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E.S.R. LINEWIDTHS IN Mn^{2+}/MgO

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The electron spin resonance linewidths of Mn^{2+} in single crystal MgO have been examined at both 9GHz and 30GHz over the temperature range 273K to 90K for manganese concentrations ranging from 880ppm to 4900ppm. For each of the doped crystals observations were made of the linewidth and lineshape as a function of polar angle; there were no changes in either 'g' value or hyperfine constant 'A' with polar angle over the temperature range. The predicted angular variations of linewidth for these manganese concentrations were also calculated, from the Van Vleck dipolar theory, and comparison showed that the observed linewidths were about sixty times less than expected. It was found that the peak-to-peak linewidths were concentration dependent (closely following a $(\text{concentration})^{1/2}$ law) and that the lineshape was Lorentzian. The E.S.R. data confirmed that Mn^{2+} entered the lattice substitutionally, occupying magnesium sites, even at the highest concentrations.

INTRODUCTION

Electron Spin Resonance (E. S. R.) results of the iron group ions Fe^{3+}, Cr^{3+} and Co^{2+} in single crystals magnesium oxide (MgO) have recently been reported by Thorp et al [1, 2, 3]. In all these materials it was found that the experimental linewidths were much narrower than those predicted from the Van Vleck model of dipolar broadening theory. It has been found that these dopant ions substitute at magnesium sites even though they have values of valence and ionic radius which differ significantly from that of the host cation Mg^{2+} [viz, $R(Fe^{3+})$ = 0.645 Å, $R(Cr^{3+})$ = 0.615 Å , $R(Co^{2+}$ = 0.735 Å and $R(Mg^{2+}$ = 0.72 Å [4]. In both Fe^{3+}/MgO (1) and Cr^{3+}/MgO [2] the observed linewidths were found to be independent of dopant concentration; in the case of Co^{2+}/KgO [3] however there was a slight increase in linewidth with concentration thought to be due to increasing cross-relaxation between the hyperfine lines of Co^{2+}. As part of a programme to extend the studies to other dopant ions we have now examined manganese doped magnesium oxide single crystals Mn^{2+}/MgO. The ESR spectrum of Mn^{2+}/MgO were first reported by Low [5, 6] who determined the characteristic parameters of the Spin-Hamiltonian for the transitions $\triangle M_S = \pm 1$, $\triangle M_I = 0$ (where M_S and M_I refer to the electronic and nuclear spins respectively) for a cubic crystalline field. This spectrum has since been reported by Auzins *et al.* [7] and by Rubio *et al.* [8]. However, little detailed information is as yet available regarding the sites occupied by the dopant ions at various dopant levels or on the nature of the interactions between the dopant atoms.

The divalent ion of manganese has the electronic configuration of $3d^5$, $^6S_{5/2}$ and the effective ionic radius $R(Mn^{2+})$= 0.82 Å which is about 15% greater than that of Mg^{2+}. In the MgO lattice the ground state $^6S_{5/2}$ splits into a two-fold and four-fold degenerate level [5]. The spectrum of Mn^{2+} is further complicated by the fact that there is a large hyperfine structure caused by the nuclear spin I = 5/2 of 55 Mn. It has been reported that in Mn^{2}+/MgO the hyperfine constant 'A' was greater than the cubic field splitting parameter 'a' [5]. It is expected therefore that the ESR spectrum of Mn^{2+}/MgO single crystal for the transitions governed by $\triangle M_S = \pm 1$, $\triangle M_I$= 0 should consist of six hyperfine groups with five fine structure (FS) lines in each. In the present work the experimental hyperfine linewidths for the ($\triangle M_S$ = +½→ – ½, $\triangle M_I$ = 0) have been measured and compared with widths calculated from dipolar theory; the effects of dopant size and of concentration dependent cross-relaxation the hyperfine lines in Mn^{2+}/MgO have also been investigated.

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EXPERIMENTAL TECHNIQUES)

The doped single crystals on which measurements were made were obtained from W & C Spicer Ltd (Cheltenham, U.K) having been grown by electrofusion using pure powdered manganese oxide and pure powdered magnesia as starting materials. The manganese concentrations in the specimens examined ranged from 880ppm to 4900ppm by weight, these have been determined by optical spectrographic analysis (Johnson-Matthey Ltd) to an accuracy of about 2%. The crystal colour varied from very pale pink at the lowest concentration to pink at 4900ppm manganese.

