

Model of Thermally Activated Hopping Motion in Solids*

G. L. SEWELL

Bartol Research Foundation of The Franklin Institute, Swarthmore, Pennsylvania

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A simple idealized model is formulated for the purpose of deriving the transport properties of a particle that moves through a lattice primarily by means of thermally activated jumps. In its present form, the model is designed to represent the gross features of the properties of a "small polaron," that have been derived from previous microscopic theories. The model consists of a single particle, confined to a set of equivalent localized states, which may move either by tunneling or by thermally activated jumps. The properties of the model are solved exactly for the case when there are only two sites. The solution exhibits how the thermally activated and tunneling processes combine to transfer the particle from site to site. The various transport properties of the model are then obtained for the cases when the particle is trapped at a color center (idealized by two-site model) and when it moves through a periodic lattice. These properties are derived from those of the "natural" motion of the system, in the absence of any applied field, by means of the fluctuation-dissipation theorem.

I. INTRODUCTION

THE properties of an electron in a solid are governed by its interactions with the static field due to the crystal structure and with the phonons. The electron-phonon interaction leads to the formation of a "polaron," comprising the electron and its accompanying lattice polarization. Theoretical investigations¹⁻⁵ have shown that, in cases of strong electron-lattice coupling, the polaron may be described in terms of localized states. In each of these states, the electron is bound to a site and is surrounded by the lattice polarization which it induces. Polarons of this kind are often referred to as "small polarons."

The polaron may move from site to site as a result of weak residual interactions, since the original electron-lattice interaction is not completely accounted for in the formation of the polaron. Thus, it may move either by tunnel effect (adiabatic processes) or by phonon-activated jumps. It has been shown³⁻⁵ that the latter processes predominate at high enough temperatures. In this case, the particle may be considered to hop from site to site in a random manner, due to its residual interaction with the phonons. Preliminary calculations³⁻⁶ have been made for the mobility of a carrier in a periodic lattice due to this mechanism. The calculations agree qualitatively, as regards order of magnitude and temperature dependence, with the previously anomalous experimental results⁷ for α -Fe₂O₃ and N₇O. Similar calculations may be shown to account qualitatively for observations⁸ of Debye losses in the above oxides and quartz, due to electrons trapped at color centers. Thus, we have ex-

perimental evidence that the properties of carriers in certain materials may be described by the hopping polaron theory.

It has also been established⁹ that the carriers responsible for impurity conduction in certain materials likewise move by the phonon-activated hopping mechanism. Here, however, one has the added complications that the sites where the carriers may be localized are randomly arranged and not mutually equivalent.

To sum up, the previous work has shown that, under certain specified conditions, the carriers in a solid move primarily by the hopping mechanism. However, it has not led to a formal theory of the various transport processes due to this mechanism. Such a theory would require an analysis of the time dependence of the observables of the carriers—not merely a calculation, as in the previous theories, of the jump transition rates.

The object of the present paper is to provide a simplified formal theory of transport properties of carriers that move primarily by hopping. In order to gain further insight into the nature of the problems involved, it is useful to first re-express the earlier theories in terms of observables of the "dressed" physical particle, i.e., the polaron, rather than the electron. As will be shown in the Appendix, this may be done formally by applying a canonical transformation to the electron-phonon model employed in the previous theories. This transformation expresses the Hamiltonian for the model, which we henceforth refer to as model *A*, in terms of polaron creation and annihilation operators and lattice dynamical variables [Eqs. (A8)–(A15)]. In this model, the carrier is confined to a set of localized states centered at certain lattice sites. The carrier moves from site to site as a result of two weak renormalized interactions, \mathcal{H}_1 and \mathcal{H}_2 . The former interaction is static and governs the tunneling motion of the particle. The interaction \mathcal{H}_2 couples the particle to the phonons and thus governs the jump processes.

The mathematical form of \mathcal{H}_2 is very complicated.

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¹ H. Fröhlich, Arch. Sci. (Geneva) **10**, 5 (1957).

² G. L. Sewell, Phil. Mag. **36**, 1361 (1958).

³ G. Yamashita and T. Kurosawa, J. Phys. Chem. Solids **5**, 34 (1958); J. Phys. Soc. Japan, **15**, 802 (1960).

⁴ H. Fröhlich and G. L. Sewell, Proc. Phys. Soc. (London) **74**, 643 (1959).

⁵ T. Holstein, Ann. Phys. (N. Y.) **8**, 343 (1959).

⁶ G. L. Sewell, Proc. Phys. Soc. (London) **76**, 985 (1960).

⁷ F. G. Morin, Phys. Rev. **93**, 1195, 1199 (1954).

⁸ G. Volger, Disc. Faraday Soc., **23**, 63 (1957).

⁹ Cf. N. F. Mott and W. D. Twose, Suppl. Phil. Mag. **10**, 107 (1961).

Because of this, we simplify the theory by employing a new formalism that takes account of only the bare essentials of the interactions governing the motion of the particle. For this purpose, we first re-examine the part played by the phonons in determining the properties of this motion. It may be seen from the previous theories^{3-5,9} that the essential role of the phonons is to provide a thermal reservoir which interacts with an assembly of carriers, via the interaction \mathcal{H}_2 , and brings them into thermal equilibrium. The hopping motion is simply the means whereby the free energy of the carriers is dissipated so that equilibrium is attained. Thus, the jump processes are thermally activated ones, governed by the dissipative interaction \mathcal{H}_2 .

Now it is known that the effects of dissipative forces on a mechanical system generally depend only on certain gross properties of those forces.¹⁰ For example, it has been shown by quantum theoretical treatments^{10,11} that the Brownian motion of an oscillator in interaction with a reservoir depends only on certain gross properties of that interaction. These considerations suggest that, in the particular case of the above-described model *A*, the dynamical properties of a carrier should likewise be governed only by the gross properties of the interaction, \mathcal{H}_2 , between carrier and reservoir. Assuming this to be the case—and the assumption is supported by an argument in the concluding section—then we may obtain the dynamical properties of a carrier on the basis of a suitable idealized model, which is simpler than *A* and which represents certain essential properties of *A*.

In the present paper, we propose such a model, which is referred to as *B*, for the purpose of studying the dynamical properties of thermally activated hopping motion. At this stage, *B* should be regarded as a heuristic model, designed for the purpose of studying the hopping mechanism rather than for direct application to any real solids. Nevertheless, it is argued in the concluding section that the resultant transport theory, in which the transport properties are expressed in terms of phenomenological constants, should apply to small polarons in solids.

The model *B* consists of a particle confined to a set of equivalent sites.¹² The particle moves from site to site as a result of two weak interactions. The first interaction, H_1 , is static and leads to tunneling. The second interaction, H_2 , couples the particles to a thermal reservoir, Γ . In this idealized model, there is no need to regard Γ as consisting specifically of phonons. The important thing is that H_1 and H_2 are so chosen as to contain the principal gross properties of \mathcal{H}_1 and \mathcal{H}_2 of model *A*. Thus, the particle in the new model corresponds qualitatively to a small polaron, not an electron.

Our procedure in deriving the theory is as follows: In Sec. II, we define the formalism for the model *B*. In the subsequent sections, we investigate its properties by means of a quantum-theoretical treatment which is free from the *ad hoc* assumption, made in previous theories, that the particle moves from site to site in a Markovian manner. Accordingly, in Sec. III, we investigate the problem of how the agencies of tunneling and thermal activation combine to transfer the particle from site to site. We treat this problem on the basis of a two-site model whose properties may be solved exactly. The basic question concerned with this problem is: What is the probability, $P(t)$, that a particle, known to be initially at one site, is to be found at the other site at time t ? It is shown that P may be expressed in the form

$$P(t) = \frac{1}{2}(1 - e^{-\gamma t} \cos \Omega t), \quad (1.1)$$

where γ and Ω are phenomenological constants representing thermally activated and tunneling processes. The temperature dependence of these constants is such that

$$\begin{aligned} \gamma < \Omega & \text{ for } T < T_c, \\ \gamma > \Omega & \text{ for } T > T_c, \end{aligned} \quad (1.2)$$

where T_c is a certain critical temperature. It follows from (1.1) that P approaches its equilibrium value, $\frac{1}{2}$, by damped oscillations. If $\gamma > \Omega$, i.e., if $T > T_c$, the exponential term predominates over the oscillatory one, so that the particle moves primarily by thermally activated jumps. In this case $\frac{1}{2}\gamma$ may be interpreted as a jump frequency. On the other hand, if $T < T_c$, the oscillatory motion predominates, so that the particle moves primarily by tunneling.

