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# Multiband electron spin resonance spectroscopy of rare-earth S ions in glasses: the isospectral frequency ratio method

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**Abstract.** Results of ESR studies of the rare-earth S ions  $Gd^{3+}$  and  $Eu^{2+}$  in oxide glasses at various microwave frequencies in the range 2.7–10.3 GHz are presented. The spectra of two different centres (different ions or the same ion in different glasses), obtained separately and with appropriately chosen frequencies  $\nu_1$  and  $\nu_2$ , respectively, coincide after being normalized with respect to both the frequency and the maximum absorption intensity. The isospectral frequency ratio (IFR)  $\nu_1/\nu_2$  remains constant for a given pair of centres. It is shown that for such centres the ratio of each pair of equivalent fine-structure (FS) parameters is equal to the IFR.

Therefore, if the FS parameters are determined for a rare-earth S ion in a certain glassy matrix, these parameters can be readily obtained in all cases, when the IFR can be determined.

## 1. Introduction

In the last decade, substantial progress has been made in understanding the ESR spectra of rare-earth S ions  $Gd^{3+}$  and  $Eu^{2+}$  in glasses and other disordered solids. The experimental ESR spectra of these ions, usually obtained in the X band ( $\nu = 9.5$  GHz), contain a number of singularities (sharp features) characterized by effective  $g$ -values  $g_{\text{eff}} = 2.0$ , 2.8 and 5.9. There has been a serious controversy concerning the adequate choice of the corresponding spin Hamiltonian, as well as alternative concepts of several sites or a single type of site with broadly distributed fine-structure (FS) parameters responsible for these features (Chepeleva 1972, Nicklin *et al* 1973, Griscom 1980, Čugunov and Kliava 1982, 1984, Iton *et al* 1983, Kliava *et al* 1984, Brodbeck and Iton 1985, Kliava 1986, 1988). At present it seems to be generally acknowledged that the correct choice is the 'rhombic' spin Hamiltonian

$$\mathbf{H} = g\beta\mathbf{B} \cdot \mathbf{S} + D[\mathbf{S}_z^2 - \frac{1}{3}S(S+1)] + E(\mathbf{S}_x^2 - \mathbf{S}_y^2) \quad (1)$$

where all symbols have their usual meanings and  $S = \frac{7}{2}$  (Čugunov and Kliava 1982, Brodbeck and Iton 1985, Kliava 1986, 1988). On the basis of this spin Hamiltonian, Čugunov and Kliava (1982), Kliava *et al* (1984) and Brodbeck and Iton (1985) have demonstrated that the so-called U spectrum (in view of its *ubiquity*), most frequently observed in the X-band ESR of  $Gd^{3+}$  in various disordered solids, arises from a single site of rhombic symmetry with distributed FS parameters. It should be noted, however,

that substantially different numerical estimates of the FS parameters have been obtained by these workers. Čugunov and Kliava (1982, 1984) have attributed the U spectrum to the strong ligand field category ( $D_0 \approx 0.5 \text{ cm}^{-1}$ ) whereas Brodbeck and Iton (1985) have demonstrated that spectra of this type are characteristic rather for the intermediate ligand-field case, with  $D_0 \approx 0.05 \text{ cm}^{-1}$  (the zero subscript denotes average values).

Beginning with the detailed  $\text{Gd}^{3+}$  ESR study in soda-silica glass (Nicklin *et al* 1973), attention has been drawn to transformations of the rare-earth ESR spectral shapes in glasses as the microwave frequency is switched from X band to other bands (Čugunov and Kliava 1984, Brodbeck and Iton 1985). These transformations yield very important data indispensable for a quantitative estimation of the spin-Hamiltonian parameters from the experimental ESR spectra.

In this paper, some results of more systematic ESR studies of  $\text{Gd}^{3+}$  and  $\text{Eu}^{2+}$  ions in glasses in various microwave bands are presented. Particular emphasis is put on lower-frequency bands, where the most significant transformations of the ESR spectral shapes for the rare-earth ions in glasses occur.

## 2. Samples and experimental results

Glasses of molar compositions  $\text{BaO-P}_2\text{O}_5$  and  $\text{MgO-P}_2\text{O}_5$  with 0.2 wt%  $\text{Gd}_2\text{O}_3$  as well as  $\text{SiO}_2\text{-Al}_2\text{O}_3$  with 1.5 wt%  $\text{Eu}_2\text{O}_3$  have been chosen for this study.

