DEUTERON NUCLEAR MAGNETIC RESONANCE INVESTIGATION
OF LaNi_5D_x COMPOUNDS

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M. S. Thesis Submitted to Iowa State University

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Deuteron nuclear magnetic resonance investigation
of LaNi_5D_x compounds

by

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I. INTRODUCTION

Much interest has been shown in the last few years in metal-hydrogen systems. This interest has been three-fold. First, the diffusion rate of hydrogen in a lattice has been shown at room temperature to be comparable in magnitude to molecular motion in a liquid. Even at moderate temperatures, diffusion is rapid. No other interstitial atom moves as fast nor so readily. Secondly, the simplicity of the hydrogen atom has led investigators to believe that the metal-hydrogen system should be the simplest metal-interstitial system to understand. Third, due to interest in a hydrogen fueled economy, certain metal hydrides possess excellent potential for technical application as hydrogen storage compounds.¹⁻³ One of these compounds is lanthanum nickel hydride LaNi_5H_x ($0 < x < 7$).

Lanthanum nickel hydride crystallizes in a structure related to the hexagonal CaCu_5 crystal structure. Much attention has been given to its hydrogen absorption properties, for it can absorb hydrogen to twice the density of liquid hydrogen, i.e., $\sim 6.2 \times 10^{22}$ atoms/cm³. It has been found to absorb and deabsorb hydrogen at high rates under moderate pressure and temperature with small sensitivity to impurities.⁴ At room temperature under 2.5 atm. of hydrogen, LaNi_5 forms $\text{LaNi}_5\text{H}_{6.7}$ with a 25% volume increase, while the c/a ratio remains constant at 0.792.⁵

Deuteron nuclear magnetic resonance (NMR) provides a useful probe for the study of solids. Deuteron NMR not only samples the magnetic environment; it also samples the electrical environment through coupling of

the local electric field gradient tensor and the quadrupole moment of the deuteron. The typically small values of deuteron couplings reflect the very small deuteron quadrupole moment and the weak effective field gradients. Thus, one is not able to apply zero-field methods (i.e., nuclear quadrupole resonance). Quadrupole couplings are deduced from their effect on the NMR spectrum. Due to the small quadrupole couplings, first order perturbation theory suffices at typical laboratory magnetic field strengths.⁶

Many NMR studies, which have been reviewed elsewhere,^{7,8} have been made on binary metal hydrides, whereas few investigations of ternary metal hydrides have been reported.^{9,10} In the present work, the temperature dependence, from 4.2 K to 380 K, of the deuteron quadrupole interaction in LaNi_5D_x ($0.9 \leq x \leq 7$) has been investigated. State-of-the-art NMR techniques and strong magnetic fields (~ 24 kOe) were employed.

II. THEORY

A. Nuclear Quadrupole Interaction

Classically, when a charge distribution $\rho(\vec{x})$ is placed in an external electrostatic field with potential $V(\vec{x})$, there exists an energy of interaction

$$E = \int_V d^3x \rho(\vec{x}) V(\vec{x}) \quad (1)$$

where the volume V encloses $\rho(\vec{x})$. When a nucleus of A nucleons ($A = N + Z$, N neutrons and Z protons of charge e) is placed in a lattice, it experiences an external field from the surrounding non-s-type electrons. Nuclei have dimensions on the order of 10^{-12} cm and atoms 10^{-8} cm, so it is appropriate to expand the potential about the origin (center of mass of the nucleus). Eq. (1) then becomes

$$E = ZeV(0) + \sum_i \left(\frac{\partial V(\vec{x})}{\partial x_i} \right)_{\vec{x}=0} P_i + 1/2 \sum_{ij} \left(\frac{\partial^2 V(\vec{x})}{\partial x_i \partial x_j} \right)_{\vec{x}=0} Q_{ij} + \dots \quad (2)$$

where i and j range over 1, 2, and 3, and $(x_1, x_2, x_3) = (x, y, z)$. The first term expresses the monopole (Coulomb) interaction resulting from the nuclear charge

$$Ze = \int_V d^3x \rho(\vec{x}) \quad (3)$$

This energy is a constant and of no real interest in NMR. The second term in Eq. (2) involves the nuclear dipole moment

$$P_i = \int_V d^3x x_i \rho(\vec{x}) \quad (4)$$

which is zero for nuclei since they possess a definite ground state parity.¹¹ Analogously, all terms in Eq. (2) containing an odd power of x_i similarly vanish. One is left with the quadrupole moment term

$$E = 1/2 \sum_{ij} V_{ij} Q_{ij} + \dots \quad (5)$$

where

$$V_{ij} \equiv \left(\frac{\partial^2 V(\vec{x})}{\partial x_i \partial x_j} \right)_{\vec{x}=0}, \quad (6)$$

and

$$Q_{ij} = \int_V d^3x x_i x_j \rho(\vec{x}) \quad (7)$$

is the nuclear quadrupole moment.

The transition to quantum mechanics is made through the correspondence, $\rho(\vec{x}) \rightarrow \sum |\Psi(\vec{x})|^2 e$. Following the notation of R. H. Good and T. J. Nelson,¹² consider a nucleus with spin $\vec{I}$ in the absence of an external electrostatic field. The wavefunction is $\Psi_m^I(\vec{x}_1 s_1, \vec{x}_2 s_2, \dots, \vec{x}_A s_A)$ where $\vec{x}_\alpha$ is the spatial coordinate of the α^{th} nucleon. Non-relativistically, the wavefunction obeys the following eigenvalue equations:

$$\begin{aligned} \mathcal{H}_0 \Psi_m^I &= E \Psi_m^I \\ \vec{I} \cdot \vec{I} \Psi_m^I &= I(I+1) \Psi_m^I \\ I_z \Psi_m^I &= m_I \Psi_m^I \\ P \Psi_m^I &= \pm \Psi_m^I \end{aligned} \quad (8)$$

where the eigenfunctions are chosen to be orthonormal

$$\langle \Psi_m^I | \Psi_{m'}^I \rangle = \langle I m | I m' \rangle = \delta_{mm'}. \quad (9)$$

The wavefunction is $(2I+1)$ -fold degenerate with energy E and (spin)^{parity} equal to $(I)^\pm$.

