PHYSICAL REVIEW B VOLUME 12, NUMBER 10 15 NOVEMBER 1975

Elasticity measurements in the layered dichalcogenides $TaSe_2$ and $NbSe_2$

M. Barmatz, L. R. Testardi, and F. J. Di Salvo
Bell Laboratories, Murray Hill, New Jersey 07974

(Received 23 June 1975)

We have measured the Young's modulus and internal friction in the two-dimensional layered dichalcogenides $2H$-$TaSe_2$ and $2H$-$NbSe_2$ using a vibrating reed technique. Weak elastic anomalies are observed at the incommensurate charge-density-wave transitions in $TaSe_2$ and $NbSe_2$ at 121 and 30 K, respectively. Heating and cooling measurements through these transitions show hysteresis effects of less than 0.3 K, which may be attributed to experimental uncertainties. At the commensurate charge-density-wave transition near 90 K in $TaSe_2$, the Young's modulus and internal friction exhibit extrema, which are an order of magnitude larger than the anomalies at the incommensurate transition. Furthermore, there are large hysteresis effects (~5 K), which verify the first-order nature of this transition. At all the charge-density-wave transitions, the internal friction maximum occurs at a lower temperature than the modulus minimum. At the $NbSe_2$ superconducting transition, $T_c = 7.2$ K, the Young's modulus undergoes a smeared-out discontinuity of ~6 ppm and a change in slope. We observe no other anomalies (e.g., a commensurate transition in $NbSe_2$) down to 1.3 K. Estimates of the uniaxial stress dependence and expansivity anomaly at these transitions are also given.

I. INTRODUCTION

The layered dichalcogenides have received considerable attention in recent years as a result of their two-dimensional anisotropic properties[1-3] and associated electronic instabilities.[3] Recent electron-diffraction studies of these materials[4] reveal the existence of superlattice structures which are attributed to the formation of charge-density waves (CDW's). Experiments indicate that there are three symmetry-related CDW's in the basal plane of these hexagonal crystals. The metal coordination within a layer may be octahedral or trigonal prismatic, and the layers may be stacked in a variety of ways, leading to a number of polytypes[2] ($1T$, $2H$, $4Hb, \ldots$). Most of these polytypes are now known to be unstable toward CDW formation.[5]

In this paper, we present elastic measurements in the $2H$ polytype (trigonal prismatic coordination) of the layered dichalcogenides $TaSe_2$ and $NbSe_2$. Young's modulus and internal-friction measurements in the frequency range 0.5–5 kHz were carried out from 1.3 to 300 K using a vibrating-reed technique.[6] Detailed measurements were taken at the commensurate and incommensurate transitions induced by the CDW's. The commensurate transition in $TaSe_2$ shows elastic hysteresis effects over a 5-K interval which clearly demonstrates the first-order character of the transformation as predicted by theoretical models.[7-9] On the other hand, the incommensurate transition in $TaSe_2$ exhibits small hysteresis effects, which may be associated with experimental uncertainties. The lack of (observable) hysteresis as well as the shape of the modulus anomaly strongly suggest (but cannot prove) that these transitions are predominantly second order. We also report resistivity measurements which confirm the hysteresis findings of the elastic measurements.

II. CHARGE-DENSITY WAVES

The CDW's may be thought of as periodic variations of the conduction electron density which produce a lattice distortion of the same period.[10] The wave vector of the periodic distortion $\vec{q}_0$ is determined by a particular spanning wave vector of the Fermi surface. At high temperatures, the structure of these layered compounds is undistorted; however, as the temperature is lowered below an onset temperature T_0, the CDW's form and are detectable as sharp satellite spots in electron-diffraction patterms.[4] Generally, the periodicity of the CDW distortion is not a simple multiple of a lattice spacing just below T_0, and, therefore, this is designated the incommensurate charge-density-wave (ICDW) transformation. At some lower temperature $T_d < T_0$, the periodicity of the CDW may become locked in to a small multiple of a lattice spacing leading to a commensurate charge-density-wave (CCDW) transition. Whether a CDW becomes locked in to the lattice periodicity has been shown to depend on sample composition[11] and pressure.[12]

In the case of $2H$-$TaSe_2$, anomalous behavior in the electrical resistivity[13,4] and magnetic susceptibility[14,13,4] near 120 K were explained[4] in terms of CDW formation. It was assumed,[4] however, that the CDW's initially formed commensurate with the lattice, i.e., $T_d = T_0$. Preliminary elastic measurements[15] revealed, in addition to a weak anomaly near 120 K, a large modulus minimum and internal friction maximum near 90 K which suggested a second phase transition. In contrast, previous resistivity and magnetic susceptibility measurements showed only smooth and slowly varying behavior near 90 K. Subsequently, high-precision neutron scattering measurements[8] showed that the CDW's in $2H$-$TaSe_2$ are actually a few percent out of commensurability at the onset temperature ($T_0 = 122.3$ K), and the elastic anomalies near 90 K are associated with the lock-in or commensurate transition. The neutron study also showed that the CDW's in $2H$-$NbSe_2$ ($T_0 = 33.5$ K) is again only a few percent out of commensurability, but the CDW's remain incommensurate down to at least 5 K.

III. TECHNIQUE

Measurements of the Young's modulus and internal friction were carried out using a vibrating-reed technique which is described in detail elsewhere.[6,16] The single-crystal samples, grown by the iodine chemical vapor transport technique,[17] were prepared in the form of thin reeds, approximately 7–12 mm long, 1–2 mm wide, and 0.05–0.15 mm thick. The $2H$ polytype of $TaSe_2$ and $NbSe_2$ are hexagonal, and the samples were oriented with the layers (basal plane) in the plane of the reed. One end of each specimen was soldered with indium to a copper block as shown in Fig. 1. The reeds were excited into flexural vibrations with an electrostatic transducer situated on one side of the free end. An identical receiver transducer detected the amplitude of vibration through the modulation of the receiver capacitance.

