at transitions from plastic to orientationally ordered phases, but may also apply in other order-disorder transitions of molecular crystals, e.g., in the ammonium halides.

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Role of Disorder in a Class of One-Dimensional Conductors*

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It is shown that the class of one-dimensional "metallic" conductors based on tetracyanoquinodimethan is not to be viewed as dominated by disorder. The experimental measurements of the electrical conductivity, magnetic susceptibility, and nuclear relaxation rates are each inconsistent with the disorder model. It is concluded that the electronic properties of these tetracyanoquinodimethan salts are primarily determined by band and interaction effects.

In a recent paper Bloch, Weissman, and Varma (BWV)[1] have asserted that the electronic properties of the highly conducting tetracyanoquinodimethan (TCNQ) salts are the result of lattice disorder. We demonstrate in this Letter that this assertion is untenable, that the disorder theory as applied to these one-dimensional (1D) conductors is not consistent with the experimental results, and that in the TCNQ salts (where sufficient data are available) the electronic properties are primarily determined by band and interaction effects.

The assertion of BWV is based upon the following arguments: (i) Disorder causes localization of wave functions in 1D, and (ii) the low-temperature conductivity of the TCNQ salts can approximately be fitted by $\log\sigma \sim (T_0/T)^{1/2}$ as derived for a disordered 1D system by analogy with the earlier work on 3D systems.[2-4] It is further claimed that the high-temperature conductivity arises not from a metal, but is determined by classical diffusion through the localized states, such that $\sigma = \sigma_D = (nNe^2/k_BT)\nu_{ph}a^2$, where n is the density of electrons on the chain, N is the number of chains per unit area, ν_{ph} is characteristic phonon frequency which drives the diffusion, and a is the lattice constant. The disorder, according to BWV, arises from the long-range Coulomb interaction of $(\mathrm{TCNQ})^-$ with the asymmetric charge distribution in the randomly oriented cation donor molecules.

Given the presence of random potentials, the question of the possible importance of disorder must be treated more quantitatively. If Δ_d is the rms disorder potential and W is the bandwidth in absence of disorder, then the ratio W/Δ_d describes the relevant regimes.[5] For $W/\Delta_d \gg 1$, disorder plays only a peripheral role (band tailing, etc.). Indeed, even in this case the "band" wave functions are strictly speaking not of infinite extent; this is irrelevant, however, as crystal imperfections and defects will clearly set an upper limit to the extent of wave functions in real samples. In this limit one can view such systems as long but finite chains with electrons interacting via the electron-electron Coulomb interaction as described previously.[6,7] In the opposite limit, $W/\Delta_d < 1$, the disorder would dominate and the wave functions would be localized to approximately a single lattice site. We give below analyses of the conductivity, magnetic susceptibility, and nuclear relaxation time; in each case the data are inconsistent with the disorder model.

The strongest argument of BWV arises from the low-temperature conductivity. If one assumes dominance of disorder, the low-temperature conductivity would result from the variable-range hopping mechanism proposed by Mott.[2] In 1D the problem can be simply viewed as a diffusion process. The conductivity can be written as σ

$=Nn_{\rm eff}e\mu$, where $n_{\rm eff}=\rho(0)k_BT$. $\rho(0)$ is the density (per unit length) of localized states near the Fermi energy. The mobility μ is given by the Einstein relation $\mu=eD/k_BT$. The diffusion constant D may be written as the hopping distance squared times the probability:

$$D=R^2\nu_{\rm ph}\exp[-2\alpha R-1/R\rho(0)k_BT]. \qquad (1)$$

This form of D is a statement of Mott's variable-range hopping idea, where $R>a$ is the variable range and α describes the decay of the wave function at its edges. Maximization of σ with respect to R yields $[k_BT<2\alpha/\rho(0)]$,

