Variable temperature scanning tunneling microscopy studies of the charge density wave phases in tantalum disulfide

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Variable temperature scanning tunneling microscopy has been used to elucidate details of the nearly commensurate charge density wave (CDW) phase in $1T$-TaS_2. Large-area images show that the nearly commensurate phase has a hexagonal domain structure, and that the domain period exhibits a strong temperature dependence. Real-space and two-dimensional Fourier transform analyses of atomic resolution images further demonstrate that within the domains the CDW is approximately commensurate with the atomic lattice, and that between domains the CDW amplitude decreases and the CDW phase changes. In addition, disorder observed in the hexagonal domain structure at low temperatures is suggested to be due to domain wall pinning.

I. INTRODUCTION

Incommensurate systems such as charge density waves (CDW) and gases physisorbed on surfaces can exhibit a variety of interesting structures.[1-10] These structures range from the uniform incommensurate superlattice to domain-like phases in which approximately commensurate domains are separated by incommensurate domain walls. Domain-like phases are relatively well understood theoretically and have been predicted for a number of incommensurate systems.[1-5] Unfortunately, experimental data reported to support domain-like structures (e.g., the observation of second- and higher order diffraction satellites) have often been controversial.[6,7] Determination of the detailed structure and temperature dependence of domain-like phases is, however, crucial to test and further develop theoretical models of these interesting incommensurate systems.

Recently it has been shown that high-resolution real-space images determined by scanning tunneling microscopy (STM) can provide a direct and unambiguous characterization of domain-like structures for incommensurate CDW systems,[11-13] and herein we report further studies of the intralayer structure of the hexagonal domain-like nearly commensurate CDW phase in $1T$-TaS_2. The nearly commensurate CDW phase is one of several temperature-dependent CDW phases observed in $1T$-TaS_2;[14] the nearly commensurate phase exists between 353 and 183 K on sample cooling. The other CDW phases include a high-temperature (353–543 K) uniformly hexagonal incommensurate phase and low-temperature (<183 K) hexagonal commensurate phase that have been unambiguously characterized by electron and x-ray diffraction experiments.[14]

II. EXPERIMENTAL

Single-crystal samples of $1T$-TaS_2 were grown over a three week period by iodine transport in a 950–880 °C temperature gradient.[11] The CDW phase transition temperatures for these crystals were determined by variable temperature resistivity measurements and are found to agree with reported values.[14] The STM used in these studies is based on a commercial instrument (Nanoscope, Digital Instruments, Inc., Santa Barbara, CA) that has been modified to carry out variable temperature experiments. The STM is located in a vacuum can that was placed in a dewar. Rough temperature control was achieved by using different cryogens in the dewar, while a sample heater was utilized for additional temperature control. The sample temperature was measured using a calibrated thermocouple placed next to the sample and is believed to be accurate to within ± 0.5 °C. Images were recorded in the constant current mode on freshly cleaved sample surfaces using platinum-iridium (80%–20%) alloy tips. The general procedures used to process and analyze the digital image data have been described previously.[11,12]

III. RESULTS AND DISCUSSION

A 38×38 nm^2 gray scale STM image of the surface of $1T$-TaS_2 recorded at 298 K is shown in Fig. 1. The key result shown in this image is the hexagonal domain structure (period ≈ 7.2 nm) that is defined by the periodic modulation of the CDW (period ≈ 1.2 nm) amplitude. The hexagonal domain structure defined by the 7.2 nm periodic modulation in CDW amplitude is very reproducible; this domain structure has been observed on many independent crystals that have come from different growth batches. Crystal defects and impurities, which are common in poor quality samples can, however, strongly pin and distort the domain structure as we have shown in doping studies of TaS_2.[15,16] Hence, STM studies must be carried out on high quality samples in order to address the intrinsic properties of this phase.

