

## Proposed Excitonic Mechanism of Color-Center Formation in Alkali Halides\*

HERBERT N. HERSH

*Zenith Radio Corporation, Chicago, Illinois*

(Received 14 March 1966)

A mechanism for vacancy generation in perfect crystals is proposed in which it is assumed that the progenitor for color-center formation is a dissociating  $X_2^{*-}$  (excited) molecule: if this molecule is initially created, or subsequently placed, in an excited vibronic, predissociative, or repulsive state, it may dissociate into a normal halide ion and an uncaged atomic halogen fragment  $X$  moving into an interstitial position and leaving behind a vacancy, according to the reaction  $X_2^{*-} \rightarrow X_{\text{int}} + \square + X^- + e$ . The relative probabilities of dissociation and radiation depend on the openness and other parameters of the lattice. Capture of the electron and motion of the interstitial halogen atom results in the formation of  $F$  centers and  $H$  and other  $V$  (halogen) centers, depending on the temperature. A general photochemical interpretation which can account for the formation and nature of the halogen centers as well as the  $F$  centers is presented. The key part of the suggested mechanism is the molecular dissociation of molecules which can (1) provide the momentum needed for the generation of the Schottky and Frenkel defects noted *after* irradiation, and (2) account for the  $X_2^{*-}$  luminescence (major process) noted *during* irradiation. On the basis of the proposed mechanism the uv colorability of KI has been predicted and made plausible, as well as such divergent color-center phenomena as the uv-induced formation of  $F$  and  $V$  centers in  $\text{KCl:H}$  and  $\text{KCl:I}$ , and the UV-induced generation of  $V_k$  centers in  $\text{KI:Tl}$  and strained KI.

### 1. INTRODUCTION

WHEN an alkali halide crystal is exposed to high-energy radiation, vacancies, interstitials, and color centers are formed. Many studies of the behavior of these radiation products have been made<sup>1</sup> as well as speculations on the mechanism of their production.<sup>2-5</sup> If the energetic photons that are responsible for the formation of color centers had momenta comparable to that of moving halide ions there would be no serious problem in understanding how vacant lattice sites are formed after irradiation: a knock-on collision would be energetically feasible and favorable from a momentum point-of-view. Since an x-ray photon is almost momentumless, the basic problem, therefore, is somehow to impart to the halide ion sufficient momentum or kinetic energy to displace it. Although none of the previously proposed mechanisms is generally accepted it has been assumed in all of them that *ionizing* radiation is necessary for color center production, and an excitonic (i.e. non-ionizing) mechanism has been precluded.<sup>1</sup>

In this paper it is proposed that the radiation which produces the color centers also generates, as a major transient, dihalide molecules, and that the molecular dissociation of these can plausibly account for the generation of vacancies and interstitials; also it is suggested that color centers can be produced by an excitonic mechanism. In addition a general photochemical interpretation of color-center phenomena is used which can account for the formation and nature

of the various  $V$  centers as well as  $F$  centers. A brief presentation of the over-all viewpoint is given in Sec. 2 before presenting a mechanism to explain the formation of vacancies and interstitials and the formation of various kinds of  $V$  centers.

### 2. CHEMICAL APPROACH TO COLOR CENTERS

#### a. Photochemical Processes in Alkali Halides

By comparing the optical spectra of  $V$  bands with the spectra of irradiated aqueous solution of alkali halides or the absorption spectra of halogen gases, it has been noted that the production of  $V$  centers parallels the photochemistry of halide ions in solution.<sup>6</sup> By assuming that an alkali halide crystal ( $AX$ ) represents a solid matrix in which photochemical reactions involving halide ions can occur, it is possible to compare solid state phenomena involving  $V$  centers with photochemical phenomena in solutions involving halogen molecules and ions. From a chemical viewpoint the photochemical products ( $X_2^-$ ,  $X_2$  and  $X_3^-$ ) of an irradiated glass or liquid solution containing a halide have similar optical absorptions to the  $V$  centers  $V_K$ ,  $V_1$ , and  $V_2$  or  $V_4$  in irradiated crystals. To complete the analogy it would be desirable to find a mechanism in the crystal which would allow moving interstitial atoms or excited ions to react with each other or with normal halide ions to form halogen molecules<sup>7</sup> of different kinds.