$$\sigma=\sigma_D(2\alpha a)^{-1}\exp[-(T_0/T)^{1/2}], \qquad (2)$$

where σ_D is the classical diffusion-limited conductivity as given above and $T_0=8\alpha/\rho(0)k_B$. We sketch this derivation because of the simplicity of the analysis in 1D and because we are particularly interested in the prefactor of the exponential. Equation (2) is inconsistent with the conductivity data as presented by BWV. Although the plot of logσ versus $T^{-1/2}$ is approximately linear, the extrapolated intercept disagrees with Eq. (2) by more than 4 orders of magnitude for the N-methyl-phenazinium salt (NMP)(TCNQ) [Fig. 1(a)].[8] To obtain the measured prefactor requires $\alpha^{-1}\simeq10^4a$, a distance so large as to be meaningless. Moreover, the extrapolated prefactor disagrees with the measured high-temperature conductivity by 10^4, in contrast to the BWV assertion. The discrepancy is even greater for the 1D Pt chain compound $\mathrm{K_2Pt(CN)_4Br_{0.3}(H_2O)_{2.3}}$, where the disorder arises from the random interstitial positions of the $\mathrm{Br^-}$ ions.[1] The discrepancy in this case is roughly 6 orders of magnitude. As a result of this discrepancy in magnitude, Brenig, Döhler, and Heyszenau[9] have attempted to apply a 2D variable-range hopping theory to the TCNQ conductors. Again, for (NMP)(TCNQ), the prefactor is off by at least 4 orders of magnitude.

In contrast, we note that plotting the conductivity data as logσ versus T^{-1} leads to a reasonable high-temperature extrapolation as shown in Fig. 1(b) for (NMP)(TCNQ). The deviations above the straight line at high temperatures result from fluctuations associated with the metal-insulator transition and from the decrease of the magnitude of the Hubbard gap as the system goes from insulator to metal.[6] This does not mean that imperfection is completely unimportant in these materials. For example, the deviations from linearity of logσ versus T^{-1} at the lowest temperatures in Fig. 1(b) and the finite ac conductivity[10] of (NMP)(TCNQ) below the metal-insulator transition probably result from either band tailing into the Hubbard gap or nonstoichiometry as a result of slight disorder, impurities, or defects. The large ac conductivity in the ordered (alkali)$^+$(TCNQ)$^-$ salts

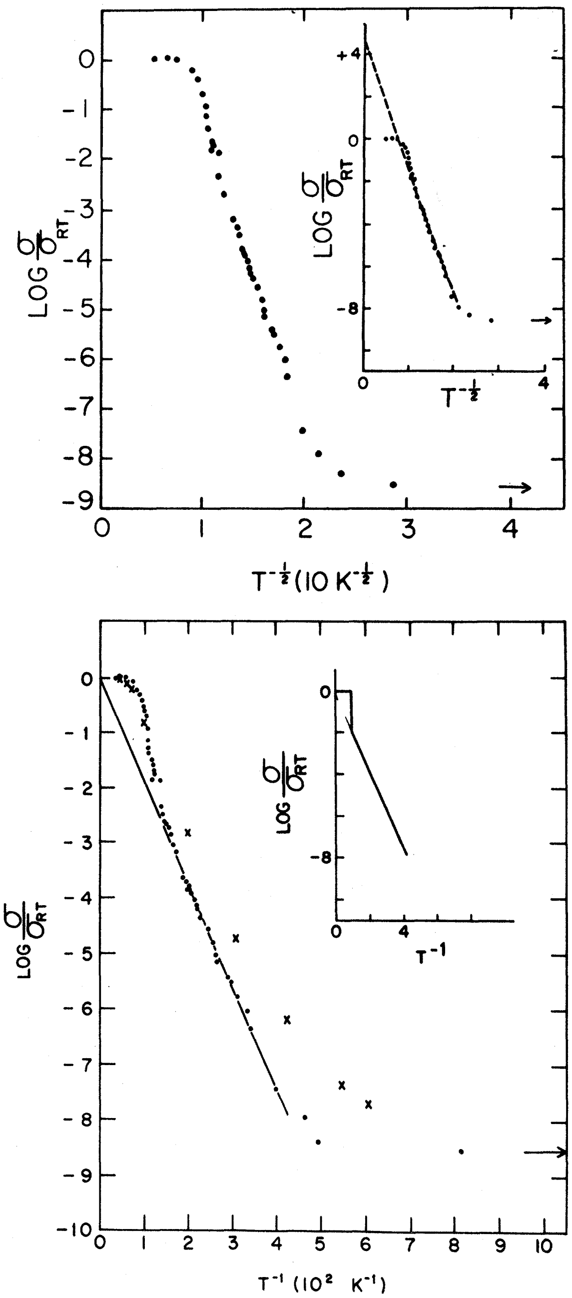

FIG. 1. (a) Temperature dependence of the conductivity of (NMP)(TCNQ) plotted as $T^{-1/2}$. (b) Temperature dependence of the conductivity of (NMP)(TCNQ) plotted as T^{-1}. Circles, this work and Ref. 6; crosses, from Ref. 10. Inset, scale drawing of the resistivity under conditions of a sharp phase transition.

