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First Principle Calculation of the Magnetocrystalline Anisotropy Energy of FePt and CoPt Ordered Alloys

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The spin-polarized band calculations including spin-orbit interaction for $L1_0$ FePt and CoPt ordered alloys have been performed with LMTO-ASA method in the frame of local spin density functional approximation. It has been shown that strong uniaxial magnetic anisotropy of both alloys is brought about by a large spin-orbit coupling of Pt atom and a strong hybridization of Pt *d* bands with highly polarized Fe (Co) *d* bands. The obtained magnetocrystalline anisotropy energy (MAE) is about 16×10^6 J/m^3 for FePt and 9×10^6 J/m^3 for CoPt. It is also found that both MAE's have a trend of increase with increasing axial ratio c/a in the vicinity of measured c/a. This can be regarded as being associated with the behavior that the MAE's decrease with increasing band filling.

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

§1. Introduction

$L1_0$ (CuAu) type CoPt,[1] FePt[2] and MnAl[3] ordered alloys exhibit strong magnetic anisotropy and then have a potential application to the hard magnetic materials. Though in general, a magnetic anisotropy is partially attributed to magnetostatic dipole-dipole interaction, practical use requires much stronger uniaxial magnetic anisotropy originating from the magnetocrystalline anisotropy. An origin of the magnetocrystalline anisotropy is considered to lie in the microscopic (electronic) nature such as crystalline electric field and spin-orbit interaction. Besides these electronic feature, however, a necessary condition for the uniaxial magnetic anisotropy is that the crystal structure considered has a uniaxial anisotropy.

In fact, the alloys mentioned above form tetragonal structure with a uniaxial anisotropy through axial ratio (c/a) different from unity. However, it has not yet been clarified how the axial ratio relates to the magnetocrystalline anisotropy or magnetic easy direction both qualitatively and quantitatively. On the other hand, $L1_0$ structure of these alloys is very simple and typical crystal structure for binary transition metal ordered alloys, and the investigation of these systems is expected to give us much information about the magnetocrystalline anisotropy of transition metal systems.

In the previous paper,[4] we reported calculated results of magnetic properties of MnAl containing magnetocrystalline anisotropy energy (MAE). In the present work CoPt and FePt are adopted to obtain a systematic understanding about the MAE of 3*d*-5*d* transition metal alloys. Although the MAE of CoPt and FePt have been already calculated within a first principles theory by Daalderop *et al.*,[5] our main concern lies in the relationship between the MAE and the axial ratio (c/a) of the $L1_0$ structure.

§2. Method of Calculation

The linear-muffin-tin orbital (LMTO) method[6,7] with atomic-sphere-approximation (ASA) has been employed to perform a semi-relativistic band calculation without spin-orbit interaction in the framework of local spin density (LSD) functional approximation. We use the exchange-correlation term that takes the form of Barth and Hedin[8] with parameters given by Janak.[9] 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 use s, p and d basis functions for Fe (Co) and Pt atoms. The density of states are evaluated by the tetrahedron method.

For the calculation of magnetic moments including orbital moments and the MAE, a spin-orbit interaction is introduced in the LMTO Hamiltonian. We have followed the manner given by Andersen[6] for evaluating the spin-orbit coupling and constructing the spin-orbit matrix in the LMTO Hamiltonian. With use of the force theorem,[10] the MAE can be obtained as a difference between sums of eigenvalues of the Kohn-Sham equation over occupied states

$$\Delta E=\sum_{i,k}^{\text{occ.}}\varepsilon_i([100],k)-\sum_{i,k}^{\text{occ.}}\varepsilon_i([001],k), \quad (1)$$

where $\varepsilon_i([n],k)$ is the Kohn-Sham eigenvalue calculated for the magnetization direction of $[n]$. In this step the number of k-points in the summation is set at 18928 in the full Brillouin zone (BZ). For dealing with the rotation of the magnetization direction, we take the unitary transformation of the structure constants in the LMTO matrices, which corresponds to the rotation of the total angular momentum j, as introduced by Ebert.[11]

According to Brooks,[12] effects of the orbital polarization term originating from Hund's second rule should generally be included for the calculations of MAE and orbital magnetic moments since it is not taken into account in the LSD approximation. In the present study, however, we drop the orbital polarization term because the results by Daalderop *et al.* indicate that it does not play a decisive role in MAE for CoPt and FePt.

