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Penetration depth studies of organic and heavy fermion superconductors in the Pauli paramagnetic limit

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Abstract

We report penetration depth and resistivity measurements on a number of organic and heavy fermion superconductors in the Pauli paramagnetic limit using a self resonant tank circuit based on a tunnel diode oscillator (TDO). We call a superconductor Pauli limited when the interaction of the applied magnetic field with the electron spin limits the superconducting state, in contrast to orbital limiting, the traditional effect where vortices eventually destroy the superconducting state. In the Pauli limit, H_{c2} can change from a second order to a first order phase transition at low temperatures, or in a very clean sample a new superconducting state with a spatially varying order parameter has been predicted, which we refer to as the FFLO state. We have done extensive experiments that show a range of Pauli limited behavior in anisotropic superconductors. Our results for α-$(ET)_2NH_4Hg(SCN)_4$, κ-$(ET)_2Cu(NCS)_2$, and $CeCoIn_5$ show that the nature of the Pauli limiting state is sensitive to the mean freepath in the sample. In $CeCoIn_5$ we have observed clear evidence of the FFLO state using our TDO method, and our data agrees with specific heat and magnetization measurements. We also show that the application of pressure will suppress the Pauli limiting in κ-$(ET)_2Cu(NCS)_2$.

1. Introduction

In most superconductors, the application of a magnetic field will eventually destroy the superconductivity due to the orbital effect, commonly known as the formation of vortices. A qualitative explanation of this effect is that because the cores of the vortices are normal (actually the superconducting order parameter goes to zero only at the exact center of a vortex), the increased density of vortices driven by the applied magnetic field eventually displaces the superconducting phase.

If there were a way to prevent formation of the vortices, the ultimate limit for superconductivity would be when the magnetic energy, $\mu_b H$, overcomes the binding energy of the Cooper pairs. When the magnetic energy is large enough to polarize the antiparallel paired electrons, the superconducting state would no longer exist. This limit was first described in a paper by Clogston and often is called the Pauli paramagnetic limit [1,2]. Soon after the Clogston paper, it was found that the upper critical field of a Pauli limited superconductor changes from a continuous to a first-order transition below $t = T/T_c \simeq 0.56$ [3]. After further study, it was proposed that if the magnetic field were able to interact with the electron spins and the superconductor were clean (the mean free path greater than the superconducting coherence length), the Cooper pairs could have non-zero momentum, and the order parameter would become spatially modulated [4,5]. This new type of superconducting state is commonly called the FFLO or LOFF state after the theorists who predicted it.

During the 40 years since the introduction of this theory, physicists have looked for a superconductor in which the orbital motion is suppressed, so that the spin interaction or Pauli limiting dominates the high field physics. Two properties of superconductors can suppress the orbital contribution. If the material is layered, that is, quasi-one- or two-dimensional (Q1D or Q2D), the carriers in certain orientations could not freely move from one layer to another, and the vortices could not form as easily. If the spaces between the conducting layers are large enough (larger than the superconducting coherence length, the nominal size of the vortices), the vortices could fit between the low resistance layers of a Q2D superconductor and not affect the superconducting state. Another way to subdue

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the orbital motion of the quasiparticles is to increase their effective mass. This effect is well known by many physicists who have measured the slope of the critical field versus temperature in the superconducting phase diagram. This slope is determined by the effective mass of the quasiparticles, and the larger the effective mass, the greater the slope near T_c, and the higher the critical fields for a given T_c.

Given these two suggestions, the search for Pauli limited superconductors has focused on two types of materials; the highly anisotropic organic superconductors and the heavy fermion superconductors. The cuprates, although highly anisotropic, are intrinsically dirty, and therefore are not good candidates. Ideally, we should be able to measure a few critical parameters that will indicate if a material is in the Pauli limit at low temperatures or in more interesting cases has an FFLO state. The two critical parameters are the Maki [3] parameter $\alpha=\sqrt{2}H_{c2}^0/H_P$, where H_p is the Pauli limiting field, $H_{c2}^0=0.7T_c\frac{dH_{c2}}{dT}|_{T_c}$ is the orbital critical field [3], and r, a measure of how clean the system is. Most of these parameters come from routine measurements. In the ratio $r=\ell/\xi$, ℓ the mean free path can be calculated from the scattering time and the Fermi velocity. These values are in turn related to the Dingle temperature, T_D, the Fermi energy, and the effective mass, which can all be measured by Shubnikov-de Haas (SdH) or de Haas-van Alphen oscillations. The other necessary parameter for finding r is the superconducting coherence length, ξ, which is found from the measurement of H_{c2} versus temperature.

