

## Surface Superstructures Fluctuating in the Quasi-One-Dimensional Organic Conductor $\beta$ -(BEDT-TTF)<sub>2</sub>PF<sub>6</sub> Observed by Scanning Tunneling Microscopy

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Two types of surface structures were observed at  $\sim 280$  K by scanning tunneling microscopy on a crystal surface of  $\beta$ -(BEDT-TTF)<sub>2</sub>PF<sub>6</sub>. One is a structure which corresponds to the expected crystal structure determined by X-ray diffraction measurement, and the other is a modulated structure with two-fold periodicity perpendicular to the one-dimensional conductive axis. Fluctuation between these two types of structures in the same area was observed by scanning tunneling microscopy, with a surface defect used as a positional marker. Occurrence of a double tip effect was considered but concluded not to be responsible for the observed change.

KEYWORDS: STM, BEDT-TTF, fluctuation, surface reconstruction, double tip

### 1. Introduction

On semiconductor and metal surfaces, energetic instability is reduced by surface reconstruction accompanied by charge and strain redistributions. Recently, such surface reconstruction has also been found by scanning tunneling microscopy (STM) to occur on surfaces of organic materials with low-dimensional conductivity, i.e. BEDT-TTF based compounds [BEDT-TTF: bis(ethylenedithio)-tetrathiafulvalene].<sup>1,2)</sup> A common characteristic property that appears in the surface reconstructions observed in these organic materials is that the electronic structure of the molecular rows is modulated with two-fold periodicity in the direction perpendicular to the most conductive axis of the materials.

Recently, a remarkable surface reconstruction was observed on the surface of  $\beta$ -(BEDT-TTF)<sub>2</sub>PF<sub>6</sub>, where the surface superstructure was found to be formed by alternate missing rows of PF<sub>6</sub> molecules.<sup>3)</sup> By comparison of the electronic structures of the BEDT-TTF molecules in the top and second layers, the occurrence of charge redistribution in the surface layers expected for this material was confirmed. If the charge transfer plays an important role in the surface reconstruction, the stability of the surface electronic and molecular structures must strongly affect the degree of surface reconstruction of materials. In the case of  $\beta$ -(BEDT-TTF)<sub>2</sub>PF<sub>6</sub>, it is known that a phase transition caused by charge density wave (CDW) formation occurs at  $\sim 297$  K,<sup>4)</sup> which suggests increased instability of this material at room temperature compared to other BEDT-TTF based compounds. Three different phases were observed on the surface, when the surface layer was BEDT-TTF molecules.<sup>2)</sup> The observed structures may be related to fluctuation of the surface instability. However, since the structures were observed separately, details of the mechanism for the structure formation are unknown.

In this work, in order to understand the surface reconstruction observed for  $\beta$ -(BEDT-TTF)<sub>2</sub>PF<sub>6</sub> in more detail, we attempted to observe directly the structural change appearing on the BEDT-TTF terminated surface of this material.

### 2. Experimental

$\beta$ -(BEDT-TTF)<sub>2</sub>PF<sub>6</sub> crystals were grown using the electrochemical oxidation method via a layer-by-layer mechanism. They are black, flake shaped, and elongated in the conductive *c*-direction. For STM observation, the crystals were fixed onto copper plates using conductive silver epoxy resin, and the STM observations were performed at room temperature in air. All images were taken in the constant current mode.

### 3. Result and Discussion

STM images taken continuously on the crystal *a-c* plane are shown in Fig. 1. It took about 13 s to acquire each image. In these images, the bright spots form row structures aligned along the most conductive *c*-axis, which are ordered with a periodicity of the half lattice constant in the direction of the *a*-axis. In a comparison of the observed surface structure with those in the STM images previously obtained,<sup>1,2)</sup> this surface is determined to be terminated by BEDT-TTF molecules.

