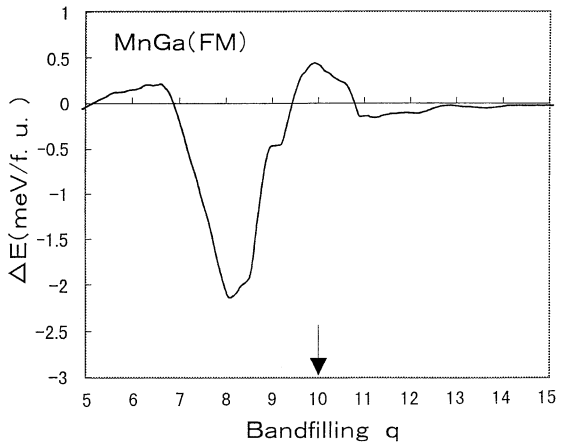

Fig. 6. Magnetocrystalline anisotropy energy (MAE) defined by ΔE of MnGa as a function of band filling q. The arrow indicates the actual valence electron number in the formula unit.

4. Summary

In order to gain insight into the intrinsic magnetic properties of CuAu-type MnNi and MnGa, the electronic and magnetic structures have been investigated by LMTO-ASA based on the LSD. The results are summarized as follows.

The d electrons of Mn atoms in MnNi are considerably localized, which gives rise to large spin polarization within each Mn atom. To realize the inter-atomic coupling (electron hopping) by keeping both the large spin polarization and the Pauli principle, the magnetic moments of Mn atoms are forced to be arranged anti-ferromagnetically. The anti-parallel arrangement of the moments lowers the electronic energy by forming a pseudo-gap in the energy bands. This is brought about by both a staggered potential and the number of d electrons close to the half-filled state. The magnetic moment of the Mn atom is shown to be restricted in the c-plane with a value of 3.29 μ_B. The calculated value of K_u is -9.7×10^5 J/m^3.

In MnGa, the d electrons in Mn atoms have a relatively strong itineracy through a hybridization with the delocalized p electrons of Ga atoms and the intra-atomic exchange splitting is decreased. This brings about the empty states in the majority spin states. In this situation electrons favor the ferromagnetic arrangement of the moments since it gives a flat potential for electrons and lowers the energy gravity of the occupied states. The key feature is that the hybridization between p and d electrons maintains a sharp peak of the d bands, which suppresses the kinetic energy consumption for the ferromagnetic arrangement of spins. The magnetic moments are found to be 2.51 and -0.09 μ_B for Mn and Ga, respectively, with uniaxial anisotropy. The value of K_u is 2.6×10^6 J/m^3.

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