Unusual temperature dependence of the London penetration depth in all-organic \(\beta'' - (ET)_2SF_5CH_2CF_2SO_3\) single crystals

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The temperature dependence of the in-plane, \(\lambda_\parallel(T)\), and interplane, \(\lambda_\perp(T)\), London penetration depth was measured in the metal-free all-organic superconductor \(\beta'' - (ET)_2SF_5CH_2CF_2SO_3\) (\(T_c \approx 5.2\) K). \(\Delta\lambda_\parallel(T) \propto T^3\) up to 0.5 \(T_c\), a power law previously observed only in materials thought to be \(p^-\) wave superconductors. \(\lambda_\perp\) is larger than the sample dimensions down to the lowest temperatures (0.35 K), implying an anisotropy of \(\lambda_\perp/\lambda_\parallel \approx 400 - 800\).

74.70.Kn, 74.25.Nf

Despite intensive study, neither the pairing mechanism nor the symmetry of the order parameter has been conclusively established in organic superconductors of the \(\kappa - (BEDT-TTF)_2X\) class. (Henceforth \textquotedblleft BEDT-TTF\textquotedblright \ will be abbreviated by \"ET\".) For the most thoroughly investigated materials, \(\kappa - (ET)_2Cu(NCS)_2\) \((T_c \approx 9.5\) K) and \(\kappa - (ET)_2Cu[N(CN)_2]Br\) \((T_c \approx 12\) K), there is some evidence for a \(d^-\) wave pairing \([4]\). However, recent penetration depth measurements revealed an unusual fractional power law variation, \(\Delta\lambda(T) \propto T^{3/2}\), unlike that of any other superconductor \([3]\). While this exponent is consistent with a novel three-fluid model \([3]\), it is also suggestive of a magnetic excitation. In this paper we report penetration depth measurements in \(\beta'' - (ET)_2SF_5CH_2CF_2SO_3\), a recently synthesized all-organic superconductor free of metallic ions and in which magnetism is likely to be negligible. This material is a strongly two dimensional, extreme type II superconductor with \(T_c \approx 5.2\) K. It is metallic between 10 and 150 K and semiconducting from 150 up to 410 K \([3]\). The upper critical field parallel to the conducting planes exceeds the Pauli limit by 18% raising the possibility of either an inhomogeneous pairing state \([3]\) or spin triplet order parameter \([3]\). We determine the London penetration depth for supercurrents both along \((\lambda_0)\) and perpendicular \((\lambda_\perp)\) to the conducting planes. The penetration depth is extremely anisotropic, with \(\lambda_\perp\) roughly 800 times larger than \(\lambda_0\). Notably, \(\lambda_0 \propto T^2\) which might imply an energy gap with nodes, but is difficult to reconcile with either \(p^-\) or \(d^-\) wave models in two dimensions. We suggest that this power law may arise from the unusual phonon spectrum in this material.

Single crystals of \(\beta'' - (ET)_2SF_5CH_2CF_2SO_3\) were grown at Argonne National Laboratory by an electrocrystallization technique described elsewhere \([3]\). The high conductance layers correspond to the \(ab\) plane and the \(c^*\) axis is normal to the planes. This designation is similar to cuprates, while different from the \(\kappa - (ET)_2X\) materials. The room-temperature interplane resistivity is roughly 700 \(\Omega\) cm while the in-plane resistivity is about 0.2 \(\Omega\) cm \([3]\). Two crystals - 0.5 \(\times\) 0.5 \(\times\) 0.3 mm\(^3\) and 0.8 \(\times\) 0.6 \(\times\) 0.3 mm\(^3\) were used for measurements. Each had a transition temperature of approximately 5.2 K. A third crystal was used to measure the absolute penetration depth. The penetration depth was measured with an 11 MHz tunnel-diode driven LC resonator \([9]\). Samples were mounted on a movable sapphire stage with temperature controllable from 0.35 K to 50 K. The low noise level, \(\Delta f_{\text{min}}/f_0 \approx 5 \times 10^{-10}\), resulted in a sensitivity of \(\Delta\lambda \leq 0.5\) Å for our samples. An rf field was applied either perpendicular to the conducting planes to probe \(\Delta\lambda_\parallel(T)\) or along the \(a^-\) axis to probe \(\Delta\lambda_\perp(T)\).

