Phase Diagram of the Heavy-Fermion Superconductor UPt_3

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A phenomenological free energy which includes a novel coupling between vector superconducting and magnetic order parameters is deduced for UPt_3. Analysis of this free energy leads to a phase diagram in the H-T plane in agreement with experiment, and identifies the symmetry of the different phases. Some further experiments are suggested.

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Soon after the discovery[1] of superconductivity in heavy-fermion compounds, it was suggested[2] that this superconductivity could not be of the conventional s-wave symmetry and experiments were suggested to look for alternatives. Shortly thereafter, ultrasonic attenuation α_s measurements[3] in UPt_3 were shown to be inconsistent with conventional pairing with a gap on the entire Fermi surface. Especially persuasive were experiments[4] which revealed that in the superconducting phase, the temperature dependence of transverse sound attenuation with **q** in the basal plane (of the hexagonal crystal UPt_3) was different for polarization in the basal plane ($\sim T$) from that for polarization along the c axis ($\sim T^2$). In the normal state the two were identical. Thus the symmetry of the ultrasonic tensor was different in the normal and the superconducting phase.

These experiments could be understood[5] on the basis of superconducting states with gap functions that have zeros on the Fermi surface along lines in the basal plane. Group-theoretical analysis[6] revealed that such states were not allowed in the triplet-odd-parity manifold of states. The (lowest-dimensioned) superconducting states with lines of zeros are the singlet "d-wave" states which in a hexagonal crystal have the basis,

$$\text{class I: } k_z k_y,\ k_z k_x; \quad \text{class II: } k_x k_y,\ k_x^2 - k_y^2 . \tag{1}$$

The two classes can be treated in parallel. In this basis set, the superconducting order parameters allowed are

$$\eta = \eta_1 \equiv (10), \quad \eta_2 \equiv (01) . \tag{2}$$

The interpretation of the ultrasound experiments requires nodal lines of the gap in the basal plane. This means class I in (1) is favored. The analysis below can, however, be done either with class I or II.

The d-wave superconducting (SC) states were found[7] to be favored if superconductivity was promoted by antiferromagnetic (AFM) fluctuation. Strong AFM fluctuations have been discovered in UPt_3 through inelastic-scattering experiments.[8] These experiments reveal that UPt_3 also has an AFM transition at $T_N \simeq 5$ K, far above the superconducting transition temperature, $T_c \simeq 0.5$ K. The ordered staggered moment is surprisingly small ($\approx 0.02\mu_B$) and the magnetic structure is longitudinal, and as shown in Fig. 1. Ultrasound and torsional-oscillator measurements[9] have since suggested that there are several distinct phases in the B-T plane in the superconducting AFM state. Recently, two distinct specific-heat anomalies in the B-T plane have been identified[10] in high-quality crystals of UPt_3. Complementing these is the discovery[11] that the AFM order changes along the newly discovered phase boundaries. The intensity of the $(1,\frac{1}{2},0)$ reflection in neutron-scattering experiments decreases at the lower transition. In view of the smallness of the ratio T_c/T_N, moment reduction is improbable and this reduction is most likely due to a reorientation of the ordered moments. The simplest reorientation would involve simultaneous rotation through an angle θ of all spins in the ordered structure of Fig. 1(a). This is equivalent to the addition of a transverse component [as in Fig. 1(b)] to the ordered structure, and a concomitant reduction in the longitudinal component. Further experiments to test this interpretation will be to study other superlattice peaks whose wave vectors **q** are induced at other angles ϕ with respect to the ordered moments. For example, from the dipole selection rules, the $(\frac{1}{2},0,0)$ intensity is proportional to $\sin^2\phi$, which implies that a Bragg peak forbidden for the purely longitudinal structure would become allowed when $m_t \neq 0$.

