Signature of Unconventional Superconductivity in a Copper-based Metal-Organic Framework with Perfect Kagome Structure

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Recently, the superconductivity in a metal-organic framework (MOF) has been discovered for the first time in copper(II) benzenehexathiolate ([Cu₂(C₆S₆)]ₙ, Cu-BHT). The Cu atoms form a two-dimensional perfect Kagome lattice, which has the potential to host a metallic quantum spin liquid state. Here we present high-precision measurements of in-plane magnetic penetration depth λ in Cu-BHT films down to 40 mK. The temperature dependence of λ shows a non-exponential, quasi-linear behavior at low temperatures, suggesting that unconventional superconductivity with low-energy quasiparticle excitations is realized in this system. With the reported non-Fermi liquid behavior, this finding implies that MOFs can provide a flexible platform to investigate the superconducting pairing mechanisms in the presence of spin frustration and strong quantum fluctuations.

Metal-organic frameworks (MOFs), a subclass of coordination polymers (CPs), are crystalline materials consisting of metal ions and bridging organic molecules [1]. In the last decades, they have attracted increasing interest in materials chemistry because of their potential for applications such as catalysis, gas sensing, separation, and storage [2]. On the other hand, in the context of condensed matter physics, they have not attracted so much attention until the past few years, because they are typically insulating or show trivial magnetic properties like most of the organic compounds. However, recent theoretical studies propose that some MOFs have the potential to be a playground of novel physical phenomena, such as high-temperature ferromagnetism, half-metallic ferromagnets, Z₂ topological insulator, and Kitaev spin liquids [3–7]. Among them, atomically layered two-dimensional (2D) MOFs are one of the fascinating materials not only for applications but also in the context of fundamental properties. Considerably high electrical conductivity in some 2D MOFs [8–10] is interpreted by band transportation mechanisms, which allow the delocalization of electrons in the whole 2D plane. This motivates researchers to explore novel physical phenomena by designing 2D conductive MOFs. For instance, a theoretical study predicts the coexistence of frustrated local spins and itinerant electrons in a 2D MOF material [11]. At the time of its discovery, Cu-BHT films exhibit a negative slope in the temperature dependence of electrical resistance indicating that metallicity is not complete. The limitation of conductivity can be explained by the electron hopping process model between different metallic nanosheets or crystalline domains, and such small crystal domains are observed in scanning electron microscope (SEM) images. Furthermore, the small value of thermopower and the observation of Fermi edge in ultraviolet photoemission valence-band spectrum support the metallic nature of Cu-BHT.

Recently, films of Cu-BHT with significantly improved quality have been synthesized. The metallic behavior is found in the temperature dependence of electrical resistivity. More importantly, they show a superconducting transition at Tc ≈ 0.25 K [12] and this is the first report of superconductivity in CPs. A theoretical study based on first-principles calculations reported that the electron-phonon coupling constant (0.51) for bulk Cu-BHT can lead to superconductivity at Tc ≈ 1.58 K from the Allen-Dynes formula [13]. This value is not far from the experimental Tc, and thus the conventional s-wave superconducting state of Bardeen-Cooper-Schrieffer (BCS) type has been proposed as a candidate of the pairing state. However, recent heat capacity and magnetic susceptibility measurements have revealed strong quantum spin fluctuations possibly related to the 2D Kagome lattice of Cu²⁺ ions with S = 1/2 spin (Fig. 1(b)). Quantum spin fluctuations can promote unconventional superconducting pairing states of non-BCS type, which have been widely discussed in strongly correlated systems including high-Tc cuprate, iron-based, heavy-fermion and organic superconductors. It is therefore quite important to experimentally determine whether the superconductivity in Cu-BHT...
has conventional or unconventional nature.

To identify the pairing nature of superconductivity, measurements of low-energy density of states (DOS) of quasiparticles provide crucial information because the superconducting gap structure, which is intimately related to the pairing mechanisms, has a profound influence on the quasiparticle excitation spectrum. Magnetic penetration depth \( \lambda \), which is one of the most fundamental properties of superconductors, is a sensitive probe of low-energy quasiparticle excitations and it directly relates with the superfluid density through \( \rho_s \propto \lambda^{-2} \) \cite{15}. In conventional \( s \)-wave superconductors, the superconducting gap function \( \Delta(k) \) in the momentum space is constant \( (\Delta_0) \), and the change of penetration depth \( \Delta \lambda(T) = \lambda(T) - \lambda(0) \) shows thermally activated temperature dependence of \( \propto \exp(-\Delta_0/T) \) well below \( T_c \). On the other hand, unconventional superconductors may have strong \( k \)-dependence on the gap function. In particular, the antiferromagnetic spin fluctuation mechanism predicts sign-changing gap structure, which often leads to gap nodes where \( \Delta(k) \) becomes zero. Such nodes are observed in \( d \)-wave superconductors including cuprates and some organic materials. In this instance, DOS remains finite even at low energies due to quasiparticle excitations emerging from the nodal region of the anisotropic gap, which results in a power-law behavior of low-temperature penetration depth \( \Delta \lambda(T) \propto T^\alpha \). In this Letter, we report on the measurements of temperature dependent in-plane magnetic penetration depth \( \Delta \lambda(T) \) in the high-quality thick films of Cu-BHT down to \( \sim 40 \) mK. We find non-exponential, quasi-linear temperature dependence of \( \Delta \lambda(T) \) at low temperatures, pointing to the presence of line nodes in the superconducting gap, a signature of unconventional superconductivity.

