Unusual temperature dependence of the London penetration depth in all-organic β''-$(ET)_2SF_5CH_2CF_2SO_3$ 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 β''-$(ET)_2SF_5CH_2CF_2SO_3$ ($T_c \approx 5.2$ 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 $\lambda_\perp/\lambda_\parallel \approx 400-800$.

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Despite intensive study, neither the pairing mechanism nor the symmetry of the order parameter has been conclusively established in organic superconductors of the κ-(BEDT-TTF)$_2X$ class. (Henceforth ''BEDT-TTF'' will be abbreviated as ''ET.'') For the most thoroughly investigated materials, κ-$(ET)_2Cu(NCS)_2$ ($T_c \approx 9.5$ K) and κ-$(ET)_2Cu[N(CN)_2]Br$ ($T_c \approx 12$ K), there is some evidence for *d*-wave pairing.[1,2] 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.[2] While this exponent is consistent with a three-fluid model,[3] it is also suggestive of a magnetic excitation. In this paper we report penetration depth measurements in β''-$(ET)_2SF_5CH_2CF_2SO_3$, 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 and up to 410 K.[4] The upper critical field parallel to the conducting planes exceeds the Pauli limit by 18%, raising the possibility of either an inhomogeneous pairing state[5,6] or a spin triplet order parameter.[7] We determine the London penetration depth for supercurrents both along ($\lambda_\parallel$) and perpendicular ($\lambda_\perp$) to the conducting planes. The penetration depth is extremely anisotropic, with $\lambda_\perp$ roughly 800 times larger than $\lambda_\parallel$. Notably, $\lambda_\parallel \propto T^3$, which might imply an energy gap with nodes, but it 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 β''-$(ET)_2SF_5CH_2CF_2SO_3$ were grown at Argonne National Laboratory by an electrocrystallization technique described elsewhere.[8] 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 κ-$(ET)_2X$ materials. The room-temperature interplane resistivity is roughly 700 Ω cm while the in-plane resistivity is about 0.2 Ω cm.[9] Two crystals—$0.5\times0.5\times0.3$ mm^3 and $0.8\times0.6\times0.3$ 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.[10] Samples were mounted on a movable sapphire stage with temperature controllable from 0.35 to 50 K. The low noise level, $\Delta f_{min}/f_0 \approx 5\times10^{-10}$, resulted in a sensitivity of $\Delta\lambda \leq 0.5$ Å for our samples. An rf field of magnitude $H_{ac} \approx 0.03$ Oe 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 entire cryostat was surrounded by a triple μ-metal shield that reduced the stray dc field to less than 0.005 Oe. Small values of magnetic fields and perfect reversibility ensure that the samples were in the Meissner state and that the observed results are not due to vortices.

The resonator frequency shift due to the superconducting sample $\Delta f \equiv f(T) - f_0$ is given by[10]

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

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.*[10] For $\lambda \ll R$, $\tanh R/\lambda \approx 1$, and the change in λ with respect to its value at low temperature is $\Delta\lambda = -\delta f R/\Delta f_0$, where $\delta f \equiv \Delta f(T) - \Delta f(T_{min})$. In the parallel orientation ($H \| ab$) we had to use the full expression Eq. (1) to estimate $\lambda_\perp$ due to the weak screening in that direction.

Figure 1 shows the frequency variation measured in two orientations for zero dc magnetic field. For ($H \| ab$) the rf screening is controlled by $\lambda_\perp(T)$ and is much weaker than in the ($H \| c^*$) orientation, where the relevant screening length is $\lambda_\parallel(T)$. Since all three crystal dimensions were roughly

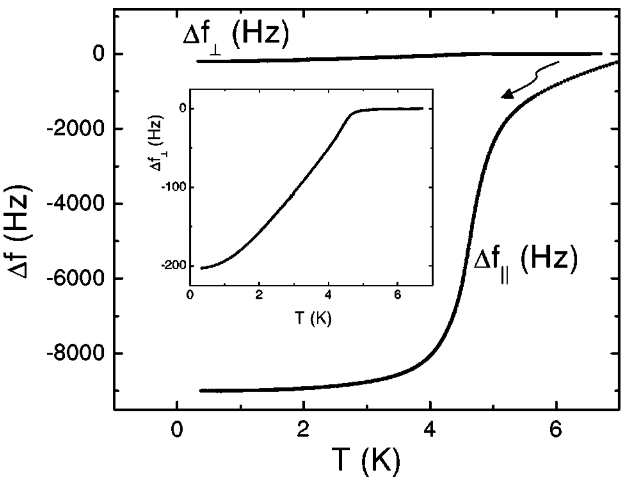

FIG. 1. Frequency variation in parallel ($\Delta f_{\perp}$) and perpendicular ($\Delta f_{\parallel}$) orientations of the magnetic with respect to superconducting layers. Usual notation in terms of current flow is used. Inset: expanded view of $\Delta f_{\perp}(T)$. Note substantial difference in shielding ability for two orientations.