In Sec. IV we use the fluctuation-dissipation theorem to obtain the frequency-dependent dielectric constant of the same two-site model, which may be considered to be an idealized representation of a carrier trapped at a color center. These properties are found to be very simple, and to correspond to those of certain classical systems which, in the absence of any applied field, approach thermal equilibrium via damped oscillations. Thus, in the notation of Eqs. (1.1) and (1.2), the model behaves as a Debye dielectric of $T > T_c$, i.e., if the particle moves primarily by the jump mechanism. On the other hand, if $T < T_c$, the system absorbs energy very strongly from fields of frequency close to the tunneling frequency Ω .

In Sec. V, we derive the frequency-dependent electrical properties for an assembly of particles in a periodic lattice, again using the fluctuation-dissipation theorem. We confine our calculations to cases where the carriers move primarily by thermally activated processes so that tunneling may be ignored. It is shown by a wave-mechanical treatment that, to a very good approximation, the relation between the static conductivity and the jump frequencies, $\frac{1}{2}\gamma$, is the same as that for an assembly of particles which hop from site to site in a

¹⁰ I. R. Senitzky, Phys. Rev. **119**, 670 (1960), cf. discussion on dissipation in Sec. I.

¹¹ J. Schwinger, J. Math. Phys. **2**, 407 (1961).

¹² The equivalence of the sites prevents our theory from being directly relevant to impurity conduction (reference 9), where the carriers are confined to randomly arranged impurity sites.

Markovian manner. This Markovian property of the jumps was assumed *ad hoc* in previous theories.³⁻⁵ We also show that the frequency dependence of the ac conductivity is negligible unless the period of the applied field is comparable with a certain parameter τ that corresponds to a jump transit time. In relating the gross properties of the model to those of model *A*, we find that τ is of the order of magnitude of some mean period of the lattice vibrations in a solid. Consequently, we see that the electrical conductivity is not significantly dependent on frequency ω unless ω is very large, i.e., comparable with the phonon frequencies in a solid.

In Sec. VI, we derive the thermoelectric power and thermal conductivity for the model of Sec. V. The calculations of these coefficients are greatly simplified by the circumstance that the carriers may be treated as monoenergetic, to a high degree of approximation, since the interactions leading to level broadening are very weak. Because of this, the ratio of the heat current \mathbf{Q} to the electric current \mathbf{J} is a constant, independent of the driving forces. Thus, it is a simple matter to relate the thermoelectric properties of the model to this constant ratio, as may be seen by considering the Peltier effect. It may also be seen that, in the monoenergetic approximation, the thermal conductivity of the model is zero, since the particles cannot transport heat without carrying an electric current, i.e., because $\mathbf{Q}=0$ when $\mathbf{J}=0$.

In the concluding section we provide arguments that the main results of our theory should be applicable to small polarons in real solids.

In the Appendix, we reformulate the previous theories^{1-5,9} (model *A*) in terms of observables of the polarons rather than the electrons.

II. THE MODEL *B*

As explained in Sec. I, we define the model *B* as one that consists of a single particle, which is confined to a set of equivalent localized states, and which moves as a result of two interactions. The first interaction H_1 is static and leads to tunneling. The second interaction H_2 couples the particle to a thermal reservoir Γ and leads to jumps. Thus, the Hamiltonian for the model is

$$H = H_0 + H_1 + H_2 + H_\Gamma, \quad (2.1)$$

where H_0 is the basic Hamiltonian for the particle, whose eigenstates are localized ones, ϕ_α , centered at sites A_α with position vectors a_α ; and H_Γ is the Hamiltonian for the reservoir. This reservoir need not be considered to be formed by phonons in the case of the idealized model *B*—as was pointed out in Sec. I. The form of H is chosen so as to possess certain gross features of the model *A*, given by [(A8)–(A15)] in the Appendix. Thus, the particle of model *B* corresponds to a polaron, not an electron.

We stipulate that the thermal conditions are appropriate for a classical treatment of Γ . Further, we neglect the influence of the weak interaction H_2 on the prop-

erties of Γ . (Actually, it is argued in the concluding section that the form of our resultant transport theory does not depend on these simplifications.) Thus, we treat Γ as the source of a classical fluctuating field, Φ , that acts on the particle. The statistical properties of Φ then depend on Γ . However, as we are concerned with the dynamical properties of the particle, not Γ as such, we define our model in terms of postulated statistical properties of Φ rather than Γ . This enables us to eliminate the Γ variables from our theory, since the relevant properties of the reservoir are buried in those of Φ . Our definitions of the properties of Φ are based partly on specific properties of model *A*, partly on general properties of thermally generated fields.

The interaction between particle and Φ may now be represented by a given time-dependent contribution, H_2' , to the Hamiltonian for the particle. The form of H_2' may easily be obtained from H_2 and H_Γ , using the methods adopted in the Appendix for the classical treatment of the reservoir in model *A* [see derivation of (A23)]. Thus, the properties of the particle may be obtained from the Hamiltonian

$$H' = H_0 + H_1 + H_2', \quad (2.2)$$

which involves the particle coordinates and time only.

Since, in our model, the particle is confined to the localized states ϕ_α , discussed above, it follows that the Hamiltonian H' may be completely specified in terms of matrix elements between those states. Now the part H_0 has been defined to be diagonal with respect to the ϕ_α 's. Also the eigenvalues of H_0 must all be equal, since the sites A_α are mutually equivalent. These eigenvalues may therefore be arranged to be zero, simply by measuring energies from a suitable standard value. In this case the diagonal, as well as off-diagonal, matrix elements of H_0 will be zero, so that

$$H_0 = 0. \quad (2.3)$$

We define the matrix elements of H_1 , H_2' , as having the same general form as the corresponding ones for model *A*, given by (A23c, d). Thus, we define

$$\langle \phi_\alpha^* | H_1 | \phi_\beta \rangle = \frac{1}{2} \hbar \Omega_{\alpha\beta}, \quad \alpha \neq \beta, \quad (2.4a)$$

$$= 0, \quad \alpha = \beta, \quad (2.4b)$$

and

$$\langle \phi_\alpha^* | H_2' | \phi_\beta \rangle = \frac{1}{2} \hbar F_{\alpha\beta}(t), \quad \alpha \neq \beta, \quad (2.5a)$$

$$= 0, \quad \alpha = \beta, \quad (2.5b)$$

where the Ω 's are constants and the F 's are fluctuating functions of the time t . We assign the same value to Ω in (2.4) as that obtained for model *A* in earlier theories (i.e., $\frac{1}{2} \hbar \Omega$ is the quantity denoted by W , calculated in reference 2). The functions $F(t)$ are defined to be real fluctuating functions of time, whose statistical properties are defined below. The functions F will *not* be equated to the corresponding ones, \mathcal{F} , of model *A*. It may, in fact, be seen from Eqs. (A11), (A12), (A15),

(A18), and (A21) that \mathfrak{F} is not real. The main thing, however, is that the parameters characterizing the phenomenological properties of H_2 are defined so as to equal the corresponding ones for \mathcal{H}_2 . This suffices to ensure that the gross properties of the dissipative forces are the same for the models A and B .

Since the statistical properties of the F 's depend ultimately on Γ , we denote the mean value of any quantity G , formed from the F 's, by $\langle G \rangle_\Gamma$. Thus, corresponding to the fact the mean value of \mathfrak{F} for model A is zero [Eq. (A22)] we postulate that

$$\langle F_{\alpha\beta}(t) \rangle_\Gamma = 0. \quad (2.6a)$$

Also, we define the autocorrelation function, governing the statistical properties of $F_{\alpha\beta}$, by the equations

$$\langle F_{\alpha\beta}(t_1)F_{\alpha\beta}(t_2) \rangle_\Gamma = f_{\alpha\beta}(t_1-t_2) = f_{\alpha\beta}(t_2-t_1). \quad (2.6b)$$

It may be seen that f must depend on t_1 and t_2 only through their difference simply because the thermal conditions for Γ are stationary in the situations under consideration. It is convenient to introduce two time integrals of f , namely,

$$g_{\alpha\beta}(t) = \int_0^t f_{\alpha\beta}(t') dt', \quad (2.7a)$$

and

$$h_{\alpha\beta}(t) = \int_0^t g_{\alpha\beta}(t') dt' = \frac{1}{2} \int_0^t \int_0^t f_{\alpha\beta}(t'-t'') dt' dt''. \quad (2.7b)$$

