Molecular structure of a crystal phase coexisting with κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ studied by scanning tunneling microscopy

Hidemi Shigekawa, Koji Miyake, Haruhiro Oigawa, and Yasuo Nannichi
Institute of Materials Science, University of Tsukuba, Tsukuba 305, Japan

Takehiko Mori
Department of Organic and Polymeric Materials, Tokyo Institute of Technology, Tokyo 152, Japan

Yoshio Saito
National Laboratory for High Energy Physics, Tsukuba 305, Japan
(Received 5 July 1994; revised manuscript received 30 August 1994)

By using scanning tunneling microscopy (STM), a molecular structure was found to coexist in a (BEDT-TTF)$_2$Cu(NCS)$_2$ crystal grown at room temperature, in addition to the well-known κ phase with metal-superconductor phase transition at $\sim$10 K. The obtained two-dimensional structure of the phase was close to that of the α-(BEDT-TTF)$_2$Cu(NCS)$_2$ crystal previously reported as a charge-transfer salt with metal-insulator transition at $\sim$200 K. The temperature dependence of I-V (tunneling current–bias voltage) curves measured by STM showed both phase transition properties. A superstructure with a 2×2 unit cell formed by modulated charge density on the BEDT-TTF molecules was also observed for the phase, which was formed by uniting two BEDT-TTF molecules.

Since the discovery of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ [BEDT-TTF is bis(ethylenedithio)-tetrathiafulvalene], many studies have been conducted due to its transition at high temperature and ambient pressure to the superconducting phase ($\sim$10 K). However, there still remain several basic problems, e.g., sample dependence on the conductivity above $\sim$100 K. Recently, from the results of electron-spin resonance and x-ray diffraction measurements, at least three different phases other than the κ phase have been proposed to exist in the (BEDT-TTF)$_2$Cu(NCS)$_2$ compound;[1,2] however, the existence and structures of these phases have neither been confirmed nor established. Among the phases, the α phase, which is considered to exhibit a metal-insulator transition at $\sim$200 K, has a peculiar characteristic: when the growth temperature of the crystal was maintained at 293 K, single crystals of the superconducting κ phase of (BEDT-TTF)$_2$Cu(NCS)$_2$ were obtained as usual, whereas when the growth temperature was kept at 283 K, the single crystal of the α phase was obtained.[2] Since a slight difference in growth conditions led to completely different structures, i.e., superconductor or insulator, much effort has been made to study this phase in detail, but to date it has been unsuccessful. In order to conduct detailed studies, we must characterize the microscopic structure of the (BEDT-TTF)$_2$Cu(NCS)$_2$ compound on an atomic scale.

In this paper, we present the results obtained by scanning tunneling microscopy (STM) on the (BEDT-TTF)$_2$Cu(NCS)$_2$ crystal. It is also intriguing to study this material on an atomic scale because the charge-density wave (CDW) occurring in two-dimensional organic conductors has not yet been observed in real space.

A single crystal was prepared by the electrochemical oxidation of BEDT-TTF in a 1,1,2-trichlorethane solution under the constant current of 1.5 μA at room temperature using potassium thiocyanate, copper (I) thiocyanate, and 18-crown-6 ether as the supporting electrolytes and platinum rods as the electrodes.[3] Temperature variation of about 10 K, which is considered to affect the growth condition of the α phase, was not controlled. The obtained crystals had a distorted hexagonal shape similar to κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ crystals grown under such procedures. The crystal was fixed onto a copper plate with conductive silver epoxy and STM observations

