Novel transition from dimer Mott to charge order phase in a quarter-filled organic salt

Internal degrees of freedom are a central idea penetrating into diverse fields of fundamental physics. In condensed matter physics, an electron in solids possesses the charge, spin and orbital degrees of freedom, each of which exhibits various ordered states at low temperatures. A quintessential example is an ordered state of the spin degree of freedom manifesting itself in a permanent magnet. A unique feature in this field is that a novel internal degree of freedom can be artificially introduced in some complex solids. In a crystal composed of clusters, the intra-cluster lattice vibration called "rattling" is observed and controlled.

The cluster degree of freedom closely couples with the electron correlation effect, leading to intriguing electronic states. This is seen in a family of the quasi two-dimensional organic salt R_2X (R_2: a dimer organic molecule, X: an anion), where one hole from the monovalent anion X^- exists per dimer (per two donor molecules). Basically, such a quarter-filled nature leads to a metallic state (Fig. 1(a)), but the strong correlation effect varies the system drastically. As shown in Fig. 1(b), in the weakly dimerized case, the correlated hole is localized on the molecular site owing to the long-range nature of Coulomb interaction to form a charge order. On the other hand, under strong dimerization, the hole is localized on the dimer to act as a Mott insulator (dimer Mott insulator, Fig. 1(c)). Theoretically, these two insulating states are suggested to change into each other by tuning materials parameters such as the transfer energy and the Coulomb repulsion [1]. Thus, the materials located near the border of such insulating phases may have an instability toward another insulating state. This instability originates from the charge degrees of freedom in the dimer, which can be regarded as a cluster structure in the crystal. Recent dielectric measurements indeed suggested the instability to a charge order hidden in a κ-type dimer Mott insulator [2]. However, there is no direct spectroscopic evidence of charge disproportionation, leaving it controversial whether the instability toward the charge order exists in the dimer Mott phase. To examine this issue, we here explore the opposite case where the instability to the dimer Mott phase is hidden in a charge-ordered dimer-type organic salt through the infrared microspectroscopy performed at beamline **BL43IR** [3].

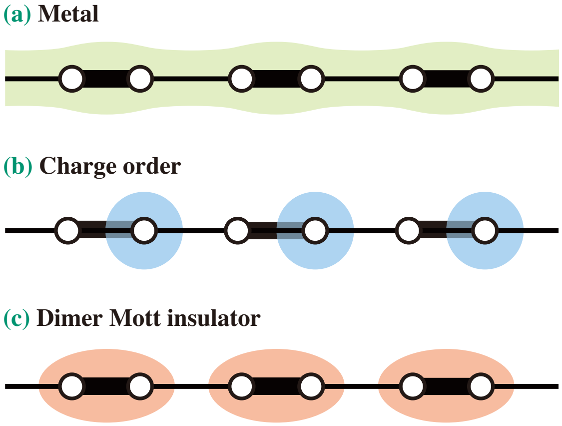

Fig. 1. Schematic electronic states in the quarter-filled organic salt R_2X. The open circles represent the organic molecules R and thick line shows the dimerization of two molecules. The color-shaded area represents the electron distribution. The closed-shell anion X is omitted. **(a)** A metallic state in weak correlation case. **(b)** The charge ordered state induced by the long-range Coulomb repulsion. **(c)** The dimer Mott insulating state.

We focus on the dimer-type organic salt β-(*meso*-DMBEDT-TTF)$_2$PF$_6$ (R=*meso*-DMBEDT-TTF, X=PF$_6$), which exhibits a charge order below T_c = 70 K. The charge order pattern determined by the synchrotron radiation X-ray study is of checkerboard type (left inset of Fig. 2). We note that the checkerboard-type charge order can be regarded as an electric dipole order, because the charge disproportionation occurs within a dimer. The main panel of Fig. 2 displays the optical conductivity spectra obtained from the Kramers-Kronig analysis for the reflectivity data. The distinct feature newly found is a pronounced peak structure at around 0.6 eV, which is enhanced with lowering temperature from 300 K down to T_c. This mid-infrared peak can be assigned to a dimer peak, a transition from bonding to anti-bonding orbitals of dimerized molecules, as widely observed in dimerized organic salts. Importantly, the dimer-peak intensity is enhanced with decreasing temperature in the dimer Mott insulating phase, while it is reduced in a correlated metallic phase [4]. The enhancement of the dimer-peak intensity down to T_c then indicates that the high-temperature phase in this material can be regarded as a dimer Mott insulating phase (right inset of Fig. 2). Thus, the charge order transition at T_c is a transition from dimer Mott to charge order phase due to the internal change degree of freedom in the dimer.

