Surface superconductivity in the heavy-fermion superconductor UPt_3

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We present a study of the surface critical field $H_{c3}(\Phi,\Theta,T)$ measured for two needlelike whiskers of UPt_3. Dominant surface effects were observed in the angular dependence of the critical field by means of ac-resistivity measurements. These surface superconductivity effects show a surprisingly nonlinear thermal variation of H_{c3} contrary to behavior expected from conventional theory, where $H_{c3}/H_{c2} = 1.69$ is predicted. The ratio H_{c3}/H_{c2} is strongly depressed from its initial value 1.7 when going from the A to the C phase as the temperature is decreased. It seems to remain constant in the C phase for even lower T. Nevertheless, for temperatures close to T_{c+} it is possible to describe the angular behavior of $H_{c3}(\Theta,\Phi)$ with a standard model by introducing an effective-mass anisotropy of the heavy quasiparticles. These results are compared to recent H_{c3} calculations for different representations of the order parameter and seem to provide a direct evidence for the suppression of one component of the order parameter at the surface. The restrictions imposed by these measurements on the choice of the representations of the unconventional order parameter will be discussed by also taking into account the limitations imposed due to the temperature dependence of the basal plane H_{c2} modulation. [S0163-1829(96)04142-2]

I. INTRODUCTION

The superconductivity of the heavy-fermion compound UPt_3 presents a variety of different phenomena. Specific-heat,[1] thermal-expansion,[2] and ultrasonic attenuation measurements[3] showed the phase diagram to be composed of three different superconducting phases which join in a tetracritical point. Commonly, these three phases are designated now by the letters A, B, and C, representing the high-temperature–low-field, the low-temperature–low-field, and the low-temperature–high-field phase, respectively (review, e.g., Ref. 4). We will use the notation T_{c+} and T_{c-} to identify the two successive transitions into the A and the B phase in zero applied magnetic field. Several theoretical models have been proposed to account for the three superconducting phases (review, e.g., Ref. 5). A main distinction between these different proposed models resides in the temperature dependence of H_{c2}(T) in the hexagonal plane. Early resistivity measurements on whiskers by Taillefer[6] and Behnia,[7] testing the H_{c2} line between the normal and the superconducting state, showed the discontinuity of $\partial H_{c2}/\partial T$ at $(T^\star,H^\star)$ for every field direction in the basal plane. But also the angular variation of the resistivity $[\rho(\Phi)]$ measured in the middle of the superconducting transition exhibited very sharp, pronounced peaks with a periodicity of 60°. This observed anisotropy in the critical field of the hexagonal plane was difficult to explain in the framework of the existing models. We wish to stress here the importance of surface effects in such transport measurements which allow us to explain the former experiments.

In this paper we present a detailed analysis of the angular and thermal variation of the critical fields measured on whiskers of UPt_3. The results strongly depend on the particular shape of the specimen and can only be analyzed by taking into account predominent surface effects, as already previously noticed.[8] The interpretation of the measurements in terms of surface superconductivity, exhibiting a suppression of the ratio H_{c3}/H_{c2} with decreasing temperature, also provides a satisfying explanation for the former results obtained in Refs. 6 and 7.

II. EXPERIMENTAL DETAILS

We studied needlelike whiskers of UPt_3 which were grown by a bismuth-flux method.[9] They have typical dimensions of $0.1\times0.15\times5\ \mathrm{mm}^3$ with their c axis parallel to the axis of the whisker. The samples exhibit a nearly hexagonal cross section with the surface normals possessing a sixfold symmetry. Laue diffraction patterns showed the surface normals to be parallel to the a axis of the hexagonal lattice. We use the notation $a^\star$ to designate the direction perpendicular to each a axis. The planar surfaces of the as-grown whiskers have a polished appearance with well defined sharp edges on the total length and nearly no irregularities on a scale of 10 μm. Whiskers 1 and 2 have a superconducting transition at $T_{c+}=508$ and 501 mK, respectively, with a typical transition width of $\Delta T_c=18$ mK as measured by conventional four-point ac resistivity using indium-soldered contacts. Their normal-state resistivity at 530 mK was 1.35 and 1.03 $\mu\Omega$ cm, respectively, which is a factor of 2 more elevated

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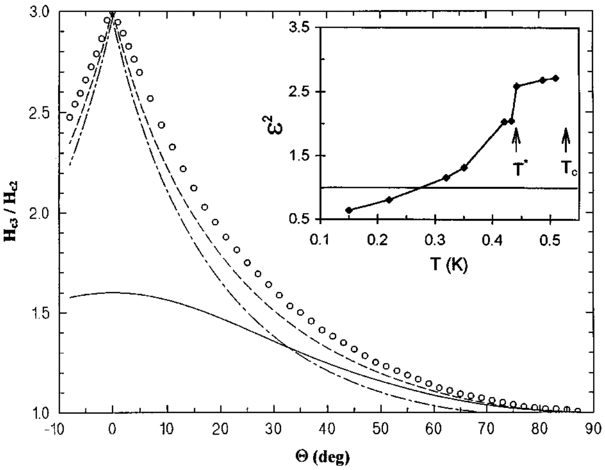

FIG. 1. $H_{c3}(\Theta)$ between the basal plane ($\Theta=90°$) and the c axis at $t=0.923$. The solid line shows the $H_{c2}(\Theta)$ anisotropy calculated for an effective mass ratio of 1.8. The dashed and the dashed-dotted lines show theoretical $H_{c3}(\Theta)$ curves calculated using formulas by Yamafuji *et al.* (Ref. 12) (extended to anisotropic superconductors) and Minenko *et al.* (Ref. 17), respectively. The inset represents the thermal variation of the parameter ε^2 as extracted from the measurements of $H_{c2}(\Theta,T)$ (Ref. 21) using formula (2) (see text for details).

