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Neutron-Diffraction Study of Antiferromagnetism in UO_2*

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Antiferromagnetism in UO_2 has been investigated in a detailed single-crystal neutron-diffraction study. Work on this material was prompted by a general interest in unpaired $5f$ and $6d$ electron distributions for different valence states of uranium in simple compounds. The form factor determined in the present case indicates a $5f^2$ electronic configuration with an effective moment slightly less than $1.8\mu_B$ for the U^{4+} ion. The magnetic ordering of the first kind, reported earlier by Henshaw and Brockhouse, is confirmed, but their proposed [111] orientation for the magnetization axis is not. The axis is found to be within the alternating ferromagnetic sheets. In the course of the diffraction study it was found that the paramagnetic-to-antiferromagnetic transition is an unusually sharp one, especially for such a simple magnetic system. Accordingly, the temperature dependence of magnetic neutron intensities was investigated through the Néel point. From the sharpness of the transition (50% of the magnetization is established within 0.03° below the Néel temperature), and the absence of a critical scattering peak, it is concluded that the transition is of the first order.

I. INTRODUCTION

The antiferromagnetic transition at about 30°K in UO_2 was first detected in the specific-heat measurements of Jones, Gordon, and Long.[1] Magnetic measurements below 90°K had not been reported at that time, but on the basis of the Curie-Weiss behavior of the susceptibility at higher temperatures,[2,3] Jones *et al.* concluded that the transition is one involving antiferromagnetic ordering. This was confirmed later by the magnetic measurements of Arrott and Goldman[4,5] and by the neutron-diffraction study of Henshaw and Brockhouse.[6] More recent susceptibility measurements have been published by Leask, Roberts, Walter, and Wolf.[7]

While the basic antiferromagnetic ordering configuration was described in the brief report of Henshaw and Brockhouse,[6] working only with data from a powdered specimen they were unable to make more than a qualitative statement on the uranium form factor. It is evident from their work, however, that the form factor must have considerable $5f$ character, since the magnetic-intensity observations extended beyond the angular range to be expected from $6d$ electrons. This is in line with accumulating chemical and x-ray crystallographic evidence of recent years (e.g., see Wells[8] and Zachariasen[9]) which has tended to favor $5f$ rather than $6d$ levels for the outer-electron configurations of all but the first two of the actinide elements. This has not, by any means, been regarded as a settled point, however (cf. Selwood[10]). The neutron study of Shull and Wilkinson[11] on ferromagnetic UH_3 has provided the most direct and reliable information for a uranium compound, but even in this case, while evidence for $5f$ dominance appears to be convincing, the error limits are too large for quantitative use of the results.

In the present paper we are reporting the results of a detailed single-crystal neutron-diffraction study of antiferromagnetism in UO_2. The experimental data have yielded an accurate form factor for the U^{4+} ion, which clearly demonstrates the $5f$ character of the outer-electron configuration. The form-factor determination was the original objective of the investigation; however, in the course of temperature dependence studies of magnetic scattering in the vicinity of the Néel point, it was found that the transition is a remarkably sharp one, and in fact appears to be of first order. A first-order paramagnetic-antiferromagnetic transition is quite unusual, and is of particular interest in the case of UO_2 since this is such a simple highly symmetrical crystal.

II. PRELIMINARY DETAILS

A. Crystallography

UO_2 crystallizes in the cubic fluorite-type (CaF_2) structure (see Fig. 1). The space group is Fm3m (O_h^5) with 4 U on the face-centered (a) sites and 8 O in the (c) coordinate set (all combinations of $\frac{1}{4}$ and $\frac{3}{4}$ over

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TABLE I. F^2 comparison for nuclear peaks used in determination of scale factor and Debye-Waller parameters at 5°K.

h	k	l	$F^2_{\text{calc.}}$	$F^2_{\text{obs.}}$	h	k	l	$F^2_{\text{calc.}}$	$F^2_{\text{obs.}}$
0	0	6	0.94	0.97	6	6	2	0.50	0.52
4	4	2	0.94	0.95	0	0	10	0.34	0.33
2	2	6	0.85	0.84	6	6	6	0.28	0.34
4	4	6	0.59	0.57					

x, y, and z). The lattice constant at room temperature is $a_0=5.4704\pm8$ Å.[12] An extensive neutron diffraction study of the UO$_2$ crystal structure has been carried out recently by Willis[13] from room temperature to 1100°C.

