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Hopping conduction in quasi-one-dimensional disordered compounds*†

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Using a percolation construction we evaluate the temperature dependence of the phonon-assisted dc hopping conductivity of a model appropriate to a class of anisotropic quasi-one-dimensional conductors in which the electronic states in the vicinity of the Fermi level are localized because of intrinsic and/or extrinsic static disorder. We find temperature dependences of the general form $\ln[\sigma(T)/\sigma_0] = -[T_0(m)/T]^{1/m}$ where m is weakly temperature dependent and has the value 4 for asymptotically low temperatures, $T \rightarrow 0$ K. With increasing temperature the interchain hopping distances become smaller and m decreases gradually. In a model in which the two transverse directions are equivalent, m decreases to 2.91 when all allowed interchain hops are to the nearest chain only. The percolation channel is three-dimensional. For a model in which the two transverse directions are inequivalent, the percolation channel becomes two-dimensional at high temperatures when all interchain hops along the more difficult direction become more difficult than the critical percolation hop. In this case m decreases to 2.70. With further increase in temperature the percolation construction breaks down in both cases. The observed conductivity of NMP-TCNQ (N-methylphenazinium tetracyanoquinodimethane) is found to be in good agreement with our results.

I. INTRODUCTION

Recently there has been considerable controversy[1-6] regarding the temperature dependence of the dc hopping conductivity in two classes of compounds[7-9] which consist of weakly coupled linear parallel chains of strongly coupled atoms or molecules. The electrical conductivity is highly anisotropic, and therefore, these compounds have been treated as almost one-dimensional conductors. This paper is concerned only with those of these compounds in which the electronic states in the vicinity of the Fermi level are localized because of intrinsic and/or extrinsic static disorder. The most prominent examples are salts of the organic ion-radical tetracyanoquinodimethane[10,11] (TCNQ) and the square planar complexes of transition metals like platinum and iridium.[12,13] Three different interpretations have been suggested: Epstein *et al.*[14] have discussed the TCNQ salts in terms of the one-dimensional Hubbard model and the assumption of a metal to insulator transition. Kuse and Zeller[15] and Rice and Bernasconi[16] introduced the interrupted strand model in which the crystal is considered to consist of linear metallic strands interrupted by insulating lattice defects. A criticism of these models already exists in the literature[1,2] and we shall not repeat the arguments here. Bloch, Weisman, and Varma proposed a model in which the highly conducting quasi-one-dimensional (QOD) compounds are disordered. Actually these compounds have a well-defined lattice structure; however, because of the random presence of charges or dipoles, the conduction electrons experience a potential which varies randomly along the chains.[1] Because of these potential fluctuations, all electronic states are localized[17-20] and consequently the electronic conductivity must be due to phonon-activated hopping from one localized state to another.

Following Mott's argument[21,22] that at low temperatures an electron, instead of hopping to a near neighbor, can hop to a distant but energetically more favorable state, Bloch, Weisman, and Varma proposed (from dimensional considerations only) a temperature dependence of the form

$$\ln[\sigma(T)/\sigma_0] = -(T_1/T)^{1/2} , \tag{1.1}$$

where T_1 is a constant. Recently, however, Kurkijarvi[3] showed that for a single infinite chain the hopping conductivity should have the temperature dependence

$$\ln[\sigma(T)/\sigma_0] = -(T_0/T) \tag{1.2}$$

rather than that of (1.1). Kukijarvi's calculation is not realistic because the QOD compounds consist of a macroscopically large number of parallel chains, each of finite length $\mathfrak{L}$, rather than of a single infinite chain. More recently Brenig, Döhler, and Heyszenau[4] have shown that the conductivity of an infinitely long chain is of the form (1.2), but that of a collection of parallel noninteracting chains of finite length is of the form (1.1). The resultant conductivity, however, depends on the length of the chains and therefore violates Ohm's law. Also, the construction of Brenig, Döhler, and Heyszenau is analogous to that of Miller and Abrahams,[23] whereas it is possible[24-27] to obtain a lower net resistance by seeking complete paths of lowest impedance. A model which corrected these shortcomings of the BDH model was proposed by Shante, Varma, and Bloch.[5] The

Shante-Varma-Bloch approach is similar to that of Ambegaokar, Halperin, and Langer[25] (AHL) but involves probabilistic considerations of finding a fraction of chains in which an electron can percolate down the entire length of the chain without ever having to go through a very large impedance. However, the percolation aspects of their calculation are insufficiently rigorous.

In all of these calculations the QOD conductors have been treated as if they were strictly one-dimensional even though there is a finite, though much smaller, conductivity in directions transverse to the highly conducting axis. In this paper we discuss a model which includes the interchain couplings (which are much weaker than the intrachain couplings) and accounts for the anisotropic lattice constant (the interchain separation being much larger than the intrachain intermolecular separation). We find that within the standard percolation models[24-27] the hopping conductivity has a temperature dependence of the form

$$\ln[\sigma(T)/\sigma_0] = -[T_0(m)/T]^{1/m} \ , \qquad (1.3)$$

where m is weakly temperature dependent and, for three- (two-) dimensional anisotropic conductors, has the value 4 (3) for asymptotically low temperatures $T \to 0$ K. With increasing temperature, the maximum transverse hopping distances become comparable to the interchain separation and m decreases to a value which depends on the details of the model.

We have considered the following two models: (a) The two transverse directions, denoted by X and Y, are equivalent in the sense that the maximum hopping distances, X_m and Y_m along the two directions, measured in units of the respective lattice constants, X_0 and Y_0 are equal: $\Delta = X_m/X_0 = Y_m/Y_0$. In this case the factor m in (1.3) decreases to $m = 2.91$ when $\Delta \gtrsim 1$. Because of the interchain hops the percolation channel is three dimensional. (b) In the second model we consider $\Delta_x > \Delta_y$, where $\Delta_x = X_m/X_0$ and $\Delta_y = Y_m/Y_0$. In this case there exists a region where $\Delta_x \gtrsim 1$ and $\Delta_y < 1$. Thus there are no allowed hops along the Y direction, the percolation channel becomes two dimensional and m decreases to 2.70. In both models, any further increase of temperature causes all interchain hops to get excluded from the critical percolation subnetwork, all chains become essentially decoupled, and the percolation model breaks down. The conductivity would then have an activated behavior, i.e., $m = 1$. Whether or not there exists a transition region in which m decreases gradually, rather than abruptly, from 2.7 to 1, has not been investigated because a simple percolation construction cannot be defined in this region.

To simplify the presentation of the anisotropic case we first review, in Sec. II, the isotropic case and the correspondence between percolation[28-31] and hopping conduction.[24-27] In the same section we summarize the arguments given by Kirkpatrick[27] to show that hops more difficult than the critical percolation hop do not alter the dominant exponential temperature dependence as determined by the critical hop. In Sec. III we consider first an anisotropic two-dimensional model which is simpler to investigate and yet brings out the essential features of the anisotropic models. The analysis is then generalized to anisotropic three-dimensional cases. An appropriate extension of Kirkpatrick's arguments to the anisotropic case is discussed in Sec. III D. In Sec. III E we estimate the effects of multiphonon processes and find that these effects are probably very small for QOD conductors. We close this section with an analysis of the conductivity of N-methylphenazinium (NMP)-TCNQ. A summary of our results is given in Sec. IV.

II. HOPPING CONDUCTION AS PERCOLATION: ISOTROPIC CASE

A. Percolation construction

The isomorphism between hopping conduction and a percolation problem proceeds in two steps: (i) The hopping rate Γ_{ij} between two localized states i and j can be viewed as a conductance G_{ij} connecting the nodes i and j of an electrical network, and (ii) the resistance network exhibits a percolation threshold behavior in the sense that if one constructs a subnetwork by retaining only a fraction x ($x < 1$) of the conductances in the original network, the conductivity, as a function of x, has the form

$$\begin{aligned} &\sigma(x) = 0, \quad x < x_c \ , \\ &\sigma(x) \propto (x - x_c)^{\zeta}, \quad x > x_c \ . \end{aligned} \qquad (2.1)$$

Here x_c is the critical concentration and ζ is a critical exponent. Equation (2.1) has been experimentally demonstrated by, e.g., Last and Thouless[32] and has been established from extensive numerical solutions of random resistance networks by Kirkpatrick[26] who found $\zeta \simeq \frac{3}{2}$ for three-dimensional networks with nearest-neighbor connections. The connection between the hopping rate Γ_{ij} and the conductance G_{ij} was established by Miller and Abrahams[23] and subsequently in a simpler and general form by AHL[25]

$$G_{ij} = (e^2/kT)\Gamma_{ij} \ . \qquad (2.2)$$

In general, $\Gamma_{ij} = \langle n_i(1 - n_j)\gamma_{ij}\rangle$, where n are the occupation numbers and γ_{ij} is the intrinsic transition rate. For single-phonon processes

$$\gamma_{ij} = \gamma_0 \exp[-2\alpha R_{ij} - \beta|E_j - E_i|\Theta(E_j - E_i)] \ , \quad (2.3)$$

where the prefactor γ_0 contains the details of the hopping interaction and depends but weakly on the energies E_i and the hopping distance R_{ij}. Here, $\beta = 1/kT$ and α is the coefficient of exponential decay of the localized states whose wave functions are $\psi(r) = \psi_0 \exp(-\alpha r)$. Θ is the Heaviside step function, being zero for negative arguments and unity for positive arguments. G_{ij} can now be expressed as

$$G_{ij} = G_0 \exp(-f_{ij}) \ , \tag{2.4}$$

where

$$f_{ij} = 2\alpha R_{ij} + \beta F(E_i, E_j) \ , \tag{2.5}$$

$$F(E_i, E_j) = |E_i|\Theta(E_i) + |E_j|\Theta(-E_j) + |E_j - E_i|\Theta(E_j - E_i) \ , \tag{2.6}$$

and $G_0 = e^2\gamma_0/kT$.

