PHYSICAL REVIEW B VOLUME 33, NUMBER 12 15 JUNE 1986

Elastic interactions between hydrogen atoms in metals. II. Elastic interaction energies

Arthur I. Shirley* and Carol K. Hall†
Department of Chemical Engineering, Princeton University, Princeton, New Jersey 08544
(Received 20 February 1986)

The fully harmonic lattice approximation derived in a previous paper is used to calculate the elastic interaction energies in the niobium-hydrogen system. The permanent-direct, permanent-indirect, induced-direct, and induced-indirect forces calculated previously each give rise to a corresponding elastic interaction between hydrogen atoms. The latter three interactions have three- and four-body terms in addition to the usual two-body terms. These quantities are calculated and compared with the corresponding two-body permanent elastic interactions obtained in the harmonic-approximation treatment of Horner and Wagner. The results show that the total induced elastic energy is approximately $\frac{1}{3}$ the size of the total permanent elastic energy and opposite to it in sign. The total elastic energy due to three-body interactions is approximately $\frac{1}{4}$ the size of the total two-body elastic energy, while the total four-body elastic energy is approximately 5% of the total two-body energy. These additional elastic energies are expected to have a profound effect on the thermodynamic and phase-change behavior of a metal hydride.

I. INTRODUCTION

In a previous paper [hereafter called I (Ref. 1)] the authors derived a second-order perturbation theory for the Hamiltonian of a metal hydride. This theory, which was called the fully harmonic lattice approximation (FHLA) goes beyond the customary harmonic-approximation treatment of Horner and Wagner[2,3] in that it includes second-order terms for the hydrogen-hydrogen and metal-hydrogen potentials as well as for the metal-metal potential. The inclusion of these terms gave rise to additional hydrogen-metal forces that do not appear in the harmonic-approximation treatment. In this paper the elastic interaction energies associated with these new forces are calculated for the hydrogen-niobium system and shown to contain three- and four-body terms (in addition to the two-body terms obtained in the harmonic approximation) which are of significant magnitude to affect the thermodynamic properties and phase-change behavior of a metal hydride.

Our development of the FHLA to describe the mechanical and thermodynamic properties of metal hydrides has been motivated by the apparent failure of harmonic-approximation treatments to predict the experimentally observed ordered phases of solid solutions at high hydrogen concentrations (see Refs. 4–7, and also I). The harmonic approximation was also felt to be inadequate because it does not yield many-body interactions which are known to be significant in concentrated metal hydrides.[8–10] Furthermore, the harmonic-approximation theories do not explain such well-known experimental phenomena as nonlinearities in $\Delta V/V$ versus concentration curves[11–14] or the variation in a hydride's elastic constants with concentration.[15,16]

In the derivation of the FHLA, the hydrogen-hydrogen, metal-metal, and hydrogen-metal potentials are expanded out to second order in the hydrogen and metal displacements. This analysis results in a differentiation between two types of forces between hydrogen atoms and metal atoms: the *direct* forces which act directly between an isolated hydrogen atom and its metal neighbors, and the *indirect* forces which are effective forces between a hydrogen atom and a metal atom due to the presence of neighboring hydrogen atoms. The indirect and direct forces can be broken down into two components: a *permanent* contribution which is the force between a hydrogen atom and a metal atom in a lattice which has the elastic properties (or couplings) of the pure (hydrogen-free) metal lattice, and an *induced* contribution (acting in the hydrogen-free lattice) which corrects the permanent contribution for the effects of the hydrogen atoms on the couplings. (Thus one could think of the permanent forces acting in the real lattice or the permanent plus the induced forces acting in the ideal lattice.) In contrast, the Horner and Wagner harmonic-approximation treatment yields only permanent-direct forces. The direct and indirect forces and their permanent and induced components were evaluated in I from experimental data on the hydrogen-niobium system. The results showed that the indirect forces have $\frac{1}{10}$ the magnitude of, and opposite sign to the direct force, while for each force the induced part was approximately $\frac{1}{3}$ the size of the permanent part and opposite to it in sign.

In this paper the elastic energy terms in the FHLA are evaluated using the force data calculated in I. The permanent-direct, permanent-indirect, induced-direct, and induced-indirect forces will each give rise to a corresponding elastic interaction between hydrogen atoms. The latter three interactions have three- and four-body terms in addition to the usual two-body (pairwise) term. In the harmonic theories derived previously[2–7] only permanent-direct interactions were considered with the exception of work by Trinkhaus[17] and Kramer[6] who performed calculations of induced interactions. Our results show that the total induced elastic energy is approximately $\frac{1}{3}$ the size of the total permanent elastic energy and opposite to it in sign. The total elastic energy due to three-body interactions is approximately $\frac{1}{4}$ the size of the total two-body elastic energy, while the total four-body energy is only about 5% the size of the total two-body elastic energy. These additional elastic energies are expected to have a profound effect on the thermodynamic and phase-change behavior of a metal hydride.

The total elastic energy for a metal hydride is evaluated for two different lattice boundary conditions: periodic (infinite lattice) and free surface (finite lattice). For periodic boundary conditions, the two-, three-, and four-body elastic interaction terms calculated from the forces in the FHLA are just summed over all hydrogen and metal atoms. For finite-lattice boundary conditions, the hydrogen atoms are assumed to be distributed homogeneously throughout the lattice so that the microscopic hydrogen-metal forces within the bulk of the crystal sum to zero. The only contribution to the elastic energy in this case comes from forces acting at the surface; this energy can be expressed in terms of macroscopically measurable quantities such as the strain and the compliance. The difference between the finite-lattice and infinite-lattice elastic energies (when both are evaluated for a homogeneous distribution of hydrogen atoms) is the so-called free-surface correction[2,3] which, when written as a sum of many-body terms and added to the infinite-lattice elastic interaction energies, makes the resulting interaction energies applicable to real, finite crystals. The free-surface correction evaluated in the FHLA is significantly different from the free-surface correction found in Horner and Wagner's harmonic-approximation treatment. At concentrations $c=1$, the difference in chemical potential between the FHLA and the harmonic approximation arising from the free-surface correction is almost 1 eV.

In order to determine the effect that the many-body elastic energies calculated here have on the phase-change behavior of a metal hydride it is necessary to perform a statistical mechanical calculation of the free energy. Unfortunately the Monte Carlo method for the calculation of free energies is ill suited to calculations involving greater-than-two-body interactions especially on the complex interstitial lattice appropriate to the hydrogen-niobium system. In part III of this series,[18] renormalization-group techniques are used to simplify the lattice geometry and transform the Hamiltonian to a new model in which hydrogen atoms sit on a simple cubic lattice and have relatively short-range interactions. The free energy of the new model (which still contains many-body interactions) is solved using the Kikuchi cluster-variation technique and the phase diagrams are calculated.

II. REVIEW OF RESULTS FROM PAPER I

In this section we review the notation and results of paper I in which we calculated the permanent and induced components of the direct and indirect forces and the associated displacements, stresses, and strains.

In paper I, we considered a lattice model containing N hydrogen atoms distributed over a subset of N_{H} tetrahedral interstitial sites in a bcc metal lattice containing N_L metal atoms. The metal atom sites are denoted by m and n and the interstitial sites are denoted by a, b, c, or d. In the hydrogen-loaded lattice the metal sites m and the interstitial sites a are displaced to new locations by $\mathbf{v}^m$ and $\mathbf{u}^a$, respectively, from their respective equilibrium positions in the hydrogen-free lattice, $\mathbf{R}^m$ and $\mathbf{Q}^a$. The occupation index $\tau_a=(0,1)$ defines which interstitial sites are occupied. The atomic volume of the pure metal is $\Omega=V/N_L$ where V is the total volume of the crystal. Greek character subscripts indicate x, y, or z directions. A double summation convention is assumed throughout the paper.

The forces between hydrogen atoms and metal atoms can be separated into direct and indirect forces as described in I and each of these forces can be broken down into permanent and induced contributions. The total permanent-direct force on metal atom m in the direction μ exerted by all the hydrogen atoms is

$$-\Psi_\mu^m(\tau)=+\sum_a {}^a\psi_\mu^m \tau_a \ , \tag{1}$$

where ${}^a\psi_\mu^m$ is defined to be the force of a H atom at site a on a metal atom at site m. The total permanent-indirect force on metal atom m in the direction μ is

$$-\Theta_\mu^m(\tau)={}^{1/2}\sum_{a,c} ({}^{ca}\theta_\mu^m+{}^{ac}\theta_\mu^m)\tau_a\tau_c \ , \tag{2}$$

where ${}^{ca}\theta_\mu^m$ is the indirect force exerted by a hydrogen atom at c on a metal atom at site m due to the presence of a H atom at a. The total induced-direct force on metal atom m in the direction μ is

$$-\Psi_\mu^{I,m}(\tau)=-\sum_{a,b} {}^b\psi_\mu^{I,m}\tau_a\tau_b \ , \tag{3}$$

where ${}^b\psi_\mu^{I,m}$ is the induced-direct force on metal atom m by hydrogen atom b in the μ direction caused by the displacement field (or coupling changes) due to a. The total induced-indirect force on metal atom m in the direction μ is

$$\Theta_\mu^{I,m}(\tau)=-\sum_{a,b,c} {}^b\theta_\mu^{I,m}\tau_a\tau_b\tau_c \ , \tag{4}$$

where ${}^b\theta_\mu^{I,m}$ is the induced-direct force on metal atom m by hydrogen atom b in the μ direction caused by the displacement field (or coupling changes) due to the pair (a,c).