The roughly circular domains contain high amplitude CDW maxima and are separated by diffuse low amplitude domain walls. A profile of the surface corrugation taken along the lines in Fig. 1(a) quantitatively shows the relatively high CDW amplitude within the domains (A) and the lower CDW amplitude within the domain walls (B) [Figs. 1(b), 1(c)]. These profiles clearly demonstrate that the decrease in CDW amplitude at the domain wall is significantly larger than variations in the CDW amplitude within the domains themselves. Additionally, the image and corrugation profile indicate that the domain walls are relatively diffuse; that is, the CDW amplitude does not abruptly decrease over one wavelength between domains. These results are in quali-

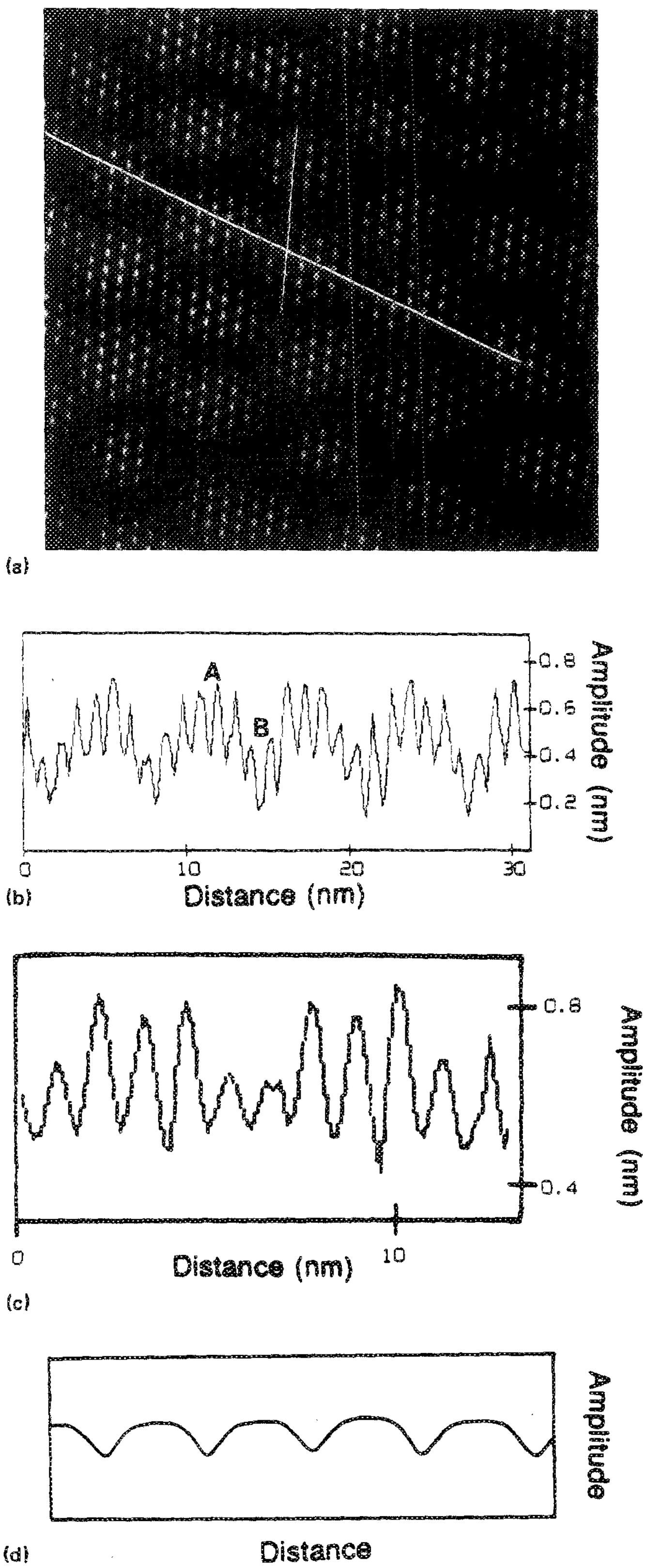


FIG. 1. (a) 38×38 nm² STM image of 1*T*-TaS_2 recorded at 298 K with a tunneling current of 2 nA and a bias voltage of 10 mV (sample vs tip). (b) Profile of the CDW amplitude across the centers of four adjacent domains indicated by the longer line in (a). Region A corresponds to the domain and region B to the domain wall. (c) Another profile of the CDW amplitude across two adjacent domains. (d) Theoretically predicted variation