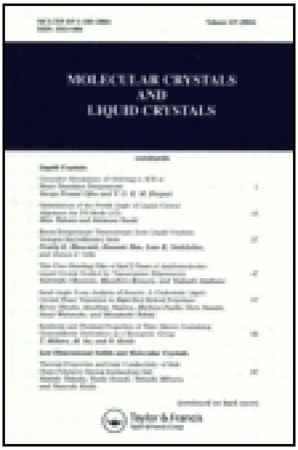

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Frequency-Dependent Conductivity of Quasi-One-Dimensional Electronic Conductors

S. Alexander [a], J. Bernasconi [b], W. R. Schneider [b], R. Biller [c] & R. Orbach [c]

[a] Racah Institute of Physics, Hebrew University, Jerusalem, Israel

[b] Brown Boveri Research Center, CH-5405, Baden, Switzerland

[c] Department of Physics, University of California, Los Angeles, CA, 90024, USA

Version of record first published: 14 Oct 2011.

Mol. Cryst. Liq. Cryst., 1982, Vol. 85, pp. 121–128
0026-8941/82/8501-0121$06.50/0

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

FREQUENCY-DEPENDENT CONDUCTIVITY OF QUASI-ONE-DIMENSIONAL ELECTRONIC CONDUCTORS

S. ALEXANDER
Racah Institute of Physics, Hebrew University, Jerusalem, Israel

J. BERNASCONI and W.R. SCHNEIDER
Brown Boveri Research Center, CH-5405 Baden, Switzerland

R. BILLER and R. ORBACH
Department of Physics, University of California, Los Angeles, CA 90024, USA

Received for publication August 31, 1981

For a one-dimensional model system, described by a master equation with random hopping rates $W_{n,n+1} \propto \exp(-\Delta_{n,n+1}/T)$, the frequency and temperature dependent electrical conductivity $\sigma(\omega,T)$ is calculated within the framework of an Effective-Medium approximation. Using a specific distribution of barrier heights, $\hat{\rho}(\Delta) \propto \exp(-\Delta/T_m)$ for $\Delta_{min} < \Delta < \Delta_{max}$, the model is shown to account quantitatively for the measured (Zettl, Grüner, and Clark) frequency and temperature dependence of Reσ and Imσ in the quasi-one-dimensional conductor $Qn(TCNQ)_2$.

I. INTRODUCTION

Peculiar frequency and temperature dependences of the complex electrical conductivity, $\sigma(\omega,T)$, are observed almost universally in quasi-one-dimensional conductors[1-4]. The dc conductivity, Re $\sigma(0,T)$, of such systems is generally activated, and Re $\sigma(\omega,T)$ appears to increase from its dc value at a temperature dependent crossover frequency

$\omega_{c.o.}(T)$. It saturates at a constant value, Re $\sigma(\infty,T)$, at high frequencies, and the ratio Re $\sigma(\infty,T)$/Re $\sigma(0,T)$ decreases towards one with increasing temperature. The dielectric constant, $\varepsilon(\omega,T) \propto -$ Im $\sigma(\omega,T)/\omega$, is strongly frequency dependent, and exhibits a pronounced peak as a function of temperature.

We have shown[5] that disorder, combined with one-dimensional transport, can account for all these features, and in the following we shall summarize some details and consequences of our investigations. Our simple one-dimensional model is a variant of the random barrier model[6] introduced originally to describe the anomalous behavior of $\sigma(\omega,T)$ in the one dimensional superionic conductor hollandite. It is based on the existence of impurity-induced potential barriers which divide the one-dimensional system into segments of average length L_0, and on the assumption that for all frequencies and temperatures of interest the intrinsic segment conductance is much larger than the intersegment transfer rates

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

Here, $\Delta_{n,n+1}$ represents the barrier height, and ω_{at} is an attempt frequency. The transport properties of the system are then completely dominated by the probability distribution $\rho(W)$ of the (mutually independent) transfer rates $W_{n,n+1}$, and can be described[6,7] by a master equation of the form

$$\frac{dP_n}{dt} = W_{n,n-1}(P_{n-1}-P_n) + W_{n,n+1}(P_{n+1}-P_n) \quad , \tag{2}$$

where P_n denotes the excess charge on segment n.