Several discussions of the phase diagram of UPt_3 ap-

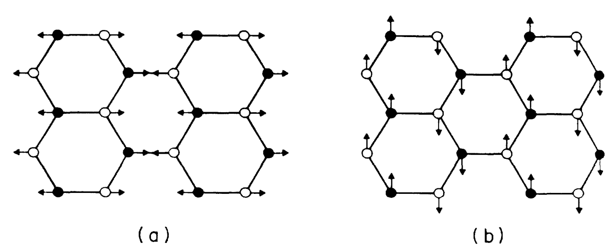

FIG. 1. (a) The longitudinal antiferromagnetic structure m_l observed in Ref. 11 below 5 K. (b) The transverse antiferromagnetic structure m_t. The measurements of Ref. 11 are consistent with an admixture of m_l and m_t to the left of the dashed line in Fig. 2(a).

peared.[12,13] In particular, Joynt pointed out that, in the presence of AFM order, two superconductive transitions can occur at $B=0$. This and subsequent work does not consider possible change of the symmetry of the AFM together with the change of superconductive symmetry. In this framework a phase diagram in the B-T plane with B in the a-b plane with three distinct phases as reported[9,10] cannot be obtained.[14] We have found that the special features of d-wave superconductive symmetry and basal-plane AFM order in a hexagonal crystal allow an unusual invariant in the free energy. Analysis with such an invariant leads to the observed phase diagram and an identification, different from previous work, of the superconductive and AFM symmetry of each phase.

The symmetry of UPt_3 below T_N with the AFM structure of Fig. 1(a) is orthorhombic. Therefore, η_1 and η_2 no longer form a 2D irreducible representation; rather, each is a 1D representation and one of them will become unstable at a higher temperature than the other. The AFM structure in the low-temperature–low-field phase is found[11] to have the same **q** vector as the high-temperature–high-field longitudinal phase which we denote by m_l. Given the large anisotropy in UPt_3, which confines the spins to the plane, the simplest structure consistent with observations[11] is a rotation, by an angle θ, of all the ordered moments. Equivalently the ordered structure acquires a transverse component, and, in general, can be written as $\alpha m_l+\beta m_t$ $(|\alpha|^2+|\beta|^2=1)$. Figure 1(b) shows the pure transverse structure m_t. Given the basis vectors η_1, η_2, m_l, and m_t, the free energy (in the absence of an external field) has the form

$$F=F_{SC}+F_M+F_{SC\text{-}M}\,, \tag{3}$$

$$F_{SC}=\frac{\alpha}{2}|\eta|^2+\frac{\beta_1}{4}|\eta|^4+\frac{\beta_2}{4}|\eta^2|^2\,, \tag{3a}$$

$$F_M=\frac{a_l}{2}m_l^2+\frac{a_t}{2}m_t^2+\frac{b_l}{4}m_l^4+\frac{b_t}{4}m_t^4+b_{lt}m_l^2m_t^2\,, \tag{3b}$$

$$F_{SC\text{-}M}=(d_{1l}|\eta_1|^2+d_{2l}|\eta_2|^2)m_l^2+(d_{1t}|\eta_1|^2+d_{2t}|\eta_2|^2)m_t^2+d_3(\eta_1^*\eta_2+\eta_2^*\eta_1)m_lm_t\,. \tag{3c}$$

The free energy actually has full hexagonal symmetry, but Eq. (3) has been written in a form adapted to the orthorhombic symmetry of the AFM phase. This structure has a single **q** vector, but there are two others equivalent by symmetry. There are quartic terms in the free energy which are products of m_l's with two different q's which pick out the single **q** structure. These and analogous terms with m_t's have been omitted from F, since we take the AFM structure above T_{c1} as given.

With just one magnetic order parameter (m_l or m_t), this form of the free energy has been written down before.[13] With both m_l and m_t there appears, besides the obvious new terms, the very interesting third term in $F_{SC\text{-}M}$. As we shown below, it is crucial in determining the phase diagram. This unusual term, *linear* in two different symmetries of superconductivity and two different symmetries of AFM, is allowed for the following reason. First, m_l and m_t are assumed to be of the same wave vector, as observed. So their product is invariant under the operations of spin flip or translation. Second, they lie in the basal plane, so that reflection about the x-z or the y-z plane changes the sign of one of them but not the other. But this reflection changes the sign of either the superconductor basis vector k_zk_x or k_zk_y. Thus the complete term is an invariant