Miller and Abrahams[23] evaluated the effective resistance of the network by choosing the optimum impedance at each successive hop. Their result is thus a lower bound to the actual conductivity. In the percolation models developed by AHL[25] and by Pollak,[24] one takes an over-all view and seeks complete paths of lowest net resistance, obtaining thereby a much better lower bound. This is achieved by picking a cutoff G deleting all conductances less than G and then varying G so that the fraction x of conductances left in the network is equal to the critical value x_c. The critical cutoff G_c is then the largest conductance such that the reduced network, composed only of conductances $G_{ij} \geqslant G_c$, contains a connected path large enough to span the entire system. According to the percolation model, the over-all conductivity of the original network is $\sigma = G_c/L$, where L is some length scale. Furthermore, the dominant exponential temperature dependence of σ is determined by G_c. Numerical studies[27,33,34] have shown these arguments to be substantially correct. [We have here considered only the single-phonon contributions to the intrinsic rate γ_{ij}. Inclusion of multiphonon processes, as stressed by Emin,[35] would modify (2.3). We shall discuss this in Sec. III E where we shall also see that the percolation analysis of this and of Sec. III can be carried out even after an appropriate generalization of (2.3) to include the multiphonon contributions.]

Let us define

$$f_c = \ln(G_0/G_c) \ , \tag{2.7}$$

and express the condtion $G_{ij} \geqslant G_c$ in a dimensionless form as follows:

$$r_{ij} \leqslant 1 - F(e_i, e_j) \ . \tag{2.8}$$

Here

$$r_{ij} = R_{ij}/R_m \ , \tag{2.9}$$

$$R_m = (1/2\alpha) f_c \ , \tag{2.10}$$

$$e_i = E_i/E_m \ , \tag{2.11}$$

and

$$E_m = kT f_c \ . \tag{2.12}$$

Any initial or final state with energy greater than E_m will not satisfy the inequality (2.8), no matter what the other parameters are. These states therefore will not occur in the critical network. Furthermore, R_m is such that hops with $R_{ij} > R_m$ will not satisfy the condition $G_{ij} \geqslant G_c$.

For an evaluation of G_c we have to make correspondence with a percolation problem. The standard percolation theory[28] treats problems in which either the bonds or the sites are removed with a constant probability. Hopping conduction is a correlated bond-site percolation problem because not only all sites with $E > E_m$ must be removed but also all bonds with $f_{ij} > f_c$ must be removed. AHL solved the correlated problem approximately by associating with each site i a sphere of radius $R_i = R_m(\frac{1}{2} - |e_i|)\Theta(\frac{1}{2} - |e_i|)$ and assuming that sites i and j are bonded when their associated spheres intersect.

Instead of the overlapping-sphere construction we make the following correspondence with a bond percolation problem.[33,36] Construct a reduced, but not yet critical, network by ignoring all sites with energy $E > E_m$. In this reduced network there are no further restrictions on the sites, but all bonds with $f_{ij} > f_c$ must be dropped. One can now evaluate the average number $B(f_c)$ of bonds retained at each site, and require it to be equal to the corresponding critical number B_c obtained from the bond percolation theory. This procedure seems more convenient to generalize to the anisotropic case of concern to us than that of AHL. In any event, by numerical solutions of Kirchoff's equations, Kirkpatrick[26] has shown that close to the percolation threshold, the conductivity in correlated networks is indistinguishable from that for the uncorrelated bond and site percolation problems.

We next evaluate $B(f_c)$, the average number of bonds at a site with $f_{ij} < f_c$. The critical value f_c is then determined by requiring that

$$B(f_c) = B_c \ . \tag{2.13}$$

For a given site of energy e_i, $-1 \leqslant e_i \leqslant 1$, the inequality (2.8) and the physical constraint $r_{ij} > 0$, determine the allowed range of variables e_j and r_{ij}. This allowed range is depicted in Fig. 1. In terms of the density of states without spin $\rho(E)$ the number of allowed final states, or equivalently, the number of allowed bonds attached to the site i is

$$\int_{-E_m}^{E_m} dE_j\,\rho(E_j)V(R_{ij})\Theta(R_{ij})\Theta(R_m-R_{ij}) \;, \qquad (2.14)$$

where $V(R_{ij})$ is the accessible space, being $2R_{ij}, \pi R_{ij}^2$ and $\frac{4}{3}\pi R_{ij}^3$ in one, two, and three dimensions, respectively. The average number of allowed bonds at a site is now given by

$$B(f_c)=C_d R_m^d(f_c)E_m(f_c)\mu_d \;, \qquad (2.15)$$

where d is the dimensionality, C_d is 2, π, or $\frac{4}{3}\pi$ for $d=1$, 2, or 3, respectively, and

$$\mu_d=\int_{-1}^{+1} de_i\,\rho(e_i)\int_{-1}^{+1} de_j\,\rho(e_j)r_{ij}^d\Theta(r_{ij})\Theta(1-r_{ij})\bigg/\int_{-1}^{+1} de_i\,\rho(e_i) \;. \qquad (2.16)$$

For $d=3$ and an energy-independent density of states ρ_3

$$B(f_c)=(\pi\rho_3 k/40\alpha^3)Tf_c^4 \;. \qquad (2.17)$$

Combining it with (2.13) we obtain the critical conductance G_c:

$$G_c=G_0\exp[-(T_0/T)^{1/4}] \;, \qquad (2.18)$$

where

$$T_0=40B_c\alpha^3/\pi\rho_3 k \;. \qquad (2.19)$$

Similarly, for $d=2$,

$$G_c=G_0\exp[-(T_0/T)^{1/3}] \;, \qquad (2.20)$$

where now

$$T_0=16B_c\alpha^2/\pi\rho_2 k \;, \qquad (2.21)$$

ρ_2 being the two-dimensional energy-independent density of states.

In a bond percolation problem where only nearest neighbor bonds are allowed with a constant probability, B_c is an approximate dimensional invariant[28]

$$B_c=d/(d-1) \qquad (2.22)$$

for d-dimensional lattices. Because of this dimensional invariance, Ziman[37] had argued that B_c would remain unchanged even for systems which do not have a well defined lattice structure, like the amorphous materials where (2.18) has been experimentally observed.[38] Pike and Seager[33] showed that B_c does not remain an exact dimensional invariant when longer hops are included but that it does approach the limiting values

$$B_c=\begin{cases} 2.80 & \text{for } d=3 \\ 4.50 & \text{for } d=2 \end{cases} \qquad (2.23)$$

for all d-dimensional lattices when the bonding distances become large compared to the underlying lattice constant and the density of allowed sites becomes small. They further showed that B_c is not temperature dependent in any case, including the cases intermediate between (2.22) and (2.23). We shall hereafter take (2.23) as the appropriate values for B_c whenever hopping distances are very large and the values (2.22) when the hopping range becomes comparable to the lattice constant.

B. Corrections to the AHL conductivity

The AHL construction gives a lower bound to the conductivity of a network whose individual conductivities vary over a large range of magnitudes. The lower bound is a consequence of the fact that the critical subnetwork corresponds to replacing all $G_{ij}<G_c$ by 0 and, through the introduction of L, all $G_{ij}\geqslant G_c$ by G_c in the original network. Furthermore, the cutoff G_c is exact only in the asymptotic limit $T\to 0$. For all finite temperatures, hops with conductance less than G_c also contribute to the over-all conductivity and therefore the optimal cutoff should be somewhat larger than G_c. As stated previously, AHL and Pollak assume the conductivity to be

$$\sigma=G_c/L \;, \qquad (2.24)$$

where L is some characteristic length which may be temperature dependent. In this subsection we discuss how the AHL lower bound can be strengthened and show that L and hops with $G<G_c$ do not alter the dominant exponential temperature dependence as determined by the percolation construction. To do so, we shall follow the arguments introduced by Kirkpatrick[27] for nearest-neighbor hopping: We let the cutoff f be somewhat larger

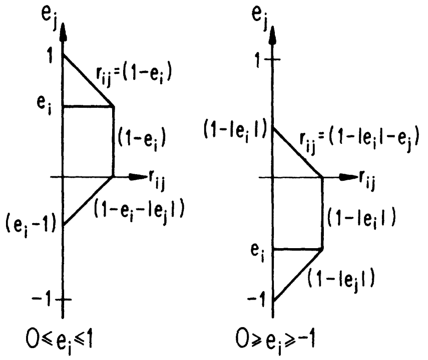

FIG. 1. Allowed range of values of e_i and r_{ij} for evaluation of integrals in (2.16) and (3.10).

than the percolation cutoff f_c and then determine f by optimizing the conductivity expressed as a function of f.

