Phase Diagram of UPt_3 in the E_{1g} Model

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(Received 28 November 1994)

The phase diagram of the unconventional superconductor UPt_3 is explained under the long-standing hypothesis that the pair wave function belongs to the E_{1g} representation of the point group. The main objection to this theory has been that it disagrees with the experimental phase diagram when a field is applied along the c axis. By a careful analysis of the free energy, this objection is shown to be incorrect. This singlet theory can also explain the unusual anisotropy in the upper critical field curves, often thought to indicate a triplet pair function, given that the in-plane susceptibility is Van Vleck-like and the out-of-plane susceptibility is Pauli-like.

PACS numbers: 74.70.Tx, 74.20.De, 74.25.Dw

Unconventional superconductivity is a state of matter under intense discussion at the present time, in both high-T_c materials [1] and the older heavy fermion superconductors. In this latter class of materials the most studied and best characterized is UPt_3. The d-wave E_{1g} state was originally proposed as the pairing symmetry on microscopic grounds [2]. It posits a two-component gap function which transforms as $(k_x k_z, k_y k_z)$ with corresponding line nodes where the Fermi surface intersects the plane $k_z = 0$ and point nodes where it intersects the line $k_x = k_y$. Evidence for this specific pattern of nodes comes, for example, from ultrasound [3] and heat conduction [4] experiments. E_{1g} also explains the pressure dependence of the phase diagram [5]. E_{1g}, along with other two-dimensional representations of D_{6h}, has a two-component order parameter (OP). This leads to a number of unusual predictions which have been confirmed by experiment, for example, the split transition in specific heat measurements [6] and the kink in the lower critical field curve [7]. A two-component OP is usually (though not always [8]) accepted for UPt_3.

In spite of the fact that E_{1g} has the proper nodal structure and number of components, a number of alternatives have been proposed because of perceived deficiencies of the theory. One objection usually given is that E_{1g} cannot explain the observed phase diagram in the field-temperature (H-T) plane when $\mathbf{H}$ is along the c axis [9]. A second objection to E_{1g}, a singlet theory, is that the upper critical field curve $H_{c2x}(T)$ for $\mathbf{H}$ in the basal plane crosses the curve $H_{c2z}(T)$ for $\mathbf{H}$ perpendicular to the basal plane [10] and that this is characteristic of triplet theories [11]. In this Letter we show that both objections are unfounded.

It has been clear for several years that the E_{1g} theory correctly predicts the exceedingly unusual phase diagram in the H-T plane when $\mathbf{H}$ is in the basal plane [12]. There are three superconducting phases meeting the normal phase at a tetracritical point. Two of these, the A and C phases, are conventional distorted Abrikosov lattices formed by one of the two components of the OP. The third, the B phase, consists of two interpenetrating lattices, one formed by each component. The phases are separated by second-order phase boundaries whose properties (such as the specific heat jump ΔC_V) may be calculated. These conclusions and the conclusions of the present paper follow from the free energy density for the E_{1g} theory:

$$
\begin{aligned}
f = {} & \alpha_0(T - T_x)|\eta_x|^2 + \alpha_0(T - T_y)|\eta_y|^2 + \beta_1(\boldsymbol{\eta}\cdot\boldsymbol{\eta}^*)^2 + \beta_2|\boldsymbol{\eta}\cdot\boldsymbol{\eta}|^2 \\
& + \sum_{i,j=x,y} (K_1 D_i\eta_j D_i^*\eta_j^* + K_2 D_i\eta_i D_j^*\eta_j^* + K_3 D_i\eta_j D_j^*\eta_i^*) + K_4 \sum_{i=x,y} |D_z\eta_i|^2 + (\alpha_0\epsilon\Delta T)(\hbar c/2e) \\
& \times \sum_{i=x,y} (|D_i\eta_x|^2 - |D_i\eta_y|^2) + a_z H_z^2 \boldsymbol{\eta}\cdot\boldsymbol{\eta}^* + a_x(H_x^2 + H_y^2)\boldsymbol{\eta}\cdot\boldsymbol{\eta}^* + a_d|\mathbf{H}\cdot\boldsymbol{\eta}|^2. \qquad (1)
\end{aligned}
$$

