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Thermal expansion, ultrasonic velocity, and attenuation measurements in TiS_2, $TiSe_2$, and $TiS_{0.5}Se_{1.5}$

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Measurements have been made of the velocity and attenuation of ultrasonic plate mode waves in TiS_2, $TiSe_2$, and $TiS_{0.5}Se_{1.5}$ between 4 and 300 K. $TiSe_2$ exhibits large anomalies associated with the occurrence of a charge-density-wave transition near $T_c = 200$ K. Measurements of the expansion coefficient and of the a-axis uniaxial stress dependence of T_c have also been made, and these measurements, together with other data in the literature, are discussed in terms of the Ehrenfest relationships. A large discrepancy is observed between results obtained from thermal expansion and those obtained from elastic properties. The temperature dependence of the velocity in $TiSe_2$ below T_c is accounted for by an anharmonic contribution and an electron-phonon contribution, which reflects the opening of an energy gap on the Fermi surface by the charge-density wave. Above T_c, the velocity changes are found to be affected by fluctuations over a wide temperature range and it is suggested that these fluctuations are associated with the phonon mode softening near the L point of the Brillouin zone as T_c is approached. Reduced-dimensionality effects are suggested.

I. INTRODUCTION

The existence of a commensurate charge-density wave (CDW) in the group-IV layered transition-metal dichalcogenides is well established and the effects of the CDW on electrical and thermal properties of these materials have been investigated in detail.[1] In this paper, we report measurements of the velocities of propagation of 10-MHz ultrasonic pulses along the basal planes of TiS_2, $TiSe_2$, and the mixed compound $TiS_{0.5}Se_{1.5}$. The thermal-expansion coefficients were also measured using a capacitance dilatometer.

The measurements of velocity and absorption of longitudinal ultrasonic waves were performed to clarify the unique features of the macroscopic behavior of $TiSe_2$ and its mixed compound near the CDW phase-transition temperature T_c. The semimetallic character of $TiSe_2$ is now a rather well-established[2] experimental fact. However, there remains a controversy regarding the origin of the CDW phase transition. One proposed mechanism[3,4] is a Fermi-surface-driven CDW with the accompanying periodic lattice distortion. Wilson *et al.*[5] suggested an excitonic insulator model with a direct Coulomb interaction between the Γ holes and the L electrons. The third possible mechanism is an intrinsic softening of the phonon branch at the L point, where the transition can be described as a phonon-driven antiferroelectric distortion.[6] Finally, a band Jahn-Teller effect was suggested by Hughes[7] where the low-temperature lattice distortion lowers the total electronic energy. Our acoustic measurements will give indications that fluctuations near the CDW phase transition are controlled by a reduced dimensionality of the phonon modes near the L points. As such, it was not possible to discriminate between the two above-proposed mechanisms, but we propose a new line of thinking to orient further researches on this question.

Section II describes the experimental technique used to measure the propagation characteristics of elastic waves. In Sec. III the velocity results for TiS_2, $TiSe_2$, and $TiSe_{0.5}Se_{1.5}$, as well as attenuation and thermal-expansion data, are presented. In Sec. IV the stress dependence of T_c is obtained using the Ehrenfest relations and the possible contribution of fluctuations above T_c is estimated. In Sec. V the velocity and attenuation data for $T > T_c$ are qualitatively analyzed in terms of a model including fluctuations which are argued to have a reduced dimensionality. A comparison of the velocity data and the calculated magnetic susceptibility results obtained using the semimetallic model is made in Secs. VI and VII, where we attempt to decompose the observed temperature dependence into an anharmonic part, a conduction-electron contribution, and possibly a contribution from fluctuations near T_c. In Sec. VII, the results for the mixed compounds $TiS_{0.5}Se_{1.5}$ are briefly reviewed. Finally, conclusions are drawn on the role of fluctuations and the relative contributions from phonon-driven and Fermi-surface-driven instabilities to the CDW phase transition.

II. EXPERIMENTAL DETAILS

The samples were 5–7 mm in length, about 3 mm wide and 0.05 mm thick. They were grown in quartz ampoules by an iodine vapor transport from powders of the respective compounds.

Velocity and attenuation measurements were made by monitoring the phase and amplitude of $\frac{1}{2}$-μs-long, 10-MHz ultrasonic pulses that were propagated along the samples in the a-b plane. Since the sample thickness was much less than an acoustic wavelength, the acoustic energy propagated as plate modes. For a system with hexagonal symmetry the first Lamb mode has a velocity given by

$$v_p = \left[\frac{C_{11}}{\rho}\right]^{1/2}\left[1-\frac{C_{13}^2}{C_{11}C_{33}}\right]^{1/2}, \qquad (1)$$

where ρ is the density, C_{ij} are the elastic constants with the conventional notation, and the c axis is perpendicular to the slab sample. The experimental arrangement and the method employed for the continuous recording of the velocity as a function of temperature was identical to that described before.[8,9] The attenuation was measured by monitoring the amplitude of the first Lamb mode using a box-car integrator. The changes in sound velocity that were observed near the CDW transition were larger than those normally encountered in the layered compounds, and in the attenuation measurement it was necessary to allow the box-car gate to shift and follow the acoustic signal as the temperature was varied.

The thermal expansion was measured in a capacitance dilatometer. Details concerning the experimental arrangement have been reported elsewhere.[10] Basal-plane expansion measurements were made by constraining the samples in a jig described in Ref. 10. Expansion measurements along the c axis could not be obtained with sufficient resolution since only very thin platelets of $TiSe_2$ were available. Fractional changes in length could be determined to 2 parts in 10^7. Temperatures were measured with a copper-Constantan thermocouple for temperatures above 60 K and with a calibrated Lakeshore cryotronics germanium resistance sensor for temperatures below 70 K.

