A Simple Model for Coupled Magnetic and Quadrupolar Instabilities in Uranium Heavy-Fermion Materials

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We present a mean-field calculation of the phase diagram of a simple model of localized moments, in the hexagonal uranium heavy-fermion compounds. The model considers a non-Kramers quadrupolar doublet ground state magnetically coupled with a singlet excited-state, favoring in-plane van-Vleck magnetism, as has been conjectured for UPt$_3$. The Hamiltonian which defines the model is Heisenberg like in both, magnetic and quadrupolar moments. No Kondo effect physics is included in the calculations. Among our main results are: (i) for zero intersite quadrupolar coupling, the magnetic order is achieved by a first order transition above a critical intersite magnetic coupling value which becomes second order at higher coupling strengths. (ii) for finite intersite quadrupolar coupling, at temperatures below a second order quadrupolar ordering transition, the minimal magnetic coupling value is increased, but (a) the magnetic ordering temperature is enhanced above this value, and (b) the ordering of first and second order transitions in the phase diagram is reversed. By considering the general structure of the Ginsburg-Landau free energy, we argue that the Kondo effect will not modify the shape of the phase diagram, but will modify the quantitative values at which transitions occur.
I. INTRODUCTION

The unusual commensurate, weak moment magnetic order present in heavy electron superconductors such as UPt$_3$ [and its related alloys U(Pt$_{1-x}$Pd$_x$)$_3$ and (U$_{1-x}$Th$_x$)Pt$_3$] and URu$_2$Si$_2$ has so far resisted explanation in any simple terms. It is difficult to believe the small moment order represents itinerant spin density wave formation, since, for example, UPt$_3$ displays no appropriate nesting features on the Fermi surface at the appropriate antiferromagnetic wave vector. It is difficult to account for the order in terms of frustration effects since the ordered structures are remarkably simple. In the case of URu$_2$Si$_2$, moreover, there is evidence that the magnetic order parameter is not the ‘primary’ one, in the sense that despite the large entropy involved in the 17.5K magnetic transition (the entropy involved is larger than in the 1.2K superconducting transition) the effective moment is too small to be consistent with the size of the ordered moment. Indeed, it has been suggested that some other “hidden” order drives the transition (such as quadrupoles).

Recently results coming from different directions altogether make it prudent to consider quadrupolar (and octupolar) ordering possibilities in these materials: it has been noted that the quadrupolar Kondo model believed to be previously restricted to cubic uranium based materials is in fact possible for hexagonal (UPt$_3$) and tetragonal (URu$_2$Si$_2$) materials as well. In this model the heavy fermions arise from local uranium quadrupole moments associated with ground crystal field doublets quenched by (predominantly) the orbital motion of itinerant electrons. Thus, the low lying degrees of freedom may be essentially quadrupolar.

The relevance of the quadrupolar Kondo model to this class of materials has been put on firmer footing by the discovery of the cubic material Y$_{1-x}$U$_x$Pd$_3$, which appears to display a dilute limit quadrupolar Kondo effect. Moreover, all known heavy fermion superconductors possess the appropriate symmetry groups to yield a quadrupolar Kondo effect or magnetic two-channel Kondo effect (CeCu$_2$Si$_2$), a point bolstered by the recent discovery of two hexagonal heavy-electron superconductors (UPd$_2$Al$_3$ and UNi$_2$Al$_3$) which also possess magnetic order.
In the quadrupolar Kondo picture, a context for weak moment magnetic order can arise naturally from two distinct sources: (i) for cubic symmetry, all magnetic character is in excited states, and for hexagonal and tetragonal symmetry, in plane magnetic character is in excited states. Thus, the magnetic response is van Vleck in character yielding a built in stability against magnetic ordering and a region of weak moment order. (ii) For hexagonal and tetragonal symmetry, the $c$-axis character of the local uranium doublets is weakly magnetic, but primarily octupolar.

In this paper, we shall focus our attention on (i), with the particular goal of examining how quadrupolar order can induce or at least enhance magnetic ordering tendencies. While it is well known that quadrupolar order will always be induced as a secondary order parameter at a magnetic transition, it seems to be less well known, at least in the heavy fermion field, for magnetic order to be induced or enhanced by the coupling to quadrupolar degrees of freedom. Such physics is known in UO$_2$, for example, where the antiferromagnetic phase transition is first order due to a coupling between magnetic and quadrupolar order parameters [6].

