Calculation of β as a function of temperatures gives

$$\beta=\beta_0^2\langle r^{-3}\rangle(1+3e^{-E_1/kT}+5e^{-E_2/kT})^{-1}\times\left[\frac{40}{3E_1}+e^{-E_1/kT}\left(-\frac{40}{3E_1}+\frac{26}{E_2-E_1}-\frac{2}{kT}\right)+e^{-E_2/kT}\left(-\frac{26}{E_2-E_1}+\frac{332}{9(E_3-E_2)}-\frac{32}{3kT}\right)\right], \quad \text{(A1)}$$

where all the related parameters are defined above in this article.

At 300°K for instance, $\beta=0.54$ (giving $H_{\text{int}}=1.54H_0$) instead of a value of $\beta=0$, when the excited ionic levels are ignored. This relatively large correction would be important for the determination of nuclear gyromagnetic ratios of excited states of europium isotopes using angular correlation technique.

Note added in proof. Recent Mossbauer measurements carried out by I. Nowik and S. Öfer in this laboratory, and to be submitted for publication shortly, show that at 80°K H_{eff} is about 750 kOe, in very good agreement with the present calculations.

PHYSICAL REVIEW VOLUME 130, NUMBER 4 15 MAY 1963

Boltzmann Equation for Polarons*

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(Received 27 December 1962)

The Feynman description of the polaron is used to write down a polaron Boltzmann equation. This equation is then used to discuss the drift mobility problem. In the limit of low temperatures, the Boltzmann equation is rearranged to exhibit elastic resonance scattering and it is solved exactly. The evaluation of the drift mobility thus obtained is compared with the results of other calculations. Other applications of the polaron Boltzmann equation are briefly discussed.

INTRODUCTION

In this paper, we calculate the drift mobility of an electron in a polar crystal (a polaron) by making use of a model due to Feynman.[1–3] Our procedure will be to use the Feynman model to derive a Boltzmann equation which may then be solved to find the mobility. Extensive study[4–7] has already been devoted to this mobility problem. The primary novel feature of the present work is the use of a Boltzmann equation in conjunction with the Feynman model.

We begin from the Fröhlich Hamiltonian for an electron in a polar crystal. We take all the optical phonons to have the same frequency and the electron-phonon matrix element to be proportional to the inverse of the magnitude of the phonon wave vector. In units in which $\hbar$, the phonon frequency, and the electron band mass are all equal to unity the Fröhlich Hamiltonian is[8]

$$H=\mathbf{p}_e^2/2+U(\mathbf{r}_e,t)+\sum_{\mathbf{q}} a_{\mathbf{q}}^\dagger a_{\mathbf{q}} +\sum_{\mathbf{q}}\left(\frac{4\pi\alpha}{\sqrt{2}Vq^2}\right)^{1/2}(a_{\mathbf{q}}e^{i\mathbf{q}\cdot\mathbf{r}_e}+a_{\mathbf{q}}^\dagger e^{-i\mathbf{q}\cdot\mathbf{r}_e}). \quad (1)$$

Here, $\mathbf{p}_e$ and $\mathbf{r}_e$ are electron momentum and position operators; $a_{\mathbf{q}}^\dagger$ and $a_{\mathbf{q}}$ are operators which create and destroy a phonon with wave vector $\mathbf{q}$; V is the volume of the system; α is a dimensionless coupling constant which measures the strength of the electron-phonon interaction. $U(\mathbf{r},t)$ is a scalar potential for a force externally applied to the system. At the space-time point $\mathbf{r}$, t, this force is, of course, $-\nabla U(\mathbf{r},t)$. We shall use this force to set the polaron in motion so that we may measure its mobility.

In the weak coupling limit, $\alpha\ll 1$, we can apply a perturbation expansion in the electron-phonon interaction. We can take the basic electronic states to be plane wave states and write a Boltzmann equation to describe how phonon emission and absorption processes change the population of these states.[4] However, when α is comparable with or greater than unity this description of the electronic states breaks down. Every electron now travels with a cloud of phonons about it and this cloud substantially modifies all the electronic properties.

