Field-induced magnetism in itinerant f-electron systems: U, Pu, and Ce

Anders Hjelm
Department of Technology, Uppsala University, Box 534, S-751 21 Uppsala, Sweden

Joakim Trygg, Olle Eriksson, and Börje Johansson
Condensed Matter Theory Group, Department of Physics, Uppsala University, Box 530, S-751 21 Uppsala, Sweden

John Wills
Theoretical Division, Los Alamos National Laboratory, New Mexico 87545
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We demonstrate, by means of first-principles calculations, that in the field-induced magnetic state of α-cerium and α-uranium the spin and orbital moments are coupled parallel rather than antiparallel as expected from Hund's third rule. This behavior gives a magnetic form factor for α-uranium in very good agreement with experiment. The calculated form factor of α-cerium, when assuming that the f electron is itinerant, is very different from the localized Ce^{3+} form factor, and we propose that a measurement of the magnetic form factor of α-Ce can indicate whether the f state is localized or itinerant. The field-induced magnetism of plutonium is shown to be almost exclusively of orbital character and the induced spin density of plutonium is highly anomalous.

I. INTRODUCTION

Normally, the spin and orbital moments couple antiparallel in systems with less than half-filled electronic shells, while systems with more than half-filled shells have parallel coupling between the moments. This is understood to be caused by spin-orbit coupling and the effect is often referred to as Hund's third rule,[1] well-known from atomic physics but also observed for itinerant electron systems.[2] For instance, the spin and orbital moments of UN were, from first-principles calculations, predicted to be large and antiparallel.[2] Several other itinerant electron systems displaying large spin and orbital moments have since then been discovered and it seems that metallic systems with large spin and orbital moments are almost exclusively found in f electron materials.[3,4] Furthermore, for all itinerant f electron systems the shell is less than half filled and an antiparallel configuration of the magnetic moments is expected. As an example of an itinerant $5f$ electron compound where both the spin and orbital moments are large we mention UFe_2.[4,5] In this material the net $5f$ moment is almost zero whereas the individual $5f$ spin and orbital components are large and antiparallel. This gives rise to several striking characteristics of the magnetic properties of UFe_2. For instance the magnetic form factor, which in the dipole approximation can be represented as[6]

$$f(q) = \mu(\langle j_0\rangle + C_2\langle j_2\rangle), \tag{1}$$

is quite anomalous. [In Eq. (1) μ is the total magnetic moment, C_2 the ratio between the orbital moment, and the total moment, $q = \sin\theta/\lambda$ is the momentum transfer with θ and λ being the scattering angle and the neutron wavelength, respectively, and $\langle j_n\rangle$ $(n = 0, 2)$ are radial averages of spherical Bessel functions weighted with the spin density.] The shape of $\langle j_0\rangle$ is very different from the shape of $\langle j_2\rangle$. The former has a maximum at $q = 0$ and is monotonically decreasing up to $q \approx 0.6$, whereas the latter equals zero at $q = 0$ and increases initially up to a maximum at $q \approx 0.25$ (for a typical f spin density). At larger q values $\langle j_2\rangle$ is also decreasing up to $q \approx 0.6$. We indicate this behavior of $\langle j_0\rangle$ and $\langle j_2\rangle$ in Fig. 1. If the spin and orbital moments are large and antiparallel the resulting total moment can be small, which will result in a large value for C_2 and the corresponding form factor is then dominated by the $\langle j_2\rangle$ function. This is the situation found in, for instance, UFe_2.[4,5] If the magnetism is dominated by the spin contribution (such as in the $3d$ systems) the C_2 value is small and the form factor is very

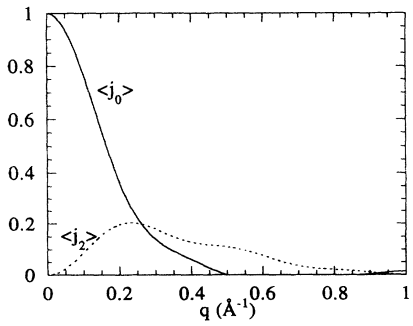

FIG. 1. A typical example of the form of the $\langle j_0\rangle$ and $\langle j_2\rangle$ functions (solid and dashed lines, respectively), calculated for fcc-U at the volume of the α phase. q is the momentum transfer.

similar to the $\langle j_0 \rangle$ function in Fig. 1.

Paramagnetic systems can be investigated and analyzed in a similar way, but in this case an external magnetic field has to be present in order to induce a magnetization density in the material. The induced magnetic moments are also considerably smaller than the spontaneous ones.