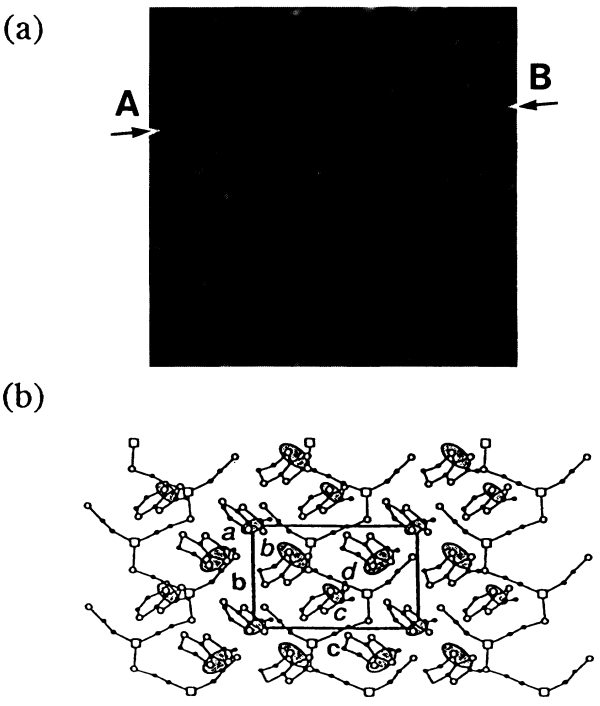

FIG. 1. (a) STM image of a (BEDT-TTF)$_2$Cu(NCS)$_2$ crystal ($V_t=-22$ mV, $I_s=2.8$ nA, 6.5×6.5 nm^2). (b) Molecular arrangement of the (BEDT-TTF)$_2$Cu(NCS)$_2$ crystal projected on the crystal b-c plane (□, Cu; ○, S; ●, C; ○, N) (Ref. 4).

were performed over the crystal surface. No particular surface preparation for STM observation was carried out except for rinsing in deionized water.

Figure 1(a) shows a current image obtained over the surface corresponding to the b-c plane of the κ phase. The tip voltage was -22 mV. The observed periodic four-type protrusions and the observed size of the unit cell is 0.80×1.31 nm^2, which agrees well with that of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$, 0.8440×1.3124 nm^2, as determined by x-ray diffraction. A schematic structure of the b-c plane of the κ phase is shown in Fig. 1(b).[4] Since the lobes of the highest occupied molecular orbital 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. 1(b) by ellipses, which should be compared with the STM image obtained.[4,5] The size of the lobes increases with the degree of distortion of the upper hexagonal ring of the molecule, which is indicated by two kinds of ellipses having two different sizes in Fig. 1(b). The molecular arrangement in the observed image is in good agreement with the structure shown in Fig. 1(b) and is quite similar to the STM image previously obtained for κ-(BEDT-TTF)$_2$Cu(NCS)$_2$.[4] The same structure was observed with the opposite bias voltage.

As expected, the structure of the κ phase was mainly observed all over the surface; however, another structure, as shown in Fig. 2 ($V_t=-22$ mV, $I_s=2.8$ nA), was found to be partially included in the crystal. The structure of the observed image in Fig. 2 appears to be similar to the structure of the κ phase, but is completely different in detail. For example, the molecular arrangement along A-B in Fig. 2 is more or less aligned on a straight line compared to the zigzag structure along A-B in Fig. 1(a). The observed size of the unit cell, enclosed by lines in Fig. 2, 0.96×1.07 nm^2, agrees well with the value for the α-(BEDT-TTF)$_2$Cu(NCS)$_2$ crystal, $0.9052(2)\times1.0854(5)$ nm^2, as determined by x-ray diffraction.[2]

The crystal structure of α-phase salt belongs to a triclinic system, and the preliminary lattice parameters determined by x-ray diffraction are $a=0.9052(2)$ nm, $b=1.0854(5)$ nm, $c=1.7471(3)$ nm, $\alpha=100.95(3)$, $\beta=97.34(2)$, $\gamma=90.37(3)$, and $V=1.672(2)$ nm.[3] The BEDT-TTF molecules are dimerized in the crystal and the hexagonal rings at both ends of the BEDT-TTF molecule are distorted, as shown in Fig. 3(a). Since the STM image of the BEDT-TTF molecule reflects the structure of π orbitals on the S atoms in the molecules, rings containing S atoms, the orbitals of which are considered to be less disturbed by the distortion of the rings, are marked by hatched areas in the figure. The schematic structure of the a-b plane of the α-(BEDT-TTF)$_2$Cu(NCS)$_2$ crystal is drawn in Fig. 3(b), where the upper two rings of the BEDT-TTF molecules, which are closer to the crystal surface, are drawn together with the anions, similarly to that shown Fig. 1(b). Two kinds of ellipses with two different sizes indicate the positions of S atoms in the two kinds of distorted rings shown in Fig. 3(a). The structure of the molecular chains along A-B in Fig. 2 seems to be aligned along a straight line compared to that of the α phase along the (**b-a**) axis, as shown in Fig. 3(b). However, the straight molecular arrangement along the a axis is in good agreement with that in Fig. 2. In order to discuss the details further, fine crystal parameters of the α phase are necessary.

