

Anisotropic Broadening of Linewidth in the Paramagnetic Resonance Spectra of Magnetically Dilute Crystals

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The effects of mosaic structure on the anisotropic broadening of the linewidth in paramagnetic resonance spectra of dilute crystals is investigated. A general formula for the line shape and the linewidth at half maximum is derived.

The half-width of the spectrum of Gd^{3+} in the single crystal of ThO_2 is measured as a function of the angle of the magnetic field with respect to the cubic axes. Good agreement is found with the above theory. The average deviation of the crystallites from the symmetry axis is found to be about 0.12° . Small deviations from the agreement indicate a compensating defect approximately along the $[100]$ direction which gives rise to a small axial distortion.

INTRODUCTION

THE linewidth in paramagnetic resonance spectra in single crystals is caused by a number of different mechanisms. It is customary to classify these into two groups, homogeneously and inhomogeneously broadened lines. In homogeneously broadened lines the absorbed energy is distributed over all the spins within the envelope of the linewidth. Examples of such broadening are dipole-dipole interactions between like spins, and spin-lattice interactions. Examples of inhomogeneous broadening are hyperfine interactions, impurities and defects near the paramagnetic ion, and mosaic structure in nearly perfect crystals.

In the description of paramagnetic resonance one employs a spin Hamiltonian which describes the observed resonance spectrum, in a shorthand notation, by means of a few experimentally determined parameters. It is usually assumed that these parameters have sharp values. These parameters are related to other parameters such as a static crystal field potential, to the spin-orbit coupling, and to the Coulomb interaction integrals. The presence of various impurities, dislocations, and other defects may cause stresses in the crystals. In general these stresses will change the point symmetry. In some cases these stresses may preserve the point symmetry about the paramagnetic ion but may change slightly the energy level spacings between the ground state and higher excited states. The changes in energy level spacing can be traced to variations in the crystal field potential, and to a minor degree in the magnitudes of the spin-orbit coupling of the Coulomb energy, and in changes in the amount of covalent bonding. The effect of all this is to give rise to a distribution of values of the various parameters in the spin Hamiltonian. In some cases, the point symmetry is changed only very slightly so that the different lines cannot be resolved. If the linewidth is measured when the spectrum is observed

along the direction of the deviation from the dominant point symmetry, it will be found to be broadened. In all of the above mechanisms the linewidth is essentially independent of whether one observes the spectrum at zero magnetic field or at strong magnetic fields. They are also a contributory factor in the linewidths observed in the optical spectra in paramagnetic crystals.

Another type of broadening is caused by the presence of mosaic structure in a nearly perfect crystal. In such a crystal the various crystallites make slightly different angles with respect to a fixed direction such as an externally applied magnetic field. These discrete and finite changes in the direction of the crystal axes cause a broadening in an anisotropic paramagnetic resonance spectra where the position of the absorption line is a function of the angle of the magnetic field with respect to the local crystal field axes. The linewidth at zero magnetic field differs from that measured at strong magnetic fields.

In this paper, we present evidence for the existence of mosaic structure in one particular crystal and discuss, in general, a method of determining aspects of the mosaic structure by means of paramagnetic resonance. In the cases where this method can be used, it has certain advantages from those employed in x rays or in optical spectroscopy. Using x rays one encounters difficulties in that the penetration depth of x rays in a crystal is small. One can, therefore, only explore a small fraction of a large single crystal. In highly dilute paramagnetic samples, it is exceedingly difficult to find changes in lattice distances, since x rays measure the average lattice distance in the crystals, and may only indirectly give information regarding changes in point symmetry near the paramagnetic ion. Optical methods seem to be limited to polished transparent doubly refracting crystals and, when used with paramagnetic substances, to highly concentrated samples.¹ Measurement of the

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¹ N. Yu. Ikornikova, *Doklady Acad. Nauk SSSR* **801**, 403 (1951).

linewidth of the optical absorption or fluorescence spectra of very sharp lines which are split into a number of Zeeman levels in an external magnetic field could possibly be used for the observation of the anisotropy in linewidth. This method is very similar, in principle, to that to be discussed in this paper but is, however, limited to those ions showing the very sharp optical absorption lines.

