

## Effects of X Irradiation at 78°K on Plastically Deformed KI

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Imperfections were deliberately introduced into good crystals of KI, giving rise to a structure sensitivity to radiation not heretofore observed. After x irradiation at 78°K, energy is stored in the form of  $I_2^-$  and  $E$  centers. The  $E$  centers are electron centers produced as the only complements of the  $I_2^-$  centers. Absorption of light in the  $E$  band releases free electrons which recombine with the  $I_2^-$  molecules, giving rise to characteristic emission. (The same emission occurs during x irradiation.) Light-sum measurements show that the characteristic emission during x irradiation is reduced by 11% as compared to annealed crystals, because some of the absorbed energy is stored as  $E + I_2^-$  centers, later to be released as characteristic luminescence. The imperfections introduced into the KI crystal by the plastic deformation act as electron (rather than hole) traps. Lattice defects in KCl and KBr behave similarly.

### 1. INTRODUCTION

STUDIES of imperfections in alkali halides have usually been concerned with color centers produced in almost perfect single crystals.<sup>1</sup> These studies using good single crystals have certain disadvantages in that the imperfection content is relatively low. The present paper describes the behavior of materials in which the imperfection content is deliberately increased. Such specimens exhibit phenomena which occur only accidentally and to a negligible extent in good crystals; the phenomena are therefore usually ignored although they are of importance to any understanding of imperfections in solids. The purpose of this paper is to present an over-all survey of the phenomena observed in highly imperfect crystals and thereby broaden the experimental basis upon which theories of imperfect crystals are based. Items of particular interest are:

(1) Do imperfections act like impurities? If so, like cationic or anionic ones?

(2)  $X_2^-$  centers do not occur in pure annealed alkali halides ( $A^+X^-$ ) in the initial stages of coloration except as transients. It has been shown that transient ( $X_2^- - e$ ) molecules are produced during x irradiation<sup>2</sup>; it might therefore be expected that, at 78°K, an imperfection could trap the more loosely bound electron from the ( $X_2^- - e$ ) molecule, resulting in the enhanced formation of  $X_2^-$  centers in pure but deformed alkali halides.

(3) The well-known effect of enhanced  $F$ -center yield in plastically deformed crystals is considerably diminished at 78°K. Are other phenomena occurring?

In this study which is confined to plastically deformed KI crystals, these questions are answered and a new kind of structure sensitivity is reported. In addition, further insights have been gained into phenomena such as recombination luminescence and optical stimulability in *doped* crystals.

<sup>1</sup> This topic is well surveyed in J. Schulman and D. Compton, *Color Centers in Solids* (The Macmillan Company, New York, 1962).

<sup>2</sup> M. Kabler, *Phys. Rev.* **136**, A1296 (1964); R. B. Murray and F. J. Keller, *ibid.* **137**, A942 (1965); H. N. Hersh, *ibid.* **148**, 928 (1966).

### 2. SUMMARY OF PREVIOUS RELEVANT WORK

A general survey of the effects of plastic deformation on color-center formation may be found in Ref. 1. The major observed feature in deformed alkali halides is an initially enhanced rate for formation of  $F$  centers at room temperature.<sup>3</sup> It is important to distinguish this type of structure sensitivity (first reported by Smekal and Przibram) from the structure sensitivity at low temperatures reported in the present paper which does *not* involve  $F$  centers.

In previous work with deformed crystals, almost no attention was paid to the kind of  $V$  centers formed simultaneously with the  $F$  centers (however, see Chang<sup>4</sup>), although it has always been implicitly assumed that enhanced  $V$ -center formation accompanies enhanced  $F$ -center formation.

Almost no work on plastically deformed crystals irradiated at low temperatures is available except for scattered brief reports on luminescence and energy-storage phenomena by Ueta, Panizza, and others in KCl and KBr; also Hirai and Scott have studied trapping phenomena in additively colored KCl.<sup>5</sup> Little detailed work has been reported on KI except in annealed crystals.

In annealed KI at 78°K the major centers produced by irradiation are  $F$  and  $V_2$ . The characteristic 370-m $\mu$  luminescence of annealed pure KI during irradiation at this temperature has been shown to be due to an  $I_2^-$ -\* center.<sup>2</sup> Under the conditions of irradiation used in this paper  $V_K$  (i.e.,  $I_2^-$ ) centers are not found in pure undeformed KI.<sup>6</sup>

<sup>3</sup> See K. Przibram [*Irradiation Colours and Luminescence* (Pergamon Press, Ltd., London, 1956)] and A. Smekal [*Handbuch der Physik*, edited by H. Geiger and Karl Scheel (Julius Springer-Verlag, Berlin, 1933), 2nd ed. Vol. 24/2] for earlier work on the influence of mechanical deformation on color-center formation.

<sup>4</sup> R. Chang, *Phys. Status Solidi* **5**, 81 (1964).

<sup>5</sup> E. Panizza, *Phys. Letters* **10**, 37 (1964); M. Hirai and A. B. Scott, *J. Chem. Phys.* **44**, 1752 (1966); N. H. Hersh and W. B. Hadley, *Phys. Rev. Letters* **10**, 437 (1963); H. N. Hersh and R. Jarka, *Bull. Am. Phys. Soc.* **9**, 543 (1964).

