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Room-Temperature Deformation Luminescence in Alkali Halides*

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Emission of light by crystals mechanically deformed at room temperature after γ irradiation at 35°C has been studied. Spectra of several alkali halides were measured, and the intensity of the luminescence investigated in relation to γ dose, strain, and strain rate. The deformation luminescence (DL) intensity becomes nearly constant beyond a certain value of plastic strain, and varies as a fractional power of the strain rate. Coloration, bleaching, annealing, and other studies show that the DL is related to F and M centers but also depends upon the presence of another, unidentified center.

INTRODUCTION

Light emission by irradiated alkali halides undergoing deformation or other mechanical working has been investigated by several workers in the past.[1] Trinks[2] studied this triboluminescence, as it was called, in NaCl and KCl and later Metz *et al.*[3] investigated it in LiF, KBr, and NaCl. In the present work, the dependence of this luminescence (here called deformation-induced luminescence and abbreviated DL) on γ dose, strain, and strain rate has been studied over a greater range of these variables than has hitherto been used. In addition, spectra of the DL of several alkali halides have been measured, and an attempt has been made to relate the DL to processes involving specific color centers.

EXPERIMENTAL

Single crystals of nominally pure alkali halides from the Harshaw Chemical Company, the Isomet Corporation, and the Optovac Corporation as well as two crystals of KCl grown at this laboratory were used in this study. Ingots from these sources are abbreviated H, I, O, and R, respectively. Samples for each experiment were always cleaved from a single ingot, and were used in their "as received" condition; that is, they were not pretreated in any way. All deformations were carried out in compression along the long dimension of the samples. A table-model Instron, the crosshead speed of which could be set in steps from 0.005 to 10 cm/min, was used for all deformations except those in which spectral data were sought. For the spectral runs, samples were compressed at 0.07 cm/min in an apparatus consisting of a heavy aluminum crosspiece driven through double lead screws. The samples, normally $2\times4\times12$ mm, could be positioned reproducibly at the same spot on the load cell by means of a guide and push rod so that corresponding faces of the samples were presented to the detecting equipment for each run. The detector was an EMI 9558AQ multiplier phototube (MPT), cooled to dry-ice temperature. For general DL runs (those not involving spectral data), the detector was maintained 8 cm from the specimen and was equipped with an appropriate combination of interference and glass filters to ensure less than 0.1% transmission at wavelengths other than the intended ones. For DL spectra, the specimens were held 7 cm from the entrance slit of a Bausch and Lomb 500-mm monochromator which could scan the range from 200 to 750 nm.[4] The monochromator was normally used at a spectral slitwidth of 5 nm (3-mm slits), but widths of 8 nm (5-mm slits) were used for very weak luminescence. The relative spectral response of the analyzing system was measured above 290 nm by the usual method of comparison to a black-body radiator. Any second-order grating response was removed with a 1-mm Pyrex filter which could be inserted in the light path.

The output of the MPT was linearly amplified by an electrometer, then fed through an active low-pass filter of variable time constant and recorded on the Y axis of an X-Y recorder. This system was linear over the entire range of MPT currents experienced. For general DL runs, the X axis of the recorder was run in its "time" mode, but for spectral runs, it was fed from a wavelength pickoff on the monochromator. Precision of the recorded wavelengths was better than ±1 nm over the entire range of measurement. Ultraviolet-excited luminescence of each ingot was measured using a 60-W deuterium lamp in conjunction with a Bausch & Lomb quartz-fluorite illuminator lens. Exciting wavelengths down to 205 nm were used, and the resulting luminescence was analyzed with the monochromator and detector already described. The gamma source was a 3.3×10^6 R/h ^{60}Co unit. The source temperature was approximately 35°C for the samples used, and was controlled to ±1°C. Samples to be irradiated were wrapped in aluminum foil, coded, and placed on a brass stand which could be reproducibly positioned in the source. Upon removal from the source, they were left in their wrappings for at least one hour to allow the afterglow to decay to a value well below that expected from the DL. Samples were opened, and all measurements made in darkness. Response due to any spurious room light was negligible in comparison to the MPT dark current.

For most of the alkali halides, it was necessary to

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* Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corporation.

[1] For a review of the general subject of triboluminescence, see K. Przibram, *Irradiation Colours and Luminescence* (English transl.: Pergamon Press, Ltd., London, 1956).

[2] J. Trinks, Sitzber. Akad. Wiss. Wien, IIa, **147**, 217 (1938).

[3] F. I. Metz *et al.*, J. Phys. Chem. **61**, 86 (1957).

[4] 1 nm (nanometer) = 1 mμ.