Of the three classes of Bragg reflections responsible for nuclear scattering in UO$_2$, only one yields intensities sufficiently weak to avoid severe extinction effects (for a crystal of the size used in the present study), and the much stronger reflections of the other two classes were used only for crystal orientation and checks on reproducibility of experimental conditions. The "weak" class, which consists of reflections with $h+k+l=4n+2$, is subject to double-Bragg-scattering errors, but, as shown by Willis, these errors are in general negligibly small in UO$_2$. The intensities observable in this class are of about the same order of magnitude as the magnetic intensities, and consequently, in addition to their principal usefulness in establishing an absolute scale factor, they provided a convenient means for checking for extinction and other possible systematic errors in the magnetic data. They were used also to derive a Debye-Waller correction for the experimental magnetic form factor. The correction was not large (about 5% at the highest angle), but the weak nuclear reflections are much more strongly affected, since the U and O contributions are of opposite sign, and accurate Debye-Waller parameters were necessary for the precise determination of the scale factor. The scale factor and extinction corrections were cross-checked by comparison of the single-crystal results with powder data. As discussed later, two powder samples of slightly different stoichiometry were used, which further provided a check on the effect of a small excess of oxygen, to which UO$_2$ is particularly susceptible, on the effective U^{4+} moment, and on the character of the transition. An independent check on extinction was made by studying the temperature dependence of strong-weak intensity ratios in the single-crystal magnetic data.

The Debye-Waller temperature parameters for uranium and oxygen at 5°K were determined from the "weak" single-crystal reflections by adjustment for the best horizontal linear plot of $\ln(F_{\text{obs}}/F_{\text{calc}})^2$ versus $(\sin^2\theta)/\lambda^2$. Starting values of B_{U} and B_{O} were determined using the first four sets of B's found by Willis[13] (at 293, 486, 598, and 728°K) in a two-Debye calculation of the type discussed by Hofmann *et al.*[14] It may be of interest that these starting values, $B_{\text{U}}=0.051\times10^{-16}$ cm^2 and $B_{\text{O}}=0.254\times10^{-16}$ cm^2, were not much different from those finally adopted: $B_{\text{U}}=0.082\times10^{-16}$ cm^2 and $B_{\text{O}}=0.248\times10^{-16}$ cm^2. A comparison of calculated and observed F^2 values is given in Table I. Two lower angle observations (002) and (222) have been omitted since these were clearly affected by extinction.

B. Experimental

The UO$_2$ single crystal was a pear-shaped specimen of about 6 mm in length and 3 mm maximum diameter. The length was roughly parallel to a [111] direction in the crystal. The measured density was 10.97 ± 0.01 g/cm^3 as compared to the calculated value of 10.96 g/cm^3 for pure UO$_2$. The crystal was mounted with the rotation axis parallel to a [110] direction for the diffraction measurements.

The two powder samples were analyzed chemically, and for the formula UO$_{2+\Delta}$ gave $\Delta=0.010\pm0.017$ and $\Delta=0.05\pm0.01$. A precision lattice-parameter determination at room temperature on the purer powder sample yielded $a_0=5.4705\pm3$ Å, in close agreement with the value cited above.[12] The neutron-diffraction results from the purer powder sample were in very close agreement with the single-crystal results (with an absolute scale factor determined independently in each case), whereas the $\Delta=0.05$ sample led to a U^{4+} moment about 7% low, consistent with a simple dilution effect resulting from uranium in higher oxidation states. All three samples were kept in sealed aluminum specimen containers in an atmosphere of helium.

The diffraction measurements were carried out with the samples mounted in a Linde CF-76 variable-temperature Dewar. Sample temperatures were controlled to ±0.02°K on a relative scale and the absolute temperature was calibrated to ±0.2°K in the temperature dependence studies through the Néel point. Data for the magnetic form factor were collected at 5°K.

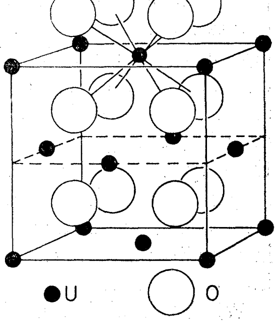

FIG. 1. Crystal structure of UO$_2$. Fluorite-type (CaF$_2$).

