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Clustering and electron spin resonance linewidths in Fe/MgO

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Electron spin resonance linewidths and integrated intensities for the $\frac{1}{2} \rightarrow -\frac{1}{2}$ transition of Fe^{3+} in cubic sites in single-crystal MgO have been examined at 9 GHz between 293 and 90 K for iron concentrations between 100 and 12 900 ppm. Very little of the iron is present in cubic sites as isolated Fe^{3+} ions. It is suggested that this is partly caused by clustering, even at extremely low concentrations. The measured linewidths, which agree well with those reported previously, have been analysed in terms of Kittel and Abrahams' dipolar broadening theory. The highest measured Fe^{3+} concentrations give linewidths comparable with those predicted, but for most samples the measured linewidths are considerably broader than those calculated. This broadening may be caused by interactions with the undetected iron, which accounts for the major fraction. There is no evidence for exchange narrowing of the Fe^{3+} lines for the range of concentrations examined.

1. Introduction

In a previous electron spin resonance (ESR) study of Fe/MgO single crystals, Thorp *et al.* [1] reported that the linewidth was independent of total iron content over the concentration range 140 to 8500 ppm. The authors also noted (on the assumption that the total iron content corresponded to the Fe^{3+} concentration) that the observed ESR linewidths were very much less than those expected on the basis of Van Vleck's dipolar broadening theory [2] and suggested that this discrepancy, coupled with the Lorentzian rather than Gaussian lineshapes, might indicate the presence of exchange narrowing. There is however considerable evidence that the precipitation of impurity clusters is important in Fe/MgO, even at extremely low concentrations, and this could have a significant bearing on the interpretation of ESR data. Various workers [3–6] have studied the precipitation of impurity clusters in magnesium oxide and their observations, together with the more recent work of de Biasi [7] and Weeks *et al.* [8], suggest that considerable clustering of iron impurity ions takes place. In circumstances where clustering takes place, the exchange interactions between neighbouring paramagnetic ions would alter their behaviour in such a way that they would not contribute to the single-ion spectrum, and so clustering could lead to a measured linewidth less than that obtained by calculations based on total dopant concentration. In addition, there is the question of valency: iron in the Fe^{2+} state will not contribute to the Fe^{3+} spectrum and so a mixture of valency states could lead to a further narrowing of the linewidth.

In an attempt to resolve this problem we have made more detailed studies, both theoretical and experimental, of the ESR spectrum of iron-doped magnesia and, in particular, have not only remeasured the linewidth but also made an estimate of the number of spins actually contributing to the Fe^{3+} line (by comparison with a standard sample). This measured concentration has then been used to calculate the linewidth, for comparison with experiment. In this new estimation of the predicted linewidths, use has been made of the Kittel and Abrahams development [9] of Van Vleck's model for dipolar broadening since this is felt to be the more appropriate approach in view of the highly dilute nature of the paramagnetic species in the samples investigated.

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2. Experimental techniques

Single crystals, grown by arc-fusion, were obtained from W. and C. Spicer Ltd (Cheltenham). The iron concentration ranged from a nominal zero (MgO = 99.99%, the 4N sample) to 12900 ppm, the values quoted by the manufacturer having been determined to ± 2% by X-ray fluorescence analysis. With the exception of the 4N sample, which was a "cloudy" white, the crystals were clear, but coloured green to varying degrees, the most heavily doped being the darkest coloured, and *vice versa.* Thin slices a few millimetres square and approximately 0.3 mm thick were cleaved from these crystals for examination in the spectrometer.

In all, seven samples were investigated, the spin concentration and linewidth being determined first for samples in the "as-received" state, and then after the samples had been "solution treated". The solution treatment involved heating the samples to 1673 K in a platinum boat in oxygen at atmospheric pressure for 24 h, followed by quenching to room temperature in oxygen. This heat treatment was intended to disperse the dopant ions as homogeneously as possible, whilst the oxygen atmosphere minimized the conversion of Fe^{3+} to Fe^{2+} [6, 10].

A Varian 9 GHz V-4502 spectrometer system was used. For the determination of linewidths, spectra were obtained with the sample placed at the centre of a rectangular cavity resonating in the TE_{102} mode, the magnetic field being modulated at 100 kHz. The field calibration for these spectra was obtained by using a proton resonance magnetometer whose probe was placed in the magnet gap adjacent to the cavity.

