

E.S.R. BEHAVIOUR OF Mn^{2+} IN CaO

M.D. Hossain* and J.S. Thorp

*Department of Applied Physics and Electronics,
University of Durham, U.K.*

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The electron spin resonance spectrum of Mn^{2+} in single crystal CaO has been examined at both 9 GHz and 30 GHz over the temperature range 273K to 90K; the manganese concentration was 280 ppm. The fine structure lines overlapped, giving a six-line spectrum in which the experimental peak to-peak derivative width of the $M = +\frac{1}{2}$ to $M = -\frac{1}{2}$ transition was (1.7 ± 0.1) mT. The predicted angular variation of linewidth for this manganese concentration has been calculated from Van Vleck's dipolar theory and comparison shows that the observed linewidth is about twenty five times less than expected. Lineshape analysis, taken in conjunction with previously reported data, confirmed that the line widths are concentration dependant and showed that (at 2800 ppm Mn) the lineshape was Lorentzian.

INTRODUCTION

Evidence has been accumulating for a number of years that the linewidth characteristics of electron spin resonance spectra due to a particular paramagnetic species are closely related to the structural features of the host lattice and to the extent to which the crystal under investigation may be regarded as a magnetically dilute system. Studies of this kind have included ESR examinations of $Nd^{3+}/CaWO_4$ [1], $Gd^{3+}/CaWO_4$ [2] and Cr^{3+}/Al_2O_3 [3], in all of which a good fit was found between the experimental observations and the predictions of Van Vleck's [4] dipolar broadening theory, and more recently of Fe^{3+}/MgO [5], Cr^{3+}/MgO [6], Co^{2+}/MgO [7] and Gd^{3+}/MgO [8] where, by contrast, the experimental line widths were much narrower than expected. As part of a programme to extend the studies to other host lattices we have now examined manganese doped calcium oxide single crystals, Mn^{2+}/CaO . Early observations of the ESR spectra of Mn^{2+}/CaO were given both by Low [8] and by Shuskus [9] who calculated the characteristics parameters of the Spin-Hamiltonian for the transitions $\Delta M_s = \pm 1$, $\Delta M_l = 0$ (Where S and I denote the electronic and nuclear spin respectively) for a cubic crystalline field. Later measurements on both single crystal and polycrystalline Mn^{2+}/CaO have also been reported [10,11]. However, there is little detailed information available either on the question of the linewidth characteristics or on the nature of the interactions between the dopant atoms.

The divalent manganese ion has the electronic configuration $3d^5$, $^6S_{5/2}$. The ESR spectrum of Mn^{2+} is compli-

cated by the fact that there is a large hyperfine structure caused by the nuclear spin $I = 5/2$ of ^{55}Mn . It has been found (9) that in Mn^{2+}/CaO the hyperfine interaction is greater than the cubic field splitting. The ESR spectrum of a Mn^{2+}/CaO single crystal would therefore be expected to consist of six hyperfine groups with five fine structure (FS) lines in each. This paper presents the results of the linewidth measurements made for the hyperfine transition corresponding to the ($m_s = +\frac{1}{2} \rightarrow M_s = \frac{1}{2}$) FS lines and discusses their significance in relation to dipolar broadening mechanisms.

EXPERIMENTAL TECHNIQUES

The doped single crystals which measurements were made were obtained from W & C Spicer Ltd. (Cheltenham), having been grown by electrofusion using pure powdered calcia and pure powdered manganese oxide as starting materials. The manganese concentration in the specimen examined was 2800 ppm, this having been determined by optical spectrographic analysis (Johnson-Mathy Ltd) to an accuracy of about 2%. Optical and X-ray examination showed that the crystalline quality was good. The crystal was light brown in colour and specimens having dimensions of 9mm x 5mm x 2.1mm (chosen to suite the size of the 9GHz spectrometer cavity) were cut from it using a diamond cutting wheel.

The ESR measurements were made using a 9GHz spectrometer and a 30 GHz spectrometer each of which was equipped with phase sensitive detection giving output spectra in first derivative form. The spectra were recorded by sweeping the magnetic field slowly through a known

*Present Address: Department of Applied Physics and Electronics, University of Rajshahi, Rajshahi, Bangladesh.

range. At 9GHz, measurements were made at temperatures between 293K and 90K, but at 30GHz spectra were only examined at 293K.

