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Electronic Structure and Magnetocrystalline Anisotropy Energy of MnAl

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The spin-polarized band calculations including spin-orbit interaction for τ-phase ($L1_0$) MnAl have been performed with LMTO-ASA method in the frame of LSD. It has been predicted that the MnAl has a magnetic moment of 2.4 μ_B with a help of the tetragonal distortion from cubic B2 to $L1_0$ structure. The magnetocrystalline anisotropy energy (MAE) is obtained as (0.26 ± 0.01) meV/f.u. This leads to 1.5×10^6 J/m^3 for magnetic anisotropy constant which is comparable to the measured value $\sim 10^6$ J/m^3. The dependence of the MAE on axial ratio c/a also reflects the influence of the tetragonal distortion, that is, the MAE shows drastic change from negative to positive at the vicinity of $c/a = 0.7071$ which corresponds to cubic B2 lattice. For larger value of c/a, MAE decreases with increasing c/a and goes into negative again for $c/a > 1.2$.

[the LMTO method, electronic structure, LSD functional approximation, MnAl, magnetocrystalline anisotropy energy, magnetic moment]

§1. Introduction

Magnetocrystalline anisotropy energy (MAE) is a key feature in the magnetic properties for permanent magnets. In high performance rare earth-transition metal intermetallic compounds, $4f$ electrons in the rare earth play a major part of MAE. However, the contribution from the $3d$ transition metals is not generally negligible at a room temperature region. The MAE originating from the $4f$ electrons can well be understood with a crystalline electric field analysis using one-ion Hamiltonian,[1] though there still remain quantitative problems in terms of the adjustable parameters. The MAE due to the transition metal lattice, on the other hand, must be treated with a spin-polarized band calculation including spin-orbit interaction.[2-9] However, so far it is very hard to get the satisfactory results of the magnetic anisotropy behavior of transition metal systems, both qualitatively and quantitatively. The difficulty mainly lies in minute quantities of the MAE relative to the band energy.

In this sense, MnAl and CoPt attract much concern because of their large MAE without rare earth ions. YCo_5 and related compounds also have large MAE originating to Co atoms. But, MnAl and CoPt form very simple and typical crystal structure of binary transition metal ordered alloys, and then the investigation of these materials is expected to give us much information about the MAE of transition metal systems. In addition, because the ordered τ-phase MnAl is metastable, the intrinsic properties such as magnetic moment and MAE have not yet been clarified, both experimentally and theoretically.

In the present work, the spin-polarized band calculations for MnAl have been performed in the frame of local spin density functional (LSD) approximation including spin-orbit interaction. We focus our attention to the relationship between the MAE and axial ratio c/a of τ-phase MnAl, because it is not clear how an elongation or collapse of the tetragonal structure relates to MAE. Further we have examined the influence of the calculation conditions on MAE such as number of $\boldsymbol{k}$-points in the Brillouin Zone (BZ), procedure dealing with the rotation of magnetization direction and correction to the atomic sphere approximation (ASA) in the liner-muffin-tin orbital (LMTO) method.

§2. Method of Calculation

For the calculations of the magnetic moments and the total energies, the LMTO method[10,11] with ASA has been employed to perform a semi-relativistic band calculation without spin-orbit interaction in the frame of LSD. The exchange-correlation term takes the form of Barth and Hedin[12] with parameters given by Janak.[13] The core charge density is calculated with the Dirac equation for a free atom and the result is used as a so-called frozen core. For valence states, we have employed *s*, *p* and *d* basis functions for Mn and *s* and *p* for Al atoms. The density of states are evaluated by tetrahedron method.

For the calculation of orbital magnetic moments and the MAE, the spin-orbit interaction is introduced in the LMTO Hamiltonian. We have followed the manner given by Andersen[10] for evaluating the spin-orbit coupling and constructing the spin-orbit matrix in the LMTO Hamiltonian. With use of the force theorem,[14] the MAE can be obtained as a difference of sums over occupied eigenvalues of the Kohn-Sham equation

$$\Delta E[\hat{n}]=\sum_{i,\boldsymbol{k}}^{\text{occ.}}\varepsilon_i(\hat{n},\boldsymbol{k})-\sum_{i,\boldsymbol{k}}^{\text{occ.}}\varepsilon_i(\boldsymbol{k}), \qquad (1)$$