#### b. Photophysical Processes in Alkali Halides

In paramagnetic resonance and optical absorption experiments the  $V_K$  and  $H$  center exhibit some molec-

\* Presented at the International Symposium on Color Centers in Alkali Halides, Urbana, Illinois, 11, Oct. 1965.

<sup>1</sup> J. Schulman and W. Compton, *Color Centers in Solids* (The Macmillan Company, New York, 1962).

<sup>2</sup> F. Seitz, *Rev. Mod. Phys.* **18**, 384 (1964); **26**, 7 (1954).

<sup>3</sup> (a) J. H. O. Varley, *Nature* **174**, 886 (1954); *J. Nucl. Energy* **1**, 130 (1954). (b) C. C. Klick, *Phys. Rev.* **120**, 760 (1960); (c) V. H. Ritz, *ibid.* **133**, A1452 (1964).

<sup>4</sup> R. E. Howard, S. Vosko, and R. Smoluchowski, *Phys. Rev.* **122**, 1460 (1961).

<sup>5</sup> F. E. Williams, *Phys. Rev.* **126**, 70 (1962).

<sup>6</sup> H. N. Hersh, *Phys. Rev.* **105**, 1410 (1957).

<sup>7</sup> These different molecules are the core of the different numbered  $V$  centers, some of which may well be extrinsic, i.e. associated with impurities and/or imperfections. More specific knowledge of the actual local environment (whether it be foreign cations, positive-ion vacancies, dislocations or a perfect region of the crystal) is required for complete models of the  $V$  centers.

ular properties remarkably independent of the crystal, i.e. their epr<sup>8</sup> and optical absorption<sup>9</sup> properties allow them to be described, respectively, as a substitutional and an interstitial  $X_2^-$  molecule. Many experiments in molecular spectroscopy demonstrate conclusively that molecules dissociate as a direct result of absorption of light in the continuous portions of their absorption spectra or if prepared in a repulsive or *predissociative* state.<sup>10</sup> Energies of 1.5 to 4 eV, depending on the molecule, are commonly necessary for dissociation, and are given up as kinetic energy of atomic fragments in the case of the association of two atoms to form a molecule in a repulsive or predissociative state. One of the tests for predissociation is the absence of fluorescence. Thus it may be that excited  $X_2^-$  or other molecular halogen centers exhibit similar properties in crystals (to the extent that crystal geometry allows).<sup>11</sup>

These considerations, taken as a whole, provide an over-all viewpoint of color center phenomena which is the following: (1) by virtue of the high electron affinity of halogen atoms, halogen molecules of different kinds are somehow and somewhere formed inside the crystal from the interactions of moving halogen atoms with halide ions, and (2) the excited states of molecules formed during the irradiation can be involved in color-center phenomena (perhaps by dissociation).<sup>12</sup>

### c. Luminescence during Irradiation

Most previous workers in the field have had to infer what went on during the irradiation from the known properties of the crystals after the radiation was turned off.<sup>2-5</sup> (Thus it was not until 1958 that it was conclusively proved that interstitials are formed)<sup>13</sup> A closer look at the experiments reveals some additional facts which should be noted. The most suggestive of these is the following: while the radiation is on, the most pronounced phenomenon at low temperatures is the generation of a characteristic luminescence; after the radiation is turned off, only stable color centers, such as  $F$ ,  $H$  and  $V_2$ , are seen, and the characteristic luminescence centers have disappeared. (It is shown below that the luminescence centers are actually produced by the radiation rather than existing prior to it.)

<sup>8</sup> T. G. Castner and W. Känzig, *J. Phys. Chem. Solids* **3**, 178 (1957).

<sup>9</sup> H. N. Hersh, *J. Chem. Phys.* **31**, 909 (1959).

<sup>10</sup> A. G. Gaydon, *Dissociation Energies*, (Chapman and Hall, Ltd. London, 1953).

