Phase diagram for UPd_3 subject to symmetry-breaking stress and magnetic field

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We show on the basis of a Landau theory that UPd_3 will exhibit a number of distinct quadrupolar ordered phases and a tetracritical point, when subject to symmetry-breaking stress and magnetic field. Without the symmetry-breaking fields, a transition to a quadrupolar ordered triple-Q phase occurs. The two fields split this transition and at the tetracritical point, the unmodulated, single-, double-, and triple-Q phases coexist. In agreement with the requirement of thermodynamic stability, our theory predicts that no phase may occupy more than 180° of the angle at the tetracritical point. The splitting of the transition to the quadrupolar ordered phase, which has been observed in a number of experiments, could be explained by our results.

I. INTRODUCTION

UPd_3 is a hexagonal crystal with space group $P6_3/mmc$. The uranium ions, because of their unfilled $5f$ shells, have fluctuating multipole moments, most importantly magnetic dipole and electric quadrupolar moments. At $T_1 \approx 7$ K and $T_2 \approx 4.5$ K two phase transitions occur associated with a modulation of wave vector $\frac{1}{2}\mathbf{a}^*$ (cf. Fig. 1).[1–8] The absence of neutron spin-flip scattering between T_1 and T_2 suggests the first transition to be due to quadrupolar ordering, whereas the existence of neutron spin-flip scattering below T_2 suggests the second transition to be due to magnetic ordering.[5] Through a symmetry analysis identifying the possible order parameters, and a comparison of these results with neutron diffraction results, earlier work[7] on the phase between T_1 and T_2 identified the symmetry of the order parameter. The order parameter describes an ordering of the uranium ion quadrupoles, and a simultaneous displacement of all ions.

The number of phase transitions observed in UPd_3 strongly depends on sample preparation. Andres *et al.*[1] performed specific heat measurements in zero external field with five differently prepared samples. Depending on the sample, they found zero to three transitions instead of the two transitions expected in zero field. In thermal expansion measurements in zero external field, Ott *et al.*[2] and Zochowski and McEwen[6] also found three transitions. The variation with sample preparation in number and sharpness of the transitions suggests internal strain in the samples to be the cause. In the following, we will study a splitting of the transition to the quadrupolar ordered phase in symmetry-breaking stress and magnetic field.

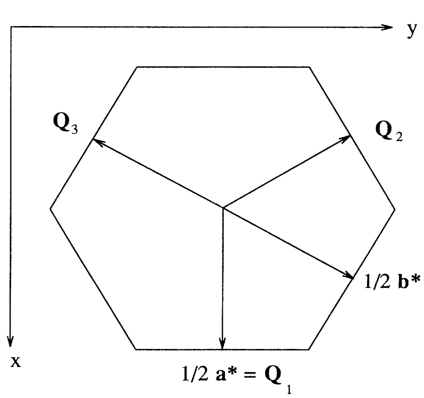

FIG. 1. Definition of axes in reciprocal space. $\mathbf{Q}_2$ and $\mathbf{Q}_3$ are in the star of $\mathbf{Q}_1$.

The star of the modulation wave vector $\mathbf{Q}_1 = \frac{1}{2}\mathbf{a}^*$ is formed by the vectors $\mathbf{Q}_2$ and $\mathbf{Q}_3$, obtained from $\mathbf{Q}_1$ by rotations of $\pm 2\pi/3$ (cf. Fig. 1). The modulated phase of UPd_3 can be a superposition of up to three plane waves with wave vectors $\mathbf{Q}_1$, $\mathbf{Q}_2$, and $\mathbf{Q}_3$. Depending on the number of modulation directions, these cases are called single-, double-, and triple-Q ordered phases. The quadrupolar ordered phase in UPd_3 is triple Q.[7]

When *one* symmetry-breaking field that couples to the order parameter is applied in the basal plane, the three directions $\mathbf{Q}_1$, $\mathbf{Q}_2$, and $\mathbf{Q}_3$ are no longer equivalent. Thus we expect an additional single-Q or double-Q phase to be wedged between the unmodulated and the triple-Q phase.

