PHYSICAL REVIEW B VOLUME 33, NUMBER 10 15 MAY 1986

Off-center self-trapped excitons and creation of lattice defects in alkali halide crystals

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(Received 17 January 1986)

Self-consistent calculations and experimental evidence indicating that self-trapped excitons in alkali halides relax spontaneously to an off-center configuration are examined in relation to radiation-induced lattice defect formation. The theoretical results show that the shift of the diatomic halogen core in relaxation of the self-trapped exciton (STE) from D_{2h} to C_{2v} point-group symmetry is quite large (e.g., about 4 a.u. in KCl). The clear implication is that the STE triplet state which is responsible for the well-known π-polarized recombination luminescence is effectively a nearest-neighbor *F-H* pair, analogous in many ways to the *F-H* pair configuration which is known to constitute the STE luminescent state in alkaline-earth-metal fluorides. From this new perspective, in which conversion of an STE to an *F-H* pair reduces to conversion of a nearest-neighbor *F-H* pair to a more distant *F-H* pair, a number of formerly puzzling aspects of photochemical *F*-center generation can be rationalized quite simply.

I. INTRODUCTION

A. Self-trapped excitons

Since its discovery[1,2] in 1964, the self-trapped exciton in alkali halides has been regarded essentially as an electron bound to a V_K center. The V_K center, or self-trapped hole, is a covalently bonded diatomic halogen molecular ion which is formed immediately upon photoionization of a halide ion, i.e., upon generation of a hole in the valence band of an alkali halide. The V_K center is stable at low temperature in a crystal with electron traps and is furthermore paramagnetic, so that its structure has been determined quite accurately by electron paramagnetic resonance (EPR) (Ref. 3) and by electron-nuclear double resonance (ENDOR) (Ref. 4). The bonded halide ions in the V_K center occupy equivalent sites lying along a [110] crystal axis, and the pair is centered on the midpoint between two nearest-neighbor halide sites, having point symmetry D_{2h}.

When an electron recombines with a self-trapped hole via states of the self-trapped exciton (STE), the resulting luminescence is polarized (σ and/or π bands) with respect to the V_K symmetry axis.[1,2] The fact that the dipole moment of recombination luminescence is correlated with the orientation of the V_K center before recombination provided the first experimental basis for the conventional model of a STE as an electron trapped at a V_K center. It has been possible to analyze lifetimes,[5,6] magneto-optical data,[7,8] excited-state EPR,[9,10] and much of the excited-state absorption spectroscopy[11,12] on the basis of the "on-center" V_K+e^- model for the STE.

The spectra of excited-state absorption originating in the π-luminescent STE triplet state exhibit transitions of the hole within the self-trapped exciton; these lie roughly between the V_K band and the H band.[11–13] (An H center is a bonded diatomic halogen molecular ion situated as a split interstitial on a halide-ion site and oriented along [110] in alkali halides.[14]) The excited-state absorption spectra also exhibit a sequence of transitions of the electron bound to the self-trapped hole. The spectrum of electron transitions seemed at first to fit qualitatively an "*M*-center model," wherein the bound electron experiences a pair of attractive centers symmetrically located along a [110] axis and has D_{2h} site symmetry.[12] Such a model predicts that the σ-polarized absorption transition from the lowest a_{1g} electron orbital to the first b_{3u} orbital will be the lowest energy transition. Theoretical calculations of STE electronic structure, taking the self-trapped hole to have the fixed configuration of the V_K center, consistently predicted that the a_{1g}-b_{3u} transition should occur at much lower energy than any of the observed transitions.[15,16] Calculated energies for this transition in NaCl ranged from 0.7 to 1.1 eV, compared to 2 eV for the lowest observed transition. A careful search in NaCl verified (with a detection limit of 2% of the predicted oscillator strength) that no transition of the STE exists between 0.1 and 2 eV.[17] Furthermore, when pulsed laser bleaching was used to determine the polarization of the lowest absorption transition, it was found to be π polarized,[18,19] in contrast to the *M*-center model. Subsequent more detailed measurements have shown the typical ordering of excited-electron orbitals of the STE to be b_{2u}, b_{1u}, and b_{3u}, in order of ascending energy.[20]

Excited-state EPR has been performed on STE triplet states by optical detection methods.[9,10] The data exhibit a seven-line hyperfine pattern (for halogen nuclear spin $\frac{3}{2}$) similar to that of a V_K center[3,21] or *H* center.[21] The widths of the hyperfine components are significantly broader than for the V_K center or *H* center, due mainly to the interaction of the STE electron with surrounding nuclei. Significantly, in all cases the investigators remarked on how similar the hyperfine linewidths of the STE are to those of the *F* center. The seven-line pattern suggests that the hole in the STE interacts with two equivalent halogen nuclei, but the breadth of the EPR hyperfine components does not permit a distinction between exact equivalence and small inequivalence of the halogen nuclear sites solely on this basis.