where $\varepsilon_i(\hat{n},\boldsymbol{k})$ and $\varepsilon_i(\boldsymbol{k})$ are the Kohn-Sham eigenvalues calculated for magnetization direction of $\hat{n}$ and [001], respectively. Generally, there are two ways to deal with rotating the magnetization direction. One is to rotate the spin quantization axis with respect to the crystal axis. In this case, the spin-orbit matrix, $\boldsymbol{l}\cdot\boldsymbol{s}$, is given as

$$\begin{aligned}\boldsymbol{l}\cdot\boldsymbol{s}=\;&l_x((\alpha_2 s_{x'}+\alpha_1\alpha_3 s_{y'})/p+\alpha_1 s_{z'})\\&+l_y((-\alpha_1 s_{x'}+\alpha_2\alpha_3 s_{y'})/p+\alpha_2 s_{z'})\\&+l_z(-p s_{y'}+\alpha_3 s_{z'}),\end{aligned} \qquad (2)$$

where $(\alpha_1, \alpha_2, \alpha_3)$ is the direction cosine of the new spin quantization axis z' and $p=(\alpha_1^2+\alpha_2^2)^{1/2}$. This treatment was first employed by Mori *et al.*[2] and recently by Li *et al.*[7] Another way was introduced by Ebert[4] and is to rotate the magnetization direction by a unitary transformation of structure constants,

$$\begin{aligned}\tilde{S}_{L',L}(\boldsymbol{k})=&\sum_{L''}\sum_{L'''}D_{L',L''}{}^*(\alpha,\beta,\gamma)S_{L'',L'''}(\boldsymbol{k})\\&\times D_{L,L'''}(\alpha,\beta,\gamma),\end{aligned} \qquad (3)$$

where (α, β, γ) are the Euler angles specifying the rotation and $D_{L',L''}$ $(L=(l, m))$ are the rotation matrix[15] of the spherical harmonics. This operation corresponds to the rotation of the total angular momentum $\boldsymbol{j}=\boldsymbol{l}+\boldsymbol{s}$ with respect to the crystal frame and thus can be considered more appropriate than the former way for investigation of the MAE. So in the present study we basically take the latter method throughout the paper except for examining the difference in the results derived by these two ways.

Figure 1 shows the crystal structure of τ-phase MnAl with L1$_0$ structure.[15] As shown in Fig. 1, the L1$_0$ structure can be reduced to the primitive structure which is regarded as a tetragonally distorted B2 type structure. In the

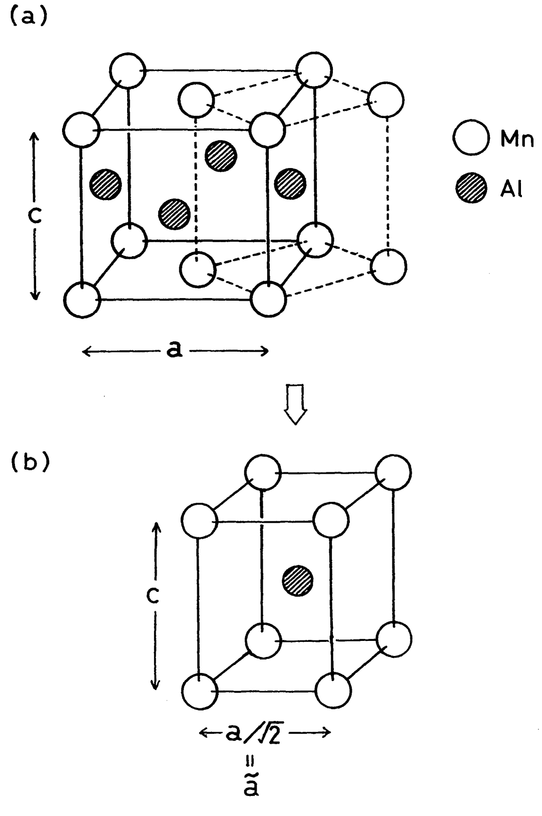

Fig. 1. Crystal structure of τ-phase MnAl with (a) L1$_0$ (a=3.93 Å, c=3.56 Å) and (b) tetragonally distorted B2 ($\tilde{a}$=2.779 Å, c=3.56 Å) representations.

present work we basically adopted the $L1_0$ structure as a unit cell including four atoms in the cell, (0, 0, 0), (1/2, 1/2, 0) for Mn and (1/2, 0, 1/2), (0, 1/2, 1/2) for Al. The primitive structure, the smallest unit cell including two atoms, is also employed only to investigate the influence of choosing the unit cell on the MAE. The atomic sphere (Wigner-Seitz) radius is set at $r_{WS}=2.8082$ a.u. for each atom.

