

STRUCTURE OF MATTER  
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## A Superposition Model of Metal–Hydrogen Interaction in Intermetallic Compound Hydrides

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**Abstract**—A model in which the metal–hydrogen interatomic interaction potential in the solid phase is described by the Gauss normal distribution function was suggested to explain and predict equilibrium isotopic effects in hydrogen–intermetallic compound hydride systems. The quantum mechanical variational principle was used to parametrize the Gauss potentials for Group IV and V transition metals in the approximation of local modes for hydrogen atom vibrations. These potentials were transferred to intermetallic compounds with Laves phase structures. Calculations performed in a similar way gave the temperature dependences of separation coefficients for hydrogen isotopes that were close to experimental for both stoichiometric and superstoichiometric forms of  $AB_2$  compounds. These results prove the applicability of the representation of the potential for hydrogen in intermetallic compounds as a superposition of the potentials of separate metal atoms, which allows simple criteria for the search for systems with the largest isotopic effect to be formulated and substantiated.

### INTRODUCTION

Transition metal and intermetallic compound hydrides exhibit substantial isotopic effects, which, under equilibrium conditions, result in the concentration of the heavy hydrogen isotope in the solid hydride phase or the gas phase brought in contact with the solid. In practice, this property of hydrides can be used in schemes for separating hydrogen isotopes on an industrial scale [1]. The vast diversity of intermetallic compounds absorbing substantial amounts of hydrogen opens up a possibility for the search for some optimal hydride system (systems). Naturally, there exists a set of optimization parameters, a complete and thorough study of which is a complex physicochemical problem. In this work, our goal was to consider one of the criteria for the search for promising (for separation of hydrogen isotopes) intermetallic compounds, namely, the equilibrium isotopic effect proper, which is numerically characterized by the separation coefficient

$$\alpha = x(1-y)/y(1-x), \quad (1)$$

where  $x$  and  $y$  are the concentrations of the heavy isotope in the solid (hydride) and gas phases, respectively.

Abundant data have been collected [2] on separation coefficients for both pure metals (Pd, V, Ti, Zr, U, etc.) and intermetallic compounds of various structures. The latter include compounds of the TiFe (AB), TiCr<sub>2</sub> (AB<sub>2</sub>), and LaNi<sub>5</sub> (AB<sub>5</sub>) types. Nevertheless, the number of compounds studied thus far amounts to dozens, whereas the number of intermetallic compounds is virtually infinite, because of the possibility of continuously varying their composition provided by the formation of solid solutions and the superstoichiometry phe-

nomenon. Clearly, experimental studies of isotopic equilibria for infinitely many systems with intermetallic compounds require an infinitely long time. On the other hand, a fairly simple, but reliable, theoretical model describing thermodynamic isotopic effects for hydrogen in systems with solid hydride phases might be very useful, both for estimating whole classes of intermetallic compounds as systems for separating hydrogen isotopes, and for studying the behavior of a selected system in more detail.

Such a model should satisfy the sole and, at the same time, severe requirement, namely, it should be based on *some parameters characterizing the nature of the metals constituting the intermetallic compound under consideration*. As the thermodynamic isotopic effect is determined by the energy spectrum of the vibrational states of hydrogen in a metallic matrix [2], these parameters should describe various atom–atom interactions in the hydride phase, first and foremost, metal–hydrogen interactions

$$U_{\text{Me-H}} = U_{\text{Me-H}}(r_{\text{Me-H}}, \{p_i\}_{\text{Me}}), \quad (2)$$

where  $r_{\text{Me-H}}$  is the metal–hydrogen internuclear distance, and  $\{p_i\}_{\text{Me}}$  is a set of parameters characterizing the metal. From this point of view, the model of the Einstein three-dimensional harmonic oscillator, which most often correctly describes the temperature dependence of separation coefficients, is by itself insufficient for solving the problem. Indeed, hydrogen atom vibrations in such a model are, in essence, empirical in character being quantitatively unrelated to the nature and the structure of the metallic matrix. These relations can only be established by correctly selecting metal–hydrogen interaction potential (2). The vibrational problem

can then be solved by expanding this potential in powers of hydrogen displacements in the vicinity of its equilibrium position followed by calculating the natural frequencies of the oscillator in the harmonic approximation. Stationary perturbation theory can be applied to find necessary anharmonic corrections. Nevertheless, it appears that we cannot *a priori* decide at what term this perturbation series should be truncated, and each particular case requires serious additional analysis. For this reason, we used a somewhat different approach based on selecting a fairly convenient and flexible potential and applying the variational technique [3].

