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The Band Structure of Solid Solutions of Hydrogen Isotopes in Palladium at Low Temperatures

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Abstract—The energy bands of hydrogen isotopes in palladium corresponding to their ground vibrational state were calculated by the variational method using a model metal–hydrogen interaction potential and an extended basis set of harmonic oscillator wave functions. The obtained band width for protons (~6 meV) was indicative of the possibility of hydrogen quantum diffusion at low temperatures. The conclusion was made that tunneling at low temperatures caused by the special features of the anisotropic hydrogen–lattice interaction potential to a considerable extent determines the high mobility of hydrogen in metals.

INTRODUCTION

Hydrogen dissolved in metals has a high mobility at low temperatures, which exceeds the mobility of other intercalation impurities by several orders of magnitude. One of the possible reasons for this is weak interaction between hydrogen and metal lattices, which results in low potential barriers between equilibrium positions. Another reason is the possibility of quantum diffusion (tunneling), which does not require thermal activation of jumps [1]. To understand which of the two reasons predominates, we must study the mechanism of hydrogen–lattice interactions in detail. Solving this problem by quantum-chemical calculations [which lay claim to a high accuracy] and the construction of the corresponding interatomic interaction potentials on their base [while subsequently solving the problem of the motion of the hydrogen atom], although possible in principle, not only involves enormous amounts of computation but also requires solving certain problems fundamental in character. In this work, we make an attempt at answering the question posed above by simplifying the problem conditions, that is, through using several theoretical presumptions and experimental findings for modeling the hydrogen–lattice interaction potential.

PROBLEM STATEMENT

The authors [2] suggested a method for calculating the energy of hydrogen atom vibrations in metal and intermetallic compound crystal lattice interstices based, first, on the expansion of the vibrational wave function of the proton into a series in the eigenfunctions of the three-dimensional harmonic oscillator and, second, on representing the periodic hydrogen–lattice interaction potential in the form

$$U(\mathbf{r}) = \sum_{\mathbf{R}}\sum_{\mathbf{d}_i} A_i \exp\{-\alpha_i(\mathbf{r}-\mathbf{R}-\mathbf{d}_i)^2\}. \qquad (1)$$

Here, **r** is the radius vector of the hydrogen atom, constants A_i and α_i characterize the *i*th metal atom in the unit cell, and the summation is over both all metal lattice vectors **R** and all unit cell basis vectors $\mathbf{d}_i$. For convenience of parametrization, the *A* value was assumed to be constant, and each metal was characterized by a single parameter $\alpha_i = 1/\rho_i^2$, where ρ_i had the physical meaning of the effective metal–hydrogen interaction radius. The vibrational problem was solved by the Ritz variational method [3].

Consider the assumptions made in [2]. First, because the mass of the hydrogen atom is small compared with the mass of an arbitrary *d*- or *f* metal, metallic sublattice vibrations were ignored. The second assumption was that of a strong localization of the wave functions. According to the Bloch theorem, the wave functions of the proton in a periodic lattice potential have the general form

$$\Psi_{n,\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{R}} \psi_n(\mathbf{r}-\mathbf{R})e^{i\mathbf{k}\cdot\mathbf{R}}, \qquad (2)$$

and the energy eigenvalues corresponding to the given quantum state *n* are

$$E_n(\mathbf{k}) = \langle n, 0|\mathbf{H}|n, 0\rangle + \sum_{\mathbf{R}\neq 0}\langle n, 0|\mathbf{H}|n, \mathbf{R}\rangle\cos(\mathbf{k}\cdot\mathbf{R}). \qquad (3)$$

Here, **k** is the wave vector, $|n, \mathbf{R}\rangle \equiv \psi_n(\mathbf{r}-\mathbf{R})$ is the Wannier function, and **H** is the one-particle Hamiltonian [4]. The suggestion that the Wannier functions are localized is equivalent to the assumption that the first term of sum (3) makes the major contribution to the energy, there is no dependence on the wave vector, and the sum over $\mathbf{R} \neq 0$ in (3) can be ignored. The third assumption used in [2] was the selection of the simplest basis set for representing the Wannier functions, namely,

$$\psi_n(\mathbf{r}) = \chi_{n_x}(x, \omega_x)\chi_{n_y}(y, \omega_y)\chi_{n_z}(z, \omega_z), \qquad (4)$$

where $\chi_{n_x}(x, \omega_x)$ etc. are the eigenfunctions of one-dimensional harmonic oscillators with frequencies ω, which serve as variational parameters, and the n's are the quantum numbers.