We have performed mean field calculations on a simple model of potential relevance to the hexagonal uranium heavy fermion superconductors. In this model, each uranium ion possesses a doublet quadrupolar ground state magnetically coupled to an excited singlet state. The uranium ions are placed on a lattice with the structure of UPt$_3$ (though the point symmetry is taken to be $D_{6h}$ rather than $D_{3h}$). We then turn on nearest neighbor in-plane and out-of-plane quadrupolar and magnetic coupling and study the resulting phase diagram. We find a rich structure, ranging from van Vleck magnetism with a tricritical point and critical exchange strength to alternately suppressed and enhanced magnetic order below a second order quadrupolar transition. We discuss the phase diagram using both the full mean field calculations and Landau theory in regions of validity.

While the model does not produce a full explanation of the ordering in bulk UPt$_3$ (for which the specific heat shows no transition and the neutron elastic scattering peaks are not true resolution limited Bragg peaks) it may be of relevance to the Pd and Th doped alloys and to the new hexagonal superconductors. In any case, it represents the beginning of an al-
ternative view of collective phenomena in the heavy fermion materials which may ultimately provide a unifying view of the heavy fermion state, superconductivity, and magnetism.

The outline of the paper is as follows: Section II provides an overview of the model. Section III develops the mean field approximation to this model. Section IV discusses our results in terms of Landau theory, paying special attention to the role of the orientation dependent coupling between quadrupolar and magnetic order parameters. Finally, in Section V we conclude and point out explicit experimentally relevant features of our model.

II. MODEL

In the section II-A we write a single-site Hamiltonian, coupling the quadrupolar moment of the ground state of the uranium-ion with the electric-field gradient and the magnetic moment with an applied magnetic field. In the next section we introduce intersite coupling of the XY-model form for both quadrupolar and magnetic degrees of freedom. Within the mean-field approximation that Hamiltonian is equivalent to that of section II-A, but with coupling coefficients which depend self-consistently on the mean magnetic and quadrupolar moments.

A. Single-Site Hamiltonian

Having in mind the motivations given in the Introduction, we define a single-site model in which the uranium ion has a non-Kramers quadrupolar doublet ground state magnetically coupled only with an excited state. Such a crystal-field scheme may arise for a $\text{U}^{4+}, 5f^2, J = 4$ at a site of hexagonal symmetry. Fig. I defines the level structure of the model, where the doublet $|E_{\pm}\rangle$ and the singlet $|B\rangle$ are defined by

$$|E_{\pm}\rangle = u|\pm 4\rangle + v|\mp 2\rangle,$$

and

$$|E_{\pm}\rangle = u|\pm 4\rangle + v|\mp 2\rangle,$$  \hspace{1cm} (1)
\[ |B\rangle = \frac{|3\rangle + |-3\rangle}{2}, \]  
(2)

where \( |m\rangle \) are the eigenstates of the z-component of the total angular momentum \( J \). \( u \) and \( v \) are constants. The relevant matrix elements for the model we are defining are

\[ \langle B|J_\pm|E_{\mp}\rangle = 2u + \sqrt{7}v \equiv a, \]  
(3)

and

\[ \langle E_{\pm}|J_\mp^2|E_{\mp}\rangle = 2\sqrt{7}v \equiv b. \]  
(4)

Since \( u^2 + v^2 = 1 \), the constants \( a \) and \( b \) defined here are not independent.

The other \( J = 4 \) multiplet levels are not considered, so the model will be restricted to temperatures less than or equal to the first excitation energy \( \Delta \). It is clear from the level structure considered that this model favor in-plane van Vleck magnetism, and c-axis Pauli magnetism, as has been conjectured for \( \text{UPt}_3 \) [3]. The motivation for focussing on the doublet level is that it is the only degenerate level in hexagonal symmetry for \( \text{U}^{4+} \) ions, and we desire the internal degrees of freedom associated with the doublet level to allow for the Kondo effect. The formation of the many body Abriksov-Suhl-Kondo resonance is the basic paradigm for the source of heavy fermions in these materials.

