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Density functional theory of spin and orbital magnetization densities in actinide magnets

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Abstract

We summarize recent attempts to calculate the contributions to the spin and orbital magnetization densities of transition metals and actinide compounds. Emphasis is placed on the relative signs of both the local and the diffuse spin moments and the orbital contributions to the moments. Examples include Fe, Co, Ni, actinide transition metal intermetallic compounds and uranium NaCl-type monochalcogenides.

1. Introduction

The theoretical framework of self-consistent electronic structure calculations is provided by density functional theory which is independent of the particular elements composing the solid [1]. It suffices here to note that the most used approximation to the density functional, the local spin density approximation (LSDA), provides us with the potential in which the electrons move if the electron spin density is known. A knowledge of the potential and some quantum mechanics are then sufficient to calculate the spin density self-consistently.

As an example of the results of such self-consistent calculations, the partial occupation numbers of the actinide metals [2] are plotted in Fig. 1 as a function of atomic number. It has been suggested [3] that Lr, owing to relativistic effects, has an s^2p configuration in the free atom, which would modify its cohesive energy somewhat. It has also been suggested [4] that the same configuration might remain in the metal, making Lr a 3a-type metal. The self-consistent calculations [2], however, reveal that Lr is a normal d transition metal. For the next element, 104, Eriksson *et al.* [2] calculated a valence bond energy of 160 kcal mol^{-1}, a value typical for a tetravalent transition metal. The consistent success of LSDA in obtaining agreement with measurements of the cohesive properties of metals across the periodic table gives us confidence that in the case of very heavy elements, where no measurements have been made, the calculated properties are also correct.

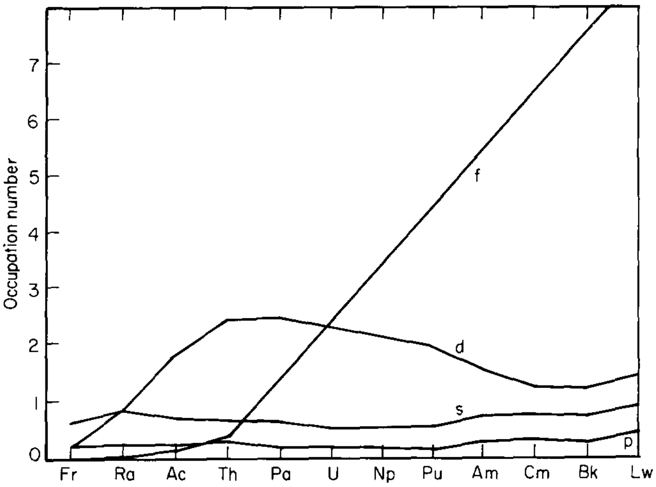

Fig. 1. The calculated s, p, d and f occupation numbers across the actinide series.

The elemental light actinide metals are not magnetic but many compounds containing them do order magnetically, and it is magnetism in the actinides which challenges LSDA. The narrow 5f bands and the large spin–orbit interaction in actinides produce the ideal situation for itinerant electrons to support the strong orbital magnetism which is one of the remarkable features of actinide magnetism.

2. The relative signs of the local, diffuse and orbital contributions to the magnetic moments

On the left-hand side of each part of Fig. 2, we have resolved the spin contributions to the magnetic moments

