X-Ray Resonant Scattering Study of the Quadrupolar Order in UPd_3

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Quadrupolar ordering in a $5f$ electron system has been observed directly for the first time, using x-ray scattering techniques. In UPd_3 at low temperatures satellite peaks appear at $(1, 0, l)$ (orthorhombic notation) with l odd and even. Both sets of peaks show a resonant enhancement of the scattering at the M_{1V} edge of U. At resonance, the dominant scattering of the l odd peaks occurs in the unrotated polarization channel, whereas for l even a significant rotated component is found. These results are discussed in terms of possible structures of the antiferroquadrupolar phases.

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Phase transitions in the solid state often result from cooperative effects involving moments of the electronic distributions of the constituent atoms. The paramagnetic-magnetic transition, for example, arises from the exchange interaction between the magnetic moments proportional to $\langle J_z \rangle$, the expectation value of the electronic angular momentum operator. The potential importance of multipolar interactions in f-electron systems has long been recognized, and in materials for which $\langle J_z \rangle = 0$, phase transitions may be driven by multipolar moments, such as the quadrupole moment proportional to $\langle J_z^2 \rangle$. By analogy with magnetic systems, transitions involving quadrupolar order are classified as ferro or antiferro, according to whether the ordering wave vector is $q = 0$ or $q = \frac{1}{2}$, respectively. Since conventional scattering probes (neutrons, nonresonant x-ray scattering, etc.) do not couple to quadrupole moments, quadrupolar order can be revealed only indirectly (e.g., via accompanying lattice distortions, or by field-induced magnetic structures) by such methods. In contrast, resonant x-ray scattering techniques offer the possibility of studying directly ordered quadrupolar structures.

In this Letter we report on a study of the order parameter of the $5f$ U quadrupole moments in UPd_3 using x-ray resonant scattering. This is the first time that quadrupolar ordering has been directly observed by x-ray resonant scattering in a $5f$ system: it is related to recent resonant scattering studies of orbital ordering in the $3d$ oxides [1–9], and to studies of quadrupolar ordering in a $4f$ system [10,11]. These are all examples of resonant scattering from aspherical distributions of charge, known more generally as Templeton scattering [12]. In a resonant scattering experiment the photon energy is tuned close to an absorption edge so as to excite virtual electric multipole transitions between a core state and an intermediate state. Interesting effects occur in the solid state if the symmetry of the intermediate state is lowered and aligned by interactions (magnetic, chemical bonding, etc.). The scattering then becomes dependent on the polarization geometry, and the scattering length itself becomes a tensor. The intermediate state probed by the resonance should ideally be the same as the states which directly drive the order. This condition is not always satisfied in the $3d$ oxides, where the dominant dipolar transition at the K edge is to the $4p$ and not the $3d$ shell, and has generated a certain amount of debate [2,3,5,8,]. Similarly, experiments on quadrupolar order in a $4f$ system have relied mainly on investigating the induced order in the $5d$ bands. In our study these particular difficulties of interpretation are not present, as the ordering of the $5f$ electrons was studied directly using dipolar transitions at the M_{1V} (3.728 keV) edge which connect $3d_{3/2}$ to $5f$ states.

UPd_3 crystallizes in the double-hexagonal close-packed structure ($dhcp$) with U ions at sites with locally hexagonal and quasicubic symmetries (space group $P6_3/mmc$, lattice parameters $a = 5.73$ Å, $c = 9.66$ Å at room temperature). Inelastic neutron spectroscopy and magnetic susceptibility measurements indicate that the crystal field splitting of the $J = 4$ multiplet of the $5f^2$ configuration results in singlet ground states ($\langle J_z \rangle = 0$) at the two sites. For the quasicubic sites the first excited doublet is almost degenerate with the ground state. In consequence the susceptibility of the quasicubic sites is much greater, at low temperatures, than that of the hexagonal sites. Bulk measurements (heat capacity [13,14], thermal expansion [15,16], magnetic susceptibility [17], ultrasound [18,19]) have revealed three phase transitions at temperatures of $T_0 = 7.6$ K, $T_1 = 6.8$ K, and $T_2 = 4.4$ K. Polarized neutron diffraction studies have indicated that two distinct antiferroquadrupolar (AFQ) phases exist in the temperature intervals $T_1 \leq T \leq T_0$ and $T_2 \leq T \leq T_1$, and that below T_2 a very weak antiferromagnetic component coexists with a third AFQ phase [20,21].