Original unit cells of the κ and α phases look completely different from each other. However, e.g., when the α phase is grown by making the direction (**b-a**) in Fig. 3(b) parallel to the c axis of the κ phase in Fig. 1(b), periodicity in the direction of the α phase is 1.413 nm and is closer to the value of the lattice constant along the c axis of the κ phase, 1.3124 nm. This may be the reason for the

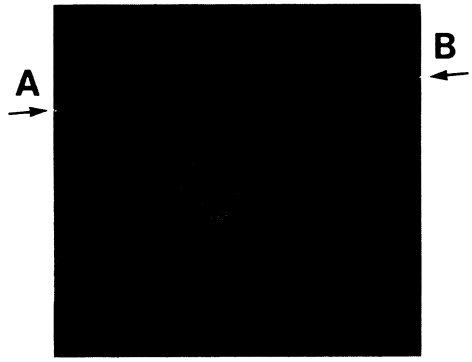

FIG. 2. STM image of a (BEDT-TTF)$_2$Cu(NCS)$_2$ crystal surface ($V_t=-22$ mV, $I_s=2.8$ nA, 6.5×6.5nm^2).

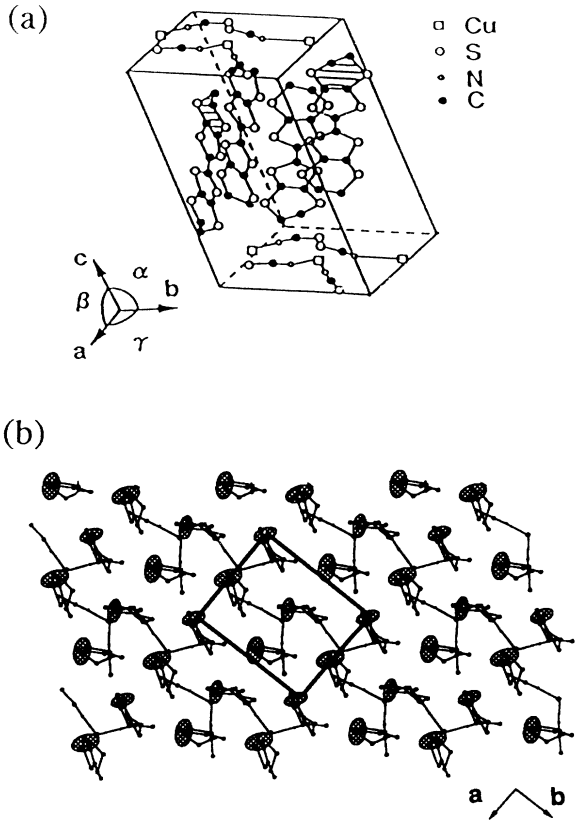

FIG. 3. (a) Crystal structure of α-(BEDT-TTF)$_2$Cu(NCS)$_2$. (b) Molecular arrangement of the α-(BEDT-TTF)$_2$Cu(NCS)$_2$ crystal projected on the crystal a-b plane (□, Cu; ○, S; ●, C; ○, N).

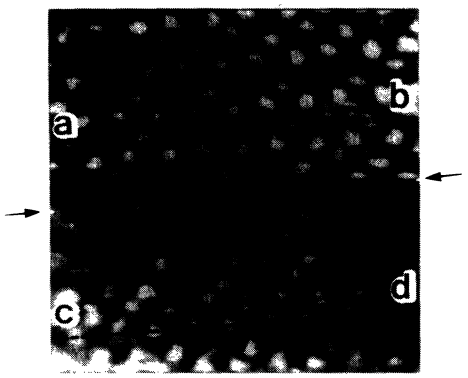

FIG. 4. STM image of a domain structure in a (BEDT-TTF)$_2$Cu(NCS)$_2$ crystal surface. Domain boundary is indicated by arrows.

growth of the α phase under conditions similar to those required for growth of the κ phase. Actually, the κ phase [Fig. 1(a)] and the alternative phase (Fig. 2) were observed to satisfy this directional relationship.

