Phase diagram of UPt$_3$ in the $E_{1g}$ model

K. A. Park and Robert Joynt

Department of Physics and Applied Superconductivity Center

University of Wisconsin-Madison

1150 University Avenue

Madison, Wisconsin 53706

(March 23, 2022)

Abstract

The phase diagram of the unconventional superconductor UPt$_3$ is explained under the long-standing hypothesis that the pair wavefunction 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 also explains the unusual anisotropy in the upper critical field curves, often thought to indicate a triplet pair function.

PACS Nos. 74.70.Tx, 74.25.Dw, 74.20.De.
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] and has had good success in explaining a large class of experiments. It posits a two-component gap function (in contrast to the d-wave states believed to be relevant to high-$T_c$) which transforms as $(k_xk_z, k_yk_z)$ 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 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. The objection usually given is that $E_{1g}$ cannot explain the observed phase diagram in the field-temperature ($H$-$T$) plane when $H$ 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 $H$ in the basal plane crosses the curve $H_{c2z}(T)$ for $H$ 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 predicts correctly the exceedingly unusual phase diagram in the $H$-$T$ plane when $H$ 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 $\Delta C_V$) may be calculated. These conclusions and the conclusions of the present paper follow from the free energy density for the $E_{1g}$ theory:

$$f = \alpha_0(T - T_x)|\eta_x|^2 + \alpha_0(T - T_y)|\eta_y|^2 + \beta_1(\eta \cdot \eta^*)^2 + \beta_2|\eta \cdot \eta|^2$$  \hspace{1cm} (1)

$$+ \sum_{i,j=x,y} (K_1 D_i \eta_j D_j^* \eta_i^* + K_2 D_i \eta_i D_j^* \eta_j^* + K_3 D_i \eta_i D_j \eta_j^*) + K_4 \sum_{i=x,y} |D_i \eta_i|^2$$

$$+ (\alpha_0 \epsilon \Delta T)(\hbar c/2e) \sum_{i=x,y} (|D_i \eta_i|^2 - |D_i \eta_y|^2)$$

$$+ a_x H_x^2 \eta \cdot \eta^* + a_x (H_x^2 + H_y^2) \eta \cdot \eta^* + a_d |H \cdot \eta|^2.$$  

Here $\eta = (\eta_x, \eta_y)$ is the two-component order parameter, and $K_1, K_2, K_3, K_4, \alpha_0, \beta_1, \beta_2,$ $a_x, a_z, a_d$ and $\epsilon$ are constants and $\Delta T = T_x - T_y$. 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 $A$ is the vector potential and $-e$ is the charge on an electron. The coupling of the staggered magnetization to $\eta$ is responsible for the temperature splitting $\Delta T$. The existence and need for the term proportional to $\epsilon$, which represents the coupling of the supercurrent to the staggered magnetization, and the terms proportional to $H^2$ was first stressed in the context of a three-component model. [13]

To obtain $H_{c2}$ we need only consider the terms quadratic in $\eta$ in Eq. (1). We minimize these terms following the Euler-Lagrange perscription of $\delta F = 0$ where $F = \int d^3xf$. When the field is in the basal plane this procedure decouples into one d.e. for $\eta_x$ and one d.e. for $\eta_y$. Hence we obtain two separate equations for $H_{c2}$. For appropriate values of the constants these two curves will cross creating the well-known kink in the upper critical field curve. Hence the A and C phases correspond to $\eta \sim (1, 0)$ and $\eta \sim (0, 1)$ in our theory. The d.e.’s for $\eta_x$ and $\eta_y$ in this case both have the same form as the corresponding equation in the more familiar single component Ginzburg-Landau theory. Hence in either phase the component of $\eta$ that is non-zero will form an Abrikosov lattice of the usual kind. The lattice will be distorted however because of anisotropy in the gradient terms due to the inequality of the $K$’s. In the B phase we have two flux lattices: one formed by $\eta_x$ and the other formed by $\eta_y$. [12] The zeroes of these flux lattices need not coincide, however. Hence, we must introduce the extra degree of freedom of the offset vector of the two flux lattices, and we
must minimize the free energy with respect to this variable. We find that the free energy is minimized for an offset vector which is one-half of a flux lattice basis vector. [4]

When $H$ is in the $z$-direction, the problem of minimizing the free energy is far more difficult to solve. The eigenfunctions of the linear problem, which we shall call $\phi_{nk}$, can be found numerically but they are complicated. Because the linear $H_{c2}$ equations do not separate into separate equations for $\eta_x$ and $\eta_y$, the $\phi_{nk}$ have both $x$ and $y$ components.

When the OP expanded in terms of the eigenfunctions: $\eta = \sum_{nk} c_{nk} \phi_{nk}$, the free energy $F$ is a 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. The fourth order terms in $F$ are complicated. If we take, for example, $\eta = c_{0k} \phi_{0k} + c_{1k} \phi_{1k}$, then terms of the form $|c_{0k}|^2 c_{0k}^* c_{1k}$ appear. The $c_{0k}$ produce, effectively, a linear term in the $c_{1k}$. It is then concluded that no second transition occurs below $H_{c2}$ in this theory, in conflict with experiment.

