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Hydrogen in lanthan–nickel storage alloys

D.V. Schur[a,*], S.Yu. Zaginaichenko[b], Z.A. Matysina[c], I. Smityukh[a], V.K. Pishuk[a]

[a]*Institute of Hydrogen and Solar Energy, P.O. Box 195, Kiev 150, 03150 Ukraine*
[b]*Institute for Problems of Materials Science of NAS, Kiev 03142, Ukraine*
[c]*Dnepropetrovsk State University, Dnepropetrovsk, 49000 Ukraine*

Abstract

A theoretical study of hydrogen solubility in lanthan–nickel storage alloys of D2d structure and $CaZn_5$ type was carried out taking into account the possible arrangement of hydrogen atoms in interstitial sites of two types. The equilibrium state equation determining the P–T–c diagram was determined and hydrogen solubility isotherms were constructed. The calculation results were compared with experimental data for hydrogen solubility in binary $LaNi_5$, $LaCu_5$ and $LaCo_5$ alloys and various ternary phases of the examined structure.

Keywords: Lanthan–nickel alloy; Equilibrium concentration; Hydrogen solubility; Isotherm

1. Introduction

The multicomponent composition of hydride systems makes possible the creation of storage systems with a controlled content of hydrogen. In $LaNi_5$ alloys the lanthanum atoms can be partially substituted by atoms of rare-earth metals (R = Nd, Pr, Sm, Er, Y, Gd) and the nickel atoms by atoms of metals (Me = Al, Cu, Fe, Mn, Si). Such additions can stabilize the structure, increase the hydrogen absorptivity, and reduce the material cost. Examples of such systems are $LaNi_4AlH_5$, $La_2Ni_9AlH_{10}$, $LaNi_{4.5}Co_{0.5}H_{8.8}$, $LaNi_3Co_2H_5$, $La_{0.8}Er_{0.2}Ni_5H_6$ and $La_{0.8}Co_{0.2}Ni_5H_6$ hydrides.

Experimental isotherms of hydrogen solubility in $La_{1-x}R_xNi_{5-y}Me_y$–H systems [1–11], in which the limiting concentration of hydrogen atoms with respect to the concentration of metal atoms varies within $1.5 \leq s \leq 6$, permits us to assume that hydrogen atoms can be placed in tetrahedral and triangular interstitial sites and also simultaneously in interstitial sites of different types.

Theoretical investigation of interstitial impurity solubility in metals and ordering alloys of cubic structure was first developed without considering correlations [12]. Correlations in the theory of solubility of interstitial impurities in binary alloys with body-centered and face-centered cubic structures were taken into consideration in Refs. [13,14]. The solubility of interstitial impurities in alloys with the hexagonal close-packed structure of AB and AB_3 type was calculated in Refs. [15,16]. In the present investigation, a calculation of hydrogen solubility in binary and ternary lanthan–nickel storage alloys of D2d structure was carried out taking into account volume effects. Knowledge of the limiting solubility of interstitial impurities can permit control of the formation of the physical properties of interstitial phases by suitable selection of specific alloying components. Therefore, the theory of the development of hydrogen solubility in examined systems, the calculation of the equilibrium equation determining the P–T–c curves, the construction of P–s isotherms, elucidation of their run, level, slope and non-linearity, the influence of R and Me metal impurities on hydrogen absorption and the determination of possible hydrogen storage in the investigated phases are of scientific and practical interest.

2. Thermodynamic potential. Equilibrium equations. Hydrogen solubility

Calculations of the thermodynamic potential for systems of the $La_{1-x}R_xNi_{5-y}Me_y$–H type and its minimization were performed on the basis of the molecular-kinetic concept to solve the above problems. The method of average energies was used in a model of pair interaction of nearest atoms, ignoring the correlation in substitution of lattice sites and interstitial sites by atoms. Lattice distortion was not taken into account because, as is well known, the interstitial hydrogen atoms in metals only increase the

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*Corresponding author.

