Effects of charge-density-wave depinning on the elastic properties of orthorhombic TaS_3

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(Received 9 December 1985)

The results of various vibrating-reed experiments on orthorhombic TaS_3 are presented. It is found that when electric fields greater than the threshold ($\mathscr{E}_T$) for charge-density-wave (CDW) depinning are applied, Young's modulus (E) decreases slowly saturating at $-\Delta E/E \sim 1\%$ for $\mathscr{E} \sim 10\mathscr{E}_T$. This saturation is surprisingly abrupt. At much lower fields, the modulus varies as the square root of the CDW velocity, and it is suggested that velocity fluctuations may cause the anomalies. The internal friction increases very rapidly above threshold, reaching a maximum for $\mathscr{E} < 2\mathscr{E}_T$, and then slowly decreases. The results are discussed from the point of view of an anelastic relaxation model, and also compared to other models which have been suggested.

I. INTRODUCTION

Orthorhombic TaS_3 (o-TaS_3) is one of a handful of quasi-one-dimensional charge-density-wave (CDW) conductors in which the CDW can be depinned from the lattice by the application of a small electric field.[1,2] The CDW is depinned for fields greater than a threshold field $\mathscr{E}_T$ (Ref. 2), leading to a rapid increase of conductivity, with field and a number of other anomalous electronic properties, which have been recently extensively reviewed by Grüner and Zettl[3] and Monceau.[4] For low fields $\mathscr{E} < \mathscr{E}_T$, the CDW is believed to be pinned by random impurities; due to the elastic stiffness of the CDW, its phase will be constant over large lengths, L_0, where the Lee-Rice coherence length L_0 is inversely proportional to the impurity concentration.[5] (For pure samples, $L_0 > 10$ μm.[3,4])

Among the different models of CDW depinning are those which treat the CDW as a classical deformable wave.[5-7] Such models predict that for $\mathscr{E} < \mathscr{E}_T$, the sample can find itself in metastable states corresponding to different configurations of Lee-Rice domains; application of a field above threshold allows the sample to equilibrate.[8,9] Many experiments have observed such metastability, manifested as hysteresis in the resistivity as a function of temperature,[10-12] electric field,[12,13] or stress.[14]

We recently reported that elastic properties of o-TaS_3 also were very anomalous for fields $\mathscr{E} > \mathscr{E}_T$.[15] Because samples are very thin (~ 3 μm), a vibrating-reed technique was used to excite flexural resonances and measure the Young's modulus (E) and internal friction (δ); it was reported that the internal friction rapidly increased above threshold ($\Delta\delta \sim 10^{-3}$–$10^{-2}$) and the modulus slowly decreased ($\Delta E/E \sim 10^{-2}$) as a function of field. Similar results for a few CDW conductors were independently reported by Mozurkewich *et al.*[16] and recently confirmed by Bourne *et al.*[17] (Also, Raman scattering measurements indicating a decrease in optical-mode frequencies for $\mathscr{E} > \mathscr{E}_T$ have since been reported.[18]) At the time, there were no models addressing the effect of CDW depinning on the elastic properties. It was suggested that the relaxation of domains (e.g., Lee-Rice phase coherent domains or velocity coherent domains)[15] or the coupling of the phonon to phasons[16] might be responsible for the observed effects.

In this paper, we discuss in detail our experimental technique, earlier results,[15,19] and subsequent measurements. We also briefly compare our results with the predictions of recent models which have been proposed. Our results, as well as those of Ref. 17, strongly suggest that CDW velocity incoherence, permitted by the internal degrees of freedom of the CDW, greatly affects the elastic properties.

II. THEORY

The first discussion of the effects of CDW depinning on the elastic properties was by Coppersmith and Varma (CV).[20] They considered the effects of a rigidly translating CDW (i.e., for fields well above threshold) on the dynamical matrix to evaluate changes in the acoustic-phonon velocity c. They found that the phonon would be Doppler shifted by the CDW drifting with average velocity v; $\Delta c/c \sim 0.01(v/c) \sim 10^{-6}$, much smaller than the observed change in modulus. (Furthermore, since in the vibrating-reed experiments standing waves are excited, only second-order Doppler shifts would be observed, making the agreement even poorer.) However, direct comparison with experiment is complicated by the fact that, experimentally, flexural oscillations are excited and the flexural velocity (c') is much less than the bulk phonon velocity; $c' \sim (qs)c \sim 10^{-3}c$, where q is the distortion wave vector and s the sample thickness.[21] Therefore, it was not clear how the CV results would be modified for flexural waves. Lehman considered the latter and showed that changes in the flexural velocity were much less than in the bulk velocity, $\Delta c'/c' \sim (qs)(\Delta c/c)$, so that the observed changes in the Young's modulus could not be caused by rigid translation of the CDW.[21]

On the other hand, Mozurkewich *et al.*[22] pointed out that when pinned the elastic constant of the CDW (K) will add to that of the lattice (E), so that the effective modulus $E'_{pin} = E + K$, while when depinned, strains in the lattice might not distort the CDW, so that $E'_{depin} = E$.

Since $K/E \sim 1\%$ (Ref. 15) (see below) decreases in the modulus comparable to the observed changes might be expected. If the CDW is depinned smoothly and abruptly (as a function of electric field), the modulus should also decrease abruptly, in contradiction to observations. However, near threshold the motion of the CDW is "jerky," effectively governed by "slip-stick" friction.[23] The effective modulus should then be given by the weighted average of the pinned and depinned moduli:

$$E' = (1-f)E'_{\text{pin}} + fE'_{\text{depin}} , \tag{1}$$

where f is the fraction of time the CDW is depinned. Both the total time (τ_1) it takes for the CDW to translate one wavelength and the time during this period that the CDW slips (τ_2) diverge as $\mathscr{E} \to \mathscr{E}_T^+$:[23]

$$\begin{aligned} \tau_1 &\sim \frac{1}{v} \sim (\mathscr{E} - \mathscr{E}_T)^{-\xi} , \\ \tau_2 &= f\tau_1 \sim (\mathscr{E} - \mathscr{E}_T)^{-\mu} , \end{aligned} \tag{2}$$

so that

$$\begin{aligned} \Delta E/E &= \frac{E' - E'_{\text{pin}}}{E} = \{[(1-\tau_2/\tau_1)(E+K) + (\tau_2/\tau_1)E \\ &\qquad - (E+K)]/E\} , \\ -\Delta E/E &= \frac{\tau_2}{\tau_1} K/E \sim (\mathscr{E} - \mathscr{E}_T)^{\xi-\mu} . \end{aligned} \tag{3}$$

In mean-field theory,[23] $\xi = \frac{3}{2}$ and $\mu = \frac{1}{2}$, so we expect the modulus to decrease linearly with the field near threshold.