RESULTS

Experimental Data. Initial measurements were made at 30 GHz in order to establish the general form of the spectrum. An example of this is shown in Fig.1. At the polar angle $\theta_H = 0^\circ$ the spectrum consists of six hyperfine lines centred on g value of about 2.0015. All the other fine structure lines (i.e. those due to the $5/2 \leftrightarrow 3/2$, $3/2 \leftrightarrow 1/2$, $1/2 \leftrightarrow -1/2$ and $-3/2 \leftrightarrow -5/2$ transitions) fully overlap with the isotropic line due to the $1/2 \leftrightarrow -1/2$ transition. This full or partial overlapping behaviour of the fine structure lines has been observed at all values of polar angles. For this reason it was not possible to measure the crystal field splitting parameter. The ν value cited is that corresponding to the centre of gravity of the two central lines of the six line spectrum. The hyperfine splitting constant A of Mn^{2+}/CaO has been deduced from the average of all the separations between successive hyperfine lines assuming the same absolute sign of A as taken [9,10] previously. The value obtained $A = 81.0 \times 10^{-4} \text{ cm}^{-1}$ agrees well with the earlier data. Close inspection of spectrum that there is an increase in the spacing of the hyperfine lines between low and high magnetic field sides by an amount of order $(A/H\nu)^2$, which is attributable to the effect of the offdiagonal terms in the magnetic hyperfine structure [11]. The close agreement between the field values at which the transitions occurred and the values expected for Mn^{2+} in an octahedral site confirmed that even at this relatively high manganese concentration (2800 ppm), it was justifiable to regard the divalent Mn^{2+} as substituting directly for Ca^{2+} .

The linewidth determinations were made for the ($m = 1/2$ to $M = -1/2$) transition. The linewidths, defined as the widths between points of maximum slope, ΔH_{ms} , were obtained directly from the derivative plots obtained at a series of polar angles and the results are shown in Fig. 2. From this it can be seen that the linewidths were almost independent of polar angle θ_H and had values of about $(1.7 \pm 0.1) \text{ mT}$.

The same specimens were also examined in a 9GHz and it was found that the linewidth results at 9GHz were identical with those obtained 30 GHz. Moreover, it was found that, at any particular polar angle, the observed linewidth was independent of temperature over the range 90K to 293K.

Theoretical Linewidths. Estimates of the linewidth and of the form of the variation of linewidth with polar

