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Vacancy-interstitial pair production via electron-hole recombination in halide crystals

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The nature of the electronic states through which band-to-band excitations or excitons evolve into *F*-*H* pairs is central to an understanding of defect production in halide crystals. The present paper develops a recent empirical model in which a self-trapped exciton becomes an *F*-*H* pair through a relaxation process that preserves the σ bond between the two halide ions on which the hole is localized. The model is shown to be consistent with relative energies of the initial and final states, and the potential surfaces which govern motion from one configuration to another have been investigated in terms of diabatic correlation rules. The defect state $F(1s)+H(\sigma_u)$ lies on a potential surface which correlates with higher levels of free and self-trapped excitons and crosses the surface corresponding to the lowest exciton state. Possible bottlenecks and associated metastable intermediate states are discussed with reference to observations from time-resolved spectroscopy. The initial ionic motion between self-trapped exciton and $F(1s)+H(\sigma_u)$ is not necessarily confined to a close-packed direction in alkali halides. The close *F*-*H* pairs observed in alkaline-earth fluorides are cited as examples of initial vacancy formation involving rotation as well as translation of an excited halide pair, and an analogous reaction path in alkali halides is suggested.

I. INTRODUCTION

The production of halide vacancies by ionizing radiation is a well-known phenomenon in simple halide crystals, although the precise nature of the production mechanism has proved difficult to determine. In alkali halides, the state created initially is the *F*-*H* pair, the *F* center being an electron trapped in a halide-ion vacancy and the *H* center the complementary interstitial atom.[1] A single ionization event, i.e., a single electron-hole (*e*-*h*) pair, is the direct precursor to *F*-*H* pair production. This fact was demonstrated by the experiments of Pooley and others,[2] which showed that ultraviolet photons absorbed in the fundamental edge of KI eventually produced intrinsic *F* centers, and also by the work of Keller and Patten,[3] which showed that *H* centers are created when conduction electrons recombine with self-trapped holes in KCl. The purpose of this paper is to summarize and correlate recent experimental data on *F*-*H* pair production in alkali and alkaline-earth halides, to develop a particular *e*-*h* recombination mechanism suggested several years ago,[4-6] and to show that this mechanism can give a reasonable account of the data provided the electronic states involved satisfy certain conditions.

Ionizing radiation also produces stable *F* centers in alkaline-earth fluorides at low temperatures,[7] although the efficiency is lower than in KCl or KBr. In the early stages of irradiation, where *F*-center production is relatively more efficient, few *H* centers are created, and impurities or other pre-existing defects may play a significant role. Ionizing radiation also produces a metastable configuration in the fluorites which may be described as an *F*-*H* pair at minimum separation. It has been observed both by EPR methods using recombination luminescence detection[8] and by transient optical-absorption spectroscopy.[9] This close *F*-*H* pair is created with high efficiency but exists for times no greater than milliseconds. In the present paper, we take the view that the primary processes responsible for efficient *F*-*H* pair production are similar in alkali and alkaline-earth halides and that the differences in pair separations are due primarily to differences in lattice structure. This premise reflects the key role played by the diatomic halogen molecular ion X_2^- in both structures.

The *H* center and the self-trapped hole (V_k center) both derive their basic structure from the X_2^-.[10] In alkali halides, the *H* center is an X_2^- centered on a halide-ion lattice site and oriented as a crowdion or split interstitial in a ⟨110⟩ halide row; in CaF_2, SrF_2, and BaF_2 the F_2^- axis lies along ⟨111⟩ and the two fluoride ions are not at equivalent sites. The self-trapped hole is essentially a covalent bond between a halide ion and a halogen atom, the two being equivalent and located near normal lattice sites. The bond axis is the nearest-like-neighbor direction, ⟨110⟩ in alkali halides and ⟨100⟩ in alkaline-earth halides.

F-*H* pair production competes with two other *e*-*h* recombination channels, heat generation and recombination luminescence. The states which originate recombination luminescence in alkali halides are triplet and singlet states of the self-trapped exciton (STE), a bound *e*-*h* pair in which the hole maintains its characteristic self-trapped morphology.[10] During *e*-*h* recombination the STE, or X_2^{2-}, also passes through states which provide entry to the *F-H* pair production channel. The first model connecting specific states of the STE with *F-H* production was suggested by Pooley.[11] It was argued that a nonradiative transition from the lowest luminescent state of the STE to the ground state of the crystal, thereby breaking the X_2^{2-} bond, would make available 4–7 eV of kinetic energy distributed between the two X^- ions and that this might be sufficient to initiate a displacement collision sequence resulting in a *F-H* pair. A solid-state analog to molecular predissociation, this idea has had considerable influence on the development of the field.[12] However, three serious difficulties have become evident, largely through results of observations in the area of time-resolved spectroscopy.

(i) The lifetime of the lowest STE state is not consistent with the rise time of defect production, whereas strict application of the original Pooley mechanism requires that they should be the same. The rise time of *F-H* pair production by pulsed high-energy electrons in KCl, KBr, and KI is nanoseconds or less, while the lifetime of the lowest STE state is microseconds or more.[1,13,14] Furthermore, experiments using two-photon absorption of laser light to create *e-h* pairs have given *F*-center rise times in the 10-psec range.[15]

(ii) Nonradiative transitions to the *ground* state with dissociation of the X_2^{2-} can only create F^+-H^- pairs initially, not *F-H* pairs. It has been known that after prolonged radiation at low temperatures F^+-H^- pairs are predominant; however, time-resolved measurements in KCl, KBr, and KI have shown that *F-H* pairs are the primary radiation product and that F^+-H^- pairs form by a secondary reaction.

(iii) The energy of the X_2^{2-} bond would be distributed between two recoiling halide ions, whereas only one would become an *F-H* pair. Previous theoretical estimates of the *F-H* pair energy in KCl indicated[16] that at least 5 eV, which is well over half the available energy, would have to be carried with *one* of the recoiling ions. Thus, only the tail of the energy distribution function for the two ions would be effective, and the *F-H* pair production efficiency would be low. On the contrary, several subsequent experiments have shown that in KCl and KBr quantum efficiencies greater than 0.1 are the rule. These experiments have included pulse radiolysis,[1,14] *F*-aggregate destruction,[17] and two-photon laser excitation.[15,18] For example, in KCl the number of *F-H* pairs formed per *e-h* pair excited is approximately 0.16 near 12 K,[15,18] 0.25–0.35 near 250 K,[17,18] and approaches 0.8 at 880 K.[18]

In response to these problems a different *F-H* pair-production mechanism was suggested and shown to be consistent, in a general sense, with experimental data available at the time.[4] A similar concept, although with significant differences in detail, was also suggested independently by Itoh and Saidoh[5] and later elaborated by Toyozawa.[6,19,20] The essential feature of this model is that *F-H* production originates in some higher STE state from which the X_2^- can move toward the initial crowdion configurations as *a unit*, without entering the strongly dissociative ground state. The sequence of ionic movements begins with the formation of a STE either directly from a free exciton or from trapping of an electron by a self-trapped hole. The X_2^- then moves as a crowdion, carrying along the hole and leaving the electron at the vacancy.