The CV (Ref. 20) and Lehman (Ref. 21) results show that the simple decrease in modulus described above should only be observed if the CDW moves nonrigidly, even at high velocities, i.e., if the internal degrees of freedom of the CDW interact with the lattice strain. Fisher pointed out that the CDW velocity is only coherent over finite lengths L equal to the Lee-Rice length L_0 at large velocities, but diverging at threshold.[23] Very recently, a few models have been proposed to describe the effect of the CDW degrees of freedom on the elastic modulus of the lattice.[17,24,25] Littlewood[24] assumed that in addition to the direct coupling of the strain to the CDW through the displacement of the impurity sites responsible for pinning, the gradient of the strain couples to the gradient of the CDW phases (e.g., screening). He found that the pinned value of the modulus would exceed the high field, depinned value by K (the elastic constant of the CDW) plus a term of second order in the gradient coupling. Furthermore, he showed that for high fields, the modulus would saturate very slowly as $(E - E_{\text{sat}}) \sim \mathscr{E}^{-1/2}$. Sneddon[25] has proposed a model in which, in addition to being coupled through the pinning term, the strain and CDW are coupled through a sliding frictional force. He found a variation of the modulus and internal friction with electric field qualitatively very similar to that observed experimentally (see Figs. 6 and 12): the internal friction increases rapidly for fields slightly greater than $\mathscr{E}_T$ and very slowly decreases for larger fields, while the modulus decreases gradually with fields greater than $\mathscr{E}_T$. The total change in modulus is again given by the modulus of the CDW. Sneddon's model will be discussed in more detail later. Bourne *et al.*[17] have proposed a similar model and solved for the case of a CDW with a single degree of freedom. They were able to study the effect of simultaneously exciting the sample with dc and ac currents; they observed large interference effects, in which the modulus and damping return to their unperturbed low-field values, when the ac frequency was harmonically related to the "natural frequency"[3,4] of the sliding CDW. They attribute these jumps in the elastic properties to "mode-locking," i.e., the ac field locks onto the sliding CDW, causing it to slide rigidly. They have also observed weak interference effects in o-TaS_3, experimentally.[17]

Changes in the elastic properties are often considered using anelastic theory.[26,27] For the simplest case of a single relaxation time,

$$\begin{aligned} E(\omega\tau) &= E(0) + F\omega^2\tau^2/(1+\omega^2\tau^2) \\ &= E(\infty) - F/(1+\omega^2\tau^2) , \\ \delta &\equiv \text{Im}[E(\omega\tau)]/E = F\omega\tau/(1+\omega^2\tau^2) , \end{aligned} \tag{4}$$

where F is the relaxation strength of an internal variable of the system, such as temperature.[27] It is assumed that this variable couples to strain and that when distortion drives it from equilibrium, it relaxes with time constant τ. For coupling linear in the strain, Eqs. (4) follow; quadratic coupling will renormalize the modulus only.[28] In general, a finite distribution of relaxation times $F(\tau)$ must be considered; also, the relaxation may be due to defects, such as domain walls, as well as intrinsic variables.[26] For example, it has been shown that uniaxial strain changes the threshold field $\mathscr{E}_T$;[29,30] it must therefore also change the CDW velocity. (The mode-locking experiments of Ref. 17 also show that the CDW velocity couples to strain.) Therefore, strain will drive the local velocity from its equilibrium value and its relaxation may cause the observed elastic anomalies.

As discussed by Fisher,[23] the velocity is coherent over length scales $L \gtrsim L_0$, and the relaxation presumably occurs coherently within these regions very rapidly ($\tau \ll 1/\omega \sim 1$ msec). The velocity (and phase) adjustment between these regions, i.e., motion of "domain walls" is probably much slower,[7] giving rise to the peak in the damping. Note that for inhomogeneous strains ($q \neq 0$), the velocity will vary through the sample. The rigidity of the CDW will still keep the velocity coherent over lengths $\sim L$ and there will necessarily be large relaxations localized at the domain walls. Therefore, the elastic anomalies may increase with the wave vector of the phonon; the relevant scaling parameter will be qL. Furthermore, for flexural oscillations, the strain (and velocity) are inhomogeneous across the thickness of the sample and transverse domain motion might occur, further softening the crystal. Because the transverse coherence length is very small (<100 Å),[31] finite-thickness effects will not be observed. The transverse commensurability may pin the domain walls, however, so one-dimensional effects may still dominate, as assumed in the models discussed.[17,24,25]

Finally, Janossy *et al.*[32] have proposed that the CDW wavelength is modified at the two current contacts, with the CDW being compressed at the positive contact and stretched at the negative, with the distorted regions being >0.1 mm in length. Such changes may affect the local elastic modulus. Of course, if the change in modulus is linear in the CDW distortion, no net effect would be observed for the average modulus of the sample. Nonetheless, it is possible that the observed elastic anomalies are due to these distortions if ΔE is a nonlinear function of the change in wavelength.

III. EXPERIMENTAL METHODS

Crystals of o-TaS_3 were grown by vapor transport in evacuated tubes back filled with ~ 1 torr of argon which were heated to 820 K with a 50-K temperature gradient. Crystals were typically $\sim 1 \text{ cm} \times 10\ \mu\text{m} \times 3\ \mu\text{m}$ and were verified to be of the orthorhombic polytype by x-ray powder diffraction and resistivity measurements. The latter indicated a metal-semiconductor phase transition at 220 K, with an activation energy of 75 meV below the transition, consistent with published results.[33] Some crystals prepared at the University of California, Los Angeles were also studied.