Magnetic materials involving early actinides in general show spin and orbital moments of the same order of magnitude, with antiparallel coupling, and correspondingly they have large C_2 values and form factors that are heavily influenced by the $\langle j_2 \rangle$ function. Therefore, it is highly surprising that the field-induced magnetism in α-U displays a form factor that lacks this characteristic feature.[7] Instead, the field-induced magnetism in α-U gives rise to a form factor that is dominated by the $\langle j_0 \rangle$ function and the C_2 value is small. Earlier suggestions to explain this behavior have been that the orbital moment is quenched for some unknown reason, e.g., that correlation and spin-orbit effects are weaker at the Fermi level, or that the $5f$ wave functions, and hence also the spin density, are much more delocalized than expected. However, in a previous report[8] we demonstrated that this atypical behavior can be explained by the response of the orbital moment to the applied magnetic field which causes *parallel* coupling between the spin and orbital moments and our first-principles calculations, which incorporate the Zeeman operator in the crystal Hamiltonian, reproduced the experimental form factor. We here give a more detailed report on our previous results as well as present more accurate calculations for uranium. We also report on studies of field-induced magnetism in some other paramagnetic itinerant f electron materials, α-Pu and α-Ce. The rest of this paper is organized as follows. Section II describes the details of our calculations, Sec. III presents the results for U, Pu, and Ce, whereas in Sec. IV we make some concluding remarks.

II. DETAILS OF CALCULATIONS

The calculations were done with the linear-muffin-tin-orbital (LMTO) method,[9,10] and many-body effects were included by means of the local spin density approximation. Most of the calculations were done in the atomic spheres approximation (ASA)[9,10] and for an fcc crystal structure. For α-Ce this is the true crystal structure whereas for α-U and α-Pu it is an approximation. The crystal structures of α-U and α-Pu are too open and complicated to be accurately treated within the LMTO-ASA method. We have, therefore, also employed a full-potential LMTO (FP-LMTO) method[11] for the calculations of α-U, as open structures do not impose any difficulty for this method. Also, the FP-LMTO method is more accurate in the sense that there are no shape restrictions on the density or the potential, while in the LMTO-ASA method spherical symmetry is assumed. As will be seen below, the differences between the results for the fcc (LMTO-ASA) and for the α (FP-LMTO) structures are small. To our knowledge, no full-potential calculations for the α structure of plutonium have been performed, and it is more uncertain how large the structure dependent effects are in this case. Due to the complexity of this structure we have not performed calculations for Pu in the α phase (16 atoms per unit cell, monoclinic Bravais lattice).

The calculational scheme for the LMTO-ASA method, including an external magnetic field self-consistently, has recently been discussed in detail[12,13] and, therefore, we will only give a brief description here. The spin-orbit (SO) interaction, $\xi \boldsymbol{l} \cdot \mathbf{s}$, as well as the Zeeman operator, $H_Z = \mu_B \mathbf{B} \cdot (\boldsymbol{l} + 2\mathbf{s})$, were included at each variational step. When constructing the exchange-correlation potential we used the parametrization of Vosko, Wilk, and Nusair.[14] For most of the calculations we also employed the orbital polarization (OP) correction, in the form suggested in Ref. 15. The LMTO-ASA calculations were done for fcc lattices at lattice constants corresponding to the experimental α-phase volumes. The direction of the magnetic field was along the [001] direction, the irreducible part of the Brillouin zone was (1/16), and sampled at 1359 $\mathbf{k}$ points. When self-consistency was achieved the spin and orbital moments were computed as described by Brooks and Kelly.[2]

For the calculations of uranium in the α structure we have used a full-potential linear muffin-tin-orbital technique.[11] The calculations were all electron, fully relativistic, with the orbital polarization correction included as well as the Zeeman term.[16] The exchange and correlation potential was treated in the local spin density approximation using the von Barth–Hedin potential with the Janak parameterization.[17] The charge density and potential were constructed without shape restrictions inside the muffin tins as well as in the interstitial region. The basis set, charge density, and potential were expanded in spherical harmonic series within the nonoverlapping muffin-tin spheres and in a Fourier series in the interstitial region. The basis set comprised augmented linear muffin-tin orbitals.[9,10] The tails of the basis function outside their parent spheres were linear combinations of Hankel or Neumann functions with nonzero kinetic energy κ^2. The FP-LTMO basis set that we use here included four different κ values. Thus on each uranium site we place $7s$, $7p$, $6s$, $6p$, $6d$, and $5f$ orbitals. All states were contained in the same energy panel, with the $6s$ and $6p$ orbitals treated as pseudovalence states in an energy set different from the rest of the basis. Furthermore, we used a so-called "double basis" where we used two different orbitals each connecting, in a continuous and differentiable way, to Hankel or Neumann functions with different κ values. The integration over the Brillouin zone was done using 275 $\mathbf{k}$ points in the (1/4) irreducible wedge of the zone. The direction of magnetic field was the same as in the LMTO-ASA calculation and the calculation was done at the experimental lattice constant for the α phase of uranium.

