

to-metal transition.¹⁴ It will be appropriate to extend Anderson's localization theory¹⁵ to include the LRO.

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Correlated Small-Polaron Hopping Motion*

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Prior small-polaron hopping theories have tacitly assumed that the lattice relaxes rapidly enough after a jump to permit the treating of successive hops as independent. We conclude that the appropriate relaxation time is too long to permit consistent application of these theories to intermediate-mobility materials such as NiO and CoO. Furthermore, the activation energies associated with correlated hopping motion may be sufficiently small so that the mobility will not manifest an activated behavior.

As has been stressed in a number of review articles on polarons,¹⁻³ the electron-lattice interaction may be sufficiently strong in those polar materials which are characterized by rather low electronic mobilities to suggest that the carriers are to be viewed as small polarons. In particular, much effort (recently reviewed by Bosman and van Daal⁵) has been expended in order to ascertain whether the carrier drift mobility in a number of transition-metal oxides manifests the thermally activated temperature dependence predicted by both the adiabatic⁶ and non-adiabatic⁷ small-polaron hopping theories. In this Letter it is pointed out that these theories are only applicable to situations in which the mean time between small-polaron hops is substantially greater than the time characterizing

the relaxation of the lattice following a small-polaron hop⁴; the present considerations indicate that the deduced values of the drift mobility⁵ in NiO and CoO ($\sim 10^{-1}$ -1 cm²/V sec) correspond to sufficiently short hopping times so that comparison with the hopping theories of Refs. 6 and 7 is not appropriate. Furthermore, it is felt that for such "intermediate" mobilities a theory of small-polaron hopping is needed in which the probability of a hop depends on the prior experience of the carrier. Such a theory may find application to a number of intermediate mobility materials.

In addition, in this Letter it will be argued that in this intermediate regime, where successive small-polaron hops are correlated, the activation energy characterizing the drift mobility is reduced substantially from that of the uncorre-

lated theories.^{6,7} Thus it is possible, depending on the choice of physical parameters, for the small-polaron drift mobility to display a mild temperature dependence; it may even decrease with increasing temperature for sufficiently high temperatures as a consequence of the temperature variation of the pre-exponential term dominating the activated term. In addition, within this model the minimum mean time between hops (and hence maximum mobility) for which the hops are essentially uncorrelated is estimated. Finally, the effect of correlated small-polaron hops on the Hall mobility is briefly discussed.

To begin let us observe that a basic assumption of all of the prior studies of small-polaron hopping motion is that each hop may be treated as independent of the previous hops. In other words these theories ask the question: If one places a small polaron on a site in the lattice, what rate characterizes the motion of the small polaron to a neighboring site? However, in general, a better question to ponder in considering the diffusive small-polaron motion⁸ is the following: If the small polaron hops between two neighboring sites at time zero, what is the rate characterizing another hop at a time t later? If, in fact, there is no correlation between small-polaron hops both of the above questions yield the same results.

Let us now discuss a mechanism which generally produces correlations between small-polaron hops. Fundamental to our discussion is the notion that each hop of a small polaron is associated with a "coincidence event." Explicitly, let us recall^{6,7} that for a carrier to hop, the local electronic energy level associated with an occupied site must momentarily coincide with the corresponding local electronic energy level of a neighboring unoccupied site (the local electronic energy levels being a function of the lattice-vibration coordinates). Furthermore, the drift-mobility activation energy calculated in Refs. 6 and 7 is simply the minimum potential energy (in excess of the polaron binding energy) required to establish such a two-site coincidence configuration. Thus, if a small-polaron hop is to be considered independent of its previous hop one expects that the distortion associated with the first hop must relax (dissipating an amount of energy comparable with this activation energy to the remainder of the lattice) in a time which is much shorter than the mean time between small-polaron hops.

In this note we shall consider, as in most prior

work,^{2,3,6,7} the carrier-induced distortions to be associated with the optical polarization modes of the crystal. Furthermore, it should be recalled that the transfer of optical vibrational energy between neighboring unit cells (or neighboring diatomic molecules in the case of Holstein's molecular crystal model⁶) is characterized by a time of the order of the reciprocal optical bandwidth $(6\Delta\nu)^{-1}$. Thus, anticipating the subsequent discussion, the smaller the dispersion of the optical polarization mode frequencies the longer the relaxation time τ .

Let us now assume that a carrier has hopped between neighboring sites at time zero and ask for the probability per unit time that a second hop occur at a time t later. It is apparent that for sufficiently short times [$t \ll (\Delta\nu)^{-1}$] the rate characterizing a return to the initially occupied site is greater than the rate associated with a hop in a relaxed lattice since the distortions associated with the initial coincidence event will not have had time to relax. In addition, if the probability of the carrier availing itself of this increased opportunity to hop back is sufficiently large it is appropriate to view the carrier as hopping back and forth repeatedly between the two involved sites rather than sitting on a particular site; this effect tends to somewhat reduce the carrier diffusion¹⁰ from that calculated in Refs. 6 and 7.

