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A new model for the crystal field and the quadrupolar phase transitions of UPd_3

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Abstract

The double-hexagonal close-packed localized moment 5f system UPd_3 exhibits four phase transitions below 8 K. We present new measurements of the magnetic susceptibility of UPd_3 single crystals. The phase transitions are attributed to a sequence of antiferroquadrupolar ordered structures of the U 5f electrons on the quasi-cubic sites.

From a comprehensive analysis of the neutron scattering, x-ray scattering, and bulk property measurements of this system, we have deduced a new crystal field model for UPd_3. This model, which has a doublet ground state on the quasi-cubic sites with a first excited singlet some 4 meV above it, provides a qualitative understanding of the succession of quadrupolar phase transitions and order parameters of UPd_3. Moreover, the new model also explains the excitations observed, by inelastic neutron scattering, in UPd_3 at 2 K.

1. Introduction

UPd_3 is a particularly interesting system because it is one of the small number of metallic materials that exhibit long-range quadrupolar ordering. In fact it has no fewer than four phase transitions associated with different quadrupolar order parameters. These have been seen clearly by neutron scattering [1–4], x-ray scattering [5], and ultrasonic techniques [6] as well as by measurements of the heat capacity [7, 8], the magnetic susceptibility [8, 9], and the magnetostriction [10] of single crystals. The uranium 5f electrons are well localized, with the $5f^2$ configuration. Hund's rules lead to the $^3H_4$ ground state multiplet ($S = 1$, $L = 5$, $J = 4$). The large orbital moment gives rise to a strong coupling to the lattice and hence it is not surprising that this is a system in which quadrupolar effects are dominant.

UPd_3 exhibits the double-hexagonal close-packed crystal structure, with the uranium ions at sites of local hexagonal and local quasi-cubic symmetry: it has a non-ideal c/a ratio of 1.671.

The measurements referred to above reveal that phase transitions occur at $T_0 = 7.8$ K, $T_{+1} = 6.9$ K, $T_{-1} = 6.7$ K, and $T_2 = 4.4$ K. Neutron diffraction [2–4] and resonant x-ray scattering studies [5] indicate that the phase transition at T_0 is to an antiferroquadrupolar (AFQ) structure of the U 5f electrons that is accompanied by periodic lattice distortions and a doubling of the crystallographic unit cell. The unit cell in the phase below T_0 is orthorhombic, with the ordered quadrupole moments predominantly on the quasi-cubic sites, and stacked in antiphase along the c-axis. X-ray and neutron scattering results for the phases below $T_{\pm 1}$ are consistent only with a rotation and tilt of these quadrupole moments. It is not until the transition at T_2 that a weak antiferromagnetic (AFM) ordering develops, accompanied by changes in the AFQ order parameter. The AFM moments in this phase are only of the order of $\sim 10^{-2}\ \mu_B$/U atom.

The probable quadrupolar order parameters and symmetry changes for each of the four transitions have been deduced from ultrasound measurements [6], and resonant x-ray scattering [5] and neutron diffraction studies [2–4] together with group theoretical arguments [3]. From these we believe that the transition at 7.8 K is second order with probable primary order parameter $\langle Q_{x^2-y^2} \rangle$. The transition at 6.9 K is also second order, and the remaining transitions are first order, with possible order parameters $\langle Q_{zx} \rangle$ and $\langle Q_{yz} \rangle$. We believe that, in the phase below 6.9 K, only $\langle Q_{x^2-y^2} \rangle$ and $\langle Q_{yz} \rangle$ are non-zero. The system then undergoes a strongly first-order transition, at 6.7 K, to a phase in which $\langle Q_{x^2-y^2} \rangle$, $\langle Q_{zx} \rangle$, and $\langle Q_{yz} \rangle$ are all non-zero. In the final phase below 4.4 K, it appears that $\langle Q_{yz} \rangle$ vanishes again, and the transition is accompanied by the development of a small magnetic moment.

In this paper, we present a comprehensive study of the magnetic properties of UPd_3. We have made detailed measurements of the DC magnetic susceptibility from room temperature down to 0.4 K along the three main crystallographic axes. We also present magnetization measurements in fields up to 12 T. From the anomalies in the susceptibility and magnetization at the various transition temperatures, we have mapped out (B, T) phase diagrams up to $B = 12$ T and down to $T = 0.4$ K for the a-, b-, and c-axes.

We will show that it is possible to understand the physics of the phase transitions within a three-level approximation based on the quasi-cubic site energy eigenstates, the lowest two levels of which are degenerate in the high-temperature (above 7.8 K) phase. In what follows we deduce the crystal field states from the high-temperature data and explain how the phase transitions arise.

