The Free Path Length of a Nonlocalized Exciton in a Polar Crystal

A. I. ANSEL'M AND IU. A. FIRSOV
Leningrad Physico-technical Institute, Academy of Sciences, USSR
(Submitted to JETP editor December 31, 1954)
J. Exptl. Theoret. Phys. (U.S.S.R.) 30, 719-723 (April, 1956)

The free path length of a nonlocalized exciton in a polar crystal is calculated for high and low temperatures, taking into account the interaction of the electron and hole, which form the exciton, with the thermal vibrations of the lattice.

INTRODUCTION

IN an earlier article by the present authors[1], devoted to the free path length of a nonlocalized exciton in an atomic crystal, the general question of the existence of excitons was considered, and experimental results supporting this existence were presented. In the present article we give results concerning the calculation of the free path length of a nonlocalized exciton in a polar crystal at high and low temperatures, omitting the details of the computation, since they are similar to the calculations of the earlier article.

We shall, as before, consider a nonlocalized exciton as a hydrogenlike formation, made up of an electron and a hole, described by the wave function

$$\psi_{ex} = V^{-1/2} e^{i\mathbf{kR}} (\pi a_{ex}^3)^{-1/2} \exp\{-r/a_{ex}\}. \quad (1)$$

Here V is the elementary volume of the crystal, $\mathbf{k}$ is the wave vector of the forward motion of the exciton, $\mathbf{R}$ and $\mathbf{r}$ are radius vectors of the center of inertia of the exciton and of the electron relative to the hole, that is,

$$\mathbf{R} = (\mu_1\mathbf{r}_1 + \mu_2\mathbf{r}_2)/(\mu_1 + \mu_2), \quad \mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2, \quad (2)$$

where μ_1, μ_2 and $\mathbf{r}_1$, $\mathbf{r}_2$ are the effective masses and radius vectors of the electron and hole (we shall continue to use the index 1 to refer to the electron and 2 to refer to the hole). The "Bohr radius of the exciton" is

$$a_{ex} = \varkappa\hbar^2/\mu e^2, \quad (3)$$

where $\varkappa$ is the optical dielectric constant and $\mu = \mu_1\mu_2/(\mu_1 + \mu_2)$ is the reduced mass. The energy corresponding to the state (1) of the exciton is

$$E_0 = (\hbar^2k^2/2\mu_{ex}) - \mu e^4/2\varkappa\hbar^2 = \varepsilon - \Delta E, \quad (4)$$

where the mass of the exciton is $\mu_{ex} = \mu_1 + \mu_2$.

Dykman and Pekar[2] have shown that localized excitons are formed in polar crystals only under the conditions $\mu_1/\mu_2 > 10$ (or $\mu_2/\mu_1 > 10$). In the treatment which follows we shall suppose that the ratio of the effective masses of the electron and hole does not reach such large values, that is, that we have to do with a nonlocalized exciton. It should also be noted that, apart from the slow decrease of the Coulomb field with distance, the application of the hydrogenlike exciton model[3] is justified, from our point of view, to the same extent to which the application of the method of effective masses to electrons and holes in kinetic phenomena is allowed.

The interaction of an exciton in a polar crystal with the thermal vibrations of the lattice is dependent on the interaction of the electron and hole with the optical branch of the vibrations. We shall, in what follows, concern ourselves only with those collisions of excitons with phonons in which an internal excitation or dissociation of the exciton does not occur. For collisions of an exciton with a phonon of the optical branch of the vibrations, for minimum excitation of the exciton, the conservation laws give

$$\mathbf{k} \pm \mathbf{q} = \mathbf{k}', \quad (5)$$

$$\frac{\hbar^2k^2}{2\mu_{ex}} \pm \hbar\omega_0 = \frac{\hbar^2k'^2}{2\mu_{ex}} + E_1. \quad (6)$$

Here $\mathbf{q}$ is the wave vector of the phonon, ω_0 is the frequency of the optical branch of the vibrations (we shall consider ω_0 as independent of $\mathbf{q}$) and $E_1 = 3/4\,\Delta E$ is the minimum energy of excitation of the exciton.