The approximation of localized wave functions used in [2] ceases to be valid for both excited states with high quantum numbers and the ground state at low hydrogen atom vibrational frequencies ($\hbar\omega_H < 100$ meV), that is, when the overlap of the Wannier functions centered on neighboring hydrogen sublattice sites is substantial. In addition, if the shape of the potential well for hydrogen in an interstice is far from parabolic, the use of the primitive basis set (4) also leads to substantial errors. These limitations are most pronounced for palladium hydride PdH_x: according to the neutron study performed in [5], hydrogen atom vibrations at a low frequency ($\hbar\omega_H$ of 60 to 70 meV depending on the composition of the hydride) are strongly anharmonic. Nevertheless, a very small width of the proton energy band was obtained in [1]. In view of these results, the question of what is the reason for the high diffusion mobility of hydrogen in Pd is answered in this work by modifying the method suggested in [2] and performing calculations of the ground vibrational state band, using as before the fairly well grounded approximation of a static sublattice of metal atoms.

BASIS EXTENSION AND CALCULATION OF MATRIX ELEMENTS

The basis set of trial wave functions can be extended by applying a technique widely used in quantum chemistry. Let us write the Wannier function for the ground vibrational state $\psi_0(\mathbf{r})$ in the form of the linear combination

$$|0, 0\rangle = \sum_{n_x=0}^{N_x}\sum_{n_y=0}^{N_y}\sum_{n_z=0}^{N_z} a_{n_x}a_{n_y}a_{n_z}\chi_{n_x}(x, \omega_x) \times\chi_{n_y}(y, \omega_y)\chi_{n_z}(z, \omega_z), \qquad (5)$$

where a_{n_x}, a_{n_y}, and a_{n_z} are the coefficients of the expansion in orthonormalized eigenfunctions of one-dimensional harmonic oscillators. The dimension of the resulting basis set is $(N_x + 1)(N_y + 1)(N_z + 1)$. The parameters for the search for the minimum of the Hamiltonian matrix element (3) are now not only three frequencies but also the expansion coefficients. In other words, the function of the ground vibrational state includes the functions of excited harmonic oscillator states that have larger localization radii and, therefore, make larger contributions to the second term of (3). It follows that anharmonic vibrations and the extension of the basis set generally lead to the necessity of calculating the tunnel matrix elements $\langle 0, 0|\mathbf{H}|0, \mathbf{R}\rangle$ when applying the variational procedure with the extended basis set.

To calculate the corresponding integrals, we will use the following $\mathbf{H} = \mathbf{T} + \mathbf{U}$ Hamiltonian property: the kinetic energy operator is the sum

$$\mathbf{T} = \mathbf{T}_x + \mathbf{T}_y + \mathbf{T}_z \qquad (6)$$

and the potential energy operator (1) is the sum of the products

$$\mathbf{U} = \sum_{\mathbf{N}} U_{\mathbf{N}}(x)U_{\mathbf{N}}(y)U_{\mathbf{N}}(z) \qquad (7)$$

(the summation over $\mathbf{N}$ is the summation over all sites of all metallic matrix sublattices, that is, over $\mathbf{R}$ and $\mathbf{d}_i$). Such a form of the Hamiltonian allows us to use Cartesian coordinates and calculate one-dimensional integrals only. Indeed, using the normalization conditions[1]

$$\sum_{n_x=0} a_{n_x}^2 = \sum_{n_y=0} a_{n_y}^2 = \sum_{n_z=0} a_{n_z}^2 = 1 \qquad (8)$$

and the orthogonality property of the eigenfunctions of the harmonic oscillator

$$\langle\chi_{n_x}(x, \omega_x)|\chi_{n'_x}(x, \omega_x)\rangle = \delta_{n_x n'_x} \qquad (9)$$

