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The structural vacancies in palladium hydride. Phase diagram

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ABSTRACT

The theory development of structural vacancies formation in palladium hydride on the molecular-kinetic presentations is the subject of this paper. The production of vacant-ordered superstructure of Cu_3Au type has been considered at the high temperatures. The calculation of free energies of the PdH and Pd_3VH phases has been carried out. The constitution diagram defined the temperature and concentration regions of phases formation with the A1 and $L1_2$ structures and regions of two $A1 + L1_2$ phases realization has been constructed. The results of theoretical calculations are in agreement with experimental data.

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1. Introduction

The recent experimental investigations of palladium hydrides make it possible to discover their interesting properties: the structural vacancies are formed at the high pressure and at the $T_0 = 800\,°C$ temperature, the phase transition $PdH \rightarrow Pd_3VH_4$ of $A1 \rightarrow L1_2$ type (V is the vacancy) occurs (Fig. 1), i.e. the vacant-ordered superstructure of the Cu_3Au type is formed in the Pd_3VH_4 alloy [1–4]. As this takes place, the compression of crystal lattice is found, the lattice parameter decreases from the 0.412 nm to the 0.408 nm value [5] (Fig. 2).

The palladium–hydrogen system has been of continuing interest experimentally and theoretically [6–20] since the pioneering studies of Thomas Graham on palladium alloys in the nineteenth century. The various palladium alloys exhibit different characteristics of hydrogen absorption compared with palladium [6]. Graham demonstrated considerable prescience in selecting the palladium–silver alloy system for investigation of hydrogen absorption by palladium alloy. The palladium–hydrogen alloy has subsequently proven to be the

alloy of great interest. This system is unique to the extremely weak interatomic bond, the availability of vacancies both on the lattice sites and interstitial sites, the high mobility of hydrogen atoms.

The great solubility of hydrogen in palladium is found even at room temperature. The continuous variety of solid solutions appears up to the production of PdH alloy of nearly stoichiometric composition at sufficiently elevated temperatures [21–31]. The perfect fcc structure is realized in solutions and hydrogen atoms are located in the octahedral interstices [21,32]. The authors of paper [33] pointed at the possible partial occupation also of tetrapositions by hydrogen atoms. As this takes place, some positions remain vacant. The presence of vacancies at the weak bond of hydrogen atoms with crystal lattice is favourable to the high diffusive mobility of atoms. This, in turn, is liable to initiate the rearrangement of hydrogen atoms and their ordering over the octapositions.

The formation of Pd_3VH_4 alloy and the revealed ordering of palladium atoms and vacancies in [1] is associated with the Yum-Rozeri effect: the dependence of structure type on the

Nomenclature	
F	free energy of crystal
E	internal energy
G	thermodynamic probability
η	degree of long-range order
N	number of lattice sites
N_P, N_H	numbers of Pd and H-atoms
N_V', N_V''	numbers of vacant sites and vacant interstices
T	absolute temperature
a	lattice constant
c_P, c_H	concentrations of Pd and H-atoms

Fig. 2 — The experimental plot of time dependence for the crystal lattice parameter in palladium hydride at the temperature of 800 °C in the course of structural vacancies formation [1,5].

state of electronic density in crystal. The redistribution of electronic density occurs with the advent of hydrogen atoms in palladium. The electrons of hydrogen atoms fill the hole states in the o-zone of metal. The electronic density of crystal decreases [31], resulting in the reduced total energy of crystal lattice state (through the decrease of basic contribution from the electronic energy); in so doing the energies of interatomic interactions show a decrease, which raise the atoms mobility, the structure with minimal energy is formed, the vacant-ordered alloy Pd_3VH_4 is produced.

The development of statistical theory of structural vacancies formation and phase transition in palladium hydride with the superstructure production of Cu_3Au type is being given in the present paper. The free energies of PdH and Pd_3VH_4 phases are calculated for solving the raised problems. Calculations are carried out by the method of average energies, with the approximation of interatomic interaction only for the nearest atomic pairs without considering the correlation in occupation of sites and interstices of crystal lattice by palladium and hydrogen atoms respectively.

