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Electron spin resonance of transition metal ions in glasses†

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Abstract. Electron spin resonance (ESR) studies of transition metal ions in glasses have been briefly reviewed. The known relations of spin Hamiltonian parameters to structural geometries around the transition metal ion probes in glasses are summarized. Recent ESR studies in glasses based on the use of Ti^{3+}, VO^{2+}, Mo^{5+}, Cr^{3+}, Fe^{3+}, Mn^{2+} and Cu^{2+} have been emphasized. Merits of ESR in the context of structural elucidation have also been discussed.

Keywords. Electron spin resonance; transition metal ion probes; glass structure.

1. Introduction

It was thirty years ago that the first electron spin resonance (ESR) study of Cu^{2+} in soda-lime silica glasses was reported by Sands (1955). A number of important advances have been made since then and ESR has come to be used as a structural tool in the study of glasses. ESR of glasses is more complex than of crystalline powders because in addition to a distribution of 'crystallite' orientations there is an inherent distribution of crystal fields around the paramagnetic species in a glass. Such a distribution of crystal fields introduces additional breadth to the resonance absorptions due to a distribution in the values of magneto-gyric ratio g. A resonance absorption in glass is observed only if g is both isotropic and its value is somewhat insensitive to variations in the degree of distortions of local environments. A wealth of experimental data and their theoretical interpretation now available in literature suggest that g values satisfying the above conditions are quite possible in glasses. Application of ESR to the investigation of glass is essentially based on this finding.

A number of excellent reviews have been written on the subject of ESR in glasses. We particularly refer to those of Wong and Angell (1976) and Griscom (1980) which deal with all aspects of ESR in glasses in sufficient detail. The initial work on ESR of glasses was directed at investigating the magnetic behaviour of various ions in glassy matrices. In recent years studies have been directed more and more towards understanding the structure and nature of bonding in glasses. We feel that ESR of transition metal (TM) ions in glasses has been more promising in this direction. In this short review a modest effort has been made to present a summary of the recent trends in ESR of TM ions in glasses.

2. General principles

The degeneracy of energy states associated with unpaired electron spin is lifted by the application of magnetic field (Orton 1968; Abragam and Bleany 1970). In general a spin

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of value S ($S = \Sigma s_i$), has a degeneracy of $(2S+1)$ and the Zeeman field splits the manifold into $(2S+1)$ different levels. Transitions can then occur between these states by resonance absorption of energy when electromagnetic radiation of appropriate frequency is impressed upon the system. These transitions are governed by the selection rule, $\Delta m = \pm 1$, where m is the spin magnetic quantum number designating the allowed components of the spin orientation in the magnetic field. In general for an applied magnetic field of about 3000 G, transitions would occur in electron spin system for energy values in the region of a few thousand megahertz frequency. For the case of a single unpaired electron whose angular momentum is only due to the spin the Zeeman interaction gives rise to two spin states, $m = -1/2$ and $m = +1/2$, between which the transition occurs. The energy equation for such a transition is given by

$$h\nu = g_0 \beta H, \tag{1}$$

when H is the applied magnetic field, ν is the microwave frequency, β is the Böhr magneton and g_0 is the magnetogyric ratio for the spin-only case and its value is equal to 2·00234.

In general the situation is more complex. Since the electrons possess angular momentum owing to their orbital motion in addition to their spin angular momentum it often results in spin-orbit coupling. In such situation J ($J = L+S$) will be the relevent good quantum number and the Zeeman field splits the J manifold into various J states. Transitions are now governed by the selection rule $\Delta J = \pm 1$ and g_0 in equation (1) may be replaced by g_L

$$g_L = 1 + \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)}. \tag{2}$$

In rare earth ions where orbital angular momentum of inner d or f electron is not quenched (see later) by crystal fields due to the screening by outer electrons, equation (2) for g_L is found valid. Rare-earth ions generally conform to low-field description (Orton 1968). On the other hand crystal fields arising from neighbouring ions strongly perturb the orbital degeneracy of d electrons of TM ions as a result of which the orbital angular momentum is nearly quenched. The final spin states are therefore influenced to a far greater extent by crystal field than by the spin-orbit interaction. The situation arises in the so-called medium and strong crystal fields as in the case of TM ions in glasses.

The effect of the crystal field and the resulting ground state is shown in figure 1 schematically for the case of a d^1 ion (Ti^{3+} ion) placed in an octahedral coordination (Wong and Angell 1976). The d levels are first split into a triplet (t_{2g}) and a doublet (e_g). The electron occupies the orbital triplet which is at a lower energy. But the degeneracy of this triplet is further lifted by the well-known Jahn-Teller effect through a tetragonal distortion into a b_2 singlet ground state and a doublet e state (the upper doublet is also split into two singlet states, a_1 and b_1). The electron which now occupies the b_2 ground state has an effective orbital angular momentum, L' equal to zero. The situation for d^9 ion is exactly the same except that the ground state is a_1 instead of b_2. In case of d^3 ions the cubic splitting itself is enough to give a ground state whose L' is zero. For d^5 ions however the free ion ground state itself is an orbital singlet ($L' = 0$). On the other hand the TM ion with even number of electrons (like d^2, d^4, d^6 and d^8) generally do not give rise to orbital singlet ground states in the usual crystal field situations (Griscom 1980); the orbital angular momentum is not quenched. Therefore ESR of these ions is

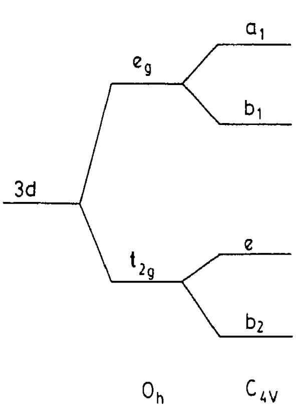

Figure 1. Energy level diagram for d^1 ion in octahedral and tetragonal crystal fields.

characterized by exceedingly short relaxation times and hence broad absorptions even at low temperatures. Usually these ions are of no interest in the ESP study of glasses.

However, we observe ESR resonance for d^1 and d^9 ions at g values slightly different from g_0. This is due to the spin-orbit coupling (Orton 1968). It arises from a small admixture of the ground state and the excited states with the same J values. In the Zeeman field such a spin-orbit coupling is represented by $\lambda\mathbf{L}\cdot\mathbf{S}$ (where λ is the spin-orbit coupling constant) and it gives rise to resonance at two principal g values (Pryce 1950):

$$g_{\parallel} = g_0\left[1-\frac{4\lambda}{\Delta E_{b_2\to b_1}}\right], \tag{3}$$

$$g_{\perp} = g_0\left[1-\frac{2\lambda}{\Delta E_{b_2\to e}}\right], \tag{4}$$

where $\Delta E_{b_2\to b_1}$ and $\Delta E_{b_2\to e}$ represents the energy difference between the levels b_2 and b_1 and b_1 and b_2 and e respectively.

In the case of d^3 and d^5 ions the spin-orbit coupling helps to lift the spin degeneracy of orbital-singlet ground state into two and three Kramers doublets respectively. Transitions between some of these levels give rise to resonances at g values very much different from g_0. This case is dealt with more clearly later in the formalism of spin Hamiltonian.

Further, the nucleus of the paramagnetic species may possess a nuclear spin I greater than zero which interacts with the electron spin giving rise to the well-known hyperfine splitting of resonance lines. Each resonance is split into $(2I+1)$ lines in such cases. The nuclear spin of neighbouring atoms can also couple with the spin-angular momentum of the unpaired electron which results in the so-called superhyperfine splitting. If the total spin of the neighbouring ions is I' the resonance is further split into $(2I'+1)$ lines.

