# Cancellation of orbital and spin magnetism in $UFe_2$

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Polarized-neutron measurements have shown that the orbital and spin magnetic moments, which individually have a value of $\sim 0.23\mu_B$, almost completely cancel on the U sublattice in the ordered Laves phase $UFe_2$. This confirms a recent theoretical prediction and raises the possibility of "magnetic" compounds with zero total moment.

Our explanation of magnetic phenomena usually starts either from the case of itinerant electrons or from a localized model involving discrete electron orbits. Although $f$ electrons ($l=3$) are usually treated as localized, there is a growing subset of compounds, including those referred to as heavy fermions, in which the strong interaction between the $f$ and conduction electrons ($s$, $p$, and $d$) gives rise to unusual properties. One consequence of this electron hybridization is the formation in some compounds of ordered magnetic moments that are much smaller than those anticipated from localized $f$ electrons. Examples involve uranium and cerium compounds such as the heavy fermions $U_2Zn_{17}$ ($0.8\mu_B$),[1] $URu_2Si_2$ ($0.03\mu_B$),[2] $CeAl_3$ ($\sim 0.05\mu_B$),[3] $UPt_3$ ($\sim 0.02\mu_B$),[4] and other materials such as UN ($0.75\ \mu_B$),[5] and $\leq 0.06\mu_B$ on the U sublattice of $UFe_2$.

Theories to treat the behavior of these unusual $f$ electrons[6] must include correlation effects, but to understand the values of the ordered moments, spin-orbit coupling must be included. It is important to realize that orbital moments can exist in systems that are essentially itinerant.[7] Moreover, since in the light lanthanides and actinides the spin and orbital moments are *opposed* to each other, the net moments may be quite small. In this connection Brooks *et al.*[8] have recently considered the itinerant magnet $UFe_2$.[9] For our purposes here the most interesting prediction of this work is that the $5f$ moment on the U site is composed of an orbital component $\mu_l = 0.47\mu_B$ and an antiparallel spin component of $\mu_s = -0.58\mu_B$. When they add the small ($s$, $p$, and $d$) contributions they get a total U moment of $-0.24\mu_B$ per atom. The negative sign indicating that the resultant moment is antiparallel to the (larger) Fe moment.

In this Brief Report, we present neutron measurements showing that these predictions[8] are qualitatively correct. In fact, our measurements show that the cancellation of $\mu_s$ and $\mu_l$ is essentially complete; the total moment on the U sublattice being zero within experimental error. Such an effect has not previously been demonstrated experimentally.

$UFe_2$ forms in the cubic fcc Laves phase ($a_0 = 7.058$ Å) and is ferromagnetic at $T_c \approx 160$ K. Neutron studies on single crystals by Yessik[10] gave the U and Fe moments as $0.03(1)\mu_B$ and $0.38(2)\mu_B$, respectively, at 84 K. Later work on polycrystalline samples[11] gave 0.06(1) and $0.59(2)\mu_B$, respectively, at 5 K. In careful magnetization experiments Aldred[12] showed that the total moment was $1.09(1)\mu_B$ per formula unit, and also that both the magnetization and $T_c$ vary slightly as a function of stoichiometry.

Our measurements have been performed on a single crystal (18 $mm^3$) cut from a larger boule grown by the Czochralski technique. The crystal was first completely characterized on a four-circle diffractometer at Risø National Laboratory, Denmark. Full details will be published elsewhere. The Fe:U ratio was 2.02(1) using accepted scattering lengths, and the weighted $R$ factor was 1.8%. The ordering temperature was 165(5) K. Polarized-neutron ($\lambda = 0.865$ Å) measurements on the same sample in a 2-T applied field were performed at the Orphée reactor, Laboratoire Leon Brillouin, Saclay, France. The Laves-phase structure is a particularly convenient one because there are certain Bragg reflections which come uniquely from each separate sublattice. If we first consider the subset from the Fe sublattice we find magnetic amplitudes that fall on a conventional Fe form factor [i.e., dependence of the magnetic scattering on momentum transfer $Q = 4\pi(\sin\theta)/\lambda$, where $\theta$ is the Bragg angle and $\lambda$ the wavelength]. These extrapolate at $(\sin\theta)/\lambda = 0$ to an Fe moment of $0.60(1)\mu_B$, in excellent agreement with the earlier study[11] on stoichiometric material.