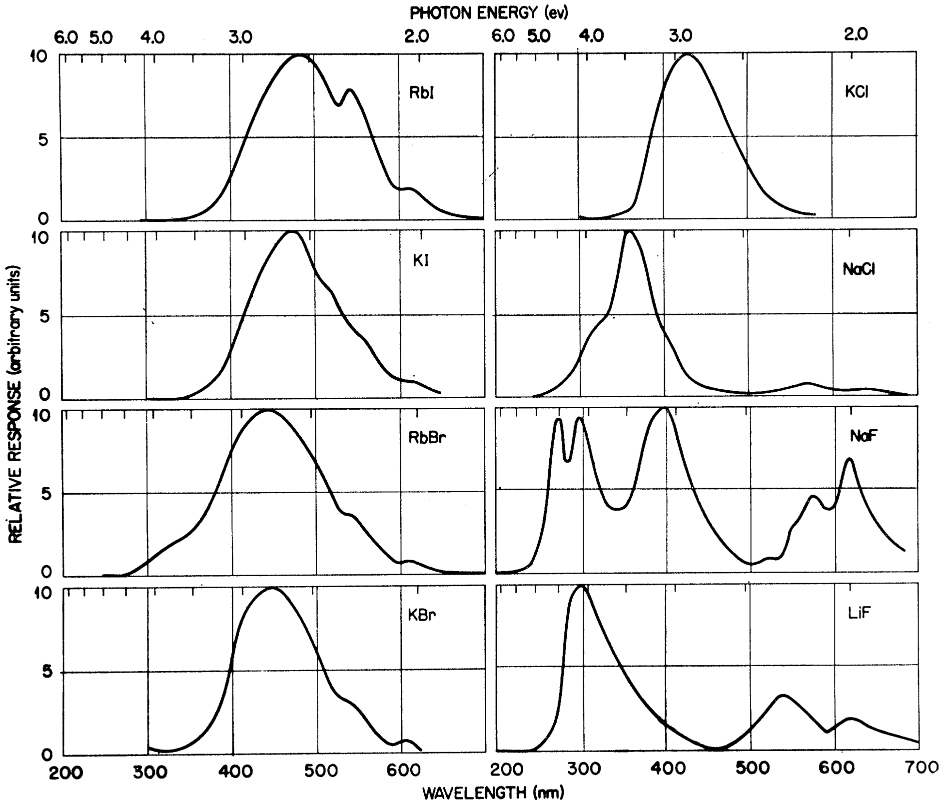

FIG. 1. Uncorrected DL spectra for 8 alkali halides. The spectra have been normalized to a peak value of 10 and dark currents subtracted. None has been corrected for self-absorption or spectrometer response.

correct the recorded intensities for absorption by the F center through the relation:

$$I_a=I_r[(1-e^{-\alpha d})/\alpha d],$$

where α is the absorption coefficient, in cm^{-1}, at the recorded wavelength, d is the thickness of the crystal in centimeters, I_a is the intensity observed if there were no self absorption, and I_r is the intensity actually recorded. This correction formula assumes point-source geometry, and the experiments were arranged to approximate such a case. A special sample holder in a Cary model 14R spectrophotometer was used in most experiments and allowed absorption measurements to be made on the same samples used for DL measurements.

RESULTS

DL Spectra

The near-ultraviolet-excited luminescence from a nominally pure, unirradiated alkali halide contains only luminescence bands which arise from various trace impurities contained in the crystal. This same crystal, if deformed either without irradiation or after additive coloration,[5] emits no detectable light. If deformed after gamma- or x-ray irradiation, however, it luminesces in one or more bands characteristic of the salt, as shown in Fig. 1 for 8 alkali halides. The spectrum of RbCl, not shown, is very similar to that of KCl. The spectra are normalized to a peak value of 10, and dark currents have been subtracted but no correction has been made for spectrometer response or self-absorption by the F center. Some of the apparent structure arises from irregularities in system response. Table I lists fully corrected peak wavelengths of the emissions and their uncertainties along with half-widths for the resolved bands with their uncertainties. Entries in the table are average values from two or more fully corrected spectra.

Peak locations for one band in each of the salts are found to fall on a single line in a Mollwo-Ivey plot[6–8] which indicates that they arise from similar events in each salt. These bands, italicized in Table I, we shall call the "main" bands. This main emission is by far the most intense band in each salt but NaF, for which it can only be said that the 270-nm band appears to be about equal in intensity to several others. (Spectrometer corrections below 290 nm are quite uncertain.) Wavelengths of the strongest DL bands have been measured

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[5] Studied here for KCl. Also studied for KBr by E. Panizza, Phys. Letters **10**, 37 (1964).

[6] E. Mollwo, Nachr. Ges. Wiss. Göttingen Math.-Physik. **Kl**, 97 (1931).

[7] H. F. Ivey, Phys. Rev. **72**, 341 (1947).

[8] Exceptions are LiF and RbBr. The emission in LiF which would lie on a Mollwo-Ivey line would be nearly out of the range of the instrument and would be more severely self-absorbed than in other alkali halides because of its greater colorability. RbBr seems to have two barely resolved bands either of which could be the proper one. Some of the other salts also give indications of such structure.