The resonator frequency shift due to superconducting sample, \(\Delta f \equiv f(T) - f_0\), is given by \([8]\):

\[
\frac{\Delta f}{f_0} = \frac{V_s}{2V_0(1 - N)} \left( 1 - \frac{\lambda}{R} \tanh \frac{R}{\lambda} \right)
\]

where \(f_0\) is the frequency in the absence of a sample, \(V_s\) is the sample volume, \(V_0\) is the effective coil volume and \(N\) is the effective demagnetization factor. The apparatus and sample - dependent constant \(\Delta f_0 \equiv V_s f_0/(2V_0(1 - N))\) was measured by removing the sample from the coil in situ \([8]\). For \(\lambda \ll R\), \(\tanh R/\lambda \approx 1\) and the change in \(\lambda\) with respect to its value at low temperature is \(\Delta\lambda = -\delta f R/\Delta f_{\text{min}}\), where \(\delta f \equiv \Delta f(T) - \Delta f(T_{\text{min}})\). In the parallel orientation \((H \parallel ab)\), however, we had to use the full expression, Eq. \([8]\) to estimate \(\lambda_\perp\) due to the weak screening in that direction.
literature values. The mainframe of Fig. 2 shows the
T dependence of the screening length in Al-coated
YBCO. The method recently developed a new method to determine
\( \lambda \) and \( \Delta \) by measuring the variation of an Al-coated
superconductor. We estimate a value of \( \Delta \lambda (0) \approx 800 \) \( \mu m \).

To date, there have been no reported measurements of the zero temperature penetration depth, \( \lambda_{\parallel} \). We recently developed a new method to determine \( \lambda_{\parallel} \) that relies upon the change in screening of an Al-coated sample as the temperature is reduced from above \( T_c \) to below \( T_c \). The inset in Fig. 2 shows the data obtained in a single crystal of YBCO. The method yields a value of 0.145 \( \pm \) 0.010 \( \mu m \) which is within 5% of literature values. The mainframe of Fig. 2 shows the method applied to \( \beta'' - (ET)_2SF_2CH_2CF_2SO_3 \). Since \( T_c \) of this material is only 5.2 K, its penetration depth is still changing at 0.35 K and the method is less reliable than for cuprate superconductors. We estimate a value of \( \lambda_{\parallel} (T = 0) = 1 - 2 \) \( \mu m \), in rough agreement with values for other ET compounds and leading to an anisotropy of 400 - 800. Our measurements provide only the average of \( \Delta \lambda_{\parallel} (T) \). Microwave conductivity measurements revealed a small in-plane anisotropy of approximately 1.35 with a maximum along the b axis.

Figure 3 shows the low temperature variation of \( \Delta \lambda_{\parallel} \) obtained in two samples of \( \beta'' - (ET)_2SF_2CH_2CF_2SO_3 \). Data for sample 2 is offset for clarity. The horizontal axis is \( T^3 \) showing that \( \Delta \lambda (T) \propto T^3 \) with a slope of 0.07 \( \mu m/K^3 \). The cubic power law is obeyed up to \( \sim T_c/2 \). The Al coated sample, shown in Fig. 2 also showed \( \Delta \lambda (T) \propto T^3 \), but below \( T_c \) the signal from \( \beta'' - (ET)_2SF_2CH_2CF_2SO_3 \) is screened by the Al coating. Both the \( n = 3 \) exponent and the wide range over which it holds are unusual and have not been observed in cuprate superconductors. To highlight the differences among superconductors, we plot in Fig. 3 the normalized low temperature variation of the penetration depth in \( \kappa = (ET)_2Cu(NCS)_2 \) (uppermost curve), \( \beta'' - (ET)_2SF_2CH_2CF_2SO_3 \) (middle curve) and polycrystalline Nb for comparison. Solid lines are the fits to \( T^{3/2} \). All data were taken in the same apparatus.

FIG. 1. Frequency variation in parallel (\( \Delta f_{\parallel} \)) and perpen-
dicular (\( \Delta f_{\perp} \)) orientations of the magnetic with respect to super-
conducting layers. Usual notation in terms of current flow is
used. Inset: zoom of \( \Delta f_{\parallel} (T) \). Note substantial difference
in shielding ability for two orientations.

FIG. 2. Measurements of the absolute value of \( \lambda_{\parallel} (0) \) in
\( \beta'' - (ET)_2SF_2CH_2CF_2SO_3 \). Inset: Same technique applied to
YBCO.

It is possible that \( \beta'' - (ET)_2SF_2CH_2CF_2SO_3 \) has an
everly anisotropic s-wave order parameter and the \( T^3 \)
variation is an effective, intermediate temperature power
law that only holds above the low temperature, exponential region. Our numerical calculations show that anisotropic s-wave states, at least in weak coupling, do not exhibit a \( T^3 \) variation over any extended range. In fact, the data in Fig. 3 shows a slight downward deviation from \( T^3 \) at the lowest temperatures, implying a decrease in the exponent - just the opposite of exponential suppression. Strictly speaking, it is the power law variation of the superfluid density \( \rho_s \) which is most directly related to the structure of the gap. \( \Delta \lambda_{\parallel} (T) \) is the mea-
sured quantity and its temperature variation only asymptoti-
cally approaches that of \( \rho_s \). The superfluid density
versus temperature was calculated from \( \Delta \lambda_{\parallel} (T) \) for
\( \lambda_{\parallel} (0) = 0.5, 1, 2, 5 \mu m \). In each case, we found that a cubic power law remained the best fit, although the range over which it held was reduced for smaller choices of \( \lambda_{\parallel} (0) \).
It is also possible that a small tilt of the $c*$ axis relative to the field may induce interplane supercurrents and create an admixture of both $\lambda_1(T)$ and $\lambda_2(T)$ in the data. If the applied field is tilted by $\theta$ relative to the $c*$ axis the additional contribution to the observed frequency shift is given by [10],

