

Low-Temperature Properties of H , V , and F Centers in KCl and KBr†

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Potassium chloride and potassium bromide crystals were exposed to x rays at 10°K. The optical absorption produced by this irradiation and the changes in optical absorption produced by subsequent annealing at higher temperatures were measured. The temperatures at which changes in optical absorption occurred were correlated with the temperatures at which free electrical charge appeared, and thermoluminescence was observed. The absorption band at 345 m μ , in KCl, which has been named the H band, is shown to result from the superposition of two or more bands, one of which is the absorption band due to self-trapped holes. In KCl, the self-trapped hole band bleaches thermally at 43°K with a release of free electrical charge. H centers disappear at 56°K with a release of free charge. The optical absorption band of the H center is shown to have its maximum at 335 m μ . In KBr, the thermal release of free charge at 30°K is attributed to the disappearance of H centers. No charge burst was observed in KBr which may be attributed to the destruction of self-trapped holes.

INTRODUCTION

THE prominent optical absorption bands that appear in KCl crystals as a result of irradiation with x rays at the temperature of liquid helium include the F and H bands. The H band, which was discovered by Duerig and Markham,¹ has its maximum at 345 m μ . The electron spin resonance experiments of Känzig and Woodruff² have established that this absorption band is due primarily to a hole center, the H center, which may be described briefly as an interstitial chlorine atom. Since the spin resonance of self-trapped holes^{3,4} has been observed in KCl exposed to x rays at liquid helium temperature, it is to be expected that the 345 m μ absorption band of Duerig and Markham is composed of overlapping absorption bands including that of the H center and that of the self-trapped hole. The work of Delbecq, Smaller, and Yuster,⁵ has located the maximum of the optical absorption band due to self-trapped holes at 365 m μ . In the present experiments, it is shown that the optical absorption due to self-trapped holes contributes to the 345-m μ band and it is established that the maximum of the absorption band of the H center is at 335 m μ .⁶ It has not been possible, however, to determine if the 345 m μ band contains a component of V_1 -center absorption. The V_1 absorption band has its maximum at 350 m μ in KCl.^{5,7}

When crystals irradiated with x rays near helium temperature are warmed to higher temperatures,

changes occur in the optical and spin resonance absorption spectra. The appearance of thermoluminescence and free charge within the crystals at definite temperatures also leads to the conclusion that some of the original centers become unstable while new centers are formed. The experiments of Känzig and Woodruff² and Teegarden and Maurer⁸ have shed considerable light upon the nature of the events that occur. The present experiments represent an attempt to compare the changes in optical absorption and the temperatures at which they occur with the temperatures at which free charge appears in KCl and KBr in order to clarify an exceedingly complex problem.

EXPERIMENTAL

The crystals of KBr and KCl, which were obtained from the Harshaw Chemical Company, were cleaved to dimensions of approximately 10×10×2 mm. The cryostat and electrodes have been described by Inchauspé.⁹

The procedure of a typical experiment for measuring charge bursts was to cool the crystal with liquid helium, expose it to x rays, apply an electric field of approximately 1500 volts/cm, and raise the temperature of the crystal at a rate of about 20°C/minute. While the crystal was being warmed, the current in the external circuit, which was the result of the thermal release of electric charge in the crystal, was measured with a vibrating reed electrometer.

The temperature of the crystal was simultaneously recorded. A thermocouple of Au+2.1% Co and Ag+0.37% Au wires was used for this purpose. This couple was calibrated against a platinum resistance thermometer which has been calibrated by the National Bureau of Standards. A less sensitive couple of copper-constantan was used in one series of experiments that resulted in the data of Fig. 1.

The optical absorption of the crystals was measured

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¹ W. H. Duerig and J. J. Markham, *Phys. Rev.* **88**, 1043 (1952).

² W. Känzig and T. O. Woodruff, *J. Phys. Chem. Solids* **9**, 70 (1958).

³ W. Känzig, *Phys. Rev.* **99**, 1890 (1955).

⁴ T. G. Castner and W. Känzig, *J. Phys. Chem. Solids* **3**, 178 (1957).

