Stress-induced metal-to-nonmetal transition in the quasi-one-dimensional superconductor $Tl_2Mo_6Se_6$

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We report a study of the effect of uniaxial stress on the electrical properties of $Tl_2Mo_6Se_6$. Stress suppresses the superconducting transition temperature and induces a metal-to-nonmetal phase transition. Nonlinear *I-V* characteristics and broadband noise measurements in the semiconducting phase suggest that the transition may be due to the formation of a charge-density or spin-density wave. A transition temperature $T_p=15\pm3$ K and energy gap $E_g=57$ K are deduced from resistance measurements in the nonmetallic state.

INTRODUCTION

The compounds with the general formula $M_2Mo_6X_6$ (M=Tl, In, Na, . . . , etc.; X=S, Se, Te) are highly anisotropic quasi-one-dimensional conductors.[1] Their structure can be thought of as chains of $(Mo_3X_3)_\infty$ running along the hexagonal c axis separated by the M element.[2] Some of these compounds exhibit a metal-semiconducting phase transition. There is speculation that these transitions are due to a fluctuating Peierls gap that is uncorrelated from one Mo chain to another.[3] $Tl_2Mo_6Se_6$ is unique among these $(Mo_3Se_3)_\infty$ chain compounds in that it is the only one found to be superconducting and the T_c is rather high, between 3 and 7 K.[4]

$Tl_2Mo_6Se_6$ samples are classified as type A or type B depending upon the temperature T dependence of their resistance R[4]. Type-A samples show a decreasing R as T is reduced to T_c, whereas type-B samples show a minimum in R near $T_m=20$ K followed by a maximum in R just above T_c. The material is highly anisotropic, as reflected by the resistivity ratio ($R_\parallel/R_\perp=10^3$), the anisotropy of the superconducting critical magnetic field H_{c2} (Refs. 4 and 5) and in polarized optical reflectance spectra.[6] The calculated Fermi surface consists of two parts; sheets and ellipsoids. The nearly planar sheets are perpendicular to the chain axis c near π/c from Γ to A. The ellipsoids are centered at A and their existence is due to the energy overlap of the a_2 band at $\pi/2$ and the e band at A.[7] It is believed that these electron pockets protect the structure from a Peierls distortion and are responsible for the superconductivity. Nohl *et al.* predicted that stress might change the occupancy of these pockets and lead to a Peierls distortion and the formation of a charge density wave (CDW).[7]

We present experimental results showing that stress indeed does suppress T_c and induces a metal-nonmetal phase transition. We also present nonlinear *I-V* characteristics and broad-band noise results which suggest that a sliding CDW or SDW might indeed occur.

EXPERIMENTS AND RESULTS

Needlelike samples of typical dimensions $2\times0.04\times0.01$ mm^3 are mounted on a pulling device described elsewhere.[8] This puller applies a uniaxial stress along the chain axis of these samples, but the axial component of the strain ϵ is calculated from a measured voltage V_p proportional to the motion of the puller. The stress σ is inferred from ϵ and Young's modulus $Y=400\pm40$ GPa.[9] Thus a 1% strain corresponds to $\sigma=4.0$ GPa.

The temperature T of the unstressed sample is slowly lowered at an average rate of 1 K/min, while a microcomputer acquires the R vs T data. At each temperature the sign of the current is reversed to eliminate errors due to thermal emfs. We use these R vs T data to characterize the quality and type of sample. The position of zero strain ($\epsilon=0$) is determined by moving one end of the sample with respect to the other end until a resistance change is detected. In this process the sample goes from being bowed (R constant and ϵ undefined) to being stressed (R changes and $\epsilon>0$). The strain is taken to be zero at the first detectable change in R. The zero is determined this way at each temperature, since differential contractions in the apparatus shift the zero as T is changed. At constant sample temperature these shifts are negligible. Because R is quadratic in ϵ (σ) in these samples, the zero of ϵ is particularly difficult to determine and is given with a precision of 0.05%. The inset in Fig. 1 shows a typical R vs ϵ curve at low temperatures.

