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# Luminescence of $\text{KCl:Bi}^{3+}$ excited at the X absorption band

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Received 21 March 1994, in final form 5 July 1994

**Abstract.** The emission from  $\text{KCl:Bi}^{3+}$  excited in the X absorption band (i.e. between the A and B absorption bands) was measured as a function of temperature. The polarized emission spectrum and the angular dependence of polarization ratio were also investigated.

The X-band excitation produces two emission bands peaking at 345 and 395 nm, the centres of which are not the same. The loosely bonded  $\text{Cl}^-$  ion arising from the substitution of  $\text{Bi}^{3+}$  ions into the KCl lattice is assumed to be the colour centre for the X-band emission. The definitive assignment of the two emission bands is presented in terms of the relaxed excited states of the perturbed  $\text{Cl}^-$  ion, in which the Jahn–Teller interaction coupling to the  $B_1$  and  $B_2$  vibronic modes is taken into account.

## 1. Introduction

Previously, we reported the absorption and the A-band emission spectra from  $\text{KCl:Bi}^{3+}$  single crystals measured at various temperatures (Kang *et al* 1994).  $\text{KCl:Bi}^{3+}$  single crystals produce very characteristic absorption bands peaking at 335, 245, 212, 207, 201 and 196 nm. The first five bands were assigned to the A, B,  $C_1$ ,  $C_2$  and  $C_3$  bands respectively, and the last band to the charge-transfer D band. It should be noted that a very uncharacteristic absorption band peaking at 270 nm appeared as a trace. For  $\text{TI}^+$ -like phosphors with an  $s^2$  electron configuration (Honma 1974), no absorption bands observed between the fundamental A and B absorption bands have been reported. For this reason, we shall call the 270 nm band the X band.

The A-band excitation produces two emission bands from  $\text{KCl:Bi}^{3+}$  peaking at 388 and 430 nm. In general,  $\text{TI}^+$ -like phosphors excited within the A absorption band emit one or two characteristic emission bands (Fukuda 1970). The results have been interpreted in terms of a model in which the Jahn–Teller (JT) effect and the spin–orbit (SO) interaction are taken into account. In the framework of the linear JT effect coupling to the  $E_g$  ( $Q_2$ ,  $Q_3$ ) mode, the X (rhombic) and  $T^*$  (tetragonal) minima can coexist on the  ${}^3T_{1u}^*$  adiabatic potential energy surface (APES) under the intermediate SO interaction (Ranfagni and Viliari 1974, Mugnai *et al* 1982, Choi *et al* 1991). When these two minima are accessible after the A-band excitation, the phosphors give rise to two A emission bands referred to as  $A_x$  and  $A_T^*$ . For  $\text{KCl:Bi}^{3+}$ , the observed experimental evidence in the two emission bands led us to assign the 430 nm emission to  $A_x$ . The 388 nm emission, however, was found to be not correlated with the  $T^*$  minimum. The reduction effect of the SO interaction on the JT effect may cause the  $T^*$  minimum to collapse to a saddle point. In this model, two types of X minima can be expected by an additional perturbation due to the cation vacancies located along one of axes perpendicular to the JT axis. The 430 nm emission was attributed to

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transitions from the  $X_2$  minimum with a low energy and the 380 nm emission was from the  $X_2$  minimum with a high energy to the ground state.

In a series of studies of luminescence of  $\text{KCl:Bi}^{3+}$  single crystals, we expanded our investigation to the X-band emission. In this study, we measured the X-band emission at various temperatures and the excitation spectrum at 78.8 K. We also investigated the polarization of the X-band emission in the hope of revealing the centre responsible for the X band.

## 2. Experimental procedure and results

The  $\text{KCl:Bi}^{3+}$  single crystals are the same as used in the previous work (Kang *et al* 1994). The optical arrangements for measurements of emission and excitation spectra and the polarization have been described in previous publications.

The intensity spectrum of the emission from  $\text{KCl:Bi}^{3+}$  excited in the X absorption band was measured at 20 K. As shown in figure 1, the X band excitation produced two emission bands for  $\text{KCl:Bi}^{3+}$ : the strong high-energy band peaking at 345 nm (3.59 eV) and the weak low-energy band peaking at 395 nm (3.14 eV). These two emission bands are totally different from the two A emission bands peaking at 388 and 430 nm. The excitation spectra of the 395 and 345 nm emission bands were measured at 78.8 K. As shown in figure 2, the excitation spectra for both emission bands differ absolutely in peak position and band width. For the 345 nm emission the excitation spectrum peaking at 272.5 nm shows a very narrow band width, while for the 395 nm emission the excitation spectrum is ranged over 240–290 nm and its intensity is weak even at 265 nm, yielding the maximum. From the excitation spectra it can be seen that the emitting centres accountable for the two emission peaks are not identical.

