Direct Observation of Charge-Density-Wave Discommensurations and Dislocations in $2H$-$TaSe_2$

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Discommensurations and dislocations in the incommensurate charge-density-wave structure of $2H$-$TaSe_2$ have been observed directly by dark-field transmission electron microscopy with use of satellite reflections produced because of the phase transition. We have imaged the domain structure in the striped phase on warming above 92 K. Discommensurations are found to have a width ~ 150 Å and their spacings vary in the expected manner with temperature.

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In the last few years systems with incommensurate periodicities, such as charge-density waves (CDW) in transition-metal dichalcogenide layered compounds and rare gases physisorbed onto surfaces, have become a subject of many extensive experimental and theoretical studies. It has been suggested theoretically[1,2] that the incommensurate phase is composed of large commensurate domains separated by narrow domain walls or discommensurations (DC's) within which the superlattice phase varies very rapidly. Thus far the experimental evidence in support of DC has come from the observation of higher-order neutron diffraction satellites of the CDW superlattice[3] and most recently from NMR measurements[4] in $2H$-$TaSe_2$.[4] Satellite intensity variations observed in the krypton/pyrolytic-graphite system have also been attributed to coherent interference from ordered commensurate domains.[5] These experiments are indirect and could be subject to ambiguity in interpretation. Moreover the detailed configuration of DC's, which is still open to conjecture at this point, cannot be obtained from these experiments.

In this Letter, we report the first direct observation of DC's and dislocations in the incommensurate CDW phase of $2H$-$TaSe_2$ by dark-field electron microscopy. This is the first time that a CDW dislocation, a defect structure in CDW proposed by McMillan,[2] has been observed by any technique. It seems clear from our data that the CDW dislocation plays an important role in the commensurate-incommensurate transition.

Thin-film samples ($\lesssim$ 1000 Å thick) were prepared for transmission electron microscopy (TEM) by cleavage of single-crystalline $2H$-$TaSe_2$ and were examined in a JOEL 200-kV electron microscope equipped with a single-tilt liquid-helium cold stage.[6] The stage provides temperature control from 16 to 400 K with a thermal stability ~ 0.1 K over a period ~ 5 min. The actual temperature of the electron-beam-irradiated area is found to be no more than 4 K above the stage reading, as judged by the appearance and disappearance of CDW satellite spots. The spatial resolution of the stage is better than 50 Å for the exposure time of 30 sec used in the present studies.

It is known from earlier neutron diffraction studies[2] that on cooling, $2H$-$TaSe_2$ has two CDW phase transitions, a normal-to-incommensurate transition at $T_{NI} = 123$ K and an incommensurate-to-commensurate transition at $T_{CI} = 90$ K. The CDW's have a triple-q structure. Very recently, high-resolution x-ray diffraction studies[7] revealed a large thermal hysteresis effect in which $T_{CI} = 85$ K on cooling and $T_{CI} = 93$ K on warming. On warming, between 93 and 112 K, the hexagonal symmetry of the triple-q CDW with wave vectors of equal magnitude was found to be broken and a new striped-domain phase[8,9] was observed. Regions of the striped phase are demarcated by one of the three CDW wave vectors which remains commensurate. The other two wave vectors become incommensurate. Within a region, parallel commensurate stripes separated by narrow DC's are expected. Above 112 K a first-order phase transition occurs and the striped-domain structure transforms to a domain structure with hexagonal symmetry.

In Fig. 1 we show an electron micrograph taken from one of the CDW satellite spots at a temperature of 100 K after warming from 20 K. The direction of the CDW wave vector which was used for imaging is also shown on the figure. The most striking feature in Fig. 1 is the appearance of parallel lines. It is important to note that these parallel lines can only be observed in CDW satellite reflections and therefore they are associated with the CDW phase transitions. Note that

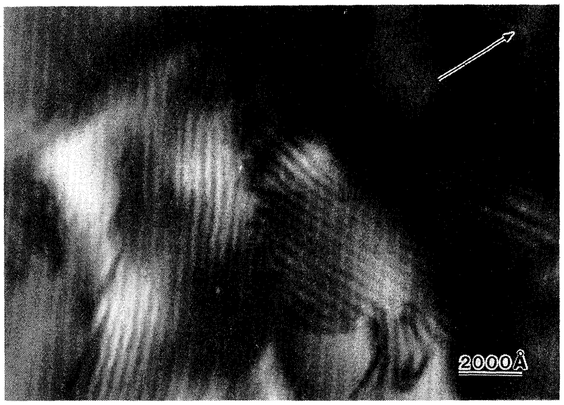

FIG. 1. Electron micrograph showing the structure of the striped-domain phase taken at a temperature of 100 K on warming. The direction of the imaging CDW wave vector is also shown. The micrograph was taken with an exposure time of 30 sec.