However, there exists a relatively simple description of the polaron which works quite well even when α is fairly large. Feynman[1] pointed out that the motion of the electron in its associated cloud of phonons was quite similar to the motion that an electron would go through if it were coupled to another particle with a harmonic oscillator coupling. If this ficticious other particle has mass M and the spring constant is k, then the Hamiltonian for this analog system is

$$H_0=\mathbf{p}_e^2/2+\mathbf{P}^2/2M+\tfrac{1}{2}k(\mathbf{r}_e-\mathbf{R})^2. \quad (2)$$

* Supported in part by the U. S. Army Research Office (Durham).
[1] R. P. Feynman, Phys. Rev. **97**, 660 (1955).
[2] Y. Osaka, Progr. Theoret. Phys. (Kyoto) **22**, 437 (1959).
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[4] D. J. Howarth and E. H. Sondheimer, Proc. Roy. Soc. (London) **A219**, 53 (1953).
[5] F. E. Low and D. Pines, Phys. Rev. **98**, 414 (1958).
[6] Y. Osaka, Progr. Theoret. Phys. (Kyoto) **25**, 517 (1961).
[7] R. P. Feynman, R. W. Hellwarth, C. K. Iddings, and P. M. Platzman, Phys. Rev. **127**, 1004 (1962), denoted as FHIP.
[8] H. Frohlich, Advan. Phys. **3**, 325 (1954).

Here, $\mathbf{P}$ and $\mathbf{R}$ are momentum and position operators for the fictitious particle.

Feynman found that, when k and M were correctly chosen, he could get an excellent description of the electronic properties by employing the Hamiltonian H_0. In particular, he calculated time-dependent correlation functions for the electron in the canonical ensemble constructed from H_0. These correlation functions enabled him to calculate the electronic energy. The parameters k and M were choosen to minimize this ground-state energy. At the end of this variational calculation, Feynman had a better, i.e., a lower energy than any previous worker.[3]

In this paper, we shall take the point of view that the model Hamiltonian (2) provides a correct zeroth-order description of the electron. We shall take the basic level scheme for the electrons to be given by the eigenvalues of (2). Then, we shall write down a Boltzmann equation for a distribution function which describes the occupation of these various levels. The scattering from one level to another will occur because of the emission and absorption of phonons. Following Feynman's discovery that the electron-phonon interaction could be treated as a perturbation when the zeroth-order Hamiltonian is H_0, we shall simply apply the golden rule for the electron-phonon interaction to calculate the transition rate into and out of the eigenstates of H_0.

We begin by examining the eigenstates of H_0. We can diagonalize H_0 by working with the set of canonical variables:

$$\begin{aligned}
&\text{center-of mass position:} && \mathbf{r}=(\mathbf{r}_e+M\mathbf{R})/(M+1),\\
&\text{total momentum:} && \mathbf{p}=\mathbf{p}_e-\mathbf{P},\\
&\text{relative position:} && \mathbf{r}_{\text{os}}=\mathbf{r}_e-\mathbf{R},\\
&\text{relative momentum:} && \mathbf{p}_{\text{os}}=(M\mathbf{p}_e-\mathbf{P})/(M+1).
\end{aligned} \tag{3}$$

In terms of these variables, the Hamiltonian H_0 is diagonalized as

$$H_0=\frac{\mathbf{p}^2}{2(M+1)}+\frac{M+1}{2M}\mathbf{p}_{\text{os}}^2+\frac{k}{2}\mathbf{r}_{\text{os}}^2.$$

Clearly, H_0 describes the motion of a compound system, a "molecule" in which the center of mass moves freely but the two particles are bound as a harmonic oscillator. The eigenstates of this Hamiltonian are labeled by the total momentum $\mathbf{p}$ and the integers n_x, n_y, n_z which describe the level of the three-dimensional oscillator. Since the oscillator frequency is

$$v=[k(M+1)/M]^{1/2}. \tag{4}$$

The energy levels are

$$E_{p,\mathbf{n}}=\frac{p^2}{2(M+1)}+(n_x+n_y+n_z+\tfrac{3}{2})v, \tag{5}$$

and corresponding eigenstates can be labeled as $|\mathbf{p},\mathbf{n}\rangle$.

In this approximation, $M+1$ represents the effective mass of the system of electron plus its cloud of phonons. In the weak-coupling limit $\alpha\ll 1$, this effective mass reduces to the electron band mass, i.e., $M\to 0$. Also, in the weak-coupling limit, the electron moves essentially freely. Hence, its coupling to the other particle, here measured by the spring constant k, also goes to zero. In the opposite limit of strong coupling, $\alpha\gg 1$, the electron appears very heavy and very strongly bound, $M\gg 1$ and $v\gg 1$. The oscillator frequency v remains uniformly greater than unity.