In addition, we also measured the effect of temperature on the emission spectra of  $\text{KCl:Bi}^{3+}$  excited at 272.5 and 264 nm. As shown in figures 3(a) and 3(b), the intensity of the 345 nm emission decreases gradually with increasing temperature but persists to a certain extent up to room temperature. For the low-energy emission band, the intensity does not change with increasing temperature up to  $T = 200$  K. Above this temperature, with increasing temperature, the intensity decreases markedly and the band width broadens. The temperature dependence of the band width indicates that the electron–lattice interaction is effective in the optical process. One finds that the peak positions of the two emission bands are almost independent of temperature. This suggests that the thermal expansion of the crystal is negligible in the optical process.

The intensity spectra of the 345 and 395 nm emissions from  $\text{KCl:Bi}^{3+}$  polarized parallel and perpendicular to the direction of the electric vector of the exciting light were also measured at 16 K. As shown in figure 4, for the 345 nm emission band the intensity polarized parallel ( $X_{\parallel}$ ) is stronger than that polarized perpendicular ( $X_{\perp}$ ) while for the 395 nm emission band the intensities of the  $X_{\parallel}$  and  $X_{\perp}$  spectra are the same. It can be assumed that absorbing and emitting dipoles responsible for each of the X emission bands could be identical since any further splitting of the polarized emission spectra are not observed. Figure 5 shows the angular dependence of the polarization ratios of the 345 and 395 nm emissions measured in the perpendicular geometry at 16 K. For the 345 nm emission, the polarization ratio  $P$  is a maximum when the exciting light is polarized at  $\alpha = 0$  or  $180^\circ$  and  $P$  is a minimum when the exciting light is polarized at  $\alpha = 90^\circ$ . It can be found that  $P(\alpha)$  of the 345 nm emission is proportional to  $\cos(2\alpha)$ . The 395 nm emission, however, is completely depolarized, independently of the angle of the electric vector of the

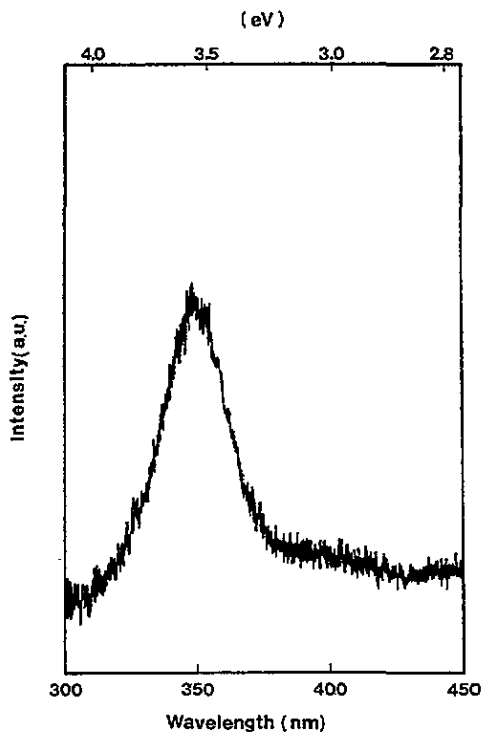


Figure 1. Emission spectra from  $\text{KCl:Bi}^{3+}$  excited at 272 nm ( $T = 20$  K) (a.u., arbitrary units).

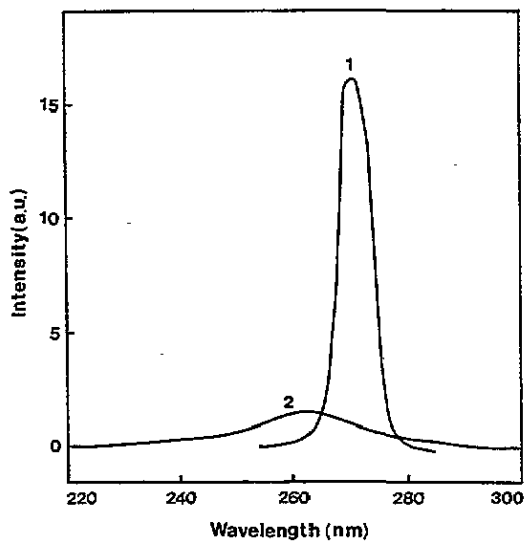


Figure 2. Excitation spectra for the 345 nm (curve 1) and the 395 nm (curve 2) emissions from  $\text{KCl:Bi}^{3+}$  ( $T = 78.8$  K) (a.u., arbitrary units).

