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Far-infrared study of the insulator–metal transition in θ -(BEDT-TTF)₂RbZn(SCN)₄ (BEDT-TTF \equiv bis(ethylene-dithio)tetrathiafulvalene)

N L Wang¹, H Mori², S Tanaka², J Dong³ and B P Clayman³

¹ Institute of Physics and Centre for Condensed Matter Physics, Chinese Academy of Sciences, PO Box 2711, Beijing 100080, People's Republic of China

² Superconductivity Research Laboratory, ISTEC, Shinonome 1-10-13, Tokyo 135-0062, Japan

³ Department of Physics, Simon Fraser University, Burnaby, British Columbia, Canada, V5A 1S6

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Abstract

We investigated the temperature-dependent infrared properties of the compound θ -(BEDT-TTF)₂RbZn(SCN)₄. At temperatures above the metal–insulator transition, the optical conductivity remains finite in the low-energy region, but shows no conventional Drude feature typical of metals. Below the metal–insulator transition temperature, the low-energy spectral weight is significantly reduced. The opening of an optical gap at about 300 cm⁻¹ is observed clearly in polarization parallel to the donor stacking direction. Analysis of both the electronic and vibronic spectra suggests a redistribution of charges in BEDT-TTF molecules as temperature decreases across the metal–insulator transition, providing strong support for a charge-ordering state at low temperatures.

Among various organic compounds containing electron-donor BEDT-TTF (abbreviated as ET) molecules, the θ -type family θ -(ET)₂X, where X is an anion, have recently attracted much attention because they show various unusual physical phenomena. The compounds have a two-dimensional (2D) layer structure consisting of ET donor sheets and insulating anion X sheets (in the *ac*-plane). Within the donor plane, the donor stacks regularly along the *c*-direction. A dihedral angle θ is formed between ET molecules in neighbouring donor columns, which is different for each compound [1]. For monovalent X⁻, half a hole is introduced into one ET^{(1/2)+} molecule, which makes a quarter-filled band. On the basis of the band picture, one would expect a metallic behaviour in those compounds. However, most of the θ -type compounds undergo very sharp metal–insulator (M–I) transitions with decreasing temperature. For θ -(BEDT-TTF)₂MM'(SCN)₄ (M = Tl, Rb; M' = Zn, Co), the resistivities jump several orders at the transition temperatures [1]. It is of great interest to understand the origin of the M–I transition in these compounds.

It is well known that a strong electron correlation can lead to a metal–insulator transition. For a half-filled system, the strong on-site Coulomb interaction would prevent two electrons

from occupying the same site, which leads to the so-called Mott metal–insulator transition. The antiferromagnetic (AF) insulating state in the κ -type ET salts can be recognized as a Mott insulating state, since the ET molecules are strongly dimerized which effectively makes the system have one hole per dimer [2, 3]. For the case of the quarter-filled band, the mechanism of the M–I transition is different. Fukuyama *et al* [4] proposed that the mutual Coulomb interactions, not only on site but also between different sites, play an important role in this situation, leading to a state where electrons are localized on every other site as in the Wigner crystal. This is a kind of charge-ordering (CO) state, which provides a route to the correlation-induced insulator transition. Recent NMR measurements [5, 6] on θ -(BEDT-TTF)₂RbZn(SCN)₄ (abbreviated as θ -RbZn) indicate the existence of two kinds of donor molecule with different amounts of charge below the metal–insulator transition temperature (T_{MI}) at 190 K, implying a CO state in the low-temperature insulating state.

Optical spectroscopy is an important technique for probing the electronic state of a material. Tajima *et al* performed the first optical reflectance measurement on θ -type ET salts. By comparing the extracted optical conductivity spectra with those calculated by means of the mean-field approximation, they concluded that the θ -RbZn salt has horizontal charge ordering below T_{MI} [7]. However, the reflectance measurement did not extend to the far-infrared region. In this case, the low-frequency extrapolation in the Kramers–Kronig transformation may affect the resultant spectra of conductivity. In addition, the vibronic features across the transition were not discussed. In this work we present a far-infrared reflectance measurement on θ -(BEDT-TTF)₂RbZn(SCN)₄. We find that the spectral change with decreasing temperature is different for the polarizations parallel and perpendicular to the donor stacking direction. The opening of a gap at about 300 cm⁻¹ below T_{MI} is clearly observed in polarization parallel to the c -axis, but a smaller gap magnitude is seen for E parallel to the a -axis. We shall see that both the electronic and vibronic spectra suggest redistribution of charges in ET molecules below the M–I transition temperature, providing further support for a CO state at low temperatures.

