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THE 38 K TRANSITION IN TTF–TCNQ VIEWED AS A PERCOLATION PHENOMENON*

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The d.c conductivity, static dielectric constant and thermopower of TTF–TCNQ have been calculated for temperatures below 54 K within a self-consistent effective medium approximation. TTF–TCNQ is assumed to consist of small regions which are semiconducting and others which are highly conducting. The conducting regions have a large negative dielectric constant, a large d.c. conductivity and a negative thermopower; the semiconducting portions have a large positive dielectric constant, an activated d.c. conductivity and a large positive thermopower. The volume fraction of conductor increases from zero at $T = 0$ to unity at 54 K. The model is the first to reproduce the observed metal–insulator transition (e.g. the d.c. conductivity anomaly) near 38 K. The dielectric constant is calculated to rise initially with temperature and then become negative as the temperature increases above 38 K. The thermopower changes sign below 54 K and increases very rapidly at 38 K.

IN THIS PAPER we discuss several properties of tetrathiofulvalene–tetracyanoquinodimethane (TTF–TCNQ) for $T < 54$ K from the viewpoint that the system is spatially inhomogeneous. We will describe TTF–TCNQ in terms of a simple model which does not contain all of the details of the system but which does possess many of the important features. As indicated by specific heat measurements,[1] at approximately 54 K TTF–TCNQ undergoes a second order phase transition. The high temperature phase is highly conducting, while at low temperatures there is semiconducting behavior.[2] Infrared studies[3] suggest that TTF–TCNQ can be described in terms of the Peierls–Fröhlich picture[4] and we will adopt the picture, although it is not essential to our model. There is an energy gap at all temperatures. The high temperature d.c. conductivity is due to a long life-time collective model which results from a one-dimensional order along the chains. Below the phase transition temperature the collective mode becomes pinned by three-dimensional ordering of the chains and the high d.c. conductivity goes away.

Like any system undergoing a second order phase transition, the low temperature phase of TTF–TCNQ has an order parameter which goes smoothly to zero at the transition temperature and which only reaches its low temperature value well below the transition. In our model the order parameter describes the amount of the material which is non-conducting. At the intermediate temperatures fluctuations and thermal excitations cause portions of the material to become conducting. Because the system is below the transition temperature these excitations have only a finite lifetime. Nonetheless, at any instant there will be a definite volume fraction f of the solid which is conducting. The system is thus spatially inhomogeneous, being composed of both conducting and semiconducting regions. If $\psi(T)$ is the order parameter of the ordered phase then $|\psi(T)|^2$ is proportional to the volume fraction $1 - f$ of *insulator*. We will use a simple mean field theory and assume that the temperature dependence of $\psi(T)$ is the same as the temperature dependence of the BCS gap parameter.

This temperature dependence is in agreement with far infrared measurements in TTF–TCNQ films.[3] The conductivity peak associated with the pinned collective mode exhibits an unusual temperature dependence. The center frequency does not shift (i.e. soften) but rather the oscillator strength of the mode diminshes rapidly between 35 K and the 54 K transition. This oscillator strength is presumably proportional to the volume fraction of insulator and it can be fit very well by $|\psi(T)|^2$ where $\psi(T)$ has the BCS gap temperature dependence.

Our model is oversimplified in at least two respects. First, there exists some experimental evidence[3,5] suggesting that insulating regions persist even above 54 K, although their volume fraction seems to be small. As long as $1 - f \lesssim 0.1$ for such temperatures, the effect on transport coefficients should be relatively weak and our conclusions would remain unchanged. Second, we are considering only one of the two molecular species in TTF–TCNQ. The structure of this system consists of alternating planes containing parallel chains of TTF or

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TCNQ molecules. If the conductivity arises from the TCNQ molecules, then the TTF planes serve merely to insulate neighboring TCNQ planes from each other. Our model is thus essentially two dimensional with all of the activity taking place in one of the planes. Recent magnetic resonance measurements,[7] however, indicate that both of the planes play a role in the magnetic susceptibility. The picture developed here considers two types of domains (phases) on one species of molecule. A complete description of the behavior of TTF–TCNQ would certainly involve taking into account both types of molecules. Bak and Emery[8] have recently constructed a theory of the structural phase transitions in TTF–TCNQ. They define a uniform order parameter for each of the two types of molecules and calculate the temperature dependence of the observed[9] neutron diffraction superlattice line along the crystallographic a direction. They do not consider transport properties. Recently, Phillips[10] has proposed a two-plane four-phase model. We expect that such a model would have transport properties similar to those found here.