exciting light, i.e.  $P(\alpha) = 0$ . The mathematical formula for angular dependence of the polarization ratio reveals that the dipoles responsible for the 345 and 395 nm emissions could be oriented along the  $C_4$  and  $C_3$  symmetry axes, respectively.

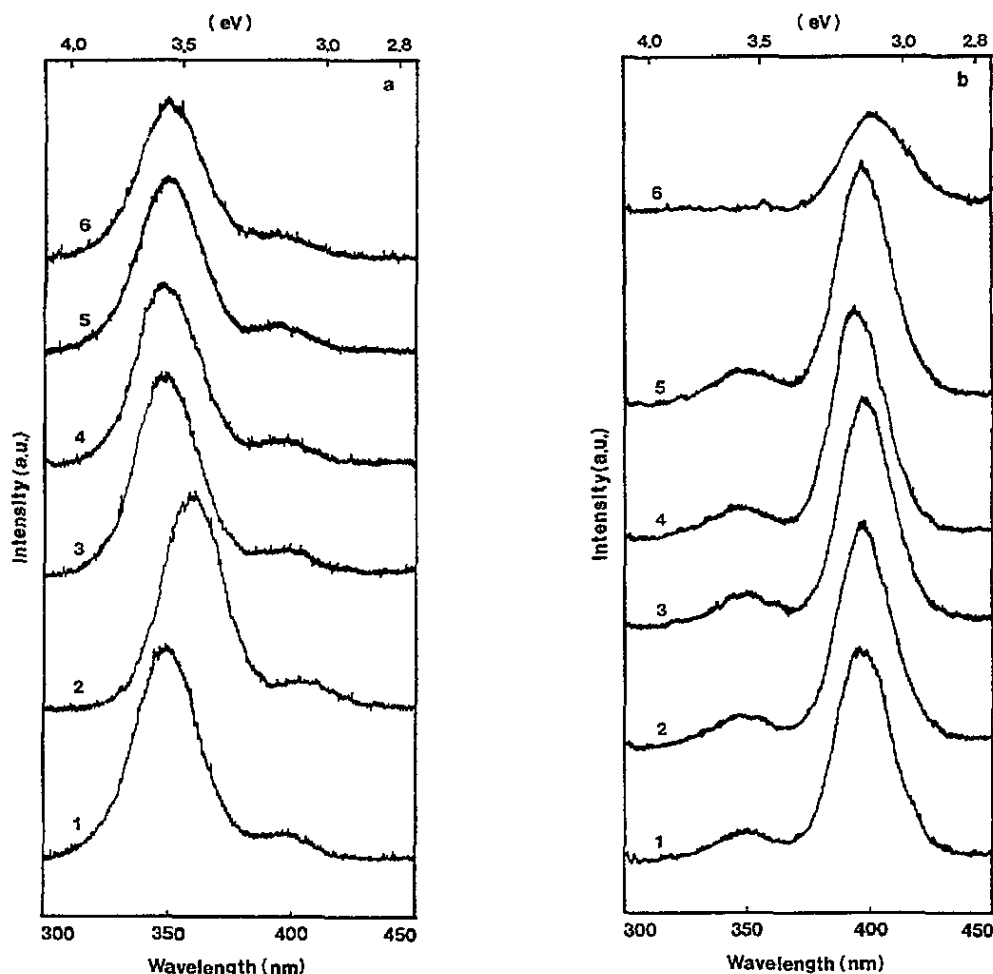


Figure 3. Emission spectra from  $\text{KCl:Bi}^{3+}$  excited at (a) 272.5 nm and (b) 264 nm as a function of temperature (a.u., arbitrary units): curves 1, 78.8 K; curves 2, 100 K; curves 3, 120 K; curves 4, 150 K; curves 5, 200 K; curves 6, 289 K.

### 3. Discussion

The main purpose of this paper is to reveal the origin of the colour centre associated with the X absorption and emission. The first question is: is the X-band transition associated with electronic states of  $\text{Bi}^{3+}$  ion in KCl?