<sup>6</sup> J. Konitzer and H. N. Hersh, *J. Chem. Phys. Solids* **27**, 771 (1966).

### 3. EXPERIMENTAL PROCEDURES

KI crystals approximately 2-mm thick and 1-cm square were plastically deformed by pressing in a square die of the same dimensions at a pressure of 8000 kg/cm.<sup>2</sup> The pressed crystals were mounted in a cell and cooled to 78°K within 30 min of pressing. The following kinds of measurements were made using standard techniques and apparatus<sup>6</sup>: (1) optical absorption at 78°K before and after irradiation at 78°K and after warm-up to specified temperatures; (2) dichroic measurements after selective bleaching; (3) thermoluminescence measurements with selective filling of traps; (4) emission measurements of optically and thermally stimulated luminescence; (5) optical stimulation spectrum after x irradiation; and (6) photoconductivity.

The crystals were obtained from the Harshaw Chemical Company and are considerably purer than those used heretofore, as discussed in Ref. 6.

### 4. RESULTS

#### A. Effect of Temperature on Color-Center Formation by X Irradiation

There is a marked temperature dependence in coloration exhibited by KI whether it be annealed or pressed. At room temperature, as is well-known, pressed crystals exhibit an enhanced initial growth rate for *F* centers. In addition to this, it has been more recently observed that the enhanced *V* band, which is observed in parallel with the *F* band, has its absorption peak shifted towards longer wavelengths.

At liquid-nitrogen temperature, KI colors very slowly, and in addition, the rate of *F* and *V*<sub>2</sub> center production is not so much affected by plastic deformation as at 300°K (although it is slightly enhanced): rather the *nature* of the induced color centers is changed.<sup>7</sup> In this study, for clarity of presentation, only results of irradiation at 78°K are presented.

#### B. Color Centers Formed at 78°K

Figure 1 shows the optical-absorption spectrum of color centers produced in a pressed crystal by x raying at 78°K. Also shown is the absorption spectrum of color centers produced in an unpressed crystal by the same irradiation. The shaded area is interpreted to represent the optical absorption due to the plastic deformation. Thus, as compared to the unpressed crystal, it may be seen that additional kinds of color centers are produced in the crystal which has been plastically deformed. The 404-mμ band is due to *V*<sub>K</sub> centers and the broad infrared absorption band out to at least 2 μ is due, as will be shown later, to one or

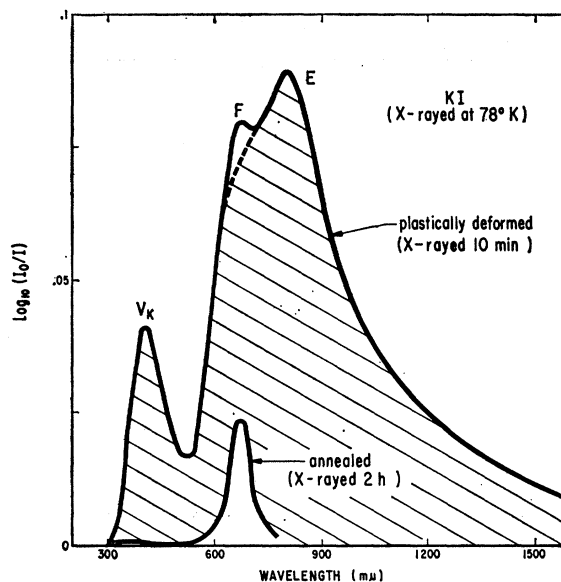


Fig. 1. Comparison of color centers produced in annealed and deformed crystal. The shaded area is a result of the plastic deformation and is due to *E* and *V*<sub>K</sub> centers.

several electron centers which are here designated for convenience as *E* centers. Neither *V*<sub>K</sub> nor *E* centers occur in pure annealed KI in the initial stages of coloration<sup>6</sup> although *V*<sub>K</sub> centers and other electron centers (believed to be thallium atoms) occur in KI:TI.<sup>8</sup> New *E* and *V*<sub>K</sub> centers cease to be generated at a relatively low total x-ray dosage while *F* centers continue to be formed (see Fig. 2).

The rapid saturation of the growth of *E* and *V*<sub>K</sub> centers is an expectation of, and in accordance with, the limited number of imperfections (which must somehow be responsible for the limited number of *E* and *V*<sub>K</sub> centers). Superposed on the relatively quick formation of *E* and *V*<sub>K</sub> centers, *F* and *V*<sub>2</sub> centers are produced by a slower process. The *F* centers are probably formed in the perfect regions of the specimen by the same vacancy-generating mechanism which operates in perfect crystals—although they seem to be produced at a slightly enhanced rate.

If a freshly pressed crystal is allowed to stand for a day at room temperature before irradiation, *E* and *V*<sub>K</sub> centers are not formed by subsequent x raying at 78°K although the slightly enhanced *F*-center formation rate remains. The reason for this must be that part of the strain has been removed by thermal annealing at 300°K. This has been proven by examination of the birefringence patterns of a pressed KI crystal: the crystal immediately after pressing is highly birefringent; upon standing for a day or more the birefringence disappears.

<sup>7</sup> H. N. Hersh and J. J. Markham, *J. Phys. Chem. Solids* **12**, 207 (1960).

<sup>8</sup> W. B. Hadley, S. Polick, R. G. Kaufman, and H. N. Hersh *J. Chem. Phys.* **45**, 2040 (1966).