The doublet ground state corresponds to the \( E_2 \) representation of the point-group \( D_{6h} \), where the eigenfunctions transform like \( x^2 - y^2 \) and \( xy \). This doublet has magnetic character along the c-axis, but only in-plane quadrupolar tensors may couple the doublet levels together. This implies we can have a quadrupolar Kondo effect. Using the Stevens operator representation [4], the corresponding quadrupolar operators are (proportional to) \( Q_{xx} = -Q_{yy} = J_x^2 - J_y^2 \) and \( Q_{xy} = Q_{yx} = (J_xJ_y + J_yJ_x)/2 \). The magnetic moment operator is \( \vec{M} = g_J\mu_B\vec{J} \), where \( g_J = 4/5 \) and \( \mu_B \) is the Bohr magneton. The doublet is connected by \( J_x \) and \( J_y \) to the excited \(|B\rangle\) singlet. [Note that while the actual point group at U sites in \( \text{UPt}_3 \) is \( D_{3h} \), the allowed crystal field spectrum is essentially identical to that of \( D_{6h} \).]

A single-site Hamiltonian \( H \) is defined coupling the quadrupolar operators with an
electric-field gradient $\nabla \vec{E}$ and coupling the magnetic moment with an external magnetic-field $\vec{H}$, at the uranium site:

$$H = H_0 - \vec{H} \cdot \vec{M} - \sum_{\alpha, \beta} (\nabla_\alpha E_\beta) \hat{Q}_{\beta \alpha},$$

(5)

where $H_0$ is the Hamiltonian for the uranium ion in the presence of the crystal field only (see Fig. 1):

$$H_0 = \Delta |B\rangle \langle B|.$$

(6)

We are measuring energies from the doublet ground-state $|E_\pm\rangle$.

For in-plane $\vec{H}$ and $\vec{E}$, the Hamiltonian Eq. (5) is written as

$$H = H_0 + AJ_+ + BJ_+^2 + h.c.,$$

(7)

where

$$A = -\frac{gJ_\mu B}{2}(H_x - iH_y)$$

(8)

and

$$B = -\frac{\lambda}{2}(\partial_{xx}E - \partial_{yy}E - 2i\partial_{xy}E).$$

(9)

The diagonalization of this Hamiltonian shows that there is a crossing of levels depending upon $\vec{H}$ and $\vec{E}$ and an interplay between the field gradient and magnetic field which depends crucially on their orientation with respect to one another. In the model defined in the next section, the coefficients $A$ and $B$ are interpreted as molecular fields acting on the uranium sites. Since those molecular fields depend on the magnetic and quadrupolar moments, a self-consistent calculation is required to obtain these moments at each temperature.

**B. The Intersite-coupling Hamiltonian**

In order to determine the molecular fields $\vec{H}$ and $\vec{E}$ present in Eq. (3) we have used a model Hamiltonian which is Heisenberg like in the magnetic moments as well in the quadrupolar moments, defined by
\[
H = H_0 - \sum_{<i,j>} (I_{\text{ab}}^m \vec{M}_i \cdot \vec{M}_j + I_{\text{c}}^m \vec{M}_i \cdot \vec{M}_j \\
+ I_{\text{q}}^m \text{Tr} \hat{Q}_i \cdot \hat{Q}_j + I_{\text{q}}^c \text{Tr} \hat{Q}_i \cdot \hat{Q}_j),
\]

where \( I_{\text{ab}}^m \) (\( I_{\text{c}}^m \)) is the coupling between the nearest-neighbour magnetic moments in the basal plane (c-axis direction) of the hexagonal lattice; \( I_{\text{ab}}^q \) (\( I_{\text{c}}^q \)) has the same meaning for the quadrupolar moments. \( \text{Tr} \) means trace over the product of the quadrupolar tensors.

