Identification of Odd-Parity Superconductivity in UPt$_3$ from Paramagnetic Effects on the Upper Critical Field

C-H. Choi and J. A. Sauls

Department of Physics & Astronomy, Northwestern University, Evanston, IL 60208

(Dated: Submitted to PRL, Received August 13, 1990)

We present a theoretical explanation of the unusual temperature-dependent anisotropy of $H_{c2}$ reported by Shivaram, et al.\cite{Shivaram} for single crystals of UPt$_3$, which we argue provides strong support for unconventional odd-parity pairing. We show that the observed low-temperature crossover in the anisotropy ratio, $H_{c2}^\perp/H_{c2}^\parallel$, can be explained by paramagnetic limiting for $H$ parallel to the sixfold axis within BCS pairing theory if the order parameter has odd-parity and there is strong spin-orbit coupling of the pair spin to the crystal axes.

The properties of the heavy Fermion superconductors (e.g. CeCu$_2$Si$_2$, UBe$_{13}$, UPt$_3$) have led to a broad effort to understand superconductors with an unconventional order parameter (we use this term to mean an order parameter which has a smaller rotational symmetry group than that of the normal metallic crystal)\cite{various}. One important area involves studies of the upper critical field, $H_{c2}$, that separates the normal metallic state from the Abrikosov state of a type II superconductor, and which can play a key role in determining the nature of the underlying order parameter\cite{various}. In this paper we present a theoretical explanation of the unusual temperature-dependent anisotropy of $H_{c2}$ reported by Shivaram, et al.\cite{Shivaram} for single crystals of UPt$_3$, which we argue provides strong support for unconventional odd-parity pairing. Theoretical arguments have been put forth by many authors (see e.g.\cite{various}) that the order parameter for UPt$_3$ transforms according to one of the non-identity representations of the hexagonal point group $D_{6h}$. These arguments are based in part on interpretations of the observed power-law temperature dependences of the ultrasonic attenuation, and also on RPA-like models of the pairing interaction. Authors\cite{various} have argued that exchange of AFM spin fluctuations suppresses pairing in the odd-parity and the even-parity identity representations, but favors an even-parity non-identity representation for the order parameter. More recent variants of the AFM exchange model\cite{various} yield odd-parity superconductivity. However, these arguments are based on models of the pairing interaction that are not grounded in a first-principles theory for the pairing instability\cite{various}. Likewise, the interpretation of the power-law behavior of the ultrasonic attenuation in terms of an unconventional order parameter is based on an assumed identification with the excitation gap, not a fundamental relationship. Therefore, considerable theoretical effort has been devoted to identifying strong tests of the symmetry of the order parameter (see e.g.\cite{various}), including the anisotropy of $dH_{c2}/dT|_T$ for tetragonal and cubic symmetry\cite{various} as well as tests of broken time-reversal symmetry\cite{various}. As yet there are no reports of positive identifications of unconventional superconductivity based on strong tests of broken symmetry. We have considerable confidence in the predictions of the BCS theory, even for unconventional pairing (e.g. $^3$He), provided we know the relevant material parameters like $T_c$, the Fermi velocity, etc., and most importantly the symmetry class of the pairing state. Thus, predictions of the BCS theory that are qualitatively different for order parameters belonging to different symmetry classes are reasonably strong tests of unconventional pairing. The loophole here is whether or not one has identified all the relevant input material parameters. Nevertheless, there is increasing evidence that UPt$_3$ has an order parameter belonging to a non-identity representation. The strongest evidence so far comes from observations of multiple superconducting phases in UPt$_3$ (see\cite{various} and references therein), which are naturally interpreted in terms of an order parameter belonging to a fundamental representation with dimensionality $d > 1$. The double transition in zero field\cite{various}, as well as the observed kinks in $H_{c2}^\parallel$ (we use $\perp$ and $\parallel$ to refer to $H \perp$ and $H \parallel$ to the sixfold axis) and $H_{c2}^\perp$\cite{various} have been interpreted in terms of a weak breaking of the hexagonal symmetry which splits the transition into a 2D representation into two nearly degenerate 1D representations\cite{various}. The existence of multiple superconducting states suggests that the order parameter belongs to one of the 2D representations: even-parity $E_{1u}$ or $E_{2g}$, or odd-parity $E_{1u}$ or $E_{2u}$.

