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ELASTIC ANOMALIES AT CHARGE DENSITY WAVE TRANSITIONS IN TaS_3 AND $NbSe_3$*

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The temperature dependence of the Young's modulus and internal friction of TaS_3 (orthorhombic) and $NbSe_3$ have been measured by the vibrating reed technique. There is a large minimum 2%, in the modulus of TaS_3 at the commensurate Peierls distortion (T_c = 222K) and the internal friction increases below T_c ($\Delta Q^{-1} \approx 5 \times 10^{-5}$), although no critical relaxation effects are observed. On the other hand, a very small minimum, $\Delta E/E \sim 0.06\%$, is observed at the upper incommensurate transition in $NbSe_3$, and a small broad increase (0.03%) at the lower transition. The measurements allow estimates to be made of the stress dependence of the transition temperature and of the electron-phonon coupling constant.

INTRODUCTION

Vibrating reed techniques provide a means of measuring elasticity (Young's modulus) and damping in crystals too small for more conventional acoustic measurements. Using the vibrating reed technique, elastic anomalies have been observed at the charge density wave (CDW) transitions in TTF-TCNQ[1], $NbSe_2$ and $TaSe_2$[2], and $NbSe_3$[3]. In the case of $TaSe_2$ and $NbSe_2$, the observed elastic and damping anomalies shed much light on the thermodynamics of their phase transitions[2,4] and the presence of discommensurations in the CDW phase.[5]

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In view of the recent high precision results of Tomic et al.[6] on the specific heat anomalies at the two incommensurate CDW transitions (at T_1=141 K and T_2=58 K) in $NbSe_3$, we have reexamined its Young's modulus with greater sensitivity than previously attained.[3] We have also measured the Young's modulus and internal friction in orthorhombic TaS_3, which undergoes a commensurate CDW transition at T_c=222 K.

THEORY

Elastic anomalies at structural phase transitions have been discussed in detail by Testardi[7,8] and Rehwald.[9] At a second order transition, the Young's modulus has an anomaly given by[8]:

$$\Delta E_i/E_i = -(E_i \Delta C_p/T_c)(\partial T_c/\partial \sigma_i)^2 \quad (1)$$

and $$\Delta E_i/E_i = E_i(\partial T_c/\partial \sigma_i)\Delta \alpha_i, \quad (2)$$

where E_i is the Young's modulus (in the i^{th} direction), σ_i is the i^{th} component of longitudinal stress, α_i is the i^{th} component of expansivity, C_p is the specific heat, and T_c is the transition temperature. Also, if the transition temperature can be expanded as a power series in stress, it can be shown that[7†]

$$\Delta(d\ell nE_i/dT) = -E_i\left[\frac{\Delta C_p}{T_c}\frac{\partial^2 T_c}{\partial \sigma_i^2} + \frac{2\Delta C_p}{T_c^2}(\partial T_c/\partial \sigma_i)^2\right] \quad (3)$$

As there is generally a specific heat maximum at the transition, Eq. (1) predicts a minimum in modulus for nonzero $\partial T_c/\partial \sigma_i$. On the other hand, a minimum in modulus implies, in a Landau expansion of the Gibbs free energy at T_c, the linear coupling of stress to the order parameter[9†], which is symmetry forbidden if the wave vector of the transition $q \neq 0$. Therefore a minimum in the modulus at a second order CDW transition, i.e. finite stress dependence of T_c, implies the breakdown of Landau theory.

It is also expected that the modulus increase below

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†References 7 and 9 discuss changes in the elastic constants, c_{ij} at phase transitions through consideration of the Helmholtz free energy $F(T,\varepsilon_{ij})$, where ε is the strain. Analogous results for the compliances, S_{ij}, can be found from consideration of the Gibbs function, $G(T,\sigma_{ij})$. The Young's modulus $E_i = 1/S_{ii}$.

