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## Investigation of the A, B, and C Bands in KBr:In by Means of Electromodulated Optical Absorption

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The effect of an electric field ( $\sim 10^4$  V/cm, rms) on the A, B, and C absorption bands of potassium bromide-indium phosphors has been studied. The A and C bands are composed of three subbands, while the B band exhibits a doublet structure. A correlation has also been found between the absorption intensities of these bands, the decrease in the A and B bands being compensated by the increase in the C band. A perturbative treatment has been used to explain the observed variation of the zeroth-order moments of A, B, and C bands.

### INTRODUCTION

Single crystals of alkali halides containing metal impurity ions with  $(ns)^2$  outermost electron configuration exhibit three absorption bands, called A, B, and C in order of increasing energy, in spectral regions where the host medium is normally transparent.<sup>1,2</sup> These absorption bands have been associated with the transition between molecular orbitals  $(a_{1g})^2 \rightarrow (a_{1g})(t_{1u})$  and assigned to  ${}^1A_{1g}({}^1S_0) \rightarrow {}^3T_{1u}({}^3P_1)$ ,  ${}^1A_{1g}({}^1S_0) \rightarrow {}^3E_u$ ,  ${}^3T_{2u}({}^3P_2)$ , and  ${}^1A_{1g}({}^1S_0) \rightarrow {}^1T_{1u}({}^1P_1)$ , respectively.<sup>3,4</sup> Transitions from the

ground state to  ${}^3T_{1u}$  and to  ${}^1T_{1u}$  are allowed, owing to their spin-orbit mixing. Transitions to  ${}^3E_u$ ,  ${}^3T_{2u}$  are partially allowed because of vibrational perturbation, as supported by the strong temperature dependence of the oscillator strength.<sup>5</sup>

Fukuda *et al.*,<sup>6</sup> studying absorption spectra of KCl:In at various temperatures, found that the A band has a doublet structure and the C band a triplet structure. According to Toyozawa and Inoue,<sup>7</sup> these structures are explained in terms of the dynamical Jahn-Teller effect with linear electron-lattice interaction which splits these bands into

three components; the quadratic interaction between the *A* and *B* bands through  $T_{2g}$  modes causes two components of the *A* band to coalesce.

Cho<sup>8</sup> reproduced theoretically the triplet structure of the *C* band by means of a Monte Carlo integration method for a variety of parameters, using the model of Toyozawa and Inoue. Honma,<sup>9</sup> applying the method of moments given by Henry, Schnatterly, and Slichter<sup>10</sup> (HSS) to the optical-absorption bands of impurity ions with  $(s)^2$  configuration in alkali halides, found that the parameters of vibronic coupling can be obtained from the moments of the *A*, *B*, and *C* bands. More recently Grasso and co-workers<sup>11,12</sup> have revealed in KBr:Tl, by means of an external electric field, a triplet structure of the *A* and *C* bands and have also observed an interaction between the *A* and *B* bands.

The aim of the present work is to report more detailed information on the fine structure of the absorption bands in KBr:In and the correlations between *A*, *B*, and *C* bands.

#### EXPERIMENTAL PROCEDURE

The samples used in this experiment were single crystals of potassium bromide containing various concentrations of indium ions and were grown by the Kyropoulos method, or colored by diffusion of indium ions into host crystals by heating the latter within an evacuated quartz tube<sup>13</sup> in saturated indium

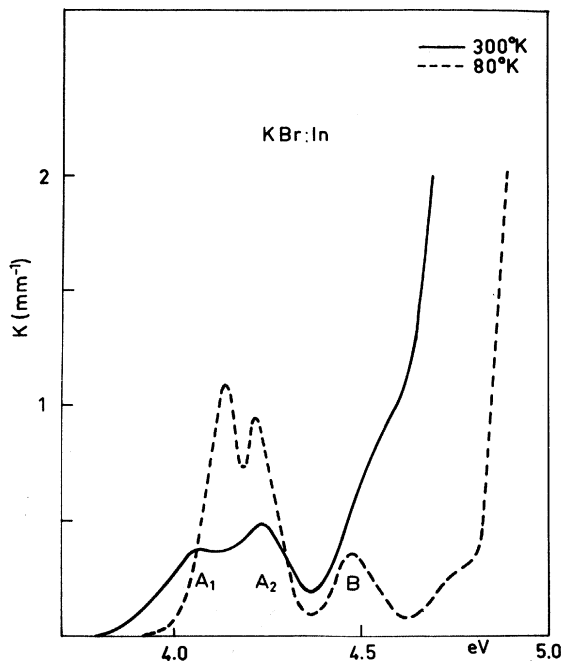


FIG. 1. Absorption spectra of the *A* and *B* bands in KBr:In at 300 and 80°K.

