Hydrogen in metals

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Usp. Fiz. Nauk **116**, 385–412 (July 1975)

This article reviews the experimental and theoretical studies of the properties of hydrogen included in metals. The problem is discussed of diffusion of hydrogen atoms in a metallic matrix, and the theory of coherent and incoherent diffusion. Phase transitions caused by elastic interactions are considered in a system of hydrogen atoms included in the interstices of a metallic matrix. The electronic properties of compounds of hydrogen with different metals, the experimental studies of the electronic band structure and of phase transitions in the electronic subsystem (metal-dielectric in cerium hydride, magnetic transitions) are reviewed. Special attention is paid to superconductivity in hydrogen-metal systems. Detailed results are presented of experimental and theoretical studies of the superconducting properties of compounds of palladium with hydrogen and deuterium, and also compounds of palladium with the noble metals and hydrogen. The effect of inclusion of hydrogen on the superconductivity of other transition metals is discussed.

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1. INTRODUCTION

The physical and chemical properties of the compounds Me—H of hydrogen with metals have been studied very intensively for many years.[1-3] The interest in these compounds stems from their potential widespread practical application, especially in nuclear technology, and also from the fact that hydrogen entering a metal is one of the fundamental causes of appearance of various defects that impair the properties of the metal. Yet, perhaps, from the standpoint of the physicist, these compounds are of greatest interest owing to the multitude of very curious and specific phenomena that manifest the substantially quantum nature of the behavior of the light hydrogen in a heavy metallic matrix.[1]

The problem of obtaining metallic hydrogen and the hypothesis that it has a rather high critical superconductive transition temperature $T_c \approx 100°K$ have substantially sharpened the question of whether the properties of metallic hydrogen can be modeled with the compounds of hydrogen with metals.[4] The discovery of superconductivity in the hydrides and deuterides PdH(D)[5] and PdAgH(D)[6] having rather high T_c $\approx 9-16°K$ has even further heightened the interest in this problem.

Some of the very interesting phenomena possessing a number of specific features that we shall principally discuss in this review are: diffusion of hydrogen in metals; gas-liquid-solid phase transitions and certain structural problems of Me—H compounds; the electronic structure of these compounds and the associated problems of modeling the properties of metallic hydrogen; and the possibility of getting high critical superconductive transition temperatures in Me—H compounds. We should immediately emphasize that the status of the theory and the experimental knowledge in most of these

problems leaves much to be desired. Actually we have many more questions on the properties of Me—H systems than answers to them.

In particular, we know that hydrogen forms with metals compounds having a very broad spectrum of bond types. The compounds of hydrogen with the alkali metals are ionic dielectrics, where hydrogen plays the role of a halogen analogous, e.g., to Cl in the compound NaCl. The compounds of hydrogen with the rare-earth metals include both covalent semiconductors and metals. The metallic type of bonding predominates in the compounds of hydrogen with the transition metals. Undoubtedly, the tendency to form different types of bonds cannot help but be reflected in the behavior of small amounts of hydrogen in various metals, and in particular, in their diffusion coefficients. Unfortunately, the theory of diffusion of hydrogen in metals is mainly phenomenological in nature, and it contains no detailed account of the features of interaction of hydrogen with the various metal ions.

We can point out the following fact as an example of our defective knowledge of the properties of Me—H compounds. Adding hydrogen to Pd leads to superconductivity, which is absent in pure Pd, whereas adding hydrogen to the superconducting Nb or V abolishes their superconductivity. We do not know the real reason for the lack of superconductivity in NbH_x or VH_x, not only because of inadequate theoretical concepts of the structure of these systems, but also because of the lack of thorough and systematic experimental studies of their properties as a function of the concentration of hydrogen.

Of course, we should not take the aforesaid as generally denying any sort of advances in studying Me—H compounds. Actually, even on the phenomenological or semimicroscopic level, people have been able to estab-

lish a whole series of regularities in the structures and properties of these compounds. Thus, for example, a governing role of the elastic interactions between the interstitial hydrogen atoms has been established in ordering processes in Me—H systems. An isotope dependence of the diffusion coefficient and a number of other effects that indicate the quantum nature of the diffusion process have been clearly revealed. A whole series of other characteristic feature of Me—H compounds has also been established, and we shall now proceed to discuss them systematically.

2. DIFFUSION OF HYDROGEN IN METALS

A characteristic feature of diffusion of hydrogen in most metals is its rapid rate. The coefficients of diffusion of hydrogen in solid metals are practically the same as in the liquids. This feature involves the extremely small atomic volume of hydrogen, in that a hydrogen molecule entering a metal unquestionably dissociates at least into individual atoms. In metals, hydrogen occupies the interstices, and migrates from one interstice to another in the diffusion process. Hydrogen can occupy different types of interstices, depending on the lattice type of the metal. For example, there are two types of interstices in a face-centered cubic lattice: octahedral (Fig. 1a) and tetrahedral (Fig. 1b). Within the framework of classical concepts, when hydrogen migrates from one interstice to another, it must overcome an energy barrier that arises from its compression by the surrounding atoms when situated in a given interstice. Hence, the diffusion coefficient D obeys well the well-known Arrhenius law

$$D = D_0 \exp\left(-\frac{E_a}{kT}\right). \quad (2.1)$$

The energy barrier E_a is determined by the elastic energy of the metal matrix that is required to separate the lattice atoms at zero temperature so as to form a cavity of dimensions equal to the volume of the hydrogen atom. Evidently, within the framework of these views, E_a depends on the elasticity of the matrix and on the dimensions of the atom of the interstitial substance, but it does not depend on the mass of this atom. The cause of diffusion in this model is the thermal vibrations of the interstitial atom. The probability of diffusion and hence also the coefficient D_0 depend on the frequency of these vibrations as $D_0 \sim \omega_0 \sim 1/\sqrt{M}$, where M is the mass of the interstitial atom. Thus, even apart from the concrete values of the coefficients D_0 and E_a themselves, the classical treatment of diffusion of hydrogen in metals leads to the nontrivial conclusion that the ratio of the diffusion coefficients of the different isotopes of hydrogen does not depend on the temperature. In particular, we should have for the diffusion coefficients of hydrogen H and deuterium D:
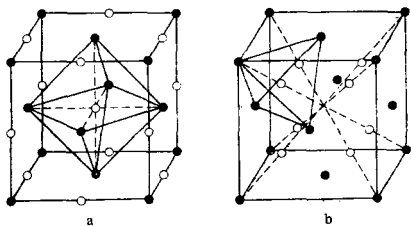

a   b

FIG. 1. The face-centered cubic lattice. ●—atom of the matrix. a) Octahedral cavities, b) tetrahedral cavities.

$$\frac{D_H}{D_D} = 1.41.$$

As analysis of the experimental data shows,[7] this relationship is known not to hold at low temperatures. Moreover, there are indications that the diffusion coefficients exceed the values that we might expect from the classical treatment, even in absolute value. Without question, all these facts indicate that we must take account of quantum phenomena in the diffusion of hydrogen in metals.

What are the characteristic features that distinguish the quantum model of diffusion from the classical model? There are two evident facts that the classical model neglects, but which exert a very substantial effect on the diffusion coefficient. First is the existence of the zero-point vibrations. In particular, these have the effect that the lattice expansion near the interstitial impurity begins to depend on the mass of the impurity. In turn, this leads to a dependence of the activation energy E_a on the mass of the impurity. Second, from the theoretical standpoint, is the following more essential circumstance. Within the framework of quantum mechanics, one can never speak of exact localization of a given impurity in a given interstice. The behavior of the impurity must be described by the Schrödinger equation, and the very intriguing possibility arises of tunneling, activationless transport of the impurity between different interstices. From this standpoint, the behavior of hydrogen in a metal can resemble the behavior of electrons, or rather, that of polarons of large mass in polar crystals. The complete construction of a quantum theory of diffusion that accounts for all of these facts is one of the very interesting and unsolved problems of solid state physics. There has recently been an entire series of studies that have undertaken attempts at a quantum treatment of light interstitial impurities.[8-11] [2]

In line with the abovesaid, the mathematical apparatus of the theory of quantum diffusion of light interstitial impurities will evidently have much in common with the polaron problem[13] and with the theory of particle transport in extremely narrow bands.[14] Now we shall briefly describe the fundamental features of the theory of quantum diffusion, while relying mainly on the results of the study of Kagan and Klinger[11] and the review of Stoneham.[15]

An atom of an interstitial impurity can occupy interstices in the crystal lattice. Here interstices of several types can exist in a given lattice (tetra- or octapores), which form somewhat peculiar sublattices. We shall restrict the treatment to diffusion of an impurity through one of these sublattices.

In each interstice of this sublattice, an impurity atom is quasilocalized in one of the levels ϵ_s in the potential well created by local lattice deformation. By analogy with the Wannier functions, we shall introduce the wave functions $| s, \nu, p \rangle$, which characterize the state of the impurity in the p-th interstice having the energy ϵ_s. The index ν denotes the set of quantum numbers that characterize the state of the phonon subsystem. Evidently, these wave functions are a reasonable zero-order approximation in the problem of quantum diffusion, since the lifetime τ of an impurity in a given interstice is rather large. That is, $\tau \gg 1/\omega_0$, where ω_0 corresponds in order of magnitude to the characteristic phonon frequencies of the solution.

However, the states introduced thus are not eigen-

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states of the translationally invariant Hamiltonian of the system. Hence transitions will occur among them.

First, transitions can occur between different discrete states ϵ_s in a given interstice, owing to interaction of the impurity with phonons. Second, transitions can occur from the interstice p to the interstice p', which, properly, define diffusion.

