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Model of excitonic mechanism for defect formation in alkali halides

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A recent model proposed by Toyozawa for defect formation in alkali halides is explicitly formulated in terms of a molecular-type model Hamiltonian, which is expanded in two vibrational modes, the stretching mode (Q_1) and the center-of-mass motion (Q_2) of the two central halogen ions X_2^-. A semiquantitative calculation shows that the predicted adiabatic instability of the Q_2 mode, due to the mixing of the two lowest states of the self-trapped exciton (A_{1g} and B_{3u}) is likely to occur at high temperatures, while the probability of radiationless transition between the two states is exceedingly small to be compatible with experiment. We propose a revised model which includes the effect of an additional mode (called $\tilde{Q}_1$) which takes account of the relaxation of other ions around the X_2^- molecule. The inclusion of this $\tilde{Q}_1$ mode resolves the difficulties of the original model of Toyozawa and among other things, gives the F-center formation time in satisfactory agreement with experiment.

I. INTRODUCTION

The mechanism by which radiation damage is produced in alkali halides has been a subject of active interest in color-center physics. Recent experimental works have established quite convincingly that the primary defects produced are pairs of F and H centers[1,2] and that some excited states of the self-trapped excitons (STE's) serve as the precursor.[3-5] It is also generally accepted that the lowest bound state of the STE from which the long-lived π luminescence is emitted is not the precursor.[6] In some systems the intensity of luminescence is correlated as a function of temperature to the F-center production yield in a complementary way.[7,8] A recent work of Bradford *et al.*[2] has determined that the formation time of F centers to be about 11 psec in KCl at 25 K.

Regarding the early stage of defect formation during which a halogen molecule ion X_2^- is squeezed out in [110] direction, leaving behind the electron in the vacant site just created, there have been several recent propositions which are all based on the translational motion of the STE, in contrast to the earlier model of Pooley[9] which is of dissociative type. These various models have been discussed and reviewed by Williams.[10] Here we shall be mainly concerned with the one proposed by Toyozawa.[11] Toyozawa suggested that the squeezing motion is due to the adiabatic instability of the lowest STE (A_{1g}) state, originating from the mixing with the second lowest (B_{3u}) state in the presence of a vibrational mode of the center of mass of the X_2^- molecule (hereafter referred to as the Q_2 mode). The mixing of the A_{1g} and B_{3u} states has two effects: first, the two adiabatic-potential surfaces do not cross, and second, with the increasing mixing the Q_2 mode eventually becomes unstable (i.e., the Q_2 mode has an effective negative force constant). The Q_2 mode instability, combined with the stretching Q_1 mode of the X_2^- molecule, squeeze out the X_2^- molecule in [110] direction, while the distorted electron wave function settles on the vacant site. According to this model, the formation time is determined by the radiationless transition from the B_{3u} state to the A_{1g} state of the STE. This model has been shown,[11] qualitatively, to be consistent with a number of experimental results.

It is the purpose of this paper to present and discuss the results of semiquantitative calculations made along this original model of Toyozawa as well as a modified version of this model, to be introduced below.

In Sec. II, we formulate explicitly the model of Toyozawa in terms of a molecule-type model Hamiltonian, assuming harmonic approximation and linear electron-ion coupling. We find, based on the results of our calculation for NaCl and LiF, that this model encounters a couple of difficulties. One is that the predicted adiabatic instability is likely to occur at high temperatures only. It is however indeed the second difficulty which seems really serious—the bottleneck in the process of defect formation, constituted by the radiationless transition between the two lowest states of the STE, is much too severe to explain the observed formation time.[2] In simple terms this is due to the fact that the equilibrium distance of the two central halogen ions does not depend in any appreciable way on the state of the electron bound to it. As the energy difference between the two electron states is about 1 eV, this renders the radiationless transition practically impossible.

Although the self-trapped hole is very strongly localized on the two halogen ions, the electron bound to it is considerably diffuse,[12] comparable to an F center. When the electron changes its orbit, we should expect that there will be changes in the response of the surrounding ions, even if the two central halogen ions are not appreciably affected. This is because the two electronic states are of different symmetry, as well as of different spatial extension. This effect is also supported by the fact that the observed transient absorption bandwidths from the lowest metastable triplet state of the STE are pretty broad,[13] indicating a considerable coupling to the lattice.

