Far-infrared electrodynamic response of $(TMTSF)_2ClO_4$ in the normal and superconducting states

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The far-infrared reflectance of $(TMTSF)_2ClO_4$ has been measured at temperatures between 0.45 and 26 K in the 10–70-cm^{-1} frequency range for light polarized along the *a*-axis conducting chains. Slow cooling of the sample permits the anions to order near 24 K and a superconducting state to develop below 1.2 K while fast-cooling yields an insulating ground state. The thermoreflectance was found to be temperature dependent below the anion ordering temperature for the slow-cooling case only. A low-frequency edge in the absolute reflectance and a peak near 30 cm^{-1}, attributed to a phonon coupled to the electronic background, are found to exhibit a strong temperature dependence in the relaxed state. The Kramers-Kronig-derived optical conductivity indicates that the 30-cm^{-1} mode becomes highly asymmetric below the ordering temperature. On entering the superconducting state it is observed to shift upward in frequency as would be the expected effect on the real part of the self-energy of a phonon coupled to the electronic system of a frequency greater than the superconducting gap.

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The temperature-dependent normal-state far-infrared optical properties of the quasi-one-dimensional organic superconductor $(TMTSF)_2ClO_4$ have been the source of considerable discussion over the years.[1–9] A brief overview was given by Cao *et al.*[6] Slow cooling of the sample permits the anions to order near 24 K resulting in metallic conductivity and the development of a superconducting state below 1.2 K while fast cooling yields an insulating ground state.[10] At room temperature the optical conductivity along the conducting chains exhibits a broad incoherent band, the low-frequency limit of which tends to a value somewhat less than the dc conductivity. As the temperature is lowered the discrepancy becomes increasingly more pronounced; the dc conductivity growing dramatically while the real optical conductivity develops a clear gap like depression below 170 cm^{-1} which is accompanied by a significant growth in intensity of phonon lines. The prevailing explanation is that the transport mechanism is via charge-density-wave fluctuations. The high dc conductivity is interpreted to result from a narrow collective mode associated with transitions across the charge-density-wave gap while the broad incoherent band is due to a strongly correlated Luttinger liquid.[9,11]

The superconducting state of $(TMTSF)_2ClO_4$ has been subject to very few studies, likely as a result of the low T_c and the fragility of the brittle, needlelike crystals. Neither the mechanism driving the superconducting instability, nor the symmetry of the superconducting order parameter have been established. In particular it is important to determine whether the superconductivity involves a phonon mediated interaction or a more exotic one since the symmetry of the gap function is likely determined by the pairing mechanism. Using the technique of nuclear magnetic resonance (NMR) Takigawa *et al.* inferred an anisotropic order parameter vanishing along lines on the Fermi surface from the absence of a coherence peak just below T_c in the nuclear relaxation rate and a T^3 dependence at lower temperatures.[12] Belin and Behnia, however, carried out thermal conductivity measurements and found that their results provided support for a nodeless superconducting gap function.[13] They argued that the NMR experiment was not carried out at sufficiently low temperatures to determine the power of *T*, however, left open the possibility of an antisymmetric order parameter. Shimahara proposed that the apparent contradiction could be resolved by a *d*-wave gap function under anion order with the pairing interaction mediated by antiferromagnetic spin fluctuations.[14] In this model the anion order eliminates the line nodes of the *d*-wave gap function and a small finite energy gap appears in the quasiparticle excitation spectrum. Near T_c the closing of the already small energy gap would cause temperature dependences of observed quantities to be similar to those for a *d*-wave gap function with line nodes, while for low temperatures behaviors corresponding to the small but finite gap are expected. On the other hand, pairing mediated by electron-phonon coupling would likely be associated with conventional BCS-like *s*-wave superconductivity. Both the magnitude of the specific heat jump[15] and the energy gap deduced from tunneling spectroscopy[16] have been found to be consistent with conventional BCS theory. Furthermore, evidence of strong electron-phonon interaction is found in infrared data as discussed below.

Herein we report a study of the far-infrared electrodynamic response of $(TMTSF)_2ClO_4$ along the *a* axis in the metallic state at temperatures which extend to the superconducting state. We cannot probe the superconducting energy gap directly because according to the tunneling and specific-heat measurements it is found to have a typical BCS value and would therefore appear at frequencies lower than those accessible. We do, however, observe a shift of the low-frequency spectral features on entering the superconducting state which indicates that the spectrum is influenced by the superconducting ground state via an electron-phonon coupling.

