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Physics

1965

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Abstract

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UDC 537.311.32

Physics

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ON THE FEATURES OF TRANSPORT AND RELAXATION PHENOMENA OF SMALL-RADIUS POLARONS

(Presented by Academician A. A. Lebedev, 16 February 1965)

1. In the present communication some essential features of relaxation and transport phenomena of localized small polarons in an ideal crystal with low mobility are discussed from a somewhat different point of view than in the quantum theory, developed in recent years, of transport phenomena of small polarons, small-radius polarons (and, in general, current carriers of this type) (see, for example, ^(1,2)).

Let us consider temperatures $T > T_0$ so high that (by the definition of T_0) the mean numbers of essential phonons $\bar{N}_{fj}(T) > 1$: in actual cases (for example, polarization phonons) for $T > T_0$ the “jump” mechanism determines the transport; for $T > T_0$ the polaron-phonon interaction (perturbation) \mathcal{H}_1 and the current $j_\mu = ev_\mu$ may be approximated by ^{(1)*}

$$\langle s_1 n_1 | \mathcal{H}_1 | s_2 n_2 \rangle \rightarrow \langle s_1 n_1 | \tilde{\mathcal{H}}_1 | s_2 n_2 \rangle \equiv \langle s_1 n_1 | \mathcal{H}_1 | s_2 n_2 \rangle \Big|_{n_1 \neq n_2},$$

$$\langle s_1 n_1 | j_\mu | s_2 n_2 \rangle \rightarrow \langle s_1 n_1 | \tilde{j}_\mu | s_2 n_2 \rangle = \frac{ie}{\hbar} \rho_\mu \langle s_1 n_1 | \mathcal{H}_1 | s_2 n_2 \rangle; \quad \rho \equiv s_2 - s_1; \quad (1)$$

v is the velocity operator; s is the vector of a site (cell); $\mu \equiv x, y, z$.

Generalizing Sewell's model ⁽⁴⁾, one may assume that for $T > T_0$ the basic unperturbed system, describing an electron strongly coupled with phonons (in a crystal with low mobility), is a small polaron (localized in some cell) and a classical equilibrium (in the theory ⁽¹⁾ the phonons are regarded as equilibrium phonon field Γ , whose Hamiltonians are \mathcal{H}_{pl} and \mathcal{H}_Γ : $\mathcal{H}_0 \equiv \mathcal{H}_{pl} + \mathcal{H}_\Gamma$.

The perturbation is determined by the action of fluctuations $\xi_\Gamma(t)$ of the phonon field on the small polaron and is described by the stochastic (polaron) operator $\hbar\hat{F}(t) \equiv \hbar\hat{F}[\xi_\Gamma(t)]$, where (in accordance with $\tilde{\mathcal{H}}_1$ from ⁽¹⁾)

$$\langle s_1 | \hat{F}(t) | s_2 \rangle \equiv \Delta_{12} Q_{12}(t); \quad \langle \hat{F} \rangle_{\Gamma} = 0; \quad \langle Q_{12}(t) Q_{21}(t') \rangle_{\Gamma} \neq 0;$$

$$\langle Q_{12}(t) Q_{23}(t') Q_{31}(t'') \rangle_{\Gamma} \neq 0; \quad \langle Q_{12}(t) Q_{23}(t') Q_{34}(t'') Q_{41}(t''') \rangle_{\Gamma} \neq 0, \quad (2)$$

where $\Delta_{12} \equiv \Delta_{s_1 s_2}$ is the electron transfer integral (and $\Delta_e \sim \Delta_{12}$ is the width of the initial electron band), which here is the initial small parameter of the model (see (8)), and $Q_{12} \equiv Q_{s_1 s_2}$ does not contain Δ_{12} . In addition,

$$\mathcal{H}_{pl} |s\rangle = \bar{\varepsilon}_0 |s\rangle, \quad [\mathcal{H}_{pl}, \mathcal{H}_{\Gamma}] = [\hat{F}, \mathcal{H}_{\Gamma}] = 0, \quad (3)$$

where $|s\rangle$ and $\bar{\varepsilon}_0 = \text{const}$ are the polaron states and term. Taking into account the usual

