the free carriers are produced by the bimolecular dissociation of excitons. The linear dependence of photocurrent on intensity at wavelengths below 3800 Å is perhaps due to direct transitions across the band gap.

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Electromodulation of the Optical Properties of Thallium-Activated Potassium Bromide

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The absorption spectrum of KBr:Tl crystals has been investigated using an ac electric field (2×10^4 V/cm, rms). The change of the absorption coefficient, versus photon energy, supports the validity of Henry, Schnatterly, and Slichter's theory concerning the zeroth-moment conservation. It is also shown that the absorption intensity of the B band is supplied, almost entirely, by the A band.

INTRODUCTION

The absorption spectrum associated with the thallium activator has stimulated the interest of many investigators.[1–3] When metal impurity ions with the $(s)^2$ outermost electron configuration, such as Tl^+, In^+, Sn^{++}, etc., are added in an alkali halide, one can observe three absorption bands which are called A, B, and C in order of increasing energy. In KBr:Tl their spectral positions at room temperature are 4.74, 5.55, and 5.87 eV, respectively. Seitz[4] has suggested a model in which he assumed that thallium is present in an alkali halide in the form of monovalent thallous ion, since this form of thallium ion is most stable at the high temperatures at which the crystals are grown. In addition, he assumed that the Tl^+ ion replaces an alkali ion of the lattice, and that the Tl^+ ions are dispersed at random through the lattice when the concentration of Tl^+ in the crystal is small. The C band was attributed to the completely allowed transition $^1S_0\rightarrow{}^1P_1$ ($^1A_{1g}\rightarrow{}^1T_{1u}$) of high oscillator strength, and the A band to the spin-forbidden transition $^1S_0\rightarrow{}^3P_1$ ($^1A_{1g}\rightarrow{}^3T_{1u}$), while the B band was attributed to the spin- and symmetry-forbidden transition $^1S_0\rightarrow{}^3P_2$ ($^1A_{1g}\rightarrow{}^3T_{2u}$) as supported by the observed temperature dependence of oscillator strength. Yuster and Delbecq[5] found the triplet structure in the C band of potassium iodide–thallium phosphors, attributing such a structure to the vibration-induced removal of the triple degeneracy of the $^1P_1$ state. Since then, several authors[2,6–9] observed the structures in the A and C bands of various alkali halide phosphors, revealing that the C band consists of three components and the A band has the doublet structure. Toyozawa and Inoue[10] have considered the possibility that the dynamical Jahn-Teller effect might be important in the case of Tl^+-type centers, and together with Cho[11] were able to reproduce theoretically the triplet structure of the C band; the calculations were made in the six-dimensional configuration coordinate space on the basis of the classical Frank-Condon approximation.

In previous papers[12,13] we confirmed experimentally both in absorption and emission that the A band shows a triplet structure and we also found an oscillator strength decrease. The present work was undertaken for the purpose of obtaining more information about A-band oscillator strength, extending measurements to B- and C-band spectral regions.

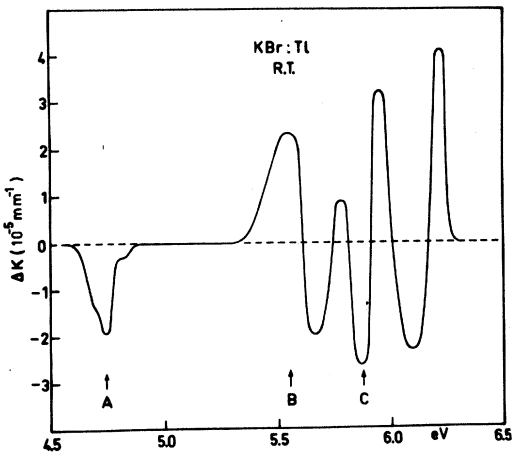

FIG. 1. Absorption spectrum at room temperature (R.T.) of a KBr:Tl crystal.

EXPERIMENTAL PROCEDURE

Single crystals of potassium bromide containing various concentrations of thallous ion were grown by the Kyropoulos method in air. The thallous ions were also introduced into the crystals by heating the latter at various temperatures in a quartz tube, previously evacuated, in an atmosphere of saturated thallium metal vapor.[14] Crystals obtained from these two different techniques agreed quite well in their absorption spectra. The sample size was $(10\times1\times0.5)$ mm^3 and before each measurement it was kept a few minutes at a temperature of 50°C below the melting point and quenched to room temperature on a copper plate to avoid the formation of paired thallous ion centers.

The electro-absorption measurements have been done at room temperature using the experimental apparatus described elsewhere.[13] A Leiss quartz-prism double monochromator in conjunction with a 200-W deuterium lamp was used in order to produce monochromatic light which crosses the sample. An ac electric field (2×10^4 V/cm, rms; $\nu=80$ Hz) was applied perpendicularly to the direction of light propagation. The transmitted light was detected by a RCA 1P28 photomultiplier, and the signal was fed to a lock-in amplifier tuned to twice the frequency of the field. The output of the lock-in was registered on a Varian recorder.

RESULTS AND DISCUSSION

A considerable amount of information is to be found in the literature[15,16] concerning the modulation effect of external electric fields on the absorption bands in solids. Nevertheless, the electron-lattice interaction makes the field effects analysis rather difficult.