We propose therefore in Sec. III a modified version of the original model of Toyozawa. We include a third mode of vibration (called $\tilde{Q}_1$ mode) which represents the relaxation of the surrounding ions other than the two central halogen ions. We remark here that a similar mode, called the "external mode" of the STE, has also been introduced by Williams and Kabler[13] in discussing the binding energy of the STE. The inclusion of this $\tilde{Q}_1$ mode, with its associated large Huang-Rhys factor, helps to resolve the two difficulties of the Toyozawa model mentioned above. We find that the adiabatic instability is very likely to occur under the experimental circumstances, but more important, the radiationless transition probability across the bottleneck is in quite satisfactory agreement with the observed F-center formation time.[2]

Finally, in Sec. IV, we make some general comments with regard to this modified version of Toyozawa's model as well as other recent models for defect formation in alkali halides.

II. TOYOZAWA'S MODEL

A. Formulation of the model

We consider first a V_K center (i.e., a self-trapped hole localized on two neighboring halogen ions) in an alkali-halide crystal of the NaCl structure. The distorted equilibrium ionic configuration for the ground state is denoted by $\{\vec{R}_1^{(0)}, \vec{R}_2^{(0)}, \vec{R}_3^{(0)}, \vec{R}_4^{(0)}, \ldots\}$, where $\vec{R}_1^{(0)}$ and $\vec{R}_2^{(0)}$ are the positions of the two halogen ions A and B which share the hole, and $\vec{R}_3^{(0)}, \vec{R}_4^{(0)}, \ldots$ are positions of the remaining ions. Choosing the z axis along $\vec{R}_1^{(0)} - \vec{R}_2^{(0)}$ (i.e., the [110] axis), we may write

$$\vec{R}_1^{(0)} = (0, 0, \tfrac{1}{2}d_0, \quad \vec{R}_2^{(0)} = (0, 0, -\tfrac{1}{2}d_0) , \tag{1}$$

where d_0 is the equilibrium separation of A and B. The change in lattice energy of the system E_L, when A and B are displaced to new positions $\vec{R}_1 = (0, 0, Z_1)$ and $\vec{R}_2 = (0, 0, Z_2)$, may be written

$$E_L(Q_1, Q_2) = \tfrac{1}{2}k_1 Q_1^2 + \tfrac{1}{2}k_2 Q_2^2 , \tag{2}$$

where

$$Q_1 = d_0 - (Z_1 - Z_2) , \qquad Q_2 = \tfrac{1}{2}(Z_1 + Z_2) \tag{3}$$

are symmetry coordinates transforming, respectively, as A_{1g} and B_{3u} under the symmetry group D_{2h} of the V_k-center system, and k_1 and k_2 are the corresponding force constants.

We next consider an extra electron bound to the V_k center, forming a STE. In accordance with Toyozawa's model,[11] we assume that the electron is only coupled to the two local modes Q_1 and Q_2. In the ionic configuration specified by $Q_1^{(0)} = Q_2^{(0)} = 0$, the electronic Hamiltonian has the form

$$H_e^{(0)} = (\vec{P}^2/2m) + V(\vec{r}, Q_1^{(0)}, Q_2^{(0)}) , \tag{4}$$

where V is the potential energy of the electron at $\vec{r}$. We are primarily concerned with the two lowest exciton states $\psi_g(A_{1g})$ and $\psi_u(B_{3u})$ of $H_e^{(0)}$,[11,12]

$$H_e^{(0)}\psi_g = \epsilon_g \psi_g , \qquad H_e^{(0)}\psi_u = \epsilon_u \psi_u \quad (\epsilon_u > \epsilon_g) , \tag{5}$$

In particular, we shall study the mixing of these two states and the resulting adiabatic-potential surfaces when the two halogen ions are displaced to new positions corresponding to $\{Q_1, Q_2\}$.

In the configuration $\{Q_1, Q_2\}$, the total Hamiltonian of the system is given by

$$H = H_e^{(0)} + V'(\vec{r}, Q_1, Q_2) + E_L(Q_1, Q_2) , \tag{6}$$

where

$$V' = V(r, Q_1, Q_2) - V(\vec{r}, Q_1^{(0)}, Q_2^{(0)}) , \tag{7}$$

Approximating the eigenstates of H by

$$\psi = \lambda\psi_g + \mu\psi_u , \tag{8}$$

we find that the lower (E_-) and upper (E_+) adiabatic-potential surfaces are given by

$$E_{\mp} = \tfrac{1}{2}(H_{gg} + H_{uu}) \mp \tfrac{1}{2}[(H_{uu} - H_{gg})^2 + 4|H_{gu}|^2]^{1/2} , \tag{9}$$

where $H_{gg} = \langle\psi_g|H|\psi_g\rangle$, $H_{gu} = \langle\psi_g|H|\psi_u\rangle$, etc., with the angular brackets denoting integration over the electronic coordinates $\vec{r}$. If we further approximate V' by