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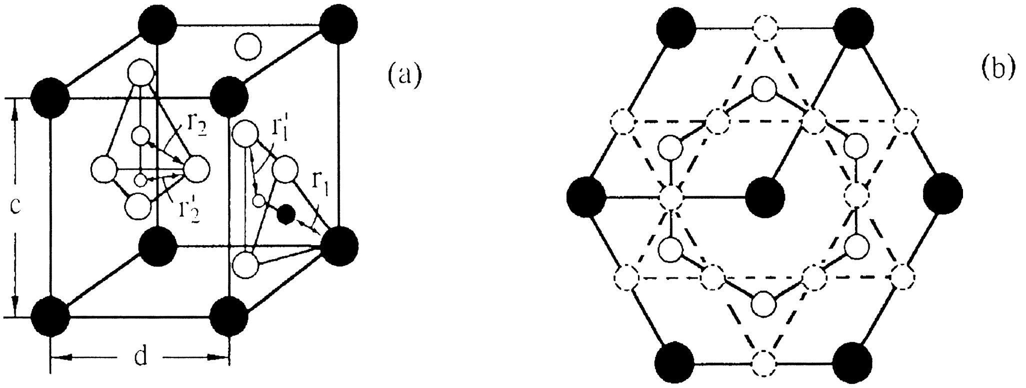

Fig. 1. D2d structure of $CaZn_5$ type. (a) Three-dimensional presentation of the lattice elementary cell. (b) Lattice presentation in projection on the equatorial plane. The elementary cell is indicated by thick lines. The sites in planes at distance $c/2$ are connected by full and dotted straight lines. (●) Sites of the first type corresponding to La and R atoms. (○ ◌) Sites of the second type corresponding to Ni and Me atoms. (● ○) Tetrahedral interstitial sites of two types. (o) Triangular interstitial sites.

lattice parameter without changing the lattice. Therefore, we allowed for the dependence of the crystal volume and lattice constant on the hydrogen concentration, for the activity of hydrogen atoms on the external pressure and for the interaction energies of atomic pairs on the interatomic distance. The D2d structure of $CaZn_5$ type [17] is shown in Fig. 1.

The thermodynamic potential of the $La_{1-x}R_xNi_{5-y}Me_y$–H system was calculated in accordance with the formula

$$\Phi = E - kT\ln G + PV - kTN_H \ln\lambda \qquad (1)$$

where k is Boltzmann's constant, T is the absolute temperature, P is the all-round pressure, λ is the activity of hydrogen atoms, N_H is the number of hydrogen atoms in the crystal, E is the configuration internal energy determined from the sum of energies of pair interactions, and G is the thermodynamic probability of the hydrogen atom distribution at interstitial sites, which is determined by the combinatorial rule.

Under the assumption that hydrogen atoms occupy positions of two types, the thermodynamic potential of the $La_{1-x}R_xNi_{5-y}Me_y$–H system is given by

$$\begin{aligned}\Phi = {} & N[(k_{11}c_1 + k_{12}c_2)(lU_{La} + rU_R) \\ & + (k_{21}c_1 + k_{22}c_2)(nU_{Ni} + mU_{Me})] \\ & + kTN\left[c_1 \ln\frac{c_1}{\mu_1} + (\mu_1 - c_1)\ln\left(1 - \frac{c_1}{\mu_1}\right)\right. \\ & \left. + c_2 \ln\frac{c_2}{\mu_2} + (\mu_2 - c_2)\ln\left(1 - \frac{c_2}{\mu_2}\right)\right] \\ & + PV_0(1 - \chi P) - kTN(c_1 + c_2)\ln(DP^{1/2}) \qquad (2)\end{aligned}$$

