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Pseudo Gap and Superconducting Gap in an Organic Superconductor κ-(BEDT-TTF)$_2$[Cu(SCN)$_2$]

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The low energy electronic structure of κ-(BEDT-TTF)$_2$Cu(SCN)$_2$ has been investigated by means of polarized reflectance over 20-5000 cm^{-1} (2.5-620 meV). The Kramers-Kronig-derived conductivity clearly demonstrates a pseudo gap of ~20 meV developed at 50 K for both the $E\|b$ and $E\|c$ polarizations. The sum rule on $\sigma_1(\omega)$ shows that the number of charge carriers is 33% larger at low temperatures ($T < 100$ K) than that at room temperature (298 K). These optical results consistently involve the observed structural and transport anomalies around 100 K as well as the Mott-insulator fluctuation around 50 K.

1. INTRODUCTION

Since the discovery of superconductivity beyond 10 K in κ-(BEDT-TTF)$_2$[Cu(SCN)$_2$] (where BEDT-TTF denotes bis(ethylenedithio)tetrathiafulvalene) [1], many studies have been reported to characterize the compound series κ-(BEDT-TTF)$_2X$ (X is a various counter anion such as [Cu(SCN)$_2$]$^-$, Cu[N(CN)$_2$]Br$^-$, *etc.*) [2]. However, some phenomena still remain open to question. For instance, the typical κ-type BEDT-TTF salts show an unusual resistivity peak about 100 K, become metallic in the lower temperature region, and finally undergo a superconducting transition around 10 K [3,4]. For X = [Cu(SCN)$_2$]$^-$, the resistivity peak magnitude shows sample dependence, and moreover, the crystals from tetrahydrofran (THF) solution do not show semiconducting behavior at all [5], without depressing the T_c as seen in the report under hydrostatic pressures [6]. What is the origin of this resistivity peak?

Here is another anomaly around 50 K: the $d\ln(\rho(T))/d\ln(T)$ curve shows a divergent peak to indicate a some kind of electronic phase transition [7]. NMR studies, from another point of view, suggest a presence of an antiferromagnetic fluctuation around this temperature [8], possibly caused by strong electron correlation [9]. If this is the case, we may see this fluctuation in far-infrared spectra. In this contribution we present the polarized far-infrared reflectance of κ-(BEDT-TTF)$_2$-[Cu(SCN)$_2$] measured on single crystals. We show the presence of a pseudo gap of ~20 meV in the conductivity spectra at 50 K. The sum rule on the conductivity indicates that the resistivity peak may be related to the change of the number of charge carriers. We discuss the temperature dependence of the low-energy electronic structure from the infrared point of view.

2. EXPERIMENTAL

Single crystals of κ-(BEDT-TTF)$_2$[Cu(SCN)$_2$], whose (100) crystal face was up to 4×2 mm^2, were prepared by a constant-current electrochemical crystallization technique in a 1,1,2-tetrachloroethylene (TCE) solution of BEDT-TTF, together with Copper(I) thiocyanate (CuSCN) and tetra-*n*-butylammonium thiocyanate to form dithiocyanate [Cu(SCN)$_2$]$^-$ anion in the solution [5]. The crystals from a THF solution, which grew only up to 2×1 mm^2, were not large enough for far-infrared measurements down to 20 cm^{-1} using ordinary mercury light source.

The temperature dependence of the polarized far-infrared reflectance was measured on a Bruker IFS 113v (20-5000 cm^{-1}) with an extensively modified

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reflectance unit, combined with a liquid He-flow type cryostat (5-300 K) equipped with a specially designed sample holder. This system has been proved to enable us to measure reliable reflectance down to 15 cm^{-1} (the lower frequency limit is restricted to the diffraction effect depending on a sample size), as described in our recent paper [10].

3. RESULTS AND DISCUSSION

3.1. Far-infrared reflectance

Figure 1 shows the temperature dependence of the polarized reflectance measured at 6.3, 50, 100, and 298 K, for the polarization $E\|b$ and $E\|c$ on the (100) crystal face. The optical anisotropy is small at all the temperatures. We can clearly see the reflectance crossover at the far-infrared region below 150 cm^{-1} as the temperature decreases from room temperature, corresponding to the resistivity peak around 100 K. The far-infrared reflectivity increases again at the lower temperatures, and in the superconducting state at 6.3 K, the value is very close to unity below 100 cm^{-1}.

3.2. Pseudo gap in conductivity spectra

In Fig.2 we show the real part of the conductivity (σ_1) obtained by a Kramers-Kronig transformation of the reflectance. We used the results of a fit by a Drude-Lorentz model [5] on the reflectance to extrapolate the measured data to low frequencies, and used our previous data at high frequencies [5]. The extrapolated zero-frequency conductivity agrees well with the reported dc results over the whole temperature region, including the semiconducting behavior down to about 100 K [3]. The mid-infrared absorption bands are assigned to interband transitions [5,11,12]; the calculated interband conductivity is in good agreement with the observed one for the $E\|c$ polarization, whereas more work may be needed for the $E\|b$ polarization to explain the experimental data.

