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Broken Hexagonal Symmetry in the Incommensurate Charge-Density Wave Structure of $2H$-TaSe$_2$

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High-resolution x-ray scattering studies show a new charge-density wave (CDW) structure on warming through the commensurate-incommensurate transition in $2H$-TaSe$_2$ at 93 K. In contrast to the fully incommensurate CDW structure seen on cooling, hexagonal symmetry is broken in the new phase and the triple-$\vec{q}$ CDW has one commensurate and two incommensurate wave vectors. At 112 K (warming) the CDW transforms to the fully incommensurate structure.

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Systems with incommensurate periodicities have been the focus of many experimental[1-4] and theoretical studies.[5-9] These systems include charge-density waves[1,2] (CDW's) and rare gases physisorbed onto surfaces.[3,4] If the incommensurate periodicity is close to registry with the host lattice, one expects the interaction between the two subsystems to favor the formation of large commensurate regions separated by narrow domain walls with rapidly varying superlattice phase.[5,6] Domain walls may be either ordered in a regular hexagonal honeycomb array or linear striped pattern, for example, as suggested by Bak and Mukamel,[7] or disordered as described by Villain.[8] These arrangements are determined by the competition between wall-wall interactions, wall-crossing energies, and entropy. There may be phase transitions from the disordered to ordered states and between the different ordered states. Thus far the evidence in support of domain walls has come from the observation of higher-order diffraction satellites of the CDW superlattice in $2H$-TaSe$_2$ (Ref. 2) and satellite intensity variations attributed to coherent interference from ordered domains in the krypton/pyrolytic-graphite systems.[3]

In this Letter we present observations of a previously undetected CDW phase in $2H$-TaSe$_2$ with broken hexagonal symmetry. In the new phase the triple-$\vec{q}$ CDW contains one commensurate and two incommensurate wave vectors. We will show that diffraction satellites identify the new phase as having the striped geometry. Further we report a first-order transition from this state to a fully incommensurate state which has the hexagonal geometry. This transition was initially seen in dilatometry studies by Steinitz and Grunzweig-Genossar.[10]

High-resolution x-ray scattering was performed on a triple-axis spectrometer with a cleaved TaSe$_2$ platelet mounted in $(h0l)$ or (hhl) scattering planes. Copper $K\alpha_1$ x rays from a 50-kW rotating anode were focused with a vertically bent LiF monochromator. A flat Ge analyzer was used on the diffracted beam. This arrangement resulted in a resolution function with a full width at half maximum of 0.003 Å^{-1} in the diffraction plane and about 0.1 Å^{-1} normal to the plane.

Neutron scattering experiments[2] have shown that on cooling[11] an incommensurate CDW forms at a normal-incommensurate (NI) transition at T_{NI} = 123 K and becomes commensurate at a commensurate-incommensurate (CI) transition at T_{CI} ~ 90 K. The CDW has a triple-$\vec{q}$ structure with

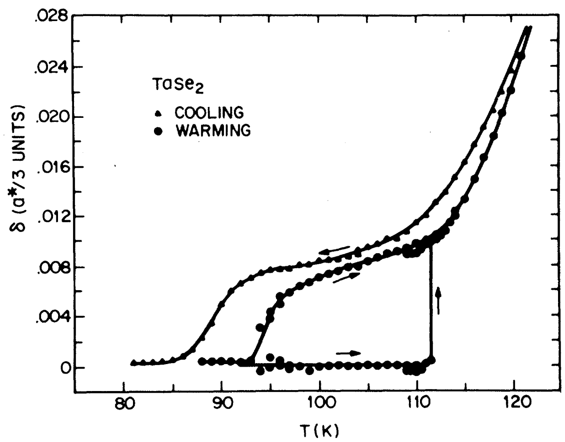

FIG. 1. Incommensurability as a function of temperature. On cooling the CDW remains in the fully incommensurate hexagonal phase until lock-in at 85 K. On warming the striped CDW phase is seen in the range 93–112 K. A phase transition between the striped and the hexagonal CDW structures occurs at 112 K.

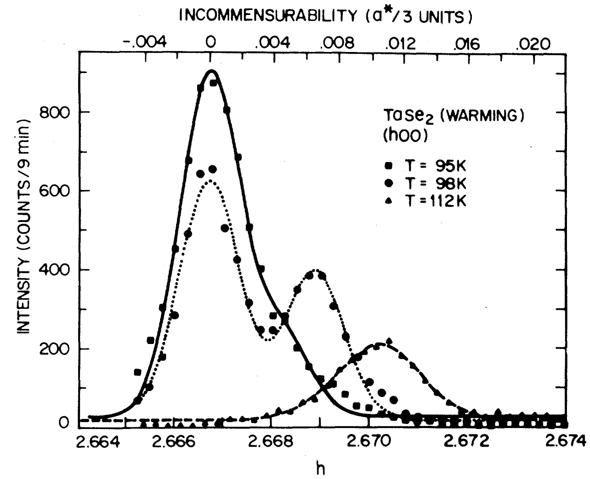

FIG. 2. Scans taken along [h00] through the ($\frac{8}{3}$ 0 0) primary superlattice position for T = 95, 98, and 112 K (warming). The two peaks are due to the striped CDW phase where one modulation wave vector is commensurate and two wave vectors are incommensurate.

