has recently been discussed by Bowe.[11] According to this interpretation for intermediate E/p_0 values generally >0.1 but <1.0 V/cm$\times$Torr where the average electron energy is many times the value of kT, the functional relationship between the drift velocity and E/p_0 is determined by the momentum transfer cross section for elastic collisions. If in this region the cross section does not decrease with energy, then the drift velocity varies with E/p_0 less than the power unity. With increasing E/p_0, a critical E/p_0 value is reached corresponding to the onset of inelastic collisions. As a result of the inelastic collisions tending to stabilize the random energy, a linear relationship between the drift velocity and E/p_0 is initially observed above the critical E/p_0 value. From Fig. 4, according to this interpre-

tation, the critical E/p_0 value in cesium corresponding to the onset of inelastic collisions appears to be ~ 2.0 V/cm$\times$Torr. Only for very low E/p_0 values, generally <0.1 V/cm$\times$Torr, where the electrons are in thermal equilibrium with the gas atoms, should any gas temperature dependence[10] be observed. The extension of electron-drift-velocity data in cesium down into this interesting energy region must await further experimental investigation.

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Thermoluminescence of X-Ray and Ultraviolet Excited CsBr Crystals*

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(Received 2 April 1964)

Thermoluminescence produced both by x irradiation of uncolored crystals and by ultraviolet irradiation of additively colored single crystals of CsBr has been studied. Glow curves were obtained over the temperature range of 90–400°K and correlated with F-band absorption. A small amount of thermoluminescence was found in nonadditively colored crystals subjected to intense ultraviolet radiation. Glow-peak temperatures and activation energies are listed.

INTRODUCTION

MOST color-center studies have been concerned with face-centered cubic NaCl-type crystals.[1] Only quite recently have investigations been carried out on color centers in x-rayed and additively colored simple cubic CsCl-type alkali halides, in particular CsBr.[2-4] Thermoluminescence studies have been reported for KBr,[5] KCl,[5-7] and NaCl.[8]

The present work involved a study of glow curves obtained in x- and ultraviolet-irradiated CsBr single crystals over the range from liquid-nitrogen temperatures to above 400°K. The positions of the glow-curve peaks in CsBr crystals from three commercial suppliers, the nature of the luminescence, activation energies for some of the glow peaks, and correlations with F-band absorption were determined for the two modes of excitation.

EXPERIMENTAL PROCEDURES

For both thermoluminescence and optical absorption measurements, single crystals of CsBr were mounted in an evacuable cryostat (patterned in part after that described by Braner and Halperin[9]), placed between the monochromator and the photomultiplier housings of a Beckman DU spectrophotometer. Glow curves were obtained on a Varian recorder connected across a resistor inserted in the meter circuit of the spectrophotometer. For large signals the response of the recorder was quite nonlinear. Optical absorption measurements were made through quartz windows in the sides of the cryostat which were heated to a temperature somewhat above room temperature to prevent the formation of vapor on the quartz windows and to thermally isolate the photomultiplier from the crystal

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and its holder at liquid-nitrogen temperatures. In addition, a vapor trap was used inside the cryostat to prevent condensable vapors from giving rise to false absorption measurements. After the crystal was placed in its holder and the cryostat was evacuated, but before the crystal holder was cooled to liquid-nitrogen temperatures, the vapor trap was cooled to this low temperature. The crystal could be rotated out of the beam to a point near a side window of thin Mylar for x irradiation. Ultraviolet irradiations were made through a quartz end window by either the hydrogen lamp through the Beckman DU monochromator or by an iron spark rich in lines in the 190–220-mμ range.

Single crystals from Semi-Elements, Harshaw and Isomet were studied. Plates approximately $20 \times 10 \times 2$ mm thick were sawn from larger crystals and polished prior to irradiation. The crystal temperature was recorded with an iron-Constantan thermocouple in good thermal contact with the outer face of the crystal. A reference thermocouple was placed in a Dewar containing liquid nitrogen for low-temperature irradiations, and in an ice-water mixture for room-temperature irradiations. The iron-Constantan thermocouple was calibrated using the freezing points of various organic and inorganic liquids. The crystal holder contained a heating element by means of which the crystal could be heated at various rates in glow-curve determinations. Generally heating rates were from 20–25°/min. X irradiations were made with a Philips copper target tube operated at 40 kVp, 20 mA, or a molybdenum tube operated at 50 kVp, 20 mA. All exposures were of 10-min duration. The ultraviolet irradiation was accomplished by two-minute exposures to the very intense light of an iron spark.

