Crossover of large to small radius polaron in ionic crystals

M I Umo†

Department of Physics, University of Calabar, PMB 1115, *Nigeria*

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The crossover of large to small radius polaron is studied in terms of the inverse-relaxation time and temperature. It is found that the small radius polaron exists at higher temperature than the large radius polaron. A formula which relates the inverse-relaxation time to the ratio of arbitrary temperature and Debye temperature of the crystal is derived. The polaron crossover temperatures in NaCl and KBr are found from plotted graphs. The straight line emerging at the Debye temperature $T_{\rm D}$ of a graph reflects the increase of the inverse relaxation time for increasing temperature up to the collapse of the small radius polaron. The relationship between the small and large radius polarons is found and known ratios of the effective and the bare masses of the electrons for the two substances are used to validate our results. The small radius polaron's mass is later compared with the mass obtained from the hopping formula and is found to be approximately equal. Finally, we point out that the crossover temperature is material-specific since it depends on the Debye and the effective dielectric function.

Keywords: large radius polaron, small radius polaron, inverse relaxation time, electron–phonon interaction

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1. Introduction

Polarons were first proposed by Landau in 1933 in Ref. [1], where the motion of an electron in ionic crystals was discussed and the study of polarons in NaCl in terms of the activation energy was proposed. A series of contributions by many researchers have been made since then, significantly by Pekar,[2] Fröhlich,[3] Landau and Pekar[4] and Feynman.[5] We shall define the Landau–Pekar–Fröhlich polaron as an electronic perturbation of ionic (and polar) crystals in such a way that the polarized lattice interacts and moves non-inertially with the electron as one entity. In polaron study, Pekar considered a variational treatment of its ground state trial wave function and obtained the calculated polaron's radius, ground state energy, coupling constant, and mass. Each of these quantities and their values has attracted attention ever since and has been used in various ways to extend and deepen the theory. Of interest is the coupling constant α which is proportional to the phonon number in the polaron: when $\alpha \geq 6$, one has a strong coupling polaron; if $1 < \alpha < 6$, an intermediate coupling polaron exists; and if $\alpha < 1$, a weak coupling polaron exists. In this paper, the small radius polaron (SRP) and the large radius polaron (LRP) are identified. The experimental facts about polarons that are important in this paper are the following: the linear size of the SRP is one lattice spacing or less, while that of the LRP is a few lattice spacings. Thus there is a reason for the motion of the SRP to be by hoping and that of the LRP to be a smooth continuous translation through the lattice. The SRP mass is greater than the LRP mass and the SRP exists at higher temperature than the LRP. Among the properties which define the state of polarons are the electron–phonon coupling constant λ, the polaron coupling constant α, the adiabatic and anti adiabatic conditions and, we may add, the Debye temperature, the effective dielectric constant ε^* and the relaxation time.

New directions and mathematical methods have been developed and employed to make qualitative improvements in the values of the quantities corresponding to the polaron's properties. The mathematical methods used in such calculations include path integrals,[6] Green's functions with diagram technique[7] and its offshoot, and the diagrammatic quantum Monte Carlo algorithm (DQMC). In addition to the polaron mass and the properties mentioned earlier, other physical quantities such as mobility, activation energy, and conductivity have received much attention in recent years.[8,9] The polaronic explanation of many processes and phenomena in metals, metallic oxides, semiconductors, and nano-systems are very topical today.[10] For example, the adoption of the concept of polarons as charge carriers gives a meaningful interpretation of the experimentally observed optical conductivity spectra, ferromagnetism, blue and green light emission, and superconductivity in $SrTiO_3$.[11] However, the question of which type of polarons (i.e., large or small) is involved is controversial. A Japanese research team[12] has used the small radius polaron (SRP) to explain superconductivity in LaFe $AsO_{1-x}F_x$ at low temperature. However, in this paper, once again we experience some confusion about the temperature range of existence of the two polaron types. We need to elucidate the temperature at which an SRP or LRP exists in a given material and the temperature direction of their crossover. In this work, starting from a high temperature $T \leq T_{\rm D}$, where $T_{\rm D}$ is the Debye temperature of the material, we shall show that the polaron crossover temperature $T_{\rm pc}$ can be accessed from the SRP side before the LRP region is accessed. Thus,