For an arbitrary cutoff f, the average number of bonds $B(f)$ at a site can be written, in analogy with (2.17),

$$B(f)=(\pi\rho_3 k/40\alpha^3)Tf^4 \ . \tag{2.25}$$

This equation determines $f(B)$. Consider

$$B=B_c+\epsilon \ , \tag{2.26}$$

where $B_c=B(f_c)$ and from (2.20)

$$f_c=(T_0/T)^{1/4} \ . \tag{2.27}$$

Near the percolation theshold, i.e., ϵ small, the conductivity has a threshold behavior as in (2.1). Hence,[27]

$$\sigma=K\epsilon^{\zeta}G_0e^{-f(B)}/L(B) \ , \tag{2.28}$$

where K is some proportionality constant. For nearest-neighbor hops, the value of ζ is[26] 1.5; we have no information on ζ for longer-range hops.

To account approximately for having replaced all $G_{ij}\geq G(f)$ by 0 and all $G_{ij}<G(f)$, Kirkpatrick[27] gives the following argument: Near the percolation threshold the network of bonds is very sparse and almost "chainlike." If we consider a chain of conductances $G_{ij}\geq G(f)$, the average conductance G per link is given by

$$\begin{aligned} G&=\langle G(f)^{-1}\rangle_{\text{av}}^{-1}\\ &=G_0\int_0^f P(f)\,df\Big/\int_0^f e^f P(f)\,df \ , \end{aligned} \tag{2.29}$$

where $G(f)=G_0e^{-f}$ and $P(f)$ is the distribution function of f_{ij}'s, as given by (2.6). Since R_{ij}, E_i, and E_j are random variables,

$$\begin{aligned} P(f)=\int d^3R\int dE_i\int dE_j\,\delta(f-2\alpha R-\beta F(E_i,E_j))\\ \times P(R)P(E_i)P(E_j) \ , \end{aligned} \tag{2.30}$$

where $P(E)$ and $P(R)$ are distribution functions for E and R, respectively. For a random distribution of energies over the range $-E_0\leq E\leq E_0$,

$$P(E)=\tfrac{1}{2}E_0 \ . \tag{2.31}$$

If we approximate $P(R)$ by

$$P(R)=2E_0\rho_3 \ , \tag{2.32}$$

we obtain

$$P(f)=(2\pi\rho_3/3E_0\alpha^3)(kT)^2f^4 \ . \tag{2.33}$$

Substituting (2.33) in (2.29) gives

$$G=\tfrac{1}{5}G(f(B))f(B) \ , \tag{2.34}$$

which implies that the conductivity σ, Eq. (2.28), should be multiplied by $\frac{1}{5}f(B)$. Finally, the only length in the problem is the maximum hopping distance, $(2\alpha)^{-1}f(B)$. The characteristic length $L(B)$ therefore must scale with $f(B)$. It is not clear how $L(B)$ should be evaluated but its scaling with $f(B)$ can be demonstrated as follows: If we regard all bonds B at a site as identical resistances in parallel,

$$\begin{aligned} L(B)&=\Big\langle\sum_i R_{ij}^{-1}\Big\rangle_{\text{av}\,i}^{-1}\Big/B\\ &=f(B)\Big\langle\sum_i r_{ij}^{-1}\Big\rangle_{\text{av}\,i}^{-1}\Big/2\alpha B \ , \end{aligned} \tag{2.35}$$

where $r_{ij}=2\alpha R_{ij}/f(B)$ is a dimensionless number. Accounting for the correction (2.34) and the above form of $L(B)$, the expression (2.28) for the conductivity becomes

$$\sigma=\sigma_1\epsilon^{\zeta}\,e^{-f(B)}B \ , \tag{2.36}$$

where all inconsequential factors have been absorbed into σ_1. Optimizing σ with respect to ϵ we obtain, to order ϵ^2,

$$\epsilon=\zeta/f'(B_c) \tag{2.37}$$

if $B_cf'(B_c)\gg 1$. The exponent $f(B)$ in (2.36) can be expanded in a Taylor series and, to order ϵ^2,

$$\begin{aligned} \sigma&=\sigma_1(4\zeta B_c)^{\zeta}(T/T_0)^{\zeta/4}\\ &\quad\times\exp[-f(B_c)-f'(B_c)\epsilon]\\ &=\sigma_0(e^2/kT)(T/T_0)^{\zeta/4}\exp[-(T_0/T)^{1/4}] \ . \end{aligned} \tag{2.38}$$

Here we have restored the factor e^2/kT which was absorbed into G_0 in going from (2.2) to (2.4) and have absorbed other preexponential factors into σ_0.

C. Remarks

The above analysis shows that the percolation criterion for determining the critical hop G_c is exact only in the asymptotic limit for $T\to 0$ when $\epsilon\to 0$. For all finite temperatures $\epsilon>0$, and the critical network does not give the optimal conductivity because hops more difficult than G_c make significant contributions. However, as long as ϵ is small and therefore the above perturbative analysis is valid, the more difficult hops contribute only to the prefactor and the dominant exponential temperature dependence is still given by the critical hop. The temperature below which ϵ is small can be estimated from (2.37): For $\zeta=1.5$,[26] and a typical $T_0=10^8$ K,[38]

$$\epsilon/B_c=\tfrac{3}{50}T^{1/4} \ , \tag{2.39}$$

which is about 0.25 for $T=300$ K and 0.16 for $T=50$ K. Thus for temperatures as high as 300 K, the temperature dependence (2.38) can be expected to hold. Indeed, the percolation models have been successful in interpreting the data up to 500 K.[39] A justification for the applicability of percolation models to such high temperatures has also been given by Pollak.[40]

Finally from a detailed numerical study of variable-range hopping conduction in three dimensions Seager and Pike[33] concluded that a good fit to the $T^{-1/4}$ law, Eq. (2.38), is obtained if the prefactor has a temperature dependence of approximately $T^{-1/2}$. The calculated prefactor has a temperature dependence $T^{-1+\zeta/4}=T^{-5/8}$ for $\zeta=\frac{3}{2}$.[26] This implies that the value of ζ for the sparse longer-range hops of the type which occur in variable-range hopping in three dimensions cannot be very different from 1.5. A prefactor of $T^{-3/5}$ has also been obtained by Ambegaokar *et al.*[34] from scaling arguments.

III. QUASI-ONE-DIMENSIONAL CONDUCTORS

A. Introduction

The quasi-one-dimensional conductors consist of long parallel columns or chains of large planar molecules like TCNQ, or molecular complexes like $\mathrm{Pt(CN)_4}$, stacked face to face with a typical separation of 3–4 Å.[7] Transverse to the chain axis the lattice constant is typically 10–15 Å.[7] In particular, for NMP-TCNQ the three lattice constants a, b, and c are 3.87, 7.78, and 15.74 Å, respectively.[41] Because of the directional nature of the π molecular orbitals (their lobes point and overlap along the chain axis) and the anisotropic lattice structure, the intrachain transfer integral $t_{\parallel}$ is a factor of 20–50 larger than the interchain transfer integral $t_{\perp}$.[42,43] Consequently the hopping rates for intrachain and interchain hops and the conductivities along different directions are highly anisotropic. Thus, the expression (2.5) for f_{ij} must now be generalized. The form of f_{ij} and, consequently, the temperature dependence of hopping conduction, depends on the nature of the localized eigenfunctions in an anisotropic disordered system.

B. Two-dimensional case

To bring out the essential features attributable to anisotropic hopping rates we shall first investigate the simpler two-dimensional case where the lattice constants are R_0 and $S_0 \gg R_0$. This model is appropriate for QOD conductors when couplings along one of the three anisotropic directions are too weak to partake in the construction of a critical percolation subnetwork. The R axis would then be identified as the highly conducting chain axis.

An investigation of[20] localization in a two-dimensional anisotropic disordered system, with transfer integrals t_R and $t_S < t_R$, shows that the critical disorder δ_c for localization of all eigenstates is given by

$$\delta_c \sim (t_R t_S)^{1/2} \tag{3.1}$$

as contradistinguished from the isotropic case ($t_R=t_S=t$) where $\delta_c \sim t$. Thus, $t_R>\delta_c>t_S$ and we expect a strong localization along the transverse (S) direction and a weaker localization in the longitudinal (R) direction. If we now ask for the overlap between two anisotropically localized wave functions centered at sites i and j, a distance $\mathcal{R}_{ij}$ apart, and make an analogy with the decay of a bound state with an anisotropic mass, we expect the following form for f_{ij}:

$$f_{ij}=2[(\alpha_R R_{ij})^2+(\alpha_S S_{ij})^2]^{1/2}+\beta F(E_i,E_j) \ . \tag{3.2}$$

Here α_R and α_S characterize the decay of the wave functions in the R and S directions, respectively, and $\beta F(E_i,E_j)$ is as in (2.6). R_{ij} and S_{ij} are the projections of $\mathcal{R}_{ij}$ along the two directions R and S, respectively. In general, the prefactor γ_0 of the hopping rate (2.3) would also be anisotropic. However, γ_0 depends on the details of the wave functions about which we have no information. For the present, therefore, we shall assume that the anisotropy of γ_0 can be approximated by an appropriate adjustment of α_R and α_S.

