JOURNAL OF SOLID STATE CHEMISTRY **11**, 114–119 (1974)

Proton NMR Studies of Lanthanum Nickel Hydride: Structure and Diffusion

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Received November 10, 1973

The proton magnetic resonance spectrum of lanthanum nickel hydride $LaNi_{5.3}H_6$ was measured over the temperature range 118°K < T < 300°K. The second moment of the absorption at 118°K is $M_2 = 13.4 \pm 0.3$ G^2. Several possible arrangements of the hydrogen atoms are discussed. Narrowing of the line above 140°K is analyzed in terms of proton diffusion and gives an activation enthalpy $E = 21 \pm 1$ kJ mol^{-1}, NMR correlation time pre-exponential 0.2 ps < $\tau_c{}^0$ < 1.6 ps and a self diffusion coefficient at 300°K of 2×10^{-12} m^2 s^{-1} < D < 2×10^{-11} m^2 s^{-1}.

Introduction

Lanthanum nickel hydride $LaNi_xH_6$ ($4.9 < x < 5.4$) is a nonferromagnetic member of a family of hydrides (*1*) derived from $CaCu_5$-type rare-earth compounds with either Ni or Co. The compounds have attracted interest because of their strong ferromagnetism (*4*) and their ability to absorb large quantities of hydrogen (*5, 6*) rapidly and reversibly at room temperature and at moderate pressures. Motivation for this study springs from an interest in materials containing highly mobile hydrogen.

Many NMR studies, which have been extensively reviewed (*7, 8*) elsewhere, have been made of binary metal hydrides whereas few investigations of ternary metal hydrides have been reported (*9*). In the present work proton magnetic resonance spectra of $LaNi_{5.3}H_6$ were recorded in the range 118°K < T < 300°K. Hydrogen self-diffusion parameters were determined from the narrowing of the spectra and an attempt was made to deduce the location of the hydrogen atoms in the structure from the second moment of the low temperature spectrum.

Experimental Details

Materials

The intermetallic compound $LaNi_x$ was prepared from pure components (3 *N* La, 4 *N* Ni) by arc melting under argon. Single phase powder patterns were obtained with CuK_α X-ray diffraction. The composition of the sample was determined by gravimetric analysis as $LaNi_{5.3}$, which is at the Ni-rich end of the $LaNi_x$ homogeneity region (*1*).

The hydride was prepared by exposing about 4 g of the powdered intermetallic compound, contained in a Pyrex bulb, to hydrogen at a pressure of about 60 atm for several hours at 296°K in a brass bomb. The sample was removed by reducing the pressure to about 7 atm and rapidly cooling the bomb at 78°K. Still at 78°K, the pressure was reduced to 1 atm, the bomb opened and the neck of the bulb quickly sealed by a flame to leave a volume of about 0.8 cm^3 above the hydride. The composition of the hydride was deduced from the published isotherm (*1, 6*) to be close to $LaNi_{5.3}H_6$.

NMR Measurements

A Varian wide line spectrometer with a 12 in. electromagnet was used to measure the

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* The work reported here was performed while on leave at the Center for Materials Research at Stanford University, Stanford, California.

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derivative absorption of the hydride over the temperature range 118°K $< T <$ 300°K. The sample was nearly cylindrical, 7 mm in diam and 15 mm high. Temperatures were held constant to better than ±1°K during each measurement and were determined from the mean emf of 2 thermocouples, held in contact with the upper and lower ends of the sample, respectively. The usual precautions were taken to avoid modulation and saturation effects. Signal to noise ratios were typically 20:1.

The rigid lattice second moment was determined by averaging repeated scans over a period of 10 hr, using a Digital Equipment Corp. PDP 8/e computer.

Results

NMR Measurements

The variation with temperature of the peak to peak separation of the derivative absorption of $LaNi_{5.3}H_6$ measured at a frequency $\nu_0 =$ 8 MHz is shown in Fig. 1. The second moment of the low temperature spectrum (118°K) at 8 MHz was calculated numerically as $M_2 = 13.4 \pm 0.3$ G^2 and was equal to the value obtained at 12 MHz, within the experimental error. The spectra were symmetrical and appeared to be Lorentzian at 296°K and Gaussian at 118°K.