Preliminary ESR measurements were made using at 9GHz spectrometer (Varian V4502). To obtain higher resolutions further data was obtained with a 30 GHz spectrometer. Each of the spectrometers was equipped with phase sensitive detection giving output spectra in derivative form. The magnetic field calibration was obtained at 9 GHz by using a proton resonance magnetometer. AT 9 GHz the cryogenic accessories available enabled spectrum to be recorded at temperatures between 293K and 90K by sweeping the magnetic field slowly through a known range; at 30 GHz however it was only possible to record spectra at 293K. Temperatures were recorded using copper-constantan thermocouples.

EXPERIMENTAL RESULTS

Spectrum Characterisation: Initial measurements were made at 9.427 GHz to establish the form of the spectrum in each specimen. An example is shown in fig. 1, which refers to a specimen containing 880ppm Mn examined at 293K. The spectrum at θ_H=0o and ϕ_H = 0° (as defined in [1]), consists of six hyperfine groups of lines with g value about 2.002. The value of ground state splitting, given by 3a = $56x10^{-4}cm^{-1}$, agrees well with the published data [5,6]. This value for 3a was obtained from measurements on the three lowest field transitions of the M_I = −5/2 pentad, which was clearly resolved at the left-hand end of the spectrum as shown in fig. 1.

The hyperfine constant A of Mn^{2+}/MgO has been deduced from the average of all the separations between successive hyperfine lines form M_S = ½↔-½ transitions and was found to be A = -82.0 x $10^{-4}cm^{-1}$; this estimate also agrees well with the published value [5, 7]. The spacing of the hyperfine lines has been found to increase between the high and low magnetic field sides by an amount of the order of $A/(h\nu)^2$; the intensity also increases by an amount of the order $A/h\nu$, where ν, is the

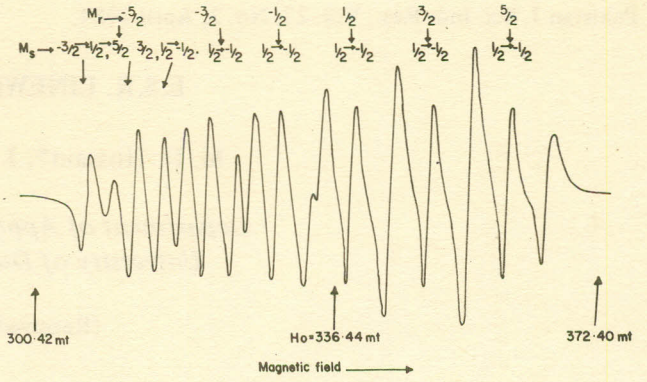

Figure 1: E.S.R. Spectrum of Mn^{2+} /Mg0 (800 ppm), 293K, θ_H = 0°, ϕ_H = 0°, f = 9.427 GHz.

resonance frequency. A similar effect was noted in the spectrum of Co^{2+} in MgO [3]. In each case it may be attributed to effects from the off-diagonal terms in the magnetic hyperfine structure [9]. The field values at which the transitions occurred were compared with the values expected for Mn^{2+} in an octahedral site. There was close agreement on this basis and in view of the similarity between fig. 1 and the spectrum reported in the literature [8], it was felt justifiable to attribute the spectrum to Mn^{2+} in octahedral sites. Even at high spectrometer sensitivity these crystals showed no sign of other paramagnetic impurities, unlike crystals previously investigated doped with Fe^{3+} [1] and Cr^{3+} [2].

There was no change in either 'g' value or hyperfine constant A with polar angle over the temperature range investigated, although the fine structure lines for the (M_S = 5/2↔3/2, 3/2↔½, − ½↔ −5/2) transitions were highly anisotropic. As θ_H was varied the spectrum repeated with a period of 90° being symmetrical about θ_H=45°. At angles near θ_H=31.5° and 58.5° the anisotropic fine structure lines overlap completely with the isotropic M_S = ½ ↔ -½ lines, showing a total of six lines only, as shown in fig. 2.

