Effect of uniaxial stress on the transport properties of $TaSe_3$

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We have measured the effect of elastic, uniaxial stress on the resistance R, the thermoelectric power (TEP), and the superconducting transition temperature T_c of $TaSe_3$. We find that there is a nearly discontinuous change in R and in the TEP at a stress σ of about 1.2 GPa at 20 K. In this change R increases by several orders of magnitude, while the TEP changes sign and increases by several orders of magnitude. At higher temperatures this change becomes less pronounced and occurs over a larger range of σ. We suggest that this change is due to a Fermi-surface topology change, a structural phase transition, or a charge-density-wave transition. We found no evidence for a metal-to-nonmetal transition just above the normal-superconducting transition at T_c.

I. INTRODUCTION

The transition-metal chalcogenides have been found to exhibit a number of interesting transitions.[1] Most are metallic at high temperatures and transform to a semiconducting, charge-density-wave, spin-density-wave, or superconducting state at lower temperatures. $TaSe_3$, however, remains a normal conductor for temperatures down to about 2.1 K,[2] where some samples become superconducting. The temperature T dependence of the resistance R of $TaSe_3$ shows a negative value of $\partial^2R/\partial T^2$ for $T>10$ K, as in Fig. 1, whereas $\partial^2R/\partial T^2 \geq 0$ for most metals.

We have studied the effect of uniaxial stress on the properties of several transition-metal trichalcogenides because they support high stresses which can have large effects on the transitions that occur in these compounds. In this paper we report the effect of stress on the properties of $TaSe_3$.

II. EXPERIMENTAL

Samples were grown by placing stoichiometric amounts of Ta (99.98% purity, Johnson Matthey) and Se (99.999% purity, Johnson Matthey) with a slight excess of Se in a quartz tube and heating for six to seven weeks. The center of the furnace was held at about 1000 K and a gradient of about 2 $K\,cm^{-1}$ was established. Samples of higher perfection were obtained from Grüner's group at UCLA. The crystal structure of $TaSe_3$ is monoclinic, with cell dimensions $a=1.0402$ nm, $b=0.3495$ nm, $c=0.9829$ nm and $\beta=106.26°$.[3] The samples grew in whiskerlike form with the b axis along the whisker.

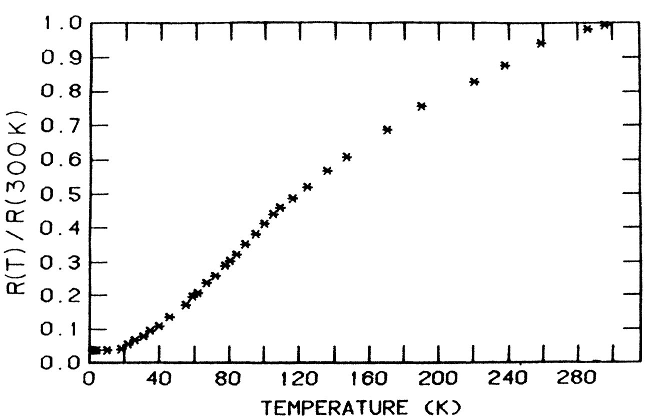

FIG. 1. Normalized resistance $R(T)/R(300\text{ K})$ versus temperature at $\sigma=0$.

The samples were mounted on a stressing device described elsewhere[4] using silver paint for the four electrical contacts. Samples were selected for small cross section (1–10 μm^2) and visual perfection, which seemed to correlate with high mechanical strength. A typical sample had length 2–3 mm. The cross-sectional area of the samples was calculated using $\rho(300\text{ K})=5\times10^{-4}\ \Omega\,\text{cm}$.[5] The residual resistivity ratio, $\mathscr{R}=R(300\text{ K})/R(4.2\text{ K})$, varied from 28 to 157. The inner (potential) contacts also served as mechanical grips. Since the samples sometimes pulled through these grips, "five-minute" epoxy was laid between the potential and current contacts on each end of the sample. Such samples did not slip through the mechanical grips.