2. Free energies of phases

The solution of these problems has been performed by calculation and analysis of crystal free energy [20,34] and we use the assumption formula:

$$F_i = E_i - kT\ln G_i, \tag{1}$$

where $i = 1$ and 2 for PdH and Pd_3VH_4 phases, E is the configuration internal energy determined by the sum of interaction energies of nearest atomic pairs PdPd, HH, PdH; G_i is the thermodynamic probability of distribution of palladium and hydrogen atoms over their positions, defined by the combinatorics rules, k is Boltzmanns constant, T is absolute temperature.

### 2.1. Free energy of PdH phase

We also introduce the following symbols:

N is the number of sites of the crystal lattice and the same is the number of octahedral O interstices,

N_P, N_V' are the numbers of palladium atoms in the lattice sites and the vacant sites,

N_H, N_V'' are the numbers of hydrogen atoms in interstitial sites and the vacant interstices,

$$N = N_P + N_V' = N_H + N_V''; \tag{2}$$

$$c_P = N_P/N, \quad c_V' = N_V'/N, \quad c_H = N_H/N \quad c_V'' = N_V''/N \tag{3}$$
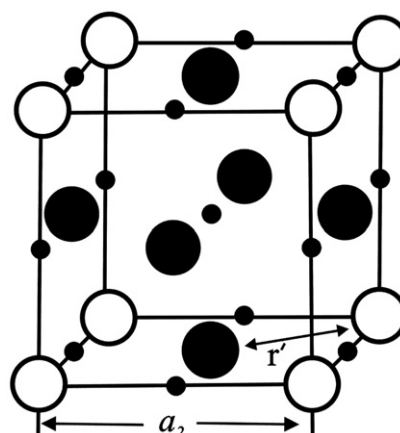
Fig. 1 — Elementary cells of lattices of the respective PdH and Pd_3VH_4 palladium hydrides. a_1, a_2, r, r' are the lattice parameters and the interatomic distances between the nearest pairs PdPd or PdH. ⬤ ● — lattice sites and interstitial sites occupied by Pd, H-atoms, respectively; ◯— vacant lattice sites V.

are concentrations of palladium and hydrogen atoms and of vacant sites and interstices,

$$c_P + c'_V = 1, \quad c_H + c''_V = 1; \tag{4}$$

N_{PP}, N_{PH}, N_{HH} are the numbers of the nearest atomic pairs PdPd, PdH, HH, $\upsilon_{PP}(r)$, $\upsilon_{PH}(a_1/2)$, $\upsilon_{HH}(r)$ are the energies with the opposite sign for interaction between atoms of these pairs at the distances indicated in parentheses (a_1 is the lattice constant, $r = a_1/\sqrt{2}$).

The configuration energy is determined by the formula

$$E_1 = -N_{PP}\upsilon_{PP} - N_{PH}\upsilon_{PH} - N_{HH}\upsilon_{HH}. \tag{5}$$

Taking into consideration the relations (3), the calculation of the numbers of atomic pairs gives the formulae

$$N_{PP} = 6Nc_P^2, \quad N_{PH} = 6Nc_Pc_H, \quad N_{HH} = 6Nc_H^2. \tag{6}$$

After substitution of these numbers (6) into (5), we get the formula for configuration energy

$$E = -6N\left(\upsilon_{PP}c_P^2 + \upsilon_{PH}c_Pc_H + \upsilon_{HH}c_H^2\right). \tag{7}$$

Thermodynamic probability is defined by the expression

$$G_1 = \frac{N!}{N_P!N'_V!} \cdot \frac{N!}{N_H!N''_V!}. \tag{8}$$

In terms of formulae (2) and (3) and using Stirling formula $\ln X! = X(\ln X - 1)$ for large X numbers, we find the natural logarithm of thermodynamical probability G_1 as follows

$$\ln G_1 = -N[c_P\ln c_P + (1 - c_P)\ln(1 - c_P) + c_H\ln c_H \\ + (1 - c_H)\ln(1 - c_H)]. \tag{9}$$

Now we find by formula (1) the free energy of the first phase for one site or interstitial site of crystal lattice

$$f_1 = F_1/N = -6\left(\upsilon_{PP}c_P^2 + \upsilon_{PH}c_Pc_H + \upsilon_{HH}c_H^2\right) + kT[c_P\ln c_P \\ + (1 - c_P)\ln(1 - c_P) + c_H\ln c_H + (1 - c_H)\ln(1 - c_H)]. \tag{10}$$

The derived formula (10) defines the dependence of free energy of the first phase on its composition (c_P, c_H concentrations), temperature T and energetic constants υ_{PP}, υ_{PH}, υ_{HH}.