where N is the number of interstitial sites occupied by hydrogen atoms, k_{ij} is the number of lattice sites of $j = 1,2$ type nearest to an interstitial site of $i = 1,2$ type, c_i is the concentration of hydrogen atoms in i-type interstitial sites in the ratio to the number of all interstitial sites occupied by hydrogen atoms, μ_i is the relative number of interstitial sites of i-type in which hydrogen atoms are placed, U_{La}, U_R, U_{Ni} and U_{Me} are energies of the interatomic interactions of LaH, RH, NiH and MeH pairs, l, r, n and m are the atomic concentrations of the La, R, Ni and Me components, respectively, V_0 is the crystal volume at $P = 0$, $\chi = -(1/V)(\partial V/\partial P)$ is the crystal compressibility, and D is the constant of proportionality in the formula describing the hydrogen atom activity to pressure $\lambda = DP^{1/2}$.

It is necessary to take into account energies U_{La}, U_R, U_{Ni} and U_{Me} as a function of pressure:

$$U_\gamma = U^{\circ}_\gamma - \alpha_\gamma P,\ \ \alpha_\gamma = \frac{1}{3}\delta\chi\left(\frac{\partial U_\gamma}{\partial\delta}\right)_{\delta_0},$$
$$\gamma = \text{La, R, Ni, Me} \qquad (3)$$

where $U_\gamma = U^{\circ}_\gamma$ at $P = 0$ and $\delta_0 = \delta_{P=0}$ is the atomic volume diameter.

By minimizing the thermodynamic potential Φ (2) we

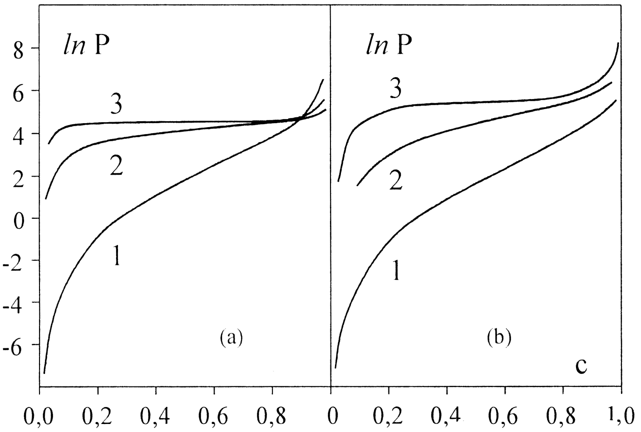

Fig. 2. Isotherms of hydrogen solubility for values $U = 1$ eV, $\alpha = 10^{-2}$ eV/Pa. (a) $D = 1$ $Pa^{-1/2}$, $1/kT = 1$, 5 and 20 eV^{-1} (curves 1, 2 and 3, respectively). (b) $D = 1$, 10 and 100 $Pa^{-1/2}$ (curves 1, 2 and 3, respectively), $kT = 1$ eV.

can calculate the total equilibrium concentration of hydrogen atoms:

$$c = c_1 + c_2$$

$$= \mu_1\left(1 + \frac{1}{DP^{1/2}}\exp\frac{U_1 - \alpha_1 P}{kT}\right)^{-1} + \mu_2\left(1 + \frac{1}{DP^{1/2}}\exp\frac{U_2 - \alpha_2 P}{kT}\right)^{-1} \quad (4)$$

where

$$U_1 = k_{11}(lU^{\mathrm{o}}_{\mathrm{La}} + rU^{\mathrm{o}}_{\mathrm{R}}) + k_{21}(nU^{\mathrm{o}}_{\mathrm{Ni}} + mU^{\mathrm{o}}_{\mathrm{Me}}),$$
$$U_2 = k_{12}(lU^{\mathrm{o}}_{\mathrm{La}} + rU^{\mathrm{o}}_{\mathrm{R}}) + k_{22}(nU^{\mathrm{o}}_{\mathrm{Ni}} + mU^{\mathrm{o}}_{\mathrm{Me}})$$
$$\alpha_1 = k_{11}(l\alpha_{\mathrm{La}} + r\alpha_{\mathrm{R}}) + k_{21}(n\alpha_{\mathrm{Ni}} + m\alpha_{\mathrm{Me}}),$$
$$\alpha_2 = k_{12}(l\alpha_{\mathrm{La}} + r\alpha_{\mathrm{R}}) + k_{22}(n\alpha_{\mathrm{Ni}} + m\alpha_{\mathrm{Me}}) \quad (5)$$