Figure 1 shows the crystal structure of FePt and CoPt with $L1_0$ structure. 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 present study we basically adopted the $L1_0$ structure as a unit cell with basis vectors $(a/2, -a/2, c)$, $(-a/2, a/2, c)$ and $(a/2, a/2, -c)$, including four atoms in the cell, (0, 0, 0), $(a/2, a/2, 0)$ for Fe (Co) and $(a/2, 0, c/2)$, $(0, a/2, c/2)$ for Pt. We chose the axial ratio c/a of 0.96 for FePt and 0.979 for CoPt from

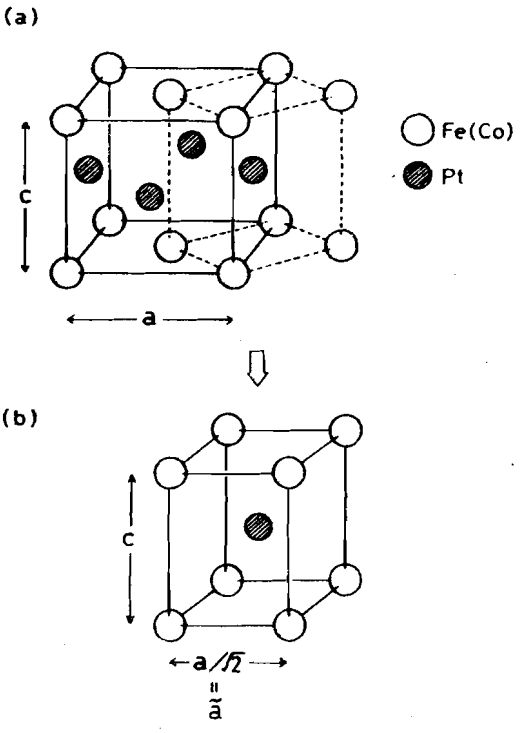

Fig. 1. Crystal structure of Fe(Co)-Pt with (a) $L1_0$ and (b) tetragonally distorted B2 representations.

the experimental data.[1,2] The atomic sphere (Wigner-Seitz) radii are set at $r_{Fe}=2.701$ a.u., $r_{Pt}=2.915$ a.u. for FePt, and $r_{Co}=2.624$ a.u., $r_{Pt}=2.901$ a.u. for CoPt, following Daalderop *et al.* The average atomic sphere radii (r_{WS}) amount to 2.8121 a.u. and 2.7694 a.u. for FePt and CoPt, respectively.

§3. Results and Discussion

3.1 *Density of states and the magnetic moments*

The spin-polarized density of states (DOS) of FePt and CoPt are shown in Figs. 2 and 3, respectively. Structures in DOS at energies higher than 0.2 Ry are mostly constructed from d bands. Both DOS's exhibit quite similar shapes and the Fermi energy (E_F) is located so as to reflect the difference of the electron numbers (1 electron); the rigid band model seems to hold for the gross feature of the DOS. Characteristic aspect commonly seen in both systems is that the d bands of Pt and Fe (Co) form bonding and anti-bonding states, re-

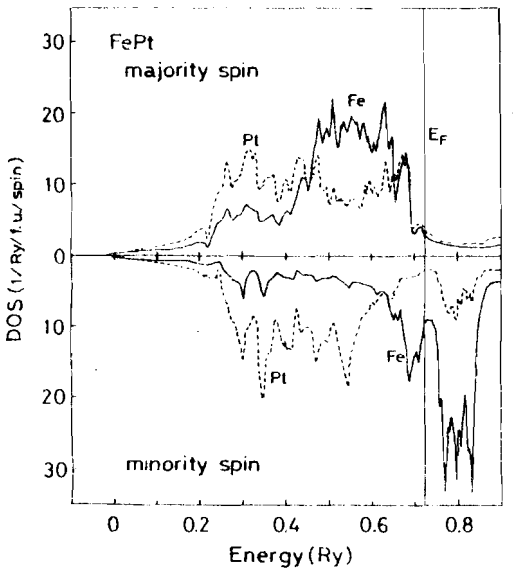

Fig. 2. Density of states of FePt. The solid and dashed lines represent partial density of states of Fe and Pt, respectively. The vertical line corresponds to the Fermi energy, E_F.

