



Self-Trapping of Excitons Beginning with Tunneling Nucleation

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The rate of self-trapping (ST) is calculated, considering that ST begins with quantum-mechanical tunneling of a free exciton to a state of nucleation less localized than the relaxed self-trapped one. Three cases appear depending on the site-diagonal and off-diagonal exciton-phonon interaction energies S_1 and S_2 relative to the half width B of the exciton band. When $S_2/B \geq 0.21$, ST through the nucleation state of two-center type predominates. When $S_2/B \leq 0.21$ and $S_1/B \leq 1.25$, only ST through that of one-center type occurs. When $S_2/B \leq 0.21$ but $S_1/B \geq 1.25$, the latter channel predominates at low temperatures but it is overcome by the former one with increasing temperature. Alkali halides except iodides are classified into the first case, RbI into the second one, and KI into the third one. The so called E_x luminescence observed only in alkali iodides should be emitted from a still unknown self-trapped state of one-center type.

§1. Introduction

In many crystals, including alkali halides,^{1,2)} rare-gas solids,³⁾ and organic molecular crystals,⁴⁾ exciton is self-trapped into a localized state with appreciable lattice distortion when the exciton-phonon interaction is strong enough.^{5,6)} Wave-like (Bloch-band) states of exciton delocalized with respect to its center-of-mass motion are not stable states in a deformable lattice in this case. Then, exciton is auto-localized inducing lattice distortion around itself, as it digs a hole containing itself. There exists, however, a potential barrier separating the free and the self-trapped exciton states in the configuration-coordinate space of lattice distortion.^{5,6)} Therefore, exciton in the free states is at least metastable against self-trapping from the standpoint of the classical description of lattice distortion. Optical excitation creates dominantly exciton in the free states with which no lattice distortion is associated, as understood from the Franck-Condon principle.⁷⁾ Exciton thus created is self-trapped by quantum mechanical tunneling through the potential barrier at low temperatures.

This initial dynamic process of self-trapping has been attracting much attention for a long

time.¹⁻³⁾ Recently, experiments probing directly the process have been performed. For example, Masumoto and others obtained the self-trapping rate at 4.2K in KI and RbI by measuring the rise time of luminescence from the self-trapped state with the use of the picosecond laser technique.^{8,9)} Many data on temperature quenching of luminescence from the free states have been reported for alkali halides and rare-gas solids for these several years.¹⁰⁻¹⁵⁾ The temperature quenching occurs because of increasing rate of self-trapping of free excitons with increasing temperature.

Theories on the initial process of self-trapping, however, are few and remain unsatisfactory. Before surveying the existing theories, let us look at the process in more detail. It should first be noted that in the course of self-trapping exciton created in the free states does not make a transition directly to the final shrunked state obtained at the relaxed lattice configuration. Self-trapping should rather be regarded as beginning with nucleation: First a state of nucleation with appreciable lattice distortion but less localized than the final shrunked one is formed by quantum mechanical tunneling, and then it shrinks inducing lattice distortion furthermore in order to stabilize itself. The self-trapping rate is a rate with which the most

probable nucleation state is formed. Moreover, self-trapping is a symmetry breaking process: The symmetry of the self-trapped state is lower than that of the lattice not only with respect to the translational symmetry but also with respect to the point-group one. For example, exciton in alkali halides is self-trapped into a state of two-center type centered at a pair of nearest-neighbor halogen ions by pulling them closer to one another.^{1,2)} Exciton in rare-gas solids is self-trapped not only into a state of two-center type but also into a state of one-center type centered at a single atom.^{3,16)} It is important here that the symmetry as well as the spatial extension of the nucleation state cannot *a priori* be anticipated because of symmetry breaking.

Rashba and his coworkers calculated in a series of papers the exponential factor of the self-trapping rate at zero degree with a continuum model, assuming that the spatial extension of the nucleation state for self-trapping is much larger than the lattice constant.⁶⁾ As will be shown in the present work, however, the spatial extension is of the order of the lattice constant in alkali halides and rare-gas solids. Then, the continuum model cannot be applied in describing the self-trapping process. Subsequently, Nasu and Toyozawa calculated the self-trapping rate still at zero degree, using a formalism not limited by the spatial extension of the nucleation state.¹⁷⁾ However, they did not take seriously that the spatial extension is of the order of the lattice constant. In fact, they calculated the rate in the simple cubic lattice which is unrealistic for alkali halides and rare-gas solids, assuming *a priori* the nucleation state of one-center type in spite of the fact that the self-trapped state of two-center type has usually been found in these crystals. When the spatial extension is of the order of the lattice constant, both the lattice structure and the symmetry of the nucleation state must be essentially important in determining the self-trapping rate. Moreover, they adopted the semiclassical approximation for phonons. As will be shown in the present work, the adiabatic potential associated with the nucleation state is lower by only several times the phonon energy than that associated with the lowest free state even at zero degree. In

this situation, the semiclassical approximation gives a rate much larger than the correct quantum mechanical treatment of phonons does, since the former gives a nonvanishing rate at zero degree even if the adiabatic potential associated with the nucleation state is higher than that associated with the lowest free state.

The present work is devoted to presenting a full quantum mechanical calculation of the self-trapping rate at finite temperatures as well as at zero degree in the face-centered cubic lattice realistic for alkali halides and rare-gas solids. (The width of the energy dispersion of exciton is roughly equal to that of hole in the valence band, which is composed of halogen *p* orbitals in alkali halides. Halogen ions crystallize in the face-centered cubic sublattice in the NaCl-type lattice of alkali halides.) The energy gain of the self-trapped state against the free state is given by the lattice relaxation energy subtracted by the loss of kinetic energy due to exciton localization. In the face-centered cubic lattice a pair of nearest neighbors have four common nearest neighbors. This makes the self-trapped state of two-center type advantageous in a point that the loss of kinetic energy is smaller therein than in the simple cubic lattice. Since the lattice binding the nucleation state is distorted already appreciably within a spatial extension of the order of the lattice constant, it seems reasonable to consider that the nucleation state with a certain symmetry changes into a relaxed self-trapped one with the same symmetry. Then it will be shown in the present work that it is essential to take into account both one- and two-center types for the nucleation state in reproducing simultaneously the self-trapping rate observed at 4.2K and the luminescence properties.

The fact that self-trapping is a symmetry-breaking process makes the problem difficult to solve. On the other hand, it makes the problem simple without defect nor impurity to trap exciton. Moreover, the lattice distortion associated with the nucleation state is, although appreciable, smaller than that associated with the relaxed self-trapped one, and it may be described within an approximation of the exciton-phonon interaction linear in the phonon coordinate.

The setup of the present paper is as follows.

The interaction to induce self-trapping is first clarified in §2. The self-trapping rate is calculated at zero degree in §3, while at finite temperatures in §4. Comparison with experiments is given in §5, and §6 summarizes the present work. Observed data on temperature quenching of free-exciton luminescence will be analyzed in the light of the present theory in the paper which just follows the present one.