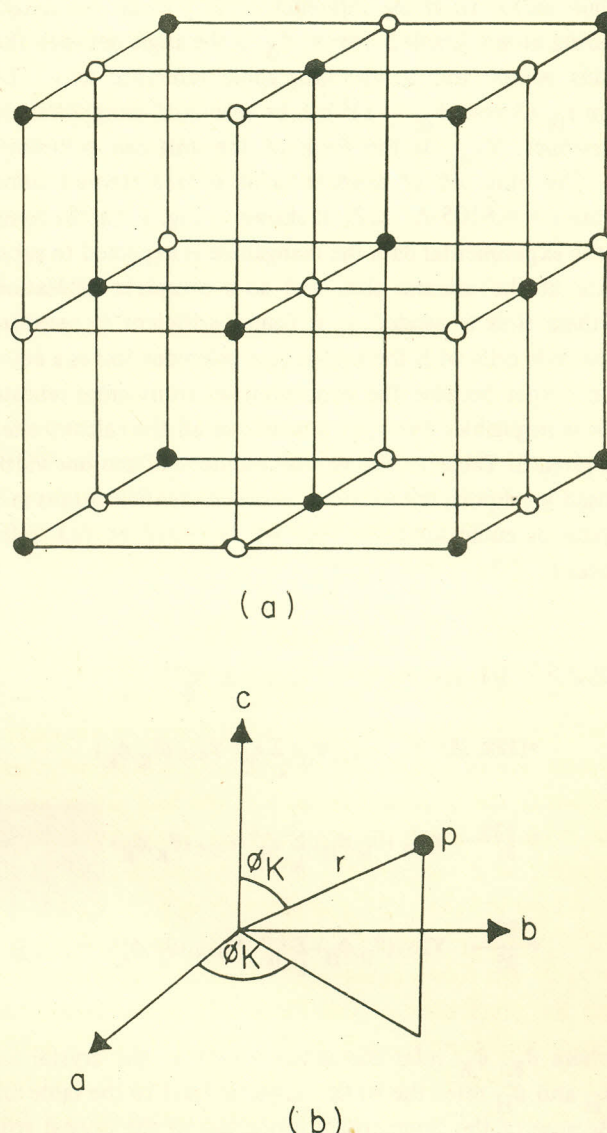


Fig. 3. The calcium oxide unit cell. (a) Atomic positions; \bullet = Calcium, \circ = Oxygen. (b) Reference axes.

angle have been made for the Mn^{2+}/CaO system on the basis that dipolar interaction between Mn^{2+} ions forms the main contribution to line broadening. Thus the calculations have been based on the second moment theory of Van Vleck [4] and for convenience the main steps are summarised below.

For like atoms the second moment, $\langle \Delta \omega^2 \rangle$ can be written:

$$\langle \Delta \omega^2 \rangle = 3/4 \cdot s(s+1)(g^2 \beta^2 h^2)^2 \cdot n \cdot \sum [r_{jk}^{-6} (3 \cos^2 \theta_{jk} - 1)^2] \quad (1)$$

where w is measured in radian sec^{-1} . n is the concentration of interacting atoms, β is the Bohr magneton, r_{jk} is the

radius vector from the reference atom j to all the neighbouring atoms labelled over k , θ_{jk} is the angle between the radius vector and a crystallographic reference axis. The term $r_{jk} (3 \cos^2 \theta_{jk} - 1)^2$ can be evaluated using spherical harmonics, Y_{1m} , if the form of the unit cell is known.

The unit cell of calcium oxide is face centred cubic having $a = 4.8105 \text{ \AA}$ [12] as shown in Fig. 3. On the basis of the experimental data the manganese is expected to substitute at the calcium sites and so a complete tabulation of these sites is needed. It is found sufficient to consider eight unit cells with the manganese reference ion as a common corner because the contribution from more remote cells is negligible. The r, θ, ϕ values of all the calcium sites are given in Table 1. The second moment of the linewidth caused by dipolar interactions between identical atoms in a crystal of cubic symmetry can be expressed as, (c.f. references 1, 2, 7).

$$\begin{aligned} \langle \Delta\omega^2 \rangle = & 3/4 S(S+1)(g^2\beta^2/h)^2 .n [4/5 \sum_k \gamma_{jk}^{-6} \\ & + (32\pi/35) . Y_{4,0}^* (\phi_H, \phi_H) \sum_k r_{jk}^{-6} Y_{4,0} (\theta_K, \phi_K) \\ & + \frac{32\pi}{35} - Y_{4,4} (\theta_H, \phi_H) \sum_k r_{jk}^{-6} Y_{4,4} (\theta_K, \phi_K) \\ & + \frac{32\pi}{35} Y_{4,-4}^* (\theta_H, \phi_H) \sum_k r_{jk}^{-6} Y_{4,-4} (\theta_K, \phi_K) \end{aligned} \quad (2)$$

where θ_K, ϕ_K refer the radius vector to the crystal axes θ_H and ϕ_H refer the static magnetic field to the same axis. Because of the symmetrical properties of the crystal structure, this equation reduces at $\phi_H = 0^\circ$ (which is the experimental case considered here) to

$$\begin{aligned} \langle \Delta\omega^2 \rangle = & \frac{3}{4} S(S+1) (g^2\beta^2/h)^2 [\frac{4}{5} \sum_k r_{jk}^{-6} \\ & + \frac{32\pi}{35} Y_{4,0}^* (\theta_H, \phi_H) \sum_k r_{jk}^{-6} Y_{4,0} (\theta_K, \phi_K) \\ & + \frac{64\pi}{35} Y_{4,4}^* (\theta_H, \phi_H) \sum_k r_{jk}^{-6} Y_{4,4} (\theta_K, \phi_K) \end{aligned} \quad (3)$$