As is shown in Fig. 1, the observed surface structure is unstable in the middle section of the surface. The unstable section spreads across the molecular rows and seems to form a boundary structure running in the direction of the *a*-axis. The molecular rows look discontinuous at the boundary. At the right side of the each image, a surface defect formed by some missing molecules exists as indicated by an arrow. With consideration of the positional relationship between the surface defect and the boundary in each image, it is clear that the boundary position has changed during the scans from Figs. 1(a) to 1(d). Since the structures of the crystal grain boundaries and surface steps were observed by the STM with fair stability, the observed structure is considered to reflect a

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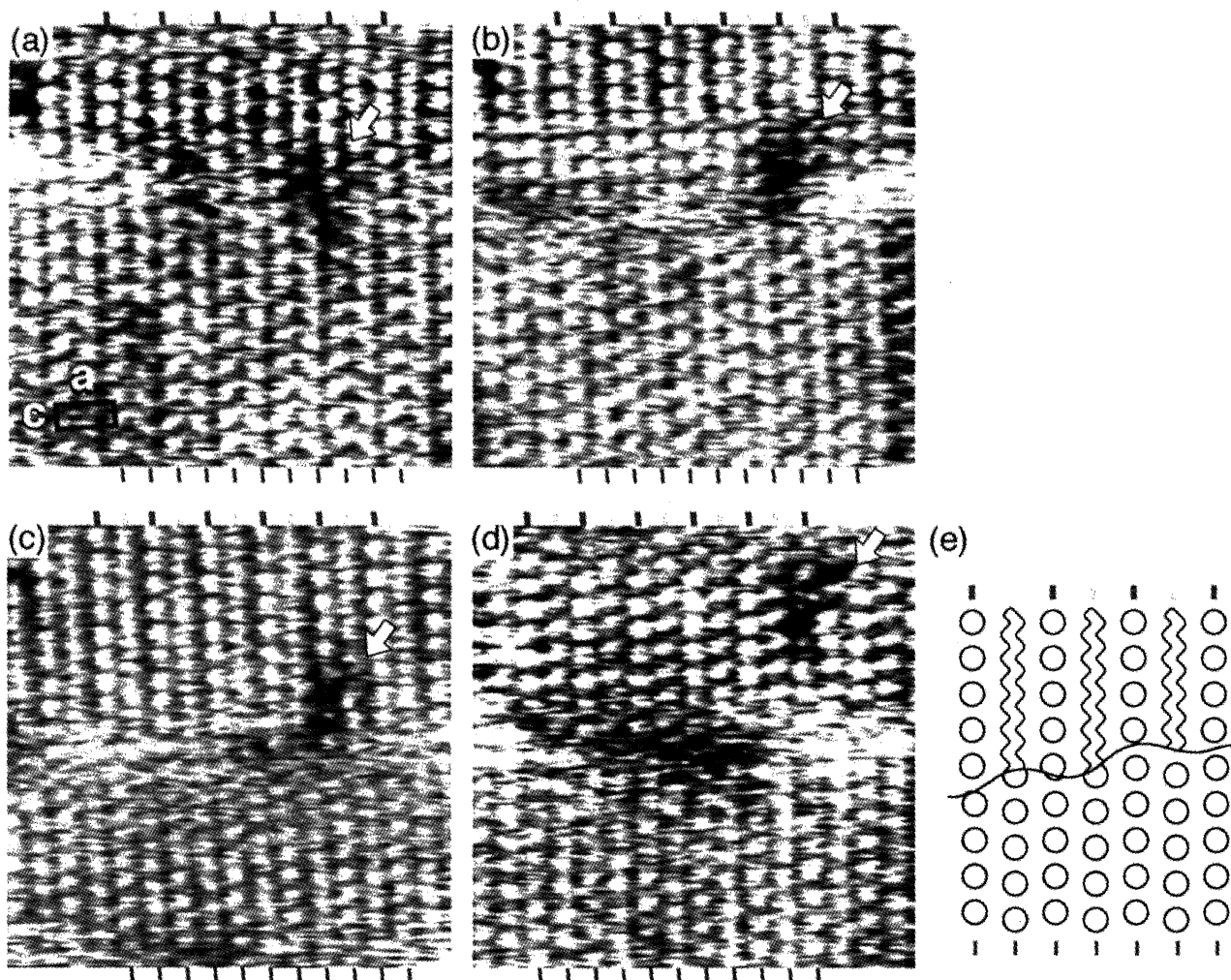


Fig. 1. STM images taken continuously on the crystal  $a$ - $c$  plane of  $\beta$ -(BEDT-TTF) $_2$ PF $_6$  ( $16 \times 16$  nm,  $V_s = -25$  mV,  $I_t = 0.43$  nA). It took about 13 s to acquire each image. The boundary structures fluctuating in the middle of the images can be compared to each other by use of the defects indicated by arrows as markers.

fluctuating boundary between different surface phases.

