Observation of an organic superconductor [bis(ethylenedithio)-tetrathiafulvalene]$_2$ [Cu(NCS)$_2$] by scanning tunneling microscopy

M. Yoshimura, K. Fujita, N. Ara, M. Kageshima, R. Shioda, and A. Kawazu
Department of Applied Physics, The University of Tokyo, Hongo 7-3-1, Bunkyo-ku, Tokyo 113, Japan

H. Shigekawa
Institute of Materials Science, University of Tsukuba, Tsukuba Science City 305, Japan

S. Hyodo
School of Science and Technology, Meiji University, Tama-ku, Kawasaki 214, Japan

(Received 10 July 1989; accepted 23 August 1989)

The surface of an organic high-T_c superconductor, (BEDT-TTF)$_2$[Cu(NCS)$_2$] [BEDT-TTF: bis(ethylenedithio)tetrathiafulvalene, $T_c = 10.4$ K under ambient pressure], was observed with a scanning tunneling microscope in air and at room temperature. The step height observed on its surface was 13.2 Å and was very close to the one layer thickness of the (BEDT-TTF)$_2$[Cu(NCS)$_2$] crystal (15.22 Å, determined by x-ray diffraction). Periodic zig-zag structures were observed along the diagonal line of the surface unit cell and agreed well with the two-dimensional BEDT-TFF molecular structure projected onto its crystal *b-c* plane.

(BEDT-TTF)$_2$[Cu(NCS)$_2$] [BEDT-TTF: bis(ethylenedithio)tetrathiafulvalene] is a very intriguing material because of the fine stability of its molecular structure in the crystal and its high transition temperature of super conductivity ($T_c = 10.4$ K under ambient pressure).[1,2] Atomically resolved electronic and geometric structure analysis of this crystal will be necessary to reveal the microscopic mechanism of this high-T_c organic superconductor.

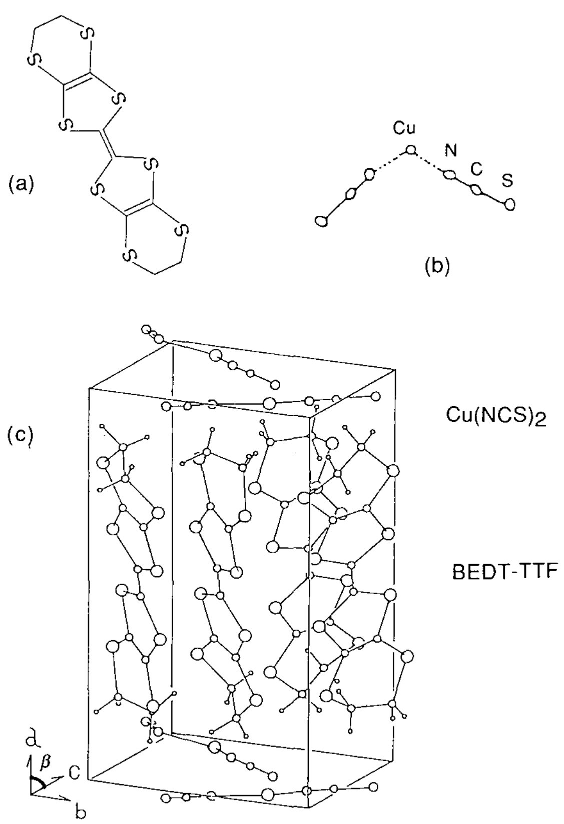

FIG. 1. (a) Molecular structure of BEDT-TTF. (b) Molecular structure of Cu(NCS)$_2$. (c) Crystal structure of (BEDT-TTF)$_2$[Cu(NCS)$_2$], which has a monoclinic structure ($a = 16.248$ Å, $b = 8.440$ Å, $c = 13.124$ Å, $\beta = 110.30°$, $V = 1688.0$ Å^3), as determined by x-ray diffraction.

