E.S.R. STUDY OF MAGNETIC INTERACTIONS IN GLASSES CONTAINING IRON

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ABSTRACT — Electron Spin Resonance (ESR) provides a useful tool not only as a probe of local structure and short range order in glasses but also of magnetic interactions in the glasses containing suitable magnetic ions. We have analysed the spectra of many glasses in the series $xFe_2O_3(PbO \cdot 2B_2O_3)$. The results of computer simulation of the spectra and the experiments on the temperature dependence of the parameters of relevant lines can be summarised as follows. For low concentration ($x < 0.1$) the peak at $g = 4.3$ is due to isolated Fe^{3+} ions in a distorted octahedral or tetrahedral coordination. The broadening of this peak can be adequately accounted for by considering temperature effects and dipolar interaction. For intermediate concentrations (approximately $0.1 \leqslant x \leqslant 0.4$) the model of superexchange interaction between strongly coupled ions, forming a pair (pair-wise interaction model) gives reasonable results in explaining, qualitatively, broad $g = 2$ absorption. For high concentrations where a fraction of iron ions is in the precipitated α-Fe_2O_3 crystalline phase, the spectra have interesting features of Ferromagnetic Resonance (FMR) and the $g = 4.3$ peak, typical of isolated Fe^{3+} ions, is more intense, indicating that these ions, left over in the glassy matrix, are comparatively diluted.

1 – INTRODUCTION

The ESR spectra of transition metal (TM) ions in the oxide glasses, specially in silicate and borate glasses have been the subject of many studies [1-9]. ESR has been used primarily as a tool to draw conclusions about valence state, coordination and the crystal field symmetry of the ion. Although there have been some studies of the resonance line shape which take the exchange interaction between magnetic ions as the dominant part of the Hamiltonian describing the states of resonance centre [10-12], we describe here an attempt to study systematically the magnetic interaction between iron ions when the concentration of the ions is varied through a wide range in the same base glass matrix.

Three ESR peaks for Fe^{3+} ions in glasses have been reported in the literature [1-4]: $g = 6$, $g = 4.3$ and $g = 2$. We did not observe $g = 6$ peak in our samples, and therefore do not discuss it. From the point of view of their microscopic origin, the spectra are determined mainly by: A) the symmetry of the crystal field at the ion and B) the interaction between the ions. There are two major symmetry environments of the ion: T_d and O_h ; T_d corresponding to Fe^{3+} ion going as network former substituting boron in BO_4 tetrahedra. Since in glass exact symmetry is rarely encountered, the spectra are due to axial ($g = 6$) or rhombic ($g = 4.3$) distortions of T_d and O_h fields. The rhombic distortion leads to $g = 4.3$ peak of Fe^{3+} ions [2]. The interaction between the ions can be magnetic dipole-dipole or exchange interaction. At large inter-ion separation we expect dipole-dipole interaction to be dominant [13-a] and at small inter-ion distances, where Fe-O-Fe configurations are possible, the dominant interaction will be the exchange interaction. As we vary the concentration of Fe_2O_3 in the glass composition we expect changes in ESR spectra to reflect in a systematic manner the resulting changes in the interactions.

A rather important issue in these glasses is that of clustering. The question has two aspects. The first one can be formulated as follows: at any given concentration is it possible that all (or a major fraction of) iron ions are in a special geometrical relation to one another or are they perfectly randomly distributed? It is clear that even in a homogeneous distribution there will be some ions, owing to statistical nature of the distribution, in a geometry favorable to exchange interaction, but these will be very few. The second aspect of the question is the following: if the special geometry configurations (clusters) start in a significant way at a definite concentration, what is that concentration? Again, the concentration which permits exchange configurations from a purely geometrical point of view will not be specially interesting. We hope that by our ongoing study of electrical [14], magnetic [13, 15] and resonance [13] properties of these glasses we can say something about this interesting question. It is expected that since some features of ESR depend on magnetic interactions resulting from special geometry, ESR can throw some light on the question of clustering.