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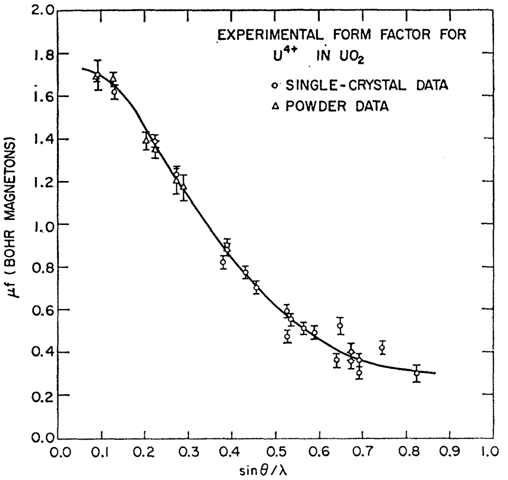

FIG. 2. Magnetic form factor for U^{4+} in UO_2.

III. MAGNETIC STRUCTURE AND FORM FACTOR

The magnetic structure of UO_2, as determined in the powder neutron-diffraction study of Henshaw and Brockhouse (HB),[6] involves ordering of the first kind, i.e., $++--$ ordering on the 000, $\frac{1}{2}\frac{1}{2}0$, $\frac{1}{2}0\frac{1}{2}$, and $0\frac{1}{2}\frac{1}{2}$ uranium sites. Henshaw and Brockhouse reported satisfactory agreement between calculated and observed intensities for six magnetic powder lines with a U^{4+} moment of about 2.1 μ_B oriented parallel to [111]. The results of the present single-crystal study confirm ordering of the first kind, but the data are definitely inconsistent with a [111] orientation for the antiferromagnetic axis and the observed moment is noticeably lower. The significant additional information on the magnetic structure that has emerged from the single-crystal study, however, is an accurate form factor which can provide a reliable basis from which an understanding of the outer-electronic properties of the U^{4+} ion may be achieved.

The results reported here are based on 23 independent ($h\,h\,l$)-type reflections collected at 5°K from a single-crystal (but multidomain) sample of UO_2. Each reflection was measured in at least two of the equivalent positions available from the [110] setting of the crystal. Neutron powder patterns at 5°K and single-crystal check scans failed to reveal any new reflections characteristic of an enlarged magnetic cell. All observations were in complete accord with the HB ordering configuration. An equal distribution of the three types of domains was assumed in all calculations. Any serious deviation from complete randomness would have shown up in a systematic way as apparent errors in the effective values of q^2 (the square of the magnetic-interaction vector), but none was detectable.

While the original cubic cell is retained in the present paper, the four-sublattice arrangement can be reduced to a two-sublattice structure by choosing a new tetragonal cell with $a=b=\frac{1}{2}\sqrt{2}a_0$ (along face diagonals of the cubic cell) and $c=a_0$. The true magnetic symmetry may, in fact, be orthorhombic, but it cannot be higher than tetragonal. In either case, a [111] moment orientation is not what one would expect on symmetry grounds. Rather, one might expect (for a collinear structure) orientations parallel to one of the cube axes, either within or perpendicular to the antiferromagnetically coupled ferromagnetic sheets, or parallel to a cube-face diagonal within the ferromagnetic sheets. The orientation perpendicular to the sheets, which can be labeled as the [001] direction in either unit cell, can be eliminated immediately using powder data alone, since this orientation would preclude observation of any of the cubic (100) peaks. The [111] orientation, and any other orientation making an angle differing from 90° from the [001] direction, can be distinguished from an XY orientation (within the sheets) on the basis of q^2 by comparing intensities at the same or neighboring values of $(\sin\theta)/\lambda$. Orientations within the XY plane cannot be distinguished from one another using a multidomain crystal, however. Calculations at an early stage in the analysis showed that the observed data could be explained only on the basis of an XY orientation.

The experimentally determined form factor, plotted as μf on an absolute scale in Bohr magnetons, is shown in Fig. 2 and a list of data is given in Table II. Several points obtained from powder data (from the purer sample) are included in the plot, and it will be noticed that an excellent fit is obtained with the single-crystal results, even though the scale factors were determined independently for each set of data. The error estimates

TABLE II. Magnetic-form-factor data from UO_2 single-crystal neutron measurements. Data corrected for temperature with $B_U=0.082\times10^{-16}$ cm².

