reflections (reflections found in phase-VI struc-
ture). This observation supports the assumption
of a rotational motion of the molecules in phase
V. The motion is cooperative, and on a local
scale the molecular structure is the same as in
phase VI. The S_B structure then appears as a
mean structure owing to a rotational disorder of
the molecules jumping to different possible posi-
tions. The same diffuse spots have also been ob-
served by de Vries and Fishel[9] for the S_B phase
of BEA. These authors proposed as a solution
that the molecules in each layer form a herring-
bone-type packing, but they did not point out that
such an order only extends to very short dis-
tances, whereas the mean structure of the quasi-
long-range order in each layer is more symmet-
rical (i.e., pseudohexagonal). Therefore, the
herringbone local array does not appear on the
Bragg spots which are characteristic of the three-
dimensional order.

We come to the conclusion that the different
phases of TBBA (V, VI, VII) which successively
appear when cooled down and before reaching
the long-range order crystalline state develop
structures less and less symmetrical and more
and more complex. Because of the layer struc-
ture and the absence of long-range three-dimen-
sional order, we can assume that these phases
are all smectic. Nevertheless, the order extent
is sufficient to define a "local" lattice. Despite
the considerable difference between the molecular
packings, the x-ray powder patterns happen to be
very similar. Therefore, without any further in-
formation, the distinction between phases V and
VI would have been very difficult if not impos-
sible. This example then emphasizes the diffi-
culty of a classification of smectic compounds[10]:
The problem of the identification of TBBA VI
and VII with some of the numerous smectic mod-
ifications already described remains open. Fur-
thermore, some questions on the distinction be-
tween such phases and some crystalline states
are still to be solved.

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Phonon-Assisted Jump Rate in Noncrystalline Solids*

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An exact calculation of the acoustic-phonon–assisted jump rate has been carried out.
It is found that while the Miller-Abrahams (single-phonon) approximation is adequate for
the study of shallow-impurity conduction at helium temperatures, it is typically inappro-
priate for the study of hopping between deep states in noncrystalline solids. In particular,
the multiphonon jump rate will display a nonactivated temperature dependence below the
Debye temperature which is similar to the often-seen $\exp[-(T_0/T)^{1/4}]$ behavior.

Recently, considerable attention has been di-
rected toward understanding the temperature de-
pendence of the electrical conductivity associated
with the hopping motion in noncrystalline solids.
Much of this interest is related to the suggestion
that the conductivity arising from the hopping of
carriers between very shallow impurity states
(such as those of Sb in Ge) should vary with tem-
perature as $\exp[-(T_0/T)^{1/4}]$ near liquid-helium
temperatures.[1] In particular, a similar temper-
ature dependence has been reported at very much
higher temperatures (of the order of 100 K) in a

number of materials in which hopping is hypothesized to occur.[2,3] In order to explain these observations, percolation theory has been utilized to justify the extension of Mott's results to such high temperatures.[2,4] In these arguments, the rate which characterizes a phonon-assisted hop between deep states at these temperatures is assumed to be essentially that which was applied by Miller and Abrahams to hops between shallow-impurity states at helium temperatures.[5,6] Specifically, the expression in question is that obtained by a perturbative calculation (lowest order in the electron-lattice coupling strength) of the rate which characterizes a hop in which only one acoustic phonon is emitted or absorbed.

The purpose of this Letter is to present the principal results of a nonperturbative calculation of the phonon-assisted jump rate in which all multiphonon jump processes can contribute to the total jump rate. It is found that although the Miller-Abrahams jump-rate expression constitutes an adequate representation of the jump rate in the highly restrictive situation to which they have applied it (hops between very shallow impurity states at helium temperatures), the perturbatively obtained expression does not in general yield even a qualitatively correct representation of the elemental (two-site) jump rate. Specifically, multiphonon transitions will in many instances provide the dominant contribution to the jump rate even as the temperature approaches absolute zero. Furthermore, it is found that the elemental jump rate will typically manifest a nonactivated temperature dependence, resembling an

$\exp[-(T_0/T)^{1/4}]$ behavior, between helium temperatures and some fraction of the Debye temperature. In fact, the present study suggests that the nonactivated temperature dependence of the electrical conductivity, which is observed in a number of noncrystalline solids in this temperature range, may arise, in the main, from the jump rate itself rather than from the percolation aspects of hopping conduction in disordered materials.

