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# E.s.r. during crystallization in $Gd^{3+}$ doped lithium-aluminium-silicate glasses

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Measurements of the electron spin resonance spectrum have been made in a $Gd^{3+}$ doped lithium-aluminium-silicate glass at various stages during the crystallization of the glass. The crystallization was induced by heat-treatment at various temperatures and took place either from the surface or from nucleation centres produced by the presence of $TiO_2$ in the glass.

The changes in the resonance spectra have been interpreted in terms of the stability of the gadolinium sites. In the presence of titanium, it is suggested that complexes are formed in the glass which involve both titanium and gadolinium ions.

Supporting measurements show that the presence of these complexes is also detectable from the more conventional structural and thermal characterization of the glasses.

## 1. Introduction

In recent years the volume of work being undertaken in an attempt to establish the nature of the glassy state has increased rapidly. In particular, electron spin resonance techniques have been used to provide information about environments of paramagnetic probe ions in the glass and about the phase transition from the glass to the crystalline state [1-6]. In this latter respect, the increasing development of glass ceramics has emphasized the importance of understanding the role played by nucleating agents in producing these materials. The most commonly used agent at the present time is $TiO_2$ although many other materials may be used for this purpose.

There are considerable differences of opinion concerning the mechanism of nucleation and subsequent crystallization [7-9] and it is by no means clear whether the $Ti^{3+}$ ions surround the developing crystallites or are taken up substitutionally, i.e. into the $\beta$-spodumene and $\beta$-eucryptite lattices of the lithium-aluminium-silicate (LAS) ceramics, for example.

All the electron spin resonance work referred to above has made use of various transition metal ions as the structure sensitive probe with which to investigate the initial stages of crystallization. Little use appears to have been made of the 4f ions of the lanthanide series however, a fact which may be associated with the reduced effects of the crystal field on these ions compared with the 3d-transition metal ions. It is possible that there is less distortion of the glass structure about a 4f impurity ion than there is about a 3d since the 4f electrons are deeply buried in the ion and consequently well screened from the crystalline electrostatic field. This is not the case for the 3d ions and it may be necessary with these to allow for some distortion of the surrounding glass matrix when evaluating the Hamiltonian for the system. As a result of this the lanthanide ions may prove more satisfactory structure sensitive probes provided that the effects of crystallization are large enough to be resolved and provided that the observed spectra are capable of interpretation. This latter point is also true for the transition metal ions of course.

Early resonance work on lanthanide ions in glass was carried out by Garif'yanov [10], Chepeleva [11] and Nicklin [12] using the $Gd^{3+}$ ion in glass matrixes which had not been heat treated. A common feature of this work was the appearance of high $g$-value resonances ($g \simeq 4$ and $g \simeq 6$) in addition to the $g = 2$ resonance to be expected for the S-state ion. To our knowledge such low field transitions for the $Gd^{3+}$ ion have most frequently been reported for glassy hosts and rarely for gadolinium substituted into a crystal lattice, although as the works of Abraham

TABLE I The composition of the various glasses used in this investigation

| Glass no. | $SiO_2$ | $Al_2O_3$ | $Li_2O$ | $TiO_2$ | $Gd_2O_3$ | MgO | CaO | BaO | $Na_2O$ | $K_2O$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 1022 | 60 | 20 | 20 | — | — | — | — | — | — | — |
| 1035 | 60 | 20 | 20 | 5.0 | — | — | — | — | — | — |
| 1036 | 60 | 20 | 20 | 5.0 | 1.0 | — | — | — | — | — |
| 1058 | 60 | 20 | 20 | — | 1.0 | — | — | — | — | — |
| 1000 | 70.8 | 2.4 | — | — | $1 \rightarrow 20$ | 2.4 | 5.0 | 1.8 | 16.4 | 1.6 |

*et al* [13, 14] and Darby [15] have shown, once a strong crystal field environment lifts the restrictions on the transition selection rules ($\Delta m = \pm 1$) then many high *g*-value resonances should be observable. The removal of these selection rules occurs because of the admixing of the wave functions caused by the large electrostatic interaction.

We have recently examined the effects of crystallization on these resonances for surface nucleated crystal growth of glasses containing no titania and for bulk nucleation caused by the addition of $TiO_2$ to the glass melt. This work has shown that the behaviour of the individual resonances is sensitive to the presence of titania and the results are described in the following.

