of Eu^{++} ions imbedded in a sea of electrons.[26,27] Although this model can approximately account for the magnetic susceptibility above the Néel temperature, our high-temperature measurements of the magnetic behavior of solid europium clearly show that the noninteracting Eu^{++} model is not a correct approximation. In fact, it appears that at high temperatures, say between 800°K and the melting point of europium (1099°K[27]), the magnetic susceptibility values are quite close to those resulting from noninteracting Eu^{+} ions. The Bohr magneton number in this range is equivalent to that of Eu^{+} ion in its ground state $^7F_6$.

The melting process produces a small anomaly in the plot of $1/\chi$ vs T curve as can be seen in Fig. 3. Liquid europium metal approximately follows the Curie-Weiss law. The magnetic moment in this state is very close to that expected from the interacting Eu^{++} system. These observations indicate that metallic europium has unusual magnetic properties and that europium is not a well-behaved rare-earth metal. This supports some previous studies on the crystal structure, density, compressibility, thermal expansion, electrical resistivity, etc.[27–30] which are out of line with the corresponding behavior for most of the rare-earth elements. At the present time we are unable to provide a theoretical justification for the possible change of valency of europium ions with respect to the temperature.

ACKNOWLEDGMENT

The authors are indebted to the following members of this Laboratory: R. C. Peck for technical assistance, R. W. Whitmore for numerical computations, and D. S. Miller for helpful discussions. Valuable conversations with A. Arrott of the Scientific Laboratory of Ford Motor Company have been greatly appreciated.

Note added in proof. Dr. Anthony Arrott of the Scientific Laboratory of the Ford Motor Company has suggested (private communications) that the valency change of europium ions is not needed for explaining our experimental results. The interacting Eu^{++} model may be applicable to metallic europium if the anomalous thermal expansion (reference 30) is taken into account.

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[27] F. H. Spedding, S. Legvold, A. H. Daane, and L. D. Jennings in *Progress in Low-Temperature Physics*, edited by C. J. Gorter (North-Holland Publishing Company, Amsterdam, 1957), Vol. II, p. 368.

[28] F. H. Spedding and A. H. Daane in *Progress in Nuclear Energy*, edited by H. M. Finniston and J. P. Howe (Pergamon Press, New York, 1956), Vol. I, Ser. V, p. 413.

[29] F. H. Spedding, J. J. Hanak, and A. H. Daane, Trans. Am. Inst. Mining Met. Engrs. **212**, 379 (1958).

[30] J. J. Hanak, Ph.D. thesis, Iowa State University of Science and Technology, Ames, Iowa, 1959 (unpublished).

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Photochemically Produced Color Centers in KCl and KBr†

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KCl and KBr crystals were exposed to unfiltered mercury arc radiation at 15°K. If an "OH" band was present in the crystals before irradiation, the ultraviolet irradiation produced an optical absorption spectrum similar to that produced by x rays at 15°K. The optical absorption spectrum and the changes in the absorption produced by annealing at higher temperatures were measured and compared with the spectra observed during similar annealing of x-irradiated crystals. In KCl the 335-mμ band, formed by the uv irradiation, bleaches thermally at 56°K as does the 335-mμ H band of x-irradiated KCl. In KBr the 381-mμ band bleaches in steps at 35°, 46°, 56°, and 80°K as compared with the 381-mμ H band in x-irradiated KBr which bleached at 30°, 46°, 56°, and 80°K. In both KCl and KBr the V_1 band appears with the disappearance of the H band. Illumination in the V_1 band causes regeneration of the H band as occurs in x-irradiated KCl and KBr. In both KCl and KBr the photoproduced H band grows by about 10% at approximately 25°K. It is concluded that the H centers bleach thermally by diffusing to and combining with other color centers. Recombination with F and α centers annihilates the H centers and leads to the formation of V_K centers, while recombination with a third center (possibly a positive-ion vacancy) results in the formation of V_1 centers.

U, U_1, U_2, O^-, and α centers are produced by the uv irradiation as well as F and H centers. The photoproduced F band may be bleached optically with negligible effect on the H band.

INTRODUCTION

When an alkali-halide crystal, which has been exposed to ionizing radiation at liquid helium temperature, is warmed, changes occur in the optical absorption spectrum. In general, at definite temperatures during warmup the various absorption bands change in magnitude and in shape. This effect, together with the appearance of thermoluminescence and free electrical charge within the crystal at some of these characteristic temperatures, leads to the conclusion that some of the original color centers become unstable while new centers are formed.

In a recent publication[1] a study was reported of the

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[1] J. Cape and G. Jacobs, Phys. Rev. **118**, 946 (1960).

properties of the optical absorption bands produced in KCl and KBr by exposure to x rays at temperatures near 10°K. It was shown that the optical absorption band, which is formed at 345 mμ in KCl and 381 mμ in KBr, is a composite of two or more overlapping bands. For example, in KCl two of these overlapping bands were identified: the *H* band at 335 mμ and the V_K band[2] at 365 mμ. It was not shown whether the V_1 absorption band[3] was present as a component of the 345-mμ band, or if it was formed as a product of the thermal bleaching of the *H* center. *H* centers bleach thermally at 56°K in KCl.[1] It was suggested that at this temperature the *H* center, an interstitial chlorine atom, becomes mobile and diffuses to neighboring *F* centers or negative-ion vacancies where it may be annihilated. The possibility that the mobile *H* center may combine with yet a third defect to produce the V_1 center was not considered. The complex structure of the 345-mμ and the 381-mμ bands of the x-irradiated salts have made it difficult to resolve these problems by optical measurements.