The flexural resonant frequencies f_n for a clamped-free rectangular reed are given by[18]

$$f_n = (\kappa / 2\pi)(k_n / l)^2 v_E \, , \tag{1}$$

where the radius of gyration $\kappa = t/(12)^{1/2}$ and t and l are the thickness and length, respectively. The k_n's are constants 1.875, 4.694, ..., corresponding to the overtones $n = 1, 2, \ldots$. The Young's modulus velocity is $v_E = (E/\rho)^{1/2}$, where E is the Young's modulus along the reed axis and ρ is the density. Thus the measured modulus corresponds to that of the basal plane of these hexagonal crystals. We have carried out measurements for the two lowest resonances in the frequency range 0.5–5 kHz.

In these dichalcogenide materials, adjacent layers are loosely coupled to one another by Van der Waals forces, and the interlayer spacing is usually much larger than the atomic spacing within a layer. For an ideal elastically two-dimensional material (i.e., having no elastic coupling between layers) Eq. (1) is no longer valid, and the reed frequency would, in fact, be zero.[19] However, for $2H$-$TaSe_2$ and $2H$-$NbSe_2$, the moduli measured by this method are reasonably high (8×10^{11}–1.8×10^{12} dyn/cm^2), and we have therefore assumed all corrections to Eq. (1) to be negligible.

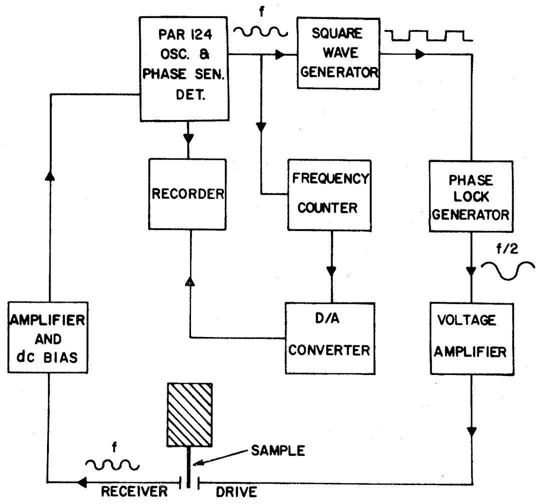

FIG. 1. Schematic of the electronics. PAR 124 is phaselocked to the antisymmetric component of the flexural resonance. Continuous record of the resonant frequency and received signal amplitude was obtained as the sample temperature changed.

Many of the samples were not of ideal rectangular geometry and led to large uncertainties [(20–50)%] in the absolute magnitude of the modulus. However, measurements of the modulus temperature dependence have a relative accuracy better than 0.2%. For this reason, all modulus measurements were presented in the dimensionless form $\Delta E/E_0 \equiv E(T)/E_0(T_R) - 1$, where T_R is a reference temperature usually associated with a particular transition or room temperature.

A detailed description of the low-temperature apparatus was reported previously.[16] The temperature of the specimen was monitored with an Au-Fe versus chromel thermocouple, situated in the copper block holding the sample. The thermocouple and a heater, also in the copper block, were used to regulate the sample temperature to better than 0.02 K. Equilibrium and drift measurements were carried out at pressures between 10^{-3} and 10^{-5} Torr, depending on the magnitude of the internal friction. Heating and cooling drift rates ranged between 0.1 and 0.3 K/min. For the fundamental resonance at any of the transitions investigated, we found reproducibility in the transition temperature and modulus minimum to be ~0.3 K and 0.1%, respectively.

The flexural resonances were investigated using the phase-sensitive detection scheme shown in Fig. 1. The Princeton Applied Research (PAR) 124 sinusodial oscillator frequency f was used to generate a square wave whose period was twice that of the incoming sine wave. This square-wave phase locked a function generator producing a sine wave of frequency $\frac{1}{2}f$. This signal was amplified and fed to an electrostatic drive transducer, which was effectively a parallel-plate capacitor with one plate (the sample) free to vibrate. The unbiased drive transducer excited the sample onto flexural vibrations at twice the applied frequency. An identical biased electrostatic receiver detected the amplitude of the vibrations through the modulation of the receiver capacitance. In a voltage-sensitive detection scheme, cable capacitance may lead to a significant loss of receiver signal. This problem was circumvented by using a current-sensitive detector (PAR 184) which had a low input impedance. The received signal contained information concerning the amplitude and phase of the reed. The PAR 124 was phase adjusted to detect the component of the displacement[20] which is in quadrature to the phase at resonance. A second phase-sensitive detector (not shown in Fig. 1) functioned as a wave analyzer and measured the total amplitude of the received signal.

The electronics could be phase locked to a flexural resonance by having the PAR dc output control the oscillator frequency. The electronic system would then track variations in the resonant frequency due to changes in external parameters (e.g., temperature). Measurements of Q could also be made in this mode of operation by determining the frequencies at the half-power points (±45° phase shift). The resonant frequency f was measured with a frequency counter and then converted to a dc signal, which could be recorded as a function of temperature. Near the phase transitions in these materials, the resonant frequency and output amplitude were simultaneously, and continuously, recorded as the sample was heated and cooled through the transformation. Separate runs were necessary for each frequency. For a constant drive voltage, the received amplitude was found to be inversely proportional to the Q^{-1} of the resonance within ~20%. Typical input voltages of 10–20 V and receiver bias voltages of 50–200 V dc introduced small strains in the samples ranging from 10^{-6} to 10^{-7}.