§2. Interaction to Induce Self-Trapping

The Hamiltonian of the exciton-phonon system written as

$$H = H_E + H_{EL} + H_L, \quad (2.1)$$

is composed of three parts of H_E describing the free center-of-mass motion of exciton, H_{EL} the exciton-lattice interaction, and H_L the free vibration of the lattice. Considering only the

nearest-neighbor transfer of exciton with transfer integral $-B/12$ in the face-centered cubic lattice, we write H_E as

$$H_E = B \sum_n a_n^\dagger a_n - \frac{B}{12} \sum_{nm} (a_n^\dagger a_m + a_m^\dagger a_n), \quad (2.2)$$

where a_n with its Hermitian conjugate written above as a_n^\dagger represents an operator annihilating an exciton at a site n , and nm with $nm=mn$ means that sites n and m compose a pair of nearest-neighbor sites. In (2.2) the free states make an energy band extending upward from zero. Note here that the lowest free state is lower by B than a state completely localized at a single lattice site without lattice distortion. Considering both the site-diagonal and off-diagonal exciton-lattice interactions with interaction energies S_1 and S_2 respectively, we write H_{EL} as

$$H_{EL} = -\sqrt{2S_1} \sum_n Q_n a_n^\dagger a_n - \sqrt{2S_2} \sum_{nm} Q_{nm} (a_n^\dagger a_m + a_m^\dagger a_n), \quad (2.3)$$

where Q_n and Q_{nm} represent phonon coordinates modifying respectively the potential energy (in the first term of (2.2)) at a site n and the transfer integral (in the second term of (2.2)) at a pair nm of nearest-neighbor sites. Considering phonon momentum operators P_n and P_{nm} conjugate respectively to Q_n and Q_{nm} with commutation relations

$$[Q_i, P_j] = i\hbar \delta_{i,j}, \quad (2.4)$$

for i and j equal to n or nm , we write H_L as

$$H_L = \frac{1}{2} \sum_n (P_n^2 + Q_n^2) + \frac{1}{2} \sum_{nm} (P_{nm}^2 + Q_{nm}^2). \quad (2.5)$$

Here a simplification has been adopted that all the phonon modes are regarded as having a same energy quantum, in order to make later calculation on multiphonon processes tractable. The nucleation state for exciton self-trapping has a spatial extension of the order of a lattice constant, as will be shown later. Then the energy quantum $\hbar\omega$ of phonons should be estimated at an energy where the density of phonon modes becomes maximum at about the edge of the Brillouin zone. Exciton in the free states interacts only weakly with all phonon modes. The phonon energy quantum is taken as the unit of energies (such as B , S_1 and S_2) hereafter.

Self-trapping is a symmetry-breaking process as mentioned in §1. Therefore, the nucleation state for self-trapping nor the interaction to induce self-trapping cannot be anticipated *a priori* from the starting Hamiltonian (2.1). We must even derive them from (2.1). Let us write the wave function of the nucleation state as

$$|d\rangle = \sum_n \gamma_n a_n^\dagger |0\rangle, \quad (2.6)$$

with a positive amplitude γ_n at a site n , where $|0\rangle$ represents the exciton vacuum. The amplitude must satisfy the normalization condition $\sum_n \gamma_n^2 = 1$. A phonon mode so constructed as to have interaction diagonal with respect to a specific exciton state $|d\rangle$ has been called the interaction mode.¹⁸⁾ In the present case its coordinate operator Q is determined by

$$\langle d | H_{EL} | d \rangle = -\sqrt{2\bar{S}} Q, \quad (2.7)$$

where \bar{S} is determined under the condition that Q is obtained by a unitary transformation from Q_n 's and Q_{nm} 's. In this case, H_L of (2.5) is diagonal with respect to both Q and its conjugate momentum operator P satisfying $[Q, P] = i\hbar$, and the part containing them is written as

$$\bar{H}_L = \frac{1}{2}(P^2 + Q^2). \quad (2.8)$$

Using $\langle d|a_n^\dagger a_n|d\rangle = \gamma_n^2$ and $\langle d|a_n^\dagger a_m + a_m^\dagger a_n|d\rangle = 2\gamma_n\gamma_m$, we get

$$\bar{S} = S_1 \sum_n \gamma_n^4 + 4S_2 \sum_{nm} \gamma_n^2 \gamma_m^2, \quad (2.9)$$

and

$$Q = -\sqrt{S_1/\bar{S}} \sum_n \gamma_n Q_n - 2\sqrt{S_2/\bar{S}} \sum_{nm} \gamma_n \gamma_m Q_{nm}. \quad (2.10)$$

Thus we have extracted a single phonon mode interacting with the nucleation state $|d\rangle$. Considering $\frac{1}{2}Q^2 - \sqrt{2\bar{S}}Q = \frac{1}{2}(Q - \sqrt{2\bar{S}})^2 - \bar{S}$, we see that \bar{S} represents the lattice relaxation energy gained by exciton localization into $|d\rangle$. Exciton localization into $|d\rangle$, on the other hand, is disadvantageous with respect to kinetic energy by an amount

$$\bar{B} = \langle d|H_E|d\rangle = B - \frac{B}{6} \sum_{nm} \gamma_n \gamma_m. \quad (2.11)$$

Thus we get the adiabatic potential associated with the nucleation state written as

$$V_d(Q) = \bar{B} - \bar{S} + \frac{1}{2}(Q - \sqrt{2\bar{S}})^2. \quad (2.12)$$

Assuming that exciton does not interact with phonons in the free states, we write the adiabatic potential associated with the f th free state with energy $E_f (\geq 0)$ along the coordinate Q as

$$V_f(Q) = E_f + \frac{1}{2}Q^2. \quad (2.13)$$

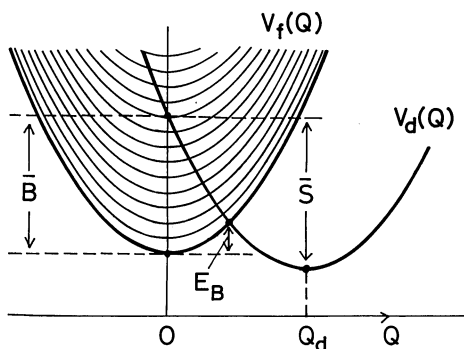


Fig. 1. Adiabatic potentials $V_f(Q)$'s and $V_d(Q)$ associated respectively with the free states and the nucleation state for self-trapping. There exists a potential barrier with height E_B between these two types of states, and \bar{S} and \bar{B} represent respectively the gain of lattice-distortion energy and the loss of kinetic energy due to localization into the nucleation state.

