Color Centers and Trapped Charge in KCl and KBr

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Potassium chloride and bromide crystals have been irradiated with x-rays at $-183°C$ and the behavior of the V_1, F, and F' optical absorption bands observed during subsequent warming to room temperature. The thermal bleaching of the V_1-band is accompanied by a decrease in the F-band, the appearance of free charge within the crystal, and luminescence. The data indicate that positive holes are released from traps during this process.

INTRODUCTION

V-CENTERS in x-rayed alkali halide crystals have recently been the subject of a number of investigations.[1-7] Many of the color centers formed by irradiation at low temperature are unstable at room temperature or below: the V_1-band,[2] for example, formed in KBr by x-raying at $-180°C$, is bleached by warming to $-140°$, and cannot be formed at the higher

FIG. 1. Cryostat. A and B, liquid nitrogen reservoirs; C, radiation shield; D, electrical lead; E, pumping line; F, crystal holder; G, rotating O-ring seal; H, crystal quartz windows.

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[1] J. Alexander and E. E. Schneider, Nature **164**, 653 (1949).
[2] Casler, Pringsheim, and Yuster, J. Chem. Phys. **18**, 887, 1564 (1950).
[3] H. Dorendorf, Z. Physik **129**, 317 (1951).
[4] Delbecq, Pringsheim, and Yuster, J. Chem. Phys. **19**, 574 (1951).
[5] W. Martienssen, Z. Physik **136**, 488 (1952).
[6] W. H. Duerig and J. J. Markham, to be published.
[7] F. Seitz, Phys. Rev. **79**, 529 (1950).

temperature.[3] The V_1-band may also be bleached by illuminating with light in the V_1-band; in either case the F-band is partially bleached at the same time.[2] Several of the V-bands have been interpreted as due to positive holes trapped at such lattice defects as positive-ion vacancies or aggregates of vacancies.[1,2,7] The V_1-band, according to Seitz,[7] may be the simple analog of the F-center, a positive hole trapped by a single positive ion vacancy. Seitz has suggested that the thermal instability of V_1-centers may, in view of the very low temperature at which it occurs, be due to ionic diffusion and combination with F-centers, rather than thermal dissociation into holes and positive ion vacancies.

The experiments to be described indicate that free charge is released within the crystal during the thermal bleaching of the V_1-band. The behavior of the F-band during this process provides strong evidence that the released charge consists of holes. Some preliminary results for KCl were previously reported;[8] this paper describes further work on KBr and improved measurements on KCl.

EXPERIMENTAL PROCEDURE

Pieces of KCl and KBr about $1.5 \times 8 \times 20$ mm were cleaved from commercial (Harshaw) crystals and mounted in a holder which permitted a dc field of the order of 1000 volts/cm to be applied along the 8-mm dimension and allowed light to be transmitted along the 1.5-mm dimension. The holder, F, was attached to the inner vessel of the cryostat shown in Fig. 1, but was insulated from it by a 0.003-inch film of polystyrene (a compromise between the requirements of good electrical insulation and good thermal contact). A radiation shield, C, at the temperature of the outer Dewar vessel surrounded the crystal except for small windows to admit light and x-rays. The external vacuum jacket was equipped with a cap which could be rotated about an O-ring seal, G, to bring either a beryllium window (1 mm thick) or a pair of crystal quartz windows, H, into alignment with the crystal. The temperature of the crystal was measured directly by a copper-constantan couple cemented in a small hole drilled in the crystal. With liquid nitrogen in both inner and outer vessels, A and B, the equilibrium temperature of the
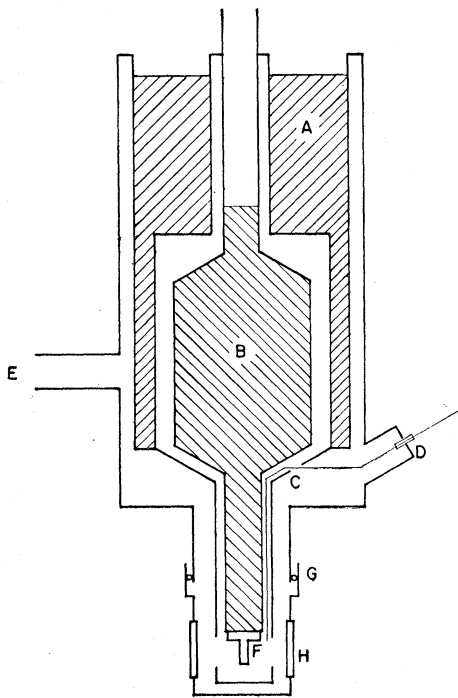
[8] Dutton, Heller, and Maurer, Phys. Rev. **84**, 363 (1951).