2. Experimental details and results

Three single crystals of UPd_3, aligned along the principal crystallographic directions were cut from larger single crystals previously used for the neutron scattering experiments: an a-axis crystal of 1.0923 g, a b-axis crystal of 0.1964 g, and a c-axis crystal of 0.7354 g. The main crystals were grown, at the University of Birmingham, using the Czochralski method with starting materials of 3N U and 4N Pd.

Magnetization and susceptibility measurements were made using a vibrating sample magnetometer (VSM) equipped with a top-loading ^{3}He cryostat, constructed by Oxford Instruments plc. Measurements were made in the temperature range 0.4–80 K and for fields up to 12 T. The cryostat is operated with the sample immersed in liquid ^{3}He for $T < 1.5$ K. For $T > 1.5$ K, the sample is cooled using ^{3}He as an exchange gas with the 1 K ^{4}He bath providing the heat sink. Further measurements at temperatures from 2 to 300 K were made using a SQUID magnetometer (MPMS7, Quantum Design) equipped with a 7 T magnet. The background signals from the sample holders were measured and found to be negligibly low in comparison with that of the sample, in each case. Figure 1 shows the results for the inverse

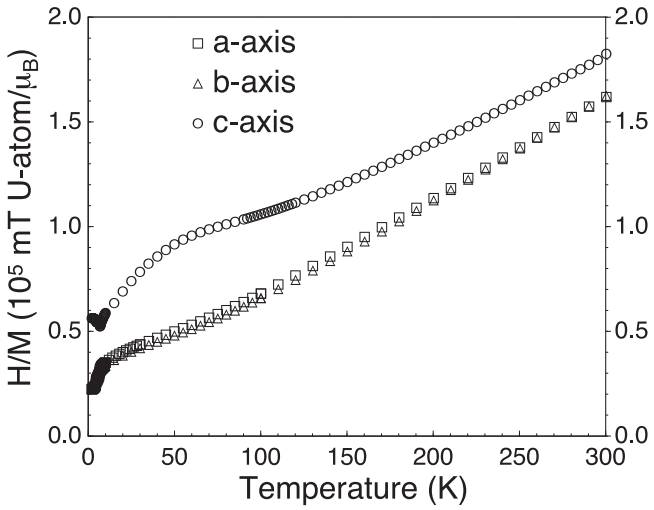

Figure 1. Inverse magnetic susceptibility of UPd_3, measured along the principal crystallographic axes.

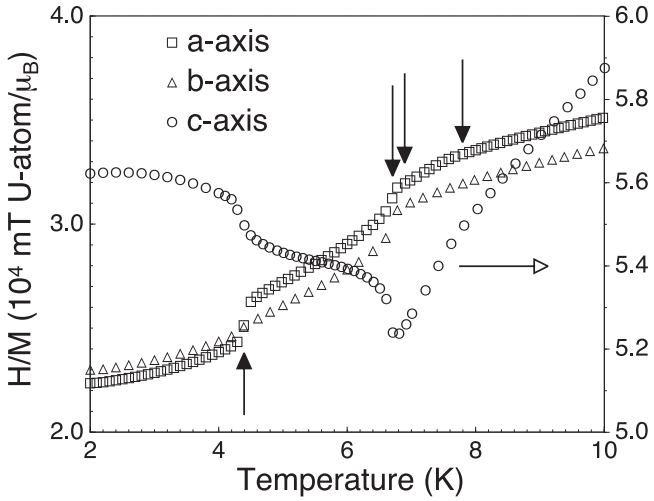

Figure 2. Inverse magnetic susceptibility of UPd_3, for temperatures between 2 and 10 K. The vertical arrows indicate the transition temperatures.

susceptibility of UPd_3 along the *a*-, *b*-, and *c*-axes, up to 300 K. Figure 2 shows the results below 10 K in detail, revealing anomalies at the phase transitions.

3. The anomalies at the phase transitions

The experimental features characterizing the phase transitions, obtained from a wide range of measurement techniques, are summarized in table 1. The first phase transition at $T_0 = 7.8$ K is very unusual. It shows up clearly in the ultrasonic data [6], and the x-ray scattering results [5] show the development of an AFQ phase corresponding to an ordering of $Q_{x^2-y^2}$ with wavevector $q = [100]$. Note that we will refer to the orthorhombic unit cell of the

Table 1. Summary of experimental findings.