The spin counts were obtained by the use of a dual cavity which was in effect two single rectangular cavities (as described above) joined end to end and resonating in a TE_{104} mode. This cavity had two sets of modulation coils, one set for each half. These coils could be driven at different frequencies, and the whole was so designed that if two different samples were placed one in each half of the cavity (at the $\frac{1}{4}$ and $\frac{3}{4}$ positions along the length) neither was affected by the other's modulation field. In practice one half of the cavity was modulated at 100 kHz, and the other half at 400 Hz. The absorption due to both samples was detected at the same crystal, but since the modulation frequencies were different the two absorption signals could be electronically separated and amplified. The signals were then displayed alongside each other in derivative form on a two-channel chart recorder. The technique involved placing a sample whose spin density was known (in this case the Varian 0.1% pitch in KCl standard) in one half of the cavity and the unknown sample in the other. Modulation and amplification were then selected to produce signals of comparable height, and the spectra recorded. The sample positions were then exchanged, and the spectra re-recorded, the only change being in the amplification. The recorder gain having been noted in each case, it was then possible to calculate the spin density for the unknown sample.

Some spectra were investigated over a range of temperatures with the use of a Varian 4540 variable temperature control unit by means of which it was possible to maintain the temperature of the sample at any desired value between 90 and 293 K (within a few degrees). The sample temperature was measured using a copper–constantan thermocouple, the cold junction of which was placed immediately adjacent to the sample.

3. Experimental results

The spectrum for Fe^{3+} in cubic sites is well established [11]. The example shown in Fig. 1 was recorded at room temperature with the applied field directed along a ⟨1 0 0⟩ axis. The centre line is almost isotropic whilst the fine structure lines are highly anisotropic (cf. [1]). Accepted values for the spin–Hamiltonian parameters are $g = 2.0033$ and $a = 203.8 \times 10^{-4}\,\mathrm{cm}^{-1}$ [12].

Preliminary investigations were carried out with each sample, both in the as-received state and after solution treatment, to search for other paramagnetic species besides Fe^{3+} in cubic sites, and also to check that the strong spectrum exhibited by each sample centred on $g \simeq 2$ was indeed due to Fe^{3+} in cubic states. These preliminary investigations were carried out using the single cavity, the field being swept over a range of approximately 0.50 T about a centre value of about 0.32 T. The only sample which showed any appreciable amount of impurity other than iron was the 4N sample which gave a relatively strong line at $g = 1.980$, presumed to be due to Cr^{3+} in cubic sites [12]. After solution treatment the intensity of the Fe^{3+} $\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transition was considerably increased relative to this line. This is illustrated in Fig. 2, where both the spectra shown are from the same sample, and it is interesting to note that whilst the heat treat-

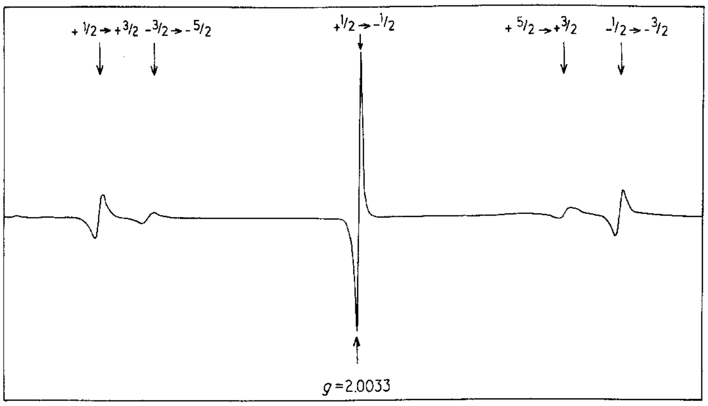

Figure 1 Spectrum of Fe^{3+} in cubic sites. As-received sample C1, 310 ppm Fe; field parallel to [100], frequency 9.20 GHz; temperature 291 K. Centre line g-value is 2.0033.

ment has considerably enhanced the central Fe^{3+} transition, it has apparently had little or no effect on the other Fe^{3+} transitions. It is worth noting also that none of the fine structure lines recorded came up to the theoretical integrated intensity when compared with the central Fe^{3+} transition; that the fine structure lines were relatively more intense in the nominally least heavily doped crystals, becoming even less intense upon solution treatment; and that after solution treatment samples E1 and F1 showed no sign of fine structure at all.

