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Reentrant Lock-in Transition of the Charge-Density Wave in $2H$-$TaSe_2$ at High Pressure

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High-pressure x-ray scattering studies of $2H$-$TaSe_2$ reveal reentrant behavior of the charge-density-wave (CDW) lock-in transition. As pressure is increased the normal-to-incommensurate CDW transition changes less than 5 K; however, the lock-in transition, initially suppressed to $T \to 0$ K at ~1.7 GPa, reappears at ~2.5 GPa. At the highest pressures (4.4 GPa) the temperature dependence of the incommensurability approaches the universal curve given by Landau theory for a single-$\vec{q}$ CDW.

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The breaking of the translational symmetry of a periodic solid by the occurrence of an incommensurate periodicity in the mass, spin, or charge density is a phenomenon of wide-spread interest.[1] Attention has focused on the generalized phase diagram describing transitions among the normal (N), commensurate (C), and incommensurate (I) phases in the transition-metal dichalcogenides.[2-7] The phase diagram can be studied with the pressure as variable, and in this Letter, we report x-ray measurements of the effect of pressure up to 4.4 GPa (44 kbar) on the transitions in the prototypical charge-density-wave (CDW) material, $2H$-$TaSe_2$. At atmospheric pressure $2H$-$TaSe_2$ has a transition on cooling to an incommensurate CDW state at $T_{IN} = 122$ K and a lock-in transition at $T_{CI} = 90$ K. In the incommensurate phase the wave vector of the CDW, $\vec{q} = (1-\delta)\vec{a}^*/3$, exhibits an initial rapid increase toward the commensurate value ($\delta \equiv 0$) with decreasing temperature but then saturates just above T_{CI}.[2] We find that the phase boundary for the lock-in transition is reentrant, being suppressed to $T < 10$ K by $P = 1.7$ GPa in agreement with earlier resistivity measurements[8,9] and then reappearing above $P \approx 2.5$ GPa. The degree of incommensurability at onset, δ_0, increases ~60% over the range of pressure up to 4.4 GPa. At the highest pressures studied, the temperature dependence of δ approaches the universal behavior predicted by Landau theory[3] in contrast to atmospheric or intermediate pressures where it is in qualitative disagreement with theory. The present results suggest that there is an interaction, not included in present theories, which becomes important below $T \sim 0.8T_{IN}$.

The high-pressure measurements were made on crystals ($\sim 0.2\times 0.2\times 0.02$ mm^3) grown by iodine vapor transport from polycrystalline powder which had been made by reaction of the pure elements in evacuated quartz tubes. A gasketed, opposed-diamond-anvil, clamp device of the Merrill-Bassett type[10] was used to generate hydrostatic pressures up to ~5 GPa. The tiny crystal and a chip of ruby were mounted in a 0.35-mm-diam hole in an Inconel gasket. The pressure-transmitting medium was a mixture of 4:1 methanol-ethanol, and the pressure calibration at room temperature was done by use of the ruby fluorescence technique.[11] With decreasing temperature there is an increase in the pressure of ~0.8 GPa caused by differential thermal contraction, but the pressure is almost constant over the range of interest, namely $T \leq 125$ K. An independent calibration of the pressure comes from a comparison of the observed lattice parameter with an interpolation of the room-temperature compressibility and the thermal expansion at atmospheric pressure.[12] The high-pressure diamond cell was mounted on a rotation stage in a closed-cycle He refrigerator so that the sample could be rotated *in situ* around the c axis to give the desired $[h0l]$ scattering plane. In order to observe the CDW reflections, which are 10^{-3} smaller than typical Bragg peaks, a high-brilliance Rigaku rotating-anode x-ray generator was used with a projected 0.2×0.2-mm^2 spot. The Mo $K\alpha$ x rays were focused by a vertically bent graphite (004) monochromator and analyzed by a flat LiF (200) crystal.

