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Dipolar line broadening in gadolinium-doped calcium tungstate

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Electron spin resonance linewidths of $Gd^{7/2}$ in single crystal calcium tungstate ($CaWO_4$) were examined experimentally and theoretically for Gd concentrations up to 0.05 at. %, the range over which single site occupation by gadolinium was maintained. The linewidths expressed as widths between points of maximum slope on derivative spectra, lay between 0.3 and 1.5 mT over the angular ranges $0° < \theta < 90°$ and $0 < \phi < 90°$ explored. There is good agreement between the form of the angular variation of linewidth and calculation based on dipolar broadening theory. Quantitatively, however, the predicted values are about five time larger than the observed linewidths; this difference may be due to exchange narrowing.

1. Introduction

A recent study of the electron spin resonance spectrum of Nd^{3+} in $CaWO_4$ showed that the width of the single line could quite successfully be explained by dipolar broadening theory [1]. Since the scheelites form an homologous series opportunity is provided for the systematic study of crystal field effects; hence, rare earth-doped scheelites have been extensively studied, though there has been little investigation of the actual linewidths. An example of this is a series of papers by Russian workers [2] in which gadolinium has been used to dope a number of different scheelites. Gadolinium, in particular, is of current interest because it has been used as a monitor ion in connection with studies on nucleation and crystallization in glasses [3]. However, in the glasses a very broad line (about 0.1 T at 9 GHz) was observed, in contrast to the generally narrow lines (1 mT or less) often seen in single crystal materials. In the present work the object is to ascertain to what extent dipolar mechanisms can account for the observed resonance linewidths of gadolinium in the known crystalline environment of calcium tungstate single crystals.

2. Experimental

Single crystal boules of Gd^{3+}:$CaWO_4$ were grown by the Czochralski process [4] by I.R.D. of Newcastle upon Tyne. The trivalent gadolinium ions were added to the powdered $CaWO_4$ in the form of the oxide Gd_2O_3 and charge compensation was by the incorporation of vacancies. As a rare earth ion gadolinium substitutes at the divalent calcium sites [5] such that one calcium vacancy is formed for each pair of gadolinium ions. Specimens were grown having nominal gadolinium concentrations between about 0.005 and 0.05%.†

The ground state of Gd^{3+} is $(4f^7)^8S_{7/2}$ and as an S-state ion gadolinium should exhibit no first order crystal field splitting. However experimentally it is found that the ground state degeneracy is removed, although the mechanism responsible is not fully understood; in the tetragonal field of calcium tungstate the $J = 7/2$ state splits into four Kramer's doublets. Paramagnetic resonance thus occurs between the Zeeman levels of these four doublets. Since the gadolinium ions substitute at the calcium sites only one resonance spectrum of seven lines is expected [6]. The energy level scheme for Gd^{3+}:$CaWO_4$ has been predicted at X-band for a specific magnetic field orientation [7]. However, there are no results or predictions for Q-band.

The resonances were observed using a Q-band spectrometer, working at 37.5 GHz, with phase-

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†The concentration figures reported in this paper refer to the percentage of calcium sites occupied by gadolinium; this is almost equivalent to the atomic percentage for calcium tungstate.

sensitive detection at 160 kHz being used to record the first derivative of the absorption line. Samples were cut with dimensions 2.5 mm × 3.5 mm × 4 mm on a diamond wheel, the *c*-axis being perpendicular to the 2.5 mm × 4 mm face. The specimen dimensions were chosen so that the samples could be mounted on a short-circuiting plunger terminating a length of thin walled stainless steel waveguide, and within the modulation loop situated on the plunger itself. Measurements were made in two planes, in the plane of the *c*-axis (100), and in the plane perpendicular to *c*, (001); the polar angle θ was defined as the angle between the *c*-axis and the magnetic field, H and ϕ as the angle between the *a*-axis and H. The full lines of Figs. 1 and 2 give the experimental isofrequency polar plots for the line positions in the two planes observed below 1.6 T. The lines were numbered one to seven in order of increasing magnetic field at $\theta = 0$ and thus it was found that on rotating the field to $\theta = 90$ the lines crossed (Fig. 1). From Fig. 2 it was clear that the crystallographic axes and the magnetic axes were not coincident. The magnetic axes, x and y, were taken as 10° from the *a*- and *b*-axes in an anticlockwise direction and the $+z$ direction was then down into the page; the four-fold symmetry of the z-axis was noticeable.