We are interested in studying the antiferromagnetic order of the model defined by Eq. (10), so that the couplings \( I_{\text{ab}}^m \) and \( I_{\text{c}}^m \) are negative. Only ferroquadrupolar coupling \( J_q \) has been considered. We have examined the effect of a coupling of the form \( \text{Tr} \vec{M}_i \cdot \hat{Q}_j \cdot \vec{M}_k \) in the Hamiltonian Eq. (10). It does not change qualitatively the mean-field phase diagram of the model, since the couplings already present in Eq. (10) give rise to a term proportional to \( M^2 Q \) in the free energy (see Eq. (19)). Hence we will drop this coupling from the Hamiltonian. The calculations are restricted to the case when \( \vec{M} \) lies in \( x \)-direction (that is the case for UPt\(_3\), as showed by neutron scattering data [8]), although it is possible to consider the general case.

III. MEAN-FIELD THEORY

A. Mean-Field Hamiltonian

The mean field approach consists in replacing the operators in the Hamiltonian by their mean values plus the respective fluctuations, and keeping the fluctuations only up to first order. Denoting the mean value of the magnetic and quadrupolar moment by \( \bar{M} \equiv g_J \mu_B m \) and \( \bar{Q} \equiv b \bar{q} \), respectively, where the matrix elements \( a \) and \( b \) are defined in Eq. (3) and Eq. (4), the mean field applied to Eq. (10) results in

\[
\frac{H}{\Delta} = \frac{H_0}{\Delta} - N(A\bar{m} + B\bar{q}) + 2 \sum_i (Am_i^x + Bq_i^{xx}) ,
\]

where \( N \) is the number of sites of the hexagonal lattice,

\[
A = \frac{(I_{\text{ab}}^m + I_{\text{c}}^m)a^2}{\Delta} \bar{m} \equiv J_m \bar{m} ,
\]
\[ B = -6 \left( \frac{I_{Q}^b + I_{Q}^c}{\Delta} \right) \bar{q} \equiv -6 J_q \bar{q}. \] (13)

The last equalities, Eq. (12) and (13), define the dimensionless magnetic coupling \( J_m \) and the dimensionless quadrupolar coupling \( J_q \), respectively. We are using deliberately the same notation \( A \) and \( B \) here as in Eq. (8) and (9) since in both cases the meaning of those parameters are the same, although in Eq. (12) and (13) \( A \) and \( B \) depend on the order parameters \( \bar{m} \) and \( \bar{q} \).

The site-independent terms of \( H \) are called the condensed energy; the other terms define a sum over an effective one-site Hamiltonian \( H_i \), which can be written in terms of the components of the total angular momentum as

\[ H_i = H_{0i} + A (J_{i+} + J_{i-}) + B (J_{i+}^2 + J_{i-}^2). \] (14)

Diagonalizing \( H_i \) in the subspace defined by the electronic levels shown in Fig. (1) we find the following expression for the free-energy per site and in units of \( \Delta \):

\[ f = -J_m \bar{m}^2 + 6 J_q \bar{q}^2 - t \ln(e^{6 J_q \bar{q}^2} + 2 e^{-\beta(1-6 J_q \bar{q}^2)} \cosh \beta C) + t \ln(2 + e^{-\beta}) \] (15)

where \( \beta = 1/t \) is the inverse of the dimensionless temperature \( t \equiv T/\Delta \). \( C \) is given by

\[ C = \sqrt{(1 + 6 J_q \bar{q})^2 + 2 J_m^2 \bar{m}^2}. \] (16)

From the free-energy, we obtain the following coupled equations for the order parameters \( \bar{m} \) and \( \bar{q} \):

\[ \bar{m} = -2 J_m \bar{m} \frac{\sinh \beta C}{C \exp[\beta(1 - 18 J_q \bar{q})/2] + 2 \cosh \beta C}, \] (17)

and

\[ \bar{q} = \frac{1 \cosh \beta C + (1 + 6 J_q \bar{q})/(2 C) \sinh \beta C - \exp[\beta(1 - 18 J_q \bar{q})/2]}{\exp[\beta(1 - 18 J_q \bar{q})/2] + 2 \cosh \beta C}. \] (18)

