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Electron spin resonance linewidths of Cr^{3+} in magnesium oxide

J. S. THORP, M. D. HOSSAIN, L. J. C. BLUCK*
Department of Applied Physics and Electronics, University of Durham, UK

Electron spin resonance linewidths of Cr^{3+} in single crystal MgO at 9 GHz and 35 GHz were examined experimentally and theoretically for a range of Cr^{3+} concentrations. In contrast to the behaviour expected from dipolar broadening the experimental peak-to-peak linewidth for the $\frac{1}{2}$ to $-\frac{1}{2}$ transition, which had a value of about 0.5 mT at 293 K, was independent of both polar angle and concentration over the range from 800 p.p.m. Cr to 15 100 p.p.m. Cr. The calculated dipolar linewidths exceeded those observed by factors of over one hundred; the ratio of moments $M_4^{1/2}/M_2^{1/2}$ derived from the experimental data lay between 1.33 and 1.39 and the lineshapes were markedly Lorentzian. The data suggested that Cr^{3+} entered the lattice substitutionally, occupying magnesium sites, that the linewidths were determined by exchange narrowing over the whole concentration range examined and that the exchange energy, whose values lay between 4 GHz and 100 GHz, varied linearly with concentration.

1. Introduction

Magnesium oxide is widely used commercially, either in its fused or powdered forms, purely for its refractory properties or, more specifically, as an electrically insulating refractory material. However, questions still remain in the latter, which has been the subject of much work over the past two decades [1, 2] regarding the role of impurities on the electrical properties and breakdown at high temperatures. An ESR study of Fe^{3+} in MgO has already been reported [3]. As part of further studies on different ions an investigation has been made of the electron spin resonance behaviour of chromium doped magnesia (Cr^{3+}/MgO) in an attempt to provide specimens of known structural characteristics on which electrical conductivity and dielectric loss measurements might subsequently be made. Some electron spin resonance data on Cr^{3+}/MgO has been reported in the literature [4–6] and the characteristic parameters of the spin-Hamiltonian calculated for cubic crystalline fields. There is, however, little detailed information available either on the question of the sites actually occupied by the dopant atoms or on the nature of the interactions between the latter. Information of this nature has recently been obtained in several materials, including doped calcium tungstate [7, 8], alumina [9, 10] and magnesium oxide [3], by making a comparison between the observed ESR linewidths and those predicted from dipolar broadening. It was decided to adopt an approach similar to that used with iron doped magnesia. This paper presents the results of the linewidth comparison made for the $\frac{1}{2} \rightarrow -\frac{1}{2}$ transition of Cr^{3+} in MgO.

2. Experimental techniques

The doped single crystals on which measurements were made were obtained from W. & C. Spicer Limited (Cheltenham), having been grown by electrofusion using pure powdered chromic oxide and pure powdered magnesia as the starting materials.

The chromium concentrations in the specimens examined ranged from 800 p.p.m. to 15 100 p.p.m; these had been determined by optical spectrographic analysis or X-ray fluorescent analysis (Johnson-Matthey Ltd.) to an accuracy of about 2%. The crystalline quality was good and neither optical examination nor X-ray back-

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*Present address: Clarendon Laboratory, Parks Road, Oxford, UK.

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reflection photographs, used to orient the specimens, revealed any evidence of macroscopic cracking, flaws, strain or mosaic formation. The crystals were coloured, varying from light green at 800 p.p.m. Cr to dark green at 15 100 p.p.m. Cr; optical absorption spectroscopy revealed features which were indicative of Cr^{3+}. Visual examination showed the coloration, and hence the doping level, to be quite uniform over each of the individual specimens, which typically had dimensions of 8.5 mm x 6 mm x 2.1 mm chosen to suit the 9 GHz spectrometer cavity.

