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ESR line broadening in Cr^{3+}/MgO at liquid helium temperatures

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Line broadening has been observed at 9 GHz in the ESR absorption spectrum of Cr^{3+} in MgO in the liquid helium temperature range, for a range of Cr^{3+} concentrations from 800 7400 ppm. The broadened linewidths at 4.2 K are about two times larger than those at 77 K and depend on polar angle. The lineshapes are Gaussian, in contrast to the Lorentzian lineshape between 293 and 77 K. The broadening is interpreted by the combined effects of strain, due to the charge misfit of Cr^{3+} and the host cation, and temperature which causes both exchange striction and departure from the cubic symmetry to a lower symmetry. Analysis of the linewidth data gives $\Delta D = (5.25 \pm 0.40) \times 10^{-4}\ \text{cm}^{-1}$ and confirms that the total linewidth, ΔH_t, is given by $\Delta H_t = \Delta H_0 + |(2\Delta D/g\beta) \cos \theta_H|$ where ΔH_0 is the linewidth independent of concentration, temperature and polar angle, θ_H.

1. Introduction

The electron spin resonance (ESR) linewidths for transition metal ions in diamagnetic host crystals can arise from various mechanisms. Firstly, there is homogeneous broadening which includes effects due to interaction of the spin system with lattice vibrations, dipole–dipole interactions between like and unlike spins, fluctuations in the microwave frequency and variations in the relative slope of Zeeman split energy levels. Secondly, inhomogeneous broadening processes must be considered and these include the effects of unresolved nuclear hyperfine structure, thermal fluctuations in the crystalline field parameters and local strain produced in the vicinity of the impurity ion by defects which arise in effecting charge compensation if the impurity ion has a valency differing from that of the host cation. In addition, other mechanisms may occur in special circumstances as, for example, broadening due to the "10/3" effect [1].

The present work has examined the linewidths of Cr^{3+} occurring as substitutional ions in MgO [2, 3] in the liquid helium temperature range; previous studies [3] have shown that the linewidth was determined by exchange narrowing at temperatures down to 77 K.

Chromium-doped MgO in which Cr^{3+} is in cubic symmetry has been studied extensively by means of ESR [2–8]. The Cr^{3+} ion has the $3d^3$ electronic configuration. In a crystal field of cubic (octrahedral) symmetry the ground state is an orbitally non-degenerate $^4A_2$ (^4F) state with spin $S = 3/2$. Since zero field splitting is absent [2, 3] at perfectly cubic sites, the allowed ESR transitions $(+3/2 \rightarrow +1/2)$, $(+1/2 \rightarrow -1/2)$ and $(-1/2 \rightarrow -3/2)$ coincide and a single ESR line should result; however, a four-fold hyperfine spectrum due to the isotope ^{53}Cr ($I = 3/2$), having a separation of about $16.3 \times 10^{-4}\ \text{cm}^{-1}$ between successive components, has been observed [2, 3, 9]; superhyperfine lines due to neighbouring ^{25}Mg nuclides have also been reported [10]. The temperature dependence of the axial field splitting D of charge-compensated Cr^{3+} ions in MgO and the isotopic shift in the crystalline field energy between ^{52}Cr and ^{53}Cr has been reported both experimentally [11] and theoretically [12] to be maximum at low temperature; the pressure dependence of the isotopic g shift has also been reported [13]. However, the hyperfine splitting constant A has been found to be independent of temperature. Dipolar coupling to paramagnetic impurities other than cubic Cr^{3+} and anisotropic hyperfine coupling to ^{25}Mg were considered [14] as a source of inhomogeneous broadening at liquid helium temperatures.