†Corresponding author. E-mail: umohphy@yahoo.co.uk

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we find that $T_{pc} \approx T_D/2$ for all materials exhibiting polaron crossover. The crossover of polarons may be studied by some parameters peculiar to the polaron states. Such studies have been carried out on ionic crystals such as KCl, LiF, and LiCl in terms of optical absorptions, thermopower measurements and dc conductivity.[13] The polaron crossover temperature has been observed at $T_{pc} = 130$ K in WO_{3-x} while transiting from the SRP to LRP regions. This result sets the Debye temperature of tungsten trioxide at approximately 300 K. Measurements of the Seebeck coefficient of oxygen deficient BaBiPbO compound reveal a polaron crossover temperature around 200 K.[13] From these studies, one observes that the transition or crossover from SRP to LRP is not a matter of mere extrapolation from the SRP, but a rather serious physics which arises from the complex dynamical behavior of the system.[14] In general, the SRP and LRP are similar in nature to the Holstein or molecular crystal polarons which only occur in one dimension.[15] However, in the present paper, we shall study the polaron crossover in terms of the traditional inverse relaxation time which is directly related to the transition probability $W(\boldsymbol{k}, \boldsymbol{k}')$ of the electron–phonon interaction. This interaction can be elastic or inelastic. At high temperature, the absorption and emission of phonons by electrons occur elastically, so that when equilibrium is established and under suitable conditions (adiabatic or anti-adiabatic) polarons are formed. At low temperature, the electron–phonon interaction only allows for a predominant absorption of phonons. This situation does not auger well for polaron formation, but since polarons nevertheless are observed at such low temperature, phonon emission must take place albeit delayed.[2] Therefore, the electron–phonon interaction in the low temperature regime could also be assumed to be elastic with the condition that the limit of any integral that appears must be worked out from the now slightly different energy conservation delta function of the Fermi golden rule. In recent times, the study of the polaron crossover has received a lot of stimuli through the work of Zoli and Das.[16] The polaron crossover from large to small was studied in one, two, and three dimensions through the behavior of the effective mass. At the crossover, the polaron effective mass was estimated to be of the order of 5–50 times the electron mass in accordance with the dimension and the value of the adiabatic parameter. The authors used the modified Lang–Firsov (MLF) transformation to obtain the polaron mass enhancement factor. The polaron mass enhancement is accompanied by a reduction of the polaron size. A good indicator of the crossover can be served by the electron–phonon (el–ph) correlation function.

For the molecular theory of the polaron, Holstein adopted the discrete non-linear Schrodinger equation for electrons, in which the el–ph coupling g controls the nonlinearity. The el–ph coupling strength then drives the polaron crossover from the LRP to the SRP for a given value of the adiabatic parameter.[6,17] Another use of the MLF in conjunction with phonon averaging in the study of the crossover of polarons is the paper of Choudhury and Das[19] in which one dimensional material was investigated. Their results agree well with the numerical analyses using density matrix renormalization group (DMRG) particularly in the low and intermediate range of el–ph coupling. Polaron crossover has also been studied in the adiabatic region by means of the spectral function $A(k,w)$, which is the imaginary part of the retarded single particle Green function. When the polaron crossover region is approached at intermediate el–ph coupling, the spectral function exhibits multiphonon resonances at low energy.[20,21]

Additionally, we note the experimental results of Lanzara *et al.*,[22] which supported the crossover of the large to small polarons across a metal–insulator (MI) transition. The experiment was carried out with Mn K-edge x-ray absorption on $La_{0.75}Ca_{0.25}MnO_3$ up to high momentum transfer across the metal–insulator transition. The data has been interpreted as a crossover of the large polaron characterized by a long Mn–O bond in the metallic phase at $T < 170$ K, into the small polaron at $T > 170$ K, characterized by a longer Mn–O bond.

The significance of the relaxation time can be traced to the adiabatic and anti-adiabatic conditions of polaron formation. The adiabatic condition states that for the formation of the strong coupling polaron, it is necessary that the electron in the potential well of the polaron moves faster than the heavy lattice ion,[2] i.e., $\tau_e = r_0/v \ll 1/w$ or equivalently $\tau_e \ll \tau_{ion}$ where τ_e and τ_{ion} are the electron and ion time of motion, respectively over the same distance r_0, v is the electron velocity and w is the ionic optical frequency. The anti-adiabatic condition is the reverse of the adiabatic. The rest of this paper is organized as follows. In Section 2, we derive the transition probability in terms of the full screening of the ion by the polaron's electron. Section 3 deals with the Boltzmann transport equation in the elastic and inelastic continuum, the formula for the inverse relaxation time is obtained in terms of the ratio T/T_D and the curves of inverse relaxation time versus temperature are plotted for two substances. In Section 4, we obtain a simple relationship between the LRP and SRP, and explicit values of the ratio of masses are obtained and verified. Section 5 examines the hopping motion of the SRP and uses the mass of the SRP found thereby to check against the masses in Section 4. The conclusion is given in Section 5.