($\delta_{n_x n'_x}$ is the Kronecker delta symbol), it is easy to show by direct calculation that the local matrix elements $\langle 0,0|\ldots|0,0\rangle$ of the kinetic and potential energy operators for the ground state take the form

$$\langle 0, 0|\mathbf{T}|0, 0\rangle = \sum_{j=x,y,z}\sum_{n_j}\sum_{n'_j} a_{n_j}a_{n'_j}\langle\chi_{n_j}|\mathbf{T}_j|\chi_{n'_j}\rangle, \qquad (10)$$

$$\langle 0, 0|\mathbf{U}|0, 0\rangle = \sum_{\mathbf{N}}\prod_{j=x,y,z}\sum_{n_j}\sum_{n'_j} a_{n_j}a_{n'_j}\langle\chi_{n_j}|U_{\mathbf{N}}(j)|\chi_{n'_j}\rangle \qquad (11)$$

(henceforth, the arguments and parameters of the harmonic oscillator functions will be omitted). For brevity, we will use the notation

$$\langle\chi_{n_j}|\mathbf{T}_j|\chi_{n'_j}\rangle = t(n_j, n'_j), \qquad (12)$$

$$\langle\chi_{n_j}|U_{\mathbf{N}}(j)|\chi_{n'_j}\rangle = u(\mathbf{N}, n_j, n'_j). \qquad (13)$$

Integrals (12) and (13) are calculated analytically (see [1, 6, 7]),

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[1] The only normalization condition for wave function (5) is $\sum_{n_x}\sum_{n_y}\sum_{n_z} a_{n_x}^2 a_{n_y}^2 a_{n_z}^2 = 1$. However, for cubic symmetry, which is considered in this work, degeneracy leads to conditions (8).

$$t(n_j, n'_j) = \frac{w_j}{4}\{\delta(n_j, n'_j)(2n_j + 1) - \delta(n_j, n'_j - 2)[(n_j + 1)(n_j + 2)]^{1/2} - \delta(n_j, n'_j + 2)[n_j(n_j + 1)]^{1/2}\}, \tag{14}$$

$$u(\mathbf{N}, n_j, n'_j) = A^{1/3}\left(\frac{w_j}{w_j + \alpha_{\mathbf{N}}}\right)^{1/2}\exp\left(-\frac{w_j\alpha_{\mathbf{N}}}{w_j + \alpha_{\mathbf{N}}}N_j^2\right) \times \sum_{r=0}^{\min(n_j, n'_j)}\left[\frac{n_j!}{r![(n_j - r)!]^2}\frac{n'_j!}{r![(n'_j - r)!]^2}\right]^{1/2} \times \left[\frac{\alpha_{\mathbf{N}}}{2(w_j + \alpha_{\mathbf{N}})}\right]^{\frac{n_j + n'_j}{2} - r} H_{n_j + n'_j - 2r}\left(\left(\frac{w_j\alpha_{\mathbf{N}}}{w_j + \alpha_{\mathbf{N}}}\right)^{1/2}N_j\right), \tag{15}$$

where $w_j = \omega_j M/\hbar$ (M is the mass of the hydrogen atom), $H_n(\ldots)$ are the Hermitian polynomials, $\mathbf{N} = (N_x, N_y, N_z)$ is the radius vector of the metal atom is position in the frame of reference where the origin is at the equilibrium position of the hydrogen atom, and $\alpha_{\mathbf{N}}$ is the corresponding parameter of the metal–hydrogen interaction potential.

Let us turn to the tunnel matrix elements. The $\langle 0, 0|\mathbf{T}|0, \mathbf{R}\rangle$ term will be calculated using the property of the completeness of the basis set of the eigenfunctions of the harmonic oscillator,

$$\sum_m |\chi_m, \mathbf{R}\rangle\langle\chi_m, \mathbf{R}| = 1. \tag{16}$$

We then have

$$\langle\chi_{n_j}, 0|\mathbf{T}_j|\chi_{n'_j}, \mathbf{R}\rangle = \sum_m \langle\chi_{n_j}, 0|\chi_m, \mathbf{R}\rangle\langle\chi_m, \mathbf{R}|\mathbf{T}_j|\chi_{n'_j}, \mathbf{R}\rangle = \sum_m S_{n_j, m}(R_j)t(m, n'_j), \tag{17}$$

where the overlap integral is [7]

$$S_{n, m}(R_j) = \exp(-\rho_j^2)\left(\frac{2^n m!}{2^m n!}\right)^{1/2} L_m^{n-m}(2\rho_j^2)\rho_j^{n-m}. \tag{18}$$

