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CONTRIBUTION TO THE THEORY OF PHONON-ASSISTED TRANSFER OF ELECTRONIC EXCITATION ENERGY

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The probability of the transfer of electronic excitation energy between impurities in a solid via the virtual phonon field is calculated within the framework of perturbation theory. The transition probability is $W \backsim (\delta/\Delta)^{2n}/n^2$, where n (a multiple of the lattice constant) is the distance between impurities, δ is the phonon band width, and Δ is the energy difference between the electron and phonon levels. This mechanism can be important for the transfer of low-lying electronic and electron-vibrational excitations.

V. R. NAGIBAROV and I. A. Nagibarova have treated the problem of the transfer of electronic excitation energy between impurities in a solid via the virtual phonon field.[1] However, their result, a power-law dependence of the transfer probability W on the distance R between impurities ($W \backsim R^{-4}$), is incorrect when the electronic excitation energy exceeds the maximum phonon energy. We shall show that $W \backsim e^{-\alpha R}$ holds true in both the one-dimensional and three-dimensional cases, and that this result is directly associated with the analytic properties of the function $\omega^2(k)$, where ω and k are the frequency and quasimomentum of the phonons.

1. STATEMENT OF THE PROBLEM

We shall consider two impurity atoms[1)] a and b in a crystal lattice. The separation of these atoms is taken to be large enough so that any exchange interaction between them can be neglected. Let the electronic excitation energy of the crystal differ greatly from the impurity excitation levels, so that energy transfer via virtual excitons will be ineffective.[2-4] We shall also neglect direct transfer of energy between a and b via inductive resonance[1].

The Hamiltonian of the system is

$$\hat{H} = \hat{H}_{ea}(\mathbf{r}_a, \mathbf{R}) + \hat{H}_{eb}(\mathbf{r}_b, \mathbf{R}) + \hat{H}_f. \tag{1}$$

Here $\hat{H}_{ea}(\mathbf{r}_a, \mathbf{R})$ and $\hat{H}_{eb}(\mathbf{r}_b, \mathbf{R})$, the Hamiltonians of the electron systems of atoms a and b, depend on the atomic electronic coordinates $\mathbf{r}_a$ and $\mathbf{r}_b$ and on the lattice-atom coordinates R; $\hat{H}_f$ is the lattice Hamiltonian (i.e., the phonon Hamiltonian). We shall assume that the phonon spectrum and wave functions are independent of the electronic states of the impurity atoms; we thus assume only a weak electron-phonon interaction (for electrons of the impurities). We then have the conventional equation

$$\hat{H}_e(\mathbf{r}, \mathbf{R}) = \hat{H}_e(\mathbf{r}, \mathbf{R}^0) + \sum_p \left.\frac{\partial \hat{H}_e}{\partial \mathbf{R}_p}\right|_{\mathbf{R}_p = \mathbf{R}_p^0} \delta \mathbf{R}_p, \tag{2}$$

where R_p^0 represents the equilibrium coordinates of the lattice atoms. The second term in the right-hand member of (2) will be considered a perturbation that induces transitions between the eigenstates of $\hat{H}_0$, where

$$\hat{H}_0 = \hat{H}_{ea}(\mathbf{r}_a, R^0) + \hat{H}_{eb}(\mathbf{r}_b, R^0) + \hat{H}_f. \tag{3}$$

The perturbation operator is

$$\hat{V} = \sum_p \left.\frac{\partial \hat{H}_{ea}(\mathbf{r}_a, \mathbf{R}_p)}{\partial \mathbf{R}_p}\right|_{\mathbf{R}_p = \mathbf{R}_p^0} \delta \mathbf{R}_p + \sum_p \left.\frac{\partial \hat{H}_{eb}(\mathbf{r}_b, \mathbf{R}_p)}{\partial \mathbf{R}_p}\right|_{\mathbf{R}_p = \mathbf{R}_p^0} \delta \mathbf{R}_p. \tag{4}$$

The initial state of the system is $|i\rangle = |0_a\rangle|1_b\rangle n_k\rangle$, and its final state is $|f\rangle = |1_a\rangle|0_b\rangle|n_k\rangle$, where $|0_{a,b}\rangle$ is the ground state of the impurity a or b, and $|1_{a,b}\rangle$ is the excited state of a or b. (Assuming nondegenerate excited impurity states for simplicity). We shall consider the resonant transfer of energy ($E_i = E_f$); therefore the phonon populations n_k will not be changed. Then the energy transfer probability W_{ab} in second order of perturbation will be

$$W_{ab} = \frac{2\pi}{\hbar} \left| \sum_l \frac{\langle f|\hat{V}|l\rangle\langle l|\hat{V}|i\rangle}{E_f - E_l} \right|^2 \nu(E_f), \tag{5}$$

where $\nu(E_f)$ is the final-state density per unit energy interval.