Because the samples of o-TaS_3 are extremely thin, elastic properties were measured using a modified vibrating-reed technique. In the conventional vibrating-reed experiment,[34] the sample is mounted as a cantilever and the resonant frequency f and quality factor Q of flexural resonances are measured. The resonant frequency of the nth flexural mode is given by[34,35]

$$f_n = (a_n s / l^2)(E/\rho)^{1/2} , \tag{5}$$

where a_n is a constant, s the sample thickness, l the length, and ρ the density. The Young's modulus is given by $E = 1/S_{33}$, where S_{ij} is the compliance tensor and $\hat{z}$ is the chain direction. Q^{-1} gives the friction, which includes the external friction with the clamping material and residual atmosphere as well as the internal friction ($\delta \equiv \text{Im}E/|E|$). For the fundamental, $a_0 = 0.161$.[35]

Changes in the resonant frequency, e.g., as a function of temperature, therefore directly give changes in the modulus; $\Delta E/E = 2\Delta f/f$ (if one assumes that effects of thermal contraction are much smaller). As described in Ref. 36, changes in frequency of order 2 mHz (typically $f_0 \sim 500$ Hz) can be measured by utilizing the sample as the phase-shifting element of a phase-lock loop. The oscillations are excited and detected by electrostatic coupling to drive and pickup electrodes spaced ~ 1 mm from the sample; no transducers are in direct contact with the sample. A buffer amplifier is mounted on the charged pickup electrode; it is sensitive to changes in the sample capacitance of the order of 10^{-7} pF,[36] corresponding to sample motions of $\sim 1\ \mu$m. The quality factor can easily be found by introducing phase shifts into the phase-lock loop to measure the bandwidth, typically $Q \sim 10^3$. Changes in the quality factor, e.g., over small temperature ranges, are generally found by measuring the amplitude of the signal. The change in internal friction is given by $\Delta\delta = \Delta 1/Q$.

To measure changes in modulus as a function of voltage across the sample, $V \equiv \mathscr{E} l$, it is necessary to mount a lead on the "free" end. Because of the fine size of the samples, it is not possible to do this such that the end remains free. A change in the boundary condition at this end only changes the constant a_n in Eq. (5); for example, for the fundamental "clamped-clamped" resonance, $a_0' = 1.03$;[35] it is desirable to use this mode because there will be no effect on the resonant frequency from the elasticity of the attached wire. However, it is difficult to avoid either bending or stressing the sample, especially as the temperature changes. If uniaxial stress σ is applied to the sample, the resonant frequency of the fundamental is given by[15,35]

$$f_0 = (\gamma a_0' s / l^2) \left\{ \left[E + \left[\frac{0.54}{\gamma} \right] \left[\frac{l}{s} \right]^2 \sigma \right] \Big/ \rho \right\}^{1/2} . \tag{6}$$

γ depends on σ, but is of order unity. [$\gamma = 0.45$ for $\sigma (l/s)^2 \gg E$, giving the familiar result for a string under tension.] Because $(l/s)^2 \sim 10^6$, small stresses can greatly increase the resonant frequency.

Two different techniques were used to avoid large stresses. For some samples, the free end was glued to a bent 50-μm-diam constantan or silver wire with silver paint. For some such samples, the resonant frequency was lower than expected, indicating that the wire was also vibrating slightly. When cooled, the resonant frequency of these samples generally would not vary in the expected manner (i.e., as the modulus previously measured in a "clamped-free" configuration), but overall changes were small and the expected anomaly observed at T_c[36] indicated that effects from stress or the elasticity of the wire were not large (generally $\lesssim 50\%$).

For other samples, the free end was glued with silver paint to a fiber of $TaSe_3$, of dimensions comparable to the sample. ($TaSe_3$ has no phase transitions above 2 K and its conductivity remains metallic.[37]) The $TaSe_3$ was bent and clamped at roughly a right angle to the sample for stress relief and a large ($\sim 1\text{-mm}^3$) ball of paint was used to inertially confine one resonant flexural mode to the sample. In this configuration, many modes of oscillation, i.e., shear and flexural modes of both fibers, could be excited. The "correct" TaS_3 flexural mode was picked out by measuring the temperature dependence of all modes of large amplitude and comparing with the results for the sample before it was clamped. As shown in Fig. 1, agreement (within 10%) could be achieved and voltage dependent measurements were only made on these "quasi-stress-free" modes.

It will be noticed that the temperature dependence of the modulus shown in Fig. 1 is similar to those previously measured,[36] but that the size of the minimum at T_c is half of those shown in Ref. 36. In fact, we found that the elastic anomaly at T_c is sample dependent, varying in size from 0.5—2 % and presumably reflects the sample breaking into Lee-Rice domains in the CDW state.[36]

After clamping the sample and determining the "correct" mode, the sample was cooled and its temperature held stable ($\Delta T < 30$ mK) in a low pressure of helium gas (typically 500 m torr) to reduce the effects of Joule heating. A computer-controlled voltage supply varied the voltage across the sample, while the current, shift in

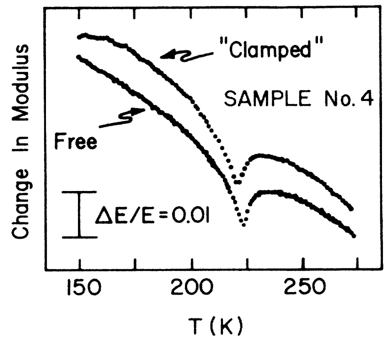

FIG. 1. Relative change in the Young's modulus versus temperature before and after adding a $TaSe_3$ "clamp." The vertical offset is arbitrary. (Reprinted from Ref. 19.)

resonant frequency, and amplitude of resonant signal were simultaneously measured. Measurements were made slowly (~ 1 point/min) to allow the phase-lock loop to have a long time constant (100 s) and keep the frequency shift measurements as precise as possible. Care was also taken to not overdrive the sample resonance (i.e., the quality factor and resonant frequency were independent of the ac driving voltage, typically 15 V) and frequency errors due to the finite loop gain were kept negligible. Generally, before taking data at any temperature, it was necessary to "condition" the sample with a large current to allow the sample to equilibrate, i.e., to remove the sample from a metastable state (see below).[8,9]

Typical results are shown in Fig. 2. It is seen that at voltages greater than the depinning threshold, at which the resistance decreases, the modulus (i.e., frequency) decreases and the internal friction increases sharply. Similar results were observed in all of the more than 20 samples studied. Note that the modulus also decreases very slightly below threshold; as shown in the inset, this decrease is proportional to the Joule power dissipated in the sample and thus to its average temperature change. Such heating effects could be reduced by increasing the pressure in the chamber and were usually kept negligible ($\Delta E/E < 10^{-5}$). When not negligible, we corrected the modulus shift for heating effects:

$$\Delta E(V)/E_0 \,|_T = 2\Delta f/f - mP(V) , \qquad (7)$$

where $P(V)$ is the power dissipated and m the empirically determined slope.

