

Charge and magnetic states of Ni ions in the GdNi₂ Laves phase synthesized at different pressures

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The lattice constant, Curie temperature, and magnetization curves were measured for GdNi₂ samples synthesized at ambient and high pressure up to $P_{\text{syn}}=8$ GPa. All these parameters exhibited a marked change in the samples synthesized at about 5 GPa and higher. The quadrupole interaction of ¹⁸¹Ta at the Ni sites was studied by the time-differential perturbed angular correlation method with the GdNi₂ samples doped with ¹⁸¹Hf. A factor of ≈ 1.5 difference of quadrupole frequencies for the samples prepared at low pressure (<5 GPa), and at pressure ≥ 5 GPa was observed. These results are considered as evidence of the change of the Ni ions' charge and magnetic states in the samples prepared at elevated pressures to be due to a reduction of the population number of the 3d band which is close to $n_d=10$ in the "normal" state. The "high-pressure" state is infinitely stable at room temperature but can be destroyed at $T\approx 400$ °C. [S0163-1829(97)05906-7]

INTRODUCTION

The intermetallic compound GdNi₂ is the Laves phases with the cubic structure of the MgCu₂ type (C15). The point symmetry of the Gd site is cubic, and that of Ni- $\bar{3}m$. It is ferromagnetic with $T_C=85$ K.¹ It is also known that the magnetic moment of Ni ions is zero, which is considered a consequence of the complete filling of the 3d band ($n_d=10$).²

It has recently been shown³ that Ni ions in the isostructural paramagnetic Laves compound YNi₂ acquired a non-zero magnetic moment, provided this compound was synthesized (melted and crystallized) at high pressure: namely, in the samples prepared at $P_{\text{syn}}=8$ GPa it amounted to about $0.36\mu_B$ [whereas in samples prepared at ambient pressure $\mu(\text{Ni})=0$]. It is evidently a consequence of the change of the band structure of the alloy leading to a decrease of the 3d-band population number ($n_d<10$).

The question arises naturally if such a rearrangement of the 3d band is a common phenomenon in Ni-based intermetallics. For example, Cava *et al.*⁴ indicated the important role of the Ni 3d-band structure in determining the properties of new superconductors RNi₂B₂C (*R* represents rare earths). It has been shown recently^{5,6} that synthesis of YNi₂B₂C at $P_{\text{syn}}=8$ GPa lowers the transition temperature from about 15 K for the "normal" phase to ≈ 10 K, which may be a result of such a rearrangement.

Here we report the results of the study of the crystallographic and magnetic properties of GdNi₂ prepared at the P_{syn} values from normal to 8 GPa. We also used the method of time-differential perturbed angular correlation of γ rays (TDPAC) in an attempt to detect possible changes of magnetic and charge states of the Ni ions by observing the elec-

tric quadrupole and magnetic dipole hyperfine interaction of the impurity ¹⁸¹Ta nuclei in the samples doped by the radioactive ¹⁸¹Hf.

EXPERIMENTAL DETAILS

The samples of GdNi₂ for the x-ray-diffraction and magnetic studies were prepared at different pressures up to 8.0 GPa by melting of the constituent materials. The purity of Ni was 99.99%, and that of Gd, 99.9%. The chamber designed by Khvostantsev *et al.*⁷ was used for generation of high pressure. The preparation procedure was described in Ref. 8. For the TDPAC measurements, a small amount of Hf with high specific activity of ¹⁸¹Hf isotope ($T_{1/2}=42$ d) was added into the melt.

The 114-mm Debye-Scherrer chamber and Ni-filtered CuK α radiation was used in the x-ray-diffraction studies of the samples. The NaCl inner reference standard was added for an accurate determination of the lattice constants. The composition of the samples was confirmed by x-ray microanalysis.

For the Curie temperature determination samples were cooled in a zero field down to 4.2 K and after that the *M-T* curves were measured in a magnetic field of 0.05 T using a SQUID magnetometer.

The magnetization curves of the samples were measured using the Princeton Applied Research vibrating sample magnetometer.

