Triple-Q quadrupolar order in UPd_3

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Abstract. An analysis of new (presented below) and existing neutron diffraction experiments demonstrates that the ordered phase of UPd$_3$ which exists between 4.5 and 7 K is described by an order parameter of B$_{2g}$ symmetry, and that the ordered state is triple-Q with space group $P\bar{3}m1$. The order parameter describes an ordering of uranium ion quadrupoles and an associated ion displacement wave.

1. Introduction

The uranium ions in UPd$_3$, having unfilled 5f shells, will have fluctuating magnetic dipole, electric quadrupole and higher-order multipole moments. As the temperature is lowered in UPd$_3$, there are successive phase transitions at $T_1 \simeq 7$ K and $T_2 \simeq 4.5$ K. The phase existing between T_1 and T_2 is thought to be due to the ordering of uranium ion quadrupoles, but the details of this quadrupolar order have not yet been determined. In this article, we report the results of a neutron diffraction experiment, and through an analysis of this and other available diffraction data, determine the detailed nature of the quadrupolar ordering.

Heat capacity measurements [1] and thermal expansion measurements [2, 3] show phase transitions at T_1 and T_2. A study of the Bragg reflections using polarized neutrons [4] showed that there was no spin-flip scattering between T_1 and T_2, thus leading to the conclusion that in this temperature range quadrupolar ordering had occurred. Previous neutron scattering work has also studied in some detail the magnetic excitations [5, 6, 7, 8].

One reason for our interest in UPd$_3$ is the relative rarity of ionic quadrupolar ordering. A 1990 review [9] of quadrupolar interactions identified three cases of ferroquadrupolar order three cases of antiferroquadrupolar order, and noted UPd$_3$ as a transition of possibly quadrupolar origin; the possibility that quadrupolar order occurs in UPd$_3$ was first raised in [1] and reiterated in [5, 6] which reported that new Bragg peaks had been observed below 7 K. In UPd$_3$, the ordering involves both ion displacements and quadrupolar ordering, and it is through the contribution of the ion displacement modes to the nuclear Bragg scattering that the character of the quadrupolar ordering reveals itself.

Another point of interest is that the ordered state will be shown to be a triple-Q state (triple-Q is defined below). It can be somewhat difficult to distinguish experimentally between single-, double- and triple-Q states, but we show how this can be done in the present case through the study of the effects of a secondary order parameter. The possibility

that UPd$_3$ might exhibit a triple-Q phase has been raised previously [5] but no evidence for or against this suggestion has yet been published.

Finally, it should be noted that the Bragg reflections associated with the ordering are extremely weak (typically four orders of magnitude weaker than the crystallographic Bragg peaks), have been observed only with neutrons, and that long counting times are required. (A high-precision x-ray search, using a crystal from which Bragg reflections had been observed using neutrons, failed to see these reflections [10]). It is therefore important to make judicious use of symmetry arguments to ensure that the required definitive information can be obtained from measurements of a small number of Bragg reflections.

2. Quadrupolar order parameters

In UPd$_3$, the stacking sequence of the four atomic planes in the unit cell is ABA′C, as it is for the double-hexagonal close-packed structure. The positions of the uranium ions in the four layers are indicated by the open circles in the column labelled CS (or in any of the other columns) of figure 1. The space group of the high-temperature phase is $P6_3/mmc$.

A given uranium ion can have five linearly independent quadrupole moments which will be denoted by Q_{zz}, $Q_{x^2-y^2}$, Q_{xy}, Q_{yz} and Q_{zx}. The last four of these have zero average value in the high-temperature phase. The average value of the quadrupole moment Q_{zz} cannot serve as an order parameter because it is non-zero above the transition temperature. However, the deviation of Q_{zz} from its average value, δQ_{zz}, can contribute to the formation of an order parameter if it varies from ion to ion.

Diffraction experiments [4, 5] have shown that the ordering at 7 K is associated with a modulation of wavevector $\frac{1}{2}a^*$. Also, the phase transition at T_1 is continuous within the accuracy of experiments. Since the little cogroup of the wavevector $\frac{1}{2}a^*$ is D$_{2h}(mmm)$, the possible symmetries of the order parameters can be classified according to the irreducible representations of D$_{2h}$. Corresponding to each irreducible representation of D$_{2h}$ there will be a certain number of linearly independent quadrupolar symmetry modes of that symmetry. A complete set of linearly independent symmetry modes of the uranium ion quadrupole moments is described by figure 1 and table 1. It is convenient to describe only the ions within the orthorhombic unit cell shown in figure 1 since the periodic repetition of this cell gives the entire crystal. Since each uranium ion has five linearly independent quadrupole moments, and since there are four uranium ions in the high-temperature hexagonal unit cell, there are 20 linearly independent quadrupolar symmetry modes, in agreement with the number of symmetry modes listed in table 1.