When studying the high-field saturation behavior of the modulus, considerable heating was encountered ($\Delta E/E \sim 1\%$) and extrapolation from the low-field region was not sufficiently precise. In such cases, the high-field frequency shift was plotted versus power, and when the frequency shift was found to be proportional to power over a large range, it was assumed that the "isothermal" modulus had saturated. Because large currents were needed, results for quasi-stress-free crystals were generally very noisy at high fields due to fraying of the $TaSe_3$ fiber, and results were obtained for samples clamped with a wire, preventing quantitative measurements of the magnitude of the modulus decrease. Typical results are shown in Fig. 3. The saturated modulus was then found from the high-voltage data by a linear fit, $E_{sat}(P) = mP + b$. This procedure works because changes in modulus due to CDW depinning and to heating are both small and can be treated as independent first-order perturbations; such a procedure obviously cannot be applied to the resistance, and no attempt has been made to correct the resistance data for Joule heating effects.

During some runs, the resonant frequency (at $V=0$)

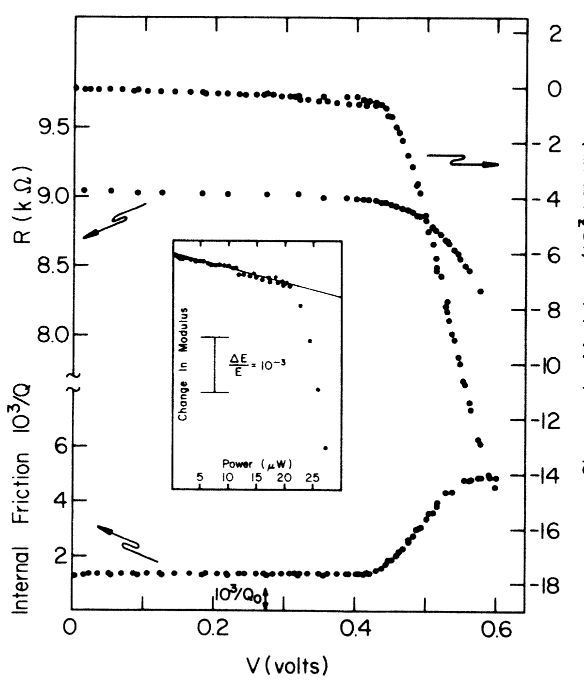

FIG. 2. Resistance, 1/(Quality Factor), and relative change in modulus versus voltage for a sample (sample 1) clamped with constantan wire at 149 K. Q_0 is the quality factor in vacuum at zero voltage. Inset: $\Delta E/E_0$ versus Joule power. The line shows the proportionality below threshold. (Reprinted from Ref. 15.)

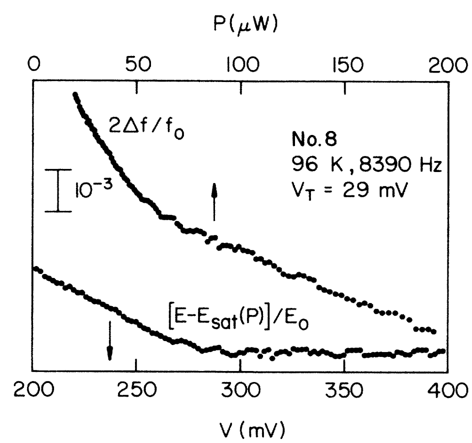

FIG. 3. High-field variation of resonant frequency (versus Joule power) and modulus (versus voltage) for a sample clamped with silver wire (not stress free). The saturated value of the modulus is given by fitting the frequency shift $E_{sat}/E_0 = 2\Delta f/f = mP + b$, at high power. The vertical offsets are arbitrary.

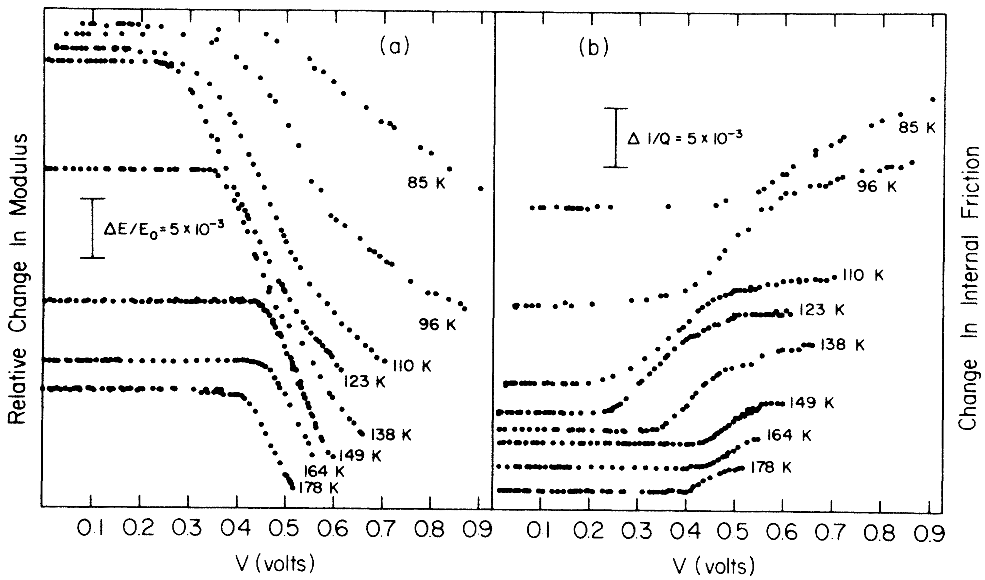

FIG. 4. (a) relative change in modulus and (b) change in $1/Q$ versus voltage at several temperatures for sample 1 (not stress free). The vertical offsets are arbitrary. The thresholds for resistance changes (not shown) are the same as for the modulus and damping. (Reprinted from Ref. 15.)

drifted slightly, presumably due to drift in temperature, sample metastability, sample creep, or drift in the VCO (voltage-controlled oscillator) offset. When these drifts were small (<10 mHz) they were corrected for by assuming they occurred linearly with time. In a few cases, the zero was measured before and after each point.

Finally, we endeavored to test the hypothesis of Ref. 32 by checking whether the change in modulus was due to the distortion of the CDW at the contacts. To isolate one side of the sample elastically, half the sample was coated with insulating paint which mechanically clamped that side, limiting vibrations to the unpainted side. There was noticeable thermal stress in the sample, but modulus and quality factor changes could be measured. Both polarities of voltage were applied.