Figure 4 shows a STM image of a domain structure ($V_t = -22$ mV, $I_s = 2.8$ nA). The domain boundary is indicated by arrows. In consideration of the zigzag features along a-b and c-d in Fig. 4, the upper and lower domains are thought to correspond to the κ and the alternative phase, respectively. The periodicities along a-b and c-d are 1.32 and 1.38 nm, respectively, which agree well with the values of the κ and the α phase structures in these directions (1.3124 and 1.413 nm, respectively). Distortion around the boundary is possibly caused by the 7% incommensurate structure between both phases along the a-b and c-d directions. Since the image was taken in the constant-height mode, step height at the boundary could not be determined here.

In order to examine the electronic property of the crystal, the temperature dependence of the I-V (tunneling current–bias voltage) curve was measured. Figure 5 shows a series of I-V curves measured at curves a, 277; b, 175; c, 27.7; d, 7.8; and e, f, 78 K. Since it was difficult to maintain a constant distance between the tip and the sample upon changing temperature, measurements were performed under the conditions of (V_t, I_s) for curves a, (0.05 V, 0.5 nA); b, (0.32 V, 0.5 nA); c, (1.0 V, 0.5 nA); d, (0.20 V, 0.5 nA); and e, (0.199 V, 0.5 nA) for each measurement. Therefore, even if absolute values cannot be compared, relative features can be discussed well.

As shown in Fig. 5, conductivity decreased with temperature and the semiconductor character appeared at 175 K, supporting the existence of a molecular structure

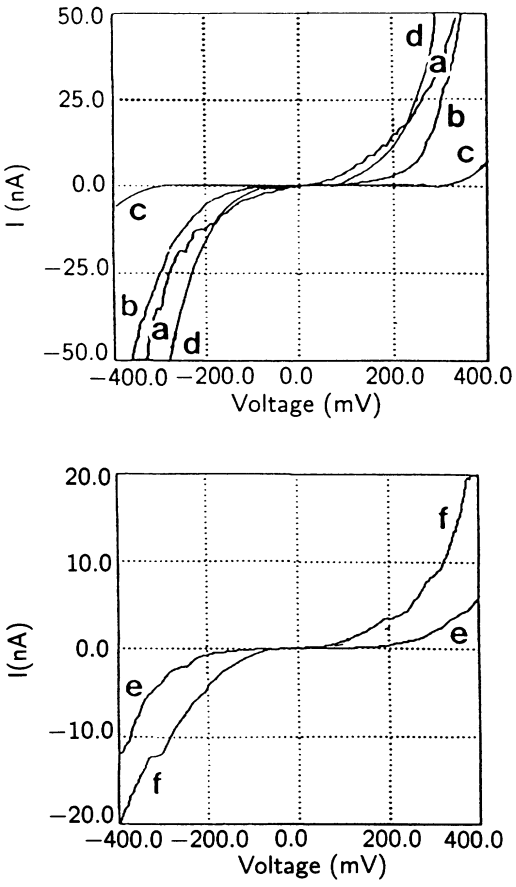

FIG. 5. Series of I-V curves measured at curves a, 277; b, 175; c, 27.7; d, 7.8; and e, 78 K. I-V curve f, measured at 78 K under soft contact of the tip with the sample surface.