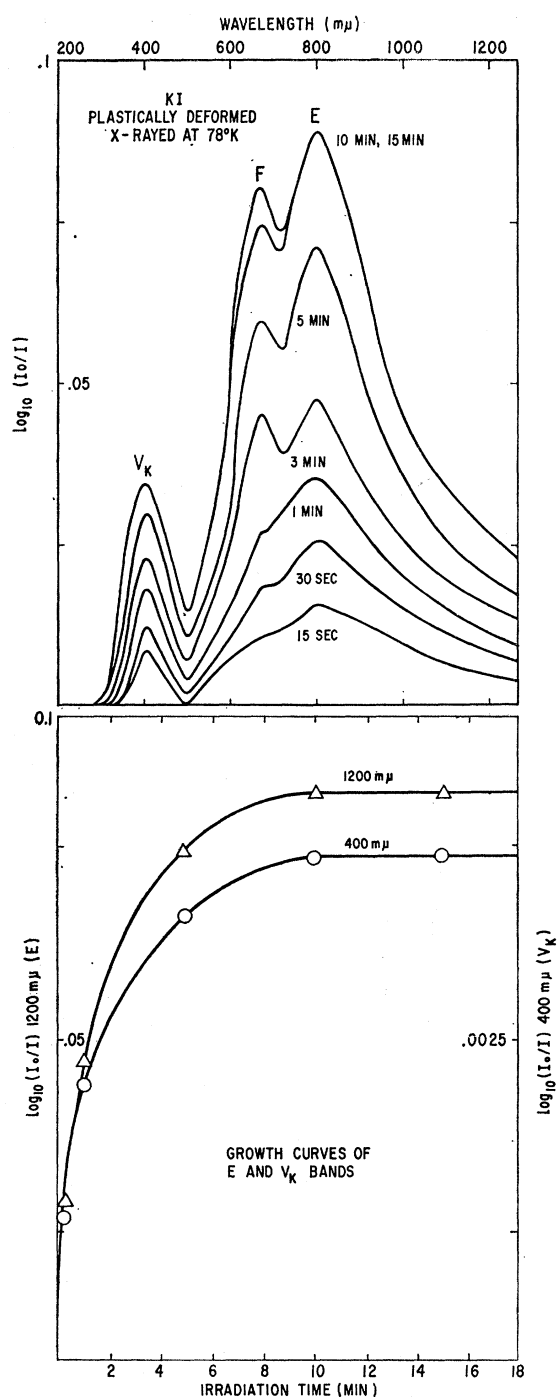


FIG. 2. (Upper) Absorption spectra after x raying for various times from 15 sec to 15 min. (Lower) Growth curves of  $E$  and  $V_K$  centers.

If a pressed crystal is heated to 300°C for a few minutes, it will recrystallize; such a sample also yields no  $E$  and  $V_K$  centers upon low-temperature x irradiation and no enhancement in  $F$ -center production rate. Thus, the large mosaic substructure of a pressed sample

remaining after the annealing is not responsible for the  $E$  and  $V_K$  centers; other, unknown, defects are.

### C. Interactions of Color Centers Produced at 78°K

If the x-rayed pressed crystal is irradiated with visible or infrared light, most of the induced optical absorption disappears, accompanied by a strong violet luminescence. On the other hand, warming the crystal to room temperature results in strong blue-violet thermal glow peaks and changing optical absorption. These effects do not occur in annealed KI, but are due to interactions of the characteristic centers of the pressed crystals, as detailed below.

#### 1. Optical Bleaching and Luminescence

If the crystal is irradiated with near-infrared light, it is quickly bleached and its optical absorption is reduced as shown in curves 2 and 3 of Fig. 3 (upper). The  $F$  band is not initially affected even if  $F$  light is used for the bleaching. The difference plot shown in Fig. 3 (middle) shows the optical absorption of only those centers which have been annihilated by the bleaching light: The bleached bands are the  $V_K$  and the  $E$ . Normalized band-shape plots show that the bleached bands have the same shape as the  $E$  and  $V_K$  bands of Fig. 1.

A detailed study of the bleaching behavior shows that  $E$  and  $V_K$  centers are quantitatively proportional to each other at each stage of the bleaching. Figure 3 (lower) shows that the  $E$ -center concentration approaches zero as the  $V_K$  centers completely disappear.

During the bleaching process, the crystal emits violet light which disappears completely when all the  $E$  and  $V_K$  centers are gone. Coupled with the growth experiments of Sec. 4.B [see Fig. 2 (lower)], these observations show conclusively that  $E$  and  $V_K$  centers (but not the  $F$  centers) grow and are bleached together. In analogy with recent studies by Kaufman and Hadley<sup>9</sup> they are probably produced and remain in pairs, the cognates being closer to each other than to other pairs.

#### 2. Optically Stimulated Luminescence and Photoconductivity

Those wavelengths that are most effective in stimulating the violet emission are shown in the stimulation spectrum of Fig. 4. The bleaching light simultaneously generates photoconductivity. Within experimental error the spectral photoconductivity curve<sup>10</sup> matches the stimulability curve of Fig. 4, indicating that free electrons are liberated by the bleaching radiation. Corrected curves would show band peaks at 800 and 670 mμ (where the  $E$  and  $F$  bands are located), in-

<sup>9</sup> R. G. Kaufman and W. B. Hadley, *J. Chem. Phys.* (to be published).