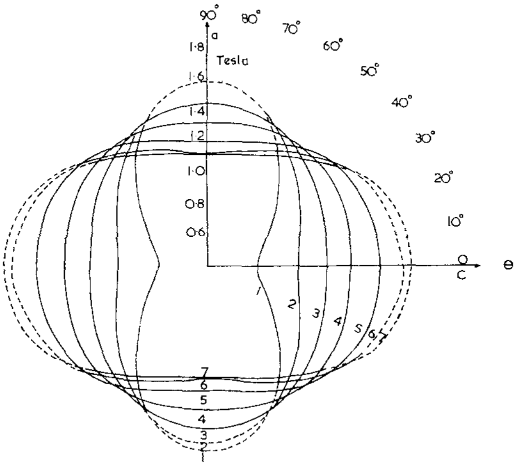

Figure 1 Polar plot in the plane of *c* for Gd:CaWO$_4$; 37.5 GHz.

As with the isofrequency plots, the linewidth measurements were made for the angles of θ and ϕ but only over the range of angles 0° → 90° due to the two-fold symmetry of θ and the four-fold symmetry of ϕ (Figs. 1 and 2). The actual measurements involved the peak to peak derivative width, ΔH_{ms}. Since all the main transitions were of measurable intensity at room temperature (293 K) it was not thought necessary to monitor the linewidths fully at lower temperatures. However the resonance linewidths were of the same order (0.4 mT) at 4.2 and 293 K; hence spin lattice relaxation could be neglected as a broadening mechanism.

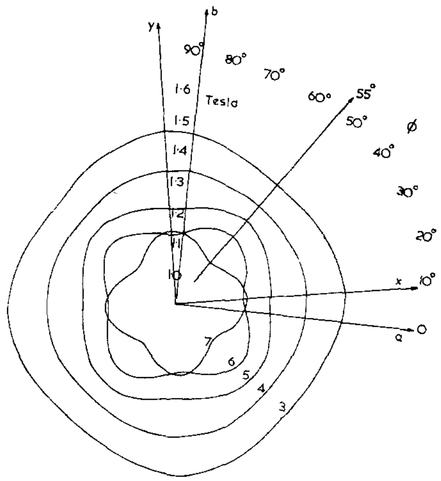

Figure 2 Polar plot in the plane perpendicular to *c* for Gd:CaWO$_4$; 37·5 GHz.

It was noticed that on increasing the nominal gadolinium concentration from 0.01 to 0.05 % a number of extra lines of smaller intensity appeared as well as the main transitions. These lines have been attributed to Gd^{3+} sites having symmetry lower than the tetragonal symmetry of the main lines. Anomalous lines were first noticed in Ce:CaWO$_4$ [8] and it was proposed that they were due to local charge compensation in a chemically uncompensated material, that is a nearest neighbour calcium vacancy. As the concentration of the rare earth ion increases so does the number of vacancies and hence the probability of one occupying an adjacent site. Because of this effect the detailed measurements were confined to nominal gadolinium concentrations of 0.05 % and below.

