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INDUCED MAGNETIZATION DENSITY IN THE 5f SYSTEM UAl_2

V. C. Rakhecha, G. H. Lander, and R. M. Moon

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Induced Magnetization Density in the 5f System UAl_2[a)]

V. C. Rakhecha[b)] and G. H. Lander

Argonne National Laboratory, Argonne, Illinois 60439, USA

R. M. Moon

Oak Ridge National Laboratory,[c)] Oak Ridge, TN 37830, USA

ABSTRACT

Using a polarized-neutron diffractometer we have studied the induced magnetization density in the unit cell of the 5f system UAl_2. Measurements have been made on single crystals at 4.2 K with an applied magnetic field of 42.5 kOe (induced magnetic moment 0.0344 μ_B per mole). Neutron wavelengths of 1.067 and 0.785 Å and different crystal thicknesses have been used to correct for and eliminate any effects from extinction. It is found that the major part of the magnetization density appears as a contribution localized at the U site, exhibiting a form factor similar to that of the f^3 free ion, and extrapolating in the forward direction to the value given by the bulk susceptibility. However, there are two interesting aspects of the density. First, the form factor points differ significantly from a smooth curve. This indicates asphericity in the 5f electron distribution arising from the crystalline environment of the U atoms. Second, and more unusual, finite magnetic scattering amplitudes have been observed for a series of reflections to which the centrosymmetric density at the U site cannot contribute. We consider this as strong evidence of noncentrosymmetric bonding involving the 5f-6d electrons.

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INTRODUCTION

The 5f electrons in actinide systems are spatially more extended than the 4f electrons in lanthanides and this feature allows for the possibility that the 5f electrons participate in chemical bonding. The spatial extent of the 5f electrons also results in a wide range of magnetic behavior, ranging from localized moments to itinerant magnets [1]. Several studies of intermetallic actinides show that the 5f electrons lie at or close to the Fermi level [2] and over the last few years a number of neutron investigations have attempted to probe the behavior of the unpaired "magnetic" electrons [3,4].

One of the most interesting series of actinide systems crystallize in the C-15 fcc Laves phase, in which the actinide-actinide separation is quite small

and the possible direct 5f-5f interaction therefore large. Indeed, in a series of Np systems [5] one can see the transition from localized to itinerant to non-magnetic behavior, all as a function of lattice spacing. The compound UAl_2 is an exchange-enhanced paramagnet with no long-range magnetic ordering, but strong spin fluctuations [6]. The magnetic susceptibility of UAl_2 is Curie-Weiss like for $T > 60$ K, almost temperature-independent for $25 < T < 60$ K, and then rises rapidly for $T < 25$ K. We have undertaken a polarized-neutron study of UAl_2 to delineate more carefully the role of the unpaired electrons; in particular we wish to search for possible bonding effects [4] or those effects associated with the hybidization of d electrons as was found [7] in $CeSn_3$, which has a susceptibility behavior very similar to that of UAl_2.

EXPERIMENTAL DETAILS

Measurements were carried out on single crystals on the polarized-neutron diffractometer at the High-Flux Isotope Reactor at Oak Ridge National Laboratory. The experiment consists of measuring the ratio of the Bragg scattered intensity when the neutron spins are first parallel and then antiparallel to the sample magnetization. From this ratio, and a knowledge of the nuclear structure amplitudes, the magnetic structure amplitudes for each Bragg reflection can be deduced.

An external magnetic field of 42.5 kOe was applied parallel to the <110> direction and the sample temperature was 4.2 K. Under these conditions the induced moment in the forward direction is 34.4×10^{-3} μ_B/mole. We have checked this directly by measuring the susceptibility of one of our crystals as a function of temperature. To eliminate effects of extinction and possible multiple Bragg scattering, measurements were made on two specimens, one a pillar $3 \times 3 \times 12$ mm^3 with the long axis parallel to <110> and the other a 0.4 mm thick disc with (110) face, and at two wavelengths 1.067 and 0.785 Å. Small corrections (<2%) have to be made for incomplete incident polarization, flipping efficiency, and diamagnetism but all are known reliably. Corrections necessary for extinction [8] were not large and were found consistently within the set of measurements ($g \simeq 276$, $r \simeq 16$ microns) by employing the dependence of observed polarization ratios on different wavelengths and effective beam path lengths. In brief, a least squares procedure was applied directly to the observed ratios which, as a function of parameters g and r, brought into convergence the final γ-values (see table I for explanation) within each group of equivalent Bragg reflections. The final averaged values of γ are given in table I. In this table, 'μ_F' values at each U

site have also been derived from Y, assuming there is moment density only on U.