§3. Results and Discussion

3.1 *Density of states and the magnetic moments*

The spin-polarized density of states (DOS) of $L1_0$-MnAl with $c/a=0.9058$ ($c/\tilde{a}=1.281$ in primitive cell) is shown in Fig. 2. The long tail in the range 0–0.5 Ry is attributed mainly to the Al *s* states and partly to the Mn *s* states. The Al *p* states have a small component around 0.6 Ry while the Mn *p* states spread over the valence band. The main structure between 0.5 and 0.9 Ry is due to the Mn *d* bands. The Fermi energy, E_F is pinned at the dip position of the DOS constructed of the *d* states, which stabilizes the system with a help of spin polarization. In fact, E_F of paramagnetic state is found to be located at the highest peak in DOS, which satisfies the Stoner criteria sufficiently.

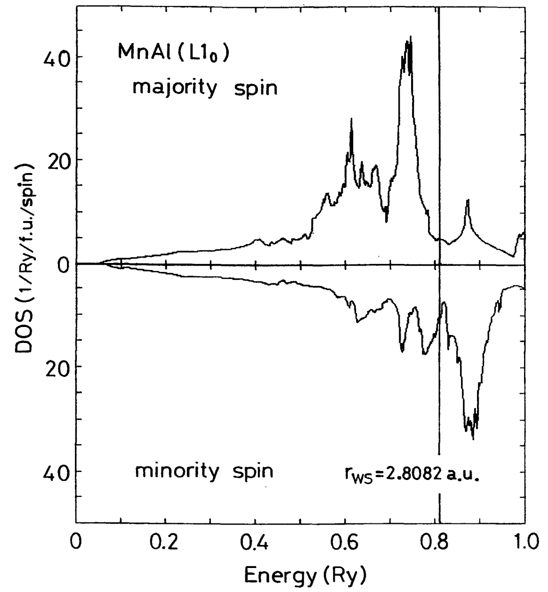

Fig. 2. Density of states of $L1_0$-MnAl with $c/a=0.9058$. The vertical line corresponds to the Fermi energy, E_F.

The local magnetic moment estimated within each atomic sphere is 2.422 μ_B for Mn atom and $-0.097\,\mu_B$ for Al atom. The total moment per formula unit amounts to 2.325 μ_B. The value seems too large comparing with the value expected from several measurements, $\sim 1.5\,\mu_B$.[16,17] According to Blau *et al.*,[18] the local moment of Mn atom should be larger than 1.5 μ_B, because the τ-phase MnAl is observed only near the composition $Mn_{1.11}Al_{0.89}$ and the excess Mn in the Al sublattice are coupled antiferromagnetically to the Mn sublattice. They have performed a band calculation for paramagnetic B2 cubic structure (mean lattice constant 2.98 Å), and estimated the theoretical value M_{Mn}^{theo} from the Stoner theory of (1.8 to 2.0) μ_B which coincides with the measured value M_{Mn}^{exp} of their best sample. Actually, for the cubic B2 structure we also get a Mn moment of 2.039 μ_B and total moment of 1.975 μ_B. This is consistent well with the value estimated by Blau *et al.* To inspect why M_{Mn} in the $L1_0$ phase is so larger than that in B2, we show in Fig. 3 DOS of cubic B2 type MnAl with the same volume as $L1_0$ type. The DOS of minority spin states are quite similar to paramagnetic DOS by Blau *et al.* and the positions of E_F both in majority and minority spin states are well agreeable to their prediction. Comparing with the DOS of $L1_0$ type in Fig. 2, it is found that the DOS of the minority spin at E_F in B2 is much higher than that in $L1_0$. This provides an aspect that the tetragonal distortion from cubic B2 to $L1_0$ structure gives a splitting of the *d* bands by destroying the degeneracy at the E_F and it may further promote the spin polarization. This may be regarded as a so-called solid state Jahn-Teller effect as Blau *et al.* pointed out. Such speculation is supported by the results shown in Fig. 4 where the M_{Mn} are plotted as a function of c/a. We find that M_{Mn} starts to grow just above $c/a=0.7071$ ($c/\tilde{a}=1$), which reflects that E_F gets out of the peak in DOS. At the measured value $c/a=0.9058$, M_{Mn} becomes stable by pinning E_F in the dip of DOS. In Fig. 4, we have also shown the total energies of the crystal as a function of c/a. Under the condition of the constant unit cell volume, the results indicate that the most