For the Mn^{2+} ion $S = 5/2$ and $g = 2.0015$ (13) so atomic part of the equation 3 can be evaluated as

$$(3/4) .S (S+1) (g^2 \beta^2/h)^2 .n = 7.0035 \times 10^{-25} .n \quad (4)$$

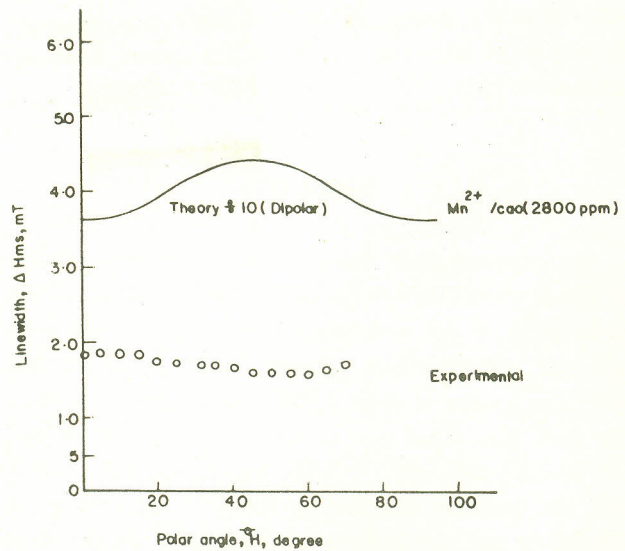


Fig. 1. E.S.R. spectrum of $\text{Mn}^{2+}/\text{CaO}$, 293K. $\theta = 0^\circ$, 30GH_z , 2800 ppm.

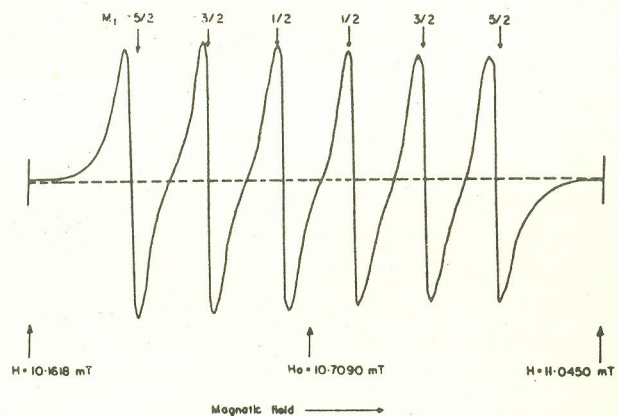


Fig. 2. Comparison of predicted and observed line width with polar angles. Full line dipolar theory, circles are experimental points. $T=293\text{K}$, $f_0=30\text{GH}_z$.

expressed in units of $(\text{radian sec}^{-1} \text{ cm}^{-6})$.

Using Table 2, the geometrical part of the Equation-3 can be partially evaluated leading to the final equation

$$\begin{aligned} \langle \Delta\omega^2 \rangle = & 7.0035 \times 10^{20} .n [7.15864 - 2.327 Y_{4,0}^* (\theta_H, \phi_H) \\ & - 2.7561 Y_{4,4}^* (\theta_H, \phi_H)] \end{aligned} \quad (5)$$

The total dipolar broadening is given by the square root of the sum of the second moments of the individual dipolar interactions. This must be converted into the peak-to-peak derivative linewidth, ΔH_{ms} , for comparison with the experi-

Table 1. Values of r , θ , and ϕ for calcium sites in eight unit cells of CaO , taking the common corner as the origin of the polar co-ordinates.

