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Surface superstructures of quasi-one-dimensional organic conductor β-(BEDT-TTF)$_2$PF$_6$ crystal studied by scanning tunneling microscopy

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Two kinds of superstructures were found at ~280 K by scanning tunneling microscopy on the crystal surface of β-(BEDT-TFF)$_2$PF$_6$, a quasi-one-dimensional organic conductor with a metal-insulator phase transition at ~297 K. One has a structural modulation which is perpendicular to the one-dimensional conductive axis, similar to that previously observed on a TTF-TCNQ crystal surface. The other has a twofold periodicity along the one-dimensional conductive axis, as expected from the theory. Under the assumption that the former is an intermediate structure caused by the interaction between neighboring one-dimensional molecular chains, superstructures which have been observed in BEDT-TTF compounds could be explained well.

Organic conductors of BEDT-TTF compounds [BEDT-TTF-bis(ethylenedithio)-tetrathiafulvalene] have been attracting considerable attention and have been studied extensively because of their high potential designability as superconductive materials.[1] On the other hand, since they have low-dimensional conductivity, they are also very intriguing for the study of phase transitions such as those caused by charge density waves (CDW). Scanning-tunneling-microscopy (STM) study has been used to verify the CDW phase transition of MX_2 (M transition metal, X chalcogen atoms) materials such as TaSe$_2$ on an atomic scale.[2-5] However, despite the recent success of STM studies, there still remain several fundamental problems concerning the superstructures of organic materials. For example, according to the STM study of the Peierls transition appearing in a tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) crystal, the observed charge modulation at ~80 K was perpendicular to the quasi-one-dimensional axis of the crystal, instead of having the expected twofold periodicity along the one-dimensional conductive axis.[6] Similar charge density modulation was observed for an α-(BEDT-TTF)$_2$I$_3$ thin film with a CDW phase transition at 160 K.[7] Chainlike CDW phases were also found in graphite intercalation compounds.[8-10] Important roles of one-dimensional conductive chains in two-dimensional conductive materials have been pointed out. Therefore, elucidation of the formation mechanism of surface structures in organic materials is important, and further study on the atomic scale is urgently required.

In this paper, we present the results obtained for the β-(BEDT-TTF)$_2$PF$_6$ crystal with quasi-one-dimensional conductivity. Since the CDW phase transition occurs at ~297 K, i.e., around room temperature, this material is very useful for STM study around critical temperature in consideration of the effect of the CDW fluctuation. Superstructures appearing in other quasi-two-dimensional BEDT-TTF compounds will also be discussed.

Figure 1 shows the crystal structure of β-(BEDT-TTF)$_2$PF$_6$ obtained by x-ray diffraction. The crystal data are orthorhombic, with space group *Pnna*, $a=1.4960(4)$, $b=3.2643(7)$, $c=0.6664(2)$ nm, and $V=3.2546$ nm^3. It is the first organic conductor in which quasi-one-dimensional conductivity in the direction parallel to the molecular plane, along the c axis, was seen, and a metal-insulator transition was observed at ~297 K ($=T_c$).[11-13] According to the calculation by the Hückel method,[12] strong dimerization of BEDT-TTF molecules is expected to form uniform half-filled metallic chains along the c axis above T_c. The anisotropy of the resistivity increases rapidly around T_c, and below T_c, the lattice constant in the direction of the c axis becomes doubled due to accompanying $2k_F$ CDW. Therefore, double periodicity should

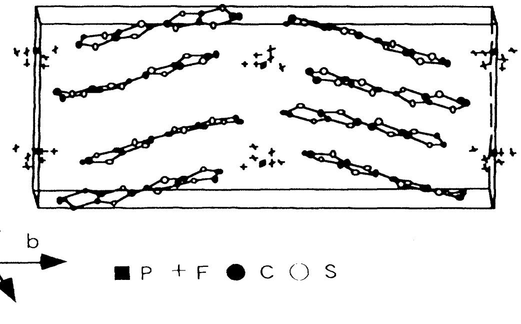

FIG. 1. Crystal structure of β-(BEDT-TTF)$_2$PF$_6$ determined by x-ray diffraction.