## 2. Experimental

Various glasses were prepared from high purity $Li_2CO_3$, $Al_2O_3$, $SiO_2$, $TiO_2$ and $Gd_2O_3$ by heating 100 *g* quantities of the well-mixed constituents at 1450° C for 8 h. Homogeneity was improved by intermediate crushing and remelting. Nucleation and crystallization were induced by further heat-treatment in the temperature range from 600 to 900° C. This heat-treatment was carried out in two ways, either by heating at a fixed temperature in this range after warming directly from room temperature or alternatively by heating in this range after a previous preheating treatment (nucleation) at a lower temperature. These different methods lead to two different types of crystallization behaviour, as is well known for the lithium-aluminium-silicate system [16]. Differential thermal analysis (DTA) was used to establish the nucleation and crystallization temperatures required for these heat-treatments.

The glasses prepared for this examination are listed in Table I, in which the detailed compositions are given.

The crystallographic structure of the heat-treated glasses was determined using conventional Debye-Scherrer X-ray diffraction techniques and the percentage crystallization estimated either from the relative intensities of the dominant lines of these diffraction patterns or from low magnification electron micrographs obtained from carbon replicas of the surfaces of freshly broken chips of the glasses.

Electron spin resonance measurements were made using a conventional X-band reflection spectrometer with field modulation at 180 Hz.

### 2.1. Structural and related data

The differential thermal analysis results showed the presence of two endotherms in the glasses containing titanium, but only one in the base glass LAS 1022. The low temperature endothermic peak $T_N$, for the titanium doped glasses, is thought to correspond to the nucleation process [17] and occurs some tens of degrees below the dominant exothermic, crystallization peak $T_C$. The lower peak is at least an order of magnitude smaller than the crystallization peak and as a result the nucleation transition was frequently difficult to detect.

Fig. 1 shows the DTA results for the LAS 1022, LAS 1035 and LAS 1036, specimens and there are two features which are evident from these results. First the presence of 5 at. % $TiO_2$ in the glass causes the crystallization temperature to be lowered by approximately 50° C and at the same time the width of the corresponding peak in the DTA output is drastically decreased. Secondly, if as little as 1 at. % $Gd_2O_3$ is added to the glass in addition to the 5 at. % $TiO_2$ the temperature of crystallization is immediately returned to the value corresponding to the base glass and the transition region is again broadened. The nucleation temperature however, is essentially unchanged between the glasses containing only titanium and those containing both titanium and gadolinium.

As indicated earlier two methods were used for crystallization of the glass, either direct crystallization at some temperature or a nucleation treatment followed by crystallization at a higher temperature. In both of these techniques the