The properties of random one-dimensional systems of this type have recently been investigated in some detail[7-9]. The conductivity $\sigma(\omega,T)$ corresponding to these model systems can be written as[8,9]

$$\sigma(\omega,T) = \frac{n_o e^2 L_o^2}{kT} \langle D(-i\omega)\rangle \quad , \tag{3}$$

where the generalized diffusion constant $\langle D(z)\rangle$ is given by

$$\langle D(z)\rangle = \frac{1}{2} z^2 \sum_{n=-\infty}^{\infty} n^2 \langle \tilde{P}_n(z)\rangle \quad . \tag{4}$$

Here n_o is the density and e the charge of the charge carriers, and <...> denotes an average with respect to the probability distribution of the $W_{n,n+1}$. The $\tilde{P}_n(z)$ are determined by

$$z\tilde{P}_n + W_{n,n-1}(\tilde{P}_n-\tilde{P}_{n-1}) + W_{n,n+1}(\tilde{P}_n-\tilde{P}_{n+1}) = \delta_{n,o} \quad , \tag{5}$$

i.e. by the Laplace transform of Eq.(2), subject to the initial condition $P_n(0) = \delta_{n,o}$.

II. EFFECTIVE-MEDIUM APPROXIMATIONS

To investigate the behavior of $\langle D(-i\omega)\rangle$ over the whole frequency range, Effective-Medium-type approximations have been proved to be very useful[6,8,9]. The random $W_{n,n+1}$ in Eq.(5) are replaced by an effective, frequency dependent transfer rate $W_{eff}(z)$, which is determined by a suitably chosen self-consistency equation. It follows that $\langle D(z)\rangle$ is approximated by $W_{eff}(z)$, and we have analyzed[8,9] two different self-consistency conditions. One of them is obtained by applying Kirkpatrick's resistor network Effective-Medium theory[10] to the electrical network analog corresponding to Eq.(5)[8,9]. It is equivalent to that obtained by the Single-Bond Coherent Potential Approximation and leads to

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

where W_{eff} and g_{eff} are related by

$$g_{eff} = \left[\frac{1}{W_{eff}} + \frac{1}{g_{eff}+z}\right]^{-1} \quad . \tag{7}$$

We note that z, g_{eff}, and W_{eff} are complex quantities, and that Eqs.(6) and (7) can easily be solved numerically for $W_{eff}(z)$.

For arbitrary $\rho(w)$, this Effective-Medium approximation reproduces the exact $\omega\to\infty$ asymptotic behavior[9] of the real and imaginary part of $\langle D(-i\omega)\rangle$. For $\omega \to 0$ it leads to the same ω-dependence for $\langle D(-i\omega)\rangle$ as has been obtained[8,9] from a general scaling hypothesis for the $\langle \tilde{P}_n(z)\rangle$. We therefore expect that $W_{eff}(-i\omega)$ represents a very accurate approximation to $\langle D(-i\omega)\rangle$ over the entire frequency range.

III. THE BARRIER HEIGHT DISTRIBUTION

Within our model, the detailed behavior of $\sigma(\omega,T)$ is completely determined by the properties of the transfer rate distribution $\rho(w)$ which, through Eq.(1), arises from a barrier height distribution $\hat{\rho}(\Delta)$. For our subsequent discussion, we shall choose the specific form

$$\hat{\rho}(\Delta) \propto \exp(-\Delta/T_m) \quad , \quad \Delta_{min} < \Delta < \Delta_{max} \quad , \qquad (8)$$

which leads to

$$\rho(w) \propto w^{-\alpha(T)} \quad , \quad W_{min} < w < W_{max} \quad , \qquad (9)$$

where $\alpha = 1 - T/T_m$, $W_{min} = \omega_{at}\exp(-\Delta_{max}/T)$, $W_{max} = \omega_{at} \cdot \exp(-\Delta_{min}/T)$, and where the probability densities $\hat{\rho}(\Delta)$ and $\rho(w)$ are, of course, properly normalized.

A barrier height distribution of this type with $\Delta_{max} \to \infty$, has been shown[6] to lead to a remarkably accurate and detailed description of the anomalous properties of $\sigma(\omega,T)$ in the one-dimensional superionic conductor hollandite. In the following we shall demonstrate that the truncated distribution of Eq.(8), with finite values for Δ_{min} and Δ_{max}, also leads to a reasonably accurate description of both the frequency and temperature dependence of $\sigma(\omega,T)$ in the quasi-one-dimensional electronic conductor $Qn(TCNQ)_2$. We note, however, that in this case the quality of the description is not very sensitive to the precise analytic form of $\hat{\rho}(\Delta)$, in contrast to the situation in hollandite[6].

