

## Simulation of phase diagrams in $\text{LaNi}_5\text{-H}_2(\text{D}_2)$ system and inversion of isotopic effect

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Simulation of phase transitions in IMC-hydrogen systems based on modified scheme of perturbation theory provides correct description of main characteristics of phase diagrams within a wide pressure range of hydrogen isotopes (6 decimal orders and wider). The obtained data on thermodynamic parameters of  $\alpha$ - $\beta$  transition allows to describe inversion of isotopic effect in  $\text{LaNi}_5\text{-H}_2(\text{D}_2)$  system. Data on solubility of hydrogen isotopes in  $\text{LaNi}_5$  at pressures up to 500 atm. have been obtained; data on parameters of the critical points of  $\alpha$ - $\beta$  equilibrium (for which experimental data are absent) have been also obtained. The proposed calculation scheme does not use any fitting parameters or empirical correlations and is based on atomic characteristics of the hydrogen subsystem and metallic matrix which are physically meaningful.

Моделирование фазовых переходов в системах ИМС-водород на базе модифицированной схемы теории возмущений дает правильное описание основных особенностей фазовых диаграмм в широком диапазоне давлений изотопов водорода (6 порядков и более). Полученные сведения о термодинамических параметрах  $\alpha$ - $\beta$ -перехода позволяют описать инверсию изотопного эффекта в системе  $\text{LaNi}_5\text{-H}_2(\text{D}_2)$ . Получены также данные о растворимости изотопов водорода в  $\text{LaNi}_5$  при давлениях до 500 атм и о параметрах критической точки  $\alpha$ - $\beta$ -равновесий, экспериментальные сведения о которых отсутствуют. Предложенная вычислительная процедура не использует подгоночных параметров или эмпирических корреляций и опирается на атомные характеристики водородной подсистемы и металлической матрицы, имеющие ясный физический смысл.

Mathematical simulation of phase diagrams in hydrogen-metal hydride systems makes it possible to reduce or exclude expensive and lasting investigations. In the work [1] of the series devoted to application of thermodynamic perturbation theory for description phase equilibria in metallic hydrides and intermetallic compounds (IMC), the following results are presented. Development of the model of non-ideal lattice gas of hydrogen ions based on the perturbation theory allows to reproduce the main peculiarities of phase diagrams for IMC- $\text{H}_2$  systems in the region of disordered phases. The obtained results for PCT (pressure-composition-temperature) diagrams for

$\text{LaNi}_5\text{-H}_2$  systems agree with experimental data.

In this work, phase diagrams of  $\text{LaNi}_5\text{-D}_2$  system are simulated in the frame of the proposed method with the aim to evaluate isotopic effect in IMC hydrides taking the  $\text{LaNi}_5$  intermetallic compound as an example. Apart from purely practical applications (isotope separation, hydrogen enrichment, etc.), the problem is of a large interest from physical point of view. In particular, it is of interest whether the molecular statistic models are applicable at all to description of fine peculiarities in phase equilibria. One of those peculiarities is no doubt the inversion of isotopic effect in

LaNi<sub>5</sub>-H<sub>2</sub>(D<sub>2</sub>) system at environmental temperatures.

The new approach to the problem of phase equilibria calculation in metallic hydrides consists in determination of the hydrogen subsystem properties of metallic hydride and also of equilibrium H<sub>2</sub> molecular phase within the unified method, namely, modified scheme of thermodynamic perturbation theory (MPT) [2]. This method represents properties of the systems being investigated in the form of series in parameters describing differences between the real interaction potential of particles and potential of zero approximation system.

Thermodynamic description of the hydrogen subsystem in the region of disordered phases (in particular,  $\alpha$  and  $\beta$  ones) was carried out basing on the model of non-ideal (interacting) lattice gas of hydrogen atoms. For calculations, both the direct interaction between hydrogen atoms and indirect "deformational" contributions to the potential energy due to the lattice expansion caused by hydrogen dissolution were taken into consideration. The equilibrium properties of the lattice gas were defined for the basic case of interstitial solution with a unique type of equivalent interstitials. In this work, we shall restrict our consideration to differences in phase equilibria for LaNi<sub>5</sub>-H<sub>2</sub> and LaNi<sub>5</sub>-D<sub>2</sub> systems, that is, for two hydrogen isotopes, protium H and deuterium D. In what follows, the term "hydrogen" will stand both for H and D.

