# Direct Observation of Growth and Melting of the Hexagonal-Domain Charge-Density-Wave Phase in $1T$-$TaS_2$ by Scanning Tunneling Microscopy

Xian Liang Wu and Charles M. Lieber
*Department of Chemistry, Columbia University, New York, New York 10027*
(Received 23 August 1989)

A variable-temperature scanning tunneling microscope has been used to elucidate the structure of the nearly commensurate (NC) charge-density-wave (CDW) phase in $1T$-$TaS_2$. Between 230 and 350 K the NC CDW phase consists of a hexagonal array of commensurate domains separated by diffuse domain walls where the CDW phase and amplitude change. The average domain period and size increase continuously as the temperature is lowered over this range. Microscopic details of this growth process are discussed.

PACS numbers: 71.45.Lr, 61.16.Di, 64.70.Kb

Weakly interacting incommensurate systems such as charge-density waves (CDW) and gases physisorbed onto surfaces have been the focus of considerable theoretical[1-5] and experimental[6-11] effort since these systems can exhibit a variety of distinct structures. In particular, when the period of an incommensurate superlattice is close to registry with the atomic lattice, the ground state of the system may consist of commensurate domains separated by domain walls (where the phase changes) rather than a uniformly incommensurate structure.[1-5,8-11] To date, experimental support for domainlike incommensurate phases has rested mainly on the observation of second- and higher-order diffraction satellites. These measurements are by nature indirect and their interpretation has been controversial for several incommensurate structures including the nearly commensurate (NC) CDW phase in $1T$-$TaS_2$.[7,8] Determination of the detailed structure and temperature dependence of such domain phases is, however, crucial for testing and developing theoretical models of these interesting incommensurate systems. In this Letter we present new results obtained with a scanning tunneling microscope (STM) that directly characterize the temperature dependence of the intralayer structure of the NC hexagonal-domainlike CDW phase in $1T$-$TaS_2$. We show that between 230 and 350 K the NC CDW phase consists of a hexagonal array of commensurate domains separated by diffuse walls where the CDW phase and amplitude change. We also demonstrate that both the period and domain size increase significantly as crystals are cooled over this temperature interval. Notably, microscopic details of this continuous growth process have been elucidated from the analysis of real-space CDW-lattice images.

The NC CDW phase is one of four distinct temperature-dependent CDW phases in $1T$-$TaS_2$.[6,12] These include a hexagonal incommensurate (IC) phase (543 to 353 K), the NC phase (353 to 183 K on cooling and 283 to 353 K on warming), a triclinic incommensurate phase (223 to 283 K on warming), and a low-temperature commensurate (C) phase. Early theoretical work by Nakanishi and Shiba predicted that the NC phase would have a hexagonal domain structure.[3] Experimental studies[7,8,13-17] have, however, been proposed to support either this theoretically predicted domain structure or a structure in which the CDW superlattice phase and amplitude are uniform. None of these investigations have been able to determine unambiguously the structure of this phase, although we have recently shown by STM that at 298 K the intralayer CDW structure of $1T$-$TaS_2$ consists of a hexagonal array of domains and is not uniform.[17]

Single-crystal samples of $1T$-$TaS_2$ were grown over a three week period by iodine transport in a 950° to 880 °C temperature gradient.[17] The CDW phase-transition temperatures for these crystals were determined by variable-temperature resistivity measurements and are found to agree with reported values.[6,12] The STM used in these studies is based on a commercial instrument[18] that has been modified[16] to carry out variable-temperature experiments. The samples were cleaved in an air or argon atmosphere and covered with oil. The temperature was measured using a calibrated thermocouple placed next to the sample and is believed to be accurate to within $\pm 0.5$ °C. Images were recorded in the constant-current mode using platinum-iridium (80-20) alloy tips. The digital image data were processed and analyzed as described previously.[17,19]