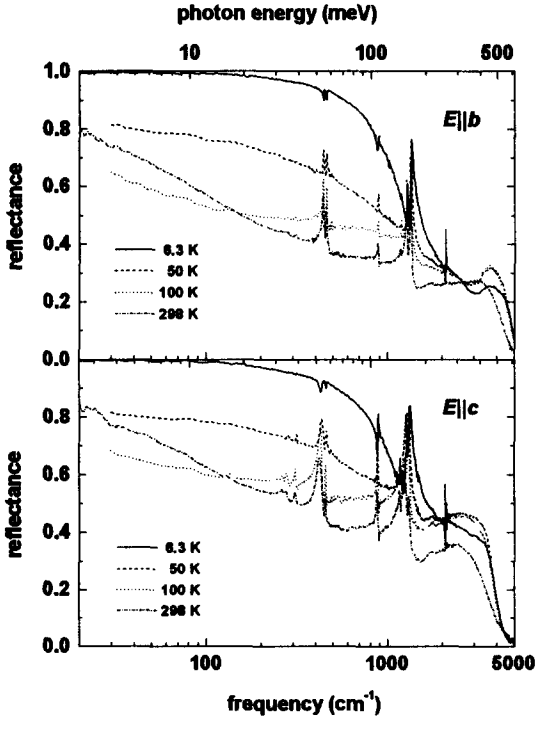

Figure 1. Temperature dependence of polarized reflectance of κ-(BEDT-TTF)$_2$[Cu(SCN)$_2$].

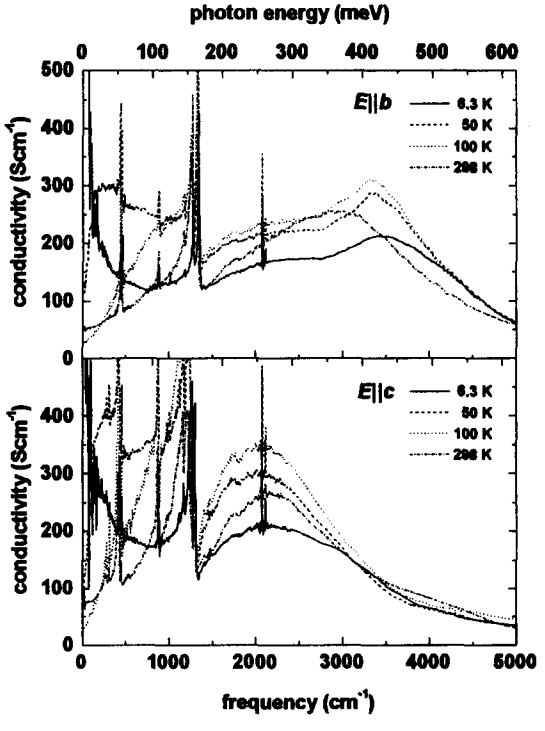

Figure 2. Real part of conductivity of κ-(BEDT-TTF)$_2$[Cu(SCN)$_2$] by a Kramers-Kronig analysis.

The most prominent feature in the conductivity is a suppressed Drude contribution at low frequencies at all temperatures except 6.3 K. In the 50 K spectra, the conductivity shows a sharp drop below ~150 cm^{-1} (~20 meV) to evidence a pseudo gap for both the $E\|b$ and $E\|c$ polarizations. This spectral aspect agrees with the picture of the Mott-insulator fluctuation around 50 K [7-9]. As the temperature decreases, the pseudo gap vanishes, and the material has a very clean-metal character ($\gamma < 25$ cm^{-1} for the Drude parameter) in the superconducting state at 6.3 K.

3.3. Superconducting gap invisible in reflectance

We sought the superconducting gap in far-infrared region by reflectance; the change through the superconducting transition, R(6.3 K) / R(14 K) was investigated. The resulting reflectance ratio is shown in Fig. 3. The dip at 390 cm^{-1} comes from an absorption band of a black-polyethylene filter inside a bolometer detector, and is not intrinsic. The ratio is almost flat and slightly higher than unity over the entire measured range of 20-600 cm^{-1}, indicating the absence of a gap-originated structure as predicted in the theoretical study [13]. This feature suggests a clean-limit superconductivity, being consistent with the report by a bolometric technique [14]. We are now trying to measure the reflectance change between the superconducting and normal states by applying a current to break the superconductivity.

