Pressure Dependence of the Metal-Insulator Transition in Tetrathiofulvalinium Tetracyanoquinodimethane (TTF-TCNQ)*

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(Received 15 October 1973)

Measurements of the conductivity of single-crystal TTF-TCNQ are reported for pressures 0–20 kbar and temperatures 20–273°K. The metal-insulator transition temperature increases about 1°K/kbar. The conductivity at 273°K increases by a factor of 4.5 at 20 kbar, while the peak conductivity near the metal-insulator transition remains independent of pressure. These results are discussed in terms of current models describing the properties of TTF-TCNQ.

The organic salt tetrathiofulvalinium tetracyanoquinodimethane (TTF-TCNQ) has been of great interest recently because it exhibits high room-temperature conductivity and metallic behavior down to about 60°K where it undergoes a metal-insulator (MI) transition.[1,2] The metallic state is quasi one-dimensional (1D) and results from strong π-orbital overlap along separate TCNQ and TTF chains.[3] The transition to the insulating state has been attributed to the Peierls instability in one dimension, although no direct evidence from x-ray or neutron scattering has been reported that supports this hypothesis. Measurements of the magnetic susceptibility,[4] thermopower,[5] microwave conductivity,[6] and optical reflectivity[7,8] have been reported recently and are consistent with the Peierls interpretation, but do not definitely rule out other possible causes of the MI transition.

We report here the first measurements of the pressure dependence of the conductivity σ in TTF-TCNQ. We find that the MI transition temperature T_{MI}, as signaled by a conductivity maximum, increases from 54 to 70°K for a 0–16-kbar pressure change. In addition, for the same pressure variation, the temperature dependence of σ changes dramatically above T_{MI}; the room-temperature σ increases by a factor of 4.5, whereas the conductivity at T_{MI} is hardly altered. These results imply that it is unlikely that superconducting fluctuations are responsible for the high conductivity in our sample and indicate that the MI transition is not of the Mott-Hubbard type as has been proposed[9] for N-methyl-phenazinium tetracyanoquinodimethane (NMP-TCNQ). Our results are consistent with the idea of a Peierls-like instability causing the MI transition, but suggest that interchain, and hence more than 1D, interactions are important, particularly near T_{MI}.

The temperature dependence of σ along the b axis of TTF-TCNQ single crystals was measured with an ac (20 Hz) four-probe technique using silver-paste contacts with the current leads covering the entire end of the sample. "Typical" atmospheric-pressure values of σ were found, i.e., $\sigma(300°K) = 200–600\ \Omega^{-1}\ cm^{-1}$, with $\sigma(60°K)/\sigma(300°K) \sim 10$ to 15. No evidence of anomalously large conductivity was found in any of the samples. Permutations of the leads were made during the σ measurements to ensure that the observed results were representative of bulk properties. Deterioration of sample conditions during temperature and pressure cycling could easily be determined by lead permutation and by unusual phase changes in the ac signal. A self-clamp technique[10] was employed to provide the hydrostatic pressure environment in a 1:1 mixture of n-pentane and isoamyl alcohol.[11] The pressure was changed near room temperature and was determined at low temperature by a superconducting Pb manometer situated next to the sample. The pressure difference between room temperature and low temperature (~7°K) is 1–2 kbar. Further details of the experimental techniques will be discussed elsewhere.

The variation of the resistivity ρ along the b axis with temperature and pressure is shown in Fig. 1. The runs above atmospheric pressure were made on the same sample and showed only slight hysteresis with cycling of the temperature. The atmospheric-pressure run was made on a different sample from the same batch. Measure-

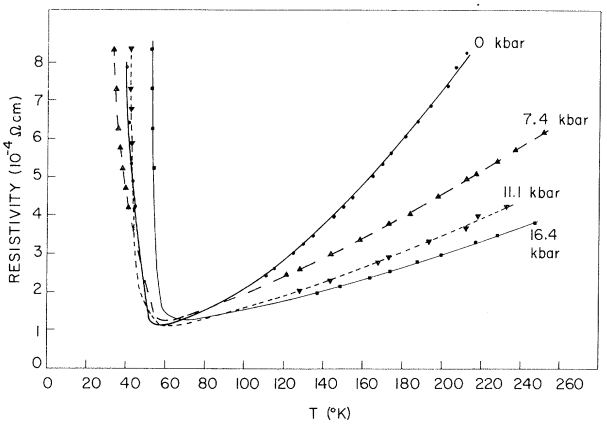

FIG. 1. Single-crystal TTF-TCNQ resistivity versus temperature for several pressures. The resistivity is measured along the crystallographic b axis. For clarity, the actual data points have been deleted near the MI transition.