<sup>10</sup> The photoconductivity measurements were made by G. Ban of this laboratory.

dicating that both curves follow the optical-absorption curve of the  $E$  and  $F$  centers. Furthermore, as shown in the lower curve of Fig. 5, the stimulability follows the  $E$  and  $V_K$  concentrations, all of which pass through zero at the same time. The fact that all curves pass through

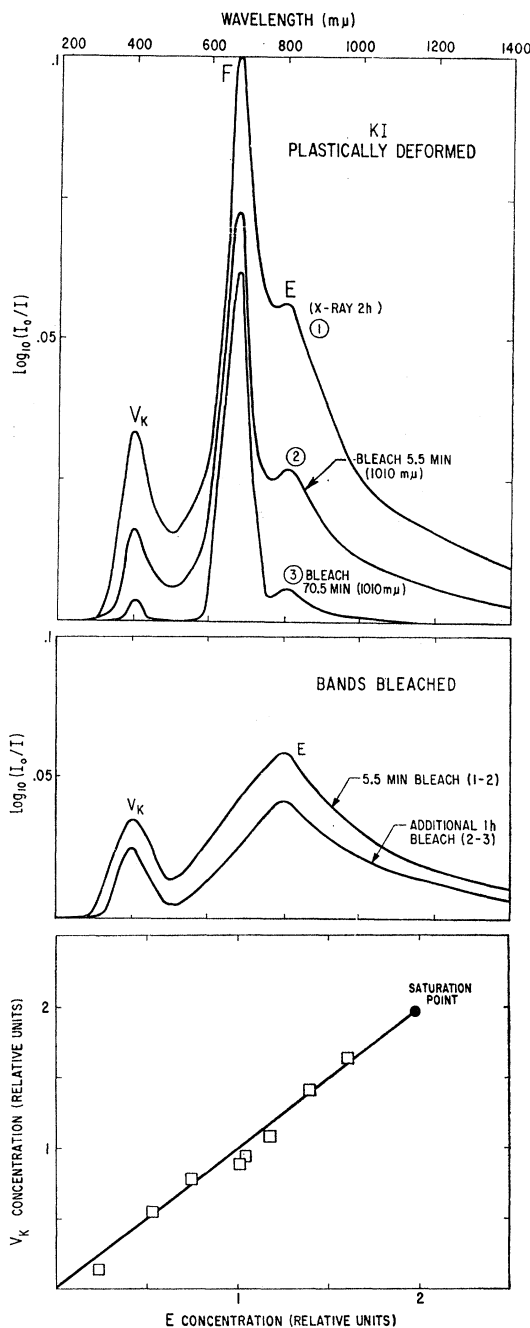


FIG. 3. (Upper) Optical absorption before and after irradiation using 1010- $m\mu$  light. (Middle) Absorption of only those centers bleached out (difference plot);  $F$  centers are not bleached. (Lower) Proportionality between  $E$ - and  $V_K$ -center concentrations (curve passes through zero at  $[E]=0$ ). In relative units the line passes through absolute zero in both coordinates.

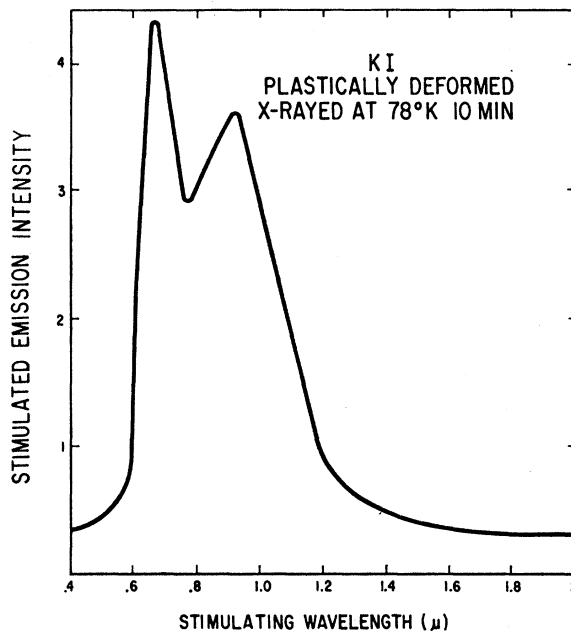


FIG. 4. Wavelengths most effective in stimulating 370- $m\mu$  emission (uncorrected for characteristics of light source, monochromator and photomultiplier). A similar spectral dependence exists for photoconductivity. Absolute corrections might place the peaks at 670 and 800  $m\mu$ .

zero suggests that there may be a one-to-one correspondence between the  $E$  and  $V_K$  centers. The upper curve of Fig. 5 shows the growth of the stimulability which also follows the growth curve of the  $E$  and  $V_K$  centers.

The effect of standing at room temperature for some time prior to x irradiation is to remove the stimulability and photoconductivity as well as the  $E$  and  $V_K$  centers.

These experiments, therefore, show the following: (1) After brief irradiation of a pressed crystal, energy is stored in the form of  $V_K$  and  $E$  centers; (2) the  $E$  centers are electron centers produced as complements of the  $V_K$  (hole) centers; (3) the absorption of light in the  $E$  band ionizes the  $E$  centers and generates free electrons in the conduction band; (4) the recombination of these moving electrons with trapped holes is responsible for the violet emission.