All these situations may be analysed by employing a spin Hamiltonian in the framework of perturbative quantum mechanics. A general spin Hamiltonian (Griscom 1980) which takes care of all terms adequately is given as

$$\mathscr{H} = \beta\tilde{H}\cdot\tilde{\tilde{g}}\cdot\tilde{S}+\tilde{I}\cdot\tilde{\tilde{A}}\cdot\tilde{S}+\tilde{S}\cdot\tilde{\tilde{D}}\cdot\tilde{S} \tag{5}$$

The first term on the right side of (5) corresponds to the Zeeman term, the second term indicates the hyperfine interactions and the third term expresses the total effect of the crystal field. A is known as the hyperfine splitting constant and D is a crystal field parameter. g, A and D are tensor quantitites. In an actual calculation of the eigenvalues of the Hamiltonian by perturbation method a knowledge of the hierarchy of the magnitude of these terms is required. Since the term corresponding to hyperfine splitting is least in energy, it is the last term in the perturbation treatment. The explicit form of spin Hamiltonian appropriate for particular ions in various situations is given in later sections. The details of perturbative treatment of the Hamiltonian is also given for some cases.

In an actual experiment the frequency of the microwave energy is kept constant and the magnetic field is varied. The spectrum corresponds to a derivative of the microwave absorption as a function of magnetic field. The spectrum contains information about various ESR or spin Hamiltonian parameters. The knowledge of these parameters gives insights into the structure and bonding aspects of glasses. A complete knowledge of spin Hamiltonian parameters is obtained from simulating the spectral features by varying these parameters and fitting the simulated spectrum to the experimental one. The computer simulation of ESR spectra of TM ions in glasses has been reported by various workers (Taylor and Bray 1970; Kliava and Purans 1980; Bals and Kliava 1983).

In an ESR experiment variation of the microwave absorption is studied as a function of magnetic field. Most of the ESR studies reported for TM ions in glasses have been performed in the X-band (~ 9 GHz) frequency, except for a few low frequency measurements. In places where low frequency (S-band) measurements are quoted, we state that specifically.

3.1 *d^1 ions (Ti^{3+}, VO^{2+} and Mo^{5+})*

The ESR spectrum of d^1 ions in glasses can be described by the following axially symmetric spin Hamiltonian:

$$H = g_{\parallel} H_z S'_z + g_{\perp}(H_x S'_x + H_y S'_y) + A_{\parallel} I_z S'_z + A_{\perp}(I_x S'_x + I_y S'_y), \tag{6}$$

where the parallel and perpendicular signs indicate the corresponding components of the parameters. $S' = 1/2$ and $I = 0$ for ^{48}Ti and 7/2 for ^{57}V. g values are given by (3) and (4). The derivation of these equations is based on pure electric field effects of the surrounding ions and the spin-orbit coupling effects. The covalency effects had not been considered. If the covalency effects are also included, Kivelson and Lee (1964) have shown that (3) and (4) become

$$g_{\parallel} = g_0 \left[1 - \frac{4\alpha^2 \beta^2 \lambda}{E_{b_2 \to b_1}} \right], \tag{7}$$

$$g_{\perp} = g_0 \left[1 - \frac{\delta^2 \beta^2 \lambda}{E_{b_2 \to e}} \right], \tag{8}$$

$$A_{\parallel} = -P[\beta^2(\tfrac{4}{7} + \kappa) + \Delta g_{\parallel} + \tfrac{3}{7}\Delta g_{\perp}], \tag{9}$$

$$A_{\perp} = P[\beta^2(\tfrac{2}{7} - \kappa) + \tfrac{11}{4}\Delta g_{\perp}], \tag{10}$$

where α^2, β^2 and δ^2 are measures of in-plane σ bonding, in-plane π bonding and out-of-plane bonding respectively. Slight variations in (7) to (10) have been given by various workers for various d^1 ions. We shall point out these differences at appropriate places.

3.1a *Ti^{3+}*: Yafaev and Yoblokov (1962) and Garif'yanov and Tokareva (1964) were the first to study ESR of Ti^{3+} in alkali silicate and phosphate glasses. They observed resonances with g varying from 1·92–1·94. These spectra are characterized by short spin-lattice relaxation times and large negative g shifts ($g < g_0$) attributable to small trigonal field splitting of low lying orbital triplet resulting from the predominantly octahedral field. This is the reason why ESR of Ti^{3+} in many systems is not observable at room temperature. Peterson and Kurkjian (1972) studied the low frequency (0·5 GHz) ESR of calcium borate glasses containing ^{47}Ti ($I = 5/2$) and ^{49}Ti ($I = 7/2$) which substituted for the natural ^{48}Ti ($I = 0$) and conclusively assigned the resonance to Ti^{3+}. They could observe hyperfine splitting in 0·5 GHz measurements (S-band) which they showed is due to the fact that linewidths at low frequencies become narrower (figure 2).

Kurkjian and Peterson (1974) later applied ESR of Ti^{3+} to the study of Ti^{3+}–Ti^{4+} equilibrium in TiO_2-SiO_2 glasses at low frequencies (S-band). They found that Ti^{3+} concentration increases with the partial pressure of hydrogen and temperature. The kinetics of oxidation and reduction has been found to be governed by the rapid outward and inward diffusion of hydrogen molecules. These authors have also pointed out that Ti^{4+} ions in six-fold coordination only are reduced by hydrogen which results in six coordinated Ti^{3+} ions in the melt. Ti^{4+} ions most of which are present in 4-fold coordination are difficult to reduce, Iwamoto *et al* (1983b) have studied Ti^{3+}–Ti^{4+} reaction in reduced sodium silicate glasses and found that Ti^{3+} ions are coordinated preferentially to nonbridged oxygens. They also suggest that $[Ti^{3+}O_4^- O_2^-]$ and $[Ti^{3+}O_3^- O_3^{2-}]$ complex ions are most probable in the reduced sodium silicate glasses.

3.1b *VO^{2+}*: Several ESR investigations of ESR glasses reported in literature are based on the use of V^{4+} ion. ESR spectrum of V^{4+} is rich in hyperfine structure due to the ^{51}V nucleus ($I = 7/2$) and can be easily observed at room temperature. A typical spectrum is given in figure 3. The axially symmetric spin Hamiltonian given in (6) which is appropriate for V^{4+} ions was analysed first by Hochstrasser (1966) and Hecht and Johnson (1967). They independently reached the conclusion that V^{4+} ion in glasses is present as vanadyl, VO^{2+} ion. Many researchers (Toyuki and Akagi 1972; Bogomolova

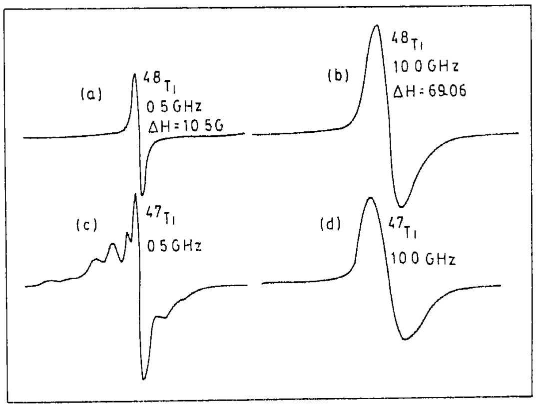

Figure 2. ESR spectra of $30CaO \cdot 69B_2O_3 \cdot 1TiO_2$ glass. (**a**) and (**c**) were obtained at 0·5 GHz and (**b**) and (**d**) at 10 GHz. The samples of (**c**) and (**d**) were enriched to 75 % ^{47}Ti (after Peterson and Kurkjian 1972).

