Ab initio investigation of magnetism in two-dimensional uranium systems

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The orbital and spin magnetic moments and the x-ray-magnetic circular-dichroism (XMCD) spectra at the $M_{4,5}$ edges of the U atoms in a UAs/Co multilayer and in an α-U film are calculated within the framework of the density-functional theory in combination with the local-spin-density approximation, the generalized-gradient approximation, and the local-density-approxiamtion+U method. The antiparallel arrangement between the U and Co spin magnetic moments at the interface results in the vanishing of ferromagnetism for the case of very thin Co layers. The U moments decay rapidly with the distance from the film surface. The magnitude of the magnetic-dipole term $\langle T_z \rangle$, which appears in the spin XMCD sum rule, is small. The different exchange-correlation treatments do not yield qualitatively different results.

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Both the subject of actinides and the issue of magnetism in two-dimensional systems, such as multilayers or films, represent interesting topics in contemporary solid-state physics. The joint problems from the two fields are therefore even more challenging. Actinides and actinide compounds exhibit very different magnetic behaviors, such as Pauli paramagnetism, localized and itinerant magnetism, and heavy fermions.[1,2] It is expected that the properties would change when going from bulk to two-dimensional materials. For example, a δ-like state for the surface behavior of α plutonium was predicted by means of *ab initio* calculations.[3] Plasket *et al.*[4] produced UAs/Co multilayers in an attempt to increase the Curie temperature of the amorphous UAs/Co alloy due to the induced polarization of U atoms through the exchange coupling to the Co layers. The first results, which came from magneto-optical measurements,[5] were promising, but they were not reproduced with polarized-neutron-reflectivity experiments[6] because the main contribution to the measured signal arises from the Co atoms, while the sensitivity to the U moment was too low. As an alternative approach, Kernavanois *et al.*[7] performed a measurement of the x-ray-magnetic-circular dichroism (XMCD), which is element specific.[8] The results were in agreement with the magneto-optical data from Ref. 5. The same technique may be suitable for detecting the finite magnetic moment at the surface of uranium that was predicted theoretically.[9]

The XMCD spectroscopy is based on the difference in the absorption coefficients $\mu^+(\epsilon)$, $\mu^-(\epsilon)$, and $\mu^0(\epsilon)$ for circularly right, circularly left, and linearly polarized x rays. The $5f$ contributions to the magnetic orbital $m_l=-\mu_B\langle l_z\rangle$ and spin $m_s=-\mu_B\langle\sigma_z\rangle$ moments are related to the absorption coefficients at the $M_{4,5}$ edges, via the sum rules[10,11]

$$\langle l_z\rangle = \frac{3I_m N_h}{I_t}, \tag{1}$$

$$\langle \sigma_z\rangle = \frac{3I_s N_h}{I_t} - 3\langle T_z\rangle, \tag{2}$$

$$I_m = \int [(\mu_c)_{M_5} + (\mu_c)_{M_4}]d\epsilon, \tag{3}$$

$$I_s = \int \left[(\mu_c)_{M_5} - \frac{3}{2}(\mu_c)_{M_4}\right]d\epsilon, \tag{4}$$

$$I_t = \int [(\mu_t)_{M_5} + (\mu_t)_{M_4}]d\epsilon, \tag{5}$$

with the XMCD signal $\mu_c=\mu^+-\mu^-$ and the total absorption coefficient $\mu_t=\mu^++\mu^-+\mu^0$. The symbols $(\mu_{c,t})_{M_{4,5}}$ in Eqs. (3)–(5) denote that the integration is to be performed over the energy integral corresponding to the $M_{4,5}$ edges. There are some problems connected with the application of the sum rules on experimental data. The exact number of holes N_h in the f band is not directly measurable, nor is the expectation value $\langle T_z\rangle$ of the magnetic dipolar operator

$$\hat{T}_z = \frac{1}{2}[\sigma - 3\hat{\mathbf{r}}(\hat{\mathbf{r}}\cdot\sigma)]_z, \tag{6}$$

