

The ESR spectrum of Gd^{3+}/MgO

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Electron spin resonance studies have been made at 9.1 GHz on Gd^{3+}/MgO single crystals grown by electrofusion and containing low gadolinium concentrations. A single isotropic line having $g = 1.992 \pm 0.00024$ was observed in contrast to the seven line spectrum reported by Abraham. The experimental peak-to-peak linewidth for the $-\frac{1}{2} \leftrightarrow +\frac{1}{2}$ transition at 293 K was 0.3 mT and was independent of polar angle. This was nearly one hundred times less than the calculated dipolar linewidth and analysis verified that the lineshape was Lorentzian indicating exchange narrowing. The linewidth was independent of temperature from 4.2 to 293 K and the exchange energy derived for a gadolinium concentration of 310 ppm was 15 GHz. A discussion is given of the cubic field splittings of Gd^{3+} in oxide crystals and a comparison made of the exchange energies of transition group ions in the MgO lattice.

1. Introduction

Electron spin resonance (ESR) studies of some iron group ions (Fe^{3+} , Cr^{3+} and Co^{2+}) in single-crystal MgO have been described by Thorpe *et al.* [1-3] in connection with the determination of exchange energies and, as an extension of this work, the Gd^{3+}/MgO system has now been examined. Several reports of ESR spectra of rare earth group ions in MgO have been given (e.g. Er^{3+} in 1964 [4], Eu^{2+} in 1971 [5], Dy^{3+} and Yb^{3+} in 1974 [6]) where the spectra corresponded to a site of cubic symmetry. Particular interest attaches these works to the work of Abraham *et al.* on Gd/MgO in 1971 [5]. The trivalent gadolinium ion has seven unpaired electrons in the 4f unfilled shell which make it half-filled and give rise to a ground state $4f^7$, $^8S_{7/2}$; in a cubic field it can split into two doublets and a quadruplet and the lowest level is a Kramers doublet. As an S-state ion, gadolinium should exhibit no first order crystal field splitting, a feature discussed by Bleaney and Stevens [7]. However, ground-state splittings of Gd^{3+} were observed in CaO [8], SrO [9] and MgO [5]; the observed splitting mechanisms were more complex than a simple linear dependence on the crystal potential. Van-Vleck and Penney [10] have suggested that the splitting arising from the combined action of the cubic field and spin-orbit interaction will be very small. The ionic

radius of Gd^{3+} in octahedral co-ordination is 0.938 Å [11]. In single-crystal MgO, gadolinium is expected to enter into the lattice by substitution at the octohedral site as, in the octahedral position, the ratio of cation radius lies between 0.732 and 0.414 [12]. The ionic radius ratio between Gd^{3+} and O^{-2} (1.40 Å) is 0.670, which lies in the range of quoted values [12]. In the host crystal MgO, the linewidths of iron group ions such as Cr^{3+} [2], Co^{2+} [3] and Fe^{3+} [1] have been shown to be determined by exchange narrowing, while the linewidth of Gd^{3+} in $CaWO_4$ is determined by dipolar broadening mechanisms [13].

2. Experimental techniques

The doped single crystal on which measurements were made was obtained from W. and C. Spicer Ltd (Cheltenham), having been grown by electrofusion.

The gadolinium concentrations in the specimen which was the only sample available was 310 ppm, this has been determined by optical spectrographic analysis (Johnson-Matthey Ltd) to an accuracy of about 2%. The crystalline quality was good and neither optical examination nor X-ray back reflection photographs, used to orientate the specimens, revealed any evidence of macroscopic cracking, flaws, strain or mosaic formation. This led us to assume that the sample was of good

crystalline quality. The crystal which had dimensions $9.8 \text{ mm} \times 5 \text{ mm} \times 2.2 \text{ mm}$ was cloudy-white; a similar colour has been reported by Abraham *et al.* [14] for MgO single crystal doped with Gd^{3+} .

