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ORBITAL EFFECTS IN ACTINIDE SYSTEMS

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ABSTRACT

Actinide magnetism presents a number of important challenges; in particular, the proximity of $5f$ band to the Fermi energy gives rise to strong interaction with both d and s like conduction electrons, and the extended nature of the $5f$ electrons means that they can interact with electron orbitals from neighboring atoms. Theory has recently addressed these problems. Often neglected, however, is the overwhelming evidence for large orbital contributions to the magnetic properties of actinides. Some experimental evidence for these effects are presented briefly in this paper. They point, clearly incorrectly, to a very localized picture for the $5f$ electrons. This dichotomy only enhances the nature of the challenge.

I. Introduction

Elsewhere in this volume Holden and Loewenhaupt have discussed properties of actinide magnetism in terms of the magnetic response function $\chi''(Q,\omega)$ as measured by inelastic neutron scattering. They have shown that the situation is complex and that in only one metallic uranium system (UPd_3) studied so far can a simple localized picture of the $5f$ electrons be correct.¹ In this short paper I shall present a few examples of large orbital effects in actinide magnetism. These all point to localized magnetism despite the contradiction of the preceding remarks.

II. What is a localized moment?

We know that for uranium and beyond the $5f$ electron states

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are populated. To have some understanding of a localized f electron we can turn to lanthanide (4f) series. As one progresses across the series one follows Hund's rule and Russell-Saunders coupling such that

$$\vec{S} = \sum_i \vec{s}_i, \quad \vec{L} = \sum_i \vec{l}_i \quad \text{and} \quad \vec{J} = \vec{L} + \vec{S},$$

where \vec{s}_i and \vec{l}_i are the spin and orbital momenta of each 5f electron, and the total \vec{J} component defines the magnetic moment, through $\vec{\mu} = g\vec{J}$, where g is the Lande factor. All this is quite conventional and in every textbook on magnetism. To answer the question posed in this section, localized magnetism of f electrons, really requires a well-defined spin and orbital component. (Except for a half-filled shell when $L = 0$). The orbital component implies long-time correlations of the f electrons around a particular nucleus.

There are other consequences of localized systems. The orbital degeneracy can be lifted by an electrostatic crystal-field potential. Strong spin-orbit interactions mean that \vec{L} and \vec{S} are frequently not good quantum numbers and we have also to take account of higher L and S states. This has to be treated in a so-called intermediate coupling.²

We can see from this what really distinguishes localized from itinerant (or even intermediate valence) systems is the presence of a large orbital moment. Americium systems present a good example. None so far have been found that are magnetic. This is ascribed to there being a $J = 0$ ground state composed of $\vec{L} = +3$, $\vec{S} = -3$ contributions. Band structures calculations of Ni, for example, do project out an orbital moment but it is small.

III. Magnetic anisotropy and magnetoelastic effects

One consequence of a large orbital moment is magnetic anisotropy and magnetoelastic effects. The actinide ferromagnets have some of the highest anisotropies known. Figure 1 shows the magnetization of UTe along the three principle axes.³ Note that the easy axis is $\langle 111 \rangle$ and that the magnetization in the other directions is exactly the projection of the moment along the nearest $\langle 111 \rangle$ in this direction. The anisotropy in UTe, and more recently in Pu ferromagnets PuSb and Pu α s, is enormous, much bigger than anything observed in the 3d or even the 4f series.

Magnetoelastic effects are basically coupling between the lattice and orbital wavefunctions. For example, such effects in an itinerant system such as chromium are very small, but in a system with a large orbital moment, e.g., Er or Dy, they are appreciable. Table I shows some of the lattice distortions of

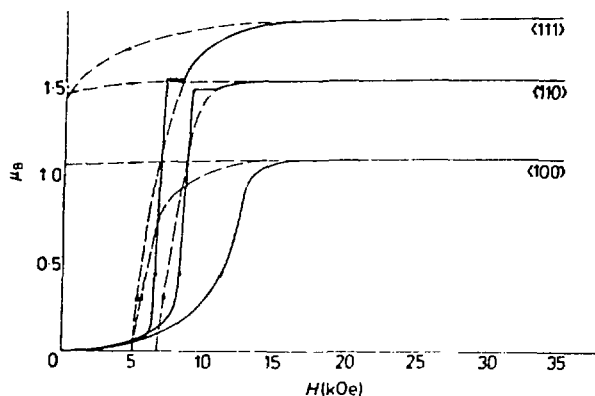


Fig. 1 Magnetization (reduced to μ_B) against applied field for three principal directions in UTe at 1.5 K (Ref. 3).

actinide ferromagnets.⁴ These distortions are very large. They show a strong coupling to the lattice, presumably through the orbital moment, and are consistent with the anisotropy illustrated in Fig. 1.