Measurements of the TDPAC spectra for the well-known 133–482 keV γ -ray cascade proceeding via the 482-keV isomeric state in ¹⁸¹Ta (spin $I=5/2$, half-life $T_{1/2}=10.8$ ns, quadrupole moment $Q=2.51$ b, *g* factor $g=1.30$) were performed using the automatic three-detector scintillation coincidence spectrometer with a time-resolution $2\tau_0=1.7$ ns.

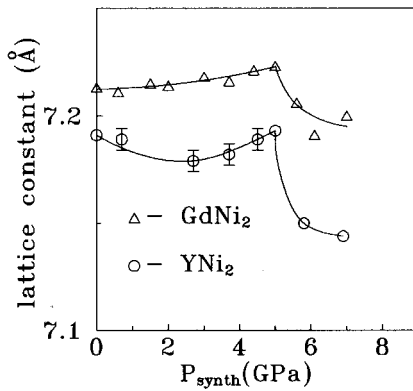


FIG. 1. The lattice constants for the GdNi₂ (triangles) and YNi₂ (circles) samples prepared at different values of pressure. The reflexes 751 and 844 were used for the determination. The GdNi₂ diffractogram was measured with the inner NaCl standard and the uncertainties of the *a* values are of an order of the points size.

The TDPAC spectra for the samples prepared at $P_{\text{syn}}=0.8, 3.7, 5.1, 6.1, 7.9$ GPa and at normal pressure were measured.

The ¹⁸¹Hf-doped samples were prepared as follows. A Hf-Ni alloy with an atomic concentration ratio close to 1:2 was prepared and irradiated in a reactor in the neutron flux of $2 \times 10^{13} \text{ s}^{-1} \text{ cm}^{-2}$ for 200 h for activation of ¹⁸¹Hf. A small amount (<1 wt. %) of this alloy was then added into the melt. After melting and crystallization the ingots were crushed and checked for the uniformity of the radioactivity distribution over their volume. The specific activity of ¹⁸¹Hf was usually high enough so that about some tens of milligrams of the resultant alloy were sufficient for TDPAC measurements. Clear and bright crumbs from the inner part of an ingot were taken and crushed into powder in order to eliminate possible texture effects.

Most of the measurements were made at room temperature; for the 7.9 GPa sample measurements at 11 K were also carried out. In the latter case, a compact flow-type helium cryostat was used.

The methods of the TDPAC data treatment are well developed and described elsewhere.⁹ At $T \geq 80$ K the samples are paramagnetic, and the perturbation coefficients $G_{22}(t)$ extracted from the anisotropy time spectra are functions of electric quadrupole interaction parameters: the quadrupole frequency $\nu_Q = eQV_{zz}/h$, the asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$, where V_{ii} ($i=x, y, z$) are the principal-axis components of the electric-field gradient (EFG) with $|V_{xx}| \leq |V_{yy}| \leq |V_{zz}|$, and a relative width of the quadrupole frequency distribution due to lattice defects and other imperfections: $\gamma_Q = \delta\nu_Q/\nu_Q$. In the treatment procedure we proposed a Lorentzian shape of the frequency distribution. The Fourier analysis and the least-squares fitting was used for the EFG parameter determination.

EXPERIMENTAL RESULTS AND DISCUSSION

All samples of GdNi₂ synthesized at different values of pressure, from ambient up to 8 GPa, were of single-phase C15 structure.

In Fig. 1 the lattice constant dependence on the synthesis pressure for GdNi₂ is presented (triangles) together with that

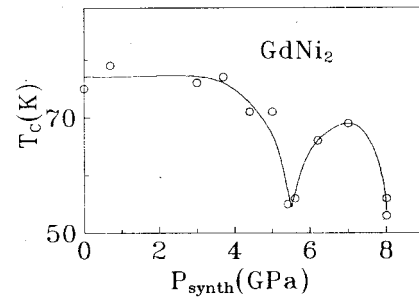


FIG. 2. The Curie temperature values of GdNi₂ samples prepared at different values of P_{syn} .

for YNi₂ (open circles). It can be seen that in both cases the lattice constant, after a smooth rise at $P_{\text{syn}} < 5$ GPa drops abruptly at $P \approx 5$ GPa, from 7.223 to 7.200 Å for GdNi₂ (0.3%), and from 7.193 to 7.150 Å for YNi₂ (0.6%). It should also be noted that for all samples single upsplit lines in the Debyeograms were observed, i.e., we did not encounter samples in which two crystal phases (“low pressure” and “high pressure”) coexisted.