Figure 1 shows $V_d(Q)$ together with $V_f(Q)$ for various f 's. The lowest one of $V_f(Q)$ for $E_f=0$ crosses $V_d(Q)$ at

$$Q = \bar{B}/\sqrt{2\bar{S}}, \quad (2.14)$$

where the lattice-distortion energy amounts to

$$E_B = \frac{1}{4}\bar{B}^2/\bar{S}. \quad (2.15)$$

Note that E_B represents the height of the potential barrier for self-trapping. When $|d\rangle$ has an amplitude $\gamma_n (=1)$ only at a single lattice site, we have $\bar{S} = S_1$ and $\bar{B} = B$. When $|d\rangle$ has an amplitude $\gamma_n (=1/\sqrt{2})$ only at a single pair of nearest-neighbor sites, we have $\bar{S} = \frac{1}{2}S_1 + S_2$, and $\bar{B} = 11B/12$. Both \bar{S} and \bar{B} decrease as the spatial extension of $|d\rangle$ increases.

Now, let us construct a Hamiltonian written as

$$H_d = |d\rangle(\bar{B} - \sqrt{2\bar{S}}Q)\langle d| + H_L, \quad (2.16)$$

which gives the zeroth-order Hamiltonian describing the nucleation state $|d\rangle$ interacting with phonons through the interaction mode Q of (2.10). Interaction between the nucleation state $|d\rangle$ and one of the free states $|f\rangle$ is induced by the remaining part $H - H_d$ of the total Hamiltonian H of (1.1) not included in H_d . In fact, $\langle d|H - H_d|d\rangle$ vanishes. To be more exact, the matrix element J of the interaction deviates from $\langle f|H - H_d|d\rangle$ since $\langle f|d\rangle \neq 0$.¹⁹⁻²¹⁾ However, $\langle f|d\rangle$ is an infinitesimal quantity of the order of $1/\sqrt{N}$ with N representing the total number of lattice sites in the crystal. In this case, within the first order in $1/\sqrt{N}$, we get $J = \langle f|H - H_d|d\rangle$,¹⁷⁾ which gives

$$J = \langle f|d\rangle(E_f - \bar{B} + \sqrt{2\bar{S}}Q) + \langle f|H_{EL}|d\rangle, \quad (2.17)$$

where E_f represents the energy of the free state $|f\rangle$. This matrix element J depends on phonon coordinates through Q and $\langle f|H_{EL}|d\rangle$.

Since $|d\rangle$ is localized enough, $|f\rangle$ in (2.17) can be approximated by the wave function $|f_0\rangle = N^{-1/2} \sum_n a_n^\dagger|0\rangle$ of the lowest free state with $E_f=0$. Moreover, the phonon coordinates contained in J can be estimated at the saddle point between the adiabatic potentials associated with the free and the nucleation states, that is, at a point with the minimum potential

energy of H_L of (2.5) obtained under the condition (2.14). The saddle point is given by $\sqrt{2S_1} Q_n = \gamma_n^2 S_1 \bar{B}/\bar{S}$ and $\sqrt{2S_2} Q_{nm} = 2\gamma_n \gamma_m S_2 \bar{B}/\bar{S}$. With these simplifications, (2.17) can be cast into

$$J = g \bar{B} / \sqrt{N_d}, \quad (2.17')$$

with

$$N_d = (\langle f_0 | d \rangle)^{-2} = N / (\sum_n \gamma_n)^2, \quad (2.18)$$

$$g = \frac{S_1 \sum_n \gamma_n^3 + 2S_2 \sum_{nm} \gamma_n \gamma_m (\gamma_n + \gamma_m)}{[\sum_n \gamma_n][S_1 \sum_n \gamma_n^4 + 4S_2 \sum_{nm} \gamma_n^2 \gamma_m^2]}, \quad (2.19)$$

where we have used $\langle f_0 | a_n^\dagger a_n | d \rangle = \langle f_0 | a_m^\dagger a_n | d \rangle = \gamma_n / \sqrt{N}$ for $|d\rangle$ defined by (2.6). When the nucleation state $|d\rangle$ has an amplitude $\gamma_n (=1)$ only at a single lattice site, we have $N_d = N$ and $g = 1$. When $|d\rangle$ has an amplitude $\gamma_n (=1/\sqrt{2})$ at a single pair of nearest-neighbor sites we have $N_d = N/2$ and $g = 1$. When $|d\rangle$ has an amplitude $\gamma_n (\simeq 1/\sqrt{L})$ over $L (\geq 1)$ lattice sites, we have $N_d \simeq N/L$. In this case, there are about $zL/2$ nearest-neighbor pairs in the region covered by $|d\rangle$ when each lattice site has z nearest neighbors, and the numerator of (2.19) for g is about $S_1/\sqrt{L} + 2zS_2/\sqrt{L}$ while the denominator is about $\sqrt{L}(S_1/L + 2zS_2/L)$. Then we have $g \simeq 1$ again. Therefore it is reasonable to regard g as unity and N_d as the degeneracy number of the nucleation state $|d\rangle$ which means the possible number of $|d\rangle$ allowed in the crystal. Thus we approximate (2.17)' as

$$J = \bar{B} / \sqrt{N_d}. \quad (2.17'')$$

This result extends the previous result obtained in ref. 22 on the matrix element \bar{J} of an interaction which induces nonradiative capture

of a free carrier by a deep-level defect in semiconductors. The deep-level defect gives rise to a completely localized defect level deep in the forbidden gap, and ref. 22 gives $\bar{J} \simeq B/\sqrt{N}$. The previous result can be obtained as a limiting case of (2.17)'' of the nucleation state with amplitude only at a single lattice site.

We must discuss here whether or not the self-trapping rate can be calculated by the perturbation theory second order in J of (2.17)''. This problem has been discussed in ref. 22 mentioned above only at temperatures higher enough than the Debye one. Following it, we can conclude that the perturbation theory cannot be applied at such high temperatures and the adiabatic description of the exciton-phonon system may be more appropriate there. At temperatures considerably lower than the Debye one, however, it seems reasonable to consider that transition between the free and the nucleation states occurs by quantum mechanical tunneling through the potential barrier and it may be treated by the perturbation theory so long as the potential barrier is high enough amounting at least to several times the phonon energy quantum.

Now let us calculate the rate W_f of transition of exciton from the f th free state $|f\rangle$ with energy E_f to the nucleation state $|d\rangle$ by the perturbation theory second-order in the interaction matrix element J of (2.17)'' between them. Since N_d in (2.17)'' represents the degeneracy number of the nucleation state, W_f obtained should be the same as the rate of transition from a state $|f\rangle$ to a nondegenerate state $|d\rangle$ obtained under the Hamiltonian

$$H_f = |f\rangle (E_f + \bar{H}_L) \langle f| + |d\rangle (\bar{B} - \sqrt{2\bar{S}} Q + \bar{H}_L) \langle d| + \bar{B} (|f\rangle \langle d| + |d\rangle \langle f|), \quad (2.20)$$

where \bar{H}_L represents the Hamiltonian of the interaction mode given by (2.8). Note here that the exciton-phonon interaction (2.3) has been replaced by that through the interaction mode Q in (2.20). Hamiltonians essentially the same as H_f of (2.20) have well been investigated for a long time since Huang and Rhys²³⁾ as the simplest model Hamiltonian describing multiphonon nonradiative transition between two electronic states.²⁴⁾ The transition rate W_f at temperature T is given by