III. EXPERIMENTAL RESULTS

The velocity results are shown in Fig. 1. The experiment actually measures changes in the ultrasonic pulse travel time. To obtain velocity changes the data were corrected for length changes in the sample due to thermal expansion. The thermal-expansion corrections amount to only a few percent at room temperature and low-resolution thermal-expansion data is adequate for making the corrections. The thermal-expansion data for $TiSe_2$ was taken from Wiegers[11] and for TiS_2 from Wittingham and Thompson.[12] Our own a-axis measurements on the mixed compound were used to correct the travel times for $TiS_{0.5}Se_{1.5}$. Absolute velocity measurements can be made to an accuracy of about 10%. The values for the room-temperature plate-mode velocities in TiS_2, $TiSe_2$, and the mixed compound are 6.0×10^5, 4.4×10^5, and 4.4×10^5 cm/s, respectively.

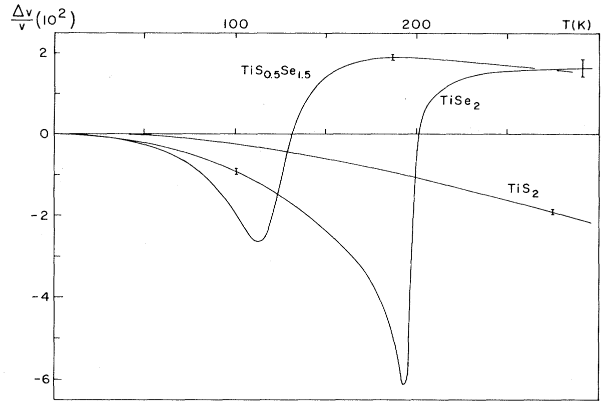

FIG. 1. Ultrasonic velocity data as a function of temperature for TiS_2, $TiSe_2$, and $TiS_{0.5}Se_{1.5}$. Data for the three samples have been arbitrarily normalized at 0 K.

The results for TiS_2, which has no CDW transition, are featureless and the overall change in the velocity between 4 and 300 K is about 2%. For $TiSe_2$ the change in the velocity of sound is marked by a gradual decrease starting at 250 K followed by a rapid decrease at the CDW transition temperature with a slow recovery below the transition. The general features of the curve are similar to the low-frequency results of Barmatz *et al.*[13] and the magnitude of the softening at the transition is comparable to the softening they report for their results at a measuring frequency of 0.64 KHz. The transition for the mixed compound is depressed by the expected amount as estimated from T_c, but it also considerably broadened. It is possible that the broadening is an intrinsic property of the compound. It is more likely, however, that the broadening is caused by variations in the stochiometry of the sample.

The attenuation results shown in Fig. 2 display well-pronounced attenuation peaks at the CDW transitions and the attenuation peak which is rather narrow for $TiSe_2$ (5 K) coincides with the dip in the velocity.

No hysteresis in the position of the attenuation and velocity features on thermal cycling was observed to within 0.3 K, the reproducibility of our temperature measurement. Notice that the attenuation peaks extend over a much narrower temperature interval than the change in velocity.

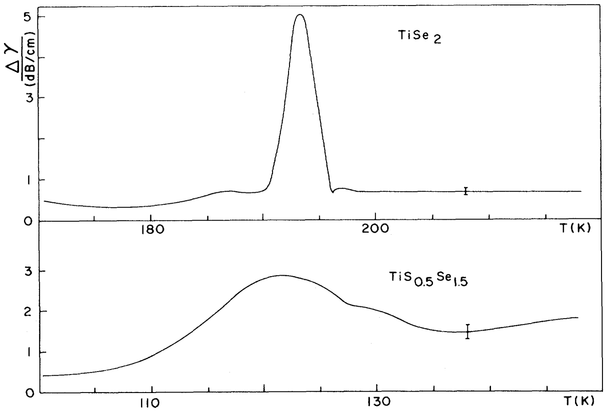

FIG. 2. Ultrasonic attenuation as a function of temperature for $TiSe_2$ and $TiS_{0.5}Se_{1.5}$.

The thermal-expansion results are shown in Figs. 3 and 4. The mixed compound was measured from 4 to 300 K, and between 80 and 300 K the expansion coefficient is constant and of magnitude $\alpha_a = 15.1\times 10^{-6}\ \mathrm{K}^{-1}$. To the resolution of our measuring system, no anomaly in the a-axis expansion was visible at the CDW transition temperature. It is quite likely that the considerable width of the transition in the mixed compound has made the observation of such an expansion-coefficient change impossible. The corresponding results in $\mathrm{TiSe_2}$ (Fig. 4) do, however, show a clear change in the expansion coefficient at the CDW transition of magnitude $\Delta\alpha_a \simeq -2.5\times 10^{-6}\ \mathrm{K}^{-1}$. There does not appear to be any significant length discontinuity at the transition. These results, together with an absence of hysteresis, support suggestions that the transition is second order. Thermal-expansion measurements using x-ray techniques were reported previously by Wiegers[11] for the a- and c-axis directions in $\mathrm{TiSe_2}$. The magnitude of α_a we obtain agrees well with that obtained in Ref. 11. Wiegers reported a c-axis expansion coefficient discontinuity at the CDW transition of $\Delta\alpha_c \simeq 7.5\times 10^{-6}\ \mathrm{K}^{-1}$ but no discontinuity in α_a.