### 3. Emission Spectra

The emission spectrum of the optically stimulated violet light is shown in Fig. 6 (solid line). It consists of two bands at 302 and 370  $m\mu$ . These same emissions occur in unpressed KI at less than 100°K under the following conditions: (1) During x-ray excitation and (2) during uv excitation (where the light is absorbed in the first exciton band). Thus, the emission, which also occurs during uv and x-ray excitation of pressed KI, is characteristic of annealed pure KI. The emissions also occur as major components of the optically stimulated emission of KI:Tl. In KI:Tl the  $I_2^-$  band is somewhat masked by overlapping impurity bands. In pressed KI,

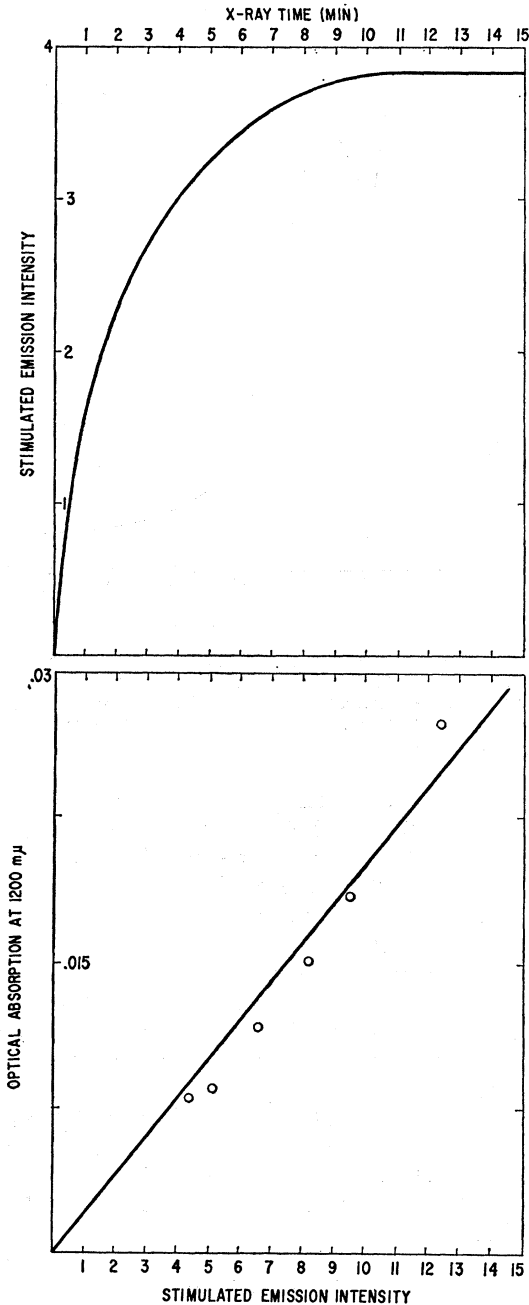


FIG. 5. (Upper) Growth of optical stimulability with x-ray dose. (Lower) Relationship of stimulability to concentration of  $E$  and  $V_K$  centers. Both curves pass through absolute zero at the origin of the graphs.

detailed study of the unobscured  $I_2^-$  absorption band shows that the emission is quantitatively and directly proportional to the concentration of  $I_2^-$  (i.e.,  $V_K$ ) centers (as well as the stimulating intensity); thus on the basis of the photoconductivity studies [Sec. 4. C. (2)] the major emission process demonstrably involves the following step:  $e + I_2^- \rightarrow (I_2^- \cdots e)$ . This is in accord with Kabler's inference<sup>2</sup> based on polarized emission

experiments that the emission center is an  $I_2^-$  center (although he assumed a tunneling mechanism for the recombination at 4.2°K); it also suggests that uv and x radiation produce a similar center which may also be described as an incipient  $I_2^-$  center containing an additional electron. It is inferred that the effect of the imperfections prepared by the plastic deformation is to trap this additional electron and allow the formation of  $I_2^-$ .

#### 4. Thermally Stimulated Luminescence and Changes in Absorption Spectra Upon Warming

We shall consider some properties of the x-rayed crystal as it is warmed to room temperature emitting light at several characteristic temperatures on the way. Figure 7 (upper) shows the glow curve. Figure 8 shows the absorption spectrum at 78°K after warming the crystal past each successive glow peak. The upper curve of Fig. 8 shows the absorption spectra after x-raying at 78°K and corresponds to the temperature region below 110°K on the glow curve. If the crystal is warmed to about 165°K a double glow burst having the emission characteristic shown in Fig. 6 (dashed curve) occurs in the temperature region between 120 and 160°K and the absorption changes. Within experimental error ( $\pm 10^\circ\text{C}$ ) the major double glow peak and the maximum rate of disappearance of the  $E$  and  $V_K$  seem to be correlated. Beyond 175°K the crystal has lost its optical stimulability. Below 175°K the optical stimulability (shown in Fig. 5 to be proportional to the  $E$  and  $V_K$  concentrations) appears to be proportional to the light sum of the major double glow peak.

