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Anomalous Frequency-Dependent Conductivity in Disordered One-Dimensional Systems

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Conduction by classical charge carriers is investigated for a one-dimensional system interrupted by barriers with a random distribution of activation energies. Under certain conditions the transport properties are dominated by disorder, and the model predicts an anomalous low-frequency conductivity $\sigma(\omega) \sim (-i\omega)^{\nu}$, with $\nu = (1-T/T_m)/(1+T/T_m)$, for $T < T_m$, and a mobility transition at $T = T_m$. The model is shown to describe recent experiments on the one-dimensional superionic conductor hollandite ($K_{1.54}Mg_{0.77}Ti_{7.23}O_{16}$).

The transport properties of real (quasi) one-dimensional (1D) systems are inherently sensitive to the presence of imperfections and disorder.[1] In this Letter we investigate classical 1D charge transport and represent the influence of imperfections by potential barriers with a random distribution of activation energies. We demonstrate that this randomness can completely dominate the diffusive or low-frequency behavior of the system. In particular, an exponential distribution of large activation energies is shown to lead to an anomalous power-law dependence of the low-frequency conductivity, with a temperature-dependent exponent. Under certain idealizations we also predict the existence of a finite delocalization temperature above which the 1D dc conductivity becomes nonzero. The anomalous conductivity behavior predicted by our model is somewhat similar to that observed in certain amorphous materials.[2]

We shall compare our theoretical results to those obtained experimentally on the 1D ionic conductor hollandite[3] ($K_{1.54}Mg_{0.77}Ti_{7.23}O_{16}$). In this compound the mobile K^+ ions reside in substoichiometrically ($\sim\frac{3}{4}$) occupied, noncommunicating channels. The state of order within these channels has been analyzed by diffuse-x-ray experiments.[4] These results indicate that the intrinsic barrier for the diffusion of the K^+ ions is only of the order of 0.1 eV. Because of the very high anisotropy of the ionic mobility it must, however, be expected that the macroscopic conductivity is dominated by the effects of crystal defects and impurities which impose additional barriers of variable height on the long-range ionic motion. The idealized *variable-barrier model* which we use is very simple, so as to keep the number of parameters small, but nevertheless be adequate to describe the situation in hollandite. We further believe that the general features of our results should be of fairly universal importance for 1D transport in real systems.

We consider a classical 1D conducting system whose intrinsic properties can be described by a diffusion constant

$$D_0 = a^2\Gamma_0 \tag{1}$$

(or a mobility $\mu_0 = D_0/k_B T$), where a is a hopping distance and Γ_0 a transfer rate. We further assume the existence of imperfections which divide the 1D system into segments of average length L. The charge transfer between adjacent segments, say n and $n+1$, is governed by a thermally activated process,

$$\Gamma_{n,n+1} = \Gamma_{n+1,n} = f_0 \exp[-\Delta_{n,n+1}/k_B T], \tag{2}$$

where $\Delta_{n,n+1}$ represents an activation energy and f_0 an effective attempt frequency given by

$$f_0 \sim (a/L)\Gamma_0. \tag{3}$$

The high-frequency response of the system is determined by its intrinsic properties (D_0, μ_0); i.e., by the processes within the segments. We are, however, interested in low frequencies,

$$\omega \ll (a/L)^2 \Gamma_0, \tag{4}$$

and temperatures such that

$$\Gamma_{n,n+1} \ll (a/L)\Gamma_0. \tag{5}$$

In this limit the dynamics of the system is dominated by the intersegment transfer rates $\Gamma_{n,n+1}$, and can be described by coupled rate equations for the charges q_n on the segments,

$$\frac{dq_n}{dt} = \sum_{\sigma=\pm 1} \Gamma_{n,n+\sigma}\left[(q_{n+\sigma} - q_n) + \frac{eLE(t)}{k_B T}\sigma q_{n+\sigma}\right], \tag{6}$$

where e is the charge of the individual charge carriers and $E(t) = E_0 e^{i\omega t}$, the external electric field. Equation (6) simply relates the transfer current $J_{n,n+1}$ to the density difference across the barrier, $\rho_n(L/2) - \rho_{n+1}(-L/2)$, where $\rho_n(x)$, $-L/2 \le x \le L/2$, is obtained from solving the intrinsic diffusion equation (with the appropriate boundary conditions) within each segment.[5] We note that local-field effects can be neglected, and that a random distribution of segment lengths does not seen to have important qualitative effects in the limit we are considering.