The value of the Pauli limit is problematic because it is a difficult quantity to determine. For a BCS superconductor, H_p is simply 1.84 T_c, where H_p is in tesla and T_c is in kelvin. However, the BCS approximation is poor for organic superconductors and useless for heavy fermions. Our solution to this problem has been to use a calculation suggested by McKenzie [7,8] that uses specific heat data near the superconducting transition to calculate the condensation energy, U_C, and the electron susceptibility, χ_e, to find to H_p via,

$$U_c=\frac{\mu_0}{2}\chi_e H_P^2, \tag{1}$$

where χ_e is the Pauli paramagnetic susceptibility. We further argue that although U_c can be found by the specific heat jump at T_c, χ_e is not easily measured. In many cases, Landau diamagnetism or the contributions of inner core electrons augment the susceptibility measurement and obscure the measurement of χ_e. This being the case we propose that Wilson's ratio can be used to find χ_e from the Sommerfeld constant $\gamma=C/T$, where C is the specific heat [9,10].

Assuming that we have found good values for H_P, H_{c2}^0, ℓ, and ξ, we will be able to predict which materials will exhibit Pauli limiting effects or the FFLO state. Gruenberg and Gunther [17] claim that if the Maki parameter $\alpha>1.8$, an FFLO state is possible, or H_{c2} could become a first-order transition below $t=0.55$. H_{c2} is normally a second-order transition in type II superconductors. Although Ref. [17] has certain assumptions that are only valid for BCS superconductors, this threshold is useful for the purpose of comparing different materials. The parameters described in this section are listed for a few superconductors of interest in Table 1.

2. Experimental

The critical fields and resistivity measurements reported and referenced here all were based on penetration depth measurements made with a tunnel diode oscillator (TDO) [18,19]. The TDO offers the advantage of not requiring contacts on the sample, and therefore, eliminates problems like contact resistance and additional stress. The experiments were carried out at frequencies between 53 and 1200 MHz. For small changes in frequency the frequency shift is proportional to the London penetrationdepth or the skin depth depending on whether the sample is in the superconducting or the metallic state. The oscillating magnetic field of the coil was always oriented perpendicular to the conducting planes, so that the penetration depths, and the resistivity measured in the normal state, are in-plane values.

3. Data

In Fig. 1 we show the critical fields for three different materials all scaled by their critical temperatures and Pauli limiting fields. Starting with α-$(ET)_2NH_4Hg(SCN)_4$, it is clear that this material is Pauli limited. Its critical field follows the functional form $\sqrt{1-T/T_c}$ for $t>0.5$, which is the same temperature dependence as the superconducting energy gap [20,21]. This should be true, because as Clogston pointed out, in a Pauli limited superconductor H_{c2} should be found when the Zeeman energy of the electrons is equal to the superconducting energy gap. At low temperatures, $t<0.5$, the energy gap does not change appreciably and thus the critical field does not change either.

Table 1
These parameters will help determine which materials are good candidates for a first-order H_{c2} transition or the FFLO state

Sample	H_{c2}^0 (T)	H_P (T)	α	$\xi\|$ (Å)	ℓ (Å)	$r=\ell/\xi$
$CeCoIn_5\|$	45 [11]	7.3 [12]	6.1	44	1800	41
$CeCoIn_5\perp$	17	4.8	3.7	44	1500	34
α-$(ET)_2NH_4Hg(SCN)_4$	>12 [19]	2.1 [13]	>5.7	628	600 [19]	0.96
κ-$(ET)_2Cu(NCS)_2$	>47 [15,16]	19.5 [14]	>2.4	60	720	12
κ-$(ET)_2Cu(NCS)_2$ 1.75 kbar	>11 [24]	4.5 [24]	>3.5	363	600	1.7

H_{c2} is the extrapolated value from the slope near T_c times 0.7 [6]. For κ-$(ET)_2Cu(NCS)_2$ or other Pauli limited superconductors the slope near T_c is not related to the coherence length and $H_{c2}^{\|}$ is estimated from $H_{c2}^{\perp}$ and the anisotropy of the London penetration depth [29]. To be consistent, we always compare ℓ and ξ in the parallel direction (in the conducting planes) to calculate r. The mean free path for κ-$(ET)_2Cu(NCS)_2$ under pressure is estimated.

