Tetrathiafulvalene Tetracyanoquinodimethane (TTF-TCNQ): A Zero-Bandgap Semiconductor?*

U. Bernstein, P. M. Chaikin, and P. Pincus
Department of Physics, University of California, Los Angeles, California 90024
(Received 25 March 1974)

We present numerical calculations based on a tight-binding model for the organic conductor tetrathiafulvalene tetracyanoquinodimethane (TTF-TCNQ). The model consists of anisotropic planar TTF and TCNQ bands coupled together by an interplanar transfer integral, which produces a nearly zero-bandgap semiconductor. The calculations are compared with experiments and it is found unlikely that all of the data can be explained simultaneously by a noninteracting electron band structure. We then discuss how many-body effects may affect the model and lead to a metal-insulator transition as observed.

There is mounting experimental evidence that the organic charge transfer salt tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ), at high temperature ($T > T_c \cong 60°K$), is a highly anisotropic narrow-band metal with small Coulomb correlation effects.[1-10] At lower temperatures ($T < T_c$) the salt behaves as a small-bandgap semiconductor with a nonmagnetic ground state. The purpose of this note is to present a simple noninteracting electron tight-binding band picture which correlates some of the known magnetic and transport properties in the high-temperature region. With a knowledge of the results of band theory it is then possible to envision several mechanisms for the observed metal-insulator transition. It is also greatly helpful to see which of the properties can be explained by one-electron physics and which require many-body interactions.

Our model is to consider parallel uniform chains of TCNQ and TTF molecules where one nondegenerate molecular orbital is associated with each molecule. This leads to the tight-binding Hamiltonian,

$$\begin{aligned}\mathcal{H} = &- t_Q \sum_{i,j,\sigma} (c_{i,j,\sigma}{}^{\dagger} c_{i+1,j,\sigma} + \text{H.c.}) - t_F \sum_{i,j,\sigma} (b_{i,j,\sigma}{}^{\dagger} b_{i+1,j,\sigma} + \text{H.c.}) \\ &- t_Q' \sum_{i,j,\sigma} (c_{i,j,\sigma}{}^{\dagger} c_{i,j+1,\sigma} + \text{H.c.}) - t_F' \sum_{i,j,\sigma} (b_{i,j,\sigma}{}^{\dagger} b_{i,j+1,\sigma} + \text{H.c.}) \\ &- j \sum_{i,j,\sigma} (c_{i,j,\sigma}{}^{\dagger} b_{i,j,\sigma} + \text{H.c.}) + \epsilon_0 \sum_{i,j,\sigma} c_{i,j,\sigma}{}^{\dagger} c_{i,j,\sigma}, \end{aligned} \tag{1}$$

where t_Q and t_F are, respectively, the transfer integrals along the highly conducting b axis for the TCNQ and TTF stacks; t_Q' and t_F' are the c-axis TCNQ or TTF transfer integrals; j is the a-axis TCNQ-TTF transfer integral; ϵ_0 is the electron affinity of TCNQ relative to the ionization potential of TTF corrected by the Madelung energy; $c^{\dagger}$, c, $b^{\dagger}$, b are TCNQ or TTF creation and destruction operators. The strong temperature dependence and magnitude of the spin susceptibility[10] and thermoelectric data[3] leads us to a model with narrow bands of order $4|t_F| \simeq 0.1$ eV and $4|t_Q| \approx 0.4$ eV. The anisotropy of the transport properties require $|t_F'|$, $|t_Q'|$, $j \ll |t_Q|$. Bond lengths and photoemission experiments suggest that the electronic structure of TTF-TCNQ corresponds to about one-electron transfer from a TTF to a TCNQ molecule: $0 < \epsilon_0 < 2|t_Q| + 2|t_F|$.[8,11]

The energy bands which result from the Hamiltonian (1) are described by the following relation:

$$\begin{aligned}\epsilon(\vec{k}) &= \tfrac{1}{2}(\epsilon_F + \epsilon_Q) \pm \tfrac{1}{2}|(\epsilon_F - \epsilon_Q)^2 + 16 j^2 \cos^2 k_a a|^{1/2}, \\ \epsilon_F &= -2t_F \cos k_b b - 2t_F' \cos k_c c, \\ \epsilon_Q &= -2t_Q \cos k_b b - 2t_Q' \cos k_c c + \epsilon_0, \end{aligned} \tag{2}$$

where the wave vector $\vec{k}$ has components (k_a, k_b, k_c).