Placed in an external electrostatic field, the hamiltonian becomes

$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_Q$ where $\mathcal{H}_Q$ is represented by

$$\mathcal{H}_Q = \sum_{\alpha=1}^A e_{\alpha} V(\vec{x}) \quad (10)$$

and incorporates the effect of the quadrupole interaction. From Eq. (5)

$\mathcal{H}_Q$ becomes

$$\mathcal{H}_Q = \frac{1}{2} \sum_{ij} V_{ij} \sum_{\alpha=1}^A e_{\alpha} x_{\alpha i} x_{\alpha j} + \dots \quad (11)$$

where $\mathcal{H}_Q$ causes the splitting of the $2I + 1$ nuclear levels. By first order perturbation theory, the energies are given by the eigenvalues of the $(2I + 1) \times (2I + 1)$ matrix

$$\begin{aligned} \mathcal{H}_{mm'} &= \langle Im | \mathcal{H}_Q | Im' \rangle \\ &= \frac{1}{2} \sum_{ij} V_{ij} \langle Im | \sum_{\alpha=1}^A e_{\alpha} x_{\alpha i} x_{\alpha j} | Im' \rangle \\ &= \frac{1}{2} \sum_{ij} V_{ij} \langle Im | \sum_{\alpha=1}^A e_{\alpha} (x_{\alpha i} x_{\alpha j} - \frac{1}{3} \delta_{ij} r_{\alpha}^2) | Im' \rangle. \end{aligned} \quad (12)$$

Since Laplace's Eq. is satisfied at the nucleus, the added $-\frac{1}{3} \delta_{ij} r_{\alpha}^2$ has a zero value for $V_{ij} \delta_{ij}$ is zero. Since $x_{\alpha i} x_{\alpha j} - \frac{1}{3} \delta_{ij} r_{\alpha}^2$ is a covariant second rank tensor operator, one is able to apply the Wigner-Eckart theorem. In particular, one may write

$$\begin{aligned} &\langle Im | \sum_{\alpha=1}^A e_{\alpha} (x_{\alpha i} x_{\alpha j} - \frac{1}{3} \delta_{ij} r_{\alpha}^2) | Im' \rangle \\ &= \text{constant} \langle Im | I_i I_j + I_j I_i - \frac{2}{3} \delta_{ij} \vec{I} \cdot \vec{I} | Im' \rangle \end{aligned} \quad (13)$$

where the constant term is independent of i, j, m , and m' . Substitution into Eq. (12) yields

$$\mathcal{H}_{mm'} = \frac{1}{2} \sum_{ij} V_{ij} \frac{Qe}{2I(2I-1)} \langle I m | I_i I_j + I_j I_i | I m' \rangle \quad (14)$$

where the constant term is chosen to be $\frac{Qe}{2I(2I-1)}$ by convention. Here Q is called the quadrupole moment of the nuclear level and is interpreted by setting $i = j = 3$ and $m = m' = I$ in Eq. (13)

$$\langle II | \sum_{\alpha=1}^A e_{\alpha} (z_{\alpha}^2 - \frac{1}{3} r_{\alpha}^2) | II \rangle = \frac{Qe}{2I(2I-1)} \langle II | (2I_z^2 - \frac{2}{3} \vec{I} \cdot \vec{I}) | II \rangle = \frac{Qe}{3}$$

$$\text{implying } Q = \frac{1}{e} \langle II | \sum_{\alpha=1}^A e_{\alpha} (3z_{\alpha}^2 - r_{\alpha}^2) | II \rangle. \quad (15)$$

The electric field gradient (EFG) tensor is symmetric ($V_{ij} = V_{ji}$), and therefore is diagonalizable by an appropriate choice of coordinate axes. By convention the principal axes are chosen such that

$$|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|. \quad (16)$$

The EFG tensor is also traceless ($\nabla^2 V(\vec{x}) = 0 = V_{xx} + V_{yy} + V_{zz}$) implying that only two independent parameters, defined as

$$\eta = \frac{V_{xx} - V_{yy}}{V_{zz}} \quad \text{and} \quad eq \equiv V_{zz}, \quad (17)$$

are required.

By Eqs. (16) and (17) and Laplace's Eq., η is limited between the values $0 \leq \eta \leq 1$. In the principal axes system, it can be shown that

$$V_{ij} = \frac{eq}{2} \begin{pmatrix} \eta-1 & 0 & 0 \\ 0 & -\eta-1 & 0 \\ 0 & 0 & 2 \end{pmatrix}. \quad (18)$$

Substituting into Eq. (14), one obtains finally:

$$\mathcal{H}_{mm'} = \left(\frac{e^2 q Q}{h} \right) \frac{h}{4I(2I-1)} \langle I m | [3I_z^2 - \vec{I} \cdot \vec{I} + \eta(I_x^2 - I_y^2)] | I m' \rangle \quad (19)$$

where $\frac{e^2 q Q}{h}$ is known as the quadrupole coupling constant.

B. Magnetic Dipole (Zeeman) and Nuclear Quadrupole Interaction

Nuclei with a non-zero spin ($\vec{I}$) possess a magnetic moment

$$\vec{\mu} = \gamma \hbar \vec{I} \quad (20)$$

where γ is the gyromagnetic ratio and $\hbar$ is Planck's constant divided by 2π . Consider a nucleus placed in an external magnetostatic field ($\vec{H}_0$) in the Z-direction. The moment ($\vec{\mu}$) will couple with the field with a hamiltonian

$$\mathcal{H} = -\vec{\mu} \cdot \vec{H}_0, \quad (21)$$

yielding $(2I+1)$ equally spaced energy levels with

$$E_m = -\gamma \hbar H_0 m_I \quad (22)$$

where m_I refers to the quantum numbers of I_z ($-I$ to I in steps of one).

The nuclear moment will precess about the field at a frequency

$$\nu_0 = \frac{\gamma}{2\pi} H_0 = \gamma H_0 \quad (23)$$

known as the Larmor frequency. If one transmits a radiofrequency field at this frequency normal to the applied field $\vec{H}_0$, transitions will occur between adjacent levels, and these can be detected by an NMR experiment.

Combining the Zeeman and quadrupole interactions, the hamiltonian becomes

$$\mathcal{H} = h\nu_0 I_z + \frac{e^2 q Q}{4I(2I-1)} [3I_z'^2 - \vec{I} \cdot \vec{I} + \eta(I_{x'}^2 - I_{y'}^2)] \quad (24)$$

where the primes denote the EFG principal axes. In general, the laboratory axes and principal axes will not coincide as shown in Fig. 1. By use of the Euler angles and a coordinate transformation, one may find the following relation:

$$\begin{pmatrix} I_{x'} \\ I_{y'} \\ I_{z'} \end{pmatrix} = \begin{pmatrix} \cos\psi & \cos\theta\sin\psi & \sin\theta\sin\psi \\ -\sin\psi & \cos\theta\cos\psi & \sin\theta\cos\psi \\ 0 & -\sin\theta & \cos\theta \end{pmatrix} \begin{pmatrix} I_x \\ I_y \\ I_z \end{pmatrix} \quad (25)$$

The Euler angle $\phi = 0$ by symmetry of I_z .