An important fact should be noted: the initial IMC crystalline structure in the majority of cases does not differ from that of the crystalline matrix in hydride (deuteride) phases of IMC-hydrogen systems in the region of disordered  $\alpha$  and  $\beta$  phases. In this case, the chemical potential  $\mu_X$  of hydrogen ( $X = H, D$ ) component of IMC hydride/deuteride has the form (including the members of the second order):

$$\beta\mu_X^+(\theta, T) = \ln \frac{\theta}{1-\theta} + \frac{W_1\theta}{T(1+\alpha C_s\theta)} + \frac{W_2\theta^2}{T^2(1+\alpha C_s\theta)^2}, \quad (1)$$

where  $\beta = 1/kT$ ;  $\mu_H^+ = \mu_H - \mu_H^{st}$ ;  $\mu_H^{st}(T)$  is the chemical potential in the standard state [1];  $\theta = C/C_s$ , hydrogen concentration;  $C = n_{\text{IMC}} \cdot c$ , hydrogen concentration in the form of X/IMC relation, that is, per formula unit of IMC;  $n_{\text{IMC}}$ , number of atoms in the formula unit,  $c$ ,

hydrogen concentration in X/Me units, that is, per one matrix atom;  $\alpha = c^{-1}(\Delta V(c)/V)$ , the dilatation coefficient of IMC lattice at hydrogen dissolution. Values  $C_s$  [H/IMC], the sorption capacity of IMC, or the maximum number of interstitial positions of H(D) atoms in the phase region being investigated, and  $c_s$  [X/Me], the maximum concentration  $c$ , are bound by the relation  $C_s = n_{\text{IMC}} \cdot c_s$ . The  $W_1$  and  $W_2$  constants providing the relationship between macroscopic properties of IMC-hydrogen interstitial solutions and microscopic (atomic) characteristics of hydrogen subsystem and IMC metallic matrix are:  $W_1 = 2I_1 n_M (\sigma_1^3 / v_0) E_1 c_s$ ,  $W_2 = (3I_2 / 4I_1^2) W_1^2$ , where  $I_1 = -5.585$ ,  $I_2 = 1.262$  are MPT parameters for H(D) gas;  $n_M$  is the number of the matrix atoms in the unit cell;  $v_0$ , the cell volume at  $C = 0$ ;  $E_1$  [K] and  $\sigma_1$  [m] are parameters of X-X interaction potential  $u_X(r) = kE_1\phi(r/\sigma_1)$  [2].

In the course of protium and deuterium absorption in intermetallic compound LaNi<sub>5</sub> in the region of  $\alpha$ - $\beta$  equilibria, the sublattice of T-interstitials can be supposed to be mainly filled; that is, thermodynamic functions of the lattice gas describe equilibrium isotherms with one "plateau" in double phase ( $\alpha + \beta$ ) regions. In order to calculate decomposition curves for homogenous phases of LaNi<sub>5</sub>-H<sub>2</sub>(D<sub>2</sub>) systems, it is necessary to find parameters in the equation (1). According to [3-6] the value of  $C_s$  is equal to 6.7 ( $c_s = 1.12$ ) for both systems. Stable combinations of  $E_1\sigma_1^3$  responsible for mutual atom-atom interaction between protium and deuterium are related approximately as  $(E_1\sigma_1^3)_D = 0.97(E_1\sigma_1^3)_H$  [4, 5, 7]. The dilatation coefficient of the LaNi<sub>5</sub> lattice is higher in the case of deuterium dissolution than in the case of protium by about 5 % [4, 7]; at  $\alpha_H = 0.20$  [6], the  $\alpha_D$  value is 0.21. In this case,  $W_1$  and  $W_2$  constants for the systems being investigated are as follows:  $W_1^{(H)} = -2.521 \cdot 10^3$  K,  $W_2^{(H)} = 1.929 \cdot 10^5 \text{K}^2$  [1];  $W_1^{(D)} = -2.444 \cdot 10^3$  K,  $W_2^{(D)} = 1.813 \cdot 10^5 \text{K}^2$ .