$$W_f = 4\pi^2 v \bar{B}^2 e^{-S(2n+1)} \left(\frac{n+1}{n} \right)^{p/2} I_p(2\bar{S} \sqrt{n(n+1)}), \quad (2.21)$$

with

$$p = \bar{S} - \bar{B} + E_f, \quad n = 1/[\exp(1/k_B T) - 1],$$

and

$$v = \omega/(2\pi), \quad (2.22)$$

where energies \bar{S} , \bar{B} , E_f and $k_B T$ are measured in units of the energy quantum $\hbar\omega$ of phonons

whose oscillation frequency is represented by ν , and $I_p(x)$ represents the modified Bessel function of the p th order. In (2.21) W_f is to be regarded as a smooth function of p since it was calculated with a usual procedure of smoothing out sharp peaks in the density of phonon modes with a single frequency at the final state for transition.^{23,24)} This procedure can be justified since the interaction mode should in reality be composed of normal modes with various frequencies and the nucleation state with a degeneracy number of the order of N with a single set of \bar{S} and \bar{B} should in reality be distributed with various sets of \bar{S} and \bar{B} . In our case, the initial state $|f\rangle$ with energy E_f constitutes a continuous band, and we must average W_f over various E_f 's as

$$W = \sum_f W_f \exp(-E_f/k_B T) / \sum_f \exp(-E_f/k_B T). \quad (2.23)$$

Especially at zero degree W of (2.23) is given by

$$W_0 = \begin{cases} 4\pi^2 \nu \bar{B}^2 e^{-\bar{S}} \bar{S}^{-\bar{B}} / \Gamma(\bar{S} - \bar{B} + 1), & \text{for } \bar{S} \geq \bar{B} \\ 0, & \text{otherwise} \end{cases} \quad (2.24)$$

where $\Gamma(x)$ represents the Gamma function. Scaled rate W_0/ν is a function of only \bar{S} and \bar{B} . Figure 2 shows contour lines of W_0/ν written in the (\bar{S}, \bar{B}) plane. W_0/ν increases with increasing \bar{S} or with decreasing \bar{B} .

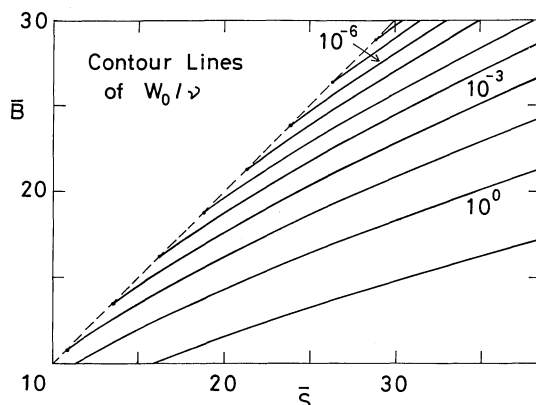


Fig. 2. Contour lines of W_0/ν of the self-trapping rate W_0 of zero degree scaled by the oscillation frequency ν of the interaction mode of phonons, written in the (\bar{S}, \bar{B}) plane.

§3. Self-Trapping Rate at Zero Degree

The wave function (2.6) of the nucleation state $|d\rangle$ for self-trapping determines \bar{S} and \bar{B} as shown respectively by (2.9) and (2.11), and they determine through (2.24) the rate W_0 with which the nucleation state itself is formed at zero degree. We consider two types of the nucleation state of

One-center type;

$$\gamma_n = \left[\frac{2(\tanh \kappa)^3}{1 + (\tanh \kappa)^6} \right]^{1/2} \times \exp[-\kappa(|n_x| + |n_y| + |n_z|)], \quad (3.1)$$

and Two-center type;

$$\gamma_n = \sinh \kappa \sqrt{2 \tanh \kappa} \times \exp \left[-\kappa \left(\left| n_x - \frac{1}{2} \right| + \left| n_y - \frac{1}{2} \right| + |n_z| \right) \right], \quad (3.2)$$

where the site n is specified by three integral numbers n_x , n_y and n_z satisfying $n_x + n_y + n_z =$ even integer in the face-centered cubic lattice. Note that γ_n of (3.1) is centered at the lattice site $(n_x, n_y, n_z) = (0, 0, 0)$ while γ_n of (3.2) is centered at the pair of nearest-neighbor sites $(0, 0, 0)$ and $(1, 1, 0)$ lying in the $[1, 1, 0]$ direction.

Figure 3 shows \bar{B}/B as a function of $\tanh \kappa$ and also as a function of \bar{S}/S_1 for $S_2/S_1 = 0.0, 0.15$ and 0.3 for the nucleation state of one-center type, while Fig. 4 shows those for the nucleation state of two-center type. Both the loss \bar{B} of kinetic energy and the gain \bar{S} of lattice-relaxation energy due to exciton localization into the nucleation state $|d\rangle$ decrease as the degree of exciton localization $\tanh \kappa$

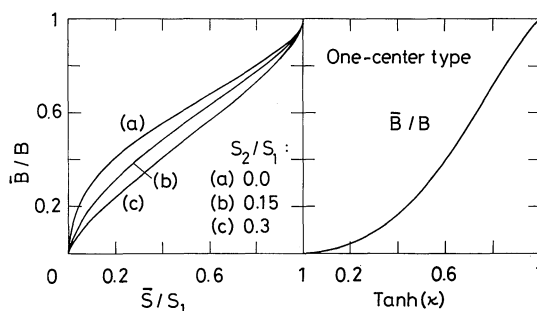


Fig. 3. Relation between $\tanh \kappa$ and \bar{B}/B and those between \bar{B}/B and \bar{S}/S_1 for the nucleation state of one-center type at $S_2/S_1 = 0.0, 0.15$ and 0.3 .

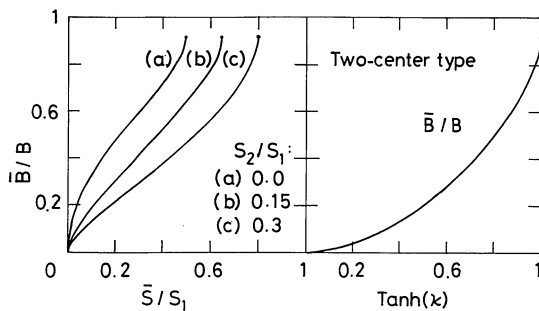


Fig. 4. Relation between $\tanh \kappa$ and \bar{B}/B and those between \bar{B}/B and \bar{S}/S_1 for the nucleation state of two-center type at $S_2/S_1 = 0.0, 0.15$ and 0.3 .

decreases. Note here that \bar{B} is an increasing function of \bar{S} although \bar{S} dependence of \bar{B} is much different between one- and two-center types of the nucleation state, as seen from the comparison between Figs. 3 and 4. For the two-center-type state \bar{S} and \bar{B} approach respectively $\frac{1}{2}S_1 + S_2$ and $11B/12$ in the limit of $\tanh \kappa = 1$ of complete localization, while for the one-center-type one \bar{S} and \bar{B} approach respectively S_1 and B in the limit of $\tanh \kappa = 1$.