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be observed along the *c* axis by STM.

A single crystal was prepared by the conventional electrochemical oxidation method. The crystal was fixed onto a copper plate with conductive silver epoxy and STM observations were performed on the crystal surface. No particular surface pretreatment for STM observation was carried out except for rinsing in deionized water. All STM images shown in this paper were obtained in the constant-height mode using a PtIr tip. No particular correction was performed.

Figure 2(a) shows a STM image obtained over the crystal *a*-*c* plane at ~280 K. The unit cell obtained is 1.6×0.62 nm^2, which agrees well with the crystal structure obtained by x-ray diffraction, $1.4960(4)\times0.6664(2)$ nm^2. A schematic of the crystal *a*-*c* plane structure is shown in Fig. 2(b). Since the lobes of the highest occupied molecular orbital (HOMO) around the S atoms in the hexagonal ring are large according to the *ab initio* calculation, the positions of the lobes of the S atoms in the uppermost rings are marked in Fig. 2(b) by ellipses, which should be compared with the STM image obtained.[14,15] Since BEDT-TTF molecules along the *a* axis are alternately placed about 0.1 nm from the surface, BEDT-TTF molecules are alternately marked by ellipses in the direction of the *a* axis. The molecular arrangement in the observed image in Fig. 2(a) agrees well with the crystal structure shown in Fig. 2(b).

Since $T_c = \sim 297$ K, the CDW phase is expected to appear around room temperature. In fact, two different kinds of superstructures were observed at ~280 K, which are shown in Figs. 3(a) and 4(a). In consideration of the unit cell determined in Figs. 3(a) (1.5×0.7 nm^2) and 4(a) (1.6×1.2 nm^2), schematic structural models are shown in Figs. 3(b) and 4(b), respectively, where BEDT-TTF molecules corresponding to the bright STM protrusions in Figs. 3(a) and 4(a) are marked by solid ellipses.

The observed superstructure in Fig. 3(a) has a charge modulation along the *a* axis as compared to the normal structure shown in Fig. 2. Since the quasi-one-dimensional conductive axis is in the direction of the *c* axis, the observed modulation is perpendicular to the one-dimensional conductive axis, unlike that expected from the theory. This structure is similar to those previously observed for the TTF-TCNQ crystal surface at ~80 K and for α-(BEDT-TTF)$_2$I$_3$.[6,7] On the other hand, the superstructure shown in Fig. 4(a) has a twofold periodicity along the one-dimensional conductive axis (*c* axis), which is in good agreement with the theoretical expectation of the CDW phase and the result of x-ray-diffraction measurement. The $\frac{1}{2}$ lattice constant modulation remains along the *a* axis in Fig. 4(a). This does not contradict to the result of x-ray-diffraction measurement; however, detailed calculation is necessary to understand it. The most frequently observed structure at ~280 K had the modulation perpendicular to the one-dimensional conductive axis [Fig. 3(a)].

Recently, a 2×2 superstructure with modulated charge density, formed by uniting two BEDT-TTF molecules, was observed by STM of an α-(BEDT-

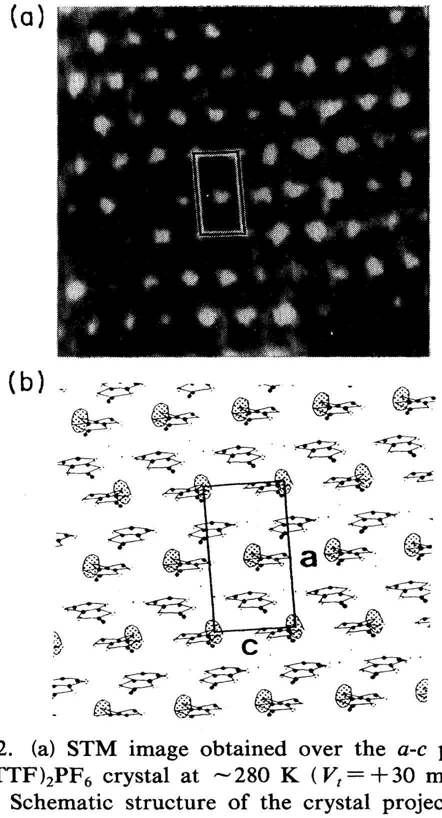

FIG. 2. (a) STM image obtained over the *a*-*c* plane of β-(BEDT-TTF)$_2$PF$_6$ crystal at ~280 K ($V_t = +30$ mV, $I_s = 500$ pA). (b) Schematic structure of the crystal projected on the crystal *a*-*c* plane.