The equivalence of the two forms for h , given in the last equation, follows from the fact that

$$f(t'-t'') = f(t''-t').$$

We define $f_{\alpha\beta}$ so that it represents general gross features of the statistical properties of a fluctuating field due to any thermal source. Thus, we postulate that $f_{\alpha\beta}(t)$ is a decreasing function of $|t|$, which contains a temporal parameter $\tau_{\alpha\beta}$. This parameter represents a decay time for $f_{\alpha\beta}$, i.e., a "memory time" for the fluctuating quantity $F_{\alpha\beta}(t)$. Hence,

$$f_{\alpha\beta}(t) \text{ and } \int_t^\infty f_{\alpha\beta}(t') dt' \sim 0 \text{ for } t \gg \tau_{\alpha\beta}.$$

It follows from (2.7) that we may write, for $t \gg \tau_{\alpha\beta}$,

$$g_{\alpha\beta}(t) = g_{\alpha\beta}(\infty) = \gamma_{\alpha\beta}, \quad (2.8a)$$

$$h_{\alpha\beta}(t) = \gamma_{\alpha\beta} t. \quad (2.8b)$$

In order to relate the model to previous theories, we define τ as some mean period of a lattice vibration, since that would be the "memory time" for a fluctuating field generated by lattice vibrations. [This may easily be verified for model A on deriving the statistical properties of $\mathfrak{F}_{\alpha\beta}(t)$ from Eqs. (A10), (A15), (A18), and (A21)]. More precise specification of τ beyond its order of magnitude is not necessary for the purposes of the present theory.

The parameter $\gamma_{\alpha\beta}$ is a very significant one which will be shown in Sec. III to correspond to twice the transition rate for jumps from A_α to A_β . Therefore, in relating the model to previous theories, we simply equate γ to twice the polaron jump frequency, as calculated in those theories on the basis of model A .

Thus, we see that the properties of the model are defined in terms of parameters γ , Ω , τ , to which we assign values that equal the corresponding quantities for model A , and which have been calculated in the earlier theories.¹⁻⁵ This enables us to specify the properties of these parameters. First we note that, in model A , γ and Ω are much less than either the phonon frequencies of kT/\hbar , where k is the Boltzmann constant. Thus, the parameters of the model B satisfy the inequalities

$$\gamma, \Omega \ll \tau^{-1}, kT/\hbar. \quad (2.9)$$

Further, in model A , γ and Ω are temperature dependent, possessing positive and negative temperature coefficients, respectively. It has been shown⁵ that, for A , $\gamma >$ or $< \Omega$ according to whether $T >$ or $< T_c$, a certain critical temperature, and that the range where $\gamma/\Omega \approx 1$ is very small. Thus

$$\gamma \gg \Omega \text{ for } T > T_c, \quad (2.10a)$$

$$\gamma \ll \Omega \text{ for } T < T_c, \quad (2.10b)$$

except in a very narrow transition region around T_c . We likewise incorporate these relations into our definition of model B .

In order to specify completely the statistical properties of $F_{\alpha\beta}$, we require the average values of products $F_{\alpha\beta}(t_1) \cdots F_{\alpha\beta}(t_n)$ for all n . We choose our definitions so that they represent general phenomenological properties of fluctuating fields due to thermal sources. Thus, we define the statistical properties of $F_{\alpha\beta}$ to be equivalent to those commonly ascribed¹³ to the thermally generated fluctuating field acting on a Brownian particle; i.e., we postulate the relations¹⁴

$$\langle F_{\alpha\beta}(t_1) \cdots F_{\alpha\beta}(t_{2n+1}) \rangle_\Gamma = 0, \quad (2.11a)$$

$$\begin{aligned} \langle F_{\alpha\beta}(t_1) \cdots F_{\alpha\beta}(t_{2n}) \rangle_\Gamma \\ = \sum \prod_{\text{pairs}} \langle F_{\alpha\beta}(t_i) F_{\alpha\beta}(t_j) \rangle_\Gamma. \end{aligned} \quad (2.11b)$$

An important quantity, whose value we subsequently

¹³ M. C. Wang and C. E. Uhlenbeck, Rev. Mod. Phys. **17**, 323 (1945).

¹⁴ It should be noted that the relations (2.11) would not be applicable to any reservoir, for all times t_1, \dots, t_n . However, they would be valid for any reservoir whenever no three of these lie within an interval of the order of the "memory time" τ , since then one could neglect triple-time correlations. This restricted validity of (2.11) would suffice for our purposes, since we shall be concerned only with time intervals $\gg \tau$, so that triple-time correlations would be unimportant, whatever the reservoir. It may, in fact, be confirmed that this restricted validity of (2.11) would yield our Eq. (2.12). This can be demonstrated by means of methods employed in notes at the end of the paper by G. E. Uhlenbeck and L. S. Ornstein, Phys. Rev. **36**, 823 (1930).

require, is

$$\left\langle \exp \left[i \int_0^t F_{\alpha\beta}(t') dt' \right] \right\rangle_{\Gamma}.$$

On expanding the exponential in an infinite series, averaging the resultant terms according to (2.6) and (2.11), and using (2.7b), we obtain the equation

$$\left\langle \exp \left[i \int_0^t F_{\alpha\beta}(t') dt' \right] \right\rangle_{\Gamma} = e^{-h_{\alpha\beta}(t)}. \quad (2.12)$$

This completes our formulation of the model in the absence of any applied field. The application of an electric field, $\mathbf{E}(t)$, leads to an extra term

$$H_{\text{app}} = -\mathbf{m} \cdot \mathbf{E}(t) \quad (2.13)$$

in the Hamiltonian, where \mathbf{m} is the dipole moment due to the particle. For an elementary point particle, \mathbf{m} is the product of electric charge and position vector. In the case of the present model, we define \mathbf{m} so that it corresponds to the value for a polaron, given by model *A* [Eq. (A24)]. Thus

$$\langle \phi_{\alpha}^* | \mathbf{m} | \phi_{\beta} \rangle = -e_0 \mathbf{a}_{\alpha} \delta_{\alpha\beta}. \quad (2.14)$$

III. THE BASIC PROCESS

We now investigate how the agencies of tunneling and thermally activated processes combine to transfer the particle from site to site. For this purpose, we derive the properties of the model, formulated in the previous section, for the case when there are only two sites A_1 and A_2 . Defining the corresponding localized states ϕ_1 and ϕ_2 as in Sec. II, we see that the basic problem to be solved is: What is the probability, $P(t)$, that a particle, known to be in the state ϕ_1 at $t=0$, is to be found in the state ϕ_2 at time t ?

It is convenient to describe the two-site model in terms of a matrix representation. Thus, we represent the state vectors ϕ_{α} by

$$\phi_1 = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{and} \quad \phi_2 = \begin{pmatrix} 0 \\ 1 \end{pmatrix}, \quad (3.1)$$

and the observables ξ by 2 by 2 matrices

$$\xi = \begin{pmatrix} \xi_{11} & \xi_{12} \\ \xi_{21} & \xi_{22} \end{pmatrix} \quad (3.2)$$

It is useful to introduce the Pauli matrices and the unit matrix

$$\begin{aligned} \sigma_1 &= \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, & \sigma_2 &= \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \\ \sigma_3 &= \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, & 1 &= \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \end{aligned} \quad (3.3)$$

since any 2 by 2 matrix may be expressed as a linear combination of the above matrices.

