Reports

Hexagonal Domain-Like Charge Density Wave Phase of TaS_2 Determined by Scanning Tunneling Microscopy

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The structure of the room-temperature charge density wave (CDW) phase in octahedrally coordinated tantalum disulfide, 1T-TaS_2, has been a controversial issue for over 15 years. Large-scale scanning tunneling microscope images of the intralayer structure of this phase exhibit a domain-like pattern defined by a variation in the maximum CDW amplitude. The circular domains, consisting of high-amplitude CDWs, are arranged in a regular hexagonal lattice (period 73 ± 3 angstroms) that is rotated relative to the CDWs. In addition, from the analysis of atomic resolution images it was determined that there is a well-defined phase shift between the CDWs in adjacent domains, and that within a domain the CDW superlattice is commensurate with the atomic lattice. These results provide evidence for the hexagonal discommensurate CDW phase in 1T-TaS_2 and also suggest an explanation for the long-standing controversy concerning the structure of this phase.

CENTRAL TO CURRENT RESEARCH efforts in condensed-matter physics and chemistry is the elucidation of electronic and structural factors that govern phase transitions in metallic materials (*1*). One such transition, which involves a simultaneous periodic distortion of the conduction electron density and the crystal lattice, is the metal to charge density wave (CDW) transition (*2–6*). The CDW phase was first predicted theoretically in 1954 (*2*); however, this phase was not observed experimentally until almost 20 years later (*3, 4*). Thus far, CDWs have been observed and studied in a host of low-dimensional inorganic and organic materials (*5*), and, although significant advances have been made, key details of the structure and dynamics of the CDW phase remain uncertain in many systems (*6*). Herein we describe investigations with the scanning tunneling microscope (STM) (*7*) that resolve the long-standing controversy concerning the structure of the room temperature CDW phase in octahedrally coordinated TaS_2, 1T-TaS_2 (*8–13*).

Four distinct temperature-dependent CDW phases have been proposed for 1T-TaS_2 on the basis of evidence from diffraction and transport studies (*4, 14*). The CDW wavelength in all of these phases is ≈11.8 Å, whereas the lattice distortions are much smaller (≤0.2 Å). Although the properties of three of the CDW phases have been well characterized (*4, 14, 15*), the detailed structure of the fourth one, which exists between 283 and 353 K, is controversial (*8–12*). The two models that have been developed describe the intralayer structure of this phase as either nearly commensurate (*4, 8*) (NC model) or domain-like discommensurate (*9*) (DC model). In the NC model the CDW amplitude and phase are uniform, and the superlattice defined by the CDWs is rotated ≈12° relative to the atomic lattice at 300 K. In the DC model, however, the CDWs define a hexagonal domain-like structure with a period of ≈67 Å. Within the domains the CDWs are commensurate with the lattice, and between domains the CDW amplitude decreases and the CDW phase changes. Despite the basic differences between the NC and the DC models, experimental studies including diffraction (*8, 9*), high-resolution electron microscopy (*10*), photoemission (*11*), and scanning tunneling microscopy (*12, 13*) have been unable to identify unambiguously the structure of this CDW phase (*16*).

To characterize the intralayer structure of the room-temperature CDW phase in 1T-TaS_2, we have carried out detailed investigations using the STM. Coleman *et al.* were the first to show that the STM could be used to observe a CDW (*17*). Since this initial report the STM has been used to image CDWs in a number of materials (*18, 19*), and more recently it has also been utilized to study key local properties of these phases (*12, 13, 20*). The STM is particularly well suited to investigate the local structure of the CDW phase because it can be used to simultaneously probe the charge modulation and the atomic lattice in real space. Hence, the STM can be used to evaluate directly the structure of the CDW superlattice as well as its orientation with respect to the underlying atomic lattice. These local properties are significantly different for the NC model than for the DC model.

Single crystals of 1T-TaS_2 were prepared by iodine vapor transport in sealed quartz tubes as described in (*13, 21*). Cleavage of the resulting plate-like crystals exposes

