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An investigation of the magnetic structure of uranium nitride by neutron diffraction

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Abstract. The magnetic structure of uranium nitride at liquid helium temperature has been studied by neutron diffraction. It is found that this substance is antiferromagnetic with ordering of the first kind. A value of 0·75 μ_B has been found for the magnetic moment at a uranium atom, and a form factor curve has been obtained. Good agreement is found between the experimental form factor and a theoretical calculation based on the assumption that the uranium atoms are triply ionized and have a $5f^3$ configuration.

1. Introduction

Most magnetic structures investigated by neutron diffraction have been compounds of the iron-group transition elements or the rare earths. This paper describes the application of these techniques to an actinide compound, uranium mononitride, which is antiferromagnetic with a Néel temperature of 53 °K. UN has the face-centred cubic, sodium chloride structure with $a = 4{\cdot}89$ Å (Rundle *et al.* 1948, Mueller and Knott 1958). It is an interstitial compound with a high melting point (about 2850 °c), metallic lustre and low electrical resistivity ($1{\cdot}6 \times 10^{-4}$ Ω cm). The electronic configuration of the uranium atom in this compound is not known, so that a determination of the magnetic structure, besides being of intrinsic interest, is important for the information it can give about the electron distribution in this substance.

2. Experimental details

The majority of the measurements were made using single-crystal specimens but, in addition, some measurements were made with powders to eliminate extinction effects. All the specimens were provided by Dr. R. M. Dell of Chemistry Division, A.E.R.E. The two single crystals used were extracted from an ingot supplied by the Battelle Memorial Institute. One crystal was almost a rectangular parallelepiped 0·95 cm × 0·65 cm × 0·35 cm, and the other was an irregular piece roughly 0·6 cm × 0·3 cm × 0·3 cm. The powdered material was prepared at A.E.R.E. It consisted of stoichiometric $UN_{1\cdot00}$ together with 1·7 mole% UO_2.

The experiments were carried out at the PLUTO reactor, using neutrons of wavelength 1·08 Å for the single-crystal measurements and 1·05 Å for the powder measurements. The specimens were mounted in a liquid-helium cryostat, and the temperature was measured with a copper–constantan thermocouple whose reference junction was at 0 °c. Integrated intensities were measured for all the obtainable magnetic reflections and one or two nuclear reflections. Only two-dimensional data could be collected for one mounting of a crystal. With the crystal at 12 °K, three sets of such data were measured: (i) with the large crystal and a [110] axis vertical, (ii) with the same crystal and a

[100] axis vertical and (iii) with the smaller crystal and a [112] axis vertical. A total of 19 non-equivalent magnetic intensities was measured. These were corrected for absorption, extinction and contamination by the $\frac{1}{2}\lambda$ component of the neutron beam. Absorption corrections were calculated using a programme written by the author for a Mercury computer, based on the method first used by Busing and Levy (1957). Extinction effects were estimated by comparing results from single crystals with those from powders. The magnetic intensities are not much affected by extinction, the intensity of the strongest magnetic reflection, 110, being only 1/700 of that of the strongest nuclear reflection, 200. The correction for $\frac{1}{2}\lambda$ contamination was necessary, because each magnetic reflection *hkl* was superimposed on a nuclear reflection $2h\ 2k\ 2l$ derived from the 0·54 Å neutrons. The even–even–even nuclear reflections are strong because all the atoms scatter in phase. Two methods of correction were used. (i) Intensities were measured at both 12 °K and 77 °K. At the latter temperature only the $\frac{1}{2}\lambda$ nuclear scattering is observed, since the material is paramagnetic. The 77 °K intensity was subtracted from the 12 °K intensity after correcting for the change in the Debye factor. (ii) Intensities at 12 °K were measured with a filter in the incident beam. This filter, a disk of ^{239}Pu 0·010 in. thick, has transmission factors of 53% and 4% for 1·08 Å and 0·54 Å neutrons. The corrections deduced by the two methods were consistent.

