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Optical and ESR investigation of borate glasses containing single and mixed transition metal oxides

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The optical and electron spin resonance (ESR) spectra of barium borate glasses, containing the oxides of V, Fe and Cu separately and in mixed proportions, have been studied. The optical spectra of the single transition metal (TM) oxide glasses showed the usual features, while those for the mixed glasses showed single bands without showing individual features of the single TM oxide glasses. However, the linear plots of optical density against composition revealed the presence of two valence states for each TM element, and this was confirmed by ESR results as well. The ESR spectra of the mixed glasses showed a complicated interaction pattern for two different TM ions, in comparison with those of the glasses containing a single TM ion. For the Fe–V glasses, the progressively vanishing hyperfine structure of the VO^{2+} complex with increasing addition of iron oxide is discussed in terms of nuclear spin relaxation, cross-relaxation between two spin systems and spin diffusion within the vanadium spin system. The covalency of the VO^{2+} complex and the number of distorted Fe^{3+} ions were found to decrease with increasing addition of Fe_2O_3 replacing V_2O_5. Similar features were noted for the Cu–V glasses; the spectra of Cu–Fe glass also showed a strong interaction between two different TM ions. It has been suggested that all the possible four valence states (for a given mixed glass) from two different TM elements are present, and that pairing of two different TM ions from two dissimilar TM elements occurs, facilitating the formation of "associates" (e.g. V^{4+}–O–Fe^{3+}).

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1. Introduction

During the last decade or so there has been considerable activity in the field of semiconducting oxide glasses containing a single transition metal (TM) oxide (see, for example, Bandyopadhyay *et al.* [1], for references). TM ions can remain in two (or more) valence states in glasses, and charge transfer is due to electron hopping from lower to higher valence states. By contrast, almost no work has been reported on glasses containing two different 3d TM oxides together, except Bogomolova *et al.* [2] who worked on vanadium phosphate glasses doped with copper oxide. However, recently Bandyopadhyay and Isard [3, 4] reported conductivity data of borate glasses containing oxides of V, Fe and Cu singly and in mixed proportions. The higher conductivity and lower activation energy of the mixed TM oxide glasses in comparison with those of the single TM oxide glasses were interpreted as due to small polaron hopping between ions of two different TM elements, paired as associates (e.g. V^{4+}–O–Fe^{3+}).

It is important to study the spectroscopic behaviour of such glasses to see the possibility of associate formation and study the interaction between different TM ions in relation to those in the glasses containing a single TM oxide. Compared

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to a huge amount of work done on the optical spectroscopy of oxide glasses containing a very low concentration of a single TM oxide [5], not much work has been reported on mixed TM oxide glasses or on glasses containing a high concentration of a single TM oxide which actually show semiconduction behaviour. Van de Graaf *et al.* [6] ascribed the spectrum observed in a borosilicate glass containing both iron and titanium to the formation of Fe^{2+}–O–Ti^{4+} associates. From the shift in the band positions of different TM ions to a lower energy in a potash–zinc–borosilicate glass containing titanium, Veinberg [7] concluded that the observed changes could be ascribed to the presence of M–O–Ti^{4+} associates (where M stands for Fe^{2+}, Cu^{2+}, Mn^{2+}, Ni^{2+}, etc.). Paul [8] observed a shift in the height and position of the differential absorption curve of a soda–alumina–borosilicate glass containing both cerium and titanium, and this behaviour was ascribed to the presence of Ce^{3+}–O–Ti^{4+} associates. All the above work refers to a very low concentration of TM ions.

Similarly, compared to the considerable amount of work done on the electron spin resonance (ESR) spectra of glasses containing a single TM ion [9], very little work has been published on glasses containing mixed TM ions. Bogomolova *et al.* [10] studied the effect of Co^{2+} (spin I) on the ESR spectra of Cu^{2+}, V^{4+}, Mn^{2+} and W^{5+} (spin II) in different glasses and suggested a cross-relaxation process between the two spin systems; spin diffusion within the vanadium spin system was also suggested. Abdrakhmanov *et al.* [11] studied a high titanium phosphate glass doped with different amounts of CuO, V_2O_5, MoO and WO_3. The effect of Cu^{2+}, V^{4+} and Mo^{5+} was thought to be mainly oxidizing Ti^{3+} to Ti^{4+}. Bogomolova *et al.* [12] also studied a barium phosphate glass containing both V_2O_5 and CoO, and V_2O_5 and CuO. In the former system the decrease of ESR signal intensity of V^{4+} was ascribed to spin diffusion, and in the latter a chemical exchange of the form: $V^{4+} + Cu^{2+} \rightarrow V^{5+} + Cu^{+}$ was proposed; the possibility of the formation of Cu^{2+}–V^{4+} pairs, by exchange interactions, was discussed.

In the case of optical spectroscopy, studies on the charge transfer reaction (metal → metal) in glasses are limited, considering the large amounts of work done on crystals [13]. In all the above work, Ti^{4+} was used (with other TM ions) which does not give any band in the visible and near infrared (i.r.) region. No work has yet been reported on the spectra of more complicated systems such as Fe–V, Cu–V and Cu–Fe in glasses, because all these metals in different valence states have several bands in the i.r., visible and ultra violet (u.v.) regions. An attempt is made here to study such spectra in a $2BaO–3B_2O_3$ glass. In the case of ESR spectroscopy, the presence of different TM ions was not rigorously proved while discussing the interaction between them. Therefore, in the present work, ESR spectra have also been measured and the results are correlated with those of optical spectra to throw light on the presence of different valence states and the possible interaction between them in mixed TM oxide glasses, in relation to single TM oxide glasses.

2. Experimental procedure

The glasses were prepared with the base glass composition as $2BaO \cdot 3B_2O_3$. Three glasses were prepared with 5, 10 and 20 mol % respectively of V_2O_5, two glasses with 5 and 10 mol % Fe_2O_3 and also two glasses with 5 and 10 mol % Cu_2O. Iron–vanadium and copper–vanadium mixed glasses were prepared with a total TM oxide content of 10 mol % starting with a high percentage of vanadium and replacing V_2O_5 by Fe_2O_3 and Cu_2O at 1 mol % steps. Only one copper–iron glass was prepared with 5 mol % Cu_2O and 5 mol % Fe_2O_3. The glasses were melted from analar grade raw materials in alumina crucibles at 1130° C for 45 min under an air atmosphere.

Chemical analyses, for the determination of the concentrations of different TM ions in single TM oxide glasses, were carried out using standard procedures. The batch compositions of the mixed TM oxide glasses and the chemically analysed compositions of the glasses containing a single TM oxide (along with their respective redox ratios) are given in Table I. A difference of 5% was observed between the batch and chemically analysed compositions of the single TM oxide glasses. Therefore, an allowance of 5% was given when plotting the optical density data for the mixed TM oxide glasses against composition.

The optical spectra were measured using a Cary 14 spectrophotometer in a range of 5000 to 25 000 cm^{-1} on polished specimens of thicknesses ranging from 0.1 to 3.0 mm, depending on the nature and concentration of the TM ions.

