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Infrared study of the properties of the normal (metallic) phase of κ-(ET-$^{13}C_4)_2$Cu(CN)[N(CN)$_2$]☆

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Abstract

Infrared (IR) properties of κ-(ET-$^{13}C_4)_2$Cu(CN)[N(CN)$_2$] crystals in the normal (metallic) phase are reported. Deviations from conventional metallic properties are found and assigned to a strong electron correlation effect.

Keywords: Organic superconductor; Strongly correlated metal; Optical study

1. Introduction

The family of 10 K organic superconductors κ-(ET)$_2$X continues to attract considerable interest due to a remarkably rich phase diagram, which includes an insulating antiferromagnetic phase next to the superconducting phase, as well as a metallic phase with properties quite different from those of a conventional metal [1]. κ-(ET)$_2$Cu(CN)[N(CN)$_2$] (T_c = 11.2 K for ET-H$_8$, 11.0 K for ET-$^{13}C_4$, and 12.3 K for ET-D$_8$) (below called as κ-CN), in contrast to κ-(ET)$_2$Cu(NCS)$_2$ and κ-(ET)$_2$Cu[N(CN)$_2$]Br, does not display distinctive semiconductive behavior down to T_c, although the resistivity versus temperature (R–T) dependence changes its curvature from negative to positive with pressure [2]. Here we report infrared (IR) properties of $^{13}C_4$ substituted κ-CN crystals in the normal (metallic) phase along the b- and c-axes in the conducting plane.

2. Experiment

Black rectangular plate-like crystals of 1.8 mm × 0.8 mm × 0.01 mm dimensions were grown electrochemically [3]. Polarized reflectivity was measured with a Bruker IFS 113v (100–700 cm^{-1}), and FT-IR Nicolet Magna 760 (600–12000 cm^{-1}) and multi-channel detection system Atago Macs 320 (11 000–33 000 cm^{-1}) combined with IR microscope.

3. Results

The optical conductivity spectra obtained by a Kramers–Kronig analysis of the reflectivity spectra are shown in Fig. 1. The oscillator strength (Fig. 2) was calculated from the integrated conductivity up to 1 eV at 300 and 12 K.

4. Discussion

4.1. Optical conductivity

At high temperatures, most of the spectral weight is contained in broad mid-IR peak centered at 0.25 and 0.35 eV for $E\|c$ and $E\|b$, respectively. While the position of the peak for $E\|b$ is reasonably consistent with the calculation of the inter-band optical transitions, the peak for $E\|c$ appears at an energy half of that predicted [4]. The electron correlation, not accounted for by the tight-binding band calculation, should certainly affect the band diagram and the density of states in κ-(ET)$_2$X crystals.

Two distinctive temperature regions can be found. From 300 K down to 100–150 K, intensity of the mid-IR peak

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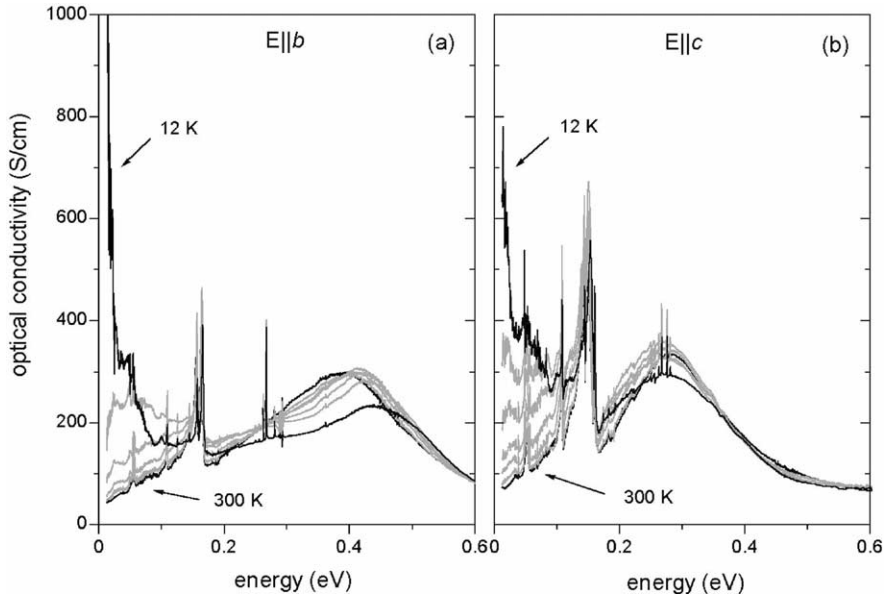

