Stress dependence of the charge-density-wave transitions in $NbSe_3$ and TaS_3

R. S. Lear, M. J. Skove, and E. P. Stillwell
Department of Physics and Astronomy, Clemson University, Clemson, South Carolina 29631

J. W. Brill
Department of Physics and Astronomy, University of Kentucky, Lexington, Kentucky 40506
(Received 24 October 1983)

We have measured the change in the charge-density-wave (CDW) transitions in monoclinic $NbSe_3$ and orthorhombic TaS_3 caused by stress applied along the high-symmetry (growth) axis. For the upper transition in $NbSe_3$, $dT_1/d\sigma = -4.4$ K/GPa for stresses up to 5 GPa, the increase in the resistance due to the transition, ΔR, is almost unaffected, and the critical field for motion of the CDW, E_c, increases with stress. For the lower transition in $NbSe_3$, $dT_2/d\sigma = -0.4$ K/GPa, ΔR more than doubles at 5 GPa, and E_c is relatively unaffected. The 222-K transition in TaS_3 decreases at a rate of -15 K/GPa for low stresses. At stresses above 2.5 GPa the resistance of TaS_3 begins to increase again, possibly due to a second stress-induced CDW transition. Both thermal hysteresis and stress hysteresis are seen in TaS_3 between about 100 and 200 K.

I. INTRODUCTION

The transition-metal trichalcogenides $NbSe_3$ and TaS_3 have interesting charge-density-wave (CDW) transitions in which all or part of the conduction electrons are condensed into a CDW state and the lattice undergoes a periodic displacement which has the same wavelength as the CDW, but which may or may not be commensurate with the lattice spacing. The electrons which are condensed into the CDW state do not contribute to the conductivity at low frequencies and low electric fields. For applied electric fields greater than a threshold E_c, the conductivity increases dramatically due to the depinning of the CDW from the lattice. For reviews of the transport properties of these materials see Refs. 1–3. The transitions show little or no hysteresis, and only weak anomalies in the specific heat and elastic constants.[4,5]

The pressure dependencies of these transitions have been studied in $NbSe_3$ by Chaussy *et al.*,[6] Briggs *et al.*,[7] and Richard and Monceau,[8] and in TaS_3 by Ido *et al.*[9] They find that both the incommensurate CDW transitions in $NbSe_3$ and the CDW transition in orthorhombic TaS_3 shift to lower temperatures (T) with pressure, and that the magnitude of the lower-T transition in $NbSe_3$ decreases with pressure until it disappears at 0.5 GPa. At the same pressure $NbSe_3$ becomes superconducting at about 2 K. Since all the transition-metal trichalcogenides are highly anisotropic, it is of interest to measure the stress dependence of these transitions also.

II. EXPERIMENTAL PROCEDURE

Samples were grown by placing stoichiometric amounts of the constituents in a quartz growth tube and sealing off the tube under vacuum. The growth tube was then kept at 1000 K for several weeks. Whiskers which were formed in this process were removed with tweezers and mounted on the four contacts of the stressing apparatus, which has been described elsewhere.[10] The stress is applied between the inner two (potential) contacts. Our samples were typically $1.5\times0.002\times0.002$ mm^3. Silver paint was used to make all four contacts, and proved to be strong enough mechanically for the tension applied to most samples. Occasionally a sample pulled through the silver paint at high stress. Because of this, an additional mechanical glue, such an epoxy or cyanoacrylic glue, was placed outside or between the two electrical contacts on either side. The stressing apparatus with the sample mounted on it was placed in a helium-filled cavity in a gas-flow cryostat whose temperature could be controlled between 4 and 300 K with a precision of ±0.1 K. Except during measurements of the critical electric field all sample currents were kept smaller than the current at which the resistance became non-Ohmic. The fiber samples were bowed with the puller mechanism to prevent breakage by thermal contraction during temperature changes. At each steady temperature the zero of strain was taken to be the position of the puller at which the first detectable change in the resistance of the sample occurred. The strain along the growth axis was measured and the uniaxial stress was calculated from this strain using the Young's moduli previously measured.[5] The stress could be applied reversibly at any temperature, but small thermal expansions made it difficult to vary the temperature at constant stress (other than zero stress).