The ESR spectra were recorded at room tem-

TABLE I The compositions and optical data for all the glasses

Glass* number	TM oxide (Mol%)			C†	Position of the peak (cm^{-1})	Optical density per cm
	V_2O_5	Fe_2O_3	Cu_2O			
1V	4.75	–	–	0.29	9 740‡	2.3
2V	9.50	–	–	0.33	9 770	4.6
3V	19.40	–	–	0.19	9 810	6.1
1F	–	4.72	–	0.20	10 170	9.2
2F	–	9.46	–	0.12	10 150	11.0
1C	–	–	4.70	0.05	13 000	54.0
2C	–	–	9.40	0.30	12 700	77.0
FV1	9.00	1.00	–	–	10 200	3.8
FV2	8.00	2.00	–	–	10 200	4.9
FV3	7.00	3.00	–	–	10 220	6.2
FV4	6.00	4.00	–	–	10 200	7.4
FV5	5.00	5.00	–	–	10 250	8.5
FV6	4.00	6.00	–	–	10 250	9.8
FV7	3.00	7.00	–	–	10 200	11.0
FV8	2.00	8.00	–	–	10 200	12.3
FV9	1.00	9.00	–	–	10 250	13.4
CV1	9.00	–	1.00	–	12 900	22.0
CV2	8.00	–	2.00	–	12 900	33.0
CV3	7.00	–	3.00	–	13 000	43.0
CV4	6.00	–	4.00	–	12 900	56.0
CV5	5.00	–	5.00	–	13 100	65.0
CV6	4.00	–	6.00	–	13 100	79.0
CV7	3.00	–	7.00	–	13 000	90.0
CV8	2.00	–	8.00	–	12 900	101.5
CV9	1.00	–	9.00	–	12 800	113.0
CF5	–	5.00	5.00	–	13 900	73.0

*V = vanadium glass, F = iron glass, C = copper glass, FV = iron–vanadium glass.

†CV = copper–vanadium glass and CF = copper–iron glass. C = V^{4+}/V_{total}, Fe^{2+}/Fe_{total} and Cu^{+}/Cu_{total} for the V, Fe and Cu glasses respectively.

‡The positions of the second band for glasses 1 V, 2 V and 3 V are 16 800, 16 900 and 17 000 cm^{-1} respectively.

perature on a Hilger and Watts Microspin spectrometer operated at *X*-band frequency. The coarsely powdered glass sample, contained in a fused quartz tube, was introduced into the resonance cavity operating in the H_{011} mode. The magnetic field modulation frequency employed was 100 kHz. The magnetic field was calibrated using a proton resonance probe, and it was swept at approximately 50 G min^{-1}. 1 G field markers were placed on the spectra at approximately 60 G

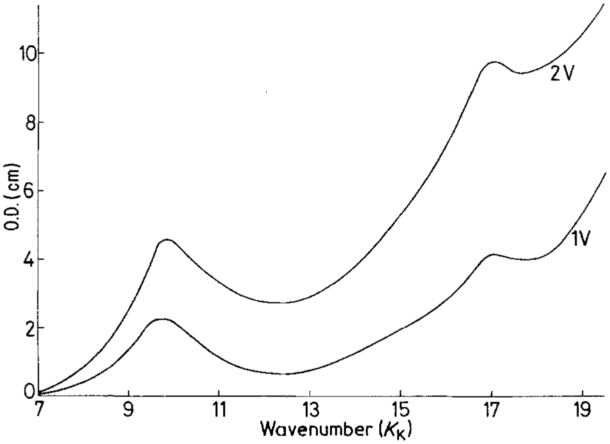

Figure 1 The optical spectra of vanadium glasses.

intervals. 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. Optical spectra

3.1.1. Vanadium glasses

The absorption spectra of glasses 1V and 2V are shown in Fig. 1. The principal features are a broad band around 10 000 cm^{-1} and a relatively weak band around 17 000 cm^{-1} and an absorption tail at high wavenumbers. The height of the first peak increased in proportion to the concentration of V_2O_5. The positions of the two peaks moved slightly towards higher wavenumbers with increasing V_2O_5 content. The steep rise in optical density (O.D.) at high wavenumbers became more marked as the concentration of V_2O_5 increased; there was also a marked shift of this absorption tail from higher to lower wavenumbers with increasing V_2O_5.

The two absorption peaks are typical for V^{4+} complexed as VO^{2+} within a distorted octahedral site, and can be assigned to $b_2 \rightarrow e_\pi^*$ and $b_2 \rightarrow b_1^*$ transitions, based on the molecular orbital scheme proposed by Ballhausen and Gray [14]. The rise of O.D. at high wavenumbers is ascribed to the tail of the metal → ligand charge transfer band of the V^{5+} ion; the absorption of the glasses studied was too high to observe the peak of this band in the near u.v. region. However, the shift of this tail to lower energy with increasing V_2O_5 (i.e. with increasing concentration of V^{5+}) justifies the assignment of this tail to the V^{5+} ion; because with increasing concentration of V^{5+}, the effective V^{5+}–O distance decreases, which facilitates the charge transfer. Similar observations in vanadium phosphate glasses have been reported by Anderson [15]. From a survey of the literature [16–18] and the observed shift in the position of the tail, it is suggested that the V^{5+} ions could have both octahedral and pentagonal co-ordination in these glasses.

No band due to the V^{3+} ion could be observed in any of the glasses studied. The presence of V^{3+} in oxide glasses is known to produce absorption bands around 14 500 and 22 500 cm^{-1} respectively, and these two bands are assigned to

$$^3T_{1g}(\mathrm{F}) \rightarrow {}^3T_{2g} \text{ and } {}^3T_{1g}(\mathrm{F}) \rightarrow {}^3T_{1g}(\mathrm{P})$$

transitions respectively [19]. The second band could have been obscured by the strong charge transfer tail of V^{5+}, but the first one should have been well separated from any other bands due to either V^{4+} or V^{5+}, if V^{3+} was present. The spectra of these glasses did not show any sign of the 14 500 cm^{-1} band even when they were analysed in a Du Pont 310 "Curve Resolver" assuming a Gaussian function. It should be mentioned that Johnston [20] was unable to detect the presence of any V^{3+} in a vanadium silicate glass melted in a highly reducing atmosphere. Therefore, the occurrence of V^{3+} in these glasses, melted under an air atmosphere, was thought to be improbable.

3.1.2. Iron glasses

The absorption spectra of glasses 1F and 2F are shown in Fig. 2. Both the glasses show a single band around 10 000 cm^{-1} and a steep rise at high wavenumbers. The values of O.D. at this peak position were in proportion with the concencentration of Fe^{2+}. This band can be assigned to the transition $^5T_{2g} \rightarrow {}^5E_g$ of the Fe^{2+} ion in accordance with the Orgel diagram for a d^6 ion in an octahedral field [21]. The distortion of the octahedral site, if any, will be very similar in both glasses, because the above band is observed in almost similar positions. The peak of the charge transfer band of Fe^{3+} could not be observed, because of the strong absorption. However, from the shift of the observed tail to lower energy and increase in its height with increasing Fe_2O_3 content, this absorption tail could be ascribed to Fe^{3+}. The co-ordination of Fe^{3+} is very difficult to predict from the observed spectra, because any spin-forbidden band due to Fe^{3+} is obscured by the strong charge transfer tail.

