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Anomalous behavior of the Ni bonding strength in some $LaNi_{5-x}Al_xH_y$ compounds

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The nuclear resonant photon scattering technique was utilized to investigate the Ni cohesion variation in $LaNi_{5-x}Al_x$ intermetallics and some of their hydrides. The resonantly scattered intensity (RSI) of 7.646-MeV γ rays by ^{62}Ni was measured for $0 \le x \le 1.5$, and was analyzed by utilizing a reference pure-Ni scatterer. The RSI drops significantly at $x = 0.25$ and increases gradually for $0.25 < x \le 1.5$. The investigated hydrides ($0.5 \le x \le 1.5$) exhibit higher RSI values than the corresponding unhydrided intermetallics. An apparent correlation between the Ni cohesion and hydrogen uptake is suggested to be the key for understanding the puzzling hydriding characteristics of this and other aluminum-substituted intermetallic systems.

$LaNi_{5-x}Al_x$ ($0 \le x \le 1.5$) compounds have been extensively investigated since the discovery of their interesting hydriding properties in 1977.[1,2] The variation of the hydrogen-sorption behavior of this system as a function of x, however, has not been comprehensively understood. The Al substitution for Ni drastically and monotonically increases the hydride stability but concomitantly the hydrogen-absorption ability is gradually inhibited toward high Al concentrations ($x \approx 1.5$). In this work we provide an explanation of that puzzling behavior, based on nuclear resonant photon scattering (NRPS) experimental results of the Ni cohesion in $LaNi_{5-x}Al_x$ ($0 \le x \le 1.5$) and in $LaNi_{5-x}Al_xH_y$ ($0.5 \le x \le 1.5$). We utilized the overlap between one of the incident gamma lines from the $Fe(n,\gamma)$ source at 7.646 MeV with a nuclear level in the ^{62}Ni isotope.[3] This overlap gives rise to a resonance scattering signal whose cross section σ_s is proportional to the overlap integral of the two Doppler-broadened shapes of the incident γ line and the resonance level. It was shown[3] that under certain conditions, the value of σ_s in the $Fe(n,\gamma)$-^{62}Ni scattering process is strongly dependent on temperature variations of the scatterer and therefore on its effective temperature T_{eff}.

Explanatory remarks and terminology associated with NRPS may be found in Refs. 4–7 and references therein. We briefly mention here that the terms effective temperature, T_{eff}, vibrational energy, bonding strength, and resonant scattering intensity (or R values) are interrelated to each other and may be used interchangeably to designate how strong a specific atom is bonded in a certain compound. The NRPS experiment measures in fact the mean kinetic atomic energy, including the zero-point motion. In the harmonic approximation it equals half of the total mean atomic energy, $k_B T_{eff}$, obtained by integration over the whole phonon frequency spectrum, where k_B is the Boltzmann constant. It may be stated that a high resonantly scattered intensity (RSI) reflects a strong cohesion (or high T_{eff}) of the scattering atom and vice versa. We have demonstrated in the past[4,5] that the numbers obtained for the cohesion are in good agreement with those obtained from inelastic neutron scattering for some simpler systems; we hence believe to have established our technique as quantitative.

T_{eff} of a certain element in a compound may be obtained by an experimental comparison of the relevant RSI with the scattered intensity by the pure element at a certain temperature, T, provided that $T_{eff}(T)$ of the pure element is given.[4] In the present case T_{eff} of pure Ni is known from neutron inelastic scattering,[8] as well as from our earlier results.[4] Formally, the scattered intensity $C(Ni^*,T,\theta)$ of Ni (the asterisk denotes a certain chemical state determining the atomic bonding strength) at angle θ and temperature T depends on the nuclear parameters Γ_0, Γ, δ, g of the level, on the effective temperature T_{eff} of the resonant nucleus, and on the effective temperature T_S of the (n,γ) source:

$$C(Ni^*,T,\theta)=f(\Gamma,\Gamma_0,\delta,g,T_{eff},T_S) .$$

Γ and Γ_0 are the total and the partial ground-state radiative widths, respectively, δ is the energy separation between the incident gamma line and the resonance level, and g is a statistical factor which depends on the spins of the resonance and the ground states. The explicit form of the scattering intensity is given elsewhere.[9] It is convenient to utilize the experimentally measured ratio R:

$$R(Ni^c,Ni^p,T_1,T_2,\theta)=C(Ni^c,T_1,\theta)/C(Ni^p,T_2,\theta) . \quad (1)$$