INTERPRETATION OF DATA

The compound UAl_2 ($a_0 = 7.78$ Å) has the cubic Laves-phase structure (space group Fd3m). The U-sub-lattice has the diamond structure and the site symmetry is $\bar{4}3m$, which is noncentrosymmetric. The near neighbor environment of U consists of 4 Al triangles set in a tetrahedral arrangement and another tetrahedron of 4 U atoms rotated by 90° about a cubic axis with respect to the aluminium tetrahedron. As a general consequence the density (charge or magnetization) about the U site can be non-centrosymmetric due to chemical bonding effects. Contributions from this noncentrosymmetric density appear in certain types of reflections e.g., (222), (422), (622),... which nominally contain no contribution from the U sub-lattice [9]. In the simple diamond structure these reflections are nominally forbidden, and their measurement to determine the bonding charge density and anharmonic contribution has represented a tour de force for diffraction over the years [10]. In the case of the Laves phase UAl_2, one also has contributions to the "forbidden" reflections from the Al sublattice and in view of the discovery of a small polarization associated with the Ge site in UGe_3 [4], we cannot exclude the possibility of a similar polarization at the Al sites in UAl_2. In principal, an accurate moment density map can delineate these two contributions. In practice, such maps are subject to experimental and termination errors and are completely dominated by the large centrosymmetric contribution at the U site.

In Fig. 1 we plot the (μf)/mole as a function of scattering angle. Note that the "Al-only" reflections (222), (622), (266) are not included on this Figure. Also plotted is the U ($5f^3$) form factor using the dipole approximation [11], the latter normalized to 35.2×10^{-3} μ_B/mole in the forward direction (i.e., after removing diamagnetic contribution from bulk susceptibility). We observe that the experimental points exhibit a form factor similar to the f^3 free ion, although we cannot easily distinguish [11] between $5f^2$ and $5f^3$. The major contribution to the density thus comes from a free-ion like density which resides at the uranium site and describes the f like states at the Fermi surface. However, the form factor points deviate significantly from a smooth curve. Qualitatively, these deviations should originate from the effect of crystalline environment of U-ions and any possible polarization present on Al sites. We have

attempted to determine possible crystal-field effects by evaluating the magnetic form factor for states belonging to different representations of a cubic field [11], but no clear trend seems to emerge from this analysis. Since neutron inelastic scattering [12] has not been able to observe any crystal field states, this inadequacy of the conventional crystal- field model is not surprising. Further, it can be shown that a pure cubic crystal field on $U(f^2)$ or $U(f^3)$ cannot give rise to a noncentrosymmetric density for which there appears strong evidence from the experimental data on forbidden reflections. Thus one is led to invoke the hybridization of U 5f-6d electrons and/or their hybridization with Al 3p states, which can naturally result in a non-centrosymmetric density. There are, therefore, present three small effects which can give rise to asphericity in magnetization density: the pure crystal field whose effect is seen to be significant from our analysis, the hybridization of U 5f-6d and Al 3p states and the possible polarization on Al sites. Sorting these out represents a complex problem.

Measurements of the "forbidden" reflections have been reported earlier in at least two itinerant Laves-phase compounds, $ZrZn_2$ [13] and $TiBe_{1.8}Cu_{0.2}$ [14], although in neither case has a quantitative analysis in terms of bonding orbitals been presented. In the case of the more analogous system $CeAl_2$, no values for the "forbidden" reflections are given in the literature [15], but would be of interest.

In conclusion, our experiment shows a number of intriguing effects in the form factor of UAl_2. We believe the noncentrosymmetric contribution contains information about the hybridization of the 5f-6d and 3p electrons, and we are presently hoping to model such effects and compare them with experiment.