We can easily note two possibilities for transitions of the second type. Either a transition occurs from $|s, \nu, p\rangle$ to $|s, \nu, p'\rangle$, or $|s, \nu, p\rangle \rightarrow |s', \nu', p'\rangle$. We can neglect transitions with change of the index s if we assume that the width of the level is small in comparison with the spacing between levels: $\Gamma_s \ll |\epsilon_s - \epsilon_s'|$. This makes it possible to treat independently the diffusion on different levels having the diffusion coefficients D^s. Then the overall diffusion coefficient is

$$D = Z^{-1} \sum_s D^s \exp\left(-\frac{\epsilon_s}{kT}\right), \qquad (2.2)$$

where $Z = \sum_s \exp(-\epsilon_s/kT)$.

The transition $|s, \nu, p\rangle \rightarrow |s, \nu, p'\rangle$ is not accompanied by any changes in the phonon system. These transitions lead to the so-called coherent diffusion. The transitions $|s, \nu, p\rangle \rightarrow |s, \nu', p'\rangle$ are accompanied by rearrangement of the phonon state of the system, and they lead to incoherent diffusion. The coherent transitions give rise to a width Δ_s in the energy levels. However, it is small in comparison with all the energy parameters of the problem, and in particular, $\Delta_s \ll \hbar\omega_0$. The overall width Γ_s of the level mainly arises from two-phonon transitions at a particular interstice.

Evidently, only coherent diffusion can occur in the system when T = 0, but its contribution must decline with increasing temperature. According to the estimates of[8], the temperature range in which coherent diffusion plays the governing role is fantastically small: $T \le 10^{-17}$°K. This estimate was based on the following arguments.

Only one transition channel $|s, \nu, p\rangle \rightarrow |s, \nu, p'\rangle$ exists for coherent diffusion, whereas a macroscopically large number of channels $|s, \nu, p\rangle \rightarrow |s, \nu', p'\rangle$ exists for incoherent diffusion from p to p'. The small contribution of each channel in the case of incoherent diffusion is compensated by the summation over all possible channels. This does not happen in the case of coherent diffusion, and hence it can be comparable with incoherent diffusion only at very low temperatures.

Kagan and Klinger[11] showed that this argument is completely false. A correct account taken of many-phonon transitions in a given interstice gives the result that the contribution of coherent diffusion contains no macroscopic smallness as compared with the total contribution of incoherent diffusion. Moreover, it turns out that when the impurity is weakly bound to the lattice, coherent diffusion makes the decisive contribution to the total diffusion over a very broad temperature range.

Without taking up the details of the calculations,[11] we shall describe the physical pattern of the diffusion of light interstitial impurities.

As we have mentioned, coherent diffusion plays the major role in the case of weak binding of the impurity to the lattice (weak polaron effect), and it leads to bandwise transport of the impurities, with account taken of specific transitions at a given interstice. Here the co-

herent diffusion coefficient on the level s depends on the temperature as

$$D_c^s \sim \left(\frac{\hbar\omega_0}{kT}\right)^9.$$

Evidently, in this case at low enough temperatures where only the lowest levels are occupied, the overall diffusion coefficient D of (2.2) will practically coincide with D_c^1. At higher temperatures, diffusion on the upper levels, which is characterized by a certain activation energy, will begin to dominate.

The main factor that destroys the bandwise character of the motion of impurities is the fluctuations in the position of the energy levels in adjacent interstices that arise from the interaction of the impurity with the lattice vibrations. The relative shifts of the levels can considerably exceed Δ_s. These fluctuations in the level positions lead to localization of impurities, similarly to what happens in the statistical scatter of levels (Anderson localization[16]). However, there is a fundamental difference in this case from Anderson localization that involves the fact that the shift of the levels fluctuates in time for each fixed pair of nodes. This has the effect that the impurity cannot become completely localized, owing to the width Γ_s of the levels. However, the effective free path becomes extremely small: $l \ll a$ (a is the interatomic distance). Evidently, in the case of strong binding of the impurity to the lattice, the described mechanism at high enough temperatures (kT $\ge \hbar\omega_0$) will cause breakdown of coherent diffusion, and incoherent, saltatory diffusion will prove to dominate. However, as before, coherent diffusion will play the major role at low temperatures. In this case, Fig. 2 schematically depicts the temperature-dependence of the overall diffusion coefficient. Analytical calculation of the exact value of T_D is at present very difficult. This is due to the lack of reliable data on the hydrogen-metal interaction potentials and on the shape of the potential well for hydrogen lying in an interstice.

We should note immediately that the theoretical model discussed up to now treats the diffusion process in an ideal crystal. Existence of defects or of other impurities very strongly influences the coherent-diffusion process. Interaction of the impurity atoms with one another also disrupts coherent diffusion. As was shown in[11], even a very small concentration of impurity actually abolishes coherent diffusion. Impurities have much less effect on incoherent diffusion.

Hence it is of great interest to calculate the incoherent diffusion coefficient.[8] Later on we shall briefly discuss the results of these calculations and their relationship to the experimental data on diffusion of hydrogen in metals.

The rate of incoherent diffusion is determined by the matrix element

$$W_{pp'} = \langle s, \nu, p | \mathscr{H} | s, \nu', p'\rangle,$$

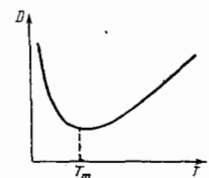where $\mathscr{H}$ is the complete Hamiltonian of the system.

FIG. 2. Temperature-dependence of the diffusion coefficient.

Within the framework of the adiabatic approximation (the wave function of the light impurity is able to adjust adiabatically to the motion of the heavy atoms of the metallic matrix), we can represent the complete wave function as the product of the wave function of the impurity, which depends parametrically on the lattice coordinates $\Phi_p^s(r, R)$, and the wave function of the lattice $\varphi_p^s(R)$:

Then

$$|s, v, p\rangle = \Phi_p^s(r, R)\,\varphi_p^s(R).$$

$$W_{pp'} = \int dR\varphi_p^{s*}(R)\,J_{pp'}^s(R)\,\varphi_{p'}^{s'}(R),$$

where $J_{pp'}^s(R) = \int dr\Phi_p^{s*}(r, R)\,\mathcal{H}\Phi_{p'}^s(r, R).$

If we neglect the discreteness of the states in each interstice (this fact is not important in incoherent diffusion), we can drop the index s, while introducing whenever necessary the density of states.

Now let us assume that the matrix element $J_{pp'}$, does not depend on the configuration of the metallic matrix, i.e., on R. Then at high enough temperatures ($kT \gtrsim \hbar\omega_0$), the transition probability for saltatory diffusion per unit time is

$$W_{pp'} = \sqrt{\frac{\pi}{4\hbar^2 E_a kT}}\,|J_{pp'}|^2\exp\left(-\frac{E_a}{kT}\right),$$

which greatly recalls the classical expression (2.1), where the "activation energy" is equal to

$$E_a = \frac{1}{2}\sum_q M\omega_q^2\left|\frac{\Delta Q_q}{2}\right|^2.$$

ΔQ_q is the change in the normal coordinate of vibrations of the mode ω_q in the jump of the impurity, and M is the mass of an atom of the metallic matrix. Estimates performed within the Debye approximation show that the size and behavior of E_a as a function of the mass of the impurity and the temperature qualitatively agree well with the experimental data for body-centered cubic metals.

There is another possibility, that $J_{pp'} = J_{pp'}(R)$. Such a situation occurs in face-centered lattices. The distinction between this situation and the preceding one can be understood in the very simple model depicted in Fig. 3. The "direct" transition in Fig. 3a corresponds to $J_{pp'}$, which does not depend on R. In the transition shown in Fig. 3b, the motion of the impurity excites the vibrations of the two atoms that lie astride the jump. This causes an additional increase in the energy barrier by some quantity E_s. A situation similar to this happens in face-centered lattices. If we assume that $J_{pp'}(R) = 0$ when the atoms being excited lie closer than some critical distance, and $J_{pp'} = J_0$ in the other cases, then the rate of diffusion is

$$W_{pp'} = \frac{1}{4\hbar}|J_0|^2(E_a E_s)^{-1/2}\exp\left[-\frac{E_a + E_s}{kT}\right].$$

It has been possible within the framework of this theory[8] to derive an expression for the activation energy that contains only fully determined quantities such as the mass of the metal atom, its Debye frequency, the elastic moduli, and the change in volume upon adding hydrogen. The calculated values of E_a for different metals proved to be in rather good, even quantitative
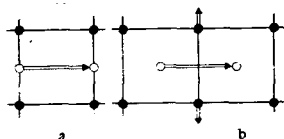

FIG. 3. "Direct" transition (a), and diffusion with excitation of vibrations of the nearest atoms (b).

agreement with the experimental data. The temperature- and isotope-dependences of the diffusion coefficient at high temperatures were also well described.

As for the variations at low temperatures, we should note here first of all the very wide scatter in the experimental data themselves.[3,7] The methods of measuring diffusion that are based on studying the passage of hydrogen through metal foils or on relaxation effects in absorption of ultrasound and in other properties (the Gorsky effect[17]) lead to very large errors at low temperatures. Measurements by NMR and other resonance methods also do not nearly always give direct information on the diffusion coefficient. Apparently no one has yet succeeded in observing a temperature-dependence of the diffusion coefficient similar to that shown in Fig. 2. To do this, as we know, we need experiments with far purer metals. In closing this section, we would like to call attention to the following rather curious phenomenon. The existence is well known of an entire class of substances (such as AgI, Ag_2S, Ag_3SI, and $RbAg_4I_5$) that are called solid electrolytes. They show an anomalously high ionic conductivity comparable with that of the fused salts.[18] The appearance of such a high conductivity is explained[19,20] by the melting of one of the sublattices of the compound, while the other component remains in the solid state. An analogous change in the diffusion coefficient also occurs in the Me—H compounds near the ordering temperature.[21] In the Me—H compounds that are metals, the increase in ionic conductivity is considerably masked by the higher electronic conductivity. However, this phenomenon should be manifested more clearly in dielectric and semiconducting Me—H compounds.

