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# Experimental heat capacities of $\text{LaNi}_5$ , $\alpha\text{-LaNi}_5\text{H}_{0.36}$ , and $\beta\text{-LaNi}_5\text{H}_{6.39}$ from 5 to 300 °K. Thermodynamic properties of the $\text{LaNi}_5\text{-H}_2$ system<sup>a)</sup>

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The heat capacities of  $\text{LaNi}_5$ ,  $\alpha\text{-LaNi}_5\text{H}_{0.36}$ , and  $\beta\text{-LaNi}_5\text{H}_{6.39}$  were measured from 5 to 300 °K, and in the case of  $\text{LaNi}_5$  also from 300 to 350 °K. Various special techniques and unusual circumstances involved in the measurements and calculations are described. A slight enhancement of the heat capacity of  $\beta\text{-LaNi}_5\text{H}_{6.39}$  was observed in the temperature range 120 to 160 °K. The standard entropies of  $\text{LaNi}_5$ ,  $\alpha\text{-LaNi}_5\text{H}_{0.36}$ , and  $\beta\text{-LaNi}_5\text{H}_{6.39}$  at 298.15 °K were found to be  $209.9 \pm 0.5$ ,  $214.1 \pm 0.5$ , and  $271.7 \pm 0.7 \text{ J}^\circ\text{K}^{-1} \text{ mole}^{-1}$ , respectively. These results together with other thermochemical data were used to calculate the entropy and enthalpy of formation of  $\beta\text{-LaNi}_5\text{H}_{6.39}$  at 298.15 °K. The partial molar entropy of hydrogen in  $\beta\text{-LaNi}_5\text{H}_{6.39}$  was derived from our results and used to estimate the configurational entropy at 298.15 °K.

## I. INTRODUCTION

In recent years, the intermetallic alloy  $\text{LaNi}_5$  has been identified as a prototype for a hydrogen storage and energy transfer material because of its favorable kinetic and thermodynamic properties for hydrogen absorption and desorption in the temperature range from about 280 to 380 °K. In addition to its desirable properties for practical applications, the  $\text{LaNi}_5\text{-H}_2$  system, as well as other related  $\text{AB}_5\text{-H}_2$  systems, offers challenging opportunities for fundamental scientific studies to understand its behavior and thereby the behavior of other metal-hydrogen systems.

The literature contains many papers which describe various chemical, physical, and thermodynamic properties of the  $\text{LaNi}_5\text{-H}_2$  system and no attempt is made in this paper to cite all these publications or to review their contents. However, it is appropriate to mention a few of the properties of the  $\text{LaNi}_5\text{-H}_2$  system which are related to the research to be presented in this paper. Near 300 °K under proper conditions pure  $\text{LaNi}_5$  will react with hydrogen to form  $\beta\text{-LaNi}_5\text{H}_{6.7}$ .<sup>1</sup> It has been shown that  $\text{LaNi}_5$  will dissolve hydrogen to form compositions up to approximately  $\alpha\text{-LaNi}_5\text{H}_{0.4}$  and still retain the same crystal structure as the hydrogen-free alloy; above this hydrogen composition another hydride phase ( $\beta$ ) is formed with the approximate composition  $\beta\text{-LaNi}_5\text{H}_6$ ; and finally above this composition additional hydrogen can be dissolved with an accompanying lattice expansion.<sup>1-5</sup> The  $\text{LaNi}_5$  resulting from thermal decomposition of  $\beta\text{-LaNi}_5\text{H}_6$  is in the form of a fine powder which reacts rapidly with hydrogen even at 195 °K.<sup>5</sup> It has been found that exposure of this activated  $\text{LaNi}_5$  powder to small amounts of air or oxygen does not reduce its reactivity toward hydrogen.<sup>6-9</sup> The crystal density of  $\beta\text{-LaNi}_5\text{H}_6$  is about 25% less than that of  $\text{LaNi}_5$ .<sup>3</sup>

The two hydride compositions chosen for this study were  $\alpha\text{-LaNi}_5\text{H}_{0.36}$  and  $\beta\text{-LaNi}_5\text{H}_{6.39}$ . The phase stability information available in the literature<sup>1-5</sup> indicated that for temperatures of 300 °K and lower that compositions of  $\alpha\text{-LaNi}_5\text{H}_{0.4}$  or lower hydrogen content would remain as a single phase. For the  $\beta$ -hydride a composition of  $\beta\text{-LaNi}_5\text{H}_{6.2}$  or higher hydrogen content would be expected to be a single phase at 300 °K and lower temperatures. However, no precise information concerning phase stability versus hydrogen composition is known below 195 °K. Structure studies<sup>10-12</sup> have indicated that the hydrogen atoms are located in several different tetrahedral interstitial sites in the  $\text{LaNi}_5$  lattice. The occupation of the sites is dependent upon the total hydrogen content. It has not been established whether or not cooling these hydrides to temperatures approaching absolute zero results in a phase with complete order with respect to the hydrogen interstitials. In any event, it was our intent to choose  $\alpha$ - and  $\beta$ -hydride compositions, each of which was likely to remain as a single well-defined phase below 300 °K.

Prior to this research, no experimental heat capacities of  $\text{LaNi}_5\text{H}_x$  had been measured. It was therefore the objective of this research to determine the heat capacities of  $\text{LaNi}_5$  and of the  $\alpha$ - and  $\beta$ -forms of  $\text{LaNi}_5\text{H}_x$  from 5 to 300 °K and to derive their entropies  $S^\circ$ , enthalpy measurements  $H^\circ(T) - H^\circ(0)$ , and Gibbs energy function  $-[G^\circ(T) - H^\circ(0)]/T$ . Further, we then would be able to combine these thermodynamic results with thermodynamic data (i.e., equilibrium hydrogen pressure measurements and entropies and enthalpies of reaction) reported here and in the literature to extend our present understanding of the  $\text{LaNi}_5\text{-H}_2$  system. Finally, we will discuss the various contributions to heat capacity and entropy of  $\alpha$ - and  $\beta\text{-LaNi}_5\text{H}_x$ .

## II. EXPERIMENTAL

### A. $\text{LaNi}_5$ samples

The  $\text{LaNi}_5$  sample was prepared by arc melting the pure metals La (99.98%) and Ni (99.995%) under an inert atmosphere. The alloy was remelted five times and then transferred to a quartz tube which was sealed under argon; a final anneal of the sample in the quartz tube was

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carried out at 1350 °K for two hours. X-ray results showed only one phase with lattice constants  $a = 5.015 \pm 0.007$  Å and  $c = 3.980 \pm 0.007$  Å for the hexagonal CaCu<sub>5</sub> structure; these values were in good agreement with lattice constant values in the literature.<sup>1,2,10,12</sup> Chemical analyses of the LaNi<sub>5</sub> sample performed at Argonne National Laboratory are summarized in Table I. The representation of metal-atom composition of this sample containing six atoms per formula weight is La<sub>0.997</sub>Ni<sub>5.003</sub>, as determined by the analytical data. Except in Tables II–VIII where the exact formulas of our samples are stated, we will use the less exact LaNi<sub>5</sub> formula.

Since our LaNi<sub>5</sub> sample contained a significant amount of oxygen, we attempted to determine how this oxygen was present in the sample. It has been shown that the direct attack of oxygen or of an oxygen-containing substance can decompose the LaNi<sub>5</sub> surface to form La(OH)<sub>3</sub> or La<sub>2</sub>O<sub>3</sub> and free nickel and that the presence of the free nickel seems to promote reaction with hydrogen.<sup>7–9</sup> A good indication of significant amounts of free nickel in LaNi<sub>5</sub> (and consequently an oxidized form of lanthanum) is a strong temperature dependence of the magnetic susceptibility.<sup>8</sup> The magnetic susceptibility of our LaNi<sub>5</sub> sample from 5 to 300 °K is shown in Fig. 1 and only a relatively small increase in magnetic susceptibility with decreasing temperature is seen. Our measured susceptibility at 300 °K agrees with the result of Schlappbach *et al.*<sup>8</sup> It appears that most of the oxygen in the LaNi<sub>5</sub> sample is not present as one or more lanthanum oxide-containing phases, but may be located in interstitial sites.

Heat capacity measurements were made using the LaNi<sub>5</sub> sample before exposing it to hydrogen. To be sure that the LaNi<sub>5</sub> contained no significant amounts of dissolved hydrogen, the sample was heated in vacuum (pressure  $< 1 \times 10^{-5}$  Torr) at 870 °K just prior to the start of the heat capacity measurements.

## B. Sample encapsulation

Our plan was to measure the heat capacity of LaNi<sub>5</sub> from 5 to 350 °K, to convert the entire LaNi<sub>5</sub> calorimetric sample to  $\beta$ -LaNi<sub>5</sub>H<sub>x</sub> and to measure its heat

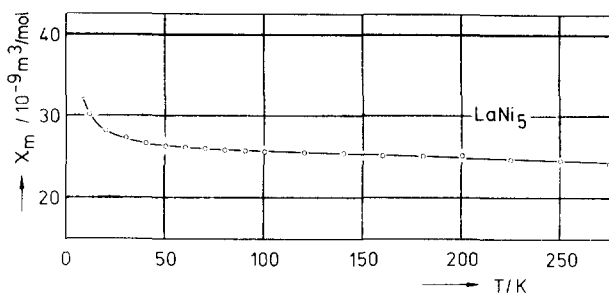


FIG. 1. The magnetic susceptibility of the LaNi<sub>5</sub> sample from 5 to 300 °K.

capacity from 5 to 300 °K, to decompose the  $\beta$ -hydride and prepare the  $\alpha$ -LaNi<sub>5</sub>H<sub>x</sub> calorimetric sample and to determine its heat capacity. It was decided to load the LaNi<sub>5</sub> into specially designed copper capsules so that all three sets of heat capacity measurements listed above could be made using the same copper capsules. These capsules terminated at one end with a small copper tube for adding or removing hydrogen so that there was no need to remove the LaNi<sub>5</sub> alloy after the original loading.

