PHYSICAL REVIEW B

CONDENSED MATTER

THIRD SERIES, VOLUME 46, NUMBER 19 — 15 NOVEMBER 1992-I

Static Young's modulus obtained by dilatometry on TaS_3 in the drifting charge-density-wave state

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(Received 8 July 1992)

We report measurements of the static Young's modulus of orthorhombic TaS_3 in the drifting charge-density-wave state. In contrast to vibrating-reed and ultrasonic measurements of the Young's modulus, the static modulus softening was observed to be less than 0.001% for electric fields up to eight times the threshold field for non-Ohmic conduction. A relaxation model using a field-dependent distribution of relaxation times was used to calculate the frequency dependence of the modulus and internal friction anomalies. A comparison with experimental data suggests the possibility that if the softening is relaxational, then a high- and a low-frequency relaxation regime may exist in this material.

The nature of the charge-density-wave (CDW) state in quasi-one-dimensional conductors such as $NbSe_3$ and TaS_3 has been the subject of extensive investigations in recent years.[1] One of the most interesting properties of these materials is the softening of the Young's and shear modulus when electric fields in the samples exceed the threshold value for Ohmic behavior of the sample resistance. The field-dependent modulus softening and the accompanying field-dependent internal friction has been observed repeatedly by many authors in vibrating reed as well as in ultrasonic experiments.[2–6] In TaS_3 the Young's modulus softening at kHz frequencies amounts to about 1–2% of the modulus while the effect at the upper transition in $NbSe_3$ is generally an order of magnitude smaller. The effects in the shear modulus are even larger than this. The importance of understanding the frequency dependence of the Young's modulus softening has been emphasized by Xiang and Brill.[7] Vibrating-reed measurements[8] taken as low as 50 Hz suggest that the effect might saturate below 100 Hz. At higher frequency the softening decreases and falls to less than 0.1% at 10 MHz. Recent measurements of the Young's modulus down to <0.1 Hz,[9] however, showed that the softening at very low frequency is more than an order of magnitude smaller than that near 50 Hz, thus suggesting the existence of a maximum in the frequency dependence of the modulus softening. Determination of the behavior of the very low frequency or, preferably, the static Young's modulus is of crucial importance for the development of theoretical models for the effect. We report here measurements of the electric-field dependence of Young's modulus in TaS_3 under static conditions.

The Young's modulus was measured with a tunneling capacitance dilatometer. Absolute length changes were determined with a capacitor that had one plate fixed and the other in the form of a stiff cantilever. The position of this lower plate was controlled by a piezoelectric tube. The lower plate also carried a brass frame which acted as the sample support structure. As shown in Fig. 1, the sample fibers were glued at the top to this frame and at the bottom to the end of a weak cantilever that carried a freshly cleaved piece of highly oriented pyrolytic graphite (HOPG) on its upper surface. A tungsten tunneling tip fixed relative to the upper capacitor plate monitored the position of this graphite surface. A constant tunneling current and hence constant tip-cantilever distance was maintained through feedback signals to the piezotube with the help of standard scanning-tunneling-microscope electronics. The cantilever force constants were about 500 N/m and the tension in the samples depended on the initial bias applied to the cantilevers prior to gluing. The actual strains applied to the samples were determined by locating the CDW phase transition with the help of four probe-resistance measurements and the published[10] strain dependence of the transition in TaS_3. At applied stresses of a few tenths of MPa, length changes of the samples in the above arrangement are determined largely by temperature changes and thus through the thermal-expansion coefficient.[11] To a good approximation, the fractional change in strain, $\Delta\epsilon/\epsilon \equiv \Delta Y/Y$, and thus at higher stresses a large contribution to sample length changes can be expected from changes in the Young's modulus so that the electric-field dependence of the static modulus can be investigated.

Samples of orthorhombic TaS_3 were grown by the iodine vapor transport technique. Typical sample dimensions were $5\times10\times7000\ \mu m^3$.

