

Velocity of ultrasonic waves in $2H$ -NbSe₂, $2H$ -TaS₂, and $1T$ -TaS₂

M. H. Jericho and A. M. Simpson

Department of Physics, Dalhousie University, Halifax, Nova Scotia B3H 3J5, Canada

R. F. Frindt

Physics Department, Simon Fraser University, Burnaby, British Columbia V5A 1S6, Canada

(Received 21 April 1980)

We have measured the temperature dependence of the velocity of 10-MHz ultrasonic pulses which were propagated along the layers of the dichalcogenides $2H$ -TaS₂, $1T$ -TaS₂, and $2H$ -NbSe₂. In $2H$ -TaS₂ the plate mode velocity shows little temperature dependence above the charge-density-wave onset temperature of about 78 K, but shows an increased stiffening below it. In $1T$ -TaS₂ the charge-density wave becomes commensurate near 170 K and the velocity undergoes a steplike stiffening, while the sound attenuation displays a large peak at this temperature. Both velocity and attenuation show strong hysteresis near this transition. Attention is drawn to the similarity between the velocity anomalies and corresponding anomalies in the magnetic susceptibility. It is suggested that the elastic anomalies might be caused by the d -band electrons. Band deformation potentials of the order of 1 eV and estimates of anharmonic background contributions to the velocity are obtained.

I. INTRODUCTION

The existence of charge-density waves (CDW) in the group VB transition-metal layer dichalcogenides is well established and the effects of the CDW on electrical and thermal properties of these materials have been investigated in detail. In this paper, we report measurements of the velocities of propagation of 10-MHz ultrasonic pulses along the basal planes of $2H$ -NbSe₂, $2H$ -TaS₂, and $1T$ -TaS₂. Young's-modulus measurements on $2H$ -NbSe₂ and $2H$ -TaSe₂ using a vibrating reed technique have already been reported by Barmatz *et al.*,¹ who observed small elastic anomalies at CDW onset temperatures and a very pronounced modulus softening in $2H$ -TaSe₂ at the commensurate charge-density wave (CCDW) to incommensurate charge-density wave (ICDW) transition.

Elastic measurements have been helpful in improving our understanding of A15 compounds²⁻³ and of quasi-one-dimensional materials such as tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ).⁴ In the latter, for example, the stiffening of the material below the Peierls transition was interpreted in terms of charge transfer from the TTF to the TCNQ molecular stacks. In both of these cases, a close connection between the elastic anomalies and the anomalies in the paramagnetic susceptibility was pointed out. From our measurements it appears that in some layered compounds a similar connection might exist, although a detailed analysis is difficult at the present time, owing to the fact that the susceptibility and, in particular, its anisotropy is poorly understood.

Section II describes the experimental technique used to measure the propagation characteristics of

elastic waves. In Sec. III the velocity results for $2H$ -NbSe₂ and $2H$ -TaS₂, as well as attenuation and velocity measurements on $1T$ -TaS₂ are presented.

A comparison of velocity data and magnetic susceptibility results is made in Sec. IV, where we attempt to decompose the observed temperature dependence of the plate modulus into an anharmonic part and a conduction-electron component. We obtain an estimate for the metal d -band deformation potential and put an upper limit on the magnitude of a magnetic anomaly in $2H$ -NbSe₂ at its CDW transition.

II. TECHNIQUE

All samples except a $2H$ -TaS₂ sample, referred to as Dalhousie sample, were prepared at Simon Fraser University (S.F.U.). The samples were in the form of platelets several mm in length and width. Their thickness ranged from 68 μ m for $1T$ -TaS₂ to about 10 μ m for $2H$ -NbSe₂ with a thickness of 50 μ m and less for the other samples. Two ends were made parallel by cutting with a razor blade in a special jig. They were then mounted between two quartz transducers in a manner shown in Fig. 1. The samples were bonded to the transducers with epoxy in such a way that acoustic coupling without electrical contact to the transducer electrode was obtained. By attaching fine gold leads to one edge of the sample just outside the acoustic beam, it was then possible to measure velocity, attenuation, and electrical conductivity simultaneously during a temperature sweep. Such a capability is particularly useful in a study of materials whose properties can depend somewhat on sample history. Attaching electrical leads to one edge of a wide sample can

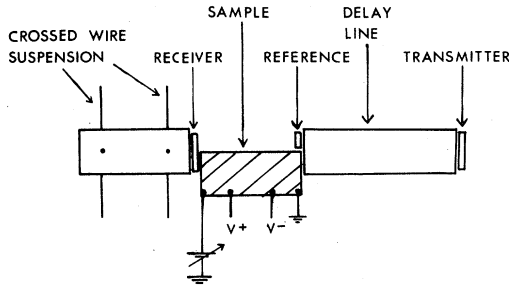


FIG. 1. Sample mounting and arrangement of electrical leads for resistance measurements.

