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Charge order and its fluctuation in α-type BEDT-TTF charge transfer salts

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Among a variety of BEDT-TTF charge-transfer salts, the α-type BEDT-TTF salts shows rich properties such as charge ordering, superconductivity, zero-gap state or Dirac fermion, persistent photoconduction, photoinduced phase transition, and non-linear optical response. We investigate the charge order and fluctuation of charge order in α-type BEDT-TTF salts including α′-(BEDT-TTF)$_2$IBr$_2$, α-(BEDT-TTF)$_2$I$_3$, and α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$ by means of infrared, Raman, and far-infrared spectroscopy. We estimated the kinetic energy of α'-(BEDT-TTF)$_2$IBr$_2$, α-(BEDT-TTF)$_2$I$_3$, and α-(BEDT-TTF)$_2$NH$_4$Hg (SCN)$_4$ from the integration of the optical conductivity at room temperature. Figure 1 shows the data of kinetic energy of α-type BEDT-TTF salts estimated from band calculation and optical conductivity. The kinetic energy of all three compounds is much smaller than the calculated kinetic energy and they are in a good relationship with the lattice parameter ratio *c/a*.

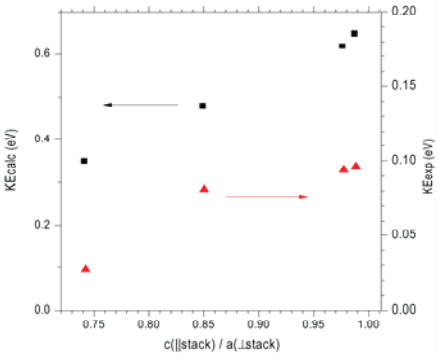

Fig.1 kinetic energy of α-type BEDT-TTF salts (frome left site to right site are α'-(BEDT-TTF)$_2$IBr$_2$, α-(BEDT-TTF)$_2$I$_3$, α-(BEDT-TTF)$_2$CsCd(SCN)$_4$ and α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$) estimated from band calculation (■) and optical conductivity (▲)

As shown in Fig. 1, the bandwidth of α'-(BEDT-TTF)$_2$IBr$_2$ is narrowest among the α-type BEDT-TTF salts. This compound shows a semiconductor-to-insulator phase transition at ~200 K in electrical resistivity. We investigated the infrared and Raman spectra of α'-(BEDT-TTF)$_2$IBr$_2$ using ^{13}C-substituted BEDT-TTF salt, and showed clear evidence that the low-temperature high-resistivity phase is a charge-ordered state. The horizontal stripe of charge order is most stable, but dislocation can be easily generated because a diagonal stripe is energetically very close to the horizontal stripe. The increase of inter-site hopping rate, symmetry change from $P1$ to $P\bar{1}$, and the appearance of density of state near Fermi energy in the high-temperature phase indicate that this semiconductor-to-insulator transition is an order-disorder phase transition of localized charge. This means that the conduction electrons

are localized (incoherent) in the whole temperature range; they are diffusively moving from one site to the adjacent site above ~200 K, and they are crystallized with long-range order forming a horizontal stripe below ~200 K. This localized electronic state in the whole temperature range is ascribed to the very narrow bandwidth.

α-$(BEDT\text{-}TTF)_2I_3$ with intermediate bandwidth shows a metal-insulator phase transition at ~135 K in electrical resistivity. We investigated the infrared and Raman spectra of low-temperature phase using ^{13}C- and d_8-substituted BEDT-TTF salts. The complete assignment of ν_2, ν_3, and ν_{27} is consistent with the charge-ordered state. The amplitude of charge order is smaller than that of α'-$(BEDT\text{-}TTF)_2IBr_2$, which is consistent with the bandwidth. The temperature dependence of the infrared-active ν_{27} mode of α-$(BEDT\text{-}TTF)_2I_3$ is qualitatively different from that of α'-$(BEDT\text{-}TTF)_2IBr_2$, which appears to be consistent with the metal-insulator transition. However, the linewidth in the metallic phase of α-$(BEDT\text{-}TTF)_2I_3$ is much broader than that of the Raman spectrum of wide-bandwidth metallic compound, α-$(BEDT\text{-}TTF)_2NH_4Hg(SCN)_4$. The Drude response by conduction electrons does not grow in the metallic phase of α-$(BEDT\text{-}TTF)_2I_3$ in contrast to the well developed Drude response at room temperature in α-$(BEDT\text{-}TTF)_2NH_4Hg(SCN)_4$. This characteristic behavior means that the scattering rate of conduction electrons is so large that the wavevector (momentum) cannot be well defined any more. This result suggests that the conduction electrons in the high-temperature phase of α-$(BEDT\text{-}TTF)_2I_3$ have not metallic (coherent) character but diffusive (incoherent) character. The broad linewidth of ν_2 and ν_{27} of α-$(BEDT\text{-}TTF)_2I_3$ suggests the fluctuation of charge order. This suggestion is consistent with the localized nature of the electronic state in high-temperature phase.

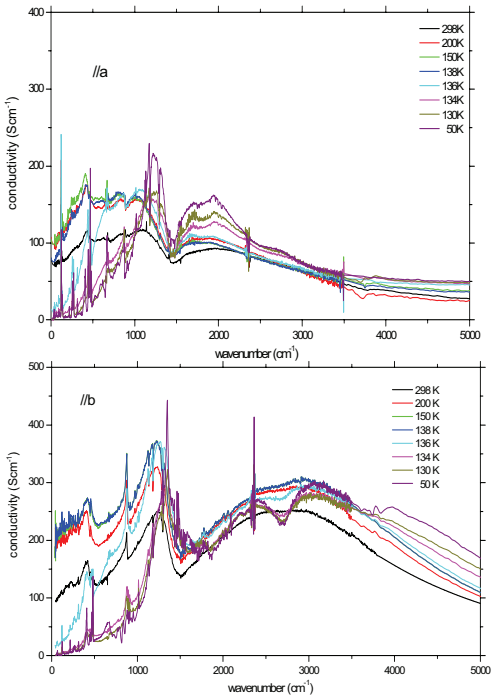

Fig. 2 Optical conductivity measured on the (001) plane with polarizations of E//a and E//b.

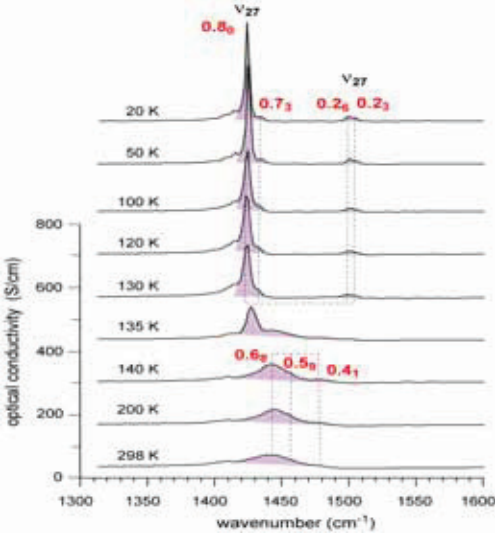

Fig 3 Optical conductivity of α-$(BEDT\text{-}TTF)_2I_3$ measured on [110] with the polarization of E //c.