Charge-Density-Wave Domains in $1T$-TaS_2 Observed by Satellite Structure in Scanning-Tunneling-Microscopy Images

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The domain structure in the nearly commensurate charge-density-wave phase of $1T$-TaS_2 has been experimentally determined. Fourier-transformed scanning-tunneling-microscopy images display fine satellite structure in excellent agreement with that predicted by the amplitude- and phase-domain model of Nakanishi and Shiba. Earlier analyses of scanning-tunneling- and atomic-force-microscopy images of $1T$-TaS_2 in the nearly commensurate phase are shown to be inadequate for the unambiguous identification and characterization of domain structure.

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The notion of competing periodicities finds application to many physical systems, including Josephson junctions, solid-solid interfaces, defect structure, and charge-density waves (CDW's). In the case of CDW's, the periodicity of the density wave is in general dictated by details of the Fermi surface of the host material and unrelated to the underlying lattice structure. CDW-lattice interactions can, however, modify the CDW structure.[1]

The layered compound $1T$-TaS_2 is a two-dimensional conductor which supports a rich spectrum of CDW phases.[2,3] One of the most intriguing is the so-called nearly commensurate (NC) phase, which exists between 353 and 183 K upon sample cooling. Diffraction studies[3] show that in the NC phase the CDW is *on average* incommensurate with the underlying lattice. The hexagonal CDW superstructure is rotated from the underlying lattice by a temperature-dependent angle which approaches the commensurate value of 13.9° at 183 K (at lower temperatures the CDW is commensurate).

In a theoretical study, Nakanishi and Shiba[4] suggest that in the NC phase of $1T$-TaS_2 the energetically favorable configuration is not a uniformly incommensurate CDW but rather a well-ordered amplitude- and phase-modulated-domain structure. In this model, the CDW is on average incommensurate, but within a domain (comprising roughly 35 CDW maxima room temperature) the CDW is predicted to be largely commensurate with the underlying lattice. While it is difficult to verify such domain structure by conventional diffraction experiments, local surface probes such as scanning tunneling microscopy (STM) and atomic-force microscopy (AFM) are well suited to this task.

In an early STM study of the different CDW phases of $1T$-TaS_2, Thomson *et al.*[5] found no clear evidence for the predicted domain structure in the NC phase of $1T$-TaS_2 [the expected domains were, however, identified in the triclinic (T) phase, which exists when the sample is warmed from 223 to 283 K]. In a subsequent study of the NC phase, Wu and Lieber[6] observed domainlike structure in real-space STM images with amplitude and phase modulation in apparent agreement with the theoretical predictions. They found that the CDW was commensurate inside domains, and that the commensurate region contained ~18 CDW maxima at 298 K, thus comprising about 50% of the domain area. Recent STM and AFM studies by Slough and co-workers[7] and Garnæs *et al.*[8] show evidence for amplitude-modulated-domain structure, but suggest that the CDW in the NC phase of $1T$-TaS_2 is continuously incommensurate, as opposed to having large commensurate regions (with the CDW superlattice oriented at 13.9° to the atomic lattice) separated by localized discommensurations. This conclusion is in direct conflict with the phase modulation findings of Wu and Lieber.

We have studied the NC phase of $1T$-TaS_2 by computer modeling and STM imaging. Through our modeling we find that real-space analyses (of the kind used in previous STM and AFM studies) can give erroneous results with respect to possible amplitude- and phase-domain structure. By examining fine satellite structure in our Fourier-transformed STM images, however, we demonstrate conclusively that amplitude and phase domains do exist in the NC phase of $1T$-TaS_2, in excellent agreement with those predicted theoretically.

It is instructive to consider a computer-generated image of how the surface of $1T$-TaS_2 might look to an STM or AFM probe if the CDW were uniformly incommensurate with absolutely no amplitude- or phase-domain structure. Figure 1(a) shows such an image, which we generated by superposing three sine waves to represent the atomic lattice with three additional sine waves which produce the uniformly incommensurate CDW. The atomic lattice constant ($a_0 = 3.346$ Å) and CDW wave vector (wavelength $\lambda_{CDW} = 11.74$ Å) have been chosen to agree with those of $1T$-TaS_2 in the NC phase at room temperature, and the CDW amplitude has been assigned 3 times the amplitude of the lattice modulation, in approximate agreement with the amplitude ra-