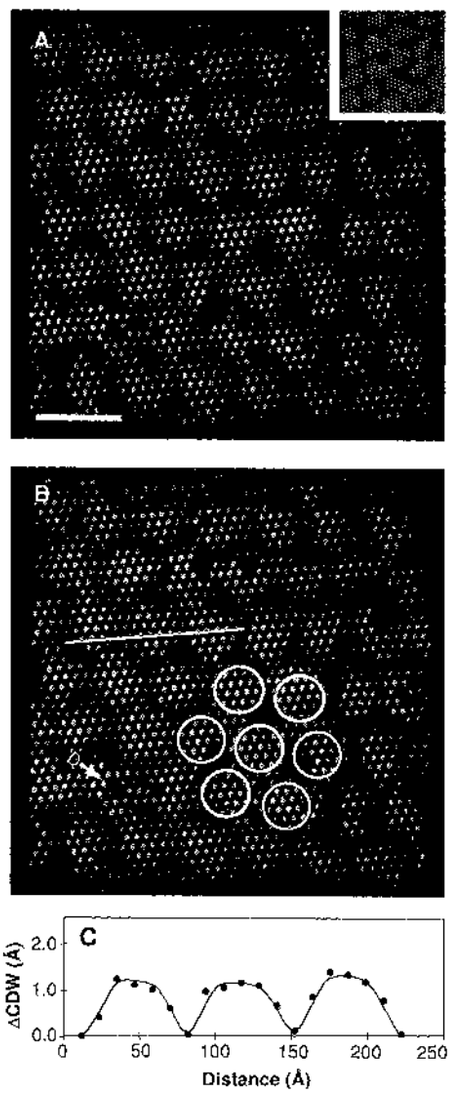

Fig. 1. (**A**) STM image of 1T-TaS_2 recorded with a Pt-Ir (80% platinum, 20% iridium) tip at a tunneling current of 2 nA and a sample versus tip bias voltage of 10 mV; this image was not filtered prior to display. The single crystal sample of 1T-TaS_2 was grown over a 3-week period with a 70°C gradient (low temperature 900°C). The CDW phase transition temperatures for these crystals, determined with variable-temperature resistivity measurements, are the same as reported previously (*4, 10*). The bar in this image is 100 Å. The inset shows ≈22 domains. (**B**) The same image as in (A) except that seven domains have been circled to highlight the symmetry of this phase. An apparent defect (D) is also marked. (**C**) Difference in the maximum CDW amplitude along the line marked in (B).

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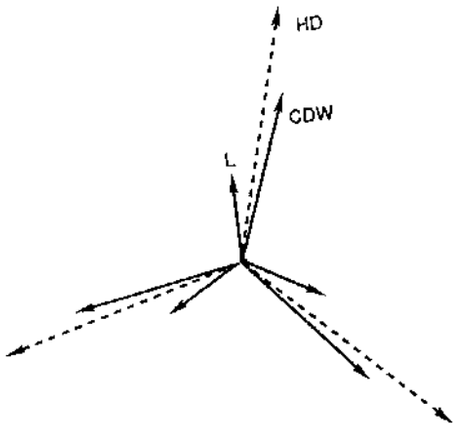


Fig. 2. Vectors illustrating the relative orientation of the hexagonal domain structure (HD), CDW, and the atomic lattice (L) for the three symmetry-related directions. Counterclockwise rotation of the HD and CDW vectors relative to L is also possible.

atomically flat surfaces that are ideal for STM studies. A typical gray-scale image, recorded in the constant current mode with a commercial STM (*22*), is shown in Fig. 1A. The light areas in this image correspond to apparent surface protrusions and the dark areas to depressions. The CDW maxima (white spots) define a regular hexagonal superlattice with an average wavelength ±1 SD (*23*) of 11.8 ± 0.3 Å, in agreement with earlier diffraction and STM measurements. A more significant feature of Fig. 1A is, however, the new periodic modulation in the CDW amplitude that defines domains consisting of relatively high-amplitude CDW maxima separated by lower amplitude regions (domain boundaries). These approximately circular domains of high-amplitude CDWs are arranged in a regular hexagonal superstructure with a period of 71 ± 2 Å (Fig. 1B). The modulation of CDW amplitude between the domains and boundaries is quantitatively displayed in a profile of the surface corrugation (Fig. 1C). Statistical analysis of corrugation data for the entire image yields a difference in CDW amplitude (that is, domain-domain boundary) of 1.0 ± 0.2 Å.

To explore the limits for which this new CDW structure can be observed, we have imaged 1T-TaS_2 by using a variety of experimental conditions. Specifically, the same periodic domain-like structure was found for sample-tip bias voltages between −100 and +100 mV, for tunneling currents between 0.5 and 6 nA, and with different tunneling tips. This domain-like CDW structure has also been observed with different 1T-TaS_2 samples, including ones grown in an independent laboratory (*24*). The domain period (73 ± 3 Å) and the amplitude difference (1.1 ± 0.2 Å) between the domains and boundaries, which were determined with these different samples, are similar to the ones obtained for Fig. 1. In short, the domain-like CDW superstructure is observed in different samples with a range of instrumental parameters, and hence we believe that it is intrinsic to 1T-TaS_2 and not the result of surface contamination or other artifacts (*25*).