We have seen above that \bar{S} and \bar{B} are not independent of one another. We have seen in §2 that W_0/ν representing the rate with which the nucleation state is formed at zero degree is a function of only \bar{S} and \bar{B} , as explicitly shown in Fig. 2. Then, let us draw a curve relating \bar{B} and \bar{S} obtained above into Fig. 2, as done in Fig. 5. Figure 5 shows explicitly a case of the nucleation state of one-center type with $S_1/B = 1.3$,

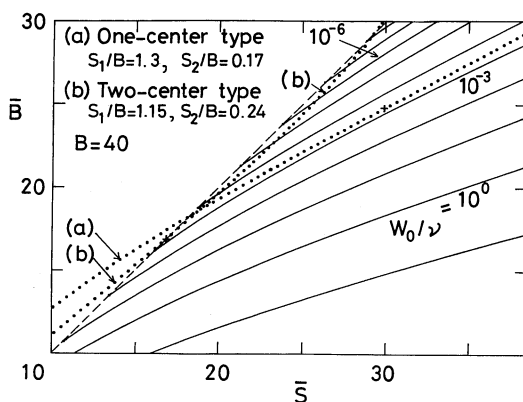


Fig. 5. Trace of a point of (\bar{S}, \bar{B}) written together with contour lines of W_0/ν ; (a) for the nucleation state of one-center type at $S_1/B = 1.3$, $S_2/B = 0.17$ and $B = 40$ and (b) for that of two-center type at $S_1/B = 1.15$, $S_2/B = 0.24$ and $B = 40$. On each trace W_0/ν becomes maximum at a cross mark.

$S_2/B = 0.17$ and $B = 40$ and that of two-center type with $S_1/B = 1.15$, $S_2/B = 0.24$ and $B = 40$. Figure 5 shows also by a cross mark a point where W_0/ν becomes maximum along a curve relating \bar{B} and \bar{S} . The determination of this point is, however, much different between one- and two-center types of the nucleation state, as seen in Fig. 5: Because of the \bar{S} dependence of \bar{B} , the point for the one-center-type state has a tendency to drop in the region of $\bar{S} > \bar{B}$, while that for the two-center-type state just on the line of $\bar{S} = \bar{B}$. The point obtained above determines the most probable nucleation state for self-trapping together with its formation rate, which we regard as the self-trapping rate at zero degree as in ref. 17.

Thus we can determine the self-trapping rate W_0 divided by the oscillation frequency ν of the interaction mode at zero degree as a function of the energy gain B of the free exciton state due to its delocalization and the site-diagonal and off-diagonal exciton-phonon interaction energies S_1 and S_2 respectively. Since a hole composing an exciton is much heavier than an electron, B can be estimated at the half width of the valence band which is about 0.3–0.5 eV in alkali halides and rare-gas solids.^{1–3, 25, 26} The energy quantum $\hbar\omega$ of the interaction mode can be estimated at an energy where the density of acoustic modes becomes maximum at about the zone boundary, which is around 10 meV (giving $\nu \sim 2 \times 10^{12} \text{ sec}^{-1}$) in these crystals.^{27–29} Therefore, B can roughly be estimated at 40 in units of $\hbar\omega$. Unfortunately, however, no reliable estimation of both S_1 and S_2 is available. Figure 6 shows contour lines of W_0/ν written in the $(S_1/B, S_2/B)$ plane for $B = 40$. In the dotted upper region R , self-trapping of exciton takes place through the nucleation state of two-center type. In the lower right region Q filled with open circles, it takes place through the nucleation state of one-center type although self-trapping through the two-center-type state is not impossible but has a smaller rate. In the lower middle region P , self-trapping takes place through the nucleation state of one-center type and no stable self-trapped state of two-center type can be formed. In the remaining lower left region, no stable self-trapped state of either one- nor two-center types can be formed.

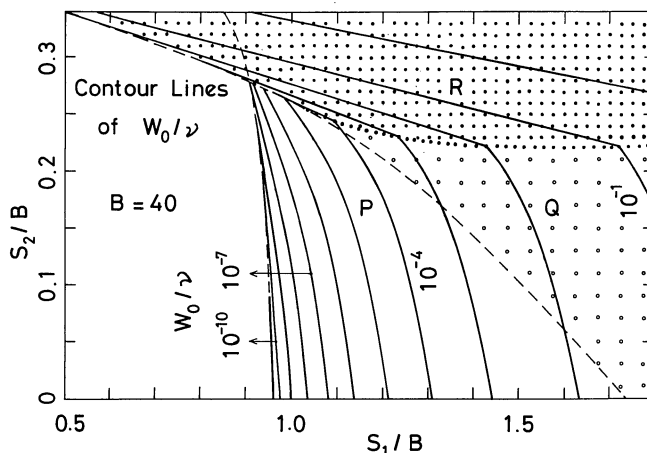


Fig. 6. Contour lines of W_0/v for $B=40$ written in the $(S_1/B, S_2/B)$ plane, where S_1/B and S_2/B represent respectively the site-diagonal and off-diagonal exciton-phonon interaction energies scaled by the half width B of the exciton band.

§4. Self-Trapping Rate at Finite Temperatures

As discussed in §2, it may be reasonable to limit our discussion in a temperature region of $k_B T \lesssim \frac{1}{2} \hbar \omega$. Now we treat W given by (2.23). It can be shown that the maximum value of W is obtained in a situation of $\bar{S} < \bar{B}$ as temperature is increased. When $\bar{S} < \bar{B}$, the adiabatic potential associated with the nucleation state is higher than that associated with the lowest free state in Fig. 1. In this situation, besides the forward process in which exciton in the nucleation state relaxes inducing lattice distortion furthermore in order to stabilize itself, we must take into account also the backward process in which exciton in the nucleation state evaporates back to the free states before the forward process takes place. When $\bar{S} < \bar{B}$, it can occur that the backward process gets a rate not negligible compared with the forward one.