The crystal chosen for this investigation was a single crystal of ThO_2 , containing a small amount (less than 0.01%) of Gd^{3+} . The spectrum of Gd^{3+} in this crystal has been previously investigated.² The point symmetry about the Gd^{3+} ion is cubic. It has the advantage that the lines are among the narrowest known in paramagnetic resonance of transition ions in single crystals. In addition, the Th^{232} nucleus and the dominant oxygen isotope have no nuclear magnetic moments. Therefore, the spin-spin interactions do not contribute appreciably to the linewidth. The spectrum of gadolinium is complicated in that each electronic line is split into a number of hyperfine lines, since the two isotopes 155 and 157 each have a spin of $\frac{3}{2}$ and an abundance of about 15% each.^{3,4} The hyperfine interaction constants A of the gadolinium isotopes in ThO_2 are 4.5 and 5.7 gauss, respectively. The contributions of the hyperfine lines to the linewidth make it difficult to measure accurately the half-width at certain angles in which the linewidth becomes an appreciable fraction of this separation. On the other hand, since A is isotropic to a high accuracy, the hyperfine lines could be used as internal calibration for measuring the linewidth. As will be shown below, we have good evidence that mosaic structure can explain the angular variation of the linewidth.

THEORY

Let us assume that the nearly perfect crystal consists of a large number of perfect crystallites which differ only in that the crystal axes point in slightly different directions. Consider that a coordinate system is attached to each crystallite, in which the coordinate axes coincide with the crystal axes. Let θ, φ denote the coordinates in such a system, and θ_0, φ_0 the coordinates in a fixed system. Let $G(\theta_0, \varphi_0; \theta, \varphi)$ describe the rotation distribution function. Then $G(\theta_0, \varphi_0; \theta, \varphi)d\theta d\varphi \sin\theta$ is the number of crystallites in which the crystallite coordinates lying within the solid angle θ and $\theta+d\theta$ and φ and $\varphi+d\varphi$, coincide with the direction θ_0, φ_0 in the fixed coordinate system. The choice of such a distribution function referred to a fixed direction has advantages over the choice of a distribution function using Eulerian angles. The fixed direction in our experiment is the direction of the magnetic field. We are interested in the number of those crystallites for which the crystal axes will coincide with this direction of the magnetic field. Obviously, a

rotation of the crystal about the axis along this preferred direction does not cause any change in the spectrum.

The frequency of the transition between any two paramagnetic levels in an external field H can be described by

$$\nu = F(H, \theta, \varphi). \quad (1)$$

Let ν_0 be the frequency for a given crystallite whose symmetry axis coincides with the direction of the magnetic field. Then, since

$$\Delta\nu = \nu_0 - \nu = F(H, \theta_0, \varphi_0) - F(H, \theta, \varphi), \quad (2)$$

the line shape of the disoriented crystal can be expressed as

$$g(\Delta\nu)d\nu = \int_{\Omega} \int G(\theta_0, \varphi_0; \theta, \varphi) d\theta d\varphi \sin\theta, \quad (3)$$

where Ω is the solid angle confined between the spheres $\Delta\nu = \text{const}$ and $\Delta\nu + d\nu = \text{const}$. It has been assumed here that the transition probability is equal in all directions, an adequate assumption for $\Delta u = \pm 1$ transitions when $h\nu$ is bigger than the initial splitting.

In order to evaluate the line shape it is convenient to transform the old coordinate system $\theta, \varphi, r = \text{const}$ to a different coordinate system $\Delta\nu(\theta, \varphi), u(\theta, \varphi)$, and $r = \text{const}$. In this new coordinate system $u(\theta, \varphi)$ is chosen so that the integral can be easily evaluated. In this new coordinate system, Eq. (3) is given by

$$g(\Delta\nu)d\nu = \int_{\Delta\nu}^{\Delta\nu+d\nu} \int_{u_{\min}}^{u_{\max}} G(\theta_0, \varphi_0; \theta, \varphi) \times \sin\theta \frac{\partial(\theta, \varphi)}{\partial(u, \Delta\nu)} du d\nu, \quad (4)$$

where $\partial(\theta, \varphi)/\partial(u, \Delta\nu)$ is the Jacobian. Similarly, the line shape can be found for the case when the frequency is kept constant and the magnetic field is varied. In this case

$$H = f(\nu, \theta, \varphi), \quad (5)$$

and

$$g(\Delta H) = \int_{\Delta H}^{\Delta H+dH} \int_{w_{\min}}^{w_{\max}} G(\theta_0, \varphi_0; \theta, \varphi) \times \sin\theta \frac{\partial(\theta, \varphi)}{\partial(w, \Delta H)} dw, \quad (6)$$

where $\Delta H = f(\nu, \theta_0, \varphi_0) - f(\nu, \theta, \varphi)$ and w is chosen in a similar manner to u .

