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On the possibility of "high-temperature" electrical superconductivity of the superhydride $Pd(H)_{n-x}$

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Hydrogen is the simplest and at the same time very important and interesting chemical element. Under pressure ≈ 500 GPa hydrogen molecules form a metal phase. According to theory, "metallized" hydrogen is a "high-temperature" superconductor, ie it is characterized by almost zero electrical resistance in the entire temperature range of this phase. Hydrogen compounds with atoms of other elements, for example, with atoms of metals, form a stable metal phase ("hydrides") under the action of much lower pressure ≤ 100 GPa. At the same time some hydrides (H_3S, LaH_{10} etc.) are superconductors at temperatures $T \leq 200$ K. An urgent and very intriguing task for researchers is to identify new substances (including new "metal" hydrides) that are stable at normal (atmospheric) pressure and at the same time have "high-temperature" superconductivity. This paper discusses the possibility of obtaining such a material on the basis of a solid solution of hydrogen in palladium $Pd(H)_{n-x}$. Palladium metal has two unique physicochemical properties: first, it is able to extremely actively absorb hydrogen (up to ≈ 10^3 volumes of H_2 molecule per volume of Pd atom) and, secondly, in the process of dissolving hydrogen in this metal, dissociation of molecules easily occurs H_2. In this case, each electron of the hydrogen atom is combined with the valence electrons of the palladium metal lattice (there is a "collectivization" of electrons), and the H^+ nucleus is converted into a proton, ie into a particle with extremely low mass and size. Thus, the "metallization" of the hydride $Pd(H)_{n-x}$ can occur without the action ofadditional external pressure. The analysis carried out in this paper shows that the specific crystal structure of this substance and the features of the energy spectrum of its electronic subsystem, enhance the electron-phonon interaction and, accordingly, determine the possibility of "high-temperature" superconductivity.

Keywords: high-temperature superconductivity, palladium hydride, electron-phonon interaction.

Про можливість "високотемпературної" електричної надпровідності супергідриду $Pd(H)_{n-x}$. *Ю.І.Бойко, В.В.Богданов, Р.В.Вовк, Б.В.Гриньов*

Водень є найпростішим і, водночас, дуже важливим та цікавим хімічним елементом. Під тиском ≈ 500 GPa молекули водню утворюють металеву фазу [1]. Відповідно до теорії, "металізований" водень є "високотемпературним" надпровідником, тобто характеризується практично нульовим електричним опором у всьому температурному інтервалі існування цієї фази. Сполуки водню з атомами інших елементів, наприклад, з атомами металів, формують стабільну металеву фазу ("гідриди") під дією значно меншого тиску ≤ 100 GPa. При цьому деякі гідриди (H_3S, LaH_{10} та ін.) є надпровідниками при температурах $T \leq 200$ К. Актуальним і вельми інтригуючим завданням для дослідників є виявлення нових речовин (у тому числі й нових "металевих" гідридів),

які є стабільними за нормального (атмосферного) тиску і водночас мають "високотемпературну" надпровідність. У даній роботі обговорюється можливість одержання такого матеріалу на основі твердого розчину водню в паладії $Pd(H)_{n-x}$. Металевий паладій має дві унікальні фізико-хімічні властивості: по-перше, він здатний надзвичайно активно поглинати водень (до $\approx 10^3$ об'ємів молекули H_2 на один об'єм атома Pd) і, по-друге, у процесі розчинення водню в цьому металі легко відбувається дисоціація молекул H_2. При цьому кожен електрон атома водню поєднується з валентними електронами металевої решітки паладію (відбувається "колективізація" електронів), а ядро H^+ перетворюється на протон, тобто на частинку з надзвичайно малою масою та розміром. Таким чином, "металізація" гідриду $Pd(H)_{n-x}$ може відбуватися без дії додаткового зовнішнього тиску. Аналіз, проведений у даній роботі, свідчить про те, що специфічна кристалічна структура цієї речовини та особливості енергетичного спектру його електронної підсистеми, сприяють посиленню електрон-фононної взаємодії та, відповідно, зумовлюють можливість прояву "високотемпературної" надпровідності.

