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A study of interaction between copper and manganese in a soda-borate glass by ESR

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The ESR spectra of 30 Na_2O–70 B_2O_3 glasses, containing very low amounts of copper and manganese singly and in mixed proportions, have been studied. The copper glass shows that Cu^{2+} is present in a distorted octahedral environment. The manganese glass shows that Mn^{2+} is also present in an octahedral site possibly with some distortion. The mixed copper–manganese glasses show that both Cu^{2+} and Mn^{2+} are present with Cu^+ and Mn^{3+}, and that there is a considerable interaction between these two ions giving rise to the exchange coupled Cu^{2+}–Mn^{2+} pairs. The covalency of Cu^{2+}–O bonding decreases in the mixed glasses. The possibility of spin diffusion and nuclear relaxation in the Mn^{2+} site is proposed to account for the absence of the Mn^{2+} hyperfine lines in the spectra of mixed glasses. The possibility of nuclear relaxation of the Cu^{2+} site is not completely ruled out from the broadening of the hyperfine lines in the mixed glasses, as compared to that in the copper glass.

1. Introduction

In the past few years interest has grown in the field of electronic conduction in oxide glasses containing mixed transition metal (TM) oxides [1–3]. Spectroscopic behaviour of such glasses is also very interesting [4–7]. In the previous ESR investigations, higher concentrations of TM ions have been used. In order to see the effect of interactions between two TM ions, it is important to study glasses containing low amounts of TM ions. In the present investigation, the ESR spectra of a 30 Na_2O–70 B_2O_3 glass containing a very low amount of copper, manganese and copper and manganese have been studied.

2. Experimental

The glasses were prepared with the base glass as 30 Na_2O–70 B_2O_3. Five glasses were prepared. The compositions and melting temperatures are given in Table I.

The ESR spectra were recorded at room temperature and at 77 K on a Hilger and Watts microspin spectrometer operated at X-band frequency with a magnetic field modulation frequency of 100 kHz. The coarsely powdered glass sample, contained in a quartz tube, was introduced into the resonance cavity operating in the H_{011} mode. The sample weight (about 0.2 g) and the other experimental conditions were kept identical to make the results of these glasses comparable to each other.

3. Results and discussion

3.1. Copper glass

The room temperature spectrum due to Cu^{2+} for glass C2 is shown in Fig. 1. The spectrum at 77 K

TABLE I The compositions and melting temperatures of the glasses

Glass No.	Composition*	Melting temperature (° C)
C2	0.5 wt% Cu_2O	1050
M2	0.6 wt% MnO	1050
CM1	0.5 wt% Cu_2O + 0.6 wt% MnO	900
CM2	0.5 wt% Cu_2O + 0.6 wt% MnO	1050
CM3	0.5 wt% Cu_2O + 0.6 wt% MnO	1200

*The base glass is 30 Na_2O–70 B_2O_3.

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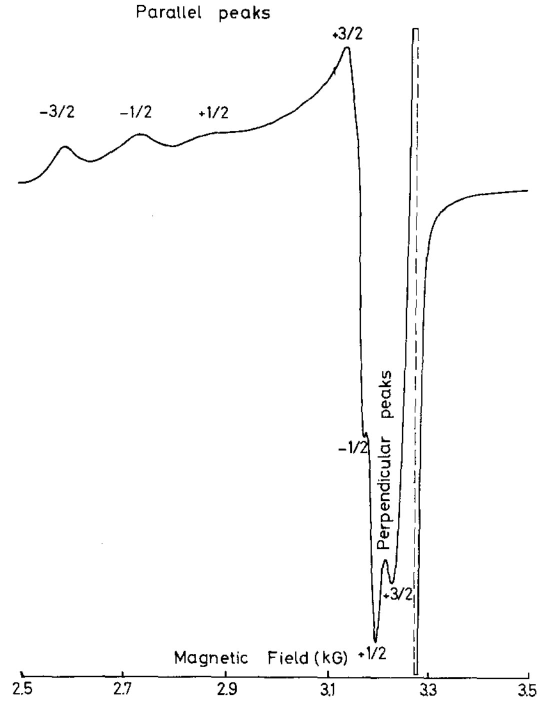

Figure 1 The room temperature ESR spectra of glass C2.

did not show much difference except that the lines were sharper and more intense. This spectrum can be described by an axial spin Hamiltonian characterized by the components $g_{\|}$ and $g_{\perp}$ of the g-tensor and components of $A_{\|}$ and $A_{\perp}$ of the hyperfine tensor

$$\mathcal{H} = g_{\|}\beta_0 H_z S_z + g_{\perp}\beta_0(H_x S_x + H_y S_y) + A_{\|}S_z I_z + A_{\perp}(S_x I_x + S_y I_y). \quad (1)$$

Here β_0 is the Bohr magneton; H_x, H_y and H_z are the components of the magnetic field; S_x, S_y, S_z and I_x, I_y, I_z are the components of the spin operators of the electron and the nucleus, respectively.