Recently, Kingsley[4] has shown that at liquid helium temperatures, irradiation with ultraviolet light of KBr and KCl crystals containing hydroxyl ion impurity[5,6] produces a less complex optical absorption in the region of the *H* band. In particular, a narrow band at 335 mμ was formed in KCl. Kingsley's data indicated that this band was probably due to *H* centers with little or no contribution from V_K or V_1 centers. In addition, the relative concentration of *F* centers to *H* centers was very much smaller in the uv-irradiated crystals than in those exposed to x rays. The greater simplicity of the optical spectrum of the uv-irradiated crystals suggested that a study of their optical and thermal properties might shed further light on the structure and properties of the *H* and V_1 centers.

The present paper deals with the optical absorption spectra formed in KCl and KBr by ultraviolet radiation as contrasted with the spectra formed by x rays.[1] The effects on these spectra of thermal and optical bleaching are studied in an attempt to gain information concerning the mechanism of photoproduction and the structure of some of the color centers. The results of these studies support the hypothesis[1] that the *H* center becomes mobile at the temperature at which its resonance disappears.[7] The data indicate that the V_1 centers are formed as a product of the thermally destroyed *H* centers. Finally, speculations are presented as to the structure of the V_1 center and the mechanism for optical bleaching of photoproduced *F* centers.

EXPERIMENTAL

For optical absorption measurements, the crystals of KBr and KCl were cleaved to dimensions of approximately 10×10×2 mm. After cleaving, the sample was mounted in a double vessel cryostat of the type described by Dutton and Maurer.[8] With liquid helium in the inner Dewar, the sample was cooled to between 10°K and 20°K. After cooling, the crystal was darkened by exposure, through the quartz windows of the cryostat, to radiation from a quartz mercury arc lamp[9] situated at a distance of approximately 3 in. from the crystal. The sample temperature was determined with a thermocouple of Au+2.1% Co vs Ag+0.37% Au.

Optical absorption data were taken with a Cary model 14*R* automatic recording spectrophotometer. When it was desired to bleach the crystal optically, the "Infrared-No. 2" tungsten lamp of the spectrophotometer was used with a suitably chosen optical filter placed between the lamp and the cryostat.

To produce changes in the absorption spectrum by warming the crystal, room-temperature helium gas was blown into the inner vessel of the cryostat until all the liquid helium had evaporated, and the sample had warmed to the desired temperature. At this point, in most cases, liquid helium was again transferred and the sample recooled to about 15°K.

POTASSIUM CHLORIDE

If a crystal of KCl containing sufficient hydroxyl ion impurity to cause a measurable "OH" absorption band, is exposed to unfiltered mercury arc radiation at liquid helium temperature, *F* and *H* centers are produced.[4] After irradiation, if the crystal is warmed, the *H* band decreases and changes shape in much the same way that occurs in x-irradiated KCl.[1] The principal effects are illustrated in Fig. 1. Curve 1 of Fig. 1 shows the absorption at 15°K of a Harshaw KCl crystal which has been freshly cleaved to a thickness of 0.35 cm, mounted in a cryostat, and cooled with liquid helium. The absorption band at 203.5 mμ is the ultraviolet band of the hydroxyl ion.[5,6] After an irradiation of 30 min with the mercury arc, the *F* band has been formed at 538 mμ and a band has appeared at 335 mμ. The properties of the 335-mμ band indicate it is the *H* band. In addition to the *F* and *H* bands, other ultraviolet bands are formed at 307 mμ, 235 mμ, 210 mμ, 195 mμ, and ≃185 mμ.

Curves 3, 4, and 6 of Fig. 1 illustrate the manner in which the 335-mμ band decreases and changes shape as the sample temperature is raised. The behavior is

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[2] The *H* center is essentially a neutral halogen atom situated interstitially along a halogen ⟨110⟩ axis. W. Känzig and T. O. Woodruff [J. Phys. Chem. Solids **9**, 70 (1958)]. The V_K band is the optical absorption band of the self-trapped hole. W. Känzig, Phys. Rev. **99**, 1890 (1955); T. G. Castner and W. Känzig, J. Phys. Chem. Solids **3**, 178 (1957).

[3] R. Casler, P. Pringsheim, and P. Yuster, J. Chem. Phys. **18**, 887, 1564 (1950).

[4] J. D. Kingsley, Air Force Office of Scientific Research, Technical Notes Nos. 1 and 2, AFOSR-TN 60-634 and 60-635, University of Illinois, May and June, 1960 (unpublished).

[5] J. Rolfe, Phys. Rev. Letters **1**, 56 (1958).

[6] W. H. Etzel and D. A. Patterson, Phys. Rev. **112**, 1112 (1958).

[7] W. Känzig and T. O. Woodruff, J. Phys. Chem. Solids **9**, 70 (1958).

[8] D. Dutton and R. J. Maurer, Phys. Rev. **90**, 126 (1953).

[9] A G. E. "Uviarc" 250 watt quartz envelope mercury vapor lamp.

