Fizika Nizkikh Temperatur, 2003, v. 29, No. 6, p. 710–714

Vibrational dynamical and thermodynamical characteristics of the superlattices based on the metal-hydrogen system

S.B. Feodosyev, I.A. Gospodarev, V.I. Grishaev, and E.S. Syrkin

B. Verkin Institute for Low Temperature Physics and Engineering of the National Academy of Sciences of Ukraine, 47 Lenin Ave., Kharkov, 61103, Ukraine
E-mail: feodosiev@ilt.kharkov.ua

Received December 19, 2002

The phonon spectra and vibrational thermodynamical characteristics of the Pd–H superlattices are investigated. Results of our calculations give a possibility to agree the data of neutronographic and calorimetric experiments and explain for the such systems the atomic mean square amplitudes and correlations between ones.

PACS: **63.20.–e**

1. Introduction

The fact of absorption of hydrogen by metals, particularly by palladium, is known from the middle of 19th century. It is widely used in applied purposes in particular for puritying of hydrogen. In 70th, and then in the end of 80th years of the last century study of physical properties of Pd experienced the natural boom. As the result many of these properties, for example electronic, were investigated very explicitly and in detailes (see, for example, [1]). However the dynamics of crystal lattice and oscillatory properties of such systems to the present time are studied obviously unsufficiently.

From results existing up to now, it is necessary to mention neutronographic investigation of the law of a dispersion of phonons of a solid solution $PdD_{0.63}$ fulfilled on 1974 [2]. On this basic it is possible to judge interatomic interaction and oscillatory spectrum of hydronized palladium. It is known that the contribution of oscillations of lattice into the different dynamic and thermodynamic characteristics of Pd–H can be essential and even defining. Therefore the comparison of the data received in [2] with results of different measurements of such characteristics is important and actual.

So in the recently published report [3] the measurement of temperature dependences of heat capacity PdH_x is carried out at different values of concentration of hydrogen x. It was revealed, that at $T \gtrsim 10$ K the heat capacity grows with growth of x, while the electronic component with growth of concentration of hydrogen sharply decreases [1] (the form of temperature dependence at $T \to 0$ in [3] at $x = 0.71$ also directly shows it). Directly from [2] the sign of change of the lattice contribution to a heat capacity with growth of x is not obvious. Really, the increasing of a value of a lattice constant for approximately 5% should noticeably weaken the interaction between Pd atoms, and reduce the frequency of their oscillations giving the determining contribution in lattice heat capacity. But the appearance of new neighbors for these atoms that is hydrogen atoms more close than other Pd atoms can compensate this weakening of links. Besides it is important to find out how such weakening of interatomic interaction (if it takes place) effects the amplitude values of atomic oscillations that is stability of crystal lattice.

The calculation at microscopic level is necessary to answer these questions of oscillatory thermodynamic characteristics of crystal structures like Pd–H. This report is devoted to such calculation for the case, when concentration of hydrogen in palladium is high, and it is possible to consider its allocation as uniform enough.

2. Interatomic interaction in solutions Pd–H and their phonon heat capacity

Crystal lattice of palladium is a cubic face-centered one. The dissolved atoms of hydrogen take in it octa-

hedral positions [1] and at high concentrations it is possible to speak about ordering of a solution in some superstructure.

Here we study two kinds of such superstructures: the first one corresponds to when the atoms of hydrogen disposed in the centers of *ribs* of cubes of a lattice Pd, and the centers of cubes remain empty (R-filling) and another one when the centers of cubes also are filled (V-filling). The case of R-filling corresponds to a $PdH_{0.75}$ composition; V-fillings corresponds to PdH. V-filling represents an immersion one in another of two fcc lattices of identical period with detrusion on value $a_0/2$ along the edge of cube (a_0 is a lattice constant). R-filling corresponds to formation in V-filling of periodic (with a period a_0) system of vacancies in a sublattice of hydrogen.