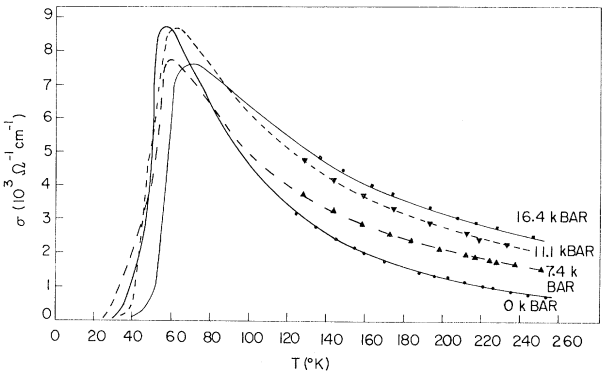

FIG. 2. The same data as Fig. 1 plotted as conductivity σ to clarify the location of the conductivity peaks.

ments of several samples from the same batch showed only a slight variation in T_{MI} (± 2°K) at atmospheric pressure. In Fig. 2 the same data as in Fig. 1 are plotted as conductivity versus temperature to clarify the location of the conductivity peaks. The shift of T_{MI} with pressure for several samples is shown by the solid curve of Fig. 3, with T_{MI} defined by the conductivity maximum. Several other features of the resistivity results are noteworthy. First, there is a small shoulder in ρ at ~45°K which disappears as pressure increases. This shoulder is too small to be seen clearly in Fig. 1 but was a reproducible feature of $\rho(T)$ in all our samples. The origin of the shoulder is unknown, but it may result from separately conducting TCNQ and TTF chains which undergo MI transitions at slightly different temperatures. The application of pressure could then increase the interchain coupling such that only one MI transition occurs. Second, we find that the temperature dependence of ρ above T_{MI} changes significantly with pressure. The pressure variation of σ at 273°K is shown in Fig. 3, and it should be noted that it is markedly larger than the change near T_{MI}. The temperature dependence of ρ has been fitted with $\rho = a + bT + cT^2$ over the range $T_{MI} \leq T \leq 300$°K in an attempt to characterize the effect of applying pressure. The primary result is that the atmospheric-pressure resistivity is dominated by a substantial quadratic term which is suppressed by the application of pressure, so that at high pressure the linear and quadratic terms have approximately the same magnitude. Perlstein *et al.*[4] have found that the conductivity perpendicular to the b axis has a linear temperature dependence above T_{MI}, and hence, our results may again indicate that interchain coupling is becoming significant under pressure. Third, we have found that at atmospheric pressure our samples often broke during

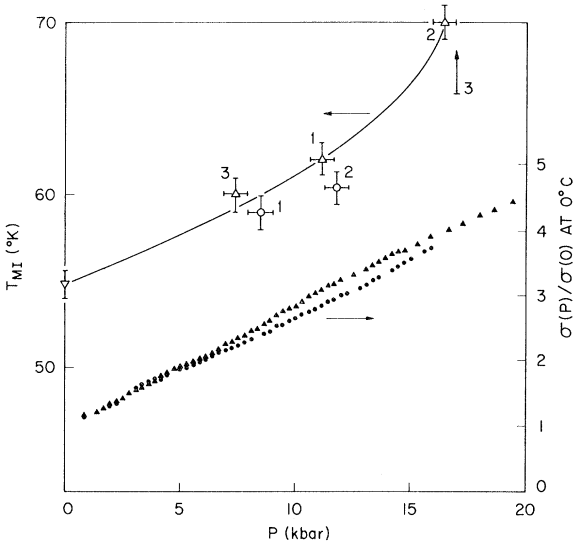

FIG. 3. Pressure dependence of the metal-insulator transition temperature T_{MI} and the b-axis conductivity of single-crystal TTF-TCNQ at 273°K. T_{MI} was defined as the temperature of maximum conductivity. The order of the pressure runs on two different samples (open triangles and open circles) is indicated by the number near the T_{MI} data points. Only a lower limit for T_{MI} could be determined for the highest-pressure run on one sample (open circles). The 273°K conductivity data (filled circles and filled triangles) are for two samples, both with $\sigma(300°K) \sim 300\ \Omega^{-1}\ cm^{-1}$ and both cycled in pressure several times.

cooling in the pressure fluid, whereas with the application of pressure we have successfully cooled and warmed the samples through the transition without breakage or other deterioration. This suggests that some change in physical dimensions occurs in TTF-TCNQ upon cooling through the MI transition. The compressibility and thermal expansion are not known for TTF-TCNQ, and hence we are not able to estimate the change in the lattice constant for our range of pressure and temperatures. The data below T_{MI} could not be fitted with any reasonable form because of the shoulder at 45°K and the limited temperature range. Experiments are in progress to measure $\rho(P, T)$ to lower temperatures.

