HYPERFINE STRUCTURE OF ELECTRON PARAMAGNETIC RESONANCE SPECTRA OF THE VANADYL ION IN VANADIUM-CONTAINING GLASSES

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HYPERFINE STRUCTURE OF ELECTRON PARAMAGNETIC RESONANCE SPECTRA OF THE VANADYL ION IN VANADIUM-CONTAINING GLASSES

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The electron paramagnetic resonance of the V^{4+} ion in glassy compounds has been investigated by a number of authors (^{1,2}). These studies showed that at sufficiently low concentrations of V^{4+} the EPR spectra have a hyperfine structure caused by the interaction of the unpaired electron with the nuclei of the isotope V^{51} (nuclear spin $I^{51} = 7/2$). From work on the investigation of EPR in crystalline compounds it is known that the magnitude of the hyperfine-structure constant depends to a considerable extent on the character of the chemical bond between the paramagnetic ion and the ligands. Solving the question of the character of the chemical bond in glassy substances plays a primary role in understanding the laws of glass formation and the nature of the glassy state of solids. In this connection, the study of the hyperfine structure of EPR spectra in glasses is of definite interest. In the present work an attempt has been made to examine the hyperfine structure of V^{4+} in various vanadium-containing oxide glasses in order to study the change in the character of chemical bonds in glass as a function of its composition.

Borate, silicate, and phosphate glasses containing 5 cat.% vanadium and 25 cat.% alkali and alkaline-earth elements were investigated (see Tables 1 and 2). Measurements were carried out on a standard RE-1301 radiospectrometer at room and nitrogen temperatures.

1. Figure 1 shows an EPR spectrum typical of vanadium-containing glasses, which may be described by the spin Hamiltonian for the case of axial symmetry

$$\hat{\mathscr{H}} = g_{\|}\beta H_z\hat{S}_z + g_{\perp}\beta(H_x\hat{S}_x +$$

$$+H_y\hat{S}_y) + AI_z\hat{S}_z + B(I_x\hat{S}_x + I_y\hat{S}_y), \tag{1}$$

Figure 1: EPR spectrum of the VO2+ ion in glass of the system P2O5–V2O5–BaO, composition P 60 cat.%, V 5 cat.%, Ba 35 cat.%, at 77 K

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where $S = 1/2$, $I = 7/2$, and the remaining parameters are given in Tables 1 and 2. The parameters of this spin Hamiltonian were determined by means of the well-known formula for finding the h.f.s. lines in crystals

$$H(m) = H_0 - Km - \frac{B^2}{4H_0}\frac{A^2 + K^2}{B^2}[I(I+1) - m^2], \qquad (2)$$

where $H_0 = h\nu_0/g\beta$; I is the nuclear spin; m is the magnetic quantum number of the nucleus; $g^2 = g_\parallel^2 \cos^2\theta + g_\perp^2 \sin^2\theta$; $K^2 g^2 = A^2 g_\parallel^2 \cos^2\theta + B^2 g_\perp^2 \sin^2\theta$.

As is seen from Fig. 1, the observed EPR spectra are the result of a complex superposition of h.f.s. components from V^{4+} ions located–

Fig. 1. EPR spectrum of the VO^{2+} ion in glass of the system P_2O_5–V_2O_5–BaO of composition P 60 cat.%, V 5 cat.%, Ba 35 cat.% at 77 K.

···in ligand fields whose symmetry axes are arbitrarily oriented in the external magnetic field. Owing to the considerable anisotropy of the g-factor in the glasses studied, it is possible to determine rather accurately the position of the hfs lines corresponding to $\theta = 0$; the accuracy of determining the positions of the hfs lines for $\theta = 90°$ and the corresponding spectral parameters is considerably lower, because the spectral lines for the perpendicular orientation are completely overlapped by the central part of the spectrum for the parallel orientation.

Table 1

EPR spectral parameters for vanadium-containing glasses at liquid-nitrogen temperature

No.	System	P	Si	B	Ba	V	A, 10^{-4} cm^{-1}	B, 10^{-4} cm^{-1}	$g_\parallel$	$g_\perp$
1	P_2O_5–BaO–V_2O_5	60		–	35	5	172± 3	68 ± 5	1.924± 0.001	1.972± 0.002
2	SiO_2–BaO–V_2O_5		60	–	35	5	161± 3	58 ± 5	1.931± 0.001	1.977± 0.002
3	B_2O_3–BaO–V_2O_5			60	35	5	157± 3	55 ± 5	1.935± 0.001	1.982± 0.002

2. It is known that, in the case of vanadium, the electronic configuration $3d^1$ may be realized for the ion V^{4+} or for the ion VO^{2+}, in which vanadium is bound by a double covalent bond to an oxygen atom. In both cases,

EPR spectra of axial symmetry can be described by spin Hamiltonian (1). In work (^{3}) a criterion was proposed that makes it possible to distinguish EPR spectra of V^{4+} and VO^{2+} ions depending on the relationship between the parameters of this spin Hamiltonian: for V^{4+}, $A > B$ when $g_{\parallel} > g_{\perp}$, whereas for VO^{2+}, $A > B$ when $g_{\parallel} < g_{\perp}$.

A comparison of the parameters given in Table 1 shows that they satisfy the second condition, i.e., that the EPR spectra observed by us in glasses may be assigned to the VO^{2+} ion. This assumption is also supported by the insignificant changes in the parameters of the spin Hamiltonian in glasses of the most varied composition (Tables 1 and 2, works (^{1},^{2})), which indicates the presence of a vanadium complex stable for all glasses. Finally, attention should be drawn to the good agreement of these parameters with the constants of the spin Hamiltonian for the vanadyl ion in other compounds (^{4},^{5}).