IV. RESULTS

A. $2H$-TaSe$_2$

The $2H$-TaSe$_2$ samples were oriented with the layers in the phane of the reed and the reed axis along the crystallographic a axis. Measurements of the modulus and internal friction from 1.3 to 300 K are shown in Fig. 2. In this initial experiment, the internal friction was determined from a record of the free decay of the resonant amplitude, i.e., $Q^{-1}=(\pi f \tau_e)^{-1}$, where τ_e is the time for the amplitude to decrease by a factor e^{-1}. The modulus data were normalized to the room-temperature value E_0 (300 K) $=(1.2\pm 0.4)\times 10^{12}$ dyn/cm^2, which is the average for several measured samples. This surprisingly large modulus suggests that there is a rather strong elastic coupling between adjacent layers.[19]

The modulus has an unusually weak temperature dependence in the range 150–300 K. Below 150 K, the modulus begins to decrease and reaches a shallow minimum at ~121 K. We associate this modulus anomaly with the incommensurate or onset (ICDW) transformation. At a slightly lower temperature near 90 K, we find elastic anomalies which are approximately an order of magnitude larger than those of the higher temperature ICDW. While these elastic measurements near 90 K indicated the existence of a phase transition, it was precision neutron measurements[8] that confirmed the presence of the commensurate (CCDW) transition near this temperature. The strong coupling between the elastic properties and the CDW's appears to extend down to liquid-helium temperatures.

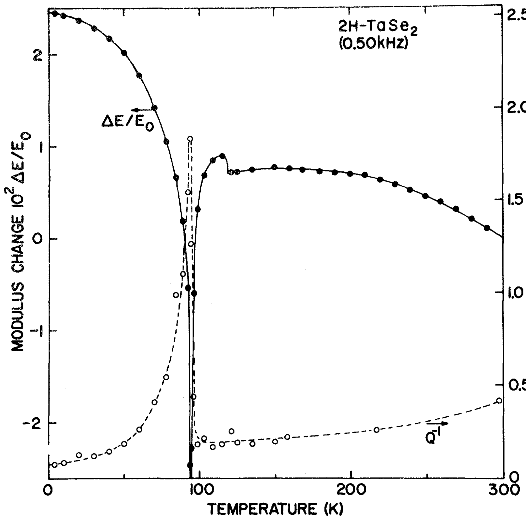

FIG. 2. Temperature dependence of the modulus and internal friction in $2H$-TaSe$_2$ from 1.3 to 300 K. A small elastic anomaly occurs at the incommensurate CDW transition at $T\simeq 121$ K, while a much larger anomaly takes place at the commensurate transition near 90 K. At 300 K, the modulus temperature dependence is $(1/E)(\partial E/\partial T)=1.0\times 10^{-4}$ K^{-1} and E_0(300 K) $=1.2\times 10^{12}$ dyn/cm^2.

Both the ICDW and CCDW transformations were studied in considerable detail using the phase-lock technique, which allowed continuous monitoring of the modulus and internal friction as the system was slowly heated and cooled through a transformation. With this procedure, elastic hysteresis effects could be easily detected. Continuous elastic measurements for the two lowest flexural modes near the incommensurate transformation ($T_0 = 121.1$ K) are presented in Fig. 3. These measurements were taken while cooling through the transition at a rate of 0.2 K/min. We have normalized each set of data to the corresponding modulus minimum in each case. In this way we may compare the relative shapes of the curves without knowing the absolute values. Both modulus curves reach a minimum at the same temperature ($T_{\min} = 121.1 \text{ K} \equiv T_0$) which we associate with the ICDW transition. In the present experiments, a thermocouple was used to measure the temperature. The absolute value of T_0 may be uncertain by approximately 1 K, and thus it is consistent with the onset temperature determined from the neutron measurements[8] ($T_0 = 122.3$ K). The small modulus minimum observed here is consistent with measurements of the integrated heat of transition which yield the very small value ~1 cal/mole.[21] Heating and cooling modulus curves were also found to overlap near the transition to better than 0.3 K. This difference may be associated with experimental uncertainties such as small differences in the drift rates. Thus, this ICDW transition shows very little if any hysteresis effect.

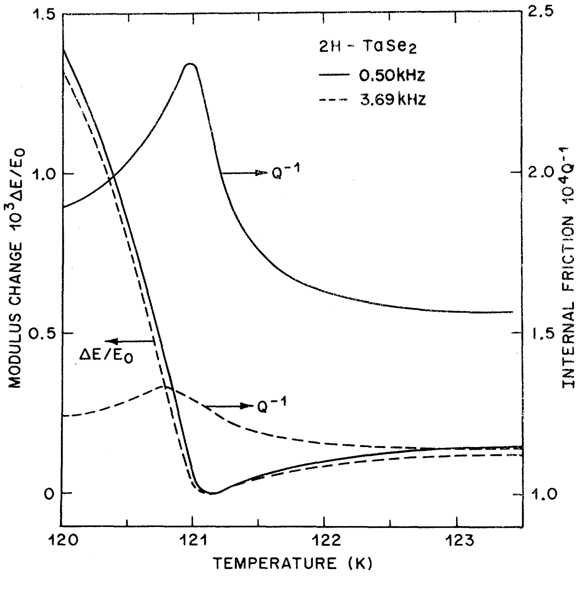

FIG. 3. Modulus and internal-friction measurements near the incommensurate transition in $2H$-TaSe$_2$. Solid and dashed curves correspond, respectively, to the fundamental and first-overtone resonance. At each frequency, the modulus measurements were normalized to the corresponding minimum value. The modulus has only a shallow minimum at the transition ($T_0 = 121.1$ K), however, it experiences a very strong temperature-dependent increase at lower temperatures. At both frequencies, the internal-friction maximum is at a lower temperature than the modulus minimum.