A series of grey-scale images recorded between 240 and 360 K with a bias voltage of 10 mV and a tunneling current of 2 nA are shown in Fig. 1. Similar results were observed when the temperature was either lowered or raised over this temperature range. In the smaller images both the CDW (period $\approx$ 12 Å) and the atomic lattice (period=3.35 Å) are resolved. A novel feature of the images of the NC phase [Figs. 1(a)–1(c)] is the periodic modulation in the CDW vertical corrugation that defines domains consisting of relatively high-amplitude CDW maxima that are separated by regions (domain walls) in which the CDW amplitude is lower.[17] Images recorded in the constant-height mode at room

 

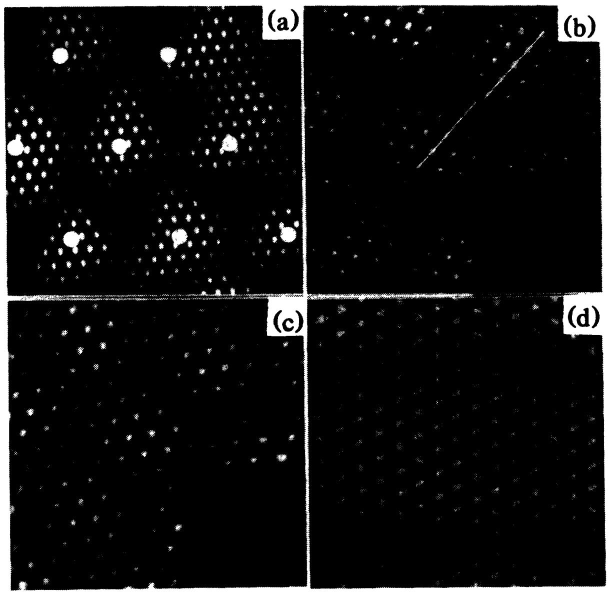


FIG. 1. A series of STM images of $1T$-$TaS_2$ recorded with a 2-nA tunneling current and a +10-mV bias voltage at sample temperatures of (a) 242 K, (b) 298 K, (c) 349 K, and (d) 357 K. The images are of (a) $300\times300$, (b) $175\times175$, and (c), (d) $155\times155$ Å$^2$ areas. The insets in (b) and (c) are $300\times300$ Å$^2$ as in Fig. 1(a). The domain center positions for an ideal hexagonal structure are marked with white dots in (a) and are clearly different from the center positions of the two domains in the upper right corner. Lines drawn through the CDW maxima of two adjacent domains in (b) highlight the one-lattice-period CDW phase shift that occurs between domains.

temperature also exhibit these same features, in contrast to the results reported in Ref. 16. The approximately circular domains of high-amplitude CDW maxima are arranged in a hexagonal superstructure with a period that depends strongly on temperature [see insets of Figs. 1(b) and 1(c)]. The variation in the amplitude of the CDW maxima within the domains, $0.07\pm0.05$ Å, is significantly smaller than the $(0.6\pm0.2)$-Å decrease in the CDW amplitude that occurs at the domain walls.[20] This decrease in amplitude at the domain-wall regions has been observed for every sample examined and is also independent of temperature (230–350 K). In addition, evaluation of atomic-resolution images demonstrates that at all temperatures between 230 and 350 K the CDW undergoes a well-defined one-lattice-period phase shift across the domain walls. This phase change is highlighted by lines through the CDW's in two adjacent domains in Fig. 1(b). The one-lattice-period phase shift represents an important feature that distinguishes this domainlike phase from a uniformly NC phase. Furthermore, images of the IC phase [Fig. 1(d), $T=357$ K] exhibit the expected[6,16] uniform triple CDW structure and show no evidence for domainlike features, in contrast to our results for the NC phase; hence, it is unlikely that the domain structure in Figs. 1(a)–1(c) is due to imaging artifacts.