In work (^{2}) it was shown that the EPR spectrum of the vanadyl ion in solids can be observed at high temperatures (from liquid-nitrogen temperature and above) only in the case when the V^{4+} ion, formally included in the vanadyl complex, is in octahedral coordination.

Thus, for all the glasses we have studied, the EPR spectrum can be identified with the V^{4+} ion bound in a VO^{2+} complex and situated in an octahedral environment of oxygen atoms.

3. With the same symmetry of the environment of the paramagnetic ion, changes in the character of the chemical bond of this ion with the ligands lead to a simultaneous change in several spectral parameters. It has been established that an increase in the degree of covalency of the bond between the paramagnetic ion and the ligands leads to a decrease in the contributions of the orbital moment to the value of the g-factor and to a decrease in the value of the hyperfine-structure constant. Therefore, in order to draw conclusions about changes in the parameters of the spin Hamiltonian as the result of a change in the degree of covalency of the paramagnetic-ion–ligand bond, it is necessary to make sure that the spectral parameters shift in accordance with these requirements.

It is easy to see from the example of the compositions listed in Table 1 that, as the constants A and B decrease from composition No. 1 to composition No. 3, $g_{\parallel}$ and $g_{\perp}$ increase while the degree of anisotropy of the g-factor remains constant, $g_{\perp}-$

$-g_{\parallel} = 0.046$. This fact indicates that the covalency of the vanadium–oxygen bond increases when the glass former is replaced in the sequence $P_2O_5 \rightarrow SiO_2 \rightarrow B_2O_3$.

The possibility of a freer redistribution of charge density in the structural units of glass, as compared with crystals, accounts for the fact that an increase in the degree of covalency of the cation–oxygen bond in glasses with different cations is accompanied by a decrease in the covalency of the paramagnetic ion–oxygen bond and a corresponding increase in the hyperfine splitting.

Table 2

EPR spectrum parameters for "parallel orientation" in phosphate glasses with different modifiers at liquid-nitrogen temperature

No.	System	A, 10^{-4} cm^{-1}	$g_\parallel$	No.	System	A, 10^{-4} cm^{-1}	$g_\parallel$
4	P_2O_5—Li_2O—V_2O_5	183 ± 2	1.902 ± 0.001	8	P_2O_5—MgO—V_2O_5	182 ± 3	1.902 ± 0.001
5	P_2O_5—Na_2O—V_2O_5	180 ± 2	1.911 ± 0.001	9	P_2O_5—CaO—V_2O_5	177 ± 3	1.924 ± 0.001
6	P_2O_5—K_2O—V_2O_5	179 ± 2	1.912 ± 0.001	10	P_2O_5—SrO—V_2O_5	166 ± 3	1.932 ± 0.001
7	P_2O_5—Cs_2O—V_2O_5	177 ± 1	1.926 ± 0.001	11	P_2O_5—BaO—V_2O_5	169 ± 3	1.932 ± 0.001

Note. Composition in cation percent: P 70%, R 25%, V 5%; R is an alkali or alkaline-earth element.

Consequently, the decrease in the hyperfine-structure constant of the VO^{2+} spectrum when the glass formers are replaced in the direction $P_2O_5 \to SiO_2 \to B_2O_3$ indicates not only an increase in the degree of covalency of the vanadium–oxygen bond, but also a decrease in the degree of covalency of the cation–oxygen bond from P–O to B–O. If one uses the Pauling electronegativity system ($X_B = 2.0$; $X_{Si} = 1.8$; $X_P = 2.1$), then one may say that the Si–O bond should be more ionic than the B–O bond. The more ionic character of the B–O bond in comparison with Si–O, established by our experiments, is apparently due to the specific distribution of bonds in the $[BO_4]$ tetrahedron, where the valence shell of the boron atom lacks one electron for the formation of ordinary covalent bonds.

4. In view of the low accuracy in determining the parameters B and $g_\perp$, the influence of bond covalency on the EPR spectra of VO^{2+} in phosphate glasses with different modifiers was assessed from the change in A and $g_\parallel$.

From the data given in Table 2 it follows that the degree of covalency of the V–O bond in phosphate glasses containing oxides of alkali (Li, Na, K, Cs) and alkaline-earth elements (Mg, Ca, Sr, Ba) increases with successive substitution of alkali metals from Li to Cs and alkaline-earth metals from Mg to Sr (the reason for the increase in hfs splitting in barium glass as compared with strontium glass is not clear). This fact indicates an increase in the degree of ionicity of the alkali metal–oxygen bond from Li to Cs and of the alkaline-earth metal–oxygen bond from Mg to Sr, and is in direct agreement with Pauling electronegativity.

It should be noted that, when an alkali metal is replaced by an alkaline-earth metal of the same row of the periodic system, the expected dependence between the magnitude of the hyperfine splitting of V^{4+} and the degree of ionicity of the metal—oxygen bond is violated. This is apparently due to the different number of oxygen atoms introduced by a singly and a doubly charged cation at equal (in percentage terms) metal content.

5. Thus, the investigations we have carried out show that EPR spectra in glasses are very sensitive to changes in the character of the chemical bond between the different elements making up the glass when its composition is changed. A direct quantitative assessment of chemical-bond parameters from EPR spectra in glasses is at present diffi-

cannot be obtained because of the absence of reliable data on the optical spectra (and, consequently, on the splitting between the energy levels that determine the constants of the EPR spectra) and the complexity of calculating the magnitude of the *s*-configuration interaction. However, a comparative estimate of these parameters in different glasses seems possible to us after a detailed study of the EPR spectra over a wide range of changes in glass compositions.

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