One can now order all conductances $G_{ij}=G_0 \times\exp(-f_{ij})$ in a decreasing order, construct a critical subnetwork consisting of all conductances $G_{ij}\geq G_c$ and determine G_c as in Sec. II. As long as this network includes intrachain ($R_{ij}>0, S_{ij}=0$) as well as interchain ($R_{ij}>0, S_{ij}>0$) hops, it is a two-dimensional network and therefore amenable to a percolation analysis. However, an evaluation of G_c requires a value for B_c, the average number of bonds at a site. For an isotropic d-dimensional percolation problem ($d>1$), $B_c \simeq d/(d-1)$ when only nearest-neighbor bonds are considered, Eq. (2.22). With increasing bonding radius, B_c increases[33] and saturates at the values given in (2.23). There are no estimates of B_c for a percolation problem in which (i) because of the anisotropic hopping rates the number of, or equivalently the probability p_S for an interchain hop to be allowed is different from p_R, the probability for an intrachain bond to be allowed; and (ii) because of the anisotropic lattice structure, the bonding distance compared to the underlying lattice constant is small for interchain hops and large for intrachain hops.

For purposes of establishing the temperature dependence, the exact value of B_c is not really necessary. All the same, an estimate of B_c can be obtained as follows: (i) With only nearest-neighbor bonds, the critical probability for percolation on a square lattice (coordination number equal to 4) is[28]

$p_c = 0.5$ and therefore $B_c = 2$. Sykes and Essam[44] have shown that when bonds are allowed with different probabilities p_R and p_S along directions R and S, respectively, the critical percolation condition is

$$p_R + p_S = 1 \ . \tag{3.3}$$

Thus there is no unique critical probability p_c. However, it is straightforward to show that there exists a unique B_c and that it has the same value, 2, as for the isotropic case. Even though this invariant result is for a specific lattice we may expect it to be generally true to within a few percent. (ii) The effect of different bonding radii in different directions is not very clear. If all interchain hops were near neighbor and intrachain hops were long ranged a crude estimate for B_c could be the mean $(1.50\times 2.80)^{1/2} = 2.05$ in two dimensions and $(1.50\times 1.50\times 2.80)^{1/3} = 1.85$ in three dimensions. However, interchain hops have a longitudinal component as well. Furthermore, with increasing bonding radius, B_c increases very rapidly from its value (2.22) for nearest-neighbor bonding only to its saturation value (2.23). Therefore, as an approximation, we shall continue to use the values (2.23) for B_c.

To evaluate G_c we express the condition $G_{ij} \geq G_c$ in a dimensionless form:

$$r_{ij} \leq \{[1 - F(e_i, e_j)]^2 - s_{ij}^2\}^{1/2} \ . \tag{3.4}$$

Here

$$\begin{aligned} &s_{ij} = S_{ij}/S_m, \quad r_{ij} = R_{ij}/R_m \ , \\ &S_m = (1/2\alpha_S)f_c, \quad R_m = (1/2\alpha_R)f_c \ , \\ &f_c = \ln(G_0/G_c) \ , \end{aligned} \tag{3.5}$$

and the e_i are defined as in (2.11). At very low temperatures when both R_m and S_m are much larger than the respective lattice constants R_0 and S_0 we expect the anisotropy effects to be unimportant. These effects are most significant when, at somewhat higher temperatures, $R_m \gg R_0$ but $S_m \gtrsim S_0$. To investigate this region we define

$$\Delta = S_m/S_0 \tag{3.6}$$

and

$$\nu = S_{ij}/S_0 \ . \tag{3.7}$$

Δ is the *maximum* transverse hopping distance measured in units of the interchain separation S_0, and is a continuous parameter which increases monotonically with decreasing temperatures. ν is the *actual* transverse hopping distance in units of S_0, and is a discrete parameter. We have suppressed the subscripts on the left-hand side of (3.7) and measured ν relative to the chain containing the initial site i. Thus $\nu = 0$ implies an intrachain hop. $\nu = 1$ is a hop to either of the two nearest-neighbor chains. For a given Δ, let $\nu(\Delta)$ be the largest integer such that $\nu(\Delta) \leq \Delta$. Then $\nu(\Delta)$ represents the farthest accessible chain in the critical network and the set of numbers $\{\nu\} = 0, 1, 2, 3, \ldots, \nu(\Delta)$ represent all accessible chains for a given Δ. Of course, for $\nu \neq 0$ there are two equivalent chains. We shall represent this by assigning weights W_ν such that $W_0 = 1$ and $W_\nu = 2$ for $\nu > 0$.

In a given chain ν, i.e., for a given transverse hopping distance s_{ij}, an electron can hop along the chain axis for a maximum distance R_{ij} as given by (3.4). Thus if ρ_1 is the energy-independent density of states in each chain, the number of accessible final states or equivalently the number of allowed bonds is

$$\int_{-E_m}^{E_m} dE_j \, (2R_{ij})\rho_1 \Theta(R_{ij})\Theta(R_m - R_{ij}) \ . \tag{3.8}$$

Averaging over E_i and summing over all accessible chains ν gives the total average number of allowed bonds. This then must equal critical percolation value B_c. Thus

$$B_c = E_m(G_c)R_m(G_c)\rho_1 g(\Delta(G_c)) \ , \tag{3.9}$$

where

$$g(\Delta) = \sum_{\nu=0}^{\nu(\Delta)} \tfrac{1}{2} W_\nu \int_{-1}^{+1} de_i \int_{-1}^{+1} de_j \, (2r_{ij})\Theta(r_{ij})\Theta(1 - r_{ij}) \ . \tag{3.10}$$

For the assumed uniform spacing of chains ρ_1 is related to the two-dimensional density of states ρ_2 by

$$\rho_1 = S_0 \rho_2 \ . \tag{3.11}$$

Substituting for r_{ij} from (3.4) with $s_{ij} = \nu/\Delta$, we obtain

$$g(\Delta) = \sum_{\nu=0}^{\nu(\Delta)} W_\nu \left[\left(1 + \frac{2\nu^2}{\Delta^2}\right)\left(1 - \frac{\nu^2}{\Delta^2}\right)^{1/2} - 3\left(\frac{\nu}{\Delta}\right)^2 \cosh^{-1}\!\left(\frac{\Delta}{\nu}\right) \right] \ . \tag{3.12}$$

Equation (3.12) can be numerically evaluated for arbitrary values of $\Delta \geq 1$. As shown in Fig. 2, $g(\Delta)$ is a smooth and monotonically increasing function of Δ.

In principle, (3.9) and (3.12) determine the critical hop G_c. However, Δ and therefore $g(\Delta)$ is itself a function of G_c. For asymptotically large Δ, i.e., $S_m \gg S_0$, $g(\Delta)$ has a simple functional dependence on Δ:

$$g(\Delta) = \tfrac{1}{4}\pi\Delta \ , \tag{3.13}$$

which on substitution in (3.9) gives the two-dimensional temperature dependence[36,45] [(2.20)], with

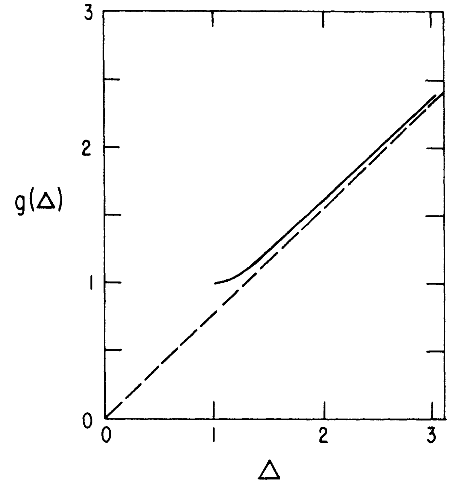

FIG. 2. Function $g(\Delta)$, Eq. (3.12), for the two-dimensional case. For $\Delta \gg 1$, $g(\Delta)$ has the asymptotic form (dashed line) $\frac{1}{4}\pi\Delta$. Deviations from the asymptotic form, for small Δ, lead to temperature dependences of the general form (3.16) with parameters as in Table I.

$$T_0 = 16B_c\alpha_R\alpha_S/\pi k\rho_2 \ . \tag{3.14}$$

In the isotropic limit $\alpha_R = \alpha_S$ this is exactly equal to the previous result (2.21).