When *two* symmetry-breaking fields are simultaneously applied in the basal plane, e.g., stress and a magnetic field, they favor either the same or a different additional phase. In the former case, the temperature region in which the phase exists becomes larger. In the latter case, the single-Q and the double-Q phase compete. At some value of field strengths, a transition occurs from one phase to the other. In particular, a tetracritical point[9] should occur, at which the unmodulated, single-, double-, and triple-Q phases coexist.

This article is organized as follows: We present the expression for the Gibbs free energy of UPd_3 under stress and in a magnetic field derived on the basis of Landau theory, and construct the phase diagram. We show the theoretical existence of a tetracritical point, and find the space groups associated with the different phases. We prove that thermodynamic stability requires a 180° rule[10] to exist for tetracritical points and that our theory is consistent with this rule. We then discuss existing experimental evidence for the occurrence of an additional single- or double-Q phase. In particular, we show how our theory could account for thermal expansion measurements by Zochowski and McEwen.[6]

II. GIBBS FREE ENERGY IN STRESS AND MAGNETIC FIELD

According to Ref. 7, the order parameter describing the quadrupolar order in UPd_3 has three real components (η_1, η_2, η_3) where η_i represents the amplitude of an ordered quadupole-moment and ion-displacement wave of B_{2g} symmetry and corresponding to wave vector $\mathbf{Q}_i$. The Gibbs free energy describing the interaction of the order parameter with stress and magnetic field is

$$\begin{aligned}\mathcal{G} = {} & A\sum_{k=1}^{3}\eta_k^2 + B\left(\sum_{k=1}^{3}\eta_k^2\right)^2 + C\sum_{\substack{k\neq l\\ k,l=1}}^{3}\eta_k^2\eta_l^2 - \frac{1}{2}\sum_{i,j=1}^{6}s_{ij}\sigma_i\sigma_j + \sum_{i=1}^{6}\Lambda_i\sigma_i\\ & + [g_{1r}\,(\sigma_1+\sigma_2) + g_{1z}\,\sigma_3]\sum_{k=1}^{3}\eta_k^2 + g_2\,[(2\eta_1^2-\eta_2^2-\eta_3^2)(\sigma_1-\sigma_2) - 2\sqrt{3}\,(\eta_2^2-\eta_3^2)\,\sigma_6]\\ & + [G_{1r}\,(H_x^2+H_y^2) + G_{1z}\,H_z^2]\sum_{k=1}^{3}\eta_k^2 + G_2[(2\eta_1^2-\eta_2^2-\eta_3^2)(H_x^2-H_y^2) - 2\sqrt{3}(\eta_2^2-\eta_3^2)H_xH_y]. \qquad (1)\end{aligned}$$

This free energy has been constructed in such a way as to be invariant under the operations of the space group $P6_3/mmc$ of the high-temperature phase of UPd_3. The terms in A, B, and C give a description of the transition to the quadrupolar ordered phase which occurs at $T_1 \approx$ 7 K and which has been discussed in detail in Ref. 7; here $A = \alpha(T - T_1)$ with $\alpha > 0$, $C < 0$ so that the transition is to a triple-Q phase, and $3B + 2C > 0$ for stability. The values of the coefficients A, B, and C in the Gibbs free energy (1) will, in general, differ from those of the coefficients in the Helmholtz free energy of Ref. 7. The quantities σ_i represent the components of the stress tensor in Voigt notation,[11] i.e., $\sigma_1 \equiv \sigma_{xx}$, etc. Also, s_{ij} is the elastic compliance matrix and Λ_i represents the effect of thermal expansion.