The two variables considered in greatest detail were the angular dependence of the linewidths and the gadolinium concentration. The three samples (samples 1, 2 and 3) used had nominal gadolinium concentrations of 0.005, 0.01 and 0.05 % respectively and were within the range over which single site substitution by gadolinium for calcium was maintained. At these

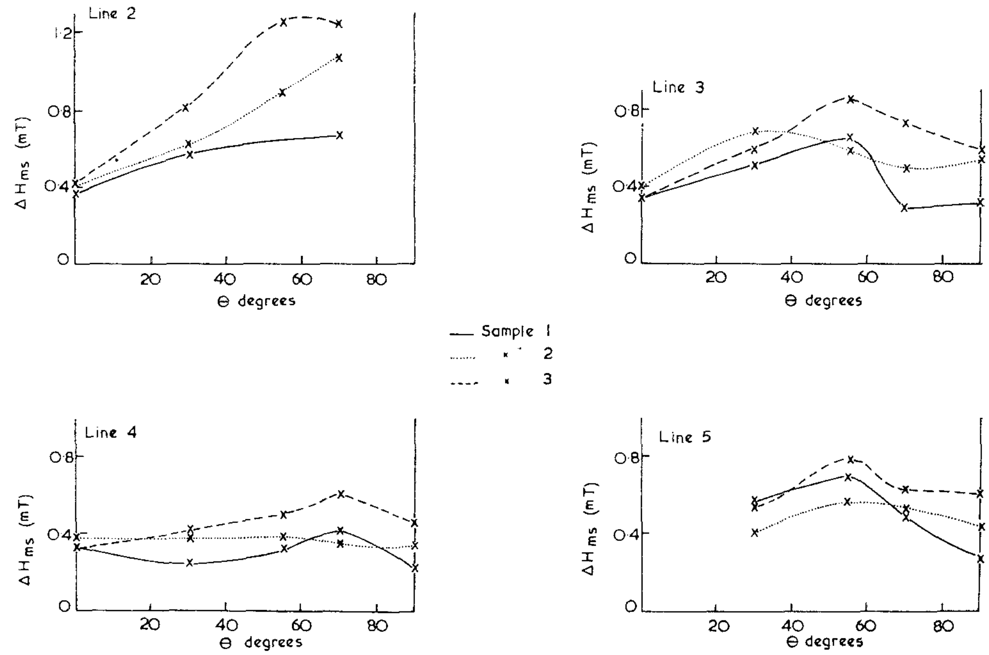

Figure 3 Linewidth plot for Gd:CaWO$_4$ samples in the plane of *c*; 37.5 GHz, 293K.

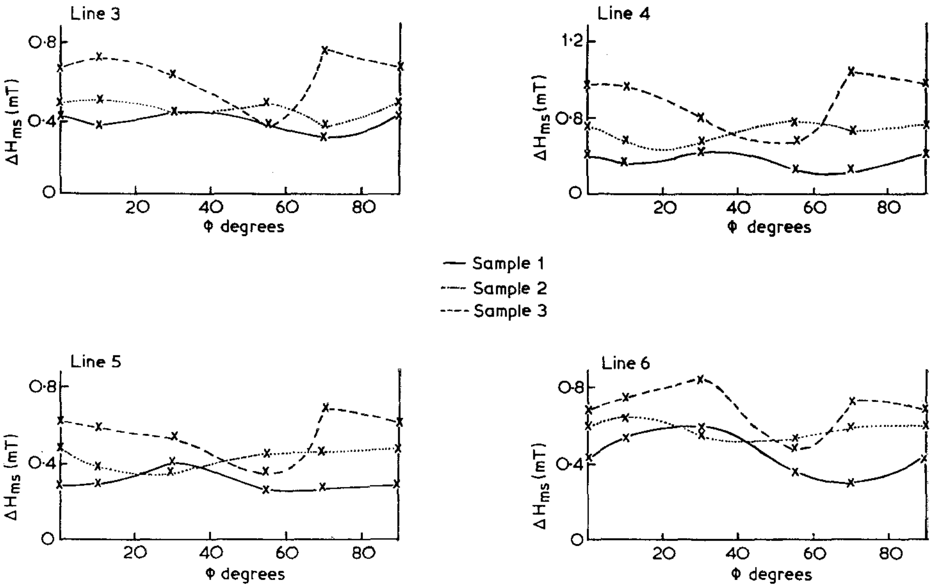

Figure 4 Linewidth plot for Gd:CaWO$_4$ in the plane perpendicular to *c*; 37.5 GHz, 293K.