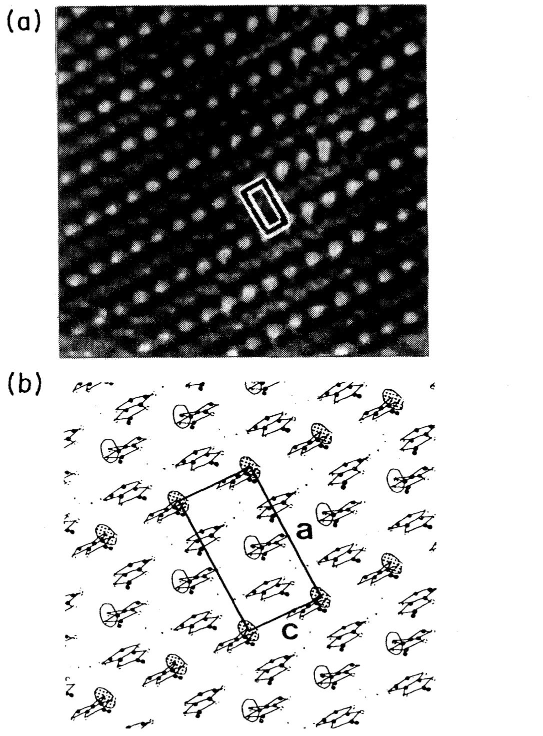

FIG. 3. (a) Superstructure of β-(BEDT-TTF)$_2$PF$_6$ crystal surface obtained at ~280 K ($V_t = +30$ mV, $I_s = 600$ pA), and (b) its schematic structural model.

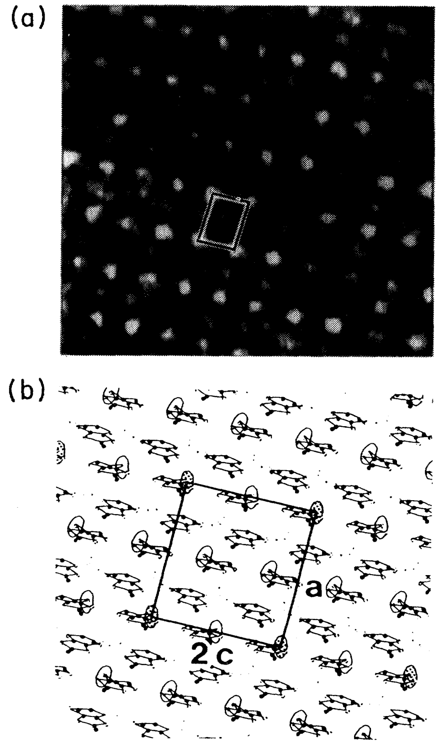

FIG. 4. (a) Another superstructure of β-(BEDT-TTF)$_2$PF$_6$ crystal surface obtained at ~280 K ($V_t=+30$ mV, $I_s=500$ pA), and (b) its schematic structural model.