Ni^c and Ni^p denote Ni in compound c, and pure Ni, respectively. It is also convenient to set $T_1 = T_2 = 298$ K (room temperature). Equation (1) can be used to derive the effective temperature $T_{\mathrm{eff}}(Ni^c, T_1)$. The parameters necessary for this calculation were reported[3,9] to be $\Gamma = 0.48$ eV, $\Gamma_0 = 0.64$ eV, $\delta = 14.35$ eV, $g = 3$, and $T_{\mathrm{eff}}(Ni^p, 298\ \mathrm{K}) = 324$ K. Figure 1 represents the calculated values of R versus T_{eff} for Ni. The experimental values of T_{eff} for Ni in the various compounds may be deduced from the measured values of R and the use of Fig. 1.

The $LaNi_{5-x}Al_x$ ($x = 0, 0.1, 0.25, 0.5, 1, 1.5$) intermetallic compounds were prepared in an arc furnace under argon atmosphere by melting the weighted fraction of the pure metals on a water-cooled copper hearth. The $CaCu_5$-type hexagonal structure of all the intermetallics was confirmed by x-ray diffraction, and was in good agreement with previously published results.[1] The samples were crushed to powder and fire-sealed in glass cylindrical holders. $LaNi_{5-x}Al_x$ ($x = 0.5, 1, 1.5$) hydrides were also prepared and identically sealed. More details will be published elsewhere. Identical glass holders were filled up with pure Ni powder, La_2O_3, and Cu for comparison and background subtraction purposes. All the Ni-containing samples consisted of 8–10 g Ni.

The filled cylindrical glass targets were put in a photon beam from the Fe(n,γ) reaction using thermal neutrons from the IRR-2 reactor. The source was in the form of six separate iron disks, placed along a tangential beam tube and near the reactor core yielding typical intensities of approximately 10^5 photons/cm^2 sec per strong gamma line at the scatterer. The photon source contained several discrete gamma lines, Doppler broadened by the thermal motion of the Fe atoms. The temperature of the iron disks during reactor operation was 600 K. More details on the experimental system may be found elsewhere.[9]

The scattered photons from the targets were detected in a 40-cm^3 Ge(Li) diode placed at 135° with respect to the photon beam and the spectrum was analyzed with a multichannel analyzer. Four targets, located simultaneously on a circular horizontal plane, were rotated in and out of the beam for short, 30-min runs. The scattered intensities were normalized to that from pure Ni kept at the same temperature, and were accumulated in four different memories of the analyzer. The experimental results were confirmed by permutating the targets among the various positions on the circular plane holder. In this way the possibility of deviations in the scattering intensities due to small variations of the target heights above the scattering plane and inhomogeneity of the incident beam has been ruled out.

A typical scattered photon spectrum from a Ni target, as measured by a Ge(Li) detector, is given in Ref. 3. The integrated intensity of this spectrum in the energy range $E = 6.5-7.7$ MeV was measured with the various targets kept at room temperature. The intensity ratios (after self-absorption and background corrections) are given in Table I, together with the values of $T_{\mathrm{eff,Ni}}$ extracted from Fig. 1 and the measured values of R. The present results (Fig. 2) of the $LaNi_{5-x}Al_x$ ($0 \le x \le 1.5$) system and of some of the corresponding hydrides exhibit the following features. (1) A sharp decrease of the resonantly scattered intensity by Ni in $LaNi_{5-x}Al_x$ occurs at $x = 0.25$. (2) A significant increase of R is observed for $0.25 < x \le 1.5$, the value of 1.035 being reached for $x = 1.5$. (3) The R values measured for the three hydrides $LaNi_{5-x}Al_xH_y$ ($x = 0.5, 1, 1.5$), are in general higher than in the corresponding unhydrided compounds. It is interesting to note that these R values are all around the same value, i.e., 1.045.