create problems if accurate resistivity measurements are desired. For the purposes of correlating electrical and acoustical measurements near a phase transition, however, we feel, that the lead arrangement shown in Fig. 1 is adequate. Sound-velocity measurements were made by comparing the phase of the signal propagated through the sample with the signal at the beginning of the sample. The phase comparison was accomplished by passing the $\frac{1}{2}$ - μ s long 10-MHz-rf pulses into the signal and carrier channels, respectively, of an MC1596L modulator-demodulator chip. Automatic recording of the phase changes with temperature was achieved, as described in Ref. 5. The accuracy of travel-time measurements of the plate mode was limited to about one period of the sound wave and, for the sample lengths used, this implied an absolute velocity uncertainty of about 10% to 15%. Changes in travel time with temperature could, however, be measured with a resolution of about 15 ps for good signals, which amounts to a velocity sensitivity of about 1 in 10^5 .

The propagation of high-frequency elastic waves in thin foils is described by theories on elastic waveguides and an examination of the mode spectrum in isotropic thin plates suggests that if the sound wavelength is much larger than the plate thickness, then the first Lamb mode which represents a quasilongitudinal wave should have the highest propagation velocity. All measurements presented were made on this mode. In isotropic materials, the velocity of this mode is given by

$$V_p = \left(\frac{E}{\rho(1 - \sigma^2)} \right)^{1/2},$$

where E is Young's modulus, σ the Poisson's ratio, and ρ the density of the sample. For anisotropic materials the situation is more complex, but for hexagonal crystals with the c axis perpendicular to the plane of the foil, the basal plane is a plane of isotropy and the plate mode velocity is again given by the above expression. E and σ can be expressed in terms of the elastic constants and for hexagonal plates we have

$$V_p = \left(\frac{C_{11}}{\rho} \right)^{1/2} \left(1 - \frac{C_{13}^2}{C_{11}C_{33}} \right)^{1/2}. \quad (1)$$

In many hexagonal systems, such as Zn, Cd, Yt, the second term in the parentheses contributes, at most, 10% to V_p and, at most, 1% to its temperature dependence. In these systems the plate mode then describes essentially the behavior of C_{11} , although the detailed behavior of the temperature dependence of V_p will, in general, be affected by C_{13} and C_{33} as well. The above expressions for the velocity are valid in the limit of sound wavelength, λ , being much larger than the sample thickness, d . For isotropic plates the dependence of the plate mode velocity on λ/d has been determined.⁶ In our samples, λ/d was between 4 and 40 and we estimate that our observed velocities for pulse propagation in the basal plane are, at most 8% below the limiting velocity. The experimental error in the determination of the absolute magnitude of the velocities due to exact phase matching is larger than this and is believed to constitute the major source of error.

We have also attempted to measure the damping of 10-MHz pulses as functions of temperature. This implies monitoring the amplitude of the plate mode signal as the temperature is changed. At sufficiently low temperatures where thermal expansion effects are negligible, such measurements should give fairly good information about the damping. At elevated temperatures, however, the sample-to-transducer bond can be affected by thermal expansion of the sample, transducer-bond material, and transducers. The signal amplitude in this type of experiment is largely governed by insertion losses at the sample edges, and variations in amplitude of the acoustic pulse with temperature does not necessarily yield the temperature dependence of the sound attenuation. Near the ICDW-to-CCDW transition in 1T-TaS₂, however, amplitude changes were so pronounced and of such a form that we believe they represent true changes in the ultrasonic attenuation.

The sample temperature was measured with a copper-Constantan thermocouple between 60 and 300 K and with a calibrated Lakeshore Cryotronics germanium thermometer between 4 and 70 K. Both sensors were in contact with the aluminum delay line and the sample chamber was filled with helium exchange gas. In the overlap region, the temperatures obtained with the two sensors agreed to better than 0.3 K and absolute temperature measurements were made to about the same accuracy. The data were recorded on an x - y recorder as a graph of temperature sensor output on the x axis versus signal amplitude (for attenuation) or change in double pulse frequency (for

velocity measurements). Subsequently, a Hewlett-Packard 9830 calculator and 9864 digitizer were used to digitize points from the graphs and compute the corresponding temperature and changes in attenuation or velocity. The primary graphs were continuous records so that near features of interest, the density of digitized points could be increased. In this way, details of the behavior near the phase transitions were not lost in the data-handling process.