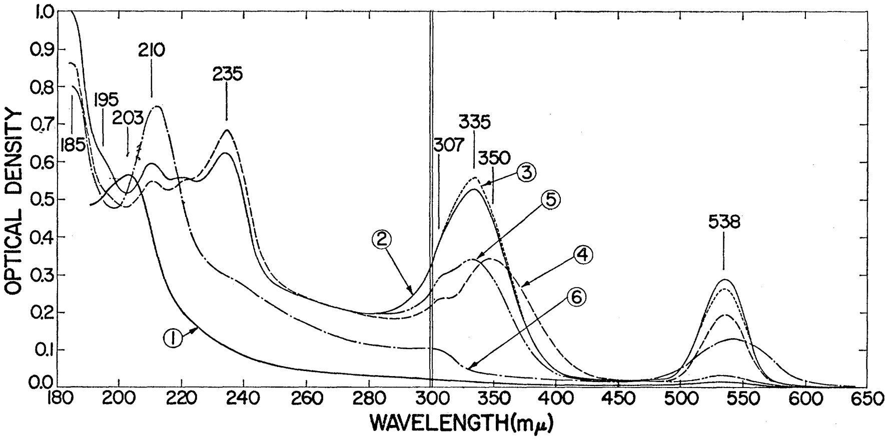

FIG. 1. Optical absorption spectra of KCl:OH exposed to ultraviolet light at 15°K and annealed at higher temperatures. (1) Before exposure to uv, (2) after irradiation for 30 minutes with ultraviolet light at 15°K, (3) after warming to 40°K, (4) after warming to 65°K and recooling to 15°K, (5) after 4 minutes irradiation with tungsten lamp and Corning 5-58 filter, (6) after warming to 230°K. Note that the wavelength scale changes at 300 mμ.

very similar to that of the *H* band in x-irradiated KCl.[1] The principal difference is that no significant decrease in the 335-mμ band occurs when the crystal temperature reaches 42°K. At 42°K, in x-irradiated KCl, a significant decrease in the optical density in the neighborhood of the *H* band accompanies the disappearance of V_K centers (self-trapped holes).[1,2] One concludes that few V_K centers are formed in KCl by ultraviolet light. The initial "*H*" band formed by x-ray peaks at 345 mμ.[10] The wavelengths at half maxima are $\lambda_v \simeq 315$ mμ and $\lambda_r \simeq 372$ mμ. The ultraviolet-produced *H* band of Fig. 1 peaks at 335 mμ with half maxima at $\lambda_v \simeq 305$ mμ[11] and $\lambda_r \simeq 363$ mμ. However in the case of the 345-mμ band formed by x rays, the component of this band caused by *H* centers may be isolated by subtraction of the absorption bands left after warming to 47°K and 60°K.[1] Between these temperatures, it is known that *H* centers disappear.[7] The subtracted band peaks at 335 mμ with half maxima at 308 mμ and 363 mμ, respectively, in good agreement with the ultraviolet-produced 335-mμ band. The presence of a substantial V_K band at 365 mμ[2] and possibly a V_1 band[3] at 350 mμ would explain why the peak of the initial band is shifted to 345 mμ in the x-irradiated samples. It seems clear that the 335-mμ band formed by ultraviolet light is the *H* band.

Growth was observed in the 335-mμ band at 25°K. This is shown by curve 3 of Fig. 1 which is the absorption spectrum taken after warming to 40°K. This result agrees with the observation of Känzig and Woodruff[7] that an increase occurs in the paramagnetic resonance of *H* centers below 42°K. As a result of warming to 40°K, the *F* band has decreased slightly. The decrease in the *F* band occurs gradually with increasing temperature, whereas the growth in the *H* band occurs very sharply at 25°K.

Following warmup to 40°K, the crystal was warmed further to 65°K and then recooled to 15°K. This procedure, illustrated by curve 4 of Fig. 1, caused the complete disappearance of the *H* band and the appearance of a new band at 350 mμ. This is presumably the V_1 band. The 335-mμ band was bleached thermally at 56°K in the ultraviolet irradiated KCl just as is the *H* band in x-irradiated KCl. A further decrease occurred in the *F* band as a result of warming to 65°K.

Curve 5 of Fig. 1 illustrates how the *H* band may be regenerated optically[12] by illumination in the "V_1" band which appeared at 350 mμ on warming to 65°K. Regeneration was accomplished by radiation from the Cary IR#2 tungsten lamp and a Corning 5-58 filter. The light transmitted through the 5-58 filter is absorbed in the long wave tail of the V_1 band (see Fig. 2, curve 2). During regeneration with filter 5-58, the *F* band is bleached. The bleaching rate of the *F* band, however, does not parallel the growth rate of the *H* band. After regeneration has reached saturation, continued illumination causes the *F* band to continue to decrease in an uninterrupted manner. After repeated cycles in which the *H* band is destroyed by warming to 60°K, and then regenerated optically, the *F* band has disappeared completely, yet the cyclic conversion between V_1 and *H* centers may be continued. This suggests that the optical conversion of V_1 centers to *H* centers does not involve *F* centers directly. Possibly, when present, the *F* centers are bleached during regeneration because of absorption of light in the L_1 band[13] at 360 mμ.

Curve 6 of Fig. 1 shows the result of warming the crystal to 230°K. This has caused the disappearance of the 235-mμ band in addition to the expected disappearance of the V_1 band.[8,12] The *F* band and the 210-mμ band have grown as a result of this procedure.

The results of a typical group of a series of experiments carried out on KCl are recorded in Table I. In each case, a KCl sample was exposed to ultraviolet radiation at about 15°K and then heated to higher temperatures to bleach the optical bands thermally, or exposed to light of various wavelengths to bleach the bands optically. The optical absorption spectrum was

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[10] W. H. Duerig and J. J. Markham, Phys. Rev. 88, 1043 (1952).

[11] Obtained by subtracting the 307-mμ band.

[12] K. J. Teegarden and R. J. Maurer, Z. Physik **138**, 284 (1954).

