Magnetic Penetration Depth in the Organic Superconductor κ-[BEDT-TTF]$_2$Cu[NCS]$_2$

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We report the first direct measurement of the effective magnetic penetration depth in oriented single crystals of κ-[BEDT-TTF]$_2$Cu[NCS]$_2$, with $T_c(5\text{ G}) \approx 9$ K. Results yield an effective in-plane value of $\lambda_{\text{eff}}^{bc}(0) \approx 9800$ Å (for $H_{\text{ext}} \approx 3$ kG), and a temperature dependence consistent with conventional s-wave pairing. Comparison with the London penetration depth, $\lambda_L(0)$ (estimated to be ≈ 5100 Å), indicates a tendency toward dirty-limit superconductivity, with the ratio of coherence length over mean free path of $\xi_0^{bc}/l_{bc} \approx 2.7$. From our results, it appears unnecessary to invoke any unconventional pairing schemes to explain the superconductivity in this material.

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The organic superconductors are a novel group of materials, having superconducting transition temperatures in the intermediate range between the heavy-fermion and high-T_c systems. As in the case of these other superconducting families, the most fundamental questions surrounding the organic superconductors concern the nature of the mechanism(s) responsible for the attractive quasiparticle interactions and the symmetry properties of the resulting ground state. Theorists have proposed a number of pairing schemes[1-3] based on a variety of mediating quasiparticles ranging from phonons to excitons. Owing to the rich magnetic phenomena observed in all of the organics, and their low dimensionality, there has been considerable speculation concerning magnetic mechanisms; in lower dimensions, spin fluctuations become more important, making the possibility of spin-mediated pairing more likely.

The magnetic penetration depth, $\lambda(T)$, which measures the length over which magnetic fields are attenuated in a superconductor, is one of the most fundamental properties of superconductivity. From the low-temperature limit, $\lambda(T \to 0)$, it is possible to estimate the ratio of the superconducting carrier density, n_s, to the effective carrier mass, m^*, while the temperature dependence of the penetration depth provides information regarding the ground-state symmetry. Unlike other bulk techniques, which often suffer from flux-pinning effects, muon-spin rotation (μ^+SR) directly probes the field distribution inside the superconductor, providing an absolute measure of λ. Furthermore, we expect that μ^+SR will be useful in studying the dynamics of the local magnetic fields which are of particular interest in the organic materials. Indeed, μ^+SR has proved invaluable in the study of the penetration depth and antiferromagnetic correlations in the high-T_c and heavy-fermion systems.[4,5]

The first organic superconductor, [TMTSF]$_2$ClO$_4$ (TMTSF denotes tetramethyltetraselenafulvalene), having a T_c of ~ 1 K, was discovered[6] in 1980. Subsequent developments have led to higher-T_c materials, exhibiting a variety of novel electronic and superconducting properties, coupled to their dimensionality; these systems are generally characterized by their low dimensionality and low carrier concentration. The [BEDT-TTF]$_2X$ [BEDT-TTF denotes bis(ethylenedithio)tetrathiafulvalene] series of materials is unique due to its two-dimensional character; fluctuations are expected to be less important than in one-dimensional systems, making conventional pairing schemes more favorable. Recently, an ambient-pressure compound of this series, with $X=$Cu[NCS]$_2$, has been developed;[7] the α modification has a metal-semiconductor transition at 200 K, whereas the κ modification exhibits a record $T_c \approx 10$ K. Of particular interest is the observation of a peak in $1/T_1$ of the ^{1}H NMR relaxation[8] at $T \approx 5$ K. This peak has been variously attributed to a second superconducting phase,[9] a spin-density wave,[10] a structural transition,[11] or flux melting.[8,12] Since the Cu[NCS]$_2$ system exhibits the highest ambient-pressure T_c of any organic and exhibits fascinating magnetic behavior, it is the ideal choice to begin our systematic study of these materials.

The κ-[BEDT-TTF]$_2$Cu[NCS]$_2$ crystals used in the present study (typical dimensions $5 \times 5 \times 0.05$ mm^3) were grown according to the general procedure of Urayama *et al.*[7] The relatively large quantity of material used in the present work was obtained by harvesting the crystals from two separate large-scale electrochemical crystal growth experiments conducted under galvanostatic conditions with a current of 1.5–3.0 μA (applied potential of