3. Experimental results and analysis

Measurements were made on a 17g single crystal of UPd$_3$ using the TAS 7 spectrometer at Risø National Laboratory. The crystal was mounted with a real-space b axis vertical, so that the horizontal scattering plane contained the [$\bar{1}$ 2 0] and [0 0 1] directions in reciprocal space. Reflections at positions ($\frac{1}{2}$ 1 ℓ) where $\ell = 0$, 1, 2, 3, 4 were examined. By tilting the cryostat, the ($\frac{1}{2}$ 0 3) and ($\frac{1}{2}$ 0 4) reflections could be brought into the scattering plane. The intensities of the ($\frac{1}{2}$ 1 ℓ) reflections, studied for the first time, could thus be normalized to the intensities of ($\frac{1}{2}$ 0 ℓ) peaks measured previously. Figure 2 shows the measured intensity of the ($\frac{1}{2}$ 1 3) Bragg reflection as a function of temperature. The intensity observed above T_1 ~7.5 K was determined to be due to background scattering. Thus, although absent above T_1, the ($\frac{1}{2}$ 1 3) reflection is clearly present in the ordered
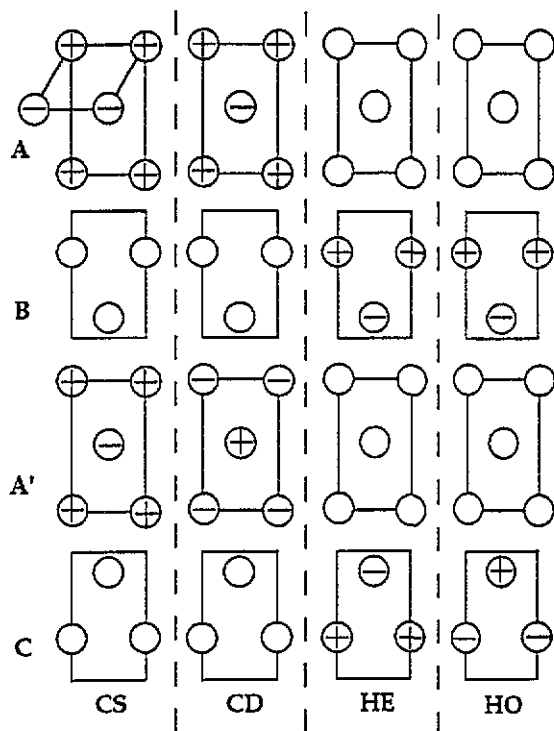
Figure 1. The quadrupolar symmetry modes. The four columns labelled CS (Cubic Same), CD (Cubic Different), HE (Hexagonal Even), and HO (Hexagonal Odd) represent four different configurations of uranium ion quadrupole moments. Each column shows the uranium ions (represented by open circles) in the four different layers (called A, B, A′ and C) of the unit cell of the single-Q quadrupolar phase. (At the top left the rhombic basal plane unit cell of the high-temperature phase is also shown). In the symmetry mode labelled Q_{xy}^{CD} in table 1, for example, the uranium ion circles containing + or − signs in column CD represent uranium ions with quadrupole moment Q_{xy} equal to $+\eta$ or $-\eta$, respectively, where η is a number. The other quadrupolar symmetry modes listed in table 1 are defined in an analogous way. Since each of the four above configurations can be applied to each of the five different quadrupole moments (Q_{xy}, Q_{xz}, etc.) a total of 20 symmetry modes is obtained. The column HO also describes the displacements of the uranium ions in a B_{2g} symmetry mode; there are no basal-plane displacements, and the displacements along the positive and negative c-axes (all of the same magnitude) are indicated by + and − signs, respectively.

phase between T_1 and T_2 (as well as below T_2). The ($\frac{\bar{1}}{2}$ 1 3) reflection is absent in the high-temperature phase as a result of the existence of the $\{\sigma|\frac{1}{2}c\}$ glide plane (where σ is a reflection in a plane normal to $a_1{}^*$). Since this glide plane is preserved in the cases where the order parameter has A_g, B_{1g}, B_{2u} or B_{3u} symmetry, the observation of the ($\frac{\bar{1}}{2}$ 1 3) reflection below T_1 excludes these four symmetries as possibilities for the order parameter.