IV. RESULTS

A. General behavior

Results for a sample (not quasi-stress-free) at a number of temperatures are shown in Fig. 4. It is seen that the anomaly in quality factor decreases as the temperature approaches the transition; at 100 K, $\Delta 1/Q \sim 1\%$, orders of magnitude larger than the presumed internal friction with the CDW pinned. ($1/Q_0 \sim 10^{-3}$ includes substantial "external" friction.) After a small transition region above V_T (see Sec. IV D), the variation of modulus with voltage has positive curvature, but the saturation is very slow. At the lowest temperatures, the threshold behavior gets washed out, as has also been reported for the resistivity.[2]

After completing these measurements, we checked whether the anomalies in the measured friction and resonant frequency were in fact due to changes in the elastic properties and not, for example, due to changes in the quality of the clamp or sample dimensions, by deliberately stressing the sample to pass into the "vibrating string" limit of Eq. (6). The sample was pulled on until its resonant frequency had increased by a factor of 17; i.e., $(l/t)^2(\sigma/E) \sim 1200$. The results at 123 K are shown in Fig. 5. There is no significant change in either frequency (corrected for Joule heating) or quality factor for the stressed sample ($\Delta f/f, \Delta 1/Q < 2\times 10^{-5}$), whereas

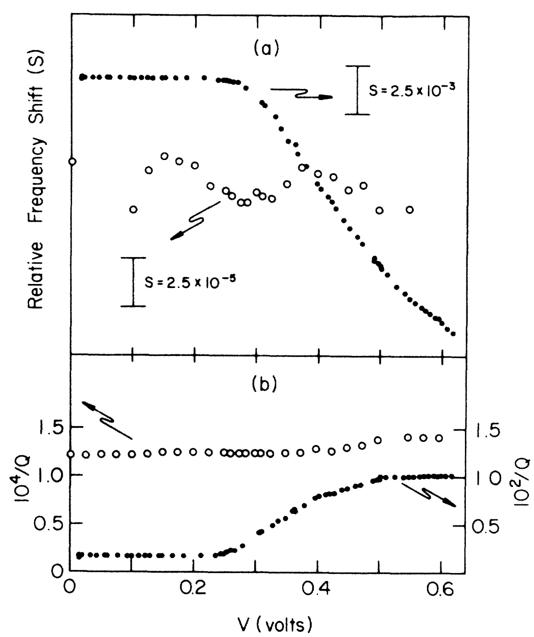

FIG. 5. (a) Relative change in frequency corrected for Joule heating, $S = \Delta f/f_0 - mP/2$ and (b) $1/Q$ versus voltage for sample 1 at 123 K. The closed circles are for the unstressed sample ($f_0 = 1.3$ kHz) and the open circles are for the highly stressed sample ($f_0 = 22$ kHz). Note the two-order-of-magnitude difference of scale for the two cases.

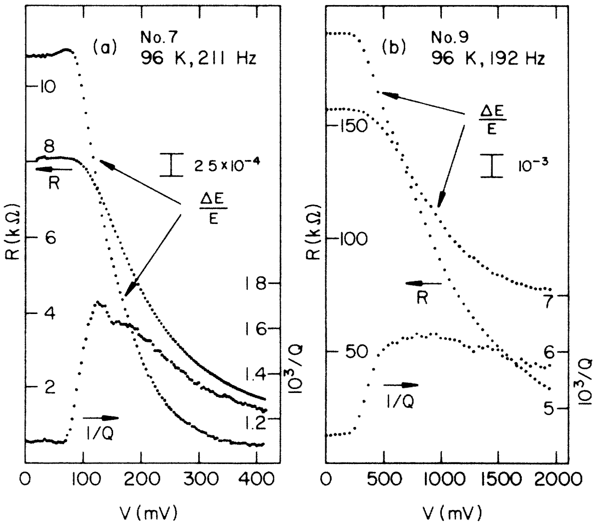

FIG. 6. Variations of modulus $1/Q$, and resistance versus voltage for two samples; sample 7 is quasi-stress-free. The moduli are approximately corrected for Joule heating; the resistances are not.

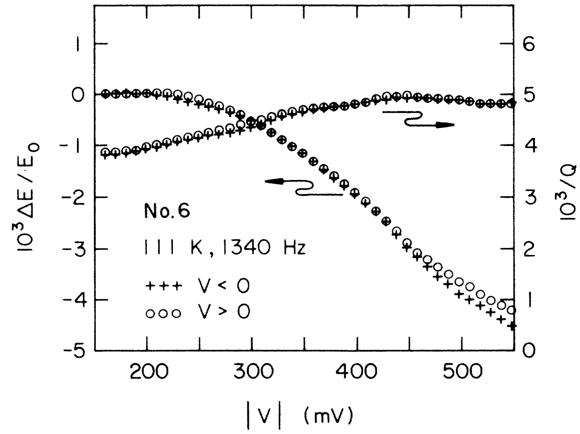

FIG. 7. Voltage dependence of the modulus and internal friction for a sample which is mechanically clamped on one side, for voltages of both polarities.

changes of $\sim 1\%$ are observed for the unstressed sample, indicating that these changes are indeed due to changes in (the real and imaginary parts of) the modulus.

The modulus and internal friction shown over larger voltage ranges are shown for two samples in Fig. 6. It is seen that the modulus only saturates at a voltage $V \sim 10V_T$. After reaching a maximum at $V \sim 2V_T$, the internal friction slowly decreases for both samples. This behavior was observed in most samples, although for a few δ stayed at its high value. The very slow falloff observed for sample 9 was most common.

B. Polarity dependence

The results of the current polarity-dependence experiment are shown in Fig. 7. There is no strong polarity dependence observed in either the internal friction or modulus. (The variation in modulus observed above 450 mV is comparable to the scatter between different runs for this sample; the large scatter is probably caused by Joule-heating-induced differential thermal expansion cracking the insulating paint slightly.) Thus, the observed anomalies in Young's modulus and internal friction are not primarily caused by changes in the CDW wave vector near the contacts, although small second-order effects ($\Delta E/E \sim 10^{-4}$) cannot be ruled out.

