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Low-temperature heat-capacity study of Haucke compounds $CaNi_5$, YNi_5, $LaNi_5$, and $ThNi_5$

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Low-temperature heat capacities of some Haucke compounds ($CaNi_5$, YNi_5, $LaNi_5$, and $ThNi_5$) were studied. The electronic specific-heat constants of these compounds are nearly the same and slightly smaller than that of pure nickel. The Deybe temperatures of these compounds show a wider variation than the electronic specific-heat constants. It is found that the lattice rigidity of these four compounds varies considerably, with that of $LaNi_5$ being the softest, followed by $CaNi_5$, $ThNi_5$, and YNi_5 in order of increasing rigidity. This appears to influence their hydrogen absorption capacity. The relative softness is correlated with the Ni–Ni distances in the midplane [3(*g*) sites], and it is suggested that the Ni atoms in this plane play a critical role in governing the hydrogenation behavior of these materials.

I. INTRODUCTION

Many intermetallic compounds of $CaCu_5$-type structure (Haucke compound) are known to absorb large quantities of hydrogen at ambient temperatures and pressures, and have great potential as hydrogen storage media. The typical compound, $LaNi_5$, absorbs hydrogen gas at room temperature and ~2.5 atm (Ref. 1) to form $LaNi_5H_{6.2}$ which has a proton density ($\sim 6.2 \times 10^{22}$ protons/cm^3) about 50% greater than that of liquid hydrogen. However, many isostructural compounds do not react with hydrogen gas to form hydrides even up to high hydrogen pressures (100 atm or higher) at room temperature.[1,2]

There have been several theories and semiempirical rules to account for the stability of metal hydrides, which is assumed to be proportional to the equilibrium hydrogen-gas pressure over metal hydrides.[3] One may classify these theories into two broad categories, i.e., electronic and elastic ones. For example, Ebisuzaki and O'Keefe[4] have applied Friedel's screened proton model to transition metals and had some success in correlating solid solubilities of hydrogen with the density of states in those metals and their alloys, and predicting limiting compositions of hydride phases. This approach seems to be reasonable since it is known that the Friedel oscillation is operative in the formation of ordered states in alloys. However, this treatment does not take into consideration the fact that a metal lattice expands with hydrogen absorption. Alefeld,[5] on the other hand, has developed a theory on the metal-hydrogen phase diagrams based on the elastic interactions between dilation centers (in this case, hydrogen) in metals. This has been applied successfully to systems such as Nb-H, V-H, and others.[5] Since hydrogen absorption definitely changes the electronic structure of metals, it appears that some elaboration for electronic factors may be needed in this elastic theory of metal hydrides.

In view of the present status of theories, there seems to be a need to have more experimental information on metals with regard to their hydrogen absorption. The low-temperature (1–20 K) heat-capacity measurements of normal metals yield information about the density of states at Fermi surface (the electronic specific-heat constant, γ) and the elastic behavior (Debye temperature at absolute zero, Θ_D). There have been only a few measurements of this kind with regard to hydrogen absorption in metals.[6,7]

We have measured the low-temperature heat capacity of some representative $CaCu_5$-type compounds, $CaNi_5$, YNi_5, $LaNi_5$, and $ThNi_5$. These were chosen because they are isostructural, are not expected to show any unusual behavior in their low-temperature heat capacities (e.g., no magnetic ordering), and some absorb a large quantity of hydrogen under mild conditions ($CaNi_5$ and $LaNi_5$) while others do not (YNi_5 and $ThNi_5$).

II. EXPERIMENTAL

Intermetallic compounds were prepared by fusing constituent elements in a water-cooled arc furnace. The ingots were melted several times, turning them over each time to insure the homogeneity of samples, and were annealed at about 800° C for two weeks (YNi_5, $LaNi_5$, and $ThNi_5$). The compound $CaNi_5$ was supplied by the International Nickel Co., Inc. through their subsidiary the Ergenics Division of

MPD Technology Corporation, Inc., and its preparation is similiar to the others. Powder x-ray-diffraction patterns of samples were taken by using a Debye-Scherrer camera (Cu$K\alpha$ radiation), and the patterns show no extraneous phases in these compounds. The lattice parameters were refined with the Nelson-Reiley method. Metallographic examination of the four samples showed no extraneous phases except $CaNi_5$ sample, which contained a second phase. An areal analysis indicated that less than 1% of the second phase was present and it is most likely the Ca_2Ni_7 phase. The chemical analysis of the $CaNi_5$ also gave the composition of $CaNi_{4.948}$ instead of $CaNi_{5.000}$.