crystal was $-183°C$. By introducing an electric heater into the inner vessel the crystal could be warmed at a rate of about 5°C per minute.

The electric field was supplied by dry cells. Currents were measured with a commercial electrometer of the vibrating-reed type (Applied Physics Corporation), connected as a voltage amplifier across a 10^{10}-ohm Victoreen resistor. The noise level was about 10^{-14} amp, the chief source of disturbance apparently being thermal stresses in the crystal and insulators while the system was being warmed. Runs on unirradiated crystals were frequently made to check on spurious effects, and care was taken to establish reproducibility of interesting events. Polarization effects were negligible, owing to the small quantities of charge collected and the very small range of the charge carriers.

The source of x-rays was a beryllium-windowed, molybdenum-target tube operated at 50 kv and 20 ma. The crystals were exposed for 1 to 2 hours at about 2 inches from the tube window.

Electrical measurements were made as follows. The crystal was first irradiated with x-rays in the dark at $-183°C$ and its absorption spectrum determined. Then an electric field was applied and the crystal warmed to room temperature, while current and temperature were recorded automatically as functions of time. The crystal was then cooled again to $-183°$ and its optical absorption remeasured.

Luminescence was observed by a similar procedure,

FIG. 3. (a) Absorption spectrum of KBr crystal after irradiation; (c) Change in absorption after warming momentarily to $-148°C$; (d)–(g) Further changes in absorption as crystal is warmed to the temperatures indicated; (h) Further change in absorption after crystal has been held at $+40°$ for two hours; (b) Absorption spectrum at completion of the run. All curves measured at $-183°$. Rates of warming and cooling were approximately 5°/min.

using as detector a cesium-antimony photocell with very small dark current.

To establish correlation between certain peaks in the current-time curves obtained in this way (Figs. 2 and 5) and changes in the absorption spectrum, two methods were used. The first, applied to KCl, was to observe the V_1-band continuously while the crystal was warmed, using a low level of illumination, and to note that bleaching of the band was simultaneous with the appearance of a current peak. The second, applied to both materials, was to measure the absorption of the irradiated crystal, first at the low irradiation temperature, and again at the same low temperature after the crystal had been warmed momentarily to some higher temperature T which corresponded roughly with a current peak; a succession of such measurements were made after a single irradiation. (This resembles the pulse-annealing technique except for the very slow rates of warming and cooling, 5° to 10° per minute.)

Optical measurements were made with a Leiss double monochromator equipped with Quarzglas prisms (unfortunately not useful below 2400A), using a hydrogen discharge lamp as source and a cesium-antimony cell as detector in the ultraviolet and a
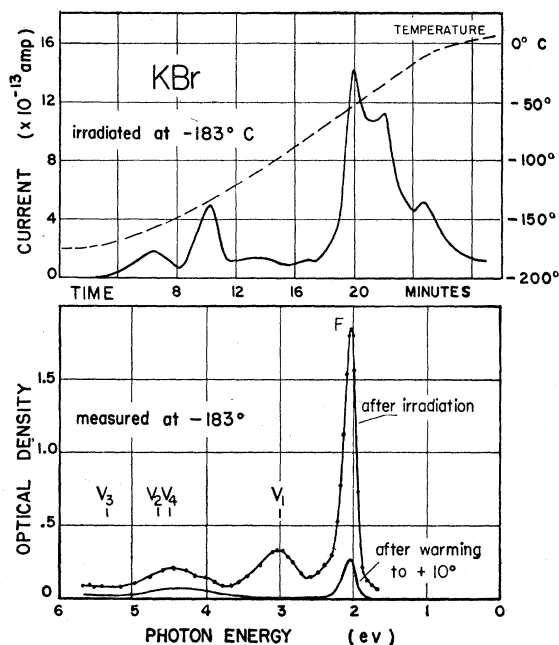