Anisotropic Broadening in Nearly Perfect Crystals

In the preceding section no restrictive assumptions have been made regarding the choice of the distribution function. In well-annealed crystals one may assume that the misorientation of the various crystallites is small, so that the axes of rotation will differ only by a small angle

² W. Low and D. Shaltiel, J. Phys. Chem. Solids **6**, 315 (1958).

³ W. Low, Phys. Rev. **103**, 1309 (1956).

⁴ W. Low and D. Shaltiel, Phys. Rev. **115**, 424 (1959).

α . We shall also assume that this angle α is distributed isotropically about the average value of the direction of the crystal axis which should coincide with the direction of this axis in a perfect crystal. This last assumption is plausible for cubic crystals. For noncubic crystals, or crystals having a defect near a paramagnetic ion along a preferential direction, α will not be isotropic.

With these assumptions, we derive (see Appendix) an expression for the distribution function:

$$G(\Phi) = C\Phi \int_{\alpha=\Phi}^{\alpha_{\max}} \frac{P(\alpha)d\alpha}{2\alpha^2[1 - (\Phi/\alpha)^2]^{\frac{1}{2}}}; \quad (7)$$

Φ is the angle between the directions θ_0 , φ_0 and θ , φ , and $\Phi \leq \alpha$; $P(\alpha)$ is the probability that the axis of the crystallite is rotated by the angle α . The integral is cut off at a maximum angle α_{\max} . We assume that the $P(\alpha)$ is so constructed that it falls to zero very fast for all angles larger than α_{\max} and therefore contributes a negligible amount to the integral for large α .

Since Φ is small we can write

$$\Phi = [\Delta\varphi^2 \sin^2\theta_0 + \Delta\theta^2]^{\frac{1}{2}}, \quad (8)$$

where $\Delta\theta = (\theta_0 - \theta)$ and $\Delta\varphi = (\varphi_0 - \varphi)$.

Expanding Eq. (2) in a Taylor's series and using the first term in the expansion, we obtain

$$\begin{aligned} \Delta\nu &= F(H, \theta_0, \varphi_0) - F(H, \theta, \varphi) \\ &= -\frac{\partial F}{\partial \theta} \Delta\theta + \frac{\partial F}{\partial \varphi} \Delta\varphi \\ &= a\Delta\theta + b\Delta\varphi. \end{aligned} \quad (9)$$

We set $u = \Phi$ and evaluate the Jacobian by means of Eqs. (8) and (9). Substituting the Jacobian as well as $G(\Phi)$ of Eq. (7) into Eq. (4), we obtain the expression

$$\begin{aligned} g(\Delta\nu) &= C \int_{\Phi_1}^{\alpha_{\max}} \frac{\Phi^2 \sin\theta}{b\Delta\theta - a\Delta\varphi \sin^2\theta} \\ &\quad \times \int_{\alpha=\Phi}^{\alpha_{\max}} \frac{P(\alpha)d\alpha}{\alpha^2[1 - (\Phi/\alpha)^2]^{\frac{1}{2}}} d\Phi, \end{aligned} \quad (10)$$

with $\Phi_1 = \Delta\nu[(b^2 \sin^2\theta + a^2)/(a^2 + b^2)^{\frac{1}{2}}]$ and C a normalization factor.

Similarly, when measuring at constant frequency, one obtains the line shape function

$$\begin{aligned} g(\Delta H) &= C' \int_{\Phi_2}^{\alpha_{\max}} \frac{\Phi^2 \sin\theta}{b\Delta\theta - a\Delta\varphi \sin^2\theta} \\ &\quad \times \int_{\alpha=\Phi}^{\alpha_{\max}} \frac{P(\alpha)d\alpha}{\alpha^2[1 - \Phi^2/\alpha^2]^{\frac{1}{2}}} d\Phi, \end{aligned} \quad (11)$$

with $\Phi_2 = \phi_1(\Delta H/\Delta\nu)(\partial F/\partial H)$.