The technique of ESR analysis we have applied for low concentrations consists, essentially, of simulating ESR spectra on a computer using a suitable but manageable Hamiltonian. A similar technique is applied to the high concentration, $x = 0.5$ sample, this time using a ferromagnetic resonance model [16, 17]. On the computer we can also generate the temperature variation of the intensities, expected from a given interaction model [10-13]. Despite this rather powerful technique, it is needless to say that due to uncertainties on some basic issues (like possible sites of Fe^{3+} ion) we can draw unambiguously only qualitative conclusions; and even that only when supplemented by information from other measurements.

2 — EXPERIMENTAL PROCEDURE

The standard technique of glass melting in air was used and the only detail worth mentioning is that we used a twice melting procedure to ensure homogeneity. The X-band (9.5 GHz) ESR spectra were taken on a Varian E-109 machine capable of fields up to 10 Kilogauss. A circulating Nitrogen cryostat permits cooling up to approximately 100 K.

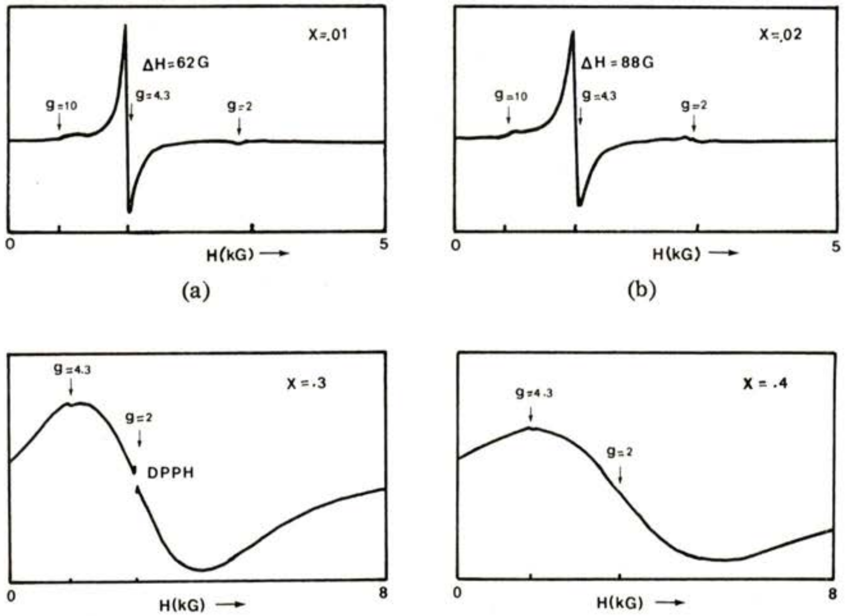
3 — LOW AND INTERMEDIATE CONCENTRATION

3.1 — *Peak intensities and widths*

From the point of view of magnetic interaction, we can discuss the results in three concentration regimes:

1. Low concentration ($0.01 \leqslant x \leqslant 0.1$): In this region the line-width is dominated by weak long range dipole-dipole interaction between the magnetic moments of Fe^{3+} ions. As the concentration of ions in the glass increases, the average distance between Fe^{3+} ions decreases. This results in an increased dipolar

interaction and consequently the width ΔH of the $g = 4.3$ line is expected to increase with concentration [13-a]. In Fig. 1a, 1b we show two typical spectra ($x = 0.01$, 0.02) and indicate the corresponding values of $(\Delta H)_{4.3}$.



(a) (b)

(c) (d)

Fig. 1 — E.S.R. spectra of $x = 0.01$, 0.02, 0.3, 0.4 samples, at room temperature, of the glass system $xFe_2O_3(PbO \cdot 2B_2O_3)$.