a CDW transition because the opening of the gaps at the Fermi surface will reduce the electronic screening of acoustic phonons. The screened phonon frequency is given by:[10]

$$\omega^2(\vec{q}) = \omega_o^2(\vec{q})\{1-[g^2(\vec{q})\chi(\vec{q})/\hbar\omega_o(\vec{q})]\} \quad (4)$$

where $\omega_o(\vec{q})$ is the unscreened phonon frequency, $g(\vec{q})$ is the electron-phonon coupling constant, and $\chi(\vec{q})$ is the susceptibility. In the long wavelength limit, this becomes[11]

$$\omega^2(0) = \omega_o^2(0)\{1-[g^2(0)N(\varepsilon_F)/\hbar\omega_o(0)]\}=\omega_o^2(0)[1-\lambda(0)] \quad (5)$$

where $\lambda(0)$ is the usual dimensionless electron-phonon coupling constant (at q=0) and $N(\varepsilon_F)$ is the density of states. Tiedje pointed out that consequently the modulus should increase as the density of states decreases at a CDW transition:[11]

$$\Delta E/E = \Delta\omega^2(0)/\omega_o^2(0) = -\lambda(0)\Delta N(\varepsilon_F)/N(\varepsilon_F) \quad (6)$$

Such an enhancement has been observed in $TaSe_2$[2] and TTF-TCNQ[1]. In the latter, large q=0 electron-phonon coupling has been interpreted as being due to stress dependent charge transfer between TTF and TCNQ bands.[1]

EXPERIMENTAL

Single crystals of $NbSe_3$ and orthorhombic TaS_3 of typical dimensions 3μm x 15μm x 2mm were mounted as cantilevers by glueing one end to a copper rod with silver paint. The free end was placed between two electrodes which respectively excited and detected flexural resonances in the crystals through capacitive coupling. The apparatus and electronics are described in detail elsewhere.[12] The resonating crystal acts as amplifier and phase shifter in a phase-lock-loop, allowing its frequency, proportional to the square root of the modulus along the chains, to be measured continuously as a function of temperature. The internal friction, Q^{-1}, was found by measuring the width of the resonance by introducing phase shifts into the loop.

The resonant frequencies of a cantilevered reed of rectangular cross-section undergoing flexural vibration are given by:[13]

$$f_n = a_n t/\ell^2 \sqrt{E/\rho} \quad (7)$$

where t is the thickness, ℓ the length, and ρ the mass density. The a_n are constants: 0.1614, 1.012, 2.834,.... For all crystals discussed here, with one exception (see below), only the fundamental was measured. As very small changes in frequency (1 mHz) were detectable, very precise measurements ($\Delta E/E \sim 10^{-5}$) in the relative change in modulus were possible. However, because of the thinness and imperfect morphologies of the crystals, it is likely that flexural vibrations were accompanied by twisting, so the effective modulus measured may include significant (and temperature dependent) contributions from the shear modulus. Determination of the thickness of a few samples with a SEM give values of $E=(2.5\pm.5)\times 10^{12}$ dynes/cm^2 for $NbSe_3$ and $E=(3.5\pm.5)\times 10^{12}$ dynes/cm^2 for TaS_3, values comparable to those of tungsten!

RESULTS AND DISCUSSION

A. TaS_3

The temperature dependence of the modulus for two samples of TaS_3 are shown in Figure 1. The differences for the two crystals is probably due to twisting of the reeds; an overtone observed for sample #1 at a frequency 6.54 times that of the fundamental, in surprisingly good agreement with the expected frequency ratio (6.27), suggests that these modes occur with little twisting.

The anomaly is very wide, with downward curvature of the modulus observable to room temperature, consistent with electron diffraction results showing precursor Peierls fluctuations on independent chains locking in at the transition.[14] In addition to the large minimum, the low temperature modulus appears enhanced over the extrapolated high temperature behavior, although the large breadth of the transition makes meaningful extrapolation impossible.

The magnitude of the specific heat anomaly can be estimated from Eq. (1). Ido et al.[15] have measured the pressure dependence of T_c, $\partial T_c/\partial p = -\sum_{i=1}^{3} \partial T_c/\partial \sigma_i = -1.3$ K/kbar, and from measurements of the pressure dependence of the CDW gap, concluded that interchain coupling has a weak effect of the pinning of the CDW. We therefore assume $-\partial T_c/\partial p \sim \partial T_c/\partial \sigma_{//} \sim 1$K/kbar, where $\sigma_{//}$ is the longitudinal stress along the chains, and take $\Delta E/E \sim 2\%$. We find: $\Delta C_p \sim 0.65$ R and $\Delta\alpha \sim -5 \times 10^{-6}$ K^{-1}. These results, of course depend strongly on the choice of $\partial T_c/\partial \sigma_{//}$.