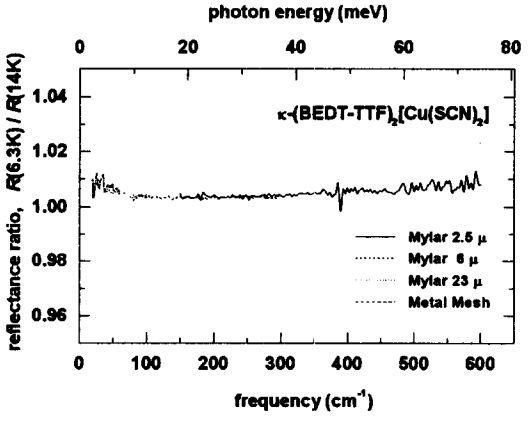

Figure 3. Reflectance ratio between the superconducting and normal states, R(6.3 K) / R(14 K).

The preliminary result also showed a gapless feature in the superconducting state.

3.4. Anomaly in sum rule above 100 K

The effective number of charge carriers participating in optical transitions at frequencies less than ω is given by the following equation,

$$n_{eff}(\omega)\frac{m}{m^*} = \frac{2mV_{cell}}{\pi e^2}\int_0^{\omega}\sigma_1(\omega')d\omega' \qquad (1)$$

where e and m are the free-electron charge and mass, respectively, m^* is the effective mass, and V_{cell} is the volume occupied by one formula unit. For the latter, we take a half of the unit cell (Z=2), *i.e.*, V_{cell} is equal to the formal volume for one hole.

Figure 4 shows the temperature dependence of the effective number of the charge carriers thus obtained. One can find that only the curve at 298 K for both the $E\|b$ and $E\|c$ polarizations separates from the

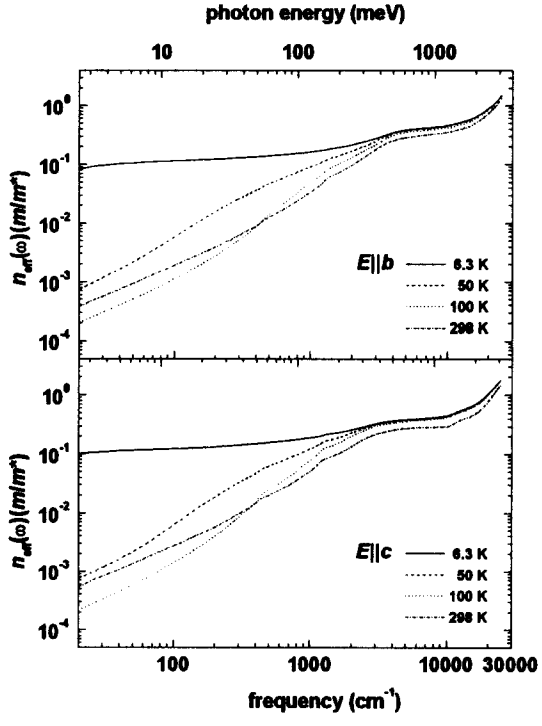

Figure 4. Effective number of charge carriers $n_{eff}(\omega)$, calculated by a sum rule on the conductivity.

others up to 25000 cm^{-1} (3.1 eV), whereas the others join around 5000 cm^{-1} (0.6 eV). Generally, the sum rule must be conserved after the charge carriers exhaust their oscillator strengths. The discrepancy between the data above and below 100 K therefore suggests the presence of an electronic phase-transition occurring between 100 K and room temperature; the number of charge carriers is estimated to be about 33% larger at low temperatures (T < 100 K) than that at 298 K. This transition is probably related to the resistivity peak around 100 K. The Hall effect study, however, did not show any indication of anomaly above 100 K [15].

In κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br, the resistivity peak around 100 K is claimed to be caused by a structural phase transition originating from ethylene group orderings in the BEDT-TTF molecules, and to be affected by the temperature prehistory of the samples [16-18]. In case of κ-(BEDT-TTF)$_2$-[Cu(SCN)$_2$], on the contrary, this kind of feature has not been observed in the resistivity although some structural anomalies have been reported around 100 K [19,20]. The mechanism and the origin of the 100 K anomaly in the resistivity as well as in the sum rule are still open to question. Further works may be necessary to achieve consistent understandings.

4. CONCLUSION

We have investigated the low energy electronic structure of κ-(BEDT-TTF)$_2$[Cu(SCN)$_2$] by means of polarized reflectance. We found the pseudo gap in the conductivity (σ_1) at 50 K for both the $E\|b$ and $E\|c$ polarizations, which gap is attributed to the Mott-insulator fluctuation around this temperature. The sum rule on the conductivity suggest the presence of an electronic phase-transition above 100 K, probably related to a semiconductor-to-metal transition observed in the resistivity.

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