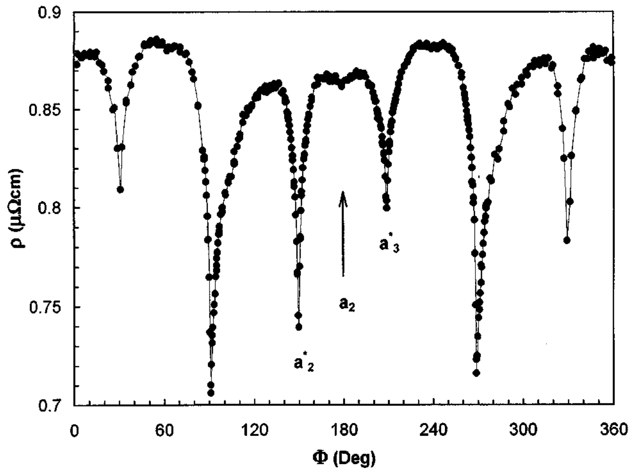

FIG. 2. $\rho(\Phi)$ measured on whisker 2 at $t=0.923$ for an applied field of $|H|=0.1$ T. The sharp minima appear for the magnetic field being parallel to a surface. Also shown are the crystalline orientations a_2, $a_2^\star$, and $a_3^\star$ with respect to the $\rho(\Phi)$ data.

than the value of Czochralski-grown single crystals [~ 0.5 $\mu\Omega$ cm at 530 mK (Ref. 8)].

The samples were mounted on the cold finger of a miniaturized dilution refrigerator and placed in the center of an assembly of three superconducting coils. The magnetic field with a maximum field strength of 0.85 T can be oriented in any spatial direction with an angular accuracy of 0.1° and a stability of the overall magnetic-field amplitude better than 0.1%. The choice of a low current density $J=0.1$ A/cm^2 for the ac resistivity ensured that no additional broadening of the resistive superconducting transition $\rho(T)$ (e.g., due to depinning effects) was observed in applied magnetic fields. The angular and thermal variations of the critical fields were measured as described in Ref. 8. The so-determined critical fields do not depend on the measurement procedure. In the following we designate by the angle Θ the direction of the applied field with respect to the c axis (e.g., $\Theta=0{:}H\|c$) and by the angle Φ the direction of H in the hexagonal plane with respect to one crystallographic a axis, which we named a_2 (see Fig. 2 for definition).

III. SURFACE CRITICAL FIELDS

The angular variation of the critical field was measured for several temperatures on both samples. First we will consider the critical field variation between the c axis and the hexagonal plane with $\Phi=0°$. In Fig. 1 we show its angular variation measured on whisker 2 at a temperature of $T=470$ mK ($t=T/T_c=0.923$) between the c axis and the hexagonal plane (see also Ref. 8). A pronounced peak is observed for the orientation of the external field parallel to the c axis. This sharp maximum can be understood in the framework of surface superconductivity as proposed by Saint-James and de Gennes.[10] They consider the boundary condition $\partial\psi/\partial x=0$ at the surface of the superconductor to the vacuum. They showed that a small superconducting layer of thickness $\sim 1.695\xi_0$ exists below the surface in external magnetic fields stronger than H_{c2} up to a value of H_{c3} ($\simeq 1.7\,H_{c2}$) when the direction of the field is oriented parallel to the surface. Their approach has been extended by several authors[11–15] to describe the measured temperature variation (near T_c and near $T=0$ K) and the angular variation of H_{c3}, also for anisotropic superconductors.[16,17] Considering an isotropic superconductor with a superconductor to vacuum interface and using a variational calculation,[18] the angular variation of the surface critical field H_{c3} can be approximated by

$$H_{c3}(\Theta)/H_{c2}=(|\sin\Theta|+\sigma\cos\Theta)^{-1};\quad \sigma=\sqrt{1-\frac{2}{\pi}}\tag{1}$$

with Θ being the angle between the surface and the field direction. It can readily be seen from this expression, that a peaklike maximum is expected in $H_{c3}(\Theta)$ for small values of Θ. This angular variation can be identified in the measured $H_{c3}(\Theta)$ curve which is represented in Fig. 1.