III. RESULTS

Figure 1 shows a typical resistance-stress (R-σ) curve near the upper CDW transition in $NbSe_3$. These data are consistent with those of three other samples. From a set of such R-σ curves at different temperatures, Fig. 2, which shows R-T curves with σ as a parameter, was made. The transition (T_c) was taken to be the temperature at which the slope of the R-T curve was most negative. For $NbSe_3$ we denote the upper transition with a

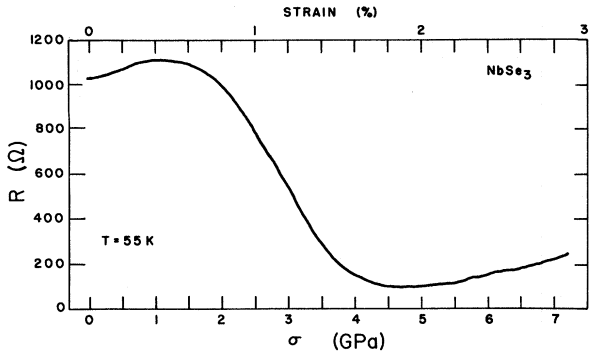

FIG. 1. Resistance of a $NbSe_3$ sample as a function of stress. The sample was 1.4 mm long and had a room-temperature resistance of 2.44 kΩ. The temperature was slightly below the lower CDW transition. The stress has moved the sample through the transition (which occurs at 57 K at zero stress) at 5 GPa and then the subsequent resistance increase is the "normal" state piezoresistance.

subscript 1 and the lower transition with a subscript 2. A plot of T_1 versus stress is shown in Fig. 3. From this plot we find $dT_1/d\sigma = -4.4 \pm 0.1$ K/GPa. The uncertainty in all our estimates does not include the systematic errors such as those due to nonuniform cross sections in the sample and to the uncertainty in Young's modulus. In comparison, dT_1/dP, the *pressure* derivative, is -40 K/GPa.[7]

Similar results for the lower transition in $NbSe_3$ are shown in Fig. 4. Note that T_2 is less dependent on stress, but the magnitude of the transition is greatly enhanced by stress, as may be seen in Fig. 2. We find $dT_2/d\sigma = (-0.4 \pm 0.2$ K/GPa$) + (-0.4 \pm 0.1$ K/GPa$^2)\sigma$. In comparison, $dT_2/dP = -63$ K/GPa.[7]

Figure 5 shows dV/dI versus E for $NbSe_3$ at a temperature below T_2. The electric field at which dV/dI starts to decrease is taken to be E_c, the critical field for depinning of the CDW. Figures 6 and 7 show E_c versus

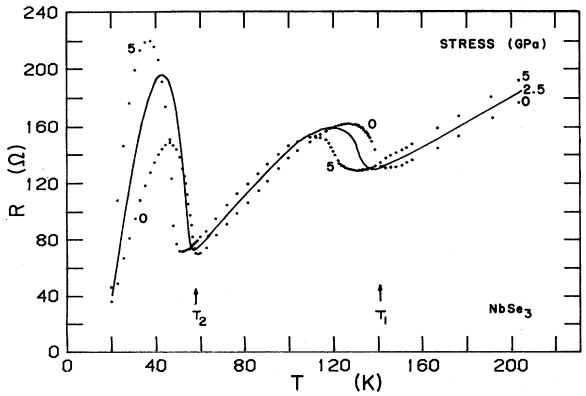

FIG. 2. Resistance of a $NbSe_3$ sample as a function of temperature with stress as a parameter. The sample was 1.5 mm long and had a resistance of 250 Ω at room temperature. The temperature at which the curves have their steepest negative slopes were taken to be T_1 and T_2.

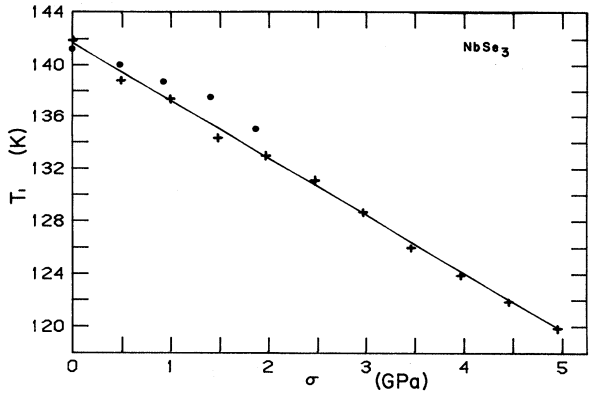

FIG. 3. T_1 as a function of stress. The transition shifts reversibly and linearly downward as the stress is increased. ● and + correspond to different samples.

