Non-Ohmic Electrical Conduction in the Highly One-Dimensional Semiconductor Methyltriphenylarsonium Tetracyanoquinodimethane

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(Received 3 April 1979)

We have observed deviations from Ohm's law in single crystals of methyltriphenylarsonium tetracyanoquinodimethane: $Me\varphi_3As(TCNQ)_2$. We propose a model based upon tunneling of electrons through barriers in the conducting strands. Electrical conductivity and electron and nuclear magnetic resonance are used to accomplish a successful quantitative test of the model.

A number of papers have appeared in recent years discussing deviations from Ohm's law in crystals of one-dimensional conductors. The explanations for this behavior include excitation of solitary waves in a weakly pinned charge-density wave system,[1,2] depinning of charge-density waves,[3] space-charge-limited currents,[4] and phonon-assisted hopping through random barriers.[5]

We have observed deviations from Ohm's law in single crystals of methyltriphenylarsonium tetracyanoquinodimethane $Me\varphi_3As(TCNQ)_2$, a highly[6] one-dimensional semiconductor with a Peierls crystal structure.[7] We propose a tunneling model, based upon electrostatic (Coulomb) barriers caused by charged imperfections distributed along the conducting strands, and employ the Wentzel-Kramers-Brillouin (WKB)[8] method in the resistivity calculation.

The height of the Coulomb barriers is obtained by taking the Coulomb repulsion energy (e^2/r) equal to that of two electrons separated a distance r of 10 Å (the same as that between the ends of a TCNQ molecule). A value of about 1 eV is obtained. When one takes into account the effect of the heterocyclic cations $(Me\varphi_3As)^+$ a somewhat smaller value would be expected. LeBlanc[9] estimates that heterocyclic cations reduce the repulsive energy of two electrons on one TCNQ molecule by about a factor of 5. Our situation is similar; we assume the height of the barrier will be approximately 0.2 eV.

A rough estimate of the width of the barrier can be had by realizing that the potential will be of the general form e^2/r. Assuming the distance of closest approach between the conduction electron and the electron on the imperfection is 10 Å, a reasonable width is of order 20 Å. We assume the

bandwidth to be considerably smaller than the barrier height; Conwell[10] apparently considers 0.04 eV a reasonable estimate in similar compounds.

Using the WKB method to determine the charge tunneling through the barrier, we assume that the total voltage applied across the crystal is the sum of equal drops across each barrier in any chain. The current flowing in a TCNQ stack will be proportional to the difference between the transmission coefficients in the "forward" and "reverse" directions. In the forward direction, the WKB method gives a transmission coefficient

$$\Theta_1 = \frac{|\Psi(x=a_0)|^2}{|\Psi(x=0)|^2}$$

$$= \exp\left(\frac{-2}{h}\int_0^{a_0}[8\pi^2 m\,\Delta V(x)]^{1/2}dx\right). \tag{1}$$

We evaluate the integral using $\Delta V(x) = V_0 - \alpha x$, where $\alpha = e\epsilon/ca_0$, a_0 is the barrier width, c is the number of barrier imperfections per unit length along the chain, and e is the absolute value of the electronic charge. The parameter ϵ is the voltage applied across the crystal divided by the length of the crystal in the chain direction, and m is the electronic mass.

We consider the case $\alpha x < V_0$. Using a series expansion for $[8\pi^2 m(V_0 - \alpha x)]^{1/2}$ we find a forward transmission coefficient

$$\Theta_1 = \exp\left[\gamma\left(\frac{e\epsilon}{4V_0 c} + \frac{e^2\epsilon^2}{24V_0^2 c^2} - 1\right)\right], \tag{2}$$

where $\gamma = 2h^{-1}(8\pi^2 m)^{1/2}V_0^{1/2}a_0$.