From (5) and (6) it is easy to show that the condition of nonexcitation of the exciton during a collision with a phonon of the optical branch has the form:

$$\gamma = \varepsilon/(E_1 - \hbar\omega_0) < 1. \quad (7)$$

For an overwhelming number of excitons we may

replace ϵ by $3/2\, k_0 T$ in this expression; thus,

$$\bar{\gamma} = 3k_0 T / 2(E_1 - \hbar\omega_0) < 1. \quad (7a)$$

Since in polar crystals $\varkappa^2 \sim 5$, we have $E_1 \sim \mu/m_e$ ev. The energy $\hbar\omega_0$ is of the order of hundredths of an electron volt. Hence, if the ratio μ/m_e is not very small, then the inequality (7a) will be fulfilled up to high temperatures, of the order of thousands of degrees.

By substituting $E_1 = 0$ (the exciton is not excited) into (6), it is easy to determine the lowest and highest values of q for high and low temperatures. For high temperatures ($k_0 T \gg \hbar\omega_0$):

$$q_{\min} = 0, \quad q_{\max} = 2k. \quad (8)$$

For low temperatures ($k_0 T \ll \hbar\omega_0$):

$$q_{\min} = \sqrt{2\mu_{ex}\omega_0/\hbar + k^2} - k, \quad (8a)$$
$$q_{\max} = \sqrt{2\mu_{ex}\omega_0/\hbar + k^2} + k.$$

In calculating the free path length of the exciton we shall make the assumption that the average time of the free path between two successive collisions with the lattice vibrations is much less than the average lifetime of the exciton.

PROBABILITY $W_{kk'}$ FOR AN EXCITON TRANSITION DURING ABSORPTION AND EMISSION OF A PHONON

As the energy of excitation U for the interaction of an exciton with the vibrations of a polar lattice we take the energy of interaction of the electron and the hole with the optical branch of the vibrations[4]:

$$U = -e\sum_q \varphi_{1q}(\mathbf{r}_1) + e\sum_q \varphi_{2q}(\mathbf{r}_2), \quad (9)$$

$$\varphi_{1q}(\mathbf{r}_1) = -\frac{2\pi i Z e C_1}{\sqrt{MN}\, a_0^3 q}\,(a_q e^{iq\mathbf{r}_1} - a_q^* e^{-iq\mathbf{r}_1}). \quad (9a)$$

Here Z is the charge number of the ions, $M = M_1 M_2/(M_1 + M_2)$ is the reduced mass of the ions, a_0 is the lattice constant, N is the number of cells in the fundamental volume of the crystal V, C_1 is a constant of the order of unity, taking account of the deformation of the electron shells during collisions of the ions, the a_q are the normal coordinates of the lattice vibrations. An analogous expression, depending on $\mathbf{r}_2$, may be written for $\varphi_{2q}(\mathbf{r}_2)$, that is, for a hole. The constant C_2 will be different from C_1, since the electron and the hole are in different quantum states.

The wave function for the zeroth approximation of the system, consisting of exciton and crystal, has the form

$$\Psi(\mathbf{R}, r_1 a_q) = V^{-1/2} e^{i\mathbf{kR}} (\pi a_{ex}^3)^{-1/2} \times \exp\{-r/a_{ex}\} \prod_q \Phi_{N_q}(a_q), \quad (10)$$

where $\Phi_{N_q}(a_q)$ is the oscillator wave function of the normalized vibration a_q.