FIG. 2. Upper part: Current and temperature as functions of time as a KBr crystal is warmed with a dc field of 950 volts/cm applied, after irradiation with x-rays for 1 hour at $-183°C$. Lower part: The absorption spectrum of the crystal before and after warming. The indicated positions of V-bands are after Dorendorf (reference 3).
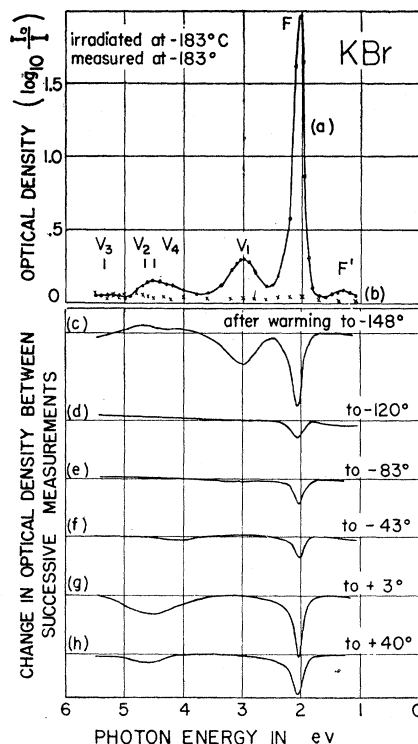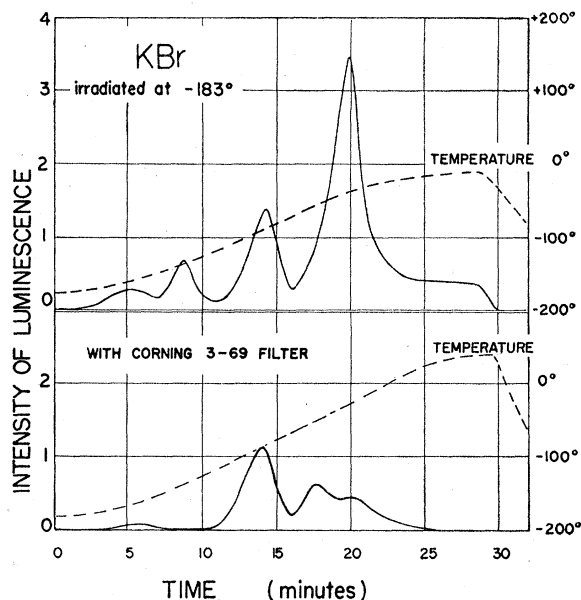
FIG. 4. Glow curves in KBr. The unit of intensity corresponds roughly to 10^9 quanta per second total emission. The upper curve was measured by a cesium-antimony cell sensitive to wave lengths below 6500A; the lower curve was measured under similar conditions but through a filter which transmits wavelengths above 5500A. The large peak at 20 minutes in the upper curve is resolved into two peaks when the filter is introduced.

tungsten lamp and dark-current-balanced cesium-silver oxide cells in the visible and near infrared. The absorption is expressed in terms of optical transmission before and after irradiation rather than in terms of the absorption constant, since the coloration varies with depth due to strong absorption of the x-rays. The penetration depth for beryllium-filtered 50-kv molybdenum radiation, as measured by Duerig and Markham,[6] is of the order of 0.05 to 0.1 mm.

