Photoproduction of V_1 Centers in KBr Crystals*

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KBr crystals have been irradiated with monochromatic light of a wavelength of 190 millimicrons at liquid nitrogen temperature. When an electric field is applied to the crystal and its temperature subsequently raised, a burst of current is observed at $-150°C$, which corresponds to the destruction of V_1 centers. Evidence is presented that F centers and V_1 centers are created simultaneously by absorption of photons in the tail of the fundamental band of the crystal.

INTRODUCTION

ABSORPTION of light in the tail of the fundamental band of alkali-halide crystals does not give rise to photoconductivity.[1] Smakula[2] has further found that photons absorbed in the same spectral region generate F centers. The quantum yield of this reaction is unity at the beginning of the irradiation and drops to zero when the concentration of F centers has reached a value of the order of 10^{14} cm^{-3}. This experiment suggests[3] that an exciton may migrate from the place where it is created to a place where it may generate an F center, transferring its electron to a negative-ion vacancy. It is the purpose of this work to investigate what happens to the hole associated with the electron in the exciton. A plausible assumption is that the hole becomes trapped to form a type of V center.

The V bands are generally observed in alkali-halide crystals which have been irradiated by x-rays, γ rays, fast electrons, or additively colored in halogen vapor. These bands lie in the ultraviolet region of the spectrum and have been attributed by Seitz to holes associated with different kinds of vacancy aggregates.[3]

The limiting concentration of F centers obtained at liquid nitrogen temperature by ultraviolet irradiation corresponds to an optical transmission in the maximum of the F band of about 98% in a crystal 2 mm thick. As the V bands are much broader than the F band, the optical detection of V centers in the same concentration is difficult. On the other hand, Dutton and Maurer[4] have observed a burst of current during the thermal destruction of V_1 centers in KBr and KCl crystals irradiated with x-rays at liquid nitrogen temperature. The magnitude of the signal depends on both the number of destroyed centers and the schubweg (migration distance) of the charge carriers. The schubweg is likely to increase with a decreasing concentration of centers and it can be expected to be rather large for concentrations of the order of 10^{14} cm^{-3}. Therefore such a method of detection seems particularly suitable in the case of small concentrations, and has been used in the experiments described below.

EXPERIMENTAL

KBr crystals were used because the tail of the fundamental absorption band lies in an easily accessible region of the ultraviolet spectrum. In addition, data on photoproduction of F centers and thermal destruction of V_1 centers are available for KBr, from Smakula's and Dutton and Maurer's work.

The crystals of KBr were supplied by the Harshaw Chemical Company. A plate of approximately $13\times13\times2$ mm was mounted in a cryostat between two electrodes and irradiated at liquid nitrogen temperature with monochromatic light of 190 millimicrons. A Farrand grating monochromator was used with a Hanovia high-voltage hydrogen lamp. The band width was 8 millimicrons. At this wavelength, 60% of the incident light is absorbed by the crystal. The number of incident photons was measured with a calibrated cesium-antimonide photocell and was approximately 2×10^{11} per second. The area of the illuminated surface of the crystal was 12 mm^2. The cryostat and the electrode arrangement are described by Dutton and Maurer[4] and Inchauspé.[5] The temperature of the crystal was measured by a copper-constantan thermocouple fastened to the crystal.

In a typical run, after the crystal had been irradiated at $-185°C$, its temperature was raised at a rate of approximately 0.3°C per second. At the same time, an electric field of 1800 volts/cm was applied to the crystal and the current through a series resistor of 10^{10} ohms was measured with a vibrating reed electrometer. The temperature of the crystal was simultaneously recorded.