Using the $dhcp$ unit cell, satellite reflections are observed in the neutron scattering experiments at $(\frac{1}{2}, 0, l =$ odd) below T_0, and additionally at $(\frac{1}{2}, 0, l =$ even) below T_1. In this paper, we will index our results using the orthorhombic unit cell shown in Fig. 1, which has

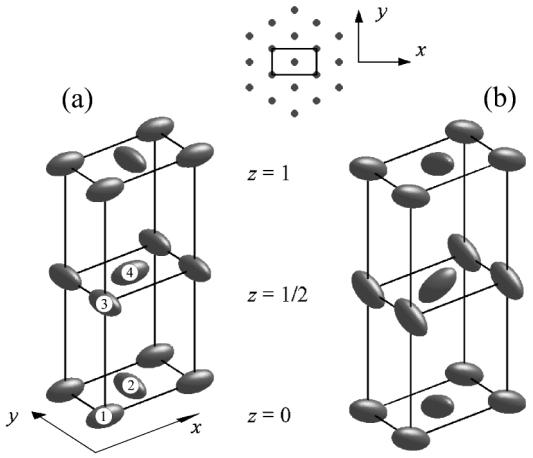

FIG. 1. The AFQ structures in UPd_3 shown in an orthorhombic unit cell. (a) The U $5f$ quadrupole moments on the quasicubic sites are represented as ellipsoids. Within one basal (x-y) plane there is a doubling of the unit cell along x. For the phase between $T_1 \leq T \leq T_0$ there is an antiphase stacking of quadrupole moments along z. (b) Possible structure of the AFQ phase below T_1, where the quadrupoles on sites 1(2) and 4(3) are rotated in antiphase around the $y(x)$ axis.

orthogonal axes with $a = \sqrt{3}\,a_{dhcp}$, $b = a_{dhcp}$, and $c = c_{dhcp}$. Analysis of the neutron data indicates that the ordered quadrupole moments are predominantly at the quasicubic sites. It is important to note that the neutron does not couple to the quadrupole moment directly, and the satellites observed in neutron scattering experiments arise from lattice distortions that accompany the quadrupolar order. Satellites at l = odd (l = even) correspond to antiphase (in-phase) stacking of scattering centers at the quasicubic sites along the c axis, the so-called cubic different (CD) and cubic same (CS) structures, respectively [21,22]. The proposed $Q^{\mathrm{CD}}_{x^2-y^2}$ arrangement of the AFQ moments on the quasicubic sites for $T_1 < T < T_0$ is shown schematically in Fig. 1a. Below T_1, a rotation and tilt of the quadrupoles, as shown schematically in Fig. 1b, are required to explain the results. A previous x-ray scattering experiment failed to observe any satellite reflections [23].

A single crystal of UPd_3 was grown by the Czochralski technique. From this ingot a thin disk of 5 mm diameter, 1 mm thick, was cut with the face perpendicular to the c axis. (Samples from this ingot were also used for the neutron scattering experiments.) The surface of the disk was polished using diamond paste down to 0.2 μm. The mosaic of the sample was 0.02° at an x-ray energy of 11.248 keV, and approximately 10 times larger at 3.728 keV, indicating some degree of remanent near-surface damage.

The x-ray scattering experiments were performed at the ID20 beam line, ESRF, Grenoble, France. The sample was placed in a helium flow cryostat, which required us to operate the diffractometer in the horizontal plane. In this configuration the incident beam was linearly polarized ($\geq$98%) in the scattering plane, which by convention is labeled π polarization. (Polarization perpendicular to the scattering plane is labeled σ.) The sample was mounted so that reflections of the type $(h, 0, l)$ could be accessed. When required, an Al(111) polarization analyzer was mounted on the 2θ arm of the diffractometer. By rotating the polarization analyzer around the scattered beam it was possible to measure either the unrotated (π-π) or rotated (π-σ) components of the scattering. Experiments were performed both on and off resonance. The resonant scattering experiments were performed for energies around the M_{IV} edge of U at 3.728 keV. Experience has shown that at this edge the resonant scattering cross section is dominated by electric dipole (virtual) transitions connecting $3d_{3/2}$ to $5f_{5/2}$ states. Off resonance an energy of 11.248 keV was selected to match the 90° scattering condition for the Al(333) reflection.