Here $\boldsymbol{\eta} = (\eta_x, \eta_y)$ is the two-component order parameter, and K_1, K_2, K_3, K_4, α_0, β_1, β_2, a_x, a_z, a_d, and ϵ are constants. The D's are momentum operators: $D_x = -i\partial/\partial x + (2e/\hbar c)A_x$, and similarly for D_y and D_z. Here $\mathbf{A}$ is the vector potential and $-e$ is the charge on an electron. The coupling of the staggered magnetization to $\boldsymbol{\eta}$ is responsible for the temperature splitting $\Delta T = T_x - T_y$. The existence and need for the term proportional to ϵ and the terms proportional to H^2 were first stressed in the context of a three-component model [13]. The free energy above is, purely from a symmetry point of view, generic to all E representations (E_{1g}, E_{1u}, E_{2g}, and E_{2u}) [14]. However, the cross-coupling terms proportional to K_2 and K_3 are small in the latter cases if basis functions are chosen with the proper nodal structure [15–17]. Since we keep these terms and find they are not small, we refer

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to this free energy as the E_{1g} free energy, and note that our results therefore support this specific representation.

To obtain H_{c2} we need only consider the terms quadratic in $\boldsymbol{\eta}$ in Eq. (1). When the field is in the basal plane, we obtain two separate equations for H_{c2}. These two curves cross, creating the well-known kink in the upper critical field curve. Hence the A and C phases correspond to $\boldsymbol{\eta} \sim (1,0)$ and $\boldsymbol{\eta} \sim (0,1)$. In the B phase we have two flux lattices: one formed by η_x and the other formed by η_y [12]. The singularities of these flux lattices need not coincide. We find that the free energy is minimized for an offset vector for the two lattices which is one-half of a flux lattice basis vector [18].

When $\mathbf{H}$ is in the z direction, the problem of minimizing the free energy is far more difficult to solve. Let ϕ_{nk} be the eigenfunctions of the linear problem. Because the linear H_{c2} equations do not separate into separate equations for η_x and η_y, the ϕ_{nk} have both x and y components. When the OP expanded in terms of the eigenfunctions, $\boldsymbol{\eta} = \sum_{nk} c_{nk}\phi_{nk}$, the free energy F is a quartic polynomial in the coefficients, $F = F(c_{nk})$. Here n is a level index (no longer a Landau level index) and k is the momentum in the y direction. Part of the argument against E_{1g} runs as follows. At H_{c2}, some of the c_{0k} become nonzero. If we examine the fourth-order term $|c_{0k}|^2 c_{0k}^* c_{1k}$, we see that the c_{0k} produce, effectively, a linear term in the c_{1k}. It is then concluded that no second transition consists below H_{c2} in this theory, in conflict with experiment.

However, a more careful analysis of all the possibilities must be carried out. The energy of the OP configuration represented by a single ϕ_{nk} is independent of k. When many k's are present, the minimization of F leads to only some of the c_{0k} becoming nonzero at H_{c2} with the formation of the usual hexagonal lattice: $c_{nk} \sim \delta_{n,0}(H_{c2} - H)^{1/2} C_k$. Let $2\pi/q$ be the periodicity of the flux lattice in the y direction. Then $C_k = 0$ unless $k = mq$, where m is an integer. As usual, $C_k = 1\,(i)$ for $m =$ even (odd). A dangerous fourth-order term in F has the form $\beta^{01}_{k_1k_2k_3k_4} c^*_{0k_1} c_{0k_2} c^*_{0k_3} c_{1k_4}$. Momentum conservation implies that the coefficient $\beta^{01}_{k_1k_2k_3k_4}$ is only nonzero if $k_1 - k_2 + k_3 - k_4 = 0$. For an interpenetrating lattice where the offset vector is one-half of a flux lattice basis vector, k_1, k_2, and k_3 are integer multiples of q, whereas k_4 is half an odd integer times q. Thus the k's never sum to zero and all dangerous terms vanish. The c_{1k}'s for the second lattice never appear in first order or, by a similar argument, in third order. *The second lattice appears by a second-order transition in the E_{1g} theory for all directions of the applied field.* This is in agreement with experiment and in conflict with previous theoretical conventional wisdom. The transition breaks the flux lattice symmetry because the lattice now has a basis.