The permanent forces acting on metal atom m cause permanent displacements which are given by

$$v_\mu^{0,m}=D_{\mu\nu}^{0,mn}[\Psi_\nu^n(\tau)+\Theta_\nu^n(\tau)] \ , \tag{5}$$

where $D_{\mu\nu}^{0,mn}$ is the Green's function of the hydrogen-free lattice. These displacements can be broken down into a direct and indirect part. The direct displacement of metal atom m due to H atom a acting via the direct force ${}^a\psi_\mu^m$ is given by

$${}^a w_\mu^m=-D_{\mu\nu}^{0,mn}\ {}^a\psi_\nu^n \tag{6}$$

and the indirect displacement of metal atom m due to the pair (a,c) acting via the indirect force ${}^{ac}\theta_\mu^m+{}^{ca}\theta_\mu^m$ is

$${}^{(a,c)}s_\mu^m=-D_{\mu\nu}^{0,mn}({}^{ca}\theta_\nu^n+{}^{ac}\theta_\nu^n) \ . \tag{7}$$

Thus the total permanent displacement of metal atom m is

$$v_{\mu}^{0,m}=\sum_{a}\left[{}^{a}w_{u}^{m}+\sum_{c}{}^{(a,c)}s_{\mu}^{m}\tau_{c}\right]\tau_{a}\ . \tag{8}$$

It is very difficult to calculate the induced displacements so these were not calculated in paper I.

In order to relate induced quantities to permanent quantities it is necessary to introduce the t matrix which is defined so that the Green's function for the hydrogen-loaded lattice, $D_{\mu\nu}^{mn}$, can be approximately related to the Green's function of the hydrogen-free lattice $D_{\mu\nu}^{0,mn}$ by

$$D_{\mu\nu}^{mn}\simeq D_{\mu\nu}^{0,mn}+D_{\mu\alpha}^{0,mr}t_{\alpha\lambda}^{rp}D_{\lambda\nu}^{0,pn}\ . \tag{9}$$

The t matrix is itself approximated by

$$t_{\mu\nu}^{mn}=\sum_{b}{}^{b}t_{\mu\nu}^{mn}\tau_{b}\ . \tag{10}$$

Values for ${}^{b}t_{\mu\nu}^{mn}$ were obtained from Kramer[6] using measurements of polarizability by Schober and Lottner.[15]

The t matrix can be used to calculate the direct and indirect forces in terms of the permanent-direct and -indirect displacements by

$$\begin{aligned}{}^{b}\psi_{\mu}^{I,m}&={}^{b}t_{\mu\nu}^{mn}\,{}^{a}w_{\mu}^{n}\ ,\\ {}^{b}\theta_{\mu}^{I,m}&={}^{b}t_{\mu\nu}^{mn}\,{}^{(a,c)}s_{\nu}^{n}\ .\end{aligned} \tag{11}$$

In order to determine values for the permanent and induced components of the direct and indirect forces it is useful to define corresponding force-dipole tensors which relate the macroscopically measured stresses and strains to the microscopic forces. The permanent-direct, permanent-indirect, induced-direct, and induced-indirect force-dipole tensors are given, respectively, by

$$P_{\mu\nu}=-(1/N)R_{\mu}^{m}\Psi_{\mu}^{m}(\tau)\ , \tag{12a}$$

$$\Pi_{\mu\nu}=-(N_{L}/N^{2})R_{\mu}^{m}\Theta_{\mu}^{m}(\tau)\ , \tag{12b}$$

$$P_{\mu\nu}^{I}=-(1/N^{2})R_{\mu}^{m}\Psi_{\nu}^{I,m}(\tau)\ , \tag{12c}$$

$$\Pi_{\mu\nu}^{I}=-(N_{L}^{2}/N)R_{\mu}^{m}\Theta_{\mu}^{I,m}(\tau)\ . \tag{12d}$$

The dipole tensors can be determined from the macroscopically measured stress

$$\sigma_{\mu\nu}=(1/\Omega)\sum_{x}\left[P_{\mu\nu}^{(x)}+\sum_{y}\Pi_{\mu\nu}^{(x,y)}c_{y}\right]c_{x}\ , \tag{13}$$

which when multiplied by the measured elastic compliance $S_{\nu\lambda\iota\mu}$ of the hydrogen-loaded lattice gives the macroscopically measured total strain $\epsilon_{\iota\lambda}$, i.e.,

$$\sigma_{\mu\nu}S_{\mu\nu\iota\lambda}=\epsilon_{\iota\lambda}\ . \tag{14}$$

The superscripts (x) and (x,y) on the direct and indirect force-dipole tensors in Eq. (13) indicate which interstitial sublattice the defects causing the forces are on and $c_{x}=N_{x}/N_{L}$ where N_{x} is the number of hydrogen atoms on the xth sublattice. Note that all possible sublattices are summed over. The permanent strain can be obtained from the stress and the elastic compliances of the unloaded lattice using

$$\sigma_{\mu\nu}S_{\mu\nu\iota\lambda}^{0}=\epsilon_{\iota\lambda}^{0}\ . \tag{15}$$

It is also convenient to define an induced stress $\sigma_{\mu\nu}^{I}$ such that

$$\epsilon_{\iota\lambda}=S_{\mu\nu\iota\lambda}^{0}(\sigma_{\mu\nu}+\sigma_{\mu\nu}^{I})\ . \tag{16}$$

The induced stress is an effective stress which when added to the measured stress gives the same strain in the hydrogen-free lattice (with elastic compliances $S_{\mu\nu\iota\lambda}^{0}$) as occurs in the hydrogen-loaded lattice (which has elastic compliances $S_{\mu\nu\iota\lambda}$). The induced stress can be written in terms of the induced force-dipole tensors as

$$\sigma_{\mu\nu}^{I}=(N_{\mathrm{H}}^{y}/\Omega)\sum_{x,z}\left[P_{\mu\nu}^{I,(x)}+\sum_{y}\Pi_{\mu\nu}^{I,(x,y)}c_{y}\right]c_{x}c_{z}\ . \tag{17}$$

In paper I the goal was to calculate values for the permanent and induced components of the direct and indirect forces for the hydrogen-niobium system and also to calculate the permanent displacements. Since these are microscopic quantities, they cannot be measured directly. They can, however, be inferred from macroscopic measurements of strain versus hydrogen concentration and elastic compliance versus hydrogen concentration using Eqs. (1)–(15). The sequence of steps is the following: Using Eq. (14) the stress can be determined from the measured strain and elastic compliances. When this is combined with information on volume dilation, assumptions about the range of the hydrogen-metal force and Eq. (13), the permanent-direct and permanent-indirect force-dipole tensors are obtained. Equations (12a) and (12b) then yield the permanent-direct and -indirect forces. The permanent displacements follow from Eqs. (6) and (7) and a knowledge of the pure lattice Green's function. The induced-direct and -indirect forces then follow from Eq. (11) combined with Kramer's (6) value for the t matrix.

In paper I it was also desired to calculate the induced stress since this plays a role in the evaluation of the elastic energies. This can be accomplished by first determining the induced force-dipole tensors from Eqs. (12c) and (12d) and then applying Eq. (17) to get the induced stress.

III. ELASTIC INTERACTIONS IN THE FHLA

A. General expression for the elastic energy

In this section we derive a general expression for the total elastic energy of a metal lattice containing hydrogen atoms. Our derivation is based on the concept that an elastic interaction between two defects will occur when the forces exerted by one defect do work along the metal-atom displacements caused by the other defect. The defects in our case will be single hydrogen atoms, pairs of hydrogen atoms, etc. Since the above concept is unfamiliar to most readers we will illustrate it by reviewing the Horner-Wagner harmonic-approximation treatment of elastic interactions.

