Breakdown of Hund's Third Rule for Induced Magnetism in U Metal

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An example of a breakdown of Hund's third rule for a system with less than a half filled electronic shell is presented. By means of spin polarized electronic structure calculations including the relativistic effects and a Zeeman term, we demonstrate that in the field induced magnetic state of uranium *the spin and orbital moments are coupled parallel rather than antiparallel as stipulated by Hund's third rule.* This provides an explanation for the measured field induced magnetic form factor of uranium metal.

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It has recently become well documented that itinerant f magnets in addition to the spin moment possess a substantial orbital magnetic moment [1–7]. The most direct experimental verification of this property has been obtained from neutron scattering experiments, showing an anomalous behavior of the f magnetic form factor as a direct consequence of the large orbital component. In this light, it becomes a contradiction that the prototype system for itinerant f electron states, uranium metal, appears to behave most normally in this respect. The measured induced magnetic form factor [8] shows a monotonic decrease as a function of the scattering wave vector Q, a behavior very similar to, for instance, the $3d$ ferromagnets. This atypical and unexpected behavior has not been addressed theoretically until now.

To illustrate the experimental and theoretical background more clearly we note that the magnetic form factor can be written (in the dipole approximation) [9]

$$f(Q) = \mu(\langle J_0\rangle + C_2\langle J_2\rangle), \tag{1}$$

where μ is the total magnetic moment, C_2 is the ratio between the orbital and total moment, i.e., $C_2 = \frac{\mu_{\text{orb}}}{\mu}$, and Q is the momentum transfer. $\langle J_0\rangle$ and $\langle J_2\rangle$ are averages of spherical Bessel functions for the spin density. The shape of $\langle J_0\rangle$ and $\langle J_2\rangle$ is very different; $\langle J_0\rangle$ equals 1 when Q is zero and then decreases monotonically with Q, whereas $\langle J_2\rangle$ is zero at $Q = 0$, increases initially, and then reaches a maximum at $Q \sim 0.25$. Normally, i.e., for systems where the orbital moment is small, C_2 is negligible and the resulting form factor has the same shape as the $\langle J_0\rangle$ function. This is, for instance, the case for all the $3d$ magnets. However, magnetism in itinerant f electron systems is considerably more exotic since for all known systems the orbital moment is large and therefore C_2 is substantial. The resulting form factor therefore has an appreciable contribution from the $\langle J_2\rangle$ function and thus has a unique shape [1–7]. There are even cases where the form factor is dominated by the $\langle J_2\rangle$ contribution [4,5]. It has been demonstrated that the unusually large values of C_2 in f electron systems with less than half filled shells have two causes [1–4]; the orbital moment is of the same magnitude as the spin moment *and* the spin and orbital moments are coupled antiparallel. The latter effect is stipulated by Hund's third rule. Thus, for these systems the total moment is substantially smaller than the individual spin and orbital moments, resulting in a large C_2 and therefore a unique shape of the magnetic form factor.

This Letter has mainly been motivated by neutron scattering measurements on uranium metal where the magnetic moment is induced by an external field [8]. The measured form factor lacks the usual fingerprint of a large C_2; instead the shape of the form factor is very similar to the $\langle J_0\rangle$ function yielding a quite low value for C_2 [8]. This behavior is most surprising and differs from actinide systems which spontaneously spin polarize [1–7]. There are other examples of uranium systems which are paramagnetic at low temperatures and have a field induced moment accompanied with a small C_2 [10].

Intrigued by these experimental observations we have studied this phenomenon theoretically on uranium metal, by means of self-consistent electronic structure calculations which include an external field $\mathbf{B}$. The method we have used was recently discussed in detail [11,12] and therefore we will only give a brief description here. The calculations were based on the local spin density approximation (LSDA) and the basis functions employed were the linear muffin-tin orbitals in the atomic sphere approximation (LMTO-ASA) [13,14]. The spin-orbit interaction, $\xi\mathbf{l}\cdot\mathbf{s}$, as well as the Zeeman operator, $H_Z = \mu_B\mathbf{B}\cdot(\mathbf{l} + 2\mathbf{s})$, were included at each variational step. When constructing the exchange-correlation potential we used the parametrization of Vosko, Wilk, and Nusair [15]. For some of the calculations we also employed the orbital polarization correction, in the form suggested in Ref. [16]. For simplicity the calculations were done for