3. Results

At 12 °K reflections were observed with indices *hkl* (based on the face-centred cubic cell) which were a mixture of odd and even integers. Reflections with half-integral values of the indices, such as $\frac{1}{2}00$, $\frac{1}{2}\frac{1}{2}0$, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ and $1\frac{1}{2}0$, were sought but were not observed. From these results the magnetic structure illustrated in figure 1 is deduced. In this structure, known as ordering of the first kind (see, for example, Goodenough 1963) ferromagnetic sheets parallel to the (001) planes are antiferromagnetically coupled. The magnetic unit cell is a cube of the same size as the face-centred cubic chemical cell but is centred on one face only, so that the symmetry of the structure is reduced from cubic to tetragonal. The further observation that reflections of the type *h*00, 0*k*0 or 00*l* do not occur for odd values of the non-zero index indicates that the magnetic moments are

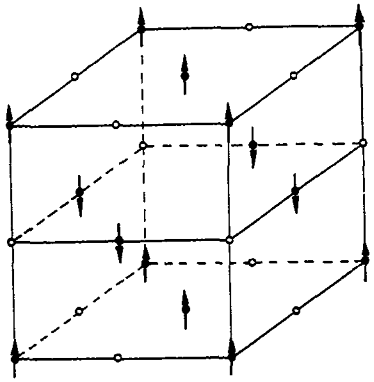

Figure 1. The magnetic structure of uranium nitride. The arrows at the positions of the uranium atoms indicate the directions of the magnetic moments and the open circles represent the nitrogen atoms. The magnetic unit cell is the same size as the chemical cell and the magnetic moments lie in ferromagnetic sheets parallel to (001).

perpendicular to the ferromagnetic sheets. Three types of domain are possible with this structure as the ferromagnetic sheets may be parallel to (100), (010) or (001). These are referred to later as domains type 1, 2 and 3. Each magnetic reflection originates from only one type of domain. Thus type 1 domains produce reflections for which h differs in parity from k and l, type 2 domains produce reflections for which k differs from h and l, and type 3 domains produce reflections for which l differs from h and k. (The reflections for which h, k and l are all of the same parity are purely nuclear. There are no 'mixed' reflections from this structure.)

In order to obtain the magnetic form factor, it is necessary to relate intensities derived from different domains. All the reflections measured with a [110] or [112] axis vertical are from type 3 domains, but reflections from all three types of domain are obtained with a [100] axis vertical. As the proportions of the crystal volume occupied by the three types of domain are unknown, symmetry relations must be used to put all the reflections on the same scale. The largest reflections in the three groups obtained with [100] vertical are 011 (type 1), 012 (type 2) and 021 (type 3). Since 012 and 021 are equivalent, reflections from domains of types 2 and 3 can be placed on a common scale. The reflections obtained with [112] vertical include $1\bar{1}0$ and $20\bar{1}$ (both from type 3 domains). Since these reflections are equivalent, respectively, to 011 and 012, their ratio may be used to put all the reflections obtained with [100] vertical on a common scale, together with those obtained with [112] vertical. (It is found that, with [100] vertical, the volumes occupied by the three types of domain are equal to within 5%.) Reflections obtained with [110] vertical can now be placed on the same scale as the others, since 011 and $1\bar{1}0$ are equivalent. (It should be noted that, although the symmetry within one domain has been reduced to tetragonal, the *hkl* reflection from type 1 domains and the *lkh* reflection from type 3 domains are equivalent.)

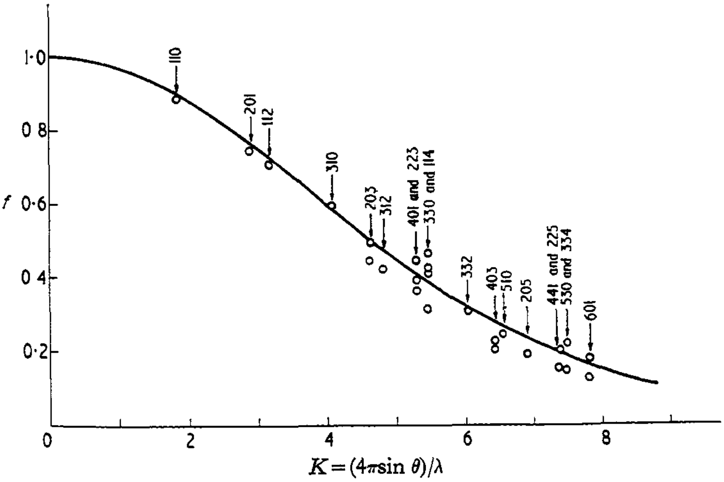

Figure 2. The amplitude form factor for the magnetic scattering of neutrons from the uranium ions in UN plotted as a function of $(4\pi \sin\theta)/\lambda$. The experimental points are shown as open circles, and the continuous curve is obtained from the theoretical calculation by Johnston (1965, to be published), assuming the configuration of the ions to be $5f^3$. The indexing of the reflections is appropriate to type 3 domains. Measurements of equivalent reflections obtained from different domains (or crystals) are plotted as independent observations.

