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NMR Study of Gd-Ni Intermetallic Compounds*

by

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Abstract

The spin echo ^{155}Gd and ^{157}Gd NMR was used to study the intermetallic compounds Gd_2Ni_{17}, $GdNi_5$, $GdNi_3$, $GdNi_2$ and GdNi. These compounds have different crystal structures and order ferri- or ferromagnetically. The measurements were performed at 4.2 K and 1.5 K. The NMR spectra were compared to computed line positions obtained from the diagonalization of the complete hyperfine hamiltonian. The differences in the values of B_{hf} at the two sites of Gd in Gd_2Ni_{17} and $GdNi_3$, of the order of 18 T and 6 T, respectively, may be justified, in a semi-quantitative way, through the RKKY model. We observed a strong quadrupole interaction at the Gd sites in the compounds $GdNi_5$, Gd_2Ni_{17}, and in one of the sites of the compound $GdNi_3$; in all these cases, the values of V_{zz} are higher than $7.0 \times 10^{21} V/m^2$. The NMR results in GdNi are consistent with a direction of magnetization along the **b** axis. No NMR signal could be unambiguously attributed to ^{61}Ni nuclei. This work presents the first NMR results of the Gd–Ni intermetallic compounds.
Key-words: Intermetallic compounds, NMR, Hyperfine fields.

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^{155}Gd and ^{157}Gd NMR was used to investigate the magnetic properties of the intermetallic compounds of the Gd-Ni series. No signals from ^{61}Ni nuclei were obtained, due to the low abundance of this isotope. The samples were prepared from high purity elements, in an arc furnace. The GdNi sample was prepared by crushing a single crystal. The measurements were made at 4.2 K (or 1.5 K in one case). The NMR spectra were fitted to determine the line positions, and compared to positions obtained through computer diagonalization of the total hyperfine (hf) hamiltonian.

The $GdNi_2$ compound crystallizes in the $MgCu_2$ structure (cubic). Gd atoms occupy one single site, 8(a) [1]. The NMR spectrum shows two narrow lines, at 14.7(1) and 19.2(1) MHz. The ratio of these frequencies (0.766(1)) is very close to the ratio of the gyromagnetic ratios of the Gd isotopes (0.7630) [2] and therefore, are associated to the transitions between the +1/2 and -1/2 nuclear hf sub-levels. The lines that appear in the spectrum at 26.5(4), 47.0(4) and 54.0(4) MHz are attributed to transitions involving other levels.

The Gd_2Ni_{17} compound crystallizes as Th_2Ni_{17} (hexagonal). Gd atoms occupy sites 2(c) and 2(b) [1]. The NMR spectrum exhibits lines associated to the two sites (Fig. 1). Both sites show narrow lines, at the frequencies 5.93(1) and 7.79(1) MHz for site 2(d), and 29.63(1) and 38.94(1) MHz for site 2(b), with a ratio of frequencies of 0.7609(1), agreeing with the ratio of the γ's. The $B'_{hf}s$ were calculated through these pairs of lines, for each site of Gd. The dashed lines near 10 MHz show the NMR response of nuclei excited at 29.63 and 38.94 MHz. These are ghost lines that appear for multiples of the main frequency (2X or 3X) [3]. No lines were observed corresponding to transitions to nuclear levels other than $\pm 1/2$, in the range of 2 - 100 MHz; we assume that such lines appear above 100 MHz. The lower limits of V_{zz} were computed assuming $\eta = \theta = 0$; these limits correspond to $V'_{zz}s$ that led to lines above 100 MHz.

The $GdNi_5$ compound crystallizes with the $CaCu_5$ structure. The Gd atoms occupy only one site, 1(a) [1]. Two narrow lines are observed in the spectrum, at 30.48(1) and 39.97(1) MHz. The ratio of these frequencies (0.7626(6)) agrees with the ratio of the $\gamma's$. No other resonance lines, arising from transitions between other levels, were detected in the range 2-100 MHz; we believe these lines to be above 100 MHz.

