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Positronium in alkali halides: Tunneling from the delocalized to the self-trapped state

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The tunnel transition of positronium (Ps) from its stable delocalized state to the metastable localized state in alkali halides is investigated theoretically using the formalism developed by Nasu and Toyozawa for excitons [J. Phys. Soc. Jpn. **50**, 235 (1981)]. The tunneling rate between these two states is found to have the exponential dependence on the parameter $B/\hbar\omega$ (B is half of the Ps bandwidth, ω is the averaged frequency of the longitudinal acoustic phonons), whereas the potential barrier height between the two states is mainly determined by the bandwidth B and is proportional to B. A fitting procedure taking into account the quantum tunneling of Ps between the delocalized and the self-trapped state is proposed for the theoretical interpretation of the experimental data on Ps self-trapping. The procedure yields the numerical values of the parameters of Ps self-trapping (the tunneling rate and the potential barrier height) in qualitative agreement with those calculated theoretically. [S0163-1829(98)06218-3]

I. INTRODUCTION

Positronium (Ps) formation in alkali halide crystals has presently been well established by means of the positron annihilation technique.[1–3] In the crystals with low enough concentration of defects, the Ps atom has been experimentally found to form in two types of states: the delocalized (Bloch-like, free) type and the localized one.[3,4] The formation of the Bloch-type positronium is confirmed by observing very narrow peaks (the central peak and the side peaks appearing at the momentum corresponding to the reciprocal lattice vectors of the sample crystal) in the momentum distribution of the annihilation radiation at sufficiently low temperatures (typically less than a few tens K).[5–10] This type of positronium is completely delocalized.

As the temperature increases it is observed[4,11–14] that the central Ps peak becomes drastically wider and the side peaks disappear, indicating the localization of positronium in the crystal volume of the order of the lattice constant. This effect was attributed to a temperature activated transition of the free delocalized Ps to the self-trapped state.[12–14] Analogous phenomenon is known for holes and excitons in crystal dielectrics.[15,16] For instance, it is known[15,16] that the ground stable state of an electron in alkali halide crystals is delocalized, whereas the ground states of excitons and holes are localized. This is connected with the broad band of the electron (the band mass is $\sim m_0$, the free-electron mass) and with the comparatively narrow bands [the band masses are $\sim(5-10)m_0$] of the excitons and holes in these crystals. For excitons, moreover, additional metastable states exist that are delocalized. The Ps atom can be regarded to some extent as an ''isotope'' of the exciton, and, in this sense, for positronium in alkali halides an analogous situation takes place with the only difference being that, since the Ps band is less narrow than that of the exciton [the Ps band mass is $\sim(2.5-4)m_0$ (Ref. 14)], the ground stable state of Ps in alkali halides is delocalized and the metastable one is localized. In other words, since Ps is lighter, it is more difficult to be localized than the exciton in the same material.[15]

According to theoretical studies of the electron and exciton[17–22] (see also Refs. 15 and 16), the free and the localized states are separated by the adiabatic potential barrier due to the short-range nature of the interaction with longitudinal acoustic phonons. The double-well structure of the adiabatic potential, in turn, results in a two-component character of the emission spectra of the decaying particle. The two components originate from the delocalized and the self-trapped excitonic states, giving a narrow and a broad decay spectrum, respectively.[15]

The temperature activated transition of positronium from the delocalized to the self-trapped state was observed experimentally for a number of alkali halide crystals such as NaF,[11] KCl,[13] KI,[3] etc.[14] The temperature of the self-trapping (the temperature at which half of all the Ps atoms decay from the self-trapped state) was experimentally estimated to be $T_{\mathrm{ST}} \sim 150$, 65, and 50 K for NaF,[12] KCl,[13] and KI,[14] respectively. The experimentally observed fractions of the self-trapped Ps in KI and KCl were compared with the predictions of a simple classical model.[3,12–14] A deviation was observed at $T<T_{\mathrm{ST}}$ of the experimental fraction from the value expected. It was suggested that this deviation was possibly attributed to the tunneling of the delocalized Ps through the adiabatic potential barrier into the self-trapped state. An attempt was made to explain this deviation by phenomenologically introducing an effective temperature.[3]

The purpose of the present paper is to investigate the Ps tunneling between the free and the self-trapped state theoretically, and to clarify the role of this purely quantum process in the temperature activated transition of Ps from one state to another. Although the analogous tunnel transition for the exciton was already studied in a number of works,[23–27] it is impossible merely to extend the excitonic theory to positronium. Additional analysis is necessary for positronium, taking into account the metastability of the self-trapped state.

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We consider the interaction of Ps with longitudinal acoustic phonons within the adiabatic approximation. The Ps interaction with optical phonons is assumed to be negligibly small due to the electroneutrality of Ps.[28] In Sec. II the basic equations are derived for the positronium-acoustic-phonon coupling constant, for the parameters of the adiabatic potential (the barrier height and the tunneling path length), and for the Ps tunneling rate from the free to the self-trapped state. Following the general theory for the exciton,[24] we introduce a trial interaction mode and formulate the interaction of Ps with acoustic phonons in terms of this mode only. The potential barrier height, the tunneling path length, and the Ps tunneling rate from the stable delocalized to the metastable self-trapped state are written in terms of the trial interaction mode. Then the degree of localization of the trial mode is regarded as a variational parameter to be chosen so that the barrier height is minimal and the tunneling rate is maximal.