doping levels all the first order ($\Delta M = 1$) transitions were easily observable at room temperature. It was not possible to measure each linewidth for all seven gadolinium transitions at every angle because of the upper limit (1.6 T) of the magnetic field available. Consequently, in the plane parallel to the *c*-axis the variations for transitions 2, 3, 4 and 5 were obtained (Fig. 3) and in the plane perpendicular to the *c*-axis those for transitions 3, 4, 5 and 6 (Fig. 4). A comparison of these data with theory is made in Section 5 but it may be noted here that in all cases the lines were quite narrow; the total variation observed in ΔH_{ms} was only from about 0.3 to 1.5 mT for all samples and angles.

3. Theory

3.1. Introduction

The calculation of the dipolar broadening of the electron spin resonance lines of $\mathrm{Gd^{3+}{:}CaWO_4}$ will follow the same scheme previously adopted by Brown *et al.* [1] in the study of $\mathrm{Nd^{3+}{:}CaWO_4}$. It is assumed that the principal homogeneous broadening mechanism is dipole-dipole interaction between gadolinium ions, and the magnitude of the homogeneous broadening is calculated using Van Vleck's second moment theory [9]. The steps in the calculation have previously been described in detail [1] and only the basic outline and results will be presented here.

3.2. Second moments

The second moment of the linewidth caused by dipolar interaction between identical atoms has been derived [9] to be:

$$\langle \Delta\omega^2 \rangle = \tfrac{3}{4} S(S+1)(g^2\beta^2/\hbar)^2 . n \sum_k [(r_{jk}^{-6})(3\cos^2\theta_{jk} - 1)^2] \quad (1)$$

where $\langle \Delta\omega^2 \rangle$ is the second moment, ω being measured in radians per second; g is the Landé g-factor of the atoms, of spin S; 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; n is the concentration of active sites.

Using spherical harmonics one can expand the $(3\cos^2\theta_{jk} - 1)^2$ term, making the deletions relevant to a crystal of tetragonal symmetry [1].

$$\begin{aligned}(3\cos^2\theta - 1)^2 = \tfrac{4}{5} &+ \frac{32\pi}{21} Y_{2,0}^*(\theta_{\mathrm{H}},\phi_{\mathrm{H}}) \,.\, Y_{2,0}(\theta_k,\phi_k)\\ &+ \frac{32\pi}{35} Y_{4,0}^*(\theta_{\mathrm{H}},\phi_{\mathrm{H}}) \,.\, Y_{4,0}(\theta_k,\phi_k)\\ &+ \frac{64\pi}{35} Y_{4,4}^*(\theta_{\mathrm{H}},\phi_{\mathrm{H}}) \,.\, Y_{4,4}(\theta_k,\phi_k) \,. \quad (2)\end{aligned}$$

θ_{H} and ϕ_{H} refer the static magnetic field to the crystal axis, while θ_k and ϕ_k refer the radius vector to the same axis. Thus the final equation becomes:

$$\begin{aligned}\langle \Delta\omega^2 \rangle = \tfrac{3}{4} S(S+1)(g^2\beta^2/\hbar)^2 . n \Bigg[&\tfrac{4}{5} \sum_k (r_{jk}^{-6})\\ &+ \frac{32\pi}{21} Y_{2,0}^*(\theta_{\mathrm{H}},\phi_{\mathrm{H}}) \sum_k (r_{jk}^{-6}) Y_{2,0}(\theta_k,\phi_k)\\ &+ \frac{32\pi}{35} Y_{4,0}^*(\theta_{\mathrm{H}},\phi_{\mathrm{H}}) \sum_k (r_{jk}^{-6}) Y_{4,0}(\theta_k,\phi_k)\\ &+ \frac{64\pi}{35} Y_{4,4}^*(\theta_{\mathrm{H}},\phi_{\mathrm{H}}) \sum_k (r_{jk}^{-6}) Y_{4,4}(\theta_k,\phi_k)\Bigg] \cdot \quad (3)\end{aligned}$$

The standard forms of the spherical harmonics are well known [6] and are specified completely by θ and ϕ.

