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LETTER TO THE EDITOR

Magnetic x-ray powder diffraction from antiferromagnetic uranium dioxide

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Abstract. We report the first successful measurement of a magnetic x-ray powder diffraction (MXP) peak from an antiferromagnet, obtained in this instance by exploiting the strong uranium M_4 magnetic resonance in UO_2 . In the experiment, the challenge has been to overcome the relative weakness of MXP relative to high levels of fluorescence background radiation. The interpretation of our data as magnetic diffraction rests on three findings. First, the signal vanishes as the sample temperature is raised through the critical temperature, at which long-range order vanishes. Secondly, the diffraction intensities are shown to exhibit a pronounced resonance structure close to the U M_4 edge. Lastly, the scattering cross-section is found to be in remarkably good agreement with a simple calculation.

In recent years, magnetic x-ray diffraction has emerged as an important new tool for studying antiferromagnetism in single crystals [1–11]. Measurements on powder samples, on the other hand, have remained exclusively in the realm of neutron scattering. The hurdle to performing a successful magnetic x-ray powder diffraction (MXP) experiment arises from the relative weakness of the diffraction peaks compared to competing fluorescence and charge scattering processes. With photon energies far from any absorption edge resonance, non-resonant magnetic diffraction intensities may be typically six to eight orders of magnitude lower than the strong charge reflections [1–4]. Furthermore, diffraction from powdered samples is almost swamped by the background of diffuse scattering. Set against this gloomy background, the huge resonance enhancements discovered in some magnetic ions, notably the celebrated actinide M_4 magnetic resonance, which can approach a per cent of the charge peak intensities [7–11], represents an obvious route by which to realize MXP in uranium compounds. However, close to resonance, the photoelectric absorption becomes extremely strong, reducing the elastic scattering signals and simultaneously generating a large increase in fluorescence background radiation. The key to a successful measurement is therefore high photon flux combined with good energy selectivity of the scattered radiation, to discriminate against fluorescence.

The sample chosen for this first step towards MXP from an antiferromagnet was a powder of the cubic semiconductor uranium dioxide, which undergoes a sharp (first-order) para- to antiferromagnetic phase transition [12–15] at $T_N = 30.8$ K. The type-I ordered structure consists of alternately directed ferromagnetic sheets (figure 1), and although there remains some debate about the precise ordering *within* the planes [15, 16], we have employed a model in which all moments are collinear and aligned with the z -axis. The ordered moment of the U^{4+} ions is $1.74 \mu_B$ [15].

For the present measurements, we have adopted an experimental geometry which optimizes the diffraction intensities and fluorescence discrimination, while providing only

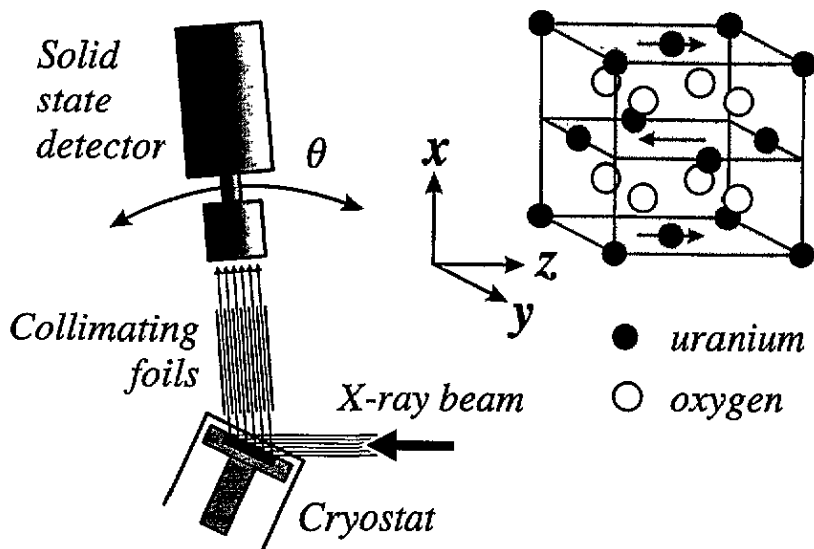


Figure 1. A schematic diagram of the experimental layout (left) and the assumed magnetic structure of UO_2 .

modest angular resolution. The purpose of this work is to demonstrate that MXPD is possible even with an unfocused bending magnet radiation source of a second-generation synchrotron. If this can be achieved then, by implication, measurements of extremely high quality will be possible with a high-flux insertion device on a third-generation machine.