$2H$-$TaSe_2$ is hexagonal with $a = 3.435$ Å and $c = 12.7$ Å at room temperature and atmospheric pressure and $a = 3.385$ and $c = 12.1$ Å at 4.4 GPa.[12] Below $T_{IN} = 122$ K a triple-$\vec{q}$ CDW and associated periodic lattice distortion develop with wave vectors from the star of $\vec{q} = \pm(1-\delta)\vec{a}^*/3$. Typical scans of the CDW reflection near $(\frac{4}{3},0,0)$ taken on cooling and warming at $P = 4.4$ GPa are shown in Fig. 1. The lock-in occurs near $T = 100$ K at $P = 4.4$ GPa. The commensurate position at each temperature was determined by interpolating between the observed positions of the (100) and (200) Bragg reflections which had been calculated from a least-squares fit with a Gaussian line shape of the appropriate longitudinal $(h00)$ scan. Mesh scans were taken periodically around the Bragg peaks to check the alignment. The position of the peak can be determined with an accuracy of one-tenth of the full width at half maximum which corresponds to an error in δ of ± 0.003.

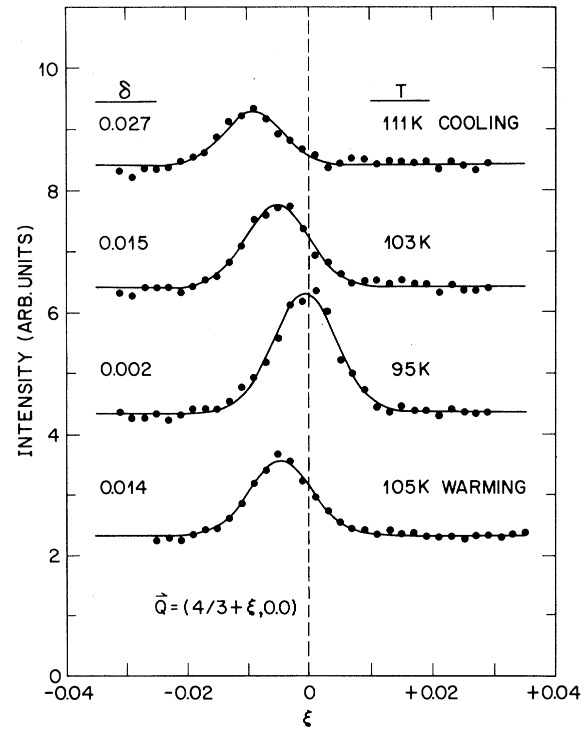

FIG. 1. Longitudinal $(h00)$ scans through the CDW reflection at $(\frac{4}{3}+\xi, 0, 0)$ at several temperatures at $P = 4.4$ GPa showing a reversible lock-in transition at $T \approx 100$ K. The solid curves are least-squares fits by a Gaussian line shape. The different curves have been successively displaced by two units for clarity.

The behavior of δ versus temperature in different regions of the phase diagram is indicated by representative curves in Fig. 2. The behavior at all pressures can be represented by superimposing a lock-in transition onto a curve with the general form observed at $P = 1.7$ GPa. Typical of the data below $P = 1.7$ GPa is the high-resolution scan taken at atmospheric pressure.[13] As the pressure is increased, the lock-in temperature is suppressed until it disappears near $P = 1.7$ GPa. The absence of lock-in was observed in three different samples and was determined from the CDW reflections near $(\frac{4}{3},0,0)$, $(\frac{8}{3},0,0)$, and $(\frac{10}{3},0,0)$. In addition, δ vs T was studied in the diamond cell at $P = 1$ atm after a series of temperature cycles at various elevated pressures, and a normal lock-in was observed on cooling near 90 K. At $P = 3$ GPa lock-in is observed again with δ varying in a way qualitatively similar to the low-pressure region. At higher pres-