Salts of θ -(BEDT-TTF)₂RbZn(SCN)₄ were prepared by an electrochemical method [1]. Optical reflectivity spectra were measured from 50 cm⁻¹ to 9500 cm⁻¹ on a Bruker 113v spectrometer using an *in situ* coating technique [8]. In order to avoid a supercooled state of the high- T metallic phase, the cooling rate between 200 K and 180 K was made very slow—about 0.1 K min⁻¹. The optical conductivity was calculated via a Kramers–Kronig analysis of the reflectivity. Appropriate extrapolations—the Hagen–Rubens relation for measurement at high T and a constant value for measurement at low T —were used below 50 cm⁻¹ for this analysis. In fact, the conductivity in the frequency range of the measurements was found to be insensitive to different extrapolations at low ω . For the high-frequency region, we extrapolated the measured spectrum at 9500 cm⁻¹ as constant to 150 000 cm⁻¹, above which an ω^{-4} -relation was employed.

Figure 1 shows room temperature reflectance and conductivity spectra of θ -(BEDT-TTF)₂RbZn(SCN)₄ in the polarizations $E \parallel c$ and $E \parallel a$. The spectra exhibit several remarkable features. First, the reflectance is much less than unity at low frequencies in both polarizations. The calculated conductivity spectra exhibit a broad electronic band centred around 2000 cm⁻¹ for both polarizations. Such a feature was observed in other organic salts, and was suggested by us to originate from the formation of small polarons [9]. The spectra are far from the conventional Drude response typical of metals. Nevertheless, the optical conductivity remains finite in the limit of $\omega \rightarrow 0$. The observation indicates that the material at high temperature, though not a good metal, is not a gapped insulator either. Second, there exists considerable spectral anisotropy over a wide frequency range. The reflectivity in the a -direction is significantly larger than that in the donor stacking direction (c -axis). Consequently, the conductivity has a higher spectral weight in the polarization of $E \parallel a$. This

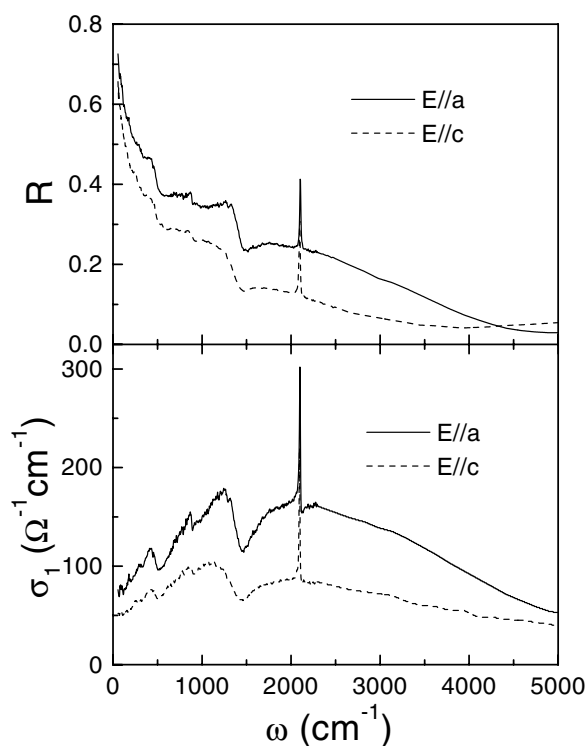


Figure 1. The frequency dependence of the reflectivity and conductivity for $E \parallel c$ and $E \parallel a$ at room temperature.

is consistent with the theoretical calculation indicating that the transverse transfer integral (t_p) is larger than that along the stacking direction (t_c) [1]. Third, the vibrational response displays distinctive electron–phonon coupling characteristics. Except for a sharp phonon appearing at 2100 cm^{-1} which is attributed to the C–N stretching mode of the anion, the spectra exhibit several vibrational modes superimposed on electronic spectra near 1350 cm^{-1} , 850 cm^{-1} , and 470 cm^{-1} . They have typical Fano line shapes caused by the strong electron–molecule–vibration (EMV) coupling: an antiresonance or dip preceded by a peak on the low-frequency side in the infrared conductivity spectrum. The vibronic structure is a characteristic feature of organic conductors [10].

