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Pressure effects on the charge-density-wave phases in $2H$-TaSe$_2$

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The transition temperatures from the commensurate to incommensurate phase (T_d) and from the incommensurate to normal phase (T_0) in $2H$-TaSe$_2$ have been determined as a function of hydrostatic pressure up to 18 kbar. We found that while T_0 increases only slightly with pressure, T_d falls rapidly as $(1-P/P_c)^{1/2}$ under pressure, extrapolating to a critical pressure P_c of 17 kbar for the complete stabilization of the incommensurate phase. We conclude that the interlayer coupling can not be neglected in discussing the stability of the charge-density-wave state.

INTRODUCTION

Recently the anomalous properties of layered transition-metal dichalcogenides have been the subject of great interest, because of their associated electronic instabilities attributed to charge-density-wave (CDW) formation.[1] The trigonal prismatic coordinated compound $2H$-TaSe$_2$ undergoes two intrapolytypic transitions upon cooling as evidenced, e.g., by a sharp resistance kink[2] at ~122 K and a small drop in the resistance[3] at ~90 K. Neutron scattering experiments[4] demonstrated that $2H$-TaSe$_2$ is a normal metal above 122 K, and forms a CDW state below 122 K with an incommensurate superlattice which subsequently becomes commensurate below 90 K. The normal to incommensurate phase (N-I) transition at temperature T_0 is second order (or weakly first order at the best),[3,4] whereas the incommensurate to commensurate phase (I-C) transition at temperature T_d is first order.[3,4]

We have measured resistively both the T_d and the T_0 for $2H$-TaSe$_2$ as a function of hydrostatic pressure up to 18 kbar. We find that while T_d decreases rapidly with pressure, T_0 increases under pressure with a large quadratic term. The T_d results can be understood qualitatively in terms of the phenomenological Landau theory of CDW states.[4,5] Our pressure data together with those from elastic and neutron scattering[4] measurements also suggest that interlayer coupling is not negligibly small. The present study demonstrates that $2H$-TaSe$_2$ is a unique example of a CDW system in which the commensurate phase can be totally inhibited and the formation of the incommensurate CDW state enhanced, by the application of pressure.

EXPERIMENTAL RESULTS

The sample investigated was cut with dimensions of $8 \times 2 \times {\sim}0.8$ mm^3 (thickness) from a $2H$-TaSe$_2$ single crystal grown from the iodine-vapor-transport technique. The electrical resistance (R) along the layers was determined by a standard four-probe ac technique operating at 10 Hz as a function of temperature between 4.2 and 300 K under different compressions up to 18 kbar. Leads were attached to the sample with an ultrasonic soldering iron using indium solder, and indium contacts were lapped over the edges of the sample to make contact with all layers. Both the thermal and pressure cyclings did not generate any breaks in R, typical for a troubled contact in layered-compound study. The modified self-clamp technique[6] was used to provide the hydrostatic pressure environment in a 1:1 fluid mixture of n-pentane and isoamyl alcohol. The pressure was generated by a press and locked by the clamp at room temperature. The pressurized sample together with the clamp was then removed from the press and slowly cooled inside a ^{4}He cryostat. No noticeable shift in either the resistance or transition temperature was detected after the sample was immersed in the pressure medium for two months, indicating that the pressure medium is chemically inert to the sample. A superconducting Pb manometer situated next to the sample was used to measure the pressure at low temperature. Since the pressure change due to cooling usually is small,[7] the quoted pressure is that determined at low temperature (~7 K). The temperature of the sample was determined by an Alumel/Chromel thermocouple[8] at the immediate vicinity of the sample inside the high-pressure medium. All electrical leads were brought out from the high-pressure environment by Stycast 2850 FT epoxy seals.

At atmospheric pressure, the temperature dependence of R for our $2H$-$TaSe_2$ sample is similar to that previously observed.[3] The N-I phase transition is characterized by a distinct ~1.5% resistance kink at 122 K, and does not exhibit any thermal hysteresis of more than 0.05 K. The I-C phase transition is less conspicuous. Only a small decrease appears in R at 92 K on cooling. However, the thermal hysteresis loop (~3 K), characteristic of a first-order transition, helps to locate the I-C phase transition. The shapes of both transitions are shown in the inserts of Figs. 1 and 2, where T_0 and T_d are also defined. R decreases almost linearly with decreasing temperature above T_0 and quadratically below T_0. The resistance ratio of our sample between 300 and 4.2 K is 170. The application of hydrostatic pressure does not change R more than (0.2–2)% at temperatures below the resistance kink, but slightly suppresses the temperature slope of R above T_0. The maximum reduction of R at 300 K observed is only 4.4% in contrast to ~20% for $2H$-$NbSe_2$.[9]