Many of the samples showed a group of two or three very weak lines at a field value of approximately 0.1 T. It was difficult to assign these lines with certainty, but an estimate of the g-value was obtained by comparison with the cubic-site Fe^{3+} spectrum. This comparison gave $g \simeq 6$ and the lines are therefore tentatively assigned to Fe^{3+} in lower symmetry sites [8, 13]. The amplitude of these lines increased with solution treatment, but was always extremely small compared with the cubic-site spectrum. None of the samples examined showed any sign of Fe^{2+} at temperatures down to 90 K (in view of the short relaxation time of this ion, considerably lower temperatures would be required for its detection).

The linewidth measurements were made on the

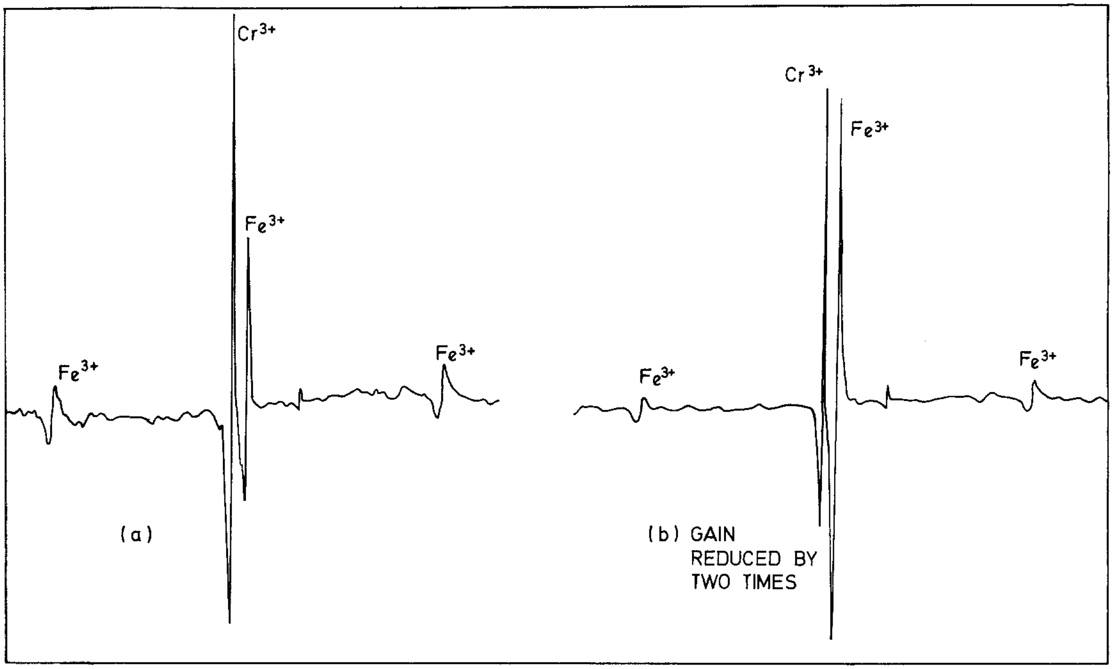

Figure 2 Relative intensities of the Fe^{3+} spectrum (a) before and (b) after heating in oxygen at 1400° C for 24 h; 4 N sample.

TABLE I Measured linewidths for the Fe^{3+} $\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transition. Field applied along [100] at 9.2 GHz and at room temperature

Sample	Nominal concentration (ppm wt)	Linewidth ΔH_{ms} (mT)	
		As-received	Solution-treated
A1	4N	0.49	0.58
C1	310	0.54	0.64
D1	2300	0.50	0.86
E1	4300	0.53	1.03
F1	8500	0.69	1.16
G1	11 900	0.63	0.98
H1	12 900	0.57	1.11

$\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transition, with the applied field directed along a ⟨1 0 0⟩ direction, the width ΔH_{ms} being the separation between the peaks of the derivative curve. Values of the measured widths are given in Table I, and it can be seen that the linewidths appear to be independent of the "nominal" dopant concentration. (The "nominal" concentration is that quoted by the manufacturer and is given in ppm by weight.) For the as-received samples ΔH_{ms} agreed well with values reported previously [1] and in every case ΔH_{ms} was increased by solution treatment, in some cases by a factor of almost two times.

