

Stimulated luminescence of KI single crystals

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Luminescence is observed in KI with red and/or infrared stimulation after previous uv preexposure. The results indicate the onset of band-to-band transitions and provide evidence for the thermal dissociation of self-trapped excitons. A commonly observed emission in KI at 3.0 eV is observed through stimulation. A model for this emission is presented.

I. INTRODUCTION

When single crystals of KI are irradiated with ionizing radiation two luminescence bands are observed.¹⁻³ These bands are located at 3.3 and 4.2 eV. When the excitation energy is near the first exciton absorption band a third emission has been reported by several investigators.^{3,4} This emission is at 3.0 eV and is especially strong below 30 K. Both the 3.3-eV and the 4.2-eV emissions are believed to be intrinsic due to the radiative decay of the self-trapped excitons, $^3\Sigma_u^+ \rightarrow ^1\Sigma_g^+$ and $^1\Sigma_u^+ \rightarrow ^1\Sigma_g^+$ transitions, respectively. However, the origin of the 3.0-eV emission is not as clear.

Several models of the low-energy emission have been proposed over the years. These models include luminescence associated with: (1) optically generated defects, (2) energy transfer to impurities or defects by proper (free) excitons, (3) $(V_K + e^-)$ (self-trapped exciton) formation near some nonideal lattice point, and (4) $(V_K + e^-)$ state arrived at via a tunneling mechanism.³⁻⁷ Perhaps the most detailed study of the 3.0-eV emission was done by Nishimura (Ref. 4). His results support (4) whereby a proper exciton may self-trap via two different processes: a tunnel effect to the 3.0-eV state at low temperatures and a thermally assisted process over an energy barrier to the 3.3-eV state.

The work described here reports the results of photostimulated luminescence experiments on single crystals of KI. Photostimulated luminescence is observed by first irradiating the sample with light in the region of the fundamental absorption. Some of the electrons which are excited into the conduction band become shallowly trapped. Subsequent irradiation with red and/or infrared light releases these electrons which then radiatively recombine with holes yielding the luminescence. The results of these experiments

suggest a thermal dissociation of the self-trapped exciton and provide information regarding the nature of the 3.0-eV emission.

II. EXPERIMENTAL PROCEDURE

A schematic of the apparatus is shown in Fig. 1. Direct luminescence is observed by exposing the crystal with uv light from the deuterium lamp which is passed through the preexposure monochromator which has a band pass of 6.0 nm. The direct luminescence is detected by a phototube after passing through the emission monochromator which has a band pass of 12 nm. Both the excitation and emission spectra for the direct luminescence are then recorded on a strip-chart recorder after appropriate dc amplification.

The stimulated luminescence is observed by expos-

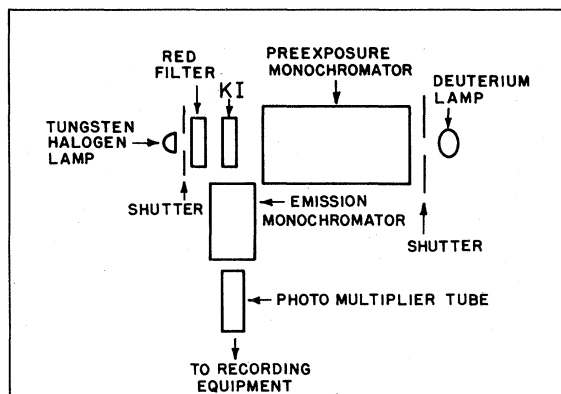


FIG. 1. Experimental arrangement.

ing the sample to uv light for the desired preexposure time, then closing the shutter between the lamp and the preexposure monochromator for a selected period of time (dark time) until a second shutter is opened, allowing the crystal to be flooded with red light. The red light is obtained from a tungsten-halogen lamp that has been filtered to provide $\lambda > 650$ nm. This stimulated luminescence is recorded as a short-lived spike on the strip-chart recorder. Two types of stimulated spectra are obtained in the above manner: (1) preexposure spectra are recorded by fixing the emission monochromator setting and varying the preexposure energy for a fixed preexposure time and dark time; and (2) stimulated emission spectra are recorded by fixing the preexposure monochromator setting and varying the emission monochromator for a fixed preexposure time and dark time.

