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## Identification of a Class of Disordered One-Dimensional Conductors

Aaron N. Bloch and R. Bruce Weisman\*

*Department of Chemistry, Johns Hopkins University, Baltimore, Maryland 21218*

and

C. M. Varma†

*Department of Physics and The James Franck Institute, The University of Chicago, Chicago, Illinois 60637*

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We find that over thirty solids having high one-dimensional conductivity form a class of materials whose electronic properties are determined principally by structural disorder.

Recently, considerable experimental work<sup>1-7</sup> has been reported on a number of highly conducting solids in which the propagation of electrons is confined effectively to one dimension. The most prominent examples are some of the "mixed-valence" complexes<sup>8</sup> of platinum and iridium, and certain salts of the organic ion-radical tetracyanoquinodimethan (TCNQ).<sup>9</sup> Here we recognize the central significance, for the electronic properties of these materials, of a fact which has been overlooked in previous interpretations: X-ray crystallographic data, where available,<sup>8,11,12</sup> show them to be structurally disordered. Indeed, this is to be expected on chemical grounds<sup>10</sup> for the entire class. Exact theorems have been proven<sup>13</sup> stating that all electronic states in any disordered one-dimensional structure are localized.

The existence of such a class of materials thus acquires special significance.

Electronic conductivity in disordered one-dimensional systems can occur only by phonon-assisted hopping,<sup>14</sup> and we find that the available data are understood on this basis. Moreover, we find that the magnetic susceptibility, the optical properties, and the ac conductivity all consistently support the same point of view. Our work resolves certain difficulties in the treatment by Epstein *et al.*<sup>4</sup> of the *N*-methyl-phenazinium salt NMP-TCNQ as a realization of the one-dimensional Mott-Hubbard model, and in the interpretation by Kuse and Zeller<sup>7</sup> and others<sup>5-8</sup> of  $K_2Pt(CN)_4Br_{0.3} \cdot 2.3H_2O$  as a one-dimensional metal.

It will be convenient for our purposes to divide

these materials into three groups. By I we shall mean any of the twenty or so known "mixed-valence" square-planar complex platinum salts of which the most widely studied example is  $\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{0.3} \cdot 2.3\text{H}_2\text{O}$  (we shall refer to this prototype specifically as Ia). Among the organic systems, we single out as II the simple<sup>9</sup> NMP-TCNQ salt studied extensively by Epstein *et al.*,<sup>4</sup> and refer to the highly conducting complex<sup>9</sup> TCNQ salts collectively as III. Specific examples are quinolinium TCNQ<sub>2</sub> (IIIa) and acridinium TCNQ<sub>2</sub> (IIIb). The crystal structures of all three groups are qualitatively similar in that they all contain arrays of infinite, parallel, periodic chains of stacked planar anions. In I, the interchain channels are found<sup>8</sup> to contain a random array of ions, and we infer that they exert on the conduction electrons a potential which varies randomly along the chains. The situation is somewhat different in II and III, where all lattice sites are occupied, but the organic cations are asymmetric, and can occupy their lattice sites in either of two inequivalent orientations. X-ray studies<sup>11,12</sup> suggest that the distribution of orientations is random, presumably with effects similar to those in I. This form of disorder could be eliminated by preparing a form of II or III with a symmetric cation, but attempts to do so<sup>9</sup> have led to drops of several orders of magnitude in the conductivity<sup>15</sup> and to crystal structures<sup>16</sup> resembling those expected from the well-known Peierls distortion<sup>17</sup> of a one-dimensional electron gas. These observations are consistent with the fact that the logarithmic divergence in the dielectric constant which gives rise to the Peierls distortion occurs only for an ordered array.

