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Frequency-dependent charge transport in a one-dimensional disordered metal

S. Alexander
Racah Institute of Physics, The Hebrew University, Jerusalem, Israel

J. Bernasconi and W. R. Schneider
Brown Boveri Research Center, CH-5405 Baden, Switzerland

R. Biller, W. G. Clark, G. Grüner, R. Orbach, and A. Zettl
Department of Physics, University of California, Los Angeles, California 90024
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We report observation of the frequency- and temperature-dependent conductivity and dielectric constant of the organic conductor quinolinium dietetracyanoquinodimethanide [Qn(TCNQ)$_2$]. The experimental results are analyzed in terms of a random-barrier classical hopping model, with a specific distribution of barrier heights specified by three parameters. The model successfully fits both the real and imaginary parts of the conductivity over a very wide range of frequencies and temperatures.

Quinolinium ditetracyanoquinodimethanide [Qn(TCNQ)$_2$] is the prototype of organic conductors in which the charge transport is highly anisotropic with various evidence suggesting an important role for disorder in the transport properties.[1,2] Although different models have been proposed to describe the temperature dependence of the dc conductivity [$\sigma_{dc}(T)$], which is metallic at high (240 K) temperatures (T), and semiconducting at low T, recent NMR experiments[3] demonstrate that $\sigma_{dc}(T)$ is determined by a temperature-dependent electron mobility. The strong decrease of $\sigma_{dc}(T)$ at low temperatures then suggests the increased role of disorder.

In this Communication, we report the first observation of a frequency (ω)-dependent conductivity [$\sigma(\omega,T)=\sigma'(\omega,T)+i\sigma''(\omega,T)$] and dielectric constant ($\epsilon \propto \sigma''/\omega$) caused by single-electron motion in a highly anisotropic metal over a wide range of frequencies. We suggest that the temperature dependence of both quantities reflects the pecularities of random transport in one dimension, and we claim that the entirety of the experimental observations can be accounted for by a simple random barrier classical hopping model.

The quantities $\sigma(\omega,T)$ and $\epsilon(\omega,T)$ were measured along the high-conductivity direction at selected frequencies between dc and 420 MHz using several radio frequency bridge circuits. In all cases, a two-probe configuration was used. It is important that both dc and ac measurements are made simultaneously on the same samples. In this way, the effect of sample and geometry variations can be minimized, and all measurements normalized to $\sigma_{dc}(T)$ at room temperature. Careful checks of the dependence of $\sigma(\omega,T)$ and $\epsilon(\omega,T)$ on sample dimensions showed that the effect of contact resistance was negligible. This was further substantiated by an experiment which showed that $\sigma_{dc}(T)$ measured in our apparatus gave the same temperature dependence as $\sigma_{dc}(T)$ using a four-probe method. Except for $\epsilon(\omega,T)$ to be discussed later, our estimated experimental uncertainties are indicated by error flags or scatter in our data.

We exhibit $\sigma'(\omega,T)$ including earlier measurements[4] at 9.14 GHz in Fig. 1. Only a small representative fraction of the points actually measured are presented. The full dependence of $\sigma(\omega,T)$ on ω for selected temperatures is exhibited in Fig. 2. Finally, $\epsilon(\omega,T)$ vs T is plotted in Fig. 3 at two frequencies plus data from Holczer and Janossy.[4] Evaluation of $\epsilon(\omega,T)$ was carried out using the relation $\epsilon=(3.5\times10^{-12})RC\sigma'$, where R is the sample resistance (in Ω), C is its capacitance (in F), and σ' is expressed in $(\Omega\,\mathrm{cm})^{-1}$. The room-temperature values of ϵ represent averages measured on several samples with different resistances.

The first point to be noted from Figs. 1–3 is that the strong ω dependence of σ and ϵ immediately rules out various models in which the temperature dependence of σ_{dc} is interpreted in terms of extended electron states,[5] as well as models in which ϵ measured at microwave frequencies is interpreted as the static dielectric constant.[4] The overall behavior of the frequency and temperature dependence of σ is similar to that found in three-dimensional amorphous semiconductors,[6] where $\sigma_{dc}(T)$ is accounted for by excitations across a mobility gap (i.e., to extended states) while the frequency-dependent part arises from localized states in the gap region. Recent NMR measurements,[3] however, demonstrate that $\sigma_{dc}(T)$