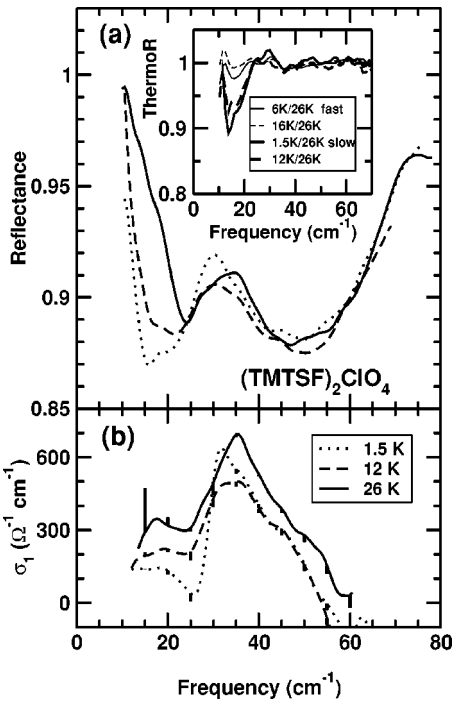

FIG. 1. Temperature dependence of the normal-state far-infrared (a) reflectance and (b) real optical conductivity of slowly cooled $(TMTSF)_2ClO_4$ along the *a* axis. In (b) the vertical lines at 5-cm^{-1} intervals indicate uncertainty in the optical conductivity as a result of selecting a different low-frequency extension for the Kramers-Kronig analysis as discussed in the text. The inset to (a) compares the slow- and fast-cooled thermoreflectance.

A mosaic of eight needle-like single crystals of $(TMTSF)_2ClO_4$, synthesized by electrocrystallization,[13] was constructed for the measurements. The crystals were aligned parallel with each other along the *a* axis to obtain a surface as flat and continuous as possible. The far-infrared reflectance was measured using a step-and-integrate Martin-Puplett-type polarizing interferometer with 2-cm^{-1} resolution at temperatures ranging from 0.45 to 26 K obtained using a helium-3 cryostat. A holographic far-infrared grid polarizer was used to polarize the light along the *a* axis of the crystal. At every temperature typically 16–20 scans (of 10-min duration each) were averaged. An *in situ* gold evaporation was used to obtain the absolute reflectance.[17] With this technique the absolute reflectance is correct to approximately $\pm 1\%$ while the relative error between the curves at different temperatures is less. High-frequency extensions to enable Kramers-Krönig analysis to obtain the optical conductivity were taken from literature data[6,18] as discussed below.

Figure 1(a) (main part) shows the *a*-axis reflectance of $(TMTSF)_2ClO_4$ at three temperatures in the normal state measured upon warming after slowly cooling the sample below 40 K at a rate of approximately 0.1 K/min in order to reach the relaxed state in which the anions are ordered and a superconducting ground state exists.[10] Note that both the peak near 30 cm^{-1} and the rising low-frequency reflectance are strongly temperature dependent. Additional measurements for which the sample was fast cooled through the anion ordering temperature at a rate of 15–20 K/min to favor the insulating spin-density-wave state indicate that this strong temperature dependence is associated with the relaxed state. The inset to Fig. 1(a) shows the thermoreflectance, defined to be the ratio of the reflectance at low temperature to that at 26 K which is above the ordering temperature, for both the slow- and fast-cooled sample. The slow-cooled curves have considerable structure, in particular at low frequencies. The fast-cooled results, however, make only small excursions from unity, on the order of a percent, indicating that the reflectance is essentially independent of temperature in this range.

The peak near 30 cm^{-1} has been identified in earlier work as a coupled electron-phonon mode.[1–3,5] Eldridge *et al.* proposed that it is a zone-boundary acoustic phonon activated as a result of zone folding which accompanies the formation of the ordered anion superlattice.[5] In their work the mode was observed to broaden dramatically for temperatures above the anion ordering transition, however, it was found that its intensity remained constant to ≈ 75 K, beyond which it was too broad to measure. Above the anion ordering transition they proposed that the absorption would occur due to defect-induced one-phonon processes along the entire phonon branch. The rising reflectance between 50 and 75 cm^{-1} can be attributed to the leading edge of a strongly temperature-dependent phonon as also observed in Refs. 5 and 6. Unlike the 30-cm^{-1} mode, this mode appears to gain oscillator strength as the low-frequency gap forms, presumably due to the onset of charge-density-wave order.[6]

The origin of the low-frequency edge is somewhat uncertain. According to Refs. 1 and 2 the rising low-frequency reflectance is the falling edge of a phonon feature centered at 7 cm^{-1}. In other measurements a phonon mode was not observed at 7 cm^{-1},[4,8,9] and thus the rising low-frequency reflectance was assumed to be the plasmalike edge of the zero-frequency mode which gives rise to the large dc conductivity.[8,9] We infer from the strong sharpening of this feature in this narrow temperature range that it is highly sensitive to the electronic structure. In Ref. 2 this feature, like the one near 30 cm^{-1}, is attributed to an electron-phonon coupled mode.