* The notation is the same as in (1): $|sn\rangle \equiv |s\rangle \cdot |n^{(s)}\rangle$ and $n \equiv (\dots N_{fj} \dots)$; $\varepsilon_{sn} = \varepsilon_n \sum_{fj} \hbar \omega_{fj} N_{fj}$ is the energy of the system (localized small polaron + phonons with “displaced” centers).

of the definition of the mobility tensor $u_{\mu\nu}(\omega)$ (3), calculating in it the trace in the basis $|s\rangle$, we obtain $u_{\mu\nu}$ in the form *

$$u_{\mu\nu} \equiv u_{\mu\nu}(\omega = 0) = |e| \beta \int_0^{\infty} dt \exp(-\varepsilon t) \text{Re} \langle v_{\nu}(0) U^+(t) v_{\mu}(t) U(t)^{pl} \rangle_{\Gamma}, \quad \varepsilon \rightarrow +0 \quad (4)$$

where \bar{A}^{pl} and $\langle A \rangle_{\Gamma}$ are, respectively, equilibrium averages over the polaron and phonon variables, for example, $\langle A \rangle_{\Gamma} = \text{Sp} \exp(\beta F_{\Gamma} - \beta \mathcal{H}_{\Gamma})$, $\beta \equiv 1/kT$; $U(t) \equiv \hat{T} \exp\{-i \int_0^t dt' \hat{F}(t')\}$, \hat{T} is the time-ordering operator; ω is the field frequency. Taking into account that $\langle s_1 | v_{\nu}(t) | s_2 \rangle \rightarrow i \rho_{\nu} \Delta_{12} Q_{12}(t)$, one can obtain regular expansions (in \hat{F}) for $u_{\mu\nu}$:

$$u_{\mu\nu} = \sum_{l_1=0}^{\infty} \sum_{l_2=0}^{\infty} u_{\mu\nu}^{(L)}, \quad u_{\mu\nu}^{(L)} \equiv u_{\mu\nu}^{(l_1+l_2)} = |e| \beta \sum_{\bar{\rho}_1 \dots \bar{\rho}_{l_1}} \sum_{\bar{\rho}'_1 \dots \bar{\rho}'_{l_2}} \rho_{1\nu}(\bar{\rho}'_{l_2} - \bar{\rho}_{l_1})_{\mu} I_{l_1 l_2} Z_{l_1 l_2}.$$

$$I_{l_1 l_2} \equiv \Delta_{0 \bar{\rho}_1} \Delta_{\bar{\rho}_1 \bar{\rho}_2} \dots \Delta_{\bar{\rho}_{l_1} \bar{\rho}'_{l_2}} \dots \Delta_{\bar{\rho}'_{l_2} 0};$$

$$Z_{l_1 l_2} \equiv \text{Re} \left\{ i^{l_1+l_2} (-1)^{l_2} \int_0^{\infty} dt \int_0^t dt_1 \dots \int_0^{t_{l_1-1}} dt_{l_1} \int_0^t dt'_{l_2} \dots \int_0^{t'_2} dt'_1 \hat{\Psi}_{l_1 l_2} \right\}, \quad (5)$$

$$\hat{\Psi}_{l_1 l_2} = \left\langle Q_{0\bar{\rho}_1}(0) Q_{\bar{\rho}_1 \bar{\rho}_2}(t_1) \cdots Q_{\bar{\rho}_{i_1} \bar{\rho}'_{i_2}}(t) \cdots Q_{\bar{\rho}'_{i_0}}(t'_1) \right\rangle_{\Gamma},$$

where, generally speaking, the correlators $\hat{\Psi}_{l_1 l_2}$ are complex functions. As in other stochastic models, it is assumed that correlators of equilibrium fluctuations of the type $\hat{\Psi}_{l_1 l_2} \rightarrow 0$ as $t \rightarrow \infty$ sufficiently rapidly, so that quantities of the type

$$\gamma \equiv \text{Re} \int_0^{\infty} dt \hat{\Psi}_{00}(t), \quad \delta \equiv \text{Im} \int_0^{\infty} dt \hat{\Psi}_{00}(t) \quad (6)$$