II. THE BOLTZMANN EQUATION FOR POLARONS

We describe the state of the polaron system by giving the distribution function $f(\mathbf{p},\mathbf{n},\mathbf{r},t)$ which gives the occupation of the state $|\mathbf{p},\mathbf{n}\rangle$ for particles in the neighborhood of the space-time point $\mathbf{r}$, t. In our calculation of the mobility, we want to know the average velocity induced by the external force. Since the electron and the fictitious particle remain bound together, the average electronic velocity is the same as the average center-of-mass velocity, i.e., the average electron velocity in the neighborhood of $\mathbf{r}$, t is

$$\mathbf{v}(\mathbf{r},t)=\int d^3p\sum_{\mathbf{n}}\frac{\mathbf{p}}{M+1}f(\mathbf{p},\mathbf{n};\mathbf{r},t)\Big/\int d^3p\sum_{\mathbf{n}}f(\mathbf{p},\mathbf{n};\mathbf{r},t). \tag{6}$$

Our level scheme in terms of $\mathbf{p}$ and $\mathbf{n}$ remains appropriate whenever the external scalar potential varies sufficiently slowly in space and time. In particular, this demands that the frequencies contained in $U(\mathbf{r},t)$ be $\ll v$ and the wave numbers be much smaller than the inverse radius of the bound state. When these conditions hold the Boltzmann equation takes the simple form

$$\left[\frac{\partial}{\partial t}+\frac{\mathbf{p}\cdot\nabla_r}{M+1}+F(\mathbf{r},t)\cdot\nabla_{\mathbf{p}}\right]f(\mathbf{p},\mathbf{n};\mathbf{r},t)=\left.\frac{\delta f}{\delta t}\right|_{\text{collision}}. \tag{7}$$

Here $\mathbf{F}(\mathbf{r},t)=-\nabla U(\mathbf{r},t)$ is the external force on the electron which is the same as the force on the center of mass of the bound system. The $M+1$ appears in (7) because the velocity of the center of mass is $\mathbf{p}/(M+1)$.

To get the collision term we apply the golden rule. The number of particles in the state $|\mathbf{p},\mathbf{n}\rangle$ is diminished by both processes in which the electron induces the emission of the phonon and also processes in which phonons are absorbed. First, we calculate the absorption rate. According to the golden rule this rate is

$$\sum_{\mathbf{q},\mathbf{p}',\mathbf{n}'}\frac{4\pi\alpha}{\sqrt{2}Vq^2}\bar{N}|\langle\mathbf{p},\mathbf{n}|e^{-i\mathbf{q}\cdot\mathbf{r}_e}|\mathbf{p}',\mathbf{n}'\rangle|^2\times 2\pi\delta(E_{p,\mathbf{n}}-E_{p',\mathbf{n}'}+1), \tag{8}$$

Here $\bar{N}$ is the equilibrium number of phonons in the state labeled by $\mathbf{q}$ at the temperature β^{-1}:

$$\bar{N}=(e^{\beta}-1)^{-1}. \tag{9}$$

To get the absorption rate, this number is multiplied by the electron-phonon matrix element squared and finally 2π times the energy conservation delta function. In computing the matrix element we use, of course, the eigenstates $|\mathbf{p}',\mathbf{n}'\rangle$ of H_0. Finally, this result is summed over all phonon wave vectors $\mathbf{q}$ and all final states $|\mathbf{p}',\mathbf{n}'\rangle$. The matrix element is easily computed if we notice that the electron-position operator can be decomposed as

$$\mathbf{r}_e=\mathbf{r}+[M/(M+1)]\mathbf{r}_{\text{os}},$$

and the eigenstates can also be decomposed as

$$|\mathbf{p},\mathbf{n}\rangle=|\mathbf{p}\rangle|\mathbf{n}\rangle,$$

so that the matrix element in (8) is

$$\langle\mathbf{p}|e^{-i\mathbf{q}\cdot\mathbf{r}}|\mathbf{p}'\rangle\langle\mathbf{n}|\exp\left(-i\mathbf{q}\cdot\mathbf{r}_{\text{os}}\frac{M}{M+1}\right)|\mathbf{n}'\rangle$$
$$=\delta_{\mathbf{p}+\mathbf{q},\mathbf{p}'}\langle\mathbf{n}|\exp\left(-i\mathbf{q}\cdot\mathbf{r}_{\text{os}}\frac{M}{M+1}\right)|\mathbf{n}'\rangle.$$