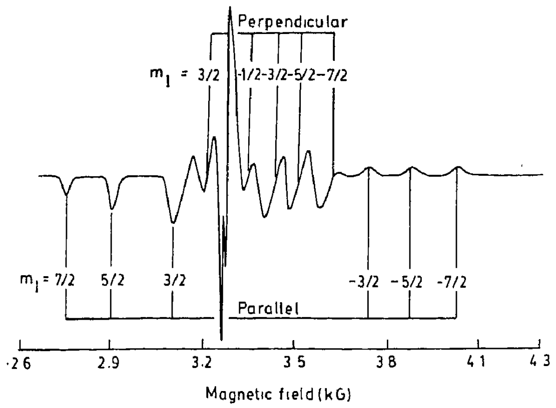

Figure 3. A typical ESR spectrum of VO^{2+} in a vanadium glass. Both parallel and perpendicular components of hyperfine structure are well resolved (after Bandyopadhyay 1981).

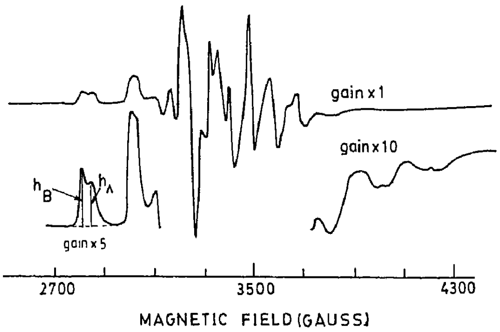

Figure 4. Representative ESR spectrum of VO^{2+} in $63BeO\text{-}37P_2O_5$ glass showing two sets of hyperfine structure (after Hosono *et al* 1980).

et al 1974; Paul and Assabghy 1975; Momo *et al* 1981b; Bandyopadhyay 1981; Seth *et al* 1983; Bogomolova *et al* 1983b) employed ESR of VO^{2+} to study the structure of glasses. Recently structural anomaly of phosphate glasses has been investigated in great detail. Bogomolova *et al* (1978a) studied $RO\text{-}B_2O_3$ glasses (R = Mg, Ca, Sr, Ba, Pb, Zn) and found two sets of hyperfine structure (HFS-A and HFS-B) in $MgO\text{-}P_2O_5$ and $ZnO\text{-}P_2O_5$ systems and one set of hyperfine structure (HFS-A) for other systems. They concluded that the coexistence of two kinds of local structures is the origin of the anomalous ESR spectra of $MgO\text{-}P_2O_5$ and $ZnO\text{-}P_2O_5$ glasses (Kordes *et al* 1953). Hosono *et al* (1980) made a detailed analysis of the ESR of VO^{2+} in $RO\text{-}P_2O_5$ and $R'_2O\text{-}P_2O_5$ glasses (R = Bi, Mg, Sr, Ba, Ca, Ni, Pb, Zn, Cd and R′ = Li, Na, Cs, Ag). A spectrum showing two sets of hfs is shown in figure 4. They found a correlation between the ionic potential (Z/R) of network modifiers and the appearance of two hyperfine structures. Their results are summarized in figure 5. Though it was shown that the super-position of two hyperfine structures was observed only for systems with network modifiers whose $Z/R \geqslant 2$, this study has not satisfactorily explained the anomaly.

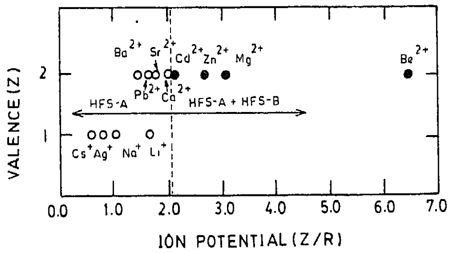

Figure 5. Correlation between the ionic potential of the network modifier and the appearance of the two sets of hyperfine structure, HFS-A and HFS-B in the ESR of VO^{2+} incorporated into metaphosphate glasses (after Hosono *et al* 1980).

Bogomolova *et al* (1983b) in another study of VO^{2+} in binary Al_2O_3-P_2O_5 and SiO_2-P_2O_5 glasses and ternary Al_2O_3-P_2O_5-SiO_2 and Al_2O_3-P_2O_5-B_2O_3 glasses have shown that the behaviour of ESR spectra is even more complex. Though they found two kinds of hyperfine structure for aluminophosphate glasses ($Z/R \simeq 5/2$ for Al^{3+}) in accordance with Hosono's correlation, only HFS-B has been observed for silicophosphate glasses ($Z/R \simeq 10$ for Si^{4+}). However these authors have found an excellent agreement of the ESR parameters of V^{4+} ions in crystalline $AlPO_4$ and SiP_2O_7 powders with those of HFS-B spectrum from aluminophosphate, alumino-silico-phosphate and alumino-boro-phosphate glasses. It has been suggested that the electronic structure of paramagnetic species responsible for HFS-B spectrum in glasses acts as modifiers and are situated in relatively small holes of three-dimensional phosphate networks.

In another interesting application of ESR of VO^{2+}, Sunandana and Bhatnagar (1984) studied hopping conduction in V_2O_5-MO_2 glasses (M = Ge, Se, Te). They have examined the spectra in the temperature range 298–498 K and observed dramatic and reversible temperature dependences by way of progressive broadening and eventual disappearance of the hyperfine structure. This behaviour has been attributed to a thermally activated delocalization of the $3d^1$ electron spin leading to hopping electronic conduction. They have also found that covalency of the V-O bond increases from GeO_2 to TeO_2 to SeO_2.

3.1c *Mo^{5+}*: Garif'yanov and Fedotov (1963) were the first to report ESR of Mo^{5+} ions in borate and phosphate glasses. They studied temperature and frequency dependence of the Mo^{5+} spectra. A typical spectrum is given in figure 6. Baugher and Parke (1972) studied ESR of Mo^{5+} in phosphate glasses and analysed the spectra using the spin Hamiltonian given in (6). They found that coordination of Mo^{5+} ion is highly distorted from octahedral symmetry. They suggested that Mo^{5+} is present as a molybdenyl ion, MoO^{3+} in phosphate glasses. However, in a recent study of B_2O_3-Na_2O-MoO_3 glasses, Simon and Nicula (1983) suggest three different site symmetries (cubic, axial and rhombic) for Mo^{5+} from their analysis of resonance lineshapes. They have also investigated the effect of composition, MoO_3 concentration and preparation temperature on the ESR spectra. Increasing Na_2O content has the effect of altering the 4-coordinated borons which in turn affect the concentration of Mo^{5+} ions in various symmetries. The effect of holding time of the melt on the equilibrium concentration of Mo^{5+} which may reduce further to Mo^{4+} has also been studied. It was suggested that ESR of Mo^{5+} is a good probe to study the structure of borate glasses.