III. RESULTS

A. α uranium

The calculated spin and orbital moments for uranium are presented in Table I. The magnetic field strength

TABLE I. Calculated spin and orbital moments in uranium, in an external field of 7 T. The calculations were done at various levels of approximation with or without the orbital polarization, OP, and with or without the $\mathbf{B} \cdot \boldsymbol{l}$ coupling in the Zeeman operator. The first four lines are calculated for the fcc structure using the LMTO-ASA method, while the last line contains results from a calculation in the α structure using a FP-LMTO method.

Zeeman term	OP	Spin moment	Orbital moment	Total moment	C_2	Expt. moment
Spin only	No	0.0040	-0.0026	0.0014	-1.8	
Spin only	Yes	0.0049	-0.0048	0.0001	-60	
Spin and orbital	No	0.0021	0.0028	0.0049	0.6	
Spin and orbital	Yes	0.0012	0.0042	0.0054	0.8	
Spin and orbital	Yes	0.0009	0.0038	0.0047	0.8	0.0049[a]

[a]Reference 7.

used in the experiments[7] for α-U was 7 T and this value was, therefore, used also in the present calculations. In the experiment the induced moment was estimated to be $0.0049\mu_B$ per atom. This value is in good agreement with our calculations (cf. Table I) when both the spin and orbital interactions with the external field are included. Also, the calculated value for C_2 is low, in agreement with experiment.[7] We will return to this fact in more detail below when discussing the magnetic form factor. On the other hand, our calculated (LMTO-ASA) moments, when neglecting the $\mathbf{B} \cdot \boldsymbol{l}$ term, yields a total moment much smaller than the experimental value and the magnitude of the C_2 constant then becomes huge, $\sim$60 (cf. Table I). However, the most important result presented in Table I is that when the external field $\mathbf{B}$ is interacting with both the spin and orbital moment *these moments are parallel*, and this coupling gives rise to a low C_2 value. This is opposite to what Hund's third rule stipulates for uranium. Namely, it is expected that the spin-orbit coupling, $\xi \boldsymbol{l} \cdot \mathbf{s}$, will cause an antiparallel alignment.[2] However, *the interaction between the magnetic field and the spin and orbital moments in the Zeeman operator favors a parallel alignment*, and there will, therefore, be a competition between the spin-orbit energy and the Zeeman polarization energy. Apparently, even in metallic systems with a very large spin-orbit coupling (uranium) an external magnetic field can induce a parallel coupling between the spin and orbital moments, despite the fact that the $5f$ shell is less than half filled.

We have also performed a calculation for α-uranium in the true crystal structure using a FP-LMTO method. The difference in calculated magnetic moment compared to the LMTO-ASA method is small (cf. Table I). However, both the spin moment and the orbital moment are somewhat reduced compared to the LMTO-ASA results and this brings the total magnetic moment very close to the moment deduced from experiment.

The parallel coupling between the spin and orbital moments in α-U is a breakdown of Hund's third rule, in the sense that the total spin and orbital moments of each site are parallel, although the f shell is less than half filled. However, if we make a closer investigation of the electronic structure we find that the perturbation from the external field is minor. In the absence of an external magnetic field the expectation value of the orbital moment projected on the spin-up states is quite large, antiparallel to and of exactly the same size as the expectation value of the orbital moment projected on the spin down states, due to the spin-orbit coupling. Thus, in the nonmagnetic state the net magnetic moment is exactly zero, for a paramagnetic metal. However, if we apply an external magnetic field, the population of one spin channel is increased while the other one is decreased, causing a small field-induced spin moment. Simultaneously, the m_l projected states also shift in energy and repopulation occurs, due to the orbital term in the Zeeman operator, in such a way that the orbital moments of each spin channel is increased in the direction that is parallel to the field. This will create a small orbital moment parallel to the field direction. Simultaneously, the spin-split bands acquire an antiparallel component to the orbital moment due to the spin-orbit coupling. When the spin and orbital contributions to the total moment are added, the Zeeman effect gives a larger contribution to the total orbital moment than the combined effect of spin splitting and spin-orbit coupling does (a more detailed analysis is given below), and both the spin and orbital moments of the site will be parallel to the applied field. Nevertheless, in each spin channel the orbital moment is antiparallel to the spin moment, and in that sense Hund's third rule is still valid. In this context it is appropriate to remark that this effect can only occur in metallic systems that are not spontaneously spin polarized.

The picture presented above can be used to obtain a simple estimate of the spin-orbit energy which, together with the Zeeman energy, demonstrates that our calculations provide the correct behavior for uranium metal and that the parallel coupling will be found irrespective of the size of the magnetic field (the special case of a metamagnetic phase transition will be discussed below). The energy of the spin-orbit splitting in the metal can be estimated as

$$E_{\mathrm{SO}}^0 \approx \xi[S_z^{\uparrow} L_z^{\uparrow} + S_z^{\downarrow} L_z^{\downarrow}] \,, \tag{2}$$