$$V' \approx \left(\frac{\partial V'}{\partial Q_1}\right)_0 Q_1 + \left(\frac{\partial V'}{\partial Q_2}\right)_0 Q_2 , \tag{10}$$

and make use of symmetry arguments and Eqs. (2) and (5), we readily obtain

$$H_{gg} = \epsilon_g + aQ_1 + \tfrac{1}{2}k_1Q_1^2 + \tfrac{1}{2}k_2Q_2^2 , \qquad H_{uu} = \epsilon_u + bQ_1 + \tfrac{1}{2}k_1Q_1^2 + \tfrac{1}{2}k_2Q_2^2 , \qquad H_{gu} = cQ_2 , \tag{11}$$

with

$$\begin{aligned} a &= \langle \psi_g | (\partial V'/\partial Q_1)_0 | \psi_g \rangle , \\ b &= \langle \psi_u | (\partial V'/\partial Q_1)_0 | \psi_u \rangle , \\ c &= \langle \psi_g | (\partial V'/\partial Q_2)_0 | \psi_u \rangle . \end{aligned} \tag{12}$$

Substituting (11) into (9) gives the final result

$$E_{\mp} = \tfrac{1}{2}\{(\epsilon_g + \epsilon_u + aQ_1 + bQ_1 + k_1Q_1^2 + k_2Q_2^2) \mp [(\epsilon_u - \epsilon_g + bQ_1 - aQ_1)^2 + 4c^2Q_2^2]^{1/2}\} , \tag{13}$$

which is the basis for the following discussions.

The adiabatic potentials are shown schematically in Fig. 1. On the plane $Q_2 = 0$, the lower (upper) curve has a minimum at $Q_{1,g} = -a/k_1$ ($Q_{1,u} = -b/k_1$) and they cross at $Q_1^C = (\epsilon_u - \epsilon_g)/(a - b)$. The stability of the systems against Q_2 distortion at various points on the lower potential curve, assuming classical mechanics, is determined by the sign of the curvature

$$\left.\frac{d^2E_-}{dQ_2^2}\right|_{Q_2 = 0} = k_2 - \frac{2c^2}{|\epsilon_u - \epsilon_g + (b - a)Q_1|} . \tag{14}$$

For our present purpose, we assume that $(a - b)$ is positive and consider only the region of interest, $Q_1 < Q_1^C$. In this case, the curvature is positive for $Q_1 < Q_1^T$ and negative for $Q_1 > Q_1^T$, with the turning point coordinate Q_1^T given by

$$Q_1^T = \frac{\epsilon_u - \epsilon_g - 2c^2/k_2}{a - b} . \tag{15}$$

Thus, the system is unstable against Q_2 distortion (or center-of-mass motion) for $Q_1 > Q_1^T$ (see Fig. 1). This instability leads to the translational motion of the two halogen ions along [110] direction and the subsequent formation of an *F* center and an *H* center as proposed by Toyozawa.[11]

B. Numerical calculation

The value of Q_1^T, which is crucial for the testing of Toyozawa's model, depends on the parameters in (13). Numerical estimates of these parameters have been obtained for NaCl and LiF. The energy difference $\epsilon_u - \epsilon_g$ is taken from Ref. 12 to be 1.0 eV. The force constant k_1 is simply taken to be the force constant of the free halogen molecule ions as calculated in Ref. 14 for Cl_2^- and Ref. 15 for F_2^-. k_2 is calculated based on the work of Das *et al.*[16] and Jette *et al.*[17] as follows. First, we employ the equilibrium distance d_0 of the two halogen ions as estimated in Ref. 18. The displacements of the nearest-neighboring alkaline ions are then determined by Eq. (2.10) of Ref. 17. Next we assume a small displacement of the center of mass of the two halogen ions from this equilibrium configuration and calculate the change in the Madelung energy and the Born-Meyer energy in second order of the displacement. Finally, we include the small contribution from the polarization energy as given in Ref. 17, assuming a perfect crystal configuration.

The wave functions ψ_g and ψ_u, required for the calculation of a, b, and c, are assumed to be single Slater functions centered on the midpoint of the two halogen ions determined in the pseudopotential calculation of Song *et al.*[12] The perturbation V' in (10) may be approximated as the change in potential energy of an electron due to the displacements of two point ions of charge $\frac{1}{2}|e|$:

$$V' = \sum_{i=1,2} \tfrac{1}{2} e^2 \left(\frac{1}{|\vec{r} - \vec{R}_i|} - \frac{1}{|\vec{r} - \vec{R}_i^{(0)}|} \right) \tag{16}$$