The absorption spectrum of  $\text{KCl:Bi}^{3+}$  was reported in the previous publication (Kang *et al* 1994). In comparison with the A absorption band ( $^1S_1 \rightarrow ^3P_1$ ) from 310 to 360 nm, the X absorption band is located at a much higher energy. In general, optical transitions due to any aggregations of impurity ions, e.g. dimer or trimer, appear as a shoulder to those of isolated ions at low energies. First, we can rule out the possibility that the X-band transition could be correlated with the  $^3P_1$  ( $^3T_{1u}$ ) state of  $\text{Bi}^{3+}$  ion. The B absorption band peaking at 245 nm, attributed to the  $^1S_0 \rightarrow ^3P_2$  transition, is partially allowed by lattice vibrations. Here, the energy gap between the X and the B absorption bands is too large to

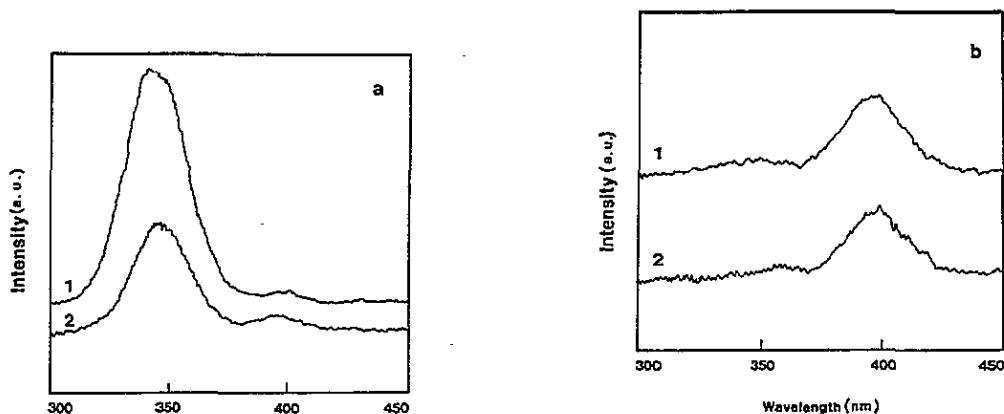


Figure 4. Polarized emission spectra from  $\text{KCl:Bi}^{3+}$  excited at (a) 272.5 nm and (b) 264 nm (a.u., arbitrary units): curves 1, the  $\Pi$  spectrum; curves 2, the  $\Sigma$  spectrum ( $T = 16$  K).

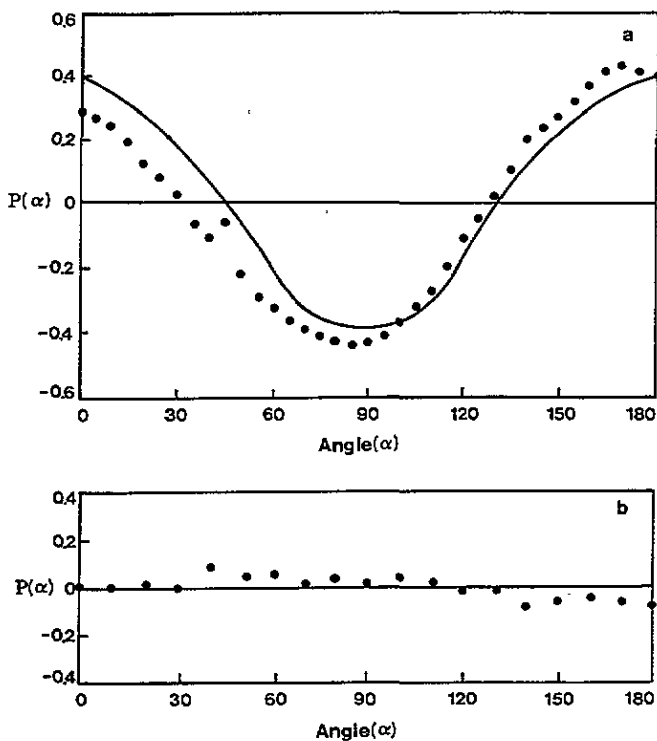


Figure 5. Angular dependence of the polarization ratio for (a) the 345 nm and (b) the 395 nm emission from  $\text{KCl:Bi}^{3+}$  ( $T = 16$  K). The angular dependence for the 345 nm emission can be formulated by  $0.4 \cos(2\alpha)$ .

correlate these two bands. Accordingly, we assume that the X band could not be attributed to electronic transitions of  $\text{Bi}^{3+}$  aggregates.