3.1.3. Copper glasses

The absorption spectra of glasses 1C and 2C are shown in Fig. 3. Both the glasses show a single band around 13 000 cm^{-1}. The values of O.D. of this band were found to increase in proportion to the Cu^{2+} concentration in these glasses. This band can be assigned to the transition $d_{x^2-y^2} \rightarrow d_{z^2}$ of the Cu^{2+} ion in a distorted octahedral site [21]. The distortion will be higher in glass 1C than in glass 2C, because the observed band appeared at a higher wavenumber for the former. It should be pointed out that the weak band, due to distortion splitting ($d_{x^2-y^2} \rightarrow d_{xy}$ transition) around 7600 cm^{-1} was not observed. An attempt

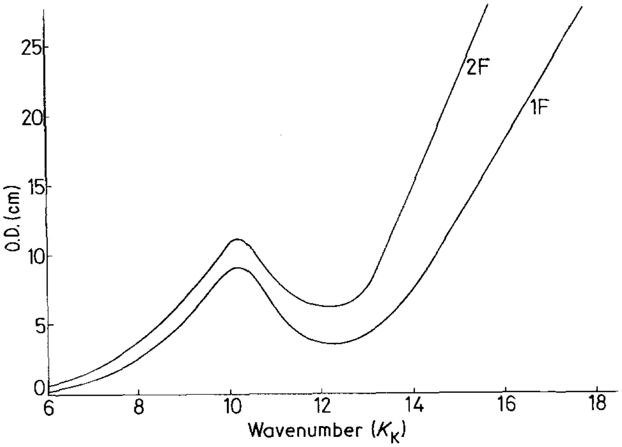

Figure 2 The optical spectra of iron glasses.

to analyse these spectra in a 310 curve resolver did not reveal the presence of any other bands, either due to this transition or due to the transition $d_{x^2-y^2} \rightarrow d_{yz,zx}$ at higher energy. This is due to the high concentration of Cu^{2+} in these glasses and also to the high molar extinction coefficient of Cu^{2+} ion in borate glasses.

As for vanadium and iron glasses, the peak of the charge transfer band of these glasses due to Cu^+ could not be observed because of the strong absorption. However, the observed shift of the absorption tail to lower energy and the increase in its height from glass 1C to 2C could be ascribed to the Cu^+ ion, because the latter has a higher concentration of Cu^+ ions. The co-ordination of Cu^+ is very difficult to predict from this tail, because any spin forbidden band due to Cu^+ would be obscured by the strong charge transfer tail. However, the radius ratio of Cu^+/O suggests that Cu^+ is octahedrally co-ordinated in borate glasses [22], but the presence of tetrahedral Cu^+ cannot be ruled out.

3.1.4. *Mixed TM oxide glasses*

It is very difficult to chemically analyse a glass containing two different transition elements for all the ions with all possible valence states. Hence, the absorption spectra could be useful in showing which ions occur. However, the spectra of all the mixed TM oxide glasses studied showed a single absorption band and a strong cut-off edge at high energies. An attempt to analyse the observed spectra in the 310 curve resolver did not reveal the presence of any other band. It was not possible to assign the bands from their respective positions, but the variation of the intensity with proportion of the two TM elements strongly suggested that an ion from each element contributed to the bands.

A typical spectrum for glass FV5 is shown in Fig. 4; the spectra for all the other glasses showed the same feature. A broad band around 10 200 cm^{-1} was observed for all nine glasses.

A typical spectrum for glass CV5 is shown in Fig. 5, which is representative of all the other copper–vanadium glasses. A broad band around

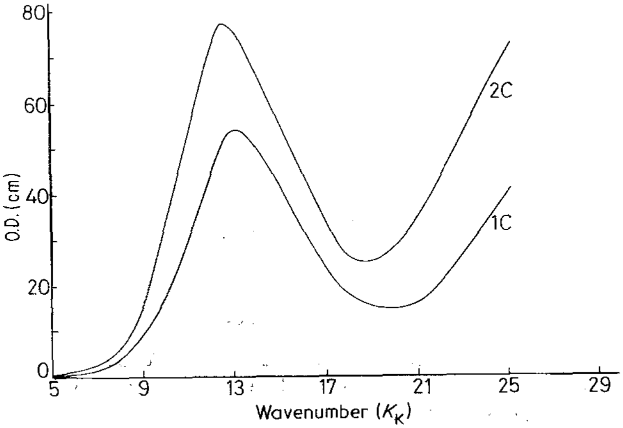

Figure 3 The optical spectra of copper glasses.

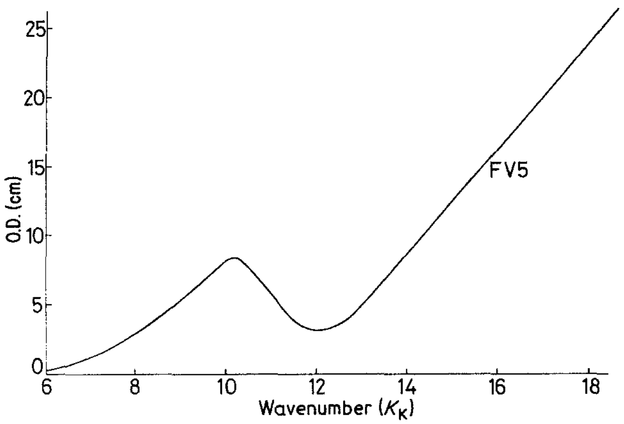

Figure 4 Typical optical spectrum of a mixed Fe–V glass.

13 000 cm^{-1} was observed for all nine glasses. The positions of the peaks and the values of O.D. are given in Table I. The spectrum for glass CF5 is shown in Fig. 5, which also shows a single broad band at 13 900 cm^{-1}.

Let us first discuss glass FV5, which is actually equivalent to a combination of glasses 1V and 1F. It is noted that, while the O.D. of the absorption band in FV5 is slightly lower than that in 1F, it is more than three times higher than that in 1V. If this band were due to V^{4+} only, the concentration of V^{4+} in FV5 would have to be three times that in 1V. This seems very unlikely from the point of view of the thermodynamics of oxidation–reduction reactions between iron and vanadium in the melt. Furthermore, such a change in the V^{4+}/V total ratio in borate glasses cannot affect the resistivity and activation energy as much as the observed differences between glasses 1V and FV5 [1, 3, 4]. Due to the short melting time, it is not unexpected that these mixed glasses contain both V^{4+} and Fe^{2+} ions, because equilibrium may not have been attained. Both these ions show bands at about the same energy which could produce a strong physical overlap to give rise to a single band.

The values of O.D. for glass FV1 to FV9 are plotted against mol% Fe_2O_3, in Fig. 6, along with those for the vanadium and iron glasses for comparison. It is seen that a straight line is obtained with a finite value of O.D. at zero Fe_2O_3 content (i.e. at 9.5 mol% V_2O_5), which almost corresponds to that of glass 2V. From the nature of this plot, it can be suggested that each point on the plot represents the value of O.D. for both V^{4+} and Fe^{2+} ions. This also suggests that the extent of the redox reaction in these glasses, melted under identical conditions, is the same and in proportion to increasing Fe_2O_3 and decreasing V_2O_5 contents. Hence, it can be assumed that all mixed iron–vanadium glasses contain both V^{4+} and Fe^{2+} ions together with V^{5+} and Fe^{3+} ions. A similar conclusion can be drawn about the presence of Cu^{2+}

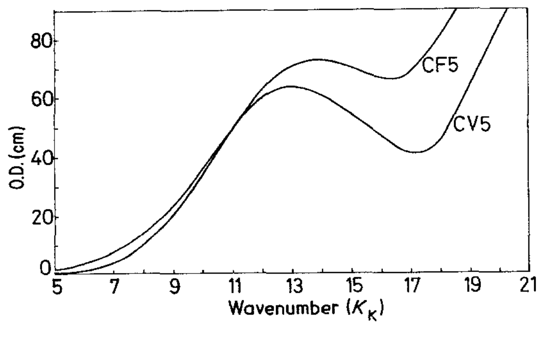

Figure 5 Typical optical spectra of mixed Cu–V and Cu–Fe glasses.