For comparison with the smooth angular variation of $H_{c2}(\Theta)$, which is due to an anisotropy of the Fermi surface, we also plotted this function (solid line) in Fig. 1 using the formula of the anisotropic mass model:

$$\frac{H_{c2}(\Theta)}{H_{c2}(90°)}=(\varepsilon^2\cos^2\Theta+\sin^2\Theta)^{-1/2}\tag{2}$$

with $\varepsilon=(m_\|/m_\perp)^{1/2}=1/1.63$. This value ε can be deduced from the ratio of the initial slopes $\partial H_{c2}/\partial T$ at T_{c+}, where $(\partial H_{c2,\|c}/\partial T)/(\partial H_{c2,\perp c}/\partial T)=\varepsilon^{-1}$ (Ref. 18) using the H_{c2}(T) anisotropy given in Ref. 8. The pronounced maximum can obviously not exclusively be described by the anisotropy of the Fermi surface which nevertheless has to be considered within the detailed description. Trying to determine the angular variation of the surface critical field H_{c3}, Yamafuji *et al.*[12] and Minenko[17] proposed approximative formulas for isotropic and anisotropic superconductors, respectively. Here, anisotropic (isotropic) designates the case of an elliptical (spherical) Fermi surface leading to anisotropic effective masses of the quasiparticles. The dashed line in Fig. 1 represents the calculated $H_{c3}(\Theta)$ curve from the Yamafuji model, which has been extended by coordinate transformation to include the principal axis anisotropy $(z=z'/\varepsilon, H_x=\varepsilon H'_x, \varepsilon^2=m_\parallel/m_\perp)$. As the model contains no free parameters the accordance is surprisingly good for temperatures close to T_{c+}. Unfortunately, the boundary condition in this model is only respected for the orientation of H perpendicular to the surface,[17] it therefore can only be considered as an approximate solution. A more elaborate calculation by Minenko[17] for anisotropic superconductors, can give a more accurate account of the angular variation but is restricted to a smaller angular range due to the choice of the trial functions (dashed-dotted line in Fig. 1). In either case, the ratio

$$\frac{H_{c3}(0°)}{H_{c3}(90°)}=\left(\frac{m_\perp}{m_\parallel}\right)^{1/2}\sigma^{-1};\quad \sigma^{-1}=1.695 \tag{3}$$

is given by both models and represents the exact solution for an infinite superconductor-vacuum surface. We have shown that the angular dependence of the measured critical fields close to T_{c+} can be qualitatively well explained by assuming the existence of a thin superconducting surface layer of thickness $d\sim\xi_0$ for magnetic fields superior to H_{c2} (see also Ref. 8). Therefore we identify now the measured values of the critical fields to be equal to the surface critical field $H_{c3}(\Theta,T)$ (see Ref. 22). As can be readily calculated from Fig. 1 and Eq. (3), even the absolute value of $H_{c3}(\Theta=0°)/H_{c2}(\Theta=90°)\sim 1.67$ is encountered when taking into account the Fermi-surface anisotropy via the effective mass ratio $\varepsilon=(m_\parallel/m_\perp)^{1/2}=1/1.8$. For $H\|c$, the crude approximation of only one infinite superconductor-vacuum interface seems to describe reasonably well the experimental results.

Now we consider the angular variation of the resistivity $\rho(\Phi)$ and the surface critical field $H_{c3}(\Phi)$ for a rotation of the magnetic field in the basal plane $(\Theta=90°)$. Our measurements of $\rho(\Phi)$, at a temperature coinciding with the midpoint of the resistive transition, show marked peaks with a periodicity of 60° (see Fig. 2) similar to those observed by Taillefer in earlier measurements.[6] These peaks occur every time the magnetic field is oriented parallel to a surface, hence the sixfold symmetry of the surface normals is projected into the angular variation of the resistivity. The corresponding critical field measurements performed on the same whisker are shown in Fig. 3. The characteristic discontinuitylike enhancement for $H_{c3}(\Phi)$ reflects the sixfold symmetry of the surface normals. Qualitatively, this angular variation can also be described by assuming not only one ideal infinitely extended surface, but a superposition of six ''ideal'' surfaces at angles of $\Phi_n=(2n+1)\pi/6$ $(n=1,2,\ldots,6)$ which reflects the experimentally encountered situation. The angular variation of the critical field using Eq. (1) can be approximated by

$$\frac{H_{c3}(\Phi)}{H_{c2}}=\max|[|\sin(\Phi-\Phi_n)|+\varepsilon_n^\star|\cos(\Phi-\Phi_n)|]^{-1}|_n \tag{4}$$

with $\varepsilon_n^\star=H_{c2}/H_{c3}(\Phi_n)|_n$ varying for every considered surface (n). Thus $\varepsilon_n^\star$ incorporates the finite-size effects. As we