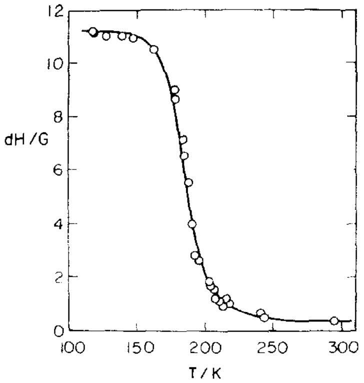

FIG. 1. Temperature variation of the line width of the proton magnetic resonance absorption in $LaNi_{5.3}H_6$. The curve was calculated using Eq. (2) and Eq. (3) and is the best fit to the experimental data.

Discussion

The Structures of $LaNi_5$ and $LaNi_5H_6$

X-ray diffraction shows (*10*) that $LaNi_5$ has a hexagonal structure belonging to the space group *P6/mmm* with $a_0 = 5.017$ A, $c_0/a_0 = 0.794$ and $V = 86.6$ A^3; and that $LaNi_5H_6$ (*2*) may belong to the same space group with $a_0 = 5.440$ A, $c_0/a_0 = 0.792$ and $V = 110.5$ A^3. Hydrogen atoms were, of course, not located by the X-ray diffraction.

Both structures may be described as layer structures. Referring to Fig. 2, it is seen that the layer of $LaNi_5$ at $z = 0$ consists of a hexagonal array of La atoms with Ni(*g*) (*g* is the Wyckoff notation for the position (*11*)) atoms trigonally surrounded by La atoms. The layer at $z = 0.5$ consists entirely of Ni(*c*) atoms, derived from a close-packed layer by the removal of atoms lying above La atoms in the $z = 0$ layer. Assuming that $LaNi_5H_6$ belongs to *P6/mmm*, hydrogen atoms could be located at any of the interstitial positions shown in Table I. Moreover, it is possible that several positions are simultaneously occupied. The positions *f*, *m* and *o* are shown in Fig. 2.

Alternatively, the structures may be described as tunnel structures. The framework is built up of chains of Ni atoms, formed by tetrahedra joined up by sharing faces (at $z = 0.5$) and corners (at $z = 0$). The tunnels are formed, parallel to the *c*-axis, from 6 of the tetrahedral chains by sharing corners of the tetrahedra (at $z = 0.5$). The La atoms are

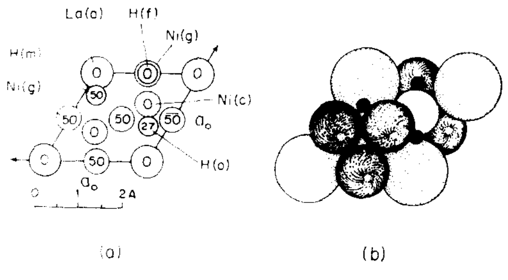

FIG. 2. Structure of $LaNi_5H_6$. (a) The hexagonal arrangement projected along its *c* axis. Lower-case letters are the Wyckoff notation, numerals denote the heights of atoms in units of $c_0/100$ A. (b) A packing drawing of the structure seen along its *c* axis, H atoms are black, the La atoms are dotted and the two kinds of Ni atoms are swirled and open. The H positions are hypothetical.

TABLE I

STRUCTURAL DATA FOR $LaNi_5H_6$

Atom	Wyckoff notation	Coordinates[a] x	y	z	No. of sites in cell	Radius of atom (A)
La	*a*	0	0	0	1	1.83 (1.69)[b]
Ni	*c*	1/3	2/3	0	2	1.31 (1.21)[b]
Ni	*g*	1/2	0	1/2	3	1.36 (1.25)[b]
H	*b*	0	0	1/2	1	0.33
H	*f*	1/2	0	0	3	0.26
H	*h*	1/3	2/3	0.37	4	0.30
H	*m*	.13	1/4	1/2	6	0.35
H	*n*	.40	0	.11	12	0.41
H	*o*	.20	.40	.27	12	0.39

[a] General coordinates for hydrogen are estimates.
[b] Radius in $LaNi_5$.

located in these tunnels. For $x > 5$, La atoms are replaced by a pair of Ni atoms, aligned along the *c*-axis. The possible hydrogen positions *m*, *n*, and *o* lie on the walls of the tunnels whereas, positions *f* and *h* are buried in the Ni framework. The *b* positions lie on the axes of the tunnels, between La atoms. Regarding the structures of both $LaNi_5$ and $LaNi_5H_6$ as being built of close-packed hard spheres, with Ni(*g*) atoms touching each other, the atomic radii of the atoms were calculated. The hydrogen positions were estimated to be at the centers of the largest spheres that could be accommodated in the interstices. These results are shown in Table I.