To proceed further with the analysis, note that for each order parameter symmetry listed in table 1, a set of parametrized ion-displacement symmetry modes can be found by standard group theory methods. As an example, the uranium ion displacements in a B_{2g} mode are shown in figure 1. Neglecting Debye–Waller factors, the intensity of the Bragg reflection at wave vector K is proportional to $|F(K)|^2$ where $F(K) = \sum f_i \exp[iK \cdot (R_i + u_i)]$, R_i is the high-temperature (above T_1) position of ion i, u_i is the displacement of ion i for the

Table 1. Classification of the uranium ion quadrupolar symmetry modes defined in figure 1 and its caption according to their symmetry.

Irreducible representation	Quadrupolar symmetry modes
A_g	$\delta Q_{zz}^{HE}, Q_{x^2-y^2}^{HE}, \delta Q_{zz}^{CS}, Q_{zx}^{CD}, Q_{x^2-y^2}^{CS}$
B_{1g}	$Q_{zy}^{HE}, Q_{xy}^{CD}, Q_{zy}^{CS}$
B_{2g}	$Q_{zx}^{HE}, \delta Q_{zz}^{CD}, Q_{x^2-y^2}^{CD}, Q_{zx}^{CS}$
B_{3g}	$Q_{xy}^{HE}, Q_{zy}^{CD}, Q_{xy}^{CS}$
A_u	Q_{zy}^{HO}
B_{1u}	$\delta Q_{zz}^{HO}, Q_{x^2-y^2}^{HO}$
B_{2u}	Q_{xy}^{HO}
B_{3u}	Q_{zx}^{HO}
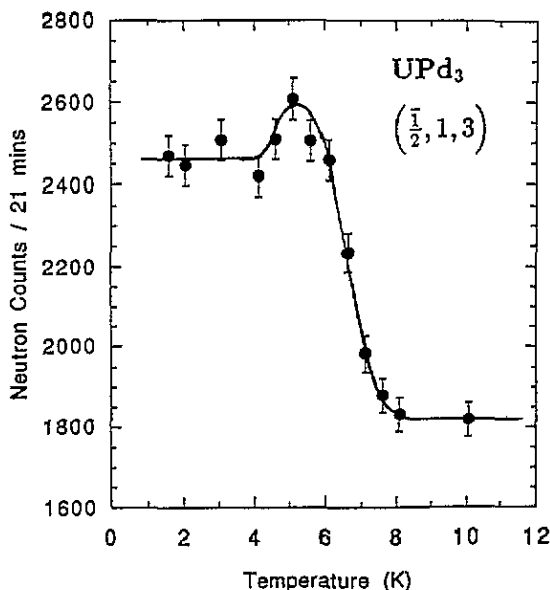
Figure 2. The *intensity of the* $(\bar{\tfrac{1}{2}}\ 1\ 3)$ *reflection as a function of temperature. The counting time was 21 minutes per point.*

symmetry mode in question, the sum is over the ions in an appropriate unit cell and f_i is the average scattering length for U or Pd as appropriate.

For both the A_u and the B_{3g} modes, the structure factor $F(K)$ is zero at $K = (\tfrac{1}{2}\ 0\ \ell)$. (This is because, for these wavevectors, $K \cdot u$ is zero for the U ions, and the sum of the contributions from the Pd ions cancels to zero.) Since the $(\tfrac{1}{2}\ 0\ 3)$ and $(\tfrac{1}{2}\ 0\ 4)$ reflections are relatively strong reflections [4], A_u and B_{3g} can be excluded as possible order parameter symmetries.