⁵ C. J. Delbecq, B. Smaller, and P. H. Yuster, *Phys. Rev.* **111**, 1235 (1958).

⁶ C. J. Delbecq and P. H. Yuster (private communication). (In recent unpublished experiments, Delbecq and Yuster have isolated the H -center absorption band at 335 m μ in KCl by absorption of radiation in the V_1 band.)

⁷ C. J. Delbecq, B. Smaller, and P. H. Yuster, *Phys. Rev.* **104**, 599 (1956).

⁸ K. J. Teegarden and R. J. Maurer, *Z. Physik* **138**, 284 (1945).

⁹ N. Inchauspé, *Phys. Rev.* **106**, 898 (1957).

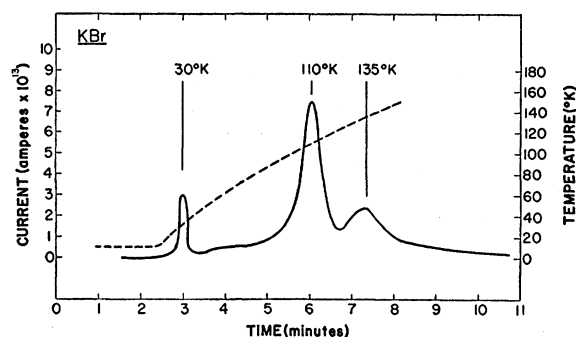


FIG. 1. Thermal release of trapped charge in KBr irradiated with x rays at 20°K. Current in external circuit is plotted as the solid curve, and the crystal temperature by the dashed curve. (Crystal thickness 2.3 mm.)

with a Beckman DU spectrophotometer. The optical density of the samples was determined relative to an aperture before and after exposure of the crystals to x rays, and it is the change in optical density as a result of irradiation that is shown in subsequent figures. In a typical experiment, the crystal was cooled with liquid helium, and its optical density spectrum was determined over the range 225 $m\mu$ to 1240 $m\mu$. The crystal was then exposed to x rays, and its absorption spectrum was remeasured. The crystal was then warmed to a prescribed temperature, recooled with liquid helium, and its optical absorption spectrum measured again. This procedure was repeated for successively higher annealing temperatures. The annealing temperatures were prescribed by the observed charge bursts in the separate experiments described above.

POTASSIUM BROMIDE

The thermal release of charge during the warming of a KBr crystal is shown in Fig. 1. This crystal was exposed at 20°K for one hour to the radiation from a beryllium windowed, molybdenum target x-ray tube. The tube was operated at 30 kilovolts and 20 ma, and was placed at a distance of seven inches from the crystal. Three charge bursts were observed as the crystal was warmed from 20°K after the irradiation. The current peaks at 110°K and 135°K were observed by Dutton and Maurer¹⁰ in crystals irradiated at 78°K. These current peaks have been attributed to the thermal destruction of V_1 and F' centers, respectively. The F' current peak in Fig. 1 is smaller than the V_1 peak; whereas, in the work of Dutton and Maurer the F' peak was larger than the V_1 peak. Optical absorption measurements on KCl and KBr crystals have shown that few F' centers are formed by x irradiation near helium temperature.^{1,8}

The three current peaks at 30°K, 110°K, and 135°K are accompanied by bursts of thermoluminescence. The work of Känzig and Woodruff has shown that the spin resonance of the H center in KBr disappears at a tem-

¹⁰ D. Dutton and R. J. Mauer, Phys. Rev. **90**, 126 (1953).