The electron spin resonance measurements were made using both a 9 GHz spectrometer and a 35 GHz spectrometer each of which was equipped with phase sensitive detection giving output spectra in derivative form. As with the previous Fe^{3+} doped specimens some difficulty was experienced in matching the spectrometer cavity. The match between the input waveguide and the cavity depended quite critically on the size of the specimen and on the temperature; at 9 GHz it was again found necessary to use a continuously variable matching unit [3]. This difficulty was less important at 35 GHz where the spectrometer used a shorted waveguide assembly [11] rather than a cavity. At 9 GHz spectra were recorded at temperatures between 293 and 77 K by sweeping the magnetic field slowly through a known range and at 35 GHz at 293 K. The magnetic field calibrations were obtained using proton or lithium resonance magnetometer systems in which the probe could be located exactly in the position normally occupied by the specimen.

3. Experimental results

Initial measurements were made at 9 GHz to establish the form of the spectrum in each specimen. An example of this is shown in Fig. 1 which refers to a specimen containing 800 p.p.m. Cr examined at 293 K. The spectrum at $\theta_H = 0°$ shows a single strong isotropic line at about $g = 1.98$, accompanied by four hyperfine lines with a separation between the components of about 17.5 G. The field values at which the transitions occurred were compared with the values expected for Cr^{3+} in an octahedral site. There was close agreement and on this basis and in view of the similarity between Fig. 1 and the spectrum reported by Low [4], it was felt justifiable to attribute the spectrum to Cr^{3+} in octahedral sites. The hyperfine lines are due to the isotope ^{53}Cr ($I = \frac{3}{2}$) which has an abundance of 9.5%; the A value, $A = 16.16 \times 10^{-4}\ \text{cm}^{-1}$, deduced from the component separation agrees very closely with published values. The resonance field value for the $\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transition was the same for all specimens even at the highest concentration (15 100 p.p.m.). Some weak additional lines were observed which were attributed to impurities, but these were well removed from the main Cr^{3+} line examined. Measurements of the magnetic field values at resonance for the $\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transition and line width determinations were made at $\theta_H = 0°$. There was no change in either the resonance field or the linewidth with polar angle at temperatures down to 77 K. The $\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transition was used for detailed linewidth studies. The linewidth, defined as the width between points of maximum slope, ΔH_{ms}, was obtained directly from the derivative plots. At room temperature $\Delta H_{ms} \cong 0.5$ mT. This is comparable to values reported in the literature. In order to check whether there was any appreciable contribution to linewidth due to spin lattice relaxation, the spectra were recorded at 77 K. The linewidths measured were only slightly larger than those at 300 K, e.g. 0.53 mT compared with 0.50 mT, suggesting that any contribution was very small.

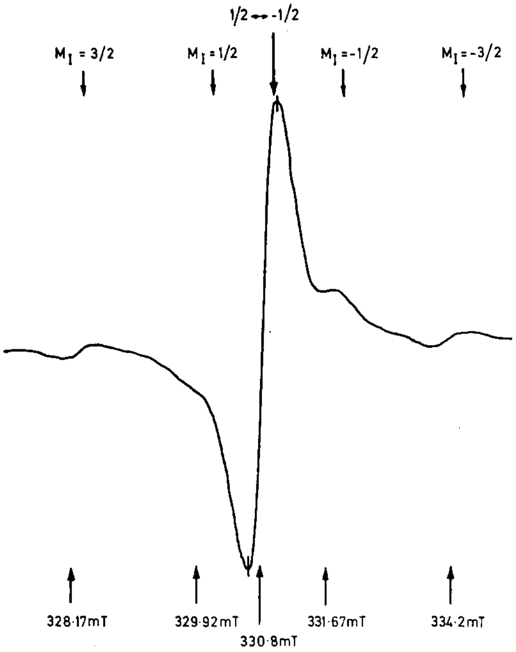

Figure 1 ESR spectrum of Cr^{3+}/MgO; 293 K, $\theta_H = 0°$, 9.167 GHz, 800 p.p.m. Cr.