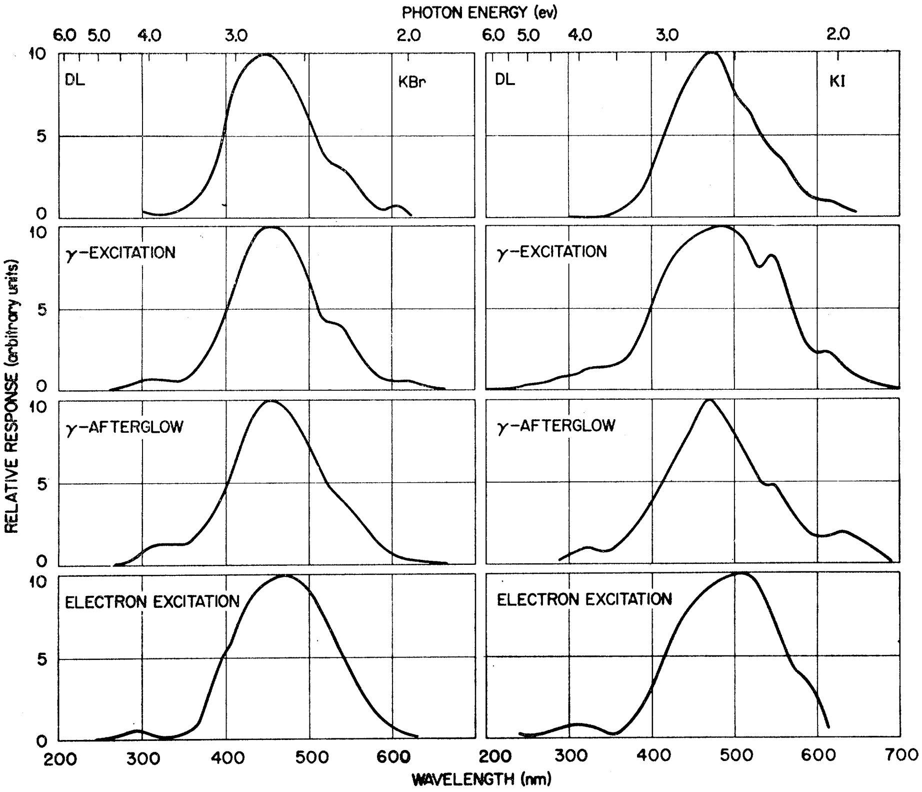

FIG. 2. Comparison of typical spectra obtained for KI and KBr under conditions of (a) deformation of γ-irradiated crystal, (b) γ excitation, (c) afterglow following γ excitation, and (d) 80-keV electron excitation. The spectra have been normalized to a peak value of 10 and dark currents subtracted. None have been corrected for self-absorption or spectrometer response.

by Leider[9,10] for several alkali halides. His measured peak locations fall within the expected error of the present measurements if allowance is made in his data for the effects of photographic plate response and self-absorption. For instance, his uncorrected measurement of the major DL band in NaBr, which was not studied in this work, is 370 nm. Using the Mollwo-Ivey relation, the main band for NaBr is expected to fall near 390 nm, which is sufficiently good agreement.

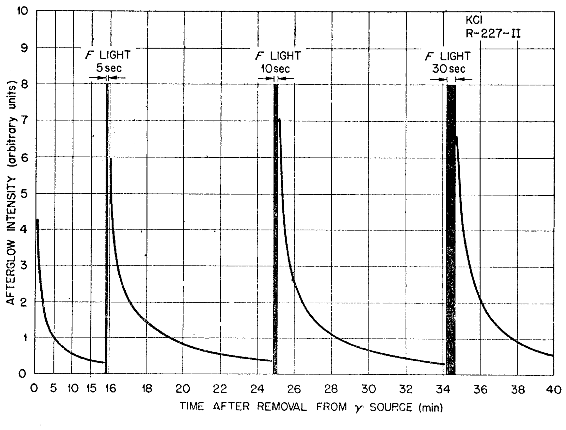

FIG. 3. Re-stimulation of 430-nm emission in KCl *R*-227. Note the scale change at 15 min.

It might be noted that these main bands appear in luminescence spectra of all the alkali halides under other types of high-energy excitation. Figure 2 illustrates this for KI and KBr under conditions of (a) deformation after γ irradiation, (b) γ excitation, (c) γ-induced afterglow, and (d) 80-keV electron bombardment. All of the salts showed similar correspondences. An afterglow also existed following deformation which had the same spectrum as the γ-induced afterglow although it was much weaker. Because of the existence of the same main band in each, one should be able to investigate the DL afterglow by experiments on the more easily studied γ afterglow. In turn, any knowledge gained about the final luminescent event should also apply to the DL and high-energy-excited luminescence mechanisms due to the appearance of the same main band in their spectra. The following experiment utilized the γ-induced afterglow. A crystal from one of the ingots used previously was irradiated in the gamma source for one hour, then placed in front of an MPT covered by a Corning filter to select the main emission band. The afterglow was recorded until it had decayed at least an order of magnitude, after which the crystal was illuminated with *F* light for a few seconds and the luminescence again recorded. Figure 3 shows that the afterglow was restimulated. The figure presents data only for KCl crystal *R*-227, but the effect was the same in commercial KBr, KI, and KCl. The restimulated afterglow of the less pure crystals actually showed a

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[9] H. R. Leider, Phys. Rev. **110**, 990L (1958).