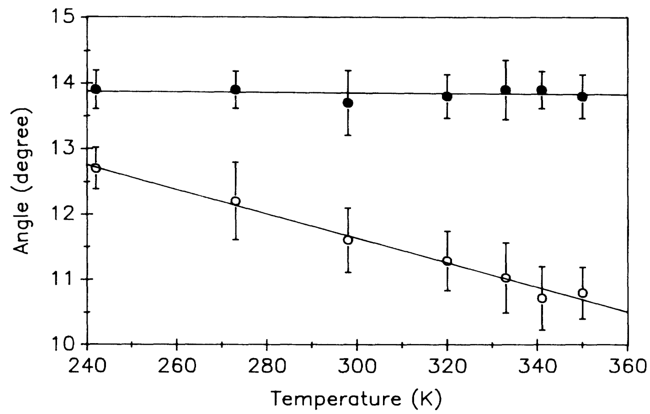


FIG. 2. The CDW–atomic-lattice orientation angle as a function of temperature. The STM data were obtained from measurements made locally within domains (●) and by averaging across several domains (○). The error bars represent ±1 standard deviation. The discontinuity at the NC-IC transition (353 K) is not shown.

The observation of a reproducible decrease in the CDW amplitude and an abrupt one-lattice-period phase change at the domain walls is consistent with the theoretical analysis of the hexagonal-domain phase in $1T$-$TaS_2$ (Ref. 3) and our recent room-temperature measurements.[17] In addition, a general requirement for a domainlike phase is that the superlattice (CDW or gas overlayer) is commensurate with the atomic lattice in the domains. For $1T$-$TaS_2$ the commensurability condition is met with a well-defined 13.9° rotation of the CDW superlattice. Since the CDW superlattice and atomic lattice have been simultaneously imaged in this study we have been able to evaluate the CDW-lattice orientation locally within single domains. Results from the analysis of an extensive series of images recorded at temperatures between 240 and 350 K are shown in Fig. 2. We find that within a given domain the CDW-lattice angle is close to the commensurate value of 13.9° and that this angle is independent of temperature.[21] In addition, we have determined that the "average" CDW-lattice orientation angle defined using a CDW vector that spans several domains exhibits a significant temperature dependence (Fig. 2). Previously, similar temperature-dependent variations in the orientation angle have been proposed to support a uniform NC phase structure;[7,16] however, from our work it is apparent that this conclusion is due to the inability to resolve the phase change that occurs between domains.[17]

One of the most interesting features evident from the analysis of images recorded between 230 and 350 K is the strong temperature dependence of the hexagonal domain structure. The temperature-dependent changes in the hexagonal-domain period are clearly evident when comparing Fig. 1(a) with the insets of Figs. 1(b) and 1(c) since these three images (recorded at 242, 298, and

349 K, respectively) all cover $300\times300$ Å$^2$ areas. We have summarized the domain-period and domain-size versus temperature data in Fig. 3. The period increases linearly from $58\pm3$ to $94\pm4$ Å between 349 and 230 K with a clear discontinuity at the first-order IC-NC transition (353 K). This discontinuity has not been shown in Figs. 2 and 3, however. We also find that the domain size, which is characterized by the number of commensurate CDW maxima per domain,[22] increases on cooling. It is likely that the energetic contribution from lock-in of the CDW to the atomic lattice in the domains drives the growth process. Although temperature-dependent changes of a striped-domain CDW phase in $2H$-$TaSe_2$ have been reported,[9,10] we note that the observed growth (melting) of the hexagonal domain structure in $1T$-$TaS_2$ on cooling (warming) occurs over an order-of-magnitude larger temperature range and in this respect is quite remarkable. Furthermore, our images in which the CDW's and atomic lattice are simultaneously resolved can be used to assess directly microscopic details of the growth and melting process.

First we consider the domain walls. Nakanishi and Shiba have predicted that the boundaries between domains should sharpen as the temperature is decreased.[3] In contrast, we observe diffuse domain walls that are 2–3 CDW periods wide (ca. 24–36 Å) and nearly independent of temperature.[23] Sharp domain walls on the order of a single CDW period are not experimentally observed near the NC-C transition and, in fact, are not expected since there is a significant strain energy associated with the CDW and lattice distortions required to form such a domain wall.[24] We have also considered the atomic details of the CDW phase shift across a domain wall. Two structural models for the lattice-period phase change that occurs across 2-CDW-period-wide domain walls are shown in Fig. 4; other possibilities that involve greater distortions of the CDW have been considered[24] but will not be discussed here.

