Low-temperature far-infrared absorption in the antiferromagnetic organic superconductor κ-(BETS)$_2$FeBr$_4$

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Organic salt κ-(BETS)$_2$FeBr$_4$ is a unique compound in which local moment antiferromagnetism of Fe^{3+} ions (below Néel temperature T_N of 2.5 K) coexists with bulk superconductivity (below the superconducting transition temperature T_C=1.1 K). To probe this unique coexistence we studied the low-temperature far-infrared optical response in a frequency range of 7–40 cm^{-1}, a characteristic energy range for superconducting and magnetic gaps. Measurements were undertaken using a polarizing interferometer and a He^3 cryostat in a temperature range 0.5–2.8 K. The spectrum shows a clear change on crossing both T_N and T_C. An absorption feature below T_N is interpreted as a signature for the formation of a magnetic pseudogap. The observed increased reflectance relative to the normal state at temperatures below T_C sets a value of the superconducting energy gap Δ_0 in the strong coupling regime, $2\Delta_0 \approx 8k_bT_C$.

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Coexistence and competition of superconductivity and magnetism is one of the central topics in modern condensed matter physics. In most cases, superconductivity with high-transition temperatures occurs on the border of magnetic order, implying a magnetically mediated mechanism of superconductivity with an exotic order parameter.[1,2] On the other hand, the response of a phonon-mediated superconducting state to coexisting spin-density-wave magnetism was considered theoretically and was found to depend on whether the magnetism is commensurate or incommensurate.[3–6] There are very few examples of the coexistence of this type, which sometimes leads to the exotic phenomenon of re-entrant superconductivity.[7]

κ-(BETS)$_2$FeBr$_4$ is an organic conductor with exotic low-temperature behavior (where BETS is bis(ethylenedithio)-tetraselenafulvalene).[8–11] The crystal structure of the salt is closely related to the well-known layered κ-type BEDT-TTF-based high-T_C organic superconductors (where BEDT-TTF is bis(ethylenedithio)-tetrathiafulvalene). The layers of the organic BETS molecules and of the inorganic FeBr$_4^-$ anions alternate along the *b* axis. Inside the two-dimensional *ac*-conduction planes BETS molecules are arranged in dimers. Molecular orbitals of BETS molecules in the layers provide the main contribution to the electronic band structure. Four bands dominate electronic structure close to the Fermi energy, with a midgap between the upper and lower two branches. As a result of the strong dimerization of the donor molecules, the upper band is essentially half-filled. Similar to many other κ phases, κ-(BETS)$_2$FeBr$_4$ has a two-dimensional Fermi surface with closed and open sheets.[12] The *d* electron shell of iron ions in the FeBr$_4^-$ anion is in the high (S=5/2) spin state and the local moments order antiferromagnetically below T_N=2.5 K. Interestingly enough, superconductivity with the same T_C is found in the isoelectronic salt κ-(BETS)$_2$GaBr$_4$, in which the magnetic moment is removed from the lattice.[13] This implies that superconductivity is not caused by magnetic interactions of the Fe ions but may respond to their presence.

Figure 1 shows the *ac*-plane electrical resistivity of κ-(BETS)$_2$FeBr$_4$ normalized to its room temperature value

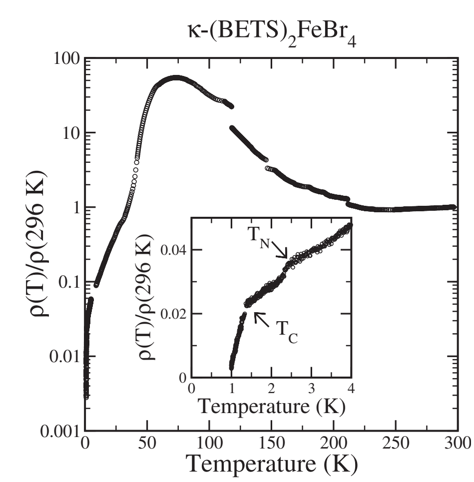

FIG. 1. Temperature dependence of electrical resistivity of κ-(BETS)$_2$FeBr$_4$, presented normalized by its room-temperature value. Inset shows zoom of the low-temperature part, showing anomalies in resistivity at T_N and T_C.

measured using a four-probe technique. The abrupt steps near 125, 150, and 200 K are extrinsic due to the sample developing cracks on cooling. It can be seen that the electrical resistivity of κ-(BETS)$_2$FeBr$_4$ is typical of a strongly correlated metal. Upon lowering the temperature it initially decreases slightly, reaching a minimum near 200 K. On further cooling the resistivity increases until a local maximum is reached near 60 K, below which it decreases rapidly by several orders of magnitude. The temperature below which the resistivity starts its sharp decline is sometimes referred to as the "coherence temperature," by analogy with heavy fermion materials.