In the harmonic approximation, the total elastic energy is given by $\frac{1}{2}\Psi_{\mu}^{m}(\tau)v_{\mu}^{0,m}$, where $-\Psi_{\mu}^{m}(\tau)$ is the total force of the hydrogen atoms on the metal atom at m, and $v_{m}^{0,m}$ is the displacement of m (in the ideal lattice) caused by the forces exerted by the H atoms. The total force can be written as the sum of the forces exerted by the individual hydrogen atoms as in Eq. (1) and the displacement can be written as the sum of the displacements of m caused by the individual hydrogen atoms as in Eq. (8) (with ${}^{(a,c)}s_{\mu}^{m}$ set to zero). The total elastic energy is then,

$$\begin{aligned}\tfrac{1}{2}\Psi_{\mu}^{m}(\tau)v_{\mu}^{0,m} &= \tfrac{1}{2}\sum_{a} {}^{a}\psi_{\mu}^{m}\,{}^{a}w_{\mu}^{m}\tau_{a} \\ &\quad + \tfrac{1}{2}\sum_{\substack{a,b \\ a\neq b}} \left(\tfrac{1}{2}\,{}^{a}\psi_{\mu}^{m}\,{}^{b}w_{\mu}^{m} + \tfrac{1}{2}\,{}^{b}\psi_{\mu}^{m}\,{}^{a}w_{\mu}^{m}\right)\tau_{a}\tau_{b}\,, \\ &= \tfrac{1}{2}\sum_{a} W_{aa}\tau_{a} + \tfrac{1}{2}\sum_{\substack{a,b \\ a\neq b}} W_{ab}\tau_{a}\tau_{b}\,. \end{aligned} \tag{18}$$

The first term,

$$W_{aa} = {}^{a}\psi_{\mu}^{m}\,{}^{a}w_{\mu}^{m}\,, \tag{19}$$

is called the self-energy, and is not of concern here. The final term,

$$W_{ab}\tau_{a}\tau_{b} = \tfrac{1}{2}\,{}^{a}\psi_{\mu}^{m}\,{}^{b}w_{\mu}^{m} + \tfrac{1}{2}\,{}^{b}\psi_{\mu}^{m}\,{}^{a}w_{\mu}^{m}\,, \tag{20}$$

may be interpreted as the elastic interaction energy between H atoms at sites a and b. It has the form of a work term in which the forces exerted by one defect (say, defect a) on the metal atoms do work along the displacements arising from another defect (defect b).

In the FHLA both the permanent and induced parts of the direct and indirect forces contribute to the elastic interactions. Since the indirect forces are forces exerted by pairs of hydrogen atoms, the elastic interactions will include three- and- four-body interactions, W_{abc} and W_{abcd}, as well as the usual pairwise interaction term W_{ab}. In the remainder of this section, we systematically calculate the two-, three-, and four-body interaction terms.

The two-body elastic interaction energy between hydrogen atoms at a and b is the force exerted on the metal atoms by a hydrogen atom at a multiplied by the metal-atom displacements caused by a hydrogen atom at b plus a similar term with a and b interchanged:

$$\begin{aligned} W_{ab} &= \tfrac{1}{2}\,{}^{a}\psi_{\mu}^{m}\,{}^{b}w_{\mu}^{m} + \tfrac{1}{2}\,{}^{b}\psi_{\mu}^{m}\,{}^{a}w_{\mu}^{m} \\ &\quad + \tfrac{1}{2}\,{}^{a}\psi_{\mu}^{I,m}\,{}^{b}w_{\mu}^{m} + \tfrac{1}{2}\,{}^{b}\psi_{\mu}^{I,m}\,{}^{a}w_{\nu}^{m}\,. \end{aligned} \tag{21}$$

We can write Eq. (21) as

$$W_{ab} = {}^{a}\psi_{\mu}^{m}\,{}^{b}w_{\mu}^{m} + {}^{a}\psi_{\mu}^{I,m}\,{}^{b}w_{\mu}^{m} = W_{ab}^{0} + W_{ab}^{I}\,, \tag{22}$$

where

$$\begin{aligned} W_{ab}^{0} &= {}^{a}\psi_{\mu}^{m}\,{}^{b}w_{\mu}^{m} = {}^{a}\psi_{\mu}^{m}\,D_{\mu\nu}^{0,mn}\,{}^{b}\psi_{\nu}^{n} = {}^{a}w_{\mu}^{n}\,{}^{b}\psi_{\mu}^{n}\,, \\ W_{ab}^{I} &= {}^{a}\psi_{\mu}^{I,m}\,{}^{b}w_{\mu}^{m} = {}^{b}w_{\mu}^{m}\,{}^{a}t_{\mu\nu}^{mn}\,{}^{b}w_{\nu}^{n} = {}^{a}w_{\mu}^{m}\,{}^{b}\psi_{\mu}^{I,m}\,. \end{aligned} \tag{23}$$

(A more general expression would include terms such as ${}^{a}\psi_{\mu}^{I,m} = {}^{a}t_{\mu\nu}^{mn}\,{}^{c}w_{\nu}^{n}$, but these would give three-body terms.) The term W_{ab}^{0} in Eq. (22) is called the *permanent* elastic interaction energy, while the term W_{ab}^{I} is called the *induced* elastic interaction energy. Throughout the rest of this paper we will use the superscript 0 to indicate a permanent interaction, and the superscript I to indicate an induced interaction.

The three-body elastic interaction between an isolated hydrogen atom at b and a pair of H atoms at a and c, is

$$\begin{aligned} W_{abc} &= \tfrac{1}{2}\,{}^{b}\psi_{\mu}^{m}\,{}^{(a,c)}s_{\mu}^{m} + \tfrac{1}{2}\left({}^{ac}\theta_{\mu}^{m} + {}^{ca}\theta_{\mu}^{m}\right){}^{b}w_{\mu}^{m} \\ &\quad + \tfrac{1}{2}\,{}^{b}\theta_{\mu}^{I,m}\,{}^{(a,c)}s_{\mu}^{m}\,. \end{aligned} \tag{24}$$

[Terms such as ${}^{b}\theta_{\mu}^{I,m}\,{}^{(a,c)}s_{\mu}^{m} = {}^{(d,e)}s_{\mu}^{m}\,{}^{b}t_{\mu\nu}^{mn}\,{}^{(a,c)}s_{\nu}^{n}$, $(d,e)\neq(a,c)$ have been left out since these would be more than three-body interactions.] A term ${}^{b}\psi_{\mu}^{I,m}\,{}^{a}w_{\mu}^{m} = {}^{c}w_{\nu}^{n}\,{}^{b}t_{\mu\nu}^{mn}\,{}^{a}w_{\mu}^{m}$ could also be included, but when summed over all c its net contribution vanishes because $\sum_{c}{}^{b}\psi_{\mu}^{I,m} = {}^{b}t_{\mu\nu}^{mn}\sum_{c}{}^{c}w_{\nu}^{n} = 0$. Using Eqs. (6) and (7), it is found that the first and second terms in Eq. (24) are equal, so that the three-body elastic interaction energy becomes

$$\begin{aligned} W_{abc} &= {}^{b}\psi_{\mu}^{m}\,{}^{(a,c)}s_{\mu}^{m} + \tfrac{1}{2}\,{}^{b}\theta_{\mu}^{I,m}\,{}^{(a,c)}s_{\mu}^{m} \\ &= W_{abc}^{0} + \tfrac{1}{2}W_{abc}^{I}\,, \end{aligned} \tag{25}$$

where

$$\begin{aligned} W_{abc}^{0} &= {}^{b}\psi_{\mu}^{m}\,{}^{(a,c)}s_{\mu}^{m} = {}^{b}\psi_{\mu}^{m}D_{\mu\nu}^{0,mn}\left({}^{ca}\theta_{\nu}^{n} + {}^{ac}\theta_{\nu}^{n}\right), \\ W_{abc}^{I} &= {}^{b}\theta_{\mu}^{I,m}\,{}^{(a,c)}s_{\mu}^{m} = {}^{(a,c)}s_{\mu}^{m}\,{}^{b}t_{\mu\nu}^{mn}\,{}^{(a,c)}s_{\nu}^{n}\,. \end{aligned} \tag{26}$$

It will be noted that there is only one term contributing to W_{abc}^{I} in Eq. (24) as opposed to two terms contributing to W_{ab}^{I} in Eq. (21), i.e., a term like ${}^{b}w_{\mu}^{m}\,{}^{(a,c)}t_{\mu\nu}^{mn}\,{}^{b}w_{\nu}^{n}$ does not appear in Eq. (25). This is because there is no t matrix defined for the pairs (a,c), but only for the isolated H atom at a or the isolated H atom at c. This is a consequence of Eq. (10), which defines the total t matrix $t_{\mu\nu}^{mn}$ to be the sum of the t matrices ${}^{b}t_{\mu\nu}^{mn}$ associated with the individual H atoms. This also means that there is no four-body induced elastic interaction, since this would require a term ${}^{(a,c)}s_{\mu}^{m}\,{}^{(b,d)}t_{\mu\nu}^{mn}\,{}^{(a,c)}s_{\nu}^{n}$. Therefore, the four-body elastic interaction W_{abcd} will have only a permanent contribution W_{abcd}^{0}:

$$\begin{aligned} W_{abcd} &= \tfrac{1}{2}\left({}^{ca}\theta_{\mu}^{m} + {}^{ac}\theta_{\mu}^{m}\right){}^{(b,d)}s_{\mu}^{m} + \tfrac{1}{2}\left({}^{bd}\theta_{\mu}^{m} + {}^{db}\theta_{\mu}^{m}\right){}^{(a,c)}s_{\mu}^{m} \\ &= \left({}^{ca}\theta_{\mu}^{m} + {}^{ac}\theta_{\mu}^{m}\right){}^{(b,d)}s_{\mu}^{m} \\ &= \left({}^{ca}\theta_{\mu}^{m} + {}^{ac}\theta_{\mu}^{m}\right)D_{\mu\nu}^{0,mn}\left({}^{bd}\theta_{\nu}^{n} + {}^{db}\theta_{\nu}^{n}\right) = W_{abcd}^{0}\,. \end{aligned} \tag{27}$$