Temperature-dependent reflectivity and conductivity spectra for polarization parallel to the donor stacking direction ($E \parallel c$) are shown in figure 2. The spectra above T_{MI} do not show much T -dependence. However, dramatic change occurs below 190 K . The reflectivity is significantly reduced in the far-infrared region, but enhanced somewhat at frequencies higher than 1500 cm^{-1} . As a result, a redistribution of spectral weight in $\sigma_1(\omega)$ is observed as the temperature decreases across 190 K . The missing spectral weight below 2000 cm^{-1} is transferred to the frequencies higher than 2000 cm^{-1} . The calculated optical conductivity has almost no spectral weight at very low frequencies, suggesting the opening of a gap below T_{MI} . The gap magnitude in the donor stacking direction is estimated to be about 300 cm^{-1} by a linear extrapolation of the conductivity onset as indicated by a solid line in the figure. Another remarkable observation is that, accompanying the redistribution of the electronic excitations, most of the antiresonances of the EMV modes become the ordinary (Lorentzian) vibrational

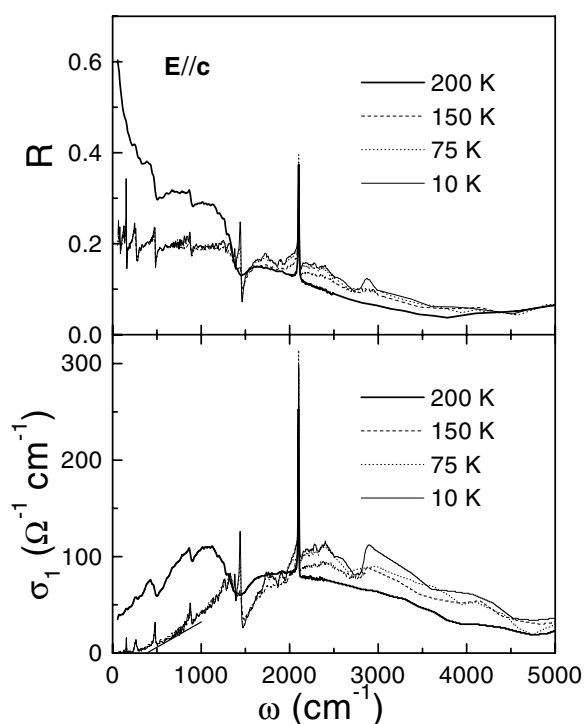


Figure 2. The frequency dependence of the reflectivity and conductivity for $E \parallel c$ at different temperatures.

peaks, whose maxima correspond to the minima of the antiresonances. In addition, a new dip appears in the conductivity spectra at around 2800 cm^{-1} .

Figure 3 shows spectra for the polarization $E \parallel a$ at several temperatures. The spectra evolve with temperature in a similar way to those for $E \parallel c$. However, the spectral weight for $E \parallel a$ is reduced over a much broader frequency range in the insulating state. Moreover, the conductivity starts to increase at much lower frequency in comparison with the case for polarization of $E \parallel c$. This suggests that the gap magnitude is much smaller in this polarization. We noticed that our conductivity spectra at low temperature are different from the earlier data obtained by Tajima *et al* [7]. In their work, except for the sharp phonon peaks, there is almost no spectral weight below 2000 cm^{-1} . Since the far-infrared reflectance was not measured in their experiment, the missing spectral weight must be due to the low- ω extrapolation in their Kramers–Kronig calculation.

The observation of an optical gap below T_{MI} is a notable result in this work. We emphasize that the differences between the situations for the two polarizations are not artifacts caused by the Kramers–Kronig analysis of the experimental reflectance data, since different low- ω extrapolations actually do not alter the conductivity spectra in the measured frequency region. As we shall see, the anisotropy of optical responses correlates well with the different parameters of electronic correlations in the two directions.