Many hypothetical arrangements of hydrogen atoms in $LaNi_5H_6$ were considered but only 5 trial structures, defined in Table II are discussed in this paper. All the available sites in structures I and II are filled by hydrogen, whereas in structures III and IV there are more than 6 sites available to the hydrogen atoms. Structure IV was suggested by analogy with the arrangement of hydrogen atoms deduced for $PrCo_5D_4$ from neutron diffraction data (*12*). When 4 sites are occupied in $PrCo_5D_4$, ordering and a hexagonal to orthorhombic distortion occurs. No distortion has been observed in $LaNi_5H_6$, suggesting that the sites are randomly occupied. Structure V is imaginary, corresponding to a hexagonal close-packed array with $a_0 = 2.82$ A, i.e., a very uniform arrangement in which the concentration of hydrogen atoms is the same as in $LaNi_5H_6$.

The equilibrium hydrogen pressure over $NiH_{0.6}$ has been estimated to be $>2 \times 10^4$ atm (*7*), therefore it is probable that sites associated with tunnels in $LaNi_5H_6$ are occupied but not those embedded in the Ni-framework.

Theoretical and Observed Second Moments

To assess how closely the trial structures approximate the true structure of $LaNi_5H_6$,

TABLE II

SECOND MOMENTS OF TRIAL STRUCTURES

Trial structure	Site (i)	Relative No. (ω_i)	Probability of occupancy (α_i)	Second moment (M_2/G^2)
I	*m*	1	1	283
II	*n*[a]	1	1	49
III	*o*	1	½	21.2
IV	*f*	⅓	⅔	130
	m	⅔	⅔	
V	(hexagonal close-packed array)			9.5

[a] Half the *n* sites are occupied in an ordered manner.

the theoretical second moment of the proton spectrum of each structure was calculated using Van Vleck's formula for the dipolar broadening in a rigid lattice and compared with the observed value of the second moment. In this case where inequivalent sites may be occupied, the calculation was facilitated by using the expression (*13*, *14*)

$$M_2 = C_{ij} \sum_{ij}^{N} \omega_i \alpha_i \alpha_j S_{ij} \Big/ \sum_{k}^{N} \omega_k \alpha_k \qquad (1)$$

where $C_{ij} = 3/5\,\gamma_I{}^2 \hbar^2 I(I+1)$, in the case where the spin at site i is identical to the spin at site j, or $4/15\gamma_S{}^2 \hbar^2 S(S+1)$, in the case where the spins are nonidentical, ω_i is the relative number of i sites, α_i is the probability that an i site is occupied, and $S_{ij} = \sum_{j=1} r_{ij}^{-6}$ where the origin is placed at site i and the summation extends over all j sites.

In addition, the second moment of the spectrum of hydrogen atoms in a hexagonal close-packed array was calculated using the value $S_{ij}(\text{hex}) = 14.45\ a_0^{-6}$ taken from the literature (*15*). The results of these calculations are shown in Table II.

In Fig. 1 it is seen that below 140°K the line width is approximately constant, indicating a rigid lattice. The independence of the second moment at 118°K on field strength indicates that the line width is dipolar in origin. In Table II it is seen that the second moment calculated for the hcp structure (V) is closest to the experimental value of 13.4 G^2, suggesting that in the actual structure hydrogen atoms are relatively uniformly distributed. Of the moments calculated for the trial structures that for III, in which *o* sites are randomly occupied, is nearest to but significantly larger than the observed value. Neither adjustment of the coordinates of the *o* site, nor the assumption of another rigid arrangement of hydrogen atoms over the sites allowed in the space group *P6/mmm* resulted in a significantly smaller calculated second moment. Now it might appear, at first sight, that a loss of hydrogen from the sample could explain the small observed second moment but this is not so. A mixture of $LaNi_5H_6$ and a hydrogen-poor phase of approximate composition $LaNi_5H_{0.5}$ (*6*) would result and the NMR absorption of $LaNi_5H_6$, reduced in intensity but not in width, would swamp the very much weaker, narrower absorption due to $LaNi_5H_{0.5}$, so that the effect on the observed second moment would be negligible. It is interesting to note that structure IV, suggested by the $PrCo_5H_4$ structure, must be rejected.