The experimentally determined linewidth parameter is the peak to peak width, ΔH_{ms}, of the first derivative of the resonance line. This is related to Equation 3 by

$$\Delta H_{\mathrm{ms}} = \sqrt{(\langle \Delta\omega^2 \rangle)}/\pi \ \mathrm{Hz} \,. \quad (4)$$

To convert this frequency width into a magnetic field width, the parameter $\partial\nu/\partial H$ must be calculated from the experimental evaluation of g as a function of polar angle, θ, in $\mathrm{Gd^{3+}{:}CaWO_4}$. Then,

$$\Delta H_{\mathrm{ms}} = \frac{\sqrt{(\langle \Delta\omega^2 \rangle}}{\pi} \cdot \frac{\partial H}{\partial \nu} \ \mathrm{Tesla} \,. \quad (5)$$

The evaluation of Equation 3 requires knowledge of the crystal lattice (to derive the values of r, θ, ϕ) and of the particular values of S and g for the gadolinium atom.

3.3. The crystal lattice

Calcium tungstate crystallizes in the tetragonal system [6, 11], has four molecules to the unit cell and has the lattice parameters $a = b = 5.243$ Å and $c = 11.376$ Å. A polar co-ordinate system is used with θ as the angle between the c-axis and the radius vector and ϕ as the angle between the a-axis and the projection of the radius vector on the a-b plane. The gadolinium reference atom is taken to be the origin of co-ordinates, and the calculation is performed over the eight unit cells having this atom as a common corner. This is the same physical situation as that considered by Brown *et al.* [1] in their calculation on $\mathrm{Nd^{3+}{:}CaWO_4}$, from which it can be seen that an extension to cover more unit cells would not affect the answer significantly.

3.4. The gadolinium-gadolinium interaction

Equation 3 is best handled in two parts – the "atomic" part outside the square brackets, and the "geometric" part inside the square brackets. Evaluation of the "atomic" part only required the knowledge of g and S for gadolinium. It is worth stressing the point here that Equation 3 is valid only for those atoms whose magnetic moment is given by $g\sqrt{[S(S+1)]}$. Gadolinium has a spectroscopic state $^8S_{7/2}$, is an S-state ion, and has a magnetic moment given by this formula with $g = 2$ and $S = 7/2$. Thus Equation 3 is directly applicable. (This is in contrast to the case of neodymium [1], where the magnetic moment is given by $g\sqrt{[J(J+1)]}$ with $g = 8/11$ and $J = 9/2$). The "atomic" part can now be evaluated:

$$\tfrac{3}{4}\, S(S+1)\,(g^2\beta^2/\hbar)^2 \,.\, n = 1.256n \times 10^{-24}\,(\text{rad sec}^{-1})\,\text{cm}^6\,. \quad (6)$$

Using Table I from Brown *et al.* [1], the "geometric" part of Equation 3 can be partially evaluated, leading to the final equation:

$$\langle \Delta\omega^2 \rangle = 1.256 \times 10^{21} . n[1.2928 + 0.9032\, Y_{2,0}{}^*(\theta_{\mathrm{H}}, \phi_{\mathrm{H}}) - 0.9411\, Y_{4,0}{}^*(\theta_{\mathrm{H}}, \phi_{\mathrm{H}}) + 0.9866\, Y_{4,4}{}^*(\theta_{\mathrm{H}}, \phi_{\mathrm{H}})]\,. \quad (7)$$

Now, $Y_{2,0}{}^* = Y_{2,0}$ and $Y_{4,0}{}^* = Y_{4,0}$, and by taking $\phi = 0°$, $Y_{4,4}{}^* = Y_{4,4}$. In this way the equation is totally real, and by substituting values of n and θ corresponding to the values used experimentally, curves of dipolar broadening as a function of polar angle, θ, can be derived. Using the transformation of Equation 5, ΔH_{ms} can be calculated and compared with the experimental values. The general curves (which include $\sqrt{n}$ as a factor in the linewidth) are given in Fig. 5.