Two sets, each consisting of four peaks, are usually designated as parallel and perpendicular hyperfine peaks. The peak positions may be related to the principal values of the g and A tensors by [8]

$$h\nu = g_{\|}\beta_0 H + m_I A_{\|} + (15/4 - m_I^2)\frac{A_{\perp}^2}{2g_{\|}\beta_0 H} \quad (2)$$

$$h\nu = g_{\perp}\beta_0 H + m_I A_{\perp} + (15/4 - m_I^2)\frac{A_{\perp}^2 + A_{\|}^2}{4g_{\perp}\beta_0 H}. \quad (3)$$

Here m_I is the nuclear magnetic quantum number of the copper nucleus whose spin I is 3/2 for both Cu^{63} and Cu^{65} (the natural abundances are 69% and 31% respectively). The perpendicular peak at $m_I = -3/2$ could not be observed because of the overlap of the spectrum with the central resonance line, while the resolution of the parallel peak at $m_I = 3/2$ was very poor. However, from the observed positions of the other peaks and using Equations 2 and 3, the values of $g_{\perp}, g_{\|}$, $A_{\perp}$ and $A_{\|}$ were calculated, and are shown in Table II. These results correspond very well with those obtained by Imagawa [9] for Cu^{2+} ion in a distorted octahedral site.

The octahedral configuration of Cu^{2+} (i.e. covalent character) satisfies the condition for applying the analysis by molecular orbital scheme developed by Maki and McGarvey [10], and slightly modified by Kivelson and Neiman [11].

The coefficients α^2, β^2 and δ^2 indicates the covalent character of $Cu^{2+}O_6$ octahedra and they are related to the spin Hamiltonian parameters by the equations given in references [10, 11]. These equations contain the terms ΔE_{xy} and ΔE_{xz}, which are the energies of the transitions $B_{2g} \rightarrow B_{1g}$ and $E_g \rightarrow B_{1g}$ respectively. These two transitions were observed by Zaman [12] at 12 600 cm^{-1} and 16 600 cm^{-1} respectively in 30 Na_2O–70 B_2O_3 glasses containing less than 1 wt% Cu_2O. Therefore, taking these values for ΔE_{xy} and ΔE_{xz}, the solutions of the equations of references [10, 11] yield values of α^2, β^2 and δ^2 and they are shown in Table II for glass C2. These values are typical for a covalent $Cu^{2+}O_6$ octahedra present in soda–borate glasses [9].

TABLE II The ESR parameters* of the glasses

Glass No.	$g_{\perp}$	$g_{\|}$	$\lvert A_{\perp}\rvert$ ($\times 10^{-4}$ cm^{-1})	$\lvert A_{\|}\rvert$ ($\times 10^{-4}$ cm^{-1})	α^2	β^2	δ^2
C2	2.0650	2.3270	26.00	150.00	0.82	0.85	0.89
CM1	2.0620	2.3300	24.00	147.00	0.83	0.87	0.91
CM2	2.0600	2.3350	22.00	144.00	0.85	0.89	0.93
CM3	2.0570	2.3390	21.00	142.00	0.87	0.92	0.95

*The maximum error for the g-values was ± 0.0012 and ± 1.5 for the A-values.

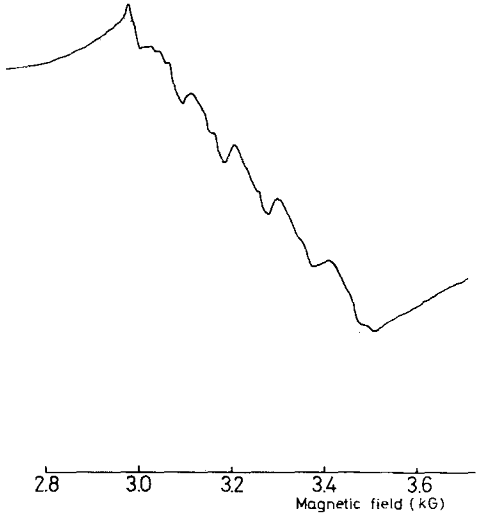

Figure 2 The room temperature ESR spectra of glass M2.