According to the expression (1) for chemical potential of the H(D) lattice gas, the parameters of the critical point of  $\alpha$ - $\beta$  equilibria are:  $T_c = -0.2163W_1/(1+\alpha c_s)$ ,  $C_c = \theta_c \cdot C_s$ , where  $\theta_c = 0.46/(1 + 0.54\alpha c_s)$ . For LaNi<sub>5</sub>-H<sub>2</sub>(D<sub>2</sub>) systems, this gives  $T_c^{(H)} = 445$  K,  $T_c^{(D)} = 428$  K and  $C_c^{(H)} = 2.75$  H/LaNi<sub>5</sub>,

$C_c^{(D)} = 2.73$  D/LaNi<sub>5</sub>; experimental data about positions of critical points are not available. The  $C_i(T) = C_s \cdot \theta_i(T)$  branches of the decomposition curves for LaNi<sub>5</sub>-H<sub>2</sub>(D<sub>2</sub>) homogenous phases into disordered phases  $i = \alpha, \beta$  are defined by equilibrium conditions:

$$\begin{cases} p_X(\theta_\alpha, T) = p_X(\theta_\beta, T) \\ \mu_X^\pm(\theta_\alpha, T) = \mu_X^\pm(\theta_\beta, T), \end{cases} \quad (2)$$

where  $p_X$  is the pressure of lattice X-gas,  $X = H, D$ .

Calculations of CT diagrams for LaNi<sub>5</sub>-H<sub>2</sub>(D<sub>2</sub>) systems were performed starting from the consequence of conditions (2) — the rule of equal areas (confinned by the  $\mu_X^\pm(\tilde{\theta})$  curve and straight line  $\mu_X^\pm(PL)$ ), which at the specified temperature  $T < T_c$  is fulfilled in the  $(\mu_X^\pm - \tilde{\theta})$  plane [2]:

$$p_X^{(\beta)} - p_X^{(\alpha)} = \text{const} \int_{\tilde{\theta}_\alpha}^{\tilde{\theta}_\beta} [\mu_X^\pm(PL) - \mu_X^\pm(\tilde{\theta})] d\tilde{\theta} = 0. \quad (3)$$

Here  $\tilde{\theta} = \theta/(1 + \alpha c_s \theta)$ ; dependences  $A^{(PL)} = A^{(\alpha\alpha)}(T) = A^{(\beta\beta)}(T)$ , where  $A^{(i)}(T) \equiv A(\theta_i, T)$ , are values of the function  $A = p_X, \mu_X^\pm$  at the phase boundaries  $i = \alpha, \beta$ , that is, in the pressure "plateau" and lattice X-gas chemical potential "plateau". Having found the coordinates  $\tilde{\theta}_i(T)$  according to (3), it is possible to obtain the branches of decomposition curves  $\theta_i(T)$  according to the dependence inverse to  $\tilde{\theta}(\theta)$ , that is, values  $\theta_i = \tilde{\theta}_i/(1 - \alpha c_s \tilde{\theta}_i)$  satisfying equations (2).

In Fig. 1, boundaries of the disordered phase regions are shown (CT decomposition curves) for LaNi<sub>5</sub>-H<sub>2</sub> and LaNi<sub>5</sub>-D<sub>2</sub> systems calculated from equilibrium conditions of  $\alpha$  and  $\beta$  phases according to the rule of equal areas (3). Values of critical parameters for  $\alpha$ - $\beta$  equilibriums that were found above correspond to coordinates of  $C_H$  and  $C_D$  points in the Figure. Estimation data for boundaries of  $(\alpha+\beta)$  region in LaNi<sub>5</sub>-H<sub>2</sub>(D<sub>2</sub>) system which were obtained from deuterium desorption isotherms are given for comparison according to the figures presented in [3].

The temperature dependences  $p_{X_2}^{(PL)}(T)$  of hydride (deuteride)  $\beta$ -phases decomposition pressure, that is, pressure of hydrogen ions in the "plateau" of the  $p_{X_2}(C)$  isotherms in

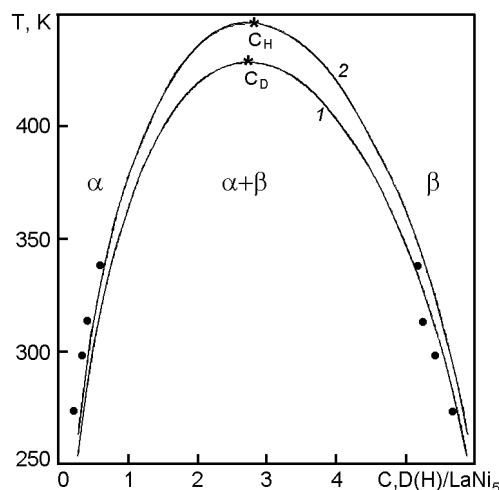


Fig. 1. Decomposition curves of homogenous phases (CT diagrams) for LaNi<sub>5</sub>-H<sub>2</sub>(D<sub>2</sub>) systems into disordered  $\alpha$  and  $\beta$  phases (calculation). •, experimental data for LaNi<sub>5</sub>-D<sub>2</sub> [3]. \* $C_H$ , \* $C_D$ , critical points of  $\alpha$ - $\beta$  equilibria. 1 - LaNi<sub>5</sub>-D<sub>2</sub>, 2 - LaNi<sub>5</sub>-H<sub>2</sub>