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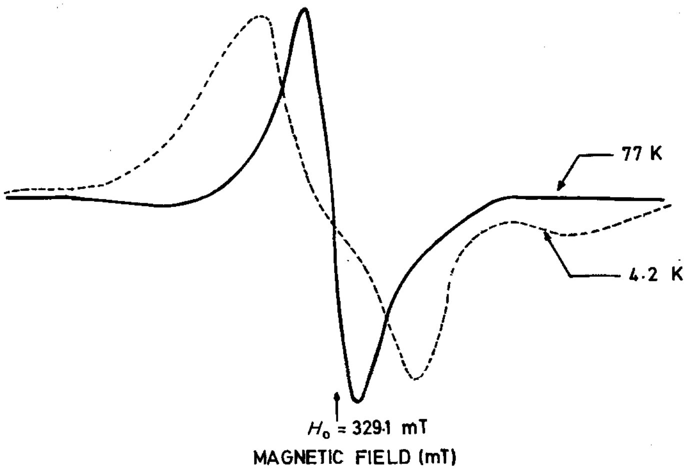

Figure 1 Line broadening of $\frac{1}{2}$ to $-\frac{1}{2}$ transition of Cr^{3+}/MgO; 77 K and 4.2 K, $\theta_H = 0°$, 9.12 GHz, 800 ppm Cr.

The linewidths of Cr^{3+} in cubic sites of MgO in the temperature range 293 to 77 K measured by Thorp *et al.* [3] were determined by exchange narrowing and the linewidth was independent of both temperature and concentration. Here, by contrast, the observed linewidths at liquid helium temperatures increase with decreasing temperature.

2. Experimental techniques

The doped single-crystals on which measurements were made were obtained from W. and C. Spicer Ltd (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 to 7400 ppm; these samples had been used in the previous study [3]. Measurements were made with a 9 GHz spectrometer [15] which was equipped with a helium cryostat. The magnetic field calibrations were obtained using a proton resonance magnetometer. A stabilized microwave source was used to minimize fluctuations to microwave frequency, and, to avoid saturation effects, the incident microwave power to the cavity was kept below 200 μW; the small amplitude field modulation frequency was 125 Hz.

3. Results

Initial measurements were taken to establish the form of the spectrum at 4.2 K in each specimen. An example of this is shown in Fig. 1, which refers to a specimen containing 800 ppm Cr^{3+} examined at 4.2 and 77 K. Other low and medium concentration samples similarly showed a broader linewidth at 4.2 than at 77 K. For concentrations up to 7400 ppm Cr^{3+} the 4.2 K linewidth was rather more than two times the 77 K linewidth. there was no change in resonance field with temperature down to 4.2 K. The variation of linewidth with polar angle θ_H has also been found in the liquid helium temperature range and, for a specimen containing 800 ppm Cr^{3+}, this is shown in Fig. 2. The maximum linewidths were observed at $\theta_H = 0°$. A linewidth variation with temperature has been found only below about 15 K. Above 15 K the

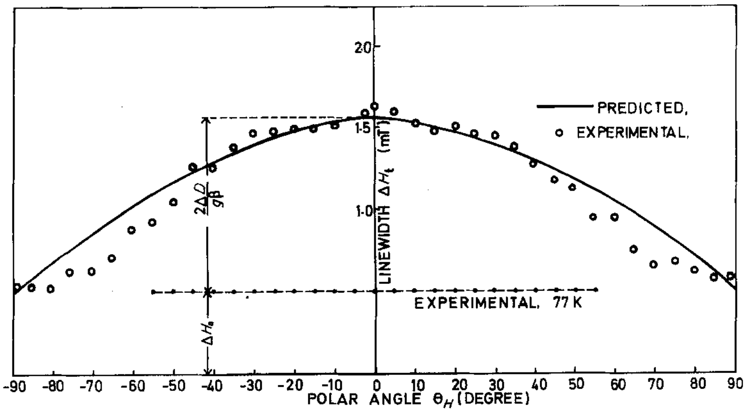

Figure 2 Linewidth variation with polar angle θ_H. Cr^{3+}/MgO (800 ppm), 4.2 K, 9.12 GHz.

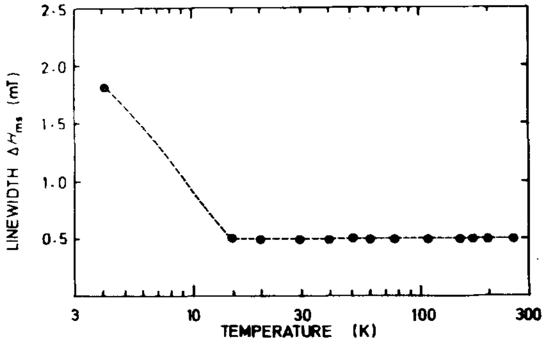

Figure 3 Variation of linewidth plotted against temperature. 9.1 GHz, $\theta_H = 0°$, Cr^{3+}/MgO (800 ppm).

width of the resonance line was independent of temperature as shown in Fig. 3.