	$T_2 = 4.4 \pm 0.1$ K	$T_{-1} = 6.7 \pm 0.05$ K	$T_{+1} = 6.9 \pm 0.05$ K	$T_0 = 7.8 \pm 0.1$ K
Ultrasound	Pronounced softening in C_{44} and C_{66}, softening in C_{33}, with large anomalies in α_{33} and α_{44}.	Softening in C_{66}, small dip in C_{44}. Small peaks in α_{33} and α_{44}. Hysteresis in C_{33} and C_{44}.	No softening in C_{33} on cooling, step increase with small peak in α_{33}. No softening in C_{44}, small α_{44} peak. No hysteresis in C_{33} and C_{44}.	Very large softening in C_{66}. Softening in C_{33} with small peak in α_{33}. No softening in C_{44}.
$\Delta\alpha_{33}$ (cm^{-1})	0.4	0.01	0.005	0.04
$\Delta\alpha_{44}$ (cm^{-1})	1	0.04	0.01	None
ΔC_{33} (GPa)	−1	+1.5	None	−2
ΔC_{44} (GPa)	−2	−0.6	None	None
ΔC_{66} (GPa)	−4	−4	−3	−21
Transition	Monoclinic (magnetic) ← trigonal triple q (g'_{44} negative ⇒ AFQ ordering) First order	Trigonal triple-q ← monoclinic First order	Monoclinic ← orthorhombic Second order	Orthorhombic ← hexagonal Second order
Order parameters	$\langle Q_{x^2-y^2}\rangle$, $\langle Q_{zx}\rangle$	$\langle Q_{x^2-y^2}\rangle$, $\langle Q_{yz}\rangle$, $\langle Q_{zx}\rangle$	$\langle Q_{x^2-y^2}\rangle$, $\langle Q_{yz}\rangle$	$\langle Q_{x^2-y^2}\rangle$
Specific heat	Peak exists but difficult to see—applied field kills it.		Peak	Broad peak—applied field enhances it.
Magnetic susceptibility	Peak		Peak	

Table 1. (Continued.)

Neutron scattering/ sound velocity		AFQ ordering on quasi-cubic U sites	
Inelastic neutron scattering, low energy	At 1.7 K, four peaks at 1.30, 1.67, 2.20, and and 2.62 meV. At 3.5 K, 1.67 meV peak decreases, others unchanged.	At 5 K, modes move closer together and decrease in intensity. Four peaks at 1.41, 1.77, 2.15, and 2.56 meV. At 6.20 K, excitation very damped, not possible to observe modes directly. At 7.10 K, no excitations distinguishable but scattering much greater than background $\Rightarrow$ at least one very damped mode.	At 9.9 K, similar to 6.2 K and below, not possible to distinguish different excitations.
Inelastic neutron scattering, higher energy	Data at 2 and 10 K. Four modes at $\sim$4, 8, 14, and 16 meV. 14 and 16 meV modes interact and exchange intensity. Fifth mode apparent at $\sim$20 meV only when $\boldsymbol{Q}$ lies in the basal plane. Intensity of all modes decreases at higher temperature $\Rightarrow$ crystal field excitations with depopulation of ground state. All transitions transverse, except $\sim$20 meV longitudinal.		

Table 1. (Continued.)

	$T_2 = 4.4$ K	$T_{-1} = 6.8$ K	$T_0 = 7.8$ K
Neutron diffraction, unpolarized neutrons in 4 T	(1, 0, 2) peak drops sharply.	(1, 0, 2) peak develops. Small anomaly in (1, 0, 1) peak	← (1, 0, 1) scattering develops.
Neutron diffraction, polarized (a-axis) neutrons in 4.6 T	Moments on both sites ∼0.06 μ_B at 120 K. Hexagonal sites decrease very little to ∼0.05 μ_B at 0 K. Cubic sites increase. For $T < 20$ K, $\chi_{cubic} \gg \chi_{hex}$.		
	(1, 0, 2) scattering predominantly SF + field-induced reflection at (1, 0, 0) ⇒ antiferromagnetic, moments along z (c-axis).	For $T_1 < T < T_0$, (1, 0, 1) scattering entirely NSF ⇒ arising from structural components and from magnetic moments parallel to a-axis. Intensity ≫ in zero field ⇒ ferrimagnetic structure, moments parallel to field direction.	
	Q_{zy} (CS), Q_{zy} (HE).	$Q_{x^2-y^2}$ (CD).	
X-ray resonant scattering	Peaks at (1, 0, 3) and (1, 0, 4) in (π–σ) continue to increase somewhat, peak at (1, 0, 3) in (π–π) constant below T_2. At T_2, intensity of peaks may change discontinuously.	Peak develops at (1, 0, 4), predominantly in (π–σ) channel, peak at (1, 0, 3) increases strongly in (π–π), much smaller peak at (1, 0, 3) in (π–σ) also develops and increases.	Peak develops above T_0 at (1, 0, 3) in (π–π) only and increases strongly. No peak at (1, 0, 4).
Entropy (integrated specific heat)	No change at T_2. Smooth decrease to zero at 0 K.	Large drop at T_1.	Decreases smoothly with depopulation, slight anomaly at ∼8.1 K. No change at T_0.