[13] See Fig. 2. The L_1 band is presumed to arise from a conducting excited state of the *F* center. F. Lüty (private communication to Professor R. J. Maurer).

TABLE I. The changes produced by thermal and optical bleaching in the peak heights of the bands formed in KCl by ultraviolet light.

		Changes in optical density at band maximum							
Crystal	Treatment of Crystal	F	H	307 mμ	235 mμ	210 mμ	195 mμ	185 mμ	0.7 μ–1.5 μ
KCl, Sample *A*	(1) 20 min uv at 15°K	+0.20	+0.58	+0.04	+0.8	+0.4	+0.03	+0.5	
	(2) Warm to 43°K	−0.02	+0.05	···	···	−0.03	−0.02	···	
	(3) Warm to 60°K	−0.06	$\rightarrow V_1$	···	···	−0.10	−0.02	···	
	(4) Warm to 80°K, cool to 15°K	−0.02	−0.10	···	+0.07	+0.05	···	−0.05	
	(5) 30 sec white light	−0.06	60%	···	+0.02	+0.03	···	···	
	(6) 4 min 5-58^{a}	−0.05	100%	···	···	+0.02	···	···	
	(7) Warm to 43°K	···	+0.01	···	···	−0.01	···	···	
	(8) Warm to 61°K	···	$\rightarrow V_1$	···	−0.02	−0.02	···	+0.02	
	(9) Warm to 80°K	···	−0.02	···	···	···	···	···	
	(10) Warm to 135°K	+0.12	-0.15^{b}	···	−0.7	+0.10	···	···	
	(11) Warm to 200°K	+0.09	···	···	−0.1	+0.25	···	···	
KCl, Sample *B*	(1) 45 min uv at 15°K	0.30	0.30	0.02	0.5	0.3	0.02	0.5	···
	(2) Warm to 85°K, cool to 15°K	−0.05	$\rightarrow V_1$	···	c	c	c	c	···
	(3) 2 min white light	−0.22	100%	···	0.02	0.02	···	c	···
	(4) 5 min white light	−0.03	···	···	c	c	c	c	···
	(5) Warm to 150°K	0.15	-0.13^{b}	···	−0.45	0.05	···	c	···
KCl, Sample *C*	(1) 30 min uv at 15°K	0.28	0.53	0.03	0.60	0.40	0.04	0.5	
	(2) Warm to 62°K, cool to 15°K	−0.09	$\rightarrow V_1$	···	0.04	−0.04	−0.02	−0.10	
	(3) 3 min 5-58	−0.15	100%	···	0.03	0.02	···	0.02	
	(4) 4 min 5-58	−0.02	···	···	0.01	0.01	···	0.01	
	(5) Warm to 60°K, cool to 15°K	···	$\rightarrow V_1$	···	···	···	···	···	
	(6) 3 min 5-58	−0.02	100%	···	···	···	···	···	
	(7) Warm to 230°K	0.15	-0.30^{b}	···	−0.45	0.15	···	−0.10	

[a] For transmission properties of the optical filters refer to Fig. 5.
[b] V_1 band bleaches.
[c] Not measured.

taken at each interval between these procedures. The first column of Table I lists the successive treatments of the KCl sample; for example, exposure to light of a given wavelength, or warming to a prescribed temperature. In the succeeding columns are recorded the changes each procedure produced in the various optical absorption bands.

In the first group of data, steps 1 to 11 are the successive treatments of KCl sample *A*. This sample was first exposed at 15°K to radiation from a quartz mercury arc lamp for 20 min. This produced an *F* band whose optical density at band maximum was 0.20, and an *H* band of peak height 0.58 as shown under step 1 in the second and third columns, respectively. The succeeding columns list the magnitudes of the various other bands which were produced by the ultraviolet radiation. The data of step 1 may be compared with curve 2 of Fig. 1. Following the radiation of step 1, the KCl crystal was warmed to 43°K and the optical absorption remeasured at that temperature. This procedure, recorded as step 2 of group *A*, resulted in a growth in the *H* band of 0.05 unit, and a decrease in the *F* band of 0.02 unit. Warming to 60°K, step 3, caused the appearance of the V_1 band at 350 mμ, and a further decrease in the *F* band. After the crystal was warmed to 80°K and recooled to 15°K, step 4, illumination in the V_1 band, steps 5 and 6, caused the regeneration of the *H* band to saturation. This is shown in the third column of Table I where the percentage of the regenerated *H* band is recorded for each step during regeneration. Warming and regeneration, steps 1 to 6, caused the *F* band to disappear entirely. Steps 7, 8, and 9 show that the thermal behavior of the regenerated *H* band is identical to that of the initial *H* band. Furthermore, the regenerated band exhibits identical bleaching

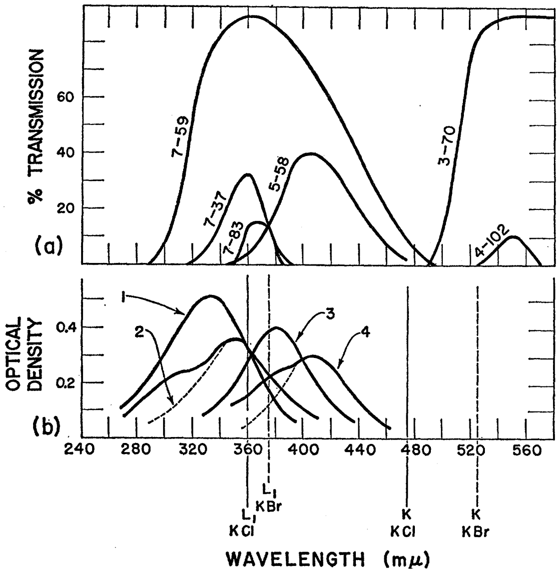

FIG. 2(a). Transmissivity vs wavelength of various Corning optical filters through which KCl and KBr crystals were optically bleached. (b) The *H* and V_1 bands of KCl and KBr. Curve 1 is the *H* band of KCl, curve 2 the V_1 band; curve 3 the *H* band of KBr and curve 4, the KBr V_1 band. The bands are drawn below the filter spectra on the same wavelength scale to permit comparison of the optical absorption bands with the transmission spectra of the filters.

