Upon reinstating the subscript i and evaluating the echo envelope function at $t=\tau$, substitution of Eq. (A9) into Eq. (A3) gives

$$V_i(\tau)=V(0)\left[1-2\sin^2\delta_i\sin^2\left(\frac{K_i^+\tau}{2}\right)\sin^2\left(\frac{K_i^-\tau}{2}\right)\right]$$

$$=V(0)\left[1-2\left(\frac{B_i\omega_n}{K_i^+K_i^-}\right)^2\sin^2\left(\frac{K_i^+\tau}{2}\right)\sin^2\left(\frac{K_i^-\tau}{2}\right)\right],$$

where $V(0)=Ng\beta\hbar S(S+1)\omega_e/3kT$.

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Paramagnetic Resonance Linewidths in Some Rare-Earth Double Nitrates

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We have measured the paramagnetic resonance linewidth δH at microwave frequencies for the three trivalent rare-earth ions Ce, Nd, and Sm present in small concentrations in $La_2Mg_3(NO_3)_{12}\cdot 24H_2O$. The linewidths appear to be strongly dependent upon the angle θ between the c axis of the crystal and the magnetic field, and in most cases the observed linewidths seem to be reasonably well explained by a simple theory which assumes a spatial distribution of paramagnetic resonance g values throughout the crystal.

I. EXPERIMENTAL APPARATUS AND PROCEDURES

We have measured the angular dependence of the paramagnetic resonance linewidth of trivalent cerium, neodymium, and samarium in a host matrix of lanthanum magnesium nitrate. The measurements were made in the liquid helium temperature range at frequencies around 9 kMc/sec, 23 kMc/sec, and 36 kMc/sec. Four different microwave spectrometers were used, each being a simple transmission or reflection system. The derivative peak-to-peak linewidth was measured as a function of the angle θ between the magnetic field H and the crystalline c axis. The crystals were grown from a saturated aqueous solution in a desiccator at 0°C, the high-purity rare-earth salts being obtained from the Lindsay Chemical Company. The crystals used were clear and visually free from imperfections. Concentrations of paramagnetic rare-earth ions ranged from approximately 0.003 to 0.2 at. %. In all cases, measurements were made on the single resonance line arising from the even isotopes.

The measurements on the Sm-doped crystal were made for a single crystal only, weighing approximately 100 mg, and at the single frequency $\nu=9.25$ kMc/sec. The relatively small g factors of the Sm ion combined with the limit on the strength of our magnetic field prevented us from making measurements at higher frequencies.

Where measurements were made for the same ion at different frequencies, the same sample was used for all frequencies, and the angle of rotation about the c axis was kept unchanged.

II. THEORY AND EXPERIMENTAL RESULTS

Of the several possible factors contributing to the width of a paramagnetic resonance line, we consider only two: first, the width caused by the interaction of the paramagnetic ion with the surrounding nuclei; and second, a possible spatial distribution of g values throughout the crystal, perhaps caused by lattice strains. Lattice strains as a contribution to paramagnetic resonance linewidths have also been considered by

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Feher and Weger,[1] and by Shaltiel and Low.[2] Other factors, such as spin-spin interaction, spin-lattice interaction, zero-field splitting, and unresolved hyperfine structure, we consider negligible or nonexistent.

A given paramagnetic ion will resonate in a field given by

$$H=h\nu/g\beta-H_d, \tag{1}$$

where ν is the (fixed) microwave frequency, β is the Bohr magneton, $g=(g_{\parallel}^2\cos^2\theta+g_{\perp}^2\sin^2\theta)^{1/2}$ is the g value for the ion, and H_d is the local magnetic field produced by the surrounding nuclear dipoles. We shall assume that $g_{\parallel}$, $g_{\perp}$, θ, and H_d may vary spatially throughout the crystal, and that this variation gives rise to the observed linewidth. Furthermore, we shall assume that each of these four parameters varies independently of the others. With these assumptions, the mean-square linewidth $\langle\delta H^2\rangle$ is given by

