

Hartree–Fock study of orbital magnetic moments in 3d and 5f magnets and X-ray magnetic circular dichroism

T. Jo

Department of Quantum Matter, ADSM, Hiroshima University,
Higashi-Hiroshima 739-8526, Japan.
E-mail: jo@sci.hiroshima-u.ac.jp

The spin (M_s) and orbital magnetic moments (M_o) of the uranium 5f state in the ferromagnetic compound uranium sulfide (US) and of the cobalt 3d state in various transition-metal superlattices are calculated on the basis of a tight-binding model, in which the intra-atomic f – f or d – d multipole interaction is taken into account using the Hartree–Fock (HF) approximation. The parameters in the model are determined on the basis of available first-principles calculations. For US, the calculated ratio M_o/M_s and magnetic circular dichroism spectrum for U $M_{4,5}$ absorption are in good agreement with the experimental results. Inclusion of the expectation values of the spin-off-diagonal operators in addition to the number operators in the 5f state is found to be crucially important when describing the 5f magnetic state. A difference in enhancement of M_o of the Co atom between the Co/Pd and Co/Cu superlattices is discussed on the basis of a semi-quantitative calculation, assuming ferromagnetism.

Keywords: orbital moment; uranium sulfide; superlattice; Hartree–Fock approximation; X-ray magnetic circular dichroism.

1. Introduction

In magnets, the atomic spin (M_s) and orbital (M_o) magnetic moments are basic quantities and their separate determination is therefore important. In addition to the traditional method to measure M_s and M_o (Bonnenberg *et al.*, 1986), the recently developed technique of X-ray magnetic circular dichroism (XMCD) with core-to-valence X-ray absorption (Chen *et al.*, 1995) combined with several sum rules (Thole *et al.*, 1992; Carra *et al.*, 1993) has attracted much attention as a method for site- and symmetry-selective determination of M_s and M_o . From the theoretical point of view, the first-principles local-density approximation (LDA) of density-functional theory is a typical method for calculating magnetic quantities and has been successfully applied to various substances, especially 3d transition-metal systems (Morruzi *et al.*, 1978).

In the LDA theory, the Kohn–Sham equation is described by the local potential including the spin-dependent electron density. The electric current, which describes M_o , is not, however, included. This means that there is no theoretical framework within which to determine M_o self-consistently in the LDA, and M_o is calculated as a quantity induced by M_s through the spin-orbit interaction (SOI). As a result, LDA theory is known to underestimate M_o in some cases. In bulk 3d transition metals, M_o is about one tenth of M_s (Bonnenberg *et al.*, 1986) and M_o is sometimes neglected, *i.e.* the success of the first-principles LDA approach relies on the experimental fact that $M_o \ll M_s$. In 4f rare earths, M_o and M_s are mostly atom-like, *i.e.* determined by the Hund rule, and a solid-state effect is in many cases irrelevant. In 5f actinide systems, especially in uranium systems, M_o and M_s of the 5f state are determined by solid-state effects, *i.e.* they are dependent on the atomic environment. LDA theory applied

to ferromagnetic U compounds underestimates M_o (Kraft *et al.*, 1995).

Many theoretical attempts to improve the underestimation of M_o have been made. They may be roughly classified into two categories. An example of the first category is the so-called current-density-functional theory, which was formulated to extend the density-functional theory to include the orbital current, which describes M_o , as an extra degree of freedom (Vignall & Rasolt, 1987; Skudlarski & Vignall, 1993; Higuchi & Hasegawa, 1997). An explicit form of the contribution of the current density is, however, at present unknown and a tentative application of the theory to Co still underestimates M_o of the Co atom (Ebert *et al.*, 1997). The other category includes the so-called orbital polarization (OP) (Brooks, 1985; Eriksson *et al.*, 1990) and LDA + U (U is an electron–electron interaction parameter) approaches (Solovyev *et al.*, 1998), intended to calculate M_o practically. For problems with the OP approach, the reader is referred to the work of Solovyev *et al.* (1998) and Shishidou *et al.* (1999). In the LDA + U approach, the wavefunctions are prepared by the LDA calculation, the multipole intra-atomic interaction between electrons is taken into account for the state of interest and the Hartree–Fock (HF) calculation is performed. The essential part of the LDA + U approach seems to be reproduced if an appropriate multi-orbital tight-binding Hamiltonian (Hubbard model) is prepared. In fact, for the antiferromagnet CoO, the HF calculations, with rotational invariance, based on both LDA + U (Solovyev *et al.*, 1998) and an extended Hubbard model (Shishidou & Jo, 1998) are found to give similar results for both M_o of Co ($\sim 1 \mu_B$) and of the stable magnetic structure.