III. RESULTS

2H-TaS₂

We have made measurements on three different samples obtained from two different sources and they all show the same general features with some variation in quantitative results. 2H-TaS₂ samples are generally wrinkly in appearance and for this reason this material was the most difficult to investigate ultrasonically. The low-temperature plate velocity was measured to be 3.6×10^5 cm/s \pm 10%. Figure 2 shows the overall variation of signal travel time with temperature on a sample grown at S.F.U. This sample had a resistance ratio $R(300)/R(4) \approx 60$. In Fig. 2 the travel time decreases with decreasing temperature in a manner similar to that found for 2H-TaSe₂ by Barmatz *et al.*¹ Between 150 K and the CDW onset temperature, T_0 , there is little temperature dependence, and below T_0 the travel time decreases rapidly and continues to decrease down to 4.2 K. Between 300 K and about 200 K, the signal-to-noise ratio for the received echoes was poor, and part of the observed variations in the results for different samples and between thermal cycling of the same sample was attributed to poor signal quality. Below 200 K, the signal quality improved significantly and the reproducibility was considerably

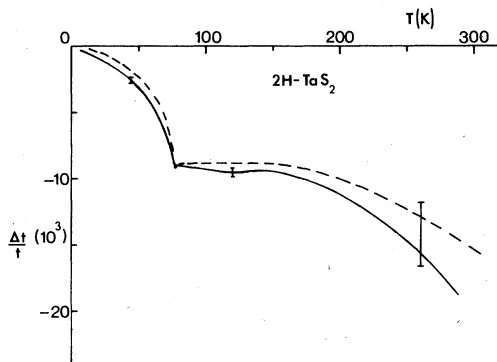


FIG. 2. Change in pulse travel time $\Delta t/t \equiv [t(0) - t(T)]/t(0)$ with temperature for 2H-TaS₂. Solid line is the experimental result; dashed line is the expected behavior according to Eq. (2).

better. The error bars in Fig. 2 represent the range of uncertainty in the data due to the above difficulties. The true velocity variation is obtained by subtracting out the change in sample length due to thermal expansion. This is not known for the a axis of 2H-TaS₂. However, Givens and Fredericks⁷ have measured the a axis expansion of the similar material, 2H-NbSe₂, above 150 K. Using this result as a guide, the small slope shown in Fig. 3 above 100 K is comparable to that to be expected from thermal expansion alone. The true velocity change may thus be flat or have a small positive slope in this region.

If we make a smooth extrapolation of the high-temperature behavior just above T_0 , we find that the excess velocity at 4.2 K is 0.9% (\pm 0.1). Correcting the curve for lattice-expansion effects is expected to change the result very little in this region, since the expansion coefficient should tend to zero as the temperature goes to zero. Moreover, Steinitz *et al.*⁸ have measured the discontinuities in lattice parameters occurring at the CDW phase transitions in 2H-TaSe₂. Assuming that the sulfide shows similar magnitude discontinuities (about 1 part in 10^5), the effect would be negligible compared to the rapid increase in velocity observed. We also note that near 4 K the velocity continues to change linearly with temperature with a slope of -8×10^{-5} K⁻¹. This observation is similar to that made by Barmatz *et al.*¹ in 2H-NbSe₂, and contrasts with our own measurement of an aluminum foil where the residual slope in $\Delta v/v$ at 4 K is no greater than -10^{-6} K⁻¹. Thermodynamic considerations suggest that elastic constants like thermal-expansion coefficients should have zero slope as T goes to zero. The reason for the finite slope in some of the layered compounds is not clear and the only other materi-

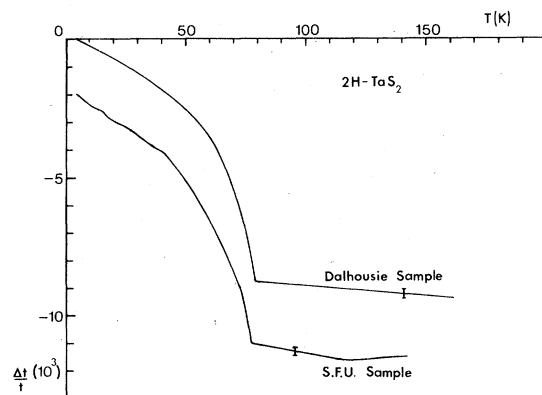


FIG. 3. Change in pulse travel time with temperature for two 2H-TaS₂ samples grown by different groups. The data for the S.F.U. sample has been displaced downwards by 2×10^{-3} for clarity.

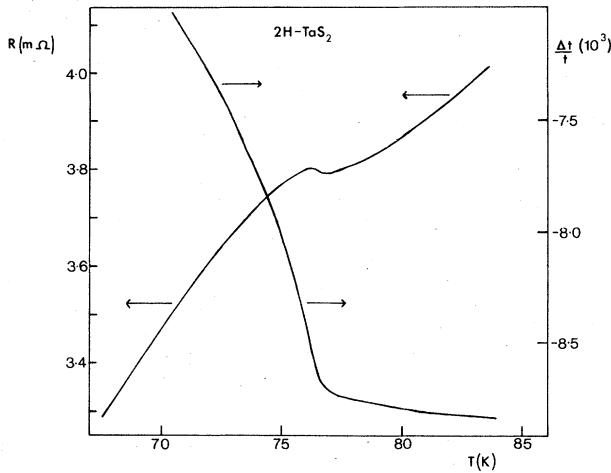


FIG. 4. Temperature dependence of pulse travel time and simultaneous resistance data on the Dalhousie $2H\text{-TaS}_2$ sample near the CDW onset temperature.

als that we are aware of that have significant temperature coefficients of velocity near 4 K are the amorphous materials⁹ and copper containing dislocations.¹⁰ Figure 3 shows the detailed variation of the pulse travel time near T_0 for the S.F.U. sample and also for a sample grown at Dalhousie. The latter had a resistance ratio $R(300)/R(4) = 36$. The results for these two samples are very similar.