Expanding δR_p in (4) in terms of the creation operators a_k^+ and annihilation operators a_k, we have

$$\delta \mathbf{R}_p = \sum_{\mathbf{k},\mu} \mathbf{e}_{\mathbf{k},\mu} (a_{\mathbf{k},\mu} e^{i\mathbf{k}\mathbf{R}_p} + a_{\mathbf{k},\mu}^+ e^{-i\mathbf{k}\mathbf{R}_p}) \left(\frac{\hbar}{2M\omega_{\mathbf{k},\mu}} \right)^{1/2} \tag{6}$$

(k is the phonon quasimomentum, μ is the phonon branch index, $\omega_{k,\mu}$ is the frequency, $e_{k,\mu}$ is the unit polarization vector, M is the crystal mass); substituting (6) and (4) in Eq. (5), we obtain, after some elementary transformations,

$$W_{ab} = \frac{2\pi}{\hbar} \left| \frac{\hbar^2}{\rho\Omega} \sum_{p',p} \alpha_{p'}^{\nu} \alpha^{\delta}_{p} \sum_{\mathbf{k},\mu} T_{\nu\delta}(\mathbf{k}, \mu) \frac{\cos(\mathbf{k}\mathbf{R}_{p'p})}{E^2 - \hbar^2\omega_{\mathbf{k},\mu}^2} \right|^2 \nu(E_f). \tag{7}$$

Here

$$\alpha_p{}^{\delta} = \left\langle 0_a \left| \frac{\partial \hat{H}_{ea}(\mathbf{r}_a, \mathbf{R}_p)}{\partial R_p{}^{\delta}} \right| 1_a \right\rangle, \quad \alpha_{p'}{}^{\nu} = \left\langle 1_b \left| \frac{\partial \hat{H}_{eb}(\mathbf{r}_b, \mathbf{R}_{p'})}{\partial R_{p'}{}^{\nu}} \right| 0_b \right\rangle,$$
$$T_{\nu\delta}(\mathbf{k}, \mu) = e_{\nu}(\mathbf{k}, \mu) e_{\delta}(\mathbf{k}, \mu), \tag{8}$$

E is the impurity electronic excitation energy, $R_{p'p} = R_p - R_{p'}$, Ω is the crystal volume, and ρ is the crystal density.

[1)] Only atoms are mentioned for the sake of simplicity, but these could be replaced by molecules.

2. CALCULATION OF THE TRANSFER PROBABILITY

Let us consider in greater detail the quantity

$$I_\mu = \frac{1}{\Omega}\sum_{k}{}' T_{\gamma\delta}(\mathbf{k},\mu)\frac{\cos(\mathbf{k}\mathbf{R}_{p'p})}{E^2-\hbar^2\omega^2_{\mathbf{k},\mu}}\ .$$

Converting the summation into an integral, we obtain

$$I_\mu = \mathrm{Re}\frac{1}{(2\pi)^3}\int T_{\gamma\delta}(\mathbf{k},\mu)\frac{\exp(i\mathbf{k}\mathbf{R}_{p'p})}{E^2-\hbar^2\omega^2_{\mathbf{k},\mu}}\,dk. \tag{9}$$

We shall assume $E > \hbar\omega_{\mathbf{k},\mu}$. We cannot integrate (9) in its general form, since the analytic function $\omega^2_\mu(\mathbf{k})$ is unknown. However, $\omega^2_\mu(\mathbf{k})$ is a periodic function of $\mathbf{k}$ with the period of the reciprocal lattice, and is analytic for real values of $\mathbf{k}$ except perhaps at the branch points. Equation (9) gives essentially a Fourier coefficient in the expansion of a function $T_{\gamma\delta}(\mathbf{k},\mu)/[E^2-\hbar^2\omega^2_\mu(\mathbf{k})]$, which is periodic and analytic for real values of $\mathbf{k}$. Then as $n = R/d$ increases the Fourier coefficient decreases exponentially.[2] Therefore when $\omega^2_\mu(\mathbf{k})$ is replaced in (9) by any approximate expression we must be careful not to introduce any additional singularities (see[6] regarding this aspect). In[1] $\omega^2_\mu(\mathbf{k})$ was replaced by a Debye approximation, leading to a discontinuity of $d\omega^2_\mu(\mathbf{k})/dk$ at the Brillouin zone boundary. The power-law dependence of W on R was derived in this way.