It should be noted that the  $F$  centers play no essential role in the loss of  $E$  and  $V_K$  centers either optically or thermally. This is indicated by these facts: (1) No thermal  $F$  bleaching occurs during the warmup to 175°K; (2) the same glow-curve and optical absorption changes occur for crystals containing very few  $F$  centers (crystals x rayed for only a very short time); (3) the rates of formation and of optical bleaching of the  $F$

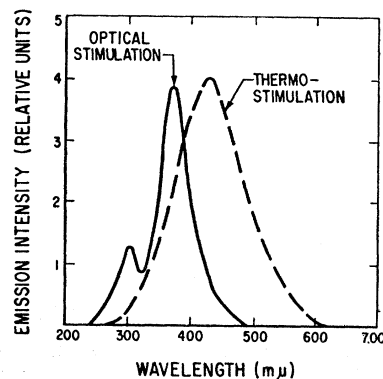


FIG. 6. Emission spectra (a) during optical irradiation and (b) during first thermoluminescent glow peak.

band are considerably different than that of the  $E$  and  $V_K$  bands (Sec. 4.A).

The glow curve shown in Fig. 7 (upper) containing five glow peaks, was obtained by x raying at 78°K and warming up. It is interesting to note that glow peaks numbered 3, 4, and 5 can also be obtained by the following procedure. The crystal is x rayed at room temperature and then irradiated with  $F$  light at 78°K (middle curve) and then warmed up. It is also noteworthy that the first and second glow peaks can be obtained by irradiating at 78°K with Hg-arc light instead (lower curve). These alternative procedures for obtaining glow curves separate the peaks into two groups: The first group contains the first and second peaks and the second group the other three higher-temperature peaks. It is very likely that the group-II glow peaks result from moving electrons released from thermally unstable electron traps; these electron traps were filled by the  $F$ -light irradiation. The origin of the group-I glow peaks is less certain. On the one hand,  $I_2^-$  molecules (i.e., holes) are known to move in this temperature region. On the other hand, it is not known whether electron or hole traps are filled using Hg-arc radiation: Such uv radiation could fill electron traps by  $L$ -band absorption (most likely) or fill hole traps by  $V$ -band absorption (however, there is no conclusive evidence that  $V$ -band irradiation ever generates free holes in any alkali halide). Thus, these interesting data (Fig. 8) await further interpretation.<sup>11</sup>

#### D. Partition of Absorbed Energy into Immediate and Delayed Luminescence

During x irradiation at 78°K, KI emits 302- and 370- $\mu$ m light with relatively high efficiency. The total amount of light emitted may be measured as a "light sum" in arbitrary units by the time-integrated photo-

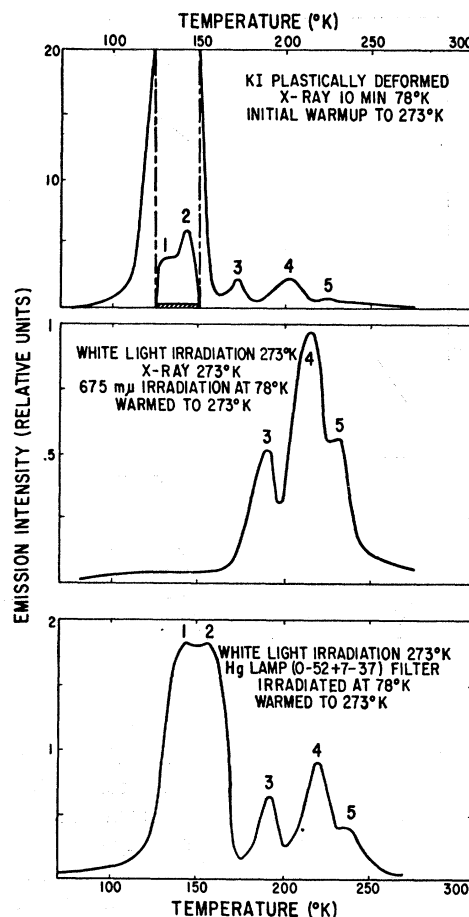


Fig. 7. (upper) Thermoluminescence of crystal x rayed at 78°K; (middle) Thermoluminescence induced by 675- $\mu$ m irradiation; and (lower) thermoluminescence induced by uv irradiation. (Apparent differences in glow-peak temperatures are experimental errors due to unreproducible thermal contact with thermocouple and to different warming rates.)

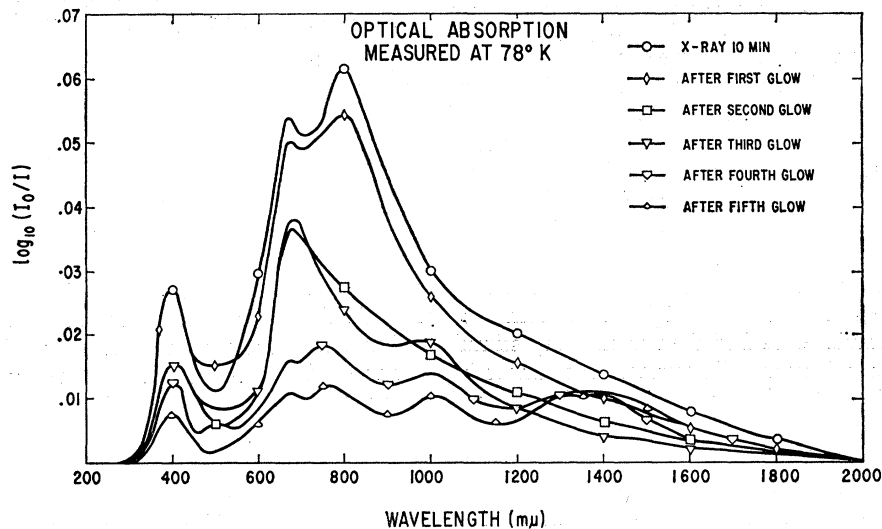


Fig. 8. Optical absorption after warming past each glow peak. (Many of the actual points were left off the figure for clarity.)