In general the wave functions in a weakly disordered material are extended over several lattice sites. Accordingly, we assign to each wave function  $\psi_i$  (of energy  $E_i$  near the Fermi energy) centered on the site  $i$ , a length  $L$ . We denote by  $\alpha$  the rate of decay of the wave function at its edges, and ignore the energy dependences of  $\alpha$ ,  $L$ , and the density of states  $\rho_0$ . The probability  $\Gamma_{ij}$  of hopping between two states  $i$  and  $j$  depends upon, among other things, the overlap of the wave functions and thus on  $\alpha R_{ij}$ , where  $R_{ij}$  is some length which depends on the detailed structure of the wave function and the distance  $|x_i - x_j|$ . Following Mott<sup>18</sup> and Ambegoakar, Halperin, and Langer,<sup>19</sup> (AHL) we have that

$$\begin{aligned} \Gamma_{ij} &\approx \gamma_0 \exp(-2\alpha R_{ij} - E_{ij}/kT), \quad R_{ij} > L \\ &\approx \gamma_0 \exp(-E_{ij}/kT), \quad R_{ij} < L, \end{aligned} \quad (1)$$

where  $\gamma_0$  is of the order of a typical phonon frequency and  $E_{ij} \approx |E_i| + |E_j| + |E_i - E_j|$  if the energies  $E_i$  and of the eigenstates are much greater than  $kT$ . Since  $L$  is larger than the lattice constant  $a$ , our band consists of a dense set of strongly overlapping states; the theories of Mott and AHL, which start from a condition of strong localization, must therefore be applied with care. However, the temperature dependence of the conductivity follows from purely dimensional arguments; and we believe that our introduction of  $R_{ij}$ , which is not in general equal to  $|x_i - x_j|$ , contains the correct physics for the present problem. The Mott and AHL theories applied to one dimension predict for the conductivity

$$\ln \sigma \sim -(T_0/T)^{1/2}, \quad (2)$$

where  $T_0 = \alpha v_c / k\rho_0$ , with  $v_c$  a dimensionless constant representing the number of states in a region of length  $2R_{\text{max}} = \alpha^{-1}(T_0/T)^{1/2}$  having energies within  $E_{\text{max}} = \frac{1}{2}k(TT_0)^{1/2}$  of the Fermi level.

In Fig. 1 we have replotted as  $\log \sigma$  versus  $T^{-1/2}$  some of the published conductivity data for I, II,

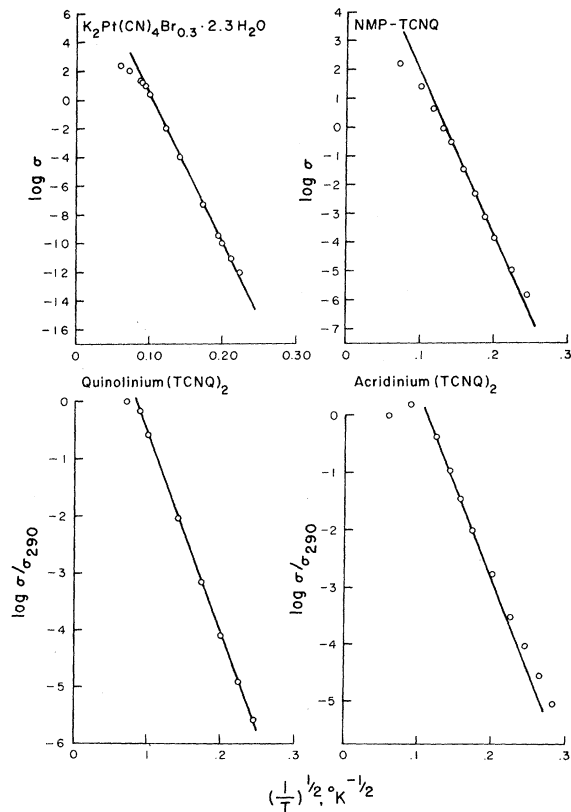


FIG. 1. Conductivity  $\sigma$  of I (Ref. 7), II (Ref. 1), IIIa (Ref. 3), and IIIb (Ref. 3) replotted versus  $T^{-1/2}$ . For I and II,  $\sigma$  is in  $\Omega^{-1} \text{cm}^{-1}$ . For IIIa and IIIb,  $\sigma_{290}$  is the conductivity at 290 K.