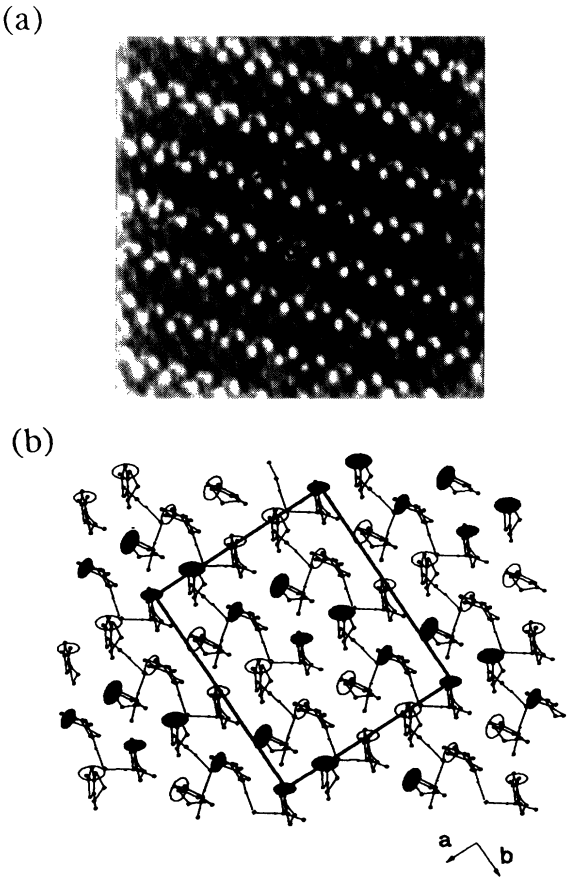

FIG. 6. (a) STM image of a (BEDT-TTF)$_2$Cu(NCS)$_2$ crystal with periodic modulation in charge density ($V_t = 23$ mV, $I_s = 2.7$ nA, 9×9 nm^2). (b) Molecular arrangement of α-(BEDT-TTF)$_2$Cu(NCS)$_2$. A 2×2 unit cell with modulated charge density on the BEDT-TTF molecules is indicated by hatched and open ellipses.

that exhibits a metal-insulator transition such as the α phase ($T_c = 200$ K). Actually, the electronic character became almost insulative around 30 K. However, as expected, when the sample temperature was decreased to ~ 15 K, an abrupt increase in conductivity began to be observed, which was attributed to the transition into the superconducting phase occurring in the κ-(BEDT-TTF)$_2$Cu(NCS)$_2$. When the STM tip was softly contacted onto the sample surface at 78 K where CDW was thought to be formed, the metallic character was recovered again, as shown in Fig. 5 (curves *e* and *f*). This recovery of the metallic character may be related to the disturbance of the CDW phase due to a distortion of the crystal surface caused by the contact.[6-8] The *I-V* characteristics should be measured for both phases by directly observing changes in the structural images. However, when the temperature was decreased, imaging became very unstable, similarly to a previous report on the STM measurement of the TTF-TCNQ (tetrathiafulvalene-tetracyanoquinodimethane) surface,[7] and a direct observation of the structural changes could not be achieved.

Figure 6(a) shows a STM image obtained on the same surface at ~ 280 K. The molecular arrangement is similar to the original structure of the alternative phase; however, there exists a 2×2 periodic modulation in the brightness, as shown in the figure. A unit cell is drawn in Fig. 6(a). The measured size of the unit cell is 1.72×2.19 nm^2, which is close to that of the 2×2 structure of the α phase (1.81×2.17 nm^2). Figure 6(b) shows a schematic structure of the α-(BEDT-TTF)$_2$Cu(NCS)$_2$ crystal, which is similar to that in Fig. 3(b). By comparing the schematic structure with the STM image in Fig. 6(a), positions of the *S* orbitals forming the 2×2 structure are marked by hatched ellipses here. There is good agreement between the obtained image and the 2×2 structure. As is shown in Figs. 6(a) and 6(b), a superstructure with modulated charge density is formed by uniting two BEDT-TTF molecules. Since details of the α phase have not been studied yet, it is difficult to analyze the α phase on an atomic scale. However, when two-dimensional BEDT-TTF conductive layers in the α phase have a $2k_F$-like CDW originating from the BEDT-TTF dimer unit, formation of such a structure as shown in Fig. 6(b) can be expected. In the case of the TTF-TCNQ, a superstructure was imaged at much higher temperatures (~ 80 K) than the transition temperature (~ 50 K).[7] By using x-ray diffraction, CDW was observed even at ~ 200 K. Therefore, partial CDW formation can be expected at high temperatures such as ~ 280 K for the α-(BEDT-TTF)$_2$Cu(NCS)$_2$ crystal.[9]

In conclusion, a structure was found to coexist in κ-(BEDT-TTF)$_2$Cu(NCS)$_2$, the molecular and electronic properties of which agree with those of α-(BEDT-TTF)$_2$Cu(NCS)$_2$, which was previously reported as a charge-transfer salt with metal-insulator transition at ~ 200 K. A 2×2 superstructure with modulated charge density was also observed at ~ 280 K, which was formed by uniting two BEDT-TTF molecules and might account for a CDW occurring.