The dependence of the strains e_i on the stresses σ_i and on the order parameter can be obtained from the relation $e_i = -\partial G/\partial\sigma_i$, which gives

$$\begin{aligned} e_1 &= s_{11}\,\sigma_1 + s_{12}\,\sigma_2 + s_{13}\,\sigma_3 - \Lambda_1\\ &\quad -g_{1r}\sum_{k=1}^{3}\eta_k^2 - g_2\,(2\eta_1^2-\eta_2^2-\eta_3^2),\\ e_2 &= s_{21}\,\sigma_1 + s_{22}\,\sigma_2 + s_{23}\,\sigma_3 - \Lambda_2\\ &\quad -g_{1r}\sum_{k=1}^{3}\eta_k^2 + g_2\,(2\eta_1^2-\eta_2^2-\eta_3^2),\\ e_3 &= s_{31}\,\sigma_1 + s_{32}\,\sigma_2 + s_{33}\,\sigma_3 - \Lambda_3\\ &\quad -g_{1z}\sum_{k=1}^{3}\eta_k^2,\\ e_4 &= s_{44}\,\sigma_4,\\ e_5 &= s_{44}\,\sigma_5,\\ e_6 &= 4\,s_{66}\,\sigma_6 + 2\sqrt{3}\,g_2\,(\eta_2^2-\eta_3^2). \qquad (2)\end{aligned}$$

III. THEORETICAL PHASE DIAGRAMS FOR FIELDS ALONG SYMMETRY AXES

We now discuss the phase diagrams implied by the Gibbs free energy $\mathcal{G}$ given above, where we ignore from now on terms not containing the order parameter. We only consider fields along one of the symmetry axes x, y, and z.

Because stress and magnetic field enter symmetrically in $\mathcal{G}$, they may be used interchangeably in the following arguments. We will sometimes use F_{kk} to stand for either σ_{kk} or H_k^2, $\{k \in x, y, z\}$, and Γ_{1r}, Γ_{1z}, and Γ_2 to stand for g_{1r} or G_{1r}, g_{1z} or G_{1z}, and g_2 or G_2, respectively.

Introducing the Gibbs free energy $\mathcal{G}_0$ in zero field

$$\mathcal{G}_0 = A\sum_{i=1}^{3}\eta_i^2 + B\left(\sum_{i=1}^{3}\eta_i^2\right)^2 + C\sum_{\substack{i\neq j\\ i,j=1}}^{3}\eta_i^2\eta_j^2, \qquad (3)$$

we have for a field F_{zz} (i.e., one of σ_{zz} or H_z^2),

$$\mathcal{G} = \mathcal{G}_0 + \Gamma_{1z}\,F_{zz}\sum_{i=1}^{3}\eta_i^2. \qquad (4)$$

This amounts to a renormalization of A to $A + \Gamma_{1z}F_{zz}$, i.e., a field along the z axis changes the transition temperature, but does not induce a new phase. The same is true for two simultaneous fields along the z axis (i.e., the presence of both σ_{zz} and H_z^2).

A. Phase diagram for one field along a symmetry axis in the basal plane

Let us first discuss one field along the x axis. The free energy is

$$\mathcal{G} = \mathcal{G}_0 + \Gamma_{1r}\, F_{xx} \sum_{i=1}^{3} \eta_i^2 + \Gamma_2\, (2\eta_1^2 - \eta_2^2 - \eta_3^2)\, F_{xx}. \quad (5)$$

Note that the η_i do not enter equivalently. Further calculation shows that the initial transition as the temperature is lowered is to a single-Q ($F_{xx}\Gamma_2 < 0$) or double-Q ($F_{xx}\Gamma_2 > 0$) phase, followed by a transition to the triple-Q phase.

If the field is along the y axis, we only need replace Γ_2 by $-\Gamma_2$. Thus, if F_{xx} induces a single-Q phase with $|\eta_1| > 0$, then F_{yy} induces a double-Q phase with $|\eta_2| = |\eta_3| > 0$, and vice versa.