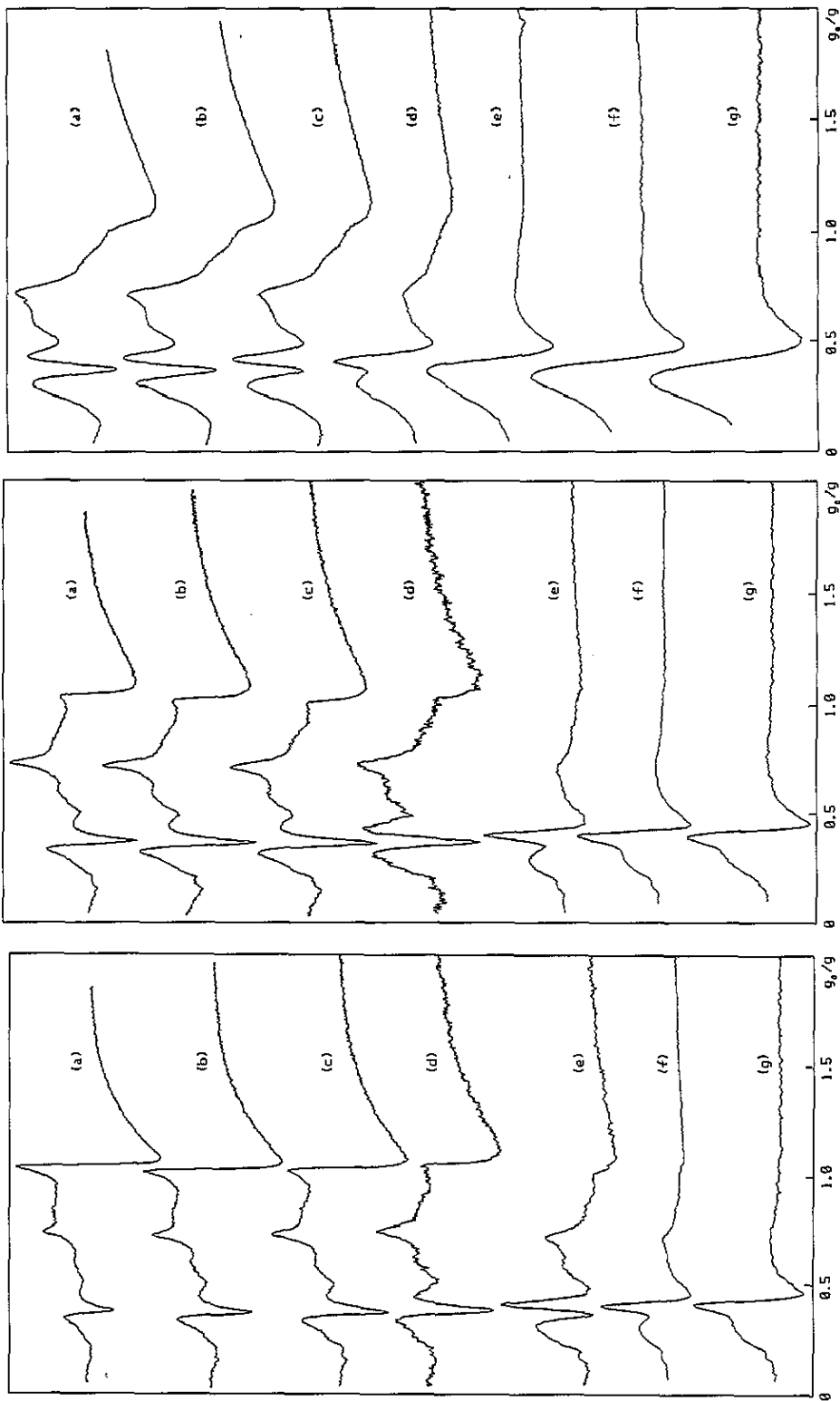
Spectra have been recorded in the following microwave bands:  $S_1$  ( $\nu = 2.7 \text{ GHz}$ ),  $S_2$  ( $\nu = 3.5 \text{ GHz}$ ),  $C_1$  ( $\nu = 4.6 \text{ GHz}$ ),  $C_2$  ( $\nu = 6.9 \text{ GHz}$ ),  $X_1$  ( $\nu = 8.5 \text{ GHz}$ ),  $X_2$  ( $\nu = 9.5 \text{ GHz}$ ) and  $X_3$  ( $\nu = 10.3 \text{ GHz}$ ). A homodyne ESR spectrometer with 100 kHz modulation made by two of us (Čugunov and Mednis 1989) has been used, with a number of klystron generators and appropriate waveguide or coaxial tracts. Measurements have been carried out at room temperature; however, we have verified that no variations in the spectral shapes occur as the temperature is lowered to 77 K.