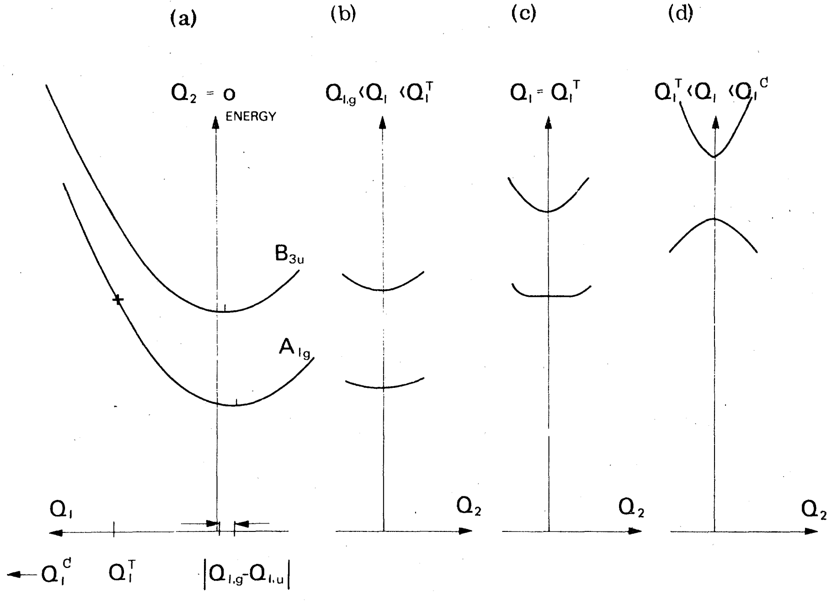

FIG. 1. Adiabatic potentials [Eq.(13)] as a function of Q_1 for $Q_2 = 0$ (*a*), and as a function of Q_2 for various values of Q_1 (*b*), (*c*), (*d*). Coordinates of various points of interest are defined in Sec. IIB.

TABLE I. Parameters in Eq. (13) for the adiabatic potentials, and the Q_1 coordinates of various points of interest (defined in Sec. II. B) for NaCl, KCl (Ref. 19) and LiF. α_0 denotes the Bohr radius.

	NaCl (KCl)	LiF
$d_0(a_0)$	5.19	3.94
$\epsilon_u - \epsilon_g$ (eV)	1.0	1.0
$k_1(\text{eV}/a_0^2)$	1.21	2.54
$k_2(\text{eV}/a_0^2)$	0.27	0.83
$a\,(\text{eV}/a_0)$	0.29	0.48
$b\,(\text{eV}/a_0)$	0.03	0.03
$c\,(\text{eV}/a_0)$	0.22(±40%)	0.41(±40%)
$Q_{1,u} - Q_{1,g}\ (a_0)$	0.21	0.18
$Q_1^C\ (a_0)$	4.0	2.2
$Q_1^T\ (a_0)$	$2.5\begin{pmatrix}-54\%\\+36\%\end{pmatrix}$	$1.3\begin{pmatrix}-68\%\\+45\%\end{pmatrix}$
$Q_1^P\ (a_0)$	1.1	0.72

The parameters are then evaluated according to (12).

The results of our calculation are presented in Table I. The values for NaCl are also found appropriate for KCl.[19] Since c is the most sensitive parameter in the determination of Q_1^T and since we have only employed rather crude wave functions in this work, we have allowed for a ±40% change in our calculated values for c as shown in Table I. Values of the Q_1 coordinates of various points of interest defined above are also listed. Q_1^P is the coordinate at which the lower potential curve has the same energy as the minimum of the upper potential curve ($Q_{1,g} < Q_1^P < Q_1^C$).

C. Discussions

Before assessing the results of the preceding calculation, we shall first examine the values of the parameters used here. We start from those which are better known. The force constant k_1 for the stretching mode Q_1 is known with considerable reliability for free X_2^- molecule from several calculations.[14,15,17] This parameter only changes (decreases) slightly when the surrounding lattice is taken into account.[17,20] The presence of a more or less loosely bound electron may modify the force constant, but this effect is believed to be small. It thus seems reasonable to assume the value for the free X_2^- molecule for both the A_{1g} and the B_{3u} states. The force constant k_2 for Q_2 mode is not as easy to obtain. It is not hard to believe that it is considerably smaller than k_1. Our simple point ion lattice calculation gives values for NaCl and LiF which are similar to those used by Smoluchowski *et al.*[21] The electronic energy difference $\epsilon_u - \epsilon_g$ is taken to be about 1 eV for both NaCl and LiF following the results of pseudopotential calculation.[12] The level B_{3u} has not been assigned in an unambiguous way.[5,13] A recent work of Williams[5] indicates that a precursor state in KCl is reached from the A_{1g} state after a laser excitation of energy 1.79 eV. We will elaborate more on this point when we discuss the $\tilde{Q}_1$ mode.