For the transition temperatures we find (keeping in mind to change the sign of Γ_2 for a field along y) (a) if the initial transition on lowering the temperature is to single-Q (i.e., $F_{xx}\Gamma_2 < 0$):

$$\begin{aligned} T_{1Q} &= T_1 - \frac{1}{\alpha}\,(\Gamma_{1r} + 2\,\Gamma_2)F_{kk}, \quad k \in \{x, y\}, \\ T_{3Q} &= T_1 - \frac{1}{\alpha}\left[\Gamma_{1r} + 2\left(1 + \frac{3B}{2C}\right)\Gamma_2\right] F_{kk}; \end{aligned} \quad (6)$$

(b) if the initial transition on lowering the temperature is to double-Q (i.e., $F_{xx}\Gamma_2 > 0$):

$$\begin{aligned} T_{2Q} &= T_1 - \frac{1}{\alpha}\,(\Gamma_{1r} - \Gamma_2)\, F_{kk}, \quad k \in \{x, y\}, \\ T_{3Q} &= T_1 - \frac{1}{\alpha}\left[\Gamma_{1r} - 4\left(1 + \frac{3B}{2C}\right)\Gamma_2\right] F_{kk}; \end{aligned} \quad (7)$$

where T_{1Q}, T_{2Q}, and T_{3Q} are the transition temperatures to the single-, double-, and triple-Q phase, respectively.

All phase transitions are second order. The phase diagrams are depicted qualitatively in Fig. 2. Note that the slope of the phase boundaries may be positive or negative depending on the relation between Γ_{1r} and Γ_2.

B. Phase diagram for two fields along symmetry axes in the basal plane

We now consider both stress and magnetic field along the x axis. Cases in which one or both fields are along the y axis can straightforwardly be obtained by changing the sign of g_2 and G_2 appropriately. The free energy is

$$\begin{aligned} \mathcal{G} = \mathcal{G}_0 &+ (G_{1r}\, H_x^2 + g_{1r}\sigma_{xx}) \sum_{i=1}^{3} \eta_i^2 \\ &+ (G_2 H_x^2 + g_2\sigma_{xx})(2\eta_1^2 - \eta_2^2 - \eta_3^2). \end{aligned} \quad (8)$$

The transition temperatures are obtained by generalizing Eqs. (6) and (7). There are two possibilities.

One possibility is that G_2 and $g_2\sigma_{xx}$ have the same sign. In this case both fields induce the same phase, and the phase diagram is the three dimensional analog of Fig. 2. The other and more interesting possibility is that G_2 and $g_2\sigma_{xx}$ have different signs. Now one field tries to induce a single-Q phase, whereas the other field tries to induce a double-Q phase. The phase diagrams can be shown to qualitatively look as depicted in Fig. 3, where one field is held at a fixed nonzero value. Particularly we find all transition temperatures to coincide at the point

$$G_2\, H_x^2 = -g_2\, \sigma_{xx}, \quad T_c = T_1 - \frac{1}{\alpha}\,(G_{1r}H_x^2 + g_{1r}\sigma_{xx}). \quad (9)$$

At this point the unmodulated, the single-, double-, and triple-Q phases all coexist. Note that this point will always exist for some combination of fields along the x and y axis, regardless of the signs of G_2 and g_2 realized in practice.

The primitive unit cell of the single-Q phase is twice as large, and the primitive unit cell of the double- and triple-Q phase is four times as large as it is in the unmodulated phase. The space groups of the phases are found by inspection to be as listed in Table I.

Note that at the transition between negative and positive σ_{xx}, when $\mathbf{H} = \mathbf{0}$ and $T_c = T_1$, the four phases also coexist. However, as we will discuss elsewhere in detail,[12] the situation is more complex in this case.

C. The tetracritical point

The point at which all four phases coexist is a tetracritical point:[9] All phase transitions are second order, and

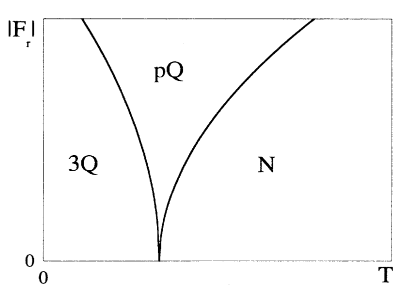

FIG. 2. Phase diagram of UPd$_3$ in one field $F_r = \sqrt{F_{rr}}$ along the x or y axis vs temperature T. N is the unmodulated phase, pQ stands for either single- or double-Q, and $3Q$ is the triple-Q phase. The slopes of the phase boundaries may both have the same sign.