Several models[12] have been proposed to explain the unusual behavior of conducting 1D materials like the TCNQ salts and the mixed-valence complexes of platinum. For instance, the properties of NMP-TCNQ have been attributed to Coulomb correlations (a Mott-Hubbard system) and/or to 1D disorder. On the other hand, the platinum complexes have been interpreted with a Peierls-instability model and also a disorder model. The existing experimental evidence seems to support the Peierls model for the platinum complexes, with the situation in the TCNQ salts still unclear. Below we discuss our results in terms of some of the present models.

First, the fact that T_{MI} increases with pressure appears to rule out the possibility that the MI transition results from electron correlation effects, i.e., a Mott-Hubbard transition. One would expect t (the transfer integral) to increase and U_{eff} (the effective Coulomb interaction[9]) to decrease with increasing pressure, leading to wider bands, a smaller Hubbard gap, and hence, a stabilization of the metallic state to lower temperature.[13] To confirm this point, we are in the process of measuring the shift of the MI transition temperature in NMP-TCNQ, a system in which correlation effects have been shown to be important.[9]

Our results also indicate that the large increase in σ with pressure observed at 273°K is not due to superconducting fluctuation effects. If it were, $d\sigma/dP$ would be expected to increase as kT is lowered, not to decrease markedly, as observed (Fig. 1). An attempt to fit our data with the exponential form proposed by Anderson, Lee, and Saitoh[14] to be appropriate for superconducting fluctuations gave poor fits to straight lines at all pressures, although the slopes corresponded to transitions in the 500°K range, as those authors suggested.

The increase of T_{MI} with pressure is at least consistent with current theories ascribing the MI transition to a Peierls-like instability.[15-17] Mean-field theory predicts $T_P{}^{MF} \sim \epsilon_F e^{-1/\lambda}$, where λ is the electron-phonon coupling constant and ϵ_F the Fermi energy. In the tight-binding model, ϵ_F is proportional to t and will increase with pressure. The dependence of λ on pressure is not so obvious. Patton and Sham[16] have shown that λ increases with pressure in the tight-binding limit; hence, in that limit $dT_P{}^{MF}/dP$ will be positive in agreement with experiment. Lee, Rice, and Anderson[15] and Rice and Strässler[17] consider the effect of fluctuations and interchain coupling on the Peierls transition. They show that in one dimension T_P is reduced to zero by the effects of fluctuations; however, weak interchain coupling leads to a 3D transition at $T_P \sim \frac{1}{4} T_P{}^{MF}$. The 3D transition temperature corresponds to what we have defined as T_{MI} and is proportional to the magnitude of the interchain coupling and the coherence length along the chain. Since we expect the interchain coupling to increase with pressure, $dT_P{}^{3D}/dP$ will again be positive in agreement with experiment.

The most puzzling feature of our data is the insensitivity of ρ near T_{MI} to increases in pressure, while at higher temperature it decreases significantly. This result is not obviously explained by any existing theory. In a tight-binding limit,[9] $\rho = \hbar^2\pi/4Ne^2t\tau a^2$, and we expect the pressure-induced increase in t to lead to a decrease of ρ at all temperatures (the temperature dependence of ρ is contained in the scattering rate $1/\tau$ and possibly in t, if lattice contraction is significant). Since this is not observed, the behavior of ρ must be caused by unusual changes in the scattering rate or in the Peierls fluctuations with pressure. The substantial decrease in the quadratic term in resistivity under pressure also suggests changes in the scattering mechanism. It is tempting to suggest that interchain scattering contributes significantly to the resistivity near the MI transition, and thus, the expected increase in this scattering rate with pressure could offset a decrease in the single-chain scattering rate or an increase in t near T_{MI}, but not at higher temperatures.

In conclusion, the rapid increase of σ at high temperature and the insensitivity of σ at T_{MI} under hydrostatic pressure suggest that the maximum σ at T_{MI} is very unlikely to be caused by superconducting fluctuations. The observation

of a positive pressure effect on T_{MI} is consistent with predictions of current theories based on the Peierls instability. The results also suggest that interchain coupling is important in TTF-TCNQ, particularly near the metal-insulator transition temperature.

We wish to thank G. Castro, R. Schumaker, and U. T. Mueller-Westerhoff for providing the TTF-TCNQ single crystals. We have benefitted from conversations with P. W. Anderson, S. Doniach, L. J. Sham, and P. A. Lee.