Rough determinations of the spectral distributions of the various glow peaks were obtained using an ultraviolet transmitting filter (Corning S7–54) and visible transmitting filters (Corning S4–96 and S3–74) placed between the crystal and the blue photomultiplier tube
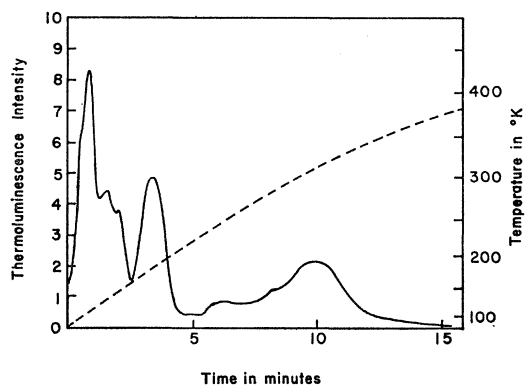

FIG. 1. Recorder trace of typical glow curve of CsBr single crystal colored by 10 min. of x irradiation (Cu target, 40 kVp, 20 mA) at liquid-nitrogen temperature. The corresponding heating curve of temperature versus time is shown as a dashed line.

of the spectrophotometer. The output of the photomultiplier was amplified by the Beckman circuit and the voltage across the null meter was fed into a recorder.

RESULTS

A. X-Rayed Crystals

The recorder trace of a typical glow curve in CsBr is shown in Fig. 1. The heating curve of temperature versus time is shown on the same graph. The most prominent peaks are the low-temperature ones. X irradiations were carried out at both liquid-nitrogen and room temperatures. Room-temperature irradiation considerably enhanced those peaks occurring above that temperature (see Fig. 2).
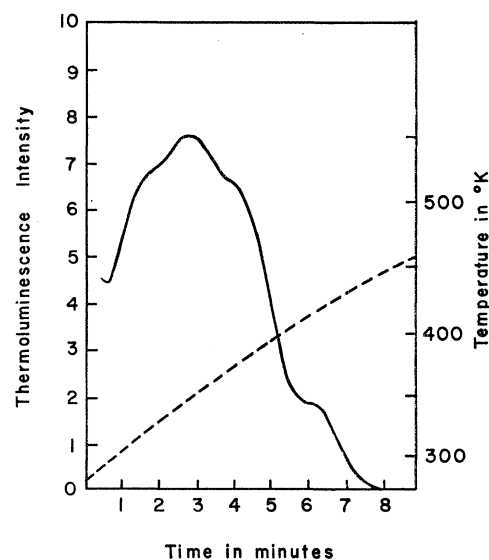

FIG. 2. Recorder trace of glow curve of CsBr crystal colored by 10 min of x-irradiation (Cu target 40 kVp, 20 mA) at room temperature. The corresponding heating curve of temperature versus time is shown as a dashed line. The peaks above 310°K can now be resolved. The actual intensity of thermoluminescence cannot be directly compared with that of Fig. 1 since different phototube sensitivities were used.

To assist in differentiating the various glow peaks, several techniques suggested by Halperin's work[6] were employed: the use of filters, thermal pretreatment which enhances some peaks over others, partial bleaching with F light (645 mμ) prior to warming the crystal and warming past one or several glow peaks with a subsequent cooling and later warming. All of these devices aided in obtaining the glow peaks for CsBr listed in Table I. Data on crystals from three different suppliers of crystals are tabulated.

Several of the same peaks occur in crystals from all three sources. The data for Isomet crystals were fragmentary, and hence not as reliable. The 153°K peak was difficult to resolve from the 145°K peak, and this could be done only in the Semi-Elements crystals. The

212 and 230°K peaks were very weak in comparison with other peaks, and again could be resolved only in Semi-Elements crystals.