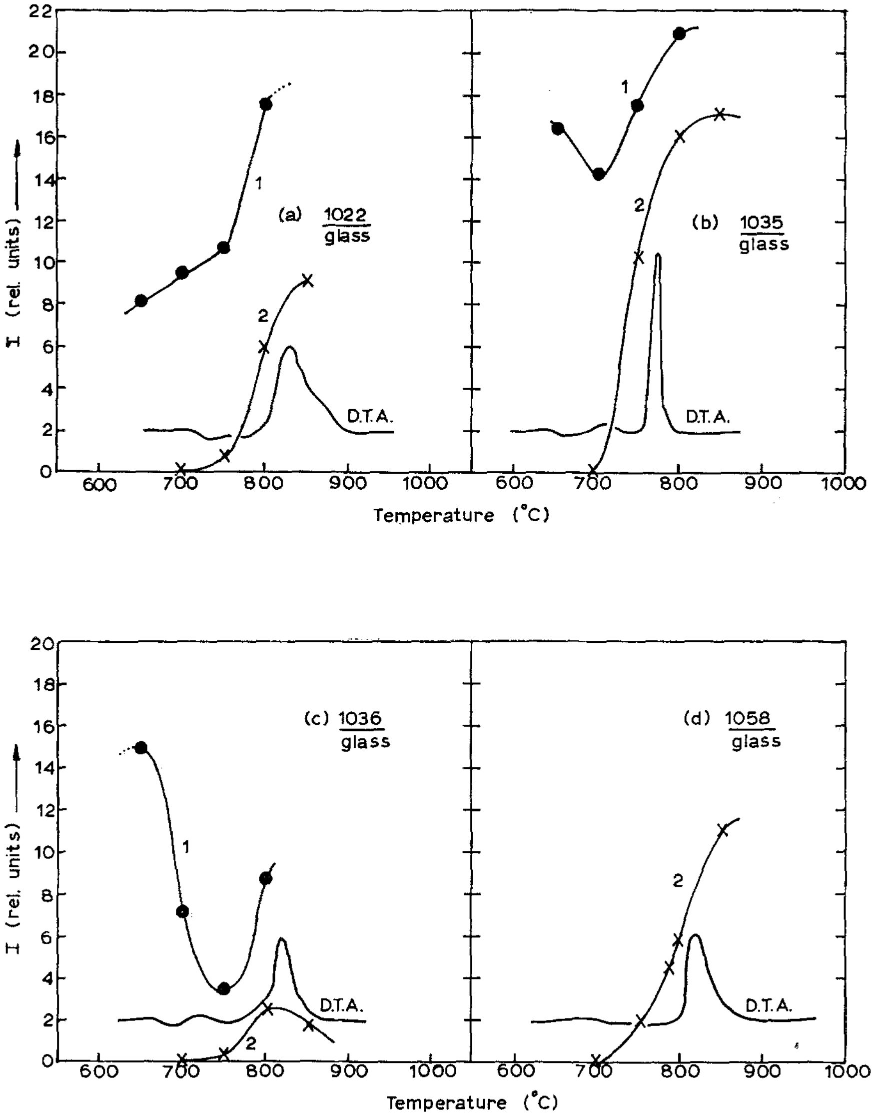

*Figure 1* DTA and degree of crystallization of glasses 1022, 1035, 1036 and 1058. Curves 2 represents the degree of crystallization in samples held for 1 h at these temperatures whilst curves 1 are for samples after a subsequent heating at 850°C for 1 h.

X-ray diffraction patterns showed the presence of only the $\beta$-eucryptite phase and as Table II shows, the derived lattice parameters are essentially insensitive to the titanium or gadolinium additions.

The extent of crystallization and the crystallite size were found to depend strongly upon the composition however, for a given heat-treatment. The degree of crystallization, as estimated from the intensities of several of the diffraction lines for standard sample and exposure conditions, are shown in Fig. 1, superimposed on the DTA output. For a single heat-treatment, little crystallization was detected at temperatures less than those corresponding to the crystallization peak. Above $T_c$ however, the percentage crystallization rose rapidly before passing through a maximum. Again there is a marked difference between the LAS 1035 ($TiO_2$ only) and LAS 1036 ($TiO_2$ + $Gd_2O_3$) glasses; for the latter composition the maximum amount of the crystalline phase was almost an order of magnitude less than

TABLE II Derived lattice parameters of glasses crystallized for 1 h at 850° C after nucleation (for 1 h) at the temperatures shown.

| | Sample heated for 1 h at these temperatures followed by 1 h at 850° C | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 650° C | | | 700° C | | | 750° C | | | 800° C | | |
| | *a* | *c* | A.V. | *a* | *c* | A.V. | *a* | *c* | A.V. | *a* | *c* | A.V. |
| 1022 | 5.26 | 11.17 | 267.6 | 5.18 | 10.98 | 255.1 | 5.25 | 10.97 | 261.8 | 5.21 | 11.08 | 260.5 |
| 1035 | 5.27 | 10.94 | 263.1 | 5.40 | 11.15 | 281.6 | 5.23 | 11.23 | 266.0 | 5.11 | 11.00 | 248.7 |
| 1036 | 5.24 | 11.10 | 263.9 | 5.28 | 11.13 | 268.7 | 5.20 | 10.96 | 256.6 | 5.25 | 11.03 | 263.3 |

A.V. = unit cell volume.
*a*, *c* dimensions are in Å and A.V. is in Å$^3$.

that for the specimens containing only $TiO_2$.