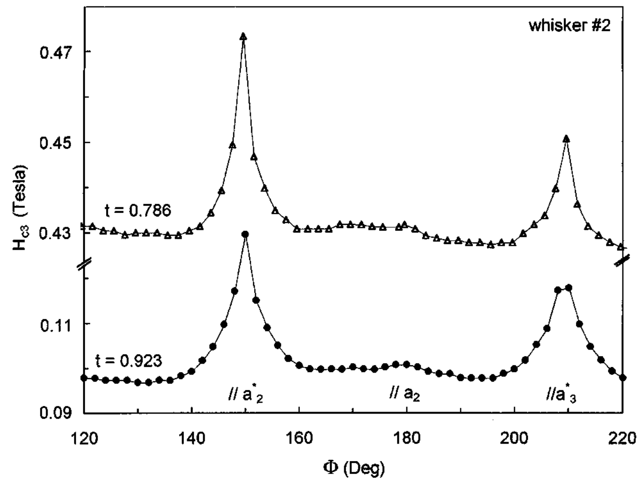

FIG. 3. $H_{c3}(\Phi,T)$ measured on whisker 2 at temperatures of $t=0.923$ (△) and $t=0.786$ (●). The suppression of the H_{c3} relative to the $H_{c2}^\star$ with decreasing temperature is clearly visible.

have already demonstrated in Ref. 8, the measurements of $H_{c3}(\Phi)$ can be represented by formula (4) (see continous line in Fig. 1 of Ref. 8). The parameters used for the fit were $\varepsilon_1^\star=0.831$ and $\varepsilon_2^\star=0.739$. Their ratio $\varepsilon_1^\star/\varepsilon_2^\star\approx 1.12$ corresponds roughly to the ratio of the related surface areas which had a value of 1.2. This relation between the geometry of the superconductor to vacuum interface and the value of H_{c3} has already been investigated by van Gelder *et al.*[19] on thin films with a wedge edge geometry. They have shown the actual geometry to be the dominant factor for the absolute value of $\varepsilon^\star=H_{c2}/H_{c3}$. Hence the finite sizes of the real surfaces are influencing significantly the ratios $H_{c3}(\Phi_n)/H_{c2}$ for the three principle directions of the field in the basal plane parallel to the surfaces.

Furthermore, one notices that the critical fields for $H\|a$ ($H\perp$ surfaces) do not correspond to the bulk H_{c2} as the magnetic field is not perpendicular to all of the surfaces but only to one. Therefore the value of the critical field, which we will designate by $H_{c2}^\star$, is enhanced over H_{c2} due to a still persisting small surface superconductivity contribution.

IV. H_{c3} PHASE DIAGRAM

The phase diagram (Fig. 4), as determined for whisker 2, shows several characteristics which we will consider in the following sections. The overall anisotropy between $H\|c$ and $H\perp c$ shows the same behavior as observed in most experiments. Nevertheless, we would like to focus attention on several particularities of the H_{c3} phase lines. First of all, one notes that the slope of $H_{c3}(\|c)$ close to T_{c+} is steeper than $\partial H_{c2}/\partial T$ for higher fields ($H>0.5$ T), contrary to the expected thermal variation (cf. Ref. 2). This behavior is strongly correlated to the influence of the surface on the critical field as will be shown in the next section. On the other hand, a significant anisotropy of H_{c3} can be observed for the a and the $a^\star$ directions in the hexagonal plane, which also changes with decreasing temperature. The linear $H_{c3}(T)$ dependence at higher fields can be used to determine the tetracritical point to be at $T^\star=395$ mK and $H^\star=0.42$ T $(H\|a^\star)$, where it starts to deviate from the linear depen-

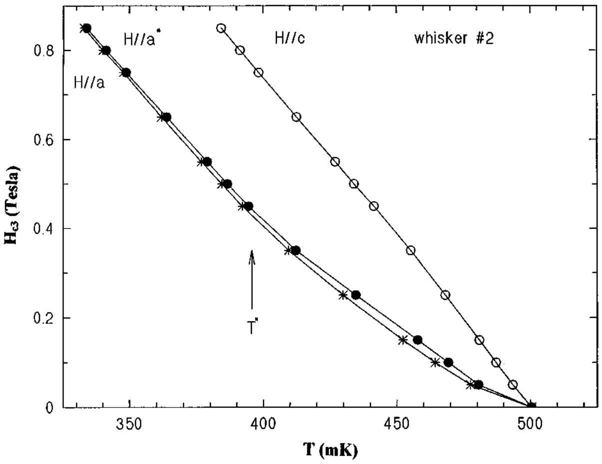

FIG. 4. Phase diagram of the surface critical field $H_{c3}(T)$ showing the anisotropy between $H\|c$ (○) and $H\perp c$. The in-plane anisotropy for the whisker 2 can be observed for $H\|a$ (⋆) and $H\|a^\star$ (●).