Using the results of Eqs. (24) and (25), the energy levels are given by

$$E_m = -h\nu_0 m + \frac{h\nu_0}{12} [3m^2 - I(I+1)][3\cos^2\theta - 1 + \eta\cos 2\psi(\cos^2\theta - 1)] \quad (26)$$

where the fundamental quadrupole frequency ν_Q is defined as

Fig. 1. The principal axes of the EFG (the primed axes) are located with respect to the laboratory axes (unprimed axes) by the Euler angles θ and ψ .

$$\nu_Q = \frac{3e^2qQ}{2I(2I-1)}, \quad (27)$$

where m now refers to the lab frame quantum number. The transition frequencies will be

$$\nu(m \rightarrow m-1) = \frac{E_{m-1} - E_m}{h} = \nu_0 - \frac{\nu_Q}{2} \left(m - \frac{1}{2}\right) [\beta] \quad (28)$$

where $\beta = [3 \cos^2 \theta - 1 + \eta \cos 2\psi (\cos^2 \theta - 1)]$. For the deuteron ($I = 1$), the two transition frequencies are

$$\begin{aligned} \nu(1 \rightarrow 0) &= \nu_0 - \frac{\nu_Q}{4} [\beta] \\ \nu(0 \rightarrow -1) &= \nu_0 + \frac{\nu_Q}{4} [\beta]; \end{aligned} \quad (29)$$

refer to Fig. 2 for an energy level diagram.

1. Polycrystalline lineshapes

In NMR experiments, metal single crystals have the inconvenience of the skin depth effect. Using polycrystalline metal powders with the size of the crystallites less than the skin depth circumvents this difficulty. Polycrystalline powders will, however, modify the NMR lineshape.

For $\eta = 0$, consider each crystallite as a unit vector randomly distributed in a unit sphere with all tails at the origin. The intensity of the signal between ν and $\nu + d\nu$ is proportional to the number of crystallites (vectors) lying between θ and $\theta + d\theta$. This is proportional to the fraction of the total spherical area between θ and $\theta + d\theta$

Fig. 2. The energy level diagram of a spin 1 nucleus experiencing both a Zeeman and a quadrupole interaction. The magnetic field splits the levels equally. The quadrupole interaction then perturbs these levels in a manner that is dependent on θ , ψ , and η . The values given for the energy differences are in frequency units and are exaggerated for convenience.

$$I(\nu) d\nu \propto \left| \frac{dA}{A} \right| = \left| \frac{2\pi \sin\theta d\theta}{4\pi} \right| = \frac{1}{2} |d \cos\theta|; \quad I(\nu) \propto \frac{1}{2} \left(\left| \frac{d\nu}{d \cos\theta} \right| \right)^{-1}. \quad (30)$$

For the deuterium transition $\nu(0 \leftrightarrow -1)_{\eta=0}$, one has

$$\frac{d\nu}{d \cos\theta} = \frac{3}{2} \nu_Q \cos\theta. \quad (31)$$

Solving for $\cos\theta$ in Eq. (29), one obtains the intensity distribution function

$$I(\nu) \propto \frac{1}{3\nu_Q \left(\frac{\nu - \nu_0}{\nu_Q} + \frac{1}{4} \right)^{\frac{1}{2}}}. \quad (32)$$

This function is displayed in Fig. 3. The lineshape has two interesting features: the singularity at $\theta = 90^\circ$ and the step at $\theta = 0^\circ$. In an NMR spectrum one detects both of the transitions given by Eq. (29), the $(1 \leftrightarrow 0)$ transition being the mirror image of $(0 \leftrightarrow -1)$ about ν_0 . The spectrum consists of the two outer weak steps ($\theta = 0^\circ$) with $\Delta\nu_{\text{steps}} = \nu_Q$, and the two strong inner singularities ($\theta = 90^\circ$) with $\Delta\nu_{\text{sings}} = \frac{\nu_Q}{2}$.

For $\eta \neq 0$ the lineshapes are more complicated due to the added Ψ dependence. The intensity distribution functions in this case have been calculated by Bloembergen and Rowland¹¹ and by Cohen and Reif.⁶ As η increases from zero, the singularities split into a shoulder and weakened singularity with the shoulder moving toward the steps while the weakened singularities move toward ν_0 . The steps grow in intensity but remain fixed in position, as can be seen in Figs. 4 and 5. The splittings between the corresponding features are as follows:

Fig. 3. The low frequency satellite distribution function for $\eta = 0.0$, 0.5 , and 1.0 . The distribution functions are normalized to π .

Fig. 4. The powder absorption derivative lineshapes shown for fixed ν_0 and varying η . Note the splitting of the singularities (largest peaks at $\eta = 0.0$) as η increases from 0.

Fig. 5. The remainder of the derivative lineshapes are shown. The shoulders emerge from the singularities and move outward as the weakened singularities move toward the center.

$$\Delta\nu_{\text{steps}} = \nu_Q \quad (33)$$

$$\Delta\nu_{\text{singularities}} = \frac{\nu_Q}{2} (1-\eta) \quad (34)$$

$$\Delta\nu_{\text{shoulders}} = \frac{\nu_Q}{2} (1+\eta) . \quad (35)$$

Measurement of any two of these splittings will determine η and ν_Q .

The spectrum in Fig. 3 was calculated by using delta function lineshapes for each crystallite. Physically, however, this is not the case. Broadening of the lineshapes occurs from the nuclear dipole-dipole interaction and from non-uniqueness of the electric field gradient. The nature of the dipole-dipole interaction gives rise to an approximately Gaussian lineshape. The EFG distribution arises from defects, impurities, etc., in the lattice and can also be approximated by a Gaussian lineshape. An example of Gaussian broadening for a fixed value of η is shown in Fig. 6. A Gaussian function of half-width σ was folded into the $\eta \neq 0$ polycrystalline distribution function. The last lineshape shown is typical of room temperature spectra obtained in the present investigation.