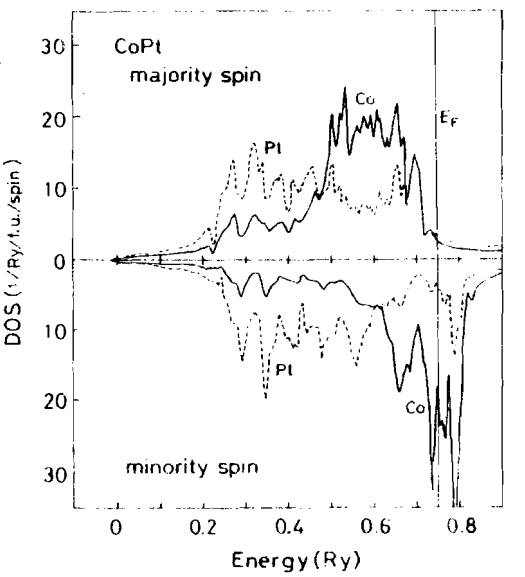

Fig. 3. Density of states of CoPt. The solid and dashed lines represent partial density of states of Co and Pt, respectively. The vertical line corresponds to the Fermi energy, E_F.

spectively, in the minority spin state, while in the majority spin state the *d* bands of Pt and Fe (Co) highly overlap in the same energy region below E_F. This means that both *d* bands in the majority spin state strongly hybridize each other.

In Table I, we show the calculated values of the spin-orbit coupling of *d* orbitals and the resultant orbital and spin magnetic moments estimated within each atomic sphere. The spin magnetic moments of Fe and Co are enhanced compared with those of their elemental metals because the large amount of the minority spin *d* bands of Fe (Co) are raised above E_F by the Pt *d* bands. On the other hand, the Pt *d* bands are almost fulfilled both in majority and minority spin states. This can be a main reason why they do not give a main contribution to the magnetic moments both in spin and orbital components. It should be noted, however, that the spin-orbit coupling of Pt is found about ten times larger in magnitude than those of Fe and Co. By this effect, together with the strong *d-d* hybridization between Pt and Fe or Co, the orbital moments of Fe and Co are enhanced compared with their elemental metals ($0.06\,\mu_B$, $0.09\,\mu_B$, respectively). It is found that the calculated magnetic moments can reach the experimental values given in Table I with the help of the orbital

Table I. Spin-orbit couplings ξ of *d* orbital (in mRy), the spin magnetic moments S (in μ_B), the orbital magnetic moments L (in μ_B), total magnetic moments M_t and measured magnetic moments M_{ex}. Notation TM in the suffices means Fe or Co. The data in the parenthesis are results by Daalderop *et al.* (ref. 5).

	ξ_{TM}	ξ_{TM}	ξ_{Pt}	ξ_{Pt}	S_{TM}	L_{TM}	S_{Pt}	L_{Pt}	M_t	M_{ex}
FePt	4.46	3.33	40.85	38.99	2.93	0.08	0.33	0.05	3.40	3.4
					(2.91	0.08	0.34	0.07)		
CoPt	5.56	4.80	40.89	39.11	1.91	0.11	0.38	0.07	2.46	2.4
					(1.86	0.12	0.32	0.06)		

moments.