Regarding the nature of the electronic states through which these processes occur, two recent experimental results are of particular importance. First, rise-time data on *F*-center production by two-photon laser excitation[15] indicate that, beginning with a virgin KCl crystal, only about 10 psec are required for the laser pulse to create an *F* center *in its ground state*, a process which entails the dissipation of some 2–3 eV. The speed of this process implies an almost continuous emission of phonons, which in turn indicates that no metastable intermediate states, no bottlenecks due to low state densities, and no large energy barriers can be involved. The second experiment determined, for the first time, the energy of a state or narrow band of states capable of acting as precursors to *F-H* pairs.[21] An electron beam pulse was used to produce a number of STE's in their lowest triplet state, and a laser pulse was timed to excite these STE's into a higher group of states. The laser excitation was found to produce a large additional number of *F* centers, indicating a precursor among these higher states.

Most of the key experiments have been done with KCl, and we shall use this crystal as a paradigm with, however, frequent reference to other halides. Although our conclusions will be somewhat limited in detail, we expect the concepts involved to have broad validity among simple halide compounds. Our discussion will first review the energetics of the STE and obtain estimates for the energies of $F+H$ and F^++H^- states relative to the perfect lattice. We shall next correlate these states by means of schematic potential surfaces and explore the ways in which such surfaces can be related to experiment. A description of the nonradiative relaxation process based on nonadiabatic or diabatic correlations among states will be suggested and shown to provide a consistent model which is in general agreement with experiment. Finally, the more limited range of data available for the fluorites will be shown to be compatible with the model, i.e., with a similar set of potential surfaces. Details of the replacement sequence occurring after the interstitial is well formed will not be of concern here; this interesting and complex area has been emphasized in the alkali halide work of Itoh and has been reviewed by him.[22]

II. INITIAL AND FINAL STATES

A. Energy levels

For the metastable configurations of the STE and F-H pair, several of the principal energy levels can be located with some degree of reliability. Figure 1 shows levels obtained for KCl. It is convenient to label these configurations by a pair of coordinates ($\vec{r}$, $\vec{R}$), where $\vec{r}$ is the internuclear distance of the X_2^- and $\vec{R}$ represents the average separation of the vacancy and interstitial. $\vec{R}$ can be defined by $\vec{R}=\sum_i \vec{d}_i$, where $\vec{d}_i$ is the instantaneous displacement of each halide nucleus from its initial equilibrium position and the sum is over all nearby halides. Assuming for the moment that $\vec{r}$ and $\vec{R}$ are along the same nearest-like-neighbor direction, the three most important configurations correspond to perfect lattice $(a/\sqrt{2}, 0)$, the lowest triplet state of the STE $(r_0, 0)$, and a well-formed F-H pair (r_1, R_1). For KCl and several other crystals, $r_0 \approx r_1 \approx 0.6a/\sqrt{2}$. The arguments to follow should be independent of R_1 as long as R_1 is taken to be greater than a few lattice spacings.

At $(a/\sqrt{2}, 0)$ in Fig. 1 is the well-known valence exciton spectrum terminating in the conduction band (cb). The STE levels at $(r_0, 0)$ are taken from Ref. 14, where they were obtained by a combination of emission and absorption spectroscopy originating in the lowest triplet state, the measured trap depth for the self-trapped hole, empirical estimates of r_0, and calculations of the ground-state potential. The state designations are those of a homonuclear diatomic molecule, the orbitals of the hole and electron being indicated; the crystal field need not be taken into account for these purposes. The lowest states of the STE, ${}^{1,3}\Sigma_u^+(\sigma_u, \sigma_g)$, are designated A for convenience. Beginning at the edge near P in Fig. 1 there is a dense, Rydberg-like sequence of states comprising higher excitations of the electron and terminating at the self-trapped hole state ${}^2\Sigma_u^+(\sigma_u)$. Individual states in this sequence are not indicated, although certain spectral features have been given tentative assignments.[14] A higher state ${}^{1,3}\Sigma_g^+(\sigma_g, \sigma_g)$, which involves hole excitation and which is degenerate with cb, is also shown. There are several other states near P which result from hole excitations to π_u and π_g orbitals but which do not contribute significantly to the transient optical spectra in fluorides and chlorides.

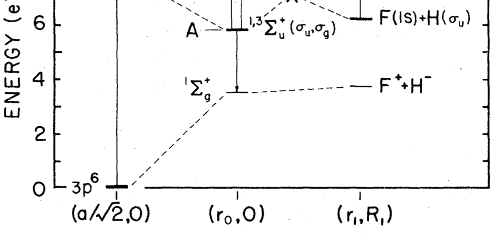

FIG. 1. Energy levels of the unrelaxed exciton, self-trapped exciton, and F-H pair in KCl are shown. Symbols, definition of coordinates, and deduction or estimation of the energy levels are described in the text.

Some of the observed optical transitions are indicated schematically in Fig. 1. The transition from A to a state ${}^3\Sigma_g^+(\sigma_u, \sigma_u)$ near P is the lowest-energy optical excitation of the STE that has been observed.[14] A recent search for transient infrared absorption in pulse irradiated NaCl conclusively demonstrated the absence of any allowed STE transitions throughout the range 0.1–1.5 eV.[23] Thus as presently understood, the STE is not expected to have odd parity states other than A in the energy range from the ground state ${}^1\Sigma_g^+$ up to at least 1 eV above A. In several crystals, including NaCl but not KCl, there exists a second, higher-energy luminescent transition known to originate from a ${}^1\Sigma_u^+(\sigma_u, \sigma_g)$ state near the energy designated P in Fig. 1. Experimental observations of laser induced intersystem crossing[21] have shown that in NaCl this state lies at, or just below, the triplet state (or states) populated by the lowest-energy optical transitions from ${}^3A$.

States of the well-separated F-H pair are shown on the right-hand side of Fig. 1. These states are specified by a hydrogenic orbital for the F-center electron and a molecular orbital for the H-center hole, and their energies have been determined on the basis of the arguments which follow. We recall that F centers can be created in KCl by excitation of STE's initially in the ${}^3A$ state with pulsed laser light (1.79 eV) absorbed in the low-energy edge of the STE spectrum.[21] Thus, a narrow band of STE levels near 7.5 eV must include an efficient precursor to F-H pair production, meaning that the lowest F-H pair state, $F(1s) + H(\sigma_u)$, must lie well below 7.5 eV. For

TABLE I. $F+H$ creation cycle for KCl.

Step	Energy (eV)	Source
1. Cl^- from lattice site to ∞	+4.8	Theory [a]
2. Remove e from Cl^-	+3.6	Expt
3. Return Cl^0 to form H center	+1.4	Theory [b]
4. Return e to cb	−0.6	Expt [c]
5. Vacancy $+e(\mathrm{cb}) \rightarrow F(1s)$	−1.9	Theory [d]
Total	7.3	

[a] P. D. Schulze and J. R. Hardy, Phys. Rev. B 6, 1580 (1972).

[b] G. J. Dienes, R. D. Hatcher, and R. Smoluchowski, Phys. Rev. 157, 692 (1967).

[c] T. Sasaki, Y. Iguchi, H. Sucawara, S. Sato, T. Nasu, A. Ejiri, S. Onari, K. Kojima, and T. Oya, J. Phys. Soc. Jpn. 30, 580 (1971).