2.2. Free energy of Pd_3VH_4 phase

The second phase is ordered and for calculation of its free energy F_2 we enter the complementary symbols as: $N_1 = 3N/4$, $N_2 = N/4$ are the numbers of sites of first and second types valid respectively for palladium atoms and vacancies V,

$$N = N_1 + N_2 = N_P + N'_V = N_H + N''_V; \tag{11}$$

ν_1, ν_2 are concentrations of sites of first and second type,

$$\nu_1 = N_1/N = 3/4, \quad \nu_2 = N_2/N = 1/4, \tag{12}$$

$N_P^{(1)}$, $N_P^{(2)}$, $N_V^{(1)}$, $N_V^{(2)}$ are the numbers of palladium atoms and quantities of vacant sites of first and second type;

$P_P^{(1)}$, $P_P^{(2)}$, $P_V^{(1)}$, $P_V^{(2)}$ are the a priori probabilities of substitution of the lattice sites of the first and second type with palladium atoms and probabilities of vacation of these sites. They are estimated by the following formulae

$$P_P^{(1)} = N_P^{(1)}/N_1, \quad P_P^{(2)} = N_P^{(2)}/N_2, \quad P_V^{(1)} = N_V^{(1)}/N_1, \quad P_V^{(2)} = N_V^{(2)}/N_2. \tag{13}$$

These probabilities are connected by the relations

$$P_P^{(1)} + P_V^{(1)} = 1, \quad \nu_1 P_P^{(1)} + \nu_2 P_P^{(2)} = c_P, \\ P_P^{(2)} + P_V^{(2)} = 1, \quad \nu_1 P_V^{(1)} + \nu_2 P_V^{(2)} = c'_V. \tag{14}$$

In this case

$$\eta = \left(P_P^{(1)} - c_P\right)\big/\nu_1 \tag{15}$$

is the order parameter in palladium atoms distribution in the lattice sites.

Equations (13) and (14) allow one to find the probabilities dependence on c_P, c'_V concentrations and order parameter

$$P_P^{(1)} = c_P + \nu_2\eta, \quad P_P^{(2)} = c_P - \nu_1\eta, \quad P_V^{(1)} = c'_V - \nu_2\eta, \quad P_V^{(2)} = c'_V + \nu_1\eta. \tag{16}$$

The calculation of the PdPd, PdH, HH pairs numbers gives the expressions

$$N_{PP} = 3NP_P^{(1)}\left(P_P^{(1)} + P_P^{(2)}\right), \quad N_{PH} = \frac{3}{2}Nc_H\left(3P_P^{(1)} + P_P^{(2)}\right), \quad N_{HH} = 6Nc_H^2. \tag{17}$$

Substituting the relations (17) in formula (5) for the second phase, we get the configuration internal energy of the second phase

$$E_2 = -3N\left[P_P^{(1)}\left(P_P^{(1)} + P_P^{(2)}\right)\upsilon'_{PP} + \frac{1}{2}c_H\left(3P_P^{(1)} + P_P^{(2)}\right)\upsilon'_{PH} + 2c_H^2\upsilon'_{HH}\right], \tag{18}$$

where the primed energetic symbols indicate that atomic pairs interactions are taken for the second phase.

Thermodynamic probability of the second phase is determined by the rules of combinatorics by the following equation:

$$G_2 = \frac{N_1!}{N_P^{(1)}!N_V^{(1)}!} \cdot \frac{N_2!}{N_P^{(2)}!N_V^{(2)}!} \cdot \frac{N!}{N_H!N'_V!}. \tag{19}$$

The natural logarithm of thermodynamic probability, in view of formulae (13), (3), (4), is written as

$$\ln G_2 = -N_1\left(P_P^{(1)}\ln P_P^{(1)} + P_V^{(1)}\ln P_V^{(1)}\right) - N_2\left(P_P^{(2)}\ln P_P^{(2)} + P_V^{(2)}\ln P_V^{(2)}\right) \\ - N[c_H\ln c_H + (1 - c_H)\ln(1 - c_H)]. \tag{20}$$