Before solving equations (17) and (18) numerically, we describe a few limits where it is possible to study these equations analytically. There is no solution other than the trivial
\( \bar{m} = 0 \) and \( \bar{q} = 0 \) if \( J_m < -1/2 \) and \( J_q = 0 \). A pure magnetic phase \((\bar{m} \neq 0, \bar{q} = 0)\) does not exist, but a pure quadrupolar phase \((\bar{m} = 0, \bar{q} \neq 0)\) exists for \(|J_m| < (1 + 3J_q)/2\) and \(J_q \neq 0\). In that phase, for \( T << \Delta \) one has \( \bar{q} \approx 0.5 \tanh (6\beta J_q \bar{q}) \), which implies the quadrupolar degrees of freedom are playing the role of a pseudospin 1/2. In this regime, a second-order critical line appears at \( t_{eq} \approx 3J_q \). The other regimes of Equations (17) and (18) are studied numerically. The next section discusses the phase diagram obtained by studying the stabilities of the solutions \( \bar{m} \) and \( \bar{q} \) for different temperatures and values of the coupling coefficients \( J_m \) and \( J_q \).

### B. Phase Diagrams

Fig. 2 shows the phase diagram of the model defined by Eq. (11). The main features of this diagram are the enhancement of the critical temperature and the interchange between first and second-order transitions when the quadrupolar coupling \( J_q \) is introduced.

We first consider the case when \( J_q = 0 \). Both order parameters, \( \bar{m} \) and \( \bar{q} \), are critical simultaneously and despite the fact that we do not have quadrupolar coupling in this case, the ground state described by the Hamiltonian \( H \), Eq. (11), has quadrupolar degrees of freedom and for different temperatures the stability of this ground state against the intersite magnetic coupling causes the tricritical point (denoted by TP), separating the first-order and second-order transitions. The coordinates of this tricritical point are \( J_m = -1.05 \) and \( t_c = 0.300 \). The line of second order is obtained from the limit \( \bar{m} \) and \( \bar{q} \) going to zero in Eq. (17) and Eq. (18) and is given by: \( e^{\beta_c} = (J_m - 1/2)/(J_m + 1) \). Near this line \( \bar{m} \) follows the usual \((t_c - t)^{1/2}\) behavior characteristic of the order parameter in mean-field theory; \( \bar{q} \) is proportional to \( \bar{m}^2 \), which is characteristic of the secondary order-parameter. The first-order line extends from the tricritical point to \( J_m = -1/2 \); below this point no order is found for either \( \bar{m} \) or \( \bar{q} \).

For non-zero \( J_q \) we have simultaneously first-order transition for both order parameters only above the critical-end-point, denoted CEP in Fig. 2. Below this point the transitions are
separated in one line of second-order, purely quadrupolar transition at \( t_{cq} = 6J_q/(2 + e^{-1/t_{cq}}) \), and another line of first-order purely magnetic transition. This latter line has a tricritical point, denoted TP, becoming second-order below this point and finishing at \( t = 0 \) and \( J_m = -(1 + 3J_q)/2 \); below this value of \( J_m \) one has only quadrupolar order. In Table I we have listed positions of the points CEP and TP for a few values of \( J_q \). Fig. 3 shows typical behavior of both order-parameters with temperature, in different parts of the phase diagram.

Besides changing the values of the critical temperatures and separating the phases below the CEP, the intersite quadrupolar coupling has a more dramatic effect on the phase diagram, inverting the nature of the phases with respect to the TP: the first-order transition occurs below the TP when \( J_q = 0 \), and exactly the opposite occurs when \( J_q \neq 0 \). We believe this complicated effect of the indirect magnetic-quadrupolar coupling generated by the Hamiltonian Eq. (10) exists even for a very small quadrupolar coupling. This is confirmed by Landau’s mean field theory, which is discussed in the Section IV.

C. Specific-Heat Jumps

Table II shows numerical calculations of the value of the specific heat jumps, \( \Delta C \), for the second-order magnetic transitions for different quadrupolar coupling \( J_q \). For zero \( J_q \), \( \Delta C \) is never less than \( 6J/\text{mol} - K \). For non-zero \( J_q \), \( \Delta C \) is a very sensitive function of \( J_m \), giving values of \( \Delta C \) around \( 2J/\text{mol} - K \) for \( J_q = 0.05 \), and \( J_m = -0.6 \), which is the experimental value of \( \Delta C \) for the compound \( U_{1-x}\text{Th}_x\text{Pt}_3 \). For these \( J_m \) and \( J_q \), and considering that the Neel temperature is equal to \( 6K \) for this compound, the model also gives the value of energy splitting \( \Delta \) of the crystal field as \( 70K \), which is the order of magnitude expected for this material. Naturally we will have corrections to the specific-heat jump when including explicitly the interaction with the conduction-band electrons. If these corrections are not too large, the model shows that a very small quadrupolar coupling, about one order of magnitude smaller than the magnetic coupling, is necessary to obtain the magnitude of the
IV. LANDAU’S MEAN-FIELD THEORY