IV. STRESS DEPENDENCE OF T_c

The behavior of, and the interrelationship between, thermodynamic quantities near a second-order phase transition are often discussed successfully with the help of Ehrenfest-type relations and particularly with Testardi's form of the relationships.[14] At the phase-transition temperature we then have

$$\Delta\alpha_i = -\left[\frac{\partial \ln T_c}{\partial \sigma_i}\right]\Delta C_P\,, \qquad (2)$$

$$\Delta s_{ij}^{T} = \left[\frac{\partial \ln T_c}{\partial \sigma_i}\right]\left[\frac{\partial \ln T_c}{\partial \sigma_j}\right]T_c \Delta C_P\,, \qquad (3)$$

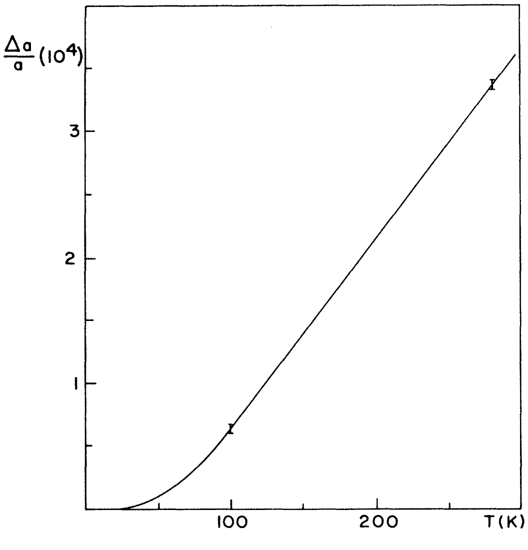

FIG. 3. Thermal expansion $10^4\,\Delta a/a$ as a function of temperature for $\mathrm{TiS_{0.5}Se_{1.5}}$.

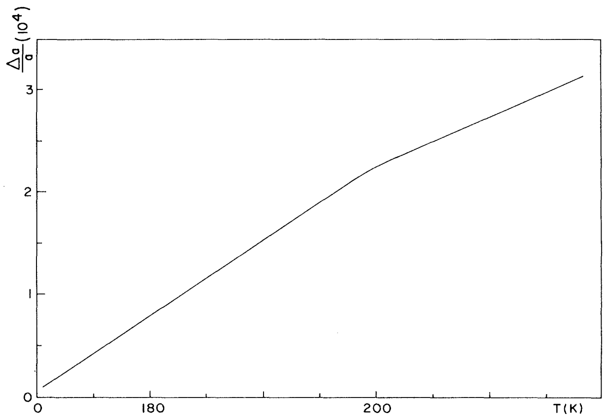

FIG. 4. Thermal expansion $10^4\,\Delta a/a$ as a function of temperature for $\mathrm{TiSe_2}$.

where $\Delta\alpha_i$, Δs_{ij}^T, and ΔC_P are the finite jumps in the linear thermal-expansion coefficient, the isothermal longitudinal elastic compliance, and the constant-pressure specific heat at the transition temperature. σ_i is the uniaxial stress in the i direction. Note that the derivation of the Ehrenfest relations (2) and (3), based on the method of thermodynamics, is a mean-field approximation in the language of statistical methods. Critical fluctuations near a second-order λ point which are absent from the Ehrenfest relations may impair their use. In such a case, generalized Pippard equations[15] may be used to relate at a given temperature the various thermodynamic quantities which change very rapidly in the vicinity of the λ point or the scaling hypothesis may be invoked to relate the critical point exponents.

In $\mathrm{TiSe_2}$, the Ehrenfest relations (2) and (3) may be checked for consistency since finite jumps in the various thermodynamic quantities may be estimated from independent data. Specific-heat measurements have shown a small peak at the CDW transition which has been approximated[16] by a mean-field model with a step discontinuity at the transition temperature of -1.15 J/mole K. The experimentally observed jumps in the linear thermal-expansion coefficient are $\Delta\alpha_c = 7.5\times 10^{-6}\ \mathrm{K}^{-1}$ (Ref. 11) and $\Delta\alpha_a = -2.5\times 10^{-6}\ \mathrm{K}^{-1}$ from our measurements. From the first Ehrenfest relation [Eq. (2)] and the above data, we obtain, for the stress dependence of T_c derived from thermal expansion, $(\partial T_c/\partial\sigma_c)_{\mathrm{TE}} = 5.16$ K/kbar and $(\partial T_c/\partial\sigma_a)_{\mathrm{TE}} = -1.75$ K/kbar where the subscript TE denotes a value derived from thermal-expansion measurements.

The stress dependence of T_c is often derived from the velocity of sound or the jump in the Young's modulus using the second Ehrenfest relation [Eq. (3)]. In $\mathrm{TiSe_2}$, since the elastic constant C_{13} ($C_{13} = C_{44}$; see Ref. 11) is much smaller[17] than C_{11}, as a first approximation the first Lamb mode propagating in the a-b plane is considered to be purely longitudinal. In such a limit, Eq. (3), written for the Young's modulus jump ΔE_a, becomes

$$\frac{\Delta E_a}{E_a^2} = -\frac{1}{T_c}\left[\frac{\partial T_c}{\partial \sigma_a}\right]_e^2 \Delta C_P \ , \tag{4}$$

where the subscript e denotes a value obtained from elastic measurements. With the use of the discontinuity of ΔC_P as estimated by Craven[16] and the discontinuity of Young's modulus obtained from sound velocity measurements, Eq. (4) gives a second estimate for the absolute value of the stress dependence of T_c, $|(\partial T_c/\partial \sigma_a)_e| = 10$ k/kbar.[18] There is thus a considerable disagreement between the basal-plane stress dependence of T_c as obtained from thermal expansion compared to that obtained from elastic measurements. It is instructive to compare the uniaxial stress dependence of T_c with measurements of the hydrostatic pressure dependence using

$$\left[\frac{\partial T_c}{\partial p}\right]_{\mathrm{TE}} = -\left[\frac{\partial T_c}{\partial \sigma_c} + 2\frac{\partial T_c}{\partial \sigma_a}\right]_{\mathrm{TE}} . \tag{5}$$

From our results, we obtain $(\partial T_c/\partial P)_{\mathrm{TE}} = -1.66$ K/kbar. Friend *et al.*[1] and Ogasawara *et al.*[19] have measured the pressure dependence of T_c from the pressure dependence of the transport properties. They report a nonlinear depression of T_c with pressure with a mean rate of $\Delta T_c/\Delta P \simeq -1$ K/kbar for P up to 5 kbar. This is reasonably close to the value calculated above.