The purpose of the present work is to review recent HF calculations of M_s and M_o made on the basis of an extended Hubbard model including the intra-atomic multipole interaction, for ferromagnetic US and superlattices of Co atoms in Pd or Cu matrixes. Parameters of the one-electron part of the model are determined on the basis of data available from first-principles LDA calculations. Among the Slater integrals describing the multipole interaction, the HF value of F^0 for an atom assuming a suitable electron configuration is, in metals, reduced to a considerable extent by a screening effect, while that of F^k with $k \neq 0$ is only reduced to 90–70% (Norman, 1995). In the calculations described here, suitable reductions from the HF values for F^k with $k \neq 0$ are assumed and values of F^0 are determined so that the calculated total moment $M_s + M_o$ agrees with the experimental result; the obtained ratio M_o/M_s is compared with the experimental value.

For US with NaCl structure, in addition to various magnetic measurements (Tillwick & de V. du Plessis, 1976; Lander *et al.*, 1991), XMCD has recently been observed (Collins *et al.*, 1995). Through an HF calculation with rotational invariance, the role of the multipole exchange interaction described by the Gaunt coefficient (Condon & Shortley, 1959) is clearly seen to be important in the estimation of M_o , which is the case for atoms obeying the Hund rule. Since the establishment of the XMCD sum rules relating M_s and M_o , the enhancement of M_o of Co or Fe compared with the bulk metal has been reported in many XMCD experiments on magnetic multilayers (Wu *et al.*, 1992; Tischer *et al.*, 1995; Nakajima *et al.*, 1998). The reported enhancement factor of M_o is at most ~ 2 . For example, an enhancement of M_o of bulk hexagonal close packed (h.c.p.) Co from $\sim 0.15 \mu_B$ to $\sim 0.25 \mu_B$ has been reported, which is still much smaller than M_s of $1.6 \mu_B$. For Co or Fe impurities in Cs metals, on the other hand, a recent LDA + U calculation (Kwon & Min, 2000) has predicted a value for M_o of $\sim 3 \mu_B$, *i.e.* almost atom-like, as for rare earths. In the present work, M_o of Co atoms in a Pd or Cu matrix is calculated assuming ferromagnetism. The relation between M_o and the atomic

environment is discussed and it is shown that M_o of Co can be comparable to M_s if Co is surrounded by Cu atoms as nearest neighbours.

2. Model

We assume the Hamiltonian

$$H = H_1 + H_2,$$

where H_1 denotes the multipole d - d or f - f interaction, and the spin-orbit interaction in d or f orbit is given by

$$H_1 = \sum_{i,v_1,v_2,v_3,v_4} \langle i\nu_1, i\nu_2 | (1/r_{12}) | i\nu_3, i\nu_4 \rangle a_{i\nu_1}^+ a_{i\nu_2}^+ a_{i\nu_4} a_{i\nu_3} \\ + \sum_{i,v_1,v_2} \langle i\nu_1 | \zeta l s | i\nu_2 \rangle a_{i\nu_1}^+ a_{i\nu_2},$$

with i and ν being the lattice point and the combined index of the magnetic and spin quantum numbers of the d or f orbit, m and σ , respectively; ζ denotes the spin-orbit coupling constant. The matrix element of the d - d or f - f interaction is expressed in terms of the Slater integral F^k and the Gaunt coefficient $c^k(lm, lm')$, with $l = 2$ and $k = 0, 2$ and 4 for the d orbit, and $l = 3$ and $k = 0, 2, 4$ and 6 for the f orbit, as follows (Condon & Shortley, 1959):

$$\langle \nu_1 \nu_2 | (1/r_{12}) | \nu_3 \nu_4 \rangle = \delta_{\sigma_1 \sigma_3} \delta_{\sigma_2 \sigma_4} \delta_{m_1+m_2, m_3+m_4} \\ \times \sum_k F^k c^k(lm_1, lm_3) c^k(lm_4, lm_2).$$