three modulation wave vectors of equal magnitude and hexagonal symmetry. Thus $|\vec{q}_1|=|\vec{q}_2|=|\vec{q}_3| =[1-\delta(T)]a^*/3$ where $a^*=4\pi/a_0\sqrt{3}\approx 2.114$ Å^{-1} and $\delta(T)$ is the temperature-dependent incommensurability. In Fig. 1 we show $\delta(T)$ for both heating and cooling. The data were obtained from scans along [h00] through the $[(8+\delta)/3,0,0]$ superlattice peak with use of scans through (300) to determine a^* precisely. The cooling data agree with the earlier lower-resolution neutron results; we find a single incommensurate peak at $[(8+\delta)/3,0,0]$ for $T_{\rm CI}<T<T_{\rm NI}$. The incommensurability approaches zero continuously with $T_{\rm CI}$(cooling) = 85 K; however, previous authors have reported a first-order CI transition.[2,10,12-14] We see no evidence on cooling of a phase transition between $T_{\rm NI}$ and $T_{\rm CI}$, but there is a gradual change in slope of $\delta(T)$ near 112 K.

The behavior of $\delta(T)$ on warming is radically different from the cooling data. First, the CDW becomes incommensurate at a higher temperature, $T_{\rm CI}$ (warming) = 93 K. Second, two distinct CDW peaks are visible as shown in Fig. 2. One peak occurs at the commensurate value of $h=\frac{8}{3}$ while the second becomes progressively more incommensurate with increasing temperature. A phase transition occurs at 112 K and the commensurate peak vanishes abruptly. Above 112 K a single incommensurate CDW peak is again observed.

In general, the multiple-peak structure which we observe on warming between 93 and 112 K could result from macroscopic coexistence of spatially separate commensurate and hexagonally incommensurate regions. If this were the case, scattering at the second-order satellites with reduced wave vectors $\vec{q}\,'=\vec{q}_i-\vec{q}_j$ would simply consist of a commensurate peak, coming from the regions with commensurate CDW's, surrounded by a set of three peaks [see Fig. 3(a)] coming from the hexagonal incommensurate regions. A scan along [hh0] with our resolution would therefore show in addition to a commensurate peak at $h=\frac{4}{3}$, two incommensurate peaks at $h=\frac{4}{3}-\delta$ and $\frac{4}{3}+\frac{1}{2}\delta$.

Figure 4 shows scans along [hh0] near ($\frac{4}{3}$ $\frac{4}{3}$ 0). The presence of scattering in this vicinity at all temperatures below $T_{\rm NI}$ on both heating and cooling extends the triple-$\vec{q}$ conclusion of Ref. 1 to include the entire temperature range where CDW's exist. However, the most dramatic feature of these data is that there is *no* commensurate peak for the temperature range 92–112 K where we observe the two-peak structure at the primary position. Rather, at least two incommensurate peaks are observed. Together with the primary peak data in Fig. 2, these observations rule out the macroscopic-coexistence model and can be used to determine uniquely the wave-vector structure of the new phase. First we note that the absence of a second-order commensurate peak implies that only *one* CDW wave vector is commensurate, say $\vec{q}_1$. The other wave vectors $\vec{q}_2$ and $\vec{q}_3$ are incommensurate and they can be deduced

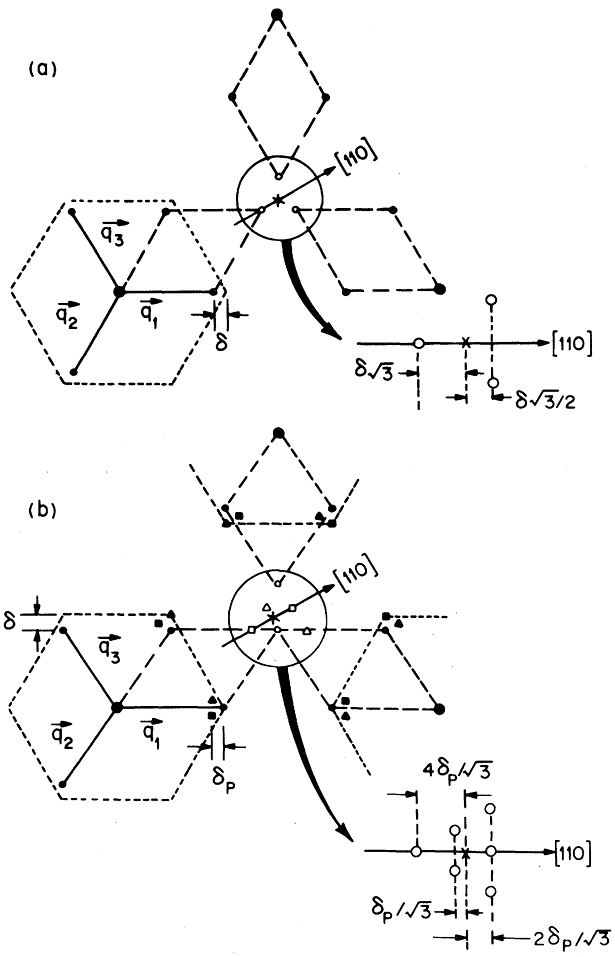

FIG. 3. Schematic plots of reciprocal space showing (a) the fully incommensurate hexagonal CDW structure and (b) the one-dimensionally incommensurate striped CDW phase. The large circles are the $TaSe_2$ lattice. The small filled symbols are the primary superlattice peaks and the open symbols are the second-order CDW peaks.