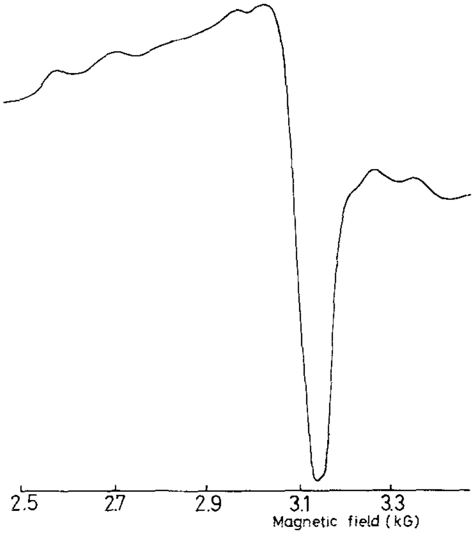

Figure 3 The room temperature ESR spectra of glass CM1.

3.2. Manganese glass

The room temperature ESR spectrum due to Mn^{2+} is shown in Fig. 2 for glass M2. The spectrum at 77 K remained unchanged. The Mn^{2+} spectra in borate glasses have been studied by various authors [13–15]. The six lined hyperfine structure centred around $g = 2$, observed in Fig. 2, is typical for such glasses. The spectrum is inhomogeneously broadened by magnetic dipole–dipole interaction. Due to this reason the hyperfine structure is not very clearly resolved, as normally observed in glasses [16]. This type of spectrum can be described by a spin Hamiltonian [16] appropriate for Mn^{2+} ($S = 5/2$, $I = 5/2$) in a crystal field of axial symmetry

$$\mathcal{H} = g\beta_0 HS + D[S_z^2 - 1/3S(S+1)] + ASI - g_I\beta_I I \qquad (4)$$

The line positions were calculated up to the third order in D and A, yielding the values of $g = 2.00$, $A = 84 \times 10^{-4}\ \mathrm{cm}^{-1}$ and $D_{av} = 89 \times 10^{-4}\ \mathrm{cm}^{-1}$. These values represent an overall deviation from the cubic symmetry. However, the high value of A suggests that Mn^{2+} is octahedrally co-ordinated in this glass, possibly with some distortion.

3.3. Copper–manganese glasses

The room temperature spectrum for glass CM1 is shown in Fig. 3. The spectra for glasses CM2 and CM3 are very similar to that shown in Fig. 3, except that the intensity of the central resonance line was relatively weaker in these glasses and the observed hyperfine lines were broadened. The spectra at 77 K were very similar to those at room temperature, except that the individual hyperfine lines were sharper, which is ascribed to a spin–lattice relaxation effect. It is noted from Fig. 3 that, although most of the copper hyperfine lines are observed as in glass C2, the hyperfine structure due to Mn^{2+} has been completely washed out. Since both the Cu^{2+} and Mn^{2+} ions have long spin–lattice relaxation times, the vanishing of Mn^{2+} spectra could not be due to cross-relaxation phenomena [5]. It could possibly be due to spin diffusion within Mn^{2+} spin system and also due to nuclear relaxation [5]. Alternatively, it could be suggested that a reaction of the type

$$Cu^{2+} + Mn^{2+} \rightarrow Cu^{+} + Mn^{3+} \qquad (5)$$

takes place in the melt when glasses are melted with both Cu_2O and MnO. The thermodynamic behaviour for such a system is not known. However, from the known behaviour of the individual oxides [17, 18]

$$2\,CuO \rightarrow Cu_2O + \tfrac{1}{2}\,O_2 \qquad (6)$$

$$Mn_2O_3 \rightarrow 2\,MnO + \tfrac{1}{2}\,O_2 \qquad (7)$$

with increasing temperature. Therefore, if we neglect the interaction between the individual oxides between 900 and 1200° C for glasses CM1 to CM3, Equations 6 and 7 show that these glasses should contain mainly Mn^{2+} and Cu^{+}. However, the observed spectra show the presence of only Cu^{2+}. But the comparison of overlap regions near $g = 2$ in Figs. 1 and 3 show that there could be some Mn^{2+} present in glasses CM1 to CM3. Therefore, it is reasonable to assume that the reaction of Equation 5 is partially complete in these glasses; the glasses were also not equilibrated at the melting temperatures. However, with increasing temperature, the Cu^+ concentration increases, which is reflected in the decrease of the intensity of the Cu^{2+} lines.