In [4] force constants of pure Pd were reduced under the data of neutronographic measurments. Density of phonon states of palladium $\nu(\omega)$ being constructed during this operation rather unsignificantly differs from the relevant performance being calculated in frameworks of approximation of central interaction of the nearest neighbors. It once again confirms that fact that in closely-packed crystals at description of interatomic interaction as a rule we can be restricted with such approximation. Potential $\varphi(\mathbf{r}, \mathbf{r}')$ of interaction of atoms with equilibrium positions determined by position $\mathbf{r}$ and $\mathbf{r}'$ one can consider to be a pair one and isotropic: $\varphi(\mathbf{r}, \mathbf{r}') = \varphi(\Delta)$ ($\Delta \equiv \mathbf{r} - \mathbf{r}'$).

Then the matrix of force constants $\Phi_{ik}(\mathbf{r}, \mathbf{r}')$ looks like:

$$\Phi_{ik}(\mathbf{r}, \mathbf{r}') = \Phi_{ik}(\Delta) = -\alpha(\Delta)\frac{\Delta_i \Delta_k}{\Delta^2} - \beta(\Delta)\delta_{ik}, \quad (1)$$

where δ_{ik} is a Kronecker symbol; parameters α and β characterize, respectively, central and uncentral interaction between atoms:

$$\beta(\Delta) = \frac{\varphi'(\Delta)}{\Delta}; \quad \alpha(\Delta) = \varphi''(\Delta) - \beta(\Delta). \quad (2)$$

In a Fig. 1 the dependences of force constants α and β both with Einstein frequency of fcc crystal with central interaction of the nearest neighbors from varying of interatomic distance (lattice constant) are shown. For definiteness, as potential $\varphi(\Delta)$ we chose the Lennard-Jones potential. Let us mark, that as we will be interested with varying of force constants with «swelling» of a lattice that is at $\Delta > \Delta_0(\varphi'(\Delta_0) = 0)$, the area of applicability of presented here results is

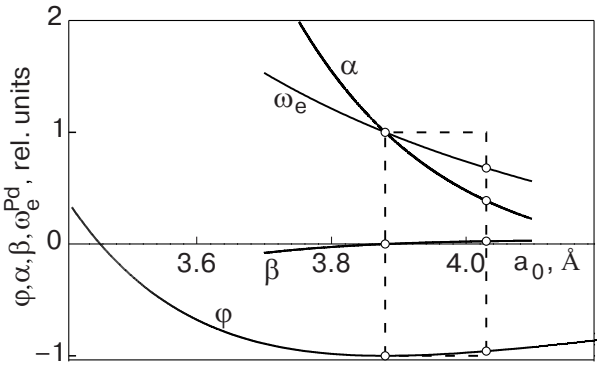

Fig. 1. Relative change with increase of a lattice constant of potential of interatomic interaction φ, force constants α, β, and Einstein oscillation frequency of atoms of palladium ω_e. All quantities are given in relative units: $\alpha(a_0) = \omega_e(a_0) = -\varphi(a_0) = 1$ ($a_0 \approx 3.88$ Å is a lattice constant of pure Pd).

much wider than the area of applicability of Lennard-Jones potential, because at $\Delta > \Delta_0$ for the majority of crystals the van der Waals attraction between atoms is in typical ($\varphi \sim \Delta^{-6}$). The values $\alpha(\Delta_0)$ and $\omega_e(\Delta_0)$ are accepted to be equal to unit (the value $\beta(\Delta_0)$ is given in units of $\alpha_0 \equiv \alpha(\Delta_0)$), and $\varphi(\Delta_0) \equiv -1$. One can see that at increase of a lattice constant from $a_0 = 3.88$ Å (lattice constant of a pure Pd) up to $a_0 \approx 4.03$ Å (palladium with concentration of hydrogen 0.7–1.0 — look, for example, [1]) the quantity of central interaction between atoms of Pd decreases more than twice, and the Einstein frequency of palladium atom does it approximately in 1.5 times. From the neutronographical data [2]*, it is possible to restore the constants of interatomic interaction in a solid solution Pd–H. According to these data the maximum frequency of acoustical band ≈ 6 THz (maximum oscillation frequency of a lattice of a pure palladium ≈ 7 THz); the width of a gap also is ≈ 6 THz and maximum frequency of optical oscillations is ≈ 21 THz. As hydrogen is lighter than palladium for approximately 106.4 times rather small width of the gap and essential dispersion of optical phonons allow one to assume that the interaction of palladium with hydrogen is much weaker than the Pd ↔ Pd one. Force constants being reduced on data from [2]** are in the good agreement with above estimation made on the basis of the carried out analysis of potential of interatomic interaction. If we accept for unity the value of force constant describing central interaction of the nearest

* These data also are given and are analyzed in [1].

