Tetrathiafulvalene (TTF) and its derivatives have provided numerous kinds of conducting charge-transfer complexes that show phase transitions such as superconducting, metal-insulator (MI), and magnetic ones. They have been extensively studied to understand the mechanisms and develop new functional systems along with the aim to afford molecular devices. The 1/4-filled-band conductor \((\text{EDO-TTF})_2\text{PF}_6\) (EDO-TTF = ethylenedioxytetrathiafulvalene) is one of them and shows quite a peculiar MI transition at \(T_{\text{MI}} = 280\) K accompanying the changeover from para- to diamagnetism. The MI transition has been considered as a particular example that shows the cooperative actions of Peierls distortion, charge ordering and anion ordering together with molecular deformation [1,2]. Recently, ultrafast photoswitching from the insulator to the metallic phase has also been reported [3,4]. The peculiar phase transition in \((\text{EDO-TTF})_2\text{PF}_6\) is quite an attractive for a better understanding of cooperative and coherent phenomena in organic conductors.

The charge ordering pattern in the insulating phase has been suggested to be \([0,0,+1,+1,\ldots]\), despite the fact that in most 1/4-filled-band conductors the ordering pattern \([0,+1,0,+1,\ldots]\) is found as a result of strong neighbor-site Coulomb repulsion [1,2]. However, there has been no direct evidence of the charge ordering pattern. In this study, we present direct evidence for an ordering of \((\text{EDO-TTF})^+\) and \((\text{EDO-TTF})^0\) visualized in \((\text{EDO-TTF})_2\text{PF}_6\) charge density distributions [5].

The charge density distributions were obtained from the synchrotron radiation powder diffraction data by a combination of the maximum entropy method (MEM) and the Rietveld method. The experiment was carried out using the large Debye-Scherrer camera at beamline BL02B2. The wavelength of incident X-ray was 1.0 Å. Data were measured for the metallic phase at 285 K and for the insulator phase at 260 K. In the structure analysis procedures, the reliability factors based on the Bragg intensities of the final Rietveld fitting were 3.75% and 3.38% for the metallic and insulator phases, respectively. The reliability factors based on the structure factors for the final MEM charge densities were 2.85% and 5.28% for the metallic and insulator phases, respectively.

The equi-charge-density surfaces at 260 K are shown in Fig. 1 at 0.7 e Å\(^{-3}\). In both the metallic and the insulator phases, the layers of EDO-TTF molecules form columns by a head-to-tail stacking perpendicular to the molecular plane; \(\text{PF}_6^-\) anions are located at the cavities between the EDO-TTF layers. Compared with the metallic phase, the unit cell is doubled in the insulator phase, corresponding to the Peierls instability. The \(\text{PF}_6^-\) anions are disordered in the metallic phase (the overlapping of two octahedra with a tilt of about 50°), whereas they are ordered in the insulator phase. Two types of \((\text{EDO-TTF})_2\text{PF}_6\) molecule are present in the insulator phase (flat and bent molecules) while only one \(\text{EDO-TTF}\) is crystallographically unique in the metallic phase.

The charge states of \(\text{EDO-TTF}\) and \(\text{PF}_6\) can be examined from the charge density distributions by counting the number of electrons around them. In the metallic phase, \(\text{EDO-TTF}\) has \(+0.6(1)\) e and \(\text{PF}_6\) has \(-1.2(1)\) e. In the insulator phase, flat \(\text{EDO-TTF}\) has...
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