

more highly energetic ones (not observed in our experiment) are defined as microvoids and cracks. On the whole, such interpretation in the given experiment is obvious because when straining the samples it is just dislocations and grain boundaries that give rise to pores and cracks.

Conclusion

It was stated that deformations of zirconium alloy E-125 result in trap formation with different hydrogen

bond energies. The primary type of traps depends on deformation degree. Bond energy and quantity of hydrogen captured in the traps depend on value of deformation as well as on sequence of deformation and saturation operations. The values of bond hydrogen energies are estimated in the traps under study, the most probable identification of traps is given.

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Literature

1. Duglas D. Material study of zirconium. – Moscow: Atomizdat, 1975. – 360 p.
2. Nikulin S.A., Rozhnov A.B., Babukin A.V. a. o. The structure and resistance to destruction of zirconium alloys for atomic power engineering // Material science and thermal treatment of metals. – 2005. – № 5. – P. 8–17.
3. Turin Y.I., Chernov Y.I., Krening M., Baumbakh Ch. Radioactively stimulated evolution of hydrogen from metals. – Tomsk: TSU, 2000. – 263 p.
4. Turin Y.I., Chernov Y.I., Krening M., Baumbakh Ch. Excitement of hydrogen subsystem in metals and alloys by ion radiation // Proceedings of Tomsk Polytechnic University. – 2000. – V. 303. – № 3. – P. 51–61.
5. Woodraf D., Delchar T. Modern methods of surface investigation. – Moscow: Mir, 1989. – 564 p.

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DIELECTRIC RESPONSE FUNCTION PdH_x SYSTEM

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The calculations of electron structure of pure Pd and PdH_x (x=1,2,3) system have been made ab initio in the range of local density approximation. Total energy of PdH_x system has been calculated for the cases of different coordination of hydrogen atom (oct- and tetrahedral), the conclusion on their most probable location in metal lattice has been made. In the approximation of constant matrix element the imaginary part of permittivity constant function $\epsilon_2(\omega)$ has been calculated. It was stated that dissolution of hydrogen in palladium increases values of the function $\epsilon_2(\omega)$ in the investigated range of energies from 2 to 24 eV. Therefore in the case of radiation impact on PdH_x system one can expect intensive excitement of the crystal electron subsystem, and, hence, decrease of potential barriers for hydrogen atom movement.

Introduction

A unique ability of palladium to dissolve large quantity of hydrogen was discovered by T. Graham as early as in 1886. Hydrogen dissolution changes the physical properties of palladium considerably [1, 2]: increases lattice parameter, decreases conductivity and magnetizability, raises hardness and strength, decreases plasticity, results in embrittlement. PdH_x system is diamagnetic and possesses superconductivity; whereas pure Pd is paramagnetic and as it is known does not exhibit superconductivity [3]. It is evidently that these changes of palladium properties are connected with modification of its atomic and electron structure when dissolving hydrogen in it.

Dissolving hydrogen palladium retains its type of crystal lattice. At small concentration of hydrogen ($x < 0,03$) the so called α -phase PdH_x is formed. At high concentration of hydrogen ($x > 0,6$) the solution is changed into β -phase with peculiar for the phase change of

the first type the uneven change of lattice constant. Dissolving in palladium hydrogen atoms occupy in interstitial spaces of its face-centred cubic (FCC) crystal lattice. FCC lattice is known to have two types of interstitial spaces: tetrahedral and octahedral. Based on the data of neutron diffraction [4–6], it was inferred that hydrogen atoms occupy octahedral interstitial spaces in FCC lattice of palladium forming PdH monohydride with NaCl structure. However, there are some data on concentration and temperature dependencies of electrical resistance of PdH monohydride as well as neutron structure investigations [3, 6], indicating the transformation of hydrogen atoms from oct- into tetrahedral type at temperature of order 50 K.

