Free and self-localized Wannier–Mott excitons in ionic crystals and activation energy of their mutual thermal conversion

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The adiabatic approximation (strong-coupling limit) is used in a theoretical analysis of the coexistence of polarizing and nonpolarizing excitons in an ionic crystal. Calculations are made of their energies and of the height of a potential barrier which has to be overcome for conversion from the nonpolarizing to the polarizing exciton state. The difference between the energies of these excitons can change sign with the values of the crystal parameters. The barrier may ensure a long lifetime of the excitons with the higher energy.

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An activation energy is not required for the formation of a polaron from a band electron: this process is accompanied by a monotonic reduction in the energy of a system (see § 8 in Ref. 1) and is completed in a time of the order of 10^{-12} sec. A similar conversion of a free into a polarizing exciton requires overcoming of a potential barrier[2-4] which may occur by activation or by the tunnel effect. An analysis and a short review of this process can be found in Ref. 5. In this case the lifetime of an exciton with the higher energy may be longer. Thus, in accordance with this qualitative theory, free and polarizing excitons may coexist and undergo transitions from one state to the other and vice versa.

This topic is now attracting considerable interest because the coexistence of two types of exciton and their mutual thermal conversion have been observed experimentally in a wide range of substances, including ionic crystals,[6-8] rare gases,[9] etc. We shall consider only the limiting case of strong coupling of carriers to optical vibrations of a crystal when the states of an electron and a hole follow adiabatically relatively slow oscillations of inertial polarization. It is also assumed that the effective radii of the ψ clouds of an electron and a hole are considerably greater than the lattice constant. In this case the states of a system can be analyzed by methods developed earlier for polarons and local centers.[1] We shall use a model of a polarizing electron introduced initially by Dykman and Pekar.[10,11]

In general, the optimal physical model of a self-localized state depends on the relationship between a number of competing parameters. This specific problem has been considered recently[13] for the nonpolarization interaction with the lattice when self-localization (self-trapping) always occurs within a distance equal to the lattice constant.[12] The same problem is encountered also in the case of the polarization interaction. For example, we can begin from electron and hole polarons which become bound to form a Wannier–Mott exciton (see, for example, Ref. 14). If the ψ clouds of the electron and hole do not overlap, the polarons interact with one another in accordance with the Coulomb law $e^2/\varepsilon_0|\mathbf{r}_1-\mathbf{r}_2|$.

The polaron radii are[1]

$$r_{pi}\approx 10\ m_0 r_B/\mu_i c_0, \qquad c_0=\varepsilon_\infty^{-1}-\varepsilon_0^{-1}, \tag{1}$$

where r_B is the Bohr radius and μ_i ($i=1$ or 2) are the effective masses of the electron and hole. The radius of the hydrogen-like motion in the j-th quantum state is

$$r_j=m_0 j^2 r_B \varepsilon_0/M, \tag{2}$$

where M is the reduced mass of two polarons. The mass of each of them is

$$M_i\approx 0.02\alpha_i^4\mu_i. \tag{3}$$

Here, α is the dimensionless polaron coupling constant. The clouds do not overlap if $r_j \gg r_{pi}$, which is equivalent to

$$5\varepsilon_0 c_0 j^2/\alpha_l^4 \gg 1, \tag{4}$$

where α_l refers to the lighter of the two particles.

In the strong-coupling case considered here we have $\alpha_l \gtrsim 10$ and the inequality (4) may be satisfied in practice only for very high values of j. Therefore, in considering the ground state of an exciton ($j=1$) we shall follow Refs. 10 and 11 and use a model in which an electron and a hole move adiabatically in a common polarization potential well.

Applying the methods developed earlier[1] we have to find the state of an electron and a hole $\psi(\mathbf{r}_1, \mathbf{r}_2)$ corresponding adiabatically to an arbitrary inertial polarization of a crystal $\mathbf{P}(\mathbf{r})$ by extremizing the functional

$$F[\psi,\mathbf{P}]=\left\langle\psi^*\left|-\frac{\hbar^2}{2\mu_1}\Delta_1-\frac{\hbar^2}{2\mu_2}\Delta_2-\frac{e^2}{\varepsilon_\infty r_{12}}\right|\psi\right\rangle - \int \mathbf{P}(\mathbf{r})\mathbf{D}[\psi,\mathbf{r}]\,d\tau+\frac{2\pi}{c_0}\int \mathbf{P}^2(\mathbf{r})\,d\tau \tag{5}$$

with respect to ψ keeping $\mathbf{P}(\mathbf{r})$ fixed. Here, $\mathbf{D}[\psi, \mathbf{r}]$ is the electrostatic induction of a $|\psi|^2$ cloud of the electron and hole charges:

$$\mathbf{D}[\psi,\mathbf{r}]=e\int|\psi(\mathbf{r}_1,\mathbf{r}_2)|^2\left[\frac{\mathbf{r}-\mathbf{r}_2}{|\mathbf{r}-\mathbf{r}_2|^3}-\frac{\mathbf{r}-\mathbf{r}_1}{|\mathbf{r}-\mathbf{r}_1|^3}\right]d\tau_1 d\tau_2. \tag{6}$$