RESULTS

Examples of the data are given in Figs. 2–7. The results, summarized in Table I, are as follows: (1) The V_1-band is bleached, with the release of charge and luminescence, at $-158°$ in KBr and $-145°$ in KCl. (2) Partial bleaching of the F-band occurs at the same time, in so far as can be determined. In KCl, warmed to $-160°$, the F-band had not begun to bleach appreciably, but bleaching had occured after warming to $-100°$. (3) Current and luminescence peaks at $-130°$ in KBr and $-68°$ in KCl are due to thermal ionization of F'-centers. The corresponding effect in NaCl was observed by Gudden and Pohl[9] at $+90°$. These are the temperatures at which the "thermally increased range" of photoelectrons from F-centers begins,[10] and the largest decrease in the F'-band occurs in the present experiments (Figs. 3 and 6). (4) Luminescent glow peaks unaccompanied by an observable release of charge

[9] B. Gudden and R. W. Pohl, Z. Physik 31, 651 (1925).
[10] G. Glaser, Gött. Nachr. 3, 31 (1937).

occur at $-88°$ in KBr and at $-36°$ in KCl. No change occurs in the absorption spectrum, at least in the limited region under observation, except a decrease in the F-band. (5) Of the additional current peaks observed in KBr, one (at $-27°$) may be associated with the disappearance of the V_4-band.[3]

The spectral composition of the luminescence in KBr was examined by taking a series of glow curves under the same conditions of excitation but with various sharp-cut-off filters in front of the detector. These measurements showed that the glow peaks have different spectra, but were inadequate to establish any definite pattern of behavior. The peak associated with V_1-centers, presumably due to the recombination of holes, is transmitted well by a filter which cuts off below 5000A, while the glow peak associated with disappearance of F'-centers, is practically extinguished by a filter which cuts off below 3800A; the peak at $-27°C$, which seems to be associated with the disappearance of V_4-centers, has a much smaller component at wave lengths above 5000A than the luminescence accompanying the disappearance of V_1-centers. The luminescent yield is small and is estimated as one quantum per 10^4 to 10^5 centers destroyed. Sharma[11] has reported similar glow curves obtained with potassium iodide.

Of the KCl luminescence, only the phosphorescence at $-183°C$ after x-ray irradiation was examined in this way. Of this radiation, 70 percent was transmitted by Corning filter 9–53 (cutoff about 3000A) and 6 percent by filter 0–52 (cutoff about 3800A).
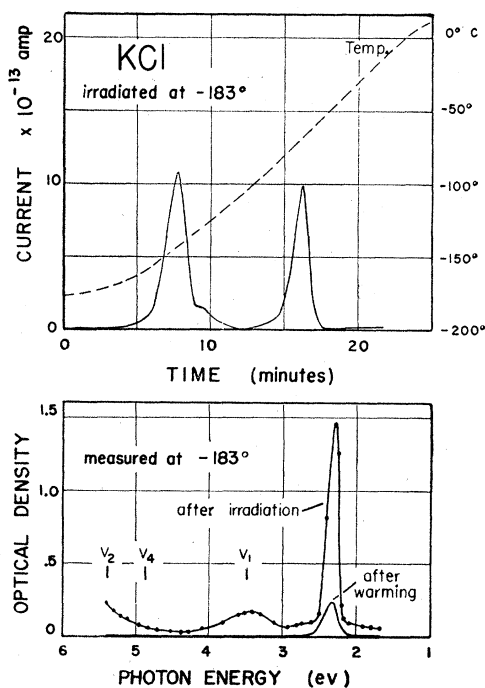

FIG. 5. Similar to Fig. 2, for KCl. The field in this case was 680 volts/cm.

[11] J. Sharma, Phys. Rev. 85, 692 (1952).

A relation originally derived by Smakula[12] and given in somewhat simpler forms by Mollwo and Roos[13] may be used to compute the concentration of color centers from the height and half-width of the absorption band. Using the numerical constants appropriate to KCl, the number of color centers per unit area is

$$\frac{N}{A} = \left(\frac{1}{f} \times 2.44 \times 10^{16} HD\right) \text{ cm}^{-2}, \qquad (1)$$