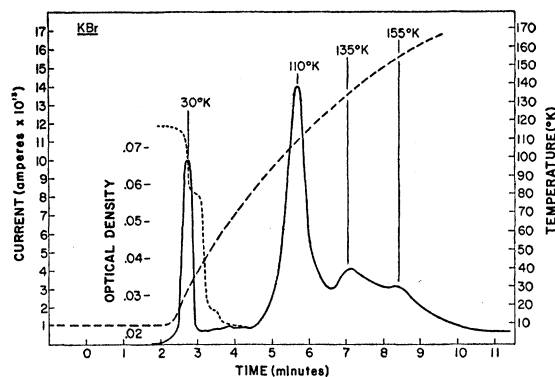


FIG. 2. Optical density and release of trapped charge in KBr exposed to x rays at 10°K. Optical density at 381 $m\mu$ is plotted as the dotted curve, the current in external circuit as the solid curve, and the crystal temperature by the dashed curve. (Crystal thickness 1.9 mm.)

perature between 20 and 40°K, so that the current peak and thermoluminescence that occur at 30°K are probably associated with the thermal destruction of H centers.

A series of current peaks observed in KBr exposed to x rays at 10°K is shown in Fig. 2. There is a small current peak at 155°K, and the three peaks at 30, 110, and 135°K that occur after irradiation at 20°K are also present.

The optical density of the crystal at 381 $m\mu$ was measured as a function of time and temperature. The results are shown by the fine dashed curve of Fig. 2. The " H " absorption band has its maximum at 381 $m\mu$ and, as Fig. 2 shows, the optical density at this wavelength decreased by approximately 25% at 30°K, the temperature of the first current peak and thermoluminescent burst. The optical density decreased by <40% at 46°K and by about 5% at 56°K. Current or thermoluminescent bursts were not observed at these temperatures.

POTASSIUM CHLORIDE

The thermal release of trapped charge in KCl is illustrated in Fig. 3. These data were obtained from a crystal that had been irradiated for 80 minutes at a temperature of 10°K. The x-ray tube was operated at 50 kilovolts and 20 ma, and its beryllium window was located at a distance of two inches from the crystal. These experimental conditions were used in all the experiment with KCl crystals.

The data of Fig. 3 were obtained with the crystal temperature rising at a rate of approximately 15°K/minute. Current peaks occur at 43°K and 54°K. These current peaks have been reported by Teegarden and Maurer⁸ in crystals exposed to x rays at 35°K, but they report a current peak at 68°K which was not observed in the present experiment. Thermoluminescence was observed at 43°K and at 56°K. As illustrated in Fig. 3, the optical density at the maximum of the 345 $m\mu$

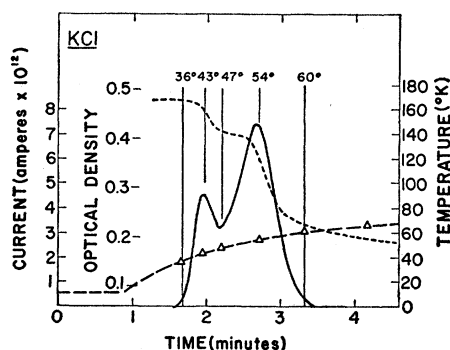


FIG. 3. Optical density and release of trapped charge in KCl exposed to x rays at 10°K. Optical density at 345 m μ is plotted as the dotted curve, the current in external circuit as the solid curve, and the crystal temperature by the dashed curve. (Crystal thickness 2.5 mm.)

absorption band decreased by approximately 15% at 43°K and by approximately 40% at 56°K.

The optical density as a function of photon energy after exposure of a KCl crystal to x rays at 10°K is plotted as curve (1) of Fig. 4. The absorption band at 3.6 eV (345 m μ) and the small band at 2.7 eV have been called the *H* and *V*₀ bands, respectively, by Duerig and Markham.¹ After obtaining the data of curve (1), Fig. 4, the crystal was warmed to 48°K at a rate of about 20°K/minute and cooled as rapidly as possible to 10°K. The absorption spectrum was remeasured, and is shown as curve (2) of Fig. 4. The difference of curves (2) and (1) is plotted as curve (5). Curve (5) has a minimum at 3.4 eV (365 m μ) where the maximum of the absorption band caused by self-trapped holes occurs.⁵ The spin resonance of the self-trapped hole disappears on warming to 43°K, according to Känzig and Woodruff.² One concludes that the absorption band at 345 m μ that is formed on exposure of KCl to x rays at 10°K is not caused by a single center, but is due to the superposition of two or more bands. One of these is an absorption band of self-trapped holes which are formed during the irradiation and disappear on warming the crystal at 54°K.