Although attention has recently been focussed on the Ginzburg-Landau region, where anomalies in $H_{c2}^\perp$ or $H_{c2}^\parallel$ have been observed, the low-temperature measurements of $H_{c2}^\perp$ and $H_{c2}^\parallel$ contain an important clue to the identification of the order parameter. While measurements of the parallel critical field are considerably larger than those measured in the basal plane for $T > 200$ mK, Shivaram, et al.\cite{Shivaram} found that $H_{c2}^\parallel$ was strongly suppressed relative to $H_{c2}^\perp$ below $\sim 200$ mK. A plot of the anisotropy ratio from\cite{Shivaram} $R(T) = H_{c2}^\perp/H_{c2}^\parallel$ (inset of Fig. 1) crosses unity at $T \simeq 200$ mK from $R(T_c) \simeq 0.6$ to $R(T \rightarrow 0) \simeq 1.25$. This crossover in the anisotropy ratio is a unique feature of UPt$_3$ that has so far not been explained by BCS theory, even with an unconventional order parameter, but is qualitatively and quantitatively accounted for within BCS theory if: (i) the uniaxial anisotropy of the Fermi surface is included, (ii) the paramagnetic coupling to the field is included, and (iii) the order parameter belongs to one of the following odd-parity ($S = 1$) representations: $E_{1u}$, $A_{1u}$, $A_{2u}$, $B_{1u}$, or $B_{2u}$, appropriate for strong spin-orbit coupling of the Cooper pair spin to the lattice.

The Fermi surface anisotropy determines the anisotropy ratio near $T_c$, where the paramagnetic coupling is unimportant, while the interplay between the paramagnetic effect, strong

Published Version: [Phys. Rev. Lett. 66 484 (1991)]
spin-orbit coupling and the spin of the Cooper pairs for odd-parity pairing is crucial for explaining the crossover in the anisotropy ratio at low temperatures. For even-parity states, the upper critical field is bounded by the paramagnetic effect for all directions of field. But for odd-parity states, there is no paramagnetic suppression of superconductivity if the external field is perpendicular to the direction along which the Cooper pairs have zero total spin, i.e. \( \mathbf{S} = 0 \); whereas other orientations of the magnetic field relative to \( \mathbf{S} \) will be a pair-breaking\(^{[19]} \). Thus, the paramagnetic limit can have a dramatic effect on the anisotropy of \( H_{c2} \) for odd-parity states with strong spin-orbit coupling, which serves to lock the Cooper pair spin to the crystal lattice.

The results presented here are based on the quasiclassical theory of superconductivity (we use the notation of Alexander, \textit{et al.}\(^{[20]} \)), which allows us to incorporate an anisotropic Fermi surface, paramagnetic coupling, spin-orbit coupling, impurity scattering and an unconventional order parameter into our calculations. The formalism and details of the calculations presented here are contained in a forthcoming article\(^{[21]} \).

We present results for the clean limit, \( 1/\tau_{\text{imp}} \ll 2\pi T_c \), appropriate for high-quality single crystals of \( UPt_3 \). The central equation is the linearized weak-coupling gap equation; for odd-parity \( (S = 1) \) pairing,

\[
\Delta(k, \mathbf{R}) = 2\pi T \sum_{\tau} \int d\tau \int d^2 k' \, n(k') \mathcal{V}(k, k') \times 
\exp \left\{ -2\pi \left[ |\mathbf{e}| - \text{sgn}(\mathbf{e}) \mathbf{v} \cdot \mathbf{d} \right] \times 
\left[ 1 + \{\cos(2\pi\mu H) - 1\} \hat{\mathbf{h}} \otimes \hat{\mathbf{h}} \right] \Delta(k', \mathbf{R}) \right\},
\]