Consequently, the expression (8) for the rate of phonon absorption is

$$\int\frac{d^3p'}{(2\pi)^3}\sum_{\mathbf{n}'}2\pi\delta(E_{p,\mathbf{n}}-E_{p',\mathbf{n}'}+1)\bar{N}W_{\mathbf{p},\mathbf{n};\mathbf{p}',\mathbf{n}'},\quad(10)$$

where

$$W_{\mathbf{p},\mathbf{n};\mathbf{p}',\mathbf{n}'}=\frac{4\pi\alpha}{\sqrt{2}}\frac{|\langle\mathbf{n}|\exp[i(\mathbf{p}-\mathbf{p}')\cdot\mathbf{r}_{\text{os}}M/(M+1)]|n'\rangle|^2}{(\mathbf{p}-\mathbf{p}')^2}\quad(11)$$

describes the transition rate between the states $|\mathbf{p},\mathbf{n}\rangle$ and $|\mathbf{p}',\mathbf{n}'\rangle$. The rate of emission of phonons is given by a form very similar to (8) except that $\bar{N}\rightarrow\bar{N}+1$ and inside the energy conservation delta function $1\rightarrow-1$. The rate of scattering into the state $|\mathbf{p},\mathbf{n}\rangle$ can be calculated in exactly this same way. When all these results are combined the collision term takes the form

$$\left.\frac{\delta f}{\delta t}\right|_{\text{collision}}=-\int\frac{d^3p'}{(2\pi)^3}\sum_{n'}2\pi W_{\mathbf{p},\mathbf{n};\mathbf{p}',\mathbf{n}'}$$
$$\times\delta(E_{p,\mathbf{n}}-E_{p',\mathbf{n}'}+1)[\bar{N}f(\mathbf{p},\mathbf{n};\mathbf{r},t)$$
$$-(\bar{N}+1)f(\mathbf{p}',\mathbf{n}';\mathbf{r},t)]$$
$$+\delta(E_{p,\mathbf{n}}-E_{p',\mathbf{n}'}-1)[(\bar{N}+1)f(\mathbf{p},\mathbf{n};\mathbf{r},t)$$
$$-\bar{N}f(\mathbf{p}',\mathbf{n}';\mathbf{r},t)].\quad(12)$$

[The reader might argue that there should, in fact, be extra scattering terms in (12) resulting from the difference between H_0 and $p_e^2/2$. This difference indeed contributes to higher order scattering processes; but it cannot induce real transitions in first order. Hence, it is omitted from the present analysis.]

There are three features which make the Boltzmann equation obtained by substituting (12) into (7) different from the standard transport equation for electrons in a polar crystal. The first is the relatively trivial fact that the effective mass, $M+1$, appears instead of the electron band mass. The second is that the n's serve as a set of extra state labels so that more kinds of transitions need to be considered. Finally, the appearance of the factor

$$\left|\langle\mathbf{n}|\exp\left[i(\mathbf{p}-\mathbf{p}')\cdot\mathbf{r}_{\text{os}}\frac{M}{M+1}\right]|\mathbf{n}'\rangle\right|^2$$

in W tends to prevent large momentum transfers from contributing appreciably.

To see this fact in more detail consider the case $\mathbf{n}=\mathbf{n}'=\mathbf{0}$. Then (9) becomes[9]

$$W_{\mathbf{p},0;\mathbf{p}',0}=\frac{4\pi\alpha}{\sqrt{2}}\frac{\exp[-(M/v)(\mathbf{p}-\mathbf{p}')^2/2(M+1)]}{(\mathbf{p}-\mathbf{p}')^2}.\quad(13)$$

The factor (13) includes an exponential cutoff at high momentum transfer. This cutoff occurs because the electron is continually emitting and absorbing phonons. It does not stand still long enough to achieve sufficient localization to be noticed by the very short wavelength phonons. In other words, because of its random motion, the electron is a diffuse structure and it is quite transparent to short-wavelength phonons.[10]

It should be pointed out that we have not derived a Boltzmann equation for the polaron system. Instead, we have simply assumed that the "molecules" of the Feynman model have sufficiently well-separated collisions so that the Boltzmann equation concept is valid. Consequently, we cannot make any statement about the range of validity of our analysis.

III. MOBILITY CALCULATIONS

We wish to compute the average velocity which appears as the linear response to a weak force for the particular case in which the force is independent of space and time. Because of this independence $f(\mathbf{p},\mathbf{n};\mathbf{r},t)$ is itself independent of space and time. We write

$$f(\mathbf{p},\mathbf{n};\mathbf{r},t)=f_0(\mathbf{p},\mathbf{n})[1+\varphi(\mathbf{p},\mathbf{n})],\quad(14)$$

where f_0 is the complete equilibrium distribution function

$$f_0(\mathbf{p},\mathbf{n})\sim\exp(-\beta E_{p,\mathbf{n}})\quad(15)$$

and $\varphi(\mathbf{p},\mathbf{n})$ represents the deviation from equilibrium. Notice that when f is replaced by f_0 in the collision term (12) that term vanishes. After a bit of algebra we

[9] The harmonic oscillator matrix elements are evaluated in, for example, J. Schwinger, Phys. Rev. **91**, 728 (1953).