2. Electron–phonon transition probability

Let us start with the Fermi golden rule which states that the transition probability of a particle from the initial energy state m to the final energy state n for the electron–phonon interaction is

$$W_{mn} = \frac{2\pi}{\hbar} \left| \langle n | \mathcal{H}_{e-p} | m \rangle \right|^2 \delta \left(E_n - E_m \mp \hbar\omega_1 \right), \qquad (1)$$

where $\hbar\omega_{\rm l}$ is the phonon energy. In particular, we may designate the electron initial state by $|k\rangle$ and final state by $|k'\rangle$, the phonon initial state by $|N_q+1/2\rangle$, and final state by $|N_q+1/2\mp1/2\rangle$, and then the expressions for the electron–phonon initial and final states are $|k,N_q+1/2\rangle$ and $|k',N_q+1/2\mp1/2\rangle$, respectively. An example of the electron–phonon Hamiltonian is the Fröhlich model Hamiltonian

$$\mathcal{H}_{\rm Fr}=-{\rm i}\left(\frac{2\pi e^2\hbar\omega_{\rm l}}{\epsilon^*}\right)^{1/2}\sum_q\frac{1}{q}\left(b_q\,{\rm e}^{{\rm i}qr}-b_q^+\,{\rm e}^{-{\rm i}qr}\right). \quad (2)$$

We make a notation that

$$A=-{\rm i}\left(\frac{2\pi e^2\hbar\omega_{\rm l}}{\epsilon^*}\right)^{1/2},\quad \frac{1}{\epsilon^*}=\frac{1}{\epsilon_\infty}-\frac{1}{\epsilon_0}, \quad (3)$$

where $\omega_{\rm l}$ is the longitudinal optical frequency and $1/\epsilon^*$ is the inverse effective dielectric function obtained from the high frequency dielectric function ϵ_∞ and the static dielectric constant ϵ_0, and then $H_{\rm Fr}$ can be written as

$$\mathcal{H}_{\rm Fr}=A\sum_q\frac{1}{q}\left(b_q\,{\rm e}^{{\rm i}qr}-b_q^+\,{\rm e}^{-{\rm i}qr}\right), \quad (4)$$

which can be substituted in Eq. (1) in place of $H_{\rm e-p}$. Taking note of the electron–phonon states, we have the transition probability

$$\begin{aligned}W_{\rm tr}&=\frac{1}{\hbar}\langle k',N_q+1/2\pm1/2||\mathcal{H}_{\rm Fr}|^2|k,N_q+1/2\pm1/2\rangle\\&\quad\times\delta\left(E_n-E_m\mp\hbar\omega_{\rm l}\right)\\&=\pm\frac{1}{\hbar}\frac{|A|^2}{q^2}\left(n_q+\frac{1}{2}\mp\frac{1}{2}\right)\delta\left(E(k')-E(k)\mp\hbar\omega_{\rm l}\right), \quad (5)\end{aligned}$$

where n_q is the Bose–Einstein distribution for phonons

$$n_q=\left({\rm e}^{\hbar\omega_{\rm l}/k_{\rm B}T}-1\right)^{-1}. \quad (6)$$

From Eq. (5), one can extract the value of the matrix element of the Fröhlich electron–phonon interaction as[22]

$$M^2=\frac{|A|^2}{q^2}=\frac{2\pi e^2\hbar\omega_{\rm l}}{\epsilon^*}\frac{1}{q^2}, \quad (7)$$

with q being the phonon wave vector.

The transition probability can now be written as

$$W_{\rm tr}=\pm\frac{1}{\hbar}M^2\left(n_q+1/2\mp1/2\right)\delta\left(E(k')-E(k)\mp\hbar\omega_{\rm l}\right). \quad (8)$$

For possible use later, equation (8) can be written as

$$W_{\rm tr}=\pm\frac{2\pi e^2\omega_{\rm l}}{\epsilon^*}\frac{1}{q^2}\left(n_q+1/2\mp\hbar\omega_{\rm l}\right). \quad (9)$$

The factor $1/q^2$ provides some form of screening in the system. However, to take account of the full screening that quantity must be expressed in the form[23]

$$\frac{1}{q^2}\to\frac{q^2}{\left(q^2+k_{\rm TF}^2\right)^2}, \quad (10)$$

where

$$k_{\rm TF}=\left(\frac{6\pi ne^2}{\varepsilon_{\rm F}}\right)^{1/2} \quad (11)$$

is the Thomas–Fermi screening wave vector and $\varepsilon_{\rm F}$ is the Fermi energy. When there are no free electrons in the system, $k_{\rm TF}=0$. Physically, there is always full screening in metals and ionic crystals which allows for the correct relaxation for all processes. Theoretically, should the screening be partial, then the relaxation time would deviate from its nominal value. Thus, with full screening, the transition probability becomes

$$\begin{aligned}W_{\rm tr}&=\pm\frac{2\pi e^2\omega_{\rm l}}{\epsilon^*}\frac{q^2}{\left(q^2+k_{\rm TF}^2\right)^2}\left(n_q+1/2\mp1/2\right)\\&\quad\times\delta\left(E(k')-E(k)\mp\hbar\omega_{\rm l}\right). \quad (12)\end{aligned}$$