where σ denotes the vector of the Pauli matrices. The integrations in Eqs. (3)–(5) have to be performed over the energy interval which corresponds to the electron $3d\rightarrow 5f$ transition. It is important to note that the limits of this energy interval are not uniquely defined in the experiment and that it is assumed that the electron $3d\rightarrow 5f$ transition is the only relevant contribution to the absorption signal in this energy range. Above all, the sum rules are derived for the atomic case. In spite of all these limitations, the XMCD analysis, particularly at the $L_{2,3}$ edges, has been proven to be a very successful tool for investigations of the magnetism in transition-metal systems of various dimensionalities. However, there is less research about the validity of the sum rules for other materials, for example, actinides, especially in systems other than bulk. Hence, the subject of the present paper is a comparison of the magnetic moments calculated directly from the electronic structure with the moments obtained from the theoretical XMCD spectra by using Eqs. (1) and

(2). The theoretical approach is complementary to an experiment since some of the abovementioned uncertainties, particularly ones related to the number of holes, the $\langle T_z \rangle$ term and the integration limits, can be reduced to a minimum. This enables us to investigate the validity of the sum rules (1) and (2) without the influence of other effects present in the experiment, which are hard to control. The number of holes N_h is well defined. The integrations in Eqs. (3)–(5) are carried out over the interval between the Fermi energy E_F and the upper limit E_C, which is related to the N_h and to the f-resolved density of states $n_f(\epsilon)$ as $N_h = \int_{E_F}^{E_C} n_f(\epsilon) d\epsilon$. The $\langle T_z \rangle$ term is simply calculated as the expectation value of Eq. (6).

The calculations were performed within the framework of the density-functional theory by applying the WIEN97 code,[12] which adopts the full-potential linearized-augmented-plane-wave (FLAPW) method.[13] The Brillouin-zone (BZ) integrations were carried out with the modified tetrahedron method[14] by using 600 and 550 k points for the UAs/Co multilayer and the U film, respectively. The plane-wave cutoff parameter was set to 11.4 Ry for both systems. In order to investigate the influence of correlation effects, the exchange-correlation contribution to the effective potential was calculated by using different schemes, namely, the local-spin-density approximation (LSDA),[15] the generalized-gradient approximation (GGA),[16] and the LDA+U method.[17,18] The parameters U and J, which appear in the LDA+U scheme, were set to $U=2$ eV and $J=0.5$ eV.[19] The contribution of the spin-orbit coupling (SOC) was calculated in the second-variational scheme,[20,21] since it was demonstrated that a more rigorous treatment, for example, the first-variational scheme,[22] did not yield substantially different results for uranium, although the magnitude of the $5f$ uranium SOC interaction is comparable to the corresponding bandwidth. The absorption coefficients $\mu^+(\epsilon)$, $\mu^-(\epsilon)$, and $\mu^0(\epsilon)$ as a function of the photon energy ϵ were calculated using Fermi's golden rule in a nonrelativistic dipole approximation that is based on the evaluation of the matrix element for the operator $\hat{\mathbf{p}} \cdot \mathbf{e}$, with $\mathbf{e}$ denoting the polarization vector of the light.[23–25] However, note that the current implementation of the density functional theory cannot simulate the excited states which would result from a hole in the $3d$ state.

