

Electronic structure of the organic superconductor κ -(BEDT-TTF)₂Cu(NCS)₂ [where BEDT-TTF is bis(ethylenedithio)tetrathiafulvalene] studied by scanning tunneling microscopy

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The bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) molecules in κ -(BEDT-TTF)₂Cu(NCS)₂ crystals were observed directly by scanning tunneling microscopy. Carrier distribution observed on the BEDT-TTF molecules were in good agreement with the electronic structure calculated by an *ab initio* method based on the dimerized molecular structure determined by x-ray diffraction. The layer structure consisting of a stack of alternate conductive and insulating layers was clearly observed.

Organic superconductors have been studied extensively because of their high potential designability for the superconductivity.¹⁻⁶ They have a layer structure consisting of a stack of alternate conductive and insulative layers. The critical temperature strongly depends on the molecular structures in those layers. Recently, band structures have been calculated on the basis of their molecular structures determined by x-ray diffraction, and the experimental results on the electronic structures, such as the Fermi surface, of those materials have been the subject of considerable attention.⁷ Since those calculations were performed using the molecular orbitals, it is very important to directly study the electronic structures of the molecules in the crystals in order to check the theoretical models and to understand the relationship between the molecular structure and the superconductivity.

In this paper, we present the results of the scanning tunneling microscopy (STM) observation of the κ -(BEDT-TTF)₂Cu(NCS)₂ crystal [BEDT-TTF is bis(ethylenedithio)tetrathiafulvalene] which was the highest T_c organic superconductor in ambient pressure ($T_c = 10.4$ K) until recently.⁸ The STM image of the BEDT-TTF molecule in the crystal was interpreted satisfactorily by the electronic structure calculated by the *ab initio* method.

The crystal structure of κ -(BEDT-TTF)₂Cu(NCS)₂ determined by x-ray diffraction is monoclinic (a : 1.6248 nm; b : 0.8440 nm; c : 1.3124 nm; β : 110.30°; V : 1.688

nm³ at 298 K), and consists of a stack of alternate BEDT-TTF layers and Cu(NCS)₂ layers parallel to the a axis (Fig. 1).^{9,10} The hexagonal ring at one end of the BEDT-TTF molecule is more distorted than that at the other side of the crystal, as shown in Fig. 1 by the hatched cross.

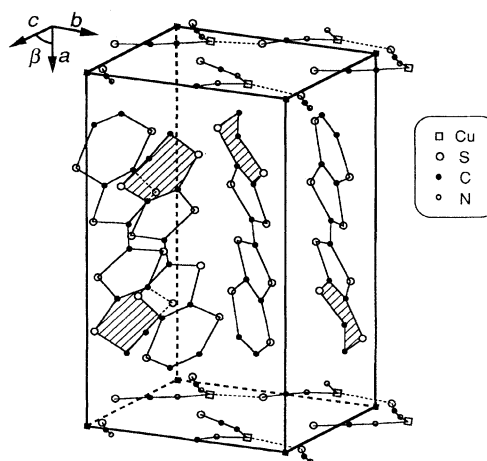


FIG. 1. Crystal structure of κ -(BEDT-TTF)₂Cu(NCS)₂. Distorted hexagonal rings are marked by hatching. (\square : Cu; \circ : S; \bullet : C; \circ : N).

A single crystal was prepared by the electrochemical oxidation of BEDT-TTF in a 1,1,2-trichloroethane solution under the constant current of $1.5 \mu\text{A}$ at room temperature using potassium thiocyanate, copper (I) thiocyanate, and 18-crown-6 ether as the supporting electrolytes and platinum rods as the electrodes.⁹ The crystal has a distorted hexagonal shape and the size is about $0.05 \text{ mm} \times 2 \text{ mm} \times 1 \text{ mm}$ in the directions of a^* (perpendicular to the b - c plane), b and c axes, respectively.

