M. I. KLINGER

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Abstract

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M. I. KLINGER

THEORY OF KINETIC PHENOMENA AT LOW MOBILITY OF CURRENT CARRIERS*

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I. A. F. Ioffe showed (see ([1])) that, as follows from experimental investigation of a number of semiconductors, the mobility of the latter u is anomalously small, and the transport mechanism is qualitatively different from the usual one, with $u(T) \sim \exp(-\mathcal{E}_0/kT)$ at high T (see also ([2],[3])). These ideas served as the stimulus for carrying out the present work. According to ([1]), the indicated transport mechanism has the character of jumps of the current carrier between sites s and s', mainly ions of a transition metal (π-ions). According to the assumption of ([2]), the current carrier is a small-radius polaron ([6]), and in ([4]), and then more carefully (but for a very special model of a one-dimensional molecular chain) in ([5]), attempts were made by the method of the theory of quantum transitions to calculate the mean probability $\overline{W}_{ss'}(T)$ of the jump $s \to s'$ of a small polaron, accompanied by multiphonon transitions with conservation of the phonon energy $\varepsilon(n)$ (below we are speaking of an ideal crystal).

Although useful estimates and a formula of the type $u(T) \sim \exp(-\mathcal{E}_0/kT)$ were obtained in ([4],[5]), it seems to us that these works do not give a solution of the problem of low mobility posed in ([1]), since they are unsatisfactory and insufficient in the following fundamental points.
1) In ([4],[5]) the expression for $\overline{W}_{ss'}$ contains an infinity which is removed in different ways, i.e., not uniquely: in ([4]) a rather arbitrary replacement is made

$$\infty = \int_{-\infty}^{\infty} \exp[X\cos\xi]\, d\xi \to \int_{-\pi}^{\pi} \exp[X\cos\xi]\, d\xi = 2\pi I_0(X),$$

($I_0(X)$ is a Bessel function), whereas in ([5]) removal of the divergence is achieved by a subtraction procedure adopted from visual considerations (after a preliminary investigation of $\overline{W}_{ss'}$ in this particular model), the justification of which in ([5]) cannot be regarded as sufficient (cf. ([9])).
2) Taking into account 1) and the fact that in ([4],[5]) transport by jumps of the current carrier is opposed, as an alternative (or competing) one, to band-type transport, there arise–and cannot be considered solved–the questions of the compatibility of the postulated jump mechanism with the presence, as a consequence of the translational symmetry of the crystal, of a current-carrier band and, in connection with this, of rigorously derived criteria of the theory.
3) In ([4],[5]) $\overline{W}_{ss'}$ was calculated only in special models; the formula $\mathcal{D} = a^2\overline{W}_{ss'}$,

for $\mathcal{D} = \frac{kT}{e} u$, was postulated ($a$ is the lattice constant), and the question of calculating other kinetic coefficients could not be considered by such a method.

II. The present communication is devoted to the formulation of a general theory, free of the limitations and difficulties noted above, of transport phenomena in an ideal crystal by small polarons or other polarizing carriers of small radius (transport in a disordered system is the subject of another communication). The usual band-wave theory of transport, based on a Boltzmann-type kinetic equation, is inapplicable to the indicated phenomena, since the criterion

$$u > \frac{e\hbar}{m^*\Delta}\left(> \frac{e}{\hbar}a^2\right); \qquad \Delta \equiv \min\{kT, \Delta_b\};$$

is not satisfied; m^*, Δ_b are the mean effective mass and the width of the carrier band. We shall single out here only the principal features of the system, the idea of the method, and the results of the theory, as far as possible independent of a concrete model. Here and below, by a model is meant a concrete form of the electron-pho-

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interaction and of the main Hamiltonian $\mathcal{H}_0$. The system under study is an electron (hole) in the field of the vibrating ions of a three-dimensional ionic crystal, whose cell, neutral as a whole, contains positive and negative ions, including at least one n-ion; moreover, the long-range character of the interaction of the electron with the polarization may be taken into account. Let

$$|spn^{(s\rho)}\rangle = |sp\rangle \cdot |n^{(s\rho)}\rangle,$$

where $|pS\rangle$ and $|n^{(s\rho)}\rangle$ are the state vectors of the polarizing carrier (small polaron) in cell s and of the phonon system; $n^{(s\rho)} = n$ is the set of phonon numbers, and for simplicity it suffices to restrict oneself to the ground states. The dependence of $n^{(s\rho)}$ and $|n^{(s\rho)}\rangle$ on s, ρ is due to the fact that, when s and ρ change, the configuration of the ions displaced under polarization changes, i.e., the centers of the phonon oscillators $q_{fj}^{s\rho}$ (f is the quasi-momentum, j the phonon branch with frequency ω_{fj}). It is essentially necessary to single out in the full Hamiltonian $\mathcal{H}$ of the system the main Hamiltonian $\mathcal{H}_0$ of the unperturbed system and the small perturbation $\lambda_0\mathcal{H}'$ in such a way that they explicitly do not depend on the choice of s; for this purpose we assume that $\mathcal{H}_0 = \{\mathcal{H}\}_d$ and $\lambda_0\mathcal{H}' = \{\mathcal{H}\}_{nd}$, i.e., respectively the diagonal and nondiagonal (in the $sn^{(s)}$-representation) parts of $\mathcal{H}$, and thus $\mathcal{H} = \mathcal{H}_0 + \lambda_0\mathcal{H}'$,

