

## THE EPR SPECTRA FOR COOPER IONS IN MIXED ALKALI CADMIUM PHOSPHATE GLASSES

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### Abstract

The aim of the present investigation is to study, from theoretical point of view, the nature of the site symmetry of  $\text{Cu}^{2+}$  in lithium-sodium mixed alkali cadmium phosphate glasses (hereafter referred to as LiNaCdP) from the nature and splitting of EPR and optical bands as a function of mixed-alkali effect MAE. The host glass is  $x\text{Li}_2\text{O} + (20-x)\text{Na}_2\text{O} + 20\text{CdO} + 59.5\text{P}_2\text{O}_5 + 0.5\text{CuO}$ , with  $x = 10$ . The electron paramagnetic resonance spectra for  $\text{Cu}^{2+}$  doped mixed alkali cadmium phosphate (LiNaCdP) glasses are calculated from perturbation theory method (PTM), to understand the nature and symmetry of dopant. The results obtained for spin Hamiltonian parameters ( $g_{\parallel}, g_{\perp}$ ) indicate that the cooper ion enters in the glass matrix into a tetragonal elongated octahedral site.

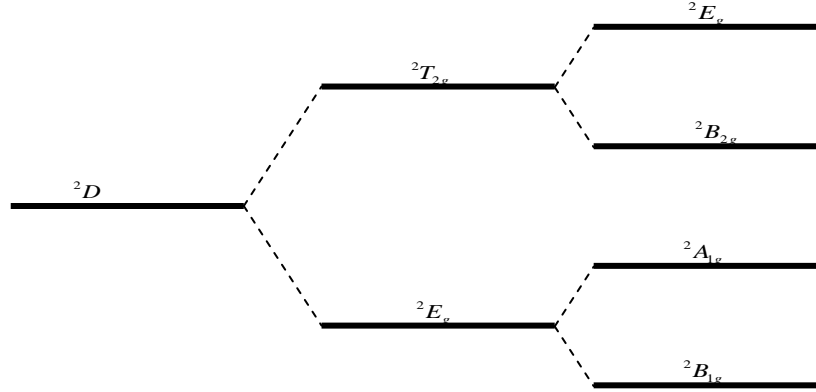
## 1. Introduction

Mixed-alkali in glasses has attracted much attention, due to its technological and theoretical interests in describing the physics and chemistry of glasses [1]. Transition metal oxide containing phosphate glasses exhibit in semi-conducting nature and the electrical conduction is observed due to the hopping of electrons [2]. So, these glasses have attracted a great deal of attention because of their potential applications in the development of new tunable solid-state lasers, solar-energy converters, and fiber-optic communication devices [2]. Transition metal ions are used to probe the glass structure, because their responses to surrounding actions are very sensitive [3].

In this paper we have been investigated, from theoretical point of view, the nature of the site symmetry of  $\text{Cu}^{2+}$  in lithium-sodium mixed alkali cadmium phosphate glasses (hereafter referred to as LiNaCdP) from the nature and splitting of EPR and optical bands as a function of mixed-alkali effect MAE. The host glass is  $x\text{Li}_2\text{O} + (20-x)\text{Na}_2\text{O} + 20\text{CdO} + 59.5\text{P}_2\text{O}_5 + 0.5\text{CuO}$ , with  $x = 10$  [4]. So, we calculate the g factors for  $\text{Cu}^{2+}:\text{LiNaCdP}$ .

## 2. Method of calculation

Cu<sup>2+</sup> replace Cd<sup>2+</sup> in the LiNaCdP glasses. The free ion term for Cu<sup>2+</sup> (d<sup>9</sup>) is <sup>2</sup>D. In an octahedral crystal field, it splits into <sup>2</sup>E<sub>g</sub> and <sup>2</sup>T<sub>2g</sub> with the former being the ground state. <sup>2</sup>E<sub>g</sub> generally splits due to Jahn Teller distortion to <sup>2</sup>B<sub>1g</sub> and <sup>2</sup>A<sub>1g</sub> and the <sup>2</sup>T<sub>2g</sub> level to <sup>2</sup>B<sub>2g</sub> and <sup>2</sup>E<sub>g</sub>. The energy difference between <sup>2</sup>A<sub>1g</sub> and <sup>2</sup>B<sub>2g</sub> depends on the degree of distortion [4].