In order to relate the phase transition as observed by velocity changes to results from other workers, we have made simultaneous measurements of the sound velocity and of the resistance on the Dalhousie sample. Figure 4 shows the results in the vicinity of T_0 . The resistance curve is essentially the same as results in the literature, although the data are somewhat more rounded than the best reported,¹¹ presumably because our sample was large and perhaps less homogeneous. The value of T_0 as determined from the discontinuity in slope of the velocity curve occurs close to the minimum in the resistance curve.

The variation of the velocity in the vicinity of T_0 in $2H\text{-TaS}_2$ is very similar to that found by Bar-matz *et al.*¹ for $2H\text{-TaSe}_2$ near the onset temperature of 121 K. In the latter material, the continued stiffening of the lattice on cooling is interrupted, however, by the second transition to the CCDW state near 90 K. All our measurements on $2H\text{-TaS}_2$ showed less than 0.5 K hysteresis effects on heating and cooling.

1T-TaS₂

This material has a CDW onset temperature of about 600 K and exists in a nearly commensurate state below 350 K. On further cooling, the CDW q

vectors rotate until, near 170 K (T_d), the CDW becomes commensurate with the lattice. It is known that the behavior near the lower transition on thermal cycling is dependent on whether or not the temperature is raised beyond the upper transition. In our apparatus, the temperature could not be raised above the upper transition, however, and the results are thus for the case where the sample temperature was cycled between 4 and 300 K only. Figure 5 shows the variation in signal travel time with temperature for a plate mode propagating in the basal plane. The plate mode velocity was $3.1 \times 10^5 \text{ cm/s} \pm 10\%$. To get the true velocity variation this curve again has to be corrected by subtracting out the effects of expansion of the lattice. Givens and Fredericks⁷ have made x-ray measurements of the a axis in $1T\text{-TaS}_2$ from 70 to 500 K and report a constant expansion coefficient of $12.7 \times 10^{-6} \text{ K}^{-1}$, with no discontinuities at the phase transitions. Our own dilatometer measurements show a discontinuous decrease of the a axis of 0.1% upon cooling through T_d .

Features of the curve shown in Fig. 5 are that (a) there is a large hysteresis in T_d , as reported previously in other properties,¹² which is about 50 K for our sample; (b) while not discontinuous, the warming transition is considerably narrower (about 1 K wide) than the width of the cooling transition; this cooling width varies with sample and with thermal cycling; (c) the background temperature dependence of velocity near 200 K is approximately the same above and below the transition, with 10% of the variation accounted for by the thermal expansion of the a axis; (d) at the pulse transition there is a steplike change in velocity of magnitude $5(\pm 1) \times 10^{-3}$ in $\Delta t/t$. About 1×10^{-3} of this can be accounted for by the change in a axis dimension at the transition; (e) the data

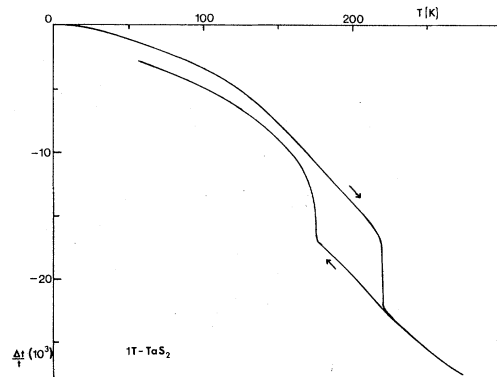


FIG. 5. Change in pulse travel time with temperature for $1T\text{-TaS}_2$ near the lock-in transition. A strong hysteretic behavior in the commensurate state is evident in this sample.

show a linear slope of $-1 \times 10^{-5} \text{ K}^{-1}$ in $\Delta t/t$ near 4 K, a factor of 8 smaller than in $2H\text{-TaS}_2$, but still an order of magnitude greater than in the aluminum foil.