We can now consider the U moment and its form factor. First, we have the reflections from the U sublattice alone. These magnetic amplitudes are shown as solid points in Fig. 1. Note particularly the low value of the innermost U-only reflection, the (220) at $(\sin\theta)/\lambda = 0.2$ $Å^{-1}$. Second, we may subtract the Fe contribution from the mixed reflections and consider the remaining contribution (open points in Fig. 1) as arising from uranium only.

 

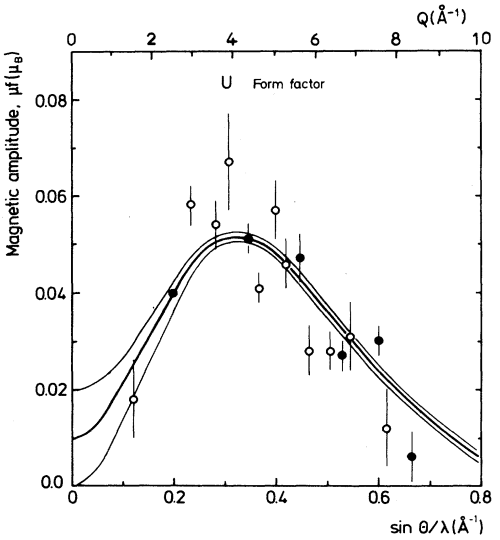


FIG. 1. The magnitude of the magnetic scattering on the U sublattice as a function of $(\sin\theta)/\lambda (=Q/4\pi)$. The extrapolation to $Q=0$ gives the magnetic moment. Solid points are from Bragg reflections coming from the U sublattice only. The open points come from Bragg reflections that have both U and Fe contributions, but the Fe contribution has been subtracted. The Fe contribution is similar to metallic Fe and falls monotonically to zero at $(\sin\theta)/\lambda = 0.6$ Å$^{-1}$. The solid central line is the fit to Eq. (2) with the outer lines representing the limits defined by the error bars and the strong correlation between $\mu$ and $C_2$.

The extrapolation of this form factor to $(\sin\theta)/\lambda = 0$ gives, by definition, the total magnetic moment on the U sublattice. We see qualitatively before any further analysis that this is approximately zero, and that the form factor shows a maximum at $(\sin\theta)/\lambda \simeq 0.35$ Å$^{-1}$.

To understand the shape of this curve we note that in the dipole approximation[13] the product of the moment and the normalized form factor can be written as

$$\mu f(Q) \approx \mu_s \langle j_0 \rangle + \mu_l (\langle j_0 \rangle + \langle j_2 \rangle) , \quad (1)$$

where $\mu$ is the total moment, $\mu_s$ is the spin component, normally $2\langle S \rangle$, $\mu_l$ is the orbital component, normally $\langle L \rangle$, and $\langle j_0 \rangle$ and $\langle j_2 \rangle$ are Bessel transforms[14] of single $5f$ electron charge-density distribution $U^2_{5f}(r)$. Noting that $\mu = \mu_s + \mu_l$ we rearrange Eq. (1) to give