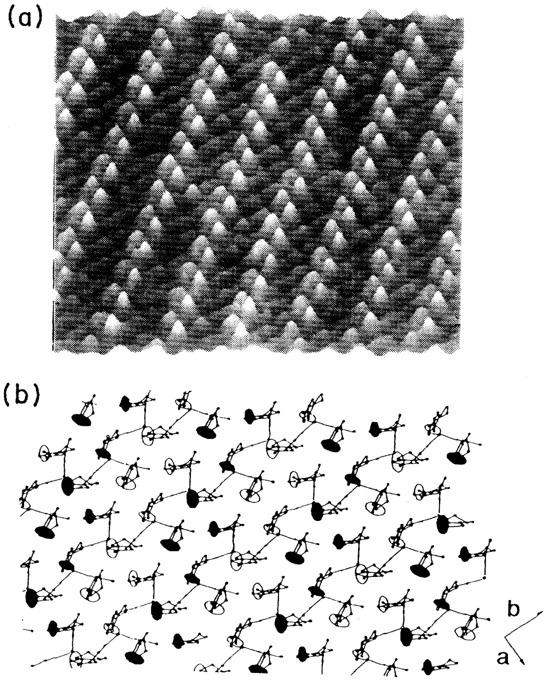

FIG. 5. (a) STM image obtained over the a-b plane of α-(BEDT-TTF)$_2$Cu(NCS)$_2$ ($V_t=+23$ mV, $I_s=2.7$ nA, 9×9 nm^2). (b) Schematic structure of the crystal projected on the crystal a-b plane (Ref. 14).

TTF)$_2$Cu(NCS)$_2$ crystal, a quasi-two-dimensional organic conductor of the BEDT-TTF compound with a metal-insulator phase transition at ~200 K.[13] According to a recent band calculation, this material has a peculiar metallic Fermi surface along the (a-b) direction;[16] therefore, the observed charge modulation can be understood as being ordered perpendicular to the metallic axis of (a-b). A STM image and its schematic structure are shown in Fig. 5.

Similar charge-density modulation was observed by STM in an α-(BEDT-TTF)$_2$I$_3$ crystal which has a CDW phase transition at 135 K, and in its thin film.[7] The observed unit cell was $\sim 2.1\times1.4$ nm^2 ($a\times b$), about twice as long in the direction of the a axis than that of the bulk crystal (0.92 nm). Since the most conductive axis is in the direction of the crystal b axis, the observed double periodicity was perpendicular to the most conductive one-dimensional axis. In addition, the conductance behavior of the α-(BEDT-TTF)$_2$I$_3$ thin films was found to be different from that of the single crystal; the former shows a gradual drop of conductance around 160 K, while an abrupt metal-insulator transition was observed at 135 K for the latter. Recently, a similar change in critical temperature was observed in TTF-TCNQ thin films.[17] Therefore, some surface effect seems to exist in thin films, which may be related to the increase of the critical temperature.

In order to study the electronic structure of β-(BEDT-TTF)$_2$PF$_6$ around T_c, I-V (tunneling current-bias voltage) curves were obtained. Figure 6 shows a series of I-V curves obtained at (a) 304 K, (b) 230 K, and (c) 202 K, under the conditions of (tip bias voltage V_t, set current I_s) (a) (50 mV, 1.0 nA), (b) (200 mV, 0.5 nA), and (c) (200 mV, 0.5 nA). As is shown in Fig. 6, the electronic property at 304 K is metallic, and conductivity decreased with temperature, as expected. However, metallic electronic states partially remained on an atomic scale even at 230 K between the energy gap, indicating fluctuation of the CDW, which is considered to be the reason for the appearance of three different structure types at ~280 K.

Generally, due to the interaction among the one-dimensional chains, CDW phases along the one-dimensional chains shift by the amount of π relative to each other; thereby, the Peierls transition is stabilized. However, when fluctuation becomes larger, correlation of

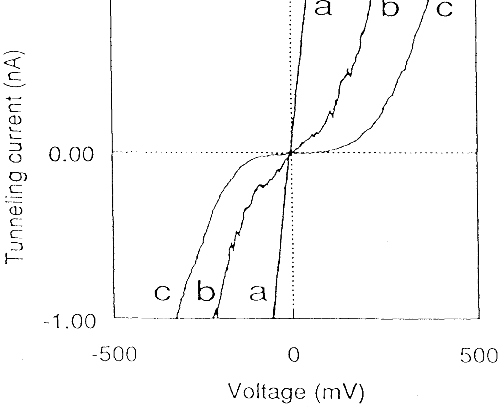

FIG. 6. Series of I-V curves measured at (a) 304 K, (b) 230 K, and (c) 202 K.

