INVESTIGATION OF ELECTRON PARAMAGNETIC RESONANCE IN GLASSES CONTAINING TWO TRANSITION ELEMENTS

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INVESTIGATION OF ELECTRON PARAMAGNETIC RESONANCE IN GLASSES CONTAINING TWO TRANSITION ELEMENTS

THE EFFECT OF COBALT ON THE E.P.R. SPECTRA OF Cu^{2+} IN OXIDE GLASSES

(Presented by Academician L. A. Artsimovich, October 31, 1967)

The investigation of electron paramagnetic resonance (E.P.R.) of glasses containing two d-oxides is of interest, first, from the point of view of studying the mechanisms of electrical conductivity of these glasses and, second, from the point of view of studying the interactions of paramagnetic particles of two types, statistically distributed in a crystallographically disordered solid.

In the present work the E.P.R. of glasses of quaternary systems is investigated: X–CuO–CoO–BaO, where $X = B_2O_3, SiO_2, P_2O_5$. The compositions studied were: $60X + m\mathrm{CuO} + n\mathrm{CoO} + [40 - (m+n)\mathrm{BaO}]$, where the content of the components is expressed in cation percent, and the quantities m and n lie in two regions: 1) $m + n = 4$; 2) $m + n = 20$. For comparison, the E.P.R. spectra of the corresponding samples of ternary systems were also studied: X–CuO–BaO and X–CoO–BaO.

Table 1

Number of "isolated" Cu^{2+} centers participating in E.P.R. absorption at liquid-nitrogen temperature as a function of glass composition

Composition No.	$BO_{1.5}$	SiO_2	$PO_{2.5}$	CuO	CoO	BaO	Number of centers, 10^{19} cm^{-3}
1277	60	–	–	2	–	38	15
1265	60	–	–	2	2	36	0.72
1125	60	–	–	2	20	18	No signal
1271	–	–	60	2	–	38	3.75

Figure 1: EPR spectra

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Composition No.	$BO_{1.5}$	SiO_2	$PO_{2.5}$	CuO	CoO	BaO	Number of centers, 10^{19} cm^{-3}
1250	–	–	60	2	2	36	1.5
1195	–	–	60	2	20	18	0.3
363	–	–	60	10	–	30	12
1127	–	–	60	10	10	20	0.3
358	–	–	60	15	–	25	6.5
1128	–	–	60	15	5	20	0.8
1679	–	60	–	2	–	38	1.1
1673	–	60	–	2	2	36	0.6
1075	–	60	–	2	20	18	No signal

E.P.R. measurements were carried out on a standard RE-1301 spectrometer at room, liquid-nitrogen, and, for individual samples, helium temperatures. The concentrations of paramagnetic ions were determined using a standard sample of $CuSO_4 \cdot 5H_2O$.

Experimental Results and Discussion

1. EPR spectra of Cu2+

The EPR of Cu2+ in glassy substances has been studied by a number of authors (1-3). Copper was introduced into these substances in small amounts (~ 0.05 wt.%). To solve the problems stated above, the study must be carried out on samples with a high content of paramagnetic particles. In Fig. 1a, c are shown the EPR spectra obtained by us for Cu2+ in borate and silicate glasses containing 60 cat.% X,

Fig. 1. EPR spectra: **a** and **b**–Cu2+ in silicate glasses Nos. 1679 and 1673 (Table 1), respectively, at 77°K; **c** and **d**–Cu2+ in borate glasses Nos. 1277 and 1265 (Table 1), respectively, at 77°K; **e**–Co2+ in glass of composition $BO_{1.5}$ 60 cat.%, BaO 38 cat.%, CoO 2 cat.% at 4.2°K.

38 cat.% BaO and 2 cat.% CuO (by synthesis). The spectra shown can be analyzed with the aid of the spin Hamiltonian

$$\mathcal{H} = g_{\parallel}\beta H_z S_z + g_{\perp}\beta(H_x S_x + H_y S_y) + A I_z S_z + B(I_x S_x + I_y S_y). \qquad (1)$$

Fig. 2. Dependence of the number of "isolated" centers of Cu^{2+} contributing to the EPR spectrum of Cu^{2+} at 77° K on the content in borate (1) and phosphate (2) glass at a glass-former concentration of 60 cat.%

Figure 2: Fig. 2. Dependence of the number of "isolated" centers of Cu^{2+} contributing to the EPR spectrum of Cu^{2+} at 77° K on the content in borate (1) and phosphate (2) glass at a glass-former concentration of 60 cat.%

The parameters of this spin Hamiltonian have been determined for silicate glass in accordance with the method developed in (1, 3) and are equal to: $S = 1/2$, $I^{63,65} = 3/2$, $g_{\parallel} = 2.39$, $g_{\perp} = 2.05$, $A = 123$ oersted, $B \simeq 25$ oersted. For borate glass it is difficult to determine the parameters of (1), with the exception of $g_{\text{eff}} = 2.09$, since hyperfine structure is absent in it. The values of the parameters of the spin Hamiltonian (1) make it possible to consider that the Cu2+ ions are surrounded by oxygen atoms forming an axially distorted octahedron.

The reason for the absence of hyperfine structure in the EPR spectrum of borate (and also phosphate) glasses is connected with the higher concentration of Cu2+ in comparison with silicate glass at the same copper content in them, which is due, in turn, to the difference in the oxidation–reduction potentials of the matrix into which the copper was introduced. An estimate of the Cu2+ concentration from the EPR spectra shows that, upon the introduction of 2 cat.% CuO, borate glasses are distinguished by the highest Cu2+ content ($\sim$ 100% of the total amount of dissolved copper), followed by phosphate glasses ($\sim$ 30%), and finally silicate glasses ($\sim$ 8%).