T with σ as a parameter for $NbSe_3$ near the upper and lower CDW transitions. As is also the case for pressure,[8] E_c below T_2 is not strongly dependent on stress. E_c for the higher temperature CDW *is* quite stress dependent, so much so that we could not measure it at the highest stresses because heating occurred before the CDW depinned.

The CDW transition in orthorhombic TaS_3 leads to a semiconducting state rather than a new metallic state as in $NbSe_3$. Thus our results are best shown on a plot of $\ln(R)$ versus $1000/T$ with σ as a parameter, as in Fig. 8. Four other samples gave similar results. Taking the transition temperature for TaS_3, T_p, to be the temperature at the steepest slope on such a plot, Fig. 9 is obtained. From this plot we find $dT_p/d\sigma = -15.1$ K/GPa, comparable to the pressure derivative, $dT_p/dP = -13$ K/GPa.[9] It is also possible to estimate the activation energy W from the slope of the $\ln(R)$ versus $1000/T$ curve at temperatures below the transition region. Here we assume that $\ln(R) = A + W/kT$. Figure 10 shows W as a function of σ. We find $W = 72 \pm 5$ meV, and $dW/d\sigma = 12 \pm 2$ meV/GPa. The activation energy at zero stress is in reasonable agreement with that of Sambongi *et al.*,[11] 75

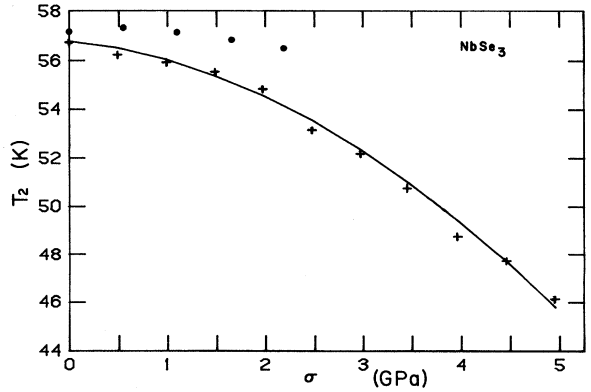

FIG. 4. T_2 as a function of stress. The transition shifts reversibly and quadratically downward as the stress is increased. ● and + correspond to different samples.

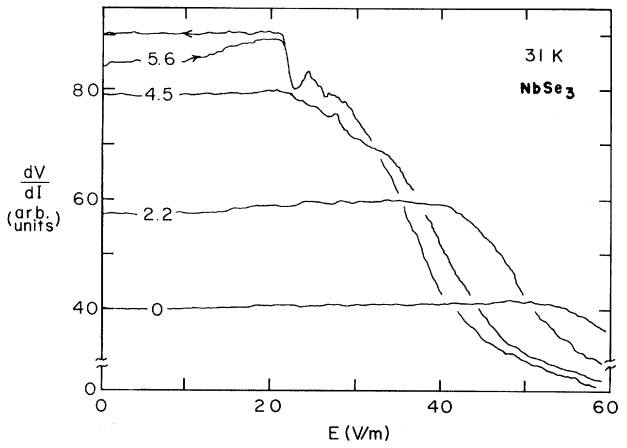

FIG. 5. Differential resistance dV/dI of the sample of Fig. 2 as a function of the electric field between the potential contacts, with stress in GPa as a parameter. The sample had a residual resistance ratio of 50. At 31 K, the resistance of the sample at stresses above ~ 3.0 GPa depends on the history of the sample. After stress is increased from zero dV/dI follows the lower curve. After a field $E > E_c$ is applied, dV/dI follows the upper curve.

