Surface superconductivity and order parameter suppression in UPt$_3$

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We show that a recent measurement of surface superconductivity in UPt$_3$ (Keller et. al., Phys. Rev. Lett. 73, 2364 (1994)) can be understood if the superconducting pair wavefunction is suppressed anisotropically at a vacuum to superconductor interface. Further measurements of surface superconductivity can distinguish between the various phenomenological models of superconducting UPt$_3$.

Superconductivity in hexagonal UPt$_3$ exhibits many properties unique among superconductors. The most striking of these is the pressure temperature magnetic field phase diagram that shows several superconducting phases [1–3]. For example, a graph or the upper critical field for fields in the basal plane ($H_{c2}^{ab}$) versus temperature exhibits a kink at a temperature $T^*$ [4]. This kink can be explained in terms of a generalized Ginzburg-Landau model in which the order parameter has two complex components, $\eta_1$ and $\eta_2$ [5,6]. For temperatures below $T^*$, one of these components orders at $H_{c2}^{ab}$, whereas for temperatures above $T^*$ the other component orders at $H_{c2}^{ab}$. Recently, a detailed study of surface superconductivity in UPt$_3$ by Keller et. al. has produced puzzling features not observed in other superconductors [7,8] (see also [9]). In particular, the ratio of the upper critical field for surface superconductivity ($H_{cs}$) to that for bulk superconductivity has an unusual temperature dependence [8]. Furthermore, different surfaces of the UPt$_3$ whisker were observed to have different values of $H_{cs}$ [9,10]. It is argued here that the reason for this unusual temperature dependence is that one of the components for the order parameter (say $\eta_1$) is suppressed at the surface (and hence cannot sustain surface superconductivity); the transition at $H_{cs}$ is thus to a superconducting $\eta_2$ state, both below and above $T^*$. Order parameter suppression at a superconductor to vacuum interface is known not to occur in conventional isotropic superconductors [11] but is expected on theoretical grounds (although not yet observed experimentally) for some unconventional superconductor symmetries [12,13]. We believe the observed behavior of $H_{cs}/H_{c2}$ in UPt$_3$ is the only evidence to date of an anisotropic suppression of the superconducting order parameter at a vacuum to superconductor interface. This interpretation of the measurements of Keller et. al. imposes strong constraints on existing phenomenological models of superconductivity in UPt$_3$ and indicates that such measurements can provide a new technique for determining the symmetry of anisotropic superconductors.

In this article we will initially consider surface superconductivity for the $E$-REP Ginzburg-Landau models proposed by by Machida and Ozaki [3] and by Hess et. al. [14] and improved by Sauls [8] (an important element of these models is the hexagonal symmetry breaking due to the basal plane antiferromagnetism [15,16]). We then show how the inclusion of symmetry dependent surface contributions to the free energy is essential for understanding the experiments. Finally, we show how surface superconductivity studies can distinguish between these models, the 1D-REP model [18], and the AB model [16].

For the odd parity $E_{2u}$ and $E_{1u}$ models the gap function is described by the pseudo-spin pairing gap matrix $\Delta(\vec{r},\vec{k}) = i\eta_1(\vec{r})d_1(\vec{k}) \cdot \vec{\sigma} + \eta_2(\vec{r})d_2(\vec{k}) \cdot \vec{\sigma} \gamma$, where $\sigma_i$ are the Pauli matrices. We will assume that $d_1(\vec{k}) = d_3(\vec{k}) \hat{z}$; this form of the gap function is required in the $E_{2u}$ model to account for the gap nodal structure implied by experiment [8]. For the even parity $E_{2g}$ and $E_{1g}$ models the form of the gap matrix is $\Delta(\vec{r},\vec{k}) = i\gamma_1(\vec{r})\psi_1(\vec{k}) + \eta_2(\vec{r})\psi_2(\vec{k})$. The free energy density for these $E$-REP models is

$$F = \alpha_0(T - T_c)\vec{\eta} \cdot \vec{\eta} - \gamma(|\eta_1|^2 - |\eta_2|^2) + \kappa_1^+|D_1\eta_2|^2 + \kappa_1^-|D_1\eta_1|^2$$

$$\kappa_1^+|D_2\eta_2|^2 + \kappa_1^-|D_2\eta_1|^2 + \kappa_2(D_1\eta_1)(D_2\eta_2)^* + \kappa_3(D_1\eta_2)(D_2\eta_1)^* + \vec{h}^2/8\pi - \vec{h} \cdot \vec{H} \gamma \kappa_1^+$$