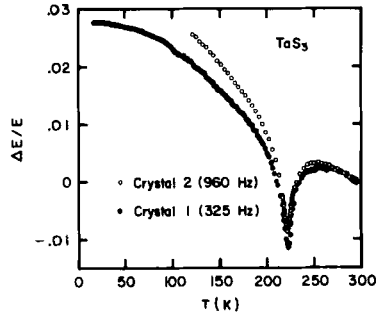

FIGURE 1 Relative change in Young's modulus (from room temperature) vs. temperature for orthorhombic TaS_3.

However the above value of C_p is a reasonable estimate of the specific heat anomaly, assuming that it is predominantly electronic in origin; for example, it is comparable to those observed in $NbSe_3$.[6] Therefore a much smaller parallel stress dependence of T_c would imply a non-negligible phonon contribution to ΔC_p.

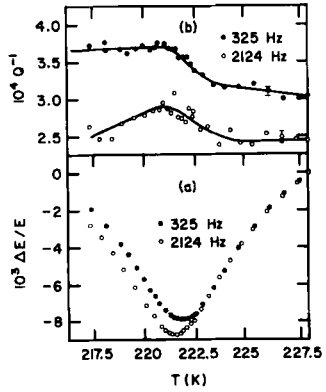

FIGURE 2 a) Change in Young's modulus (normalized at 227K) vs. temperature for TaS_3 crystal #1, as determined from the fundamental (325 Hz) and first overtone (2124 Hz).

b) Internal friction vs. temperature for the two modes. Lines are guide to eye.

The modulus and damping near the transition, for both fundamental and overtone of crystal #1, are shown in Figure 2. These data were taken with temperatures stabilized to < 30 mK; no hysteresis was observed ($\Delta T < 0.1K$). The modulus minima occured at 221.8 K and 221.5 K for the two modes, slightly above the reported temperature of the peak in dlnR/dT.[15] (For crystal #2, the modulus minimum was at 221.5 K and no enhanced damping ($\Delta Q^{-1} < 3 \times 10^{-5}$) was observed). Although there is an increase in internal friction below T_c (for crystal #1), no sharp relaxation peak (i.e. no critical damping) was observed. The large size of the modulus minimum, mode dependence of the temperature of the minimum, and the long tail in the damping into the low temperature state have previously been observed at the first order lock-in transition in $TaSe_2$[2]. The sample dependence of the friction and its rapid growth (for sample #1) at 224 K suggest that it is due to the growth and motion of domain walls under the applied stress. The pinning of the domains increases below T_c, and the internal friction decreases as the damping rate falls below the resonant frequency. These result are discussed in detail in reference 12.

B. $NbSe_3$

The modulus vs. temperature for three crystals of $NbSe_3$ is shown in Figure 3. Again, the differences between these

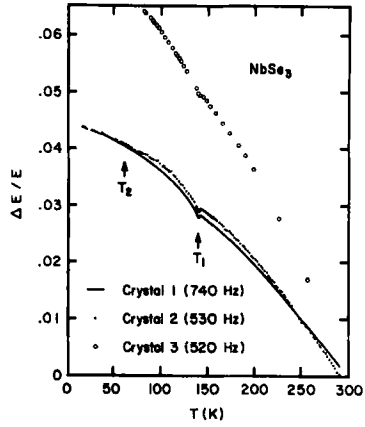

FIGURE 3 Relative change in Young's modulus (from room temperature) vs. temperature for $NbSe_3$.

samples, as well as those of reference 3, are probably due to twisting; of the several samples, #1 and #2 had the best morphologies and clamps and the data for them is considered most reliable.