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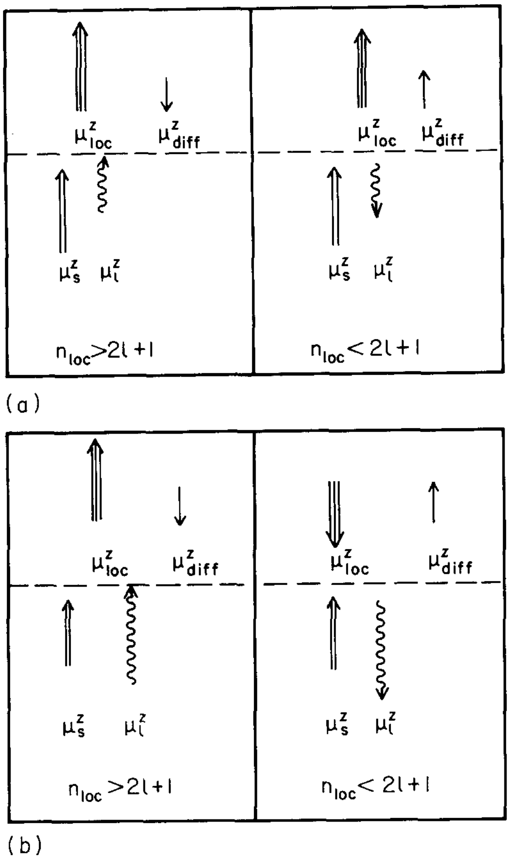

Fig. 2. Possible contributions to the total magnetic moments from local and diffuse spin densities and the orbital densities for orbital moments (a) less than and (b) greater than the spin moments. In (a) and (b) the left-hand and right-hand sides correspond to the narrow bands being respectively more and less than half-filled. The left-hand side of (a) corresponds to Fe, Co or Ni whereas the right-hand side of (b) corresponds to the actinide site in an actinide compound.

of late transition metals into local and diffuse parts (the orbital moments belong almost entirely to the 3d or local electrons). Here, in accordance with common usage, by local part we mean the 3d contribution and by diffuse part we mean the sp contribution, which is also that part of the moment whose density lies mainly in the interstitial region of the crystal and is not detected in neutron diffraction experiments under normal circumstances. Both the exchange interaction and hybridization between local and diffuse electrons influence the relative sign of the local and diffuse moments. Exchange interactions between the local and diffuse moments are always positive in LSDA and lead to parallel polarization in the absence of other influences. In Fe, Co and Ni the spin moments are small and the exchange interactions between local and diffuse moments small enough that hybridization dominates. The origin of the relative signs of the diffuse and local moments is therefore hybridization between the 3d and sp electrons. The 3d bands are more than half-filled and the Fermi energy lies close to the bottom of the broad, free electron like, sp bands. The hybridization is therefore similar to that between an early transition metal (the sp conduction band system) and a late transition metal (the 3d band system) and results in the relative sign of the local and diffuse moments being negative [5–7]. In Fe, Co and Ni the diffuse part of the moment is antiparallel to the local part.

The light actinides with itinerant 5f electrons are early 5f transition metals. The diffuse electron density is dominated by the 6d density and also constitutes an early transition metal system. The 5f moments then polarize parallel to the 6d moments. In the actinides, therefore, both exchange and hybridization lead to parallel polarization of the local and diffuse moments as shown on the right-hand side of Fig. 2(a).

Calculations for Fe, Co and Ni [8] yielded orbital contributions to the moments of $0.08\mu_B$, $0.14\mu_B$ and $0.05\mu_B$ for Fe, Co and Ni respectively. The orbital contributions to the moments are parallel to the spin contributions of $2.13\mu_B$, $1.52\mu_B$ and $0.57\mu_B$ for Fe, Co and Ni respectively, since the 3d bands are more than half-filled. Such a situation is shown graphically on the left-hand side of Fig. 2(a). However, light actinides have a less than half-filled 5f band, and therefore the induced orbital moment is antiparallel to the 5f spin moment as shown on the right-hand side of Fig. 2(a). Thus there are two sign changes occurring between the right- and left-hand sides of the figure (the transition metal and actinide), for both diffuse and orbital moments.

The diffuse spin moment is actually antiparallel to the total moment in uranium compounds as is verified by comparison of the measured relative magnitudes of 5f and total moments in neutron scattering and magnetization experiments [9, 10] and from the interpretation of spin polarized photoemission experiments on uranium chalcogenides [11] and deduced from magneto-optical spectroscopy [12]. However, the calculated diffuse moment (right-hand side of Fig. 2(a)) is always parallel to the total spin moment in actinide NaCl-type compounds. Only if the orbital component of the moment at the uranium site is larger than, and antiparallel to, the spin component can theory and experiment be consistent. This situation, which is consistent with all known data, is shown graphically on the right-hand side of Fig. 2(b). Several relativistic energy band calculations have yielded orbital moments which are larger than the spin moments in compounds containing actinides [13–15].