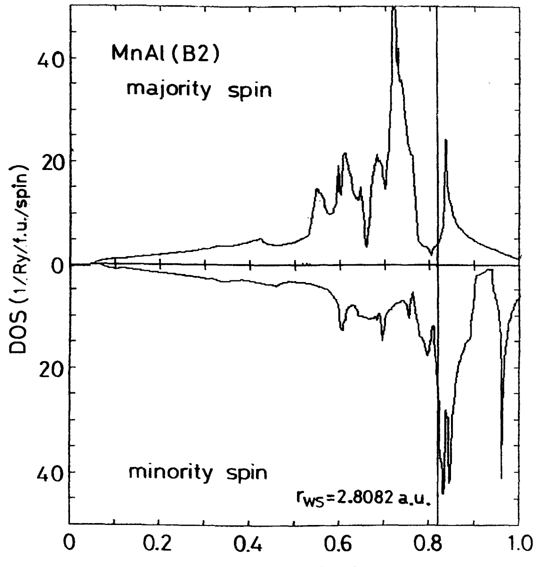

Fig. 3. Density of states of cubic B2-MnAl with the same volume as $L1_0$ type in Fig. 2.

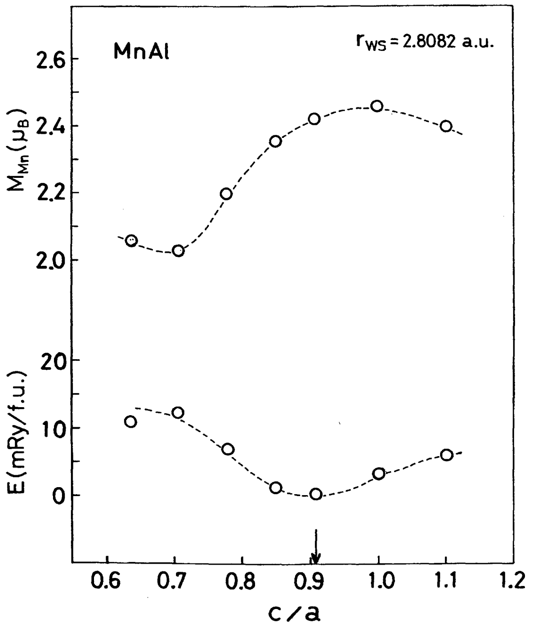

Fig. 4. Magnetic moment of Mn atom, M_{Mn} and the total energy of MnAl as a function of axial ratio c/a. The arrow indicates the measured c/a (=0.9058).

preferable axial ratio is around c/a=0.9058. Therefore the tetragonal distortion makes the system stable, being accompanied with the enhancement of the spin polarization.

Table I. Spin-orbit coupling ξ (in Ry), the spin magnetic moments s_z (in μ_B) and the orbital magnetic moments l_z (in μ_B) estimated within each atomic sphere in MnAl.

	$\xi_p^{\uparrow}$	$\xi_p^{\downarrow}$	$\xi_d^{\uparrow}$	$\xi_d^{\downarrow}$	s_z	l_z
Mn	0.0092	0.0092	0.0032	0.0025	2.442	0.059
Al	0.0016	0.0017	—	—	−0.095	−0.003

In Table I, we show the calculated values of the spin-orbit coupling and the resultant orbital and spin magnetic moments estimated within each atomic sphere. Though the spin-orbit coupling is larger in p states than in d states in Mn, the orbital moments of p character are negligible. This is because the p states spread over the valence band and then the spin-orbit splitting is smeared out. The orbital moment of Mn atom is almost the same as one of bcc-Fe (~0.06 μ_B[19)]) and does not give a drastic change to the total magnetic moment. As a result, the total magnetic moment including the orbital moment reaches 2.4 μ_B, though the value is still larger by about 20% than the value given by Blau *et al.*