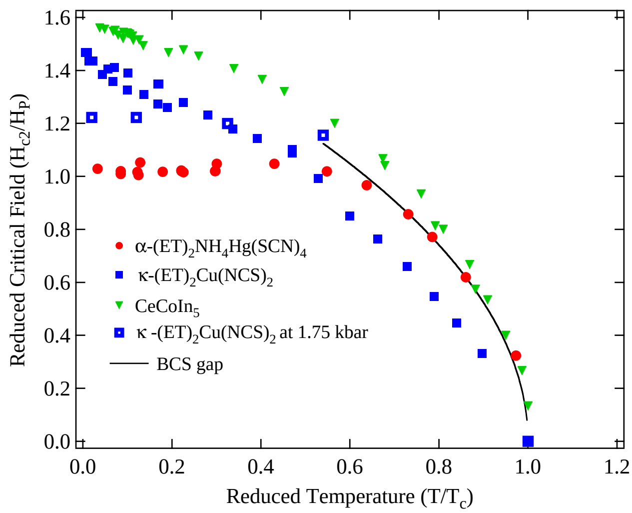

Fig. 1. The critical fields with the magnetic field oriented parallel to the conducting planes of α-$(ET)_2NH_4Hg(SCN)_4$ [18], κ-$(ET)_2Cu(NCS)_2$ [22,23] and this work, κ-$(ET)_2Cu(NCS)_2$ at 1.75 kbar[24], and $CeCoIn_5$ [9] as a function of temperature.

At the other extreme is $CeCoIn_5$. This material is most interesting because it shows evidence of the FFLO state [26,27, 9] in addition to exceeding the Pauli Limit and having a first order H_{c2} transition when $t<0.5$. It also follows the BCS gap equation well at high temperatures, although the high temperature region does not follow $\sqrt{1-T/T_c}$ quite as well as α-$(ET)_2NH_4Hg(SCN)_4$, but it is possible that our calculation of H_P may be slightly off. The critical field of κ-$(ET)_2$-$Cu(NCS)_2$ exceeds the Pauli limit, and the phase transition becomes first order below $t=0.4$. The contrast with $CeCoIn_5$is that, using the same experimental method, there is no evidence in our data for the FFLO state down to 50 mK [25], as has been claimed by others [28]. It is interesting to note that by increasing the pressure on κ-$(ET)_2Cu(NCS)_2$ the phase diagram looks more similar to α-$(ET)_2NH_4Hg(SCN)_4$. The main effect of increasing the pressure is the suppression of T_c and H_{c2} and the correlated increase in the coherence length.

For all of these materials $\alpha>1.8$, which according to Ref. [17] suggests that all of these materials are Pauli limited. The parameter that is most different between materials is r, and this suggests that the relative mean free path is the most important parameter that determines the details of the Pauli limited state. Notice that the two materials which have $r>10$ exceed the Pauli limit, and the materials with $r<10$ show no change in H_{c2} below $t<0.5$. This being said it is important to check the origins and accuracy of ℓ and $\xi\cdot\ \xi$ comes from critical field measurements, and can be estimated by the slope of H_{c2} versus T near T_c. In the parallel direction this method is valid only if the temperature is above T^* [29]. Below T^* layers in the superconductor become Josephson coupled, the superconductor is Pauli limited and the coherence length is not related to H_{c2}. For highly 2D superconductors such as κ-$(ET)_2Cu(NCS)_2$ and α-$(ET)_2NH_4Hg(SCN)_4$, ξ perpendicular can be calculated by using $H_{c2}^{\perp}$ and the anisotropy as found by measuring the anisotropy of the London penetration depth.