For the B_{2g} mode, $F(K)$ calculated to first order in the displacements u_i for the $(\tfrac{1}{2}\ 0\ 2\ell)$ series of reflections has the parametrized form

$$F_{B_{2g}}(\tfrac{1}{2}\ 0\ 2\ell) = C\ell\left[1 + a\cos(1/6\pi + \ell\pi) + b\cos(1/3\pi - \ell\pi)\right].$$

The analogous expression for the B_{1u} mode is

$$F_{B_{1u}} \left(\tfrac{1}{2} \ 0 \ 2\ell \right) = C' \left[1 + a' \sin \left(1/6\pi + \ell\pi \right) + b' \sin \left(1/3\pi - \ell\pi \right) \right] .$$

The measured intensity of the $(\tfrac{1}{2} \ 0 \ 0)$ reflection is about six times smaller than that of the $(\tfrac{1}{2} \ 0 \ 4)$ reflection at 6 K (i.e. in the quadrupolar phase) — see [4]. This result can not possibly be accounted for by an order parameter of B_{1u} symmetry for which these two reflections have equal calculated intensities (note that $F_{B_{1u}}(\tfrac{1}{2} \ 0 \ 2\ell) = F_{B_{1u}}(\tfrac{1}{2} \ 0 \ 2\ell + 4)$); when Debye–Waller factors are included, the discrepancy will be even worse. For the B_{2g} mode, however, the calculated intensity, being proportional to ℓ^2, does give a $(\tfrac{1}{2} \ 0 \ 0)$ reflection which is much weaker (in fact of zero intensity) than the $(\tfrac{1}{2} \ 0 \ 4)$ reflection. The remaining puzzle now is why there is any observed intensity at all in the $(\tfrac{1}{2} \ 0 \ 0)$ reflection. We will explain this remaining weak $(\tfrac{1}{2} \ 0 \ 0)$ scattering through the presence of a secondary order parameter. (Finally, for completeness, we note that the B_{2g} mode also gives Bragg scattering at the $(\tfrac{1}{2} \ 0 \ 2\ell + 1)$ positions, which is consistent with the experimental observations.)

4. Landau theory

Let Q_1, Q_2 and Q_3 be three wavevectors lying in the basal plane, with $Q_1 = \tfrac{1}{2}a^*$, and with Q_2 and Q_3 being the result of rotating Q_1 by $2\pi/3$ and by $4\pi/3$ about the c axis, respectively. We take η_1, η_2 and η_3 to be the amplitudes of the B_{2g} order parameters associated with these three wavevectors (this order parameter will be a combination of ordered quadrupolar moments and ion displacement modes). The appropriate Landau free energy for this problem has the form

$$F = A \sum_i \eta_i^2 + B \left(\sum_i \eta_i^2 \right)^2 + C \sum_{i \neq j} \eta_i^2 \eta_j^2 .$$

Here $A = \alpha(T - T_1)$, giving a phase transition to an ordered phase at $T = T_1$. Also, for $C > 0$, the phase transition will be to a single-Q phase with only one of the η_i not equal to zero. For $C < 0$, the ordered phase will be a triple-Q phase with all η_i having the same magnitude. (Terms of the form $\eta_1 \eta_2 \eta_3$ are excluded from the free energy by symmetry requirements.) The triple-Q phase has the space group $P\bar{3}m1$.

Since distortions of B_{2g} symmetry cannot account for the weak Bragg scattering at $(\tfrac{1}{2} \ 0 \ 0)$, we look for a secondary order parameter which can do so. Distortions of A_g symmetry associated with wavevectors Q_1, Q_2 and Q_3 (their amplitudes are defined to be ξ_1, ξ_2 and ξ_3) are the sought after distortions. These A_g distortions contribute additional terms to the free energy of the form

$$F' = A' \sum_i \xi_i^2 + D[\eta_1 \eta_2 \xi_3 + \eta_1 \xi_2 \eta_3 + \xi_1 \eta_2 \eta_3] .$$

Clearly, distortions of A_g symmetry (non-zero ξ_i) will be induced only in the triple-Q state (where $\xi_3 = -[D/(2A')]\eta_1 \eta_2$, etc.) and not in the single-Q state. Bragg scattering at $(\tfrac{1}{2} \ 0 \ 0)$ is allowed for distortions of A_g symmetry.

In principle, the intensities of the scattering from the primary order parameter B_{2g} and from the secondary order parameter A_g should be characterized by different critical exponents. Unfortunately, due to the extreme weakness of the Bragg reflections due to

the lattice distortions, the quality of the diffraction data obtained up to the present is not sufficiently high to allow us to obtain, even roughly, these critical exponents.

