Recombination Luminescence from V_K Centers in Potassium Iodide*†

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This paper reports experiments with KI to determine whether the near-uv emission characteristic of the "pure" crystal arises from the recombination of an electron with a V_K center. KI crystals containing Tl or Eu, when irradiated at 77°K with 1.7-MeV electrons, exhibit absorption bands due to V_K and F centers. Illumination of an irradiated crystal in the F band or near infrared results in attenuation of V_K absorption bands and in emission of the 302- and 371-mμ bands characteristic of the pure crystal, as well as in Tl^+ emission. Thermal or optical destruction of V_K centers results in attenuation of the 302- and 371-mμ bands, while the Tl^+ emission remains. Preferential orientation of V_K centers by bleaching with polarized light at liquid-helium temperature or at 77°K results in a polarization of both these emission bands. Assuming that the orienting transition is σ polarized, the 302-mμ band is polarized parallel to the V_K axis, and the 371-mμ band perpendicular. It is concluded that these bands do arise from the radiative decay of a V_K-plus-electron center.

INTRODUCTION

ALL nonactivated alkali iodides emit luminescence in the near ultraviolet region of the spectrum upon excitation by sufficiently energetic photons or charged particles. This emission is typically very weak at room temperature and increases rapidly as the crystal is cooled to liquid-nitrogen or liquid-helium temperature. At low temperatures the quantum efficiency for this emission upon excitation in the fundamental band region is high, of order 1 for KI (Ref. 1) and NaI (Ref. 2), and the scintillation efficiency, upon excitation by gamma rays, is such that approximately one photon is emitted per electron-hole pair (produced by the incident radiation) for NaI (Ref. 3) and CsI (Ref. 4). The emission bands characteristic of nonactivated alkali iodides at low temperature (nominally liquid-nitrogen temperature) are summarized in Table I.[5–9]

Various experimental results indicate that these emission bands arise from a transition characteristic of the pure crystal, and are not associated with impurity atoms. The 295-mμ emission in NaI has been attributed by Van Sciver[10] to the radiative decay of a localized exciton, and the 370-mμ emission in KI was shown by Teegarden and Weeks[7] to arise from the recombination of an electron with a trapped hole, though the identity of the trapped-hole center was not established. Studies of the scintillation process in CsI (Ref. 11) led to the suggestion that the uv emission (near 330 mμ at room temperature) might arise from the radiative decay of an excited state resulting from the recombination of an electron with a self-trapped hole (V_K center) and that this process might be responsible for the characteristic uv emission in the other alkali iodides.

In order to examine this proposed recombination mechanism, experiments have been performed on the production of color centers and the luminescence processes in activated and nonactivated crystals of KI. The principal objective has been to focus attention on the self-trapped hole in order to determine whether there exists a correlation between the self-trapped hole and the characteristic uv emission.

EXPERIMENTAL METHODS

Low-temperature irradiations and measurements of absorption spectra, emission spectra, excitation spectra, and thermoluminescence glow curves were carried out with a rotatable-base cryostat which was obtained commercially. Crystal samples were rectangular in shape and were typically 2 mm thick. The cryostat base could be rotated while under vacuum so that the radiation beam was admitted through a thin aluminum window; the base was then rotated through 90° to align quartz windows for spectral measurements. The crystal temperature was indicated by a copper-constantan

TABLE I. Luminescence emission bands of nonactivated alkali iodides.

Crystal	Peak λ (mμ)	References
LiI	366, 403	5
NaI	295	2
KI	302, 371	This work, also 6–8
RbI	318, 425	7
CsI	326, 361	9

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thermocouple attached to the sample mounting block made of copper. In most of the experiments reported here the crystal was irradiated with a beam of 1.7-MeV electrons from a Van de Graaff accelerator; the electron current density during irradiation was typically of order 10^{-2} μA/cm^2.

Absorption spectra were measured with a Cary Model-14 recording spectrophotometer. Emission spectra were obtained with a Bausch and Lomb grating monochromator of 500-mm focal length whose dispersion is 3.3 mμ/mm. The photomultiplier detector at the monochromator exit slit was either a quartz window RCA 6903 (for use to 200 mμ) or a multialkali cathode RCA 7265 (for scanning in the red to 700 mμ). The response function of the monochromator-detector combination was measured with a calibrated lamp, and all emission spectra reported here have been corrected. Monochromatic light for excitation spectra was obtained from a Beckman DU quartz spectrophotometer.