$$\begin{aligned}\langle\delta H^2\rangle&=\left(\frac{\partial H}{\partial g_{\parallel}}\right)^2\langle\delta g_{\parallel}^2\rangle+\left(\frac{\partial H}{\partial g_{\perp}}\right)^2\langle\delta g_{\perp}^2\rangle\\&\quad+\left(\frac{\partial H}{\partial\theta}\right)^2\langle\delta\theta^2\rangle+\left(\frac{\partial H}{\partial H_d}\right)^2\langle\delta H_d^2\rangle\\&=\langle\delta H_d^2\rangle+\left(\frac{h\nu}{g^3\beta}\right)^2\{g_{\parallel}^2\cos^4\theta\langle\delta g_{\parallel}^2\rangle\\&\quad+g_{\perp}^2\sin^4\theta\langle\delta g_{\perp}^2\rangle+(g_{\perp}^2-g_{\parallel}^2)^2\cos^2\theta\sin^2\theta\langle\delta\theta^2\rangle\}\\&=A+B\left[\frac{h\nu\cos\theta}{g^2(\theta)\beta}\right]^2+C\left[\frac{h\nu\sin\theta}{g^2(\theta)\beta}\right]^2\\&\quad+D\left[\frac{h\nu\sin\theta\cos\theta}{g^3(\theta)\beta}\right]^2,\end{aligned} \tag{2}$$

where $A=\langle\delta H_d^2\rangle$, $B=\langle\delta g_{\parallel}^2\rangle$, $C=\langle\delta g_{\perp}^2\rangle$, and $D=(g_{\perp}^2-g_{\parallel}^2)^2\langle\delta\theta^2\rangle-\langle\delta g_{\perp}^2\rangle g_{\parallel}^2-\langle\delta g_{\parallel}^2\rangle g_{\perp}^2$.

If it happens that $g_{\parallel}^2\ll g_{\perp}^2$, expression (2) may be simplified to read

$$\langle\delta H^2\rangle=\langle\delta H_d^2\rangle+(h\nu/g^2\beta)^2(g_{\perp}^2\cos^2\theta\langle\delta\theta^2\rangle+\sin^2\theta\langle\delta g_{\perp}^2\rangle) \tag{3}$$

for angles θ not too small.

The observed derivative peak-to-peak linewidth δH_{pp} will be related to δH by a constant K:

$$\delta H_{pp}^2=K\langle\delta H^2\rangle, \tag{4}$$

where K is a number of order unity which depends on the exact line shape. If H_d, $\delta g_{\parallel}$, $\delta g_{\perp}$, and $\delta\theta$ are normally distributed, we should observe a normal, or Gaussian line shape, and for that case, $K=4$.

In most cases, the observed line shape is approximately Gaussian, although for the case of the Nd-doped crystal, the line shape does not remain precisely Gaussian at higher frequencies: the "wings" of the line become qualitatively somewhat larger than one would expect for a Gaussian shape. In spite of this, we attempt to fit our observed data to curves of the form of Eqs. (2) or (3), as shown in Figs. 1 through 5, assuming $\langle\delta H_d^2\rangle$, $\langle\delta g_{\parallel}^2\rangle$, $\langle\delta g_{\perp}^2\rangle$, and $\langle\delta\theta^2\rangle$ to be constants, independent of θ and ν. The observed linewidths are quite anisotropic, and in the case of the Ce-doped crystal, the degree of anisotropy seems quite noticeably dependent on the size of the crystal. Figure 1 shows data for a crystal weighing approximately 200 mg; Fig. 2 shows data for a small piece of the same crystal, weighing approximately 15 mg. The larger crystal appears to have the greater linewidth anisotropy. In the case of Nd, such size-dependent behavior was less noticeable. Data (not shown) at 8.78 kMc/sec for a crystal weighing approximately 200 mg, and containing approximately 0.003 at. % Nd, were nearly identical to the data of Fig. 3, taken at 9.5 kMc/sec for a crystal weighing approximately 15 mg, and containing 0.1 atomic percent Nd. For Sm, where we have data on one crystal only, we have no experimental information on such size-dependent behavior.