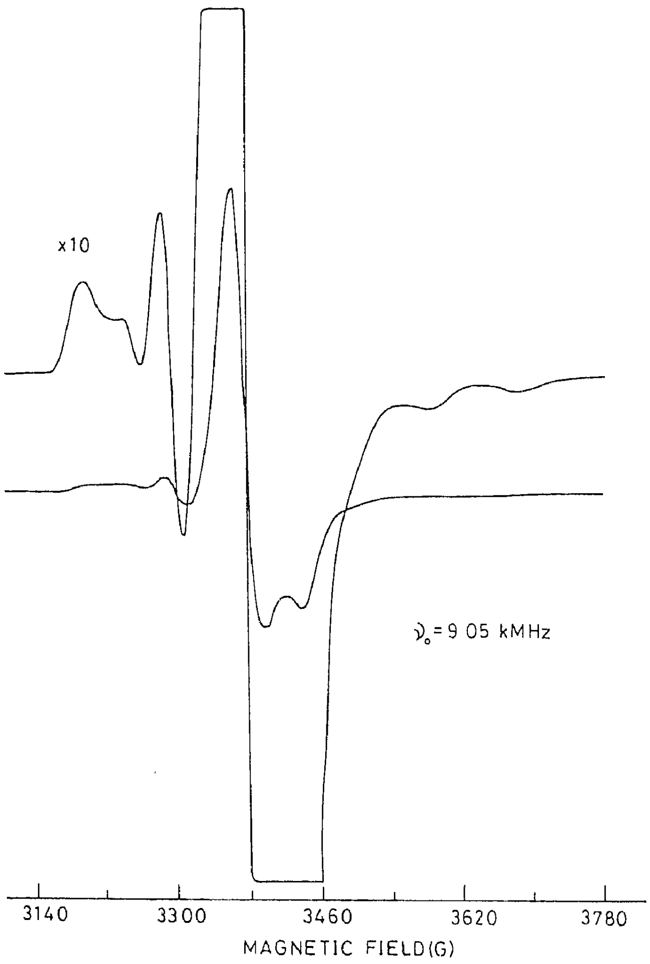

Figure 6. A typical ESR spectrum of Mo^{5+} in a potassium phosphomolybdate glass (after Selvaraj and Rao 1985).

Sperlich (1973) studied the hyperfine structure of MoO_3-TeO_2 and MoO_3-P_2O_5 glasses enriched with ^{95}Mo isotope. They found that *d*-electron is mainly localized on one molybdenum site. The transfer rate of the *d*-electron (hopping frequency) is lower than the hyperfine splitting in frequency units even at room temperature. ESR of Mo^{5+} has also been used to estimate Mo^{5+}/Mo_{total} in MoO_3-containing glasses (Patel and Bridge 1983; Selvaraj and Rao 1985).

There have been few reports on the ESR of Cr^{5+} ions. These results are discussed along with the spectra of Cr^{3+}. However, no significant ESR spectra of W^{5+} ions (see Wong and Angell 1976 for earlier reports) have appeared in recent times.

3.2 d^3 (Cr^{3+}) and d^5 (Fe^{3+} and Mn^{2+}) ions

We noted earlier that the degeneracy of odd electron TM ions is partially lifted by the crystal field giving rise to Kramers doublets. Application of the Zeeman field splits the spin degeneracy of the Kramers' doublets. As the crystal field splitting is normally much greater than the Zeeman energy in glasses, resonances are observed due to transition within the Zeeman-split Kramers doublet. The spin Hamiltonian (Bleaney and Stevens 1953) employed for these ions is given below:

$$\mathscr{H} = g_0 \beta H + D[S_z^2 + \tfrac{1}{3}S(S+1)] + E(S_x^2 - S_y^2), \tag{11}$$

where D and E are the crystal field parameters representing axial and rhombic distortions respectively. It may be seen that the crystal field effects enter as second order terms in spin quantum number. Castner *et al* (1960) were the first to apply the above spin Hamiltonian successfully to explain the ESR spectra of Fe^{3+} (d^5) ions in glasses. In this classic work they assumed the primacy of the crystal field terms and treated Zeeman term as a perturbation. It is clear from the Hamiltonian in (11) that by dropping all terms other than DS_z^2, *i.e.*, by switching on the axial crystal field, the degeneracy is lifted giving rise to $\pm m$; $\pm(m-1)\ldots\pm\frac{1}{2}$ states for the odd electron TM ions. This accounts for the resulting Kramers doublets. The two crystal field parameters D and E can be combined into a single parameter by taking the ratio $E/D = \lambda$ (not to be confused with spin-orbit coupling constant). The spin Hamiltonian can then be analysed with the limiting values of λ. It has been shown (Wickman *et al* 1965) that $\lambda = 0$ to $\frac{1}{3}$ covers practically all significant crystal field situations arising in solids from fully axial ($\lambda = 0$) to fully rhombic ($\lambda = \frac{1}{3}$) symmetry. For these extreme values of λ, g values for which resonances occur for d^3 and d^5 ions are summarized below:

	$\lambda = 0$	$\lambda = \frac{1}{3}$
d^3	$g_\parallel = 2$ $g_\perp = 5$	—
d^5	$g_\parallel = 2$ $g_\perp = 6$	$g_{\text{eff}} = 4{\cdot}3$

It is significant that in the case of d^5 ions $g_{\text{eff}} = 4{\cdot}3$ resonance observed for rhombic symmetry has been found to be remarkably isotropic. The actual variation of the individual g_x, g_y and g_z for d^5 ions as a function of λ (Wickman *et al* 1965) is shown in figure 7.

3.2a *Cr^{3+}*: Though the ESR of Cr^{3+}, a d^3 ion, has not been widely studied in glasses, few interesting studies have been reported recently. A typical spectrum is given in figure 8. The spin Hamiltonian given in (11) was first analysed for Cr^{3+} by Garif'yanov and Zaripov (1964) and later more exactly by Zakharov and Yudin (1965). The latter authors had shown that the transitions in the two Kramers doublets yield two resonances at $g_\perp = 5{\cdot}0$ and $g_\parallel = 1{\cdot}77$ in agreement with their experimental results. Recently Fuxi *et al* (1982) have pointed out that the transitions can occur not only within the Kramers doublets but also between the levels in different Kramers doublets.

Landry *et al* (1967) noted that as the concentration of chromium increases, the resonance at $g \simeq 2{\cdot}0$ becomes more dominant. This feature was attributed to exchange-coupled Cr^{3+} ion pairs. The low field feature (at $g \simeq 5{\cdot}0$), which reduces in intensity as the concentration of chromium increases, was attributed to isolated, octahedrally coordinated Cr^{3+} ions. Recently Ardelean *et al* (1984) have investigated the concentra-

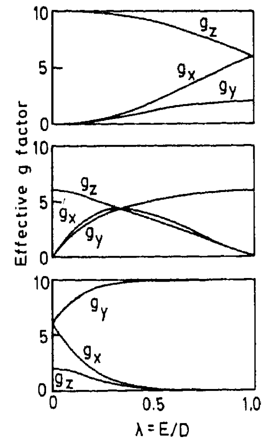

Figure 7. The effective g values for the spin Hamiltonian given in equation (11) plotted against $\lambda = E/D$ (after Wickman *et al* 1965).