are finite, i.e., finite correlation times τ_{γ} and τ_{δ} exist. If one assumes, as appears natural (and in agreement with theory ⁽¹⁾), that the same τ_{γ} and τ_{δ} determine the characteristic correlation times for other $\hat{\Psi}_{l_1 l_2}$, then $\tau_{\gamma}, \tau_{\delta}$ (and γ, δ) are the principal parameters describing such a stochastic model of high-temperature transport of localized small polarons. If τ_{γ} and τ_{δ} differ substantially, then, taking into account (5), the form of the dependence $\Delta_{12}(H)$, and also from comparison with (1), that $\tau_{\delta} \approx \delta$ and $\tau_{\gamma} \geq \gamma$ (see (10)), one may, to order of magnitude, write ** ($H \parallel OZ$)

$$u_{xx}^{(L)}(H=0) \sim u_{xx}^{(0)} \left\{ c_L (w_e \tau_{\delta})^L + c'_L \tau_{\gamma}^{[L]} \tau_{\delta}^{L-[L]} w_e^L \right\}, \quad c_L \lesssim 1; \quad c'_L \lesssim 1,$$

$$u_{xy}^{(L)}(H \ll H_0) \Big|_I \sim \frac{H}{H_0} |e| \beta a^2 w_e^2 \left\{ b_L \tau_{\delta} (w_e \tau_{\delta})^L + b'_L (w_e \tau_{\delta})^L [\gamma \delta_{L,2l+1} + \tau_{\delta} \delta_{L,2l}] \right\}, \quad b_L \lesssim 1; \quad b'_L < 1, \quad (7)$$

$$u_{xx}^{(0)}(H=0) \sim u_0 \hbar \beta w_e^2 \gamma; \quad |u_{xy}^{(1)}(H \ll H_0)| \Big|_{\Gamma} \sim u_0 \frac{H}{H_0} \hbar \beta w_e^3 (b_1 \tau_{\delta}^2 + b'_1 \gamma \tau_{\gamma}),$$

where $w_e \equiv \Delta_e / \hbar$; $[L] \equiv \{L \text{ for } L = 2l; L - 1 \text{ for } L = 2l + 1\}$;

* Analogously, one can calculate any kinetic coefficient σ_{MN} of small polarons in this model under the action of weak “external” forces (allowance for Kubo-type formulas) ⁽³⁾.

** The index I denotes the case when, in the plane perpendicular to the magnetic field, three diagonal nodes may be mutually nearest neighbors, i.e. $|\Delta_{12}| \sim |\Delta_{23}| \sim |\Delta_{31}|$; II denotes the other case.

$u_0 = |e|a^2/\hbar$; $H_0 = \hbar c/|e|a^2$; a is the lattice constant ($u_0 \sim 1 \text{ cm}^2/\text{V} \cdot \text{sec}$ for $a \sim 3 \text{ \AA}$). In the case $\gamma < \tau_\delta < \tau_\gamma$ and $\gamma\tau_\gamma \ll \tau_\delta^2$ (as in ⁽¹⁾ for $T \ll \mathcal{E}/k$), in the main approximation in the small parameters $w_e\tau_\delta \ll 1$ and $w_e\tau_\gamma \ll 1$:

$$u_{xx} = u_{xx}^{(0)}(H = 0) \sim u_0 \hbar \beta \gamma w_e^2 \ll u_0;$$

$$|u_{xy}|_1 = u_{xy}^{(1)}(H \ll H_0)_1 \sim u_0 \frac{H}{H_0} \hbar \beta w_e^3 \tau_\delta^2 \ll u_0. \quad (8)$$

The mean charge currents I_μ and energy currents S_μ are connected by the simple formula

$$S_\mu \approx \tilde{\varepsilon} I_\mu; \quad \tilde{\varepsilon} = \text{const}; \quad \eta \approx \frac{1}{eT}(\xi - \tilde{\varepsilon}); \quad \chi_{\mu\mu} \ll T \sigma_{\mu\mu} \left(\frac{k}{e}\right)^2, \quad (9)$$

where ξ is the chemical potential, i.e., the energy transfer is basically of the convection type (η , χ , and σ are, respectively, the thermoelectric power, the thermal conductivity at zero current, and the electrical conductivity).