where H is the width of the absorption band at half-maximum, in electron volts, D is the optical density $= \log_{10}(I_0/I)$, and f is the oscillator strength of the transition. f has been measured chemically for the F-band in KCl by Kleinschrod,[14] who found $f = 0.81$ in this case. Oscillator strengths have not been determined for other materials and other absorption bands. Estimates of the numbers of color centers involved, with
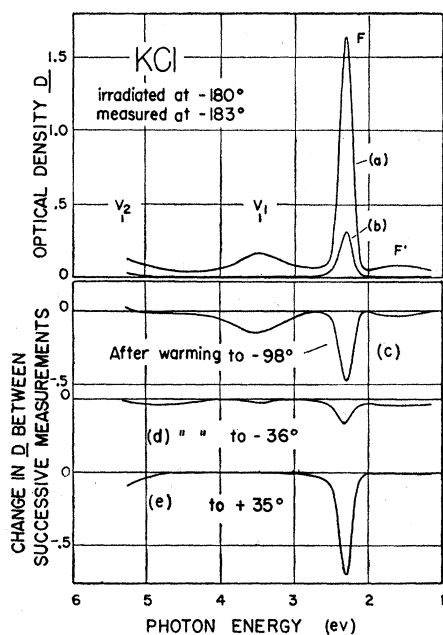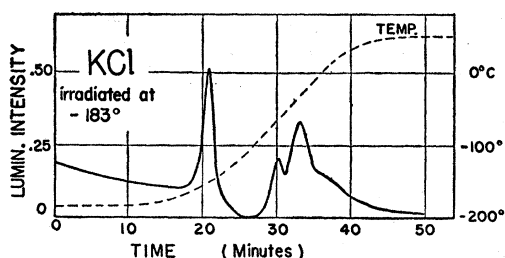

FIG. 6. Similar to Fig. 3, for KCl.

FIG. 7. Glow curve in KCl. The observation began 15 minutes after removal from the x-ray beam. The phosphorescence at $-183°$ has a decay time of about 9 minutes.

[12] A. Smakula, Z. Physik 59, 603 (1930).
[13] E. Mollwo and W. Roos, Gött. Nachr. 1, 107 (1934).
[14] F. Kleinschrod, Ann. phys. 27, 97 (1936).

TABLE I. The temperatures at which current maxima were observed on warming of crystals irradiated with x-rays at $-183°$C. The rate of heating was $5°$C per minute. Temperatures listed are mean values from several observations, variation among individual runs was of the order of $\pm 3°$C. Trap depths are calculated from $E = 1.08kT \ln s$. ** denotes a glow peak unaccompanied by a current peak.

Temperature of current peak (°C)	Principal change in optical absorption	Spectral character of luminescence	Trap depth (ev)
	KBr		
-158	V_1-band	($\lambda > 5000$A)	0.23
-130	F'-band	($\lambda < 3800$A)	0.29
** -88	?	($\lambda > 5000$A)	0.38
-48	?	?	0.46
-27	V_4-band	($\lambda > 5000$A)	0.50
	KCl		
-145	V_1-band	?	0.26
-68	F'-band	?	0.42
** -36	?	?	0.49

the assumption that $f = 1$ and the data of Figs. 3 and 6, are given in Table II.

A comparison of the total number of color centers destroyed with the total charge collected is given in Table III. If N charge carriers are released, and each drifts an average distance w in the direction of the field before it is trapped, the total charge measured will be

$$Q = New/d, \qquad (2)$$

where d is the separation of the electrodes. Assuming the presence of one type of trap, w can be written

$$w = \mu E\tau = \mu E \frac{1}{C_t \sigma_t v}, \qquad (3)$$

where $\tau =$ mean free time, $E =$ electric field, $C_t =$ density of traps, $\sigma_t =$ trap cross section, $v =$ thermal velocity $= 10^7$ cm/sec, and $\mu =$ mobility. A small volume element $dxdydz$ which has a density n of centers able to release charge carriers and a density C_t of traps will contribute to the total charge an amount

$$dQ = \frac{eE\mu}{d\sigma_t v} \frac{n}{C_t} dxdydz. \qquad (4)$$

TABLE II. Concentration of color centers in crystals irradiated with x-rays at $-183°$C and change in concentration observed during warming of crystals. The numbers listed in columns 3, 4, and 5 are the quantity (Nf/A) calculated from Eq. (1) with $f = 1$.