the heterogeneous  $(\alpha+\beta)$  phase region, may be presented in the form of conventional equation

$$\ln p_{X_2}^{(PL)}(T) = - \frac{\Delta H_{\beta \rightarrow \alpha}^{(X)}}{RT} + \frac{\Delta S_{\beta \rightarrow \alpha}^{(X)}}{R}, \quad (4)$$

where  $\Delta H_{\beta \rightarrow \alpha}^{(X)}, \Delta S_{\beta \rightarrow \alpha}^{(X)}$  correspond to enthalpy and entropy of  $\beta$ -phase decomposition. These parameters in MPT scheme have the following form:

$$\begin{aligned} \Delta H_{\beta \rightarrow \alpha}^{(X)} &\cong H_{X_2}^0 + 2RT\Delta_{\beta \rightarrow \alpha}, \\ \Delta S_{\beta \rightarrow \alpha}^{(X)} &\cong S_{X_2}^0 - 2R\Delta_{\beta \rightarrow \alpha}, \end{aligned} \quad (5)$$

where  $H_{X_2}^0, S_{X_2}^0$  are enthalpy and entropy, respectively, of H<sub>2</sub>(D<sub>2</sub>) in the standard state of ideal gas [8]; the quantity  $\Delta_{\beta \rightarrow \alpha}$  corresponds to relative difference in specific enthalpy  $h_X$  of the lattice X-gas  $h_X^{(i)}(T) \equiv h_X^{(st)}(T) + h_X^+(\theta_i, T)$  on the boundaries of homogenous phases  $\theta_\alpha(T), \theta_\beta(T)$ .

As well as in the case of decomposition of hydride  $\beta$ -phase of LaNi<sub>5</sub>-H<sub>2</sub> [1], we shall define the parameters (5) for the range of operating parameters in the isolated (critical) point. We will get the following expression for enthalpy of non-ideal lattice gas [2] and for critical concentration  $\theta_c = 0.46/(1+0.54\alpha c_s)$  in the general form:

$$\begin{aligned}
 \left| -\Delta_{\beta \rightarrow \alpha}^{(c)} = \frac{\partial(\beta h_X^{\pm})}{\partial \theta} \right|_{\substack{T=T_c \\ \theta = \theta_c}} &= \quad (6) \\
 = \frac{1}{\theta_c(1 - \theta_c)} + \frac{1}{\theta_c^2} \left[ \ln(1 - \theta_c) - \frac{0.763}{1 + \alpha_X c_s} \right].
 \end{aligned}$$

According to (6), for LaNi<sub>5</sub>-D<sub>2</sub> system at  $\theta_c^{(D)} = 0.408$ ,  $\Delta_{\beta \rightarrow \alpha}^{(c)} = 2.72$ . Taking into account the parameters for LaNi<sub>5</sub>-H<sub>2</sub> that were found before, we will obtain the following set of thermodynamic parameters [1] of the  $\beta \rightarrow \alpha$  phase transition in LaNi<sub>5</sub> hydrides and deuterides: enthalpy [kJ/mole]  $\Delta H_{\beta \rightarrow \alpha}^{(H)} = 29.8$ ;  $\Delta H_{\beta \rightarrow \alpha}^{(D)} = 31.7$ ; entropy [J/(K·mole)]  $\Delta S_{\beta \rightarrow \alpha}^{(H)} = 104$ ,  $\Delta S_{\beta \rightarrow \alpha}^{(D)} = 110$ . The  $p_{X_2}^{(PL)}(T)$  dependences obtained for both systems according to (4)–(6), are compared in Fig. 2 with experimental data [3] on the pressure in the "plateau" of H<sub>2</sub> and D<sub>2</sub> desorption isotherms.