The total elastic energy, H_{elast}, will be the sum of the elastic interactions for a given configuration of hydrogen atoms $\{\tau_{a}\}$,

$$\begin{aligned} H_{\text{elast}} &= \tfrac{1}{2}\sum_{a,b} W_{ab}\tau_{a}\tau_{b} + \tfrac{1}{2}\sum_{a,b,c} W_{abc}\tau_{a}\tau_{b}\tau_{c} \\ &\quad + \tfrac{1}{8}\sum_{a,b,c,d} W_{abcd}\tau_{a}\tau_{b}\tau_{c}\tau_{d}\,. \end{aligned} \tag{28}$$

The coefficients in front of each summation are "weights" that correct for overcounting in the sums. In each of the summations it is assumed that $a\neq b\neq c\neq d$. We can separate H_{elast} into a *permanent* elastic energy H_{elast}^{0} and an *induced* elastic energy H_{elast}^{I}:

$$H_{\text{elast}} = H_{\text{elast}}^{0} + H_{\text{elast}}^{I}\,. \tag{29}$$

The energy H_{elast}^{0} is found by summing the permanent elastic interactions for a given configuration:

$$\begin{aligned} H_{\text{elast}}^{0} &= \tfrac{1}{2}\sum_{a,b} W_{ab}^{0}\tau_{a}\tau_{b} + \tfrac{1}{2}\sum_{a,b,c} W_{abc}^{0}\tau_{a}\tau_{b}\tau_{c} \\ &\quad + \tfrac{1}{8}\sum_{a,b,c,d} W_{abcd}^{0}\tau_{a}\tau_{b}\tau_{c}\tau_{d}\,. \end{aligned} \tag{30}$$

The energy H^I_{elast} is calculated in a similar fashion from the induced elastic interactions,

$$H^I_{\text{elast}}=\tfrac{1}{2}\sum_{a,b} W^I_{ab}\tau_a\tau_b+\tfrac{1}{4}\sum_{a,b,c} W^I_{abc}\tau_a\tau_b\tau_c\ . \tag{31}$$

The coefficient in front of the sum over W^I_{abc} in Eq. (31) is different from that in front of the sum over W^0_{abc} in Eq. (30) because of the $\frac{1}{2}$ multiplying W^I_{abc} in Eq. (25).

B. Results for the elastic interactions on an infinite lattice

The infinite-lattice permanent and induced interactions can be calculated from the permanent and induced forces and the permanent displacements calculated in paper I for hydrogen in niobium using Eqs. (23), (26), and (27). The calculated two-body interactions are given in Table I, the three-body interactions are given in Table II, and the four-body interactions are given in Table III. The calculations have been done only for hydrogen atoms on the x sublattice (where the tetragonal axis of the H atom lies in the x direction). Not all of the interactions that were calculated are shown. The values that are shown are for the interactions with small H-H separations, since these interactions tend to be the largest.

The pair interactions W^0_{ab} and W^I_{ab} agree roughly with the previous calculations of Horner and Wagner,[2,3] and Kramer,[6] respectively, as shown in Table I, but a direct comparison is difficult since those authors used different force-dipole tensor values and different force models from those used in the present calculations. Horner and Wagner used an isotropic force-dipole tensor having $P=5.33\times10^{-12}$ erg, while Kramer used an isotropic force-dipole tensor having $P=4.33\times10^{-12}$ erg. Our calculations used $P=(A+2B)/3=5.73\times10^{-12}$ erg (Ref. 1). Horner and Wagner used a force model that included forces exerted by a hydrogen atom on its nearest and next-nearest neighboring metal atoms. The same model has been used in our calculations. Kramer[6] considered two different force models. The elastic interactions listed in Table I under "model I" were calculated by Kramer using a model that considered only nearest-neighbor forces, while the elastic interactions listed under "model II" were calculated using the same force model as was used by Horner and Wagner and the present calculations. It can be seen that there is considerable disagreement between Kramer's model I elastic interactions and the calculations using the next-nearest-neighbor force model, for both W^0_{ab} and W^I_{ab}. Johnston and Sholl[19] have also noted that the nearest-neighbor model gives much larger relaxation energies than a model with forces out to next-nearest neighbors, even when the force-dipole tensor is the same. We see that W^I_{ab} is anywhere from 0 to 37% of W^0_{ab}, and of opposite sign.

The three-body interactions W^0_{abc} shown in Table II are typically an order of magnitude smaller than W^0_{ab}. The W^0_{abcd} are about two orders of magnitude smaller than W^0_{ab}. Both the permanent and induced elastic interactions oscillate between positive and negative values as the distance between the defects r increases, but the induced interactions die out more quickly with increasing distance because of their r^{-6} dependence, whereas the permanent interactions have a r^{-3} dependence.[20,21]

Although the three- and four-body interactions are much smaller than the two-body interactions, there are a greater number of them so they make a sizable contribution to H_{elast}. This can be seen by considering the total energy due to each type (permanent, induced) of n-body ($n=2,3,4$) interaction. These total energies are given by the individual summed terms in Eq. (42) for the permanent interactions and Eq. (53) for the induced interactions, and are tabulated in Table IV for both finite and infinite lattices. (The finite-lattice values will be discussed in the next section.) The two-body induced interactions have a total energy of from $\frac{1}{4}$ to $\frac{1}{3}$ the total of the two-body permanent interactions, but the three-body induced interactions are negligibly small. The three-body permanent interactions are also about $\frac{1}{4}$ the size of the two-body energy, and the total four-body contribution is on the order of 5% of the two-body energy. From these numbers it is clear that ignoring the induced interactions

TABLE I. Comparison of $\tilde{W}^0_{ab}$ and $\tilde{W}^I_{ab}$ with the values calculated by Horner and Wagner, and Kramer.

$4(Q^b-Q^a)/a$			W^0_{ab}(K)				W^I_{ab}(K)	
					Kramer (5)			Kramer
x	y	z	This work	H-W(2)	Model I	Model II	This work	Model I
0	0	0	−4122	−4174	−9995	−4812	1528	2828
2	0	0	−1961	−1967	605	−2155	196	−101
0	2	2	−579	−589	−1975	−625	108	221
2	2	2	−210	−212	548	−252	−9.8	29
0	0	4	353	377	−4.4	452	−2.7	−5.0
4	0	0	−217	−183	−355	−166	−0.3	−2.2
2	0	4	703	688	1662	780	7.0	
2	4	0	−57	−61	−126	−54	−1.4	
4	2	2	−7.4	−16	−147	52	0.5	

$\text{TRACE}(P_{\mu\mu})/3=5.33\times10^{-12}$ erg for Horner-Wagner (Refs. 2 and 3).
$\text{TRACE}(P_{\mu\mu})/3=4.33\times10^{-12}$ erg for Kramer (Ref. 6).
$\text{TRACE}(P_{\mu\mu})/3=5.73\times10^{-12}$ erg for this work (Ref. 1).

TABLE II. Permanent and induced three-body elastic interactions for various defect-defect separations and orientations.

			$4[(\mathbf{Q}^c-\mathbf{Q}^a)]/a$ (x,y,z)							
			(0,2,2)		(0,−2,2)		(2,−2,2)		(2,2,−2)	
	$4(\mathbf{Q}^b-\mathbf{Q}^a)/a$		$\tilde{W}^0_{abc}$	$\tilde{W}^I_{abc}$	$\tilde{W}^0_{abc}$	$\tilde{W}^I_{abc}$	$\tilde{W}^0_{abc}$	$\tilde{W}^I_{abc}$	$\tilde{W}^0_{abc}$	$\tilde{W}^I_{abc}$
x	y	z	(K)	(K)	(K)	(K)	(K)	(K)	(K)	(K)
0	0	0	96	1.6	96	1.6	60	0.6	60	0.6
2	0	0	61	0.02	61	0.02	98	−0.7	98	−0.7
0	2	2	96	1.6	58	0.1	65	0.6	10	−0.4
2	2	2	61	0.1	22	0.02	13	0.01	10	1.8
0	0	4	58	0.1	58	0.1	13	0.01	−33	−0.04
4	0	0	13		13		31		31	
2	0	4	22		22					
2	4	0	55		−2.3		10		10	

and the elastic energy due to the indirect forces as is done in most methods using the harmonic approximation gives an incomplete description of the elastic energy of a metal hydride.

