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Optical Absorption and Thermoluminescence of X-Ray-Irradiated KBr Crystals at Room Temperature

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Two thermoluminescence peaks are observed in KBr crystals that are x irradiated at room temperature. The 185 °C peak can be removed by annealing the crystal for several hours at 400 °C and is attributed to highly localized defects. The 152 °C peak is proposed to be due to the liberation and recombination of the electrons from the *F* centers. The single glow peak obtained at 152 °C is analyzed by the area method and initial-rise method to give thermal trap depths of 0.55 ± 0.04 and 0.61 ± 0.02 eV, respectively. The optical absorption measurements indicate that *F* and V_2 centers are formed in the crystal during the x-irradiation process. The thermoluminescence spectra has been analyzed to consist of one narrow emission band centered at 3.08 eV. This thermoluminescence process is found to be nearly first order and an energy-level diagram is proposed to correlate the optical absorption and emission spectra.

I. INTRODUCTION

Mehendru and Radhakrisha[1] have previously reported thermoluminescence (TL) of pure and impurity-doped KBr crystals. Two types of *F* centers[2-10] have been postulated to explain a variety of experimental data. The fast stage of *F* centers are the ones formed by electrons trapped at anion vacancies initially present in the crystals, whereas the slow stage are electrons trapped at anion vacancies created during the x-irradiation process. Jain and Mehendru[10] have postulated an intimate correlation between the growth of the *F* centers and the growth of the areas under the thermoluminescence peaks in KCl. In KCl crystals a heating rate of 40 °C min^{-1} gave two peaks at 135 and 190 °C and have been interpreted by Jain and Mehendru as corresponding to the growth of the fast and slow stages of the *F* centers, respectively. For a heating rate of 40 °C min^{-1} in pure KBr crystals, Mehendru and Radhakrisha[1] have observed two peaks at 90 and 150 °C which they attempted to interpret as the growth of the fast and slow stages of the *F* centers, respectively.

Guilani, Gustinetti, and Stella[11] report that lithium impurities in KBr crystals stabilize interstitial halogen atoms at 300 °K in the form of V centers which have a maximum optical absorption peak at 306 nm. The number of stabilized interstitials is limited by the diffusion of anion vacancies and their recombination with the interstitials. As a result the lithium impurities introduce a rapidly saturating first stage in the *F*-center growth curve.

Murti, Murthy, and Ramasastry[12] report four TL glow peaks in x-ray-irradiated KBr and KBr : Cu crystals at room temperature. They report that each glow peak has first-order kinetics for a heating rate of 40 °C min^{-1}. The peaks occur at 86, 104, 119, and 186 °C with thermal trap depths of 0.86, 0.97, 1.00, and 1.05 eV, respectively. The 104 °C peak has been related to the presence of Cu^+ ions in the crystal. They also deduce that the thermal excitation energy of the *F* centers to the relaxed excited state to be about 1.7 eV. Murti[12] *et al.* also report a 160 °C peak to be dominant in crystals obtained from Hilger and Watts Co.

Jain and Jain[13] report that in additively colored KBr crystals the excess electronic conductivity is due to *M* centers below 150 °C and to colloids between 300 and 450 °C. They measured the optical and thermal stability of the *F*, *M*, and *R* bands.

This investigator has observed only a 152 °C peak (40 °C min^{-1} heating rate) in spectroscopically pure KBr crystals obtained from the Harshaw Chemical Co. A 185 °C peak also is present initially in the crystals but can be annealed out by heating in the oven at 400 °C for several hours. A 90 °C shoulder could be made to appear in the TL glow curve if the crystal was rapidly quenched from 600 °C to room temperature. This 90 °C shoulder is attributed to an impurity since it saturates rapidly and the 152 °C peak is attributed to the *F* center. The 185 °C peak is probably due to localized defects producing a small internal stress that can be removed by annealing.

The trap depth of the 152 °C peak is calculated by the "initial-rise method" and by the area method given by Halperin and Braner.[14] The process is nearly first order for most of the data.