and III. The agreement with theory is particularly impressive for IIIa and Ia, where it persists over twelve orders of magnitude in the conductivity. We suspect that the departures at the lowest temperatures are manifestations of inter-chain tunneling: As  $R_{\max}$  becomes much larger than the distance between chains, tunneling must eventually become insensitive to the anisotropy of the crystal, and the three-dimensional  $T^{-1/4}$  law<sup>18,19</sup> should hold. More extensive low-temperature studies are needed to test this conjecture, but it is clear that the present data suggest such behavior, particularly in IIIb.

The departures at high temperatures, on the other hand, are to be expected from our one-dimensional model, and can in fact be used to estimate  $\alpha L$  and  $\nu_c$  as follows. Our analysis up to this point can hold only for large  $R_{\max}$ : It must break down when  $R_{\max}$  becomes so short that no  $\Gamma_{ij}$  which contributes to the conductivity depends strongly on  $R_{ij}$ . From (1) this is true above a temperature  $T_H$  such that

$$R_{\max}(T_H) = \frac{1}{2} \alpha^{-1} (T_0/T_H)^{1/2} = L, \quad (3)$$

whence

$$T_H = T_0/4\alpha^2 L^2. \quad (4)$$

For  $T > T_H$  there are at least  $\nu_c$  states within the energy interval  $2E_{\max}(T_H)$  which overlap the initial state  $i$  strongly. The activation energy is then of the order of the average energy separation between these states:

$$\ln \sigma \sim \frac{-k(T_0 T_H)^{1/2}}{kT\nu_c} = -(2\alpha L\nu_c)^{-1} \frac{T_0}{T}, \quad T > T_H. \quad (5)$$

Such behavior can persist with increasing temperature only until  $kT$  is of the order of the activation energy. This will of course occur at a temperature  $T_D$  defined by

$$T_D = T_0/2\alpha L\nu_c. \quad (6)$$

Above  $T_D$ , the conduction must be essentially diffusive, with a conductivity given by the Ein-

stein equation in the limit  $T \gg T_D$ :

$$\sigma = (Nne^2/kT) \langle \gamma_0 \rangle \langle (x_i - x_j)^2 \rangle. \quad (7)$$

Here  $N$  is the number of chains per unit cross-sectional area and  $n$  is the electron density on the chains. If at these temperatures  $\langle (x_i - x_j)^2 \rangle$  is of order  $a^2$ , and if  $\langle \gamma_0 \rangle \approx 10^{12} \text{ sec}^{-1}$ , the conductivity calculated from (7) agrees well with the experimental values<sup>1-7</sup> of ca.  $1-3 \times 10^2 \Omega^{-1} \text{ cm}^{-1}$  measured at room temperature for I, II, and III. We note that we are not dealing here with a transition to the metallic state as usually defined: The mean free path  $\lambda$  calculated from the one-dimensional nearly free-electron formula  $\sigma = 2Ne^2/\pi\hbar$  is of order  $a$ . Under this condition there can be no long-range phase coherence, and the conduction process is described more appropriately in terms of Brownian motion than of wave propagation.

It is difficult to measure  $T_D$ , but if we identify it as the temperature at which the conductivity passes through a maximum, we can combine (5) and (7) to determine

$$\nu_c^2 \approx T_0 T_D / T_H^2. \quad (8)$$

Since  $\nu_c$  depends only upon the dimensionality of the system, the ratio (8) should be a constant of the entire class of materials: Its invariance then represents a test of the crude theory presented here. We have applied (4) and (8) to the data of Fig. 1 to compute  $\alpha L$  and  $\nu_c$  for II, IIIa, and IIIb;  $\nu_c$  cannot be determined for Ia because  $T_D$  is presumably higher than the temperature at which the compound decomposes. The results are listed in Table I. We consider the agreement among the computed values of  $\nu_c$  excellent in view of the approximations involved and the difficulty in reading the data from the published graphs.

