# ELECTRON PARAMAGNETIC RESONANCE SPECTRUM OF Cu(II) IN CESIUM PHOSPHATE GLASSES

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## Abstract

## Full Text

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## PHYSICS

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# ELECTRON PARAMAGNETIC RESONANCE SPECTRUM OF Cu(II) IN CESIUM PHOSPHATE GLASSES

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A high sensitivity ([1–3]) of the EPR spectra of Cu(II) ions to structural changes in oxide glasses has been established. It therefore appears useful to study the EPR spectrum of this ion in glasses of the $Cs_2O$—$P_2O_5$ system. The properties of this system have been little studied, while the large ionic radius and high coordination numbers of $Cs^+$ in crystalline compounds make it possible to suppose that these glasses may have a structure different from that of other alkali phosphate glasses. For comparison, the EPR spectra of Cu(II) in sodium phosphate glasses of corresponding composition were also studied. In the present work phosphate glasses containing 20–50 mol.% $Cs_2O$ (or 10–50 mol.% $Na_2O$) were investigated. The paramagnetic $Cu^{2+}$ ions were introduced into these glasses as a small admixture of CuO (0.1–1 wt.% in excess of 100%). The glasses were melted from reagents (analytical grade): $Cs_2CO_3$, $Na_2CO_3$, and $NH_4H_2PO_4$, in a laboratory electric furnace, followed by cooling of the melt in air.

EPR measurements were carried out on an RE-1301 three-centimeter-band radiospectrometer at room and liquid-nitrogen temperatures.

**Fig. 1.** EPR spectrum of Cu(II) in a glass containing $Cs_2O$ 45 mol.%, $P_2O_5$ 55 mol.%; CuO 0.5 wt.%

## Experimental results and discussion

Figure 1 shows a typical EPR spectrum of $Cu^{2+}$ in cesium phosphate glasses. It is characteristic that, in contrast to borate glasses, which have larger hyperfine-splitting constants, in alkali phosphate glasses the hyperfine structure in the perpendicular orientation is, as a rule, not resolved. Such spectra are described by an axially symmetric spin Hamiltonian, which has been discussed repeatedly (see, for example, ([1–3])). The parameters of this spin Hamiltonian for the glasses we investigated are given in Tables 1 and 2.

1. Table 1 presents the results of studying the dependence of the EPR spectral parameters on the concentration of CuO for two glass compositions in the $Cs_2O$—$P_2O_5$ system. From these data it follows that, for glasses of one composition melted simultaneously (marked by *), the parameters $A_\parallel$, $g_\parallel$, and $g_\perp$ do not depend on the CuO content (within the investigated range of CuO concentrations) to within the accuracy of the measurement errors. A certain difference in the parameters in glasses 1 and 5 for composition No. 1 and 8 for composition No. 4, obtained in another melting, is apparently due to the nonidentity of their actual composition (chemical analysis was not performed), associated with a difference in the maximum melting temperatures.

**Table 1**

**Dependence of the parameters of the EPR spectra of Cu(II) in cesium phosphate glasses on the CuO content**

| Specimen No. | CuO, wt.% | $g_\parallel$ | $g_\perp$ | $A_\parallel \cdot 10^{-4}$, $cm^{-1}$ | Specimen No. | CuO, wt.% | $g_\parallel$ | $g_\perp$ | $A_\parallel \cdot 10^{-4}$, $cm^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|
| | | **N1 $20Cs_2O \cdot 80P_2O_5$** | | | | | **N4 $35Cs_2O \cdot 65P_2O_5$** | | |
| 1 | 0.2 | $2.43_4$ | $2.06_8$ | $107^*\pm 12$ | 5 | 0.2 | $2.42_5^*$ | $2.06_5$ | $140^*\pm 15$ |
| 2 | 0.5 | $2.43_4$ | $2.06_8$ | $107^*\pm 12$ | 6 | 0.5 | $2.42_5^*$ | $2.06_5$ | $140^*\pm 15$ |
| 3 | 1.0 | $2.43_4$ | $2.06_8$ | $107^*\pm 12$ | 7 | 1.0 | $2.42_5^*$ | $2.06_5$ | $140^*\pm 15$ |
| 4 | 2.0 | $2.43_4$ | $2.06_8$ | $107^*\pm 12$ | 8 | 2.0 | $2.42_5^*$ | $2.06_5$ | $140^*\pm 15$ |

**Table 2**

**Dependence of the parameters of the EPR spectra of Cu(II) and of the $\sigma$-bond coefficient ($\alpha^2$) on the glass composition**

| Specimen No. | $100x$ | $g_{\parallel}$ | $g_{\perp}$ | $A_{\parallel} \cdot 10^{-4}$, $cm^{-1}$ | $\alpha^2$ | Specimen No. | $100x$ | $g_{\parallel}$ | $g_{\perp}$ | $A_{\parallel} \cdot 10^{-4}$, $cm^{-1}$ | $\alpha^2$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $x\mathbf{Cs_2O}$ $(1-x)\mathbf{P_2O_5}$ $+$ **0.5 wt.% CuO** | | | | | | $x\mathbf{Na_2O}$ $(1-x)\mathbf{P_2O_5}$ $+$ **0.5 wt.% CuO** | | | |
| 1 | 20 | $2.44_2$ | $2.06_7$ | $110 | | | | | | | |

