HYPERFINE STRUCTURE OF THE PARAMAGNETIC-RESONANCE SPECTRA OF Cu(II) IN CERTAIN OXIDE GLASSES

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Abstract

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HYPERFINE STRUCTURE OF THE PARAMAGNETIC-RESONANCE SPECTRA OF Cu(II) IN CERTAIN OXIDE GLASSES

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1. It has been established (1) that the parameters of the electron paramagnetic resonance (EPR) spectra of VO^{2+} in various oxide glasses show a clear correlation with the chemical nature of the elements constituting the glass. In the present work an attempt has been made to carry out an analogous study for Cu(II) in similar glasses. Such a study should reveal the features of the incorporation of Cu(II) into the glass matrix in comparison with VO^{2+}, and also makes it possible to verify the conclusions concerning the nature of the chemical bonds between the elements in the glass matrix, drawn in (1) on the basis of an analysis of the behavior of the EPR spectra of VO^{2+}.

Fig. 1. Typical EPR spectrum of Cu(II) in oxide glass

The dependence of the EPR spectra of Cu(II), present as an impurity (0.5—2 cat.%), on the nature of the glass former (P_2O_5, SiO_2, B_2O_3) and of the modifier (elements of the alkali and alkaline-earth groups of the periodic system) was investigated in the simplest binary glasses. The compositions of the glasses studied are given in Tables 1 and 2. EPR measurements were carried out on an RE-1301 radiospectrometer operating in the 3-centimeter range, at room and liquid-nitrogen temperatures.

2. A typical EPR spectrum of Cu(II) observed in glasses is shown in Fig. 1. A method for analyzing such spectra was proposed by Sands (2) and developed in subsequent works. The spectrum can be described by a spin Hamiltonian of axial symmetry:

$$\mathcal{H} = g_{\|}\beta H_z S_z + g_{\perp}\beta(H_{xS}x + H_{yS}y) + AI_{zS}z + B(I_{xS}x + I_{yS}y), \qquad (1)$$

where $S = 1/2$ (electronic configuration Cu^{2+}—$3d^9$) and $I^{63,65} = 3/2$. The remaining parameters of the spin Hamiltonian are given in Tables 1 and 2.

3. Analysis of the data presented in Tables 1 and 2 shows that in all the glasses investigated $g_{\|} > g_{\perp} > 2.002$. This fact, as well as the fact that the Cu(II) spectrum is observed at room temperature, indicates octahedral coordination of Cu(II) in all the samples studied.

In work (^{3}) material was presented, selected on the basis of literature data, on the empirical comparison of the parameters of the EPR spectra of Cu(II) and the geometry of the corresponding complex, established on the basis of X-ray investigations. Such a comparison confirms that in oxide glasses Cu(II) is indeed located at the center of an elongated octahedron, in which the internuclear distances Cu^{2+}—O^{2-} in the equatorial plane and along the tetragonal axis should be of the order of 2 and 2.5 Å, respectively. Such an environment of Cu(II) can, with a sufficiently good approximation, be regarded as a square plane and the theory developed for square-planar complexes of Cu(II) (^{4,5}) can be used.

4. It is known that, for the same symmetry of the environment of a paramagnetic ion by ligands in different compounds, differences in the character of the chemical bond paramagnetic ion—ligand lead to a simultaneous change in several EPR spectral parameters. Thus, an increase in the degree of covalency of the bond is, as a rule, accompanied by a simultaneous decrease in the difference $|g - 2.0023|$ and in the constants of the hyperfine structure (h.f.s.).

Table 1

Parameters of the EPR spectra of Cu(II) as a function of the glass former

Composition no.	$BO_{1.5}$	SiO_2	$PO_{2.5}$	BaO	CuO	$g_{\|}$	$g_{\perp}$	$\|A\| \cdot 10^{-4}$, cm^{-1}	$\|B\| \cdot 10^{-4}$, cm^{-1}	α^2
1	65	–	–	34.5	0.5	2.31_9	2.05	150$±3|[illegible]		

For copper compounds, an anomalous picture has been found (^{6,7}): with an increase in the covalency of the copper—ligand bond, a decrease in $|g - 2.0023|$ is indeed observed, but the h.f.s. constants increase in absolute value (being negative in sign).