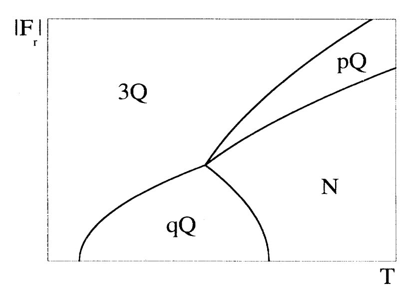

FIG. 3. Examples of phase diagrams of UPd$_3$ in two fields along symmetry axes in the basal plane. One field F_r (e.g., H_x) is varied vs temperature T, whereas the other field (e.g., σ_{xx}) is held fixed at a nonzero value. Label for phases as in Fig. 2. If pQ is single-Q, then qQ is double-Q and vice versa.

TABLE I. Space groups of phases.

Phase	Space group
Unmodulated	$P\frac{6_3}{m}mc$
Single-Q	$P\frac{2_1}{n}\frac{2}{m}\frac{2_1}{n}$
Double-Q	$C\frac{2_1}{b}\frac{2}{m}\frac{2}{c}$
Monoclinic triple-Q	$C1\frac{2}{m}1$

have the prescribed group-subgroup relationship (cf. Table I). The space groups of the single-Q and double-Q phase are subgroups of the space group of the unmodulated phase. The space group of the triple-Q phase is a subgroup of the space groups of both the single-Q and the double-Q phase.

Note that the space group of the triple-Q phase is different, in fact of lower symmetry, from that found earlier[7] in the case of zero fields: Because of the asymmetry introduced by the fields, the amplitudes η_i of the modulation have no longer equal magnitude. In the absence of symmetry-breaking fields, the triple-Q phase is trigonal, whereas in the presence of such fields it is monoclinic.

The slope of all phase boundaries will in general be different, and may be positive or negative. Inspecting Eqs. (6) and (7), keeping in mind $1 + 3B/2C < 0$, we find that only those combinations of slopes are possible, where no phase occupies more than 180° of the angle at the critical point.

In fact, this means our analysis conforms with the requirement of thermodynamic stability, which we will show to imply such a "180°" rule for tetracritical points. The proof is an extension of the 180° rule for certain classes of higher order triple points by Wheeler.[10]

For a second order phase transition described by the free energy $\mathcal{G}(\eta, T, F)$, with order parameter η and fields T and F, the slope $s_{A,B}$ of the phase boundary between phases A and B is given by the Ehrenfest relations[13]

$$s_{A,B} = \frac{\Delta\alpha_{A,B}}{\Delta\beta_{A,B}} = \frac{\Delta\beta_{A,B}}{\Delta\gamma_{A,B}}, \tag{10}$$

provided the quantities in the denominators are finite. Here $\Delta\alpha_{A,B} = \alpha_A - \alpha_B$, etc. , and

$$\alpha = -\frac{\partial^2\mathcal{G}}{\partial T^2}, \quad \beta = \frac{\partial^2\mathcal{G}}{\partial T\partial F}, \quad \gamma = -\frac{\partial^2\mathcal{G}}{\partial F^2}. \tag{11}$$

If phase B is more ordered (i.e., of lower symmetry) than phase A, stability demands that the specific heat jump $T^{-1}\Delta\alpha_{A,B} > 0$. Note that we have $\Delta\alpha_{3Q,pQ} = \Delta\alpha_{3Q,qQ} + \Delta\alpha_{qQ,N} - \Delta\alpha_{pQ,N}$, with the notation of Fig. 2, and all these $\Delta\alpha_{ij} > 0$. Thus

$$\begin{aligned} s_{3Q,pQ} &= \frac{\Delta\alpha_{3Q,pQ}}{\Delta\beta_{3Q,pQ}} \\ &= \Delta\alpha_{3Q,pQ}\left(\frac{\Delta\alpha_{3Q,qQ}}{s_{3Q,qQ}} + \frac{\Delta\alpha_{qQ,N}}{s_{qQ,N}} - \frac{\Delta\alpha_{pQ,N}}{s_{pQ,N}}\right)^{-1}, \end{aligned} \tag{12}$$

relating the four slopes at the tetracritical point. It is easy to see that neither a combination of slopes as in Fig. 4(a) with $\{s_{3Q,pQ}, s_{pQ,N} > 0,\ s_{3Q,qQ}, s_{qQ,N} < 0\}$ nor a combination as in Fig. 4(b) with $\{s_{3Q,pQ}, s_{pQ,N} < 0,\ s_{3Q,qQ}, s_{qQ,N} > 0\}$ are possible solutions.