Spectroscopic studies on KCl:Ge<sup>0</sup> and KCl:Ge<sup>4+</sup> single crystals have also been conducted at our laboratory. According to the preliminary results for these crystals (Kang *et al.* 1995), the 340 and 395 nm emission bands have also been strongly observed in not only KCl:Bi<sup>3+</sup> but also KCl:Ge<sup>0</sup> and KCl:Ge<sup>4+</sup> phosphors. The excitation spectra for these two emissions are almost the same no matter what the impurity ions in the KCl single crystal are (table 1). This experimental evidence on the 340 and 395 nm emissions suggests that the X band transitions could not be connected directly to the electronic structures of the impurity ion but may be connected to a defect arising from the substitution of an impurity into the lattice.

**Table 1.** Observed X emission from KCl single crystals doped with impurities.

Phosphors	$\lambda_{exc}$ (nm)	$\lambda_{em}$ (nm)	$P(\alpha)$
KCl:Bi <sup>3+</sup>	265	395	0
	272.5	345	0.4 cos(2 $\alpha$ )
KCl:Ge <sup>0</sup>	265	395	0
	275	345	0.3 cos(2 $\alpha$ )
KCl:Ge <sup>4+</sup>	265	395	0
	275	345	0.3 cos(2 $\alpha$ )

The next question is: is the X-band transition therefore connected to Cl vacancies? Electron centres or hole centres should be considered when answering this, on the assumption that these centres can be created by irradiation with the exciting light. Among the electron centres connected to Cl<sup>-</sup> vacancies (such as the F, M and R centres and aggregates of F centres) the F centre is the most attractive since it has the highest excitation energy ( $E_{exc} = 2.313$  eV and  $E_{em} = 1.215$  eV) (Fowler 1968). In addition to the absorption band of the F centre, the irradiated KCl crystals show additional higher-energy bands, namely K, L<sub>1</sub>, L<sub>2</sub> and L<sub>3</sub> bands in order of increasing energy (Lüty 1968). These additional bands, however, have been found to have very small oscillator strengths compared with that of the F band. Our crystals did not produce the F absorption band so that the X band could not be attributed to these additional bands. The V<sub>K</sub> centre (or the self-trapped hole) and the H centre (or the interstitial Cl<sub>2</sub><sup>-</sup>) are well known in some detail as hole centres. For KCl crystals upon irradiation, the V<sub>K</sub> centre shows two absorption bands peaking at 365 and 750 nm and the H centre shows one absorption band peaking at 336 nm (Farge and Fontana 1979). Comparing the optical properties of the X band with those of Cl<sup>-</sup> vacancies, we can rule out the centres connected to Cl<sup>-</sup> vacancies. Thus, we are led to consider a perturbation effect of the substituted Bi<sup>3+</sup> on Cl<sup>-</sup> ions in the lattice, resulting in an interstitial Cl<sup>-</sup> ion or a loosely bonded Cl<sup>-</sup> ion.

When one of the six K<sup>+</sup> ions surrounding the Cl<sup>-</sup> ion is substituted by the Bi<sup>3+</sup> ion, interspacing may occur since the ionic radius of Bi<sup>3+</sup> (0.96 Å) is smaller than that of K<sup>+</sup> (1.33 Å) (figure 6). The central potential with O<sub>h</sub> symmetry is forced to be reduced. It is possible that the interspacing could loosen the binding of one of the neighbouring Cl<sup>-</sup> ions. The perturbation arising from substitution of impurity ions with smaller size is well understood for the F<sub>A</sub> centre of KCl single crystals doped with Li<sup>+</sup> or Na<sup>+</sup> (Lüty 1968). Furthermore, the Cl<sup>-</sup> ion may be in the interstitial position at a site of symmetry C<sub>4v</sub>, depending on the magnitude of the perturbation. Electronic transitions of the loosely bonded Cl<sup>-</sup> ion will require a higher energy than those of the F or F<sub>A</sub> centres, but less energy than the intrinsic transitions of the Cl<sup>-</sup> ion at the valence band as shown in figure 6.

Here, we regard the loosely bonded  $Cl^-$  ion (hereafter referred to as  $(Cl^-)^*$ ) as the X-band centre with the assumption that the exciting light is not strong enough to trap an electron at the defect.