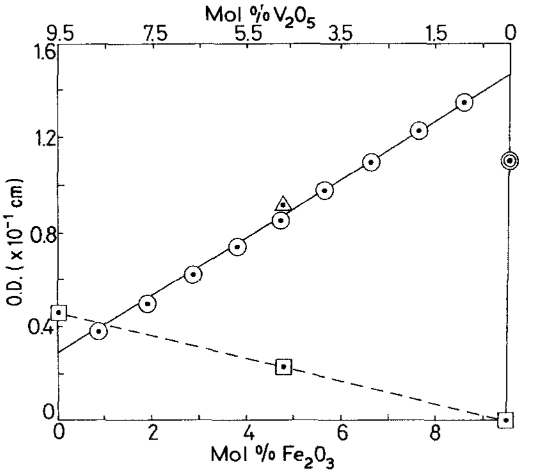

Figure 6 Optical density against mol% Fe_2O_3 for mixed Fe–V glasses: ⊙ glasses FV1 to FV9, ⊡ vanadium glasses, △ glass 1F and ◎ glass 2F.

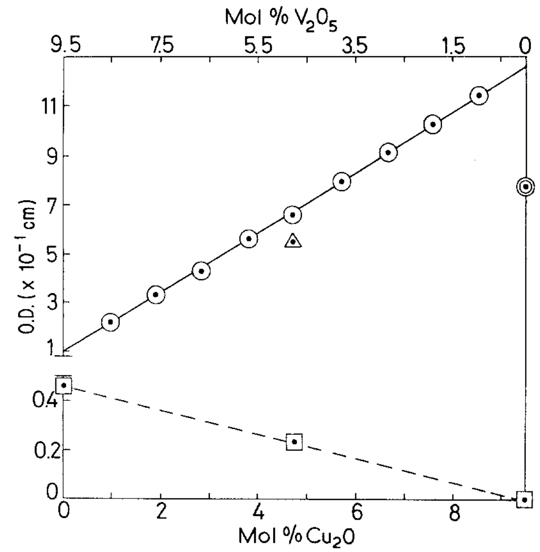

Figure 7 Optical density against mol% Cu_2O for mixed Cu–V glasses: ⊙ glasses CV1 to CV9, ⊡ vanadium glasses, △ glass 1C and ◎ glass 2C.

and V^{4+} along with Cu^+ and V^{5+} in all the Cu–V mixed glasses (see Fig. 7).

It is seen from Figs. 1, 2 and 4 that the cut-off absorption edge at FV5 is at a higher energy than that of either 1V or 1F. By comparing the O.D. values of these glasses, it seems likely that the total concentration of the oxidized states ($Fe^{3+} + V^{5+}$) in FV5 is higher than the sum of V^{5+} in 1V plus Fe^{3+} in 1F. Accordingly, this cut-off edge should move to lower energy, if it was due either to Fe^{3+} or to V^{5+} ions. Therefore, it is suggested that a strong interaction is taking place between different TM ions facilitating the formation of the Fe^{2+}–O–V^{5+} and V^{4+}–O–Fe^{3+} associates, and that the charge transfer processes can take place in these associates. However, the possibility of the charge transfer processes involving the individual ions cannot be completely ruled out. This necessitates a more detailed work in this system.

It is seen from Figs. 1, 3 and 5 that the cut-off absorption edge of glass CV5 is at a lower energy than that of either 1V or 1C. By comparing the O.D. values of these glasses, it seems likely that the total concentration of ($V^{5+} + Cu^+$) in CV5 is lower than the sum of V^{5+} in 1V plus Cu^+ in 1C. Therefore, the cut-off edge should move to higher energy if it was either due to Cu^+ or to V^{5+} ions. Hence, it is suggested that there is a strong interaction taking place between different TM ions facilitating the formation of the Cu^+–O–V^{5+} and V^{4+}–O–Cu^{2+} associates. However, the effect of

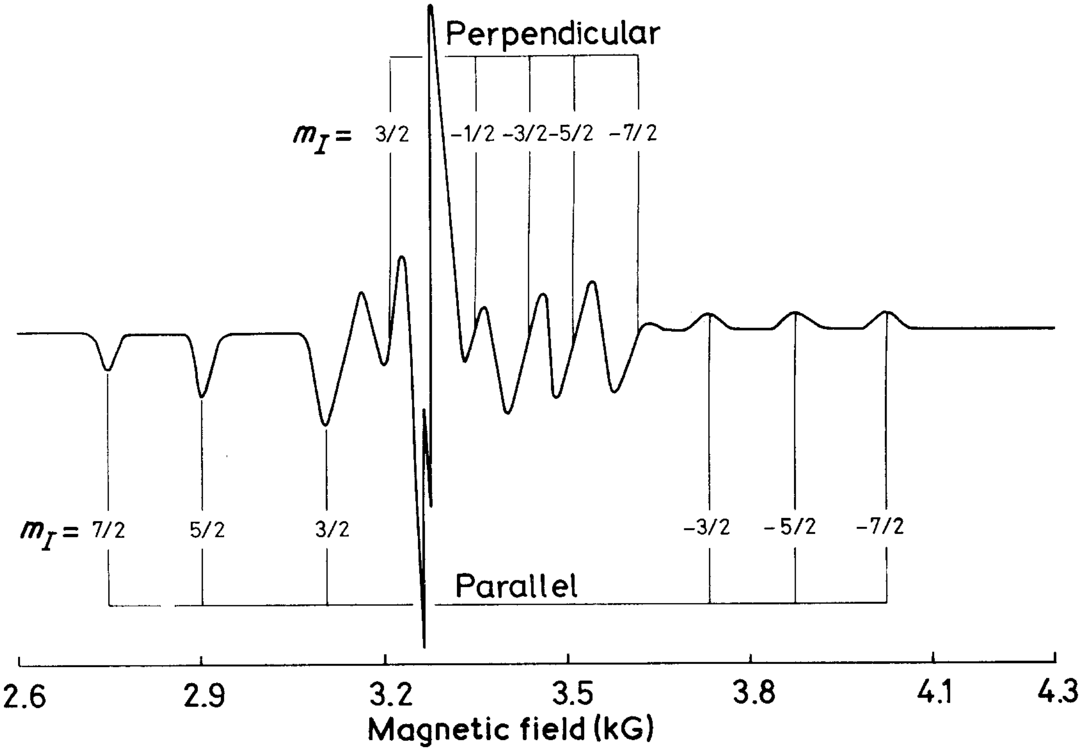

Figure 8 A typical ESR spectrum of V^{4+} in a vanadium glass.