During recent experiments information about hydrogen behavior in palladium lattice exposed to the action of ionized radiation has been obtained. So, the experimental data on radioactive stimulated hydrogen migration and desorption from palladium including

corpuseular (non-equilibrium) form in the wide temperature range exposed to electron X-rays and γ -radiation [7, 8]. In the authors' opinion of these works such hydrogen behaviour is conditioned by its ability to absorb and accumulate energy if ionized radiation during the time sufficient for some jumps from its initial state. However, no microscopic mechanisms of this phenomenon have been suggested up to now. Posing the problem of creation of such microscopic model in the first stage we tried to find out how the presence of hydrogen in the lattice influences the ability of crystal electron subsystem to absorb the radiation energy of external action. To answer this question the information on electron and atomic structure of the hydride investigated is necessary. Taking into account the dispersion law $E(k)$ for the wavelets of solid body (in the given case it is electron system) one can calculate function of system response to the external excitement (frequency dependency of complex dielectric impermeability).

In present work the formation of PdH_x compounds for $x=1, 2, 3$ of element components Pd и H_2 has been investigated on the basis of *ab initio* calculations of total energy. The densities of electron states $N(E)$, dispersion curves $E(k)$, distribution of charge density and imaginary part of dielectric function $\varepsilon_2(\omega)$ have been calculated.

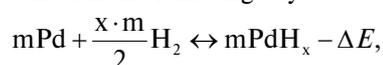
Methods and calculations

In the context of the theory of density functionals self-consistent calculations of electron structure of the PdH_x system and pure Pd were made by linearization method of adjoint plane waves. Correlation-change effects were considered by using generalized gradient approximation PW91 [11]. Radii of MT spheres of Pd and H atoms were chosen to be equal 2,3 and 1,0 atm. un. correspondingly, that permitted free motion of hydrogen atoms in tetra- and octahedral interstice of FCC palladium lattice. Disintegrating the wave function within the MT spheres into spheric harmonics all the members up to $l=8$ for Pd and up to $l=4$ for H were taken into account. On disintegrating the wave function into adjoint plane waves up to 120 basis functions per atom were taken into consideration.

At each iteration of coordination the Hamiltonian proper values were calculated in 40 k -points of irreducible part of Brillouin zone (IPBZ). To construct the density of electron state $N(E)$ integration in IPBZ was made by linear method of tetrahedrons on the grid of 90 k -points. Function smoothing $N(E)$ was made by Gaussians with mean-square width 0,14 eV. The imaginary part of dielectric function $\varepsilon_2(\omega)$ was calculated in the approximation of constant matrix element on the grid of 1200 k -points in IPBZ.

Results and discussions

The process of hydrogen dissolution in palladium can be presented in the following way:



where heat of hydrogen dissolution

$$\Delta E = E(\text{PdH}_x) - E(\text{Pd}) - \frac{x}{2}E(\text{H}_2).$$

Here $E(\text{PdH}_x)$ and $E(\text{Pd})$ – total PdH_x and pure Pd system energies correspondingly. $E(\text{H}_2)$ – energy necessary for the dissociation of H_2 molecule. The value obtained for dissociation energy $E(\text{H}_2)$ made up $-30,96144$ eV. In table 1 the results of parameter calculation of lattice and solution heat of the hydrides involved are presented. It is seen that the results obtained for lattice parameters are well consistent with both experimental [2, 14, 15] and calculated data of other authors [12, 13, 15]. As for the heat of hydride formation the situation turned out to be complex. Thus, if one does not take into account the zero-point energy of hydrogen atom in metal, their tetrahedral coordination is energetically more efficient. Energy accounting of these oscillations in harmonic approximation resulted in the conditions where octahedral interstice became more energetically efficient for hydrogen atoms.