C. Calculation of the elastic energy of a finite lattice

It has long been recognized[2,3] that the choice of boundary conditions for a lattice will affect the elastic energy of defects in the lattice. On the microscopic level the placement of the metal atoms is roughly periodic, and the displacement fields near a defect (assumed to be in the bulk of the metal) should be determined using periodic boundary conditions (infinite lattice). Far from the defect, however, the influence of the free surface of a finite crystal will affect these displacements, and the use of periodic boundary conditions is no longer valid. In this section the macroscopic elastic energy of hydrogen atoms in a finite metal lattice is calculated. In order to calculate the macroscopic quantities we assume that the hydrogen atoms are homogeneously distributed throughout the lattice (i.e., $\tau_a=\langle\tau_a\rangle$). In the first part of this section we will calculate the permanent elastic energy in terms of the force-dipole tensors and the elastic constants. Again we will use the FHLA to relate the microscopic hydrogen-metal forces and the metal-atom displacements to the macroscopic stresses and strains.

TABLE III. Permanent and induced four-body elastic interactions for various defect-defect separations.

						$4(\mathbf{Q}^c-\mathbf{Q}^a)/a$		
						(0,2,2)	(2,−2,2)	(2,2,2)
$4(\mathbf{Q}^b-\mathbf{Q}^a)/a$			$4(\mathbf{Q}^d-\mathbf{Q}^a)/a$			$\tilde{W}^0_{abcd}$	$\tilde{W}^0_{abcd}$	$\tilde{W}^0_{abcd}$
x	y	z	x	y	z	(K)	(K)	(K)
0	0	0	0	2	2	−34	3.2	−15
			2	−2	2	3.2	−29	−1.2
			2	2	2	−15	−1.2	−29
2	0	0	2	−2	2	−1.2	−14	1.0
0	2	2	0	0	0	−34	3.2	−15
			0	0	4	3.5	−6.7	3.1

The total permanent elastic energy, H^0_{elast}, can be written in terms of the microscopic forces and displacements,

$$H^0_{\text{elast}}=\tfrac{1}{2}\sum_{a,b}{}^{b}\psi^m_\mu\,{}^{b}w^m_\mu\,\tau_a\tau_b+\tfrac{1}{2}\sum_{a,b,c}{}^{b}\psi^{m}_\mu\,{}^{(a,c)}s^m_\mu\,\tau_a\tau_b\tau_c$$
$$+\tfrac{1}{8}\sum_{a,b,c,d}({}^{ca}\theta^m_\mu+{}^{ac}\theta^m_\mu)\,{}^{(b,d)}s^m_\mu\,\tau_a\tau_b\tau_c\tau_d\ . \qquad (32)$$

It is desirable to get H^0_{elast} into a form that depends on the total forces and displacements. By inserting Eqs. (6) and (7) into Eq. (32) and summing the terms together, we achieve the result

$$H^0_{\text{elast}}=\tfrac{1}{2}\sum_{a,b}\left[{}^{a}\psi^m_\mu+\tfrac{1}{2}\sum_{c}({}^{ac}\theta^m_\mu+{}^{ca}\theta^m_\mu)\tau_c\right]D^{0,mn}_{\mu\nu}$$
$$\times\left[{}^{b}\psi^n_\nu+\tfrac{1}{2}\sum_{d}({}^{db}\theta^n_\nu+{}^{bd}\theta^n_\nu)\tau_d\right]\tau_a\tau_b\ . \qquad (33)$$

Equation (33) can now be written as a sum over all m of the product of the permanent force on metal atom m

$$\Psi^m_\mu(\tau)+\theta^m_\mu(\tau)=-\sum_{a}\left[{}^{a}\psi^m_\mu+\tfrac{1}{2}\sum_{c}({}^{ac}\theta^m_\mu+{}^{ca}\theta^m_\mu)\tau_c\right]\tau_a\ , \qquad (34)$$

and the permanent displacement of metal atom m

$$v^{0,m}_\mu=-D^{0,m}_{\mu\nu}\sum_{b}\left[{}^{b}\psi^m_\mu+\tfrac{1}{2}\sum_{d}({}^{bd}\theta^m_\mu+{}^{db}\theta^m_\mu)\tau_d\right]\tau_b\ , \qquad (35)$$

i.e., H^0_{elast} becomes

$$H^0_{\text{elast}}=\tfrac{1}{2}[\Psi^m_\mu(\tau)+\Theta^m_\mu(\tau)]v^{0,m}_\mu\ . \qquad (36)$$

In the bulk of the crystal the forces $\Psi^m_\mu(\tau)+\Theta^m_\mu(\tau)$ will vanish because of lattice symmetry (recall that we are considering a perfectly homogeneous distribution of H atoms), but near the surface they do not vanish since the surface atoms are unattached on the outside.[2,3] Instead, these forces cause a homogeneous deformation of the lattice; i.e., $v^{0,m}_\mu=\epsilon^0_{\mu\nu}R^m_\nu$, where $\epsilon^0_{\mu\nu}$ is the strain that occurs in the pure metal as the result of the stress $\sigma_{\iota\lambda}$, see Eq.

TABLE IV. Sums of interaction energies for two-, three-, and four-body interactions for H atoms in niobium.

		Finite lattice boundary conditions		
$\sum_b \widetilde{W}^{0,xx}_{ab}$ (K)	$\sum_b \widetilde{W}^{I,xx}_{ab}$ (K)	$\frac{1}{2}\sum_{b,c} \widetilde{W}^{0,xxx}_{abc}$ (K)	$\frac{1}{2}\sum_{b,c} \widetilde{W}^{I,xxx}_{abc}$ (K)	$\frac{1}{4}\sum_{b,c,d} \widetilde{W}^{0,xxxx}_{abcd}$ (K)
−4020	1696	1049	5.6	−182
		Infinite lattice boundary conditions		
$\sum_b W^{0,xx}_{ab}$ (K)	$\sum_b W^{I,xx}_{ab}$ (K)	$\frac{1}{2}\sum_{b,c} W^{0,xxy}_{abc}$ (K)	$\frac{1}{4}\sum_{b,c} W^{I,xxx}_{abc}$ (K)	$\frac{1}{4}\sum_{b,c,d} W^{0,xxxx}_{abcd}$ (K)
−7084	1955	1326	205	−424

(15). Thus, Eq. (36) becomes

$$H^0_{\text{elast}} = \tfrac{1}{2} R^m_\nu [\Psi^m_\mu(\tau) + \Theta^m_\mu(\tau)] \epsilon^0_{\mu\nu} \, . \tag{37}$$

Inserting Eqs. (15) and (23) of I into Eq. (37) produces

$$H^0_{\text{elast}} = -(\Omega N_L/2) \sigma_{\mu\nu} S^0_{\mu\nu\iota\lambda} \sigma_{\iota\lambda} \, , \tag{38}$$

for a homogeneous distribution of H atoms. Equation (38) is significant in that it shows H^0_{elast} to be dependent on the boundary conditions of the crystal, and therefore to be a macroscopic quantity. This expression is a familiar result in elasticity theory,[20] and is also valid in the harmonic approximation (where $H_{\text{elast}} = H^0_{\text{elast}}$).

The concentration dependence of H^0_{elast} is found by inserting Eq. (13) into Eq. (38):

$$H^0_{\text{elast}} = (-N_L/2\Omega) \sum_{x,y} \left[P^{(x)}_{\iota\mu} + \sum_z \Pi^{(x,z)}_{\iota\mu} c_z \right] S^0_{\iota\mu\nu\lambda} \left[P^{(y)}_{\iota\mu} + \sum_w \Pi^{(y,w)}_{\iota\mu} c_w \right] c_x c_y \, , \tag{39}$$

which can be expanded to give

$$H^0_{\text{elast}} = -(N_L/2\Omega) \left[\sum_{x,y} P^{(x)}_{\iota\mu} S^0_{\iota\mu\nu\lambda} P^{(y)}_{\nu\lambda} c_x c_y + \sum_{x,y,w} P^{(x)}_{\iota\mu} S^0_{\iota\mu\nu\lambda} \Pi^{(y,w)}_{\nu\lambda} c_x c_y c_w + \sum_{x,y,z,w} \Pi^{(x,z)}_{\iota\mu} S^0_{\iota\mu\nu\lambda} \Pi^{(y,w)}_{\nu\lambda} c_x c_y c_w c_z \right] . \tag{40}$$