### A VARIATIONAL THEORY OF LOCAL HYDROGEN ATOM VIBRATIONS IN A PERIODIC GAUSS POTENTIAL

Consider a hydrogen atom in a crystal lattice formed by metal atoms or, in an intermetallic compound, atoms of several metals. The mass of the hydrogen atom is small in comparison with the mass of any *d*- or *f*-metal; lattice vibrations can therefore be ignored, and the lattice can be considered static. According to the Bloch scheme [4], the wave functions of a proton in the periodic potential of the lattice have the general form

$$\Psi_{n,\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{R}} \psi_n(\mathbf{r} - \mathbf{R}) e^{i\mathbf{k} \cdot \mathbf{R}}, \quad (3)$$

where index *n* plays the role of a set of quantum numbers (1*s*, 2*s*, 2*p*, etc.),  $\mathbf{k}$  is the wave vector, and  $\mathbf{R}$  is the crystal lattice vector. As the summation in (3) is over all lattice vectors, eigenenergies  $E_n(\mathbf{k})$  are given by

$$E_n(\mathbf{k}) = \sum_{\mathbf{R}} \langle n, 0 | H | n, \mathbf{R} \rangle e^{i\mathbf{k} \cdot \mathbf{R}}, \quad (4)$$

where the notation  $|n, \mathbf{R}\rangle = \psi_n(\mathbf{r} - \mathbf{R})$  is used, and *H* is the one-particle Hamiltonian. Equation (4) can be rewritten as

$$E_n(\mathbf{k}) = \langle n, 0 | H | n, 0 \rangle + \sum_{\mathbf{R} \neq 0} \langle n, 0 | H | n, \mathbf{R} \rangle \cos \mathbf{k} \cdot \mathbf{R}, \quad (5)$$

where the first term makes the major contribution to the energy if the  $|n, \mathbf{R}\rangle$  functions are well localized; that is, the  $\langle n, 0 | n, \mathbf{R} \rangle$  integral virtually equals zero.

Clearly, the localization condition is satisfied. It follows from the inelastic neutron scattering spectra of hydrides of many metals that the energies of optical vibrations of protium in tetrahedral interstices are, as a rule, of 100–150 meV [5, 6], which corresponds to the radius of localization of the wave function of the ground vibrational state (*n* = 1*s*) equal to 0.3–0.25 Å. Because distances between neighboring interstices are of 1 Å or larger, hydrogen atoms prove to be “bound” to the corresponding interstices of the metallic matrix. As a result, energy values cease to depend on the wave vector,

$$E_n = \langle n, 0 | H | n, 0 \rangle \equiv \langle n | H | n \rangle. \quad (6)$$

Note that the approximation of local modes is inapplicable to states with high quantum numbers *n* and cannot be used if the dynamics of the metallic lattice is taken into account, or hydrogen atoms are involved in substantial interactions with each other. At temperatures of the order of 373 K and below, the population of excited states with high energies is, however, negligibly small. For this reason, we will only consider the lowest (that is, well localized) levels. Next, because of the small mass of hydrogen, taking into account vibrations of heavy metal atoms, can only cause an insignificant broadening of optical levels. Lastly, it appears that H–H interactions should be explicitly included only in consideration of hydrides of palladium and some palladium-based alloys whose optical phonon branches are characterized by strong dispersion [5, 6].

The next step toward model construction requires selecting an H–Me periodic potential created by matrix atoms. It can be assumed that interaction of some metal atom *i* with hydrogen has the form of the Gauss normal distribution function

$$u_i(r) = A_i \exp(-\alpha_i r^2), \quad (7)$$

where the  $A_i$  and  $\alpha_i$  constants characterize the nature of the metal, and *r* is the metal–hydrogen internuclear distance. The pair potential in such a form (further referred to as the Gauss potential) was selected from the following considerations. First, the Gauss function very rapidly decreases as distance increases, which makes it possible to take into account only few metal atoms constituting the nearest environment of hydrogen. (In this work, the summation of the potential was conducted over 27 unit cells of the metallic matrix in all calculations; this number proved to be more than sufficient.) Secondly, the factorization of (7)

$$u_i(r) = A_i \exp(-\alpha_i x^2) \exp(-\alpha_i y^2) \exp(-\alpha_i z^2) \quad (8)$$

facilitates calculations in the Cartesian coordinate system directly related to the crystal lattice. Thirdly, for harmonic oscillator wave functions,  $\langle n | u_i | n \rangle$ -type integrals are calculated analytically, which also substantially decreases the amount of necessary calculations.

The property of the Gauss potential to take on a finite value at *r* = 0 (where the real potential should tend to infinity) by no means distorts the physical picture. As mentioned, the radius of localization of the wave functions describing several lowest vibrational states is much smaller than the equilibrium metal–hydrogen distance; for this reason, in calculations of the corresponding potential energy matrix elements, the finite character of  $u_i(0)$  cannot lead to a serious error or confusion.

Lastly, note that the use of a linear combination of Gauss functions as an approximation to the real metal–hydrogen potential (if such a potential can be obtained in quantum-chemical or other calculations) does not introduce difficulties of a fundamental character.

Prior to writing down the complete periodic potentials and performing calculations, consider one more characteristic of the  $u_i(r)$  function. According to (7), such an atom-atom potential is characterized by two independent parameters for each metal. To maximally simplify the model, it can be assumed that  $A_i$  is the same for all metals; the nature of the metal is then characterized by a single parameter, which can be written as  $\alpha_i = 1/\rho_i^2$ . The  $\rho_i$  value has the dimension of length and, therefore, plays the role of the effective radius of the metal atom.