We have plotted the phase boundaries obtained by minimizing the free energy in the following approximation. The eigenvalues of the linear H_{c2} operator are obtained by a truncation of the infinite matrix. The lowest eigenvalue, which is a function of H and T, gives the H_{c2} curve. The next lowest eigenvalue gives a bare inner transition line. This must be corrected by an effective field term because the existing lattice lowers the transition temperature of the new one. This correction involves only one coupling constant which is obtained by fitting to the data [19]. The result is shown in Fig. 1. We have not attempted to fit the data for $T < 0.4T_c$ since the linear temperature dependence of the first two terms in Eq. (1) breaks down there.

There is no tetracritical point for $\mathbf{H} = H\hat{\mathbf{z}}$; this is due to level repulsion. We regard this as a virtue of the theory, because the experimental data show that to call the phase diagram isotropic is an exaggeration. The H_{c2} curve for $\mathbf{H} = H\hat{\mathbf{z}}$ does not have a kink, only a flat region well reproduced by the theory, and the data are consistent with only two superconducting phases, as the present theory predicts for this field direction. We find that the phase diagram for *both* field directions can be fitted by the same set of parameters, and the only numerical coincidence which arises when this is done is that $K_2 \approx K_3$ [19]. This is actually a consequence of approximate particle-hole symmetry, and the fact that it comes out of the fit is further evidence that the overall picture is correct.

To understand the directional dependence of H_{c2}, it is first necessary to discuss the magnetic susceptibility of UPt_3. This issue is complicated by the fact that all renormalizations involved are not well understood. Since UPt_3 is a Fermi liquid, however, the starting point must be the single-particle states calculated in band theory, which account very well for the Fermi surface [20]. The states near the Fermi surface are predominantly derived from uranium $5f$ orbitals with $j = 5/2$. In the isolated

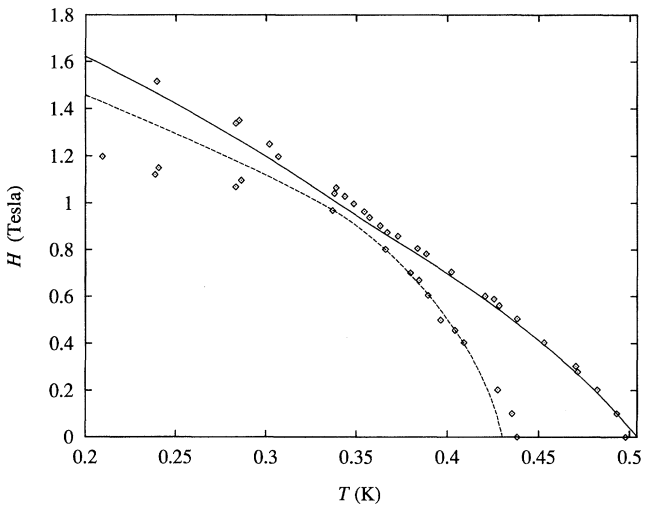

FIG. 1. Phase diagram when the field is in the z direction. The lines are the theoretical fits to H_{c2} (solid line) and the inner transition (dashed line). The data points are from ultrasonic velocity measurements and are taken from Ref. [28], Fig. 3.

atom, these would be 6-fold degenerate. Near the Γ point the hexagonal crystal field splits the 6-fold degenerate state into three doublets: $j_z = \pm 5/2$, $j_z = \pm 3/2$, and $j_z = \pm 1/2$. The splittings can be inferred from bands calculated in the local density approximation. Probably the most accurate to date are the linearized argumented plane wave results of Wang *et al.* [20], which give a splitting of order 0.1 eV and a bandwidth of order twice this. The six (not three, because of the two U atoms in the unit cell) bands constructed from these states cross the Fermi energy. These features of UPt_3 suggest that it is likely to be an example of a system in which the magnetism is Van Vleck-like in the plane and Pauli-like along the c axis, which is expected to be a general feature of hexagonal U-based systems [21].