Table 2

Parameters of the EPR spectra of Cu(II) as a function of the modifier

Figure 2

Figure 2: Figure 2

Composition no.	X	$g_\parallel$	$g_\perp$	$\lvert A\rvert \cdot 10^{-4}$, cm^{-1}	Composition no.	Y	$g_\parallel$	$g_\perp$	$\lvert A\rvert \cdot 10^{-4}$, cm^{-1}
		Composition 65 $PO_{2.5}$+ 35 $XO_{0.5}$					**Composition** 78 $PO_{2.5}$+ 22 YO		
4	Li	2.45_8	2.08_0	119 [illegible]					

Note. In compositions nos. 4-14, copper in an amount of 0.7 cat.% was introduced in excess of 100%.

Comparison of the spectral parameters for Cu(II) in glasses differing in the glass former (Table 1) shows that, upon replacement of the glass former in the series $B_2O_3 \to SiO_2 \to P_2O_5$, an increase in the g-factor and a decrease in the h.f.s. constants are observed; i.e., the covalency of the copper—oxygen bond decreases from borate glass to phosphate glass. An analogous effect for the vanadium—oxygen bond was found in work ([1]).

The dependence of the EPR spectra of Cu(II) on the nature of the modifier is expressed more weakly than on the nature of the glass former. However, the data given in Table 2 indicate that, in glasses containing alkali elements as modifiers, the Cu—O bond is more ionic than in the case of glasses with alkaline-earth modifiers, which was also observed for V—O bonds in vanadium-containing glasses ([1]).

Consequently, although Cu(II) and V(IV) form complexes of different geometry in one and the same glass matrix, the chemical bonds within these complexes obey regularities arising not only from the nature of the transition element itself, but also from the elements of the glass-forming framework.

5. A theoretical analysis of the parameters of the EPR spectra of Cu(II) in a square-planar complex was given in the approximation of molecular-orbital theory in papers ([4], [5]). It follows from this analysis that an estimate of the coefficients of the π bonds in the complex is possible only when optical-absorption data are available, whereas for determining the parameters of the σ bond in the plane of the square, EPR data are sufficient.

Fig. 2. Dependence of the parameter of the σ bond (α^2) on the electronegativity of the modifier according to Pauling.
I —alkali group in phosphate glasses; *II* —alkaline-earth group in phosphate glasses; *III* —alkali group in borate glasses; *IV* —alkaline-earth group in borate glasses.

The coefficient α^2, which is a measure of the density of the unpaired electron on the copper $3d_{x^2-y^2}$ orbital participating in the formation of the antibonding σ orbital of the complex and, according to (^{5}), is a characteristic of the covalency of the σ bonds in the plane of the square, can be calculated from the formula

$$\alpha^2 = -(A/P) + (g_\parallel - 2) + {}^3/_7(g_\perp - 2) + 0.04, \tag{2}$$

where

$$P = 2\gamma_{\mathrm{Cu}}\beta\beta_{\mathrm{N}} \left\langle d_{x^2-y^2} \left| \frac{1}{r^3} \right| d_{x^2-y^2} \right\rangle \simeq 0.036 \text{ cm}^{-1}.$$

The results of calculating α^2 for the glasses studied are given in Table 1 and in Fig. 2. The coefficient α', which characterizes the delocalization of the unpaired electron onto the σ orbitals of the ligands in the plane of the square, is determined from the normalization condition

$$\alpha^2 + \alpha {a'}^2 - 2\alpha\alpha' S = 1, \tag{3}$$

where S is the overlap integral of $d_{x^2-y^2}$ and σ orbitals, equal to 0.076 for oxygen ligands (^{5}). The coefficients β_1^2 and β^2, characterizing π bonds in the plane and outside it, respectively, can be determined from the electronic absorption spectra and the EPR spectrum. Since it may be assumed that the delocalization of the unpaired electron onto the axial ligands is practically small, $\beta^2 \simeq 1$, while β_1^2 can be calculated from the formula

$$g_\parallel - 2.002 = -\frac{8\lambda_0\alpha\beta_1}{\Delta E_{B_2\to B_1}} \left[\alpha\beta_1 - \alpha'\beta_1 S\right], \tag{4}$$