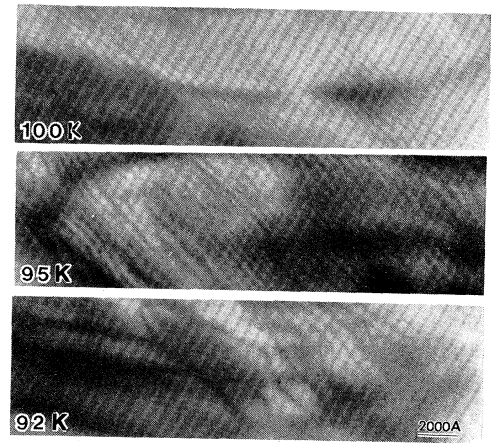

FIG. 2. Images showing the evolution of a region in the striped phase as temperature is increased through 92, 95, and 100 K. Note the decrease of DC spacings as the temperature increases.

there are two sets of lines in different regions running at an angle $2\pi/3$ to each other and that these lines both make an angle of $2\pi/3$ to the direction of the imaging CDW wave vector. No lines running parallel to the imaging CDW wave vector can be seen. This is what we expect from a striped-domain structure where the DC's are parallel to the CDW wave vector which remains commensurate. Along the DC planes no phase changes are expected and therefore regions with DC's parallel to the direction of the imaging CDW wave vector would not be visible and only the regions with DC's not parallel to the imaging direction can be seen. This condition has been checked experimentally for all three directions of the triple-q CDW wave vectors. Lines of DC are well defined with width $\lesssim 150$ Å. Separation of DC (L) is about ~ 350 Å at 100 K as shown in Fig. 1. This separation agrees well with the x-ray diffraction result[7] from which L can be obtained ($L = 2\pi/3\delta$) by using the measured data of the incommensurability δ. Regions of the striped phase are found to be quite irregular in size and shape varying from a few thousand angstroms to $\gtrsim 5$ μm. Furthermore, DC's in a region are not strictly straight but tend to be slightly wavy.

A crucial test of the observation of DC's in the striped-domain phase as described above is to vary the temperature and observe the change of spacing between DC's. In Fig. 2 we show the evolution of a striped domain at temperatures 92, 95, and 100 K. At 92 K, the average spacing between DC's is ~ 1000 Å, although the spacing is rather nonuniform. At 95 K the spacing has decreased to ~ 450 and a 350 Å DC spacing is again observed at 100 K. This result agrees very well with the DC spacing L deduced from the x-ray diffraction measurements of δ.[7] It is noted that the width of the DC seems to decrease a small amount as the temperature increases. The lines visible in the figures are in reality DC "planes", seen in projection, which must therefore run almost perpendicular to the sample surface (i.e., along the c axis). This is consistent with the theoretical considerations that, because of the Coulomb interaction between CDW's on successive layers of the $TaSE_2$ crystal, a DC in one layer must be near a DC of the same phase slip in the corresponding CDW in a neighboring layer.

Another interesting feature in Fig. 2 is that lines of DC become irregular and less parallel as they get farther apart. This can be understood by considering the repulsive interaction[8,9] between DC's in the striped phase. This interaction gets stronger when L becomes smaller. With a given density of DC's the strong repulsive interaction would tend to keep DC lines parallel to each other. When DC's are far apart the repulsive force becomes weak and the lines can take other shapes as required by local conditions, such as strains, defects, impurities,[10] etc.

