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ABSTRACT

The magnetic form factor of uranium in UO_2 has been examined by means of neutron diffraction. Uranium dioxide (CaF_2 structure) orders antiferromagnetically at 30.8 K with the type I magnetic structure. The intensities of 1250 magnetic Bragg reflections (reducing to 71 independent hkl values and giving full three-dimensional data for $\sin \theta/\lambda \leq 0.83 \text{ \AA}^{-1}$) have been measured with a well-characterized stoichiometric single crystal at 5°K. The values of (uf) plotted versus $\sin \theta/\lambda$ show considerable asphericity for $\sin \theta/\lambda > 0.5 \text{ \AA}^{-1}$. Comparisons with free-ion (+ crystal field) calculations give an experimental magnetic moment of 1.78 (4) μ_B and indicate that the general shape of the form factor is in agreement with theory for low scattering angles, but that the nonspherical contributions at higher angles are at least a factor of five greater than expected. The significance of these results is discussed in terms of the extended nature of the $5f$ wavefunctions in UO_2 .

INTRODUCTION

Measurements of the magnetic form factor yield direct information on the radial extent of the unpaired electrons. This information is of particular value in the actinides since, in contrast to $3d$ and $4f$ systems, the nature of magnetism in $5f$ systems appears to be strongly correlated with the extent of overlap between neighboring $5f$ ions. The form factor is also sensitive to the electronic ground state of the ion - a problem especially difficult to resolve in actinide systems. Since theoretical calculations have suggested that the $5f^2 : {}^3H_4$ ground state is appropriate for UO_2 , a measurement of the magnetic form factor should be able to provide precise information on the spatial extent of the $5f$ electrons. In addition, the antiferromagnetic structure of UO_2 is simple type I with an ordered moment $\approx 1.8 \mu_B / \text{U atom}$,¹ which are features that tend to simplify both the experiment and interpretation of the data.

EXPERIMENTAL

A UO_2 single crystal ($1.6 \times 2.4 \times 5.1$ mm) was heated for 6 h at 1950°C in a 10^{-6} to 5×10^{-7} torr vacuum to ensure the stoichiometric composition.² The room temperature lattice constant, $a=5.4702(2)\text{\AA}$, agrees well with values found in the literature.³ The neutron diffraction experiments were performed at the CP-5 reactor using an instrument capable of collecting 3-dimensional crystallographic data at low temperature.⁴ The neutron wavelength was $\lambda=0.992\text{\AA}$. Specimen characterization as well as parameters needed for processing the magnetic intensities were obtained at 80 and 5°K by measuring the nuclear Bragg reflections, with the results summarized in Table I. Extinction corrections were $\sim 5\%$ for the weak nuclear reflections, whereas for the magnetic data only the (100) and (110) reflections required significant corrections (4 and 2% respectively). Azimuthal (Σ) scans on four magnetic reflections at 5°K suggested that the effects of multiple scattering are negligible. The first-order phase transformation characterized on this sample by $T_N 30.7(2)^\circ\text{K}$ is in excellent agreement with the literature.¹

The intensities of 1250 magnetic Bragg reflections (reducing to 71 independent hkl values for $\sin \theta/\lambda \leq 0.83\text{\AA}^{-1}$) were collected at 5°K from a multidomain UO_2 single crystal. The magnetic intensities were consistent with UO_2 being a type I antiferromagnet with a $\langle 001 \rangle$ propagation direction and moments in the XY plane. The domain populations were equal (within experimental error), thus precluding a unique determination of the moment direction in the XY plane. A $\langle 100 \rangle$ or $\langle 110 \rangle$ direction for the moments appears most probable,⁵ and the magnetic unit cell symmetry is then orthorhombic. The experimentally determined product of the magnetic moment (μ , in Bohr magnetons) and the form factor (f) is shown in Fig. 1. Three points of interest are: (a) the slow fall-off of the form factor with $\sin \theta/\lambda$ suggests a $5f^2$ rather than $6d^2$ outer-electron configuration, (b) the U^{4+} effective moment and the magnitude of the form factor anisotropy for $\sin \theta/\lambda > 0.5 \text{\AA}^{-1}$ are in agreement with the limited zone data of Frazer et al.,¹ (c) the anisotropy in the form factor for $\sin \theta/\lambda > 0.5 \text{\AA}^{-1}$ is clearly outside experimental error.