We are interested in the region where Δ is small. For $\Delta \lesssim 4$, $g(\Delta)$ deviates from its asymptotic form, Fig. 2, and has no simple dependence on Δ. We therefore adopt the following approximate procedure: Consider the various ranges $\nu_j \leqslant \Delta < \nu_{j+1}$, where ν_j is the jth member of the ordered set $\{\nu\} = 1, 2, 3, \ldots, \nu(\Delta)$. (We do not consider the range $0 \leqslant \Delta < 1$ because in that case $S_m < S_0$, i.e., there are no interchain hops, and we cannot construct a two-dimensional percolation channel.) In each of these ranges we approximate $g(\Delta)$ by

$$\tilde{g}(\Delta) = A_j\Delta^{n_j} \simeq g(\Delta) \ . \tag{3.15}$$

The two parameters A_j and n_j are determined by requiring that $\tilde{g}(\nu) = g(\nu)$ for $\nu = \nu_j$ and $\nu = \nu_{j+1}$. For instance, $g(1) = 1$ implies $A_1 = 1$ and $g(2) = 1.622$ implies $n_1 = 0.698$. With these boundary conditions, $\tilde{g}(\Delta)$ is a continuous piecewise-smooth function and is a very good approximation to $g(\Delta)$. Substituting (3.15) in (3.9) gives a temperature dependence of the form

$$\ln(G_0/G_c) = (T_j/T)^{1/m_j} \ , \tag{3.16}$$

where

$$T_j = (\alpha_R/k\rho_1)(2\alpha_S S_0)^{n_j} 2B_c/A_j \ , \tag{3.17}$$

and $m_j = 2 + n_j$ has the maximum value 3 for asymptotically large Δ, i.e., asymptotically low temperatures. In the first interval, $1 \leqslant \Delta < 2$, $g(\Delta)$ has the form

$$g(\Delta) = \Delta^{0.70} \ , \tag{3.18}$$

which implies

$$\ln(G_0/G_c) = (T_1/T)^{1/2.70} \ , \tag{3.19}$$

where

$$T_1 = (2\alpha_R B_c/k\rho_1)(2\alpha_S S_0)^{0.70} \ . \tag{3.20}$$

This temperature dependence would hold as long as $\Delta = (1/2\alpha_S S_0)f_c$ stays in the range $1 \leqslant \Delta \lesssim 2$. The extent of this temperature region is $T_{1l} \leqslant T \leqslant T_{1u}$, where

$$T_{1u} = 6.5T_{1l} = T_1/(2\alpha_S S_0)^{2.70} \ . \tag{3.21}$$

For temperatures $T > T_{1u}$, $\Delta < 1$ and, as remarked earlier, the two-dimensional percolation construction breaks down because there are no interchain hops. The conductivity would then follow the activated form (1.2). For $T < T_{1u}$, the conductivity is of the form (3.19). Thus T_{1u} can be identified from the data. T_1 can then be obtained from a fit to (3.19). The present two-dimensional model is not directly applicable to any real physical system, but for the sake of argument let us consider, $T_1 = 4\times 10^5$ K and $2\alpha_S S_0 = 15$. Then $T_{1u} = 269$ K and $T_{1l} = 41$ K.

As the temperature decreases below T_{1l}, Δ becomes larger than 2 and the temperature dependence changes as in (3.16). In the region $2 \leqslant \Delta < 3$,

$$g(\Delta) = 0.84(\Delta)^{0.94} \ , \tag{3.22}$$

which implies that $m = 2.94$ and

$$T_2 = T_1(2\alpha_S S_0)^{0.24}/0.84 \tag{3.23}$$

is known in terms of T_1 and $2\alpha_S S_0$. The extent of this temperature region is $T_{2l} \leqslant T \leqslant T_{2u}$, where

$$T_{2u} = 3.3T_{2l} = T_{1l} \ . \tag{3.24}$$

Successive lower temperature regions can be analyzed as above. The range of some of these regions and the corresponding temperature dependences are summarized in Table I.

In deriving (3.9) we had made a continuum approximation for the distribution of states within a chain, i.e., for a hopping distance R_{ij}, the number of available states was approximated by $2R_{ij}\rho_1$. For interchain hops, we had a proper discrete sum, Eq. (3.12). Table I shows that for $\Delta = S_m/S_0 \gtrsim 3$, the results are indistinguishable from that for $\Delta \gg 1$. Similarly, we may expect that (3.9) would be valid for $R_m/R_0 \gtrsim 3$. This condition is easily satisfied, even when $\Delta = 1$, because of the anisotropic hopping rates and the lattice constants.

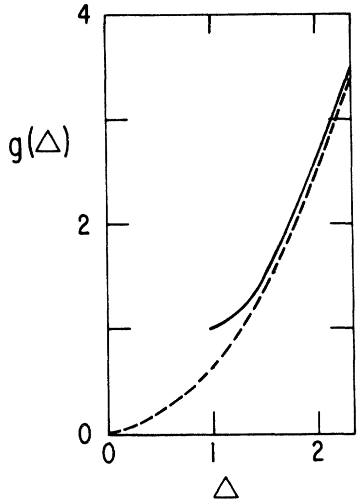

FIG. 3. Function $g(\Delta)$, Eq. (3.12), for the three-dimensional case. For $\Delta \gg 1$, $g(\Delta)$ has the asymptotic form (dashed line) $\frac{1}{5}\pi\Delta^2$. Deviations from the asymptotic form lead to the temperature dependences of the general form (3.16) with parameters as in Table II.

C. Three-dimensional case

An appropriate generalization of (3.2) for an anisotropic three-dimensional conductor would be

$$f_{ij} = 2[(\alpha_R R_{ij})^2 + (\alpha_x X_{ij})^2 + (\alpha_y Y_{ij})^2]^{1/2} + \beta F(E_{ij} E_j) \ . \tag{3.25}$$

Here X_{ij} and Y_{ij} are projections of the actual hopping distance $\mathcal{R}_{ij}$ along the two transverse directions X and Y, respectively. As before, we represent the highly conducting chain axis by R. The decay rates of the anisotropically localized wave function along different directions are represented by corresponding subscripts to α. Let R_0, X_0, and Y_0 be the three lattice constants and define

$$\begin{gathered} X_m = (1/2\alpha_x) f_c, \quad Y_m = (1/2\alpha_y) f_c \ , \\ f_c = \ln(G_0/G_c) \end{gathered} \tag{3.26}$$

and

$$\begin{gathered} \Delta_R = R_m/R_0, \quad \Delta_x = X_m/X_0, \\ \Delta_y = Y_m/Y_0, \quad \nu_x = X_{ij}/X_0, \quad \nu_y = Y_{ij}/Y_0 \ . \end{gathered} \tag{3.27}$$

Consider a system in which the conductivities are such that

$$\sigma_R \gg \sigma_x > \sigma_y \ , \tag{3.28}$$

i.e., of the two transverse directions, it is easier to hop along the X direction. Thus,

$$\Delta_x = \eta \Delta_y \equiv \Delta \ , \tag{3.29}$$

where $\eta \geqslant 1$ for $\sigma_x \geqslant \sigma_y$.[46] Further, let us define

$$\nu^2 = \nu_x^2 + \eta^2 \nu_y^2 \ . \tag{3.30}$$

TABLE I. Anisotropic two-dimensional case, Sec. III B. For different ranges of the maximum transverse hopping distance, Δ, A, and m are the coefficients defined in (3.15) and (3.16), respectively. T_u and T_l define the temperature region where Δ is in the specified range and can be evaluated from equations like (3.21).

Range of Δ	A	m	T_u/T_l
1–2	1.000	2.698	6.489
2–3	0.844	2.943	3.298
3–4	0.810	2.981	2.357
4–5	0.798	2.991	1.949
5–6	0.793	2.995	1.726
⋮	⋮	⋮	⋮
29–30	0.785	3.000	1.111

The intersections of the chain centers with a plane normal to the chain axis define the (X, Y) lattice. Consider a hop from a localized state centered at a site i of a chain a to another localized state centered at a site j of any chain b. Then ν_x, ν_y are the coordinates in the (X, Y) lattice of the point of intersection of chain b with respect to the point of intersection of chain a. Thus both ν_x and ν_y can have the values 0, 1, 2, . . . , etc. We shall assume that the set of numbers $\{\nu\}$ defined by (3.30) have been arranged in an increasing order. Thus, fo. $\eta = 1$,

$$\{\nu\} = 0, 1, \sqrt{2}, 2, 5, \ldots, \tag{3.31}$$

and for $\eta = 2$,

$$\{\nu\} = 0, 1, 2, \sqrt{5}, \sqrt{8}, \ldots, \text{etc.} \tag{3.32}$$

In terms of these parameters, the condition $G_{ij} = G_0 \exp(-f_{ij}) \geqslant G_c$ for constructing a critical percolation subnetwork can be expressed as

$$r_{ij} \leqslant \{[1 - F(e_i, e_j)]^2 - (\nu/\Delta)^2\}^{1/2} \ , \tag{3.33}$$

where r, e, and $F(e_i, e_j)$ are as defined in (2.8). The number of allowed bonds is again given by (3.9) and $g(\Delta)$ has the same form as (3.12) except that now Δ and ν are as defined by (3.29) and (3.30), respectively. Also, the weight factors W_ν are to be reevaluated for every set $\{\nu\}$. Furthermore, the linear density of states, ρ_1, in (3.9) is related to the volume density of states ρ_3 by

$$\rho_1 = \rho_3 X_0 Y_0 \ . \tag{3.34}$$

For asymptotically large Δ, $g(\Delta)$ can be expressed as (see Fig. 3)

$$g(\Delta) = \pi\Delta^2/5\eta \ , \tag{3.35}$$

where $\Delta^2 = \Delta_x \Delta_y \eta$. Substituting (3.34) and (3.35) in (3.9) gives the three-dimensional temperature dependence (2.18) with

$$T_0 = 40 B_c \alpha_R \alpha_x \alpha_y / \pi \rho_3 k \ . \tag{3.36}$$

In the isotropic limit, $\alpha_R = \alpha_x = \alpha_y$, this is identical to the previous result (2.19).