Of greater importance is the fact that for $t \ll (\Delta\nu)^{-1}$ the rate characterizing a hop to a "new" site is also expected to be greater than the jump rate associated with a relaxed lattice because the region surrounding the occupied site will deviate substantially from its equilibrium configuration. In fact, for such times the activation energy characterizing a hop to a new site is the additional energy, beyond that required for the initial hop, needed to form another coincidence; in Holstein's model this energy is $\epsilon_3 - \epsilon_2 \sim \epsilon_2/3$, where ϵ_3 and ϵ_2 are the activation energies characterizing three-site and two-site coincidences, respectively.

In light of the previous comments, it is useful at this point to view the rates associated with a return jump and a jump to a "new" site as possessing activation energies which depend on the time between the "initial" hop and the succeeding hop.¹¹ Thus the activation energy appropriate to a return hop $E_A^r(t)$ is essentially zero for $t \ll (\Delta\nu)^{-1}$ and increases monotonically¹² with time (as the initial distortions dissipate) to the value characterizing a hop in a relaxed lattice. The

activation energy associated with a hop to "new" site $E_A(t)$, however, may not rise monotonically from its initial value $E_A(0) \sim \epsilon_2/3$ to its relaxed value $E_A(\infty) \sim \epsilon_2$. This phenomenon (present in an explicit calculation which utilizes Holstein's one-dimensional molecular crystal model¹³) arises as a result of the fact that as the initially distorted sites relax the neighboring sites receive energy from the initially distorted sites and become somewhat distorted themselves. The net result is that the additional vibrational energy required to form a coincidence may actually decrease with time until a substantial portion of the energy involved in the initial coincidence is exchanged between the sites in the region of the initial hop. Actually a complete discussion of this property of the jump rates involves the detailed consideration of the relative phases of the oscillations at the initially distorted site and the relevant unoccupied neighbor and hence will not be discussed in detail here.¹⁴

At this point let us observe that for $t \gg (\Delta\nu)^{-1}$ a substantial portion of the energy of the initial distortion has been transferred back and forth among those ions that are in the vicinity of the initial coincidence. Therefore it is reasonable to consider the distortions associated with the sites adjacent to the occupied site to be comparable with one another. In this situation the jump rates associated with a hop to any of the adjacent sites are all essentially equal. Thus for $t \gg (\Delta\nu)^{-1}$ the activation energies $E_A(t)$ and $E_A^r(t)$ approach one another.

The time which characterizes both rates becoming a single constant rate equal to the uncorrelated jump rate is defined as the relaxation time. A good estimate of this relaxation time can be made by realizing that the effects of the residual distortion of the occupied site are only significant when the difference between the activation energies required for a two-site coincidence with and without a residual distortion is greater than the energy associated with a thermally produced distortion. Furthermore, one can show that for sufficient lattice relaxation $[(\Delta\nu)t \gg 1]$ the difference between the activation energy associated with the residual distortion and the activation energy appropriate to a relaxed lattice, denoted by $\Delta E_A(t)$, is given by

$$\Delta E_A(t) \simeq -\epsilon_2[A(t)/A(0)], \quad (1)$$

where $A(t)$ is the time dependent amplitude of the difference between the residual distortion of the

occupied site and an unoccupied neighboring site.¹⁵

Let us now view the localized distortion as being composed of a linear superposition of all of the optical polarization mode states. Assuming the following vibrational dispersion relation (appropriate to a narrow-band isotropic cubic crystal):

$$\nu_{\vec{k}} = \nu_0 + (\Delta\nu)[\cos k_x + \cos k_y + \cos k_z], \quad (2)$$

where \vec{k} is the phonon wave vector ($-\pi \leq k_x \leq \pi$, $-\pi \leq k_y \leq \pi$, $-\pi \leq k_z \leq \pi$) and ν_0 is a typical optical mode frequency, it then follows that at sufficiently long times, $(\Delta\nu)t \gg 1$, the amplitude of the relative distortion $A(t)$ decreases with time as $[(\Delta\nu)t]^{-3/2}$ corresponding to the fall of the center of the wave packet which described the initial distortion. Therefore replacing the ratio $[A(t)/A(0)]$ of Eq. (1) by $[(\Delta\nu)t]^{-3/2}$ and defining the relaxation time τ by the condition

$$|\Delta E_A(\tau)| \sim \kappa T/2, \quad (3)$$

we find

$$\tau \sim (\Delta\nu)^{-1}(2\epsilon_2/\kappa T)^{2/3}. \quad (4)$$

Thus the mean time between hops t_{hop} must certainly be much greater than τ in order for the theories of uncorrelated small polaron^{6,7} to be strictly applicable. In terms of the drift mobility μ_D , related to the hopping time via the relation