C. Knight Shift

The relationship in Eq. (23) is assumed to hold for only diamagnetic materials. It is found in metallic materials that ν_0 is shifted to ν_m by a factor $(1+\chi)$ where χ is known as the Knight shift. Thus,

$$\nu_m = \nu_0(1+\chi) , \quad (36)$$

Fig. 6. A spin-one quadrupole split lineshape is shown for a constant value of η but with varying half-widths σ .

and $\mathcal{K}$ usually is expressed in percent. Its value is a couple percent or less in most metals. When an NMR measurement is made at constant magnetic field, the Knight shift is given by

$$\mathcal{K} = \frac{\nu_m - \nu_0}{\nu_0}, \quad (37)$$

whereas at constant frequency it is given by

$$\mathcal{K} = \frac{H_0 - H_m}{H_m}. \quad (38)$$

Generally, the Knight shift has spatial orientation dependence, and is anisotropic. The deuterium resonances in this investigation were found not to exhibit any such shift anisotropy, so only the isotropic Knight shift will be considered. In transition and rare-earth metals this can arise from the overlap of unpaired 's' conduction electrons with the nucleus, 'd' and 'f' electron core polarization, and 'd' and 'f' electron orbital contributions.¹³

The 's'-contact term can be written as

$$\mathcal{K}_s = \frac{8\pi}{3} \langle |\psi_{\vec{k}}(0)|^2 \rangle_F V \beta^2 N_S(\epsilon_F) \quad (39)$$

where $N_S(\epsilon_F)$ is the density of s-electron states at the Fermi energy, β is the Bohr magneton, $\langle |\psi_{\vec{k}}(0)|^2 \rangle$ is the probability density of the conduction s-electrons evaluated at the nucleus and averaged over the Fermi surface, and V is the volume over which $\psi_{\vec{k}}(\vec{x})$ is normalized. Since the Pauli-spin susceptibility is related to $N_S(\epsilon_F)$ by

$$\chi_p^s = \beta^2 N_S (\epsilon_F) , \quad (40)$$

one may write

$$\chi_s = \frac{8\pi}{3} \langle |\psi_k(0)|^2 \rangle_F V \chi_p^s . \quad (41)$$

This contribution to the shift is positive and temperature independent for one is dealing with electrons at the Fermi level.

Core-polarization arises from the unpairing of inner-s core-electron spins as a result of an exchange interaction with unpaired 's', 'p', 'd', and 'f' character electrons.¹³ The core-polarization term may be written as

$$\chi_{\text{core}}(T) = \frac{8\pi}{3} V \langle |\psi|^2 \rangle_{\text{cp}} \chi_{f,d}(T) \quad (42)$$

where $\langle |\psi|^2 \rangle_{\text{cp}}$ represents the spatial distortion and subsequent core-polarization. In case of narrow 'd' or 'f' bands, $\chi_{f,d}(T)$ is large, possibly dominating over χ_s , and very often is temperature dependent. The χ_{core} term is almost always negative.

The orbital contribution is proportional to the Van Vleck susceptibility. The Van Vleck susceptibility, as in molecules with Van Vleck paramagnetism, has its origins from the mixing of higher orbital states of non-vanishing orbital moments into the ground state.¹³

III. EXPERIMENTAL METHODS

A. Sample Preparation

The samples were prepared by D. K. Thome and B. J. Beaudry of the Metallurgy Division of the Ames Laboratory. High purity La (Ames Lab. - 99.99%) was arc-melted with Ni (99.99%) six or seven times. The LaNi_5 button was crushed and put into a 10 mm O.D. pyrex tube and evacuated. It was then exposed to H_2 gas (99.999%) at 500 psi two times and again evacuated. Finally, the sample was exposed to D_2 gas at 250 psi. The D_2 gas was obtained from the Matheson Company and was 99.5% atomic wt. minimum. By use of a high pressure gauge and mercury manometer, a known volume of D_2 gas was pumped off till the desired concentration was achieved. The sample tube was then immersed in liquid nitrogen and sealed off (flame annealed).

1. Analysis

Two different LaNi_5 buttons were prepared with the difference being mainly in the grade of Ni used. B. J. Beaudry prepared the deuterides with reagent grade Ni ($x = 3.4, 5.75$); D. K. Thome prepared the deuterides from purer Ni ($x = 0.9, 3.6, 5.7, 6.7$). The majority of the measurements were made with Thome's samples. Analysis by spark source mass spectrometer for the La and Ni used in each button is listed in the Appendix.

B. Experimental Measurements

Nuclear magnetic resonance spectra were obtained by conventional cross-coil NMR techniques of Bloch, Hansen, and Packard.¹⁴ A block diagram of the equipment is shown in Fig. 7. The spectrometer was a

Fig. 7. Block diagram of NMR apparatus.

wide-line induction spectrometer.¹⁵ Two radio frequency transmitters were used: a quartz crystal oscillator built at Ames Laboratory¹⁵ with a stability of 5 Hz/hr. and a General Radio Model 1061 frequency synthesizer with a stability of ± 1 Hz. The probe used was a Varian Associates 8-16 MHz Model V4230B cross-coil probe.

All experiments were run at constant frequency (~ 15.5 MHz) and variable magnetic field. The frequency was monitored via a CMC Model 880B frequency counter. The magnetic field scan was obtained by use of a Varian Mark II Fieldial and Varian VFR 2515 External Sweep Adaptor used in conjunction with a Varian 15" electromagnet (up to 25 kOe). The technique of signal averaging was obtained by driving the magnet scan from the channel advance signal in the RIDL Model 24-2 400 Channel Analyzer. A one-to-one correspondence is maintained between memory channel and magnetic field by use of a linear interface amplifier.¹⁶ Thus, one is able to add each scan to all previous scans stored in the Analyzer memory, with the signal-to-noise ratio proportional to the square root of the number of scans.

The signal is further enhanced by means of phase sensitive detection using a lock-in-amplifier. The d.c. signal from the phase sensitive detector is fed into a Voltage to Frequency Converter (Vidar Model 241) which converts the d.c. signal to a sine wave with a frequency proportional to the input voltage. Conventional audio modulation techniques¹⁴ (80 Hz) were used to obtain the derivative of the NMR absorption spectrum.

Saturation determinations were made for each sample at each temperature at which spectra were recorded. Thus, at each temperature small

radio frequency fields were employed to avoid saturation (equalization of the population of the nuclear states). Typical run times were of the order of two to five hours.

C. Variable Temperature Equipment

Spectra were recorded from 4.2 K to 380 K by means of liquid coolant baths for the fixed temperatures of 4.2 K and 77 K, and by passage of hot or cold nitrogen gas over the sample (100 K to 380 K). The dewars were finger dewars adapted for NMR probe use. A diagram of the helium dewar is shown in Fig. 8. The nitrogen gas blowing apparatus was an adapted Varian V-4257 Variable Temperature System, the main feature being a gas flow dewar insert designed for Varian probes. The insert was connected to hot or cold N₂ sources by means of a dewar pipe. A diagram is shown in Fig. 9.

A copper-constantan (Cu-Con) thermocouple was placed at the bottom of the sample and one at ~5 cm above the sample. The latter was used to monitor the change in temperature of the exhaust gas. Temperature gradients across the samples were typically 2 K or less, and temperature stability was within 1 K. Specific details of this apparatus may be found in K. P. Roenker's Ph.D. thesis.¹⁷

Fig. 8. The glass double dewar used in liquid helium experiments.