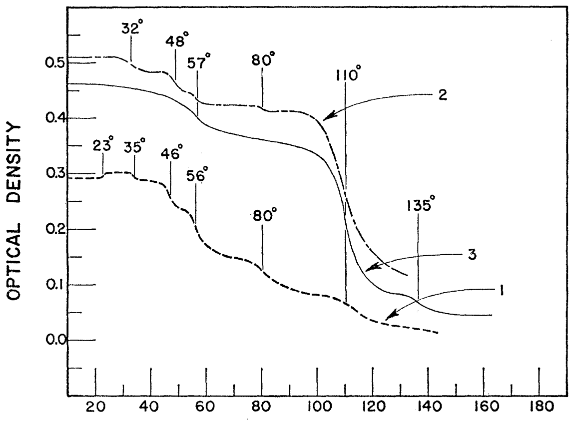

FIG. 3. The optical density at the peaks of the F, H, and α bands as they change with temperature during warmup of a KBr crystal uv irradiated at 15°K. Curve 1 is the optical density at 381 mμ, the maximum of the H band; curve 2, the optical density at 201 mμ, the peak of the α band; curve 3, the F band at 599 mμ. Warming rate approximately 5°/min.

and regeneration properties whether F centers are or are not present.

As may be seen in each of the groups of data A, B, and C, measurement of the absorption spectrum after the crystal had been warmed to above 130° revealed that the 235-mμ band had disappeared almost entirely, a substantial growth had occurred in the 210-mμ band, and there was a large decrease in the 185-mμ band. Accompanying these changes in the ultraviolet bands, warming to 130°K caused significant growth in the F band. This result may be seen in each of the groups of data of Table I and is illustrated also on Fig. 1, curve 6. These results are identical to the observations of Kerkhoff[14] for KCl:OH irradiated with ultraviolet light at 80°K. In agreement with the conclusions of Kerkhoff, the 185, 210, and 235-mμ bands are identified with the O^-, U, and U_2 bands.[15] In addition to these bands, it may be noted from Fig. 1 that the ultraviolet irradiation produced a small band at 307 mμ. This band overlaps the H and V_1 bands and is stable to temperatures above 230°K. (See Fig. 1, curves 2–6.) A similar 307-mμ band was not detected in x-irradiated KCl.[1] Possibly the band is generated by the same photochemical mechanism which produces H and U-type centers from OH$^-$ centers.

POTASSIUM BROMIDE

The irradiation with ultraviolet light of a crystal of KBr containing "OH" impurity produces F, H, and α bands[4] at 15°K. Warmup of the irradiated KBr crystals causes the peak heights of the principal bands to change in a characteristic way. This is illustrated for the F, H, and α bands of KBr in Fig. 3. The optical density at 381 mμ, the peak of the H band, was measured as a function of temperature during warmup. The results are shown as curve 1 of Fig. 3. As the crystal was warmed, the optical density at 381 mμ increased suddenly at 23°K. With continued warming at a rate of about 5° per minute, curve 1 shows that the peak optical density of the 381-mμ band decreased at 35°, 46°, 56°, 80°, and 110°K. Curve 2 shows that the optical density at 201 mμ, the peak of the α band, as a function of temperature. Decreases in the α band occurred at nearly the same temperatures as those at 381 mμ. The F band, curve 3, decreased gradually over the temperature range below 100°K, and exhibited a pronounced decrease only at 56°K. Both the F and α bands showed large decreases at 110°K.

Fig. 4 shows the absorption bands in ultraviolet irradiated KBr as the appear after warming to just above each of the characteristic bleaching temperatures of Fig. 3. Curve 1 shows the absorption of a Harshaw KBr crystal which has been freshly cleaved, mounted in the cryostat, and cooled to 15°K with liquid helium. In addition to the fundamental absorption in the near ultraviolet caused by the exciton bands, there appears a small "OH" absorption band at 215 mμ. Curve 2 is the absorption spectrum after 2-hr exposure to unfiltered mercury arc radiation. In addition to the α, H, and F bands at 201, 381, and 599 mμ, respectively, bands are formed at 228, 271, and 316 mμ. The 228- and 271-mμ bands have been observed by Kerkhoff[14] in KBr:OH exposed to ultraviolet light at 80°K. Kerkhoff has identified them with the U and U_2 bands,[15,16] respectively. The 316-mμ band appears to correspond to the 307-mμ band of KCl (Fig. 1) inasmuch as both appear to the short wavelength side of the H band and remain stable at temperatures above the bleaching