The first direct experimental indication that the STE may not simply be an electron bound to a V_K center came from optical ENDOR studies in KCl.[22] It was found that the ENDOR spectra representing interaction of the STE electron with neighboring nuclei give contact interactions very similar to those of the *F* center, indicating a similar extent of the wave functions. Furthermore, a four-line ENDOR pattern interpreted in terms of two different quadrupole splittings for the central chlorine nuclei is a strong indication that the STE is displaced from the centrosymmetric site (D_{2h}) to an off-center position in the lattice (C_{2v} symmetry).[22]

Following the experimental indication by ENDOR of an off-center STE, Leung and Song[23] employed the model of Toyozawa[24] to show that off-center displacement of the STE is indeed rather likely in KCl, and its displacement was estimated to be about 0.5 a.u. Subsequent calculations by Leung, Brunet, and Song (LBS) in which the electron state and the lattice relaxation were determined simultaneously[25,26] predicted that the off-center STE should be quite general among the alkali halides, and that the amount of off-center relaxation might be large, in the neighborhood of 3 a.u. (about 1.6 A). Still more recent calculations to be discussed in this paper indicate an off-center relaxation of about 4 a.u. in KCl, which corresponds to displacement of the Cl_2^- molecular ion to an *H*-center site. Much better agreement with the energies of excited-electron transitions of the STE were obtained for the off-center configuration.[25,26]

It seems fair to say, that whereas the V_K+e^- model of the on-center STE can reasonably account for the polarization and lifetime of luminescence and for the optically detected EPR spectrum, calculations based on that model have failed to properly reproduce the excited-state electron transition energies within the STE. The simple V_K+e^- model fails to account for the inequivalent nuclear quadrupole splittings observed by ENDOR. Furthermore, the contact interaction with neighboring nuclei for the STE in KCl as calculated by a pseudopotential technique assuming the on-center V_K+e^- model[15] fails to reproduce the values found by ENDOR.[22]

The off-center STE can account for the observed polarization of recombination luminescence if its off-center motion is along [110], preserving the axis of the diatomic halogen molecular ion which is the core of the STE. The STE triplet luminescence lifetimes depend principally on the halogen spin-orbit coupling[5,8] and should be relatively insensitive to an axial shift of the halogen molecular ion. After providing additional background in this paper, we will discuss how optically detected EPR of the STE may indicate nearly equivalent halogen nuclei despite a large off-center relaxation of the pair. In summary, we believe that all existing data on the STE are consistent with a lower point symmetry than D_{2h}. Conversely, assumption of D_{2h} symmetry for the STE leads to serious difficulty with theoretical calculation of STE excited-electron states, and it contradicts the existing optical ENDOR data for KCl.

B. *F*-*H* pair formation

Hall *et al.* first noted that ultraviolet light in the exciton absorption bands of an alkali halide crystal is sufficient to produce *F* centers.[27] Furthermore, in certain alkali halides the temperature dependence of the *F*-center-formation yield was found to be anticorrelated with the STE π luminescence.[28,29] It was therefore proposed that *F* centers are formed by nonradiative decay of self-trapped excitons.[28,30] Subsequent work has continued to support this basic hypothesis, although the *way* in which nonradiative STE decay leads to *F*-center generation has remained a topic of active interest and diverse opinion (reviewed in Refs. 31 and 32).

Time-resolved spectroscopy has shown that the primary (first-formed) defects are *F* centers and *H* centers, created as pairs.[13,33] The pairs will be labeled by *F*-*H* separation as nearest-neighbor [$(F\text{-}H)_{NN}$], next-nearest-neighbor [$(F\text{-}H)_{NNN}$], etc.[34] Close-neighbor *F*-*H* pairs appear to be unstable against mutual annihilation, with lifetimes as short as tens of picoseconds at room temperature.[35] It has now been reasonably well established that the anticorrelation of the temperature-dependent yield of *F* centers and of STE π luminescence is a consequence of diffusive transport of a halogen atom among potential minima on the lowest excited adiabatic potential surface, which is common to the STE π-luminescent state and the *F*-*H* pair.[35–39] It has been shown by LBS that the equilibrium configuration of the self-trapped exciton at low temperature in many alkali halides is probably very close to that of a nearest-neighbor *F*-*H* pair. It is already well known that STE luminescence in alkaline-earth fluorides is emitted from a nearest-neighbor *F*-*H* pair that forms spontaneously when an electron and self-trapped hole come together, rather than from a V_K center plus electron;[40,41] the latter relaxes spontaneously and quickly into the former. We propose that a similar sequence occurs in alkali halides. The main difference is that relaxation from V_K+e^- to $(F\text{-}H)_{NN}$ in CaF_2 involves a rotation of the symmetry axis of the diatomic fluorine molecular ion from [100] to [111] making it easy to observe. The corresponding relaxation in alkali halides is simply a translation along [110]; the latter presents a more subtle problem for detection.