H_2 denotes the interatomic electron transfer and the atomic level,

$$H_2 = \sum_{i,j} \sum_{\mu_1, \mu_2} t_{ij}^{\mu_1, \mu_2} a_{i\mu_1}^+ a_{j\mu_2},$$

with μ being the combined index of the magnetic and spin quantum numbers of all the orbits including d and f .

For the multipole d - d or f - f interaction in H_1 , we apply the HF approximation: the first term of H_1 is replaced by

$$\sum_{i,v_1,v_2,v_3,v_4} \left[\langle i\nu_1, i\nu_2 | (1/r_{12}) | i\nu_3, i\nu_4 \rangle \right. \\ \left. - \langle i\nu_1, i\nu_2 | (1/r_{12}) | i\nu_4, i\nu_3 \rangle \right] \langle a_{i\nu_2}^+ a_{i\nu_4} \rangle a_{i\nu_1}^+ a_{i\nu_3},$$

with $\langle a_{i\nu_2}^+ a_{i\nu_4} \rangle$ being the expectation value of the operator including the number operator. By diagonalizing the obtained one-body Hamiltonian, we calculate M_s and M_o :

$$M_s = \mu_B \sum_m (\langle a_{m\downarrow}^+ a_{m\downarrow} \rangle - \langle a_{m\uparrow}^+ a_{m\uparrow} \rangle)$$

and

$$M_o = \mu_B \sum_{m,\sigma} m \langle a_{m\sigma}^+ a_{m\sigma} \rangle.$$

The lattice point index i is omitted for simplicity.

3. 5f state and $M_{4,5}$ XMCD in US

Taking into account the U $5f$, $6p$, $6d$ and $7s$ orbitals, and the S $3s$, $3p$ and $3d$ orbitals, the parameters in H_2 are determined by a first-principles LDA calculation with the full-potential linear augmented plane wave (FLAPW) method in the paramagnetic state without the $5f$ spin-orbit interaction. $F^0 = 0.76$, $F^2 = 5.530$, $F^4 = 4.669$ and $F^6 = 2.881$ eV are adopted in the Hamiltonian H_1 . For details, the reader is referred to the work of Shishidou *et al.* (1999), including the F^0 dependence of M_s and M_o . As a result of the presence of a large M_o , magnetic anisotropy exists. Values of M_{5f} ($= M_s + M_o$) of 1.70 for the [111] direction, 1.51 for the [110] direction and 1.28 for the [001] direction are obtained, in units of μ_B . By comparing the total energies among

Table 1

Comparison of calculated $5f$ magnetic moments in uranium sulfide.

LDA = local-density approximation. SOI = spin-orbit interaction. OP = orbital polarization. HF = Hartree-Fock. FLAPW = full-potential linear augmented plane wave. ASW = augmented sphere wave. LMTO = linearized muffin-tin orbital. TB = tight binding.

Method	Reference	M_{5f} (μ_B)	M_s (μ_B)	M_o (μ_B)
LDA + SOI FLAPW	Oguchi (1998)	0.55	-1.66	2.21
LDA + SOI ASW	Kraft <i>et al.</i> (1995)	1.1	-1.5	2.6
LDA + SOI LMTO	Brooks (1985)	1.1	-2.1	3.2
OP LMTO	Brooks (1985)	1.8	-2.2	4.0
OP (scaled HF)	Severin <i>et al.</i> (1993)	1.61	-1.51	3.12
HF TB	This work	1.70 [†]	-1.49	3.19
Spin-diagonal HF TB	This work	1.56	-1.78	3.34
Neutron measurement	Wedgwood (1972)	1.70	(-1.31)	(3.0)

[†] This value is adjusted to the experimental value.

the three directions, the [111] direction is found to be the easy axis in accordance with the experiment and hereinafter the magnetic moments are presented along the easy axis.