The linear coupling constants a, b, and c are harder to determine. The shift in the equilibrium distance ($Q_{1,u} - Q_{1,g}$) of the two central halogen ions as the electron changes its orbit from A_{1g} to B_{3u} is determined by $(a-b)/k_1$. Our calculated values (see Table I) show that this shift is quite small, in agreement with the suggestions of other authors.[10] This fact will be critically important when we discuss Toyozawa's adiabatic instability. The parameter c is the most crucial one, as it determines the mixing between the two states A_{1g} and B_{3u}. Also the turning point at Q_1^T, where the Q_2 mode effective force constant becomes zero, depends in a critical way on the value of c. The values of c as we found in Sec. II B give the turning point coordinate Q_1^T at 2.5 a_0 for NaCl and $1.3a_0$ for LiF (a_0 is the Bohr radius), approximately at the midpoint to the respective crossing point Q_1^C. These values of Q_1^T situate the turning point at about 3.5 eV (NaCl) and 1.8 eV (LiF) above the respective minimum of the B_{3u} state (see Fig. 1). If one varies c by about 40%, with all the other parameters unchanged, Q_1^T varies in a substantial way as shown in Table I. The largest value of c brings the instability point Q_1^T somewhat close to the minimum of the B_{3u} state. One interesting point to remark is the sign of c we have obtained. Depending on the sign of c, the electron wave function of the lower state (formally A_{1g}) will have larger amplitude on the vacant site just created or on the opposite site. A simple check confirms that we have the anticipated distortion of the A_{1g} wave function with larger amplitude on the vacant site corresponding to an F center, as was predicted by Toyozawa.[11]

At this point, we are in a position to make some basic assessment regarding the adiabatic instability, as well as the bottleneck in the radiationless transition between the A_{1g} and B_{3u} states. There are two aspects, as mentioned in Sec. I, which oblige us to modify this model. First, the turning point at Q_1^T us too high above the minimum of the B_{3u} state for the instability to be operative at temperatures of experimental interest[2] (except for the largest values of c; see Table I). This depends strongly on the value of the mixing coefficient c of this model, which is evaluated only approximately. It is obvious, however, that the instability as proposed by Toyozawa may be operative at high temperatures. The second, in fact the more serious, difficulty is that the probability of radiationless transition from the B_{3u} to the A_{1g} state is too small. At low temperatures ($T \rightarrow 0$ K), this transition probability is determined by the square of the overlap integral between the lowest vibrational wave function of the B_{3u} state and a highly excited ($\approx$ the 30th for NaCl and KCl) vibrational wave function of the A_{1g} state. Because the shift of the equilibrium position of these two vibrational states (i.e., $Q_{1,u} - Q_{1,g}$) is small, the transition probability is found to be hopelessly small in comparison with the observed formation time of 11 psec. in KCl.[2] This point has also been raised in a recent paper by Williams.[10] At high temperatures, the activation energy for this radiationless process, as determined by the energy difference between the crossing point and the minimum of the upper state,[22] is found to be about 10 eV for NaCl and KCl and 6 eV for LiF. Such large activation energies would render radiationless transition almost impossible even at high temperatures.

As already discussed in considerable details in the introduction, the difficulty of Toyozawa's model to account for the observed F-center formation time is directly related to the fact that the electron states are only weakly coupled to the Q_1 mode. However, based on the observed broad absorption bandwidths of the STE,[13] we do expect considerable difference in the relaxation of the lattice around the STE for the two electronic states, although the distance between the two central halogen ions does not change appreciably. We shall assume that the lattice relaxation may be represented by a single effective mode ($\tilde{Q}_1$), and accordingly, we modify Toyozawa's model by including this additional mode into the analysis. This is the subject of Sec. III.

III. MODIFICATION OF TOYOZAWA'S MODEL

It is straightforward to generalize the treatment given in Sec. II A to include the coupling of the STE states to one more vibrational mode $\tilde{Q}_1$, in addition to Q_1 and Q_2. We assume that the $\tilde{Q}_1$ mode has symmetry A_{1g} and represents effectively the relaxations of all the ions other than the two central halogen ions. Alternatively $\tilde{Q}_1$ may be viewed as analogous to the breathing mode that broadens and shifts transitions in M centers.[23] The separation of these three modes, Q_1, Q_2, and $\tilde{Q}_1$ is only approximate, but is convenient for our discussion.