a	b	c	$r(\text{\AA})$	θ°	ϕ°	a	b	c	$r(\text{\AA})$	θ''	ϕ''
-1/2	1/2	0	3.4015	90	45	-1/2	1	-1/2	5.8916	114.09	116.56
-1/2	1/2	0	3.4015	90	135	-1/2	-1	1/2	5.8916	65.91	243.44
-1/2	-1/2	0	3.4015	90	225	1/2	-1	1/2	5.8916	65.91	296.55
1/2	-1/2	0	3.4015	90	315	-1/2	-1	-1/2	5.8916	114.09	243.44
0	1/2	1/2	3.4015	45	90	1/2	-1	-1/2	5.8916	114.09	296.56
0	-1/2	1/2	3.4015	45	270	1	1/2	1/2	5.8916	65.91	26.57
0	-1/2	-1/2	3.4015	135	270	1	-1/2	1/2	5.8916	65.91	233.43
0	1/2	-1/2	3.4015	135	90	1	1/2	-1/2	5.8916	114.09	26.57
1/2	0	1/2	3.4015	45	130	1	-1/2	-1/2	5.8916	114.09	333.43
-1/2	0	1/2	3.4015	45	180	-1	1/2	1/2	5.8916	65.91	153.43
1/2	0	-1/2	3.4015	135	0	-1	-1/2	1/2	5.8916	65.91	206.56
-1/2	0	-1/2	3.4015	135	180	-1	1/2	-1/2	5.8916	114.09	153.43
0	0	1	4.8105	0	-	-1	-1/2	-1/2	5.8916	114.09	206.56
0	0	-1	4.8105	180	-	1	0	1	6.8030	45	0
1	0	0	4.8105	90	0	-1	0	-1	6.8030	45	180
0	1	0	4.8105	90	90	1	0	-1	6.8030	135	0
-1	0	0	4.8105	90	180	-1	0	-1	6.8030	135	180
0	-1	0	4.8105	90	270	0	1	1	6.8030	45	90
1/2	1/2	1	5.8916	35.26	45	0	-1	1	6.8030	45	270
-1/2	1/2	1	5.8916	35.26	135	0	1	-1	6.8030	135	90
-1/2	-1/2	1	5.8916	35.26	225	0	-1	-1	6.8030	135	270
1/2	-1/2	1	5.8916	35.26	315	1	1	0	6.8030	90	45
1/2	1/2	-1	5.8916	144.74	45	-1	1	0	6.8030	90	135
-1/2	1/2	-1	5.8916	144.74	135	-1	-1	0	6.8030	90	225
-1/2	-1/2	-1	5.8916	144.74	225	1	-1	0	6.8030	90	315
1/2	-1/2	-1	5.8916	144.74	315	1	1	1	8.3320	54.74	45
1/2	1	1	5.8916	65.91	63.44	-1	1	1	8.3320	54.74	135
-1/2	1	1/2	5.8916	65.91	116.56	-1	-1	1	8.3320	54.74	225
1/2	1	-1/2	5.8916	114.09	62.44	1	-1	1	8.3320	54.74	315
						1	1	-1	8.3320	125.26	45
						-1	1	-1	8.3320	125.26	135
						-1	-1	-1	8.3320	125.20	225
						1	-1	-1	8.3320	125.26	315

mental results. This is done by using the equation

$$H_{ms} = \frac{\sqrt{\langle \Delta\omega^2 \rangle}}{\pi} \frac{3H}{\partial\nu} \quad \text{Tesla} \quad (6)$$

where the parameter $\frac{\partial H}{\partial\nu}$ is obtained from the relation $\frac{\partial H}{\partial\nu} = h/g\beta$.

Under the experimental conditions used in the present equation experiments $\phi_H = 0$ and by substituting the value

of $n = 0.0028$ for the Mn^{2+} concentration together with the appropriate values of θ_H the theoretical curve for the variation of dipolar linewidth ΔG_{ms} with polar angle can be obtained. This is shown by full line in Fig. 2.