T_0 was found to be enhanced by hydrostatic pressure with $dT_0/dP = +(3.5 \pm 0.2) \times 10^{-4}$ Kbar^{-1} and $d^2T_0/dP^2 = -(7.4 \pm 0.5) \times 10^{-8}$ Kbar^{-2} at low pressure, as shown in Fig. 1, where the numbers represented the sequential order of the experimental runs. The presence of a large negative quadratic term in the pressure behavior of T_0 is consistent with the recent observation[3] of the unusually sharp rise in Young's modulus below T_0. On the other hand, T_d is drastically suppressed by hydrostatic pressure, as shown in Fig. 2 where the vertical bar indicates the thermal hysteresis of T_d. No I-C transition was detected for pressure >15 kbar down to 4.2 K. However it should be pointed out that it became increasingly difficult to identify the I-C transition as T_d was suppressed toward lower temperature. This is because of the small sample resistance at low temperature which makes the ~1.5% thermal-hysteresis R loop associated with the I-C transition less apparent at low temperature. Therefore an upper limit of 25 K was set for T_d at pressure >15 kbar. T_d fits well the relationship of $T_d(P) = 92.5(1 - P/P_c)^{1/2}$ K with a critical pressure $P_c = 17$ kbar for the complete suppression of the commensurate state, as shown in Fig. 2, although such a pressure behavior is expected for a first-order transition in a metal only as $T \rightarrow 0$ K. We found that $dT_d/dP = -(2.7 \pm 0.1) \times 10^{-3}$ Kbar^{-1} and $d^2T_d/dP^2 = -(8.0 \pm 0.5) \times 10^{-8}$ Kbar^{-2} at atmospheric pressure.

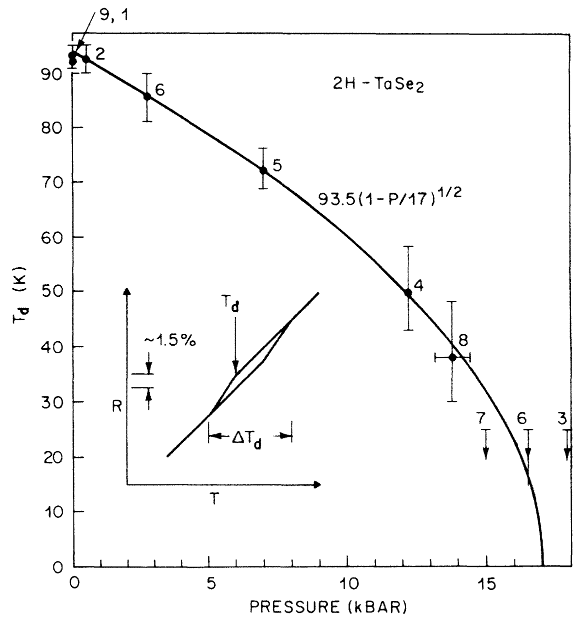

FIG. 2. Pressure dependence of T_d. The circular dot represents T_d defined in the insert, the vertical bar the thermal hysteresis, and the horizontal bar the uncertainty in pressure.

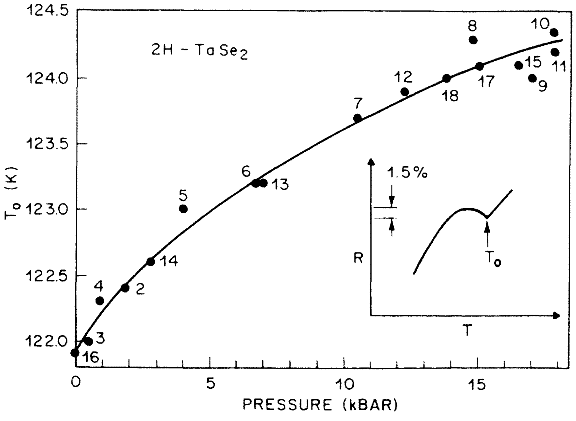

FIG. 1. Pressure dependence of T_0.

DISCUSSION

It has been shown that a metal will exhibit an electronic instability providing that the electron response function diverges at a wave vector $\vec{q}_0$. This can occur if the Fermi surface of the metal contains parallel pieces or nesting sections,[10,11] or if two-dimensional saddle points[12] in the band structure exist near the Fermi level. A CDW will result when the electron-phonon interaction is strong enough to balance off the Coulomb repulsion, and a spin density wave when the exchange dominates.[11] The characteristic band structure[13] and the strong electron-phonon coupling of these materials make them particularly susceptible to the formation of CDW states. Below T_0, where the thermal energy is overcome by the energy gain of the CDW states, an incommensurate CDW forms. Further reduction of energy is achieved as the CDW locks into a commensurate geometry at T_d by a slight change of $\vec{q}_0$. In $2H$-TaSe$_2$ the incommensurate state has a $\vec{q}_0 = \frac{1}{3}(1+\delta)\vec{a}^*$ where $\vec{a}^*$ is the reciprocal-lattice vector and δ the temperature-dependent incommensurateness.[4] $|\delta|$ decreases from $\simeq 0.02$ to 0 at T_d.