With increasing temperatures, Δ becomes small and $g(\Delta)$ deviates from its asymptotic form (3.35). When Δ lies in the range $\nu_j \leq \Delta \lesssim \nu_{j+1}$, where $\{\nu\}$ is the previously defined ordered set, $g(\Delta)$ has the general form

$$g(\Delta) = A_j (\Delta)^{n_j} \ , \tag{3.37}$$

where Δ is an appropriate combination of Δ_x and Δ_y. Consider first the isotropic case $\Delta_x = \Delta_y \equiv \Delta$, i.e., $\eta = 1$ in (3.29). In the range $0 \leq \Delta < 1$, there are no interchain hops, and the percolation construction breaks down. Thus the first interval that we shall consider is $1 \leq \Delta \lesssim 2$ for which

$$g(\Delta) = (\Delta)^{0.91} \ , \tag{3.38}$$

and therefore

$$\ln(G_0/G_c) = (T_1/T)^{1/2.91} \ , \tag{3.39}$$

with

$$T_1 = 2\alpha_R B_c (2\alpha_\perp S_0)^{0.91} / k\rho_1 \ , \tag{3.40}$$

where $\alpha_\perp S_0 \equiv \alpha_x X_0 = \alpha_y Y_0$ for the case $\eta = 1$. As in Sec. III B, the temperature region $T_{1l} \lesssim T \leq T_{1u}$, where (3.39) is appropriate can be determined to be

$$T_{1u} = 2.74 T_{1l} = T_1/(2\alpha_\perp S_0)^{2.91} \ . \tag{3.41}$$

Successive lower-temperature regions can be investigated as in Sec. III B. The parameters characteristic of different temperature regions are summarized in Table II.

Next we consider the case where the two transverse directions are inequivalent. In particular, consider $\eta = 2$, i.e.,

$$\Delta_x = 2\Delta_y \equiv \Delta \ . \tag{3.42}$$

As usual, we do not consider the region $0 \leq \Delta < 1$ because then there are no interchain hops. The next lower-temperature region, $1 \leq \Delta \lesssim 2$, is interesting because whereas $\Delta_x > 1$, Δ_y is less than one. Thus there are no allowed hops in the Y direction and the percolation channel is rigorously two dimensional. Indeed, $g(\Delta)$ has the form (3.18) and the temperature dependence is the same as in (3.19)–(3.21) with $2\alpha_x X_0$ replacing $2\alpha_S S_0$.

The next lower-temperature region corresponds to $2 \leq \Delta \lesssim \sqrt{2}$. In this case both Δ_x and Δ_y are larger than one and the percolation channel is three dimensional though most of the hops are confined to the R-X planes. Table III summarizes the relevant parameters for different temperature regions in this case.

D. Corrections to percolation conduction

The above analysis shows that for asymptotically low temperatures, $T \to 0$ K, the temperature dependence of hopping conduction in an anisotropic system is indistinguishable from that of an isotropic conductor. With increasing temperatures, the transverse hopping distances become small and they begin to sample the discreteness and the anisotropy of the lattice. Correspondingly, the temperature dependence deviates from its isotropic form.

As observed in Sec. II, for all finite temperatures hops more difficult than the critical hop also contribute to the conductivity. However, the arguments of Sec. II B can be easily generalized to show that these hops contribute only to the preexponential and that the dominant exponential temperature dependence is always determined by the critical hop which, as we have shown above, is sensitive to the details of the anisotropy. Similarly, the lower bound to the conductivity as de-

TABLE II. Three-dimensional case, Sec. III C, when the two transverse directions are equivalent (see Table I caption).

Range of Δ	A	m	T_u/T_l
1–$\sqrt{2}$	1.000	2.905	2.737
$\sqrt{2}$–2	0.717	3.867	3.820
2–$\sqrt{5}$	0.743	3.814	1.530
$\sqrt{5}$–$\sqrt{8}$	0.661	3.960	2.536
$\sqrt{8}$–3	0.651	3.973	1.264
⋮	⋮	⋮	⋮
$\sqrt{13}$–4	0.628	4.000	1.515

TABLE III. Three-dimensional case when the two transverse directions, X and Y, are inequivalent and the corresponding maximum hopping distances are related by $\Delta_x = 2\Delta_y$ (see Table I caption).

Range of Δ	A	m	T_u/T_l
1–2	1.000	2.698	6.489
2–$\sqrt{5}$	0.842	2.947	1.389
$\sqrt{5}$–$\sqrt{8}$	0.517	3.553	2.305
$\sqrt{8}$–3	0.373	3.866	1.256
3–$\sqrt{13}$	0.326	3.988	2.082
⋮	⋮	⋮	⋮
5–$\sqrt{29}$	0.314	4.000	1.346

termined by the percolation construction can be strengthened by the "chain correction" introduced in Sec. II B.

Inclusion of hops more difficult than the critical hop increases the cutoff $f = \ln(G_0/G)$ and the average number of bonds at a site B to values somewhat larger than the corresponding critical values $f_c = \ln(G_0/G_c)$ and B_c, respectively. Thus, instead of the general form (3.16) we have

$$f(B) = (T_n/T)^{1/m} , \tag{3.43}$$

where $m = n + 2$ and T_n is of the form (3.17) with B_c replaced by B. Near the percolation threshold, i.e., $B - B_c = \epsilon$ small, the conductivity can be expressed as in (2.26):

$$\sigma = K\epsilon^{\zeta} G_0 e^{-f(B)}[C/L(B)] . \tag{3.44}$$

Here C represents the chain correction introduced by Kirkpatrick[27] and discussed briefly in Sec. II B. K is a proportionality constant and $L(B)$ is some characteristic length. In writing (3.44) we have assumed that just as in the isotropic case, the conductivity has a threshold behavior of the kind (2.1). We have no information on the exponent ζ for the anisotropic case. For the isotropic case with nearest neighbor hops only, $\zeta = 1.5$ in three dimensions.[26]

The chain correction can be evaluated as in (2.29) with an appropriate generalization for $P(f)$. For instance, when the two transverse directions are equivalent, i.e., $\alpha_x X_0 = \alpha_y Y_0 \equiv \alpha_\perp S_0$,

$$P(f) = \int dR \int d^2S \int dE_i \int dE_j P(R)P(S)P(E_i)P(E_j)\delta(f - 2\alpha_R R - 2\alpha_\perp S - \beta F(E_i, E_j)) , \tag{3.45}$$

where $P(R)$, $P(S)$, and $P(E)$ are distribution functions for R, S, and E, respectively. If, as in Sec. II, we take $P(E) = \frac{1}{2}E_0$, $P(R) = \rho_3 S_0^2(2E_0)$, and $P(S) = \rho_3 R_0(2E_0)$,

$$P(f) = \tfrac{2}{3}\pi(\rho_3/E_0\alpha_R\alpha_\perp^2)(kT)^2 f^4 \tag{3.46}$$

after the substitution $(2E_0)(S_0^2R_0)\rho_3 = 1$. For the isotropic case, $\alpha_R = \alpha_\perp$, this is identical to (2.33). As in (2.34) the chain correction is proportional to $f(B)$.

For the isotropic case, the characteristic length was shown to scale with the maximum hopping distance, $R_m = (2\alpha_R)^{-1}f(B)$, Eq. (2.35). In the present anisotropic case there are two length scales: R_m and $S_m = (2\alpha_S)^{-1}f(B)$. An appropriate generalization of (2.35) for $L(B)$ is

$$\begin{aligned} L(B) &= \left\langle \left(\sum_j R_{ij} + \sum_k S_{ik} \right)^{-1} \right\rangle_{\text{av}\,i}^{-1} \Big/ B \\ &= f(B) \left\langle \left(\sum_j \frac{r_{ij}}{\alpha_R} + \sum_k \frac{s_{ik}}{\alpha_S} \right)^{-1} \right\rangle_{\text{av}\,i}^{-1} \Big/ 2B , \end{aligned} \tag{3.47}$$

where r_{ij} and s_{ik} are dimensionless numbers R_{ij}/R_m and S_{ik}/S_m, respectively. Thus $L(B)$ again scales with $f(B)$ because both R_m and S_m scale with $f(B)$. Obviously a similar result would hold when the two transverse directions are inequivalent. Substituting $L(B)$ and the chain correction in (3.44) leads to

$$\sigma = \sigma_1 \epsilon^{\zeta} e^{-f(B)} B , \tag{3.48}$$

where we have absorbed all inconsequential factors into σ_1. The conductivity can now be optimized with respect to ϵ to obtain

$$\sigma = \sigma_0(e^2/kT)(T/T_n)^{\zeta/m} \exp[-(T_n/T)^{1/m}] , \tag{3.49}$$

where, as in (2.38), we have restored the factor e^2/kT. Equation (3.49) shows that, as for the isotropic case, the hops more difficult than the critical hop do not affect the major exponential temperature dependence determined by the critical hop.

E. Multiphonon processes

For the transition rate characterizing a phonon-assisted hop we have considered a form, Eq. (2.3), which is essentially the same as applied by Miller and Abrahams[23] (MA) to hops between shallow impurity states and by AHL[25] to the percolation model for amorphous materials. This corresponds to hops in which only one acoustic phonon is emitted or absorbed and is obtained by a perturbative calculation to lowest order in electron-phonon coupling constant. This imposes an asymptotically low-temperature condition: $kT < |E_i - E_j| < \hbar\omega_D$, the Debye energy. AHL argued that (2.3) may also be valid, under suitable conditions, for energy differences $|E_i - E_j|$ large compared to $\hbar\omega_D$. [A more detailed discussion of the hopping processes in various regimes where (2.3) is valid is given by Holstein[47].] An exact calculation of the transition rate by Emin[35] shows that whereas (2.3) is appropriate for the case discussed by MA, it constitutes an inadequate representation, at high as well as low temperatures, of the elemental two-site jump rate in general and for amorphous germanium and silicon in particular because the multiphonon processes, not included in (2.3), provide a strong temperature-dependent contribution. We argue below that for QOD conductors (2.3) is adequate at low temperatures and that its generalization to include temperature-dependent multiphonon contributions at high temperatures does not significantly alter the basic temperature dependences derived from (2.3).