Here, $\rho_j = R_j w_j^{1/2}/2$, $L_m^{n-m}(\ldots)$ are the generalized Laguerre polynomials, and $n \geq m$ (because the overlap integrals are invariant with respect to permutations of the indices, this condition can always be satisfied). By virtue of (14), the sum over m in (17) contains no more than three nonzero terms. We then have for the tunnel matrix elements of kinetic energy components

$$\langle 0, 0|\mathbf{T}_x|0, \mathbf{R}\rangle = \left(\sum_{n_x}\sum_{n'_x} a_{n_x}a_{n'_x}\sum_m S_{n_x, m}(\rho_x)t(m, n'_x)\right) \times \left(\sum_{n_y}\sum_{n'_y} a_{n_y}a_{n'_y}S_{n_y, n'_y}(\rho_y)\right)\left(\sum_{n_z}\sum_{n'_z} a_{n_z}a_{n'_z}S_{n_z, n'_z}(\rho_z)\right) \tag{19}$$

(similar equations can be written for $\mathbf{T}_y$ and $\mathbf{T}_x$). The total tunnel matrix element of the kinetic energy operator is the sum of the coordinate components (19).

As in the derivation of (15), $\langle 0, 0|\mathbf{U}|0, \mathbf{R}\rangle$ will be calculated taking into account that the product of two normal distribution functions is itself a normal distribution function. We will also use the theorem for the summation of Hermitian polynomial arguments,

$$H_n(x + y) = 2^{-n/2}\sum_{k=0}^{n}\binom{n}{k}H_{n-k}(x\sqrt{2})H_k(y\sqrt{2}),$$

where $\binom{n}{k}$ are the binomial coefficients. This allows us to go from the integrals with wave functions centered at various crystal space points to the integrals with functions centered at one point. Fairly simple calculations show that the matrix elements of the coordinate components of the potential energy operator related to the metal atom in site $\mathbf{N}$ are

$$\langle n_j, 0|U_{\mathbf{N}}(j)|m_j, R_j\rangle = \Delta u_j(\mathbf{N}, n, m, R_j) = \frac{A^{1/3}}{2^n 2^m (n!m!)^{1/2}}\left(\frac{w_j}{w_j + \alpha_{\mathbf{N}}}\right)^{1/2} \times \exp\left[-\frac{w_j R_j^2}{4}\right]\exp\left[-\frac{w_j\alpha_{\mathbf{N}}}{w_j + \alpha_{\mathbf{N}}}\left(N - \frac{R_j}{2}\right)^2\right] \times \sum_{k=0}^{n}\sum_{l=0}^{m}\binom{n}{k}\binom{m}{l}H_k(0)H_l[\pm R_j(w_j + \alpha_{\mathbf{N}})^{1/2}] \times \sum_{r=0}^{\min(n-k, m-l)} 2^r r!\binom{n-k}{r}\binom{m-l}{r}\left[\frac{\alpha_{\mathbf{N}} - w_j}{\alpha_{\mathbf{N}} + w_j}\right]^{\frac{n+m-k-l}{2} - r} \times H_{n+m-k-l-2r}\left[\left(\frac{2w_j}{\alpha_{\mathbf{N}}^2 - w_j^2}\right)^{1/2}\left(\alpha_{\mathbf{N}}N + w_j\frac{R_j}{2}\right)\right], \tag{20}$$

where the upper and lower signs of the Hermitian polynomial argument correspond to $w_j > \alpha_{\mathbf{N}}$ and $w_j < \alpha_{\mathbf{N}}$, respectively. Further, constructing the products of the coordinate components of $\mathbf{U}$ and summing over the metal lattice sites, we obtain the tunnel matrix element of the potential energy operator

$$\langle 0, 0|\mathbf{U}|0, \mathbf{R}\rangle = \sum_{\mathbf{N}} \prod_{j = x, y, z} \sum_{n_j} \sum_{n'_j} a_{n_j} a_{n'_j} \Delta u_j(\mathbf{N}, n_j, n'_j, R_j). \tag{21}$$

To summarize, we obtained equations for all the matrix elements of a one-particle Hamiltonian in an extended basis set of the wave functions of the harmonic oscillator. This allows us to directly turn to seeking a minimum of (3) at $n = 0$ (the ground state). The optimization can be performed by one of the numerical methods; in this work, we use the direct search method.

