

## DIRECT OBSERVATION OF CHARGE ORDERING PATTERN IN AN ORGANIC CONDUCTOR $(\text{EDO-TTF})_2\text{PF}_6$

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  $[0,0,+1,+1,\dots]$ , despite the fact that in most 1/4-filled-band conductors the ordering pattern  $[0,+1,0,+1,\dots]$  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  $0.7 \text{ e}\text{\AA}^{-3}$ . 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  $50^\circ$ ), whereas they are ordered in the insulator phase. Two types of EDO-TTF molecule are present in the insulator phase (flat and bent molecules) while only one EDO-TTF is crystallographically unique in the metallic phase.

The charge states of 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, EDO-TTF has  $+0.6(1) \text{ e}$  and  $\text{PF}_6^-$  has  $-1.2(1) \text{ e}$ . In the insulator phase, flat EDO-TTF has

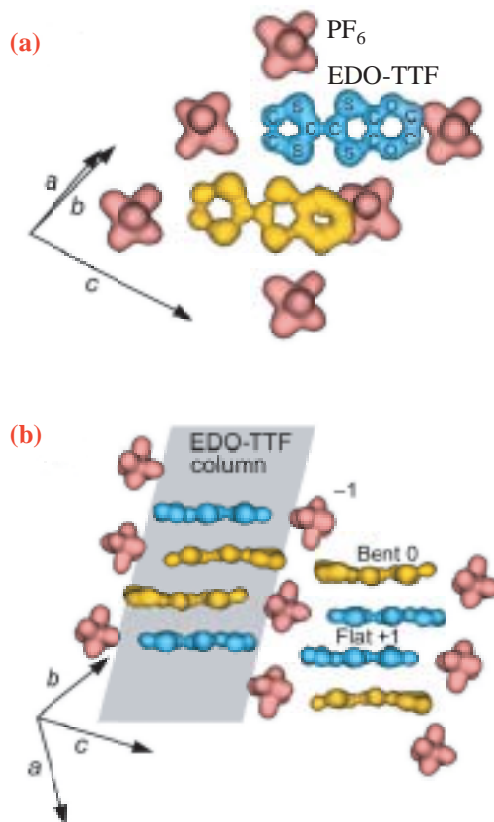


Fig. 1. MEM equi-charge-density surfaces of insulator phase of  $(\text{EDO-TTF})_2\text{PF}_6$  at  $0.7 \text{ e}\text{\AA}^{-3}$ . The view in (a) is along the EDO-TTF stacking direction; (b) the side view of the EDO-TTF column is shown.  $\text{PF}_6^-$  is colored in red. The flat and bent EDO-TTF molecules are colored in blue and yellow, respectively.

+0.8(1) e, bent EDO-TTF has +0.2(1) e, and  $\text{PF}_6^-$  has -1.0(1) e. Thus, flat EDO-TTF in the insulator phase has an excess charge concentration close to +1 e. The positive charge is concentrated mainly on one sulfur atom in the flat molecule, the nearest sulfur atom to the  $\text{PF}_6^-$  anion. The distance between the sulfur atom and the anion is shortened by the molecular displacement caused by the MI transition. Therefore, it is considered that the local electrostatic interaction between the sulfur atom and the anion contributes to the hole trapping on the sulfur atom and to anion ordering. The charge-rich and -poor EDO-TTF molecules alternate with a periodicity of  $2k_F$  nesting vector of the Fermi surface due to the Peierls instability. As a result, the [0,0,+1,+1,...] ordering of charges is along the nesting vector as shown in Fig. 2.

The lower equi-charge-density surface of the EDO-TTF column in the insulator phase at  $0.13 \text{ e}\text{\AA}^{-3}$  is shown in Fig. 3. A weak intermolecular overlapping of charge density between flat molecules can be observed as two S-S bonds, whereas it cannot be observed between flat and bent molecules and between bent molecules. In other words, the flat (EDO-TTF)<sup>+</sup> molecules in the insulator phase are dimerized to provide a spin singlet state. From the viewpoint of intermolecular orbital interactions, this dimerization assists the neighboring of two (EDO-TTF)<sup>+</sup> causing the [0,0,+1,+1,...] charge-ordering pattern.

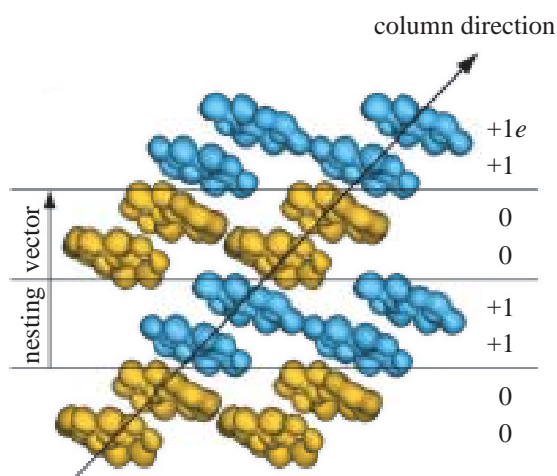


Fig. 2. MEM equi-charge-density surface of EDO-TTF layer at  $0.7 \text{ e}\text{\AA}^{-3}$  and charge ordering pattern in the insulator phase viewed along  $c$ -axis.

This study revealed that the molecular displacements observed in the MI transition of  $(\text{EDO-TTF})_2\text{PF}_6$  assist the anion ordering and the electrostatic and electronic stabilization of the crystal structure in the insulator phase. The cooperation in this peculiar MI transition shall be regarded as a result of the displacement and deformation of EDO-TTF molecules during the phase transition.

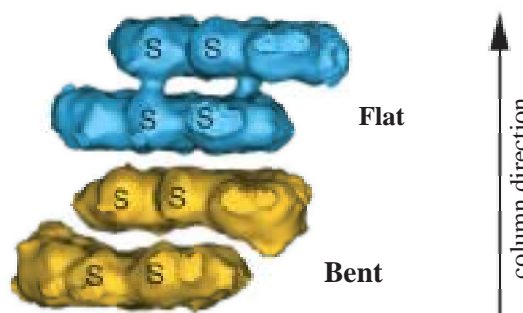


Fig. 3. Side view of lower MEM equi-charge-density surface of EDO-TTF column in the insulator phase. The surface is at  $0.13 \text{ e}\text{\AA}^{-3}$ .

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