The hydrogen pressures in equilibrium with the LaNi<sub>5</sub>H<sub>x</sub> samples were in the range of one to several atmospheres near 300 °K and therefore it was desirable that the free volume inside the capsules be small as possible because the large enthalpy change associated with the release of hydrogen from the solid hydride into the free volume could cause large uncertainties in the measured heat capacities above about 250 °K. A total 46.665 g of LaNi<sub>5</sub> alloy was loaded into seven copper capsules. Each cylindrically shaped copper capsule was 0.69 cm in diameter and 5.1 cm long (approximately 1.6 cm<sup>3</sup> volume per capsule available for sample). After the LaNi<sub>5</sub> was loaded into a capsule, a copper end cap was soldered (50–50 Pb–Sn) over the open end of the capsule. A small copper capillary tube (0.2 cm in diameter and ~5 cm long) had been previously silver brazed to the end cap; this tube was used to admit hydrogen to the alloy in the capsule for hydride preparations (see later section) and it was sealed with a special pinch-off tool after the proper amounts of hydrogen and helium exchange gas had been added. All manipulations involving the sample were carried out in a helium-filled dry box or by use of a leak-free gas handling system.

## C. Activation of the LaNi<sub>5</sub> and preparation of the hydride

Following measurements of the heat capacity of LaNi<sub>5</sub>, the alloy in each capsule was converted to  $\beta$ -LaNi<sub>5</sub>H<sub>x</sub> for the first time and then hydride was thermally decomposed to produce the alloy in the form of a fine powder which reacts rapidly with hydrogen; this procedure is called activation of the LaNi<sub>5</sub>. Since the 25% volume expansion which occurs during activation would distort or split the copper capsules they were held to shape in a heavy brass support during formation of the hydride. The initial conditions necessary to start the activation were about 27 atm hydrogen pressure in the temperature range 300 to 345 °K. After the reaction was completed, the hydrogen was pumped from the sample near room temperature and then for 20 h at 350 °K

TABLE I. Chemical analyses of LaNi<sub>5</sub> samples  $w$  = mass fraction.

Elements <sup>a</sup>	$10^2 w$	Comments
La	$67.85 \pm 0.07^b$	Wet chemical analyses
Ni	$31.98 \pm 0.03^b$	Wet chemical analyses
O	$0.05 \pm 0.01^c$	Inert gas fusion technique
N	$0.004 \pm 0.002$	Kjeldahl method

<sup>a</sup>Spectrochemical analysis for trace elements showed the following significant amounts of impurities ( $10^6 w$ ): Al, 100; Cu, 25; Fe, 30.

<sup>b</sup>These values correspond to a Ni-to-La mole ratio of  $5.021 \pm 0.005$  or to the formula La<sub>0.997</sub>Ni<sub>5.003</sub> which has a molecular mass of 432.16 g mole<sup>-1</sup>.

<sup>c</sup>Oxygen analyses were made on the LaNi<sub>5</sub> as received from Denver Research Institute and on a portion of dehydrided alloy after the heat capacity measurements were completed; the values were equal within the stated error.

TABLE II. Experimental heat capacity of La<sub>0.997</sub>Ni<sub>5.003</sub>, at constant pressure  $M(\text{La}_{0.997}\text{Ni}_{5.003}) = 432.16 \text{ g mole}^{-1}$ .

$T$ (°K)	$C_p^\circ$ (J K <sup>-1</sup> mole <sup>-1</sup> )	$T$ (K)	$C_p^\circ$ (J K <sup>-1</sup> mole <sup>-1</sup> )	$T$ (K)	$C_p^\circ$ (J K <sup>-1</sup> mole <sup>-1</sup> )
5.34	0.262	22.69	7.252	131.28	117.35
5.53	0.269	23.65	8.116	141.43	121.96
5.61	0.274	24.94	9.341	151.50	125.89
6.86	0.363	26.04	10.46	161.57	129.19
6.97	0.371	27.45	11.97	171.59	132.10
7.43	0.404	30.25	15.21	181.64	134.76
8.68	0.526	33.30	19.02	191.75	137.11
8.77	0.541	36.62	23.42	201.88	139.06
9.30	0.608	40.25	28.41	211.82	140.95
10.70	0.830	44.25	34.07	221.93	142.54
10.73	0.836	48.68	40.42	232.02	144.09
11.22	0.941	53.40	47.23	242.05	145.45
12.59	1.291	58.53	54.21	252.03	146.88
12.66	1.309	64.38	61.96	262.02	147.84
13.19	1.479	70.89	69.94	272.02	149.07
14.55	1.985	78.08	78.01	282.01	150.11
14.65	2.026	85.73	85.91	292.01	151.19
15.23	2.278	85.99	86.18	302.01	152.08
16.65	2.985	90.77	90.70	312.01	152.77
17.29	3.343	94.92	94.17	321.52	153.61
18.65	4.171	99.72	97.85	331.51	154.46
19.34	4.646	104.84	101.49	341.49	155.10
20.55	5.508	110.01	105.04		
21.42	6.190	120.77	111.74		

(final pressure  $< 1 \times 10^{-5}$  Torr). In separate experiments under the same conditions it was found that this treatment resulted in a hydride of the composition  $\alpha$ -LaNi<sub>5</sub>H<sub>0.11±0.01</sub>. Sufficient hydrogen was then added to the sample in each capsule to form the final composition  $\beta$ -LaNi<sub>5</sub>H<sub>6.39±0.01</sub>. The hydrogen reaction was carried out at 195 °K and then the temperature was lowered to 77 °K where the hydrogen equilibrium pressure is negligible. Then the free volume of each capsule was determined volumetrically using helium gas and finally a measured amount of <sup>3</sup>He gas ( $P \approx 25$  Torr) was added to each capsule and the capsules were subsequently sealed (see above) at 195 °K. After completing the heat capacity measurements of  $\beta$ -LaNi<sub>5</sub>H<sub>6.39</sub> the capsules were opened in the dry box, readied and attached to the gas-handling system and finally evacuated for 20 h at 400 °K (final pressure  $< 1 \times 10^{-5}$  Torr). The hydride composition under these conditions was established to be  $\alpha$ -LaNi<sub>5</sub>H<sub>0.076±0.006</sub>. Then hydrogen was added, as described above for the  $\beta$ -hydride, to obtain a final composition  $\alpha$ -LaNi<sub>5</sub>H<sub>0.360±0.006</sub>. The capsules were again sealed with known amounts of <sup>3</sup>He exchange gas. <sup>3</sup>He rather than <sup>4</sup>He was used to minimize the chance that significant amounts of helium would adsorb on the finely powdered hydrides below 15 °K.

#### D. Calorimeter and calorimetric apparatus

A gold-plated copper calorimetric vessel (internal volume  $\approx 34 \text{ cm}^3$ ) was used to contain all seven loaded copper capsules. This vessel was evacuated and then <sup>4</sup>He exchange gas ( $P \approx 70$  Torr) was added to promote rapid heat interchange between the seven capsules and the calorimetric vessel. Details of the adiabatic calori-

metric apparatus and the measuring circuits have been described in previous publications.<sup>13,14</sup>

#### E. Heat capacity calculations

The heat capacity of the calorimeter including the seven empty capsules was determined in a separate series of measurements. The usual corrections were applied to allow for small differences in the amounts of copper, gold, solder, helium exchange gas and grease between the empty capsules plus calorimeter and the loaded capsules plus calorimeter. In the cases of the two hydrides it was also necessary to apply significant corrections above about 250 °K due to the release of hydrogen from the solid hydrides into the free volume in each capsule. In separate experiments we found that below 300 °K and down to below 195 °K, the hydrogen above our  $\alpha$ - and  $\beta$ -LaNi<sub>5</sub>H<sub>x</sub> samples is rapidly absorbed when the temperature is lowered and rapidly evolved as the temperature is increased. During a heat capacity run, as the temperature increases in the electrical heating period, hydrogen is released with the absorption of heat. To allow for this effect we have applied a correction by adding  $-T(d/dt)(V_F dP/dT)$  to the measured heat capacity, where  $V_F$  is the sum of the free volumes in the seven capsules and  $P$  is the hydrogen pressure at temperature  $T$ .<sup>15,16</sup> The values of  $V_F$  amounted to  $5.917 \text{ cm}^3$  for  $\alpha$ -LaNi<sub>5</sub>H<sub>0.36</sub> and  $4.674 \text{ cm}^3$  for  $\beta$ -LaNi<sub>5</sub>H<sub>6.39</sub>. The equilibrium hydrogen pressure for each case was evaluated from experimental data and fitted to an equation of the form

$$\log P_{\text{Torr}}(T) = \frac{A}{T} + B. \quad (1)$$

TABLE III. Experimental heat capacity of La<sub>0.997</sub>Ni<sub>5.003</sub>H<sub>0.36</sub>, at constant pressure  
 $M(\text{La}_{0.997}\text{Ni}_{5.003}\text{H}_{0.36}) = 432.53 \text{ g mole}^{-1}$ .