Contrary to the previous section, which treated the molecular-field-theory free energy exactly, now we want to use the Landau’s mean field theory, which is valid in the limit of small order parameters, i.e., near a second-order transition. This theory, although limited, can describe some of the features of the phase diagrams.

A. Free Energy

The Landau’s mean-field theory uses an approximation for the free energy, valid near the region where the order parameters \( \bar{m} \) and \( \bar{q} \) are small. Expanding the free energy given by Eq. (15) around \( \bar{m} = 0 \) and \( \bar{q} = 0 \) we have:

\[
\begin{align*}
    f &= \alpha_m \bar{m}^2 + \beta_m \bar{m}^4 + \gamma_m \bar{m}^6 + \alpha_q \bar{q}^2 + \beta_q \bar{q}^4 + \delta_{mq} \bar{m}^2 \bar{q} + \epsilon_{mq} \bar{m}^2 \bar{q}^2 + \ldots ,
\end{align*}
\]

where the coefficients are functions of the temperature \( t \) and of the couplings \( J_m \) and \( J_q \). They are listed in Table II.

For \( J_q = 0 \), only the three first terms on the right hand side of Eq. (19) survive and the critical temperatures for second-order transitions are obtained from the equation \( \alpha_m(t_c, J_m) = 0 \), whose solutions agree with the numerical results. The coefficient \( \beta_m(t, J_m) \) is negative (positive) for temperature less (greater) than 0.30032, and \( \gamma_m \) is positive (negative) for temperature less (greater) than 0.46370, for all \( J_m \). That means we have first (second) order for critical temperatures less (greater) than 0.30032. The point where both coefficients, \( \alpha_m \) and \( \beta_m \), vanish simultaneously determines the tricritical point (TP) and that is at \( t_{\text{TP}} = 0.30032 \) and \( J_{m\text{TP}} = -1.07140 \), also in agreement with the phase diagram Fig. (2).

The quadrupolar-coupling \( J_q \) complicates the analysis of the free energy Eq. (19). Now, the second-order magnetic transition (dashed line in Fig. 2) has non-zero quadrupolar order-parameter \( \bar{q} = q_0 \), so the free energy in fact should be written as
\[ f = \alpha_m'(t, J_m, q_0)m^2 + \beta_m'(t, J_m, q_0)m^4 + \ldots, \]  

where \( q_0 \) is the equilibrium value of \( \bar{q} \) on the critical line \( (\bar{m} = 0) \), and is given by \( q_0 = \left(-\alpha_q/2\beta_q\right)^{1/2} \). The critical temperature for the magnetic transition now is the solution of \( \alpha_m'(t, J_m, q_0) \approx \alpha_m + \gamma q_0 + \delta q_0^2 + \ldots = 0 \), which gives \( t_c \) close to the numerical results, mainly near (but at left of) the tricritical point where \( q_0 \) is not too big. To calculate \( \beta_m' \) needs some care. Using the expansion (19) \( \beta_m' \) will have divergent terms at \( t_{cp} \), which invalidate its expansion around the tricritical point since this point occurs always near \( t_{cp} \).

For \( J_q = 0 \) those terms do not exist and \( \beta_m' = \beta_m \). We have computed \( \beta_m' \) through its definition: \( \beta_m' = (\partial^4 f/\partial m^4)/4! \), calculated at \( \bar{m} = 0 \) and \( \bar{q} = q_0 \), where \( q_0 \) is obtained from the numerical solution of the Eq. (17) and Eq. (18). \( \beta_m' \) showed no divergence and, although \( \beta_m \) can be negative, \( \beta_m' \) is positive for \( t \leq t_{TP} \), which explains why we have a second-order transition when \( J_q \neq 0 \) instead of a first-order one when \( J_q = 0 \). Unfortunately, Landau’s mean-field theory does not work well right above the tricritical point TP since \( \bar{m} \) does not go to zero, and in fact \( \bar{m} \) has a big jump at the critical temperature and so \( \bar{q} \) has a discontinuity at this line (see Fig. 3e). For large \( J_m \), however, the jumps in both order parameters at the critical line become small, thus the expansion (19) gives a reasonable description of the model in this limit.

