Coexistence of two charge-density waves of different symmetry in $4Hb$-$TaSe_2$

F. J. Di Salvo
Bell Laboratories, Murray Hill, New Jersey 07974

D. E. Moncton
Bell Laboratories, Murray Hill, New Jersey 07974
and Brookhaven National Laboratory, Upton, New York 11973*

J. A. Wilson and S. Mahajan
Bell Laboratories, Murray Hill, New Jersey 07974

(Received 22 December 1975)

The physical properties of $4Hb$-$TaSe_2$ suggest the development of two charge-density waves (CDWs) of different symmetry. Electron and neutron diffraction studies establish that layers with octahedral and trigonal prismatic (TP) coordination undergo independent transitions to CDW states similar to $1T$-$TaSe_2$ and $2H$-$TaSe_2$, respectively. Although the "octahedral-CDWs" exhibit three-dimensional ordering, the "TP-CDWs" are uncorrelated due to weak interlayer forces. The possibility of a two-dimensional phase transition and the role of impurities are discussed.

The variety of physical phenomena observed in layered compounds[1] and their relation to charge-density wave (CDW) instabilities[2,3] has stimulated detailed studies of their lattice properties.[4] $TaSe_2$ has layered structure, consisting of strongly bonded Se-Ta-Se sandwiches that are weakly bonded to each other. In the $4Hb$ polytype the Ta coordination alternates from octahedral in one layer to trigonal prismatic (TP) in the next. We find that the properties of $4Hb$-$TaSe_2$ reflect those of both $1T$-$TaSe_2$,[2] in which all layers are octahedral, and of $2H$-$TaSe_2$,[4-6] in which all layers are TP. Neutron- and electron-diffraction data show that two CDWs of different symmetry develop in $4Hb$-$TaSe_2$. Quite unexpectedly, however, the CDW in the TP layers is found to exhibit *only* two-dimensional long-range order, the individual layers being uncorrelated.

Single crystals of $4Hb$-$TaSe_2$ were prepared in sealed quartz tubes by the iodine-vapor-transport technique. The tube was quenched in water from a growth temperature of 800 °C, to retain this metastable polytype at room temperature (the room temperature stable polymorph is $2H$-$TaSe_2$). X-ray diffraction confirmed the $4Hb$ structure,[7] with hexagonal axes of $c = 25.15$ Å, $a = 3.455$ Å. A few weak superlattice lines were also observed. Resistivity measurements were performed by the four-point method using either ultrasonic indium- or silver-paste contacts. The magnetic susceptibility of single crystals was determined by the Faraday method.

The electrical resistivity (ρ) of $4Hb$-$TaSe_2$ (parallel to the layers) is compared with that of $1T$-$TaSe_2$ and $2H$-$TaSe_2$ in Fig. 1. In $1T$-$TaSe_2$ an incommensurate CDW forms at $T_0 \approx 600$ K, and a first-order transition at $T_d = 473$ K to a commensurate CDW state is accompanied by a jump in ρ. In $2H$-$TaSe_2$ CDW onset causes a sudden change in ρ near $T_0 = 122$ K. For this compound the subsequent transition to the commensurate state at $T_d = 90$ K is accompanied by a 1% change in ρ.[8] In comparison, the resistivity of $4Hb$-$TaSe_2$ indicates *both* a first-order transition ($T_{d1} = 410$ K) as in $1T$-$TaSe_2$, and a drop in ρ (near $T_{02} \approx 75$ K)[9] as in $2H$-$TaSe_2$. The transition at T_{02} also influences the magnetic susceptibility (χ) of $4Hb$-$TaSe_2$ as shown in Fig. 2. Both $\chi_{\parallel}$ (to c axis) and $\chi_{\perp}$ have a

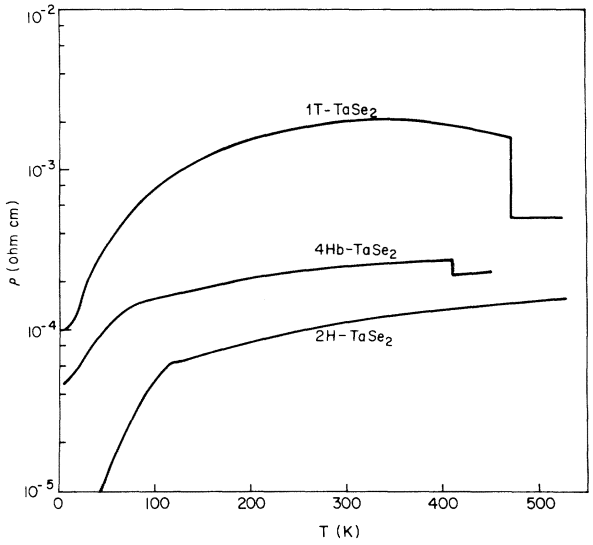

FIG. 1. Basal plane resistivity in the direction perpendicular to the c axis of $1T$, $2H$, and $4Hb$-$TaSe_2$. $4Hb$-$TaSe_2$ shows both a first-order transition at $T_{d1} = 410$ K as in $1T$-$TaSe_2$ and a knee at $T_{02} \approx 75$ K as in $2H$-$TaSe_2$ [the resistivity ratio of this $2H$ sample, $\rho(295\text{ K})/\rho(4.2\text{ K}) = 210$].