Polarization measurements and preferential orientation of V_K centers were performed with a Glan-Thompson prism.

The crystals used in this study were obtained commercially from Harshaw, Semi-Elements, and Isomet. Most of the experimental work was done with two ingots of KI(Tl), each of which contained 10^{-3} mole fraction of Tl; these crystals are designated hereafter simply as KI(Tl).

For measurements of emission spectra during x-ray excitation, the crystal was irradiated with x rays from a molybdenum target operated at 40 keV and a maximum current of 15 mA. The x rays were filtered only through the thin mica-beryllium window of the x-ray tube and an 0.008-in. aluminum window on the cryostat.

X-RAY EXCITED EMISSION IN KI AND KI(Tl)

The features of the luminescence emission spectrum with which we will be concerned are illustrated in the spectra observed during x-ray excitation of both nonactivated KI and KI(Tl), as shown in Figs. 1 and 2. The crystal whose spectrum is shown in Fig. 1 was a nominally pure sample obtained from Isomet; the absorption spectrum at liquid-nitrogen temperature (LNT) revealed no absorption bands between 1.5 μ and the onset of the fundamental band at 230 mμ and below. In particular there was no trace of the thallium absorption bands at 282 and 233 mμ. Knowing the relationship between thallium concentration and the absorption coefficients of these bands,[12] we conclude that the thallium concentration was less than 5–10 parts per billion. Further, there was no evidence of the prominent Tl^+ emission band near 425 mμ in any of the emission spectra measured from this crystal in the range from room temperature (RT) to liquid-helium temperature (LHT). In contrast to this, the x-ray excited emission

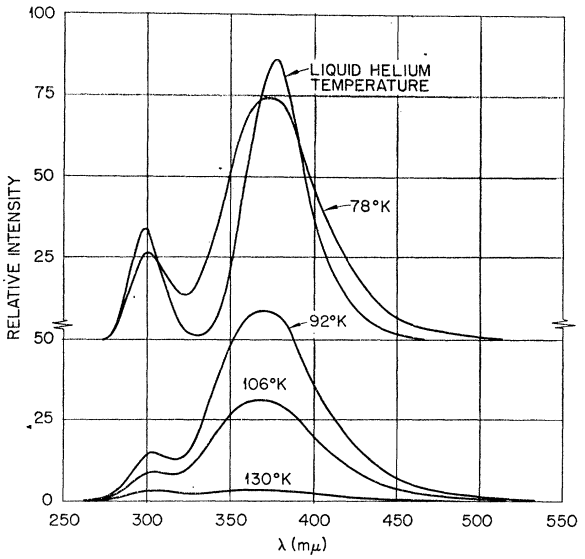

FIG. 1. X-ray excited emission from nonactivated KI at various temperatures. These spectra (and all others) have been corrected for the monochromator-detector response function. The monochromator band pass was 2–3 mμ in all cases.

spectrum at RT from a crystal of KI containing ~25-ppb thallium exhibits a prominent Tl^+ emission band. We conclude that the spectra of Fig. 1 are not influenced by the presence of thallium. In the nonactivated crystal, only two bands are observed in the region 200–700 mμ at low temperature; the peak wavelengths are measured at 302 and 371 mμ at LNT, and at 299 and 376 mμ at LHT.

Spectra are shown in Fig. 1 at temperatures up to 130°K. At higher temperatures the emission becomes progressively weaker; the RT spectrum is composed of two bands, a broad band centered near 515 mμ and a weaker band at ~310 mμ. Fieschi and Spinolo[6] discuss the 515-mμ band and suggest that it may be due to O_2^-. The intensity of the short-wavelength band decreases monotonically by a factor of ~100 from LNT to RT. The 371-mμ band was not observed above 145°K.

Emission spectra from KI(Tl) at various temperatures are shown in Fig. 2. At high temperatures the spectrum consists only of the prominent Tl^+ emission at ~420 mμ. At LNT it is observed that the emission spectrum exhibits the 302- and 371-mμ bands characteristic of the nonactivated crystal, and in addition a prominent band whose (displaced) peak occurs at 422 mμ and a weaker band occurring just to the long-wavelength side of the 302-mμ band. Both of the latter bands have been identified as Tl^+ emission bands, with peak wavelengths at LNT given as 426 and 304 mμ.[13] At LHT the KI(Tl) spectrum exhibits the two bands characteristic of nonactivated KI, and in addition bands whose peak wavelengths occur at 287, ~308, 336, and