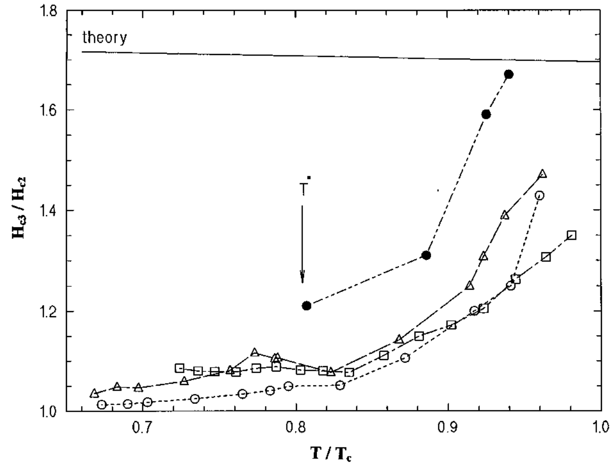

FIG. 5. Temperature variation of H_{c3} relative to H_{c2} measured for $H\|c$ (●), $H\|a_3^\star$ (△) and $H\|a_2^\star$ (○), evaluated from a phase diagram with basal plane H_{c2} anisotropy in Ref. 7 (□) and compared to theoretical prediction by Hu *et al.* (Ref. 15) (solid line). The value of $H_{c2}(\|a)$ used to determine the ratio H_{c3}/H_{c2} is probably an overestimation of the real H_{c2} in the basal plane due to a still persisting surface contribution. Therefore, the H_{c3}/H_{c2} appear to have a reduced value for field directions in the hexagonal plane compared to the $H\|c$ geometry.

dence. In the following analysis we will only consider the phase line $H_{c3}(T)$. Therefore, we will refer to the temperature range $T>T^\star$ ($T<T^\star$) as the A (C) phase, respectively. The change in slope $\partial H_{c3}/\partial T$ can be distinguished for all directions of the field in the basal plane also at intermediate angles (cf. Ref. 6).

V. TEMPERATURE DEPENDENCE OF H_{c3}

The $H_{c3}(\Theta,T)$ data ($\Phi=0°$) were analyzed according to formula (3) using the effective-mass ratio ($m_\|/m_\perp$) determined from $H_{c2}(\Theta)$ measurements.[20,21] Here we take the ratio $\varepsilon^2=m_\|/m_\perp$ as a parameter to describe the change in $H_{c2}(\Theta)$ as a function of temperature [formula (2)]. The analysis of the $H_{c2}(\Theta)$ curves of Ref. 21 provided the thermal variation of the parameter ε^2, as represented in the inset of Fig. 1. Therefore, for every $H_{c3}(\Theta,T)$ curve it is possible to calculate the H_{c3}/H_{c2} ratio. The results are summarized in Table I and shown in Fig. 5. The data taken on both whiskers for $H\|c$ are represented by the solid dots. The surface superconductivity is apparently strongly suppressed in the A phase, where it is reduced from a value close to 1.7 at T_{c+} to ~ 1.2 below $T^\star$.

Now we will discuss the temperature dependence of H_{c3} when the magnetic field is only rotated in the hexagonal plane ($\Theta=90°$). For the directions of the magnetic field parallel to the $a_2^\star$, a_2, and $a_3^\star$ directions (defined in Fig. 2), the temperature evolution of the critical fields were carefully determined by $\rho(T)$ measurements in constant applied magnetic fields. From these phase lines the ratios $H_{c3}(\|a_2^\star)/H_{c2}^\star(\|a_2)$ and $H_{c3}(\|a_3^\star)/H_{c2}^\star(\|a_2)$ were determined for the temperature range of 0.65 T_c to T_c. The data is also represented in Fig. 5. One clearly sees the decrease of the surface critical field relative to the H_{c2} for decreasing temperatures also in the basal plane. The value of $H_{c2}^\star(\|a_2)$ is probably an overestimation of the real H_{c2} in the basal plane due to a still persisting surface contribution.[22] Therefore, the $H_{c3}/H_{c2}^\star$ curves do not show the same absolute values for both of the directions $H\|c$ and $H\perp c$. The so-determined ratios H_{c3}/H_{c2} coincide with values determined directly from the $H_{c3}(\Phi)$ curves shown in Fig. 3 (see also data for whisker 1 in Ref. 8).

In the classical theory for surface superconductivity, the temperature variation of H_{c3} has been evaluated theoretically by several authors.[11,13–15] For an s-wave superconductor the surface critical field H_{c3} is expected to increase from the initial value of 1.695 towards a value of 1.99(2.09) when considering specular (diffuse) reflexion of the quasiparticles at the surface.[14] Hu and Korenman[15] expanded the Ginzburg-Landau free energy near T_c to sixth order and obtained two correction terms to the $H_{c3}(T)$ dependence:

$$\frac{H_{c3}}{H_{c2}}\simeq 1.695\star[1+0.614(1-t)-0.577(1-t)^{3/2}]. \quad (5)$$

TABLE I. Temperature evolution of the H_{c3}/H_{c2} determined for $H\|c$ under consideration of the global anisotropy of H_{c2} (see text for details).

No.	$t=T/T_c$	$m_\|/m_\perp$ (from Ref. 20)	$H_{c3}(0°)/H_{c3}(90°)$	$(H_{c3}/H_{c2})_{\rm calc}$
1	0.925	1.63	2.6	1.59
1	0.886	1.62	2.12	1.31
1	0.807	1.37	1.65	1.21
2	0.94	1.8	3.0	1.67

The solid line in Fig. 5 represents this temperature variation of $H_{c3}(T)$ for comparison with the experimental results. One clearly observes the significant difference between the classical H_{c3}(T) prediction and the measurements.