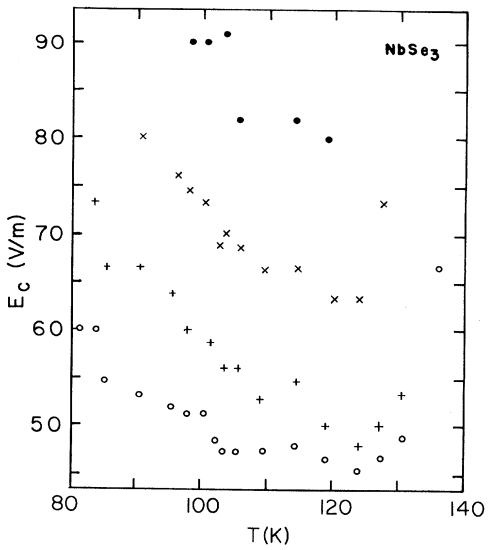

FIG. 7. Critical field of the sample of Fig. 2 as a function of temperature near the upper transition with stress as a parameter. o at zero stress, + 's at 1.1 GPa, ×'s at 2.2 GPa, and ● at 3.4 GPa. For stresses above 3.4 GPa the sample heated before the critical current was reached.

meV. Ido *et al.*[9] find the pressure derivative dW/dP is -3 meV/GPa. Note that the pressure and stress derivatives of W have opposite signs, in contrast to the pressure and stress derivatives of T_p, which have the same sign. We will return to this point later.

In TaS_3, for temperatures below T_p and above 190 K, the R-σ relation is similar to that shown in Fig. 11 at 198 K. There is a large reduction in R with σ, due to a reduction of T_p with stress to less than 198 K. After this initial reduction almost no further change in R occurs. As T is lowered further, an unexpected increase in the resistance shows up at high stress. Figure 11 shows the evolution of this stress-dependent resistance anomaly as the temperature is decreased. Finally, at a temperature around 70 K, the stress anomaly disappears. In a following paper, we plan to show that the behavior at higher currents, where the CDW is depinned, indicates that a second CDW transition may occur at high stress in this temperature region.

In the temperature range 70—190 K in which the anomalous stress dependence of R occurs, Higgs and Gill[12] found that the R-T curves were hysteretic. We find this to be true also. Furthermore, the resistance depends on the stressing history of the sample as shown in Fig. 12. Higgs and Gill also found that the resistance of the sample after a high-current pulse is neither that measured

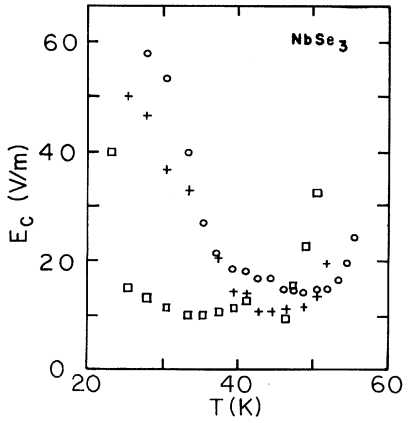

FIG. 6. Critical field of the sample of Fig. 2 as a function of temperature near the lower temperature transition with stress as a parameter. o at zero stress, + 's at 2.2 GPa, and □ at 4.5 GPa.

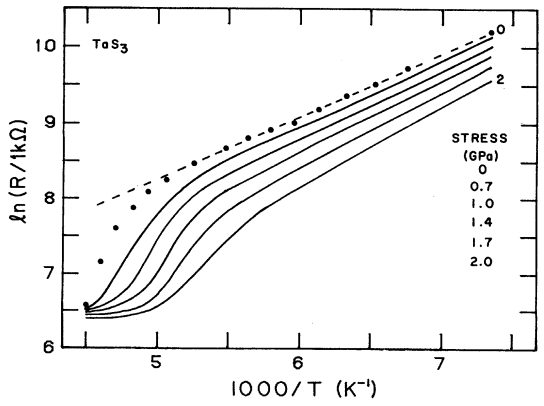

FIG. 8. Logarithm of the resistance of a TaS_3 sample as a function of the inverse temperature, with stress as a parameter. The sample was 1.6 mm long and had a room-temperature resistance of 625 Ω. The slope of the curve at a temperature well below T_p was taken as a measure of the activation energy. The temperature at which the curve has the steepest negative slope was taken to be T_p.