An example of the output from the dual-channel system used to count spins is shown in Fig. 3. In order to estimate the number of spins in the unknown sample, it was necessary to record two such spectra, giving a total of four curves. All four curves were first integrated numerically, and the absorption curves obtained were then integrated using Simpson's rule to give the area under each. In practice the integrations were carried out over half the derivative and the final result doubled, as the lineshapes were reasonably symmetrical. The spin density for the sample was then obtained from the equation (derived in [14])

$$N_B = N_C \left(\frac{A_{B1}}{G_{B1}} \frac{A_{B2}}{G_{B2}} \frac{G_{C1}}{A_{C1}} \frac{G_{C2}}{A_{C2}} \right)^{1/2} \qquad (1)$$

where the subscripts B and C refer to "unknown" and "standard" respectively, subscripts 1 and 2 refer to channels 1 and 2, N is the number of spins per unit volume, A the area under the absorption curve and G the amplifier/recorder gain.

Values of spin densities obtained in this way are listed in Table II. If the relative intensities of the fine structure line obeyed theory, it would be possible to use the figures of Table II to derive reasonable figures for the number of Fe^{3+} ions in cubic sites in each sample. However, as we have seen above, the relative integrated intensities of the fine structure lines are in practice trivial compared with that of the $\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transition. Allowing for the inaccuracies inherent in the method, it is therefore felt reasonable to consider that the figures in Table II represent the number of Fe^{3+} ions per unit volume of sample, to within a factor of 2 or 3. For easier comparison with the nominal impurity concentration the spin density figures have been converted to impurity ppm by weight and these figures are also given in Table II.

4. Discussion

4.1. Fe^{3+} concentrations

Since factors such as linewidth depend upon concentration it is essential to consider first of all the

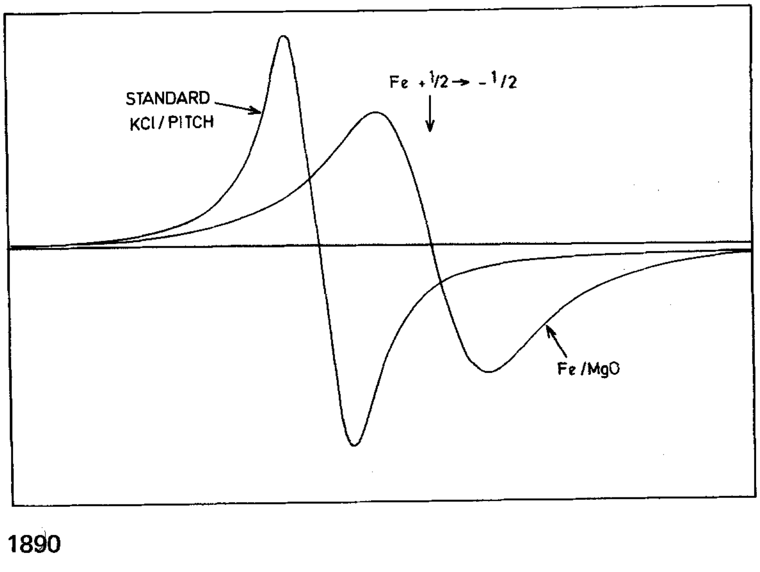

Figure 3 Dual cavity spectra of standard and Fe/MgO samples (pens offset, so the *g*-values are not directly comparable).

TABLE II Measured concentrations of isolated Fe^{3+} ions

Sample	Nominal concentration (ppm wt)	As-received		Solution-treated	
		Spin density ($\times 10^{15}\ mm^{-3}$)	ppm (wt)	Spin density ($\times 10^{15}\ mm^{-3}$)	ppm (wt)
A1	4N	0.79	20	4.26	110
C1	310	2.31	60	8.36	216
D1	2300	2.40	62	18.20	471
E1	4300	1.70	44	15.60	404
F1	8500	1.07	28	14.70	380
G1	11900	1.21	31	19.20	497
H1	12900	0.79	20	12.40	321

question of the numbers of isolated Fe^{3+} ions in the sample. It can be seen from Table II that in every case the measured quantities are considerably less than the nominal concentrations; that in every case solution treatment increases the numbers of isolated Fe^{3+} ions; and that the variation of numbers of isolated ions with nominal concentration follows the same trend (Fig. 4) in the as-received and solution-treated states. When compared with the total iron content of the samples the quantity of isolated Fe^{3+} ions is remarkably small. Presumably the iron which is not included in the spectrum examined is either:

(a) not in the Fe^{3+} state,

(b) not in cubic sites,

(c) clustered in such a way that it does not contribute to the isolated-ion signal.