<sup>11</sup> A. A. Braner and M. Israeli, Phys. Rev. 132, 2501 (1963); B. Bosacchi, R. Fieschi, and P. Scaramelli, *ibid.* 138, A1760 (1965).

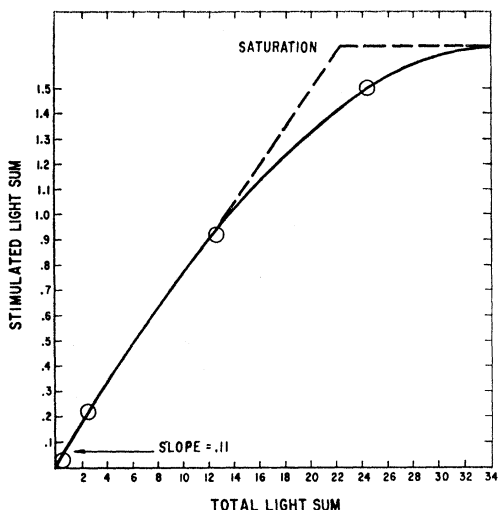


FIG. 9. Curve indicating the fate of the absorbed x-ray energy. The initial slope indicates that 11% of the energy of the absorbed x rays is stored rather than immediately released as characteristic luminescence. Data taken at greater total light-sums show that the stimulated light-sum saturates at the level indicated by the dashed line.

multiplier current. After the x radiation is turned off, the light emission ceases. Subsequent optical stimulation with  $E$  light, as noted above, generates further light of the same emission characteristic until exhaustion of all the  $E$  and  $V_K$  centers. It is interesting to compare the light sum of this optically stimulated luminescence with that of the (immediate) x-ray stimulated luminescence, for this is a measure of how the absorbed energy is partitioned. (Such a comparison is most meaningful before the crystal has become saturated with  $E$  and  $V_K$  centers because, thereafter, the optically stimulated light sum becomes constant and the x-ray stimulated light sum can be increased without limit. During this early stage, almost no  $F$  centers are produced, and it has been shown that  $F$  centers play no significant role in the light sums.) Figure 9 is a plot of the optically stimulated light sum versus the total light sum (i.e., x ray + optically stimulated) for several doses of x rays. The slope of the curve at any point is the fraction of absorbed energy showing up radiatively as stored energy. At high doses (where saturation begins to set in) the curve deviates from the initial straight line and quickly becomes horizontal as the limit of  $E$  and  $V_K$  growth sets in. The figure shows that at the onset of irradiation 11% of the total light sum comes from optically stimulated rather than from x-ray stimulated luminescence. This may be compared to almost 0% for annealed KI and 50% for KI:Ti.<sup>12</sup> The optically stimulated light sum is a measure of the stored energy and is obtained at the expense of the x-ray stimulated im-

mediate luminescence. The energy initially absorbed in deformed KI from the x-ray beam is thus conserved and partitioned into two large fractions which ultimately yield the same total light sum.

## 5. GENERAL CONCLUSIONS

A consideration of the above data leads to the following general conclusions in addition to those specific ones described above:

- (1) When KI is plastically deformed, it develops color centers not found in annealed KI.
- (2) These centers, the  $E$  and  $V_K$ , give rise to the phenomena of infrared stimulability, recombination luminescence, thermoluminescence, bleaching effects, etc. described above.
- (3) The trapping of electrons at imperfections gives rise to the  $E$  centers which thereby stabilize the intrinsic hole center ( $V_K$  center). Although it appears to behave as a distinct center, the  $E$  center may be a number of closely similar electron centers having overlapping optical absorptions in the same region of the spectrum.
- (4) The formation of  $E$  and  $V_K$  centers results from the filling of already-present imperfections rather than from a vacancy-generation process such as is responsible for  $F$  and  $V_2$  centers.
- (5) The  $E$  centers are produced and destroyed with the  $V_K$  centers and both behave as if they effectively form a separate subsystem from the  $F$  and  $V_2$  centers normally produced at 78°K in annealed KI.
- (6) Optical ionization of the  $E$  center generates a free electron (rather than a tunnelling electron) which recombines with the trapped hole.
- (7) The emission resulting from this recombination is intrinsic to pure KI, being due to  $I_2^{-*}$  luminescence centers.
- (8) KI is "soft," i.e., the active imperfections anneal out at room temperature in less than one day, and no  $E$  and  $V_K$  centers can thereafter be produced.