CALCULATING THE ENERGY OF THE GROUND STATE OF HYDROGEN ISOTOPES IN PALLADIUM

Consider the results of our calculations performed for hydrogen isotopes (protium, deuterium, and tritium) in the palladium lattice. The metal has a face-centered cubic (FCC) structure, and the dissolved hydrogen is localized in octahedral interstices. The theory described above ignores H–H interaction, and the calculations were therefore only performed for the α phases, that is, for solid solutions with low concentrations of interstitial hydrogen. The crystal lattice constant of α-PdH_x is $a = 3.8902$ Å [8]; that is, it virtually coincides with the lattice constant of the pure metal. The hydrogen–lattice interaction potential parameters (A_{Pd} and α_{Pd}) were selected to reproduce the ground state energies of protium and deuterium at $\mathbf{k} = 0$. These energies were estimated based on the results obtained in [5], where the anharmonic corrections were taken into account by expanding the potential into powers of atomic displacements from the equilibrium positions while retaining the first nonvanishing terms,

$$\begin{aligned} V(x, y, z) &= C_2(x^2 + y^2 + z^2) + C_4(x^4 + y^4 + z^4) \\ &\quad + C_{22}(x^2y^2 + x^2z^2 + y^2z^2). \end{aligned} \tag{22}$$

The coefficients of this expansion, $C_2\hbar/\omega m = 50 \pm 0.5$ meV, $C_4(\hbar/\omega m)^2 = 6.3 \pm 1$ meV, and $C_{22} \approx 0$ ($\omega = (2C_2/m)^{1/2}$ is the harmonic frequency), were determined from the inelastic neutron scattering spectra of α-PdH_x at the level of first-order stationary perturbation theory. It can be shown that first-order perturbation theory gives the energy of the ground state in the form

$$E = \frac{3}{2}\hbar\omega + \left(C_4 + \frac{C_{22}}{3}\right)\left(\frac{3\hbar}{2\omega m}\right)^2,$$

whence it follows that $E_{\mathbf{H}} = 89 \pm 1.5$ meV for protium and $E_D = 60 \pm 1$ meV for deuterium. The calculations show that the closest agreement with these estimates is attained for $A_{Pd} = 4.4$ eV and $\rho_{Pd} = 0.6$ Å.

The profiles of the corresponding periodic potential in various directions are shown in Fig. 1. Note that the potential grows monotonically in the [100] direction within the unit cell as the distance from the cell center increases, because metal atoms that occupy cube face centers lie along the path of hydrogen in this direction. The potential oscillates with the amplitude ~45 meV in the [110] direction, and this is one of the most probable directions of hydrogen diffusion into a neighboring octahedral interstice. As concerns the [111] direction, it contains additional local minima corresponding to tetrahedral interstices. The localization of hydrogen in these interstices is, although possible, unfavorable energetically: evaluations show that the energy of the ground state in a tetrahedral interstice is 50–60 meV higher, and that the hydrogen atom displays an affinity for to octahedral wells. It follows that, for instance, unlike potential (22), which is only weakly anisotropic, potential (1) much more correctly reproduces the special features of the interstitial space of the crystal lattice.

