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# Surface structure of the organic conductor $\beta$-(BEDT-TTF)$_2$I$_3$ observed by scanning tunneling microscopy [where BEDT-TTF is bis(ethylenedithio) tetrathiafulvalene]

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Superstructure was observed on the surface of the organic conductor $\beta$-(BEDT-TTF)$_2$I$_3$ [where BEDT-TTF is bis(ethylenedithio)tetrathiafulvalene] by scanning tunneling microscopy; this shows that surface reconstruction for organic materials can occur. The column structure of BEDT-TTF molecules along the [011] direction was stable and the reconstruction was completed as a result of the change in the relative arrangement of these columns. Many defects consisting of the voids of the BEDT-TTF molecules were also observed. These imperfections of the crystal surface are considered to be due to the instability of the anion structure.

Characterization of organic materials at an atomic scale is very important from fundamental and practical points of view, because their properties strongly depend on the local arrangement of molecules. Scanning tunneling microscopy (STM) is known to be a powerful method by which to investigate the geometric and electronic structures of the materials with atomic resolution, and many useful results have been reported for the semiconductor surfaces since its invention by Binnig *et al.*[1] This method is also successfully applied to the study of organic materials such as liquid crystals,[2] DNA,[3] and organic conductors.[4-7]

In this paper, we present the surface structure of $\beta$-(BEDT-TTF)$_2$I$_3$ crystal as observed by STM. (BEDT-TTF)$_2$I$_3$ is known to have the most diverse phases of crystal structures at room temperature among the BEDT-TTF salts.[8] Among these crystal structures, $\beta$-(BEDT-TTF)$_2$I$_3$ is the most intensively studied structure because of the existence of two or more superconducting phases with different critical temperatures ($T_c$).[9,10] It is shown that the structural stability of this material is closely related to the structure of the anion layer.

According to the x-ray-diffraction analysis, the crystal has a triclinic structure and $P\bar{1}$ symmetry [Fig. 1(a)].[8] The crystal parameters are as follows: $a=1.5243$ nm, $b=0.9070$ nm, $c=0.6597$ nm, $\alpha=109.73°$, $\beta=95.56°$, $\gamma=94.33°$, and $V=0.8489$ nm$^3$. The hexagonal rings at one end of the BEDT-TTF molecules in the crystal are slightly distorted and are indicated by hatches in the figure. The crystal consists of the alternating stacked structure of (BEDT-TTF) layers and I$_3$ layers. Figure 1(b) shows the top view of the crystal $bc$ plane. Concerning the BEDT-TTF molecules, only the upper two rings which are closer to the surface are drawn for simplicity. In the (BEDT-TTF) cation layers, the (BEDT-TTF) molecules are stacked face to face to form a column along the [001] direction. The topmost layers of BEDT-TTF salt crystals are considered, generally, to be anion layers.[5-7]

Through the half-electron transfer from each (BEDT-TTF) molecule to the I$_3$ molecules, the cation layers become conducting and the anion layers become insulating. According to the band calculation, this material is an example of an isotropic two-dimensional organic conductor.[8]

The $\beta$-I$_3$ crystal was prepared in the conventional chemical oxidation of (BEDT-TTF) molecules. The surface was shiny and no particular surface treatment for the STM observation was carried out except for rinsing by deionized water, as was performed for the observation of the other BEDT-TTF salt materials.[5-7] STM measurements were performed over the crystal $bc$ plane in air and at room temperature with a Pt-Ir tip in the constant-height mode.