where ξ is the spectroscopic spin-orbit parameter, which for uranium is 0.21 eV. $S_z^{\uparrow}$, $L_z^{\uparrow}$, $S_z^{\downarrow}$, and $L_z^{\downarrow}$ denote the expectation values of the components of the spin and orbital momenta in the z direction, where arrows indicate spin-up and spin-down projected states, respectively. In the nonmagnetic case we have $S_z^{\uparrow} = -S_z^{\downarrow}$ and $L_z^{\uparrow} = -L_z^{\downarrow}$ and the total spin and orbital momenta, $S_z^{\uparrow} + S_z^{\downarrow}$ and $L_z^{\uparrow} + L_z^{\downarrow}$ are zero. If an external field induces small spin and orbital momenta (s_z and l_z) the spin-orbit energy is

modified to

$$E^1_{\rm SO} \approx \xi \left[\left(S^\uparrow_z + \frac{s_z}{2} \right) \left(L^\uparrow_z + \frac{l_z}{2} \right) + \left(S^\downarrow_z + \frac{s_z}{2} \right) \left(L^\downarrow_z + \frac{l_z}{2} \right) \right] = \xi [S^\uparrow_z L^\uparrow_z + S^\downarrow_z L^\downarrow_z] + \xi 2 \frac{s_z}{2} \frac{l_z}{2} = E^0_{\rm SO} + \frac{\xi}{2} s_z l_z. \quad (3)$$

So the spin-orbit energy difference between the nonmagnetic and the magnetized states, which governs the antiparallel coupling, can be estimated as $\frac{\xi}{2} s_z l_z$, where s_z and l_z are the expectation values of the spin and orbital momenta in the induced state. Furthermore, when induced by an external field B these momenta can be written as $-\frac{\chi_s}{2} B$ and $-\chi_l B$,[18] where χ_s and χ_l are the spin and orbital contributions to the susceptibility, respectively, in units of Bohr magnetons per atom and per tesla. Consequently, the spin-orbit energy can be estimated as $\frac{\xi}{2} \frac{\chi_s}{2} B \chi_l B$. The competing energy is the orbital Zeeman energy, $\mu_B B l_z$, or $-\mu_B B \chi_l B$. The gain in energy from the orbital Zeeman term will be larger than the spin-orbit energy (and, therefore, the moments will be parallel) whenever

$$\mu_B B^2 \chi_l > \frac{\xi}{2} B^2 \frac{\chi_s \chi_l}{2} \quad (4a)$$

or

$$\chi_s < 4\mu_B/\xi. \quad (4b)$$

As long as the susceptibilities are field independent this inequality relation is also field independent. For uranium, the expression to the right in Eq. (4b) is 11.2×10^{-4} μ_B atom^{-1} T^{-1}. From our calculated density of states at the Fermi level (for the α structure) we estimate the Pauli spin susceptibility to be 1.7×10^{-4} μ_B atom^{-1} T^{-1}, which means that an exchange enhancement factor larger than 6.4 is needed in order to make the spin-orbit energy larger than the orbital part of the Zeeman energy. The Stoner product for α-U is approximately 3, and our explicit first-principles calculations show that the enhancement factor is even smaller, and thus the parallel coupling between spin and orbital moments can be explained and shown to be independent of the field strength. The latter requires that the susceptibilities are approximately constant, which they sometimes are not, e.g., at a metamagnetic phase transition.

The discussion above implies that if the spin susceptibility is sufficiently large the coupling between the spin and orbital moments will be antiparallel. In order to investigate this in more detail we have calculated the magnetic response of U at expanded volumes, since the spin susceptibility is expected to increase with volume. In Fig. 2 we show the field-induced spin and orbital moments of U at various volumes. The calculations presented in Fig. 2 were all performed for an fcc lattice with the LMTO-ASA method, and included a field of 7 T in the Zeeman operator and no orbital polarization. Notice from Fig. 2 that at smaller volumes the coupling between the spin and orbital moments is parallel whereas at volumes larger than $\sim$ 27 Å^3 the coupling is antiparallel. Surprisingly, at larger volumes it is the orbital moment that is parallel to the applied field while the spin moment is antiparallel. This effect serves as a useful illustration of different competing effects in metallic paramagnetic systems with large angular momenta. As shown in an earlier paper[13] large orbital contributions to the paramagnetic susceptibility is possible in f electron systems, several times larger than the spin contribution. Therefore, it is reasonable to expect that the orbital moment is aligned with the external field, and the question is whether the spin moment is parallel or not. This question finds it answer by comparing the spin term of the Zeeman operator and the spin-orbit energy. The spin moment will be parallel to the applied field when

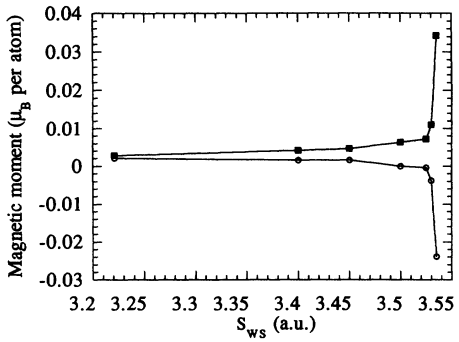

FIG. 2. The calculated spin (circles) and orbital (squares) moments of fcc-uranium at a magnetic field of 7 T as a function of Wigner-Seitz radius (proportional to the lattice constant). The calculations do not use the OP correction.