4. Discussion

Three salient features emerge from an initial comparison between the experimental 4.2 K results for the as-grown crystals and those reported for temperatures above 77 K [3]. In the first place, the observed linewidths are about two times larger than the reported 77 K values [3]. Secondly, the linewidths are dependent on polar angle. Thirdly the lineshapes are Gaussian in contrast to the Lorentzian lineshape [3] found between 293 and 77 K.

Although the line is broadened at liquid helium temperature, the observed linewidth is about 50 times less than that predicted from the dipolar broadening theory [3]. The ratios $M_4^{1/4}/M_2^{1/2}$ (where M_2 and M_4 are respectively the second and fourth moments) were greater than unity, as shown in Table I, which indicated that exchange narrowing is still present at low temperatures. In Fe^{3+}/MgO, broadening due to the "10/3" effect under exchange narrowing conditions at liquid helium temperatures has been described in the literature [16]. The "10/3" effect predicts a Lorentzian lineshape, unlike the lineshape observed here in Cr^{3+}/MgO; details of the lineshape analysis are given in Fig. 4 and Table I. A close examination of the absorption lineshapes, shown in Fig. 4, reveals a pair of shoulders. These are indicative of the fact that in a slightly distorted octahedral field, the $\pm 3/2 \leftrightarrow \pm 1/2$ transitions occur at field values slightly different from that of the $\pm 1/2$ transition. Similar shoulders on the absorption line of Cr^{3+}/MgO have been reported [17].

Now the possible broadening mechanisms will be considered. The Cr^{3+} ions occupy the Mg^{2+} site substitutionally [2, 3]. The extra positive charge on the trivalent Cr^{3+} must be compensated for to ensure stability. It has been reported that in Cr^{3+}/MgO [5] and Fe^{3+}/MgO [18] charge compensation is affected by Mg^{2+} vacancies located along one of the cube axes. One would expect that these vacancies are distributed throughout the crystal at random. The uneven localized charge distribution of the vacancies probably causes Cr^{3+} to be slightly displaced from the original crystal lattice positions. The temperature dependence of the crystal field splitting due to thermal expansion of the host crystal has been reported [19]. Presumably, due to the combined effect of temperature and displacements, a distortion from octahedral symmetry will result; this will cause some zero field splitting, which would explain the splitting of the resonance line to $M = \pm 3/2 \leftrightarrow \pm 1/2$ at low temperatures. Similar splitting of the spectrum to Cr^{3+} in chrome alum in isomorphous aluminium alum has been reported at about 160 K [20], although a single line was observed at room-temperature. In addition, these distortions in the crystal may play a role in exchange striction [21],

TABLE I Lineshape data for a range of chromium concentrations together with derived values of ΔD; 9.1 GHz; 4.2 K; $\theta_H = 0°$.

Chromium concentration (ppm)	ΔH_{ms} (Obs.) at 77 K (mT)	ΔH_{ms} (Obs.) at 4.2 K (mT)	$M_4^{1/4}$* / $M_2^{1/2}$ at 4.2 K	ΔH_{ms} (Obs.)* / $\Delta H_{1/2}$ (Obs.) at 4.2 K	Lineshape	ΔD (cm^{-1})
800	0.50	1.60	1.226	0.848	Gaussian	5.08×10^{-4}
1300	0.60	1.82	1.259	0.776	Nearer to Gaussian	5.17×10^{-4}
3600	0.80	2.06	1.251	0.960	Gaussian	5.72×10^{-4}
4200	0.60	1.58	1.26	0.821	Nearer to Gaussian	4.53×10^{-4}
5000	0.70	1.86	1.28	0.839	Nearer to Gaussian	5.36×10^{-4}
6200	0.60	1.84	1.345	1.02	Gaussian	5.82×10^{-4}
7400	0.60	1.70	1.274	0.948	Gaussian	5.08×10^{-4}

*Figures in columns 4 and 5 have been obtained by using the procedure described in [3].