3.2 *Magnetocrystalline anisotropy energy*

Because the MAE is quite sensitive to the calculation condition, it is difficult to judge the adequacy of the obtained MAE. In this sense, as pointed out by Daalderop,[6)] the ΔE vs bandfilling q plot is useful as a probe of the sensitivity of the MAE to details of the band structure such as splitting features due to spin-orbit interaction and rearrangement of the band occupation due to the change of the magnetization direction. Figure 5 shows the MAE ΔE[100] of $L1_0$-MnAl as a function of the bandfilling q with several conditions of the calculation. It is found from Fig. 5 that 11616 k-points in the full BZ seem to be sufficient to get reasonable convergence. As for the treatment of the magnetization direction, the calculation of MAE with the rotation of the spin quantization axis (eq. (2)) gives a slight shift to higher energy side in MAE. Calculations of MAE for some other systems have convinced ourselves that this trend can be commonly seen in ferromagnetic materials. So we are led to consider that the rotation of only spin axis leaving the orbital axis fixed may consume extra energy which should not be accounted in

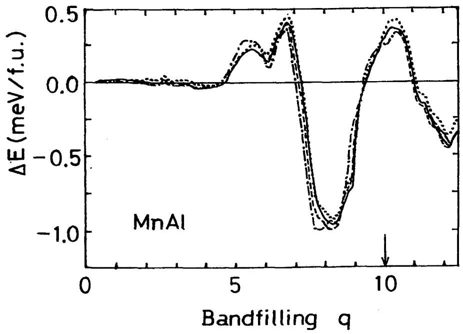

Fig. 5. Magnetocrystalline anisotropy energy ΔE[100] of L1_0-MnAl as a function of bandfilling, q. The arrow indicates the valence electron number in a formula unit. Solid line represents the result with a condition of 28800 k-points in the BZ, no combined correction term, and transformation of structure constant matrix for rotation of the magnetization. Dashed line is with 11616 k-point, dashed dotted line is with a combined correction term and the dotted line is with a rotation of the spin quantization axis for rotation of the magnetization direction.

the MAE intrinsically. The influence of the inclusion of the correction to the ASA (combined correction term[10]) is found not to be large in the present system. So the combined correction term has been dropped hereafter, though it may not be always needless in the MAE of other systems.

The MAEs given above are the energy difference in between the directions of [100] and [001] in L1_0 representation. However, there is no assurance that the easy direction of the magnetization in the c-plane is [100]. In order to examine the easy direction in the c-plane, we have further performed the calculation for ΔE[110] with L1_0 structure and ΔE[100] with tetragonally distorted B2 unit cell in which system [110] direction corresponds to [100] direction in L1_0 structure. At the valence electron number, $q=10$, both the MAEs for [110] direction in L1_0 and [100] direction in distorted B2 structure are larger than that for [100] direction in L1_0 structure by about 0.01 meV/f.u. This means that the magnetization restricted in the c-plane prefers [100] direction in the L1_0 structure or [110] in distorted B2 structure. However, the value of 0.01 meV/f.u. is comparable to the variation range of the MAE in accordance with the calculation condition. So, at this stage, we can insist only that the MAE is almost constant when the magnetization lies in the c-plane. Above inspection permits us to determine the MAE of τ-phase MnAl of (0.26±0.01) meV/f.u. This leads about 1.5×10^6 J/m^3 of magnetic anisotropy constant. The measured value is around 10^6 J/m^3 at low temperature.[16] Although there might be difficulty in comparison between the calculation and experiments since MnAl samples in experiments slightly differ from stoichiometric one, the calculated MAE is considered to be consistent with the experiments with a reasonable accuracy.

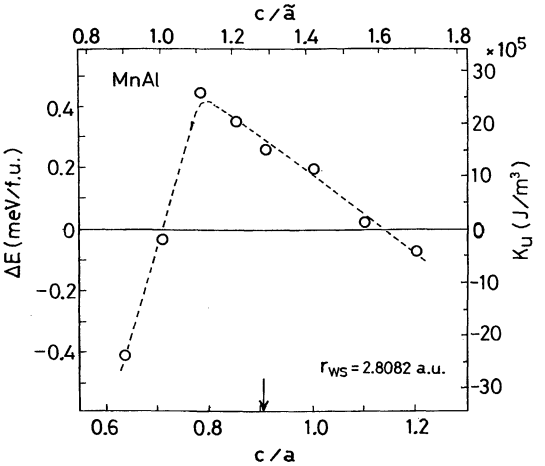

Fig. 6. Magnetocrystalline anisotropy energy ΔE[100] of L1_0-MnAl as a function of c/a. The arrow indicates the measured c/a (=0.9058).