It may easily be seen from Eqs. (2.2)–(2.5) that, in the above representation, the Hamiltonian for the system is given by

$$H' = \frac{1}{2} [\Omega + F(t)] \sigma_1, \quad (3.4)$$

where the suffixes on Ω and F have been dropped. The dynamical properties of the model may be expressed in terms of the evolution operator, $U(t)$, which satisfies the Schrödinger equation

$$i\hbar [dU(t)/dt] = H' U(t), \quad (3.5a)$$

with

$$U = 1 \quad \text{at} \quad t = 0. \quad (3.5b)$$

It follows from Eqs. (3.4) and (3.5) that

$$U(t) = \exp \left[\frac{1}{2} i \theta \sigma_1 \right] = 1 \cos(\theta/2) + i \sigma_1 \sin(\theta/2), \quad (3.6a)$$

where

$$\theta = \Omega t + \int_0^t F(t') dt' \quad (3.6b)$$

We now treat the problem of the transfer of the particle from site to site. Given that the particle is initially in the state ϕ_1 , its wave function at time t is

$$\phi_1(t) = U(t) \phi_1.$$

Hence, by (3.1), (3.3), and (3.6a)

$$\phi_1(t) = \phi_1 \cos(\theta/2) + i \phi_2 \sin(\theta/2).$$

The probability that the particle is to be found in the state ϕ_2 at time t is, therefore,

$$P(t) = \langle \sin^2 \theta/2 \rangle_{\Gamma}.$$

Consequently, by (3.6b),

$$P(t) = \frac{1}{2} \text{Re} \left\langle 1 - \exp \left\{ i \left[\Omega t + \int_0^t F(t') dt' \right] \right\} \right\rangle_{\Gamma},$$

and, therefore, by (2.12)

$$P(t) = \frac{1}{2} [1 - e^{-h(t)} \cos \Omega t]. \quad (3.7)$$

This equation enables us to analyze the roles played by thermal activation and tunneling, since the exponential and cosine terms are due, respectively, to the former and latter processes. First we note that, by (2.7)–(2.9), unless $t \gg \tau$,

$$\Omega t \ll 1$$

and

$$h(t) < \gamma t \ll 1.$$

Consequently, it follows from (3.7) that P differs significantly from zero only for times $t \gg \tau$. For such times it follows from (2.9) and (3.7) that

$$P(t) = \frac{1}{2} [1 - e^{-\gamma t} \cos \Omega t] \quad \text{for} \quad t \gg \tau, \quad (3.8)$$

so that $P(t)$ approaches its equilibrium value $\frac{1}{2}$ by damped oscillations.

This result may be explained very simply. For the static interaction H_1 alone, in the absence of H_2 , would lead to a splitting of the levels of the two-site model. The energy levels of the model would differ by $\hbar\Omega$, so that the motion of the system would correspond to oscillations of frequency Ω . The "switching-on" of the interaction H_2 between particle and reservoir would then lead to dissipative processes which damp out the oscillations. The significance of the term $h(t)$, rather than γt , in the exponential term in (3.7) when $t \lesssim \tau$, is that the interactions governing the dissipative processes have a duration $\approx \tau$; and that consequently the processes are not Markovian¹⁵ until a time $\gtrsim \tau$ has elapsed.

Let us now analyze the formulas (3.7), (3.8) further. It follows immediately from (3.8) that the thermally activated processes predominate over tunneling in transferring the particle from site to site if $\gamma \gg \Omega$, i.e., by (2.10), if $T > T_c$. In this case the formula (3.8) may be written

$$P(t) = \frac{1}{2}(1 - e^{-\gamma t}),$$

which is formally identical with that for a classical particle confined to a pair of potential wells that are separated by a barrier.¹⁵

It is of interest to interpret the significance of the parameters τ and γ with regard to the jump mechanism. For this purpose we note that, in cases where tunneling may be neglected ($\Omega \rightarrow 0$), Eq. (3.7) reduces to

$$P(t) = \frac{1}{2}(1 - e^{-h(t)}).$$

It follows from this equation and (2.7b) that, if $P_\alpha(t)$ ($\alpha = 1, 2$) denotes the probability that the particle is in the state ϕ_α at time t , i.e., if

$$P_1(t), P_2(t) = 1 - P(t), P(t),$$

then

$$dP_2/dt = -dP_1/dt = -\frac{1}{2}g(t)[P_2(t) - P_1(t)].$$

This signifies that $\frac{1}{2}g(t)$ may be regarded as the transition rate at which the particle is transferred from site to site. Now, by (2.7a) and (2.8a), $g(t)$ increases from zero at $t=0$ to a steady value $\frac{1}{2}\gamma$ in time $t \approx \tau$. Consequently, we may regard τ as the jump transit time and $\frac{1}{2}\gamma$ as the steady-jump transition frequency attained after time τ .

IV. DIELECTRIC PROPERTIES

In this section, we derive the dielectric properties of the two-site model. For this purpose, we obtain the response of the model to classical applied electric field, $E(t)$, directed from A_2 to A_1 . We take this line to be the x axis, with 0 as the midpoint of A_2A_1 . Thus, the x coordinates of A_1 and A_2 are a and $-a$, respectively, where $2a$ is the distance between the sites.

¹⁵ Cf. L. Van Hove, *Physica* **23**, 441 (1957); and R. Zwanzig, *Phys. Rev.* **124**, 983 (1961), for general treatments of non-Markovian effects in irreversible processes.

By Eq. (2.13) the application of the field $E(t)$ along Ox leads to an extra term

$$H_{\text{app}} = -mE(t), \quad (4.1)$$

in the Hamiltonian, m being the dipole operator. Since the coordinates of A_1, A_2 are $\pm \frac{1}{2}a$, it follows from (2.14) and (3.3) that, in the representation of Sec. III,

$$m = -ae_0\sigma_3. \quad (4.2)$$

The mean dipole strength at time t , due to the application of the field, may be written

$$\bar{m}(t) = \int_{-\infty}^t K(t-t')E(t')dt', \quad (4.3)$$

where the response function K is determined by the dynamical properties of the model. Thus, the mean dipole moment induced by a simply periodic field

$$E(t) = E(\omega)e^{i\omega t}, \quad (4.4)$$

is given by

$$\bar{m}(t) = K(\omega)E(\omega)e^{i\omega t}, \quad (4.5)$$

where

$$K(\omega) = \int_0^\infty K(t)e^{-i\omega t}dt. \quad (4.6)$$

The function $K(t)$ may be related to the spontaneous thermal fluctuations of the dipole moment by means of the fluctuation-dissipation theorem. Thus¹⁶

$$K(t) = -(1/2kT)\langle\{\dot{m}(t), m\}_+\rangle_{\text{av}}, \quad (4.7)$$

where $m(t)$ is the Heisenberg operator corresponding to m , $\{\ \ \}_+$ denotes anticommutator, and $\langle \ \ \rangle_{\text{av}}$ denotes equilibrium thermal average for the closed system comprising particle and Γ , in the absence of any applied field. The Hamiltonian H for this closed system is given by (2.1). Since the weak interactions H_1 and H_2 lead to particle level broadenings $\hbar\Omega$, $\hbar\gamma$ which are much less than kT [by (2.9)], it follows from (2.1) that we may replace the averaging operation $\langle \ \ \rangle_{\text{av}}$ by the product of averages over the particle system H_0 and the reservoir Γ . Thus, if ρ_0 is the equilibrium density matrix for H_0 , then

$$\langle \dots \rangle_{\text{av}} = \langle \text{Tr}(\rho_0 \dots) \rangle_\Gamma.$$

Hence, by (4.7)

$$K(t) = -(1/2kT)(d/dt)\langle \text{Tr}[\rho_0\{m(t), m\}_+] \rangle_\Gamma. \quad (4.8)$$

¹⁶ R. Kubo, *J. Phys. Soc. Japan*, **12**, 570 (1957). Actually, the exact form of the response of a quantum-mechanical system is not, in general, given by the above equation (4.7). Instead, the right-hand side, $C(t)$, say, of (4.7) is generally replaced by $\int_{-\infty}^\infty C(t')\chi(t-t')dt'$, where $\chi(t) = (4\pi kT/\hbar) \log \coth(\pi kT|t|/\hbar)$. However, if the conditions are such that $\hbar T/\hbar$ is much greater than any other frequency concerned, then we may replace $\chi(t)$ by $\delta(t)$. These conditions are certainly fulfilled in the present case. For, since Γ and the applied field may be treated classically for the given model, $\hbar T/\hbar$ must be much greater than either ω or the natural frequencies of Γ (e.g., τ^{-1}). In addition, it is much greater than γ, Ω , by (2.9).

