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ON THE NATURE OF CHEMICAL BONDS IN THE VANADYL COMPLEX FOR SOME OXIDE GLASSES ACCORDING TO PARAMAGNETIC RESONANCE DATA AND ELECTRONIC ABSORPTION SPECTRA

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In the preceding work (^1), the dependence of the parameters of the hyperfine spectra of e.p.r. of VO^{2+} in oxide glasses on the type of glass former and modifier was investigated, and a clear correlation of these parameters with the chemical composition of the glass was established (on passing from one system to another). The aim of the present work is to interpret certain e.p.r. data obtained in (^1) and supplemented by measurements of electronic absorption spectra, in the light of the molecular-orbital (m.o.) theory for vanadyl complexes, and also to continue the investigation of the dependence of the e.p.r. spectra of VO^{2+} in oxide glasses on their composition (chiefly on the ratio between the contents of modifiers and glass formers within a single system).

The e.p.r. measurements were carried out on an RE-1301 spectrometer at liquid-nitrogen temperatures; the electronic absorption bands were recorded with an SF-4 spectrophotometer.

The following were investigated: 1) the dependence of the parameters of the e.p.r. spectra and of the positions of the bands in the electronic absorption spectra of VO^{2+} on the type of glass former in the systems B_2O_3—BaO—V_2O_5, SiO_2—BaO—V_2O_5, and P_2O_5—BaO—V_2O_5, where the content of glass former remained constant (60 cat.%), while the content of V_2O_5 varied from 1 to 5 cat.%; 2) the dependence of the e.p.r. spectra of VO^{2+} on the concentration of the modifier in the systems P_2O_5—BaO and P_2O_5—CaO, containing a constant amount of V_2O_5 (5 cat.%). The results obtained are given in Table 1 and in Fig. 1.

Theory. From the e.p.r. data (^1) it follows that in oxide glasses vanadium, introduced in the form of an oxide in an amount of 5%, exists in the stable form

of the molecular vanadyl ion VO^{2+}, with one unpaired electron in the outer shell (configuration $3d^1$). The possibility of observing e.p.r. lines of VO^{2+} at high temperatures, indicating a more—

Table 1

Parameters of e.p.r. spectra, positions of electronic absorption bands, and coefficients of chemical bonds for vanadyl complexes in certain vanadium-containing glasses. Glass composition: $60\,XO_n$—$38\,BaO$—$2\,V_2O_5$

Glass former X	$g_\parallel$	$g_\perp$	$A\cdot 10^{-4}$, cm^{-1}	$B\cdot 10^{-4}$, cm^{-1}	$\Delta E_{b_{2g}\to b_{1g}}$, cm^{-1}	$\Delta E_{b_{2g}\to e_{\pi x}}$, cm^{-1}	α^2	γ^2	K_v	$P\beta_2^2\cdot 10^{-4}$, cm^{-1}
P_2O_5	1.924	1.972	172	68	15 600	11 600	0.92	0.99	0.845	121
SiO_2	1.931	1.974	161	58	15 600	9 000	0.84	0.71	0.755	122
B_2O_3	1.935	1.978	157	55	16 500	9 000	0.84	0.60	0.747	119

spin-lattice relaxation times, as well as the values of the EPR spectral parameters ($g_\parallel < 2$), make it possible to assume, in accordance with the theory of Ballhausen and Gray ([2]), that in the glasses studied by us vanadyl forms a complex of symmetry of the C_{4v} type, and that the unpaired electron is localized on a nonbonding orbital of the b_{2g} type (in the description by the MO LCAO method ([2,3])). The b_{2g} orbital is constructed from the $3d_{xy}$-orbital of V^{4+} and the $2p$-orbitals of the oxygen ligands lying on the x and y axes in the (xy) plane. The coefficients β_1 and β_1' at the $3d_{xy}$- and $2p$-orbitals, respectively, are determined by the degree of localization of the unpaired electron on the corresponding orbital and, thus, may serve as a characteristic of π-bonding in the equatorial plane of the vanadyl complex. Similarly, the b_{1g}-orbital of the complex is constructed from the $3d_{x^2-y^2}$-orbital of V^{4+} and the σ-orbitals of the equatorial ligands, and the $e_{\pi x}$-orbital is constructed from the $3d_{xz}$-orbital of V^{4+} and the p-orbitals of vanadyl oxygen; the corresponding coefficients (α and γ) at the d-functions may serve as characteristics of σ-bonding in the equatorial plane and of π-bonding of V with vanadyl oxygen.