At sufficiently high temperature, all alkali halides that have been investigated exhibit thermally activated primary *F*-center formation.[42–45] In most cases it proceeds with an activation energy roughly comparable to that for *H*-center migration, suggesting the importance of diffusive transport of the halogen interstitial on the lowest STE/*FH* adiabatic potential surface.[35–39] On the other hand, certain crystals, including KCl, KBr, and RbBr, also exhibit a nonvanishing *F*-*H* pair formation yield (up to about 15%) at temperatures as low as 4 K. At such temperatures, diffusive transport of halogen atoms in thermal equilibrium with the lattice cannot be important. Furthermore, the low-temperature process of *F*-center formation is very fast,[33,43] and the *H* center appears to preserve the orientation of the self-trapped exciton.[46] Halogen atoms are ejected from the crystal surface with nonthermal energies (about 1 eV) by the low-temperature defect-formation process, but only with thermal energy ($\lesssim 0.025$ eV) by the temperature-dependent process.[47] In crystals such as KI, RbI, and NaBr, only the temperature-dependent defect-formation process is observed. It is only in these crystals that anticorrelation of *F*-center yield with STE luminescence yield and lifetime[48] is observed.[36,37] Finally, it has been observed that when a laser pulse excites self-trapped excitons which have relaxed to the lowest (π-luminescent) state at low temperature, there occurs an enhancement of the low-temperature *F*-center-formation yield.[18,49,50]

Collectively, the above data seem to suggest two distinct mechanisms of defect formation: one of which is thermally activated and occurs universally in the alkali halides at elevated temperature, the other being effective in certain crystals at low temperature and apparently deriving energy for ejection of the halogen atom from excited states of the STE. We believe that these two apparently distinct channels of defect production can be given a unified account in a simple picture. One purpose of the present paper is to describe the adiabatic potential surfaces which can account for both defect production channels.

II. THEORETICAL METHOD AND RESULTS

This paper is less a presentation of new theoretical results than an examination of the implications for defect formation of recent calculations on STE structure (LBS, Refs. 25 and 26). Using those results, we can now understand the nearly universal close correspondence of the energy minima for STE and *F*-*H* pair configurations and the surprisingly small barrier against halogen diffusion out of the STE, which are required by the model of thermally activated *F*-center formation discussed in Refs. 35–39. The off-center relaxation of the lowest STE level also suggests a mechanism that can channel excited-state energy into translational acceleration of a halogen pair at low temperature. First we will give a brief overview of the computational methods employed to examine STE electronic structure in alkali chlorides[25] and potassium halides.[26] Then we will describe the results which have particular relevance to defect formation.

The electronic energy of the STE was studied within the framework of the one-electron Hartree-Fock approximation (extended-ion model), using the hybrid method developed by Song *et al.*[51] The various terms (including exchange) for the outer shells were treated explicitly, using a set of interpolation formulas, while the deep cores were represented by the first two orders of the ion-size parameters.[52] The required wave functions for the V_K center were taken from the work of Gilbert and Wahl.[53] A basis of floating 1*s* Gaussians was used to represent the excited electron.[51] Because it turns out that the electron wave function distorts substantially between the two symmetries D_{2h} and C_{2v}, from 8 to 14 of the floating Gaussians were required for adequate representation.

In the most recent work, the V_K molecular ion core and 39 neighboring ions are allowed to displace. The total energy of the system for a given lattice configuration $\{R_j\}$ is

$$E_{\text{tot}}(\{R_j\})=E_{\text{el}}(\{R_j\})+E_{\text{lattice}}(\{R_j\}) , \tag{1}$$

where E_{lattice} is the sum of the Coulomb and (Born-Mayer) repulsive energies of the lattice and E_{el} is the lowest eigenvalue of the electron Hamiltonian. For each $\{R_j\}$ obtained by a small trial displacement of one of the ions, the secular determinant was solved. When the total energy converged to within 0.003 eV, the process was stopped and the equilibrium configuration was assumed to have been reached. The electronic polarization energy was added at the end of the minimization using the Mott-Littleton method in the lowest order. Since the system is electrically neutral, it is felt that this is an acceptable approximation. The above method was applied to determine the equilibrium configuration of the STE in NaCl, KCl, RbCl, KBr, and KI.[25,26] In each case it was found that at equilibrium the STE is situated off center along the molecular axis of the V_K center, corresponding to a lowering of symmetry from D_{2h} to C_{2v}. The neighboring ions are also found to move appreciably toward a distorted configuration. In terms of the local modes appropriate to the symmetry of the V_K center, the new lattice configuration is a superposition of the a_{1g} (breathing) mode and the b_{3u} mode. The first mode corresponds to the stretching motion of the molecule as well as to the breathing motion of the first cation shell. The second mode corresponds to the axial translation of the molecule as well as to the parity-breaking distortion of the cations surrounding the molecule. These two modes correspond, respectively, to the Q_1 and Q_2 modes introduced in earlier works on the adiabatic instability of the STE in alkali halides.[23,24]

Specifying the low-lying states of the STE in the format of (hole orbital, electron orbital), we have for D_{2h} symmetry, in order of increasing energy, (b_{3u},a_{1g}), (b_{3u},b_{3u}), (b_{3u},b_{2u}), and (b_{3u},b_{1u}). We will confine our attention to states involving the b_{3u} hole orbital, and therefore indicate only the electron orbital in the discussion to follow.