(1)

where $\vec{B} = \vec{\eta} = (i2e/hc)\vec{A}$, $\vec{h} = \vec{\eta} \times \vec{\eta}$, $\vec{H}$ is the applied field, $i$ and $j$ refer to indices $x$ (and 1) and $y$ (and 2), and $\kappa_1^\pm = \kappa_1(1 \pm \delta_1)$. The convention $\sigma_x\eta_1 = -\eta_1$ for even parity representations and $\sigma_y\eta_1 = \eta_1$ for the odd parity representations fixes the axes and $\sigma_x$ is a reflection in a plane normal to the $\vec{a}$ crystallographic axis (these conventions allow the discussion of surface superconductivity to occur on the same footing for the even and odd parity representations). For the calculation of $H_{c2}$ and $H_{cs}$ higher order terms in $\eta_1$ and $\eta_2$ in Eq. 1 can be omitted. The coefficients $\gamma$ and $\delta_1$ arise from the coupling to the antiferromagnetic moment. The gradient terms with coefficients $\kappa_2$ and $\kappa_3$ give rise to anisotropy in $H_{c2}$. This has been observed to be of the order $0.01H_{c2}^{ab}$. It has also been argued by Sauls [8] that these terms are small relative to $\kappa_1$ in the $E_{2u}$ model. We will therefore solve for $H_{cs}$ to first order in $\lambda = (\kappa_2 + \kappa_3)/2\kappa_1$. The linearized Ginzburg-Landau equation given by the free energy in Eq. 1 is
In the presence of this surface free energy density the boundary conditions are

\[ \alpha \vec{\eta} = \left( \begin{array}{ccc} \kappa_1 D_y^2 + \kappa_2 D_y^2 + \kappa_3 D_y^2 \, & -\gamma \kappa_2 D_x D_y + \kappa_3 D_y D_z \\ \kappa_3 D_x D_y + \kappa_2 D_y D_z \, & \kappa_1 + 3 \kappa_2 y^2 + \gamma + \gamma^2 \end{array} \right) \vec{\eta} \] (2)

where \( \kappa_{1,23} = \kappa_1^2 + \kappa_2 + \kappa_3 \).

We will consider the geometry in which the superconductor occupies the half space \( y > 0 \). The surface normal will be taken to be along the \( \vec{a} \) (or \( y \)) direction and the antiferromagnetic moment along the \( \vec{a}^* \) (or \( x \)) direction. The field will be chosen to lie along the \( \vec{a} \) or \( \vec{a}^* \) directions. This geometry will allow for a comparison to be made with the measurements of Keller et. al. [10].

The off diagonal terms in Eq. 2 containing \( \kappa_2 \) and \( \kappa_3 \) vanish in the determination of the upper critical field for the field orientations chosen above when there is no surface present. In the presence of a surface normal along \( \vec{a} \) it can be shown that to first order in \( \lambda \) these terms have no effect. In this limit the Ginzburg-Landau equations decouple for the \( \eta_1 \) and \( \eta_2 \) components. When the field lies along \( \vec{a} \) then the upper critical field (denoted \( H_{c2}^a \)) is given by

\[ \sqrt{\kappa_1^+ \kappa_4^+ \mu^2 [H_{c2}^a]^2} = -\alpha + \gamma, \quad \eta_2 \neq 0 \quad \eta_1 = 0 \] (3)