The attenuation of the sound waves was also measured as a function of temperature with the result shown in Fig. 6. The background attenuation was virtually the same and nearly constant, above and below the transition. On cooling, there was an increase in signal before the main wide attenuation maximum. The temperature at which the attenuation started to increase rapidly was within 1 K of the temperature at which the velocity started to increase rapidly. On warming, there was a single narrow peak in the attenuation with the temperature of the maximum attenuation coinciding with the step decrease in velocity within 1 K. This attenuation structure is strongly dependent on sample quality, for when the measurements were repeated after attaching leads for a simultaneous measurement of resistance but otherwise not disturbing the sample, it was found that the background attenuation was no longer flat, that the cooling dip near 177 K vanished, and that the attenuation peak was significantly broader on cooling, but not on warming. In all thermal cycles, the existence of large attenuation peaks at the cooling and heating transitions was a reproducible feature, however. Our resistance measurements also showed that the maxima in the attenuation coincided with the positions of the well-known resistance edges found in this material. The lack of detailed reproducibility of the attenuation curves prevented a study of the effect of heating and cooling rates on the observations. However, results for velocity and attenuation reported here were made at sufficiently slow temperature drift rates (less than 1 K/min near the transitions)

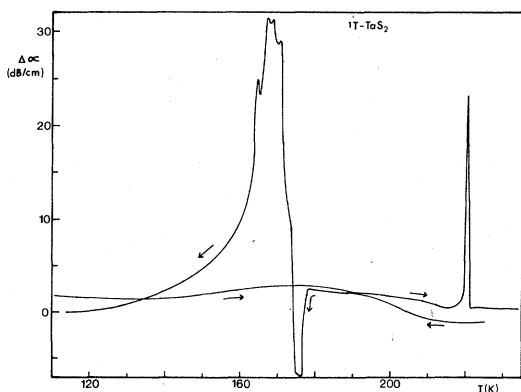


FIG. 6. Variation of pulse amplitude which has been expressed as an attenuation with temperature in the $1T\text{-TaS}_2$ sample. The broad peak near 170 K and the very sharp peak near 220 K were very reproducible features.

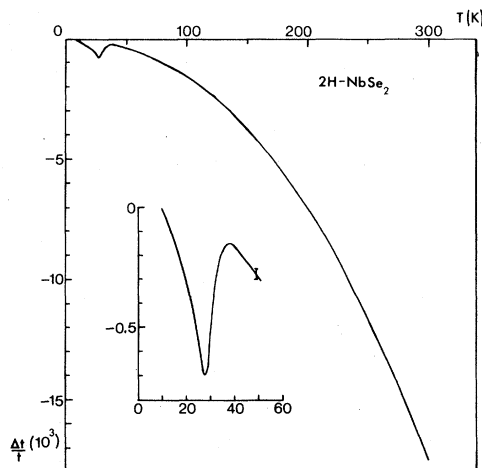


FIG. 7. Variation of pulse travel time with temperature for $2H\text{-NbSe}_2$. Insert is the detailed behavior near the CDW onset temperature.

that this should not be an important factor.

$2H\text{-NbSe}_2$

The velocity results on a sample with a resistance ratio of about 66 are shown in Fig. 7. As for the other samples, the temperature dependence of the travel time is given. The a -axis thermal expansion was measured to be about $6 \times 10^{-6} \text{ K}^{-1}$ near room temperature so that in that temperature range the actual velocity curve would be about 5% above the curve shown in Fig. 7. The results were normalized to the value at 10 K. The results are qualitatively very similar to the results of Barmatz *et al.*¹ and also of Skolnick *et al.*,¹³ with a dip in the velocity at the CDW onset temperature of about 28 K. The dilatometer measurements showed that there are no accompanying anomalies in the sample length greater than 3 parts in 10^{-7} . The low-temperature value of V_p was equal to $3.7 \times 10^5 \text{ cm/s}$. Feldman¹⁴ estimated the elastic constants for $2H\text{-NbSe}_2$ and with his first set of values ($C_{13} = 3.1 \times 10^{11}$ and $C_{33} = 4.6 \times 10^{11} \text{ dyn/cm}^2$), we estimate, from Eq. (1), $C_{11} = 10.8 \times 10^{11}$. This implies a Young's modulus of about $0.8 \times 10^{12} \pm 30\% \text{ dyn/cm}^2$, which is considerably smaller than the value obtained by Barmatz *et al.*¹ Feldman's second set of values for C_{13} and C_{33} yield a 10% smaller value for C_{11} .

IV. DISCUSSION

The most striking feature of the results on $2H\text{-TaS}_2$ is the softening of the velocity as the onset temperature is approached from below and the relatively flat region up to about 175 K. It is in this temperature region that anharmonic effects generally produce a much stronger temper-