The elastic measurements at this onset transition show unusual static and dynamic properties. An unusual feature of the modulus behavior at the ICDW transition in TaSe$_2$ is the shape of its temperature dependence. From reasonably general arguments[22] one expects the temperature dependence of the modulus anomaly to be the same as the specific-heat (C_p) anomaly near T_0 with the magnitudes of these two quantities differing only by a scaling factor of $-T(d\ln T_0/d\sigma)^2$. Since the specific heat usually rises on cooling through a second-order transition, one expects, and generally finds, that the modulus undergoes a decrease at that temperature. Figures 2 and 3 show that at the 121-K transition in TaSe$_2$ the major change in the modulus is a rapid increase on cooling through T_0. It is possible that the small dip in E just before this increase (see Fig. 3) is related to the specific-heat rise. However, the sharp rise below this minimum could indicate an unusually large and rapid drop in C_p just below T_0. (Accurate measurements of C_p at this transition have not been published.) Two other explanations, equally anomalous, which come from the thermodynamic treatment[22] are that (i) the order parameter has an extremely large uniaxial stress dependence, and (ii) the transition temperature has a large quadratic uniaxial stress dependence. Specific-heat measurements should clarify, somewhat, this behavior.

The internal friction at each frequency shows a maximum at a temperature below the corresponding modulus minimum. At the transition $T = T_0$, the internal friction associated with the transformation is finite and has a tail extending into the high-temperature phase. This type of behavior has previously been reported in both fluids[23] and solids[24] near critical points, and the sound attenuation was interpreted in terms of two processes. One process is due to fluctuations in the order parameter and leads to attenuation symmetric about the transition, while the second is a relaxation process associated with the order parameter and contributes only below the transition. In the case of the ICDW transitions in the layered dichalcogenides, the order parameter is the amplitude of the CDW distortions. At present, the detailed coupling mechanism between the CDW's and the phonons is not understood and thus we will qualitatively interpret the internal-friction measurements below the transition in terms of a relaxation model.

For a single relaxation process, the internal friction and Young's modulus dispersion may be represented by

$$Q^{-1}(\omega, T) = A(T)[\omega\tau/(1 = \omega^2\tau^2)]\,, \qquad (2)$$

$$[E(\omega, T) - E(0, T)]/E(0, T)$$
$$= A(T)[\omega^2\tau^2/(1+\omega^2\tau^2)]\,, \qquad (3)$$

where τ is the characteristic relaxation time for the process. The first-overtone internal-friction maximum is seen to be approximately twice as far below T_0 as the fundamental maximum. By assuming the relaxation time has a power-law divergence $\tau = \tau_0 |T/T_0 - 1|^{-\zeta}$ and using the condition $\omega\tau = 1$ at the maximum, we calculate the following estimates for the relaxation-time coefficient and exponent:

$$\tau_0 = 3 \times 10^{-12} \text{ sec and } \zeta = 2.9\,. \qquad (4)$$

The most unusual feature of the loss measurements associated with the transformation is that the fundamental internal-friction maximum is approximately four times larger than the first-overtone maximum. A detailed analysis of the data shows that this anomalous behavior is not consistent with a simple relaxation model as given by Eqs. (2) and (3) since the temperature dependence of Q^{-1} is not that predicted by Eq. (2).

The experimental result that, for the ICDW transition in TaSe_2, the acoustic loss is larger at the lower frequency is a puzzling and nontrivial finding. This is certainly not what one would expect for an electronic loss mechanism where the limiting relaxation frequencies are far in excess of the low frequencies used in this experiment. Such low relaxation frequencies as appear here are more characteristic of atomic loss mechanisms (e.g., diffusion, point defects, dislocations, etc.) or macroscopic loss mechanism (e.g., domain-wall motion). The nature of such a "slow" loss mechanism at a charge-density wave transformation is not, at present, understood. The experiments do suggest, however, that an unexpected loss phenomena is occurring at this transition. The concept of phononlike distortions or dislocations in the charge-density wave, recently discussed by McMillan,[9] may be a possible explanation for the unusual low frequency loss at the ICDW transition.

Elastic measurements near the CCDW transition in $2H$-TaSe_2 are shown in Fig. 4. These continuous measurements were taken by initially heating the system through the transition and then reversing the process by introducing ~10^{-3} Torr of ^{4}He gas to cool the specimen down again. The initial heating curves show elastic extrema near 92.5 K, while the subsequent cooling curves lead to weaker elastic anomalies near 87.3 K. These measurements reveal a large elastic hysteresis of greater than 5 K at this lock-in transformation, which clearly demonstrates its first-order character. To within ~0.3 K, the temperatures of these elastic anomalies were independent of drift rates in the range 0.1–0.3 K/min so long as the initial starting temperature was at least 5 K away from the transition. This type of behavior is characteristic of first-order transitions. In both the heating and cooling measurements, the internal-friction maximum occurs at a temperature approximately 0.4 K below the modulus minimum. The occurrence of Q^{-1}_{max} below T_0 is a similar feature to both transitions in TaSe_2. However, the temperature difference between the extrema of Q^{-1}_{max} and E is dependent upon frequency for the ICDW but not for the CCDW transition. However, there are significant frequency-dependent hysteresis effects at the CCDW transition which are shown in Fig. 5. These heating curves for the fundamental and first-overtone modes reveal a difference of ~1.7 K in the temperature of the corresponding modulus