It is conceivable that future NMR studies may reveal that the observed moment is not the rigid lattice value and that some motion, e.g., localized tunnelling, causes significant narrowing at a temperature below 118°K.

Motional Narrowing

Turning now to the motion of the hydrogen atoms it is seen in Fig. 1 that above 140°K the line width narrows to a very small value indicating the onset of hydrogen diffusion. The data were analyzed using the expression (*14*, *16*)

$$1/\tau_c = \frac{\alpha\gamma(dH - dH_1)}{\tan\{\pi[(dH - dH_1)/(dH_2 - dH_1)]^2/2\}} \qquad (2)$$

where τ_c is the NMR correlation time for the interaction between 2 spins, is the gyromagnetic ratio, dH is the observed line width, dH_1 is the line width of the motionally narrowed line, dH_2 is the line width before narrowing and α is a numerical constant probably with the value $2 < \alpha < 10$, depending on the line shape (*14*, *16*).

From this analysis τ_c values were obtained as a function of temperature and these are plotted in Fig. 3 as $\log_{10}\alpha\tau_c$ against $1/T$. The observed linear relationship of these quantities indicates that the τ_c values obey the Arrhenius equation

$$\tau_c = \tau_c{}^0 \exp{(E/RT)}. \qquad (3)$$

Values of $E = 21 \pm 1$ kJ mole^{-1} and $\alpha\tau_c{}^0 = 2.6 \pm 0.6$ ps were chosen by trial and error to give a good fit between the values of dH and T, calculated using Eq. (2) and Eq. (3), and the observed values. A theoretical curve of dH against T, thus derived, is shown in Fig. 1.

The dwell time between net atomic displacement is $\tau_n = 2\tau_c$ because the interaction between two spins is interrupted when either spin jumps. The mean time between jumps

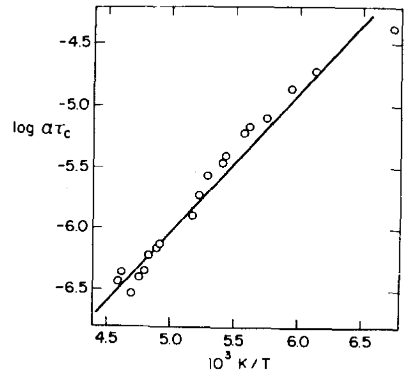

FIG. 3. Temperature dependence of NMR correlation time for $LaNi_5H_6$. The straight line is a plot of $\alpha\tau_c = 2.6 \times 10^{-12} \exp(21 \text{ kJ mole}^{-1}/RT)$.

(jump correlation time) $\tau = f\tau_n$, where f is a correlation factor which depends on the diffusion mechanism (probably $0.5 < f < 0.7$), because successive jumps may be correlated and cause no net displacement (*18*, *19*). Therefore, the best estimate for the jump correlation time preexponential factor is $0.2 \text{ ps} < \tau_c{}^0 < 2 \text{ ps}$.

The theory of random flights gives the expression

$$D = d^2/n\tau \qquad (4)$$

where D is the self diffusion coefficient, d is the jump distance and n is the number of jump paths. If the hydrogens jump between o sites then the average value of d^2/n is approximately 1.6 A^2. Therefore, the best estimate for the diffusion constant preexponential factor is $8 \times 10^{-9} \text{m}^2\text{s}^{-1} < D_0 < 8 \times 10^{-8} \text{m}^2\text{s}^{-1}$ and for the diffusion constant at 300°K is $2 \times 10^{-12} \text{m}^2\text{s}^{-1} < D < 2 \times 10^{-11} \text{m}^2\text{s}^{-1}$.