$T$ (K)	$C_p^\circ$ (JK <sup>-1</sup> mole <sup>-1</sup> )	$T$ (K)	$C_p^\circ$ (JK <sup>-1</sup> mole <sup>-1</sup> )	$T$ (K)	$C_p^\circ$ (JK <sup>-1</sup> mole <sup>-1</sup> )
5.54	0.266	25.82	10.21	107.40	104.21
5.87	0.295	27.59	12.11	117.59	111.04
7.29	0.402	28.40	13.03	127.72	116.86
7.70	0.435	30.40	15.41	137.70	121.95
9.17	0.613	33.46	19.25	147.71	126.37
9.62	0.671	36.81	23.75	157.77	130.29
11.13	0.943	40.52	28.88	167.79	133.72
11.63	1.055	44.62	34.75	177.77	136.90
13.13	1.473	49.38	41.58	187.77	139.77
13.66	1.643	49.63	42.09	197.79	142.37
15.19	2.255	54.11	48.43	207.81	144.73
15.72	2.504	54.90	49.58	217.83	146.82
17.28	3.326	59.68	55.99	227.85	148.91
17.77	3.608	60.35	57.03	237.86	150.88
19.37	4.640	66.38	64.75	247.87	152.56
19.80	4.933	72.99	72.80	257.89	154.33
21.44	6.177	80.39	80.94	267.92	155.85
21.87	6.521	80.73	81.28	277.93	157.50
22.49	7.054	88.59	89.26	287.93	159.06
23.52	7.971	88.84	89.40	297.93	160.44
25.10	9.480	97.72	97.03		

TABLE IV. Experimental heat capacity of La<sub>0.997</sub>Ni<sub>5.003</sub>H<sub>6.39</sub>, at constant pressure  
 $M(\text{La}_{0.997}\text{Ni}_{5.003}\text{H}_{6.39}) = 438.61 \text{ g mole}^{-1}$ .

$T$ (K)	$C_p^\circ$ (JK <sup>-1</sup> mole <sup>-1</sup> )	$T$ (K)	$C_p^\circ$ (JK <sup>-1</sup> mole <sup>-1</sup> )	$T$ (K)	$C_p^\circ$ (JK <sup>-1</sup> mole <sup>-1</sup> )
5.65	0.360	50.43	58.11	137.15	145.24
5.93	0.394	55.72	66.45	139.08	146.43
7.30	0.589	61.22	74.45	140.32	147.57
7.52	0.626	67.41	82.84	141.08	147.70
8.99	0.931	74.25	91.50	143.07	148.85
9.33	1.017	81.74	100.16	145.06	149.81
10.62	1.410	82.49	101.04	147.06	150.98
11.22	1.626	90.05	108.94	149.05	151.84
12.49	2.180	90.68	109.59	150.34	152.75
13.20	2.558	99.63	117.44	151.06	152.81
14.48	3.344	105.03	121.52	153.06	153.76
15.23	3.875	107.07	123.20	156.06	155.04
16.48	4.874	109.15	124.86	160.05	156.89
17.31	5.614	109.47	125.39	160.35	157.19
18.49	6.754	111.18	126.48	164.04	158.58
19.39	7.706	113.18	127.98	170.38	161.52
20.49	8.969	115.18	129.64	180.38	166.33
21.43	10.08	117.18	131.10	190.35	171.42
22.57	11.56	119.18	132.68	200.35	176.69
23.55	12.88	119.90	133.35	210.35	181.96
24.84	14.73	121.18	134.03	211.63	182.62
25.91	16.35	123.17	135.61	221.62	187.97
27.35	18.59	125.17	136.59	231.63	193.05
28.50	20.47	127.17	138.36	241.57	197.98
30.11	23.13	129.16	139.80	251.42	202.70
33.11	28.27	130.24	140.93	261.32	208.38
36.42	34.08	131.16	141.24	271.29	214.48
40.06	40.40	133.16	142.62	281.25	221.70
44.04	47.31	135.15	143.92	291.21	230.04
48.59	54.98	137.07	145.09	298.71	236.94

The constants  $A$  and  $B$  for  $\alpha$ -LaNi<sub>5</sub>H<sub>0.36</sub> were found to be (assuming a constant hydrogen content of the solid hydride)  $A = -1358$  and  $B = 6.894$  based upon a comparison of data we obtained with literature values.<sup>5</sup> This correction amounts to only 0.08% of the heat capacity (Table III) near 300 °K and even less at lower temperatures.

For the case of  $\beta$ -LaNi<sub>5</sub>H<sub>6.39</sub> this correction was larger, as expected. Since no appropriate hydrogen equilibrium values for this hydride composition were available we obtained the experimental values given in Table V using a portion of our calorimetric sample. In the temperature range from 250 to 300 °K, the constants  $A = -1929.6$  and  $B = 9.880$  represent the best fit to the pressures in Table V. The calculated corrections amounted to 0.5% near 250 °K and to 4.1% near 300 °K of the heat capacities (Table IV). The decrease of hydrogen content of the  $\beta$ -LaNi<sub>5</sub>H<sub>x</sub> sample in the calorimeter at 300 °K compared to a low temperature (~200 °K) where essentially all the hydrogen would be in the solid hydride ( $x = 6.39$ ) amounted to  $x = 0.013$ . It was assumed that the <sup>3</sup>He in the capsules did not influence the hydrogen pressures.

All the various corrections, including the dominant correction of the heat capacity of the empty capsules plus calorimeter, ranged between 47% and 67% of the heat capacities reported in Tables III and IV.

### III. HEAT CAPACITY RESULTS

The experimental molar heat capacities of LaNi<sub>5</sub>,  $\alpha$ -LaNi<sub>5</sub>H<sub>0.36</sub> and  $\beta$ -LaNi<sub>5</sub>H<sub>6.39</sub> are given in Tables II, III, and IV, respectively. The approximate temperature increments for the individual heat capacity determinations were as follows: for  $\bar{T} < 20$  °K,  $\Delta T \approx 2$  °K; for  $20$  °K  $< \bar{T} < 100$  °K,  $\Delta T \approx 0.1 \bar{T}$ ; and for  $\bar{T} > 100$  °K,  $\Delta T = 10$  °K. Corrections for these finite temperature increments were applied to all values in Tables II–IV by means of the formula given in a previous publication.<sup>14</sup> The estimated probable errors of the heat capacity values in Tables II–IV are 5% at 5 °K, 1% at 15 °K, 0.5% at 20 °K, and 0.25% above 30 °K.

After the first series of determinations in the tem-

TABLE V. Hydrogen equilibrium<sup>a</sup> pressures for La<sub>0.997</sub>Ni<sub>5.003</sub>H<sub>6.39</sub>.

$T$ (K)	H <sub>2</sub> pressure (Torr <sup>b</sup> )
202.5	3.96
209.0	6.96
219.4	16.4
229.2	35.6
239.3	73.7
249.3	132
259.6	280
269.2	523
279.6	971
289.0	1620
291.8	1830

<sup>a</sup>These pressures were obtained by desorption of a small amount of hydrogen from the hydride.

<sup>b</sup>1 Torr = 1/760 atm.

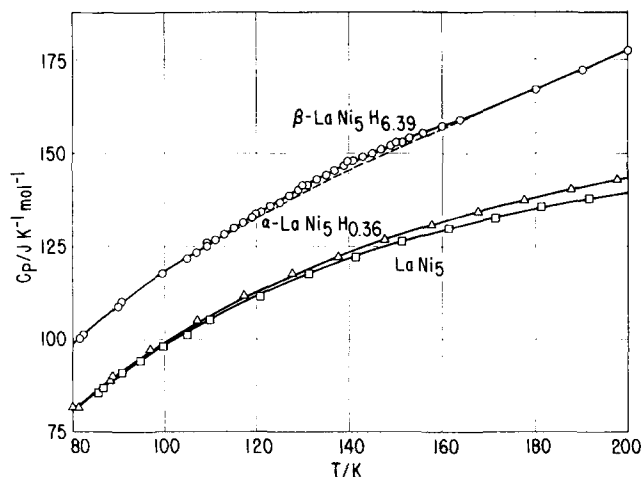


FIG. 2. The heat capacity of  $\beta$ -LaNi<sub>5</sub>H<sub>6.39</sub> from 80 to 200 °K; the dashed section indicates the expected "normal" heat capacity between 120 and 160 °K (see text). The heat capacities of LaNi<sub>5</sub> and  $\alpha$ -LaNi<sub>5</sub>H<sub>0.36</sub> are shown for comparison.

perature range 100 to 200 °K were completed for  $\beta$ -LaNi<sub>5</sub>H<sub>6.39</sub> it was noted that the heat capacities at  $T = 140.32$  and  $150.34$  °K (Table IV) were high by about 1% and 2%, respectively, compared to a smooth curve drawn through data points just above and below these temperatures. We therefore made additional measurements in this temperature region as follows: from 104 to 154 °K with  $\Delta T \approx 2$  °K, and 154 to 162 °K with  $\Delta T \approx 4$  °K. All these results, together with the curves for LaNi<sub>5</sub> and  $\alpha$ -LaNi<sub>5</sub>H<sub>0.36</sub> for comparison, are presented graphically in Fig. 2. The dashed line from about 120 to 160 °K represents the expected "normal"  $C_p$  for  $\beta$ -LaNi<sub>5</sub>H<sub>6.39</sub>. A possible cause for this small anomaly will be discussed in a later section of this paper.

### IV. DERIVED RESULTS AND COMPARISONS

#### A. Thermodynamic functions

The molar heat capacities listed in Tables II–IV were fitted by the method of least squares to two overlapping polynomials, one covered the temperature span from 5 to 40 °K and the second from 20 to 300 °K. Values of the functions  $C_p^\circ$ ,  $S^\circ$ ,  $H^\circ(T) - H^\circ(0)$ , and  $-[G^\circ(T) - H^\circ(0)]/T$  at selected temperatures from 5 to 350 °K for LaNi<sub>5</sub> are given in Table VI and from 5 to 300 °K for  $\alpha$ -LaNi<sub>5</sub>H<sub>0.36</sub> and  $\beta$ -LaNi<sub>5</sub>H<sub>6.39</sub> in Tables VII and VIII, respectively. The probable errors associated with the functions in these three tables are estimated to be 0.25% above 30 °K.