Eq. (4) defines the *P–T–c* diagram of the system in the

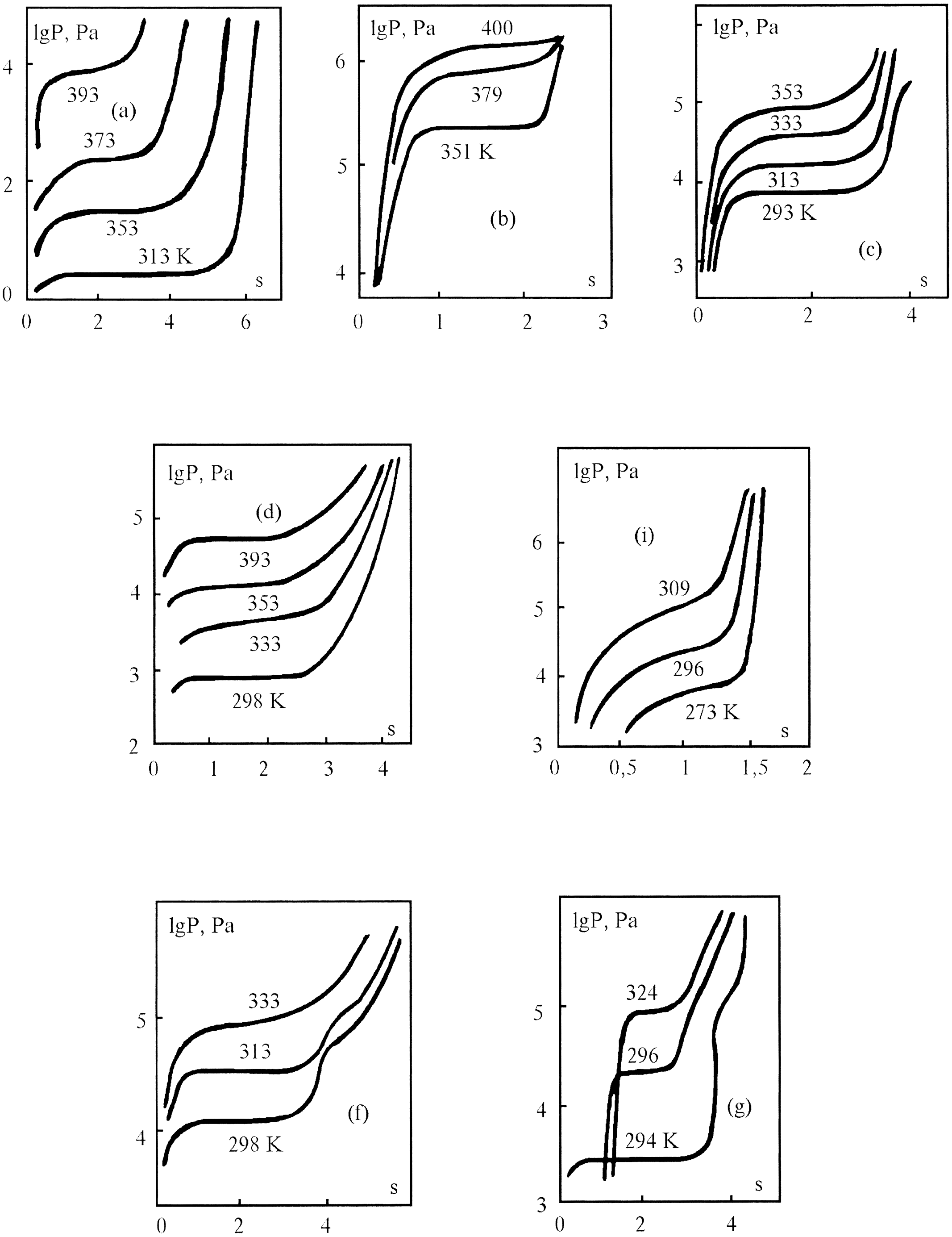

Fig. 3. Experimental isothermal curves of hydrogen solubility in $LaNi_5$ [10] (a), $LaCu_5$ [3] (b) and $LaCo_5$ [11] (c) binary alloys and $LaNi_4Al$ [1] (d), $LaNi_4B$ [1] (e), $LaNi_3Co_2$ [7] (f) and $LaCo_4B$ [1] (g) ternary alloys at the temperatures indicated.

equilibrium state. It is evident from this equation that, in the case under consideration, the isotherms ($P^{1/2}$ dependence on c at $T = \text{const.}$), isobars ($\ln c$ dependence on $1/T$ at $P = \text{const.}$) and isopleths ($\ln P$ dependence on $1/T$ at $c = \text{const.}$) are not linear functions as in the case of pure metals in the absence of volume effects and uniformity of hydrogen atom positions with low hydrogen solubility.

If the hydrogen atoms are arranged in interstitial sites of one type ($\mu_1 = 1$, $\mu = 0$), the formula defining the hydrogen solubility with reference to the number of interstitial sites of this type is

$$c = c_1 = \left(1 + \frac{1}{DP^{1/2}} \exp \frac{U - \alpha P}{kT}\right)^{-1}, \ U = U_1,$$
$$a = \alpha_1, \ \mu_1 = 1 \tag{6}$$

At low hydrogen solubility ($c \ll 1$), formula (6) is simplified to

$$c = DP^{1/2} \exp \frac{-U + \alpha P}{kT} \tag{7}$$

and it follows that, at $\alpha = 0$, all the mentioned regularities of the P–T–c curves must manifest themselves as in the case of pure metals.

3. Discussion of results. Comparison with experiment