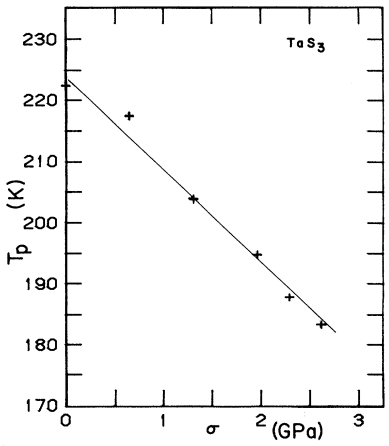

FIG. 9. T_p as a function of stress for the TaS_3 sample of Fig. 8. For these low stresses T_p decreases reversibly and linearly, with $dT_p/d\sigma = -15 \pm 1$ K/GPa.

with increasing T nor that measured with decreasing T, but approximately halfway between. We find the same behavior, but in addition a fourth resistance is measured after a stress application is made. This is illustrated in Fig. 13 which shows the stress dependence of two different states of the sample at a temperature below T_p. State A is obtained after a large current pulse and state B is obtained after the stress passes through 2 GPa. Stress changes that do not go through 2 GPa do not give the full hysteresis. One can go back and forth between these two states as many times as desired. Notice that at stresses beyond 2 GPa there is also hysteresis, both with current and with stress that passes through the "critical" stress of 2 GPa. Since we cannot vary the temperature at constant stress we do not know if temperature hysteresis exists in a sample with 2 GPa of applied stress.

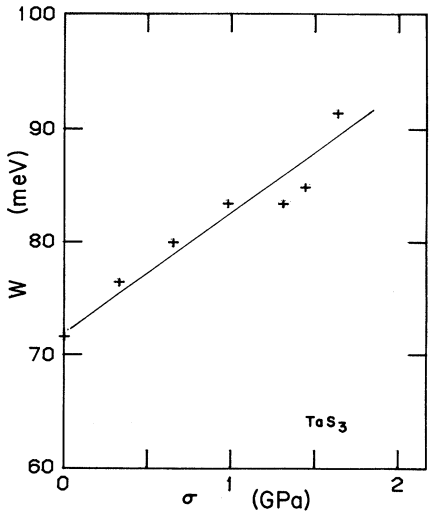

FIG. 10. Activation energy W for the TaS_3 sample of Fig. 8 as a function of stress. $dW/d\sigma = 12 \pm 1$ meV/GPa.

IV. DISCUSSION

The stress derivative $dT_c/d\sigma_i$ is thermodynamically related to anomalies in the specific heat C_p, the isothermal elastic compliance s_{ii}, and the thermal expansion α_i, measured at the transition. Since it is not known for sure what the orders of these transitions are, it is of interest to compare the anomalies in these response functions with our results. The measured anomalies in the response functions are not simple steps in their values so that the Ehrenfest relations for second-order transitions or those obtained for a Landau theory or under more general assumptions by Testardi[13] may not strictly hold. We will assume them nevertheless. These relations are

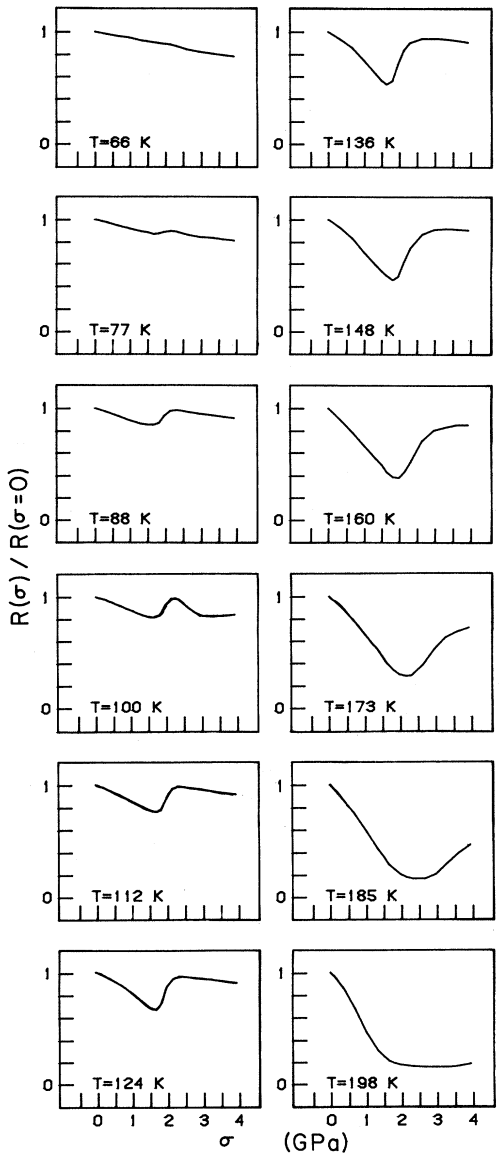

FIG. 11. Stress dependence of the resistance of the TaS_3 sample of Fig. 8 at various temperatures. The nonlinear "bump" on the curve is evident from 66 to 185 K, approximately the temperature range in which the resistance shows temperature hysteresis.