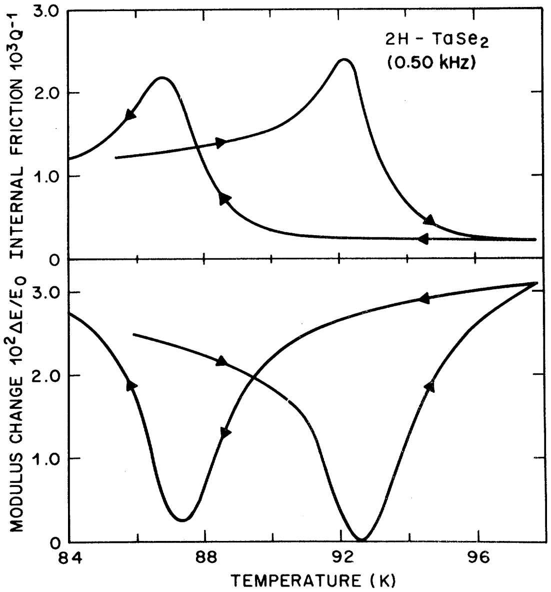

FIG. 4. Continuous heating and cooling curves of the elastic properties near the commensurate transition in $2H$-TaSe_2 ($T_d \simeq 90$ K). Modulus measurements were normalized to the modulus minimum obtained upon heating. Measurements correspond to drift rates of ~ 0.2 K/min. Large elastic hysteresis (~ 5 K) clearly demonstrates the first-order character of this transition. For both heating and cooling, the internal-friction maximum occurs at a temperature lower than the modulus minimum.

minimum. On cooling runs, the modulus minimum for the first overtone also lies ~1.7 K above the corresponding minimum for the fundamental. Superposition of the modulus curved at the two frequencies gives a maximum modulus difference of ~1.5×10^{-3}, which is consistent with the measured internal friction assuming a relaxation process. As was the case at the incommensurate transition, the elastic loss of the first overtone due to the CDW coupling is less than that of the fundamental.

We have also carried out resistivity measurements in $2H$-TaSe$_2$ to investigate the CCDW transformation. Previous resistivity measurements[4] did not observe anomalous behavior near 90 K, however, the present high-resolution data show a weak hysteresis in the resistivity over the range 86–93 K, with the resistivity on cooling about 1% above that on heating. This resistivity hysteresis covers essentially the same temperature range as the elastic hysteresis, and also demonstrates that this transition is first order.

B. $2H$-NbSe$_2$

The measurements in $2H$-NbSe$_2$ were carried out in a similar manner as for $2H$-TaSe$_2$. Figure 6 presents modulus measurements in $2H$-NbSe$_2$ sample No. 1 over a wide temperature range. As the temperature is reduced, the modulus increases by over 2% from its room-temperature value, $E_0(300\text{ K})\approx1.8\times10^{12}$ dyn/cm^2, and then experiences a dip with a minimum at 29.8 K. We associate the temperature of this minimum with the ICDW transition. A second sample No. 2 showed a much larger modulus increase of ~5.5% between 300 and 50 K, however the onset CDW transition occurred at the same temperature ($T_0=29.8$ K). Reheating from 4.2 K reproduces the cooling data to ~5 K above T_0. At higher temperatures, however, the measured modulus is smaller than that obtained on the cooling run. The cause of this change is unknown.

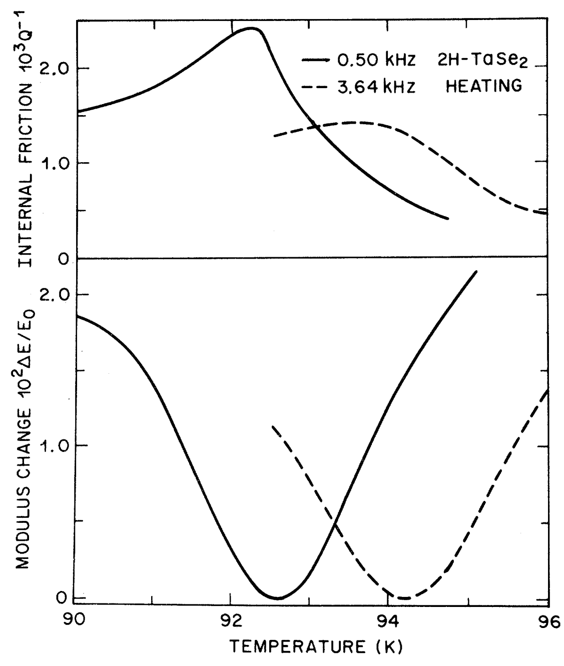

FIG. 5. Heating curves for the modulus and internal friction near the commensurate transition in $2H$-TaSe$_2$. Solid and dashed curves correspond, respectively, to the fundamental and first overtone. For each frequency, E_0 is the corresponding modulus minimum. Curves correspond to a heating rate of 0.2 K/min. Difference in the temperature of the modulus minimum at each frequency indicates that the elastic hysteresis at this transition is frequency dependent.

Recent neutron measurements[8] in $2H$-NbSe$_2$ found the ICDW transition at $T_0=33.5$ K, which is several degrees higher than the value reported here. This difference is outside the combined temperature uncertainty in the two experiments. We suggest this discrepancy may be due to differences in sample preparation. Measurements of the temperature dependence of the electrical resistivity of the two samples used in the acoustic studies near the ICDW transition show an anomalous increase in resistivity starting near 35 K and reaching a maximum magnitude of ~5% near 30 K. These results have been previously obtained by Harper.[25]

The modulus and internal friction in the low-

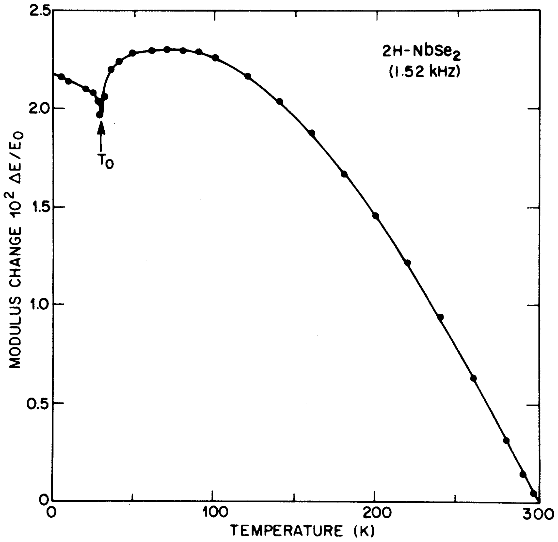

FIG. 6. Temperature dependence of the reed modulus in $2H$-NbSe$_2$ from 1.3 to 300 K. The modulus reaches a minimum at the incommensurate CDW transition, $T_0=29.8$ K. At 300 K, the modulus temperature dependence is $(1/E)(\partial E/\partial T)=1.56\times10^{-4}\text{ K}^{-1}$ for a modulus of $E_0(300\text{ K})=1.8\times10^{12}$ dyn/cm^2.