Novel behavior arises as a result of the interaction between the π orbital conduction electrons of the BETS donor and the localized spins of the magnetic anion. When the Fe^{3+} spins undergo antiferromagnetic (AFM) ordering below T_N $=2.5$ K, the resistivity of κ-(BETS)$_2$FeBr$_4$ exhibits a small steplike decrease due to the resulting loss of magnetic scattering (see inset to Fig. 1). At 1.5 K the resistivity begins to decrease rapidly and reaches zero within experimental uncertainty at $T_C=1.1$ K as κ-(BETS)$_2$FeBr$_4$ undergoes a transition to the superconducting state.

Superconductivity in κ-(BETS)$_2$FeBr$_4$ has two superconducting domes in the magnetic field oriented parallel to the conducting plane.[14–16] It is bulk in nature, as revealed by thermal-conductivity measurements.[17] The nature of this coexisting antiferromagnetic/superconducting state is of great interest. To further characterize this unusual coexistence of superconductivity and magnetism herein we report far-infrared reflectance measurements of single crystals of κ-(BETS)$_2$FeBr$_4$.

A dominant feature of the superconducting state is the formation of a gap in the spectrum of single-electron excitations below T_C. According to weak coupling BCS theory, the magnitude of the gap in the limit $T\rightarrow 0$ is expected to be $2\Delta=3.5k_BT_C$. Strong coupling would lead to $2\Delta > 3.5k_BT_C$. Tunneling[18] and infrared[19] spectroscopic techniques have been used to determine the magnitude of the gap in conventional superconductors. In the infrared measurements, the reflectance, R, of the sample becomes identically equal to unity for energies below 2Δ. This leads to a notable although small change in the reflectance of a metal on crossing over into the superconducting state. For a simple metal one expects R to exhibit a Drude frequency dependence in the normal state which drives R to unity only in the limit of zero frequency. Thus, the superconducting gap can be studied by taking ratios of the reflectance of a sample below and above T_C. As the frequency approaches 2Δ the sample in the superconducting state begins to absorb radiation so the ratio of the superconducting to the normal-state reflectance peaks at a value greater than unity near 2Δ, and then approaches unity at higher frequencies, when the normal and superconducting state reflectance becomes the same.

This classical behavior has been observed in a number of superconducting materials including Pb,[20] boron-doped diamond,[21] and CaAlSi.[22] For many exotic superconductors, however, including organics, the electron coupling mechanism and the gap symmetry have not been incontrovertibly established. For an anisotropic superconducting gap function with nodes, absorption starts at frequencies below the superconducting gap and thus determination of the gap from optical measurements of the superconducting to normal-state reflectance is not straightforward.[23,24]

In materials exhibiting antiferromagnetic ordering, a partial energy gap (pseudogap) appears on parts of the Fermi surface affected by the magnetic Brillouin-zone boundaries. In the reflectance spectrum the pseudogap gives rise to a finite frequency peak in the optical conductivity. This behavior has been observed in the classical spin-density-wave system, Chromium,[25] and in antiferromagnetic heavy fermion materials UCu_5,[26] UPd_2Al_3 and UPt_3,[27] and URu_2Si_2 (Ref. 28) in the hidden order state. Only a fraction of the Fermi surface may be affected by the magnetic phase transition; the remainder contributing to low-frequency free-electron transport. The resistivity of these heavy fermion materials shows a temperature dependence similar to that of κ-(BETS)$_2$FeBr$_4$. The zero-frequency free-electron peak in the optical conductivity is very narrow if the magnetic transition occurs at a temperature well below the onset of coherence. In such a case the AFM absorption feature appears essentially as a peak on a very low background conductivity (assuming that the electronic transitions occur at higher frequencies). This is the case for URu_2Si_2. If, on the other hand, the magnetic transitions occur at a temperature comparable to the coherence temperature, as in UCu_5, or in a material that does not show low-temperature heavy electron behavior, such as Chromium, the gap excitation appears as a small peak or shoulder on the Drude background.