Further evidence for the inhibition of the crystallization process by gadolinium comes from the results obtained for specimens subjected to a double heat-treatment. The glasses containing $TiO_2$ both show a double peak in the percentage crystallization curves in agreement with other workers [18], however when $Gd_2O_3$ is also added to the glass the amount of crystallization developed by the second heating at temperatures above 700° C is much less than for the glasses containing only $TiO_2$. This is clearly seen in Fig. 1 and it is evident that while the nucleation efficiency appears to be unaffected by the addition of gadolinium, the subsequent crystallization is severely inhibited by its presence. Surprisingly, however, the LAS 1058 specimens, containing $Gd_2O_3$ only, showed quite extensive crystallization after the single heat-treatment.

The electron micrographs also showed these differences, the grain size in the LAS 1035 glasses being greater than that in the LAS 1036 glasses for comparable heat-treatment.

### 2.2. Electron spin resonance

E.s.r. absorption was anticipated only for those glasses containing $Gd^{3+}$ ions. However, specimens of all the glasses prepared were examined in order to eliminate the possible existence of impurity resonances (for example from $Fe^{3+}$) which might interfere with the $Gd^{3+}$ spectra. Resonances were never found in any specimen which did not contain gadolinium, a feature which also confirmed that the titanium ions in the LAS 1035 and LAS 1036 specimens were in the non-magnetic $Ti^{4+}$ state. In a later phase of the work the titanium ions were deliberately converted to the $Ti^{3+}$ state by solarization with X-rays, and under these conditions sharp and intense absorptions were observed in the vicinity of $g = 2.0$. The nature of these results will be described in a later publication and it is necessary here to comment only on the fact that in the present work the absence of these $Ti^{3+}$ resonances in the glasses containing titania may be taken as evidence for the existence of only non-magnetic $Ti^{4+}$ ions in these glasses. Consequently any possible influence of these ions on the observed spectrum due to cross relaxation phenomena can be ruled out. In further support of this conclusion, the temperature dependence of the spectra for glasses containing both gadolinium and titanium ions was not typical of that to be expected for a resonance spectrum dominated by cross relaxation [19].

The resonance spectra for three gadolinium concentrations (0.09, 0.2 and 1.0 at. %) were examined in preliminary measurements in order to determine the optimum conditions for the present investigation. The general form of the spectra in the range from $H = 0$ to 8 kOe is the same for all the compositions with relatively sharp resonances at $g \simeq 5.9$ and 4.3 and a much broader high intensity resonance with its centre field corresponding to $g \simeq 2.0$. This is shown for glass LAS 1058 (1.0 at. % Gd) in Fig. 2. There is also evidence of some further structure associated with this large peak in the vicinity of $g = 2.0$ but it has so far proved impossible to resolve this satisfactorily. The location of the $Ti^{3+}$ resonance observed in titanium containing samples after X-ray irradiation is indicated in this figure. There is no evidence for this resonance in this material, before irradiation.

The only variation evident from decreasing the gadolinium concentration is associated with the broad central resonance which decreases in intensity but there is no change in its half-width.

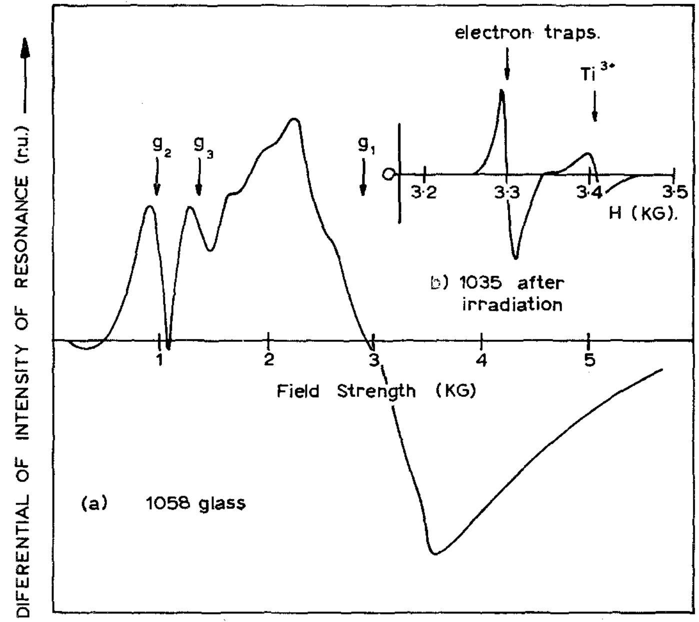

*Figure 2* Differential of e.s.r. signal for glasses (a) 1058 (b) 1035 after X-ray irradiation.