Let us analyze the results obtained and examine formula (6). Quantitative evaluation of distances r_1, r_1', r_2 and r_2' for concrete systems of the investigated structure has shown that the variation in these magnitudes is 8–10%. This means that energies U_1 and U_2 and coefficients α_1 and α_2 differ insignificantly. Therefore, for a crude estimation of the equilibrium hydrogen concentration it is possible to examine formula (6) for the arrangement of hydrogen atoms in interstitial sites of one type and of two types.

In reports [1–11] concerning investigations of the P–T–c diagrams of $La_{1-x}R_xN_{5-y}Me_y$–H systems, the hydrogen concentrations were determined as the ratio N_0, the number of matrix atoms La, R, Ni and Me, and for different systems of the examined type it was assumed that the maximum limiting value is $\neq 1$ ($c_{\lim} \to 1$), in correspondence with formula (6), but >1:

$$s_{\lim} = v c_{\lim} \ (v = N/N_0) \tag{8}$$

and equals 2, 2.7, 4 and 6, where v is the concentration of interstitial sites occupied by hydrogen atoms in the ratio of the lattice site number.

Isotherms of hydrogen solubility in alloys of the $CaZn_5$ type, constructed using formula (6), are shown in Fig. 2. It is clear from Fig. 2 that the hydrogen concentration c tends to approach $c \to c_{\lim} = 1$ and $s \to s_{\lim} = 1$ as pressure P increases. The character of the $\ln P$ dependence on c is determined to a considerable extent by the temperature and the activity of the hydrogen atoms. With decreasing temperature (Fig. 2a) or increasing activity (Fig. 2b) the plots become more gently sloped and a plateau appears, the length of which increases with decreasing temperature and increasing hydrogen atom activity.