<sup>11</sup> Alkali halide molecules themselves dissociate into alkali and halogen atoms, e.g.  $\text{NaCl (vapor)} + h\nu (3.8 \text{ eV}) \rightarrow \text{Na} + \text{Cl}$ . The photodissociation of iodine molecules to produce I atoms occurs in sunlight (2 eV). In both cases no net reaction occurs because of recombination. In a solid, products would be possible only if the atoms moved far enough away in the interstices.

<sup>12</sup> Of course the chemical behavior is a manifestation of more fundamental electronic interactions. It should be possible to develop a self-consistent electronic approach on the basis of the chemical approach which will account more quantitatively for the interactions of the molecule with the lattice.

<sup>13</sup> W. Känzig and T. O. Woodruff, *J. Phys. Chem. Solids* **9**, 70 (1958).

### d. Relationship between Luminescence and Color-Center Formation

In many photochemical systems the onset of reaction is accompanied by a drop-off in luminescence.<sup>14</sup> As shown in Fig. 1, in pure KI<sup>15</sup> there is virtually no intrinsic color center formation below 90°K and the luminescence is quite high. At 120°K and higher temperatures, where the  $F$  and  $V_2$  rates are high, the luminescence is very low. This figure is typical of that for photochemical systems in which the luminescence center is known to be the first product of photolysis and also the source of the subsequent photochemical products.<sup>16</sup> In the present view the luminescence center is the generator of the vacancy and interstitial halogen atom. It is required that we identify the luminescence center more specifically to treat color center production photochemically, namely as a series of subsequent chemical reactions in a chemically active crystalline alkali halide matrix.

A further observation is that in KI both x rays and uv irradiation give rise to the same luminescence emis-

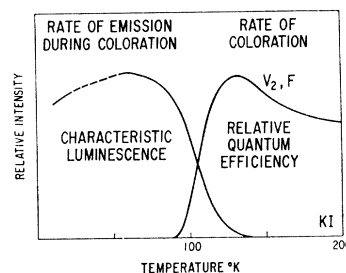


FIG. 1. Rates of emission and coloration under uv or x-ray excitation as a function of temperature. The sharp temperature dependences near 110°K indicate a correlation between the quenching of luminescence and the onset of coloration.

sion spectrum having the same temperature dependence as the coloration efficiency.<sup>15,17</sup> These facts suggest that color center formation and characteristic luminescence have the same origin.

### e. Identity of Luminescence Center

In working with plastically deformed KCl, KBr and KI, (which had been briefly x rayed and therefore contained  $E$  centers and  $X_2^-$  molecules)<sup>18-20</sup> it has been

<sup>14</sup> S. Glasstone, *Textbook of Physical Chemistry* (D. Van Nostrand, Inc., New York, 1946) 2nd ed., p. 1168.

<sup>15</sup> J. Konitzer and H. N. Hersh, *J. Phys. Chem. Solids* **27**, 771 (1966).

<sup>16</sup> For example,  $A + h\nu \rightarrow A^*$ ;  $A^* \rightarrow A + h\nu'$  or  $A^* + A \rightarrow A_2$ , where  $A^*$  is the first product of photolysis and  $A_2$  is the photochemical product, in this case a dimer.

<sup>17</sup> Hall, Pooley, Runciman, and Wedepohl, *Proc. Phys. Soc. (London)* **A84**, 719 (1964).

<sup>18</sup> H. N. Hersh and W. Hadley, *Phys. Rev. Letters* **10**, 437 (1963).

<sup>19</sup> H. N. Hersh, G. Ban, and M. Lesondak, *Bull. Am. Phys. Soc.* **9**, 88 (1964).

<sup>20</sup> H. N. Hersh and R. Jarka, *Bull. Am. Phys. Soc.*, **9**, 543 (1964).