3. PHASE TRANSITIONS AND STRUCTURE OF Me—H COMPOUNDS

There are at least two approaches to the problem of the structure of Me—H compounds. In line with one of these approaches, the hydrides are treated as chemical compounds of ionic, covalent, or metallic types,[22] whose structure is determined by metal-hydrogen bonds. We have actually used the other, earlier approach[23] to these compounds in discussing diffusion problems, and it consists in treating these compounds as interstitial solutions, where the small-dimensioned hydrogen atoms occupy cavities in the metal lattice. This approach is primarily inapplicable for describing the ionic hydrides of the alkali metals, where the lattice of the Me—H compound differs substantially from the lattice of the alkali metal, and also for the series of covalent hydrides of the rare-earth metals. As the experimental studies of the structure of the transition-metal hydrides have shown,[24] interstitial-solution model is quite satisfactory for describing them. The structure and properties of the Me—H compounds within the framework of the interstitial-solution model are better studied, both theoretically and experimentally. The behavior of hydrogen in transition metals can serve as an excellent embodiment of the favorite model, well-studied by theoreticians, of a lattice gas.[25] Just as in the theoretical model,[26] the properties of interstitial hydrogen show gas-liquid-solid transitions. The peculiarity of these transitions and the contrast with the transitions in free hydrogen involve the fact that they occur within the rigid lattice of the metallic matrix.

Hydrogen in the transition metals is not the only ex-

ample of a phase transition of one of the components of a compound while the other keeps its unchanged lattice. As we have noted, a similar phenomenon, i.e., melting of one of the sublattices, occurs also in the solid electrolytes.[18-20] Analogous phenomena can also occur in the ionic and the covalent hydrides. However, these phenomena have been less studied, and moreover, they are determined by hydrogen-metal bonds that are specific to each class of hydrides. Yet the interaction between the hydrogen atoms included in a transition metal, which is responsible for the phase transitions in these systems, is universal in nature in all of the transition metals. However, in itself, this interaction directly shows the specifics of the phase transition within the metallic matrix that distinguishes these transitions from those in free hydrogen. Hereinafter in this section, we shall not treat the problems of the ionic and covalent hydrides, but shall discuss only the metallic hydrides of the transition metals as a clear example of the existence of a specific interatomic interaction in a condensed medium.

A hydrogen atom lying in an interstice of a metallic lattice deforms it by repelling the neighboring metal atoms. In turn, they displace the next metal atoms. Consequently, a long-range displacement field arises in the metal that declines as $1/r^2$ away from the included hydrogen atom. The symmetry and magnitude of this displacement field depend on the symmetry of the crystal and the local symmetry of the site of the hydrogen atom. For a given crystal, the magnitude and symmetry of this field can be described by using the elastic dipole moment tensor P_{ij}. This quantity plays the same role for an elastic displacement field as does the electric dipole moment for the electric field. The interaction of two interstitial hydrogen atoms also occurs via this elastic displacement field. This is a long-range interaction, and it behaves at great distances like a dipole-dipole interaction. Multipole moments can also prove to be important at short distances.

Zener[27] first proposed the idea of the dominant role of the deformation interaction in determining the structure of solid alloys. This idea was consistently developed for describing phase transitions in solid alloys, and in particular, in terstitial alloys in the studies of Khachaturyan.[28] We immediately emphasize that such an effective interaction among hydrogens in an interstitial alloy is no exceptional phenomenon in the physics of condensed phases. The interaction between two hydrogen atoms included in a transition metal is ultimately of the same type as the interaction between the electrons in the metal that gives rise to the superconducting state. Of course, there is an essential quantitative difference between these interactions that arise from the fact that substantially different phonons participate in producing them.

We have already noted that the effective long-range interaction that arises between two hydrogen atoms included in a metal is not an exceptional phenomenon in the physics of condensed systems. Moreover, we can say that such an interaction is rather a universal property of condensed systems. Even if the condensed medium is formed of atoms having short-range pairwise forces, the existence of collective excitations of the phonon type has the result that the effective interatomic interaction in such a medium becomes long-range. The appearance in condensed media of effective

long-range many-particle interactions leads to features in the behavior of the structure factor $S(q)$ of a liquid for small momenta q and to a number of other phenomena that have been discussed, e.g., by Kemoklidze and Pitaevskiĭ[29] as applied to liquid helium.

Hence the problem might be only that of the size of the long-range interactions and of their effective contribution to various phenomena in condensed media. In particular, the elastic interactions between impurities also exist in substitution alloys, but there they play no determining role in the structure of the alloy. One can estimate the contribution of deformational interaction of point defects to the ordering energy of an alloy.[28] In order of magnitude, this contribution is: $V \sim v \lambda u_0^2$, where v is the volume of a unit cell of the solvent, λ is the characteristic elastic modulus, and u_0 is the concentration coefficient of linear expansion of the lattice owing to the presence of the defect. If we select typical values of the cited quantities for interstitial alloys: $v \approx 10^{-23}$ cm^3, $\lambda \approx 10^{12}$ erg/cm^3, and $u_0 \approx 1$, we have $V \approx 1$ eV. For substitution alloys, typical values are $u_0 \approx 10^{-2}$. These values correspond to an energy $V \approx 10^{-4}$ eV, or $V \approx 1°$K. Thus, in substitution alloys, the contribution of the deformation energy to the ordering energy is substantially smaller than the contribution of energy of other origins, which is of the order of the phase transition temperatures, i.e., 10^2 °K. Apparently, this also happens in the ionic hydrides, where the structural transitions are most likely determined by the energy of the metal-hydrogen bond, rather than by the elastic interactions between the hydrogen atoms.

Without taking up the theoretical and experimental study of gas-liquid phase transitions in transition metal-hydrogen compounds, which are described within the framework of the self-consistent field theory by the van der Waals equation with an effective dipole-dipole interaction,[25,30] we shall proceed to a brief discussion of liquid-solid transitions. We note only that, owing to the long-range nature of the dipole-dipole interaction, an entire series of nontrivial effects also arises in gas-liquid phase transitions. In particular, it turns out that the properties of these transitions can depend on the boundary conditions and on the shape of the specimen. The theory of these phenomena has been presented in more detail in a recent study by Wagner and Horner.[31a] The experimental manifestations of the features of the gas-liquid phase transition in such a system have been described in[24,31b].

We must first take up the problem of the difference between the phases of interstitial hydrogen. The gas and liquid differ only in density, and the corresponding phase transition can be accompanied only by a small increase in the lattice parameter of the metallic matrix. However, here the original symmetry of the matrix (cubic for the metals of interest to us) is conserved, and additional Bragg reflections do not arise.

Yet if a periodic ordering of the interstitial hydrogen atoms occurs over equivalent interstices, new Bragg planes appear, although the original cubic symmetry can persist. We can call such a phase transition a liquid-solid transition. However, there are evidently other possibilities involving loss of cubic symmetry. Actually, as we have noted earlier, hydrogen can occupy two types of positions in cubic metal lattices: octa- and tetra-cavities. Figure 1 shows their arrangement for a
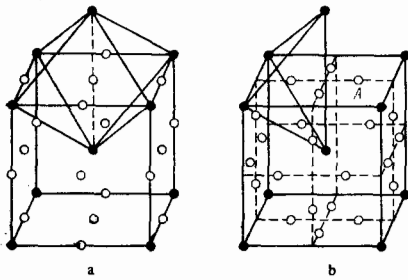
FIG. 4. The body-centered cubic lattice. ●—atom of the matrix. a) Octahedral cavities, b) tetrahedral cavities.

f.c.c. lattice, and Fig. 4 shows them for a b.c.c. lattice. The f.c.c. lattice has only one octa-position and two tetra-positions per atom of the metallic matrix, and all of these interstices possess cubic symmetry. In the b.c.c. lattice, both the octahedron (Fig. 4a) and the tetrahedron (Fig. 4b) for inclusion are slightly compressed along one of the fundamental cubic axes. Since the interstitial hydrogen atom repels its closer neighbors more strongly, inclusion of H into one of the interstices of the b.c.c. lattice leads to a small tetragonal deformation of the original cubic structure. Consequently, a phase transition can occur in the b.c.c. lattice that involves preferential arrangement of the impurities in interstices having a particular axis of tetragonality (e.g., points A and B in Fig. 4b) and loss of the original symmetry. However, new Bragg planes may not arise here. Evidently, this phase transition is analogous to a liquid-anisotropic liquid (liquid crystal) transition. And finally, "solidification of the liquid crystal" can occur when the atoms included in interstices having a given axis of tetragonality become periodically ordered. This is accompanied by appearance of new Bragg reflections.

All of these ideas on the possible types of phase transitions in Me—H systems agree with the results of experimental studies. Thus, for example, it is known that only one gas-liquid phase transition occurs in palladium hydride, which has a f.c.c. lattice. Phase transitions of the remaining types have also been observed in the hydrides of b.c.c. metals (Nb, Ta, V).