Henry, Schnatterly, and Slichter[17] (HSS) showed that these difficulties can be partly overcome using the method of moments for the absorption spectra. They used an original method to predict line-shape variations that occur when an external perturbation, such as an electric field, a magnetic field, or stress, is applied. Their analysis is restricted to centers with orbital singlet ground states and they have been able to take the electron-lattice interaction into account computing the changes in the moments of the absorption line shape that occur when the external perturbation is applied. In fact, although the calculations of one or several moments cannot predict the line shape in detail, the moments can, however, be easily compared with experimental results. Even neglecting the mixing of nondegenerate electronic states by the lattice and the applied perturbation and limiting to use a linear electron-lattice interaction, HSS found that the area of the band remains constant when an external perturbation is applied, while the change in the first and second moments are independent of the electron-lattice interaction.

The shape function $f(E)$ is related to the absorption coefficient by the relation

$$f(E)=CK(E)/E$$

with

$$C=(4\pi^2N/\hbar cn)\,(F_{\text{eff}}/F_0)^2,$$

where N is the number of impurities per unit volume, n is the refraction index of the host crystal, and F_{eff} is the ratio of the local electric field to the average field in the medium. The exact estimation of the effective field ratio is very difficult because it depends on the nature of the wave function of the impurity.[18] For a localized impurity, it is possible to use the following relation:

$$F_{\text{eff}}/F_0=1+\tfrac{1}{3}(n^2-1).$$

With this assignment for the shape function, the zeroth moment ("area") is defined as

$$E_0=\int f(E)\,dE.$$

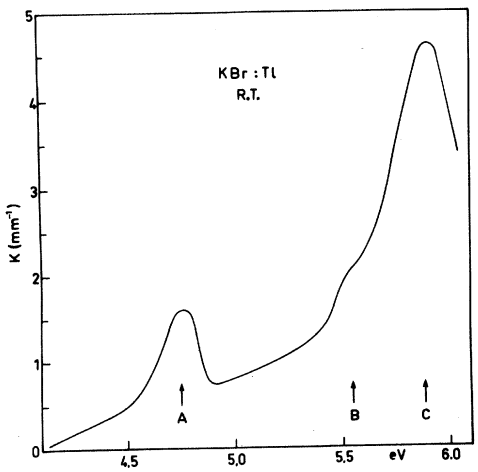

FIG. 2. Change of the absorption coefficient of a KBr:Tl crystal versus photon energy, due to an applied electric field (2×10^4 V/cm, rms) at room temperature.

The first moment ("center of gravity") is defined as

$$\bar{E}=E_0^{-1}\int Ef(E)\,dE.$$

The second moment ("halfwidth") measured about $\bar{E}$ is

$$\langle E^2\rangle=E_0^{-1}\int(E-\bar{E})^2f(E)\,dE.$$

Honma[19] has reformulated and extended the method given by HSS to the absorption bands of alkali halides containing heavy-metal ions with $(s)^2$ configuration. He obtained the following expression for R, the ratio of the dipole strength of the C band to that of the A band:

$$R=\frac{1+\lambda^2(1-x)+[1+2\lambda^2x(1-x)]^{1/2}}{1+\lambda^2x-[1+2\lambda^2x(1-x)]^{1/2}},$$

where

$$x=(E_B-E_A)/(E_C-E_A),$$

and λ is a parameter that takes account of the small difference between the radial wave functions for the singlet and triplet state. When $\lambda=1$ the relation corresponds to that obtained by Sugano.[20] A remarkable agreement has been found between theoretical and experimental data assuming $\lambda=0.8$. Honma[19] also obtained a theoretical expression that shows how the intensity of the B band is supplied by the C band as well as the A band:

$$I^B=6(\mu\nu\langle s\,|\,P_x|\,p_x\rangle)^2[(E_B-E_A)^{-1}+(E_C-E_B^{-1})]^2F_2(T),$$

where μ and ν denote the mixing coefficients between the states $|\,^1T_{1u}\rangle$ and $|\,^3T_{1u}\rangle$, $\langle s\,|\,P_x|\,p_x\rangle$ are the matrix elements of the electric dipole moment, and

$$F_2(T)=\tfrac{1}{12}(2b^2+3c^2)kT=0.226\times10^{-4}T\ \text{eV}^2\quad\text{for Tl}^+,$$

and b and c are the linear electron-lattice coupling constants. The theory shows that the area of the shape function cannot be changed by the external perturbation, on account of the spectroscopic stability principle, although the zeroth-moment change can be different from zero for an individual band. So in order to have information from the measurements of zeroth-moment variation in a single band, it is necessary to consider the mixing of the excited state of such a band with the other center states. As a consequence of the observed zeroth-moment decrease[12] we extended experimental measurements to bands B and C.

Figure 1 shows an absorption spectrum at room temperature of a potassium bromide crystal containing a low concentration of thallium. The modulated absorption spectrum is reported, as a function of the energy of the photons, in Fig. 2, where one can observe a negative change of the absorption coefficient in the region of the A band, while in the B-band region a positive change is present and C band reveals its triplet structure maintaining the zeroth moment almost unchanged.

Closer inspection of Fig. 2 shows that the area, according to HSS theory, remains constant throughout the whole spectrum, and that the oscillator-strength transfer occurs almost entirely between A and B bands. On the contrary, examining the values of the energy distances between B states and other states, one should expect an increase of the B-band intensity at the expense of the C-band intensity according to the experimental data of Tsuboi and Kato.[21] In fact they, investigating the absorption spectra of the B bands in alkali halide thallium crystals over the temperature range from 10 to 300°K, observed a correlation between absorption intensities of the B and C bands, indicating that the C state is a main mixing state to the forbidden B state.

It is our opinion, that this discrepancy between the effects of temperature and electric field could be clarified by studying the structure of thallium center by means of two-photon spectroscopy using cascade generation of harmonic frequencies of Nd-glass lasers.

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