2. Intermediate concentration ($0.1 \leqslant x \leqslant 0.4$): In this region the effect of exchange interaction between Fe^{3+} is noticeable. This manifests itself in two different ways: A) effect on the $g = 4.3$ peak; B) appearance and evolution of a broad $g = 2$ absorption. So far as the $g = 4.3$ peak is concerned the width does not change visibly within this region. Moreover, as the number of ions participating in the exchange pairs increases, the number of isolated ions contributing to the dipole broadened $g = 4.3$ peak decreases leading to a loss of intensity in that resonance. The presence of a broad resonance at $g = 2$ is due to exchange interaction [9-13], direct or superexchange via bridging oxygen ion,

between the Fe^{3+} ions. As expected, the intensity of this peak increases with concentration. In Fig. 1c, 1d we show two typical spectra of intermediate concentrations, $x = 0.3$ and 0.4. From this and other spectra, the relative increase in the intensity of the $g = 2$ peak at the cost of $g = 4.3$ peak is clearly evident. Room temperature values of the intensity ratios, $I_{g=2} / I_{g=4.3}$, for different values of x, are shown below.

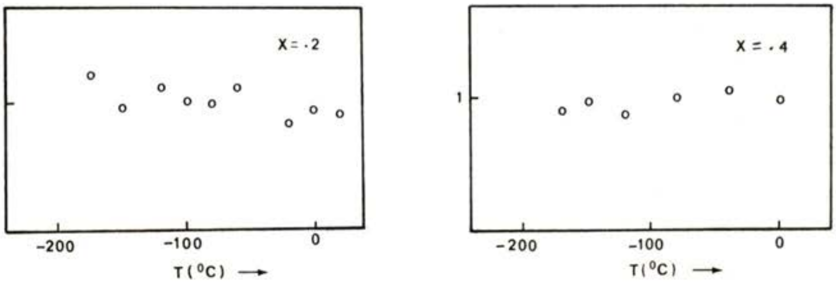


Fig. 2 — Variation of the intensity of $g = 2$ absorption line with temperature, in arbitrary units, for $x = 0.2$ and $x = 0.4$.

x	0.1	0.2	0.3	0.4
$I_{g=2} / I_{g=4.3}$	0.35	5	100	100

3.2 — *Temperature effects*

The effect of temperature variation on the spectra of $x = 0.2$ and $x = 0.4$ specimens can be summarised as follows:

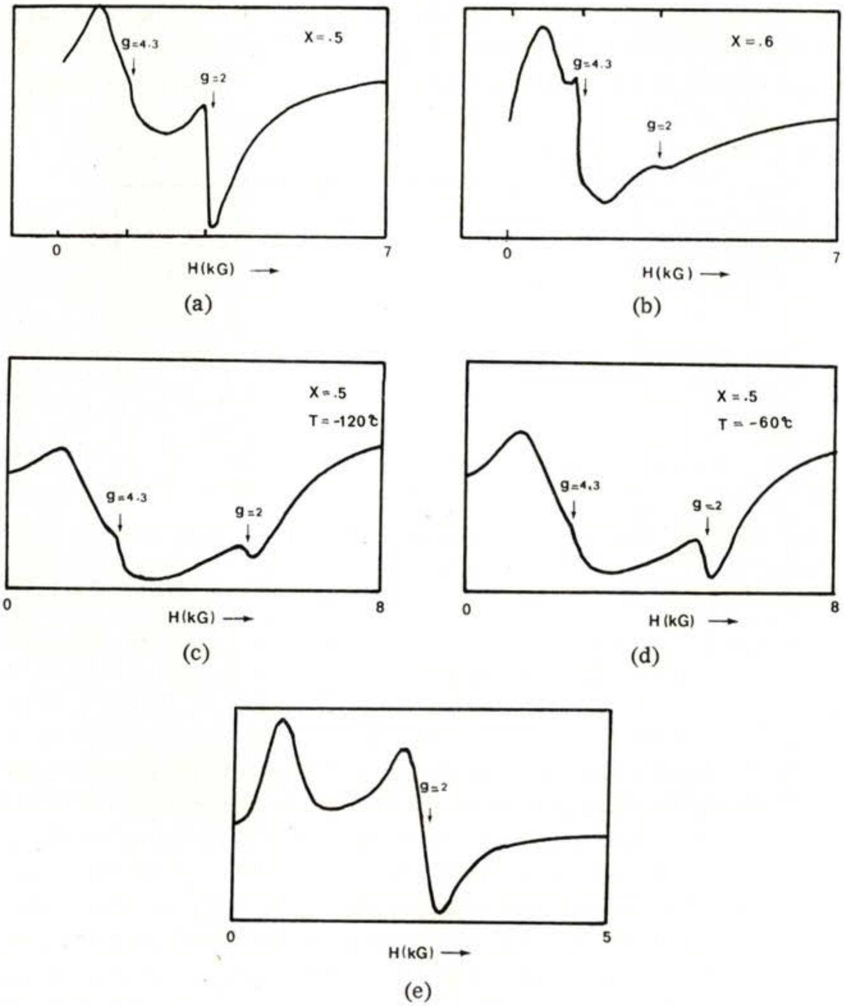
1. The intensity of the $g = 4.3$ peak decreases with the increase of temperature (see Fig. 5 for $x = 0.2$ sample). This behaviour is easily attributed to interaction with the phonons.
2. The intensity of the $g = 2$ peak remains relatively constant in the temperature region 100 K - 300 K. Actually, for the sample $x = 0.2$ the intensity slightly decreases with increasing temperature, while for $x = 0.4$ there is a marginal increase (Fig. 2).