Fig. 1. Dependence of the hyperfine-structure constant A of the VO^{2+} ion on the content of modifier (Ca(I) or Ba(II)) in glasses of the systems P_2O_5—BaO and P_2O_5—CaO, containing 5 mol.% $VO_{2.5}$

On the basis of data on the hyperfine splittings of EPR spectra in certain nitrogen-containing vanadyl complexes, the authors ([2,3]) showed that $\beta_1^2 \simeq 1$, i.e., that the π-bonds in the equatorial plane of vanadyl complexes of C_{4v} symmetry are practically ionic in character. The coefficients α^2 and γ^2 can then be

determined by combining EPR data and electronic absorption spectra with the aid of the formulas

$$g_{\perp} = g_e\{1 - [\lambda\gamma^2/\Delta E_{b_{2q}\to e_{\pi x}}]\}, \tag{1}$$

$$g_{\parallel} = g_e\{1 - [4\lambda\alpha^2/\Delta E_{b_{2q}\to b_{1q}}]\}, \tag{2}$$

where g_e is the g-factor of the free electron; ΔE is the splitting of the corresponding energy levels; λ is the spin-orbit coupling constant.

The hyperfine-structure constants of the EPR spectra can be used to estimate the magnitude of the Fermi contact interaction K_v. If in the expression for A and B, given in ([2,3]), one neglects certain terms that contribute $\leq 5\%$, then

$$K_v = \frac{2}{7}\frac{A+2B}{A-B}, \tag{3}$$

$$\beta_1^2 P_v = B/({}^2/_7 - K_v), \tag{4}$$

where $P_v = 2\gamma_v\mu_0\mu_v\langle d_{xy}|r^{-3}|d_{xy}\rangle$.

Results and discussion. Table 1 gives experimental EPR data in glasses of the systems XO_n—BaO—$VO_{2.5}$ (where X = P, Si, B, and n = 2.5; 2 and 1.5, respectively). Since these data, within the measurement error, do not depend on the V content in the range from 1 to 5 mol.%, they are given only for one composition in each system. The EPR spectral parameters presented practically coincide with the parameters published earlier ([1]) for analogous systems, and indicate a sufficiently good reproducibility of the EPR results in glasses melted at different times according to the identical procedure and from the same starting materials. EPR data for these systems were discussed by us in ([1]).

2. In the electronic absorption spectra of vanadium in the investigated borate and silicate glasses, three bands are observed; the position of two

of them is given in Table 1; the third in both types of glasses lies at 21 000 cm^{-1}. In phosphate glasses two absorption bands are observed, the positions of which are given in Table 1. The results obtained agree well with the results of studies of the optical spectra of vanadium ([4,5]) and, in accordance with existing concepts, the band at 21 000 cm^{-1} can be identified with the V^{3+} ion, while the bands $(15–16.5)\cdot10^3$ cm^{-1} and $(9–12)\cdot10^3$ cm^{-1} with the vanadyl ion for the transitions $b_{2g} \to b_{1g}$ and $b_{2g} \to e_{\pi x}$, respectively.

3. The parameters of the EPR and electronic absorption spectra given in Table 1 can be used to estimate the coefficients of the chemical bonds α^2 and γ^2 from formulas (1) and (2) *. The only quantity unknown for these formulas is the constant λ. In accordance with the considerations set forth

in ([3]) concerning possible values of λ for the vanadyl ion, and following ([6]), we take $\lambda = 165$ cm^{-1}. It follows from our data that λ for the vanadyl ion cannot lie outside the interval $160 \leq \lambda \leq 190$ cm^{-1}.

4. The values obtained for α^2 and γ^2, depending on the type of glass former, do not contradict the conclusions drawn by us in ([1]) on the basis of a qualitative analysis of only the EPR spectra, i.e., the decrease of α^2 and γ^2 in the direction
$P_2O_5 \rightarrow SiO_2 \rightarrow B_2O_3$ indicates an increase in the degree of covalency of the bonds of vanadium with the oxygen ligands and, correspondingly, an increase in the ionicity of the bond between the glass-forming cation and oxygen in the same direction. The high sensitivity of the parameter γ^2 to the value of $g_\perp$, on the one hand, and the low accuracy in determining $g_\perp$ (± 0.002), on the other, as well as a certain uncertainty in the choice of λ, do not allow us to draw conclusions about the nature of the high degree of covalency of the π-bonding of vanadium with vanadyl oxygen in borate and silicate glasses.