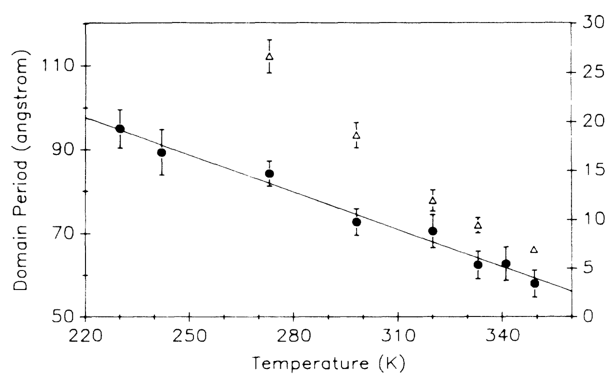


FIG. 3. A plot of the NC-CDW-phase domain period (●) and domain size (△) vs temperature. The domain size is characterized by the number of commensurate CDW maxima per domain (Ref. 22). The discontinuity at the NC-IC transition (353 K) is not shown.

Notably, statistical analysis of the distances experimentally determined between the closest CDW maxima in adjacent domains [Fig. 4(c)] demonstrates that Fig. 4(a) more accurately depicts the details of the phase change across a domain wall.

This analysis indicates that only discrete values are possible for the separation between adjacent domains. Hence, continuous growth of the domain structure on cooling requires that there be fluctuations in the domain size and domain-wall width. Experimentally, we find that the average domain period changes continuously, although at a given temperature the distribution of periods about the average is non-Gaussian. Further analysis of the domain structure shows that this non-Gaussian distribution is due to local fluctuations in the domain-wall width and domain size, and that the NC CDW phase is, in fact, quasiperiodic and not rigorously hexagonal [for example, see Fig. 1(a)]. On the basis of these results we

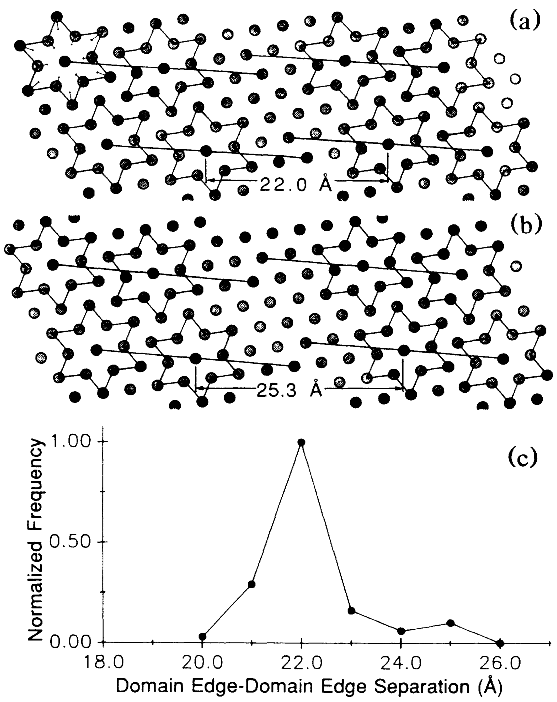


FIG. 4. (a),(b) Two model structures for the one-lattice-period CDW phase shift that occurs between adjacent domains. The shaded circles in (a) and (b) represent the atomic lattice. Each commensurate CDW maximum [located at the solid circles in (a) and (b)] is associated with 13 lattice sites that form a star-shaped cluster; the lattice distortions for one cluster are indicated by arrows in (a). The expected commensurate positions for a CDW maximum associated with either the left or right domain are represented by half-filled circles in the boundary region. These positions highlight the different distortions of the CDW (compression and stretching) that give rise to the phase shift in (a) and (b). (c) Normalized frequency of the experimentally determined distance between CDW maxima at the edges of adjacent domains.

suggest that continuous growth and melting of this domainlike CDW phase occurs via localized distortions or fluctuations of the hexagonal structure which results in a quasiperiodic packing of the commensurate domains.[25]

In summary, a variable-temperature tunneling microscope has been used to elucidate the intralayer structure of the hexagonal-domain NC CDW phase in $1T$-$TaS_2$. We demonstrate that between 230 and 350 K the intralayer structure of this phase consists of commensurate domains separated by diffuse domain walls in which the CDW undergoes a well-defined one-lattice-period phase shift and the amplitude decreases by 0.6 Å. The domain period and size also increase (decrease) continuously on cooling (warming) over this temperature range. In addition, we have shown that only discrete domain-wall widths are likely, and that the continuous changes of domain structure between 230 and 350 K occur via local fluctuations in the domain-wall width and domain period.