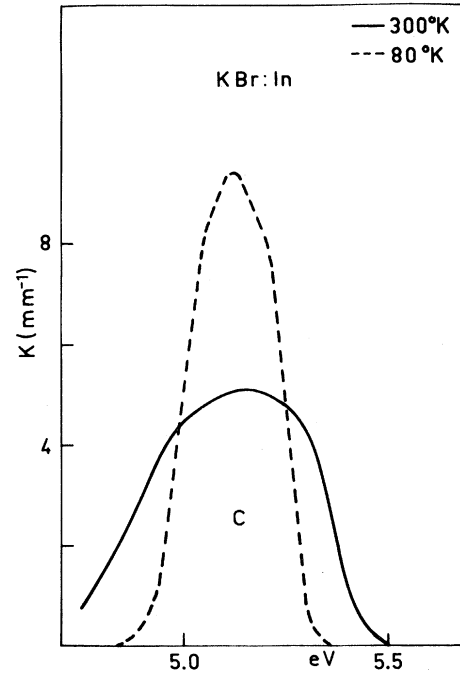


FIG. 2. Absorption spectra of the *C* band in KBr:In at 300 and 80°K.

metal vapor near the melting point. The size of the samples was  $10 \times 1.2 \times 1$  mm<sup>3</sup>. Before optical measurements all specimens were wrapped with aluminum foil and quenched from about 550°C to remove dimer centers. Thereafter the samples were mounted on the copper sample holder and put in an evacuated chamber, where they were slowly heated to 100°C for a few days before each measurement, at the bottom of a conventional liquid-nitrogen cryostat, which can maintain the sample at any desired temperature between about 80 and 300°K. The sample temperature was measured by a combination of an iron-constantan thermocouple and a potentiometer. The electroabsorption measurements were carried out at room and liquid-nitrogen temperatures using the experimental apparatus described elsewhere.<sup>14</sup> Light from a XBO 450-W Osram xenon lamp was monochromated by a Leiss quartz prism double monochromator and focused onto the sample by a Tetrasil lens. An ac modulating electric field ( $\sim 10^4$  V/cm, rms,  $\nu = 80$  Hz) was applied perpendicular to the direction of light propagation. Since the change in optical absorption is independent of the polarity of the applied voltage, the frequency of the modulation will be twice that of the applied voltage. The transmitted radiation was detected by a RCA 1P28 photomultiplier, and the ac signal was measured by a lock-in amplifier tuned to  $2\nu$ . The output of the lock-in amplifier was registered on a Varian recorder.

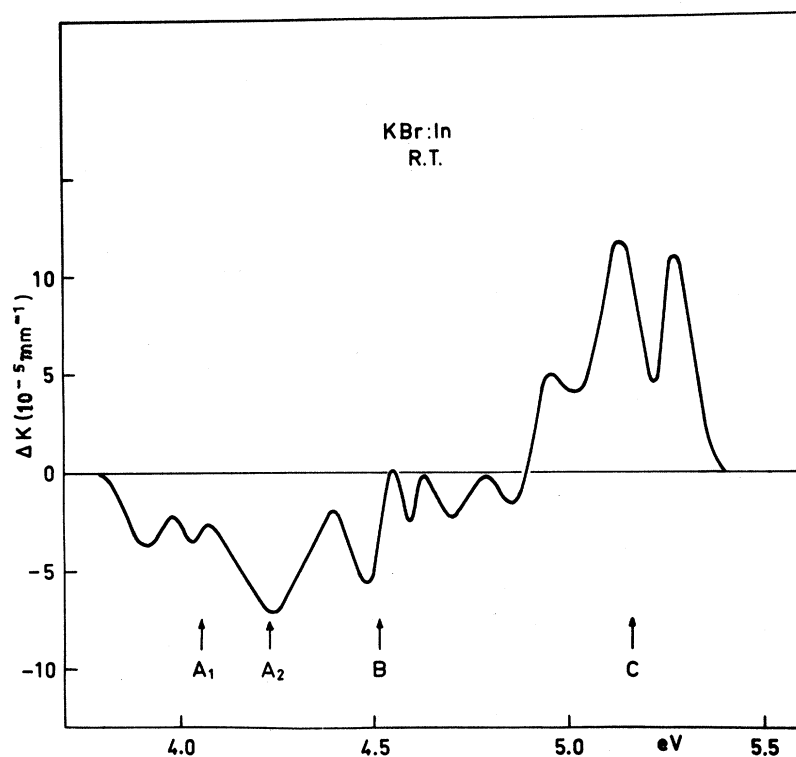


FIG. 3. Change of the absorption coefficient of a KBr:In crystal vs photon energy, due to an applied electric field ( $\sim 10^4$  V/cm, rms) at room temperature.