Fig. 9. The construction of the variable temperature apparatus used in N₂ gas blowing experiments.

IV. RESULTS

A. $4.2 \text{ K} < T < 300 \text{ K}$

The deuterium resonance spectra at 300 K appeared as the last spectrum shown in Fig. 6 ($\sigma = 0.25$). The major inner peaks are the broadened singularities, the smaller outer peaks being the steps. At all temperatures below 300 K, and the resulting lineshape appeared as two broad singularities, slightly split, down to approximately 200 K. The singularities in the last spectrum shown in Fig. 6 are still much more clearly defined than those in spectra obtained in the range $T < 300 \text{ K}$. From 200 K to 160 K, the spectra appeared as broad, unsplit single lines. At 160 K and below, additional features appear on the unsplit line, as shown in Fig. 10 for $x = 5.75$ at 140 K. In Fig. 10, these features refer to peaks 1 and 6, and 2 and 5. All deuterium concentrations of $x > 3$ had these characteristic features. The $x = 0.9$ sample was not run below room temperature due to the excessive time required to record the spectrum (~ 24 hrs. at 300 K). It was found that the greater the deuterium concentration, the more resolved were the features. All spectra retained the shape shown in Fig. 10 even at 4.2 K. Shown in Fig. 11 is a plot of quadrupole splitting versus temperature for each sample. The splitting refers to the innermost singularity peaks (ΔH_{34} in Fig. 11). Each value is an average of reverse (high to low magnetic field) and forward (low to high magnetic field) scans of the spectrum. The trend in the data is characteristic of the data reported by T. K. Halstead in the proton resonance of LaNi_5H_6 .⁹

Fig. 10. Spectrum of $\text{LaNi}_5\text{D}_{5.75}$ at 140 K.

Fig. 11. Quadrupole line splitting versus temperature for LaNi_5D_x samples with $x = 3.4, 3.6, 5.7, 5.75$, and 6.7 .

Fig. 12. Knight shift versus temperature for LaNi_5D_x samples with $x = 3.6, 5.7, \text{ and } 6.7$. Note the similar values for each sample.

The Knight shift measured for each sample in the range $77 \text{ K} \leq T \leq 300 \text{ K}$ is shown in Fig. 12. The shift position was taken as the midpoint of the innermost singularity peaks. The large uncertainties at low temperatures are due to the very small shifts since the uncertainty in the peak positions are comparable to the shift values themselves. The Knight shift values are an average of reverse and forward scans through the resonance. This was done to eliminate systematic errors in magnetic field calibration due to magnetic field lag or time constant lag.

To complement the Knight shift data, a preliminary measurement of the susceptibility of LaNi_5 was made by Paul Burgardt of the Solid State Division of Ames Laboratory. A measurement of the susceptibility of the hydride was not made because a small enough sample tube could not be obtained. The measurements yielded a temperature independent χ of $\sim 5 \times 10^{-6} \text{ gram}^{-1}$, which certainly indicates that LaNi_5 is a simple Pauli paramagnetic metal with a high susceptibility, comparable to that of vanadium.

B. $T \geq 300 \text{ K}$

The deuterium resonance spectrum was observable in this temperature range up to a certain temperature T_c at which the quadrupole pattern was no longer detectable ($T_c = 380 \text{ K}$ for $x = 6.7, 5.7$ and $T_c = 360 \text{ K}$).

for $x = 3.6$). In the range $300 \text{ K} \leq T \leq T_c$ the spectrum exhibited two distinct features: that of the quadrupole split pattern and a single narrow line located midway between the singularities of the quadrupole pattern. Due to the considerable difference in T_1 (spin-lattice relaxation time) between the narrow line and the quadrupole pattern, the narrow line usually appears only as a bump in the spectrum. This can be seen in Fig. 13, a typical 300 K spectrum. At temperatures $T \geq 300 \text{ K}$, only the steps and singularities were obtained for $x > 3$. The steps in the $x = 0.9$ case were never observed due to the very large broadening of the singularities which caused the steps to be unresolved.

One of the principal difficulties in this temperature range was the measurement of the asymmetry parameter η . As one will recall, measurement of any two features of the quadrupole pattern will determine η . At all temperatures the shoulders were never resolved from the singularities, even with very small modulation amplitudes. It was found that the splittings between the singularities were always greater than $\nu_Q/2$, which for $\eta \neq 0$ does not correspond to Eq. (34). Since the singularity splittings suggest the use of Eq. (35), it was assumed that the singularity position was an approximate shoulder position. Thus, by Eq. (35) η was determined for each sample for $T \geq 300 \text{ K}$. The results are listed in Table 1.

Fig. 13. Room temperature spectrum of LaNi₅D_{6.7}. Note the appearance of the narrow line at the D₂O position.

Table 1. Values of η for each sample of LaNi_5D_x for $T \geq 300$ K

Concentration	Temperature	η
$x = 6.7$	300 K	0.17 ± 0.03
	$T > 300$ K (320 K, 340 K, 360 K)	$0.14 \rightarrow 0.19 \pm 0.04$
$x = 5.7$	300 K	0.17 ± 0.03
	$T > 300$ K (320 K, 340 K, 360 K)	$0.21 \rightarrow 0.26 \pm 0.04$
$x = 3.6$	300 K	0.17 ± 0.03
	$T > 300$ K (320 K, 340 K)	$0.21 \rightarrow 0.26 \pm 0.04$

Since the steps were resolvable, ν_Q was always obtained for $T \geq 300$ K. In Fig. 14 is a plot of ν_Q versus concentration at 300 K. It should be noted that the value of ν_Q for $x = 0.9$ was obtained by assuming $\eta = 0.17$ since all other samples had this value at 300 K. Shown in Fig. 15 is the deuterium resonance for $x = 6.7$ as a function of temperature for $T \geq 320$ K. This sequence was typical of all samples. The narrow line at 380 K is saturated and overmodulated (the modulation amplitude is too large for the corresponding linewidth) in Fig. 15. In Fig. 16 is shown a plot of ν_Q versus T for each sample up to the temperature at which the quadrupole pattern vanishes.

Initially, when measured at high temperatures, the narrow line in each sample appeared as in Fig. 17. Initially, for $x = 6.7$ $\Delta H_{\text{H.F.P.}}$ was ~ 1.50 e and for $x = 3.6$ $\Delta H_{\text{H.F.P.}}$ was ~ 1.00 e. When rerun a month later, the high field peak (H.F.P.) had vanished in both cases. Both concentrations yielded an unsplit single line with $\Delta H \sim 0.7$ e for

Fig. 14. Deuterium lowest pure quadrupole frequency (ν_Q) versus concentration x in LaNi_5D_x at 300K.