According to the aforesaid, the total periodic potential of a metallic matrix for a hydrogen atom has the form

$$U(\mathbf{r}) = A \sum_{\mathbf{R}} \sum_i \exp\{-\alpha_i(\mathbf{r} - \mathbf{R} - \mathbf{d}_i)^2\}, \quad (9)$$

where the summation is over all crystal lattice vectors and all unit cell basis atoms, and  $\mathbf{d}_i$  is the basis vector for the  $i$ th metal atom in the unit cell.

Solutions to the Schrödinger equation with the Hamiltonian

$$H = \mathbf{P}^2/2M + U(\mathbf{r}), \quad (10)$$

where  $\mathbf{P}$  is the momentum operator, and  $M$  is the mass of the hydrogen atom, will be sought with the use of the variational technique for the basis set of the wave functions of the three-dimensional harmonic oscillator [3]

$$\begin{aligned} & \chi(\mathbf{r}, \omega_x, \omega_y, \omega_z, n) \\ &= \chi_x(x, \omega_x, n_x) \chi_y(y, \omega_y, n_y) \chi_z(z, \omega_z, n_z). \end{aligned} \quad (11)$$

The  $\chi_j(j, \omega_j, n_j)$  functions, where  $j = x, y, z$ , are the eigenfunctions of one-dimensional harmonic oscillators with frequencies  $\omega_j$ , and  $n_j = 0, 1, 2, \dots$  are the corresponding quantum numbers. Let us write the true wave functions of our system  $\psi_m(\mathbf{r})$  in the form of linear combinations of the harmonic oscillator functions

$$\psi_m(\mathbf{r}) = \sum_m c_{mn} \chi_n(\mathbf{r}, \omega_x, \omega_y, \omega_z, n). \quad (12)$$

The expansion coefficients for the ground-state function  $c_{0n}$  and the  $\omega_j$  values form the set of parameters for varying the  $\langle 0|H|0\rangle$  matrix element until it reaches a minimum, after which the  $c_{mn}$  coefficients for  $m > 0$  are found by orthogonalization.

Let us simplify the procedure. Suppose that all  $c_{mn}$  coefficients except  $c_{m0}$  are negligibly small, that is

$$\psi_n(\mathbf{r}) = \chi_n(\mathbf{r}, \omega_x, \omega_y, \omega_z, n). \quad (13)$$

For the matrix elements of the kinetic energy operator, we then have [7]

$$\left\langle n \left| \frac{\mathbf{P}^2}{2M} \right| n \right\rangle = \sum_j \hbar \omega_j \left( \frac{n_j}{2} + \frac{1}{4} \right), \quad (14)$$

where  $\hbar$  is the Planck constant. The matrix elements of the potential energy operator are calculated by the scheme

$$\begin{aligned} & \langle n|U(\mathbf{r})|n\rangle \\ &= A \sum_{\mathbf{R}} \sum_i \prod_j \langle n_j | \exp\{-\alpha_i(r_j - R_j - d_{ij})^2\} | n_j \rangle, \end{aligned} \quad (15)$$

$$\begin{aligned} & \langle n_j | \exp\{-\alpha_i(r_j - R_j - d_{ij})^2\} | n_j \rangle \\ &= \frac{1}{2^{n_j} n_j!} \tilde{w}_{ij}^{1/2} e^{-\zeta_{ij}^2} \sum_{m=0}^{n_j} 2^m m! \binom{n_j}{m}^2 \tilde{\alpha}_{ij}^{n_j-m} H_{2(n_j-m)}(\zeta_{ij}). \end{aligned} \quad (16)$$

The notation used in (15) and (16) is as follows:  $\mathbf{r} = (r_x, r_y, r_z)$ ,  $\mathbf{R} = (R_x, R_y, R_z)$ ,  $\mathbf{d}_i = (d_{ix}, d_{iy}, d_{iz})$ ,  $\binom{n_j}{m}$  are binomial coefficients,  $H_{2(n_j-m)}(\zeta_{ij})$  are the Hermite polynomials,

$$\tilde{w}_{ij} = w_j/(\alpha_i + w_j), \quad (17)$$

$$\tilde{\alpha}_{ij} = \alpha_i/(\alpha_i + w_j), \quad (18)$$

$$\zeta_{ij} = (R_j + d_{ij} - \delta_j)[\alpha_i w_j/(\alpha_i + w_j)]^{1/2}, \quad (19)$$

$$w_j = \frac{\omega_j M}{\hbar}, \quad (20)$$

and  $\delta = (\delta_x, \delta_y, \delta_z)$  is the radius vector of the equilibrium position of hydrogen in the interstice. The last value was introduced because it is more convenient to use the coordinate system with the origin at a metal atom rather than hydrogen. In deriving (16), we used the equation [8]

$$\begin{aligned} & \int_{-\infty}^{\infty} e^{-(x-y)^2} H_m(ax) H_n(ax) dx \\ &= \sqrt{\pi} \sum_{k=0}^{\min(m,n)} 2^k k! \binom{m}{k} \binom{n}{k} \\ & \times (1 - a^2)^{(m+n)/2-k} H_{m+n-2k} \left[ \frac{ay}{(1-a^2)^{1/2}} \right]. \end{aligned}$$