#### EXPERIMENTAL RESULTS AND DISCUSSION

Figures 1 and 2 show absorption spectra of KBr:In measured at room and liquid-nitrogen temperatures. At both temperatures the A band consists clearly of two well-resolved  $A_1$  and  $A_2$  subbands whose peaks at  $80^\circ\text{K}$  are centered at 4.14 and 4.21 eV, respectively. The B band, which looks like a shoulder at room temperature, shifts toward lower energy with decreasing temperature, becoming observable separately from the C band and revealing no fine structure. The C band appears broad and shows weak triplet structure.<sup>15</sup> In Fig. 1 one can also observe at liquid-nitrogen temperature the presence of a small shoulder between the B and the C bands which has been attributed to paired activator ions.<sup>5</sup>

The modulated absorption spectrum at room temperature is reported as a function of the energy of the photons in Fig. 3. This spectrum exhibits a negative change of the absorption coefficient in the region of the A and B bands, while in the C band region a positive change is present. Moreover, it shows well-resolved triplet structure of the A and C bands similar to that previously observed<sup>12</sup> in KBr:Tl, and doublet structure of the B band previously not so clearly revealed experimentally. The spectrum of Fig. 3 also exhibits a negative peak in the region between the B and C bands that could be attributed to electric field effects on the

paired activator ions.

The observed triplet structure of the A band presents convincing evidence for the Toyozawa-Inoue theory.<sup>7</sup> In fact, the low-energy component of this band is approximately doubly degenerate and the electric field induces a local asymmetry that removes the remaining degeneracy. The doublet structure of the B band shown in Fig. 3 is in rather good agreement with previous theoretical and experimental results.<sup>16,17</sup>

Esser and Levy,<sup>17</sup> examining at various temperatures the absorption bands in KCl:Tl and using a computerized best-fit procedure, found that the B band was best fitted by two subbands. The experimental values agree well with the theoretical results of Lemos *et al.*,<sup>16</sup> who suggested that the B band should exhibit doublet structure since their computation reveals that only transitions to the two  $^3E_u$  states are nonnegligible.

A careful examination of Fig. 3 shows that the area, according to the theory of HSS,<sup>10</sup> remains constant throughout the whole spectrum, and that the oscillator strength transfers entirely to the C band at the expense of the A and B bands. Figure 4 shows the linear dependence of  $\Delta K/K$  at 5.10 eV upon the square of the electric field, expected a Stark effect.

In order to interpret the results we adopt the following procedure.<sup>9,18</sup> The total Hamiltonian is divided into two parts, an unperturbed one which

gives the sharp absorption lines and a perturbing one which causes the coupling between the states of the unperturbed Hamiltonian. It is convenient to take as the zeroth-order Hamiltonian of the  $\text{In}^+$  ion

$$H_0 = H_E + H_{SO}, \quad (1)$$

where  $H_E$  is the two-electron electronic Hamiltonian containing the potential energy due to the cubic crystalline field, and  $H_{SO}$  the spin-orbit interaction. The zeroth-order wave functions are eigenfunctions of the Hamiltonian which includes exchange, spin-orbit, and static  $O_h$  crystal-field interactions and take the form

$$\begin{aligned} |C^i\rangle &= \mu |^1T_{1u}^i\rangle + \nu |^3T_{1u}^i\rangle, \\ |B^i\rangle &= |^3T_{2u}^i\rangle \text{ and } |^3E_u^i\rangle, \\ |A^i\rangle &= -\nu |^1T_{1u}^i\rangle + \mu |^3T_{1u}^i\rangle. \end{aligned} \quad (2)$$