Fig. 15. Temperature dependence of the LaNi₅D_{6.7} spectrum. Note the increasing amplitude of the narrow line. The ν_0 value increases with increasing temperature.

Fig. 16. Deuterium lowest pure quadrupole frequency (ν_Q) versus temperature for $\text{LaNi}_5\text{D}_{3.6}$, $\text{LaNi}_5\text{D}_{5.7}$, and $\text{LaNi}_5\text{D}_{6.7}$.

Fig. 17. Narrow line of $\text{LaNi}_5\text{D}_{6.7}$ at 380K. The quadrupole pattern was not detectable.

$x = 6.7$ and $\Delta H \sim 0.65$ Oe for $x = 3.6$. When these samples were rerun at 300 K, the steps were not as well resolved and the singularities had broadened about half as much. This was found not to be the case when the samples were cooled below 300 K. It appears that heating the samples causes irreversible effects.

C. LaNi_5 Exposed to D_2 Gas at 77 K (~ 83 psi Over Pressure)

It was found in the proton resonance investigation of LaNi_5H_x that a very narrow line appears superimposed on the broad line at low temperatures. Since LaNi_5 is over 80% nickel and since nickel adsorbs hydrogen readily, one might expect a surface state of the hydride to exist.

D. K. Thome, in preparing the hydrides, discovered that LaNi_5 does not hydride at 77 K. The following experiment was then undertaken: a sample of LaNi_5 was immersed in liquid nitrogen and D_2 gas was added at 83 psi over pressure. This sample was kept at 77 K throughout an NMR investigation of the ^2D resonance. Measurements were made over a four day period under identical conditions, and the results are shown in Fig. 18. Spectrum A refers to the first day, B to the second, and so on. The strength of the high field peak increases in time until only an unsplit line remains. Spectrum A has the appearance of an anisotropic Knight shift resonance. It should be noted that the picture presented by this sequence of traces is only qualitative, and is not quantitative. This is due in part to the fact that the scans shown were not all made in the same direction.

Fig. 18. Time dependence of the LaNi_5 spectrum at 77K with 83 psi D_2 gas over pressure. A refers to day one, B to day two, C to day three, and D to day four.

V. DISCUSSION

A. $4.2 \text{ K} < T < 300 \text{ K}$

As an aid in interpreting the NMR results, the crystal structure of LaNi_5 is shown in Fig. 19. LaNi_5 crystallizes in space group $P6_3/mmm$. Upon hydriding, the lattice isotropically expands 25%, retaining the same crystal structure. A neutron diffraction study of $\text{LaNi}_5\text{D}_{6.8}$ has been reported, yielding 38 possible interstitial sites for the deuterium atoms.¹⁸ A c-axis (z) view is shown in Fig. 20, with most of the interstitial sites listed. Some sites were excluded due to overlap of symbols.

The NMR spectra in this temperature region suggest occupation of inequivalent hydrogen sites. The three peaks visible in the spectra, as in Fig. 10, suggest the occurrence of several different quadrupole interactions. If one assumes the lineshapes are not due to quadrupole interactions, then the observed splittings ($\sim 20 \text{ Oe}$) are much too large (approximately 5 times in this temperature region) for any other known broadening mechanism for deuterium. An explanation for the large broadening and poor resolution is not known at this time. Further attempts at computer synthesis will be made to try to explain the large broadening.

A preliminary calculation of the EFG tensor at the various deuterium sites in the rigid lattice was performed by Dr. T. Pinter of the Computer Division of the Ames Laboratory. This calculation was based on the expanded lattice parameters, and as a first approximation

Fig. 19. Atom positions of LaNi_5 (hexagonal CaCu_5 type crystal structure).

- Lanthanum
- Nickel, A-site
- Nickel, B-site

Fig. 20. C-axis view of LaNi_5 hydride. Z refers to the distance up the C-axis in units of C.

placed a +3 charge on the lanthanum atoms and a zero charge on the nickel atoms. This assumption of zero charge on the nickel is consistent with the Pauli-paramagnetic behavior of LaNi_5 . The values of q , ν_Q , and η determined from the lanthanum ion contribution alone are listed in Table 2.

Table 2. Calculated rigid lattice EFG, ν_Q , and η for LaNi_5D_x

Wyckoff designation	Hydrogen Site Number	q 10^{+24} cm^{-3}	ν_Q (^{20}D) kHz	η
b	1	1.172	171.4	0
f	3	0.560	81.9	0
h	4	-0.115	16.9	0.716
m	6	0.626	91.5	0.565
n	12	-0.148	21.7	0.803
o	12	0.759	110.9	0.152

It should be noted that screening of the La^{+3} charges has not been considered, nor has the contribution to the EFG due to the deuterium ions. Sternheimer shielding and/or anti-shielding effects¹⁹ have also been neglected since no estimates have been made of these for the deuteron in metallic systems.

As is evident from Table 2, sites m, n, and o have the greatest number of sites and account for 30 of the 38 sites per unit cell. Thus,

analysis of the data in this temperature region will be based on these three sites. The values of the splittings ΔH_{34} , ΔH_{25} , and ΔH_{16} (refer to Fig. 10) are listed in Table 3 for various samples in this temperature region.

Table 3. Line splittings for LaNi_5D_x at $T \leq 150$ K

Concentration	T K	ΔH_{34} Oe	ΔH_{25} Oe	ΔH_{16} Oe
x = 6.7	140	23.5 ± 1.5	37.3 ± 1.5	94.3 ± 1.5
x = 5.75	140	20.7 ± 1.5	46.5 ± 1.5	88.2 ± 1.5
x = 3.6	150	19.2 ± 1.5	43.4 ± 1.5	77.4 ± 1.5
x = 6.7	4.2	19.0 ± 2.0	39.1 ± 2.0	80.0 ± 2.0
x = 5.7	4.2	22.2 ± 2.0	41.4 ± 2.0	84.6 ± 2.0
x = 3.6	4.2	24.5 ± 2.0	38.0 ± 2.0	83.7 ± 2.0

Since only singularity peaks were resolved in this temperature region, it was assumed that the shoulders were not resolvable from the singularities, and that the lineshapes observed were composites of several quadrupole interactions. Thus, the singularity peaks were assumed to be an approximate shoulder position. On the basis of the observed singularity splittings (ΔH_{16} and ΔH_{34}), and using the values of η in Table 2 for the m, n, and o sites, and Eq. (35), the ν_Q values listed in Table 4 were obtained for various samples.