It is true that terms of the form $E\eta_1^2\xi_1^2$ can also be added to F', giving a contribution to F' which is quadratic in ξ_1 of the form $F' = (A' + E\eta_1^2)\xi_1^2 + \ldots$; for $E < 0$, such terms could cause the appearance of a non-zero A_g distortion in the single-Q phase with $\eta_1 \neq 0$, but only at a temperature below T_c where $A' + E\eta_1^2$ becomes < 0. ($A' > 0$ is necessary because ξ_l is the secondary order parameter.) An examination of the neutron scattering data [4] reveals that non-zero $(\frac{1}{2} \, 0 \, \ell)$ reflections appear at the same temperature for $\ell = 0, 3$ and 4, which can only be consistent with the triple-Q possibility. A pictorial
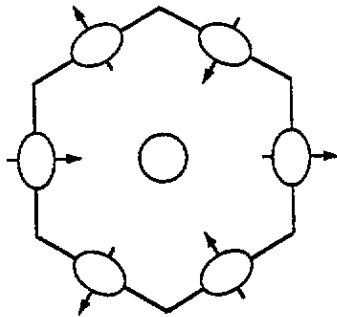

Figure 3. Partial pictorial description of the quadrupolar order. The circle and the ellipses represent the uranium ions at the cubic A-layer sites (see figure 1) of the Wigner–Seitz unit cell of the ordered phase. In the high-temperature phase (above T_1) the uranium ions will have non-zero quadrupole moments Q_{zz} corresponding to the uranium ions having a spheroidal charge distribution with the c axis being the axis of revolution. The $Q_{x^2-y^2}^{CD}$ contribution to the order parameter results in the charge distribution of an ion no longer being spheroidal, but acquiring the symmetry of an ellipsoid with its three principal axes having unequal lengths; the ellipses indicate the relative orientations of these ellipsoids (one principal axis remains normal to the basal plane) for the different uranium ions in the A-layer unit cell (the central ion remains spheroidal). The effect of the Q_{zx}^{CS} contribution to the order parameter can be visualized by imagining that the ellipsoidal charge distribution for each ion is rotated by a small angle in the positive direction about an appropriate rotation axis; this rotation axis lies in the basal plane and is indicated for each ion by a straight line with an arrow attached to give the sense of the axis; the central ion is not rotated.

representation of the quadrupolar order at the cubic A-layer sites in the triple-Q state is shown in figure 3. According to table 1, there are three linearly independent B_{2g} modes which contribute to the cubic site A-layer quadrupolar order, namely the δQ_{zz}^{CD}, the $Q_{x^2-y^2}^{CD}$ and the Q_{zx}^{CS} symmetry modes. In the high-temperature phase (above T_1), all of the cubic site uranium ions have identical spheroidal charge distributions characterized by the quadrupole moment Q_{zz} (which is the only non-zero component of the quadrupole moment tensor). Below T_1, the presence of the triple-Q δQ_{zz}^{CD} modes can be shown to result in additional contributions to the Q_{zz} moments of the cubic site ions such that, if the central ion of the unit cell (see figure 3) has an additional Q_{zz} moment of q, then the ions on the edges of the unit cell will have additional Q_{zz} moments of $-1/3q$. The qualitative features of the $Q_{x^2-y^2}^{CD}$ and the Q_{zx}^{CS} contributions to the order in the triple-Q state are described in figure 3. This picture of the quadrupolar order is consistent with the $P\bar{3}m1$ space group symmetry which we have determined for the quadrupolar phase. Similar descriptions of the order in the other layers can be found by combining the information in table 1 with the results of the Landau theory sketched above.

From figure 3, it is clear that the unit cell of the quadrupolar phase is four times as large as the unit cell of the high-temperature phase. Note that there are four possible ways of centering the unit cell on different uranium atoms. Also, corresponding to each of these possibilities, there are two ways of orienting the rotation axes, one corresponding to figure 3, and the other in which the sense of each rotation axis is reversed. Thus, in total, the quadrupolar phase will have eight distinct domains.

5. Conclusion

This article has identified the symmetry of the order parameter (which has a mixed quadrupole moment and ion displacement character) as B_{2g}. The specific quadrupole moments participating in the transition are thus known from table 1, and this should stimulate work on microscopic models to further elucidate the microscopic forces driving the transition (e.g. are these quadrupole-quadrupole type interactions or are they more closely related to the forces involved in ordinary structural phase changes). Also, the ordered phase has been identified as triple-Q as a result of a study of the effects of a secondary order parameter, and the space group of this phase has been established as $P\bar{3}m1$.

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       (We make use of peak intensities of Bragg reflections taken from the figures of this article. The relative peak intensities are proportional to the relative integrated intensities to within about 20%. Due to the extreme weakness of the reflections, more accurate measurements of the integrated intensities would be very time-consuming.)
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