AFQ ordered phase, introduced in [5]. However there is hardly any discernible effect on the specific heat (or entropy) at T_0. Similarly there is only a very small change in the magnetic susceptibilities as shown in figure 1.

There is no evidence that the transition at T_0 is not second order. These observations are consistent with the three-level scheme for the low-lying crystal field levels that we propose in section 3 only if the off-diagonal term for the operator corresponding to $Q_{x^2-y^2}$ is very small indeed.

The two transitions at $T_{\pm 1}$ are extremely close to each other. They were first distinguished separately in the ultrasound study [6], and can just about be deduced from the later x-ray data [5]. The main entropy changes occur at these transitions. There are sharp changes in the susceptibilities at T_{-1} and T_2. For further details, refer to table 1.

3.1. The crystal field states in the high-temperature phase

Early neutron scattering investigations by Buyers and co-workers [1] revealed well-defined crystal field excitations in UPd_3, demonstrating that the 5f electrons are localized in this compound. The strong mode observed at around 15 meV was attributed to the hexagonal sites, with a $J_z = |0\rangle$ ground state and $J_z = |\pm 1\rangle$ excited doublet. This interpretation is supported by the subsequent polarized neutron diffraction measurements of the separate susceptibilities of the two sites [4]. For the hexagonal sites at low temperatures, χ_z tends to zero, whilst the basal plane susceptibility becomes temperature independent. The crystal field splitting is far too big for the hexagonal sites to play any role in the phase transitions and so this paper will focus on the quasi-cubic sites. We will now consider how the crystal field states at the cubic sites may be deduced from a study of the entropy, susceptibility χ_z, and the neutron scattering results.

The magnetic contribution to the entropy up to $T = 30$ K has been deduced from the available specific heat measurements [7]. In the phase above T_0, it is not compatible with a singlet ground state on both sublattices. However, the entropy above the first phase transition is well described by a doublet ground state on one sublattice and a singlet ground state on the other sublattice, provided that the excited singlet state on the first sublattice is at a much lower energy than the excited states of the second sublattice. In other words, we deduce that the ground state on the hexagonal sites is indeed a singlet, but that the ground state on the quasi-cubic sites is a doublet. Inelastic neutron scattering measurements above T_0 show an excitation at $\sim$4 meV which we attribute to the quasi-cubic sites.

Above T_0, χ_z follows a clear Curie–Weiss behaviour as shown in figure 2. Since χ_z for the hexagonal sites is zero when the excited doublet is not occupied (i.e. for $T \ll 160$ K), the measured χ_z at these temperatures is entirely due to the quasi-cubic sites. The value of the Curie–Weiss constant, θ, is -50.7 K. It is interesting that this is comparable with the value of the exchange deduced by Murray and Buyers from the dispersion in their neutron scattering data.

Taken together, the entropy and χ_z are clear evidence that the crystal field state ground state in the high-temperature phase is a doublet on the cubic sites. The wavefunctions for the ground doublet and first excited singlet were estimated by considering the lack of entropy change at the first phase transition, together with the values of J_z (=1.6) and J_x (=0.9) deduced from the magnetic susceptibilities in the high-temperature phase. The allowable symmetries of the wavefunctions are discussed in section 4.

The expressions that we give in figure 3 are possible wavefunctions but there are certainly others that would fit the data as well. Since the crystal field Hamiltonian for the quasi-cubic sites contains six independent parameters and has nine basis states, it was not possible to use these wavefunctions to deduce the values of the crystal field parameters.

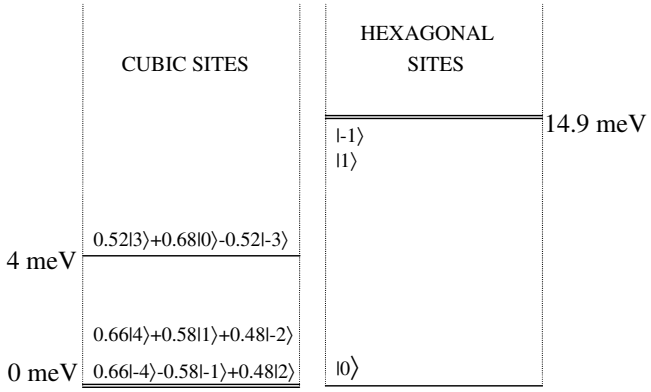

Figure 3. The low-lying levels of the new crystal field level scheme for UPd_3 proposed in this paper.