For the ground vibrational state, the matrix element of the Hamiltonian takes the form

$$\begin{aligned} \langle 0|H|0\rangle &= \frac{\hbar^2}{4M} \sum_j w_j + A \sum_{\mathbf{R}} \sum_i \prod_j \sqrt{\frac{w_j}{\alpha_i + w_j}} \\ & \times \exp \left\{ -\frac{\alpha_i w_j}{\alpha_i + w_j} (R_j + d_{ij} - \delta_j)^2 \right\}. \end{aligned} \quad (21)$$

The  $w_j$  values should be adjusted to minimize (21). As is clear from general quantum-mechanical considerations, the  $\delta$  radius vector approximately corresponds

to the position of the minimum of the potential function in the interstice. In the absence of strict limitations by symmetry, this parameter, however, may and should play the role of an additional variational parameter.

The matrix elements of excited states are calculated by (15), (16) with the use of the optimized parameters of the ground-state wave function.

In the section that follows, we apply this model to some metal and intermetallic compound hydrides.

### APPLICATION TO HYDRIDE SYSTEMS

*Metals (parametrization of the method).* Group IV and V transition metal hydrides possess the most characteristic properties of metal hydrides except PdH<sub>x</sub>. We will consider titanium, zirconium, vanadium, and niobium hydrides. Common to them is the ability to form dihydrides MeH<sub>x</sub> ( $x \approx 2$ ) with a fluorite-type structure, in which hydrogen atoms occur in tetrahedral interstices  $\delta = (1/4, 1/4, 1/4)$  of the FCC metal matrix lattice. Although this structure is different from that of pure metals, the compounds undergo structural phase transitions at certain hydrogen concentrations [9]. The unit cell parameters of the corresponding dihydrides and the frequencies of local hydrogen atom vibrations measured by inelastic incoherent neutron scattering are listed in Table 1.

The available structural data were used to solve the inverse vibrational problem; that is, we determined the parameters of the Gauss metal–hydrogen interaction potentials describing the experimental frequencies of the local modes. The arbitrariness involved in selecting the  $A$  constant was removed by the introduction of an additional harmonicity criterion, namely, the virial ratio

$$\vartheta = \langle 0|T|0\rangle / \langle 0|U|0\rangle, \quad (22)$$

where  $T$  and  $U$  are the kinetic and potential energy operators, respectively. For the harmonic oscillator, the strict equality  $\vartheta = 1$  holds. In solving the problem by the variational method, the basis functions of the harmonic oscillator are used, and such an approximate solution can only be physically meaningful if the total potential for the hydrogen atom in the interstice is insignificantly different from harmonic; that is,  $\vartheta \approx 1$ . This is substantiated by the neutron studies of most transition metal hydrides [5, 6] except PdH<sub>x</sub>, where hydrogen occupies octahedral interstices. From the point of view of a harmonic description of all four metal dihydrides, the most suitable  $A$  constant value was  $A = 4.25$  eV.

The corresponding  $\rho_i$  parameter values, the local mode frequencies for hydrogen, and the virial ratios  $\vartheta$  are listed in Table 2, which also contains harmonic ratios  $f$ ; that is, the ratios between the ground state oscillator energies for protium and deuterium. For the ideal harmonic oscillator,  $f = \sqrt{2} \approx 1.414$ .

**Table 1.** Neutron diffraction and inelastic scattering data on the structure and hydrogen local modes for Group IV and V transition metal hydrides with CaF<sub>2</sub>-type structures

Phase	$x$	$a$ , Å	$\hbar\omega_{\text{H}}$ , meV
$\gamma$ -TiH <sub>x</sub>	$\sim 2$	4.454 [9]	149 [2]
$\delta$ -ZrH <sub>x</sub>	2	4.779 [9]	139 [6]
$\gamma$ -VH <sub>x</sub>	1.5–1.7	4.271 [9]	160 [2]
$\delta$ -NbH <sub>x</sub>	2	4.55 [9]	148 [2]

Note:  $x$  is the composition,  $a$  is the FCC unit cell parameter, and  $\hbar\omega_{\text{H}}$  is the local mode frequency.

These results show that the effective metal–hydrogen interaction radii,  $\rho_i$ , correlate with the atomic radii of the corresponding metals, or, which is the same, with the unit cell parameters of the hydrides. In all metal hydrides, the behavior of hydrogen in tetrahedral interstices insignificantly deviated from harmonic.