#### B. Extrapolation to 0 °K and electronic and lattice heat capacities

To obtain values of  $S^\circ$  and  $H^\circ(T) - H^\circ(0)$  shown in parentheses for  $T = 5$  °K in Tables VI–VIII it was necessary to extrapolate to 0 °K and to assume  $S^\circ = 0$  at 0 °K. Heat capacity data below about 12 °K were fitted to equations of the form

$$C_p = \gamma T + \beta T^3 + \delta T^5, \quad (2)$$

where  $\gamma T$  represents the contribution associated with the conduction electrons,  $\beta T^3$  represents the contribution of

TABLE VI. Thermodynamic functions for La<sub>0.997</sub>Ni<sub>5.003</sub>.

$T$ (K)	$C_p$ (J K <sup>-1</sup> mole <sup>-1</sup> )	$S^\circ(T)$ (J K <sup>-1</sup> mole <sup>-1</sup> )	$H^\circ(T) - H^\circ(0)$ (J mole <sup>-1</sup> )	$-[G^\circ(T) - H^\circ(0)]/T$ (J K <sup>-1</sup> mole <sup>-1</sup> )
5	0.238	(0.224)	(0.57)	(0.110)
10	0.708	0.507	2.73	0.234
15	2.177	1.024	9.35	0.401
20	5.106	2.017	26.97	0.669
25	9.043	3.594	62.69	1.086
30	14.90	5.779	123.0	1.679
35	21.23	8.542	213.1	2.453
40	28.07	11.82	336.2	3.415
45	35.17	15.53	494.2	4.548
50	42.33	19.61	688.0	5.850
60	56.22	28.57	1181.5	8.878
70	68.93	38.21	1808.4	12.38
80	80.13	48.16	2555	16.22
90	89.81	58.17	3406	20.33
100	98.11	68.08	4347	24.61
110	105.2	77.77	5364	29.01
120	111.3	87.20	6448	33.47
130	116.6	96.32	7588	37.95
140	121.2	105.14	8778	42.44
150	125.2	113.64	10011	46.90
160	128.7	121.84	11282	51.33
170	131.8	129.74	12584	55.71
180	134.4	137.33	13915	60.04
190	136.7	144.67	15271	64.30
200	138.7	151.74	16648	68.50
210	140.6	158.55	18045	72.62
220	142.2	165.13	19460	76.68
230	143.8	171.49	20890	80.66
240	145.2	177.64	22335	84.58
250	146.5	183.59	23793	88.42
260	147.7	189.36	25264	92.19
270	148.9	194.96	26748	95.89
280	149.9	200.4	28242	99.53
290	150.9	205.7	29746	103.1
300	151.8	210.8	31260	106.6
310	152.7	215.8	32782	110.0
320	153.5	220.7	34313	113.5
330	154.3	225.4	35852	116.7
340	155.0	230.0	37399	120.0
350	155.8	234.5	38953	123.2
273.15	149.2	196.7	27217	97.06
298.15	151.7	209.9	30979	106.0
	$\pm 0.4$	$\pm 0.5$	$\pm 77$	$\pm 0.3$

the lattice vibrations according to the Debye equation in the low temperature approximation, and  $\delta T^5$  allows for contributions not accounted for by the  $\beta T^3$  term. The values for the constants,  $\gamma$ ,  $\beta$  and  $\delta$  for the three cases are listed in Table IX. The appropriate integrals derived from Eq. 2 were then used to calculate the values of  $S^\circ(5)$  and  $H^\circ(5) - H^\circ(0)$  given in Tables VI–VIII. The main purpose for calculating the parameters given in Table IX was to derive the values of the entropy and enthalpy increment at 5 °K. However, the values  $\gamma$  and  $\beta$  are of obvious fundamental interest in that  $\gamma$  is proportional to the density of states at the Fermi surface and  $\beta$  can be used to calculate the Debye temperature  $\theta_D$ . A discussion of the significance of the electronic specific heats in metal–hydrogen systems has been published recently.<sup>17</sup> To obtain the most reliable values of  $\gamma$  and  $\beta$  it is necessary to have accurate heat capacities for well-characterized samples in the temperature range about 1–10 °K, but especially in the range below 5 °K.

No previous results for the  $\alpha$ - and  $\beta$ -hydrides have been published, but there are two sets of low-temperature heat capacities for LaNi<sub>5</sub>. Nasu *et al.*<sup>18</sup> have measured the heat capacity of LaNi<sub>5</sub> from 1.6 to 4.2 °K and from a fit of their data to the equation  $C_p = \gamma T + \beta T^3$  they found  $\gamma = 3.43 \times 10^{-2}$  J °K<sup>-2</sup> mole<sup>-1</sup> and  $\beta = 2.99 \times 10^{-4}$  J °K<sup>-4</sup> mole<sup>-1</sup>. Heat capacity measurements from 1 to 5 °K by Thome and Gschneidner<sup>19</sup> gave  $\gamma = 3.65 \times 10^{-2}$  J °K<sup>-2</sup> mole<sup>-1</sup> and  $\beta = 2.69 \times 10^{-4}$  J K<sup>-4</sup> mole<sup>-1</sup>. Although these two sets of  $\gamma$ 's and  $\beta$ 's are in fair agreement, it is not too surprising that our values (also see footnote for Table IX) obtained at temperatures higher than the others are significantly different. Obviously the values obtained at the lower temperatures are to be preferred. However, it is worth noting that our values of  $\gamma$  for LaNi<sub>5</sub> and for the two hydrides suggest that  $\gamma$  does not change radically as hydrogen is added to LaNi<sub>5</sub>. Also, it can be concluded from the  $\beta$  values in Table IX that the lattice heat capacity of  $\beta$ -LaNi<sub>5</sub>H<sub>6.39</sub> at low temperatures, where contributions

TABLE VII. Thermodynamic functions for La<sub>0.997</sub>Ni<sub>5.003</sub>H<sub>0.36</sub>.

$T$ (K)	$C_p^\circ$ (J K <sup>-1</sup> mole <sup>-1</sup> )	$S^\circ(T)$ (J K <sup>-1</sup> mole <sup>-1</sup> )	$H^\circ(T) - H^\circ(0)$ (J mole <sup>-1</sup> )	$-[G^\circ(T) - H^\circ(0)]/T$ J K <sup>-1</sup> mole <sup>-1</sup>
5	0.230	(0.208)	(0.53)	(0.102)
10	0.734	0.495	2.74	0.221
15	2.173	1.018	9.43	0.389
20	5.079	2.008	26.98	0.659
25	9.387	3.578	62.56	1.075
30	14.91	5.762	122.89	1.666
35	21.28	8.531	213.1	2.442
40	28.18	11.82	336.6	3.404
45	35.33	15.55	495.3	4.542
50	42.54	19.64	690.0	5.840
60	56.51	28.65	1186	8.883
70	69.29	38.34	1816	12.39
80	80.58	48.35	2567	16.26
90	90.38	58.42	3423	20.38
100	98.83	68.39	4370	24.69
110	106.1	78.16	5396	29.11
120	112.5	87.67	6490	33.59
130	118.1	96.90	7643	38.11
140	123.0	105.8	8849	42.63
150	127.3	114.5	10101	47.13
160	131.1	122.8	11393	51.60
170	134.5	130.9	12721	56.03
180	137.6	138.6	14082	60.40
190	140.3	146.2	15472	64.72
200	142.9	153.4	16888	68.97
210	145.2	160.4	18328	73.16
220	147.4	167.2	19791	77.29
230	149.4	173.8	21275	81.34
240	151.2	180.2	22778	85.33
250	153.0	186.4	24299	89.25
260	154.6	192.5	25837	93.11
270	156.2	198.3	27391	96.89
280	157.8	204.1	28961	100.6
290	159.3	209.6	30547	104.3
300	160.7	215.0	32148	107.9
273.15	156.7	200.2	27884	98.12
298.15	160.5	214.1	31850	107.3
	$\pm 0.4$	$\pm 0.5$	$\pm 80$	$\pm 0.3$

from the optical modes associated with hydrogen vibrations would be negligible, is very much higher than either LaNi<sub>5</sub> or  $\alpha$ -LaNi<sub>5</sub>H<sub>0.36</sub> (see later discussion).

### C. Heat capacity of LaNi<sub>5</sub>—comparison with literature values of 300 °K

Marzouk *et al.*<sup>20</sup> have measured the heat capacity of LaNi<sub>5</sub> from 5 to 300 °K. Compared to our heat capacities in Table VI, Marzouk *et al.*<sup>20</sup> are 38% lower at 10 °K, 1.1% lower at 20 °K and 1.5% to 2.2% higher at 25 °K and up to 300 °K. Thome and Gschneidner<sup>19</sup> also made measurements of LaNi<sub>5</sub> up to 25 °K and compared to data in Table VI their heat capacities are 7.3% lower at 6 °K, 0.7% higher at 9 °K, and about 2.3% higher from 12 to 20 °K. These comparisons suggest that differences are due in part to errors associated with the calorimetric measurements (i.e., temperature scale) and in part to real differences in the chemical and physical properties of the samples; this latter effect is most likely to be very important below 10 °K. Further discussion of this matter in the absence of adequate sample characterization is not appropriate. However, it should be noted that

the rather significant heat capacity differences below 10 °K have little effect on the thermodynamic functions at higher temperatures (i.e., 298.15 °K) so that thermodynamic calculations of practical interest based upon derived values can be made with relatively small uncertainty limits. For example, the value of the function  $-[G^\circ(298.15^\circ\text{K} - H^\circ(0))/T]$  as reported for LaNi<sub>5</sub> in Table VI is  $106.0 \pm 0.3$  J °K<sup>-1</sup> mole<sup>-1</sup> and the value reported by Marzouk *et al.*<sup>20</sup> is 107.2 J °K mole<sup>-1</sup> (no uncertainty given).