$$\mu_D = (ea^2/\kappa T)1/t_{\text{hop}}, \quad (5)$$

the condition for the applicability of the uncorrelated small polaron hopping theories is

$$\mu_D \ll \frac{ea^2}{\kappa T} (\Delta\nu) \left(\frac{\kappa T}{2\epsilon_2} \right)^{2/3}, \quad (6)$$

i.e.,

$$\mu_D \ll \left[\frac{ea^2}{h} \left(\frac{h\nu_0}{\kappa T} \right) \right] \left[\left(\frac{\Delta\nu}{\nu_0} \right) \left(\frac{\kappa T}{2\epsilon_2} \right)^{2/3} \right]. \quad (7)$$

Observing that the first bracketed term of Eq. (7) is typically of the order of $1 \text{ cm}^2/\text{V sec}$ and that the second bracketed term is usually considerably less than unity (at most $\sim 10^{-1}$), it is clear that the uncorrelated theory certainly cannot be consistently applied to materials with drift mobilities greater than $10^{-1} \text{ cm}^2/\text{V sec}$. In particular, accepting the deduced magnitude of the drift mobilities in NiO and CoO (10^{-1} - $1 \text{ cm}^2/\text{V sec}$) precludes consistent application of the uncorrelated hopping theories^{6,7} to these materials. Thus it becomes useful to discuss what one might expect from a small-polaron theory which considers correlation effects.

It is evident that if the average time that a carrier remains on a site is much less than $(\Delta\nu)^{-1}$, the activation energy associated with small-polaron diffusion is considerably less than its relaxed value. In fact, considering (within the nonadiabatic approach⁷) only the correlation between successive small-polaron jumps, one finds in Holstein's model that the diffusion activation energy in this situation is roughly $\epsilon_2/3$, i.e., one-third the value calculated in Ref. 7. In addition, the activation energy of the adiabatic theory⁶ generally contains additional terms (dependent upon electronic transfer integrals) which serve to further reduce the drift mobility activation energy. Thus it is within the realm of small-polaron theory for there to be small-polaron hopping motion characterized by a sufficiently small drift mobility activation energy so that the temperature dependence of the mobility is rather mild.

It should be commented that the Hall mobility will also be affected by lattice relaxation effects. In particular, for $(\Delta\nu)t_{\text{hop}} < 1$ the Hall mobility activation energy will be smaller than that calculated for a relaxed lattice^{6,9,16} and, as in these prior studies, it will be smaller than the drift mobility activation energy. Finally, it is important to recall^{6,9,16} that the ratio of the Hall to drift mobilities is proportional to $\exp[E_{\text{drift}} - E_{\text{Hall}}]/\kappa T$, this quantity generally being sufficiently large in the preceding works¹⁷ [$\approx \exp(2\epsilon_2/3\kappa T)$] so that in most instances the calculated Hall mobility is greater than the drift mobility. However, in the situation being discussed here this factor is considerably smaller¹⁸ [$\approx \exp(\epsilon_2/6\kappa T)$]; thus it is possible for the small-polaron Hall and drift mobilities to be comparable. In fact, in the adiabatic theory [cf. Eq. (9.8) of Ref. 6] the Hall mobility may be considerably smaller than the drift mobility.

As a result of the above considerations it is concluded that it is within the domain of small-polaron theory for both Hall and drift mobilities to possess sufficiently small activation energies to permit the pre-exponential temperature dependence of the mobility expressions to play an important role in determining the temperature dependence of the mobilities. Such a situation is characterized by mobilities which do not display a simple activation-type temperature dependence and which are associated with a hopping time which is less than or comparable with the reciprocal of the optical phonon bandwidth.

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¹¹The notion that the essential relaxation related time dependence of these rates occurs as a time dependent "activation energy" is supported by a detailed calculation for Holstein's molecular crystal model.

¹²Actually, in addition to the time dependences of $E_A(t)$ and $E_A^*(t)$ due to the relaxation of the coincidence distortion, there is relatively rapid oscillatory time dependence (characterized by a typical vibrational frequency ν_0) which merely reflects the oscillatory nature of the lattice. Suppressing this latter time dependence by time averaging the rates over a vibrational period $(\nu_0)^{-1}$ we obtain the results discussed here.

¹³All of the arguments concerning the time dependence of the jump rates have been verified in a lengthy study of the one-dimensional small-polaron model of Ref. 7: D. Emin, *Phys. Rev. B* (to be published).

¹⁴A classical study of the relaxation of Holstein's model lattice (Ref. 7) after a coincidence event is the subject of a future publication.