ature dependence. The general shape of the curve below T_0 is very similar to the behavior of the velocity of compressional modes observed at low temperatures for TTF-TCNQ (Ref. 4) and some of the A15 compounds.³ In these materials the anomalies were attributed to the conduction bands, and charge transfer between one-dimensional bands for volume-nonconserving distortions played an important part in the interpretation. We suggest that in $2H$ -TaS₂ and $2H$ -TaSe₂ the conduction band also plays an important role in determining the temperature dependence of the elastic constants. In this quasi-two-dimensional situation a compression along the basal plane, for example, would then produce a Fermi-surface distortion which would be a function of position on the Fermi surface. In the normal state, the strain energy of the electrons could be reduced by having electrons transfer from regions of high energy to regions of lower energy on the Fermi surface and thereby give rise to a soft elastic constant. At low temperatures, in the charge-density-wave state, energy gaps appear over the Fermi surface and it is conceivable that the extent to which electrons can become rearranged will be reduced. The electronic strain energy will then remain high and the elastic constant will be stiffer. These effects can be expected to be significant whenever the density of states near the Fermi level is large, a situation which is generally believed to be the case for the $2H$ compounds under investigation here.¹⁵ A quantitative evaluation of this model requires a detailed knowledge of the Fermi-surface distortions under strain, as well as knowledge of the location of the energy gaps on the Fermi surface, and will not be attempted here. Instead, we will attempt to obtain a qualitative explanation for the general shape of the velocity curves. The conduction-band contribution to the elastic constants will be dependent on the density of electron states near the Fermi level. The same applies to the behavior of the Pauli spin susceptibility in these materials. We can therefore expect a relationship between the sound velocity and the paramagnetic susceptibility. Such a relationship was already pointed out by Bernstein,¹⁶ who showed that for a spherical Fermi surface the form of the temperature-dependent part of the bulk modulus was identical to the temperature-dependent term in the Stoner susceptibility expression. In one dimension, a first-order contribution to certain elastic constants has generally been written in the form^{3,4}

$$C(T) = u^2 \int N(\epsilon) \left(-\frac{\partial f}{\partial \epsilon} \right) d\epsilon,$$

where C is an elastic constant, u is a deformation

potential, and $N(\epsilon)$ is the density of electron states. The close connection with the paramagnetic susceptibility is thus evident. For a complex Fermi surface we cannot expect such a simple proportionality between sound velocity and paramagnetic susceptibility, since different averages over the Fermi surface will, in general, be involved for the two quantities. In the layered compounds, however, because of the high isotropy within the basal plane, we might expect that the above relationship will lead to a qualitative description of the conduction-band contribution to the temperature dependence of the plate modulus or to C_{11} . The conduction-band contribution to an elastic constant could then be written as

$$C_{el}(T) = \frac{u^2}{\mu_B^2} \chi_{par}(T),$$

where χ_{par} is the Pauli spin susceptibility and μ_B is the Bohr magneton. The temperature dependence of an elastic modulus is also determined by lattice anharmonic effects, that is, the anharmonic interaction of acoustic phonons with the whole phonon spectrum.¹⁷ Our main concern here is the temperature dependence of the plate mode velocity and it is convenient to express the softening of the velocity relative to its value at $T = 0$ in terms of an anharmonic contribution and a contribution from the conduction band so that we write

$$\begin{aligned} \frac{\Delta V}{V} &= \frac{[V(T) - V(0)]}{V(0)} \\ &= \frac{[V_0(T) - V(0)]}{V(0)} - \frac{u^2 \rho}{2 \mu_B^2 E_p(0) M} [\chi_{par}(T) - \chi_{par}(0)]. \end{aligned} \quad (2)$$

In Eq. (2) $[V_0(T) - V(0)]/V(0)$ represents the anharmonic contribution to $\Delta V/V$, $E_p(0)$ is the plate modulus at $T = 0$, M the molecular weight, ρ the density, and $[\chi_{par}(T) - \chi_{par}(0)]$ represents the change in the paramagnetic susceptibility [measured in (emu/mole)]. The velocity measurements can now be combined with magnetic-susceptibility data to obtain information about the anharmonic background, as well as estimates of the order of magnitude of the deformation potential in the $2H$ layered compounds. One difficulty that is encountered is the observed anisotropy in the magnetic susceptibility¹⁸ which is not properly understood at the present time. Both χ_{\perp} and χ_{\parallel} show very similar temperature dependences but their magnitudes differ considerably. The temperature dependence of each component, in the normal state, is qualitatively what one might expect when the Fermi level is close to a sharp peak in the density of states and the sharp decrease in the susceptibility in the CDW state is generally at-

tributed to the decrease in the density of states when the energy gaps open up on the Fermi surface. It appears likely that the anisotropy is caused by spin-orbit interaction effects¹⁹ so that the density of states will still play a central role in the temperature dependence of the susceptibility. We expect the paramagnetic susceptibility without spin-orbit effects to be somewhat closer to χ for H perpendicular to the c axis but in the absence of a detailed calculation, we have used data on powders to obtain representative quantities for $[\chi_{\text{par}}(T) - \chi_{\text{par}}(0)]$ and assumed that all diamagnetic contributions to χ are temperature independent. The anharmonic contribution was chosen to have the simple form