[10] See the discussions of T. D. Schultz and P. M. Platzman, in Proceedings of the Scottish University Summer School on Excitations in Semi-conductors [Oliver Boyd Ltd., London (to be published)].

see that we can simplify the collision term as

$$-f_0(\mathbf{p},\mathbf{n})\int\frac{d^3p'}{(2\pi)^3}\sum_{n'}2\pi W_{\mathbf{p},\mathbf{n};\mathbf{p}',\mathbf{n}'}$$
$$\times[\delta(E_{p,\mathbf{n}}-E_{p',\mathbf{n}'}+1)\bar{N}+\delta(E_{p,\mathbf{n}}-E_{p',\mathbf{n}'}-1)(\bar{N}+1)]$$
$$\times[\varphi(\mathbf{p},\mathbf{n})-\varphi(\mathbf{p}',\mathbf{n}')]. \quad (16)$$

On the left-hand side of our Boltzmann equation we have $\mathbf{F}\cdot\nabla_{\mathbf{p}}f(\mathbf{p},\mathbf{n})$. Since we only want to consider the linear effect of the force, we can replace this by

$$\mathbf{F}\cdot\nabla_{\mathbf{p}}f_0(\mathbf{p},\mathbf{n})=-\frac{\beta\mathbf{F}\cdot\mathbf{p}}{M+1}f_0(\mathbf{p},\mathbf{n}). \quad (17)$$

The common factor f_0 may be cancelled out of (16) and (17) leaving an integral equation for φ of the form

$$\frac{\beta\mathbf{F}\cdot\mathbf{p}}{M+1}=\int\frac{d^3p'}{(2\pi)^3}\sum_{\mathbf{n}'}2\pi W_{\mathbf{p},\mathbf{n};\mathbf{p}'\mathbf{n}'}$$
$$\times[\delta(E_{p,\mathbf{n}}-E_{p',\mathbf{n}'}+1)\bar{N}+\delta(E_{p,\mathbf{n}}-E_{p',\mathbf{n}'}-1)(\bar{N}+1)]$$
$$\times[\varphi(\mathbf{p},\mathbf{n})-\varphi(\mathbf{p}',\mathbf{n}')]. \quad (18)$$

Once we have calculated φ, we can calculate the velocity, $\mathbf{v}$, by making use of Eq. (6). In the limit of small $\mathbf{F}$ and hence small φ,

$$\mathbf{v}=\int\frac{d^3p}{(2\pi)^3}\sum_{\mathbf{n}}\frac{\mathbf{p}}{M+1}\varphi(\mathbf{p},\mathbf{n})f_0(\mathbf{p},\mathbf{n})\Big/\int\frac{d^3p}{(2\pi)^3}\sum_{\mathbf{n}}f_0(\mathbf{p},\mathbf{n}). \quad (19)$$

Then the drift mobility is given as the coefficient μ in the relation

$$e\mathbf{v}=\mu\mathbf{F}, \quad (20)$$

where e is the magnitude of the electronic charge.

For very low temperatures, $\beta\gg1$, the only contribution to $\mathbf{v}$ in (19) occurs for $\mathbf{n}=0$ and $p^2/2(M+1)\ll1$. In this limit, Eq. (18) is relatively simple. The second delta function in (18) cannot contribute because its argument is always smaller than zero when $\mathbf{n}=0$ and $p^2/2(M+1)<1$. (The vanishing of this term reflects the impossibility of processes in which a low-energy polaron emits a phonon and also processes in which a low-energy polaron is produced by the absorption of a phonon.) In this range of energies, the other delta function only contributes for $\mathbf{n}'=0$, since $v>1$. Thus, by making use of (18) and (13), we find

$$\frac{\beta\mathbf{F}\cdot\mathbf{p}}{M+1}=\frac{\alpha\bar{N}}{\pi\sqrt{2}}\int d^3p'\frac{\exp[-(M/v)(\mathbf{p}-\mathbf{p}')^2/(M+1)]}{(p-p')^2}$$
$$\times\delta(\epsilon_p-\epsilon_{p'}+1)[\varphi(\mathbf{p},0)-\varphi(\mathbf{p}',0)] \quad \text{for} \quad \epsilon_p<1. \quad (21)$$

Here we have used the abbreviation ϵ_p for the kinetic energy of the "molecule," $p^2/2(M+1)$.