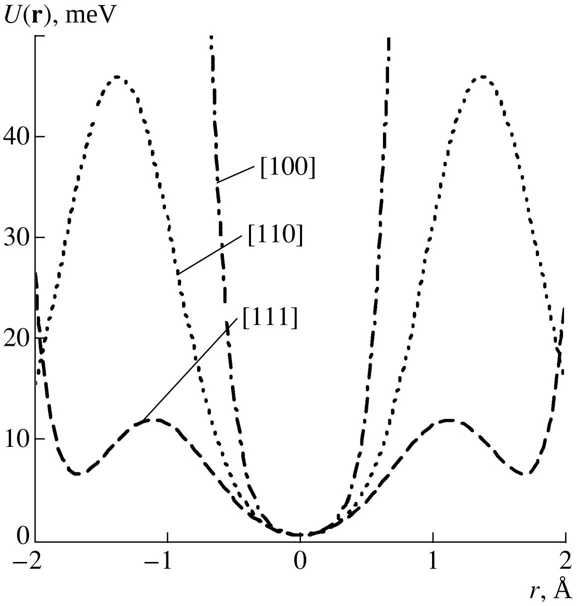

Fig. 1. Profiles of the periodic hydrogen–lattice interaction potential for α-PdH_x in various crystallographic directions.

The calculations show that the necessary number of independent basis functions in expansion (5) reduces to three; these are the eigenfunctions of the ground and second and fourth excited states of the one-dimensional harmonic oscillator. The inclusion of functions with even larger quantum numbers does not cause substantial changes in the results, since the correction to the energy is less than 1 meV. The functions with odd quantum numbers, which are odd with respect to the change in the sign of the argument, cannot be present in the expansion of the ground state function.[2]

The tunnel matrix elements rapidly decrease as the distance increases, and it is therefore sufficient to perform the summation in (3) over the 12 nearest neigh-

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[2] With real coefficients.

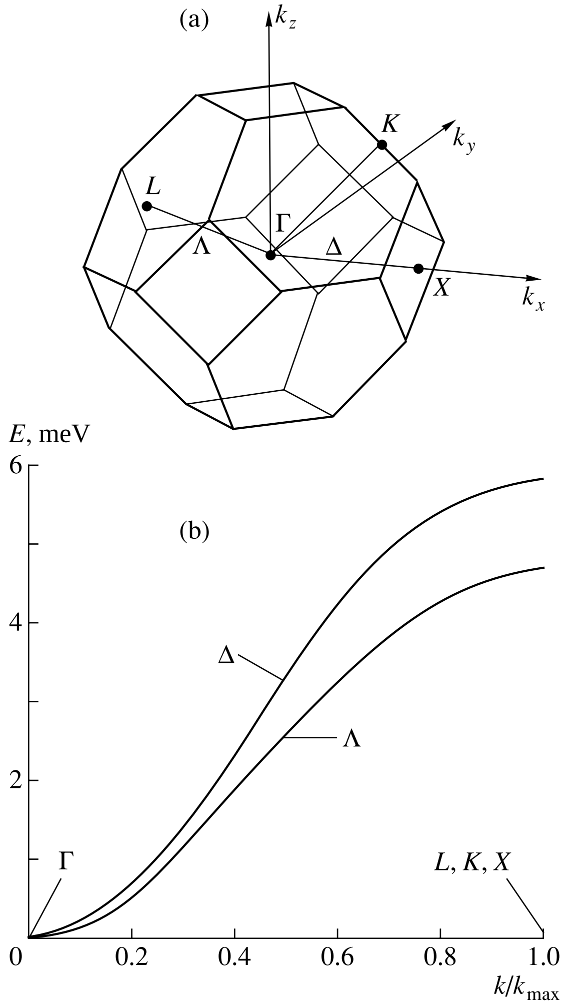

Fig. 2. First Brillouin zone of the FCC lattice; dispersion curves for protons in palladium.

bors in the FCC lattice, for which the tunnel matrix elements are equal. We then have

$$E_0(\mathbf{k}) = \langle 0, 0|\mathbf{H}|0, 0\rangle$$
$$+ \langle 0, 0|\mathbf{H}|0, a/\sqrt{2}\rangle \sum_{\mathbf{R}} \cos(\mathbf{k}\cdot\mathbf{R}) = I + JF(\mathbf{k}), \quad (23)$$

where $\mathbf{R} = a/\sqrt{2}\,(\pm 1, \pm 1, 0)$ with all coordinate permutations in parentheses, and I and J are the local and tunnel matrix elements of the Hamiltonian.