1.5–2.5 V), as described below. Recrystallized BEDT-TTF (150 mg) was dissolved in the anode compartment of an electrochemical H cell containing filtered 1,1,2-trichloroethane electrolyte solution (250 ml), under an atmosphere of argon. The electrolyte mixture was prepared by stirring KSCN (97 mg), CuSCN (122 mg), and 18-crown-6 (529 mg) in dry, distilled 1,1,2-trichloroethane (250 ml) overnight under argon. Crystal growth was complete in 2–3 months. The structure of κ-[BEDT-TTF]$_2$Cu[NCS]$_2$ is monoclinic ($a = 16.248$ Å, $b = 8.440$ Å, and $c = 13.124$ Å, $\beta = 110.30°$),[7] having 118 atoms (two formula units) per unit cell. The BEDT-TTF cations form a relatively isotropic, two-dimensional conducting layer in the b-c plane, while the Cu[NCS]$_2$ anions are arranged in one-dimensional chains along the b axis, forming insulating layers between the BEDT-TTF molecules. The dc magnetization was measured on a representative subset of the sample material (unoriented), and is shown in Fig. 1. The data were taken on field cooling in 5 Oe and indicate a T_c (onset) of ~ 9 K.

The time-differential μ^+SR technique is described elsewhere,[13] so only a brief description will be given here. Energetic (4.2 MeV) positive muons, produced at the TRIUMF accelerator facility, are stopped in the sample where they decay (with an intrinsic lifetime of ~ 2.2 μs) via the weak interaction $\mu^+ \rightarrow e^+ + \bar{\nu}_\mu + \nu_e$, emitting the positron preferentially along their final spin-polarization direction. Since the muons are created with spins aligned opposite to their momentum, it is possible to follow the time evolution of the muon-spin direction after thermalizing in the sample; normally a clock is started when the muon enters the sample region, and stopped upon the subsequent detection of the decay positron. The resulting time spectrum represents an ensemble average of $\sim 10^6$ such events. Transverse-field geometry was used in the present work, where the magnetic field is applied perpendicular to the initial muon polarization. Such a configuration yields a spin-relaxation function, $G_{xx}(t)$, consisting of a relaxation envelope which modulates a precessing muon amplitude. The experiments were conducted on field cooling with the external field (~ 3 kG) applied along the beam momentum to help focus the incident muons. In order to conform with transverse-field geometry, the muon spins were rotated perpendicular to their momentum using a crossed-field separator upstream of the sample. The crystals were assembled into a flat mosaic sample with their a axes aligned along the applied field direction, and mounted on a 99.999%-pure silver foil (high-purity silver exhibits no appreciable relaxation of the muon spin).

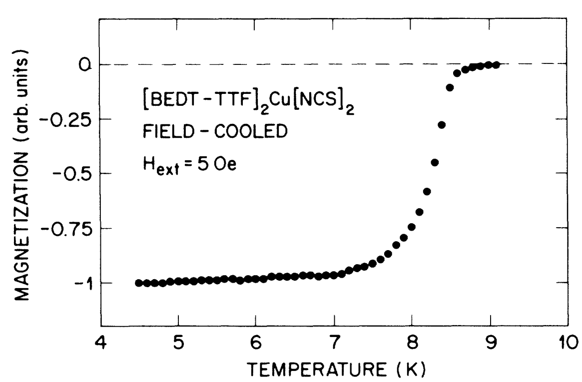

FIG. 1. Magnetization curve (taken on field cooling in 5 Oe) for a representative subset of the κ-[BEDT-TTF]$_2$-Cu[NCS]$_2$ crystals. The data show an onset for superconductivity at $T_c \approx 9$ K.

In a type-II superconductor, the application of an external magnetic field induces the formation of a flux lattice with the vortices parallel to the field direction, typically arranged with triangular symmetry. The field distribution, $\rho(B)$, associated with the vortex lattice leads to dephasing or relaxation of the muon spin polarization. While the exact form of $\rho(B)$ has been calculated for this situation,[14] the line shape can be approximated by a Gaussian having the same second moment $\langle(\Delta B)^2\rangle = 2\sigma^2/\gamma_\mu^2$ (higher moment corrections are negligible within our statistical resolution), where σ is the relaxation rate of the precessing muon-spin ensemble and γ_μ ($= 2\pi \times 13.55$ MHz/kG) is the muon gyromagnetic ratio. For a perfect triangular lattice, the effective penetration depth, λ_{eff}, can be determined from the width of the field distribution via the equation[14] (true for the fields used in the present work)

$$\langle(\Delta B)^2\rangle = 2\sigma^2/\gamma_\mu^2 = 0.00371\phi_0^2\lambda_{\text{eff}}^{-4}, \tag{1}$$

where ϕ_0 is the magnetic flux quantum ($= 2.068 \times 10^{-7}$ G cm^2). Accompanying the increase in relaxation rate in the superconducting state is a (negative) shift, Δf, in the muon precession frequency arising from the sample diamagnetism. For the sample and field geometry employed in the present study, the demagnetizing factor, n_d, approaches 1, thus greatly reducing Δf [$\propto B - H \sim (1-n_d)4\pi M$, where M is the magnetization]. Although the demagnetizing currents are often nonuniform, they are confined to the sample surface and do not, therefore, contribute to the field inhomogeneities in the bulk material. Since the muon probes the bulk of the sample (at depths well beyond the penetration depth, λ), the relaxation experienced by the muon is insensitive to surface currents, and thus entirely due to the vortex lattice.