In Sec. III we explain how to incorporate the tunneling rate into the formulas previously proposed for the analysis of the self-trapping,[14] and thus to take into account the possibility of the tunnel self-trapping of Ps at $T<T_{\mathrm{ST}}$. We fit the new formula to the experimental data for Ps in KCl (Ref. 13) and in KI (Ref. 14) and get the numerical values for the Ps tunneling rate from the free delocalized to the self-trapped state, and for the barrier height and the energy difference between the two states.

In Sec. IV we perform the numerical calculations of the barrier height, the tunneling path length, and the tunneling rate for Ps in KI, KCl, and in NaF in terms of the theoretical relations obtained in Sec. II. We also discuss the results obtained in two previous sections.

II. ADIABATIC POTENTIAL FOR POSITRONIUM SELF-TRAPPING AND POSITRONIUM TUNNELING RATE FROM THE DELOCALIZED TO THE SELF-TRAPPED STATE

Below we will basically follow the theory of the tunnel self-trapping of exciton developed by Nasu and Toyozawa,[24] which will, however, be modified to take into account the essential features of the Ps self-trapping. We start with the Hamiltonian $\mathcal{H}$ of Ps coupled with the field of longitudinal acoustic phonons. Ps is assumed to be in the ground $1S_{1/2}$ internal state during the whole self-trapping process, since the typical energies of the acoustic phonons (~ 0.01 eV) are much less than the energy difference between the ground and the first excited state of Ps (~ 5 eV). The wave function of Ps can, in such a case, be factorized in the form

$$\Psi=\phi(\mathbf{n})|1S_{1/2}\rangle, \tag{1}$$

where $\phi(\mathbf{n})$ denotes the center-of-mass wave function, and $\mathbf{n}$ is the center-of-mass coordinate of the Ps atom expressed in the units of the lattice constant. The Hamiltonian of the Ps averaged over the internal degrees of freedom takes the form

$$H=\langle 1S_{1/2}|\mathcal{H}|1S_{1/2}\rangle=H_{\mathrm{Ps}}+H_{\mathrm{ph}}+H_{\mathrm{int}}. \tag{2}$$

The first term in Eq. (2) denotes the band energy of Ps in the tight-binding approximation

$$H_{\mathrm{Ps}}=B-\frac{B}{3}\sum_{j=x,y,z}\cos(-i\nabla_j), \tag{3}$$

where B is the half of the Ps bandwidth, and ∇_j ($j=x,y,z$) is the jth Cartesian component of the gradient operator of $\mathbf{n}$. The crystal is assumed to have a simple cubic structure. In contrast to the case of the exciton,[26] such an assumption appears to be fairly natural for Ps, since the experiment shows that Ps in alkali halides hardly distinguishes the anion and the cation and only ''sees'' the simple cubic lattice.[8,10] The second term in Eq. (2) is the phonon Hamiltonian. It is written in the adiabatic approximation as

$$H_{\mathrm{ph}}=\frac{\hbar}{2}\sum_{\mathbf{q}}{}'\ \omega_{\mathbf{q}}(C_{1\mathbf{q}}^2+C_{2\mathbf{q}}^2), \tag{4}$$

where $C_{k\mathbf{q}}$ ($k=1,2$) are the dimensionless coordinates of the standing phonon wave of the cosine ($k=1$) or the sine ($k=2$) type with the wave vector $\mathbf{q}$, $\omega_{\mathbf{q}}=uq$ the frequency of the acoustic wave, u the sound velocity, and $\Sigma'_{\mathbf{q}}$ denotes the summation over the half of the first Brillouin zone. The third term in Eq. (2) is the Ps–acoustic-phonon interaction. It can be represented in the form

$$H_{\mathrm{int}}=-S\sqrt{\frac{2}{N}}\sum_{\mathbf{q}}{}'\ \hbar\omega_{\mathbf{q}}\sqrt{\frac{\bar{q}}{q}}L_{\mathbf{q}}\{C_{1\mathbf{q}}\cos(\mathbf{q}\cdot\mathbf{n})+C_{2\mathbf{q}}\sin(\mathbf{q}\cdot\mathbf{n})\}, \tag{5}$$

where $S=E_d/\sqrt{\hbar\omega M u^2}$ is the dimensionless coefficient, E_d the deformation potential constant (it is assumed to be the same for the electron and the positron in the Ps atom, since the deformation potential corresponds to the variation of the band structure of the particle with changing the interionic distances, and the lowest positron band in alkali halides is not considerably different from the conduction band of the electron,[29]) M the mass of the elementary cell, N the total number of the elementary cells of the crystal, $\bar{q}=\Sigma_{\mathbf{q}}|q|/N$ the averaged phonon wave vector, and $\omega=u\bar{q}$ the averaged acoustic phonon frequency. The factor $L_{\mathbf{q}}$ comes from the relative motion of the electron and the positron in the Ps atom[30,31]

$$L_{\mathbf{q}}=2\left\langle 1S_{1/2}\middle|\cos\left(\frac{\mathbf{q}\cdot\mathbf{r}}{2}\right)\middle|1S_{1/2}\right\rangle=\frac{2}{(1+q^2a_B^2/16)^2}, \tag{6}$$

where $\mathbf{r}$ is the relative motion coordinate and a_B is the Bohr radius of Ps.