Evidence that not all the Fe^{3+} ions are in cubic sites has been suggested by the lines at $g \simeq 6$ in many of the spectra. These lines are thought to be Fe^{3+} ions in sites of other symmetry.

According to the theory of the oxidation–reduction behaviour of iron in magnesium oxide, at room temperature most of the iron should be Fe^{3+} for the concentrations investigated, although the fraction does vary with concentration [6, 10]. Heating the samples should increase the amount of Fe^{2+}, although this increase can be kept to a minimum by carrying out the heating in an oxygen atmosphere. We should therefore obtain a decrease

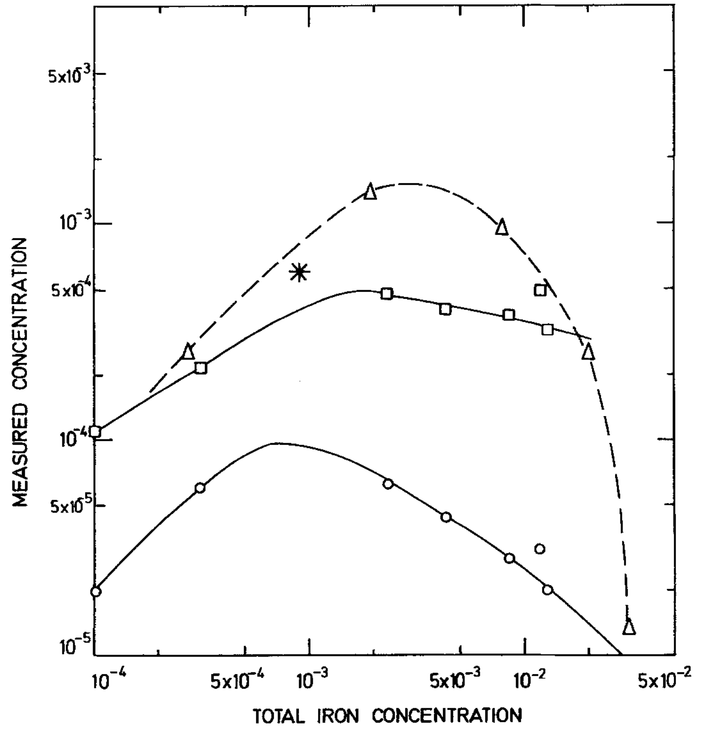

Figure 4 Variation of measured concentration of isolated Fe^{3+} ions versus total iron concentration (all ppm by weight). ○, As-received samples; □, solution-treated samples; △, de Biasi [7]; * Wicks and Lewis [15].

in the spectral integrated intensity after we have quenched the samples from 1673 K. In every case we obtain an increase, for some samples by a factor of ten times. Presumably, although we are converting some Fe^{3+} to Fe^{2+}, we are at this temperature dissolving clusters of ions which previously did not contribute to the isolated Fe^{3+} signal, and which, during heat treatment, become isolated and contribute. It can be seen from Fig. 4 that for the samples with nominal iron concentration > 2000 ppm the free-ion spectrum decreases in intensity with increased concentration. This type of behaviour has been reported previously by de Biasi [7] and we have presented his data on the graph in Fig. 4 for comparison. Whilst the behaviour of his samples exhibits a much sharper peak than ours, the order of magnitude of spectral intensities is in general very similar, and the trends with increasing concentrations are likewise similar.

It was suggested by de Biasi that the decrease in the number of isolated ions with increased iron concentration for all but the lowest concentrations is due to clustering. Whilst both the slope and curvature of our plots are considerably less than those presented by de Biasi, the similarities suggest that the overall behaviour of our samples is also dictated by non-random clustering effects. Wicks and Lewis [15] have also reported a measurement of Fe^{3+} isolated-ion spectral intensity, which they compared with total iron concentration in their sample. This value is plotted on Fig. 4 and it can be seen that there is again reasonable agreement with our measured values for similar concentrations.