From the observed spectra, the ESR parameters for Cu^{2+} were calculated for glasses CM1 to CM3, as described in Section 3.1, and are given in Table II. It is seen that the covalency of the $Cu^{2+}O_6$ octahedra decreases significantly in the mixed Cu–Mn glasses compared with that in the copper glass C2. Comparison of the A values shows that there is a decrease of hyperfine interaction at the Cu^{2+} nucleus, which was reflected by the decrease of the intensities of the hyperfine lines between glasses CM1 to CM3. Since the hyperfine structures of both Cu^{2+} and Mn^{2+} are observed around $g = 2.0$, it seems likely that the interaction between these two ions can form Mn^{2+}–O–Cu^{2+} associates. The observed differences between the spectra of different glasses could possibly account for such a situation. The formation of exchange coupled pairs of two TM ions of two dissimilar TM elements has been proposed in other glasses as well [4, 7, 19].

4. Conclusion

The comparison of the ESR spectra of soda–borate glasses containing copper and manganese singly and in mixed proportions have shown that both the Cu^{2+} and Mn^{2+} ions are present in the mixed glasses along with Cu^+ and Mn^{3+}. There is a considerable interaction between Cu^{2+} and Mn^{2+} ions giving rise to Cu^{2+}–Mn^{2+} exchange coupled pairs. While the possibility of spin diffusion and nuclear relaxation cannot be completely ruled out for Mn^{2+} to account for the absence of the hyperfine lines in glasses CM1 to CM3, the weakening of Cu^{2+} hyperfine lines in these glasses show that there could be some amount of nuclear relaxation at the Cu^{2+} nucleus as well. The ESR spectra on such systems show that there is a need for more theoretical and experimental work in this field.

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References

1. A. K. BANDYOPADHYAY and J. O. ISARD, *J. Phys. D* 10 (1977) L99.
2. *Idem*, "Amorphous and Liquid Semiconductors", edited by W. E. Spear (1977) p. 683.
3. L. D. BOGOMOLAVA *et al.*, *Sov. Phys. Solid State* 15 (1974) 2477.
4. A. K. BANDYOPADHYAY, *J. Mater. Sci.* submitted.
5. L. D. BOGOMOLOVA *et al.*, *Sov. Phys. Solid State* 14 (1969) 243.
6. R. S. ABDRAKHMANOV *et al.*, *Izv. Akad. Nauk. SSSR* 7 (1971) 1240.
7. L. D. BOGOMOLOVA *et al.*, *Sov. Phys. Solid State* 18 (1973) 61.
8. B. BLEANY *et al.*, *Proc. Roy. Soc., A* 228 (1955) 147.
9. H. IMAGAWA, *Phys. Stat. Solidi*, 30 (1968) 469.
10. A. H. MAKI and B. R. McGARVEY, *J. Chem. Phys.* 29 (1958) 31.
11. D. KIVELSON and R. NEIMAN, *ibid.* 35 (1961) 149.
12. M. S. ZAMAN, private communication.
13. H. W. de WIJN and R. F. VAN BALDEREN, *J. Chem. Phys.* 46 (1967) 1381.
14. D. L. GRISCOM and R. E. GRISCOM, *J. Chem. Phys.* 47 (1967) 2711.
15. E. I. ABDRASHITOVA and N. R. YAFAEV, *Sov. Phys. Solid State* 9 (1968) 2500.
16. J. WONG and C. A. ANGELL, "Glass Structure by Spectroscopy" (Marcel Dekker Inc., New York, 1976) p. 555.
17. S. BANERJEE and A. PAUL, *J. Amer. Ceram. Soc.* 57 (1974) 286.
18. A. PAUL and D. LAHIRI, *ibid.* 49 (1966) 565.
19. L. D. BOGOMOLOBA, *J. Non Cryst. Solids* 30 (1979) 379.

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