Table I

Lattice distortions in the ordered state of actinide ferromagnetics with the NaCl crystal structure; a_0 is the lattice parameter, T_c is the ordering temperature, at which the distortion, either rhombohedral (R) or tetragonal (T), begins.⁴ In the rhombohedral phase "c" is defined as a unit length along the $\langle 111 \rangle$ direction, "a" in a direction perpendicular to this.

Compound	a_0 (\AA) at 300K	T_c (K)	Distortion	$10 \frac{4}{a} \frac{c-a}{a}$
US	5.49	178	R	+ 105
USE	5.75	160	R	+ 81
UTe	6.16	104	R	+ 67
NpC	5.00	220	R	+ 23
NpN	4.90	87	R	- 52
PuP	5.66	126	T	- 31

IV. Neutron elastic scattering-magnetic form factors

The magnetic moment of the neutron interacts with both the spin and orbital moment of the unpaired electrons around the nucleus. Since these electrons have a spatial distribution ($1 - 2\text{\AA}$), comparable to the neutron wavelength then we will see a decrease in the magnetic scattering amplitude for increasing

momentum transfer Q . This implies a form factor which is related to the total magnetization density through the Fourier transform

$$f(\vec{Q}) = \int M(\vec{r}) e^{i\vec{Q} \cdot \vec{r}} d\vec{r} .$$

Scattering from orbital moments is quite easily distinguished from spin-only scattering. We show, for example, in Fig. 2 the form factor of the induced magnetic moment in α -U at low temperature⁵. We know that the $5f$ wavefunctions of α -U are very broad and strongly hybridized so that we should not expect an orbital moment, and none is apparent. For such a well-localized system as UO_2 the reverse, of course, is true.^{6,7}

Form factors are therefore ideal at showing whether or not an orbital moment is present. A particularly interesting form factor is that of Sm^{3+} or Pu^{3+} in which the $6H_{5/2}$ configuration is the ground state. Since both $L(=5)$ and $S(=5/2)$ are large and opposed to each other, the ground state J value ($=5/2$) is small. Furthermore, because the spin distribution is more extended in real space than the orbital contribution, regions of negative (with respect to \vec{J}) magnetization density exist around the nucleus. The resulting form factor gives a peak at $Q \neq 0$, and this has been clearly seen in Sm compounds.⁸ In Pu systems the situation is complicated by the need to take into account the large spin-orbit coupling, but the two form factors measured so far are essentially flat for small Q values.^{9,10} This is a clear signature of an orbital contribution.

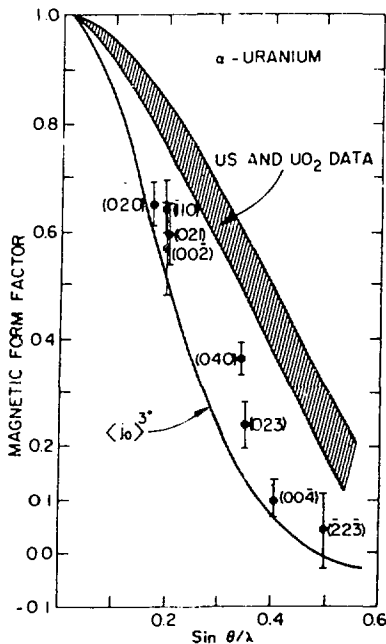


Fig. 2 Experimental magnetic form factor for α -uranium metal compared to $\langle j_0 \rangle$ and combined results on uranium in compounds - hatched region (Ref. 5)

Another important aspect of form factors is that they can be thought of as measuring the time-averaged localized moment. The modifier "time-averaged" is important. Nickel is not usually thought of as a localized system; however, the form factor agrees well with atomic calculations.¹¹ The reason is that the hopping time of the itinerant d electrons is much less than their resident time at a particular site, so the "time-average" misses the hopping aspect. On the other hand, if electrons have wavefunctions that are spread out in real space, then the Fourier transform of this will be a sharp peak in Q space. Since the most accurate form factors are measured at Bragg peaks (with polarized neutrons utilizing the interference between magnetic and nuclear scattering), a diffuse electron distribution is often missed. Its presence is then inferred from the difference between the μ_{local} extrapolated from the neutron work at finite Q and μ_{total} measured by bulk susceptibility and by definition at Q = 0. The difference is then called the "conduction electron polarization", μ_{cep} . This quantity has been the subject of much interest in iron, nickel, gadolinium,¹² and in lanthanide compounds, and also exists in actinide systems.³ Unfortunately, neutrons have difficulty in measuring the small Q ($< 1 \text{ \AA}^{-1}$) region because in normal systems (with moderate lattice parameters) there are no Bragg peaks. Other methods of measuring f(Q) through the spin waves, the magnetovibrational scattering, or the diffuse scattering in the paramagnetic phase are difficult and subject to rather large uncertainties.