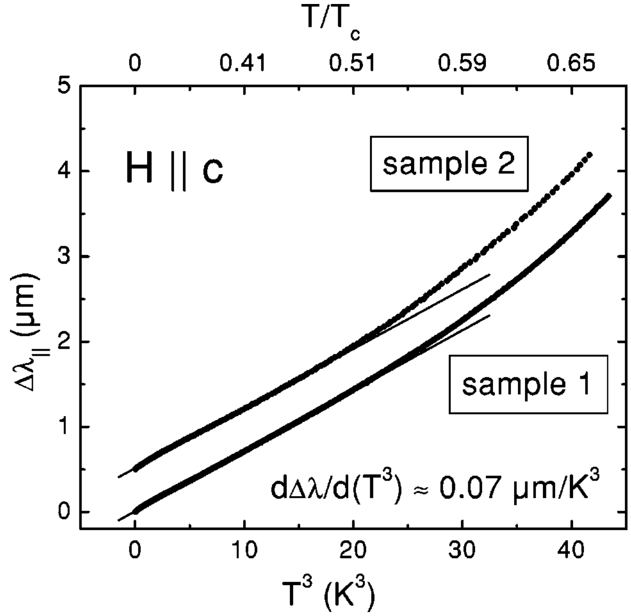

FIG. 3. $\Delta\lambda_{\parallel}(T)$ measured in two different crystals. (Data for sample 2 are offset for clarity.) Solid lines show fits to T^3 power law.

comparable, this indicates that $\lambda_{\perp}$ is several hundred times larger than $\lambda_{\parallel}$. The inset shows an expanded view of the $\Delta f_{\perp}(T)$ curve. From the total frequency variation and using Eq. (1) we estimate $\lambda_{\perp}(0) \approx 800$ μm.

To date, there have been no reported measurements of the zero-temperature penetration depth $\lambda_{\parallel}(T=0)$. We recently developed a new method to determine $\lambda_{\parallel}(T=0)$ that relies upon the change in screening of an Al-coated sample as the temperature is reduced from above T_c(Al) to below T_c(Al).[11] The inset to Fig. 2 shows the data obtained in a single crystal of Y $Ba_2Cu_3O_{7-\delta}$ (Y-Ba-Cu-O). The method yields a value of 0.145 ± 0.01 μm, which is within 5% of literature values. The mainframe of Fig. 2 shows the method applied to β''-$(ET)_2SF_5CH_2CF_2SO_3$. 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 $\lambda_{\parallel}(T=0)=1-2$ μm, in rough agreement with values for other ET compounds,[2] 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.[4]

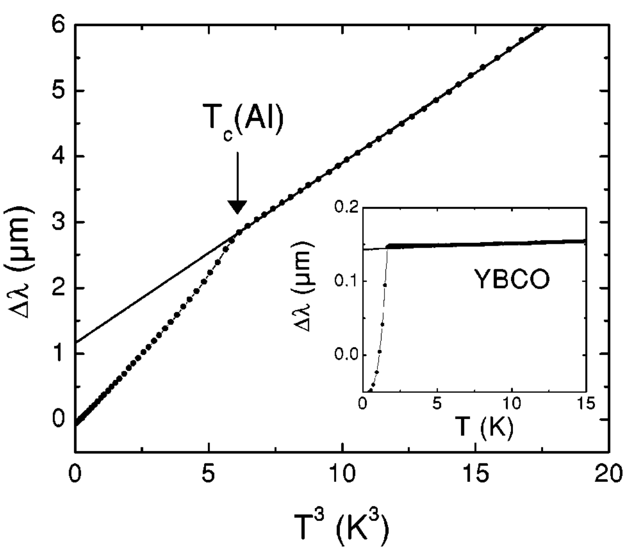

FIG. 2. Measurements of the absolute value of $\lambda_{\parallel}(0)$ in β''-$(ET)_2SF_5CH_2CF_2SO_3$. Inset: Same technique applied to Y-Ba-Cu-O.