*Intermetallic AB<sub>2</sub>-type compounds (calculation of separation coefficients).* Given the parameters of the metal–hydrogen interaction potential for various metals, we can directly approach the problem of determining the separation coefficients for hydrogen isotopes X and X\* in systems with intermetallic compound hydrides. According to [1],

$$\alpha_{\text{XX}^*} = Z_{\text{X}^*}Z_{\text{XX}} / Z_{\text{X}}Z_{\text{XX}^*}, \quad (23)$$

where  $\alpha_{\text{XX}^*}$  is the separation coefficient in the region of low concentrations of the heavier hydrogen isotope X\*,  $Z_{\text{X}}$  and  $Z_{\text{X}^*}$  are the partition functions for the isotopic forms of the hydride phase, and  $Z_{\text{XX}}$  and  $Z_{\text{XX}^*}$  are the partition functions for molecular hydrogen in the gas phase. The ratio between the two latter values is given by [10]

$$\ln \frac{Z_{\text{XX}}}{Z_{\text{XX}^*}} = \sum_{n=0}^4 a_n \left( \frac{300}{T} \right)^n, \quad (24)$$

where  $T$  is the absolute temperature in Kelvin, and  $a_n$  are the tabulated coefficients of the Bron polynomial [10] for the XX and XX\* molecules. In the Einstein approximation of independent harmonic oscillators, the vibrational component of the partition function of hydrogen in the hydride phase is given by [11]

$$Z = \prod_{i=1}^3 \left[ \sinh \left( \frac{\hbar\omega_i}{2kT} \right) \right]^{g_i}, \quad (25)$$

where  $g_i$  is the statistical weight of the local mode with the  $\omega_i$  frequency (by virtue of the normalization conditions,  $\sum_i g_i = 3$ ), and  $k$  is the Boltzmann constant. If  $\hbar\omega_i \gg kT$ , the hyperbolic sine can be replaced by an exponential function in (24), which is equivalent to complete neglect of the spectrum of excitations. A wealth of experimental data [2] show that the latter con-

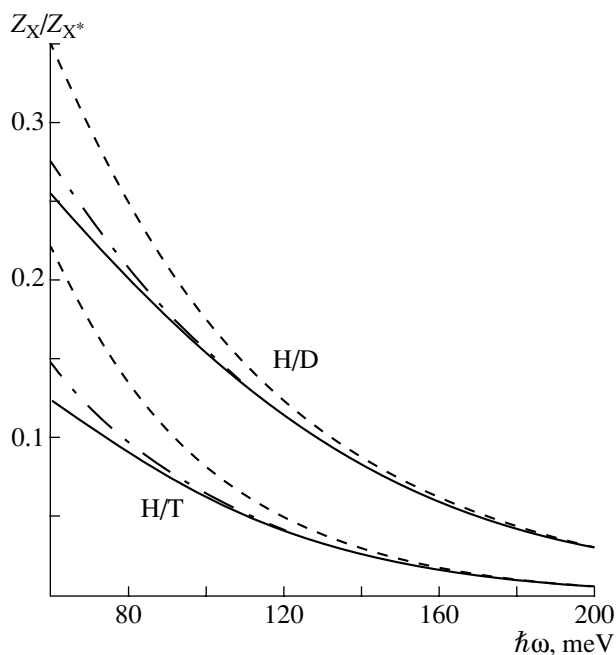
**Table 2.** Calculation data on Group IV and V transition metal hydrides with CaF<sub>2</sub>-type structures

Hydride phase	$\rho_i$ , Å	$\hbar\omega_H$ , meV	$\vartheta$	$f$
$\gamma$ -TiH <sub>x</sub>	0.88	149	1.021	1.419
$\delta$ -ZrH <sub>x</sub>	0.94	138	1.025	1.420
$\gamma$ -VH <sub>x</sub>	0.86	159	1.013	1.415
$\delta$ -NbH <sub>x</sub>	0.91	148	1.007	1.417

Note:  $\rho_i$  is the potential parameter,  $\hbar\omega_H$  is the local mode frequency, and  $\vartheta$  and  $f$  are the virial and harmonic ratios (see text).

dition does hold for most metal and intermetallic compound hydrides. As concerns deuterium and tritium-containing phases, they can be treated, taking into account, the contribution of only the first excited state of each local mode. The  $Z_X/Z_{X^*}$  ratio between the partition functions of the hydride phases is shown in Fig. 1 as a function of the frequency of the triply degenerate local mode. These ratios were calculated taking into account (a) the ground, (b) the ground and first excited, and (c) all harmonic oscillator states at  $T = 293$  K. The coalescence of curves (b) and (c) at  $\hbar\omega > 100$  meV substantiates the conclusions drawn above.

As follows from the neutron diffraction data [12–15] on the corresponding deuterides, deuterium atoms in AB<sub>2</sub>-type intermetallic compounds (Laves phases) predominantly occupy A<sub>2</sub>B<sub>2</sub>-type tetrahedral interstices (here, A is the metal with the larger, and B, with the



**Fig. 1.** Ratio  $Z_X/Z_{X^*}$  between partition functions of hydride phases as a function of the frequency of the triply degenerate local mode calculated taking into account the ground (dashed lines), ground and first excited (dot-dash lines), and all (solid lines) harmonic oscillator states ( $T = 293$  K).

smaller crystallographic radius). There are exceptions to this rule, when the population of AB<sub>3</sub> tetrahedra becomes nonzero (ZrV<sub>2</sub>). In systems of the first type, the excitation spectrum comprises three different frequencies, and in systems of the second type, there is one nondegenerate and one doubly degenerate mode. Nevertheless, the splitting of the energy levels of the excited states has no effect on the separation coefficient in two limiting cases: (a) if the isotopic effect is determined by the contribution of only the ground state and (b) if the splitting is small in comparison with the excitation energy. Condition (b) is almost always satisfied; strong splitting of the first excited state was observed experimentally only in unsaturated phases of Group V metal hydrides with a low-symmetry local environment of hydrogen atoms [2].