2. Table 2 gives the parameters of the EPR spectra of Cu(II) as a function of the $Cs_2O$ and $Na_2O$ content.

Consideration of these results shows that:

a) in the $Cs_2O$ concentration interval from 20 to 50 mol.% the parameters $g_{\parallel}$, $g_{\perp}$, and $A_{\parallel}$ change monotonically;

b) the character and range of these changes for cesium phosphate and sodium phosphate glasses of analogous compositions are identical;

c) the absolute value of the parameters depends little on the chemical nature of the alkali over the entire composition range studied, as was established earlier ([3]) using one composition of alkali-phosphate glasses as an example;

d) the character of the change in the spectral parameters (a decrease in $g_{\parallel}$ and $g_{\perp}$ and an increase in $A_{\parallel}$) indicates an increase in the ionicity of the bonds in the glass matrix as the alkali content increases in the interval 20-50 mol.%;

e) the abrupt change in the parameters of the Cu(II) EPR spectra at alkali contents above 50 mol.% is apparently associated with structural changes in the glass and requires further study.

## Estimation of the unpaired-electron density on the copper atom in glasses

1. The character of the change in the parameters of the Cu(II) EPR spectra may serve as a qualitative characteristic of the change in the degree of covalency of the copper-ligand bond in the glass as a function of its composition. For a quantitative estimate of the nature of the bonds in the glass, as shown in works ([1–3]), one can use the coefficients $\alpha^2$, $\beta_1^2$, $\beta^2$ in the theory of MacGarvey-Maki ([4]) and Kivelson-Neiman ([5]).

The cesium phosphate glasses studied by us are extremely unstable to the action of moisture, as a result of which it is very difficult to obtain reliable optical spectra for them. Therefore, for these glasses only the parameter $\alpha^2$ can be estimated; for its calculation only EPR data are used.

It should be noted that, for estimating $\alpha^2$ in glasses, the formula ([1–3]) is usually used

$$\alpha^2 = -\left(A_\parallel/P\right) + \left(g_\parallel - 2\right) + \frac{3}{7}\left(g_\perp - 2\right) + 0.04, \tag{1}$$

which was obtained in ([5]) approximately and requires discussion in connection with the possibility of applying it to oxide glasses.

2. First, the last term (0.04) in formula (1) was calculated in ([5]) for nitrogen ligands. Its magnitude is composed of two terms:

$$D_1 = -\rho f_1 - \mu f_2 \quad \text{and} \quad D_2 = -\frac{11}{6}\mu f_2,$$

where

$$\rho = \lambda_0\alpha\beta_1/\Delta E_{xy}; \qquad \mu = \lambda_0\alpha\beta/\Delta E_{xz};$$

$$f_1 = 8\left[\alpha'\beta_1 S + \alpha'(1-\beta_1^2)^{1/2}\frac{T(n)}{2}\right]; \qquad f_2 = \frac{6}{7}\left[\alpha'\beta S + \alpha'(1-\beta^2)^{1/2}\frac{T(n)}{\sqrt{2}}\right].$$

(The quantities $\alpha$, $\beta$, $\beta_1$, $\Delta E_{xy}$, $\Delta E_{xz}$, $S$, $T(n)$, $\lambda_0$ are given in the notation of Kivelson and Neiman ([5]).) We estimated the term $D_1+D_2$ for some oxide glasses on the basis of our experimental EPR data for Cu(II) in aluminosilicate glasses, for which we were able to determine the positions of the electron-absorption bands, and the data of ([2]) on the EPR of Cu(II) in sodium borate glasses (for which the electron-absorption bands are also given). The calculation was carried out assuming $S = 0.076$, $T(n) = 0.22$, and $\lambda_0 = -828$ cm$^{-1}$. From the data of Table 3 it is seen that the value of the last term in formula (1) is $\sim 0.03$.

3. A second important factor that can introduce substantial errors into the estimate of $\alpha^2$ by formula (1) is the assumption that $k = \alpha^2 k_0$, where $k_0 = 0.43 \pm 0.02$. In ([6]) it is asserted that calculating $\alpha^2$ without this assumption can lead to a change in $\alpha^2$, depending on the composition of the compound under study, in the opposite direction. In order to check this assertion, we studied the EPR of Cu(II) in strontium borate glasses.* The presence of a sufficiently well resolved hyperfine structure in the perpendicular orientation makes it possible to estimate the value $A_\perp$, which enters into a formula that does not contain the assumption of constancy of $k_0$, and also to calculate the value of $k_0$ for different glasses.