The sample was cooled to base temperature (~1.6 K) and a search was made for satellite reflections. With the diffractometer operated in a 2-axis mode, and the photon energy close to the M_{IV} edge of U, peaks were found at positions (1,0,3) and (1,0,4), indexed with respect to the orthorhombic unit cell of Fig. 1. These were the only satellite reflections accessible within the kinematical constraints at this energy. In Figs. 2a and 2b the energy dependencies are shown of the scattered intensity for the two satellite peaks. Both peaks display a clear resonance close to the M_{IV} edge. The resonant energies of the peaks were the same and equal to 3.725 keV, some 3 eV lower than the nominal position of the M_{IV} edge.

The temperature dependencies of the satellites at (1,0,3) and (1,0,4) were then investigated by performing rocking

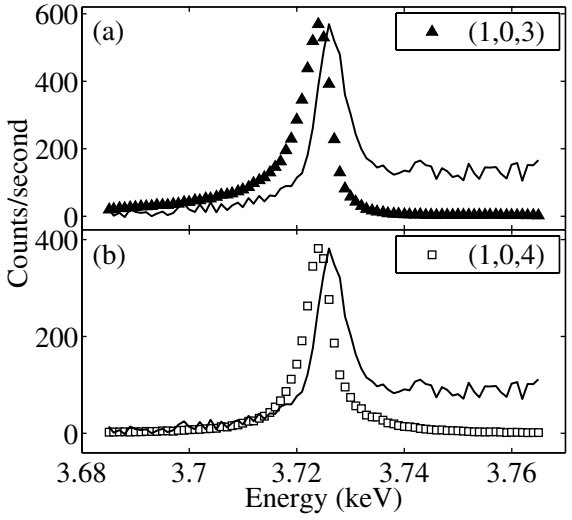

FIG. 2. Scans in 2-axis mode of the x-ray energy at (a) ▲ $(1, 0, 3)$ and (b) □ $(1, 0, 4)$ at 1.6 K. The fluorescence spectra are represented by the solid lines and have been scaled to the data.

curve scans, at the resonant energy, as the sample was cooled from 20 K to base temperature. In Fig. 3a the temperature dependencies of the intensities of the peaks are summarized. The scattering at (1,0,3) is clearly present at temperatures above T_0, with a width which reduces continuously until $\sim T_1$, as shown in Fig. 3b. This indicates the presence of strong dynamical fluctuations in the quadrupolar structure, which can be correlated with the broad anomalies observed around T_0 in the bulk properties of UPd_3. Our x-ray experiments have probed the structure on a time scale of 10^{-18} s, revealing fluctuations not seen on the 10^{-12} s time scale of the neutron scattering studies. At T_1 the (1,0,3) intensity increases abruptly, and the (1,0,4) reflection appears to exhibit a first-order transition with no critical scattering evident above T_1 in this case. At T_2 both reflections show a discontinuity in their intensities. From these results a picture emerges of distinct and potentially competing order parameters: critical fluctuations first build up at (1,0,3), but before long-range order is established, a first-order transition occurs at T_1 into a structure associated with (1,0,4).

The polarization dependence of the satellites was investigated by mounting the Al(111) polarization analyzer. Rocking curve scans at 1.6 K through the satellite peaks revealed that the (1,0,3) peak occurs predominantly in the unrotated (π-π) channel, whereas the (1,0,4) peak is found mainly in the rotated (π-σ) channel. The scattering intensities were then measured at selected temperatures, as summarized in Fig. 4. Particularly noticeable is the development of the (1,0,3) (π-σ) component in the temperature interval $T_2 < T < T_1$.

From the energy scans in Fig. 2 it is clear that the satellite intensities decreased rapidly as the energy was tuned away from the M_{IV} edge, and were in fact unobservable for energies more than 50 eV from the edge. However, by increasing the energy to 11.248 keV, thereby increasing the cryostat transmission from 2% to almost 100%, it was possible to detect nonresonant peaks at $(1, 0, l)$ with l odd and even, in the (π-π) channel only. These correspond to the peaks observed in neutron scattering experiments, and arise from a lattice distortion that accompanies the antiferroquadrupolar order.