## VI. DISCUSSION

### A. $\beta$ -LaNi<sub>5</sub>H<sub>6.39</sub>—heat capacity anomaly 120–160 °K

The heat capacities of LaNi<sub>5</sub> and  $\alpha$ -LaNi<sub>5</sub>H<sub>0.36</sub> are nearly identical below 100 °K and the  $C_p^\circ$  of the  $\alpha$ -hydride gradually becomes larger at higher temperatures. However, at 300 °K,  $C_p^\circ(\text{LaNi}_5)/6 = 25.3$  J °K<sup>-1</sup> (g-at.)<sup>-1</sup> and  $C_p^\circ(\alpha\text{-LaNi}_5\text{H}_{0.36})/6.36 = 25.3$  J °K<sup>-1</sup> (g-at.)<sup>-1</sup> and this circumstance strongly suggests that the hydrogen interstitials in the  $\alpha$ -hydride exert but little influence on the elastic constants of the LaNi<sub>5</sub> host metal. In agree-



TABLE VIII. Thermodynamic functions for La<sub>0.997</sub>Ni<sub>5.003</sub>H<sub>6.39</sub>.

$T$ (K)	$C_p^s$ (J K <sup>-1</sup> mole <sup>-1</sup> )	$S^s(T)$ (J K <sup>-1</sup> mole <sup>-1</sup> )	$H^s(T) - H^s(0)$ (J mole <sup>-1</sup> )	$-[G^s(T) - H^s(0)]/T$ (J K <sup>-1</sup> mole <sup>-1</sup> )
5	0.293	(0.234)	(0.62)	(0.110)
10	1.206	0.659	3.94	0.265
15	3.706	1.550	15.34	0.527
20	8.391	3.208	44.71	0.972
25	14.97	5.775	102.39	1.659
30	22.94	9.172	196.73	2.615
35	31.59	13.35	332.9	3.842
40	40.38	18.15	512.9	5.325
45	48.99	23.40	736.4	7.038
50	57.27	29.00	1002.2	8.952
60	72.68	40.82	1653.2	13.27
70	86.44	53.08	2450	18.08
80	98.39	65.42	3376	23.23
90	108.6	77.62	4412	28.59
100	117.5	89.53	5544	34.09
110	125.6	101.1	6760	39.66
120	133.3	112.4	8055	45.26
130	140.5	123.3	9424	50.84
140	146.9	134.0	10862	56.40
150	152.4	144.3	12359	61.92
160	157.1	154.3	13907	67.38
170	161.4	164.0	15499	72.78
180	166.0	173.3	17136	78.11
190	171.0	182.4	18820	83.36
200	176.4	191.3	20557	88.54
210	181.9	200.1	22348	93.64
220	187.2	208.6	24194	98.67
230	192.2	217.1	26091	103.6
240	197.0	225.4	28037	108.5
250	202.1	233.5	30033	113.4
260	207.6	241.5	32081	118.1
270	213.7	249.5	34186	122.9
280	220.7	257.4	36357	127.5
290	229.0	265.3	38604	132.1
300	238.2	273.2	40940	136.7
273.15	215.8	252.0	34862	124.4
298.15	236.4	271.7	40501	135.9
	$\pm 0.6$	$\pm 0.7$	$\pm 101$	$\pm 0.3$

ment with the above result, Fischer *et al.*<sup>12</sup> found by neutron diffraction that  $\alpha$ -LaNi<sub>5</sub>D<sub>0.25</sub> had the same structure (hexagonal, space group  $P6/mmm$ ) as pure LaNi<sub>5</sub>; however, a small elongation along the  $a$ -axis of the  $\alpha$ -deuteride was reported.<sup>12</sup>

The formation of  $\beta$ -LaNi<sub>5</sub>H<sub>6</sub> from LaNi<sub>5</sub> is accompanied by a  $\sim 25\%$  lattice expansion due to the additional hydrogen located in interstitial sites. As was first deduced by Bowman *et al.*<sup>10</sup> and substantiated by others<sup>11,12</sup> the space group of the  $\beta$ -hydride is  $P31m$  which is a lower symmetry derivative of the  $P6/mmm$  space group assigned to LaNi<sub>5</sub>. This change in structure is reflected in a much higher lattice heat capacity of  $\beta$ -LaNi<sub>5</sub>H<sub>6.39</sub> compared to LaNi<sub>5</sub>. This change can readily be seen by making the comparison at low temperatures (10 to 50 °K) (see Tables VI–VIII or a plot in another publication<sup>21</sup>) since at these temperatures the contribution of the acoustic modes is very large compared to the contributions from the conduction electrons and from the optical modes associated with hydrogen vibrations. As can be seen in Fig. 2, there is a small enhancement in the heat capacity of  $\beta$ -LaNi<sub>5</sub>H<sub>6.39</sub> in the temperature range 120–160 °K;

the dashed line below the experimental points (circles) corresponds in our judgment to a “normal” heat-capacity curve. Several NMR investigations of  $\beta$ -LaNi<sub>5</sub>H<sub>x</sub> have been reported in the literature.<sup>11,22–24</sup> Barnes *et al.*<sup>11</sup> and Halstead<sup>22</sup> indicated that above about 140 °K there is a rapid diffusive motion of the hydrogen in the  $\beta$ -hydride. According to Gualtieri and Wallace,<sup>6</sup> LaNi<sub>5</sub> does not react with hydrogen below 140 °K. The entropy associated with the small anomaly in the heat capacity of  $\beta$ -

TABLE IX. Values of the coefficients in the equation  $C_p = \gamma T + \beta T^3 + \delta T^5$  which were used to represent the measured heat capacities below 12 °K.

Sample	$\gamma$ [J °K <sup>-2</sup> mole <sup>-1</sup> ]	$\beta$ [J °K <sup>-4</sup> mole <sup>-1</sup> ]	$\delta$ [J °K <sup>-6</sup> mole <sup>-1</sup> ]
LaNi <sub>5</sub> <sup>a</sup>	$4.37 \times 10^{-2}$	$1.25 \times 10^{-4}$	$1.40 \times 10^{-6}$
$\alpha$ -LaNi <sub>5</sub> H <sub>0.36</sub>	$3.92 \times 10^{-2}$	$2.67 \times 10^{-4}$	$6.68 \times 10^{-7}$
$\beta$ -LaNi <sub>5</sub> H <sub>6.39</sub>	$4.09 \times 10^{-2}$	$6.83 \times 10^{-4}$	$1.15 \times 10^{-7}$

<sup>a</sup>Fitting the measured data with the more simple equation  $C_p = \gamma T + \beta T^3$  resulted in the values:  $\gamma = 4.08 \times 10^{-2}$  [J °K<sup>-2</sup> mole<sup>-1</sup>],  $\beta = 2.66 \times 10^{-4}$  [J °K<sup>-4</sup> mole<sup>-1</sup>].

TABLE X. Some derived thermodynamic functions for the LaNi<sub>5</sub>-H<sub>2</sub> system at 298.15 °K.

$\Delta S_{\alpha-\beta}^{\circ}$ J °K <sup>-1</sup> (mole H <sub>2</sub> ) <sup>-1</sup>	-111.5 ± 0.5
$\Delta S_{\beta}^{\circ}$ J °K <sup>-1</sup> (mole H <sub>2</sub> ) <sup>-1</sup>	-111.2 ± 0.5
$\Delta\{H^{\circ}(T) - H^{\circ}(0)\}_{\alpha-\beta}$ J (mole H <sub>2</sub> ) <sup>-1</sup>	-5599 ± 70
$\Delta\{H^{\circ}(T) - H^{\circ}(0)\}_{\beta}$ J (mole H <sub>2</sub> ) <sup>-1</sup>	-5488 ± 70
$\Delta H_{\beta} = \Delta H_{\alpha-\beta}$ kJ (mole H <sub>2</sub> ) <sup>-1</sup>	-30.40 ± 0.35
$\Delta H_f^{\circ}$ kJ (mole $\beta$ -LaNi <sub>5</sub> H <sub>6.39</sub> ) <sup>-1</sup>	-244.7 ± 6

LaNi<sub>5</sub>H<sub>6.39</sub> between 120 and 160 °K amounts to  $S = 0.4$  J °K<sup>-1</sup> mole<sup>-1</sup>, which is small compared to the minimum entropy of  $S = R \ln 2$  usually associated with an order-disorder phase transition. Consistent with the above information we suggest that the cause of the anomaly may be that a small net change in the distribution of hydrogen atoms among the available tetrahedral interstitial sites<sup>10-12</sup> occurs in the region 120 to 160 °K and that the hydrogen "freezes" in certain tetrahedral sites at lower temperatures.

### B. Entropy and enthalpy of formation of $\beta$ -LaNi<sub>5</sub>H<sub>6.39</sub>

In another publication<sup>21</sup> we calculated the entropy of formation of  $\beta$ -LaNi<sub>5</sub>H<sub>3.39</sub>,  $\Delta S_{\beta}^{\circ}$ , according to the equation

$$\Delta S_{\beta}^{\circ} = \frac{2}{6.39} S^{\circ}(\beta\text{-LaNi}_5\text{H}_{6.39}) - \frac{2}{6.39} S^{\circ}(\text{LaNi}_5) - S_{\text{H}_2}^{\circ}, \quad (3)$$

and the entropy of transition of the  $\alpha$ - to the  $\beta$ -hydride  $\Delta S_{\alpha-\beta}$ , according to the equation

$$\Delta S_{\alpha-\beta}^{\circ} = \frac{2}{(6.39 - 0.36)} S^{\circ}(\beta\text{-LaNi}_5\text{H}_{6.39}) - \frac{2}{(6.39 - 0.36)} S^{\circ}(\alpha\text{-LaNi}_5\text{H}_{0.36}) - S_{\text{H}_2}^{\circ} \quad (4)$$