The UAs/Co multilayer was modelled with a supercell, based on a face-centered-cubic (fcc) stacking sequence along the (001) direction as presented in Fig. 1. The experimental lattice parameter $a=0.355$ nm for fcc Co was used. It turns out that the calculations performed on supercells with fewer Co layers do not result in a magnetic solution, in agreement with experiments at 300 K (Ref. 4), where no magnetic ordering was observed for the multilayers with the Co layer thinner than 1 nm. However, the present theoretical results do not prove the thesis that the absence of magnetism is due to the interdiffusion of U and As atoms into the Co layer. Furthermore, in the case of larger supercells, with more UAs layers, a finite magnetic moment at the U sites was found just at the interface, while in experiments[7] the magnitude of the moment increased with an increasing UAs thickness. The calculated spin $\langle \sigma_z \rangle$ and orbital $\langle l_z \rangle$ magnetic moments, obtained with the LDA+U method, are presented in Fig. 1. As demonstrated in Table I for the case of the U $5f$ moments, the LSDA and GGA do not give qualitatively different results, although the Coulomb repulsion U, in terms of the LDA+U method, enhances the orbital moments by about a factor of 2 (3) relative to the LSDA (GGA) values. In contrast to the low-temperature experiments[7] on the multilayers with amorphous UAs bilayers, carried out in the presence of high magnetic fields, the magnitude of the orbital moments are smaller than the magnitude of the spin moments. The magnitude of the total magnetic moment $|\langle l_z \rangle + \langle \sigma_z \rangle| \approx 0.1$ is much smaller than the corresponding experimental values[7] between 0.4 and 1.1. However, the LMTO calculations[26,27]

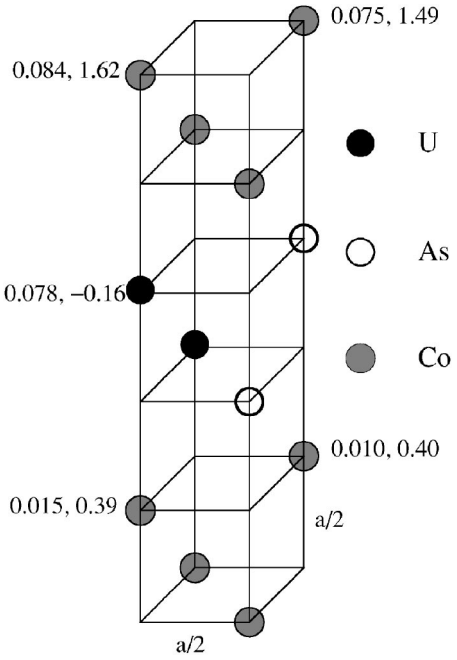

FIG. 1. A part of the As/Co-multilayer supercell, which is based on the fcc Co unit cell with the lattice parameter a. The numbers $\langle l_z \rangle$, $\langle \sigma_z \rangle$ represent the spin and orbital moments at particular U and Co sites obtained by applying the LDA+U method for the $5f$ U states.

TABLE I. A comparison between the $5f$ contribution to the orbital $\langle l_z \rangle$ and the spin $\langle \sigma_z \rangle$ magnetic moments at the U sites in the UAs/Co multilayer, calculated directly from the electronic structure, and obtained from the theoretical XMCD spectra by using the sum rules (1) and (2).

	$\langle l_z \rangle$	$\langle l_z \rangle$ from Eq. (1)	$\langle \sigma_z \rangle$	$\langle \sigma_z \rangle$ from Eq. (2)	$\langle \sigma_z \rangle$ from Eq. (2), $\langle T_z \rangle = 0$
LSDA	0.033	0.034	−0.138	−0.105	−0.109
GGA	0.025	0.027	−0.169	−0.121	−0.104
LDA+U	0.078	0.068	−0.162	−0.128	−0.138

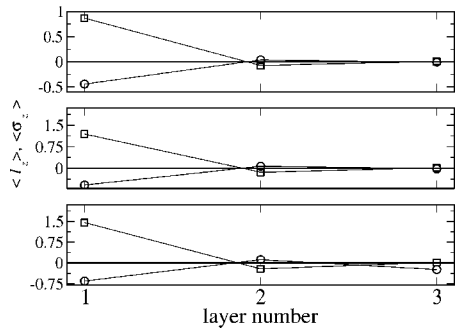

FIG. 2. The $5f$ orbital $\langle l_z \rangle$ (circles) and the spin $\langle \sigma_z \rangle$ (squares) magnetic moments as a function of the layer number for U film, calculated with the LSDA (upper graph), GGA (middle graph), and LDA+U method (lower graph).