The variations of the R values reflect directly the variation in the bonding strength of the nickel atoms in the different compounds. The very distinct change of the Ni bonding strength in the $LaNi_{5-x}Al_x$ system as a function of x may be qualitatively explained as follows: the substitution of the Ni atoms by the larger Al atoms expands the original $LaNi_5$ hexagonal lattice. At relatively small

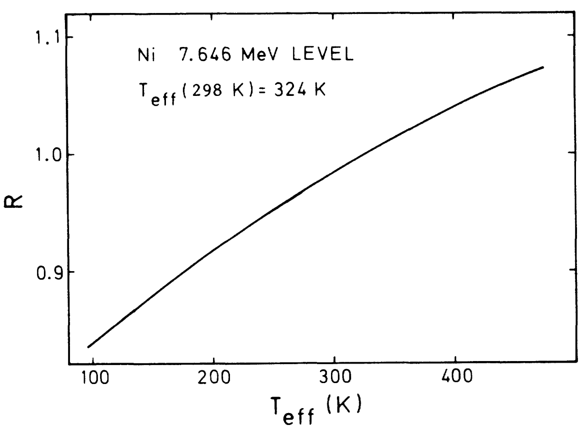

FIG. 1. Calculated values of the relative scattered intensity $R(Ni^c, Ni^p, 298\ \mathrm{K}, 135°)$, defined in relation (1), with a predetermined $T_e(Ni^p, T = 298\ \mathrm{K}) = 324$ K, vs T_{eff}. The results are obtained for a scatterer thickness of 1 cm.

TABLE I. Measured scattered intensity ratios R [see Eq. (1)], with accuracy of about 2%, normalized to pure nickel (after background and self-absorption corrections) and deduced effective temperature $T_{\mathrm{eff,Ni}}$ at $T = 298$ K. The numbers in parentheses indicate errors.

Compound	R	$T_{e,\mathrm{Ni}}$ (K)
Ni (metal)	1	324(3)[a]
$LaNi_5$	1.013	349(30)
$LaNi_{4.9}Al_{0.1}$	1.019	360(41)
$LaNi_{4.75}Al_{0.25}$	0.920	202(36)
$LaNi_{4.5}Al_{0.5}$	0.946	239(30)
$LaNi_4Al$	0.966	269(21)
$LaNi_{3.5}Al_{1.5}$	1.035	391(36)
$LaNi_{4.5}Al_{0.5}H_{5.8}$	1.046	413(40)
$LaNi_4AlH_{4.9}$	1.041	403(33)
$LaNi_{3.5}Al_{1.5}H_{3.8}$	1.049	418(43)

[a] Reference 1.

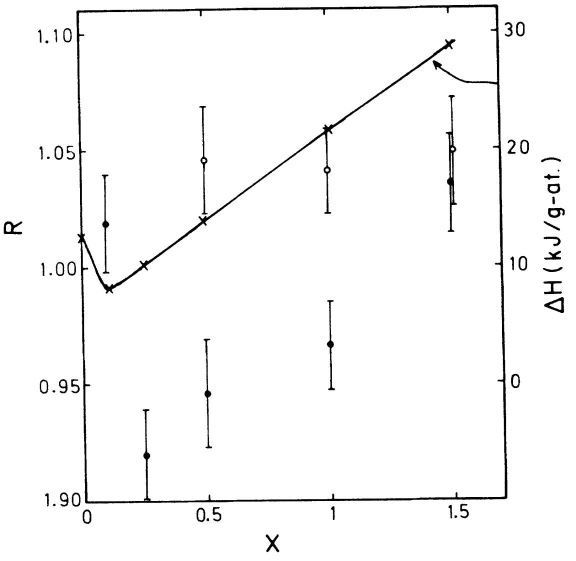

FIG. 2. Measured scattered intensity ratios R relative to pure Ni [see also Eq. (1)] for $LaNi_{5-x}Al_x$ (●) and $LaNi_{5-x}Al_xH_y$ (○) vs x. A simplified estimation of the heats of formation (×) of the intermetallic compounds is also shown.

