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Optical and electrical properties of an organic superconductor di[bis(ethylenedithio) tetrathiafulvalenium] dithiocyanocuprate(I), $(BEDT\text{-}TTF)_2[Cu(SCN)_2]$

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A single crystal of $(BEDT\text{-}TTF)_2[Cu(SCN)_2]$ was prepared and its reflectance spectrum and electrical resistivity were investigated. The optical anisotropy was found to be very small. The spectrum in the infrared region was concluded to be dominated by the interband transitions for the directions parallel to both *b* and *c*. From the analysis of the spectra measured at 25 K, the effective masses were estimated to be $m_b^* = 5.5m_e$ and $m_c^* = 4.1m_e$, respectively. The material was proved to be metallic over the temperature range from 300 down to 10 K, and become superconductive at 11 K.

Recently an organic cation-radical salt of BEDT-TTF [bis(ethylendithio)tetrathiafulvalene], $(BEDT\text{-}TTF)_2[Cu(SCN)_2]$, was found to exhibit a superconducting transition at 10.4 K, which is the highest among the T_c hitherto reported for organic superconductors.[1] The crystal structure solved by Urayama *et al.* quite resembles that of $\kappa\text{-}(BEDT\text{-}TTF)_2I_3$ which also exhibits a superconducting transition at 3.5 K.[2,3] In these crystals, BEDT-TTF molecules form the dimeric units and these units are arranged so as to make a checkered pattern as shown in Fig. 1.[4] We have studied systematically the optical spectra of various different types [α,[5] α',[6] β,[7-9] β',[10] β'',[11] δ,[10] and θ (Ref. 12)] of the BEDT-TTF salts, aiming to elucidate the relation between the crystal structures and the electronic structures. From this point of view, the κ-type salts are of great interest because of the unique molecular arrangement. The electrical behavior of $(BEDT\text{-}TTF)_2[Cu(SCN)_2]$ reported by Urayama *et al.* showed a curious phenomenon:[1] the observed temperature dependence of electrical resistivity was semiconductive from room temperature down to 90 K and turned to be metallic in the region lower than 90 K, whereas $\kappa\text{-}(BEDT\text{-}TTF)_2I_3$, a nearly isostructural salt, behaved metallic over the whole temperature region.[3] Urayama *et al.* have interpreted this phenomenon as being caused by the impurity and/or the disorder of the counter anion.[1]

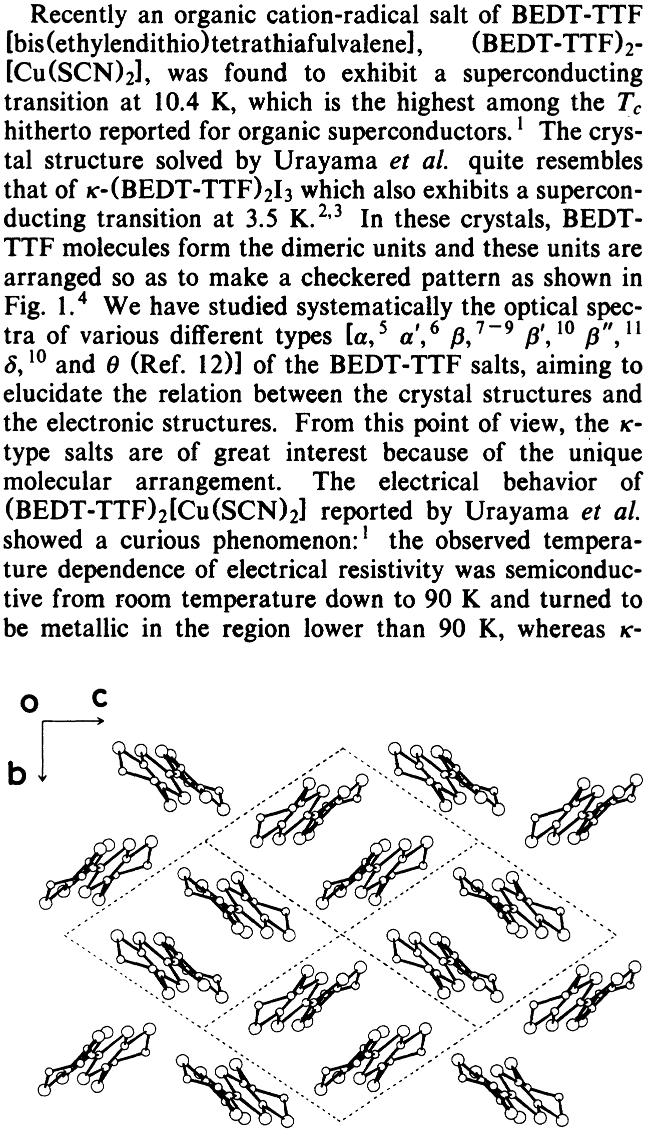

FIG. 1. Crystal structure of $(BEDT\text{-}TTF)_2[Cu(SCN)_2]$ projected along the *a* axis (see Ref. 4). The dimeric units are encompassed by the dotted lines.