The sample was placed in a variable temperature Dewar in which T could be controlled within 0.1 K between 1.5 and 300 K. At each T of interest, the resistance R or the thermoelectric power (TEP) was measured as a function of stress σ. While T was being changed, the sample was bowed to prevent accidental damage. The zero of σ was taken to be the point at which R changed by 0.1%. The effect of stress on R and the TEP was found to be reversible and repeatable, hence σ was assumed to be elastic. The stress was calculated from the measured sample length and extension, assuming the stress to be linear in strain with a Young's modulus $Y\approx250$ GPa. Since Y has not yet been directly measured, we assumed it to be approximately the same as that of $NbSe_3$.[6] This is in accord with the compressibility K measurements on $TaSe_3$ of Yamaya and Oomi,[7] who found $K_a=12\times10^{-4}\ \text{kbar}^{-1}$, $K_b=5.4\times10^{-4}\ \text{kbar}^{-1}$, and $K_c=9.6\times10^{-4}\ \text{kbar}^{-1}$. If it is assumed that the shear components of the compressibility tensor s_{12} and s_{23} are small compared to s_{22}, then Yamaya and Oomi's results give $Y_b=1/s_{22}=1/K_b=190$

TABLE I. Sample characteristics for resistance-stress measurements.

Sample	$\mathscr{R}$	$R(\Omega)$ ($T=296$ K, $\sigma=0$)	l (mm)	$\frac{R(296\text{ K})}{l}$ (Ω/mm)	T_P (K)	$\Delta R(\sigma)/R$[a] $T=296$ K	$T=100$ K	$T=77$ K	$T=50$ K	$T=22$ K
1	30	875	1.45	603.4	38	1.0	40.3	93.6	199	559
2	29	1378	1.72	801.1	31	1.6	54	104	210	646
3[b]	28	2943	1.98	1486.4	77		30	42	53	160
4	28	830	2.05	404.8	25	1.47	35	90	201	698
5	111	710	2.01	353.2	79	1.6	52.4	79.2	142	192
6	131	739	1.98	373.2	< 1.6	1.52	43	170	746	9500
7	136	3167	1.95	1624.1	4	1.57	49.8	147	571	5200
8[c]	157	80	1.65	48.5	47					

[a]Sample taken at $\sigma=2.5$ GPa.
[b]Sample broke at $T=120$ K.
[c]The only sample to exhibit superconductivity.

kbar as a lower limit.

Because of small thermal expansions due to thermal gradients in the apparatus, T could not be changed at constant σ. Instead, the T dependence of R at constant σ was extracted from the R-σ measurements made at constant T.

Thermal contact to the sample was made through the same copper wires through which electrical contact was made. A copper heat sink that was in thermal contact with two of these copper wires was electrically heated to raise its temperature several degrees K above another copper heat sink at the other end of the sample. Also in thermal contact with the copper heat sinks were the junctions of a copper versus Au 0.07 at. % Fe thermocouple which was used to measure the temperature difference between the ends of the sample during the thermopower measurements. This temperature difference was about 2 K, but varied somewhat with the absolute temperature.

III. RESULTS

A. Resistance

Table I gives a summary of characteristics of the samples used in these experiments.

The room-temperature piezoresistance of $TaSe_3$, typical of all samples, is shown in Fig. 2(a). The large value of $\partial(\ln R)/\partial\sigma$ is unusual, as is the nonlinearity of the R-versus-σ relation. At lower temperatures, the piezoresistance becomes even larger and the nonlinearity more pronounced. Note the scale changes on the vertical axes in Figs. 2(b) and 2(c). At temperatures below 20 K, the form of the R-versus-σ curve is essentially independent of temperature and has a sharp increase in the resistance at $\sigma \approx 1.2$ GPa. Evidently a transition of some form occurs at this stress, a transition which is smeared out at higher temperatures. We have taken the stress at which $\partial(\ln R)/\partial\sigma$ is a maximum to be the boundary stress σ_c between two states of the sample, the low-stress state S_l in which the resistance is low and metallic, and the high-stress state S_h in which the resistance is high and nonmetallic.