In a theoretical point of view, there remains a physical interest about the relationship between MAE and the axial ratio c/a. So we have performed the calculations of MAE for several c/a. Figure 6 shows the calculated results. The MAE decreases with increasing c/a around the measured point $c/a=0.9058$, while it drastically changes its sign from negative to positive near the point, $c/a=0.7071$, corresponding to the cubic B2 structure. We can consider that the abrupt change around $c/a=0.7071$ may be closely related to the change of the Jahn-Teller splitting of the highly degenerated down spin DOS around E_F. In order to gain insight into the spin-orbit splitting in this region, MAE ΔE vs q for several c/a are shown in Fig. 7. When $c/a=0.7071$, it seems that MAE does not have meaningful values at any q. This may be reasonable because the

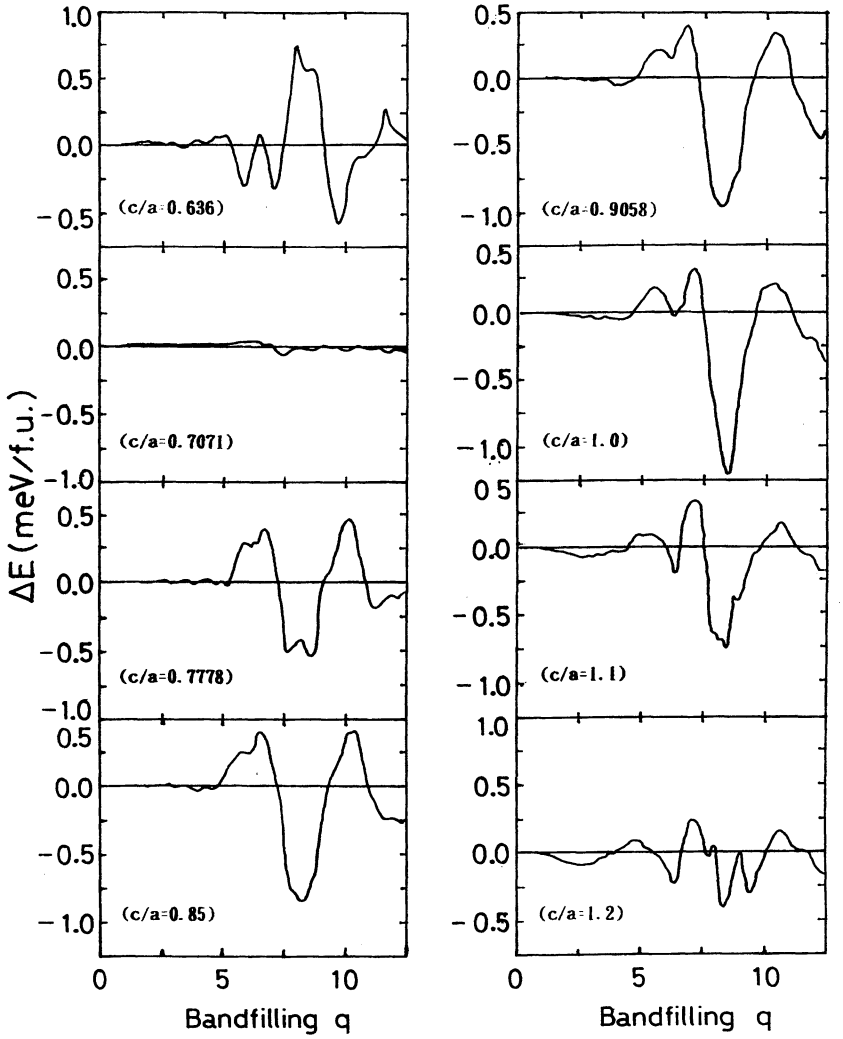

Fig. 7. Magnetocrystalline anisotropy energy ΔE[100] as a function of bandfilling, q for several c/a.

structure is cubic at this point, though MAE does not necessary vanish since the magnetization direction in the c-plane is assumed at [110] instead of [100] in the B2 unit cell. Roughly speaking, the sign of MAE in the range $7<q<12$ is turned out to be inverse across the point $c/a=0.7071$. This behavior may reflect the fact that the crystal field splitting of the Mn d states due to the tetragonal distortion is opposite depending on the direction of distortion of $c/\tilde{a}>1$ and of $c/\tilde{a}<1$, and then the order of the energy levels split by the spin-orbit interaction is changed. It should be noted, however, that the change of sign is not always the same for any system, and may depend on the relative position of the energy level of each constituent and electron number in it. At the value of c/a higher than 1.2, we find that MAE goes into negative again. For Mn monolayer as an extreme limit of c/a we obtained planar anisotropy with antiferromagnetic arrangement which is consistent with the result by Freeman and Wu.[20]