In our experiments we chose the measurements made

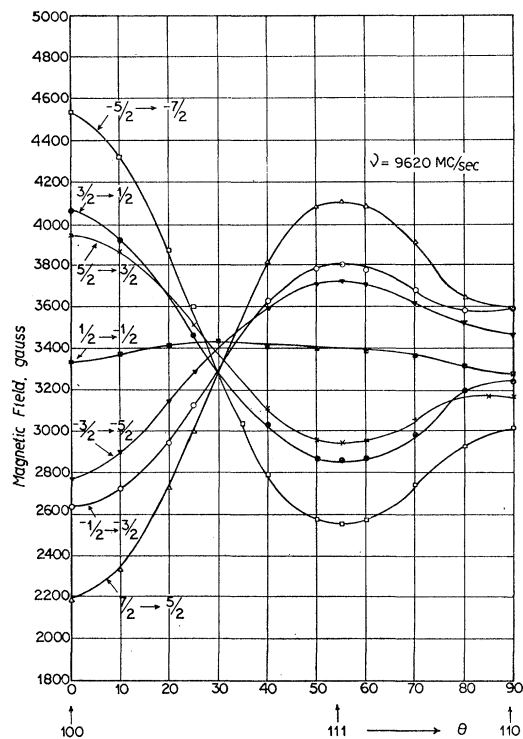


FIG. 1. The paramagnetic resonance spectrum of Gd^{3+} in the single crystals of ThO_2 in strong magnetic field. The solid line is the calculated spectrum and the various points the measured spectrum for the $\Delta M = \pm 1$ transitions.

in a plane where $b=0$. Equations (8) and (9) simplify to

$$\Delta\varphi = \frac{(\Phi^2 - \Delta\nu^2/a^2)^{\frac{1}{2}}}{\sin\theta},$$

and Eq. (11) reduces to

$$\begin{aligned} g(\Delta H) &= \frac{C'}{a} \frac{\partial F}{\partial H} \int_{\Phi=(\Delta H/a)(\partial F/\partial H)}^{\alpha_{\max}} \left[\frac{\Phi^2}{a[\Phi^2 - (\Delta\nu)^2/(a^2)^{\frac{1}{2}}]} \right] \\ &\quad \times \int_{\alpha=\Phi}^{\alpha_{\max}} \frac{P(\alpha)d\alpha}{\alpha^2(1 - \Phi^2/\alpha^2)^{\frac{1}{2}}} d\Phi. \end{aligned} \quad (12)$$

In order to evaluate these integrals we need to know something about the rotation function $P(\alpha)$. For computational reasons we shall assume a Gaussian distribution $P(\alpha) = (2/\pi^{\frac{1}{2}}\alpha_0) \exp(-\alpha^2/\alpha_0^2)$. For any other distribution, the integral has similarly to be evaluated numerically and will give results which differ only by a numerical weighting factor from the one presented below.

Using a Gaussian distribution, the half-width at half intensity is given by a simple expression (which could have been anticipated)

$$\Delta H = (a/2)\alpha_0/(\partial F/\partial H). \quad (13)$$

We shall use this expression for the particular case of

TABLE I. Linewidth of $\Delta M = \pm 1$ transition of Gd^{3+} in the single crystal of ThO_2 along the $[100]$, $[111]$, and $[110]$ directions.^a

Direction	$\frac{5}{2} \leftrightarrow \frac{7}{2}$	$\frac{3}{2} \leftrightarrow \frac{5}{2}$	$\frac{1}{2} \leftrightarrow \frac{3}{2}$	$-\frac{1}{2} \leftrightarrow +\frac{1}{2}$	$-\frac{3}{2} \leftrightarrow -\frac{1}{2}$	$-\frac{5}{2} \leftrightarrow -\frac{3}{2}$	$-\frac{7}{2} \leftrightarrow -\frac{5}{2}$
$[100]$	4.8 ± 0.25	4.4 ± 0.2	3.6 ± 0.2	2.6 ± 0.15	3.3 ± 0.2	3.8 ± 0.2	5.3 ± 0.25
$[111]$	5.8 ± 0.25	4.8 ± 0.2	4.0 ± 0.2	2.7 ± 0.15	4.4 ± 0.2	4.2 ± 0.2	5.9 ± 0.25
$[110]$	5.2 ± 0.25	4.5 ± 0.2	3.8 ± 0.2	2.9 ± 0.15	3.5 ± 0.2	3.9 ± 0.2	5.8 ± 0.25

^a Linewidths measured in gauss.