3. Boltzmann transport equation

The polaron effect takes place most significantly in ionic and polar solids and consists of an electron interacting with optical vibrations or phonons. In complex crystals, the high frequency phonons are optical, and should the acoustic phonons be incorporated in this theory, its wave vector must be significantly greater than zero. Mainly in order to avoid singularities in the iso-energetic acoustic hypersurface,[18] the phonons and hence the polarons considered in this work are optical. The analysis made in this section is, however, general for all polaron types. A situation arises where the exchange of longitudinal optical phonons from the polarized ion with the electron soon reaches equilibrium. This equilibrium may be described by the transition probability in one direction per unit time by $W_{\rm tr}(\boldsymbol{k},\boldsymbol{k}')$ and in the reverse direction by $W_{\rm tr}(\boldsymbol{k}',\boldsymbol{k})$, where $\boldsymbol{k}$ is the wave vector state of the electron. The Boltzmann transport equation (BTE) can now be written in the variant form as

$$\begin{aligned}\frac{\partial f}{\partial t}&=-\boldsymbol{v}\boldsymbol{\nabla}_{\boldsymbol{r}}f-\frac{1}{m}\boldsymbol{F}\boldsymbol{\nabla}_{\boldsymbol{v}}f+\sum_k\left\{W_{\rm tr}(\boldsymbol{k}',\boldsymbol{k})f(\boldsymbol{k}')\left[1-f(\boldsymbol{k})\right]\right.\\&\quad\left.-W_{\rm tr}(\boldsymbol{k},\boldsymbol{k}')f(\boldsymbol{k})\left[1-f(\boldsymbol{k}')\right]\right\}, \quad (13)\end{aligned}$$

with the Pauli exclusion principle being taken into account and

$$f=\left({\rm e}^{(\varepsilon-\mu)/k_{\rm B}T}+1\right)^{-1} \quad (14)$$

the Fermi–Dirac function, $\boldsymbol{v}$ the electron's velocity, $\boldsymbol{r}$ the position vector, $\boldsymbol{F}$ the force on the electron while m is its mass. In the stationary state,

$$\frac{\partial f}{\partial t}=\left(\frac{\partial f}{\partial t}\right)_{\rm field}+\left(\frac{\partial f}{\partial t}\right)_{\rm coll}, \quad (15)$$

where the field term is

$$\left(\frac{\partial f}{\partial t}\right)_{\rm field}=-\boldsymbol{v}\boldsymbol{\nabla}_{\boldsymbol{r}}f-\frac{1}{m}\boldsymbol{F}\boldsymbol{\nabla}_{\boldsymbol{v}}f, \quad (16)$$

and the collision term is

$$\left(\frac{\partial f}{\partial t}\right)_{\rm coll}=\sum_{\boldsymbol{k}'}\left\{W_{\rm tr}(\boldsymbol{k}',\boldsymbol{k})f(\boldsymbol{k}')\left[1-f(\boldsymbol{k})\right]\right.$$

$$-W_{\rm tr}(\boldsymbol{k},\boldsymbol{k}')\left[1-f(\boldsymbol{k}')\right]\}$$
$$=\sum_{\boldsymbol{k}'}W_{\rm tr}(\boldsymbol{k},\boldsymbol{k}')\left\{f(\boldsymbol{k}')-f(\boldsymbol{k})\right\}. \quad (17)$$

In the last equality, the principle of detail balancing has been used. Let us write $f(\boldsymbol{k})$ in the form[2]

$$f(\boldsymbol{k})=f_0(\varepsilon)+f_1(\boldsymbol{k}), \quad (18)$$

where

$$f_1(\boldsymbol{k})=-\frac{\partial f_0}{\partial\varepsilon}\chi(\varepsilon)\boldsymbol{k}, \quad (19)$$

and $\chi(\varepsilon)$ is a function of energy.

We now introduce the relaxation time τ by

$$\frac{1}{\tau}=-\frac{1}{2\pi}\sum_{\boldsymbol{k}'}W_{\rm tr}\left(\boldsymbol{k},\boldsymbol{k}'\right)\frac{\Delta k_\chi}{k_\chi}. \quad (20)$$

During the scattering of electrons on phonons, we have $\boldsymbol{k}'=\boldsymbol{k}\pm\boldsymbol{q}$ or in terms of energy $\varepsilon_{\boldsymbol{k}'}=\varepsilon_{\boldsymbol{k}}+\hbar\omega_q$. Then, $\Delta\boldsymbol{k}=\boldsymbol{k}'-\boldsymbol{k}=\pm\boldsymbol{q}$; $\Delta k_\chi=q_\chi$, and as a result

$$\frac{1}{\tau}=-\frac{1}{2\pi}\sum_{\boldsymbol{q}}W_{\rm tr}\left(\boldsymbol{k},\boldsymbol{q}\right)\frac{q_\chi}{k_\chi}. \quad (21)$$