[10] H. R. Leider (private communication of unpublished results).

TABLE I. Location of DL peaks for various alkali halides. Locations of main bands italicized; see text.

Salt	Peak location and uncertainty (nm)	Full width at half-maximum (eV)	Average relative height[a]
RbI	630±30	···	*S*
	525±15	0.7±0.1	10
KI	615±20	···	*S*
	515±10	0.8±0.1	10
RbBr	570±30	···	*S*
	465±10 *495*±10	1.0±0.2	10
	325±20	···	*S*
KBr	*465*±5	0.8±0.1	10
RbCl	510±20	···	1
	430±10	0.5±0.1	10
KCl	520±20	···	*S*
	430±10	0.7±0.1	10
NaCl	610±20	···	<1
	362±5	0.6±0.1	10
	318±10	···	*S*
	282±10	···	*S*
NaF	610±10	0.4±0.1	10
	410±10	0.6±0.1	5
	334±20	0.5±0.1	7–10
	306±5	0.4±0.1	6
	270±5	0.5±0.1	6
LiF	650±20	···	···
	560±20	0.3±0.1	···
	290±10	···	···

[a] *S* indicates that the peak was a shoulder on the main band.

positive initial slope upon termination of the *F* light which produced a concave downward curvature in the luminescence lasting from a few seconds in the commercial KCl to several minutes in KI and KBr.

Only main DL bands have been used in this study. The spectra have been presented first to show that the results of the experiments, which almost exclusively used KCl, should be applicable to processes involving the main band in other alkali halides.

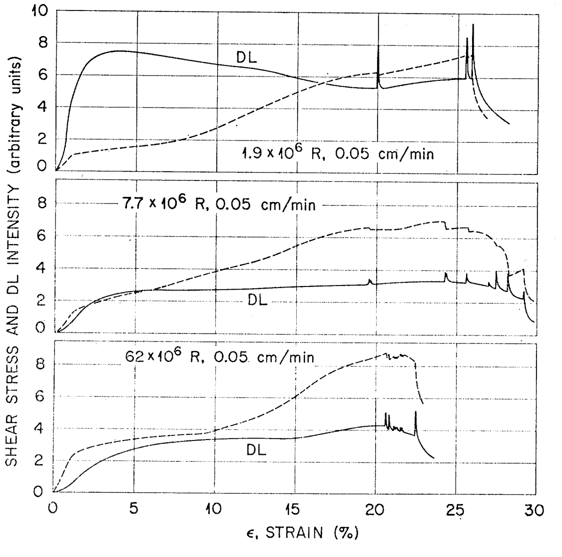

FIG. 4. Stress-strain (dashed) and DL-strain (solid) curves for KCl *H*-223 at 0.05 cm/min crosshead speed and γ doses shown.

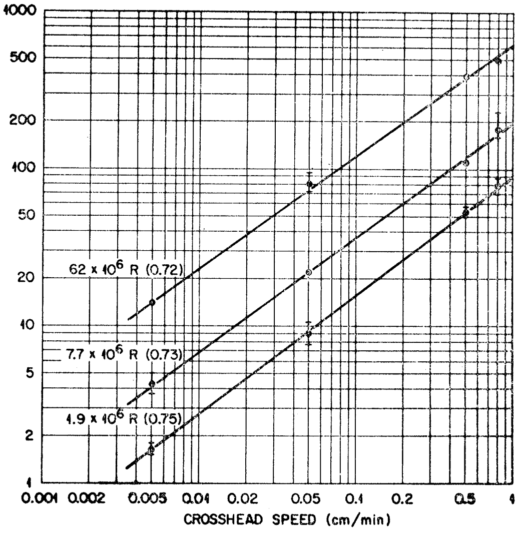

FIG. 5. Crosshead-speed dependence of DL from *H*-223 at three doses. The slope of each line is shown in parentheses. Each datum point represents the average of three determinations.

General Characteristics of the DL

Upon initation of deformation, the DL intensity immediately begins rising, goes through an inflection point near the yield point of the specimen, and eventually reaches a more or less steady value. However, the strain at which this steady value or saturation is reached is dependent upon the rate of deformation, the irradiation dose, and the particular slip system activated. For low γ doses, the DL decreases after remaining at a maximum value for a short time, but for heavier doses, the DL slowly increases after the initial saturation. Figure 4 compares the DL-versus-strain curve with the stress-versus-strain curve at three doses. It can be seen that the regions in which the DL saturates are those in which the stress rate is about constant.

For all specimens of KCl and KI, the DL intensity is proportional to a fixed power of the deformation rate for all doses, but the power varies with the ingot used. Figure 5 is a plot of the logarithm of the DL versus the logarithm of the deformation rate in centimeters/minute for ingot *H*-223 for three different γ doses. The slopes of the lines are very nearly the same and measure 0.73±0.02. That is, the DL varies as the 0.73 power of the deformation rate regardless of the dose. Figure 6 presents similar information for three other ingots.

