Behavior of Charge Density Waves in a One-Dimensional Organic Conductor Visualized by Scanning Tunneling Microscopy

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Charge density waves (CDW) in a tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) single crystal have been studied with molecular resolution using a low temperature scanning tunneling microscope (STM). For the first time the periodicities of the CDW along both the *a* and *b* axes have been observed and were found to be coincident with those of the $2k_F$ CDW. The influence of crystal singularities on the ordering of the CDW along the *a* axis was also revealed. [S0031-9007(98)07263-9]

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One-dimensional organic conductors have attracted much attention due to their unique conduction mechanism. Some of them exhibit peculiar electronic behavior such as superconductivity or the Peierls transition. It has been proved that their characteristic molecular arrangement in a crystalline phase plays a crucial role in these electronic properties. The Peierls transition [1] has been attributed to the strong interaction between the electron system and the crystal lattice. This transition is associated with a charge density wave (CDW) that is a hybrid of electron wave and phonon.

Tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) is one of the typical compounds that exhibit the Peierls transition. The CDW in a TTF-TCNQ crystal have been studied mainly by scattering methods using x-rays [2–7] and neutrons [8–10]. It has been proved that the Peierls transition at 53 K is associated with CDW having a wave number twice the Fermi wave number ($2k_F$ CDW), whereas $4k_F$ CDW also exists for a wide temperature range [3]. These experimental techniques, however, can only give information averaged over a large volume of the crystal. Therefore, little knowledge has been gathered about the local appearance of CDW.

The invention of scanning tunneling microscopy (STM) [11] has enabled close studies of local structures or phenomenon at the atomic scale. Its adaptability to various imaging conditions such as temperature or atmosphere has made it one of the major imaging tools. Consequently, the STM has been expected to be a promising tool for investigation of structure and electronic properties of organic conductors. The *ab* plane of a TTF-TCNQ crystal has been imaged with STM [12–14] and atomic force microscopy (AFM) [15] with molecular resolution at room temperature. On the other hand, there has been only one report on a CDW-like superstructure below the Peierls temperature [16]. In this report, however, the modulation periodicity along the *b* axis, which is the most pronounced structure in the CDW phase, is not imaged. In addition, the appearance of the periodicity along the *a* axis does not coincide with the true CDW structure. Therefore, we consider these results to be due to artifacts such as multi-tip interference.

In the present study, STM observation of a TTF-TCNQ single crystal was performed at low temperature (LT) with particular emphasis placed on the following: (1) Imaging of the both periodicities along the *a* and *b* axes. (2) Comparison of the periodicity along the *a* axis with the theoretical prediction on its temperature dependence. (3) Effect of surface singularities on the ordering of CDW.

The TTF-TCNQ single crystals were synthesized by the diffusion method in acetonitrile solution for longer than three months. Because at a temperature below 53 K bulk conductivity of this crystal is depressed considerably, a special procedure is required at each stage of STM observation at low temperatures. Steps, cracks, or other defects blocking the *b* axis must also be taken into account as obstacles to conduction. Therefore, in mounting the crystal onto a sample holder, special care was expended to ensure the conduction paths along the *b* axis from the observation point. The low-temperature (LT) STM employed was constructed by UNISOKU Co., Ltd. For LT measurement, in order to avoid condensation of residual gas on the surfaces of the tip or the sample, the STM was cooled down to the observation temperature prior to introduction of the sample and the tip. In addition, the tip was occasionally cleaned during the observation by a voltage pulse in order to remove TTF or TCNQ molecules adsorbed onto the tip, because they form an insulation layer unless they are in a crystalline phase. This procedure was also useful in reducing the multiple-tip effect on the obtained images. All the images presented here are obtained in constant-height mode. The bias voltage applied to the STM tip is -70 to $+150$ mV; i.e., the images reflect the local density of state around the Fermi level.

The molecular arrangement of this crystal is illustrated in Fig. 1(a). Because of the closely packed configuration