With (3), we are interested in studying the region below T_N where $m_l\neq 0$. Choose $d_{1l}<d_{2l}$ so that η_1 becomes nonzero first, at T_{c1}. The terms in (3) second order in η_2 and m_t are

$$\frac{\tilde{a}_2}{2}\eta_{2r}^2+\frac{\tilde{a}_{2i}}{2}\eta_{2i}^2+\frac{\tilde{a}_t}{2}m_t^2+2d_3m_lm_t\eta_1\eta_{2r}\,, \tag{4}$$

where

$$\tilde{a}_2=\alpha+(\beta_1+\beta_2)\eta_1^2+d_{2l}m_l^2\,, \tag{4a}$$

$$\tilde{a}_{2i}=\alpha+(\beta_1-\beta_2)\eta_1^2+d_{2l}m_l^2\,, \tag{4b}$$

$$\tilde{a}_t/2=a_t/2+b_{lt}m_l^2+d_{1t}\eta_1^2\,. \tag{4c}$$

We have chosen η_1 to be real and separated η_2 into its real, η_{2r}, and imaginary, η_{2i}, parts. η_{2i} here, and later with a magnetic field, is uncoupled to other variables in the linearized problem. From (4) we immediately get a *second transition at T_{c2} where both η_{2r} and m_t are simultaneously nonzero.* T_{c2} is given by

$$\tilde{a}_2\tilde{a}_t=(2d_3m_l\eta_1)^2\,. \tag{5}$$

Below T_{c2} superconductivity thus occurs with the order parameter $\eta_1+\delta\eta_2$. Simultaneously antiferromagnetism occurs with $m_l+\epsilon m_t$. The relative magnitude of $\delta(T)$ and $\epsilon(T)$ can be determined from the fourth-order terms.

Above we have taken $\beta_2<0$ so that at the second transition $\eta_{2r}\neq 0$ and $\eta_{2i}=0$. With the opposite assumption, $\beta_2>0$, which is predicted by weak-coupling theory, one would have $\eta_{2i}\neq 0$ at the second transition unaccompanied by any change in the symmetry of the AFM order. The experimental evidence seems to favor $\beta_2<0$. It enables, see below, the detailed phase diagram to be obtained (see, however, Ref. 14).

A principal experimental result,[11] that at the second superconducting transition, the AFM order simultaneously changes, is thus explained through the last term in

$F_{SC\text{-}M}$. Previous suggestions[13] for the observed transitions at $B=0$ have been that *hexagonal* UPt_3 *by itself* might have parameters such that the phase $\eta_3 \equiv \eta_1 + i\eta_{2i}$ is favored but that a symmetry-breaking field (AFM order) might, near T_{c1}, force the η_1 or η_2 phase. At low enough temperature, higher-order terms in η may conspire to force the transition to a linear combination of η_1 and η_2 and ultimately towards the η_3 phase. This scenario requires $\beta_2 > 0$.

Consider next the phase diagram in a magnetic field. As usual, we add to the free energy, Eq. (3), the gradient terms appropriate for hexagonal symmetry,[12,13]

$$F_V = \int d^3r\, \kappa_1 |p_i \eta_j|^2 + \kappa_2 (p_i\eta_i)(p_j\eta_j)^* + \kappa_3 (p_i\eta_j)(p_j\eta_i)^* + \kappa_4 |p_z \eta_i|^2 , \tag{6}$$

where $p_i = \partial_i - i2eA_i/c$ and $\mathbf{A}$ is the vector potential.

The linearized Ginzburg-Landau equations following from (3) and (6) are

$$(\alpha_1 + \kappa_{123}p_x^2 + \kappa_1 p_y^2 + \kappa_4 p_z^2)\eta_1 + (\kappa_2 p_x p_y + \kappa_3 p_y p_x)\eta_{2r} = 2d_3 m_l m_t \eta_{2r} , \tag{6a}$$

$$(\kappa_3 p_x p_y + \kappa_2 p_y p_x)\eta_1 + (\tilde{\alpha}_2 + \kappa_1 p_x^2 + \kappa_{123} p_y^2 + \kappa_4 p_z^2)\eta_{2r} = 2d_3 m_l m_t \eta_1 . \tag{6b}$$

Here $\kappa_{123} = \kappa_1 + \kappa_2 + \kappa_3$. The equation for η_{2i} remains uncoupled from the other variables. Here $\alpha_{1,2} = \alpha + d_{1,2l} m_l^2$.