In the absence of a coupling term j we would have two independent bands. If they have transfer integrals of the same sign the result will be a metal or a semimetal. If the bands were separated we would have an indirect-gap semiconductor. This contradicts the low-temperature conductivity and dielectric-constant measurements,[5-7] which require accessible states at an energy ≈ 0.01 eV. If t_F and t_Q have opposite signs there will be a line of degeneracy in the (k_b, k_a)

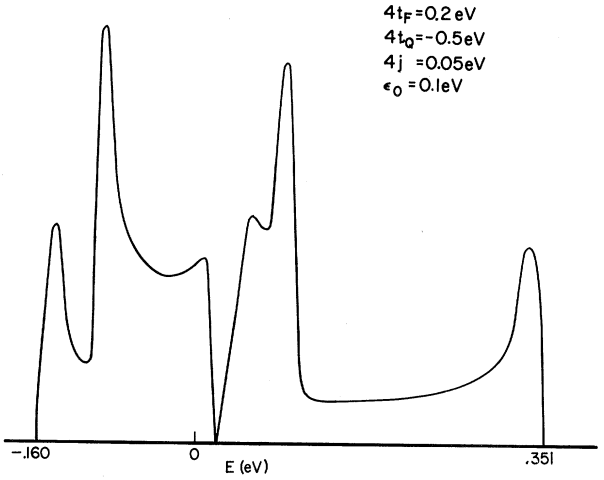

FIG. 1. Density of states as a function of energy for the dispersion relation of Eq. (2) for a particular set of transfer integrals (Ref. 13).

plane. If t_F' and t_Q' are negligible, the interplane coupling j will then split this degeneracy at all but one point ($k_a = \pi/2a$) producing a zero-bandgap semiconductor. Finite c-axis transfers give rise to a small but finite density of states at the Fermi energy. It is clear that the Fermi energy coincides with this point of degeneracy. The sign of the transfer integral is governed by the symmetry of the atomic or molecular wave functions and the crystal structure.[12]

Some physical insight into the predictions of this model can be gained by looking at a typical density-of-states plot (Fig. 1). The effect of the interplane coupling is to dig a hole in the density of states (of width approximately j) which is shifted from the center of the narrower band as the separation of the bands (ϵ_0) is increased. Plots of the temperature dependence of the susceptibility, conductivity, and thermopower for particular sets of variables are shown in Figs. 2 and 3. The energy scales which determine the temperature variation of the conductivity and susceptibility are both the interchange coupling j and the bandwidth of the narrow band. The thermopower crossing temperature is set mostly by bandwidth of the narrow band, but also is sensitive to the band separation ϵ_0. The magnitude of the susceptibility at high temperatures is sensitive to the TTF bandwidths; the conductivities and thermopower are sensitive to the TCNQ bandwidths.

With reasonable values for the parameters the model reproduces much of the transport properties but does not give a good fit to the suscepti-