After obtaining the data of curve (2), Fig. 4, the crystal was warmed to 76°K and recooled rapidly to 10°K. The optical density of the crystal after this procedure is shown by curve (3) of Fig. 4, and the difference between curves (3) and (2) is shown as curve (6). Curve (6) has a minimum of 3.7 eV. One concludes that this is the location of the maximum of the optical absorption band due to *H* centers, since the spin resonance of *H* centers disappears at 56°K.² The absorption band with a maximum at 3.54 eV in curve (3) is attributed primarily to *V*₁ centers with a small contribution from self-trapped holes. Spin-resonance studies indicate that on warming an irradiated crystal there is a reappearance of self-trapped holes between 50 and 60°K.²

After the data of curve (3), Fig. 4, were obtained, the crystal was warmed to 136°K and cooled to 10°K. The optical density after this procedure is shown as curve (4) of Fig. 4. The *V*₁ absorption band has disappeared as expected.

The spectral region of the *F* and *F'* bands is shown in Fig. 5. Curve (1) shows the optical density of a KCl crystal after exposure to x rays at 10°K. No optical absorption in the *F'* region is detectable after x irradiation at liquid helium temperatures.^{1,8} After warming the crystal to 48°K and recoiling to 10°K, the optical density at the peak of the *F* band had decreased by approximately 25%. As curve (5), of Fig. 5 shows, there was a small increase in the optical density in the near infrared region of the spectrum where the *F'* band is located. The optical density at 10°K, after warming the crystal to 67°K, is shown as curve (3). The *F* band has decreased by about 15%. Curve (6), the difference between curves (2) and (3), indicates there was no detectable change in the optical density in the spectral region of the *F'* band. The result of a subsequent warming of the crystal to 130°K and recoiling to 10°K is shown by curve (7), the difference between curves (3) and (4). There was a decrease of about 15% in the magnitude of the *F* band, and a decrease in the optical density in the spectral region of the *F'* band as a result of this procedure.

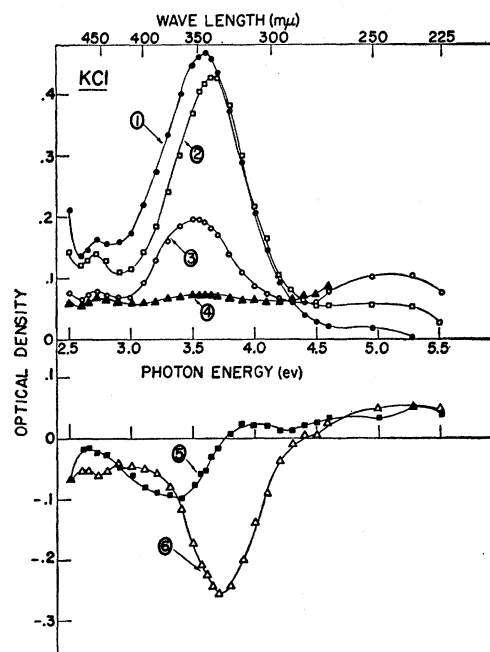


FIG. 4. Ultraviolet absorption spectrum of KCl exposed to x rays at 10°K and annealed at higher temperatures. (1) after irradiation with x rays at 10°K, (2) after warming to 48°K, (3) after warming to 76°K, (4) after warming to 136°K. Curve (5) is the difference of curves (2) and (1). Curve (6) is the difference of curves (3) and (2). Crystal thickness 3.1 mm.

DISCUSSION

Spin resonance and optical data establish that *F* and *H* centers and self-trapped holes are formed by exposing KCl to x rays at 10°K. If *F'* centers are formed, their concentration is so small as to be undetectable optically. It is not known if the center responsible for the *V*₁ absorption band is formed. If it is not formed during x irradiation at 10°K, the present data indicate that it is formed on subsequent annealing at higher temperature. In the following, some speculations are offered to explain the observed bleaching and generation properties of the *H* center.