The hexagonal domain-like CDW structure that we observe supports the DC model for the room-temperature CDW phase in 1T-TaS_2. Specifically, the hexagonal domain structure, the domain period, and the variation of the CDW amplitude between the domains and boundaries are all consistent with this model (Table 1).

We have also investigated a number of other key properties of the room-temperature CDW phase, including (i) the orientation of the hexagonal domain-like structure with respect to the CDW superlattice, (ii) the relationship of the CDW phases in adjacent domains, and (iii) the orientation of the CDW maxima in the domains relative to the atomic lattice. From the analysis of images recorded on different samples we find that the hexagonal domain structure is rotated 6° ± 1° relative to the CDW superlattice in a single domain. This rotation is opposite to the direction of rotation of the CDW superlattice relative to the atomic lattice (Fig. 2). Rotation of the hexagonal domain structure implies that a phase shift occurs between the CDWs in adjacent domains. To characterize the relative phase between the CDWs in adjacent domains, we have recorded high-resolution images in which both the atomic lattice and the CDW superlattice are resolved. In a typical atomic resolution image containing four domains (Fig. 3) there are well-defined phase shifts of one lattice period between the CDWs in adjacent domains. The one-lattice-period phase shift between domains has been observed in all of the 30 atomic resolution images examined. This phase shift represents an important feature that distinguishes the DC model from the NC model. In addition, this phase shift has been detected in each of the symmetry-related directions of the hexagonal domain structure.

We have also characterized the orientation of the CDWs with respect to the lattice using atomic resolution images such as Fig. 3. Within a given domain a similar array of atoms (small spots, separation 3.4 ± 0.2 Å) was observed at each CDW maximum, indicating that the CDW is approximately com-

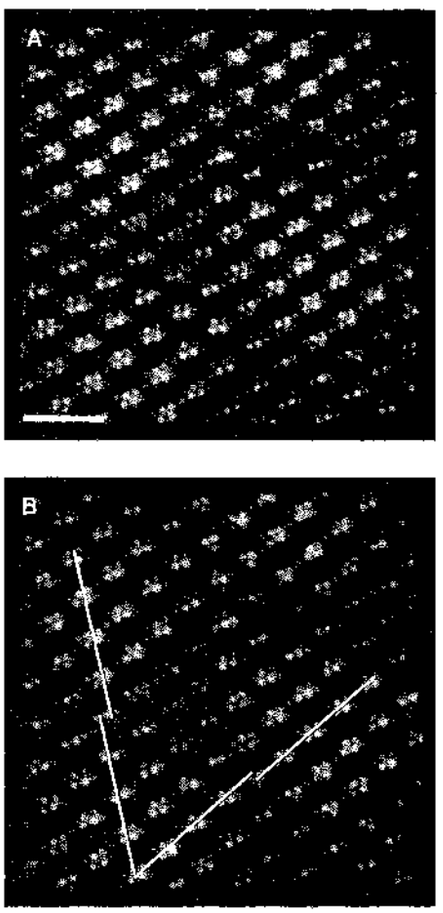
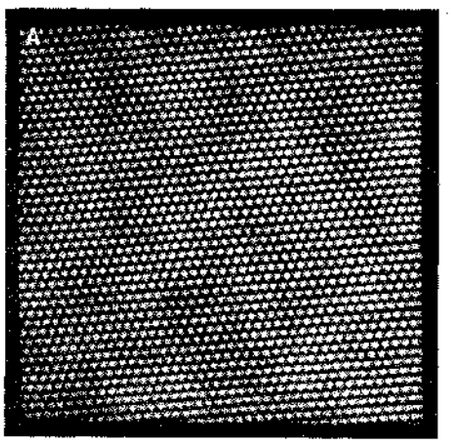


Fig. 3. (**A**) Atomic resolution raw data of 1T-TaS_2 recorded with a tunneling current of 2 nA and a bias voltage of 10 mV. The domains are located near the four corners of this image. The bar is 25 Å. (**B**) Low-pass filtered data from (A). Lines have been drawn through three adjacent domains to highlight the one-lattice-period phase shift.

Table 1. Comparison of the CDW properties determined from STM measurements and predicted by the DC and NC models for 1T-TaS_2.