These equations must now be solved together with the equation obtained from (4) by minimizing with respect to m_t. This assumes that a magnetic field (below H_{c2}) causes no reorientation of the AFM structure. This is certainly true with the field applied in the z direction; the anisotropy pinning the staggered moment to the basal plane is much too large. So far, there is no evidence[15] that fields less than 15 kG applied in the basal plane lead to any spin reorientation either. Were such an effect to occur, it is straightforward but messy to include in the analysis to follow.

Here we shall present only the results of the analysis of Eqs. (6a), (6b), and (4). First we consider the case with B parallel to the z axis. Then the diagonal terms of (6) lead[13(b)] to two equally spaced Landau ladders, with energies $\alpha_1 + (n_1 + \frac{1}{2})\hbar\omega$ and $\alpha_2 + (n_2 + \frac{1}{2})\hbar\omega$, where $\omega = B(\kappa_1\kappa_{123})^{1/2}$. In this approximation, the ground-state energy is $\alpha_1 + \hbar\omega/2$, since $\alpha_1 < \alpha_2$. This state is coupled, by matrix elements proportional to B, to the states in the other ladder with even n_2. This coupling leads to a term in the ground-state energy of the form $-cB^2/(\alpha_2 - \alpha_1)$, where c involves a sum over all even n_2. The interladder coupling also leads to an admixture, of order B, of η_{2r} in the order parameter.

When the temperature decreases further, there comes a point at which

$$\tilde{\alpha}_2 - \frac{4d_3^2 m_l^2 \eta_1^2}{\tilde{\alpha}_t} + \frac{\hbar\omega}{2} = 0 . \tag{7}$$

At this point, if $B=0$, as discussed, η_{2r} appears spontaneously as a new order parameter. When $B \neq 0$, this is not a true phase transition, since η_{2r} is already finite at higher temperatures, but (7) defines a region where η_{2r} (and m_t) increases rapidly with decreasing T at constant B; see Fig. 2(a). When η_1 is not too large, (7) describes a curve which is, in general, not parallel to $H_{c2}(T)$. This is as observed. We suggest that the feature in the specific heat along (7) should decrease as B is increased.

In transverse field the situation is somewhat different. If this field is parallel or perpendicular to m_l, in most cases the magnetic field does not mix η_1 and η_2. With the field in the m_l direction, the critical field is given[13(b)] by either

$$\alpha_1 + \frac{B\sqrt{\kappa_1\kappa_4}}{2} = 0 \quad \text{or} \quad \alpha_2 + \frac{B\sqrt{\kappa_{123}\kappa_4}}{2} = 0 , \tag{8}$$

while if it is transverse to m_l, we obtain

$$\alpha_1 + \frac{B\sqrt{\kappa_{123}\kappa_4}}{2} = 0 \quad \text{or} \quad \alpha_2 + \frac{B\sqrt{\kappa_1\kappa_4}}{2} = 0 . \tag{9}$$