the CDW phase between the neighboring one-dimensional chains is disturbed, resulting in the increase of the interaction energy. Therefore, some reconstruction, such as the observed modulation [Fig. 3(a)], may occur to reduce the interaction energy between the neighboring one-dimensional chains. On semiconductor surfaces, surface reconstruction such as dimer buckling is known to reduce the surface energy by disrupting the structural symmetry; this is observed on Si(100) and GaAs(011) surfaces.[18]

In consideration of the fact that thin films of TTF-TCNQ and α-(BEDT-TTF)$_2$I$_3$ have been found to have higher, but dull critical temperature of the metal-insulator transition, i.e., gradual drop of conductance,[7,17] theoretical calculation is necessary to clarify the surface effect in organic materials.

Among the BEDT-TTF compounds, β-(BEDT-TTF)$_2$I$_3$ is the most intensively studied structure because it has two or more superconducting phases with different critical temperatures. Surface reconstruction in organic materials was reported for the first time for this material. The relationship between the bulk (b,c) and the observed reconstructed surface (b',c') unit cells is represented well by[19,20]

$$\begin{bmatrix} b' \\ c' \end{bmatrix} = \begin{bmatrix} 0 & -2 \\ 1 & 1 \end{bmatrix} \begin{bmatrix} b \\ c \end{bmatrix} .$$

However, the reason for this surface reconstruction is not clear.

According to the discussion above, a superstructure should occur along the direction perpendicular to the most conductive axis due to the interaction among the neighboring one-dimensional chains caused by fluctuation. Recent band-structural calculation shows that the crystal has a metallic property along the b axis. Therefore, modulation is expected to occur along the c axis, which is different from the observed structure. However, it is possible to understand the observed molecular arrangement as a 2×2 superstructure, which is similar to the structure of β-(BEDT-TTF)$_2$PF$_6$ in Fig. 4. If the structure in Fig. 4 is assumed to be a phase which appears at lower temperatures following the intermediate structure shown in Fig. 3, the 2×2 structure observed on the β-(BEDT-TTF)$_2$I$_3$ crystal surface is considered to be in the second stage of the phase transition: the CDW state. Lower instability of the β-(BEDT-TTF)$_2$I$_3$ crystal compared to other BEDT-TTF compounds, which may cause a stronger surface effect, is a possible reason for this. In order to understand the formation mechanism of the surface superstructure of organic materials, further study such as temperature dependence of the STM images must be performed.

In summary, in addition to the normal CDW phase, a superstructure with a modulation perpendicular to the one-dimensional conductive axis was found by STM on a β-(BEDT-TTF)$_2$PF$_6$ surface at $\sim$280 K, the structure of which is similar to that previously observed on a TTF-TCNQ crystal surface around its critical temperature. Under the assumption that the new structure is an intermediate phase caused by the interaction between neighboring one-dimensional molecular chains upon fluctuation of the CDW around critical temperature, superstructures which have been observed in other BEDT-TTF compounds could also be explained well.