Table 1. Lattice parameters and solution heat of palladium hydrides

System	Lattice parameters, Å			Heat of hydrogen solution, eV		
	Present work	Theory	Experiment	Present work	Theory	Experiment
Pd	3,93	3,97 [12]	3,89 [2]	–	–	–
PdH	4,08	4,06 [13] 4,15 [12]	4,09 [2]	-0,533 -0,462*	-0,143 [13] -0,500 [15]	-0,21 [14] -0,122 [15]
PdH ₂	4,47	4,40 [13]	–	-0,692 -0,238*	-0,216 [13]	–
PdH ₃	4,66	4,64 [13]	–	1,311	–	–

The results obtained with regard to zero-point energy of hydrogen atoms in harmonic approximation are marked with asterisks

Table 2. Local orbital distribution of valent charge Q (in electron charge units) for pure palladium and PdH_x systems at $x=1, 2, 3$. The values of electron state density at Fermi level $N(E_F)$ (in units, state./eV/el.cell)

System	Atom	Q_s	Q_p	Q_d	Q_{MT}	Q_{int}	Q_{tot}	$N(E_F)$
Pd	Pd	0,274	0,201	7,796	8,299	1,701	10	2,64
PdH	Pd	0,214	0,210	7,908	8,356	2,261	11	0,49
	H (oct.)	0,363	0,018	0,001	0,383			
PdH ₂	Pd	0,197	0,236	7,907	8,364	2,814	12	0,13
	H (tetr.)	0,392	0,017	0,001	0,411			
PdH ₃	Pd	0,210	0,198	7,892	8,318	3,615	13	1,42
	H (oct.)	0,305	0,010	0	0,315			
	H (tetr.)	0,361	0,014	0,001	0,376			

In table 2 the following designations are used: Q_{tot} – a total charge in low-level cell, Q_{int} – a charge in the interatomic region, Q_{MT} , Q_s , Q_p , Q_d – a charge in MT-spheres and its s -, p - and d -components. $N(E_F)$ – a magnitude of electron state density at Fermi level.

In fig. 1 and in table 2 the calculated electron state densities for pure Pd and PdH_x ($x=1, 2, 3$) systems with different atom coordination of hydrogen are presented. The results obtained are well consistent with the data obtained by the other authors [16, 17].

From comparison of zone structures of pure Pd and Pd-H systems one can see some peculiarities of electron structure of metallic hydride appearing as a result of hydrogen dissolution.

1. filling Pd *d*-zone due to electrons of dissolved hydrogen;
2. lowering the conductivity zone bottom due to hybridization of *s*-states of hydrogen with *s*-, *p*- and *d*-states of Pd atoms;
3. Fermi level shift up with respect to the Pd *d*-zone top, that results in decrease of electron state density of the system at Fermi level.

In fig. 1 it is also seen that the appearance of hydrogen in the Pd lattice results in a pseudoslot in the elec-

tron spectrum of Pd-H system. For PdH compound this pseudoslot is in the energy range ~ 4 eV. With the increase of hydrogen concentration it goes down the energy owing to filling the electron states by electrons of hydrogen atoms. For PdH₂ system with tetrahedral coordination of hydrogen atoms Fermi level falls into pseudoslot, the compound acquiring semimetal properties. Further growth of hydrogen concentration results in PdH₃ system becoming again a metal as the pseudoslot falls more than 1 eV lower Fermi level. The presence of pseudoslot in electro spectrum of Pd-H system indicates the appearance of covalent constituent of bonding force between atoms of palladium and hydrogen in addition to the metallic type of bonding common to pure palladium.