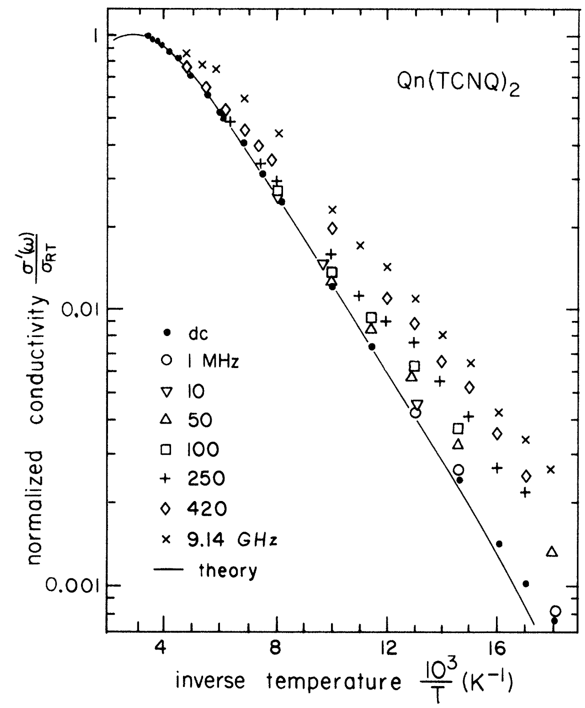

FIG. 1. Temperature dependence of $\sigma'(\omega,T)$ in $Qn(TCNQ)_2$. The solid line represents the best fit to the data for $\sigma_{dc}(T)$. The model parameters are $\Delta_{min}=290$ K, $\Delta_{max}=600$ K, $T_m=320$ K, and $\omega_{at}=1.9\times10^{11}$ sec^{-1}, and the fitting procedure is outlined in the text. The data at 9.14 GHz are taken from Holczer and Janossy (Ref. 4).

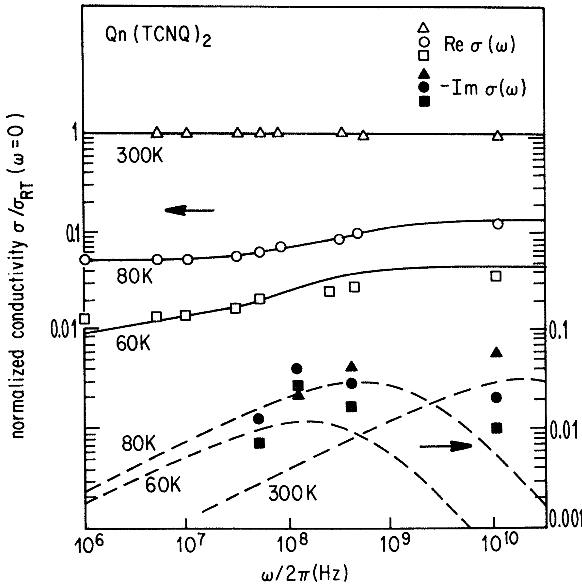

FIG. 2. $\sigma'(\omega,T)$ (full curves) and $-\sigma''(\omega,T)$ (dashed curves) vs frequency, calculated for three different temperatures using the parameters listed in the caption to Fig. 1. The experimental data for $Qn(TCNQ)_2$ below 9.14 GHz are our own (□, ■: 60 K; ○, ●: 80 K; and △, ▲: 300 K), while those at 9.14 GHz are from Holczer and Janossy (Ref. 4). The open points are the real part of the conductivity; the closed points are the imaginary part. The scale for $-\sigma''(\omega,T)$ has been shifted downward by a decade to avoid confusion with $\sigma'(\omega,T)$.

for $Qn(TCNQ)_2$ reflects temperature-dependent diffusion along the chain direction. The number of electrons participating in the charge transport is independent of the temperature, and the strong decrease of $\sigma_{dc}(T)$ at low temperatures is caused by a strong decrease in the one-dimensional diffusion constant. We propose, therefore, that $\sigma_{dc}(T)$ and $\sigma(\omega,T)$ do not signify different carriers, but rather that both reflect one-dimensional diffusion processes associated with random barriers.

The random potentials responsible for electron localization in one dimension at low temperatures in $Qn(TCNQ)_2$ have been attributed to randomly oriented Qn ions[7] (weak disorder) and impurities on the TCNQ chains[8] (strong disorder). We shall assume that the electrical transport is determined mainly by high mobility segments of average length L_0, exhibiting metallic conduction, separated by large barriers with a (random) distribution of heights.