Linewidth Results: The linewidth determinations were made at ϕ = 0 for the (M_S = ½↔−½, ΔM_I = 0) transitions. The linewidth, defined as the width between points of maximum slope, ΔH_{ms}, was obtained directly from the derivative plots. The polar angle independent linewidths were found for values of θ_H between 0° and 20° and also between 70° and 90°; some typical values obtained at θ_H = 0° and 5° are recorded in Table 1. For values of θ_H between 20° and 70° a variation in linewidth has been observed, but this variation is probably largely due to alteration of the degree of overlap of the anisotropic fine structure lines with the M_S = ½↔½ isotropic line. This variation appears to be periodic.

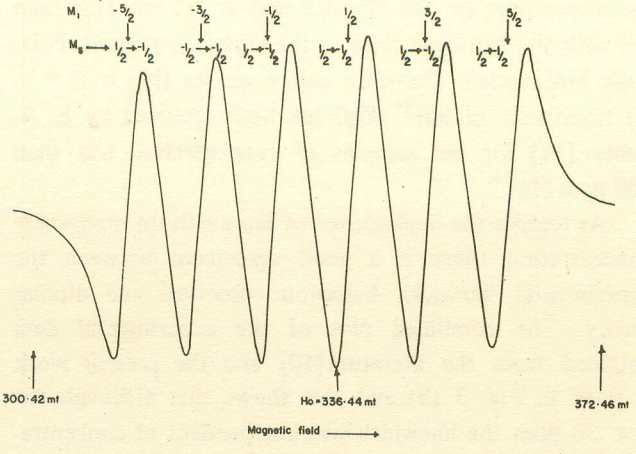

Figure 2: E.S.R. Specturm of Mn^{2+}/MgO (4900) ppm), 293K, θ_H 35.5°, $\phi_H = 0°$, f = 9.427 GHz.

giving maximum linewidths at $\theta_H = 31'5°$ and 58'5°, at which angle all the lines of any pentad overlap exactly.

The linewidth values at $\theta_H = 0°$ for the M_S ½↔−½ transitions of Mn^{2+}/MgO are plotted as a function of concentration in fig. 3 (b). This also includes the linewidth data taken from the literature [10], after conversion into peak-to-peak linewidths on the assumption of Lorentzian lineshape. The graph shows that over a substantial range the measured linewidths are proportional to (concentration)^x, where the exponent x has the value x = 0'499, obtained from the solid line of fig. 3 (b). This value of x is very close to the predicted dipolarlinewidth value of x = 0'50 (fig. 3 (a)). A similar variation of linewidth with concentration was reported previously for Co^{2+}/MgO [3], but in that material calculation from the data given in [3] yields a value x = 0.3. Returning to consideration of Mn^{2+}/MgO the linewidths for the M_S = ½ ↔ ½) transition were found to be narrower than all other lines (where they could be distinguished). Both the derivative linewidth and lineshape were found to be independent of temperature over the range 90K to 293K. The results obtained at the higher frequency of 29'27GHz were very similar with those obtained 9'427GHz, the only difference being in the amplitudes of the derivative lines recorded at ...$_H$ = 31'5° (as illustrated by fig. 4). At 29'27 GHz all the six lines are virtually equal in amplitude, in contrast to the situation of 9'427 GHz where the amplitudes are significantly unequal. This demonstrates the importance of the intensity term of amount A/(hν) which is higher at 9'427 GHz than at 29'27 GHz.

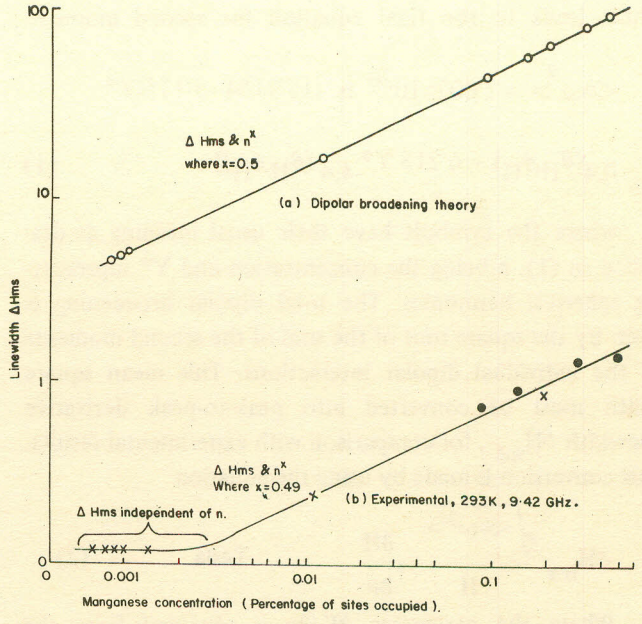

Figure 3. Comparison of predicted and observed variation of linewidth with concentration (a) Dipolar broadening; (b) Experimental, where o - present data; x - data taken from reference - (10).