of the CDW amplitude across the centers of four domains [See K. Nakanishi and H. Shiba, J. Phys. Soc. Jpn. **43**, 1839 (1977)]. These calculated results agree closely with a smooth curve drawn through the amplitude maxima in (b).

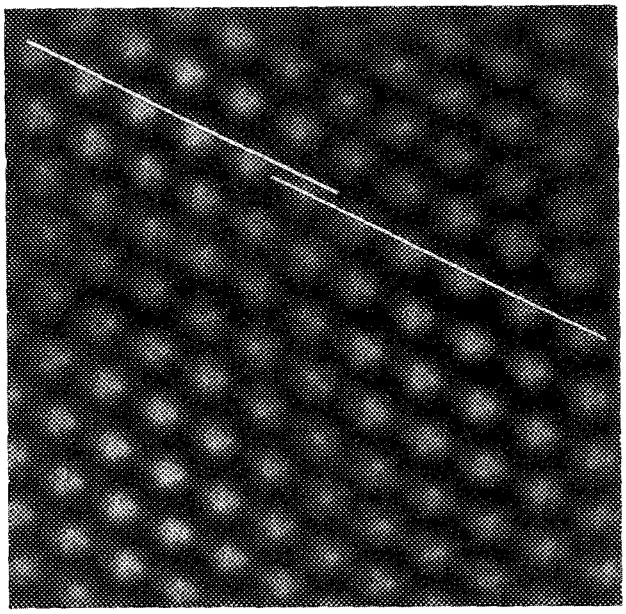
tative agreement with the amplitude profiles calculated theoretically by Nakanishi and Shiba [Fig. 1(d)].[3]

In addition to the periodic modulation of the CDW amplitude that we observe, there are two other key features that are expected of a domain-like phase.[2,3] First, the CDW superlattice should be approximately commensurate with the underlying lattice within the domains. Secondly, the CDW phase should change across the domain walls, although the phase is expected to be approximately constant within the domains. It is especially important to recognize that it would be physically unreasonable to observe a long-period amplitude modulation of the CDW superlattice [e.g., Fig. 1(a)] without the formation of commensurate domains since it costs energy to vary the CDW amplitude.[2,3] The formation of approximately commensurate domains in which there is an energetically favorable CDW–lattice interaction stabilizes the domain-like phase.