To the best of our knowledge, neither normal nor superconducting state optical properties of κ-(BETS)$_2$FeBr$_4$ have been reported previously, although some work has been done on related materials. Polarized infrared reflectance of a single crystal of κ-(BETS)$_2$FeCl$_4$ has been studied in the midinfrared spectral region 650–5500 cm^{-1} using an IR microscope at room temperature.[29] κ-(BETS)$_2$FeCl$_4$ is isostructural with κ-(BETS)$_2$FeBr$_4$ and similarly exhibits antiferromagnetic ordering with $T_N=0.45$ K and superconductivity with T_C $=0.1$ K. One important difference is that while the resistivity of κ-(BETS)$_2$FeBr$_4$ exhibits a maximum near 60 K, that of κ-(BETS)$_2$FeCl$_4$ retains metallic behavior down to the lowest temperatures.[9] Olejniczak *et al.*[29] compared the infrared spectra of κ-(BETS)$_2$FeCl$_4$ with the spectra of BEDT-TTF-based compounds and concluded that despite the substitution of the fulvalene sulfur atoms in BEDT-TTF with selenium atoms in the BETS-based conductor, which resulted in some shifts in frequency and intensity of the intramolecular vibrations, the overall characteristics of the vibrational and electronic excitations were essentially the same in the two families of compounds.

The low-frequency low-temperature optical properties of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$, which has a Fermi surface of the same topology as κ-(BETS)$_2$FeBr$_4$,[30] have been investigated by Kornelsen *et al.*[31] κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ undergoes a transition to the superconducting state at $T_C=10.4$ K, however, does not exhibit magnetic ordering. Kornelsen *et al.*[31] used a bolometric absorption technique to probe the superconducting state. In a frequency range below the expected BCS gap of 25 cm^{-1}, they found no decrease in absorption at a temperature of $0.5T_C$ compared to that above T_C. They suggested that the lack of change in the optical response below T_C was due to either the sample being in the clean limit or the superconducting gap having nodes. On the other hand, Klein *et al.*[32] performed microwave surface impedance measurements in the superconducting state to obtain the real part of the optical conductivity from which they ruled out a nodal gap.

Here we present polarized low-frequency far-infrared measurements of κ-(BETS)$_2$FeBr$_4$ at low temperatures with the goal of investigating changes in the electromagnetic absorption taking place upon entering the antiferromagnetic and superconducting regimes.

We carried out frequency-dependent measurements of the electromagnetic response of single crystals of κ-(BETS)$_2$FeBr$_4$ at various temperatures using a Martin-Pupplett-type polarizing interferometer and a ^{3}He cryostat. This combination of instruments is optimized for measurements at very low frequencies. We used three crystal pieces of total surface area $\approx 17\ \text{mm}^2$ that came from a rhombohedral-shaped crystal.

Preliminary measurements at room temperature in the midinfrared indicated that the reflectance is higher along the *c* axis. In the rhombus-shaped crystals of κ-(BETS)$_2$FeBr$_4$ the long diagonal corresponds to the *a* axis. These two facts were used to determine the orientation of each crystal piece. To increase the signal intensity, we constructed a sample holder in which the three samples were studied concurrently by mounting them on individual copper posts, oriented with their crystallographic axes parallel, so that the reflection from each piece was maximized.[33]

In Fig. 2 we present the ratios of the reflectance at selected temperatures. These ratios represent the relative change in the reflectance between the two temperatures and are referred to as "thermal reflectance" ratios. Incomplete cancellation of interference fringes caused by windows, filters, beam splitters, *etc.* within the optical path results in the oscillations in the data on the order of $\pm 1.5\%$. Putting this extrinsic effect aside, it can be seen that (1) the thermal reflectance ratio is essentially unity at higher frequencies (implying the same reflectance for the two temperatures investigated) and (2) a notable deviation from unity is observed at lower frequencies. The left and right columns of panels in Fig. 2 show the thermal reflectance ratios for the *a* and *c* axis, respectively. Top panels (a) and (b) in Fig. 2 show the thermal reflectance ratios for the samples in the superconducting state at 0.5 K to that in the antiferromagnetic state above T_C at 1.4 K. The panels (c) and (d) show the ratio of the superconducting state reflectance at 0.5 K to the reflectance at 2.8 K in the paramagnetic normal state above T_N. These plots show that for both the *a*- and *c*-axis polarizations, that the reflectance at the lowest frequencies is higher in the superconducting state, than it is at both 1.4 and 2.8 K. The panels (e) and (f) show the ratio of the reflectance within the antiferromagnetic state at 1.4 K to that in the paramagnetic normal state above T_N, at 2.8 K. Panels (g) and (h) show the ratio of the reflectance at 1.9 K in the antiferromagnetic state to that at 2.8 K in the paramagnetic normal state. For both latter sets of ratios, the reflectance at the lowest frequencies is lower in the antiferromagnetic regime than in the paramagnetic regime. Within the experimental uncertainty of $\pm 1.5\%$ no significant anisotropy is found for polarization along the *c* axis and *a* axis (the latter being an easy axis for antiferromagnetism).