The crystal was fixed onto a copper plate with conductive silver epoxy and the STM observations were performed over the crystal a - b and b - c planes in air at room temperature using Pt-Ir tips. The crystal surface was very shiny. No particular surface preparation for the STM observation was carried out except for rinsing in deionized water.

Figure 2(a) shows the current image obtained over the crystal a - b plane. The tip voltage to the sample was 22.9 mV. Alternate bright and dark bands can be seen along the b axis. The line profile along line A_1 - A_2 in Fig. 2(a) is shown in Fig. 2(b). The period of this structure is 1.70 nm and is close to the lattice constant along the a axis (1.6248 nm). According to the results obtained by techniques such as ESR, electron spectroscopy for chemical

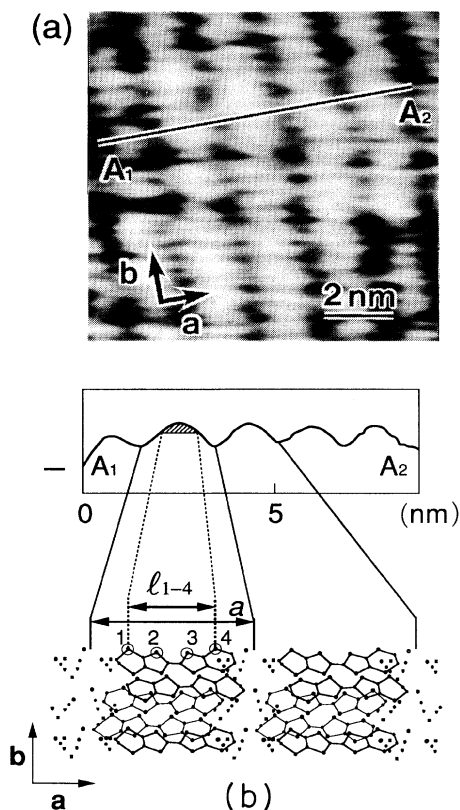


FIG. 2. (a) Current image of the crystal a - b plane ($V_t = 22.9$ mV, $10.2 \text{ nm} \times 10.2 \text{ nm}$). (b) Cross section along line A_1 - A_2 in (a). (a : lattice constant; l_{1-4} : distance between two S atoms in the hexagonal rings at both ends of BEDT-TTF molecule (0.86 nm)].

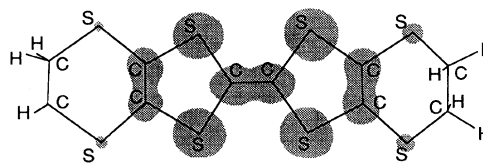


FIG. 3. HOMO structure of BEDT-TTF molecule at $|\phi|^2 = 0.081 \text{ bohr}^{-3}$ calculated by the *ab initio* method. The shape of the hexagonal ring on the right-hand side is more distorted than on the left-hand side.

analysis (ESCA), and x-ray-diffraction measurements, through the transfer of a half-electron from each BEDT-TTF molecule to the $\text{Cu}(\text{NCS})_2$ layers, the $\text{Cu}(\text{NCS})_2$ layers become insulative and the BEDT-TTF layers become two-dimensionally conductive.¹⁰ Actually, the typical value of the conductivity normal to the b - c plane is about 600 times as small as that in the b - c plane.¹¹ STM would not work well in a constant current mode over the a - b plane because of the presence of those low-current regions. Therefore, the periodic band image is expected to reflect the alternate stacking structure of the conductive BEDT-TTF cation layers and the insulative $\text{Cu}(\text{NCS})_2$ anion layers.