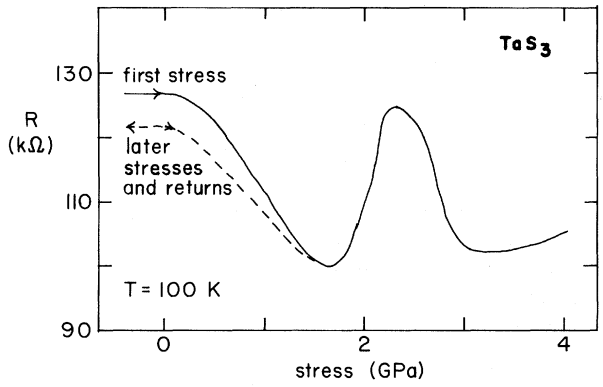

FIG. 12. Resistance of the sample of Fig. 8 as a function of stress showing the history-dependent behavior. The sample temperature was raised and allowed to equilibrate before the stress was applied. All data reported in this paper are for the behavior observed after applying and releasing the stress one time. When the temperature is raised, a stress pulse will reset the resistance to a new, lower value, which is not the same resistance as that after a large current is applied.

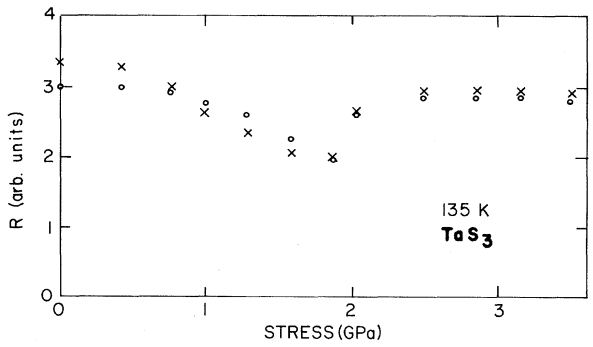

FIG. 13. Resistance as a function of stress for two states of a TaS_3 sample. The sample was 0.93 mm long and had a room-temperature resistance of 4.69 kΩ. The state denoted by + 's is the state of the sample after a large current was applied while the sample was at constant stress (state *A* of the text). The state of the sample denoted by ○ is the state of the sample after the stress was passed through 2 GPa, keeping the current well below that necessary to move the CDW (state *B* of the text).

$$\Delta C_p = \frac{\Delta s_{ii}}{T_c}\left[\frac{d(\ln T_c)}{d\sigma_i}\right]^{-2}, \tag{1}$$

$$\Delta \alpha_i = -\frac{\Delta s_{ii}}{T_c}\left[\frac{d(\ln T_c)}{d\sigma_i}\right]^{-1}. \tag{2}$$

Tomić *et al.*[4] have measured ΔC_p near the upper and lower CDW transitions in $NbSe_3$, and Brill[5] has measured Δs_{ii} [=1/(Young's modulus)] near all three transitions reported here. The values they obtained are shown in Table I.

The specific-heat anomalies observed in $NbSe_3$ are more than 4 times larger than those predicted from the elastic-constant anomalies and the stress derivative of T_c. The experimental uncertainties are large, particularly in the value of Young's modulus. Thus it may be that the Ehrenfest relations hold. It may also be that the transition is a continuous one rather than second order, so that the Ehrenfest relations are not applicable. The experimental anomalies in C_p and s_{ii} are difficult to measure. The experimental results of Brill and Tomić *et al.* do not exclude a jump in the response functions as would be seen at a second-order transition nor an exponential divergence as would be seen if the role of fluctuations were important and that transition continuous. If there is indeed an exponential divergence, the data do not allow even an estimate of the critical exponents of the response functions so that we cannot pursue this possibility further. Another explanation of the possible failure of the Ehrenfest relations is given by Caillé *et al.*[14] for $TiSe_2$. They propose that fluctuations in the lattice modes near the Brillouin-zone boundary affect the long-wavelength elastic properties more than the specific heat and thermal expansion, which measure averages over the entire phonon spectrum. This results in a larger critical region for the elastic constants than for the specific heat or thermal expansion and a failure of Eq. (1). Thermal-expansion measurements may clear the experimental situation sufficiently well to distinguish these possible explanations for the discrepancies shown in Table I.