Our measurements relating to the isolated Fe^{3+} spectrum also appear to be in overall agreement with those reported by Weeks *et al.* [8]. However, at the gains used in our measurements we did not detect either the lines which they ascribe tentatively to Fe^{3+}/vacancy trimers, or the broader ferrimagnetic resonances centred around $g = 2$, even after solution treatment.

There are two other points to be made in this context. One is that although measurement of absolute spin densities is notoriously unreliable, we have found the results for different samples of the same nominal concentration to be reproducible to within 10%. The other is that we have checked the spin count values measured for samples C1 and E1 (as listed in Table II) by comparing the two samples with each other in the dual cavity, rather than with the standard. The ratio of spin densities measured in this way agrees to within 6% with the ratio obtained by taking the figures in Table II.

We conclude that the measured values of the number of isolated ions contributing to the Fe^{3+} ESR spectrum are not unreasonable to within a factor of two and, further, that the iron which does not contribute to this spectrum is either in the Fe^{2+} state, or is Fe^{3+} in some form of cluster.

4.2. Linewidth considerations

We turn now to the question of linewidths and consider first of all the calculations of linewidths. In previous work on Fe/MgO [1] the linewidth data was interpreted in terms of Van Vleck's Gaussian dipolar broadening [2]. The discrepancy between the observed and calculated linewidths and lineshapes was taken to indicate exchange narrowing. Similar conclusions have been drawn in studies on Cr/MgO [16] and Co/MgO [17]. However, materials to which Van Vleck's theory can be reasonably applied [18] are in general paramagnetic salts, the *most* dilute cases being those where waters of hydration are present. In these salts the ions are at separations of next-nearest-neighbour magnitude. When the paramagnetic species are brought closer, for example, by removing the water of hydration, exchange forces become stronger and the ESR linewidths become considerably narrowed. When the water of hydration is present the increased separation is sufficient to decrease the exchange narrowing considerably. The theory provides a reasonable fit with experiment, as is illustrated in Table III where some of Van Vleck's data are presented. If we dilute these salts the exchange effects become negligible, as the exchange interaction falls off with separation more rapidly than the dipolar interaction.

TABLE III Some of Van Vleck's dipolar line broadening data [18]

Substance	Linewidths $\Delta H_{1/2}$ (mT)	
	Experimental	Calculated
$MnCl_2 \cdot 4H_2O$	141	153
$MnCl_2$	75	295
$MnSO_4 \cdot 4H_2O$	115	156
$MnSO_4$	66.5	352
$Mn(NO_2)_2 \cdot 6H_2O$	121	103.3
MnF_2	47	702

Clearly our samples fall into the "very dilute" range and for this reason we have used the Kittel and Abrahams [9] result to calculate linewidths. The theoretical peak-to-peak linewidth (in tesla) is given by

$$H_{\rm ms} = 1.955 f^{1/2} \langle \Delta\nu^2 \rangle^{1/2} \frac{\partial H}{\partial \nu}. \qquad (2)$$

Here f is the cation site fraction of dopant ions. A small error may arise as a result of the assumption that the line is a truncated Lorentzian shape, but in view of the relative uncertainty of the concentration measurement, we may reasonably ignore this error. We see immediately from Equation 2 that:

(a) The expected linewidth will be directly proportional to concentration, since $\langle \Delta\nu^2 \rangle$ contains a term in f. This is in direct contrast with the result

$$\Delta H_{\rm ms} \propto f^{1/2}$$

which is obtained using the Gaussian relationship [2].

(b) The predicted linewidth will be very much smaller than that calculated previously, since $f \ll 0.01$.

Values of $\Delta H_{\rm ms}$ calculated using the measured concentrations of isolated Fe^{3+} ions are listed in Table IV where they are compared with experimental values for samples before and after heat treatment. Values calculated using the Gaussian relationship and nominal concentrations are also shown for comparison. Those samples which have the highest measured concentrations exhibit linewidths which are of the same order of magnitude as the calculated linewidths, but in the majority of cases the measured linewidths are in excess of the calculated values, in some cases by as much as thirty times. In addition, the measured linewidths do not appear to follow the predicted concentration dependence since the linewidth only increases by a factor of about two times for a concentration increase of thirty times. Without more information regarding the states and sites of the majority of the iron it is difficult to be specific, but the line broadening is presumably a result of the interaction between the isolated Fe^{3+} ions and both the clusters of Fe^{3+} and any Fe^{2+} ions present.