A theory of phase transitions involving ordering of interstitial alloys has been developed by Khachaturyan,[28] and it is based on treating the following Hamiltonian:

$$\mathscr{H} = \mathscr{H}_0 + \frac{1}{2} \sum_{r, r'} V(r, r') c(r) c(r'),$$

Here $\mathscr{H}_0$ = const., $V(r, r')$ is the interaction potential of two interstitial hydrogen atoms, and c = 1 or 0, depending on whether there is a hydrogen atom in a given interstice or not. The summation is performed over all of the cells of the lattice and over all equivalent cavity positions. The distribution of hydrogen atoms in the metal lattice can be described by using a one-particle distribution function:

$$n(r) = \langle c(r) \rangle,$$

Here the symbol $\langle \ldots \rangle$ denotes averaging over the Gibbs ensemble. The following expression for the distribution function arises from the variational principle of the free-energy minimum with respect to $n(r)$:

$$n(r) = \left\{ \exp \left[-\frac{\mu - \Phi(r)}{kT} \right] + 1 \right\}^{-1}, \quad (3.1)$$

Here $\Phi(r)$ is the overall potential acting on the H atom

at the point r arising from all the rest of the H atoms. In the self-consistent field approximation,

$$\Phi(r) = \sum_{r'} V(r, r') n(r'). \quad (3.2)$$

When (3.2) is taken into account, Eq. (3.1) is a non-linear finite-difference equation in n(r). Suris[32] has shown that this equation is asymptotically exact in the limit of high and low temperatures. Since it is actually a self-consistent field equation, naturally, it is poorly applicable near the phase-transition point itself. As we know, the width of this region depends on the radius of interatomic interaction. For the compounds of H with the transition metals, the region where this equation fails proves to be rather small, owing to the long-range nature of the elastic interaction between the hydrogen atoms. The meaning of Eq. (3.1) is very transparent. Since a sort of Pauli principle is realized in a solid alloy, i.e., a given node either contains a hydrogen atom or it doesn't, the occupation of the nodes of hydrogen atoms in an interstitial alloy is expressed by a Fermi distribution.

The theory presented here of phase transitions in an interstitial alloy takes no account at all of the quantum behavior of the light hydrogen atom in a metal. The possible manifestation in Me—H systems of such purely quantum features as zero sound or superfluidity of vacancions[10,33] has not yet been discussed, Evidently, these phenomena can arise only at temperatures below the Fermi degeneracy temperature of the protons. Even for free protons at densities corresponding to the density of hydrogen dissolved in a metal, the temperature $T_F^p \ll 1°K$. However, it is generally extremely hard to estimate this temperature for interstitial alloys. Although the phase-transition temperatures are considerably higher than T_F^p, the quantum effects involving the zero-point vibrations of the hydrogen atoms prove to be rather significant, even at these temperatures. In particular, the existence of the zero-point vibrations and their contribution to the energy of the crystal give rise to an isotope-dependence of the liquid-solid transition temperature.[34]

Within the framework of classical concepts of exact localization, one can solve Eq. (3.1) by the method of static concentration waves.[28] The essence of this method consists in seeking a solution for n(r) in the form of a superposition of several static concentration waves,

$$n(r) = c + \frac{1}{2} \sum_j \{ Q(k_j) \exp(ik_j r) + \text{c.c.} \},$$

Here $\exp(ik_j \cdot r)$ is a static plane wave, k_j is a non-zero wave vector lying in the first Brillouin zone, and $Q(k_j)$ is the amplitude of the wave. We shall not discuss here the concrete solutions of the self-consistency equation, and those interested can acquaint themselves with these studies in the book of Khachaturyan.[28] We note only that using the concentration-wave method in solving Eq. (3.1) not only permits one to describe theoretically the ordering processes, but also it substantially simplifies the process of establishing the structure of a compound from source data obtained, e.g., by slow neutron scattering.

Considerable progress has recently been attained in studying structural transitions in transition-metal hydrides by using neutron scattering. Somenkov, Shil'shtein et al.[35-38] have studied the hydrides of Ta,

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Nb, and V. They established that the hydrogen atoms in Ta, Nb, and V generally occur in tetrahedral interstices. They have detected liquid-solid transitions of the interstitial hydrogen in these compounds, together with the associated ordering processes. Somenkov[24] has given a brief review of these results, and has discussed them, and we shall recommend one to refer there for a more detailed study of this problem. In concluding this section, we wish to take up a rather curious effect of ordering of the isotopes of hydrogen over the interstices of a matrix that is caused by the quantum zero-point vibrations of the interstitial atoms.[38] Usually, ordering processes are caused by direct interaction forces between atoms, and accounting for lattice dynamics only amounts to small corrections to the fundamental interaction. The existence in hydrogen of two isotopes of large mass difference leads to a very substantial difference in the frequencies of the optical vibrations of the interstitial atoms. In a first approximation, they depend only on the type of position occupied and the mass of the interstitial atom. Figure 5 shows the energy diagram of the local vibrations of hydrogen and deuterium in the tetra-pores and octa-pores of cerium trihydride CeH_3. The frequencies of the local vibrations are so high that only the zero-point vibrations at the optical frequencies contribute to the free energy of the crystal at the actual temperatures used in the experiment.[39] Inasmuch as, in line with Fig. 5, $\omega_H^{(T)} - \omega_H^{(O)} > \omega_D^{(T)} - \omega_D^{(O)}$, it is quite evident from the free-energy minimum that hydrogen lies in the octa-pores in the ordered state, and deuterium in the tetra-pores, of which, moreover, there are as twice as many. Thus, the fully disordered state must become ordered with decreasing temperature. There is no phase transition in this case, since this ordering is not a cooperative process. The energy difference of the zero-point vibrations serves here as a sort of external field. Figure 6 shows the calculated and experimental curves of the temperature-dependence of the ordering parameter $\eta = c_H^{(O)} - c_H^{(T)}$, where $c_H^{(O)}$ and $c_H^{(T)}$ are the probabilities that hydrogen will lie in an octa-pore or a tetra-pore, respectively. The experimental data actually indicate an ordering of the hydrogen isotopes. The sharp difference between η_{exp} and η_{theor} at low temperatures apparently involves the relatively low mobility of hydro-

gen in the trihydride (all the interstices are occupied, and the usual mechanism of diffusion via free pores is blocked).

4. ELECTRONIC PROPERTIES OF Me—H COMPOUNDS

The high solubility of hydrogen in metals and the broad region of homogeneity of the solutions provide great possibilities for studying the electronic properties of these compounds. It might seem that no significant difficulties should exist in theoretically describing the properties of the Me—H compounds, owing to the extremely simple electronic structure of the hydrogen atom. Yet this is far from the truth. In fact, as we have noted in the Introduction, Me—H compounds have a very broad spectrum of types of Me—H bonds, and correspondingly, extremely varied electronic properties. From the standpoint of electronic properties, the most interesting compounds are those of the transition and rare-earth metals. We shall mainly discuss these compounds in this section. At the end of this section in discussing the possibility of modeling the properties of metallic hydrogen by using the Me—H compounds, we shall briefly take up the properties of the hydrides of the alkali metals, which are of very considerable interest in this regard.[4]

Before we proceed to discuss the theoretical models of the electronic structure of the compounds of the transition and rare-earth metals with hydrogen, we shall note the very interesting (as we see it), experimental data on these compounds. First, there is the metal-dielectric phase transition in cerium hydride as the hydrogen concentration increases to a composition corresponding to $CeH_{2.8}$. No changes in the structure of the compound are observed in this transition. Temperature measurements on monocrystals of cerium hydrides having compositions from $CeH_{2.7}$ to $CeH_{2.8}$ show that the metal-dielectric transition occurs at $T_C \approx 250°K$. Here exact x-ray measurements show that the fluorite-type cubic structure undergoes a slight tetragonal distortion below T_C.[3)] Second is the experimentally observed transformation of the ferromagnetic ally $Pd_{1-x}Mn_x$ with x < 4% into the antiferromagnetic $Pd_{1-x}Mn_xH_y$ upon adding hydrogen[40] up to a concentration $y \gtrsim 0.7$. Third is the discovery of superconductivity[5,6] in the alloys of Pd and Pd-Ag with hydrogen, which we shall discuss in greater detail in the next section of this review.

Two alternative models (anion and proton) are used to describe the electronic properties of Me—H compounds. In the former, hydrogen lying in an interstice of the metallic lattice attracts to itself an electron of the metal, and is converted into the negatively charged ion H^-. On the other hand, the proton model is based on the assumption that the hydrogen atom gives up its electron to the conduction band of the metal, and is converted into a positively charged proton. The proton model is historically earlier.[23] The grounds for it were the high solubility of hydrogen in metals caused by the small radius of the proton, and the earlier, and as it turned out, not fully accurate calculations of the band structure of Pd. According to these calculations, Pd has about 0.6 holes per atom in the d-band. Owing to the strong Coulomb correlations in the d-band, Pd is paramagnetic with a high susceptibility. In the proton model, addition of hydrogen diminishes the number of d-holes and correspondingly, also the paramagnetism
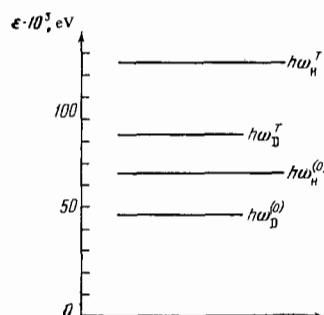
FIG. 5. Energy diagram of the local vibrations of hydrogen and deuterium in Ce(H, D)$_3$. ($\omega_{H(D)}^{(T, O)}$ is the frequency of the vibrations of hydrogen (or deuterium) in a tetra- or octapore.)
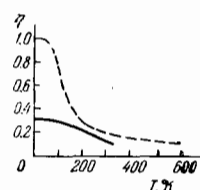
FIG. 6. The theoretical (dotted) and experimental curves for the temperature-dependence of the order parameter.

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of Pd. The transition of Pd from the paramagnetic to the diamagnetic state occurs just at the hydrogen concentration $c = 0.65$.[41,42]

The proton model explains, indeed qualitatively, an entire series of phenomena in the Me—H compounds. However, the quantitative agreement has proved to be not too good. According to new, more accurate calculations, Pd proves to have not 0.6, but only 0.36 holes per atom in the d-band,[43] and the proton model cannot explain strictly qualitatively an entire series of other phenomena in Me—H compounds. Primarily, this refers to Knight-shift experiments, nuclear magnetic relaxation, and the Mössbauer effect.[22] But especially great difficulties within the framework of the proton model arise in attempts to describe the metal-dielectric transition in cerium hydride and in describing the semiconductor properties of the series of rare-earth hydrides.