To measure the electric-field dependence of the dilation, a slow voltage ramp was applied to the sample and the differential resistance and the output of the capacitance bridge were monitored simultaneously. An example of such a voltage sweep is shown in Fig. 2. The field sweep started at $E=-0.82$ V/cm and reached $+0.9$ V/cm after about 6 min. The threshold or CDW depinning field for this sample was about 100 mV/cm. Except for a small drift in the dilation signal in the amount of 3 ppm attributed to the measured drift in the dilatometer temperature from 112.35 to 113.02 K, no effects in the dilation on crossing threshold field could be observed. The maximum power dissipated in the samples was ~ 30 μW, which is too small to produce significant sample heating. If we use 350 GPa for the Young's modulus of TaS_3, then the stress applied to the sample for the results in Fig. 2 was about 2.4 GPa. This implies that the fractional change in Young's modulus at $E/E_T=8$ was less than 6×10^{-5}. This is over two orders of magnitude smaller than the effects observed in the vibrating-reed experiments and is consistent with the recent results of Tritt,

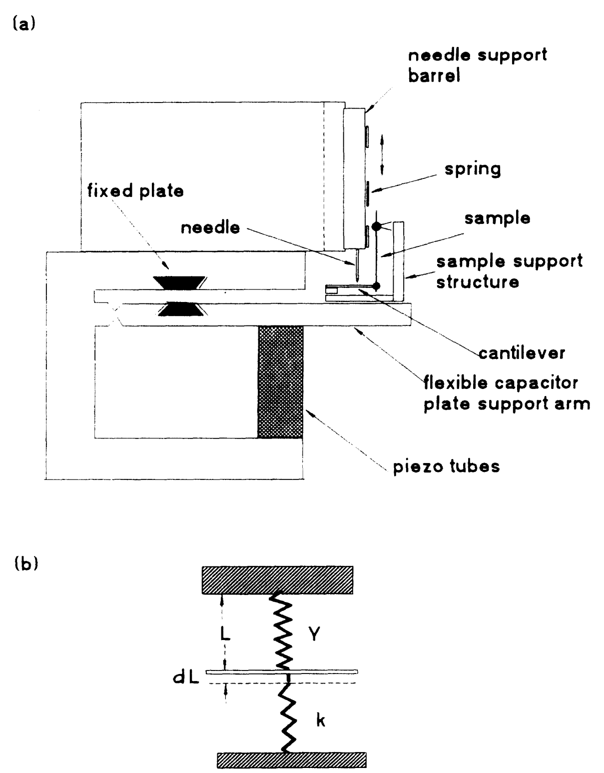

FIG. 1. (a) Sketch of the tunneling dilatometer. The movable lower plate of the dilatometer capacitor carries the sample support structure. The sample is fixed to this structure at the top and to a weak cantilever at the bottom. Negative feedback electrical signals act on a piezotube attached to the movable capacitor plate and thus maintain a constant distance between the cantilever surface and the tungsten tunneling needle. (b) Shows a spring representation of the sample (Young's modulus Y) and the cantilever (force constant k). At stress levels of a few GPa changes in Young's modulus can produce measurable changes in sample length (dL).

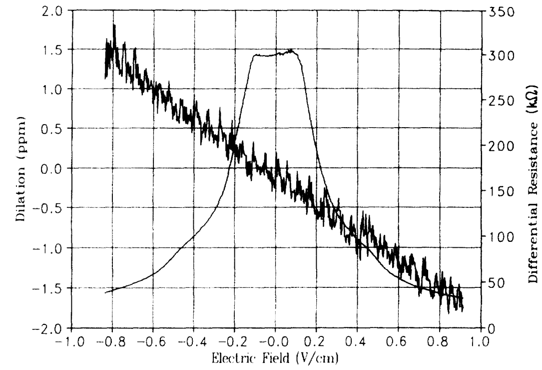

FIG. 2. Simultaneous measurements of differential resistance and dilation (dL/L) for an o-TaS_3 sample at ~ 112.7 K. From measurements of the shifts in the resistance anomalies at the CDW transition temperature the applied strain was determined to be $\sim 0.7\%$. Except for a temperature-related small drift, no anomaly in the dilation on crossing the threshold field, E_t, could be observed.

Skove, and Ehrlich[9] of $0<\Delta Y/Y<0.2\%$ for near static conditions.