It could be argued that the specific-heat anomaly does not represent the mean-field specific-heat jump but that the anomaly is dominated by fluctuations. It would then be more appropriate to eliminate ΔC_P from the Ehrenfest relations. In that case we obtain

$$\frac{\Delta \alpha_a}{\Delta \alpha_c} = \frac{(\partial T_c/\partial \sigma_a)_{\mathrm{TE}}}{(\partial T_c/\partial \sigma_c)_{\mathrm{TE}}} \simeq = -0.33 \ . \tag{6}$$

Combining this with the hydrostatic pressure result, Eq. (5), we obtain

$$\left[\frac{\partial T_c}{\partial \sigma_a}\right]_P \simeq -1.0 \ , \tag{7}$$

$$\left[\frac{\partial T_c}{\partial \sigma_c}\right]_P \simeq 3.0 \ , \tag{8}$$

in K/kbar, where the subscript P denotes values obtained from measurements under an hydrostatic pressure. These estimates are reasonably consistent with those obtained using the specific-heat jump. Alternatively we can eliminate the specific heat and write

$$\left[\frac{\Delta E}{E^2}\right] \Big/ \Delta \alpha_a = \left[\frac{\partial T_c}{\partial \sigma_a}\right]_e \simeq -59 \tag{9}$$

(in K/kbar), and from Eq. (6),

$$\left[\frac{\partial T_c}{\partial \sigma_c}\right]_e \simeq 180 \ , \tag{10}$$

also in K/kbar. These estimates, when substituted in Eq. (5), give, for $\partial T_c/\partial P$, a result $[(\partial T_c/\partial P) \simeq 60$ K/kbar$]$ in total disagreement with the experimental result.[19] However, one might in this case argue that $(\partial T_c/\partial P)$ is the difference of two large numbers and the inevitable uncertainties in the estimates for the uniaxial stress coefficients could allow for the possibility of having $\partial T_c/\partial \sigma_c$ nearly equal in magnitude to $2(\partial T_c/\partial \sigma_a)$ to explain the small observed value of $\partial T_c/\partial P$. We, therefore, determined $\partial T_c/\partial \sigma_a$ directly by measuring the resistivity and its temperature derivative for $TiSe_2$ samples as a function of a-axis stress up to 0.5 kbar. We conclude from these measurements that $|\partial T_c/\partial \sigma_a|$ is less than 2 K/kbar. These measurements are, therefore, in qualitative agreement with the estimates for the stress coefficients obtained from the specific-heat and thermal-expansion data but are not consistent with estimates made from sound-velocity measurements.

Two possible sources for the above discrepency are the following: (a) The difference between the isothermal and adiabatic elastic compliances, and (b) contributions to the jump of the velocity of sound arising from off-diagonal elastic compliances neglected in Eq. (4).

We can make a rough quantitative estimate of the first contribution. The elastic measurements allow us only to calculate the adiabatic elastic compliances. To establish a comparison with the isothermal parameters derived from linear thermal-expansion coefficients, the isothermal elastic compliances must be estimated. The relation between isothermal and adiabatic constants is given[20] by

$$s_{ij}^S = s_{ij}^T - \alpha_i \alpha_j T/C_P \ . \tag{11}$$

With the use of the specific-heat measurement of Craven *et al.*[16] ($C_P \simeq 65$ J/K mole) and our measured value of α_a, along with the jumps in these quantities, the jump in the Young's modulus arising from the last term in Eq. (11) is estimated to be at most 10% of the jump measured adiabatically. This is, therefore, not the source of the discrepancy observed above.

In relation to the second contribution (b), an estimate of the jumps in the off-diagonal elastic compliances s_{ij}^T is obtained from Eq. (3) and the stress dependence of T_c obtained from thermal-expansion data. With the use of Eq. (1) and the general relationships between elastic compliances and elastic constants for hexagonal crystals,[20] the change of velocity is related to changes in s_{ij}^T. Because of the small value of C_{13} compared to C_{11} in $TiSe_2$, the above-mentioned contribution to the jump in the velocity of sound amounts to only a few percent, and is, therefore, also not responsible for the discrepancy between sound-velocity and thermal-expansion estimates.

Before we examine other reasons for the inconsistency in the results for $\partial T_c/\partial \sigma$ from the Ehrenfest relations, it is instructive to take a closer look at the nature of the CDW transition in $TiSe_2$. This material is the only known layered transition-metal dichalcogenide which has a second-order phase transition from a normal semimetallic system to a commensurate CDW phase and periodic lattice distortion, as all the other dichalcogenides[18] have a first-order transition under similar conditions. Thus we expect for $TiSe_2$, contrary to the other transition-metal dichalcogenides, that CDW and lattice fluctuations are large above T_c and that as a consequence pretransitional effects on the elastic properties may be important. Independent of the particular mechanism involved, the Brillouin-zone