About $\frac{2}{3}$ of the commercial, and virtually all of the purer samples deform on the geometrically "favored" slip system.[11,12] Glide in this "favored" system occurs in {110} planes that intersect the broad face of the

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[11] A. Hikata *et al.*, J. Appl. Phys. 34, 2154 (1963).

[12] F. Agulló-Lopez and P. W. Levy, Proc. Brit. Ceram. Soc. 1, 183 (1964).

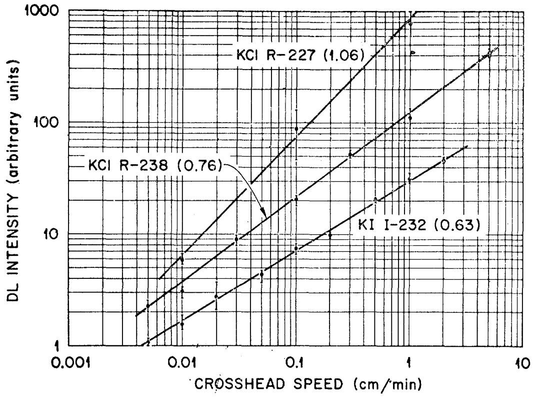
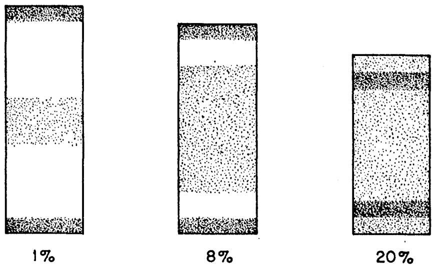
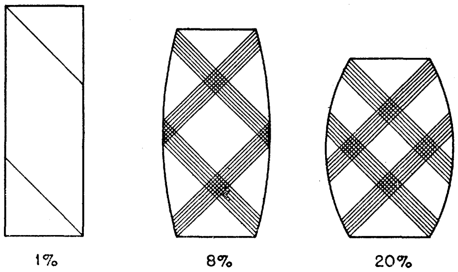


FIG. 6. Crosshead-speed dependence of DL for KCl ingots *R*-227, *R*-238, and KI ingot *I*-232. Slopes are in parentheses. The relative intensities shown were chosen for clarity of presentation and do not represent the actual differences in DL response among the crystals. The data points are average responses of three separate samples with the exception of *R*-227 for which only two specimens were available for each point. The error bars are the extreme limits of individual determinations.

sample horizontally in ⟨100⟩ directions. The final shape of the sample for this type of slip is a bow or an "S" with the broad faces curved and the narrow faces planar. The DL appears as a diffuse glow when viewed on the broad face of the sample. It begins at the ends of the sample immediately upon contact by the crosshead, presumably from surface irregularities of various types. At the yield point of the sample, the glow spreads quickly over the entire surface with the exception of one band about 1 mm wide separated from each end of the sample by about 1 mm. These dark bands apparently undergo nearly pure rotation during a large portion of the deformation, but even they begin to glow after severe strain hardening has occurred. For those samples which deform in the "unfavored" manner, a barrel shape results when viewed on the broad face, and the DL is seen to originate in a series of fine, parallel bands along ⟨110⟩ directions. These bands appear first near the ends of the specimen, then spread to the rest of the face as deformation progresses. New bands appear suddenly, broaden, and even shift position until a symmetric pattern is established. Late in the deformation, the dark portions of the pattern become filled in with diffuse light and the band pattern disintegrates into a general glow. The appearance of the crystals at various stages in the deformation is sketched in Fig. 7 for both the "favored" and "unfavored" modes of deformation.[13]



(*a*) "FAVORED" SLIP



(*b*) "UNFAVORED" SLIP

FIG. 7. Appearance of DL light patterns when viewed on the broad face when the slip planes activated are "favored" (a) or "unfavored" (b). A 1% strain represents the pattern just after yield, 8% the fully developed pattern, and 20% the pattern just before fracture, i.e., after severe strain-hardening has developed.

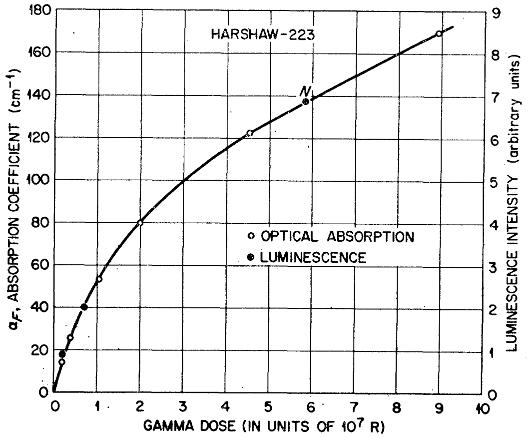


FIG. 8. α_F- and DL-versus-dose curves for KCl crystal *H*-223. Each DL datum point is the average response of three samples.