Figure 1 shows a typical result of the effect of ϵ (σ) on the R vs T curves, ln(R) is shown on the ordinate axis due to large resistance change. For both the stressed and the unstressed samples, there are two regimes: a metallic

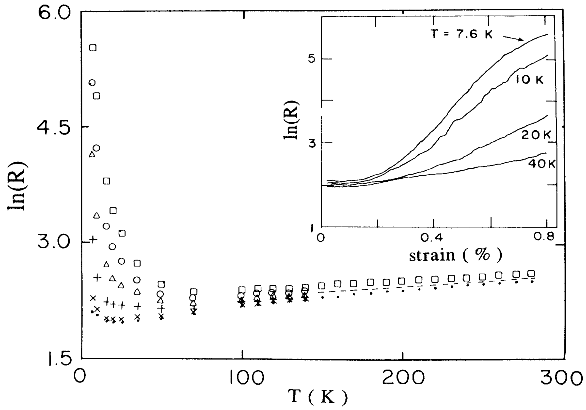

FIG. 1. The temperature dependence of the resistance vs strain of a type-B sample. Note the logarithm scale on the R axis. The strain ϵ is given by $\epsilon=0$ for dots, 0.15 for crosses, 0.30 for plus signs, 0.45 for triangles, 0.6 for circles, and 0.75 for squares. The isothermal $\ln(R)$ vs ϵ curves are shown in the inset: the number next to each curve indicates the temperature.

regime ($dR/dT>0$) at high temperatures and a nonmetallic ($dR/dT<0$) regime below a temperature $T_m(\epsilon)$ at which $R(\epsilon,T)$ is a minimum. Stress increases the resistance at all temperatures investigated, with the relative change $\Delta R/R_0$ increasing at lower temperature. The linear behavior of $R(\epsilon,T)$ vs T in the metallic regime remains for all ϵ. In the nonmetallic regime a plot of $\log_{10}[R(\epsilon,T)/R_0]$ vs $1000/T$ as in Fig. 2 shows a linear relationship for $\epsilon<0.75\%$. A deviation from linearity with a tendency toward saturation at low temperatures ($T<20$ K) is observed for higher strain. The inset in Fig. 2 shows a plot of $d\{\ln_{10}[R(\epsilon,T)]\}/d(1000/T)$. A rather broad peak centered around $T_p=15\pm3$ K is observed. Increasing ϵ to a maximum of 1.1% does not affect T_p but the peak becomes more pronounced. For $\epsilon<0.75\%$

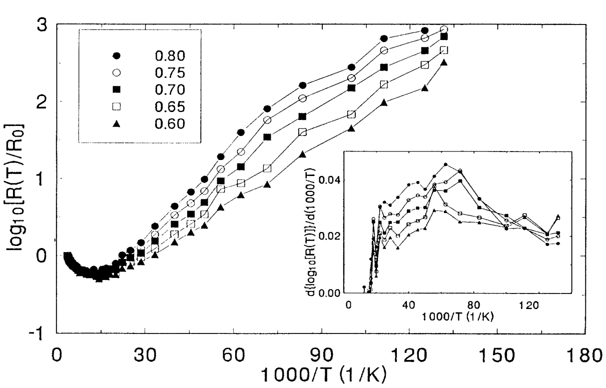

FIG. 2. Plot of $\ln_{10}[R(\epsilon,T)/R_0]$ vs $1000/T$. The legends are given in the box; the numbers refer to the values of ϵ in %. The same legends hold for the inset. The inset shows plots of $d\{\ln_{10}[R(\epsilon,T)]\}/d(1000/T)$ for different values of ϵ. A broad peak is observed at $T=15$ K. All the curves for $\epsilon>0.6\%$ converge to a stress independent value of $E_g=57$ K at $T<10$ K.