The value of D indicates that hydrogen is very mobile in $LaNi_5H_6$ at room temperature, being comparable with D for hydrogen in β-PdH_x (*20*) and NbH_x (*21*), and is almost as high as for Na^+ in sodium β-alumina (*22*), a so-called superionic conductor. The high mobility suggests that the hydrogen atoms can diffuse via a rather open path and that there is an excess of sites, of similar energy, available to them. This may be taken as further evidence for a structure like III, in which about half of the sites in the tunnel are occupied, and against structures such as I and II.

Assuming that the optical vibration frequency is given by the expression

$$\nu_0 = 1/(2\pi n p \tau_c{}^0) \qquad (5)$$

for structure VI, where the number of jump paths $n \simeq 3.5$ and the probability that a neighbouring site is occupied $p = 7/12$, a value of 3×10^{10} Hz $< \nu_0 < 3 \times 10^{11}$ Hz was obtained. Low optical frequencies are typical of superionic conductors (*22*).

Acknowledgments

The author wishes to thank Professor R. A. Huggins, Dr. M. S. Whittingham from Stanford, and Dr. P. G. Dickens from Oxford for helpful discussions. Also, thanks are due to Dr. L. D. Clark for writing the data acquisition program. The work was supported by the Environmental Protection Agency under grant No. 801337, at Stanford University.

References

1. K. H. J. BUSCHOW AND H. H. VAN MAL, *J. Less-Common Metals* **29**, 203 (1972).
2. J. H. N. VAN VUCHT, F. A. KUIJPERS, AND H. C. A. M. BRUNING, *Philips Res. Repts.* **25**, 133 (1970).
3. H. H. VAN MAL, K. H. J. BUSCHOW, AND F. A. KUIJPERS, *J. Less-Common Metals* **32**, 289 (1973).
4. H. ZIJLSTRA AND F. F. WESTENDORP, *Solid State Comm.* **7**, 857 (1969).
5. F. A. KIUJPERS AND H. H. VAN MAL, *J. Less-Common Metals* **23**, 395 (1971).
6. H. H. VAN MAL, *Chemie Ingenieur Technik* **45**, 80 (1973).
7. W. M. MUELLER, J. P. BLACKLEDGE, AND G. G. LIBOWITZ, "Metal Hydrides," Academic Press, New York (1968).
8. G. G. LIBOWITZ, "MTP Int. Rev. of Science" **10**, *Solid State Chemistry* (L. E. J. Roberts, Ed.), Butterworths, London (1971).
9. J. H. N. VAN VUCHT, *Philips Res. Repts.* **18**, 1 (1963).
10. J. H. WERNICK AND S. GELLER, *Acta Cryst.* **12**, 662 (1959).
11. "International Tables for X-Ray Crystallography" (Int. Union of Crystallography), Kynoch Press, Birmingham (1965).
12. F. A. KUIJPERS AND B. O. LOOPSTRA, *J. Phys. (Paris)* **32**, C1-658 (1971).
13. H. T. WEAVER, *J. Chem. Phys.* **56**, 3193 (1972).
14. B. STALINSKY, C. K. COOGAN, AND H. S. GUTOWSKY, *J. Chem. Phys.* **34**, 1191 (1961).

15. H. S. Gutowsky and B. R. McGarvey, *J. Chem. Phys.* **20**, 1472 (1952).

16. H. S. Gutowsky, G. E. Pake, and R. Bersohn, *J. Chem. Phys.* **22**, 643 (1954).

17. M. S. Whittingham, P. S. Connell, and R. A. Huggins, *J. Solid State Chem.* **5**, 321 (1972).

18. M. Eisenstadt, *Phys. Rev.* **132**, 630 (1963).

19. T. G. Stoebe, T. O. Ogurtani, and R. A. Huggins, *Phys. Status Solidi* **12**, 649 (1965).

20. W. Spalthoff, *Z. Phys. Chem.* **39**, 258 (1961).

21. B. Stalinsky and O. J. Zogal, *Bull. Acad. Polon. Sci. Ser. Sci. Chim.* **13**, 397 (1965).

22. M. S. Whittingham and R. A. Huggins, *Chem. Phys.* **54**, 414 (1971).