DISCUSSION

Overlapping of the Fine Structure Lines. An important

feature which emerges from comparison between the experimental spectrum observed with this crystal and those reported in the literature [9, 10, 14] is that here we see a spectrum of six lines instead of a spectrum of six groups of five fine structure lines reported previously. A spectrum of six-lines indicate the overlapping of all the fine structure transitions ($M_s = \pm 5/2 \leftrightarrow \pm 3/2, \pm 3/2 \leftrightarrow \pm 1/2$) with the central $1/2 \leftrightarrow -1/2$ transitions. It follows from the spin-Hamiltonian for a states ions (having $S = 5/2$) in a cubic lattice with a strong magnetic field, that the maximum separation between the transitions $+5/2 \leftrightarrow +3/2$ and $-5/2 \leftrightarrow -3/2$ is $4a/g\beta$ (where 'a' is the crystal field splitting parameter) and that it will be observed at the polar angle $\phi_H = 0^\circ$ [11]. The reported 'a' value of Mn^{2+}/CaO is $5.9 \times 10^{-4} \text{ cm}^{-1} = 0.63 \text{ mT}$ (9); thus, the possible maximum separation between the $\pm 5/2 \leftrightarrow \pm 3/2$ transitions is 2.52mT. It has been reported by Low[13] that the linewidth of the $\pm 5/2 \leftrightarrow \pm 3/2$ transition in Mn^{2+}/CaO was about twice as wide as that of the $1/2 \leftrightarrow -1/2$ transition when H was parallel to the (100) direction. Therefore, for the $1/2 \leftrightarrow -1/2$ transition, the linewidth will be greater than 0.6mT and will overlap with the $\pm 5/2 \leftrightarrow \pm 3/2$ transitions and produce a single broad line. It has also been reported in the literature[9] that the fine structure lines in Mn^{2+}/CaO were resolved for a manganese concentration of 580 ppm. Here is the present specimen the concentration is about five times larger. It seems likely therefore that the overlapping of the transitions $\pm 5/2 \leftrightarrow \pm 3/2$ and $\pm 3/2 \leftrightarrow \pm 1/2$ with the $1/2 \leftrightarrow -1/2$ central fine structure line is due to higher concentration of Mn^{2+} in CaO and this suggests that the linewidth is concentration dependant.

Linewidth Characteristics. Comparison of the experi-

mental and theoretical data given in Fig. 2 shows that the predicted dipolar linewidth is about twenty five times larger than the observed linewidth and also there is no convincing experimental evidence for the linewidth maximum expected at $\rho_H = 0$. This result is similar to those recently found by the authors several transition group ions in magnesium oxide, to which more detailed reference is made later. In order to establish the form of the line broadening an analysis of the lineshape was undertaken. The usual method of determining whether an ESR line has Gaussian or Lorentzian shape [15] is to find the ratio of the peak-to-peak derivative width (ΔH_{ms}) to the width at half-height of the absorption spectrum (ΔH_1); for a Gaussian line $\Delta H_{ms}/\Delta H_1 = 0.846$ whereas for a Lorentzian line the value of the ratio is 0.577. Here the experimentally recorded derivative plot was integrated numerically to give the absorption spectrum. From this the width at half height (ΔH_1) was deduced and the ratio $\Delta H_{ms}/\Delta H_1$ derived; the value found was 0.567 in close agreement with that expected for a Lorentzian lineshape.

This similarities between the present linewidth examination of Mn^{2+}/CaO and the previous studies on doped MgO referred to above are brought out by reference to Table 3.

This lists the values of the factor by which the predicted linewidth (derived from Van Vleck dipolar broadening theory) exceeds that observed experimentally, the ratio $\Delta H_{ms}/\Delta H_1$ and also the moment ratio $M_4/M_2^{1/2}$. (The latter quantity, in which M_2 and M_4 are respectively the second