$$\mu f(Q) = \mu (\langle j_0 \rangle + C_2 \langle j_2 \rangle) , \quad (2)$$

where $C_2 = \mu_l/\mu$. The functions $\langle j_0 \rangle$ and $\langle j_2 \rangle$ always (i.e., independent of whether we assume $U^{3+}$ or $U^{4+}$) have the character[14] that at $Q=0$ $\langle j_0 \rangle = 1$, $\langle j_2 \rangle = 0$, and for increasing $Q$ $\langle j_0 \rangle$ decreases, whereas $\langle j_2 \rangle$ has a maximum at $(\sin\theta)/\lambda \approx 0.3$ Å$^{-1}$. The solid line in Fig. 1 represents a least-squares analysis giving $\mu = 0.01\mu_B$ and $C_2 \simeq 23$. The quantity well defined is $\mu C_c [= \mu_l$ the orbital moment from Eq. (2)] and this is $0.23(1)\mu_B$, but there is a strong correlation between the two individual values. We have also allowed variations in the anisotropy of the Fe form factor, which would affect the position of the open points in Fig. 1, but find no significant aspherical part. Adding a small $C_4\langle j_4 \rangle$ term ($C_4 \approx -2$) in Eq. (2) also slightly improves the fit for $(\sin\theta)/\lambda \geq 0.4$ Å$^{-1}$. However, the main point is not so much the precise value of $C_2$, but the obvious *cancellation* of $\mu_s$ and $\mu_l$, such that $|\mu_l + \mu_s| \leq 0.01\mu_B$. This is exactly the prediction of Brooks *et al.*[8] Within the dipole approximation[13] we can also estimate $\mu_s$ and $\mu_l$ individually, since $\langle j_0 \rangle$ is negligible for $(\sin\theta)/\lambda \geq 0.45$ Å$^{-1}$. This gives $\mu_l \approx \mu_s \approx 0.23\mu_B$, values that are about a factor of two less than calculated by Brooks *et al.*

Cancellation of the orbital and spin components also occurs in $Sm^{3+}$ compounds, such as SmN (Ref. 15) and $SmCo_5$.[16] In these materials the $4f$ electrons are localized and there is a mixture of the excited $J = \frac{7}{2}$ state into the $J = \frac{5}{2}$ ground-state wave function as the temperature is raised, or under the influence of a crystal-field interaction. However, this is unique to the $4f^5$ configuration and because of the larger spin-orbit coupling cannot even occur appreciable in the analogous $5f^5$ configuration. We have discussed this in a recent paper on $PuFe_2$.[17] In $UFe_2$ the electrons are essentially itinerant[9] and the $f$ count[8] is about 2.7 so that there is no analogy between this situation and that of $Sm^{3+}$; moreover the cancellation here is a ground-state property, predicted to be independent of temperature.

Partial cancellation of $\mu_l$ and $\mu_s$ has been seen previously in $UNi_2$ (Ref. 18) and $PuFe_2$.[17] Clearly $d$ electrons in these Laves phase compounds strongly hybridize with the $f$'s, but it is not necessary that the $d$ element carry a moment (indeed it does not in $UNi_2$). Experimentally it should be possible to find a system that has a microscopic magnetization density (i.e., finite $\mu_l$ and $\mu_s$) but a zero *macroscopic* moment. UN under pressure[7] is predicted to be such a system, but compounds at ambient pressure, even with reasonably high ordering temperatures, should exist if the hybridization can be correctly tuned. Since the orbital moment $\mu_l$ is mainly responsible for anisotropy, these systems may exhibit both anisotropic magnetization and magnetoelastic interactions. In $UFe_2$ a large rhombohedral distortion[19] is indeed observed with x rays. However, if the total moment is zero no domains need be formed. A phase transition to ferromagnetism or antiferromagnetism will be detected by specific-heat measurements, for example, because $\mu_s$ is the order parameter,[7] but not by magnetization experiments.