With the description of the model complete, one can anticipate the consequences for various physical properties. The rapid increase in the d.c. conductivity which has been observed[2] at 38 K is a percolation transition corresponding to a sufficient amount of conductor being present that a conducting path forms throughout the material. The microwave dielectric constant[11] first increases due to the large polarizability of the conducting regions. At the percolation transition the dielectric constant becomes characteristically metallic (negative).[12] The thermoelectric power shows a large change towards semiconducting behavior[13] at the percolation transition. There is structure in the thermal conductivity[14] at 38 K, also characteristic of a percolation transition. Diffuse X-ray scattering experiments[15] show spots at 20 K (characteristic of three-dimensional order) and streaks at 55 K (characteristic of only one-dimensional order). At 40 K the X-ray experiments show a superposition of spots and streaks. This is probably the strongest evidence for inhomogeneities in TTF–TCNQ.[16]

In order to use this model for quantitative calculations, one requires a method of computing the effective transport coefficients of a randomly inhomogeneous system composed of separate metallic and semiconducting regions. The best analytic approach for such problems is the self-consistent effective medium approximation (EMA).[17] In this approach one computes the fields and currents inside each inhomogeneity as if the actual environment of the inhomogeneity were replaced by self-consistently determined homogeneous medium (the "effective medium").

We have used the EMA to calculate the d.c. conductivity, $\sigma(T)$, d.c. dielectric constant $\epsilon_1(T)$, and

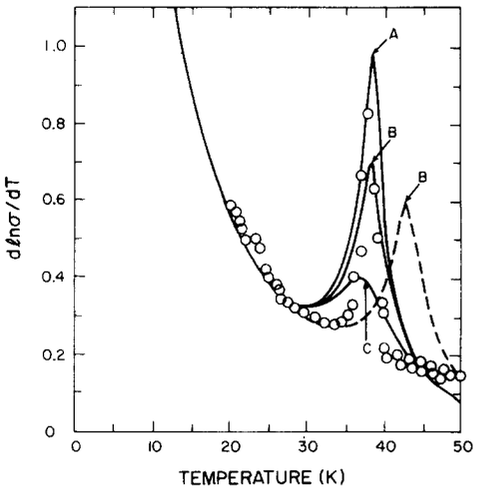

Fig. 1. Logarithmic derivative of the conductivity versus temperature. Experimental data are shown as open circles.

thermopower $S(T)$ of TTF–TCNQ between 20 and 54 K. We have obtained σ and ϵ_1 from the real and imaginary parts of a complex dielectric function $\epsilon_{\text{eff}}(\omega, T) = \epsilon_1(\omega, T) + (4\pi i/\omega)\sigma(\omega, T)$ evaluated in the limit $\omega \to 0$.[18] Within the EMA, $\epsilon_{\text{eff}}(\omega, T)$ satisfies the following equation

$$(1-f)\frac{\epsilon_{\text{eff}} - \epsilon_i}{g\epsilon_i + (1-g)\epsilon_{\text{eff}}} + f\frac{\epsilon_{\text{eff}} - \epsilon_m}{g\epsilon_m + (1-g)\epsilon_{\text{eff}}} = 0. \tag{1}$$

Here f is as before the volume fraction of metal, and $\epsilon_m(\omega, T)$ and $\epsilon_i(\omega, T)$ are the (complex) dielectric functions characterizing the metallic and semiconducting regions. The quantity g denotes a depolarization factor describing the shapes of the inhomogeneities, assumed all identical. For the present model, which assumes that transport arises entirely from within the TCNQ planes, these shapes are of necessity two-dimensional; the corresponding g's may vary from nearly zero (needle parallel to the applied field) to nearly one (needle perpendicular to the field). For circles $g = 1/2$.

We have solved equation (1) for $\sigma(T)$ and $\epsilon_1(T)$ using parameters appropriate to TTF–TCNQ. The results are shown in Figs. 1 and 2. The conductor was assigned to be characterized by a temperature-independent Drude dielectric function with plasma frequency[3] $\omega_p = 7.5 \times 10^{13}\ \text{sec}^{-1}$. The relaxation time was chosen so that the d.c. conductivity $\sigma_m = \omega_p^2\tau/4\pi$ was comparable with the measured[19] conductivity of TTF–TCNQ at 58 K. In Fig. 1 curve A is for $\sigma_m = 70{,}000\ \Omega^{-1}\ \text{cm}^{-1}$, curves B for $\sigma_m = 30{,}000\ \Omega^{-1}\ \text{cm}^{-1}$ and curve C for $\sigma_m = 7000\ \Omega^{-1}\ \text{cm}^{-1}$. For the semiconducting regions we have used an activated d.c. conductivity,[2] $\sigma_i = 30{,}000\, e^{-E/T}\ \Omega^{-1}\ \text{cm}^{-1}$ with $E = 220$ K. The low