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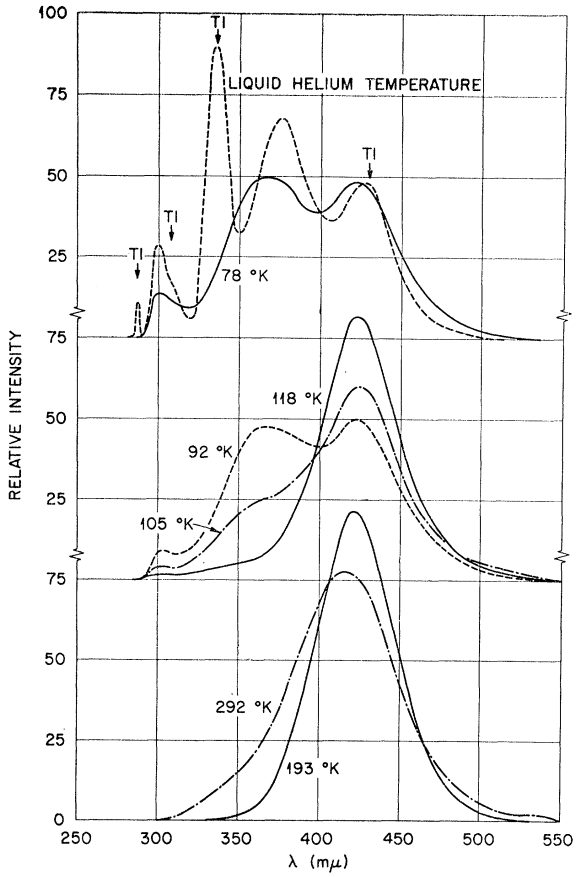

FIG. 2. X-ray excited emission from KI(Tl) containing 10^{-3} mole fraction of Tl at various temperatures. Peak wavelengths of known Tl bands are indicated. The monochromator band pass was 1.3 mμ in all cases.

428 mμ. Each of these latter bands has been identified as Tl^+ luminescence.[13,14] The 287-mμ band appears sharp in Fig. 2 as a consequence of strong thallium absorption bands on either side (see Fig. 6 of Ref. 12).

We also call attention to the temperature dependence of the two bands characteristic of the host crystal in the spectra of KI(Tl), Fig. 2, viz., the 302- and 371-mμ bands. These bands are observed prominently only at 105°K and below, and are barely discernible in the 118°K spectrum.

ABSORPTION SPECTRA AND THERMAL STABILITY OF SELF-TRAPPED HOLES

The absorption spectrum of KI(Tl) at liquid-nitrogen temperature exhibits sharp thallium absorption bands in the near-ultraviolet region and is otherwise transparent throughout the visible and near infrared. The principal thallium absorption bands at 77°K occur at 282 and 233 mμ. Upon irradiation by x rays or electrons at LNT, several broad absorption bands are introduced in the visible and near infrared which are known from previous work[15,16] to arise from optical absorption of F centers and V_K centers. In addition, sharper bands are produced in the ultraviolet region (denoted as P bands) and these have been previously interpreted[16] as due to transitions in Tl^+ ions perturbed by the presence of holes trapped nearby. Radiation-induced absorption bands in KI(Tl) are shown at LNT in Fig. 3. The principal V_K absorption bands are located at 404 and 800 mμ. As the crystal is slowly warmed above LNT, it is observed that the V_K bands disappear abruptly near 105°K, and are replaced by new absorption bands which are presumed to be associated with other trapped-hole centers. A thermoluminescence glow peak occurs in the same temperature region as that in which the V_K centers disappear: the peak was recorded at 106°K for a warming rate of almost 2°/min. Glow peaks which were observed at higher temperatures (177 and 245°K) are associated with the disappearance of other color centers as revealed by the absorption spectrum. Details of these processes have been discussed previously by Hersh.[16]

The principal point for the present work is the fact that self-trapped holes become thermally unstable near 105°K. Warming through this region results in a thermoluminescence glow peak whose emission spectrum was observed to be characteristic of Tl^+ (426-mμ band). Simultaneously, the P_1 and P_3 thallium perturbation bands were observed to increase sharply. It is concluded that holes which are released from the self-trapped state may be annihilated at Tl^0 sites which were produced during irradiation by electron capture at Tl^+, or they may be trapped in a stable configuration at or near a Tl^+ site as revealed by the enhanced thallium perturbation bands.