where the sum is over Matsubara frequencies, \( \tau = \nabla \mathbf{R} + i \frac{2\pi}{T} / A \) includes the coupling to the field through the vector potential \( A(\mathbf{R}) \). The density of states, \( n(k') \), Fermi velocity, \( \mathbf{v} \), and the pairing interaction, \( \mathcal{V}(k, k') \), are functions of position, \( k, k' \), on the Fermi surface, as is the effective magnetic moment, \( \mu \), that determines the paramagnetic coupling to the field. The uniaxial tensor, \( \hat{\mathbf{h}} \otimes \hat{\mathbf{h}} \), is defined by the direction of magnetic field, \( \hat{\mathbf{h}} \). For even-parity states the scalar \( (S = 0) \) order parameter satisfies a similar equation to (1) with \( \hat{\mathbf{h}} \otimes \hat{\mathbf{h}} \rightarrow 1 \). The upper critical field is then computed as the largest value of \( H \) for which eq. (1) has a nontrivial solution. Note that the paramagnetic term is unimportant close to \( T_c \) for both odd- and even-parity states; however, it has an effect on \( H_{c2} \) at lower temperatures, except for odd-parity states with \( \Delta = \perp \mathbf{H} \).

Our calculations of \( H_{c2} \) for \( UPt_3 \) depend on the following material parameters: (i) principal Fermi velocities, \( v^\parallel \) and \( v^\perp \), to parametrize our uniaxial model for the Fermi surface; (ii) an effective moment for quasiparticles, \( \mu \) (The effective moment is in general a crystal tensor. However, our conclusions are insensitive to this structure, so \( \mu \) is taken to be a single parameter here. A more detailed discussion of this point is given in ref\(^{[21]} \)); and (iii) a transition temperature, \( T_c \), (in zero field) determined by the most attractive pairing channel, which will be one of the irreducible representations of the point group \( D_{6h} \). We assume that only one pairing channel is significant, thus excluding an accidental degeneracy of two representations. We also omit all symmetry breaking fields that might reduce the 2D representations to nearly degenerate 1D representations. Thus, the calculations we present do not show the kink in \( H_{c2}^\parallel \) near \( T_c \), but since we are interested in the effect of paramagnetism on the intermediate- and low-temperature behavior of \( H_{c2} \) this is not a serious limitation.

It is useful to introduce the coherence lengths, \( \xi^\parallel = v^\parallel / 2\pi T_c \), \( \xi^\perp = v^\perp / 2\pi T_c \), and a magnetic field scale, \( H_0 = (\hbar c/2e) / \pi \xi^\perp \), as well as the dimensionless parameters:

\[
\eta = \left( \frac{\xi^\parallel}{\xi^\perp} \right)^2, \quad \hbar = \frac{H}{H_0}, \quad \bar{\mu} = \frac{\mu H_0}{\pi T_c}.
\]

We have solved eq. (1) for the upper critical field of the odd-parity representations (and a similar equation for the even-parity representations) of the hexagonal group with \( \mathbf{H} \) along \( \hat{z} \), the axis of six-fold symmetry, and also for \( \mathbf{H} \) in the basal plane.

We first consider solutions for the odd-parity 2D representations, \( E_{1u} \) and \( E_{2u} \), and also the \( B_{1u} \) representation, which for our purposes is representative of all the 1D odd-parity states. Consider the \( E_{1u} \) order parameter (see e.g. Ref\(^{[22]} \)),

\[
\Delta(k, \mathbf{R}) = \hat{z} \left[ \eta^+ (\mathbf{R}) f^+(k) + \eta^- (\mathbf{R}) f^-(k) \right],
\]

where \( f(k) \) is given in table I. Note that \( \Delta \) is along \( \hat{z} \), so that the Cooper pair spin is in the basal plane. The amplitudes \( \eta^\pm (\mathbf{R}) \) satisfy a homogeneous equation that depends on \( H \) and is simply obtained from eqs. (1) and (3). The order parameter and upper critical field are obtained for all temperatures by a standard method of introducing raising and lowering operators and a set of eigenfunctions \( \{\phi_\nu(\mathbf{R})\} \) of the harmonic oscillator problem\(^{[23]} \).

When the magnetic field is along \( \hat{z} \), the maximum value of \( H \) occurs for \( (\eta^+, \eta^-) \sim (\phi_2, c\phi_0) \). Without paramagnetism, \( h_{c2}^0 \) has the limiting values shown in table I. Since the pairs have \( S_z = 0 \), the paramagnetic term reduces \( h_{c2}^0 \). Fig.