The entropy values for the  $\alpha$ - and  $\beta$ -hydrides were taken from Tables VII and VIII. In agreement with findings of Wicke and Brodowsky<sup>25</sup> we found for this metal-hydrogen system where the maximum hydrogen content of the  $\alpha$ -phase,  $\alpha_{\text{max}}$ , is small compared to the minimum hydrogen content of the  $\beta$ -phase,  $\beta_{\text{min}}$ , i.e.,  $\alpha_{\text{max}} \ll \beta_{\text{min}}$ , that  $\Delta S_{\beta}^{\circ} = \Delta S_{\alpha-\beta}^{\circ}$  within probable error limits from 100 to 300 °K<sup>21</sup> (see Table X for values at 298.15 °K). The values of  $\Delta S_{\beta}^{\circ}$  at 195, 273.15, and 298.15 °K were found to be  $-106.5 \pm 0.5$ ,  $-110.8 \pm 0.5$ , and  $-111.2 \pm 0.5$  J °K<sup>-1</sup> (mole H<sub>2</sub>)<sup>-1</sup>, respectively. It is apparent that there is a small, but definite, temperature variation of  $\Delta S^{\circ} = \Delta S_{\alpha-\beta}^{\circ}$ ; this temperature dependence was not previously established on the basis of equilibrium pressure data alone.<sup>4, 5, 26, 27</sup> Our value  $\Delta S_{\beta}^{\circ}$  at 298.15 °K is in reasonable agreement with values

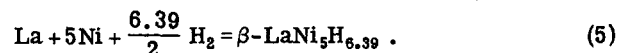
$[-107$  to  $-110$  J °K<sup>-1</sup> (mole H<sub>2</sub>)<sup>-1</sup>] from equilibrium hydrogen pressure measurements just above and below 298.15 °K.<sup>21</sup> This agreement supports our assumption that  $S^{\circ}(0 \text{ °K}) = 0$  for  $\beta$ -LaNi<sub>5</sub>H<sub>6.39</sub> and indicates that any disorder at 0 °K associated with the interstitial hydrogen must be small or negligible relative to  $S^{\circ}(298.15 \text{ °K})$ .

We have calculated values for the change in the enthalpy increments,  $[H^{\circ}(T) - H^{\circ}(0)]$ , using equations analogous to Eqs. (3) and (4) above, to obtain  $\Delta[H^{\circ}(T) - H^{\circ}(0)]_{\beta}$  and  $\Delta[H^{\circ}(T) - H^{\circ}(0)]_{\alpha-\beta}$  and these two quantities were found to be equal within error limits between 100 and 300 °K<sup>21</sup> (also see Table X). A 273.15 °K absorption isotherm was measured using a portion of our LaNi<sub>5</sub> sample and the pressure (near the center of the plateau) was found to be  $P_{\alpha-\beta} = 673 \pm 67$  Torr. From the equation  $\Delta H(273.15 \text{ °K})_{\alpha-\beta} = T [R \ln P(273.15 \text{ °K})]_{\alpha-\beta} + \Delta S^{\circ}(273.15 \text{ °K})_{\alpha-\beta}$  we calculated  $\Delta H(273.15 \text{ °K})_{\alpha-\beta} = -30.24 \pm 0.35$  kJ (mole H<sub>2</sub>)<sup>-1</sup>. Correcting this to 298.15 °K we found the value  $-30.40 \pm 0.35$  kJ (mole H<sub>2</sub>)<sup>-1</sup> as given in Table X. The value of  $\Delta H(195 \text{ °K})_{\alpha-\beta}$  was calculated to be  $-29.20 \pm 0.35$  kJ (mole H<sub>2</sub>)<sup>-1</sup> and thus we have established that  $\Delta H_{\alpha-\beta}$  has a small variation with temperature. These results are compared with  $\Delta H_{\alpha-\beta}$  values derived from equilibrium hydrogen pressures and with a direct calorimetric determination<sup>28</sup> and general agreement was found.<sup>21</sup> Within the limits of error we find  $\Delta H_{\alpha-\beta} = \Delta H_{\beta}$  at near 298.15 °K.

Two values for the heat of formation of LaNi<sub>5</sub> at 298.15 °K,  $\Delta H_f^{\circ}(\text{LaNi}_5)$ , have been published recently. Diaz *et al.*<sup>29</sup> reported  $\Delta H_f^{\circ}(\text{LaNi}_5) = -127.6 (\pm 4)$  kJ mole<sup>-1</sup> and Semenenko *et al.*<sup>30</sup> reported  $-126.3 (\pm 7.5)$  kJ mole<sup>-1</sup>. The error limit for the first value was not reported by Diaz *et al.*<sup>29</sup> and represent the present authors' assessment, and the value given by Semenenko *et al.*<sup>30</sup> was their error limit. Using the average of these two values of  $\Delta H_f^{\circ}(\text{LaNi}_5) = -127 \pm 6$  kJ mole<sup>-1</sup> and our value of  $\Delta H_{\beta} = -30.40 \pm 0.35$  kJ (mole H<sub>2</sub>)<sup>-1</sup> we calculate at 298.15 °K:

$$\Delta H_f^{\circ}(\beta\text{-LaNi}_5\text{H}_{6.39}) = \frac{6.39}{2} \Delta H_{\beta} + \Delta H_f^{\circ}(\text{LaNi}_5) = -224 \pm 6 \text{ kJ mole}^{-1},$$

which represent the enthalpy change for the reaction



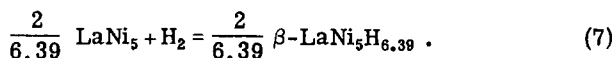
### C. Entropy effects associated with the formation of $\beta$ -LaNi<sub>5</sub>H<sub>6</sub>

The hydrogen plateau pressures in the  $\alpha + \beta$  LaNi<sub>5</sub>H<sub>x</sub> two-phase region can be represented by the relationship

$$\ln P_{\text{H}_2} = \frac{\Delta H}{RT} - \frac{\Delta S}{R}, \quad (6)$$

where  $\Delta H$  is the enthalpy of formation of the  $\beta$ -phase from the  $\alpha$ -phase for the reaction of one mole of hydrogen,  $\Delta S$  is the entropy change per mole of hydrogen, and  $R$  is the molar gas constant. It has been proposed<sup>3, 31</sup> that the plateau pressures for a large number of metal-hydrogen systems, including AB<sub>5</sub>-hydrogen systems, can be estimated from values of  $\Delta H$  alone because the

$\Delta S$  effect is due mostly to the high entropy of hydrogen (130.6 J °K<sup>-1</sup> mole<sup>-1</sup> at 298.15 °K) as its entropy is lost when it enters the interstitial sites of the metal or alloy. It has been indicated by Gruen and Mendelsohn<sup>32</sup> that configurational entropies of AB<sub>5</sub>-hydrides can be of considerable importance in the magnitude of the hydrogen plateau pressures. A more detailed knowledge of the various entropy effects associated with the formation of  $\beta$ -LaNi<sub>5</sub>H<sub>x</sub> would be of obvious benefit for a proper understanding of the fundamental properties of this and perhaps other metal-hydrogen systems. In the discussion below we calculate, either from experimental data or reasonable estimates, the various entropy changes for the reaction:



If we ascribe changes in the thermodynamic functions accompanying the formation of  $\beta$ -LaNi<sub>5</sub>H<sub>6.39</sub> [Eq. (7)] to the effects related to the presence of the interstitial hydrogen in the hydride and if the phase boundary compositions ( $\alpha_{\max}$ ,  $\beta_{\min}$ ) are nearly temperature independent, as can be assumed from published isotherms,<sup>1,4,5,26,27</sup> then the partial molar entropy per mole of H<sub>2</sub> in  $\beta$ -LaNi<sub>5</sub>H<sub>6.39</sub> can be calculated as previously discussed for the palladium-hydrogen system<sup>25</sup> by the relationship:

$$\begin{aligned} \bar{S}_{\text{H}_2}^{\beta} &= \frac{2}{6.39 - 0.36} S^{\circ}(\beta\text{-LaNi}_5\text{H}_{6.39}) \\ &\quad - \frac{2}{6.39 - 0.36} S^{\circ}(\alpha\text{-LaNi}_5\text{H}_{0.36}) \\ &= \Delta S_{\alpha-\beta}^{\circ} + S_{\text{H}_2}^{\circ} \end{aligned} \quad (8)$$

In the present instance we have previously shown that  $\alpha_{\max} < \beta_{\min}$  and therefore we can write:

$$\begin{aligned} \bar{S}_{\text{H}_2}^{\beta} &= \frac{2}{6.39} S^{\circ}(\beta\text{-LaNi}_5\text{H}_{6.39}) \\ &\quad - \frac{2}{6.39} S^{\circ}(\text{LaNi}_5) = \Delta S_{\beta}^{\circ} + S_{\text{H}_2}^{\circ} \end{aligned} \quad (9)$$

At 298.15 °K we find  $\bar{S}_{\text{H}_2}^{\beta} = -(111.2 \pm 0.5) + 130.57 = 19.4 \pm 0.5$  J °K<sup>-1</sup> (mole H<sub>2</sub>)<sup>-1</sup>. The entropy of hydrogen was taken from Haar *et al.*<sup>33</sup>

We now consider the various entropy contributions to  $\bar{S}_{\text{H}_2}^{\beta}$  and will follow the discussion given by O'Keefe and Steward<sup>34</sup> involving the following equation:

$$\bar{S}_{\text{H}_2}^{\beta} = S_{\text{optical}} + S_{\text{lattice}} + S_{\text{el}} + S_{\text{conf}} \quad (10)$$

where  $S_{\text{optical}}$  is the vibrational (optical phonon branch) entropy associated with the hydrogen atoms in the hydride,  $S_{\text{lattice}}$  is the additional lattice entropy occasioned by the dilation of LaNi<sub>5</sub> to form the  $\beta$ -hydride (~25% volume increase),  $S_{\text{el}}$  is the entropy change which occurs on addition of the electrons from the hydrogen in the hydride to the alloy conduction band, and  $S_{\text{conf}}$  is the configurational entropy.