We prepared single crystals of $(BEDT\text{-}TTF)_2[Cu(SCN)_2]$ by the method a little different from the previous one, paying attention to the purity of the material, and investigated the optical and electrical properties.

Single crystals of $(BEDT\text{-}TTF)_2[Cu(SCN)_2]$ were prepared by the following procedure. Copper (I) thiocyanate was added to the tetrahydrofuran solution of tetra-*n*-butylammonium thiocyanate, to form dithiocyanocuprate (I). Then BEDT-TTF was dissolved into the solution, from which the salt crystals were formed by the electrochemical method applying a constant current (1 μA) for one week. Some lumps of single crystals were grown on the Pt anode. The crystal was identified by the x-ray oscillation and Weissenberg photographs. The electrical resistivity was measured over the temperature range 4.2–300 K, by means of a four-probe method by applying a low-frequency current of 10 μA. The unnested voltage was satisfactorily small. The polarized reflectance spectrum was measured at 25, 50, 100, and 293 K over the wave-number region 450–25000 cm^{-1}, by use of a microspectrophotomeric technique. The details of the apparatus and the cooling system have been described elsewhere.[8,13]

Figure 2 shows the temperature dependence of electrical resistivity, measured on one of the crystals obtained in the present study. The room-temperature conductivity is ca. 20 $S\,cm^{-1}$. The resistivity steeply decreased below 100 K and the superconducting transition appeared at 11 K. These features are nearly the same as those of the previous report by Urayama *et al.*[1] However, the behavior observed above 100 K is significantly different from the reported results: the crystal remains metallic above 100 K instead of showing a semiconductive behavior. We found that the electrical behavior above 100 K did somewhat vary depending on the batch from which the crystal was taken out. Seemingly, the resistivity in this temperature range is very sensitive to the impurity or the lattice defect, introduced in the process of the crystal growth.

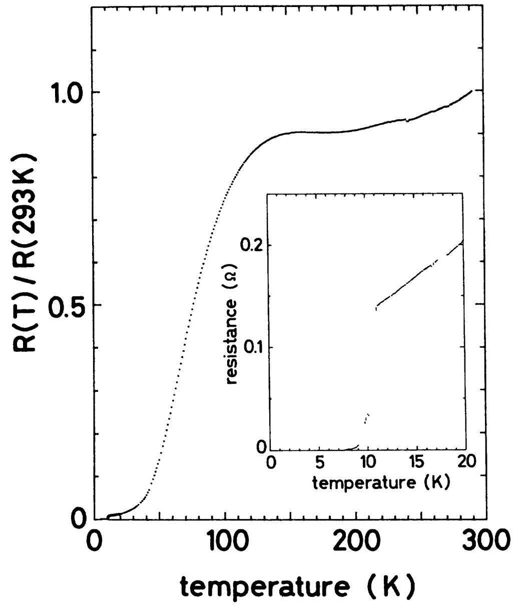

FIG. 2. Temperature dependence of electrical resistivity of (BEDT-TTF)$_2$[Cu(SCN)$_2$] measured along the b axis. The inset shows the resistance near the superconducting transition temperature.

Figures 3(a) and 3(b) show the temperature dependence of the polarized reflectance spectra measured on the (100) crystal face. At room temperature, the reflectivity is quite low over the whole observed region and the spectral shape is not the Drude type that is expected for a typical metal. The low reflectivity indicates a markedly high electron-phonon scattering rate, which may be also related to the low electrical conductivity observed at room temperature. Another characteristic feature found in the infrared region is the appearance of the peak around 2000–3000 cm^{-1} together with the strong vibrational structure induced by the electron-molecular-vibration coupling.[14] These two features are essentially the same both for the $\|b$ and $\|c$ polarizations. From the study of the reflectance spectra of the BEDT-TTF cation-radical salts,[5–12] we have previously found that the peak at 2000–3000 cm^{-1} appears for the polarization parallel to the crystal axis along which the arrangement of BEDT-TTF molecules is dimeric, whereas extremely small for the polarization parallel to the regularly arranged direction, and have proposed that this peak is associated with the interband transition between the bands split by the strong intermolecular interaction within the dimer. Since in (BEDT-TTF)$_2$[Cu(SCN)$_2$] there are two kinds of orientation of the dimeric unit and they are almost mutually perpendicular, the 2000–3000 cm^{-1} peaks are expected to appear for both the $\|b$ and $\|c$ polarizations. The contribution of the interband transition is predominant in the spectra observed at room temperature, the intraband transition forming a broad background in the region below 3×10^3 cm^{-1}, which increases on lowering the temperature as shown in Fig. 3.