V. SUMMARY AND CONCLUSIONS

We have calculated the phase diagram of a simple model which includes intersite quadrupolar coupling between uranium ions in the hexagonal lattice. The model has some of the physics found in the hexagonal uranium-based materials, like the in-plane van Vleck magnetism, magnetic character along the c-axis and degrees of freedom to allow the possibility of quadrupolar-Kondo effect. We have shown that the intersite quadrupolar coupling between uranium ions enhances the critical temperature and plays the fundamental role in defining the nature of the transitions in the phase diagram.

Based on the magnitudes of the specific-heat jumps and the magnetic moment \( \bar{m} \) given
by the model around the tricritical point (TP) when $J_q$ is of order $|J_m|/10$, we speculate this region as most probable to find the hexagonal uranium-doped compounds. We are performing a model calculation based on the Coqblin-Schrieffer [10] formalism to determine whether this coupling constant ratio can be realized in practice.

Naturally, the model defined here represents just the first step in the development of a model for the antiferromagnetic transition in U-heavy-fermion materials. We should next introduce explicitly the conduction electrons, in hence the Kondo effect. The natural question is what features of the mean-field phase diagram will survive. The structure of the phase diagram near the tricritical point for non-zero $J_q$ appears essentially due to the terms $\delta_{mq}\bar{m}^2\bar{q}$ and $\epsilon_{mq}\bar{m}^2\bar{q}^2$ in the free-energy, Eq. (15), generated by the Hamiltonian (11). Gufan et al. [9] using Landau’s mean-field theory have analysed the phase diagram of a free energy of the form given by (19), and they also found the same topology we have around the multicritical points. Those terms in our model are always present as long as we have ferroquadrupolar coupling and the hexagonal symmetry.

The Kondo effect will not alter the structure of the Ginsburg-Landau free energy which is dictated purely by symmetry considerations. However, will renormalize the GL coefficients. We don’t expect the phase diagram to be strongly modified in the absence of intersite quadrupolar coupling, since the physics of the magnetic susceptibility remains that of van Vleck with only slight modification of the low temperature values relative to the case of zero Kondo temperature. However, once we turn on intersite quadrupolar coupling, we will dramatically renormalize the coefficients. In particular, wherever a $1/T$ appears, in our expressions, we realize that at a first pass this is the single-site quadrupolar susceptibility of the U ions, and given the quadrupolar Kondo effect, which is two-channel, this will diverge logarithmically [12]. Using the single site susceptibility of the two-channel model as a guide, we will effect the replacements $\delta_{mq} \approx 1/T \rightarrow 1/T_K \ln(T_K/T)$ and $\epsilon_{mq} \approx 1/T \rightarrow 1/T_K \ln(T_K/T)$ where $T_K$ is the Kondo temperature. This will not remove the second-order quadrupolar and magnetic transitions in our phase diagram, but will renormalize the transition temperatures downwards. As a result of this we anticipate that we may
obtain similar reduced moment values and specific heat jumps to UPt$_3$ with larger intersite quadrupolar couplings.

In addition to this exploration of how the Kondo effect modifies our already interesting results, we would like to explore the effects of magnetic field through magnetostrictive coupling to see whether we can understand the metamagnetic transition observed in pure UPt$_3$ below 20K in fields of order 20T [11].