In the next section we shall show that the term $\varphi(\mathbf{p}',0)$ contributes very little to the right-hand side of (21). For the moment, however, let us simply neglect this term. Then (21) is of the form

$$\frac{\beta\mathbf{F}\cdot\mathbf{p}}{M+1}=\Gamma(\epsilon_p)\varphi(p,0) \quad \text{for} \quad \epsilon_p<1, \quad (22)$$

where

$$\Gamma(\epsilon_p)=\frac{\alpha\bar{N}}{\pi\sqrt{2}}\int d^3p'\frac{\exp[-(M/v)(\mathbf{p}-\mathbf{p}')^2/(M+1)]}{(\mathbf{p}-\mathbf{p}')^2}$$
$$\times\delta(\epsilon_p-\epsilon_{p'}+1) \quad (23)$$

is the rate of occurrence of phonon absorption processes in which the polaron is both initially and finally in the lowest oscillator level.

For very small p,

$$\Gamma(0)=2\alpha\bar{N}(M+1)^{1/2}e^{-M/v}.$$

We can determine the mobility by substituting

$$\varphi(\mathbf{p},0)=\frac{\beta\mathbf{F}\cdot\mathbf{p}}{(M+1)\Gamma(0)} \quad (24)$$

into (19) to find that the average velocity is

$$\mathbf{v}=\frac{\mathbf{F}}{(M+1)\Gamma(0)}$$

and hence

$$\mu=\frac{e}{(M+1)\Gamma(0)}=\frac{e}{2\alpha\bar{N}(M+1)^{3/2}\exp(-M/v)}. \quad (25)$$

The result (25) for the low-temperature mobility was previously obtained in reference 6. However, in reference 7 a somewhat different result was obtained. Here, the mobility, which was calculated for all temperatures and all frequencies, reduces in the zero-frequency, low-temperature limit to

$$\mu_{\text{FHIP}}=\frac{3}{2\beta}\frac{e}{(M+1)\Gamma(0)}. \quad (26)$$

This differs by a factor of $3/(2\beta)$ from (25). However, there exists no real disagreement between our conclusions and those of FHIP because the authors of FHIP take great pains to point out that the perturbation theory they employ fails in the zero-frequency limit. The source of this failure can be seen in the fact that their dc mobility was derived by extrapolating the high-frequency form of $\varphi(\mathbf{p},0)$ to lower frequencies. This gave a result which can be expressed in the present language as

$$\text{FHIP:} \quad \varphi(\mathbf{p},0)=\varphi_0\mathbf{p}\cdot\mathbf{F} \quad \text{for all } p. \quad (27)$$

Here φ_0 is a constant which is to be determined self-

consistently. In our work we have assumed that for low temperatures

$$\varphi(\mathbf{p},0)=\varphi_0\mathbf{p}\cdot\mathbf{F} \quad \text{for} \quad \epsilon_p<1, \qquad =0 \quad \text{for} \quad \epsilon_p>1. \tag{28}$$

It is well known[4,11] that in a variational calculation based upon the ordinary Boltzmann equation, the assumption (27) leads to an incorrect estimate of the low-temperature mobility. In fact, the error produced in the variational calculation by this incorrect assumption is just the extra factor of $3/(2\beta)$ which appears in μ_{FHIP}.[12] Equation (27) is wrong because $\varphi(\mathbf{p},0)$ is greatly reduced by phonon emission processes whenever the energy of the particle is above the emission threshold.

In order to make this point more firmly, in the next section we calculate $\varphi(\mathbf{p},0)$ from our polaron Boltzmann equation with the aim of establishing the validity of (28).

Resonance Scattering

At this point, we return to Eq. (21). This equation can be written in terms of the variables

$$\epsilon_p=p^2/2(M+1),$$
$$\mathbf{\Omega}=\mathbf{p}/|\mathbf{p}|,$$
$$\varphi(\mathbf{p},0)=\varphi(\epsilon,\mathbf{\Omega}),$$

as

$$\beta\mathbf{F}\cdot\mathbf{\Omega}\left(\frac{2\epsilon}{M+1}\right)^{1/2}=\Gamma(\epsilon)\left[\varphi(\epsilon,\mathbf{\Omega})-\int\frac{d\mathbf{\Omega}'}{4\pi}\varphi(\epsilon+1,\mathbf{\Omega}')P_{\epsilon+1\to\epsilon}(\mathbf{\Omega}'\to\mathbf{\Omega})\right]. \tag{29}$$