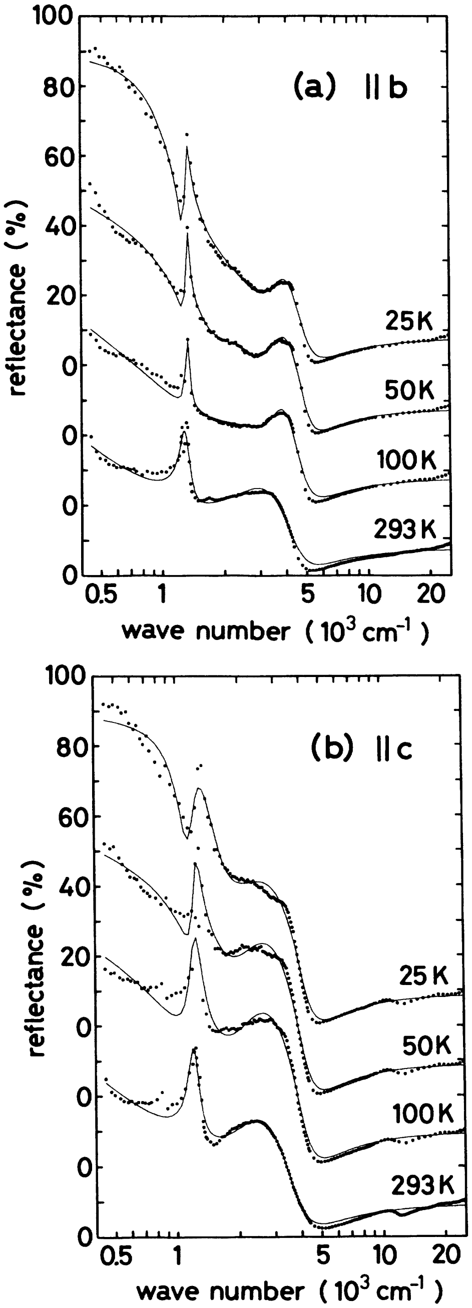

FIG. 3. Temperature dependence of reflectance spectra (a) for the $\|b$ polarization and (b) for the $\|c$ polarization. The circles indicate the observed reflectivity, and the solid lines show the simulated curves according to the model function (see text).

We analyzed the reflectance spectra by the method of a dispersion analysis using the model function for the complex dielectric function, described by the equation

$$\epsilon(\omega)=\epsilon_c-\frac{\omega_p^2}{\omega(\omega+i\gamma)}-\sum_j\frac{\Omega_{pj}^2}{(\omega^2-\omega_j^2)+i\Gamma_j\omega}\ , \tag{1}$$

where ϵ_c stands for the frequency-independent dielectric constant, ω_p and γ are the plasma frequency and the relaxation rate of the charge carriers, and ω_j, Γ_j, Ω_{pj} are the parameters of the Lorentz oscillators for simulating the interband transitions and the vibrational structures. The results of the analysis are given in Table I, and the

TABLE I. Analysis of the reflectance spectra by the Drude-Lorentz model.

	T (K)	ϵ_c	ω_P (eV)	γ (eV)	Ω_{pj} (eV)	Γ_j (eV)	ω_j (eV)	Ω_T[a] (eV)
$\parallel b$	293	3.2	0.47	0.38	0.15	0.016	0.16	0.84
					0.68	0.27	0.39	
	100	3.2	0.65	0.38	0.094	0.0053	0.17	0.93
					0.43	0.29	0.33	
					0.50	0.15	0.46	
	50	3.2	0.62	0.096	0.095	0.0037	0.17	0.93
					0.39	0.20	0.30	
					0.57	0.18	0.46	
	25	3.2	0.55	0.033	0.093	0.0048	0.16	0.99
					0.70	0.45	0.28	
					0.44	0.17	0.47	
$\parallel c$	293	3.6	0.60	0.43	0.18	0.014	0.15	0.85
					0.57	0.19	0.30	
	100	3.7	0.66	0.23	0.23	0.012	0.15	0.94
					0.63	0.18	0.30	
	50	3.6	0.69	0.16	0.17	0.0089	0.15	0.93
					0.60	0.19	0.30	
	25	3.5	0.64	0.039	0.19	0.021	0.15	0.95
					0.67	0.26	0.30	