In order to reduce the background associated with the stimulated luminescence a Corning 7-59 glass filter is inserted between the sample and the emission monochromator when observing the 3.0- and the 3.3-eV luminescence. A Corning 7-54 filter is used when observing the 4.2-eV emission.

The data reported here were taken on samples cleaved from a single block of "pure" KI obtained from the Harshaw Chemical Company. These samples showed slight evidence of TI ($\sim 10^{-9}M$ fraction) when attempts were made to observe the TI emission by excitation in the characteristic TI excitation bands.

III. RESULTS AND DISCUSSION

One of the difficulties associated with the study of the 3.0-eV emission is its close proximity to the 3.3-eV emission. The half widths of both bands are about 0.40 eV which results in an extensive overlap. However, two properties of these bands help to reduce the overlap problem: (1) The relative intensities as a function of temperature are different. At temperatures < 30 K the 3.0-eV band dominates. As the temperature increases the relative intensities of the bands change in a complimentary manner; the 3.0-eV emission decreases as the 3.3-eV emission increases, resulting in a dominance of the 3.3-eV emission at higher temperatures. (2) The excitation spectra of the two bands are different. The low-energy luminescence is excited by light in the exciton absorption region, while the high-energy luminescence is excited predominantly by band-to-band excitation (especially at low temperatures). Both of the above characteristics are illustrated in Refs. 3 and 4.

The stimulated emission spectra for preexposure in the band-to-band region at 15 K yields two bands peaking at 4.20 and 3.35 eV. The preexposure spectra for each of these bands are shown in Fig. 2. Both of these spectra are consistent with the interpretation of the direct luminescence spectra at this tempera-

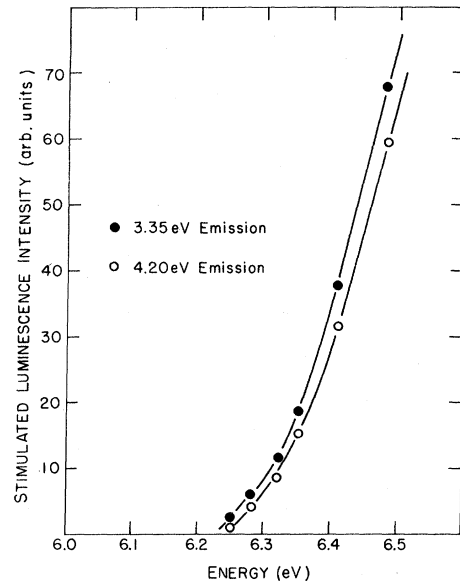


FIG. 2. Preexposure spectra for the 3.35- and the 4.20-eV emissions at 15 K. Preexposure time = 2.0 min; dark time = 2.0 sec.

ture. Namely, they result from a radiative recombination of a conduction-band electron with a self-trapped hole. In the stimulated luminescence case the conduction-band electron comes from the excitation of an electron which became trapped after excitation into the conduction band by a uv photon.