In order to evaluate $K(t)$, it remains for us to derive the properties of ρ_0 and $m(t)$. The particle density matrix ρ_0 is simply equal to $Z \exp(-H_0/kT)$, where Z is a normalization constant. Therefore, by (2.3), (3.3)

$$\rho_0 = \frac{1}{2} \mathbf{1}. \quad (4.9)$$

The Heisenberg operator $m(t)$ may be expressed, in a usual way, in terms of the Schrödinger operator m and the evolution operator $U(t)$, defined by (3.5). Thus,

$$m(t) = U^*(t) m U(t),$$

which reduces, by (3.3), (3.6a), and (4.2), to

$$m(t) = -ae_0(\sigma_3 \cos\theta - \sigma_2 \sin\theta).$$

Therefore, by (3.3), (4.2), and (4.9)

$$\rho_0 \{m(t), m\}_+ = e_0^2 a^2 \cos\theta \mathbf{1}.$$

On substituting this formula into (4.8), we obtain

$$K(t) = -(e_0^2 a^2 / kT) (d/dt) \operatorname{Re} \langle e^{i\theta} \rangle_{\Gamma}.$$

Hence, by (3.6b) and (2.12),

$$K(t) = -(e_0^2 a^2 / kT) (d/dt) [e^{-h(t)} \cos\Omega t]. \quad (4.10)$$

We shall, henceforth, restrict the theory to cases where the frequency of the applied field is much less than τ^{-1} , i.e.,

$$\omega \ll \tau^{-1}. \quad (4.11)$$

This signifies that we are concerned only with applied fields whose frequencies are much less than typical phonon frequencies in solids. It may be seen from (2.9) that the condition (4.11) does not prevent ω from exceeding the frequencies, γ, Ω . Now, by (2.8b), (4.6), and (4.11), we may replace $h(t)$ by γt in (4.11), i.e.,

$$K(t) = -(e_0^2 a^2 / kT) (d/dt) [e^{-\gamma t} \cos\Omega t]. \quad (4.12)$$

This result is formally identical with that obtained by Fröhlich¹⁷ for the dielectric properties of certain classical systems which approached equilibrium, in the absence of an applied field, by damped oscillations. Therefore, in interpreting our formula for $K(t)$, we may make direct use of Fröhlich's analysis of the properties of dielectrics with response functions of the above form.

Thus, if $\gamma \gg \Omega$, i.e., if thermally activated processes predominate over tunneling, the system behaves as a Debye dielectric and leads to appreciable dielectric losses whenever the frequency of the applied field becomes comparable with the jump frequency γ . On the other hand, if $\Omega \gg \gamma$, i.e., if tunneling processes predominate, then the system absorbs energy very strongly from fields whose frequencies are close to the tunneling frequency Ω (resonance absorption!). Thus, it follows from (2.10) that one obtains Debye losses or resonance absorption according to whether $T >$ or $< T_c$.

It is a trivial matter to obtain the frequency-depend-

ent dielectric properties of the model from (4.6) and (4.12).

V. CONDUCTION IN PERIODIC LATTICE

In this section we obtain the response of the particle to an external field when it moves through a periodic lattice. This enables us to derive the electrical properties of an assembly of n such carriers in the lattice, provided that $n \ll N$. For in this case, the particles may be treated as moving independently of one another. Thus, the current density \mathbf{J} , due to the applied fields, is related to the mean drift current \mathbf{j} of a single particle by the equation

$$\mathbf{J} = n_0 \mathbf{j},$$

where n_0 is the number density of particles. We may relate \mathbf{j} , and thence \mathbf{J} , to the applied field by means of the fluctuation-dissipation theorem. Thus, denoting rectangular coordinate components, by μ, ν , and proceeding as in Sec. IV, we see that the response of the system to an applied field

$$\mathbf{E}(t) = \mathbf{E}(\omega) e^{i\omega t} \quad (5.1)$$

is given by

$$J_{\mu}(t) = \sigma_{\mu\nu}(\omega) E_{\nu}(\omega) e^{i\omega t} \quad (5.2)$$

where

$$\sigma_{\mu\nu}(\omega) = \int_0^{\infty} \sigma_{\mu\nu}(t) e^{-i\omega t} dt, \quad (5.3)$$

and

$$\sigma_{\mu\nu}(t) = (n_0 / 2kT) \langle \operatorname{Tr} [\rho_0 \{ \dot{m}_{\mu}(t), \dot{m}_{\nu}(0) \}_+] \rangle_{\Gamma}. \quad (5.4)$$

The equilibrium density matrix for H_0 is easily seen to be given by [c.f., (4.9)]

$$\langle \phi_{\alpha}^* | \rho_0 | \phi_{\beta} \rangle = (1/N) \delta_{\alpha\beta}.$$

Hence, by (5.4),

$$\sigma_{\mu\nu}(t) = (n_0 / NkT) \operatorname{Re} \sum_{\alpha} \langle \langle \phi_{\alpha}^* | \dot{m}_{\mu}(t) \dot{m}_{\nu}(0) | \phi_{\alpha} \rangle \rangle_{\Gamma}.$$

Since all sites are equivalent, the terms in the above contribute equally to σ . Therefore, we may write

$$\sigma_{\mu\nu}(t) = (n_0 / kT) \operatorname{Re} \langle \langle \phi_0^* | \dot{m}_{\mu}(t) \dot{m}_{\nu}(0) | \phi_0 \rangle \rangle_{\Gamma},$$

where ϕ_0 is the state centered at A_0 , say, which is chosen to be the origin of spatial coordinates. This formula may be conveniently expanded in the form

$$\sigma_{\mu\nu}(t) = (n_0 / kT) \operatorname{Re} \sum_{\alpha} \langle \langle \phi_0^* | \dot{m}_{\mu}(t) | \phi_{\alpha} \rangle \rangle_{\Gamma} \times \langle \langle \phi_{\alpha}^* | \dot{m}_{\nu}(0) | \phi_0 \rangle \rangle_{\Gamma}. \quad (5.5)$$

Equations (5.3) and (5.5) express the frequency-dependent conductivity $\sigma_{\mu\nu}(\omega)$ in terms of the "natural" motion of the system in the absence of the applied field.

We now determine the electrical properties for cases where the thermally activated processes predominate over tunneling, i.e., where $T > T_c$. Thus, in deriving the dynamical properties of the system we ignore H_1 , i.e., by (2.2) and (2.3) we put H' equal to H_2' . The evolution

¹⁷ H. Fröhlich, *Theory of Dielectrics* (Oxford University Press, New York, 1949), p. 98.

operator U is then given by

$$i\hbar(d/dt)U(t) = H_2'U(t), \quad (5.6a)$$

with

$$U(t) = 1 \quad \text{at } t=0. \quad (5.6b)$$

Now we may express the Heisenberg operator $d\mathbf{m}(t)/dt$ in terms of $U(t)$ and the Schrödinger operator \mathbf{m} by the equation

$$\mathbf{m}(t) = U^*(t)\mathbf{m}U(t).$$

Hence, by (5.6a),

$$i\hbar d\mathbf{m}(t)/dt = U^*(t)[\mathbf{m}, H_2']_- U(t), \quad (5.7)$$

where $[\]_-$ denotes a commutator. The operator U may be expressed as a power series in H_2' , i.e., by Eqs. (2.5) and (5.6)

$$\langle \phi_\alpha^* | U(t) | \phi_\beta \rangle = \delta_{\alpha\beta} - \frac{1}{2}i \int_0^t F_{\alpha\beta}(t') dt' + \text{higher order terms.} \quad (5.8)$$

In the calculations that follow, we include only the lowest order contributions to σ . This approximation, which is discussed further at the end of this section, is justified in view of the weakness of the interaction H_2' . Thus, we calculate U and $\mathbf{m}(t)$ to zero and first order, respectively, in H_2' ; i.e., we shall approximate (5.8), (5.7) by

$$U(t) = 1,$$

and

$$i\hbar d\mathbf{m}(t)/dt = [\mathbf{m}, H_2']_-.$$

Hence

$$i\hbar \langle \phi_\alpha^* | d\mathbf{m}(t)/dt | \phi_0 \rangle = \sum_\beta [\langle \phi_\alpha^* | \mathbf{m} | \phi_\beta \rangle \langle \phi_\beta^* | H_2' | \phi_0 \rangle - \langle \phi_\alpha^* | H_2' | \phi_\beta \rangle \langle \phi_\beta^* | \mathbf{m} | \phi_0 \rangle].$$

It follows from this equation, (2.5), (2.11), and the definition of A_0 as origin of spatial coordinates that

$$\langle \phi_\alpha^* | d\mathbf{m}(t)/dt | \phi_0 \rangle = -\frac{1}{2}ie_0 \mathbf{a}_\alpha F_{\alpha 0}(t). \quad (5.9a)$$

Hence, also

$$\langle \phi_0^* | d\mathbf{m}(t)/dt | \phi_\alpha \rangle = -\frac{1}{2}ie_0 \mathbf{a}_\alpha F_{\alpha 0}(t), \quad (5.9b)$$

since F is defined to be real. On substituting appropriate components of (5.9a, b) into (5.5), we obtain the equation

$$\sigma_{\mu\nu}(t) = (n_0 e_0^2 / 4kT) \sum_\alpha a_{\alpha\mu} a_{\alpha\nu} \langle F_{\alpha 0}(t) F_{\alpha 0}(t) \rangle_t,$$

where $a_{\alpha\mu}$, $a_{\alpha\nu}$ are μ , ν components of \mathbf{a}_α . Hence, by (2.6b) and (5.3), the frequency-dependent conductivity is given by

$$\sigma_{\mu\nu}(\omega) = \frac{n_0 e_0^2}{4kT} \sum_\alpha a_{\alpha\mu} a_{\alpha\nu} \int_0^\infty f_{\alpha 0}(t) e^{-i\omega t} dt. \quad (5.10)$$