Figure 3 shows the low temperature variation of $\Delta\lambda_{\parallel}(T)$ observed in two samples of β''-$(ET)_2SF_5CH_2CF_2SO_3$. 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 μm/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(Al) the signal from β''-$(ET)_2SF_5CH_2CF_2SO_3$ 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. 4 the normalized low-temperature variation of the penetration depth in κ-$(ET)_2Cu(NCS)_2$ (uppermost curve), β''-$(ET)_2SF_5CH_2CF_2SO_3$ (middle curve), and polycrystalline Nb for comparison. Solid lines are the fits to $T^{3/2}$, T^3, and $\sqrt{\pi\Delta(0)/2T}\,\exp(-\Delta(0)/T)$ variations. All data were taken in the same apparatus.

It is possible that β''-$(ET)_2SF_5CH_2CF_2SO_3$ has an extremely 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-

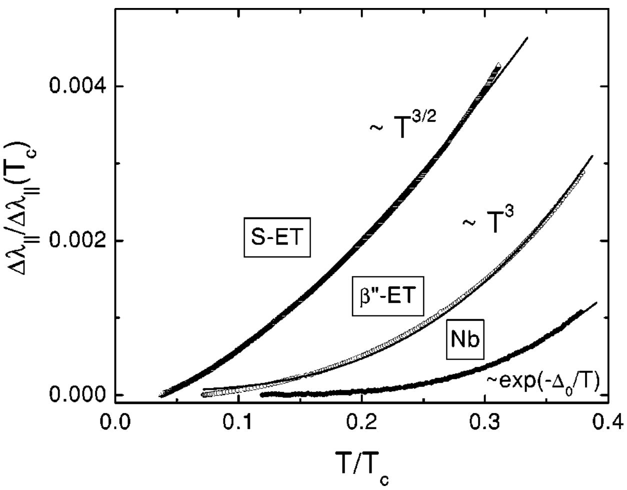

FIG. 4. Comparison of the temperature variation of $\Delta\lambda_{\parallel}(T)$ in different systems. From bottom to top: polycrystalline Nb (solid line is a fit to a standard weak-coupling *s*-wave BCS low-temperature expansion with $\Delta(0)/T_c = 1.76$); β''-$(ET)_2SF_5CH_2CF_2SO_3$ (solid line is a fit to T^3); κ-$(ET)_2Cu(NCS)_2$ (solid line is a fit to $T^{3/2}$).

law variation of the superfluid density ρ_s that is most directly related to the structure of the gap. $\Delta\lambda_{\parallel}(T)$ is the measured quantity and its temperature variation only asymptotically approaches that of ρ_s. The superfluid density versus temperature was calculated from $\Delta\lambda_{\parallel}(T)$ for $\lambda_{\parallel}(0) = 0.5$, 1, 2, and 5 μm. 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 $\lambda_{\parallel}(T)$ and $\lambda_{\perp}(T)$ in the data. If the applied field is tilted by θ relative to the c^* axis the additional contribution to the observed frequency shift is given by[10]

$$\Delta f_{\text{tilt}} = \frac{f_0 V_s}{2V_0}\left(1 - \left[\frac{\lambda_{\parallel}}{d} + \frac{\lambda_{\perp}}{w}\right]\right)\sin^2(\theta). \tag{2}$$

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°. To be conservative, we considered a misalignment of 5° and using the data for $\Delta\lambda_{\perp}(T)$ from Fig. 1, calculated a maximum misalignment error of 4% in our determination of $\Delta\lambda_{\parallel}(T)$ versus temperature. This value is too small to change our conclusion about the presence of an $n = 3$ exponent.

A T^3 variation of $\lambda_{\parallel}$ is unusual, but was predicted for a three-dimensional *p*-wave superconductor with an equatorial line of nodes: the so-called polar state with $\Delta(\hat{k}) = \Delta_0(T)\hat{k}\cdot\hat{l}$.[12,13] Here, $\hat{l}$ is the axis of gap symmetry, which must lie parallel to the vector potential $\vec{A}$ in order to obtain a cubic power law. If $\hat{l}$ is perpendicular to $\vec{A}$ the dependence is linear in *T*. The relevance to our data is questionable since β''-$(ET)_2SF_5CH_2CF_2SO_3$ 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. Superconducting quantum interference device 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.[12,13,15] The latter might be an issue in β''-$(ET)_2SF_5CH_2CF_2SO_3$ 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 a *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.[16] β''-$(ET)_2SF_5CH_2CF_2SO_3$ 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.[17] 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, β''-$(ET)_2SF_5CH_2CF_2SO_3$ 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 with the coupling of electrons to low frequency, localized vibrations can give a temperature 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 β''-$(ET)_2SF_5CH_2CF_2SO_3$ to help determine the parity of the order parameter.

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