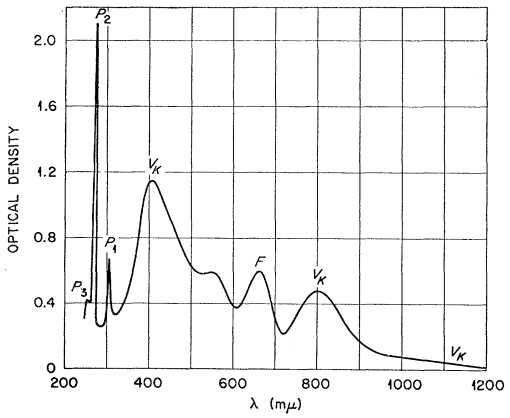

FIG. 3. Radiation-induced absorption bands in KI(Tl) (10^{-3} mole fraction Tl). Crystal was irradiated with 1.7-MeV electrons and spectrum was measured at LNT.

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EXCITATION OF LUMINESCENCE

In order to examine the proposed recombination mechanism, it is necessary to prepare a crystal which contains both V_K centers and a source of electrons. This may be achieved through irradiation with 1.7-MeV electrons by either of two methods: (a) irradiation of KI(Tl) at LNT which yields strong V_K absorption and a weak F band, and (b) irradiation of KI(Tl) at RT which introduces a strong F band, and subsequent irradiation at LNT which introduces strong V_K absorption. The radiation-induced absorption spectrum of KI(Tl) irradiated as in (a) above is shown in Fig. 3. It was observed for crystals of KI(Tl) irradiated as in either (a) or (b) above, that illumination with monochromatic light in the F-band region at LNT was found to result in a luminescence whose spectrum is the same as that observed during x-ray excitation at LNT, Fig. 2. The principal features of the optical excitation of this luminescence in KI(Tl) at LNT are listed below.

(1) The excitation spectrum is the same for the two principal luminescence emission bands, the 426-mμ band characteristic of Tl^+, and the 371-mμ band characteristic of the host crystal.

(2) The excitation spectrum exhibits a peak occurring at the peak wavelength of the F band (665 mμ) and a broader band centered near 1.03 μ [see Fig. 4, curve (a)].

(3) Identification of the excitation peak at 665 mμ with the F band is further supported by a bleaching experiment. After measuring the excitation spectrum shown in curve (a) of Fig. 4, the crystal was optically bleached with F light, eliminating virtually all of the F centers as revealed by the absorption spectrum. The excitation spectrum was remeasured and is shown as curve (b) of Fig. 4. It is observed that the only feature of the spectrum which has changed significantly is the attenuation of the peak at 665 mμ. It is concluded that this peak in the excitation spectrum arises from the release of electrons from F centers and their subsequent recombination at luminescence centers.

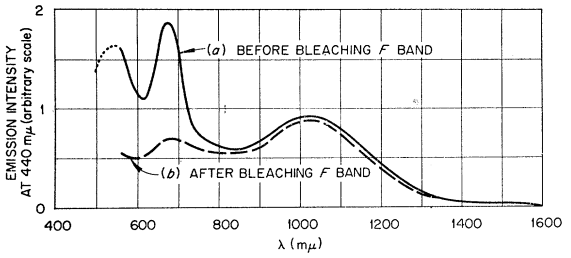

FIG. 4. (a) Excitation spectrum of the principal Tl^+ emission band in KI(Tl), irradiated and measured at LNT. The analyzing monochromator was set to accept 440-mμ light to minimize overlap with the 371-mμ emission. This spectrum has been corrected for the wavelength dependence of excitation intensity, and gives the emission intensity (in arbitrary units) per photon absorbed as a function of the wavelength of the exciting light. (b) After optically bleaching with 665-mμ light.

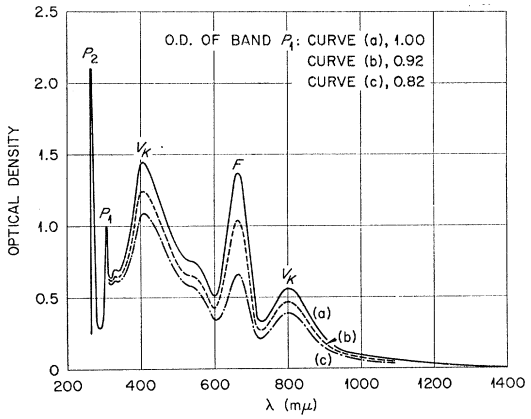

FIG. 5. (a) Absorption spectrum of KI(Tl) irradiated at RT and then at LNT, measured at LNT. (b) After optical excitation in the F band. (c) After further optical excitation in the F band.