[d] R. F. Wood and U. Opik, Phys. Rev. 179, 783 (1969).

convenience, this STE precursor state is designated P, and its approximate location is so marked in Fig. 1.

The energy of an F-H pair can be calculated[4,24] by means of a Born-Haber cycle involving the following steps: (i) remove a normal lattice ion to infinity; (ii) separate the ion into an atom and free electron; (iii) return the atom to an interstitial position to form an H center; (iv) place the electron at the bottom of the cb; (v) trap the electron to form an $F(1s)$ center. Experimental or theoretical values for all of these steps are available and are given for KCl in Table I. The resulting $F(1s)+H(\sigma_u)$ energy is 7.3 eV. By a similar procedure, an $F+H$ formation energy for NaCl of approximately 7.6 eV can be obtained. In Fig. 1, $F(1s)+H(\sigma_u)$ is placed at 6.2 eV. Although lower than the 7.3 eV obtained through the above cycle, this value is consistent with uncertainties occurring principally in steps (i), (iii), and (iv). For example, step (iii) fails to take account of covalent bonding of the H center to lattice ions, which is at least several tenths of a volt. Furthermore, in relation to the STE energies, the 6.2 eV energy allows about 1.0 eV to be dissipated in the lattice during the process $P \rightarrow F(1s)+H(\sigma_u)$. If the latter state were as low as 5 eV, nonradiative processes such as $A \rightarrow F(1s)+H(\sigma_u)$ and ${}^2\Sigma_u^+(\sigma_u) \rightarrow F^+ + H(\sigma_u)$ would become possible, at least in terms of final-state energy, but such processes have not been observed. In addition, Purdy and Murray[25] have observed in KCl a low-temperature thermoluminescence at 2.32 eV which can be interpreted as normal intrinsic luminescence, ${}^3A \rightarrow {}^1\Sigma_g^+$, initiated by thermally activated recombination $F(1s)+H(\sigma_u) \rightarrow {}^3A$. A similar process has been observed in KBr.[26] Our 6.2 eV placement of $F(1s)+H(\sigma_u)$ makes this process energetically feasible at least in principle. However, the probable existence of an energy barrier between ${}^3A$ and the well-separated F-H pair argues for a low probability of this radiative recombination event, apparently in agreement with the observed weakness of the luminescence.

Relative to $F(1s)+H(\sigma_u)$, the higher $F+H$ levels are known from spectroscopy. The $F^+ + H^-$ energy in Fig. 1 is obtained from a calculation of Frenkel-pair formation energies by Schulze and Hardy.[27] Since this calculation pertains to the relaxed lattice configuration for the F^+-H^- pair, the energy of $F^+ + H^-$ at (r_1, R_1), which is the lattice relaxation characteristic of $F(1s)+H(\sigma_u)$, must be somewhat higher than shown. One can argue on empirical grounds that the $F^+ + H^-$ potential surface intersects the $F(1s)+H(\sigma)$ surface near the latter's minima along R, as will be discussed in Sec. III B.

The problem of available kinetic energy in a bond-breaking model for F-H production is immediately apparent from Fig. 1. Excitations as low as 8 eV can produce F centers, yet if the halogens of the X_2^{-2} were to recoil in opposite directions, one of them would have to carry more than 6 eV in order to reach $F(1s)+H(\sigma_u)$.

B. Correlations

Since the three configurations of Fig.1 represent one system of ions and electrons, the states must correspond to continuous potential surfaces whose energies depend on the coordinate $(\vec{r}, \vec{R})$. There will be significant displacements of nearby ions in addition to those halides on which the hole and electron are localized, but this can be taken into account conceptually by assuming $(\vec{r}, \vec{R})$ to represent complex motions parallel to the principal potential valleys of a more general multidimensional configuration space. The energy levels specified in Fig. 1 describe only small regions of the infinite array of potential surfaces which can be regarded as characterizing the system. The overall forms of these surfaces are clearly the primary factor in determining the

F-H pair production channel. However, symmetry arguments are the only *a priori* means presently available by which their full extent from exciton to STE to $F+H$ can be characterized.

In order to establish correlations, we consider first the simplest example, that of a diatomic molecular system. For a one-electron system the number of elliptical, parabolic, and azimuthal nodal surfaces of the electron orbital are each conserved for all internuclear distances.[28] This provides unique correlations between the united-atom and separated-atoms limits. It has been argued[29,30] that these correlations can also represent the many-electron case when levels are not too closely spaced. These correlations are not valid in the usual adiabatic limit, where crossings of states having the same overall symmetry are avoided. However, in atomic collisions or chemical reactions the system can pass through a crossover region so rapidly that a substantial change in the wave function is improbable, and the state remains unaffected by the crossing. Theoretical descriptions of these so-called diabatic processes have been developed by Lichten and others and have been found experimentally to characterize many low-energy atomic processes including NaCl collisions and He-He$^+$ charge exchange. Although departures from two-center symmetry can obviously be significant in the present problem, the diabatic approximation should nevertheless be applicable as long as the process is rapid and the nodal structure of primary electron orbitals remains well defined. We shall not attempt to expand the theoretical foundation for diabatic states into the realm of solids, but shall instead deal with the *F-H* collision problem in terms of diatomic analogs and apply correlation rules developed for diatomic molecules by Barat and Lichten.[30] These rules, in their most useful form, specify that the difference between the quantum numbers n and l for a given orbital is the same in the united atom and separated atoms limits; that is, $n-l$ is conserved. Also the orbital angular momemtum m parallel to the two-center axis is conserved as the separation varies. After developing diabatic correlations for the *F-H* production problem, we shall consider the conditions under which this description should be valid.

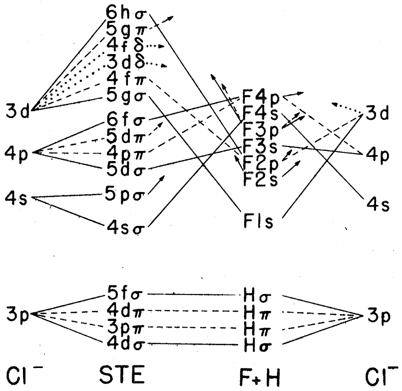

FIG. 2. Diabatic correlation of orbitals of the chloride ion, self-trapped excition, and *F-H* pair in KCl. Orbital notation and correlation rules are described in the text.

The simplest diatomic analog for *F-H* production is a lattice ion moving to an interstitial position. The F center and the Cl interstitial are the separated atoms, and since the F center is a vacancy (Madelung potential plus electron), perfect lattice corresponds to the united atom. By contrast, in atomic collision processes the united-atom limit is approached only at high projectile energies. The right-hand side of Fig. 2 illustrates schematically the resulting correlations for the valence orbitals and several of the lowest Rydberg orbitals. The interstitial has been allowed to relax into the H-center configuration, the only effect being a splitting of the $3p$ orbitals. For orbitals above Cl($4s$) and $F(2s)$ the energy sequence is somewhat conjectural, particularly regarding the relative locations of the d orbitals. Nevertheless, these uncertainties do not alter the crucial fact that the lowest F-center level $F(1s)$ does not correlate with $4s$ but crosses it. Furthermore, although $4p$, $3d$, $5s$, etc. may mix with each other near the perfect lattice configuration, the $F(1s)$ orbital correlates with $3d$ and thus should have substantial $3d$ character during the initial stage of *F-H* separation.