Our experimental set-up is illustrated in figure 1. Unfocused synchrotron radiation was extracted from a dipole magnet, some 32 m from the powder target in station 8.4 of the SRS, Daresbury Laboratory, with an estimated flux of $\sim 6 \times 10^8$ photons $\text{s}^{-1} \text{mm}^{-2}$ within the 1.3 eV bandwidth of a germanium (111) channel-cut monochromator. To reduce beam attenuation, helium bags eliminated all residual air paths. The target—a compressed 13 mm diameter disk of UO_2 powder—was attached to the cold finger of a displax cryostat, very close to the flat 0.1 mm beryllium vacuum window. A single driveable θ -axis (figure 1) rotated a high-energy-resolution solid state detector around the fixed target, inclined at 25° to the (1 mm vertical \times 12 mm horizontal) beam. Scattering was in the vertical plane. The most unusual feature of the diffractometer geometry was the use of a set of low-resolution (FWHM = 0.5°) angle-defining parallel foils placed close to the sample position, with no axial divergence (Soller) slits. This approach maximized the detection efficiency while maintaining symmetric line shapes for reflections with $\theta \sim 90^\circ$, albeit with modest wavevector resolution.

Most of the diffraction scans were performed at a fixed wavelength of $\lambda \simeq 3.326 \text{ \AA}$, close to the centre of the $\text{U } M_4$ white line, where the magnetic resonance in a number of uranium compounds is known to be maximum [7–11]. By repeatedly scanning over an angular range which included the position of the (102) pure magnetic reflection, a peak was indeed observed (figure 2) at precisely the expected angle, with a maximum count rate of around 20 cps on a background some 20 times higher. Despite a somewhat inaccurate temperature calibration (due to the absence of a radiation shield), the estimated sample temperature of $T \simeq 23 \text{ K}$ was well below the 30.8 K Néel point. From the graph, the diffraction peak is unquestionably statistically significant.

Having established the existence of a diffraction peak at the (102) position, it was

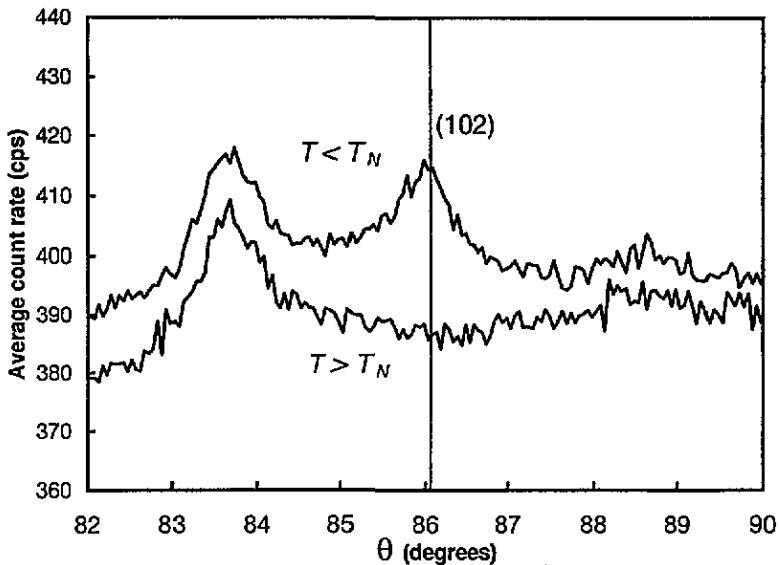


Figure 2. Diffraction scans centred on the expected (102) magnetic peak position (vertical line). Low-temperature data were recorded at around 23 K; high-temperature data were recorded close to 50 K. The transition temperature for UO_2 is $T_N = 30.8$ K. The peak to the left of the (102) is clearly not associated with the antiferromagnetic structure, and is probably an impurity—possibly $\beta\text{-UO}_3$. Note that the vertical scales have been offset for clarity.

important to verify its magnetic origin. This required three crucial confirmatory steps. First, a magnetic Bragg reflection should vanish in the paramagnetic phase. The data in figure 2 for signals observed above and below the ordering temperature confirm that it does. Secondly, magnetic scattering should exhibit a sharp resonant energy dependence. Again this was confirmed, by performing measurements over a range of photon energies; our data are displayed in figure 3. Finally, one can check that the cross-section of the magnetic reflection is in accord with theoretical predictions. Most of the remainder of this letter is concerned with this last, most demanding task. First, though, we establish the relation between the observed intensities, I_{hkl} , and the cross-section.