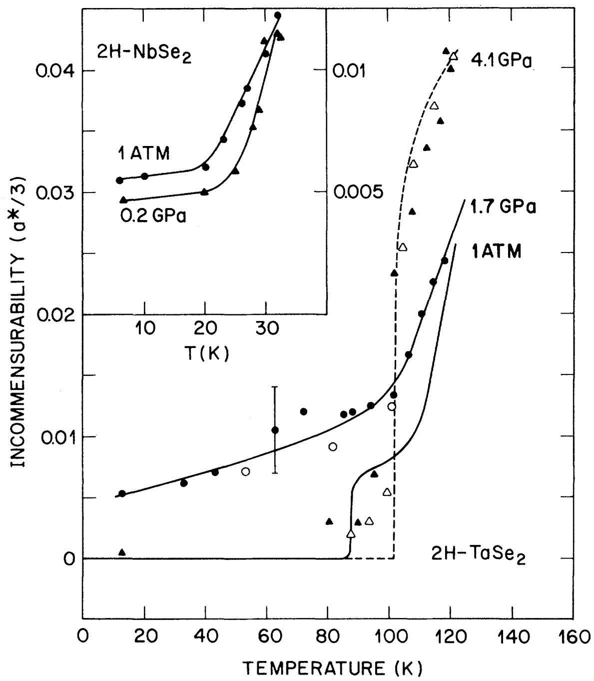

FIG. 2. Incommensurability, δ, vs temperature at $P\sim 0$, $P=1.7$, and 4.1 GPa. The curve at $P=1$ atm is from Ref. 13. Closed and open symbols were taken on cooling and warming, respectively. The solid curves are guides to the eye. The dashed curve is the universal curve given by Landau theory as described in the text. The inset shows similar curves for $2H$-$NbSe_2$ from Ref. 14.

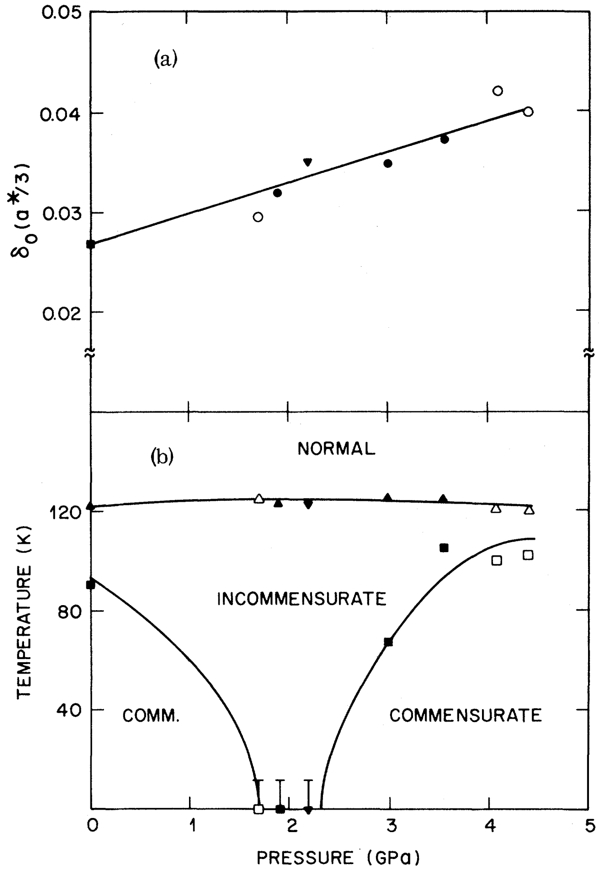

FIG. 3. (a) Incommensurability at onset, δ_0, vs pressure and (b) the temperature-pressure phase diagram for the CDW transitions in $2H$-$TaSe_2$. The phase boundaries below $P=1.8$ GPa are from Ref. 8 and the different symbols represent different samples.

sures the temperature of the lock-in transition has risen above the temperature at which δ vs T begins to saturate and $\delta(T)$ evolves to the shape demonstrated by the data of Fig. 2 for $P=4.1$ GPa.