TABLE II The ESR parameters of the glasses

Glass number	Spectra due to	$g_\perp$	$g_\parallel$	$\lvert A_\perp \rvert$ ($\times 10^4$ cm^{-1})	$\lvert A_\parallel \rvert$ ($\times 10^4$ cm^{-1})	$\lvert A'_\perp \rvert$ ($\times 10^4$ cm^{-1})	$\lvert A'_\parallel \rvert$ ($\times 10^4$ cm^{-1})	$(1-\gamma^2)$	$(1-\alpha^2)$	$\frac{\Delta g_\parallel}{\Delta g_\perp}$
1V	V^{4+}	1.9370	1.9670	57.64	165.1	29.30	78.40	0.31	0.44	1.88
1V	V^{4+}	1.9677	1.9315	58.40	165.8	29.02	78.20	0.32	0.40	2.04
3V	V^{4+}	1.9686	1.9260	59.20	165.3	28.60	77.40	0.34	0.35	2.27
FV1	V^{4+}	1.9598	1.9330	53.90	158.8	27.80	76.50	0.17	0.41	1.64
FV2	V^{4+}	1.9580	1.9345	53.00	157.6	27.40	76.10	0.13	0.43	1.52
FV3	V^{4+}	1.9550	1.9365	52.20	156.4	27.00	75.60	0.07	0.44	1.39
CV1	V^{4+}	1.9620	1.9328	54.20	160.6	28.20	77.50	0.21	0.41	1.73
	Cu^{2+}	2.040	2.420	–	145.0	–	–	–	–	–
CV2	V^{4+}	1.9600	1.9340	53.50	159.2	27.90	77.10	0.17	0.42	1.61
	Cu^{2+}	2.020	2.440	–	142.0	–	–	–	–	–
1C	Cu^{2+}	2.078	2.375	–	155.0	–	–	–	–	–
2C	Cu^{2+}	2.060	2.395	–	150.0	–	–	–	–	–

the charge transfer bands from the individual ions on the observed adsorption edge cannot be ruled out.

The same feature is noted for glass CF5 in that the cut-off edge of this glass is shifted to a lower energy compared to that in either 1C or 1F. Following the above discussion, it is suggested that the charge transfer processes can take place in the Fe^{2+}–O–Cu^{2+} and Cu^{+}–O–Fe^{3+} associates in this mixed glass as well. However, a definite conclusion about the existence of different TM ions cannot be made for this mixed glass as for the other two.

3.2. ESR spectra

3.2.1. Vanadium glasses

A typical spectrum is shown in Fig. 8. In contrast to the results of other workers, the hyperfine structure is well resolved [23, 24]. The spectrum can be described by an axial spin Hamiltonian

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

The principal results of the above spin Hamiltonian is that the eight hyperfine components of the electron nuclear spin interaction have envelopes with divergencies at magnetic field positions

$$H_{\parallel}(m_I) = H_{\parallel}(0) - A_{\parallel}(m_I) - \frac{A_{\perp}^2}{2H_{\parallel}(0)}[I(I+1) - m_I^2] \qquad (2)$$

and shoulders at positions

$$H_{\perp}(m_I) = H_{\perp}(0) - A_{\perp}(m_I) - \frac{(A_{\parallel}^2 + A_{\perp}^2)}{4H_{\perp}(0)}[I(I+1) - m_I^2]. \qquad (3)$$

Here m_I is the nuclear magnetic quantum number ranging from $-7/2$ to $+7/2$; $H_{\parallel}(0) = h\nu/g_{\parallel}\beta_O$ and $H_{\perp}(0) = h\nu/g_{\perp}\beta_O$, where ν is the spectrometer frequency. The extreme points which are relatively pure can readily be identified on the experimental spectrum; we observed five perpendicular components and six parallel components as shown in Fig. 8 for different values of m_I.

The spin Hamiltonian parameters ($g_{\perp}$, $g_{\parallel}$, $A_{\perp}$ and $A_{\parallel}$) were calculated by an iterative procedure giving the best fit to the quadratic Equations 2 and 3; and are given in Table II. The 60% confidence limits, determined by normal statistical methods, were maximum ± 0.0009 for the g-values and ± 0.4 for the A-values. It is seen from Table II that there is a slight increase in $g_{\perp}$, while $g_{\parallel}$ shows a steady decrease from glass 1V to 3V. The values of both $A_{\perp}$ and $A_{\parallel}$ increase between glasses 1V and 3V. These results are quite similar to those reported earlier [1]; however, there is a slight difference in the g- and A-values results due to different redox ratios in these three glasses compared to those of their counterparts studied in the previous work. The present results can also be interpreted as the V^{4+} ion being complexed as a VO^{2+} ion within a tetragonally distorted octahedral site, which is consistent with the results of the absorption spectra, and the V^{4+}–O bonding becomes increasingly covalent with increasing V_2O_5 content.

From the analysis of the above results, it is found that there is a considerable amount of covalency. Therefore, taking the covalency of the V^{4+}–O bonds into consideration

$$g_{\perp} = g_e[1 - (\gamma^2\beta^2\lambda/E_1)] \qquad (4)$$

$$g_{\parallel} = g_e[1 - (4\alpha^2\beta^2\lambda/E_2)] \qquad (5)$$

$$A_{\perp} = P\left[\beta^2\left(\frac{2}{7} + K\right) - \frac{11}{4}\Delta g_{\perp}\right] \qquad (6)$$

$$A_{\parallel} = -P\left[\beta^2\left(\frac{4}{7} + K\right) + \Delta g_{\parallel} + \frac{3}{7}\Delta g_{\perp}\right] \qquad (7)$$

where K is proportional to the amount of isotropic Fermi contact interaction, $\Delta g_{\perp} = g_e - g_{\perp}$; $\Delta g_{\parallel} = g_e - g_{\parallel}$ and $P = 2\beta_O\beta_N\gamma_O\langle d_{xy}|r^{-3}|d_{xy}\rangle$. β_N is the nuclear magneton, γ_O is the gyromagnetic ratio, g_e is the free electron value equal to 2.0023, E_1 and E_2 are the energies of the transitions $b_2 \rightarrow e^*$ and $b_2 \rightarrow b_1^*$ respectively.

The expressions $(1 - \gamma^2)$ and $(1 - \alpha^2)$ are degrees of covalency; the covalency increases as their values increase, the former gives an indication of the influence of the π-bonding between the V^{4+} ion and the vanadyl oxygen; while the latter indicates the influence of the σ-bonding with equilateral ligands; here β^2 is a measure of the in-plane π-bonding with the equilateral ligands, which is taken to be equal to 1 for many oxide glasses containing VO^{2+} ion, as the b_2 orbital is assumed strictly non- (in-plane π) bonding [25].

Taking $\beta^2 = 1$ and assuming $\lambda = 249\,cm^{-1}$ [26], the values of $(1 - \gamma^2)$ and $(1 - \alpha^2)$ were calculated from Equations 4 and 5 using the peak frequencies from the observed absorption spectra of these glasses, and are given in Table II. It is seen that, while $(1 - \gamma^2)$ remains almost constant, the values of $(1 - \alpha^2)$ decrease. This means that the degree of covalency of the σ-bonding decreases with increasing V_2O_5 content. However, further analysis of the hyperfine tensor components show a reverse trend. From the molecular orbital theory, it can be shown that the components $A_\perp$ and $A_\parallel$ consist of the contributions $A'_\perp$ and $A'_\parallel$ of the $3d_{xy}$ electron to the hyperfine structure and the $P\beta^2K$ term arising due to the anomalous contribution of the s-electrons. Equations 6 and 7 can be split into their component parts

$$A_\perp = P\left(\frac{2}{7}\beta^2 - \frac{11}{14}\Delta g_\perp\right) - P\beta^2K = A'_\perp - P\beta^2K \tag{8}$$

$$A_\parallel = -P\left(\frac{4}{7}\beta^2 + \Delta g_\parallel + \frac{3}{7}\Delta g_\perp\right) - P\beta^2K = A'_\parallel - P\beta^2K. \tag{9}$$

The values of $A'_\perp$ and $A'_\parallel$ were calculated using the above equations and are also given in Table II. It is seen that both these parameters show a steady decrease between glasses 1V and 3V indicating an increase of covalency in the V^{4+}–O bonds with increasing V_2O_5 content. The decrease of the anisotropic contribution of the $3d_{xy}$ electron to the hyperfine splittings is brought about by the increasing screening of the $3d_{xy}$ orbital from its nucleus through overlap of the electron orbits of the surrounding oxygen ligands. This produces an expansion of the $3d_{xy}$ orbital resulting in a decreased interaction of this magnetic electron with the vanadium nucleus.