For the specific, truncated probability density $\rho(w)$ of Eq.(9), our Effective-Medium analysis of section II leads to the following prediction for the asymptotic dependences of $W_{eff}(-i\omega)$[5]:

$$W_{eff}(-i\omega) = a_0 + a_1(-i\omega)^{1/2} + \ldots \quad , \quad \omega \to 0 \quad , \qquad (10)$$

$$W_{eff}(-i\omega) = b_o - b_1/(-i\omega) + \ldots \quad , \quad \omega \gg W_{max} \quad ,(11)$$

where the expansion coefficients $a_i(T)$ and $b_i(T)$ can easily be calculated from Eqs.(6), (7), and (9).

It follows that Re $\sigma(\omega,T)$ increases from a dc value, $\sigma_{dc}(T) \propto a_o(T)/T$, to a high frequency value, $\sigma_\infty(T) \propto b_o(T)/T$. The explicit temperature dependence of σ_{dc} is given by

$$\sigma_{dc} \propto \frac{T_m - T}{T^2} \frac{\exp(-\Delta_{max}/T)}{1-\exp[-(\Delta_{max}-\Delta_{min})(1/T-1/T_m)]} \quad , \quad (12)$$

and it further turns out that

$$\omega_{c.o.}(T) \propto T\,\sigma_{dc}(T) \quad , \quad (13)$$

where $\omega_{c.o.}$ denotes the crossover frequency at which Re $\sigma(\omega,T)$ starts to increase. The ratio $\sigma_\infty/\sigma_{dc}$ is large at low T, and decreases towards one with increasing temperature.

The dielectric constant, $\varepsilon(\omega,T) \propto -\text{Im}\,\sigma(\omega,T)/\omega$, is predicted to vary as $\omega^{-1/2}$ at low frequencies and as ω^{-2} at high frequencies. As a function of T, it exhibits a pronounced peak if ω is not too large.

We finally note that the $(-i\omega)^{1/2}$ term in the low frequency expansion of $\langle D(-i\omega)\rangle \approx W_{eff}(-i\omega)$, Eq.(10), leads to a $t^{-3/2}$ long time tail in the memory kernel of the associated non-Markovian master equation[11]. If confirmed experimentally, the existence of such long time tails may turn out to become an important aspect of transport in low-dimensional conductors.

IV. APPLICATION TO $Qn(TCNQ)_2$

The results of the preceding section indicate that our model can account, at least qualitatively, for all the features exhibited by $\sigma(\omega,T)$ in quasi-one-dimensional electronic conductors. To obtain a quantitative description of the complete $Qn(TCNQ)_2$ data[3], however, we have to determine the values of Δ_{min}, Δ_{max}, and T_m. From the measured[3] ratios of $\sigma_{dc}(300K)/\sigma_{dc}(80K)$ and $\sigma_\infty(80K)/\sigma_{dc}(80K)$, we obtain[5] $\Delta_{min} \approx 290K$ and $\Delta_{max} \approx 600K$, if $T_m \approx 320K$. The

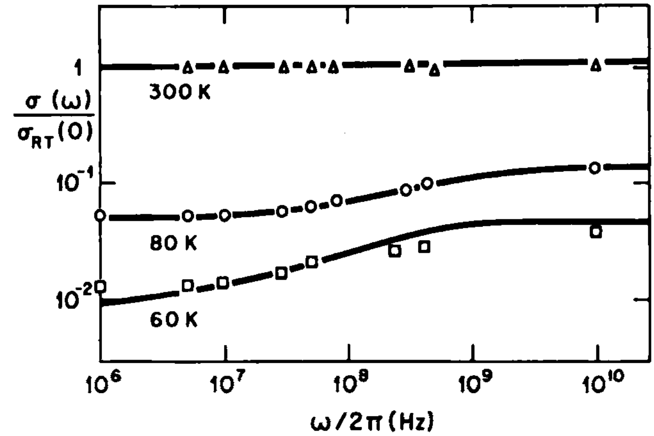

FIGURE 1 Model results for Re $\sigma(\omega,T)$ [full curves] vs. frequency for three different temperatures. The model parameters are Δ_{min} = 290K, Δ_{max} = 600K, T_m = 320K, and ω_{at} = 1.9×10^{11} sec^{-1}. The experimental data are from Ref.3.

dependence of Δ_{min} and Δ_{max} on T_m, however, is very weak, and it does not seem possible to determine the precise form of $\hat{\rho}(\Delta)$ between its cutoffs from the present experimental data.