Spectra have been recorded in a frequency-normalized digital form in order to facilitate a comparison between spectral shapes obtained in various bands. In figures 1-3 the spectra are displayed as functions of  $g_0/g$ , where  $g_0$  is the  $g$ -factor for the free electron:

$$g = h\nu_c/\beta B_r. \quad (2)$$

Here  $\nu_c$  is the microwave frequency and  $B_r$  is the resonance magnetic field.

It is seen that the X-band ESR spectra of rare-earth ions in all three glasses can be classified as typical U spectra, with the most conspicuous sharp feature at  $g_{\text{eff}} \approx 6.0$ . At lower-frequency bands this feature gradually vanishes and another broader feature centred at  $g_{\text{eff}} \approx 5.0$  arises. At the  $C_1$  band this feature predominates in all three cases (see figures 1-3). The striking resemblance between the spectra of *different* rare-earth ions (or of the same ion in *different* glassy matrices) taken at two *different*, appropriately chosen microwave frequencies  $\nu_1$  and  $\nu_2$  is somewhat unexpected. Several examples of such a correspondence are shown in figures 4 and 5. After normalizing such pairs of spectra with respect to both the maximum intensity of absorption and the microwave frequency, they coincide almost completely. The worse agreement between the spectral shapes of  $\text{Gd}^{3+}$  and  $\text{Eu}^{2+}$  in the region around  $g \approx 2.0$  is probably due to spin-spin interactions which begin to alter the ESR spectral shapes of rare-earth ions as their concentration exceeds approximately 0.5 wt%.



**Figure 1.** Room-temperature frequency-normalized ESR spectra of  $Gd^{3+}$  in  $MgO-P_2O_5$  glass for various microwave frequencies: curve (a) 10.3 GHz; curve (b) 9.5 GHz; curve (c) 8.5 GHz; curve (d) 6.9 GHz; curve (e) 4.6 GHz; curve (f) 3.5 GHz; curve (g) 2.7 GHz.

**Figure 2.** Room-temperature frequency-normalized ESR spectra of  $Gd^{3+}$  in  $BaO-P_2O_5$  glass for various microwave frequencies: curve (a) 10.3 GHz; curve (b) 9.5 GHz; curve (c) 8.5 GHz; curve (d) 6.9 GHz; curve (e) 4.6 GHz; curve (f) 3.5 GHz; curve (g) 2.7 GHz.

**Figure 3.** Room-temperature frequency-normalized ESR spectra of  $Eu^{2+}$  in  $SiO_2-Al_2O_3$  glass for various microwave frequencies: curve (a) 10.3 GHz; curve (b) 9.5 GHz; curve (c) 8.5 GHz; curve (d) 6.9 GHz; curve (e) 4.6 GHz; curve (f) 3.5 GHz; curve (g) 2.7 GHz.

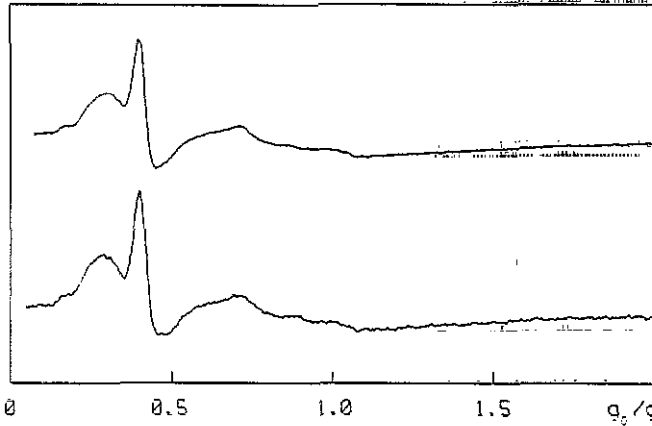


Figure 4. Comparison of the ESR spectra of  $Gd^{3+}$  in  $MgO-P_2O_5$  glass at 3.5 GHz (upper curve) and in  $BaO-P_2O_5$  glass at 4.6 GHz (lower curve). The spectra have been normalized with respect to both the maximum absorption intensity and the microwave frequency.