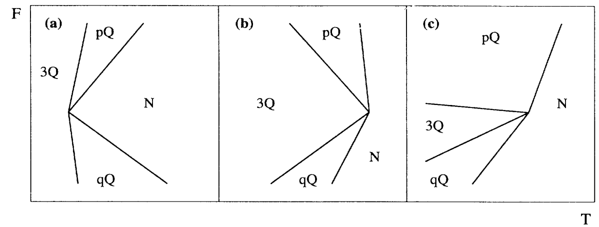

FIG. 4. Examples of phase diagrams breaking the 180° rule. Label for phases as in Fig. 2.

Of course there are other combinations of slopes, not described by these relations, that break the 180° rule [cf. Fig. 4(c)]. However, all these cases can be brought to fit either (a) or (b) by an nonsingular affine transformation of the fields $(T', F') = M\,(T, F)^t + (T_0, F_0)$, where M is a nonsingular 2×2 matrix and (T_0, F_0) an arbitrary vector. A nonsingular affine transformation conserves the concavity of the thermodynamic potential in T and F, and thus the sign of the specific heat. It also conserves the positive sign of the jump in α_{AB}, when B is of lower symmetry then A.[10] It also transforms half planes into half planes, and thus does not affect whether a particular phase occupies more than 180° of the angle. Therefore after executing the transformation, the argument can continue as above. In the case of Fig. 4(c), the transformation may be thought of as a composition of the following: (i) rotation such that all phase boundaries lie in the left half plane; (ii) compression of one axis such that neither qQ nor the pQ occupy more than 90° of the angle at the critical point; and (iii) rotation such that qQ and pQ are comprised entirely in the lower left and upper left quadrant, respectively.

In this section we have derived different phase diagrams which are possible for UPd_3 in stress and magnetic field. In particular we have shown theoretically the existence of a tetracritical point, at which the unmodulated, a single-, double-, and monoclinic triple-Q phase coexist.

IV. EXPERIMENTAL EVIDENCE FOR A SINGLE- OR DOUBLE-Q PHASE

Experiments with UPd_3 in which stress and magnetic field vary independently have not been performed, and thus a tetracritical point has not been observed. However, as pointed out in the Introduction, there is some evidence that single- and double-Q phases do indeed occur when stress or a magnetic field is applied.

Comparison of theoretical results with thermal expansion measurements

We now attempt to interpret in terms of our theory the thermal expansion measurements in zero and nonzero magnetic field by Zochowski and McEwen,[6] reproduced in Fig. 5. In nonzero magnetic field, there is clear ev-

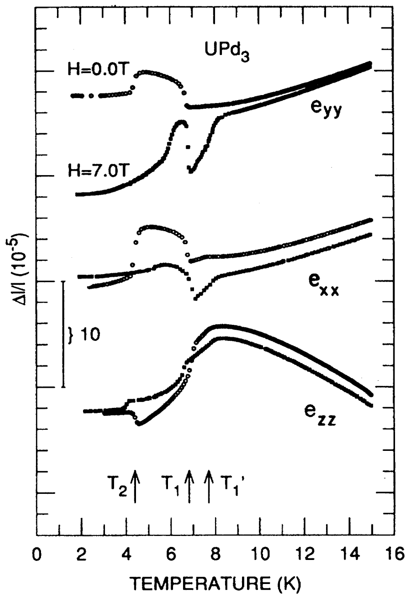

FIG. 5. Thermal expansion of UPd_3, measured along the symmetry axes. (○) represents zero field data and (■) represents data taken at $H = 7$ T, where the field is always along the axis of measurement. The arrows indicate the transition temperatures in zero magnetic field at T_1' to single- or double-Q, at T_1 to the triple-Q quadrupolar ordered phase and at T_2 to the magnetically ordered phase. The data for each axis have been displaced vertically for ease of representation. Reprinted from Ref. 6.

idence for a third phase transition in addition to those to the triple-Q quadrupolar ordered phase and to the magnetically ordered phase. In zero field, this additional phase is also weakly manifest at T_1', which is at a slightly lower temperature than in nonzero magnetic field.