Emin[35] analyzed the jump rate in three different temperature regions, which we denote by TR 1 etc. In the low- and high-temperature regions, TR 1 and TR 3, respectively, the jump rate is simply activated and can therefore be represented as in (2.3). The jump rate is nonactivated in TR 2 but, as we shall see, contributes insignificantly to the total temperature dependence. The low-temperature (TR 1) jump rate [Eq. (4), Ref. 35] is

$$\Gamma_{ij} = J_{ij}^2 e^{-2s_0} e^{-\beta\Delta\Theta(\Delta)} \left(\frac{2\pi}{\hbar\Delta}\right) \sum_{n=1}^{\infty} \frac{B^n(\Delta)}{n!(2n-1)!} , \quad (3.50)$$

where $2s_0 = 3\gamma(\omega_m/\omega_D)^2$, $B(\Delta) = 3\gamma(\Delta/\hbar\omega_D)^2$, and n is the number of phonons involved. Here ω_D is the Debye frequency, ω_m the maximum-energy phonon with which a carrier can interact, Δ a typical intersite energy difference, and $\gamma = z^2/Mv^2\hbar\omega_D$, where z is the deformation potential constant, v the sound velocity, and M the atomic mass. (For amorphous Ge and Si, $\gamma \approx 10^2$.[35]) Further, let a and r represent the lattice constant and radii of the impurity states (localized wave functions), respectively. The MA approximation (also used by AHL[25]), in which one neglects all but $n = 1$ terms and replaces $\exp(-2s_0)$ by unity, requires $2s_0 \ll 1$ and $B(\Delta) \lesssim 1$. According to Emin these conditions are nearly met in the MA case, since $\omega_m/\omega_D = a/r < 10^{-1}$ and $\Delta \approx 10^{-3}$–10^{-4} eV, but are grossly violated in noncrystalline solids were $a \approx r$, and $\Delta \approx 10^0$–10^{-2} eV.[35] For QOD conductors, however, the wave functions are not as strongly localized as in Ge and Si. Typically, $r \sim 10a$.[1] (Because of the anisotropic localization[20] and consequent anisotropic shape of the wave function, one should really define some average r. However, this would not qualitatively change the order of magnitude estimates of this section.) In amorphous Ge and Si states are localized near charged traps whose density is very small: typically, $\rho \lesssim 10^{19}$ $\text{eV}^{-1}\,\text{cm}^{-3}$.[38] In disordered one-dimensional conductors all states are localized[17-19] and therefore their density is large: $\rho \approx 10^{21}$ $\text{eV}^{-1}\,\text{cm}^{-3}$. Also the bandwidths and disorder are very small. Thus $\Delta \approx 500$ K. Furthermore, γ is much smaller because the atomic mass M has to be replaced by molecular mass, of TCNQ for instance. v and ω_D have the same order of magnitude. Thus $\gamma \approx 10$ rather than ≈ 100. These values of a/r, Δ, and γ are consistent with Emin's criterion for validity of (2.3).

As the temperature is raised beyond the region of validity of (3.50) various kinds of multiphonon processes contribute to the jump rate which is "progressively less dependent on Δ and increases with temperature in a nonactivated manner" in TR 2 and is simply activated in TR 3, with an activation energy[35]

$$E_A = 0.25\gamma\hbar\omega_D(\omega_m/\omega_D)^3 \ . \quad (3.51)$$

Thus the jump rate should, instead of (2.3) be given by

$$\gamma_{ij} = \gamma_0 F(T) \exp[-2\alpha R_{ij} - \beta|E_j - E_i|\Theta(E_j - E_i)] \ , \quad (3.52)$$

and a corresponding expression for the anisotropic case. Here $F(T)$ is the multiphonon contribution to the temperature dependence of the elemental jump rate (for $E_i = E_j$) and maybe nonactivated as in TR 2 or simply activated with activation energy (3.51). In either case, $F(T)$ does not depend on i or j and can therefore be absorbed into the factor G_0 of (2.4). The percolation analysis can now be carried out as before to obtain a temperature dependent conductivity of the form

$$\sigma(T) = \sigma_0 F(T) T^{\zeta/m} \exp[-(T_n/T)^{1/m}] \quad (3.53)$$

instead of (3.49). We now argue that for the QOD conductors $F(T)$ is very weakly temperature dependent and can be ignored. The strongest T dependence of $F(T)$ is in the high-temperature region TR 3 where it has an activated behavior. The activation energy [from (3.51)] with typical values $\omega_m/\omega_D \approx 10^{-1}$, $\omega_D \approx 10^2$ °K, and $\gamma \lesssim 100$, is $E_A \lesssim 2$ °K which is insignificant in the temperature region $50 < T < 200$ °K of interest to us. ($\omega_m/\omega_D \approx 10^{-1}$ is probably an underestimate for ω_m since $\omega_m/\omega_D = a/r$ is not expected to be a good approximation in this case. However, $\gamma \lesssim 100$ is an overestimate.) Similarly, in the lower-temperature region where $F(T)$ is nonactivated, its temperature dependence is too weak to mask the much stronger exponential factor in (3.53). In any event (3.53) shows that the total temperature dependence of the hopping conductivity is determined by a percolation effect as well as by the nonactivated temperature dependence of the pairwise-hopping rate due to multiphonon transitions. The two contributions are neither competing nor complimentary but are simultaneously present. Here we have discussed in detail the percolation aspects of hopping conduction and given a crude and by no means conclusive discussion of contributions from multiphonon processes. We conclude that the temperature dependence of the elemental jump rate due to multiphonon processes, which maybe playing a significant role in amorphous Ge and Si as observed by Emin[35] is, subject to a more careful estimate, irrelevant for QOD conductors.

F. Comparison with experiments

Coleman *et al.*[48] have reported conductivity measurements on high-purity NMP-TCNQ in which the curvature in the plot of $\log_{10}[\sigma(T)/\sigma(295\text{ K})]$ vs T^{-1} is somewhat smaller than that in the earlier data of Schegolev *et al.*[49] From this Coleman *et al.* concluded that the intrinsic temperature dependence was of the activated form (1.2) rather than the form (1.1) proposed by BWV.[1] The analysis of this section shows that the hopping conductivity in a quasi-one-dimensional conductor has a temperature dependence of the form (3.49) where m is weakly temperature dependent, being 4 for asymptotically low temperatures, $T \to 0$ K, and 1 at higher temperatures when the percolation construction breaks down. The intermediate values of m depend on the details of the model and, in particular, on the relative anisotropy of the two weakly conducting transverse directions. Because of the very small crystal dimensions[50] (typically $5\times0.5\times0.05$ mm^3) the magnitudes and therefore the anisotropy of the two transverse conductivities has not yet been measured. We have therefore analyzed the data of Ref. 48 within a model where the two transverse directions are equivalent, Table II. In any event, the values of m for this case are not significantly different from those of a typical model with inequivalent transverse directions, Table III. Thus, we consider $m = 1.0$ (activated), 2.91, and 3.87 in successively lower-temperature regions, which have yet to be identified.

Recently, Gogolin *et al.*[51,52] have investigated the joint influence of structural disorder and phonons on the transport properties of quasi-one-dimensional conductors. At sufficiently high temperatures when the effective electron-phonon interaction energy becomes much larger than the rms random potential, the electronic states, localized by the static random potential, become delocalized by the phonons and consequently the conductivity increases more rapidly with increasing temperatures than expected from the activated fit at lower temperatures. We choose the point of inflection in σ vs T as an overestimate of the temperature above which the activated form ceases to hold. For NMP-TCNQ the point of inflection is 140 K. The lowest temperature at which the conductivity has been measured is 18 K.[48] From a least-squares analysis of the conductivity data in the temperature range 18–140 K, we find that (3.49) gives the best fit (minimum rms error) with the following parameters:

$$
\begin{aligned}
&m = 1.0 \text{ and } E_{\text{act}} = 509\text{ K} \\
&\text{for } 140 \leq T \leq 100\text{ K}, \\
&m = 2.91 \text{ and } T_1 = 1.33\times10^6\text{ K} \\
&\text{for } 100 \leq T \leq 38\text{ K, and} \\
&m = 3.87 \text{ and } T_2 = 6.06\times10^7\text{ K} \\
&\text{for } 38 \leq T \leq 18\text{ K.}
\end{aligned}
\tag{3.54}
$$

The transition temperatures, 100 and 38 K, were identified as follows: The data was least-squares fitted to the activated form in the range $140\text{ K} \leq T \leq T_a$ and T_a varied over the entire range 18–140 K. For $T_a < 100$ K, the rms error increases sharply. Similarly, $m = 2.91$ was fitted in the range $100\text{ K} \leq T \leq T_b$ and T_b varied over the range 18–100 K. For $T_b < 38$ K, the rms error increases significantly. A final refinement was made by considering the entire range 18–140 K and varying T_a and T_b to minimize the total rms error.