It is not from the standpoint of energy minimization that the nucleation state and the associated interaction mode are determined. Therefore, exciton in the nucleation state relaxes to stabilize itself. The relaxation rate, that is the rate of the forward process mentioned above, can be estimated at the oscillation frequency ν of the interaction mode. The rate W' of the backward process, on the other hand, can be estimated back from the rate W of (2.23): When $\bar{S} < \bar{B}$, participating mainly as the initial states in W are free states with energy

around $\bar{B} - \bar{S}$ whose occupation probability per state is given by $p = \exp [-(\bar{B} - \bar{S})/k_B T] / (V n_T)$, where n_T represents the effective density of free states in the crystal with volume V . Using the effective mass M of exciton given by $(6\hbar^2/B)(N/4V)^{2/3}$ in the case of nearest-neighbor transfer of exciton in the face-centered cubic lattice, we write

$$n_T = \left(\frac{M k_B T}{2\pi \hbar^2} \right)^{3/2} = \frac{N}{V} \frac{1}{4} \left(\frac{3 k_B T}{\pi B} \right)^{3/2}. \quad (4.1)$$

On the other hand, the final state in W is the nucleation state whose degeneracy number in the crystal is given by N_d of (2.18). Therefore, from the principle of microscopic reversibility, we should have $p W' N_d \simeq W$. When $\bar{S} > \bar{B}$, participating mainly as the initial states in W are free states with energy around zero, whose occupation probability per state is given by $1/(V n_T)$, and we should have $(V n_T)^{-1} W' N_d \simeq W$. Thus we get

$$W' \simeq \begin{cases} (V n_T / N_d) \exp [(\bar{B} - \bar{S})/k_B T] W, & \text{for } \bar{S} < \bar{B} \\ (V n_T / N_d) W, & \text{for } \bar{S} > \bar{B}. \end{cases} \quad (4.2)$$

Note that W' for $\bar{S} < \bar{B}$ is the same as obtained from the relation of detailed balance. At zero degree where $\bar{S} > \bar{B}$, the backward process is forbidden since $n_T = 0$ originating from that only one state participates as the initial state in W while the final state is innumerable de-

generated.

Thus we have known that after making a transition from the free to the nucleation states with rate W exciton relaxes into the lowest self-trapped state with probability of about $1/(1+W'/v)$. The self-trapping rate W_T at finite temperatures is given by

$$W_T = \text{Maximized } W/(1+W'/v), \quad (4.3)$$

which can be calculated with the same procedure as described in §3. In reality, however, W'/v is at most one tenth at the nucleation state determined by (4.3) even at the highest temperature (around $\frac{1}{2}\hbar\omega/k_B$) concerned. But its presence excludes correctly a situation that the lowest point of $V_d(Q)$ falls within the region of the multiple curves of $V_f(Q)$'s in Fig. 1. The situation cannot be allowed from the standpoint of the adiabatic approximation.

Figure 7 shows the Arrhenius plot of W_T/v obtained when (a): $S_1/B=1.3$, $S_2/B=0.17$ and $B=40$ for the nucleation state of one-center type, and that obtained when (b): $S_1/B=1.15$, $S_2/B=0.24$ and $B=40$ for the nucleation state of two-center type. The value W_0/v of W_T/v at zero degree is also shown by an arrow on the left ordinate. The case (a) was chosen in the

region P in Fig. 6. Since no stable self-trapped state of two-center type can be formed in the region P , the self-trapping rate is given by a rate through the nucleation state of one-center type, with a temperature dependence as shown by the curve (a) of Fig. 7, at all temperatures. The case (b) was, on the other hand, chosen in the region R . In this region self-trapping through the nucleation state of two-center type is more rapid than that through the one-center-type state even at zero degree, and W_T increases more rapidly with increasing temperature along the curve (b) than along the curve (a), as seen in Fig. 7. Therefore, in the region R self-trapping through the nucleation state of two-center type predominates at all temperatures, giving a temperature dependence as shown by the curve (b) of Fig. 7.

Figure 8 shows the Arrhenius plot of W_T/v obtained when $S_1/B=1.3$, $S_2/B=0.21$ and $B=40$ chosen in the region Q in Fig. 6 for the two cases (a) and (b) of the nucleation state of one- and two-center types respectively. The value W_0/v of W_T/v at zero degree is also shown by an arrow on the left ordinate. In the region Q self-trapping through the nucleation state of one-center type predominates over that through

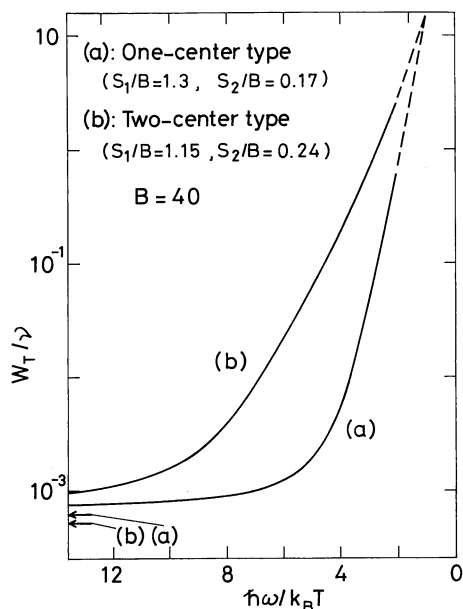


Fig. 7. Arrhenius plot of W_T/v ; (a) for one-center-type self-trapping obtained at $S_1/B=1.3$, $S_2/B=0.17$ and $B=40$ and (b) for two-center-type one obtained at $S_1/B=1.15$, $S_2/B=0.24$ and $B=40$.

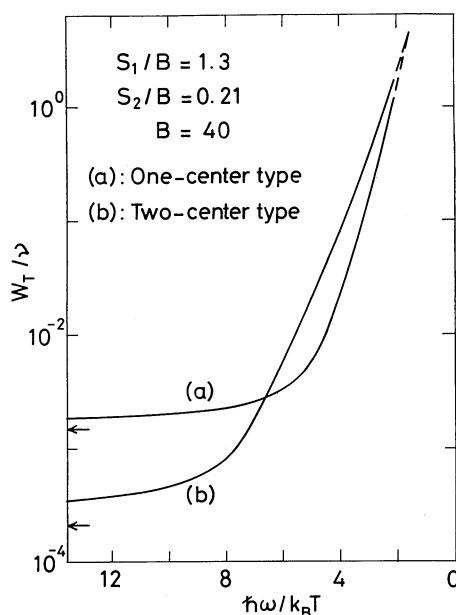


Fig. 8. Arrhenius plot of W_T/v obtained at $S_1/B=1.3$, $S_2/B=0.21$ and $B=40$; (a) for one-center-type self-trapping and (b) for two-center-type one.

the nucleation state of two-center type at low temperatures. In the example shown in Fig. 8, W_T/v is about ten times larger on the curve (a) than on the curve (b) at zero degree. However, W_T/v increases more rapidly along the curve (b) than along the curve (a) when temperature is increased. Accordingly, in the region Q not far from the boundary between regions Q and R in Fig. 6, a crossover occurs in which self-trapping through the nucleation state of one-center type dominating at low temperatures is overcome by that through the nucleation state of two-center type with increasing temperature. In the example shown in Fig. 8, W_T/v is about several times larger along the curve (b) than along the curve (a) around temperatures of $\hbar\omega/k_B T \approx 4$.