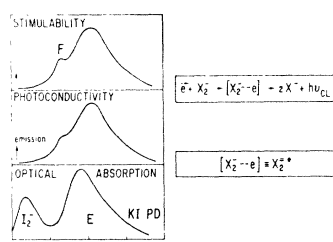
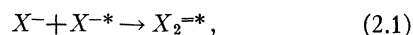


FIG. 2. Optical absorption, photoconductivity, and optical-stimulation spectra of plastically deformed KI x rayed at 78°K. The recombination of a moving electron and a  $V_K$  center yields an  $X_2^{=}$  molecule. The same luminescence is generated during uv or x-ray excitation at low temperatures.

observed in photoconductivity and infrared-stimulated luminescence studies, that when the moving electron recombines with the  $X_2^-$  center the recombination can be quantitatively correlated with the characteristic excitonic luminescence generated; this was therefore conceived to be due to a transitory molecule composed of an  $X_2^-$  center containing an additional bound electron. This is shown for KI in Fig. 2. In experiments using oriented  $X_2^-$  centers, Kabler,<sup>21</sup> and Murray and Keller<sup>22</sup> have given conclusive proof of this, and that the additional electron spends a long enough time on the  $X_2^-$  center that it is meaningful to talk of it as an  $X_2^{=}$  molecule. One characteristic of such a molecule must be that it is derived from two nonequivalent  $X^-$  ions (otherwise there would be no net binding); this is signified by the symbol  $X_2^{=}$ . It can be prepared in two ways: (1) excitation of the crystal by ionizing or ultraviolet rays in accordance with the equation of formation in Table I, and (2) recombination of a moving electron and immobile self-trapped hole in accordance with the equation given in Fig. 2, i.e.,



and



### 3. PROPOSED MECHANISM

Thus it can be said with certainty that during x-ray and uv excitation there exists in the crystal a high

TABLE I. Fates of  $X_2^{=*}$ .

0 Formation	$X^- + h\nu \rightarrow X^{=*}$ (primary exciton)
(by irradiation)	$X^{=*} + X^- \rightarrow X_2^{=*}$ (relaxed exciton)
1 Luminescence	$X_2^{=*} \rightarrow 2X^- + h\nu'_{CL}$ (characteristic luminescence)
2 Heat	$X_2^{=*} \rightarrow 2X^- + h\nu''$ (heat)
3 Ionization	$X_2^{=*} \rightarrow X_2^- + e$
4 Dissociation	$X_2^{=*} \rightarrow X_2^{=*} - X_{int} + X^- + \square + e$ (vacancy-interstitial generation)
5 Reactions to form	(a) $X_{int} + X^- \rightarrow X_{2int}^-$ ( $V$ center generation)
Halogen	(b) $X_{int} + X_{int} \rightarrow X_{2int}$
Molecules	$X_{2int} + X^- \rightarrow X_{3int}^-$

<sup>21</sup> M. N. Kabler, Phys. Rev. **136**, A1296 (1964).

<sup>22</sup> R. B. Murray and F. J. Keller, Phys. Rev. **137**, A942 (1965).

steady-state population of  $X_2^{=*}$  molecules, some of which radiatively decay to the ground state. What happens to those that do not? It is proposed that the molecules are all initially formed in an excited or predissociative state and that the successful dissociation of *some* of them generates vacancies and halogen interstitials, and that radiative transitions of undissociated molecules generate the characteristic emission, as will be described.

We list in Table I five possible fates to which the  $X_2^{=*}$  molecule is subject once it has been prepared: it can fluoresce, heat up the crystal, ionize, dissociate or react with other species, in all cases giving up a few or many phonons to the lattice. These are competing processes with characteristic different probabilities in different alkali halides.

Processes (1) and (2) can explain the characteristic luminescence at low temperature and at least part of its drop-off at higher temperatures. It may be seen that a drop-in exciton luminescence with temperature is not necessarily due only to the onset of phonon generation, but could be due to the onset of other nonradiative processes.