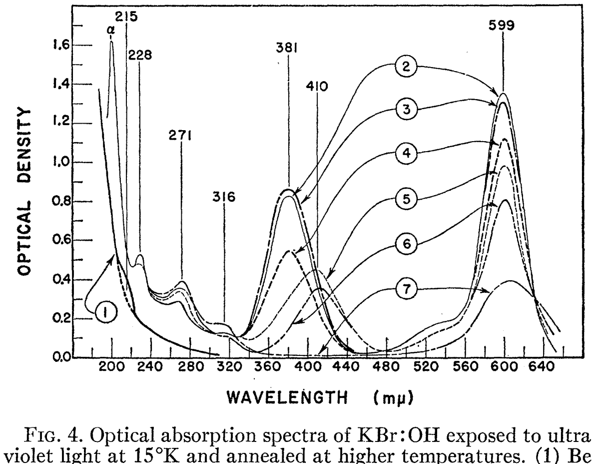

FIG. 4. Optical absorption spectra of KBr:OH exposed to ultraviolet light at 15°K and annealed at higher temperatures. (1) Before exposure to uv, (2) after irradiation with ultraviolet light for 2 hours at 15°K, (3) after warming to 25°K, (4) after warming to 47°K, (5) after warming to 60°K, (6) after warming to 86°K, (7) after warming to 120°K.

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[14] F. Kerkhoff, Z. Physik **158**, 535 (1960).

[15] C. J. Delbecq, B. Smaller, and P. H. Yuster, Phys. Rev. **104**, 599 (1956).

[16] The 271-mμ band has been called the U' band by Rolfe (reference 5), and the U'' band by Thomas [H. Thomas, Ann. Physik **38**, 601 (1940)].

TABLE II. The changes produced by thermal and optical bleaching in the peak heights of the bands formed in KBr by ultraviolet light.

		Changes in optical density at maximum of band						
Crystal	Treatment of Crystal	F	H	α	316 mμ	271 mμ	228 mμ	0.7 μ–1.5 μ
KBr, Sample *A*	(1) 35 min uv,[a] at 15°K	0.55	0.29	0.60				
	(2) 2 min 7-59	−0.25	−0.02	0.25				
	(3) 6 min 5-58[b]	−0.07	−0.01	0.07				
	(4) 11 min 3-70	−0.12	−0.01	0.12				
KBr, Sample *B*	(1) 1 hr uv, at 16°K	0.72	0.55	Off scale				···
	(2) 25 min 5-58	−0.37	−0.04	Increase				···
	(3) Warm to 47°K	−0.07	−0.12	···				···
	(4) Warm to 62°, cool to 17°K	−0.01	$\rightarrow V_1$	Decrease				
	(5) 8 min 5-58	−0.08	90%	Increase				
	(6) 17 min 5-58, 1 hr 3-70	−0.18	−0.04	Increase				
	(7) Warm to 68°, cool to 17°K	···	$\rightarrow V_1$	Decrease				
	(8) 10 min 5-58	−0.01	100%	Increase				
KBr, Sample *C*	(1) 17 min uv, at 12°K	0.17	0.29	1.17	0.02	0.07	0.05	···
	(2) 30 min 5-58	−0.16	−0.02	0.15	0.01	0.03	0.01	···
	(3) 6 min 2-64	···	···	···	···	···	···	···
	(4) 48 min 7-37	0.04	···	−0.04	···	···	···	···
	(5) 5 min white light	−0.03	···	0.03	···	···	···	
	(6) Warm to 49°K	···[c]	−0.08[d]	−0.20	···	···	−0.02	
	(7) Warm to 62°, cool to 14°K	···[c]	$\rightarrow V_1$	−0.03	···	0.03	···	
	(8) 17 min 7-37	0.02	0.06	−0.01	···	···	···	
	(9) Warm to 84°, cool to 14°K	···	−0.10	−0.05	···	0.02	···	
	(10) 16 min 7-37	···	0.07	···	···	−0.01	···	
	(11) Warm to 47°K	···	−0.04[d]	−0.03	···	···	···	
	(12) Warm to 170°K	···	−0.12[e]	−0.70	···	−0.11	···	
KBr, Sample *D*	(1) 90 min uv, at 17°K	0.28	0.19	0.40				
	(2) Warm to 62°, cool to 17°K	−0.03	$\rightarrow V_1$	−0.04				
	(3) 7 min 7-83	−0.06	75%	0.06				
	(4) 11 min 4-102	−0.03	···	0.03				
	(5) 12 min 7-37	···	100%	···				
	(6) Warm to 70°, cool to 17°K	−0.02	$\rightarrow V_1$	−0.03				
	(7) 18 min 7-37	···	100%	···				
	(8) 5 min white light	···	···	···				

[a] Irradiated with a Bausch and Lomb spark generator.
[b] For transmission properties of optical filters, refer to Fig. 5.
[c] *F* band unmeasurably small.
[d] V_1 band half grown.
[e] V_1 band bleaches.

temperature of the V_1 center. The fact that these bands have not been observed in x-irradiated KBr or KCl[1] and are not produced by the uv irradiation of crystals in which the "OH" band is absent, suggests that they are caused by a center which is a by product of the photoproduction mechanism for *H* centers.

Curve 3 of Fig. 4 is the absorption spectrum measured after the crystal had been warmed to 25°K. At 25°K the *H* band had grown by about 5% while the *F* band had decreased by a similar amount. However, reference to Fig. 3 indicates that the decrease in the *F* band is not related to the growth in *H* inasmuch as the *F* band did not change suddenly at 23°K. Following warming to 25°K, the crystal was warmed to 47°K and the absorption spectrum measured at that temperature. Curve 4 shows that the *F* band continued to decrease and the *H* band had diminished appreciably. Due to lack of space, changes in the α band are not shown on Fig. 4. On warming to 60°K, curve 5, the *F* band decreased further, and a band appeared at 410 mμ. The 410-mμ band is presumably the V_1 band. Further warming of the crystal to 86°K, curve 6, caused more *F* centers to disappear and further growth in the 271-mμ band.