4. Dipolar broadening

It will be assumed in this calculation that the main contribution to homogeneous line broadening is dipole–dipole interaction between Cr^{3+} ions. The second moment of the linewidth caused by dipolar interaction between identical atoms in magnesium oxide lattice has been shown [3] to be

$$\langle\Delta\omega^2\rangle = \tfrac{3}{4}S(S+1)(g^2\beta^2/\hbar)^2 \times n \times \left[\frac{4}{5}\sum_k (r_{jk}^{-6}) + \frac{32\pi}{35}Y_{4,0}^*(\theta_H,\phi_H)\sum_k r_{jk}^{-6}Y_{4,0}(\theta_k,\phi_k) + \frac{64\pi}{35}Y_{4,4}^*(\theta_H,\phi_H)\sum_k r_{jk}^{-6}Y_{4,4}(\theta_k,\phi_k)\right] \quad (1)$$

where $\langle\Delta\omega^2\rangle$ is the second moment, ω being measured in radian per second; g is the Landé g-factor of the atoms, of spin S, β is the Bohr magneton; n is the concentration of the interacting atoms, r_{jk} is the radius vector from the reference atom j to all the neighbouring atoms labelled over k; θ_H and ϕ_H refer the static magnetic field to the crystal axes, while θ_k and ϕ_k refer the radius vector to the same axes. The standard forms of the spherical harmonics are well known [12] and are specified completely by θ and ϕ.

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 the peak to peak derivative linewidth, ΔH_{ms}, for comparison with experimental results. This is done using the equation

$$\Delta H_{ms} = \frac{\sqrt{\langle\Delta\omega^2\rangle}}{\pi}\partial H/\partial\nu \qquad \text{tesla} \quad (2)$$

where the parameter $\partial H/\partial\nu$ is obtained from the experimental isofrequency plots obtained for each crystal.

For Cr^{3+}, $S = 3/2$ and $g = 1.98$ [4] and so the atomic part of the equations can be evaluated as

$$\tfrac{3}{4}S(S+1)(g^2\beta^2/\hbar)^2 n = 2.8757 \times 10^{-25} n(\text{rad sec}^{-1})^2 \text{ cm}^6 \quad (3)$$

Using Table A-II of [3] the geometrical part of the equation can be partially evaluated leading to the final equation,

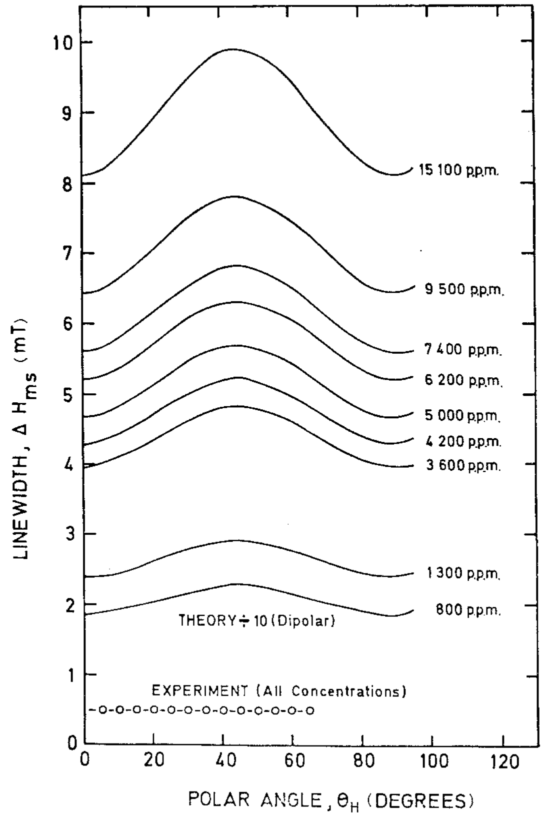

Figure 2 Comparison of predicted and observed variation of linewidth with polar angle; full lines, dipolar broadening theory; broken line, experimental.

$$\langle\Delta\omega^2\rangle = 2.8757 \times 10^{20} n \times [15.9184 - 5.175\,Y_{4,0}^*(\theta_H,\phi_H) - 6.218\,Y_{4,4}^*(\theta_H,\phi_H)] \quad (4)$$

For $\phi_H = 0°$ the equation is totally real and by substituting the experimental values of n and θ_H curves of dipolar broadening as a function of polar angle can be derived. Using the transformation of Equation 2. ΔH_{ms} can then be calculated and compared with experimental values. The theoretical curves for the variation of dipolar linewidth with polar angle are given by the full lines in Fig. 2, which also includes the experimental data shown by the broken line. The predicted concentration dependence of linewidth is compared with the experimental data obtained at 293 K in Fig. 3 in which the concentration is expressed as the percentage number of sites occupied.