h	k	l	$(\sin\theta)/\lambda$ (Å^{-1})	μf (Bohr magnetons)	σ (μf)
0	0	1	0.092	1.70	0.07
1	1	0	0.130	1.62	0.03
1	1	2	0.224	1.39	0.03
0	0	3	0.275	1.23	0.03
2	2	1	0.275	1.23	0.04
2	2	3	0.378	0.82	0.03
3	3	0	0.389	0.88	0.03
1	1	4	0.389	0.90	0.03
3	3	2	0.430	0.77	0.03
0	0	5	0.458	0.70	0.03
2	2	5	0.526	0.47	0.03
4	4	1	0.526	0.59	0.03
3	3	4	0.534	0.55	0.03
1	1	6	0.565	0.51	0.03
4	4	3	0.589	0.49	0.03
0	0	7	0.641	0.36	0.03
5	5	0	0.648	0.52	0.04
5	5	2	0.673	0.40	0.04
3	3	6	0.673	0.36	0.04
2	2	7	0.692	0.30	0.03
4	4	5	0.692	0.36	0.03
1	1	8	0.744	0.42	0.03
0	0	9	0.824	0.30	0.04

plotted with the single-crystal data points are substantially larger than those derived only from counting statistics. Possible additional sources of error considered in the estimates were differences in equivalent reflections, double Bragg scattering, extinction, absorption, and occasional overlapping with the weak broadened Al powder lines from the cryostat and sample holder. Extinction corrections were made for the first two single-crystal points (001) and (110), but were found to be negligibly small for the remaining reflections. The corrections were determined by comparing the temperature dependence of these relatively strong peaks to that of weaker magnetic peaks, especially in the immediate vicinity of the Néel point. The corrected values agree very well with the powder data.

There are three main points of interest in the form-factor results:

(1) The curve falls off much too slowly with increasing $\sin\theta/\lambda$ to be explained by a $6d^2$ configuration, even if a large orbital contribution is considered, and hence must be interpreted in terms of $5f^2$ levels.

(2) The U^{4+} effective moment, obtained by extrapolation to zero angle, appears to lie between 1.7 and 1.8 Bohr magnetons.

(3) The deviations of some observations from the smooth curve appear to be well outside experimental error, suggesting some degree of asphericity in the magnetization density distribution. An attempt was made to analyze the data for this by Fourier methods, but the results were inconclusive.

IV. MAGNETIC PHASE TRANSITION

The temperature dependence of the magnetic intensities has been investigated in detail through the Néel temperature. The measurements were made on the two strongest magnetic reflections (001) and (110) of the single crystal as well as the (001) reflection of powder samples. These observed intensities were scaled to 100 at 5°K and are shown in Fig. 3. The two sets of single-crystal data are in excellent agreement and indicated an extremely sharp phase transition at 30.8°K. The temperature dependence of the powder data near the transition is somewhat less steep, as might be expected from the inherently higher degree of imperfection of polycrystalline samples. Nevertheless, the agreement is quite satisfactory.

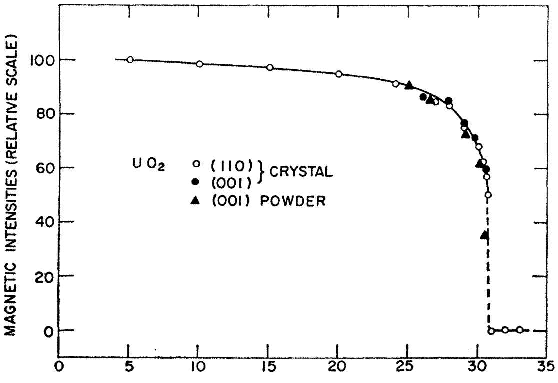

FIG. 3. Temperature dependence of magnetic scattering in UO$_2$.

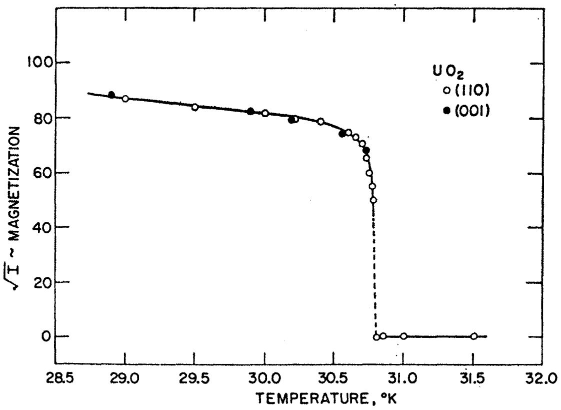

FIG. 4. Details of neutron measurements through the Néel temperature. Data scaled to 100 at 5°K.

The details of the change in intensity in the immediate vicinity of the Néel temperature are shown in Fig. 4. In this figure, the coordinate is taken as a square root of the intensity scaled to 100 at 5°K, which in the first approximation is proportional to the magnetization. The data clearly indicate that the antiferromagnetic phase transition in UO$_2$ is of the first order. More specifically, it can be stated that 50% of the magnetization is established within a range of 0.03°K below the Néel temperature, or within $\Delta T/T_N = 0.001$.