The dominant relaxation component in the time spectra was fitted assuming a Gaussian line shape of the form (the time-dependent relaxation function is essentially the Fourier transform of the internal field distribution)

$$G_{xx}(t) = \exp(-\sigma^2 t^2), \tag{2}$$

and the resulting σ are plotted as a function of temperature in Fig. 2(a). The observed increase in $\sigma(T)$, below T_c, arises from the formation of the vortex lattice and associated inhomogeneous field distribution. The corresponding values for the in-plane effective penetration depth, $\lambda_{\rm eff}^{bc}(T)$, have been calculated using Eq. (1) and are shown in Fig. 2(b).

Conventional BCS, *s*-wave superconductivity is characterized by a pair-breaking density of states which is exponential in temperature due to the nonvanishing gap function. Consequently, the temperature dependence of $\lambda_{\rm eff}$ is expected to be relatively independent of temperature as T approaches zero, while near T_c, $\lambda_{\rm eff}(T)$ is well described by a T^4 dependence derived from mean-field theory. Incorporating these two limits, $\lambda_{\rm eff}(T)$ is well described by the two-fluid equation[15]

$$\lambda_{\rm eff}(T) = \lambda_{\rm eff}(0)[1-(T/T_c)^4]^{-1/2}. \tag{3}$$

Although Eq. (3) is a good approximation, it is not identical to the exact numerical calculation in which $\lambda_{\rm eff}(T)$ depends on specific material parameters such as the mean free path, l, and the coupling strength. Alternatively, if there exist nodes in the gap function, one expects an enhancement in the pair-breaking density of states, resulting in a power-law temperature dependence at low temperatures.[16] The curves plotted in Figs. 2(a) and 2(b) represent a fit to the data assuming the relations defined by Eqs. (1) and (3), which gives $\lambda_{\rm eff}(0) \approx 9800$ Å, and a corresponding transition temperature (at 3 kG) of ~ 7.5 K. The suppression of T_c with field is consistent with that observed in resistivity measurements in this field orientation,[17] and the curvature near T_c is the result of the subtraction of a relatively large background component associated with the nuclear dipolar field distribution. The excellent agreement of the data with Eq. (3) strongly suggests consistency with conventional *s*-wave pairing. We, however, caution the reader that the exponent on T/T_c is not completely constrained by the present data.

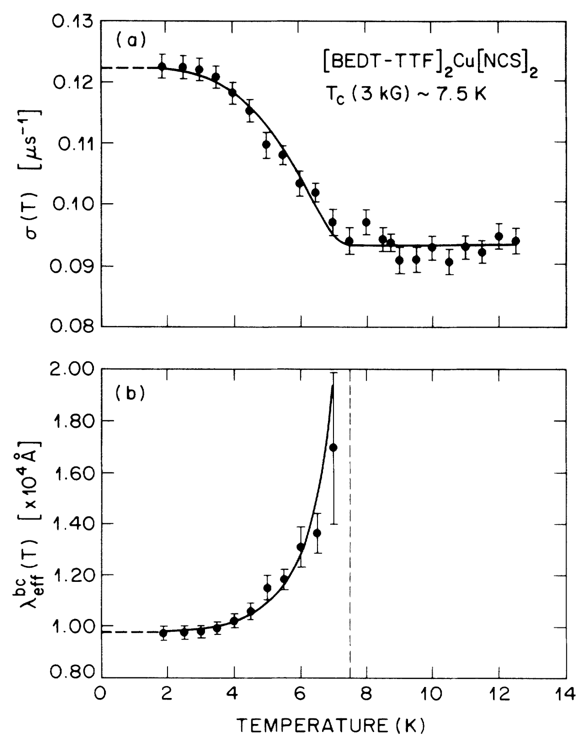

FIG. 2. Temperature dependence of the (a) Gaussian relaxation rate, σ, and (b) associated in-plane effective magnetic penetration depth, $\lambda_{\rm eff}^{bc}$, for κ-[BEDT-TTF]$_2$Cu[NCS]$_2$. The data were taken on field cooling in 3 kG (directed along the a axis) and exhibit an effective T_c of ~ 7.5 K.