The experimental isotherms of the hydrogen solubility in some binary systems of the investigated structure [1,3,7,9,11] are presented in Fig. 3. For all systems, there is a plateau or one appears with decreasing temperature and becomes elongated with decreasing temperature. From the behaviour of the isotherms for each system it is possible to determine the limiting hydrogen solubility $s_{\lim}$ and the assumed type of interstitial site occupied by the hydrogen atoms. From this, a temperature change can cause a redistribution of the hydrogen atoms on interstitial sites of another type.

Theoretical isotherms of the hydrogen solubility in the ternary systems $La_{1-x}R_xNi_5$–H and $LaNi_{5-y}Me_y$–H illustrate the effect of concentrations x and y of impurities R and Me and of the interstitial site type (v values) on the behaviour of the isotherms (see Fig. 4). The isotherms of hydrogen solubility were constructed using Eq. (6) for different v, x and y values and

$$\Delta U = \tfrac{1}{6}(U_R - U_{La}) \text{ or } \Delta U = \tfrac{1}{3}(U_{Me} - U_{Ni}) \tag{9}$$

It can be seen from Fig. 4 that the isotherms level increase at the expense of concentration x or y at $\Delta U > 0$ and decrease at $\Delta U < 0$ in comparison with $x = y = 0$. The R or Me impurity can initiate the transition of hydrogen atoms to interstitial sites of another type and that will change the limiting solubility $s_{\lim} = v$, which in its turn will change the behaviour of the isotherms. The change of isotherm behaviour with variation of v at $x = y = 0$ is

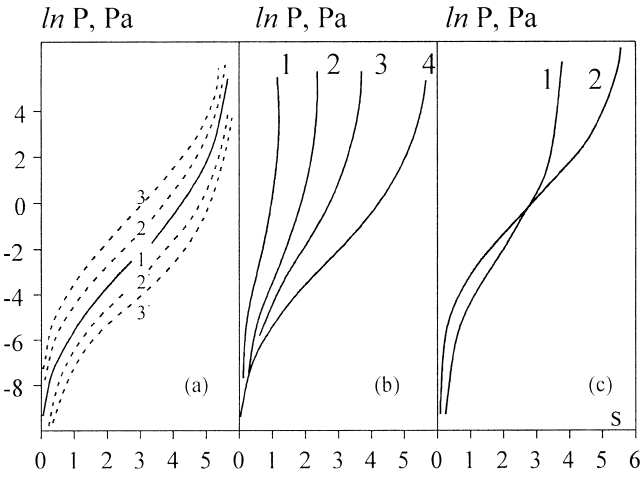

Fig. 4. Isotherms of hydrogen solubility for $U/kT = -1$, $\alpha = 10^{-3}$ eV/Pa and different v, x, y and $\Delta U/kT$ values. (a) $v = 6$, $x = y = 0$ (curve 1), $x = 2y = 0.5$ (curves 2 and 2′), $x = 2y = 1$ (curves 3 and 3′), $\Delta U/kT = 1$ (curves 2 and 3), $\Delta U/kT = -1$ (curves 2′ and 3′). (b) $x = y = 0$, $v = 1.5$, 2.7, 4 and 6 (curves 1, 2, 3 and 4, respectively). (c) $\Delta U/kT = 1$, $y = 0$ and 1 (curves 1 and 2), $v = 4$ and 6 (curves 1 and 2).

shown in Fig. 3b. Fig. 3c shows an example of the relative position of the isotherms when the Me impurity causes a redistribution of hydrogen atoms over interstitial sites of different type and in doing so changes the v value and the limiting solubility s_{lim} and increases the isotherm level at the expense of $\Delta U > 0$. All these regularities are in qualitative agreement with experimental data.