<table>
<thead>
<tr>
<th>Rep. Order Parameter</th>
<th>( h_{c2}(0) )</th>
<th>(-T_c dh_{c2}/dT )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E_{1u} ) ( \phi_2 )</td>
<td>0.77</td>
<td>1.08</td>
</tr>
<tr>
<td>( E_{2u} ) ( \phi_0(\mathbf{S}_0) \kappa_0 )</td>
<td>0.37</td>
<td>0.59</td>
</tr>
<tr>
<td>( B_{1u} ) ( \phi_0(\mathbf{S}_0) \kappa_0 )</td>
<td>0.65</td>
<td>0.84</td>
</tr>
<tr>
<td>( E_{1e} ) ( \phi_2(k_3^3 - 3k_3^2) \kappa_0 )</td>
<td>0.32</td>
<td>0.53</td>
</tr>
<tr>
<td>( E_{1e} ) ( \phi_0(k_3^3 - 3k_3^2) \kappa_0 )</td>
<td>0.92</td>
<td>1.07</td>
</tr>
<tr>
<td>( E_{1e} ) ( \phi_2(k_3^3 - 3k_3^2) \kappa_0 )</td>
<td>1.15</td>
<td>1.51</td>
</tr>
<tr>
<td>( E_{1e} ) ( \phi_0(k_3^3 - 3k_3^2) \kappa_0 )</td>
<td>0.70</td>
<td>0.96</td>
</tr>
</tbody>
</table>
1 shows the reduction in $h_2^\parallel (T)$ at low temperatures due to paramagnetic limiting as well as the absence of a paramagnetic effect near $T_c$. By contrast, $h_2^\perp (T)$ is independent of the paramagnetic effect because the pairs have no amplitude with zero spin projection for directions in the basal plane.

In table I and fig. 1 we summarize the results for the $E_{1u}$ representation as a function of $T/T_c$ for relevant choices of the effective mass ratio $\eta$ and scaled effective moment $\bar{\mu}$. Both $h_2^\parallel$ and $h_2^\perp$ are scaled in units of $H_2$. $h_2^\parallel$ is then independent of $\eta$, while $h_2^\perp$ scales as $1/\sqrt{\eta}$. As noted earlier the paramagnetic effect can significantly reduce the value of $h_2^\parallel$ at low temperatures, whereas it has no effect on $h_2^\perp$. Thus, by adjusting $\eta$ and $\bar{\mu}$, we obtain $h_2^\parallel$ and $h_2^\perp$ that crossover at an intermediate temperature. We have a crossover around $0.4 T_c$ for $\eta = 3.37$ and $\bar{\mu} = 0.68$; the inset of fig. 1 shows the anisotropy ratio $h_2^\parallel/h_2^\perp$ as a function of $T/T_c$ for this choice of parameters, compared with the experimental values from $^{11}$ Fig. 1 also shows the measured values of $H_2^\parallel$ and $H_2^\perp$ compared with the theoretical calculations. We have purposely chosen slightly different values for $T_c$ of $H_2^\parallel$ and $H_2^\perp$, which emphasizes the discrepancy in the narrow temperature interval of the double transition, but provides a better fit to the data away from $T_c$. An essentially perfect fit to the full temperature range, including the region of the double transition, can be obtained by including the splitting of the $E_{1u}$ representation by a weak symmetry breaking field $^{13}$.

For the $E_{2u}$ representation the order parameter,

$$\Delta(k_f, R) = \eta_+ (R) \left( \frac{\hat{x} + i \hat{y}}{\sqrt{2}} \right) f(k_f) + \eta_- (R) \left( \frac{\hat{x} - i \hat{y}}{\sqrt{2}} \right) f^* (k_f) ,$$

(4)

differs significantly in its magnetic structure from that of $E_{1u}$. When $H \parallel \hat{z}$ the upper critical field is independent of the paramagnetic term and has a maximum eigenvalue for $(\eta_+, \eta_-) \sim (\phi_0, 0)$, and for fields in the basal plane $H_{2, \perp}$ is quite sensitive to $\bar{\mu}$. We can obtain a very weak crossover in the anisotropy ratio even without the paramagnetic term for the limited range $2 < \eta < 3$; however, this crossover is much too weak to account for that observed in $UPt_3$, and becomes more isotropic as $\bar{\mu}$ is increased (see $^{21}$ for details).

