

Lattice dynamics of metal hydrides

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(Received 10 October 1980)

A simple nonstoichiometric model of metal hydrides is proposed and applied to the study of the phonon dispersion curves and composition-dependent Young's moduli of PdH_x (D_x) system. The model can readily take into account the temperature and composition dependence of the metal hydride properties including phase changes.

I. INTRODUCTION

The interest in metal-hydrogen systems stems from their potential technological applications as fuel for transportation,¹ energy-storage devices,² and moderator and blanket in fission and fusion reactors, respectively.³ Metal-hydrogen systems can be classified by the nature of the hydrogen bonding into principle categories of covalent, saline, and metallic hydrides. The covalent hydrogen model⁴ assumes formation of covalent bonds between hydrogen and metal atoms. The saline, or hydride-anion model⁵ assumes ionic bonding accomplished by transfer of an electron from metal to hydrogen. The metallic, or screened-proton model⁶ assumes that the hydrogen enters the metal as a proton contributing its electron to the d -band states of the metal.

Metallic hydrides exhibit metallic properties and the study of their electronic structure⁷ has indicated that the bonding is largely metallic, similar to that of d electrons in pure transition metals, but the results are not inconsistent with the notion that some ionicity could also be present. Neutron-diffraction studies⁸ have shown that the metal-hydrogen systems can be considered as interstitial alloys in which the hydrogen atoms reside in the interstices of the host metal lattice.

The lattice-dynamics treatment of the metallic hydrides has been complicated by the nonstoichiometry and consequent loss of translational symmetry because of random distribution of hydrogen atoms in the metallic interstices.⁹ The only nonstoichiometric model of metallic hydrides presently available¹⁰ increases the size of the unit cell from a^3 to $(na)^3$, $n=2, 3, \dots$, and randomly distributes the appropriate number of hydrogen atoms among the interstices of the larger "supercell" in order to obtain the correct H/M ratio. This model suffers from large computation times and prohibitively so if the results become sensitive to the size of the supercell.

In this paper we present a simple model of the nonstoichiometric metal hydrides which considers

average interaction force constants and average hydrogen mass in arriving at the dynamical matrix of a conventional Born-von Kármán lattice-dynamics treatment utilizing the stoichiometric structure. In Sec. II the theoretical development of the nonstoichiometric model is given. Section III considers the application of the model to the calculation of the dispersion curves of $\text{PdD}_{0.63}$ and composition-dependent Young's modulus. Section IV includes discussion and concluding remarks.

II. THEORY

In the structure of a metallic hydride, MH_x , the metal atoms are located at the lattice points of a periodic crystal structure. The hydrogen atoms, on the other hand, randomly occupy interstitial sites of type i with a probability of site occupation P_i . In order to transform the random positions of the hydrogen atoms to that of an equivalent ordered arrangement, we make the following simplifying assumptions:

(a) The mass at an interstitial site of type i is replaced by the average hydrogen mass $xP_i m$, where x is the composition in MH_x and m is the mass of the hydrogen atom.

(b) The hydrogen-metal interaction force constants are given by

$$xP_k \phi_{xy}^{MH}(l', kk'), \quad (1)$$

where $\phi_{xy}^{MH}(l', kk')$ is the stoichiometric interaction force constant between hydrogen atom k in unit cell 0 with metal atom k' in unit cell l' .

(c) The hydrogen-hydrogen interaction force constants are given by

$$(xP_k)(xP_{k'})\phi_{xy}^{HH}(l', kk'), \quad (2)$$

where $\phi_{xy}^{HH}(l', kk')$ is the stoichiometric H-H interaction force constant. The resultant dynamical matrix, \underline{D} , takes the form

$$\underline{D} = \begin{pmatrix} \underline{D}^{MM} & \underline{D}^{HM} \\ \underline{D}^{MH} & \underline{D}^{HH} \end{pmatrix} \quad (3)$$

and has dimension $3(n+i) \times 3(n+i)$, where n is the number of metal atoms per unit cell and i is the number of interstitial sites per unit cell. The dynamical matrix elements are given by

$$D_{xy}^{MM}(\vec{q}, kk') = \sum_{l'} (m_k m_{k'})^{-1/2} \phi_{xy}^{MM}(l', kk') e^{i\vec{q} \cdot \vec{r}_{kk'}^{l'}}, \quad (4)$$