The molecular structures of BEDT-TTF and Cu(NCS)$_2$ are shown in Figs. 1(a) and (b). Their molecular arrangement in the crystal of (BEDT-TTF)$_2$[Cu(NCS)$_2$], determined by x-ray diffraction, is shown in Fig. 1(c).[3] The (BEDT-TTF)$_2$[Cu(NCS)$_2$] crystal has a monoclinic structure which consists of alternating stacked layers of two-dimensional networks of BEDT-TTF molecules and Cu(NCS)$_2$ molecules ($a = 16.248$ Å, $b = 8.440$ Å, $c = 13.124$ Å, $\beta = 110.30°$, $V = 1688.0$ Å^3) [Fig. 1(c)]. Through the electron transfer from BEDT-TTF layers to Cu(NCS)$_2$ layers, the former layers have two-dimensional conductivity in the crystal *b–c* plane, while the latter layers become insulative.

Scanning tunneling microscopy (STM) observations were performed over the crystal *b–c* plane. A platinum–iridium tip was used. Figure 2(a) shows a line scan image of the crystal surface obtained by the constant current mode (-0.3 V tip to sample, 3 nA). A step-like structure exists on the surface, and its cross section is drawn in Fig. 2(b). The step height obtained experimentally is about 13.2 Å and is very close to the thickness of the one-layer (BEDT-

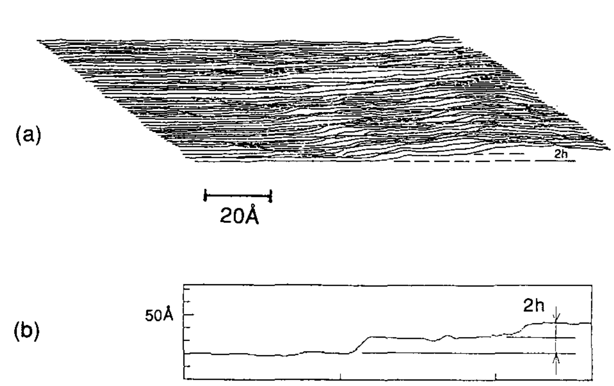

FIG. 2. (a) Line scan image of the (BEDT-TTF)$_2$[Cu(NCS)$_2$] crystal obtained by the constant current mode (-0.3 V tip to sample, 3 nA). Scan area is 130×61 Å^2. (b) Cross section of the step structure in (a). Step height **h** is 13.2 Å.

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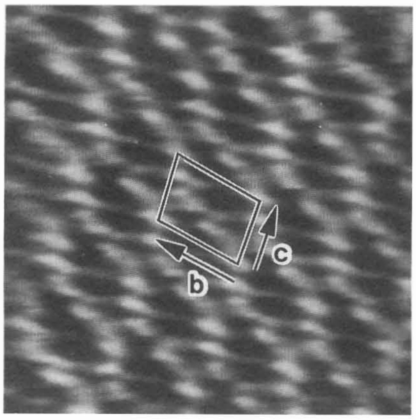

FIG. 3. Grey scale image of the $(BEDT-TTF)_2[Cu(NCS)_2]$ surface obtained by the constant current mode (46 mV tip to sample, 4.47 nA). Scan area is 60×60 Å^2. Periodic zig–zag structure is observed along the diagonal line of the unit cell (9.6×15.0 Å^2).

$TTF)_2[Cu(NCS)_2]$ crystal, as determined by x-ray diffraction (15.22 Å).

Figure 3 shows a gray scale image of $(BEDT-TTF)_2[Cu(NCS)_2]$ obtained by the constant current mode (46-mV-tip to sample, 4.7 nA, scan area 60×60 Å^2). Periodic zig-zag structure can be observed along the diagonal line of the unit cell drawn in the figure (about 9.6×15.0 Å^2 no drift correction). The same structure was observed with the opposite bias voltage of − 46 mV, which indicates that the surface has a metallic property, and the periodic structure in Fig. 3 is expected to correspond to the surface structure of BEDT-TTF layers. In addition, the STM image had a strong tunneling voltage dependence.[4] Figure 4 shows a magnified image with a bias voltage of + 66 mV which has a finer structure along the crystal *b* axis (no drift correction). The structure consists of four kinds of protrusions [labeled with A, B, C, D in Fig. 4(a)] which are supposed to correspond to the four BEDT-TTF molecules in the unit cell of the BEDT-TTF layer. A top view of the BEDT-TTF layer, projected onto the crystal *b–c* plane, is shown in Fig. 4(b). When the crystal axis as determined by x-ray diffraction is taken into consideration, two choices for the unit cell are possible [drawn in Fig. 4(a)].