(BZ) phonon mode which goes soft at the phase transition could be considered coupled to the elastic strains by terms in the Gibbs free energy which are linear in the strain and quadratic in the order parameter. In such a case the strain is a secondary order parameter and the ultrasonic velocity measures the inverse of the correlation function. With the use of a simple scaling hypothesis on the Gibbs free energy $G(T,\sigma_i)$ expressed as a function of the temperature T and the axial stress components σ_i, the critical exponents are linked by the relation

$$\mu+\alpha-2\nu=0\ , \tag{12}$$

where μ, α, and ν are, respectively, the static critical exponents of the isothermal elastic compliances s_{ij}^T, of the specific heat at constant pressure C_P, and of the linear coefficient of thermal expansion α_i. From the specific-heat data,[16] we conclude that α is small since only a quasidiscontinuity is observed as predicted by mean-field theory where $\alpha=0$. From Eq. (12), we obtain that μ, the critical exponent of the isothermal elastic compliance is roughly equal to 2ν. Our measurements of the linear coefficients of thermal expansion show no divergent behavior characteristic of fluctuations (Fig. 4). This is easily understood if ν is of order unity and if the critical or fluctuation-dominated region for α_i is small around T_c, being smeared out by the strain or defect-broadened transition width. The width of the fluctuation dominated region around T_c for a particular property of the system is controlled not only by the critical exponent but also by the strength of the term arising from fluctuations when compared with the background contribution. The periodic lattice distortion principally affects the lattice modes near the BZ boundary (points L) by folding them back to the origin of the distorted BZ leaving most of the phonon spectrum unchanged. Properties of the system which are controlled by the entire phonon spectrum such as the specific heat and thermal expansion are less affected by the above fluctuations whereas the slope of the acoustic branch at the origin is more influenced by the appearance of a new optical mode at $q=0$ in the distorted BZ. We believe that this explains the absence of observable fluctuation effects on the specific heat and thermal expansion, whereas the long-wavelength elastic properties have a measurable critical region. We now claim that the gradual decrease in $\Delta v/v$ starting at $T\simeq T_c+50$ K results from the effect of critical fluctuations on the elastic compliance when the elastic strains are coupled to the square of the fluctuating normal-mode coordinate which goes soft at $T=T_c$. The square of the velocity of sound being proportional to the inverse of the elastic compliance, the divergent compliance gives rise to a decrease in the velocity of sound. Secondly, since the critical exponent $\mu\simeq2\nu$, the effect on the velocity of sound is felt over a larger temperature region than for thermal expansion as explained above. This suggestion is supported by at least one other measurement. Strong diffuse scattering from fluctuations has been observed in $Ti_{1+x}Se_2$ ($x\simeq0,02$) above T_c up to at least room temperature using electron and x-ray diffraction.[4] Similar behavior has also been measured for the high-temperature phase of β-quartz and for the cubic phase of $KMnF_3$.[21–25] In view of the above discussion we suggest that the failure of Eq. (3) is a direct consequence of the soft mode at the BZ L point. The soft mode leads to large fluctuations and hence long precursor effects for the sound velocity above T_c. Furthermore, below the transition the slope of the acoustic branch near $q\rightarrow0$ is partly controlled by the frequency of the new optical mode at the center of the distorted BZ in the commensurate CDW state. For a commensurate second-order phase transition, the frequency of this mode should be zero at $T=T_c$ and it will increase to a finite value as $T\rightarrow0$. The repulsion between this optical mode and the acoustic mode at $q\rightarrow0$ will determine, in part, the value of the velocity of sound for $T\rightarrow0$. These two effects together make an extrapolation to estimate the mean-field value of $\Delta v/v$ at the transition temperature very difficult. The new optic mode near the BZ center, as well as fluctuations, have a much smaller effect on the specific heat and thermal expansion, and estimates of $\partial T_c/\partial\sigma$ from Eq. (2) should be more reliable.

V. TEMPERATURE DEPENDENCE OF THE ULTRASONIC PROPERTIES FOR $T>T_c$ IN $TiSe_2$

As seen in Fig. 1 the decrease in the velocity of sound in $TiSe_2$ for $T>T_c$ starts well above T_c near $T\simeq250$ K. Since critical fluctuations in the soft-BZ mode affect the elastic properties over such a wide temperature range, it is expected that the effective dimensionality d of the periodically deformed lattice is less than 3. Indeed, we argue that as the phonon frequency at L softens, the dispersion of the phonon modes, as measured from L in the reciprocal space, is anisotropic in the reciprocal q space. This anisotropy at $T>T_c$ leads to a correlation range ξ which is anisotropic and reflects itself in a reduced dimensionality of the correlated regions of the periodically distorted lattice. Such soft-mode frequencies which are very nearly two-dimensional have been observed before for a structural phase transition in $KMnF_3$.[23,24] Indeed, in $KMnF_3$, x-ray[23] and neutron[24] inelastic scattering has shown that the dispersion of the lowest-energy phonon branches around the superlattice Bragg reflections, which goes soft at $T=T_c$, is anisotropic. In addition to this, it is very interesting to compare the anomalies in elastic properties of $KMnF_3$ as obtained from ultrasonic velocity measurements with observations on $TiSe_2$ as seen on Fig. 1. Aleksandrov *et al.*[22] have measured the temperature dependence of the velocity of longitudinal waves in $KmNF_3$ and their experimental observation (see Fig. 1 of Ref. 22) has a remarkable resemblence to our observation for $TiSe_2$. This is an additional reason to argue for an effective reduced dimensionality in $TiSe_2$.

In contrast to the velocity results, the ultrasonic attenuation extends only a few degrees around T_c. This behavior is easily understood in the framework of a model Hamiltonian proposed by Pytte[26] to consider the general problem of the interaction between a long-wavelength acoustic strain and an optical soft-mode coordinate. In his analysis, Pytte uses a coupling linear in strain and quadratic in the order parameter. For symmetry reasons, such a coupling is also the lowest allowed term in our problem. For $T > T_c$, fluctuations in the scattering terms renormalize the ultrasonic sound velocity according to the following law:

$$\frac{\Delta v}{v} \sim \frac{1}{\epsilon_0^{4-d}} , \tag{13}$$

where d is the effective dimensionality of the system and ϵ_0 is the energy of the mode at the BZ that goes soft at T_c. For the ultrasonic attenuation γ, two regimes have to be differentiated,

$$\gamma_u \sim \frac{1}{\epsilon_0^{4-d}} \quad \text{if } \Gamma \ll \epsilon_0 \text{ (or } T \gg T_c\text{)} \tag{14}$$

and

$$\gamma_0 \sim \frac{1}{\epsilon_0^{6-d}} \quad \text{if } \Gamma \gg \epsilon_0 \text{ (or } T \gtrsim T_c\text{)} \tag{15}$$

where Γ is the BZ soft-mode damping. Equation (14) is the underdamped soft mode for $T \gg T_c$, while Eq. (15) is for the overdamped soft mode for T close to T_c. We then see that contrary to the ultrasonic velocity [Eq. (13)], the critical exponent for the ultrasonic attenuation changes as we approach T_c going from $4-d$ for $T \gg T_c$ to $6-d$ for $T \rightarrow T_c$ where $\Gamma \gg \epsilon_0$ ($\epsilon_0 \rightarrow 0$). This crossover between two possible regimes results in a narrow domain of temperature where the critical fluctuations dominate the behavior over the background contribution to the ultrasonic attenuation.