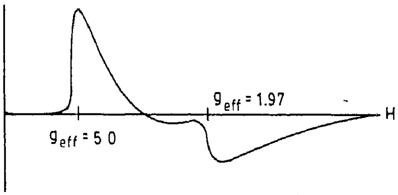

Figure 8. ESR spectrum of Cr^{3+} in alumino-zinc phosphate glass containing 0·57 wt % Cr_2O_3 (after Landry *et al* 1967).

tion dependence of spectrum in $xCr_2O_3 \cdot (1-x)[3B_2O_3\text{-}PbO]$ glass and found a similar behaviour. However they found evidence for the presence of both Cr^{3+} and Cr^{5+} in glasses. Cr^{5+} ions which are in small proportion produce resonance at $g = 1{\cdot}98$. This resonance is superimposed upon another resonance at $g = 1{\cdot}97$ due to exchange coupled Cr^{3+} ion pairs. Earlier, Iwamoto and Makino (1980) investigated the state of chromium ions in soda-silicate glasses under various oxygen pressures. In glasses produced in air or under moderately reducing conditions, three ESR absorptions were observed near $g = 2{\cdot}0$ (sharp), $g = 2{\cdot}0$ (broad) and $g = 5{\cdot}0$. These three absorptions were assigned to isolated Cr^{5+} ions, strongly coupled Cr^{3+} ion pairs and isolated Cr^{3+} ions in orthorhombic crystal field respectively. An absorption attributable to weakly coupled Cr^{3+} ion pairs was observed near $g = 2{\cdot}3$ in glasses produced in reducing atmosphere.

In an interesting application of ESR of Cr^{3+} ions Zhilinskaya *et al* (1983) investigated the effect of pressure treatment, temperature and annealing on the structure of chalcogenide glasses. They found that the ESR parameters of Cr^{3+} impurity ions in AS_2Se_3 glass and $5Cu95As_2Se_3$ glass varied considerably by the application of pressure. The variations have been attributed to pressure-induced structural changes which affect locally the crystal field splitting of Cr^{3+} energy levels. However, these pressure-induced effects could be annealed out at the glass transition temperatures. The ionic state of copper and its contributions to the observed ESR spectra have not been clearly discussed. In another interesting study Bruckner *et al* (1980) have employed the ESR of Cr^{3+} to investigate structural anisotropies in silicate glass fibres. They have found that the short-range order of Cr^{3+} ion is identical in nature both in bulk and fibre glasses. The Cr–O bonding in CrO^{3+} is less covalent in the fibre than in the bulk glass. It was also found to be orientation-dependent. In another study of Cr^{3+} in phosphate, fluorophosphate and fluoride glasses, Fuxi *et al* (1982) found g values to be highest in phosphate and lowest in fluoride glasses. Such an observation is in agreement with the fact that the ionicity of Cr–O bond is lowest in phosphate and highest in fluoride glasses.

3.2b *Fe^{3+}*: The ESR spectrum of Fe^{3+} in glasses is characterized by a sharp, well-defined resonance at $g = 4{\cdot}3$ and relatively weak resonances at $g = 2$, 6 and 10. A typical spectrum is shown in figure 9. As stated earlier in this section, the features of ESR spectrum of Fe^{3+} in glasses were successfully explained by Castner *et al* (1960) by using the spin Hamiltonian given in (11). These authors associated the $g = 4{\cdot}3$ resonance with Fe^{3+} in a network-forming (tetrahedral) site. However, it was shown by Loveridge and Parke (1971) that this resonance can be produced by rhombic symmetry of either octahedral or tetrahedral coordination of Fe^{3+}. These authors have described different possible coordination environments associated with resonances at $g = 2$, 4·3 and 6. The $g = 2{\cdot}0$ resonance can be caused by both axiality of the crystal field and spin-spin interaction. The spin-spin interaction appears to be the primary cause of $g = 2{\cdot}0$ resonance in glasses containing higher concentration of Fe^{3+} ions (Kurkjian and Sigety 1968; Moon *et al* 1975). Peterson *et al* (1974) have argued that $g = 4{\cdot}3$ resonance of Fe^{3+} can also result from a large spread of $g_\perp$ (6·0) and $g_\parallel$ (2.0) resonances along with a substantial negative correlation. This suggestion is repudiated in the work of Momo *et al* (1981a) who showed that the $g = 4{\cdot}3$ resonance is due to Fe^{3+} ions in rhombic sites in their studies of selected silicate glasses.

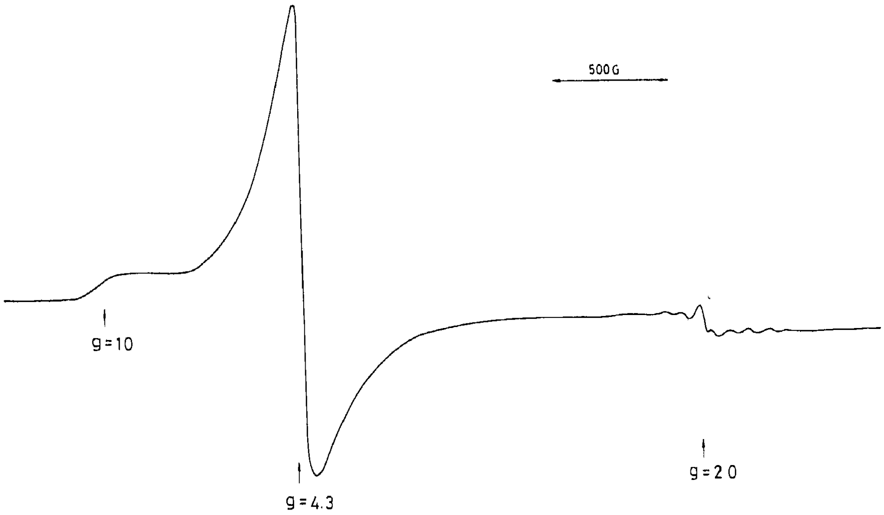

Figure 9. ESR spectrum of Fe^{3+} in PbO-PbF$_2$ glass (after Rao and Rao 1985).

The spectral features are essentially similar for silicate, borate and phosphate glasses and their variation with Fe^{3+} ion concentration is also similar (Kurkjian and Sigety 1968; Wong and Angell 1976). It has been reported that in $Na_2O \cdot B_2O_3$ glasses the features (width and intensity) of $g = 4{\cdot}3$ resonance are affected very little by the variation of Na_2O content (Loveridge and Parke 1971). However, Danielson and Schreurs (1980) have found changes in line shape and intensity of $g = 4{\cdot}3$ resonance with composition in $x\text{MO} \cdot y\ Al_2O_3 \cdot z\ SiO_2$ glass containing 0·1 mol% Fe_2O_3 (M = Ca, Sr, Ba, Mg). The effect is most pronounced in Ba and Sr glasses, less so in Ca glass and quite small in Mg glass. They attributed this behaviour to change in coordination from four-fold to six-fold for Fe^{3+} ion without sufficiently corroborative evidence for such an assignment. Iwamoto *et al* (1983a) recently have investigated the state of Fe^{3+} ion and Fe^{3+}-F^- interaction in $xCaF_2 \cdot (1-x)CaO \cdot SiO_2$ $(0 \leqslant x \leqslant 0{\cdot}3)$ glasses by ESR. Two resonances were observed near $g = 2{\cdot}0$ and $g = 4{\cdot}3$ which were assigned to Fe^{3+} ions with dipole-dipole interactions and isolated Fe^{3+} ions in rhombic symmetry, respectively. The relative magnitude of Fe^{3+} centres giving rise to dipole-dipole interaction depended on CaF_2 content and it exhibited a maximum at 10 mol% of CaF_2. Iwamoto *et al* (1983a) discussed this behaviour in the light of 1*s* binding energy of and negative partial charge on fluorine; the latter quantities behave in a similar way with composition. A similar composition dependence of line intensity of $g = 2{\cdot}0$ resonance has been found in BaO-B_2O_3 glasses (Kishore *et al* 1984). The intensity of $g = 2{\cdot}0$ resonances shows a maximum at 40 mol% BaO while the intensity of $g = 4{\cdot}3$ resonance shows a minimum at the same composition. This anomalous composition dependence of intensities has however not been clearly understood.