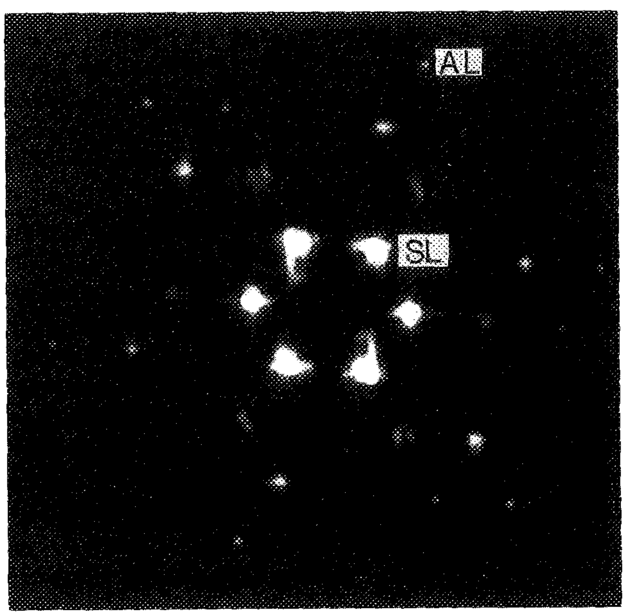
For 1*T*-TaS_2 the commensurability condition is met by a 13.9° rotation of the CDW superlattice relative to the atomic lattice.[14] We have used atomic resolution images such as Fig. 2 to evaluate the crucial CDW-lattice orientation angle directly. Notably, analysis of the images demonstrates that the CDW-lattice orientation angle within domains is always close to the 13.9° angle expected for a commensurate domain.[11,12] We thus conclude from these real-space measurements that the CDW is approximately commensurate within the domains. Our results for the domain-like structure at 298 K also have been confirmed recently in an analysis of electron diffraction data.[17] We have also calculated the two-dimensional Fourier transform (2DFT) of images of the nearly commensurate phase to connect these results with diffraction studies. The 2DFT power spectra of one typical image is shown in Fig. 2(b). The power spectrum exhibits sharp first-order peaks corresponding to the atomic lattice, although the CDW peaks are broader. It is likely that the angular spread of the CDW peaks with respect to the atomic lattice corresponds to a contribution from the approximately commensurate domains (i.e., the peak maxima are oriented at 13.9°) and the incommensurate domain walls. The absence of distinct peaks makes it difficult, however, to prove on the basis of these reciprocal space data that the domains are commensurate. Hence, for this system we believe that using the real-space image data to evaluate the CDW-lattice orientation angle is more reliable than 2DFT methods.

In addition, the atomic resolution images [Fig. 2(a)] can be used to evaluate the CDW phase between two adjacent domains. Analysis of these data demonstrate that there is a well-defined one-atomic-period phase shift of the CDW across the domain wall that separates two domains; this phase shift is highlighted by the lines through the CDW maxima in two adjacent domains in Fig. 2(a). The CDW phase is, however, approximately constant across the domains. We observe the phase shift between domains and the approximately constant phase within domains for all high quality atomic resolution images, and further note that filtering inferior data smears out these key features.

Lastly, we have investigated the temperature dependence of the hexagonal domain structure. The 27×27 nm² images presented in Fig. 3 show a dramatic temperature-dependent



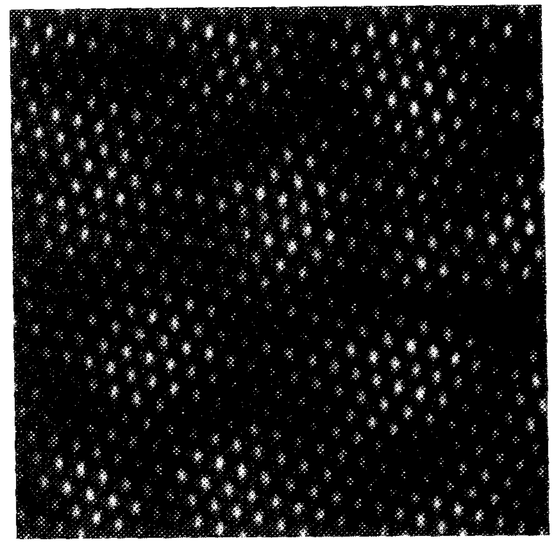
(a)



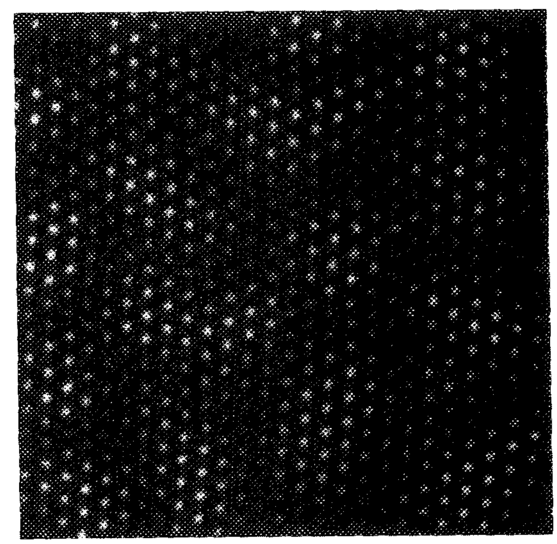
(b)