After this extremization, $F[\psi_{\mathbf{P}}, \mathbf{P}]$ depends only on $\mathbf{P}(\mathbf{r})$ and represents the potential energy of the polarization vibrations of the ions. The equilibrium self-consistent polarizations of a crystal and the saddle point of a potential barrier can be found by varying $F[\psi_{\mathbf{P}}, \mathbf{P}]$ with respect to $\mathbf{P}(\mathbf{r})$. Thus, in these configurations F is stationary with respect to ψ and $\mathbf{P}$. These quantities can

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be found conveniently by varying $F[\psi, \mathbf{P}]$ first with respect to $\mathbf{P}$ for a fixed ψ, and then with respect to ψ itself.

Extremization of the functional (5) with respect to $\mathbf{P}$ gives

$$\mathbf{P}_\psi = \frac{c_0}{4\pi} \mathbf{D}[\psi, \mathbf{r}]. \tag{7}$$

As a result, Eq. (5) becomes

$$F[\psi, \mathbf{P}] = J[\psi] = \left\langle \psi^* \left| -\frac{\hbar^2}{2\mu_1}\Delta_1 - \frac{\hbar^2}{2\mu_2}\Delta_2 - \frac{e^2}{\varepsilon_\infty r_{12}} \right| \psi \right\rangle - \frac{c_0}{8\pi}\int \mathbf{D}^2[\psi, \mathbf{r}]\, d\tau. \tag{8}$$

This functional has to be varied now with respect to ψ.

The absolute minimum of $J[\psi]$ was found by direct variational methods in 1952 (Refs. 10 and 11). It was found that, depending on the parameters μ_1/μ_2 and $\varepsilon_\infty c_0$, it corresponds to free or self-localized excitons. However, the saddle points were not found because at that time it was not yet known that various types of exciton could coexist when separated by a potential barrier. We shall use a more flexible approximation $\psi(\mathbf{r}_1, \mathbf{r}_2)$ in the direct variational method and we shall analyze all the stationary points $J[\psi]$.

A test wave function will be selected in the form

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = C_N \exp\{-\lambda^2(r_1^2 + \beta r_2^2 + 2\delta \mathbf{r}_1\mathbf{r}_2)\}, \tag{9}$$

where λ, β, and δ are the variational parameters, and C_N is the normalization constant. We shall find it convenient to use not the functional J itself but its ratio to the energy of a nonpolarizing exciton calculated for a function similar to Eq. (9). Variation with respect to λ gives the value of this ratio

$$J_0 \equiv \frac{J}{|E_0|} = -\frac{1}{8}\frac{1+k}{1+\beta k}(\beta - \delta^2) \times \left\{ 2 \Big/ \left(\frac{1+\beta}{2} + \delta\right)^{1/2} + \varepsilon_\infty c_0 \left[1 + \beta^{-1/2} - \left(\frac{8}{1+\beta}\right)^{1/2} \right] \right\}^2, \tag{10}$$

where

$$k = \frac{\mu_1}{\mu_2} \leqslant 1, \qquad E_0 = -\frac{e^4\mu_1}{\varepsilon_\infty^2 \hbar^2}\frac{4}{3\pi}\frac{1}{1+k}.$$

We carried out more accurate calculations when a test function with a large number of variational parameters was a sum of terms of the type given by Eq. (9). It was found that although $J_{\min}$ for the lowest minimum and E_0 decreased considerably (and E_0 reached practically the exact value), their ratio hardly differed from that found from Eq. (10). Hence, we may expect to obtain a reasonable estimate on this basis for J_0 at the saddle point.

Introducing

$$b = {}^1/_2(1+\beta), \quad x = (b+\delta)^{1/2}, \quad 2/\gamma = \varepsilon_\infty c_0 (1 + \beta^{-1/2} - 2b^{-1/2}),$$

we find that the condition for an extremum of J with respect to δ gives the following equation for x:

$$2x^5 + \gamma x^4 - (1+\beta)x^3 - {}^1/_4\gamma(1-\beta)^2 = 0, \tag{11}$$

which has just one real root for a given value of β. The condition for an extremum of J with respect to β gives an equation which makes it possible to determine k as a function of β:

$$\frac{k}{1+\beta k} = \frac{1}{\beta - \delta^2} - \frac{x\gamma}{2(x+\gamma)}\left\{ \frac{1}{x^3} + \varepsilon_\infty c_0 \left(\frac{1}{\beta^{3/2}} - \frac{1}{b^{3/2}} \right) \right\}. \tag{12}$$