Calculating the matrix element of the transition by the general rule

$$U_{kk'} = \int \Psi^*(\mathbf{R}, r, a_q)\, U \Psi(\mathbf{R}, r, a_q)\, d\mathbf{R}\, d\mathbf{r}\, da_q, \quad (11)$$

we obtain for the transition probability associated with the absorption and emission of phonons the expressions:

$$W^+_{kk'} = wN_q Q(q)\,\delta(\varepsilon_{k'} - \varepsilon_k - \hbar\omega_0), \quad (12)$$
$$W^-_{kk'} = w(N_q + 1) Q(q)\,\delta(\varepsilon_k - \varepsilon_k + \hbar\omega_0).$$

Here $w = 8\pi^3 Z^2 e^4 C_1^2/VMa_0^3\omega_0 q^2$, N_q is the quantum number of the normal vibrations, δ is a delta function expressing the law of conservation of energy and

$$Q(q) = [(1 + \beta_1^2 q^2)^{-2} - s(1 + \beta_2^2 q^2)^{-2}]^2, \quad (12a)$$

where $\beta_1 = \varkappa\hbar^2/2\mu_1 e^2$, $\beta_2 = \varkappa\hbar^2/2\mu_2 e^2$ and $s = C_2/C_1$. In order of magnitude β_1 and β_2 are equal to a_{ex}.

FREE PATH LENGTH OF AN EXCITON AT HIGH AND LOW TEMPERATURES

The free path length of an exciton is $l = \tau v$. The velocity of the exciton is $v = \hbar k/\mu_{ex}$, while at high temperatures ($k_0 T \gg \hbar\omega_0$) the relaxation time τ is determined by the formula[5]

$$\frac{1}{\tau} = -\sum_q \frac{\Delta k_x}{k_x}(W^+_{kk'} + W^-_{kk'}). \quad (13)$$

Calculation gives

$$l = l_1 F(x), \quad l_1 = \frac{a_0}{2\pi}\left(\frac{\hbar\omega_0}{C_1 Ze^2/a_0}\right)^2 \frac{M}{\mu_1}\frac{\varepsilon}{k_0 T}. \quad (14)$$

Here l_1 is the free path length of an electron with energy ϵ equal to the energy of the forward motion of the exciton. The function $F(x)$, depending on the dimensionless variable $x = a_{ex}^2 k^2 = 2\mu_{ex} a_{ex}^2 \epsilon/\hbar^2$, determines the deviation of the free path length of the exciton from the free path length of an electron of the same kinetic energy:

$$\frac{1}{F(x)} = \frac{\alpha_1+\alpha_2}{\alpha_1 x}\left[\frac{s^2}{3\alpha_1^2}\left(1-\frac{1}{(1+\alpha_1^2 x)^3}\right)\right. \tag{14a}$$

$$+\frac{1}{3\alpha_2^2}\left(1-\frac{1}{(1+\alpha_2^2 x)^3}\right)$$

$$-\frac{2s}{1-(\alpha_1/\alpha_2)^2}\left(\frac{2/\alpha_2^2}{1-(\alpha_2/\alpha_1)^2}\ln\frac{1+\alpha_2^2 x}{1+\alpha_1^2 x}\right.$$

$$\left.\left.+\frac{x}{1+\alpha_2^2 x}+\left(\frac{\alpha_1}{\alpha_2}\right)^4\frac{x}{1+\alpha_1^2 x}\right)\right],$$

where $\alpha_1 = \mu_1/\mu_{ex}$ and $\alpha_2 = \mu_2/\mu_{ex}$. Thus, the function $F(x)$ depends only on two parameters: $s = C_2/C_1$ and $g = \mu_2/\mu_1$.