Here, $\Gamma(\epsilon)$ is the phonon absorption rate defined by Eq. (23) and $P_{\epsilon+1\to\epsilon}$ is defined by

$$\begin{aligned}&\Gamma(\epsilon)P_{\epsilon+1\to\epsilon}(\mathbf{\Omega}'\to\mathbf{\Omega})\\&=2\sqrt{2}\alpha\bar{N}\int_0^\infty dp'p'^2\,\delta(\epsilon_p-\epsilon_{p'}+1)\exp\left[-\frac{M}{v}\frac{(\mathbf{p}-\mathbf{p}')^2}{2(M+1)}\right]\\&=2\alpha\bar{N}[(\epsilon+1)(M+1)]^{1/2}\\&\quad\times\frac{\exp\{-(M/v)[\mathbf{\Omega}\epsilon^{1/2}-\mathbf{\Omega}'(\epsilon+1)^{1/2}]^2\}}{[\mathbf{\Omega}\epsilon^{1/2}-\mathbf{\Omega}'(\epsilon+1)^{1/2}]^2}.\end{aligned} \tag{30}$$

From Eq. (29) $P_{\epsilon+1\to\epsilon}(\mathbf{\Omega}'\to\mathbf{\Omega})$ represents the probability that, in a phonon emission process, a particle with initial energy $\epsilon+1$ and direction $\mathbf{\Omega}'$ would have the direction $\mathbf{\Omega}$ after the emission. This probability is normalized so that

$$\int\frac{d\mathbf{\Omega}}{4\pi}P_{\epsilon+1\to\epsilon}(\mathbf{\Omega}'\to\mathbf{\Omega})=\int\frac{d\mathbf{\Omega}'}{4\pi}P_{\epsilon+1\to\epsilon}(\mathbf{\Omega}'\to\mathbf{\Omega})=1. \tag{31}$$

[11] J. M. Ziman, *Electrons and Phonons* (The Clarendon Press, Oxford, England, 1962), p. 344.

[12] F. Garcia Moliner (private communication), noted this feature of μ_{FHIP}.

Thus, $P_{\epsilon+1\to\epsilon}(\mathbf{\Omega}'\to\mathbf{\Omega})$ represents an angular correlation factor for an emission process. Because of detailed balancing symmetry, $P_{\epsilon+1\to\epsilon}(\mathbf{\Omega}'\to\mathbf{\Omega})$ also represents the angular correlation factor which gives the probability that, after an absorption process a particle with initial energy ϵ and direction $\mathbf{\Omega}$ would have final direction $\mathbf{\Omega}'$. This dual role of P is indicated by writing

$$P_{\epsilon\to\epsilon+1}(\mathbf{\Omega}\to\mathbf{\Omega}')=P_{\epsilon+1\to\epsilon}(\mathbf{\Omega}'\to\mathbf{\Omega}). \tag{32}$$

Equation (29) involves $\varphi(\epsilon+1,\mathbf{\Omega}')$. For $\mathbf{n}=0$ and $\epsilon>1$, the Boltzmann equation (18) involves both terms proportional to $\bar{N}$ and terms proportional to $\bar{N}+1$. Since $\bar{N}$ is $\ll1$ for low temperatures, we neglect it and find

$$\begin{aligned}\frac{\beta\mathbf{F}\cdot\mathbf{p}'}{M+1}=\frac{\alpha}{\pi\sqrt{2}}\int d^3p''\,\delta\left(\frac{p'^2}{2(M+1)}-\frac{p''^2}{2(M+1)}-1\right)\\\times\frac{\exp[-(M/v)(\mathbf{p}'-\mathbf{p}'')^2/2(M+1)]}{(\mathbf{p}'-\mathbf{p}'')^2}\\\times[\varphi(\mathbf{p}',0)-\varphi(\mathbf{p}'',0)].\end{aligned} \tag{33}$$

We multiply this equation by $\bar{N}$, write $p'^2/2(M+1)=\epsilon+1$ and utilize our definitions of Γ and P to write (33) as

$$\bar{N}\beta\mathbf{F}\cdot\mathbf{\Omega}'\left[\frac{2(\epsilon+1)}{M+1}\right]^{1/2}=\Gamma(\epsilon)\left[\varphi(\epsilon+1,\mathbf{\Omega}')-\int\frac{d\mathbf{\Omega}''}{4\pi}\varphi(\epsilon,\mathbf{\Omega}'')P_{\epsilon\to\epsilon+1}(\mathbf{\Omega}''\to\mathbf{\Omega})\right]. \tag{34}$$

Notice that we begin from a particular value of the energy, say ϵ, for $\epsilon<1$. Equation (29) tells us that because of phonon emission processes $\varphi(\epsilon,\mathbf{\Omega})$ is determined by $\varphi(\epsilon+1,\mathbf{\Omega}')$. However, Eq. (34) tells us that because of phonon absorption process $\varphi(\epsilon+1,\mathbf{\Omega}')$ is itself determined by $\varphi(\epsilon,\mathbf{\Omega}'')$. Hence, we can eliminate $\varphi(\epsilon+1,\mathbf{\Omega}')$ from the pair of Eqs. (29) and (34).