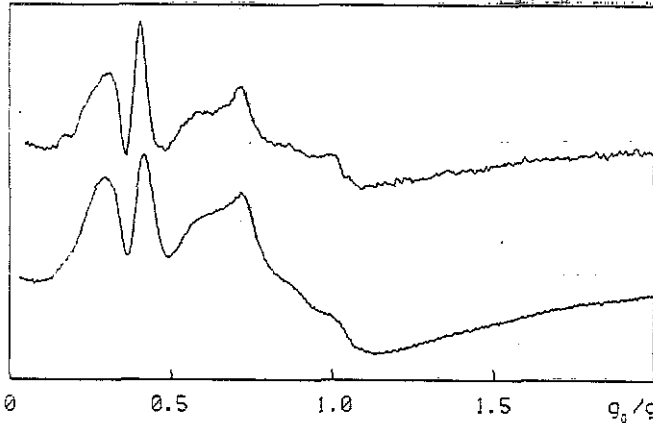


Figure 5. Comparison of the normalized (see the caption for figure 4) ESR spectra of  $Gd^{3+}$  in  $MgO-P_2O_5$  glass at 4.6 GHz (upper curve) and  $Eu^{2+}$  in  $SiO_2-Al_2O_3$  glass at 8.5 GHz (lower curve).

The most significant feature of the coincidence of the spectral shapes is the invariability of the *isospectral frequency ratio* (IFR)

$$r = \nu_1 / \nu_2. \quad (3)$$

For instance, for  $Gd^{3+}$  in  $MgO-P_2O_5$  and  $BaO-P_2O_5$  glasses (see figure 4) one obtains  $2.7/3.5 \approx 0.77$ ,  $3.5/4.6 \approx 0.76$  and  $6.9/9.5 \approx 0.73$ . Thus, the average IFR in this case is

$$\left\langle r \left( \frac{MgO-P_2O_5 : Gd_2O_3}{BaO-P_2O_5 : Gd_2O_3} \right) \right\rangle \approx 0.75. \quad (4)$$

Analogously, in the case of  $Gd^{3+}$  in  $MgO-P_2O_5$  glass and  $Eu^{2+}$  in  $SiO_2-Al_2O_3$  glass the IFRs are  $3.5/6.9 \approx 0.51$  and  $4.6/8.5 \approx 0.54$ , the average value being

$$\left\langle r \left( \frac{MgO-P_2O_5 : Gd_2O_3}{SiO_2-Al_2O_3 : Eu_2O_3} \right) \right\rangle \approx 0.53. \quad (5)$$

A comparison of the ESR spectra series for  $Gd^{3+}$  in  $BaO-P_2O_5$  glass and  $Eu^{2+}$  in  $SiO_2-Al_2O_3$  glass yields the IFRs  $4.6/6.9 = 0.67$  and  $6.9/9.5 = 0.73$ . So,

$$\left\langle r \left( \frac{BaO-P_2O_5 : Gd_2O_3}{SiO_2-Al_2O_3 : Eu_2O_3} \right) \right\rangle \approx 0.70. \quad (6)$$

One can readily verify that these IFR values are mutually consistent. Indeed,

$$\begin{aligned} \left\langle r \left( \frac{MgO-P_2O_5 : Gd_2O_3}{SiO_2-Al_2O_3 : Eu_2O_3} \right) \right\rangle : \left\langle r \left( \frac{BaO-P_2O_5 : Gd_2O_3}{SiO_2-Al_2O_3 : Eu_2O_3} \right) \right\rangle &\approx 0.76 \\ &\approx \left\langle r \left( \frac{MgO-P_2O_5 : Gd_2O_3}{BaO-P_2O_5 : Gd_2O_3} \right) \right\rangle. \end{aligned} \quad (7)$$