where \( \alpha = \alpha_0(T - T_c) \). If \( \gamma > 0 \) and \( \delta_1 \leq 0 \) or \( \gamma < 0 \) and \( \delta_1 \leq 0 \) then the two solutions will cross at a temperature \( T^* \). This crossing gives rise to the kink in \( H_{c2}^a(T) \) that is observed in experiment. For the field along the \( \vec{a}^* \) direction the upper critical field for surface superconductivity (denoted \( H_{c3}^{a,*} \) where \( a \) refers to the surface normal and \( a^* \) to the field direction) can be found using the exact solution for conventional superconductors [12]; this yields

\[ \sqrt{\kappa_1^+ \kappa_4^+ (1 + \lambda) \mu^2 [H_{c3}^{a,*}]^2} = -\alpha - \gamma, \quad \eta_1 \neq 0 \quad \eta_2 = 0. \] (4)

where \( \mu^2 = 0.59010 \). An immediate consequence is that \( H_{c3}^{a,*} \) will have a kink where the two solutions cross. This kink will occur at the approximately \( T^* \) (the difference is of order \( \lambda \)). Note that \( H_{c3}^{a,*}/H_{c2}^a = 1/\mu^2 + O(\lambda) \) for all temperatures in this model. Keller et. al. [10] have observed that this ratio is strongly temperature dependent. This model cannot account for the observed behavior.

Qualitatively different behavior from that presented above arises when the surface free energy is considered [14]. For conventional isotropic superconductors with order parameter \( \psi \), the surface free energy takes the form \( g \int_{surface} |\psi|^2 dS \). For \( g > 0 \) this term suppresses surface superconductivity. However, superconductor to insulator or vacuum boundaries of isotropic superconductors are well described by \( g = 0 \) [12]. For anisotropic superconductors this is not necessarily the case. For the E-REP models and the geometry defined above the surface free energy density has the form

\[ F_{surface} = g_1 |\eta_1|^2 + g_2 |\eta_2|^2. \] (6)

In the presence of this surface free energy density the boundary conditions are

\[ -(\kappa_1 D_y \eta_1 + \kappa_3 D_z \eta_2) = g_1 \eta_1 \]
\[ -(\kappa_1 + 3 \kappa_2 y^2 D_y \eta_1 + \kappa_2 D_z \eta_1) = g_2 \eta_2. \] (7)

Assuming that the coefficients are field independent one can find \( H_{c3}^{a,*} \) by using the method similar to that used for an isotropic superconductor [12]. For convenience we set \( \lambda = 0 \) in the remainder of this article (the corrections \( O(\lambda) \) are easily obtained). The solution is given by

\[ H_{c3}^{a,*}/H_{c2}^a = \frac{1}{\mu^2(l_i - l_i^2)} \] (8)

where \( i \) refers to the solutions \( \vec{\eta}_1 = (1,0) \) or \( \vec{\eta}_2 = (0,1) \), \( l_1 = [H_{c2}^a/H_{c3}^{a,*}]^{1/2} g_1/(\kappa_1 \alpha_0(T_c - T))^{1/2} \), \( l_2 = [H_{c2}^a/H_{c3}^{a,*}]^{1/2} g_2/(\kappa_1 \alpha_0(T_c - T))^{1/2} \), \( T_c^\pm = T_c \pm \gamma/\alpha_0 \), and \( \mu(l_i) \) is defined by

\[ \int_0^\infty (2u - \mu - l_i^2) e^{-(u - \mu)^2} u^{(1 + \mu^2 - l_i^2)/2} du = 0. \] (9)
Insight into the values of the coefficients \( g_1 \) and \( g_2 \) can be obtained from the microscopic model originally studied by Ambegaokar et. al. for superfluid \(^3\)He [2] and extended to anisotropic superconductors by Sigrist and Ueda [13] and also by Samokhin [14]. The microscopic weak coupling analysis of [13] and [14] indicates that for a specularly reflecting surface with normal \( \vec{n} \), \( g_1 = 0 \) if \( P_{\vec{n}} \Delta(\vec{k}) = \Delta(\vec{k}) \) where \( P_{\vec{n}} \Delta(\vec{k}) = \Delta(\vec{k} - 2\vec{n} \cdot \vec{k}\vec{n}) \) and that \( g_1 = \infty \) or \( g_1 \approx \alpha_0 T_c \zeta_0 \) [13] \((\zeta_{0,1} \text{ is the zero temperature coherence length})\) if \( P_{\vec{n}} \Delta(\vec{k}) = -\Delta(\vec{k}) \). This is in agreement with experiments for conventional isotropic superconductors for which \( P_{\vec{n}} \Delta(\vec{k}) = \Delta(\vec{k}) \) for all surface normals (note that this model is exactly solvable for \( H_{\text{eff}} \)).