1. Introduction

For more than a century of discovering the phenomenon of mercury superconductivity (virtually zero electrical resistance), this unique phenomenon has been observed in a large number of different chemical elements and substances: in metals, double or triple metal alloys and more complex compounds. However, the number of superconductors used in practice is still very limited. The main reason for this situation is that the superconducting state occurs only at very low temperatures. For example, for many single-element metals, this effect is observed at temperatures ≤ 10 K and only for some metal alloys at temperatures ≤ 40 K.

A very significant breakthrough in the study of superconductivity was the discovery in 1986–1987 of the so-called "high-temperature" superconductors (HTSC) — complex polycomponent compounds containing atoms of various elements, in particular copper and oxygen atoms (mixed cuprate oxides) [1, 2]. An important distinctive feature characteristic of this group of substances is that they retain superconductivity at temperatures above the boiling point of liquid nitrogen (77 K) — relatively cheap and affordable refrigerant. For example, it was found that the compound $HgBa_2Ca_2Cu_3O_{10-x}$, synthesized in 1993, turns into a superconducting state at the temperature $T_c \simeq 164$ K [3]. This record value of T_c remained for more than twenty years. Most of the research done during this time has focused on finding new compounds that have superconductivity at even higher temperatures. The main purpose of these studies was to search for substances with a transition temperature $T_c \approx 300$ K (room temperature). And in 2015 a new compound was discovered that transitions to the superconducting state at temperature $\simeq 203$ K. This substance was a compound of sulfur and hydrogen (H_3S) [4]. However, it turned out that this substance turns into a superconductor only under significant pressure $P \geq 150$ GPa. In 2019, the superconductivity record was broken again. It was found that during the compression of the "superhydride" of lanthanum (LaH_{10}) under pressure $\simeq 170$ GPa its superconductivity is detected already at temperature $T_c \simeq 260$ K [5]. Experimental detection of this, so far the maximum value of the transition temperature T_c, played a very important role in further progress towards the main goal: obtaining a substance having superconductivity at room temperature. This is due to the fact that theoretically the superconductivity of metals solid solutions with hydrogen under high pressure is associated with the effect of "collectivization" of valence electrons of hydride-forming elements. In the initial state, the hydrides studied in [4, 5] were not metals, but were dielectrics, that is, they were substances in which there are no "collectivized" electrons. Under the external pressure, the valence electrons of the hydride-forming atoms combine and form a "gas" of "free electrons", ie there is a kind of "metallization" of dielectrics. The value of the pressure required for the full implementation of this process is determined by the requirement to convert electrons into a "degenerate" (quantum) state [6]. In addition to the effect of electrons "collectivization" in hydrides under the pressure, conditions are also realized that contribute to the formation of their special crystal structure. The small size of hydrogen atoms allows to form a specific structure with a unit cell in the form of a kind of "cell" formed by hydrogen atoms, in the center of which is a metal atom (clathrate-like structure) [6]. The formation of such a structure of "metallized" hydrides is accompanied by the appearance of individual crystallographic directions, characterized by the minimum pos-

sible distances between the nearest neighboring atoms. This circumstance, as well as the small mass of hydrogen atoms, cause the generation of high-frequency phonons in hydrides. Both of the above factors, ie the "collectivization" of electrons and the emergence of high-frequency mode in the phonon spectrum of "metallized" hydrides, ultimately provide the realization of the increased value of the transition temperature of these compounds to the superconducting state. Thus, the above results of experiments with hydrides, played an important role in the study of superconductivity. They confirmed the correctness of the basic physical ideas about the nature of this phenomenon in metals, metal alloys, as well as in "metallized" hydrides. The data from these experiments are in complete agreement with the conclusions of the microscopic theory of superconductivity published in 1957 (BCS theory) [7]. According to this theory, the reason for the superconductivity effect in metals and in "metallized" compounds is the interaction of quantum particles: phonons and electrons. As a result of the phonon attraction of electrons, new quantum particles are formed in the "gas" of "collectivized" electrons — "Cooper" pairs of electrons or bosons. These particles are able to move under the action of an electric field without scattering, ie without loss of energy and thus realize the electrical superconductivity. According to the BCS theory, the value of the transition temperature of metals in the superconducting state Tc is described by the following relation:

$$T_c \simeq \theta \cdot \exp(-1/\mu). \quad (1)$$

Here θ is the Debye temperature, μ is the electron pairing constant by phonons, which characterizes the efficiency of phonon electron attraction. For metals and metal alloys, the Debye temperature is characterized by a value $\theta \simeq 300$ K, and the value of the pairing constant μ reaches the maximum value $\simeq$ (0.1–0.3) and, accordingly, the value of T_c in this case is $\simeq$ (10–40 K), which agrees well with the experimental data.

Thus, in classical metals and metal alloys, the "pairing" of electrons is realized only at very low temperatures. In the case of "metallized" hydrides under pressure, the "gas" of "collectivized" electrons has a specific energy spectrum with a high density of states at the Fermi level, which causes an increase in the pairing constant to values $\mu \geq 1$. In addition, in hydrides, due to the appearance of high-frequency phonons, about one and a half to two times the Debye temperature. For such values of the parameters θ and μ, equation (1), which characterizes the transition temperature T_c, does not work, and the dependence $T_c(\mu)$ describes by different relationship [8]:

$$T_s \simeq 0.2 \cdot \theta\, \mu^{1/2}. \quad (2)$$

From this relation it follows that the hydrides transition temperature to the superconducting state under pressure, due to the "collectivization" of electrons, should increase to values $\simeq$ (200–250 K), which was also found in the experiments described in the works [4–6]. Thus, the detection of "high-temperature" superconductivity of some hydrides under pressure played a very important role in confirming the correct understanding of the physical nature of this phenomenon in metals and in "metallized" compounds. However, this discovery did not solve another important problem: the possibility of using these substances in practice. The very low temperature T_c for metals and their alloys, as well as the need to apply high pressure in the case of hydrides complicate and make economically unprofitable to use of superconducting metals and hydrides for practical purposes. In this regard, a very important task of modern research on the phenomenon of superconductivity is still the search for new compounds, including new hydrides, which would have this property not only at technically acceptable temperatures (preferably at room temperature), but also at normal (atmospheric) pressure.

This article discusses the possibility of realizing the effect of superconductivity under conditions close to normal. It is proposed to use a saturated solid solution of hydrogen in palladium PdH_{n-x} as the object of study.

2. Reasoning of the possibility of electrical superconductivity in solid solution $Pd(H)_{n-x}$ at temperatures approaching room temperature and at atmospheric pressure

Palladium (Pd) in its physical and chemical properties occupies a special place in a number of transition precious metals. This is a chemical element of the tenth group of the fifth period of the periodic table of elements with atomic number 46. Its electronic configuration is $4d^{10}$, atomic weight 106.42 g/mol, crystal lattice parameter 3.89 E, Debye temperature 274 K, melting