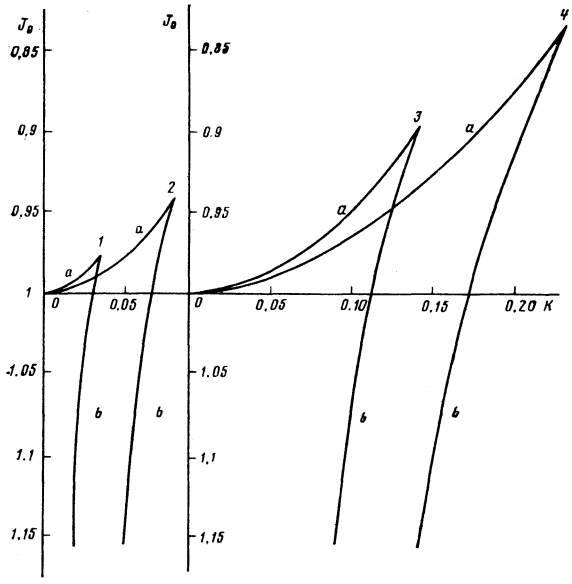

FIG. 1. Dependences of the absolute energies at a saddle point (curve *a*) and of the energy of a polarizing exciton (curve *b*), measured in units of the free-exciton energy, on the ratio of the effective masses of an electron and a hole. The number of the curve is identical with the value of $4\varepsilon_\infty c_0$.

Thus, variation of β makes it possible to plot the dependence of the stationary values of J_0 on the mass ratio k. The results are given in Fig. 1. Curve *a* describes the position of a saddle point of a potential barrier and corresponds to the same value of $\varepsilon_\infty c_0$ as curve *b* which touches it. Curve *b* represents the energy of a polarizing exciton. Moreover, there is an extremum of J, equal to E_0, at $\beta = 1$ and $\delta = -1$, which corresponds to a nonpolarizing exciton. On increase in the mass ratio and approach to the point of contact between curves *a* and *b* the excess of the potential barrier above state *b* is canceled out and the minimum of J_0 represented by curve *b* disappears, i.e., beyond the point of contact there is polarizing exciton (within the framework of the adopted adiabatic approximation). For $J_0 \leqslant -1$ our numerical results (curves denoted by *b*) agree with those deduced from the analytic formula (25) in Ref. 11, which (rewritten in our notation) is

$$J_0 = -{}^1/_8(1+k)\{[2^{3/2} + \varepsilon_\infty c_0(1-2^{3/2})]^2 + (\varepsilon_\infty c_0)^2/k\}. \tag{13}$$

This formula is obtained from Eq. (10) in the limit of high values of β. It corresponds to the sum of the energies of a polaron formed from a heavy particle [second term in Eq. (13)] and of an F center formed from a light particle and the same polaron.

It is remarkable that the barrier height W is small compared with the exciton binding energy $|E_0|$. Moreover, since curve *b* in Fig. 1 drops very steeply, it follows that throughout most of the range of k the barrier height is considerably less than the self-localization energy, i.e., it is considerably less than the difference between the energies of free and polarizing excitons. This is in qualitative agreement with the experimental results.[6-8]

It must be stressed that the adiabatic approximation is valid only if for fixed positions of the ions the energy

spectrum of the electon subsystem is discrete and the distances between its levels are much greater than $\hbar\omega$. In the case of a free exciton this is not true, i.e., a different approximation method should be used (for example, the method of weak or intermediate electron–phonon coupling). In this case we can regard the hydrogen-like motion of an electron and a hole as the zeroth approximation and introduce the electron–phonon interaction as a perturbation so that in the second approximation we obtain a small reduction in the exciton energy and the resultant polarization of the crystal. Approximately the same results are obtained also in the intermediate coupling approximation.[14,15] The small effects are not shown in Fig. 1 and a nonpolarizing exciton is more correctly called a weakly polarizing one.

The effective mass method and macrocalculations of the crystal polarization used above are valid if the radius of a carrier with a large effective mass exceeds the lattice constant. If the polarization of a crystal changes little the effective radius of an exciton compared with the case of a free exciton, for which

$$r_{1\,\mathrm{eff}}+r_{2\,\mathrm{eff}}\approx\hbar^2\varepsilon_\infty/\mu_1 e^2 \quad (\mu_1\leqslant\mu_2), \tag{14}$$

then $r_{2\mathrm{eff}}/r_{1\mathrm{eff}}\approx\mu_1/\mu_2\leqslant 1$ and the radius $r_{2\mathrm{eff}}$ may be smaller than the lattice constant even if $r_{1\mathrm{eff}}$ exceeds it. In this case an analysis of the internal motion in an exciton shows that particle 2 forms a low-mobility small-radius polaron whose energy has to be found by microcalculations, instead of the macrocalculations which give the last term in Eq. (13).

If a polarizing exciton has a very deep polarization well exceeding the Coulomb interaction between an electron and a hole, the effective radii are much smaller than those given by Eq. (14). We cannot exclude the possibility that the polarization potential well at a saddle point is shallower and the effective radii still satisfy the relationship (14). We may then find that, because of the small effective radii, a polarizing exciton cannot be analyzed by continuum methods, whereas the height of the potential barrier can still be determined by these methods (curve *a* in Fig. 1 still remains meaningful, whereas curve *b* is now meaningless).

The height of the potential barrier has been determined so far only for some alkali halide crystals.[6-8] Unfortunately, these crystals do not obey the large-radius criterion and the theoretical results cannot be regarded as quantitatively correct.

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