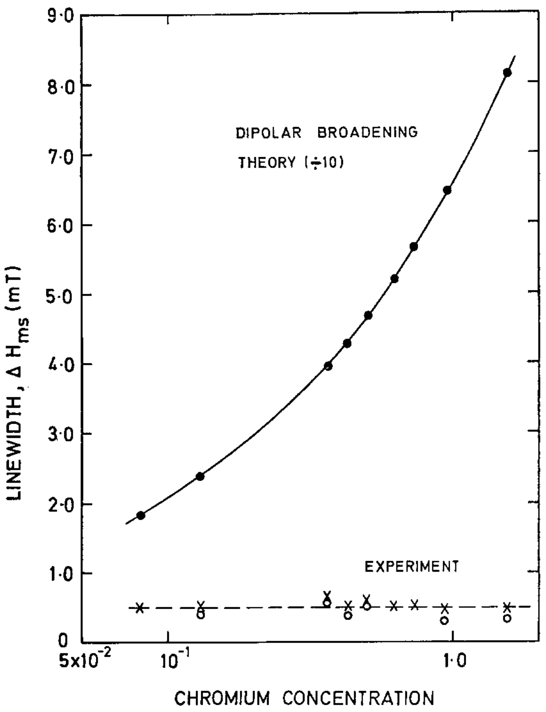

Figure 3 Comparison of predicted and observed variation of linewidth with concentration; full line, dipolar broadening theory; broken line, experimental, $\theta_H = 0°$, 293 K (x 9.1 GHz, ○ 35 GHz).

TABLE I Comparison of predicted dipolar linewidth with observed linewidth in different materials.

Material	Predicted linewidth (dipolar model)	Reference
Cr^{3+}/Al_2O_3 (Ruby)	5 times larger than observed	Grant *et al.* [9]
$Nd/CaWO_4$	Agreed closely with that observed	Brown *et al.* [7]
$Gd/CaWO_4$	7 times larger than observed	Thorp *et al.* [8]
Double-doped $Cr/Ti/Al_2O_3$	7 times larger than observed	Thorp *et al.* [10]
Fe^{3+}/MgO	100 times larger observed	Thorp *et al.* [3]

5. Discussion

Three salient features emerge from an initial comparison between the experimental results for the as grown crystals and those predicted on the basis of dipolar broadening. In the first place the predicted linewidths are about 160 times larger than the observed linewidths; secondly, the linewidth appears to be almost concentration independent, in marked contrast to the (concentration)$^{1/2}$ variation expected; thirdly, the observed linewidth appears independent of polar angle in contrast to the angular dependence predicted, which shows a maximum near $\theta = 45°$.

The discrepancy in the magnitude of the linewidth is far greater than those encountered in other materials in which similar comparisons have been made, Table I. In the examples of Table I there was a reasonably good fit between the forms of the predicted and observed angular variation of the linewidth and also between the predicted and observed linewidth versus concentration variation except for Fe^{3+}/MgO which gave exchange narrowed linewidths. The large numerical disparity in Cr^{3+}/MgO suggested that a strong narrowing mechanism was involved and to substantiate the possibility of exchange narrowing the following evidence, shown in Table II, was deduced from analysis of the lineshapes.