** We did not take aim of precision calculations of force constants on data of work [2], as the results of our work have a qualitative character.

neighbors in lattice of a pure palladium, we shall have for the Pd–H solution:

$$\alpha_{Pd\leftrightarrow Pd} \approx 0.48;\ \alpha_{Pd\leftrightarrow H} \approx 0.12;\ \alpha_{H\leftrightarrow H} \approx 0.05;$$
$$\beta_{Pd\leftrightarrow Pd} \approx 0.05;\ \beta_{Pd\leftrightarrow H} = \beta_{H\leftrightarrow H} = 0. \quad (3)$$

On the base of these force constants it is possible at once to assume that during hydrogenization the low-temperature phonon heat capacity of a palladium should noticeably increase. Really, the basic contribution to this characteristic is done by oscillations of heavy atoms of Pd, whose interaction in comparison with the lattice of a pure palladium (because of «swelling» of lattice) is attenuated more than twice. The additional interaction of palladium with hydrogen taking place here is much less, than even attenuated interaction between atoms of metal. The Einstein frequency of oscillation of atoms of palladium, because of interaction Pd ↔ H, will be higher, than the one shown at Fig. 1 at value of lattice constant relevant to hydrogenized palladium, but is noticeably lower, than the one for pure Pd. That fact should stipulate higher values of a heat capacity at low temperatures.

The results of more precise calculations of temperature dependence of a phonon heat capacity of solid solutions Pd–H are shown at Figs. 2 and 3. The calculations are carried out by $\mathcal{J}$-matrices method [5–7] using force constants (3). Figure 2 demonstrates the dependences $C_v(T)$ for pure palladium (solid line), the one for solutions of PdH_x: the dashed line corresponds to $x = 0.75$ (R-filling), and dots to $x = 1.00$ (V-filling). Really at implantation of hydrogen the phonon heat capacity noticeably increases because of growth of lattice constant approximately for 5%.

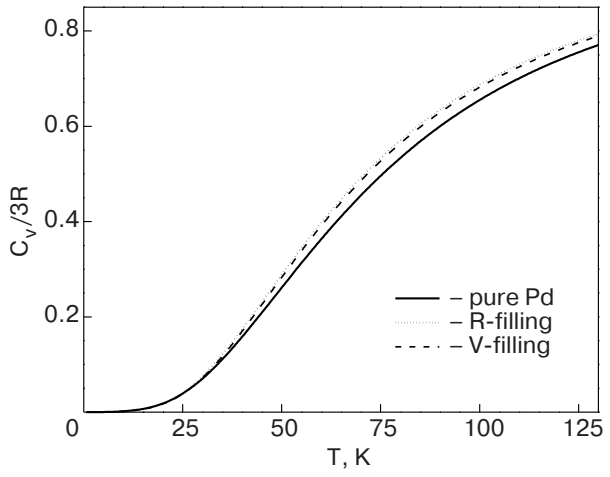

Fig. 2. Temperature dependences of a phonon heat capacity of pure Pd (solid line), $PdH_{0.75}$ (R-filling is presented as dashed line) and PdH (V-filling is presented as dashed line with points).