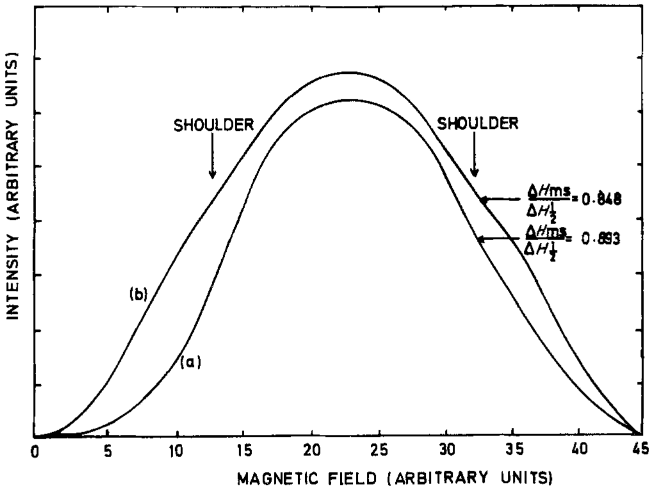

Figure 4 Comparison of integrated lineshapes for (a) 7400 ppm and (b) 800 ppm Cr at 4.2 K; 9.1 GHz, $\theta_H = 0°$.

the phenomenon whereby the lattice tends to distort so as to lower the exchange energy until it is balanced by elastic forces. So, the broadening observed here at low temperature may be strain broadening, due to a charge misfit of Cr^{3+} from the host cation. The strain model has been used to explain the anisotropic broadening of Mn^{2+}, Fe^{3+} and Cr^{3+} ESR absorption lines in MgO [22, 23] and optical absorption lines of Cr^{3+}/MgO at low temperatures [24].

Another possible source of line broadening, described by Stoneham [25] is due to point defects. The point defect model arises essentially from a size difference effect and is not likely to make an important contribution here because the ionic radius of the doping ion (Cr^{3+}, 0.615 Å) is less than that of the cation (Mg^{2+}, 0.72 Å) [26].

To explain the spectrum at low temperature, the spin Hamiltonian (neglecting hyperfine action) can be used,

$$\mathscr{H}_s = g\beta H S_z + D(S_z^2 - \tfrac{5}{4}), \qquad (1)$$

where g is the g-factor, β is the Bohr magneton, H is the magnetic field, S_z is the z-component of spin and $2D$ is the zero field splitting energy. Since Cr^{3+} has $S = 3/2$, three lines would be observed representing, for an energy level, W, the transitions

$$W \pm \tfrac{3}{2} \rightarrow W \pm \tfrac{1}{2} = g\beta H \pm 2D \qquad (2)$$

and

$$W + \tfrac{1}{2} \rightarrow W - \tfrac{1}{2} = g\beta H. \qquad (3)$$

Three resolved lines are not observed; instead a single broad line is seen. Because of this, it was not possible to measure the value of D exactly, but the change in D, ΔD, was determined by taking the difference in the positions of the peaks of the derivative lines observed at 77 and 4.2 K. The shift of peak along the magnetic field axis due to the internal strain is $\Delta D/g\beta$ and the best estimate of ΔD, as shown in column 7 of Table I, is $(5.25 \pm 0.40) \times 10^{-4}\ \text{cm}^{-1}$. This is comparable to the value of $\Delta D = (1.2 \pm 0.2) \times 10^{-4}\ \text{cm}^{-1}$ observed by Serway *et al.* [23] assuming strain and tetragonal symmetry, for measurements on the $M = 3/2 \rightarrow \pm 1/2$ transition in a Cr^{3+}/MgO sample containing 10 ppm Cr^{3+}. It has been reported by Van Wieringen *et al.* [4] that the linewidth of the $\pm 3/2 \rightarrow \pm 1/2$ transition in Cr^{3+}/MgO was twice as wide as that of the $1/2 \leftrightarrow -1/2$ transition, with H parallel to the (1 0 0) direction. On this basis and taking the reported linewidth value of 0.5 mT [3] for the $\pm 1/2$ transition, one could observe the three resolved lines separately if the value of $\Delta D/g\beta$ is greater than 2.5 mT (i.e. $24 \times 10^{-4}\ \text{cm}^{-1}$).