By means of simple transformations of the expressions obtained in ([5]), one can arrive at the following formulas:

$$\alpha^2 = \frac{7}{6}\left\{\frac{|A_\parallel|}{P} - \frac{|A_\perp|}{P} + \left(g_\parallel - 2\right) - \frac{5}{14}\left(g_\perp - 2\right)\right\} + \frac{7}{6}(D_1 - D_2), \qquad (2)$$

$$\alpha^2 = \frac{1}{k_0}\left\{\frac{A_\parallel + 2A_\perp}{3} + \frac{g_\parallel + 2g_\perp}{3} - 2\right\} + \frac{D_1 + 2D_2}{3k_0}, \qquad (3)$$

which do not contain the assumption of constancy of $k_0$.

Table 4 gives the values of $\alpha^2$ and $k_0$, calculated by formulas (1)**, (2), and (3).

From Table 4 it follows that

a) the direction of change of the value of $\alpha^2$ calculated by formulas (1) and (2) remains unchanged;

b) the value of $k_0$ changes only insignificantly for different glasses and, for the glasses we studied, lies in the interval 0.435–0.445. Comparison with the values of $k_0$ calculated in ([4]) for lithium- and sodium-borate glasses confirms that the value of $k_0$ in glasses does not go beyond the limits $0.43 \pm 0.02$;

c) the insignificant difference in the absolute values of $\alpha^2$, calculated by

* The strontium borate glasses were prepared by N. V. Petrovykh, to whom the authors express their gratitude for the samples provided.

** Formula (1) was used to calculate $\alpha^2$ with replacement of the last term, 0.04, by 0.03.

according to formulas (1) and (2), which exceeds the measurement errors, is connected with the difference in the magnitude of $k_0$.

Thus, from what has been set forth above it follows that, since the direction of change of $\alpha^2$ does not depend on the assumption of the constancy of $k_0$ (and, as a rule, we are interested in the relative character of the change in $\alpha^2$) and since the absolute values of $\alpha^2$ differ only slightly when calculated with and without this assumption, for estimating the value of $\alpha^2$ one may use formula (1) (with the corresponding correction of the last term), since it is not possible to determine the value $A_\perp$, entering into formula (2), for all glasses.

**Table 3**

**Estimate of corrections to formula (1)**

| Glass composition | $g_\parallel$ | $g_\perp$ | $A_\parallel \cdot 10^{-4}$, $cm^{-1}$ | $\Delta E_{xy}$, $cm^{-1}$ | $\Delta E_{xz}$, $cm^{-1}$ | $\alpha^2$ | $\beta_1^2$ | $D_1$ | $D_2$ | $D_1+D_2$ |
|---|---|---|---|---|---|---|---|---|---|---|
| $Al_2O_3$ 2.332 $O$ 2.084 $SiO_2$ | | | 133 | 13000 | – | 0.76 | 0.90 | 0.027 | 0.004 | 0.031 |
| $Al_2O_3$ 2.330 $\cdot$ 2.002 | | | 136 | 12700 | – | 0.77 | 0.87 | 0.027 | 0.004 | 0.031 |
| $2B_2O_3 \cdot Na_2O$* | | | | 12600 | – | 0.825 | 0.805 | 0.026 | 0.004 | 0.030 |
| $0.98B_2O_3 \cdot 0.02Na_2O$* | | | | 12500 | 23800 | 0.855 | 0.910 | 0.024 | 0.004 | 0.028 |

**Note.** Results for compositions marked with an asterisk are taken from work ([2]).

**Table 4**

**Calculation of the quantities $\alpha^2$ and $k_0$ for strontium borate glasses**

| $x$ | $\Delta g_\parallel$ | $\Delta g_\perp$ | $A_\parallel \cdot 10^{-4}$, $cm^{-1}$ | $A_\perp \cdot 10^{-4}$, $cm^{-1}$ | $\alpha^2(1)$ | $\alpha^2(2)$ | $k_0$ |
|---|---|---|---|---|---|---|---|
| 20 | 0.306 | 0.053 | 165 | 28 | 0.817 | 0.809 | 0.435 |
| 29 | 0.306 | 0.051 | 163 | 30 | 0.811 | 0.798 | 0.442 |
| 40 | 0.305 | 0.050 | 163 | 30 | 0.809 | 0.793 | 0.444 |
| 57 | 0.290 | 0.043 | 166 | 32 | 0.799 | 0.785 | 0.442 |

**Note.** Composition of the glasses: $x$SrO $(100-x)B_2O_3$; $\alpha^2(1)$ and $\alpha^2(2)$ mean that $\alpha^2$ was calculated by formulas (1) and (2), respectively.

4. From the data of Table 2, which gives the values of $\alpha^2$ for the cesium phosphate and sodium phosphate glasses studied by us, it follows that in the range of variation of alkali content from 10 to 50 mol.% the value of $\alpha^2$ remains practically constant and decreases abruptly on going to a higher alkali content.

## Conclusions

In the region of low alkali content (up to 50 mol.%) the structure of cesium phosphate glasses should not differ substantially from the structure of sodium phosphate glasses. The change in the parameters of the EPR spectra in glasses of both systems is monotonic in character, which does not contradict literature data on the dependences of other properties of various alkali-phosphate glasses on alkali content (up to 50 mol.%).

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*Note: Figure translations are in progress. See original paper for figures.*