confirms this interpretation.[11]

The disorder model fails on comparison with the experimental data of nuclear relaxation times in the TCNQ metallic systems. A detailed analysis of T_1 for (NMP)(TCNQ) yields results fully consistent with this system undergoing a transition from metal to insulator as the temperature is decreased below 200°K.[7] We emphasize here the data from the salt (quinolinium)$(\mathrm{TCNQ})_2$, where the relaxation time obeys the Korringa relation, $T_1T = \mathrm{const}$, above 130°K (Fig. 2). A temperature dependence of this form is again inconsistent with the BWV assertion, for in the diffusion regime one would predict $T_1^{-1} \simeq \frac{1}{4}(A/\hbar)^2 \nu_{\mathrm{ph}}^{-1}$ as for a collection of spins (hyperfine constant A) with correlation time on a given site limited by the hopping frequency. This has the wrong temperature dependence and is off by nearly 2 orders of magnitude in comparison with experiment. In contrast, the band picture predicts $1/T_1 = \pi\hbar(A/\hbar)^2 \times \eta^2(0) k_B T$. Comparison with the results of Fig. 2 shows not only the proper temperature dependence, but also gives $\eta(0) = 12$, in rough agreement with the value of 3.8 states/eV per TCNQ molecule obtained from the temperature-independent Pauli susceptibility. The larger value inferred from T_1 is consistent with some enhancement of both T_1^{-1} and χ_p, as is expected from interaction effects.[7]

The disorder model fails on comparison with the experimental data of magnetic susceptibility in the TCNQ systems. BWV have argued that the wave functions are localized to order one lattice constant by disorder. In this regime the fraction of unpaired spins is given by U/Δ_d, where U is the local Coulomb interaction.[12] Thus one would predict $\chi = \chi_{\mathrm{P}} + \chi_{\mathrm{C}}$[12] (a Pauli term and a Curie-Weiss term) such that $\chi_{\mathrm{C}}/\chi_{\mathrm{P}} = U/(T+\theta)$. To explain the magnitude of the low-temperature Curie-Weiss term[6,13] requires $k_{\mathrm{B}}^{-1} U_{(\mathrm{NMP})(\mathrm{TCNQ})} \simeq 500$°K and $k_{\mathrm{B}}^{-1} U_{\mathrm{Q}(\mathrm{TCNQ})_2} \simeq 10$°K. The factor of 50 change in the Coulomb energy simply on changing the cation is impossible to accept, especially since the quinolinium molecule is more asymmetric and should lead to a shorter localization length. Moreover, any polarizability argument would fail since the larger NMP molecule would be more effective in reducing U. In addition to failing in the systematics of the different systems, the disorder model is inconsistent with the (NMP)(TCNQ) data which shows Curie-Weiss behavior below 200°K and a temperature-independent Pauli susceptibility above 200°K, not a sum of the two throughout (Fig. 3). The solid curve in Fig. 3 is a fit of $\chi = A + B/(T+\theta)$ to the data, where B is determined from the initial slope at low temperature and A is χ_{P}. Furthermore, if the high-temperature conductivity were diffusion limited,[1] the susceptibility should be temperature dependent, approaching a Curie-Weiss law (since $k_{\mathrm{B}}T \sim \Delta_d$), again in disagreement with experiment. In contrast, the band-interaction picture is capable of explaining all these data without inconsistency.[6,7]

We conclude that the electronic properties of these 1D conductors are determined by band and interaction effects with disorder playing only a peripheral role. The evidence is particularly