We have investigated ESR of Fe^{3+} in lead oxide-lead halide glasses (Rao and Rao 1985). The spectral features are quite drastically affected by composition in PbO-$PbCl_2$ glasses. In $PbCl_2$-rich composition $g = 6{\cdot}0$ resonance has been observed in addition to $g = 4{\cdot}3$ resonance. The intensity of $g = 6.0$ resonance increases and the intensity of $g = 4{\cdot}3$ resonance decreases with increasing $PbCl_2$ content suggesting that more (axially) symmetric sites are available for Fe^{3+} in $PbCl_2$-rich glasses. However, the spectra of PbO-PbF_2 glasses do not show such composition dependence. This difference between the two glass systems can be attributed to the difference in sizes of chloride and fluoride ions as also the tendency of fluorine to enter network positions.

Komatsu and Soga (1980) studied the crystallization process of sodium-iron-silicate glass and found that the $g = 4{\cdot}3$ resonance disappears and $g = 2{\cdot}0$ resonance sharpens in the process of crystallization. They attributed this behaviour to the removal of distortions and randomness in the environment of Fe^{3+} ions during crystallization. Baiocchi *et al* (1980) who studied the high temperature ESR of Fe^{3+} in lead silicate glass also observed the disappearance of $g = 4{\cdot}3$ resonance and narrowing of $g = 2{\cdot}0$ resonance at high temperature. However, these authors have attributed the narrowing of $g = 2{\cdot}0$ resonance to diffusion of Fe^{3+} ions in the glass as diffusion causes narrowing due to reduction of dipolar broadening.

The clustering tendency of Fe^{3+} ions in $2OFe_2O_3[3B_2O_3\ (1-x)PbOxGeO_2]$ glasses has been reported by Burzo *et al* (1980). At high temperatures of equilibration isolated Fe^{3+} ion sites appear to be favoured. But with increasing GeO_2 in the glass (which increases oxygen concentration) there appears a maximum in $g = 4{\cdot}3$ resonance as a function of x. This is perhaps due to larger distortion of tetrahedra in intermediate compositions.

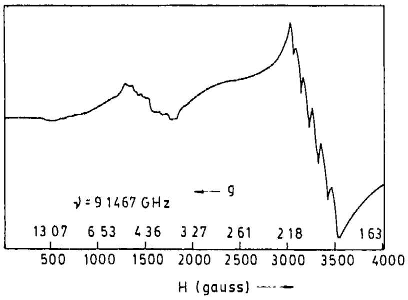

Figure 10. A typical ESR spectrum of Mn^{2+} in a silicate glass (Schreurs 1978).

3.2c *Mn^{2+}*: The ESR spectrum of Mn^{2+} in oxide glasses are characterized by an intense resonance at $g = 2{\cdot}0$ with hyperfine structure, an absorption at $g = 4{\cdot}3$ and a distinct shoulder at $g = 3{\cdot}3$. In chalcogenide glasses the spectra are qualitatively similar to those of oxide glasses though the relative intensity of $g = 4{\cdot}3$ resonance is greatly enhanced in some systems (Wong and Angell 1976). A typical spectrum of Mn^{2+} in an oxide glass is given in figure 10. Although Mn^{2+} shares the same $3d^5$ $(^6S_{5/2})$ electronic structure as Fe^{3+}, its ESR spectra are generally quite different, firstly due to the addition of hyperfine structure ($I = 5/2$ for ^{55}Mn) and secondly due to generally much smaller crystal field splittings. Spin Hamiltonian which includes hyperfine interaction also is appropriate for this case:

$$\mathscr{H} = g\beta H\,.\,S + D[S_z^2 - \tfrac{1}{3}S(S+1)] + E(S_x^2 - S_y^2) + A.S.I. \tag{12}$$

On the basis of the treatment of the spin Hamiltonian by Castner *et al* (1960) for Fe^{3+}, Tucker (1962) suggested existence of two distinct sites: one with large E value (rhombic case) giving rise to $g = 4{\cdot}3$ resonance and the other with both D and E very much less than Zeeman energy giving rise to predominant resonance at $g = 2{\cdot}0$. de Wijn and van Balderen (1967) and Griscom and Griscom (1967) were the first to attempt a detailed explanation of the ESR spectron of Mn^{2+} in oxide glasses in terms of the spin Hamiltonian parameters. Griscom and Griscom (1967) suggested that the Mn^{2+} sites in alkali borate glasses are characterized by $(E/D) \sim 1/3$ and $(D)/h \sim 2$ GHz. Further they suggested that a broad distribution of sites with different D and E values with a probable constraint of $E/D \sim 1/3$ is present in these glasses. A transition can be observed only if the resonance energy is stationary with respect to variations in D and E. Similar conclusions were drawn by Taylor and Bray (1972) from their study of ESR of Mn^{2+} in strontium borate (crystalline and glassy).

The magnitude of the hyperfine splitting constant A provides a measure of covalency between Mn^{2+} ion and its ligands. Van Wieringen (1955) empirically determined a positive correlation between A and ionicity of the manganese-ligand bond. On this basis it was found that Mn^{2+} is quite ionic in alkali borate and phosphate glasses ($A = 92$ G) and less ionic in silicate glasses ($A = 86$–88 G) (Schreurs 1978; de Wijn and van Balderen 1967). We have investigated ESR spectra of Mn^{2+} in K_2SO_4-$ZnSO_4$ glasses (Sundar and Rao 1982) and lead oxide-lead halide glasses (Rao and Rao 1985) and found that Mn^{2+} is highly ionic in sulphate glasses ($A = 92$G) and less ionic in lead oxide-lead halide glasses ($A = 82$G). However, we find a slight variation in ionicity of

Mn^{2+} in the latter glasses with composition. Griscom and Griscom (1967) correlated variation of relative intensity of a hyperfine line of $g = 2{\cdot}0$ resonance with a change in network of borate glasses with alkali oxide concentration.

The hyperfine structure at $g = 4{\cdot}3$ resonance in chalcogenides is well resolved although it is complicated by additional structure. This feature has been employed in the study of structural aspects of chalcogenide glasses (Watanabe *et al* 1976; Kumeda *et al* 1978; Zhilianskaya *et al* 1980; Durney 1980; Kaitai *et al* 1983; Barnier *et al* 1983). The hyperfine splitting constants of Mn^{2+} in chalcogenides are very low ($A = 60$–65G) suggesting that Mn^{2+} is very strongly covalently bonded in these glasses. It was also suggested (Watanabe *et al* 1976) that $g = 4{\cdot}3$ resonance arises from the Mn^{2+} ions incorporated into the network. It is generally believed that Mn^{2+} is four-coordinated in chalcogenide glasses except in $GaS_{3/2}$-GeS_2-MnS glass (where the value of hyperfine splitting constant is slightly higher $A = 71$ G) in which Mn^{2+} has been shown to be six-coordinated by UV-visible spectroscopy (Barnier *et al* 1983). Kumeda *et al* (1978) investigated the structural changes in chalcogenide glasses by monitoring the hyperfine structure of the resonance at $g = 4{\cdot}3$ induced by various processes such as annealing, illumination or application of high pressure. These processes cause a change of lineshape of the hyperfine structure and also hyperfine splitting constant both of which reflect the bonding characteristics around manganese. From these studies it has been concluded that the randomness of amorphous structure decreases by annealing and increases by illumination or application of pressure. Additional hyperfine structure at $g = 4{\cdot}3$ resonance has been the subject of study of many investigations (Lazukin *et al* 1975; Chepeleva *et al* 1977; Schreurs 1978; Zhilinskaya and Lazukin 1982). Lazukin *et al* (1975) interpreted the double hyperfine structure at $g = 4{\cdot}3$ in chalcogenide glasses as the superposition of two unequal sextets with a shift in the isotropic g factor ($\Delta g \simeq 0{\cdot}08$). Schreurs (1978) found superposition of these different hyperfine structures with $\Delta g \simeq 0{\cdot}024$. However, these explanations are not unique. Zhilinskaya and Lazukin (1982) attribute the additional hyperfine structure to the forbidden hyperfine transitions.