x values ($x \approx 0.25$) the Ni bonding strength is drastically decreased because of increased distance of the nickel atoms to its neighbors. Further increase of the Al content, although accompanied by further expansion, enhances the Ni bonding because of increased d-p hybridization. These trends may be put on semiquantitative grounds by considering the heats of formation of $LaNi_{5-x}Al_x$. In order to stress the Ni bonds we look only on $LaNi_{5-x}$ and $Ni_{5-x}Al_x$ as composing the intermetallics, and neglect $LaAl_x$. The average heat of formation (of $LaNi_{5-x}$ and $Ni_{5-x}Al_x$), calculated according to Miedema's model,[10,11] is presented in Fig. 2. In spite of the simplified way of averaging, the trends presented by $|\Delta H|$ agree quite well with those of R, i.e., $|\Delta H|$ initially decreases with x and then increases with further increase of x. $|\Delta H|$ exhibits however (Fig. 2) much higher stability as also demonstrated by measured enthalpies of formation of $LaNi_5$ and $LaNi_4Al$.[12] It should, however, be borne in mind that we have measured the isolated contribution of Ni to the bonding strength of the $LaN_{5-x}Al_x$ intermetallics. The NRPS is probably the best available experimental technique to obtain such a microscopic insight into compounds.

In view of our results we suggest that the decreased hydrogen-absorption capacity in $LaNi_{5-x}Al_x$ for high values of x is associated with the increased bonding or rigidity of the lattice. This may be formulated as a *rule of reverse capacity* (RRC)—in resemblance to the rule of reverse stability[13] in the following way: The hydrogen absorption capacity of isostructural intermetallic compounds *may* decrease with increasing of the lattice rigidity and vice versa—the capacity *may* increase with decreasing of the lattice rigidity (softening). "May" stresses that the RRC does not represent sufficient conditions. For example, softening of the lattice will not cause an increased hydrogen-absorption capacity if (1) hydrogen-absorbing elements are not present in the intermetallic—in such case there is not any hydrogen absorption and (2) the hydrogen capacity of the unsoftened intermetallic is so high that any further increase of the hydrogen content is limited by other factors such as repulsion between too closely located hydrogen atoms. This is probably the reason for the nonincreased hydrogen absorption in $LaNi_{5-x}Al_x$ for small values of x.

In view of the present results for the Al influence on the bonding strength, we suggest that the systems $Zr(Fe_{1-x}Al_x)_2$, $Zr(Co_{1-x}Al_x)_2$ (Ref. 14), and $ThNi_{5-x}Al_x$ (Ref. 15) present a comprehensive demonstration of the RRC. In all these cases the Al-free compounds do not absorb any significant quantities of hydrogen. Substituting small amounts of the above $3d$ metals by Al leads probably to the softening of the intermetallic lattice as in the present case, and to a sharp increase of the H capacity. Further substitution of the $3d$ metals by Al, accompanied probably by a concomitant stiffening of the crystal lattice, causes at first a gradual decrease and finally completely inhibits the hydrogen absorption. On the other hand, the stability of the hydrides monotonically increases with the increase of the Al content in consistency with the higher affinity of Al to hydrogen than that of Fe, Co, or Ni. Additional Al-containing systems[16] exhibit similar behavior.