Figure 2(a) shows an STM image of the crystal $bc$ plane ($3.2\times3.2$ nm$^2$). The sample voltage $V_s$ was kept at 30.2 mV during the measurement. Since almost the same image was observed for the inverse voltage, the STM image is considered to reflect the metallic property of the electronic structure of the conductive BEDT-TTF layer, as was observed for other BEDT-TTF salt crystals.[5-7] Two alternative kinds of linear arrays, $C_1$ and $C_2$, of the protrusions along the [011] direction can be seen. As is shown in the figure, the spacings between the lines along

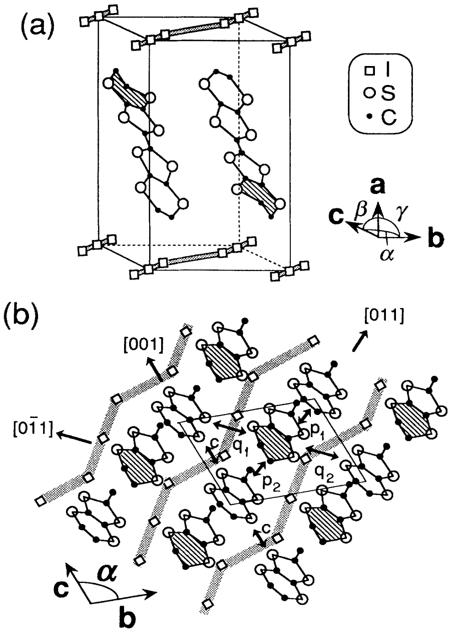

FIG. 1. (a) Crystal structure of β-(BEDT-TTF)$_2$I$_3$. Distorted hexagonal rings are hatched lines (□, I; ○, S; ●, C). (b) Molecular arrangement projected onto the crystal *bc* plane.

the [001] direction are not unique, but they have a periodic structure consisting of two alternative different spacings of $D_1=0.84$ nm and $D_2=0.68$ nm.

Figure 2(b) shows the line profiles along $C_1$ and $C_2$. There are two kinds of maxima on each line, which correspond to protrusions with different brightness and shape in Fig. 2(a). The values of the intermolecular overlap of the highest occupied molecular orbital of the BEDT-TTF molecules shown in Fig. 1(b) are as follows: $p_1=-24.5$, $p_2=-8.4$, $q_1=-12.7$, $q_2=-6.8$, $c=-5.0\times10^{-3}$.[8] Since the intrastack overlap $p_1$ is the largest, and the $p_2$ overlap is much smaller, the BEDT-TTF molecules in the crystal are considered to be slightly dimerized in the column along the [011] direction. The side view of the BEDT-TTF molecule structure in the column is drawn in Fig. 2(b). Each dimer unit is shown in the figure linked with the dashed line. The sulfur atoms in the topmost hexagonal ring of the right-hand-side molecule of the dimer unit are about 0.1-nm higher in vertical position than the left-hand side. Since the calculation shows the highest occupied molecular-orbital concentration on the S atoms in the hexagonal ring,[5] the right-hand-side molecule is considered to bear a brighter protrusion in the STM image. Taking these factors into consideration, the dimer structure can be assigned to the protrusions observed along $C_1$ and $C_2$. In Fig. 2(b), the dimer structure under each profile is drawn in the same structure of the bulk crystal, while the shape of the profile is different between $C_1$ and $C_2$, as mentioned later. The sulfur atoms in the hexagonal ring of BEDT-TTF molecules are arranged under the maximum points of each line profile. Excellent agreement can be seen in the figure.

A possible unit cell is drawn in Fig. 2(a), the size of which is $1.52\times1.05$ nm$^2$. The surface periodicity in the