The states  $|A^i\rangle$ ,  $|B^i\rangle$ , and  $|C^i\rangle$  correspond to the excited states of the  $A$ ,  $B$ , and  $C$  absorption and the index  $i$  refers to the three states corresponding to  $M_j = 1, 0, -1$ . The parameters  $\mu$  and  $\nu$  are the spin-orbit mixing coefficients between the states  $|^1T_{1u}^i\rangle$  and  $|^3T_{1u}^i\rangle$  and can be expressed in terms of  $G$ ,  $R$ , and  $\lambda$  by

$$\mu^2 - \nu^2 = \frac{G + \frac{1}{4}R}{[(G + \frac{1}{4}R)^2 + \frac{1}{2}(\lambda R)^2]^{1/2}}, \quad (3)$$

where  $G$  is the exchange energy,  $R$  the parameter of the spin-orbit interaction, and  $\lambda$  is a parameter

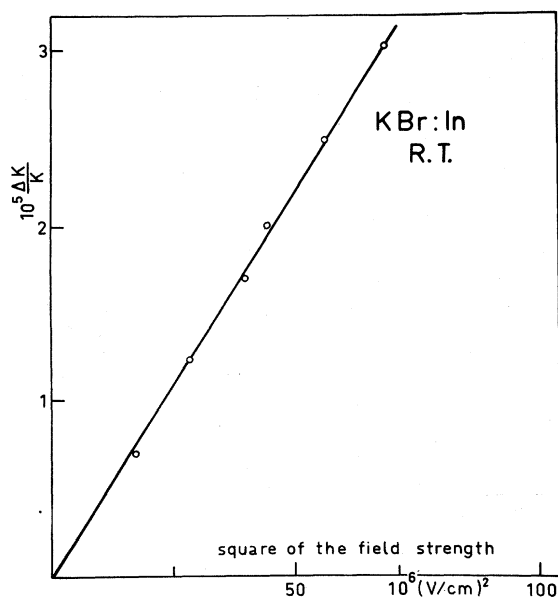


FIG. 4. Dependence of  $\Delta K/K$  on the squared field strength at 5.10 eV.

introduced by King and Van Vleck<sup>19</sup> to take account of the small difference between the radial wave functions for the singlet and triplet states. To keep  $|A^i\rangle$  and  $|C^i\rangle$  normalized we have  $\mu^2 + \nu^2 = 1$ . The perturbing Hamiltonian  $H_1$  is written in the form

$$H_1 = H_{eL} + H_f, \quad (4)$$

where  $H_{eL}$  is the electron-lattice interaction and  $H_f$  the Hamiltonian due to the externally applied field. For an electric field  $E$  in the  $z$  direction the perturbation operator  $H_f$ , which is of odd parity, is

$$H_f = -P_z E, \quad (5)$$

where  $P_z$  is the dipole operator. The energy matrix elements between states of equal parity are zero:

$$\langle \Psi_k^o | H_f | \Psi_k^o \rangle = 0, \quad (6)$$

where  $|\Psi_k\rangle$  represents anyone of the states in Eq. (2) and the index  $o$  refers to their odd parity. This means that there is no first-order Stark effect. The change of the zeroth-order moment  $M_{0k}$  due to the external perturbation is therefore obtained from the first-order wave functions  $|a\rangle^{(1)}$  and  $|\Psi_k\rangle^{(1)}$  by

$$\frac{\Delta M_{0k}}{M_{0k}} = \sum_i \frac{|\langle a | P_z | \Psi_k \rangle^{(1)}|^2 - |\langle a | P_z | \Psi_k^i \rangle|^2}{M_{0k}}, \quad (7)$$

where  $|a\rangle$  represents the ground state.

Using the perturbation theory to first order in  $H_f(E_k - E_n)^{-1}$ ,  $|\Psi_k\rangle^{(1)}$  is given by

$$\begin{aligned} |\Psi_k\rangle^{(1)} &= |\Psi_k\rangle + \sum_{n \neq k} \frac{\langle \Psi_n | H_f | \Psi_k \rangle}{E_k - E_n} |\Psi_n\rangle \\ &+ \sum_{m \neq k, n} \frac{\langle \Psi_m | H_f | \Psi_n \rangle \langle \Psi_n | H_f | \Psi_k \rangle}{(E_k - E_m)(E_k - E_n)} |\Psi_m\rangle + \dots \end{aligned} \quad (8)$$

A similar expression is valid for the perturbed ground state.