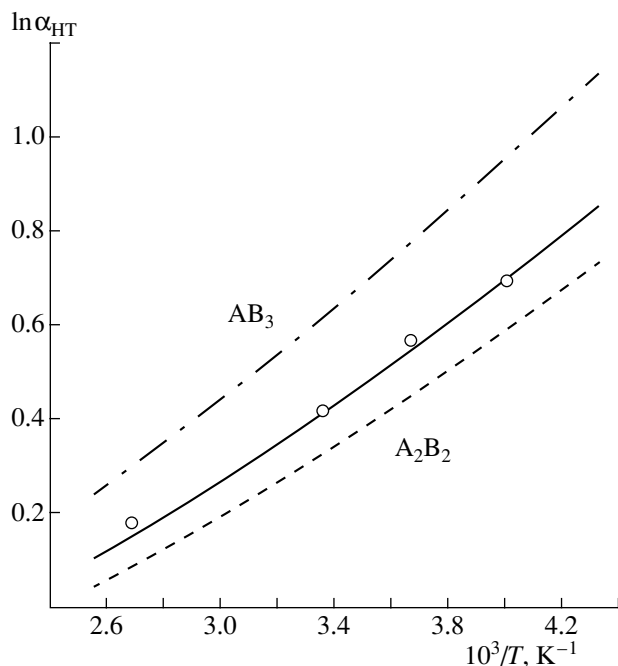
It follows that, for each type of occupied interstices, one averaged triply degenerate frequency  $\hbar\omega$  can be used in partition function calculations. For the harmonic oscillator, this frequency equals 2/3 of the ground state energy. A preliminary analysis also showed that, within the framework of the model under consideration,

$$\omega_x = \omega_y = \omega_z = \omega, \quad (26)$$

which allows a smaller number of wave function parameters to be used. The difference between the ground state energies obtained with and without the use of simplification (26) does not exceed 1 meV; that is, this difference is within the error of experimental determinations of separation coefficients. The last remark that should be made concerns the identity of the structures of the isotopically substituted hydride phase forms. The structural data of neutron diffraction experiments, as a rule, refer to metal deuterides. It is, however, known [16] that tetrahedral and octahedral site population probabilities in VH<sub>x</sub> differ from those in VD<sub>x</sub>. It, however, appears that vanadium is rather an exception, and isotopic polymorphism is not characteristic of a large number of other metal hydrides [9]. Data on the influence of isotopic substitution of hydrogen on the structure of intermetallic compound hydrides are still lacking; we will assume that there is no such influence.

Let us use the *superposition principle* and transfer the metal–hydrogen potentials determined for pure metal hydrides to intermetallic compound hydrides. By way of example, consider several hydride systems based on ZrB<sub>2</sub> (B = V, Cr, and Mn).

**ZrV<sub>2</sub>.** This compound has a MgCu<sub>2</sub>-type structure. At fairly high deuterium pressures approximately corresponding to the ZrV<sub>2</sub>D<sub>5</sub> solid phase composition, tetrahedral interstices Zr<sub>2</sub>V<sub>2</sub> and ZrV<sub>3</sub> in the matrix of the intermetallic compound are occupied by deuterium. The partial population of ZrV<sub>3</sub> sites amounts to about 30%. The cubic unit cell parameter is  $a = 7.913$  Å [12, 13]. The  $\alpha_{HT}$  separation coefficient was calculated with the use of the metal–hydrogen pair interaction poten-



**Fig. 2.** Temperature dependences of the  $\alpha_{\text{HT}}$  separation coefficient in the  $\text{ZrV}_2$ -based system. Open circles correspond to experimental data, and dashed and dot-dash lines were obtained on the assumption that interstices of one type only were populated.