C.M.L. acknowledges support of this work by the David and Lucile Packard Foundation and the National Science Foundation.

[1]F. C. Frank and J. H. van der Merwe, Proc. Roy. Soc. London **198**, 205 (1949).

[2]W. L. McMillan, Phys. Rev. B **14**, 1496 (1976).

[3]K. Nakanishi and H. Shiba, J. Phys. Soc. Jpn. **43**, 1839 (1977).

[4]P. Bak, D. Mukamel, J. Villain, and K. Wentowski, Phys. Rev. B **19**, 1610 (1979).

[5]J. P. McTague and A. D. Novaco, Phys. Rev. B **19**, 5299 (1979).

[6]J. A. Wilson, F. J. DiSalvo, and S. Mahajan, Adv. Phys. **24**, 117 (1975).

[7]C. B. Scruby, P. M. Williams, and G. S. Parry, Philos. Mag. **31**, 255 (1975).

[8]K. Nakanishi, H. Takatera, Y. Yamada, and H. Shiba, J. Phys. Soc. Jpn. **43**, 1509 (1977).

[9]C. H. Chen, J. M. Gibson, and R. M. Fleming, Phys. Rev. Lett. **47**, 723 (1981).

[10]Y. Koyama, Z. P. Zhang, and H. Sato, Phys. Rev. B **36**, 3701 (1987).

[11]J. Cui, S. C. Fain, Jr., H. Freimuth, H. Wiechert, H. P. Schildberg, and H. J. Lauter, Phys. Rev. Lett. **60**, 1848 (1988).

[12]S. C. Bayliss, A. M. Ghorayeb, and D. R. P. Guy, J. Phys. C **17**, L533 (1984).

[13]H. P. Hughes and R. A. Pollak, Commun. Phys. **1**, 61 (1976).

[14]G. van Tendeloo, J. van Landuyt, and S. Amelinckx, Phys. Status Solidi **64**, K105 (1981).

[15]A. Yamamoto, Phys. Rev. B **27**, 7823 (1983).

[16]R. E. Thomson, U. Walter, E. Ganz, J. Clarke, A. Zettl, P. Rauch, and F. J. DiSalvo, Phys. Rev. B **38**, 10734 (1988).

[17]X. L. Wu and C. M. Lieber, Science **243**, 1703 (1989).

[18]Nanoscope, Digital Instruments, Inc., Santa Barbara, CA.

[19]X. L. Wu, P. Zhou, and C. M. Lieber, Phys. Rev. Lett. **61**, 2604 (1988).

[20]The difference in CDW vertical corrugation is determined between the atomic peaks of the CDW maxima in the domain and in the domain wall, and hence are not a superposition of the atomic and CDW deflections. The domain wall corresponds to the region between two adjacent domains. The amplitude difference reported in Ref. 17 (1 Å), however, was determined between the CDW maxima in the domain and in the hollow between three adjacent domains.

[21]The similar array of atoms at the CDW maxima within domains indicates qualitatively that the CDW is commensurate. In addition, the small variations observed in these arrays are expected on the basis of theoretical calculations for the domainlike phase (Ref. 3).

[22]Within a domain the commensurate CDW maxima have a similar array of atomic peaks (Ref. 21), but since the domain walls are not sharp the exact value of this quantity is uncertain. Nevertheless, we believe that the general trend in our results is correct.

[23]The density of domain wall does, however, decrease on cooling. McMillan postulated that domain walls can be removed from the system by CDW dislocations (Ref. 2), although we have been unable to find direct evidence for dislocations in $1T$-$TaS_2$.

[24]X. L. Wu and C. M. Lieber (unpublished).