temperature region is shown in Fig. 7 for sample No. 2. These are equilibrium measurements taken by cooling in a step-wise manner through this temperature region. This material has a very low elastic loss along this direction. As was the case in $2H$-TaSe$_2$, the internal-friction maximum, which has an asymmetric shape, occurs below the temperature of the modulus minimum. We also observe a weak modulus anomaly, but no anomaly in the elastic loss, at the superconducting transition at $T = 7.2$ K. A discussion of the elastic properties near the superconducting transition will be given below. At the ICDW transition, the modulus experiences a dip of $\Delta E/E_0 \sim 2\times10^{-3}$ relative to a hypothetical modulus background determined by extrapolating the high- and low-temperature modulus to T_0 assuming no phase transition. At a second-order phase transition, the Young's modulus, measured along the ith direction, the specific heat, and the expansivity are related by the expressions[15,22]

$$\left(\frac{\partial T_c}{\partial \sigma_i}\right)^2 = -\frac{\Delta E_i}{E_i^2}\frac{T_c}{\Delta C_p}, \tag{5}$$

$$\Delta\alpha_i = \frac{\Delta E_i}{E_i^2}\Big/\frac{\partial T_c}{\partial \sigma_i}, \tag{6}$$

where T_c is the transition temperature and σ_i and α_i are the uniaxial stress and expansivity, respectively, along the ith direction. All Δ's correspond to the difference of a given parameter between the high- and low-temperature phases. Assuming this incommensurate transition is second order, we may use Eqs. (5) and (6), the present results, and recent specific-heat measurements[25] to calculate the absolute magnitude of the uniaxial stress dependence of the transition temperature and the expected expansivity change. For a uniaxial stress in the basal plane, we obtain

$$\left|\frac{\partial T_0}{\partial \sigma_b}\right| = 0.6 \pm 0.2 \text{ K/kbar} \tag{7}$$

and

$$|\Delta\alpha_b| = (3.4 \pm 1.7)\times10^{-5} \text{ K}^{-1}. \tag{8}$$

The uniaxial stress dependence is just one component of the hydrostatic pressure dependence of the ICDW transition temperature. For a hexagonal system, we have

$$\frac{\partial T_0}{\partial P} = -\left(\frac{2\partial T_0}{\partial \sigma_b} + \frac{\partial T_0}{\partial \sigma_c}\right), \tag{9}$$

where σ_c is the stress along the c axis. The present measurement of $|\partial T_0/\partial\sigma_b|$ may be compared to recent preliminary neutron scattering measure-

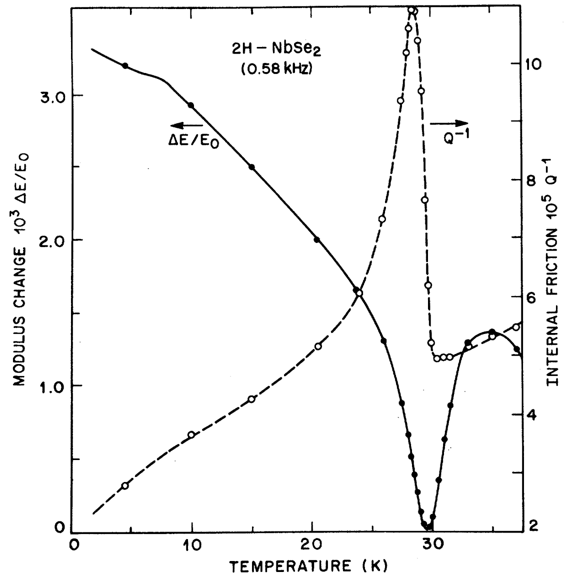

FIG. 7. Elastic measurements near the incommensurate transition in $2H$-NbSe$_2$. Modulus measurements were normalized to the modulus minimum, E_0(29.8 K) $= 1.88\times10^{12}$ dyn/cm^2. Modulus and internal friction exhibit a minimum and a maximum, respectively, near T_0.

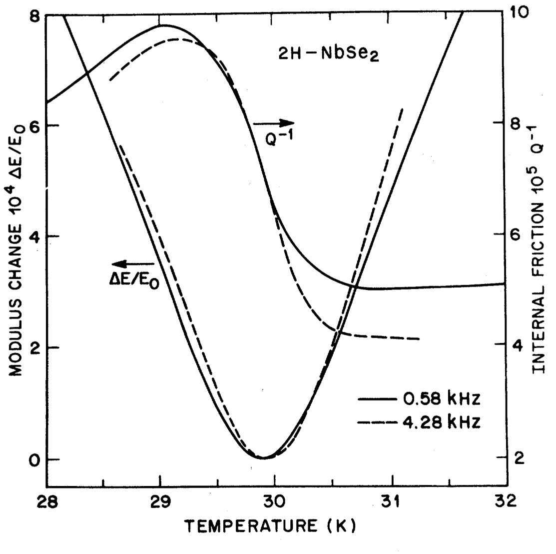

FIG. 8. Continuous heating curves of the modulus and internal friction in the vicinity of the $2H$-NbSe$_2$ incommensurate transition. Solid and dashed curves correspond, respectively, to the fundamental and first-overtone flexural resonance. Moduli for each frequency are normalized to the corresponding modulus minimum. Within experimental uncertainty (~0.3 K), the modulus minima occur at the same temperature $T_0 \equiv 29.8$ which is consistent with a second-order transformation, as was the case for the $2H$-TaSe$_2$ incommensurate transformation. Internal-friction maximum at each frequency occurs at a temperature below the corresponding modulus minimum.

ments[12] which show that the absolute value of the hydrostatic pressure dependence is

$$\left|\frac{\partial T_0}{\partial P}\right| \lesssim 1 \text{ K/kbar}$$

and probably is negative in sign. More accurate hydrostatic measurements are necessary in order to obtain $\partial T_c/\partial \sigma_c$ from Eq. (9).