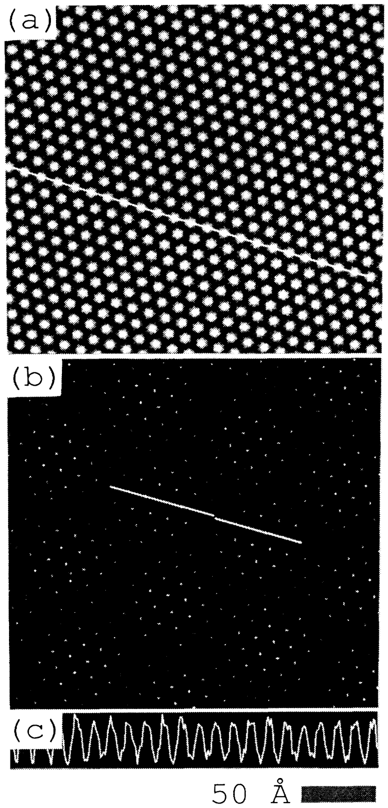

FIG. 1. (a) Computer-generated model image of $1T$-TaS_2 at room temperature illustrating interference between atomic lattice and CDW. (b) Same image as (a) with gray scale adjusted to emphasize interference "domains." Computer-drawn lines pass through maxima in adjacent domains to show one-atomic-lattice-constant phase slip. (c) Intensity line scan through (a) demonstrating apparent CDW amplitude modulation.

tio suggested by real STM images.[9] Despite the fact that Fig. 1(a) represents a uniformly incommensurate CDW *with no inherent amplitude or domain structure of any kind,* there appear in the image *apparent* amplitude and phase "domains." The domain features can be emphasized by readjusting the discrimination level for the image gray scale so that only CDW maxima are resolved, as shown in Fig. 1(b) for the same computer-generated image. (We note that a similar gray-scale readjustment has been routinely applied to real $1T$-TaS_2 STM data by other groups to emphasize apparent domain structure.) Figure 1(b) clearly and strikingly gives the impression of a domainlike modulation of the CDW. However, this impression is false: The origin of the apparent domains is simply interference (or "beating") between the CDW and the underlying lattice that produces moiré fringes.

The interference domains display both apparent phase and amplitude modulation of the CDW. Apparent amplitude modulation is obvious in Fig. 1(b), and can also be extracted from Fig. 1(a) by measuring the CDW intensity along a line of maxima, as is shown in Fig. 1(c). The apparent phase modulation can be seen by sighting at a glancing angle along a line of CDW maxima in Fig. 1(b); the maxima are not collinear, and there is an apparent phase shift of one atomic lattice constant from one domain to the next, as emphasized by the lines drawn in Fig. 1(b) in two adjacent domains. Furthermore, a local measurement of the orientation of the CDW maxima obtained simply by drawing a straight line through the maxima in a given domain [see Fig. 1(b)] and measuring the angle relative to the atomic lattice yields a rotation angle of 13.9°, which is the commensurate angle. Ironically, the interference domains of Figs. 1(a) and 1(b) have wavelength and orientation identical[10] to the true phase and amplitude domains predicted by Nakanishi and Shiba.

Because of the inevitable interference effect just described, it seems that any identification of true phase and/or amplitude domains from a real-space NC $1T$-TaS_2 image is questionable. The interference effect is, we believe, the origin of the discrepancy between the STM analysis of Wu and Lieber[6] and the STM and AFM analyses of Slough and co-workers[7] and Garnæs *et al.*[8]

Fortunately, it is possible to avoid the complications of the interference effect and determine the true domain structure by a careful analysis of the Fourier transform of real-space STM or AFM images. In the model of Nakanishi and Shiba, the CDW order parameter for the domain-modulated structure contains a strong Fourier component at the uniformly incommensurate CDW wave vector and lesser Fourier components which always differ from the uniformly incommensurate wave vector by a *domain wave vector* (or a sum of domain wave vectors). The three domain wave vectors $\mathbf{k}^{(l)}$ are defined by $\mathbf{k}^{(l)}=3\mathbf{q}^{(l)}-\mathbf{q}^{(m)}$, for cyclic permutations of l, m, and n, where $\mathbf{q}^{(l)}=\mathbf{Q}^{(l)}-\mathbf{Q}_c^{(l)}$; $\mathbf{Q}^{(l)}$ are the wave vectors of the uniformly incommensurate CDW's, and $\mathbf{Q}_c^{(l)}$ are the wave vectors of the commensurate CDW's. No Fourier component is expected at the commensurate CDW wave vector as the uniformly incommensurate CDW wave vector and the commensurate wave vector do not differ by a sum of domain wave vectors.[11] The lesser Fourier components are responsible for inducing the domainlike modulation. A true domain modulation of the type envisaged by Nakanishi and Shiba can therefore be identified by appropriate fine-structure *satellite spots* in the Fourier transform of an STM or AFM image of $1T$-TaS_2.