FIG. 2. (a) An 11.5×11.5 nm^2 atomic resolution image of 1*T*-TaS_2 recorded at 298 K with a tunneling current of 2 nA and a bias voltage of 10 mV. The brighter areas in this image correspond to three domains. Lines drawn through the CDW maxima in two domains highlight the one lattice period phase shift that occurs across the domain wall. This phase shift can be seen clearly by viewing the image at an oblique angle along the lines. (b) A 2DFT power spectrum of the image in (a). The first-order atomic lattice and CDW superlattice peaks are marked by an AL and a SL, respectively.

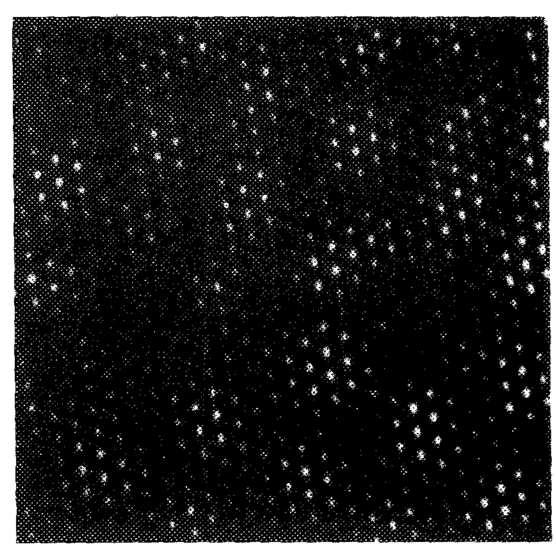
change in the domain period for the nearly commensurate phase. Specifically, as the temperature is lowered from 350 K, the onset of the nearly commensurate phase, to 240 K the average domain period increase from 5.8 to 9.0 nm.[12] At all temperatures for which the hexagonal domain structure has been observed we find that the CDWs are approximately commensurate within the domains and that there is a phase



(a)



(b)



(c)

FIG. 3. A series of 27×27 nm^2 STM images of 1*T*-TaS_2 recorded at (a) 242 K, (b) 273 K, and (c) 350 K; the tunneling current and bias voltage were 2 nA and 10 mV, respectively.

shift between domains as discussed above for the 298 K data. Additionally, the domain walls remain relatively diffuse between 350 and 240 K, and do not sharpen as predicted theoretically by Nakanishi and Shiba.[3]

It is also important to consider that the density of domain walls must decrease as the sample is cooled. A decrease in domain wall density requires that domain walls or CDW dislocations[2] are removed from the system. It is possible that movement of the walls or dislocations occur by thermally activated flow or hopping in analogy to vortex motion in type II superconductors, although we have not yet observed domain wall motion or CDW dislocations. We do note that STM images of the hexagonal domain structure exhibit increasing disorder at low temperature,[12] and suggest that this disorder could result from domain wall pinning. Indeed, it is interesting to speculate that the hysteresis in the low-temperature nearly commensurate/commensurate CDW transition may be due to domain wall pinning. Additional STM studies are currently in progress to address this issue.

IV. CONCLUSIONS

In summary, variable temperature STM has been used to elucidate details of the nearly commensurate CDW phase in $1T$-TaS_2. Large-area images show that the nearly commensurate phase has a hexagonal domain structure, and that the domain period exhibits a strong temperature dependence. Real-space and 2DFT analyses of atomic resolution images further demonstrate that within the domains the CDW is approximately commensurate with the atomic lattice, and that between domains the CDW amplitude decreases and the CDW phase changes. These new results further support our previous reports[11,12] and a recent diffraction study.[17] In addition, we have found that the hexagonal domain structure exhibits increasing disorder at low temperatures and propose that this disorder is due to pinning of the domain walls.

ACKNOWLEDGMENTS

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