Känzig and Woodruff² have posulated the formation of interstitial negative halide ions during x irradiation at 10°K. They assume that at 42°K the interstitial negative halide ion loses an electron and becomes an *H* center. The released electron may annihilate self-trapped holes or convert *F* centers to *F'* centers. It is possible, however, that the center assumed by Känzig and Woodruff to be responsible for the *V*₁ absorption band is formed at 10°K. Since this center is, according to Känzig and Woodruff, a chlorine molecule in a negative ion vacancy, the capture by it of an electron will convert it into an *H* center. According to the present speculation, the electrons that yield the observed current at 43°K are responsible for the increase in the *H* center concentration at 43°K² by converting the Känzig-Woodruff centers¹¹ into *H* centers. The observed decrease in the concentration of self trapped holes at 43°K is due to annihilation by electrons. These electrons are assumed to come from shallow traps which may or may not be interstitial negative halide ions.

A tentative explanation of the observed effects at 56°K may be offered in the following manner. It is assumed that the *H* center, an interstitial chlorine atom, becomes mobile at this temperature and diffuses to a neighboring *F* center where mutual annihilation occurs. The recombination energy ionizes the *F*-center electron which is the cause of the 56°K current peak. A self-trapped hole is left at or near the site of the original *F* center. The observed increase in the concentration of self-trapped holes at 56°K is explained in this manner. It is also possible that mobile *H* centers diffuse to negative ion vacancies and combine with them. Self-trapped holes will be formed by such a reaction. It is necessary to assume that the freed electrons react with hole centers and not with *F* centers to explain the nonappearance of the *F'* band at 56°K.

¹¹ This is the chlorine molecule in a negative ion vacancy.

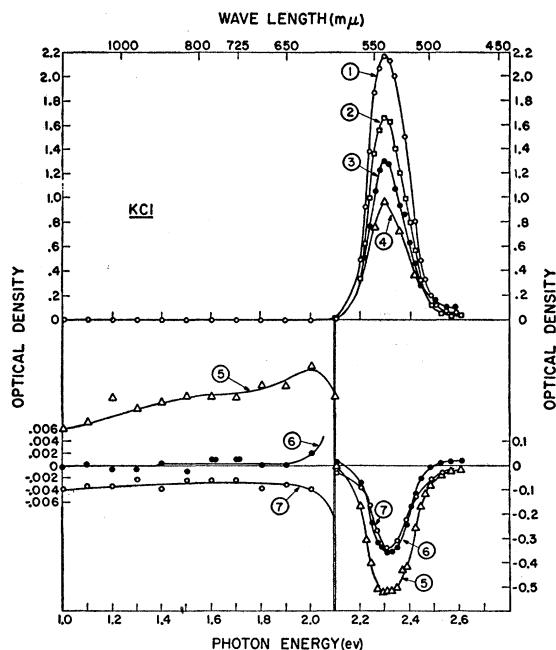


FIG. 5. Visible and near infrared absorption spectrum of KCl exposed to x rays at 10°K and annealed at higher temperatures. (1) after irradiation with x rays at 10°K, (2) after warming to 48°K, (3) after warming to 67°K, (4) after warming to 130°K. Curves (5), (6), and (7) are the differences between (2) and (1), (3) and (2), (4) and (3), respectively. Crystal thickness 2.7 mm. Note that the optical density scale is not the same for all curves.

Känzig and Woodruff² have suggested that an electron is thermally released from an *H* center at 56°K and that the electron is captured by a neighboring *F* center to form an *F'* center. This suggestion predicts the appearance of the *F'* band, and does not offer an explanation for the observed appearance of self-trapped holes. It further predicts that the *V*₁ center of Känzig and Woodruff, a chlorine molecule in a negative ion vacancy, is formed at 56°K as a result of the loss of the electron by the *H* center. On the other hand, the hypothesis given here for the disappearance of *H* centers at 56°K does not predict the formation of the Känzig-Woodruff *V*₁¹¹ centers at that temperature. For this reason, it is suggested that these centers are formed during exposure to x rays at 10°K but it is not required that they are responsible for the *V*₁ absorption band.

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