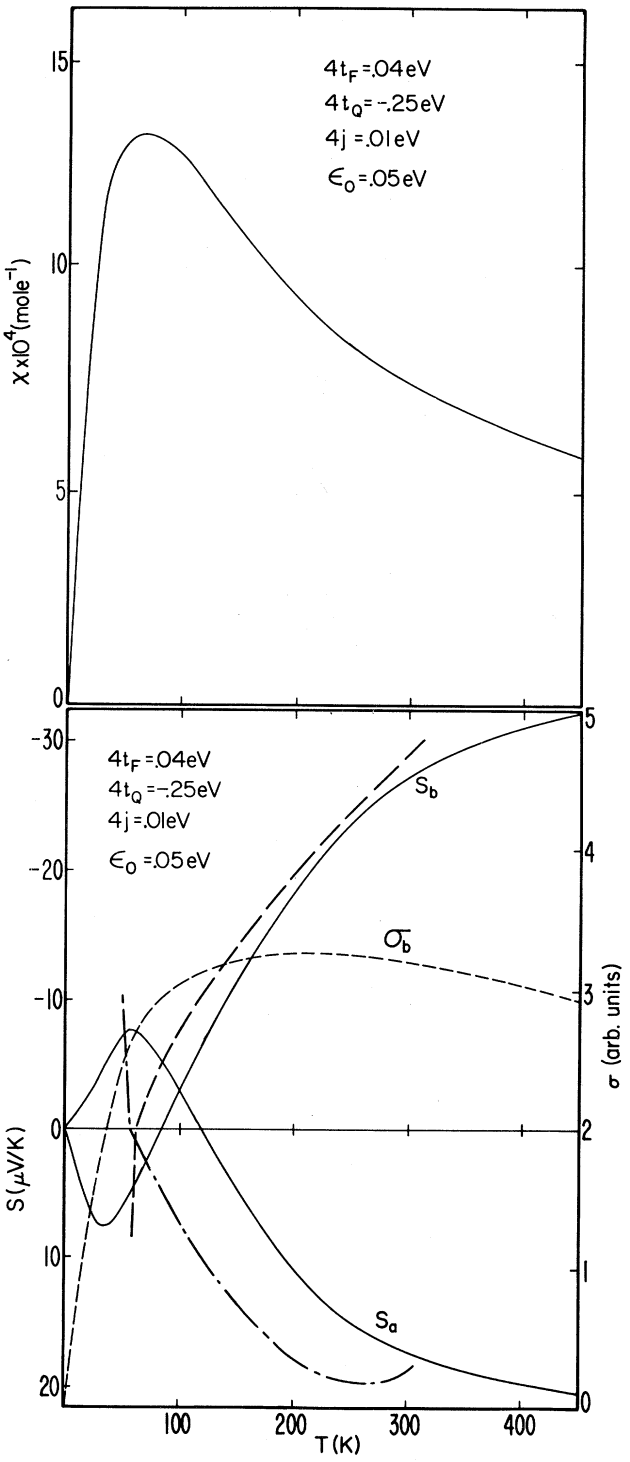

FIG. 2. (a) Temperature dependence of the susceptibility for a particular set of variables. (b) Temperature dependence of the b- and a-axis thermopower for the values used above. The dashed line is the experimental data for the b axis, the dash-dotted line is for the a axis (Ref. 14).

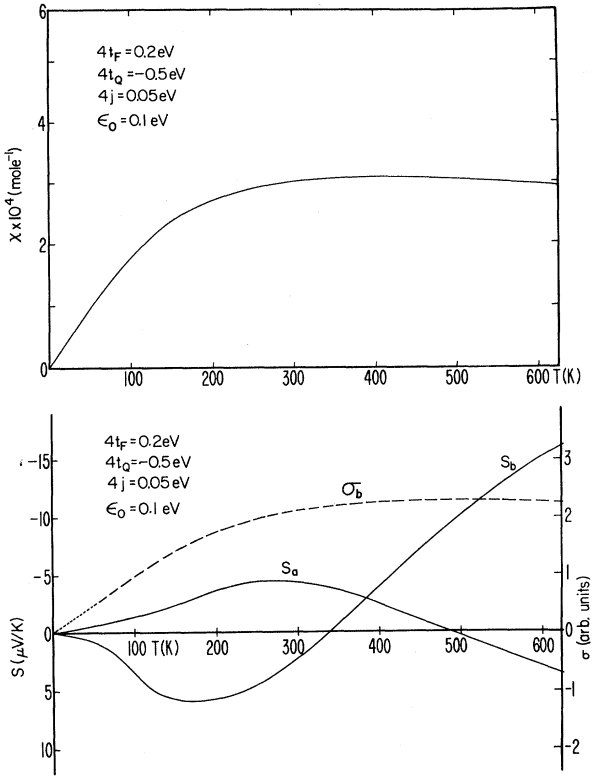

FIG. 3. Temperature dependence of the susceptibility, conductivity, and thermopowers for another set of parameters.

bility. The thermopower is highly anisotropic being negative in the b direction while positive in the a direction with both crossing zero close in temperature and near the maximum in the conductivity. This unusual behavior is remarkably similar to the experimentally observed a- and b-axis thermopower (see Fig. 2; the calculation is *not* a best fit, but rather one taking reasonable values) and is a strong point for the model.[15]

We have used the Boltzmann equation to compute the transport coefficients and we have explicitly factored out the scattering time (τ) so that the effects we show are entirely due to band structure. Including a temperature-dependent τ of the usual phonon type ($\tau \sim T^{-1}$) will multiply the conductivity by T^{-1} but will not affect the thermopower as it is a ratio of transport coefficients.[14] The conductivity will therefore fall off faster than $1/T$ above the conductivity maximum, approaching T^{-2} at high temperature.

It should be noted that the measured anisotropy in the conductivity dictates the allowed ratios of the transfer integrals along the major axis. In the case where the density of states is dominated by the transfer in one direction ($t_{\parallel} \gg t_{\perp}$) the anisotropy varies approximately as

$$\sigma_{\parallel}/\sigma_{\perp} \approx (t_{\parallel}/t_{\perp})^2.$$

This is true both for a single-band model and for our two-band model, where $\sigma_{\parallel} = \sigma_b$, $\sigma_{\perp} = \sigma_a$, and $t_{\parallel}$ is the larger of t_F or t_Q.

There are several other appealing features of this model especially above 60°K. The EPR g value is halfway between the TTF and the TCNQ solution values.[16] The nuclear spin-lattice relaxation rate T_1^{-1} also shows that there is strong coupling between TTF and TCNQ chains near the Fermi surface.[9] In the present model the Fermi energy sits in a hole in the density of states caused by the admixture of the bands. The electron states directly accessible for relaxation are thus partly on TTF and partly on TCNQ chains.