$GdNi_3$ crystallizes with the structure of $NbBe_3$ (rhombohedral symmetry); Gd atoms ocupy sites 3(a) and 6(c) [1]. Figure 1 shows the NMR spectrum obtained at 1.5 K; the

lower temperature was used due to the very weak NMR signal. The spectrum is very complex, being very difficult to associate the lines to individual sites. The lines at the frequencies 21.22(2) and 27.54(6) MHz, of frequencies in the ratio 0.770(1), very close to the ratio of the $\gamma's$ are attributed to the site 6(c) (trigonal point symmetry) [4]. The other lines of the spectrum are related to site 3(a) (approximately cubic [4]). No other resonance lines, associated to other levels were observed for site 6(c) of Gd, in the range 5-100 MHz.

GdNi crystallizes with the CrB structure; Gd atoms are located on a single site (4(c)) [1]. The NMR spectrum (figure 1) is very complex for a single crystallographic Gd site. Varying systematically the hf parameters we reproduced it reasonably well.

The Gd_2Ni_{17} compound has two crystallographic sites of Gd, 2(b) and 2(d) [1]. The 2(b) site has a very similar neighborhood to that of site 1(a) of Gd in $GdNi_5$. It is reasonable to expect that the hf interactions will show similar behavior. For these sites, the lower limits of V_{zz} have comparable magnitude; the B_{hf}'s are also very close (table). B_{hf} in the 2(d) site of the compound Gd_2Ni_{17} is very low compared to the value obtained for the site 2(b). Steenwijk et al. [5] have considered that this difference may originate from different transferred hf fields.

We have calculated the RKKY sum for the two sites of Gd in Gd_2Ni_{17}, $r \leq 40$ Å, and we obtained the same behavior described by Steenwijk et al. Since the transferred hf field is proportional to the RKKY sum, to each value of k_F corresponds a ratio of B_{hf} of the two sites. For $k_F = 0.83$ Å^{-1} this ratio is 3.4; this corresponds to a c.e. concentration of ≈ 4.7 electrons/f.u., in agreement with [5].

$B'_{hf}s$ at the Gd sites 3(a) and 6(c) in $GdNi_3$ are comparable (table). The ratio $B^{Gd3(a)}_{transf}/B^{Gd6(c)}_{transf} \approx 1.4$. For $k_F = 0.72$ Å^{-1}, the ratio of the sums is 1.3. For $k_F = 0.72$ Å^{-1} it follows a c.e. density of ≈ 3.3 electrons/f.u. This value is reasonable, since one has one Gd per f.u., this atom contributing with 3 electrons.

$V'_{zz}s$ obtained for the 8(a) site of Gd in $GdNi_2$, and the 3(a) site of Gd in $GdNi_3$, are in the same range. The $B'_{hf}s$ are also very close. This shows that these sites behave more or less in the same way, in terms of magnetic and electrostatic interactions. The 8(a) site has cubic point symmetry. Tomala et al. [4] state that the site 3(a) of Gd in $GdNi_3$, has 'approximately cubic' point symmetry. This justifies the similarities observed here. The $V'_{zz}s$ for these two sites are very large for pure S-state ions in sites of cubic symmetry [6].

For the 4(c) site of Gd in GdNi, we found $\eta = 0.51(5)$ and the angles θ and ϕ equal to $90^o(8)$ and $106^o(15)$, respectively. The low symmetry of this site, justifies the value found for η. Computing the lattice EFG tensor using a point charge model, for $r \leq 40$ Å, we get $\eta = 0.67$, which agrees roughly with our experimental value. The values of θ and ϕ derived here indicate that $\vec{B}_{hf}$ is localized along the positive direction of the crystalline axis b, in agreement with neutron diffraction measurements [7].

The 8(a) site in $GdNi_2$ has cubic point symmetry. The site 3(a) of Gd in $GdNi_3$, has 'approximately cubic' point symmetry. The large $V'_{zz}s$ found here for these high symmetry sites suggest that the Gd ion is not in a pure S-state [8].