At the centre of the magnetic resonance the integrated intensity ratio between the magnetic (102) and the chemical (220) reflections was determined to be 0.22%. After making a modest correction for the differences in sample absorption and Lorentz factors, this ratio was reduced to 0.18%, with an estimated uncertainty of perhaps 20%, arising mainly from errors in data normalization for primary beam flux variations. For a particular experimental geometry, the corrected integrated intensities scale with the unit-cell cross-section ($d\sigma/d\Omega$) and the multiplicity of the powder reflection (M). One can therefore write the (102) magnetic cross-section as

$$\left(\frac{d\sigma}{d\Omega}\right)_{102} = \frac{M_{220}}{M_{102}} \left(\frac{d\sigma}{d\Omega}\right)_{220} \frac{I_{102}}{I_{220}} \quad (1)$$

where the multiplicities of the (220) reflections in the chemical cell and the (102) reflections of the magnetic cell are $M_{220} = 12$ and $M_{102} = 8$, respectively. (The magnetic multiplicity is discussed later.) The magnetic cross-section can therefore be deduced with a knowledge of the chemical cross-section, which is given in terms of the unit-cell chemical structure factor, $F_c(\mathbf{k})$ —the Fourier transform (with wavevector \mathbf{k}) of the charge density. The expression

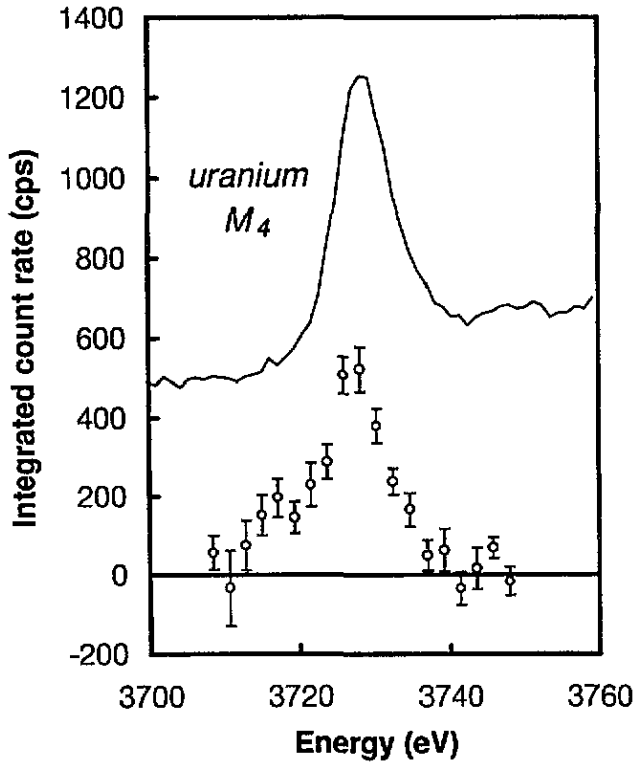


Figure 3. The uranium M_4 absorption-edge resonance determined from fluorescence (solid line) and the integrated magnetic diffraction intensities (error bars). The slightly broadened widths of both of these lines are largely due to sample absorption variations, which have not been corrected for.

required in equation (1) is (see, for example, [19])

$$\left(\frac{d\sigma}{d\Omega}\right)_{220} = r_e^2(\boldsymbol{\varepsilon}' \cdot \boldsymbol{\varepsilon})^2 F_c^2(\mathbf{k}) \Rightarrow r_e^2 \frac{1}{2} \{1 + \cos^2 \theta + P_3 \sin^2 \theta\} F_c^2(\mathbf{k}). \quad (2)$$

Here, $r_e \simeq 2.818 \times 10^{-5} \text{ \AA}$ is the classical electron radius, $\boldsymbol{\varepsilon}$ and $\boldsymbol{\varepsilon}'$ are the primary and secondary photon beam polarization vectors, θ is the angle between the primary and secondary beams, and P_3 is one of the Stokes parameters which describe the state of polarization in the primary beam. The extreme values, $P_3 = +1$ and -1 , correspond to complete linear polarization perpendicular to, and within the plane of scattering, respectively. With our diffractometer, $P_3 \simeq +1$ to a good approximation [4]. The structure factor for the (220) reflection in UO_2 can be expressed in terms of the atomic form factors $f(\mathbf{k})$ of the uranium and oxygen ions,

$$F_c(220) = 4f_{\text{U}^{4+}}(\mathbf{k}) + 8f_{\text{O}^{2-}}(\mathbf{k}). \quad (3)$$