Light actinides are early 6d transition metals. Therefore, in actinide transition metal intermetallics, when the transition metal is a late transition metal, the spins on the transition metal and actinide sites are coupled antiparallel. The total moments on the atoms will only be parallel if the orbital moment of the actinide is opposite to, and greater than, the spin moment, as it is for light actinides. The mechanism for the ferrimagnetic spin–spin coupling is now A 5f–M 3d hybridization. Since the gap between the unhybridized spin-down A 5f and M 3d bands is smaller than between the unhybridized spin-up bands, hybridization and spin transfer are greater for the spin-down bands and the interaction between the M 3d and A 5f spin moments is ferrimagnetic.

3. Spin and orbital angular momentum densities

The magnetization density is responsible for the magnetic scattering of neutrons [16]. The magnetic form factor is given by [16, 17]

$$F(Q) = (\langle j_0 \rangle_s m_s^z + \langle j_0 + j_2 \rangle_l m_l^z)/m^z \quad (1)$$

where the total ground state moment is the integral of the moment density given by $m^z(r) = \mu_B[l^z(r) + 2s^z(r)]$ in terms of the orbital angular momentum and spin densities. Here $\langle j_i \rangle_\alpha = 4\pi[\int j_i(Qr) r^2 n_\alpha(r)\, dr]/m_\alpha^z$ where $\alpha = s$, l denotes the spin or orbital density and moment. Typical radial integrals are plotted in Fig. 3. Clearly $\langle j_2 \rangle$ contributes only when there is an orbital contribution to the moment. Furthermore the way in which $\langle j_2 \rangle$ contributes depends critically on the relative signs and magnitudes of the spin and orbital moments. We illustrate this schematically in Figs. 3(b), 3(c) and 3(d) where we have drawn form factors for m_s^z and m_l^z parallel, $m_s^z < m_l^z$ but m_s^z and m_l^z antiparallel, and $m_s^z > m_l^z$ with m_s^z and m_l^z again antiparallel. It is relatively difficult to extract the orbital moment when the spin and orbital contributions are parallel, as in a heavy rare earth or late transition metal, since the tail in the measured form factor arising from the dependence of $\langle j_2 \rangle$ on the scattering vector appears only as a bump at large scattering vectors. However, when orbital and spin moments are antiparallel, especially if they are almost cancelling, the tail in the form factor arising from the orbital contribution to the magnetization density develops into a prominent bump which has been observed in several actinide compounds [18].

In the presence of both spin polarization and spin–orbit interaction there is a net current, and it is from this current that the orbital moment arises. The orbital moment density may be calculated from the orbital angular momentum density, a readily computable quantity [13]. The first attempt to calculate an orbital moment for an itinerant electron metal was by Singh and coworkers [8] for Fe and Ni with reasonable results although the orbital moments were very small. Subsequently Brooks and Kelly and coworkers [13] calculated the orbital moment density and form factor of UN and obtained an orbital moment larger than the spin moment. Similar calculations [13] for the uranium monochalcogenides, which are ferromagnets, showed that a large orbital contribution to the moment density is a common feature in uranium compounds.

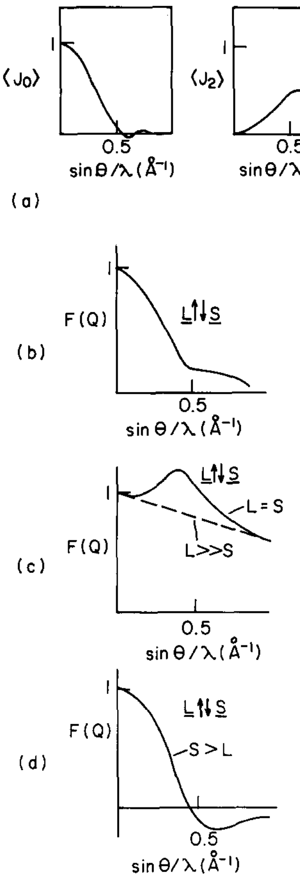

Fig. 3. Schematic illustration of the spin and orbital contributions to the form factors obtained by adding the Bessel functions shown in (a) in various ways depending on whether the orbital spin contributions are parallel or antiparallel.