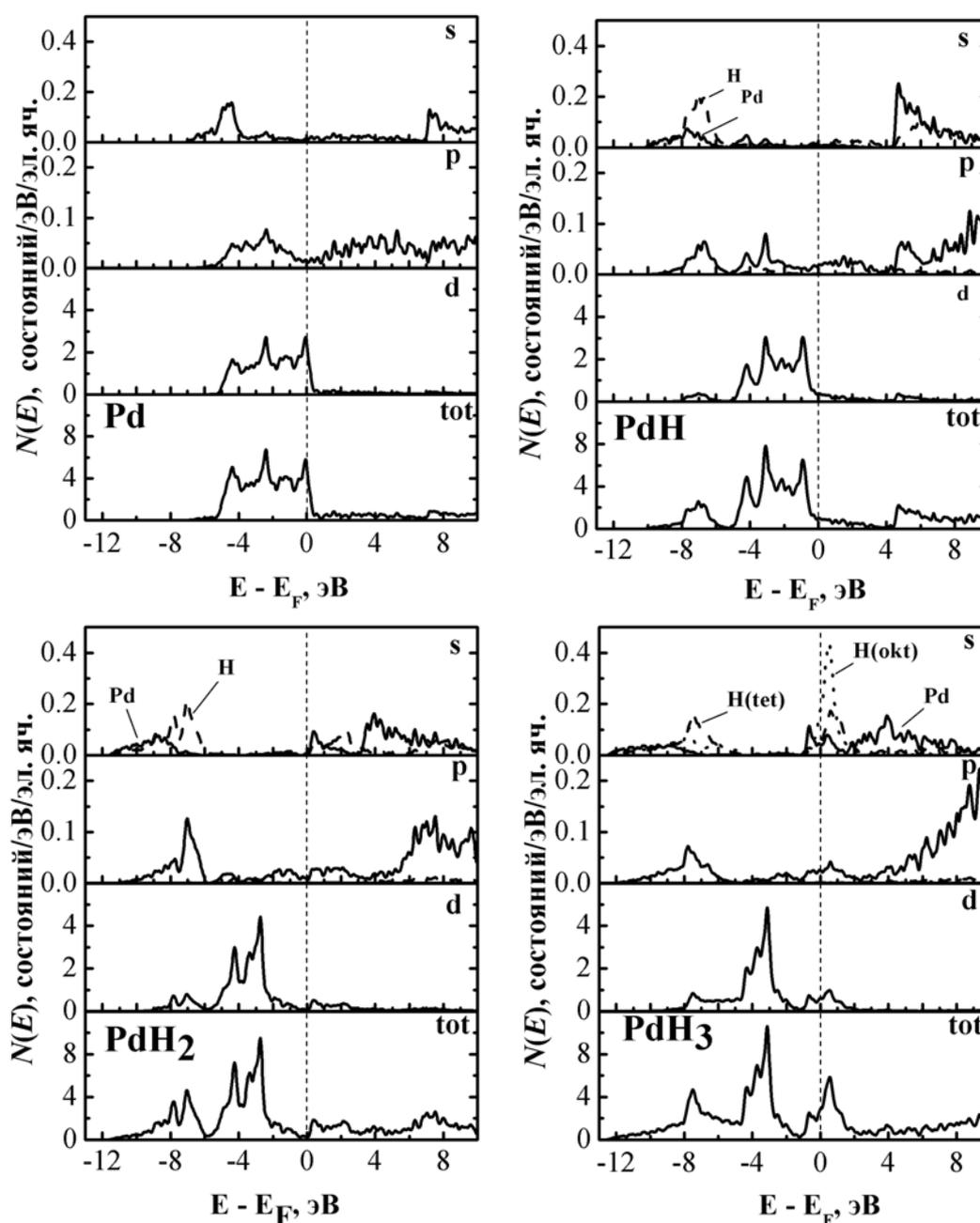


Fig. 1. Density of electron states of pure Pd and PdH_x compounds

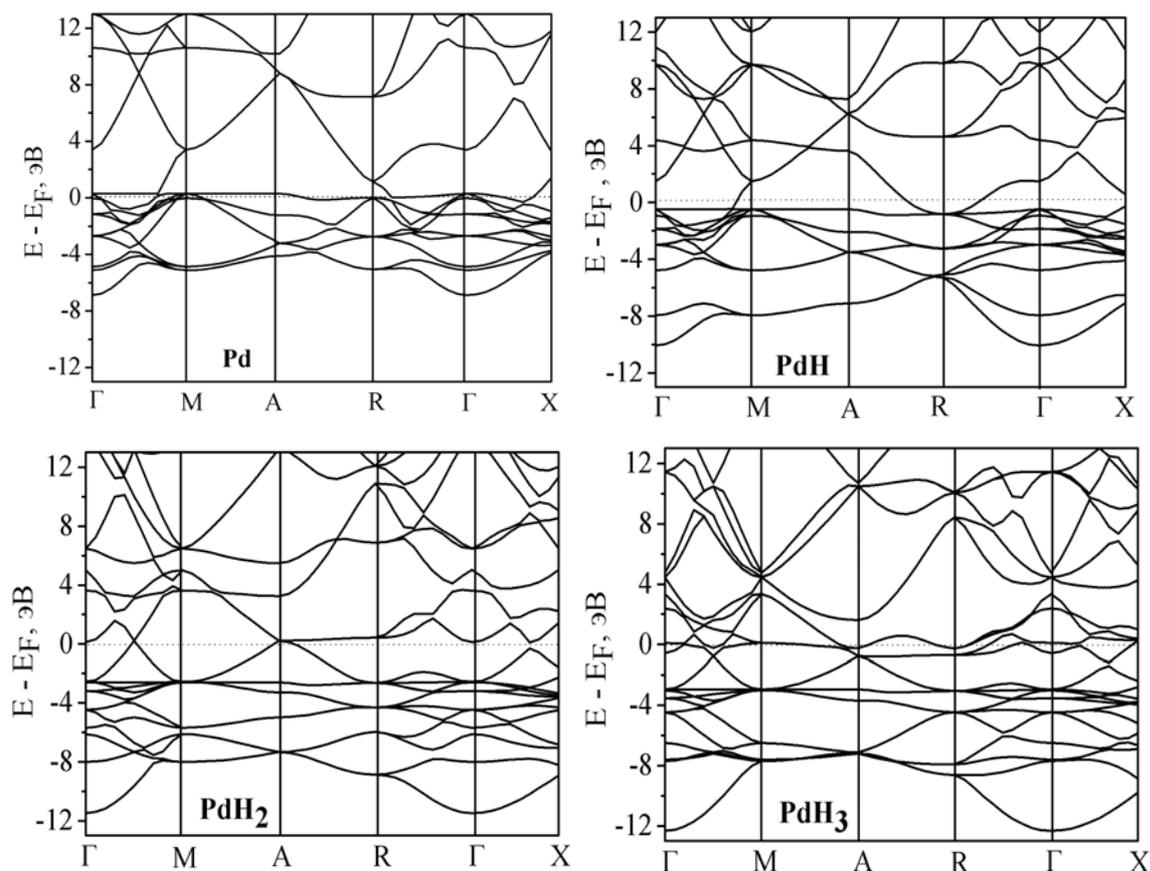


Рис. 2. The dispersion curves for Pd and PdH_x compounds

The decrease of state density on Fermi level is known to result in reduction of screening ability of electrons on conductivity zone. Actually, according to [2] model excess charge in metal is screened by electrons of conductivity zone, the density of which exponentially coincides with the increase of distance and is characterised by screening radius $\sim [N(E_F)]^{-1/2}$. Thus, if the density of states is great, the radius of screening is small like in pure palladium as even the nearest neighbours do not feel the replacement of matrix atom by hydrogen atom [2]. For the considered PdH_x systems the density of states at Fermi level is lower than in pure palladium (table 2), therefore they are expected to increase the screening radius and, consequently, to increase the life time of electron excitation.