The Knight-shift and NMR experiments definitely indicate differing behavior of the interstitial hydrogen from that of a free proton, and they fit better the ion of hydrogen H^-. An entire series of other experimental data also fits far better into the framework of the anion model.[44] Figure 7 (from[45]) shows the difference in the consequences from the proton and anion models. It schematically depicts the band structure of metallic yttrium and of its dihydride within the framework of the proton and anion models.

In addition to the difference in the occupancy of the 1s-band of hydrogen, which is not shown in Fig. 7, a difference in the band structure in these models arises from the fact that the crystal splitting of the d-level of the Y ion occurs in an essentially different way for the positive and negative H ions.

One can understand the possible appearance in a metal of both positive and negative hydrogen ions from a very simple analysis of the shielding conditions of this ion in a transition metal. Friedel[46] has conducted such a treatment for dilute solutions of H, and we shall now repeat it briefly. The specifics of the shielding in the transition and rare-earth metals arises from the presence of narrow d-bands and practically discrete f-states. In the rare-earth metals, the f-states overlap but little with the interstitial hydrogen, and most likely, they do not participate in shielding. Thus shielding arises from the c- and d-electrons. The transfer of one hydrogen atom into the metal is accompanied by a change in the energy of the system of

$$U \approx I - W + \langle V_t \rangle,$$

(I = 1 Ry is the ionization energy of a hydrogen atom, W is the work function of the given metal, and $\langle V_t \rangle$ is the energy of interaction between the shielded potential of the proton [$V_t = -4\pi e^2/q^2 \epsilon(q)$ and $\epsilon(q)$ is the static dielectric constant]) and the electrons and ions of the metal in the first order in V_t.

The quantity $\langle V_t \rangle$ is determined by the nature of the shielding in the given metal. Evidently, the shielded charge is distributed about the proton so as to minimize the energy $\langle V_t \rangle$. We shall neglect the contribution to $\langle V_t \rangle$ of the interaction of the proton with the ions, while assuming that the potential of the proton is rather strongly shielded at the interatomic distances.

It is reasonable to use the rigid-band model[47] for dilute solutions of hydrogen. Here the presence of the impurity causes the bands of the solvent metal to be
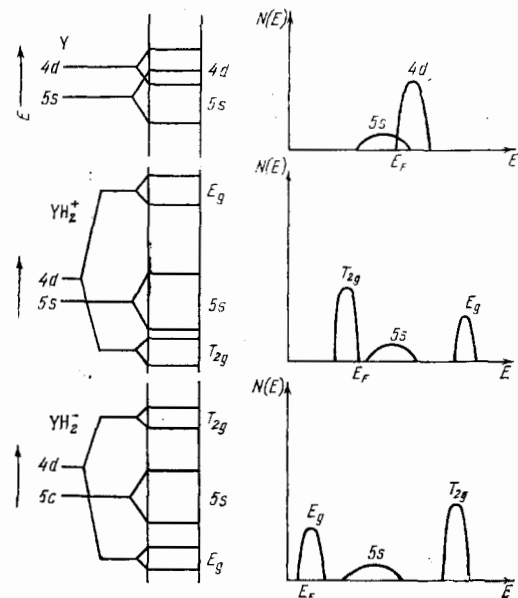

FIG. 7. Diagram of the electronic structure of Y metal and of the dihydride YH_2, according to the proton and anion models.

shifted en masse by the amount $\langle kj | V_t | kj \rangle$, where $| kj \rangle$ is the Bloch function of the band j. (Here we have used the Born approximation. That is, we assume that there are no virtual bound states and the phase shifts are small.)

Then, evidently,

$$\langle V_t \rangle = \langle k, s | V_t | k, s \rangle N_s + \langle k, d | V_t | k, d \rangle N_d,$$

Here N_s and N_d are the densities of s and d electrons. The overall shielding charge is determined by Friedel's rule

$$1 = Z_s + Z_d, \qquad (4.1)$$

where Z_s and Z_d are the shielding charges of the s and d electrons localized near the impurity.

Denoting by n_s and n_d the densities of states in the s and d bands that correspond to the Bloch functions $| k, s \rangle$ and $| k, d \rangle$, we can write:[47]

$$Z_s = -n_s(\varepsilon_F) \langle k, s | V_t | k, s \rangle,$$
$$Z_d = -n_d(\varepsilon_F) \langle k, d | V_t | k, d \rangle.$$

Finally we get

$$\langle V_t \rangle = -\frac{N_d}{n_d(\varepsilon_F)} Z_d - \frac{N_s}{n_s(\varepsilon_F)} Z_s. \qquad (4.2)$$

Now we can determine Z_s and Z_d by minimizing $\langle V_t \rangle$ with account taken of the condition (4.1). (Evidently, Eq. (4.2) must also contain positive terms that correspond to the increase in energy owing to electron-electron interaction. We must take them into account in minimizing $\langle V_t \rangle$.)

Let us study the shielding in different transition metals.

a) At the end of the series of transition metals (Ni, Pd), the density N_d of d electrons is maximal, whereas the density of states $n_d(\epsilon_F)$ is not maximal, though large. Then $N_d/n_d(\epsilon_F) \approx N_s/n_s(\epsilon_F)$, and the minimization of (4.2) gives $0 < Z_s < Z_d < 1$, which corresponds to an H^+ ion.

b) In the first half of the series of transition metals, N_d is much smaller, while $n_d(\epsilon_F)$ is maximal, and the

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minimization of $\langle V_t \rangle$ gives $Z_s > 1$ and $Z_d < 0$. Over-shielding occurs here, and the shielding charge of the s electrons is compensated by the decrease in the number of d electrons in the region of the impurity. However, owing to the fact that the wave functions $|k, d\rangle$ are quasilocalized at the lattice modes, and they weakly overlap in the region of the interstices, the situation that $Z_s > 1$ and $Z_d < 0$ corresponds to an H^- ion. Analysis of the experimental data on energy of solution and on relaxation phenomena apparently confirms this conclusion of the preferability of the proton model for the metals at the end of the series, but the anion model for the beginning of the series.

Of course, both the proton and the anion models per se are rather crude, and are chemical, rather than physical models. A correct description of the Me—H compounds requires a calculation of the exact electronic band spectrum. Naturally, only within the framework of this description can one justify the use of the approximate proton and anion models and establish their degree of applicability. Such a program has been carried out most systematically in the studies of Switendick.[48,49]

Calculations performed by the method of combining plane waves with the crystal potential, as calculated in the Hartree-Fock self-consistent approximation, lead to the following picture for the hydrides of the rare-earth and transition metals.

First of all, the rigid-band model based on the bands of the original metal has proved to be absolutely false in many cases. In the dihydrides of the rare-earth metals (REM), one new band arises that is formed by the 1s state of hydrogen and lies below the Fermi level. An energy gap arises in the spectrum of states. In the dihydrides of the divalent REM, the Fermi level falls in this gap, and correspondingly, they are semiconductors. In the dihydrides of the trivalent REM, the Fermi level passes above this gap. With increasing hydrogen concentration in the composition MeH_x with $x > 2$, a second additional band arises, and the Fermi level for the trivalent REM lies in the forbidden energy region. Here the width of this region increases as the hydrogen concentration approaches $x = 3$.

In the transition metals, where a phase transition to the dihydride does not occur, but the hydrogen is arbitrarily distributed over the interstices (i.e., in compounds like VH, NiH, and PdH), new bands do not arise involving the electrons of hydrogen. Here hybridized states are produced that lie near the Fermi surface. Although the rigid-band approximation is not applicable in this case as well, yet qualitatively this situation is rather close to the proton model.

The band-structure calculations permit us to describe rather well many experimentally-observed phenomena in the Me—H compounds. In particular, the possibility arises of explaining the metal-dielectric transition of $CeH_{2.8}$ within the framework of a one-particle band spectrum. The decrease in the magnetic transition temperatures in the series of REM hydrides as compared with the pure metals also becomes understandable.[39,50] Actually, the magnetic structures in the REM arise from indirect exchange between the magnetic electrons lying in the f levels. Indirect exchange interaction of the Ruderman-Kittel type is due to the free conducting electrons. As the hydrogen concentration increases in the REM hydrides, the number of these elec-

trons decreases, in agreement with Switendick's calculations, just as in the anion model. Hence, the indirect exchange interaction also decreases, along with the critical magnetic transition temperature. Unfortunately, there are as yet no exact, quantitative comparisons of this model with the experimental data. Hence it is yet premature to speak of its degree of accuracy. Undoubtedly also, the study of the phase transition in $CeH_{2.8}$ and an elucidation of how well a very simple one-particle treatment corresponding to Switendick's model can describe it accurately are also of considerable interest. This is all the more interesting in that very similar phenomena occur also in the series of oxides of the transition metals, which can also be treated as interstitial solutions of oxygen.