This expression can be compared to the result obtained when Eq. (30) is evaluated in the limit of a homogeneous distribution of hydrogen atoms on each sublattice, $\langle \tau_a \rangle_x \rightarrow N_x$. To do this we convert the summation over interstitial sites in Eq. (30) into an initial summation in which site a is on the xth sublattice, site b is on the yth sublattice, site c is on the zth sublattice, and site d is on the wth sublattice, and then a second summation over all sublattices. Thus, in the limit of a homogeneous distribution of H atoms on each sublattice, Eq. (30) becomes

$$\begin{aligned} H^0_{\text{elast}} = {} & (N_L/2) \sum_{x,y} \left[(N_L/N^y_{\text{H}}) \sum_b W^{0,xy}_{ab} \right] c_x c_y + (N_L) \sum_{x,y,z} \left[(N_L^2/2N^y_{\text{H}} N^z_{\text{H}}) \sum_{b,c} W^{0,yz}_{abc} \right] c_x c_y c_z \\ & + (N_L/2) \sum_{x,y,z,w} \left[(N_L^3/4N^y_{\text{H}} N^z_{\text{H}} N^w_{\text{H}}) \sum_{b,c,d} W^{0,xyzw}_{abcd} \right] c_x c_y c_z c_w \, , \end{aligned} \tag{41}$$

where N^x_{H} is the number of interstitial sites on the xth sublattice. The sum $\sum_b W^{0,xyz}_{ab}$ is restricted to sites b on the yth sublattice surrounding site a on the xth sublattice. Similar definitions apply to $\sum_{b,c} W^{0,xyz}_{abc}$, etc. For the tetrahedral sublattices in bcc metals, $N_L/N^x_{\text{H}} = 1$.

A comparison of Eqs. (40) and (41) allows one to write

$$\sum_b W^{0,xy}_{ab} = -(1/\Omega) P^{(x)}_{\iota\mu} S^0_{\iota\mu\nu\lambda} P^{(y)}_{\nu\lambda} \, ,$$

$$\tfrac{1}{2} \sum_{b,c} W^{0,xyz}_{abc} = -(1/\Omega) \Pi^{(x,z)}_{\iota\mu} S^0_{\iota\mu\nu\lambda} P^{(y)}_{\nu\lambda} \, , \tag{42}$$

$$\tfrac{1}{4} \sum_{b,c,d} W^{0,xyzw}_{abcd} = -(1/\Omega) \Pi^{(x,z)}_{\iota\mu} S^0_{\iota\mu\nu\lambda} \Pi^{(y,w)}_{\nu\lambda} \, .$$

The evaluation of H^I_{elast} for a finite lattice is done in a similar manner, although it cannot be reduced to a simple function of stress and strain like H^0_{elast} in Eq. (38). If the terms in Eqs. (23) and (26) are inserted into Eq. (31), H^I_{elast} can be written as

$$\begin{aligned} H^I_{\text{elast}} = {} & \tfrac{1}{2} \sum_{a,b} {}^a w^m_\mu \, {}^b t^{mn}_{\mu\nu} \, {}^a w^n_\nu \, \tau_a \tau_b \\ & + \tfrac{1}{4} \sum_{a,b,c} {}^{a,c} s^m_\mu \, {}^b t^{mn}_{\mu\nu} \, {}^{(a,c)} s^n_\nu \, \tau_a \tau_b \tau_c \, . \end{aligned} \tag{43}$$

With the definitions for the induced forces ${}^b\psi^{I,m}_\mu$ and ${}^b\theta^{I,m}_\mu$ [Eqs. (6) and (7)], Eq. (43) becomes

$$\begin{aligned} H^{I}_{\text{elast}} &= \tfrac{1}{2}\sum_{a,b} {}^{b}\psi_{\mu}^{I,m}\,{}^{a}w_{\mu}^{m}\,\tau_a\tau_b \\ &\quad + \tfrac{1}{4}\sum_{a,b,c} {}^{b}\theta_{\mu}^{I,m}\,{}^{(a,c)}s_{\mu}^{m}\,\tau_a\tau_b\tau_c \;. \end{aligned} \tag{44}$$

In this form H^{I}_{elast} cannot be written in terms of the total forces and total displacement as H^{0}_{elast} was in Eq. (36), and so cannot be derived as a function of stress and strain. The final result we are looking for, however, is a relationship similar to Eq. (40), in which H^{0}_{elast} was given as a function of the permanent force-dipole tensors. An expression for H^{I}_{elast} that is analogous to Eq. (40) can be achieved by assuming that if the defects are placed in a regular fashion, then the strain fields of the defects will be approximately additive. This is equivalent to saying that a contribution to the homogeneous strain can be assigned to each defect.

The contribution from an individual defect to the total strain field can be found by considering Eq. (8) which, in the limit of a regular or spatially average distribution of defects, $\sum_a \tau_a \rightarrow N_L \sum_x c_x$, becomes

$$\begin{aligned} v_{\mu}^{0,m} = -N_L \sum_{x} \Biggl[& (N_L/N_{\text{H}}^{x})\,{}^{a}w_{\mu}^{m} \\ & + \tfrac{1}{2}\sum_{y} (N_L^2/N_{\text{H}}^{x}N_{\text{H}}^{y}) \Biggl[\sum_{c} {}^{(c,a)}s_{\mu}^{m} \Biggr] c_y \Biggr] c_x \;. \end{aligned} \tag{45}$$

The summation has been broken up so that a is on the xth sublattice and c is on the yth sublattice. The factor N_L/N_{H}^{x} is again unity for tetrahedral sites in bcc metals, and can be ignored. A macroscopic expression for the displacement $v_{\mu}^{0,m}$ can also be found for a homogeneous strain $\epsilon_{\mu\iota}^{0}$ by writing $v_{\mu}^{0,m} = \epsilon_{\mu\iota}^{0} R_{\iota}^{m}$, as a function of the permanent force-dipole tensors using Eqs. (13), (15), and (36) of I:

$$v_{\mu}^{0,m} = (S_{\mu\iota\nu\lambda}^{0}/\Omega) \left[\sum_{x} \left\{ P_{\nu\lambda}^{(x)} + \sum_{y}\sum_{k} {}^{k}\Pi_{\nu\lambda}^{(x,y)} c_y \right\} c_x \right] R_{\iota}^{m} \;, \tag{46}$$

where k is the interstitial shell number, defining what shell of interstitial sites c is in with respect to a. Equations (45) and (46) have the same concentration dependence, so that we can equate terms to get

$${}^{a}w_{\mu}^{m} = -(S_{\mu\iota\nu\lambda}^{0} P_{\nu\lambda}^{(x)}/\Omega N_L) R_{\iota}^{m} \tag{47}$$

and

$${}^{(c,a)}s_{\mu}^{m} = -(S_{\mu\iota\nu\lambda}^{0}\;{}^{k}\Pi_{\nu\lambda}^{(x,y)}/\Omega N_L) R_{\iota}^{m} \tag{48}$$

for a and c on the xth and yth sublattices, respectively.

Equations (47) and (48) can be combined with the expressions for the induced force-dipole tensors ${}^{b}P_{\nu\lambda}^{I,a}(=R_{\nu}^{m}\;{}^{b}\psi_{\lambda}^{I,m})$ and ${}^{b}\Pi_{\nu\lambda}^{I,(a,c)}(=R_{\nu}^{m}\;{}^{b}\theta_{\lambda}^{I,m})$ [Eq. (70) of I] to become

$$\begin{aligned} H^{I}_{\text{elast}} &= -(1/2\Omega N_L) \sum_{a,b} {}^{b}P_{\lambda\nu}^{I,(a)} S_{\nu\lambda\iota\mu}^{0} P_{\iota\mu}^{(x)} \tau_a\tau_b \\ &\quad -(1/2\Omega N_L) \sum_{a,b,c} {}^{b}\Pi_{\lambda\nu}^{I,(a,c)} S_{\nu\lambda\iota\mu}^{0}\;{}^{k}\Pi_{\iota\mu}^{(x,z)} \tau_a\tau_b\tau_c \;. \end{aligned} \tag{49}$$

For the case of a homogeneous distribution of H atoms, $\tau_a \simeq \langle \tau_a \rangle = \sum_x c_x$ and $\sum_b \tau_b = N_L \sum_x c_x$. Equation (49) may be written as

$$\begin{aligned} H^{I}_{\text{elast}} &= -(1/2\Omega) \sum_{x,y} \left[\sum_{a} {}^{b}P_{\lambda\nu}^{I,(a)} \right] S_{\nu\lambda\iota\mu}^{0} P_{\iota\mu}^{(x)} c_x c_y \\ &\quad -(1/2\Omega) \sum_{x,y,z}\sum_{k} \left[\sum_{a} {}^{b}\Pi_{\lambda\nu}^{I,(a,c)} \right] S_{\nu\lambda\iota\mu}^{0}\;{}^{k}\Pi_{\iota\mu}^{(x,z)} c_x c_y c_z \end{aligned} \tag{50}$$

which becomes

$$\begin{aligned} H^{I}_{\text{elast}} &= -(N_L/2\Omega) \sum_{x,y} P_{\lambda\nu}^{I,(y)} S_{\nu\lambda\iota\mu}^{0} P_{\iota\nu}^{(x)} c_x c_y \\ &= -(N_L/2\Omega) \sum_{k}\sum_{x,y,z} {}^{k}\Pi_{\lambda\nu}^{I,(y)} S_{\nu\lambda\iota\mu}^{0}\;{}^{k}\Pi_{\iota\mu}^{(x,z)} c_x c_y c_z \end{aligned} \tag{51}$$

when the expressions from Eq. (89) of paper I are inserted. This expression for H^{I}_{elast} depends only on the permanent and induced force-dipole tensors, in analogy with the expression for H^{0}_{elast} in Eq. (40). Because these quantities are macroscopic, H^{I}_{elast} is also macroscopic; i.e., it will depend on the boundary conditions of the crystal.