We shall now attempt to evaluate I_μ. We select the axis $x \parallel R_{pp'}$, and assume that $\omega^2_\mu(\mathbf{k})$ has the period $k^0_\alpha \sim 2\pi/d$ in the x direction, where d is the lattice period, and can be expanded in a Fourier series:

$$\omega_\mu{}^2(k_x,k_y,k_z) = \sum_n A_{n\mu}(k_y,k_z)\cos\left(\frac{2\pi n k_x}{k_x{}^0}\right). \tag{10}$$

We now have

$$I_\mu = \mathrm{Re}\left(\frac{1}{2\pi}\right)^3\iint dk_y\,dk_z\int dk_x\,T_{\gamma\delta}(k_x,k_y,k_z,\mu)\frac{\exp[ik_xR_{pp'}]}{E^2-\hbar^2\omega_\mu{}^2}, \tag{11}$$

where ω^2_μ is given in (10).

The integral in (11) is taken over one cell of the reciprocal lattice. With the aid of (10) it can be shown that all the poles of the integrand in (11) are symmetrically located with respect to the real axis in the complex k_x plane. Shifting the path of integration into the complex k_x plane and including the contribution of only the nearest pole, we obtain

$$I_\mu = \mathrm{Re}\frac{1}{8\pi^2}\iint dk_y dk_z\,T_{\gamma\delta}(k_y,k_z,\widetilde{k}_x,\mu) \times\frac{\exp[-\widetilde{k}_x{}''(k_y,k_z)R_{pp'}+i\widetilde{k}_x{}'(k_y,k_z)R_{pp'}]}{(E-\varepsilon_\mu)\hbar\partial\omega(k_y,k_z,k_x)/\partial k_x|_{k_x=\widetilde{k}_x}}, \tag{12}$$

where ϵ_μ is the average energy of the μ-th phonon band, and $\widetilde{k}_x(k_y,k_z) = \widetilde{k}'_x + i\widetilde{k}''_x$ is a pole of the integrand in (11). We have, in order of magnitude,

$$\widetilde{k}_x{}'' \approx \frac{1}{d}\ln\frac{E^2-\varepsilon_\mu{}^2}{2\varepsilon_\mu\delta}, \tag{13}$$

where δ_μ is the width of the μ-th phonon band. Most of the contribution to (12) comes from the region near the minimum of $\widetilde{k}''_x(k_y,k_z)$ in the (k_y,k_z) plane. By the method of steepest descent we obtain

$$I_\mu = AT_{\gamma\delta}\frac{1}{E^2-\varepsilon_\mu{}^2}\frac{1}{d^2R}\exp(-k''R)\cos(k'R), \tag{14}$$

where A is a numerical coefficient of the order of unity, while k'' and k' are the minimal values of $\widetilde{k}''$ and $\widetilde{k}'$.

We emphasize that (14) is applicable to both optical and acoustic phonons, because I_μ is determined by a pole of the integrand in (11) that lies in the complex k_x plane for any phonon branch. For acoustic phonons k' is close to the boundary of the Brillouin zone, and for the optical branches k' varies, within the boundaries of the zone, depending on the energy-spectral structure of the particular branch.

For the acoustic phonon branch in the one-dimensional case $[\omega_k = 2cd^{-1}\sin(kd/2)|]$ we can calculate I exactly; if $E \gg \epsilon = 2\hbar c/d$ (where c is the velocity of sound) we have

$$I = \frac{1}{d}\frac{1}{E^2}\left(\frac{\varepsilon}{E}\right)^{2R/d}. \tag{15}$$