The mean free path can also be difficult to estimate. One pitfall which affects the measurement of ℓ for κ-$(ET)_2$-$Cu(NCS)_2$ is that the measurement of T_D can be underestimated due to the presence of magnetic breakdown. A recent correction to this problem can be found in Ref. [30] where ℓ for the samples used in this study where found to be 720 Å, 20% lower than previous estimates.

Sample variation should also be taken into account, and characterizing each sample used in an experiment is important. To this end we have recently found that we can measure the SdH oscillations in $CeCoIn_5$ using our TDO technique. This is a remarkable ability, because the oscillations in resistance are only one part in 1000 of the total change in resistance. Fig. 2a shows a typical TDO signal for $CeCoIn_5$ with the magnetic field applied perpendicular to the most conducting planes. The prominent feature is the sharp critical field transition at 5 T, above which the TDO is measuring the skin depth of the normal metallic state. Within the normal state a line can be fit to the data and subtracted to reveal high quality SdH oscillations as shown in Fig. 2b. This represents a resistance measurement with a resolution of one part in 10^7. Careful analysis of similar oscillations at different angles shows a roughly cylindrical Fermi surface as has been found by the de Haas-van Alphen effect [31,32]. Fig. 3 shows the evolution of the frequencies versus angle. Further analysis of T_D shows that $\ell=1800$ Å for this sample.

The details of the parameters in Table 1 will eventually provide a starting point for a more quantitative approach to the nature of superconductors in the Pauli limit. As of now, the correlation between the parameter r and the shape of the phase diagrams give a hint of where the experiments and theory should concentrate. In particular, pressure experiments in all of these materials will provide insight into how these phase

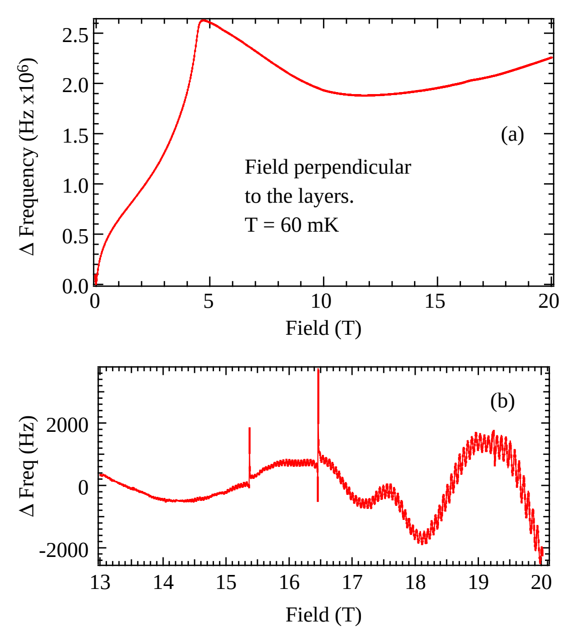

Fig. 2. The TDO signal showing (a) the superconducting transition in $CeCoIn_5$ and (b) SdH oscillations hidden in the data when the background is subtracted out. The spikes in the data are copper NMR lines.

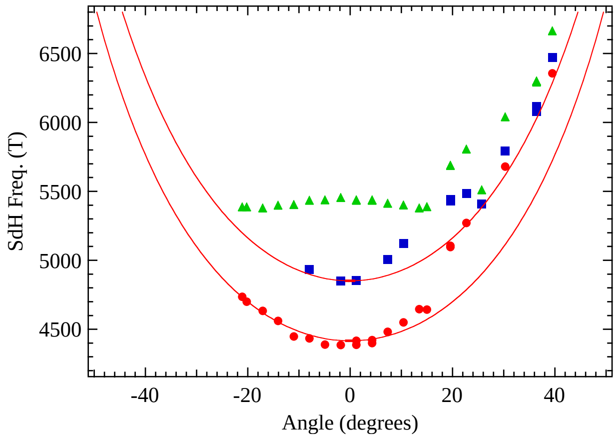

Fig. 3. At least three series of oscillations, corresponding to three extrema of the Fermi surface of $CeCoIn_5$ are seen in this Fig. The lines are functions of 1/cos to form a guide for the eye.

diagrams evolve from having H_{c2} exceed the Pauli limit to forcing H_{c2} to be at the Pauli limit.

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