3.2 *Magnetocrystalline anisotropy energy*

Figures 4 and 5 show the MAE (ΔE in eq. (1)) for FePt and CoPt, respectively, as a function of band filling q. As pointed out by Daalderop *et al.*,[5] the ΔE vs. band filling 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 the spin-orbit interaction and rearrangements of the band occupation due to the change of the magnetization direction. Moreover, because the MAE is quite sensitive to the calculational condition, the ΔE vs. q plot is also meaningful when we make a comparison of the calculated results with those by other people. In Figs. 4 and 5 we show also the calculated results by Daalderop *et al.* without the orbital polarization correction. Qualitatively the present results agree with their data. Although the amplitudes of $\Delta E(q)$ are considerably smaller in our results than that of Daalderop *et al.*, much discrepancy can not be seen, especially at the actual valence electron number, $q=18$ and 19 for FePt and CoPt, respectively. So we are led to conclude that there is no essential difference between our results and those of Daalderop *et al.*, except for minor differences which may originate from numerical details.

As for the behavior of $\Delta E(q)$ of FePt and CoPt, both profiles exhibit a similar shape around each valence electron number. However, the peak position of $\Delta E(q)$ of CoPt is shifted as large as about $\Delta q \sim 0.5$ from that of FePt. Apart from the difference in the axial ratio of FePt and CoPt, this indicates that it is difficult to predict MAE of one system from $\Delta E(q)$ of another system, on a basis of the rigid band model.

Figures 6 and 7 show ΔE at each valence electron number of FePt and CoPt, respectively, as a function of axial ratio (c/a) under the constant unit cell volume. For any c/a, the atomic sphere radius of each atom is fixed at

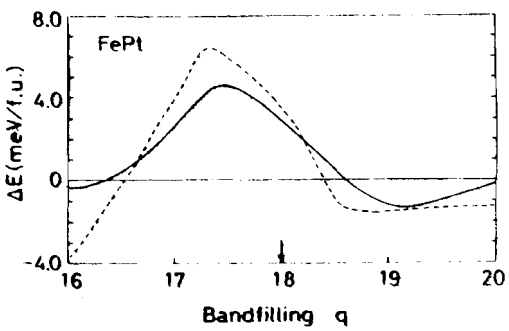

Fig. 4. Magnetocrystalline anisotropy energy ΔE of FePt as a function of band filling, q. The arrow indicates the valence electron number in the formula unit. Solid line represents the present result. Dashed line is the result by Daalderop *et al.* (ref. 5) without the orbital polarization correction.

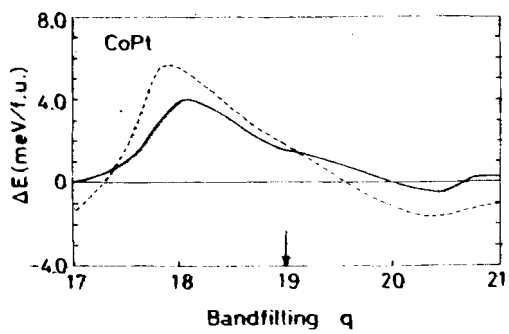

Fig. 5. Magnetocrystalline anisotropy energy ΔE of CoPt as a function of band filling, q. The arrow indicates the valence electron number in the formula unit. Solid line represents the present result and dashed line by Daalderop *et al.* (ref. 5) without the orbital polarization correction.

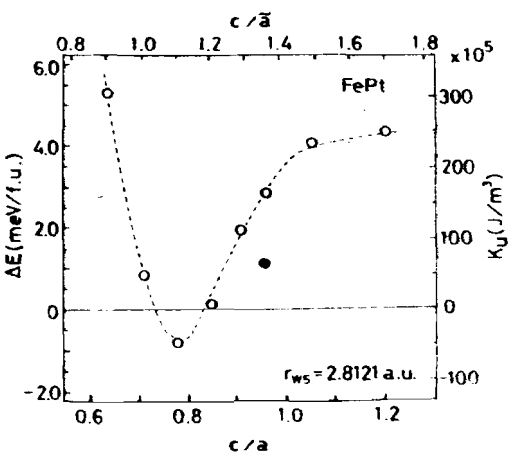

Fig. 6. Magnetocrystalline anisotropy energy ΔE of FePt as a function of c/a under the constant average atomic sphere radius, $r_{WS}=2.8121$ a.u. The closed circle indicates the measured value of magnetic anisotropy constant K_u at room temperature (ref. 2).