We now assume that the activation energies $\Delta_{n,n+1}$ are independently distributed according to a probability density

$$W(\Delta) = \begin{cases} W_0 \exp(-\Delta/k_B T_m), & \Delta_0 \le \Delta \le \Delta_1 \\ 0, & \text{otherwise,} \end{cases} \tag{7}$$

which, according to Eq. (2), leads to a probability density

$$\rho(\Gamma) = \begin{cases} \rho_0(T)\Gamma^{-\alpha}, & \Omega_1 \le \Gamma \le \Omega_0 \\ 0, & \text{otherwise,} \end{cases} \tag{8}$$

for the transfer rates $\Gamma_{n,n+1}$, where

$$\alpha = 1 - T/T_m \tag{9}$$

and

$$\Omega_i = f_0 \exp[-\Delta_i/k_B T], \quad i = 0, 1. \tag{10}$$

It can be shown[5] that the experimental results on hollandite imply the assumption of a strongly decreasing $W(\Delta)$, and the chosen exponential form of Eq. (7) is convenient for the mathematical analysis of the model. The lower cutoff Δ_0 has to be large enough to satisfy Eq. (5), and for our subsequent discussion it is important that $\Omega_1 \ll \Omega_0$.

Diffusion equations corresponding to Eq. (6) have recently been investigated in some detail[6] for general distributions $\rho(\Gamma)$ of the transfer rates. The dynamical quantities of the system can be expressed in terms of infinite continued fractions $g(\omega)$ of the form[6]

$$g(\omega) = \cfrac{1}{\cfrac{1}{\Gamma_{12}} + \cfrac{1}{-i\omega + \cfrac{1}{\cfrac{1}{\Gamma_{23}} + \cdots}}}. \tag{11}$$

At least for the calculation of single-particle correlation functions it has been shown[6] that in the low-frequency (long-time) limit the corresponding distribution function $f_\omega(g)$ can be replaced by a δ function located at $g_{\text{eff}}(\omega)$ which is determined by

$$g_{\text{eff}} = \int d\Gamma\, \rho(\Gamma)\left[\frac{1}{\Gamma} + \frac{1}{-i\omega + g_{\text{eff}}}\right]^{-1}. \tag{12}$$

This $g_{\text{eff}}(\omega)$ can be considered to define a nonrandom homogeneous system with an effective transfer rate

$$\Gamma_{\text{eff}}(\omega) = g_{\text{eff}}(\omega)[g_{\text{eff}}(\omega) - i\omega]/(-i\omega), \tag{13}$$

which, in general, is frequency dependent.[7] For a nonrandom system, on the other hand, the conductivity can easily be evaluated from Eq. (6). Using linear-response theory, we obtain

$$\sigma(\omega) = (e^2 n_0 L^2/k_B T)\Gamma_{\text{eff}}(\omega), \tag{14}$$

where n_0 is the density of charge carriers. We emphasize that the determination of the conductivity as given by Eqs. (12) to (14) is not implied

directly by the arguments of Ref. 6. On a large distance scale, however, appropriate to our small-frequency limit, $\Gamma_{\rm eff}(\omega)$ should represent the correct behavior of the random system, as can be demonstrated by an explicit scaling argument.[8] On the other hand it is interesting to note that Eqs. (12) to (14) also lead to the exact high-frequency conductivity of a random system described by Eq. (6).