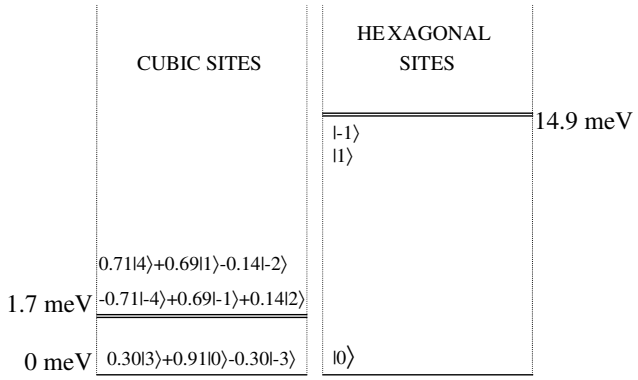

Figure 4. The low-lying levels of the crystal field level scheme for UPd_3 proposed by Buyers *et al* [1].

Our new level scheme differs from that of Murray and Buyers, shown in figure 4, who used their crystal field fit from the hexagonal sites to estimate the crystal field splitting on the cubic sites. This led them to believe that there was also a singlet ground state on the cubic sites. They regarded this as very satisfactory because it immediately explained why UPd_3 does not order magnetically.

Since we have clear evidence for a magnetic doublet on the cubic sites albeit with a rather small J_z-value, but a sizable Curie–Weiss temperature, magnetic ordering would indeed be possible. However, the hexagonal crystal structure will frustrate simple antiferromagnetism and so reduce any transition temperature to well below $|\theta|$. The quadrupolar interactions are strong and so the reason that there is no magnetic ordering seems to be that the quadrupolar transitions occur first.

From the matrix elements J_x connecting our crystal field wavefunctions, we would expect the magnetic susceptibility χ_x for the quasi-cubic sites to be entirely Van Vleck in form. In fact, the experimental data show that it increases with every phase transition. We believe that this behaviour can be explained by the effects of the quadrupolar order parameters, since at every phase transition more of the singlet is mixed into the former doublet states, pushing up the value of J_x each time. We also expect a large, but temperature-independent contribution to χ_x from the hexagonal sites.

4. What is special about a three-level system?

We believe that the physics of the phase transitions arises from the special nature of this three-level system. Our model for the transitions is based on the quasi-cubic site energy eigenstates, the lowest two levels of which are degenerate in the high-temperature (above 7.8 K) phase. We consider the effect of each of the four quadrupolar and three magnetic operators on this system.

Since the total angular momentum, J, is a good quantum number, the wavefunctions are expressed in the $|J_z\rangle$ basis, within a manifold of constant J. Inspection of the crystal field Hamiltonian for the quasi-cubic sites reveals that doublet states always have the form

$$|d_1\rangle = a|4\rangle + b|1\rangle + c|{-2}\rangle$$

$$|d_2\rangle = a|{-4}\rangle - b|{-1}\rangle + c|2\rangle$$

and singlet states are either of the form

$$|s\rangle = d|3\rangle + e|0\rangle - d|{-3}\rangle$$

or of the form

$$|s\rangle = \frac{1}{\sqrt{2}}(|3\rangle + |{-3}\rangle).$$

The following analysis takes the former singlet as the appropriate state, although all the arguments can be shown to hold for the latter form also.

We may write the crystal field Hamiltonian in matrix form for these three states as

$$H_{cf} = \begin{pmatrix} \Delta & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

where the first excited singlet lies at an energy Δ above the ground state doublet. We have estimated Δ at 4 meV from the neutron scattering data.

Then, from these general states given above, the matrix elements of the operators can be calculated, and shown to have the following symmetrical forms:

$$Q_{x^2-y^2} = \begin{pmatrix} 0 & A & A \\ A & 0 & B \\ A & B & 0 \end{pmatrix} \qquad Q_{zx} = \begin{pmatrix} 0 & A' & A' \\ A' & 0 & B' \\ A' & B' & 0 \end{pmatrix}$$

$$Q_{xy} = \begin{pmatrix} 0 & -A\mathrm{i} & A\mathrm{i} \\ A\mathrm{i} & 0 & -B\mathrm{i} \\ -A\mathrm{i} & B\mathrm{i} & 0 \end{pmatrix} \qquad Q_{yz} = \begin{pmatrix} 0 & A'\mathrm{i} & -A'\mathrm{i} \\ -A'\mathrm{i} & 0 & B'\mathrm{i} \\ A'\mathrm{i} & -B'\mathrm{i} & 0 \end{pmatrix}.$$

For the crystal field scheme detailed in figure 3, the values of these matrix elements are $A = 5.5$, $B = 0.0$, $A' = 3.3$, and $B' = 1.8$.