The ESR measurements were made using a conventional 9 GHz spectrometer [1], which was equipped with a helium cryostat. Spectra were recorded in the range 4.2 to 293 K by sweeping the magnetic field slowly through a known range. The magnetic field calibrations were obtained using a proton resonance magnetometer system in which the probe could be located exactly in the position normally occupied by the specimen.

3. Experimental results

The ESR spectrum of gadolinium in MgO has been recorded at 9.1 GHz. Only one isotropic line was observed where the seven transitions coincide at $h\nu = g\beta H$, where h is Planck's constant, ν is the frequency, g is the Lande g -Factor, β is the Bohr magneton and H is the magnetic field. (It is interesting to note that single line transitions corresponding to an effective spin $S' = 1/2$, of Cr^{3+} in MgO [2, 15], Co^{2+} in MgO [3] and Dy^{3+} in MgO and SrO [6] have been observed instead of transitions corresponding to the spin value $S > 1$.) A typical spectrum of the single line transition at $\theta_H = 0^\circ$ at different temperatures is shown in Fig. 1. The g value of the line is 1.992 ± 0.0002 which is the same as the value reported for the $1/2 \leftrightarrow -1/2$ by Abraham [5]. Measurements of the magnetic field values at resonance and linewidth determinations were made as functions of both polar angle and temperature. There is no change in resonance field with temperature. There is a small variation of resonance field with polar angle; the field departs by up to 0.3 mT from its value at $\theta_H = 0^\circ$, when it lies in the (1 0 0) plane. The variation of resonance field has also been reported elsewhere [5] where it was found, for the case in which the magnetic field lay in the (1 1 0) plane that the resonance magnetic field changed by up to 1.2 mT over a similar range of polar angle at 77 K. On the basis of the very close agreement between the g value measured here and that reported in [5] it was felt justified to attribute the spectrum to Gd^{3+} in octahedral sites. Some very weak additional lines were observed, which were due to Fe^{3+} and Mn^{2+} as impurities. The linewidth (defined as the width between points of maximum slope, ΔH_{ms}) was obtained directly from the derivative plots. The measured line-

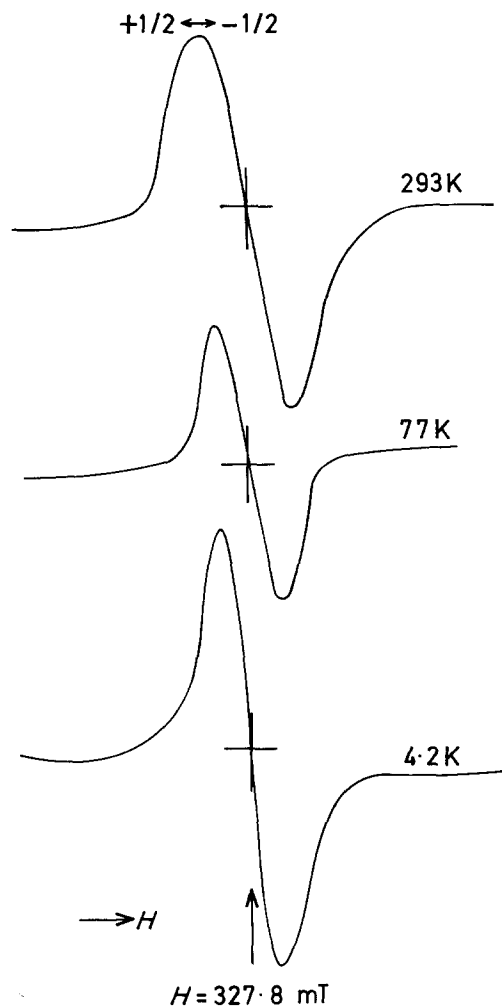


Figure 1 Derivative line of $\text{Gd}^{3+}/\text{MgO}$, $\theta_H = 0^\circ$, 9.14 GHz and 310 ppm Gd.

width at room temperature was about 0.3 mT, which was independent of polar angle as shown in Fig. 2. This behaviour of the rare-earth group S-state ion Gd^{3+} is in marked contrast (in the MgO lattice) to the linewidth variation with polar angle θ_H of the iron group S-state ion Fe^{3+} (where ΔH_{ms} increased with the increasing value of θ_H [1]). In order to check whether there was any appreciable linewidth contribution due to spin-lattice relaxation, the spectra were recorded as a function of temperature from room temperature down to 4.2 K; the linewidths remained constant which shows that the relaxation effect on linewidth is negligible.