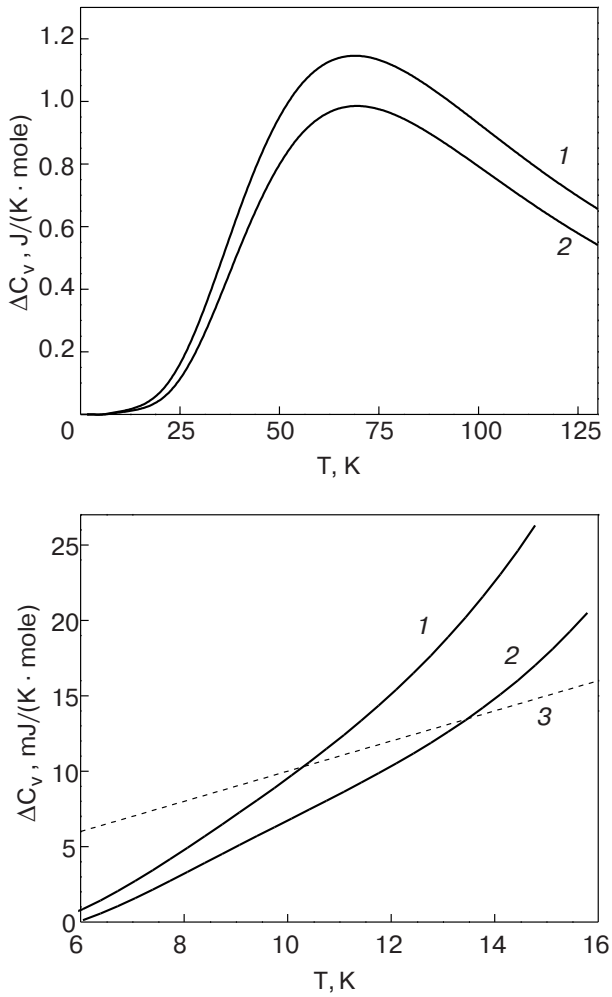

Fig. 3. Difference of lattice heat capacities of hydrogenized Pd and of a pure Pd: curve *1* shows R-filling; a curve *2* is for V-filling. The dependences $\Delta C_v(T)$ in a broad interval of temperatures are presented at the top, these dependences for low temperatures are presented below (in larger scale). The dashed curve *3* is electronic heat capacity of pure palladium [1,4].

In a Fig. 3 the temperature dependences of difference of lattice heat capacities $\Delta C_v(T)$ of hydrogenized Pd and of a pure one are shown. On the upper side of this figure the diagrams of these functions are shown in a wide interval of temperatures, and at the bottom one — at low temperatures.

On both parts of this figure the curves *1* and *2* show the values $\Delta C_v(T)$ for R- and for *V*-filling, respectively. The fact that the curve *1* lays above the curve *2* is apparent within the framework of our model, as at identical value of a lattice constant the case of R-filling corresponds to more «friable» structure. For the answer to the question how such nonmonotonic character of concentration dependence of a heat capacity can really be observed, it is natural to investigate the concentration dependence of value of lattice constant

in the indicated range of concentrations. Comparison of curves *1* and *2* with temperature dependence of electronic heat capacity of pure palladium [1,4] (curve *3*, presented as the dashed line on the bottom of a figure) shows that already at $T \approx 10$–12 K the growth of phonon part in heat capacity is able to compensate *any* (down to zero) decrease of its electronic component. This result agrees with the one in [3] and at any rate qualitatively explains such effect.

3. Mean square amplitudes and correlation of oscillations of atoms in solid solutions Pd–H

Growth of lattice constant at saturation by hydrogen of crystals of Pd and stipulated by it decrease of force constants of palladium atoms must, at the first sight, stipulated growth of amplitude of oscillations of these atoms, that can result in destabilising of a lattice. For finding out this problem we have fulfilled calculations of mean square vibration amplitudes of atoms for both palladium and hydrogen, within the framework of the same models, by the same method of $\mathcal{J}$-matrices.

The mean square vibration amplitudes of atoms of a crystal lattice are one of the main characteristic of the crystal. Besides that on their behavior it is possible to judge about stability of a crystal and about temperature of its melting. These values determine dispersion of sound and electromagnetic waves in crystal. The mean square amplitude of atom with a position vector $\mathbf{r}$ in crystallographic direction i is determined as $\sqrt{\langle |u_i^2(\mathbf{r})| \rangle_T}$, where $\langle |u_i^2(\mathbf{r})| \rangle_T$ is mean square displacement, diagonal element of correlator $\langle |u_i(\mathbf{r}) u_k(\mathbf{r}')| \rangle_T$ at $i = k$ and $\mathbf{r} = \mathbf{r}'$ is as follows:

$$\left\langle |u_i(\mathbf{r}) u_k(\mathbf{r}')| \right\rangle_T = \frac{\hbar}{2\sqrt{m(\mathbf{r}) m(\mathbf{r}')}} \times$$

$$\times \int_{\mathcal{D}} \frac{1}{\sqrt{\lambda}} \coth\left(\frac{\hbar\sqrt{\lambda}}{2kT}\right) \frac{1}{\pi} \operatorname{Im} \mathcal{G}_{ik}(\lambda, \mathbf{r}, \mathbf{r}') d\lambda \ . \qquad (4)$$

Here $m(\mathbf{r})$ is mass of atom with a position vector $\mathbf{r}$; λ is square of eigen frequency; $\mathcal{G}_{ik}(\lambda, \mathbf{r}, \mathbf{r}')$ is relevant element of Green's tensor of lattice; T is temperature; $\hbar$ and k are Planck and Boltsmann constants, respectively.