In the final step, the crystal was warmed to 120°K. The absorption spectrum measured at that temperature is shown by curve 7. The V_1 band has disappeared in agreement with the results for V_1 centers produced by x-rays in KBr at 80°K.[8] At the same temperature at which the V_1 centers (the 410-mμ band) disappear, about 110°K, the *F* and α bands both decreased sharply (see Fig. 3). Possibly the mechanism for the disappearance of V_1 centers involves the annihilation of negative-ion vacancies.

A series of experiments were carried out in which KBr crystals which had been exposed to ultraviolet light at temperatures near 15°K were then heated to higher temperatures or exposed to light of various wavelengths. The optical absorption spectrum was measured at each interval between these procedures. A typical group of such experiments are recorded in Table II. The data in the first column describe the successive treatments of the KBr crystal. In succeeding columns are shown the changes that occur in the optical absorption bands because of these treatments. In the following, the conclusions derived from the series of experiments are outlined, and the steps in the data of

Table II from which these conclusions may be inferred are indicated.

(1) At 15°K, light absorbed in the *F* band (step 4 of group *A*), the *K* band (step 4 of group *D*), and probably the L_1 band[13] (steps 2 and 3 of group *A*; 2, 5, 6, and 8 of group *B*; and 3 of group *D*) bleaches the photoproduced *F* centers and forms α centers. The electrons released from the *F* centers become captured by unidentified centers. The effect of these bleaching procedures on other optical bands is very small.

(2) Warming the crystal to about 60°K causes the *H* band to bleach thermally and the V_1 band to appear. If *F* centers are present, both the *F* and α bands decrease simultaneously with the disappearance of the *H* band and the growth of the V_1 band. If *F* centers are absent, only the α band decreases (steps 3 and 4 of group *B*; 6, 7, 9, and 11 of group *C*; and 2 and 6 of group *D*).

Following thermal bleaching of *H* centers by warming to 60°K, if the crystal is recooled to 15°K, then: (3*a*) Light absorbed in the spectral region of the V_1 band, 360 mμ to 460 mμ, partially regenerates the *H* band[17] while destroying the V_1 band. If *F* centers are present, they are bleached by this procedure and commensurate growth occurs in the α band (steps 5 and 8 of group *B*; step 3 of group *D*). After the *H* band has been regenerated to saturation while the V_1 band has disappeared completely, continued illumination with regenerating light continues to bleach *F* centers and produce α centers. If no *F* band is present before regeneration, light absorbed in the V_1 band regenerates the *H* band with negligible effect on any of the other bands (steps 7 and 8 of group *D*); (3*b*) Light absorbed in the spectral region 300 mμ to 380 mμ regenerates the *H* band at the expense of the V_1 band as does the light absorbed in the region 360 mμ to 460 mμ (conclusion 3*a*). However, if no *F* centers have been optically bleached before this procedure, the procedure does not effect the *F* and α bands (step 10 of group *C* and step 5 of group *D*). If the *F* band has been optically bleached before this procedure, the procedure *restores* the *F* band at the expense of the α band (steps 4 and 8 of group *C*).

(4) The center formed by capture of the *F* center electron during optical bleaching does not absorb light in the spectral region to the red of the *F* band implying that the electrons are not captured by other *F* centers to form *F′* centers (steps 1, 2, 3, and 4 of group *C*). Rather, it appears that this center absorbs light in the region 300 mμ to 380 mμ causing the electron to return to a negative ion vacancy (conclusion 3*b*).

SUMMARY AND CONCLUSIONS

Thermal Bleaching of *H* Centers

The irradiation with ultraviolet light of KBr or KCl containing "OH" impurity produces *F*, *H*, and α centers at 15°K. If the crystal is then warmed continuously, the *H* band bleaches thermally at certain characteristic temperatures. The thermal destruction of *H* centers is accompanied by the formation of V_1 centers. When *F* and α centers are present, some of them are destroyed simultaneously with the disappearance of the *H* centers. The thermally destroyed *H* band may be regenerated by recooling the crystal and optically bleaching the V_1 band. The regenerated *H* band bleaches thermally in steps at the same characteristic temperatures as the original one. It is possible to regenerate *H* centers from V_1 centers without affecting the concentration of *F* or α centers (filter 7-37), and regeneration is possible when all *F* centers have been previously bleached. In the latter case the α band remains unaffected regardless of which filter is used to effect the regeneration. One concludes that the reaction, whereby *H* centers form V_1 centers when the crystal is warmed and the reverse reaction, whereby *H* centers are regenerated optically from V_1 centers, are processes which do not involve *F* or α centers.

To explain these observations, it is assumed that at sufficiently high temperature, e.g., 56°K in KCl, the *H* center becomes mobile. It follows that *F* and α centers may be annihilated during the thermal destruction of *H* centers because of combination of the mobile *H* centers with *F* centers and negative ion vacancies. This mechanism was suggested previously[1] to account for the observed effects accompanying the disappearance of *H* centers in x-irradiated KCl. The hypothesis agrees with the conclusion from the present data that the decrease in the concentration of *F* and α centers is an indirect result of the disappearance of *H* centers.