The transition probability of Eq. (12) for phonon absorption (the upper sign) becomes

$$W_{\rm tr}^{+}(\boldsymbol{k},\boldsymbol{q}) = \frac{2\pi e^2\omega_{\rm l}}{\epsilon^*}\frac{q^2}{\left(q^2+k_{\rm TF}^2\right)^2}n_q$$
$$\times\delta\left(E\left(\boldsymbol{k}+\boldsymbol{q}\right)-E\left(\boldsymbol{k}\right)-\hbar\omega_q\right), \quad (22)$$

and for phonon emission

$$W_{\rm tr}^{-}\left(\boldsymbol{k},\boldsymbol{q}\right) = -\frac{2\pi e^2\omega_{\rm l}}{\epsilon^*}\frac{q^2}{\left(q^2+k_{\rm TF}^2\right)^2}\left(n_q+1\right)$$
$$\times\delta\left(E\left(\boldsymbol{k}-\boldsymbol{q}\right)-E\left(\boldsymbol{k}\right)+\hbar\omega_q\right), \quad (23)$$

so that

$$\frac{1}{\tau}=-\frac{1}{2\pi}\sum_{\boldsymbol{q}}W_{\rm tr}^{+}\left(\boldsymbol{k},\boldsymbol{q}\right)+\sum_{\boldsymbol{q}}W_{\rm tr}^{-}\left(\boldsymbol{k},\boldsymbol{q}\right). \quad (24)$$

Passing from summation to integration in Eq. (24) and using Eqs. (22) and (23), we have

$$\frac{1}{\tau} = -\frac{2\pi e^2\omega_{\rm l}}{(2\pi)^4\epsilon^*}\int_{q_{\rm min}}^{q_{\rm max}}\int_0^{\pi}\int_0^{2\pi}\frac{q^2\,{\rm d}q}{\left(q^2+k_{\rm TF}^2\right)^2}$$
$$\times\left\{n_q\delta\left(E(\boldsymbol{k}+\boldsymbol{q})-E(\boldsymbol{k})-h\omega_q\right)\right.$$
$$\left.-\left(n_q+1\right)\delta\left(E(\boldsymbol{k}-\boldsymbol{q})-E(\boldsymbol{k})+\hbar\omega_q\right)\right\}$$
$$\times\frac{q^3}{k}\frac{\cos\alpha}{\cos\beta}\sin\vartheta\,{\rm d}\vartheta\,{\rm d}\varphi. \quad (25)$$

Then, equation (25) becomes

$$\frac{1}{\tau} = -\frac{m}{(2\pi)^3\hbar^2k^2}\frac{2\pi e^2\omega_{\rm l}}{\epsilon^*}\int_{q_{\rm min}}^{q_{\rm max}}\frac{q^4}{\left(q^2+k_{\rm TF}^2\right)^2}$$
$$\times\left\{n_q\int_0^{\pi}\cos\vartheta\sin\vartheta\,\delta\left(\frac{q}{2k}+\cos\vartheta\right){\rm d}\vartheta\right.$$
$$\left.-\left(n_q+1\right)\int_0^{\pi}\cos\vartheta\sin\vartheta\,\delta\left(\frac{q}{2k}-\cos\vartheta\right){\rm d}\vartheta\right\}. \quad (26)$$

The two integrals in the brackets add up to give $(q/2k)(2n_q+1)$, therefore, equation (25) becomes

$$\frac{1}{\tau}=-\frac{m}{4\pi^2\hbar^2k^3}\frac{e^2\omega_{\rm l}}{\epsilon^*}\left(2n_q+1\right)\int_{q_{\rm min}}^{q_{\rm max}}\frac{q^5}{\left(q^2+k_{\rm TF}^2\right)^2}{\rm d}q, \quad (27)$$

which is applicable to both absorption and emission of phonons in the system. The integral in Eq. (27) is elementary or can be taken from the table of integrals (see Ref. [25] for example). The result of the integration is

$$\int_{q_{\rm min}}^{q_{\rm max}}\frac{q^5\,{\rm d}q}{\left(q^2+k_{\rm TF}^2\right)^2} = \left[\frac{q^2}{2}\right]_{q_{\rm min}}^{q_{\rm max}}-k_{\rm TF}^2\left[\ln\left(q^2+k_{\rm TF}^2\right)\right]_{q_{\rm min}}^{q_{\rm max}}$$
$$-\frac{k_{\rm TF}^4}{2}\left[\frac{1}{q^2+k_{\rm TF}^2}\right]_{q_{\rm min}}^{q_{\rm max}}. \quad (28)$$

Since the elastic and inelastic interactions occur at high and low temperatures, respectively, then limits of q should be made explicit in Eq. (28). In the delta function in Eq. (12), if the last term is ignored, the law of energy conservation for the elastic interaction is obtained (in the high temperature regime) as $q=\pm2k\cos\vartheta$, so that

$$q_{\rm min}=0,\ \ q_{\rm max}=2k. \quad (29)$$

In the high temperature range $k_{\rm B}T\gg\hbar\omega$, or $k>k_0$, where $k_0=\sqrt{2m\omega_{\rm l}/\hbar}$, the emission and absorption of phonons take place with an equal force ($q\equiv q^{(\rm e)}, q\equiv q^{(\rm a)}$, where (a) is the absorption and (e) is the emission. However, if we retain the last term in the delta function in Eq. (12), the inelastic interaction condition (in the low temperature regime, $k_{\rm B}T\ll\hbar\omega_{\rm l}$, or, $k<k_0$) is

$$q^2\pm2kq\cos\vartheta\mp\frac{2m\omega_{\rm l}}{\hbar}=0, \quad (30)$$

with solutions

$$q_1\equiv q^{(\rm a)} = -k\cos\vartheta+\sqrt{k^2\cos^2\vartheta+k_0^2};$$
$$q_2\equiv q^{(\rm e)} = k\cos\vartheta-\sqrt{k^2\cos^2\vartheta+k_0^2}. \quad (31)$$