$$\mathcal{H}_0|sn^{(s)}\rangle = \varepsilon(n)|sn^{(s)}\rangle, \qquad \varepsilon(n) = (sn^{(s)}|\mathcal{H}|sn^{(s)}), \tag{1}$$

$$(sn^{(s)}|\mathcal{H}'|s'n'^{(s')}) = (sn^{(s)}|V_{s'}|s'n'^{(s')}),$$

where $V_{s'}$ is the Hamiltonian of the interaction of the electron with all the ions (fixed at the sites), except s'-x. Let us emphasize that the unperturbed system and $\mathcal{H}_0$ include the entire linear (in the displacement) interaction of an electron localized at a site with phonons of all branches, acoustic and optical, which may be sufficiently strong (for $\Phi(0) \gg 1$, see below); it is this region that is considered. In this sense, the following treats transport in a system with strong electron-phonon coupling. The method is based on calculating the kinetic coefficients σ_{AB} (for brevity, for stationary processes), starting from their general expressions ([7],[9]), when it is sufficient to consider (see ([9]), I.4–9)

$$\mathcal{D}_{AB} = \frac{1}{2}\beta N_e \int_{-\infty}^{\infty} \frac{dl}{2\pi}\ \mathrm{Re}\langle BR_l^+ AR_l^- \rangle, \tag{2}$$

where $\beta = (kT)^{-1}$; N_l is the carrier concentration; B, A are the operators of electron fluxes (charge, energy); $\langle Z\rangle \equiv \mathrm{Sp}\exp(\beta F - \beta\mathcal{H})Z$; Sp is taken in the system $|sn^{(s)}\rangle$, orthonormalized and, in a sufficiently complete approximation, complete (one may orthogonalize $|sn^{(s)}\rangle$ and set $(sn^{(s)}|s'n'^{(s')}) = \delta_{ss'}\delta_{nn'}$); in (2)

$$R_l^{\mp} = (\mathcal{H}_0 + \lambda_0\mathcal{H}' - l \mp i\varepsilon)^{-1}_{\varepsilon\to+0}.$$

The operator $\exp(-\beta\mathcal{H})$ can also be expressed through R_l^+, and the main idea of the method of calculating $\mathcal{D}_{AB}$ here consists in passing from the formal series $R_l^{\mp}$ in λ_0 (convergent for not too small ε) to a modified series $R_l^{\mp}$, taking into account the finite lifetime of the states $|sn^{(s)}\rangle$ (and convergent for all ε). For this it is essential that: a) the energy spectrum of the system, in the present case of the phonon subsystem, is continuous (finite branch width); b) there exist singular properties of the matrix elements, i.e.,

$$(sn^{(s)}|\mathcal{H}'\hat{\mathcal{L}}_1 \dots \hat{\mathcal{L}}_k\mathcal{H}'|s'n'^{(s')}) \sim \begin{cases} O(N^0), & \text{for } n = n', \\ O(N^{-z/2}), & \text{for } n \neq n', \end{cases} \tag{3}$$

where z is the number of phonon numbers differing in the sets n and n'; $\hat{\mathcal{L}}_i|sn^{(s)}\rangle = \mathcal{L}_i(sn^{(s)})|sn^{(s)}\rangle$; N is the number of ions (atoms) in the crystal; moreover, it is shown that, in the case considered here, which differs appreciably from the usually investigated ([8]) case, the modified series $R_l^{\mp}$ can be obtained by introducing special diagrams of transitions $sn \to s'n'$ and summing their contribution.