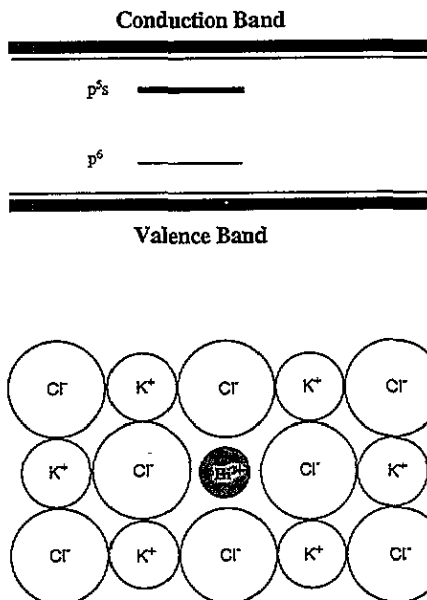


Figure 6. Schematic representations of structure and electronic states of the loosely bonded  $Cl^-$  ions as the X centre.

The ground state of  $(Cl^-)^*$  is non-degenerate  $^1S_0$ , while the excited state is expected to be  $^3P_J$  and  $^1P_1$ . The SO interaction may split  $^3P_J$  into  $^3P_2$ ,  $^3P_1$  and  $^3P_0$  in order of increasing energy. If we denote the electronic states by the appropriate irreducible representations of the  $C_{4v}$  symmetry group, the reduced static potential would split the fivefold  $^3P_2$  state into the non-degenerate  $^3A_1$ ,  $^3B_1$  and  $^3B_2$  states and the twofold  $^3E$  state. The optical transitions  $^1A_1 \rightarrow ^3A_1$  and  $^1A_1 \rightarrow ^3E$  are partially allowed with small oscillator strength by the orbital selection rule, while the optical transitions  $^1A_1 \rightarrow ^3B_1$  and  $^1A_1 \rightarrow ^3B_2$  are totally forbidden by the SO selection rule. Upon irradiation with the polarized exciting light, the orientation of the electric dipole is possibly conserved in transitions between the  $A_1$  and  $A_1$  states. For the transitions between the  $A_1$  and  $E$  states, the vector of the emitting dipole could be perpendicular to that of the exciting dipole. If we take into account the polarizations and the relative intensities of the two emission bands, the 272 nm excitation could be attributed to transitions from the ground  $^1A_1$  state to the excited  $^3A_1$  state, and the 265 nm excitation to transitions from the  $^1A_1$  state to the  $^3E$  state.

Let us try to understand the features of the X-band emission on the basis of the coordination diagram of the excited states. Taking into account the Stoke's shifts for the two emission bands (0.92 eV for the 345 nm band and 1.54 eV for the 390 nm band), one can find that the twofold  $^3E$  excited state becomes more stabilized than the excited  $^3A_1$  state. The stabilization would arise from the electronic-vibrational interaction and/or the off-diagonal elements of the SO interaction. The stabilization due to the latter could not be expected in these excited states.



For detailed assignment of the X-band emission from  $\text{KCl:Bi}^{3+}$ , we shall discuss the energy-level scheme of the relaxed excited states (RESS) in terms of the JT effect coupling to the vibronic modes under the  $C_{4v}$  symmetry. Since the JT energy  $E_{JT}$  is approximately half the Stokes shift, it is expected that the JT stabilization is not negligible. Here, we confine our consideration of the JT effect on the non-degenerate  $A_1$  and doubly degenerate E states of the  $C_{4v}$  system to only a qualitative analysis. Among the 15 vibronic modes, the  $A_1(Q_A)$ ,  $B_1(Q_{B_1})$ ,  $B_2(Q_{B_2})$ , and  $E(Q_\theta, Q_\epsilon)$  modes are active in vibronic interactions. The  $B_1$ ,  $B_2$  and E vibronic modes transform as  $x^2 - y^2$ ,  $xy$  and  $(xz, yz)$ , respectively. The non-degenerate  $A_1$  state is unaffected by the JT effect.