If we assume that the dominant interaction between the ions is pair-wise exchange [11, 12] of antiferromagnetic type, we can attribute the appearance of the observed $g = 2$ peak to this interaction. The peak becomes broader if, along with the exchange field, the original distorted crystal field of isolated ions is also included in the Hamiltonian. Thus we verify the qualitative features of the observed peak in the pair exchange interaction model, except the temperature behaviour of the resonance centered at $g = 2$. Within this model, where exchange interaction is assumed to be dominant, an increase in the peak intensity with temperature is predicted [10-12]. In our case the peak in the glass $x = 0.4$ follows the predicted behaviour if we assume very small values of J, but the observed temperature variation in the $x = 0.2$ sample, though weak, is in the opposite sense. This leads us to suspect that, in the present case, the exchange interaction is not sufficiently large; we estimate $J < 0.5\ \mathrm{cm}^{-1}$.

4 – HIGH CONCENTRATION

For samples $x = 0.5$ and $x = 0.6$ a Mössbauer study [15] indicates the presence of crystalline α-Fe_2O_3 (Hematite) in these glasses. This introduces major changes in the corresponding ESR spectra. The room temperature spectra of these two glasses are shown in Fig. 3a and 3b. In both spectra we notice a background signal spread over a rather large range of the applied field. However, the most interesting feature of these samples is the behaviour of the sharp $g = 2$ peak.

In the sample $x = 0.5$ the pronounced $g = 2$ peak can be attributed to the superparamagnetic behaviour of the small particles of Hematite. This has also been observed in other glasses where a segregated phase is present [18-20]. In order to interpret and draw some conclusions from the temperature behaviour of this peak we recall some rather well known facts about α-Fe_2O_3. The bulk form of Hematite shows weak ferromagnetism at room temperature, when the spins lie in the c-plane. At about 260 K (T_M) Morin transition takes place and the pure antiferromagnetic phase corresponding to the configuration of all spins lining up along the c-axis is more stable. The behaviour of small particles of α-Fe_2O_3 is, however, different. T_M decreases with the decreasing size of the particles [21-24], so much so that Yamamoto [23] did not observe any transition in the sintered sample with particle diameter less then 200 Å. For small particles, a gradual decrease is generally observed in the properties characteristic of superparamagnetism with increasing particle size. The spectra of the x = 0.5 sample taken at different temperatures confirm the above mentioned general behaviour. In Fig. 3c and 3d we show two of these spectra (T = − 120°C, T = − 60°C).