There is no corresponding change in the higher $g$-value line intensities and again the half-widths are independent of composition, consequently we can assume that there are no appreciable interactions between the $Gd^{3+}$ ions leading to exchange narrowing of the lines in the concentration studied. These features are typical of those found by earlier workers with gadolinium doped glasses and we have used a 1.0 at. % gadolinium concentration employed in the previous investigations of other workers and direct comparison of the various sets of results should therefore be more meaningful.

The resonance spectrum of the 1 at. % $Gd^{3+}$ sample (Fig. 2) is similar to that found by these earlier workers [10-12] using other types of glass matrix.

It was found that after heat-treatment the intensities of the $g_2$ and $g_3$ resonances (see Fig. 2) decrease with respect to the $g_1$ resonance as the heat-treatment temperature is increased above about 600°C. This decrease, which is shown in Fig. 3, occurred for both the LAS 1036 (Gd and Ti doped) and LAS 1058 (Gd doping only) glasses. However, the detailed variation of the intensity ratio of the $g_2$ and $g_3$ resonances ($I_2/I_3$) depends upon the composition of the glass under investigation. For the LAS 1058 glasses, increasing the temperature of heat-treatment led to a sudden increase in $I_2/I_3$ above about 800° C. This temperature corresponds to the onset of surface nucleated crystallization as described earlier. Fig. 4 shows the variation of this ratio with increasing heat-treatment temperature. Fig. 4 also shows the behaviour of the glasses containing both titanium and gadolinium for which the results are obviously different, the $I_2/I_3$ ratio decreasing with increasing nucleation heat-treatment temperature. Comparison with the DTA and crystallization data of Fig. 1 suggests that these variations in the intensity ratio are associated with the onset of crystallization, differences occurring due to the different methods of nucleation.

## 3. Discussion

The changes caused in the transition temperatures by the addition of $TiO_2$ and $Gd_2O_3$, either separately or together, to the glass melts are evident from the results given in Fig. 1. The normally wide range of the crystallization transition at $T_c$ is appreciably narrowed by the addition of $TiO_2$ in agreement with other workers, and corresponds to an increase in the crystallization efficiency caused by the action of the titanium ions as nucleating agents. As mentioned earlier the precise role played by these ions is not yet understood. With gadolinium

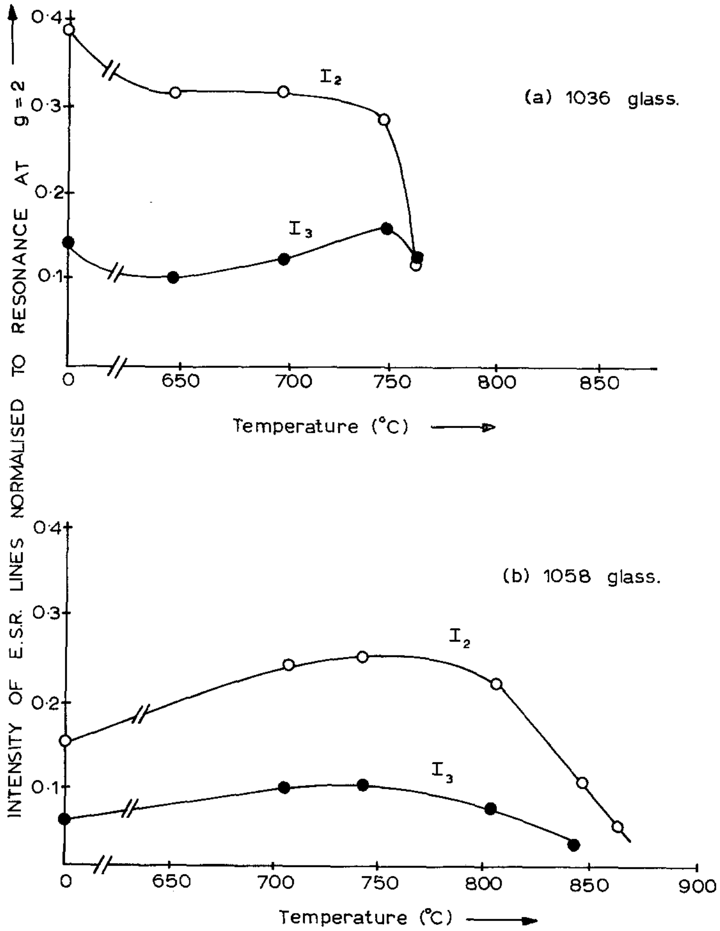

*Figure 3* Relative intensities of high *g*-value resonances in glasses (a) 1036 (b) 1058 with heat-treatment.