The low-temperature calorimeter was checked by measuring the heat capacity of the 1965 Calorimetry Conference copper standard. The measured electronic specific-heat constant and the Debye temperature were in agreement with literature values within 0.8% or better.

The low-temperature heat capacity (in mJ/g-at. K) of normal metals (C_p) can be expressed as $C_p = \gamma T + \beta T^3$, where γ is the electronic specific-heat constant and β is related to the Debye temperature, Θ_D, by the expression $\beta = (\frac{12}{5}\pi^4 \mathcal{R})(1/\Theta_D)^3$, where $\mathcal{R}$ is the gas constant ($\mathcal{R} = 8.317$ J/g-at. K). The results of heat-capacity measurements were analyzed in terms of the above relationship, since the plot of C_p/T vs T^2 is linear at temperatures below $\frac{1}{50}\Theta_D$. A least-squares fit program was used to obtain the coefficients, γ and β.

III. RESULTS AND DISCUSSION

A. Electronic specific-heat constant

The results of the heat-capacity measurements are given in Table I along with the hydrogenation plateau pressure, the amount of hydrogen absorbed, and some other physical parameters of the RNi$_5$ compounds. Our results for $LaNi_5$ are in reasonable agreement with those published by Nasu *et al.*,[8] who found $\gamma = 5.72$ mJ/g-at. K^2 and $\Theta_D = 341$ K. The electronic specific constants for the four metals are nearly the same (< 9% difference between the lowest and largest value), but they show a linear variation with electron concentration (see Fig. 1). Furthermore, it is noted from Table I that the γ's for the RNi$_5$ compounds are slightly less (10 to 17%) than that of pure Ni. It is concluded from these results that the density of states at the Fermi surface, which is proportional to γ, probably is not an important factor in determining the hydrogenation characteristics of these RNi$_5$ phases. This is especially evident for the isoelectronic compounds YNi_5 and $LaNi_5$, where γ's are virtually identical but YNi_5 does not easily form a hydride while $LaNi_5$ readily forms $LaNi_5H_{6.2}$ (see Fig. 2 and Table I). It is true that there are several interactions which also contribute to the experimental electronic specific-heat constant, i.e., the electron-electron and electron-phonon, but these would be expected to be about the same for all four compounds. Thus the variation in γ probably represents the varia-

TABLE I. Hydrogenation properties, electron concentration (e/a), and unit-cell volume of and the low-temperature heat-capacity results on some Haucke compounds.

Compound	Hydrogenation at 25 °C Plateau pressure (atm)	Hydrogenation at 25 °C RM_5H_x x	e/a	γ $\left(\frac{\text{mJ}}{\text{g-at. K}^2}\right)$	Θ_D (K)	Unit-cell volume (Å^3)	κ (arbitrary units)
$CaNi_5$	0.5[a]	4.2[a]	8.67	5.86	441	85.08	2.24
	25.0[a]	6.2[a]		. . .	. . .	. . .	
YNi_5	>100	b	8.83	6.06	450	80.81	1.77
$LaNi_5$	2	6.2	8.83	6.08	351	86.80	2.74
$GdNi_5$	120	2–3	8.83	. . .	. . .	82.58	. . .
$ThNi_5$	>100	b	9.00	6.38	366	83.30	2.05
Ni	3400 ± 70	~4.2[c]	10.00	7.08	473	65.63[d]	1.67

[a] Hydrogenation takes place to two steps, see Fig. 2.

[b] No hydrogen is absorbed up to pressures of 100 atm.

[c] Number of hydrogen atoms absorbed per six nickel atoms.

[d] Six times the atomic volume of pure nickel.