It is interesting to note that both pressure and elastic stress, which would naively be expected to have opposite effects, lower the temperature of the CDW transitions in these materials. However, application of uniaxial stress,

TABLE I. Comparisons between response functions at CDW transitions.

		Measured			Predicted	
	T_c (K)	$\frac{d(\ln T_c)}{d\sigma}$ (GPa^{-1})	Δs_{ii}[a] (GPa^{-1})	ΔC_p[b] (J/m^3K)	ΔC_p (J/m^3K)	$\Delta \alpha_i$ (K^{-1})
TaS_3	222	-7×10^{-2}	5.7×10^{-5}		5.2×10^{4}	4×10^{-6}
$NbSe_3$						
upper transition	141	-3.1×10^{-2}	2.2×10^{-6}	7.3×10^{4}	1.6×10^{4}	5×10^{-7}
lower transition	57	-7×10^{-3}	$<1\times10^{-7}$	1.6×10^{4}	$<3.6\times10^{4}$	$<2\times10^{-7}$

[a]Reference 5.
[b]Reference 4.

like pressure, causes a contraction transverse to the direction of the "whisker" (chain) axis of these materials. This contraction apparently predominates in affecting the transition temperatures. It is possible to estimate an "average" Poisson ratio ν for $NbSe_3$ using the isothermal compressibility K_b along the chain axis measured by Yamaya *et al.*[15] and the Young's modulus E_b along the chain direction measured by Brill,[5] all measured at room temperature. This average gives the sum of the strains in two directions perpendicular to the whisker direction divided by 2 as a fraction of the strain along the whisker axis:

$$\nu = -(s_{21}+s_{23})/(2s_{22}) = (1-E_bK_b)/2 \sim 0.34 .$$

This is indeed a normal value for a Poisson ratio, and indicates that in $NbSe_3$ there is significant transverse contraction under uniaxial stress. It is also possible to compare the transverse contraction due to 1 GPa of stress to that due to 1 GPa of pressure, again using the results of Yamaya *et al.*:[15]

$$(\epsilon_1+\epsilon_3)_p/(\epsilon_1+\epsilon_3)_\sigma = (K_a+K_c)E_b/2\nu \simeq 7.3 .$$

Therefore, if all the stress dependencies of T_1 and T_2 were due to the Poisson contraction, we would expect $(dT/dP)/(dT/d\sigma) \sim 7.3$ (assuming isotropy in the a-c plane). This is in rough agreement with the ratio observed for T_1 (9.1), but much less than that for T_2 (160). This indicates that the lower transition is much more sensitive to longitudinal strain ϵ_2 than is the upper transition. The nearly perfect cancellation of the increase in T_2 due to longitudinal expansion with the decrease due to Poisson contraction is remarkable and allows the quadratic dependence of T_2 on stress to be clearly evident at higher stresses. The much stronger ϵ_2 dependence of the lower transition is also reflected in the increase in the magnitude of the resistance anomaly which *decreases* under pressure.

This increase in the resistance anomaly implies that the number of electrons condensed into the CDW state increases under strain. If we let $\alpha = (R_L - R_H)/R_L$, where R_H is the resistance at high electric field and R_L is the resistance at low electric field, then α is a measure of the number of electrons condensed into the CDW state, ρ_e. We see from Fig. 2 that α is increased by a factor of 2 by 5 GPa stress below T_2, but that α near T_1 is essentially unaffected by stress. On the other hand, $\Delta T_1/T_1 \simeq \Delta T_2/T_2 \simeq 0.15$ at 5 GPa. If we suppose that the CDW gap Δ is proportional to the transition temperature, then the fractional change of both Δ_1 and Δ_2 at 5 GPa is about 0.15. In the Lee-Rice model,[16] the threshold field is given by