$$\left(\frac{V_p(T) - V(0)}{V(0)}\right) = \alpha T^2 + \beta T^4,$$

since such an expression gave reasonable representation for temperature dependence of the plate mode velocity above the CDW transition in the $2H\text{-NbSe}_2$ sample for which anharmonic effects should dominate. By using the susceptibility data given by Wilson¹² on $2H\text{-TaS}_2$ and letting $\alpha = 1.9 \times 10^{-7}$, $\beta = 5.1 \times 10^{-14}$, and $u^2\rho/2\mu_B^2 E_p(0)M = 225$ (emu/mole)⁻¹, we obtained the dashed curve in Fig. 2. This curve has the general features of the experimental curve, i.e., it shows the characteristic softening of the lattice as the CDW transition is approached from below and a relatively flat region above this temperature. The anharmonic contribution to the temperature dependence for the above values α and β is shown in Fig. 8. In $2H\text{-NbSe}_2$ the magnetic susceptibility has a relatively weak temperature dependence so that the data in Fig. 7 should represent largely the anharmonic component in this material. The derived anharmonic contribution for $2H\text{-TaS}_2$ is thus com-

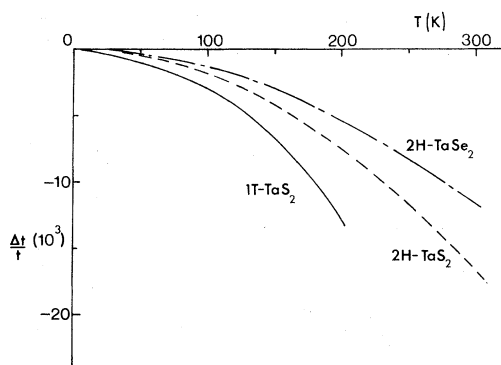


FIG. 8. Expected anharmonic contribution to pulse travel time according to Eq. (2). --- plate mode in $2H\text{-TaS}_2$; -.-.- Young's-modulus velocity in $2H\text{-TaSe}_2$; for comparison our plate mode measurements on $1T\text{-TaS}_2$ in the commensurate state are also given.

parable to that found in $2H\text{-NbSe}_2$.²⁰ Our plate mode velocity value then gives a deformation potential of about 0.7 eV. This is comparable to the d -electron band width.¹⁵ It is interesting to note at this point that deformation potentials for tight-binding d bands were shown by Mitra²¹ to be of the order of the bandwidth.

A similar analysis for the Young's-modulus data on $2H\text{-TaSe}_2$ as obtained by Barmatz *et al.*¹ is complicated by the ICDW-to-CCDW transition near 90 K in this material. This transition is very pronounced in the elastic measurements but seems to have no effect on the magnetic susceptibility. The density of states thus does not appear to change significantly at this second transition and Eq. (2) would simply give a modulus stiffening below 121 K, very much like that observed for $2H\text{-TaS}_2$. To obtain a fit to the data above 121 K with Eq. (2), an allowance for a possible shift in the $T = 0$ value of the velocity in the absence of the second transition must be made, and a constant δ should be subtracted from the right-hand side of Eq. (2). This parameter then is the offset of the low-temperature intercepts on the velocity axis between the observed behavior and that expected in the absence of the second transition. We obtained a good fit above 121 K to the data of Barmatz *et al.*¹ shown in their Fig. 2 for $\alpha = -1.4 \times 10^{-7}$, $\beta = 1.1 \times 10^{-13}$, $\delta = 3.58 \times 10^{-3}$, and $u^2\rho/2\mu_B^2 E_p(0)M = 245$ (emu/mole)⁻¹. The derived anharmonic background shown in Fig. 8 and the deformation potential of about 0.9 eV are thus very similar to the values found for $2H\text{-TaS}_2$.

The anomaly in $2H\text{-NbSe}_2$ near 28 K does not show the stiffening of the lattice seen in $2H\text{-TaS}_2$ and also at the upper transition in $2H\text{-TaSe}_2$. Instead, the behavior is much more like that seen at the ICDW-to-CCDW transition near 90 K in $2H\text{-TaSe}_2$. If any stiffening takes place in addition to the observed modulus softening, it is probably less than 2×10^{-4} in $\Delta V/V$. If we assume that for $2H\text{-NbSe}_2$, u is of the same order as for the Ta compounds, then we expect a susceptibility anomaly of at most, 1×10^{-6} emu/mole. This is well within the noise of susceptibility measurements reported so far.