4. Dipolar broadening

It will be assumed in this calculation that the main

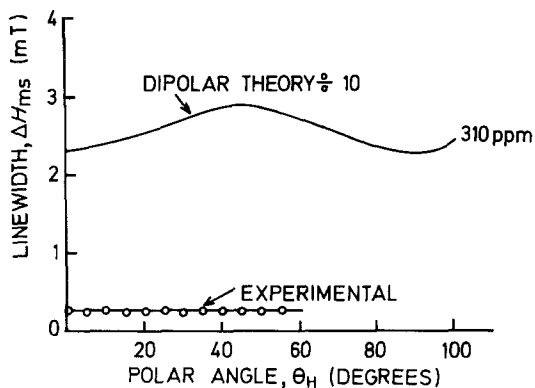


Figure 2 Comparison of predicted and observed variation of linewidth with polar angle Gd³⁺/MgO (310 ppm), $\pm 1/2$ transition.

contribution to homogeneous line broadening is dipole-dipole interaction between Gd³⁺ ions. The second moment $\langle \Delta\omega^2 \rangle$ of the linewidth caused by dipolar interaction between identical atoms in the magnesium oxide lattice has been derived in the literature [1]. For Gd³⁺, $S = 7/2$ and $g = 1.992$ [5] and so the atomic part of the second moment is $1.2073 \times 10^{-24} \cdot n$ (rad sec⁻¹)² cm⁶, which leads to the final equation for second moment

$$\begin{aligned} \langle \Delta\omega^2 \rangle = & 1.2073 \times 10^{21} \cdot n \\ & \times [15.9184 - 5.175Y_{4,0}^*(\theta_H, \phi_H) \\ & - 6.218Y_{4,4}^*(\theta_H, \phi_H)] \end{aligned} \quad (1)$$

where n is the concentration of the interacting ions, and θ_H and ϕ_H refer the static magnetic field to the crystal axis (see also [1]). Using the transformation equation and considering $\theta_H = 0^\circ$, the peak-to-peak derivative linewidths ΔH_{ms} can be evaluated and compared with experimental values. The general curve for the variation of linewidth with polar angle is given in Fig. 2 which also shows the experimental values of linewidth.

5. Discussion

5.1. Crystal field splitting

One salient feature emerges from an initial comparison between the experimental results for the as-grown crystal and those reported in the literature [5], in which a spectrum of seven lines was observed instead of the single transition found here. The observation of only one line indicates that the cubic field splitting is zero. Similar reduction of the cubic splitting for Gd³⁺ in CaO and SrO [16] and Cr³⁺ in MgO [2, 15] has been

reported. The observed linewidth of Gd³⁺/MgO was half that for the S-state ion Fe³⁺ in MgO [1] for the same concentration (310 ppm). Thus the narrow linewidth ($\Delta H_{ms} = 0.3$ mT) and the general behaviour of the spectrum showed that the cubic symmetry was preserved to a high order, despite the fact that gadolinium has a larger valency and ionic radius (0.97 Å) than the host lattice cation Mg²⁺ (ionic radius of 0.72 Å). In this case it is necessary for a lattice to distort in order to accept the larger ion, i.e. the neighbours move away from their normal positions. Here the experimental result showed that if any distortion is present, it would be uniform leaving the local symmetry completely unchanged. Substitution of trivalent ions Fe³⁺ and Cr³⁺ for the divalent cation Mg²⁺, without disturbing the octahedral cubic symmetry has been reported [1, 2].