This argument is, however, not correct. The actual Hilbert space for the functional $F$ is infinite-dimensional and a careful analysis of all the possibilities must be carried out. The energy levels labelled by the integer $n \geq 0$ are highly degenerate, the eigenvalues being independent of $k$, which may take the value of any allowed wavevector $k = 2\pi \times $ integer$/L_y$, where $L_y$ is the length of the sample in the $y$-direction. The energy of the OP configuration represented by $\phi_{nk}$ is independent of $k$. The minimization of $F$ leads to 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 $m = \text{even(odd)}$. A dangerous fourth order term in $F$ has the form: $\beta_{k_1k_2k_3k_4}^{01} c^*_{0k_1} c_{0k_2} c^*_{0k_3} c_{1k_4}$. Momentum conservation implies that the coefficient $\beta_{k_1k_2k_3k_4}^{01}$ 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 $c_{1k}$ 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. 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 $H = H^z$; 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 $H = H^z$ 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. Another part of the argument against $E_{1g}$ has been that fine tuning of parameters is required to fit the data. Our fit does not require any fine-tuning. We find that the phase diagram for both field directions can be fit by the same set of parameters, and the only numerical coincidence which arises when this is done is that $K_2 \approx K_3$. 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 accounts very
The states near the Fermi surface are predominantly derived from uranium 5f orbitals with \( j = 5/2 \). In the isolated atom, these would be 6-fold degenerate. In the hexagonal crystal field, there is an effective Hamiltonian of the form
\[
H_{\text{crystal field}} = B_h (j_z^2 - j(j+1)/3),
\]
where \( B_h \) is a constant. This splits the six-fold degenerate state into three doublets at the \( \Gamma \) point: \( j_z = \pm 5/2, j_z = \pm 3/2, \) and \( j_z = \pm 1/2 \). There is also an even-odd splitting from the fact that there are two U atoms per unit cell. The six bands constructed from these states cross the Fermi energy, and the crystal field splitting is of the same order as the bandwidth. The average occupation of the 5f level is between 2 and 3. 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 \( (g_{\text{eff}} \mu_B)^2 N(\varepsilon_F) \), while the latter is of order \( (g_{\text{eff}} \mu_B)^2 / |B_h| \). Here \( g_{\text{eff}} \) is an effective g-factor for the coupling of the field to the total angular momentum of the band or bands involved. It is a dimensionless number of order unity. The Landé factor for \( \ell = 3, s = 1/2 \), and \( j = 5/2 \) is \( 6/7 \).

The Van Vleck susceptibility is given by
\[
\chi_{ii} = 2n\mu_B^2 \sum_{\alpha,\beta} \left| \frac{\langle \alpha | L_z + 2S_z | \beta \rangle}{E_\beta - E_\alpha} \right|^2 f_\alpha (1 - f_\beta). \tag{2}
\]
Here \( f_\alpha, f_\beta, E_\alpha, E_\beta \) are occupation factors and energies of the states \( \alpha \) and \( \beta \). In view of the greater multiplicity of the interband transitions, we expect the Van Vleck susceptibility to be very important - indeed it may dominate the total. If \( H \) is along the c-axis, then the relevant matrix element (with \( \hbar = 1 \)) is:
\[
\left| \frac{\langle \alpha | L_z + 2S_z | \beta \rangle}{E_\beta - E_\alpha} \right|^2 = (36/49) j_z^2 \delta_{\alpha,\beta}. \tag{3}
\]
In the approximation that states of different \( j_z \) do not mix (negligible intersite interactions), then the perturbation introduced by \( H \) is diagonal, and the occupation factors then imply that the Van Vleck susceptibility is zero for this direction. If \( H \) is in the x-direction, the corresponding expression for the square of the matrix element is
\[
\left| \frac{\langle \alpha | L_x + 2S_x | \beta \rangle}{E_\beta - E_\alpha} \right|^2 = (36/49)(5/2 - j_z)(5/2 + j_z + 1) \tag{4}
\]
if the states $\alpha$ and $\beta$ 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 $\chi_{xx}$, on the other hand, comes only from the pair $(-1/2,1/2)$ when this state is occupied.

Summing up these considerations, we expect that $\chi_{zz}$ will be dominated by the Pauli contribution, while $\chi_{xx}$ will be dominated by the Van Vleck contribution. There are two effects which can vitiate these conclusions. Intersite effects will mix states of different $j_z$, and this will modify this ionic picture. 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. Experiment confirms these theoretical arguments. It is found that $\chi_{xx}$ is considerably larger than $\chi_{zz}$ 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. This peak is absent in the smooth curve for $\chi_{zz}(T)$, and in the the specific heat $C_V(T)$. This is consistent with the idea that the physical origins of $\chi_{zz}$ and $\chi_{xx}$ are different, and that the density of states at the Fermi level determines $\chi_{zz}$ but not $\chi_{xx}$. Thus experiment confirms the theoretical picture.