We interpret the additional phase between T_1 and T_1' in zero magnetic field as being a single- or double-Q phase stabilized by a symmetry-breaking stress, which is induced through the measuring technique.[14] The measurements in Fig. 5 were made using a capacitance dilatometer, in which the sample is glued to the plates of the capacitor. The dilatation is measured in a direction perpendicular to the plates. Generally, capacitor plates and sample will have different thermal expansion coefficients. Therefore, when the apparatus is cooled, the UPd_3 sample experiences uncontrolled stress in the plane of the plates. For the e_{xx} and e_{yy} measurements, this stress will break the hexagonal symmetry and induce a single- or double-Q phase between the normal and triple-Q phase.

Note that the presence of an additional phase in a symmetry-breaking field provides further evidence, in addition to what has been presented in Ref. 7, for the interpretation of the quadrupolar ordered phase in zero field as a triple-Q. It follows from Eq. (1) that if the quadrupolar phase in zero field was single Q, then a field in the basal plane would not be symmetry breaking, and no additional phase would be induced.

In Fig. 5 the strain at the transition to the triple-Q phase at T_1 is discontinuous. However, our Landau theory predicts it to be continuous. A possible explanation is that this discontinuity is fluctuation induced.[15] This question is not investigated in detail here.

Now we compare the experimental results in Fig. 5 and the predictions for the temperature dependence of the strains in Eqs. (2). Note that in Fig. 5 the magnetic field is always applied along the axis of measurement of the strain. We first remark that according to Eqs. (2), only the strains e_{zz}, e_{xx}, e_{yy}, and e_{xy} exhibit a change in slope at a phase transition. In Fig. 5 e_{zz}, e_{xx}, e_{yy} indeed show such changes, whereas e_{xy}, e_{xz}, and e_{yz} have not been measured. Also from Eqs. (2) we expect $e_{xx} \approx e_{yy}$ in zero magnetic field, provided the stress due to gluing the sample to the capacitor plates is approximately the same in both cases; from Fig. 5 this appears to be the case.

It follows from Eq. (1) that the expression for the amplitude of the modulation η_i in a single- or double-Q phase is

$$\eta_{1,1Q}^2 = -\frac{\alpha}{2B}\,(T - T_z^{1Q}),$$
$$\eta_{2,2Q}^2 = \eta_{3,2Q}^2 = -\frac{\alpha}{2(2B+C)}\,(T - T_z^{2Q}), \qquad (13)$$

where

$$T_z^{1Q} = T^{1Q} - \frac{1}{\alpha}\,g_{1z}\sigma_{zz}, \quad T_z^{2Q} = T^{2Q} - \frac{1}{\alpha}\,g_{1z}\sigma_{zz}, \quad (14)$$

and T^{1Q} and T^{2Q} are the transition temperatures to the single- and double-Q phase, previously given by Eqs. (6) and (7). Thus in the expression for η_i, only the transition temperature depends on the strength of stress or magnetic field. Consequently, the change of the slope of e_{kl} as a function of temperature at a transition depends neither on the field strength nor on the nature of the field. However, e_{xx} and e_{yy} have different slopes.

For e_{xx} in zero magnetic field, a phase transition occurs at T_1', to what we interpret as a a single- or double-Q phase. In nonzero magnetic field, the transition is more pronounced. In particular, the slope of e_{xx} is steeper in the latter case, contradicting the result of the last paragraph. A possible explanation is that the stress is inhomogeneous, such that the transition to the single- or double-Q phase occurs only in a small fraction of the sample, so that in this case the average strain is smaller. In fact, for e_{yy} in zero magnetic field, no transition at T_1' is discernible at all.