In order to investigate the nature of this ICDW transition in more detail, we made continuous heating and cooling measurements near the transition. Heating curves for the fundamental and first overtone are shown in Fig. 8. As was the case with the ICDW transition in $TaSe_2$, we find heating and cooling curves overlap near the transition to better than 0.3 K. The absence of observable hysteresis is consistent with a transformation of second order. The attenuation maximum at both frequencies occurs ~0.8 K below the temperature of the corresponding modulus minimum. Furthermore, the magnitude of the elastic loss in this temperature region and the temperature of the maximum internal friction for these two frequencies essentially coincide. It should also be noted that the inflection point in the internal-friction curves coincides closely with the modulus minimum. These properties cannot be explained by a simple relaxation model.

In comparing the elastic properties at the ICDW transitions in $NbSe_2$ and $TaSe_2$ (see Fig. 3), we find considerably different behavior. However, the temperature dependence of the modulus and internal friction in $NbSe_2$ appears to be similar in shape to that found at the CCDW transition in $TaSe_2$ (see Fig. 4). Any complete theory of these CDW transformations must take these unusual elastic properties into account.

The question arises as to whether the CDW's in 2*H*-$NbSe_2$ become commensurate with the lattice at any temperature. Neutron measurements[8] did not reveal a commensurate transformation down to 5 K. We have carried out modulus measurements in 2*H*-$NbSe_2$ to low temperatures, as shown in Fig. 9, in an attempt to detect such a lock-in transition. This material is known[26] to be a superconductor below $T_c = 7.2$ K. A weak modulus anomaly is observed at the superconducting transition; however, we find no other anomalies in this low-temperature region down to 1.3 K which might be associated with the CCDW transition. At the lowest temperatures measured, the modulus has not reached its limiting zero slope which is required by thermodynamic arguments at absolute zero and, indeed, shows a positive curvature versus temperature. Since the slope of E vs T is proportional to the entropy as $T \rightarrow 0$, the failure to see the expected zero slope suggests the possibility of further elastic anomalies (e.g., transformations) at lower temperatures.

At the superconducting transition the modulus shows a change in slope, and an extrapolation of the modulus temperature dependence above and below T_c leads to a modulus discontinuity of ~6 ± 3 ppm smeared out over a 0.3 K temperature interval. The specific-heat discontinuity at this second-order transition has been measured,[27,25] and may be used in Eqs. (5) and (6) with the modulus results to obtain

$$\left|\frac{\partial T_c}{\partial \sigma_b}\right| = 0.028 \pm 0.015 \text{ K/kbar} \tag{10}$$

and

$$|\Delta\alpha_b| = (2.4 \pm 1.7) \times 10^{-7} \text{ K}^{-1}. \tag{11}$$

Recently, Sambongi[28] measured the dependence of the superconducting transition temperature on a uniaxial stress applied parallel to the c axis and obtained

$$\frac{\partial T_c}{\partial \sigma_c} = 0.018 \pm 0.002 \text{ K/kbar}.$$

The hydrostatic pressure dependence is reported[29] to be positive and in the range

$$\frac{\partial T_c}{\partial P} \sim 0.04 - 0.095 \text{ K/kbar}.$$

The present results together with those of Sambongi[28] are consistent with the pressure results (within the large combined experimental uncertainties). Furthermore, choosing the algebraic sign so that $\partial T_c/\partial \sigma_b$ is negative gives $\Delta\alpha_b > 0$.

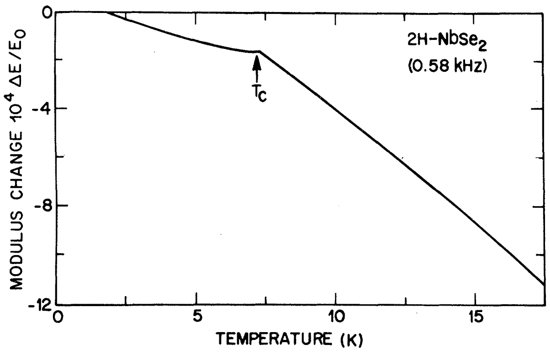

FIG. 9. Modulus temperature dependence near the 2*H*-$NbSe_2$ superconducting transition, $T_c = 7.2$ K. Measurements were arbitrarily normalized to the modulus at the lowest temperature ($T_R = 1.3$ K). There is a change in slope of the modulus at T_c. Extrapolation of the modulus above and below the transition leads to a discontinuity at T_c of ~6 ± 3 ppm. The modulus slope at the lowest temperatures is still increasing, and suggests possible further anomalies at still lower temperatures.

A thermodynamic analysis[22] of the large change in dE/dT at the superconducting transition indicates a quadratic dependence of T_c on stress of magnitude

$$\frac{d^2T_c}{d\sigma^2} \simeq (2.8 \pm 1.5) \times 10^{-21} \text{ K cm}^4 \text{ dyn}^{-2}$$

at zero stress. This initial curvature, if extrapolated to high stresses (ignoring higher-order terms), would lead to a positive deviation of T_c from linear behavior, amounting to ~0.14 K at 10 kbar for uniaxial stresses parallel to the basal plane. Sambongi[28] has recently observed $d^2T_c/d\sigma^2 > 0$ for stresses perpendicular to the basal plane. Although a negative curvature appears to be present in the pressure results of Smith *et al.*,[29] an accurate determination is not possible. In any case, the sign of d^2Tc/dp^2 cannot be determined from the two uniaxial stress results given above, but also involves additional terms of the form $d^2T_c/d\sigma_i d\sigma_j$. The tendency of T_c to saturate at high pressures may be related to a pressure-induced shift in a CCDW or ICDW transition toward the superconducting T_c.