A much more prominent discontinuity was observed in the dependence of the Curie temperature on the synthesis pressure (Fig. 2). The drop of the T_C at $P_{\text{syn}}=5$ and ≈ 7.9 GPa amounts to about 30%.

In Fig. 3 the magnetization curves in the fields up to 1.3 T for samples prepared at $P_{\text{syn}}=3.7, 4.4, 5.0$ GPa, and at normal pressure [Fig. 3(a)] and $P_{\text{syn}}=5.0, 6.1, 7$ GPa [Fig. 3(b)] are shown. In the magnetic field below 1.3 T the saturation could not be reached, and thus we could not compare saturation moments for the samples prepared at different pressure. But it can be seen that the sample prepared at $P_{\text{syn}}=5.0$ GPa is characterized by a most steep rise of the M vs B curve at low-field values, i.e., by the highest value of permeability.

It should be noted that abrupt changes of the lattice constant and Curie temperature and maximal permeability are observed in the sample synthesized at about 5 GPa.

The TDPAC spectra taken at room temperature (i.e., in the paramagnetic state) for the samples prepared at normal pressure, and at $P_{\text{syn}}=3.7, 5.1, 7.9$ GPa are shown in Figs. 4(a)–4(d). It can be seen that in all cases the correlation is strongly perturbed by the electric quadrupole interaction (EQI). This means, first of all, that Hf impurity atoms do not substitute for Gd at the sites with cubic point symmetry. This is contrary to the case of RFe₂ Laves phase where nearly 100% of Hf impurities (at concentrations <1%) occupied the cubic substitutional sites.^{10,11} Presumably, this is a reflection of the fact that there does not exist the Laves compound HfNi₂.¹²

The results of the fit of these spectra are presented in Table I and shown by the solid lines on the graphs.

In all TDPAC spectra of the samples prepared at $P_{\text{syn}} \geq 5$ GPa, the perturbation due to a well-defined quadrupole precession characterized by a small asymmetry parameter and a narrow frequency distribution was observed [see Figs. 4(c) and 4(d) and Table I]. These parameters averaged over spectra of the samples prepared at 5.1, 6.5, and 8.0 GPa are as follows:

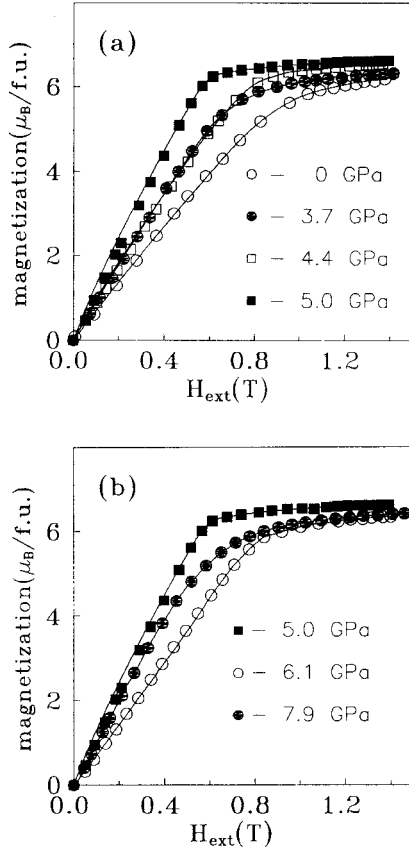


FIG. 3. Magnetization curves of the GdNi_2 samples measured at 4.2 K for (a) the samples prepared at ambient pressure (open circles) and at $P_{\text{syn}}=3.7$ GPa (solid circles), 4.4 GPa (open squares), and 5.0 GPa (solid squares), and (b) the same for $P_{\text{syn}}=5.0$ (solid squares), 6.1 GPa (open circles), and 7.9 GPa (solid circles).

$$\nu_Q = 457(3) \text{ MHz}, \quad \eta = 0.09(2), \quad \text{and} \quad \gamma_Q = 0.012(5).$$