These calculations allow us to rewrite Eq. (27) as

$$\frac{1}{\tau}=\frac{11m^*e^2\omega_{\rm l}}{8\pi^2\hbar^2k^3\epsilon^*}\left(2n_q+1\right)k_{\rm TF}^2, \quad (32)$$

where

$$(2n_q+1)\cong2\langle n_q\rangle_0\cong2\frac{k_{\rm B}T}{\hbar\omega_{\rm l}}\left(1-\frac{\hbar\omega_{\rm l}}{k_{\rm B}T}\right)=2\frac{T}{T_{\rm D}}\left(1-\frac{T_{\rm D}}{T}\right), \quad (33)$$

and $T_{\rm D}$ is the Debye temperature of the solid. Thus,

$$\frac{1}{\tau}=\frac{33}{8\pi^2}\frac{e^2}{\hbar\epsilon^*}\frac{T}{T_{\rm D}}\left(1-\frac{T}{T_{\rm D}}\right)k_{\rm TF}. \quad (34)$$

We write Eq. (34) in the form

$$\frac{1}{\tau} = \Gamma \frac{T}{T_D}\left(1 - \frac{T}{T_D}\right), \tag{35}$$

where Γ for NaCl and KBr are, respectively,

$$\Gamma_{NaCl} = \frac{33e^2}{8\pi^2\hbar\epsilon^*} k_{TF} = 17 \times 10^{14}\ s^{-1};$$
$$\Gamma_{KBr} = 15 \times 10^{14}\ s^{-1}, \tag{36}$$

and the inverse dielectric quantity $1/\epsilon^* = 0.257$ for the former[26] and 0.22 for the latter.[27] Using Eq. (34) or Eq. (35), we present $1/\tau$ against T for the two crystals in Fig. 1.

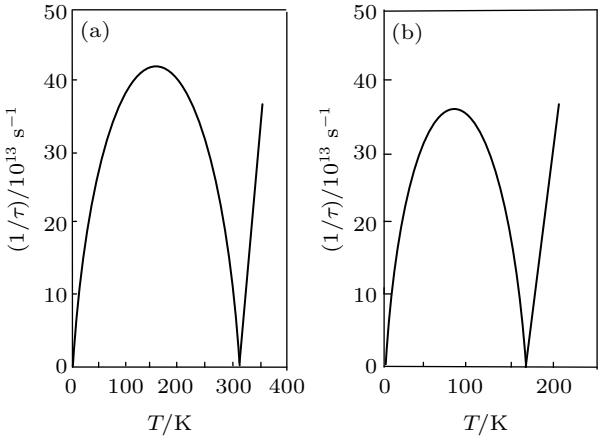


Fig. 1. Graphs of inverse relaxation time $1/\tau$ versus temperature T. (a) NaCl, the polaron crossover temperature is $T_{pc} \cong 162$ K and (b) KBr, $T_{pc} \cong 90$ K. The small radius polaron (SRP) exists in the region $T > T_{pc}$ and the large radius polaron (LRP) at $T < T_{pc}$. The straight lines indicate the steepness of the polaron collapse rate.

4. Polaron mass ratios

Let us consider the motion of the LRP, beginning with its mean free path length given as $l = v\tau$, where v is its linear velocity and τ is the time of motion, we write

$$l = \left(\frac{3k_BT}{e}\right)^{1/2}\left(\frac{e}{m^*}\right)^{1/2}\tau, \tag{37}$$

where m^* is the effective mass of the polaron. For the LRP and SRP, we write respectively

$$l_L^2 = \frac{3k_BT_L\tau^2}{m_L^*},$$
$$l_s^2 = \frac{3k_BT_S\tau^2}{m_s^*},$$

so that

$$l_L^2 - l_s^2 = 3k_B\tau^2\left(\frac{T_L}{m_L^*} - \frac{T_s}{m_s^*}\right), \tag{38}$$

where T_L and T_s are FWHM temperatures at opposite sides of the curves (see Fig. 1) containing the LRP and SRP, respectively. We can now make the following approximations:

$$l_L = \eta l_s,\ \ m_L^* = \eta m_s^*, \tag{39}$$

where

$$\eta < 1,\ \ m_L^* < m_s^*;\ \ l_L < l_s, \tag{40}$$
$$\eta > 1,\ \ m_L^* > m_s^*;\ \ l_L > l_s. \tag{41}$$

so equation (38) becomes

$$m_s^{*2}v_s^2 = \frac{3k_B}{\eta^2 - 1}\left(\frac{T_L}{\eta} - T_s\right). \tag{42}$$