We have imaged $1T$-TaS_2 with an STM (Ref. 5) (constant-height mode, tip bias of -10 mV, tunnel current of 3 nA), using high-quality samples grown in our laboratory and at Cornell University. Figure 2(a) is an unfiltered image of $1T$-TaS_2 in the NC phase at

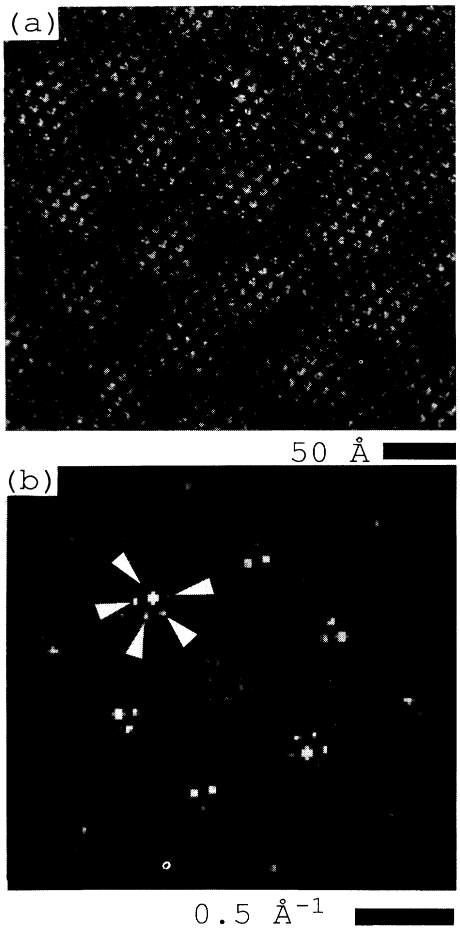

FIG. 2. (a) STM image of $1T$-TaS_2 obtained at $T=295$ K in the NC phase. (b) Fourier transform of (a). Satellite spots near hexagonally arranged CDW peaks are clearly evident; arrows identify five such spots. Different satellite spots have different intensities, consistent with theoretical predictions.

$T=295$ K. The dominant bright spots are CDW maxima. A periodic brightness variation of the CDW maxima is observed, similar to that reported in previous studies (and attributed there to domainlike modulations). As emphasized previously, these real-space modulations do not in themselves demonstrate true CDW domain structure. Figure 2(b) shows the two-dimensional Fourier transform of the data of Fig. 2(a). In the Fourier-transform image of Fig. 2(b), a hexagonal reciprocal lattice is observed with the six large peaks, corresponding to the fundamental CDW frequencies, surrounding the center (the hexagon is slightly distorted due to thermal drifts and imperfections in the piezoelectric scanning tube). Surrounding each fundamental CDW peak, there are several satellite spots, some of which are identified by small arrows in the figure. Satellite spots are also evident around higher-order CDW peaks. It is important to note that different satellite peaks associated with a given

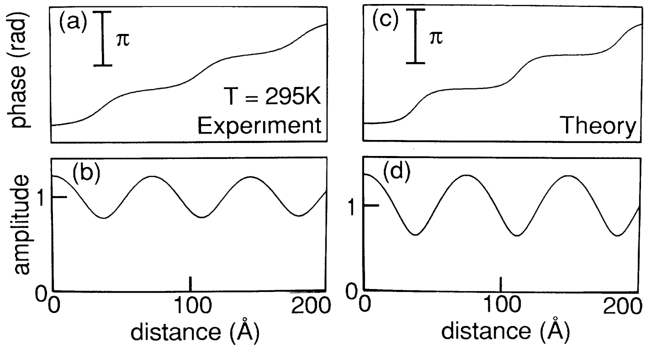

FIG. 3. (a) Real-space phase variation and (b) amplitude modulation A/A_{avg} of the CDW in $1T$-TaS_2 in the NC phase reconstructed from the Fourier coefficients and wave vectors extracted from the Fourier transform of Fig. 2(a). (c) Real-space phase variation and (d) amplitude modulation A/A_{avg} of the CDW predicted by the Nakanishi and Shiba theory.

CDW fundamental have different intensities. This is not an imaging artifact, but rather implies an amplitude *and* phase modulation of the CDW and that the CDW amplitude modulation envelope is not purely sinusoidal.

Using the measured Fourier coefficients of a first-order CDW peak and its first-order satellites together with the CDW peak and satellite positions, we can reconstruct the real-space phase and amplitude modulation function of one of the three simultaneously occurring CDW's, as shown in Figs. 3(a) and 3(b). We determine the intensity of a Fourier peak from the integrated pixel intensity and its position (i.e., wave vector) from a weighted average of the coordinates of pixels within the peak. Figures 3(a) and 3(b) show that the domain structure has a real-space wavelength (measured through the centers of domains) of 72 ± 3 Å, and that the CDW is close to being commensurate over an appreciable part of the domain. The CDW amplitude is modulated with a fractional modulation amplitude of about 0.44. The troughs of the amplitude modulation envelope are distinctly narrower than the crests. Hence, as already demonstrated by the satellite intensity pattern, the CDW amplitude modulation is not strictly sinusoidal. The domain boundaries are not sharp, but rather comprise more than 50% of the domain dimension. In going from one domain to the next, the CDW phase slips by a factor of $\delta\phi=0.61\pi \pm 0.03\pi$ rad, which corresponds favorably with the theoretically predicted[4] phase slip of $\delta\phi=0.615\pi$ rad. To compare our data further with the theory, we have calculated the real-space phase and amplitude variations from the theory of Nakanishi and Shiba, using their predictions for the Fourier coefficients of the modulation function[4] at 295 K. The results of those calculations, shown in Figs. 3(c) and 3(d), are in excellent agreement with those reconstructed from our data.