$$D_{xy}^{HM}(\vec{q}, kk') = \sum_{l'} (m_k m_{k'})^{-1/2} x P_k \phi_{xy}^{HM}(l', kk') e^{i\vec{q} \cdot \vec{r}_{kk'}^{l'}},$$

and

$$D_{xy}^{HH}(\vec{q}, kk') = \sum_{l'} (m_k m_{k'})^{-1/2} (x P_k) \times (x P_{k'}) \phi_{xy}^{HM}(l', kk') e^{i\vec{q} \cdot \vec{r}_{kk'}^{l'}}, \quad (5)$$

$$C_{\alpha\gamma, \beta\lambda} = -\frac{1}{2v_a} \sum_{l'} \left(\sum_{kk'} \phi_{\alpha\beta}^{MM}(l', kk') (\vec{r}_{kk'}^{l'})_{\gamma} (\vec{r}_{kk'}^{l'})_{\lambda} + \sum_{kk'} x^2 P_k P_{k'} \phi_{\alpha\beta}^{HH}(l', kk') (\vec{r}_{kk'}^{l'})_{\gamma} (\vec{r}_{kk'}^{l'})_{\lambda} + 2 \sum_{kk'} x P_k \phi_{\alpha\beta}^{HM}(l', kk') (\vec{r}_{kk'}^{l'})_{\gamma} (\vec{r}_{kk'}^{l'})_{\lambda} \right), \quad (7)$$

where v_a is the unit-cell volume.

Hence, from Eqs. (6) and (7) utilizing the dynamical matrix of Eq. (3) the composition-dependent dispersion curves and elastic constants of a nonstoichiometric metal hydride can be calculated. The calculation can then be extended to include other thermodynamic and spectral properties. At this point it must be clarified that the force constants $\phi_{xy}(l', kk')$ are not composition independent and in calculating composition-dependent properties the variations of ϕ and x should also be taken into account.

III. CALCULATIONS

As an application of the proposed model, in this section we will consider the calculation of the dispersion curves and composition-dependent Young's modulus of $\text{PdH}_x(\text{D}_x)$. The phonon dispersion curves of $\text{PdD}_{0.63}$ have been measured by coherent inelastic scattering of neutrons and the results have been successfully fitted with a 12 force-constant stoichiometric dynamical matrix.¹² A nonstoichiometric calculation,¹³ based on a supercell of 108 Pd atoms on an fcc lattice with 68 D atoms randomly distributed on 108 octahedral sites, has been successful in fitting the dispersion curves using, also, a 12-parameter force-constant model.

The palladium hydride phase diagram at room temperature consists of a solid solution α phase ($\text{H}/\text{Pd} < 0.05$) and a NaCl-defect structure β phase ($\text{H}/\text{Pd} > 0.6$). X-ray-diffraction studies at room temperature¹⁴ have shown the α phase to have a lattice parameter of 3.89 Å and the β phase to have a lattice parameter of 4.02 Å. For $\text{PdD}_{0.63}$ the lattice constant has been measured¹² to be

where \vec{q} is the phonon wave vector and $\vec{r}_{kk'}^{l'}$, the interatomic separation. The equation of motion is defined as

$$\omega^2 \vec{U} = \underline{D} \vec{U}, \quad (6)$$

where ω is the frequency of vibration and $\vec{U}(k, \vec{q})$ the displacement amplitude of the k th atom. The dispersion curves ω vs \vec{q} can be calculated once the structure and the force-constant values are known.

Using the method of long waves,¹¹ and observing that the stoichiometric structure of all hydrides is centrosymmetric, the elastic constants $C_{\alpha\gamma, \beta\lambda}$ are given by

4.052 Å. Neutron diffraction studies of the β phase¹⁵ have indicated that of the two octahedral and tetrahedral sites of the fcc lattice, at room temperature only the octahedral site is occupied by the hydrogen atom and hence $P_{\text{oct}} = 1$ and $P_{\text{tet}} = 0$.

If considering only the nearest-neighbor Pd-Pd (3 force constants), D-D (3 force constants), and Pd-D (2 force constants) interactions, all of the dispersion branches except for the high-energy optical branch along [001] and [111] can be fitted to the experimental observations. The high-energy optical branch is strongly dependent on the next-nearest D-D (2 force constants) interaction and with inclusion of these parameters, which brings the total number of unknown force-constant parameters to ten, a satisfactory agreement with the measured dispersion curves can be obtained. Table I gives the force-constant values, and Fig.