Now let us discuss the detailed structures of the two domains separated by the boundary in Fig. 1. In the lower area, the molecules are equivalently imaged, while in the upper area, the molecular rows seem to have a two-fold periodicity in the direction of the  $a$ -axis; molecular rows change in form alternately as indicated by the two different bars in Fig. 1. Molecules in the rows indicated by the white bars look slightly darker and smaller than those in the rows indicated by the solid bars. In addition, the molecules tend to run together instead of appearing separately along the rows with less brightness. A structural model for the images is schematically shown in Fig. 1(e).

For clarification of the two structures observed in Fig. 1, Fig. 2 shows the structural change observed more clearly; the structures in Figs. 2(a) and 2(b) correspond to those in the upper and lower areas in Fig. 1, respectively. These images were also taken in continuous scans, and it required about 37 s to acquire each image. In Fig. 2, the surface defects indicated by the arrows in the two images are identical, demonstrating that the structural changes occurred the same area. In comparison of Figs. 2(a) and 2(b), it is clear that they show two differ-

ent surface structures which are similar to those obtained previously; one is a structure which corresponds to that expected from the crystal structure determined by X-ray diffraction measurement (Fig. 2(b)), and the other is a modulated structure with two-fold periodicity perpendicular to the one-dimensional conductive axis, the  $c$ -axis (Fig. 2(a)).<sup>2)</sup>

Schematic models of the crystal  $a$ - $c$  plane corresponding to those in Figs. 2(a) and 2(b) are shown in Figs. 2(c) and 2(d), respectively. In the schematics, the upper two rings of the BEDT-TTF molecules, which are closer to the surface, are shown. Since alternate BEDT-TTF molecules along the  $a$ -axis are about 0.1 nm from the surface, the positions of the HOMO lobes of the S atoms in the uppermost rings of alternate BEDT-TTF molecules are indicated by ellipses in the direction of the  $a$ -axis.<sup>1-3)</sup>

The observed unit cell in Fig. 2(b) corresponds well with that of the crystal surface in Fig. 2(d), and the characteristic features of the STM image are consistent with those expected from the ideal crystal structure determined by X-ray diffraction measurement.

On the other hand, the image in Fig. 2(a) shows a structure different from that of the ideal one; the brightness of the molecular rows is modulated with two-fold

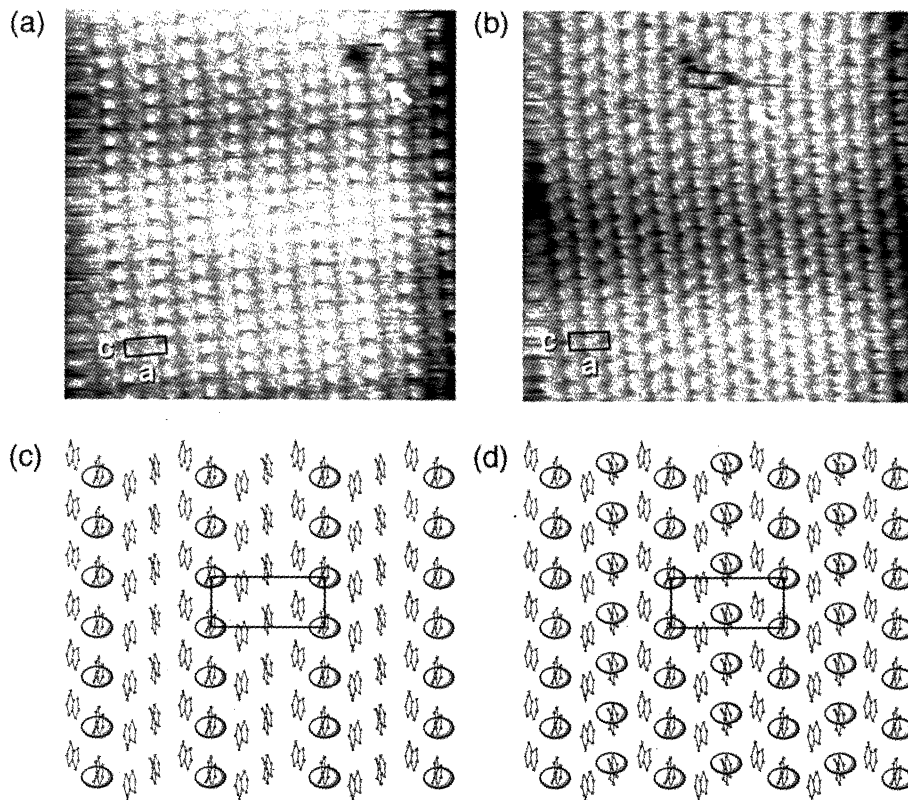


Fig. 2. (a), (b), STM images obtained in a continuous scans over the same area of the  $\beta$ -(BEDT-TTF) $_2$ PF $_6$  surface (12  $\times$  12 nm,  $V_s = 64$  mV,  $I_t = 1.27$  nA). It took about 37 s to acquire each image. Schematic structures corresponding to (a) and (b) are shown in (c) and (d), respectively.