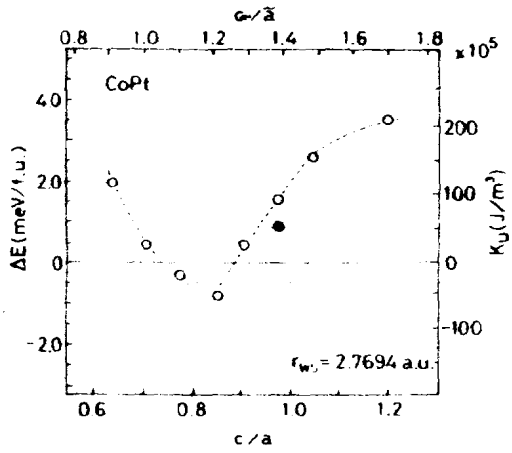

Fig. 7. Magnetocrystalline anisotropy energy ΔE of CoPt as a function of c/a under the constant average atomic sphere radius, $r_{ws}=2.7694$ a.u. The closed circle indicates the measured value of magnetic anisotropy constant K_u at room temperature (ref. 1).

the value given in §2. As can be understood easily from Fig. 1, $c/a=1/\sqrt{2}$ (~ 0.7071, $c/\tilde{a}=1$) corresponds to the case where the primitive cell of this system falls in the cubic B2 structure. Therefore, if $E[100]$ ($=\sum_{i,k}^{occ}\varepsilon_i([100], k)$) and $E[110]$ have a same value, ΔE ($=E[100]-E[001]$) at this point must be vanished because [110] in the $L1_0$ representation corresponds to [100] in the B2 representation. However, ΔE of both FePt and CoPt takes positive value at this point. On the other hand, the calculated result of $E[110]-E[001]$ is also found to have positive value of same degree, whereas $E[110]-E[001]$ must be exactly zero when $c/a=1/\sqrt{2}$ ($c/\tilde{a}=1$). The relatively large value of ΔE at this point is considered to reflect a numerical error which may be caused by the practical way of a BZ division. Generally, the calculation of ΔE is strongly affected by a construction of the k-mesh in the BZ, such as number of k-points and shape of the tetrahedra. Furthermore the BZ reflects the shape of crystal structure. Thus the change of the axial ratio may also affect the accuracy of calculated ΔE. Actually, ΔE of CoPt and FePt are quite sensitive to c/a, and they cut across zero at c/a slightly larger than $1/\sqrt{2}$.

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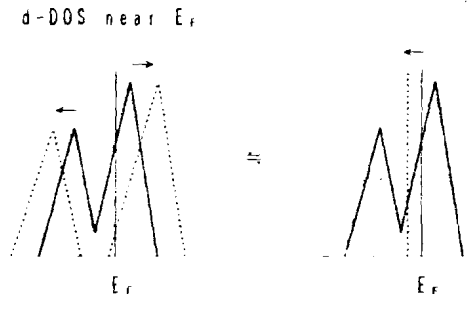
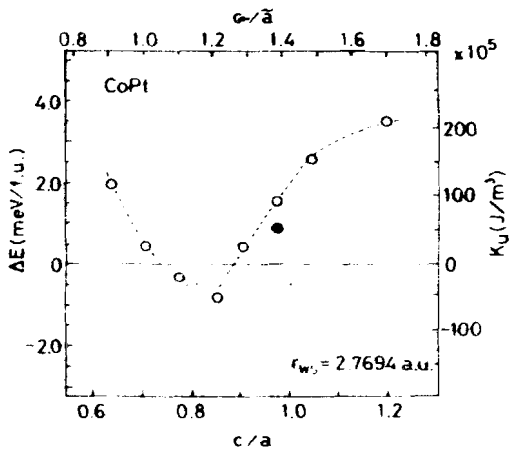


Fig. 8. Schematic representation of the effects of changing of c/a and the band filling on the electronic structure near E_F. Tetragonal distortion with increasing c/a may give similar effect caused by a decrease in band filling because the tetragonal distortion moves a portion of the d bands above E_F.