Thus it may be seen that, for the four quadrupolar operators, only two possible symmetries exist, i.e. that shared by $Q_{x^2-y^2}$ and Q_{zx}, and that of Q_{xy} and Q_{yz}. The matrix elements of $Q_{x^2-y^2}$, for example, have the same symmetry as those of Q_{zx}, but the same magnitude as those belonging to Q_{xy}. This has important consequences in terms of the effect of one operator on the expectation value of another, and therefore for the possible linear combination of quadrupolar Stevens operators which may contribute to the order parameter in each phase. It may be seen, for instance, that a non-zero $\langle Q_{x^2-y^2}\rangle$ automatically implies that $\langle Q_{zx}\rangle$ is also finite, and an exactly similar situation arises for $\langle Q_{xy}\rangle$ and $\langle Q_{yz}\rangle$. It is to be expected that the magnitude of the matrix elements of $Q_{x^2-y^2}$ and Q_{xy} are the same, as are those of Q_{zx} and Q_{yz}, since

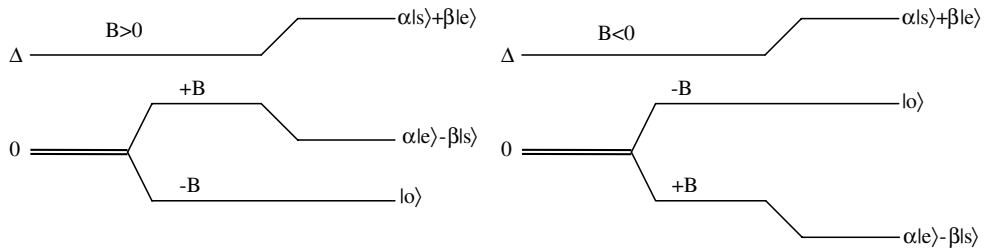

Figure 5. Eigenfunctions and eigenvalues of $H_{cf} - J_{x^2-y^2}\langle Q_{x^2-y^2}\rangle Q_{x^2-y^2}$. $|\mathrm{e}\rangle$ and $|\mathrm{o}\rangle$ denote the even and odd combinations of the doublet ground state $|\mathrm{e}\rangle = \frac{1}{\sqrt{2}}(|d_1\rangle + |d_2\rangle)$ and $|\mathrm{o}\rangle = \frac{1}{\sqrt{2}}(|d_1\rangle - |d_2\rangle)$.

the structure is quasi-cubic. If the analysis is carried out for the other form of the singlet, the matrices for $Q_{x^2-y^2}$ and Q_{xy} are found to be

$$Q_{x^2-y^2} = \begin{pmatrix} 0 & C & -C \\ C & 0 & B \\ -C & B & 0 \end{pmatrix} \qquad Q_{xy} = \begin{pmatrix} 0 & -C\mathrm{i} & -C\mathrm{i} \\ C\mathrm{i} & 0 & -B\mathrm{i} \\ C\mathrm{i} & B\mathrm{i} & 0 \end{pmatrix}$$

and the symmetry of these with the other two quadrupolar operators is exactly similar to the former case.

An important difference between Q_{xy} and Q_{yz} and the other two operators is that, for these two, the eigenvalues are unchanged by the transformation of the order parameter $Q \to -Q$, whereas for $Q_{x^2-y^2}$ and Q_{zx} they are different. This is illustrated in the figures 5 and 6 below. By treating the A- and B-terms as having two separable effects, it can be seen that the downward shift of the ground state is dependent on the sign of the matrix element B, since this determines whether it is the odd or even combination of the original doublet states which becomes the ground state. The A-term always mixes the singlet into the even combination, whilst the odd state remains pure. In Landau theory, $Q \neq -Q$ requires that the expansion for the free energy must contain a third-order term in Q, and so the phase transition must be first order, but for $Q = -Q$ the free energy is even in Q and may lead to a second-order transition. Thus we find that the symmetry of the operator $Q_{x^2-y^2}$ is consistent with its being the primary order parameter at the second-order transition at 7.8 K only if the value of the matrix element B is essentially zero, this also being in agreement with the lack of entropy change at this transition. The development of Q_{yz} at T_{+1} is consistent with the observed second-order transition at this temperature, with the first-order transition at T_{-1} having order parameter Q_{zx}. We believe that the parallel symmetries of $Q_{x^2-y^2}$ and Q_{zx} mean that the development of Q_{zx} at T_{-1} enhances $Q_{x^2-y^2}$, and that this can be seen in the x-ray scattering data [5] as an enhancement of the $(1, 0, 3)$ peak in the $(\pi$–$\pi)$ channel, following the development of the $(1, 0, 4)$ peak in the $(\pi$–$\sigma)$ channel at T_{-1}. Although the matrix element B of $Q_{x^2-y^2}$ is vanishingly small, the corresponding B'-element for Q_{zx} is comparatively large, and hence it is at this transition that a sudden drop is seen in the entropy, owing to the splitting of the ground state doublet.