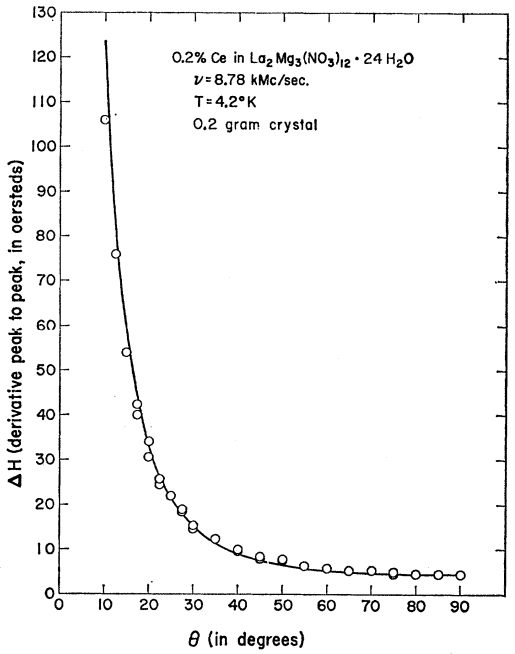

FIG. 1. Data and fitted theoretical curve for the linewidth of Ce^{3+} in lanthanum magnesium nitrate. The curve represents Eq. (3) of the text with $\langle\delta H_d^2\rangle=3.2$ Oe^2, $\langle\delta g_{\perp}^2\rangle=0.43\times10^{-6}$, $\langle\delta\theta^2\rangle=0.36\times10^{-6}$, and $K=4$.

In fitting the curves, we use the following g-values: Ce: $g_{\perp}=1.83$, $g_{\parallel}=0.02$; Nd: $g_{\perp}=2.71$, $g_{\parallel}=0.368$; Sm: $g_{\perp}=0.36$, $g_{\parallel}=0.74$. These are values which we have measured, and they are in substantial agreement with values reported by Leask *et al.*[3] for Ce and by Cooke and Duffus[4] for Nd and Sm.

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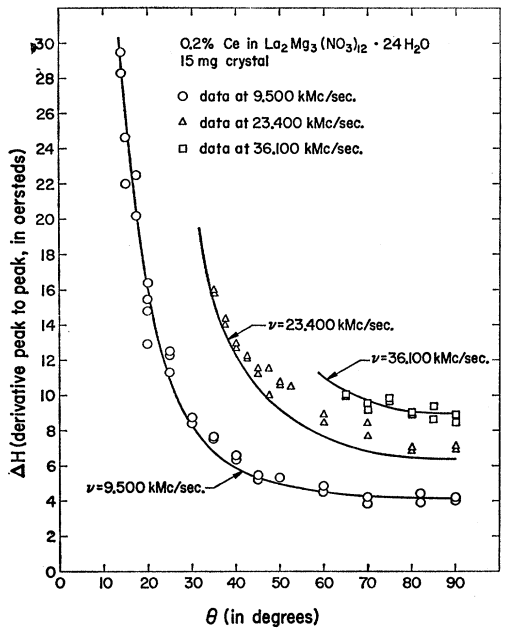

FIG. 2. Data and fitted theoretical curves for the linewidth of Ce^{3+} in lanthanum magnesium nitrate at 4.2°K. All three curves represent Eq. (3) of the text with $\langle \delta H_d^2 \rangle = 3.2$ Oe^2, $\langle \delta g_\perp^2 \rangle = 0.27\times10^{-6}$, $\langle \delta\theta^2 \rangle = 0.62\times10^{-7}$, and $K=4$.

In fitting the data for Ce, we neglect $g_\parallel$ with respect to $g_\perp$, and hence use Eq. (3). The results are shown in Figs. 1 and 2.

In fitting the data for Nd, we may use Eq. (3) only for $\theta > 30°$. The data of Fig. 3 was fit in this manner. The Nd data of Fig. 4 and the Sm data of Fig. 5 were fit using the complete expression of Eq. (2), where a least squares fit was made using an IBM-7094 computer.