For our specific distribution $\rho(\Gamma)$ of Eq. (8) the low-frequency behavior of $\Gamma_{\rm eff}(\omega)$ becomes

$$\Gamma_{\rm eff}(\omega)/\Omega_0 \approx \begin{cases} \alpha^{2/(2-\alpha)}(-i\omega/\Omega_0)^{\alpha/(2-\alpha)}, & 0 \ll \alpha < 1 \\ -2/\ln(-i\omega/\Omega_0), & \alpha = 0 \\ -\alpha/(1-\alpha), & \alpha < 0, \end{cases} \tag{15}$$

where we have neglected the lower cutoff in $\rho(\Gamma)$, i.e., $\Delta_1/k_BT \to \infty$. This is the main result of our idealized model which, for $\alpha > 0$, i.e., $T < T_m$, thus predicts an anomalous low-frequency behavior of the conductivity,

$$\sigma(\omega) = C(T)(-i\omega)^{\nu(T)} \tag{16}$$

with a temperature-dependent exponent

$$\nu = (1 - T/T_m)/(1 + T/T_m). \tag{17}$$

The dc conductivity $\sigma(0)$ therefore vanishes for $T < T_m$, and the system is an insulator with no proper mobility or diffusion constant. In this sense the charge carriers are (quasi) localized, though of course not confined to any finite region. Above T_m, $\sigma(\omega)$ becomes approximately frequency independent at low frequencies and $\sigma(0)$ is nonzero, so that T_m defines a mobility transition analogous to an insulator-to-metal transition.

We note that, according to the arguments of Ref. 8, the lower cutoff in $\rho(\Gamma)$ only becomes important for $\alpha > 0$ (i.e., $T < T_m$) and frequencies

$$\omega < [f_0 \exp(-\Delta_1/k_BT)]^{2-\alpha}, \tag{18}$$

and the residual conductivity for $T < T_m$ is given by

$$\sigma(0) = \frac{e^2 n_0 L^2}{k_B T}\left\langle\frac{1}{\Gamma}\right\rangle^{-1} = \frac{e^2 n_0 L^2}{k_B T} f_0 \left(\frac{T_m}{T} - 1\right)\left(\exp\left[\frac{\Delta_1 - \Delta_0}{k_B T_m} - \frac{\Delta_1}{k_B T}\right]\left\{1 - \exp\left[-\frac{\Delta_1 - \Delta_0}{k_B T}\left(1 - \frac{T}{T_m}\right)\right]\right\}^{-1}\right). \tag{19}$$

It exhibits an essentially exponential temperature dependence if T is not very close to T_m.

The investigation of the channel-axis conductivity of single-crystal hollandite of the composition $K_{1.54}Mg_{0.77}Ti_{7.23}O_{16}$ has shown that the room-temperature dc conductivity is unmeasurably small [$< 10^{-9}$ $(\Omega\ {\rm cm})^{-1}$]. For frequencies between 1 kHz and 1 MHz, however, an anomalous ac conductivity with a power-law frequency dependence as given by Eq. (16) is observed. Figure 1 shows the frequency dependence of the real and imaginary part of σ for different temperatures, and the temperature dependence of the exponent ν is displayed in Fig. 2. These results demonstrate the excellent and detailed agreement with the predictions of Eqs. (16) and (17), and for the samples used we deduce a value of the order of 410 K for T_m.