In Fig. 5, we also compare our experimental results to hitherto uninterpreted results available in the literature. Behnia[7] showed a phase diagram $H_{c2}(T)$ anisotropic in the basal plane, which was determined during the same measurements as reported in Ref. 6. We analyzed these data to extract the ratio H_{c3}/H_{c2} when supposing that also surface superconductivity was encountered. This data is also reported in Fig. 5 by the open squares. Surprisingly, the same strong suppression of the surface critical field with decreasing temperature in the *A* phase is observed for their measurements. Here we would like to emphasize that the former measurements were performed on whiskers prepared differently by rapid quenching of a UPt_3 melt in an UHV zone refining installation. Also early measurements by Kleiman *et al.*,[23] determining the phase diagram by mechanical torsional oscillator experiments, claim the observation of surface superconductivity. The H_{c3}/H_{c2} ratio, extracted from their phase diagram, also exhibits a strong suppression in the *A* phase, although the initial ratio close to T_c is far more elevated ($H_{c3}/H_{c2}\approx 2.8$ at $T/T_c\approx 0.94$) than the theoretical value of 1.695.

VI. DISCUSSION

Our measurements clearly show that the surface critical field (or H_{c3}/H_{c2}) in the basal plane $[H_{c3}(\Phi,\Theta=90°)]$ and along the *c* axis $[H_{c3}(\Phi=0°,\Theta)]$ is strongly suppressed in the *A* phase with decreasing temperature (see Fig. 5) and exhibits an essentially constant temperature evolution in the *C* phase. This temperature dependence is contrary to the verified predictions of the ''classical'' theory, where the ratio H_{c3}/H_{c2} should slightly increase towards $T=0$ K. These results seems to be strengthened by earlier, unanalyzed data of Behnia[7] and Kleiman *et al.*[23] One has to keep in mind when interpreting these results in the framework of the classical surface superconductivity theory, that these models consider an ideal superconductor-vacuum surface with a conventional *s*-wave order parameter.

Recent theoretical efforts by Samokhin,[24] Agterberg and Walker,[25] and Chen and Garg[26] focus on the calculation of H_{c3} for different possible representations of the order parameter belonging either to the one-dimensional representations (1D-REP) $A_i, B_i, A_i\oplus B_j$ or to the two-dimensional representations (2D-REP) E_i in the framework of a Ginzburg-Landau (GL) free-energy expansion. Samokhin[24] and Chen and Garg[26] each give complementary information for all possible order parameters on the boundary conditions and the suppression of certain components due to the presence of a boundary. According to the analysis by Samokhin, the order parameters belonging to the 1D-REP (A_1, A_2, B_1, B_2) give the ratio H_{c3}/H_{c2} to be independent from temperature over the entire validity range of the GL theory (refer to Ref. 24). This dependence is not observed for the measured data. The same conclusion is reached by Agterberg and Walker,[25] while analyzing the data of Ref. 8.

A. 1D Models

Here, we would like to recall the basic idea of the 1D-REP models (either A,B or mixed $A\oplus B$) (Refs. 27–29) to provide a basis for the following discussion. The superconducting ground state is assumed to be formed by two independent order parameters (η_1 and η_2) belonging to different 1D representations and exhibiting slightly different transition temperatures (T_{c+} and T_{c-}, respectively). Also the slope $\partial H_{c2}/\partial T$ differs in general between η_1 and η_2, being steeper for the latter in order to reproduce the $H_{c2}(T)$ phase diagram. Therefore, the *A* phase will be formed only by η_1, the *B* phase by η_1 and η_2 being simultaneously present, and the *C* phase only by the η_2 order parameter. Independent of the orientation of the applied magnetic field with respect to the crystallographic axes in these models the phase diagram always exhibits a tetracritical point. Also no additional mechanism like a symmetry breaking field (i.e., the antiferromagnetic ordering) is required as it is the case for the 2D models, which we will discuss later.

Concerning the mixture of two different types of order parameters ($A_1\oplus B_1$, $A_{1g}\oplus B_{2g}$, and $A_{1u}\oplus B_{2u}$) Chen and Garg[26] considered three different geometries of surface normals (n) along the a, $a^\star$, and the c axes, representing also our experimentally encountered situation ($n\|a^\star$). While also analyzing our data of Ref. 8, they conclude that the combination $A_{1u}\oplus B_{2u}$ could probably not be realized, as H_{c3} is predicted to be linearly proportional to H_{c2} over the entire temperature range ($H_{c3}=1.695H_{c2}$), which is contrary to the observations.

Now for both of the other considered combinations of mixed order parameters ($A_1\oplus B_1$ and $A_{1g}\oplus B_{2g}$) only the component η_2 is suppressed due to the boundary condition, whereas the component η_1 maintains the surface superconductivity even to fields higher than $H^\star$. This implies that the ratio H_{c3}/H_{c2} has a value of 1.695 in the *A* phase, due to the presence of η_1. As the H_{c2} in the *C* phase is given by η_2, possessing an enhanced slope $\partial H_{c2}/\partial T$ relative to the *A* phase, the H_{c3}/H_{c2} will exhibit a reduced value for temperatures $T<T^\star$. Ideally, H_{c3}/H_{c2} should present a step change in its value at $T^\star$ from its initial value of 1.695 to a value of 1.1. This value of H_{c3}/H_{c2} ($=1.1$) in the *C* phase can be estimated from the ratio $(\partial H_{c2,A}/\partial T)/(\partial H_{c2,C}/\partial T)$ in slopes of the H_{c2} ($=0.645$ for sample 1 in Ref. 8) between the *A* and *C* phases. Compared to our experiments this step change in H_{c3}/H_{c2} would only be encountered for perfectly linear $H_{c3}(T)$ and $H_{c2}(T)$ phase lines. Now, if one considers a more continuous variation of the slope between the *A* phase and the *C* phase, H_{c3}/H_{c2} will be expected to show a continuous decrease from its inital value 1.695 already in the *A* phase. This thermal variation, which we named suppression of H_{c3}/H_{c2} in the *A* phase, seems to be encountered for our experiments.

