Comparison of the charge ordering phase transition in α-$(ET)_2I_3$ and α'-$(ET)_2IBr_2$

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1. Introduction

It has been well known that the metal-insulator transition of α-$(ET)_2I_3$ is accompanied by charge ordering. In the charge-ordered state, the inversion symmetry is broken, and a strong second harmonic generation suggesting ferroelectricity is reported.[1] α'-$(ET)_2IBr_2$, which has a similar crystal structure, exhibits a semiconductor- semiconductor transition at around 200K [2] To make a comparative study of α-$(ET)_2I_3$ and α'-$(ET)_2IBr_2$, we measured the infrared, Raman, and reflection spectra of these compounds.

2. Experimental technique

The Raman-active υ_2 mode was distinguished from the υ_3 mode with the aid of α'-(^{13}C-ET)$_2IBr_2$, where the central C=C was substituted by ^{13}C. The infrared-active υ_{27} mode was measured on the (110) crystal face with the polarization of E//c, which direction is perpendicular to the conducting layer. The reflectivity data were collected using the FT-IR, Bruker FIR-66v (50-650cm^{-1}) and Nicolet Nexus 870 (650-10000cm^{-1}) combined with the microscope, Spectratech IR-Plan. The gold was evaporated on the sample crystal to calibrate the 100% reflectivity without removing the crystal from a sample holder.

3. Results and discussion

Both in the Raman and infrared spectra of α'-$(ET)_2IBr_2$, the charge-sensitive υ_2 and υ_{27} modes are split already at room temperature, and the spectra of high-temperature phase is essentially the same as those of low-temperature phase. This result shows that the conduction electrons are localized loosing the coherence. Based on the analysis of the linewidth, we speculate that these localized charges are short-range ordered. On lowering temperature, the broad linewidth continuously decreases and levels off at around 200K as shown in Fig.1(c). This result suggests the view that the short-range ordered domains are slowly fluctuating above 200K, and they condenses into a long-range ordered state at 200K. Combining the frequencies of υ_2 and υ_{27} modes, the charge distribution in the charge-ordered state is estimated to be ($+0.9_4$, $+0.8_3$, $+0.1_7$, $+0.0_9$). The unit cell with $P\bar{1}$ space group accommodates four molecules, two of which are crystallographically independent. The appearance of four signals suggests the breaking of inversion symmetry. The breaking of symmetry was actually confirmed by the splitting of the asymmetric stretching mode of IBr_2^- at 155 cm^{-1} below 200K. Therefore, the charge-ordering pattern is a horizontal stripe (A_R, B'_R, A'_P, B_P) or diagonal stripe (A_R,B_R, A'_P, B'_P), where the A and B are the crystallographically independent sites, A' and B' are the sites connected by the inversion center with A and B, respectively, and P and R denote the charge poor and charge rich. In contrast to α-$(ET)_2I_3$, the linewidth at 4.2K is broad (10cm^{-1}). We therefore consider that charge-ordered state is rather disordered due to the competition between the horizontal and diagonal stripes. As shown in Fig.1(b), the far-infrared region becomes transparent in the charge-ordered state. The optical gap is close to the activation energy of the resistivity of the low-temperature phase.

Observing the infrared-active υ_{27} mode, we confirmed that the metal-insulator transition at 135K is originated from the charge ordering. Since the linewidth at 4.2K is very narrow (≤4cm^{-1}), the charge-ordered state is long-range ordered. This is consistent with the structural characteristics that the

horizontal stripe is the unique arrangement. The υ_2 and υ_{27} modes at high-temperature suggest that the coherence of the conduction electrons is not broken. However, the linewidth of high-temperature phase is broad (~ 40cm^{-1}). This broad linewidth is attributed to a dynamical fluctuation of charge order. The fluctuation rate is estimated to be ~50cm^{-1}. It has been theoretically predicted that the fluctuation rate is softened when the inter-site Coulomb interaction V increases and approaches the critical value V_c.[3] The slow fluctuation rate supports this theoretical prediction. As shown in Fig.2, the optical conductivity of α-$(ET)_2I_3$ shows a feature very different from a metal down to the phase transition temperature. The Dude response exhibits an over-damped feature, namely, the charges are strongly scattered. The slow fluctuation of charge order seems to be related to this strong scattering.