The transition is completely reversible: the R-versus-σ curves were the same for increasing and decreasing σ and could be repeated as many times as desired. No evidence of hysteresis was found, nor was any nonlinear conductivity found to within one part in 10^3 for fields as high as 100 V/m in the low-stress state and 5000 V/m in the high-stress state.

The value of the resistivity ρ in the high-stress state ρ_h is sample dependent, changing by a factor of 60 from sample to sample. There is a tendency for samples of high residual resistivity ratio ($\mathscr{R}$) to have a large ρ_h but a

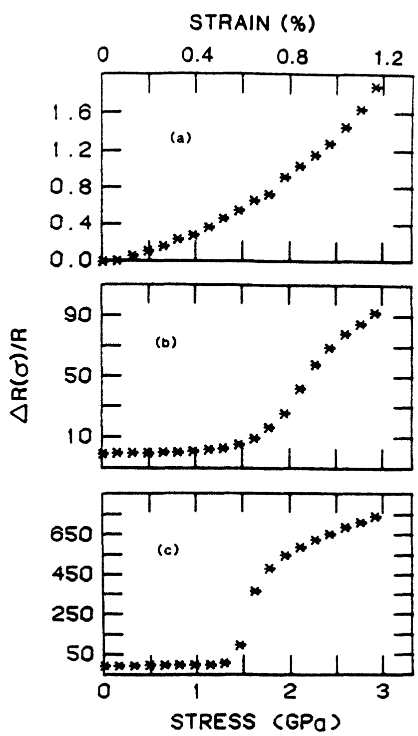

FIG. 2. Differential resistance $\Delta R(\sigma)/R$ versus stress for sample 4 at (a) $T=296$ K, (b) $T=84$ K, and (c) $T=22$ K.

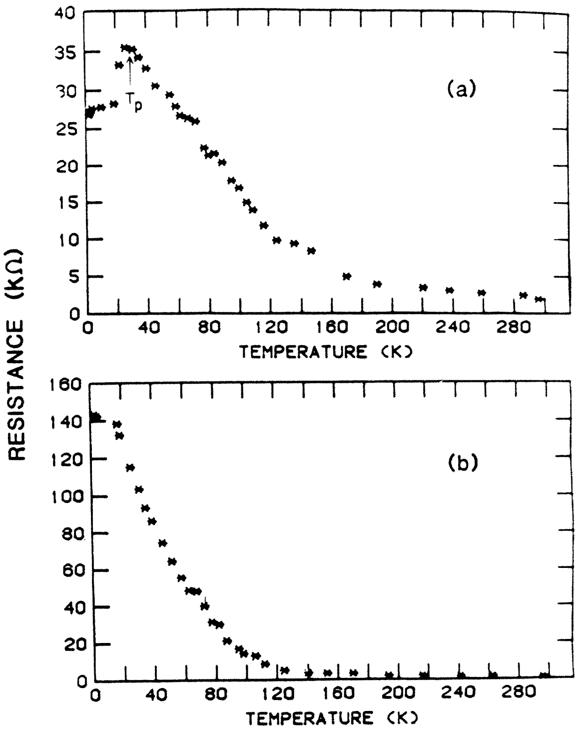

FIG. 3. Resistance at high stress $R(\sigma > \sigma_c)$ versus temperature for (a) sample 4 at $\sigma = 2.59$ GPa showing a resistance maximum, and (b) sample 6 at $\sigma = 2.53$ GPa showing no maximum.