With the value of the quadrupole moment of the ^{181}Ta isomeric state quoted above, the main component of the electric-field gradient is

$$V_{zz} = 7.5(3) \times 10^{17} \text{ V cm}^{-2}.$$

It should be noted that none of the observed EQI parameters correspond to any of the Ni-Hf intermetallic compounds studied by Gerda *et al.*¹² On the other hand, small values of the η and γ_Q parameters for the high-pressure samples we consider as evidence of the ^{181}Hf - ^{181}Ta probe's localization at the Ni substitutional sites with the $\bar{3}m$ point symmetry. The precession amplitude at this frequency amounts to about 40% of its maximum value; the remainder of the probes are located at sites with highly disordered environments determining a fast drop of the anisotropy during the first few nanoseconds as seen in Fig. 4.

The samples prepared at P_{syn} in the range 3–4 GPa showed essentially two-component frequency spectra. Besides the component with $\nu_Q = 457$ MHz another one with $\nu_Q = 300$ MHz was present with a comparable intensity, as can be seen in Fig. 4(b) ($P_{\text{syn}}=3.7$ GPa) and Table I. In the sample prepared at 0.8 GPa, the only distinct frequency component was that at $\nu_Q = 270(10)$ MHz (see Table I). Spectra

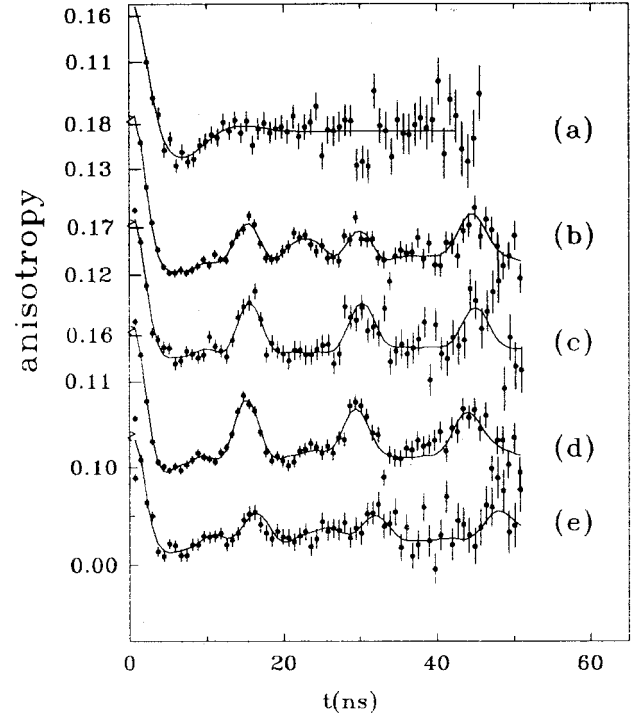


FIG. 4. ^{181}Ta TDPAC spectra taken at room temperature for the GdNi_2 samples prepared at (a) ambient pressure, (b)–3.7 GPa, (c)–5.1 GPa, (d)–7.9 GPa, (e)–7.9 GPa and annealed at 400 °C for about 5 h.

of the samples prepared at normal pressure were characterized by nonperiodic perturbation corresponding to a rather broad distribution of the quadrupole frequency with an average value $\langle \nu_Q \rangle = 280(37)$ MHz with $\gamma_Q \approx 0.4$.

An additional experiment was performed with the sample synthesized at 7.9 GPa and annealed at 400 °C for about 5 h. The corresponding spectrum is shown in Fig. 4(e). Its analysis revealed the presence of the component with $\nu_Q = 280$ MHz which was absent in the original spectrum, Fig. 4(d). The common abundance of the higher- and lower-frequency components was equal to the initial abundance of the 457-MHz fraction.

We propose that the 280-MHz component in the spectrum Fig. 4(e) corresponds to the “low-pressure” phase, and that a comparatively short annealing at comparatively low temperature induced a transition of the “high-pressure” phase into the “low-pressure” one.

Considering the nature of the “low-pressure” and “high-pressure” phases, we can assume the following two possibilities.

(i) At $P_{\text{syn}} < 5$ GPa the Hf impurity atoms do not implant into the GdNi_2 lattice (or implant into it only partly at $P_{\text{syn}} \approx 3\text{--}4$ GPa), and form some separate Hf-Gd-Ni phase (or phases).