The recombination of *H* centers with *F* and α centers is expected to produce holes which could become self-trapped to form V_K centers.[2] Since the V_K band peaks at 385 mμ in KBr,[18] the growth of the V_1 band at 410 mμ makes it difficult to detect whether the V_K band appears with the disappearance of *H* centers. However, in the case of KCl, Känzig and Woodruff[7] have established that the electron spin resonance of the V_K center appears when the *H*-center resonance is destroyed by warming to 56°K.

The hypothesis that *H* centers are annihilated by diffusing to and combining with *F* and α centers suggests that the V_1 center results from the combination of an *H* center with a third defect. As an example, the mobile *H* center may be expected to encounter a positive ion vacancy. Since the *H* center is neutral, there are no electrostatic forces to inhibit such a combination. One expects the hole of the resulting center to be described by a *P*-like state made up of halogen *P* functions. Consequently, on the basis of the Jahn-Teller theorem, it is likely that combination of an *H* center and a positive-ion vacancy would result in a configuration of lower than cubic symmetry. An example of a possible

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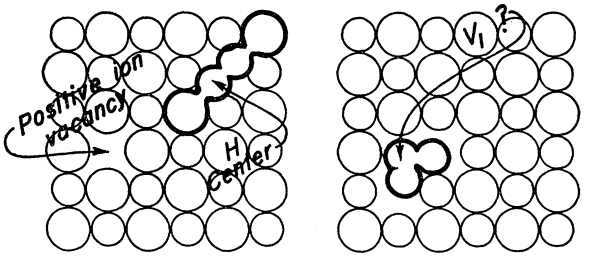
[17] In each thermal bleaching-optical regeneration cycle, the regenerated *H* band is smaller than the previous one.

[18] C. J. Delbecq and P. H. Yuster (private communication to J. D. Kingsley).



(a) (b)

FIG. 5. (a) shows H center and positive ion vacancy before heating of crystal permits H center to diffuse towards vacancy. (b), same region of crystal after warming to 60°K showing one conceivable configuration of the center resulting from combination of H center and positive ion vacancy. (This may be the V_1 center.)

structure is shown in Fig. 5. The hole is depicted as being shared by three halogen ions in a ⟨110⟩ oriented configuration. Delbecq and Yuster[18] have shown that the V_1 center relaxes into ⟨110⟩ symmetry at sufficiently low temperatures. On the other hand, the combination of an H center and a positive ion vacancy leaves an unpaired electron spin so that the resulting center is paramagnetic. Känzig and Woodruff[7] were unable to detect any resonance which may have appeared with the disappearance of the H-center resonance. For this reason, these authors argued that the V_1 center was probably diamagnetic. If this were true, it would be likely that the center with which the H center combined to form a V_1 center would be itself paramagnetic, and one would seek a second resonance disappearing simultaneously with the disappearing H-center resonance.

With a few exceptions, the properties of the photoproduced H band are identical to those of the H band produced by exposure to x rays. A notable exception is that few V_K centers are formed during the initial irradiation by ultraviolet light. In the case of KBr, there is evidently a difference in that the H centers of x-irradiated crystals disappear below 40°K,[7] whereas the photoproduced H centers convert to V_1 centers above 47°K (see Figs. 3 and 4). The uv-irradiated crystals are distinguished also by the fact that they contain much fewer F centers in proportion to the number of H centers than do the x-irradiated crystals. Thus in uv-irradiated crystals, it is possible to optically bleach the F band almost entirely with negligible effect on the H band.

Optical Bleaching of *F* Centers

If a KCl or KBr crystal containing F, H, α, and the various "U" centers is irradiated with light absorbed to the long wave side of the H band, the F band is caused to bleach and commensurate growth occurs in the α band, simultaneously. The fact that this is observed to occur when the crystal is illuminated through any of the various Corning optical filters 7-83, 5-58, 4-102, 7-59, and 3-70 suggests the possibility that F centers may be bleached by excitation of either the F, K, or L_1 bands.

For KBr it was shown that the bleached F band may be restored by illumination in the spectral region from 300 to 380 mμ (filter 7-37). Light absorbed in this region would be expected to excite the U_1 band.[15] It is possible that during bleaching of F centers, the electrons are captured by U_2 centers to form U_1 centers. Delbecq and Yuster[19] have concluded that for those F centers which are sufficiently close to U_2 centers, tunneling may occur from an excited state of the F center to the U_2 center according to[20]

$$H_i^0(U_2)+[e]\xrightarrow{h\nu(F),\ \rho}\square+H_i^-(U_1), \tag{1}$$

where the symbol ρ indicates that the distance separating the F and U_2 centers must be not too great. It may be further supposed that if the F center is excited into a conducting state such as the L_1 band, tunneling is not required, and the electron may be captured by a U_2 center at greater distances than the minimum separation ρ. Restoration of the F centers through light passed by filter 7-37 would take place by excitation in the U_1 band. According to Delbecq and Yuster,[19] tunneling may occur from excited U_1 centers to α centers forming F and U_2 centers. This is represented by

$$H_i^-(U_1)+\square\xrightarrow{h\nu(U_1),\ \rho}[e]+H_i^0(U_2). \tag{2}$$

In this case, ρ indicates a minimum distance below which back tunneling from the ground state of the F center would occur.

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[19] C. J. Delbecq and P. H. Yuster, Phys. Rev. **104**, 607 (1956).

[20] The symbolism is as follows: $\square$ = negative ion vacancy (α center), $[e]=F$ center, $[H^-]$ = hydrogen ion in negative-ion vacancy (U center), H_i^- = interstitial hydrogen ion (U_1 center), and H_i^0 = interstitial hydrogen atom (U_2 center).