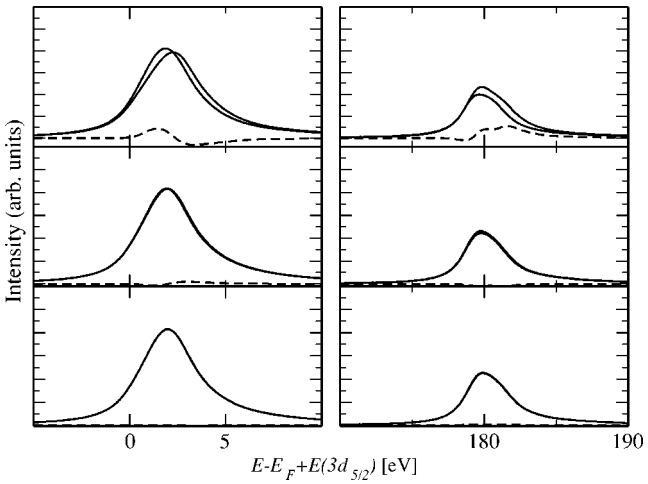

FIG. 3. The calculated absorption spectra for two polarizations (solid lines) and the XMCD signal (dashed lines) for the surface (upper graph), the second (middle graph), and the third (lower graph) layer of U film obtained by using the LDA+U method. The M_5 edge is shown on the left and the M_4 edge on the right panel.

on bulk U_3As_4 alloy yielded $|\langle l_z \rangle| > |\langle \sigma_z \rangle|$ already within the basic LSDA (Ref. 27) and even more when the Hund's rule was explicitly taken into account in terms of the orbital-polarization (OP)[28] contribution to the Hamiltonian. The results of the latter calculations[26] were also in a good agreement with experimental values. We satisfactory reproduced these results for the U_3As_4 alloy by using the FLAPW method. The OP term added to the LSDA increased the magnitude of the $\langle l_z \rangle$ for the UAs/Co multilayer to 0.051 which is still much less than the magnitude of the calculated $\langle \sigma_z \rangle$ and even below the LDA+U value. According to Lander *et al.*,[29] the hybridization of the $5f$ and $3d$ states in the actinide intermetallic compounds reduces $|\langle l_z \rangle|$ with the strongest effect in uranium materials. The hybridization in the modeled UAs/Co interface is strong due to a relatively small interatomic distance, which is determined by the fcc Co lattice parameter. In order to prove this hypothesis we performed a calculation for the multilayer with the lattice constant increased by 10%. As expected, the LSDA+OP ratio $-\langle l_z \rangle / \langle \sigma_z \rangle$ grew from 0.37 for the case of the fcc Co lattice constant to 1.03. Hence, the discrepancy between the experimental data for the amorphous UAs/Co multilayers and the theoretical results for the corresponding ordered material is to a large extent governed by the difference in the interatomic distances, which are for the ordered material fixed and determined by the Co crystal if an epitaxial growth is assumed. Some discrepancy might be also due to the difference in the ratio of atomic concentrations, [U]/[As] between the calculation ([U]/[As]=1) and the experiment[7] ([U]/[As]=1.5) since the results of the superconducting quantum interference device (SQUID) measurements[30] exhibited a pronounced composition dependence. We believe that the agreement with the experiment might be improved if a calculation allowing the relaxation of the UAs layers could be performed. At the interface there is an antiparallel alignment between the calculated U and Co spin moments, as explained by Lander *et al.*[29] The Co moments in the interface layer are drastically reduced relative to the moments in other layers or in the bulk, which is consistent with the vanishing of magnetism in the case of thin Co layers, as mentioned earlier.