$S_{\text{optical}}$  can be calculated if the hydrogen vibration frequencies and degeneracies are known. Although these frequencies have not been determined for  $\beta$ -LaNi<sub>5</sub>H<sub>6.39</sub>, it is possible to infer a reasonable average frequency

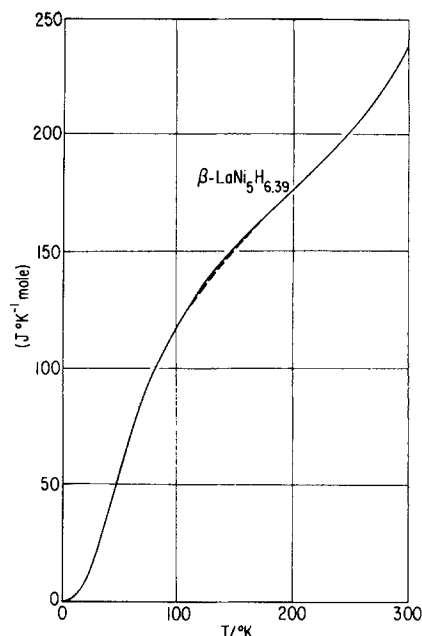


FIG. 3. The heat capacity of  $\beta$ -LaNi<sub>5</sub>H<sub>6.39</sub> from 0 to 300 °K.

from experimentally derived frequencies for hydrogen believed to be in tetrahedral sites in other metal hydrides as reported in the literature. We cite the following hydrides and their journal references from which we concluded that the hydrogen frequencies in tetrahedral sites average  $1000 \pm 90$  cm<sup>-1</sup>: ZrH<sub>2</sub>,<sup>35,36</sup> YH<sub>2</sub>,<sup>37,38</sup> YH<sub>3</sub>,<sup>37,39</sup> UH<sub>3</sub>,<sup>37,40</sup> VH<sub>0.2</sub>-VH<sub>1.2</sub>,<sup>41</sup> VH<sub>1.49</sub>-VH<sub>1.71</sub>,<sup>41</sup> LaH<sub>2</sub>,<sup>42,43</sup> LaH<sub>3</sub>,<sup>42</sup> CeH<sub>3</sub>,<sup>42,44</sup> From Einstein harmonic-oscillator functions,<sup>45</sup> we then calculate  $S_{\text{optical}} = 1.6$  J °K<sup>-1</sup> (mole H<sub>2</sub>)<sup>-1</sup> at 298.15 °K for a hydrogen frequency of 1000 cm<sup>-1</sup>. If an average frequency of 900 cm<sup>-1</sup> is assumed  $S_{\text{optical}} = 2.5$  J °K<sup>-1</sup> (mole H<sub>2</sub>)<sup>-1</sup>. From these considerations we take  $S_{\text{optical}} = 2 \pm 1$  J °K<sup>-1</sup> (mole H<sub>2</sub>)<sup>-1</sup> at 298.15 °K.

To calculate a reliable value for  $S_{\text{lattice}}$  we can use our accurate heat capacity values for LaNi<sub>5</sub> and  $\beta$ -LaNi<sub>5</sub>H<sub>6.39</sub> in conjunction with the Debye theory in the following manner. At sufficiently low temperatures, in the range 50–90 °K, the only two significant expected contributions to the heat capacities of the alloy and the hydride are the lattice (acoustic phonon branch) contributions and that associated with the conduction electrons. Figure 3 is a plot of  $C_p$  of  $\beta$ -LaNi<sub>5</sub>H<sub>6.39</sub> from 0 to 300 °K. In the region from 50 to 90 °K the curve is smooth with no obvious anomalous contribution as might be observed if a significant disorder process associated with H atoms in interstitial sites was occurring at these temperatures. Other reasons for choosing this temperature range for this calculation were that  $\gamma T$  is only about 4% to 5% of  $C_p$ ,  $C_p$  values are known to  $\pm 0.25\%$ , and the expected  $\theta_D$  values would be several times larger than the absolute temperatures involved and therefore the method will be reasonably sensitive to heat capacity differences. The lattice entropy calculations were made at 10 °K intervals from 50 to 90 °K as shown in Table XI.  $\theta_D$  values were calculated from heat capacity values in Tables VI and VIII and from the equation  $C_{\text{lattice}} = C_p - \gamma T$ ;  $\gamma$  values are

TABLE XI. Calculated lattice entropies of LaNi<sub>5</sub> and  $\beta$ -LaNi<sub>5</sub>H<sub>6.39</sub> at 298.15 °K.

T (°K)	$\theta_D$ (°K)		$S_{\theta_D}$ (298.15 °K) (J °K <sup>-1</sup> mole <sup>-1</sup> )		$S_{\text{lattice}}$ (298.15 °K) <sup>a</sup> J °K <sup>-1</sup> (mole H <sub>2</sub> ) <sup>-1</sup>
	LaNi <sub>5</sub>	$\beta$ -LaNi <sub>5</sub> H <sub>6.39</sub>	LaNi <sub>5</sub>	$\beta$ -LaNi <sub>5</sub> H <sub>6.39</sub>	
50	298.5	249.9	203.2	228.8	8.0
60	305.4	253.9	199.9	226.6	8.4
70	310.8	254.8	197.5	226.0	8.9
80	315.2	253.1	195.5	227.0	9.9
90	318.9	249.4	193.8	229.1	11.0
...	312.1 <sup>b</sup>	254.2 <sup>b</sup>	196.9	226.4	9.2

<sup>a</sup>  $S_{\text{lattice}} = (2/6.39) [S_{\theta_D}(\beta\text{-LaNi}_5\text{H}_{6.39}) - S_{\theta_D}(\text{LaNi}_5)]$ .

<sup>b</sup> These values of the  $\theta_D$  were selected to give the best value of  $S_{\text{lattice}}$  (298.15 °K) as discussed in the text.

given in Table IX. It can be seen in Table XI, that  $\theta_D$  values for  $\beta$ -LaNi<sub>5</sub>H<sub>6.39</sub> are fairly constant, but that those for LaNi<sub>5</sub> increase with increasing temperature. In the case of LaNi<sub>5</sub> it is reasonable to choose  $\theta_D$  so that  $S_{\theta_D}$  is nearly equal to the lattice entropy which can be calculated directly from  $S^\circ(\text{LaNi}_5, 298.15 \text{ °K})$  in Table VI. Thus,  $S_{\theta_D}(\text{LaNi}_5, 298.15 \text{ °K}) = S^\circ - \gamma T = 209.9 - 0.0437 \times 298.15 = 196.9 \text{ J °K}^{-1} \text{ mole}^{-1}$ . This entropy corresponds to  $\theta_D = 312.1 \text{ °K}$  for LaNi<sub>5</sub> and if we then estimate  $\theta_D$  of  $\beta$ -LaNi<sub>5</sub>H<sub>6.39</sub> as 254.2 °K (see Table XI) we then arrive at our best estimate of  $S_{\text{lattice}} = 9.2 \pm 1.5 \text{ J °K}^{-1} \text{ (mole H}_2\text{)}^{-1}$  (see equation given as footnote in Table XI). The stated probable error is an estimate by the authors.

$S_{e1}$  at 298.15 °K can be calculated directly from the values of  $\gamma$  given in Table IX. We find

$$S_{e1} = \frac{2}{6.39} (4.09 \times 10^{-2} - 4.37 \times 10^{-2}) 298.15 \\ = -0.3 \pm 0.1 \text{ J °K}^{-1} \text{ (mole H}_2\text{)}^{-1}.$$

A value of  $S_{\text{conf}}$  can now be calculated by substitution in Eq. (10) and the result at 298.15 °K is

$$S_{\text{conf}} = \bar{S}_H^\beta - S_{\text{optical}} - S_{\text{lattice}} - S_{e1} \\ = (19.4 \pm 0.5) - (2 \pm 1) - (9.2 \pm 1.5) + (0.3 \pm 0.1) \\ = 8.5 \pm 1.9 \text{ J °K}^{-1} \text{ (mole H}_2\text{)}^{-1}.$$

This value of  $S_{\text{conf}}$  is much lower than the one calculated by Gruen and Mendelsohn<sup>32</sup> who obtained  $S_{\text{conf}} = 42 \text{ J °K}^{-1} \text{ (mole H}_2\text{)}^{-1}$  for  $\beta$ -LaNi<sub>5</sub>H<sub>6.5</sub> based upon a total of 33 equally available hydrogen sites per unit cell which represents one molecule of  $\beta$ -LaNi<sub>5</sub>H<sub>6.5</sub>. On the basis of structural considerations Bowman *et al.*<sup>10</sup> and on the basis of NMR results Barnes *et al.*<sup>11</sup> concluded that in the  $\beta$ -hydride three hydrogens are always in H<sub>II</sub> sites (Bowman *et al.*<sup>10</sup> notation), and additional hydrogen may be distributed randomly over six H<sub>I</sub> sites. If we then assume for  $\beta$ -LaNi<sub>5</sub>H<sub>6.39</sub> that 3.39 hydrogens can randomly occupy six sites at 298.15 °K, we can calculate the configurational entropy involved using Stirling's approximation formula<sup>46</sup>

$$\ln \omega = -6N [\theta \ln \theta + (1 - \theta) \ln(1 - \theta)], \quad (11)$$

where  $N$  is the Avogadro number and  $\theta$  is the occupied fraction of the 6N available sites per mole of  $\beta$ -LaNi<sub>5</sub>H<sub>6.39</sub>. Then for  $\theta = 3.39/6$  we find

$$S_{\text{conf}} = \frac{2}{6.39} k \ln \omega = 10.7 \text{ J °K}^{-1} \text{ (mole H}_2\text{)}^{-1},$$

where  $k$  is the Boltzmann constant ( $1.381 \times 10^{-23} \text{ J °K}^{-1} \text{ (molecule}^{-1}\text{)}$ ). Since this statistical calculation of  $S_{\text{conf}}$  is at best only approximate and is based upon somewhat speculative structural considerations, the agreement between this value and  $S_{\text{conf}} = 8.5 \pm 1.9 \text{ J °K}^{-1} \text{ (mole H}_2\text{)}^{-1}$  calculated above from Eq. (10) is considered satisfactory. For  $\beta$ -LaNi<sub>5</sub>H<sub>6.39</sub> the configurational entropy per mole of hydride is  $6.39/(8.5 \pm 1.9) = 27 \pm 6 \text{ J °K}^{-1} \text{ mole}^{-1}$  at 298.15 °K compared to the value of  $S^\circ = 271.7 \text{ J °K}^{-1}$  as given in Table VIII.