In obtaining the reverse transmission coefficient Θ_2, we use Eq. (1) with $\Delta V(x) = V_0 + e\epsilon/c + \alpha x$. The result differs from Θ_1 only in the sign of the first term in parentheses and

$$\Delta\Theta = (\Theta_1 - \Theta_2) = \left[1 - \exp\left(\frac{-\gamma e\epsilon}{2V_0 c}\right)\right]\exp\left[\gamma\left(\frac{e\epsilon}{4V_0 c} + \frac{e^2\epsilon^2}{24V_0^2 c^2} - 1\right)\right]. \tag{3}$$

The current will be equal to the product of $\Delta\Theta$ and the number of charge carriers incident on the barrier per unit time. A zero-order estimate of the magnitude of the current can be obtained by considering the electronic velocity to be of order $v \approx (3k_BT/m)^{1/2}$ and the concentration of charge carriers per unit length $n = (2d)^{-1}\exp(-\Delta/k_BT)$. The cations donate one electron per every two TCNQ molecules; these are spaced about $d = 3.3$ Å apart. In a length l of a conducting strand there will be about nl electrons, each of which will impinge on the barrier at roughly the frequency v/l. We obtain a crude estimate for the number of charge carriers incident on the barrier per unit time nv, and thus have an approximate expression for the current in a conducting strand:

$$i = nev\,\Delta\Theta = C_0 T^{1/2}\exp(-\Delta/k_BT - \gamma)\left[1 - \exp\left(\frac{-\gamma e\epsilon}{2V_0 c}\right)\right]\left\{\exp\left[\gamma\left(\frac{e\epsilon}{4V_0 c} + \frac{e^2\epsilon^2}{24V_0^2 c^2}\right)\right]\right\}, \tag{4}$$

where $C_0 = (e/2d)(3k_B/m)^{1/2}$.

The Coulomb potential will be screened to some extent as a result of a redistribution of the conduction electrons. We take the Thomas-Fermi screening length[11] $\lambda \simeq 4\times10^{-5}L^{-1/6}$ cm$^{1/2}$, where L is the number of charge carriers per cm^3, as a rough estimate of the range of the screening. Screening is introduced to emphasize that our model predicts the occurrence of non-Ohmic behavior in semiconductors. In materials with small activation energies of conduction, one expects to see deviations from Ohm's law appear gradually as the temperature is lowered (and the screening becomes less effective). This is widely observed.[5, 12-14]

We have grown single crystals of $Me\varphi_3As(TCNQ)_2$ using the method of Melby et al.[15] The TCNQ was gradient sublimed and the $Me\varphi_3AsI$ was purified by multiple recrystallization from solution. The final single crystals were grown from highly purified acetonitrile in a dry argon atmosphere.

An approximate measure of the imperfection level was obtained through low temperature (2 to 4.2 K) proton spin-lattice relaxation time (T_1) measurements, and through ESR experiments (at $T = 95$ K). We find $T_1 \approx 100$ sec in single crystals at 4.2 K; T_1 changes little as the temperature is lowered to 2.0 K. Essentially the same T_1 is found in crystals in which the hydrogen sites on the TCNQ molecules are deuterated. In diamagnetic crystals at low temperature, a concentration N of paramagnetic impurities per unit volume is approximately related to T_1 and the nuclear spin-spin relaxation time T_2 by[16, 17] $N \approx 50T_2/(4\pi a^3 T_1)$, where a is the nuclear separation distance. From cw NMR measurements we obtain $T_2 = 2.1\times10^{-5}$ sec; taking $a = 2.5$ Å, N is found to be 5.3×10^{16} cm^{-3}. In selectively deuterated and nondeuterated crystals, T_1 is essentially the same; the imperfections are thus approximately evenly distributed between the TCNQ and $Me\varphi_3As$ ions. Taking the volume of a TCNQ ion as 2.5×10^{-24} cm^3, we estimate the fraction f of TCNQ sites with charged imperfections to be $f \approx 1.4\times10^{-6}$.