Thick films of Cu-BHT were synthesized by an interface reaction method, as described in Refs. \cite{12} \cite{13}. The in-plane size of as grown Cu-BHT films are larger than \( 1 \times 1 \) mm\(^2\) whereas the thickness is smaller than a few \( \mu \)m. Cu-BHT films were cut into small pieces of samples about \( 350 \times 350 \) \( \mu \)m\(^2\). The temperature variation of the in-plane magnetic penetration depth \( \Delta \lambda(T) \) was measured by using the tunnel diode oscillator (TDO) technique operating at resonant frequency \( f \sim 14 \) MHz in a dilution refrigerator down to \( \sim 40 \) mK \cite{15}. The sample was mounted on a sapphire rod with Apiezon N grease and inserted into a copper coil that is a part of the \( rf \) circuit. The shift in the resonant frequency \( \Delta f \) directly reflects the change in the magnetic penetration depth, \( \Delta \lambda = G \Delta f \). The geometric factor \( G \) depends on the geometry of the sample and the coil \cite{17}. Samples were cooled slowly (with a rate less than \( 1.0 \) K/min) to avoid introducing cracks.

Figure 1(c) shows the normalized resistivity \( R(T)/R(300 \) K) as a function of temperature down to \( 4 \) K measured by the standard four-probe method. We observe metallic temperature dependence down to the lowest temperature (see inset), with a residual resistivity ratio \( (\sim 1.2) \) similar to that for the superconducting samples with high crystallinity in the previous report \cite{14}.

Figure 2(a) shows the temperature dependence of the normalized TDO frequency shift below \( 0.5 \) K in two Cu-BHT films. Both films show a clear diamagnetic transition around \( 0.25 \) K, confirming the superconducting ground state in this system. Here, we define the superconducting transition temperature \( T_c \) as the onset of the frequency shift \( \Delta f \), as shown in the Fig. 2(b). We note that the SEM images of the upside surface of our Cu-BHT films (inset of Fig. 2(a)) indicate a very flat surface with no apparent grains or small domains, implying that the superconducting screening current flows near the edges of the entire film. This is confirmed from the comparison with the result for ground powder of sample \#1 (Fig. 2(c)). If the supercurrents on small grains or nanostructures dominate the \( \Delta f \) signal, the amplitude of \( \Delta f \) in the powder sample is not expected to be reduced dramatically compared with the data in films of the same volume \cite{18} \cite{19}. However, our results indicate that the films exhibit orders of magnitude larger signals than the powder sample, in which the superconducting signal is below the experimental noise owing to the small mass

FIG. 1. (a) The crystal structure of Cu-BHT projected along c-axis direction. The dashed line indicates the unit cell. (b) The same structure with highlights of Cu atoms forming a perfect Kagome lattice. (c) Temperature dependence of normalized electrical resistivity \( R(T)/R(300 \) K) in a Cu-BHT film. Inset: The same plot up to \( 50 \) K.
of $\sim 1 \mu g$. This clearly demonstrates that the obtained $\Delta f(T)$ reflects the superconducting diamagnetic signal of the entire film.

Having established that the observed frequency shift comes from the temperature dependence of the penetration depth in the superconducting state of Cu-BHT, now we focus on the low temperature behavior. Figure 3(a) depicts the variation of penetration depth $\Delta \lambda$ for sample #1 and #2 as a function of $T/T_c$, where each curve is normalized by $\Delta \lambda(0.5T_c)$ and compared with the BCS temperature dependence (dashed line). In BCS superconductors, isotropic fully gapped structure leads to the exponential temperature dependence of $\Delta \lambda(T) \sim \exp(-\Delta_0/k_BT)$ at low temperatures, and thus $\Delta \lambda$ is almost $T$-independent below about $0.2T_c$. In stark contrast to this, both Cu-BHT films show steeper slopes at low temperatures below $0.2T_c$, where quasi-linear temperature dependence is observed as shown in the inset of Fig. 3(a). Figure 3(b) shows the same data plotted against $(T/T_c)^2$ at low temperatures, which clearly indicates that the low-temperature behavior of penetration depth in Cu-BHT deviates strongly from the one in the conventional $s$-wave superconductor.