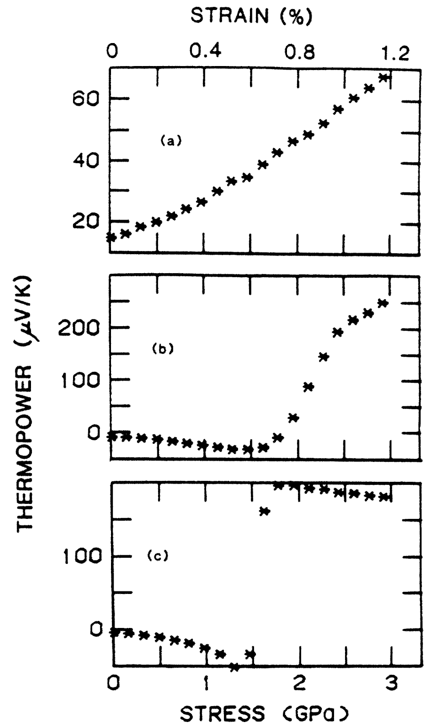

FIG. 5. Thermoelectric power versus stress for sample 4 at (a) $T = 296$ K, (b) $T = 84$ K, and (c) $T = 22$ K.

large $\mathscr{R}$ does not guarantee a large ρ_h. Evidently the sample properties that affect the $\mathscr{R}$ are not identical to those which affect ρ_h. The range of stress over which the transition occurs appears to be independent of sample.

The temperature dependence of the resistance in the high-stress state shows two types of behavior (Fig. 3). As T is lowered, R either (a) rises to a maximum and then decreases, or (b) rises monotonically reaching no maximum to the lowest T measured, 1.6 K. Type-b behavior occurred in two samples with $\mathscr{R}$ of 131 and 136. Type-a behavior was observed in samples with $30 \ll \mathscr{R} \ll 157$. Just below the temperature at which the resistance began to rise, the resistance showed thermal activation. Activation temperatures could only be imprecisely determined, but were roughly consistent with the temperatures at which the resistance began to rise.

The boundary stress σ_c varies with T as shown in Fig. 4.

B. Thermoelectric Power (TEP)

The TEP was linear in the temperature difference measured across the sample for all temperatures and stresses in these measurements. The TEP at 300 K increased from ~ 10 μV/K at zero stress to ~ 60 μV/K at $\sigma = 3$ GPa (Fig. 5). At lower T it is clear that the transition in the resistance is accompanied by a similar transition in the TEP, with the same σ_c. At 22 K the TEP, negative at zero stress, becomes more negative with increasing stress

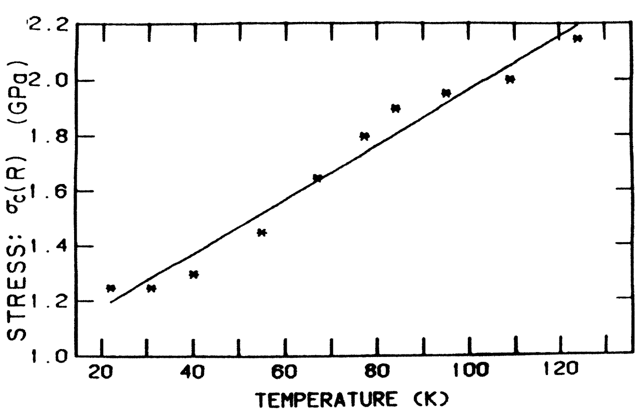

FIG. 4. Critical stress σ_c for high-resistance state versus temperature. The slope is $(9.8 \pm 0.6) \times 10^{-3}$ GPa/K.

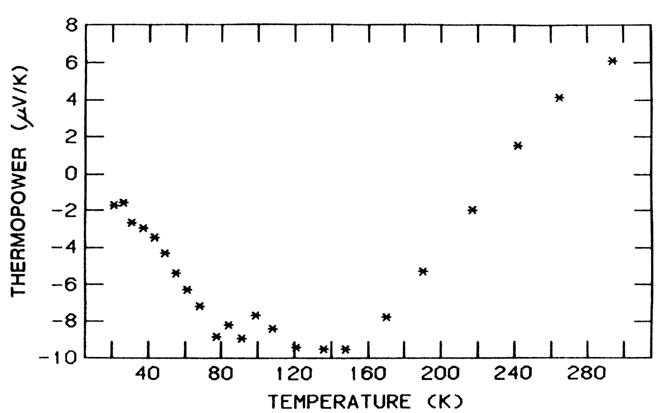

FIG. 6. Thermoelectric power versus temperature at $\sigma = 0$.