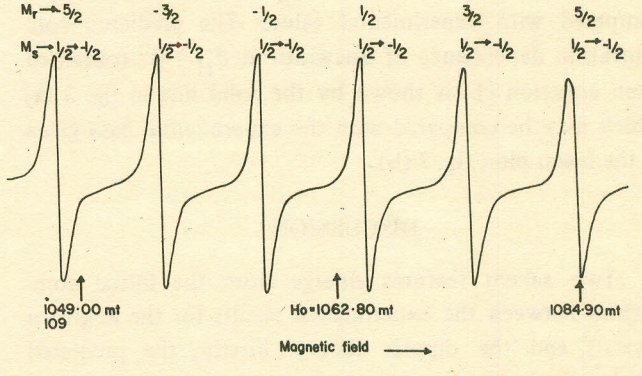

Figure 4: The derivative lineshape at 29.78 GHz, $\theta_H = 31.5°$, $\phi_H = 0°$, 293K, Mn^{2+} / MgO (880 ppm).

DIPOLAR BROADENING

It has been assumed in the calculations made here that the main contribution to homogeneous line broadening is dipole-dipole interaction between isolated Mn^{2+} ions. Expressions for the second moment ⇋

Expressions for the second moment $\langle\Delta\omega^2\rangle$ of the linewidth caused by dipolar (Van Vleck model) interaction between identical atoms in the magnesium oxide lattice have been derived in the literature [1]. The approach used in (1) has been adopted here. For Mn^{2+}, S = 5/2

and g = 2.0014 (5) giving a value of the atomic part of the second moment of 7'002 x 10^{-25} .n. (rad $sec^{-1})^2$ cm^6, which leads to the final equation for second moment.

$$\langle \Delta\omega^2 \rangle = 7'002 \times 10^{20} \text{ .n. } [15'9184 - 5'175\ Y^*_{0,4}(\theta_H,\phi_H) - 6'218\ Y^*_{4,4}(\theta_H,\phi_H)] \quad (1)$$

where the symbols have their usual meaning as described in (1), n being the concentration and Y* representing spherical harmonics. The total dipolar broadening is given by the square root of the sum of the second moments of the individual dipolar interactions. This mean square width must be converted into peak-to-peak derivative linewidth ΔH_{ms}, for comparison with experimental results. This conversion is made by using the equation

$$\Delta H_{ms} = \frac{\sqrt{\langle \Delta\omega^2 \rangle}}{II} \frac{\partial H}{\partial \nu} \text{ Tesla} \quad (2)$$

Where the parameter $\dagger K/\partial\nu$ is obtained from the experimental isofrequency plots obtained for each crystal. For $\phi_H = 0^o$ equation (1) is totally real and by substituting the experimental values of n and θ_H, the peak-to-peak derivative linewidths ΔH_{ms} can be evaluated and compared with experimental values. The predicted concentration dependence of linewidth at $\theta_H = 0^o$ (obtained from equation (1) is shown by the solid line in fig. 3 (a) which may be compared with the experimental data given in the lower plot, fig. 3 (b).

DISCUSSION

Two salient features emerge from the initial comparison between the experimental results for the as-grown crystals and the dipolar theory. Firstly, the predicted dipolar linewidths are about sixty times larger than the observed linewidths at $\theta_H = 0^o$; this is an effect similar to those reported for Fe^{3+}/MgO (1), Cr^{3+}/MgO (2) and Co^{2+}/MgO (3), in each of which systems the observed linewidths were found to be about 100 times less than those predicted dipolar broadening theory. Secondly, the angular dependence of the linewidth differs from the expected. Experimentally it was found that there are two maxima for each concentration separated by regions of relatively angle independent behaviour between $\theta_H = 0^o$ and $\theta_H = 20^o$ also between $\theta_H = \theta_H = 70^o$ and $\theta_H = 90^o$. This behaviour is at variance with the predictions from dipolar theory according to which the linewidths should show one maximum only (at $\theta_H = 45^o$) and have a continuous angular dependence between $\theta_H = 0^o$ and $\theta_H = 90^o$.