We can now relate the individual components of Eq. (51) to the induced interaction energies in Eq. (31). For a homogeneous distribution of H atoms $\sum_a \tau_a = \sum_x c_x$, Eq. (31) becomes

$$\begin{aligned} H^{I}_{\text{elast}} &= (N_L/2) \sum_{x,y} \left[(N_L/N_{\text{H}}^{y}) \sum_{b} W_{ab}^{I,xy} \right] c_x c_y \\ &\quad + (N_L) \sum_{x,y,z} \left[(N_L^2/4N_{\text{H}}^{y}N_{\text{H}}^{z}) \sum_{b,c} W_{abc}^{I,yz} \right] c_x c_y c_z \;, \end{aligned} \tag{52}$$

where the superscripts x, y, and z restrict the summations over a, b, and c to a on the xth sublattice, b on the yth sublattice, etc. A comparison of Eq. (52) with (51) gives the following relationships:

$$\begin{aligned} \sum_{b} W_{ab}^{I,xy} &= -(1/\Omega) P_{\lambda\nu}^{I,(y)} S_{\nu\lambda\iota\mu}^{0} P_{\iota\mu}^{(x)} \;, \\ \tfrac{1}{2}\sum_{b,c} W_{abc}^{I,xyz} &= -(1/\Omega) \sum_{k} {}^{k}\Pi_{\lambda\nu}^{I,(y)} S_{\nu\lambda\iota\mu}^{0}\;{}^{k}\Pi_{\iota\mu}^{(x,z)} \;, \end{aligned} \tag{53}$$

since $N_L/N_{\text{H}}^{x} = 1$. These expressions will be used in a following section to determine the elastic energy in a finite lattice and to compare with the result for a lattice with periodic boundary conditions.

D. Free-surface correction to the elastic interaction

In a statistical mechanics calculation of a metal-hydride free-energy, the short-range and long-range elastic interaction terms are treated separately. The short-range elastic interactions between hydrogen atoms may be evaluated assuming an infinite lattice since the lattice atoms will deviate only slightly from their periodicity in the interior of the metal. These short-range interactions are summed into the so-called reference system Hamiltonian H_0 and the free energy associated with the Hamiltonian, the reference system free energy $F_0(N,T)$, is calculated. The longer-range elastic interactions between hydrogen atoms must be evaluated using the real boundary condition, since the long-range strain fields of the H atoms will interact with the stresses acting at the surface of the metal. This additional energy that is present in the real lattice but does not occur in the infinite lattice is the free-surface correction.

Because the free-surface correction to the elastic interaction energy is long range, the free energy associated with this correction may be calculated using the mean-field approximation (1). Since a mean-field treatment is equivalent to treating the system as though the hydrogen atom were uniformly distributed, the free-surface correction may be evaluated assuming a homogeneous distribution. Thus the free-surface correction is $H_{\text{elast}} - \widetilde{H}_{\text{elast}}$, where the infinite lattice Hamiltonian $\widetilde{H}_{\text{elast}}$ is given by the sum of H^0_{elast} [Eq. (41)] and H^I_{elast} [Eq. (52)], and the finite lattice Hamiltonian H_{elast} is given by the sum of H^0_{elast} [Eq. (40)] and H^I_{elast} [Eq. (51)]. The total free energy $F(N,T)$ of the crystal with a free surface is found by adding $F_0(N,T)$ and the free-surface correction

$$F(N,T) = F_0(N,T) + (H_{\text{elast}} - \widetilde{H}_{\text{elast}}) \ . \tag{54}$$

The free-surface correction per interstitial site is

$$\begin{aligned}(1/N_{\text{H}})(H_{\text{elast}} - \widetilde{H}_{\text{elast}}) = \tfrac{1}{2} \Bigg[& \sum_{x,y} \left[(N_{\text{H}}/N^y_{\text{H}}) \sum_b (\Delta W^{0,xy}_{ab} + \Delta W^{I,xy}_{ab}) \right] \tau_x \tau_y \\ & + \sum_{x,y,z} (N^2_{\text{H}}/N^y_{\text{H}} N^z_{\text{H}}) \left[\sum_{b,c} \Delta W^{0,yz}_{abc} + \tfrac{1}{2} \sum_{b,c} \Delta W^{I,yz}_{abc} \right] \tau_x \tau_y \tau_z \\ & + \sum_{x,y,z,w} \left[\tfrac{1}{4} (N^3/N^y_{\text{H}} N^z_{\text{H}} N^w_{\text{H}}) \sum_{b,c,d} \Delta W^{0,xyzw}_{abcd} \right] \tau_x \tau_y \tau_z \tau_w \Bigg] \ ,\end{aligned} \tag{55}$$

where $\Delta W = W - \widetilde{W}$, the difference between the finite lattice and infinite lattice elastic interactions, and $\tau_x = c_x(N_L/N_{\text{H}})$. Equation (55) can be written as

$$\begin{aligned}(1/N_{\text{H}})(H_{\text{elast}} - \widetilde{H}_{\text{elast}}) = \tfrac{1}{2} \Bigg[& \sum_{x,y} \gamma^{xy}_1 \tau_x \tau_y + \sum_{x,y,z} \gamma^{xyz}_2 \tau_x \tau_y \tau_w \\ & + \sum_{x,y,z,w} \gamma^{xyzw}_3 \tau_x \tau_y \tau_z \tau_w \Bigg] \ ,\end{aligned} \tag{56}$$

where the quantities γ^{xy}_1, γ^{xyz}_2, and γ^{xyzw}_3 are defined here to be

$$\begin{aligned}\gamma^{xy}_1 &= (N_{\text{H}}/N^y_{\text{H}}) \sum_b (\Delta W^{0,xy}_{ab} + \Delta W^{I,xy}_{ab}) \ , \\ \gamma^{xyz}_2 &= (N^2_{\text{H}}/N^y_{\text{H}} N^z_{\text{H}}) \left[\sum_{b,c} \Delta W^{0,yz}_{abc} + \tfrac{1}{2} \sum_{b,c} \Delta W^{I,yz}_{abc} \right] \ , \\ \gamma^{xyzw}_3 &= (N^3_{\text{H}}/4 N^y_{\text{H}} N^z_{\text{H}} N^w_{\text{H}}) \left[\sum_{b,c,d} \Delta W^{0,xyzw}_{abcd} \right] \ .\end{aligned} \tag{57}$$

If the free-surface correction is computed in the harmonic approximation, as is done by Horner and Wagner,[2,3] the result is simply the part of Eq. (55) that is due to $\Delta W^{0,xy}_{ab}$:

$$\begin{aligned}(1/N_{\text{H}})(H_{\text{elast}} - \widetilde{H}_{\text{elast}})_{\text{harmonic}} &= \tfrac{1}{2} \sum_{x,y} \left[(N_{\text{H}}/N^y_{\text{H}}) \sum_b \Delta W^{0,xy}_{ab} \right] \tau_x \tau_y \\ &= \tfrac{1}{2} \sum_{x,y} \gamma^{xy}_0 \tau_x \tau_y \ ,\end{aligned} \tag{58}$$

where the coefficient γ^{xy}_0 is given by

$$\gamma^{xy}_0 = (N_{\text{H}}/N^y_{\text{H}}) \sum_b \Delta W^{0,xy}_{ab} \ . \tag{59}$$

In the following discussion Eqs. (58) and (59) will be called the harmonic-approximation formula for the free-surface correction, while Eqs. (56) and (57) will be called the FHLA formula for the free-surface correction.