The TL emission spectra is a narrow band centered at 3.08 eV and is the same for both the 152 and 185 °C peaks. The optical density of the *F* band is approximately linear when plotted as a function of the TL peak intensity indicating a strong correlation between this TL peak and the *F* centers. The optical absorption measurements are correlated with the emission spectra using the 7.13-eV conduction-band–valence-band transition.

II. EXPERIMENTAL

Single crystals 5×5×0.5 mm of spectroscopically pure KBr were obtained from the Harshaw Chemical Co. The x-irradiation was carried out with a Philips x-ray-diffraction unit (Cu target) operating at 35 kV with beam currents between 10-20 mA. Each crystal was colored on one side only and a nickel filter was used so the copper $K\alpha$ line was the principal source of x irradiation.

The optical absorption measurements were performed with a Coleman 124 Perkin-Elmer double-beam spectrophotometer. Optical absorption measurements were performed before and after x irradiation and after the TL experiment.

An RCA 6199 photomultiplier tube powered by a Power Design 2-kV–10-mA power supply, a Keithly 600A electrometer, two Varian G-14 strip chart recorders along with a Houston Instrument omnigraphic 2000 *X-Y* recorder were used for detecting and recording the thermoluminescence intensity, temperature, and heating rate. A 200-W soldering iron with a variac was used to heat the crystal, and a copper-constantan thermocouple with the reference junction at 0 °C was used to measure the temperature. The TL spectra were analyzed with an ultraviolet-infrared monochrometer model No. F-11-20 made by Orion Optics Corp. At room temperature when the monochrometer was placed in front of the photomultiplier the dark current was many times greater than the TL-induced current. This difficulty was obviated by packing dry ice around the photomultiplier tube and thereby reducing the dark current to an acceptable level.

III. RESULTS AND DISCUSSION

Typical optical absorption and TL curves are shown in Figs. 1 and 2. The *F*-center absorption band has its onset at 780 nm and reaches its maximum at 625 nm while the V_2 center has its onset at 308 nm (4.02 eV) and reaches its maximum at 265 nm (4.67 eV). It is possible that V_3 centers are also present but the broadness of the V_2 band is enough to make any separate absorption of the V_3 center not discernable. If the crystal is annealed for several hours at 400 °C and after the crystal is allowed to cool slowly to room temperature, the *F*-center optical absorption and the 152 °C TL peak are increased after exposing the crystal to the same x-ray dose while keeping the geometry nearly the same as possible. The *F*-center optical absorption and the 152 °C TL peak decreased after successive

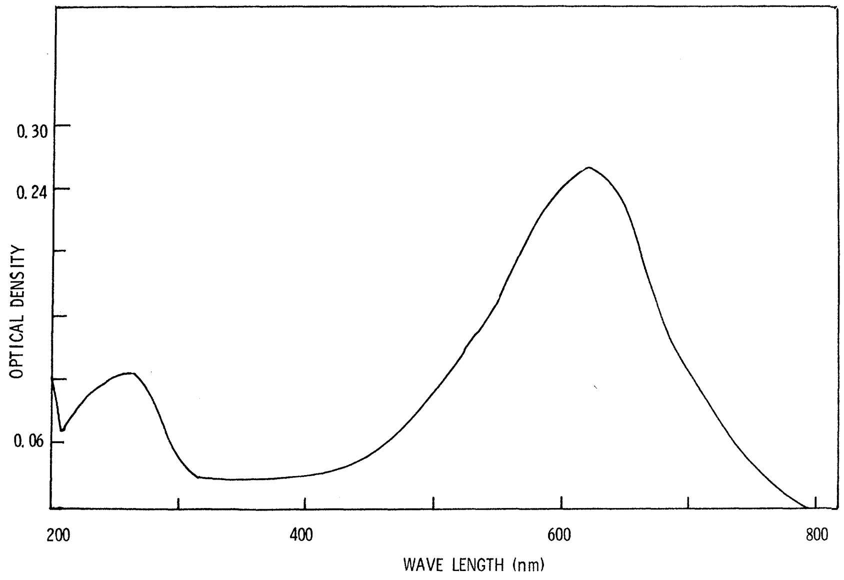

FIG. 1. Optical absorption spectra for spectroscopically pure KBr crystals at room temperature. Optical density as a function of wavelength measured in nm. The broad band at 625 nm is due to the *F* center whereas the smaller absorption occurring at 265 nm is due to the V_2 center.