The observed total linewidth ΔH_t when H lies in a (1 0 0) plane can be written as

$$\Delta H_t = \Delta H_0 + \left| \left(\frac{2\Delta D}{g\beta} \right) \cos\theta_H \right| \qquad (4)$$

where ΔH_0 represents a linewidth independent of polar angle θ_H, temperature and concentration and is taken to be the width of the $M = \pm 1/2$ transition, when the zero field splitting energy, $2D$, is zero and the Zeeman field is along a cube axis. This can be considered to be the intrinsic linewidth in the absence of internal strain. The comparisons between the observed linewidth at 4.2 K and the linewidth according to Equation 4 are shown in Fig. 2. The line broadening was maximum at $\theta_H = 0°$, which indicates the direction of strain in the crystal lattice. Thus it can be assumed that the Cr^{3+}/MgO crystal lattice acquires a strain at low temperature due to the vacancies (caused by charge misfit), along one of the cube axes. Strain effects due to poor annealling have been reported for Ni^{2+} in magnesium oxide [27] and Cr^{3+} in yttrium aluminium garnet [28]. To examine the effect of heat treatment in removing strain two of the as-received Cr^{3+}/MgO specimens (800 and 3600 ppm) were heated at 1000° C for 12 h in air and cooled slowly down to room temperature, (4 h). The linewidths of these samples at 4.2 K fell from 1.6 to 0.91 mT and from 2.06 to 0.81 mT, respectively. The resulting values are close to the linewidths at 77 K and were independent of polar angle θ_H. The 800 ppm Cr specimen (for which the room-temperature linewidth was 0.7 mT) was then heated in air at 1000° C for 12 h and cooled down to room temperature much more quickly (1 h). The linewidth at room-temperature increased to 1.2 mT and became polar angle dependent showing a similar variation to that observed before at 4.2 K, and indicating the presence of considerable strain. The reactions between vacancies and Cr^{3+} ions in MgO crystal as a function of temperature have been discussed by Glass [29]; where the valency of the Cr^{3+} ion is unchanged the vacancies are essentially immobile up to 900° C but diffuse into the lattice at temperatures above 900° C. The heat treatment of the specimens in air at 1000° C for 12 h followed by a slow cool down to room temperature creates this mechanism of charge compensation of the Cr^{3+} ion whereas quick cooling creates strain in the specimen.

Using ESR techniques, Watkins and Feher [30] found that the strain coupling coefficients for Cr^{3+} in cubic sites of MgO were $G_{11} = 0.6 \pm 0.6$ and $G_{44} = 4.2 \pm 0.6$ (with dimensions of cm^{-1} per unit strain). The stress coefficient G_{ii} is related to the strain coupling coefficient C_{ii} through the elastic stiffness coefficient [22]. Using the value of coefficient quoted by Watkins and Feher, the stress coefficients were calculated by Serway *et al.* [23] and have values $C_{ii} = (2.8 \pm 2.8) \times 10^{-8}$ cm N^{-1}. It has been reported by Feher [22] that the change in crystal field splitting parameter D in MgO due to pressure P along the (1 0 0) axis is given by

$$\Delta D = \tfrac{3}{2} C_{ii} P. \qquad (5)$$

Using the quoted values [23] for C_{ii} and taking $\Delta D = (5.25 \pm 0.40) \times 10^{-4}$ cm^{-1}, the pressure P experienced in the crystal at low temperature along (1 0 0) is $(6.25 \pm 0.8) \times 10^3$ N cm^{-2}. Walsh [13] measured the shift of the "g"-factor as a function of hydrostatic pressure and found that a "g"-shift of $+0.0025$ corresponds to a pressure of 10^5 N cm^{-2}. The derived pressure is about sixteen times less than Walsh's value, so it is not surprising that no g-shift at low temperature was seen in this work.

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