The pressure of hydrogen isotopes in the "plateau" of similar solubility isotherms for metal-hydrogen and IMC-hydrogen systems may be lower for the heavier isotope D<sub>2</sub> (normal isotopic effect) or higher (inverse isotopic effect) than for H<sub>2</sub>. It is seen from Fig. 2 that, depending on temperature, both normal and inverse effect can be observed in LaNi<sub>5</sub>-H<sub>2</sub> system. At the temperature  $T_i$  when these isotopic pressures are equal, the inversion of isotopic effect occurs. Intersection of calculated dependences  $p_{X_2}^{(PL)}(T)$  takes place at  $(\Delta H_{\beta \rightarrow \alpha}^{(D)} - \Delta H_{\beta \rightarrow \alpha}^{(H)}) / (\Delta S_{\beta \rightarrow \alpha}^{(D)} - \Delta S_{\beta \rightarrow \alpha}^{(H)}) = 317$  K; experiment [3] gives  $T_i = 308$  K as an average for different samples.

From the equation (4), one an analytical expression for relationship between equilibrium pressures of hydrogen isotopes (at  $T < T_c$ , K) can be obtained:

$$\ln \left( \frac{p_{D_2}^{(PL)}}{p_{H_2}^{(PL)}} \right) = 0.72 - \frac{228.5}{T}, \quad (7)$$

as well as the pressure values at critical points of  $\alpha$ - $\beta$ -equilibria:  $p_{H_2}^{(c)} = 86$  atm.,  $p_{D_2}^{(c)} = 75$  atm. Experimental data on the parameters of critical points for these equilibria in LaNi<sub>5</sub>-H<sub>2</sub>(D<sub>2</sub>) are absent to date.

The nature of inverse isotopic effect is associated mainly with lower energy of D–D interaction in the lattice in comparison with H–H interaction. The vibration amplitude of

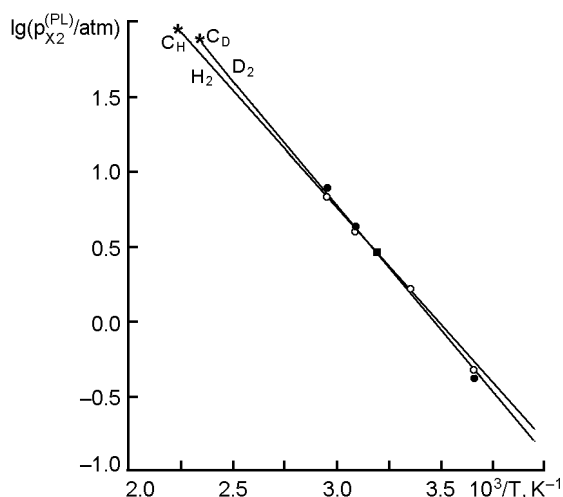


Fig. 2. Logarithm of hydrogen isotope pressure in the "plateau" of  $p_{X_2}(C)$  isotherms in double-phase region ( $\alpha + \beta$ ) as a function of inverse temperature, calculations according to (4). Experimental data on hydrogen desorption [3]:  $\circ$  – H<sub>2</sub>,  $\bullet$  – D<sub>2</sub>. Critical points of  $\alpha$ - $\beta$  equilibria:  $*C_H$ ,  $C_D$  (calculations);  $T_i$ , temperature of isotopic effect inversion.

D atoms in interstitials is less than that of H atoms [4]; their smaller volume results eventually in the above-mentioned differences in  $(E_1\sigma_1^3)$  combinations for interaction of isotopic atoms. On the other hand, differences in zero vibration energy between protium and deuterium atoms in the metallic or IMC lattice are of a large importance. The competition of these two factors can explain the nature of isotopic effect (normal or inverse). As for the effect inversion, in general, it should take place in any system, as straight lines in the Fig. 2 never run in parallel. However, such inversion can occur in the systems where significant temperature extension of double-phase region ( $\alpha + \beta$ ) exists, though this is not a sufficient condition. For example, for Pd–H<sub>2</sub>(D<sub>2</sub>) system with inverse isotopic effect and very wide temperature range of  $\alpha$ - $\beta$  equilibria (no less than 400 K), the dependences (2) may intersect at about 1000 K which is much higher than the critical temperature of  $\alpha$ - $\beta$  transition (~570 K) [2].