Table 4. Calculated values of ν_Q for LaNi_5D_x at $T \leq 150$ K

Concentration	T K	ν_Q ΔH_{34} site n kHz	ν_Q ΔH_{16} site m kHz	ν_Q ΔH_{16} site o kHz
x = 6.7	140	22.6	56.1	76.2
x = 5.75	140	27.8	71.0	96.4
x = 3.6	150	22.4	60.2	81.8
x = 6.7	4.2	23.1	64.3	87.3
x = 5.7	4.2	26.1	64.2	87.2
x = 3.6	4.2	28.9	63.0	85.6

Comparing Table 2 with Table 4, there exists a possible correlation of site n with the ΔH_{34} peaks and of site o and the ΔH_{16} peaks. However, the ΔH_{25} peaks do not appear to correlate with the Table 2 values of ν_Q . Based on the lineshapes and this preliminary data, it appears likely that several quadrupole interactions are being observed from inequivalent hydrogen sites in the lattice.

One would expect from Eqs. (41) and (42) that the Knight shift data would follow the susceptibility measurements. However, this is not quite the case. χ remains constant down to ~ 100 K while the Knight shift begins decreasing at $\sim 250 \rightarrow 200$ K. The extremely small, but measurable, shifts and the similar trend in each sample may suggest some systematic error in measurements at low temperatures. Over most of the temperature range, the Knight shifts have, within uncertainties,

a near zero value. Shifts of the deuteron (and proton) NMR in metallic hydrides are generally extremely small, so the present results are not unusual.¹⁷

The results of Fig. 11 (quadrupole splitting versus temperature) show the apparent thermal (motional) averaging of the ^2D quadrupole interaction with increasing temperature. T. K. Halstead's investigation of the proton linewidth temperature dependence in $\text{LaNi}_{5.7}\text{H}_6$ indicates motional narrowing beginning at 150 → 160 K.⁹ It can be seen in Fig. 11 that this appears also to be the case with the deuteron quadrupole couplings. One may note an anomalous bump in Fig. 11 for the higher concentrations ($x = 5.75, 6.7$) at 140 K to 160 K while the lower concentrations level off more in this region. An explanation for the anomalous bump is not known at this time. The increasing splitting of the $x = 3.4$ and $x = 5.75$ samples at $T \leq 100$ K may be due in part to their high iron impurity content (~ 450 ppm by weight). The three samples ($x = 3.6, 5.7, 6.7$) containing less iron (~ 12 ppm) yield substantially smaller splittings at 4.2 K (see Fig. 11).

B. $T \geq 300$ K

From the lineshapes in this temperature region, it appears that diffusional averaging is not entirely isotropic, but that the deuterium still occupies certain interstitial sites preferentially. J. L. Anderson et al. reported on the basis of neutron diffraction studies that $\text{LaNi}_{5.7}\text{D}_{6.8}$ at room temperature may represent an intermediate state between a completely random hydride at elevated temperatures and a

completely ordered state at lower temperatures.¹⁸ Since inversion symmetry is a property of the crystal space group, one would expect a vanishing v_Q to result from equal occupation of all sites. The spherical average of $(3\cos^2\theta-1)$ in Eq. (26), with $\eta=0$, is zero. However, a non-vanishing v_Q is obtained in all samples.

From Fig. 14 (v_Q versus concentration x at 300 K), we see that v_Q is not very strongly dependent on the deuterium concentration. Because of this, one expects that just including lanthanum in the EFG calculations is not a poor approximation. One can also interpret Fig. 14 as indicating that the more deuterium atoms one inserts into the lattice, the more expanded the lattice becomes. Since the EFG is proportional to $1/R^3$ or $1/\text{volume}$, the smaller v_Q 's should correspond to a larger lattice volume. The v_Q at 300 K for $x = 3.6$ is 10% greater than v_Q for $x = 6.7$.

J.H.N. van Vucht et al. have reported that at 322 K and with a pressure of 1 atm of H_2 gas over the hydride, 99% of the hydrogen in the hydride escapes in 5 minutes.¹ It is, therefore, likely that as the temperature is increased above 300 K, the hydrogen is driven out of the lattice. Since v_Q is proportional to $1/\text{volume}$, the 27% increase in v_Q for the $x = 6.7$ sample from 300 K to 360 K corresponds almost exactly to the 25% volume increase upon hydriding and, hence, is very likely attributable to the shrinking of the lattice due to loss of deuterium. The loss of the deuterium would also explain the disappearance of the quadrupole split pattern at higher temperatures.

As for the narrow line observed at high temperatures, there are at least four possible explanations for this resonance:

1. It is due to D_2 gas in the sample tube.
2. It arises from deuterium in the solid-solution α -phase.
3. It arises from a deuterium surface film.
4. It results from deuterium gas which is exchanging with the surface film.

Investigators have believed that the $LaNi_5$ hydrogen system is a two-phased system on the basis of the pressure-composition isotherm data.^{1,2,4} As is typical of metal-hydrogen systems, the α -phase is regarded as the solid-solution of hydrogen, and the β -phase as the $LaNi_5$ hydride. However, the neutron diffraction data do not indicate a crystal phase change upon hydriding, but only an isotropic 25% volume increase.¹⁸

Since the possibility of a surface state may exist, electron scanning micrographs of a sample of $LaNi_5H_x$ which had been hydrided ~ 5 times were obtained by Dr. J. Verhoeven of the Metallurgy Division of the Ames Laboratory. Investigators have previously reported particle sizes on the order of 5 to 15 μm .^{1,5} As seen in Fig. 21, $LaNi_5$ hydride exhibits much surface area from numerous cracks and fissures and has cracked particles on the order of 5 to 15 μm . Picture B is a magnification of the left hand corner of picture A.

Based on these possibilities, the NMR of a sample of deuterium gas (35 psi) was investigated at 300 K. It was found to have a very weak

Picture A. 950X. One inch $\sim 27\mu\text{m}$.

Picture B. 4700X. One inch $\sim 5\mu\text{m}$.

Fig. 21. Electron scanning micrographs of LaNi_5H_x .

signal, requiring a minimum of 200 minutes to resolve the lineshape even with overmodulation. Typically, a modulation amplitude 1/5 of the linewidth or less is required. In the case of deuterium gas, an amplitude 1/3 of the linewidth was needed. Under the same experimental conditions, the NMR from D_2O had the same linewidth as the gas (~ 0.35 Oe). It should be noted that the high temperature linewidths reported were 0.7 to 1.3 Oe. Also, the higher temperature spectra were easily resolved and did not require overmodulation. On this basis, it appears that it is not simply deuterium gas at higher temperatures that is being observed. Spin-lattice (T_1) and spin-spin (T_2) relaxation time measurements by pulsed NMR methods are needed to correlate with the linewidth measurements obtained in the present investigation.