Fig. 1. The conductivity of $^{13}C_4$ compound at 300, 250, 200, 150, 100, 50, and 12 K for $E\|b$ (left) and $E\|c$ (right). Thick lines show the spectra at two extreme temperatures.

increases and the peak position experiences a slight blue shift. This is reminiscent of the insulating κ-$(ET)_2X$ crystals, such as κ-$(ET)_2Cu[N(CN)_2]Cl$ and κ-$(ET)_2Cu_2(CN)_3$, where the mid-IR peaks appear at energies similar to those in metallic crystals, but are commonly interpreted as intra- and inter-dimer charge transfer bands which are temperature-dependent on account of the lattice contraction. At 100 K, the Drude peak in the far-IR starts to develop. Below 100–150 K, the intensity of the mid-IR peak decreases. However, it is not until below 50 K that Re $\varepsilon(\omega)$, which indicates metallic response, becomes negative for both polarizations. This is consistent with the curvature of the *R–T* behavior, which becomes positive at ~30 K.

4.2. Oscillator strength

The oscillator strength in the far-IR at 12 K is substantially higher than at 300 K for both polarizations, while the total oscillator strength at 1 eV seems unchanged. Therefore, the spectral weight from the mid-IR peak is shifted to the Drude peak. N_{eff} saturates at around 1 eV (the total bandwidth) to ca. 0.8*e* for both polarizations, and measures joint intra- and inter-band oscillator strength. This value is less than half of the number of conduction carriers available in a unit cell. The reduction of N_{eff} should be assigned to the effect of the band structure and of the electron interactions. While the electron–phonon interaction gives rise to strong deviations from the Drude behavior, the total oscillator strength is not expected to change. On the other hand, the presence of the electron–electron correlations is known to reduce the optical oscillator strength through localization of the wavefunction and decrease in the magnitude of transfer integrals [5]. Therefore, the difference between the expected and observed N_{eff} involves the effect of both the band mass and electron correlation.

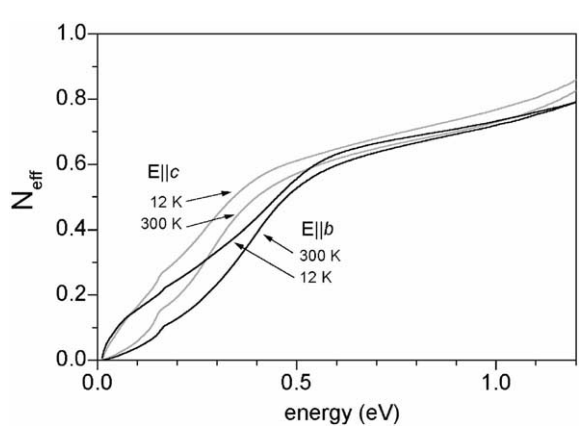

Fig. 2. The oscillator strength of $^{13}C_4$ compound at 300 and 12 K for $E\|b$ and $E\|c$.

The value of N_{eff} at 1 eV gives the estimate of the plasma frequency $\omega_p = 7860\ cm^{-1}$ and optical effective mass $m^* = 1.76m_e$. However, it does not reveal the significant temperature dependence of the pure intra-band mass in the far-IR, which is obviously much enhanced at high temperatures and decreases at 12 K. It is impossible to deduce the intra-band term in the sum rule calculation, since so many contributions in the spectrum are overlapped. Therefore, an analysis of the experimental spectra with a Drude–Lorentz model including Fano function to describe the strong EMV features is necessary.

5. Conclusion

Normal (metallic) phase properties of κ-$(ET)_2Cu(CN)[N(CN)_2]$ crystals were studied by means of IR spectroscopy. The optical conductivity spectra display a transfer of

spectral weight from the mid-IR peaks to the Drude peak in the far-IR below about 100 K. Integration of the optical conductivity over all occupied states up to 1 eV gives the plasma frequency $\omega_p = 7860\,\mathrm{cm}^{-1}$ and optical effective mass $m^* = 1.76 m_e$.

Acknowledgements

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