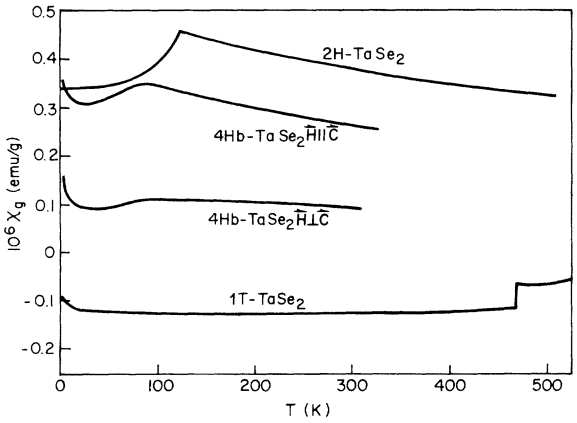

FIG. 2. Magnetic susceptibility of single crystal $4Hb$-$TaSe_2$, both for $\vec{H} \| \vec{c}$ and $\vec{H} \perp \vec{c}$, shows a peak similar to that in $2H$-$TaSe_2$ (shown here for a powder sample), and absent from the susceptibility of $1T$-$TaSe_2$ (also powder).

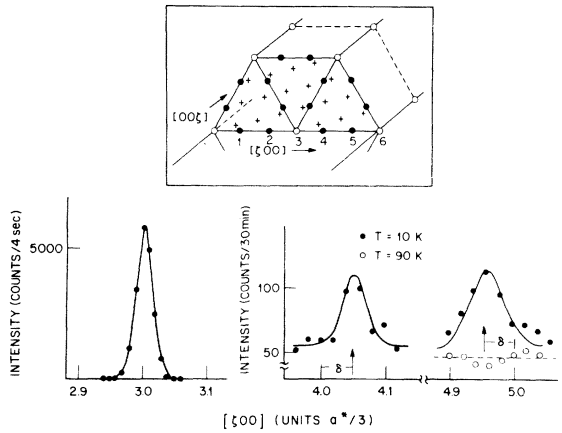

FIG. 3. Elastic neutron scattering along $[\zeta 00]$ in $4Hb$-$TaSe_2$, showing incommensurate superlattice peaks at $\zeta = \frac{1}{3}(4+\delta)a^*$ and $\zeta = \frac{1}{3}(5-\delta)a^*$, and the (300) Bragg peak of the undistorted structure. The inset displays the reciprocal lattice of the undistorted phase (open circles), a commensurate $3a$ superlattice (full circles), and the commensurate $\sqrt{13}a$ superlattice (crosses).

peak which, except for rounding, is similar to that seen in $2H$-$TaSe_2$. These properties suggest that (i) different CDWs exist in the octahedral and TP layers, and (ii) these CDWs may be similar to those in the respective pure octahedral or TP "parent" compound.[10] In fact, the entropy change in $4Hb$-$TaSe_2$ at T_{d1} (0.32 cal/mole K)[7] is nearly half the value obtained for $1T$-$TaSe_2$ at T_d (0.78 cal/mole K),[11] as expected from the 1 : 2 ratio of octahedral layers in the two structures. We now discuss the results of electron- and neutron-diffraction studies which verify the above speculations.

Above $T_{d1} = 410$ K, 200-kV transmission-electron-diffraction patterns show sharp satellite spots separated from the main Bragg peaks by wave vector $\vec{q} = 0.265\ \vec{a}^*$, indicating an incommensurate CDW. The satellite intensity decreases smoothly with increasing temperature, and vanishes at $T_0 \approx 600$ K. The entire pattern is essentially the same as $1T$-$TaSe_2$ above T_d (except in $1T$-$TaSe_2$ $\vec{q} = 0.285\ \vec{a}^*$) showing that three symmetry-related CDWS are present, separated by 120° about the c axis. Furthermore, below the transition at $T_{d1} = 410$ K a superlattice identical to that of $1T$-$TaSe_2$ below $T_d = 473$ K (i.e., $a' = \sqrt{13}\,a$)[12] is observed. From the similarity of these patterns, and from the analogous behavior of the $1T$ and $4Hb$ resistivity in this temperature range, we conclude that this CDW in $4Hb$-$TaSe_2$ occurs in the octahedral layers.