Practically all the compounds of the transition metals with hydrogen are metallic. A very simple rigid-band proton model describes their behavior qualitatively fairly well. In all of them, the electronic heat capacity and susceptibility decline with addition of hydrogen,[44] which primarily involves the decrease in density of states owing to the addition of electrons from hydrogen, However, these changes do not agree with the rigid-band model quantitatively. The calculations of Switendick[49] for the hydrides of Pd and Ni permitted him to get quite a reasonable quantitative agreement with these data. The existence near the Fermi surface of hybridized electronic states from the 1s band of hydrogen permits us to hope for a reasonable description of the data on the Knight shift, NMR, the Mössbauer effect, and positron annihilation in these compounds. According to these data, hydrogen occurs in the metal not in the form of a proton, but it has about 0.1—0.6 electron per atom.[51,52] The photoemission measurements of the density of electron states in the compound PdH[53] (Fig. 8) are also rather well described in this model. Perhaps the time is now ripe to return to the experimental finding[40] that had been mentioned at the beginning of this section of the conversion of the ferromagnetic alloy $Pd_{1-x}Mn_x$ ($x < 4\%$) upon adding hydrogen into the antiferromagnetic compound $Pd_{1-x}Mn_xH_y$ with $y \geq 0.7$. According to[40], the ferromagnetism in $Pd_{1-x}Mn_x$ is not determined solely by the magnetic moments of the Mn ions, but is enhanced by the strong paramagnetism of the d electrons of Pd. The decrease in the density of states in Pd upon adding hydrogen actually abolishes this contribution to the magnetic properties of the alloy $Pd_{1-x}Mn_x$. The situation that arises greatly recalls the behavior of Mn in Cu, while the additional decrease in the free flight path of the electrons owing to scattering by H establishes an antiferromagnetic, or rather, disordered distribution of the magnetic moments localized on the Mn ions. In the next section in discussing superconductivity in Me—H compounds, we shall again return to discussing the electronic properties of the transition-metal hydrides.

Now we would like to take up a problem that has been

FIG. 8. The relationship between the number of ejected electrons and their energy. The energy of the incident radiation $h\nu = 21.2$ eV. The states sp — 1s are bonding hybridized Pd–H states that shield the proton in the Pd lattice. They arise from the sp state of Pd and the 1s state of H.

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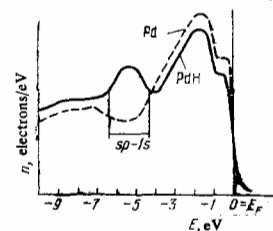
recently noted in many studies on Me—H compounds: the problem of modeling the properties of metallic hydrogen by using the Me—H compounds. This problem is often mentioned even when treating the hydrides of the transition metals. In the light of the above-presented ideas on the structure and properties of the compounds of the transition metals with hydrogen, the properties of the interstitial hydrogen in this case evidently have nothing in common with metallic hydrogen. First, the structure of hydrogen within a metal lattice is determined by the specific elastic interactions, rather than by the electronic interactions, as in free hydrogen.[54] Second, the electronic properties of the transition-metal hydrides also have little in common with metallic hydrogen, since here special bands associated with the 1s states of hydrogen are not produced.[48,49] In this regard, the higher hydrides of the alkali and rare-earth metals are far more attractive. Primarily, these compounds are favorably distinguished from the transition-metal hydrides by the fact that, in them (namely in the alkali-metal hydrides), the electrons of the metal occur in a broad s band, the same as the 1s band of hydrogen. Hence the electrons do not transfer to the metal ions, but can be found also on the H ions. As we have noted, an electronic band is also formed in the higher hydrides of the rare-earth metals that involves the electrons of hydrogen. Formation of this band at the Fermi surface might lead to the appearance of a number of specific properties characteristic of metallic hydrogen, in particular, a high critical superconductive transition temperature.

Unfortunately, most of these compounds are dielectrics. Hence they cannot directly manifest the properties of metallic hydrogen. However, perhaps they can be transformed to the metallic state by applying high pressure to them. As Gillman[4] has shown, this pressure will be substantially lower than the transition pressure of pure hydrogen to the metallic state. This involves the fact that a rather considerable dielectric constant exists within the matrix that substantially lowers the energy difference between the dielectric and metallic states. Concrete estimates were made in[4] for the compound LiH_2F.

Actually, the binding energy of the H_2 molecule is 52 kcal/mole, and the binding energy of metallic H is 11 kcal/mole. If we consider that the dielectric constant of LiF is $\epsilon = 3.7$, the energy difference between the two states will be only 10 kcal/mole. This difference corresponds to a pressure of only 40 kbar, in contrast to 2.5 Mbar for pure hydrogen. Moreover, the distance between the hydrogen atoms in the molecule is $d_H = 0.746$ Å, while with the dielectric constant in LiF taken into account, $d_H = 1.43$ Å. The distance between the pores in LiF where the hydrogen atoms lie is $d = 2.01$ Å. According to the data of Drickamer,[55] this distance will become equal to $d = 1.43$ Å even at 600 kbar. Of course, these estimates seem too crude, and we can hardly treat them very trustingly. One thing is indubitable: in discussing the problem of modeling the properties of metallic hydrogen, we must pay far more attention to compounds that are dielectrics and semiconductors under ordinary conditions.

5. SUPERCONDUCTIVITY IN Me—H SYSTEMS

Until recently, the only Me—H compound in which a superconductive state had been found was the higher hydride of thorium Th_4H_{15}.[56] Curiously, no signs of superconductivity had been observed in the hydrides of the superconductive metals Nb, V, and La down to very low temperatures of the order of 0.1°K. Usually the treatment of superconductive properties is based on the very simple formulas proposed by Bardeen, Cooper, and Schrieffer.[57] In particular, the critical temperature of the superconductive transition in the BCS theory is written in the form

$$T_c = 1.14\Theta_D \exp\left[-\frac{1}{N(0)V}\right], \qquad (5.1)$$

Here Θ_D is the Debye temperature of the metal, V is the interelectronic binding constant, and $N(0)$ is the density of states of the electrons at the Fermi surface. Addition of hydrogen to transition metals like Nb, V, and Ta decreases $N(0)$. Such a phenomenon is experimentally observed, for example, in the decrease in electronic heat capacity.[58] According to Eq. (5.1), a decrease in $N(0)$ should lead to a sharp decline in T_c. Very often the lack of superconductivity in metal hydrides is explained in this way. In fact the situation is far more complex. The critical temperature T_c is expressed in terms of the properties of the normal metal in a more complex way than is implied by the BCS formula (5.1), namely,

$$T_c = \bar{\omega} \exp\left(-\frac{1+\lambda}{1-\mu^*}\right),$$

Here $\bar{\omega}$ is some mean phonon frequency, ($\hbar = 1$), λ is the electron-phonon coupling constant, and μ^* is the Coulomb pseudopotential, which for most superconductors is a very small quantity of the order of 0.1—0.2. As has been noted empirically by McMillan,[59] the electron-phonon coupling constant λ for many transition metals is practically independent of the density of states of electrons at the Fermi surface. Hopfield[60] has theoretically corroborated this fact. Hence the decrease in density of states of electrons in Nb, V, and a number of other metals cannot in itself yet explain the decrease in T_c. An essential point here is the behavior of the electron-phonon coupling constant λ. It would be extremely interesting to study the behavior of λ upon adding hydrogen to metals. Such a possibility exists. As Hopfield[61] and Maksimov and Motulevich[62] have shown, the electron-phonon coupling constant can be determined from optical measurements at room temperature. Such an investigation would also permit one more thoroughly to study the dependence of λ on the density of states of the electrons and to test the accuracy of the statements of[59,60] that it depends weakly on $N(0)$.

Measurements of the resistance of these metals at different H concentrations[63–65] cast a certain amount of light on the changes that occur in the transition metals as hydrogen is added to them and on the reason for the decrease in the electron-phonon coupling constant. Figure 9[62] shows a typical graph of such a relationship for the system Ta—D. The deep trough in the resistance near the concentration $c_D = 0.5$ involves the ordering of the deuterium at the composition Ta_2D. The next trough in $\Delta\rho$ appears near $c_D = 1$ with formation of the hydride TaD. The fact is extremely important in this graph that the absolute value of the resistance for Ta_2D and for pure Ta is practically the same. An analogous situation occurs in the compounds V—H[64] and Nb—H.[65]

The following explanation of this behavior of the resistance suggests itself. Addition of hydrogen to a transition metal substantially changes the band structure of
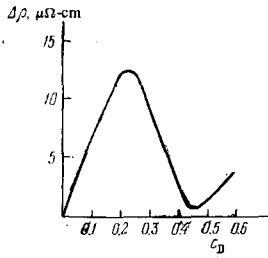
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$\Delta\rho$, $\mu\Omega$-cm

FIG. 9. The relationship between the D concentration and the excess resistance of the Ta—D system as compared with pure Ta. The measurements were performed at $T = 9°C$.

the metal involving the d electrons, but it hardly alters the s states. Since mainly the light s electrons participate in electrical transport, the resistance of the pure metal and of the ordered Me—H compound are practically the same. However, the d electrons make the fundamental contribution in the transition metals to the density of states and to the electron-phonon coupling constant, which determines the value of the critical superconductive transition temperature. As hydrogen is added to the metal, its electrons fill the d band, which comes to lie below the Fermi surface. Then it no longer exerts hardly any effect on the properties of the electrons at the Fermi surface. Hence the density of states at the Fermi surface sharply diminishes. The decrease in the constant λ upon going from a metal having d electrons to a metal having almost free s electrons, as occurs in the hydrides of Nb, V, and Ta, can involve a decrease in the matrix element for electron-ion interaction or the small number of these s electrons.

Quite recently superconductivity has been found in the hydrides of palladium[5] and of alloys of palladium with noble metals.[6] The unexpectedly high values of T_c of up to 11°K in the system Pd—H (D) and up to 10°K in the systems Pd—Ag—H (D) have attracted considerable attention of researchers toward these compounds. There is currently a rather large number of studies, both experimental and theoretical, concerned with the superconducting properties of these compounds. Yet the first stimulus to many investigators, after the discovery of such rather high T_c's, was to associate these T_c's with the presence in PdH of a matrix of metallic hydrogen. In fact, according to the estimates existing in a number of studies,[66,67] the critical temperature of the superconductive transition in metallic hydrogen should be very high, of the order of 100°K. However, as was shown in the last section of this review in discussing the electronic properties of Me—H compounds, these hypotheses of the existence in PdH of an independent subsystem of metallic hydrogen are completely groundless. One of the confirmations of this is the study of the isotope effect in the systems PdH and PdD.[68] If the hydrogen subsystem were to make the fundamental contribution to the appearance of superconductivity, then the critical temperature T_c for the different isotopes of hydrogen should behave like $M^{-1/2}$, and be considerably smaller for deuterium. Yet the experimental data show the completely opposite picture, namely, the critical temperature of the deuterium compounds is higher than that of hydrogen: $T_c^D = 11°K$, $T_c^H = 9°K$. In order to understand the reason for the appearance of the superconductive state in the PdH compounds and the role of hydrogen in this, we must first find the properties of Pd itself. And most importantly, we must understand why Pd itself lacks superconductivity.