The variation of the experimental linewidths for (M_S = 1/2 →1/2) transitions with polar angle between θ_H = 20^o and $\theta_H = 70^o$ is due to the variation of overlap of the anisotropic (± 5/2 →± 3/2 and ± 3/2 →± 1/2) lines [5] with the isotropic lines as the crystal is rotated. Polar angle independent linewidth behaviour for (M_S = ½ → – ½) transitions of Mn^{2+}/MgO has been reported by E. R. Feher [11] for the samples of concentration less than 100 ppm Mn^{2+}.

As regards the dependence of linewidth on manganese concentration there is a good agreement between the experimental linewidth behaviour observed and dipolar theory. The combined plot of the experimental data obtained from the literature [10] and the present work is given in Fig. 3 (b) and this shows that although for n < 30 ppm the linewidth was independent of concentration; above n ≈ 30ppm the linewidth began to change with concentration as n^x, where x = 0.49. This behaviour follows very closely the $n^{0.5}$ variation predicted by dipolar broadening theory and was found to hold up to concentration of 4900ppm Mn. Further, experimental evidence which is helpful in clarifying the mechanism of line broadening is usually obtained from lineshape analysis and moment comparisons. Here the shapes of the observed derivative lines were compared with the Lorentzian lineshape expression for a derivative line, [12]

$$L_{y'(H)} = \frac{16\left(\frac{H-H_0}{1/2\,\Delta H_{ms}}\right)}{\left[3+\left(\frac{H-H_0}{1/2\,\Delta H_{ms}}\right)^2\right]}$$

in order to obtain values of the lineshape factor.

Close agreement was found between the observed derivative lineshapes and those corresponding to the Lorentzian lineshape expression of equation (3). This analysis confirmed that the observed lineshapes were Lorentzian since a lineshape factor of 0'577 was obtained. It was assumed that the line was symmetrical about the midpoint. The ration $M_4^{1/4}/M_2^{1/2}$ (where M_2 and M_4 are respectively, the second and fourth moments) was then derived and the results are tabulated in Table 1. The values of the ratio are similar to the figures quoted in the literature [1, 2, 3] for Fe/MgO, Cr/MgO and Co/MgO.

The present comparison of theory and experiment shows that, apart from the numerical discrepancy in the magnitudes of the linewidths, the predicted concentration dependence is observed although the lineshapes are Loren-

Table 1. Linewidth data for a range of manganese concentrations at temperature 293K; 9,427 GHz.

Manganese Concentration (ppm)	Polar-angles θ_H (degree) ϕ_H=0	ΔH_{ms} (mT) Measured	ΔH_{ms} (mT) Prediction from dipolar theory	Moment ratio $M_4^+/M_2^{1/2}$
	0°	0.77	48.77	
880				1.40
	5°	0.67	49.12	
	0°	0.92	60.8	
1400				1.45
	5°	0.83	61.2	
	0°	1.38	87.54	
2900				1.35
	5°	1.17	88.17	
	0°	1.34	109.0	
4900				1.50
	5°	1.51	109.80	

tzian. Two additional broadening mechanisms may have some influence in the present context; these are firstly the size effect [13], which would give a Lorentzian lineshape though with a linewidth proportional to concentration and secondly cross-relaxation between hyperfine lines [14], which would produce a more Lorentzian than Gaussian lineshape, and has been shown to be important in Co^{2+}/MgO. Cross relaxation is important when the dipole-dipole interaction is very small in comparison to the Zeeman interaction and the crystal field splitting [15]. Although neither effect has been considered in detail in making the present comparison it may be noted that the ionic radius of Co^{2+} is about 2% larger than the ionic radius of Mg^{2+} and the hyperfine constant A is $98'0 \times 10^{-4} cm^{-1}$ and the effective spin S' = ½ (3). In Mg^{2+}/MgO however the ionic radius of Mn^{2+} is about 15% greater than that of Mg^{2+}, the hyperfine constant (A= 82 x $10^{-4} cm^{-1}$) is about 20% less than in Co/MgO and the effective spin is S = 5/2. It thus appears that the probabilities for contributions to the linewidth from both the size effect and cross-relaxation are likely to be greater in Mn^{2+}/MgO than in Co^{2+}/MgO and should be taken into account.

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