The curves in Fig. 1 show the calculated total energy (lattice and electronic) for STE states in KCl which are labeled by the excited electron orbital appropriate to D_{2h} symmetry: a_{1g}, b_{1u}, b_{2u}, and b_{3u}. These curves are based on calculations by Song, Adair, and Leung.[54] The abscissa is a measure of the axial shift, along [110], of the bond-

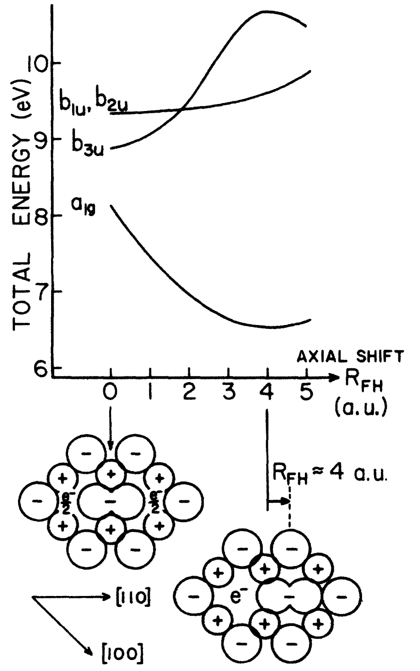

FIG. 1. Total energy (sum of the defect electron energy and the change of the lattice energy relative to the perfect lattice) versus the translational coordinate R_{FH} of the STE in states designated by the electron orbital in D_{2h} symmetry: a_{1g}, b_{3u}, b_{1u}, and b_{2u}. The curves are based on calculated results of Song, Adair, and Leung (Ref. 54) for KCl, in which 41 ions were allowed to move as the energy was minimized. The minimum of the a_{1g} curve at the coordinate $R_{FH}=4$ a.u. corresponds to the equilibrium STE configuration from which π luminescence is emitted. This configuration closely resembles a nearest-neighbor *F*-*H* pair. In the lower part of the figure, pictorial representations of lattice configurations for the "on-center" and "off-center" STE are shown, viewed in a (001) plane having its [110] axis horizontal. The circles are drawn to scale representing the Pauling ionic radii of the ions and their positions are given by the calculation.

ed Cl_2^- molecular ion. Although we focus here on the motion of the Cl_2^- in defining the abscissa of the plot, motions of the 39 other ions which were allowed to move are included implicitly since the energy was minimized at each stage. The measure of axial shift used here is R_{FH}, given in atomic units (1 a.u.$=$0.529 A). R_{FH} is zero when the Cl_2^- is located symmetrically about the midpoint of the initial Cl^--ion position, as illustrated in the diagram at the lower left of Fig. 1. This is the configuration appropriate to the on-center STE or V_K+e^-. As axial relaxation progresses, R_{FH} describes the distance from the center of the Cl_2^- in the initial V_K configuration to the center of the shifted Cl_2^-. Thus, R_{FH} approximates the separation of the developing *F* center and *H* center. Accompanying this shift in position, the energy of the state labeled a_{1g} falls by almost 1.5 eV relative to its energy at $R_{FH}=0$. Thus, the on-center STE in its lowest electronic state is unstable against a shift to nonzero R_{FH}. The calculations of Ref. 54 represented here show that the relaxation proceeds until an energy minimum is reached for $R_{FH}=4$ a.u. (The equilibrium value of R_{FH} in KCl was found to be 3 a.u. in Ref. 25, where only 12 ions were allowed to move.)

The ion positions corresponding to the luminescent STE state, or minimum of the a_{1g} energy surface at $R_{FH}=4$ a.u., are diagrammed in the lower right of Fig. 1. The calculated ion positions are plotted, using the Pauling ionic radii for K^+ and Cl^- to represent ion size. It is clear that the equilibrium configuration of the STE found by these calculations is an *H* center adjacent to an *F* center. If the displacement is indeed 4 a.u., then the "*H* center" has already passed the presumably largest hurdle—repulsion by the central cation pair—while still in the π-luminescent STE configuration. It was the simultaneous treatment of relaxation of the excited electron and the lattice ions in the energy minimization process which allowed the cation repulsive barrier to be overcome so readily.[25,26,54]

This is in contrast to an earlier calculation[55] in which the lattice relaxation was computed independently of the excited electron, after which the CNDO method was employed to include the excited electron in evaluating total energy in the presence of the previously determined lattice distortion. This approach afforded no opportunity for *interaction* of the excited electron with the Cl_2^- halogen core and surrounding ions to affect the relaxation. We have seen that the instability induced by this interaction is in fact crucial. It is therefore not surprising that the calculation in Ref. 55 yielded quite different conclusions about the energy needed to move from the on-center to the off-center $[(F\text{-}H)_{NN}]$ configuration.