cycles of irradiation and measurement. This phenomenon can be explained in terms of annealing out the initial vacancies that contribute to the *F*-center absorption. A graph of the 152 °C TL peak intensity versus the *F*-center optical density is shown in Fig. 3. This nearly linear relationship suggests that this TL peak is due to the destruction of *F* centers. After many exposures the 152 °C peak stopped decreasing and the 185 °C peak started to reappear probably due to the cumulative x-ray dose causing defects in the crystal. No optical absorption measurement could be found to correspond to the 185 °C peak. A 90 °C peak would also appear after many runs or after rapidly quenching the crystal to room temperature from 600 °C. This peak also had no corresponding optical absorption peak and is probably due to a divalent impurity entering the crystal. All attempts to relate the magnitude of the V_2 absorption to the *F*-center optical density and the TL intensity were unsuccessful.

The initial-rise method is applied to determine the trap depth and is shown as a graph in Fig. 4 which yields a value of 0.61 ± 0.02 eV. The uncertainty is due to the standard deviation of the slope

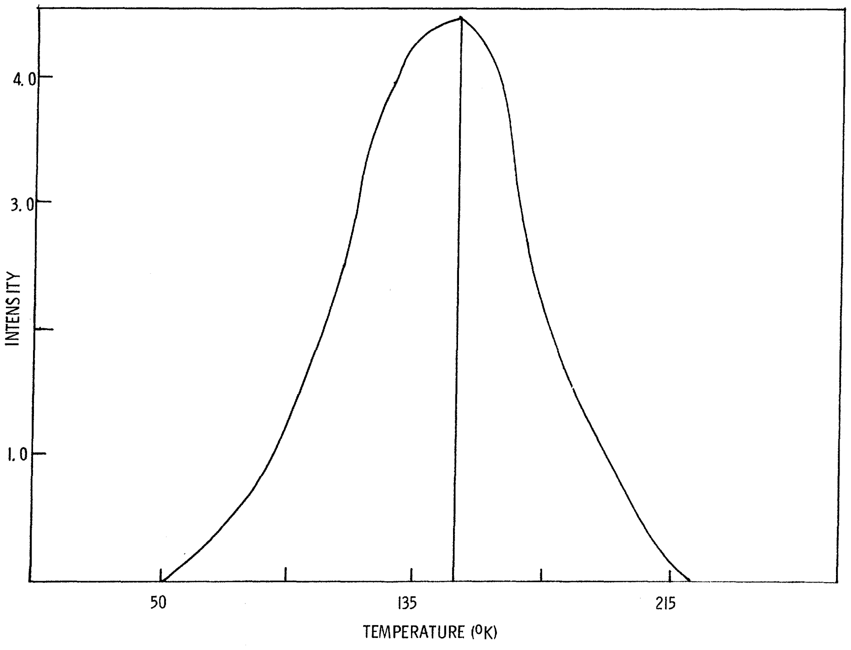

FIG. 2. TL intensity (arbitrary units) vs temperature (°C).