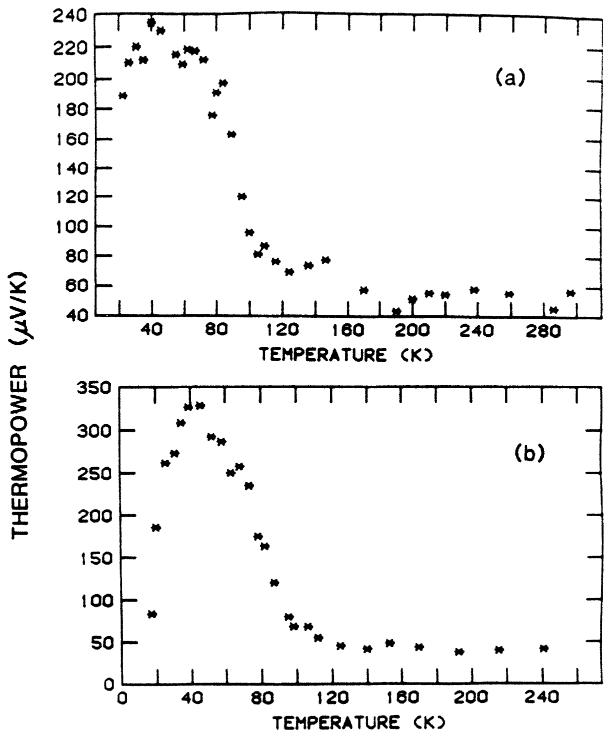

FIG. 7. Thermoelectric power at high stress, $\sigma > \sigma_c$, versus temperature for (a) sample 4 at $\sigma = 2.53$ GPa, and (b) sample 6 at $\sigma = 2.53$ GPa.

until a narrow region around 1.5 GPa it goes from -50 μV/K to $+200$ μV/K. As T was decreased, the TEP at zero stress decreased to a minimum of ~ -10 μV/K at 140 K (Fig. 6), while at higher stress the TEP increased as T decreased (Fig. 7).

The temperature dependence of σ_c obtained from the TEP gives essentially the same results as that obtained from R. The slopes $\partial\sigma_c/\partial T$ obtained from TEP and R are, respectively, $8.7 \pm 1 \times 10^{-3}$ GPa/K and $9.8 \pm 0.6 \times 10^{-3}$ GPa/K. The TEP results are nearly sample independent.

C. Superconductivity

Of the many samples checked down to 1.6 K, only two samples were superconducting, and we were able to stress only one of these. It was unlike other samples in that it had a much larger cross-sectional area (determined from R/l measured at 300 K). This sample was not stressed before its temperature was reduced below the superconducting transition temperature T_c. It was slightly bowed as mentioned above. The resistance did not go to zero in the superconducting state down to $T = 1.6$ K, but rather $R(1.6\text{ K})/R(4.3\text{ K}) = 0.1$. After the sample had been stressed the first time, this ratio was 0.4, as shown in Fig. 8. A similar result has been found in the pressure experiments of Yamaya *et al.*[8] Successive stressing produced no further changes. The resistive transition was reproducible with σ and T changes thereafter.

As shown in Fig. 8, the effect of uniaxial stress along the growth axis is to broaden the transition, and increase

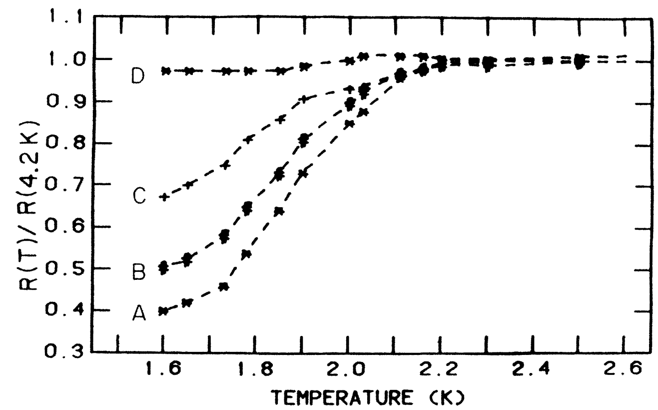

FIG. 8. Normalized resistance $R(T)/R(4.2\text{ K})$ versus temperature showing the effect of stress on the superconducting transition. A, $\sigma = 0$; B, $\sigma = 0.6$ GPa; C, $\sigma = 1.0$ GPa; and D, $\sigma = 2.5$ GPa.