Property	Results (298 K)		
	STM	DC model	NC model
Overall structure	Hexagonal domain	Hexagonal domain	Uniformly NC
Domain period	73 ± 3 Å	≈67 Å	
Domain orientation	6° ± 1°		
Difference in CDW amplitude (domain-boundary)	1.1 ± 0.3 Å	>0	0
CDW orientation	13.7° ± 0.5° (domain)	13.9° (domain)	Uniform 12°
Domain-domain phase shift	One lattice period	One lattice period	

mensurate (*20*). To determine in a more quantitative manner whether the CDWs in the domains are commensurate, we measured the angle between the atomic lattice and the CDW superlattice. The experimental angle of 13.7° ± 0.5° (*23*) is similar to the 13.9° angle that is expected for a commensurate domain (*4, 9*). We have also measured an "average" orientation angle, which ignores the important domain structure, by using a vector spanning several domains to define the CDW direction. As expected (*26*), this average angle, 11.6° ± 0.5°, is smaller than the orientation angle determined in the well-defined domains. Thus, an orientation angle consistent with the NC model is found when one incorrectly assumes that the CDW phase is uniform across several domains. This analysis suggests why previous diffraction and STM data, collected from areas larger than a single domain, would yield an orientation angle consistent with the NC model (*4, 8, 12*).



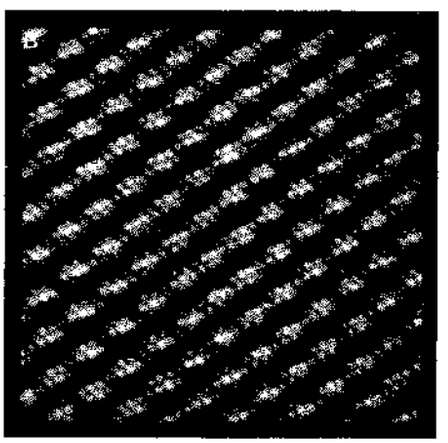


Fig. 4. Fourier transform–filtered images of Fig. 1A (**A**) and Fig. 3A (**B**). In the Fourier transform method, frequency spectrum peaks corresponding to the CDW superlattice and the atomic lattice are saved and then transformed back to image space. The images are the same size as Fig. 1A and Fig. 3A, respectively.

Because the data obtained from our atomic resolution and large-area images so clearly favor the DC model (Table 1), we have considered why earlier STM studies have failed to detect it (*12, 13, 17*). One factor that may play an important role is the image size. The hexagonal domain structure is easily observed in images such as Fig. 1A; however, this structure with a domain period of 73 Å is more difficult to identify in a smaller image such as Fig. 3, which is similar in size to images previously reported (*12, 13, 17*). We believe that another critical factor is the method used to process the primary image data. For example, when we filter our raw data files (Figs. 1A and 3A) using a standard Fourier transform method (*12*), the hexagonal domain structure and the phase shift between domains are not easily detected in the resulting images (Fig. 4, A and B). In addition, the CDW lattice orientation angle determined from Fourier transform–filtered atomic resolution images, 11.7° ± 0.5°, is similar to the "average" angle discussed earlier. These observations suggest that STM image processing must be carried out with caution to avoid losing important local data that raw STM images can provide.

Lastly, we address the effect of crystal defects and impurities on the structure of the DC phase. For example, apparent holes, which have been attributed to surface defects (*20*), are observed at random CDW sites in our images (Fig. 1A). The hexagonal domain structure is not significantly distorted by the holes, indicating that the CDWs are not strongly pinned to these sites (*27*). In contrast, we have found that nonperiodic domains are present in 1T-TaS_2 doped with niobium (*28*). Although it was suggested that the domains were the result of an impurity-driven CDW localization (*28*), it now appears that the niobium impurities only distort the hexagonal domain-like phase intrinsic to pure 1T-TaS_2.

In summary, we have used the STM to characterize the key properties (Table 1) of the room-temperature CDW phase in 1T-TaS_2. Our experimental data provide what we believe to be unambiguous evidence for the hexagonal discommensurate CDW phase in 1T-TaS_2 and resolve the long-standing controversy concerning the structure of this CDW phase. These results together with data from future high-resolution STM investigations should provide a unique opportunity to increase our understanding of the fundamental properties of these low-dimensional materials.

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23. All of the error limits reported here are ±1 SD. They were calculated from a data set consisting of at least 60 independent measurements (wavelength, angle, and so forth) that were typically obtained as follows: 5 independent data points per image, 3 images per crystal (where each image corresponds to a different region of the crystal), and 5 independent crystals. The standard deviations for the domain period and difference in CDW amplitude for Fig. 1 were determined for 6 wavelength and 30 amplitude measurements.
24. Independent samples of 1T-TaS_2 were provided by F. DiSalvo and P. Rauch (Cornell University).
25. Although surface contamination may cause variations in the observed CDW amplitude, it is unlikely that surface contamination or defects would give rise to a periodic amplitude change that is the same in different samples.
26. Because the domain structure is rotated relative to the CDWs in a single domain (Fig. 2), the "average" CDW lattice orientation angle measured across several domains will be less than in a single domain.
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