The most striking feature in the data is the extremely small size of the anomalies (see Figures 4 and 5), as compared to TaS_3. This might seem reasonable, as the amplitude of the lattice distortion is expected to be less for incommensurate transitions than for commensurate, so the stress dependence of T_c due to the anharmonic coupling of the soft mode to the q=0 acoustic phonon would be less, but this interpretation of the results is confused by the fact that the pressure dependences of the transition temperatures are greater in $NbSe_3$[16] ($\partial T_1/\partial p = \partial T_2/\partial p = -4$K/kbar) than in TaS_3!

In the analysis of the data given below, we assume the transitions to be second order, and use the specific heat results of Tomic et al.[6]. It should be mentioned that other researchers[17] have not observed anomalies comparable to those of Tomic, who also observed hysteresis and latent heat at the transitions. If in fact the transitions are first order, Eq. (1-3) do not rigorously apply, although they may be expected to hold approximately if the first order character is small.

Results for the two samples near T_1 are shown in Figure 4. The modulus minimum occurs at 141.1 K, in good agreement with other measurements,[18] with no observable hysteresis ($\Delta T < 0.1$K). The anomalies for three samples, as determined by extrapolating the high temperature dependence, varied from $\Delta E/E = 4 \times 10^{-4}$ to 7×10^{-4}, slightly smaller than those reported previously.[3] There is also an increase in slope on cooling through T_1 which varied from $d\ln E/dT = 8.8 \times 10^{-5}$ K^{-1} to 10.4×10^{-5} K^{-1}. No anomaly in friction was observed ($\Delta Q^{-1} < 5 \times 10^{-6}$). Taking $\Delta C_p = .45R$,[6] we calculate: $|\partial T_1/\partial \sigma_{//}| \sim 0.2$ K/kbar, $|\Delta \alpha_{//}| \sim 1 \times 10^{-6}$K^{-1}, and $\partial^2 T_1/\partial \sigma_{//}^2 \sim -7 \times 10^{-3}$ K/kbar^2.

Results for four samples at T_2 are shown in Figure 5. No minimum ($\Delta E/E < 3 \times 10^{-5}$) or anomaly in friction ($\Delta Q^{-1} < 2 \times 10^{-5}$) was observed for any sample. There is a small sample dependent increase in slope below 60 K, $\Delta d\ln E/dT = (2.6 \pm 1.2) \times 10^{-5}$ K^{-1}. Using the result[6] $\Delta C_p = 0.1$ R, we find: $|\partial T_2/\partial \sigma_{//}| < .07$ K/kbar, $|\Delta \alpha_{//}| < 2 \times 10^{-7}$ K^{-1}, and $\partial^2 T_2/\partial \sigma_{//}^2 \sim -4 \times 10^{-3}$ K/kbar^2.

The stress dependences of both transition temperatures are much less than the pressure dependences, implying that $|\partial T_1/\partial \sigma_{\perp}| \sim 10|\partial T_1/\partial \sigma_{//}|$ and $|\partial T_2/\partial \sigma_{\perp}| > 30|\partial T_2/\partial \sigma_{//}|$, and that the transitions depend most strongly on interchain

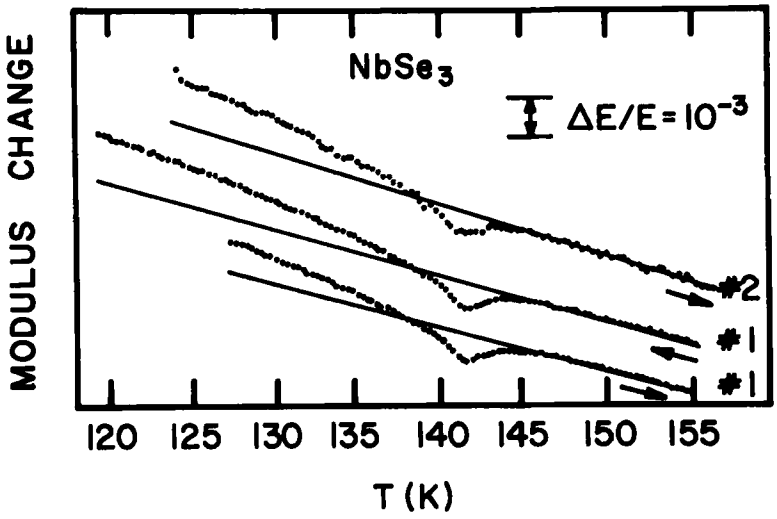

FIGURE 4 Change in Young's modulus vs. temperature of $NbSe_3$ near T_1. Vertical displacement is arbitrary. Arrows denote direction of temperature change. ($|dT/dt|<0.5K/min.$) Solid lines are extrapolation of pretransition behavior.