The modified expansion of $R_l^{\mp}$ has the compact matrix form

$$(\alpha_1|R^{\mp}|\alpha_2) = \mathcal{D}_l^{\mp}(\alpha_1)\delta_{\alpha_1\alpha_2} - (\alpha_1|D_l^{\mp}\cdot\hat{J}(\lambda_0\mathcal{H}'R_l^{\mp})|\alpha_2), \tag{4}$$

$$\mathcal{D}_t^{\pm}(\alpha_1) = \left(\varepsilon(\alpha_1) - l - \lambda_0^2 G_l^{\pm}(\alpha_1) + i\varepsilon\right)^{-1}\Big|_{\varepsilon\to+0}, \qquad G_l^{\pm}(\alpha_1) \equiv (\alpha_1|\{\hat{G}_l^{\pm}\}_d|\alpha_1),$$

$$\hat{G}_l^{\pm} = \widetilde{G}_l^{\pm} - \lambda_0\hat{J}\left(\mathcal{H}^{0'}\mathcal{D}_l^{\pm}\hat{G}_l^{\pm}\right), \qquad \hat{G}_l^{\pm} \equiv \mathcal{H}^{0'}D_l^{\pm}\mathcal{H}^{0'}, \tag{5}$$

where $\alpha \equiv (s, n^{(s)} = n)$; $\hat{J}(...)$ means that these relations have the meaning of iterative expansions in λ_0, in which: a) repeated, and those preceding in $D_l^{\pm}$, $|\alpha\rangle$, including $|\alpha_1\rangle$ and $|\alpha_2\rangle$, if only there is no condition $\{...\}_d$, when $\alpha_1 = \alpha_2$, are excluded; b) the sets n may be repeated for different $|s\rangle$.

III. The theory developed here is the theory of high-temperature transfer at low mobility of polarizing carriers, i.e., in the region of sufficiently high T ($> T_{\text{cr}}$, see below). A detailed analysis of expressions (4), (5) shows that (for $N \to \infty$, volume $\Omega \to \infty$, $\Omega N^{-1} = \text{const}$) the principal criteria for the applicability of the theory (i.e., the applicability of perturbation theory to the calculation of $\mathcal{D}_{AB}$) are the conditions

$$\eta \equiv \Delta_{\text{cp}}/\hbar\Gamma < 1, \qquad \zeta \equiv \Gamma/\omega_e < 1, \tag{6}$$

and in this sense η, ζ are small parameters of the theory. In (6)

$$\Delta_{\text{cp}} = \Delta_c^* \exp[-\Phi(T)], \qquad \Phi(T) = \sum_{fj}\frac{1}{2}\lambda_j(f)\,\text{cth}\,\frac{\beta\hbar\omega_{fj}}{2}, \tag{7}$$

$\Delta_c \equiv 2\nu|(s|\lambda_0\mathcal{H}^{0'}|s')|$ is the width of the band of the current carrier without allowance for lattice polarization (for example, of the electron); $\lambda_j(f) \equiv \frac{1}{2\hbar}\omega_{fj}(q_{fj}^s - q_{fj}^{s'})^2$; s, s', as above, are nearest π-sites, whose number is ν; Δ_{cp} and Γ are respectively the mean widths of the band and of the level (see (9)) localized in the carrier cell, with allowance for lattice polarization (small polaron $*$); ω_e is the characteristic phonon frequency (the choice of ω_e and the concrete form of $\lambda_j(f)$ are determined by the model). Since, for sufficiently strong electron-phonon coupling, $\Phi(0) = \sum_{fj}\frac{1}{2}\lambda_j(f) \equiv \frac{\lambda}{2} > 1$ and $\Phi(T)$ increases with T, so that Δ_{cp} rapidly decreases, while Γ usually (at appreciable T) increases with T, the condition $\eta < 1$ is realized at $T > T_{\text{cr}}$, if

$$\Delta_{\text{cp}}(T_{\text{cr}}) = \hbar\Gamma(T_{\text{cr}}). \tag{8}$$

1) The meaning of the criterion $\eta < 1$ may be seen in the fact that transfer is effected by transitions of a packet, localized in a cell, of waves of the polaron-band type (and of a similar small-polaron type) between cells, but

only if the lifetime of the packet in the cell $\sim \Gamma^{-1}$ is less than its mean spreading time $\sim \hbar/\Delta_{\text{cp}}$. In this sense this is a new type of polaron-band transport, distinct from band-wave transport (possible for a continuous phonon spectrum). 2) Since ω_e^{-1} is the characteristic time of lattice polarization, the criterion $\Gamma^{-1} > \omega_e^{-1}$, i.e., $\zeta > 1$, is the condition for quasistationarity of the state of lattice polarization around the carrier (electron) in the cell.

IV. Let us note also some principal results of the theory.

1. In the principal approximation, in an ideal crystal, for $H \neq 0$ and $H = 0$ (H is the magnetic field), the thermoelectric emf $\gamma = \frac{k}{e}\mu$, μ being the chemical potential; the thermal conductivity of the current carriers $\chi = 0$, and the coefficient of the transverse Nernst effect $Q_\perp = 0$ (the appearance of $\Delta\gamma \equiv \gamma - \frac{k}{e}\mu \neq 0$, $\chi \neq 0$, $Q_\perp \neq 0$ is possible in a nonideal crystal under certain conditions).