The estimates (8)–(9) and the criteria of the theory $w_e\tau_\gamma \ll 1$ and $w_e\tau_\delta \ll 1$ are equivalent to the estimates for $u_{\mu\nu}$, η , χ , and to the criteria of smallness of Δ_e from ⁽¹⁾, if one sets

$$\varepsilon \equiv \varepsilon_0 - \delta\varepsilon, \quad \delta\varepsilon \text{ is the binding energy of a small polaron,}$$

$$\gamma = \tau_\gamma e^{-\mathcal{E}/kT}; \quad \tau_\gamma = \hbar(\mathcal{E}/kT)^{-1/2};$$

$$\tau_\delta \approx \delta = \{\hbar/\mathcal{E} \text{ for } \mathcal{E} > kT; \hbar\beta \text{ for } \mathcal{E} < kT\}. \quad (10)$$

In such a model the structure of the terms of the expansions (7) for $u_{\mu\nu}$ is noticeably simpler than in ⁽¹⁾, and the estimate of the convergence criteria of the expansions supplements and confirms the criteria of smallness of Δ_e found in ⁽¹⁾ (for such small Δ_e the adiabatic correlation of the state of a small polaron with the lattice vibrations may be neglected) ⁽⁸⁾.

- Let us define the characteristic times τ_i of interaction and τ_c of current correlation as the damping times of the essential part, respectively, of the correlators of the perturbations \mathcal{H}_1 (for $H = 0$) and of the currents, and let us denote by τ_R the relaxation time of the carrier current.

As follows from the general expressions for the kinetic coefficients of the Kubo type ⁽³⁾, weakly nonequilibrium transport is determined by the character of the free relaxation in the system, and, as follows from ⁽¹⁾, for the transport of local small polarons at high T the character of the relaxation at small times $t \lesssim \tau_c \lesssim \tau_i \ll \tau_R$ is essential.*

In the case under consideration of equilibrium phonons it is convenient to consider the relaxation of the density matrix $R_{ss'}(t)$ of local small polarons, already averaged over phonons (for example, $R_{ss'}(t)$ describes the stochastic model of the system considered above).** It is natural to assume that the relaxation equation for $R_{ss'}(t)$ has the same form as for $R_{sn;s'n'}(t)$ according to ⁽⁶⁾***, and then, in the lowest approximation in \mathcal{H}_1 , the relaxation equation corresponding to it for the part even in H , $R_{ss'}^{(0)}(t, H) = R_{ss'}^{(0)}(t, -H)$, has the form

$$\frac{dR_{ss'}^{(0)}(t)}{dt} = \int_0^t dt' \sum_{s''} \{g_{ss''}^{(0)}(t-t')R_{s''s'}^{(0)}(t') - g_{s''s'}^{(0)}(t-t')R_{ss''}^{(0)}(t')\}, \quad (11)$$

$$g_{ss'}^{(0)}(t, H) = \sum_{nn'} \exp(\beta F_0 - \beta \varepsilon_n) \cos \omega_{nn'} t |\langle sn | \mathcal{H}_1 | s'n' \rangle|^2 = g_{ss'}^{(0)}(t, -H);$$

$$\omega_{nn'} = \frac{\varepsilon_n - \varepsilon_{n'}}{\hbar},$$

and describes the relaxation of small polarons during their diffusion by means of

* The times τ_c are different for quantities even and odd in H : for even $\tau_c \rightarrow \tau'_c = \tau_\gamma \sim \tau_i$, and for odd $\tau_c \rightarrow \tau''_c \sim \tau_i$.

** One may assume that the perturbation F is also dissipative in the sense of Van Hove.

*** At large $t \sim \tau_R$ the relaxation of small polarons is mainly Markovian; an essential contribution to it is made by the non-Markovian features of the process (11) at times of order t .

simplest two-site independent “hops.” However, even for $t \lesssim \tau_i$ the transition matrix $g_{ss'}^{(0)}(t)$ does not contain a contribution from coherence of the interactions, and the phase “memory” is due only to the time dependence $\cos(\omega_{mn}t)$; therefore the non-Markovian features of the process (11) at times of order t should not be significant. On the contrary, for $t \lesssim \tau_i$ the higher approximations $g_{ss'}^{(L)}$ with