The inclusion of this extra mode $\tilde{Q}_1$ does not make the algebra more complicated, and we shall only give here the useful results. In place of (13), the adiabatic-potential surfaces are now given by

$$\begin{aligned} E_{\mp} = {} & \tfrac{1}{2}(\epsilon_g + \epsilon_u + aQ_1 + bQ_1 + \tilde{a}\tilde{Q}_1 + \tilde{b}\tilde{Q}_1 \\ & + k_1 Q_1^2 + k_2 Q_2^2 + \tilde{k}_1 \tilde{Q}_1^2) \\ & \mp \tfrac{1}{2}\{[\epsilon_u - \epsilon_g + (b-a)Q_1 + (\tilde{b}-\tilde{a})\tilde{Q}_1]^2 \\ & + 4c^2 Q_2^2\}^{1/2} \end{aligned} \tag{17}$$

where $\tilde{a}$ and $\tilde{b}$ are defined similarly as a and b by (12) with Q_1 replaced by $\tilde{Q}_1$, and $\tilde{k}_1$ is the force constant for the $\tilde{Q}_1$ mode.

Based upon the discussion in the preceding section which shows that the Q_1 mode is unable to account for the observed instability of the STE (because the coupling coefficients a and b are small), we can safely ignore the Q_1 mode in our following discussion. Thus the treatment given in Sec. II A and Fig. 1 may straightforwardly be applied to the present case with Q_1 now replaced by $\tilde{Q}_1$. The turning point $\tilde{Q}_1^T$ is now given by

$$\tilde{Q}_1^T = \frac{\epsilon_u - \epsilon_g - 2c^2/k_2}{\tilde{a} - \tilde{b}} . \tag{18}$$

The crossing point coordinate $\tilde{Q}_1^C$ is given by

$$\tilde{Q}_1^C = -(\epsilon_u - \epsilon_g)/(\tilde{b} - \tilde{a}) . \tag{19}$$

For clarity, the two potential curves along $\tilde{Q}_1$ are shown in Fig. 2.

Parameters $\tilde{a}$, $\tilde{b}$, and $\tilde{k}_1$ relevant to the $\tilde{Q}_1$ mode

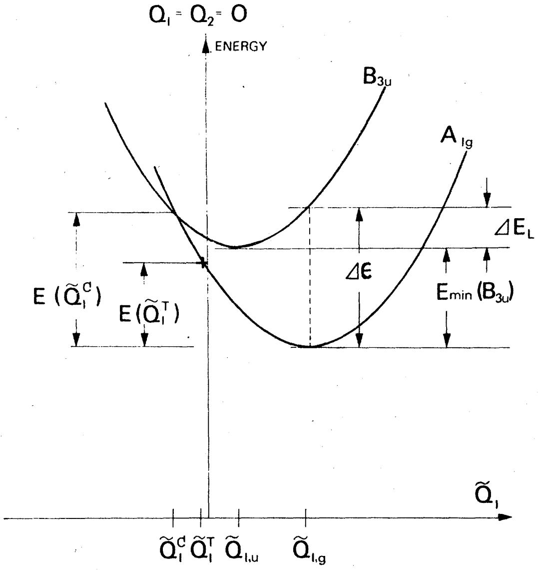

FIG. 2. Adiabatic potential [Eq.(17)] as a function of $\tilde{Q}_1$ with $Q_1 = Q_2 = 0$. $E(\tilde{Q}_1^C)$, $E(\tilde{Q}_1^T)$, and $E_{\min}(B_{3u})$ are the energies (relative to the minimum of the lower A_{1g} state) at the crossing point, the turning point, and the minimum of the upper B_{3u} state, respectively. $\Delta\epsilon$ is the optical-absorption energy and ΔE_L is the strain energy.

are not readily accessible by simple calculations as was the case for Q_1 and Q_2. It is possible, however, to obtain useful information from such data as the absorption bandwidth for $A_{1g} \rightarrow B_{3u}$, or the Stokes shift between the two bands (see Fig. 2). There is no observed luminescence for $B_{3u} \rightarrow A_{1g}$, but Ref. 13 gives some idea about the absorption bandwidth at very low temperatures. If one assumes that the $\tilde{Q}_1$ mode is responsible for the broadening,[13] and make use of the theory of Huang-Rhys for the line shape,[24] one obtains the following useful relations:

$$\begin{aligned} \Delta E_{\text{Stokes}} &= 2\Delta E_L = 2S\hbar\tilde{\omega}_1 , \\ \Delta E_L &= \tfrac{1}{2}(\tilde{a} - \tilde{b})^2/\tilde{k}_1 , \end{aligned} \tag{20}$$