the resistance at lower temperatures, with no apparent change in the onset temperature within our precision of 50 mK at 2.5 GPa. Yamaya and Abe[9] found $\partial T_c/\partial\sigma = (8 \pm 1) \times 10^{-2}$ K/GPa for stress along the sample axis and reported no irreversible behavior. Their largest stress was ~ 0.44 GPa. Yamaya *et al.*[8] found $\partial T_c/\partial P = -0.75 \pm 0.03$ K/GPa.

Tajima and Yamaya[10] have reported an anomalous resistance increase at low current densities in some of their samples just above T_c. We lowered our current densities to 1 A/m^2 to check for this anomaly, at which density an effect sufficient to double the resistance was observed by Tajima and Yamaya, but we found no anomaly. Others reporting no anomaly are Harker *et al.*[11] with $J = 0.1$ A/m^2, and Yamaya *et al.*[8] with $J = 0.01$ A/m^2.

IV. DISCUSSION AND CONCLUSIONS

Three types of transition are suggested by these results for $TaSe_3$: (a) charge-density-wave (CDW) transition, (b) an electron transition of the Lifshitz type,[12] and (c) a structural transition. Any of these transitions could lead to R decreasing exponentially with increasing T. CDW transitions are observed in this family of compounds at $\sigma = 0$, notably in $NbSe_3$ and TaS_3. The R-versus-T curve for $TaSe_3$ ($\sigma > 1.5$ GPa) is similar to that of TaS_3 except in the region with $T < 10$ K, in which dR/dT for TaS_3 saturates.[13] However if the transition we observe is a CDW transition, the critical electric field for CDW motion is much higher than in TaS_3,[14] or $NbSe_3$.[15] Furthermore, uniaxial stress along the chain axis lowers T_c for almost all CDW transitions,[16] presumably by increasing the three-dimensional character of the material as the interchain separation decreases. Thus we would not expect stress to cause a CDW transition. There is, however, some evidence for an additional CDW transition in TaS_3 at high stress.[17] Until diffraction experiments under stress are performed, superlattice formation cannot be ruled out.

In a Lifshitz transition there is a Fermi-surface topology change, but no structural change. For $TaSe_3$, this change would be induced by stress (as in the experiment of Overcash *et al.*[18]). The transition would cause at least a portion of the Fermi surface to disappear, leaving either a semimetal with a very few electrons (type-a resistive behavior), or a semiconductor with a very small band gap (type-b resistive behavior). Whether the sample was semimetallic or semiconducting might depend sensitively on the sample properties. This would explain the large changes in resistance during the transition as well as the sample dependence of dR/dT at low temperatures.

The transition-metal trichalcogenides occur in many allotropes, with the difference between allotropes of a given compound often being a slight rearrangement of the chains of metal trichalcogenide prisms, such as the difference between orthorhombic and monoclinic TaS_3. It may be that stress along the chain axis favors a new arrangement of the chains in $TaSe_3$ This could lead to a new electronic structure that is a semimetal with few electrons or a semiconductor with a very small gap as in the Lifshitz transition. Such a structural phase transition usually displays hysteresis, either because it is a first-order transition or because it has a martinsitic character. We observed no hysteresis. Again, diffraction experiments under stress could detect such a transition.

We cannot give a definite answer as to what type of transition occurs in $TaSe_3$. Perhaps low-temperature magnetoresistance measurements now in progress or diffraction experiments under stress will give a definite answer.

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