Table I. Summary of magnetic scattering amplitudes. F_N is the nuclear structure amplitude per mole. γ is the ratio of magnetic to nuclear structure amplitudes after all corrections, including atomic diamagnetism, have been made. Fractional error estimates for γ can be obtained from those for μf.

hkl	$\sin\theta/\lambda$	F_N	$\gamma \times 10^4$	μf (mμ_B) Per mole
111	0.111	$-U/\sqrt{2}+Al$	254.05	33.6 (7)
022	0.182	U	94.44	29.6 (4)
311	0.213	$U/\sqrt{2}+Al$	57.81	28.6 (5)
222	0.223	$2Al$	-2.82	-0.7 (2)
400	0.257	$U-2Al$	391.75	22.5 (3)
133	0.280	$-U/\sqrt{2}+Al$	159.62	21.2 (3)
422	0.315	U	65.45	20.5 (3)
333	0.334	$U/\sqrt{2}+Al$	40.05	19.8 (4)
511	0.334	$U/\sqrt{2}+Al$	39.80	19.7 (4)
044	0.364	$U+2Al$	29.31	16.7 (4)
622	0.426	$2Al$	0.34	-0.1 (3)
444	0.445	$U-2Al$	160.48	9.3 (2)
155	0.459	$-U/\sqrt{2}+Al$	76.63	10.2 (4)
711	0.459	$-U/\sqrt{2}+Al$	83.15	11.0 (3)
266	0.560	$2Al$	2.57	0.7 (3)

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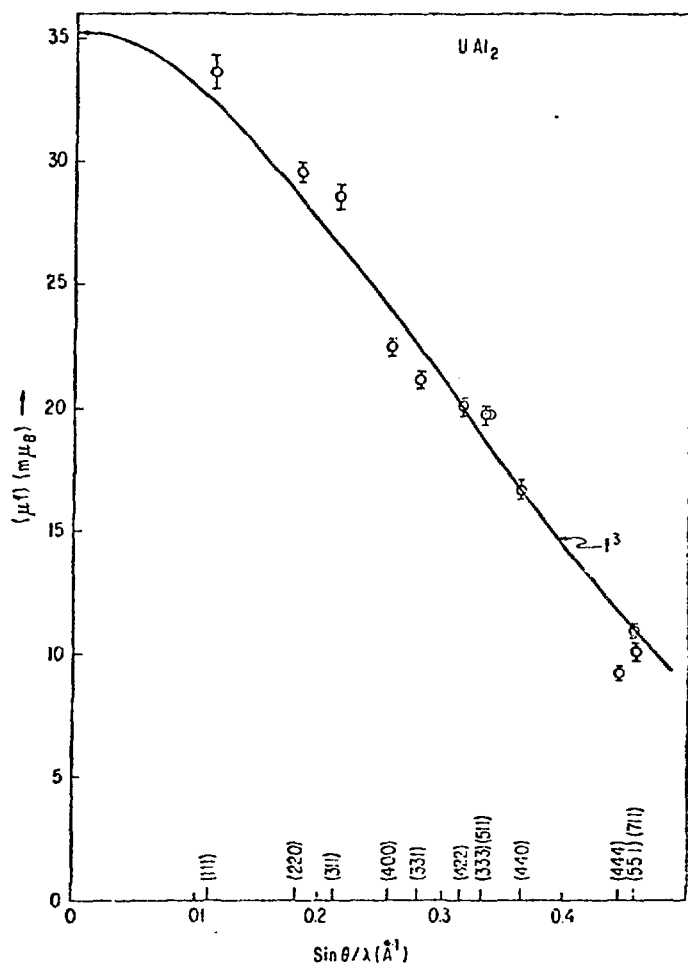   Schweizer and J. L. Buevoz, J. Appl. Phys.
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U Al$_2$

(μf) (mμ_B)

$\sim$ I^3

[111] [220] [311] [400] [331] [422] [333][511] [440] [444] [711]
[551]

Sin θ/λ (Å^{-1})

Fig. 1. Open circles are the experimental μf values per mole of UAl$_2$. Continuous curve is the U(5 f^3) form factor in dipole approximation normalized to 35.2 in forward direction.