(4) Optical excitation at 665 mμ (F light) and at 1.1 μ yields the same emission spectrum. It is concluded that excitation in the broad infrared band centered near 1.03 μ results in the liberation of electrons from shallow traps, and these electrons subsequently produce the luminescence at recombination centers. This observation is in accord with the results of Hersh,[16] who attributed the infrared stimulability to the release of electrons from capture sites associated with the presence of thallium, possibly from Tl^0 centers.

(5) Liberation of electrons by optical excitation at LNT in the F band had the effect of decreasing the V_K absorption bands and the P_1 and P_2 bands (the P_3 band is very weak and was not studied). These effects are illustrated in Fig. 5, showing in curve (a) the radiation-induced absorption spectrum of KI(Tl) which had been irradiated at RT and then at LNT. Curve (b) was recorded after optical excitation in the F band, and curve (c) was recorded after further excitation by F light. The optical density of the P_2 band was not measured accurately in the experiment of Fig. 5; however, in a subsequent experiment it was observed that the P_2 band was also reduced by optical bleaching with F light. These results are interpreted as showing that the release of electrons from F centers (with associated attenuation of the F band) is accompanied by annihilation of V_K centers and the annihilation of those centers (Tl^++nearby hole) responsible for the P_1 and P_2 bands. Since F-band excitation leads to an emission spectrum exhibiting luminescence bands characteristic of both thallium and the host crystal (as in Fig. 2), we are led to the tentative interpretation at this point of the 302- and 371-mμ emission bands as due to the recombination of electrons with V_K centers. The thallium emission bands, due to the radiative decay of Tl^+ in an excited state, are presumed to result from the recombination of electrons with Tl^+ plus hole centers.

LUMINESCENCE EMISSION FROM OPTICAL EXCITATION

We turn next to a consideration of the luminescence emission spectrum of irradiated KI(Tl). A crystal of KI(Tl) was irradiated at LNT, introducing V_K bands, P bands, and the F band as discussed previously. Illumination of the crystal at 1.1 μ at LNT resulted in a luminescence emission whose spectrum, shown in the upper curve of Fig. 6, is the same as that observed by x-ray excitation. The crystal was then allowed to warm slowly while the thermoluminescence glow at 426 mμ was followed as a function of time. When the thermoluminescence glow had passed its first peak (at $\sim$105°K), the crystal was cooled promptly to LNT and the emission spectrum resulting from 1.1-μ stimulation was again recorded, see lower curve of Fig. 6. It is seen that the 302- and 371-mμ bands were eliminated, leaving only the Tl^+ emission. It is also noted (see ordinates of Fig. 6) that the thallium emission band at 426 mμ was strongly enhanced.

As indicated previously it is known from studies of the absorption spectrum that self-trapped holes are destroyed as the crystal is warmed through the first glow peak. Of those holes which are freed at this temperature, some are apparently annihilated through recombination at Tl^+ plus electron sites, giving the thermoluminescence glow, and others are trapped to form stable Tl^+ plus hole centers as evidenced by the enhancement of the P_1 and P_3 bands. The complete loss of the 302- and 371-mμ emission bands upon warming through the 105°K region is thus evidence in favor of the origin of these bands through recombination of electrons with self-trapped holes.

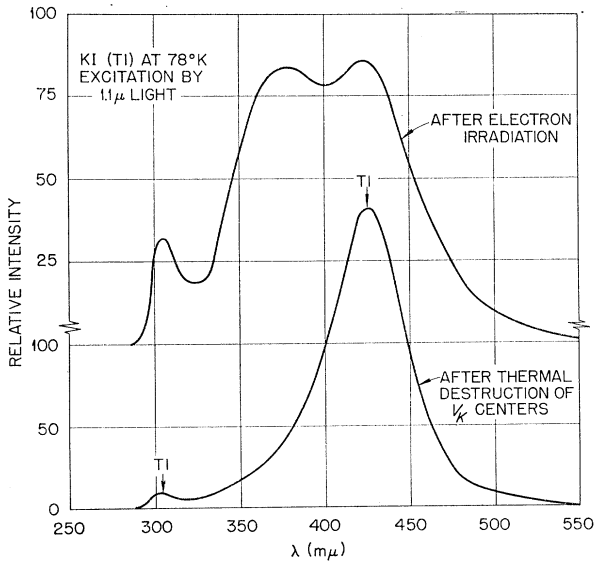

FIG. 6. Upper curve: Luminescence emission upon stimulation at 1.1 μ from KI(Tl) which was irradiated at LNT. Emission spectrum was measured at LNT. Lower curve: Emission spectrum at LNT after crystal had been warmed past first thermoluminescence glow peak, at which temperature self-trapped holes are annihilated.