This formula may be greatly simplified for all cases where the period of the applied field is much greater than the decay time τ of the function f , i.e., where the

inequality (4.11) is satisfied. In such cases we may put

$$\int_0^\infty f_{\alpha 0}(t) e^{-i\omega t} dt = \int_0^\infty f_{\alpha 0}(t) dt = \gamma_{\alpha 0},$$

by Eqs. (2.7a) and (2.8a). Consequently, Eq. (5.10) reduces to

$$\sigma_{\mu\nu}(\omega) = (n_0 e_0^2 / kT) D_{\mu\nu}, \quad (5.11a)$$

where

$$D_{\mu\nu} = \frac{1}{4} \sum_\alpha \gamma_{\alpha 0} a_{\alpha\mu} a_{\alpha\nu}. \quad (5.11b)$$

It is seen from these equations that the dependence of σ on ω is negligible for frequencies $\ll \tau^{-1}$. The significance of this may be seen from the fact that, as shown in Sec. III, τ is a jump transit time. Consequently, Eqs. (5.11) imply that σ is negligibly dependent on ω whenever the period of the applied field is much greater than the jump transit times—an obvious result, since, under these circumstances the particle responds to the external field as though the latter were static.

It is of interest to analyze why the onset of frequency dependence of electrical properties occurs at $\omega \approx \gamma$ for the two-site model and at $\omega \approx \tau^{-1}$ for the periodic lattice. In the former case, the application of the electric field leads to oscillations in the occupation probabilities for the two sites—this is how the polarization is generated. Therefore, the electrical properties become appreciably frequency dependent whenever ω becomes comparable with the natural frequency with which the site occupation probabilities become equalized, i.e., when $\omega \approx \gamma$. On the other hand, in the case of a periodic lattice, the application of an electric field to an equilibrium distribution of carriers leads to an electric current but not to a density gradient. Thus, it does not lead to oscillations in the site occupation probabilities; and, therefore, the natural rate at which these probabilities become equalized is not relevant to the onset of frequency dependence. Consequently, the electrical properties become appreciably dependent on frequency only when the period of the applied field becomes comparable with the jump transit time, i.e., when $\omega \approx \tau^{-1}$.

The properties of σ , given by (5.11), may be interpreted very simply. For, as shown in the discussion at the end of Sec. III, $\frac{1}{2}\gamma_{\alpha 0}$ is the jump frequency for transitions from A_0 to A_α when there are no other sites present. Thus, in the case of the many-site model, $\frac{1}{2}\gamma_{\alpha 0}$ is the value of that frequency given by the approximation where processes involving intermediate states on other sites are neglected. Thus, it follows from (5.11b) that, in this approximation, $D_{\mu\nu}$ is the diffusion tensor for a particle performing a random walk through the lattice. Equation (5.11a) is then simply the Einstein formula that relates conductivity to diffusion.

Summing up, the approximations we have used in order to calculate σ lead to the result that would be obtained from a treatment where it is assumed *ad hoc* that (1) the particle jumps from site to site in a Markovian manner, and (2) the jump transition rate be-

tween any pair of sites is unaltered by processes involving other sites. These assumptions were made in the previous treatments.³⁻⁵ It is clear that, in higher orders, there would be corrections to our results due to indirect processes in which a particle moves from site to site via an intermediate state on a third site. Such processes have already been taken into account by Friedman¹⁸ using a model of the type treated in the earlier theories, in order to investigate the Hall effect for thermally activated polarons.

VI. THERMOELECTRIC POWER AND THERMAL CONDUCTIVITY

In the present section, we evaluate the thermoelectric power and thermal conductivity for the model treated in Sec. V. Our derivation does not depend on whether the particles move primarily by tunneling or jumping.

We denote the chemical potential for the particles, in interaction with Γ , by ζ . Thus, it follows from (2.1) and (2.3) that the energy of a particle, as measured from this potential, is given by

$$\epsilon = -\zeta \quad (6.1)$$

in an approximation where H_1, H_2 are ignored. When these interactions are taken into account, they lead to contributions Δ_1, Δ_2 to the particle level width. Thus

$$\Delta_1 \approx h\Omega, \quad (6.2a)$$

$$\Delta_2 \approx h\gamma, \quad (6.2b)$$

since Ω, γ are tunneling and jump frequencies. It is important for our purposes to compare the order of magnitude of ϵ with those of Δ_1, Δ_2 . First, we note that the requirement, stated in Sec. V, that the mean number of particles per site $\ll 1$, signifies that

$$\exp(-\epsilon/kT) \ll 1,$$

and therefore $\epsilon \gg kT$. Consequently, by (2.9), $\epsilon \gg h\Omega$ and $h\gamma$, and hence, by (6.2),

$$\epsilon \gg \Delta_1, \Delta_2 \quad (6.3)$$

These inequalities signify that the particles may be treated as monoenergetic, to a high degree of approximation. Thus, we treat the particles as each having energy ϵ relative to the chemical potential. This means that, if \mathbf{Q} and \mathbf{J} denote the thermal and electrical current densities of the particles due to the application of an electric field \mathbf{E} and a temperature gradient ∇T , then

$$\mathbf{Q} = -(\epsilon/e_0)\mathbf{J}. \quad (6.4)$$

This equation enables us to evaluate the thermoelectric power α and the thermal conductivity K for the assembly of particles. For these coefficients are defined¹⁹

by the relations

$$\mathbf{Q} = -\alpha T \mathbf{J} \quad \text{when} \quad \nabla T = 0.$$

$$\mathbf{Q} = -K \nabla T \quad \text{when} \quad \mathbf{J} = 0.$$

It follows immediately from these relations and (6.4) that

$$\alpha = \epsilon/Te_0, \quad (6.5a)$$

$$K = 0. \quad (6.5b)$$

The lack of thermal conductivity, in the monoenergetic approximation, follows from the relation (6.4) where \mathbf{Q} is a constant multiple of \mathbf{J} . This means that the particles can transport heat by convection only.

CONCLUSION

We have constructed a simple model (B) of thermally activated hopping motion, and have derived a formal theory of transport properties of the model. This formal theory expresses the various transport coefficients in terms of phenomenological constants γ, Ω, τ [Eqs. (3.7), (3.8), (4.12), (5.11), (6.5)].

The model is formulated so as to represent the essential properties of small polarons, as obtained from earlier microscopic theories.¹⁻⁵ (model A). Criteria for the applicability of those previous theories to carriers in real solids were given in the papers concerned. We now argue that the formal theory, derived in the present paper, should apply to the same systems as the earlier theories, despite the fact that the microscopic properties of model B differ from those of A . It may be seen from Sec. II that the differences are comprised by the classical treatment of Γ , the reality of $F_{\alpha\beta}$ and the postulated relations (2.11). These latter relations were justified in footnote 14.

It suffices to base our argument on the analysis of Eqs. (3.7) and (3.8), which describe the principal dynamical properties of the carrier for model B . Our main point is that the validity of those equations is independent of the detailed microscopic properties of the interaction H_2 between particle and reservoir; and that the equations would, therefore, apply also to model A .

First we note that, as explained in the discussion following (3.8), the properties of the two-site model depend on the fact that, in the absence of the interaction H_2 , the motion of the system ($H_0 + H_1$) is oscillatory; and that the "switching-on" of the interaction between particle and reservoir leads to damping of the oscillations. Now this damping effect is a general phenomenon that occurs whenever a mechanical system is subjected to dissipative forces, due to interaction with a thermal reservoir. In particular, the natural motion of a harmonic oscillator becomes exponentially damped when brought into interaction with a reservoir—as has

that the flow of carriers, due to the applied field, does not lead to a heat current in Γ (by a "phonon-drag" type of effect). This condition is satisfied, to a very good approximation, in the present model, because of the weakness in the coupling between carriers and Γ .

¹⁸ L. Friedman, thesis, University of Pittsburgh, 1961 (unpublished).