In the special cases when $g = 1$ or $g \gg 1$ or $s = 1$, the function (14a) becomes simpler. In order to obtain a more visual representation of the change of the free path length of the exciton with the change in its energy, curves (Figs. 1 and 2) were drawn up. The dimensionless kinetic energy $a = a_{ex}^2 k^2$ is plotted as abscissa and the function $F(x; s, g)$ is plotted as ordinate. In Fig. 1, $g = 10$ for all the curves, while the parameter s ranges in value from 0.3 to 2. In Fig. 2 g ranges from 1.2 to 10, while s varies within the narrower interval from 0.85 to 1.1. The general aspect of the curves in Figs. 1 and 2 shows that the function $F(x; s, g)$ has a maximum in those cases where for $g > 1$ the ratio of the corresponding polarization constants $s < 1$. In such cases, the nearer s is to unity, that is, the smaller the difference between C_2 and C_1, the smaller is the value of x at which the maximum occurs. If g and s are both larger (smaller) than unity, then the function $F(x; s, g)$ decrease monotonically with increasing x and decreases more steeply the closer s is to unity. It must be kept in mind, however, that, in accordance with (7), the theory applies for such times as

$$x < (2\mu_{ex} a_{ex}^2/\hbar^2)(E_1 - \hbar\omega_0). \tag{15}$$

In thermal equilibrium $\epsilon = \bar{\epsilon} = 3/2\, k_0 T$ for the overwhelming number of excitons; hence, for them the factor l_1 does not depend on the temperature, and the curve $F(x; s, g)$ gives directly, in relative units, the dependence of the free path length

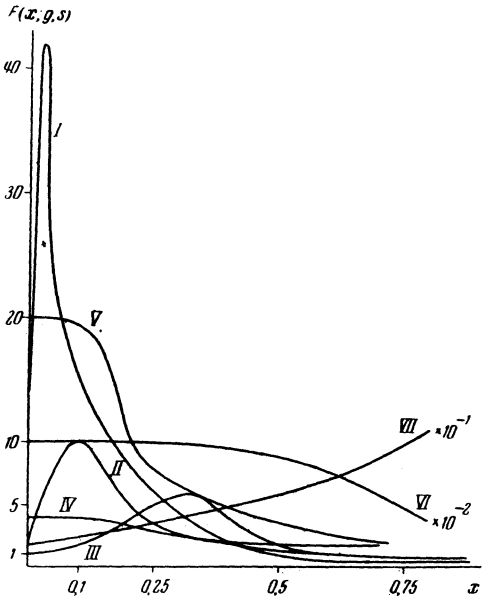

FIG. 1. $g = \mu_2/\mu_1 = 10$ for all the curves. $s = 0.9$ for curve I, $s = 0.8$ for curve II, $s = 0.7$ for curve III, $s = 1.15$ for curve IV, $s = 1.07$ for curve V, $s = 2.0$ for curve VI, $s = 0.3$ for curve VII.

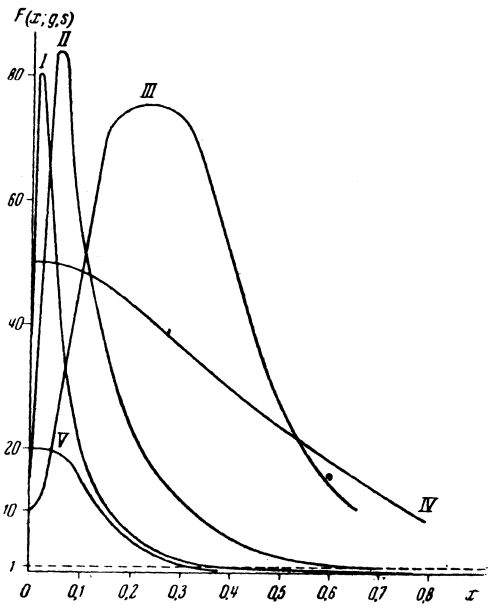

FIG. 2. $g = 10$, $s = 0.95$ for curve I; $g = 5$, $s = 0.9$ for curve II; $g = 3$, $s = 0.85$ for curve III; $g = 1.2$, $s = 1.1$ for curve IV; $g = 5$, $s = 1.1$ for curve V.

of the exciton on the temperature. On the other hand, it must be kept in mind that if we consider the free path length as a function of the average energy $\overline{\epsilon}$ of the exciton, then the change in x has not only an upper limit but also a lower limit:

$$x > (3\mu_{ex}a_{ex}^2/\hbar^2)\hbar\omega_0. \quad (15a)$$

If we consider $\mu_1 = \mu_2 = m_e$ and $\varkappa^2 \approx 5$, then the order of the interval in which x lies is from 0.01 to 1.