Relation of the DL to Color Centers

Earlier workers[2,3] speculated that the DL was connected with one or more color centers introduced by irradiation. A series of experiments were performed to investigate the relationship of DL to known color centers or to processes involving them. In Fig. 8, an *F* and a corresponding DL introduction curve for KCl ingot *H*-223 are shown. The DL curve has been normalized to the color center curve at an arbitrary point,

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[13] In some cases, fine bands occur on the narrow edges of these crystals which have no continuation when traced to the broad face. These bands are parallel to the load-cell surface and move, for the 0.05 cm/min crosshead speed, at about 1 cm/sec. At the lowest deformation rate, a series of small, fast light bursts having a rate of about 1.5 bursts/sec and a duration of <0.1 sec are often recorded. They begin a few seconds after the yield point and continue until the light output is about half its saturation value.

marked *N*. The DL cannot be correlated to growth of the *M*, *R*, or *U* centers.

The relation between DL and color center concentration was also studied by means of annealing experiments. Because each DL measurement requires destruction of the specimen, a modified isochronal annealing sequence was used which involved heating a series of identically prepared samples for equal times at different temperatures. This corresponds to a vertical cut at a particular time through a series of isothermal annealing plots. Figure 9 shows the fraction remaining of the DL, the *F* and *M* centers versus the temperature of anneal for ingot *H*-223 for 20-min annealing pulses. The DL and *M* center appear to anneal together. Neither seems to decay with first-order kinetics, but, as Fig. 10 shows, both can be fit to second-order decay kinetics and show a common activation energy of about 0.76 eV. A brief derivation of the formulas to obtain the activation energy is included as an Appendix. The data for KCl ingot *O*-103C are similar and yield the same activation energy, but an identical experiment performed on *R*-227, a much purer KCl crystal, yielded quite different data. In this ingot, the intensity of the DL was somewhat lower than that for *H*-223, the data scattered badly, and the DL and color centers persisted to considerably higher temperatures.

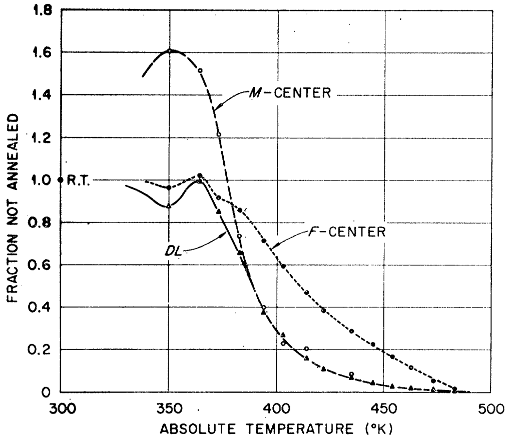

FIG. 9. Annealing behavior of the *F* and *M* centers and the DL for *H*-223 under a modified isochronal anneal; see text.

A bleaching experiment was performed to further characterize the color center dependence of the DL. In a normal bleaching experiment, the irradiated crystal is flooded with light absorbed by the *F* band. The *M* center shortly begins to grow, reaches a maximum, and eventually decays back to, or slightly below its original concentration. The *F*, on the other hand, never grows but decreases monotonically throughout the bleach. The *R* and other higher order centers grow slowly after a delay period and eventually saturate. Thus, this experiment should show rather clearly whether the bleaching behavior of the DL follows that of any one of these color centers. Because the samples are destroyed by the deformation, separate specimens had to be used for each bleaching time. The wavelength of the bleaching light used was 470 nm since the 2 mm-thick crystals would not have been optically thin to light at the peak of the *F* band (560 nm). Auxiliary experiments showed that the wavelength of the emission band found when only *F* centers were present was the same as when a large number of *M* and higher order centers were also present. A microscope-illumination lamp focused through a 470-nm interference filter into a dark, air-cooled enclosure served to bleach the samples. The outcome of this experiment, performed on samples from ingot *R*-227, is shown in Fig. 11. The DL grows, goes through a maximum at approximately the same time as the *M* center and then decays to a low value. To approximately correct for contributions

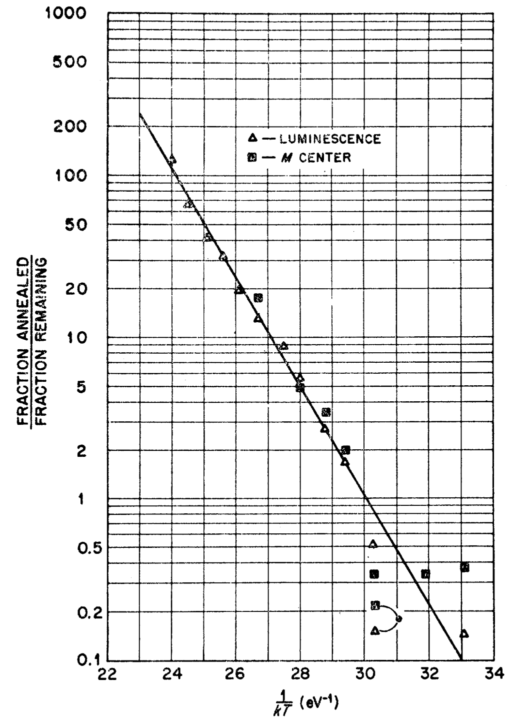

FIG. 10. Second-order Arrhenius plot of annealing data for the *M* center and the DL.