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an fcc structure at a lattice constant corresponding to the experimental volume, rather than for the observed orthorhombic structure [17]. As the external magnetic field was applied in the [001] direction, the irreducible part of the Brillouin zone was one-sixteenth, which was sampled at 1359 k points. When self-consistency was achieved the spin and orbital moments were computed as described by Brooks and Kelly [1]. As has been shown earlier, incorporation of an external magnetic field in this way reproduces the anisotropy of the Zeeman splitting over Fermi-surface sheets as well as the total susceptibilities [11,12]. These successful applications of the present theory suggest that this is a suitable tool for studies of the electronic and magnetic structure of metals in external magnetic fields.

The calculated spin and orbital moments for uranium are presented in Table I, adopting a number of different approximations. The magnetic field strength used in the experiment [8] was 7 T and this value was therefore used 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 when both the spin and orbital interactions with the external field are included ($0.0054\mu_B$ per atom). Also, the calculated value for C_2 is low, in agreement with experiment [8]. We will return to this fact in more detail below when discussing the magnetic form factor. On the other hand our calculated moments, when neglecting the $\mathbf{B}\cdot\mathbf{l}$ term, yields a total moment much smaller than the experimental value and the magnitude of the C_2 constant is huge, ~ 60 (cf. Table I). However, the most important aspect of the results presented in Table I is that when the external field $\mathbf{B}$ is interacting with both the spin and orbital moments *the coupling between these moments is parallel.* This behavior is opposite to what Hund's third rule stipulates for uranium, as it is expected that the spin-orbit coupling, $\xi\mathbf{l}\cdot\mathbf{s}$, will cause an antiparallel alignment [1]. However, *the coupling between* $\mathbf{B}$ *and* $\mathbf{l}$ *favors a parallel alignment of* $\mathbf{s}$ *and* $\mathbf{l}$, and therefore there will be a competition between the spin-orbit energy and Zeeman orbital polarization energy. Apparently, even in systems with a very large spin-orbit coupling (uranium) an external magnetic field can result in a parallel coupling between the spin and orbital moment, despite the fact that the shell is less than half filled. *We have thus found an anomalous situation where Hund's third rule does not apply.*

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 $\mathbf{B}\cdot\mathbf{l}$ coupling in the Zeeman operator.

OP	Zeeman operator	Spin moment	Orbital moment	Total moment	C_2
No	Spin only	0.0040	−0.0026	0.0014	−1.8
Yes	Spin only	0.0049	−0.0048	0.0001	−60
No	Spin and orbital	0.0021	0.0028	0.0049	0.6
Yes	Spin and orbital	0.0012	0.0042	0.0054	0.8