§4. Summary

The spin-polarized band calculations including spin-orbit interaction for τ-phase ($L1_0$) MnAl have been performed with LMTO-ASA method in the frame of local spin density functional approximation. It has been predicted that the MnAl has a potential having a magnetic moment of 2.4 μ_B in the $L1_0$ structure, while the moment goes down to 2 μ_B in the cubic B2 structure. The tetragonal distortion from cubic B2 to $L1_0$ structure also stabilize the system, which can be regarded as a so called Jahn-Teller effect. The discrepancy of the calculated magnetic moments with measurements can be considered to stem from a partial breakdown of the ferromagnetic state (to ferri-magnetic state, for instance) due to an non-stoichiometry in actual samples. As for the magnetic anisotropy, we have obtained MAE of (0.26 ± 0.01) meV/f.u., with examining the influence of calculation condition on MAE. This leads 1.5×10^6 J/m^3 for magnetic anisotropy constant, which is comparable to the measured value $\sim10^6$ J/m^3. We found that the dependence of MAE on the axial ratio c/a also reflects the influence of the tetragonal distortion, that is, MAE shows drastic change from negative to positive at the vicinity of $c/a=0.7071$ which corresponds to cubic B2 lattice. For larger value of c/a, MAE decreases with increasing c/a and goes into negative again for $c/a>1.2$. This would be connected to the result that the Mn monolayer exhibits planar anisotropy.

References

1) M. Yamada, H. Kato, H. Yamamoto and Y. Nakagawa: Phys. Rev. **B38** (1988) 620.
2) N. Mori: J. Phys. Soc. Jpn. 27 (1969) 307.
3) J. G. Gay and Roy Richter: Phys. Rev. Lett. **56** (1986) 2728.
4) H. Ebert: Phys. Rev. **B38** (1988) 9390.
5) P. Strange, H. Ebert, J. B. Staunton and B. L. Gyorffy: J. Phys.: Condens. Matter 1 (1989) 3947.
6) G. H. O. Daalderop, P. J. Kelly and M. F. H. Schuurmans: Phys. Rev. **B41** (1990) 11919; G. H. O. Daalderop, P. J. Kelly and M. F. H. Schuurmans: Phys. Rev. **B44** (1991) 12054.
7) C. Li, A. J. Freeman, H. J. F. Jansen and C. L. Fu: Phys. Rev. **B42** (1990) 5433.
8) K. Kyuno, R. Yamamoto and S. Asano: J. Phys. Soc. Jpn. **61** (1992) 412.
9) D. S. Wang, R. Wu and A. J. Freeman: Phys. Rev. **B47** (1993) 14932.
10) O. K. Andersen: Phys. Rev. **B12** (1975) 3060.
11) H. L. Skriver: *The LMTO Method*, ed. M. Cardona, P. Fulde and H. J. Queisser (Springer, Berlin, 1984).
12) U. von Barth and H. Hedin: J. Phys. **C5** (1972) 1629.
13) J. F. Janak: Solid State Commun. **25** (1978) 53.
14) A. R. Mackintosh and O. K. Andersen: *Electrons at the Fermi Surface*, ed. M. Springfold (Cambridge Univ. Press, Cambridge, 1980).
15) M. E. Rose: *Elementary Theory of Angular Momentum* (Wiley, New York, 1957).
16) N. I. Vlasova, G. S. Kandaurova, YA. S. Shur and N. N. Bykhanova: Phys. Met. Metall. **51** (1981) 1.
17) J. J. Wyslocki and A. Zygmunt: Acta Physica Polonica **A70** (1986) 29.
18) W. Blau, CH. Muller and H. Wonn: Phys. Status Solidi **A59** (1980) K203.
19) P. Soderlind, O. Eriksson, B. Johansson, R. C. Albers and A. M. Boring: Phys. Rev. **B45** (1992) 12911.
20) A. J. Freeman and Ru-qian Wu: J. Magn. Magn. Mater. **100** (1991) 497.