### 3. Theory

In order to account for the above observations, we point out that a coincidence of normalized ESR spectral shapes implies that, for the two spectra at equal frequency-normalized resonance fields  $B_r/h\nu$ , the normalized absorption intensities are the same. Implications of the IFR can be conveniently analysed within the eigenfield formalism put forward by Belford *et al* (1973). In the eigenfield problem the resonance magnetic fields are solutions of a generalized eigenvalue equation

$$\mathbf{A}_F Z = B_r \mathbf{A}_G Z \quad (8)$$

where  $\mathbf{A}_F = h\nu \mathbf{1} \otimes \mathbf{1} - \mathbf{F} \otimes \mathbf{1} + \mathbf{1} \otimes \mathbf{F}^+$  and  $\mathbf{A}_G = \mathbf{G} \otimes \mathbf{1} - \mathbf{1} \otimes \mathbf{G}^+$  are  $n^2 \times n^2$  Hermitian matrices (in the absence of hyperfine structure),  $n = 2S + 1$ ,  $\mathbf{F}$  and  $\mathbf{G}$  are  $n \times n$  Hermitian matrices, respectively, for the FS and Zeeman operator in the spin Hamiltonian,  $Z$  is the eigenvector defined as a direct product of two eigenvectors of the Schrödinger equations

$$Z = u \otimes v^+ \quad (9)$$

$$\mathbf{H}u = Eu \quad (10)$$

$$v^+ \mathbf{H} = (E - h\nu)v^+$$

and  $\mathbf{1}$  is an  $n \times n$  unit matrix. Superscripts +, as usual, mark Hermite conjugated vectors and matrices.

Consider a pair of frequency-normalized equations of type (8) corresponding to two different microwave frequencies  $\nu_1$  and  $\nu_2$  and two different ligand-field operators  $\mathbf{F}_1$  and  $\mathbf{F}_2$ :

$$(1/h\nu_1)\mathbf{A}_{F_1}Z_1 = (B_{r_1}/h\nu_1)\mathbf{A}_GZ_1 \quad (1/h\nu_2)\mathbf{A}_{F_2}Z_2 = (B_{r_2}/h\nu_2)\mathbf{A}_GZ_2. \quad (11)$$

For the  $^8S_{7/2}$  ions  $Gd^{3+}$  and  $Eu^{2+}$  the  $g$ -values are nearly isotropic and closely approach the free-electron  $g$ -value. Therefore, the  $\mathbf{A}_G$  matrices in both equations (11) are one and the same. Pre-multiplying equations (11) by  $Z_1$  and  $Z_2^+$ , respectively, and subtracting the second equation from the first, we get

$$(1/h\nu_1)Z_1^+ \mathbf{A}_{F_1} Z_1 - (1/h\nu_2)Z_2^+ \mathbf{A}_{F_2} Z_2 = (B_{r_1}/h\nu_1)Z_1^+ \mathbf{A}_G Z_1 - (B_{r_2}/h\nu_2)Z_2^+ \mathbf{A}_G Z_2. \quad (12)$$

Coincidence of normalized spectral shapes corresponding to (11) means that both the frequency-normalized resonance fields and the intensity-normalized transition probabilities in these two cases are equal to each other:

$$B_{r_1}/h\nu_1 = B_{r_2}/h\nu_2 = b_r \quad (13)$$

and

$$|\boldsymbol{\mu}Z_1|^2 = |\boldsymbol{\mu}Z_2|^2. \quad (14)$$

Here  $\boldsymbol{\mu}$  is a row vector containing all the rows of the  $n \times n$  matrix of the perturbation operator

$$\vec{\boldsymbol{\mu}} = g\beta\mathbf{B}_1 \cdot \mathbf{S} \quad (15)$$

one after the other (Belford *et al* 1973),  $\mathbf{B}_1$  being the microwave magnetic field:  $\mathbf{B}_1 \perp \mathbf{B}$ .

Since the eigenvectors are normalized, i.e.

$$Z^+Z = \sum_{\gamma=1}^n |Z_{\gamma}|^2 = \left( \sum_{i=1}^n u_i u_i^+ \right) \left( \sum_{j=1}^n v_j v_j^+ \right) = 1 \quad (16)$$

it is seen that  $Z_1 = Z_2$ . Then (12) becomes

$$Z_1^+ [(1/h\nu_1)\mathbf{A}_{F_1} - (1/h\nu_2)\mathbf{A}_{F_2}]Z_1^+ = b_r(Z_1^+\mathbf{A}_G Z_1 - Z_1^+\mathbf{A}_G Z_1) = 0. \quad (17)$$

As  $Z_1$  is not equal to zero, we get

$$\mathbf{A}_{F_1}/\mathbf{A}_{F_2} = \nu_1/\nu_2 = r. \quad (18)$$

Therefore the ratio of matrices  $\mathbf{A}_{F_1}$  to  $\mathbf{A}_{F_2}$  is equal to the IFR.