(ii) The “low-pressure” phase corresponds to the same Ni substitutional sites but with a different EFG value due to a different charge state of the Ni ions.

We propose that the experiment with the annealed sample makes the second alternative likely, because a recrystallization process accompanied by escaping of hafnium atoms from the Ni substitutional sites and formation of a new in-

TABLE I. The fitting parameters of the ^{181}Ta TDPAC spectra for the GdNi_2 samples synthesized at different pressures.

P_{syn}	ν_Q (MHz)	V_{zz} ($10^{17} \text{ V cm}^{-2}$)	γ_Q	η	Relative abundance
Ambient	280(37)	4.6(6)	0.4		~ 1.0
0.8 GPa	270(10)	4.5(3)	0.08(5)	0.39(8)	0.22(5)
3.7 GPa	(1) 300(5)	5.0(4)	0.03(3)	0.18(7)	0.14(5)
	(2) 456(3)	7.6(3)	0.012(12)	0.01(5)	0.20(5)
5.1 GPa	453(3)	7.5(3)	0.013(10)	0.04(4)	0.38(8)
6.5 GPa	463(3)	7.7(3)	0.017(10)	0.11(4)	0.37(5)
7.9 GPa	456(3)	7.6(3)	0.006(12)	0.13(4)	0.42(10)
Annealed sample	(1) 270(10)	4.5(3)	0.2		
	(2) 447(5)	7.4(4)	0.02(3)	0.07(4)	
7.9 GPa					

termetallic phase seems to be unlikely at the chosen conditions.

In Fig. 5 the quadrupole frequency values extracted from the TDPAC spectra are presented versus the P_{syn} values. It should be noted that the onset of the high-frequency ($\nu_Q = 457$ MHz) component is observed near $P_{\text{syn}} \approx 5$ GPa, i.e., just where the peculiarities of the lattice constant, Curie temperature, and magnetization are observed.

According to the first-principles band-structure calculations (see, e.g., Ref. 13) the charge density in the vicinity of a nucleus, and, consequently, the EFG, is directly connected with the local density of states, and, in our case, with the occupation number of the $3d$ band. Thus, the observed difference of quadrupole frequencies in the samples synthesized at P_{syn} below and above ~ 5 GPa may be considered as an additional evidence of the change of the $3d$ -band population in the ‘‘high-pressure’’ samples accompanied by an origin of the localized moment at Ni ions, similar to the case of YNi_2 .³

Important additional information could be obtained from studies of the magnetic hyperfine interaction ^{181}Ta in the ‘‘low-pressure’’ and ‘‘high-pressure’’ phases. We have performed the TDPAC measurements at 11 K, i.e., below T_C .

In Fig. 6 the Fourier transforms of the TDPAC spectra, measured at 300 and 11 K with the ‘‘high-pressure’’ (7.9

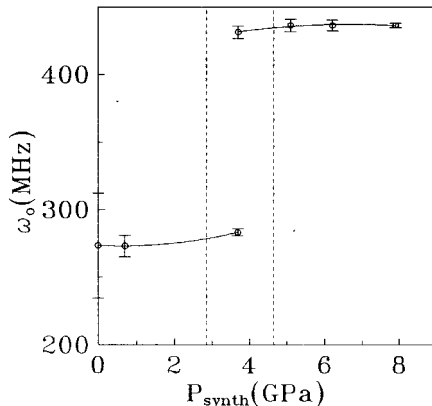


FIG. 5. The quadrupole frequency values extracted from the ^{181}Ta TDPAC spectra for the GdNi_2 samples vs P_{syn} .