In all subsequent calculations for actinide compounds the orbital contribution at the actinide site has been found to be large [13, 15]. In particular, a series of actinide compounds where a thorough analysis has been made is the AnFe$_2$ series. The results are shown in Fig. 4. Here, as in the other compounds, the induced orbital moments are very large compared with those obtained for 3d transition metals. However, although the calculated orbital moments are very large in actinides, it seems to be generally true that they are still too small compared with experiment as may be seen from Fig. 4, especially for Pu compounds.

Figure 5 shows the calculated equation of state and site-resolved magnetic moments in UFe$_2$ as a function of volume [19]. The measured uranium form factors of both UFe$_2$ and UNi$_2$ [20] showed that the cancellation between spin and orbital moments was almost complete. Other detailed studies have been made for UNi$_2$ [15]

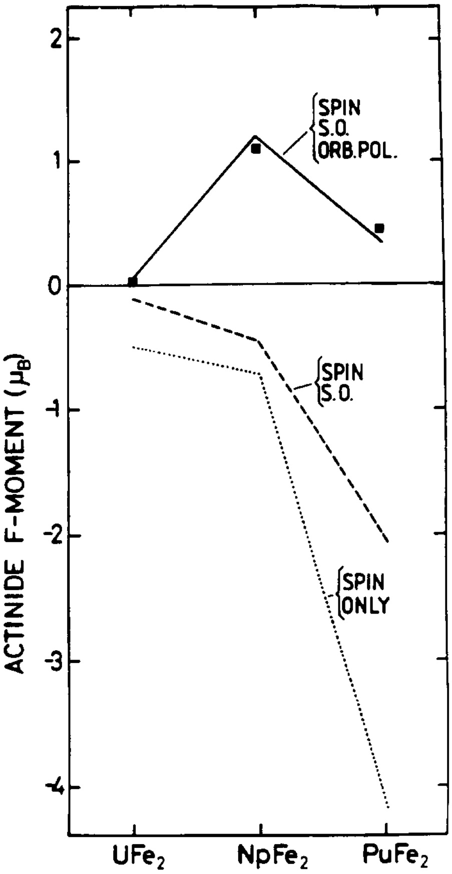

Fig. 4. The calculated actinide moments for part of the AnFe$_2$ series in several approximations: · · · · ·, ("spin only"), conventional spin-polarized calculation; – – –, results when spin–orbit interaction is added, producing an orbital contribution to the moment; ——, results when orbital polarization is included in the calculations; ■, measured moments.

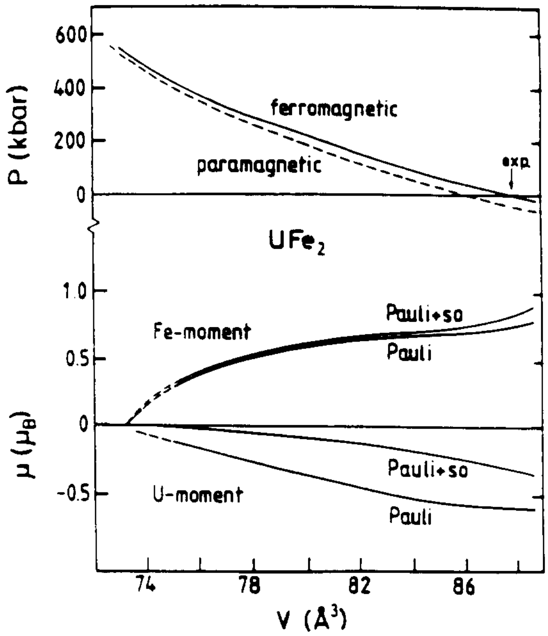

Fig. 5. The calculated equation of state (top) and site-resolved magnetic moments as a function of pressure (bottom) for UFe$_2$. The curves labelled "Pauli" are from spin-polarized calculations and those labelled "Pauli + so" are from calculations with spin–orbit coupling included.

