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Anisotropic Hyperfine Interactions in Gadolinium Metal*

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Mössbauer studies of the 86-keV transition of Gd^{155} in $Gd_{1-x}R_x$ compounds yield the hyperfine interaction parameters as a function of lattice dimensions and the angle θ between the magnetization and the c axis. The magnetic hyperfine field is anisotropic, $H_{\rm eff}(\theta=28°)/H_{\rm eff}(\theta=47°)=1.13$. The ratios between the electric field gradients in various metallic crystals are in agreement with the point-charge model. The absolute values of the gradients are about twice the theoretical values.

The results of some measurements of the hyperfine interaction parameters in Gd metal have recently been published.[1-3] In all these measurements the hyperfine field was assumed to be isotropic. The values of the magnetic hyperfine fields differ in the various measurements by as much as 20% and the values of the quadrupole interaction parameters differ by as much as 25%. In the present work the anisotropy of the hyperfine magnetic field acting on Gd nuclei in Gd metal was established. $H_{\rm eff}$ was found to change by about 13% as the angle θ between the direction of magnetization and the c axis changes between 28° and 47°. It was further found that the angle θ in Gd-metal powder is different in samples obtained from different suppliers and is different from the angle found in a Gd single crystal. The hyperfine field acting on Gd nuclei in Gd-metal single crystals was found to be 373 ± 5 kG. The quadrupole interaction parameter $[eqQ(0)/4]$ of the ground state of Gd^{155} in the metal was found to be 26.4 ± 0.7 MHz. The value of θ was determined to be $28°\pm2°$. The ratios between the electric field gradients (EFG) acting on Gd nuclei embedded in various metallic close-packed hexagonal crystals (with different lattice parameters) were found to be in agreement with the predictions of the point-charge model. The absolute values of the EFG calculated according to this model are about half of the experimental values.

Recoilless absorption studies of the 86-keV γ ray of Gd^{155} in a single-crystal absorber of Gd metal, in Gd-metal powder, and in some $Gd_{1-x}R_x$ compounds, where R is a rare-earth metal, Y, Lu, or Sc, were performed at 4.1 K. The Gd-metal single crystal was purchased from Koch Light Labs. Ltd. The source used was $SmPd_3$ at 4.1 K. Some typical spectra obtained are shown in Fig. 1. Large differences between the spectra of Gd metal, $Gd_{0.85}Tm_{0.15}$, and $Gd_{0.95}Tb_{0.05}$ are clearly seen. The experimental spectra were analyzed by least-squares computer fits. Gd metal and all other compounds investigated have the hexagonal close-packed structure, as was verified by x-ray measurements. The $4f$ contribution to the electric field gradient acting on the Gd nuclei vanishes and the gradients stem only from the lattice. It is justified, therefore, to assume that the electric field gradients are axially symmetric ($\eta=0$) and point along the c axis. The theoretical spectra were calculated by computer-diagonalizing the Hamiltonian

$$\mathcal{H}=\frac{eqQ}{4I(2I-1)}[3I_z^2-I(I+1)]+g\mu_n H_{\rm eff}(I_z\cos\theta+I_x\sin\theta)$$

for both the ground and excited states. ($I=\frac{3}{2}$ in the ground state and $I=\frac{5}{2}$ for the 86.5-keV excited state.) The wave functions of the sublevels were determined and were used to calculate the relative intensities of the transitions between the various sublevels. The ratios $g(86.5)/g(0)$ and $Q(86.5)/Q(0)$ were assumed in the analysis to be 1.235 and 0.087, respectively.[4,5] In the Gd single-crystal absorber, the direction of the γ ray was parallel to the c axis of the crystal. The analysis of the spectra yields unambiguously the values of $g_0\mu_n H_{\rm eff}$ with an accuracy of ~2%, $eqQ(0)$ with an accuracy of ~10%, and the angle θ with an accuracy of ~3°, in the various absorbers. The