¹⁹ S. de Groot, *Thermodynamics of Irreversible Processes* (Interscience Publishers, Inc., New York, 1951) p. 144. It should be noted that the above definition for α is valid only on condition

been shown by quantum-theoretical treatments.^{10,11} Consequently, since our two-site model (H_0+H_1) simulates an oscillator, it is to be expected that its motion will be similarly damped²⁰ when brought into interaction with a reservoir—irrespective of the microscopic properties of that interaction and irrespective of whether the thermal conditions are appropriate for a classical treatment of the reservoir.²¹ Thus, we consider that Eqs. (3.7) and (3.8) should apply to model *A*, as well as to *B*, since the former model also contains interactions $\mathcal{H}_1, \mathcal{H}_2$, which similarly lead to oscillation and dissipation. One may similarly argue that our other results for the transport properties of the model depend only on certain gross properties, and would thus be valid for *A* as well as *B*.

Finally, we observe that the present theory, like the previous ones, takes no account of excited states of the carrier. We now argue this is not a significant omission.

Firstly, we note that, in a real solid, the frequencies $\tilde{\omega}$, corresponding to transitions of a carrier into excited states (interband transitions) are normally much greater than the phonon frequencies ω_{ph} . Further, the frequencies ω of the applied fields considered in the present theory are all much less than ω_{ph} [c.f., Eq. (4.11)]; and, therefore, $\tilde{\omega} \gg \omega$. Consequently, neither the phonons nor the external field can induce real transitions into excited states.

On the other hand, virtual transitions cannot be ruled out. However, since H_2' is essentially a phenomenological interaction, we could easily consider it as already containing contributions due to virtual transitions into excited states. For we may regard H_2' as an effective interaction governing all transitions between localized ϕ states, including those transitions that proceed via an intermediate excited state.

With regard to virtual transitions due to the applied field, it may easily be shown that, since $\tilde{\omega} \gg \omega$, such processes merely lead to an additional frequency-independent contribution to the real part of the dielectric constant. This would not lead to any significant changes in our main results.

We therefore, conclude that the omission of excited states is justifiable for the purposes of the present theory.

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²⁰ It is possible that, for certain interactions, the motion would become "overdamped" for $T > T_c$, i.e., $\gamma \gg \Omega$, so that the cosine term on the right-hand side of (3.8) would be eliminated. However, it may easily seem that this is of no consequence to our main conclusions, since the replacement of $\cos \Omega t$ by unity in (3.8) would not substantially affect the properties of $P(t)$ when $\gamma \gg \Omega$.

²¹ Of course, the values of γ , Ω , and τ will depend ultimately on the microscopic properties of the reservoir. This does not affect the above argument, however, since we are concerned only with the relationships between the transport coefficients and the phenomenological constants γ , Ω , and τ .

APPENDIX

We re-express the contents of previous polaron theories^{1-5,9} (model *A*) in terms of observables of the "dressed" particle, i.e., the polaron, rather than the electron. It may easily be verified that the theory in this Appendix is exactly equivalent to the previous theories.

The Hamiltonian is given by

$$H = H_{\text{el}} + H_{\text{ph}} + H_{\text{int}}, \quad (\text{A1})$$

the three parts referring to the electron in a static potential due to the lattice structure, the phonons, and the electron-phonon interaction. As in the earlier theories, we consider only states which are based on a set of mutually orthogonal localized electronic states, $\psi_\alpha(\mathbf{x})$, centered at the site A_α , where \mathbf{x} is the electronic position vector. Thus, the electronic system may be described in terms of creation and annihilation operators c_α^* , c_α for those states. The quantized wave operator representing the destruction of an electron at \mathbf{x} is then

$$\psi(\mathbf{x}) = \sum_\alpha c_\alpha \psi_\alpha(\mathbf{x}). \quad (\text{A2})$$

In this notation, the Hamiltonian H_{el} may be written

$$H_{\text{el}} = H_{\text{loc}} + H_{\text{el}'}, \quad (\text{A3a})$$

where

$$H_{\text{loc}} = \sum_\alpha \epsilon_\alpha c_\alpha^* c_\alpha, \quad (\text{A3b})$$

and

$$H_{\text{el}'} = \sum_{\alpha \neq \beta} J_{\alpha\beta} c_\alpha^* c_\beta. \quad (\text{A3c})$$

Hence, ϵ and $J_{\alpha\beta}$ are constants. H_{loc} thus represents the part of H_{el} that is diagonal with respect to the localized electronic states, and $H_{\text{el}'}$ is the static interaction governing the transfer of the electron from site to site by tunnel effect. In cases where the sites are equivalent, the ϵ_α 's are all equal. However, there is no need to make this restriction for the purposes of this Appendix.

The lattice vibrations are described in terms of normal coordinates and momenta Q_λ , P_λ . Thus

$$H_{\text{ph}} = \frac{1}{2} \sum_\lambda (P_\lambda^2 + \omega_\lambda^2 Q_\lambda^2), \quad (\text{A4})$$

the ω_λ 's being constant frequencies.

The interaction H_{int} is assumed to be linear in the Q 's and may be written

$$H_{\text{int}} = H_{\text{int}'} + H_{\text{int}''}, \quad (\text{A5a})$$

where

$$H_{\text{int}'} = \sum_{\alpha, \lambda} K_{\alpha\lambda} c_\alpha^* c_\alpha Q_\lambda, \quad (\text{A5b})$$

and

$$H_{\text{int}''} = \sum_{\alpha \neq \beta, \lambda} L_{\alpha\beta\lambda} c_\alpha^* c_\beta Q_\lambda, \quad (\text{A5c})$$

where the K 's and L 's are constants. It is easily seen that $H_{\text{int}''}$ governs only processes involving the transfer of the electron from one site to another. On the other hand, $H_{\text{int}'}$ governs the properties of the electron while it remains on a site. It is this latter interaction which leads to the formation of localized polaron states.

We shall introduce a contact transformation

$$\mathcal{H} = S^* H S, \quad (\text{A6})$$

which removes the interaction $H_{\text{int}'}$, and thus takes account of the formation of the localized polaron. The operator S is given by

$$S = \exp[-(i/\hbar) \sum_{\alpha} c_{\alpha}^* c_{\alpha} M_{\alpha}(P)], \quad (\text{A7a})$$

where

$$M_{\alpha}(P) = \sum_{\lambda} (K_{\alpha\lambda}/\omega_{\lambda}^2) P_{\lambda}. \quad (\text{A7b})$$

It follows from (A1)–(A7) that the transformed Hamiltonian may be written

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{\text{ph}} + \mathcal{H}_1 + \mathcal{H}_2, \quad (\text{A8})$$

where \mathcal{H}_0 is the Hamiltonian for the “dressed” particle, i.e., the polaron, whose eigenstates are all localized ones; \mathcal{H}_{ph} is the renormalized phonon Hamiltonian; \mathcal{H}_1 is the static interaction governing the tunneling motion of the carrier, and \mathcal{H}_2 is the residual polaron-phonon interaction. Before writing down the expressions for these terms, we point out that we are concerned only with cases where there is just one carrier. Consequently, we ignore all contributions to \mathcal{H} due to terms of the form $f(P, Q) c_{\alpha}^* c_{\beta}^* c_{\gamma} c_{\delta}$, since the last two c 's would yield a zero when operating on any single-carrier state. Thus, we obtain

$$\mathcal{H}_0 = \sum_{\alpha} \epsilon_{\alpha}' c_{\alpha}^* c_{\alpha}, \quad (\text{A9})$$

where

$$\epsilon_{\alpha}' = \epsilon_{\alpha} - \frac{1}{2} \sum_{\lambda} (K_{\alpha\lambda}^2/\omega_{\lambda})$$

is the renormalized energy for the localized polaron state centered at A_{α} , and c_{α}^* , c_{α} are now creation and annihilation operators for the polaron, not the electron. The phonon Hamiltonian is unchanged by the transformation so that

$$\mathcal{H}_{\text{ph}} = \frac{1}{2} \sum_{\lambda} (P_{\lambda}^2 + \omega_{\lambda}^2 Q_{\lambda}^2). \quad (\text{A10})$$

The interactions \mathcal{H}_1 , \mathcal{H}_2 may be expressed in terms of the operators

$$\frac{1}{2} \hbar k_{\alpha\beta}(P, Q) = \exp[iM_{\alpha}(P)/\hbar] (J_{\alpha\beta} + \sum_{\lambda} L_{\alpha\beta\lambda} Q_{\lambda}) \times \exp[-iM_{\beta}(P)/\hbar], \quad (\text{A11})$$

and their thermal averages with respect to \mathcal{H}_{ph}

$$\frac{1}{2} \hbar \Omega_{\alpha\beta} = \langle \frac{1}{2} \hbar k_{\alpha\beta}(P, Q) \rangle_{\text{ph}}. \quad (\text{A12})$$

This quantity corresponds to the term W that was calculated in reference 2 and which was shown to represent the overlap integral governing the transfer of the polaron from site to site by tunneling. Thus,

$$\mathcal{H}_1 = \frac{1}{2} \hbar \sum_{\alpha \neq \beta} \Omega_{\alpha\beta} c_{\alpha}^* a_{\beta} \quad (\text{A13})$$

is the static interaction governing tunneling. One finds from (A8)–(A13) that the remaining part, \mathcal{H}_2 , of the transformed Hamiltonian, i.e., the part representing the residual polaron-phonon interaction, is

$$\mathcal{H}_2 = \frac{1}{2} \hbar \sum_{\alpha \neq \beta} k_{\alpha\beta}'(P, Q) c_{\alpha}^* a_{\beta}, \quad (\text{A14})$$

where

$$k_{\alpha\beta}'(P, Q) = k_{\alpha\beta}(P, Q) - \Omega_{\alpha\beta}. \quad (\text{A15})$$

It is important to note that, as shown in the earlier theories, the residual interactions \mathcal{H}_1 and \mathcal{H}_2 are both very weak in the cases of interest, i.e., where the original electron-phonon interaction is strong.