The notion of a restrained H capacity of stiff crystal lattices is supported also by the hydrogen-induced changes in the RSI from $LaNi_{5-x}Al_xH_y$ ($x = 0.5, 1, 1.5$), see Fig. 2. The enhanced scattered intensities by these relatively stable hydrides ($\Delta H = -39$, -53, and -61 kJ/mol H_2,[1] respectively) with regard to the corresponding unhydrided compounds are in a qualitative, but not quantitative, agreement with a previously proposed empirical rule.[17] According to this rule, the change in Debye temperature Θ_D (and hence the change in bonding strength) upon hydrogenation is proportional to the heat of hydrogen formation. Therefore, we expect for the $LaNi_{5-x}Al_xH_y$ compounds studied in this work (a) larger R values with respect to the corresponding intermetallic compounds, and (b) an increase of R with x for the three hydrides. From Table I and Fig. 2 we see clearly that the experimental data confirm (a), but do not confirm (b). This last fact is most probably due to a restraint of the hydrogen capacity, induced by the increased rigidity at larger x values. We consider this as a further evidence for the proposed RRC.

Anomaly in the values of T_{eff}. A problem associated with the significance of the $T_{\text{eff,Ni}}$ of some of the unhydrided $LaNi_{5-x}Al_x$ compounds should be pointed out. According to Lamb,[18] the effective temperature of any element should always be higher than the thermodynamic temperature T. This is due to additional contribution to the kinetic energy arising from the zero-point contribution of the solid viewed as a system of harmonic oscillators. In other words, this condition for T_{eff} stems from the contribution of the binding forces of the crystal atoms to the usual (gaslike) thermal Doppler broadening of the resonance scattering cross section. Therefore one expects the T_{eff} of all the measured samples mentioned in Table I to be higher than room temperature T at which the measurements were performed ($T = 298$ K). The fact that T_{eff} of $\text{LaNi}_{4.75}\text{Al}_{0.25}$ was found to be as low as 202 ± 36 K is clearly in sharp contrast with the above expectation.

In an attempt to try to understand this large anomaly, we could speculate two possible reasons associated with the definition of T_{eff}. (1) Lamb assumed the harmonic approximation in treating the resonance scattering cross section. It is possible that the reason for the above "discrepancy" in T_{eff} is associated with an anharmonic behavior of the Ni atoms in the relevant $\text{LaNi}_{5-x}\text{Al}_x$ compounds. The Al-induced increase of the $\text{LaNi}_{5-x}\text{Al}_x$ crystal lattice for small x values may be regarded as a thermallike expansion which is an anharmonic phenomenon. (2) Even a more basic reason may be associated with perturbing the periodicity of the Ni atoms because of their almost random (the Ni atoms occupy two unequivalent lattice sites in LaNi_5, while the Al atoms strongly prefer one of them, e.g., Refs. 19 and 20) substitution by Al atoms. Then the phonon presentation [which is a basic assumption in defining T_{eff} (Ref. 18)] for the Ni atoms may not be a valid one.[21] The influence of these two effects on σ_s should be checked in order to examine the above speculations, but this is beyond the scope of the present work.

In summary, this work reports the first experimentally derived kinetic vibrational energies of a metal element in a compound crystal matrix. In earlier works metal vibrational energies were determined either in pure elementary crystal matrices or using the Debye model, e.g., Refs. 4 and 5, and references therein. One significant outcome of the present research is the determination of the Ni cohesion variation in $\text{LaNi}_{5-x}\text{Al}_x$ compounds ($0 \le x \le 1.5$) and some of their hydrides. This parameter, previously not obtained in other works, appears to be the key for understanding the "anomalous"[22] hydrogenation characteristics in this and probably other Al-substituted intermetallic systems. Macroscopic heat-capacity measurements in $\text{LaNi}_{5-x}\text{Al}_x$ (Ref. 23) have lead to Θ_D values insensitive to x. Probably the most similar, but not as definite, conclusions may be drawn from the NMR-derived hydrogen diffusion activation energies[24] in $\text{LaNi}_{5-x}\text{Al}_x$ ($0 \le x \le 1.2$) hydrides. The second significant outcome of this work is the experimental demonstration of a new way for measuring the cohesion of one specific metal element in a compound. In neutron inelastic scattering such a quantity depends on a model analysis of the phonon spectrum. The NRPS technique may appear very useful for investigating the new high-T_c superconductors, e.g., Ref. 25, since a direct measurement of the cohesion of specific metal elements like Cu and Sr (Ref. 4) in these multiatom compounds may be obtained.

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