Next we consider the behavior below 100 K. Triple-axis neutron-diffraction measurements performed at the Brookhaven High Flux Beam Reactor reveal weak elastic scattering at 10 K which is not present above 90 K. We emphasize that this scattering is in addition to the peaks of the "octahedral-CDW" discussed previously. Scans along the $[\zeta 00]$ direction are shown in Fig. 3. The reduced wave vector for this superlattice $[\vec{q} = \frac{1}{3} \times (1+\delta)\vec{a}^*$, where $\delta \approx 0.04$ at 10 K] is similar to that found in $2H$-$TaSe_2$ ($\delta = -0.025$ at T_0).[4] This evidence supports the speculation made on the basis of the resistivity and susceptibility studies: CDW formation near $T_{02} \approx 75$ K involves specifically the TP layers. Unlike $2H$-$TaSe_2$, however, the TP-CDW does not attain the commensurate state ($\vec{q} = \frac{1}{3}\vec{a}^*$) down to 10 K. This difference between the two compounds may result from a lower lock-in energy in the $4Hb$ compound. Within a simple model,[4] this energy decreases rapidly as $|\delta|$ increases.

Thus far we have described the CDW superlattices in terms of wave-vector components in the basal plane. We conclude that the octahedral and TP layers each display characteristic CDWs which are nearly the same in the $4Hb$ material as in the parent compounds. However, the variation of scattered intensity along the $\vec{c}^*$ axis implies that the interlayer order is distinctly different in the $4Hb$ compound. This new behavior derives from the alternating-layer structure in which coupling forces between CDWs in nearest layers vanish since the waves are mutually incommensurate. Interactions between similarly coordinated layers are weak due to the large separation and possible screening provided by the intervening layer.

At 10 and 300 K the superlattice peaks of the octahedral-CDW are well-defined "points" on planes with integer c^* values, indicating long-

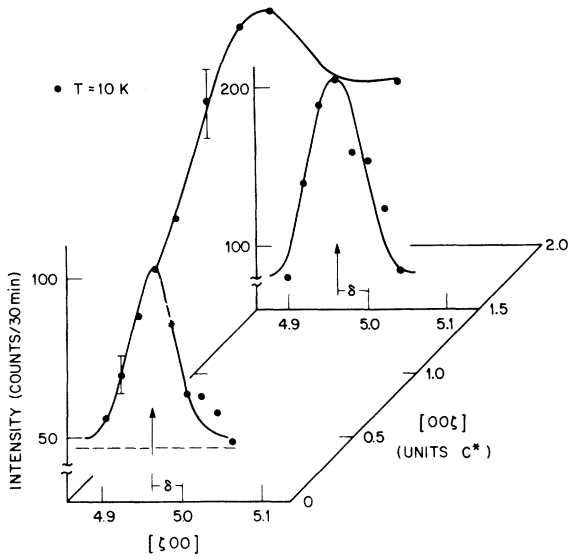

FIG. 4. Scans along [ζ00] and [00ζ] in 4*Hb*-$TaSe_2$ show the rodlike structure of the elastic scattering from the TP-CDW.

range order from layer to layer. Therefore, the CDW unit cell contains two octahedral layers, whose individual CDWs may be shifted by a relative phase to minimize the interaction energy. This ordering is simpler than that observed in 1*T*-$TaSe_2$, where the CDW unit cell involves 13 layers.[13]

In contrast to the octahedral-CDW, Fig. 4 demonstrates that scattering from the TP-CDW at $\vec{q} = \frac{1}{3}(1+\delta)\vec{a}^*$ is in the form of rods perpendicular to the basal plane. Only structure factor modulation is observed along the [00ζ] direction, and this implies that the CDW phase in each TP layer is in random sequence. These data were taken at 10 K, well below the temperature (~60 K) at which the rodlike scattering is strong enough to detect. Although low intensity prevents measurements above ~60 K, we believe that the peak in the susceptibility near 75 K signals the onset of a CDW with long, if not infinite, coherence length in the basal plane of the TP layers. These observations raise questions concerning the nature of the CDW phase transition in these layers.