In Table 1, the calculated M_{5f} , M_s and M_o values obtained by several methods are compared. The results based on the conventional LDA with SOI reveal an absolute value of M_{5f} that is too small compared with the experimental value of 1.70 μ_B (Wedgwood, 1972) because of an underestimation of M_o . Brooks (1985) applied the OP method and obtained a larger magnitude of M_o and a considerable improvement in M_{5f} . According to Severin *et al.* (1993), the individual absolute magnitudes of M_s and M_o of Brooks are too large compared with those obtained from the analysis of the magnetic form factor. Severin *et al.* (1993) performed an HF calculation in which the expectation values of only the number operators specified by the spin (σ) and magnetic quantum numbers (m) are taken into account and the exchange integrals are scaled to the LDA ('scaled HF' method). Their result is, as far as M_s and M_o are concerned, similar to ours ('HF TB') with $M_s = -1.49 \mu_B$ and $M_o = 3.19 \mu_B$, where the off-diagonal operator as well as the number operators are taken into account. In order to estimate M_o well, one should include the orbital-dependent exchange potential, which is taken into account in neither the LDA nor the OP method. The values in parentheses (Table 1) of the neutron measurement by Wedgwood (1972) are from an analysis by Severin *et al.* (1993). The calculation was also performed neglecting the spin-off-diagonal operators in the present model ('spin-diagonal HF'); the obtained M_s and M_o are apparently similar to those obtained by the HF TB method. Problems with the scaled HF and the spin-diagonal HF method will be discussed below.

Fig. 1 presents the U $3d \rightarrow 5f$ X-ray absorption spectroscopy (XAS) XMCD spectrum $\Delta F(\omega) = F_-(\omega) - F_+(\omega)$, calculated with use of the unoccupied Bloch states and energy eigenvalues obtained for HF TB on the basis of Fermi's 'Golden rule'; F_{\pm} represents the XAS spectrum for the incident positive (+) and negative (-) helicities. The Lorentzian convolution with FWHM of 4.0 eV is adopted, which represents the U $3d$ core-hole lifetime broadening. The calculated XMCD spectral shape is found to be in good agreement with the measurement by Collins *et al.* (1995), with dispersive features in the M_5 region. The M_5 to M_4 intensity ratio R_{XMCD} , determined by combining the so-called L_z (Thole *et al.*, 1992) and S_z (Carra *et al.*, 1993) XMCD sum rules, is expressed as

$$R_{\text{XMCD}} = \frac{\int_{M_5} \Delta F(\omega) d\omega}{\int_{M_4} \Delta F(\omega) d\omega} \\ = (5/2)[\langle L_z \rangle / (\langle L_z \rangle - 2\langle S_z \rangle - 6\langle T_z \rangle)] - 1,$$

where $\langle L_z \rangle = M_o/\mu_B$ and $\langle S_z \rangle = M_s/(2\mu_B)$, and $\langle T_z \rangle$ is the expectation value of the z component of the magnetic dipole operator, given by

$$\mathbf{T} = \sum_i [\mathbf{s}_i - 3\mathbf{r}_i(\mathbf{r}_i \cdot \mathbf{s}_i)/r_i^2].$$

\mathbf{s}_i and \mathbf{r}_i are the spin and the position vectors of the i th $5f$ electron, respectively. The HF TB method, taking into account the expectation value of the off-diagonal operators as well as the number operators, gives $\langle T_z \rangle = -0.36$ and $R_{\text{XMCD}} = 0.169$, which is in reasonable agreement with the observed value of 0.13 ± 0.03 (Collins *et al.*, 1995). The spin-diagonal HF TB method, on the other hand, gives $\langle T_z \rangle = -0.22$ ($\sim 60\%$ of the HF TB value) and $R_{\text{XMCD}} = 0.292$. The magnitudes of M_s and M_o (or $\langle S_z \rangle$ and $\langle L_z \rangle$) are rather insensitive to whether the spin-off-diagonal operators are included or not, since L_z and S_z are expressed by the number operators specified by m and σ . T_z is, on the other hand, expressed in terms of spin-off-diagonal operators as well as number operators and its expectation value. Furthermore, R_{XMCD} is more sensitively influenced by the extent of spin-off-diagonal mixing in the Bloch wavefunction. It has been shown that R_{XMCD} can be a severe test of wavefunction and that the HF TB method is a promising method to calculate magnetic quantities including wave functions.