Now we get the free energy f_2 for one site or interstitial site of crystal lattice of the second phase by formula (1) taking into consideration formulae (18), (20), (16), (12) and second formula of (4). This expression can be written as

$$\begin{aligned}f_2 = F_2/N = &-6\left(c_P^2\upsilon'_{PP} + c_Pc_H\upsilon'_{PH} + c_H^2\upsilon'_{HH} - \frac{1}{16}\eta^2\upsilon'_{PP}\right) \\ &+ \frac{1}{4}kT\left[3\left(c_P + \frac{1}{4}\eta\right)\ln\left(c_P + \frac{1}{4}\eta\right) \\ &+ 3\left(c'_V - \frac{1}{4}\eta\right)\ln\left(c'_V - \frac{1}{4}\eta\right) + \left(c_P - \frac{3}{4}\eta\right)\ln\left(c_P - \frac{3}{4}\eta\right) \\ &+ \left(c'_V + \frac{3}{4}\eta\right)\ln\left(c'_V + \frac{3}{4}\eta\right)\right] + c_H\ln c_H \\ &+ (1 - c_H)\ln(1 - c_H).\end{aligned} \tag{21}$$

The free energy f_2 is the function of temperature T, phase composition (concentrations c_P, c_H, c'_V), order parameter η and energetic constants.

3.   The order parameter of Pd_3VH_4 phase. Equilibrium concentration of vacancies

In the case of thermodynamic equilibrium, when $\partial f_2/\partial \eta = 0$, we find the equation defined the dependence of order parameter on phase composition and temperature

$$kT\ln\frac{(c_P + \eta/4)(c'_V + 3\eta/4)}{(c_P - 3\eta/4)(c'_V - \eta/4)} = -4\eta\upsilon'_{PP}. \tag{22}$$

Assuming in this equation that $\eta \to 0$, after a little manipulation we find the T_L temperature of stable state loss

$$T_L = -4c_P c'_V \upsilon'_{PP}, \tag{23}$$

whence it follows that energetic parameter is to be negative ($\upsilon'_{PP} < 0$).

For the phase of stoichiometric composition, when $c_P = 3/4$, $c'_V = 1/4$, the relation (22) takes the form

$$kT\ln\frac{(1 + \eta/3)(1 + 3\eta)}{(1-\eta)^2} = -4\upsilon'_{PP}\eta. \tag{24}$$

The value $\omega = -4\upsilon'_{PP} > 0$ is the ordering energy of the second phase.

The graphical representation of temperature dependence of order parameter for Pd_3VH_4 alloy of stoichiometric composition is given in Fig. 3. It is seen from this figure that temperatures of stable state loss T_L, ordering T_C and extreme point T_E appeared to be closely related. The ordering temperature T_C is determined from equation (24) and the relation $f_2(\eta) = f_2(0)$, but the temperature of maximum point is defined from the extremum condition $\partial T/\partial \eta = 0$. As is obvious from Fig. 3, the phase transition order-disorder in the second phase is the first-kind transition, the order parameter varies abruptly from the η_0 value up to zero.

The equilibrium concentration of vacancies in the second phase can be found by minimization of free energy f_2. The method of Lagrangian of uncertain multiplier is convenient to use for this purpose and we set up the function

$$\psi = f_2 + \lambda\varphi, \tag{25}$$

where λ is the Lagrangian multiplier that can be related to the condition of c_P, c'_V concentrations relation
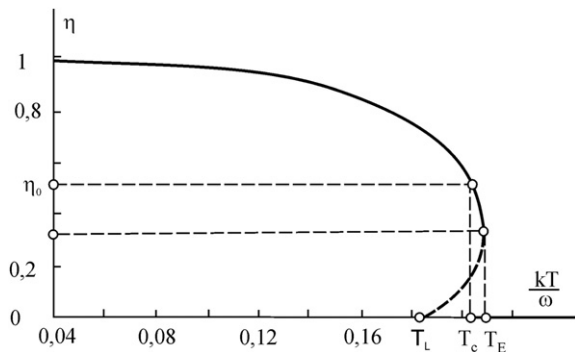
Fig. 3 – The design plot of temperature dependence of equilibrium value of order parameter for Pd_3VH_4 crystal of stoichiometric composition. T_L, T_C, T_E – temperatures of stable state loss, ordering and extreme point, respectively. The dotted part of curve corresponds to the unstable state.