Despite performing these measurements at the peak of the white-line absorption feature, no correction has been applied for anomalous dispersion. This is partly justified by the approximate nature of the present calculations, and the fact that the anomalous corrections are not well documented. We note, however, that the contribution which may at first sight appear most problematic—the *real* component arising from the white line—should cross zero

at the resonant centre, very close to the energy chosen for these measurements. Neglecting anomalous scattering may therefore be justified in the present case.

From tabulated atomic form factors [17], the unit-cell chemical structure factor for the (220) Bragg position is estimated at $F_c(220) \simeq 333$, leading to a maximum magnetic cross-section (i.e. at the resonant centre) of $d\sigma/d\Omega \simeq 295r_e^2$. We next compare this value with a theoretical interpretation of the magnetic scattering.

The dipole approximation to the resonant magnetic scattering length for a crystal unit cell containing a single resonant ion species can be written [18, 19, 22] as

$$f = -i \left(\frac{3}{4\pi q} \right) (\varepsilon' \times \varepsilon) \cdot F_m [F_{-1}^1 - F_{+1}^1] \quad (4)$$

where $q = 2\pi/\lambda$. All information pertaining to the magnetic structure is contained in the magnetic structure factor

$$F_m = \sum_j^{\text{cell}} e^{ik \cdot R_j} m_j \quad (5)$$

where m_j and R_j are, respectively, the orientation and position of the j th resonant magnetic ion in the unit cell. Probably the least accessible terms in the scattering amplitude are the dimensionless energy-dependent resonant strengths F_ν^1 for dipole excitations with a magnetic quantum number ν .

From the scattering length in equation (4), one can compile an expression for the magnetic cross-section, applied in the case to the (102) Bragg reflection,

$$\left(\frac{d\sigma}{d\Omega} \right)_{102} = |f|^2 = \left(\frac{3}{4\pi q} \right)^2 F_m^2 \langle P \rangle |F_{-1}^1 - F_{+1}^1|^2 \quad (6)$$

which, apart from some constants, requires the input of three quantities: $F_m^2 = |F_m|^2$, $\langle P \rangle$ and $|F_{-1}^1 - F_{+1}^1|^2$. Turning first to the mean polarization factor $\langle P \rangle$, we write

$$\begin{aligned} \langle P \rangle &= \langle |\hat{F}_m \cdot (\varepsilon' \times \varepsilon)|^2 \rangle \\ &\Rightarrow \frac{1}{2} \left[(\hat{F}_m \cdot \hat{q})^2 + \{\hat{F}_m \cdot (\hat{q} \times \hat{q}')\}^2 \right] (1 - P_3) \\ &\quad + \frac{1}{2} (\hat{F}_m \cdot \hat{q})^2 (1 + P_3) + (\hat{F}_m \cdot \hat{q}) \hat{F}_m \cdot (\hat{q} \times \hat{q}') P_1 \end{aligned} \quad (7)$$

where the two Stokes parameters $P_{1,3}$ completely describe linear polarization in the primary beam [19, 22]. Since $P_3 \simeq +1$ and $P_1 \simeq 0$,

$$\langle P \rangle = \langle |\hat{F}_m \cdot \hat{q}'|^2 \rangle. \quad (8)$$

That is, $\langle P \rangle$ is largest when the magnetic polarization is collinear with the *secondary* photon beam q' . (The scattering wave vector $k = q - q'$.) For diffraction from a random powder, the projection $(\hat{F}_m \cdot \hat{k})$ is fixed, and the mean polarization factor can be obtained by averaging over all crystallite orientations which satisfy the Bragg condition, with the result

$$\langle P \rangle = \frac{1}{2} \left\{ \cos^2(\theta/2) + (2 - 3 \cos^2(\theta/2)) |\hat{F}_m \cdot \hat{k}|^2 \right\}. \quad (9)$$