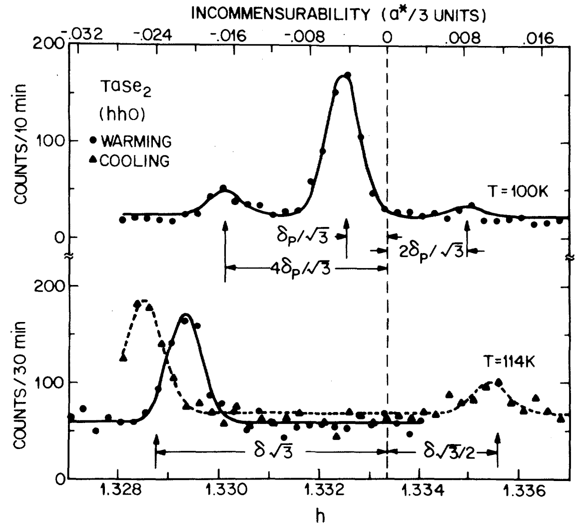

FIG. 4. Scans taken along $[hh0]$ through $(\frac{4}{3}\,\frac{4}{3}\,0)$. For $T = 100$ K (warming) three peaks characteristic of the striped CDW phase are seen. For $T = 114$ K (warming or cooling) two peaks characteristic of the hexagonal CDW phase are present.

directly from our data.

The most general form for the wave vectors allowed by our observations is (in units of $a^*/3$)

$$\vec{q}_1 = \hat{x},$$
$$\vec{q}_2 = -\tfrac{1}{2}\hat{x} - (\tfrac{1}{2}\sqrt{3} - \delta)\hat{y}, \qquad (1)$$
$$\vec{q}_3 = -\tfrac{1}{2}\hat{x} + (\tfrac{1}{2}\sqrt{3} - \delta)\hat{y}.$$

This is the structure of the striped-domain phase of Ref. 7 except that in the present case the lattice modulation is commensurate in the x direction but incommensurate by δ in the y direction. A schematic plot of the arrangement of primary and second-order diffraction satellites is shown in Fig. 3(b). Since all domain orientations are present, each of the six primary peaks in the hexagonal phase splits into three peaks in the striped phase. Scans along $[h00]$ show two peaks due to the extent of the resolution function normal to the scattering plane. The incommensurate peak is separated from the commensurate position by the projection of δ onto $[h00]$, $\delta_p = \frac{1}{2}\sqrt{3}\delta$. There are six second-order peaks in the vicinity of $(\frac{4}{3}\,\frac{4}{3}\,0)$ and scans along $[hh0]$ should show three peaks at $h = \frac{4}{3}(1 - \delta_p)$, $\frac{4}{3}(1 - \frac{1}{4}\delta_p)$, and $\frac{4}{3}(1 - \frac{1}{2}\delta_p)$ as demonstrated in Fig. 4. At the striped-hexagonal transition ($T_{SH} = 112$ K) the peak at $h = \frac{4}{3}(1 - \frac{1}{4}\delta_p)$ disappears and the structure reverts to that of the hexagonal phase.

At this stage, a number of important issues require additional comment. The sequence of events in $2H$-$TaSe_2$ is complicated by large hysteresis effects and metastability. Extrinsic effects may be very important in systems with such subtle structural differences between phases. However, the values for various transition temperatures reported elsewhere agree well with ours. One is tempted to conclude that hysteresis and metastability are intrinsic effects.

The thermodynamic order of the various transitions is also inadequately understood. The onset transition is second order experimentally, yet it should be first order because of cubic Landau terms.[2] As expected, the striped-to-hexagonal transition is demonstrably first order. Although both the striped lock-in and hexagonal lock-in transitions appear continuous in the present study, only the striped lock-in transition is expected to be continuous theoretically.[7] If this transition is indeed second order, it is potentially quite interesting to study in more detail. However, we note that an experiment in which we warmed through the commensurate-striped transition at 93 K and then cooled the *striped* phase to lock-in revealed large hysteresis effects uncharacteristic of second-order transitions.

We conclude by emphasizing a most remarkable feature of the physics of these phase transitions: the extraordinary length scale which is required to establish a physical difference between the various phases. The fact that we observe peak profiles with instrumental widths demonstrates coherence in the domain-wall pattern on a scale of $\gtrsim 3000$ Å.

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