The hydrogen chemical potential $\mu = \partial[F(N,T)/N_{\text{H}}]/\partial\tau$ may be separated into a reference term μ_0 and a contribution from the free-surface correction $\Delta\mu$ (Refs. 1 and 2). Since the latter is a mean-field quantity it is easily found to be

$$\begin{aligned}\Delta\mu &= \partial[(1/N_{\text{H}})(H_{\text{elast}} - \widetilde{H}_{\text{elast}})]/\partial\tau \\ &= \sum_{x,y} (N^x_{\text{H}}/N_{\text{H}}) \gamma^{xy}_1 \tau_y + \tfrac{3}{2} \sum_{x,y,z} (N^x_{\text{H}}/N_{\text{H}}) \gamma^{xyz}_2 \tau_y \tau_w \\ &\quad + 2 \sum_{x,y,z} (N^x_{\text{H}}/N_{\text{H}}) \gamma^{xyz}_3 \tau_y \tau_z \tau_w\end{aligned} \tag{60}$$

for the FHLA treatment, and

$$\Delta\mu_{\text{harmonic}} = \sum_{x,y} (N^x_{\text{H}}/N_{\text{H}}) \gamma^{xy}_0 \tau_y \tag{61}$$

in the harmonic approximation. The variation with hydrogen concentration of these two correction factors and their effect on phase formation will be discussed in the next section.

IV. EVALUATION OF THE FREE-SURFACE CORRECTION TO THE CHEMICAL POTENTIAL

The effect of these additional many-body and induced interactions is most easily seen by considering the free-surface correction to the chemical potential. This correction depends on the magnitude of the terms $\Delta W_{ab} = W_{ab} - \widetilde{W}_{ab}$, $\Delta W_{abc} = W_{abc} - \widetilde{W}_{abc}$, etc. With the sums in Table IV the coefficients in Eq. (57) are found to be

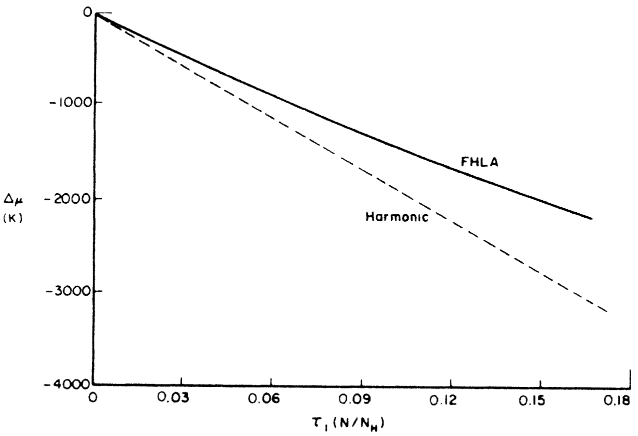

FIG. 1. Comparison of the free-surface correction to the chemical potential $\Delta\mu$ in the FHLA and in the harmonic approximation.

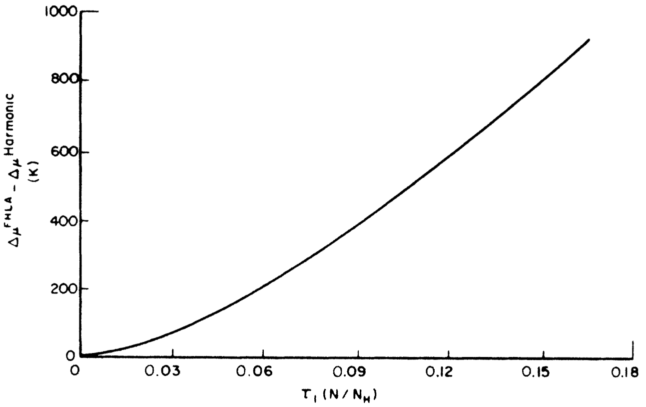

FIG. 2. The difference between the free-surface correction to the chemical potential $\Delta\mu$ in the FHLA and in the harmonic approximation.

$$\gamma_1^{xy} = -16830\ \text{K}\ ,$$

$$\gamma_2^{xyz} = -27122\ \text{K}\ ,$$

$$\gamma_3^{xyzw} = -52417\ \text{K}\ .$$

Although the three- and four-body coefficients are quite large, they are multiplied with additional τ_x terms in Eq. (55), so that their contributions to the energy are not as large as the coefficients imply. For the harmonic approximation the free-surface correction is given by Eq. (58) with the coefficient

$$\gamma_0^{xy} \equiv -18150\ \text{K}\ .$$

The value of γ_1^{xy} differs from γ_0^{xy} for Horner and Wagner because γ_1^{xy} includes $\tilde{W}^{I}_{ab}$ as well as $\tilde{W}^{0}_{ab}$ terms, while γ_0^{xy} includes only $\tilde{W}^{0}_{ab}$ terms. Using the coefficients calculated above, $\Delta\mu$ the free-surface correction to the chemical potential in the FHLA [Eq. (60)] and in the harmonic approximation [Eq. (61)] are plotted in Fig. 1. While $\Delta\mu$ for the harmonic approximation decreases linearly with τ, $\Delta\mu$ for the FHLA has a slight curvature due to the τ^2 and τ^3 terms. This curvature can be better detected by plotting the difference in the two calculated by the two methods, as shown in Fig. 2. The large difference between the values for $\Delta\mu$ in the FHLA formula and in the harmonic approximation means that critical phenomena will be suppressed to lower temperatures in the FHLA. No predictions about the magnitude of the change in critical temperatures can be made here, however, since μ will also depend on μ_0 which will be different in the FHLA treatment from its value in the harmonic-approximation treatment.

The preceding calculations demonstrate the importance of many-body effects on metal-hydride thermodynamics, and the improvement of the FHLA over the harmonic approximation in describing the changes in elastic properties and elastic energy that occur during hydrogenation. As Oates and Stoneham[8] have noted, the significance of the many-body interactions may be greatest during development of order and during nucleation of a new phase, energetically. Although the complexity of the many-body interactions makes it difficult to perform a lattice-gas calculation of the phase behavior, it is felt that results of the FHLA should be used in any further statistical mechanical calculations.

These are also the first calculations to account for the effect of the H-H forces on the elastic energy of a concentrated metal hydride. Normally a solid solution of gas atoms in a metal has a very low concentration, and defect-defect forces are assumed to be nonexistent in the calculation of elastic energies. Metal hydrides can have very high densities, however, and the additional elastic energy that comes from the H-H forces (in the form of the indirect H-H forces) is significant. These H-H forces will also cause many-body electronic interactions, but it is not possible to estimate how large these interactions will be.

ACKNOWLEDGMENT

The authors gratefully acknowledge support by the National Science Foundation, under Grant No. CHE-85-14808.

---

*Present address: ARCO Oil and Gas Company, 2300 West Plano Parkway, Plano, TX 75075.

†Present address: Department of Chemical Engineering, North Carolina State University, Raleigh, NC 27695-7905.

[1] A. I. Shirley and C. K. Hall, preceding paper, Phys. Rev. B 33, xxxx (1986).
[2] H. Wagner and H. Horner, Adv. Phys. 23, 587 (1974).
[3] H. Horner and H. Wagner, J. Phys. C 7, 3305 (1974).
[4] A. G. Khachaturyan and G. A. Shatalov, Acta Met. 23, 1089 (1975).

[5] M. S. Blanter and A. G. Khachaturyan, Phys. Status Solidi A **51**, 291 (1979).

[6] I. Kramer, Diplomarbeit in Physik, Aachen, West Germany, 1980.

[7] M. Futran, S. G. Coats, C. K. Hall, and D. O. Welch, J. Chem. Phys. **77**, 6223 (1982).

[8] W. A. Oates and A. M. Stoneham, J. Phys. F **13**, 2427 (1983).

[9] M. Futran, Ph.D. thesis, Princeton University, 1985.

[10] M. Futran and C. K. Hall, J. Chem. Phys. (to be published).

[11] M. A. Pick and R. Bausch, J. Phys. F **6**, 1751 (1973).

[12] T. Schober and H. Wenzl, Scripta Met. **10**, 819 (1976).

[13] W. Pesch, T. Schober, and H. Wenzl, Scripta Met. **12**, 815 (1978).

[14] G. Mair, K. Bickmann, and H. Wenzl, Z. Phys. Chem. (Frankfurt am Main) **114**, 29 (1979).

[15] H. R. Schober and V. Lottner, Z. Phys. Chem. (Frankfurt am Main) **114**, 203 (1979).

[16] M. Amano, F. M. Mazzola, and H. K. Birnbaum, Acta Met. **31**, 1949 (1983).

[17] H. Trinkhaus, in *Proceedings of the Conference on Fundamental Aspects of Radiation Damage in Metals, Gatlinburg, Tennessee,* National Technical Information Service, edited by M. T. Robinson and F. W. Young, Jr. (U.S. GPO, Washington, D.C., 1976), Vol. 1, p. 258.

[18] C. E. Soteros, A. I. Shirley, and C. K. Hall, (unpublished).

[19] N. A. Johnston and C. A. Sholl, J. Phys. F **10**, 2375 (1980).

[20] G. Liebfried and N. Breuer, *Point Defects in Metals I* (Springer, Berlin, 1978).

[21] P. H. Dederichs, C. Lehmann, and A. Scholz, Z. Phys. B **20**, 155 (1975).