$$\varphi \equiv 1 - c_P - c'_V \tag{26}$$

We equate the derivatives of ψ with respect to c_P and c'_V to zero

$$\frac{\partial\psi}{\partial c_P} = \frac{\partial f_2}{\partial c_P} + \lambda\frac{\partial\varphi}{\partial c_P} = 0, \quad \frac{\partial\psi}{\partial c'_V} = \frac{\partial f_2}{\partial c'_V} + \lambda\frac{\partial\varphi}{\partial c'_V} = 0 \tag{27}$$

and the following equations are derived as the result of calculation

$$\frac{1}{4}kT\left[3\ln\left(c_P + \frac{1}{4}\eta\right) + \ln\left(c_P - \frac{3}{4}\eta\right)\right] - 6\left(2c_P\upsilon'_{PP} + c_H\upsilon'_{PH}\right) - \lambda = 0, \tag{28}$$

$$\frac{1}{4}kT\left[3\ln\left(c'_V - \frac{1}{4}\eta\right) + \ln\left(c'_V + \frac{3}{4}\eta\right)\right] + 6\left(2c_P\upsilon'_{PP} + c_H\upsilon'_{PH}\right) - \lambda = 0. \tag{29}$$

By subtraction of equation (29) from (28) and elimination of the Lagrangian multiplier λ we get the formula

$$\ln\frac{(c_P + \eta/4)^3(c_P - 3\eta/4)}{(c'_V - \eta/4)^3(c'_V - 3\eta/4)} = \frac{48}{kT}\left(2c_P\upsilon'_{PP} + c_H\upsilon'_{PH}\right), \tag{30}$$

that in combination with the first equation of (4) defines the c'_V concentration of vacancies in the state of thermodynamic equilibrium.

In the particular case of absence of atomic order in the second phase, when $\eta = 0$, we have the simplified expression

$$\ln\frac{c_P}{c'_V} = \frac{12}{kT}\left(2c_P\upsilon'_{PP} + c_H\upsilon'_{PH}\right). \tag{31}$$

We get the c'_V concentration from this formula in the form

$$c'_V = \left(1 + \exp\frac{V}{kT}\right)^{-1}, \quad \text{where } V = 12\left(2c_P\upsilon'_{PP} + c_H\upsilon'_{PH}\right). \tag{32}$$

The evaluation of energetic parameter V gives the value $V = 0.1$ eV having regard to the formation of Pd_3VH_4 second phase experimentally at the temperature $T_0 = 800\ °C$ ($kT_0 = 0.092$ eV).

Fig. 4 illustrates the plot of temperature dependence of concentration of structural vacancies, constructed by formula (32) using the energetic parameter V. One can see from this figure that c'_V concentration of vacancies increases considerably with increasing temperature that can be responsible for the reformation of thermal vacancies into structural and, as this takes place, the last can become ordered. These vacancies predominantly occupy the cubes vertexes in the lattice cell, and as a result of which the vacant-ordering phase Pd_3VH_4 is realized. It should be pointed out that hydrogen atoms play a role in the formation of structural vacancies, it follows from the fact that $\upsilon'_{PP} < 0$, but $V > 0$ (see formula (32)).

4.   Phase diagram of the system

In transition from the first phase to the second the free energies of phases must be equal. Because of this, the state diagram can be defined from the condition of equality of free energies
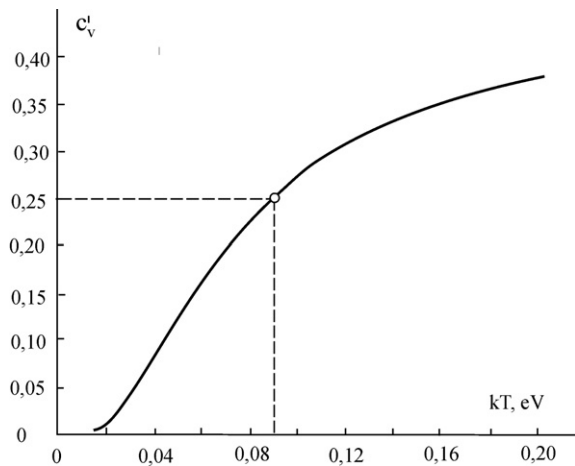
Fig. 4 – The design plot of temperature dependence of vacancies concentration in disordered second phase. The point is marked off on the curve by circle, by which the energetic parameter V is determined in formula (32).