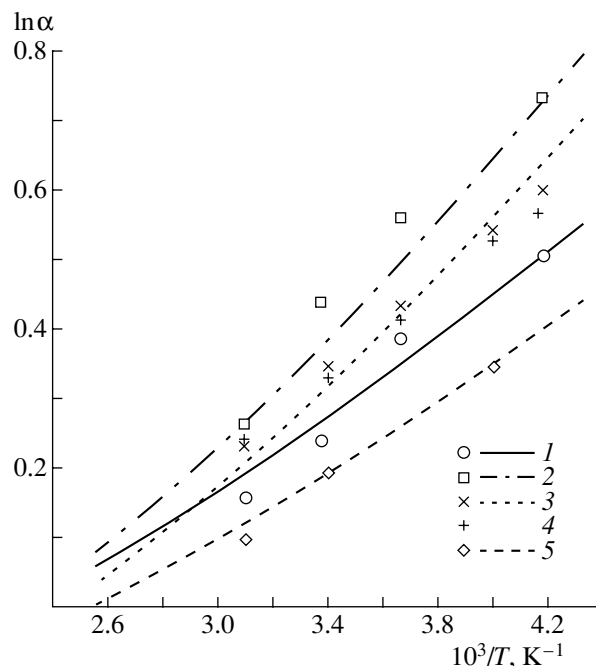
tials  $\rho_i$  determined for zirconium and vanadium (see the preceding section) taking into account the additivity of contributions of each type of interstices.

The temperature dependence of  $\alpha_{\text{HT}}$  is shown in Fig. 2. Open circles correspond to the experimental data [2]. There is close agreement between theory and experiment, which justifies the use of the superposition approach to potential modeling. For comparison, the hypothetical temperature dependences obtained on the assumption that interstices of only one type ( $\text{Zr}_2\text{V}_2$  or  $\text{ZrV}_3$ ) are occupied are also shown in the figure; neither of these two dependences correctly describes the experimental data.

**$\text{ZrMn}_{2+x}$ .** This compound has a  $\text{MgZn}_2$ -type structure. At high deuterium pressures, a saturated phase having a composition close to  $\text{ZrMn}_2\text{D}_3$  is formed. In this phase, deuterium atoms only occupy  $\text{Zr}_2\text{Mn}_2$  tetrahedral interstices. The hexagonal unit cell parameters are  $a = 5.391 \text{ \AA}$  and  $c = 8.748 \text{ \AA}$  [14].

The unknown  $\rho_i$  parameter value for Mn–H interactions was determined directly from the experimental  $\alpha_{\text{HD}}$  and  $\alpha_{\text{HT}}$  separation coefficient values in the temperature range 239–323 K; this gave  $\rho_i = 0.73 \text{ \AA}$ . The calculated temperature dependences of the separation coefficients are shown in Fig. 3.

The available data [15] on the structure of the superstoichiometric  $\text{ZrMn}_{2.75}\text{D}_{3.1}$  phase, in which manganese atoms substitute a part (about 20%) of zirconium atoms in the corresponding crystallographic sites, and on the



**Fig. 3.** Temperature dependences of the  $\alpha_{\text{HT}}$  and  $\alpha_{\text{HD}}$  separation coefficients in the  $\text{ZrMn}_{2+x}$ -based system: (1)  $\text{ZrMn}_2(\text{H/D})$ , (2)  $\text{ZrMn}_2(\text{H/T})$ , (3)  $\text{ZrMn}_{2.8}(\text{H/T})$ , (4)  $\text{ZrMn}_{3.8}(\text{H/T})$ , and (5)  $\text{ZrMn}_{2.8}(\text{H/D})$  (symbols are experimental values).

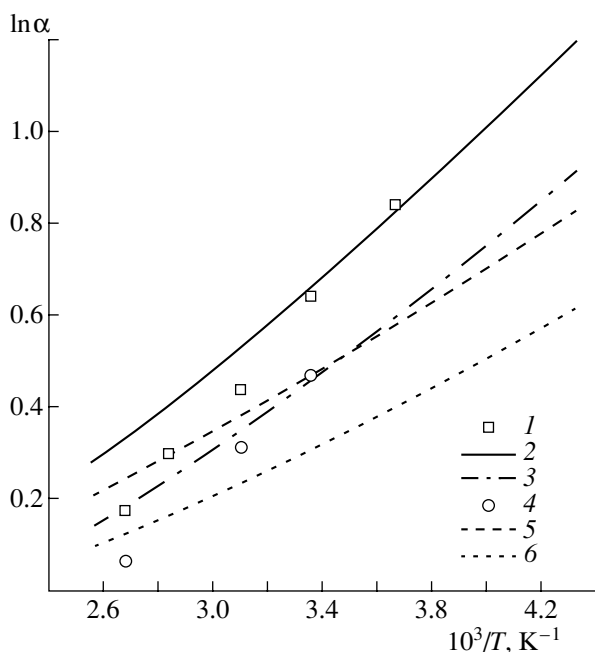
separation coefficients for  $\text{ZrMn}_{2.8}$  can be used to check the correctness of the  $\rho_{\text{Mn}}$  value cited above. The interaction potential between A and hydrogen in the structure of the  $\text{AB}_2$  matrix was written as the superposition of the corresponding potentials for A and B

$$U_{\text{A}} = sU_{\text{Mn}} + (1-s)U_{\text{Zr}}, \quad (27)$$

where  $s$  is the degree of substitution; in superstoichiometric  $\text{ZrMn}_{2.75}$ ,  $s = 0.2$ . The temperature dependences of the  $\alpha_{\text{HD}}$  and  $\alpha_{\text{HT}}$  separation coefficients calculated with the use of the macroscopic  $\text{ZrMn}_{2.75}\text{D}_{3.1}$  lattice constants  $a = 5.349 \text{ \AA}$  and  $c = 8.700 \text{ \AA}$  [15] and  $\rho_{\text{Mn}} = 0.73 \text{ \AA}$  are shown in Fig. 4. The calculation results closely agree with the experimental data.