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### TABLE I. Coordinates of the tricritical points (TP) and critical end points (CEP) in the phase diagram of the Fig. 2, for different quadrupolar coupling $J_q$.

| $J_q$ | $t_{TP}$ | $-J_m^{TP}$ | $t_{CEP}$ | $-J_m^{CEP}$ |
|-------|----------|-------------|-----------|-------------|
| 0.    | 0.30     | 1.06        | —         | —           |
| 0.05  | 0.12     | 0.64        | 0.14      | 0.70        |
| 0.1   | 0.27     | 0.79        | 0.29      | 0.83        |
| 0.2   | 0.52     | 1.01        | 0.55      | 1.10        |

### TABLE II. Coefficients of the expansion of the free energy defined in Eq. (19). Here $d = (2e^{\beta/2} + e^{-\beta/2})^{-1}$.

\[
\begin{align*}
\alpha_m &= -4d J_m^2 \sinh \beta/2 - J_m \\
\beta_m &= 2d^2 J_m^4 [(2 - \beta)e^\beta - 5\beta - 1 - e^{-\beta}] \\
\gamma_m &= 8J_m^6 (3\beta^2d^3 - 4d) \sinh[\beta/2] + 8J_m^6 \beta d^2 (5 + e^\beta) \\
\alpha_q &= 6d J_q e^{\beta/2} (2 + e^{-\beta} - 6J_q \beta) \\
\beta_q &= 108d^2 J_q^4 \beta^3 (4e^\beta - 1) \\
\delta_{mq} &= 12d J_m^2 J_q (\beta e^{\beta/2} - 2 \sinh \beta/2) \\
\epsilon_{mq} &= 36d^2 J_m^2 J_q^2 (4\beta e^{\beta/2} - 4e^{\beta/2} - 3\beta^2 + 2\beta + 2e^{-\beta})
\end{align*}
\]
TABLE III. Specific-heat jumps $\Delta C$ of the second-order magnetic transitions on the phase diagram Fig. 2, for a few values of the quadrupolar coupling $J_q$. The magnetic coupling $J_m$ are near the minimum value to give second-order transitions.

| $J_q$ | $-J_m$ | $\Delta C$ |
|-------|--------|------------|
| 0.00  | 1.10   | 6.52       |
| 0.05  | 0.60   | 1.50       |
| 0.1   | 0.68   | 0.92       |
| 0.2   | 0.85   | 1.31       |
FIGURES

FIG. 1. Level structure of the model considered in this work. The doublet ground-state \(|E\pm\rangle = u|\pm 4\rangle + v|\mp 2\rangle\) is magnetic coupled to a singlet excited-state \(\sqrt{2}|B\rangle = |3\rangle + |-3\rangle\), which has energy \(\Delta\). Here \(|m\rangle\) is the eigenstate of the z-component of the total angular momentum \(J = 4\). The other \(D_{6h}\) crystal-field levels are not included, thus restricting the model to temperatures less than \(\Delta\).

FIG. 2. Mean-field phase diagram of the model defined by the Hamiltonian Eq. (11). \(J_m\) and \(J_q\) are the dimensionless magnetic and quadrupolar coupling between the nearest-neighbouring sites, respectively, and \(t_c \equiv k_BT_c/\Delta\) is the dimensionless critical temperature. At right of the critical end point (denoted by CEP), both order parameters have the same critical temperatures. At left, the transitions are separated into one pure second-order quadrupolar (horizontal straight line) and one pure first-order magnetic transition (dashed line). This last one ends at the tricritical point (denoted TP) where a line of second-order magnetic transition begins and ends at \(t = 0\) and \(J_m = -0.5(1 + 3J_q)\). The quadrupolar coupling enhances the critical temperature \(t_c\), increases the absolute value of the minimum magnetic coupling \(J_m\) necessary to have magnetic order, and reverses the nature of the phase transitions respect to the tricritical point.

FIG. 3. Temperature dependence of the magnetic moment \(\bar{m}\) and quadrupolar moment \(\bar{q}\), obtained from Eq. (17) and Eq. (18). The temperatures on the x-axis are measured in units of the crystal-field splitting \(\Delta\), and are not in the same scale; the units of all other quantities are defined in the text. For \(J_q = 0\), Fig. (a), (b) and (c) \(\bar{q}\) has the same critical temperatures as \(\bar{m}\), and behaves like a secondary order-parameter. For \(J_q = 0.1\), Fig. (d), (e) and (f) the quadrupolar transitions are separated from the magnetic ones, except for \(|J_m| > |J_{ME}^{C}\rangle = 0.83\). For the same value of \(J_m\) the nature of the phase transitions changes according to whether \(J_q\) is present or not. No magnetic order is found without quadrupolar order.