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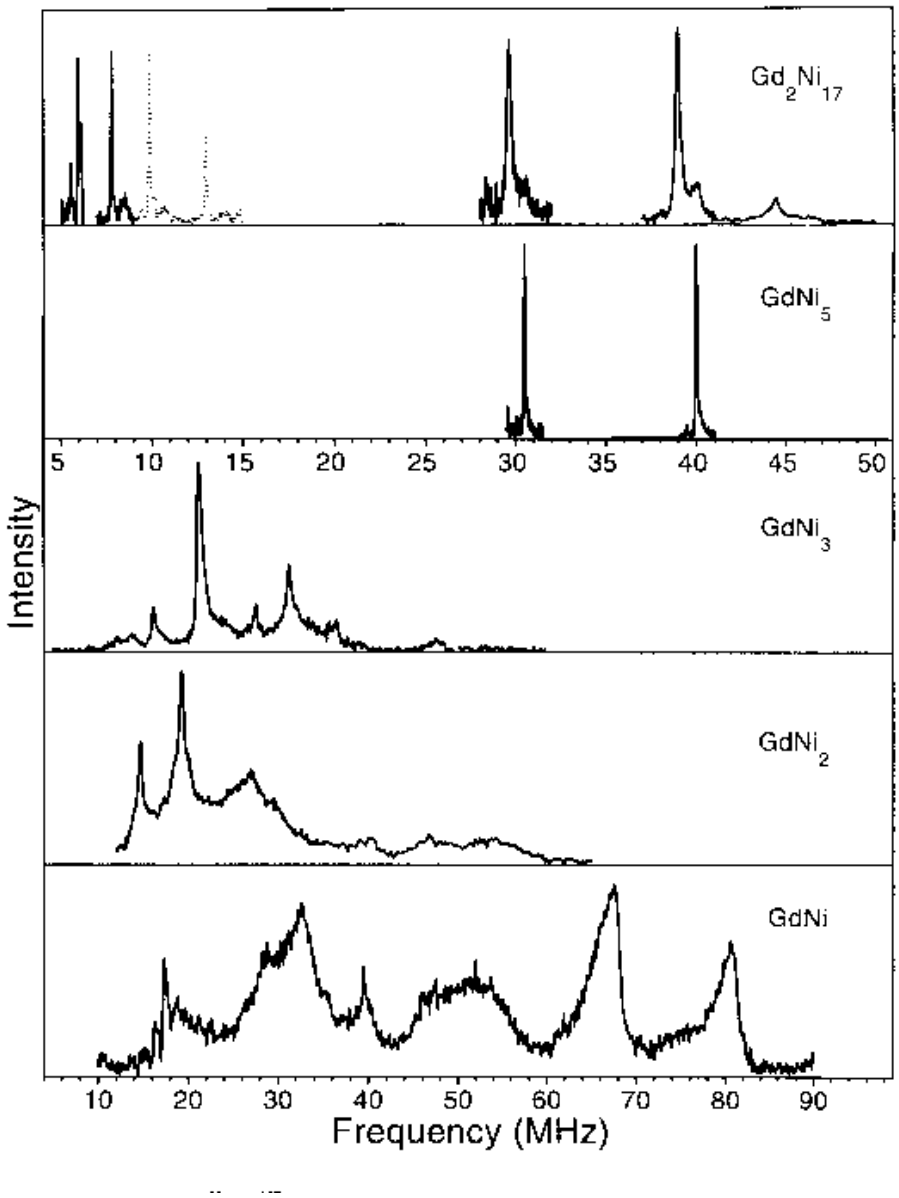

Caption: ^{155}Gd, ^{157}Gd NMR spectra of Gd-Ni intermetallic compounds at low temperature; the dashed lines are instrumental artifacts.

Compound	site	$B_{hf}(T)$	$V_{zz}(10^{21}/\mathrm{m}^2)$	η	θ(degrees)	ϕ(degrees)
GdNi	4(c)	14.5(5)	2.2(1)	0.51(5)	90(8)	106(15)
$GdNi_2$	8(a)	9.8(2)	1.90(5)	0	18(1)	0
$GdNi_3$	3(a)	10.0(1)	1.03(1)	0	18(1)	0
	6(c)	16.16(2)	>6.5(1)	0	0	0
$GdNi_5$	1(a)	23.33(1)	>7.1(1)	0	0	0
Gd_2Ni_{17}	2(b)	22.70(1)	>7.0(2)	0	0	0
	2(d)	4.54(1)	>5.8(2)	0	0	0

Table caption: Values of the hf parameters of the Gd-Ni compounds obtained by simulation.

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