With the above parameter values, however, we obtain a reasonably accurate fit to the complete data[3] for $\sigma(\omega,T)$ in $Qn(TCNQ)_2$. In Fig.1 we present our results for the frequency dependence of Re $\sigma(\omega,T)$ at three different temperatures, and in Fig.2 we exhibit the temperature dependence of the dielectric constant, $\varepsilon(\omega,T) \propto -\,\mathrm{Im}\,\sigma(\omega,T)/\omega$, at three different frequencies. In addition, a detailed comparison of the experimental data for $\sigma_{dc}(T)$ with Eq.(12), and a verification of the proportionality of $\omega_{c.o.}(T)$ and $T\sigma_{dc}(T)$, Eq.(13), can be found in Ref.3. Taking into account the simplicity of the model, and the small number of fitting parameters, the overall agreement with the rather complicated behavior of both Re $\sigma(\omega,T)$ and Im $\sigma(\omega,T)$ seems quite satisfactory.

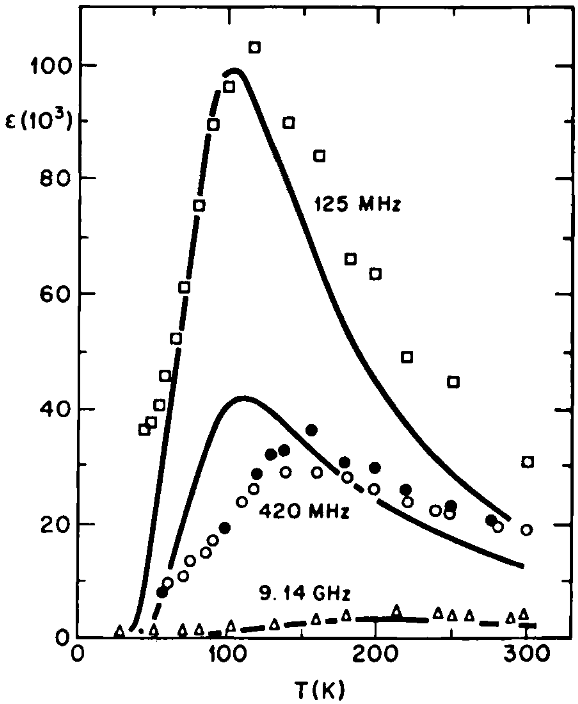

FIGURE 2 Model results for ε(ω,T) [full curves] vs. temperature for three different frequencies. Same model parameters as in Fig.1, experimental data from Ref.3.

REFERENCES

1. H. A. Pohl and M. Pollak, J.Chem.Phys. 66, 4031 (1977).
2. G. Grüner, Bull.Am.Phys.Soc. 25, 255 (1980); Chemica Scripta, 1981, accepted for publication.
3. A. Zettl, G. Grüner, and W.G. Clark, to be published; G. Grüner, A. Zettl, and W.G. Clark, these proceedings.
4. J. C. Giuntini and J. V. Zanchetta, J.de Chimie Physique (France), 1981, accepted for publication.
5. S. Alexander, J. Bernasconi, W. R. Schneider, R. Biller, and R. Orbach, to be published.
6. J. Bernasconi, H. U. Beyeler, S. Strässler, and S. Alexander, Phys.Rev.Lett. 42, 819 (1979).

7. S. Alexander, J. Bernasconi, W. R. Schneider, and R. Orbach, in Physics in One Dimension, ed. by J. Bernasconi and T. Schneider, Springer Series in Solid-State Sciences (1981), Vol. 23, p. 277.
8. J. Bernasconi, W. R. Schneider, and W. Wyss, Z. Phys. B37, 175 (1980).
9. S. Alexander, J. Bernasconi, W. R. Schneider, and R. Orbach, Rev.Mod.Phys. 53, 175 (1981).
10. S. Kirkpatrick, Rev.Mod.Phys. 45, 574 (1973).
11. J. Machta, to be published.

NOTE ADDED IN PROOF

For hopping rate distributions $\rho(w)$, for which the moments

$$m_{-k} = \int_0^\infty dw\, \rho(w) w^{-k} \quad , \quad k = 1,2 \quad ,$$

exist, R. Zwanzig (preprint) has recently shown that the first two terms of the low frequency expansion for $W_{eff}(-i\omega)$ coincide with the exact low frequency expansion of $\langle D(-i\omega)\rangle$:

$$\langle D(-i\omega)\rangle = 1/m_{-1} + \frac{m_{-2} - m_{-1}^2}{2m_{-1}^{5/2}} (-i\omega)^{1/2} + \cdots \quad .$$

For these type of hopping rate distributions at least, our Effective-Medium approximation thus becomes exact both at high and at low frequencies.