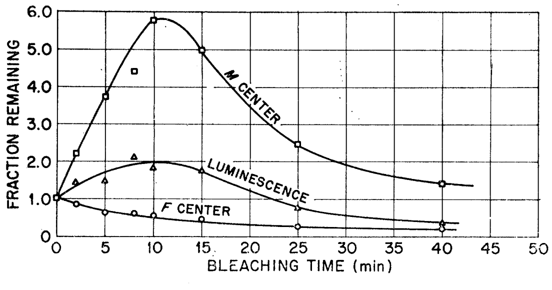

FIG. 11. Bleaching behavior of the *F* and *M* centers and the DL.

of other centers under the F absorption, $(0.8\,\alpha_M+4\,\alpha_R)$ has been subtracted from the measured α_F.[14]

DISCUSSION

The similarity of growth of the DL and F center with irradiation indicate that the F center and the DL are intimately connected. The DL bleaching behavior suggests that the DL intensity is also dependent upon the M-center concentration. This dependence apparently does not appear in the coloration curve because the M-center concentration there is only a small fraction of the F-center concentration. In the bleaching experiment, however, the concentration of M centers reached a maximum of about 40% of the F-center concentration. If the reasonable assumption is made that F and M centers play similar roles in the DL process, it can be inferred that the M center is somewhat more than twice as effective in this role than the F center. This inference can be made from the observation that the total number of filled negative-ion vacancies represented by F and M centers was constant in this experiment to within 5% up to the time at which the M center peaked, while the DL about doubled during this time. Thus the M seems to be more effective in the DL process than the two F centers it replaces.

The annealing data are more difficult to interpret. The decays of the F and M centers, at least in H-223 and O-103C, evidently do not represent thermal destruction of these centers, for Tomiki[15] has shown that the M center decays thermally with a considerably higher energy of activation than the one found here and that the F center is also more thermally stable than the present measurements would indicate. Moreover, the data apparently do not represent annihilation of the centers by interstitials, for Nadeau[16] has shown that the radiation-induced hardening in KCl (which almost assuredly is due to interstitials) anneals at much higher temperatures than those observed for the commercial crystals. The data for R-227 could reflect one or both of these effects, but scatter too badly to allow careful analysis.

So far, nothing has been said of the nature of the luminescent event which gives rise to the main emission or of the identity of the center at which this event occurs. Many authors[3,5,17–21] have proposed that electron-hole recombination is the event responsible for luminescence of alkali halides under various types of high-energy excitation, including DL. The data presented here are consistent with such a model, and in view of the "restimulability" of the afterglow by F light, would require that F and M centers furnish electrons to combine with holes trapped at some special lattice site. This mechanism requires a second type of center (the recombination center) and ionization of color centers by dislocations. Ionization of electron excess color centers by plastic deformation has actually been reported,[22,23] and additively colored material containing both F and M centers does not exhibit DL so that a second type of center must indeed be involved in the process. The data, however, are not inconsistent with a more complex DL model involving ionic motion. It is difficult to explain the continued increase and concave downward curvature of the re-stimulated afterglow after illumination is stopped if ionic motion is required, however, whereas the explanation is quite simple if only electron-hole recombination is assumed. Nevertheless, none of the data clearly support one possibility over the other. The one mechanism which seems to be excluded by the data is excited-state decay of either a color center or an impurity, since the main bands cannot be excited by uv light of 205 nm or greater wavelength[24] in uncolored, or γ-irradiated material of any of the alkali halides available or in additively colored KCl (the only additively colored salt available). If the luminescent event of the DL were such an excited state decay, there should be wavelengths above the absorption edge where the emission could be excited.

A few other observations must be mentioned briefly: The relatively large strains required to produce a steady DL output apparent in Fig. 1, are probably associated with the deformation itself and not directly with the luminescence process since the DL intensity and the glide-band pattern stabilize at about the same strain. In other words, the intrinsic intensity of the DL from a microscopic volume of the crystal which is undergoing plastic deformation seems to be about constant at any strain for a particular strain rate; the total volume involved in the plastic deformation, however, seems to keep increasing until a plastic strain of several percent is reached. Interestingly, a plot of the strain required to just reach saturation of the DL output during a deformation versus the logarithm of the irradiation dose yields a straight line over a factor of about 30 in gamma dose. The immediate onset of the DL with deformation is most probably connected with the yielding

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[14] S. Schnatterly and W. D. Compton, Phys. Rev. **135**, A227 (1964).