As we mentioned in our introductory remarks, recent experimental and theoretical works established a charge-ordering transition in this θ -type compound. NMR measurement indicated that the ET donors, which are equivalent at high T with a charge of 0.5, become inequivalent at low T [5, 6]. A disproportionation of charges like $D^{0.5+\delta}D^{0.5-\delta}D^{0.5+\delta}D^{0.5-\delta}\dots$ occurs at

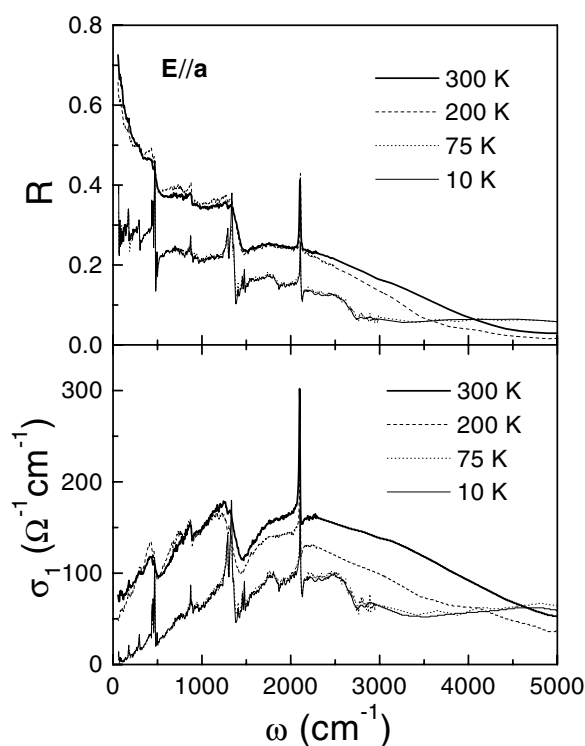


Figure 3. The frequency dependence of the reflectivity and conductivity for $E \parallel a$ at different temperatures.

T_{MI} . Therefore, there exist two kinds of ET molecule with different amounts of charge at low temperature, which implies a charge ordering below T_{MI} . The charge ratio estimated from the NMR measurements is about 1:(4–6) [5, 6], which gives $\delta = 0.30$ – 0.36 . On the other hand, x-ray diffraction measurement demonstrated that the M–I transition was associated with lattice modulation with a period doubling along the c -axis [11]; i.e. the ET donors form dimers along the c -axis. These experiments suggest that the CO is coupled with the lattice modulation. Charge-ordering formation was also suggested from theoretical studies, where the intermolecular Coulomb repulsion V was suggested to play a crucial role [4, 12, 13]. This is because the Hubbard model only taking account of the on-site Coulomb repulsion energy was believed to be always metallic at quarter-filling. Mori calculated the intersite Coulomb repulsion V as a function of the dihedral angle of the ET molecules and found that the intersite Coulomb repulsion V_c along the stacking direction is larger than V_p along the transverse direction in most of the actual θ -type salts. The CO takes the direction of the smaller intersite Coulomb repulsions in the θ -type salts [12]. Taking account of both the experimental and theoretical studies on the θ -type ET salts, the electronic states of ET donors above and below T_{MI} in the conducting layer can be summarized as in figure 4 (we assume $\delta = 0.3$ here) [14].

We argue that our anisotropic optical responses are consistent with the horizontal charge-ordering picture in figure 4. Upon cooling the sample, the dihedral angle increases because of the thermal contraction [12]. The intersite Coulomb repulsion V_c becomes effective when the lattice modulation along the c -axis takes place below 190 K; as a result, the horizontal charge ordering occurs. Since the Coulomb repulsion energy V_c is larger than V_p , while the

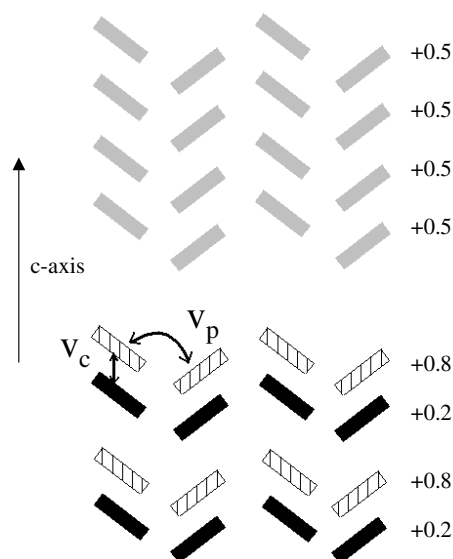


Figure 4. A schematic picture of the electronic states of ET donors above and below T_{MI} in the conducting layer.