The herein-discussed calculation is based on a model which is in fact quite general. Namely, the atomic vibratory motion is described in terms of the normal vibrational modes of the solid and, as is also customary, the electron-lattice interaction is represented by a linear dependence of the carrier's energy on the vibrational displacements. For simplicity only the carrier's interaction with the N modes of one branch of the acoustic vibrational spectrum will be considered here. The energy of a carrier occupying a state whose location is designated by the site index $\vec{g}$ is then given by

$$\epsilon_{\vec{g}} = \epsilon_{\vec{g}}^{\,0} - 2N^{-1}\sum_{\vec{q}}|\gamma_{\vec{g}}(q)|^2\hbar\omega_{\vec{q}},$$

where $\omega_{\vec{q}}$ is the eigenfrequency of the qth vibrational mode, $\epsilon_{\vec{g}}^{\,0}$ is the electronic energy in the absence of an interaction between the electron and the vibratory motion, and $\gamma_{\vec{g}}(\vec{q})$ is a measure of the electron-lattice interaction.

Following a procedure which is analogous to that employed in calculating the (nonadiabatic) small-polaron jump rate,[7] one obtains the following expression for the rate characterizing a hop from site $\vec{g}$ to $\vec{g}'$:

$$R_{\vec{g}',\vec{g}} = (J_{\vec{g}',\vec{g}}e^{-S}/\hbar)^2 e^{-\beta\Delta/2}\sum_{n=1}^{\infty}(1/n!)\int_{-\infty}^{\infty}dt\,[F(t)]^n\cos(\Delta t/\hbar). \tag{1}$$

Here $J_{\vec{g}',g}$ is the transfer integral between sites $\vec{g}'$ and $\vec{g}$, Δ is the difference between the energies of a carrier placed at sites $\vec{g}'$ and $\vec{g}$ [$\Delta > 0$ ($\Delta < 0$) for a hop upward (downward) in energy], $\beta \equiv 1/kT$,

$$S \equiv N^{-1}\sum_{\vec{q}}|\gamma_{\vec{g}'}(\vec{q}) - \gamma_{\vec{g}}(\vec{q})|^2\coth(\beta\hbar\omega_{\vec{q}}/2), \tag{2}$$

and

$$F(t) \equiv N^{-1}\sum_{\vec{q}}|\gamma_{\vec{g}'}(\vec{q}) - \gamma_{\vec{g}}(\vec{q})|^2\operatorname{csch}(\beta\hbar\omega_{\vec{q}}/2)\cos(\omega_{\vec{q}}t). \tag{3}$$

The summation index n in (1) corresponds to the total number of phonons that are emitted and absorbed in the associated jump processes. Figure 1 illustrates the one-, two-, and three-phonon processes involved in an upward hop in energy. It is noted that the terms represented in the first column all require the absorption of energy Δ from the lattice while the other higher-order processes involve the absorption of more energy. Thus at arbitrarily low temperatures only the multiphonon processes of the first column will contribute to the jump rate. In this limit, the rate will therefore be characterized simply by the activation energy Δ.
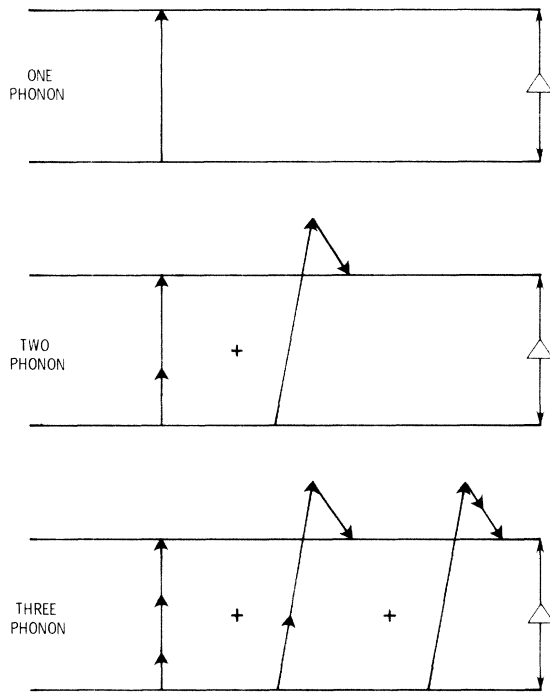
For simplicity and to provide a direct compar-