The spectral distribution of some of the peaks are as follows: the 105, 180, and 355°K predominantly ultraviolet; the 128, 145, 153, 255, 290, and 325°K mainly visible.

In an attempt to relate the various luminescent glow peaks to color centers, absorption measurements were made in the region of the most prominent absorption band of CsBr, the so-called F band, after 10 min of x irradiation, and after successively warming to 120, 160, 190, and 270°K. All absorption measurements were made at liquid-nitrogen temperatures. Figure 3 is a plot of changes in optical absorbance in the range from 400 to 750 mμ after successive heatings. Figure 4 shows the optical absorbance immediately after irradiation and again after the final heating to near room temperature.
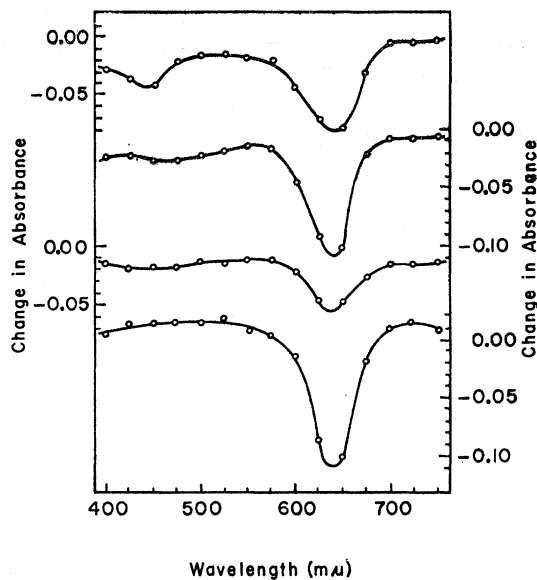

Wavelength (mμ)

FIG. 3. Change in optical absorbance of CsBr crystal after successive heatings to the indicated temperatures and subsequent coolings to liquid nitrogen temperature for absorbance measurements. Ten minutes of x-irradiation at liquid-nitrogen temperatures preceded the initial heating.

TABLE I. Temperatures, T_g, in °K of the thermoluminescent glow peaks.

Semi-Elements	Harshaw	Isomet
105°	105°	105°
128	128	128
145	144	...
153	...	...
180	180	185
212	212	...
230	...	...
255	255	250
290	290	...
310	310	...
325	325	...
355	360	...
380	380	...
415	...	...

Considerable variation in relative intensities of the various peaks were observed in the crystals from the three suppliers.

B. Additively Colored Crystals Exposed to Ultraviolet Radiation

Single crystals of CsBr were additively colored by heating in potassium vapor for twelve hours at 500°C using the well-known differential heating method. Prior to each irradiation with ultraviolet, the crystals were heated to 500°C in air for two minutes and then quenched to room temperature. Following this, the crystals were brought to liquid-nitrogen temperatures, and exposed to weak ultraviolet light, 220 mμ, for 10 min with a wide open slit in the Beckman DU spectrophotometer. This is the lower useful limit with this instrument. The luminescent peaks observed were much weaker than those obtained after x irradiation. Irradiation with ultraviolet light of 280 mμ still produced a little luminescence at the most prominent peak. Irradiation with the very intense light from a $\frac{1}{4}$-in. iron

spark which is rich in lines in the range from 190 to 220 mμ produced a greatly enhanced luminescence, but, still somewhat weaker than that produced by x irradiation.
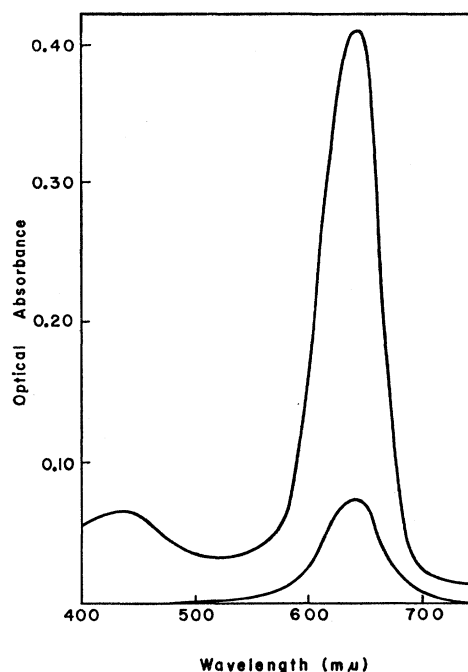

Wavelength (mμ)

FIG. 4. The optical absorbance spectrum of CsBr immediately after 10 min of x irradiation at liquid-nitrogen temperature (upper curve) and after heating to near room temperature with subsequent cooling to liquid-nitrogen temperature (lower curve).