3.5. The gadolinium-tungsten and gadolinium-calcium interactions

Calculation of the magnitudes of the Gd—W and Gd—Ca interactions gives values of ΔH_{ms} of the order of 10^{-6} T and so these dipolar broadening effects are negligible in comparison with those of the Gd—Gd interaction.

4. Discussion

As can be seen from Fig. 5 all the transitions have similar angular variations and for this reason only one transition will be used to compare theory with experiment. Fig. 5a represents the situation where the magnetic field is rotated in the $\phi = 0°$ plane (i.e. the *a-c* plane); calculations and experimental measurements have also been performed in the $\theta = 90°$ plane

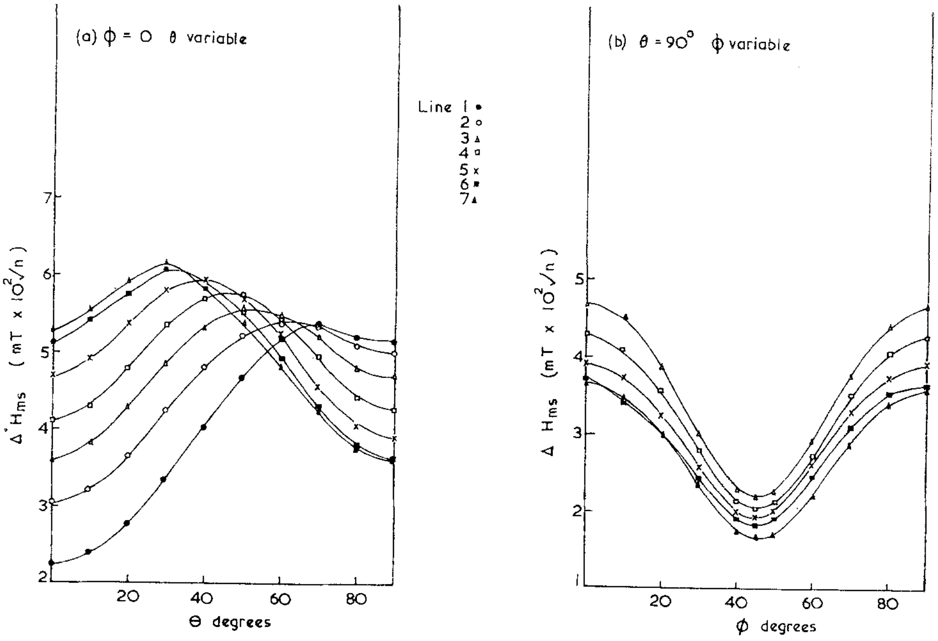

Figure 5 Angular variation of the theoretical Gd—Gd dipolar interaction.

(i.e. the *a-b* plane), see Fig. 5b. The following comparisons thus refer to one transition in the $\phi = 0°$ plane and one at $\theta = 90°$.

The samples were analysed by the Analytical Services Laboratory, Imperial College, using flame emission spectrochemistry. All three were found to contain less than 0.01% gadolinium. With the sample volumes available the method was insufficiently sensitive to determine the absolute gadolinium levels, or the relative gadolinium concentration in the samples, more accurately. (The determination of gadolinium at these trace levels is not straightforward, cf. [12]). In working out the relative percentages of calcium tungstate and gadolinium oxide used for growing the single crystals from the mixed powders no account was taken of the distribution coefficient (K) of gadolinium. This has been determined for sodium compensated gadolinium doped calcium tungstate and quoted as $K = 0.31$ [5]. Using this value the nominal concentrations would become:

sample 1, 0.0015%; sample 2, 0.003%;
sample 3, 0.015%.