C. Metastable effects

Generally, if the voltage was increased to a value above threshold and then returned to a low value, the resonant frequency was observed to change (usually $|\Delta f| < 20$ mHz, corresponding to $|\Delta E/E| < 10^{-4}$); both increases and decreases in frequency were observed. It was usually possible to "fix" the sample by applying a sufficiently large voltage, i.e., a voltage greater than any used in the subsequent run, so that changes in the $V=0$ modulus were greatly reduced. Similar changes have previously been observed in resistivity and have been attributed to the presence of metastable configurations of Lee-Rice domains.[10–12] However, there is one important difference in the observed behavior of the Young's modulus. Whereas voltages slightly above threshold were sufficient to fix the low-field resistivity of the sample, considerably larger voltages were needed to fix the resonant frequency. It was usually observed that if a given voltage ($V_1 > V_T$) was applied to the sample, the zero-voltage resonant frequency would change unless a larger voltage ($V_2 > V_1$) had previously been applied. Of course, these changes in frequency were small, unlike the large ($>10\%$) changes in resistivity,[10,12] which are nonetheless perfectly equilibrated by application of a voltage greater than threshold. This implies that the Young's modulus is sensitive to changes in the configuration of Lee-Rice domains in ways very different from the conductivity. As mentioned earlier, theories based on the Lee-Rice model have predicted that the sample should be equilibrated by application of a voltage $V > V_T$,[8,9] and we have not eliminated the possibility that the observed frequency jumps are contact effects; e.g., the rigidity of the silver paint contacts may be affected by large currents.

In some samples, the resonant frequency was observed to increase slightly ($\Delta E/E < 10^{-4}$) near threshold before decreasing; such effects were usually only slightly out of the scatter in the data and not reproducible. An example is seen in Fig. 2; what is striking is that the hysteresis occurs just below threshold, again suggesting the motion of Lee-Rice domains. For two samples, cleaner and reproducible peaks were observed near threshold; an example is shown in Fig. 6(a). Notice that the modulus starts increasing at voltages slightly below threshold (as determined by the internal friction). Large peaks in modulus at threshold have been predicted by Sneddon (see below).

The only conclusion that can be safely drawn from our present results below threshold, given the scatter and irreproducibility of the data, is that the changes in modulus observed for $V < V_T$ are two orders of magnitude smaller than those for $V > V_T$, so that changes in Lee-Rice domains cannot account for the large anomalies observed above threshold. [Very different results have been observed for $(TaSe_4)_2I$, in which there is large hysteresis in the modulus above threshold.[38]]

D. Behavior of the modulus as $V \to V_T^+$

In earlier work[19] we showed that as the voltage approached the threshold from above, the modulus varied roughly quadratically with voltage: $-\Delta E/E \sim (V/V_T - 1)^\alpha$, $\alpha = 2$; this behavior persisted up to modulus changes of $\sim 10^{-3}$, when α starts decreasing, as seen in Fig. 4. A complete set of results is shown in Fig. 8; it is seen that the quadratic behavior is observed for most samples, in contrast to $\alpha = 1$ predicted by the slip-stick model in the mean-field limit. Also, for those samples for which precise *I-V* data was obtained, we found that $I_{CDW} \sim (V/V_T - 1)^\xi$ with $\xi = 3$, in contrast to the power $\xi = \frac{3}{2}$ predicted. Monceau *et al.*[4,39] have reported that $\xi \to \frac{3}{2}$ in *o*-TaS_3 for temperatures close to T_c. We were not able to get quantitative data near V_T for higher temperatures due to Joule heating effects.

One sample, sample 9 at 103 K, had a power α significantly less than 2; in fact, $\alpha = 1.2$ and $\xi = 1.8$ at 103 K, with a difference intriguingly close to the mean-field value of 0.5. However, when this sample was warmed to 141 K, both powers were observed to increase.

For most samples we failed to extend these analyses closer than ~ 5 mV from V_T. ($V/V_T - 1 \sim 3 \times 10^{-2}$), so it is not clear that we are yet observing true critical behavior. The reasons for these failures are (i) metastable effects masked the threshold voltage, (ii) two samples exhibited a peak in modulus as described above, and (iii) for some samples slightly different thresholds were observed for CDW conductivity and elastic properties. It may be that the long samples needed for the elastic measurements were inhomogeneous, having a small distribution in threshold fields. The uncertainty in threshold voltage also prevents us from plotting the modulus versus the CDW current (i.e., the CDW velocity) in this range, as shown below, the velocity is probably the "intrinsic" variable of most interest.

E. Intermediate field behavior

The quadratic dependence on voltage extends for most samples up to $-\Delta E/E \sim 10^{-3}$; above this value the modulus starts varying more slowly.[19] In this range we could plot the change in modulus versus the CDW current, $I_{CDW} = I - V/R_0$, where R_0 is the resistance of the normal electrons; the currents were normalized to the current at threshold, $I_T = V_T/R_0$, so that I_{CDW}/I_T is proportional to the average CDW velocity (assuming that the CDW carrier density is independent of temperature well below the transition). The results are shown in Fig. 9. It is seen that $-\Delta E/E \sim I_{CDW}^{1/2}$ for $10^{-2} I_T < I_{CDW} < I_T$. At lower values of current, the exponent starts increasing, but the uncertainties in V_T and R_0 lead to large uncertainties here. At larger currents, the exponent decreases, but here Joule heating increases the current nonnegligible. Note that $I_{CDW} \sim I_T$ corresponds to $V \sim 3V_T$, where the CDW is expected to be drifting rigidly, but the fractional power observed is in clear contradiction to the Doppler-shift result of CV.[20] Also note that, as compared to the voltage dependence plotted in Fig. 8, the results for different samples are rather tightly clustered; in particular, compare the results for sample 2 at 99 K and 124 K in the two figures. This supports our contention that the CDW velocity is the intrinsic variable

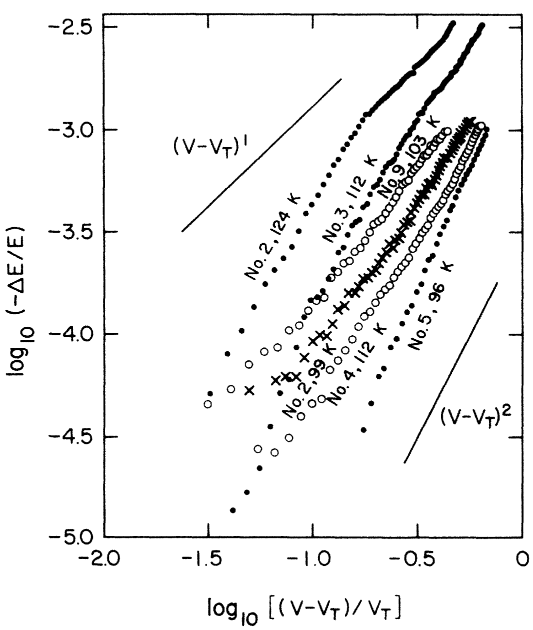

FIG. 8. Variation of the change in modulus versus voltage near threshold, V_T, for several samples. All samples except sample 9 are quasi-stress-free. The lines are guides for the eye.