A simple estimate of the spin-orbit and Zeeman orbital energies 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 [18]. The energy of the spin-orbit splitting, which governs the antiparallel coupling, is estimated as $\xi\langle l_z\rangle\langle s_z\rangle$ where $\langle l_z\rangle$ and $\langle s_z\rangle$ are the expectation values of l_z and s_z in the induced state and ξ is the spectroscopic spin-orbit parameter, which for uranium is 0.21 eV. Furthermore, the spin and orbital angular momenta induced by an external field B in a paramagnetic system can be written as $-\chi_l B$ and $-\frac{\chi_s}{2}B$ [19], where χ_s and χ_l are the spin and orbital contributions to the susceptibility, in units of Bohr magnetons per atom and per tesla. Consequently, the spin-orbit energy can be written as $\xi\chi_l B\frac{\chi_s}{2}B$. The competing energy is the orbital Zeeman energy, $\mu_B B\langle l_z\rangle$, or $-\mu_B B\chi_l B$. The gain in energy from the orbital Zeeman term will be larger than the spin-orbit energy loss (and therefore the moments will be parallel) when $\mu_B B^2\chi_l > \xi B^2\frac{\chi_l\chi_s}{2}$, or $\chi_s < 2\mu_B/\xi = 5.6\times 10^{-4}\mu_B$ atom^{-1} T^{-1}. As long as the susceptibilities are field independent this inequality relation is also field independent. From our calculations (density of states at the Fermi level) we estimate that the Pauli spin susceptibility is $1.9\times10^{-4}\mu_B$ atom^{-1} T^{-1}, which means that an exchange enhancement factor larger than 2.9 would be needed in order to make the spin-orbit energy larger than the orbital part of the Zeeman energy. When using the full Hamiltonian the enhancement factor is smaller than this value, and thus the parallel coupling between spin and orbital moments can be explained and shown to be independent of the strength of the field. If the exchange enhancement raises over 2.9 we enter a region of the energy balance where the directions of the moments are more difficult to estimate, until the enhancement is so large that spin-orbit coupling dominates, and the moments are antiparallel. In order to investigate this situation we calculated the spin and orbital moments (in an external field of 7 T) for U at an expanded volume (26.6 Å^3) where the enhancement is larger. At this volume we found that uranium is on the borderline to spontaneously polarize, and in order to avoid convergence problems we used the fixed spin moment method [20] and computed the orbital moment with the spin moment fixed at $10^{-2}\mu_B$. In agreement with the discussion above the resulting orbital moment ($3\times10^{-3}\mu_B$) was antiparallel to the spin moment.

Comparisons between our calculated magnetic form factors and the experimental data (Fig. 1) show that the agreement between experiment and theory is good only when the magnetic field is allowed to interact with the orbital as well as the spin moment. When the $\mathbf{B}\cdot\mathbf{l}$ term

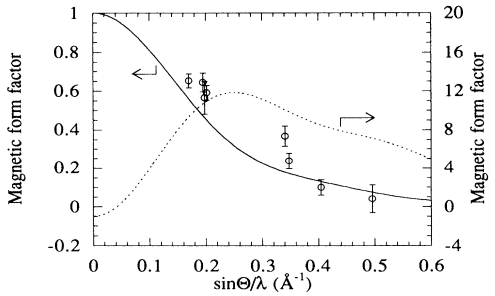

FIG. 1. The magnetic form factor of uranium metal, from experiments [8] (circles, left hand scale) and calculations including the orbital polarization correction and the orbital term in the Zeeman operator (solid line), as well as without the orbital interaction in the Zeeman operator (dashed line).

is neglected, the resulting form factor (also shown in Fig. 1) 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 very large (since the net moment is small) and the resulting form factor behaves like $\langle J_2 \rangle$, in disagreement with experiment. Our conclusion is that the interaction between the magnetic field and the orbital moment is necessary in order to describe the field induced magnetization, and that this interaction causes a parallel arrangement of the moments. *Furthermore, since the spin-orbit coupling in uranium is large we conjecture that the field induced spin and orbital moments of paramagnetic metals generally will be parallel, irrespective of the filling of the electronic shell* [21].

In summary, we have shown that in the field induced magnetic state, uranium metal has the spin and orbital moments ordered parallel, in contradiction to Hund's third rule and in sharp contrast to the free atom. This result explains the shape of the previously measured magnetic form factor as well as the magnitude of the induced moment. Based on these results we argue that all field induced magnetism in paramagnetic f electron systems should display this behavior [21]. The origin of the parallel ordering is demonstrated to be the interaction between the external magnetic field and the orbital angular momentum. It should be possible to study these effects in more detail by measuring the form factor of f electron systems which undergo a metamagnetic transition at a certain field strength (in UCoAl, for instance). Our present result suggests that the coupling between the spin and orbital moments is parallel on the low moment side of the transition and antiparallel on the high moment side. It is our hope that the present work will stimulate such experimental efforts.

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[18] As long as the system does not go through a metamagnetic transition.
[19] Here we use the relations $\mu_s = -2\langle s_z \rangle$ and $\mu_l = -\langle l_z \rangle$ where μ_s and μ_l are the spin and orbital magnetic moments.
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