However, since the analysis showed that the true concentrations were less than the nominal concentrations estimates of n have been obtained by assuming that $n = 0.010\%$ for sample 3 (i.e. the analytical figure) and deriving the values for sample 1 and 2 from this by scaling in proportion to the nominal concentration. Thus we take the values of n as 0.01, 0.002 and 0.001% for samples 3, 2 and 1 respectively. These values have been used in evaluating Equation 7.

Fig. 6 compares the theoretical and experimental linewidth variations for samples 1 and 3; Fig. 6a shows the variation for line 2 at $\phi = 0$ with θ variable and Fig. 6b gives the corresponding variation for line 4 at $\theta = 90°$ with ϕ variable. There is good agreement between the form of the angular variation of linewidth and calculation based on dipolar broadening theory. Quantitatively, however, the calculated values are between about four and seven times larger than the observed linewidths depending on the transition and polar angle.

The absolute value of ΔH_{ms} can only be regarded as giving an approximation of the linewidth because Van Vleck's formulae applied strictly to an isolated Kramers doublet only. Once a zero-field splitting is involved the formulae become approximate. The approximation can be overcome by replacing S with its projection operator. This has been done for Cr^{3+} in Al_2O_3 [13, 14] and the values of ΔH_{ms} so derived are lower than the values given by using S by about 10%. However, the form of the angular variation is unaffected, and if we bear in mind that the precise values of the calculated linewidths may be about 10% too large, any general conclusions made will be valid. Such a correction would not explain the observed

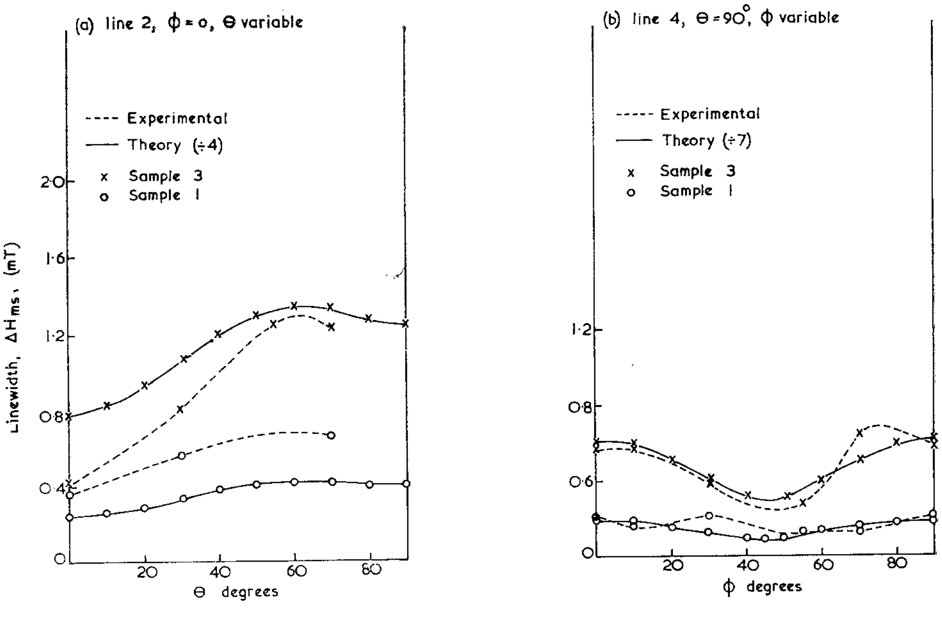

Figure 6 Comparison of theoretical and experimental linewidth variations.

discrepancy. This may be due to exchange narrowing. In most rare earths exchange interactions are unlikely because of the screened position of the 4f electrons. However, gadolinium is different in many ways from the other rare earths. This is shown in that gadolinium is one of the few rare earths to give an e.s.r. spectrum at room temperature, in contrast to the behaviour of Nd:$CaWO_4$. Furthermore, gadolinium metal is ferromagnetic below 289 K and thus it seems reasonable to assume that there may be some exchange interaction between gadolinium ions at neighbouring calcium sites in the tungstate lattice.

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