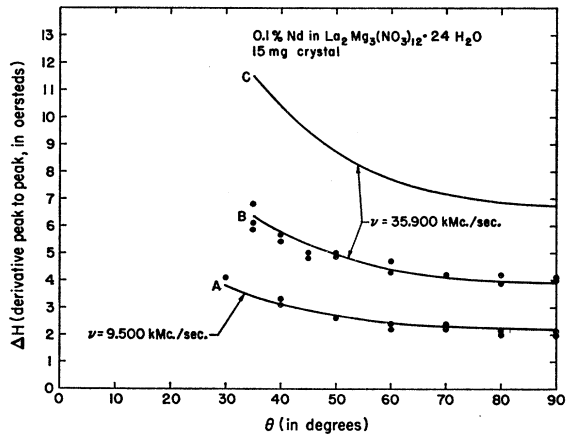

FIG. 3. Data and fitted theoretical curves for the linewidth of Nd^{3+} in lanthanum magnesium nitrate at 4.2°K. Curve A is the best fit to Eq. (3) of the text for the 9.500 kMc/sec data with $\langle \delta H_d^2 \rangle = 0.5$ Oe^2, $\langle \delta g_\perp^2 \rangle = 0.89\times10^{-6}$, $\langle \delta\theta^2 \rangle = 0.73\times10^{-8}$, and $K=4$. Curve C is the theoretical value of δH for these same parameters, but at $\nu = 35.90$ kMc/sec. Curve B is an independent fit of 35.90 kMc/sec data using $\langle \delta H_d^2 \rangle = 0.5$ Oe^2, $\langle \delta g_\perp^2 \rangle = 0.27\times10^{-6}$, $\langle \delta\theta^2 \rangle = 0.49\times10^{-9}$, and $K=4$.

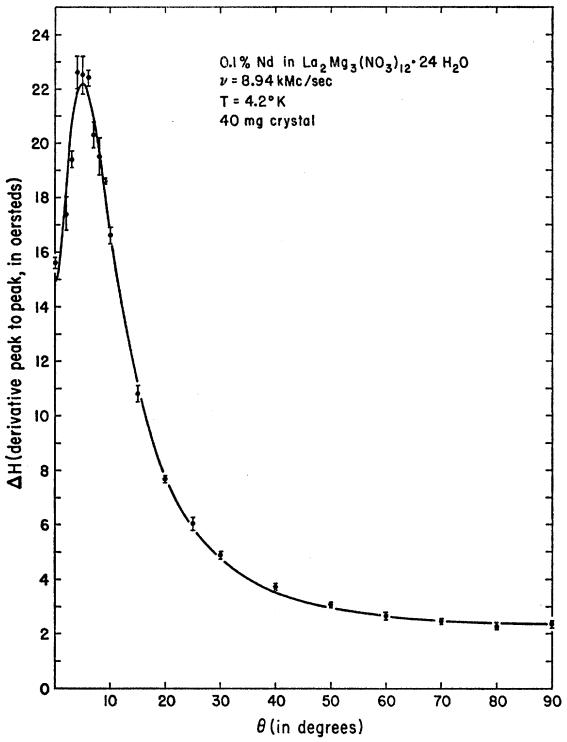

FIG. 4. Data and fitted theoretical curve for the linewidth of Nd^{3+} in lanthanum magnesium nitrate at 4.2°K. The curve represents Eq. (2) of the text with $\langle \delta H_d^2 \rangle = 0.66$ Oe^2, $\langle \delta g_\perp^2 \rangle = 0.99\times10^{-6}$, $\langle \delta g_\parallel^2 \rangle = 0.25\times10^{-7}$, $\langle \delta\theta^2 \rangle = 0.43\times10^{-7}$, and $K=4$.

The constants which seem to provide the best fit to our data for each of the three ions are listed in Table I,

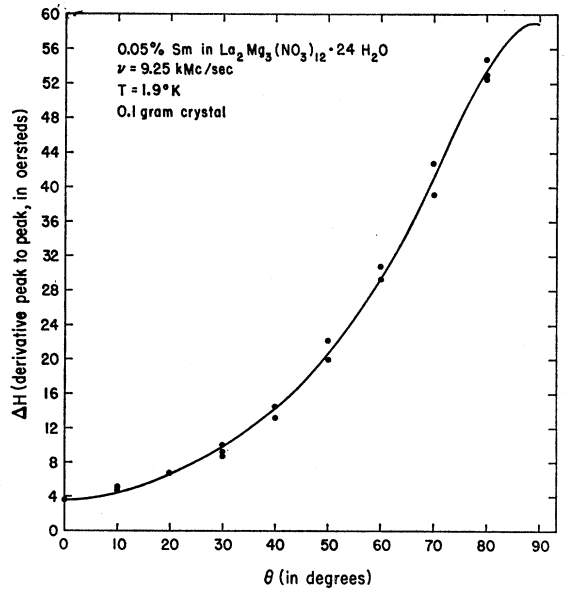

FIG. 5. Data and fitted theoretical curve for the linewidth of Sm^{3+} in lanthanum magnesium nitrate at 1.9°K. The curve represents Eq. (2) of the text, with $\langle \delta H_d^2 \rangle = 0.66$ Oe^2, $\langle \delta g_\perp^2 \rangle = 0.34\times10^{-6}$, $\langle \delta g_\parallel^2 \rangle = 0.18\times10^{-7}$, $\langle \delta\theta^2 \rangle = 1.10\times10^{-6}$, and $K=4$.