Pd closes the second row of transition 4d metals, and it has the configuration of a filled $(4d)^{10}$ shell in the

free atom. When the metal is formed from Pd atoms, the band that corresponds to the 4d shell proves to be incompletely filled. As the recent theoretical calculations and the experimental data have shown,[43] Pd has 0.36 d-holes per atom. Owing to the high density of states in the d band, Pd shows a very high Coulombic interaction between the electrons. This is precisely the type of interaction that leads to ferromagnetism in the 3d transition metals. This interaction is not strong enough in Pd to lead to ferromagnetism, but it exerts a very strong effect on many electronic properties of Pd. The theory of this interaction, which corresponds to exchange of virtual spin waves, has been developed by Doniach[69] and by Berk and Schrieffer.[70,71] The effective Coulomb interaction of electrons having opposite spins can be expressed by using the scattering t matrix. In the random-phase approximation (RPA), the t matrix has the form

$$t(q, \omega) = \frac{\overline{V}_c}{1 - N(0)\,\overline{V}_c U(q, \omega)}, \qquad (5.2)$$

Here $\overline{V}_c$ is the averaged Coulomb matrix element, $N(0)$ is the density of states of the electrons at the Fermi surface, and $U(q, \omega)$ is the Lindhart expression for the dielectric constant of a free electron gas. The existence of the effective interaction (5.2) increases the magnetic susceptibility $\chi(q, \omega)$, so that in the RPA,

$$\chi(q, \omega) = \frac{\chi_0 U(q, \omega)}{1 - N(0)\,\overline{V}_c U(q, \omega)}, \qquad (5.3)$$

where $\chi_0 = 2\mu_B^2 N(0)$. In this approximation, the condition for appearance of the ferromagnetic state $\chi(0, 0) \to \infty$, as we see from (5.3), takes the form $N(0)\overline{V}_c > 1$. As we have noted, this criterion is not satisfied in Pd, though its magnetic susceptibility is very high, precisely owing to the enhancement arising from exchange of virtual spin waves. In order to explain the meaning of the words "exchange of virtual spin waves," we shall write the spectral representation for the t matrix:

$$t(q, \omega) = \int_{-\infty}^{+\infty} \frac{F(q, E)\,dE}{\omega - E + i\delta},$$

where $F(q, E) = (1/\pi)\operatorname{Im} t(q, E)$.

In a ferromagnetic metal, where there exist well-defined excitations, or spin waves having a certain spectrum $\omega(q)$, we have $F(q, E) \approx \delta(E - \omega(q))$. The almost ferromagnetic Pd lacks undamped spin waves, and the spectral density of the t matrix differs substantially from a δ-function, being a broad bell-shaped function near $E = 0$.

A combined treatment of the electron-phonon and exchange interaction of (5.2) permits one to calculate the change in the density of states of the electrons and the critical superconductive transition temperature T_c:[72]

$$N(0) = N_b(0)(1 + \lambda_{\rm ph} + \lambda_{\rm pm}),$$

Here $\lambda_{\rm ph}$ is the electron-phonon coupling constant, $\lambda_{\rm pm}$ is the exchange interaction constant, $N_b(0)$ is the band density of states:

$$\lambda_{ph} = 2 \int_0^\infty \frac{\alpha^2(\omega) g(\omega)}{\omega}\,d\omega,$$

where $\alpha^2(\omega)g(\omega)$ is the spectral density of the electron-phonon interaction; and

$$\lambda_{pm} = 2N(0) \int_0^{2k_F} \frac{q\,dq}{2k_F^2} \int_0^\infty \frac{F(q, \omega)}{\omega}\,d\omega.$$

A calculation of the band structure of Pd[43] and com-

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parison with the experimental data on electronic heat capacity shows that $\lambda_{ph} + \lambda_{pm} = 0.76$, with $\lambda_{ph} = 0.37$, and $\lambda_{pm} = 0.39$.

We can express the critical superconductive transition temperature as follows:

$$T_c = \frac{\sqrt{\langle \omega^2 \rangle}}{1.2} \exp\left(-\frac{1 + \lambda_{ph} + \lambda_{pm}}{\lambda_{ph} - \lambda_{pm} - \mu^*}\right), \qquad (5.4)$$

Here $\langle \omega^2 \rangle$ is the mean square of the phonon frequencies, and $\mu^* \approx 0.13$ is the Coulomb pseudopotential. Since the paramagnetic interaction constant $\lambda_{pm} > \lambda_{ph}$ in pure Pd, which corresponds to an effective repulsion between the electrons, superconductivity is absent in pure Pd.

Even shortly after the discovery of superconductivity in the PdH compounds, it was clearly realized[73,74] that the fundamental reason for appearance of superconductivity in PdH is the suppression of the spin fluctuations in Pd as H is added to it. We can assume that $\lambda_{pm} = 0$ at the concentration $c_H \approx 0.7$. This is confirmed experimentally by the fact that the magnetic susceptibility of PdH not only decreases substantially in absolute value at these concentrations, but it even becomes diamagnetic.[41,42] The vanishing of the spin fluctuations in PdH involves the decrease in the density of states of the electrons as compared with pure Pd. Although, as we have noted in the last section, the "rigid" band model is inapplicable in describing the electronic structure of the Me—H compounds, yet in a more rigorous treatment[49] it turns out that the narrow d band is filled by the electrons of hydrogen as the latter is added to Pd. The Fermi level of the compound PdH falls in the broad s band, and the density of states of the electrons in PdH is practically the same as in Cu.

A theory of the superconductivity in the PdH compounds was first proposed by Benneman and Garland.[73] Relying on the calculations of the superconductive properties of the transition metals that they had developed earlier,[72] these authors calculated all the parameters that enter into the expression (5.4) for T_c of the compound PdH. The fundamental assumption contained in[73] is that the incorporated hydrogen abolishes the spin fluctuations by decreasing the density of states of the electrons, but it little affects all of the rest of the properties of Pd. As the authors of[73] see it, the most important fact is that in the compound PdH, just as in pure Pd, the electrons near the Fermi surface have the nature of strongly-coupled d electrons. Then the electron-phonon coupling constant can be written in the form:[60,72]

$$\lambda_{ph} = \frac{\Phi(\Omega)\,\eta(\Omega)}{M\langle \omega^2 \rangle}, \qquad (5.5)$$

Here $\Phi(\Omega)$ is a function that depends very weakly on $N(0)$ and on the valency of the metal, M is the mass of the unit cell, Ω is the atomic volume, and η is an atomic characteristic that expresses the gradient of the atomic potential in terms of the matrix element. Although it is too hard a problem to calculate η from "first principles," it can be found from the experimental data on T_c for different elements. It can be linearly extrapolated for alloys. The authors calculated η for the stated compounds from the experimental data on the superconductivity of U_6X compounds, where X = Cr, Mn, Fe, Co, or Ni, They calculated η for Pd, Pt, and Rh from the data on alloys of the 3d and 4d compounds. The obtained values of η permitted them to calculate

λ_{ph}, the electron-phonon coupling constant, and hence also T_c, not only for PdH, but also for PtH, RbH, and NiH. According to these calculations, we can expect superconductivity only in platinum hydride, with $T_c \approx 1°K$.

Within the framework of the approach developed by Benneman and Garland, the anomalous isotope effect in PdH was attributed to the small lattice expansion owing to incorporation of hydrogen and the consequent decrease in λ_{ph}. Here, in the opinion of the authors, the expansion is greater in incorporating hydrogen, owing to its smaller mass, than for deuterium.

The good agreement of the calculated and experimental data on T_c in PdH would have been an excellent confirmation of the correctness of the initial assumptions of the authors and of their calculations if they had not made in this study an entire series of predictions on the behavior of other hydrides on the basis of the performed studies. In particular, the authors concluded that superconductivity should be lacking in the alloys of Pd with the noble metals, where the electrons at the Fermi surface are not strongly bound, and resemble, rather, the almost free s electrons. The explanation that the authors gave for the anomalous isotope effect implied that one could increase T_c by subjecting PdH to strong pressure to decrease the interatomic distance. Both of these predictions proved false. The critical temperature of the compounds PdAgH proved to be even higher than for PdH,[6] while application of high pressures to PdH only lowered its critical temperature.[75,76] Moreover, there are experimental indications[41,77] that the lattice constant of PdD may be even larger than for PdH.

Undoubtedly, the fundamental reason why superconductivity appears in palladium hydride is the suppression of spin fluctuations. Yet all the rest of the existing data create the impression that all the other assumptions of[73], namely, the d character of the electrons at the Fermi surface and the lack of other changes in the properties of Pd, apart from the abolition of spin fluctuations upon inclusion of H, are evidently false.