The phase PCT diagrams relating the gaseous phase pressure  $p_{X_2}$  of hydrogen isotopes with  $C$ ,  $T$  parameters of hydride and intermetallic compounds can be obtained from the chemical potential equality condition for the hydride X-subsystem  $\mu_X(C, T)$

and molecular  $\mu_{X_2}(p_{X_2}, T)$  gaseous phase per one isotope atom:

$$\mu_{X_2}(p_{X_2}, T) = 2\mu_X(C, T). \quad (8)$$

After a number of rearrangements similar to [2], we can obtain (according to (8)) for  $p_{X_2}(\theta, T)$  curves intersecting single- and double-phase regions of IMC-hydrogen systems:

$$\begin{aligned} \ln p_{X_2}(\theta, T) &= \\ &= \ln p_{X_2}^{(PL)}(T) + 2\beta[\mu_X^+(\theta, T) - \mu_X^{+(PL)}(T)], \end{aligned} \quad (9)$$

where  $\mu_X^{+(PL)}$  is the chemical potential value of lattice X-gas in the "plateau" of  $\mu_X^+(\theta)$  isotherms; the value is defined by conditions (2) of the gas-liquid phase transition. The expression (9) at  $\theta < \theta_\alpha$  and  $\theta > \theta_\beta$  describes descending and ascending branches of  $p_{X_2}(C)$  isotherms, respectively, and at  $\theta_\alpha < \theta < \theta_\beta$  it gives the value  $p_{X_2}^{(PL)}$  according to Van't Hoff equation (4).

For isotherms  $T \geq T_c$  and elevated pressures  $p_{X_2}$ , we obtain:

$$\begin{aligned} \ln p_{X_2}(\theta, T) + 0.18 \frac{p_{X_2}(\theta, T)}{T} = \\ Q_X + \frac{\Delta\Phi_{X_2}^0(T)}{R} + 2\beta[\mu_X^+(\theta, T) - \mu_X^{+c}], \end{aligned} \quad (10)$$

where  $\Delta\Phi_{X_2}^0(T) = \Phi_{X_2}^0(T) - \Phi_{X_2}^0(T_c^{(X)})$ ;  $\Phi_{X_2}^0(T) = -G_{X_2}^0(T)/T$ ,  $G_{X_2}^0$  is the Gibbs energy in the standard state of ideal  $X_2$  gas [8];  $Q_X = \ln p_{X_2}^{(c)} + 0.18 p_{X_2}^{(c)}/T_c^{(X)}$ . The expression (10) provides PCT dependences above the critical point of  $\alpha$ - $\beta$  transition up to pressures of about 500 atm, that is, in the case when virial expansion of chemical potential of gaseous hydrogen phases [2] can be confined to second virial coefficient  $B_{X_2}$ .

The phase diagram of  $\text{LaNi}_5\text{-H}_2$  system at temperatures below and above  $T_c^{(H)}$  was obtained before and is presented in [1]. In this work, additional phase equilibria in  $\text{LaNi}_5\text{-D}_2$  system are calculated. The set of calculated isotherms is shown in Fig. 3 in comparison with available data on  $\text{D}_2$  desorption [3]. The predicted dependences at

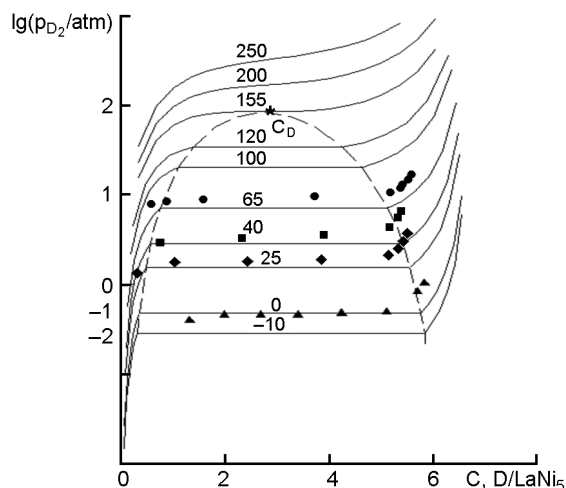


Fig. 3. PCT dependences for  $\text{LaNi}_5\text{-D}_2$  system, calculation according to (9) ( $T < T_c$ ) and (10) ( $T \geq T_c$ ). Temperatures on the isotherms are given in degrees C. The dashed line represents the boundary of double-phase ( $\alpha + \beta$ ) region in the  $(\lg p_{D_2} - C)$  plane. The critical point of  $\alpha$ - $\beta$  equilibria:  ${}^*C_D$  (calculation). Experimental data [3] on  $\text{D}_2$  desorption at temperatures:  $0^\circ\text{C}$  ( $\blacktriangle$ ),  $-25^\circ\text{C}$  ( $\blacklozenge$ ),  $40^\circ\text{C}$  ( $\blacksquare$ ),  $65^\circ\text{C}$  ( $\bullet$ ).