We wish to thank Dr. N. Kinoshita of Electrotechnical Laboratory for allowing use of their x-ray diffraction data on the α-(BEDT-TTF)$_2$Cu(NCS)$_2$ crystal. We also thank UNISOK Corp. for their help in the measurement at low temperatures. This work was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan. Support from the Iketani, Izumi, Kurata, and Mikitani Foundations is also acknowledged.

[1]U. Geiser, H. H. Wang, K. M. Donega, B. A. Anderson, J. M. Williams, and J. F. Kwak, Inorg. Chem. **25**, 401 (1986).

[2]N. Kinoshita, K. Takahashi, K. Murata, M. Tokumoto, and H. Anzai, Solid State. Commun. **67**, 465 (1988); N. Kinoshita, M. Tokumoto, K. Murata, K. Takahashi, H. Anzai, T. Mori, and K. Honda, Synth. Met. **41-43**, 2107 (1991).

[3]H. Urayama, H. Yamochi, G. Saito, K. Nozawa, T. Sugano, M. Kinoshita, S. Sato, K. Oshima, A. Kawamoto, and J. Tanaka, Chem. Lett. **1988**, 55.

[4]M. Yoshimura, H. Shigekawa, H. Nejoh, G. Saito, Y. Saito, and A. Kawazu, Phys. Rev. B **43**, 13 590 (1991).

[5]M. Yoshimura, H. Shigekawa, H. Yamochi, G. Saito, Y. Saito, and A. Kawazu, Phys. Rev. B **44**, 1970 (1991).

[6]Such an interaction may be related to the fact that superstructures of a charge density wave, expected to be formed along the one-dimensional conductive molecular rows in TTF-TCNQ and (BEDT-TTF)$_2$PF$_6$ crystals, could not be observed by STM (Refs. 7 and 8).

[7]S. Pan, A. L. Delozanne, and R. Fainchtein, J. Vac. Sci. Technol. B **9**, 1017 (1991).

[8]H. Shigekawa, K. Miyake, Y. Aiso, H. Oigawa, T. Mori, and A. Kobayashi, Synth. Met. (to be published).

[9]In fact, κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ crystal shows an anomaly in the temperature dependence of resistivity. It is metallic down to around 270 K with weak temperature dependence. However, an upturn of resistivity appears around 270 K and it continues down to ~ 90 K. This anomaly may be caused by the coexistence of the α phase. K. Oshima, H. Urayama, H. Yamochi, and G. Saito, J. Phys. Soc. Jpn. **57**, 730 (1988).

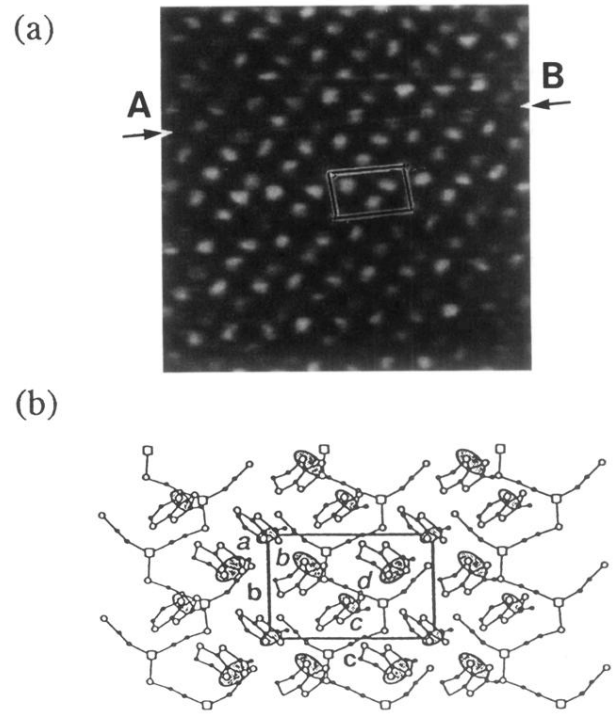

FIG. 1. (a) STM image of a $(BEDT\text{-}TTF)_2Cu(NCS)_2$ crystal ($V_t = -22$ mV, $I_s = 2.8$ nA, 6.5×6.5 nm^2). (b) Molecular arrangement of the $(BEDT\text{-}TTF)_2Cu(NCS)_2$ crystal projected on the crystal b-c plane (□, Cu; ○, S; ●, C; ○, N) (Ref. 4).