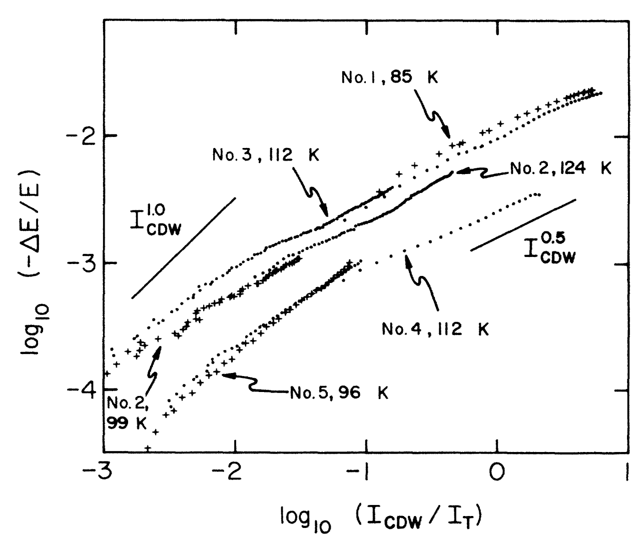

FIG. 9. Variation of the change in modulus versus the CDW current for several samples; all samples except sample 1 are quasi-stress-free. I_T is the (normal) current at threshold; I_{CDW}/I_T is proportional to the average CDW velocity. The lines are guides to the eye.

governing the change in modulus. We find that $-\Delta E/E = A(I_{\mathrm{CDW}}/I_T)^{1/2}$, where $A = (7\pm3)\times10^{-3}$.

F. High-field behavior—saturation of the modulus

The method of correcting for significant Joule heating in measuring the high-field modulus was discussed earlier; the assumption is of course, that when the change in frequency becomes strictly proportional to the Joule power, the modulus has saturated. Because heating effects rapidly become larger as the temperature increases, data have only been taken below 100 K. It is seen that although the modulus only saturates for a voltage $V_s \sim 10V_T$, it does so very abruptly, with $\Delta E/E$ apparently going to zero (i.e., below the noise level) linearly with voltage below V_s; i.e., $(E-E_{\mathrm{sat}}) \sim (V_s - V)$. Clearly, in a fit of $(E-E_{\mathrm{sat}})$ to a simple power law V^{-p} the exponent will be very large. In Fig. 10 are shown logarithmic plots of $E-E_{\mathrm{sat}}$ versus voltage for two samples. Although a single power law does not give a good fit, the best fit as $E \rightarrow E_{\mathrm{sat}}$ is $p \sim 15$, in obvious contrast to the prediction of Littlewood's model, $p=\frac{1}{2}$.[24] It should be noted that at the apparent saturation voltage V_s, the resistance *(including* the effects of Joule heating) is still an order of magnitude larger than its saturated value; in this range, I_{CDW} is an exponential function of V.[3,4]

V. DISCUSSION

The decrease in modulus with field implies that, in a relaxation model, $\tau \rightarrow \infty$ as $\mathcal{E} \rightarrow \mathcal{E}_T^+$ [see Eq. (4)]; the increase in internal friction as $\mathcal{E}$ increases above threshold then implies that $\tau \sim 1/\omega \sim 1$ ms at $\mathcal{E} \sim 2\mathcal{E}_T$, although the relaxation strength F may also vary with field. The long tail in the internal friction indicates that the relaxation time decreases slowly with field. The long time constants suggest that the relaxation is of defects in the CDW structure, i.e., the domain walls discussed earlier. Lee-Rice domains are thought to exhibit slow relaxation for $\mathcal{E} < \mathcal{E}_T$,[11] but to be frozen for $\mathcal{E} > \mathcal{E}_T$.[8,9] In addition, the small changes in modulus observed below $\mathcal{E}_T$ make it unlikely that Lee-Rice domain changes are contributing significantly to the large elastic anomalies observed above threshold. Velocity coherent domains, on the other hand, are expected to have divergent time and length scales (i.e., $F \rightarrow 0$) as $\mathcal{E} \rightarrow \mathcal{E}_T^+$. Although for unstrained samples the velocity is thought to become coherent at high fields ($\mathcal{E} > 2\mathcal{E}_T$),[23] the oscillating strain drives it out of equilibrium, as discussed earlier. The fractional power law observed, $-\Delta E/E \sim v^{1/2}$, also suggests that fluctuations in velocity cause the modulus to decrease. As mentioned before, the strength of the slow relaxation at the walls is expected to increase with q, and may be significantly larger for flexural strains than for longitudinal.

Results of a simple model calculation using Eqs. (4) are shown in Fig. 11 where we have assumed a constant relaxation strength and a single relaxation time $\tau_0 = (1.5/\omega)[\mathcal{E}_T/(\mathcal{E}-\mathcal{E}_T)]^{0.75}$. It is seen that although the basic shape of the anomalies in modulus and internal friction are easily reproduced, both anomalies in such a model will be of comparable magnitude. This result is not altered significantly by including a large distribution of relaxation times centered on τ_0; the principle effects of such a distribution are to reduce the curvature in ΔE as $\mathcal{E} \rightarrow \mathcal{E}_T$ and to increase the tail in $1/Q$. On the other hand, as seen in Figs. 6 and 4 (at high temperatures), the anomaly in modulus is generally much larger than that in internal friction. Within an anelastic relaxation model, this requires a field-dependent relaxation strength with $F(\mathcal{E},\tau)$ increasing with field for $\tau \ll 1/\omega$; i.e., the modulus at high fields must be dominated by "instantaneous" relaxations, e.g., coherent velocity relaxations.