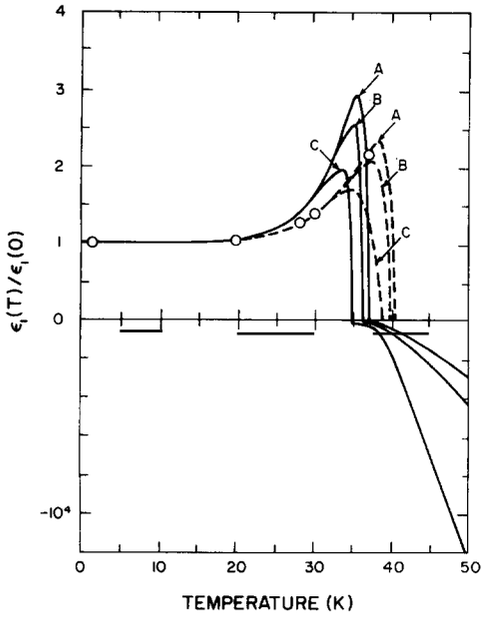

Fig. 2. Dielectric constant divided by its value at $T = 0$ plotted vs temperature. Experimental data are shown as open circles. Notice the large construction of the scale for negative values of ϵ. The dashed lines have been suppressed below zero

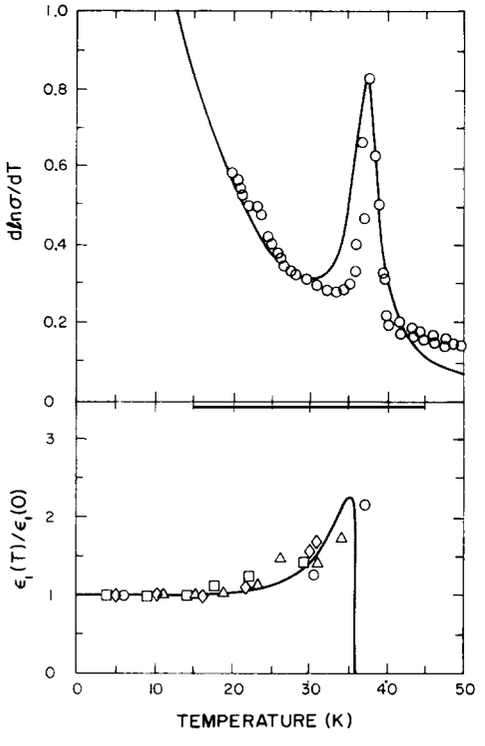

Fig. 3. Logarithmic derivative of the conductivity (upper portion) and static dielectric constant (lower portion) versus temperature for the case where the depolarization factor is temperature dependent. Experimental points are shown by various symbols.

frequency dielectric constant of the metal is $\epsilon_{m1} = 1 - \omega_p^2\tau^2$ and is between -10^6 and -10^7. The dielectric constant of the insulator was taken to be comparable with the measured[11] microwave dielectric constant of TTF–TCNQ at 4.2 K. In Fig. 2 curves A are for $\epsilon_{i1} = 5000$, curves B for $\epsilon_{i1} = 3000$ and curves C for $\epsilon_{i1} = 1000$.

Figure 1 shows d ln σ/dT vs T plotted for two shape factors, $g = 1/3$ (solid line) and $g = 1/2$ (dashed line). The open circles are the data of Etemad.[2] The calculations for $g = 1/3$, which in our model would describe elliptical domains with the long axis along the **b** crystallographic direction, give the correct temperature for the peak in d ln σ/dT although the peak is too broad. Figure 2 shows ϵ_1 vs T for the same shape factors. The open circles are representative data of Khanna *et al.*[11] Note that the scale for negative ϵ is strongly contracted; the calculated dielectric constants in fact go smoothly through zero. The drop in $\epsilon_1(T)$ followed by a sign change just below 38 K has been observed in microwave dielectric constant measurements by Gunning *et al.*[12] In the case of the dielectric constant, the best comparison with experiment is obtained for $g = 1/2$.

A better fit to the data can be obtained by assuming that the shapes of the inhomogeneities themselves vary with temperature. Figure 3 shows d ln σ/dT and $\epsilon_1(T)$ as calculated with $g = (T_c - T)/T_c$; with this choice of g, the inhomogeneities become very elongated in the high conductivity direction (parallel to the TCNQ chains) as T approaches T_c from below. This behavior is to be expected, at least roughly, since the length of the inhomogeneities along the chain is expected to vary in proportion to a coherence length, which diverges at $T \to T_c$. The parameters used are $\sigma_m = 17{,}000\ \Omega^{-1}\,\mathrm{cm}^{-1}$, $\sigma_i = 30{,}000\,e^{-220/T}\ \Omega^{-1}\,\mathrm{cm}^{-1}$, $\epsilon_{i1} = 3000$, and $\epsilon_{m1} = -6 \times 10^6$.