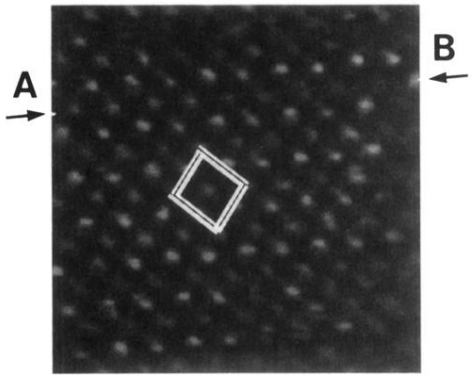

FIG. 2. STM image of a $(BEDT\text{-}TTF)_2Cu(NCS)_2$ crystal surface ($V_t = -22$ mV, $I_s = 2.8$ nA, $6.5 \times 6.5 nm^2$).

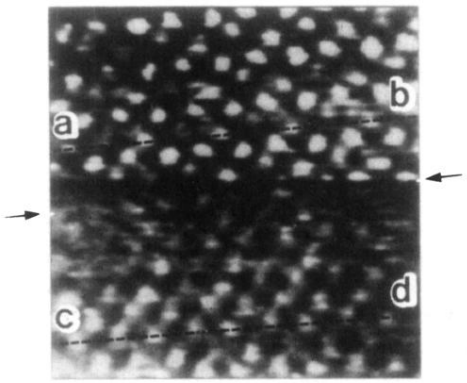

FIG. 4. STM image of a domain structure in a (BEDT-TTF)$_2$Cu(NCS)$_2$ crystal surface. Domain boundary is indicated by arrows.

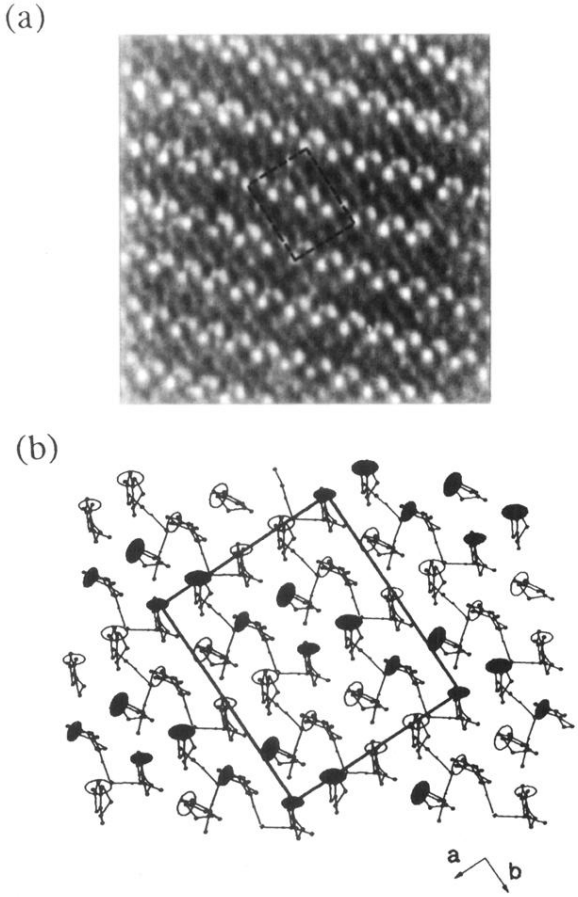

FIG. 6. (a) STM image of a $(BEDT\text{-}TTF)_2Cu(NCS)_2$ crystal with periodic modulation in charge density ($V_t = 23$ mV, $I_s = 2.7$ nA, 9×9 nm^2). (b) Molecular arrangement of α-$(BEDT\text{-}TTF)_2Cu(NCS)_2$. A 2×2 unit cell with modulated charge density on the BEDT-TTF molecules is indicated by hatched and open ellipses.