We have discussed the spontaneous distortion in terms of an adiabatic instability brought on by mixing and consequent level repulsion of a_{1g} and b_{3u} as the symmetry is lowered. Another way of looking at the energy balance is in terms of removing the halogen-atom core and its associated repulsive pseudopotential from the developing site of an *F* center. Cl_2^- is not an attractive center for an electron in free space. In the crystal, an electron is attracted to the *site* of the Cl_2^- via the Madelung potential, not to the Cl_2^- itself. In fact, the halogen core states comprise a net repulsive pseudopotential for an excited electron attempting to occupy an *F*-center-like wave function centered on the site of one or the other of the halogens bonded in the STE. The electron wave function on the nascent *F* center can achieve a substantially lower energy if it does not need to be orthogonalized to a halogen core near the center of the developing vacancy. If the electronic energy can be lowered enough by expulsion of the halogen to offset the increase in lattice strain energy, then the halogen will be spontaneously pushed out some distance. Self-trapped exciton luminescence would then occur from this relaxed configuration resembling a nearest-neighbor *F*-*H* pair, as observed in the alkaline-earth fluorides.[40,41,56] The calculations of LBS (Refs. 25, 26, and 56) have shown that the energy balance favors expulsion of a halogen. Both the theoretical[56] and experimental[40,41] evidence for this is especially clear for the alkaline-earth fluorides. We should remark that the situation described here is very close to that which occurs for self-trapped excitons and electron "bubbles" in condensed rare gases.[57,58]

As noted earlier, optically detected EPR showed that the two halogen nuclei comprising the core of the STE have nearly equal hole density, as evidenced by the V_K-like (or H-like) hyperfine pattern. This observation is consistent with a nearest-neighbor F-H pair in which the F-center electron is localized on the vacancy at one end of the H center. The trapped electron restores one negative charge to the vacancy so that each anion site surrounding the H center has an equivalent charge. If the halogen displacement were only partway to the $(F\text{-}H)_{\mathrm{NN}}$ configuration, the electron could not fully occupy the developing F center and the self-trapped hole would then be subject to distinct lack of mirror symmetry in the charge distribution, in contradiction to the EPR results. The existence of the EPR data requires that the off-center STE relaxation be either very large (about 4 a.u., close to an F-H pair) or very small.

We can be somewhat more quantitative about this. The calculations of Song, Adair, and Leung[54] have shown that the sum of the distorted-lattice Madelung potential and the potential due to the trapped electron differs by no more than about 0.1 eV at the two central halogen sites in the off-center STE, when evaluated for the full 4-a.u. equilibrium displacement calculated in KCl. Corresponding to this potential difference between the two sites, we find hole occupation probabilities of 48% and 52%, respectively, on the two halogen sites. This would split the central peak of the $\mathrm{Cl}_2{}^-$ hyperfine pattern into four subpeaks spanning about 24% of the separation between adjacent main-peak envelopes. Likewise, the adjacent main peaks would be split into three subpeaks spanning 18% of the main-peak separation, etc. But in the reported optical EPR data for the STE in KCl, each of the seven hyperfine peaks has a width of 40 to 50% of the separation between adjacent peaks. Hence, the expected splitting of hyperfine components would not be resolvable against the broadening which has already occurred due to interactions of the F-center-like electron with surrounding nuclei. Support for this hypothesis is given by the failure to observe hyperfine splitting due to the naturally occurring isotopes $^{35}\mathrm{Cl}$ (75% abundant) and $^{37}\mathrm{Cl}$ (25% abundant). These isotopes differ in nuclear moment, and hence in hyperfine constant, by 20%. By inference, then, a hole imbalance as large as 20% of the mean occupation on the two chlorine nuclei might not be detected in the hyperfine pattern.

III. DISCUSSION

A. Thermally activated *F*-center formation

We have noted that, in addition to the low-temperature process of F-center formation exhibited by some of the alkali halides, there is a thermally activated process which is apparently universal in the alkali halides at sufficiently high temperature.[42-45] Furthermore, the activation energy is often found to be comparable to the activation energy for H-center diffusion.[42-45] It has been proposed that thermally activated F-center formation proceeds by diffusion of a halogen atom out of the STE *in its lowest (π-luminescent) state.*[35-37] This diffusive motion of the halogen can also convert an F-H pair back into a STE.[59] F centers would be formed in competition with radiative decay (e.g., in KI) or nonradiative decay (e.g., in KCl) of the STE during those periods when the halogen passes through the F center during its motions on the a_{1g}/FH potential surface. This competition is believed to be the origin of the anticorrelation of F-center yield and STE luminescence observed by Pooley and co-worker[28,29] and of the high-temperature stage of thermally activated *primary* F-center formation observed in KCl and other crystals.[42-45] The process favors F-center formation at high temperature because there are more ways (sites available) for the halogen interstitial to move away from the vacancy than toward it.