charge-transfer integral t_c is smaller than t_p , the electrons have to overcome larger barrier potentials in the c -direction than in the a -direction for transport. This is in agreement with experiment, indicating that a larger gap is observed in the c -direction. The gap size is found to be scarcely reduced with increase of temperature up to T_{MI} , which is very similar to the findings for other strongly correlated systems with CO transitions—for example, the Fe_3O_4 compound [15]. As can be seen from figure 4, a charge-density wave (CDW) is actually formed along the c -direction. Therefore, the development of the optical gap below T_{MI} in the present CO state may have a similar origin to the CDW gap. However, further theoretical work is needed to elucidate the mechanism of gap formation in the CO state of the material.

We will now turn to the discussion of the vibrational features. It is well established that most of the observed phonon features are due to the totally symmetric A_g modes of intramolecular vibrations which are coupled strongly to the charge densities distributed on the donor molecules [16–18]. Thus, the dramatic change of the vibronic structure in the course of the M–I transition also reflects significant redistribution of charges on ET molecules. This is also consistent with the CO picture.

The assignments of the vibrational modes of ET-based salts were thoroughly investigated in previous studies [16–18]. In the compound under study, except for the sharp C–N stretching mode from the anion at 2100 cm^{-1} , major vibrational features occur near 1350 cm^{-1} (very broad), 850 cm^{-1} , and 470 cm^{-1} . Comparing with the previous work, we can assign the strong and broad structure near 1350 cm^{-1} to the central C=C stretching mode $\nu_3(a_g)$ and the feature near 470 cm^{-1} to the C–S stretching modes $\nu_9(a_g)$ and $\nu_{10}(a_g)$. However, the feature at 850 cm^{-1} should be assigned to the $\nu_{60}(B_{3g})$ normal mode involving the motion of four of the inner-ring carbon atoms, rather than to the $\nu_7(a_g)$ mode [16]. As noted above, those vibronic modes of ET donors change from the antiresonances at high T to the ordinary (Lorentzian) peaks at low T . Moreover, from figure 2 and figure 3, we find that the line shape is related to the relative strength of the electronic excitations: the antiresonance takes place if the vibrational mode overlaps with a higher electronic background, whereas the ordinary peak

appears when the electronic background becomes lower. We believe that the change of the vibrational structure is due to the change of the screening action of mobile charges, caused by either more localized electrons or the smaller charge density around the bonds associated with those vibrational modes below T_{MI} .

Another notable observation is that a new dip appears at a frequency near 2800 cm⁻¹ for both polarizations below T_{MI} . The feature was also observed in previous measurements by Tajima *et al*, where it was considered to be formed by two separated electronic bands. In our opinion, the dip is more probably related to the vibronic structure, i.e. an antiresonance of a vibrational mode. We assign it to the C–H stretching mode $\nu_1(a_g)$, which was usually very weak in the ET-based salts [16]. A similar feature was also observed in some other ET-based compounds in the same frequency region [19, 20]. The sizable strength of this antiresonance feature suggests a significant EMV coupling for this mode in comparison with other ET salts. This could be due to a higher charge-density distribution around the H atoms upon CO transition at low temperature. Taking account of both the low-temperature emergence of the remarkable C–H stretching vibrational feature and the change of other vibrational modes, we also draw the conclusion that there is a charge redistribution across the metal–insulator transition. A conceivable scenario is as follows. A certain amount of charges were transferred from around the inner-ring atoms of a ET molecule to the region around C–H bonds in the outer ring of another ET molecule, thus making the disproportionation of charges as depicted in figure 4. But these localized charges greatly reduce the low- ω conductivity spectral weight. Additionally, we find that the number of vibrational peaks increases at low T , which is apparently due to the structure modulation that occurred at T_{MI} .

To conclude, our far-infrared spectroscopy study revealed dramatic change of both electronic and vibrational spectra across the metal–insulator transition. The change can be well understood on the basis of the charge-ordering transition, which is consistent with the result of earlier NMR measurements.

Acknowledgments

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