[15] T. Tomiki, J. Phys. Soc. Japan **15**, 488 (1960).

[16] J. S. Nadeau, J. Appl. Phys. **34**, 2248 (1963).

[17] W. E. Spicer, Phys. Rev. **106**, 726 (1957).

[18] R. Fieschi and G. Spinolo, Nuovo Cimento **23**, 738 (1962).

[19] A. H. Morrish and A. J. Dekker, Phys. Rev. **80**, 1030 (1950).

[20] A. Halperin *et al.*, Phys. Rev. **116**, 1081 (1959).

[21] T. Timusk and W. Martienssen, Phys. Rev. **128**, 1656 (1962).

[22] A. Bohun, Czech. J. Phys. **6**, 496 (1956).

[23] M. Ueta *et al.* [J. Phys. Soc. Japan **17**, 1668 (1962)] has suggested that this ionization results from a thermal spike produced by intersection of dislocations. It seems even more probable, however, that moving dislocations directly ionize color centers as a result of the sensitivity of the electronic energy of a center to the ionic configuration. Indeed, calculations by R. F. Wood and H. W. Joy [Phys. Rev. **136**, A45 (1964)] and W. B. Fowler [Phys. Rev. **135**, A1725 (1964)] have shown that the relatively small ionic displacements resulting from relaxation around an excited F center raise the energy of the ground state nearly to the conduction band. The larger displacements experienced in plastic deformation would assuredly be capable of moving the ground-state level completely into the conduction band, causing release of the electron.

[24] Actually few, if any, of the bands in the DL spectra can be excited by ultraviolet light.

of the ends of the specimen described earlier. The inflection in the DL intensity at the yield point is caused by sudden onset of DL from the main portion of the sample which occurs after the intensity from the ends has begun to saturate. A rather large fraction of the crystal volume is swept by dislocations during a deformation[25,26] but MPT sensitivities and geometrical considerations indicate that a maximum of only about 10^{12} luminescent events occur during the longest runs. The over-all efficiency of the DL process, then, must be quite low.

CONCLUSIONS

From the data, several conclusions may be made regarding the DL process:

(1) DL spectra of the various salts are similar to those found under other conditions of high-energy excitation. In particular, one emission band in each alkali halide follows a Mollwo-Ivey relation and is common to all excitation methods studied. It is the process involving emission in this band to which the following conclusions apply.

(2) F and M centers are intimately involved and the M is the more efficacious of the two.

(3) The DL intensity is more dependent upon the rate than upon the amount of deformation beyond a certain strain and tends to be nearly constant for constant stress rate.

(4) It increases as a fractional power of the crosshead speed for all γ doses studied, but the fractional power is different for samples from different ingots.

(5) The DL involves at least two different types of centers.

Panizza has already suggested that deformation-induced luminescence could be utilized to study the deformation process itself. This would be true of many materials besides alkali halides since a large number of different compounds show DL[1]—some without irradiation. The observations made here on the places of origin of the light suggest, in particular, a means of conveniently studying various aspects of glide-band development during deformation. With the fast films now available, it should be possible to photograph active areas of the crystal by their own light.

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APPENDIX: MODIFIED ISOCHRONAL ANNEALING EQUATIONS

It is assumed that the intensity of the DL is exactly proportional to the concentration c of some entity.

First-order case:

The usual first-order rate equation for a single reactant is

$$dc/dt=-K_1c. \tag{A1}$$

The solution can immediately be written in the form

$$c=c_0e^{-K_1\tau}, \tag{A2}$$

where τ is the time interval of the anneal during which the concentration always starts at c_0 (held constant) and ends at c. K_1 is given by the usual expression

$$K_1=A_1e^{-E/kT}, \tag{A3}$$

where T is the absolute temperature, A_1 is a constant, and E is the energy of activation the exact meaning of which cannot be specified unless the process is known in detail. We define the ratio c/c_0 as X, the fraction remaining, and recognize that $0\leqslant X\leqslant 1$ for all runs. Combining Eqs. (A2) and (A3), one obtains the relation

$$\ln|\ln X|=(-E/kT)+\ln(A_1/\tau), \tag{A4}$$

where the quantities A_1 and τ are constants for this method. Thus a plot of $\ln|\ln X|$ versus $1/kT$ should yield a straight line of slope $-E$.

Second-order case:

For either a single reacting species or two species with nearly equal concentrations, the second-order rate equation is

$$dc/dt=-K_2c^2 \tag{A5}$$

which has a solution

$$(1/c_0)-(1/c)=-K_2\tau. \tag{A6}$$

Again assuming that K_2 is given by the form in Eq. (3), and defining X as before, these equations lead to the relation

$$(1-X)/X=n_0\tau A_2e^{-E/kT} \tag{A7}$$

or

$$\ln[1-X/X]=-E/kT+\ln n_0\tau A_2 \tag{A8}$$

from which a plot of $\ln[(1-X)/X]$ versus $1/kT$ should yield a line of slope $-E$, since n_0, τ, and A_2 are all constants.

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