Noting that thermal energy $(3/2)k_BT = m_s^{*2}v_s^2/2$, we obtain

$$\eta = \left(\frac{T_L}{T_s}\right)^{1/3}. \tag{43}$$

From Fig. 1(a), we can obtain the values T_L, T_s, and τ at FWHM and obtain

$$\eta = \left(\frac{48}{280}\right)^{1/3} = 0.55, \tag{44}$$

and similarly in Fig. 1(b), $\eta = (25/150)^{1/3} = 0.55$. Thus, η is a universal constant for the polaron crossover in solids. Besides the two masses mentioned above, two other characteristic masses are the electron bare mass m_e and the effective mass of the electron m_e^*; relations between the four masses can be established. Consider the distribution Eq. (6); for $k_BT > \hbar\omega_l$, a limiting condition for the existence of the SRP can be imposed as discussed by Firsov.[28] Thus, $k_BT > \hbar\omega_l \sim \hbar/\tau$, yielding $\hbar/\tau k_BT < 1$. The mobility of the electron is defined as $\mu = e\tau/m_e^*$, therefore, if we use the LRP mass $m_L^* = 321m_e^*$[29] (see Table 1), we can write[8,28]

$$\frac{\hbar}{\tau k_BT} \approx 20\frac{m_e}{m_e^*}\frac{500\ K}{T}\frac{cm^2\cdot V^{-1}\cdot s^{-1}}{\mu} < 1. \tag{45}$$

In order to satisfy Eq. (45), $m_e^* > m_e$, $\mu \gg 1$, for $T \sim 10^2$ K; therefore, the condition for the existence of the SRP and LRP is $m_S^* > m_e^* > m_e$. We can make use of Table 1 for further calculations on NaCl and KBr crystals. The data of Table 1 are taken from most relevant literature to our work.

Table 1. Mass ratios for NaCl and KBr crystals, their effective dielectric constants ϵ^* and polaron coupling constants a.

Substance	ϵ^*	a	m_e^*/m_e	m_L^*/m_e	m_L^*/m_e^*
NaCl	3.9[a]	8.9[b]	2.78[b]	432[c]	140[a]
		8.7[d]	2.78[a,d]	391[d]	
		9.19[a]		321[b]	
KBr	4.5[a]	7.7[d]	1.87[a]	0.93[e]	2.2[e]
			0.43[e]	1.87[a]	
			0.48[b]	155[d]	

[a] Ref. [26], [b] Ref. [30], [c] Ref. [4], [d] Ref. [29], [e] Ref. [33].

The unreliability of the values of m_e^* in NaCl and in other alkali based crystals was discussed by Appel.[30] In order to

use Table 1 to estimate the numerical values of the ratios of the masses, we begin with

$$\frac{m_{\rm L}^*}{m_{\rm e}^*} = 155. \tag{46}$$

In order to check the value of the coupling constant a for NaCl, we use the formula[28]

$$m_{\rm L}^* = 0.025a^4 m_{\rm e}^*, \tag{47}$$

as well as our result in Eq. (44) ($m_{\rm L}^* = 0.55m_{\rm s}^*$) to write

$$m_{\rm s}^* = 0.045a^4 m_{\rm e}^*. \tag{48}$$

Therefore, equation (46) is otherwise represented as $m_{\rm L}^* = 155m_{\rm e}^*$ to yield

$$m_{\rm s}^* = 282m_{\rm e}^*. \tag{49}$$

If we substitute the table value $a = 8.9$ in Eq. (47), we find that $m_{\rm L}^* = 156m_{\rm e}^*$ which is approximately equal to the result in Eq. (46). Therefore, based on the validity of Eq. (47), we can write Eq. (48) for $m_{\rm s}^*$ as

$$m_{\rm s}^* = 0.025a_1^4 m_{\rm e}^*, \ \ a_1 = 10.3. \tag{50}$$

Thus, contrary to the assumption that the coupling constant a does not change[25] during the transition or crossover from LRP to the SRP, we find in the present work that a change in the magnitude of a does occur. The phonons are therefore more tightly bound to the electron in the SRP than in the $T > T_{\rm pc}$. The relationship between $m_{\rm s}^*$ and $m_{\rm e}$, $m_{\rm L}^*$ and $m_{\rm e}$ can also be determined as follows:

$$\frac{m_{\rm s}^*}{m_{\rm e}} = \frac{m_{\rm s}^*}{m_{\rm e}^*}\frac{m_{\rm e}^*}{m_{\rm e}} = 282 \times 2.78 = 784,$$

thus

$$m_{\rm s}^* = 784m_{\rm e}. \tag{51}$$

Similar results for KBr are

$$m_{\rm s}^* = 0.025a_1^4 m_{\rm e}^* = 155m_{\rm e}^*, \ \ a_1 = 8.87, \tag{52}$$

$$m_{\rm L}^* = 0.025a^4 m_{\rm e}^* = 88m_{\rm e}^*, \ \ a = 7.7, \tag{53}$$

$$m_{\rm s}^* = 289m_{\rm e}, \ \ m_{\rm L}^* = 165m_{\rm e}. \tag{54}$$

The values $a = 8.9$ and $a = 7.7$ are used because their sources also contain other relevantly consistent data for this work. Mass ratios for NaCl, KBr and their LRP, SRP coupling constants a, and a_1 are shown in Table 2.