FIG. 1. Schematic representation of the processes which correspond to the $n = 1$, 2, and 3 terms in the series of Eq. (1). It is assumed in this figure that the disorder energy Δ is positive and less than that of the maximum-energy phonon with which a carrier can interact, $\hbar\omega_m$.

ison with the Miller-Abrahams result, attention will henceforth be restricted to Δ being less than the maximum-energy acoustic phonon with which the carrier can interact. In this case, the Miller-Abrahams approximation consists of ignoring all but the single-phonon ($n = 1$) term of the series while setting $S = 0$ in the prefactor. The actual

contribution of the multiphonon processes in this series is dependent on the availability of absorbable lattice-vibrational energy, on the number of vibrational states (phase space) into which phonons can be emitted, and on $|\gamma_{\vec{g}'}(\vec{q}) - \gamma_{\vec{g}}(\vec{q})|$. Although this function is in most instances unknown, it is only its typical magnitude which is of major significance in this study (its $\vec{q}$ variation affects only the detailed distribution of multiphonon processes which contribute to the total jump rate).[8] To estimate roughly the order of magnitude of the interaction and to facilitate a comparison with the Miller-Abrahams result, a generalization of the model utilized both in their study and in general discussions of the electron-lattice interaction in noncrystalline solids[9] will be adopted:

$$|\gamma_{\vec{g}'}(\vec{q}) - \gamma_{\vec{g}}(\vec{q})|^2 = \gamma(\omega_D/\omega_{\vec{q}})f^2(\hbar\omega_{\vec{q}}),$$

where the coupling constant γ is defined by $Z^2/Ms^2\hbar\omega_D$; Z is the deformation-potential constant, M is an atomic mass, s is the speed of sound, and ω_D is the Debye frequency. Denoting by $\hbar\omega_m$ the energy of the highest-energy vibrational mode with which the carrier can effectively interact, the cutoff factor $f(\hbar\omega_{\vec{q}})$ may be approximated by 1 when $\omega_{\vec{q}} < \omega_m$ and by 0 when $\omega_{\vec{q}} > \omega_m$. In the impurity-conduction case,[5] $\omega_m = \omega_D a/b$, where a is the lattice constant, b denotes the (equal) radii of the impurity states, and $a/b \ll 1$. If the radii of the localized states are less than a/C $(C \sim \frac{1}{2})$, then $\omega_m = C\omega_D$. With known values of these parameters one finds that γ is typically much larger than unity[10]: $\gamma(n\text{-Ge}) = 242$, $\gamma(p\text{-Ge}) = 119$, $\gamma(n\text{-Si}) = 175$, and $\gamma(p\text{-Si}) = 63$. Therefore, as a working hypothesis, it will henceforth be assumed that $\gamma \gg 1$.

Focusing attention on the low-temperature limit $(T \to 0$ with $\hbar\omega_m > \Delta \gg kT)$, evaluation of Eq. (1) yields

$$R_{\vec{g}',\vec{g}} = (J_{\vec{g}',\vec{g}}e^{-S_0})^2 e^{-\beta(\Delta+|\Delta|)/2}(2\pi/\hbar|\Delta|)\sum_{n=1}^{\infty}B^n(\Delta)/n\,!\,(2n-1)\,!, \tag{4}$$

where $S_0 = \frac{3}{2}\gamma(\omega_m/\omega_D)^2$ and $B(\Delta) \equiv 3\gamma(\Delta/\hbar\omega_D)^2$. As expected, the jump rate is simply activated for an upward hop in energy and temperature independent for a downward hop in energy. The contribution of each term in the sum relative to the $n = 1$ term is plotted in Fig. 2 for several values of $B(\Delta)$; it is apparent that the $n = 1$ term only dominates the series when $B(\Delta)$ is rather small. In particular, the Miller-Abrahams approximation, the neglect of all but the $n = 1$ term and the replacing of $\exp(-2S_0)$ by unity, requires both that $2S_0 \ll 1$ and that $B(\Delta) \lesssim 1$. While these conditions