Since the four sulfur atoms, which are close to the observed surface and will contribute to the STM image, labeled 1-4 in the BEDT-TTF molecules, are arranged nearly equidistant from the a - b plane [Fig. 2(b)], the tunneling current from these four sulfur atoms in a BEDT-TTF molecule should be almost equal if their electronic structure remains in the same state. The distance between the outermost two S atoms (1 and 4) of the hexagonal rings of the BEDT-TTF molecule, indicated by l_{1-4} in Fig. 2(b) as determined by x-ray diffraction, is 0.86 nm. The corresponding region is also indicated in the profile by a hatched area. As is shown in the profile in Fig. 2(b), the current intensity from the bright bands are not equal for these four sulfur atoms, which indicates the presence of the carrier concentration around the central TTF molecular part. Figure 3 shows the distribution of the highest occupied molecular orbital (HOMO) at $|\phi|^2 = 0.081 \text{ bohr}^{-3}$ calculated by an *ab initio* method. The high concentration of the carrier density on the part

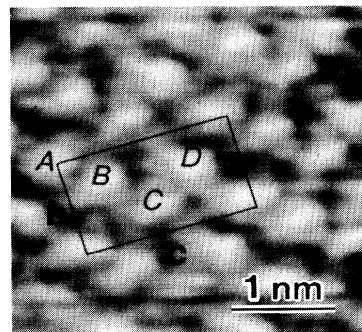


FIG. 4. STM current image of the crystal b - c plane ($V_t = -20.8$ mV, $3.7 \text{ nm} \times 3.7 \text{ nm}$).

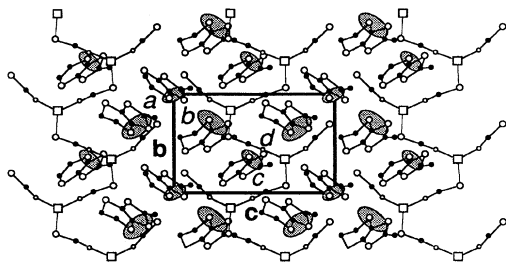


FIG. 5. Molecular arrangement of the crystal projected on the crystal b - c plane (\square : Cu; \circ : S; \bullet : C; \circ : N).

of the TTF molecule is clearly visible, which is in good agreement with the experimental result written above. Indiscernibility of the two sulfur atoms labeled 2 and 3 in the profile image may be due to the fact that the STM tip probes the lower density of state, the contour of which is rather smooth.

Figure 4 shows a current image over the b - c plane. The tip voltage was -20.8 mV. The four types of protrusions observed are labeled A - D in Fig. 4. The observed size of the unit cell is 0.97 nm \times 1.70 nm and agrees with 0.8440 nm \times 1.3124 nm as determined by x-ray diffraction for the bulk crystal.¹⁰ The difference between these values is considered to be due to thermal drift. Of the four types of protrusion, C is small and less bright. Almost the same image was obtained for the inverse voltage. This result indicates that the surface electronic structure obtained is metallic and that the STM image observed is expected to reflect the molecular structure of the conductive BEDT-TTF layer. However, since the crystal stability is assured by the sandwiched structure of the cation layers by the anion layers, the topmost layer is assumed to be an anion layer, which must be taken into consideration in order to analyze the STM images.

Figure 5 shows the top view of the molecular arrangement over the b - c plane. Since the tunneling current is very sensitive to the distance between the tip and the object, it is most important to consider only those lobes which stand out from the top rings of the molecules. Therefore, the upper two rings of the BEDT-TTF molecules which are closer to the crystal surface are drawn in the Fig. 5, together with the anion positions. Since, in the hexagonal ring, the lobes of HOMO around the S atoms are big according to the *ab initio* calculation, the positions of the lobes of the S atoms in the uppermost rings are marked in Fig. 5 by ellipses, which should be

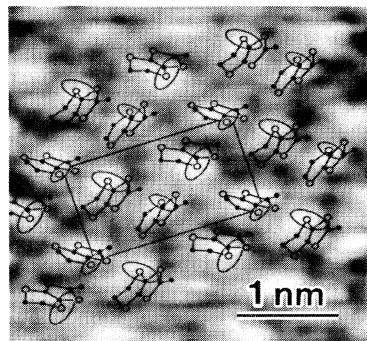


FIG. 6. STM image of the crystal b - c plane superimposed on the molecular structure drawn in Fig. 5 ($V_t = -20.8$ mV, 3.7 nm \times 3.7 nm).