Since $\bar{N}\ll1$, the left-hand side of (34) may be replaced by zero. Then (34) implies

$$\varphi(\epsilon+1,\mathbf{\Omega}')=\int\frac{d\mathbf{\Omega}''}{4\pi}\varphi(\epsilon,\mathbf{\Omega}'')P_{\epsilon\to\epsilon+1}(\mathbf{\Omega}''\to\mathbf{\Omega}'). \tag{35}$$

The result of combining (35) with (29) is

$$\beta\mathbf{F}\cdot\mathbf{\Omega}\left[\frac{2\epsilon}{M+1}\right]^{1/2}=\Gamma(\epsilon)\left[\varphi(\epsilon,\mathbf{\Omega})-\int\frac{d\mathbf{\Omega}'}{4\pi}\frac{d\mathbf{\Omega}''}{4\pi}\varphi(\epsilon,\mathbf{\Omega}'')\times P_{\epsilon\to\epsilon+1}(\mathbf{\Omega}''\to\mathbf{\Omega}')P_{\epsilon+1\to\epsilon}(\mathbf{\Omega}'\to\mathbf{\Omega}'')\right]. \tag{36}$$

This result may be best understood by multiplying it by f_0. Because the angular scattering probabilities

ntegrate to unity (36) then implies

$$\mathbf{iF}\cdot\nabla_{\mathbf{p}}f(p,0)$$
$$=-\Gamma(\epsilon)\Big[f(\mathbf{p},0)-\int\frac{d\Omega'}{4\pi}\frac{d\Omega''}{4\pi}f(\mathbf{p}'',0)\,|_{\epsilon''=\epsilon}$$
$$\times P_{\epsilon\to\epsilon+1}(\Omega''\to\Omega')P_{\epsilon+1\to\epsilon}(\Omega'\to\Omega)\Big]. \quad (37)$$

Equation (37) is naturally interpreted by looking at scatterings as a compound in which a low-energy polaron first absorbs and then emits a phonon. The rate at which this process occurs is $\Gamma(\epsilon)$; while

$$\int\frac{d\Omega'}{4\pi}P_{\epsilon\to\epsilon+1}(\Omega''\to\Omega')P_{\epsilon+1\to\epsilon}(\Omega'\to\Omega),$$

describes the angular correlation between the initial and final directions of the polaron.

This view of the scattering as a compound process has been espoused by Schultz.[3] He called this a resonance scattering process. Notice that we have derived resonance scattering only for very low temperatures; in our view the concept breaks down for higher temperatures.

Now we can see quite directly why it is possible to neglect the second term in (36) in the limit $\epsilon\to 0$. In this limit the initial and final momentum of the particle almost vanishes. Therefore, the directions of these momenta are almost irrelevant in determining the direction of the momentum in the excited state, Ω'. This means that for small ϵ, the angular correlation factors, P, may be replaced by unity. Then, (36) becomes for $\epsilon\ll 1$

$$\beta\mathbf{F}\cdot\Omega\Big[\frac{2\epsilon}{M+1}\Big]^{1/2}$$
$$=\Gamma(0)\Big[\varphi(\epsilon,\Omega)-\int\frac{d\Omega''}{4\pi}\varphi(\epsilon,\Omega'')\Big]. \quad (38)$$

However, because of the vector character of the disturbance $\varphi(\epsilon,\Omega'')\sim\mathbf{F}\cdot\Omega''$ times a function of ϵ. Thus, the angular average of φ vanishes, and the second term on the right-hand side of (38) disappears.

We can, therefore, conclude that the collision time approximation, (24), is fully justified at sufficiently low temperatures.

Another way of seeing this same result is to again make use of (35) which implies that, for very small ϵ

$$\varphi(\epsilon+1,\,\Omega')=\int\frac{d\Omega''}{4\pi}\varphi(\epsilon,\Omega'')=0.$$

Thus, we see quite directly that, above the emission threshold, the FHIP assumption (28) is quite untenable.

CONCLUSIONS

The work reported in this paper is quite incomplete. We have only calculated the drift mobility in the extreme low-temperature limit; our Boltzmann equation is capable of predicting the drift mobility for all temperatures. We have not considered the Hall mobility at all; the analysis given here can easily be extended to the case in which a magnetic field is present. Calculations of the drift and Hall mobilities at all temperatures are in progress.

Finally, the most important gap in this paper is the question of the range of validity of the Boltzmann employed here. Is this equation correct for all temperatures and coupling strengths? Is it correct in the presence of a strong magnetic field? These questions too are under investigation and it is hoped that we can report some progress in the near future.