Coleman *et al.*[48] fitted their data to an activated form ($m = 1$) in the temperature range 18–70 K. We find that this fit gives an rms error of 0.36. In the same temperature range 18–70 K, a least-squares fit with parameters as in (3.54) gives an rms error of only 0.068. Over the entire temperature range 18–140 K, an activated fit (Fig. 4) gives an rms error of 0.49 whereas the best fit (Fig. 5) as in (3.54) gives an rms error of only 0.057. Clearly, the activated form gives a poorer fit to the data. Coleman *et al.*[48] had used three parameters: E_{act}, upper temperature cutoff (70 K), and a temperature-dependent gap above 70 K. We have used five parameters: E_{act}, two transition temperatures, 100 and 38 K, and T_1 and T_2. However, there are two theoretical constraints on these parameters; and, as shown below, they

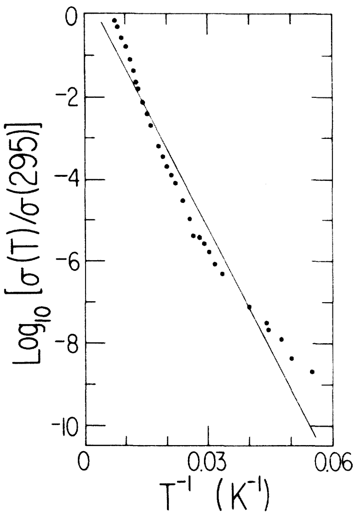

FIG. 4. Best fit (by the least-squares analysis) to the NMP-TCNQ dc conductivity data of Ref. 48, assuming that the conductivity is activated in the temperature region 140–18 K. The activation energy is 450 K and the rms error is 0.49. Figure 5 contains the best fit according to the temperature dependences proposed in this paper. The resulting rms error there is 0.057. (There were 53 data points. Not all are shown in Figs. 4 and 5.)

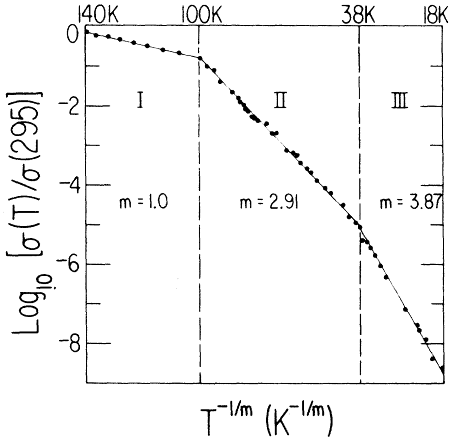

FIG. 5. Best fit (by the least-squares analysis) to the NMP-TCNQ dc conductivity data of Ref. 48 according to the temperature dependences proposed in this paper. *The data points are indistinguishable from the best-fit lines* and the rms error is only 0.057. The three regions are distinguished by different values of m in Eq. (3.49) and have different scales along the horizontal axis. The best-fit parameters are given in Eq. (3.54). The temperatures 100 and 38 K, which separate the three regions, were determined so as to minimize the rms error. (The raw data for this analysis were kindly provided by Dr. Coleman.)

are adequately satisfied: (i) From (3.54) we identify the transition temperatures, 100 and 38 K, to be the parameters T_{1u} and T_{1l}, respectively, of Eq. (3.41). Their ratio, $T_{1u}/T_{1l} = 2.63$, is in good agreement, with the theoretical value [Eq. (3.41) or Table II] of 2.74. (ii) From (3.41) we determine $2\alpha_\perp S_0 = 25.7$. Substituting for $2\alpha_\perp S_0$ and T_1 into an equation analogous to (3.23), i.e.,

$$T_2 = T_1(2\alpha_\perp S_0)/0.72 \tag{3.55}$$

gives $T_2 = 4.75\times 10^7$ K which, considering the approximations made in the analysis, especially the assumed equivalence of the two transverse directions, is in fair agreement with the value obtained from a least-squares fit to the data, Eq. (3.54).

IV. SUMMARY AND DISCUSSION

We have investigated the temperature dependence of the phonon-assisted dc hopping conductivity in a model in which hopping rates along the chain axis R and the two transverse directions, X and Y, are highly anisotropic. This simulates the anisotropic conductivities, $\sigma_R \gg \sigma_x \gg \sigma_y$, observed in disordered quasi-one-dimensional conductors like NMP-TCNQ.[7] Working within the usual percolation models[24-27] we find that the conductivity has the temperature dependence: $\ln[\sigma_0/\sigma(T)] = (T_m/T)^{1/m}$, where m and σ_0 are weakly temperature dependent. For $T\to 0$ K, $m = 4$ for an anisotropic three-dimensional conductor. With increasing temperatures, the ranges Δ_x, Δ_y, of the transverse (interchain) hops, measured in units of the corresponding lattice constants, X_0, Y_0 (which are also anisotropic) decrease and accordingly m decreases to 2.70 or 2.91 depending on the details of the model. For $\Delta_R > \Delta_x > 1$ and $\Delta_y < 1$, the percolation channel becomes two dimensional and confined to the R-X planes. At still higher temperatures when both Δ_x and Δ_y become less than one, the percolation construction would not allow interchain hops. The percolation path would be one dimensional, which is impossible, and therefore the percolation construction would break down. The conductivity would then be activated. At still higher temperatures, when the electron-phonon interaction energy becomes larger than the rms random potential, the electronic states, localized by the static random potential, become delocalized by the phonons[51,52] and consequently the conductivity increases more rapidly with increasing temperatures than expected from the activated fit at lower temperatures.

The temperature dependence of the observed conductivity of NMP-TCNQ[48] is in good agreement with these results. In the temperature region 100–140 K the conductivity is activated with an activation energy of 509 K. In the regions 100–38 K and 38–18 K (the lowest measured temperature) the conductivity has the form $\ln[\sigma_0/\sigma(T)] = (T_m/T)^{1/m}$, with $m = 2.91$ and 3.87, respectively, and $T_m = 1.33\times 10^6$ and 6.06×10^7 K, respectively. This fit is shown in Fig. 5 and has an rms error of 0.057. The best activated fit over the entire region 18–140 K is shown in Fig. 4 and has an rms error of 0.49.

The change in the temperature dependence from $T^{-1/4}$ to $T^{-1/2.91}$ or $T^{-1/2.70}$ is a purely geometrical effect reflecting the anisotropy of the lattice and/or the hopping rates. A somewhat similar change of temperature dependence due to the geometric constraints on the system was theoretically predicted[36,45] and subsequently established[45] for thin amorphous films: At very low temperatures, when the maximum hopping distance R_m is much larger than the film thickness t the hopping conductivity has a temperature-dependence characteristic of a two-dimensional system, $m = 3$ in (1.3). With increasing temperature, as R_m becomes $\lesssim t$, the temperature dependence changes to that of a three-dimensional system, $m = 4$. Thus, in thin films m increases with increasing temperatures whereas in QOD compounds m decreases with increasing temperatures. This is because in thin films one compares the maximum transverse hopping range with the maximum transverse length, the film thickness, whereas in QOD conductors one compares it with the minimum transverse length, the interchain separation.

The various values of m (Tables I–III) suggested to characterize the temperature dependence according to Eq. (3.49) were obtained by an approximate decoupling procedure, and may be regarded as values averaged over individual temperature regions determined by various ranges of interchain hopping distances. In principle, the critical hop G_c and its correct temperature dependence is to be determined from (3.9) and (3.12). m would then vary continuously with temperature rather than discontinuously as in Tables I–III. (3.9), however, cannot be directly solved since Δ and therefore $g(\Delta)$ is itself a function of G_c. We have therefore considered various specific ranges of Δ, approximated $g(\Delta)$ as in (3.37) and thereby determined m. A different decoupling procedure involving different ranges of Δ would give somewhat different values for m. However, as long as the percolation construction (two or three dimensional) is valid, the lowest value of m would be 2, corresponding to the interchain hopping range $1 \leqslant \Delta \leqslant 1 + 0^+$. The extent of the temperature region in which $m = 2$ would hold would, however, be extremely small. In fact, $m = 2$ holds only at one particular temperature when $\Delta = 1$. At higher temperatures, when $\Delta < 1$, the percolation construction breaks down and the temperature dependence cannot be determined by this analysis. At lower temperatures when $\Delta > 1$, m becomes larger than 2.

A temperature dependence of the form (1.3) with $m = 2$ has also been observed in three-dimensional energy-band tails.[53] Redfield attributed this to possible formation of QOD filamentary paths of least impedance. Formation of filaments requires some anisotropy in the magnitudes of resistances along and transverse to the filaments, and therefore considerations similar to those of Sec. III would lead to an exponent m somewhere between 2 and 3 depending on the details of the filamentary structure. Alternatively, Shklovskii[54] and Pollak[55] have shown that under suitable conditions a temperature dependence of the form (1.3) with $m = 2$ can be observed even without the formation of filamentary paths. Thus, whether or not filaments are formed during conduction in energy band tails may be determined from the exact form of the temperature dependence—$m = 2$ over an extended temperature region would imply the absence of filaments. However, it is very difficult to distinguish between various values of m in the range 2–3.

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