In the model of Sneddon,[25] the anomaly in internal friction is caused by excitation of the internal degrees of freedom of the CDW (roughly corresponding to the domain walls[7]), while the modulus anomaly is essentially a static effect (analogous to the instantaneous relaxation of the anelastic model). Its total magnitude is given by $\Delta E/E \sim K/E$, for $K \ll E$, where K is the effective modulus of the CDW, and its slow variation with voltage arises from the decrease in length scales over which the CDW is effectively pinned (analogous to the time depen-

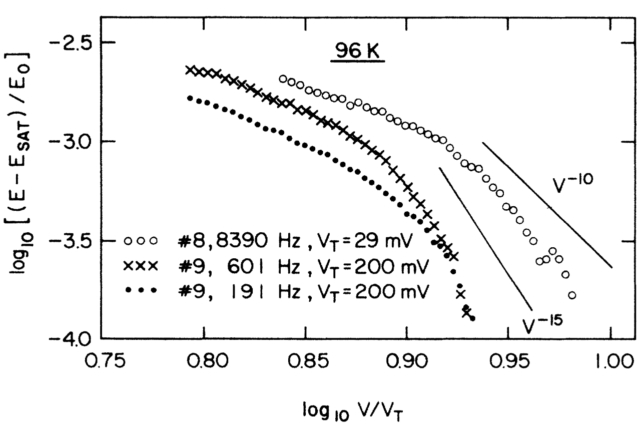

FIG. 10. Variation of the modulus above its saturated value versus voltage for two samples (not stress free); two modes are shown for one sample. E_{sat} is found as shown in Fig. 3. The lines are guides to the eye.

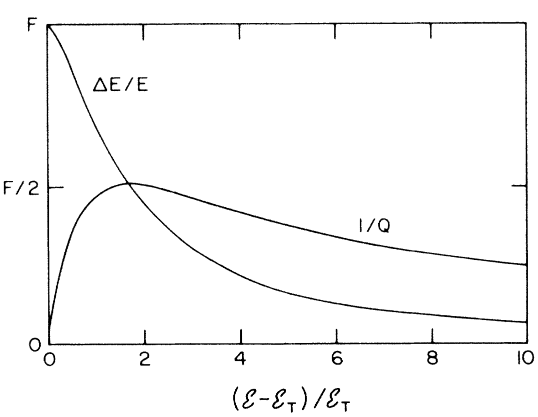

FIG. 11. Variation of modulus and internal friction for a relaxation model with a single relaxation time τ_0. The relaxation strength F is constant with field; $\omega\tau_0 = 1.5[\mathcal{E}_T/(\mathcal{E}-\mathcal{E}_T)]^{0.75}$.

dence of pinning in the slip-stick model.)[40] A plot of Sneddon's results is shown in Fig. 12. Although the anomalies in $\Delta E/E$ and $1/Q$ shown in this figure are of comparable magnitude, they have different sources and can be varied independently. The peak in modulus at threshold is an interference effect which is expected to be largely washed out experimentally due to sample heterogeneity. As mentioned above, it may be related to the small peak seen in some samples [see Fig. 6(a)]. Sneddon's model, which incorporates incommensurate rather than random impurity site pinning, is not expected to hold quantitatively at high fields, where the modulus saturates; work is in progress to determine its predictions on the velocity dependence of ΔE at intermediate fields.[40]

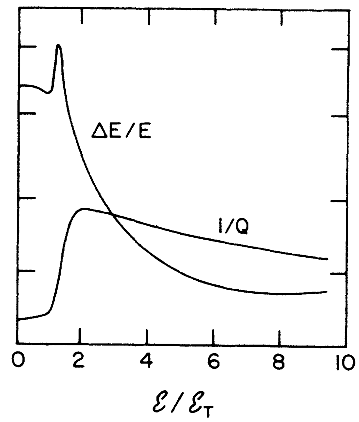

FIG. 12. Variation of modulus and internal friction in the model of Sneddon. The vertical scales are arbitrary but equal for the two quantities. (Reprinted from Ref. 25.)

Lehman's work on the CV model[21] suggests that flexural strains may couple differently to the CDW than do longitudinal strains. The one-dimensional models which treat the CDW as an elastic medium with elastic constant K all find that $E_{\rm sat}-E_0\sim -K$.[17,24,25] Since E_0 is expected to exceed the modulus of the crystal without a CDW (E_0') by $\sim K$, we expect $E_{\rm sat}\sim E_0'$. The gradual curvature of modulus with temperature and wide anomaly at T_c prevents us from estimating E_0-E_0' by extrapolating the pretransition behavior, however. In the Fukuyama-Lee model,[5]

$$K=hv_f/\lambda^2\Omega\ , \qquad (8)$$

where λ is the CDW wavelength and Ω the area per conducting chain. Estimating $v_f\sim 5\times 10^8$ cm/s from optical results,[41] we find $K\sim 2\times 10^{-2}E_0$, comparable to the observed effect, suggesting that transverse strain gradients in the flexural mode (and other finite q effects) are unimportant (e.g., due to transverse pinning of domains). However, the observed modulus decrease is sample dependent, even for quasi-stress-free modes; it is not clear if the variation $[-\Delta E/E\sim(0.4-2)\times 10^{-2}]$ is extrinsic (e.g., due to sample geometry) or intrinsic (e.g., due to impurity concentration). It would therefore be desirable to compare measurements of the elastic modulus for longitudinal strains, i.e., both ultrasonic and, especially, static ($\omega=q=0$) experiments. Brillouin scattering measurements, to determine whether the elastic anomalies persist to high frequencies and to what extent they reflect changes in the dynamic matrix of the ions rather than localized softening and losses due to CDW defects, would also be useful.

In summary, there are three salient results of our measurements which need to be addressed by theory. The basic shape and size (i.e., voltage dependence) of the internal friction and Young's modulus anomalies are qualitatively fit by the model of Sneddon.[25] The abrupt saturation of the modulus at a field $\mathcal{E}\sim 10\mathcal{E}_T$ is very striking, although the fact that the internal friction is still greater than its pinned value indicates that internal degrees of freedom can still be excited. Finally, the slow variation of modulus with CDW velocity near threshold $(-\Delta E/E\sim v^{1/2})$ provides a stringent test of any model.

ACKNOWLEDGMENTS

Large samples of TaS_3 were provided by Dr. G. Grüner of University of California, Los Angeles, who originally suggested the experiment. We have benefited greatly from many discussions with Dr. G. W. Lehman, Dr. L. Sneddon, Dr. A. Zettl, and Dr. P. B. Littlewood, who all kindly provided preprints of their related work. This research was supported in part by the National Science Foundation under Grant No. DMR-83-18189.

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