Ambegaokar et. al. showed that transform as different one dimensional representations of the hexagonal point group (one as an \( A \) and the other as a \( B \) representation). The surface free energy density takes the form

\[
g(\vec{k} \cdot \vec{n}) = |\vec{\psi}|^2 + 2g_1 |\vec{\psi}|^2 + \frac{g_2}{2}|\vec{\psi}|^2.
\]

For \( g_2 = 0 \), \( H_{c_3}^{e,a} \) is exactly solvable for \( AB \) as a one dimensional representation under spatial transformations the surface free energy density takes the form

\[
\frac{\delta \gamma}{\delta \alpha} = \frac{\partial H_{c_3}^{e,a}}{\partial \alpha} + \frac{\partial H_{c_3}^{e,a}}{\partial \alpha} \approx \frac{\partial H_{c_3}^{e,a}}{\partial \alpha}.
\]

In the 1D-REP model [18] the order parameter is a three dimensional order parameter that transforms as a \( \vec{n} \) (see below). However, experiments on UPt\(_3\) samples with a well defined kink in \( H_{c_2}^{e,a} \) will be required for a quantitative comparison.

The above discussion is relevant to specular reflecting surfaces which in fact does not account for the experimental results on UPt\(_3\) (see below). If diffusive scattering is considered then the \( \eta \) component will also be suppressed at the surface. This is taken into account by introducing \( g_2 \neq 0 \). In Fig. 2 we have plotted \( H_{c_3}^{e,a} / H_{c_2}^{e,a} \) versus temperature for \( g_1 \approx \alpha_0 T_c \zeta_0 \) and \( g_2 = \alpha_0 T_c \zeta_0 / 10 \) where \( \zeta_0 = \zeta_{0,1} / \alpha_0 T_c^{\pm} \).

Keller has given a graph of \( \Delta(T) = T_{H_{c_2}^{e,a}} - T_{H_{c_2}^{e,a}}(H) \) versus \( H \) that illustrates the temperature dependence of \( H_{c_3}^{e,a} / H_{c_2}^{e,a} \). It was observed that \( \Delta(T) \) initially increased with increasing field until it reached a maximum (at \( H \approx 0.25 \) Tesla after which it decreased with increasing field. It can be seen that for specular reflection \( \Delta(T) \) is always increasing with \( H \) (see Fig. 1a). The experimental behavior is best described by the \( \gamma > 0, \delta_1 + \delta_4 > 0 \), and the diffusive scattering values \( g_0 T_c^{\pm} \zeta_0 / 12 < g_2 < g_0 T_c^{\pm} \zeta_0 / 8 \) and \( g_1 \approx \alpha_0 T_c \zeta_0 \) (as in Fig. 2).

We have considered the simplest case in which the antiferromagnetic moment is pinned orthogonal to the surface. Other possible relative orientations of the surface and the antiferromagnetic moment are possible. Differing domain distributions at different surfaces may account for the different values of \( H_{c_3} \) observed at these surfaces (note that different values of \( g_2 \) for different surfaces also can account for the observed \( H_{c_3} \) values). A detailed study can be undertaken once a better understanding of the antiferromagnetic domain structure near the surface is achieved. We have also assumed that the whisker used by Keller et. al. can be described by the same model that describes annealed UPt\(_3\) samples. We note that Keller gives the \( H_{c_2}^{e,a} \) curve for this whisker [14]. There is a strong curvature in \( H_{c_2}^{e,a} \) at small fields and as the field increase above \( H \approx 0.25 \) Tesla (note this is approximately the same field at which \( \Delta(T) \) attains its maximum), \( H_{c_2}^{e,a} \) increases linearly with temperature. We expect that our model is qualitatively correct for this whisker. However, experiments on UPt\(_3\) samples with a well defined kink in \( H_{c_2}^{e,a} \) will be required for a quantitative comparison.

