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ABOUT THE ORIGIN OF THE D BAND IN ALKALI HALIDES WITH TL+ IMPURITIES*

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ABSTRACT

The optical absorption of excitons near monovalent impurities is examined theoretically, using a phenomenological model for the exciton and a Born Haber cycle.

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RESUMEN

Se examina teóricamente la absorción óptica de excitones cerca de impurezas monovalentes, usando un modelo fenomenológico para el excitón y un ciclo de Born Haber.

In spite of the long time that has been dedicated to the study of the optical absorption properties of alkali halides with monovalent and divalent impurities the theoretical and experimental findings have been scarce. In particular, a so called D band is detected in the high energy region in crystals such as KCl: Tl$^+$ and KCl:In$^+$, and is conjectured in the literature as due to an exciton near the impurity or a charge transfer to the impurity(1). Recently, Tsuboi(2,3) has found by experiment that the D band is composed of three bands, (D_1, D_2, D_3) in order of increasing energy, and his theoretical calculations for KCl:Tl, which include charge transfer, have agreed well with experiment. Nevertheless, we believe it is physically plausible that the exciton optical absorption existing in a pure crystal is affected by impurities in a notable manner in doped crystals, and that this absorption occurs in the range of the D band.

The purpose of this note is to examine theoretically the optical absorption of excitons near monovalent impurities, using a phenomenological model for the exciton and a Born Haber cycle(4).

A first-principles approach would employ exciton wave functions in alkali halides, which are not easily found, because they correspond to neither Wannier or Bloch functions, but to an intermediate case, investigated theoretically by the Hartree Fock method(5).

The calculation are performed for alkali halides crystal with Tl^+ impurities, and the results are compared to the values found in Fakuda's classical work$^{(1)}$ and Tsuboi's work$^{(2,3)}$.

The theory developed for calculation of the energy of formation of localized excitons in alkali halides with divalent impurities appears in a recent work of Clark *et al.*$^{(6)}$. Details about the Born-Haber cycle appear in this work. For the case of excitons near monovalent impurities, depicted in Fig. 1, ions in position 1 and 2 those who participate in the creation of an exciton. The monovalent cationic impurity is at position 3. The energy difference ΔE between a free exciton and that of Fig. 1 has two principal contributions. I) Repulsive (ΔE_r), and II) Polarization (ΔE_ρ). For the repulsive term we employed the exponential form of Born and Mayer, so the difference in repulsive energy is

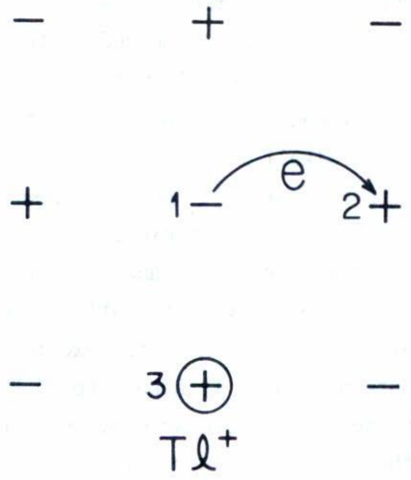
$$\exp\left[\frac{r_I + r_- - R}{\rho}\right] - C_H \exp\left[\frac{r_+ + \underline{r} - R}{\rho}\right] \quad , \tag{1}$$

where C_1 and C_H are constants depending upon the charge and the ionic species, r_+, r and r_1 are the ionic radius of the alkali, halogen and impurity ions respectively, and b the Born-Mayer interaction parameters and R the interionic distance.

The polarization energy has two contributions: one due to the interaction between the hole at position 1 and the electron at position 2, with the dipolar moment induced by them at point 3. The expression for this contribution is

$$E_p = \frac{e^2R^3}{2}\left[\frac{1}{r_{13}^4} + \frac{1}{r_{23}^4} - 2\cos\frac{(r_{13}, r_{23}}{r_{13}^2\ r_{23}^3}\right](M_I - M_+), \tag{2}$$

where M_I and M_+ are the dipolar moment of the impurity and the dipolar moment of the substituted monovalent positive ion, respectively, which are



given by

$$M_I = \frac{2\alpha_I}{\alpha_+ + \alpha_-} \; \frac{1}{4\pi} \; (1 - \frac{1}{K_0}) \quad , \tag{3}$$

$$M_+ = \frac{2\alpha_+}{\alpha_+ + \alpha_-} \; \frac{1}{4\pi} \; (1 - \frac{1}{K_0}) \quad , \tag{4}$$

where α_I, α_+, and α_- represent the polarizability of the impurity, positive and negative ions respectively.

Then, the total effect, the shift of the exciton absorption peak, by the presence of the impurity is

$$E = E_r + E_p = b \;\; C_I \exp \frac{r_I + r_- - R}{\rho} - C_H \exp \left(\frac{r_+ - r_- - R}{\rho} \right)$$

$$+ \frac{e^2 R^3}{2} \left(\frac{1}{r_{13}^4} + \frac{1}{r_{23}^4} - \frac{2 \cos(r_{13}, r_{23})}{r_{13}^2 \;\; r_{23}^2} \right) (M_I - M_+) \;\; , \tag{5}$$

where $r_{13} = r_{23} = \sqrt{2}R$.