An intriguing question is how these two correlated insulating phases compete in real space. To address this, we show the positional dependence of the local reflectivity spectra measured with high spatial resolution of 10 μm using high-brilliance synchrotron radiation light. We here evaluate the local reflectivity ratio R(184.5 meV)/R(181 meV) at each point, which gives a relative strength between the charge ordered insulating state with 184.5-meV peak and the dimer Mott insulating state with 181-meV peak [5], and plot its spatial distribution in Fig. 3. The measured surface area is 1400×100 μm² and the red- and blue-color areas indicate the dimer Mott and the charge order states, respectively. In contrast to spatially-homogeneous spectra above T_c, the low-temperature spectra are highly inhomogeneous, consisting of the competitive dimer Mott and charge order insulating states.

Obviously, the present phenomenon is different from conventional phase transition occurring at finite temperatures. The spatial coexistence consisting of dimer Mott and charge order states appears even at 10 K far below T_c, indicating that the phase transition in this material is not driven by entropy term in the free energy. We rather suggest that the materials parameters are largely varied with temperature to drive the transition. This type of transition may possess quantum nature in the sense that the transition is driven by the materials parameters. As theoretically suggested, the ground state of the two-dimensional quarter-filled organic system varies from dimer Mott to charge order state by tuning such parameters [1]. The observed spatial inhomogeneity therefore implies that this organic salt actually lies on the border between those two correlated insulating ground states in the parameter space.

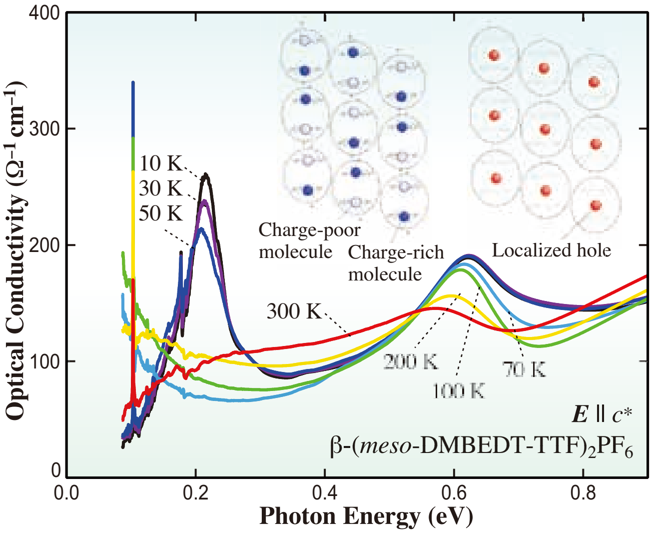

Fig. 2. The optical conductivity spectra measured at various temperatures with polarization parallel to the c^* axis. The left and right insets illustrate the charge order ($T < T_c = 70$ K) and the dimer Mott insulator ($T > T_c$) emerged in the two-dimensional molecular plane of β-(*meso*-DMBEDT-TTF)$_2$PF$_6$, respectively. Two donor molecules circled by the dotted ellipsoid are dimerized.

The anomalous transition phenomenon shown in the present study originates from the internal cluster degree of freedom, which is introduced by a unique dimer structure in the organic systems. Such a characteristic structure is also found in transition-metal oxides such as $BaIrO_3$ and $Ba_4Ru_3O_{10}$, which are consisting of Ir_3O_{12} and Ru_3O_{12} trimers, respectively. Interestingly, both compounds exhibit unusual phase transitions, in which the underlying cluster degree of freedom may play a crucial role as a ubiquitous property in the complex solids.

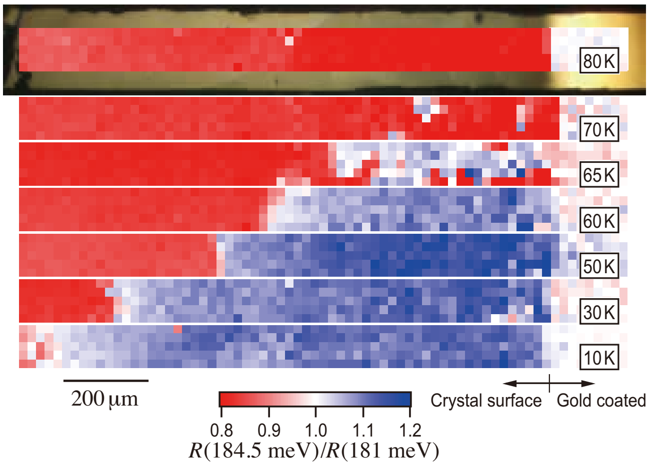

Fig. 3. The reflectivity-ratio mapping on the crystal surface of 1400×100 μm² measured at several temperatures. The color scale shows the reflectivity ratio R(184.5 meV)/R(181 meV) at each position. Red and blue areas indicate the dimer Mott and the charge ordered states, respectively. The right-side white region is a gold-coated area for measuring reference spectrum.

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