$$\mu_B B^2 \chi_s > \frac{\xi}{2} B^2 \frac{\chi_s \chi_l}{2} \quad (5a)$$

or

$$\chi_l < 4\mu_B/\xi. \quad (5b)$$

This constraint is similar to Eq. (4b), but the upper limit is now set by the orbital susceptibility. If χ_l is larger than χ_s, and both are proportional to the density of states at the Fermi level, which is a reasonable assumption, the cost in spin-orbit energy will become larger than the gain in Zeeman *spin* energy before it becomes larger than the gain in Zeeman *orbital* energy, and consequently the spin moment will turn antiparallel during the expansion. Finally, at large volumes the system polarizes with an orbital moment in the direction of the applied field, and a smaller and antiparallel spin moment.

When comparing our calculated magnetic form factor for uranium (at the equilibrium volume) with the experimental data (Fig. 3), it may be seen that the agreement between experiment and theory is very good, but only when the magnetic field is allowed to interact with the orbital as well as the spin moment. When the $\mathbf{B} \cdot \boldsymbol{l}$ term is neglected, the resulting form factor (also shown in Fig. 3) resembles the form factor of, for instance, UFe_2 or $PuFe_2$.[3,4] In this case the spin and orbital moments are antiparallel and correspondingly the magnitude of C_2 is

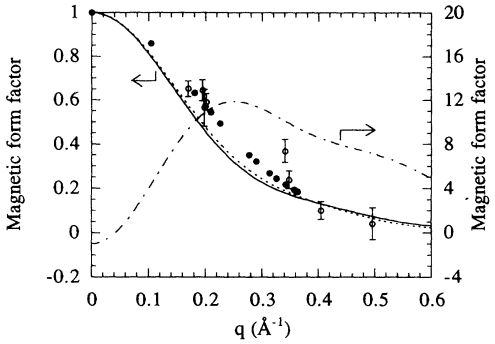

FIG. 3. The field-induced magnetic form factor $f(q)$ for α-U, calculated for the fcc structure using the LMTO-ASA method, with (solid line) and without (dashed line) the OP correction. As a comparison, the form factor calculated when omitting the orbital term in the Zeeman operator, $\mu_B \mathbf{B} \cdot \boldsymbol{l}$, is presented (dot-dashed line). Filled circles indicate the form factor calculated for the α structure using the FP-LMTO method. Finally, the experimental values (Ref. 7) are presented as empty circles.

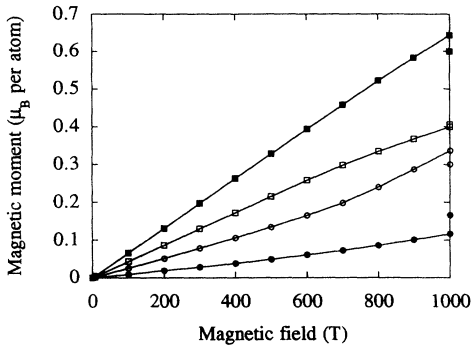

FIG. 4. The calculated magnetic response of fcc-U as a function of applied field, divided on the spin (circles) and orbital (squares) components. Filled symbols indicate calculations where the OP correction is included, while the empty symbols represent values calculated without the OP correction. The symbols at 1000 T without joining lines display values linearly extrapolated from the calculations at 7 T.

very large (since the net moment is small) and the resulting form factor behaves like $\langle j_2 \rangle$, in disagreement with experiment. These results definitely prove that the interaction between magnetic fields and metallic electrons is not sufficiently described by pure spin splitting. Also, the orbital interaction with the field is necessary to include, in order to obtain a proper description of the field-induced magnetization.

Also noteworthy in Fig. 3 is that the agreement between theory and experiment is further improved when the calculation is performed for the correct α structure, and when including nonspherical terms in the density and potential.

In many compounds uranium display f driven magnetism. As demonstrated in the present paper the interplay between exchange, correlation, spin-orbit coupling, and an external field is not at all obvious, and requires first-principles calculations in order to sort out the dominating mechanism. Of particular interest is the response to high magnetic fields, where nonlinear effects can change the balance between the competing energies, and hence create, e.g., meta-magnetic transitions. We, therefore, have investigated the high-field response of fcc-U within the present model. As shown in Fig. 4, up to fields of 1000 T no dramatic effects occur. The deviation from the low-field susceptibility is indicated in the figure by showing the values extrapolated from low fields (7 T). As can be seen, the nonlinear effects are rather small even at 1000 T, although the curve for the spin moment calculated without OP has an upward turn towards 1000 T.