4. Co/Pd and Co/Cu superlattices

In this section, the relation between M_o or M_o/M_s of transition-metal atoms and various atomic environments will be discussed. For this purpose, superlattices of Co atoms in face-centred cubic (f.c.c.) Pd or Cu hosts have been chosen, as shown in Fig. 2, for which M_s and M_o of Co will be calculated. In Fig. 2(a), linear chains of Co atoms (solid circles) are periodically embedded in the [110] direction in a three-dimensional Pd or Cu (open circles) matrix. In Fig. 2(b), Co chains are in the [100] direction. In Fig. 2(c), two-dimensional sheets of Co atoms are stacked in the [001] direction, *i.e.* forming a kind of multilayer. In Fig. 2(d), Co atoms form a three-dimensional superlattice. In Fig. 2, the lattice constant of the pure host metal, Pd or Cu, is assumed. The parameters in H_2 for pure metals, where s , p and d orbitals are taken into account, are determined according to Papaconstantopoulos (1986) in the paramagnetic state; these parameters are used in the calculation in the ferromagnetic state. The Co $3d$ majority spin states are almost filled; thus the neglect of the spin-off-diagonal operators, as discussed in the preceding section, is found to be a good approximation. The calculation for f.c.c. Co gives $M_s = 1.52 \mu_B$ and $M_o = 0.11 \mu_B$, and that for h.c.p. Co gives $M_s = 1.58 \mu_B$

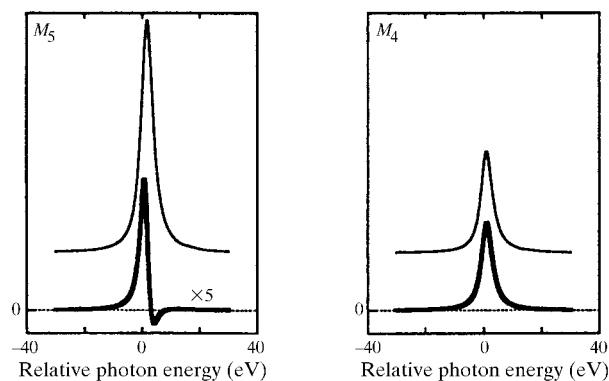


Figure 1
Calculated isotropic (thin line) and magnetic circular dichroism (thick line) spectra for U $M_{4.5}$ absorption in US as a function of relative photon energy (Shishidou *et al.*, 1999).

and $M_o = 0.13 \mu_B$. The parameters in the superlattices are estimated according to Andersen *et al.* (1978) and the Co–Pd (Cu–Pd) transfer integrals are assumed to be the arithmetic means of the Co–Co and Pd–Pd (Cu–Cu) values. For details of the calculations, the reader is referred to the work of Okutani & Jo (2000).

In Table 2, the calculated M_o and M_s of Co for the superlattices shown in Fig. 2 are presented along with the choice of quantization axes. The number of $3d$ electrons is, compared with the bulk Co, increased by ~ 0.2 in the model superlattices and M_s is decreased by $\sim 0.2 \mu_B$. The following observations regarding M_s and M_o of Co atoms can be made.

- (i) M_s is insensitive to the atomic environment and the quantization axis.
- (ii) M_o is enhanced compared with bulk Co metal in any case.
- (iii) The enhancement of M_o is much more remarkable in the Cu matrix.
- (iv) The extent of enhancement in the Pd matrix is not so sensitive to the atomic environment ($0.24 \mu_B < M_o < 0.35 \mu_B$).
- (v) The extent of enhancement in the Cu matrix is strongly dependent on the atomic environment. The enhancement is remarkable in the case where a Co atom is surrounded by Cu atoms as its nearest neighbours.
- (vi) M_o is dependent on the quantization axis, *i.e.* anisotropy exists and is more remarkable in the Cu matrix.