The average occupation of the $5f$ level is near 2. If we apply a magnetic field, there will be both a Pauli (intraband) and a Van Vleck (interband) contribution to the susceptibility. The former is of order $(g_{\rm eff}\mu_B)^2 N(\varepsilon_F)$, while the latter is of order $(g_{\rm eff}\mu_B)^2/|B_h|$, where B_h is the crystal field splitting. Here $g_{\rm eff}$ is an effective g factor for the coupling of the field to the total angular momentum of the band or bands involved. The Landé factor for $\ell = 3$, $s = 1/2$, and $j = 5/2$ is 6/7.

The Van Vleck susceptibility is the interband susceptibility due to mixing of states $|\alpha\rangle$, $|\beta\rangle$ (say) in different bands. If $\mathbf{H}$ is along the c axis, then the relevant matrix element (with $\hbar = 1$) is

$$|\langle\alpha|L_z + 2S_z|\beta\rangle|^2 = (36/49) j_z^2 \delta_{\alpha,\beta} . \qquad (2)$$

Near the Γ point, where states of different j_z do not mix, then the perturbation introduced by $\mathbf{H}$ is diagonal, and the occupation factors then imply that the Van Vleck susceptibility is zero for this direction. If $\mathbf{H}$ is in the x direction, the corresponding expression for the square of the matrix element is

$$|\langle\alpha|L_x + 2S_x|\beta\rangle|^2 = (36/49)(5/2 - j_z)(5/2 + j_z + 1) \qquad (3)$$

if the states α and β differ by one unit of j_z and is zero otherwise. The Van Vleck susceptibility comes from four distinct pairs of states: $(j_z = -5/2, -3/2)$, $(-3/2, -1/2)$, $(1/2, 3/2)$, and $(3/2, 5/2)$, whenever one of the pair is occupied and the other unoccupied. The Pauli contribution to χ_{xx}, on the other hand, comes only from the pair $(-1/2, 1/2)$ when this state is occupied. In view of the greater multiplicity of the interband transitions, we expect the Van Vleck susceptibility to be very important—indeed it very likely dominates the total. A band calculation which explicitly computes the two components reckons the Pauli contribution at (15–20)% [22], in agreement with the multiplicity argument. The matrix elements above show that a sheet of the Fermi surface will have an isotropic partial Pauli susceptibility $(\chi^P_{zz}/\chi^P_{xx} \approx 1)$ if different j_z values are well mixed in the wave function, but will be anisotropic otherwise; $j_z = 1/2$ on a sheet implies $(\chi^P_{zz}/\chi^P_{xx} \ll 1)$ and $j_z = 3/2$ or $5/2$ implies $(\chi^P_{zz}/\chi^P_{xx} \gg 1)$. Band calculations show that the parts of the Fermi surface near the Γ point and K point are predominantly $j_z = 3/2$ or $5/2$, while the remaining parts (near the A point) are well mixed [23]. Hence we expect a total Pauli susceptibility which satisfies $\chi^P_{zz}/\chi^P_{xx} > 1$.

The interaction effects give rise to the large Fermi liquid enhancement of the susceptibility, which comes chiefly from the mass term. This is expected to affect Pauli and Van Vleck terms alike [24].

It is found experimentally that χ_{xx} is considerably larger than χ_{zz} at all temperatures, in accord with the expectation that the Van Vleck contribution is large. The temperature dependence of $\chi_{xx}(T)$ is anomalous, with a peak at $T = 15$ K [25]. This peak is absent in the smooth curve for $\chi_{zz}(T)$, and in the specific heat $C_V(T)$ [26]. This is consistent with the idea that the physical origins of χ_{zz} and χ_{xx} are different, and that the density of states at the Fermi level largely determines χ_{zz} but not χ_{xx}. Thus experiments, to the extent that we have them, confirm the theoretical picture.