Our purpose in this section is to determine the adiabatic potential for the Ps self-trapping in the crystal lattice. To do so we first define a localized distortion mode of the lattice[24]

$$Q_{\mathbf{n}}=\sqrt{\frac{2}{N}}\sum_{\mathbf{q}}{}'\ \frac{\omega_{\mathbf{q}}}{\omega}\sqrt{\frac{\bar{q}}{q}}\{C_{1\mathbf{q}}\cos(\mathbf{q}\cdot\mathbf{n})+C_{2\mathbf{q}}\sin(\mathbf{q}\cdot\mathbf{n})\}, \tag{7}$$

which is, in other words, the dimensionless configuration coordinate describing the displacement of an atom from the **n**th lattice site. Equations (4) and (5) are then rewritten in terms of $Q_{\mathbf{n}}$ as

$$H_{\mathrm{ph}}=\frac{\hbar\omega}{2}\sum_{\mathbf{n}} Q_{\mathbf{n}}^2 \tag{8}$$

and

$$H_{\mathrm{int}}=-\hbar\omega S\frac{2}{N}\sum_{\mathbf{q},\mathbf{m}}{}' L_{\mathbf{q}}\, Q_{\mathbf{m}}\{\cos(\mathbf{q}\cdot\mathbf{n})\cos(\mathbf{q}\cdot\mathbf{m}) + \sin(\mathbf{q}\cdot\mathbf{n})\sin(\mathbf{q}\cdot\mathbf{m})\}, \tag{9}$$

whereupon we assume the localized distortion mode $Q_{\mathbf{n}}$ to have the following spatial distortion pattern:

$$Q_{\mathbf{n}}=Q\Phi_{\mathbf{n}}(\alpha), \tag{10}$$

$$\Phi_{\mathbf{n}}(\alpha)=\exp[-\alpha(|n_x|+|n_y|+|n_z|)/2]\tanh^{3/2}(\alpha/2),$$

where α is the reciprocal distortion radius and Q is the amplitude of the lattice distortion. We also define the trial center-of-mass wave function of Ps in the form

$$\phi(\mathbf{n},\beta)=\exp[-\beta(|n_x|+|n_y|+|n_z|)/2]\tanh^{3/2}(\beta/2), \tag{11}$$

with β, the reciprocal radius of the center-of-mass motion, being the variational parameter. In Eqs. (10) and (11) n_j ($j=x,y,z$) are the Cartesian components of **n** that are regarded to be integers ($n_{x,y,z}=0,\pm1,\pm2,\dots$) as if they were corresponding to the lattice points of the simple cubic crystal, so as to take the discreteness of the lattice into account. The functions $\Phi_{\mathbf{n}}(\alpha)$ and $\phi(\mathbf{n},\beta)$ have been chosen in such a way as to account for the existence of the two Ps states in the crystal. For example, at small $\beta\to0$ (the large center-of-mass distribution radius) one obtains $|\phi(\mathbf{n},\beta)|^2\approx(\beta/2)^3\sim1/N\to0$, indicating the absence of the localization. We then have the delocalized Ps state with the wave function $\phi(\mathbf{n},\beta)=1/\sqrt{N}$. This case corresponds to the small reciprocal distortion radius $\alpha\to0$. Accordingly, $|\Phi_{\mathbf{n}}(\alpha)|^2\to0$ too, indicating the absence of the lattice distortion around the delocalized positronium. In the opposite case of large β (the small center-of-mass distribution radius) one has $|\phi(\mathbf{n},\beta)|^2\to\delta_{|n_x|,0}\delta_{|n_y|,0}\delta_{|n_z|,0}$, i.e., the positronium is localized at the origin of the coordinate system chosen (the origin can be fixed at any atom of the crystal lattice). This then corresponds to the large reciprocal distortion radius α and, as a consequence, to the large lattice distortion at this point since $|\Phi_{\mathbf{n}}(\alpha)|^2\to\delta_{|n_x|,0}\delta_{|n_y|,0}\delta_{|n_z|,0}$. Thus both functions are the simplest ones, allowing one to describe the existence of the delocalized and completely localized Ps states in the same crystal.

The adiabatic potential U for the Ps self-trapping is defined as the total energy of Ps in the adiabatic approximation. This energy is given by averaging the Ps Hamiltonian, Eq. (2), over the trial center-of-mass wave function, Eq. (11),

$$U=\overline{H}_{\mathrm{Ps}}+\overline{H}_{\mathrm{ph}}+\overline{H}_{\mathrm{int}}. \tag{12}$$

This, in view of Eq. (3) and Eqs. (8)–(10), give us U as a function of α, β, and Q:

$$\frac{U}{B}=1-\sqrt{1-x^2}-2gF(x,y)\overline{Q}+g\overline{Q}^2, \tag{13}$$

where

$$F(x,y)=2\left(\frac{x(1+xy)}{x+y}\sqrt{\frac{2y}{1+y^2}}\right)^3,\quad x=\tanh(\beta/2),$$

$$y=\tanh(\alpha/4). \tag{14}$$

The first two terms in Eq. (13) come from the Ps kinetic energy $\overline{H}_{\mathrm{Ps}}$, the third and the forth terms are $\overline{H}_{\mathrm{int}}$ and $\overline{H}_{\mathrm{ph}}$, respectively. The parameter $\overline{Q}=Q/S$ denotes the reduced amplitude of the distortion pattern, $g=\hbar\omega S^2/2B$ is the dimensionless coupling constant of Ps with acoustic phonons. The function $F(x,y)$ has been obtained as a result of power expansion of $L_{\mathbf{q}}$ in Eq. (9) to the zeroth order in $(qa_B/4)^2$.