As noted in Ref. 36, the model of thermally activated F-center formation by halogen diffusion out of the STE requires two conditions: (1) the barriers to halogen extraction from the STE should be small, of the order of H-center migration energies, and (2) it must be almost universally true in the alkali halides that the lowest STE state and the nearest-neighbor F-H pair have about the same energy. The latter condition is necessary to allow the reversible conversion $\mathrm{STE}\leftrightarrow FH$ which is necessary to account for experiments on F-H recombination[59] and to reproduce the observed anticorrelation of F-center yield and STE luminescence *lifetime*,[48] as discussed in Refs. 36 and 37. At the time this model was proposed, the two conditions above seemed to require a great deal of coincidence in the relative location of STE and F-H pair energy levels. Furthermore, the conditions seemed to be inconsistent with the large barrier against halogen extraction from the lowest STE state which had been found by a CNDO calculation[55] and which was conventionally expected on the basis of repulsive interaction of the moving halogen atoms with neighboring pairs of cations.

The importance for F-center formation of off-center relaxation of the STE in its lowest state should now be clear. The work of LBS has strongly indicated that spontaneous relaxation of the a_{1g} level of the STE brings it to a configuration nearly identical to a nearest-neighbor F-H pair. The two puzzling conditions for F-center formation by diffusive halogen transport out of the STE are almost trivially satisfied by a large spontaneous off-center relaxation. Since the relaxed STE already is an F-H pair in this model (though unstable against electron-hole recombination), barriers to further halogen motion should be comparable to the H-center migration energy. The "large" barriers due to repulsive interaction with the central cation pair and the lattice distortion associated with injection of the halogen into an interstitial site would have already been encountered and overcome during spontaneous relaxation to the π-luminescent STE state. It should no longer be puzzling that the STE and next-neighboring F-H pair always lie at nearly the same energy in their lowest electronic state, because the STE is effectively an F-H pair in the first place. Specifically, the calculated energies of $(F\text{-}H)_{\mathrm{NN}}$ (i.e., the STE) and $(F\text{-}H)_{\mathrm{NNN}}$ are found to be so close[54] that it cannot be said which lies higher.

Some adjustment of terminology used in the earlier discussion of the mechanism[35–39] is necessary, since the earlier work assumed an on-center STE, making $(F\text{-}H)_{\rm NN}$ the first step toward defect formation. Now that $(F\text{-}H)_{\rm NN}$ is taken to be the same as the STE, the first step toward defect formation after the relaxation of the STE itself would presumably be $(F\text{-}H)_{\rm NNN}$. A qualitative sketch of the lowest STE/*FH* potential surface with a central minimum at the π-luminescent STE configuration was used by Williams and co-workers in discussing thermally activated F-center formation.[35–37]

The corresponding potential surface taking into account off-center relaxation of the STE should now have a central *maximum* in the a_{1g} surface at the on-center (D_{2h}) STE configuration, as shown in Fig. 2. The potential curves in the region of STE and V_K configurations are based on the calculated curves displayed in Fig. 1. Whereas Fig. 1 presents the curves as calculated, the energy scale in Fig. 2 has been adjusted to conform with the results of optical-absorption spectroscopy. The abscissa represents axial [110] displacement of the halogen molecular ion, where zero displacement (0) corresponds to the V_K configuration or on-center STE. Since displacement beyond the nearest-neighbor F-H pair configuration corresponds to H-center migration, successive F-H pair energy minima are shown separated by barriers of 75 meV, the measured activation energy for H-center migration and for F-center formation in KCl.