Whilst the Kittel and Abrahams' model does not fit too well, it is more appropriate and fits better than the Van Vleck model; in addition, since the measured linewidths are in all cases greater than the calculated linewidths, exchange narrowing need no longer be postulated in order to fit the calculated linewidths.

4.3. Fine structure intensities

Finally, we would mention the behaviour of the fine structure lines. According to theory [19] relative integrated intensities of the various transitions for $S = 5/2$ ions in cubic sites in a strong applied field should be as outlined in Table V: in practice all the workers who have reported the fine structure integrated intensities have found them to be considerably weaker than this. Low [11] suggested that this could be due partly to disorder in the crystal, such as randomly distributed vacancies, or excess oxygen ions. That these may be contributory factors seems reasonable in view of our experience with the spectra reported here, and also those which we have recorded on other occasions, because:

(a) The relatively most intense fine structure is always associated with the lower doping concentrations of iron. Assuming that Reppich [6] is correct then the fractional concentration of Fe^{3+} will increase with increasing iron concen-

TABLE IV Comparison of calculated and measured linewidths, $\Delta H_{\rm ms}$

Sample	As-received			Solution-treated		
	Measured concentration (cation site fraction × 10^4)	Linewidths (mT)		Measured concentration (cation site fraction × 10^4)	Linewidths (mT)	
		Calculated*	Measured		Calculated	Measured
A1	0.15	0.015	0.49	0.79	0.079	0.58
C1	0.43	0.043 (15.56)	0.54	1.56	0.156	0.64
D1	0.45	0.045 (42.58)	0.50	3.40	0.340	0.86
E1	0.32	0.032	0.53	2.91	0.291	1.03
F1	0.20	0.020	0.69	2.74	0.274	1.16
G1	0.23	0.023	0.63	3.58	0.358	0.98
H1	0.15	0.015	0.57	2.32	0.232	1.11

*Values in brackets are Van Vleck "Gaussian" values, shown here for comparison (see [1]).

TABLE V Theoretical relative intensities of the fine structure components of the Fe^{3+} cubic-site spectrum

Transition	Relative intensity
$-\frac{5}{2} \leftrightarrow -\frac{3}{2}$	5
$-\frac{3}{2} \leftrightarrow -\frac{1}{2}$	8
$-\frac{1}{2} \leftrightarrow +\frac{1}{2}$	9
$+\frac{1}{2} \leftrightarrow +\frac{3}{2}$	8
$+\frac{3}{2} \leftrightarrow +\frac{5}{2}$	5

tration, and this in turn will increase the number of vacancies required for charge compensation.

(b) Although solution treating in oxygen in every case increased the intensity of the central transition, it decreased the intensity of the fine structure transitions: in some cases (samples E1 and F1) to the extent that the fine structure disappeared altogether. Since the solution treatment is carried out in oxygen at atmospheric pressure, presumably one effect of the treatment will be to increase the number of excess ogygen ions present.

5. Conclusions

We have examined experimentally the linewidths and integrated intensities for the ESR $\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transition of Fe^{3+} in cubic sites in MgO for a range of iron concentrations between 100 and 12 900 ppm. The experimental measurements of linewidth are in good agreement with those reported previously [1]. There is considerable evidence from spin-density measurements that not all the iron is present in cubic sites in the form of isolated Fe^{3+} ions. Indeed, in the higher concentrations examined very little is in this form. It is suggested that the discrepancy between the total iron quantity and the quantity which contributes to the Fe^{3+} spectrum is partly due to clustering; that this clustering is evident even at extremely low (~ 2000 ppm) concentrations, and that heat treatment for 24 h at 1673 K does not dissolve the clusters entirely, though an improvement is obtained.

It has also been shown that whilst the highest measured concentrations of dopant give a linewidth comparable with that predicted by the Kittel and Abrahams' dipolar broadening theory, for most samples the measured linewidths are considerably broader than the calculated linewidths. It is suggested that this broadening is caused by interactions with the undetected fraction of the iron, which in every case is the larger fraction (in the case of the highest concentrations this undetected fraction is well over 99% of the total). On this analysis there is no evidence for exchange narrowing of the Fe^{3+} ESR lines in MgO for the range of concentrations examined. We have confirmed that the relative intensities of the fine structure lines due to Fe^{3+} vary with crystal treatment.

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