The form factor derived from these results is shown in figure 2, in which the experimental points are represented by open circles. The ordinates are the quantity f in the expression

$$I \propto \frac{p_0^2 f^2 \sin^2\alpha}{\sin 2\theta}$$

where I is the integrated intensity of a reflection, θ is the Bragg angle, p_0 is the magnetic scattering length per uranium atom at $\theta = 0°$ and α is the angle between the scattering vector and the direction of the magnetic moment. The values of f are plotted as a function of $(4\pi \sin\theta)/\lambda$.

A value for the magnetic moment per uranium atom is deduced from the intensity ratios of magnetic and nuclear reflections. The most accurate value is likely to be obtained from the ratio I_{110}/I_{200} measured with a powder specimen. With a single crystal the ratio I_{110}/I_{200} is strongly affected by extinction in the 200 reflection. If the ratio I_{110}/I_{111} is used to calculate the magnetic moment, a potential source of error arises because the structure factor of the 111 reflection is sensitive to a possible difference between the Debye factors for uranium and nitrogen. A value of $0{\cdot}75 \pm 0{\cdot}1\ \mu_B$ is deduced from the powder ratio I_{110}/I_{200}, the chief sources of uncertainty occurring in estimating the $\frac{1}{2}\lambda$ correction to the 110 intensity and in extrapolating the form factor to $\theta = 0°$.

The Néel temperature was determined from the temperature variation of the peak intensity of the 110 reflection, which is shown graphically in figure 3. The value obtained is 53 ± 2 °K, which may be compared with 52 °K found by Anderson (1964, private communication) from susceptibility measurements.

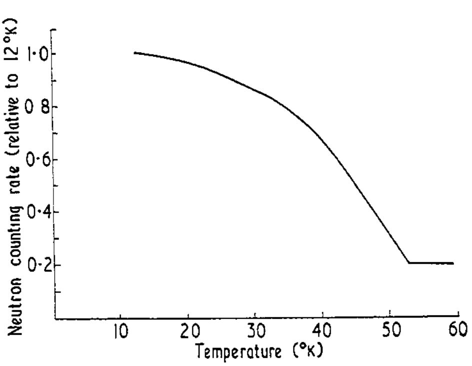

Figure 3. The temperature variation of the peak intensity of the 110 magnetic reflection. The Néel temperature is 53 °K. The rather high background is due partly to the 220 nuclear reflection produced by the 0·54 Å neutrons in the incident beam, and partly to incoherent scattering from the large sample and the vanadium walls of the cryostat.

4. Discussion

The magnetic structure determined for UN has not been found previously in any other compound with the rock salt structure, although a similar structure without the interstitial atoms occurs in γ manganese. The oxides of the iron-group transition metals, such as MnO, have ordering of the second kind, i.e. the unit cell edge is doubled and the ferromagnetic sheets are parallel to (111) planes. The compounds MX, where M is a heavy rare-earth metal and X an element of group VB, are when ordered either ferromagnetic (TbN, DyN, HoN, ErN, for which $a < 5{\cdot}6$ Å), or antiferromagnetic with ordering of the second kind (TbP, TbAs, TbSb, HoSb, ErP, ErSb, for which $a \geqslant 5{\cdot}6$ Å), or are ferrimagnetic with a multi-axial spin structure (HoP, for which $a = 5{\cdot}62$ Å)

(Child *et al.* 1963). One other antiferromagnetic nitride with a rock salt structure (CrN) has been studied and found to have ordering of the fourth kind (Corliss *et al.* 1960).

The value of 0·75 μ_B which is found for the magnetic moment appears at first to be surprisingly small. If the uranium atoms are triply ionized with three electrons remaining in the 5f sub-shell, then making the extreme assumption that Hund's rule operates, we have $S = \frac{3}{2}$, $L = 6$, $J = \frac{9}{2}$ and $gJ = 3{\cdot}3\ \mu_B$ (g is defined below). However, one would not expect to find such a large value for the magnetic moment in the solid at 12 °K, because the $J = \frac{9}{2}$ energy level is split by the cubic crystal field and the tetragonal exchange field, and at this temperature most of the ions are in the ground state. This produces a reduction in the effective magnetic moment. At higher temperatures the higher energy levels for which $J = \frac{9}{2}$ will also be occupied and the magnetic moment may be expected to approach a value of $3{\cdot}3\ \mu_B$. This is indeed found to be the case when the magnetic moment above the Néel temperature is deduced from plots of reciprocal susceptibility against temperature. The results obtained, in Bohr magnetons, are 3·0 (Trzebiatowski *et al.* 1962) and 3·1 (Allbut *et al.* 1964).