TABLE I. Best fitting parameters to the anisotropic linewidth expression, Eq. (2), for trivalent Ce, Nd, and Sm in lanthanum magnesium nitrate at liquid-helium temperatures. A Gaussian line shape is assumed.

Ion	$\langle\delta g_1^2\rangle$	$\langle\delta g_{11}^2\rangle$	$\langle\delta\theta^2\rangle$	$\langle\delta H_d^2\rangle$ (Oe^2)	Crystal weight	Fig.	Comments
Ce	0.43×10^{-6}	···	0.36×10^{-6}	3.2	200 mg	1	
Ce	0.27×10^{-6}	···	0.62×10^{-7}	3.2	15 mg	2	
Nd	0.89×10^{-6}	···	0.73×10^{-8}	0.5	15 mg	3	$\nu=9.5$ kMc/sec
Nd	0.27×10^{-6}	···	0.49×10^{-9}	0.5	15 mg	3	$\nu=35.9$ kMc/sec
Nd	0.99×10^{-6}	0.25×10^{-7}	0.43×10^{-7}	0.66	40 mg	4	
Sm	0.34×10^{-6}	0.18×10^{-7}	1.10×10^{-6}	0.66[a]	100 mg	5	

[a] This value of $\langle\delta H_d^2\rangle$ was assumed for Sm in order to get a convergent least-squares fit.

where we have put $K=4$, i.e., we have assumed a Gaussian line shape.

The value of $\langle\delta H_d^2\rangle$ may also be calculated using the Van Vleck formula[5]:

$$\langle\delta H_d^2\rangle=\tfrac{1}{3}\gamma_I^2\hbar^2I(I+1)\sum_j r_j^{-6}(1-3\cos^2\theta_j), \quad (5)$$

where I is the spin of a neighboring nucleus, such as a proton or a nitrogen nucleus, r_j is the distance from a paramagnetic ion site to the jth nucleus, and θ_j is the angle between r_j and the external magnetic field. The positions of the protons and nitrogen nuclei are known from recent x-ray crystallographic data on $Ce_2Mg_3(NO_3)_{12}\cdot24H_2O$[6]; using these known positions, Ford[7] has calculated the value of the sum in Eq. (5) for various angles between H and the crystal c axis, taking into account contributions from 560 neighboring proton sites. He has also calculated the contribution from 135 neighboring nitrate sites, but their contribution turns out to be negligible. These calculated values of $\langle\delta H_d^2\rangle$ are listed in Table II, and may be compared with the measured values listed in Table I.

TABLE II. Calculated values of $\langle\delta H_d^2\rangle$ in Oe^2 as a function of θ using Eq. (5).[a]

θ	0°	45°	75°	90°
$\langle\delta H_d^2\rangle$	0.70	0.37	0.52	0.63

[a] See Ref. 7.

III. DISCUSSION

The angular dependence of the observed linewidth seems to be reasonably well described by our simple theory for all three of the rare-earth ions investigated. However, the frequency dependence of the observed linewidth, while being reasonably well described in the case of Ce, is not well described by our theory for the Nd salt, as can be seen from Fig. 3 and Table I. The most likely explanation for this discrepancy is that for the case of Nd, the actual line shape does not seem to be independent of frequency, as mentioned earlier in Sec. II. This feature may possibly be due to the existence of macroscopic crystal strains. At any rate, we note that the theory is qualitatively correct in predicting a general increase of the observed linewidth with frequency.

The calculated values of $\langle\delta H_d^2\rangle$ seem to agree reasonably well with our measured values for both the Nd and Sm salts; that the observed value of $\langle\delta H_d^2\rangle$ is larger in the case of the Ce salt may possibly be evidence for a direct hyperfine interaction between the single $4f$ electron on the Ce ion and the surrounding nuclei. We have attempted to observe such an interaction by a double resonance experiment but the only observed signal occurred at the proton resonance frequency, and it showed no structure.

The fact that we obtain nearly identical data for two crystals containing widely different Nd ion concentrations indicates that it is reasonable to neglect spin-spin interaction as a contribution to the linewidth, at least for atomic concentrations of 0.2% or less.

Finally, of the four parameters in our theory, a glance at Table I shows that $\langle\delta\theta^2\rangle$ depends most markedly on the crystal size. This is not surprising, as this parameter may indicate a kind of "c-axis wander" which may be more dependent on crystal size than any of the remaining three parameters.

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