In another experiment the effect of optical bleaching of the V_K band at LNT was studied. A crystal of KI(Tl) was irradiated at LNT and the emission spectrum was recorded upon excitation at 1.1 μ. The crystal was then exposed to 800-mμ light for various time intervals, and the absorption and emission spectra were recorded after each interval of bleaching. Two of the emission spectra are shown in Fig. 7. The absorption spectra corresponding to curves (a) and (b) of Fig. 7 showed V_K bands whose optical densities (at 800 mμ) were 0.35 and 0.11, respectively. It is noted that the effect of bleaching the V_K centers has been to reduce the intensity of the 302- and 371-mμ bands, while the area of the principal

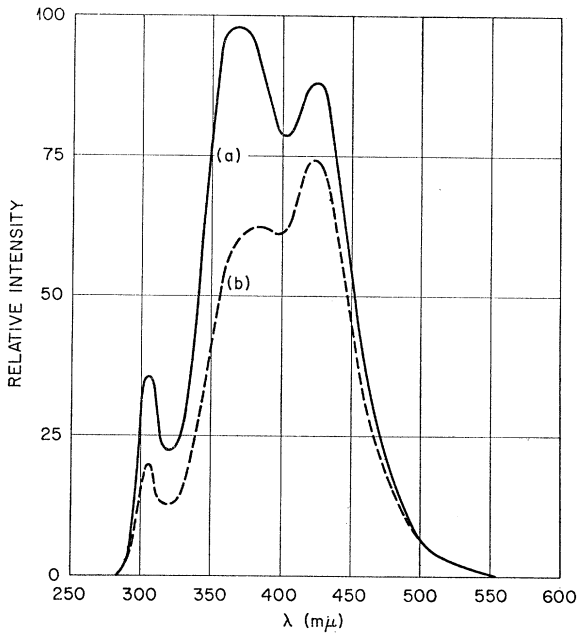

FIG. 7. Emission spectra from KI(Tl) irradiated at LNT and stimulated by 1.1-μ light at LNT, showing the effect of bleaching V_K centers with 800-mμ light: (a) before bleaching, (b) after partial bleaching of V_K bands.

thallium band has remained essentially constant. This result provides further evidence that the emission bands characteristic of the pure crystal arise from recombination with V_K centers. A quantitative study of the dependence of these bands on the density of V_K centers has not been undertaken in this work, but would be of considerable interest. Such a study would be complicated by the fact that bleaching at 800 mμ results not only in optical absorption in V_K centers, but also in the release of electrons into the crystal (see the excitation spectrum, Fig. 4). The complication of releasing electrons should not affect the qualitative conclusion of the present experiment, as we observe a progressive decrease of the 302- and 371-mμ bands relative to the Tl^+ emission

POLARIZATION OF LUMINESCENCE

It is possible to achieve a preferential orientation of V_K centers by illumination in the V_K absorption bands with polarized light.[15] It is, therefore, possible to seek a further identification of the emission bands under study by examining the polarization of the light emitted by optical stimulation of a crystal containing oriented V_K centers. Four experiments of this type have been performed with KI(Tl) and KI(Eu) (europium concentration 3×10^{-4} mole fraction). In the first experiment [with KI(Tl)], V_K centers were oriented at LHT by absorption of light in the 800-mμ V_K band with the electric vector parallel to the $[0\bar{1}1]$ direction in the terminology of Delbecq, Hayes, and Yuster.[15] Orientation bleaching was continued until maximum anisotropy was nearly achieved, i.e., the optical density of both V_K absorption bands measured with [011] light was about twice that measured with $[0\bar{1}1]$ light. Stimulation of the crystal at LHT by 1.1-μ light yields an emission spectrum which is the same as that recorded upon x-ray excitation, as shown in Fig. 2. Light emitted in the pricipal thallium bands (336 and 430 mμ) was found to be unpolarized both before and after orientation of the V_K centers. Light emitted in the 299- and 376-mμ bands was found to be unpolarized before orientation of the V_K centers, but was partially plane polarized after the orientation. The 299-mμ emission was polarized with electric vector parallel to [011] and the 376-mμ band was polarized with electric vector parallel to $[0\bar{1}1]$. The polarization properties of the V_K absorption bands in several alkali halides (including KI) have been studied previously by Delbecq, Hayes, and Yuster.[15] They concluded that the polarization properties of both the 404- and 800-mμ bands in KI were similar, both predominantly σ-polarized. They showed that bleaching with $[0\bar{1}1]$ light in either of the principal V_K absorption bands results in a preferential orientation of the V_K centers along [011]. On this basis the results of our experiments show that the higher energy emission band is polarized with electric vector parallel to the V_K axis, and the lower energy band with electric vector perpendicular to the V_K axis.