Comparison of the spectra obtained by us for Cu2+ in silicate glass (composition No. 1679, Table 1) with spectra for Cu2+ in an aqueous solution of $CuSO_4$,

penetrating into the pores of a gel obtained by γ-irradiation of polyvinyl alcohol (4), shows that the Cu^{2+} ions present in the glass in an amount of $\sim 10^{19}$ cm^{-3} are uniformly distributed over the volume occupied by the modifier ions.

We investigated the dependence of the integrated intensity of the EPR spectra of Cu^{2+} in borate and phosphate glasses (melted in identical atmospheres) on the content of the introduced copper at a constant concentration of glass former (60 cat.%). The results are presented in Fig. 2. It is characteristic that, with increasing CuO content in borate glass, the EPR signal decreases monotonically, whereas in phosphate glass the signal intensity first increases approximately in proportion to the total copper content and then begins to decrease. The decrease in the intensity of the EPR spectrum in borate glasses at CuO contents above 2 cat.% and in phosphate glasses at CuO concentrations above 10 cat.% cannot be explained by a corresponding decrease in the number of Cu^{2+} ions, since in this case the form of the spectrum should have changed substantially and a hyperfine structure should have been observed, which in fact does not occur.

Fig. 2. Dependence of the number of "isolated" Cu^{2+} centers contributing to

the EPR spectrum of Cu^{2+} at 77° K on the content in borate (1) and phosphate (2) glass at a glass-former concentration of 60 cat.%

Therefore it may be assumed that the reason for the decrease in the EPR signal is that, at high concentrations of Cu^{2+} (above $\sim 10^{20}$ cm^{-3}), groups of 2, 3, or more copper ions connected by a strong exchange interaction begin to form in the glasses. Such groups may have a nonmagnetic ground state (5), or a state providing a high multiplet character of the spectrum, excluding the possibility of observing it in a crystalline disordered system, or, finally, such groups may have exceptionally short relaxation times, making it impossible to observe the signal in the temperature range available to us. The spectrum observed by us belongs to "isolated" copper ions Cu^{2+}.

In borate glasses, where the concentration of Cu^{2+} already at 2 cat.% CuO exceeds 10^{20} cm^{-3}, groups begin to form at a lower content of introduced copper than in the case of phosphate glasses.

2. On the EPR of Co^{2+} in glasses. At nitrogen temperatures, the EPR spectrum of Co^{2+} in the class of glassy substances was previously observed only for fluoroberyllate glasses colored red (3), and, in the opinion of the authors, is associated with Co^{2+} in octahedral coordination. In the oxide glasses we investigated, containing cobalt and colored blue or violet, no EPR signal could be observed at 77° K. At 4.2° K, two samples of the following compositions were investigated: the first, B_2O_3 60 cat.%, CoO 2 cat.% and BaO 38 cat.%; the second, P_2O_5 60 cat.%, CoO 2 cat.% and BaO 38 cat.%. The samples had a violet coloration, and both gave an EPR signal whose form and position coincide with the data of work (6) and make it possible to assume that it is also due to Co^{2+} in octahedral coordination. However, the fact that the signal is observed only at helium temperatures indicates that the initial splitting of the orbital triplet ($^4T_1$) of Co^{2+} in an octahedral oxygen complex of oxide glasses is smaller than in fluoroberyllate glasses. In this case, as in crystals, short relaxation times occur for Co^{2+}, excluding the possibility of observing the EPR signal in oxide glasses at nitrogen and higher temperatures.

3. EPR spectra of glasses containing Cu^{2+} and Co^{2+} simultaneously. In the glasses we investigated, containing CuO and CoO simultaneously (in amounts $\geqslant 2$ cat.%), the EPR signals from Co^{2+} at nitrogen-

were not observed at elevated temperatures. It was also found that, under these conditions, the EPR signals of Cu^{2+} in a number of cases undergo substantial changes, which are partially reflected in Table 1 and in Fig. 1. These changes are manifested in the following: 1) upon the introduction of Co (at the expense of Ba), the number of Cu^{2+} centers contributing to the EPR signal decreases, and this decrease is the greater, the higher the content of Cu^{2+} in the corresponding glass of the ternary system; 2) upon addition of Co, a deterioration is observed in the resolution of the hyperfine structure in the EPR spectrum of Cu^{2+}, although the number of Cu^{2+} ions contributing to the observed spectrum decreases; 3) an increase in the Co concentration (at constant CuO content) is accompanied by a decrease in the Cu^{2+} signal, or even by its complete disappearance.

There are two possible principal reasons for the decrease in the integral intensity of the EPR signal of Cu^{2+} in glass upon the introduction of cobalt: 1) cobalt shifts the equilibrium $Cu^{2+} + e \leftrightarrow Cu^{1+}$ toward an increase in the content of diamagnetic Cu^{1+} ions in the glass; 2) the presence in the medium of rapidly relaxing Co^{2+} ions leads to rapid relaxation of nearby Cu^{2+} ions and to exclusion of the contribution of the latter from the total EPR signal intensity at 77° K.

Apparently, in the present case the second reason is involved, because, as our preliminary experiments have shown, cobalt has a similar effect on the EPR spectra of other ions of the iron group in glasses, whereas the "reducing" role of cobalt should, on the contrary, have led to an increase in the intensity of the corresponding EPR spectrum.

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