The considerable variation in both the magnitude of the reflectance and the presence or absence and strength of phonon features is a concern for elucidating the optical properties of $(TMTSF)_2ClO_4$.[6] Thermal cycling leading to surface deterioration is suspected to be the leading cause of the variation in the literature data.[2–4,6] The crystals used in our study were cooled only once slowly from room temperature to nitrogen temperature. They were then quenched to helium temperatures, warmed to 90 K while data was collected, and then slow cooled back to helium temperatures in order to collect data in the anion-ordered state. The data of Ref. 6 were used to extend our data to higher frequencies in the Kramers-Kronig procedure for obtaining the optical conductivity since the limit of our data was found to be in good agreement. Beyond the high-frequency limit of Ref. 6 data were taken from Ref. 18. The low-frequency extrapolation was more problematic. Given the extent of variation in the literature data in the far infrared, we used the phonon of Ref. 1 and alternatively we assumed that the reflectance follows a

Hagen-Rubens dependence below 10 cm^{-1}. These are the most reasonable extrapolations under the circumstances although the Hagen-Rubens dependence assumes Drude transport which it is clearly not.

The real conductivity calculated using the Hagen-Rubens low-frequency extrapolation consistent with the dc resistivity[19] is shown for the slow-cooled sample in the normal state in the far-infrared in Fig. 1(b). The vertical line segments at 5-cm^{-1} intervals indicate the magnitude of the difference in the optical conductivity determined using the Hagen-Rubens and the phonon low-frequency extrapolations discussed above. The effect of the low-frequency extrapolation on the optical conductivity beyond ≈ 25 cm^{-1} was negligible. It is thus clear that while there is considerable uncertainty in selecting the correct low-frequency extrapolation, it does not change the general trends observed in the data above 15 cm^{-1}. We limit the optical conductivity to 60 cm^{-1} because we could not measure the reflectance of the phonon at the upper limit of our data to high enough frequencies to determine the temperature dependence of the corresponding conductivity accurately. In agreement with previous work the lower limit of $\sigma_1(\omega)$ is orders of magnitude less than the dc conductivity which implies that the temperature and frequency dependence of the optical conductivity is not that expected for a simple metal. As discussed in the Introduction, the optical data available in the literature suggest the development at low temperatures of a mass-enhanced collective mode with width much less than the low-frequency limit of the data, superimposed upon a gapped low-conductivity single-particle band.[6] As the temperature is lowered in Fig. 1(b) the low-frequency background optical conductivity decreases in magnitude, while the 30-cm^{-1} mode becomes more asymmetric, appearing as an antiresonance. The sensitivity of this mode to changes in electronic structure support its assignment as a strongly coupled electron-phonon mode. The limit of the optical conductivity of Fig. 1(b) at the lowest frequencies shows that the gaplike depression continues to develop over this very narrow range of temperatures and thus suggests that it is strongly affected by the anion ordering.

Because acoustic modes play an important role in the superconductivity of simple metals exhibiting the conventional electron-phonon mediated pairing interaction[20,21] it is of particular interest to examine the effect of the onset of superconductivity on the mode near 30 cm^{-1}. In Fig. 2(a) we show a detail of the *a*-axis reflectance of $(TMTSF)_2ClO_4$ in the relaxed state under slow-cooled conditions at the lowest temperatures measured. The corresponding optical conductivity is shown in Fig. 2(b). In order to confirm that a superconducting ground state was attained under the experimental conditions used, ac-susceptibility measurements were carried out with a susceptometer based on the design of Ref. 22 and configured for the same He^3 cryostat that was utilized for the optical measurements. The mosaic sample used for the optical experiment was mounted within the ac susceptometer on a cold plate of the cryostat and measurements were taken upon warming from 0.4 K with both the fast- and slow-cooling procedures reproduced as closely as possible. The results are shown in the inset of Fig. 2(a). At a temperature of