It can be shown (see appendix) that, if (18) holds, then

$$\mathbf{F}_1/\mathbf{F}_2 = \nu_1/\nu_2. \quad (19)$$

#### 4. Discussion

One may compare the series of spectra shown in figures 1–3 with a series of computer-generated spectra in figure 15 of the paper by Brodbeck and Iton (1985). It is seen that only in the case of  $\text{Gd}^{3+}$  in  $\text{MgO-P}_2\text{O}_5$  glass are the transformations of the spectral shapes at different microwave frequencies more or less consistent with the results of computer simulations (see figure 1). However, we draw the reader's attention to the fact that the computer-generated spectra do not exhibit the  $g_{\text{eff}} \approx 4.0$  singularity as well as the low-field shoulder of the  $g_{\text{eff}} \approx 6.0$  singularity, which are always present in the experimental spectra (Nicklin *et al* 1973, Čugunov and Kliava 1982) and the spectra shown in figures 1(b), 2(b) and 3(a) of the present paper.

According to Brodbeck and Iton (1985), the sharp feature at  $g_{\text{eff}} \approx 6.0$  arises from a 'forbidden' transition between the lowest and the second-lowest Kramers doublets (for  $D > 0$ ). The  $g_{\text{eff}} \approx 5.0$  feature is believed to arise from transitions within the second-lowest (for  $D > 0$ ) Kramers doublet (Garif'yanov and Zaripov 1964, Čugunov and Kliava 1982).

In principle, it is known that singularities (more or less sharp features) in ESR spectra of disordered solids occur at stationary points of a hypersurface  $B_r = \text{constant}$  (Kliava 1986, 1988). It is interesting to note that the  $g_{\text{eff}} \approx 5.0$  feature is substantially broader

than the  $g_{\text{eff}} \approx 6.0$  feature. Such a distinction can be explained by the fact that, as Brodbeck and Iton (1985) have demonstrated, the  $g_{\text{eff}} \approx 6.0$  singularity corresponds to a point of the hypersurface  $B_i(D, E, \vartheta, \varphi) = \text{constant}$ , which is stationary with respect to variations in both the orientations of paramagnetic ions, and the FS parameters (a 'non-crystalline' stationary point (Kliava 1986, 1988)). On the other hand, the  $g_{\text{eff}} \approx 5.0$  singularity corresponds to a point which is stationary only with respect to variations in the orientations of ions (a 'polycrystalline' stationary point). Therefore this singularity is broadened owing to distributions of the FS parameters.

As far as the IFR is concerned, equation (19) states that, for a pair of ions which give rise to coinciding normalized ESR spectra, the ratio of each pair of equivalent parameters (corresponding to the same equivalent operator) is one and the same and equals the IFR.

In the general case the ligand-field operator in the spin Hamiltonian has the form (Abragam and Bleaney 1970)

$$\mathbf{F} = \sum_n \sum_{m=-n}^n B_n^m O_n^m = \sum_n \sum_{m=-n}^n A_n^m \langle r^n \rangle \alpha_n O_n^m \quad (20)$$

where  $B_n^m$  are FS parameters and  $O_n^m$  are equivalent operators ( $B_2^0 = D/3$ ,  $B_2^2 = E$ , etc),  $\alpha_n$  are factors of proportionality and  $\langle r^n \rangle$  are the  $n$ th moments of density distributions for unpaired electrons of the paramagnetic ions:

$$\langle r^n \rangle = \int_0^\infty r^{n+2} |R_{nl}^2| dr \quad (21)$$

where  $R_{nl}$  is a radial part of the wavefunction ( $l = 2$  and  $3$  for d and f electrons, respectively).

The parameters  $B_n^m$  and  $A_n^m$  for different  $n$  depend in a different manner on the distance  $R_j$  between the paramagnetic ion and its ligands. For instance, in the point charge model (Taylor and Darby 1972),

$$A_n^m = \frac{4\pi}{2n+1} \sum_j \frac{Z_j}{R_j^{n+1}} (-1)^m Y_n^{-m}(\vartheta_j, \varphi_j) \quad (22)$$

where  $Z_j$  and  $\vartheta_j, \varphi_j$ , respectively, are the charge and spherical coordinates of the ligand  $j$  and  $Y_n^m$  are spherical functions. Similarly, according to the superposition model of Newman and Urban (1975), which takes into account overlap and covalency effects,  $A_n^m$  can be written as follows:

$$A_n^m \langle r^n \rangle = \sum_j \bar{A}_n(R_0) \left(\frac{R_0}{R_j}\right)^{t_n} Y_n^{-m}(\vartheta_j, \varphi_j) \quad (23)$$

where the parameters  $\bar{A}_n(R_0)$  and  $t_n$  depend on  $n$ .