point 1827 K, density 12.02 g/cm^3, Fermi energy 5.48 eV. Listed above, the properties of palladium are typical for conventional classical metals. However, this element has two special physicochemical properties: first, the palladium atom is characterized by low ionization energy $\simeq$ 803.5 kJ/mol and, secondly, palladium metal is able to extremely actively absorb hydrogen, forming solid solutions (up to 10^3 vol. of H_2 molecules per volume of Pd atom [9, 10]). It is these two properties of palladium that distinguish it from other metals and, we believe, it is these properties that allow the formation of a hydride with "collectivized" electrons without additional external pressure. Indeed, palladium in its original state is a common metal with "collectivized" intrinsic valence electrons. However, this metal allows the introduction of an increased number of hydrogen atoms in its crystal lattice. In other words, a palladium-based hydride can be created without the use of additional pressure. This possibility is due to the fact that in the process of dissolving hydrogen on the metal surface, dissociation of molecules H_2 easily occurs. In this case, each electron of the hydrogen atom combines with the valence electrons of the metal lattice, and the H+ nucleus is converted into a proton, ie into a particle of extremely small mass and size [10]. This circumstance gives grounds to assume the possibility of forming in solid solution $Pd(H)_{n-x}$ of specific crystal lattice inherent in all hydrides: clathrate — like structure, which is characterized by the presence of high-frequency phonon spectrum mode. Accordingly, as a result, the Debye temperature of the formed substance should increase. Indeed, the Debye temperature $\theta \sim \nu$, and $\nu \sim 1/M^{1/2} \cdot R$ (here ν is the frequency of the generated phonons, M is the mass of the particle, R is the distance between the nearest neighboring atoms). Quantitative assessment of the Debye temperature increase degree, due to changes in the above parameters M and R, indicates the possibility of almost threefold increase in its value, ie Debye temperature can reach $\simeq 10^3$ K. In addition, it is obvious that the dissolution of hydrogen in palladium should be accompanied by a significant increase in the density of "collectivized" electrons compared to the initial state in pure metal. Indeed, as already mentioned, when dissolving hydrogen in palladium, each volume of palladium atom in the process of forming a solid solution has up to 10^3 volumes of hydrogen molecule. Thus, the density of "collectivized" electrons in a saturated solution of $Pd(H)_{n-x}$ may increase from the value $n_e \simeq 10^{23}$ 1/cm^3 up to $\simeq 10^{26}$1/cm^3, that is, increase by three orders of magnitude. The change in the concentration of free electrons should lead to an increase in two other, very important for superconductivity, characteristics of matter — the pairing constant μ and Fermi energy E_F. Indeed, according to the BCS theory,

$$\mu \simeq U \cdot (dN/dE)^*. \quad (3)$$

Here U is the potential of the electron-lattice interaction, $(dN/dE)^*$ is the density of energy states of electrons directly in the environment of the Fermi level, ie at $E \simeq E_F$, N is the number of all energy states of electrons determined by the total number of "collectivized" electrons. As $N \simeq n_e \cdot V$ (V is the volume of the sample), then increase the electron density n_e in solution $Pd{\cdot}H_x$ should cause a corresponding increase in the pairing constant μ. At the same time, the value of Fermi energy should increase

$$E_F = (h^2/8m) \cdot (3/4\,\pi)(N/V)^{2/3} \quad N^{2/3}. \quad (4)$$

Here h is the Planck constant, m is the mass of the electron.

Let's quantify the possible increase in the value of the pairing constant in solution $Pd(H)_{n-x}$, due to the increase in the density of energy states. Using the Fermi- Dirac function, which describes the energy distribution of "degenerate" electrons, it is easy to see that $dN/dE = (3N/2E_F)\cdot(E/E_F)^{1/2}$ and, therefore, directly only at the Fermi level, ie at $E = E_F$ we have:

$$(dN/dE)^* \simeq 3N/2E_F. \quad (5)$$

Accordingly, from relations (3)–(5) it follows that $\mu \sim N^{1/3}$, ie the increase in the pairing constant in the solution of hydrogen and palladium compared to pure (hydrogen-free) metal can be tenfold, ie the value of μ can reach the value $\mu \simeq 3$. According to formula (2) for this value of the pairing constant and for the value of the Debye temperature $\theta \simeq 10^3$ K the expected transition temperature T_c of the solution $Pd(H)_{n-x}$ to the superconducting state can reach the value $\simeq$ 340 K. There is no need to apply additional external pressure, as in the case of "metallization" of other hydrides.

3. Conclusions

1. Based on the analysis and quantitative estimates, it can be stated with a high degree of confidence that a saturated solid solution $Pd(H)_{n-x}$ can have electrical superconductivity with a transition temperature T_c close to room temperature at atmospheric pressure.

2. The compound $Pd(H)_{n-x}$ is characterized by the Debye temperature $\theta \simeq 10^3$ K, as well as by the increased density of energy states of electrons $(dN/dE)^*$ at the Fermi level, which, ultimately, should lead to an increase in the critical transition temperature of the substance under discussion to superconducting. Herewith the specified transition does not demand additional pressure and can be realized at atmospheric pressure.

3. The given quantitative data of some parameters are estimated and should be consistent with the experimental data.

4. The results of the experimental approbation of the conclusions will be published in addition.

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