TABLE I. Force-constant values obtained by fitting the observed dispersion curves of $\text{PdD}_{0.63}$ using the nonstoichiometric model (in 10^3 dyne/cm).

α_1	$\phi_{xx}(\frac{1}{2}00, \text{Pd-D})$	-6.87
β_1	$\phi_{zz}(\frac{1}{2}00, \text{Pd-D})$	0.79
α_2	$\phi_{xx}(\frac{1}{2}\frac{1}{2}0, \text{Pd-Pd})$	-14.4
β_2	$\phi_{zz}(\frac{1}{2}\frac{1}{2}0, \text{Pd-Pd})$	-0.5
γ_2	$\phi_{xz}(\frac{1}{2}\frac{1}{2}0, \text{Pd-Pd})$	-18.2
α_3	$\phi_{xx}(\frac{1}{2}\frac{1}{2}0, \text{D-D})$	-3.7
β_3	$\phi_{zz}(\frac{1}{2}\frac{1}{2}0, \text{D-D})$	0.45
γ_3	$\phi_{xz}(\frac{1}{2}\frac{1}{2}0, \text{D-D})$	-2.96
α_4	$\phi_{xx}(100, \text{D-D})$	0.17
β_4	$\phi_{zz}(100, \text{D-D})$	-3.33

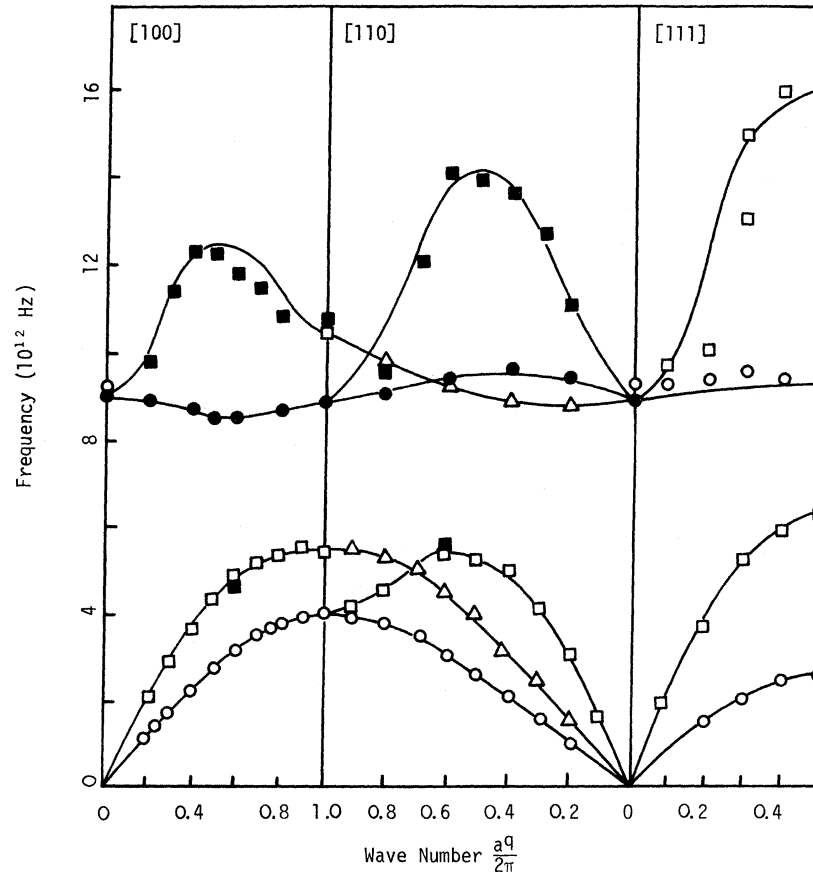


FIG. 1. Comparison of the experimental observation (Ref. 12) of the phonon dispersion curves of $\text{PdD}_{0.63}$ with the calculations of a ten-parameter nonstoichiometric lattice-dynamics model.

1 gives the comparison of calculated dispersion curves with the experimental data.