Experimental plots of the hydrogen solubility in ternary systems of $La_{1-x}R_xNi_5$ and $LaNi_{5-y}Me_y$ type for different values of x and y [1,2,4–6,8,9] are shown in Fig. 5. As illustrated in Fig. 5a–c, impurities Nd, Sm and Pr increase the isotherm level, which corresponds to a positive value of the energy difference ΔU and is evidence of a strong interaction between the hydrogen atoms and the Nd, Sm or Pr impurity atoms in comparison with La atoms. For these alloys the limiting solubility s_{lim} changes with variation of x, suggesting the partial redistribution of hydrogen atoms over interstitial sites of different types. In the $LaNi_{5-y}Al_y$

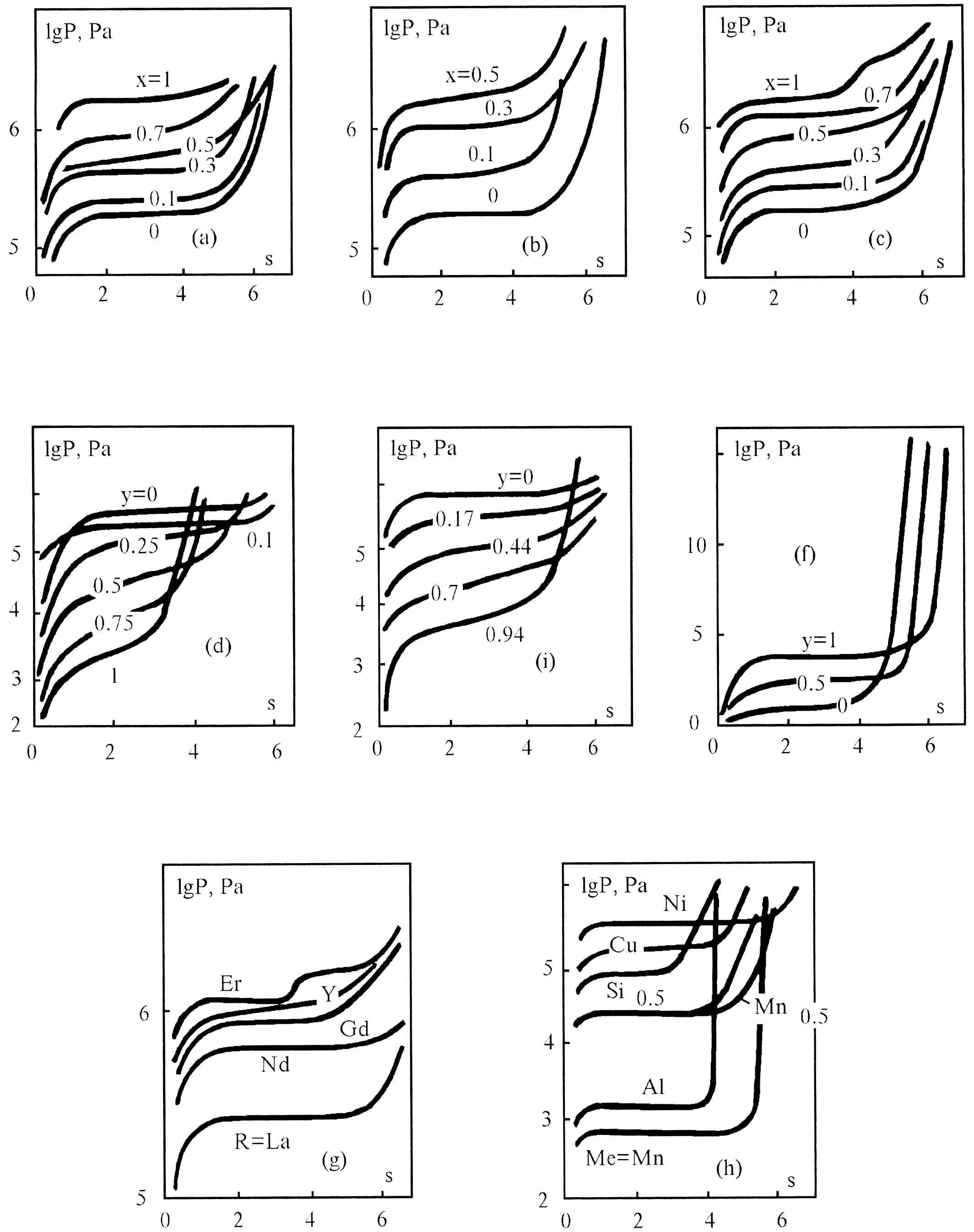

Fig. 5. Experimental isothermal curves for hydrogen solubility in $La_{1-x}R_xNi_5$ and $LaNi_{5-y}Me_y$ ternary alloys. (a) $La_{1-x}Nd_xNi_5$ [5]. (b) $La_{1-x}Sm_xNi_5$ [5]. (c) $La_{1-x}Pr_xNi_5$ [5]. (d) $LaNi_{5-y}Al_y$ [4]. (i) $LaNi_{5-y}Mn_y$ [4]. (f) $LaNi_{5-y}Fe_y$ [8]. (g) $La_{0.8}R_{0.2}Ni_5$, R=Er, Y, Gd, Nd, La [2]. (h) $LaNi_{5-y}Me_y$, Me=Mn, Al, Si, Cu, Ni [6]. (a–c) Temperature 293 K. (d–h) Temperature 313 K.

and $LaNi_{5-y}Mn_y$ systems (Fig. 5d,c) we can observe that the Me impurity changes the hydrogen solubility at low and high pressure. An aluminum or manganese impurity increases the hydrogen solubility at low pressure and decreases it at high pressure, initiating, in this case, the redistribution of hydrogen atoms from positions Q_1 to positions $\Theta_1 + Q_2'$. Such a change in the isothermal run corresponds to the case when $\Delta U < 0$, i.e. to the case of weaker interactions between hydrogen atoms and Me = Al, Mn atoms in comparison with nickel atoms. On the contrary, in the $LaNi_{5-y}Fe_y$ system (Fig. 5f), iron impurity reduces the hydrogen solubility at low pressure and increases it at high pressure, as in Fig. 4c. This corresponds to the case when $\Delta U > 0$, i.e. to the case with stronger interactions between hydrogen atoms and iron atoms in comparison with nickel atoms.