It is important to stress that it would be impossible to justify as many as four phase transitions from a two-level system. In the phases below T_{+1}, the x-ray scattering results have indicated possible AFQ structures based on an orthorhombic unit cell, in which there are four inequivalent sublattices. For an Ising system where only a single ion is taken into account, a ferromagnetic exchange would certainly be the more energetically favourable. However, with a crystal with four sublattices an AFM exchange is possible, and represents a system in which the tendency to order magnetically may be strongly frustrated by lattice effects.

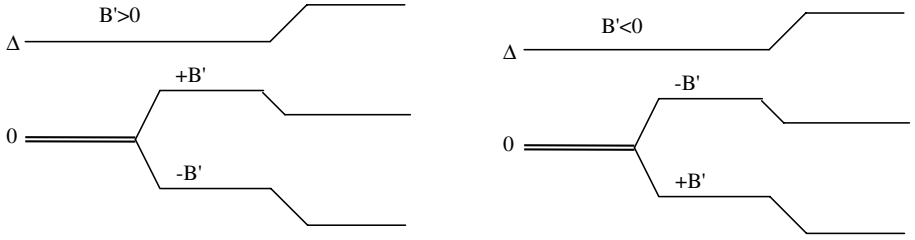

Figure 6. Eigenfunctions and eigenvalues of $H_{cf} - J_{xy}\langle Q_{xy}\rangle Q_{xy}$ and $H_{cf} - J_{yz}\langle Q_{yz}\rangle Q_{yz}$.

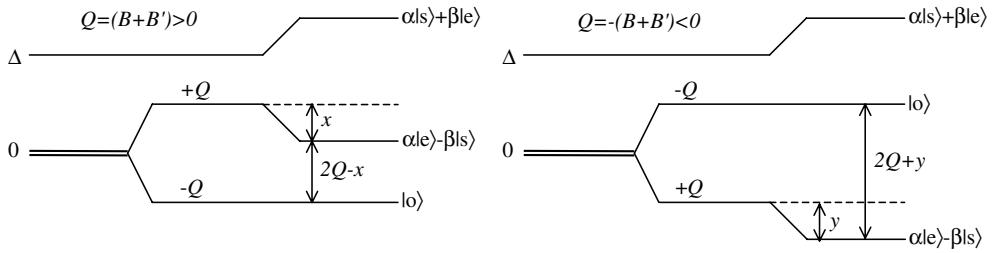

Figure 7. Energy level scheme for the low temperature phase with $\langle Q_{x^2-y^2}\rangle$ and $\langle Q_{zx}\rangle$ nonzero.

The matrix elements for the magnetic operators were found to be of the form

$$J_x = \begin{pmatrix} 0 & C & -C \\ C & 0 & 0 \\ -C & 0 & 0 \end{pmatrix} \qquad J_y = \begin{pmatrix} 0 & C\mathrm{i} & C\mathrm{i} \\ -C\mathrm{i} & 0 & 0 \\ -C\mathrm{i} & 0 & 0 \end{pmatrix} \qquad J_z = \begin{pmatrix} 0 & 0 & 0 \\ 0 & D & 0 \\ 0 & 0 & -D \end{pmatrix}$$

which would lead us to expect the magnetic susceptibility χ^{xx} to be Van Vleck in form, whilst χ^{zz} is entirely Curie type. The increase in the susceptibility χ^{xx} at every phase transition indicates progressively more and more mixing of the singlet into the ground state.

5. Mean field fit to the inelastic neutron scattering data

We have analysed the low-temperature inelastic neutron scattering results [11], by considering the energies at which we would expect dipolar excitations to occur in the four-sublattice AFQ model. If the matrix elements for the quadrupolar operators are as in section 4 above, then it is instructive to consider a Hamiltonian for a low temperature phase of the form

$$H_4 = H_{cf} - J_{x^2-y^2}\langle Q_{x^2-y^2}\rangle Q_{x^2-y^2} - J_{zx}\langle Q_{zx}\rangle Q_{zx}$$

which may be represented by the four matrices

$$H = \begin{pmatrix} \Delta & \pm A \pm A' & \pm A \pm A' \\ \pm A \pm A' & 0 & \pm B \pm B' \\ \pm A \pm A' & \pm B \pm B' & 0 \end{pmatrix} = \begin{pmatrix} \Delta & \pm P^{(\prime)} & \pm P^{(\prime)} \\ \pm P^{(\prime)} & 0 & \pm Q^{(\prime)} \\ \pm P^{(\prime)} & \pm Q^{(\prime)} & 0 \end{pmatrix},$$

so the combinations $+P, -P, +P', -P'$ form the matrix elements for each of the four sublattices. The resulting energy level schemes depend on the sign of the $Q^{(\prime)}$ matrix element, as shown in figure 7 below.