In glasses containing PbO such as PbO-SiO_2, PbO-TeO_2 and PbO-$PbCl_2$ (Bogomolova *et al* 1978; Ardelean *et al* 1980; Rao and Rao 1985), $g = 4{\cdot}3$ resonance has been found to be quite intense and a single set of hyperfine structure is well resolved, particularly in PbO-rich compositions. Rao and Rao (1985) propose that Mn^{2+} occupies network positions with a coordination polyhedra of the type, $[MnO_2Cl_4]$ in PbO-$PbCl_2$ glasses. The spectral features (particularly at $g = 2{\cdot}0$) which are drastically affected by composition, are explained by the structural model for these glasses. It was also found that the spectra of Mn^{2+} in PbO-PbF_2 glasses are quite similar to those of oxide glasses (absence of intense, well-resolved $g = 4{\cdot}3$ resonance) whereas the spectra for PbO-$PbCl_2$ glasses are similar to those of chalcogenide glasses. These differences have been attributed to differences in the role of fluorine and chlorine in glasses (as pointed out earlier in the study of Fe^{3+}).

The most important development in this field probably is the application of superposition model analysis of ESR spectra to determine distortions around d^5 ions in glasses. This method was first proposed by Newman (1971) and applied to glasses by Brodbeck and Bukrey (1981) and Kliava (1982). Brodbeck and Bukrey (1981) found from their analysis that a wide range in the magnitude of the crystal field parameters satisfy the condition for the appearance of $g = 4{\cdot}3$ resonance in Fe^{3+} while the range is much smaller in the case of Mn^{2+} ions. Hence they show that in general the intensity of $g = 4{\cdot}3$ resonance as compared to that at $g = 2{\cdot}0$ must be considerably higher for Fe^{3+}

ions than for Mn^{2+} ions. They have also shown that the resonance at $g = 4{\cdot}3$ observed in the X-band should be absent in the Q-band as indeed the case. Kliava (1982) employed a gaussian probability density function for variations in D and E in making use of the superposition model. He has shown that D_0/E_0 being equal to 3 and not (D/E) is the rigorous constraint for observing $g = 4{\cdot}3$ resonance for d^5 ions (D_0 and E_0 are the mean values of D and E respectively). It has also been argued that the distribution functions for the crystal field parameters required for $g = 2{\cdot}0$ and $g = 4{\cdot}3$ resonances have negligible overlap. Hence Kliava (1982) supports the earlier conjecture of Tucker (1962) that two dominant resonances observed in Mn^{2+} ESR may be associated with different sites even though it is admitted that demarcation of network former and network-modifier sites is difficult. Nevertheless, it would be possible to assign tentatively such positions in combination with the values of hyperfine splitting constant which are generally lower for tetrahedrally coordinated (network former) Mn^{2+} ions.

3.2d *Cu^{2+}*: ESR of Cu^{2+} in glasses was studied first by Sands (1955) in soda-lime-silicate glasses and later by Hecht (1968) in soda-boric oxide glasses and Imagawa (1968) in sodium and lithium glasses. A typical ESR spectrum of Cu^{2+} is given in figure 11. The spectra of Cu^{2+} in glasses are characterized by two principal resonances ($g_{\parallel} \simeq 2{\cdot}32$ and $g_{\perp} \simeq 2{\cdot}06$) with four-line hyperfine splitting (due to ^{65}Cu and ^{63}Cu, $I = 3/2$). A spin Hamiltonian given for d^1 ions in (6) can be used for d^9 ion also. Iwagawa's (1968) treatment of the spin Hamiltonian provides the two principal values of g involving covalency parameters and spin-orbit coupling;

$$g = g_0\left[1 - \frac{4\alpha^2\beta_1^2\lambda}{\Delta}\right], \tag{13}$$

$$g = g_0\left[1 - \frac{\alpha^2\lambda}{\Delta}\right], \tag{14}$$

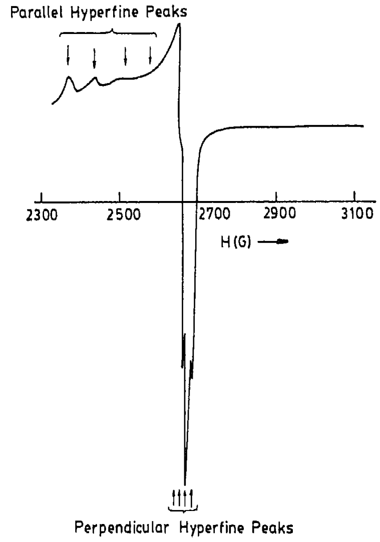

Figure 11. ESR spectrum of Cu^{2+} in a commercial ruby glass. Both parallel and perpendicular components of hyperfine structure are well resolved (after Duran *et al* 1984).

where Δ and λ are the crystal field splitting energy and spin-orbit coupling constant respectively. $(1-\alpha^2)$ represents the degree of covalency of the (in-plane) σ-bonding while $(1-\beta_1^2)$ represents the covalency of (out-of plane) π-bonding between Cu^{2+} and the ligands.