A comparison between the U $5f$ moments calculated directly from the electronic structure and the moments obtained from the theoretical XMCD spectra is given in Table I. The orbital sum rule (1) holds well for all three types of the exchange-correlation potential. The validity of the spin sum rule (2) is worse, since the resulting moments underestimate the directly calculated values by ~20% (LDA+U) to ~30% (GGA). The influence of the magnetic dipole $\langle T_z \rangle$ term is below the deviation of the sum rule $\langle \sigma_z \rangle$ from the directly calculated value, although, surprisingly, the deviation is reduced when the $\langle T_z \rangle$ is omitted from Eq. (2) in the case of the LSDA and LDA+U.

The supercell for modeling the α-U (001) film was based on the orthorhombic structure and it contained six uranium and four vacuum layers (for details, see, for example, Ref. 9). As found previously,[9] the density-functional theory predicts a magnetic ordering on the U surface. Figure 2 demon-

TABLE II. A comparison between the $5f$ contribution to the orbital $\langle l_z \rangle$ and the spin $\langle \sigma_z \rangle$ U magnetic moments at the surface of the U film calculated directly from the electronic structure, and obtained from the theoretical XMCD spectra by using the sum rules (1) and (2).

	$\langle l_z \rangle$	$\langle l_z \rangle$ from Eq. (1)	$\langle \sigma_z \rangle$	$\langle \sigma_z \rangle$ from Eq. (2)	$\langle \sigma_z \rangle$ from Eq. (2), $\langle T_z \rangle = 0$
LSDA	−0.444	−0.364	0.869	0.722	0.714
GGA	−0.576	−0.479	1.193	0.981	0.956
LDA+U	−0.655	−0.546	1.456	1.194	1.162

strates that the calculated magnetic moments rapidly decrease with an increasing distance from the surface. However, the sign of the moments alternates, so that the moments in subsequent layers are aligned antiparallel to each other. In the surface and in the next layer, where the moments are possibly measurable, the magnitude of the spin moment $\langle \sigma_z \rangle$ is about two times larger than the magnitude of the orbital moment $\langle l_z \rangle$. The enhancement of the magnitude of $\langle l_z \rangle$ due to the Coulomb repulsion is smaller than in the case of the UAs/Co multilayer, whereas the LDA+U spin magnetic moment is almost two times larger than the corresponding LSDA value. The calculated XMCD signal is pronounced just for the surface layer, as shown in Fig. 3. Hence, only the surface magnetic moments are given in Table II. Both the orbital and the spin sum rule underestimate the directly calculated magnetic moments. The deviation is below 20%. The influence of the $\langle T_z \rangle$ term is even more subtle than in the case of the UAs/Co multilayer, although the validity of the spin sum rule is worse if this term is set to zero.

In conclusion, a theoretical test based on an *ab initio* calculation proved the XMCD method to be a suitable tool for investigating the magnetism in two-dimensional U systems, that arises from the ordered 5f magnetic moments. However, the results of the calculations on the UAs/Co multilayer suggest the ferromagnetism confined at the interface, and hence to some extent disagree with the experimental data and findings. This issue might be explored by performing the x-ray-resonant-magnetic-scattering (XRMS) (Ref. 31) measurements of the magnetization profile. If ferromagnetism really exists on the surface of uranium, its presence should be readily proven by means of the XMCD, or probably even more likely the XRMS experiments.