We conclude this section by saying that only a detailed experimental study of the phonon modes by inelastic scattering experiments could reveal the shape of the dispersion surfaces around the BZ L point and provide the necessary information to decide on the correctness of the proposed mechanism. However, it is argued that if such an anisotropic screening of the lattice modes exists, it is very likely to result from Fermi-surface effects (as in the nesting model,[3,4] the excitonic insulator model,[5] or the band Jahn-Teller model[7]) since the electron conducting states are roughly two dimensional while the lattice by itself is three dimensional.

VI. TEMPERATURE DEPENDENCE OF THE ULTRASONIC VELOCITY IN TiS_2

For this material, the sound velocity decreases monotonically with temperature. TiS_2 always retains its prototype structure so that lattice anharmonicities are the only important source for the changes in sound velocity. A detailed description of anharmonic effects on the elastic constants is difficult in anisotropic systems and we have chosen to represent these effects by the simple form

$$\left[\frac{\Delta v}{v}\right]_{\text{anh}} = \frac{v(T)-v(0)}{v(0)} = AT^2 + BT^4 . \tag{16}$$

Such an expression gives reasonable representation[9] for temperature dependence of the plate-mode velocity above the CDW transition in $2H$-$NbSe_2$ and $2H$-TaS_2 where anharmonic effects should dominate. For TiS_2 we obtain a very good fit to the data (shown in Fig. 1) for $A = -2.70\times10^{-7}$ K^{-2} and $B = 3.23\times10^{-13}$ K^{-4}. In Fig. 1, only the experimental curve is given since the fitted curve follows the data points perfectly. The values for A and B are in good agreement with previously obtained data for similar materials.[9]

VII. TEMPERATURE DEPENDENCE OF THE ULTRASONIC VELOCITY FOR $TiSe_2$

The elastic behavior in this material is characterized by a gradual decrease of the velocity starting around 250 K accompanied by a very sharp drop near the phase transition followed by a relatively slow recovery of the velocity that continues to the lowest temperature. The transition is thus characterized by a very asymmetric dip in the velocity at $T = T_c$. In the interpretation of the data we adopt the point of view that the coupling described in Sec. VI between strain and soft modes give rise to the anomaly in $\Delta v/v$. We will not discuss any further the behavior above T_c since it would require a detailed free-energy expression and proper treatment of the fluctuations. This is beyond the scope of our present work and the qualitative behavior has been discussed in Sec. IV.

As seen in the Introduction, there are two possible mechanisms for the periodic lattice distortion phase transition. In both, it may be argued that a gap will open up at the Fermi surface as a result of the electron-phonon interaction. In addition to the Fermi-surface-driven instability, the second mechanism, which invokes an intrinsic softening of the BZ lattice mode, will indirectly induce a gap at the Fermi surface. In this general framework then, we attribute the gradual stiffening of the elastic constant below T_c to lattice anharmonicities, to changes in the conduction electrons through a deformation potential and finally close to T_c to fluctuations in the order parameter. In what follows we will retain only the lattice anharmonicity contribution and the conduction-electron contribution, indicating that the third term would only contribute for $T < T_c$ very close to the transition.

The conduction-electron contribution may be understood physically in the following way. The longitudinal plate mode produces a Fermi-surface distortion which varies over the Fermi surface. In the absence of the CDW, this contribution to the strain energy is reduced by transferring electrons from regions of high energy to regions of lower energy. As a result, the stiffening of the elastic constants is reduced. In the CDW state, the energy gap in the conduction electrons prevents this free redistribution of the electrons on the Fermi surface. As a result, the strain energy is higher and the elastic constants will be stiffer for larger energy gaps. A quantitative evaluation of this effect would require a detailed knowledge of the Fermi-surface distortions under strain. This is beyond the purpose of this paper and we shall attempt to obtain a semiquantitative explanation for the general shape of the velocity curves using the excitonic insulator model[27] of $TiSe_2$. Indeed, this model, with the underlying assumption of a semimetallic character of this material, has gained support recently through photoemission studies.[27] In this model, the overlap of the Ti d bands with the Se p band is expected to be about 0.1 eV. The gradual stiffening in the sound velocity below T_c would then be a consequence of the gradual opening of an energy gap at the Fermi level. Such a gradual opening of the gap is suggested by the growth in amplitude of the lattice distortion[3,28] as well as by the behavior of the magnetic susceptibility[3] below T_c.