For the doubly degenerate E state, the JT stabilization is very significant in optical relaxation processes. Since  $E \times E = A_1 + A_2 + B_1 + B_2$ , the E electronic state can be coupled to the asymmetrical  $B_1$  and  $B_2$  modes; this problem is accordingly specified as  $E \otimes (B_1 + B_2)$ . In this problem, the APES in terms of the linear vibronic interaction is specified by (Bersuker 1984)

$$E(Q_{B_1}, Q_{B_2}) = \frac{1}{2}(K_{B_1}^2 Q_{B_1}^2 + K_{B_2}^2 Q_{B_2}^2) \pm (F_{B_1}^2 Q_{B_1}^2 + F_{B_2}^2 Q_{B_2}^2)^{1/2}$$

where  $K_\Gamma$  and  $F_\Gamma$  represent the force constant of the lattice for the  $\Gamma$  mode and the strength of the coupling to the  $\Gamma$  mode, respectively. When the coupling to the  $B_1$  mode is much stronger than that to the  $B_2$  mode, i.e.  $F_{B_1} > F_{B_2}$ , two minima with the JT stabilization energy  $E_{JT} = F_{B_1}^2/2K_{B_1}$  can exist at points  $(\pm F_{B_1}/K_{B_1}, 0)$  on the APES of the E state. For the other particular case of  $E \otimes B_2$ , two minima are reduced at  $(0, F_{B_2}/K_{B_2})$  with  $E_{JT} = F_{B_2}^2/K_{B_2}$ . When  $F_{B_1} = F_{B_2}$ , the  $E \otimes (B_1 + B_2)$  problem is very similar to the  $E \otimes E$  problem, showing the trigonal minima on the APES in the space of  $(Q_\theta, Q_\epsilon)$ . Accordingly, from the JT problem it can be seen that the E state becomes much more stable than the  $A_1$  state.

The resulting energy-level scheme and the corresponding configurational coordinate diagram for the  $(\text{Cl}^-)^*$  centre in KCl single crystals are shown in figure 7. This model and the diagram give a more definitive assignment of the X-band emission from  $\text{KCl:Bi}^{3+}$  as follows: the 395 nm emission could be attributed to transitions from the more stabilized  ${}^3E$  wells to the ground state (referred to as  $X_E$ ) and the 345 nm emission from the  ${}^3A_1$  well to the ground state (referred to as  $X_{A_1}$ ). The excitation from the ground state to point A on the  ${}^3A_1$  well could mainly produce the  $X_A$  emission peaking at 345 nm. On increasing the exciting photon energy, population of the  ${}^3E$  wells can be attained via non-radiative transitions from the  ${}^3A_1$  well, which may produce the additional  $X_E$  emission peaking at 395 nm. Excitation above the point B on the  ${}^3E$  wells may mainly produce the  $X_E$ .

The polarization of the two emission bands are indicative of the nature of the excited states. Regarding the relative orientation of the  $(\text{Cl}^-)^*$  with respect to the dopant  $\text{Bi}^{3+}$  ion, two possible configurations can be expected in the excited state of  $(\text{Cl}^-)^*$ . Upon irradiation with the polarized exciting light, the emission from the axial configurations may conserve the polarization of the exciting light, while the emission from the equatorial configurations may totally depolarize. As seen in the  $F_A$  centre of KCl doped with  $\text{Na}^+$  or  $\text{Li}^+$  ions, the RESS of those states become degenerate in energy, giving rise to an identical emission band. For this case, at high temperatures, reorientation between the two configurations takes place so that the emission becomes totally depolarized. Since the polarization of the 345 nm emission from the  $(\text{Cl}^-)^*$  centre is not changed much up to a high temperature, we can rule out the possibility that the characteristics of the observed polarization of the X-band emission may arise from the two configurations of the  $(\text{Cl}^-)^*$  centre.

For exciting light polarized in the [001] direction, i.e. along the z axis, the 345 nm emission from the  $A_1$  state is polarized in the same direction, since the orientation of the