$$f_1(c_P, c_H, T) = f_2(c_P, \eta, c_H, T). \tag{33}$$

By way of illustration we consider the particular case of maximum order in the second phase, when

$$\eta_m = \begin{cases} c_P/\nu_1 = 4c_P/3 & \text{at} \quad c_P \le \nu_1, \\ c'_V/\nu_2 = 4c'_V & \text{at} \quad c_P \ge \nu_1. \end{cases} \tag{34}$$

In this case the a priori probabilities (16) take the form

$$P_P^{(1)} = \begin{cases} c_P/\nu_1, \\ 1, \end{cases} P_P^{(2)} = \begin{cases} 0, \\ (c_P - \nu_1)/\nu_2, \end{cases} P_V^{(1)} = \begin{cases} 1 - c_P/\nu_1, \\ 0, \end{cases}$$

$$P_V^{(2)} = \begin{cases} 1 & \text{at } c_P \le \nu_1, \\ (1 - c_P)/\nu_2 & \text{at } c_P \ge \nu_1. \end{cases} \tag{35}$$

Furthermore, we shall compare the f_1, f_2 free energies without components, depending only on the c_H concentration of hydrogen and let us indicate these energies as f' and f''

$$f' = f_1(c_P, c_H, T) - f_1(c_H), \quad f'' = f_2(c_P, c_H, T) - f_2(c_H). \tag{36}$$

In the particular case being considered these formulae will be written as
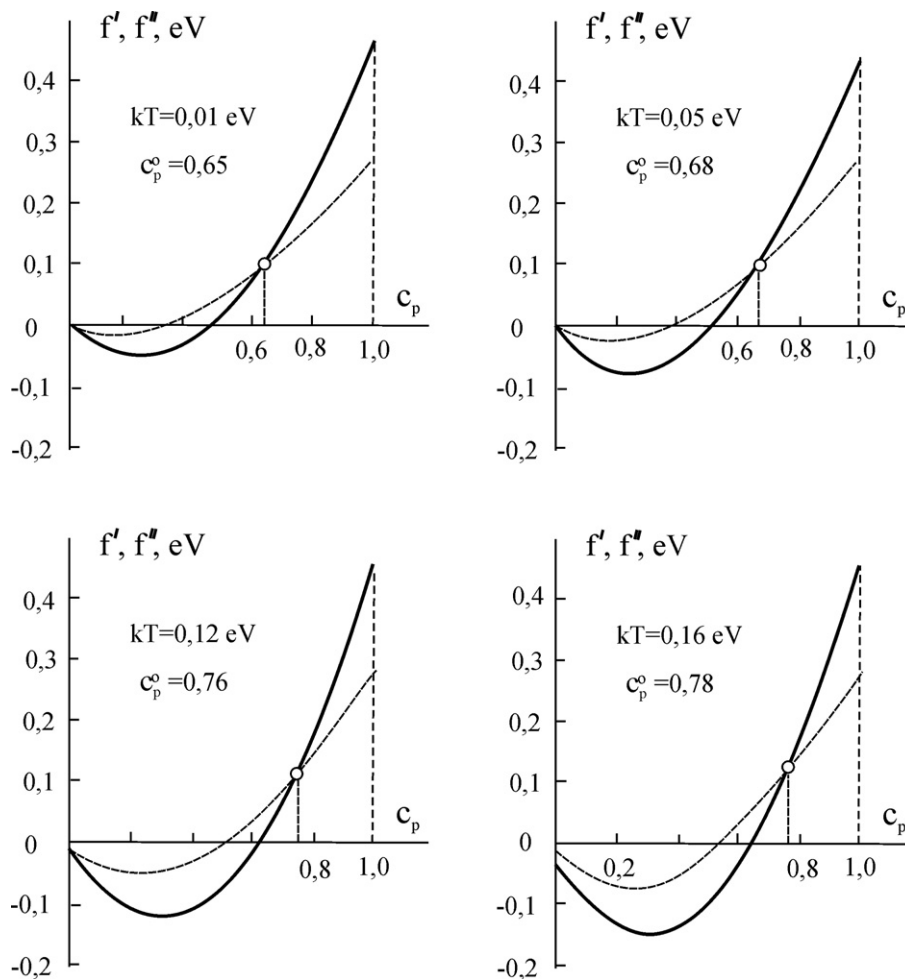
Fig. 5 – The plots for concentration dependence of free energies f', f'' (full and dotted curves, respectively) for phases with A1, L1$_2$ structures constructed by formulae (36)–(38) for different temperatures, energetic parametres (44) and maximum value of order parameter (34) in the second phase. The intersection points of $f'(c_p)$ $f''(c_p)$ functions are marked off by circles. c_p^o – concentration corresponding to the intersection point.