Result (i) arises from the fact that the Co majority spin state is almost filled and the number of minority-spin $3d$ electrons determines M_s . Results (ii), (iii), (iv) and (v) provide a picture of the environment dependence of M_o in the Pd and Cu matrices. In the case of the Pd matrix, the lattice parameter is considerably larger compared with that of bulk Co, and pure Co with such a lattice constant has M_o of $0.36 \mu_B$ as a result of a narrowing of the $3d$ state in the present model. A comparison between this value and those in Table 2(a) is suggestive. The effective Co–Co hybridization and the Co–Pd hybridization are similar to each other. The key factor in the enhancement of M_o is, in this case, the lattice parameter, while the

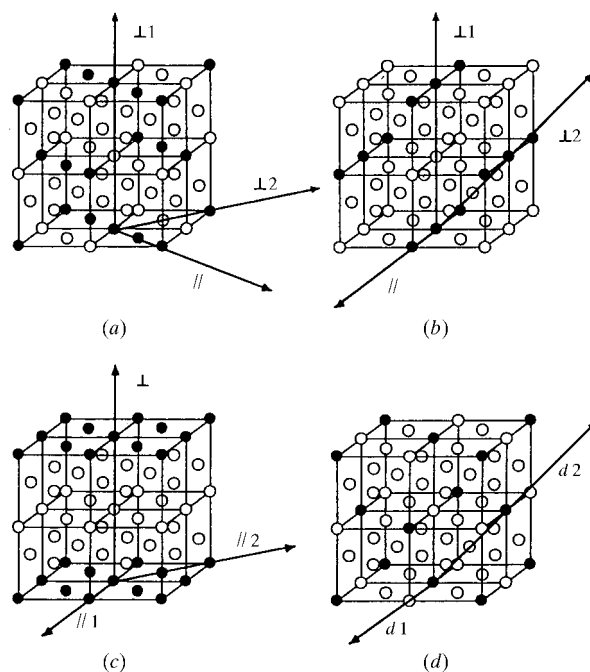


Figure 2
The superlattices composed of Co atoms (solid circles) and Pd or Cu host atoms (open circles) (Okutani & Jo, 2000).

Table 2

The calculated atomic spin (M_s) and orbital moments (M_o) of Co in the Pd and Cu matrixes shown in Fig. 2.

(a) Co in Pd matrix.

Lattice		M_s (μ_B)	M_o (μ_B)	M_o/M_s
Fig. 2(a)		1.37	0.30	0.22
	⊥1	1.36	0.26	0.19
	⊥2	1.37	0.27	0.20
Fig. 2(b)		1.37	0.24	0.17
	⊥1	1.36	0.34	0.25
	⊥2	1.38	0.35	0.26
Fig. 2(c)	⊥	1.36	0.25	0.19
	1	1.37	0.24	0.18
	2	1.37	0.24	0.17
Fig. 2(d)	d1	1.34	0.33	0.25
	d2	1.35	0.34	0.25

(b) Co in Cu matrix.

Lattice		M_s (μ_B)	M_o (μ_B)	M_o/M_s
Fig. 2(a)		1.38	0.38	0.28
	⊥1	1.38	0.63	0.46
	⊥2	1.39	0.67	0.48
Fig. 2(b)		1.33	1.43	1.07
	⊥1	1.35	1.10	0.81
	⊥2	1.35	1.48	1.09
Fig. 2(c)	⊥	1.45	0.69	0.47
	1	1.45	0.40	0.28
	2	1.45	0.32	0.22
Fig. 2(d)	d1	1.34	1.22	0.91
	d2	1.34	1.45	1.09