The experimentally determined form factor may be compared with the results of a theoretical calculation by Johnston (1965, to be published) for magnetic ions in the presence of a crystal field. He shows that to a good approximation f is proportional to

$$\langle j_0 \rangle + \frac{g_L}{g} \langle j_2 \rangle$$

where

$$g_L = \frac{J(J+1) + L(L+1) - S(S+1)}{2J(J+1)}$$

$$g = \frac{3J(J+1) - L(L+1) + S(S+1)}{2J(J+1)}$$

$$\langle j_p \rangle = \int_0^\infty \rho^2(r) \left(\frac{\pi}{2Kr} \right)^{1/2} \mathrm{J}_{p+\frac{1}{2}}(Kr)\, dr \qquad \text{for } p = 0 \text{ or } 2$$

$\rho^2(r)$ is the radial density of unpaired electron spins, J_x is the Bessel function of order x and $K = (4\pi \sin\theta)/\lambda$†.

The above formula has been evaluated for the particular case, already discussed, of a U^{3+} ion with the configuration $5f^3$ for which $S = \frac{3}{2}$, $L = 6$, $J = \frac{9}{2}$ and $g_L/g = \frac{7}{4}$. The electron densities used in calculating $\langle j_0 \rangle$ and $\langle j_2 \rangle$ were obtained from calculations by Waber (1964, private communication) for the 5f sub-shell of a neutral uranium atom with the configuration $5f^3 6d^1 7s^2$. These are self-consistent field calculations of relativistic wave functions, using the Dirac equations with Slater's (1951) approximate exchange correction. The curve obtained is shown in figure 2 and can be seen to be in good agreement with the experimental points. We may conclude that a $5f^3$ configuration is consistent with the results of the experiment, although other configurations such as $5f^1$ or $5f^2$ cannot be ruled out. The experimental results do appear, however, to rule out the possibility of a magnetic moment derived from electrons in the 6d sub-shell as this would require a form factor which diminished much more rapidly with increasing values of K.

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† The above formula can be related to the expression given by Trammell (1953) for the form factor of a free rare-earth ion. It should be noted that Trammell's functions $f_0(x)$, $f_2(x)$, $g_0(x)$ and $g_2(x)$ are related by $f_0(x) - \frac{1}{2} f_2(x) = g_0(x) + g_2(x)$ and that the functions $g_p(x)$ are related to our radial integrals $\langle j_p \rangle$ by

$$\langle j_p \rangle = \int_0^\infty \rho^2(r) g_p(Kr)\, dr.$$

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References

ALLBUTT, M., JUNKISON, A. R., and DELL, R. M., 1964, *Proc. Int. Symp. on Compounds of Interest in Nuclear Reactor Technology, Boulder, Colorado*, 1964 (New York: A.I.M.E.), pp. 65–81.
BUSING, W. R., and LEVY, H. A., 1957, *Acta Cryst.*, **10,** 180–82.
CHILD, H. R., WILKINSON, M. K., CABLE, J. W., KOEHLER, W. C., and WOLLAN, E. O., 1963, *Phys. Rev.*, **131,** 922–31.
CORLISS, L. M., ELLIOTT, N., and HASTINGS, J. M., 1960, *Phys. Rev.*, **117,** 929–35.
GOODENOUGH, J. B., 1963, *Magnetism and the Chemical Bond* (New York: John Wiley), p. 92.
MUELLER, M. H., and KNOTT, H. W., 1958, *Acta Cryst.*, **11,** 751–2.
RUNDLE, R. E., BAENZIGER, N. C., WILSON, A. S., and MCDONALD, R. A., 1948, *J. Amer. Chem. Soc.*, **70,** 99–105.
SLATER, J. C., 1951, *Phys. Rev.*, **81,** 385–90.
TRAMMELL, G. T., 1953, *Phys. Rev.*, **92,** 1387–93.
TRZEBIATOWSKI, W., TROC, R., and LECIEJEWICZ, J., 1962, *Bull. Acad. Pol. Sci. Ser. Sci. Chim.*, **10,** 395–8.