The major difference between our measurements and those of Ref. 9 as well as the vibrating-reed elastic measurements is the level of strain applied to the samples. In the vibrating-reed measurements the strain is near zero while the maximum strain reported by Tritt, Skove, and Ehrlich was 0.3%. From the 37-K shift in the transition temperature and with the help of Fig. 9 of Ref. 10 we estimate a strain of about 0.7% (Ref. 12) for the results in Fig. 2. This strain level is somewhat larger than the critical strain of 0.5% reported by Xu and Brill,[13] beyond which the shear modulus anomalies in TaS_3 begin to decrease. The strain dependence of the Young's modulus anomaly has not yet been reported but it is likely that, as is the case for the shear modulus, a significant effect will remain even at strain levels of 0.7%. The null result shown in Fig. 2 was confirmed by measurements on other samples under different strain conditions. At a strain of 0.43% and with a maximum power dissipation of 14 μW an upper limit on the modulus softening was 0.0022% in $\Delta Y/Y$ for elastic fields $E=2E_t$.

The absence of softening of the Young's modulus in the extreme low-frequency limit poses problems for a number of theories that have attempted to explain the effect. These theories generally predict a significant contribution to the modulus softening even at very low frequency.[14,15] The importance of understanding the frequency dependence of the electric-field-induced softening was already pointed out by Xiang and Brill,[7] who tried to explain the effects with the help of relaxation models. These models, however, were unable to reproduce with a single set of parameters both the modulus and internal friction results over a wide frequency range. The relaxation model was recently reconsidered by Mozurkewich,[16] who made the interesting suggestion that relaxation of the CDW to an equilibrium configuration would be faster in the sliding state than in the pinned state. A relaxation model with a relaxation time that decreases with field can in principle give small effects at very high frequency, much larger effects at lower frequency, and produce no field-dependent effects for static or near static conditions. It has been recognized (for recent comments on this point, see Refs. 8 and 14) for some time, however, that relaxation models that use a single relaxation time and relaxation strength are unable to describe in a quantitative way the modulus softening and the internal friction over the whole frequency range covered by the experiments. Instead it was suggested that a distribution of relaxation times may be needed to explain the results. Given the complex state of a pinned CDW where the CDW can be trapped locally in metastable states,[16,17] the suggestion of a distribution of relaxation times does not seem unreasonable.

To explore the effects of a distribution of relaxation times we have calculated the modulus and internal friction for a uniform spectrum of relaxation times centered about a mean value. To incorporate electric-field effects, the mean relaxation time was assumed to be the field-dependent quantity and it was assumed to shorten when the sample enters the drifting CDW state. The modulus and damping for a flat distribution function of relaxation times was discussed by Nowick and Berry.[18] The distribution is expressed in terms of the variable $z=\ln(t/t_m)$, where t_m is the mean relaxation time. The distribution function is cut off at $\pm\beta$ as shown in the inset in Fig. 3(a). In this model the modulus and internal friction are described by a mean relaxation time t_m, a cutoff parameter β, as well as the usual relaxation strength F. All three quantities can, in principle, be field dependent and for a description of the changes in the elastic properties we have six parameters that can be adjusted. To reduce the number of parameters to a manageable set we assumed that F and β are field independent and that the field dependence is contained exclusively in t_m. The expressions for the change in modulus and internal friction in going from zero field (pinned) to a large field (unpinned) are then given by

$$\frac{\Delta Y}{Y}=\frac{Y(0)-Y(E)}{Y}=\frac{F}{4\beta}\ln\left\{\frac{\cosh[x(0)+\beta]\cosh[x(E)-\beta]}{\cosh[x(0)-\beta]\cosh[x(E)+\beta]}\right\}, \quad (1)$$

$$\Delta Q^{-1}=Q^{-1}(E)-Q^{-1}(0)=\frac{F}{2\beta}\{\tan^{-1}e^{[x(E)+\beta]}-\tan^{-1}e^{[x(E)-\beta]}-\tan^{-1}e^{[x(0)+\beta]}+\tan^{-1}e^{[x(0)-\beta]}\}. \quad (2)$$