Phenomenological Landau theories of the CDW states in layer compounds were recently developed by McMillan[5] and Moncton *et al.*[4] The theories correctly describe the sequence of the CDW phase transitions, the negative impurity effects[14] on both T_0 and T_d, and the temperature dependence of the incommensurateness, δ.

The Landau theories predict a decrease in T_d as $|\delta_0|$ (δ at T_0) increases. A decrease in T_d under pressure could be due to an increase in $|\delta_0|$ and/or to a pressure dependence of the Landau parameters that also determine T_d. Diffraction studies to determine δ_0 vs pressure would show if any of the Landau parameters are indeed pressure dependent.

In the $2H$-polytypes, it seems likely that the saddle-point mechanism[12] is the microscopic source of the CDW formation. The effect of pressure on the saddle points near the Fermi level is not immediately evident, however, and thus the change of T_0 with pressure can not be easily predicted.

To determine the effects of interlayer vs intralayer atom spacings on T_0, it is necessary to obtain the uniaxial stress dependences and combine these with the appropriate elastic moduli. The former can be estimated from the behavior of the Young's modulus[3] at T_0 using a thermodynamic treatment.[15] This analysis yields $|dT_0/d\sigma_1| = (0.8 \pm 0.3) \times 10^{-4}$ Kbar^{-1} for stress in the basal plane with an undetermined algebraic sign. Combining this result with the present pressure data gives the interlayer stress derivative $dT_0/d\sigma_3 = -(5.1 \pm 1) \times 10^{-4}$ or $-(1.9 \pm 1) \times 10^{-4}$ Kbar^{-1} for the "+" and "−" signs, respectively, of $dT_0/d\sigma_1$ above.

In order to determine the strain derivatives, it is necessary to know much of the elastic modulus (stiffness) tensor. From the long-wavelength phonon-dispersion data of Moncton *et al.*[16] one calculates $C_{11} = 23$, $C_{12} = 10.7$, $C_{33} = 5.4$, and $C_{44} = 1.9$, all in unit 10^{11} dyne/cm^2 and with typical uncertainties of ~(10–15)%. The remaining tensor element obtained from the Young's modulus measurement[3] is $|C_{13}| = (7.6 + 1 \text{ or } 7.6 - 2) \times 10^{11}$ dyne/cm^2. The algebraic sign cannot be determined from the known data.[17]

Some information on the physically more relevant strain dependences of T_0 can be referred from the above results. These values indicate the importance of interlayer effects in determining T_0. For ideally-two-dimensional behavior,[18] one expects $r \equiv (dT_0/d\epsilon_\perp)/(dT_0/d\epsilon_\parallel) = 0$, where $\epsilon_\perp$ and $\epsilon_\parallel$ are strains perpendicular and parallel to the basal plane. Although there is considerable uncertainty in the calculated results as discussed above, it appears probable that $\frac{1}{3} < |r| < 2$ and, therefore, that interlayer effects are not negligible. Furthermore, for $C_{13} > 0$, $dT_0/d\epsilon_\perp \sim -100$ to -250 K, indicating that, at least to the first order in strain, the interlayer effects would enhance the T_0. A determination of the sign of C_{13} (e.g., from linear compressibility measurements) and of $dT_0/d\sigma_1$ (or $dT_0/d\sigma_3$) would lead to better estimates of the intralayer and interlayer atomic spacing effects.

The importance of interlayer interactions is evident in the band-structure calculations,[13] where the splitting at certain points in the lower d band due to interlayer interactions is equal to the bandwidth. These calculations also showed the sensitivity of these splittings to interlayer separation. It is clear that, if the band splitting changes, the separation of the saddle points from the Fermi level will change. This would establish microscopically, the pressure dependence of T_0 in the saddle-point model.[12]

In conclusion, we have found for the first time that hydrostatic pressure enhances T_0 and suppresses T_d. The rapid reduction of T_d with pressure suggests that the I-C transition sensitively depends on the details of the Fermi surface. The decrease of T_d may be associated with the enhancement of the incommensurateness under pressure or a pressure dependence of the Landau parameters. By analyzing the high-pressure data and the elastic modulus results, the contribution of the interlayer coupling is found to be important in determining the CDW state.

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[17] For $C_{13} > 0$, one finds that hydrostatic pressure leads to a small expansion of the basal plane (and a considerably larger contraction perpendicular to the plane). However, the alternate choice, $C_{13} < 0$, would also indicate relatively unique behavior, since it occurs for very few hexagonal crystals. $C_{13} > 0$ was found for $2H$-$NbSe_2$ and MoS_2 by J. L. Feldman *et al*. [Phys. Rev. B (to be published)].

[18] We assume that $\epsilon_\perp$ occurs mainly in the Van der Waals bonds and that they dominate the calculated values of $dT_0/d\epsilon_\perp$.