C. $LaNi_5$ Exposed to D_2 Gas at 77 K (~ 83 psi Over Pressure)

The explanations offered for the unsplit resonance at high temperatures could equally well account for the results for $LaNi_5$ exposed to D_2 gas at 77 K. The NMR of a pure deuterium gas sample (~ 35 psi) and of the gas in the sample tube over the $x = 6.7$ sample were easily resolved and did not require overmodulation. Each had a linewidth of ~ 0.34 Oe. However, the linewidth in the case of $LaNi_5$ exposed to D_2 gas at 77 K was ~ 1.30 Oe.

If the nuclear spin-lattice relaxation is enhanced when deuterium gas is adsorbed on the surface, it is possible to extract T_1 values from the linewidth data. In both the pure D_2 gas and the gas over the

$x = 6.7$ sample, the lineshapes appeared to be Lorentzian. For NMR in a gas, one can assume that $T_1 = T_2$, leading to a Lorentzian lineshape with $\Delta\nu(\text{linewidth}) = 1/\sqrt{3}\pi T_2 = 1/\sqrt{3}\pi T_1$. Based on this, the T_1 for the pure D_2 gas is 0.74 msec and that for the gas in the $LaNi_5$ sample at 77 K is 0.21 msec. Since the relaxation rates are additive, we may conclude that $(1/T_1) LaNi_5 + D_2 \text{ at } 77 \text{ K} = (1/T_1) \text{ pure gas} + (1/T_1) \text{ surface relaxation}$, yielding $(T_1) \text{ surface relaxation} \sim 0.29 \text{ msec}$. Thus, it appears that there is a significant surface effect contribution to the total relaxation rate.

As for the time dependence of this series of spectra, it has been reported on the basis of thermal desorption spectra and the measurement of differential heats that hydrogen is adsorbed on nickel in a physisorbed state and in two chemisorbed states.²⁰ At 77 K the formation of the two chemisorbed states was not observed. Thus, only one species, or alternatively, a mixture of the two species can be present on the surface.²⁰ At the present time, this offers only a possible explanation for the observed time dependence of the NMR spectra.

VI. CONCLUSIONS

The ^2D quadrupole interaction was observable in all the samples of LaNi_5D_x studied up to a critical temperature T_c at which the intensity of the quadrupole interaction spectrum disappeared and only a narrow unsplit line remained. The critical temperatures were 360 K for the $x = 3.6$ sample and 380 K for the $x = 5.7, 6.7$ samples. In the temperature range $4.2 \text{ K} \leq T < 300 \text{ K}$, thermal (motional) averaging of the ^2D quadrupole interaction was observable with increasing temperature. Based on preliminary electric field gradient (EFG) calculations, it appears likely that several quadrupole interactions are being observed from inequivalent deuterium sites in the lattice. However, large anomalous broadening of the spectra occurred with decreasing temperature and remains unexplained at this time.

In the temperature range $T \geq 300 \text{ K}$, it appears that diffusional averaging is not entirely isotropic and that the deuterium still occupies certain interstitial sites preferentially. The temperature dependence of the ^2D characteristic quadrupole frequency (ν_Q) and the disappearance of the ^2D quadrupole interaction signal were found to be compatible with desorption of the deuterium from the LaNi_5 lattice with increasing temperature.

Spectra obtained from D_2 gas samples under various experimental conditions (pure gas, gas above $\text{LaNi}_5\text{D}_{6.7}$, and gas within or on LaNi_5 at 77 K) may provide evidence for the identification of the solid-solution α -phase or for the existence of an adsorbed deuterium surface

film on the LaNi_5 . In addition, the spectra suggest that at 77 K rapid deuterium exchange between the gas and surface contributes to spin-lattice relaxation and, hence, to broadening of the NMR resonance.

VII. REFERENCES

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IX. APPENDIX

The impurity levels, in ppm by weight, are listed in the table below for the La and Ni used in preparation of LaNi_5D_x .

Table 5. Impurity level of metals

Impurity	D. K. Thome ($x=3.6, 5.7, 6.7$)		B. J. Beaudry ($x=3.4, 5.75$)	
	Ni (ppm)	La (ppm)	La (ppm)	
H		2	3	
C	9	5	24	
N		5	22	
O		35	38	
F	15	74	21	
Na		0.03	1	
Mg		0.02	<0.4	
Al		0.01	<2	
Si		0.42	<1	
P		<0.008	<0.1	
S		0.09	2	
Cl		0.1	4	
K		0.02	0.6	
Ca		0.06	0.4	
Sc		0.09	<0.4	
Ti		0.08	<0.4	
V		<0.007	0.1	
Cr		1.1	0.04	
Mn		0.087	<6	
Fe	6	5.1	20	
Ni		3	10	
Cu		0.62	3	
Zn		0.05	0.1	
Ga		<0.02	<0.2	
Ge		<0.06	<0.2	
Br		--	<0.2	
Y		6	2.8	
Zr		<0.5	<2	
Mo		<0.3	<2	
Ru		<0.3	<0.8	

Table 5. Continued

Impurity	D. K. Thome (x = 3.6, 5.7, 6.7)		B. J. Beaudry (x = 3.4, 5.75)	
	Ni (ppm)	La (ppm)	La (ppm)	
Rh		<0.02	<0.2	
Pd		<0.05	<0.4	
Ag		<0.009	<0.1	
Cd		<0.02	<0.1	
Sn		<0.04	<0.4	
Te		<0.2	<0.1	
Ba		<0.9	<0.6	
Ce		10	20	
Pr		2.7	0.76	
Nd		2	<0.5	
Sm		<0.5	<0.3	
Eu		<0.4	<0.2	
Gd		<2	2.4	
Tb		0.3	0.8	
Dy		2	<0.4	
Ho		3	3	
Er		2	1.1	
Yb		<0.2	<0.5	
Lu		<0.4	1	
Hf		<0.5	0.8	
Ta		0.3	2	
W		<0.7	<2	
Re		<0.2	<1	
Os		0.5	<1	
Ir		<0.09	<1	
Pt		<0.1	1	
Au		<0.05	<0.2	
Hg		0.05	0.1	
Tl		<0.02	0.1	
Pb		<0.1	0.1	
Th		0.2	0.2	
U		<2	0.2	

The analysis of the metals (La) was obtained by spark source mass spectrometry performed in the Ames Laboratory. The impurity elements F, C, and Fe were analyzed by wet chemistry, and H, N, and O were analyzed by vacuum fusion. The Ni used by B. J. Beaudry was "Reagent grade" Ni shot with Fe (.04%), C (.008%), and Pb (.008%) by weight. The Ni used by D. K. Thome was analyzed by wet chemistry which is tested only for C, F, and Fe using 1 gm of sample for each test.