We can make statements about the signs of g_{1r} and g_2. If we interpret the transition at T_1' in zero magnetic field as occurring in only a small fraction of the sample, then in the triple-Q phase at T_1 the change in the strains associated with the appearance of nonzero η_i will be $\Delta e_{xx} = \Delta e_{yy} = -g_{1r}\sum_i \eta_i^2$. We disregard the discontinuity, and look only at the slope of e_{xx} and e_{yy} as T_1 is approached from below. According to Fig. 5, $d(\Delta e_{xx})/dT \approx d(\Delta e_{yy})/dT < 0$, and since $d(\eta_i^2)/dT < 0$, g_{1r} must be negative.

Now assume $G_2 < 0$. Then for nonzero magnetic field the first transition for e_{xx} ($H_x \neq 0$) is to a single-Q phase with $|\eta_1| > 0$, and for e_{yy} ($H_y \neq 0$) it is to a double-Q phase with $|\eta_2| = |\eta_3| > 0$. In the former case the change in e_{xx} is $\Delta e_{xx} = -(g_{1r} + 2g_2)\eta_1^2$. In the latter case the change in e_{yy} is $\Delta e_{yy} = -2(g_{1r} + g_2)\,\eta_2^2$. From Fig. 5, in this phase both $d(\Delta e_{xx})/dT > 0$ and $d(\Delta e_{yy})/dT > 0$, and we conclude $g_2 > -g_{1r} > 0$.

The *additional* change in the strains for $H_i \neq 0$ for $T_2 < T < T_1$ below the transition into the triple-Q phase is [cf. Eqs. (2)] $\Delta' e_{xx} = 2(-g_{1r} + g_2)\eta_2^2 > 0$ and $\Delta' e_{yy} = (-g_{1r} + 2g_2)\,\eta_1^2 > 0$, because, from the previous paragraph, $-g_{1r} + g_2 > 0$ and $-g_{1r} + 2g_2 > 0$. From Fig. 5, disregarding the discontinuity at T_1, we find $d(\Delta' e_{xx})/dT < 0$, which is consistent with the above result. However, $d(\Delta' e_{yy})/dT \geq 0$, which is not consistent with the above result. This behavior may be due to the transition to the magnetic phase, taking place at higher temperatures in magnetic field.

If we assume $G_2 > 0$, qualitatively the same results are obtained, except that in this case $g_2 < g_{1r} < 0$. From available experimental results, it is not possible to deduce which of the fields H_x and H_y induces a single-, and which induces a double-Q phase. Neutron diffraction experiments in a magnetic field and/or applied stress would help to decide this question.

In this section we have discussed experimental evidence for the existence of a single- or double-Q phase as predicted by our theory. We also compared in detail our theoretical results for the strains with thermal expansion measurements. With the exception of the data on e_{yy} for $T < T_1$, the theory is consistent with the experimental results. Further experiments on samples subjected to known external stress would provide a valuable additional test for the theory.

V. CONCLUSION

In this article we have shown theoretically that, when subject to symmetry-breaking stress and magnetic field, UPd_3 will exhibit a number of distinct quadrupolar ordered phases, as well as a tetracritical point. Without a symmetry-breaking field, a transition occurs to a quadrupolar ordered trigonal triple-Q phase. Under external symmetry-breaking stress and magnetic field, this transition splits and a tetracritical point appears, at which the unmodulated, a single-, double-, and a monoclinic triple-Q phase coexist. We present a Landau theory of these phase transitions, based on a symmetry analysis of the crystal. We also prove that thermodynamic stability requires a 180° rule to exist for tetracritical points, limiting the angle a phase may occupy at the critical point; our results comply with that rule. We also find the space group of all phases involved. The splitting of the quadrupolar ordered phase into two or more distinct phases observed in experiment can in principle be accounted for by our theory. However, further experiments, in particular diffraction experiments performed under conditions of controlled externally applied stress and magnetic field would be useful tests for our theory.

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