where ΔE_L is the strain energy which is half the Stokes shift in this simple model, and S and $\tilde{\omega}_1$ are, respectively, the Huang-Rhys factor and the frequency of the $\tilde{Q}_1$ mode. According to the theory of line shape, one also finds that at $T = 0$ K, the full width at half-maximum (FWHM) is given by $[8S(\ln 2)]^{1/2}\hbar\tilde{\omega}_1$. Thus, even if we are unable to evaluate $\tilde{k}_1$ and $(\tilde{a} - \tilde{b})$, we can determine the energy of various points of interest on the lower potential surface with respect to the minimum of the A_{1g} state. Using (17)–(20), we readily obtain (see Fig. 2) (i) at the crossing point,

$$E(\tilde{Q}_1^C) = \tfrac{1}{2}\tilde{k}_1(\tilde{Q}_1^C - \tilde{Q}_{1,g})^2 = \tfrac{1}{4}(\Delta\epsilon)^2/\Delta E_L ; \tag{21a}$$

(ii) at the turning point,

$$E(\tilde{Q}_1^T) = \tfrac{1}{2}k_1(\tilde{Q}_1^T - \tilde{Q}_{1,g})^2 = \frac{1}{4}\frac{(2c^2/k_2 - \Delta\epsilon)^2}{\Delta E_L} ; \tag{21b}$$

(iii) at the minimum of the B_{3u} state,

$$E_{\min}(B_{3u}) = \Delta E - \Delta E_L , \tag{21c}$$

where $\Delta\epsilon$ is the optical-absorption energy for $A_{1g} \rightarrow B_{3u}$.

The parameter $\Delta\epsilon$ is not well known at the moment. Theoretical calculations give values of 0.6[12] and 1.4 eV,[25] for KCl. Absorption spectra of STE in KCl give the low-energy peaks at 1.87 and 2.12 eV,[13] but the assignment of the final states is not unambiguous. Williams[5] has observed an enhancement of F-center production in KCl when photons of 1.79 eV was absorbed, but this could be the B_{3u}^* or B_{3u} state or some other states which lead to a B_{3u} state. We therefore assume here that for both KCl and NaCl, $\Delta\epsilon$ is in the range 1.0–1.8 eV. The other parameter, the strain energy ΔE_L, is estimated from the observed absorption bandwidth[13] to be 0.5 eV for both NaCl and KCl (corresponding to a FWHM of about 0.3 eV). A strain energy of 0.8 eV for KCl is proposed by Williams and Kabler[13] in a similar situation where the B_{3u} state is replaced by the ionized electron state (V_k center). With these parameters, one obtains the various energies defined in (21a)–(21c) as shown in the upper part of Table II. The turning point which marks the onset of the adiabatic instability at $\tilde{Q}_1^T$ is located, for the range of $\Delta\epsilon$ used, between 0.30 and 0.35 eV below the bottom of the upper (B_{3u}) state, in contrast with the results obtained earlier with the original model of Toyozawa. Thus, even at low temperatures, the adiabatic instability of translational (Q_2 mode) motion of the X_2^- molecule is very likely to occur provided that the tunneling passage from the bottom of the B_{3u} state to the A_{1g} state can take place with large enough probability.

TABLE II. Energies at various points on the lower adiabatic potential [defined in Fig. 2 and Eqs. (21a–21c)] and the radiationless transition probability [Eq.(22)] for NaCl and KCl for various values of the optical-absorption ($A_{1g} \rightarrow B_{3u}$) energy $\Delta\epsilon$. All energies are in eV($c = 0.22$ eV/a_0, $k_2 = 0.27$ eV/a_0^2, $\Delta E_L = 0.5$ eV, $\hbar\omega_{\text{LO}} = 0.032$ eV for NaCl and 0.026 eV for KCl).

$\Delta\epsilon$		1.0	1.4	1.8
$E(\tilde{Q}_1^C)$		0.5	0.98	1.6
$E(\tilde{Q}_1^T)$		0.21	0.54	1.0
$E_{\min}(B_{3u})$		0.50	0.90	1.3
$W\left(\frac{1}{\text{sec}}\right)$	NaCl	5.0×10^{13}	2.1×10^{11}	4.8×10^{6}
	KCl	2.5×10^{13}	4.1×10^{10}	1.0×10^{5}

We now examine the probability of radiationless transition between these two states. We assume that the $\tilde{Q}_1$ mode may be approximated by linear combinations of longitudinal-optical (LO) phonon modes of the perfect crystal, and make use of the following expression derived by Huang and Rhys[24] for the radiationless transition probability:

$$\underset{T\to 0}{W(T)} = \frac{32\pi^3\hbar\omega_{\text{LO}}^2}{3v}\left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0}\right) \times \frac{|\langle\psi_u|e\vec{\mathrm{x}}|\psi_g\rangle|^2}{[E_{\min}(B_{3u})]^2}\frac{e^{-S}S^p}{p!} . \tag{22}$$

Here $\hbar\omega_{\text{LO}}$ is the energy of a LO phonon, v is the primitive cell volume, S is the Huang-Rhys factor already defined above, $p = E_{\min}(B_{3u})/\hbar\omega_{\text{LO}}$, and the other symbols have their usual meanings. The dipole moment is evaluated by employing single Slater functions for ψ_g and ψ_u as in Sec. II B, which gives $3.2ea_0$ for NaCl and $3.5ea_0$ for KCl. Values of S are obtained from (20) with $\Delta E_L = 0.5$ eV as before.