atomic environment dependence plays a minor role. The magnitude of $0.36 \mu_B$ can even be reduced a little by surrounding Pd atoms. In the case of the Cu matrix, on the other hand, M_o of pure Co enlarged to the Cu lattice parameter is only $0.16 \mu_B$, which is much smaller than the values given in Table 2(b). Since the effective Co–Cu hybridization is much smaller than the Co–Co hybridization in the Cu matrix and also than in pure Co metal, the neighbouring Cu atoms cause the enhancement of M_o of Co through a narrowing of the 3d state. This seems to be sensitively reflected in the strong environment dependence of M_o : in the multilayer (see Fig. 2c), a Co atom is surrounded by four Co atoms and M_o is somewhat smaller ($0.7\sim 0.4 \mu_B$) compared with the case in which the Co is surrounded by no Co atoms (Figs. 2b and 2d), where M_o is comparable to M_s .

The contribution to the magnetic anisotropy energy (MAE) (ΔE) is known to be composed of differences in the band energies (ΔE_b) and the magnetic dipole–dipole interaction energies (ΔE_{dd}) between two orientations (Szunyogh *et al.*, 1995). The band energy is lower for the magnetization direction with larger M_o ; M_s is, in the present case, insensitive to the direction. The calculated result for the Co/Cu multilayer [see Table 2(b) for the lattice shown in Fig. 2(c)] shows that M_o is much larger for the direction perpendicular to the Co layer compared with that for the parallel direction. If it is assumed that Cu atoms in the Co/Cu multilayers play a role similar to that of Au atoms in Co/Au multilayers and that the main contribution to ΔE is ΔE_b in Co/Cu, the result is qualitatively consistent with that of the first-principles calculation for Co/Au performed by Újfalussy *et al.* (1996).

Recently, enhancements of M_o , determined by XMCD measurements, have been reported for Co/Pd (Wu *et al.*, 1992), Co/Cu (Tischer *et al.*, 1995) and Co/Pt multilayer systems (Nakajima *et al.*, 1998). In these cases, and in a recent study of nanoscale Fe clusters (Edmonds *et al.*, 1999), the reported enhancement factor, compared with the bulk metals, is at most double. If the monolayer sandwich of the present study is modified to two monolayers in the calculation, M_o

of Co is considerably reduced. For a quantitative discussion, a confirmation of the atomic structure, between theory and experiment, will be needed.

5. Concluding remarks

In summary, M_s and M_o of the U 5f state in US and of the Co 3d state in various Co/Pd and Co/Cu superlattices have been calculated with an HF approximation on the basis of a tight-binding model, including the full atomic orbitals in valence states and the multipole interactions between 5f or d electrons. In US, it is stressed that inclusion of the expectation value of the spin-off-diagonal operators in addition to the number operators is crucially important when describing the Bloch state *via* an analysis of the U $M_{4,5}$ XMCD spectrum. Calculations assuming ferromagnetism reveal an enhancement of M_o of Co in both the Co/Pd system and the Co/Cu system compared with bulk Co. The enhancement in the Co/Pd system arises from the large lattice constant in the Pd matrix, while that in Co/Cu results from the small hybridization of the Co–Cu pair compared with the Co–Co pair.

The magnitudes of M_o and MAE, *i.e.* the perpendicular or parallel anisotropy in the magnetic multilayers, are subjects closely related to each other. At present, the first-principles calculation of MAE has been performed only for limited systems, although the 3d-electron number dependence (of magnetic atoms) of MAE has been discussed on the basis of simplified models (see for example Dorantes-Dávila & Pastor, 1998). It is expected that in the future these first-principles calculations will be developed further and that realistic calculations of MAE in various systems, including magnetic multilayers, will be made.

In itinerant 3d ferromagnets, the thermodynamical properties, *e.g.* the temperature dependence of magnetization, have been the main subject of theoretical studies (Moriya, 1985). So far, the temperature dependence of only M_s has been discussed; the temperature dependence of M_o has been neglected. In systems with enhanced M_o , the temperature dependence not only of M_s but also of M_o (or M_o/M_s) should be the subject of interest, especially as the latter may provide new information regarding electronic structure. Recent measurements of M_o in Co clusters on Au(111) (Dürr *et al.*, 1999) have addressed this subject from an experimental point of view.

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