TABLE II. Temperatures T_g of glow peaks in both additively colored and uncolored crystals excited by an iron spark.

Additively colored T_g	112°	128°	139°	177°	⋯	250°	325°	368°
Uncolored T_g	⋯	122°	147°	183°	205°	250°	315°	365°

The temperatures of the glow peaks in additively colored crystals are given in Table II. No decrease in F-band absorption was observed after completing a glow curve, as was found with x-rayed crystals.

C. Uncolored Crystals Exposed to Ultraviolet Radiation

Attempts to produce thermoluminescence in untreated CsBr single crystals by exposure to 220-mμ light from the hydrogen lamp in the Beckman spectrophotometer for 10 min were unsuccessful. However, exposure of virgin CsBr crystals to an intense iron spark again gave rise to thermoluminescence.[10] The magnitude of the observed peaks was of the same order as those produced in additively colored crystals exposed to the iron spark, but again somewhat less than those due to x irradiation. The peak temperatures of the glow peaks in uncolored crystals are included in Table II. No change in optical absorption could be detected in any of these crystals after exposure to the iron spark or after completion of the glow curve.

The spectral distribution of the emission from the 122, 147, 183, and 205°K peaks was predominantly in the ultraviolet, and that from the 250°K peak mainly in the visible.

CONCLUSIONS

There is a striking agreement between the positions of the peaks due to the two modes of excitation. Not all the peaks are observed in the ultraviolet excited crystals, but those that do occur agree quite closely with peaks produced by x-ray excitation, i.e., within the ±5° estimation of the order of precision of peak temperature determination.

The emission of luminescence in x-ray excited crystals is definitely accompanied by a decrease in F-band absorption as is evident in Fig. 3. Therefore, it seems evident that these glow peaks must be associated with transitions between energy levels characteristic of the crystal and its defects, not due to small amounts of impurities.

The thermal luminescence resulting from ultraviolet irradiation is not well understood. If it be due to im-

purities, the fortuitous agreement with the glow peaks in x-ray excited crystals where a definite correlation with F-band absorption exists would be hard to explain. Additional evidence for an association of glow peaks with color centers occurs in additively colored CsBr crystals. Very low levels of ultraviolet radiation will produce thermoluminescence in these crystals, but not in uncolored crystals. Presumably the color centers are responsible for this difference. Certainly much more work needs to be done before a clear answer is available.

Corresponding peaks in x-rayed and in ultraviolet-irradiated crystals produce a somewhat different spectral emission which seems to indicate that different transitions are taking place after the initial thermal excitation.

Thermal activation energies were calculated for some of the glow peaks. We employed a method used by Halperin[6] which he ascribes to Urbach[11] and Lushchik.[12] The activation energy E_T of a glow peak at temperature T_g is approximately $E_T = kT_g^2/\delta_g$, where k is the Boltzmann constant and $\delta_g = T_2 - T_g$, T_2 being the temperature of half-intensity on the falloff of the peak. It was often very difficult to isolate the various glow peaks even using the methods referred to earlier. The individual calculations for a given peak often showed a considerable variation. Values for activation energies at the various glow peaks are as follows: 0.27 eV, 105°K; 0.31 eV, 145°K; 0.40 eV, 153°K; 0.32 eV, 180°K; 0.54 eV, 255°K; 1.13 eV, 355°K; 1.04 eV, 380°K.

Note added in proof. In Fig. 3 the four curves of change in optical absorbance were obtained after successive heatings to temperatures, from top to bottom respectively, of 120, 160, 190, and 270°K.

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