Exchange narrowing line mechanisms have been examined by Van Vleck [13]. Experimental evidence for exchange narrowing is usually obtained from analysis of line shapes and especially by comparison of moments. A review of Alt'Shuler [14] gives

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

where M_2 and M_4 are respectively the second and fourth moments of the line as a criterion for exchange narrowing. An analysis of this type has been attempted as in [3] and the results are given in column three. The values of the ratio are similar to the figures quoted in the literature [3] for materials in which exchange narrowing occurs. This suggests that exchange narrowing is important, even at the lowest concentration (800 p.p.m. Cr).

It has been calculated [15] that the ratio of peak to peak derivative linewidth, ΔH_{ms}, to the width at half-height, $\Delta H_{1/2}$, of the absorption curve for Gaussian lineshape is 0.846 and for the Lorentzian lineshape is 0.577. Exchange narrowing would make the line adopt a Lorentzian shape. To confirm this, the spectra were integrated numerically giving the integrated lineshapes some of which are shown in Fig. 4. From these the widths at half-height $\Delta H_{1/2}$ have been calculated and the ratio of $\Delta H_{ms}/\Delta H_{1/2}$ derived; the values are tabulated in column four. The results substantiate that the observed lineshapes are much more akin to Lorentzian than Gaussian.

The assumption, on the above basis, of an exchange-narrowed model enables evaluation of

TABLE II Lineshape data for a range of chromium concentration together with the derived values of J and θ; 9.1 GHz, 293 K

Chromium concentration (p.p.m.)	ΔH_{ms}(obs) (mT)	$M_4^{1/4}/M_4^{1/2}$	ΔH_{ms}(obs)/$\Delta H^{1/2}$(obs)	Exchange energy, J (GHz)	Weiss constant, θ (K)
800	0.47	1.38	0.425	4.39	3.15
1 300	0.51	1.37	0.544	8.39	6.04
3 600	0.73	1.39	0.642	19.13	13.78
4 200	0.48	1.34	0.480	25.40	18.30
5 000	0.65	1.33			
6 200	0.51	1.38	0.563	41.80	30.2
7400	0.51	1.37	0.532	46.40	33.48
9 500	0.40	1.35	0.479	69.00	49.72
15 100	0.42	1.36	0.470	102.60	73.70

the exchange integral J to be made by adapting the Anderson–Weiss formula [16] to give

$$J \cong \frac{\hbar\langle\Delta\omega^2\rangle\,\text{dipolar}}{\Delta\omega} \qquad (5)$$

where $\Delta\omega$ is the absorption line half-width at half-height in frequency units [i.e. $\Delta\omega = (2\pi g\beta/h)(\frac{1}{2}\Delta H_{1/2})$] obtained from the experimental spectrum. By using Equation 1 values for $\langle\Delta\omega^2\rangle$ were obtained and thus the approximate J values for the specimens have been evaluated. Furthermore, a plot of J against concentration gives a straight line as shown by the solid line in Fig. 5 where again the concentration is expressed as the percentage number of sites occupied. If this line is extrapolated to 66.6% of cation sites occupied by Cr^{3+}, (i.e. to the point corresponding to Cr_2O_3), an exchange energy of 4.38×10^{12} Hz is obtained; this compares well with the values of 3.75×10^{12} Hz for Cr^{3+} in Cr_2O_3 (which has the Al_2O_3 crystallographic structure) [17] and of 2.49×10^{12} Hz for Cr^{3+} in MgO [18], both of which estimates were obtained from intensity measurements of ESR pair spectra. We have also calculated the