RESULTS

Figure 1 shows a current "glow curve" for a crystal of KBr which has been irradiated for three minutes at liquid nitrogen temperature with x-rays (molybdenum target tube, 30 kilovolts, 7 milliamperes). After such a short period of irradiation, it was not possible to detect

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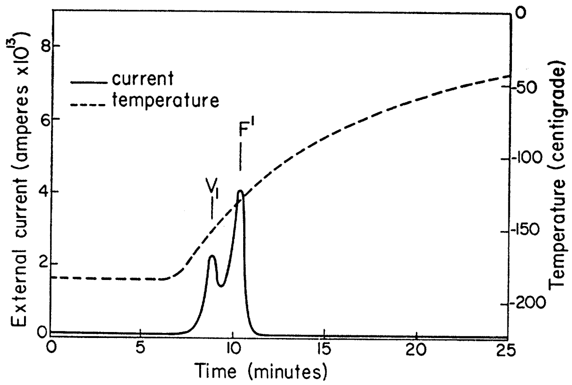

FIG. 1. Current "glow curve" for a crystal of KBr which has been irradiated for 3 minutes with x-rays at liquid nitrogen temperature. The dashed curve shows the variation of temperature of the crystal with time (right-hand scale).

any coloration of the crystal with standard optical equipment. The current glow curve shows two peaks, one at −153°C and the other at −130°C. The comparison with similar curves obtained by Dutton and Maurer indicates that the peak at −153°C is associated with the destruction of V_1 centers and the peak at −130°C with the destruction of F' centers. The burst of current associated with the destruction of F' centers is due to a motion of electrons, whereas the burst of current associated with the destruction of the V_1 centers has been attributed to a motion of holes. Further comparison of Fig. 1 with Dutton and Maurer's experiments shows that the magnitude of the observed bursts of current is about the same in both cases in spite of the fact that the concentration of centers in Dutton and Maurer's experiments was at least one hundred times larger than that in the experiment of Fig. 1. This indicates that for slightly colored crystals, a larger schubweg compensates for a smaller concentration of centers. It may be noted that unidentified bursts of current are observed in Dutton and Maurer's experiments at higher temperatures. Apparently, the centers responsible for these peaks are not created in the first stage of the darkening.

Figure 2 shows a typical current "glow curve" for a crystal of KBr which has absorbed approximately 1.2×10^{14} photons of wavelength of 190 millimicrons. There is only one burst of current at −150°C, corresponding to the destruction of V_1 centers. In addition, the luminescence glow curve (not shown) has a peak at the same temperature, in agreement with the experiments of Dutton and Maurer. As in the case of Fig. 1, it was not possible to detect the V_1 band with standard optical equipment. The limit of accuracy in the optical transmission measurements was about 1%, which corresponds to an upper limit for the concentration of V_1 centers of 3×10^{14} cm^{-3}. The concentration of photoproduced F centers was 1.3×10^{14} cm^{-3}.

In Fig. 3 (upper part) the integrated released charge at −150°C is plotted as a function of the number of photons absorbed per cm^2. Each point refers to a different crystal. For comparison, the lower part of the figure shows Smakula's results on the photoproduction of F centers with monochromatic light of 193 millimicrons. The number of absorbed photons per cm^2 has been used as abscissa instead of the number of absorbed photons per cm^3 in order to allow comparison with the data of Smakula's paper where the thickness of the crystal is not explicitly reported.[6]

The two curves in Fig. 3 are strikingly similar: they both exhibit a saturation when the number of photons absorbed per cm^2 exceeds 5×10^{14}. If one assumes that for small concentrations, the schubweg of the carriers does not depend on the concentration of centers, one is led to the conclusion that the creation of F and V_1 centers is the result of the same elementary process. The most simple suggestion is that at liquid nitrogen temperature, an exciton generates simultaneously one F center and one V_1 center in KBr crystals. The initial quantum yield for the photoproduction of V_1 centers should therefore be unity as in the case of the photoproduction of F centers.

Following the latter assumptions, one can estimate the schubweg of the holes, which is related to the released charge through the formula:

$$w_0 = (q/e)(d^2/V)(1/N), \tag{1}$$

where w_0 is the schubweg per unit electric field, q the charge released in the external circuit, e the electronic charge, V the applied voltage, and N the number of released charges. If one takes N, the number of destroyed V_1 centers, equal to the number of photoproduced F centers as measured optically in our sample,