Equation (13) must be minimized with respect to the variational parameter β (or x). The corresponding condition $\partial U/\partial x=0$, being applied to Eq. (13), gives us

$$\overline{Q}=\frac{x}{2g\sqrt{1-x^2}}\left(\frac{\partial F(x,y)}{\partial x}\right)^{-1}. \tag{15}$$

Equation (15), being substituted into Eq. (13), eliminates the reduced amplitude $\overline{Q}$, yielding

$$\frac{U}{B}=1-\sqrt{1-x^2}-\frac{x}{\sqrt{1-x^2}}F(x,y)\left(\frac{\partial F(x,y)}{\partial x}\right)^{-1} + \frac{x^2}{4g(1-x^2)}\left(\frac{\partial F(x,y)}{\partial x}\right)^{-2}. \tag{16}$$

In this way we finally get the adiabatic potential U/B as a function of the reduced amplitude $\overline{Q}$ and the reciprocal radius α (or y) of the lattice distortion. It is given by the parametric set of Eqs. (15) and (16) with x as a parameter.

The adiabatic potential obtained contains the coupling constant g whose value is not known. It can be estimated by the comparison with an experiment through the following procedure. When Ps is self-trapped, the range of the lattice distortion around it is small ($\sim a$, the lattice constant), and hence the reciprocal distortion radius α is large, yielding $y\sim1$. So, we can eliminate y from Eqs. (15) and (16) by putting $y=1$. The set of equations thus obtained gives us the adiabatic potential for the self-trapped Ps as a function of $\overline{Q}$, the minimum of which determines the energy difference between the delocalized and the self-trapped Ps states (the energy of the delocalized state is taken to be zero). The minimum condition $\partial U(g,x,y=1)/\partial x=0$ gives us the equation for g as a function of x, which, being substituted into $U(g,x,y=1)/B$, eliminates g from U/B. In this way we get the following set of two equations, the parametric representation of the adiabatic potential for the self-trapped Ps as a function of the coupling constant g:

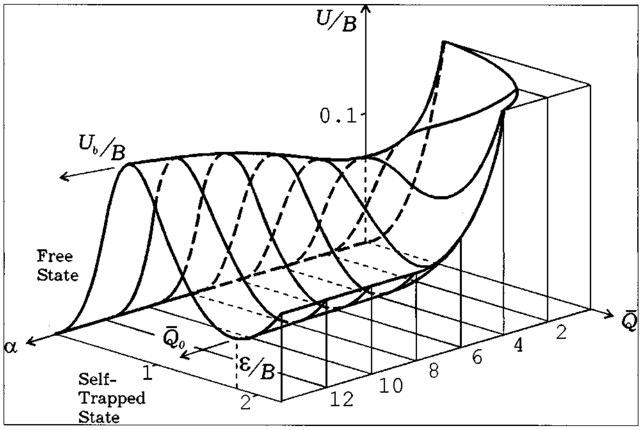

FIG. 1. The adiabatic potential for the Ps self-trapping in KI, calculated from Eqs. (15) and (16) with g determined from Eqs. (17).

$$\frac{U}{B}=1-\sqrt{1-x^2}-\frac{x^2}{6\sqrt{1-x^2}}, \tag{17}$$

$$g=\frac{1}{24x^4\sqrt{1-x^2}}.$$

Note that the set of Eqs. (17) yields $U/B\approx 1-4g$ for the self-trapped state ($x\sim 1$) in agreement with the result recently obtained by another method.[32] Putting U in the first of Eqs. (17) to be equal to $\mathcal{E}$, the experimental value of the energy difference between the stable delocalized and the metastable self-trapped Ps state, one can calculate the corresponding value of the parameter x, which lets us obtain g from the second of Eqs. (17). The value of g thus obtained is to be substituted into the parametric Eqs. (15) and (16) and in Eq. (13) for the adiabatic potential of Ps. The value $\mathcal{E}$ of the energy difference between the two Ps states can be obtained by fitting the experimental data on Ps self-trapping (see Sec. III).

The height U_b of the adiabatic potential barrier between the two states, measured from the bottom of the free Ps band, is determined by the two conditions: $\partial U/\partial\bar{Q}=0$ and $\partial U/\partial x=0$. The first one, applied to Eq. (13), gives us

$$\bar{Q}=F(x,y). \tag{18}$$

The second one, in view of Eq. (18), becomes

$$\frac{x}{\sqrt{1-x^2}}-2gF(x,y)\frac{\partial F(x,y)}{\partial x}=0. \tag{19}$$

The barrier height U_b is now obtained by substituting the root of Eq. (19) into Eq. (16) and then by minimizing the function obtained with respect to y (or α).