an energy gap $E_g'(\epsilon)$ can be estimated from the linear regime of the $\ln(R/R_0)$ vs $1000/T$ plot. E_g' and $T_m(\epsilon)$ are both approximately linear functions of ϵ. The maximum value of the E_g' (at the highest value of ϵ risked in this sample, $\epsilon=0.8\%$) is $E_g'/k=80$ K, where k is Boltzmann's constant, and its rate of change with ϵ is $\Delta(E_g'/k)/\Delta\epsilon=122$ K/% ($T_m=85$ K at $\epsilon=0.8\%$ and $\Delta T_m/\Delta\epsilon=88.3$ K/%). The last two results are obtained on a type-B sample. Type-A samples give similar results. However, these results are both sample dependent, varying approximately by a factor of 2 between type-A and type-B samples Similarly a gap E_g can be estimated for $T<15$ K and for $\epsilon>0.6\%$. The peak value of E_g is 115 K obtained for $\epsilon\approx1.1\%$. However, the inset in Fig. 2 suggests that for $T<10$ K E_g is independent of ϵ within our experimental accuracy, provided that $\epsilon>0.50\%$.

To study the effect of σ (ϵ) on T_c, T is controlled at about 7.5 to 8 K and the desired ϵ applied. The temperature is then slowly lowered below T_c at a rate of 1 K/min while R and T are monitored with a microcomputer. We found that the change in ϵ due to differential contraction in the pulling apparatus is negligible for this small temperature excursion. The results both for type-A and type-B samples are shown in Fig. 3. Whereas T_c for type-B samples decreases monotonically with stress (solid circles in the figure), type-A samples exhibit a rather peculiar behavior (open circles). The inset shows the resistive transition of a type-A sample under different values of ϵ. For $0<\epsilon<0.4\%$, T_c increases smoothly to a maximum of 7 K. The transition becomes narrower (the width of the transition is taken between 10% and 90% of the change in resistance). T_c drops sharply above $\epsilon\approx0.4\%$ and the transition broadens. For $\epsilon\geq0.6\%$ the material is not superconductivity down to the lowest measured T (2.2 K) and $dR/dT<0$.

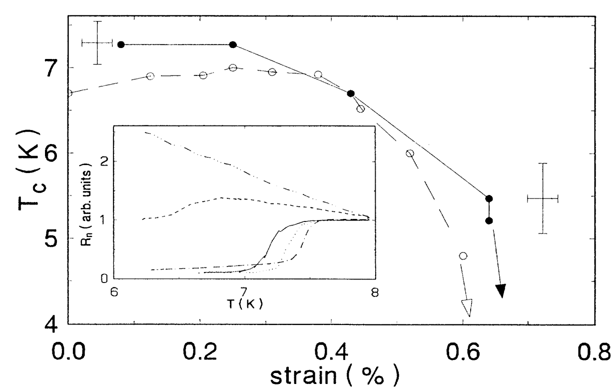

FIG. 3. The effect of ϵ on the T_c of two samples. T_c for type-B samples (solid circles), decreases monotonously. T_c for type-A samples (open circles), exhibits an initial rise to a broad maximum before it decreases steeply. The inset shows the effect of ϵ on the resistive transition of a type-A sample. The value of ϵ in % is 0.00, 0.12, 0.38, 0.46, 0.52 for the solid, the dotted, dashed-dotted, short-dashed, and dot-dot-dot-dashed lines, respectively. The resistance $R_N=R(\epsilon,T)/R(\epsilon,\ 7.5)$ is shown vs T.