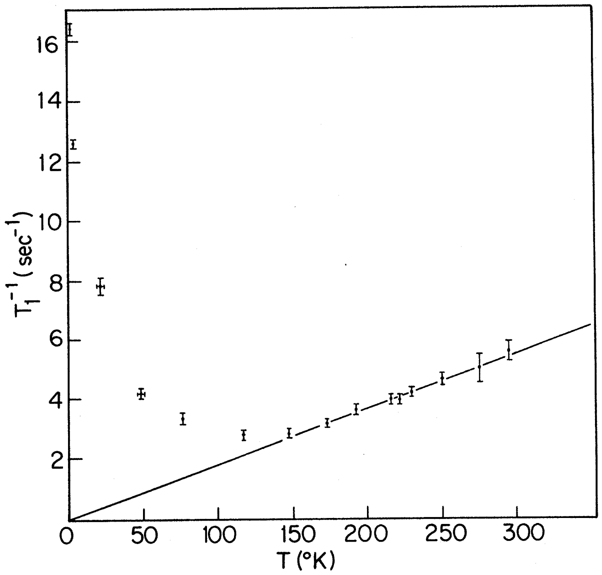

FIG. 2. Temperature dependence of T_1^{-1} for protons in (quinolinium)$(\mathrm{TCNQ})_2$.

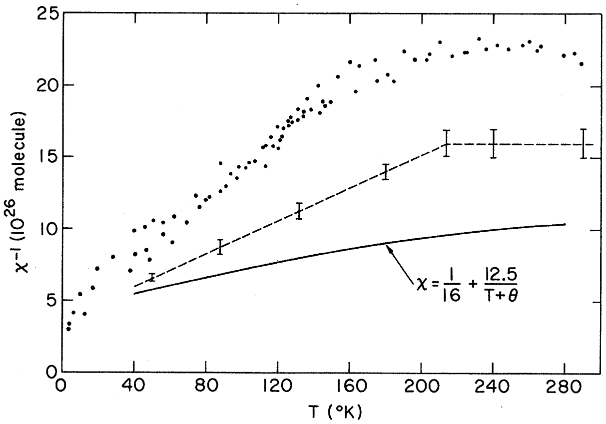

FIG. 3. Temperature dependence of χ^{-1}. (a) $(\mathrm{NMP})_{0.99}$-$(\mathrm{NEP})_{0.01}$(TCNQ) (filled circles); (b) (NMP)(TCNQ) from Ref. 6 (dashed curve); (c) predicted from the sum $\chi_{\mathrm{P}} + \chi_{\mathrm{C}}$ (solid curve).

strong for (NMP)(TCNQ), where the experimental picture is most complete. The quinolinium salt is a metal at high temperatures; the low-temperature properties are not yet well understood. However, assuming the Q$(TCNQ)_2$ chains (with $\frac{1}{4}$-filled band) remain metallic, an upper limit on the chain length can be obtained from straightforward application of spin diffusion theory to determine the contribution to the proton T_1 from paramagnetic centers at the chain ends. The result is an estimated length of order 500 lattice constants. This estimate is in reasonable agreement with the interpretation of the Curie contribution to χ[13] as arising from paramagnetic defects at chain ends.

The sensitivity of 1D systems to disorder localization can be exploited by using TCNQ compounds. As a first example we show in Fig. 3 the inverse susceptibility of $(NMP)_{0.99}(NEP)_{0.01}(TCNQ)$, where NEP denotes *N*-ethyl-phenazinium. The substitution of C_2H_5 for CH_3 on 1% of the cations has clearly observable effects. The "transition" appears to be somewhat rounded and shifted, but the major change is in magnitude. The high-temperature Pauli term is decreased in the disordered mixed crystal consistent with a spread of localized-state energies somewhat greater than the pure-system intrinsic bandwidth. The low-temperature magnetism is also decreased relative to that of the pure system as expected with increased disorder.[12,14] The disorder in this mixed (NEP)-(NMP) system probably arises from the steric effect of the larger ethyl group. The observation of a clear effect with only 1% NEP indicates that in the pure (NMP)(TCNQ) the wave functions extend to distances far greater than the length of order a lattice constant predicted by BWV. More detailed studies of the effect of *controlled* disorder are in progress and will be published separately.

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Contribution of Nonparabolicity to Longitudinal Magnetoresistance at Quantum Magnetic Fields

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In this communication we report that in the quantum region of magnetic field ($\hbar\omega_c \gg k_B T$) the nonparabolicity alone leads to a nonzero longitudinal magnetoresistance even if the energy and magnetic-field dependence of the relaxation time is ignored.

It is well known that anisotropy in the band structure of semiconductors gives rise to longitudinal effects, viz., longitudinal magnetoresistance. In the quantum region of magnetic field, i.e., where $\hbar\omega_c \gtrsim k_B T$, the dependence of electron collision frequency on electron energy and applied magnetic field also gives rise to longitudinal magnetoresistance[1] even in a semiconductor