$L \geq 1$ also describe non-Markovian relaxation processes of small polarons with correlation “memory,” due to interference of perturbations in $(L + 1)$ -site hops. For small $H \ll H_0$, putting $R_{ss'}^H = R_{ss'} + \frac{H}{H_0} \delta R_{ss'}$ (to first order in H/H_0), we obtain, in the first nonvanishing approximation in \mathcal{H}_1 , for the odd-in- H part $\delta R_{ss'}$

$$\frac{d\delta R_{ss'}^{(\lambda)}(t)}{dt} = \int_0^t dt' \sum_{s''} \left\{ (\overline{\delta g_{ss''}}(t-t'))_\lambda \delta R_{s''s'}^{(\lambda)}(t') - (\overline{\delta g_{s''s'}}(t-t'))_\lambda \delta R_{ss''}^{(\lambda)}(t') \right\}, \quad (12)$$

$\lambda \equiv \text{I or II}$, where for case I $(\overline{\delta g_{ss''}})_I = (\delta g_{ss''}^{(1)})_{I,l}$, and for case II $(\overline{\delta g_{ss'}})_{II} \equiv (\delta g_{ss'}^{(1)} + \delta g_{ss'}^{(2)})_{II}$; $\delta g_{ss'}^{(l)} \propto \mathcal{H}_1^l$.

For sufficiently small Δ_e (see (8)), equations (11), (12) describe, in the main approximation, the relaxation process of local small polarons, on the whole non-Markovian (for times $t \lesssim \tau_i$ essential for transport) and due to “hops.” When a weak electric field F_x is applied, an ordered diffusion of current carriers and a finite mobility $u_{x\nu}$ arise (for the same relaxation processes): for $|eF_x \rho_x| \ll kT$, $|\rho_x| \sim a$

$$u_{x\nu} \Big|_{\nu=x,y} \simeq \frac{|e|\beta}{q^{(\nu)}} \sum_{\bar{\rho}} \rho_\nu \rho_x g_{\bar{\rho}}^{(\nu)} \sim u_0 \hbar \beta \Omega_{(\nu)} \ll u_0, \quad (13)$$

where $q^{(\nu)}$ is determined by the number b_ν of sites (cells) “participating” in the elementary act (i.e. $b_x = 2$; $(b_y)_I = 3$, etc.);

$$\Omega_\nu \equiv \sum_{\bar{\rho}} g_{\bar{\rho}}^{(\nu)}, \quad g_{\bar{\rho}}^{(x)} \equiv \int_0^{\tau_i} dt g_{0\bar{\rho}}^{(0)}(t); \quad (g_{\bar{\rho}}^{(y)})_\lambda \equiv \frac{e}{|e|} \frac{H}{H_0} \int_0^{\tau_i} dt (\overline{\delta g_{0\bar{\rho}}}(t))_\lambda, \quad \lambda \equiv \text{I or II}; \quad (14)$$

relations (13), (14) are analogous to (8).

In the stochastic model of the nonequilibrium type considered, at high temperatures the transport of small polarons has, in the main, the character of diffusion by means of hops under the action of thermal fluctuations. This transport is determined, in contrast to ordinary (for example, Brownian) diffusion*, by the velocity correlations $\Psi_{\mu\nu}(t)$ at small times $t \ll \tau_R$ and is governed by an equation that takes into account the non-Markovian features of transport of this type. Moreover, the principal part of $\Psi_{\mu\nu}(t)$ for $u_{\mu\nu}$ is, for essential $t \lesssim t_c$, $\Psi_{\mu\nu}^{(p)}(t) \propto \exp(-qt^2) P_{\mu\nu}(t)$, where $P_{\mu\nu}(t)$ is a certain complicated oscillating function (for sufficiently small t , $\Psi_{\mu\nu}^{(p)}(t)$ decreases with t in a Gaussian manner), and similarly for $\hat{\Psi}_{00}(t)$ from (6) (see (1, 8)).

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Received
9 II 1965

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* For classical hopping diffusion (7), the substantial decay of the correlator $\Psi_{xx}(t)$ at large $t \sim \tau_R \gg \tau_i$, i.e. $t_c - \tau_R$, is essential; the relaxation and transport are described by a Markov process and $u_{xx} \sim u_0 \hbar \beta \tau_R^{-1}$, for $\Psi_{xx}^{(p)}(t) \sim (a^2/\tau_R^2) \exp(-t/\tau_R)$.

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

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