periodicity along the  $a$ -axis. The molecules in Fig. 2(c) which correspond to the ones in Fig. 2(a) are represented by solid ellipses. The modulation with two-fold periodicity has been frequently observed also in other BEDT-TTF compounds, such as (BEDT-TTF) $_2$ THg(SCN) $_4$ ,<sup>5)</sup>  $\alpha$ -(BEDT-TTF) $_2$ I $_3$ <sup>6)</sup> and  $\alpha$ -(BEDT-TTF) $_2$ Cu(NCS) $_2$ ,<sup>7)</sup> while unmodulated equivalent molecular STM images are expected from the crystal structures for all of these materials. This structure is understood to be formed because of the charge instability of the material in the surface layer.<sup>3)</sup>

Taking into account the all results, the images in Fig. 1 are considered to reflect the fluctuation between the two structures. The modulated structure (Fig. 2(b)) has been frequently observed for BEDT-TTF based compounds, and is considered to be a reconstructed structure of the material surfaces. Therefore, if the observed change is a fluctuation between the ideal and the reconstructed structures, energy difference between the two structures of this material is expected to be small at room temperature. In consideration of the fact that  $\beta$ -(BEDT-TTF) $_2$ PF $_6$  is a quasi-one-dimensional conductor and the critical temperature of the CDW phase transition of this material induced by the Peierls instability is  $\sim 297$  K, the observed structural change may be caused by the structural instability related to the phase transition.

Magnified images of the defects in Figs. 2(a) and 2(b) are shown in Figs. 3(a) and 3(b), respectively. As is shown in Fig. 3, the structure of the defects seems to have

changed slightly during the scan. Recent STM studies have shown that a single molecular vacancy defect in a surface BEDT-TTF layer could undergo a change in position during scans.<sup>8)</sup> The unstable image of a defect in Fig. 2(b) may be a result of the positional change of the defect. However, we cannot exclude the possibility that some anomalous tip geometry might have modulated the defect image. In attempting to clarify this point, we considered the possibility of occurrence of the tip effect. It is well known that contamination causes giant corrugations<sup>9)</sup> or reversal imaging<sup>10)</sup> of the corrugations, especially at atmospheric pressure. However, that is not the case here because these phenomena do not change the periodicity of the structure. Another well known effect is caused by anomalous tip geometry, such as a double tip structure.<sup>11)</sup> Such a change in the apex of the tip might have effected the observed structural change in the modulation.

In order to be able to better discuss the double tip effect, we performed image processing of the results shown in Fig. 2. Since the STM images, which have been observed generally on the surface of this material, show a structure similar to that shown in Fig. 2(b), we assumed that the structure shown in Fig. 2(a) was formed by superposition of the structure in Fig. 2(b) and Fig. 3(c) shows example of a structure which is quite similar to that in Fig. 2(a). Such a structure with the equivalent brightness of the rows was reproduced only when the two superposed images are shifted along the  $a$ -axis by half of the lattice constant in this direction. However, in that