Fig. 5g,h lends support to the above consideration. The impurities R = Er, Y, Gd, as in the case of R = Nd, Sm, Pr, reduce the hydrogen solubility, but increase the level of the isotherms. However, impurities Me = Al, Mn, Cu, Si in $LaNi_{5-y}Me_y$ alloys increase the hydrogen solubility and reduce the level of the isotherms; this effect is greater the higher the value of y.

Thus, experimental investigations of isotherms for ternary systems of the $La_{1-x}R_xNi_5$ and $LaNi_{5-y}Me_y$ type using design formulae permit us to make an estimate of the energetic parameters of the interaction between hydrogen atoms and atoms of R or Me impurities, to determine their relation to the energies of interaction between hydrogen atoms and La and Ni atoms, and to ascertain the possible redistribution of hydrogen atoms over interstitial sites of different types caused by changes in concentrations x and y.

4. Conclusions

The theory developed for hydrogen solubility in lanthanum–nickel accumulator alloys with the D2d structure makes it possible for us to substantiate the limiting solubility of hydrogen, to establish the effect of R or Me impurities in $LaNi_5$ alloy, to determine the positions of the hydrogen atom arrangement, to explain the character of the possible functional dependencies of hydrogen solubility, and to ascertain the causes responsible for these dependencies.

Such knowledge can permit the regulation of the hydrogen content of such systems by selection of the impurities at each temperature and encouraging accumulation or isolation.

5. Nomenclature

Φ	thermodynamic potential
T	absolute temperature
k	Boltzmann's constant
P	external pressure
λ	activity of hydrogen atoms
V	crystal volume
χ	compressibility of crystal
U_{La}, U_R, U_{Ni}, U_{Me}	energies of interatomic interaction of LaH, RH, NiH and MeH pairs
c	total equilibrium concentration of hydrogen atoms
s	hydrogen solubility

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