The stress-induced metal-nonmetal phase transition and the suppression of superconducting in this highly anisotropic compound poses the crucial question of the competition between CDW or SDW and superconductivity. A structural search for a Peierls distortion (CDW) or magnetic resonance measurement (SDW) will be needed to definitely resolve the presence of a CDW or SDW. However, the search for nonlinear conduction and other coherent responses typical of a DW motion (narrow-band and broadband noises, AC response studies, and memory effects[1–13]) should give an initial clue. Our initial results along these lines show that in the nonmetallic state the material exhibits nonlinear *I-V* characteristics and broadband noise as in Fig. 4. Differential conductivity measurements with a lock-in amplifier set up for broadband detection reveals the existence of two distinct threshold fields, E_1 and E_2, at 6 K and $\epsilon=0.2\%$ (this value of ϵ might have been underestimated due to the error in the determination of the $\epsilon=0$ position below T_c). Above $E_1=12$ V/m, nonlinear conductivity is observed. Above $E_2=50$ V/m broadband noise is observed. To rule out heating effects we have also done pulse *IV* measurements. We used a pulse width of 10 μs and a period of a few hundred ms. A sharp threshold field of about 75 V/m for nonlinear conductivity (typical of CDW depinning) is observed at 4.2 K under a strain of 0.3%. There is a strong sample dependence in the *I-V* characteristics. *I-V* curves similar to those observed in $K_{0.3}MoO_3$, TaS_3, and $(TaSe_4)_2I$ at low temperatures and attributed to a motion of a rigid CDW without damping[14] (Frohlich superconductivity) are also observed. Preliminary results on the stress dependence of the threshold field show that E_1 increases with stress, as in the upper transition of $NbSe_3$.[15] Our attempts to observe NBN were not successful. At the high strain, at 4.2 K and in a frequency bandwidth from 10 Hz to 50 MHz the NBN amplitude was below a baseline of 40 nV.

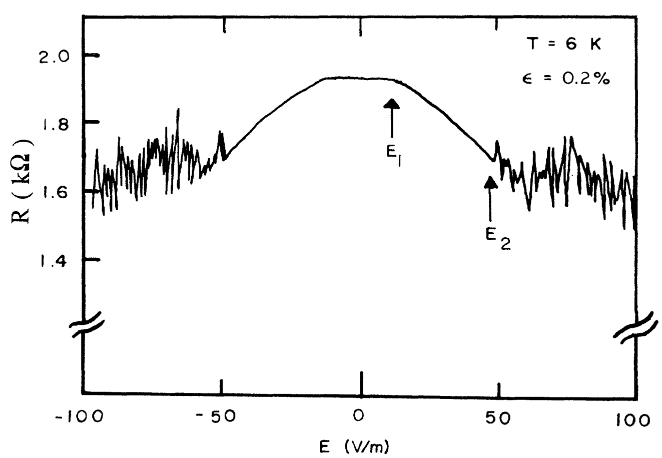

FIG. 4. The differential resistance of a sample under stress is shown on the ordinate. The two threshold fields $E_1=12$ V/m and $E_2=50$ V/m, corresponding to the onset of nonlinear differential conductance and the sudden occurrence of a broadband noise, respectively, are shown by the arrows. The data were taken on a type-*B* sample with a resistance of 1.9 $k\Omega$ at $T=6$ K and $\epsilon=0.2$.

DISCUSSION AND CONCLUSION

Previous studies of the effect of uniaxial stress on low dimensional conductors have led to a rather complex set of results. In $NbSe_3$ and *o*-TaS_3 (Ref. 15) stress is known to reduce the CDW transition temperatures T_p. In *m*-TaS_3, the lower transition temperature T_{p2} decreases with stress and the upper transition temperature T_{p1} initially increases with stress but decreases at higher stress.[16] A possible enhancement of the three dimensionality of the materials by virtue of an increased interchain coupling has been suggested as a possible mechanism. The situation is different in $TaSe_3$ (Ref. 17) and in $ZrTe_5$ and $HfTe_5$.[18] Here stress induces a *metal-nonmetal* transition. The underlying mechanism for this transition is not very clear. A Lifshitz transition,[19] a CDW transition, or a structural phase transition are possible candidates. A structural phase transition cannot be ruled out, but the observed transition is unlikely to be first order as no superheating or supercooling was observed. The quasi-one-dimensional structure seems to favor a CDW transition, but it is difficult to conclude decisively because of the absence of a structural study showing a lattice distortion and the failure to observe a NBN associated with the nonlinear conductance.