Table 2. Trigonometrical parameters for the calcium sites in 8 unit cells of CaO

$r \text{ \AA}$	$\theta^\circ k$	$\phi^\circ k$	N(No. of sites)	$Y_{4,0}(\theta_k, \phi_k)$	$Y_{4,4}(\theta_k, \phi_k)$	$Nr^{-6} \times 10^{45} \text{ cm}^{-6}$	$Nr^{-6} Y_{4,0}(\theta_k, \phi_k) \times 10^{45} \text{ cm}^{-6}$	$Nr^{-6} Y_{4,4}(\theta_k, \phi_k) \times 10^{45} \text{ cm}^{-6}$
3.4015	90	45	4	0.3174	-0.4425	2.5825	0.8197	-1.1427
3.4015	45	0	8	0.3438	0.1106	5.1649	-1.7757	0.5712
4.8105	0	-	2	0.8463	0.000	0.1614	0.1366	0.000
4.8185	90	0	4	0.3174	0.4425	0.3228	0.1025	0.1428
5.8916	35.26	45	8	-0.1528	-0.04917	0.1913	-0.0292	-0.00094
5.8916	65.91	26.57	16	-0.1087	-0.0861	0.3826	-0.0416	-0.03294
6.8030	45	0	8	-0.3438	0.1106	0.0793	-0.0273	0.0088
6.8030	90	45	4	0.3174	-0.4425	0.0396	0.0126	-0.01752
8.3320	54.74	45	8	-0.3291	-0.1967	0.0239	-0.0078	-0.00047
SUM						8.9483	-0.8120	-0.4799

and fourth moments of line if of interest because the condition that

$$M_4^{1/4} / M_2^{1/2} \gg 1$$

has been suggested by Alt'shuler [16] as a criterion for exchange narrowing. It can be seen that in all these materials the linewidth predicted from Van Vleck dipolar broadening exceeds that observed experimentally by a very considerable margin and also that they all exhibit a Loren-

Table 3. Comparison of linewidth characteristics of Mn^{2+} /CaO with those from some doped magnesium oxide single crystals

Crystal system and reference	Ratio of predicted dipolar to observed line width	Width ratio $\Delta H_{ms} / \Delta H_1$	Moment ratio $M_4^{1/4} / M_2^{1/2}$
Fe			
Fe ³⁺ /MgO (5)	100	0.48	1.48
Cr ³⁺ /MgO (6)	100	0.64	1.39
Co ²⁺ /MgO (7)	50	0.58	1.36
Gd ³⁺ /MgO (8)	100	0.59	1.33
Mn ²⁺ /CaO (present work)	25	0.57	1.39

tian lineshape. Further experiments are desirable on crystals containing lower manganese concentrations in order to establish the form of the linewidth versus concentration dependence and confirm the results deduced from the measurements on the one crystal available for examination here.

REFERENCES

1. G. Brown, G.J. Kirkby, J.S. Thorp, *J. Mat.Sci.*, **9**, 65 (1974).
2. J.S. Thorp, G. Brown and H.P. Buckley, *J. Mat.Sci.*, **9**, 1337 (1974).
3. W.J.C. Grant and M.W.W. Strandberg, *Phys.Rev.*, **135** A, 727 (1964).
4. J.H. Van Vleck, *Nuovo. Si Suppl. No. 3*, **6**, 933 (1956).
5. J.S. Thorp, R.A. Vasquez, C. Adcock, W. Hutton, *J. Mat.Sci.*, **11**, 89, (1974).
6. J.S. Thorp, M.D. Hossain, L.J.C. Bluck, *J. Mat.Sci.*, **14**, 2853 (1979).
7. J.S. Thorp, M.D. Hossain, L.J.C. Bluck, T.G. Bushell, *J. Mat.Sci.*, **15**, 903 (1980).
8. J.S. Thorp, M.D. Hossain, *J. Mat.Sci.*, **16**, 633 (1981).
9. A.J. Shuskus, *Phys. Rev.*, **127**, 1529 (1962).
10. C.O. Arian, F.S. Stone, *J. Chem. Soc. Faraday Trans.*, **75**, 2285 (1979).
11. A. Abragam, B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions*, (Clarendon Press, Oxford, 1970), p 171.
12. R.W.G. Wyckoff, *Crystal Structures* (Inter.Sci. New York, 1965), Vol. 1.
13. W. Low, R.S. Rubins, *Paramagnetic Resonance* (Low Academic Press, New York, 1963), p.79, Vol.1.
14. O.J. Rubio, P.E. Munoz, J. Boldeio, Y. Chen, M.M. Abraham, *J. Chem. Phys.*, **70**, 633 (1979).
15. C.P. Poole, *Electron Spin Resonance* (John Wiley and Sons, New York, 1967), p.775.
16. S.A. Alt'shuler and B.M. Kozyrev, *Electron Paramagnetic Resonance* (Academic Press, New York, 1964).