The most difficult experiment to fit is the susceptibility. For all values of the parameters computed, the crossing of the thermopower, maximum in the conductivity, and maximum in the susceptibility occurred very close in temperature. Experimentally the susceptibility increases quickly from $0 < T < 60$°K and then continues to increase appreciably in the region where the conductivity is quickly falling, $60 < T < 400$°K.[10] We note that including Coulomb correlations in the model would increase the magnitude of the temperature dependence of the susceptibility but would not change a falling χ to a rising one.

The absence of strong Coulomb correlations and a magnetic low-temperature state is easily seen in this model to be a result of the low density of states at the Fermi energy caused by the a-axis transfer.

We have left many things out of the model which could cause a "real" transition to occur. The most convincing evidence of a real transition is the specific-heat discontinuity seen recently by Craven *et al.*[17] Several papers have suggested that the high-temperature ($T > 60$°K) susceptibility and the phase transition in TTF-TCNQ can be explained by many-body effects such as a Peierls distortion.[1,18] Using the band structure developed above there is only one line of degeneracy between the split bands. Thus any sizable periodic distortion in the crystal which corresponds to either the $k_a = \pi/2a$ or k_b component of the k vector on this line will split the degeneracy and create a finite gap.

In particular a distortion perpendicular to the TCNQ and TTF planes changing the spacing so

that there are pairs of TTF-TCNQ planes will be commensurate and also will separate the bands.

The opening of a finite gap will alter our low-temperature results in such a way as to produce an exponential susceptibility and conductivity and an inverse temperature dependence for the thermopower (leaving the relative signs of S_A and S_B from our model unchanged unless a considerable number of impurities are present). This will bring our results closer to the experimental observations.

It is interesting to note that recent calculations show that the Peierls transition is suppressed for a single quasi-one-dimensional band as transverse bandwidths are included.[19] However in this model interplane (hence interband) transfer splits the bands to a point and allows an easy direction for the distortion.

In conclusion we have presented a realistic non-interacting electron band structure for TTF-TCNQ which we believe should be the basis for further calculations. Many of the unusual experimental properties of TTF-TCNQ are thus natural consequences of the highly anisotropic bands. However it does appear necessary to embellish the model with more sophisticated effects to allow quantitative agreement.

*Research supported by the National Science Foundation under Grants No. GH-37250 and No. NSF 35689X.

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

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

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

[4]D. E. Schafer, F. Wudl, G. A. Thomas, J. P. Ferraris, and D. O. Cowan, to be published.

[5]S. K. Khanna, E. Ehrenfreund, A. F. Garito, and A. J. Heeger, to be published.

[6]A. A. Bright, A. F. Garito, and A. J. Heeger, to be published.

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

[8]T. E. Phillips, T. J. Kistenmacher, and J. P. Ferraris, Chem. Commun. 14, 471 (1973).

[9]E. F. Rybaczewski, A. F. Garito, and A. J. Heeger, Bull. Amer. Phys. Soc. 18, 450 (1973); also E. F. Rybaczewski, E. Ehrenfreund, A. G. Garito, and A. J. Heeger, to be published.

[10]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), p. 1494; J. C. Scott, A. F. Garito, and A. J. Heeger, to be published.

[11]A. J. Epstein, P. Nielson, N. O. Lipari, and D. J. Sandman, to be published; W. D. Grobman, R. A. Pollak, D. E. Eastman, E. T. Maas, Jr., and B. A. Scott, Phys. Rev. Lett. 32, 534 (1974).

[12]A. J. Berlinsky, J. F. Carolan, and L. Weiler, Solid State Commun. 15, 795 (1974).

[13]The linear extrapolation of the density of states to zero is valid for the two-dimensional case which was used here for computational convenience. In three dimensions, the density of states would increase more sharply at low temperatures, but the essential features in the graphs are unchanged.

[14]J. M. Ziman, *Electrons and Phonons* (Oxford Univ. Press, Oxford, England, 1972), p. 384.

[15]J. F. Kwak, P. M. Chaikin, A. A. Russel, A. F. Garito, and A. J. Heeger, to be published.

[16]Y. Tomkiewicz, B. A. Scott, L. J. Tao, and R. S. Title, Phys. Rev. Lett. 32, 1363 (1974).

[17]R. A. Craven, M. B. Salamon, G. De Pasquali, R. M. Herman, G. Stucky, and A. Schultz, to be published.

[18]J. Bardeen, Solid State Commun. 13, 357 (1973); P. A. Lee, T. M. Rice, and P. W. Anderson, Phys. Rev. Lett. 31, 462 (1973).

[19]G. Beni, to be published.