The calculated values of W for NaCl and KCl are presented in the lower part of Table II for the same range of $\Delta\epsilon$ employed before. Except for the case $\Delta\epsilon = 1.8$ eV, the results obtained are compatible with the experimental observed F-center formation time of 11 psec in KCl at 25 K.[2] We should note that W is also very sensitive to S (or ΔE_L), which is only roughly estimated here. Reliable location of the B_{3u} state as well as the determination of the strain energy ΔE_L should provide important information regarding this modified version of Toyozawa's model.

IV. COMMENTS

We may conclude at this point that the inclusion of the $\tilde{Q}_1$ mode into the original model of Toyozawa can satisfactorily account for the adiabatic instability of the X_2^- molecule in [110] direction, which leads to the formation of pairs of F and H centers. We give here some physical insight regarding the role played by the $\tilde{Q}_1$ mode in this model. In an oversimplied picture, we may visualize the $\tilde{Q}_1$ mode as the breathing mode of the nearest-neighboring (nn) alkali ions to the X_2^- molecule. At the turning point at $\tilde{Q}_1^T$, these nn ions move away from the X_2^- molecule and give rise to a force squeezing out the X_2^- molecule in [110] direction. One more appealing feature of this model is that the $\tilde{Q}_1$ mode is likely to reduce the potential barrier experienced by the X_2^- molecule in its subsequent motion.

Although it is generally accepted that translation, rather than dissociation, of the X_2^- molecule is the initial motion leading to F and H defect pair formation, there have been various other proposals[10] regarding the mechanism besides the one which we have so far concerned with. We now briefly comment on two of the recent models. Itoh and Saidoh[26] proposed a mechanism in which this motion is due to an adiabatic instability (similar to Toyozawa's, although not specified) accompanied by an excitation of the self-trapped hole from its ground state B_{3u} to a π-like (B_{1u} or B_{1g}) state. This helps to explain the passage of the X_2^- molecule through the potential barrier of the nn ions. It is well known that a V_k center in its excited states is extremely mobile, with virtually no activation energy.[27,28] It is thus not clear how this rapid reorientation of the excited STE state is compatible with the idea of early coherent motion of the X_2^- molecule along [110] direction.

Another model proposed by Kabler and Williams[10,29] is based on a mechanism in which the X_2^- molecule undergoes a combined rotation and translation. The rotational motion involved seems different from the 60° jumps observed for V_k centers in alkali halides of the NaCl structure. They argued that the rotation, after which the memory of its previous orientation is lost, may have very small or no potential barrier to overcome when accompanied by a nearby bound electron (STE). This combined rotation translation is believed to operate in CaF_2 and other fluorites when the self-trapped hole F_2^- captures an electron. However, more elaboration and calculations are needed to clarify the key steps involved particularly for alkali halides. Nevertheless it was found that the activation energies for 60° jumps in alkali halides even with the complete cancellation of the lattice distortion (other than those of the two central halogen ions) are reduced by a factor of 2 to 3 compared to the corresponding values for the V_k centers.[30] It is not clear therefore whether the STE (with its hole in the ground state) can undergo rapid reorientations at low temperatures.

In conclusion, we feel that the Toyozawa model in its present modified version provides a very plausible mechanism of defect formation in alkali halides, but more detailed studies of this model (e.g., clarifying the nature of the $\tilde{Q}_1$ mode, more reliable calculation of the parameters c, k_2, $\tilde{a}$, $\tilde{b}$, etc.) are yet required for better understanding of the mechanism. Also similar studies on other models, such as the ones just described, would undoubtedly be important for an understanding of defect formation.

Note added in proof. After this paper was submitted, Williams, Kabler, and Schneider have reported that the lowest state which is reached from the metastable A_{1g} state is about 1.9 eV above A_{1g} for KCl (2.0 eV for NaCl).[31] This state is probably the B_{3u} of our model. Taking $\Delta\epsilon \simeq 1.9$ eV for KCl, we find that the strain energy ΔE_L has to be about 0.7 eV (instead of 0.5 eV) for the radiationless transition probability to be about 10^{11}/sec.

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