In these expressions $x=\ln(\omega t_m)$, where ω is the vibration frequency. To compare the above equations with experimental data the parameters were adjusted by trial and error. Even though four parameters can be adjusted we found it difficult to fit experimental data over a large range of frequencies. Although parameters could be found that gave a good fit over a large frequency range for either modulus or friction data separately, it was very difficult to simultaneously fit both quantities with the same parameter set. For the data of Refs. 7 (their Fig. 3) and 8 (their Fig. 5), which give the change in modulus and friction when E is changed from 0 to $4E_t$, a reasonable fit to both quantities could be obtained for frequencies above 2 kHz. The values for the parameters for the dash-dot curves shown in Fig. 3 are $F=0.008$, $t_m(0)=10$ sec, $t_m(4E_t)=30$ μsec, and $\beta=8$. The same set of parameters also gave the right order of magnitude for the high-frequency data of Ref. 6. Figure 3 also shows more recent lower-frequency measurements by Xu and Brill.[8] We were unable to find a single parameter set that could fit the data over the whole frequency domain now available. To describe the lower-frequency results with the above equations (dashed curves) required a second parameter set with $F=0.4$, $t_m(0)=0.07$ sec, $t_m(4E_t)=0.06$ sec, and $\beta=6$. The solid curve in Fig. 3 shows the sum of both contributions. At very low frequency, i.e., in the

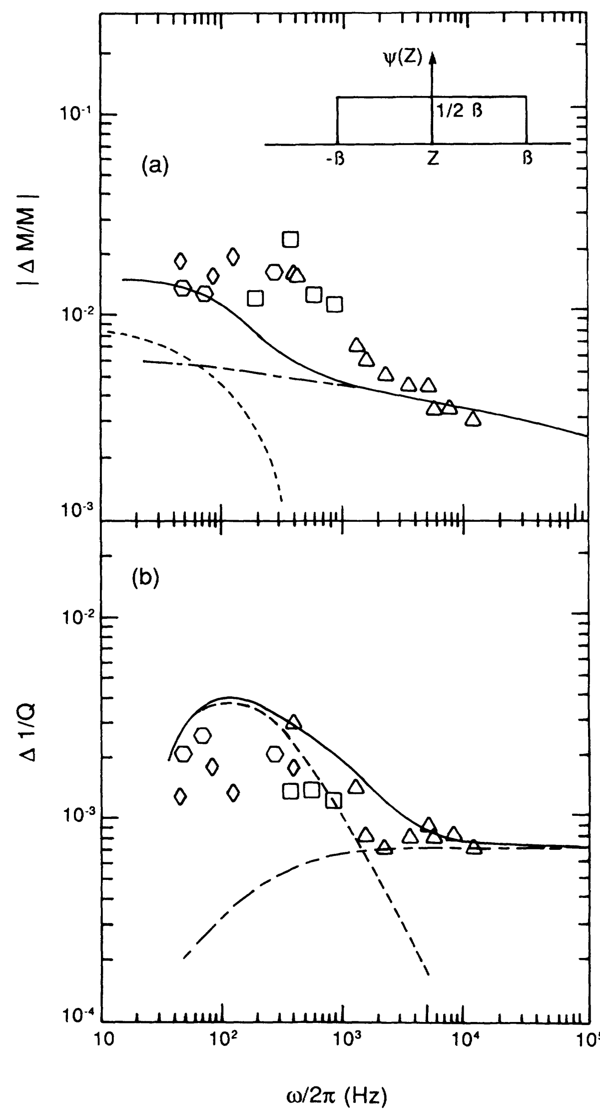

FIG. 3. Attempt to fit a relaxation model [Eqs. (1) and (2)] to Young's modulus and internal friction vibrating-reed data for a sample from Ref. 8 (see their Fig. 5). The dashed curves represent results for two independent sets of fitting parameters; the solid curve is the sum of the dashed curves.

static limit, Eq. (1) gives a vanishing modulus change in agreement with our observations. The above fits to the modulus and internal friction data are very insensitive to the choice of $t_m(0)$ and no significance can therefore be attached to the numbers quoted for $t_m(0)$. The zero-field mean relaxation time largely determines the behavior in the very-low-frequency region for which detailed data are not yet available.