3.2.2. Iron glasses

The spectrum of glass 1F is shown in Fig. 9, which is similar to that of glass 2F. There is only one resonance observed at $g = 4.3$. This spectrum is described by the usual spin Hamiltonian

$$\mathcal{H} = \beta_0 H.g.S + D[S_z^2 - 1/3S(S+1)] + E(S_x^2 - S_y^2) \tag{10}$$

where the crystal field parameters D and E determine the resonance positions. The resonance at $g = 4.3$. arises due to the transition within the middle doublet among the three Kramers doublets; the other resonances at 6.0 and 2.0 arise due to the transitions in the lowest doublet; this has been discussed by various authors [27, 28].

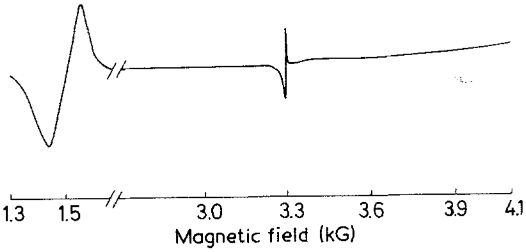

Figure 9 The $g = 4.3$ resonance due to Fe^{3+} in glass 1F.

The $g = 4.3$. resonance was ascribed by many authors as due to the tetrahedral Fe^{3+} ion [29–32]. But Kurkjian and Sigety [27] suggested that both tetrahedral and octahedral Fe^{3+} ions with rhombic distortions could produce this resonance. The latter view was also supported by Loveridge and Parke [28]. In this work we shall call these Fe^{3+} ions, responsible for this resonance, as "distorted". Although the spin Hamiltonian parameters have not been calculated from the observed spectra, the values of D were found to range between 0.24 and 0.32 cm^{-1} in different borate glasses [28], which represents the rhombic distortion of the Fe^{3+} ions.

No resonance at $g = 2.0$ was observed, but a little background absorption is apparent in the higher field region for glass 1F; this background absorption was relatively more marked for glass 2F, presumably due to the higher concentration of Fe^{3+} ions. The integrated intensity of the observed resonance was calculated as $(I \times \Delta H^2)$, where I is the peak to peak derivative intensity in some arbitrary units and ΔH is the peak to peak width in Gauss. The values for I and ΔH were obtained fitting the spectra with a differential Lorentzian function. The values of the functional constant were iterated by providing the initial values from the line shape analysis, and the values of ΔH were also iterated within ± 15% to obtain the best fit of the I values with those of the experimental spectra. The values of $(I \times \Delta H^2)$ and ΔH for glass 2F are almost half those for glass 1F. This means that in glass 2F there may not be any spin–spin interaction, because that should increase the linewidth. The $g = 4.3$ resonance was observed in different borate glasses containing a high concentration of Fe_2O_3 by various authors [28, 32], and no mention was made about the spin–spin interaction. Therefore, the observed decrease in the values of $(I \times \Delta H^2)$ and ΔH could be ascribed to the decrease of the number of "distorted" Fe^{3+} ions from glass 1F to 2F.

3.2.3. Copper-glasses

The spectrum for glass 2C is shown in Fig. 10. The Cu^{2+} ion has a nuclear spin $I = 3/2$ and therefore

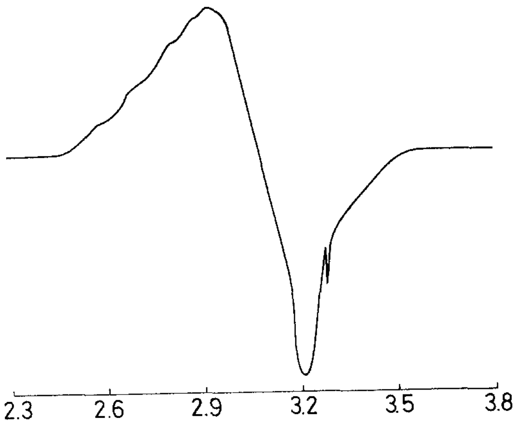

Figure 10 The ESR spectrum due to Cu^{2+} of glass 2C.

$(2I + 1)$ or four perpendicular and four parallel hyperfine components should be observed. However, as seen in Fig. 10, four weak parallel components are observed in the lower field region; but the perpendicular components are not observed at all in the higher field region, because of a high concentration of Cu^{2+} ions in this glass. Glass 1C, which has a lower concentration of Cu^{2+} ions than that of glass 2C, showed a similar type of spectrum except that the shape of the spectrum was more symmetric and the intensity of the central resonance line was lower than that of glass 2C.

The Cu^{2+} spectrum can be described by the same axial spin Hamiltonian as the V^{4+} ion (Equation 1). The peak positions may be related to the principal values of the g and A tensors by [33]

$$h\nu = g_{\parallel}\beta_0 H + m_I A_{\parallel} + \left[I(I+1) - m_I^2\right] \frac{A_{\perp}^2}{2g_{\parallel}\beta_0 H} \qquad (11)$$

$$h\nu = g_{\perp}\beta_0 H + m_I A_{\perp} + \left[I(I+1) - m_I^2\right] \frac{A_{\perp}^2 + A_{\parallel}^2}{4g_{\perp}^2\beta_0 H}. \qquad (12)$$

Since the perpendicular components were not resolved, the values of $A_{\perp}$ could not be determined. The values of $g_{\parallel}$ and $A_{\parallel}$ were first estimated from the positions of the first two peaks in the lower field region by Equations 11 and 23, and the value of $g_{\perp}$ was estimated by a fitting procedure [34]. The values are given in Table II. These values suggest that Cu^{2+} ion is in a distorted octahedral site [35], and this is consistent with the results of the absorption spectra. However, the estimated errors (maximum ± 0.009 for the g-values and ± 1.5 for the $A_{\parallel}$ values) for the parameters are too high to deduce anything about the change of covalency with Cu_2O content. Even considering the errors, it could be suggested that Cu^{2+} ions are relatively more distorted in glass 1C than in 2C, as also observed by the change of position of the absorption peak between glasses 1C and 2C.

3.2.4. Glasses containing mixed TM oxides

3.2.4.1. Iron–vanadium Glasses. The spectra of the first five Fe–V glasses (from the vanadium end) are shown in Fig. 11. It is seen that these five glasses show the symmetric resonance due to Fe^{3+} at $g = 4.3$. (it was, in fact, observed in all nine glasses), but the hyperfine structure due to V^{4+} is