We have Fourier analyzed STM images of $1T$-TaS_2 from different preparation batches and find results consistent with those described above. Although the modulation functions displayed in Figs. 3(a) and 3(b) are representative of the NC phase at room temperature, there are variations of roughly 10% in the phase slip, modulation amplitude, and domain boundary size evaluated from different images. Gross sample defects tend to destroy the domain structure. We have also performed similar Fourier-transform analyses on STM images obtained on 1T-TaS_2 at different temperatures.[12] For the NC phase, the domain structure is found to be temperature dependent in a manner consistent with predictions of the domain model.[4] In the T phase, a different satellite structure is obtained,[12] which is consistent with the stretched honeycomb model of Nakanishi and Shiba.[13]

In conclusion, we have demonstrated that interference effects obscure the direct identification of CDW domains in real-space STM or AFM images of 1T-TaS_2. From an analysis of fine satellite structure in Fourier-transformed STM images, we observe true amplitude- and phase-modulation-domain structure in the NC phase of 1T-TaS_2. The positions and intensities of the satellite spots in our Fourier-transformed images yield domain structure in excellent agreement with the predictions of the amplitude- and phase-domain model of Nakanishi and Shiba. The satellite structure identification provides unambiguous evidence for domain structure in the NC phase of 1T-TaS_2.

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[10] This correspondence is, of course, not accidental, as the most energetically favorable locations for true domains are at points of constructive interference between the atomic lattice and the CDW superlattice.

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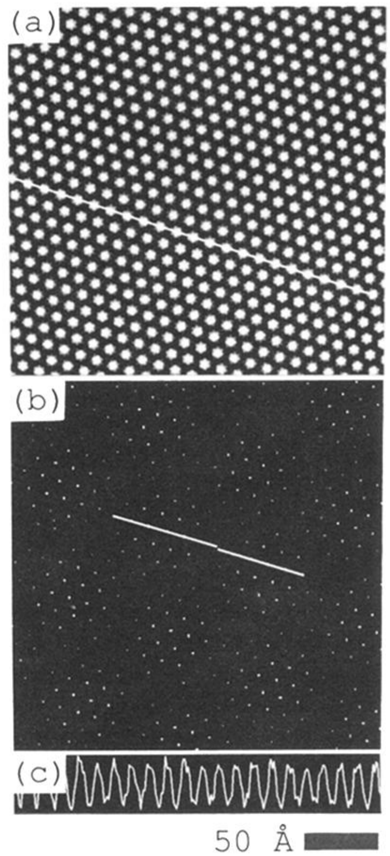

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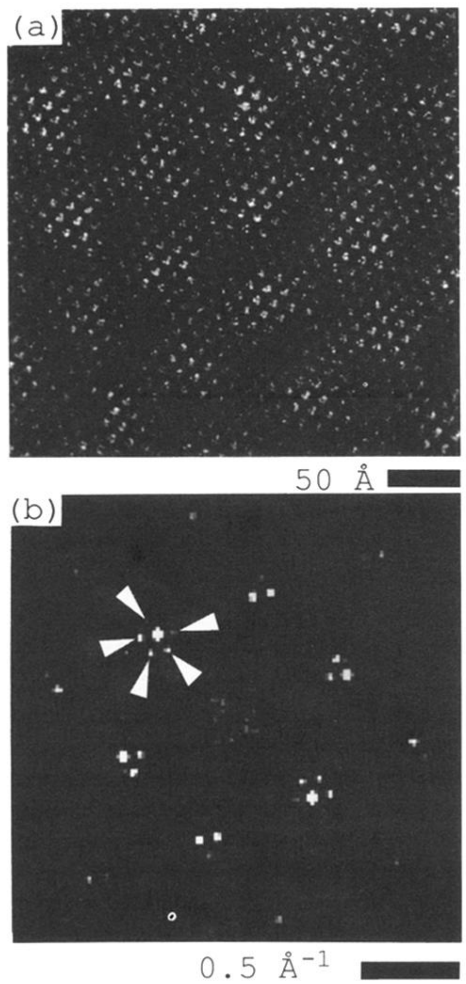

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