**Figure 1.** Splitting of the term <sup>2</sup>D.

The strongest bands correspond to the transition <sup>2</sup>B<sub>1g</sub> - <sup>2</sup>B<sub>2g</sub> at 11425 cm<sup>-1</sup> and the other band correspond to the transition <sup>2</sup>B<sub>1g</sub> - <sup>2</sup>E<sub>g</sub> at 12045 cm<sup>-1</sup>. For d<sup>9</sup> ions in the tetragonal symmetry with the ground states, according to the crystal-field theory [5, 6, 7], the three optical band positions concerning the d-d transitions are given as:

$$\begin{aligned}
 E_1 &= E(^2B_1) - E(^2A_1) = 4Ds + 5Dt \\
 E_2 &= E(^2B_1) - E(^2B_2) = 10Dq \\
 E_3 &= E(^2B_1) - E(^2E_2) = 10Dq - 3Ds + 5Dt
 \end{aligned} \tag{1}$$

The third-order perturbation formulas of g factors for d<sup>9</sup> ions in tetragonally elongated octahedral clusters are derived by the perturbation theory as:

$$g_{\parallel} = g_e + \frac{8k\zeta}{E_2} - \frac{4k\zeta^2}{E_2E_3} - \frac{(k + g_e)\zeta^2}{E_3^2}, \tag{2}$$

$$g_{\perp} = g_e + \frac{2k\zeta}{E_3} + \frac{(k - g_e/2)\zeta^2}{E_3^2} - \frac{2g_e\zeta^2}{E_2^2}, \tag{3}$$

where k is the orbital reduction factor, in our case k = 0.94, g<sub>e</sub> is the free-spin g value of 2.0023, ζ<sub>0</sub> = 829 cm<sup>-1</sup> are the value of ζ in free state. E<sub>2</sub> and E<sub>3</sub> are the energy intervals given in Eqs. (1).

$$\zeta \approx k \cdot \zeta_0 \quad (4)$$

In table 1 are shown the values of g factors for Cu<sup>2+</sup> doped in LiNaCdP.

Table 1. g factors values of Cu<sup>2+</sup> doped LiNaCdP glass, calculated by PTM.

LiNaCdP	$g_{\parallel}$ (calc.)	$g_{\parallel}$ (exp.) [4]	$g_{\perp}$ (calc.)	$g_{\perp}$ (exp.) [4]
	2.486	2.441	2.102	2.088

The covalency parameter for the in plane  $\sigma$  bonding is evaluated from the expression [4]:

$$\alpha^2 = \frac{A_{\parallel}}{0.036} + (g_{\parallel} - g_e) + \frac{3}{7}(g_{\perp} - g_e) + 0.004 \quad (5)$$

where  $A_{\parallel} = 0.0121 \text{ cm}^{-1}$  [4]. Using eqs. (4), we obtain for covalency parameter the value  $\alpha^2 = 0.8668$ .

### 3. Conclusion

Cu<sup>2+</sup> ions take position in place of Cd<sup>2+</sup> ions in the glasses. It can be seen from the Table 1, that results obtained by PTM are in good agreement with observed values [4]. Thus the EPR spectra of Cu<sup>2+</sup> in LiNaCdP are explained theoretically. As  $g_{\parallel} > g_{\perp} > g_e$  the ground state of the unpaired electron is <sup>2</sup>B<sub>1g</sub>. This observation also suggests that Cu<sup>2+</sup> ions are subjected to tetragonally elongated distortion. The covalence degree of the in-plane Cu-O- $\sigma$  bonds ( $\alpha^2$ ) in LiNaCdP glasses indicates partially covalent.

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