B. α plutonium

With the results of uranium in mind it becomes very interesting to study the magnetic response to an applied field of α-Pu. The reason for this is twofold. First, the spin-orbit coupling in Pu is larger than in U and, second, the susceptibility (at zero temperature) is larger than in U. It is thus expected that Pu is closer to the point where the spin and orbital moments change from parallel to antiparallel coupling. Unfortunately, we are not aware of any experiments performed on Pu which might have revealed whether or not the coupling is parallel. Our results are, therefore, a prediction.

As mentioned earlier, the orbital contribution to the paramagnetic susceptibility is larger than the spin contribution in uranium. Consequently, we can assume that also in plutonium the orbital moment is parallel to the applied field, and the question is whether the spin moment is parallel or not. A comparison of the energy of the spin Zeeman term and the spin-orbit energy can give a hint to the answer of that question. For Pu the criterion for a spin moment to be parallel to the applied field as well as to the orbital moment will be [compare Eq. (5b) in the previous section]

$$\chi_l < 4\mu_B/\xi = 8 \times 10^{-4} \mu_B \text{ atom}^{-1} \text{ T}^{-1}, \qquad (6)$$

since ξ is 0.28 eV per atom for Pu. The value of the orbital susceptibility, according to the model described in Ref. 13, is $3.7 \times 10^{-4} \mu_B$ atom^{-1} T^{-1}, while the self-consistently calculated value is much larger, $8.7 \times 10^{-4} \mu_B$ atom^{-1} T^{-1}. (All calculations for α-Pu are approximated with the fcc structure and make use of the LMTO-ASA method.) Thus, we see that Pu is close to the borderline where the spin can go antiparallel to the applied field and to the orbital moment. As can be seen in Table II this is confirmed in the self-consistent, first-principles calculations, including the full Zeeman operator. The spin moment is very small and in the opposite direction, because χ_l has become larger than 8×10^{-4}, and the inequality in Eq. (6) is no longer fulfilled. Thus, the field-induced magnetism in α-Pu is almost exclusively of orbital character.

In Table II, the experimental value of the susceptibility is also given, and it is close to the calculated value. The experimental value also contains diamagnetic contributions and thus the paramagnetic experimental moment is expected to be somewhat larger. It is also uncertain

TABLE II. Calculated spin and orbital moments in fcc plutonium in an external field of 10 T, in similarity to Table I.

Zeeman term	OP	Spin moment	Orbital moment	Total moment	C_2	Expt. moment
Spin only	No	0.0216	-0.0152	0.0063	-2.4	
Spin only	Yes	0.0101	-0.0110	-0.0007	15	
Spin and orbital	No	0.0062	0.0060	0.0122	0.5	
Spin and orbital	Yes	-0.0003	0.0087	0.0084	1.0	0.0098[a]

[a]Using the susceptibility in Reference 27.

how accurate it is to approximate α-Pu with an fcc crystal. However, the results mentioned above for uranium indicate that the errors are more of a quantitative nature rather than qualitative.

Next, we discuss the calculated magnetic form factor of Pu. The total form factor as well as the $\langle j_0 \rangle$ and $\langle j_2 \rangle$ functions are plotted in Fig. 5. Notice that the shape of both functions is drastically different from what we showed in Fig. 1. This is a very surprising result since, to our knowledge, all previous experience shows that the shape of $\langle j_0 \rangle$ and $\langle j_2 \rangle$ is very similar to what we showed in Fig. 1. Since the $\langle j_0 \rangle$ and $\langle j_2 \rangle$ functions are averages of spherical Bessel functions over the spin density it seems reasonable to suspect that the unusual shape of the $\langle j_0 \rangle$ and $\langle j_2 \rangle$ functions is due to the shape of the induced spin density. To investigate this we show in Fig. 6 the induced spin density of Pu corresponding to the form factor in Fig. 5. Notice that the spin density does indeed display a very unusual shape, the small spin moment obtained in the calculations is a manifestation of a spin density changing sign and thus averaging out, and not of an almost-zero density over all space. Near the nucleus, where relativistic effects are more evident, the spin-orbit energy dominates and the local spin magnetization is antiparallel. Near the interstitial region the Zeeman energy dominates and the local spin magnetization is parallel. This balance between spin-orbit energy and Zeeman energy is illustrated further in Fig. 6, by considering the l projected spin densities. The f projected density, which is most influenced by spin-orbit coupling is negative over a large region of space and reaches positive values just before the sphere boundary, while the d projected density with smaller spin-orbit coupling is dominated by the Zeeman energy and is positive for all radii.

At this point it is appropriate to remark that when the OP correction is excluded from the calculational scheme, the magnetic form factor and spin density behaves similar to uranium. Furthermore, without the OP correction a meta-magnetic phase transition to a "normal" magnetic state occurs at a few hundred teslas. This transition is absent when the OP correction is taken into account.