We now turn to the interpretation and discussion of the resonant scattering. The observation of resonant satellite peaks at the M_{IV} edge of U establishes the fact that long-range order of the $5f$ electrons occurs in UPd_3. Ordering of the $5f$ magnetic moments is ruled out by neutron scattering experiments for $T > T_2$. An explanation, more consistent with the full weight of experimental data for UPd_3, is that we are probing the ordering of the quadrupolar moments of the $5f$ shell. However, to establish a direct connection between our results and the existence of antiferroquadrupolar order it is necessary to calculate the scattered intensities from a model of the AFQ structure.

For dipolar transitions the resonant scattering amplitude A can be written in the form

$$A \propto \epsilon'^{\alpha} C^{\alpha\beta} \epsilon^{\beta}, \qquad C^{\alpha\beta} = \sum_{\mathbf{r_j}} e^{i\mathbf{Q}\cdot\mathbf{r_j}} C_j^{\alpha\beta}, \qquad (1)$$

where the second-rank tensor $C_j^{\alpha\beta}$ represents the resonant scattering length of the jth atom; ϵ^{β} (ϵ'^{α}) is the polarization vector of the incident (scattered) photon [24,25]. Using the orthorhombic unit cell there are four U atoms on the quasicubic sites at positions (0,0,0), $(\frac{1}{2}, \frac{1}{2}, 0)$, $(0, 0, \frac{1}{2})$, and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. In the $(h, 0, l)$ scattering plane $C = C_1 +$

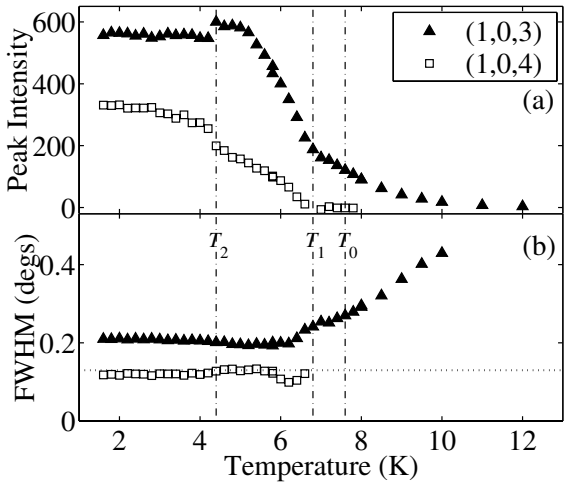

FIG. 3. (a) The peak intensity and (b) the peak full width at half maximum as a function of temperature. The horizontal line in (b) is the effective resolution of the instrument. The measurements were made in 2-axis mode at the resonant energy.

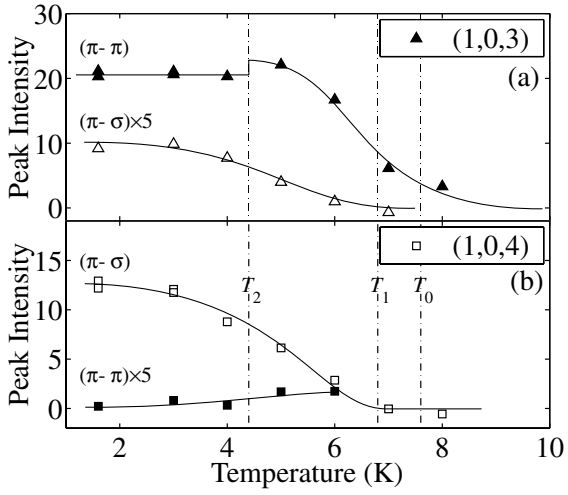

FIG. 4. Temperature dependence of the (a) (1,0,3) and (b) (1,0,4) peaks measured with the polarization analyzer at an energy of 3.725 keV. For each peak the unrotated (π-π) (filled symbols) and rotated (π-σ) (open symbols) components of the scattering were measured. The intensity of the weaker channel in each case has been corrected for feedthrough from the stronger channel, and for display has been multiplied by a factor of 5. Solid lines are guides for the eye.