$$E_c = BC\Delta/\rho_e \quad \text{(strong pinning)} ,$$

$$E_c = AV^4C^2/(t^6\rho_e) \quad \text{(weak pinning)} ,$$

where A and B are proportionality constants, C the concentration of pinning sites, V the pinning potential, and $t = (T_c - T)/T_c$. Thus in the Lee-Rice theory our results predict that E_{c2} should be lowered by $\sim 60\%$ (strong pinning) or $\sim 50\%$ (weak pinning), whereas we find E_{c2} lowered by $\sim 30\%$. At the upper transition E_{c1} *increases* by nearly a factor of 2, while ρ_e is nearly constant and Δ decreases, in qualitative disagreement with the Lee-Rice theory for either weak or strong pinning. In the quantum theory E_c depends on the gap introduced in the quasiparticle energy spectrum by pinning centers and on the coherence length of the CDW.[17] Neither of these has an obvious dependence on stress.

For TaS_3 we find $dT_p/d\sigma \sim dT_p/dP$,[9] suggesting that either the transverse compressibilities are much less than for $NbSe_3$ or the average Poisson ratio is much greater. It is very surprising that the activation energy W increases with uniaxial stress while T_p decreases. Ido *et al.*[9] found that W/T_p was independent of pressure; its independence of stress and pressure is expected if the transition is described by either mean-field theory or by three-dimensional ordering of fluctuating CDW's, as described by Lee, Rice, and Anderson,[18] assuming that $W = \Delta/2$. If the activation energy were that of defect states, its variation under pressure or stress need not be proportional to that of T_p. Recently Higgs and Gill[12] have proposed that the activated behavior of the resistivity is due to a temperature-dependent concentration of discommensurations, and not due to thermal excitations of carriers. The discommensurations would depend very differently on stress and pressure, a result which is consistent with our results.

ACKNOWLEDGMENTS

We are pleased to acknowledge helpful discussions with N. P. Ong and J. C. Gill. The research at Clemson University was supported in part by National Science Foundation Grant No. DMR 80-08351 and the research at the University of Kentucky by the Research Corporation.

[1] G. Grüner, Comments Solid State Phys. 10, 183 (1983).
[2] N. P. Ong, Can. J. Phys. 60, 757 (1982).
[3] P. Monceau, Physica 109, 1890 (1982).
[4] S. Tomić, K. Biljaković, D. Djurek, J. R. Cooper, P. Monceau, and A. Meerschaut, Solid State Commun. 38, 109 (1981).
[5] J. W. Brill, Mol. Cryst. Liq. Cryst. 81, 107 (1982).
[6] J. Chaussy, P. Haen, J. C. Lasjaunias, P. Monceau, G. Waysand, A. Waintal, A. Meerschaut, P. Molinié, and J. Rouxel, Solid State Commun. 20, 759 (1976).
[7] A. Briggs, P. Monceau, M. Nunez-Regueiro, J. Peyard, M. Ribault, and J. Richard, J. Phys. C 13, 2117 (1980).
[8] J. Richard and P. Monceau, Solid State Commun. 33, 635 (1980).
[9] M. Ido, K. Tsutsumi, T. Sambongi, and N. Môri, Solid State Commun. 29, 399 (1979).
[10] J. W. Cook, Jr., W. T. Davis, J. H. Chandler, and M. J. Skove, Phys. Rev. B 15, 1357 (1977).
[11] T. Sambongi, K. Tsutsumi, Y. Shiozaki, M. Yamamoto,

K. Yamaya, and Y. Abe, Solid State Commun. 22, 729 (1977).
[12]A. W. Higgs and J. C. Gill, Solid State Commun. 47, 737 (1983).
[13]L. R. Testardi, Phys. Rev. B 12, 3849 (1975).
[14]A. Caillé, Y. Lepine, M. H. Jericho, and A. M. Simpson, Phys. Rev. B 28, 5454 (1983).
[15]K. Yamaya and G. Oomi, J. Phys. Soc. Jpn. 52, 1886 (1983).
[16]P. A. Lee and T. M. Rice, Phys. Rev. B 19, 3970 (1979).
[17]J. Bardeen, Mol. Cryst. Liq. Cryst. 81, 1 (1982).
[18]P. A. Lee, T. M. Rice, and P. W. Anderson, Phys. Rev. Lett. 31, 462 (1973).