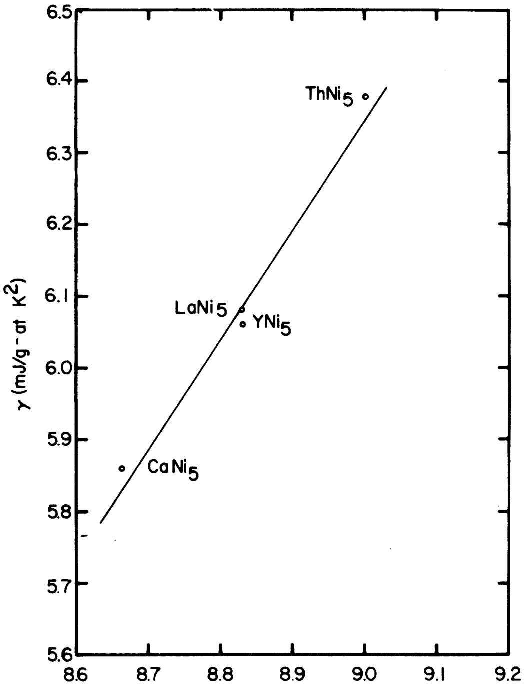

FIG. 1. Plot of electronic specific-heat constant γ as a function of electron concentration, e/a, for $CaNi_5$, YNi_5, $LaNi_5$, and $ThNi_5$.

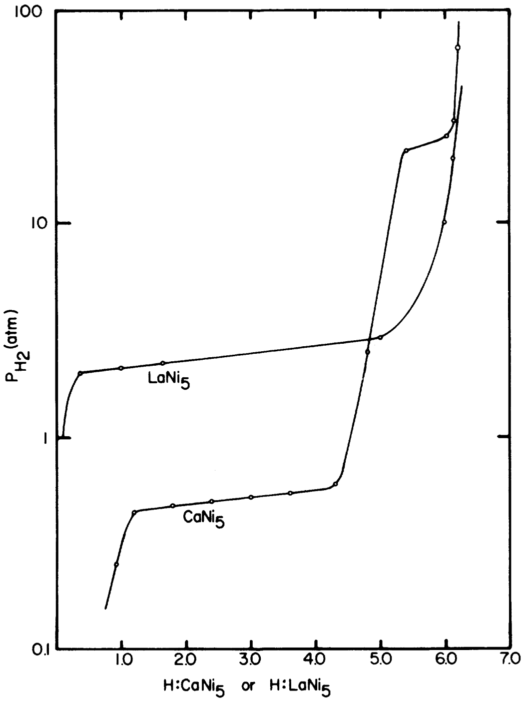

FIG. 2. Isothermal pressure-composition curves for $CaNi_5$-H_2 and $LaNi_5$-H_2 at 23 °C.

tion in the band density of states at the Fermi surface of these phases. Furthermore, this variation in γ's is consistent with the little information available on band-structure calculations on the isostructural compound RCo_5 (Ref. 9) and the related RNi_2 compounds.[10] These calculations suggest that the band structures of the transition-metal-rich compounds are quite similar to the band structure of the pure transition metal.

B. Debye temperature

The Debye temperatures of these compounds exhibit a wider variation than the electronic specific-heat constant, and $LaNi_5$ has the smallest value (Table I). The Debye temperature is a measure of the stiffness of metal lattice. The Debye theory, however, is based on the lattice vibrations of a solid continuum and involves not only the elasticity but also the mass of the atoms and the density of solid. Madelung derived a relation between the Debye temperature and the compressibility (κ), molecular weight (μ), and the density of solids (ρ): $\Theta_D = A\kappa^{-1/2}\mu^{-1/3}\rho^{-1/6}$ (where A is a constant for isostructural solids[11]). Strictly speaking, this is a high-temperature approximation, but we assume that this expression may also be used for Θ_D at absolute zero degree in the absence of the high-temperature value of Θ_D. In Table I, the values for κ for compounds studied are given in arbitrary units. Comparison of κ's for the compounds shows that $LaNi_5$ is significantly softer than the other three compounds and $CaNi_5$ is fairly soft relative to $ThNi_5$ and YNi_5. This difference in lattice stiffness may account for the observed differences in the hydriding behaviors of the four compounds if we assume that there is a critical compressibility value ($\kappa \simeq 2.1$), above which the compound exhibits good hydrogenation properties.