Using the expression (5), the corresponding results are shown in Table I and III. In table I are listed the numerical values of the constants introduced in the calculations the results shown in Table II and III agree with the peak values of band D reported by Fakuda(1) and we might conclude that the D band in alkali-halide crystals with monovalent impurities such Tl^+ is related to exciton near a Tl^+ impurity.

TABLE I

VALUES FOR THE CONSTANTS USED IN THE CALCULATIONS

$M = 1.7476$	$r_I = 1.47$(1)
$b = 0.229$ x 10-17 erg.	$M_I = 5.2$(2)
$C_H = 1$	$C_I = 1.125$

(1) Ref. (6)
(2) Ref. (9)

For the values R, r_+, r_-, M_+, M_- see Ref. (6).

On the other side, Table IV shows the experimental results of Tsuboi *et al.* for KCl:Tl, and Kl:Tl, and also a comparison with those obtained in this work. In this table one notes that the theoretical value of 5.72 eV, obtained for Kl:Tl, lies very close to the experimental value for the D_3 band. In the case of KCl:Tl, Tsuboi *et al.* have not detected the D_3 band; they presume it is hidden within the exciton band(3), while on the theoretical side they find an effect, due to charge transfer, of the order of 7.74 eV. This value is comparable to the one found in this work for the exciton: 7.68 eV.

TABLE II

ENERGY DIFFERENCE (in eV) BETWEEN A FREE EXCITON AND AN EXCITON LOCALIZED AT Tl^+ CATIONIC IMPURITY

E					
Host	Theo	Exp[+]	Host	Theo	Exp[+]
NaBr	0.562		LiI	0.364	
KBr	0.097	0.270	LiBr	0.505	
RbBr	0.089		LiF	1.363	
NaI	0.206		LiCl	0.569	
KI	0.082		NaCl	0.311	0.360
RbI	0.045		KCl	0.105	0.460
NaF	0.667		RbCl	0.074	
KF	0.273				
RbF	0.161				

[+] E(exp) Ref. (1) (Fakuda).

TABLE III

Host	D band (eV)	theo (eV)
NaCl:Tl^+	7.6	7.65
KCl:Tl^+	7.3	7.66
KBr:Tl^+	6.5	6.68

Table III. Peak position of the absorption bands due to the excitons considered in this work, compared with the peak position of the D band. The calculated values of E have been subtracted from the energy for the first exciton peak at 80°K (Ref. 10).

TABLE IV

	D_1(eV)	D_2(eV)	D_3(eV)	D (eV)
KCl:Tl$^+$	6.72	7.23	-	-
	6.71(Theo)	7.28(Theo)	7.74(Theo)	7.66
KI:Tl$^+$		5.52	5.68	-
		-	-	5.72

Table IV. Position of the absorption peak due to excitons. The calculations performed in this work appear under column D, and are compared with the experimental values reported by Tsuboi(3) for the D_1, D_2, D_3 - bands. There are also shown, in the case of KCl:Tl, the theoretical results by Tsuboi(3), obtained with a charge-transfer model.

Thus, considering the D-band resolved in the three bands found by Tsuboi *et al.*(2,3), the results seem comparable to the D_3 band, which Tsuboi interprets as due to charge transfer therefore, it is possible that both effects are mixed in the D_3-band. On the other hand, in the case of crystaline alkali-halides doped with divalent impurities such as Pb^{2+}(6) or Sn^{2+}(7), the optical apsortion of the exciton near to impurity might correspond to the D' band detected by Fakuda(1), which would be equivalent to the D_2-band obtained by Tsuboi. Calculations similar to those by Clark *et al.*(6), performed for excitons near divalent impurities, have yielded the theoretical values(7) 7.06 eV and 5.21 eV for KCl:Sn^{2+} and Kl:Sn^{2+}, respectively. The first value compares with the 7.15 eV-D' band detected by Fakuda(1) and also with the 7.11 eV-D_2-band detected by Tsuboi(2); the second value corresponds to the 5.2-eV D_{2-} band obtained by Tsuboi, the fact that the exciton peak shows a greater shift in divalent impurities is reasonable, since the coulomb contributions produces a greater effect than monovalent impurities.

In order to delucidate more clearly the D band problem and the aforementioned possibilities, more work is needed, both theoretical and experimental. On the theoretical side, it becomes necessary to conduct quantum-mechanical taking into account covalency effects, which may be of importance.

REFERENCES

1. A. Fakuda, *Sci Light* (Japanese Journal) 13 (1964) 64.
2. T. Tusboi, *Physica* 96B (1979) 341.
3. T. Tusboi, and S. Sakoda, *Phys Rev* B22 (1980) 4972.
4. F. Bassani and N. Inchauspé. *Phys Rev*. 105 (1957) 819.
5. A.M. Stoneham, *J Phys C, Solid St Phys* 7 (1974) 2476.
6. A. Clark, J.L. Marín, R. Rodríguez and C. Ruíz Mejía, *Cryst Latt Def and Amorph Mat* 10 (1984) 185.
7. R. Rodríguez and A. Clark, *Rev. Mex. de Fis.*, (To be published).
8. *CRS Handbook, Phys and Chem.* F. 179 (1976-1977).
9. J.R. Teesman and A.H. Kohn, *Phys Rev.* 92 (1953) 890.
10. J.E. Eby, K.J. Teegarden and D.B. Dutton, *Phys Rev* 116 (1959) 1099.