When KI is irradiated at 15 K with 5.76-eV light, which corresponds to an excitation in the low-energy tail of the first exciton band, the stimulated emission spectrum consists of a band peaking at 3.02 eV. This band is shown in Fig. 3 along with the 3.35-eV band for comparison. The preexposure spectrum for the

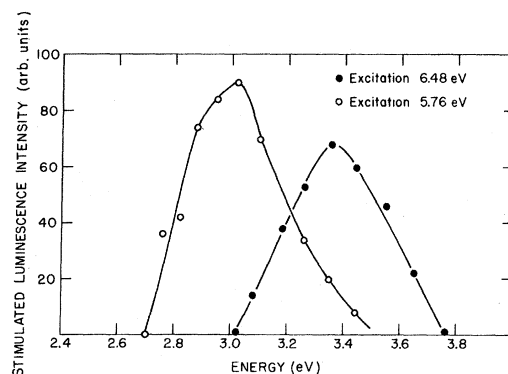


FIG. 3. Stimulated emission spectra for excitation at 5.76 and 6.48 eV at 15 K. Preexposure time = 2.0 min; dark time = 2.0 sec.

3.02-eV emission is given in Fig. 4. The 3.02-eV emission is not stimulated after preexposure in the band-to-band region but is only stimulated after preexposure in the low-energy tail of the first exciton absorption band. These results question the intrinsic nature of the 3.02-eV emission. In order for an emission to be intrinsic it must be associated with the radiative recombination of an electron with a self-trapped hole (V_k center). Such is the case for the two high-energy bands which appear as both direct luminescence and stimulated luminescence after band-to-band excitation. The fact that the 3.02-eV emission is not seen (directly or stimulated) upon band-to-band excitation does not by itself preclude it from being intrinsic since this state may be attainable through a tunneling process as suggested by Nishimura. However, when the conduction-band electron is produced by red and/or infrared stimulation after preexposure in the low-energy tail of the first exciton band *only* the 3.02-eV emission is observed. Thus the hole is not in a self-trapped state. It is important to note here that the diffusion of V_k centers at 15 K is not likely since they are immobile at this temperature.⁸⁻¹⁰ This was further verified by monitoring the stimulated luminescence as a function of dark time where we found the stimulated luminescence intensity to be independent of the dark time.

The temperature dependence of both the 3.35-eV stimulated and direct luminescence and the 3.02-eV stimulated luminescence are shown in Fig. 5. If a simple exponential dependence is assumed, then an activation energy for the process(es) competing with

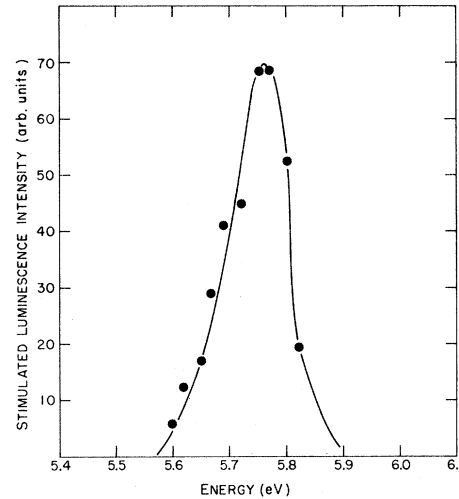


FIG. 4. Preexposure spectrum for the 3.0-eV emission at 15 K. Preexposure time = 2.0 min; dark time = 2.0 sec.

the 3.02-eV emission is found to be 0.08 eV. This value is in agreement with that value determined by direct luminescence studies for the same excitation energy.⁴

Our results lead us to suggest the following luminescence model for KI. For preexposure in the band-to-band region at low temperatures the electrons freed from shallow traps recombine with the immobile V_k centers yielding the two high-energy in-