(a) (b)

(c) (d)

(e)

Fig. 3 — (a) (b) Room temperature E.S.R. spectra for x = 0.5 and x = 0.6; (c) (d) Spectra for x = 0.5, at −120 and −60°C; (e) Simulated spectrum of ferromagnetic resonance, in the cubic model, with $2K_1 / M_s = 2500$ Gauss.

The temperature dependence of the superparamagnetic properties of small particles, has been given by Néel [25]. This was applied by Kündig et al. [24] to the Mössbauer spectra of the particles and from their data they calculated the anisotropy constant to be $K_1 = 4.7 \times 10^4$ erg cm^{-3}. If we apply a similar procedure to our ESR intensities and make the Arrehenius plot of $\log_e (I)_{p\text{-}p}$ versus $1/T$ ($(I)_{p\text{-}p}$ being the difference between maximum and minimum, proportional to the absorption intensity) for the $g = 2$ sharp resonance of the $x = 0.5$ sample we obtain the graph shown in Fig. 4, where the slope gives the anisotropy energy.

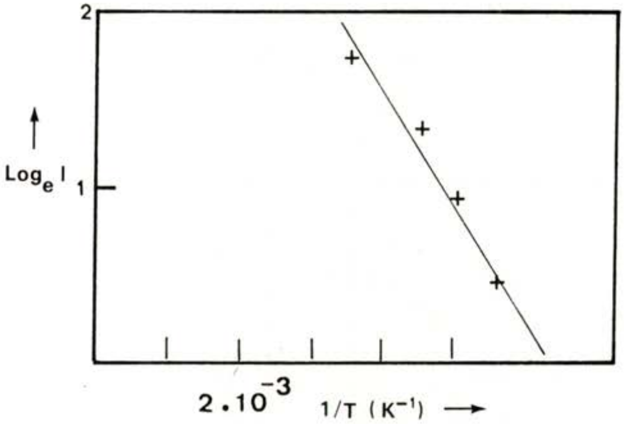


Fig. 4 — $\text{Log}_e (I)_{p\text{-}p}$ vs. $1/T$, for $g = 2$ peak of the $x = 0.5$ sample. Anisotropy energy, calculated from the slope, is 8.7×10^{-14} erg.

We can estimate the diameter of the particles employing the value of K_1 given by Kündig et al. [24]. This gives a value of 120 Å and therefore the observation of a gradual decrease in the intensity of the $g = 2$ peak instead of Morin transition agrees with the observations of Yamamoto [23] and Kündig et al. [24] on such small particles. Although the anisotropy energy for small particles can account for the results, the exact physical origin of this anisotropy is not clear; it may be due to some interactions inside the particles or simply because of the demagnetising field.

We have looked at the $g = 2$ resonance from yet another point of view. We have simulated a ferromagnetic resonance spectrum for spherical particles assuming all possible relative orientations of the applied field and the anisotropy field. The resonance condition for the cubic symmetry is given by [17, 18]

$$H(\Theta, \phi) = H_0 + (2K_1 / M_s)(1 - 5F)$$

where

$$F(\Theta, \phi) = \cos^2\Theta \sin^2\Theta + \sin^4\Theta \sin^2\phi \cos^2\phi$$

The simulated spectrum is shown in Fig. 3e. This points to a value of the anisotropy field of 2500 Gauss and from the results of Komatsu and Soga [22] for the value of effective magnetic moment in α-Fe_2O_3, we deduce that the value of K_1 as 1.4×14^4 erg cm^{-3}. Using this value the estimated particle diameter would be 180 Å. Still neither of the analyses, Néel model or computer simulation of ferromagnetic resonance, takes into account the interactions and structure specific to Hematite. We are working on a model which takes into account these features.