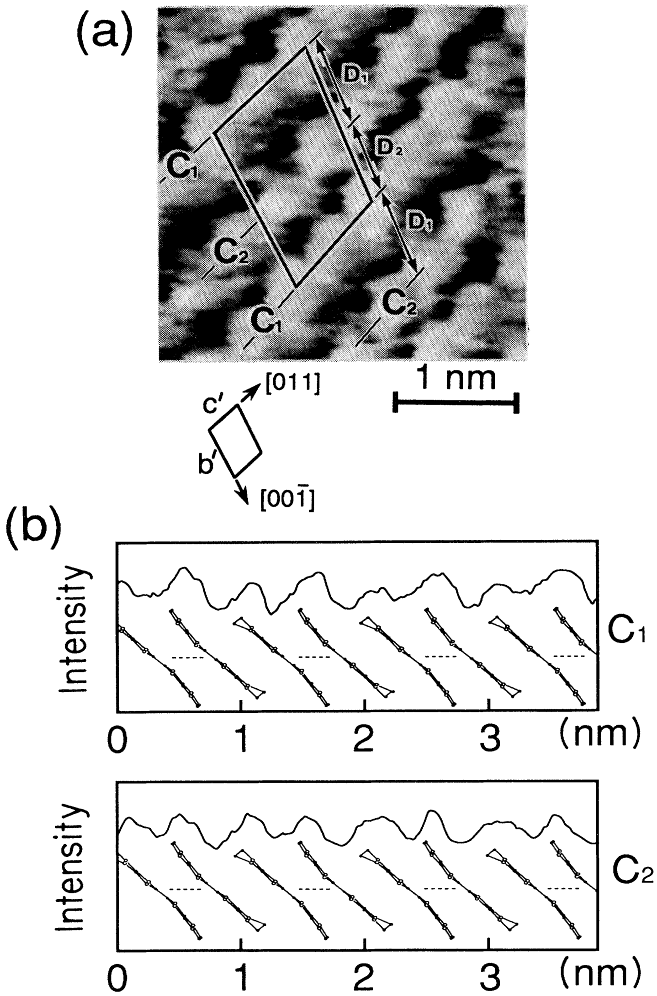

FIG. 2. (a) STM image of β-(BEDT-TTF)$_2$I$_3$ surface ($3.2\times3.2$ nm$^2$, $V_s=30.2$ mV). (b) Cross sections along columns $C_1$ and $C_2$ in (a). Dimer structure of the BEDT-TTF molecules in the bulk crystal is also shown in the figures.

[011] direction ($c'$) is very close to the crystal periodicity of 0.924 nm, and in the [001] direction ($b'$) it is almost twice that of the crystal value of 1.32 nm. Therefore, the relationship between the surface ($b',c'$) and the bulk ($b,c$) unit cells drawn in Figs. 2(a) and 1(b) can be represented by

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

Figure 3(a) shows the molecular structure of the cation layer in the bulk crystal and Fig. 3(b) shows a model to interpret the observed surface reconstruction. If the molecular columns rearrange as indicated by the arrays in Fig. 3(a), the observed surface superstructure can be reproduced as shown in Fig. 3(b). The amount of the relative slide of the columns, which is indicated by Δ in Fig. 3(b), is 0.18 nm. Rearrangement perpendicular to the surface may exist; however, the amount of change is not clear at present.

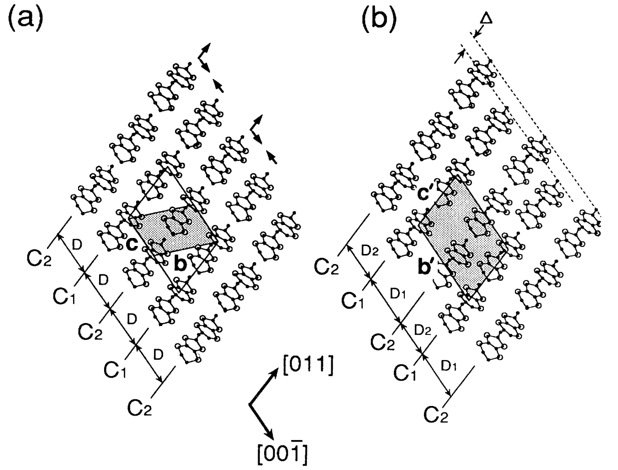

FIG. 3. BEDT-TTF molecular arrangements for (a) the bulk and (b) the surface of the $\beta$-(BEDT-TTF)$_2$I$_3$ crystal.