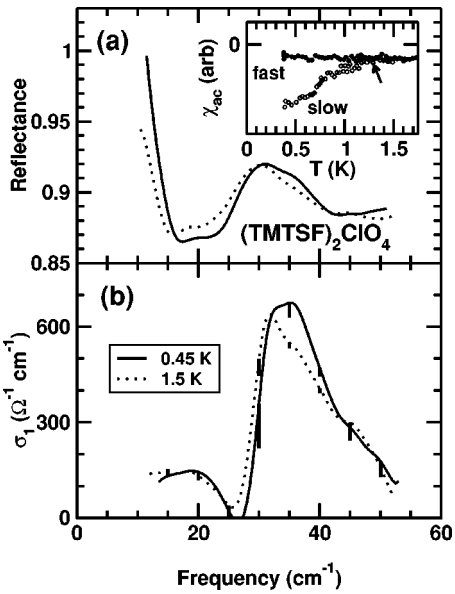

FIG. 2. Comparison of the far-infrared (a) reflectance and (b) real optical conductivity of slowly cooled $(TMTSF)_2ClO_4$ along the *a* axis at 1.5 K in the normal state with that at 0.45 K in the superconducting state. Vertical lines in (b) indicate uncertainty as discussed in the text. The inset to (a) shows the ac susceptibility measured under slow- and fast-cooled conditions. The arrow indicates where the slow-cooled data begin to deviate from the temperature independence of the fast-cooled curve due to the onset of superconductivity.

approximately 1.2 K (indicated by the arrow) the slow-cooled curve deviates from the temperature independence of the fast-cooled data as expected with the onset of superconductivity, thus confirming that the relaxed state has been reached under slow-cooling conditions and that for temperature below 1.2 K the sample is superconducting. Note that both the low-frequency edge and the 30-cm^{-1} mode in the reflectance of Fig. 2(a) (main part) shift to *higher* frequency by approximately 2 cm^{-1} upon cooling from the normal state at 1.5 K to the superconducting state at 0.45 K. There is a corresponding shift in the antiresonance near 30 cm^{-1} in the optical conductivity, shown in Fig. 2(b). This shift upward in frequency opposes the trend found in the normal state where both the 30-cm^{-1} mode and the low-frequency reflectance edge shift down in frequency with decreasing temperature. Since it has been established that these features are highly sensitive to the electronic structure, it can be assumed that this behavior is the result of the change in electronic structure upon entry into the superconducting state. For a BCS superconductor, an energy gap of $2\Delta_o = 3.53kT_c$ is expected to open up in the density of states at low temperature. A BCS superconductor with a nodeless isotropic gap function will thus have a sharp threshold of absorption at $2\Delta_o$. According to tunneling measurements $2\Delta_o$ is ≈ 2.8 cm^{-1}[16] which is below the range of accessible frequencies. However, the interaction of the superconducting carriers with strongly coupled phonon modes will also reflect this shift in the density of states giving rise to changes in phonon structure. For example, in conventional BCS superconductors such as Pb the contribution to the spectrum due

to Holstein emission, wherein a photon is absorbed and a phonon is emitted resulting in absorption thresholds with onset at the various phonon frequencies, is shifted by the gap 2Δ.[20] In the high-T_c cuprate superconductors modification of the Fermi surface, caused by the opening of the superconducting gap, results in changes in the real and imaginary parts of the self-energy (the resonance frequency and linewidth, respectively) if the phonon is coupled to the electronic system.[23] The hardening of the 30-cm^{-1} mode of $(TMTSF)_2ClO_4$ on entry to the superconducting state is consistent with its resonance frequency lying above the gap, as is the slight broadening due to the opening of an additional decay channel.[24]

It is instructive to compare these findings with the results of the above-mentioned study of thermal conductivity in this system. Since the lattice thermal conductivity below T_c appeared to be unaffected by the condensation of electrons in the superconducting condensate, Belin and Behnia[13] concluded that the acoustic phonons (which are the only thermally available modes at sub-Kelvin temperatures) are not strongly coupled to electrons. [This contrasts with the case of κ-$(BEDT\text{-}TTF)_2Cu(CNS)_2$ where thermal conductivity does detect such a coupling between low-energy phonons and electrons.[25]] Hence this new result, *i.e.*, the hardening of the optical mode at 30 cm^{-1} below T_c, which identifies a higher-energy phonon mode (which would not contribute to the thermal conductivity at low temperatures) that is coupled strongly to the electrons forming the superconducting condensate may provide new constraints for theoretical models for the mechanism of superconductivity in this system which remains an unresolved issue.

In summary, the optical properties of $(TMTSF)_2ClO_4$ have been examined along the *a* axis at low frequencies and temperatures which extend into the superconducting state. The notable temperature dependence observed when the sample was cooled slowly through the anion ordering temperature was absent when the sample was quenched quickly from liquid nitrogen to helium temperatures. This suggests that there is a strong coupling between the electronic background and the features in the reflectance below 50 cm^{-1} in the relaxed state where the sample is metallic at low temperature. In particular, the mode near 30 cm^{-1} takes on a highly antisymmetric form at low temperatures. Upon entry to the superconducting state both the 30-cm^{-1} mode and the low-frequency reflectance edge are observed to shift upward in frequency indicating that there is a coupling to excitations of quasiparticles across the superconducting gap.

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