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[1] M. S. S. Brooks, B. Johansson, and H. L. Skriver, in *Handbook of the Physics and Chemistry of Actinides*, edited by A. J. Freeman and G. H. Lander (North-Holland, Amsterdam, 1984), Vol. 1, p. 153.
[2] G. H. Lander and G. Aeppli, J. Magn. Magn. Mater. **100**, 151 (1991).
[3] O. Eriksson, L. E. Cox, B. R. Cooper, J. M. Wills, G. W. Fernando, Y. Hao, and A. M. Boring, Phys. Rev. B **46**, 13 576 (1992).
[4] T. S. Plaskett, P. Fumagalli, T. R. McGuire, R. J. Gambino, N. A. Bojarczuk, and J. Angilello, IEEE Trans. Magn. **22**, 2659 (1992).
[5] P. Fumagalli, T. S. Plasket, D. Weller, T. R. Mcguire, and R. J. Gambino, Phys. Rev. Lett. **70**, 230 (1993).
[6] D. Mannix, W. G. Stirling, D. G. Bucknall, P. W. Haycock, S. D. Brown, G. H. Lander, and T. S. Plaskett, Physica B **234–236**, 470 (1997).
[7] N. Kernavanois, D. Mannix, P. D. de Réotier, J. P. Sanchez, A. Yaouanc, A. Rogalev, G. H. Lander, and W. G. Stirling, Phys. Rev. B **69**, 054405 (2004).
[8] G. Schütz, W. Wagner, W. Wilhelm, P. Kienle, R. Zeller, R. Frahm, and G. Materlik, Phys. Rev. Lett. **58**, 737 (1987).
[9] N. Stojić, J. W. Davenport, M. Komelj, and J. Glimm, Phys. Rev. B **68**, 094407 (2003).
[10] B. T. Thole, P. Carra, F. Sette, and G. van der Laan, Phys. Rev. Lett. **68**, 1943 (1992).
[11] P. Carra, B. T. Thole, M. Altarelli, and X. Wang, Phys. Rev. Lett. **70**, 694 (1993).
[12] P. Blaha, K. Schwarz, P. Sorantin, and S. B. Trickey, Comput. Phys. Commun. **59**, 399 (1990).
[13] E. Wimmer, H. Krakauer, M. Weinert, and A. J. Freeman, Phys. Rev. B **24**, 864 (1981).
[14] P. E. Blöchl, O. Jepsen, and O. K. Andersen, Phys. Rev. B **49**, 16 223 (1994).
[15] J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13 244 (1992).
[16] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and G. Fiolhais, Phys. Rev. B **46**, 6671 (1992).
[17] V. I. Anisimov, I. V. Solovyev, M. A. Korotin, M. T. Czyżyk, and G. A. Sawatzky, Phys. Rev. B **48**, 16 929 (1993).
[18] A. I. Liechtenstein, V. I. Anisimov, and J. Zaanen, Phys. Rev. B **52**, R5467 (1995).
[19] A. N. Yaresko, V. N. Antonov, and P. Fulde, Phys. Rev. B **67**, 155103 (2003).
[20] D. J. Singh, *Plane Waves, Pseudopotentials and LAPW Method* (Kluwer Academic, Dordrecht, 1994).
[21] P. Novák (unpublished).
[22] M. Komelj (unpublished).
[23] R. Q. Wu and A. J. Freeman, J. Magn. Magn. Mater. **132**, 103 (1994).
[24] J. Kuneš, P. M. Oppeneer, H. C. Mertins, F. Schaäfers, A. Gaupp, W. Gudat, and P. Novák, Phys. Rev. B **64**, 174417 (2001).
[25] J. Kuneš, P. Novák, M. Diviš, and P. M. Oppeneer, Phys. Rev. B **63**, 205111 (2001).
[26] L. M. Sandratksii and J. Kübler, Phys. Rev. B **55**, 11 395 (1997).
[27] V. N. Antonov, B. N. Harmon, A. N. Yaresko, and A. Y. Perlov, Phys. Rev. B **59**, 14 571 (1999).
[28] O. Eriksson, M. S. S. Brooks, and B. Johansson, Phys. Rev. B **41**, 9087 (1990).
[29] G. H. Lander, M. S. S. Brooks, and B. Johansson, Phys. Rev. B **43**, 13 672 (1991).
[30] P. Fumagalli, T. S. Plaskett, T. R. McGuire, R. J. Gambino, and N. A. Bojarczuk, Phys. Rev. B **46**, 6187 (1992).
[31] J. P. Hannon, G. T. Trammell, M. Blume, and D. Gibbs, Phys. Rev. Lett. **61**, 1245 (1988).