We are able to account for the entirety of the observed behavior of $\sigma(\omega,T)$ by this simple one-dimensional model, a variant of that introduced originally to describe the anomalous behavior of $\sigma(\omega,T)$, in the one-dimensional superionic conductor hollan-

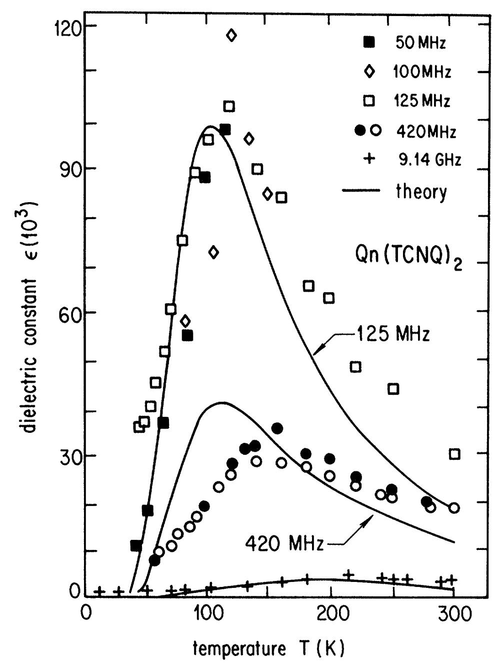

FIG. 3. Temperature dependence of $\epsilon(\omega,T)$ in $Qn(TCNQ)_2$. The solid lines are calculated using the parameters listed in the caption to Fig. 1. The data at 9.14 GHz are taken from Holczer and Janossy (Ref. 4).

dite.[9] We assume that for all frequencies and temperatures of interest, the intrinsic segment conductance is much larger than the intersegment transfer rates

$$W_{n,n+1} = \omega_{\text{at}} \exp(-\Delta_{n,n+1}/T) \quad , \tag{1}$$

where $\Delta_{n,n+1}$ represents the barrier height and ω_{at} an attempt frequency. The transport properties of the system are then completely dominated by the $W_{n,n+1}$, and can be described by a master equation.[9,10] The conductivity $\sigma(\omega,T)$ of our model system can be expressed as follows[11]:

$$\sigma(\omega,T) = (n_0 e^2 L_0^2/k_B T)\langle D(-i\omega)\rangle \quad , \tag{2}$$

where n_0 is the carrier density and e the charge. The average $\langle \cdots \rangle$ is defined with respect to the distribution of the independent random variables $W_{n,n+1}$. The frequency-dependent diffusion constant $\langle D(-i\omega)\rangle$ is defined in terms of the solution of the master equation.[10]

The barrier heights $\Delta_{n,n+1}$ are assumed to be mutually independent random variables, distributed according to a probability density $\hat{\rho}(\Delta)$ which is chosen to have the specific form[9]

$$\hat{\rho}(\Delta) \propto \exp(-\Delta/T_m), \quad \Delta_{\min} < \Delta < \Delta_{\max} \quad , \tag{3}$$

with $\hat{\rho}(\Delta) = 0$ otherwise. Together with Eq. (1), this leads to the probability density

$$\rho(w) \begin{cases} \propto w^{-\alpha}, & W_{\min} < w < W_{\max} \\ = 0, & \text{otherwise} \quad , \end{cases} \tag{4}$$

for the transfer rates $W_{n,n+1}$, where $\alpha = 1 - (T/T_m)$, and $W_{\min} = \omega_{\text{at}} \exp(-\Delta_{\max}/T)$, $W_{\max} = \omega_{\text{at}} \times \exp(-\Delta_{\min}/T)$. This distribution for w is peaked for small w between two temperature-dependent limits, such that the width of the distribution narrows as the temperature is increased. The parameter T_m determines the strength of the tendancy for $\rho(w)$ to diverge at low w (though of course it is cut off at $W_{\min}$), and thus serves as a measure of the sharpness of the distribution in w about the $W_{\min}$. For $T < T_m$, the distribution is peaked at $W_{\min}$; for $T > T_m$, the distribution rises smoothly as w increases from $W_{\min}$. In the limit of vanishingly small $W_{\min}$, this generates a transition from vanishing to finite dc conductivity at $T = T_m$.[9] It will turn out in the present case that our results are relatively insensitive to the precise value of T_m, but that it must be larger than the temperatures at which the conductivity exhibits a substantial frequency dependence. Otherwise, the distribution in w is too "flat" to yield a substantial frequency dependence to the conductivity.