As shown in Ref. 9, except in special cases, the relationship between the sound velocity variation and the paramagnetic susceptibility can be written as

$$\left[\frac{\Delta v}{v}\right]_{e\text{-ph}} = -C_2 \chi_{\text{par}}(T) \;, \tag{17}$$

where

$$C_2 = \frac{u^2}{\mu_B^2}\,\frac{1}{2\rho v^2} \;.$$

$\chi_{\text{par}}(T)$ is the Pauli-spin susceptibility, μ_B is the Bohr magneton, u is a deformation potential, ρ is the density, and v is the zero-temperature sound velocity. Unfortunately, only the total magnetic susceptibility has been measured[3] and we have no way of substracting the temperature-dependent diamagnetic contribution for this semimetallic system. Instead, to determine the significance of the electron-phonon coupling for the low-temperature behavior, we have calculated the paramagnetic susceptibility $\chi_{\text{par}}(T)$ for a simple two-dimensional model. We use the form for the conduction and valence bands suggested by White and Lucovsky,[7]

$$E_k^{\pm} = \tfrac{1}{2}\{\Delta \pm [(\Delta - 2\epsilon_k)^2 + 4V^2]^{1/2}\} \;, \tag{18}$$

where $\epsilon_k = \hbar^2 k^2/2m^*$, Δ is the overlap between the conduction and the valence band in the uniform phase, and $2V$ is the energy gap appearing for $T < T_c$. We have assumed that both valence- and conduction-band masses are the same. If the impurity concentration is not too important, the Fermi energy is at zero because of the electron-hole symmetry. The corresponding paramagnetic susceptibility can be directly obtained from Eq. (18), considering a two-dimensional electron gas. It is

$$\chi_{\text{par}} = \frac{m^* \mu_B^2}{4\pi \hbar^2 k_B T C}\left[\int_{2V}^{\infty} \frac{E}{(E^2 - 4V^2)^{1/2}} \operatorname{sech}^2\left[\frac{E}{4k_B T}\right] dE + \int_{2V}^{(\Delta^2+4V^2)^{1/2}} \frac{E}{(E^2-4V^2)^{1/2}} \operatorname{sech}^2\left[\frac{E}{4k_B T}\right] dE\right] \;, \tag{19}$$

where C is the c-axis lattice constant and k_B is the Boltzmann constant. In the case of TiSe_2, it has been found that the magnitude of the distortion grows in amplitude in an approximately BCS-type fashion.[3,28] The energy gap $2V$ will thus have the same temperature dependence: $2V = 0$ for $T > T_c$ and a BCS law for $T < T_c$.

With Δ close to 0.1 eV, as suggested by Margaritondo *et al.*,[27] it is not possible by adjusting C_2 and $2V(0)$ to obtain a fit to the data below the transition with only this mechanism. The BCS energy-gap function saturates too early [$2V(0) \simeq 1500$ K; see below] to describe the still substantial temperature dependence in the velocity below 100 K. Even though the model is oversimplified, an electron-phonon mechanism cannot account for the temperature dependence of the velocity at the lowest T. We therefore conclude that below about 100 K the temperature dependence is a result of anharmonic effects only. The anharmonic contribution was again taken to have the form of Eq. (16). The parameters A and B were fitted using the experimental data for $T < 100$ K. For $A = 0.87 \times 10^{-6}\ \text{K}^{-2}$ and $B = 0$, the dashed line in Fig. 5 is obtained for TiSe_2. As shown in Fig. 5 the difference between the experimental data points and the anharmonic contribution (the dashed curve) in TiSe_2 can be accounted for by an electron-phonon contribution with the following parameters: $2V(0) = 0.13$ eV, $\Delta = 0.1$ eV, $T_c = 195$ K, and $C_2 m^* \mu_B^2 / 4\pi \hbar^2 C = 0.003\,72$. These parameters correspond to a value of the deformation potential equal to 1.38 eV if we let $m^* = m_e$, the free-electron mass, a value quite reasonable when compared to other layered compounds.[9] Fluctuations, which should be important for $T \lesssim T_c$, were not identified in our measurements. This is reasonable since for $T < T_c$ the finite value of the order parameter serves to damp these fluctuations.

VIII. MIXED COMPOUND $\text{TiS}_{0.5}\text{Se}_{1.5}$

For the mixed compound a phase transition is still observed but with a smoother behavior. The jump in $\Delta v/v$ extends from 110 to 150 K and is less pronounced than in TiSe_2. A larger low-temperature anharmonic contribution, as well as the electron-phonon coupling, are present in this sample while its high-temperature variation is close to that of TiS_2. The ultrasonic attenuation is important over 30 K (from 105 to 135 K) instead of 6 K for TiSe_2,

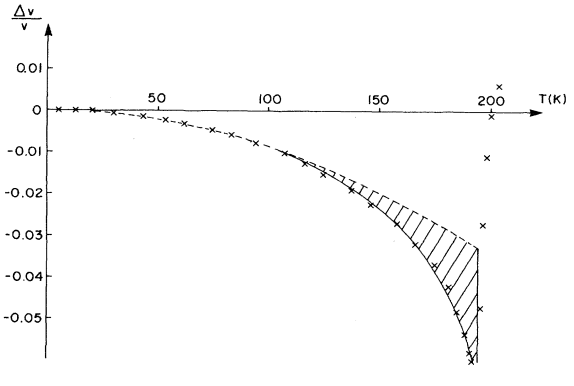

FIG. 5. Fitted curves of $\Delta v/v$ for TiSe_2. The experimental points as obtained from Fig. 1 are represented by ×'s. Dashed line is the best fit for an anharmonic contribution estimated for $T < 100$ K ($A = -0.87 \times 10^{-6}$ and $B = 0$). Solid line is the sum of the fitted anharmonic contribution (dashed line) and an electron-phonon contribution estimated with $2V(0) = 0.13$ eV, $\Delta = 0.1$ eV, $T_c = 195$ K, and $C_2 = 0.003\,72$. Shaded area represents the electron-phonon contribution.

indicating possibly a large critical region. Note that the maximum of attenuation (121.6 K) does not coincide with the maximum of $\Delta v/v$ (112 K). Our interpretation of this behavior is that stoichiometry inhomogeneities are present in the crystal which give rise to regions with different values of T_c. The resulting average response of a large number of such regions is thus measured, giving rise to wider structures in the ultrasonic measurements. This also explains the difference in the peak values of attenuation and sound velocity.