The environment of Cu^{2+} in glass is tetragonally distorted octahedron (axially elongated, D_{4h} symmetry). For such distortions $g_{\parallel} > g_{\perp}$. In borate glasses, Cu^{2+} shares oxygens which are part of the boroxyl ring in the network. The lone pair of oxygen can be involved in π-bonding with Cu^{2+} or can be delocalized into boroxyl π-system. Hence there is a competition between boroxyl ring and Cu^{2+} to share the lone pair of oxygen and any changes in the boroxyl network which tilts this balance can be sensed by changes in ESR features. ESR features are quite sensitive to changes in bonding around Cu^{2+}. In his study of sodium and lithium borate glasses, Imagawa (1968) found that α^2 is relatively insensitive to glass composition whereas β_1^2 (or $g_{\parallel}$ and $A_{\parallel}$) is affected by composition (figure 12). The sharp drop in β_1^2 above 15 mol % alkali oxide was taken to reflect a weakening in the average B–O bond strength due to the formation of four-coordinated borons. Since then an increasing number of studies of Cu^{2+} in various borate glasses ($RO\text{-}B_2O_3$ and $R'_2O\text{-}B_2O_3$; R = Ba, Sr, Pb, Zn and R′ = Li, Na, K, Tl) have been reported in literature (Bogomolova *et al* 1971; Kawazoe *et al* 1978b; Hosono *et al* 1979; Hosono *et al* 1981; Ohta *et al* 1982; Bogomolova and Jachkin 1983). In all cases, abrupt changes in $g_{\parallel}$ and $A_{\parallel}$ were noted at various concentrations of RO or R_2O for different systems. Similar behaviour was noted for $Na_2O\text{-}P_2O_5$ and $K_2SO_4\text{-}ZnSO_4$ glasses also (Kawzoe *et al* 1978b). As pointed out earlier sudden changes in $g_{\parallel}$ and $A_{\parallel}$ were attributed to changes in covalency of Cu^{2+}–O π-bonding (or weakening of B–O bonding). Kawazoe *et al* (1978a) have estimated basicities of an oxygen in alkali borate glasses by means of MO calculations for molecular models of various borate groups. They have found that the degree of delocalization of the out-of-plane non-bonding level (π-character) decreased in the composition region of 15–20 mol % alkali oxide while in-plane basicity was nearly constant over the composition of 0–35 mol % alkali oxide. However this study does not explain the abruptness of the changes in bonding or ESR parameters. According to present understanding (Bogomolova and Jachkin 1983) of Cu^{2+} spectra of borate glasses, there are three different spectra (I, II and III) with distinct ranges of $g_{\parallel}$ and $A_{\parallel}$ values. For example, spectra I, II and III are obtained for $Na_2O\text{-}B_2O_3$ glasses with $5 \leqslant Na_2O \leqslant 13$, $20 \leqslant Na_2O \leqslant 37$ and $55 \leqslant Na_2O \leqslant 75$ respectively. Step-like changes in ESR parameters observed in the region around 17 to 45

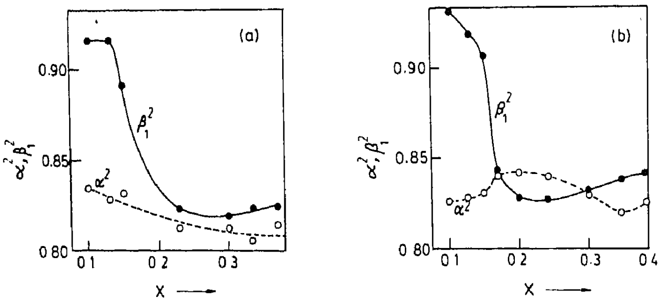

Figure 12. Variations of bonding parameters, α^2 and β_1^2 of Cu^{2+} in (**a**) $x \cdot Na_2O \cdot (1-x) \cdot B_2O_3$ and (**b**) $x \cdot Li_2O \cdot (1-x) \cdot B_2O_3$ glasses (after Imagawa 1968).

mol % alkali oxide may be attributed to change of spectra from I to II (actually a change in the overlap of spectra I and II is observed). Hosono *et al* (1983) have detected a new spectrum for borate glasses with Na_2O content smaller than 5 mol % obtained with different cooling rates. The ESR parameters of this spectrum are much the same as spectrum II, but a significant difference was observed between the thermal stabilities of these spectra. Ardelean *et al* (1984) did not find any significant modification of ESR parameters with increasing copper content in $x\text{CuO}\cdot(1-x)\ [2B_2O_3\text{-}Li_2O]$ glasses (with $x = 0$ to 30). In sodium borosilicate (Dingkum *et al* 1982) $g_\parallel$ changes moderately whereas the other spin Hamiltonian parameters and the covalency of Cu^{2+}–O bond remain almost constant. In phosphate glasses (Bogomolova *et al* 1978) also only a linear dependence of ESR parameters was noted with increasing BaO and CaO. Similarly in mixed alkali $Li_2O\text{-}Na_2O\text{-}Al_2O_3\text{-}SiO_2$ glasses (Klonkowski *et al* 1983), a monotonic decrease in the values of $g_\parallel$ and $A_\parallel$ was noted with increasing mole fraction, $[Li_2O]/([Li_2O]+[Na_2O])$. Kawazoe *et al* (1978c, 1979, 1980b) have applied ESR of Cu^{2+} to the study of immiscibility in $K_2O\text{-}CaO\text{-}B_2O_3$, $K_2O\text{-}BaO\text{-}B_2O_3$ and $K_2O\text{-}MgO\text{-}B_2O_3$ glasses. In the inhomogenous region, the spectra were found to be superposition of two or three different types of spectra (described earlier) characteristic of representative spectra observed for alkali or alkaline earth borate glasses. The inhomogenous region determined by ESR was found to be far wider than that obtained by opalescence in all the three systems. Kawazoe *et al* (1980a) have also studied the rigidity of glass network by analysing the distribution of $g_\parallel$ and $A_\parallel$ ($\delta g_\parallel$ and $\delta A_\parallel$) in silicate, borate and phosphate glasses. In similar compositions of $Na_2O\text{-}B_2O_3$ and $PbO\text{-}B_2O_3$ glasses $\delta g_\parallel$ was found to be larger for PbO-glass than for Na_2O-glass which reflects the difference in the rigidity of these glasses. In another interesting application of ESR of Cu^{2+} in glasses, the mechanism of colouration was investigated by Duran *et al* (1984). They found that both clusters of CuO and crystallites of Cu_2O are present in the glass and the reaction leading to the formation of these products by redox process is buffered by disproportionation reaction involving Sn^{2+}.

Environment of Cu^{2+} in diffusion layers produced by ion exchange in binary alkali-silicate glasses was investigated by Bogomolova *et al* (1983a). They found that isolated Cu^{2+} ions in diffusion layers are in local environments nearly identical with those for Cu^{2+} ions in bulk glasses of the same composition.

4. Concluding remarks

The use of ESR in the investigation of glasses has been increasing steadily in recent years. We have noted in this brief review that substantial amount of work has been done based on ESR of transition metal ions. A certain degree of confidence has emerged with regard to the use of spin Hamiltonian of relevant transition metal ions in ESR studies of glasses. In general ESR parameters and structural geometries appear to possess a reliable degree of correlation. In several instances such as in chalcogenides variation of structures appearing in the glassy matrix are well diagnosed by substantial composition variations of probe ion ESR spectra. Thus the merit of transition metal probe ions in ESR spectral studies of glasses is quite significant.

It is however conspicuous that a number of studies still appear to be more related to the investigation of the ESR behaviour of TM ions in glassy matrices rather than investigation of the structure of glassy matrices using ESR probes. In fact it so happens as pointed by Griscom that some of the ions like Fe^{3+} exhibit characteristic spectra with minor variations in almost all glassy matrices. TM ions appear to dictate their own local structures in glassy matrices (which we may call as "Griscom effect"). This results in a serious limitation in using transition metal ions as ESR probes. We feel that this tendency is inherently and inversely related to the ionic potential of the probe ion. In otherwords a low Z/R ion (like Cu^{2+} or Mn^{2+}) is assimilated in the glassy matrix so as to maximize entropy while a high Z/R ion (like Fe^{3+} or V^{4+}) is assimilated such that energy is maximized. It is in the former case which does not lead to 'Griscom effect' that ESR is most useful as a tool for investigating glass structure.

It is disappointing that ESR spectroscopic studies of transition metal ions in glasses have rarely been used to examine the relaxational aspects of such spectra. Parthasarathy *et al* (1982) have investigated the spin-spin relaxation behaviour of Mn^{2+} and Fe^{3+} ions in several glass systems and have arrived at useful correlation between ESR intensities and configurational entropy in the glass transition region.

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