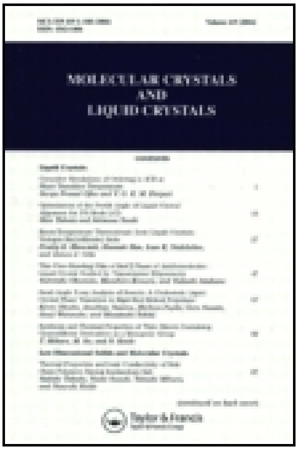

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The Electrical Conductivity of TTF-TCNQ Under Pressure

J. R. Cooper [a], D. Jérome [a], M. Weger [a] & S. Etemad [b]

[a] Laboratoire de Physique des Solides, Université Paris-Sud, 91405, Orsay, France

[b] I.B.M. Thomas J. Watson Research Center, Yorktown Heights, N.Y., 10598, U.S.A.

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The Electrical Conductivity of TTF–TCNQ Under Pressure

J. R. COOPER, D. JÉROME and M. WEGER
Laboratoire de Physique des Solides, Université Paris-Sud, 91405 Orsay, France

and

S. ETEMAD
I.B.M. Thomas J. Watson Research Center, Yorktown Heights, N.Y. 10598, U.S.A.

We have measured the *b*-axis conductivity of three single crystals of the organic charge transfer salt TTF–TCNQ from 20–300 K under hydrostatic (gas) pressures of up to 6 kilobars in an attempt to clarify some results reported a year ago[1] which indicated that there were two transitions below 60 K in this compound and what is more important that one of them was strongly pressure (p) dependent. We will also briefly mention the effect of pressure in the metallic region at higher temperatures.

The samples were prepared at the I.B.M. Laboratory. Results for the d.c. conductivity at ambient pressure for samples prepared in the same way with similar electrical contacts have just been reported in two publications by Etemad, *et al.*[2,3] The results reported here were obtained using a 4 contact a.c. method at a frequency of 70 Hz and measuring currents from 1 to 5 μA R.M.S. A copper-constantan thermocouple mounted inside the pressure bomb was used to determine the sample temperature. On most runs its calibration was checked against an external platinum thermometer. Resistance-temperature curves were continuously displayed on an X–Y recorder while slowly cooling ($\sim$2 K/minute) or warming ($\sim$0.5 K/minute) the large pressure bomb containing the sample. This method is well suited for the detection of any anomalies in the $R(T)$ curve but there are rather large uncertainties in the sample temperature (at least $\pm$1 K). The main feature we notice in the R vs T curves shown in Figures 1 and 2 is that they possess anomalies at two temperatures $T_{HIGH} = 53 \pm 1$ K and $T_{LOW} = 38 \pm 1$ K in agreement with Ref. (1) and other more recent work.[3,4] Anomalies at these temperatures were observed in all samples investigated including one from

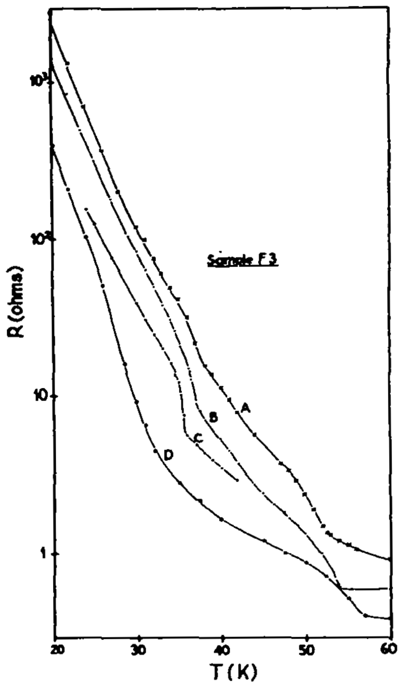

FIGURE 1 $R(T)$ curves for a TTF–TNCQ sample at: A, 100 bars; B, ambient pressure; C, 2 kilobars; D, 5 kilobars. The curves shown were recorded as T increased. Order of measurement BDCA.

another source.[5] As shown in Figures 1 and 2 the anomaly at T_{HIGH} manifests itself as a change in slope of R vs T, while that at T_{LOW} is s-shaped and in a certain pressure range almost a discontinuity in R vs T.

Neither of these two temperatures is strongly p-dependent as shown in Figure 3. T_{HIGH} increases slightly with pressure, in agreement with the work of Chu, *et al.*[6] while T_{LOW} decreases at approximately 1 K/kilobar. As a note of caution we should say that the transition at 5 and 6 kilobars were not sharp, perhaps because the helium was solid and if these two points are disregarded dT_{LOW}/dp could be as much as -2 K/kilobar.

In the region $20 < T < T_{LOW}$ the log R vs $1/T$ plots are straight within experimental error in agreement with more precise work at ambient pressure.[3] The activation energy $\Delta = 210 \pm 10$ K falls only slightly with pressure, 10 ± 4 K/kilobar but this leads to a large decrease in R.

For $T > T_{HIGH}$ R increases approximately as $A + BT^2$ and the pressure dependence comes mainly from the reduction in the T^2 term as shown in Figure 4, and in agreement with Ref. 6.