In a few systems "extra", i.e. non-localized, scattering can be seen. Good examples are the work on CeSn_3 ¹³ and CePd_3 ,¹⁴ where an additional d contribution can be seen. Note should also be made of the fact that the d polarization is parallel to \vec{J} , whereas in all other light lanthanide or actinide systems it is antiparallel. In the actinides an interesting magnetization density was obtained in UCe_3 , in which the hybridization results in a polarized spin density observable near the Ce site.¹⁵

V. Hyperfine field-magnetic moment correlations

We now turn to quite a different aspect. One of the terms that may be derived from Mossbauer spectroscopy is the hyperfine field - or strength of the magnetic interaction, H_{hf} . We show in Fig. 3 the relationship between hyperfine fields in Np systems and the ordered moments derived by neutron scattering.¹⁶ The relationship in the Np systems is as linear as in the Yb salts. Note some of the small values of the ordered moment found in the Np systems, less than $1 \mu_{\text{B}}$. Moreover, because of the very large values of H_{hf} the orbital component must contribute a major component. In contrast the hyperfine field in ordered iron is 340 kOe. The fact that H_{hf} comes so close to the free-ion Np³⁺ value suggests an essentially atomic character with this configuration. The proportionality between H_{hf} and $\langle r^{-3} \rangle$, where this

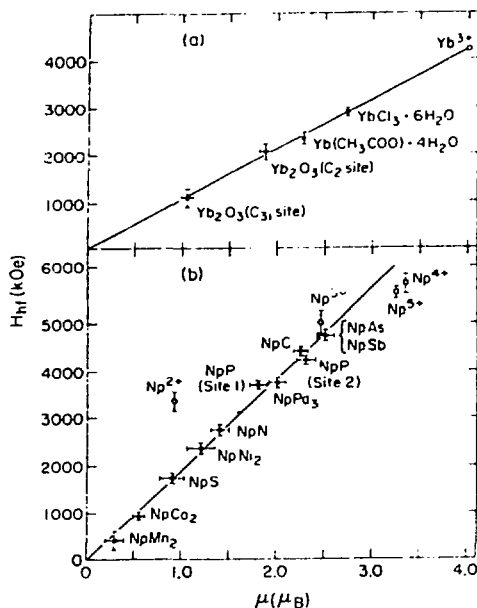


Fig. 3 Comparison between magnetic hyperfine field and electronic magnetic moment for a number of (a) Yb salts and (b) Np intermetallics. Experimental points are shown by solid circles and calculated free-ion values by open circles.

is the average value of $1/r^3$ for the open-shell electrons, remain roughly constant and only $\langle J_z \rangle$, the average value of the angular momentum, is altered in the various materials. Thus, even for systems with small moments a proportional orbital must exist.

VI. Conclusions

I have tried in this short paper to draw attention to the importance of orbital magnetism in actinide systems. The present NATO School has focussed attention on intermediate valence, unstable moments, and actinide systems. These classes have many things in common. It is interesting, for example, that recent neutron experiments on intermediate valence systems such as CeSn_3 and YbCuAl have claimed to find evidence for crystal-field transitions. The latter imply an orbital degeneracy lifted by the electrostatic field of the surrounding ions. We do not easily find crystal-field transitions in U systems, but much evidence for strong orbital contributions exists.

None of the properties discussed in this paper for actinide systems are by themselves too surprising. Similar magnetization, magnetostrictive, and form factor properties exist in the heavy rare-earths, which also have large orbital moments. What is surprising is that these localized properties are observed in systems with unusual photoemission (see the paper by Y. Baer in this volume) and neutron inelastic scattering (Holden and Loewenhaupt in this volume) measurements. In the neutron inelastic scattering, for example, it has proved very difficult to observe propagating spin-wave modes, and yet all the properties discussed in the present article would point to their existence, as indeed

is the case in normal rare-earth materials. It is this conjunction of properties that is the most interesting.

The challenge to theory is then to include both strong spin-orbit coupling and hybridization in a realistic way. Recent work by Brooks and Kelly¹⁷ on the form factors of the actinide nitrides is in step in this direction, as are the most recent calculations of Edwards in this volume, both of which start with a band description and proceed to determine the extent of f-d hybridization.

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