The major portion of the ESR signal in $Me\varphi_3As(TCNQ)_2$ has been attributed to triplet excitons.[18] As the temperature is lowered, the resonance broadens and splits. Generally some small intensity remains at the center. This center resonance is attributed to "impurities" in TCNQ compounds.[19] The triplet resonance intensity is an exponential function of temperature with an activation energy $J = 0.062$ eV. We estimate the fraction of electrons in the excited state to be $3\exp(-J/k_BT)$,[18] and compare the integrated intensity I of the imperfection resonance to that of the exciton resonance. Assuming that half of the imperfections are on the conducting TCNQ chains, we estimate the fraction f of TCNQ sites with unpaired electron impurities to be given by

$$f \approx \frac{3}{4}\frac{I(\text{imperfection})}{I(\text{exciton})}\exp(-J/k_BT). \tag{5}$$

A typical ESR spectrum is shown in Fig. 1; this crystal was grown in the same batch as the one used for the conductivity measurements plotted in Figs. 2 and 3. From that spectrum we find $f \approx 12\times10^{-6}$. Both NMR and ESR are seen to yield
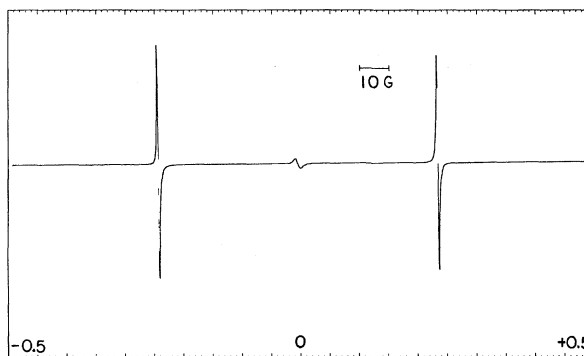

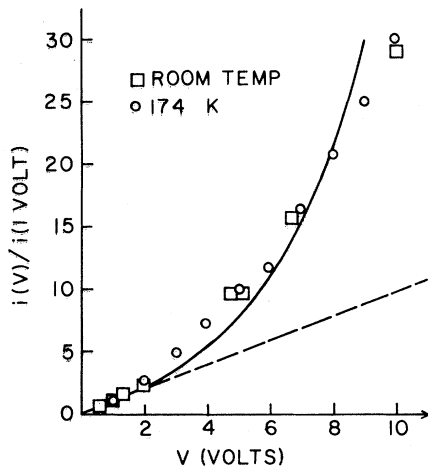FIG. 1. The ESR absorption derivative spectrum taken at $T = 95$ K and $\nu \approx 10$ GHz.

FIG. 2. The dashed line represents Ohmic behavior with "resistance" determined at 1 V. The solid line is taken from Eq. (6), with $V_0 = 0.2$ eV, $\gamma = 10$, $c = 270$ cm^{-1}. We plot $i(V)/i(1$ V) for both room temperature and 174 K.

approximately the same result: a concentration of unpaired electron imperfections of about 10^{-5}.

Having experimentally determined the approximate number of charged imperfections, and esti-

mated the values of V_0 and a_0, the value of every quantity in Eq. (4) is approximately known: c $= f/(3.3 \times 10^{-8}) \approx 300$ cm^{-1}, $V_0 \approx 0.2$ eV, $a_0 \approx 20$ Å, and $\gamma \approx 10$.

We have made both two- and four-probe resistivity measurements on more than a dozen crystals of Meφ_3As(TCNQ)$_2$ and find that the current increases more rapidly with increasing voltage than is predicted by Ohm's law. The deviation from Ohmic behavior occurs at quite small applied fields ≈ 3 to 7 V/cm. The electrical behavior of a typical crystal (cleaved from a larger crystal) measuring 0.17 cm thick with cross-sectional dimensions 0.18×0.45 cm^2 is shown in Figs. 2 and 3. A pulse technique with variable duty cycle was used to measure resistance and to eliminate Joule heating as a possible source of error.

The shape of the current versus voltage curve is absolutely independent of temperature, as illustrated in Fig. 2. This suggests a tunneling process; also the conductivity is activated, as shown in Fig. 3. (We find $\Delta = 0.41$ eV.)