Since the conduction in κ-[BEDT-TTF]$_2$Cu[NCS]$_2$ is extremely anisotropic, it can be approximated in terms of a stack of two-dimensional systems, with spacing δ between them. Within this (2D) model, the Sommerfeld constant can be written as

$$\gamma = k_B^2 \frac{\pi}{3} \frac{(m_b^* m_c^*)^{1/2}}{\hbar^2} \frac{1}{\delta}, \tag{4}$$

where m_b^* ($\approx 3m_e$) and m_c^* ($\approx 4m_e$) are the effective masses along the b and c axes,[18] and δ is equal to the a-axis layer spacing. The evaluation of Eq. (4) gives $\gamma \approx 35$ J/K^{2}m^3, in reasonable agreement with that derived using the density of states determined from the Pauli susceptibility.[18,19]

The London penetration depth is generally given by $\lambda_L(0) = [m^* c^2/4\pi n_s e^2]^{1/2}$, where n_s and m^* are as defined previously. Alternatively, this relation can be expressed as $\lambda_L(0) \propto \gamma^{1/2}/S_s$,[20] where S_s is the surface area of the Fermi surface within the first Brillouin zone, which may be deduced by assuming a half-filled band. Shubnikov–de Haas measurements indicate that this simple Fermi-surface topology is appropriate.[21] Based on these assumptions, $\lambda_L(0) \approx 5100$ Å, which is considerably lower than $\lambda_{\rm eff}^{bc}(0)$ determined by our μ^+SR measurement, implying a tendency toward dirty-limit ($\xi_0 \gg l$) superconductivity. The effective magnetic penetration depth is related to $\lambda_L(0)$ by the equation[22]

$$\lambda_{\rm eff}(0) \approx (1+\xi_0/l)^{1/2} \lambda_L(0). \tag{5}$$

The evaluation of Eq. (5) gives an in-plane ratio of $\xi_0^{bc}/l_{bc} \approx 2.7$ which, when combined with resistivity measurements,[17] yields $l_{bc} \approx 50$ Å and a clean-limit ξ_0^{bc} of ≈ 135 Å, in good agreement with the values of ξ_0 derived from H_{c2} measurements.[17] The lower critical field, $H_{c1}(0)$, is also related to $\lambda_{\rm eff}(0)$ via the equation[15]

$$H_{c1}(0) = \phi_0 \ln\kappa / 4\pi\lambda_{\rm eff}^2(0), \tag{6}$$

where $\kappa = \lambda_{\rm eff}/\xi$. This gives an estimate of $H_{c1}(0)$ of ~ 7 Oe, substantially different than that observed in some conventional magnetic measurements.[18,23] We attribute the discrepancy to the neglect of sample shape and pinning effects on the determination of H_{c1} via these other methods.

A smaller ($<10\%$) relaxation component was also observed in the time spectra, implying a second-muon-site distribution. Whether this component is intrinsic to the superconducting medium or extrinsic, however, remains a point of debate. A second muon site within the superconducting medium is not unreasonable, but it is equally possible that this signal arises from a small subset of crystallites exhibiting different properties; studies show that mechanical stress can produce a loss of superconductivity in the κ-[BEDT-TTF]$_2$Cu[NCS]$_2$ system.[24] This component may be associated with the ^{1}H NMR peak observed[8] in polycrystalline samples which may, in turn, be due to stressed regions in the material; we note with interest that $1/T_1$ does not drop below the normal-state Korringa level at T_c, as is expected for conventional systems. Whatever the case, the fact that there are no corresponding features in $\sigma(T)$ [see Fig. 2(a)] suggests that the relaxation peak does not arise from a superconducting-state or vortex-lattice transition, as has been suggested in Refs. 9 and 8, respectively.

To summarize, we have performed the first direct measurement of the magnetic penetration depth in single-crystal κ-[BEDT-TTF]$_2$Cu[NCS]$_2$. Results indicate an effective low-temperature value of $\lambda_{\rm eff}^{bc}(0) \approx 9800$ Å, and a temperature dependence consistent with conventional s-wave pairing. Comparison with an estimate of the London penetration depth, $\lambda_L(0) \approx 5100$ Å, indicates a tendency toward dirty-limit superconductivity, with $\xi_0^{bc}/l_{bc} \approx 2.7$. From our results, it appears unnecessary to invoke any unconventional pairing schemes to explain the superconductivity in this material.

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