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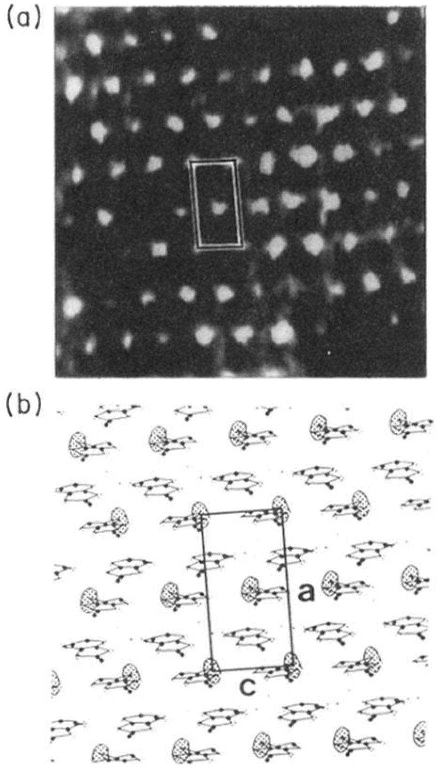
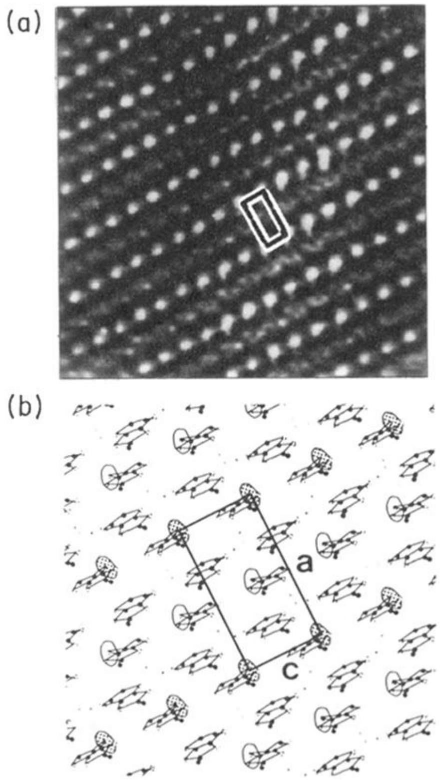


FIG. 2. (a) STM image obtained over the *a*-*c* plane of β-(BEDT-TTF)$_2$PF$_6$ crystal at ~280 K ($V_t = +30$ mV, $I_s = 500$ pA). (b) Schematic structure of the crystal projected on the crystal *a*-*c* plane.



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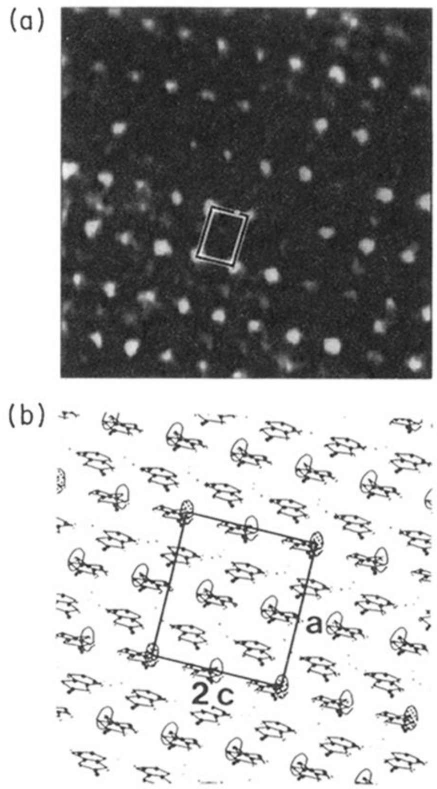

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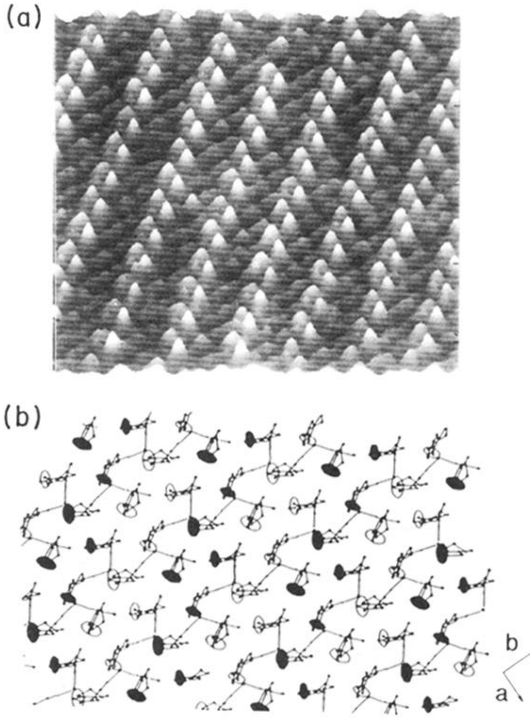

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