doping alone the results are similar to those for the base glass LAS 1022, however, it is remarkable that in the LAS 1036 glasses the effects of the addition of 5% $TiO_2$ have been almost completely negated by the simultaneous addition of 1% $Gd_2O_3$. The crystallization temperature is comparable to that in glasses containing no $TiO_2$ and the range over which crystallization occurs is correspondingly larger. The nucleation temperature is little affected by the presence of the gadolinium ions however.

There is clear evidence from the X-ray data of a double peak in the dependence of the amount of crystallization on heat-treatment temperature for glasses containing $TiO_2$ subjected to the two stage heat-treatment. This is in agreement with other workers [18], the initial peak corresponds to nucleated crystal growth; whilst the second peak is due to a rapid crystal growth in the specimen in which the lower viscosity allows a much easier path for either bulk or surface crystallization. We will refer to these peaks as the nucleation and crystallization peaks respectively. It is remarkable, however, that with both gadolinium and titanium ions present the crystallization peak is greatly diminished compared with the results for specimens containing only titanium. There seems to be no comparable effect on the nucleation peak, and it appears that while the $Ti^{4+}$ ions can perform their role in bringing about nucleation in the presence of gadolinium, the presence of this latter ion inhibits the subsequent crystal growth about the nucleation centres. The action of the gadolinium in this respect is very efficient since only 1% $Gd_2O_3$ greatly reduces the effects of 5% $TiO_2$.

The mechanism of this desensitization is unclear, as the action of the $TiO_2$ alone is not yet

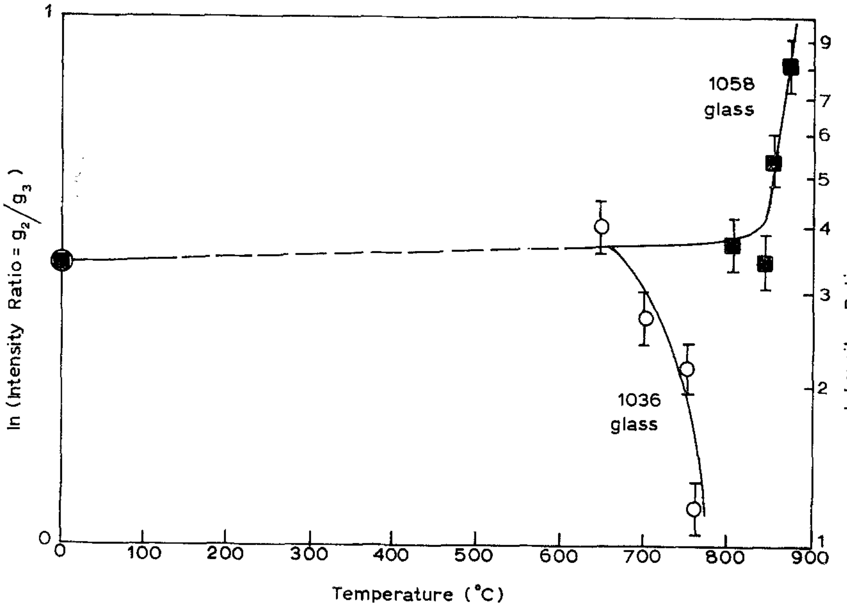

*Figure 4* A comparison of the ratio of intensities of resonances at $g \approx 5.8$ ($g_1$) to $g \approx 4.3$ ($g_2$) for Gd in glass 1058 and 1036 varying with heat-treatment for 1 h at the temperatures shown.