Using Eq. (7) the expressions for the elastic constants of $\text{PdH}_x(\text{D}_x)$ are obtained as

$$\begin{aligned}
 C_{11} &= -\frac{4}{a} [x\alpha_1 + \alpha_2 + x^2(\alpha_3 + 2\alpha_4)] \\
 C_{44} &= -\frac{2}{a} [2x\beta_1 + \alpha_2 + \beta_2 \\
 &\quad + x^2(\alpha_3 + \beta_3 + 2\alpha_4)] \\
 C_{12} &= \frac{2}{a} [-2x\beta_1 - \alpha_2 - \beta_2 \\
 &\quad + 2\gamma_2 - x^2(\alpha_3 + \beta_3 - 2\gamma_3)].
 \end{aligned} \tag{8}$$

The calculated values are compared with the elastic constants of palladium in Table II, clearly indicating the softening effect upon deuteriding. The degree of softening can be taken to be indicative of the extent to which the changes in composition produce changes in the Pd-Pd interactions.

In order to calculate the composition-dependent

Young's modulus we use the Voight-Reuss-Hill (VRH) approximation¹⁶ in calculating the shear and bulk moduli. Since Young's modulus can be calculated from either shear or bulk moduli, we have taken the average of the two expressions, i.e.,

$$E_y = \frac{1}{2} [2G_H(1+\nu) + 3K_H(1-2\nu)], \tag{9}$$

where G_H and K_H are shear and bulk moduli in the VRH approximation and ν is the Poisson's ratio. In our calculations we have assumed ν to be composition independent with a value of 0.375 cor-

TABLE II. Calculation of the elastic constants of $\text{PdD}_{0.63}$ using the nonstoichiometric model, and the comparison with the elastic constants of palladium illustrating the softening effect upon deuteriding (in 10^{12} dyne/cm²).

	C_{11}	C_{12}	C_{44}
$\text{PdD}_{0.63}$, calculated	1.861	1.225	0.683
Pd, measured ^a	2.270	1.759	0.717

^aJ. A. Rayne, Phys. Rev. **118**, 1545 (1960).

responding to that of pure palladium.¹⁷

In utilizing the expressions in Eq. (8), as previously mentioned, we must take into account the composition dependence of force-constant values, especially for Pd-Pd interactions. Assuming that in the Pd-Pd interaction potential, $V(r) = \epsilon F(r)$, only the potential strength ϵ has a continuous composition dependence, that is, $\epsilon(x) = \epsilon_0 f(x)$, then the expressions in Eq. (8) can be modified to include composition dependence of Pd-Pd force constants by multiplying α_2 , β_2 , and γ_2 by $f(x)$. We have assumed negligible composition dependence for Pd-D and D-D force constants.

In our calculations, we have taken a simple linear variation for $f(x)$, i.e.,

$$f(x) = A + Bx. \quad (10)$$

Since our equations for elastic moduli are exact at $x = 0.63$, we can use the condition $f(0.63) = 1$ to reduce the unknown parameters in $f(x)$; the relationship between A and B is given by:

$$B = \frac{1 - A}{0.63}. \quad (11)$$

We have elected to calculate A from the Young's modulus of pure palladium which has the value of 1.124×10^{12} dyne/cm².¹⁸ The calculated values of A and B are given in Table III.

In performing the calculations we have to consider the existence of two phases α and β in the calculation of the Young's modulus. These two phases have the same crystal structure and differ only in their lattice constant. For the sake of simplicity we will assume that the force constants will remain the same in both phases. The Young's modulus is then calculated for

$0 \leq x \leq 0.05$, α phase

$0.05 \leq x \leq 0.6$, lever rule average of α and β phases

$0.6 \leq x \leq 1$, β phase.

The calculations of the composition-dependent Young's modulus are summarized in Table IV and Fig. 2. It is of interest to note that although the average E_y , calculated from Eq. (9), shows

TABLE IV. Calculation of the Young's modulus of PdH_x(D_x) from shear and bulk moduli calculated using VRH approximation (in 10^{12} dyne/cm²).

x	$E'_y = 2G_H(1 + \nu)$	$E''_y = 3K_H(1 - 2\nu)$	$E_y = \frac{1}{2}(E'_y + E''_y)$
0	1.124	1.124	1.124
0.1	1.131	1.111	1.121
0.2	1.124	1.098	1.111
0.3	1.107	1.087	1.097
0.4	1.080	1.080	1.080
0.5	1.045	1.075	1.060
0.6	1.003	1.074	1.038
0.7	0.960	1.084	1.022
0.8	0.910	1.096	1.003
0.9	0.853	1.112	0.982
1.0	0.788	1.130	0.959