In Fig. 1 the result of the numerical calculation of U/B for the KI crystal is shown as a typical example of the Ps adiabatic potential energy inside the ionic crystal as a function of α and $\bar{Q}$. In this calculation the value of $\mathcal{E}$ was taken to be 0.013 eV (see Sec. III). As is seen, the adiabatic potential is nearly parabolic with respect to $\bar{Q}$ at $\alpha\ll 1$, while at moderate α it becomes a double-well structure and U_b takes its minimum. As α increases further, U_b increases as well, while the valley of the self-trapped state becomes deeper, approaching its minimum at $\alpha\gtrsim 10$.

The tunneling path length $\bar{Q}_0$ is determined as follows. According to the energy conservation, the transition ''delocalized Ps–self-trapped Ps'' takes place with the total energy $\mathcal{E}$ in the case where the localized state is metastable. Therefore, the value of x_0 (or β_0) just after the tunneling can be determined from Eq. (16) under the additional condition $U=\mathcal{E}$. The substitution of x_0 obtained into Eq. (15) gives us the tunneling path length $\bar{Q}_0$ as a function of y (or α).

To estimate the tunnel transition rate of Ps, Γ, we use the expression derived by Nasu and Toyozawa for the exciton.[24] The tunneling is assumed to occur along the trial interaction mode defined by Eq. (10). Its reciprocal distortion radius α (or y) is the variational parameter to be determined so as to maximize Γ at the final stage of the calculation. According to Nasu and Toyozawa,[24] the tunnel self-trapping rate of the exciton at zero temperature as a function of the reciprocal distortion radius, in the case where only the acoustic phonons are taken into account, is given by

$$\Gamma(y)=\omega(S'Q_c)^2\frac{2\sqrt{\pi}}{S_e\sqrt{\langle Q^2\rangle}}\exp\left(-\frac{Q_c^2}{\langle Q^2\rangle}\right), \tag{20}$$

where $S_e=SF(x_0,y)$ with $x_0=\tanh(\beta_0/2)$ being the value of x just after the tunneling, and

$$S'=S\left(\frac{1+zy}{z+y}\right)^3\left(\frac{4zy}{(1+z^2)(1+y^2)}\right)^{3/2}, \tag{21}$$

with $z=\tanh(\beta_0/4)$. The quantity

$$\langle Q^2\rangle=\left(\frac{2}{y(1+y^2)}\right)^3\frac{1}{N}\times\sum_{\mathbf{q}}\frac{\omega_{\mathbf{q}}}{\omega}\prod_{j=x,y,z}\left[1+\left(\frac{1}{y^2}-1\right)\sin^2\left(\frac{q_j}{2}\right)\right]^{-2} \tag{22}$$

is the thermally averaged amplitude squared of the trial interaction mode at $T=0$ K. The parameter Q_c is defined as follows. The adiabatic potential energy $U(Q)$ of the self-trapped state in the vicinity of the final point Q_0 of the tunnel transition is written from Eq. (13) as

$$U(Q)=-\hbar\omega S_e(Q-Q_c)+\frac{\hbar\omega}{2}Q^2. \tag{23}$$

Then the constant term for the exciton is determined from the condition $U(Q_0)=0$, because the self-trapped excitonic state is stable with the energy lower than that in the free delocalized state.

For Ps, however, the self-trapped state is metastable with the energy higher by $\mathcal{E}$ than that in the free state. Therefore, this condition evidently has to be changed to $U(Q_0)=\mathcal{E}$. Thus, for Ps we get

$$Q_c=\frac{\mathcal{E}}{\hbar\omega S_e}+Q_0\left(1-\frac{Q_0}{2S_e}\right). \tag{24}$$

As is seen from the equation $H_{\mathrm{ph}}=U(Q)$, in view of Eqs. (8) and (10), Q_c thus defined has a meaning of the crossing point of the two adiabatic potential energy surfaces extended from the initial $Q=0$ and from the final $Q=Q_0$ point of the tunnel transition, respectively, (see Fig. 1). The tunnel transition, in turn, according to Eq. (20), mainly occurs around the crossing point Q_c.

In estimating Γ by Eq. (20) we neglect the temperature dependence of the shape of the adiabatic potential for the Ps self-trapping. This can be justified by the fact that the typical self-trapping temperatures of Ps in alkali halides, as it follows from the experiment,[3,14] are low enough ($\sim$ a few tens K). Indeed, according to the instanton theoretical approach by Ioselevich and Rashba,[27] the temperature dependence of the shape of the adiabatic potential at low $T\rightarrow 0$ leads to the temperature dependence of the exponential factor and of the pre-exponential factor in the tunneling rate. For interaction with acoustic phonons these dependences are given by $(E_d^2\omega^2/\hbar\rho u^5)(T/T_D)^4$ and $(1-2T/T_D)^{-3/2}$, respectively, (ρ and T_D are the density and the Debye temperature of the crystal). It is easy to see now that both temperature-dependent factors are rather small for Ps in alkali halides at $T\lesssim T_{\mathrm{ST}}$ since the typical Debye temperatures are the quantities of the order of 10^2 K and much bigger than T_{ST}. Thus, in the first approximation, we can consider the tunneling rate to be temperature independent for Ps in alkali halides, and use Eqs. (20)–(24) for its numerical estimation. The rate, Eq. (20), must finally be maximized with respect to α to obtain the actual rate Γ of the tunnel transition of Ps between its free and self-trapped state.