The model presented above also implies informative results for \( H_{c_3}^{e,a} \). For a surface normal along the \( \vec{c} \) axis symmetry implies \( g_1 = g_2 \) in Eq. 3. It is therefore expected that \( H_{c_2}^{e,a} \) will either exhibit a kink at \( T \approx T^* \) or be suppressed. Using the microscopic arguments presented earlier it is expected that for the \( E_{2u} \) and \( E_{1g} \) representations \( H_{c_3}^{e,a} \approx H_{c_2}^{e,a} \) while for the \( E_{1u} \) and \( E_{2g} \) representations \( H_{c_3}^{e,a} > H_{c_2}^{e,a} \).

A similar analysis for different models of UPt\(_3\) results in qualitatively different behavior than that of the E-REP models. In the 1D-REP model [18] the order parameter is a three dimensional order parameter that transforms as a vector under spin rotations and as a one dimensional representation under spacial transformations. In this model the antiferromagnetic moment breaks the spin degeneracy of the order parameter. Since the order parameter transforms as a one dimensional representation under spacial transformations the surface free energy density takes the form

\[
g(\vec{k} \cdot \vec{n}) = |\vec{\psi}|^2 + 2g_1 |\vec{\psi}|^2 + \frac{g_2}{2}|\vec{\psi}|^2.
\]

for all surface normals (note that this model is exactly solvable for \( H_{c_3}^{e,a} \) using Eqs. 3 and 4). This surface free energy does not allow any anisotropy to occur between the different order parameter components. It is therefore difficult to reconcile this model with the experimental observations of Keller et. al. [13,14].

In the accidentally nearly degenerate \( AB \) model [13] the order parameter has two components of the same parity that transform as different one dimensional representations of the hexagonal point group (one as a \( A \) and the other as a \( B \) representation). The surface free energy for all surface normals takes the form \( g_A |\psi_A|^2 + g_B |\psi_B|^2 \). This model is also exactly solvable for \( H_{c_3} \). Analysis indicates that the results for \( H_{c_3}^{e,a} \) are similar to that of the E-REP models with \( \lambda = 0 \). However, a qualitative difference may occur in \( H_{c_3}^{e,a} \) between these two models. For \( H_{c_3}^{e,a} \) in the even parity \( AB \) models, microscopic analysis indicates one component will be suppressed and the other will not be.
Consequently the resulting behavior of $H_{c_2}^{a_3}$ will correspond to that of one of the two curves in Fig. 2.

In conclusion, we have, for the first time, used experimental results on surface superconductivity to yield information about the symmetry of the superconducting order parameter. In particular the experiments of Keller et. al. on UPt$_3$ can be understood if one component of the order parameter is strongly suppressed while the other component is weakly suppressed for a surface normal along the $\vec{a}$ direction. This anisotropy places a strong constraint on phenomenological models of superconductivity in UPt$_3$. Further experimental investigations of surface superconductivity can place additional constraints on these models.

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FIG. 1. $H_{c_2}^{a_3}$ (upper curves) and $H_{c_2}^{a_1}$ (lower curves) as a function of temperature for different model parameters for specular reflecting surfaces. The parameters have been chosen to agree with the experimental phase diagram for $H_{c_2}^{a_1}$. a) $\gamma > 0$, $\delta_1 + \delta_4 > 0$ b) $\gamma < 0$, $\delta_1 + \delta_4 < 0$.

FIG. 2. The ratio $H_{c_2}^{a_3} / H_{c_2}^{a_1}$ for diffusive scattering at the surface. The rightmost curve corresponds to $\gamma > 0$, $\delta_1 + \delta_4 > 0$ and the other curve to $\gamma < 0$, $\delta_1 + \delta_4 < 0$. 

4