It is instructive to examine the $LaNi_5$ structure, Figs. 3 and 4. Figure 3 shows the full hexagonal symmetry of $LaNi_5$ and defines the positional parameters of the La and Ni atoms, while the important planes showing the hard-sphere atom contacts are illustrated in Fig. 4. Considering the formation of $LaNi_5$ from the pure elements we find that there is a -7.3% decrease in the Ni–La distance relative to the metallic radii of the pure metals in the basal planes [the $2(c)$ Ni atoms and the La atoms]. For the prismatic face [the $3(g)$ Ni atoms and the La atoms] there is a $+2.5\%$ expansion in the Ni–La distance. For the midplane, which consists of only Ni atoms [the $3(g)$ Ni atoms], the Ni–Ni distance is $+0.7\%$ larger than in pure metallic Ni. These changes are summarized in Table II for the other RNi_5 compounds studied. Examination of the experimental results (Table I) and comparing these with the change in the basal plane and the prismatic face distances shows that there is no correlation. However,

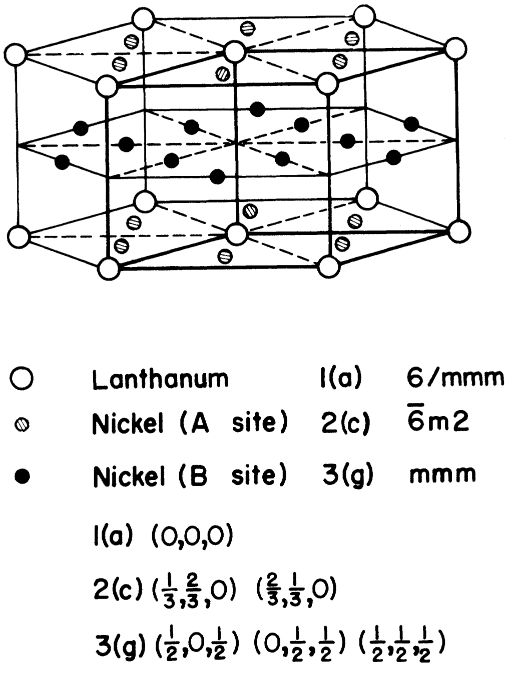

FIG. 3. $LaNi_5$ structure.

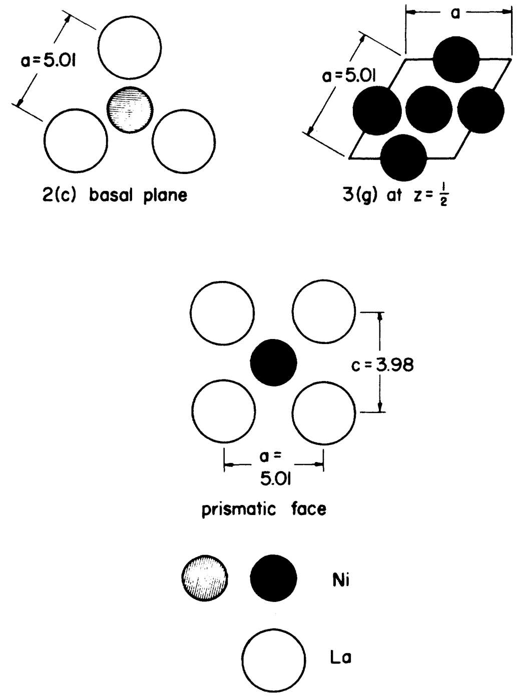

FIG. 4. Various planes in the $LaNi_5$ structure showing the hard-sphere atom contacts.

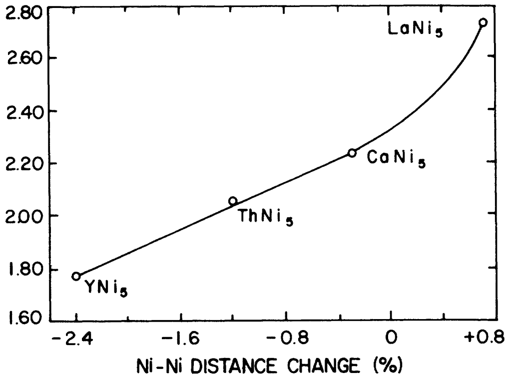

FIG. 5. Compressibility κ (in arbitrary units) vs the percent change in the Ni–Ni distance in the midplane [3(g) sites] relative to the metallic diameter in pure Ni metal.

one finds a direct relationship between the nickel atom distances in the midplane and the compressibilities (see Fig. 5). Where there is an expansion in those Ni–Ni distances, the compound is the most compressible ($LaNi_5$). And the compound which is the least compressible is the one whose Ni–Ni distances have undergone the largest contraction (YNi_5). Furthermore, *the expansion or compression of the midplane Ni atoms varies as a linear function with the unit-cell volume.* It is also known that there is a correlation between the unit-cell size of isostructural metals and the stability of their hydrides. (See Sec. III C). Thus for these RNi_5 compounds, the Ni–Ni distances in the 3 (g) sites (midplane) play an important and probably critical role in governing both the lattice dynamics (κ, Θ_D) and the hyrogenation characteristics.