In fig. 2 the dispersion curves $E(k)$ along symmetrical directions of irreducible part of Brillouin zone calculated in the context of the theory of density functionals by linearization method of adjoint plane waves are presented. The figure shows that hydrogen dissolution in palladium does not result in appearance of additional energy zones, but changes notably their course and mutual arrangement. Due to filling the holes in palladium d -zone by electrons given by hydrogen into common conductivity zone of Pd-H system, d -zone becomes narrower and falls down the energy.

In fig. 3 the calculated imaginary part of dielectric function $\varepsilon_2(\omega)$ is presented. This value connects the

zone structure and optical constants of the substance. In particular, it characterizes the ability of the substance to absorb E-field radiation.

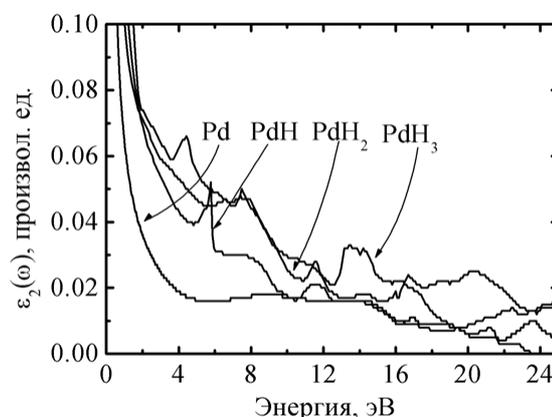


Fig. 3. Imaginary part of dielectric function $\varepsilon_2(\omega)$ for pure Pd and PdH_x systems

In the literature one could not find any data on the value $\varepsilon_2(\omega)$ calculated by us for the Pd-H system. The comparison of the results for pure palladium with the data of semiempirical calculations [17, 19] and experimental works [20] shows good agreement. On the whole, the dependence obtained $\varepsilon_2(\omega)$ accounts for the course of the experimental curve [20], but differs from the results of calculations [17, 19]. So, there is no peak

in the energy region of 4,5 eV order in our results. It should be noted that in the experiment this peak was not also observed. In fig. 3 it is seen that the values of dielectric function $\varepsilon_2(\omega)$ of the PdH_x involved are more than corresponding values of $\varepsilon_2(\omega)$ for pure palladium in the wide range of energy (approximately up to 24 eV). Thus, one can say that hydrogen solution in palladium increases the ability of the Pd-H system to absorb energy of E-field radiation. This condition together with the increase of life-time of electron excitations in Pd-H systems mentioned above can sufficiently change the behavior of PdH_x compounds in the field of ionizing radiation.

It is known that if energy in a crystal or its fragment increased, one can expect decrease of potential barriers for atom migration [21]. So, absorbing the radioactive energy effectively, electron subsystem of PdH_x compounds transfers into excitement state. This will change potential barriers for atom migration, first of all, for the lightest ones. If the life time of these excitations is long enough, the atoms will have time to make some jumps before the excitement will have relaxed. Increasing the time of radioactive action one can achieve the intensive

movement of hydrogen atoms over the crystal volume and exceed the bounds of it.

Conclusion

The calculations of electron structure of pure palladium and Pd-H system were performed. The equilibrium values of lattice parameters of PdH_x compounds for $x=1, 2, 3$ at different coordinations in palladium lattice were defined. Good agreement of the calculated values with experimental and theoretical data of the other authors was obtained. The calculation of imaginary part of dielectric function of PdH_x system was carried out. From the analysis of the results obtained was made the conclusion about increase of the ability of metal electron subsystem to absorb energy of external electromagnetic radiation and keep it during more long time than in pure palladium. A hypothesis was put forward about influence of ionizing radiation on Pd-H system that can result in hydrogen atom migration as well as in their leaving metal in equilibrium (corpuscular) state owing to lowering potential barriers caused by the excitement of equilibrium charge density in the sample volume.