B. 2D Models

In general, the ground state due to the vector order parameter $\eta=(\eta_1,\eta_2)$ of the 2D-REP models is always degenerate and the corresponding phase diagram does only exhibit one superconducting order parameter. The degeneracy of the ground-state energy can be lifted if a symmetry-breaking mechanism (generally called the symmetry-breaking field), like a coupling between the superconducting order parameter η and the magnetic moments $|\mathbf{M}|$ of the antiferromagnetism ($F=\pm\zeta|\eta\mathbf{M}|$), is introduced into the free energy. All of the below-considered 2D-REP models reproduce the phase diagram for $H\perp c$ and $H\perp\mathbf{M}$. A study of $H_{c2}(T)$ as a function of the direction of the magnetic field in the hexagonal plane[6] has shown that the tetracritical point is generally present for $H\perp c$. Most of the E models (cf. Ref. 5) require one to assume a rotation of the magnetic moment $\mathbf{M}$ under the action of H to account for the experimental facts. However, recently inelastic neutron-scattering measurements seem to indicate that the directions of $\mathbf{M}$, which are fixed along the $a^\star$ directions,[30] do not rotate under the action of an external applied magnetic field.[31] Therefore in the framework of the basic E models the isotropy of the phase diagram for $H\perp c$ seems difficult to predict. Only for the $E_{2u}^{(2)}$ representation[32] of the order parameter, recently Agterberg and Walker[33] and Sauls[34] have shown, that incorporating a static orientation of the magnetic moments is sufficient to explain the observed $H_{c2}(T)$ phase diagram.

The main problem of the different considered representations of the order parameter (E_1,E_2) resides in the problem of reproducing the tetracritical point for $H\|c$ as it has been observed experimentally.[2,3] Only recently, Sauls[5] has shown that it is possible to overcome this problem when choosing the $E_{2u}^{(2)}$ representation of the order parameter and assuming only a very weak hexagonal anisotropy of the Fermi surface (see also Agterberg and Walker[33] who extended the model further). According to this approach the phase diagram can be reproduced for $H\perp c$ and $H\|c$. Also using this model the strong uniaxial suppression of H_{c2} for $H\|c$ compared to $H\perp c$ (Refs. 20 and 21) can be explained in terms of a uniaxial Pauli limiting of the H_{c2} for $H\|c$.[35,36]

Returning to the interpretation of the measured surface critical field $H_{c3}(T)$, Chen and Garg[26] also show that it should exhibit a similar T dependence for nearly all 2D-REP as for the $A\oplus B$ models [no surface superconductivity is to be expected for $E_{2u}^{(1)}$ (Refs. 24 and 32)], when the field is oriented along the $a^\star$ direction in the basal plane. For the orientation of H along the c axis, H_{c3}/H_{c2} is calculated to increase slightly with decreasing temperature for the E_{1g}, E_{1u}, E_{2g}, and $E_{2u}^{(2)}$ representation of the order parameter.[37] Our results for $H\|c$ show also a significant decrease in the ratio H_{c3}/H_{c2} and contradict therefore the predicted T dependence. One has to notice that the calculation for the $E_{2u}^{(2)}$ representation of the order parameter with the field along the c axis was performed without the refinements introduced by Sauls[5] in order to obtain the tetracritical point in the $H_{c2}(T)$ for this direction. This particular situation was recently considered by Agterberg and Walker[25] and they show that due to the suppression of the η_2 component of the vector order parameter $\boldsymbol{\eta}=(\eta_1,\eta_2)$ at the boundary, a suppression of the surface superconductivity in the C phase is to be expected in all directions of the field with respect to the crystal axis. They conclude that the strong reduction of H_{c3}/H_{c2} may be explained with the presence of an $E_{2u}^{(2)}$ order parameter. Summing these different calculations,[24–26] there seem to remain three different possibilities for the order parameter representations: $A_1\oplus B_1$, $A_{1g}\oplus B_{2g}$, and $E_{2u}^{(2)}$.