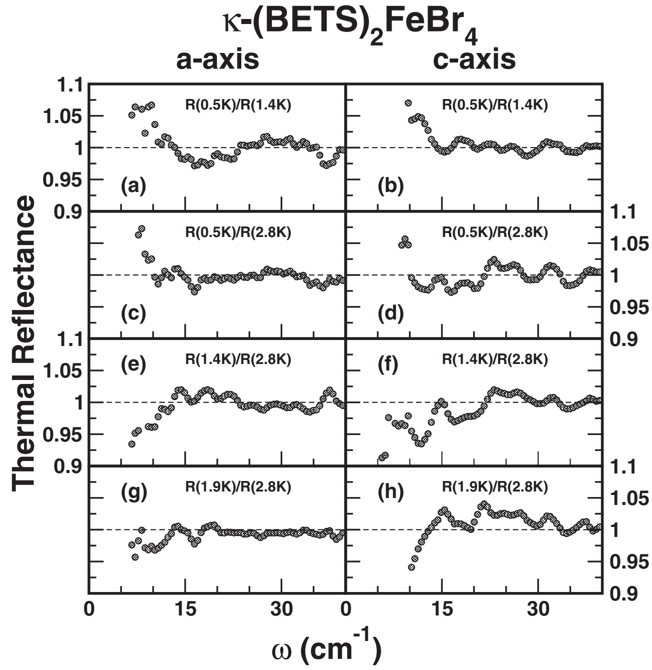

FIG. 2. Thermal-reflectance ratios of κ-(BETS)$_2$FeBr$_4$ along the *a* (left column of panels) and *c* axis (right column of panels). Panels (a) and (b) show the ratios of the reflectance at 0.5 K in the superconducting state to that at 1.4 K in the AFM normal state. Panels (c) and (d) show the ratio of the reflectance at 0.5 K in the superconducting state to that at 2.8 K in the paramagnetic normal state. Panels (e) and (f) show the ratio of the reflectance at temperatures of 1.4 K in the antiferromagnetic normal state to that at 2.8 K in the paramagnetic normal state, panels (g) and (h) show analogous ratios for measurements at 1.9 K and 2.8 K. Uncertainty in the thermal-reflectance ratio is $\approx \pm 0.015$.

These results suggest that as the temperature is lowered from 2.8 K (paramagnetic normal state) into the antiferromagnetic normal state, additional absorption occurs at frequencies below $\approx 15\ \text{cm}^{-1}$. This may be due to formation of a pseudogap at the magnetic Brillouin-zone boundary. As the temperature is lowered below T_C into the superconducting state, the reflectance becomes higher than in the normal state (both paramagnetic and antiferromagnetic). This is expected for the formation of a true superconducting gap, for which no absorption is possible for $\hbar\omega < 2\Delta$ and which leads to the ratio of the reflectance below T_C to that at temperatures above T_C exhibiting a peak. (The spectral range of our apparatus allows only observation of the falling edge of this peak). Because of the interference of the AFM state (at temperatures in the interval from T_C to T_N), it is most straightforward to look at the thermal reflectance ratio $R(0.5\ \text{K})/R(2.8\ \text{K})$ from which we infer that the increase occurs below $\approx 10\ \text{cm}^{-1}$. The low-frequency limit of our data is around $7\ \text{cm}^{-1}$ which would thus place an upper limit for $2\Delta_0$ for a conventional BCS superconductor or give the maximum of the superconducting gap for an anisotropic gap superconductor, as $2\Delta_0/kT_C < 8$.

Despite the fact that organic metals have a rich phonon spectrum which may couple to electronic degrees of freedom and be affected by superconductivity, low-lying phonon modes in the frequency range of our experiment are usually screened by the electronic component in the far infrared. Raman experiments on the higher T_C compounds κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ (Ref. 34) and κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br,[35,36] find modes with frequency as low as 19 cm^{-1}, however, no analogs were found in far-infrared absorption spectra.[31] These Raman modes are affected by the opening of the superconducting gap, as long as their frequency $\omega < 2\Delta_0$. So, if in the unlikely event that the feature observed in our experiments on κ-(BETS)$_2$FeBr$_4$ is the result of such modes, information would still be provided regarding the energies of the gaps in the electronic spectrum.

In summary, we have found that the low-frequency optical properties of κ-(BETS)$_2$FeBr$_4$ are influenced by both the magnetic and the superconducting phase transitions. We observe changes in the absorption in the far-infrared optical response on crossing both T_N and T_C. We interpret these spectral features as likely signatures of the formation of a magnetic pseudogap and a superconducting gap, respectively.

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