Literature

- Held P.V., Ryabov R.A., Mokhracheva L.P. Hydrogen and physical properties of metals and alloys. – Moscow: Nauka, 1985. – 232 p.
- Hydrogen in metals: In 2 Vols. / Edited by G. Alefeld, I. Felkl. – Moscow: Mir, 1981. – V. 1. – 475 p.; – V.2. – 430 p.
- Andriyevskiy R.S., Umanskiy Ya.S. Introduction phases. – Moscow: Nauka, 1977. – 240 p.
- Worsham J.E., Wilkinson J.R.M.K., Shull C.G. Neutron-diffraction observations on the palladium-hydrogen and palladium-deuterium systems // J. Phys. Chem. Solids. – 1957. – V. 3. – P. 303–308.
- Drexel W., Murani A., Tocchetti D., Kley W., Sosnowska I., Ross D.K. The motions of hydrogen impurities in γ -Palladium-hydride // J. Phys. Chem. Solids. – 1976. – V. 37. – P. 1135–1140.
- Ferguson G., Schindler A.I., Tanaka T., Morita T. Neutron Diffraction Study of Temperature-Dependent Properties of Palladium Containing Absorbed Hydrogen // Phys. Rev. – 1965. – V. 137A. – P. 483–487.
- Tyurin Yu.I., Chernov I.P. Storage capacity of hydrogen in solid body. – Moscow: Energoatomizdat, 2000. – 286 p.
- Tyurin Yu., Chernov I. Non-equilibrium release of atomic hydrogen from metals under irradiation // Int. J. of Hydrogen Energy. – 2002. – V. 27. – P. 829–237.
- Wimmer E., Krakauer H., Weinrt M., Freeman A.J. Full-potential self-consistent linearized-augmented-plane-wave method for calculating the electronic structure of molecules and surfaces: O_2 molecule // Phys. Rev. B. – 1981. – V. 24. – P. 864–875.
- Weinert M., Wimmer E., Freeman A.J. Total-energy all-electron density functional method for bulk solids and surfaces // Phys. Rev. B. – 1982. – V. 26. – P. 4571–4578.
- Wang Y., Perdew J.P. Correlation hole of the spin-polarized electron gas, with exact small-wave-vector and high-density scaling // Phys. Rev. B. – 1991. – V. 44. – P. 13298–13307.
- Caputo R., Alavi A. Where do the H atoms reside in PdH_x systems? // Molecular Physics. – 2003. – V. 101. – № 11. – P. 1781–1787.
- Wang X.W., Louie S.G., Cohen M.L. Hydrogen interactions in PdH_n ($1 \leq n \leq 4$) // Phys. Rev. B. – 1989. – V. 40. – P. 5822–5825.
- Tanaka T., Keita M., Azofeifa D.E. Theory of hydrogen absorption in metal hydrides // Phys. Rev. B. – 1981. – V. 24. – P. 1771–1788.
- Ageyev V.N., Bekman I.N., Burmistrova O.P. a. o. Interaction of hydrogen with metals. – Moscow: Nauka, 1987. – 296 p.
- Chan C.T., Louie S.G. Self-consistent pseudopotential calculation of the electronic structure of PdH and Pd_4H // Phys. Rev. B. – 1983. – V. 27. – P. 3325–3337.
- Bordoloi A.K., Auluck S. Frequency-dependent dielectric function of Pd and Pt // J. Phys. F: Met. Phys. – 1988. – V. 18. – P. 237–247.
- Bassani F., Parrovichini J.P. Electron states and optical transitions in solid bodies. – Moscow: Nauka, 1982. – 391 p.
- Lasser R., Smith N. V. Empirical band calculations of the optical properties of d-band metals. III. Rh and Pd // Phys. Rev. B. – 1982. – V. 25. – P. 806–814.
- Weaver J.H., Benbow R.L. Low-energy interband absorption in Pd // Phys. Rev. B. – 1975. – V. 12. – P. 3509–3510.
- Heine V. Physics of metals. I. Electrons. – Moscow: Mir, 1972. – 323 p.