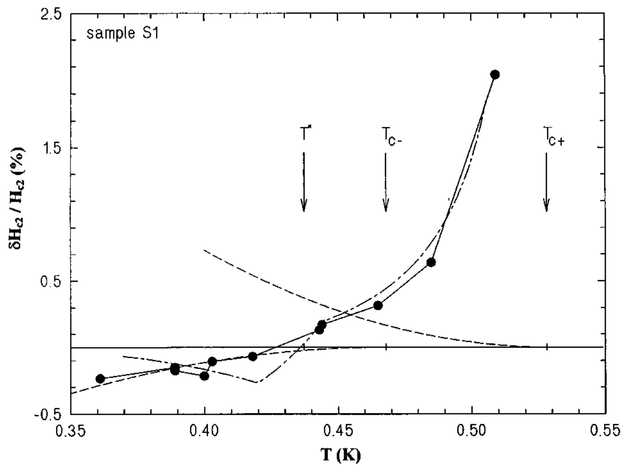

FIG. 6. Temperature variation of the $\delta H_{c2}/H_{c2}$ modulation observed during $H_{c2}(\Phi)$ measurements (Refs. 8 and 38). The two successive superconducting transitions take place at $T_{c+}=527.9$ mK and $T_{c-}=420$ mK. The H_{c2} modulation changes its sign at $T^\star\approx 437$ mK. The dashed lines represent a fit of the data for the A and C phases to the model T dependence $(1-T/T_{c\pm})^2$ determined by Mineev (Ref. 40) for order parameters of mixed $(A\oplus B)$ representation. The thermal variation in the C phase can obviously be described by the model, whereas in the A phase an opposite behavior is observed. The dashed-dotted line represents a $\delta H_{c2}/H_{c2}$ calculation by Sauls (Ref. 34) considering an $E_{2u}^{(2)}$ representation of the order parameter (see text), which we scaled by a factor of 1/20.1 to describe our results.

C. H_{c2} modulation in the hexagonal plane

At this point it seems suitable to reconsider the observed modulation δH_{c2} of the $H_{c2}(\Phi)$ in the basal plane,[8,38,39] which we observed on spark-cut single crystals, and the different theoretical models proposed for their explanation by Mineev,[40] Agterberg and Walker,[33,41] Sauls,[34] and Machida *et al.*[42] They all identify the change in sign of the modulation δH_{c2} at the tetracritical point to be related to the change in the components of the order parameter under consideration. Here once again an important feature of the observed H_{c2} anisotropy resides in its temperature variation which is significantly different between the A phase and the C phase (cf. Fig. 6). Mineev explicitly calculated the thermal variation of the expected modulation $\delta H_{c2}/H_{c2}$ for mixtures of order parameters belonging to two different one-dimensional representations $(A\oplus B)$. He showed it to be proportional to $(1-T/T_{c\pm})^2$. The dashed lines in Fig. 6 represent a fit of these formulas to the $\delta H_{c2}/H_{c2}$ data in the A and C phases. Whereas the thermal variation in the C phase is quite well described by the model, the modulation in the A phase shows a behavior inverse to the one calculated. On the other hand, Agterberg and Walker[33,41] and Sauls[34] calculated independently, while using the same $E_{2u}^{(2)}$ representation of the order parameter, that a theoretical description using this 2D representation can qualitively describe the observed H_{c2} modulation and its temperature dependence. To illustrate this qualitative accordance, we transformed (scaling factor 1/20.1) the δH_{c2} modulation calculated by Sauls[34] to be represented in Fig. 6. The calculated thermal variation of δH_{c2} shows the same behavior as the measurements except that a value of 30% close to T_c is an overestimation. The calculations by

Agterberg and Walker[41] reproduce more quantitatively the experiments.[38] Therefore, the measurement of the thermal change of the $\delta H_{c2}/H_{c2}$ modulations seems to exclude order parameters belonging to any of the one-dimensional representations.

VII. CONCLUSIONS

The measurements of the critical fields on whiskers of UPt_3 revealed pronounced surface superconductivity effects every time the magnetic field was oriented parallel to a surface. The observed angular variation of H_{c3} can be explained in the framework of classical surface superconductivity when the anisotropy of the effective masses of the quasiparticles is taken into account. Contrary to the expected small increase of the ratio H_{c3}/H_{c2} at lower temperatures, the measurements clearly show its strong suppression with temperature from a value of 1.69 at T_{c+} to a value of 1.1 in the C phase. According to the above-presented theoretical interpretations, this thermal variation of H_{c3}/H_{c2} can be taken as direct evidence for the suppression of one component of the unconventional order parameter at the surface due to the boundary condictions.

Keeping in mind that the surprising suppression of the surface superconductivity in the C phase favors either the $A_1 \oplus B_1$, the $A_{1g} \oplus B_{2g}$, or the $E_{2u}^{(2)}$ representation of the order parameter and that the thermal variation in the A and the C phase of the $\delta H_{c2}/H_{c2}$ modulation restricts the order parameter to belong to a 2D-REP, one may be tempted to conclude in favor of the $E_{2u}^{(2)}$ representation as the actually present superconducting order parameter in UPt_3. As pointed out recently by Sauls,[5] an order parameter of the $E_{2u}^{(2)}$ representation has also the required nodal structure to account for the thermal variation of the acoustic attenuation, the specific heat, and the penetration depths in UPt_3. It is possible to reach this conclusion after considering the large variety of different proposed theoretical models for both the upper critical field (e.g., Refs. 5, 40, 33, and 34) and the surface critical field[24–26] with their thermal variations.

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