STE states can be fitted into the diabatic, diatomic model by constructing correlations as if the STE were a united-atom limit, and the states are so designated in Fig. 2. The resulting correlations are self-consistent and produce continuous potential surfaces throughout the configuration space $(\vec{r},\vec{R})$. Because the STE comprises two ions, Cl$^-$ on the left-hand side of Fig. 2 represents the separated atoms limit for the STE, whereas on the right-hand side Cl$^-$ is the united atom limit for the *F-H* pair. The order of STE levels above $4s$ is only schematic and is largely immaterial to the defect production process.

The orbital correlations of Fig. 2 can be adapted directly to the electronic states of Fig. 1. The excited states involve a hole in the highest $3p$-derived orbital and an electron in various higher orbitals; the one exception shown is the ${}^{1,3}\Sigma_g^+(\sigma_g,\sigma_g)$ state at $(r_0,0)$, where the hole is $4d\sigma$ and the electron $4s\sigma$. The state A is identified with a $4s\sigma_g$ electron. The $4s$ orbital of Cl$^-$ is associated with the exciton bands below the cb, and presumably $4p$ are above the cb edge.

The most important consequence of the diabatic approach is that $F(1s)+H(\sigma_u)$ lies on a potential surface which correlates with higher levels of the STE and the free exciton, and this surface crosses the surface corresponding to the lowest states of the free exciton and the STE. This is indicated schematically by the dashed lines crossing at × in Fig. 1. Identifying P now with the effective continuation of the $F(1s)+H(\sigma_u)$ potential surface at $(r_0, 0)$, relaxation of the exciton along this surface, $P \rightarrow F(1s)+H(\sigma_u)$, is an obvious possible final step in the F-H pair production mechanism. The correlations of Fig. 2 do not require that the precursor state P be derived entirely from the $\sigma 3d$ orbital, since $5p\sigma$, $5d\sigma$, $6f\sigma$, and $5g\sigma$ orbitals are near in energy and substantial crossing and mixing of these is likely. Thus P can, in effect, include several of the lowest STE states above A. This circumstance is consistent with the fact that depopulation of A by light in the low-energy edge of the transient absorption produces F centers.

III. INTERMEDIATE STATES

A. Lattice effects

While treating the F-H system as a heteronuclear diatomic molecule is useful in establishing correlations among states, the actual shapes of potential surfaces depend upon interactions with nearby lattice ions as well as interactions between F and H. Beginning with the STE at $(r_0, 0)$, the primary interactions are among the two halide ions of the Cl_2^- core and the two nearest alkali ions in the (001) plane. Core repulsion will tend to resist the initial movement of the Cl_2^- in the $\langle 110 \rangle$ direction. But once past the two alkalis, the Cl_2^- motion will be enhanced by these forces as well as by resonance of the σ_u hole with the next Cl^- ion in the row.

A recent calculation for KCl by Itoh, Stoneham, and Harker has indicated that the potential curves for STE states having the hole in a σ_u orbital rise initially when the Cl_2^- molecular ion is displaced along a $\langle 110 \rangle$ direction.[32] This calculation also suggests that the potential curve is flat for displacement of the Cl_2^{2-} when the hole is in a π orbital. However, convergence to an energy value was obtained only for one step in the displacement, and the calculation applies strictly to displacements constrained to a $\langle 110 \rangle$ direction. Itoh and Saidoh had earlier suggested that repulsion between the Cl_2^- core and the two nearest alkalis would be minimized if the hole occupes a π orbital.[5] This suggestion was based on experiments involving propagation of a newly created H center (dynamic interstitial) which were interpreted in terms of thermally activated diffusion of H centers having the hole in an excited (π_g) orbital. Alternative interpretations have also been proposed.[33,34] The state in question, which is not shown in Fig. 1, would be $\Pi_g(\pi_g, \sigma_g)$ and would lie several tenths of a volt below P. This state would correlate diabatically with an $F(4s)+H(\pi)$ state high in the continuum or adiabatically with the $F(1s)+H(\pi)$ state which lies from 1 to 2 eV above $F(1s)+H(\sigma_u)$. From the energy levels estimated in Fig. 1 as well as the calculation of final-state energies by Itoh *et al.*[32] it appears unlikely that $F(1s)+H(\pi)$ is lower in energy than P. However, a transition from $\Pi_g(\pi_g, \sigma_g)$ to $F(1s)+H(\sigma_u)$ may occur rapidly where these surfaces approach each other, near $(a/\sqrt{2}, 0)$ or near $(r_0, 0)$. Near $(a/\sqrt{2}, 0)$ where the splittings of σ and π hole states become comparable to the halogen spin-orbit coupling, σ and π cease to have meaning. Thus, the array of states near P which might effectively feed into the $F(1s)+H(\sigma_u)$ surface with negligible delay can be considered to include $\Pi_g(\pi_g, \sigma_g)$, but it would appear unlikely that this state can remain in the production channel as R becomes larger than a fraction of the nearest-neighbor lattice distance.

On the other hand, one might expect minimum potential barriers to occur for motions which deviate *initially* from the $\langle 110 \rangle$ axis. This has been shown to be the case for the fluorites, where motion is a combination of translation and rotation.[8,9] In alkali halides, thermally activated reorientation of self-trapped holes (ionized STE's) is a closely related process involving rotation. Figure 3 illustrates a pathway of F-H pair formation, analogous to V_k reorientation, which tends to circumvent the barrier presented by the two nearest alkali ions. Several stages in the process are represented, and alongside are shown conceptual drawings of the potential energy curves connecting the precursor level P with $F(1s)+H(\sigma_u)$. A conceptual energy curve for the V_K center is also shown. The Cl_2^- depicted in Fig. 3(a) by the shaded ions vibrates in the symmetric stretching mode, librates within the $(1\bar{1}0)$ and (001) planes, and vibrates as a unit within the cage of nearest neighbor ions. In the case of the V_K center, given sufficient thermal energy, the bonded halide pair can reach positions like that shown in (b), in which the hole is shared resonantly among three halide ions labeled 1, 2, and 3. Only a small part of any vibrational period is spent in such a configuration, and immediately the hole will return to a diatomic configuration. However, if the bond now involves ion 2 or 3 instead of ion 1, the V_K center will have undergone thermal reorientation. The measured activation energy in KCl is 0.54 eV, and reorientation is ob-