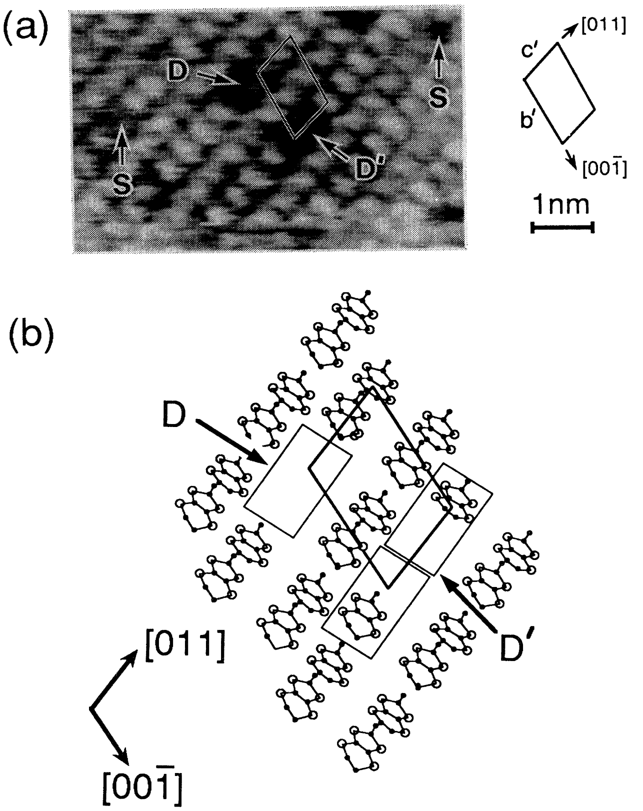

FIG. 4. (a) STM image of $\beta$-(BEDT-TTF)$_2$I$_3$ surface (6.4 ×4.0 nm$^2$, $V_s=50.0$ mV). (b) Molecular structure near the defects in Fig. 4(a).

Figure 4(a) shows an STM image of a larger area scan (6.4×4.0 nm$^2$). In order to eliminate the collisions between the tip and the sample, the bias voltage was increases ($V_s=50.0$ mV); thereby, the image of the protrusions is slightly different from the image in Fig. 2(a). Defects consisting of the void of the (BEDT-TTF) molecules can be seen. In addition to the defects of the single molecule (labeled by *S* in the figure), there are some defects consisting of the void of two molecules, as labeled by *D* and *D'* in the figure. Considering the dimer structure of the BEDT-TTF molecules in the crystal, those *D* and *D'* defects seem to be created by the dimer units. However, compared with the unit cell drawn near the defects in Fig. 4(a), defect *D'* does not correspond to the dimer unit. The relationship between the two defects *D* and *D'* is drawn in Fig. 4(b) schematically.

Since those defects and the reconstruction were not observed for the surface of (BEDT-TTF)$_2$Cu(NCS)$_2$,[5] this instability of the surface structure is considered to be a particular property of the $\beta$-I$_3$ crystal. The instability of the $\beta$-I$_3$ crystal is attributed to the unstable structure of its anion layers. In order to validate this, we observed the surface of the (BEDT-TTF)$_2$(NH$_4$)(SCN)$_4$ and (BEDT-TTF)$_2$KHg(SCN)$_4$, the anion layer of which has a three-dimensional structure where the (BEDT-TTF) molecules are strongly fixed by the network of the anions. Very stable STM images without defects were obtained as expected.[6,7]

In conclusion, the surface of the $\beta$-(BEDT-TTF)$_2$I$_3$ observed by STM contained many defects and was reconstructed to give a superstructure. These instabilities can be attributed to the unstable structure of the anion layers of this crystal. These results also indicate that the application of STM is very useful in understanding the geometric and electronic structures of the surface of organic materials at an atomic scale.