For low temperatures ($k_0T \ll \hbar\omega_0$) the possible values of q for phonons interacting with excitons lie in the narrow interval (8a). Thus, the magnitude of $\beta_{1,2}^2 q^2$ in $Q(q)$ [see Eq. (12a)] is equal, in order of magnitude, to

$$\beta_{1,2}^2 q^2 \approx \beta_{1,2}^2 \frac{2\mu_{ex}\omega_0}{\hbar} = \frac{m_e(\mu_1+\mu_2)\varkappa^2\hbar\omega_0}{4\mu_{1,2}^2}\frac{\hbar\omega_0}{V_i}. \quad (16)$$

where $V_i = 13.5$ ev is the ionizing energy of a hydrogen atom. Since $\hbar\omega_0$ is of the order of a few hundredths of an electron volt, while the factor $m_e(\mu_1+\mu_2)\varkappa^2/4\mu_{1,2}^2$ is of the order of unity, then (16) is of the order of 10^{-3}.

If, on the other hand, the absolute magnitude of the difference $(1-s)$ is not less than 10^{-2}, that is, if it is larger in order of magnitude than $\beta_{1,2}^2 q^2$, then we may put

$$Q(q) = (1-s)^2. \quad (17)$$

In this case the transition probabilities (12) and (12a) differ from the usual ones only in the constant factors $(1-s)^2$; hence, the calculated free path length of the exciton is equal to[4]:

$$l = \frac{a_0 M}{2\pi\mu_{ex}}\left(\frac{\hbar\omega_0}{C_1 Ze^2/a_0}\right)^2 e^{\hbar\omega_0/k_0T}\sqrt{\frac{\varepsilon}{\hbar\omega_0}}\frac{1}{(1-s)^2} \quad (18)$$

$$= l_1\frac{\mu_1}{\mu_1+\mu_2}\frac{1}{(1-s)^2}.$$

Here l_1 is the free path length of an electron with energy equal to the energy of forward movement of the exciton ϵ. If $|1-s| \sim 0.1$ and $\mu_1/(\mu_1+\mu_2) \sim 1$, then l is 100 times as large as l_1. We do not consider the more complicated case where $Q(q)$ may not be replaced by the constant value (17).

It should be noted that for sufficiently low temperatures the free path length of an exciton will probably be determined not by the interaction with the thermal vibrations of the lattice, but by scattering from impurities and defects in the crystal.

We make a remark concerning a localized exciton in a polar crystal, an exciton which is formed, according to Dykman and Pekar[2], only for a large ratio μ_2/μ_1 (or μ_1/μ_2). As these authors have remarked, a heavy particle here acts like a polaron, but a light particle acts like an F-center electron. An analysis of the question indicates that the free path length of such an exciton coincides in order of magnitude with the free path length of a polaron, corresponding to a heavy particle.

---

[1] A. I. Ansel'm and Iu. A. Firsov, J. Exptl. Theoret. Phys. (U.S.S.R.) 28, 151 (1955); Soviet Phys. JETP 1, 139 (1955).

[2] I. M. Dykman and S. I. Pekar, Trudy Inst. Phys. Acad. Sci., USSR 3, 92 (1952).

[3] G. H. Wannier, Phys. Rev. 52, 191 (1937).

[4] V. I. Davydov and I. M. Shmushkevich, J. Exptl. Theoret. Phys.(U.S.S.R.) 10, 1043 (1940).

[5] H. Fröhlich, *Elektronentheorie der Metalle*, 1936.

Translated by M. G. Gibbons
146