Gd^{3+} in ThO_2 . The ground state of this ion is $^8S_{7/2}$. In the cubic field of ThO_2 the angular behavior for all strong-field $\Delta M = \pm 1$ transitions can be expressed by

$$\hbar\nu/g\beta = H + A_i + B_i/H_i + C_i/H_i^2. \quad (14)$$

The constants A_i , B_i , and C_i have been evaluated by de Boer and Van Lieshout⁵ and by Lacroix.⁶ These constants are functions of the invariants p and q of the three direction cosines l , m , and n which the magnetic field makes with the cubic axes. p and q are given explicitly by

$$p = l^2m^2 + m^2n^2 + l^2n^2, \quad (15)$$

$$q = l^2m^2n^2.$$

The general form of the linewidth at half intensity is given in terms of the constants A , B , C and p , q as

$$\Delta H_i = -\frac{\alpha_0}{2} \left[\frac{\partial A_i}{\partial p} \frac{\partial p}{\partial \theta} + \frac{\partial A_i}{\partial q} \frac{\partial q}{\partial \theta} + \frac{1}{H_i} \left(\frac{\partial B_i}{\partial p} \frac{\partial p}{\partial \theta} + \frac{\partial B_i}{\partial q} \frac{\partial q}{\partial \theta} \right) + \frac{1}{H_i^2} \left(\frac{\partial C_i}{\partial p} \frac{\partial p}{\partial \theta} + \frac{\partial C_i}{\partial q} \frac{\partial q}{\partial \theta} \right) \right] \left(1 - \frac{B_i}{H_i^2} + \frac{2C_i}{H_i^3} \right)^{-1}. \quad (16)$$

EXPERIMENTAL PROCEDURE

The paramagnetic resonance spectrometer was a conventional 3-cm wavelength spectrometer using a simple

magic T , rectangular cavity, and video detection. The single crystal of ThO_2 , with less than 10^{-4} mole fraction of gadolinium, was mounted on the broad side of the H_{102} cavity. The crystal could be rotated about a horizontal axis and the magnet about a vertical axis. By rotating both the crystal and the magnet, the crystal was adjusted so that the $[100]$ direction was contained in a plane perpendicular to the vertical axis. The magnetic field could be rotated in the (110) plane.

The video detection used a wide-band amplifier with pass band of 8–10 000 cycles in order to prevent distortion of the line shape. A fixed magnitude of magnetic field modulation was used. The peak-to-peak modulation was about 10 times the linewidth. Care was taken that the center of the lines should appear at zero magnetic field modulation. All this eliminated, to a large extent, the effects of nonlinearity of the field modulation.

EXPERIMENTAL RESULTS

The measured and calculated paramagnetic resonance spectrum for the transitions $\Delta M = \pm 1$ is shown in Fig. 1. The magnetic field was rotated in the (110) plane. Table I gives the measured linewidths at half intensity at the three directions $[100]$, $[111]$, and $[110]$.

The anisotropic line broadening was obtained from the total linewidths as follows:

1. It is assumed that the anisotropic broadening gives a negligible contribution to the total linewidth along the $[100]$ direction (this is justified below).

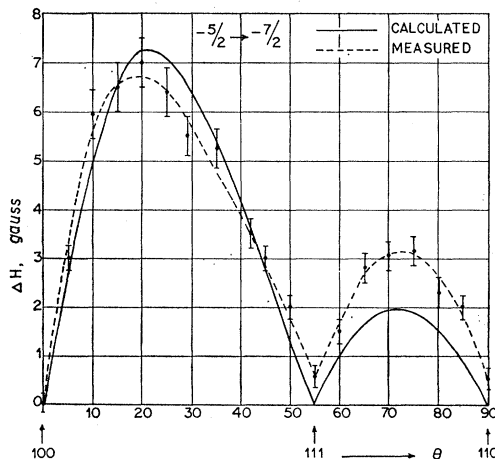


FIG. 2. The variation of the half-width ΔH as a function of the angle which the magnetic field makes with the cubic axis for the indicated one of the seven $\Delta M = \pm 1$ transitions. The solid lines are the calculated variations using Eq. (16) in the text. The dashed lines give the experimental anisotropy of ΔH .