As can be seen in Fig. 3, the slope of the heat capacity curve for  $\beta$ -LaNiH<sub>6.39</sub> increases sharply above 200 °K instead of decreasing as do the curves for LaNi<sub>5</sub> and  $\alpha$ -LaNi<sub>5</sub>H<sub>6.39</sub>. Thus if the interpretation of the  $\bar{S}_H^\beta$  [Eq. (10)] presented in this section of the discussion is accepted, it can be concluded that most of  $S_{\text{conf}}$  and  $S_{\text{optical}}$  at 298.15 °K are reflected in the enhanced  $C_p^\circ$  of  $\beta$ -LaNi<sub>5</sub>H<sub>6.39</sub> in the region above 200 °K. There is no evidence for a configurational contribution to the heat capacity below 100 °K and we have implicitly assumed that  $S^\circ(\beta\text{-LaNi}_5\text{H}_{6.39})$  is negligible or zero at  $T = 0 \text{ °K}$  for the calculation of the entropy values given in Table VIII. This latter assumption, is also in agreement with our entropy discussion in Sec. VIB above.

An extension of this investigation would be to determine these entropy effects in related AB<sub>5</sub>-H<sub>2</sub> systems (i.e., LaCo<sub>5</sub>-H<sub>2</sub>) and in ternary alloy-H<sub>2</sub> systems (i.e., LaNi<sub>5-x</sub>Al<sub>x</sub>-H<sub>2</sub>). Additional research efforts to identify the interstitial sites occupied by the hydrogen as a function of temperature and concentration as well as to determine the hydrogen vibration frequencies are highly recommended.

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- <sup>1</sup>J. H. N. van Vucht, F. A. Kuipers, and H. C. A. M. Bruning Philips Res. Rep. **25**, 133 (1970).
- <sup>2</sup>K. H. J. Buschow and H. H. van Mal, J. Less-Com. Met. **29**, 203 (1972).
- <sup>3</sup>H. H. van Mal, K. H. J. Buschow, and A. R. Miedema, J. Less-Com. Met. **35**, 65 (1974).
- <sup>4</sup>H. H. van Mal, Thesis, Technological University Delft 1976; Philips Res. Rep. Suppl. 1976, No. 1.
- <sup>5</sup>S. Tanaka, J. D. Clewley, and T. B. Flanagan, J. Catalysis **51**, 9 (1978).
- <sup>6</sup>D. M. Gualtieri and W. E. Wallace, J. Less-Com. Met. **61**, 261 (1978).
- <sup>7</sup>H. C. Siegmann, L. Schlapbach, and C. R. Brundle, Phys. Rev. Lett. **40**, 972 (1978).
- <sup>8</sup>L. Schlapbach, A. Seiler, H. C. Siegmann, T. V. Waldkirch, P. Zürcher, and C. R. Brundle, Int. J. Hydrogen Energy **4**, 21 (1979).
- <sup>9</sup>W. E. Wallace, R. F. Karlicek, and H. Imamura, J. Phys. Chem. **83**, 1708 (1979).
- <sup>10</sup>A. L. Bowman, J. L. Anderson, and N. G. Nereson, Proc. Tenth Rare Earth Res. Conf., Carefree, Arizona, 1973, p. 485.
- <sup>11</sup>R. G. Barnes, W. C. Harper, S. O. Nelson, D. K. Thomas, and D. R. Torgeson, J. Less-Com. Met. **49**, 483 (1976).
- <sup>12</sup>P. Fischer, A. Furrer, G. Busch, and L. Schlapbach, Helvetica Phys. Acta **50**, 421 (1977).
- <sup>13</sup>E. F. Westrum, Jr., J. B. Hatcher, and D. W. Osborne, J. Chem. Phys. **21**, 419 (1953).
- <sup>14</sup>D. W. Osborne, F. Schreiner, H. E. Flotow, and J. G. Malm, J. Chem. Phys. **57**, 340 (1972).
- <sup>15</sup>H. L. Hoge, J. Res. Nat. Bur. Stand. **36**, 111 (1946).
- <sup>16</sup>E. F. Westrum, Jr., G. T. Furukawa, and J. P. McCullough, in *Experimental Thermodynamics, Vol. I, Calorimetry of Non-Reacting Systems*, edited by J. P. McCullough and D. W. Scott (International Union of Pure and Applied Chemistry, London, 1968).
- <sup>17</sup>H. E. Flotow, Z. Physik Chemie Neue Folge **116**, 95 (1979).
- <sup>18</sup>S. Nasu, H. H. Neumann, N. Marzouk, R. S. Craig, and W. E. Wallace, J. Phys. Chem. Solids **32**, 2779 (1971).
- <sup>19</sup>D. Thome and K. A. Gschneidner, Jr. (private communication).
- <sup>20</sup>N. Marzouk, R. S. Craig, and W. E. Wallace, J. Phys. Chem. Solids **34**, 15 (1973).
- <sup>21</sup>D. Ohlendorff and H. E. Flotow, J. Less-Com. Met. (in press).
- <sup>22</sup>T. K. Halstead, J. Solid State Chem. **11**, 114 (1974).
- <sup>23</sup>T. K. Halstead, N. A. Abood, and K. H. J. Buschow, Solid State Comm. **19**, 425 (1976).
- <sup>24</sup>E. F. Khodosov, A. I. Lennik, G. F. Kobzenko, and V. G. Ivanchenko, Phys. Met. Metall. **44**, 433 (1977).
- <sup>25</sup>E. Wicke and H. Brodowsky, in *Hydrogen in Metals II, Topics in Applied Physics*, edited by G. Alefeld and J. Völkl (Springer, Berlin/Heidelberg/New York, 1978), Vol. 29.
- <sup>26</sup>J. L. Anderson, T. C. Wallace, A. L. Bowman, C. L. Radosevich, and M. L. Courtney, Report LA-5320 MS, Issued July 1973.
- <sup>27</sup>A. Biris, R. V. Bucur, P. Ghete, E. Indrea, and D. Lupu, J. Less-Com. Met. **49**, 477 (1976).
- <sup>28</sup>B. S. Bowerman, C. A. Wulff, and T. B. Flanagan, Z. Physik Chemie Neue Folge **116**, 197 (1979).
- <sup>29</sup>H. Diaz, A. Percheron-Guegan, J. C. Achard, C. Chatillon, and J. C. Mathieu, Int. J. Hydrogen En. **4**, 445 (1979).
- <sup>30</sup>K. N. Semenenko, K. N. Sirotina, and A. P. Savchenkova, Zh. Fiz. Khim. **53**, 2373 (1979).
- <sup>31</sup>K. H. J. Buschow, H. H. Van Mal, and A. R. Miedema, J. Less-Com. Met. **42**, 163 (1975).
- <sup>32</sup>D. Gruen and M. Mendelsohn, J. Less-Com. Met. **55**, 149 (1977) and in *Transition Metal Hydrides*, Advances in Chemistry Series **167**, (American Chemical Society, Washington, D. C., 1978).
- <sup>33</sup>L. Haar, A. S. Friedman, and C. W. Beckett, NBS Monograph **20**, 11 (1961). Also *JANAF Thermochemical Tables* (The Dow Chemical Co., Midland, Michigan, 1977).
- <sup>34</sup>M. O. Keefe and S. A. Steward, Ber. Bunsenges. Physik. Chem. **76**, 1278 (1972).
- <sup>35</sup>W. L. Whittemore and A. W. McReynolds, Phys. Rev. **113**, 806 (1959).
- <sup>36</sup>H. E. Flotow and D. W. Osborne, J. Chem. Phys. **34**, 1418 (1961).
- <sup>37</sup>J. J. Rush, H. E. Flotow, D. W. Connor, and C. L. Thaper, J. Chem. Phys. **45**, 3817 (1966).
- <sup>38</sup>H. E. Flotow, D. W. Osborne, and K. Otto, J. Chem. Phys. **36**, 866 (1962).
- <sup>39</sup>H. E. Flotow, D. W. Osborne, K. Otto, and B. M. Abraham, J. Chem. Phys. **38**, 2620 (1963).
- <sup>40</sup>B. M. Abraham, D. W. Osborne, H. E. Flotow, and R. B. Marcus, J. Am. Chem. Soc. **82**, 1064 (1960).
- <sup>41</sup>J. J. Rush and H. E. Flotow, J. Chem. Phys. **48**, 3795 (1968).
- <sup>42</sup>A. J. Maeland and D. E. Holmes, J. Chem. Phys. **54**, 3979 (1971).
- <sup>43</sup>W. L. Whittemore, "Differential Neutron Thermalization," General Atomics Report GA-5554, October 20, 1964.
- <sup>44</sup>I. Karimov, M. G. Zemlyanov, M. E. Kost, V. A. Somenkov, and N. A. Chernoplekov, Fiz. Tverd. Tela **9**, 1740 (1967). [Sov. Phys. Phys. Solid State **9**, 1366 (1967)].
- <sup>45</sup>G. N. Lewis and M. Randall, revised by K. S. Pitzer and L. Brewer, *Thermodynamics* (McGraw-Hill, New York, 1961) (see pp. 428-432).
- <sup>46</sup>T. P. R. Gibb, Jr., J. Phys. Chem. **68**, 1096 (1964).