Except for its high-frequency asymptotic expansion, a rigorous evaluation of $\langle D(-i\omega)\rangle$ does not seem possible.[11] In this Communication, we shall therefore use an effective-medium (or coherent-potential) approximation[11] to investigate the behavior of $\langle D(-i\omega)\rangle$ over the whole frequency range. It follows[9,11] that $\langle D(z)\rangle$ can be identified with an effective, frequency-dependent, transfer rate $W_{\text{eff}}(z)$,

$$\langle D(z)\rangle = W_{\text{eff}}(z) = g_{\text{eff}}(z)[g_{\text{eff}}(z) + z]/z \quad , \tag{5}$$

where W_{eff}, or g_{eff}, is determined from a self-consistency equation. We adopt that which corresponds to Kirkpatrick's[12] effective-medium theory for random resistor networks (see Ref. 11),

$$\int_0^\infty dw\,\rho(w) \frac{w - W_{\text{eff}}}{w + \frac{1}{2}(g_{\text{eff}} + z)} = 0 \quad , \tag{6}$$

and we note that z, $g_{\text{eff}}(z)$, and $W_{\text{eff}}(z)$ are complex quantities. Using an iteration procedure, Eq. (6) can easily be solved numerically.

For arbitrary $\rho(w)$, the effective medium approximation always reproduces the exact $\omega \to \infty$ limit of $\langle D(-i\omega)\rangle$. For $\omega \to 0$, it leads to the same ω dependence for $\langle D(-i\omega)\rangle$ as that conjectured[11,13] to be exact when using a general scaling hypothesis.[11,14] We expect, therefore, that $W_{\text{eff}}(-i\omega)$ will represent a quite accurate approximation of $\langle D(-i\omega)\rangle$ for the entire frequency range of these measurements (frequencies low compared to the inverse propagation time along a segment).

For the specific probability density $\rho(w)$ of Eq. (4), we obtain the following asymptotic dependences

$$W_{\text{eff}}(-i\omega) = \begin{cases} a_0 + a_1(-i\omega)^{1/2} + \dots, & \omega \to 0 \quad \text{(7a)} \\ b_0 - b_1/(-i\omega) + \dots, & \omega >> W_{\max} \quad \text{.(7b)} \end{cases}$$

According to Eqs. (2) and (5), this implies that $\text{Re}\,\sigma(\omega,T)$ increases with increasing frequency from a dc value, $A_0(T) \propto a_0(T)/T$, to a high-frequency value, $B_0(T) \propto b_0(T)/T$, whereas the dielectric constant $\epsilon(\omega,T) \propto -\sigma''(\omega,T)/\omega$ varies as $\omega^{-1/2}$ at low frequencies and as ω^{-2} at high frequencies. The expansion coefficients a_i and b_i can easily be calculated from Eqs. (6) and (4).

A reasonably accurate fit of our model results for $\sigma(\omega,T)$ to the complete Qn(TCNQ)_2 data (Figs. 1–3) can be obtained from the following procedure. For a given value of T_m, we determine $\Delta_{\min}$ and $\Delta_{\max}$ from the measured ratio of $\text{Re}\,\sigma(\omega,T)$ between high and low frequencies at $T = 80$ K, and from the measured ratio of σ_{dc} between $T = 300$ and 80 K. This leads to $\Delta_{\min} \simeq 290$ K and $\Delta_{\max} \simeq 600$ K for $T_m = 320$ K. The dependence of $\Delta_{\min}$ and $\Delta_{\max}$ on T_m is very weak, and it does not seem possible to determine T_m from the present experimental results. However, as remarked earlier, T_m must be larger than the temperatures at which the conductivity exhibits significant frequency dependence. This implies a lower limit of roughly 200 K. The value we have taken seems a reasonable compromise, and fits the strength of the frequency variation satisfactorily at the temperatures measured. With these parameters, we obtain a quite accurate fit of the measured temperature dependence of σ_{dc} between $T = 60$ and 300 K (see Fig. 1).

Using Eqs. (2), (5), and (6), we have calculated $\sigma'(\omega,T)$ and $\sigma''(\omega,T)$ over the full frequency range for several temperatures. The results are exhibited in Fig. 2, and show reasonably good overall agreement with our measurements at 420 MHz and below, and with those of Holczer and Janossy at 9.14 GHz,[4] whose data are also included.

The dielectric constant $\epsilon(\omega,T)$ follows immediately from $-\sigma''(\omega,T)/\omega$. Our model results, with no further adjustable constants, are plotted versus temperature at three different frequencies (125 MHz, 420 MHz, and 9.14 GHz in Fig. 3. Again, acceptable agreement between theory and experiment is found.

In conclusion, we have demonstrated how a simple random barrier model for hopping transport can give rise to frequency-dependent conductivities of the type exhibited by a variety of quasi-one-dimensional electronic conductors.[1–4] We should emphasize that we can account for the complicated behavior exhibited experimentally for both the real and imaginary parts of the conductivity using only a simple one-chain model. We do not invoke two different mechanisms or two competing conductivity paths.

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