The importance of these considerations for the superconducting state is simple [27]. Superconductivity affects the Pauli susceptibility in a drastic fashion. For a singlet state such as E_{1g}, the Pauli term $\chi^P_{ij}(T)$ is reduced to zero at zero temperature because it takes a finite amount of energy to break a pair and magnetize the system. Superconductivity should have no effect at all on the Van Vleck term. Hence we expect a field along the c axis to have the largest effect on superconductivity. Near T_c, the slope of H_{c2}, larger in magnitude for $\mathbf{H}$ in the z direction, is determined by the terms in F which are linear in H. The different slopes reflect the anisotropic coherence length and are not directly related to the susceptibility. As H increases, the H^2 terms become more important and cause $H_{c2}(T)$ to curve down. The anisotropy in the Pauli susceptibility then causes H_{c2z} to curve more strongly with the result that the two curves cross. To implement this quantitatively, we note that the change in the susceptibility is quadratic in η near T_c. The expression for $F_{\rm magnetic}$ which results is precisely the last three terms, proportional to H^2, in Eq. (1). The resulting fit is shown in Fig. 2. A similar fit has been performed by Yin and Maki [16] for the E_{2g} representation.

What these arguments show is that the peculiar anisotropy of the upper critical field together with the hypothesis of a *singlet* superconducting state, such as E_{1g}, fits together with a particular picture of the magnetic properties of the system. It would be interesting to see this picture checked by polarized inelastic neutron scattering which, in principle, can determine the different tensor elements of χ, and whether these have a gap (Van Vleck) or not (Pauli).

This sort of measurement thus bears on the argument that the anisotropy in H_{c2} points to a triplet state. This argument is based on the idea that the observed anisotropy

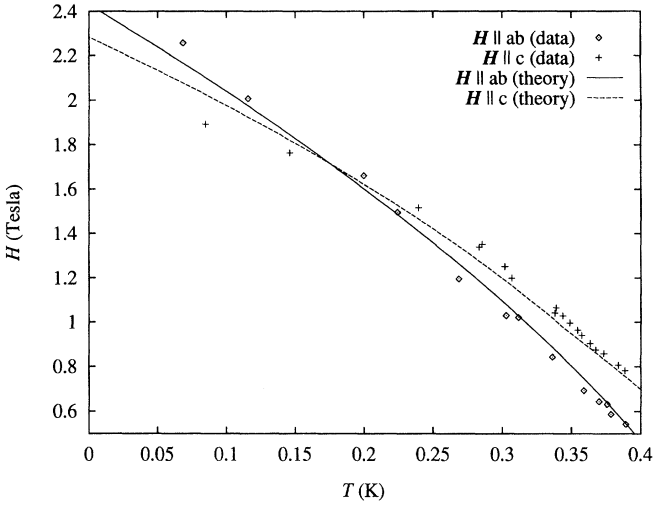

FIG. 2. The crossing of the H_{c2} line when the field is the basal plane (solid line) and the H_{c2} line when the field is in the z direction (dashed line). The data points are from ultrasonic velocity measurements and are taken from Ref. [28], Fig. 3.

in the total susceptibility is also reflected in the Pauli term, that is $\chi^P_{xx} \approx 2\chi^P_{zz}$. According to the arguments presented here, this is somewhat unlikely. In any case, new susceptibility experiments could help distinguish between the alternatives.

We conclude that the E_{1g} theory can account for two crucial aspects of the phase diagram of UPt_3: the existence and shape of the inner transition line for **H** along the c axis, and the peculiar anisotropy of the upper critical field. This removes the major objections to this theory, which otherwise gives a good account of the low temperature thermodynamics, including the position of the gap nodes, the tetracritical point, and the dependence of the phase boundary positions on applied pressure.

We are very grateful to D. L. Cox and M. Norman for useful discussions and correspondence and acknowledge the support of the National Science Foundation through Grant No. 9214739.

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