We define the polarization P as

$$P=(I_{\parallel}-I_{\perp})/(I_{\parallel}+I_{\perp}),$$

where $I_{\parallel}$ is the measured emission intensity with the polarization analyzer parallel to [011], and $I_{\perp}$ is the intensity with the analyzer parallel to $[0\bar{1}1]$. In the experiment with KI(Tl) we found $P(299\ \text{m}\mu)=0.22$ and $P(376\ \text{m}\mu)=-0.17$. Both of these numbers are, however, numerically smaller than the true value as both bands overlap thallium emission bands which are unpolarized.

A more definitive result was obtained in the second polarization experiment with KI(Eu). In this case the luminescence emission spectrum at LHT exhibited only the two bands characteristic of the host crystal

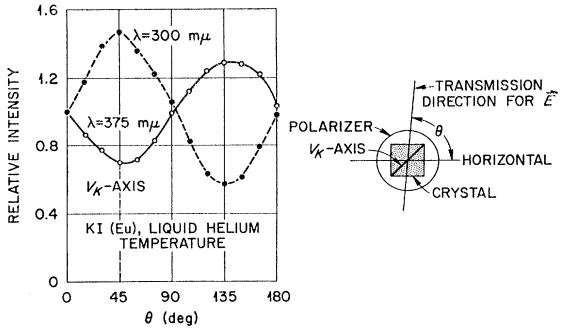

FIG. 8. Relative intensity of light transmitted through analyzing prism as a function of angle of rotation of the prism. The angle θ is measured from the horizontal to the polarization direction of the prism. The [011] direction of the crystal is at 45° and the $[0\bar{1}1]$ direction is at 135°. Experiment performed with KI(Eu) irradiated at LNT, measured at LHT, excitation by F light.

at 299 and 376 mμ. V_K centers were oriented at LHT as described above with 800-mμ light. Both bands in the emission spectrum were unpolarized before orientation, and both bands were polarized after orientation in the same sense as in the case with KI(Tl), i.e., the electric vector of light emitted at 376 mμ was perpendicular to the V_K axis, and the 299-mμ band was polarized parallel to the V_K axis. The relative intensity of the analyzed light as a function of angle of rotation of the Glan-Thompson prism is shown in Fig. 8. From this experiment we obtain $P(299\ \text{m}\mu)=0.44$, and $P(376\ \text{m}\mu)=-0.30$. These numbers cannot be directly interpreted in terms of the polarization of light from a single center, as the measured polarization arises from a crystal in which not all V_K centers are oriented along [011].

In both of the polarization experiments described above the orientation of V_K centers was achieved with 800-mμ light. In a third polarization experiment, with KI(Tl), V_K centers were oriented with 404-mμ light with electric vector along $[0\bar{1}1]$. The polarization of the emitted light was the same as that observed in earlier experiments, viz., 299-mμ light was polarized with electric vector parallel to [011] and the emission at 376 mμ was polarized with electric vector parallel to $[0\bar{1}1]$. It is concluded that bleaching in either of the two principal V_K absorption bands, with electric vector along $[0\bar{1}1]$, results in the same preferential orientation for V_K centers.