From a series of temperature cycles at different pressures, a temperature-pressure phase diagram has been constructed [Fig. 3(b)]. In addition, from extrapolations of δ vs T up to T_{IN} at different pressures, the variation of δ_0 with pressure was determined [Fig. 3(a)] and the initial slope is $(d\ln\delta_0/d\ln a)_{p\to 0}=-34$. The phase boundaries up to 1.8 GPa, shown in Fig. 3, are taken from earlier resistivity studies.[11] The data for lock-in above $P=2.5$ GPa appear to saturate near $T\approx 100$ K, but further experiments at higher pressures will be needed to look for a possible triple point between the normal, incommensurate, and commensurate phases as a function of pressure. The lock-in temperature, the sharpness of the transition, and the sharpness of the change in slope of δ vs T at lower pressures are strain dependent and become broader on successive temperature cycles. This probably results from the freezing and melting of the pressure transmitting medium on cycling the temperature.

A comparison of the properties of the chemically similar transition metal dichalcogenides $2H$-$NbSe_2$ and $2H$-$TaSe_2$ suggests that a generalized temperature-pressure phase diagram can be constructed for the two compounds by the assumption that $P=1$ atm in $2H$-$NbSe_2$ corresponds to $P\sim 1.7$ GPa in $2H$-$TaSe_2$. $2H$-$NbSe_2$ has a transition to an incommensurate CDW at $T=34$ K, but no lock-in transition has been observed down to $T=4.2$ K.[2,14] The variation of δ with temperature in $2H$-$NbSe_2$ at $P=1$ atm (shown in the inset of Fig. 2) is similar to that of $2H$-$TaSe_2$ at 1.7–2.2 GPa, and $2H$-$NbSe_2$ is approaching a commensurate phase with increasing pressure (inset of Fig. 2).[14,15]

Theoretical models for CDW transitions involve

Landau expansions of the free energy in powers of a charge-density-wave order parameter. The occurrence of a lock-in transition in a single-$\vec{q}$ CDW results from the competition between the gradient-energy term and the umklapp terms. The observed sequence of transitions as a function of temperature follows from the usual assumption that the only temperature-dependent term is the quadratic one. The presence of higher harmonics of the fundamental CDW satellite naturally leads to a temperature dependence of δ in the incommensurate phase as a result of coupling terms of the form $\varphi_\delta^2\varphi_{2\delta}$.[2] These harmonics are evidence that amplitude and/or phase modulation of the simple sine-wave CDW is occurring. In the limit of weak coupling only phase modulation is important, and the minimization of a free energy correct to all harmonic orders[3] gives a universal curve for $\delta(t)$ which is independent of the Landau parameters. This curve for the single-$\vec{q}$ CDW and also numerical results[5] for the triple-$\vec{q}$ CDW phase have the common feature that as commensurability is approached the slope of $\delta(T)$ becomes increasingly larger. As shown in Fig. 2, $\delta(T)$ may initially increase its slope below T_{IN}, but the predominant behavior is the decreasing slope as lock-in is approached in qualitative disagreement with the theoretical prediction. However, at $P = 4.1$ GPa the experimental results approach the universal curve which is shown as the dashed curve. We conclude that below temperatures of the order of $\sim 0.8T_{IN}$ there are additional contributions to the free energy which are causing $\delta(T)$ to saturate and that the universal behavior is approached only if commensurability is achieved before these contributions become important.

The pressure dependence of the lock-in transition of a single-$\vec{q}$ CDW depends on the ratio of amplitude to phase modulation[4,5] and varies as δ_0^4 for the latter.[3] As shown in Fig. 3, δ_0 increases ~60% over the range of pressure studied and therefore δ_0^4 increases by a factor of 6. This is consistent with the initial large decrease in T_{CI} but not the reentrant behavior which probably requires considering the full triple-$\vec{q}$ CDW. The free energy of the $3\vec{q}$ phase has terms which result from the interaction between the three different CDWs and the reentrant nature of the lock-in transition probably results from the competition between these new terms. It is possible that the two commensurate regions in the phase diagram represent separate triple-$\vec{q}$ and single-$\vec{q}$ phases or that they have different CDW eigenvectors. Further work is planned to attempt to answer these questions.

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