Table 2. Mass ratios for NaCl and KBr and their LRP and SRP coupling constants a and a_1.

Substance	a	a_1	$m_{\rm L}^*/m_{\rm s}^*$	$m_{\rm s}^*/m_{\rm e}^*$	$m_{\rm s}^*/m_{\rm e}$	$m_{\rm L}^*/m_{\rm e}$
NaCl	8.9[28]	10.3	0.55	282	784	432[4]
KBr	7.7[29]	8.87	0.55	155	289	165

5. The hopping motion of the SRP

The two polarons, LRP and SRP, move differently in polar and ionic lattices, according to their temperature regimes. The LRP motion is a translational Bloch type whereas the SRP moves in the crystal by hopping from one lattice site to another, and the energy $W_{\rm p}$ needed to overcome the interaction barrier is provided by the lattice vibrations and equals $\hbar\omega$.[8] The period corresponding to the vibration is longer than the time taken by the electron to traverse a distance equal to the de Broglie wave length of the ion vibration. This is an adiabatic approximation and is necessary for the formation of strong coupling polarons. The number of hops per unit time is given as

$$N_{\rm t} \approx \omega {\rm e}^{-W_{\rm H}/k_{\rm B}T}, \tag{55}$$

where $W_{\rm H} = -1/2W_{\rm p}$ is the electron hoping energy and $W_{\rm p}$ is the polaron's energy. Assuming that the vibration energy of the polaron is converted into the hop, then in the adiabatic approximation, the formula of the SRP mass[32] is

$$m_{\rm s}^* = \frac{2\hbar}{\omega R^2}{\rm e}^{\frac{W_{\rm p}}{k_{\rm B}T}}. \tag{56}$$

It is necessary to note that equation (56) refers to temperatures above $T_{\rm D}/2$ since this is the zone of existence of the SRP. In order to check whether $m_{\rm s}^*$ given by Eq. (56) coincides with the values obtained previously in Section 4, we start with basic calculations for NaCl at 300 K and $R = 5.63$ Å[30]

$$W_{\rm p} = \frac{me^4}{20\hbar^2\epsilon^{*2}} = 0.087 \text{ eV}, \tag{57}$$

and $k_{\rm B}T = 0.023$ eV. Then, we can write Eq. (57) numerically as

$$\frac{m_{\rm s}^*}{m_{\rm e}} = 786, \tag{58}$$

which approximately coincides with Eq. (51).

For KBr, we have $W_{\rm p} = 0.066$ eV, $k_{\rm B}T = 0.024$ eV where we have taken $T = 300$ K. Then using the value of the effective dielectric constant given in Table 1, we obtain

$$\frac{m_{\rm s}^*}{m_{\rm e}} = 282. \tag{59}$$

In Eqs. (58) and (59), we have used the frequency $\sim 10^{13}$ s^{-1}.

6. Conclusion

This work has been done based on the phenomenological investigations of Fröhlich and Pekar; and in particular has borrowed from the result of the later researcher. Although more than eighty years have passed since the 1933 paper of Landau, it is still difficult to extract reliable values of polaron mobility and ratios of masses of certain traditional substances. The chaotic data on NaCl from different sources, for example, acted as a stimulant for the present study. Another aspect

of this work which is the subject of the second part concerns the derivation of the crossover temperature from a Bardeen–Cooper–Schrieffer (BCS) gap-like equation emerging from the Boltzmann transport equation.

The innovations of this paper consist of the following: (i) We have made use of full screening in the theory (Eq. (10)), thus making Eq. (12) a new result; (ii) equations (32)–(35) are derived in the literature for the first time; (iii) the plotted graphs directly reflect the polaron crossover in NaCl and KBr, this is an innovative result; (iv) equation (43) is new and reveals the universal constant for polaron crossover in solids (see Eq. (44)); (v) contrary to the assumption that the polaron coupling does not change during the polaron crossover, we found that the magnitude of the coupling does change (see Eq. (50)); (vi) some results in Table 2 are new, and a few are improvements on known ratios of electronic and polaronic masses; (vii) the results in this work can be used to estimate the temperature range of existence of polarons in solids; (viii) we hope our work can bring the rather chaotic data on NaCl and KBr to some order; (ix) and the method presented in this paper can be used to study other substances, either individually or in pairs.

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