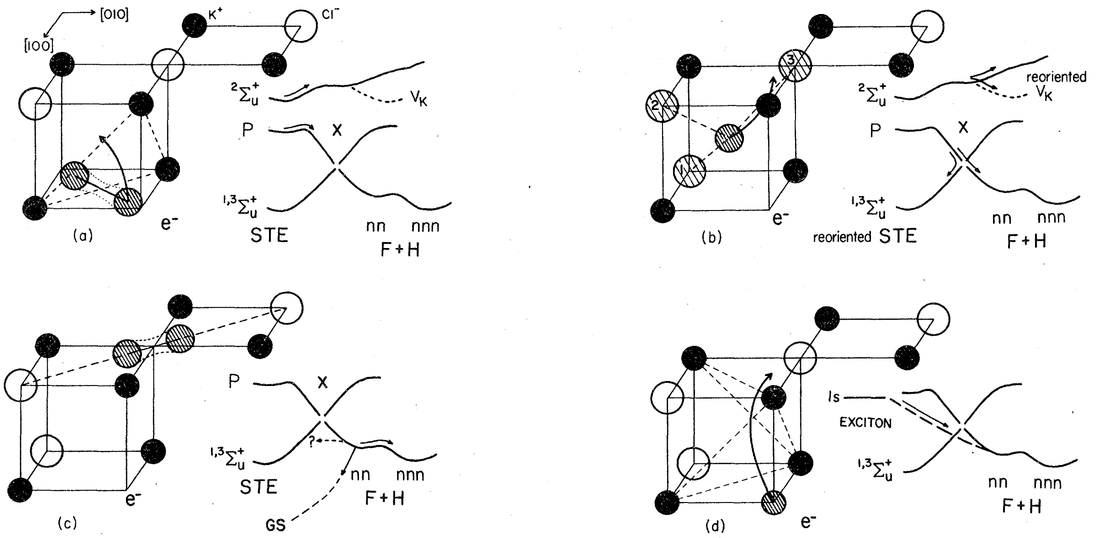

FIG. 3. (a) KCl lattice with a hole localized on a Cl_2^- ion pair (shaded). Schematic potential curves connecting self-trapped exciton and *F-H* pair are shown at the right. (b) A generalized rotation translation places an excited halide ion in roughly equal proximity to the three halide ions labeled 1, 2, 3, with the hole being shared reasonantly. Motion to one of the possible nearest-neighbor *F-H* pair configurations (c), crossing to the ground state (GS), or population of the STE state $^3\Sigma_u^+$ may occur. (d) Defect formation initiated from the lowest free exciton state, bypassing states of the self-trapped exciton.

served at temperatures above about 140 K.[35]

A significant part of the potential barrier against V_K reorientation is the electrostatic interaction of the Cl_2^- molecular ion with the crystal Madelung potential. Addition of an electron in the vicinity of the V_K center will partially screen the Madelung potential, thus reducing the barrier against achieving configuration (b). As the electron shifts toward the nascent vacancy, the Cl_2^- will polarize and the hole will shift toward the interstitial, further lowering the barrier. Thus, in the state *P*, the forces confining the Cl_2^- to the ⟨110⟩ direction may be negligible. There is evidently complete cancellation of these forces for the fluorites as discussed in Sec. IV. It is reasonable to suppose that the crossover point × would occur at roughly the configuration (b) in Fig. 3 where the Cl has just emerged from the vacancy.

When the halogen interstital is near the cube center as in (b), the three numbered halide ions become essentially equivalent and the developing *H*-center configuration may involve any one of them. In (c) we illustrate the nearest-neighbor *F-H* pair formed by bonding with ion 3. The *H* center axis is shown in a different direction from that of the original Cl_2^-. In the normal lattice, the *H* center is known to reorient with a low activation energy, 31 meV in KCl and 37 meV in KBr.[36] Thus any of the six ⟨110⟩ orientations for the *H* center in (c) would probably be accessible before the system cools completely. It is also conceivable that a ⟨111⟩ orientation might be more stable near the *F* center. We shall take $F+H_{nn}$ to designate all these configurations. Subsequent motion of the *H* center along a ⟨110⟩ close-packed row is aided by overlap of the σ hole with neighboring halide ions along the direction of motion, and by the effective crowding of the *H* center on one lattice site as opposed to the initial STE configuration. The present model does not conflict with any experiments on directionality of *H*-center motion. In fact, it is consistent with the absence of detectable polarization of *H* centers produced from aligned V_K centers observed by Hall, Hughes, and Pooley.[37]

There are three prinicpal regions in configuration space where barriers to populating the *F-H* pair and $^{1,3}\Sigma_u^+$ STE states can occur. These are at *P*, at ×, and near $F+H_{nn}$. (See Figs. 1 and 3.) In KCl, experiment shows little delay. However, the temperature dependence of the *F-H* production efficiency indicates competition from nonradiative decay to the ground state. The relative probabilities of leaving these regions by the three competing channels, $F+H$, $^{1,3}\Sigma_u^+$ STE, or ground state, can vary with temperature.

B. Transition through the crossover region

The two lowest excited potential surfaces, which include states *A* and $F(1s)+H(\sigma_u)$, both have the same symmetry, Σ^+ in the diatomic approximation and A_1 for the lattice. For sufficiently slow motion in the vicinity of ×, the crossing would be avoided, that is, the adiabatic and not the diabatic approximation would be valid.

A well-known approximate formula of Landau, Zener, and Stückelberg[31] gives, in principle, a relationship between the crossing probability, the velocity of the ions near ×, and the magnitude of the interaction between the two states at ×. Although this formula has been justified rigorously only on the basis of rather stringent assumptions, it has been found to be a fair empirical representation of a wide range of data on low-energy atomic collisions. The probability Q that the system remains in a diabatic state through a single crossing is

$$Q = \exp\left(-\frac{2\pi|V_{12}|^2}{\hbar v(d\Delta E/dR)}\right), \tag{1}$$

where $|V_{12}|$ is the interaction between the two states which cause the crossing to be avoided in the adiabatic limit, $d\Delta E/dR$ is the change with R of the energy separation of the surfaces at × assuming that they intersect, and $v = dR/dt$ is the velocity with which the system moves past ×.

On the basis of the data in Fig. 1 one can estimate some of the parameters in Eq. (1). A system which begins at P will have roughly 0.5 eV kinetic energy near ×, giving $v = 1.2\times10^5$ cm/sec if two Cl nuclei carry the momentum. Comparing Figs. 1 and 3 one might estimate $d\Delta E/dR \approx 10^8$ eV/cm, keeping in mind that the actual shapes of potential surfaces are unknown. The interaction V_{12} is the most difficult parameter to evaluate independently, since no detailed theory yet exists. Alternatively, one can choose a rough value of Q which represents the minimum for which the diabatic process might satisfy experiment, say $Q > 0.2$, and use Eq. (1) to calculate the corresponding maximum value of $|V_{12}|$. The result is $|V_{12}| \lesssim 0.04$ eV.