An effort was made to detect a thermal hysteresis effect for the first-order phase transition. First, it was established that the intensity data taken below 30.76°K, or above the Néel temperature 30.80°K, are quite reproducible irrespective of whether the approach to the given temperature is by heating or cooling. Between these two temperatures, on the other hand, the intensity data were not reproducible enough to draw positive conclusions on a thermal-hysteresis effect. The relatively large size of the single crystal may have contributed to the fluctuation of the data in this range.

As a further test of the first-order nature of the transition, it was of interest to study the magnetic scattering above the Néel temperature in more detail. If the phase transition is of the second order, one would expect to observe critical scattering near the Néel temperature. Figure 5 shows the data taken 0.2°K above the Néel temperature in comparison with the corresponding curve 0.2°K below. In these measurements the counter was held at a fixed position while the crystal was rotated through the Bragg position. While, as would be expected, some orientational correlation of magnetization density is indicated by the

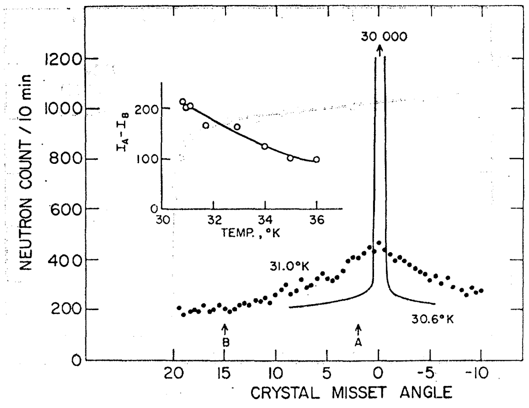

FIG. 5. Critical-scattering measurements near the Néel temperature, 30.8°K.

observation of a diffuse peak, the measurement above the Néel temperature does not show the sharp critical scattering which is characteristic of a second-order transition. This is further illustrated in the insert of Fig. 5, in which the intensity of the diffuse peak is shown as a function of temperature. The position A was selected instead of the peak position in order to avoid the effect of double Bragg scattering.

Finally, some remarks might be made concerning the transition temperature. The recent susceptibility measurements of Leask *et al.*[7] show a peak very close to the transition point of 30.8°K observed in the present study; however, the data were interpreted such that the steepest point of the χ-versus-T curve at about 29°K was taken as the Néel point. This interpretation may be justified for a second-order phase transition, but is not valid in the light of the results reported here. It is more natural to assume that the peak corresponds to the Néel temperature, in agreement with the present data.

V. DISCUSSION

The form-factor results lead to a U^{4+} moment close to the spin-only value of 2 μ_B, but it is improbable the data can be explained on this basis. The more likely situation is that large orbital effects are present, and that an explanation would be derived from crystal field splitting of the $5f^2$ free-ion $J=4$ ground state with $S=1$ and $L=5$ (other states are too high in energy to consider). Blume[15] has suggested that this might not only be the basis for explaining the form factor, or its Fourier transform, the magnetization density distribution, but also might be the origin of the first-order transition as well. Two of the expected split levels are nonmagnetic; under proper temperature-dependence conditions, it is possible that a cross-over could occur between magnetic and nonmagnetic levels at the Néel point. First-order transitions in magnetic ordering were first discussed by Bean and Rodbell[16] on a different basis with relation to the paramagnetic-ferromagnetic transition in MnAs at 40°C. In their treatment, the first-order character of the transition was attributed to a strong dependence of exchange interaction on interatomic distance, and, in this case, a relatively large change in lattice parameter is expected at the transition point. It was later[17] shown that the same result can be obtained phenomenologically if the exchange interaction has small additional biquadratic terms.[18] The biquadratic-term approach would seem to be the more likely one for a highly symmetric cubic crystal such as UO_2 if an explanation is sought in the exchange interaction rather than in the electronic configuration of the U^{4+} ion.

As this paper was being written the authors were informed by Dr. Walter Marshall that a neutron investigation of antiferromagnetism in UO_2 had also just been carried out independently by Willis and Taylor[19] with substantial experimental agreement with the results reported here.

Note added in proof. We have since become aware of some recent specific heat measurements (E. F. Westrum and J. J. Huntzicker, to be published) which demonstrate that the transition is much sharper than reported by Jones *et al.*,[1] and occurs at 30.4°K, in excellent agreement with the results reported above. We thank Professor Westrum for sending us a copy of his report prior to publication.

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