C. α cerium

The field-induced magnetic state of α-Ce is of particular interest since from such studies one might add additional evidence to clarify the true ground state of α-Ce. Namely, from the results presented above one would expect that for α-Ce the field-induced magnetism will be of such a nature that the spin and orbital moments are parallel (since the spin-orbit coupling is smaller than for U and Pu). However, this only applies if the f electrons in α-Ce are delocalized. If the ground state of α-Ce is best described by for instance a localized $4f$ level coupled to the valence states, as described by the Kondo model,[19] one might expect a magnetic response from the f electrons which is more reminiscent of a free ion behavior. In such a situation the spin and orbital moments are antiparallel and the application of a small field will not break this coupling. The magnetic response is, therefore, expected to be very different for the two models (which contend in describing the ground state of α-Ce) and an experiment

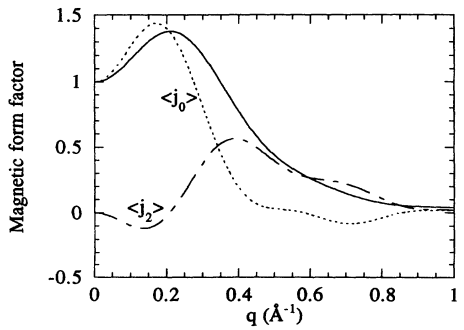

FIG. 5. The calculated field-induced magnetic form factor of fcc-Pu (solid line), including the OP correction. The dashed and dot-dashed lines show the $\langle j_0 \rangle$ and $\langle j_2 \rangle$ functions, respectively.

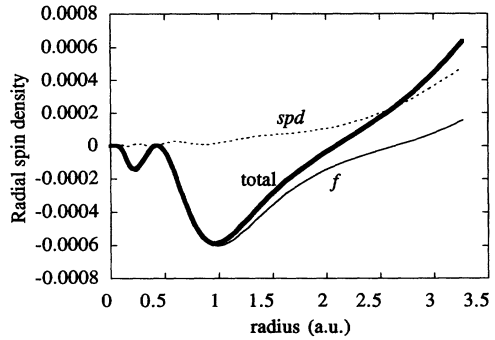

FIG. 6. The radial spin density of fcc-plutonium in a magnetic field of 10 T is shown as a thick solid line. The thin solid line indicates the contribution from the f electrons, while the dashed line shows the s, p, and d contribution. The calculations include the OP correction.

TABLE III. Calculated spin and orbital moments in α cerium in an external field of 10 T, presented as in the previous tables.

Zeeman term	OP	Spin moment	Orbital moment	Total moment	C_2	Expt. moment
Spin only	No	0.0034	-0.0012	0.0022	-0.5	
Spin only	Yes	0.0036	-0.0019	0.0017	-1.1	
Spin and orbital	No	0.0023	0.0039	0.0062	0.6	
Spin and orbital	Yes	0.0017	0.0050	0.0067	0.7	0.0095[a]

[a]Using the minimum value of the susceptibility in Reference 20.

on α-Ce aimed at studying the spin and orbital moments of the field-induced state might be very useful.

In this section, we present our calculated spin and orbital moments of α-Ce assuming itinerant f electrons. The self-consistently calculated moments in an external magnetic field of 10 T are thus presented in Table III. The corresponding magnetic moment from experiments[20] is also given. Compared to the experimental estimates the calculated values are too small, about two thirds of the measured susceptibility. If diamagnetic contributions are taken into account the difference is slightly larger. However, susceptibility measurements of α-Ce are difficult since the samples might contain minor fractions of other, magnetically ordered, phases and it is not obvious how these contributions should be accounted for.

The most important feature shown in Table III is the magnitude and direction of the orbital moment. When only the interaction between the field and the spin is considered the coupling between the spin and orbital moments are antiparallel. However, just as for U, when the full Zeeman term is treated the coupling between the spin and orbital moments is parallel. In this latter case the orbital susceptibility dominates the magnetic response. This gives rise to a magnetic form factor (Fig. 7) quite different from the form factor of the Ce^{3+} ion,[21] which also has a large orbital moment, but coupled antiparallel to the spin moment. In Fig. 7 we also display the calculated ionic (Ce^{3+}) form factor together with the measured field-induced form factor of γ-Ce.[22] The agreement between the experiment and the ionic form factor is good, as would be expected since it is well known that γ-Ce is trivalent with a localized $4f$ electron. If an experiment on α-Ce could be performed, it should be possible to distinguish whether the form factor resembles the metallic behavior calculated in the present work, or the ionic behavior, typical for the γ phase. Thus such an experiment could be used to help to determine the nature of the f electrons in α cerium.

As the energy difference between α-Ce and γ-Ce is quite small, it could be possible to induce a metamagnetic phase transition from the α to the γ phase by applying a sufficiently large magnetic field. In order to investigate this possibility we have calculated the spin and orbital magnetic moments of α-Ce as a function of field strength for large fields. The results are presented in Fig. 8. Up to 2500 T no phase transition is revealed for these fixed volume calculations. The slope of the moments show some variation across the field range, an effect that can be related to the shape of the density of states curve near the Fermi level. However, the calculations were done for a fixed volume, while a full treatment requires that also the volume is allowed to vary as a function of the applied field. We intend to do such studies in the near future.