Process (3) is an ionization process, the reverse of (2.2). If we assume that the molecule can be ionized and the electron trapped, we may predict exactly what kind of color centers will form as a result of ultraviolet excitation at low temperatures: they will be a trapped electron center and a  $V_K$  center, produced without directly going through the conduction band and without vacancy production. This has recently been verified.<sup>23</sup>

Equation (4) of Table I indicates schematically how a dissociating molecule can yield an interstitial halogen atom fragment and a vacancy in a perfect crystal. The key idea is that the association of an excited  $X^-$  and a normal  $X^-$  produces an  $X_2^{=*}$  molecule in a state which is sufficiently excited or predissociative that within one or several vibrations of the newly formed molecule it dissociates. Thus, through the formation of a covalent bond between the excited and a normal halide ion, the potential energy imparted to the ion by an almost momentless photon can be converted into kinetic energy: sufficient momentum has been gained to move a massive ion. The only place in a perfect crystal that the halogen fragment can go to is an interstitial position. The ease or the probability of the dissociation depends on the openness of the lattice, which is tighter in KI than in KCl as noted by Rabin and Klick,<sup>24</sup> as well as on other parameters. In accordance with the viewpoint described in Sec. 2, which recognizes  $V$  centers as the key to the mechanism, all of the halogen centers, including  $H$ ,  $V_2$ , etc., are believed to arise after the primary photochemical act, from ordinary chemical interactions of the various halogen products listed above. It is implicit that room-temperature coloration

<sup>23</sup> H. N. Hersh, Bull. Am. Phys. Soc. **10**, 582 (1965).

<sup>24</sup> H. Rabin and C. C. Klick, Phys. Rev. **117**, 1005 (1960).

produces as transients all of the low-temperature halogen centers.

Processes listed under (5) are some typical molecular reactions which are envisioned to occur. Equation (5a) shows the formation of an  $H$  center; (5b) shows a bimolecular chemical reaction to create  $X_3^-$  centers (which we equate with  $V_2$  centers). This view conceives of two neighboring atoms as chemically reacting rather than two holes electrostatically repelling.

Figure 3 shows the various stages of the mechanism for the generation of vacancies and interstitials in a perfect crystal. Figure 3(a) shows the perfect crystal with all of the interstitial lattice sites empty. In Fig. 3(b), an ion has absorbed a quantum of energy sufficient to excite it. Fig. 3(c) shows its association with a normal halide ion to form an excited dihalide molecule,  $X_2^{=*}$ , which in one or several vibrations dissociates. Fig. 3(d) shows the atomic halogen fragment  $X$  going into an interstitial position with kinetic energy, leaving behind its electron at the newly created vacancy; but the nature of the dissociation process<sup>10</sup> the interstitial atom moves away with at least 1 eV of kinetic energy, assuring that it will move some distance away from the  $F$  center which has formed, as shown in Fig. 3(e). Figures 3(e) and 3(f) show the capture of the interstitial atom to form an  $H$  center.

In Fig. 4 generalized qualitative potential energy curves are presented which allow a reasonable represen-

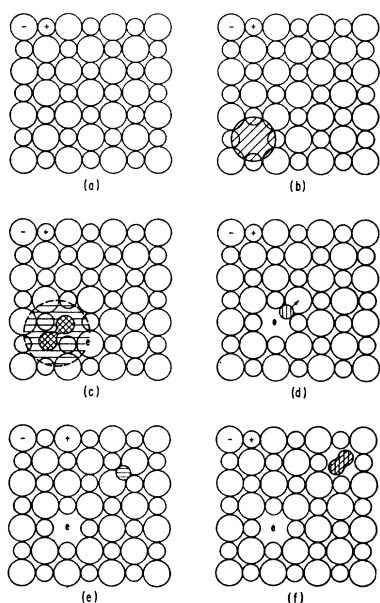


FIG. 3. Schematic representation of proposed mechanism at low temperatures, (a) perfect crystal, (b) excitation of  $X^-$  ( $X^- + h\nu \rightarrow X^{*-}$ ), (c) formation of  $X_2^{=*}$  ( $X^- + X^- \rightarrow X_2^{=*}$ ), (d) dissociation of  $X_2^{=*}$  with ejection of halogen fragment and formation of  $F$  center ( $X_2^{=*} \rightarrow X^- + e + X_{int}$ ), (e) motion of interstitial halogen atom, (f) formation of  $H$  center ( $X_{int} + X^- \rightarrow X_{2int}^-$ ). (The  $H$  center can also be represented as  $X_{4int}^{3-}$  which is the implication of the spin-resonance results: the hole is shared by 4 rather than 2 ions.)