elevated temperatures and pressures are also shown both in double-phase and in overcritical regions. There are no experimental data on hydrogen solubility in  $\text{LaNi}_5$  in this region of states. At the critical temperature  $\mu_X^{+(c)} = \mu_X^{+(PL)}(T_c^{(X)})$  and  $\Delta\Phi_{X_2}^0 = 0$ , and both expressions (9) and 10) describe the critical isotherm ( $155^\circ\text{C}$ , Fig. 3)  $p_{X_2}(\theta, T_c^{(X)})$  with inflection point  $p_{X_2}(\theta_c, T_c^{(X)}) \equiv p_{X_2}^{(c)} = p_{X_2}^{(PL)}(T_c^{(X)})$ .

To conclude, it is possible to take into account hydrogen-hydrogen attraction adequately within the frame of thermodynamic perturbation theory. This makes it possible to reproduce within the non-ideal lattice gas not only qualitative parameters of phase equilibria in IMC-hydrogen systems, but also to describe fine peculiarities, such as inversion of isotopic effect in  $\text{LaNi}_5\text{-H}_2(\text{D}_2)$ . The isotopic effect character (normal or inverse) is defined mainly by competition of two factors: lower energy of D-D interaction in the lattice as compared to the H-H one and, on the other hand, by differences in zero vibration energy of prothium and deuterium atoms in the lattice. Data on solubility of hydrogen isotopes at the pres-

sure up to 500 atm and parameters of critical point  $\alpha$ - $\beta$  equilibria have been obtained.

### References

1. V.S.Marinin, Yu.F.Shmalko, K.R.Umerenkova, *Problemy Mashinostroeniya*, **9**, 64 (2006).
2. V.S.Marinin, K.R.Umerenkova, Yu.F.Shmalko, *Functional Materials*, **10**, 614 (2003).
3. A.Biris, R.V.Bucur, *J. Less-Common Met.*, **49**, 477 (1976).
4. Hydrogen in Metals, ed. by G.Alefeld and J.Volkl, Springer, Berlin (1978).
5. A.F.Volkov, Investigation of Interaction between Hydrogen and  $\text{LaNi}_5$  Intermetallic Compound, and Optimization of Treatment with Hydrogen for Obtaining Activated Powders, Abst. Ph.D. Thesis, DPI, Donetsk, Ukraine (1989) [in Russian].
6. V.S.Marinin, Yu.F.Shmalko, K.R.Umerenkova, in: Hydrogen Materials Science and Chemistry of Carbon Nanomaterials, "NATO Security through Science. Series A: Chemistry and Biology", Springer, New York (2007), p.187.
7. V.S.Marinin, Yu.F.Shmalko, K.R.Umerenkova, Problems of Atomic Science and Technology, Series "Physics of Radiation Damages and Radiation Material Engineering", **4**, 235 (2006) [in Russian].
8. Thermodynamic Properties of Individual Compounds, ed. by V.P.Glushko, v.1, Nauka, Moscow (1978) [in Russian].

## Моделювання фазових діаграм у системі $\text{LaNi}_5\text{-H}_2(\text{D}_2)$ та інверсія ізотопного ефекту

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Моделювання фазових переходів у системах ІМС-водень на базі модифікованої схеми теорії збурень дає правильний опис основних особливостей фазових діаграм у широкому діапазоні тиску ізотопів водню (6 порядків і більше). Отримані дані щодо термодинамічних параметрів  $\alpha$ - $\beta$ -переходу дають можливість описати інверсію ізотопного ефекту у системі  $\text{LaNi}_5\text{-H}_2(\text{D}_2)$ . Також отримано дані щодо розчинності ізотопів водню у  $\text{LaNi}_5$  при тиску до 500 атм і параметрів критичної точки  $\alpha$ - $\beta$ -рівноваг, експериментальні дані щодо яких відсутні. Запропонована обчислювальна процедура не використовує корекційних параметрів або емпіричних кореляцій і спирається на атомні характеристики водневої підсистеми та металічної матриці, які є чітко зрозумілими з фізичної точки зору.