The results of calculation of temperature dependences of mean square amplitudes by $\mathcal{J}$-matrices method are shown as solid lines in Fig. 4. The curves *0* correspond to pure Pd. Curves *1* and *1′* and *3* show mean square amplitudes for Pd at the presence of hydrogen (the curve *3* is obtained for case of V-filling, the rest are for R-filling). Curve *1* corresponds to displacement of $Pd^{(0)}$ atom (in any direction), and also

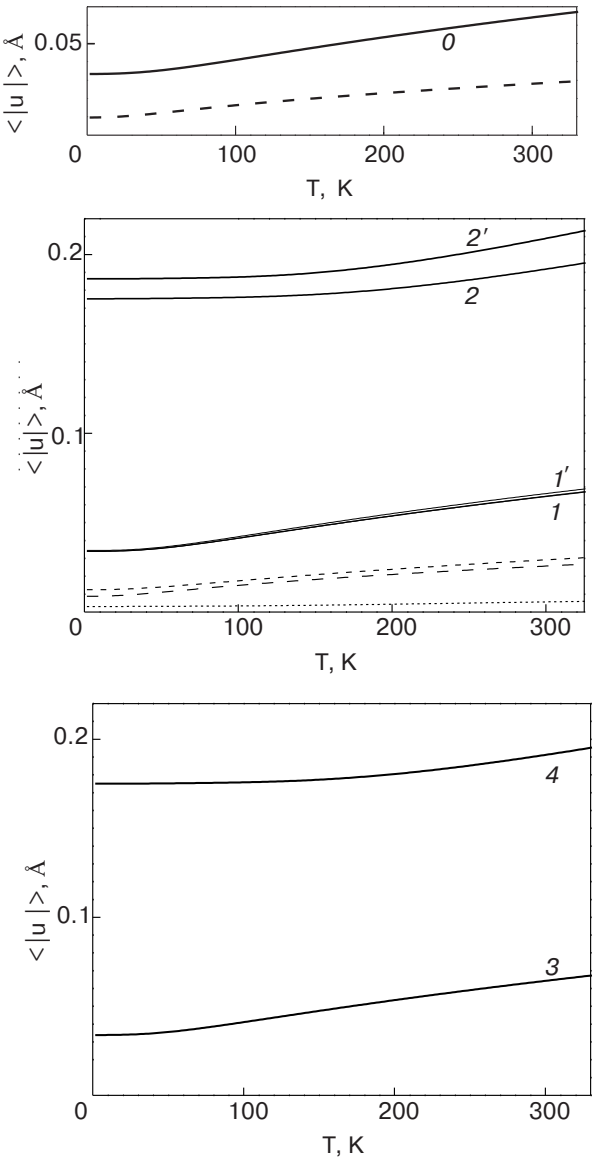

Fig. 4. Temperature dependences of mean square amplitudes and correlations of displacements. Curves *0* correspond to pure Pd: continuous line is a mean square amplitude, the dashed one is correlation of displacements of atoms Pd ↔ Pd. The curves *1* and *1′* correspond to mean square amplitudes of atoms Pd in solution $PdH_{0.75}$; *2* and *2′* are for atoms of hydrogen in the same solution (curves *1′* and *2′* correspond to displacements in direction of centre of a cube, that in this case is vacant), the long dashes are designated correlations of displacements of Pd ↔ Pd, short ones are designated for Pd ↔ H, points are designated H ↔ H. Curves *3* and *4* accordingly mean square vibration amplitudes of atoms of palladium and hydrogen in a solution PdH (V-filling).

to atom of $Pd^{(1)}$ in directions to the nearest atom of hydrogen; a curve *1′* shows displacements of $Pd^{(1)}$ in direction to center of a cube (at R-filling vacant). That is why curve *1′* lays slightly above curve *1*. The curves *0*, *1* and *3* differ from each other very little.