It can be concluded that the coincidence of normalized ESR spectra takes place only if predominant contributions to the spectral shapes are brought about by the FS parameters  $B_n^m$  with definite  $n$ -values ( $n = 2, 4$  or  $6$ ). It has been noted by a number of workers (see, e.g., Kliava 1986, 1988) that, in disordered solids, parameters with  $n = 2$  inevitably dominate over those with  $n = 4$  or  $6$ . Therefore, the coincidence of normalized ESR spectra once again justifies the use of the spin Hamiltonian (1), where only  $n = 2$  terms are retained. On the other hand, slight disagreement between a pair of normalized ESR spectral shapes in some cases may give evidence of a contribution from FS terms with higher  $n$  (if other possible explanations, e.g. concentration effects or instrumental errors, are ruled out).



Having determined the IFR, one can make quantitative comparisons of ligand-field parameters for rare-earth ions in different glasses. For instance, it follows from (4) that both the mean values and the distribution widths of  $D$  and  $E$  for  $Gd^{3+}$  in  $MgO-P_2O_5$  glass are about 1.3 times less than those for  $Gd^{3+}$  in  $BaO-P_2O_5$  glass. Thus, a certain correlation between the deviation from cubic symmetry in the environment of rare-earth ions and the ionic radii of next-nearest neighbours is inferred. From (5) and (6) one can conclude that the mean values and the distribution widths of  $D$  and  $E$  for  $Eu^{2+}$  in  $SiO_2-Al_2O_3$  glass are 1.9 times greater than for  $Gd^{3+}$  in  $MgO-P_2O_5$  glass and 1.4 times greater than for  $Gd^{3+}$  in  $BaO-P_2O_5$  glass.

Thus, if the FS parameters are determined for  $Gd^{3+}$  or  $Eu^{2+}$  in a certain glassy matrix (e.g. using computer simulations), these parameters can be readily obtained for all cases, when the IFR can be determined.

### Appendix. Derivation of equation (19)

Starting from equation (18), we rewrite it in terms of the matrix elements (Belford *et al* 1973):

$$A_{ii;jk}^{(1)} = h\nu_1 \delta_{ij} \delta_{lk} - F_{1ij} \delta_{lk} + F_{1kl} \delta_{ij} = rA_{ii;jk}^{(2)} = h\nu_1 \delta_{ij} \delta_{lk} - rF_{2ij} \delta_{lk} + rF_{2kl} \delta_{ij}. \quad (A1)$$

Therefore,

$$F_{1ij} \delta_{lk} - F_{1kl} \delta_{ij} = r(F_{2ij} \delta_{lk} - F_{2kl} \delta_{ij}). \quad (A2)$$

First, consider the case  $i \neq j$  (or  $l \neq k$ ). Then it is immediately seen that

$$F_{1ij} = rF_{2ij} \quad i \neq j. \quad (A3)$$

Now, if  $i = j$  and  $l = k$ , (A1) becomes

$$F_{1ii} - F_{1ii} = r(F_{2ii} - F_{2ii}) \quad (A4)$$

where  $i$  and  $l$  take the values  $1, 2, \dots, 2S + 1$ . Of all the equations (A4), only  $2S$  (e.g. for  $i = 1$  and  $l = 2, \dots, 2S + 1$ ) are linearly independent. The condition that the traces of  $F_1$  and  $F_2$  matrices are equal to zero yields the lacking equation

$$\sum_i F_{1ii} = \sum_l F_{2ll} (=0). \quad (A5)$$

One gets a system of  $2S + 1$  linearly independent equations for  $2S + 1$  unknown values  $F_{1ii}/F_{2ii}$ . Such a system must have a unique solution which, as one can see, is

$$F_{1ii} = rF_{2ii} \quad i = 1, 2, \dots, 2S + 1. \quad (A6)$$

Thus, equation (19) follows immediately.

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