$C_2 e^{i\pi h} + C_3 e^{i\pi l} + C_4 e^{i\pi(h+l)}$. For the $Q^{\mathrm{CD}}_{x^2-y^2}$ structure shown in Fig. 1a we have

$$C_1 = \begin{pmatrix} c_\parallel & 0 & 0 \\ 0 & c_\perp & 0 \\ 0 & 0 & c_\perp \end{pmatrix} \quad \text{and} \quad C_2 = \begin{pmatrix} c_\perp & 0 & 0 \\ 0 & c_\parallel & 0 \\ 0 & 0 & c_\perp \end{pmatrix},$$

with $C_3 = C_2$ and $C_4 = C_1$. Here $c_\parallel$ and $c_\perp$ refer to the major and minor axes of the ellipsoids. For reflections of type $(h, 0, l = \text{odd})$ the scattering amplitude is

$$C = C_1 - C_2 - C_3 + C_4 = \begin{pmatrix} 2(c_\parallel - c_\perp) & 0 & 0 \\ 0 & 2(c_\perp - c_\parallel) & 0 \\ 0 & 0 & 0 \end{pmatrix},$$

whereas for reflections of type $(h, 0, l = \text{even})$ $A = 0$. When the polarization vectors used in the experiment are included, and due consideration is made for the necessary coordinate transforms, we find that the scattering amplitude from the $Q^{\mathrm{CD}}_{x^2-y^2}$ structure is nonzero in the $(\pi\text{-}\pi)$ channel only. This is consistent with our observations of the (1,0,3) reflection for temperatures above T_1 [see Fig. 4(a)], and we conclude that the structure shown in Fig. 1a provides an adequate description of the data in this phase.

Below T_1 the (1,0,4) reflection appears mainly in the $(\pi\text{-}\sigma)$ channel. To understand the origin of this reflection a number of distortions to the orthorhombic $Q^{\mathrm{CD}}_{x^2-y^2}$ structure were considered. A necessary but not sufficient condition for producing a nonzero component in the $(\pi\text{-}\sigma)$ channel is that the scattering amplitude A has off-diagonal elements. These can be produced by allowing the ellipsoids to rotate away from the high-symmetry directions. It was found that scattering in the $(\pi\text{-}\sigma)$ channel at (1,0,4) is obtained by allowing the ellipsoids to rotate either around the x or the z axis (see Fig. 1), while for rotations around y the scattering is strictly confined to the $(\pi\text{-}\pi)$ channel.

Figure 4a shows that for the (1,0,3) reflection a significant $(\pi\text{-}\sigma)$ component also develops in the temperature interval $T_2 < T < T_1$. Our calculations reveal that an antiphase rotation of the charge densities on sites 1 and 4 around the y axis, together with an antiphase rotation of those on sites 2 and 3 around the x axis, as shown in Fig. 1b, leads to scattering in both the $(\pi\text{-}\pi)$ and $(\pi\text{-}\sigma)$ channels at (1,0,3), and in the $(\pi\text{-}\sigma)$ channel at (1,0,4). Scattering in the $(\pi\text{-}\sigma)$ channel at (1,0,4), but not at (1,0,3), may also arise from a rotation around the z axis of the charges on sites 1 and 2 in antiphase with those on sites 3 and 4. We have also calculated the scattering from the triple-**q** version of the $Q^{\mathrm{CD}}_{x^2-y^2}$ structure illustrated in Ref. [22]. This yields strong scattering in the $(\pi\text{-}\sigma)$ channel at (1,0,3), and the $(\pi\text{-}\pi)$ channel at (1,0,4), in contrast to our experimental results below T_1.

In conclusion, our resonant x-ray scattering experiments give direct evidence for antiferroquadrupolar ordering of the U ions in UPd_3, and provide new insight into the nature of the phase transitions in this compound. The structure in Fig. 1a explains our data between T_0 and T_1. At lower temperatures this structure is modified by rotations of the charge densities, as depicted in Fig. 1b. While it is possible to find AFQ structures which are consistent with our data, it is not yet possible to make an unambiguous identification of the structures below T_1 and T_2. This may become possible after the development of a diffractometer that allows azimuthal scans to be performed at low temperatures. Our calculations predict distinctly different variations of the scattered intensity as a function of the azimuthal angle for different modifications of the basic structure shown in Fig. 1a.

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