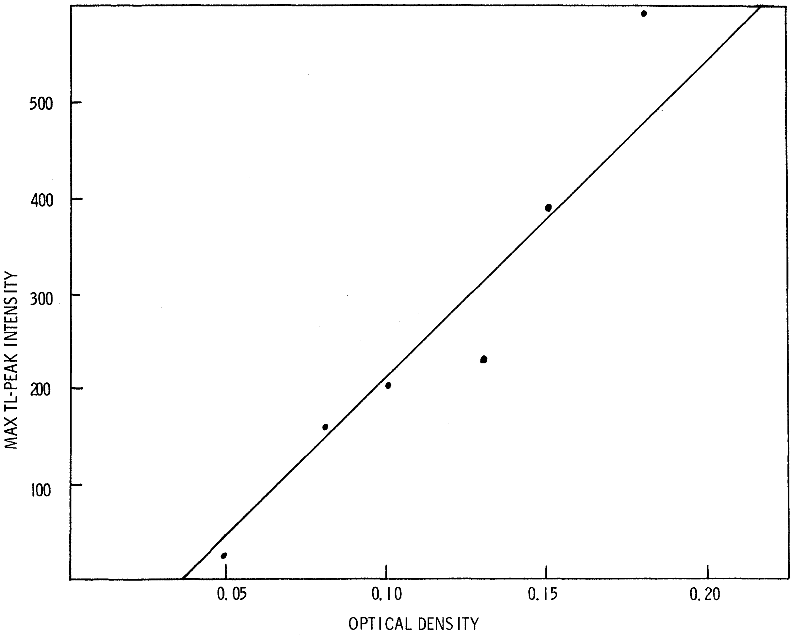

FIG. 3. 152 °C TL peak intensity (arbitrary units) vs F-center optical density. The TL peak intensity was chosen instead of the integral of the TL curve since the 90 and 185 °C peaks contributed to the area.

as determined from a least-squares fit. Several initial-rise methods were performed with values ranging from 0.52–0.63 eV.

Halperin and Braner[14] give a formula for the activation energy associated with a thermoluminescence peak

$$E=qkT_g^2/\delta\ ,$$

where T_g is the peak temperature, δ the half-width of the peak on the high-temperature side, and k Boltzmann's constant. q is a factor determined by the kinetics: $q\leq 1$ for monomolecular decays and $1\leq q\leq 2$ for bimolecular decays. Inserting $E=0.61$ eV and the measured values for δ and T_g, q is determined to be 0.98. Several other determinations of q varied from 0.78 to 0.99. The decay is thus expected to be monomolecular and nearly first order.

Halperin and Braner[14] also give a formula for calculating the trap depth in terms of the peak intensity $I(T_g)$, the peak temperature T_g, the area of the glow curve from T_g to infinity $A(T_g,\infty)$, and the Boltzmann constant k:

$$E=kT_g^2 I(T_g)/A(T_g,\infty).$$

The curve in Fig. 2 yields an activation energy of 0.55 eV. Several other determinations were made by this area method and the values ranged from 0.48–0.65 eV.

R. T. Whitlock[15] has extended the Halperin equations to show that for a true-first-order process the ratio of the thermoluminescent areas $A(T_g,\infty)$ to $A(0,\infty)$ is given by

$$[A(T_g,\infty)/A(0,\infty)]=e^{-(1-2kT_g/E)}\ .$$

The curve in Fig. 2 gives a ratio of 0.41 which agrees exactly with the theoretical calculation of 0.41.

Eby, Teegarden, and Dutton[16] give the principal absorption maxima of KBr at room temperature to be 6.60, 7.13, and 8.5 eV. Figure 5 is an energy-level diagram showing the possible transitions that correspond to the optical absorption and TL spectra

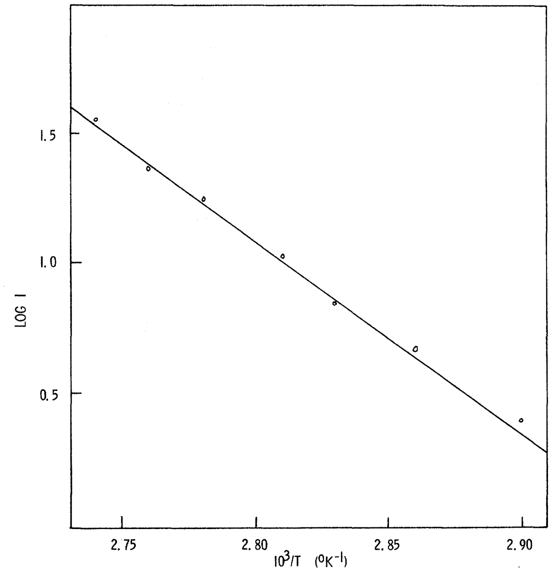

FIG. 4. Log of the TL intensity vs the inverse of the absolute temperature times 1000.