In this regard it is also interesting to compare the hydriding behavior of $LaNi_5$ and $CaNi_5$ (see Fig. 2). Many Haucke compounds which form hydrides have two hydride phases (β and γ phase).[1] This is seen

TABLE II. Change in metal-metal distances in the RNi_5 compound relative to the metallic radii of the pure metals for a coordination number of 12.

Compound	Basal plane (%)	Prismatic face (%)	Midplane (%)
$CaNi_5$	−10.9	+1.2	−0.3
YNi_5	−6.9	+3.7	−2.4
$LaNi_5$	−7.3	+2.5	+0.7
$GdNi_5$	−7.7	+3.5	−1.7
$ThNi_5$	−7.1	+3.7	−1.2

by the existence of two plateau pressures in the P-C-T curve for $CaNi_5$. $LaNi_5$ appears to be exceptional in that it has only one plateau pressure; i.e., it forms only β-phase hydride with a large hydrogen content ($LaNi_5H_{6.2}$). $CaNi_5$, on the other hand, eventually absorbs a comparable amount of hydrogen as $LaNi_5$, but first forms the β-phase hydride $CaNi_5H_{4.2}$ upon hydriding before the γ- phase hydride $CaNi_5H_{6.2}$ is formed. This is the more typical behavior of other hydride forming Haucke compounds, but the final hydrogen composition appears to be higher than that of other Haucke compounds. We believe that the large compressibility of $LaNi_5$ may account for the single hydriding plateau in this compound.

C. Other factors

Lundin and co-workers[12] have made an extensive analysis of the hydriding characteristics of ~ 50 Haucke compounds and found an excellent correlation between the size of one of the tetrahedral interstitial holes in the RM_5 phase and the stability or the free energy of formations (ΔG_f^0) of the RM_5H_x phase. Neutron diffraction studies,[13–16] however, show that several different holes may have fractional occupancy of hydrogen atoms [five in $LaNi_4MnD_6$ (Ref. 15)], and thus focusing on one particular hole is not too meaningful. Furthermore, since the lattice parameters are used to calculate the tetrahedral hole size via several complex equations, one might reasonably expect the Lundin-Lynch-Magee correlation to hold just as well if one were to use the unit-cell volume ($V = 0.86602a^2c$) instead of the interstitial hole size. Basically this has been verified by Buschow and Miedema[17] and Gruen, Mendelshohn, and Dwight.[18,19]

Comparison of the unit-cell volumes and hydrogenation behaviors reveals that if the unit-cell volume is less than ~ 82 Å^3 for the isoelectronic compounds (YNi_5, $LaNi_5$, and $GdNi_5$) the compound will not form a stable hydride. The observed hydrogenation behaviors of the other lanthanide RNi$_5$ phases confirm this observation.[1] It is seen that the behavior of $CaNi_5$ is consistent with the size limit, but $ThNi_5$, which would be expected to form a hydride, does not follow this size limit. Thus we see that size alone cannot account for the observed hydrogenation behaviors.

As noted earlier the electronic specific-heat constant increases with increasing electron concentration (Fig. 1) and the compounds $CaNi_5$ and $LaNi_5$ form hydrides, but YNi_5 and $ThNi_5$ do not. It is possible that electron concentration plays an important role in the hydrogenation behaviors of the compounds, and it may explain the anomalous behavior of $ThNi_5$ which has a favorable size factor.

Although, as noted above, the unit-cell volume is proportional to the expansion or compression of the midplane Ni atoms and thus the compressibility, the compressibility of the solid also depends upon the electronic wave functions of the valence electrons. Therefore, the compressibility embodies both parameters (size and electron concentration) and by itself appears to explain the hydrogenation characteristics of the RM_5 phases. Clearly more measurements on these types of materials are required to see if the compressibility is the critical and only parameter involved.

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