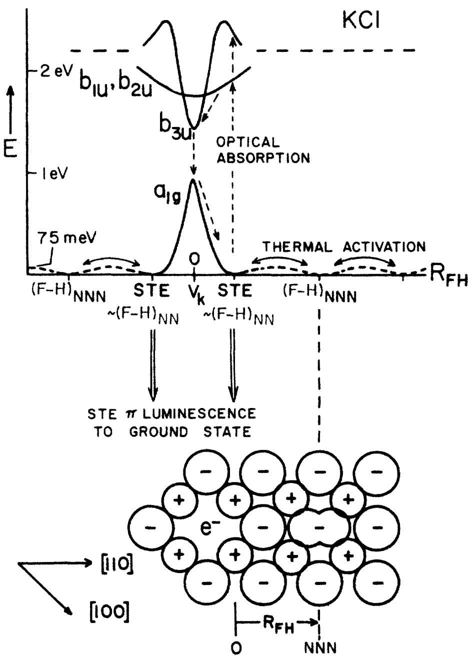

FIG. 2. (a) The curves of Fig. 1 have been redrawn here over a broader range of F-H pair separations (R_{FH} or Q_2) to exhibit explicitly the symmetry about $R_{FH}=0$ and the succession of shallow potential minima corresponding to increasing separations of the H center and F center. Thus, the full horizontal extent of Fig. 1 is compressed into the small region from the central maximum to either of the adjacent minima labeled STE. Since the calculated energy intervals represented in Fig. 1 are somewhat larger than experiment indicates, the energy scale has been adjusted in Fig. 2 to fit available empirical data. These include optical-absorption transitions for KCl as indicated, as well as the 75-meV barrier for H-center migration and primary F-H pair formation by thermal activation. In the lower part of the figure, a pictorial representation of $(F\text{-}H)_{\rm NNN}$ is shown, to be compared to the lattice configurations for V_K+e^- and for STE [or $(F\text{-}H)_{\rm NN}$] in Fig. 1.

Self-trapped excitons which have equilibrated at the off-center potential minima labeled STE may undergo radiative decay to the ground state yielding the familiar π luminescence of the STE. The H center has already been formed at this stage, but it is unstable against radiative or nonradiative recombination as long as there is significant overlap between the F-center electron and the H-center hole. Given sufficient thermal energy, the H center can migrate farther from the F center and therefore become more stable. This diffusive motion is of course not unidirectional and the H center may pass several times through the luminescent $(F\text{-}H)_{\rm NN}$ (STE) configuration. There is an *average* outward direction associated with the halogen diffusion because of the entropy argument based on site availability mentioned earlier. At temperatures too low to allow H-center migration, the nascent F center and H center are confined together and recombination dominates.

In Fig. 2, only the translational coordinate R_{FH}, closely related to the odd-parity Q_2 mode, is shown. The even-parity mode Q_1 is also important, especially in determining the minimum separation of two potential surfaces and the rate of nonradiative transition between them. Figure 2 is essentially a slice through Q_1-Q_2 space. Since the calculated potential (Fig. 1) was obtained by minimizing the lattice and electronic energy at each step, it is not a straight slice through Q_1-Q_2 space but follows the combination of Q_1 and Q_2 giving minimum energy at each stage. We may regard the more qualitative curve in Fig. 2 in the same way.

In Fig. 3, we again show the central portion of the Q_1-Q_2 space, with several slices taken parallel to Q_2 to illustrate the instability region on the a_{1g}/FH surface. At each point of the curve along Q_2, there is an approximate parabola in the Q_1 direction representing the stability with respect to Q_1. The energy minimum with respect to Q_1 may shift as relaxation along Q_2 progresses. The higher states, such as b_{3u}, will certainly have a different equilibrium position along Q_1. Thus, the relaxation from higher states to the a_{1g} surface will in general reach the lower surface at a Q_1 value removed from the energy minimum because the nonradiative transition rate is highest near the closest approach. Furthermore, the Q_2 instability should be even steeper there by virtue of stronger repulsion between the curves upon closer approach. This is very similar to the earlier discussion by Toyozawa.[24] However, the present model does not require that arrival on the lower potential surface high above its minimum be a *necessary* condition for entering the Q_2 instability. LBS have shown that the *entire* Q_1 potential curve, including its minimum, is unstable along the Q_2 coordinate. The parabolic Q_1 potential curve for the on-

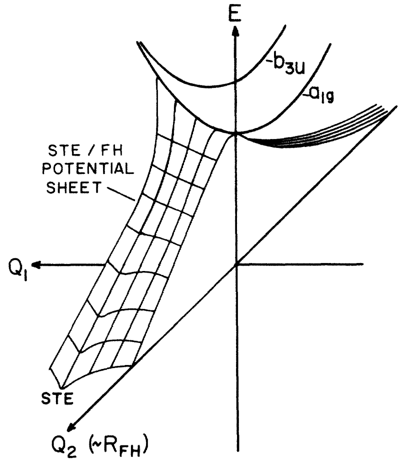

FIG. 3. Qualitative representation of the lowest STE potential surface in Q_1-Q_2 coordinate space, in the region from the central maximum ($Q_2=0$) to the STE $[(F\text{-}H)_{\text{NN}}]$ minima. Parabolic curves corresponding to slices of the a_{1g} and b_{3u} potential surfaces along Q_1 at $Q_2=0$ are shown to illustrate the probable path of nonradiative relaxation from the upper to the lower surface.

center STE with D_{2h} site symmetry is the ridge of a "saddle" in Q_1-Q_2 space.