The importance of these considerations for the superconducting state is simple. Superconductivity affects the Pauli susceptibility in a drastic fashion. For a singlet state such as $E_{1g}$, the Pauli term $\chi_{ij}^P(T)$ 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. The difference in free energies between the normal and superconducting states in a field is

$$F_{\text{magnetic}} = -\frac{1}{2} \sum_{ij} \Delta \chi_{ij}^P H_i H_j.$$ 

Here $\Delta \chi_{ij}^P = \chi_{ij}^S - \chi_{ij}^N$ where $\chi_{ij}^S$ and $\chi_{ij}^N$ are the Pauli susceptibilities in the superconducting and normal states, respectively. 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 $H$ 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 $\eta$ near $T_c$. The expression for $F_{magnetic}$ which results is precisely the last three terms, proportional to $H^2$, in Eq. (1). The resulting fit is shown in Fig. 2.

What these arguments show is that the peculiar anisotropy of the upper critical field is evidence for a singlet superconducting state, such as $E_{1g}$. This is in sharp contrast to previous arguments that the anisotropy points to a triplet state. These arguments were based on the idea that the observed anisotropy in the total susceptibility is also reflected in the Pauli term, that is $\chi_{xx}^P \approx 2\chi_{zz}^P$. According to the above arguments, this appears unlikely.

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 for useful discussions and acknowledge the support of the National Science Foundation through grant no. 9214739.
REFERENCES

[1] J. F. Annett, N. Goldenfeld, and S. Renn, Phys. Rev. B 43, 2778 (1991); a recent review is by D. Scalapino (unpublished)

[2] W. O. Putikka and R. Joynt, Phys. Rev. B 49, 701 (1989)

[3] B. S. Shivaram, Y. Jeong, T. Rosenbaum, and D. Hinks, Phys. Rev. Lett. 56, 1078 (1986); P. Hirschfeld, D. Vollhardt, and P. Wölfle, Sol. St. Comm. 59, 111 (1986)

[4] B. Lussier, B. Ellmann, and L. Taillefer (unpublished)

[5] R. Joynt, Phys. Rev. Lett., 71, 3015, (1993)

[6] R. Joynt, Supercon. Sci. Tech. 1, 210 (1988); R. A. Fisher et al., Phys. Rev. Lett. 62, 1441 (1989); K. Hasselbach, L. Taillefer, and J. Flouquet, Phys. Rev. Lett. 63, 93 (1989)

[7] D. W. Hess, T. Tokuyasu, and J. Sauls, J. Phys. Cond. Matt. 1, 8135 (1989); B. S. Shivaram, J. J. Gannon, and D. Hinks, Phys. Rev. Lett. 63, 1441 (1989)

[8] K. Machida and M. Ozaki, Phys. Rev. Lett. 66, 6293 (1991)

[9] See, for example, A. Garg, Phys. Rev. Lett. 69, 676 (1992); J. A. Sauls, Adv. in Phys. 43, 113 (1994)

[10] B. Shivaram, T. Rosenbaum, and D. Hinks, Phys. Rev. Lett. 57, 1259 (1986)

[11] C. Choi and J. Sauls, Phys. Rev. Lett. 66, 484 (1991)

[12] R. Joynt, Europhys. Lett. 16, 289 (1991)

[13] K. Machida, T. Ohmi, and M. Ozaki, J. Phys. Soc. Japan 62, 3216 (1993)

[14] K. A. Park and R. Joynt, to be published; there is a commensuration energy at this off-set vector, as in D.-C. Chen and A. Garg, Phys. Rev. B 49, 479 (1994)

[15] C.S. Wang et al., Phys. Rev. B 35, 7260 (1987)
[16] F. C. Zhang and T. K. Lee, Phys. Rev. Lett. 58, 2728 (1987); C. Varma and G. Aeppli, ibid. 58, 2729 (1987); D. L. Cox, ibid. 58, 2730 (1987)

[17] P. Frings, J. Franse, F. deBoer, and A. Menovsky, J. Mag. Mag. Mat., 31, 240 (1983)

[18] A. de Visser, A. Menovsky, and J. Franse, Physica B, 147, 81 (1987)

[19] This point has been stressed particularly by D. L. Cox (private communication)

[20] S. Adenwalla, S. W. Lin, Q. Z. Ran, Z. Zhao, J. B. Ketterson, J. A. Sauls, L. Taillefer, D. G. Hinks, M. Levy, and Bimal K. Sarma, Phys. Rev. Lett. 65, 2298 (1990)
FIGURES

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. [20], Fig. 3.

FIG. 2. Shows 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. [20], Fig. 3. The diamonds are for the case when the field in the basal plane (\( \mathbf{H} \parallel ab \)) and the crosses are for the case when the field is in the \( z \)-direction (\( \mathbf{H} \parallel c \)).