Although independent evaluation of V_{12} is beyond the scope of the present paper, some insight may be gained by means of the following rough approximation. Consider an F center and one halogen atom. The two diabatic states ψ_1 and ψ_2 which cross at × can be represented, to a first approximation, in terms of linear combination of atomic orbitals, $\psi_1 = a|F1s\rangle + b|3d\rangle$ and $\psi_2 = c|F4s\rangle - d|4s\rangle$, where the coefficients a, b, c, and d are functions of R, the F-center-halogen separation. The matrix element is $V_{12} = \langle\psi_1|V'|\psi_2\rangle$. The largest contribution to V' arises from the interpenetration of electron clouds on the two atoms at finite R.[29] With this in mind, we assume that V' is independent of electron coordinates over the region of space which provides the largest contribution of V_{12}; that is, V' depends only on R. Because of the assumed orthogonality of orbitals on a given center,

$$V_{12} = V'(bc\langle 3d|F4s\rangle - ad\langle F1s|4s\rangle). \tag{2}$$

V' is, at most, comparable to the splittings at either extreme, $R = 0$ or $R = \infty$, which implies $V' \lesssim 1$ eV. The overlap integrals in Eq. (2) are probably much smaller than unity because of differences in nodal structure and spatial extent of these orbitals, the one centered at the vacancy and the other at the interstitial. The result of this approach is then $V_{12} \ll 1$ eV. While the approximations underlying this estimate are obviously severe, the result is consistent with the limit $V_{12} \lesssim 0.04$ eV obtained above. Thus, present considerations do not rule out the possibility that a diabatic crossing at × contributes significantly to F-H pair production. The diabatic crossing in KI should be less likely than in KCl, since the product $v(d\Delta E/dR)$ is expected to be roughly four times smaller.

If the system does not pass diabatically through ×, it can become trapped briefly at the minimum of the upper (adiabatic) potential surface. With respect to coordinate r, this minimum will reflect the covalent bond between the halogen atom and one of the three numbered ions in Fig. 3(b). Curves representing schematically the intersections of potential surfaces with the plane $R = R_x$. where R_x is the F-H separation at ×, are illustrated in Fig. 4. Near the minimum the two excited-state curves are roughly parallel and separated by an energy $2|V_{12}|$. In rough approximation, the nonradiative transition rate between these two states should vary exponentially with the negative of this separation, and rates approaching 10^{11} per sec may not be unreasonable if the separation is

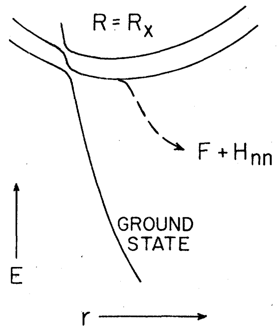

FIG. 4. Qualitative representation of the lowest three adiabatic potential curves as a function of r, the halide pair separation, when the translational coordinate R (defined in the text) corresponds to the crossing region × in Fig. 1. The dashed curve (out of plane) corresponds to R increasing toward the $F + H$ defect state.

small.

The presence of the ground-state potential surface near × may provide a more efficient path through the crossing region. It is likely that the ground state crosses the lowest excited state very near its minimum for all $R \gtrsim R_x$. That is, at $R = 0$ the ${}^{1,3}\Sigma_u^+$ state quenches thermally with a low activation energy, 12 meV for KCl,[42] indicating close proximity of the ground state. But for a given value of r, the ground-state energy will be greater as the interstitial is formed, i.e., as R increases. Therefore, for $R \geq R_x$ the ground-state surface will cross the lowest excited state even closer to its minimum, and thermal activation may not be required for nonradiative recombination. This general trend is evident also in the calculations mentioned previously.[32] Of course, as R increases beyond R_{nn} the nonradiative recombination rate will decrease because of the decreasing electronic overlap. Also, for $R > 0$ inversion symmetry is lost, and crossing with the ground state will be avoided in the adiabatic limit, as indicated in Fig. 4. But if the interaction is small, transitions from the upper to the middle surface may occur in a few vibrational periods. Since the system arrives at a saddle point, subsequent movement to $F + H_{nn}$ will be more probable than a transition to the ground-state surface.

Given these alternative channels, it would appear unlikely that delays of greater than 10 psec would be encountered in passing ×, at least for the chlorides. However, for crystals such as the iodides, delays might well be greater.

C. Close *F-H* pairs: Temperature dependence of defect production efficiency in KCl

Given thermal activation of the order of the H-center migration energy, the nearest-neighbor F-H pair in Fig. 3(c) may separate farther to become metastable for times of at least nanoseconds. We note that the 75 meV activation energy for primary defect formation in KCl between 140 and 250 K as found by Sonder,[17] and also an activation energy of roughly 75 meV between 195 and 880 K deduced from measurements with 46 psec resolution,[18] are comparable to the H-center migration energy, about 75–88 meV.[38,39] This close correspondence in KCl is probably fortuitous. In KBr, for example, the difference is greater: about 30 meV for F-H pair production[17,40] versus 90 meV for diffusion of H centers.[39] Sonder has suggested a model in which the relative probabilities of forward and backward jumps of an H center separating from an F center give a thermally activated defect formation yield with an effective barrier somewhat less than the activation energy for ordinary H center motion.[17] Although this was first envisioned as applying over several lattice spacings from the F center after the H center had been initially ejected some distance, we suggest that the critical step yielding the primary temperature dependence in KCl is thermal activation from $F + H_{nn}$ to $F + H_{nnn}$. The state $F + H_{nn}$ seems to be unobservable in KCl on the 46-psec time scale of the F center yield measurements in Ref. 18.

Suzuki and Hirai have made picosecond laser measurements of the rise of defect absorption at 694 nm in KI, inferring from analysis of the rise curve a transient component having approximately 15-psec decay time.[41] They suggest that this short-lived absorption may arise from incomplete F-H pairs, although cautioning that spectral measurements will be necessary for definite identification. Williams, Bradford, and Faust have observed roughly similar features in the rise of absorption at 532 nm in NaCl and NaBr, i.e., a leading edge of the rise curve requiring an additional component with decay time less than 20 psec for best fit.[18] If unstable close F-H pairs are indeed being observed in KI, they presumably recombine via the STE ground state or another nonradiative channel, since the measurements do not indicate a corresponding population of STE ${}^3\Sigma_u^+$ on a 10-psec time scale at low temperature.[41] The 10-psec absorption component which is seen may not be a perturbed F-like band, but rather the STE hole transition $\Sigma_u^+(\sigma_u, \sigma_g) \to \Pi_g(\pi_g, \sigma_g)$ or its analog in an intermediate-state ionic configuration such as (b) or (c) in Fig. 3.

At temperatures between 8 and 80 K the primary F-center yield in KCl as measured by pulse radiolysis,[42] is almost independent of temperature. The large electronic energy dissipated into vibrational modes during the relaxation from P to $F + H_{nn}$ can reasonably account for such a temperature-independent probability of defect formation at moderately low temperature. If at very low temperature the system were prevented from entering the channel connecting P to $F + H_{nn}$, then no defects would be formed. The small barrier found by Karasawa and Hirai[42] may have this origin.

We have previously noted experimental evidence for the occurrence of the reaction

$$F(1s) + H(\sigma_u) \to {}^3\Sigma_u^+(\sigma_u, \sigma_g) .$$

$F + H_{nn}$ may therefore be considered unstable with respect to recombination along the adiabatic potential surface leading to STE (${}^3\Sigma_u^+$). However, the observed efficiency of this reverse reaction is small, consistent with the energy barrier expected between $F(1s) + H(\sigma_u)$ and STE (${}^3\Sigma_u^+$). Recombination from the unstable configuration in Fig. 3 (b) is more likely to populate ${}^3\Sigma_u^+$. Note that the bond axis resulting from this recombination process may be different from the initial Cl_2^- bond axis in Fig. 3(a). That is, reorientation of the self-trapped exciton during relaxation from higher electronic states can occur by temporary formation of an unstable *F-H* pair precursor. Evidence that reorientation of the STE occurs during relaxation from higher states has been noted in previous work,[21,43] but the dissociative hole states were suggested as being responsible.