Although a distribution of relaxation times coupled with Mozurkewich's idea of a shorter relaxation time in the drifting CDW state can improve the agreement of a relaxation model with the experimental data over what can be obtained with a single relaxation time approach, the agreement obtained is far from satisfactory. The uniform distribution function of relaxation times assumed here is no doubt overly simplistic and a more complex distribution may give better agreement over a larger frequency range. As pointed out before,[8,16] relaxation models with a single relaxation time tend to either underestimate the modulus change or overestimate the internal friction contribution. This still tends to be a problem when a distribution of relaxation times is assumed. If relaxation models with field-dependent relaxation times describe the electric-field effects, then our results suggest that two distinct relaxation regimes with perhaps different relaxation processes may exist. A more detailed examination of this model will require a determination of the field dependence of the relaxation times. Xu and Brill[8] pointed out that the strain pattern in the samples in the static and dynamic experiments is fundamentally different. In the static modulus experiments the strain is uniform. In the dynamic experiments, however, the strain dependence of the CDW velocity will result in the establishment of phase gradients in the samples and will thus produce an inhomogeneous elastic medium. In this case one may expect the modulus anomalies to depend on the amplitude of the flexural vibration. Experiments by Xu and Brill,[8] however, showed that the modulus softening was independent of vibration amplitude. The reason for a substantial anomaly in the dynamic modulus but an absence of softening in the static modulus even at fields that exceed $8E_t$ is thus still not understood. The discrepancy clearly has important implications for theoretical models of the elastic anomalies.

[1]For reviews, see F. Monceau, *Electronic Properties of Organic Quasi-One-Dimensional Compounds* (Reidel, Boston, 1985); G. Grüner, Rev. Mod. Phys. **60**, 1129 (1988).

[2]J. W. Brill and W. Roark, Phys. Rev. Lett. **53**, 846 (1984).

[3]J. W. Brill, W. Roark, and G. Minton, Phys. Rev. B **33**, 6831 (1986).

[4]G. Mozurkewich, P. M. Chaikin, W. G. Clark, and G. Grüner, Solid State Commun. **56**, 421 (1985).

[5]X.-D. Xiang and J. W. Brill, Phys. Rev. B **39**, 1290 (1989).

[6]M. H. Jericho and A. M. Simpson, Phys. Rev. B **34**, 1116 (1986).

[7]X.-D. Xiang and J. W. Brill, Phys. Rev. Lett. **63**, 1853 (1989).

[8]Z. G. Xu and J. W. Brill, Phys. Rev. B **45**, 3953 (1992).

[9]T. M. Tritt, M. J. Skove, and A. C. Ehrlich, Phys. Rev. B **43**, 9972 (1991).

[10]R. S. Lear, M. J. Skove, E. P. Stillwell, and J. W. Brill, Phys. Rev. B **29**, 5656 (1984).

[11]Results on the expansion coefficient of TaS_3 will be published elsewhere.

[12]In Ref. 10, Lear *et al.* measured the strains applied to their samples and then calculated the stresses which appear in their Fig. 9 using their value of Young's modulus. For the conversion we used $E = 350$ GPa.

[13]Z. G. Xu and J. W. Brill, Phys. Rev. B **43**, 11 037 (1991).

[14]A. Virosztek and K. Maki, Phys. Rev. B **41**, 7055 (1990).

[15]R. Zeyher, Phys. Rev. Lett. **61**, 1009 (1988).

[16]G. Mosurkewich, Phys. Rev. B **42**, 11 183 (1990); the elastic anomalies associated with the depinning of the CDW have recently been reviewed by G. Mozurkewich in *Perspectives in Physical Acoustics*, edited by Y. Fu, R. K. Sundorfs, and P. Suntharothok-Priesmeyer (World Scientific, Singapore, 1992).

[17]P. A. Littlewood and T. M. Rice, Phys. Rev. Lett. **48**, 44 (1982); P. A. Littlewood and R. Rammal, Phys. Rev. B **38**, 2675 (1988).

[18]A. S. Nowick and B. S. Berry, *Anelastic Relaxation in Crystalline Solids* (Academic, New York, 1972).