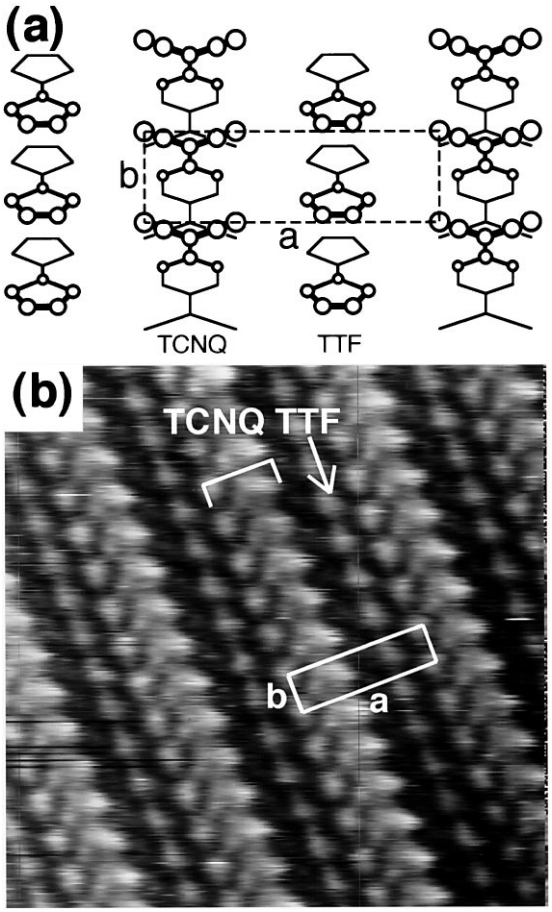

FIG. 1. (a) Molecular arrangement of TTF-TCNQ projected onto the *ab* plane. Parameters of the crystal structure are $a = 12.298$ Å, $b = 3.819$ Å, $c = 18.468$ Å, $\alpha = \beta = 90°$, and $\gamma = 104.6°$. (b) A typical STM image of the *ab* plane. The imaged area is 47 Å × 47 Å. A unit cell is indicated.

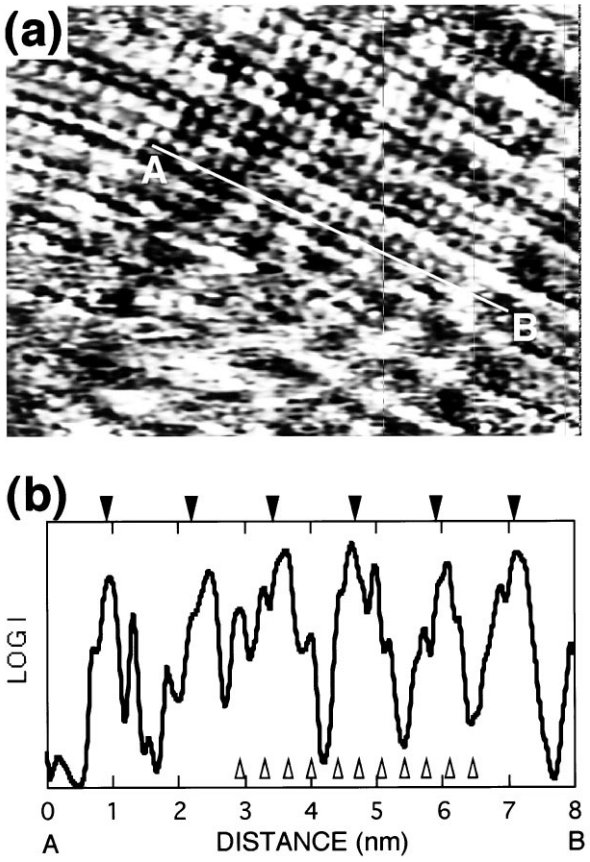

FIG. 2. (a) An STM image taken at 61 K. The imaged area is 117 Å × 88 Å. (b) A cross-sectional view along the line *A-B* on a TCNQ chain in (a). Upper and lower arrowheads indicate the positions of CDW maxima and TCNQ molecules, respectively.

along the *b* axis, the conductivity along this axis is enhanced by a factor of approximately 100 compared to conductivities along other directions. The interaction within each molecular chain along the *b* axis generates the CDW. Figure 1(b) shows an STM image of an *ab* plane obtained at RT in ultrahigh vacuum. Appearance of this image is consistent with a simulation [13] and previous results by STM [13–15] and atomic force microscopy (AFM) [16]. Both the TCNQ chain and the TTF chain are indicated in this image. Note that all the molecules within each chain appear to be equivalent at this temperature.

As the temperature decreased to below 70 K, periodic modulation on the TCNQ chains lasting during scans of several frames was observed on some limited TCNQ chains. Images with clear modulation were obtained especially near steps on the surface. Both the lifetime and the correlation range appeared to increase as the temperature decreased. Figure 2(a) shows an STM image taken at 61 K. The modulation on the TCNQ chain is clearly noticeable in this image. Figure 2(b) shows a cross-sectional view taken along a line indicated in the image. The periodicity of the modulation along the *b* axis is 12.6 ± 0.7 Å, which is in agreement with the theoretical periodicity of the $2k_F$ CDW of 12.9 Å. This appearance of the modulation was quite reproducible for different tips and samples. Therefore, it is natural to conclude that this modulation reflects $2k_F$ CDW in the TCNQ chains.

Studies with x rays [3,5] and inelastic neutrons [8] have revealed that at a temperature above 49 K the lattice deformation relevant to the $2k_F$ CDW in the TCNQ chain is transverse and is polarized along the *c* axis. Other studies suggest that the amount of displacement of the TCNQ molecule would be at most around 0.01 Å even in the case of the lowest temperature phase [6,7]. Because the images in this study are obtained in the constant height mode, it is impossible to derive the exact corrugation amplitude without a precise knowledge of the surface potential barrier height. However, it is reasonably confirmed that the observed modulation amplitude is significantly larger than 0.01 Å, which is almost the sensitivity limit of the STM. Therefore, the observed modulation is considered to reflect mainly the modulation in the conduction electron density.

Besides, in the surface layer, absence of an overlayer may relax the limitation on the molecular displacement, resulting in a substantial change in the CDW amplitude. For a detailed discussion, a theoretical calculation taking this effect into account is indispensable.