A comparison of the reported data at 9 GHz for some rare-earth ions in MgO and the present results is given in Table I.

The present ESR results and the results reported in Table I indicate the relative absences of strain in the MgO crystal lattice for substitutional rare-earth ions of larger ionic radius and valencies than the cation Mg²⁺. This is especially remarkable in MgO.

To consider the mechanism responsible for the ground state splitting of Gd³⁺ in various crystals of O_h^5 space group of comparison of splitting parameters is given in Table II.

Watanabe [17] has extended the theoretical discussion of the crystal field splitting in the S-state ions beyond the treatments of Van-Vleck and Penney [10] and Pryce [18] and he concludes that the cubic field splitting, c , would be of the form

$$c = (Dq)^2 [a - b(Dq)^2], \quad (2)$$

where Dq represents the cubic field strength, and a and b are constants depending on the detailed nature of the excited states. Assuming that Dq was small for most rare-earth ions and that the spin-orbit interaction was fairly large, Low *et al.* [19] considered that the splitting ought to be primarily proportional to the square of the potential or inversely proportional to the tenth power of the interionic distance. From Table II, the ratio of Ca-O and Mg-O distances is about 1.142 and the value of the ratio of the Sr-O and Mg-O distances is about 1.209. Assuming that substituting the trivalent gadolinium ion does not change this ratio

TABLE I Comparison of results of rare-earth ions in MgO, 9 GHz

Ion	Ionic radius [11] (Å)	Concentration (ppm)	Peak-to-peak linewidths ΔH_{ms} (mT)	Spectrum corresponds to	References
Er ³⁺	0.881	300	0.3	One octa and the other tetrahedral	[4]
Yb ³⁺	0.858	Not mentioned	0.2 $H/(1\ 1\ 1)$	Cubic site	[6]
Dy ³⁺	0.908	Not mentioned	0.2 $H/(1\ 1\ 1)$	Cubic site	[6]
Eu ²⁺	1.17	Not mentioned	Narrow $H/(1\ 1\ 0)$	Cubic site	[5]
Gd ³⁺	0.938	Not mentioned	Narrow $H/(1\ 1\ 0)$	Cubic site	[5]
Gd ³⁺	0.938	310	0.3 $H/(1\ 0\ 0)$	Octahedral cubic site	This work

appreciably, one can calculate the ratio of cubic splittings, which are

$$\frac{c_{\text{MgO}}}{c_{\text{CaO}}} : \frac{c_{\text{CaO}}}{c_{\text{SrO}}} : \frac{c_{\text{SrO}}}{c_{\text{MgO}}} = 3.77 : 1.76 : 0.149.$$

If one puts the measured cubic field splitting value of c_{CaO} and c_{SrO} from Table II in the above relation, the two values of c_{MgO} will be $174.9 \times 10^{-4} \text{ cm}^{-1}$ and $144.9 \times 10^{-4} \text{ cm}^{-1}$. The latter value of c_{MgO} is close to the measured value of c_{MgO} reported in [5]. This shows that the mechanism responsible for the cubic field splitting follows the inverse tenth power of the interionic distance. So from the spectrum of Gd³⁺ in MgO observed here and from the spectrum reported in the literature [5], it may be assumed that the cubic field splitting mechanism depends also on the crystal history. The result given here represents measurements on only one sample and is not necessarily applicable for all Gd³⁺/MgO samples.