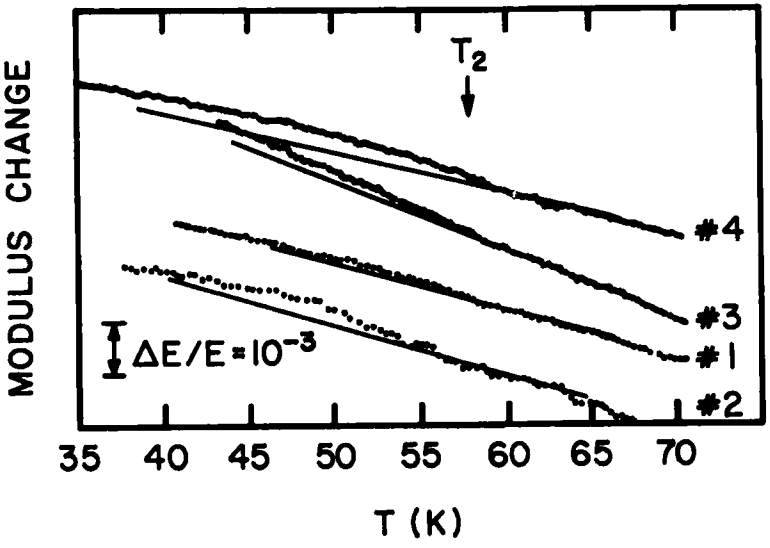

FIGURE 5 Change in Young's modulus vs. temperature of $NbSe_3$ near T_2. Vertical displacements are arbitrary. Solid lines are extrapolation of pretransition behavior.

coupling. While a non-negligible transverse stress dependence is expected in view of the three-dimensionality of the Fermi surface, in contrast to TaS_3, the smallness of $\partial T_c/\partial\sigma_{//}$ and consequent relative weak dependence of T_c's on interchain bonding is surprising. (The strain dependence of T_c, $\partial T_c/\partial\varepsilon$, will be somewhat more isotropic than $\partial T_c/\partial\sigma$ if the Young's modulus is anisotropic, as expected.) In view of the earlier caveats, there are two possible alternative explanations of the small elastic anomalies to large anisotropies in $\partial T_c/\partial\sigma$. Firstly, the transitions may have sufficient first order quality so that Eqs. (1-3) do not even hold approximately. Secondly, the results of Tomic et al. may overestimate the specific heat anomalies.

Finally we discuss the electron-phonon coupling at the transitions. The increase in slope below T_1 is probably not due to reduced electron screening, as the increase in modulus has not saturated 20K below the transition. On the other hand, the increase in modulus below T_2 does appear to saturate within a few degrees and may be due to the condensation of electrons. The average value for the four samples is $\Delta E/E = 3 \times 10^{-4}$; assuming that 30% of the electrons condense at T_2, we find $\lambda(0) = 10^{-3}$. This small value for the electron-phonon coupling constant implies that the condensing band is very narrow. For a single band[11] $\lambda/N(\varepsilon_F) \sim \beta^2/E$, where β is the bandwidth. Taking $N(\varepsilon_F) \sim 1$ state/eV-Nb atom,[6] we find $\beta \sim 0.4$ eV. Such a small bandwidth has been calculated for the niobium $d_{x^2-y^2}$ bands thought to contain most of the states at the Fermi surface.[19]

In summary, the very small anomalies observed in the Young's modulus of $NbSe_3$ imply very anisotropic stress dependence of T_1 and T_2 and the overwhelming influence of interchain bonds on the Fermi surface. In TaS_3, a much larger anomaly is observed, consistent with the one-dimensional character of the material. The increase in internal friction below the transition may be due to the hysteretic motion of domain walls.

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