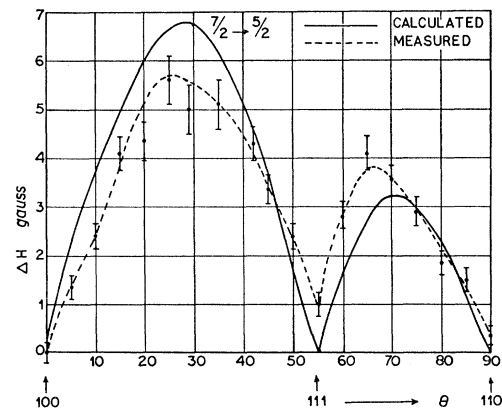


FIG. 3. The variation of the half-width ΔH as a function of the angle which the magnetic field makes with the cubic axis for the indicated one of the seven $\Delta M = \pm 1$ transitions. The solid lines are the calculated variations using Eq. (16) in the text. The dashed lines give the experimental anisotropy of ΔH .

⁵ J. de Boer and R. Van Lieshout, *Physica* **15**, 570 (1959).

⁶ R. Lacroix, *Helv. Physica Acta* **30**, 374 (1957).

2. Additivity of linewidths caused by different broadening mechanisms is assumed.

We then subtract the linewidth as observed along the [100] direction from that observed along other angles and obtain a residual linewidth. In Figs. 2-8, we have plotted this residual linewidth for all $M \rightarrow M-1$ transitions (dashed lines) as a function of the angle θ . The theoretical anisotropy is calculated in the (110) plane from Eq. (16) using

$$p = 1/4(1 + 2 \cos^2\theta - 3 \cos^4\theta),$$

and

$$q = 1/4(\cos^2\theta - 2 \cos^4\theta + \cos^6\theta).$$

It should be noticed that the first term A_i would give linewidths of equal magnitudes for the $M_i \rightarrow M_i-1$ and $M_{-i} \rightarrow M_{-i}+1$ transitions. The terms B_i/H_i and C_i/H_i^2 have to be added to account for the asymmetry. The curves are normalized so to give a best fit to the experimental data by choosing $\alpha_0 = 0.12^\circ \pm 0.02$. The good agreement between the experimental and theoretical curve shows that the theory as developed above is a good

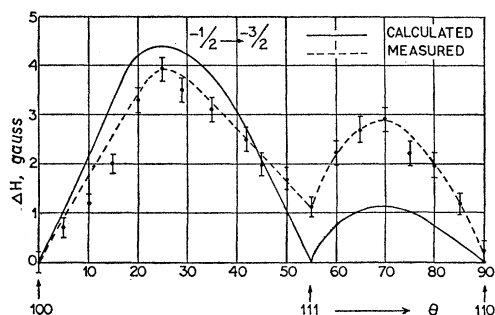


FIG. 4. The variation of the half-width ΔH as a function of the angle which the magnetic field makes with the cubic axis for the indicated one of the seven $\Delta M = \pm 1$ transitions. The solid lines are the calculated variations using Eq. (16) in the text. The dashed lines give the experimental anisotropy of ΔH .

first approximation. The value of $\alpha_0 = 0.12^\circ$ is reasonable for the average misorientation of the various crystallites. If a distribution other than a Gaussian were used, α_0 would have a different value but probably of the same order of magnitude.

The small deviations found for the $\frac{1}{2} \rightarrow -\frac{1}{2}$ transitions suggest that there is another mechanism which is responsible in part for the anisotropic broadening. This is also seen from the fact that the theoretical anisotropic broadening should be zero to first order for the [100], [111], and [110] directions. Second-order effects contribute only a negligible amount. However, the experimental curves show that there is some residual broadening along these directions. Spin-lattice relaxation or cross-relaxation effects seem to be ruled out since the linewidth for the $\frac{1}{2} \rightarrow -\frac{1}{2}$ transition decreases only slightly (about 0.4 gauss along the [100] direction) as the temperature is lowered from room to liquid nitrogen temperature.