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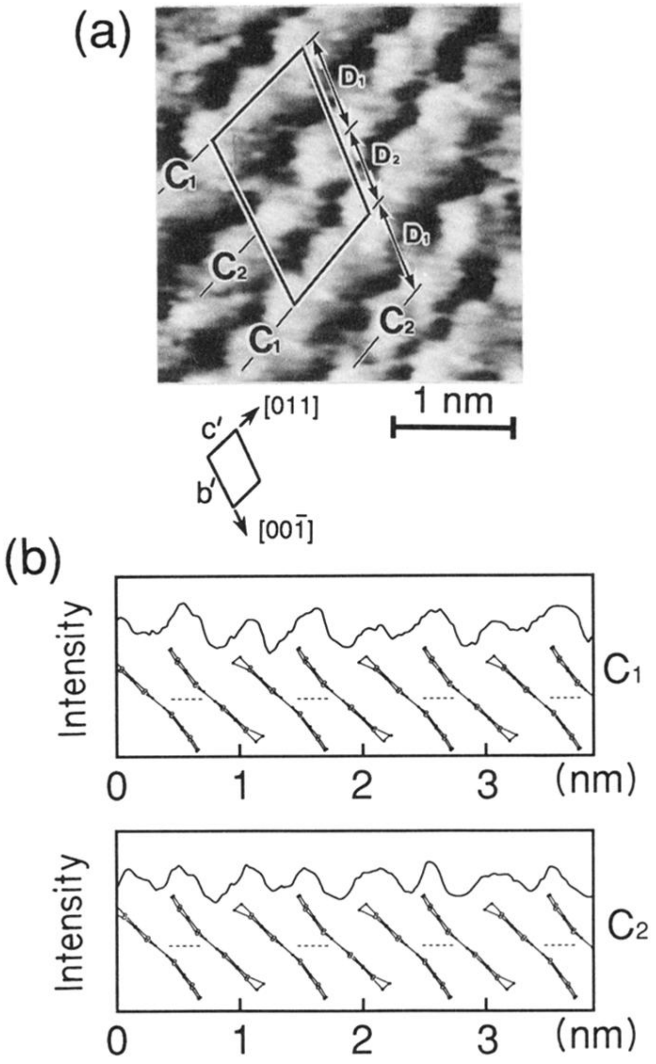

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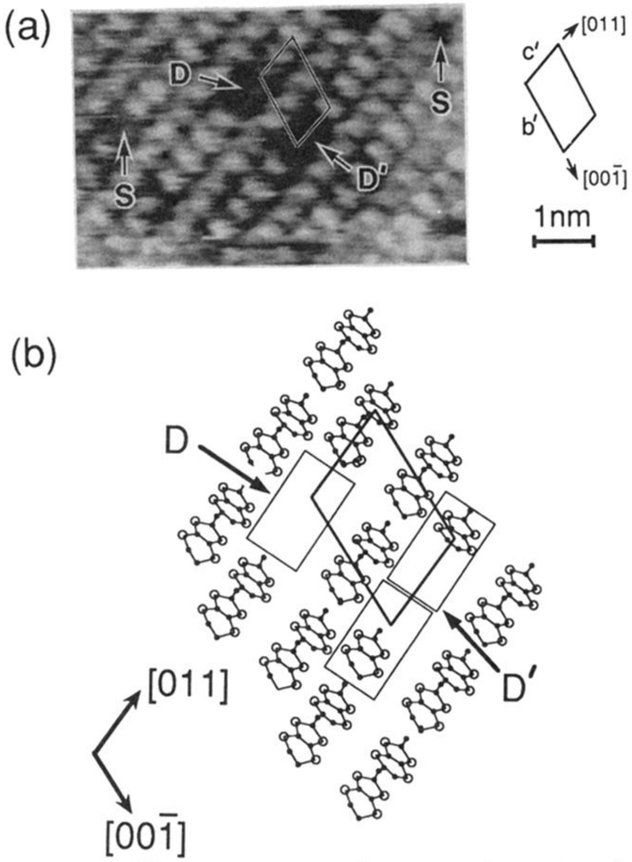

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