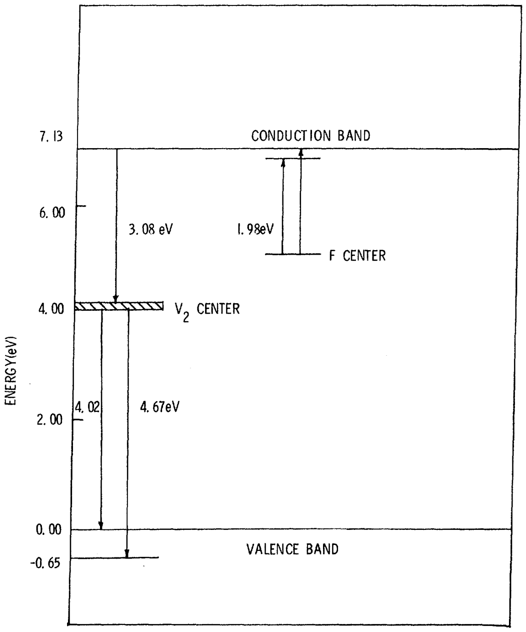

FIG. 5. Proposed energy-level diagram showing the optical absorption and TL emission spectra. The energy is in eV as measured from the top of the valence band.

measurements. The *F* center has an optical trap depth near 1.98 eV (625 nm) corresponding to the excited state of the *F* center that is near the 7.13-eV conduction band and a proposed thermal-trap depth of 0.61 eV. This energy difference between 1.3–1.4 eV is larger than the 1.0-eV difference for KCl. However, it is not an unreasonable difference. It is proposed that the electrons recombine with the V_2 center directly from the conduction band giving rise to the TL and the narrow spectral band centered at 3.08 eV (401 nm). The total half-width of the band is 2.91–3.25 eV. This recombination radiation indicates that the width of the V_2 band is about 0.34 eV, whereas the optical absorption measurements indicate it has a width of over 1.0 eV. The optical absorption of the V_2 band begins at 4.02 eV (308 nm) and reaches its maximum at 4.67 eV (265 nm). The 4.02-eV absorption could perhaps be interpreted as the threshold energy for the hole to jump to its excited state that is assumed to be very close to the valence band or an electron to jump from the valence band to the hole center. The maximum absorption occurs at 265 nm which means the hole has enough energy to jump 0.65 eV below the top of the valence band or an electron 0.65 eV deep in the valence band makes a transition to the hole center. The reason[17] for this maximum absorption could be due to the momentum distribution of the electrons in the valence band. The width of over 1.0 eV is then probably due to the valence band and is not intrinsic to the V_2 center as seen by the narrow TL emission spectrum. If the emission band 3.08 ± 0.17 eV is added to the threshold energy of 4.02 eV, the resulting answer is 7.10 ± 0.17 eV which is very near the 7.13 absorption maximum.

This proposed energy-level diagram assumes that there is no significant modification of the bands in the vicinity of the trapped hole. This assumption does indeed seem unreasonable if the V_2 center is charged with respect to the lattice. However, the energy difference in the vicinity of the V_2 center and the valence band could be uncertain by the 0.65 eV as indicated in the above discussion, if the hole makes a transition just to the top of the valence band.

IV. CONCLUSIONS

The proposed energy-level diagram fits the TL and absorption measurements well. The thermoluminescence process occurring in these pure KBr crystals is almost first order. The 152° peak is attributed to the *F* center while the 90 and 185 °C peaks are probably due to other defects.

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