DISCUSSION

The magnetic form factor can be considered as arising from two fundamental properties of the uranium ion: (a) the one-electron radial wavefunctions of the $5f$ shell, and (b) the electronic ground state of the U^{4+} ions in the lattice. In this model anisotropy is a result of the unquenched

orbital angular momentum and crystal-field effects. For (a) we have integrated relativistic Dirac-Fock wavefunctions $U_{5f}^2(r)$, supplied by Freeman and Desclaux⁶, to obtain the $\langle j_1(\vec{k}) \rangle$ functions where

$$\langle j_1(\vec{k}) \rangle = \int_0^\infty U_{5f}^2(r) j_1(kr) dr$$

in which $j_1(kr)$ is the spherical Bessel function. The radial integrals, $\langle j_1(k) \rangle$, are shown in Fig. 2. The $\langle j_0 \rangle$ component of the wavefunctions contains terms that are spherically symmetric, whereas terms in $\langle j_2 \rangle$ etc., contain aspherical contributions. Of particular interest is the angular dependence of $\langle j_0 \rangle$ in comparison with the observed data in Fig. 1. The large scatter of points about a smooth curve in Fig. 1 is a measure of the anisotropy in the form factor of UO_2 and occurs predominantly for $\sin \theta/\lambda > 0.5 \text{ \AA}^{-1}$, in which region the spherical contributions, $\langle j_0 \rangle$ in Fig. 2, have passed through zero and remain small. For (b), the electronic ground state, we choose a model that considers UO_2 an insulator with a localized $5f^2$ configuration. Within the framework of Russell-Saunders coupling this gives a 3H_4 state with a magnetic moment of $3.2\mu_B$. The wavefunctions of the free-ion model may then be characterized as $|M_J = 4\rangle$. Crystal-field calculations have been reported on UO_2 and suggest that the 5 triplet is the ground state⁷. We have calculated the neutron cross-section for such a model with the moments along either a $\langle 100 \rangle$ or $\langle 110 \rangle$ direction. In this model an exchange field polarizes the triplet to yield the magnetic moment of $1.8\mu_B$ at low temperature. The tensor-operator method^{8,9} provides a simple method of handling the magnetic scattering from ions with unquenched orbital moments and gives the cross section in the form

$$q^2 \nu f(\vec{k}) = \sum_{l=0,2,4,6} a_l \langle j_l(\vec{k}) \rangle$$

where $f(\vec{k})$ is the form factor, q^2 the square of the magnetic interaction vector, ν the magnetic moment, and a_l are coefficients.

Form factors calculated for $|M_J = 3\rangle$, and $|M_J = 4\rangle$ were fit to the experimental data with a weighting scheme based on $\sigma_{\text{obs}}(\nu f)$. To match the calculated and experimental values of (νf) for a given M_J state one parameter, the magnetic moment, was allowed to vary. The best fit gave $\nu = 1.78(4)\mu_B$. The (νf) values for $|M_J = 3\rangle$ are shown in Fig. 3. As expected, the calculated form factor (either M_J state) fits the data quite well for $\sin \theta/\lambda < 0.5 \text{ \AA}^{-1}$, but neither calculation can account for the magnitude of the anisotropy at higher angles. For $\sin \theta/\lambda > 0.5 \text{ \AA}^{-1}$ a comparison between Fig. 1 and 3 shows that the magnitude of the anisotropy is at least a factor of five greater than that predicted on the basis of the unquenched orbital moment.

Fourier transform techniques can yield the magnetization density throughout the unit cell and the data in Fig. 1 as well as the calculated form factor given in Fig. 3 were used to generate such magnetization maps. Several features have emerged from the study of the magnetization maps. First, the radial dependence of the magnetization density around the U^{4+} ion at the origin was found to be consistent with $|M_J = 3\rangle$ and incorrect for $|M_J = 4\rangle$. This is consistent with the preliminary crystal-field calculations. Second, integration techniques¹⁰ were used to calculate the magnetic moment per uranium ion from the experimental data, yielding $\mu = 1.74\mu_B$. In addition a non-zero density at the octahedral interstices (1/2,1/2,1/2, etc.) was found to represent a moment of $\sim 0.1\mu_B$. However, these results must be viewed with caution since no data were obtained for $\sin \theta/\lambda > 0.83\text{\AA}^{-1}$ and series termination effects are probably important.

A few concluding remarks appear appropriate since the experimental data presented here tend to ask (rather than answer) more questions concerning our understanding of the physics of actinide magnetism, particularly for UO_2 . We plan to do a full crystal-field calculation and hence remove some of the constraints associated with the free-ion model. These calculations may account for some of the observed anisotropy. Invoking covalency, where unpaired spin remains on the ligand ion, does not appear too promising, as pointed-out by Lovesey,¹¹ because of the symmetry associated with the cubical environment of the U^{4+} ions. Finally we plan to use polarized neutron experiments to examine the induced moment for UO_2 and compare it with the antiferromagnetic form factor of Fig. 1.

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Table I. UO_2 nuclear reflections parameter summary
at 80 and 5°K.

Parameter	T=80°K	T=5°K
Scale constant	50.4(2)	50.3(2)
Extinction parameter, g	1110(46)	1155(43)
B_u ($\text{\AA}^2$)	0.10(1)	0.07(1)
B_{gx} ($\text{\AA}^2$)	0.24(1)	0.22(1)
χ^2	1.4	1.2
Residual (weighted)	0.9%	0.6%
# observations	594	540
# indep. hkl's	32	32

Fig. 1. Experimental values for μ_f in antiferromagnetic UO_2 .

Fig. 2. Radial integrals calculated from Dirac-Fock one-electron wavefunctions for a $5f^2$ ground state.

Fig. 3. Calculated values for μf with moments along a $\langle 110 \rangle$ direction, with $|M_J = 3 \rangle$.