are nearly met in the Miller-Abrahams impurity-conduction study $(\omega_m/\omega_D = a/b < 10^{-1}$, $\Delta \approx 10^{-3}-10^{-4}$ eV), they are grossly violated in many situations which are envisaged in noncrystalline solids $(b \approx a$, $\Delta \approx 10^0 - 10^{-2}$eV). In the latter case, $B \gg 1$, the series contributes a major Δ-dependent factor, $\exp[3(3\gamma/4)^{1/3}(\Delta/\hbar\omega_D)^{2/3}]$, to the jump rate. Thus, even in the limit as $T \to 0$, multiphonon processes often substantially affect the jump rate. Finally, analysis shows that the activated temperature dependence of the jump rate manifested
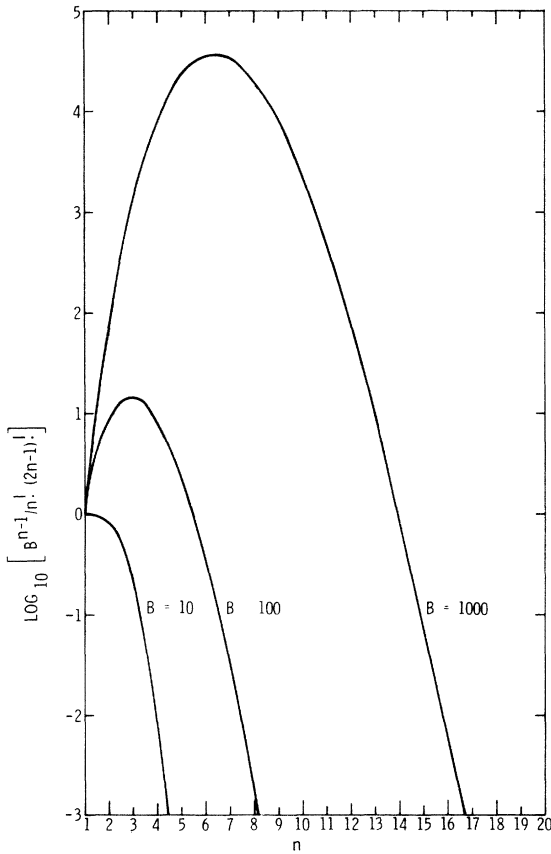
FIG. 2. The logarithm of the ratio of the contribution to the jump rate of the n-phonon processes to that of the one-phonon process in the low-temperature limit, $\Delta/kT \to \infty$, plotted versus n for three values of $B(\Delta)$. The curves only have meaning at integer values of n.

FIG. 3. The logarithm of the reduced jump rate, r $\equiv R_{\vec{g}}{}^r, \vec{g}{}'/(J_{\vec{g}}{}', \vec{g}^2/\hbar^2\omega_m)$, plotted against both θ_m/T and $(\theta_m/T)^{1/4}$ for $3\gamma(\omega_m/\omega_D)^2 = 50$, where $\theta_m \equiv \hbar\omega_m/k$; here $T_0 \simeq 4 \times 10^5 \, \theta_m$.

by Eq. (4) will prevail only at extremely low temperatures: $kT < \Delta$ in the impurity-conduction case, and $kT \ll \hbar\omega_D/2\pi\sqrt{3\gamma}$ in the multiphonon situation.

As the temperature is raised beyond the regime of validity of Eq. (4), with $2S_0 \gg 1$, processes other than those depicted in the first column of Fig. 1 make the dominant contribution to the jump rate. With increasing temperature more and more multiphonon processes contribute giving rise to a jump rate which (is progressively less dependent on Δ and) increases with temperature in a nonactivated manner. Once the temperature climbs above a point where phonon-absorption processes are no longer frozen out, $kT \gtrsim \hbar\omega_m/2$, an activated behavior, albeit with a different activation energy, is regained.