It should be emphasized that the temperature variation of $\Delta \lambda$ at the lowest temperatures gives the most important information on the low-energy quasiparticle excitations and hence the detailed superconducting gap structure. In clean superconductors with line nodes in the gap such as $d$-wave cuprates, the low-temperature $\Delta \lambda(T)$ is proportional to $T$, and in the case of point nodes, it follows as $T^2$. Such power-law behaviors ($\Delta \lambda \sim T^\alpha$) are associated with the energy dependence of quasiparticle DOS at low energies ($\sim E$ for line nodes and $\sim E^2$ for point nodes). There are a few mechanisms which may affect the exponent $\alpha$ in the
power-law temperature dependence, including impurity effect \[20\], nonlocal effect \[21\], and quantum criticality \[22\]. These effects tend to increase the exponent $\alpha$. In $d$-wave superconductors, for example, the impurity and nonlocal effects changes the low-temperature variation from $T$ to $T^2$ which can be approximated by $\Delta \lambda(T) \propto T^2/(T + T^*)$, where $T^*$ is the crossover temperature \[20\]. In quantum critical superconductors with line nodes, the $T^{1.5}$ dependence is often found, which may be related to the temperature-dependent mass renormalization \[23\]. Thus the low-temperature exponent $\alpha$ in the line node case is expected as $1 \leq \alpha \leq 2$, whereas that for point nodes should not be smaller than 2.

In the $(T/T_c)^2$ plot of Fig. 3(b), the overall temperature dependence is nearly described by the $T^2$ dependence, but in the lowest temperature region the data clearly show a convex up curvature, indicating that the exponent $\alpha$ is smaller than 2. From this behavior, we can exclude gap structures having point nodes. Of course, in such very low-$T_c$ superconductors it is difficult to access the asymptotic behavior in the zero temperature limit, and thus we cannot completely exclude the possibility of the presence of very small finite gap, which can occur in multigap superconductors. However, the obtained low-temperature data indicating a quasi-$T$-linear behavior are most consistent with the presence of line nodes in the superconducting gap function.

Now we have an open question; what is the mechanism of the possible unconventional superconductivity in Cu-BHT? As reported in the previous work \[13\], the normal-state heat capacity $C$ and magnetic susceptibility show intriguing properties. The $T$ dependence of $C/T$ below 1 K follows $C/T \sim T^{-2/3}$, which is indicative of non-Fermi liquid behavior. The Curie-Weiss analysis of the magnetic susceptibility shows an effective moment of $\mu_{eff} \sim 1.79 \mu_B$ close to that expected for $Cu^2+$ with $S = 1/2$ spin ($1.73 \mu_B$), with no sign of long-range magnetic ordering at least down to 2 K instead of a large magnitude of the Weiss temperature (1400 K) \[13\]. These results indicate that the system is close to a quantum spin liquid state with strong quantum fluctuations, which is likely associated with the spin frustration in the Kagome structure. Therefore the unconventional pairing mechanisms related to spin fluctuations in a metallic spin liquid state may be relevant here, which deserves further theoretical and experimental studies.

Finally, we look into the possibility of single-layer superconducting phase in Cu-BHT films. In the previous work, a sharp droplet in the diamagnetic signal at about 3 K is reported \[13\], which is compatible with the transition temperature of 2D single-layer Cu-BHT predicted by theoretical calculations \[13\]. Furthermore, the estimated shielding volume fraction of this 3 K phase is very low ($\sim 0.1\%$), thus this signal is considered as the indication of monolayer Cu-BHT superconducting phase. If about 0.1% of the sample volume shows superconductivity, the expected change in the frequency shift is about $\sim 0.08 \, \text{Hz}$ for sample #1 and $\sim 0.2 \, \text{Hz}$ for sample #2, which is larger than our noise level of $\sim 0.05 \, \text{Hz}$. However, in the present study, we did not observe any noticeable change in $\Delta f$ around 3 K in both samples, as shown in Fig. 4. We cannot exclude the possibility that the volume fraction of monolayer Cu-BHT in these samples are much smaller than 0.1%. Further experiments in the samples with the controlled number of layers are required to establish the possible high-$T_c$ phase in this system.

In conclusion, we have measured the magnetic penetration depth in thick film samples of Cu-BHT, which is the first 2D MOF superconductor. We found quasi-linear temperature dependence of $\Delta \lambda(T)$ at the lowest temperatures, a signature of unconventional gap structure with line nodes. Considering the flexibility of designing the crystal structure in MOFs, this superconducting system can provide a promising platform to study the relationship between quantum spin liquid and superconductivity, which is one of the central topics in condensed matter physics.

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