The results in the $Tl_2Mo_6Se_6$ compound are similar to $TaSe_3$, $ZrTe_5$, and $HfTe_5$ (Ref. 18) except for the nonlinear electrical conductivity, thus the two mechanisms, Lifshitz or CDW transition, can be forwarded and may not be contradictory in this compound A Lifshitz transition may act at low stress, with a progressive depletion of the electron pockets at the zone boundary without leading to any structural change. This mechanism may be responsible for part of the rise in the resistance of the metallic phase. As predicted from band-structure calculations,[7] a change in the occupation of the electron pockets might trigger a Peierls transition leading to the observed nonlinear conductance and noise results due to DW motion. Thus a Lifshitz transition and a Peierls transition might go hand in hand. This same mechanism would reduce the density of states at the Fermi surface N_0, which would be strongly affected by the presence of an electron pocket, and thus account for the stress-induced suppression of T_c in the type-*B* sample.

The initial rise in T_c of type-*A* samples complicates the situation. The reason why type-*A* samples should behave differently is not clear, but it is possible that N_0 may rise before falling as the electron pockets are being depleted. One can think of an even more naive picture. Stress can (as in $NbSe_3$) enhance the interchain coupling and the 3D character of the sample. The competition between a Lifshitz-transition reduction of the density of electrons at the Fermi surface and the enhanced interchain coupling can result in an electron-phonon coupling constant that goes through a maximum and, according to McMillan's equation for the T_c of isotropic superconductors, this might lead to an initial rise in T_c. It should be noted that hydrostatic pressure either suppresses T_c (Ref. 20) or is without any effect[5] and that increased dimensionality might not necessarily lead to an increase in T_c.

The phase diagram shown in Fig. 5 summarizes our interpretation of the experimental results. For type-A samples we suggest a reentrant normal-superconducting-DW phase diagram. The nature of the DW state is yet to be determined. Type-B samples would follow a similar diagram without the reentrant characteristics.

In conclusion, we have presented experimental data showing that stress induces a metal-nonmetal transition in $Tl_2Mo_6Se_6$. Our results suggest that the nonmetallic state could be the CDW state as predicted by Nohl *et al.*[7] For $\epsilon > 0.65\%$ a Peierls transition temperature $T_p = 15$ K is estimated. T_p is not affected by further stress and the energy gap E_g saturates to a stress independent value of approximately 57 K giving a ratio E_g/kT of 3.4. Nonlinear electrical conduction and broadband noise results indicate that the nonmetallic state is most likely a CDW or SDW state. Further work in structural study of the samples under stress and at low temperatures and/or search for narrow-band noise will be required to confirm these results. If confirmed, these results may give a clue to the metal to nonmetal transition observed in the general family of $M_2Mo_6X_6$ compounds. The study of the superconducting transition temperature of type-A samples provides a rather interesting CDW-SC-normal phase diagram.

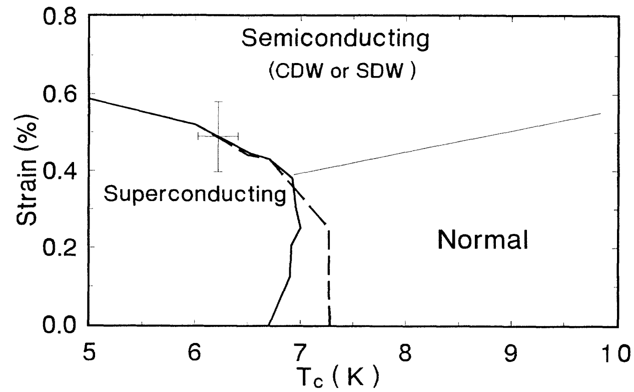

FIG. 5. The suggested phase diagram. The solid lines show the reentrant normal-superconducting-nonmetallic (CDW or SDW) character of type-A samples. The broken lines show the behavior of type-B samples.

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