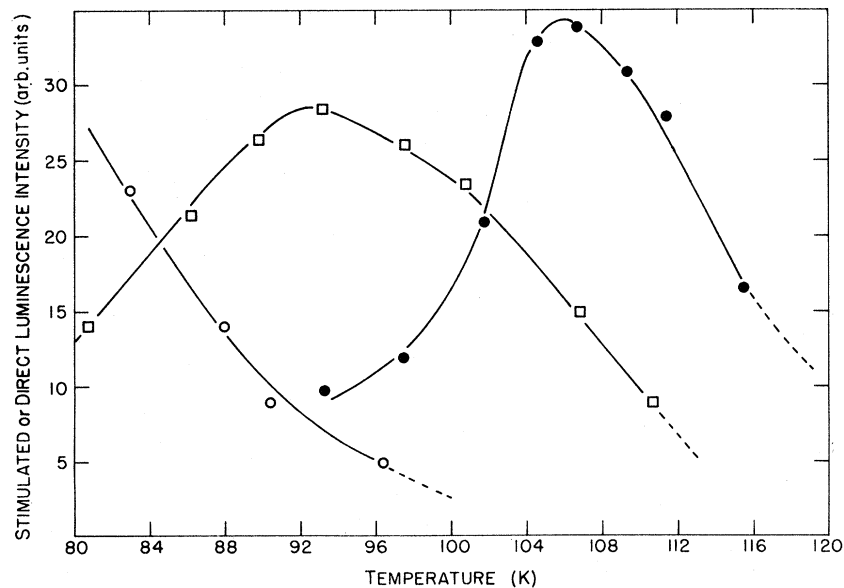


FIG. 5. Temperature dependence of luminescence: ○ 3.0-eV stimulated luminescence; preexposure: 5.76 eV. □ 3.35-eV direct luminescence; excitation: 5.76 eV. ● 3.35-eV stimulated luminescence; preexposure: 5.76 eV.

trinsic emissions. For excitation in the exciton absorption region proper excitons are created in a state which is separated from the 3.3-eV state by a potential barrier. If the temperature is low enough this barrier cannot be overcome and the exciton diffuses through the crystal, allowing for an interaction with impurities and/or defects. The result of these interactions is the creation of electrons in the conduction band, some of which eventually become shallowly trapped. Subsequent low-energy irradiation frees these electrons which radiatively recombine with the holes which are now associated with the impurities or defects. This low-temperature model parallels that which explains the luminescence phenomena in NaI with respect to the potential barrier, exciton energy transfer, and the location of the low-energy excitation "band."¹¹⁻¹³ Regarding the position of the "band," it should be noted that its location is dependent upon crystal purity and the behavior of the absorption coefficient in the tail of the fundamental absorption region.¹⁴ Therefore, caution must be used in attempting to draw correlations between samples of different purities based upon the relative positions of these "bands."

As the temperature of the sample increases the potential barrier is overcome and the 3.3-eV luminescent state becomes populated. The result is a decrease in the 3.0-eV stimulated emission and a corresponding increase in the 3.3-eV direct luminescence for low-energy excitation (see Fig. 5). As the temperature continues to increase the 3.3-eV state becomes thermally dissociated, thus freeing an electron which may subsequently become trapped. Thus one would expect to see a decrease in the 3.3-eV direct luminescence associated with an increase in the 3.3-

eV stimulated emission. This effect is also shown in Fig. 5. The authors have recently reported evidence for exciton thermal dissociation in NaI.¹⁵

IV. CONCLUSION

It was found that the 3.35- and the 4.20-eV emissions in KI can be stimulated at 15 K after preexposure with light in the band-to-band region only, whereas the 3.0-eV emission is stimulated at 15 K only after preexposure in the low-energy tail of the first exciton absorption band. A model is presented which suggests that the 3.0-eV luminescence results from the following process: (1) a proper exciton is created which is separated from the ($V_k + e^-$) state by a potential barrier; (2) the exciton interacts with an impurity or defect, freeing an electron which subsequently becomes shallowly trapped; and (3) red and/or infrared stimulation frees the electron which recombines at the impurity or defect, yielding the 3.0-eV luminescence. As the temperature increases the potential barrier is overcome, resulting in a decrease of the 3.0-eV stimulated luminescence and a corresponding increase in the ($V_k + e^-$) direct luminescence (3.35 eV). As the temperature continues to rise, the stimulated 3.35-eV emission increases at the expense of the same emission excited directly. This suggests that the ($V_k + e^-$) state becomes thermally dissociated.

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