Table 3

Composition No.	$\Delta E_{B_2\to B_1}$, cm^{-1}	α^2	$\alpha {a'}^2$	β_1^2
11	13000	0.835	0.231	0.855
12	12300	0.821	0.228	0.835

where λ_0 is the spin-orbit coupling constant for the free ion (-828 cm^{-1}), and $\Delta E_{B_2\to B_1}$ is the splitting of the B_1 and B_2 levels, determined from optical spectra and expressed in cm^{-1}.

In the electronic absorption spectra of Cu(II) in oxide glasses, one band is observed, identified with the transition $B_2 \to B_1$ (^{6}). It is assumed that the remaining bands lie in the near ultraviolet region and are masked by the intense absorption band for the charge-transfer transition.

The positions of the absorption bands for the transitions $B_2 \to B_1$ and the coefficients β_1^2 calculated on this basis for some of the borate glasses we studied are given in Table 3.

6. Analysis of the parameters of the chemical bonds given in Tables 1 and 3, and also in Fig. 2, makes it possible to draw the following conclusions:

A. The coefficients α^2, characterizing the degree of covalency of the σ bonds in the plane of the square (equal to 0.5 in the case of a purely covalent bond and 1 in the case of a purely ionic bond), have values of 0.8-0.85 in oxide glasses, indicating a fairly high degree of covalency of the bonds. Similar values of α^2 are observed in many organic complexes.

Cu(II) and, as a rule, considerably larger—in many inorganic crystals. The order of change in the value of α^2 (in the second digit after the decimal point) upon replacement of the glass former or modifier is approximately the same as in the case of organic copper complexes in which groups of different electronegativity, located two or more bonds away from the Cu(II) ion, are substituted while the ligand unit itself remains unchanged. This result is quite natural, since in the glasses we studied the replacement involved cations separated from Cu(II) by at least two bonds.

B. The direction of the change in α^2 with the glass former (Table 1) coincides with the direction of change in the total covalency of the bonds in the plane of the square and indicates an increase in the covalency of the σ bond in the series $P_2O_5 \to SiO_2 \to B_2O_3$.

C. For a given type of glass (borate or phosphate), when the modifier is replaced within one group of the periodic system, a monotonic decrease of the coefficients α^2 is observed in the direction of decreasing electronegativity (polarizing ability) of the cation. Such a character of the change in α^2 indicates a practically identical structural position, relative to the copper complex, of modifier ions belonging to the same group.

The significant decrease in α^2 when alkali modifiers are replaced by alkaline-earth modifiers with the same electronegativity indicates a different degree of influence of these cations on the distribution of spin density among the orbitals of the complex and requires special investigation.

D. The dependence of α^2 on the type of alkali modifier in phosphate glass is considerably weaker than in borate glass, which indicates the different structural role of a monovalent alkali cation in the formation of the tetrahedra $[BO_4]$ and $[PO_4]$ in the case of trivalent and pentavalent glass-forming cations. It is also of interest that, in the case of modifier ions with a high polarizing ability (Li in the alkali group, Mg in the alkaline-earth group), the coefficient α^2 is almost independent of the glass former and, conversely, depends more strongly the smaller the polarizing ability of the modifier cation.

From all that has been said it follows that, although Cu(II) forms in all the glasses studied its characteristic complexes—planar squares—the EPR spectra of

Cu(II) are exceptionally sensitive to the chemical nature of the elements forming the glass matrix, and not only to those manifestations that determine the strength of the bonds in the glass framework, but also to the spatial distribution of these bonds and the mutual arrangement of the glass elements relative to one another. Therefore, the study of the EPR spectra of Cu(II) in different glasses over a wide range of compositional variation may play an important role in investigating the structure of these glasses.

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