understood. If the titanium ions are taken up substitutionally into the growing crystal phase, as some workers believe, the action of gadolinium must be to prevent the titanium ions entering the lattice. This can occur either by changing their valence through an electron transfer process or alternatively by forming complexes including at least the $Ti^{4+(\text{or } 3+)}$ and $Gd^{3+}$ ions such that the affinity of the titanium ions for these complexes is greater than that for the growing crystal. Other workers take the view that the titanium ions reduce the lattice stability on a shell surrounding the growing crystals and so allow the glass-crystal transition to occur more easily by atomic diffusion. In this case the action of the gadolinium must be to increase the stability of the glass matrix either by adopting the role of a network former or again by forming Ti-Gd complexes which are capable of screening the effects of the $Ti^{4+}$ ions from the glass structure. Such complexes would require an extremely efficient interaction between the two types of ion as they are in the ratio of 1 (Gd):5 (Ti). There is, however, considerable evidence from other studies that some interaction does occur. These include differences in the optical absorption spectrum of solarized LAS 1036 and LAS 1035 glasses and changes in the thermoluminescence and luminescence behaviour caused by the addition of $TiO_2$ to glasses containing $Gd_2O_3$, only. The results of these measurements will be described elsewhere.

Interpretation of the resonance spectra for the specimens which have not been subjected to a heat-treatment (see for example Fig. 2) represent a considerable problem in themselves. The existence of the $g = 2$ resonance is to be expected for the $Gd^{3+}$ ion, which has an $S_{7/2}$ ground state, and the very great width of the corresponding resonance can readily be attributed to the random orientation of the applied magnetic field with respect to the symmetry axes of the "crystal field" environment about the gadolinium ion. The low field resonances corresponding to $g = 4.3$ and 5.9 are less readily explained.

In principle we can adopt the conventional spin-hamiltonian

$$\mathscr{H}_S = g\,\mu_B\,H\,.\,S + \mathscr{H}_{CF} \qquad (1)$$

to describe the splitting of the ground state $J$-manifold for probe ions situated in the electrostatic field associated with the surrounding host ions. However the $\mathscr{H}_{CF}$ term contains the well-known (see for example [20]) factors $\alpha$, $\beta$ and $\gamma$ which are identically zero for a pure S-state ion.

Consequently any observed splitting must be derived from second order effects [21] using an effective crystal field hamiltonian of the form

$$\mathscr{H}_{\mathrm{CF}} = \mathrm{S}.D.\mathrm{S} \ (= \textstyle\sum B_n^m O_n^m) \qquad (2)$$

where $D$ is a tensor arising from the second order effects of the fine structure interaction. $D$ and $g$ are then used as disposable parameters for fitting the observed data.

While this approach may be used satisfactorily in single crystal systems its application to polycrystals is more difficult since the observed spectra then contain spatial averages over all possible crystallite orientations relative to the applied field. The situation is even worse in a glass matrix where it is not at all certain that the paramagnetic resonance probe sites are identical. At best one can probably assume similar co-ordinations for the probes but the interatomic spacing of the ions in the immediate vicinity of the probe will differ from ion to ion. Consequently a second average must be made in attempting to reproduce the observed resonances and analysis in this way may be of little value unless a great deal of structural information is known about the glass matrix.

If one persists in employing the spin-hamiltonian approach to account for the main resonance of the glasses containing $\mathrm{Gd}^{3+}$, the high $g$-value resonances may be considered as forbidden ($|\Delta M_{\mathrm{S}}| > 1$) transitions, which may not be fitted by Equation 1 and we must invoke the presence of strong crystal field effects to remove the limitation imposed by the selection rules. The low field transitions are then effectively those between the crystal field split doublets of the $J = 7/2$ state. Alternatively, however, we can use the method of analysis described by Koster and Statz [22, 23] since the matrix elements contained in the expression for the oscillator strengths suggest that a great many transitions may occur between the eight levels, including some at very low field values. The hamiltonian used in this treatment is formed by using basis wave functions of the correct symmetry and Koster and Statz have shown that the matrix elements of $\mathscr{H}_{\mathrm{Z}}$ between two states $\Gamma_i$ and $\Gamma_j$ may be written.