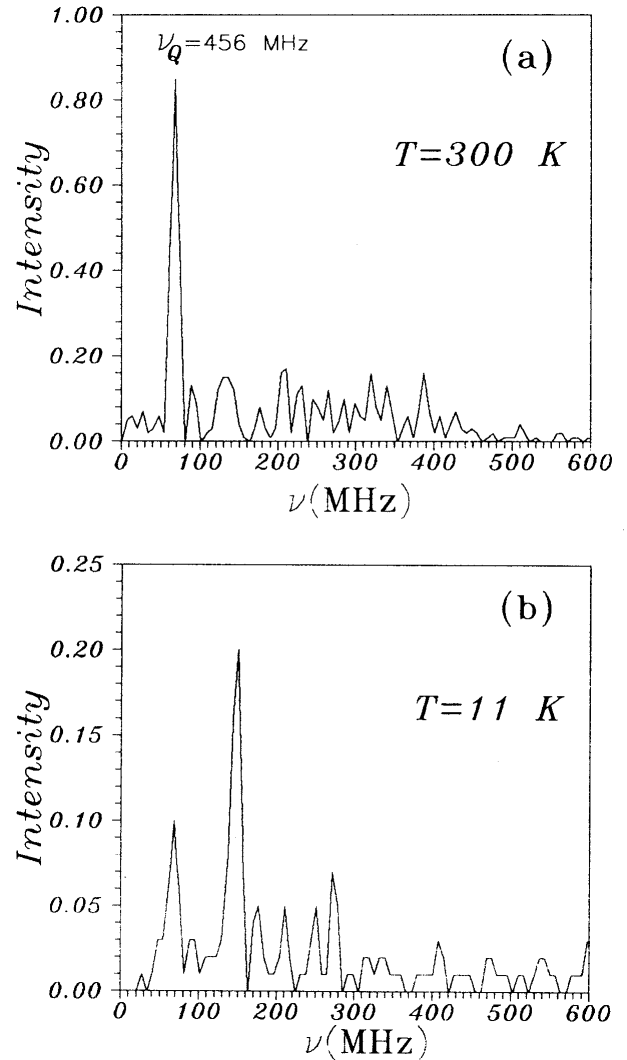


FIG. 6. Fourier transforms of the ^{181}Ta TDPAC spectra for the GdNi_2 sample prepared at $P_{\text{syn}} = 7.9$ GPa and measured at (a) 300 and (b) 11 K. Additional precession frequencies appear at $T < T_C$ due to switching of the magnetic hyperfine interaction. The frequency values on the x axis are the reciprocal of the precession periods.

GPa) sample, are shown which demonstrate a spectacular change of the precession frequency spectrum due to switching on of the magnetic hyperfine interaction. Unfortunately, there is no *a priori* information about the easy-axis direction in the ‘‘high-pressure’’ phase of GdNi_2 which could help in interpreting this spectrum, because this direction determines the number of unequivalent positions in the Ni sublattice, and the angle between the EFG main axis and hyperfine magnetic field directions. The fitting tests showed that, independent of this direction, the value of hyperfine magnetic field is confined in the range of about 10–14 T.

A broad distribution of quadrupole frequencies in the sample prepared at ambient pressure reflects a large degree of disorder around the ^{181}Ta probes which did not allow us to determine with any certainty if there was the magnetic hyperfine interaction present at $T < T_C$.

As can be seen from the data cited in Ref. 11, the hyperfine field at ^{181}Ta in the ReF_2 does not depend on the rare-earth magnetic moment: e.g., it is practically the same, about 7 T at 80 K, in SmFe_2 , where $\mu(\text{Sm}) < 0.5\mu_B$, and in GdFe_2 [$\mu(\text{Gd}) = 7\mu_B$]. On the other hand, in ZrFe_2 , where there is no $4f$ moment, $B_{\text{hf}}(\text{Ta})$ is extremely sensitive to small

changes of the $3d$ electron density induced by small admixtures of Mn or Co in the Fe sublattice.^{10,14} Taking into account these facts, we suggest that the magnetic hyperfine field at Ta is determined mainly, if not exclusively, by an interaction of its $5d$ electrons with the polarized electrons of the hybridized $4d-3d$, or $5d-3d$, band of an alloy, and, consequently, that the magnetic hyperfine interaction of ^{181}Ta in the ‘‘high-pressure’’ phase of GdNi_2 is also induced by an interaction with polarized d electrons of nearest-neighbor Ni ions.

In summary, on the basis of these observations we conclude that synthesis of GdNi_2 at high synthesis pressure $P_{\text{syn}} \geq 5$ GPa changes filling of the $3d$ band so that the Ni ions charge changes as a result.

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