From their thorough experimental study of II, Epstein *et al.*<sup>4</sup> have interpreted this system, with its half-filled band, as a realization of the simple (ordered) one-dimensional Hubbard model, and

TABLE I. Values of  $\alpha L$  and  $\nu_c$  calculated using (4) and (8) and  $T_0$ ,  $T_H$ , and  $T_D$  obtained from data and references of Fig. 1.

| Material  | $T_0$<br>(K)       | $T_H$<br>(K) | $T_D$<br>(K)     | $\alpha L$ | $\nu_c$ |
|---|--------------------|--------------|------------------|------------|---------|
| $\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{0.3} \cdot 2.3\text{H}_2\text{O}$ | $5.79 \times 10^4$ | 120          | 580 <sup>a</sup> | 11.0       | ...     |
| NMP-TCNQ  | $1.72 \times 10^4$ | 50           | 200              | 0.3        | 4.6     |
| Quinolinium TCNQ  | $6.48 \times 10^3$ | 130          | 230              | 3.5        | 4.0     |
| Acridinium TCNQ   | $5.49 \times 10^3$ | 70           | 130              | 4.4        | 4.8     |

<sup>a</sup>Estimated assuming  $\nu_c = 4.5$ .

have asserted that a Mott-Hubbard transition from semiconductor to metal occurs with increasing temperature. The apparent temperature dependence of the activation energy for conductivity would then be due to an (as yet uncalculated) continuous renormalization of the Hubbard gap as the temperature is raised. This explanation does not appear to be consistent with several experimental facts. First, at 10 K the ac conductivity of II at  $10^{10}$  Hz is known<sup>2</sup> to be 4 orders of magnitude larger than the dc; we do not believe that this can be reconciled with the Hubbard gap of 0.17 eV demanded by the experiments of Epstein *et al.*<sup>4</sup> On the other hand, this behavior, as well as the temperature dependence of the ac conductivity and dielectric constant,<sup>2</sup> is precisely what is expected<sup>20</sup> if II is disordered. Strikingly similar results have been obtained for Ia<sup>6</sup> and IIIb.<sup>2</sup> Unfortunately the ac measurements have been made at only two frequencies, so that a detailed comparison with theory is not possible. Second, x-ray measurements<sup>11</sup> have shown explicitly that II is disordered, and the fit by the  $T^{-1/2}$  law for the dc conductivity persuades us that the Mott-Hubbard transition need not be invoked for II.

That is not to say that electron correlations are totally unimportant to the properties of these materials. The temperature dependence of the magnetic susceptibility of II as well as of I and III can be understood in terms of disorder if there is a repulsion energy between opposite spins in the same localized state. As Mott<sup>21</sup> has emphasized, this will give rise to a fraction of states with unpaired spins and to a susceptibility which includes the sum of a Curie-Weiss term  $\chi_c(T)$  and a temperature-independent term  $\chi_p$ . The measured spin susceptibilities of Ia,<sup>22</sup> II,<sup>1,4</sup> and IIIa<sup>23</sup> are of approximately this form. In II,<sup>1,4</sup> the crossing point at which  $\chi_c(T) \approx \chi_p$  occurs at a temperature  $T_M$  similar to  $T_D$ , the temperature of maximum conductivity; Epstein *et al.*<sup>4</sup> have interpreted this as a manifestation of a Mott-Hubbard transition. In I<sup>22</sup> and in IIIa,<sup>23</sup> however,  $T_M$  is quite different from  $T_D$ , and in this context it becomes clear that the rough agreement in II is probably a coincidence:  $T_M$  is primarily a measure of the correlation energy and  $T_D$  of the density of states and the degree of disorder.

*Note added in proof.*—After completion of this

work, we have learned that Professor N. F. Mott and Professor W. A. Little have come to some of the same conclusions reported in this paper.

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\*Present address: Department of Chemistry, University of Chicago, Chicago, Ill. 60637.

†Permanent address: Bell Telephone Laboratories, Murray Hill, N. J. 07974.

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