2. In the principal (in η and ζ) approximation of the theory:

$*$ In particular, formulas from (4–6) are obtained when only optical phonons are taken into account, with limiting frequency $\omega_0 = \omega_e$ and branch width $\Delta\omega(\ll \omega_0)$, when $\Phi(T) = \frac{1}{2}\lambda \operatorname{cth}(\beta\hbar\omega_0/2)$ and approximation (10) is applicable for $\Gamma(T)$ (T_{cr} is close to $\hbar\omega_0/2k$, and $T_0 \gg T_{\text{cr}}$ for $\lambda \gg 1$).

A. The general formula for $u(T) \equiv \overset{0}{u}(T)$ has the form

$$\overset{0}{u} = e\beta\mathcal{D}, \qquad \mathcal{D} = \delta^2\Gamma, \qquad \delta^2 \equiv (s|(x-a_s)^2|s), \qquad \Gamma = \lim_{l\to 0}\Gamma_l;$$

$$\begin{aligned}\Gamma_l(T) =& \frac{2\pi}{\hbar}\sum_{s'nn'} \exp(\beta F_0 - \beta\varepsilon(n)) \left|\left(sn^{(s)}\,|\lambda_0\mathcal{H}'|\,s'n'^{(s')}\right)\right|^2 \\ &\times \left[\delta(\varepsilon(n) - \varepsilon(n') + l) - \delta_{nn'}\delta(l)\right] \\ =& \frac{\Delta_c^2}{4\hbar^2\omega_e\nu}\int_{-\infty}^{\infty} d\xi\, \exp\left(\frac{il\xi}{\hbar\omega_e}\right) \\ &\times \left\{\exp\left[\sum_{fj}\lambda_j(f)\operatorname{csch}\frac{\beta\hbar\omega_{fj}}{2}\cos\left(\frac{\omega_{fj}}{\omega_e}\xi\right)\right] - 1\right\}\exp\left[-2\Phi(T) - \frac{\beta l}{2}\right].\end{aligned} \tag{9}$$

Expression (9) for $\overset{0}{u}(T)$ contains no divergence, and the exclusion of transitions $\{s \to s',\, n \to n' = n\}$ follows directly from the derivation independently of the model; the meaning of this exclusion is that only transitions $\{s \to s',\, n \to n' \neq n\}$ are responsible for the redistribution of energy and quasimomentum in transport phenomena in a system with a discontinuous phonon spectrum.

From (9) it is seen that, in the principal approximation, the mobility is due to independent jumps $\{s \to s', n \to n' \neq n\}$ of the current carrier; the dynamic and statistical correlation of transitions between cells is taken into account in higher approximations and, for $\eta < 1,\ \zeta < 1$, gives a small correction to $\overset{0}{u}(T)$.

In the region $T > T_{\text{cr}}$, for $\Phi(0) > 1$ and $\sum_{fj} \lambda_j(f) \operatorname{csch} \dfrac{\beta\hbar\omega_{fj}}{2} > 1$,

$$\Gamma(T) = \frac{\Delta_c^2\sqrt{\pi}}{8\hbar^2\nu}\left[\sum_{fj}\frac{1}{2}\lambda_j(f)\operatorname{csch}\frac{\beta\hbar\omega_{fj}}{2}\cdot\omega_{fj}^2\right]^{-1/2}\exp\left(-\frac{T_0}{T}\right);$$

$$T_0 \equiv \frac{1}{4k}\sum_{fj}\lambda_j(f)\hbar\omega_{fj} \equiv \frac{\mathcal{E}_0}{k}. \tag{10}$$

B. In the principal approximation (independent jumps) the Hall mobility $\overset{0}{u}_{xy}(T) = 0$ (as do the other antisymmetric coefficients $\overset{0}{\sigma}{}^{(a)}_{AB}$, in particular, the one determining the Faraday effect); hence it follows that if $u_{xy} \neq 0$, then this is due only to the correlation of transitions indicated above, taken into account in higher approximations, i.e., in any case, $|u_{xy}|\,\overset{0}{u}{}^{-1} \ll 1$ for $\eta < 1$ and $\zeta < 1$.

It follows from the formula for u_{xy} that, in accordance with point 2 of (10), the principal $u_{xy}(\neq 0)$ is determined by the correlation of transitions (the product of their matrix elements) from a real state $a(= sn) \to a''(= s''n'')$, with $\varepsilon_a = \varepsilon_{a''}$, and virtual states $a \to a'(= s'n') \to a''$ through an intermediate site s' (the Hall angle $u_{xy}u^{-1}$ may be $\ll uHc^{-1}$). This is valid under certain conditions also for the mobilities $u_{xx}(\omega)$, $u_{xy}(\omega)$ in a disordered system, in particular, for conduction by impurities in a semiconductor—here the “jumps” are accompanied by one-phonon transitions (weak coupling, cf. [11]).

Institute of Semiconductors
Academy of Sciences of the USSR

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Note: Figure translations are in progress. See original paper for figures.