¹⁵Within Holstein's molecular crystal model, $A(t)$ is shown (in the work referred to in Ref. 13) to be the amplitude of the difference between the residual displacements from equilibrium of the occupied diatomic molecule and a neighboring diatomic molecule.

¹⁶D. Emin, to be published.

¹⁷In the nonadiabatic theory of the Hall effect in a square lattice (Ref. 16), it is shown that, while the temperature dependence of the Hall mobility is essentially the same as that calculated for a triangular lattice (Ref. 9) at sufficiently low temperatures, $\kappa T < \epsilon_4 - \epsilon_3 \approx \epsilon_2/6$, at higher temperatures the Hall mobility is multiplied by an additional factor of $(1/\kappa T)$ and the activation energy is slightly increased by the amount $\epsilon_4 - \epsilon_3$. This leads to an exponential factor of $\approx \exp(\epsilon_2/$

$2kT$) rather than the triangular lattice value quoted in the text.

¹⁸In the correlated regime, it is expected that the transition between the high- and low-temperature regime of the square lattice Hall mobility (cf. Ref. 17)

will occur at $\kappa T \approx \epsilon_5 - \epsilon_4 \approx \epsilon_2/10$. In the high-temperature correlated regime, $E_{\text{Hall}} \approx (\epsilon_5 - \epsilon_2) - (\epsilon_3 - \epsilon_2) \approx \epsilon_2/4$ while $E_{\text{diff}} \approx \epsilon_3 - \epsilon_2 \approx \epsilon_2/3$, thereby yielding an even smaller exponential factor [$\exp(\epsilon_2/12\kappa T)$] than the estimate for a triangular lattice given in the text.

Electron Relaxation Rates in Bismuth at Microwave and Far-Infrared Frequencies

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Temperature- and frequency-dependent relaxation rates in bismuth have been measured by studies of the magnetic-field-dependent reflectivity of microwave and far-infrared radiation in single-crystal samples. Retardation effects have been taken into account in the analysis of the cyclotron resonance line shapes. The temperature and frequency dependence of the relaxation rates are analyzed in terms of the theory of electron-electron scattering and the experiment provides strong support for electron-electron dominated scattering in bismuth. The experimental results are inconsistent with an electron-phonon dominated scattering mechanism.

There has been considerable interest recently in the frequency and temperature dependence of electron effective masses (m^*) and relaxation times (τ) in metals. These effects are expected from the electron-phonon interaction and electron-electron scattering, and their investigation can lead to a better understanding of electron interactions in metals. The frequency and temperature dependence of m^* and τ are determined by the line-shape analysis of measurements such as cyclotron resonance, and it is important to note that accuracy of the line-shape theory is crucial to these experiments.

The first measurements of frequency dependent relaxation times have been reported recently by Goy and Weisbuch¹ for lead and Edel'man and Cheremisin² for bismuth. In this Letter new measurements are reported of relaxation rates in bismuth over a larger frequency and temperature range than previously investigated. Moreover, in the analysis of cyclotron-resonance measurements, important corrections to the line-shape theory due to retardation effects have been considered. The relaxation rates obtained here, which are not in agreement with the measurements of Edel'man and Cheremisin, are interpreted in terms of electron-electron scattering in bismuth.

The bismuth samples were single-crystal disks (20-mm diam and 2-mm thickness) grown in graphite boats in vacuum from 99.9999% pure starting material, seeded so that the trigonal

axis was normal to the disk faces, then chemically lapped and polished. X-ray diffraction measurements were made to check the crystal orientation and the crystal quality.

At microwave frequencies of 36, 28, and 8 GHz the magnetic-field-dependent surface resistance R_s , arising from Azbel'-Kaner cyclotron resonance was studied by use of a microwave reflection spectrometer. With the magnetic field H parallel to the binary axis of the bismuth crystals the cyclotron resonance series corresponding to the mass $m^* = 0.0093m_0$ was observed. To obtain information on electron relaxation rates from these data it was first necessary to take retardation effects^{3,4} into account in the cyclotron-resonance line-shape theory. The Azbel'-Kaner theory only applies if the time dependence of the rf field can be ignored while the electrons are passing through the rf skin layer. For circular orbits this leads to the condition $\omega^2\delta/\omega_c V_F \ll 1$ for the applicability of Azbel'-Kaner theory. Here δ is the rf skin depth, V_F is the Fermi velocity, ω_c is the cyclotron frequency, and ω the rf frequency. For $\omega_c\tau < 10$ the surface impedance $Z(H)$ incorporating retardation effects can be written approximately as⁵

$$Z(H) - Z(0) \approx \frac{1}{3} Z(0) \exp\left[-2\pi\left(i\frac{\omega}{\omega_c} + \frac{1}{\omega_c\tau}\right)\right] \times \exp\left(\frac{\tilde{\omega}^2\delta}{\omega_c V_F}\right), \quad (1)$$