Curves *2* and *2′* present mean square vibration amplitudes of hydrogen atoms: in a direction along the rib, in the middle of which it is (curve *2*) and in perpendicular to it directions (curve *2′*). The curve *4*, practically coinciding with a curve *2*, corresponds to mean square amplitude of hydrogen atom at V-filling. That is we have received unexpected on the first sight result: the change of mean square amplitudes of oscillations of palladium atoms in solutions Pd–H have, in comparison with pure Pd, is very little. Because of a huge difference in mass between a palladium and hydrogen, the mean square amplitudes of unit cells of solutions Pd–H and palladium atoms practically coincide, the lattice of such solution will be practically as stable, as the lattice of a pure palladium.

In order to understand why weakening of interatomic interaction has not lead to noticeable increase of oscillation amplitudes of a palladium we shall consider correlations of displacements in the given systems. To have an opportunity to compare the values of such correlations to the ones of mean square amplitudes of a correlation it is convenient to characterize by dependence $\sqrt{\langle |u_i(\mathbf{r})u_k(\mathbf{r}')|\rangle_T}$, where the radicand is determined by relation (4). Temperature dependences of such functions for displacements of neighbor atoms along the line connecting them (when the correlation is maximum) also are shown at the same Fig. 4 (dashed lines): the long dashes correspond to correlations of displacements of Pd ↔ Pd; the short ones correspond to Pd ↔ H and dots correspond to H ↔ H. For R- and V-fillings the data of dependence practically coincide and on a fragment relevant to V-filling the diagrams of correlations of displacements are not shown.

The high value of a correlation of displacements Pd ↔ H testifies to considerable pumping-over of energy from palladium atoms to hydrogen atoms. The amplitude of oscillation of Pd atoms practically does not increase with decreasing of interatomic interaction during hydrogenization, as the palladium atoms thus «shake» atoms of hydrogen.

4. Conclusions

Thus, our microscopic calculations of thermodynamic characteristics have shown that the data of neutronographic [2] and calorimetric experiments [3] are mutually consistent. In particular it is shown, that the weakening of interatomic interactions caused by increasing of lattice constant resulted by implantation of hydrogen in a palladium gives a noticeable gain of the phonon contribution in a low-temperature heat capacity. At $T \gtrsim 10$–12 K this phonon contribution in heat capacity cancels decreasing of an electronic contribution in heat capacity happening at hydrogenization of palladium [1,4].

Also it is shown, that in a temperature range up to 400 K the value of mean square amplitudes both palladium and hydrogen is insignificant in comparison with a lattice constant (3.88 Å for a pure palladium and ≈ 4.03 Å for strongly hydrogenized one), that testifies to a major stability margin this compound. Thus the weakening of interatomic interaction at hydrogenization of metal does not give in a noticeable growth of amplitude of its eigen oscillations, and because of a strong correlation of displacements of neghboring atoms Pd ↔ H gives in padding «shake» of light hydrogen atoms.

1. *Hydrogen in Metals*, Vols. 1 and 2, G. Alefeld and J.Völkl (eds.), Springer-Verlag, Berlin – Heidelberg – New York (1978).
2. J.M. Rowe, J.J. Rush, H.G. Smith, M.M. Mostoller, and H.E. Flotow, *Phys. Rev. Lett.* **33**, 1297 (1974).
3. H. Araki, S. Harada, M. Fukuda, V. Syvokon, and M. Kubota, *Physica* **B284–288**, 1266 (2000).
4. A.P. Miller and B.N. Brockhouse, *Canadian J. Physics* **49**, 704 (1971).
5. V.I. Peresada, in: *Physics of the Condesed State* [in Russian], Kharkov (1968), p. 172.
6. V.I. Peresada and V.N. Afanas'ev, *Zh. Eksp. Teor. Fiz.* **58**, 135 (1970) [*Sov. Phys. JETP* **31**, 78 (1970)].
7. V.I. Peresada, V.N. Afanas'ev, and V.S. Borovikov, *Fis. Nizk. Tem*p. **1**, 461 (1975) [*Sov. J. Low Temp. Phys*. **1**, 227 (1975)].