Theoretically, it is not known whether a single, two-dimensional (2D) layer can undergo a phase transition in the rigorous sense. If a 2D transition is possible, one must invoke impurity pinning effects[14] to explain why the three-dimensional (3D) system with weak but necessarily finite interlayer forces does not exhibit 3D order at and below T_{02}. Within such a model the rounding of the magnetic susceptibility at 75 K would be interpreted as an impurity effect. However, if a pure 2D phase transition cannot occur, it is possible that we are observing *intrinsic* behavior, analogous to that of highly 2D magnetic systems.[15] Characteristically such a system exhibits rapid but smooth changes in physical properties in the temperature range when the 2D correlation length $\xi_{2D}(T)$ becomes large. A distinct 3D phase transition[16] occurs at a lower temperature given by $k_B T_{3D} = \xi_{2D} J_\perp$, where $J_\perp$ is the interlayer exchange. Adapted to the present case, such an interpretation would explain the rounding of the susceptibility, but predict a 3D transition at lower temperature. Since we have not observed this transition, it must occur below 10 K or be suppressed by impurities. Experiments in impure CDW systems[11,13] imply that impurity (or defect) concentrations in the 10–100-ppm range may be sufficient to suppress 3D ordering of the TP-CDWs in the present compound. Further experiments are required to firmly establish the effects of impurities.

In this study we report the novel observation of two symmetry-independent CDWs in the same compound. The octahedral-CDW is incommensurate at inception ($T_{01} = 600$ K) and locks to the commensurate $\sqrt{13}a$ superlattice at $T_{d1} = 410$ K. Measurements at and below 300 K show that this superlattice has 3D long-range order. On the other hand, the TP-CDW which forms at $T_{02} \approx 75$ K exhibits only 2D long-range order and is incommensurate down to 10 K. The behavior of 4*Hb*-$TaSe_2$ indicates that it may prove as interesting for studying the role of impurities, dimensionality, and fluctuations in phase transitions as it has been for investigating the CDW phenomenon.

We thank J. V. Waszczak for assistance in the preparation and measurements of ρ and χ of 4*Hb*-$TaSe_2$. We also acknowledge useful discussions with J. D. Axe, Y. Imry, and P. A. Lee.

*Work at Brookhaven performed under the auspices of the U. S. Energy Research and Development Administration.

[1]J. A. Wilson and A. D. Yoffe, Adv. Phys. 18, 193 (1969).
[2]J. A. Wilson, F. J. Di Salvo, and S. Mahajan, Adv. Phys. 24, 117 (1975).
[3]P. M. Williams, G. S. Parry, and C. B. Scruby, Philos. Mag. 29, 695 (1974); C. B. Scruby, P. M. Williams, and G. S. Parry, *ibid.* 31, 255 (1975).
[4]D. E. Moncton, J. D. Axe, and F. J. Di Salvo, Phys. Rev. Lett. 34, 734 (1975).
[5]R. K. Quinn, R. Summons, and J. J. Banewicz, J.

Phys. Chem. 70, 230 (1966).
[6]H. N. S. Lee, M. Garcia, H. McKinzie, and A. Wold, J. Solid State Chem. 1, 190 (1970).
[7]R. Huisman and F. Jellinek, J. Less-Common Met. 17, 111 (1969).
[8]J. M. E. Harper (private communication); C. W. Chu, L. R. Testardi, F. J. Di Salvo, and D. E. Moncton, Phys. Rev. B 14, 464 (1976).
[9]We denote the onset temperature of a CDW (usually incommensurate) by T_0, and the discontinuous incommensurate → commensurate transition temperature by T_d. The 4*Hb* system has two distinct CDWs. Therefore, we add an additional numerical subscript (e.g., T_{d1}) for clarity.
[10]The previously reported properties of 4*Hb*-TaS_2 also suggest that the behavior of the octahedral and TP layers resembles that of the respective 1*T* or 2*H* parent polymorph. However, the transition associated with the TP layers appears to be first order. See, F. J. Di Salvo, B. G. Bagley, J. M. Voorhoeve, and J. V. Waszczak, J. Phys. Chem. Solids 34, 1357.
[11]F. J. Di Salvo, J. A. Wilson, B. G. Bagley, and J. V. Waszczak, Phys. Rev. B 12, 2220 (1975).
[12]See Ref. 2 and the inset of Fig. 3.
[13]In 1*T*-$TaSe_2$ the Coulomb interaction dominates the stacking sequence of the CDW in *both* the incommensurate and commensurate state. See Ref. 2 and D. E. Moncton, F. J. Di Salvo, J. D. Axe, L. J. Sham, and B. R. Patton, Phys. Rev. B (to be published).
[14]Y. Imry and S. Ma, Phys. Rev. Lett. 35, 1399 (1975); W. L. McMillan, Phys. Rev. B 12, 1187 (1975); L. J. Sham and B. R. Patton, Phys. Rev. B 13, 3151 (1976).
[15]L. J. de Jongh, A. R. Miedema, Adv. Phys. 23, 1 (1974).
[16]Y. Imry, Phys. Rev. B 13, 3018 (1976).