*Research at Stanford sponsored in part by the Air Force Office of Scientific Research, Air Force Systems Command, U.S. Air Force, under Grant No. AFOSR 73-2435.

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[1]J. P. Ferraris, D. O. Cowan, V. V. Walatka, and J. H. Perlstein, J. Amer. Chem. Soc. 95, 948 (1973).

[2]L. B. Coleman, M. J. Cohen, D. Sandman, F. G. Yamagishi, A. F. Garito, and A. J. Heeger, Solid State Commun. 12, 1125 (1973).

[3]T. E. Phillips, T. J. Kistenmacher, J. P. Ferraris, and D. O. Cowan, J. Chem. Soc., Chem. Commun. 14, 471 (1973).

[4]J. H. Perlstein, J. P. Ferraris, V. V. Walatka, D. O. Cowan, and G. A. Candela, in *Magnetism and Magnetic Materials—1972*, AIP Conference Proceedings No. 10, edited by C. D. Graham, Jr., and J. J. Rhyne (American Institute of Physics, New York, 1973).

[5]P. M. Chaiken, J. F. Kwak, T. E. Jones, A. F. Garito, and A. J. Heeger, Phys. Rev. Lett. 31, 601 (1973).

[6]A. N. Bloch, J. P. Ferraris, D. O. Cowan, and T. O. Poehler, Solid State Commun. 13, 753 (1973).

[7]P. M. Grant, R. L. Greene, G. C. Wrighton, and G. Castro, Phys. Rev. Lett. 31, 1311 (1973).

[8]A. A. Bright, A. F. Garito, and A. J. Heeger, Solid State Commun. 13, 943 (1973).

[9]A. J. Epstein, S. Etemad, A. F. Garito, and A. J. Heeger, Phys. Rev. B 5, 952 (1972).

[10]C. W. Chu, T. F. Smith, and W. E. Gardner, Phys. Rev. Lett. 20, 198 (1968).

[11]A. Jayaraman, A. R. Hutson, J. H. McFee, A. S. Coriell, and R. G. Maines, Rev. Sci. Instrum. 38, 44 (1967).

[12]For a review of the present experimental and theoretical situation, see H. R. Zeller, in *Festkörperprobleme*, edited by H.-J. Queisser (Vieweg, Braunschweig, Germany, 1973), Vol. 13, p. 31.

[13]T. M. Rice and D. B. McWhan, IBM J. Res. Develop. 14, 251 (1970), discuss the pressure dependence of the Mott transition in Cr-doped V_2O_3.

[14]P. W. Anderson, P. A. Lee, and M. Saitoh, Solid State Commun. 13, 595 (1973).

[15]P. A. Lee, T. M. Rice, and P. W. Anderson, Phys. Rev. Lett. 31, 462 (1973).

[16]B. R. Patton and L. J. Sham, Phys. Rev. Lett. 31, 631 (1973), and private communication.

[17]M. J. Rice and S. Strässler, Solid State Commun. 13, 125 (1973), and to be published.

Critical Behavior of Anisotropic Cubic Systems in the Limit of Infinite Spin Dimensionality

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(Received 29 October 1973)

The zero-field critical behavior above T_c of ferromagnets (or ferroelectrics) with a Hamiltonian of cubic symmetry is studied, in d space dimensions, in the limit of infinite spin dimensionality, $n \to \infty$, with the cubic term of order unity, but the usual S^4 term of order n^{-1}. A diagrammatic expansion about an Ising model (instead of the normal Gaussian model) is used. Characteristic cubic behavior is discovered, with renormalized Ising-model exponents (in the Fisher sense).

Recent diagrammatic expansions of critical exponents, either in powers of ϵ $(=4-d)$ or of $1/n$ (n being the number of components of the order parameter), have greatly improved our understanding of critical phenomena.[1,2] All the existing expansions are based on a perturbation about the Gaussian or "free-field" model. This type of expansion is inappropriate for problems in which the reduced Hamiltonian deviates strongly from that of the Gaussian model. The purpose of the present note is to generalize the basis of the $1/n$ expansion for one such case. The procedure should prove useful for other similar problems.

The Hamiltonian we consider is that of a system with "cubic" anisotropy, i.e., in addition to the usual rotationally invariant exchange interactions the Hamiltonian contains a term like[3]

$$\mathcal{H}_c = v_1 \sum_{\alpha=1}^{n} \sum_{\vec{R}} (S_{\vec{R}}^{\alpha})^4, \tag{1}$$