These features are illustrated by Fig. 3, in which the logarithm of the $\Delta = 0$ jump rate is plotted versus $\hbar\omega_m/kT$ and $(\hbar\omega_m/kT)^{1/4}$. The high-
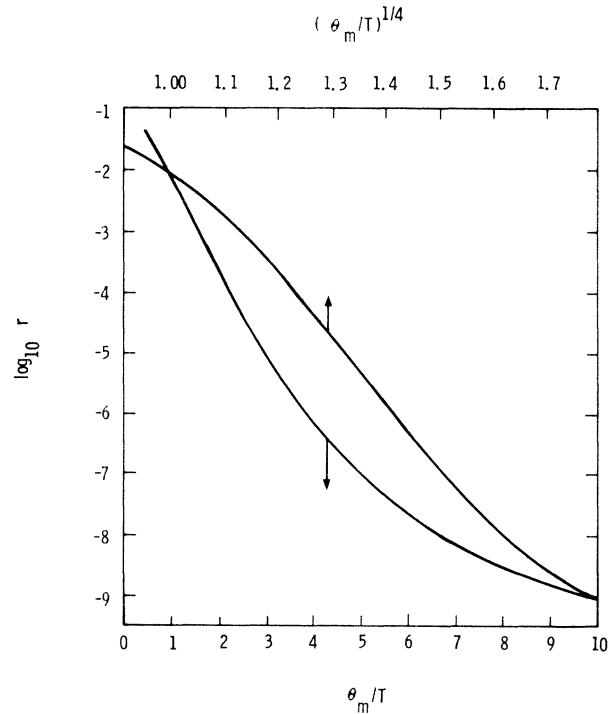
temperature activation energy is simply $E_A \equiv \frac{1}{4}\gamma\hbar$ $\times \omega_D(\omega_m/\omega_D)^3$. In the lower-temperature nonactivated region the jump rate displays a more gradual temperature dependence[11] which, as shown in the upper curve, is not unlike an $\exp[-(T_0/T)^{1/4}]$ behavior. Typically [for $\gamma(8kT/\hbar\omega_D)^4 \gg (\Delta/\hbar\omega_D)^2$], the presence of a finite Δ only modifies the jump rate by the factor $\exp(-\beta\Delta/2)$. Thus, in this regime, the factors which are related to the spacial and energetic separation of the sites between which the particle hops, $J^2 e^{-\beta\Delta/2}$, multiply a temperature-dependent factor which itself displays a $T^{-1/4}$-like temperature dependence. The electrical conductivity can then be written as a product of factors related respectively to a percolation calculation and to the elemental $\Delta = 0$ jump rates. Calculation shows that, in typical cases $(S_0 \gg 1)$, the temperature dependence of the multiphonon jump-rate factor contributes appreciably $(T_0 \sim 10^7$– 10^{10} K) to the temperature dependence of the conductivity.

Thus it is concluded that while the Miller-Abrahams jump-rate expression is appropriate to the situation to which they have applied it (shallow-impurity conduction at helium temperatures), it

is not generally applicable to the hopping situations which are envisaged in noncrystalline solids. Furthermore, it is suggested that the generally observed nonactivated temperature dependence of the dc conductivity is, at least in part, a manifestation of the multiphonon nature of acoustic-phonon—assisted hopping between well-localized states. A detailed account of the herein-summarized consideration is currently being prepared.

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Magnitude of the Deformation of the Proton-Nucleus Spin-Orbit Coupling

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A simple explanation is presented for the observed tendency of the spin-orbit part of the optical potential for a proton scattered by a nonspherical target nucleus to be more deformed than the central part. The explanation is based on the fact that the range of the central two-body force is longer than that of the two-body spin-orbit force.

The macroscopic description of inelastic scattering is based on the extended optical model, which differs from the conventional optical model in that the spherically symmetric optical potential is replaced by a deformed potential. It is now generally accepted that in addition to the real central potential, the absorptive central and spin-orbit potentials are also affected by the nuclear deformation. With respect to the spin-orbit coupling, two deformed forms have been proposed: the so-called Oak Ridge[1] and full Thomas[2] forms. The latter has been shown to be in better agreement with experiment.[2]

A general feature following from the early investigations, for both full Thomas and Oak Ridge forms, was a slight but consistent preference for a value of the experimental spin-orbit deformation parameter $\beta^{s.o.}$ larger than that for the central potential, β^{cent}. It is well known[3] that this discrepancy can partly be resolved by following Blair's suggestion[4] that the deformation distances $\alpha(\theta\varphi)$ over which the various parts of the optical potential are displaced in the deformation process are taken equal, which implies equal products βR, R standing for the radius parameter of the specific potential term considered. The relative smallness of the spin-orbit radius parameter $R^{s.o.}$, given by elastic scattering fits, then yields an increased value for $\beta^{s.o.}$. It turns out, however, that this effect is not sufficient to explain the discrepancy, the tendency being that even the product βR for the spin-orbit coupling is anomalously large. A similar tendency has been observed in later work.[5-7] Cases for which there is no clear indication of a discrepancy within the experimental accuracy have also been reported,[8] and even cases in which the discrepancy is in the opposite direction.[9] It is, however, remarkable that deviations take place almost without exception in the direction of larger spin-or-