[a] $\Omega_T = \left[\omega_P^2 + \sum_j \Omega_{pj}^2\right]^{1/2}$.

reflectivity curves simulated with those parameters are shown in Fig. 3. Since the interband transitions with small excitation energies dominate the spectrum in the infrared region, in particular at a higher temperature, it is difficult to accurately determine the parameters for the conduction band. However, we may say that the plasma frequency does not change significantly over the whole termperature region. Consequently, the number of charge carriers is not likely to change with temperature. Therefore, the temperature dependence of electrical resisitivity is probably determined by the change of the relaxation rate. Indeed, the γ value derived from the optical data steeply decreases below 100 K in parallel to the decrease of electrical resistivity. Since the contribution of the intraband transition markedly increases in the spectra at 25 K, the values of plasma frequencies estimated from the spectra are most reliable at 25 K. Assuming that the carrier density is equal to the number density of BEDT-TTF$^+$, we estimated the effective masses from the observed plasma frequencies and found to be $5.5m_e$ and $4.1m_e$ for $\parallel b$ and $\parallel c$, respectively. The anisotropic ratio of the effective mass, $m_b^*/m_c^* = 1.3$, is considerably smaller in comparison with the corresponding value in other superconducting BEDT-TTF salts, which is 3.5 for β-(BEDT-TTF)$_2$I$_3$ and 2.1 for θ-(BEDT-TTF)$_2$I$_3$.[8,12] The optical mass along the a^* axis, m_a^*, is expected to be much larger than m_b^* and m_c^*, because of the effect of the counter anions existing between the BEDT-TTF sheets. According to the effective mass approximation for the two-dimensional energy band, the Fermi energy measured from the top of the parabolic band is given by

$$E_F = \pi a n \hbar^2/(m_b^* m_c^*)^{1/2}, \qquad (2)$$

where n is the number density of holes and a is the lattice constant. The Fermi energy E_F was calculated to be 0.10 eV by this equation using the values, $n = 1.2\times10^{21}$ cm^{-3} and $a = 16.4$ Å. The density of states at the Fermi surface, which can be given by

$$D(E_F) = (m_b^* m_c^*)^{1/2}/\pi a \hbar^2, \qquad (3)$$

was calculated to be 0.76×10^{34} erg^{-1} cm^{-3}. Urayama *et al.* reported that the temperature dependence of static magnetic susceptibility was very small and likely to be explained by the Pauli paramagnetism.[1] The absolute value of the susceptibility falls in the range $(4.0\text{–}4.7)\times10^4$ emu mol^{-1} over the temperature range 12–300 K. The Pauli paramagnetic susceptibility at zero temperature, χ_p, can be expressed as $\chi_p = \frac{1}{4}(g\mu_B)^2 D(E_F)$, where μ_B is the Bohr magneton.[15] Putting the above-mentioned value of the density of states in this equation, $\chi_{p_{\rm calc}}$ was calculated to be 3.2×10^{-4} emu mol^{-1}, which is a little lower than the observed value. The static susceptibilities of most organic conductors are considerably larger than the values estimated from the simple Pauli paramagnetism.[16–18] The magnitude of the enhancement factor $\chi_{p_{\rm obs}}/\chi_{p_{\rm calc}}$ is known to be dependent of the width and the low-dimensional character of the electronic band.[19] For the narrow and/or the low-dimensional band, the susceptibility is enhanced by the electron-phonon coupling and the Coulomb interactions between the conduction electrons. The fact that the enhancement factor $\chi_{p_{\rm obs}}/\chi_{p_{\rm calc}}$ is only 1.2–1.4 in (BEDT-TTF)$_2$[Cu(SCN)$_2$] indicates that the correlation effect is fairly small in this salt, possibly by the strong two-dimensional character of the electronic structure. This conclusion is also consistent with our interpretation as regards the appearance of the 2000–3000 cm^{-1} peak that this peak is caused not by the correlation effect[20] but by the interband transitions between the band split by the intermolecular interaction within the dimeric unit.

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