In order to calculate the magnetic structure and polarization factors for UO_2 , we have adopted the slightly simplified model of the magnetic structure illustrated in figure 1. In this picture, the moments are all collinear with the \hat{z} -axis and form alternating ferromagnetic sheets in the \hat{y} - \hat{z} -plane. Writing

$$k = \frac{2\pi}{a_0} (h\hat{x} + k\hat{y} + l\hat{z}) \quad (10)$$

where a_0 is the cell constant, the magnetic structure factors are

$$F_m = \hat{z}\{1 + (-1)^{k+l} - (-1)^{h+l} - (-1)^{h+k}\}. \quad (11)$$

All reflections from this collinear structure have $\hat{F}_m = \hat{z}$, and we can write

$$|\hat{F}_m \cdot \hat{k}|^2 = \frac{l^2}{h^2 + k^2 + l^2}. \quad (12)$$

Of the 24 positive and negative permutations of the indices (102), 16 give $F_m = 0$ and the remaining eight have $F_m = 4$, so we say that $F_m = 4$ with a multiplicity (of the *magnetic cell*) of 8. Turning to the polarization factor, half of the allowed magnetic reflections have $|\hat{F}_m \cdot \hat{k}|^2 = 0$ and the others have $|\hat{F}_m \cdot \hat{k}|^2 = 4/5$. The net polarization factor is then given by equation (9), averaging the values for the two projections, with the result $\langle P \rangle = 0.347$.

The remaining and most difficult part of the theoretical interpretation is to obtain a reliable estimate of the difference in resonant strengths $[F_{-1}^1 - F_{+1}^1]$. One can begin by estimating the *sum* of the resonant strengths since it is this combination which determines the (non-magnetic) scattering amplitude for a single ion:

$$f = -\left(\frac{3}{4\pi q}\right) (\epsilon' \cdot \epsilon) [F_{-1}^1 + F_{+1}^1] \quad (13)$$

which, in turn, is related to the total x-ray *attenuation* cross-section, σ , via the optical theorem

$$\sigma = \left(\frac{4\pi}{q}\right) \text{Im} f_0 = -\left(\frac{3}{q^2}\right) \text{Im}[F_{-1}^1 + F_{+1}^1] \quad (14)$$

where f_0 is the *forward* scattering amplitude ($\theta = 0$, $\epsilon' = \epsilon$).

From the literature [20], the 'white line' at the uranium M_4 edge, which corresponds to the same excitations ($3d_{3/2} \rightarrow 5f$) as the magnetic resonance has a cross-section of $\sigma \simeq 0.0037 \text{ \AA}^2$. Since at the centre of a simple resonance, the scattering amplitude is purely *imaginary*, one can readily equate the total resonant strength with the cross-section to obtain $[F_{-1}^1 + F_{+1}^1] \simeq -0.0044$.

Finally, the difference in resonance strengths $[F_{-1}^1 - F_{+1}^1]$ can be obtained with a knowledge of the total strength and the ratio $[F_{-1}^1 - F_{+1}^1]/[F_{-1}^1 + F_{+1}^1]$. This ratio is fundamental to magnetic circular dichroism studies, and determines the polarization dependence of an attenuation spectrum. We have adopted an atomic calculation [21] of the resonance ratio for the $5f^2$ ion in intermediate coupling which, after scaling with the ratio of the measured uranium moment in UO_2 to the calculated moment, gives $[F_{-1}^1 - F_{+1}^1]/[F_{-1}^1 + F_{+1}^1] \simeq 0.34$.

Combining all the of the above results leads finally to a predicted unit-cell magnetic scattering cross-section at resonance of $250r_e^2$, which, given the approximate nature of the calculation and the large uncertainty in the attenuation cross-section, is in remarkably good agreement with the measured value of $295r_e^2$.

The findings reported here, on a single, low-resolution magnetic diffraction peak with poor signal/background ratio, are not at present of sufficiently high quality to be useful in magnetism studies. However, this is the first experiment of its kind, and the data were obtained using an unfocused beam from a simple bending magnet source of a second-generation synchrotron (the SRS). Fluxes from undulator sources installed on third-generation machines, such at the ESRF, APS and SPRING-8, will be some three to five orders of magnitude higher. Gains of this magnitude can be used to make very significant improvements in wavevector resolution, perhaps by employing crystal analyser optics which could act simultaneously as an effective fluorescence filter. It seems likely that magnetic

x-ray powder diffraction, at least from actinide compounds, will soon become a valuable addition to the growing armoury of new techniques for magnetism research.

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