IX. CONCLUSION

We have measured the thermal expansion, as well as the velocity and attenuation of plate modes in TiS_2, $TiSe_2$, and a mixed compound. The a-axis expansion measurements on $TiSe_2$ show a decrease in the expansion coefficient at T_c on warming. This is opposite to the change reported by Wiegers[11] for the c-axis expansion coefficient. These changes predict via Ehrenfest-type relations, reasonable values for the average pressure dependence of T_c. Similar relations for the elastic modulus discontinuity at the transition are, however, inconsistent with the pressure data. The reason for this has been attributed to the importance of fluctuations for the elastic properties of $TiSe_2$ near T_c as well as to the effect on the acoustic-phonon branch of a new optical mode at the center of the reconstructed BZ.

From an analysis of the temperature dependence of the sound velocity in the selenium compounds, it appears that anharmonic effects and electron-phonon deformation-potential coupling for $T < T_c$ are needed to describe the temperature dependence of the velocity. The importance of fluctuations for $T > T_c$ has been argued to result from an effective reduced dimensionality of the correlated domains of the periodically distorted lattice. This conjecture could be verified by inelastic scattering experiments near T_c to measure the dispersion relations of the phonon modes near the soft-BZ phonon.

A simple model calculation for the electron-phonon deformation-potential coupling contribution showed that such a contribution is unimportant below 100 K but that a good fit to the data for $T < T_c$ can be achieved closer to T_c for reasonable values of the parameters in the model.

Finally, the importance of fluctuations of the periodically distorted lattice which are attributed to a reduced dimensionality of the lattice modes would argue in favor of a mechanism for the CDW transition which involves intrinsically the electron states since the $TiSe_2$ lattice by itself has a three-dimensional character while the electron states have a very anisotropic two-dimensional behavior. We have started a critical study of the different CDW models involving an electronic contribution, i.e., the Fermi-surface nesting model,[3,4] the excitonic insulator model,[5] and the band Jahn-Teller model[6] to indicate which of these would lead to anisotropic screening of the phonon modes at L. Unfortunately, it was not possible to totally discard the phonon-driven model.[7]

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[1] R. H. Friend, D. Jerome, and A. D. Yoffe, J. Phys. C 15, 2183 (1982).

[2] M. M. Traum, G. Margaritondo, N. V. Smith, J. E. Rowe, and F. J. DiSalvo, Phys. Rev. B 17, 1836 (1978).

[3] F. J. DiSalvo, D. E. Moncton, and U. V. Waszczak, Phys. Rev. B 14, 4321 (1976).

[4] K. C. Woo, F. C. Brown, W. L. McMillan, R. J. Miller, M. J. Schaffman, and M. P. Sears, Phys. Rev. B 14, 3242 (1976).

[5] J. A. Wilson and S. Mahajan, Commun. Phys. 2, 23 (1977).

[6] R. M. White and G. Lucovsky, Nuovo Cimento 38B, 280 (1977).

[7] J. A. Wilson, Phys. Status Solidi B 81, 11 (1978).

[8] A. M. Simpson, W. A. Roger, and M. H. Jericho, Rev. Sci. Instrum. 51, 32 (1980).

[9] M. H. Jericho, A. M. Simpson, and R. F. Frindt, Phys. Rev. B 22, 4907 (1980).

[10] O. Sezerman, A. M. Simpson, and M. H. Jericho, Solid State Commun. 36, 737 (1980).

[11] G. A. Wiegers, Physica 99B, 151 (1980).

[12] M. S. Wittingham and A. H. Thompson, J. Chem. Phys. 62, 1588 (1975).

[13] M. Barmatz, R. C. Farrow, and F. J. DiSalvo, IEEE Ultrasonics Symp. Proc. 1977, 378.

[14] L. R. Testardi, Phys. Rev. B 12, 3849 (1975).

[15] C. W. Garland, J. Chem. Phys. 41, 1005 (1964).

[16] R. A. Craven, F. J. DiSalvo, and F. S. L. Hsu, Solid State Commun. 25, 39 (1978).

[17] W. G. Stirling, B. Dorner, J. D. N. Cheeke, and J. Revelli, Solid State Commun. 18, 931 (1976).

[18] M. Barmatz, L. R. Testardi, and F. J. DiSalvo, Phys. Rev. 13, 4637 (1976); 12, 4367 (1975).

[19] N. Ogasawara, K. Nakamura, and S. Tanaka, Solid State Commun. 31, 873 (1979).

[20] R. F. S. Hearman, *Applied Anisotropic Elasticity* (Oxford University Press, Oxford, 1961).

[21] J. D. Axe and G. Shirane, Phys. Rev. B 1, 342 (1970).

[22] K. S. Aleksandrov, L. M. Reshchokova, and B. V. Beznosikv, Fiz. Tverd. Tela (Leningrad) 8, 3637 (1966) [Sov. Phys.—Solid State 8, 2904 (1967)].

[23] V. J. Minkiewicz, Y. Fujii, and Y. Yamada, J. Phys. Soc. Jpn. 28, 443 (1970).

[24] K. Gesi, J. D. Axe, G. Shirane, and A. Linz, Phys. Rev. B 5, 1933 (1972).

[25] P. B. Miller and J. D. Axe, Phys. Rev. 163, 924 (1967).

[26] E. Pytte, in *Structural Phase Transitions and Soft Modes*, edited by E. J. Samuelsen, E. Andersen, and J. Fedder (Universitetsforlaget, Oslo, 1971), pp. 151–169.

[27] G. Margaritondo, C. M. Bertoni, J. H. Weaver, F. Levy, N. T. Stoffel, and A. D. Katnami, Phys. Rev. B 23, 3765 (1981).

[28] J. A. Wilson, A. S. Barker, Jr., F. J. DiSalvo, Jr., and J. A. Ditzenberger, Phys. Rev. B 18, 2866 (1978).