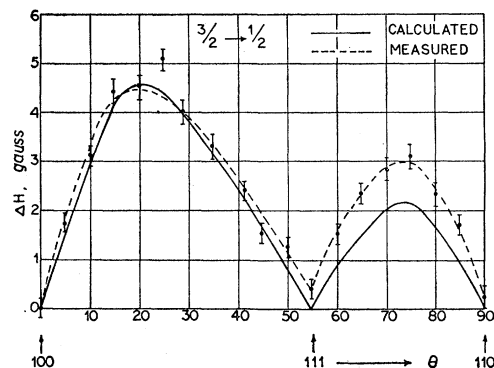


FIG. 5. The variation of the half-width ΔH as a function of the angle which the magnetic field makes with the cubic axis for the indicated one of the seven $\Delta M = \pm 1$ transitions. The solid lines are the calculated variations using Eq. (16) in the text. The dashed lines give the experimental anisotropy of ΔH .

Some indication as to the causes of this additional broadening is found from the ratio of the linewidth of the various $\pm M \leftrightarrow \pm M \pm 1$ transitions. The observed ratio of the $\pm \frac{7}{2} \leftrightarrow \pm \frac{5}{2}$, $\pm \frac{5}{2} \leftrightarrow \pm \frac{3}{2}$, and $\pm \frac{3}{2} \leftrightarrow \pm \frac{1}{2}$ transitions is 10:7:3.5. If the cause were a random distribution of the cubic zero field splitting, one would expect a ratio of 10:5:6.

A partial explanation can be given by assuming an additional small axial field along the principal cubic axes. An additional parameter to the spin Hamiltonian of the form DS_z^2 would give rise to line shifts in the ratio of 10:6.7:3.3. Assuming, therefore, a distribution of values of D centered around $D=0$ one can explain this residual linewidth. Such an axial field can be caused by some compensating positive ion, or by the absence of some oxygen ions at large distances. Some support for this conjecture is found in the fact that well-annealed crystals show some reduction in linewidth.

As seen from Table I the linewidth of the $M_i \rightarrow M_i-1$ and $M_{-i} \rightarrow M_{-i}+1$ transitions in the three principal directions, contrary to expectation, are not equal. Although this may be attributed to the errors in measurement which are close to the differences, we nevertheless

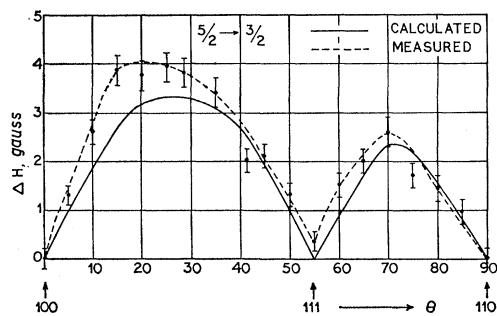


FIG. 6. The variation of the half-width ΔH as a function of the angle which the magnetic field makes with the cubic axis for the indicated one of the seven $\Delta M = \pm 1$ transitions. The solid lines are the calculated variations using Eq. (16) in the text. The dashed lines give the experimental anisotropy of ΔH .

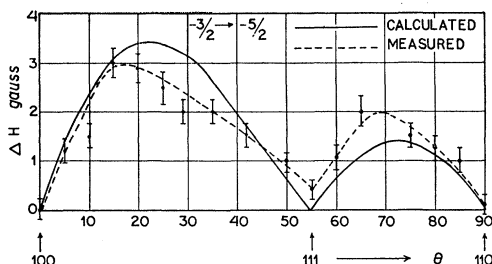


FIG. 7. The variation of the half-width ΔH as a function of the angle which the magnetic field makes with the cubic axis for the indicated one of the seven $\Delta M = \pm 1$ transitions. The solid lines are the calculated variations using Eq. (16) in the text. The dashed lines give the experimental anisotropy of ΔH .

think that the differences are real but their origins have not yet been clearly understood.

DISCUSSION

In the preceding, we have shown that the angular dependence of the linewidth can be explained by crystallites having slightly different orientation. The analysis in this particular case gave the average angle which the crystallites make with the symmetry axes. If the line shape were carefully measured as a function of the angle one could possibly get some information regarding the distribution function.