5.2. Exchange narrowing

In order to obtain information about the nature of the interaction between the dopant atoms, a

comparison was made between the measured linewidth and the predicted dipolar broadening linewidth. The theoretical curve for the variation of dipolar linewidth with polar angle is given in Fig. 2 by the full line. The measured linewidth is about 100 times narrower than the predicted dipolar linewidth at $\theta_H = 45^\circ$. The large numerical disparity suggested that there was a strong narrowing mechanism such as the exchange narrowing observed in Fe³⁺/MgO [1], Cr³⁺/MgO [2] and Co²⁺/MgO [3]. Experimental evidence for exchange narrowing is usually obtained from analysis of lineshapes and comparisons of moments. To find the lineshape factor, the observed derivative line was integrated, and the ratio of the peak-to-peak derivative linewidth to the integrated linewidth at half-height was found to be 0.591. Therefore, the observed lineshape factor is very close to the Lorentzian lineshape factor of 0.577 [20]. This Lorentzian lineshape indicates exchange narrowing. The moment ratio $M_4^{1/4}/M_2^{1/2}$ where M_2 and M_4 are respectively the second and fourth moments, was derived as 1.33. This value is similar to the figures quoted in [1, 2] for examples of exchange narrowed ESR lines. This suggests that

TABLE II Cubic field splittings of Gd³⁺ in various oxide crystals having cubic symmetry

Paramagnetic ion	Host crystal	Lattice space group	Lattice constant (Å)	Inter-ionic distance in crystals (Å)	<i>g</i> -values	Cubic field splitting c ($\times 10^{-4} \text{ cm}^{-1}$)	References
Gd ³⁺	SrO	O_h^5	5.10	2.54	1.9918	-21.6 ± 0.2	[9]
Gd ³⁺	CaO	O_h^5	4.797	2.40	1.9925	46.4 ± 0.4	[8]
Gd ³⁺	MgO	O_h^5	4.2112	2.10	1.9920	-139.8 ± 0.02	[5]
Gd ³⁺	MgO	O_h^5	4.2112	2.10	1.9920	0	This work

TABLE III Comparison of J values for different ions in MgO

Ion	Ground state	Concentration (ppm)	Exchange energy J (GHz)	References
Gd ³⁺	⁸ S _{7/2}	310	15	This work
Fe ³⁺	⁶ S _{5/2}	310	3.99	All these values have been calculated from the slope for J [21]
Cr ³⁺	⁴ F _{3/2}	310	2.03	
Co ²⁺	⁴ F _{9/2}	310	1.98	

the observed spectrum of Gd³⁺/MgO is also determined by "exchange narrowing".

The exchange energy J has been derived, by adopting the same method as in [2], and compared with the reported values for iron group ions in the MgO lattice [21] for the same concentration (Table III).

Table III shows that in MgO, Gd³⁺ has a greater exchange energy since Gd³⁺ has a higher spin value and a greater ionic radius, which causes greater overlapping between paramagnetic impurity coordinating ions than the other iron group ions, which substantiates that S-state ions have greater exchange energy than F-state ions in the same host lattice MgO, irrespective of their periodic group.

In order to maintain the neutrality of the crystal, there have to be either some positive ion vacancies or negative ion interstitials. Since the spectrum can be fitted with a simple cubic spin-Hamiltonian, $h\nu = g\beta H$, and since only a single isotropic line of narrow width was seen, the evidence seems to show that there are no interstitial ions in the neighbourhood. So one Mg²⁺ vacancy will arise for every two Gd³⁺ ions in the magnesium sites. Similar vacancy rules for charge neutralizing due to the introduction of the trivalent S-state ion Fe³⁺ in MgO have been reported [1].

The linewidth mechanisms of Gd³⁺ in the CaWO₄ lattice (substituted at calcium sites) has been shown to fit a dipolar broadening mechanism [13], which is in contrast to the present observed linewidth mechanism of Gd³⁺ in MgO. The number of Mg²⁺ cationic sites close to that occupied by one substitutional Gd³⁺ ion (corresponding to the eight unit cells of MgO around the central Gd³⁺ ion) is 64. The sphere which contains these 64 sites has a radius of 7.294 Å [1] while the corresponding radius of a sphere which contains the 64 Ca²⁺ cationic sites in CaWO₄ lattice around the substitutional Gd³⁺ ion is 13.579 Å [22]. So the same S-state ion, Gd³⁺, shows different linewidth mechanisms according to the radius of this sphere and the larger radius of sphere corresponds to the dipolar mechanism.

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