$$f' = V_1 + kT\Delta_1, f'' = V_2 + kT\Delta_2, \tag{37}$$

where the following designations are used

$$V_1 = -6\left(\upsilon_{PP}c_P^2 + \upsilon_{PH}c_Hc_P\right), \tag{38}$$

$$V_2 = \begin{cases} V_2' = -6\left(\frac{8}{9}\upsilon_{PP}'c_P^2 + \upsilon_{PH}'c_Hc_P\right) & \text{at } c_P \le \frac{3}{4}, \\ V_2'' = -6\left[\upsilon_{PP}'(c_P - c_H) + \upsilon_{PH}'c_Hc_P\right] & \text{at } c_P \ge \frac{3}{4}, \end{cases} \tag{39}$$

$$\Delta_1 = c_P \ln c_P + (1 - c_P)\ln(1 - c_P), \tag{40}$$

$$\Delta_2 = \begin{cases} \Delta_2' = \frac{3}{4}\left[\frac{4}{3}c_P \ln\frac{4c_P}{3} + \left(1 - \frac{4}{3}c_P\right)\ln\left(1 - \frac{4}{3}c_P\right)\right] & \text{at } c_P \le \frac{3}{4}, \\ \Delta_2'' = \left(c_P - \frac{3}{4}\right)\ln 4\left(c_P - \frac{3}{4}\right) + (1 - c_P)\ln 4(1 - c_P) & \text{at } c_P \ge \frac{3}{4}. \end{cases} \tag{41}$$

Note that at $c_P = 3/4$ these values are in the following relationship

$$V_2' = V_2'' = -3\left(\upsilon_{PP}' + \frac{3}{2}\upsilon_{PH}'c_H\right) \quad \text{and} \quad \Delta_2' = \Delta_2'' = 0. \tag{42}$$

From the condition of equal free energies $f' = f''$ the temperature T_0 of transition from the first phase to the second $PdH \rightarrow Pd_3VH_4$ with the change of structure fcc $\rightarrow L1_2$ can be found

$$kT_o = (V_2 - V_1)/(\Delta_1 - \Delta_2). \tag{43}$$

This formula allows the determination of concentration and temperature regions of formation of pure fcc and $L1_2$ phases, but does not make possible the estimation of area of two phases realization simultaneously that are bound to be at the first-kind phase transition.

The problem of constitution diagram construction is convenient to solve by graphical representation: to construct the plots $f'(c_P)$, $f''(c_P)$ for different temperatures and by points of these curves intersection and also by the method of common tangents to them to define the concentration dependence $T_0 = T_0(c_P)$ of the temperature T_0 of phase transition.

The plots $f'(c_P)$, $f''(c_P)$ have been constructed on the assumption that thermal vacancies in interstitial sites are of small concentrations, i.e. for the case of $c_H \approx 1/4$ using the following energetic parametres

$$\upsilon_{PP} = -0.154eV, \quad \upsilon_{PP}' = -0.056eV, \quad \upsilon_{PH} = 0.299eV,$$

$$\upsilon_{PH}' = 0.032eV. \tag{44}$$

These values are estimated approximately, not very clearly from experimental data about the temperature of transition $T_0 = 800\,°C$ between phases $PdH \rightarrow Pd_3VH_4$. It is evident from (44) that the υ_{PP} and υ_{PP}' energies have the negative values, as mentioned above. In addition, the υ_{PP}', υ_{PH}' energies are less by the absolute value than the υ_{PP}, υ_{PH} energies that agree with the statement of paper [1] about the decrease of interatomic interactions (at the expense of reduced electronic density) at the formation of vacantly-ordered superstructure in the palladium hydride.