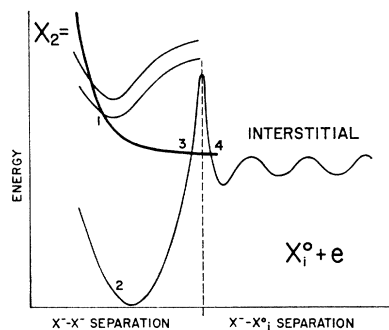


FIG. 4. Potential energy curve of  $X_2^{=*}$  depicting one radiative process (1 to 2 vertical) and two radiationless processes (which either generate phonons (3 to 2) or color centers (3 to 4)).

tation of the facts. The diagram depicts characteristic luminescence transitions as well as two nonradiative processes, one leading to heat generation and the other to color-center formation by dissociation. Vertical transitions between 1 to 2 represent characteristic luminescence (Eq. 1 of Table I), e.g., the 370- $m\mu$  emission in KI. A transition along the lower curve between 3 and 2 leads to heat generation (Eq. 2) and a transition from 3 to 4 represents a successful dissociation leading to color-center formation (Eq. 4).<sup>25</sup> The relative probabilities of dissociative and radiative processes are different in different alkali halides. Differences in the actual shapes, crossover points and minima of the curves, and sizes and masses of the halogens, can account for the differences in the rates and temperature dependences of coloration in different alkali halides and explain why KCl and KBr have such small temperature dependences, whereas a larger thermal activation is necessary in KI for the  $I_2^{=*}$  molecule to dissociate. Other things being equal, the repulsive curve must therefore cross nearer the minimum in KCl and KBr than in KI. In all cases it is assumed that it is energetically more favorable for an  $X$  atom to be ejected than an  $X^-$ , although the latter is conceivable. (In this latter case a knock-on collision or replacement substitution with a neighboring substitutional  $X^-$  would be the mechanism by which a halide ion would be displaced.) An  $X$  atom, being neutral and smaller, is also assumed to be able to move through the interstices more easily than an ion. To the extent that the luminescence will bleach the  $F$  centers, alpha centers are formed as Kabler has noted.<sup>21</sup> A recent study of KI, whose excitonic luminescence does not coincide with the  $F$  band, shows that at low temperatures both the  $\alpha$  and  $F$  center production are low.<sup>15</sup>

<sup>25</sup> A photodissociation of  $X_2^{=*}$  by near-uv or visible light is conceivable but not shown in the diagram. A simultaneous photodissociation with visible light could enhance the production of  $F$  centers by uv or x rays.

#### 4. DISCUSSION

Some divergent examples of color-center formation will be discussed which all seem explicable on the basis of the same mechanism and thereby lend support to it.

##### a. Ultraviolet Coloration of KI

It is implicit in the mechanism that alkali halides can be colored by so called non-ionizing rays of the order of 6 to 10 eV in energy. Ultraviolet colorability experiments on the formation of  $F$  centers in KI,<sup>17</sup> and on the formation of  $V_2$  centers<sup>15</sup> as well, are in accord with this.<sup>26</sup> The ultraviolet colorability experiment of Konitzer was predicated on this model. It is expected that strong excitation in the exciton bands of KCl and KBr would also result in color-center formation although Kingsley, using an unfiltered mercury arc at 15°K, found none in KBr.