B. *F*-center formation at low temperature

Figure 2 suggests that as a self-trapped exciton relaxes through higher levels such as those labeled by the electron orbitals b_{1u}, b_{2u}, and b_{3u}, it should remain near the configuration with D_{2h} symmetry (on center, V_K-like) and cross onto the a_{1g} potential surface near $R_{FH}=0$. (There are other possibilities for populating the a_{1g} surface, as suggested by Kabler[60] and Itoh and Saidoh.[61]) Since the a_{1g} surface is unstable at $R_{FH}=0$ and possesses about 1 eV excess energy at that point, an STE crossing to the a_{1g} surface near $R_{FH}=0$ will immediately experience an acceleration toward larger R_{FH}, given classically as the reciprocal of its mass times the gradient of the potential. If this event occurs at the surface, the accelerated halogen atom can retain most of its 1-eV kinetic energy as it escapes from the surface. This is observed.[47] Within the bulk of the crystal, the coherent motion of a single energetic *H* center will quickly be partitioned among a number of vibrational modes, but within roughly the same time scale, the *H* center can already have been projected (via a short replacement sequence) past the $(F\text{-}H)_{\text{NNN}}$ barrier to a position of relative stability at low temperature. Thus, we suggest that the energy for low-temperature *F*-center formation and separation is derived from stored energy of a higher electronic state, released and channeled into unidirectional motion by the adiabatic instability in a_{1g}.

This is similar to several of the excited-state mechanisms which have been proposed previously. An important conceptual difference is that here the instability propels the *H* center *toward* the configuration giving π luminescence, rather than away from it. The momentum of the halogen atom (*H* center) carries it rapidly through the luminescent STE state to an *F*-*H* pair state of larger, more stable, separation. Note that this process can account for correlation of *H*-center orientation with STE (or V_K-center) orientation.[46] The main thermal activation barriers are on the *lower* potential surface, rather than on the upper ones.

The proposed mechanism can also account for some aspects of the experiments showing that laser excitation from the lower STE level to higher levels results in enhanced *F*-center formation.[18,49,50,62] All such experiments have been performed only at low temperature and so are constrained to those specific crystals which exhibit *F*-center formation at low temperature. We may imagine the following sequence: Upon initial creation of STE's in highly excited states, relaxation leads quickly to population of the a_{1g}/FH potential surface near $R_{FH}=0$, followed by acceleration of halogen atoms toward and through the $(F\text{-}H)_{\text{NN}}$ (π-luminescent STE) configuration. Some of them (about 17% in KCl) successfully achieve stable *F*-*H* separation. A larger fraction fail to achieve stable *F*-*H* separation on the first attempt and therefore collect at the $(F\text{-}H)_{\text{NN}}$ (π-luminescent STE) potential minima awaiting decay to the ground electronic state. Since the lowest luminescent state is a spin triplet, the radiative lifetime can be quite long at low temperature, e.g., 5 msec in KCl. These self-trapped excitons can be placed back into the higher levels by a laser pulse. The entire process described above would then be repeated, with a fixed fraction achieving stable *F*-*H* separation and much of the remainder settling back into the π-luminescent STE state. Actually, a laser pulse of several nanoseconds duration can cycle a self-trapped exciton through its excited states many times. The accumulated defect yield enhancement from one laser pulse can thus be quite large, as observed.[18,49,50,62] In a real sense, the laser light may be simply pumping energy into a collection of cold equilibrated STE's, thereby giving the halogen atoms the energy they need to escape along the lower (a_{1g}/FH) potential surface. At higher temperature, they could move along the same surface in thermal equilibrium. The potential curves and associated dynamics represented in Fig. 2 provide a means of *channeling* the optical excitation energy into specific motion of separation of the *H* center and *F* center.

There is one important aspect of the laser reexcitation experiments which is not simply explained in this picture. This is the work of Tanimura and Itoh indicating that there is a state selectivity in the laser enhancement of *F*-center yield.[62] Of the three levels, b_{1u}, b_{2u}, and b_{3u}, the b_{2u} level was found to be the most effective in *F*-center yield. We cannot at present suggest a simple way of accommodating these data in the mechanism proposed above, which should, it seems, predict roughly equal enhancement in all three levels. Further theoretical and experimental examination of this issue is needed.

In summary, the calculations reported by LBS have provided strong evidence indicating that the self-trapped exciton in alkali halides exists as a nearest-neighbor *F*-*H* pair rather than a V_K+e^- center. This behavior is in close correspondence with the known structure of STE's in alkaline-earth fluorides, where both experiment and the calculations of Adair *et al.*[56] concur that the STE is a nearest-neighbor *F-H* pair. The existing data on excited-state EPR, luminescence lifetime and polarization, and absorption spectra appear to be consistent with the C_{2v} symmetry of the off-center STE. Certainly, detailed reexamination of the data with respect to the off-center STE should continue. We have shown how the essential identity of the luminescent STE state with a nearest-neighbor *F-H* pair resolves several questions associated with *F*-center generation at both low temperature and high temperature.

ACKNOWLEDGMENTS

We wish to thank M. N. Kabler for very helpful discussions and M. Adair for the use of results prior to publication.

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