However, the accuracy of the measurements and estimates of α^2 and γ^2 carried out by us is sufficient to call attention to a substantial difference in the character of incorporation of VO^{2+} into the matrix of phosphate glass, on the one hand, and of borate and silicate glasses, on the other, expressed in a significant increase in the degree of localization of the molecular orbitals of the complex on the atomic orbitals of vanadium upon transition to the phosphate matrix.

5. It follows from Table 1 that $P_\nu \beta_1^2 \simeq$ const, and the value of this product ($\sim 120 \cdot 10^{-4}$ cm^{-1}) is practically the same as in the compounds studied in ([3]). This allows us, in accordance with the estimates of ([3]), to consider $\beta_1^2 \simeq 1$ and the b_{2g} orbital nonbonding.

The magnitude of the Fermi-contact interaction, as is seen from Table 1, changes for the VO^{2+} ion depending on the glass former. The change in the isotropic hyperfine interaction in vanadyl complexes from compound to compound is explained in ([3]) on the assumption that the hyperfine splitting of the vanadyl spectra is governed by the configurational interaction of the b_{2g} orbital (which has no S-character) with the a_I- and a_{II}-orbitals, in whose construction the vanadium $4s$-orbital and the σ-orbitals of the ligands participate. Consequently, the Fermi-contact interaction should depend on the character of the σ-bonding in the vanadyl complex and, apparently, mainly on the character of the σ-bonds with the vanadyl oxygen. Then the decrease of K_ν in the direction
$P_2O_5 \rightarrow SiO_2 \rightarrow B_2O_3$ reflects an increase in the magnitude of the σ-bonding of vanadium with vanadyl oxygen.

6. As was noted in ([1]), the parameters of the EPR spectra depend on the type of modifier, although more weakly than on the glass former. In the present work the dependence of the EPR spectra on the ratio between the modifier–

* These formulas were obtained under the assumption that $\beta_1^2 = 1$. At the same time, cases are known (see, for example, ([7])) in which π-bonding occurs in the equatorial plane of the vanadyl complex. This leads to corresponding corrections in (1) and (2). We, as will be shown, consider the b_{2g} orbital nonbonding and use formulas (1) and (2).

in which both glass former and modifier in glasses of the systems P_2O_5—BaO—V_2O_5 and P_2O_5—CaO—V_2O_5. Figure 1 presents the dependence of the hyperfine-structure constant A—the quantity most accurately measured in the spectra studied—on the modifier content. The constant A, as already noted, can serve as a qualitative characteristic of the degree of covalency of the bond between V and the ligands, provided the symmetry of the crystal field is identical. The considerable increase in the constant A at modifier (M) contents above 30% indicates a change in the field surrounding V, since the mere accumulation of a large number of highly ionic M—O bonds should have led to an increase in the covalency of the V—O bonds, i.e., to a decrease in the constant A. Consequently, at M concentrations above 30% structural changes occur in the phosphate glass, as a result of which the V—O bond becomes more ionic. The nature of these changes can evidently be clarified by studying the crystallization of these glasses, since the sharp change in A and $g_\parallel$ occurs in the range of compositions approaching the limits of glass formation.

Conclusions. 1. In oxide glasses the molecular ion of vanadium forms complexes of C_{4v} symmetry; the unpaired electron belongs to the nonbonding orbital b_{2g}, localized on the $3d_{xy}$ atomic orbital of vanadium.

2. Estimation of the parameters of chemical bonds by the MO LCAO method in the Ballhausen-Gray and Kivelson-Lee approximations in various vanadium-containing glasses confirms that the covalency of the π- and σ-bonds in vanadyl complexes increases depending on the glass former in the direction $P_2O_5 \rightarrow SiO_2 \rightarrow B_2O_3$.

3. The EPR spectra of VO^{2+} in glasses of the systems P_2O_5—BaO—V_2O_5 and P_2O_5—CaO—V_2O_5 (concentration of V_2O_5 5 mol.%) are practically independent of the modifier content in the range 20-30 mol.%. The observed changes in the EPR spectra at BaO and CaO contents above 30% reflect structural changes in these glasses.

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