In another polarization experiment V_K centers were preferentially oriented in KI(Tl) at LNT by bleaching at 404 mμ. The anisotropy in the 404- and 800-mμ absorption bands is not stable for a long period at LNT, but is observed to decay such that about half the anisotropy (i.e., the difference in optical density measured with $[0\bar{1}1]$ and [011] light) is lost in two hours. The polarization properties of both the 302- and 371-mμ bands were measured within one-half hour after stopping the orientation bleaching, and both bands were again observed to be partially plane polarized, in the same sense as at LHT. We conclude

that the orientation of the V_K plus electron center is retained during the lifetime of the radiative state at LNT as well as at LHT. It should be noted that LNT is just below the temperature at which oriented self-trapped holes lose their orientation at a maximum rate, viz., 93°K.[15]

DISCUSSION

The experimental results presented above seem to provide a strong argument in favor of the origin of the 302- and 371-mμ emission bands from the recombination of electrons with V_K centers. There are three principal experimental results summarized as follows: (1) the 302- and 371-mμ bands are lost upon thermal destruction of V_K centers, (2) these bands are attenuated relative to the Tl^+ emission upon partial bleaching of the V_K centers, (3) these bands are partially plane polarized at LHT and at LNT if the V_K centers are first preferentially oriented. We further note in the emission spectrum of KI(Tl) upon x-ray excitation (Fig. 2), that the 302- and 371-mμ bands are observed only at temperatures where V_K centers are thermally stable for a period of seconds or longer, i.e., from $\sim$105°K down. This result can be understood in terms of a competition, between self-trapped holes and Tl^+ plus hole centers, for the capture of electrons released during x-ray excitation. At temperatures below $\sim$105°K a significant fraction of the holes will be promptly self-trapped and will compete effectively against Tl^+ plus hole sites for electron capture, resulting in a prominent emission of the 302- and 371-mμ bands as well as the Tl^+ emission. At a higher temperature holes created during irradiation are thermally stable in the self-trapped state only for a very short time. Absorption spectra and thermoluminescence studies indicate that holes are stably trapped to form Tl^+ plus hole centers, and the predominant luminescence mechanism is then presumably through recombination of electrons with such centers to yield Tl^+ luminescence.

Recombination luminescence from self-trapped holes in other alkali halides has recently been studied by Kabler,[17] who observed two emission bands in KBr, KI, and NaCl, and one band in KCl. His results on KI give the same emission bands as those discussed in this paper, although the polarization was not measured in detail. In KBr he observed that the polarization of the high-energy emission band was positive (parallel to V_K axis) and the low-energy band was polarized perpendicular to the V_K axis. Thus both the high- and low-energy emission bands in KBr and KI have the same polarization properties relative to the V_K axis. Polarization properties of the two emission bands have been discussed by Kabler in terms of the states of the $X^- - X^-$ diatomic molecule.

Recombination of an electron with a self-trapped hole results in an excited center which is electrically neutral; i.e., the total number of ions and electrons is the same as in the pure crystal. The excited states of this V_K plus electron center should then correspond to exciton states of the pure crystal. Emission of the 371-mμ band has been observed upon excitation in the first fundamental band region in several laboratories.[1,7,8,18] The 302-mμ band has apparently not been observed from ultraviolet excitation. In particular, Teegarden[1] has examined the emission spectrum from nonactivated KI from 2.0–5.50 eV, upon excitation in the fundamental band and finds the 371-mμ emission band only. The absence of the 302-mμ emission may be due only to the fact that a higher excitation energy is required to reach the excited state responsible for this band. Emission of the 371-mμ band upon excitation in the fundamental band region ($\sim$5.8 eV) involves a Stokes shift of 2.5 eV. A similar Stokes shift associated with the 302-mμ emission would require uv excitation at $\sim$6.7 eV (185 mμ). We note that additional exciton peaks in the absorption spectrum of KI occur[19] at 6.7, 6.9, and 7.2 eV. The two higher energy absorption bands at 6.9 and 7.2 eV have recently been interpreted by Phillips[20] as arising from L excitons, which he suggests may be described as an electron bound to a self-trapped hole. In view of the above, it would be of interest to examine the excitation spectrum of the 302-mμ luminescence to determine whether it is excited by 6.7 eV or higher energy uv.

Finally, we note the rather remarkable stability of the V_K plus electron center, as evidenced by the polarization of the emission bands even at LNT. Measurements[21,22] of the decay of the light from nonactivated KI at LNT indicate an exponential decay time of order 10^{-6} sec, a time interval many orders of magnitude longer than that required for a relaxation of the nuclei. The polarization results indicate that the excited states of the V_K plus electron center are states in which the principal lattice distortions are along the $\langle 110 \rangle$ directions, and that the original axis of the V_K center is retained even after the electron recombines.

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