The matrix elements of the perturbation operator  $H_f$  between states of the same parity vanish. Therefore the only nonvanishing matrix elements in Eq. (8) are the ones containing the mixing between the excited states and the ground state. Be-

TABLE I. Values of the parameters used in analysis of the zeroth-order moments changes (Refs. 1 and 20).

Sample	$E_A - E_0$ (eV)	$E_B - E_0$ (eV)	$E_C - E_0$ (eV)	$\mu^2$	$\nu^2$	$K^2$ (eV <sup>-2</sup> )
KBr: $\text{Ti}^+$	4.79	5.58	5.93	0.79	0.21	24
KBr: $\text{In}^+$	4.17	4.45	5.09	0.975	0.025	27

fore computing the dipole matrix elements between the perturbed ground state and excited ones it should be noted that the only states which can be reached by a dipole transition from the ground state are the  $|C^t\rangle$  and  $|A^t\rangle$  states because the transition  ${}^1A_{1g} \rightarrow {}^3E_u + {}^3T_{2u}$  is forbidden. However, it is induced by electron-phonon interactions, so that we used for the B band a state of the form<sup>18</sup>

$$|B^t\rangle = \sum_k \frac{\langle \Psi_k | H_{eL} | B \rangle}{E_B - E_k} |\Psi_k\rangle, \quad (9)$$

because only even-parity modes will contribute to the perturbation matrix. Substituting Eqs. (2) and (9) into Eq. (8) and using the expressions of  $M_{0A}$ ,  $M_{0B}$ , and  $M_{0C}$  given in Ref. 20, we obtain for the change of the zeroth-order moment of the A, B, and C bands, respectively,

$$\frac{\Delta M_{0A}}{M_{0A}} = -\frac{4E^2}{E_A - E_0} \left[ \frac{\nu^2}{E_A - E_0} + 3\mu^2 \nu^2 K^2 \left( \frac{1}{E_B - E_0} + \frac{1}{E_B - E_A} \right) + \mu^2 \left( \frac{1}{E_C - E_0} + \frac{1}{E_C - E_A} \right) \right] |\langle {}^1A_{1g} | P_z | {}^1T_{1u}^t \rangle|^2, \quad (10)$$

$$\frac{\Delta M_{0B}}{M_{0B}} = \frac{4E^2}{E_B - E_0} \left[ \nu^2 \left( \frac{1}{E_B - E_A} - \frac{1}{E_A - E_0} \right) - \mu^2 \left( \frac{1}{E_C - E_B} + \frac{1}{E_C - E_0} \right) - \frac{3\mu^2 \nu^2 K^2}{E_B - E_0} \right] |\langle {}^1A_{1g} | P_z | {}^1T_{1u}^t \rangle|^2, \quad (11)$$

$$\frac{\Delta M_{0C}}{M_{0C}} = \frac{4E^2}{E_C - E_0} \left[ \nu^2 \left( \frac{1}{E_C - E_A} - \frac{1}{E_A - E_0} \right) + 3\mu^2 \nu^2 K^2 \left( \frac{1}{E_C - E_B} - \frac{1}{E_B - E_0} \right) - \frac{\mu^2}{E_C - E_0} \right] |\langle {}^1A_{1g} | P_z | {}^1T_{1u}^t \rangle|^2, \quad (12)$$

where  $E_0$ ,  $E_A$ ,  $E_B$ , and  $E_C$  are the unperturbed electronic energies of the impurity ion, and<sup>20</sup>

$$K^2 = \left( \frac{1}{E_B - E_A} + \frac{1}{E_C - E_B} \right)^2 \left( \frac{b^2}{3} \langle Q_b^2 \rangle + \frac{c^2}{2} \langle Q_c^2 \rangle \right).$$

Using for the parameters involved in Eqs. (10)–(12) the values listed in Table I, it can be seen that our simple development gives a fairly good account of the sign of the observed relative changes of the zeroth-order moments for the A, B, and C bands in KBr:In. Moreover this development accounts for the experimental results obtained recently<sup>12</sup> in KBr:Tl.

A complete and detailed explanation of the electric field effects on the absorption intensities in alkali halides containing  $Tl^+$ -like ions is still difficult because the structure of those impurity centers is extremely complex and only their general features are well known and understood. Current models constitute a first approximation so that a complete theoretical treatment of these effects is undoubtedly required.

The general theory of electro-optical effects on these phosphors is not yet available. However we think that our results together with those obtained on KBr:Tl<sup>12</sup> may be considered a starting point for a more detailed study of the impurities in alkali halides.

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