$$\Delta f_{\text{tilt}} = \frac{f_0 V_s}{2 V_0} \left( 1 - \frac{\lambda_1}{d} + \frac{\lambda_2}{w} \right) \sin^2(\theta) \quad (2)$$

The alignment was checked at room temperature by repeatedly attaching a sample to the sapphire rod with vacuum grease and measuring the divergence of a laser beam reflected off the sample surface. The average alignment error was never more than 2 degrees. To be conservative, we consider a misalignment of 5 degrees and using the data for $\Delta \lambda(T)$ from Fig. 1, calculate a maximum misalignment error of 4% in our determination of $\Delta \lambda(T)$ versus temperature. This value is too small to change our conclusion about the presence of an $n = 3$ exponent.

A $T^3$ variation of $\lambda_1$ is unusual, but was predicted for a three dimensional $p-$wave superconductor with an equatorial line of nodes; the so-called polar state with $\Delta(\hat{k}) = \Delta_0(T) \hat{k} \cdot \hat{l}$. Here, $\hat{l}$ is the axis of gap symmetry which must lie parallel to the vector potential $\hat{A}$ in order to obtain a cubic power law. If $\hat{l}$ is perpendicular to $\hat{A}$ the dependence is linear in $T$. The relevance to our data is questionable since $\beta'' - (ET)_{2}SF_{5}CH_{2}CF_{2}SO_{3}$ is strongly two dimensional and both $d$ and $p-$wave states must have line nodes perpendicular to the $ab$ plane, giving a linear $T$ dependence. A $T^3$ dependence would then require an angular variation of the gap near the node, $\Delta(\phi) \propto \phi^{1/3}$, for which there is no obvious justification.

Previous tunnel diode measurements of the penetration depth in $UPt_3$, believed by many to be a $p$-wave superconductor, revealed intermediate exponents ranging from $n = 2-4$ depending upon surface preparation [14].

However, lower frequency measurements on the same samples gave lower power laws ($n = 1-2$) for reasons not understood, but possibly related to surface dissipation. SQUID measurements of the penetration depth in the heavy fermion material $UBe_{13}$ gave $n = 2$, which could arise either from point nodes or impurity scattering [12,13]. The latter might be an issue in $\beta'' - (ET)_{2}SF_{5}CH_{2}CF_{2}SO_{3}$ since, at the low end, our data show a slight tendency toward a lower power law, possibly $n = 2$. Recent measurements in $Sr_2RuO_4$, also thought to be $p-$wave superconductor, have shown $\lambda \approx T^3$ in one sample, attributed to a combination of impurity scattering and nonlocality in a superconductor with line nodes [14]. $\beta'' - (ET)_{2}SF_{5}CH_{2}CF_{2}SO_{3}$ is an extreme type II material and nonlocality is unlikely to be an issue until one reaches temperatures of order $(\xi/\lambda)T_c \approx 0.05$ K [7]. Finally, on general grounds $p$-wave pairing is favored in materials with a tendency toward ferromagnetism, for which there is no evidence in this material. Although the discovery of a new pairing symmetry is appealing, $\beta'' - (ET)_{2}SF_{5}CH_{2}CF_{2}SO_{3}$ is sufficiently complex that other possibilities should be considered. Recent heat capacity measurements suggest a strong-coupling $s$-wave BCS state. They also indicate the presence of optical modes in the 20-40 K energy range [18]. Some time ago, it was shown theoretically that the coupling of electrons to low frequency, localized vibrations can give a temper-
ature dependence to the effective mass and thus a power law to the London penetration depth over and above that due to the superfluid fraction [19]. For example, a phonon density of states $g(E)$ varying as $E^2$ may give rise to a $T^3$ power law for an s-wave superconductor, in the absence of vertex corrections. Under most circumstances vertex corrections raise the power to $T^5$ making the effect extremely small, but this may not be true here. Our data suggest that strong coupling calculations involving a realistic phonon spectrum may be relevant for organic superconductors. We also wish to stress the desirability of NMR measurements in $\beta'' - (ET)^3 SF_3CH_2CF_2SO_3$ to help determine the parity of the order parameter.

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