III. ANALYSIS OF EXPERIMENTAL DATA WITH THE TUNNELING EFFECT TAKEN INTO ACCOUNT

According to the model of the Ps self-trapping previously proposed,[14] the fraction f_{ST} of the self-trapped Ps is given by

$$f_{\mathrm{ST}}=\frac{\lambda_t^{\mathrm{sa}}\gamma_t}{\lambda_f^{\mathrm{sa}}(\lambda_t+\gamma_f)+\lambda_t^{\mathrm{sa}}\gamma_t}, \tag{25}$$

where λ_f^{sa}, λ_t^{sa}, γ_t, and γ_f are the Ps self-annihilation rate from the free state, that from the self-trapped state, the trapping rate from the free state, and the detrapping rate from the self-trapped state, respectively; $\lambda_t=\lambda_t^{\mathrm{sa}}+\lambda_t^{\mathrm{po}}$ is the annihilation rate from the self-trapped state with the pickoff annihilation process (λ_t^{po}) taken into account. The effect of the tunneling is not taken into account in this model. The detrapping rate γ_f is assumed to have the temperature dependence of an activation type

$$\gamma_f=\nu\,\exp\left(-\frac{U_b-\mathcal{E}}{k_BT}\right), \tag{26}$$

where ν ($\sim\omega/2\pi$) is the typical phonon frequency associated with the local deformation of the lattice, and $U_b-\mathcal{E}$ is the height of the potential barrier ‘‘seen’’ by the Ps in the self-trapped state (see Fig. 1). The trapping rate γ_t is then obtained from the statistical detailed balance

$$\gamma_t g_f(T)=\gamma_f g_t \exp\left(-\frac{\mathcal{E}}{k_BT}\right), \tag{27}$$

where

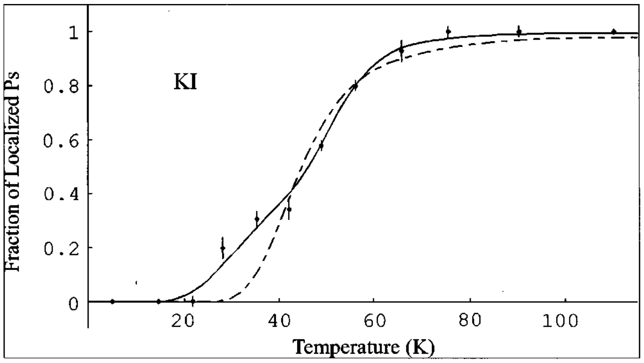

FIG. 2. Temperature dependence of the fraction f_{ST} of the self-trapped Ps in KI. The full circles show the experimental data and the dashed line is the least-squares-fitted theoretical curve of the model previously proposed ($\mathcal{E}=0.03_1$ eV, $U_b=0.04_7$ eV) (Ref. 14). The solid line represents the least-squares-fitted theoretical curve of the model proposed in the present paper ($\mathcal{E}=0.01_3$ eV, $U_b=0.05_9$ eV, $\Gamma=4.9_5\times 10^7$ s^{-1}).

$$g_f(T)=\sum_{\mathbf{k}}\exp\left(-\frac{E_{\mathbf{k}}}{k_BT}\right)=V\left(\frac{M^*k_BT}{2\pi\hbar^2}\right)^{3/2}$$

is the effective number of the free Ps states in the crystal of volume V at temperature T (here $E_{\mathbf{k}}$ denotes the lowest Ps band and M^* is the effective mass of Ps), and g_t is the number of the trapping sites in the same volume. This gives the trapping rate in the form

$$\gamma_t=\frac{g_t}{g_f(T)}\,\nu\,\exp\left(-\frac{U_b}{k_BT}\right). \tag{28}$$

In Eq. (28) the ratio $g_t/g_f(T)$ is large because the number of the possible self-trapping sites g_t is of the order of that of the unit cells. Therefore, the trapping rate γ_t is large at high temperature even if the trapping probability at a particular site in the crystal is small.

In the previous model[14] the experimental values of U_b and $\mathcal{E}$ were estimated by the least-squares fit of the experimental data for the fraction of the localized Ps to Eq. (25) with γ_f and γ_t given by Eqs. (26) and (28). As an example, in Fig. 2 the fitting curve for the KI crystal ($h\nu=0.0077$ eV, the phonon energy at which the density of the longitudinal acoustic mode is largest[33]) is reproduced from Ref. 14 by the dashed line. The curve is described by Eq. (25) taken under the assumption that $\lambda_f^{\mathrm{sa}}=\lambda_t^{\mathrm{sa}}$ and $\lambda_t=8\times 10^9$ s^{-1} (the annihilation rate of the free para-Ps in vacuum), with $\mathcal{E}=0.031$ eV and $U_b=0.047$ eV. At low temperature the significant deviation is seen of the theoretical curve from the experimental data, though at high temperature the behavior of the curve is quite satisfactory.