Figures 9 and 10 show the temperature dependence of $\tanh \kappa$, \bar{S} , \bar{B} , and E_B obtained respectively when $S_1/B=1.3$, $S_2/B=0.17$ and $B=40$ as an example of one-center-type self-trapping and when $S_1/B=1.15$, $S_2/B=0.24$ and $B=40$ as an example of two-center-type self-trapping. For one-center-type self-trapping, the temperature dependence of them can be classified into two regimes in Fig. 9: In the first regime appearing at low temperatures, the

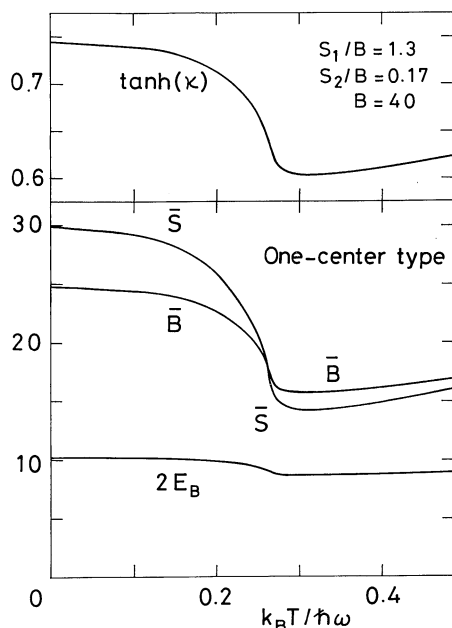


Fig. 9. Temperature dependence of $\tanh \kappa$, \bar{S} , \bar{B} and E_B for one-center-type self-trapping obtained at $S_1/B=1.3$, $S_2/B=0.17$ and $B=40$.

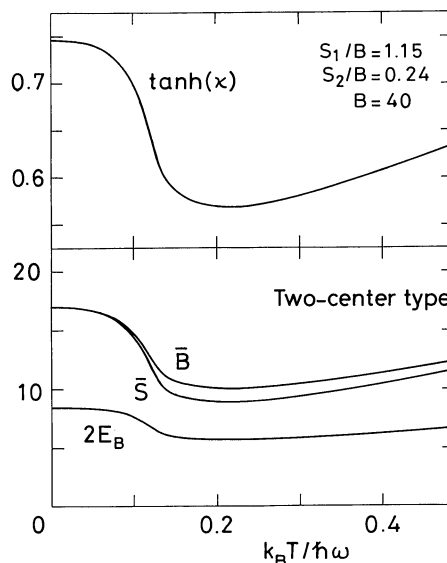


Fig. 10. Temperature dependence of $\tanh \kappa$, \bar{S} , \bar{B} and E_B for two-center-type self-trapping obtained at $S_1/B=1.15$, $S_2/B=0.24$ and $B=40$.

lattice relaxation energy \bar{S} gained in the nucleation state is larger than the energy loss \bar{B} due to exciton localization into it, although $\bar{S} - \bar{B}$ is at most several. With increasing temperature, the second regime appears in which \bar{S} is smaller than \bar{B} with $\bar{B} - \bar{S}$ being kept on the order of unity. For two-center-type self-trapping in Fig. 10, on the other hand, the first regime for $\bar{S} > \bar{B}$ is missing and the situation of $\bar{S} = \bar{B}$ at zero degree shifts into those in the second regime of $\bar{S} < \bar{B}$ with increasing temperature. The temperature dependence of the barrier height E_B for self-trapping is small even in the boundary region of the two regimes as well as in each regime. Since κ represents the rate of exponential decrease of the wave function in (3.1) and (3.2), $\tanh \kappa$ can be regarded as the degree of localization of the nucleation state. Figures 9 and 10 show that $\tanh \kappa$ ranges from about 0.7 to 0.6. For the nucleation state of one-center type, its amplitude (3.1) at twelve sites nearest-neighbor to the central one is given by $\exp(-2\kappa)$ relative to that at the central site. When $\tanh \kappa$ equals 0.7 or 0.6 respectively, $\exp(-2\kappa)$ equals 0.18 or 0.25. For the nucleation state of two-center type, its amplitude (3.2) at four sites nearest-neighbor to the central pair of sites is given by $\exp(-\kappa)$ relative to that at the central pair. When $\tanh \kappa$

equals 0.7 or 0.6, respectively, $\exp(-\kappa)$ equals 0.42 or 0.5. This fact justifies *a posteriori* our starting assumption that the spatial extension of the nucleation state should not be much larger than the lattice constant but already be of the order of it. Since \bar{S} is determined by the sum of the fourth power of the amplitude of the wave function as shown in (2.9), phonons see exciton in the nucleation state as being more localized than we see from the decay of its wave function.

§5. Comparison with Experiments

Masumoto and others obtained the self-trapping rate of $n=1$ free excitons in KI and RbI at 4.2K by measuring the rise time of luminescence from the self-trapped state with the use of the picosecond laser technique.^{8,9)} The rate can be regarded as nearly equal either at 4.2K or at zero degree, since the rate of multiphonon nonradiative transition such as the self-trapping rate depends scarcely on temperature at such low temperatures.^{23,24)} Therefore we understand that the experiments have given $W_0 \simeq (2 \text{ nsec})^{-1} \simeq 5 \times 10^8 \text{ sec}^{-1}$ for RbI and $W_0 \simeq (0.16 \text{ nsec})^{-1} \simeq 6 \times 10^9 \text{ sec}^{-1}$ for KI. Considering $\nu \sim 2 \times 10^{12} \text{ sec}^{-1}$, we see that W_0/ν is of the order of 10^{-4} in RbI while 10^{-3} in KI. Let us look at the region of $W_0/\nu = 10^{-4}$ – 10^{-3} in Fig. 6. This region overlaps very little with the dotted region R where self-trapping takes place through the nucleation state of two-center type, while it spreads largely in the regions P and Q . Therefore it seems very probable that in RbI and KI self-trapping of exciton takes place through the nucleation state of one-center type in the regions P or Q at low temperatures.

In alkali halides except iodides optical excitation in the exciton region as well as in the ionization-continuum region gives rise to two Stokes shifted luminescences called the σ and π ones both of which are emitted from the self-trapped exciton state localized on a pair of nearest-neighbor halogen ions.^{1,2,30)} In alkali iodides, however, optical excitation in the $n=1$ free exciton region gives rise to another Stokes shifted luminescence called the E_x one at least at low temperatures, although that in the $n=2$ free exciton region as well as in the ionization-continuum region gives rise to the σ and π

luminescences.^{11,12,31)} The nature, including the symmetry, of the self-trapped exciton state emitting the E_x luminescence has not been clarified. To be more exact, we can find a difference among alkali iodides concerning the E_x luminescence: Even at low temperatures optical excitation in the $n=1$ free exciton region in KI gives rise also to the π luminescence although its yield is small being about 0.1–0.2 of the E_x luminescence at 4.2K.^{8,30,32)} Moreover in KI, the π luminescence yield increases while the E_x one decreases with increasing temperature with the sum of the two being conserved, and the former exceeds the latter around 30K reaching 5–10 times the latter at higher temperatures.^{30,32)} In RbI, on the other hand, under $n=1$ free exciton excitation no sign of the π luminescence can be seen⁹⁾ and the E_x -luminescence yield is not quenched thermally below about 60K.^{32–34)}