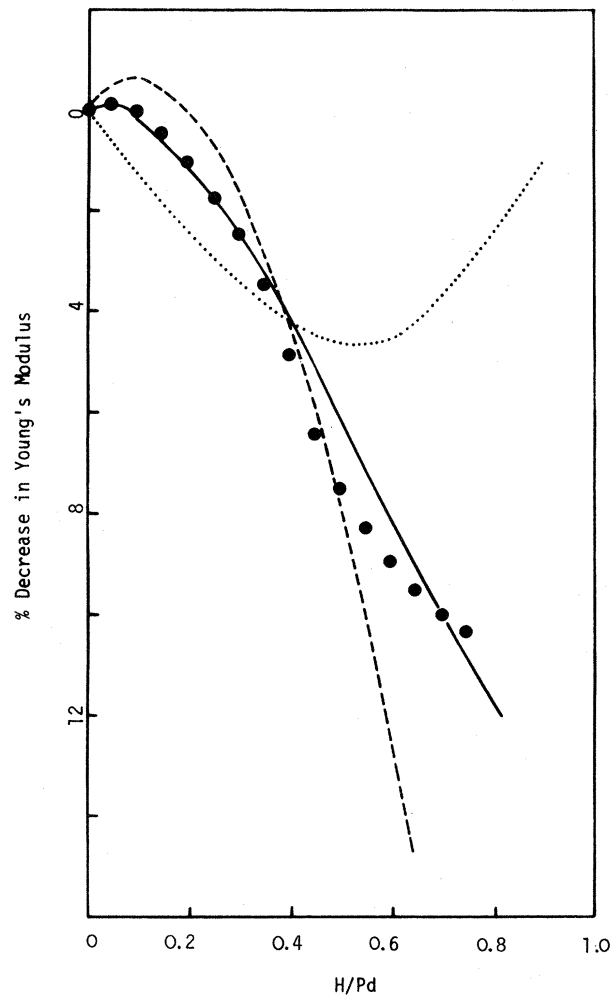


FIG. 2. Comparison of the calculated decrease in average Young's modulus (solid curve) with the experimental data (Ref. 19) (solid circles). The decrease in Young's modulus calculated from shear modulus (dashed curve) and from bulk modulus (dotted curve) are also given.

TABLE III. The values of parameters in $f(x) = A + Bx$ utilized in characterization of the composition dependence of Pd-Pd interaction force constants, calculated from shear and bulk moduli in VRH approximation.

	From shear modulus	From bulk modulus
A	1.43	1.22
B	-0.68	-0.35

good agreement with the experimental observations, the values of E_y calculated from shear or bulk moduli act only as limiting cases. This observation is essentially another manifestation of the VRH approximation.

IV. DISCUSSION

A simple nonstoichiometric model of metal hydrides has been proposed in which average hydrogen mass and average interaction force constants are utilized in a stoichiometric structure, and the standard lattice-dynamics formulations are employed in calculation of the dispersion curves and the elastic constants.

The proposed model is applied to the calculation of the dispersion curves of $\text{PdD}_{0.63}$ and composition-dependent Young's modulus of palladium hydride. A satisfactory agreement with the measurements of phonon dispersion curves is obtained using only ten force-constant parameters, as compared with twelve parameters of other lattice-dynamics model calculations. More important, the computation time for the model is considerably less than the supercell model, and explicit composition-dependent expressions for the frequencies of vibration and elastic constants can be readily derived in the proposed model.

In the calculation of the Young's modulus of

PdH_x (D_x) the model takes into account the phase changes as a function of composition. Although the phase change for palladium hydride, at room temperature, consists only of an abrupt change in the lattice constant with no structural change, the model is, however, readily applicable to phase changes where structural changes are also present. The calculations of the Young's modulus have been fitted to the data at essentially one point, $x = 0$, and the relatively good agreement between the theory and experiment is not only supportive of the model, but also indicative of the strength of VRH approximation in the calculation of the elastic moduli.

The model can easily calculate properties of metal hydrides when more than two phases are present. By making assumptions about probability of interstitial-site occupation by hydrogen atoms, the model can dynamically consider all temperature- and composition-dependent changes in the calculation of the properties of metal hydrides.

ACKNOWLEDGMENT

This work was supported in part by the U. S. Army Research Office, Durham. Contribution No. 84 for the Institute of Chemical Analysis.

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