$$\langle \Gamma_i | \mathscr{H}_{\mathrm{Z}} | \Gamma_j \rangle = \mu_{\mathrm{B}} g_1^{ij} [H_{\mathrm{X}} U_{\mathrm{X}}^1 + H_{\mathrm{Y}} U_{\mathrm{Y}}^1 + H^2 U_{\mathrm{Z}}^1]$$
$$+ \mu_{\mathrm{B}} g_2^{ij} [H_{\mathrm{X}} U_{\mathrm{X}}^2 + H_{\mathrm{Y}} U_{\mathrm{Y}}^2 + H_{\mathrm{Z}} U_{\mathrm{Z}}^2] \qquad (3)$$

where the $g^{ij}$'s are fitting parameters and the $U$'s are matrices which have been derived once and for all for many symmetries by Koster and Statz. The zero field splittings are assumed to exist *ab initio* and the level separations are then also used as fitting parameters. Unlike the spin hamiltonian approach the $g$-values are not related by simple constants and there is, in consequence, considerably more flexibility in fitting observed resonances using this method.

Unfortunately, random orientation of the distorted environments about the $\mathrm{Gd}^{3+}$ ions again make spectra interpretation extremely hazardous and until such time as a satisfactory means of analysis of e.s.r. spectra in glasses is developed it is probably more useful to attempt to employ the characteristics of the resonance spectra themselves (i.e. line width, resonance field and line intensity) as a means of obtaining information indicating possible correlations between the structural and electronic properties of glasses.

The most sensitive features of the spectrum of Fig. 2 are the low field resonances and as we have seen the relative intensities of these lines vary with heat treatment, the detailed variation depending upon the composition. The line widths and resonance fields are essentially constant however. If we take the increase in the $I_2/I_3$ ratio with heat-treatment temperature observed for the LAS 1058 glasses as the normal behaviour then the sudden drop in this quantity in the titanium containing, LAS 1036 glasses must be taken as a further indication of an interaction between the $\mathrm{Gd}^{3+}$ and $\mathrm{Ti}^{4+}$ ions.

The initial problem in the interpretation of the variation of the e.s.r. spectra is then one of establishing whether the observations are associated with a single type of gadolinium site or with two or more sites whose stability is associated with the degree and type of crystallization.

If the spectrum arises from a single atomic environment the low field resonances must arise from transitions between the strongly hybridized doublets of the $J = 7/2$ manifold. It is then difficult to see why the presence of titanium ions during crystallization should affect one of the resonance lines more than another. The most likely mechanism for such an effect would be a cross relaxation process but as we have seen the possibility of this seems to be small. It is possible, of course, that at $\mathrm{Gd}^{3+}$ sites which have a $\mathrm{Ti}^{4+}$ ion in the nearest neighbour shell, the change in the crystal field symmetry is sufficient to change the eigenfunctions of the levels involved in the low field transitions and hence the transition probability between them. Changes of this type however, would normally be accompanied by changes in the energies of the levels concerned and consequently in the resonance field values. As this is not observed we must assume that the changes are such as to leave the average resonance position the same or alternatively that a two site model is to be preferred.

In this latter case, it is convenient to consider the $g = 5.4$ and 4.3 resonances as being the low field transitions at the two sites in question. The structural evidence described earlier suggests that on crystallization with titanium present, the gadolinium and titanium ions may become jointly involved in complexes in the crystallizing glass. If this is so, then the zero field splitting of the ground state may be modified by the presence of the quadrivalent titanium ions as described in the previous section. These changes will depend on the location of the $Ti^{4+}$ ions with respect to the symmetry axis of the local electrostatic field at the $Gd^{3+}$ site.

Under these conditions the observed changes in the resonance line intensities would seem to suggest that (i) titanium is incorporated into one site in preference to another or (ii) that the crystal field is less sensitive to the presence of $Ti^{4+}$ at one of the sites compared to the other or finally (iii) that the $Gd^{3+}$ ions are ejected from one of the sites as crystallization develops. The complexes involved in these sites are almost certainly associated with non-bridging oxygen ions in the silicate matrix as considered by Barry *et al* [1-3].

At the present time it is not possible to differentiate between the models as more information is needed about the environments of the two types of "impurity" ions introduced into the matrix. It would seem to us, however, that the multiple-site case is perhaps to be preferred and the problem remaining is related to the establishment of the detailed structure of the complexes themselves, their relation to the glass as a whole and their behaviour during crystallization.

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