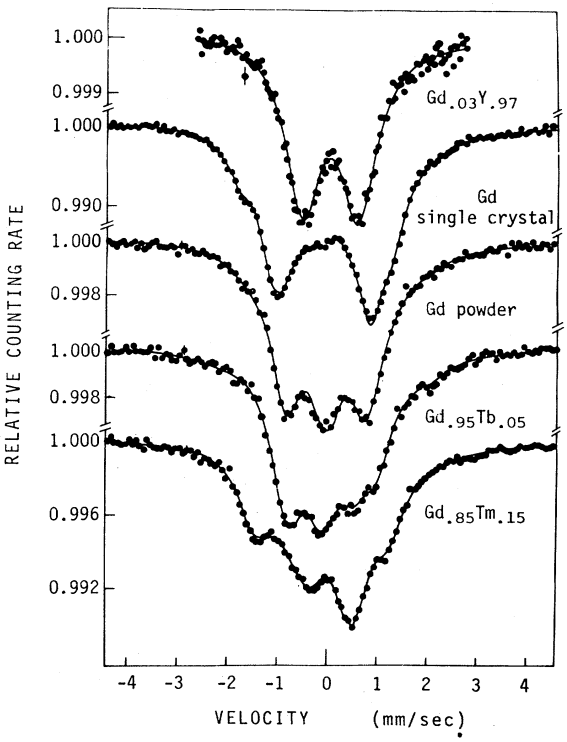

FIG. 1. Recoilless absorption spectra of the 86.5-keV γ ray of Gd^{155} in some $Gd_{1-x}R_x$ compounds at 4.2 K. The solid lines are the theoretical best fits to the experimental spectra. The upper spectrum is a typical pure quadrupole spectrum. The second spectrum was obtained using a single-crystal Gd absorber, with the direction of the γ ray parallel to the c axis of the crystal. The third spectrum was obtained using Gd powder purchased from Lunex Co., in which $\theta = 52° \pm 3°$. The fourth spectrum was obtained using a $Gd_{0.95}Tb_{0.05}$ absorber ($\theta = 88° \pm 3°$) and the lowest spectrum was obtained using a $Gd_{0.85}Tm_{0.15}$ absorber ($\theta = 8° \pm 1°$).

main results obtained are summarized in Table I. As expected, the quadrupole interactions are found to be the same, within the limits of errors, in the Gd single crystal, the Gd powders, and the $Gd_{1-x}R_x$ compounds with $x \leq 0.15$.

The results show that the angle θ in Gd-metal powder is different from that in the Gd single crystal. In the single crystal θ was found to be $28° \pm 2°$, in agreement with torque[6] and neutron-diffraction measurements.[7] Different samples of Gd powder, all 99.9% (or more) pure, obtained from various suppliers, did not all yield the same spectra. The differences between the spectra could be explained only if it was assumed that θ is not the same in all samples. Thus, e.g., θ was found to be $52° \pm 3°$ in a sample obtained from Lunex Co., whereas in samples from three other companies it was around 75°. It seems, therefore, that this angle depends very much on small amounts of impurities in the samples and on their method of preparation. It is also seen from Table I that very small amounts of Tm or Tb change θ very significantly. In $Gd_{0.97}Tb_{0.03}$ θ is ~ 90°, whereas in $Gd_{0.85}Tm_{0.15}$ $\theta = 8°$. This phenomenon is in agreement with torque measurements of the magnetocrystalline anisotropy of rare-earth impurities doped in Gd metal.[8]

TABLE I. The angle between the crystal axis and the direction of the magnetic moment, and hyperfine interaction parameters, in some $Gd_{1-x}R_x$ compounds.

Sample	θ°	$g_0\mu_n H_{\text{eff}}/h$ (MHz)	$eqQ(0)/4h$ (MHz)
$Gd_{0.85}Tm_{0.15}$	8 ± 1	45.5 ± 1.0	30.0 ± 3.0
$Gd_{0.95}Tm_{0.05}$	16 ± 2	46.0 ± 1.0	28.0 ± 2.5
Gd single crystal	28 ± 2	48.8 ± 0.5	26.4 ± 0.7
$Gd_{0.99}Tm_{0.01}$	33 ± 2	46.0 ± 1.0	30.0 ± 2.5
$Gd_{0.995}Tm_{0.005}$	47 ± 3	43.3 ± 0.7	27.5 ± 2.5
Gd (Lunex)	52 ± 3	43.3 ± 0.6	27.5 ± 2.5
Gd (others)	75 ± 3	42.8 ± 0.6	27.5 ± 2.5
$Gd_{0.99}Tb_{0.01}$	78 ± 3	42.2 ± 0.6	27.5 ± 2.5
$Gd_{0.97}Tb_{0.03}$	87 ± 3	43.1 ± 0.6	27.5 ± 2.5