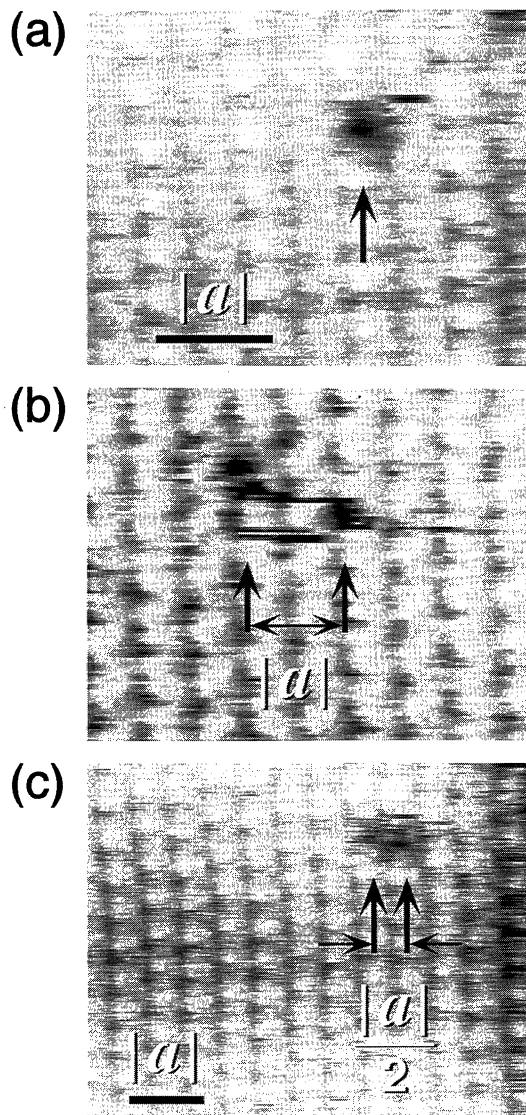


Fig. 3. (a) and (b), magnifications of the defects in Figs. 2(a) and 2(b), respectively. (c) An artificial image produced by superposition of the two images shown in Fig. 2(b), with a shift of half the lattice constant in the direction of the  $a$ -axis.

case, the observed structure in Fig. 2(a) can be interpreted as a result of the double tip formed during the interval of the scans.

In order to clarify the effect of double tip formation, we can check the structure of the surface defect indicated by the arrows in Fig. 2. Since the defect is a characteristic feature in these images, if the observed change was caused by a double tip, the change in the defect image must be produced by the tip effect. As is shown in Fig. 3(c), the artificially produced defect looks dupli-

cated. A similar structure was observed for the original defect in Fig. 2(b). However, there is some inconsistency about the distance between the duplicated defects. It is almost equal to the lattice constant of the  $a$ -axis for the image shown in Fig. 3(b). On the other hand, the distance in the artificial defect shown in Fig. 3(c) is equal to half of the lattice constant. Therefore, the observed change on the surface is probably some real fluctuation between normal and reconstructed structures of this surface as described above, which may be caused by the instability of the electronic and molecular structures of this material, due to the fact that CDW phase transition occurs at  $\sim 297$  K. Further experiments and theoretical studies are necessary to clarify the mechanism in detail.

#### 4. Conclusions

By use of surface defects as positional markers, structural change in a  $\beta$ -(BEDT-TTF)<sub>2</sub>PF<sub>6</sub> surface was observed by STM. A double tip effect was considered, but was not determined to be the cause for the observed structural change. Therefore, the observed change is possibly a structural fluctuation between the two phases of the material.

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- 1) M. Yoshimura, H. Shigekawa, H. Yamochi, G. Saito, Y. Saito and A. Kawazu: *Phys. Rev. B* **44** (1991) 1970.
- 2) H. Shigekawa, K. Miyake, A. Miyauchi, M. Ishida, H. Oigawa, Y. Nannichi, R. Yoshizaki and T. Mori: *Phys. Rev. B* **52** (1995) 16361.
- 3) M. Ishida, K. Hata, T. Mori and H. Shigekawa: *Phys. Rev. B* **55** (1997) 6773.
- 4) H. Kobayashi, T. Mori, R. Kato, A. Kobayashi, Y. Sasaki, G. Saito and H. Inokuchi: *Chem. Lett.* **1983** (1983) 581.
- 5) S. N. Magonov, G. Bar, H. -J. Cantow, J. Paradis, J. Ren, M.-H. Whangbo and E. B. Yagubskii: *J. Phys. Chem.* **97** (1993) 9170.
- 6) S. N. Magonov, G. Bar, A. Y. Gorenburg, E. B. Yagubskii and H.-J. Cantow: *Adv. Mater.* **5** (1993) 453.
- 7) H. Shigekawa, K. Miyake, H. Oigawa, Y. Nannichi, T. Mori and Y. Saito: *Phys. Rev. B* **50** (1994) 15427.
- 8) S. N. Magonov and M.-H. Whangbo: *Adv. Mater.* **6** (1994) 355.
- 9) H. J. Mamin, E. Ganz, D. W. Abraham, R. E. Thomson and J. Clarke: *Phys. Rev. B* **34** (1986) 9015.
- 10) C. J. Chen: *J. Vac. Sci. & Technol. B* **12** (1994) 2193.
- 11) M. Tomitori, F. Iwatsuki, N. Hirano, F. Katsuki and O. Nishikawa: *J. Vac. Sci. & Technol. A* **8** (1990) 222.