Equations (A8)–(A15) constitute our formulation of model A in terms of the observables for the polaron (rather than electron) and phonons. We shall now express the electron dipole operator $\mathbf{m} = -e_0 \mathbf{x}$ in terms of these operators. First, we note that, by (A2), the operator \mathbf{m} is given in the original untransformed representation by

$$\begin{aligned} \mathbf{m} &= -e_0 \int \psi^*(\mathbf{x}) \mathbf{x} \psi(\mathbf{x}) d^3 \mathbf{x} \\ &= -e_0 \sum_{\alpha, \beta} c_{\alpha}^* c_{\beta} \int \psi_{\alpha}^*(\mathbf{x}) \mathbf{x} \psi_{\beta}(\mathbf{x}) d^3 \mathbf{x}. \end{aligned}$$

In the transformed representation this becomes

$$\mathbf{m} = -e_0 \sum_{\alpha, \beta} S^* c_{\alpha}^* c_{\beta} S \int \psi_{\alpha}^*(\mathbf{x}) \mathbf{x} \psi_{\beta}(\mathbf{x}) d^3 \mathbf{x}. \quad (\text{A16})$$

As in the previous theories, we restrict ourselves to cases where the ψ 's are s states. Therefore, $\psi_{\alpha}(\mathbf{x})$ is unchanged by the transformation $(\mathbf{x} - \mathbf{a}_{\alpha}) \rightarrow -(\mathbf{x} - \mathbf{a}_{\alpha})$, where \mathbf{a}_{α} is the position vector of A_{α} . Consequently,

$$\int \psi_{\alpha}^*(\mathbf{x}) \mathbf{x} \psi_{\beta}(\mathbf{x}) d^3 \mathbf{x} = \mathbf{a}_{\alpha} \delta_{\alpha\beta}.$$

It follows from this equation, (A7), and (A16) that

$$\mathbf{m} = -e_0 \sum_{\alpha} \mathbf{a}_{\alpha} c_{\alpha}^* c_{\alpha}. \quad (\text{A17})$$

Finally, we formulate the model for cases where the thermal conditions are such that \mathcal{H}_{ph} may be treated classically. We neglect the modification of the motion of \mathcal{H}_{ph} due to its weak interaction with the particle. It follows from (A10) that the time-dependent variables $P(t)$, $Q(t)$, corresponding to the observables, P , Q is given by

$$Q_{\lambda}(t) = Q_{\lambda} \cos \omega_{\lambda} t + (1/\omega_{\lambda}) P_{\lambda} \sin \omega_{\lambda} t, \quad (\text{A18a})$$

$$P_{\lambda}(t) = P_{\lambda} \cos \omega_{\lambda} t - \omega_{\lambda} Q_{\lambda} \sin \omega_{\lambda} t, \quad (\text{A18b})$$

where Q_{λ} , $P_{\lambda} = Q_{\lambda}(0)$, $P_{\lambda}(0)$ are c numbers (classical variables) whose statistical properties are determined by the distribution function corresponding to the thermal conditions for \mathcal{H}_{ph} .

It may now be seen that, according to this classical treatment, the action of the given field, generated by \mathcal{H}_{ph} , on the particle will still be given by \mathcal{H}_2 , though with P , Q replaced by the time-dependent quantities $P(t)$, $Q(t)$. Thus, by (A8) and (A14), the Hamiltonian for the particle in the field due to the lattice is given by

$$\mathcal{H}' = \mathcal{H}_0 + \mathcal{H}_1 + \mathcal{H}_2', \quad (\text{A19})$$

where

$$\mathcal{H}'_2 = \frac{1}{2}\hbar \sum_{\alpha \neq \beta} \mathcal{F}_{\alpha\beta}(t) c_\alpha^* c_\beta, \quad (\text{A20})$$

and

$$\mathcal{F}_{\alpha\beta}(t) = k_{\alpha\beta}'(P(t), Q(t)). \quad (\text{A21})$$

It follows from (A18) and (A21) that the statistical properties of \mathcal{F} are determined by those of P , Q that were discussed following Eq. (A18). One important quantity is $\langle \mathcal{F}_{\alpha\beta}(t) \rangle_{\text{ph}}$. This is a constant, with respect to time, since we are considering only situations where the thermal conditions are steady. Therefore, by (A18) and (A21),

$$\langle \mathcal{F}_{\alpha\beta}(t) \rangle_{\text{ph}} = \langle \mathcal{F}_{\alpha\beta}(0) \rangle_{\text{ph}} = \langle k_{\alpha\beta}'(P, Q) \rangle_{\text{ph}}.$$

Consequently, by (A12) and (A15),

$$\langle \mathcal{F}_{\alpha\beta}(t) \rangle_{\text{ph}} = 0. \quad (\text{A22})$$

It is convenient to re-express the formalism for \mathcal{H}' in terms of matrix elements between single-particle states

$$|\phi_\alpha\rangle = c_\alpha^* |\rangle,$$

where $|\rangle$ is the vacuum state, i.e., $c_\alpha |\rangle = 0$ for all α . It follows from (A9), (A13), (A19), and (A20) that

$$\mathcal{H}' = \mathcal{H}_0 + \mathcal{H}_1 + \mathcal{H}'_2, \quad (\text{A23a})$$

where

$$\langle \phi_\alpha^* | \mathcal{H}_0 | \phi_\beta \rangle = \epsilon_\alpha' \delta_{\alpha\beta}, \quad (\text{A23b})$$

$$\langle \phi_\alpha^* | \mathcal{H}_1 | \phi_\beta \rangle = \frac{1}{2}\hbar \Omega_{\alpha\beta} (1 - \delta_{\alpha\beta}), \quad (\text{A23c})$$

and

$$\langle \phi_\alpha^* | \mathcal{H}'_2 | \phi_\beta \rangle = \frac{1}{2}\hbar \mathcal{F}_{\alpha\beta}(t) (1 - \delta_{\alpha\beta}). \quad (\text{A23d})$$

Also, by (A17), the dipole operator is given by

$$\langle \phi_\alpha^* | \mathbf{m} | \phi_\beta \rangle = -e_0 \mathbf{a}_\alpha \delta_{\alpha\beta}. \quad (\text{A24})$$

Density and Energy of Surface States on Cleaved Surfaces of Germanium*

D. R. PALMER, S. R. MORRISON, AND C. E. DAUENBAUGH

Honeywell Research Center, Hopkins, Minnesota

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The channel technique has been successfully applied to measurement of the properties of cleaved germanium surfaces. A clean germanium surface is highly p type with the Fermi level near the valence band at the surface. This is brought about by acceptor-like surface states close to the edge of the valence band with a density of at least $1.5 \times 10^{12}/\text{cm}^2$. The density of these low-lying surface states decreases when the surface is exposed to oxygen. A comparison is made between results on cleaved surfaces and surfaces cleaned by ion bombardment.

IN recent years a number of attempts have been made to produce atomically clean surfaces on semiconductors. A clean semiconductor surface should lend itself to a much simpler and more fruitful investigation of basic surface properties.

A number of methods have been used to produce clean surfaces, namely, ion bombardment and annealing,^{1,2} cleavage,³⁻¹⁰ vacuum heat treatment,¹¹⁻¹³ and

hydrogen reduction.¹⁴ Ion bombardment has been most widely used for studies¹⁵⁻²⁰ of the electrical properties of silicon and germanium surfaces because of the relative ease with which experiments can be done. How-

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