A similar level scheme can also be drawn for $Q' = (B - B') > 0$ and $-(B - B') < 0$. Thus in this phase, there is a dipolar coupling between the two lowest states, and we would hence expect four peaks in the neutron scattering data, at energies $2Q - x$, $2Q + y$, $2Q' - x'$,

and $2Q' + y'$ due to the splitting of the doublet and the admixture of the singlet for the four sublattices. The experimental results [11] at 1.7 K show two strong peaks at 1.68 and 2.20 meV, along with two weaker peaks at 1.28 and 2.60 meV.

The mere existence of four peaks at this temperature supports the hypothesis that there are four sublattices, since it would be impossible to justify more than two peaks with a single-ion model. The energies of the peaks allow the matrix elements P and Q to be calculated directly, and from these the matrix elements A and B may be deduced as $A \cong 0.9$, $A' \cong -0.2$, $B \cong 0.0$, and $B' \cong 1.0$. The matrix element B, which is that connecting the doublet states for $Q_{x^2-y^2}$, is therefore confirmed to be vanishingly small, as had been deduced from the lack of entropy change at the first phase transition. Thus the neutron scattering data support the hypotheses that the first phase transition at $T_0 = 7.8$ K is second order with primary order parameter $Q_{x^2-y^2}$, in which the doublet splits only very little, and that the phase below T_2 is consistent with an AFQ state with four sublattices with order parameters $Q_{x^2-y^2}$ and Q_{zx}.

Knowledge of the values of these matrix elements allows us to calculate the expectation values $\langle Q_{x^2-y^2}\rangle$ and $\langle Q_{zx}\rangle$ at $T = 0$, from which an estimate of the respective exchange interactions can be made. These calculations, when averaged over all four sublattices, yield $\langle Q_{x^2-y^2}\rangle_{T=0} \cong 1.2$ and $\langle Q_{zx}\rangle_{T=0} \cong 4.1$, from which $J_{x^2-y^2} \cong -3.0$ meV and $J_{zx} \cong 1.0$ meV. Self-consistent mean field theory predicts $J_{x^2-y^2}$ to be of the order of the crystal field splitting, Δ, with J_{zx} considerably smaller, being close to $k_B T_c$, i.e. 6.7 K. The values calculated from experiment are consistent with the expected magnitudes, since $J_{x^2-y^2}$ is equivalent to a temperature of about 35 K, and is thus slightly less than Δ, acceptably close given the tolerances of experimental data and the limits of mean field theory, particularly in a regime of four inequivalent sublattices. Mean field theories tend to give an overestimate of transition temperatures, and the calculated J_{zx} corresponds to a transition temperature of about 11.6 K.

This discussion shows how the admixture of different symmetries of distortion for the different sublattices leads to four dipolar excitations, as measured in our inelastic neutron scattering studies. A more detailed explanation of the order parameters in the various phases of UPd_3 will be given in a forthcoming publication.

6. Conclusions

We have re-analysed the available experimental data for UPd_3, and have produced both a new energy level and wavefunction scheme for the high-temperature phase, and a model for the progression of the phase transitions. Our three-level scheme has a doublet ground state with a first excited singlet some 4 meV above, consistent with neutron scattering and entropy data. We have presented possible wavefunctions for these states, derived from fitting to experimental results for the magnetic susceptibility and to low-temperature inelastic neutron scattering. The doublet ground state is absolutely necessary to explain both the entropy and magnetic susceptibilities, which we have demonstrated to obey a Curie–Weiss law.

By using this new insight into the crystal field levels in the high-temperature phase, and setting this alongside previous experimental deductions about the probable order parameters at each transition, we have developed a model for the phase transitions that has the potential to explain many of the observed anomalies. We believe that the special nature of the three-level, AF system based on a ground state magnetic doublet is what gives rise to the observed number and sequence of transitions. We have shown that this model is qualitatively consistent with x-ray scattering, magnetic susceptibility, entropy, and neutron scattering measurements. This system is particularly exciting, since we are unaware of any other three-level system with a magnetic doublet ground state and AF exchange.

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