It was found that H_{eff} in the Gd single crystal is ~ 13% larger than in Gd-metal powder. We attribute this difference to the difference in the angle θ. The field measured in the $Gd_{1-x}Tb_x$ compounds is almost independent of x (for $x \leq 0.03$) and is equal to the field found in Gd-metal powder and in $Gd_{0.995}Tm_{0.005}$. The field does not change appreciably for θ between 47° and 90°. The values of H_{eff} for such small values of x are expected to be equal to their values in pure Gd metal with the same values of θ. On the other hand, H_{eff} changes by about 13% between $\theta = 28°$ and $\theta = 47°$. Angles smaller than 28° are obtained in $Gd_{1-x}Tm_x$ compounds with $x > 0.05$. In these compounds the contribution of the polarized conduction electrons to H_{eff}, which is expected to be approximately proportional to $\langle S_z \rangle$, will depend significantly on the values of x; the dependence of H_{eff} in pure Gd on θ cannot be derived, therefore, unambiguously, from the values of H_{eff} in these compounds.

The anisotropy observed in the hyperfine field of Gd metal may stem either from an anisotropy of the conduction-electron polarization or from the fact that Gd^{3+} is not in a pure $S_{7/2}$ ground state. According to an estimate by Wybourne[9] the ground state is approximately given by $|J = \frac{7}{2}\rangle = 0.987|^8S_{7/2}\rangle + 0.162|^6P_{7/2}\rangle - 0.012|^6D_{7/2}\rangle$. Such an admixture of the $^6P_{7/2}$ to the $^8S_{7/2}$ state would have

TABLE II. Quadrupole interaction parameters and lattice dimensions of some $Gd_{1-x}R_x$ compounds. In column 2 the measured quadrupole interaction parameters are given. In column 5, theoretical values calculated by the point-charge model are given.

Sample	$eqQ(0)/4h$ expt. (MHz)	a (Å)	c (Å)	$eqQ(0)/4h$ calc. (MHz)
$Gd_{0.03}Lu_{0.97}$ (30 K)	34.2± 0.6	3.505	5.553	16.84
$Gd_{0.03}Sc_{0.97}$ (30 K)	32.3± 0.5	3.309	5.268	16.3
$Gd_{0.03}Y_{0.97}$ (30 K)	41.1± 0.4	3.650	5.741	18.84
Gd single crystal (4 K)	26.4+ 0.7	3.634	5.781	13.25
Gd powder (4 K)	27.5± 2.5	3.634	5.781	13.25

a negligible effect on the magnetic moment, but may have an appreciable effect on the hyperfine field: In the $S_{7/2}$ state the $4f$ contribution vanishes, whereas for a pure $^6P_{7/2}$ state it would be 1.1 MG. The change of this contribution as a function of θ might contribute appreciably to the changes in the hyperfine field observed in the present measurements.

The measurements of the electric field gradient acting on Gd nuclei in $Gd_{1-x}R_x$ compounds yield the dependence of the electric field gradient on the lattice parameters. The results were deduced mainly from measurements in compounds of Gd enriched in Gd^{155} with diamagnetic metals (Sc, Lu, and Y) and $x = 0.97$ at 30 K. At this temperature the magnetic hyperfine interaction in these compounds vanishes and pure quadrupole spectra are obtained. One typical quadrupole spectrum ($Gd_{0.03}Y_{0.97}$) is shown in Fig. 1. According to the point-charge model, the dependence of the electric field gradient on the lattice parameters in a simple close-packed hexagonal lattice is given by

$$q = [a^{-3}\{0.0065 - 4.3584(c/a - 1.633)\}] \times (1-\gamma_\infty)Ze, \qquad (1)$$

where a and c are the lattice constants and γ_∞ is the Sternheimer shielding factor. Column 2 in Table II gives the experimental values of the quadrupole interactions measured in the various compounds. Column 5 in the table gives the values of the electric quadrupole interactions computed from the point-charge model. These values were obtained by assuming $\gamma_\infty = -80$ and $Q(0) = 1.5$ b.[11] In all cases the ratio between the experimental value and the computed one is seen to be about 2. The formula accounts, therefore, correctly for the dependence of the EFG on the lattice parameters, yet the absolute values calculated are about half of the experimental values. The difference between the calculated and experimental values may be due to the field gradient produced by the conduction electrons. Similar results have been found previously in La[12] and Tm.[13]