As the temperature is lowered toward the commensurate lock-in phase transition the density of DC's decreases. A CDW dislocation model has been proposed by McMillan[2] in order to understand the way in which DC's are removed from the system. In this model DC's can be terminated in a CDW dislocation and then removed by the

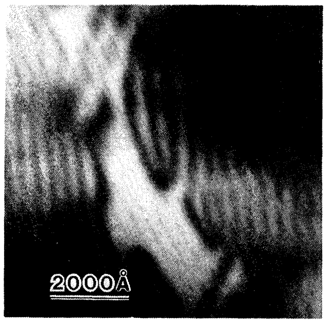

FIG. 3. Images of CDW dislocations observed in the striped phase at 100 K on warming. Note that three DC's are always required to make a CDW dislocation.

motion of these CDW dislocations. Since one DC involves a phase change of $2\pi/3$ of the CDW with respect to the lattice, it is not possible to terminate a single DC because of the nonintegral phase difference. However, three similar DC's can be brought together and joined at a point to give a total phase change of 2π along any path around that point. A point singularity like this is called a CDW dislocation. Such CDW dislocations have never been observed directly, although the Young's modulus experiments of Barmatz, Testardi, and DiSalvo[11] seem to be consistent with this CDW dislocation model. We show in Fig. 3 direct images of CDW dislocations of this kind found in the striped phase at 100 K. It is strikingly obvious in Fig. 3 that three DC's are always required to make a CDW dislocation. Recall that DC's in the striped phase are planes that extend through the entire sample thickness. The CDW dislocations shown in Fig. 3 are therefore lines perpendicular to the sample surface. It does seem from the density and temperature behavior of these dislocations that they are important in the evolution of the striped phase.

Finally we would like to mention that some residual DC's are always present in the commensurate phase even at 16 K. These residual DC's seem to be irregular in shape and little movement is observed below T_{CI}. These residual DC's in the commensurate phase could be responsible for some low-frequency acoustic loss observed by Barmatz, Testardi, and DiSalvo.[11]

In this Letter we have presented direct evidence for the existence of DC's and dislocations in the incommensurate CDW phase of $2H$-$TaSe_2$. They have been imaged directly by CDW satellite dark-field transmission electron microscopy. Recently time-dependent images associated with CDW's in $NbSe_3$ were reported obtained with a similar technique.[12] However, the interpretation of that observation is not quite so clear. We have also made observations on a cooling cycle in which CDW domains with hexagonal symmetry are expected and have also studied the striped-to-hexagonal transition on warming. Very interesting domain patterns are observed, which we will discuss elsewhere.

A great deal more information can be extracted from images such as shown here, for example concerning the kinetics and dynamics of the CDW phase transitions. The main purpose of this Letter is to demonstrate the obvious confirmation of the DC/dislocation model which is evident from this elegant technique.

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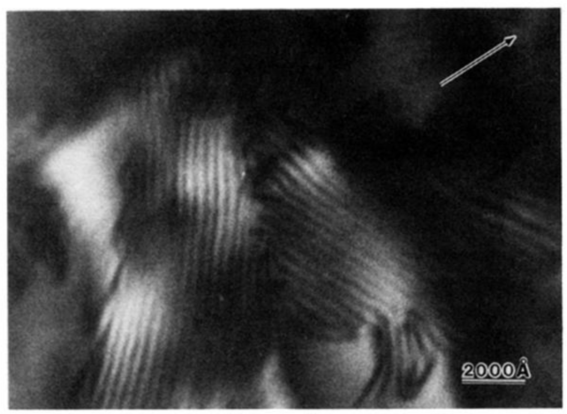

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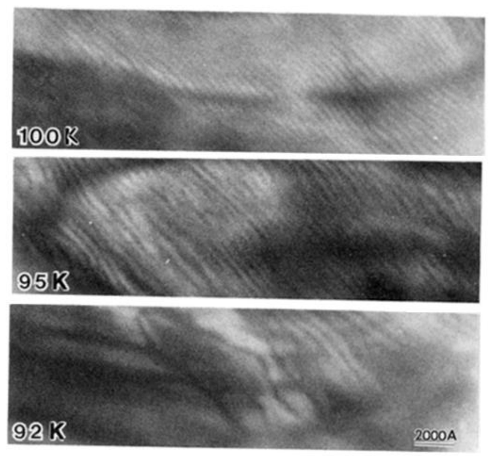

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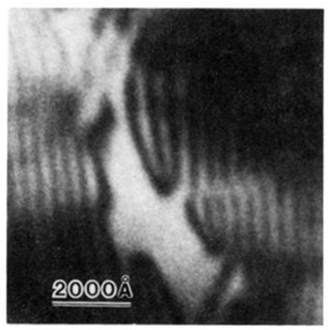

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