V. CONCLUSIONS

The CDW instabilities in the two-dimensional layered transition-metal dichalcogenides lead to unusual static and dynamic elastic effects. We have presented low-frequency modulus and internal-friction measurements in the $2H$ polytype of $TaSe_2$ and $NbSe_2$ which exhibit anomalous behavior near the CCDW and ICDW transitions. The coupling between the CDW instabilities and the lattice is found to be an order of magnitude larger at the commensurate CDW transition in $TaSe_2$ as compared to the ICDW transition in $TaSe_2$ or $NbSe_2$. The CCDW transformation in $TaSe_2$ near 90 K exhibits large elastic hysteresis (~5 K), which is characteristic of a first-order transition. On the other hand, the ICDW transitions in $TaSe_2$ and $NbSe_2$ show very little if any hysteresis and appear to be second order. If these incommensurate transitions are first order, they have only a weak first-order character as compared with the commensurate transformation.

Information concerning the dynamic properties of these CDW transitions was obtained from sound dispersion and attenuation measurements. At all the CDW transitions, the internal-friction maximum of a given frequency is at a temperature below the corresponding modulus minimum. Furthermore, the first-overtone internal friction associated with the transition is always comparable or smaller than that of the fundamental. This feature is inconsistent with simple relaxation processes where $Q^{-1} \propto \omega$ in the hydrodynamic limit.

We have shown that the vibrating-reed technique is a sensitive method for detecting and investigating the CDW transitions in the layered dichalcogenides. A more complete understanding of the thermodynamic properties of these transitions will come about as precision specific-heat and expansivity data become available to correlate with the elastic measurements. It is clear that any detailed theory of these CDW instabilities must explain the anomalous elastic properties.

ACKNOWLEDGMENTS

We wish to thank G. F. Brennert and W. A. Royer for technical assistance.

---

[1] F. R. Gamble, J. H. Osiecki, M. Cais, R. Pisharody, F. J. Di Salvo, and T. H. Geballe, Science 174, 493 (1971).

[2] J. A. Wilson and A. D. Yoffe, Adv. Phys. 18, 193 (1969).

[3] J. Edwards and R. F. Frindt, J. Phys. Chem. Solids 32, 2217 (1971).

[4] J. A. Wilson, F. J. Di Salvo, and S. Mahajan, Phys. Rev. Lett. 32, 882 (1974); Adv. Phys. 24, 117 (1975); and P. M. Williams, G. S. Parry, and C. B. Scruby, Philos. Mag. 29, 695 (1974).

[5] A. H. Thompson, Phys. Rev. Lett. 34, 520 (1975).

[6] M. Barmatz, H. J. Leamy, and H. S. Chen, Rev. Sci. Instrum. 42, 885 (1971).

[7] C. Herring, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic, New York, 1966), Vol. IV, p. 340.

[8] D. E. Moncton, J. D. Axe, and F. J. Di Salvo, Phys. Rev. Lett. 34, 734 (1975).

[9] W. L. McMillan, Phys. Rev. B 12, 1187 (1975); and unpublished.

[10] A. W. Overhauser, Phys. Rev. 167, 691 (1968).

[11] F. J. Di Salvo, J. A. Wilson, B. G. Bagley, and J. V. Waszcak, Phys. Rev. B 12, 2220 (1975).

[12] D. E. Moncton and J. D. Axe (private communication).

[13] H. N. S. Lee, M. Garcia, H. McKinzie, and A. Wold, J. Solid State Chem. 1, 190 (1970).

[14] R. K. Quinn, R. Simmons, and J. Banewicz, J. Phys. Chem. 70, 230 (1966).

[15] M. Barmatz, in *Proceedings of the 1974 IEEE Ultrasonics Symposium* (IEEE, New York, 1974), No. 74, p. 461.

[16] M. Barmatz and H. S. Chen, Phys. Rev. B 9, 4073 (1974).

[17] See, Harald Schäfer, *Chemical Transport Reactions* (Academic, New York, 1964).

[18] P. M. Morse, *Vibration and Sound* (McGraw-Hill, New York, 1948), 2nd ed., p. 151.

[19] M. Barmatz, L. R. Testardi, A. F. Garito, and A. J. Heeger, Solid State Commun. 15, 1299 (1974).

[20] See, for example, M. Barmatz and B. Golding, Phys. Rev. B 9, 3064 (1974).

[21] B. G. Bagley, F. J. Di Salvo, H. E. Bair, and E. M. Vogel (unpublished).

[22] L. R. Testardi, Phys. Rev. B (to be published).

[23] R. D. Williams and I. Rudnick, Phys. Rev. Lett. **25**, 276 (1970).

[24] See, for example, B. Golding and M. Barmatz, Phys. Rev. Lett. **23**, 223 (1969); and B. Golding, *ibid.* **34**, 1102 (1975).

[25] J. M. E. Harper, T. H. Geballe, F. J. Di Salvo, Phys. Lett. A **54**, 27 (1975).

[26] E. Revolinsky, E. P. Lautenschlager, and C. H. Armitage, Solid State Commun. **1**, 59 (1963).

[27] A. J. Bevolo and H. R. Shanks, J. Appl. Phys. **45**, 4644 (1974).

[28] T. Sambongi, J. Low Temp. Phys. **18**, 139 (1975).

[29] T. F. Smith, R. N. Shelton, and R. E. Schwall, J. Phys. F **4**, 2009 (1974).