Also shown in Fig. 3 are the experimental separation coefficients for  $\text{ZrMn}_{3.8}$ . Because of the absence of data on the structure of this superstoichiometric compound, the coefficients were not calculated. Note, however, that the separation coefficients for  $\text{ZrMn}_{2.8}$  and  $\text{ZrMn}_{3.8}$  are virtually equal, whereas for  $\text{ZrMn}_{2.8}$ , they are noticeably lower than for  $\text{ZrMn}_2$ . Therefore, there should be some factor that counterbalances this downward tendency of separation coefficients, such as, for instance, filling of  $\text{AB}_3$  tetrahedra by hydrogen.

**$\text{ZrCr}_2$ .** The structure of this compound is similar to that of  $\text{ZrV}_2$  at high temperatures and that of  $\text{ZrMn}_2$  at low temperatures. The lattice constant of the  $\text{ZrCr}_2\text{H}_4$  cubic phase equals  $7.654 \text{ \AA}$  [17]. The isotopic effect for  $\text{ZrCr}_2$  exhibits a strong temperature dependence



**Fig. 4.** Temperature dependences of the  $\alpha_{HT}$  and  $\alpha_{HD}$  separation coefficients in the  $ZrCr_2$ -based system: (1) H/T, (2) H/T ( $AB_3$ ), (3) H/T ( $A_2B_2$ ), (4) H/D, (5) H/D ( $AB_3$ ), and (6) H/D ( $A_2B_2$ ) (symbols are experimental values).

uncharacteristic of most of the other intermetallic compounds [18] (see Fig. 4). The use of  $\rho_{Cr} = 0.795 \text{ \AA}$ , which is the mean of  $\rho_V$  and  $\rho_{Mn}$ , as the potential parameter and the hypothesis that hydrogen only occupies interstices of one kind,  $Zr_2Cr_2$  or  $ZrCr_3$ , lead to the temperature dependences of the separation coefficients somewhat different from the experimental curves. The isotopic effect is, however, satisfactorily described on the assumption that hydrogen occurs in  $Zr_2Cr_2$  tetrahedra at high and  $ZrCr_3$  tetrahedra at low temperatures (Fig. 4). This may be evidence that the relative populations of interstices of different kinds depends on temperature, which is in part substantiated by neutron studies. Although the partial population of  $ZrCr_3$  interstices is still low at the temperature of measurements (about 9% at 293 K [17]), the polymorphic transformation of

**Table 3.** Averaged local vibration frequencies (meV) of hydrogen isotopes in interstices of  $ZrB_x$  ( $B = V, Cr, \text{ and } Mn$ ) intermetallic compounds

Compound	$A_2B_2$			$AB_3$		
	H	D	T	H	D	T
ZnV <sub>2</sub>	143	102	83	156	111	91
ZrMn <sub>2</sub>	144	101	82	*	*	*
ZnMn <sub>2.8</sub>	141	100	81	*	*	*
ZrCr <sub>2</sub>	148	105	85	158	112	92

\* Not calculated.

the  $ZrCr_2$  matrix [19] may influence the population ratio. On the other hand, the observed temperature dependence of the separation coefficient can be explained by a structural isotopic effect (isotopic polymorphism), as for vanadium hydride.

The calculated averaged frequencies of local hydrogen isotope vibrations in the  $A_2B_2$  and  $AB_3$  interstices of the systems considered above are listed in Table 3.

## CONCLUSION

The results of our calculations of separation coefficients for systems with  $ZrB_2$  ( $B = V, Cr, \text{ and } Mn$ ) intermetallic compound hydrides show that the model of the superposition of the Gauss metal–hydrogen pair potentials correctly reproduces experimental data. The following conclusions can be drawn:

(1) the harmonic oscillator approximation is valid for the systems under consideration; the deviations from the harmonic model do not exceed 1% for the  $A_2B_2$  and  $AB_3$  interstices;

(2) in  $AB_3$ -type interstices, the energy of the ground vibrational state of the hydrogen atom is substantially higher than in  $A_2B_2$  interstices, and population of the latter increases the separation coefficient.

The last circumstance gives a key to finding Laves phase hydrides with large  $\alpha$  values.

The developed model may well be applicable also to intermetallic compound hydrides of other classes ( $AB$  and  $AB_5$ ). It should, however, be noted that obtaining correct predictions requires the use of reliable data on the structure of hydride phases. Otherwise, the criterion of energy minimum should be used. Speculations based on the model developed in this work are, however, incapable of, for instance, answering the question why octahedral interstices with a lower energy remain unoccupied in hydrides with  $CaF_2$ -type structures. To answer this question, we must consider the minimum of the Helmholtz rather than potential energy, which explicitly includes all interatomic interactions.

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