To explain this deviation it is natural to assume that the tunneling process of Ps from the free stable state to the self-trapped metastable state (see Fig. 1) starts at low temperature and dominates up to $T\lesssim T_{\mathrm{ST}}$ over the classical self-trapping mechanism of the activation type. As an attempt to take into account the tunneling effect, we introduce the detrapping rate γ_f in the form

$$\gamma_f=\nu\,\exp\left(-\frac{U_b-\mathcal{E}}{k_BT}\right)+\Gamma, \tag{29}$$

TABLE I. The parameters of the Ps self-trapping in some alkali halides.

Crystal	$\mathcal{E}^{\mathrm{exp}}$, eV	U_b^{exp}, eV	Γ^{exp}, s^{-1}	B, eV	$\hbar\omega$, eV	g	U_b, eV	Γ, s^{-1}
KI	0.01_3	0.05_9	$4.9_5\times10^7$	0.92	0.019	0.22	0.15	1.1×10^7
KCl	0.02_7	0.08_7	$8.2_4\times10^7$	1.16	0.031	0.22	0.19	1.0×10^9
NaF	0.10_7 (Ref. 12)			2.15	0.054	0.21	0.36	6.8×10^8

where Γ, the tunnel detrapping rate, is introduced to take into account the possibility for Ps to cross the adiabatic potential barrier quantum mechanically. Note that the physical meaning of the detrapping rate Γ thus introduced, is the same as that of the tunneling rate Γ introduced in Sec. II. In view of Eq. (29), the statistical detailed balance determined by Eq. (27) gives us the following modified expression for the trapping rate from the free to the self-trapped state:

$$\gamma_t=\frac{g_t}{g_f(T)}\left[\nu\,\exp\left(-\frac{U_b}{k_BT}\right)+\Gamma\exp\left(-\frac{\mathcal{E}}{k_BT}\right)\right], \qquad (30)$$

where the second term in the brackets describes the quantum mechanical contribution to the trapping rate. Note that again, as in the case of the classical trapping described by Eq. (28) [or by the first term in the brackets in Eq. (30)], even if Γ itself is small, the tunnel trapping rate can, because of the large factor $g_t/g_f(T)$, be sufficiently big so that Ps atoms forming in the free state tunnel through the potential barrier and annihilate mainly from the self-trapped state. Therefore, the fraction of the self-trapped Ps must start to grow at lower temperature than that predicted by the classical model given by Eqs. (25), (26), and (28) (Fig. 2, the dashed line).

In the present work we used Eq. (25) with γ_f and γ_t given by Eqs. (29) and (30) to estimate U_b, $\mathcal{E}$, and Γ experimentally. The least-squares fits of the experimental data were performed for KI (Ref. 14) and for KCl (Ref. 13) [$h\nu=0.0145$ eV (Ref. 33)] crystals under the same assumptions for λ_f^{sa}, λ_t^{sa} and for λ_t as in Ref. 14. The fitting curve for KI is shown by the solid line in Fig. 2, and the results of the fits for KI and KCl are listed in Table I in the columns marked as ''exp''. The new fitting curve behaves satisfactory over the whole temperature range, indicating the importance of the quantum tunneling process for Ps in KI at least up to the temperatures $T\lesssim T_{\mathrm{ST}}$. For KCl also the fitting procedure gives good correspondence of the fitting curve to the experimental data over the whole temperature range.

IV. DISCUSSION

The results of the numerical calculation of the adiabatic potential U for the Ps self-trapping, of the barrier height U_b, and of the tunneling path length Q_0, are shown in Figs. 1, 3, and 4. Since the values of the bandwidths for Ps in alkali halides are only poorly known, we estimated them from the expression given by the standard tight-binding approximation for all the crystals under study (KI, KCl, NaF): $B=3\hbar^2/Ma^2$, where a is the distance between the nearest neighbors, and M, the Ps band mass, was simply assumed to be equal to $2m_0$, the doubled free-electron mass. The coupling constant g was estimated from Eqs. (17) under the additional condition $U=\mathcal{E}$ with $\mathcal{E}$ obtained from the fits for KI and KCl, and taken from Ref. 12 for NaF. The bandwidths and the coupling constants thus determined (see Table I) were used, as described in Sec. II, to calculate U for the KI crystal as a function of α and Q (Fig. 1), and U_b and Q_0 for KI, KCl, and NaF as functions of α (Figs. 3 and 4).

As is seen from Figs. 3 and 4, with the increase of g (see Table I) the minimum of U_b/B decreases somewhat and the tunneling path length $\overline{Q}_0$ increases, indicating that the potential barrier between the stable delocalized and the metastable self-trapped states of Ps becomes wider as its height decreases. The dependences $U_b(\alpha)/B$ in Fig. 3 take their minima at $\alpha\sim4$. These minima, in accordance with the theory described in Sec. II, determine the numerical values of the barrier heights between the two Ps states in the corresponding crystals. The values of U_b thus calculated are listed in Table I.