It is interesting to consider pictorially why neutrons can still "probe" magnetism even though the resultant moment on the U site is zero. In Fig. 2 we show the spin and orbital magnetization densities in real space as obtained by Fourier transforming the theoretical expression [Eq. (1)] within the dipole approximation. The orbital and spin moments are the integral of these quantities over all space. Here we assume they are collinear and oppositely directed. The areas in Fig. 2 are also exactly equal so that the *total* moment is zero, much as we find on the uranium sublattice in $UFe_2$. However, as is well known, the orbital magnetization density is more contracted than that of the spin in real space. We show the difference as the thick line in Fig. 2 that clearly oscillates about zero. In per-

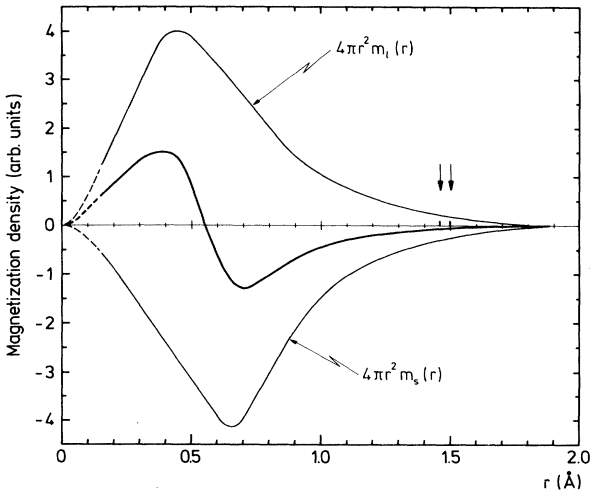


FIG. 2. Schematic representation of the orbital ($4\pi r^2 m_l$) and spin ($4\pi r^2 m_s$) components of the magnetization density as a function of the distance $r$ from the nucleus. The difference (heavy line) gives the total magnetization density. These curves have been obtained by Fourier transforming the $\mu_l$ and $\mu_s$ components in Eq. (1) using $\langle j_0 \rangle$ and $\langle j_2 \rangle$ functions of Ref. 14. Because the dipole approximation is not valid at high $Q$, these curves are not correct in real space at small $r$. Thus, for $r \leq 0.3$ Å$^{-1}$ another node should exist, and the dashed parts of the curves indicate this region. Half the nearest U-Fe and U-U distances are 1.46 and 1.51 Å, respectively, and these are marked with arrows.

forming the Fourier transform of the total magnetization density to obtain the form factor of Eq. (1) the Fourier components for $Q$ values between about 2.5 and 5 Å$^{-1}$ change the sign of the (negative) spin contribution with respect to the (positive) orbital contribution. This results in a maximum in the form factor at $Q \approx 4$ Å$^{-1}$.

We should point out that our interpretation is based on the assumption that $\mu_l$ and $\mu_s$ are collinear. Our experiments make clear that the Fe moments follow the direction of the applied field but, given the small magnitude of $\mu_l$ and $\mu_s$ on the U sublattice, we can be less certain of their collinearity. To account for this one would have to introduce odd-order spherical harmonics in the expression[13] leading to Eq. (1). The dipole approximation would then be good for small $Q$ only, and not all the magnetic amplitudes would then be expected to lie on a single smooth curve as a function of $Q$. Experiments with polarization analysis of the scattered neutrons are needed to examine this point. X-ray experiments to identify separately the $\mu_l$ and $\mu_s$ contribution and their direction would obviously be of great interest.[20]

In concluding, we point out the extreme importance of including spin-orbit coupling in any theories addressing systems that order with small magnetic moments involving $f$ electrons. For systems such as these with the Laves structure the hybridization is very strong (we show in Fig. 2 half the U-U and U-Fe interatomic distances to emphasize the amount of electron wave function overlap) and the ordered moment may reflect a cancellation between orbital and spin contributions. It is also of importance to realize that in most small moment systems the $f$ moment has been obtained by an extrapolation of the neutron data to $Q=0$. If this is done from $(\sin\theta)/\lambda \simeq 0.3$ Å$^{-1}$ in $UFe_2$ one is led[11] to a value of $\approx 0.06\mu_B$, which is clearly in error.

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