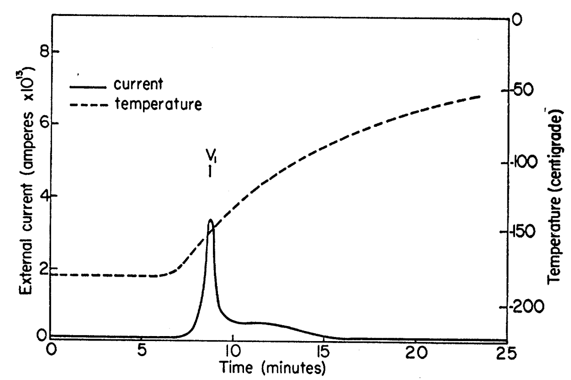

FIG. 2. Typical current "glow curve" for a crystal of KBr which has been irradiated at liquid nitrogen temperature with monochromatic light of wavelength 190 millimicrons. The number of absorbed photons was approximately 1.2×10^{14}. The dashed curve shows the variation of the temperature of the crystal with time (right-hand scale).

[6] The thickness of the crystals used by Smakula can be derived from his data on the absorption. They lead to values of limiting concentrations of F centers which depend on the wavelength of the incident light, and which are larger than the values that we have measured optically.

one has

$$w_0 = 2.7\times 10^{-9}\ \text{cm}^2/\text{volt}. \qquad (2)$$

This value of the hole schubweg can be compared with the value given by Dutton and Maurer.[4] In their crystals, the concentration of F centers, which are supposed to act as traps for holes, was 9×10^{17} cm^{-3}. The hole schubweg was evaluated equal to 3×10^{-11} cm^2/volt, a figure which is two orders of magnitude smaller than (2), probably because of the much larger concentration of centers. Further comparison can be made with the electronic schubweg as given by photoconductivity experiments in the F band.[7,5] It is found that the electronic schubweg is inversely proportional to the concentration of F centers, for concentrations larger than 10^{15} cm^{-3}, and that it reaches a constant value for smaller concentrations. The limiting value of $\eta_a w_0$ is about 10^{-10} cm^2/volt, where η_a is the probability for a photon absorbed in the F band to release an electron. There is some evidence that the value of η_a at liquid nitrogen temperature is between 1/10 and 1/100. The schubweg of the holes is then of the same order of magnitude as the schubweg of the electrons at those low concentrations.

CONCLUSION

The above experiments suggest that in KBr crystals an exciton generates simultaneously an F center and a V_1 center at temperatures where V_1 centers are stable. As no photocurrent is observed during the process, the two centers are created close to each other. In the case of the model proposed by Seitz for the V_1 center of a hole trapped at a positive-ion vacancy, the F and V_1 centers could be generated either from a vacancy pair or from a pair of jogs at a dislocation.

The occurrence of the saturation of the reaction does not result in the creation of new types of centers. In particular, F' centers are not created, even under prolonged illumination. The production of F centers by excitons is not therefore limited by the reverse reaction, namely the destruction of F centers by excitons, at these concentrations.[5,8] Rather the photoproduction of F and V_1 centers involves a type of defect whose supply is limited in the crystals and which is not regenerated as the reaction proceeds.

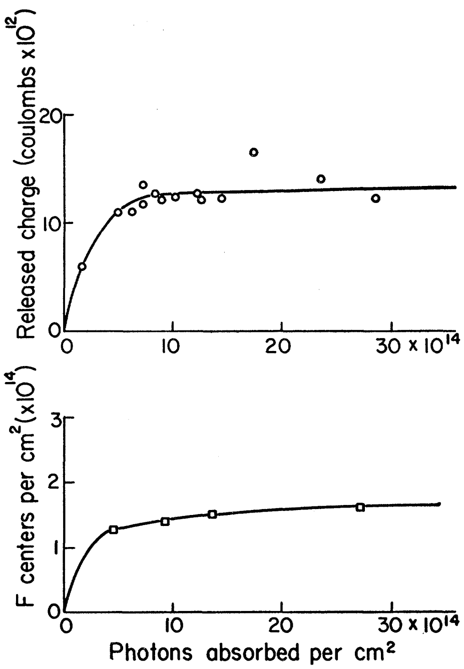

FIG. 3. Upper part: Integrated charge released at -150°C as a function of the number of photons ($\lambda = 190$ millimicrons) absorbed per cm^2 at liquid nitrogen temperature. Lower part: Number of photoproduced F centers per cm^2 as a function of the number of photons ($\lambda = 193$ millimicrons) absorbed per cm^2 at liquid nitrogen temperature (after Smakula).

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