##### b. KCl:I and KCl:H

The introduction of small amounts of  $I^-$  or  $H^-$  results in the formation of characteristic localized absorption bands on the long-wavelength side of the first exciton absorption band.<sup>3</sup> Ultraviolet or x irradiation results in the formation of  $F$  centers at the expense of the localized absorption centers. In the case of KCl:I the onset of  $F$  coloration above 200°K is accompanied by a decrease in the yield of the luminescence generated by the uv excitation.<sup>27</sup> According to the present model,  $ClI^{=*}$  and  $ClH^{=*}$  molecules are formed. Dissociation of these molecules ejects the atom with the lower electron affinity<sup>28</sup> (I and H atoms) into the interstitial volume leaving behind  $F$  centers. Under different temperature conditions the H and I atoms move through the interstices giving rise to characteristic stable centers. In the case of KCl:H,<sup>29</sup> these are  $H$  and  $H_2$ . In the case of KCl:I, Hattori and Nagata<sup>30</sup> report the formation of  $V$  centers which they believe to be  $I_2Cl^-$  molecules, on the basis of comparisons with solution spectra. (This would indicate that two mobile interstitial I atoms react to form an interstitial  $I_2$  molecule; this reacts with a substitutional  $Cl^-$ , perhaps at a special site, to form an  $I_2Cl^-_{int}$  center.)<sup>6</sup>

<sup>26</sup> It is believed that, in addition to the facts that uv coloration seems to be nonsaturating and to have the same temperature dependence of coloration as x-ray coloration, the presence of  $V_2$  centers is indicative of an intrinsic mechanism; if  $OH^-$  or  $H^-$  were present  $V_2$  centers would not form.

<sup>27</sup> L. S. Goldberg and H. Mahr, Bull. Am. Phys. Soc. **10**, 373 (1965).

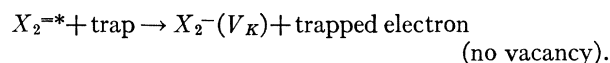
<sup>28</sup> In any heteronuclear molecule,  $XY$ , the electron charge cloud is displaced towards the more electronegative component, in this case Cl.

<sup>29</sup> C. Delbecq, B. Smaller, and P. H. Yuster, Phys. Rev. **104**, 599 (1956); **104**, 605 (1956).

<sup>30</sup> S. Hattori and N. Nagata, private communication.

##### c. KI:Tl and Plastically Deformed Pure KI

In both these cases ultraviolet irradiation at low temperatures in the region of the first exciton band gives rise to  $V_K$  centers and electron centers without going through the conduction band.<sup>23</sup> It is believed that the  $I_2^{=*}$  is ionized by the electron trap ( $Tl^+$  or lattice defect) by a tunneling process in accordance with process (3) of Table I which may be rewritten as follows:



If the trap is an  $F$  center,  $F$  centers and  $V_K$  centers should result (at the appropriate temperature).

#### 5. SUMMARY

The mechanism proposed above, while speculative, suggests new ways of looking at color-center formation. Whereas previous authors have proposed various kinds of ionization mechanisms, in this study an excitonic mechanism has been proposed. Color-center production is viewed as an induced predissociation of the same molecular species which gives rise to characteristic luminescence. The subsequent formation of various  $V$  centers (i.e., halogen centers) occurs in the dark and is governed by thermochemical considerations. The same vacancy-generating mechanism is applicable at higher temperatures and to the formation of  $V$  centers and is readily extendable to doped and imperfect crystals.

The key part of the suggested mechanism is the molecular dissociation of  $X_2^{=*}$  molecules which are temporarily present while the crystal is being irradiated with ultraviolet or x rays. This can provide the momentum needed for the generation of vacancies and interstitials noted after irradiation, and account for the characteristic luminescence which is the major process noted at low temperatures during irradiation.<sup>31</sup>

#### ACKNOWLEDGMENTS

The author is grateful for critical discussions and advice given by Dr. W. Hadley and Dr. G. Kaufman of this laboratory.

<sup>31</sup> A model of  $F$ -center production involving the radiationless decay of an exciton has very recently been proposed by Pooley [International Symposium on Color Centers in Alkali Halides, Urbana, Illinois, 1965 (unpublished)]. The mechanism (which deals only with  $F$ -center production) appears to be somewhat similar to the vacancy-generating mechanism proposed here, although differing in several details, in approach and in viewpoint. F. Pretzel has also reported on uv colorability of KI at 80°K.