In Fig. 3(d) a path is indicated whereby excitation of a 1*s* exciton is followed immediately by motion of the halogen atom toward the *H*-center configuration, bypassing the STE configuration. This process may well occur to some degree, since experiments have shown that ultraviolet illumination in the 1*s* exciton band produces *F* centers but apparently does not populate STE states higher than $^3\Sigma_u^+(\sigma_u, \sigma_g)$.[44] Furthermore, if a STE enters a dissociative excited state and relaxes to approximately the free exciton configuration, this defect production channel could be operative. If the nearest-neighbor *F-H* pair so formed does not quickly achieve a larger separation, the system could pass to STE ($^3\Sigma_u^+$) or the ground state ($^1\Sigma_g^+$). Note that the atom again need not move directly between the nearest-neighbor alkali ions, but is effectively expelled along the path of least resistance.

D. Temperature dependence in KI

Application of the present defect production model to KI presents more difficulty than in the case of KCl because the available experimental data are not consistent with a simple activation model. The temperature dependence of the production efficiency fits an activation barrier very well, but the activation energy and attempt frequency thus obtained are in conflict with the measured *F*-center rise time regardless of which STE state the barrier is assumed to be encountered in.

It was shown by Pooley that the yield of stable *F* centers in KI increases with temperature in anticorrelation with the STE luminescence.[11] Karasawa and Hirai[13] have demonstrated that the *F*-center absorption measured 20 μsec after excitation of KI can be fit from 80 to 200 K by assuming the rate of *F*-center production to be governed by the same activation energy *and* attempt frequency as determined for nonradiative decay of the STE state $^3\Sigma_u^+$. That is, the normalized *F*-center production efficiency is given by $\eta_F = \nu_N(\nu_N + \nu_R)^{-1}$, where the nonradiative decay rate is $\nu_N = \nu_0 \exp(-E/kT)$ and the radiative decay time is $\tau_R = 1/\nu_R \approx 1.8\times10^{-6}$ sec. From the data on luminescence quenching and *F*-center production it was determined that $E = 0.132$ eV and that $\nu_0\tau_R = 3.2\times10^6$. From this we can estimate $\nu_0 \approx 2\times10^{12}$ sec^{-1}, to be compared with the vibrational frequency $\nu' = 1.2\times10^{12}$ sec^{-1} required to fit the STE luminescence bandwidth as a funtion of temperature in KI.[44] For comparison, the LO phonon frequency in KI is 4×10^{12} sec^{-1}.

The coincidence of $\nu_0\tau_R$ and E as fitting parameters for both STE luminescence quenching and *F*-center production and the reasonableness of the above numbers can be interpreted in terms of *F*-center formation originating in the luminescent state $^3\Sigma_u^+$. But this explanation conflicts with the fact that *F*-center formation in KI occurs in a time much shorter than $\tau = (\nu_N + \nu_R)^{-1}$, which describes the decay of $^3\Sigma_u^+$. For example, at 95 K the measured *F*-center formation time was less than 20 nsec,[13] but the time constant for escape over the 0.132 eV barrier is $\nu_N^{-1} \approx 5\times10^{-6}$ sec. This dilemma is not resolved by assuming that the decision between entry to the defect formation channel over the 0.132 eV barrier and relaxato the luminsecent state is made in a state higher than $^3\Sigma_u^+$. The same activation energy and attempt frequency apply to any higher state in which the simple thermal activation model is applied.

In general, an 0.132-eV barrier could be encountered at *A*, *P*, or $\times$ in Figs. 1 and 3 (as adapted for KI) or at a close *F-H* pair configuration as in Fig. 3. A barrier near *P* or $\times$ could account for thermally activated *F*-center production and a corresponding decrease in relaxation to the luminescent state *A* ($^3\Sigma_u^+$). However, such a barrier would not govern the decay of population in *A*. Furthermore the "initial" population in *A*, defined as the zero time ($t = 0$) intercept of the extrapolated STE luminescence decay curve, is predicted by such a model to vary with temperature in approximate anticorrelation with *F*-center production. In contrast, Karasawa and Hirai found that the $t = 0$ intercept of luminescence as defined above is independent of temperature,[45] and the temperature dependent decay time of state *A* is described very well by the 0.132-eV barrier.[45,46] If, on the other hand, the 0.132-eV barrier in KI is assumed to govern separation of close *F-H* pairs as was suggested for the 75-meV barrier in KCl, then the remarkable agreement in *both* E and $\nu_0\tau_R$ for luminescence quenching and *F*-center production must be fortuitous. This seems unlikely. The remaining possibility is that *A* ($^3\Sigma_u^+$) is the precursor state from which the system passes over an 0.132-eV barrier to $F + H_{nn}$. This would be the same precursor suggested by Pooley,[11] but the reaction path would lie entirely on the adiabatic potential surface containing *A* and $F + H$, rather than passing to the ground-state surface containing ${}^1\Sigma_g^+$ and $F^+ + H^-$. Such a process would be consistent with essentially all the data for KI except F-center formation time, which, as we have stressed, also poses a problem for activation barrier models in general. There do not at present appear to be any very satisfactory resolutions to this dilemma.

IV. ALKALINE-EARTH FLUORIDES

We have suggested in Fig. 3 that for alkali halides the initial motion is rotation out of the ⟨110⟩ direction, but reoriented intermediate states are evidently short lived and therefore difficult to identify. In fluorite crystals, on the other hand, a reoriented metastable intermediate state is readily observable because it originates the recombination luminescence. In CaF_2, SrF_2, and BaF_2, a triplet state of the e-h pair is observed in which the two fluoride ions forming the F_2^- core are not at equivalent sites and their internuclear axis is approximately ⟨111⟩, which is not a close-packed halide direction.[8] The F_2^{2-} morphology is thus similar to that of the H center in these crystals. Figure 5(a) is an illustration of the CaF_2 lattice, with fluoride ions occupying the corners of a cube and calcium ions forming a tetrahedron about each fluoride ion. The self-trapped hole (V_K center) in fluorite is known to have a ⟨100⟩ orientation as illustrated in Fig. 5(b).[7] This lattice configuration is apparently not stable in the presence of an electron, but moves to a ⟨111⟩-oriented F-H pair configuration such as that illustrated in Fig. 5(c).[8] The F-H separation at $F+H_{nn}$ is small enough to permit characterization also as a modified STE. Radiative e-h recombination occurs in times of 5–10 msec and restores the perfect lattice.[9] It is apparent from Fig. 5 that the simplest motion which can produce $F+H_{nn}$ is a rotation of the F_2^- and simultaneous translation through a distance of roughly $\frac{1}{2}a_0$ or less. The three $F+H_{nn}$ pair configurations consistent with experiment were described in Ref. 9. All have the same point symmetry, C_{1h}.