Absorption band	Half-width H(ev)	Initial number of color centers (cm⁻²)	Number bleached (Curve C, Figs. 3 and 6) (cm⁻²)	Number bleached (Curve G, Fig. 3) (cm⁻²)
		KBr		
F	0.18	8.6×10^{15}	2.2×10^{15}	2.0×10^{15}
V_1	0.6	4.0×10^{15}	3.2×10^{15}	
V_4	~1			3.0×10^{15}
		KCl		
F	0.20	8.0×10^{15}	2.2×10^{15}	
V_1	0.7	2.7×10^{15}	2.5×10^{15}	

If we assume that (1) the traps are F-centers and (2) the ratio of F-centers to V-centers is the same at different levels of coloration, the integration of the above expression reduces to the choice of an effective volume V in which there is sufficient density of color centers so that we may expect these assumptions to hold. A reasonable choice is the area of the irradiated crystal multiplied by the penetration depth of the x-rays, which gives $V = 0.01$ cm^3. With these assumptions we may estimate the quantity.

$$\frac{\mu}{\sigma_t} = Q\frac{C_t}{Nv_1}\frac{dv}{eE}, \tag{5}$$

and such estimates are given in Table III. Some results by Glaser[10] for photoelectrons from F-centers are included for comparison.

The method described by Randall and Wilkins[15] was used to compute trap depths for the various glow peaks. The rate of thermal ionization of charge from the original traps is taken as

$$R = se^{-E/kT}, \tag{6}$$

and the trap depth E is related to the temperature T^* of maximum glow by

$$E = kT \ln s\left\{1 + \frac{\ln(kT^{*2}/\beta E)}{\ln s}\right\}, \tag{7}$$

where β is the warming rate. In our case this becomes

$$E = 1.08kT^* \ln s. \tag{8}$$

The frequency factor s was taken as $10^{9.5}$ sec^{-1}, the value obtained from glow curves in Tl-activated KCl by Bunger and Flechsig.[16] The temperatures of maximum luminescence are, within experimental error, the same as the corresponding temperatures of maximum current, as one would expect for the case in which the lifetime of the electrons or holes in their original traps is very long compared to the lifetime in the conduction band.

One further point of interest is the very low thermal ionization energy of the V_1-center, compared to the

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[15] J. T. Randall and M. H. F. Wilkins, Proc. Roy. Soc. (London) A184, 365 (1945).
[16] W. Bunger and W. Flechsig, Z. Physik 67, 42 (1931).

TABLE III. Data which permit a calculation of μ/σ, the ratio of mobility of the charged particles to the trapping cross section. Glaser (reference 10) found $\mu/\sigma = 6\times10^{14}$ volt^{-1} sec^{-1} for photoelectrons from F-centers in x-rayed KCl at $-120°$C. Mott and Gurney (reference 17) estimate σ for the F-center to be 10^{-14}–10^{-15} cm^{-2}.

Material	Current peak (°C)	Total no. of V_1-centers	Total charge measured Q (coulombs)	Average density of F-centers C_F (cm^{-3})	Average value of w/E (cm^2-volt^{-1})	μ/σ (volt^{-1} sec^{-1})
KBr	−158	4×10^{15}	4×10^{-11}	9×10^{17}	3×10^{-11}	3×10^{14}
KCl	−145	3×10^{15}	9×10^{-12}	8×10^{17}	1×10^{-11}	1×10^{14}

energy of the optical transition. A qualitative argument can be given[8] to the effect that the ratio of optical to thermal energies should be greater for trapped holes than for trapped electrons, but it does not appear that a ratio as large as 10 can be accounted for in this way. In a recent paper Kubo[17] has suggested that a small apparent trap depth may result from the fact that the crystal is not in thermal equilibrium; however, V_1-centers cannot be produced in KBr by irradiating at $-140°$ under conditions of thermal equilibrium, and the ionization of F'-centers is observed at the expected temperature. The V_4-band and an ultraviolet band, observed by Duerig and Markham[6] in crystals x-rayed at 5°K, which is bleached by warming to 78°K, seem to be other instances of small thermal excitation energies.

CONCLUSION

The thermal bleaching of the V_1 absorption band is due to thermal ionization of the centers. Since the number of F-centers which disappear when the V_1 band is bleached is approximately the same as the number of V_1-centers which disappear it is concluded that holes are released from V_1-centers and migrate to the F-centers where recombination of the free holes and trapped electrons occurs.

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[17] R. Kubo, Phys. Rev. 86, 929 (1952).