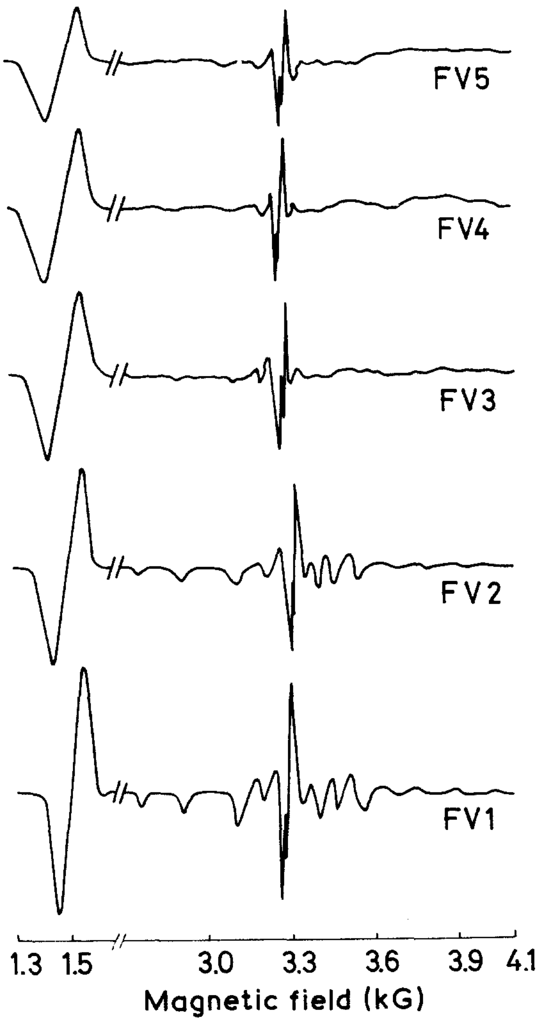

Figure 11 The ESR spectra due to V^{4+} and Fe^{3+} in mixed Fe–V glasses.

only observed clearly for the first two glasses FV1 and FV2 and less clearly for the other three (FV3–FV5). After glass FV5, no hyperfine structure was observed at all. Instead, a broad background became more marked in the higher field region, presumably due to Fe^{3+}, as in the glasses containing only iron. Both the intensity and the line-width of the Fe^{3+} resonance decreased with increasing Fe_2O_3 (i.e. decreasing V_2O_5) content. This behaviour, coupled with the observation that the intensities of the V^{4+} hyperfine components decrease with composition, suggests that there is a considerable interaction between Fe^{3+} and V^{4+} ions which obscures the hyperfine structure of the latter. However, the ESR spectra show that V^{4+} is certainly present in glasses FV1 to FV5, and it is probably present in glasses beyond FV5.

From the V^{4+} hyperfine structure of glasses FV1 to FV3, the ESR parameters were calculated according to the method described in Section 3.2.1. and are given in Table II. The calculation for glasses FV4 and FV5 gave considerable errors and, therefore, they were excluded from the analysis. The maximum error for the g-values was ± 0.0011 and ± 0.7 for the A-values. It is seen that, while $g_{\parallel}$ increases slightly compared to that in glass 2V, $g_{\perp}$ shows a considerable decrease. This indicates a decrease in covalency or tetragonal distortion along the V^{4+}–(vanadyl) oxygen bond in the mixed glasses with very little substitution (from 1 to 3%) of V_2O_5 by Fe_2O_3 in glass 2V. The values of both $A_{\perp}$ and $A_{\parallel}$ also show a significant decrease, while those of $A'_{\perp}$ and $A'_{\parallel}$ show a considerable decrease from glass 2V to glasses FV1, FV2 and FV3. This indicates a decreased interaction of the $3d_{xy}$ electron with the V^{51} nucleus. The g-values show that a small replacement of V_2O_5 by Fe_2O_3 in glass 2V involves a considerable change in V^{4+}–(vanadyl) oxygen bonding without significantly altering that along the V^{4+} and equilateral ligands. It is thought that this trend should be followed through the whole series of Fe–V mixed glasses.

Taking the values of E_1 and E_2 for glass 2V (Table I) and using Equations 4 and 5, the values of $(1-\gamma^2)$ and $(1-\alpha^2)$ were calculated for glasses FV1 to FV3 as shown in Table II. It is seen that, while $(1-\alpha^2)$ remains almost constant, $(1-\gamma^2)$ decreases from glass 2V to the mixed glasses FV1 to FV3. This again shows the change in covalency of the vanadium–oxygen bonding.

Using Equations 4 and 5, the ratio

$$\Delta g_{\parallel}/\Delta g_{\perp} = (4\alpha^2/\gamma^2)(E_1/E_2)$$

which eliminates the variable quantities, λ and β^2, and hence the uncertainities in their values, can be taken as a measure of tetragonality [26]. This will provide a more meaningful estimate of the symmetry of the octahedral V^{4+} site. Although the bonding parameters γ^2 and α^2 are involved in this expression, their values would not affect E_1 and E_2 so much that $\Delta g_{\parallel}/\Delta g_{\perp}$ is invalidated as a measure of tetragonality. The values of this ratio for the vanadium and Fe–V mixed glasses are given in Table II. Lower values of this ratio in the mixed Fe–V glasses compared to those in vanadium glasses again show the improvement of the octahedral symmetry of the V^{4+} site in mixed glasses.

The g-values show that the interaction between the electron and nuclear spin moments should increase significantly both along the perpendicular and parallel orientations, i.e. the $3d_{xy}$ electron should be increasingly localized on the vanadium nucleus in the mixed Fe–V glasses. However, the hyperfine structures are progressively destroyed in these glasses, and the values of $A'_{\perp}$ and $A'_{\parallel}$ show a steady decrease. This implies that a process of nuclear relaxation may take place in the vanadium nuclei when V_2O_5 is replaced by Fe_2O_3 in glass 2V. A similar observation was made in a barium borate glass containing V^{4+} and Co^{2+} ions by Bogomolova *et al.* [10].

Since Fe^{2+} ions having a very short spin-lattice relaxation time are also present in the mixed Fe–V glasses, they can interact with the V^{4+} ions (having longer spin-lattice relaxation time) via cross-relaxation processes between two spin systems [36]. However, this point should be verified by low temperature measurements. Another possibility is that there is a process of spin diffusion within the vanadium spin system. Following Bogomolova *et al.* [12], when the intensities of the lines corresponding to $m_I = \pm 7/2$ were compared, they showed a steady decrease with increasing Fe_2O_3 content; it was assumed that the number of V^{4+} ions contributing to the spectra does not change significantly. This behaviour could be related to a process of spin diffusion which results in a progressive disappearance of the V^{4+} hyperfine structure.

The above possibilities could be thought to be more prominent up to glass FV5, after which the influence of the Fe^{3+} ion would be more marked. Although there are various types of interaction taking place in this system, it is suggested that the

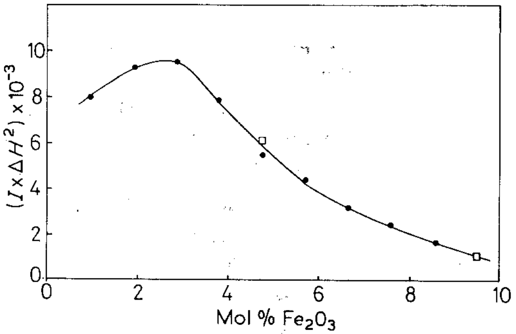

Figure 12 The integrated intensity ($I \times \Delta H^2$) of the $g = 4.3$ resonance against mol% Fe_2O_3 for mixed Fe–V glasses: ● Glasses FV1 to FV9 and ▫ glasses 1F and 2F.

strong interaction between the V^{4+} and Fe^{3+} ions may result in the formation of V^{4+}–O–Fe^{3+} associates. This is thought to be facilitated by the formation of less covalent $V^{4+}O_6$ units in the Fe–V mixed glasses.