3. CALCULATION OF THE ELECTRON-PHONON INTERACTION AND THE FINAL FORM OF W_{ab}

The final form of W_{ab} as a function of R_{ab} depends essentially on the behavior of α_p and $\alpha_{p'}$ as functions of the separation distances $R_a - R_p$ and $R_b - R_{p'}$. Let us consider

$$\alpha_p{}^\delta = \left\langle 0_a\left|\frac{\partial\hat{H}_{ea}(\mathbf{r}_a,\mathbf{R}_p)}{\partial R_p{}^\delta}\right|1_a\right\rangle.$$

After expanding $H_{ea}(r_a, R_p)$ in a series of multipole interactions and retaining only the lowest nonvanishing multipoles (the l-th multipole for the $\langle 0_a|r^l|1_a\rangle$ transition and the s-th multipole moment for the lattice atom field), we obtain

$$\alpha_p{}^\delta = \eta_p{}^\delta\frac{\hbar^{1/2}\lambda^{l+1/2}}{(2\pi)^{l+1/2}\tau_a^{1/2}}\mathscr{E}\frac{d^{s+2}}{|\mathbf{R}_p-\mathbf{R}_a|^{l+s+2}}, \tag{16}$$

where η_p is a vector having a modulus of the order of unity, λ is the wavelength for the transition $|0_a\rangle \longleftrightarrow |1_a\rangle$, τ_a is the radiation lifetime of the $|1_a\rangle$ state, d is the lattice period, and $\mathscr{E}$ is the crystal-lattice field.

If excitation energy is transferred between an exchange pair and an impurity atom (or ion),[1] we have

$$\alpha_p^{x,y,z} = \delta(\mathbf{R}_p-\mathbf{R})\frac{R_{x,y,z}}{dR}\varepsilon_{\text{обм}}, \tag{17}$$

where $\mathbf{R}$ is the radius vector between the two atoms of the exchange pair and ϵ_{exch} is the splitting of the pair level.

It is difficult to sum exactly with respect to p and p′. However, since, according to (16), α_p decreases rapidly as $|R_a - R_p|$ increases, the summation in (17) will be limited to only the lattice atoms that are closest to the impurities. Then, inserting (16) and (14) into (7), we obtain [assuming $l = 1$ in (16)]

$$W_{ab} = \frac{\hbar^5\nu(E)}{(2\pi)^6}\frac{N_a{}^2N_b{}^2}{\rho^2}\frac{1}{\tau_a\tau_b}\mathscr{E}^4\frac{1}{(E^2-\varepsilon_\mu{}^2)^2} \times\frac{1}{d^2}\left(\frac{\lambda}{d}\right)^6\frac{\exp(-2k''R_{ab})\cos(k'R_{ab})}{R_{ab}{}^2} \tag{18}$$

where N_a and N_b are the coordination numbers of the atoms a and b.

The mechanism of transfer via virtual phonons can be important only when the electronic excitation energy is not too greatly different from the phonon energy $[(E-\epsilon_\mu)/\delta_\mu \gtrsim 1]$, in which case the argument of the exponent in (18) is not too large. In order to evaluate

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[2] It can be shown that if all branches of the phonon spectrum are included the contribution of the branch points in (9) will vanish.

the effectiveness of the energy transfer mechanism under consideration we now evaluate the ratio κ between the probability of such transfer and the probability of inductive resonance transfer

$$\varkappa = \frac{\hbar^4 \mathscr{E}^4 d^2 N_a{}^2 N_b{}^2}{m^2 E^2 (E-\varepsilon_\mu)^2} n^4 \left(\frac{\delta^\mu}{E-\varepsilon_\mu}\right)^{2n} \tag{19}$$

where $n = R/d$ and m is the mass of a unit cell. For the usual electronic excitations amounting to a few electron volts and phonon energy of the order 10^{-1} eV we have $\kappa \ll 1$ and the given mechanism is ineffective.

However, our entire discussion is applicable to an excited impurity state that is equivalent to a local optical vibration. In this case the impurity excitation energy and the energy of an optical (or acoustic) phonon are often close in actual practice, and the considered energy transfer mechanism can play a large role. Thus, for $E = 0.1$ eV, $E - \epsilon_\mu = \Delta = 0.001$ eV, $\mathscr{E} = 10^7$ V/cm, $m = 5 \times 10^{-23}$ g, $d = 3 \times 10^{-8}$ cm, and $N_a = N_b = 6$ we shall have $\kappa \approx n^4(\delta/\Delta)^{2n}$, and for $\delta/\Delta = 0.8$ we shall have $\kappa > 1$ when $n < 10$.

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