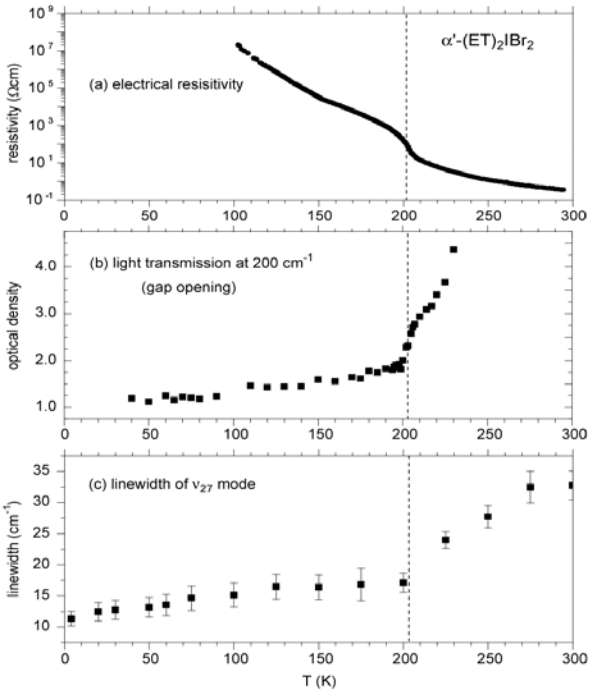

Fig.1 Resistivity, transmittance at 200cm-1, and linewidth of υ_{27}

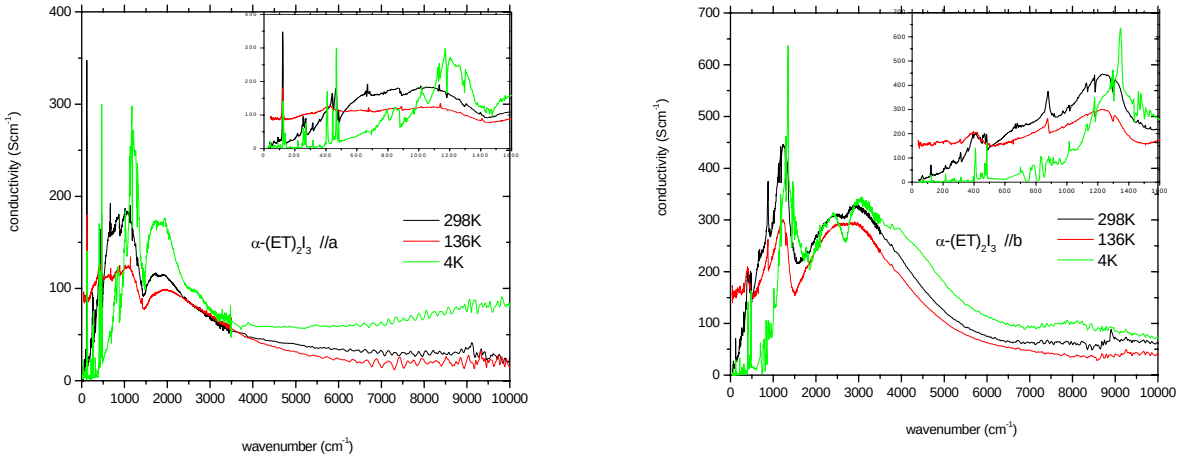

Fig 2 Optical conductivity of α-$(ET)_2I_3$

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2) Tokumoto *et al. Synthetic Metals* **19**, 215 (1987).

3) J.Merino *et al. Phys. Rev.B* **68**, 245121 (2003)