In order to see the changes occurring with Fe^{3+}, the integrated intensity ($I \times \Delta H^2$) was plotted against mol% Fe_2O_3, as shown in Fig. 12. This shows a progressive decrease in the number of "distorted" Fe^{3+} ions as Fe_2O_3 content increases; this was also observed in the glasses containing only iron. Assuming that the "distorted" Fe^{3+} ions are not favourable for forming associates with V^{4+}, it is suggested that, as Fe_2O_3 content increases in the Fe–V mixed glasses, more of the less "distorted" Fe^{3+} ions become available, resulting in the formation of the V^{4+}–O–Fe^{3+} associates. In a variety of glasses containing Fe^{3+}, the disappearance of the $g = 4.3$ resonance was associated with the appearance of the $g = 2.0$ resonance, which was ascribed to the increase in spin–spin interaction with increasing concentration of Fe^{3+} [27]. But in our case we did not observe any $g = 2.0$ resonance. This could be due to the progressive coupling of the less "distorted" Fe^{3+} ions with the V^{4+} ions to form the associates. It could be thought that the change in $g = 4.3$ resonance was due to spin–spin interaction in glasses containing more Fe_2O_3 than in glass FV5, but this should lead to an increase in ΔH, which was not observed. However, a possibility of magnetic coupling, either between the Fe^{3+} ions or between the Fe^{2+} and Fe^{3+} ions, cannot be completely ruled out [37]. More detailed work is necessary in this system to obtain a better understanding of the different magnetic interactions.

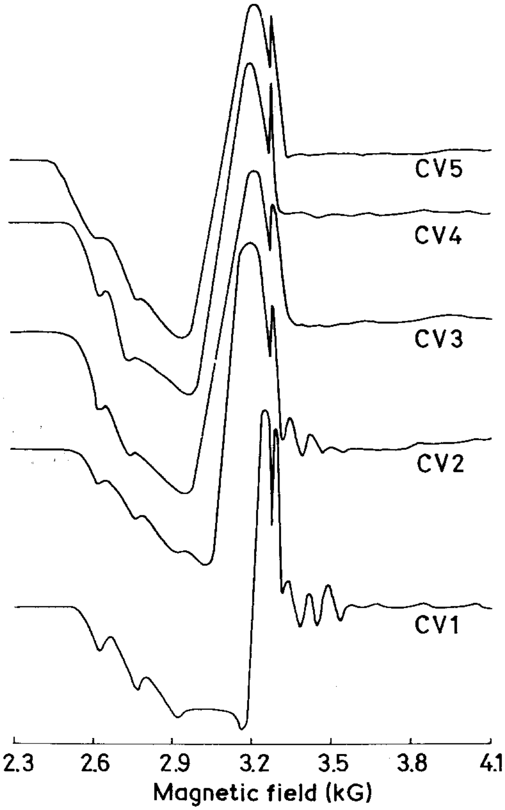

Figure 13 The ESR spectra due to V^{4+} and Cu^{2+} in mixed Cu–V glasses.

3.2.4.2. Copper–vanadium and copper–iron glasses. The ESR spectra for the first five Cu–V glasses are shown in Fig. 13. It is seen that the hyperfine structure components, presumably due to both V^{4+} and Cu^{2+} ions, are clearly observable in the first two glasses CV1 and CV2 and less clearly in the glasses CV3 to CV5. A central asymmetric resonance line was also observed for all nine glasses, presumably due to Cu^{2+} ions. This shows that Cu^{2+} ions are present in all mixed glasses; the V^{4+} ions are also present in at least these five mixed glasses. After CV5, the hyperfine structure disappears completely. From the observed spectra, it can be suggested that there is a considerable interaction taking place between Cu^{2+} and V^{4+} ions, simply because both these ions exhibit hyperfine spectra in the same region of the magnetic field. Therefore, there is a considerable overlap of the spectra due to both ions. An attempt to fit the spectra by Lorentzian analysis was not successful in separating the hyperfine components for the two ions.

However, by a comparison of the spectra of glasses CV1 and CV2 only with those of vanadium and copper glasses, some hyperfine lines due to V^{4+} were identified; only two parallel components due to Cu^{2+} could be identified in the observed spectra. The spin Hamiltonian parameters for both these ions were calculated according to the methods described in Sections 3.2.1 and 3.2.3. The values are given in Table II. The maximum error for the g-values was ± 0.012 and ± 2.5 for the $A_{\parallel}$ values for Cu^{2+} ions, and those for V^{4+} ions were ± 0.0015 and ± 0.9 respectively. In the case of Cu^{2+} ions, even considering the errors, it can be suggested that there is a decrease in distortion of the $Cu^{2+}O_6$ octahedra, as V_2O_5 is replaced by Cu_2O in glass 2V, compared to that in glasses containing only copper (see the g-values in Table II).

By comparing the g-values for the V^{4+} ions, it is seen from Table II that the tetragonal distortion of the $V^{4+}O_6$ octahedra in glasses CV1 and CV2 is much less compared with that in glass 2V. The values of $(1-\gamma^2)$ and $(1-\alpha^2)$ show that the covalency of the vanadium–oxygen bond decreases when V_2O_5 is replaced by Cu_2O in glass 2V. However, the effect is relatively less in these glasses compared to that in Fe–V glasses.

The values of $A_{\perp}$ and $A_{\parallel}$ for both Cu^{2+} and V^{4+} ions show a steady decrease in the mixed glasses CV1 and CV2, compared with those in glasses containing only vanadium or copper; the values of $A'_{\perp}$ and $A'_{\parallel}$ for V^{4+} ions show a steady decrease. This implies a decrease in the interaction between electron and nuclear spin moments with increasing Cu_2O content. Therefore, the progressive disappearance of the hyperfine structure could be interpreted as due to a process of nuclear relaxation in the vanadium nucleus and possibly in the copper nucleus as well.

This disappearance could be also due to spin diffusion within the vanadium spin system, as observed by the decrease of the intensities of the $m_I = \pm 7/2$ lines with increasing Cu_2O content. This process possibly takes place within the copper spin system as well, because the intensity of the $m_I = -3/2$ line was also found to decrease with increasing Cu_2O content in the mixed Cu–V glasses.

It is suggested that a considerable interaction takes place between the V^{4+} and Cu^{2+} ions facilitating the formation of V^{4+}–O–Cu^{2+} associates. The formation of the associates could be facilitated by the changes in covalency of both the $V^{4+}O_6$ and $Cu^{2+}O_6$ octahedra. These results along with those for the Fe–V mixed glasses give some support to the suggestions, made from our study of the absorption spectra, about the formation of different associates.

In the spectrum of glass CF5 (not shown) a very narrow resonance around $g = 4.3$ was observed due to Fe^{3+} ions, but no hyperfine structure was observed due to Cu^{2+} ions. However, an asymmetric central resonance due to Cu^{2+} ions was observed in the spectrum. The spectrum obtained suggests that there is also a considerable interaction between Cu^{2+} and Fe^{3+} ions in the copper–iron mixed glass. A more detailed work on this system is in progress.

4. Conclusion

The analysis of the optical absorption and ESR spectra of the mixed TM oxide glasses, in relation to those of the single TM oxide glasses, show the presence of all the possible valence states of two TM elements. In all the mixed glasses there is a considerable interaction between the TM ions present. It is suggested that there is a formation of different associates composed of two TM ions, one from each TM element, with one oxygen ligand. A more detailed spectroscopic study is necessary to elucidate the interaction between ions of different TM elements in the mixed TM oxide glasses with a wide variety of compositions, and consequently correlate with the electrical data, since the semiconducting behaviour of these glasses is very interesting.

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A recent Mössbauer experiment on mixed Fe–V glasses suggests that there is a pronounced structural change taking place with both the Fe^{2+} and Fe^{3+} ions when V_2O_5 is replaced by Fe_2O_3. The results will be published when the analysis is complete on the whole series of glasses.