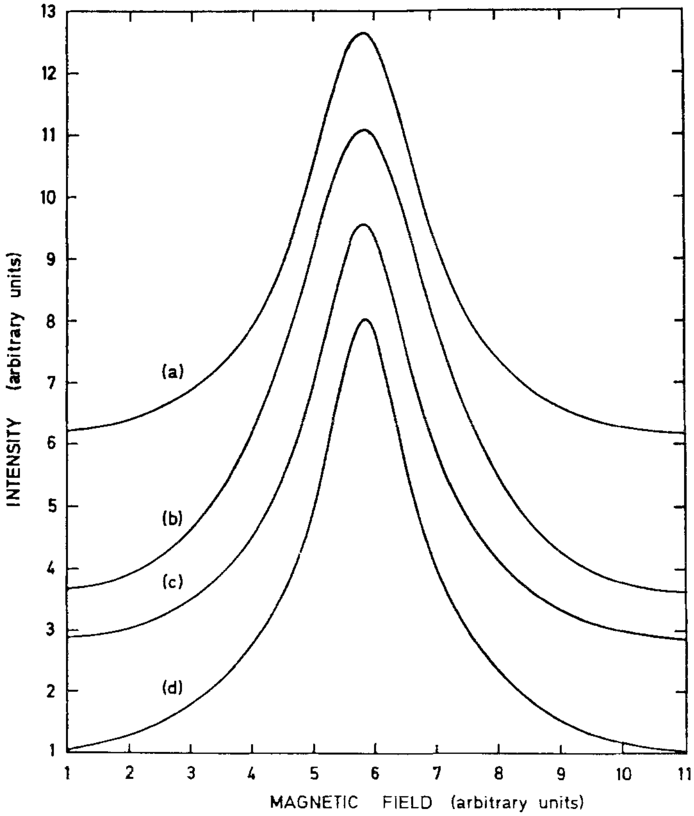

Figure 4 Integrated lineshapes for (a) 1300 p.p.m. Cr; (b) 3600 p.p.m. Cr; (c) 6200 p.p.m. Cr, and (d) 15 100 p.p.m. Cr.

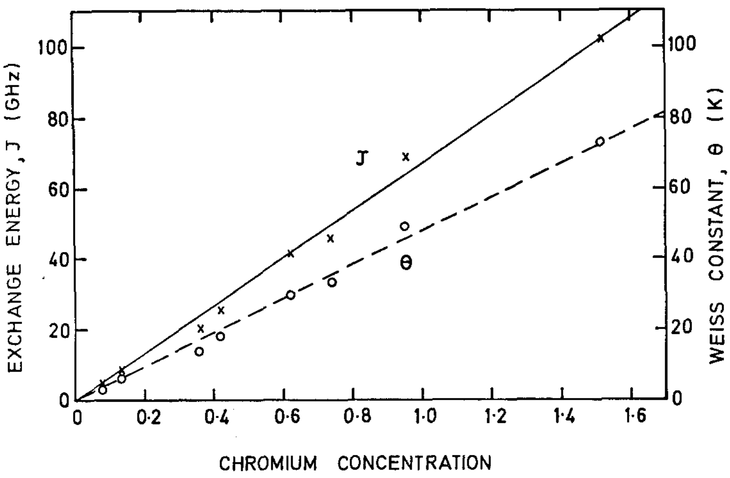

Figure 5 The variation of J and θ with chromium concentration.

values of Weiss constant, θ, from the Weiss molecular field equation

$$3k\theta = 2JzS(S+1) \qquad (6)$$

where z is the number of nearest neighbours and k is the Boltzmann constant; in the MgO lattice $z = 6$. The values of θ are tabulated in column six. A plot of θ against concentration also gives a straight line as shown by the broken line in Fig. 5. This indicates that the θ value is linearly dependent on the dopant concentration over the range examined. The slight increase in linewidth as the temperature decreases towards 77 K may be due to the unresolved superhyperfine interaction with the ^{25}Mg nuclide ($I = 5/2$) at nearest neighbour cation positions. Such a superhyperfine line has been found experimentally [19] (linewidth 0.017 mT, $A_s = 0.13$ mT) in the temperature range 77 to 220 K.

In conclusion, it may be noted that analysis of the experimental lineshapes obtained at 35 GHz gave results which were also identical to those derived from the 9 GHz data. Thus we conclude from the linewidth studies as a whole that chromium enters the magnesium oxide lattice substitutionally occupying magnesium sites at concentrations of up to at least 15 000 p.p.m.; that even at low concentrations there is a strong exchange narrowing of the ESR lines and that the exchange energy varies linearly with the chromium concentration over the range examined.

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