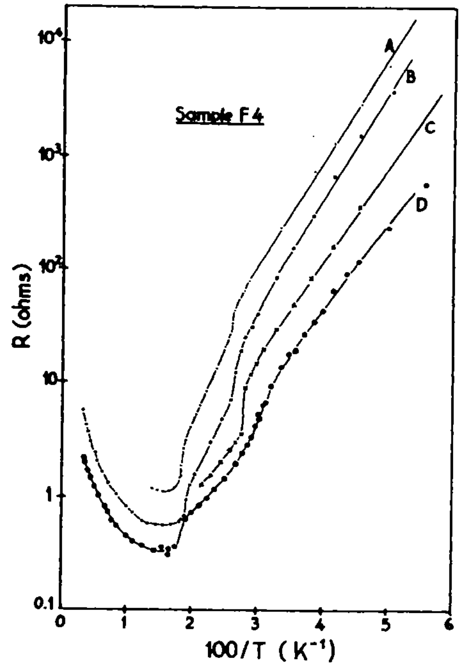

FIGURE 2 *R* vs. inverse temperature. A, 100 bars; B, 200 bars; C, 1.5 kilobars; D, 6 kilobars. Again recorded as *T* increased, measurement order CBDA.

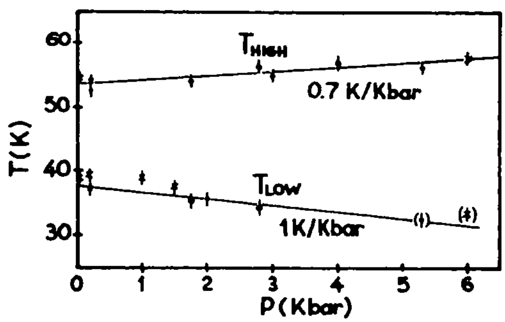

FIGURE 3 Transition temperatures T_{HIGH} and T_{LOW} versus pressure for samples F2 ○, F3 ● and F4 ×. Small differences between samples are probably due to errors in the temperature scale. The transitions at T_{LOW} were not sharp at 5 and 6 kilobars.

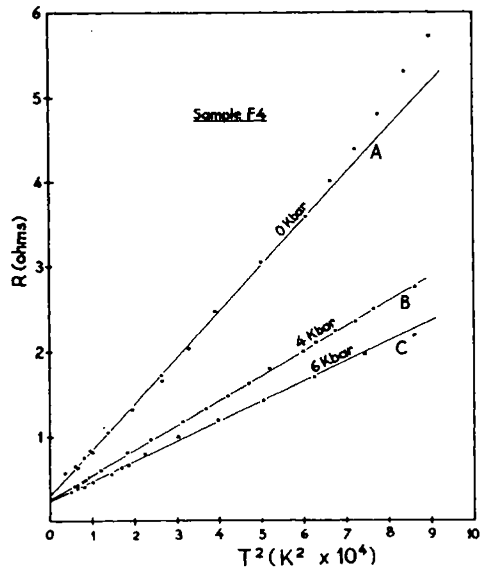

FIGURE 4 Examples of T^2 fits in the region 70–300 K.

From band structure calculations[7] and Youngs modulus measurements in TTF-TCNQ[8] it is estimated that the TCNQ bandwidth increases by 8–12 %/kilobar, i.e. 2–3 times more slowly than the measured increase in the conductivity. This is an indication that the conductivity is approximately proportional to E_F^2. Such behaviour could arise from electron–electron scattering, which would also account for the T^2 dependence,[2] or alternatively from electron–phonon scattering with a pressure independent el–phonon interaction.[1]

In the region $T_{\text{LOW}} < T < T_{\text{HIGH}}$ the behaviour of the resistivity is more complicated. For example both R and $1/R\ \mathrm{d}R/\mathrm{d}T$ are strongly reduced by relatively low pressures of 1.5–2 kilobars. In some samples $\mathrm{d}R/\mathrm{d}T$ even changed sign, (sample F2 and the sample of Ref. 1). There will undoubtedly be a renewed interest in this region because recent x-ray measurements show the existence of incommensurate one dimensional fluctuations, or a 1D Peierls distortion in this region, with the occurrence of a superstructure, i.e. 3D ordering around T_{LOW}.[9]

For the moment we are unable to understand the weak and opposite pressure dependences of T_{HIGH} and T_{LOW}. According to mean field expressions for the Peierls transition temperature $T_p = T_F \exp -1/\lambda$, and a much stronger p dependence would be expected unless there is an accidental balance between the contributions of T_F and of λ to the pressure dependence.

It will be interesting to make similar experiments on related compounds such as TSeF–TCNQ where there is only one transition at ambient pressure.[3]

References

1. D. Jérome, W. Muller, and M. Weger, *J. de Phys. Letters*, **35**, L77 (1974).
2. S. Etemad, T. Penney, E. M. Engler, B. A. Scott, and P. E. Seiden, *Phys. Rev. Lett.*, **34**, 741 (1975).
3. S. Etemad, T. Penney, and E. M. Engler, *Bull. Am. Phys. Soc.*, 496, March (1975) and to be published.
4. A. J. Berlinsky, T. Tiedje, J. F. Carolan, L. Weiler, and W. Friesen. *Bull. Am. Phys. Soc.*, 465, March (1975).
5. L. Giral and J. M. Fabre, from the University of Montpellier.
6. C. W. Chu, J. M. E. Harper, T. M. Geballe and R. L. Green, *Phys. Rev. Lett.*, **31**, 1441 (1973).
7. A. J. Berlinsky, J. F. Carolan, and L. Weiler, *Solid State Comm.*, **15**, 795 (1974).
8. M. Barmatz, L. R. Testardi, A. F. Garito, and A. J. Heeger, *Solid State Comm.*, **15**, 215 (1974).
9. F. Denoyer, R. Comes, A. F. Garito and A. J. Heeger, *Phys. Rev. Lett.* **35**, 445 (1975).