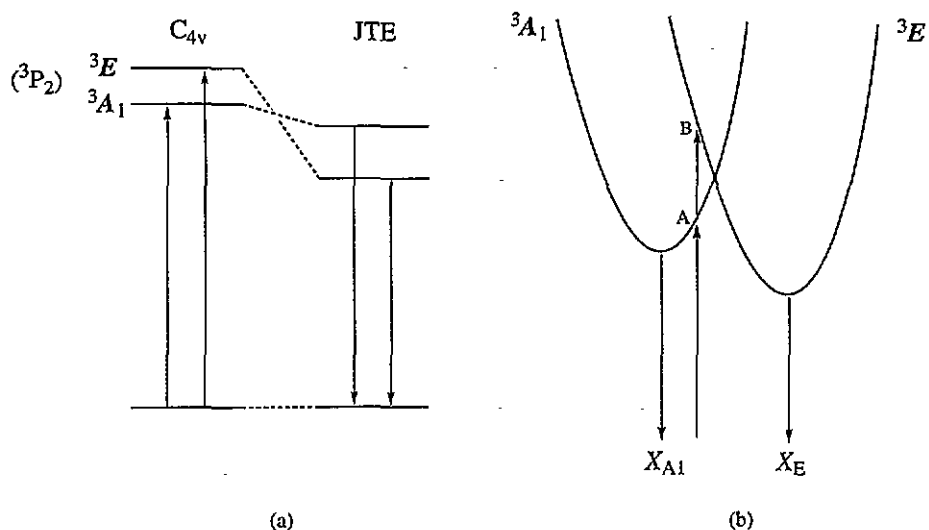


Figure 7. (a) Energy-level scheme and (b) configurational coordinate diagram for the RES of the X centre, formulated in terms of the JT coupling to the  $A_1$ ,  $B_1$  and  $B_2$  modes.

dipole is conserved in the optical processes for the  $^3A_1$  state. In this case, the angular dependence of the degree of polarization ratio is characterized by  $\cos(2\alpha)$ , where  $\alpha$  is the angle of the excitation beam with respect to the  $z$  axis. On the contrary, for the 395 nm emission from the E state, the polarization relationships could become more complicated. The vibronic coupling may play a key role in the depolarization process. The vibronic coupling to the  $B_1$  and  $B_2$  modes could result in trigonal minima on the  $^3E$  paraboloid. If this is true, emission from the trigonal minima is completely depolarized.

#### 4. Conclusions

$\text{KCl}:\text{Bi}^{3+}$  produces a very weak absorption band (called the X band) in the range between the A and B-absorption bands. The X-band excitation consists of two emission bands peaking at 345 and 395 nm, the appearance of which is very dependent on the exciting photon energy. These X-band emissions have also been found in KCl single crystals doped with impurity ions of relatively small ion size. The interspacing due to the substituted impurity ion or the cation vacancy could cause the binding of one of the neighbouring  $\text{Cl}^-$  ions to loosen. These two emission bands can be attributed to the loosely bonded  $\text{Cl}^-$  ion ( $\text{Cl}^-$ )\* with the symmetry  $C_{4v}$ .

Under the reduced static potential of  $C_{4v}$ , the  $^3A_1$  and  $^3E$  excited states arising from  $^3P_2$  could account for the X-band optical process. For the twofold  $^3E$  state, the JT coupling to the  $B_1$  and  $B_2$  vibronic modes is expected to be significant in the relaxation process. The dynamic JT interaction coupling to these vibronic modes may result in trigonal minima on the  $^3E$  paraboloids. The emission from these minima is completely depolarized for polarized exciting light. These considerations leads us to assign the two emission bands as follows: the 345 nm emission is attributed to the transition from the  $^3A_1$  RES and the 395 nm emission is from the  $^3E$  RES to the  $^1A_1$  state. Without this assumption, no treatment can account for the 345 and 395 nm emission bands from  $\text{KCl}:\text{Bi}^{3+}$ .

## Acknowledgment

This work was supported by the Korean Research Foundation.

## References

- Bersuker I B 1984 *The Jahn–Teller Effect and Vibronic Interactions in Modern Chemistry* (New York: Plenum) ch 2
- Choi K O, Lee S W, Bae H K, Jung S H, Chang C K and Kang J G 1991 *J. Chem. Phys.* **94** 6420
- Farge Y and Fontana M P 1979 *Electronic and Vibrational Properties of Point Defects in Ionic Crystals* (Amsterdam: North-Holland)
- Fowler W B 1968 *Physics of Color Centers* ed W B Fowler (New York: Academic) ch 2
- Fukuda A 1970 *Phys. Rev. B* **1** 4161
- Honma A 1974 *Sci. Light.* **23** 43
- Kang J G, Ju S K, Lee S W and Kim Y D 1995 to be published
- Kang J G, Yoon H M, Chun G M, Kim Y D and Tsuboi T 1994 *J. Phys.: Condens. Matter* **6** 2101
- Lüty F 1968 *Physics of Color Centers* ed W B Fowler (New York: Academic) ch 3
- Mugnai D, Ranfagni A and Viliani G 1982 *Phys. Rev. B* **25** 4284
- Ranfagni A and Viliani G 1974 *J. Phys. Chem. Solids* **35** 25