## 6. DISCUSSION

The above conclusions may be used to point out some general features of alkali halides which seem noteworthy:

- (1) Plastically deformed KCl and KBr have also been observed to exhibit much the same properties as KI. The phenomena described here are thus general and seem to be due to the same kind of mechanically induced imperfection. It remains to be determined whether this lattice imperfection is associated with residual impurities or is a pure crystal imperfection.
- (2) Plastically deformed crystals of KI (and other alkali halides) exhibit two kinds of energy storage after x irradiation, both of which are enhanced by plastic deformation: the conventional kind, resulting in  $F$  and  $V$  centers, involving vacancy-generation

<sup>12</sup> R. G. Kaufman and W. B. Hadley, J. Chem. Phys. 44, 1311 (1966).

processes<sup>2</sup> and most pronounced at room temperatures, and a new kind yielding  $E$  and  $V_K$  centers, most evident at low temperatures, which does not involve vacancy generation but which is due to the trapping of electrons at already-present imperfections.

(3) Plastically deformed but undoped crystals behave somewhat similarly to some doped crystals which have not been deformed. It is illuminating, for example to note the similarities between a thallium-activated alkali halide, e.g., KI:Tl<sup>+</sup>, and an imperfection-activated one. If we designate the latter as KI: $E^+$  (where  $E^+$  is the active imperfection which is associated with the modified properties of the pressed KI) we can write down some reactions and compare the behavior of the KI:Tl<sup>+</sup> and KI: $E^+$  (see Table I). The left-hand side of each "equation" represents the process *during* irradiation or stimulation, the right-hand side the results of the treatment. Table I depicts why pressed KI and unpressed KI:Tl both exhibit  $V_K$  centers, optically stimulated emission and photoconductivity and the same 302- and 370-m $\mu$  emission bands, viz. they are both KI with electron traps. The nature of the electron trap is different in the two cases; in the pressed KI,  $E$  centers are formed; in KI:Tl, Tl<sup>0</sup> centers are formed. Both of these electron centers release free electrons when optically excited in their absorption bands and give rise to 302- and 370-m $\mu$  emission when the electron recombines with the  $V_K$  center.

In the light of this, one may understand the interesting results of Teegarden and Weeks.<sup>13</sup> These authors uv-irradiated nominally unpressed KI at 78°K and observed weak energy storage which is identical with that studied here, although detailed studies could not then be made. In detailed studies with pressed and

<sup>13</sup> K. Teegarden and R. Weeks, J. Phys. Chem. Solids **10**, 211 (1959).

TABLE I. Similarities between KI:Tl<sup>+</sup> and plastically deformed KI (KI: $E^+$ ).<sup>a</sup>

	KI:Tl <sup>+</sup>	KI: $E^+$
X irradiation <sup>b</sup>	Tl <sup>+</sup> + $e$ $\rightarrow$ Tl <sup>0</sup> 2I <sup>-</sup> + $h$ $\rightarrow$ I <sub>2</sub> <sup>-</sup>	$E^+$ + $e$ $\rightarrow$ $E^0$ 2I <sup>-</sup> + $h$ $\rightarrow$ I <sub>2</sub> <sup>-</sup>
Optical stimulation:	Tl <sup>0</sup> + $h\nu$ $\xrightarrow{IR}$ Tl <sup>+</sup> + $e$ $e$ +I <sub>2</sub> <sup>-</sup> $\rightarrow$ $h\nu_{CL}$ +2I <sup>-</sup>	$E^0$ + $h\nu$ $\xrightarrow{IR}$ $E^+$ + $e$ $e$ +I <sub>2</sub> <sup>-</sup> $\rightarrow$ $h\nu_{CL}$ +2I <sup>-</sup>
Thermal stimulation:	I <sub>2</sub> <sup>-</sup> +heat $\rightarrow$ $h$ +2I <sup>-</sup> $h$ +Tl <sup>0</sup> $\rightarrow$ Tl <sup>+</sup> + $h\nu_{Tl}$	I <sub>2</sub> <sup>-</sup> +heat $\rightarrow$ $h$ +2I <sup>-</sup> $h$ + $E^0$ $\rightarrow$ $E^+$ + $h\nu_E$

<sup>a</sup>  $e$  and  $h$  stand for the free electron and hole and  $h\nu_{CL}$  is the characteristic 302- and 370-m $\mu$  recombinant luminescence.

<sup>b</sup> Alternatively these processes could occur via the relaxed exciton, (I<sub>2</sub><sup>-</sup>... $e$ ), rather than free electrons and holes, viz. (I<sub>2</sub><sup>-</sup>... $e$ )+Tl<sup>+</sup>  $\rightarrow$  Tl<sup>0</sup>+I<sub>2</sub><sup>-</sup> and (I<sub>2</sub><sup>-</sup>... $e$ )+ $E^+$   $\rightarrow$   $E^0$ +I<sub>2</sub><sup>-</sup>.

impure crystals using uv, we have observed identical but much stronger effects. It is therefore concluded that Teegarden and Weeks produced  $E$  (or impurity) and  $V_K$  centers (as well as  $F$  centers), probably arising from impure or imperfect crystals, and that the stimulability they observed at 0.8  $\mu$  is due predominantly to  $E$  (or impurity) centers rather than  $F^0$ .

In conclusion, in the above studies, imperfections were deliberately introduced into good crystals. The imperfections appear to act like cationic impurities and to give rise to intrinsic recombination processes and to a kind of structure sensitivity at low temperatures not heretofore observed. It is hoped that the further study of imperfection-activated alkali halides will yield new information on the kind of imperfection formed and on the coloration process in general.

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