There are four odd-parity, 1D representations in the limit of strong spin-orbit coupling, all of which have a similar spin structure to that of the $E_{1u}$ representation and, therefore, exhibit similar anisotropic paramagnetic effects. We choose $B_{1u}$ to illustrate the 1D representations with $\Delta(k_f, R) = \varphi(R) \hat{z} f(k_f)$. A numerical calculation of the anisotropy ratio $h_{2u}^\parallel/h_{2u}^\perp$ for $\eta = 11.0$ and $\bar{\mu} = 1.2$ gives an almost identical fit to the experimental data of $UPt_3$. As shown in fig. 1 for the $E_{1u}$ representation. Similar results can be obtained for all of the 1D odd-parity representations with suitable choices of the anisotropy and paramagnetic parameters.

The important distinction of the even-parity states is that the paramagnetic term is important for any direction of the magnetic field. For the $E_{1g}$ representation,

$$\Delta(k_f, R) = \eta_+ (R) f^+ (k_f) + \eta_- (R) f(k_f) ,$$

(5)

has a similar orbital form to that of $E_{1u}$. And not surprisingly, the solutions for $(\eta_+, \eta_-)$ are of the same form as for the odd-parity $E_{1u}$ representation; for $H \parallel \hat{z}$ the upper critical field occurs for $(\eta_+, \eta_-) \sim (\phi_2, c \phi_0)$. For $H \parallel \hat{x}$ we performed a variational calculation for $h_{2u}^\parallel$, the precision of which is $\approx 1\%$. The important point is that we do not find a crossover in the anisotropy ratio $h_{2u}^\parallel/h_{2u}^\perp$, with $h_{2u}^\parallel > h_{2u}^\perp$ at $T = 0$, for any values of $\eta$ and $\bar{\mu}$. Similar results are obtained for the other even-parity representations, and are discussed in Ref.$^{21}$

We have calculated the upper critical field for order parameters belonging to the even- and odd-parity representations of the hexagonal point group with strong spin-orbit coupling. The effects of paramagnetism and anisotropy of Fermi surface on the anisotropy of the upper critical field, in particular the crossover behavior of $h_{2u}^\parallel/h_{2u}^\perp$, were examined in detail. For odd-parity states $E_{1u}$ and $B_{1u}$, with a $\hat{z}$ parallel to $\hat{z}$, the anisotropy ratio $h_{2u}^\parallel/h_{2u}^\perp$ fits the data on $UPt_3$ well with two parameters that measure the Fermi surface anisotropy and the paramagnetic effect. Although our model for the Fermi surface anisotropy is simple, we note for comparison that the val-
ues, $\eta = 3.37$ (11.0), $H_o = 4.8T$ (9.4$T$) and $\bar{\mu} = 0.7$ (1.2), which we obtain from our fit for the $E_{1u}$ ($B_{1u}$) representation, imply an effective moment of $\mu = 0.34\mu_B (\mu = 0.30\mu_B)$, in reasonable agreement with several other estimates. The important point is that the Fermi surface anisotropy and paramagnetic coupling give rise to a crossover in the anisotropy ratio of the right magnitude and temperature dependence for realistic values of the material parameters only for odd-parity states with $\mathbf{m}$ along the $\hat{z}$-axis. In particular, for the $E_{2u}$ representation ($\Delta \pm \hat{z}$), the paramagnetic term affects only $h_{\perp}^{-2}$, and not $h_{\parallel}^{-2}$, and thus cannot account for the observed crossover. For even-parity states, the paramagnetic effect suppresses both $h_{\perp}^{-2}$ and $h_{\parallel}^{-2}$, and even tends to reduce the anisotropy of upper critical field at low temperatures. These characteristics lead us to conclude that the experimental data of Ref. provide strong support for odd-parity pairing in $UPt_3$.

We thank D. Rainer, M. Graf, and G. H. Kim for many useful discussions. The research of C.H.C. was supported by the NSF through the Northwestern University Materials Research Center grant no. DMR-8821571, and that of J.A.S. was supported by the NSF (DMR-8809854) through the Science and Technology Center for Superconductivity.

Note added 10/31/90: An independent test of the proposed model for the order parameter in $UPt_3$ is the spin-susceptibility anisotropy (from Knight shift measurements) $\Delta \parallel \hat{z}$. The spin susceptibility for $\mathbf{H} \parallel \hat{z}$ should be reduced, similar to that in conventional superconductors, while the spin susceptibility perpendicular to the $\hat{z}$ axis should be essentially independent of temperature.

---

* [sauls@northwestern.edu]