These behaviors of Stokes shifted luminescences under $n=1$ free exciton excitation together with the observed value of the self-trapping rate at 4.2K can well be explained if RbI is located in the region P in Fig. 6, KI in the region Q , and alkali halides other than iodides in the region R concerning $n=1$ free excitons. In this case, the E_x luminescence is regarded as emitted from a still unknown self-trapped state of one-center type, since it seems reasonable to consider that the nucleation state of one-center type triggering exciton self-trapping in the regions P and Q changes into a relaxed self-trapped state with the same symmetry as noted in §1. If both the deformation potential E_d and the sound velocity u do not change appreciably among alkali halides, the site-diagonal exciton-phonon interaction energy S_1 in (2.3) should roughly be inversely proportional to the mass of the unit cell. (In fact both E_d and u are nearly equal between RbI and KI.^{8,9,27)}) Similarly, if the change of the transfer integral of exciton (or hole) per unit change of the halogen-ion distance does not change appreciably among alkali halides, the site-off-diagonal exciton-phonon interaction energy S_2 in (2.3) should roughly be inversely proportional to the mass of the halogen ion. Therefore it seems reasonable to consider that S_1 should be larger in KI than in RbI, and that S_2 should be smaller in alkali iodides than in

alkali bromides, chlorides and fluorides. These tendencies are consistent with the above mentioned assignment of alkali halides into the three regions of Fig. 6. The self-trapping rate has been observed to be about ten times larger in KI than in RbI at 4.2K.^{8,9)} This fact is also consistent with that RbI should be located in the region *P* in Fig. 6 while KI in the region *Q* concerning $n=1$ free excitons. In the paper which just follows the present one, analysis is given of the temperature dependence of the quantum yield of the $n=1$ free exciton luminescence observed in RbI. The analysis supports also that RbI should be located in the region *P* concerning $n=1$ free excitons.

The exciton-phonon interaction energies are different between $n=1$ and $n=2$ free excitons. The self-trapping rate at 4.2K has not been measured for $n=2$ free excitons. However it has been known that $n=2$ free exciton excitation gives rise to the σ and π luminescences in all alkali halides. Therefore, all alkali halides should be located in the region *R* in Fig. 6 concerning $n=2$ free excitons.

We have assigned RbI as located in the region *P* concerning $n=1$ free excitons where no stable self-trapped state of two-center type can be formed, while as located in the region *R* concerning $n=2$ free excitons where a stable one can be formed. This shows that the self-trapped state of two-center type observed in RbI should mainly be formed from $n=2$ and higher free-exciton states within the present approximation of the exciton-phonon interaction linear in the phonon coordinate. It should be noted here that a very large lattice distortion is associated with the relaxed self-trapped state in all alkali halides including RbI, since its emission has a very large Stokes shift amounting to 3–4 eV of about 300–400 times the phonon energy quantum. Therefore, in order to describe correctly such a strongly relaxed state, it may be important to take into account not only the nonlinear exciton-phonon interaction but also mixing of various free exciton states with different principal quantum number n 's since the state has a large binding energy below the free exciton states at the relaxed lattice configuration. On the other hand, the lattice distortion associated with the nucleation state for self-trapping has

an energy of at most 30 times the phonon energy quantum even at zero degree as shown in Figs. 9 and 10, although it is already appreciable. Therefore, the present approximation can be applicable only in describing the nucleation state. Then the result of the present work noted in the beginning of this paragraph shows that $n=1$ free excitons in RbI have no channel for access to the self-trapped state of two-center type even if it is strongly relaxed, since no nucleation state of two-center type can be formed from the $n=1$ free exciton states.

The E_x luminescence has been observed also in CsI.^{35,36)} CsI crystallizes in the body-centered cubic lattice in which iodine ions constitute the simple cubic sublattice. Then the present calculation of the self-trapping rate in the face-centered cubic lattice cannot be applied to CsI. But the present calculation can easily be performed also for the simple cubic cubic lattice. Therefore, if we know the self-trapping rate at 4.2 K also for CsI, we will be able to perform an analysis similar to that performed in the present work also for CsI.

§6. Summary

The present work is summarized as follows:

- (1) Self-trapping begins with quantum mechanical tunneling of a free exciton to a state of nucleation for self-trapping less localized than the relaxed self-trapped state. The spatial extension of the nucleation state is already of the order of the lattice constant, and an appreciable lattice distortion is associated with it. In order to calculate the self-trapping rate in this situation, it is essentially important to take into account correctly the structure of the lattice in which the nucleation state is formed, as well as the symmetry of the nucleation state itself.
- (2) The matrix element of self-trapping between the free and the nucleation states can be approximated by the loss of kinetic energy due to exciton localization into the nucleation state divided by the square root of the possible number of the state in the crystal.
- (3) The nucleation state is not stable, and relaxes inducing lattice distortion furthermore in order to stabilize itself. It seems reasonable to

consider that the nucleation state with a certain symmetry changes into a relaxed self-trapped state with the same symmetry because of the associated lattice distortion already appreciable with that symmetry.

- (4) Three situations of self-trapping appear depending on the site-diagonal and off-diagonal exciton-phonon interaction energies S_1 and S_2 relative to the energy gain B of the free exciton state due to its delocalization: In the region P in Fig. 6, self-trapping occurs through the nucleation state of one-center type while no stable self-trapped state of two-center type can be formed. In the region R self-trapping through the nucleation state of two-center type predominates at all temperatures. In the region Q self-trapping through the nucleation state of one-center type predominates at low temperatures, but it is overcome by that through the nucleation state of two-center type with increasing temperature.
- (5) Concerning $n=1$ free excitons, RbI is located in the region P in Fig. 6, while KI in the region Q . All alkali halides with NaCl-type structure except alkali iodides are located in the region R .
- (6) The so called E_x luminescence, obtained only in alkali iodides under $n=1$ free exciton excitation, should be emitted from a still unknown self-trapped state of one-center type.
- (7) Concerning $n=2$ free excitons, on the other hand, all alkali halides are located in the region R .

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Note added in proof Very recently Eshita, Tanimura and Itoh (*Proc. Intern. Conf. Defects in Insulating Crystals*, Utah, 1984) suggested a possibility of the I_3^- configuration for the initial state of the E_x luminescence in KI and RbI, studying mutual conversion of the self-trapped excitons emitting the E_x and the π luminescences under visible light excitation. As discussed by them too, it can be considered that the I_3^- configuration is stabilized as a

result of the Jahn-Teller instability of the totally symmetric one-center-type configuration, which was proposed by the present work. The nucleation state treated in the present work relaxes inducing lattice distortions furthermore into a strongly distorted self-trapped state. It is probable that such an instability as mentioned above with a comparatively small stabilization energy may take place at the final stage of the relaxation. The author wishes to thank Professor N. Itoh of Nagoya University for showing the paper mentioned above prior to publication and valuable discussions.

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