IV. CONCLUSION

We have demonstrated that the interaction of the angular momentum with an external magnetic field results in parallel spin and orbital moments in α-Ce and α-U

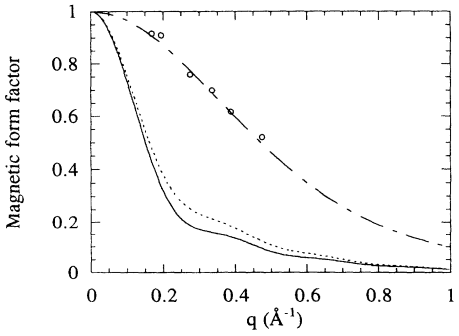

FIG. 7. The calculated field-induced magnetic form factor of α-Ce is presented, where it has been assumed that the f electron is metallic. The calculations are performed both with (solid line) and without (dashed line) the OP correction. Also presented is the form factor of γ-Ce, from calculations for the Ce^{3+} ion (dot-dashed line, Ref. 21) and experiments (circles, Ref. 22).

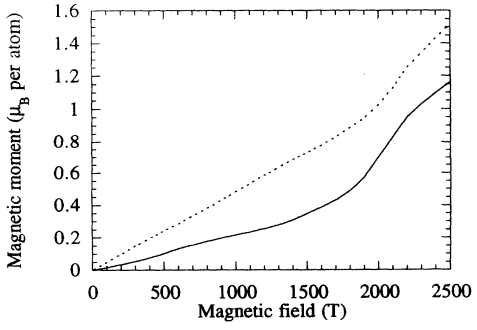

FIG. 8. The calculated magnetic response as a function of applied field strength for α-Ce. The spin (solid line) and orbital (dashed line) components are presented separately. The calculations include the OP correction.

whereas α-Pu is a borderline case where the spin moment is almost zero and the magnetism is dominated by the orbital contribution. The calculated magnetic behavior of α-U agrees very well with the measured magnetic form factor. We have presented simple arguments for why the Zeeman term drives the spin and orbital moments parallel and thus dominates over the interaction energy provided by the spin-orbit coupling. These arguments require that the "magnetic electrons" are itinerant and that the susceptibility is not dominated by either the spin or the orbital component, and that the material is not spontaneously spin-polarized (even above T_C, since short-range order can persist). In the latter case the spin and orbital moments will of course be antiparallel. Thus, if one could study f electron systems that undergo a meta-magnetic transition as a function of applied field one would presumably observe a huge difference in the shape of the magnetic form factor between the low- and high-field states. UCoAl might be a good candidate for such an experiment since it has been documented to undergo such a transition.[23]

The large orbital susceptibility (i.e., van Vleck-like) we have found for the presently studied systems might be surprising. However, for systems dominated by f electrons, the electrons have large angular momenta that can give strong interaction with the external magnetic field within the orbital term of the Zeeman operator. The possibility of large contributions to the susceptibility from the orbital states has been discussed before,[24,25] but to our knowledge the present work and the results presented in Ref. 8 are the first quantitative estimates for f metals. The present model is also a first approach to treat enhanced spin and orbital susceptibilities on the same footing, although diamagnetic effects of the conduction electrons are neglected.

Thus, the spin moments calculated in the present work are generally smaller than the orbital moments, and for α-Ce the spin susceptibility is only a factor 1.1 larger than the Pauli spin susceptibility. The enhancement of the total susceptibility is instead supplied by the orbital magnetization. Thus an "orbital paramagnet" would be a better description for α-Ce than the previously used label "exchange enhanced paramagnet". Also, the low value of the exchange enhancement in Ce explains the observations in Ref. 26, where the magnetic moment of Gd impurities in α-Ce were studied. The magnetic moment per Gd atom was found to be close to the value of pure Gd metal, whereas a large exchange enhancement in α-Ce should increase the moment per Gd atom significantly.

An experimental study of the field-induced magnetism of α-Ce might reveal if the presently assumed ground state, namely itinerant f electrons, is correct. If that is the case one would expect parallel spin and orbital moments of the field-induced state.

Plutonium is an even more extreme case since it is possible that the total moment is almost exclusively of orbital character and α-Pu may also be labeled as an "orbital paramagnet." Furthermore, the corresponding field-induced spin density in Pu is presently found to be anomalous and this results in very atypical shapes of the $\langle j_0 \rangle$ and $\langle j_2 \rangle$ functions. This result shows that the analysis of experimental data can be very misleading when $\langle j_0 \rangle$ and $\langle j_2 \rangle$ functions calculated from atomic spin densities are used to fit the experimental data. The $\langle j_0 \rangle$ and $\langle j_2 \rangle$ functions can be very dependent on the system studied.

ACKNOWLEDGMENTS

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