Fig. 5 demonstrates some plots for concentration dependence of free energies f', f'' for different temperatures. Thereafter, we construct the constitution diagram by the intersection points of these curves and by the method of common tangents to them.
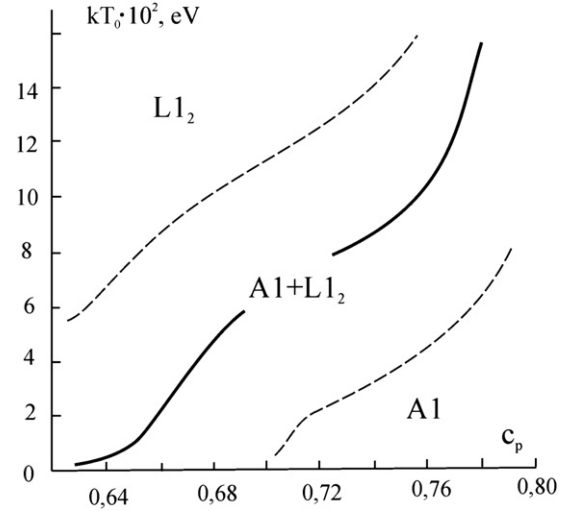
Fig. 6 – **The design constitution diagram defined the temperature and concentration regions of phases formation with A1 and $L1_2$ structures in palladium hydride. The full and dotted curves are constructed, respectively, by the intersection points of plots of $f'(c_p)$ $f''(c_p)$ functions and by the method of common tangents to them.**

The constitution diagram, determined the concentration dependence of the temperature of phase transition $PdH \rightarrow Pd_3VH_4$, is illustrated in Fig. 6. As is obvious from this diagram, the phase transitions occur in narrow concentration area in the vicinity of stoichiometric composition of the second phase. The rise in the c_P concentration tends to increase T_0 temperature. The concentration interval of fcc (A1) phase realization is narrowed down with increasing temperature, but of $L1_2$ phase, on the contrary, it becomes more wide. This finding is consistent with experimental data according to which the PdH phase is realized at low temperatures, whereas the Pd_3VH_4 phase – at high temperatures.

5. Conclusions

The elaborated statistical theory permits us to explain and justify the formation of structural vacancies in the palladium hydride with increase in temperature.

To solve the problems, a calculation of free energies f_1, f_2 of PdH and Pd_3VH_4 phases has been performed having regard to the existence of $L1_2$ superstructure (Cu_3Au type) in the second phase. From the equation of the thermodynamic equilibrium, it has been found that the concentration dependence of order parameter for the second phase that corresponds to the first-kind phase transition with the abrupt decrease of order parameter from the value of η_o to zero at the ordering temperature T_C. As this takes place, the T_L, T_C, T_E temperatures respectively of stable state loss, ordering and extremum are close to each other. But in the case being considered they are of the same order and somewhat below the T_0 temperature ($kT_0 = 0.092$ eV, $kT_L = 0.04$ eV, $kT_C = 0.047$ eV, $kT_E = 0.05$ eV). This clearly demonstrates the approximate, non much exact estimate of the υ_{PP}' energy.

The estimation of equilibrium concentration of vacancies has shown that it can be sufficiently great. This is in accordance with the possibility of structural vacancies formation with a rise in temperature.

The constitution diagram, determined the concentration and temperature regions of first and second phases formation and areas of both phases realization, has been constructed.

The concentration region of second phase formation shows the broadening at elevated temperature, that corresponds to the increase of vacancies concentration in this phase, i.e. to the formation of structural vacancies in it.

The carried out calculations give the grounds of possibility of structural vacancies formation at the solid-phase palladium hydrogenation. The comparison of obtained results with experimental data shows the qualitative agreement.

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