In summary, the step height observed on the $(BEDT-TTF)_2[Cu(NCS)_2]$ crystal (13.2 Å) was very close to the one layer thickness of the crystal as determined by x-ray diffraction (15.22 Å). The two-dimensional periodic structure of the STM images had a metallic property and was in good agreement with the BEDT-TTF molecular structure

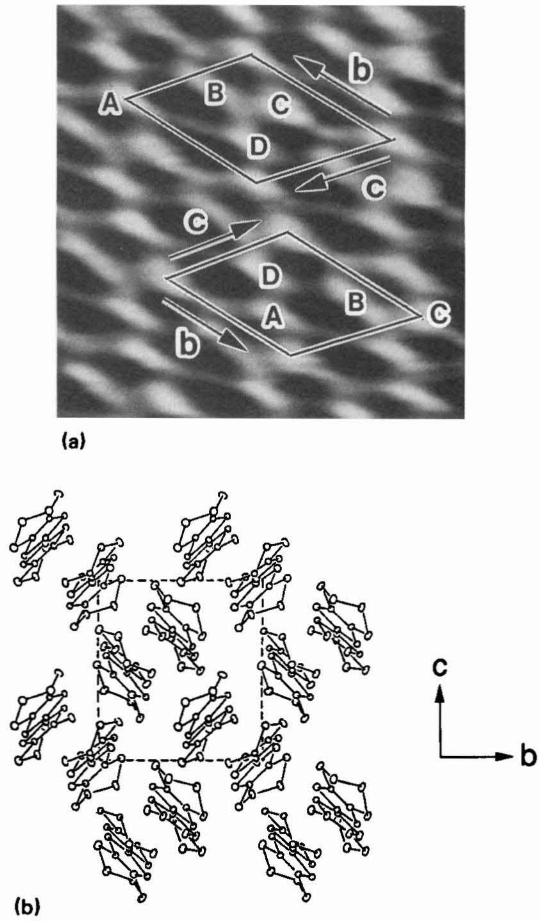

FIG. 4. (a) Grey scale image of the $(BEDT-TTF)_2[Cu(NCS)_2]$ surface obtained by the constant current mode (66 mV tip to sample, 4.6 nA). Scan area is 60×60 Å^2. Two possible unit cells are drawn with the four labeled protrusions, A, B, C, and D. (b) BEDT-TTF molecular structure projected onto the crystal *b–c* plane.

projected onto the crystal *b–c* plane.

Acknowledgment: The $(BEDT-TTF)_2[Cu(NCS)_2]$ samples used in this study were kindly supplied by Prof. G. Saito, Institute for Solid State Physics, The University of Tokyo.

[1]T. Sugano, H. Hayashi, M. Kinoshita, and K. Nishikida, Phys. Rev. B **39**, 11387 (1989).
[2]K. Oshima, T. Mori, H. Inokuchi, H. Urayama, H. Yamochi, and G. Saito, Phys. Rev. B **38**, 938 (1988).
[3]H. Urayama, H. Yamochi, G. Saito, S. Sato, A. Kawamoto, J. Tanaka, T. Mori, Y. Maruyama, and H. Inokuchi, Chem. Lett. **1988**, 463 (1988).
[4]M. Yoshimura, N. Ara, M. Kageshima, R. Shioda, A. Kawazu, H. Shigekawa, H. Mori, M. Oshima, H. Yamochi, and G. Saito, *The Physics and Chemistry of Organic Superconductors*, edited by G. Saito and S. Kagoshima (Springer, Berlin, in press).