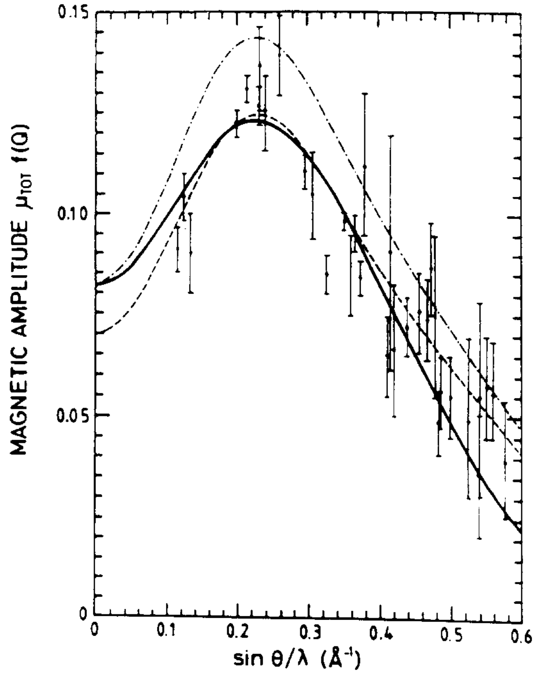

Fig. 6. A comparison of measured and calculated 5f magnetic amplitudes for UNi$_2$: ——, fit to the experimental results of ref. 20; — · —, from a self-consistent calculation with the uranium spin moment constrained to be equal to 0.47 μ_B yielding a total uranium moment of 0.082 μ_B; – – –, a slightly different constraint on the uranium moment such that it is equal to 0.07 μ_B.

where there is appreciable scattering only at the uranium site [20]. The total moment is very small but the compound is nevertheless magnetic. The calculated and measured magnetic amplitudes are shown in Fig. 6.

Comparison with experiment shows that the calculated absolute values of the orbital moments are almost always too small [13, 21]. This seems also to be true in Fe, Co and Ni [8, 22], although the larger discrepancies for the actinides are more obvious. One factor that is missing in LSDA is interaction between the orbital moments. Such an interaction is well known to be important in atoms where it is responsible for Hund's second rule. One way to approximate orbital interactions which has had some success has been suggested [13]. The functional dependence of the energy on occupation number in Hartree–Fock theory was approximated quite well by $-(1/2)E^3L_z^2$ where E^3 is a Racah parameter (a linear combination of Slater Coulomb integrals). The differential of the orbital polarization energy with respect to occupation number leads to different orbital energy levels when there is an orbital moment. The results for the $AnFe_2$ series are shown in Fig. 4. Applications to non-actinides such as Fe, Co and Ni and some cobalt compounds have also improved agreement with experiment for the orbital moments [8, 22–24]. Norman [24] has applied this and similar approximations to the transition metal oxides. More recently the enhanced orbital moments at Co sites in Co/Pd multilayers have been studied by Wu *et al.* [25] using magnetic circular X-ray dichroism. Comparison between the measurements and first principles calculations by Daalderop *et al.* [26] indicates that the orbital polarization correction is essential if agreement for the moments at the Co sites is to be obtained.

A curious anomaly occurs in the case of uranium metal where it has recently been shown that the spin and orbital moments are coupled parallel, breaking Hund's third rule [27]. The measured form factor of uranium, which in zero applied field is a paramagnet, is an induced form factor [28]. In this case the third induced spin density is so small that spin–orbit interaction, although favouring antiparallel spin and orbital moments, has less effect than the applied field which favours parallel alignment.

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