It is tempting to extend the above arguments for the $2H$ compounds also to the case of $1T\text{-TaS}_2$. In this material the susceptibility shows little temperature dependence except near the incommensurate-to-nearly-commensurate and the nearly-commensurate-to-commensurate transitions, where the susceptibility, like the electrical resistivity, makes sharp jumps. For the sound velocity this would imply, on the basis of Eq. (2), a temperature dependence determined essentially by anharmonic background effects but interrupted by

nearly discontinuous jumps which are opposite in sign to the jump in the susceptibility. This interpretation of the jumps in the velocity and the susceptibility implies that density-of-states changes accompany the transitions in $1T\text{-TaS}_2$. Equation (2) then gives $\mu \approx 0.7$ eV. In the commensurate state, the susceptibility is essentially temperature independent and the measured temperature dependence of the plate mode velocity shown in Fig. 5 must be attributed entirely to anharmonic effects. $1T\text{-TaS}_2$ would then show the largest anharmonic contributions to the velocity of the layered compounds discussed here. The CDW has a very large amplitude in $1T\text{-TaS}_2$, and considerable lattice distortions accompany the transitions. In that case, it is quite possible that other explanations for the jumps in the magnetic susceptibility and the elastic behavior can be advanced and a detailed study of elastic measurements, such as sound velocity and thermal expansion that include the upper transition, would be very helpful in furthering our understanding of the properties of this interesting material.

V. CONCLUSION

We have measured the plate modulus in $2H\text{-NbSe}_2$, $2H\text{-TaS}_2$, and $1T\text{-TaS}_2$ as functions of temperature and noted a strong similarity between

the behavior of the magnetic susceptibility and the plate mode velocity near the CDW transitions. The temperature dependence of the velocity was interpreted in terms of an anharmonic component and a component attributable to the conduction electrons. The rapid softening of the plate modulus as the CDW transition is approached from below in $2H\text{-TaS}_2$ and the surprisingly small temperature dependence in the normal state in both $2H\text{-TaS}_2$ and $2H\text{-TaSe}_2$, were interpreted in terms of an interplay between these two components. The anharmonic backgrounds suggested by the model for the layered compounds turn out to be significantly smaller than anharmonic softening in, for example, aluminum, and an order of magnitude smaller than in quasi-one-dimensional materials, such as NbSe_3 or TTF-TCNQ. The model also suggests that conduction-band deformation potentials in all four layered compounds discussed are of the order of 1 eV. The analysis in this paper was of necessity very qualitative, but it does suggest that a detailed theoretical study of this problem might be very fruitful.

ACKNOWLEDGMENTS

We are pleased to acknowledge very helpful discussions with T. M. Rice, M. Walker, A. H. MacDonald, W. Geldart, and T. Tiedje.

-
- ¹M. Barmatz, L. R. Testardi, and F. J. DiSalvo, *Phys. Rev.* **12**, 4367 (1975).
²L. R. Testardi and T. B. Bateman, *Phys. Rev.* **154**, 402 (1967).
³W. Rehwald, M. Raul, R. W. Cohen, and G. D. Cody, *Phys. Rev.* **6**, 363 (1972).
⁴T. Tiedje, R. R. Haering, M. H. Jericho, W. A. Roger, and A. Simpson, *Solid State Commun.* **23**, 713 (1977).
⁵A. M. Simpson, W. A. Roger, and M. H. Jericho, *Rev. Sci. Instrum.* **51**, 32 (1980).
⁶T. R. Meeker and A. H. Meitzler, in *Physical Acoustics*, edited by W. P. Mason (Academic, New York, 1964), Vol. 1A, Chap. II.
⁷G. L. Givens and E. Fredericks, *J. Phys. Chem. Solids* **38**, 1363 (1977).
⁸M. O. Steinitz and J. Grunzweig-Genossar, *Solid State Commun.* **29**, 519 (1979).
⁹T. N. Claytor and R. J. Sladek, *Phys. Rev. B* **18**, 5842 (1978).
¹⁰G. A. Alers, in *Physical Acoustics*, edited by W. P. Mason (Academic, New York, 1966), Vol. IVA, Chap. VIII.
¹¹J. P. Tidman, O. Singh, A. E. Curzon, and R. F. Frindt, *Philos. Mag.* **30**, 1191 (1974).
¹²J. A. Wilson, F. J. DiSalvo, and S. Mahajam, *Adv. Phys.* **24**, 117 (1975).
¹³M. S. Skolnick, S. Roth, and H. Alms, *J. Phys. C* **10**, 2523 (1977).
¹⁴J. L. Feldman, *J. Phys. Chem. Solids* **37**, 1141 (1976).
¹⁵L. F. Mattheiss, *Phys. Rev.* **8**, 3719 (1973); G. Wexler and A. M. Woolley, *J. Phys. C* **9**, 1185 (1976).
¹⁶B. T. Bernstein, *Phys. Rev.* **132**, 50 (1963).
¹⁷G. Leibfried and W. Ludwig, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1961).
¹⁸J. L. Benchimol, F. T. Hedgcock, and F. J. DiSalvo, *Solid State Commun.* **25**, 677 (1978).
¹⁹A. H. MacDonald, private communication.
²⁰We have recently measured the plate mode velocity in $1T\text{-TiS}_2$ which does not have a CDW transition (unpublished) and anharmonic effects are of the same order of magnitude as those reported in this work.
²¹T. K. Mitra, *J. Phys. C* **2**, 52 (1969).