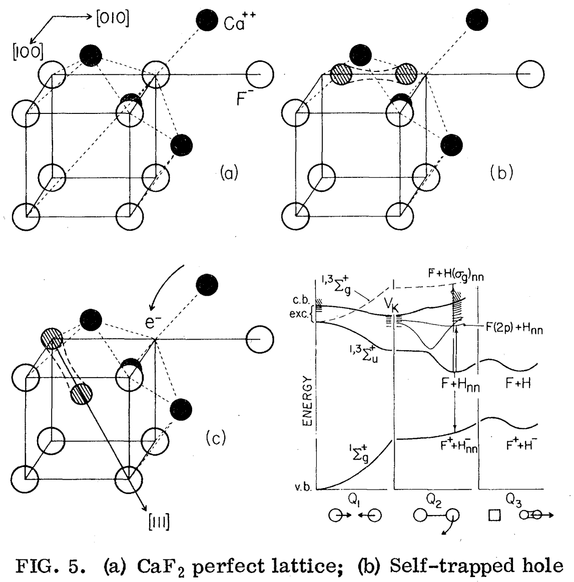

FIG. 5. (a) CaF_2 perfect lattice; (b) Self-trapped hole localized principally on the shaded ion pair; (c) Radiative e-h state having the configuration of a nearest-neighbor F-H pair. Shown at lower right are qualitative potential energy curves vs the fluoride ion pair stretching mode (Q_1), a generalized rotation (Q_2), and F-H pair separation (Q_3).

In the lower right of Fig. 5 is a conceptual drawing of energy curves for three relaxation modes of the exciton or F-H pair. Q_1 is the symmetric stretching mode appropriate to the F_2^- and the apparently unstable ⟨010⟩ self-trapped exciton. Q_2 is a generalized rotation and translation carrying the ⟨010⟩ STE to the $F+H_{nn}$ configuration. Arrows indicate observed optical absorption and emission transitions of the metastable defect pair.[9] Q_3 corresponds to separation of the F-H pair to distances where stability is no longer determined principally by the electron-hole recombination lifetime. In the fluorites, relaxation in Q_3 proceeds with small probability even though nearly every e-h pair reaches $F+H_{nn}$.

It is straightforward to construct a correlation diagram for fluorites similar to Fig. 2 for KCl. The valence shell is $2p$ rather than $3p$, and the lowest exciton orbitals are $3s$ and $3p$. However $F(1s)$ still correlates with $3d$ exciton orbitals, which lie relatively higher for F^- than for Cl^-. One expects for the fluorites an energy-level diagram approximately as shown in Fig. 5. The two states which cross in the approach to $F+H_{nn}$ have A_1 symmetry. None of the transitions thus far observed in absorption or emission appear to originate in the ⟨100⟩-oriented ${}^{1,3}\Sigma_u^+$ state, which gives strong indication that in the fluorites there is no significant minimum in this potential surface against relaxation via the generalized motion labeled Q_2.

Relative energies of levels in the STE and $F+H$ configurations can be estimated approximately for CaF_2 in a way analogous to that used for KCl. In comparison with Fig. 1, the first unrelaxed exciton in CaF_2 is at 11.2 eV. The relevant continuum state (${}^{1,3}\Sigma_u^+$) is the self-trapped hole, which does not differ significantly in KCl and CaF_2. It is thus reasonable to suppose that the A state might occur in the 7–9 eV range. On the other hand, a very rough estimate of $F(1s)+H(\sigma)$, using the cycle described in Sec. III A and based in part on a calculated energy for the fluoride-ion vacancy,[47] falls in the 6-8 eV range. Therefore, as indicated schematically in Fig. 5, the A state in the $\langle 100\rangle$ configuration may empty spontaneously into F-H_{nn}^{*}. It is possible to make one further numerical comparison for CaF_2: On the basis of the above argument one might expect the recombination luminescence to correspond roughly to the energy difference between $F(1s)+H(\sigma)$ and $F^{+}+H^{-}$. The Frenkel defect energy $F^{+}+H^{-}$ has been calculated to be about 2.6 eV,[47] and the emitted photon is around 4.4 eV. This gives an $F(1s)+H(\sigma)$ energy of about 7 eV, which is within the range of the above estimate. Differences in lattice relaxation and Coulomb attraction for nearest-neighbor and separated pairs have been neglected, but in this case the effects should tend to cancel.

Recent experiments on luminescence and transient absorption produced in MgF_2 by electron pulse excitation were discussed in terms of nearest-neighbor F-H pairs.[48] These were suggested to be analogous to the luminescent F-H pair state in fluorites, though MgF_2 differs in having the cassiterite structure. Further experiments, particularly excited-state EPR detected via the intrinsic luminescence, will be required to determine the specific configuration of the proposed nearest-neighbor F-H pair (or self-trapped exciton) in MgF_2. The time-resolved optical data[48] indicated that at temperatures below about 160 K an intrinsic state is populated with near unit efficiency by e-h pair generation, giving rise to the intrinsic luminescence and to an absorption band resembling the F band but shifted and broadened substantially. The perturbation is significantly more than the broadening of the F band found to be stable at low temperature by Sibley[49] and by Buckton and Pooley[50] and attributed by them to close pairs of F centers and interstitial centers. The recently observed transient state decays radiatively at low temperature, with the perturbed F-like absorption decreasing to less than 10^{-3} of its initial value in a few milliseconds or less. As the temperature approaches 160 K this strongly perturbed F like absorption and the intrinsic luminescence vanish together and there begins to appear a slightly perturbed F band with no associated recombination luminescence. This latter absorption component was suggested to arise from F-center–interstitial pairs which achieve larger separation (through thermally activated interstitial motion) than the radiatively unstable nearest-neighbor configuration. The production efficiency of these defect pairs at moderate separations is actually quite high, about one F center formed per five e-h pairs. However, most of them decay within a few milliseconds at room temperature, presumably by nonradiative recombination with the mobile interstitial center. Thus, in magnitude of *primary* defect yield, MgF_2 ranks as comparable with any of the alkali halides at room temperature in spite of its lack of focussing directions for replacement sequences. A similar conclusion was reached in regard to *stable* defect production in $NaMgF_3$ as studied by Seretlo, Martin, and Sonder.[51]

V. SUMMARY

It is likely that photochemical production of vacancy-interstitial pairs in these and many of the other simple halide crystals will ultimately be described within one unified model of electron-hole recombination and associated lattice relaxation. As a photochemical problem, rearrangement of a simple ionic crystal is at once simplified by the high symmetry of the lattice before rearrangement and yet is complicated by the large number of interacting ions and the typical low symmetry of the intermediate-state configurations. The latter difficulty precludes detailed calculations in all but a few rather restricted cases. Hence, in the present discussion we are at the stage of making correlations of initial and final states on general principles and of suggesting probable paths through the intermediate-state configurations. The correlation arguments given here should be quite generally applicable to halide crystals in which hole self-trapping and F-H pair production are observed, but a firmer theoretical basis for diabatic correlation rules in many-atom systems is required for further progress in this direction. Although an attempt has been made to obtain qualitative agreement with a wide range of experimental data, the arguments on intermediate configurations and pathways are still largely matters of speculation. However, by pointing out or reexamining reasonable alternatives to aspects of the qualitative models now being considered, it is hoped that the groundwork for more definitive conclusions can be laid.

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