[25]Impurities can also cause local distortions of the domain structure, although direct studies of impurity effects indicate that the present observations are intrinsic to pure $1T$-$TaS_2$; X. L. Wu and C. M. Lieber, J. Am. Chem. Soc. **111**, 2731 (1989).

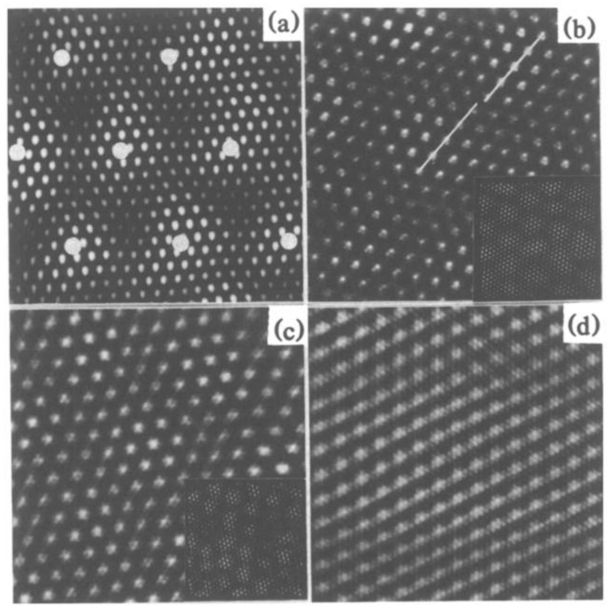


FIG. 1. A series of STM images of $1T$-$TaS_2$ recorded with a 2-nA tunneling current and a +10-mV bias voltage at sample temperatures of (a) 242 K, (b) 298 K, (c) 349 K, and (d) 357 K. The images are of (a) 300×300, (b) 175×175, and (c), (d) 155×155 Å$^2$ areas. The insets in (b) and (c) are 300×300 Å$^2$ as in Fig. 1(a). The domain center positions for an ideal hexagonal structure are marked with white dots in (a) and are clearly different from the center positions of the two domains in the upper right corner. Lines drawn through the CDW maxima of two adjacent domains in (b) highlight the one-lattice-period CDW phase shift that occurs between domains.

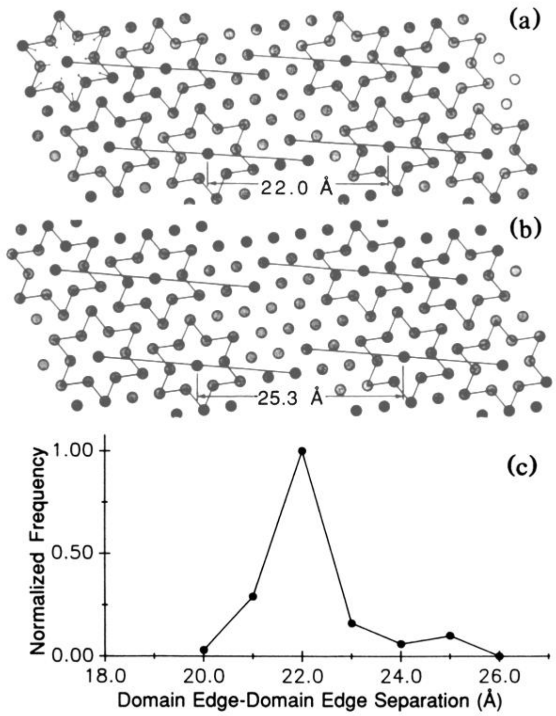


FIG. 4. (a),(b) Two model structures for the one-lattice-period CDW phase shift that occurs between adjacent domains. The shaded circles in (a) and (b) represent the atomic lattice. Each commensurate CDW maximum [located at the solid circles in (a) and (b)] is associated with 13 lattice sites that form a star-shaped cluster; the lattice distortions for one cluster are indicated by arrows in (a). The expected commensurate positions for a CDW maximum associated with either the left or right domain are represented by half-filled circles in the boundary region. These positions highlight the different distortions of the CDW (compression and stretching) that give rise to the phase shift in (a) and (b). (c) Normalized frequency of the experimentally determined distance between CDW maxima at the edges of adjacent domains.