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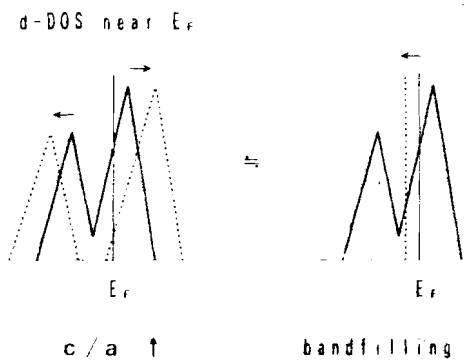
In larger value of c/a, the curves of ΔE of FePt and CoPt exhibit a similar behavior, having a stational value at around $c/a\sim 0.8$ and a positive slope against c/a in the region of $c/a>0.8$. Qualitatively, this trend can be understood in a certain degree from the profiles of $\Delta E(q)$ in Figs. 4 and 5 as follows. The tetragonal distortion splits the d bands of Fe (Co) and, then, a portion of the d bands near E_F in the minority spin state is raised above E_F. The larger the axial ratio c/a ($>1/\sqrt{2}$ at least) is, the higher the split d bands above E_F are. Roughly speaking, this may correspond to a lowering of E_F of the system as shown in Fig. 8. Figures 4 and 5 indicate that the decrease in the band filling q causes an increase in ΔE in the vicinity of each valence electron number in both systems. Thus we can consider that the sign of $d\Delta E/d(c/a)$ is connected to that of $-d\Delta E/dq$. Actually, $d\Delta E/d(c/a)$ of MnAl is negative in $c/a>0.8$ and concurrently $d\Delta E/dq$ is found to be positive, which can be seen in our previous paper.[4] In addition, we consider that the above interpretation could be an explanation also for the result that ΔE of CoPt is shifted to larger c/a by about $0.05\sim 0.1$ than that of FePt, especially in the region of $c/a>0.8$. That is, CoPt has higher E_F than FePt as is seen in DOS in Figs. 2 and 3, while increase in c/a plays a equivalent role as decreasing E_F as mentioned above. As a result, the value of ΔE of CoPt can reach that of FePt at a larger value of c/a



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than that of FePt. However, it should be noted that the rigid band model does not necessarily work well for MAE, quantitatively.

The MAE's obtained from ΔE are 2.8 meV/f.u. for FePt and 1.5 meV/f.u. for CoPt. The values are quite large as transition metal systems. This can be attributed to the fact that the Pt atom has a large spin-orbit coupling and hybridizes strongly with highly spin polarized Fe (Co) d bands. As a magnetic anisotropy constant, we obtain 16.3×10^6 J/m^3 and 9.0×10^6 J/m^3 for FePt and CoPt, respectively. These amount to two times larger than the experimental values, 7×10^6 J/m^3 for FePt[2] and 5×10^6 J/m^3 for CoPt,[1] both of which were observed at room temperature.

§4. Summary

Spin-polarized band structure calculations including the spin-orbit interaction for $L1_0$-FePt and CoPt ordered alloys have been performed with LMTO-ASA method in the framework of the local spin density functional approximation. It has been shown that a strong uniaxial magnetic anisotropy of both alloys is brought about by the large spin-orbit coupling of Pt atoms and the strong hybridization of Pt d bands with highly polarized Fe (Co) d bands. The obtained magnetocrystalline anisotropy energy (MAE) is about 16×10^6 J/m^3 for FePt and 9×10^6 J/m^3 for CoPt which are about two times larger than the experimental values at room temperature. It is also found that both MAE's have a trend that it increases with increasing c/a in the vicinity of measured axial ratio c/a. This can be understood from the behavior that the MAE's decrease with increasing band filling q because the band splitting near E_F with the tetragonal distortion (increase in c/a) gives an equivalent effect as lowering E_F (decreasing q) in the present system.

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