Our measured value of the hyperfine field, $H_{\text{eff}} = 373 \pm 5$ kG for $\theta = 28° \pm 2°$, agrees with the value cited by Seiwa *et al.*,[1] yet the value found in the present measurements for the quadrupole interaction parameter in Gd metal, $eqQ(0)/h = 108 \pm 1$ MHz, is larger by 30% than the value given in the above-mentioned work. It seems, therefore, doubtful whether the identification of the lines in the NMR spectrum was correct.

In Gd metal, θ is known to change with temperature.[6] The hyperfine interactions in Gd metal as a function of temperature have been measured by the angular correlation technique.[3] These measurements show that the temperature dependence of the reduced hyperfine field, $H_{\text{eff}}(T)/H_{\text{eff}}(0)$, deviates appreciably from the magnetization curve. This deviation may be explained by the observed dependence of the hyperfine field on θ, as measured in the present work.

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Cross Section Ratios for $(\pi^{\pm}, \pi N)$ Reactions on ^{16}O near the $\Delta(1236)$ Resonance*

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Ratios of cross sections for 200-MeV $\pi^{\pm}$ reactions on ^{16}O leading to mirror levels in ^{15}O and ^{15}N, observed by their γ decays, were measured and compared. For the first $\frac{3}{2}^-$ levels, the ratios are $(^{15}O/^{15}N)_{\pi^-} = 1.7 \pm 0.4$ and $(^{15}O/^{15}N)_{\pi^+} = 1/(1.8 \pm 0.4)$, indicating charge symmetry.

The one-step quasifree (OSQF) mechanism for $(\pi, \pi N)$ nuclear reactions, in which the incident pion scatters from an individual nucleon, appeared to be a good approximation[1] until Chivers *et al.*[2] reported that the activation-cross-section ratios $(A + \pi^- \to A - 1)/(A + \pi^+ \to A - 1)$ on ^{12}C, ^{14}N, and ^{16}O near the $\Delta(1236)$ pion-nucleon resonance are close to 1 and not to 3, as originally expected from the behavior of the pion-nucleon cross section. Similar cross-section ratios have also been determined for a variety of even- and odd-mass targets from ^4He to ^{64}Zn at incident energies ranging from 30 to 360 MeV.[2-9] A recent remeasurement at Los Alamos[10] of $\pi^{\pm}$ activation of ^{11}C from ^{12}C yielded π^+ cross sections somewhat lower than those in Ref. 2. Nearly all ratios were found to be considerably less than 3; the Los Alamos measurement yielded, at $E_\pi = 180$ MeV, $\sigma_{\pi^-}/\sigma_{\pi^+} = 1.5$. Various mechanisms have been proposed to explain these results. Besides OSQF processes, final-state interactions between the struck nucleon and the residual nucleus and inelastic pion scattering to unbound levels have been suggested.[2,11-17]

In order to test the $(\pi, \pi N)$ nuclear reaction mechanism in a different way from previous experiments, we determined, for incident π^+ near the $\Delta(1236)$ resonance energy on a water target, the ratio of π^+ cross sections,

$$R(\pi^+) \equiv \frac{\sigma(\pi^+, {}^{15}O^*(6.18, \tfrac{3}{2}^-))}{\sigma(\pi^+, {}^{15}N^*(6.32, \tfrac{3}{2}^-))},$$

producing the first $\frac{3}{2}^-$ excited levels in the residual mirror nuclei ^{15}O and ^{15}N. We then compared the result with a previously obtained ratio[18] of π^- cross sections,

$$R(\pi^-) \equiv \frac{\sigma(\pi^-, {}^{15}O^*(6.18, \tfrac{3}{2}^-))}{\sigma(\pi^-, {}^{15}N^*(6.32, \tfrac{3}{2}^-))},$$

leading to the same excited residual-nucleus levels. These ratios were determined by observing the prompt de-excitation γ rays from individual bound levels of these residual nuclei. Since the decay schemes for ^{15}O and ^{15}N[19] permit an un-