Addition of H to Pd and to Pd alloys has a far greater effect on the properties of these compounds than a simple suppression of spin fluctuations. According to the magnitude and sign of the pressure-dependence of T_c, the PdH compounds are far more reminiscent of simple metals of the type of Sn and Pb than of the transition metals. Just as undoubtedly, inclusion of H substantially increases the electron-phonon coupling constant λ_{ph}. The attempts to explain the increase in λ_{ph} and the role of hydrogen in this process have led to creation of an entire series of theories.[74,78-80] Most of these studies assume that the interaction of the electrons with the optical high-frequency vibrations of the H or D atoms contributes directly to the coupling constant λ_{ph}. Moreover, upon using the empirical relationship[59,72]

$$\lambda_{ph} \approx \frac{1}{\langle \omega^2 \rangle}, \qquad (5.6)$$

the authors of[79] consider that λ_{ph} for deuterium will be larger than for hydrogen, since $\langle \omega_D^2 \rangle < \langle \omega_H^2 \rangle$ for deuterium owing to its larger mass. This hypothesis ought to explain the existence of the anomalous isotope effect in PdH. We should immediately object that such arguments are deeply in error. One can show rigorously[81] that, in the harmonic approximation, the elec-

tron-phonon coupling constant is completely independent of the masses of the atoms comprising the alloy. Only the pre-exponential factor in the expression (5.4) for T_C depends on the masses of the atoms. In turn, this factor cannot in any case lead to an anomalous isotope effect.

Let us examine in somewhat greater detail the currently existing theoretical models and experimental data on the superconductivity of PdH, PdD, and Pd—Ag—H(D). If we use the ordinary formula (5.4) for T_C, in which we can now set $\lambda_{pm} = 0$, and take account of the fact that $\sqrt{\langle\omega^2\rangle} \approx \omega_D \approx 300°$K, we can convince ourselves that we must assume that $\lambda_{ph} \approx 0.7$ in order to explain the rather high T_C of the PdH compounds. Comparison of the density of states that one gets by measuring the electronic heat capacity of $PdH_{0.88}$, which gives the value 0.34 states/eV,[82] and by the band calculations of Switendick,[49] which give 0.2 states/eV, leads to the same value $\lambda_{ph} = 0.7$, according to the formula $N(0) = N_b(0) (1 + \lambda_{ph})$. As we have noted, $\lambda_{ph} \approx 0.37$ for pure Pd. The great increase in the electron-phonon coupling constant λ_{ph} in going from pure Pd to PdH indicates a considerable change in the electronic, and perhaps the phonon properties of this compound. The impossibility of explaining the superconductivity in PdH by suppression of paramagnon interaction alone led Ganguly[78] to the hypothesis of a substantial effect on λ_{ph} and T_C of the high-frequency optical vibrations of the hydrogen atoms. This study used an approximate formula for T_C that took account of the high-frequency vibrations:

$$T_c = \frac{\omega_{ph}}{1.45} \exp\left\{ -\left[\lambda_{ph}^* + \frac{\lambda_{op}^* - \mu^*}{1 - (\lambda_{op}^* - \mu^*) \ln(\omega_{op}/\omega_{ph})} \right]^{-1} \right\},$$

Here $\lambda_{ph}^* = \lambda_{ph}/(1 + \lambda_{ph})$, $\lambda_{op}^* = \lambda_{op}/(1 + \lambda_{op})$, λ_{ph} is the coupling constant of the electrons with the vibrations of the Pd atoms, λ_{op} is the coupling constant with the optical constants of H,

$$\mu^* = \frac{\mu}{1 + \mu \ln(\varepsilon_F/\omega_{op})},$$

where $\mu \approx 0.1$, ω_{ph} is the Debye frequency of the PdH crystal, and ω_{op} is the frequency of the optical vibrations of the hydrogen atom. Upon assuming that the Debye frequency of PdH does not differ from the same in pure Pd, while the coupling constant of the electrons with the Pd atoms also does not vary upon going to PdH, i.e., $\lambda_{ph} = 0.37$, Ganguly showed that one can explain the experimental value of T_C in PdH by assuming that $\lambda_{op} = 0.15$. According to Ganguly's results, one of the reasons for the anomalous isotope effect in the PdH system is the decrease in the Coulombic pseudopotential μ^* upon replacing hydrogen by deuterium, owing to the decrease in ω_{op} and the corresponding increase in the quantity $(\lambda_{op}^* - \mu^*)$. In Ganguly's opinion, the second reason for the increase in T_C upon replacing H with D, which makes the anomalous isotope effect evident, does not involve directly the change in mass of the isotope, but arises from the change in the force constants of the bonds of the deuterium and palladium atoms. We can conclude from the thermodynamic calculations and the neutron studies that $f_{Pd-H} > f_{Pd-D}$, where the f's are the appropriate force constants. If we take account of the fact that the frequency of the optical vibrations $\omega_{op} \approx \sqrt{f/M}$, we find from the relationship (5.6) that the electron-phonon coupling constant increases with decreasing force constant, and $\lambda_{op}^D > \lambda_{op}^H$.

The qualitative side of Ganguly's study involves esti-

mating the effect of the optical vibrations of the hydrogen atoms on T_C and their contribution to the anomalous isotope effect in the PdH system. It arouses no doubts. This is all the more true, since the other explanation of this effect[79] is simply wrong, being based on attempts to relate the change in the electron-phonon coupling constant of the alloy to the change in mass of one of the components.

As we have noted, a study by one of us[81] has rigorously proved that the change in the electron-phonon coupling constant in the alloy depends only on the change in the force constants, and not at all on the change of mass of the atoms of the components of the alloy. Yet the quantitative calculations of Ganguly seem to us much less convincing. If we use the more exact expression for T_C:

$$T_c = 1.14 \omega_{ph}^{\lambda_{ph}/\lambda} \omega_{op}^{\lambda_{op}/\lambda} \exp\left(-\frac{1+\lambda}{\lambda - \mu^*} \right),$$

where $\lambda = \lambda_{ph} + \lambda_{op}$, and we assume here that $\lambda = 0.7$, as the heat-capacity experiments imply, then the change in μ^* upon replacing H by D evidently cannot yield an appreciable increase in T_C.

The second comment on Ganguly's study was expressed by Hertel,[80] and it involves the considerable elevation in Ganguly's study of the coupling constant with the optical vibrations. The estimates given in[80] on the basis of microscopic calculations show that in any case $\lambda_{op}/\lambda_{ph} < 0.2$.

As we see it, the reason for the anomalous isotope effect in PdH involves not the direct interaction of the conduction electrons with the optical vibrations of hydrogen, but the change in the interatomic spacing in the Pd matrix upon replacing H with D. The x-ray measurements[77] show that the lattice expansion is somewhat greater when D is interstitial. Since increasing pressure decreases T_C in the PdH system,[75,76] a lattice expansion correspondingly elevates T_C. Of course, one cannot explain the overall change in the electron-phonon interaction constant from pure Pd, where $\lambda_{ph} = 0.37$, to PdH, where $\lambda_{ph} = 0.7$, by the mere change in the lattice constant and the concomitant decrease in the characteristic phonon frequencies. We must take into account the fact that PdH differs considerably in its electronic properties from pure Pd. The electronic properties of PdH recall far more those of simple metals of the type of Sn or Pb than the properties of the transition metal Pd. As we know, the overall change in the constant λ_{ph} upon going from Pd to PdH does not involve the slow variation in the parameter η that enters into Eq. (5.5). Most likely, it is due to the substantial change in the scattering processes and the actual increase in the concentration of conduction electrons, which in simple metals increases the electron-phonon coupling constant.[4]

We should note that a change in the nature of the wave functions of the electrons from s to d, while maintaining the total concentration of electrons, usually increases the electron-phonon coupling constant λ_{ph}. In particular, this phenomenon is commonly associated with the appearance of superconductivity in Cs and Ba at high pressures where isomorphous phase transitions occur in these metals that are caused by transition of the valence electrons from the s band to the d band. In this regard, PdH apparently presents a completely opposite example of increase in λ_{ph} upon changing the

nature of the electronic spectrum from strongly-bound d electrons to almost free s electrons. The decrease in the matrix elements of the electron-ion potential that occurs here is apparently compensated by the increase in the total concentration of electrons. A more precise answer to the question of the nature of the increase in the electron-phonon coupling constant in PdH and of the anomalous isotope effect will absolutely require further studies, both theoretical and experimental. In particular, a thorough study of the Knight shift and the hydrogen NMR in the compound PdH would be of great interest in elucidating the coupling force of the conduction electrons with the hydrogen atoms. In closing this section, we note that superconductivity was found quite recently in the hydrides of the alloys Pd—Cu and Pd—Au, with the high practical temperatures $T_c \approx 16.6°$ and $T_c \approx 13.6°K$.[84]

6. CONCLUSION

Usually conclusions are written in order to give the results and to formulate finally the established opinion on certain of the problems treated in the study.

Unfortunately, yet perhaps fortunately, there are not yet many clearly established facts in the problem of the Me—H compounds. It is all the more premature to present results in this problem. Much still remains here to be done, both by the experimentalists and the theoreticians.

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1)Far less attention has been paid to studying the properties of hydrogen incorporated into dielectrics or semiconductors. Perhaps this involves both the lesser practical importance of these compounds and the fact that the solubility of hydrogen in them is less by several orders of magnitude. [3]

2)The problem of diffusion of hydrogen in a crystalline matrix is of considerable interest also in astrophysics. In order to elucidate the final stage of the evolution of stars and to establish the time when the hydrogen is burned up in thermonuclear reactions, it is extremely important to know the diffusion coefficients of hydrogen and its variations as a function of the lattice type in the stellar matter. [12]

3)A more detailed presentation with references to the original experimental studies is found in the short review of Libowitz. [39]

4)A highly interesting possibility of explaining the anomalous isotope effect was proposed recently in [83]. The authors attribute the difference in T_c between PdH and PdD to a difference in the band structure of these compounds, namely, that in PdD a smaller number of electrons from D go to form bonds, than in PdH. Consequently, a somewhat larger number of electrons ≈ 0.05 lies at the Fermi surface. This increases the density of states, and correspondingly also λ in PdD.

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Translated by M. V. King