We emphasize that the qualitative features illustrated in Figs. 1–3 are quite insensitive to the choice of parameters and are in fact general characteristics of any percolation transition. The only requirement on the parameters is that $\sigma_m(T) \gg \sigma_i(T)$ at the temperature where the transition occurs, namely, at the temperature where $f(T) = g(T)$.[20]

In order to illustrate further the percolative nature of the 38 K transition, we show in Fig. 4 the thermopower $S(T)$ for TTF–TCNQ, as calculated within the EMA,[21] compared to the experimental data of Chaikin *et al.*[13] The EMA formula is[21]

$$S = \frac{\left\langle \dfrac{3K_{\mathrm{eff}}\sigma' S'}{(K' + 2K_{\mathrm{eff}})(\sigma' + 2\sigma_{\mathrm{eff}})} \right\rangle}{\left\langle \dfrac{K_{\mathrm{eff}}\sigma' + \sigma_{\mathrm{eff}}K' + 2K_{\mathrm{eff}}\sigma_{\mathrm{eff}} - K'\sigma'}{(K' + 2K_{\mathrm{eff}})(\sigma' + 2\sigma_{\mathrm{eff}})} \right\rangle}, \quad (2)$$

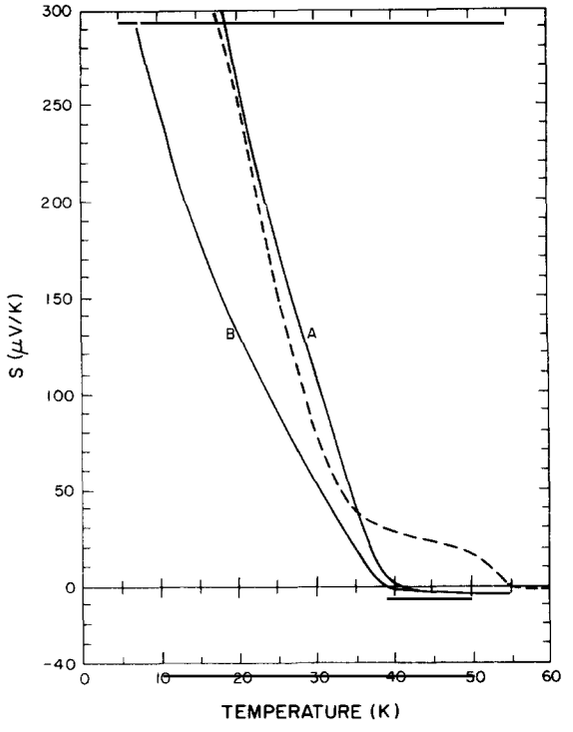

Fig. 4. Calculated thermopower versus temperature for several values of parameters. The trend of the experimental results is shown as a dashed line.

where $\langle x' \rangle$ is the average of a quantity x', to be evaluated as $fx_m + (1-f)x_i$. In equation (2), σ_i, K_i, and S_i are the electrical conductivity, thermal conductivity, and thermopower of the semiconducting regions, and σ_m, K_m, and S_m the corresponding quantities for the metallic regions. The thermal conductivity K of the inhomogeneous system obeys an equation of the same form as equation (1). Equation (2) is written for spherical inclusions ($g = 1/3$). It presumably is valid also for elliptical inclusions with $g = 1/3$. We have not considered temperature-dependent values of g because the experiment is not sufficiently reproducible from sample to sample to warrant such a detailed analysis. In evaluating equation (2), we have chosen K_m and K_i to be consistent with the data of Salamon *et al.*,[14] assuming a metallic thermopower, $S = -(k_B/|e|)T/t$, and a semiconducting thermopower $S_i = \alpha(k_B/|e|)E/T$ with $t = 1400$ K and $\alpha = 0.6$ (curve A) and 0.3 (curve B). These parameters are consistent with the high and low temperature data of Chaikin *et al.*[13] for "Penn crystals". The calculations reproduce the observed rather sharp transition from metallic to semiconducting behavior at 38 K. The discrepancy for temperatures between 38 and 54 K is presumably due to our neglect of effects from the second planes.

In conclusion, we have shown that several important transport properties of TTF–TCNQ at temperatures near 38 K are consistent with a percolative transition which we interpret as being due to the linking of metallic regions above 38 K to form a continuous network permeating the TCNQ planes. Several other experimental results near 38 K can be understood within this picture. These are (1) anomaly in the thermal conductivity;[14] (2) diffuse X-ray scattering;[15] (3) lack of specific heat anomaly;[1,14] (4) disappearance of the 38 K resistance anomaly with the introduction of impurities;[2,22] and (5) lack of evidence for soft modes.[3]

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18. In spite of the seeming divergence at $\omega = 0$, the limiting procedure does give well defined values for $\epsilon_{\mathrm{eff}}(0, T)$

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