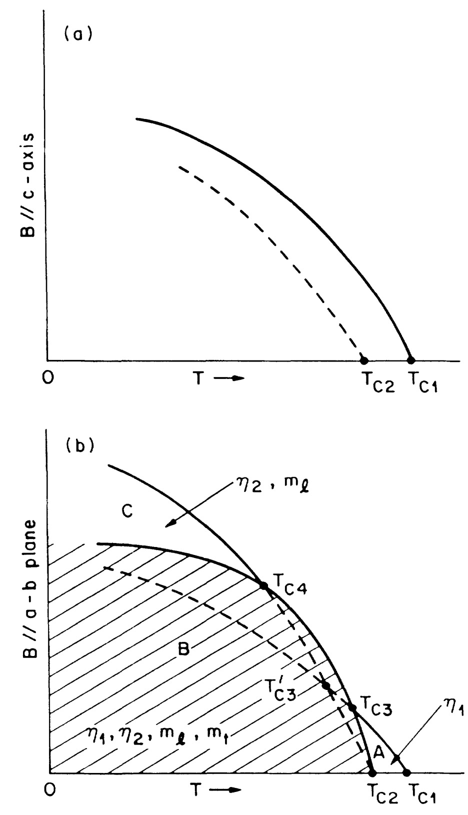

FIG. 2. (a) Phase diagram of UPt_3 with a field applied along the c axis. There is a true second-order phase transition at zero field at T_{c1} and T_{c2} but at finite fields the dashed line emanating from T_{c2} marks a crossover. (b) Phase diagram of UPt_3 with field in the basal plane with the field along m_l. A is a phase of η_1 and m_l, B of η_1, η_2, m_l and m_t, and C is likely to be a phase of η_2 and m_l. The line from T_{c3} to T_{c4} most likely marks first-order phase transitions.

In one of these cases, the two lines cross at

$$B=|\alpha_2-\alpha_1|/|\sqrt{\kappa_1\kappa_4}-\sqrt{\kappa_{123}\kappa_4}|$$

and yield a discontinuity in slope of H_{c2} vs T. We call this point T_{c3}; see Fig. 2(b).

The lower transition, which in this case remains a true transition, is now given by

$$\tilde{\alpha}_2-\frac{4d_3^2m_l^2\eta_1^2}{\tilde{a}_t}+\frac{B\sqrt{\kappa_4\kappa}}{2}=0\,, \tag{10}$$

where κ is κ_1 or κ_{123}. This will meet the H_{c2} line at the change of slope. Equation (10) gives the boundary of the mixed phase $(m_l+\epsilon m_t)$, $\eta_1+\delta\eta_{2r}$.

We have examined the character of the H_{c2} curve below T_{c3} and find that it may well be a first-order phase transition. This arises from the fact that due to the last term in (3c) a third-order term in the free energy arises and with small α_1,α_2 (which are experimentally established) and a_t (plausible from the appearance of m_t) a first-order transition to a phase with η_1,η_2 and m_t all nonzero could occur at a higher temperature than any of three possible second-order transitions.

The experimental results[9,10] indicate another line of transitions with field in the basal plane, shown beginning at T_{c4} in Fig. 2(b). [In Ref. 10(b) T_{c3} is drawn coincident with T_{c4}. This is not allowed except accidentally.] The most natural explanation is that at T_{c4} in Fig. 2(b) a transition to a phase with $\eta_1=0$, $\eta_2\neq0$ occurs. T_{c4} is given by the intersection of the line $\alpha+B(\kappa\kappa_4)^{1/2}/2=0$ with the critical field line for large B emanating from T_{c3}. This intersection must occur since phase B in Fig. 2(b), being a mixture of η_1 and η_2, has a smaller critical field than the pure phase η_2. This implies $m_t=0$ in this phase; further diffraction experiments are suggested to test this.

With the magnetic field perpendicular to m_l, the slope of the phase boundary emanating from T_{c1} is larger than that from T_{c2}. So only the A and the B phases are expected. In general, due to domain formation, a sample may have both kinds of phase boundaries.

It should be noted, in connection with interpretation of transport measurements, that due to the coupling of AFM and SC the gap structure of the quasiparticle excitation spectrum is not given either by the gap structure of SC or by that of AFM alone.

In summary, we find that the specific symmetry features of the d-wave-type order parameters, Eqs. (1) and (2), together with the coupling to antiferromagnetism with the specific symmetry features of m_l and m_t shown in Fig. 2 enable a complete understanding of the observed phase diagram in UPt_3 and provide an identification of the different phases. Some predictions for future experiments have also been made. The experimental results plus the analysis presented here and elsewhere[5,7,13] effectively seals the case for the heavy-fermion superconductor UPt_3 as an unconventional d-wave-type superconductor strongly coupled to antiferromagnetism.

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[14]In Fig. 2 of Ref. 13(b), a speculated phase diagram with B in the a-b plane is drawn with only two distinct phases made to resemble the experimental results of Refs. 9 and 10(b) which are consistent, as claimed by their authors, with three distinct phases, as in Fig. 2 here.

[15]R. N. Kleiman (private communication).