It is remarkable that the $2k_F$ CDW is observed to be frozen at a temperature higher than the Peierls transition temperature of 53 K. Existence of a $2k_F$ lattice wave itself has been confirmed at 150 K by x-ray studies [4,5], although it is considered to fluctuate. The present study suggests that local condensation of CDW is induced by the singularities such as steps, defects, and impurities above the Peierls transition temperature.

Below 53 K, the observation was even more difficult due to a local reduction in the conductivity. Stable observation was possible only in very limited areas. Tunneling spectra taken during these stable observations showed an energy gap of 50–100 mV. An image taken at a wide flat terrace at 42 K is shown in Fig. 3. In a part of this image the CDW in each TCNQ chain has a phase different from that of the neighboring chains by an almost same amount, resulting in a two-dimensional superstructure. The new periodicity along the a axis is approximately $(3.4 \pm 0.3)a$. This value is in agreement with the dependence curve of this periodicity on temperature that was predicted theoretically [17,18] and was confirmed by x-ray [3] and neutron [9] scattering experiments.

Figure 4 is an image of an area at a distance of approximately 30 nm from the area imaged in Fig. 3 on the same terrace. In this image a band-like region with an anomalous rise in the tunneling current is observed. Possible explanations for this anomalous region are defects, some impurities, and distortion due to thermal shrinkage. Obviously amplitude of the CDW adjacent to this region is enhanced substantially compared to Fig. 3. It is also noteworthy that phases of the CDW in TCNQ chains are aligned almost along the a axis. This type of phase ordering has not been previously reported either theoretically or experimentally. Local strain or disturbance in electric field due to the anomalous region is considered to have interacted with the CDW and have arranged it into this strange configuration. This configuration would be energetically unfavorable if only the Coulomb interaction between TCNQ chains is taken into account. At this temperature, the CDW in the TTF chains is also believed to contribute to the interchain interaction of the CDW [17,18]. In the present study, however, it was impossible to image the CDW in the TTF chains clearly. One explanation for this is the weaker intensity of this CDW compared with the CDW in the TCNQ chain. Another possibility is the complexity of this CDW due to contribution of the $4k_F$ component.

As the imaging area was moved away from this region, the ordering of CDW was observed to transform into the structure similar to the one imaged in Fig. 3, accompanied by decay of the CDW amplitude. Between the above two areas, a region where CDW is hardly perceptible was observed. This is considered to be a transient region between the two configurations.

Imaging at below 42 K was not successful because of insufficient tunneling current. This can be explained by an almost insulating character of the sample due to locking of the CDW in the entire crystal. For studies in this temperature range, a thin-film-like sample grown on the conductive substrate would be suitable.

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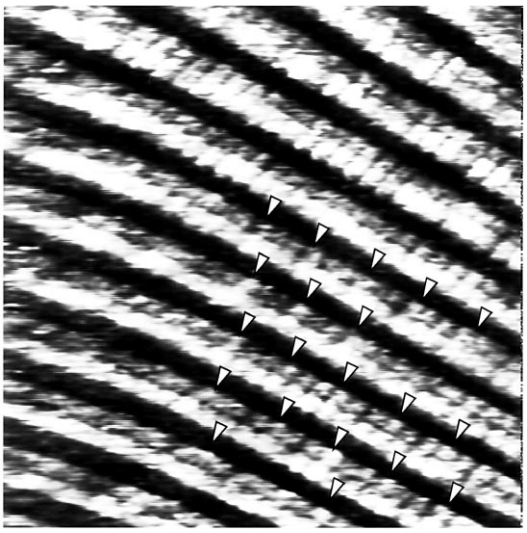

FIG. 3. An STM image taken at 42 K. Arrowheads in lower right of the image indicate noticeable peak position of CDW in TCNQ chains aligned at an approximate angle of 17° to the a axis.

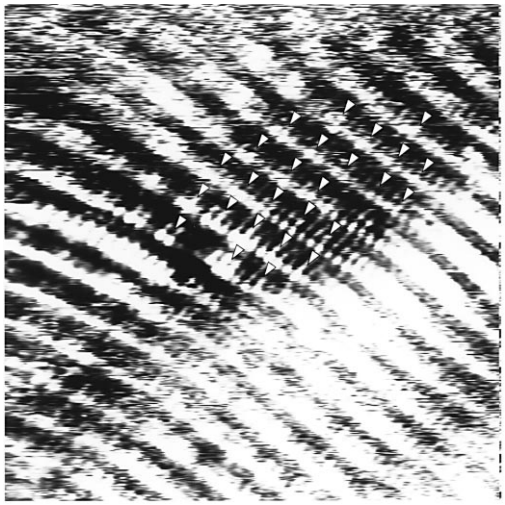

FIG. 4. An STM image taken at a position about 30 nm apart from the area in Fig. 3 at 42 K. A bandlike region with anomalous enhancement in the tunneling current is imaged in the lower right of the image. Arrowheads indicate noticeable peak position of CDW in TCNQ chains aligned almost along the a axis.

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