In Fig. 5 the α dependence of the tunneling rate Γ for KI is shown as a typical example. The dependence was calcu-

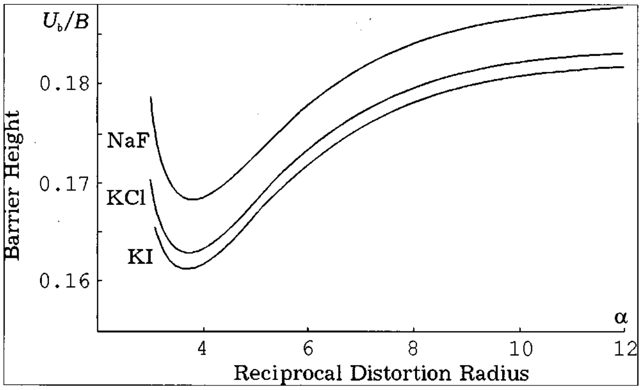

FIG. 3. The α dependence of the barrier height U_b for Ps in KI, KCl, and NaF, calculated from Eqs. (16) with g determined from Eqs. (17) and x determined from Eq. (19).

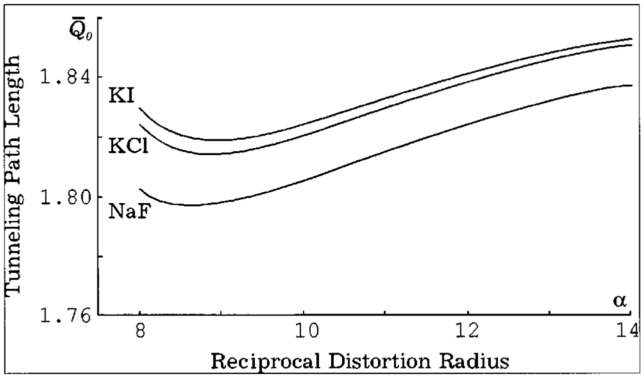

FIG. 4. The α dependence of the tunneling path length $\overline{Q}_0$ for Ps in KI, KCl, and NaF, calculated from Eq. (15) with g determined from Eqs. (17) and x_0 obtained from Eq. (16) as described in Sec. II.

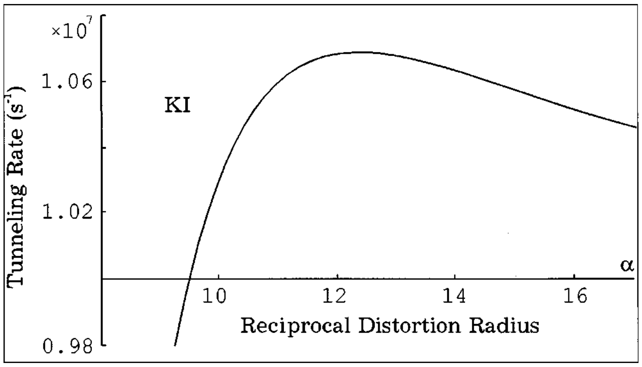

FIG. 5. The α dependence of the tunneling rate Γ obtained from Eqs. (20)–(24) for KI.

lated from Eqs. (20)–(24) with $\mathcal{E}$ taken from the fit. Similar dependences were obtained for KCl and for NaF ($\mathcal{E}$ was taken from the fit for KCl and from Ref. 12 for NaF). As is seen from the figure, $\Gamma(\alpha)$ takes its maximum at $\alpha \sim 12$. This maximum gives us the numerical value of the rate Γ of the tunnel transition of Ps between its free and self-trapped state. The values of Γ thus obtained are listed in Table I.

As is seen in Table I, the barrier heights and the tunneling rates estimated numerically, and those obtained from the fits of the experimental data, are in qualitative agreement. Although the calculated barrier heights are approximately two times higher than the experimental ones, they show the bandwidth dependence in agreement with the experiment. The same is true for the tunneling rates: the tunneling rate in KI is smaller than that in KCl, in agreement with the experiment. The quantitative disagreement of the values calculated with those obtained from the fits may be caused by the mathematical simplifications of the theoretical model. In particular, the phonon energies given by the model of the simple cubic lattice and shown in Table I, differ by a factor of approximately 2 from those used in the fits, 0.0077 eV for KI and 0.0145 eV for KCl.[33] Another source of the quantitative disagreement is the variational procedure used in the numerical calculations, since, as is known, the variational method is strongly dependent on the choice of the trial function.

Nevertheless, the qualitative agreement between the theory and the experiment lets us conclude that the potential barrier height U_b between the stable free and the metastable self-trapped state of Ps is mainly determined by the bandwidth B and increases with the bandwidth, in agreement with the predictions of the general theory for the case of the exciton.[24] The tunneling rate Γ is mainly determined by the factor $B/\hbar\omega$. This results from its Gaussian dependence on Q_c [see Eq. (20)], which is estimated from Eq. (24) as $Q_c \approx \sqrt{B/\hbar\omega}\times$(the factor weakly dependent on the type of the crystal). According to Table I, $B/\hbar\omega$ is bigger in KI than in KCl. Therefore, Γ in KI must be smaller than that in KCl, explaining qualitatively the results of the fits of the experimental data (see Table I).

Finally, it is interesting to note that, as in the case of the exciton,[24] the value of α that maximizes the Ps tunneling rate is not equal to that minimizing the potential barrier height (compare Figs. 5 and 3). This means that the tunneling path dominating in the self-trapping process at low temperatures is different from the thermal activation path that prevails at high temperatures.

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