The first Brillouin zone of the FCC lattice and the calculated dispersion curves in the directions ΓL and ΓX are shown in Fig. 2. Table 1 contains the calculation results for several points of the wave vector space. These data show that the ground vibrational state of the hydrogen atom in the palladium lattice forms an energy band ~6 meV wide. This effect is caused by a substantial overlap of the Wannier functions $|0, 0\rangle$ and $|0, a/\sqrt{2}\rangle$. The proton density profiles at low temperatures (the square of the wave function of the ground state) in the crystallographic directions [100], [110], and [111] are shown in Fig. 3. As expected, the density distribution within the octahedron is no longer spherically symmetrical because of the nonzero a_2 and a_4 values. The largest density shift is in the [111] direction, that is, toward the tetrahedral interstice.

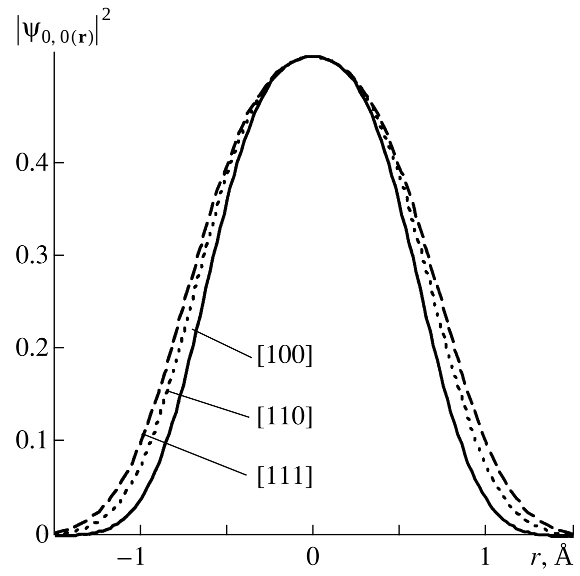

Fig. 3. Proton density profiles in α-PdH$_x$ for $T \to 0$.

The wave function parameters of the ground state and the Hamiltonian matrix elements for the three hydrogen isotopes are listed in Table 2. Note that, in spite of a decrease in the specific weight of the basis functions with high quantum numbers, vibrational motions are still substantially anharmonic for heavy tritium as well as for light protium. At the same time, the tunnel matrix element decreases in magnitude, by an order of magnitude for deuterium and two orders of magnitude for tritium. As the tunnel matrix elements determine the width of the energy band, the behavior of the heavy hydrogen isotopes in palladium at low temperatures can be characterized with high accuracy as local vibrations, whereas the band structure effects, including quantum diffusion (incoherent and, at the lowest temperatures, coherent tunneling), should be fairly pronounced for protium [1]. As the quantum diffusion coefficient D is proportional to J^2 (the Fermi Golden Rule), the kinetic isotope effects D_H/D_D and D_H/D_T should be on the order of 10^2 and 10^4, respectively, at low temperatures.

It should be specially noted that the inverse kinetic isotope effect for palladium (a higher diffusion coefficient for deuterium than for protium) at 223–373 K and higher temperatures [9] is not at variance with the above conclusion. The apparent contradiction can be explained taking into account that 300 K is a high temperature for hydrogen isotopes in palladium, and the

Table 1. Characteristics of the ground vibrational state of hydrogen in palladium

k	$F(\mathbf{k})$	$\hbar\omega_H$, meV	a_2	a_4	$E_0(\mathbf{k})$, meV
Γ	12	94	0.138	–0.060	88.8
L	0	106	0.129	–0.048	93.5
K	–3.657	109	0.129	–0.047	94.5
X	–4	110	0.129	–0.046	94.6

Table 2. Wave function parameters and Hamiltonian matrix elements at **k** = (0, 0, 0)

Isotope	$\hbar\omega_H$, meV	a_2	$-a_4$	I, meV	$-J$, meV
H	94	0.138	0.060	94.8	0.5
D	66	0.130	0.042	59.6	0.04
T	52	0.127	0.042	45.8	0.004

population of excited states at this temperature is substantial. Under these conditions, the mechanism of diffusion changes, and strongly excited, so-called *above-barrier* states become responsible for the transport of hydrogen. This follows from a fairly large experimental activation energy of diffusion (~230 meV).