The anisotropic linewidth is probably present in most crystals. In some crystals, the symmetry axis changes the direction in some manner along the crystal. Ruby is well known to show such an effect. The crystal axis may show a curvature along the boule; the deviation across a crystal of about one inch may be several degrees. The angular behavior of the $\pm \frac{3}{2} \rightarrow \pm \frac{1}{2}$ transition of Cr^{3+} in Al_2O_3 is given by $h\nu = g\beta H \pm D(3 \cos^2 \theta - 1)$. Then, $\Delta H = (D/g\beta)^{\frac{1}{2}} \sin 2\theta$ which would show a maximum linewidth for $\theta = 45^\circ$. At this angle, and for an angular spread of $\Delta\theta = 0.5^\circ$, we find $\Delta H \sim 50$ gauss. This is larger than the spin-spin interactions for all Cr^{3+} with concentration less than 0.2 mole percent of Cr^{3+} . The misalignment of the axial symmetry axis in ruby is probably one of the causes of the wide lines in the paramagnetic resonance spectra, and one of the main contributing effects to the linewidths if the spectrum is observed along a direction other than the C axis. This method

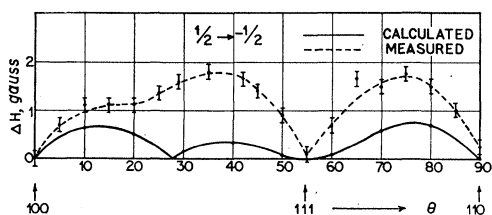


FIG. 8. The variation of the half-width ΔH as a function of the angle which the magnetic field makes with the cubic axis for the indicated one of the seven $\Delta M = \pm 1$ transitions. The solid lines are the calculated variations using Eq. (16) in the text. The dashed lines give the experimental anisotropy of ΔH .

would, therefore, be used for the investigation of how perfectly the C axis in ruby is orientated.

APPENDIX

Calculation of the Rotation Distribution Function

We shall assume that the various crystallites are disoriented with respect to a given axis in an isotropic manner. We mean by this that the axes of rotation, through which the crystallites are rotated, are isotropically distributed. In Fig. 9 the z axis was chosen for convenience as the direction in which the distribution function is calculated. Let a crystallite be rotated about an axis making an angle θ with the z axis of the crystal.

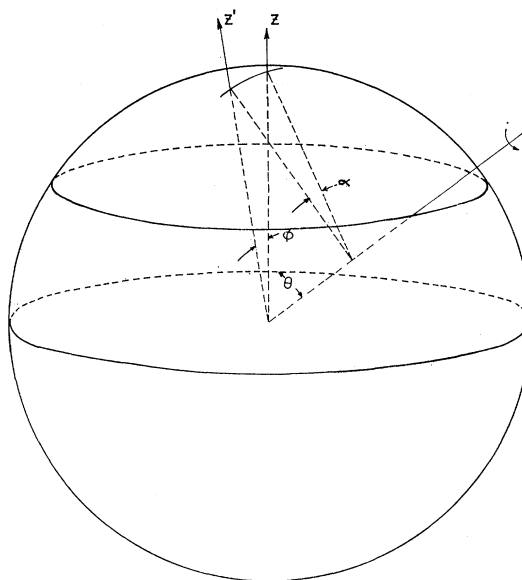


FIG. 9. Calculation of the rotation distribution function.

The angle between the new z' axis and the old axis will be Φ . For small angles of rotation

$$\Phi = \alpha \sin \theta. \quad (\text{A1})$$

The number of crystallites whose z axis is rotated between Φ and $\Phi + d\Phi$, because of a rotation by α , is proportional to $\sin \theta d\theta$. Therefore (see Fig. 9)

$$\sin \theta d\theta = \frac{\Phi}{\alpha^2} \frac{d\Phi}{(1 - \Phi^2/\alpha^2)^{\frac{1}{2}}}. \quad (\text{A2})$$

If $P(\alpha)$ is the distribution function for rotating the angle by α , we get the rotation distribution function

$$G(\Phi) = C\Phi \int_{\alpha=\Phi}^{\alpha=\max} \frac{P(\alpha) d\alpha}{\alpha^2 (1 - \Phi^2/\alpha^2)^{\frac{1}{2}}}, \quad (\text{A3})$$

where Φ has the restriction that $\Phi \leq \alpha$.