The prefactor $C(T)$ in Eq. (16) is related to the average distance L between barriers, to the lower bound of activation energies, Δ_0, and to

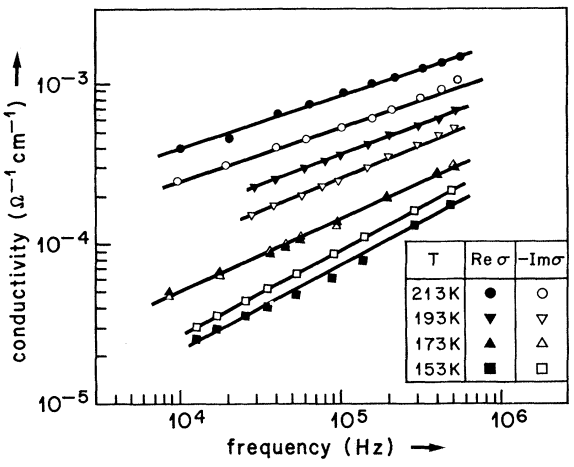

FIG. 1. Frequency dependence of the real and imaginary part of the channel-axis conductivity in hollandite for different temperatures.

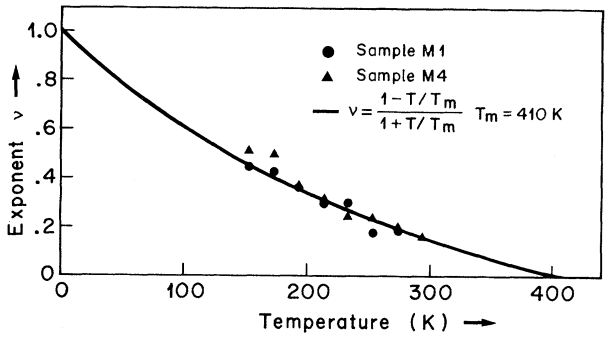

FIG. 2. Temperature dependence of the conductivity exponent ν [see Eqs. (16) and (17)].

the effective attempt frequency f_0. From a detailed analysis of the experimental data we deduce the values $L/a \lesssim 10$, $\Delta_0 \sim 0.2$ eV, and $f_0 \sim 10^{11}$ Hz. In addition, Eq. (19) and the experimental upper bound for $\sigma(0)$ of 10^{-9} $(\Omega\ \mathrm{cm})^{-1}$ lead to a lower bound for Δ_1 of the order of 2 eV.

In conclusion, we have demonstrated that a simple variable-barrier model can lead to interesting and unconventional predictions for the impurity-dominated transport properties of one-dimensional systems. It is able to explain the anomalous power-law behavior of $\sigma(\omega)$ as well as the temperature dependence of the exponent ν observed in hollandite. A detailed fit to the experimental data, moreover, leads to reasonable and consistent values for the model parameters. To our knowledge no other model for classical transport in one-dimensional systems is able to predict this rather complex conductivity behavior.

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[1]See, e.g., *Lecture Notes in Physics 65, Organic Conductors and Semiconductors* (Springer, New York, 1977); A. A. Abrikosov and I. A. Ryzhkin, Adv. Phys. 27, 147 (1978); M. J. Rice and J. Bernasconi, J. Phys. F 2, 905 (1972), and 3, 55 (1973).

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[7]Our $\Gamma_{\mathrm{eff}}(\omega)$ formally corresponds to the Laplace transform of the relaxation function $\varphi(t)$ in the "continuous-time random-walk model" of Scher and Montroll (Ref. 2). We note, however, that the determination and the physical interpretation of $\Gamma_{\mathrm{eff}}(\omega)$ is fundamentally different from their characterization of $\varphi(t)$ in terms of a site-independent hopping-time distribution.

[8]S. Alexander and J. Bernasconi, to be published.

Charge Retention in Deep-Inelastic Electroproduction

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We have measured the net charge of the forward hadrons electroproduced from a proton target and have observed a rise with increasing x $(=Q^2/2M\nu)$. This effect is expected in the quark-proton model as the electroproduction of hadrons becomes dominated by the fragmentation of u quarks. The data are also consistent with jet models in which a high-momentum leading hadron, rather than a slower hadron, is more likely to be carrying the parent quark.

The identification of final-state hadrons as the fragmentation products of fractionally charged quarks is an important but experimentally elusive feature of the quark-parton model. As a direct test of this feature, Feynman conjectured that the hadrons arising from quark fragmenta-