An analysis of the model of hydrogen isotope diffusion in metals at high temperatures shows that the transition of deuterium into the above-barrier state can in principle be easier compared with protium [10]. The explanation given in [10] is based on the model of "multiple jumps" and is as follows: For light interstitial atoms, energy loss is a slow process, and the mean kinetic energy is comparable with the height of potential barriers. According to the model of multiple jumps, a hydrogen atom in the above-barrier state (whose energy is higher then the potential barrier height) has three translational degrees of freedom and can make several elementary jumps before being localized in some interstice that is not necessarily nearest to the initial one. The diffusion coefficient is then given by the formula $D = D_{\mathrm{arr}}\langle l\rangle$, where D_{arr} is the usual activation (Arrhenius) diffusion coefficient and $\langle l\rangle$ is the mean number of jumps.

According to the simplest assumption on the energy spectra of above- and sub-barrier particles, above-barrier atoms move quasi-freely in a three-dimensional potential well of size $L \times d^2$, whereas three independent harmonic oscillators of frequency ω equal to the local level frequency correspond to each sub-barrier particle. The calculations given in [10] yield

$$D = \frac{\lambda}{6}\left(\frac{kT}{2\pi m}\right)^{1/2}\exp\left\{-\frac{1}{kT}\left[\Delta u - \frac{3}{2}\left(\hbar\omega - \frac{\pi^2\hbar^2}{md^2}\right)\right]\right\}.$$

This equation has the Arrhenius form $D = D_0\exp(-Q/kT)$. The activation energy in it, however, does not coincide with Δu but also depends on the mass of the particle m and increases as m decreases. For hydrogen and deuterium with $m_D = 2m_H$ and $\omega_D = \omega_H/\sqrt{2}$, the diffusion isotope effect takes the form

$$\frac{D_H}{D_D} = \sqrt{2}\exp\left\{-\frac{3\hbar}{2kT}\left[\frac{\pi^2\hbar}{2m_H d^2} - \left(1 - \frac{1}{\sqrt{2}}\right)\right]\omega_H\right\}, \quad (24)$$

which shows that the D_H/D_D ratio becomes smaller than one at fairly low temperatures; that is, the rate of deuterium diffusion is higher than that of hydrogen diffusion.

It should be stressed that the inverse isotope effect in the model of multiple jumps is a consequence of the discreteness of the energy spectrum of above-barrier particles; their energy is proportional to $\sim 1/m$, whereas the energy of vibrations of sub-barrier atoms is proportional to $\sim 1/m^{1/2}$. For this reason, the transition of deuterium to the above-barrier state is facilitated compared with hydrogen (the corresponding activation energy is lower).

Equation (24) shows that the inverse isotope effect only manifests itself at a certain temperature, and that the D_H/D_D value tends to decrease further below this temperature; that is, the inverse diffusion isotope effect becomes stronger. It should, however, be borne in mind that the diffusion coefficients themselves sharply decrease as the temperature drops. For this reason, a further decrease in temperature, when, according to (24), the inverse isotope effect should increase, results in that diffusion by multiple jumps (and all kinds of activation diffusion) stops. Under these conditions, a determining role is played by other diffusion mechanisms, primarily the tunnel mechanism that is considered in this work.

To summarize, the large width of the energy band corresponding to the ground state of the proton in the palladium lattice is capable of switching on the quantum diffusion mechanism at low temperatures [1]. The reason for the band behavior of hydrogen is the anisotropic hydrogen–lattice interaction potential characterized by low barriers in several crystallographic directions. We wish to stress that the low height of the barriers by no means results in a low activation energy of the above-barrier particle motions characteristic of high-temperature diffusion (see above). To completely describe the diffusion behavior of hydrogen isotopes in metals over a wide temperature range, we must perform similar calculations for the bands corresponding to excited states.

In conclusion, let us note the following: In [1], anomalously low values were obtained for the tunnel matrix elements of hydrogen isotopes in palladium (by several orders of magnitude lower than for such FCC metals as vanadium and niobium). The J values were estimated in a fairly crude approximation, that is, for one-dimensional motion in a sine-shaped periodic potential, which can hardly be considered correct for describing the interaction of hydrogen with the lattice. The calculation results obtained in this work are evidence to the contrary, namely, the J values for all metals should be comparable in magnitude. It follows that all special features of the band motion of hydrogen considered in [1] are also applicable to FCC metals.

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