compared with the STM image obtained. The size of the lobes increases with the degree of distortion of the upper hexagonal ring of the molecule (Fig. 3). Thus, as is shown in Fig. 5, the images of molecules a and c are expected to be less bright than the images of the distorted molecules b and d . In addition, the STM images of the cations are influenced by the anions in the top layer, as described elsewhere,^{12,13} so the image of molecules c , which are closer to the anion in the top layer than molecules d , must be the least bright of these protrusions. Therefore, protrusion c in Fig. 4 should be assigned to the molecules c in Fig. 5, and the protrusions A , B , and D can be assigned to a , b , and d , respectively. Figure 6 shows the STM image superimposed on the molecular structure drawn in Fig. 5. The brightness distribution in each protrusion of the STM image shows a satisfactory agreement with the theoretical model calculated by the *ab initio* method (Fig. 3).

In conclusion, BEDT-TTF molecules in the κ (BEDT-TTF)₂Cu(NCS)₂ crystal were observed by STM. The STM image was in good agreement with the calculated electronic structure of BEDT-TTF molecules in the crystal. The layer structure of the crystal, consisting of the conductive and insulative layers, was clearly observed. These results indicate that such calculation is useful in analyzing the electronic structure of these materials.

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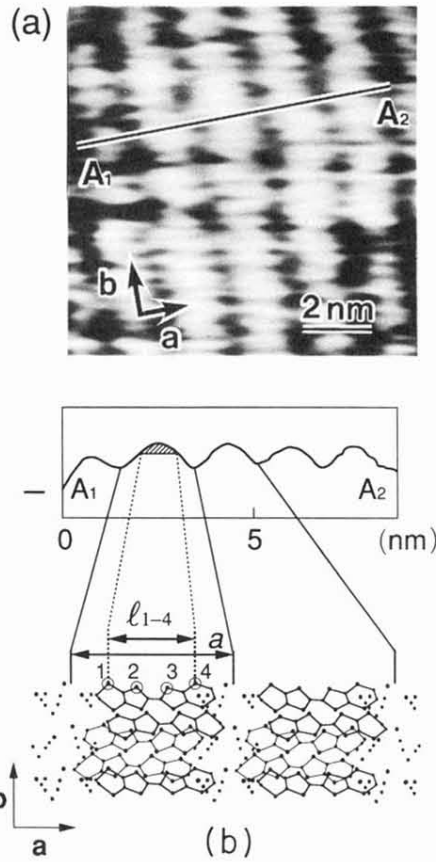


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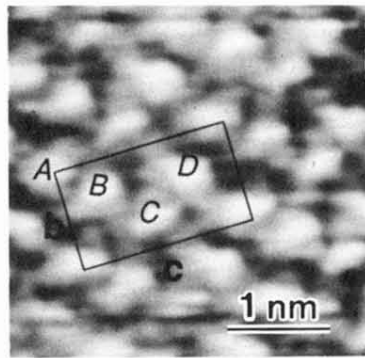


FIG. 4. STM current image of the crystal *b-c* plane ($V_t = -20.8$ mV, 3.7 nm \times 3.7 nm).

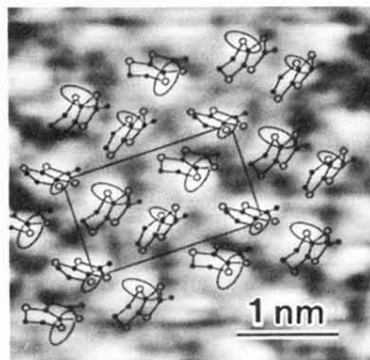


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