The fact that the sample $x = 0.6$ hardly shows the features of superparamagnetism is again in agreement with the Néel theory, according to which the anisotropy energy depends upon the volume. As a matter of fact the size of the particles in this sample is so large that their diameter, from X-ray, may be estimated to be about 1000 Å. The most noteworthy observation which we have made in this sample is the increase in the intensity of the $g = 4.3$ peak relative to the situation in the samples $x = 0.5$. From the similarity in the temperature variation of this peak in samples $x = 0.2$ and $x = 0.5$ (Fig. 5) we conclude that the peak indeed corresponds to isolated Fe^{3+} ions. However, the problem of this peak of isolated ions being more intense and sharper than in the sample $x = 0.5$ needs a more thorough analysis of the physical situation and is currently under study.

5 – CONCLUSIONS

The physical picture we deduce is the following. At very low concentration (approximately $x < 0.1$) the Fe^{3+} ions behave as independent spins and the principal interaction is dipolar. There is no noticeable clustering at this low level of concentration, barring a few exchange coupled ions allowed on statistical grounds.

As the concentration is increased, the dipolar interaction increases, but, more importantly, a significant fraction of ions form exchange coupled pairs. The dominant interaction is superexchange (antiferromagnetic) via a bridging oxygen ion. Analysis of the temperature variation of the g = 2 resonance shows that a pair-wise

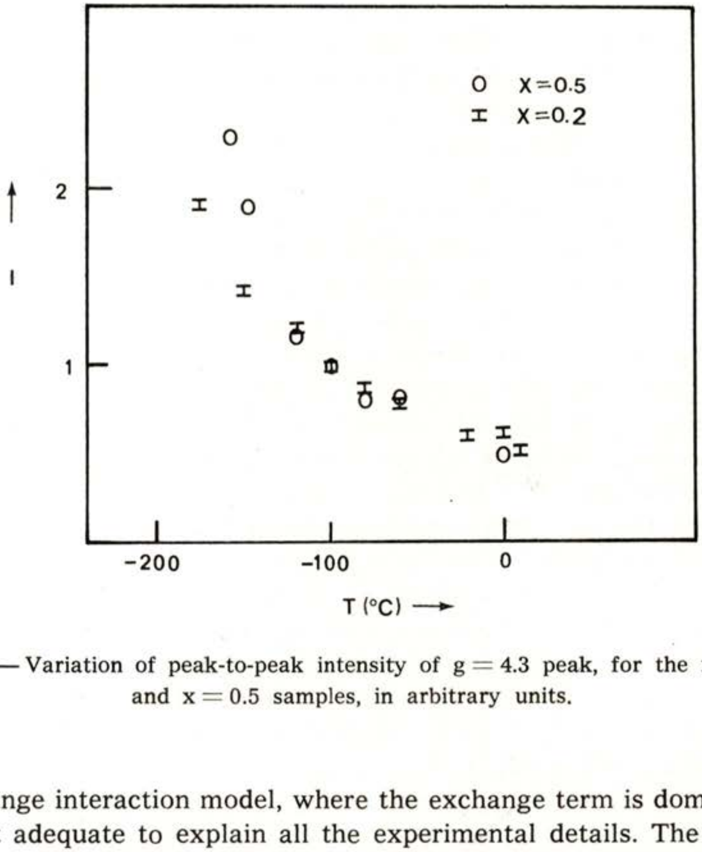


Fig. 5 — Variation of peak-to-peak intensity of g = 4.3 peak, for the x = 0.2 and x = 0.5 samples, in arbitrary units.

exchange interaction model, where the exchange term is dominant, is not adequate to explain all the experimental details. The onset of crystallite (α-Fe_2O_3) formation with increased concentration is accompanied by a sudden appearance of a sharp g = 2 peak arising from small crystallites behaving essentially like superparamagnetic particles. The size and anisotropy energy of these particles are consistent with the results obtained by other authors. As more ions go into crystallites the latter become bigger and, probably, the large anisotropy energy prevents the precession of the small magnetic moment and, therefore, no typical superparamagnetic behaviour is observed. On the other hand the g = 4.3 peak of isolated Fe^{3+} ions becomes sharper and more intense. This and some other details of spectra of these glasses with a crystalline phase, which are currently under study, cannot be explained at this moment.

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