The current in a single strand is given by Eq. (4). To find the current in a crystal of cross-sectional area A cm^2, we multiply i by the product of the number of strands per square centimeter ($\approx 10^{14}$) and the area A. Thus

$$I(\epsilon) = C_0 T^{1/2} A \, 10^{14} \exp(-\Delta/k_B T - \gamma)\left[1 - \exp\left(\frac{-\gamma e \epsilon}{2V_0 c}\right)\right] \exp\left[\gamma\left(\frac{e\epsilon}{4V_0 c} + \frac{e^2 \epsilon^2}{24 V_0^2 c^2}\right)\right]. \tag{6}$$

If we let $\gamma = 10$, $f = 9 \times 10^{-6}$ ($c = 270$/cm), and $V_0 = 0.2$ eV, a good fit to the data of Figs. 2 and 3 is obtained using Eq. (6).
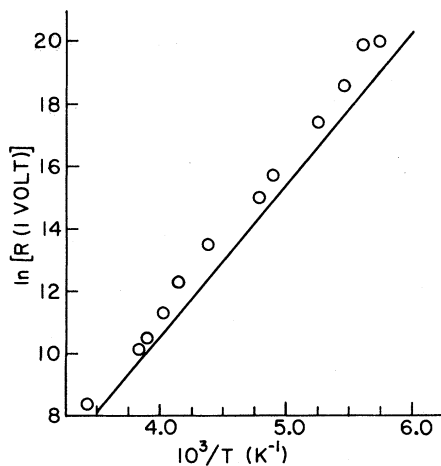

FIG. 3. Plot of $\ln(R)$ ($R = 1$ V/i) vs reciprocal temperature for the case of 1 V applied. The solid line is obtained using Eq. (6), with V_0 and c as given in the caption of Fig. 2, and $\Delta = 0.41$ eV.

In view of the approximate nature of the calculation, the fit between theory and experiment is good; furthermore, our data do not appear to be adequately explained by any of the models referred to earlier.[1-5] The models suggested by Rice, Strässler, and Schneider[3] and Kurti et al.[5] both predict behavior of the form $I = I_0 \sinh(e\epsilon\lambda/k_B T)$; our behavior with temperature is quite different. The space-charge-limited-current[20] model predicts a characteristic transient response to a pulse of applied voltage; we have been unable to observe this. Maki[21] has suggested the measurement of the low-temperature dielectric response of a system in which the soliton model is appropriate. He predicts that the low-frequency dielectric response will be an exponential function of frequency and field. We have measured dielectric response as a function of field and frequency from 1.7 to 77 K and find the dielectric constant to be constant over two orders of magnitude of frequency and applied field (50 kHz to 5 MHz, 01 to 20 V/cm).

The model put forth in this paper explains our

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Electron-Energy-Loss Study of Stage-1 Potassium-Intercalated Graphite

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Electron-energy-loss spectra of stage-1 K-intercalated graphite single crystals were obtained with a scanning transmission electron microscope. The complex dielectric function with electric polarization perpendicular to the c axis was derived by Kramers-Kronig analysis. The energy-loss peak at 2.5 eV is consistent with previous optical measurements, while the splitting of the one at 27 eV can be interpreted by folding the Brillouin zone of pristine graphite. Splittings and shifts of the interband transitions were observed and compared with calculations.

There has been considerable recent interest in the electronic properties of intercalated layer compounds[1] in general and of graphite intercalates[2-4] in particular. This interest is spurred not only by the technological potential for their very anisotropic high conductivity but also by the need for a fundamental understanding of their electronic properties.

While there are many phenomenological studies of various kinds of intercalated layer compounds, theoretical calculations of the electronic band structures have at present been limited to systems with the simplest crystal structures, i.e., stage-1 potassium-intercalated graphite C_8K,[5-7] and stage-1 lithium-intercalated graphite C_6Li.[7-] Therefore, electronic band structures based on the rigid-band model, which are proposed[10] for high-stage intercalates, have been used to interpret experimental data even for low-stage intercalates. Nevertheless, the band structure of C_8K recently calculated by Inoshita, Nakao, and Kamimura (INK) exhibits measurable deviations from that of pristine graphite. Therefore, it is important to test experimentally the validity of