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Elastic interactions between hydrogen atoms in metals. I. Lattice forces and displacements

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This is the first of a series of papers in which a second-order perturbation theory is derived for the Hamiltonian of a metal hydride. The theory, which is called the fully harmonic lattice approximation, or FHLA, goes beyond the customary harmonic treatment of Horner and Wagner to include second-order terms for the hydrogen-hydrogen and metal-hydrogen potentials. These terms account for the hydrogen-concentration dependences of a metal hydride's volume and elastic constants; their inclusion should result in a better representation of the free-energy and phase-change behavior at high hydrogen concentration. In this paper, the forces between hydrogen atoms and metal atoms are evaluated using the FHLA. Two types of forces result: direct forces, between an isolated hydrogen atom and a metal atom, and indirect forces, which are effective forces between a hydrogen atom and a metal atom caused by the presence of a neighboring hydrogen atom. Both the direct and indirect forces each have two components: a permanent part, which is equivalent to the force exerted by a hydrogen atom on a metal atom in the pure (hydrogen-free) metal lattice, and an induced part, which corrects the permanent part for the effects of the hydrogen atom on the metal-metal couplings. These four forces are evaluated for the hydrogen-niobium system. The indirect forces have one-tenth the magnitude and are of opposite sign to the direct forces. The induced component of the force is approximately one-third the size of the permanent component, and opposite to it in sign. The displacements of the metal atoms surrounding an isolated hydrogen atom or a pair of hydrogen atoms are also evaluated. These are compared with the results of previous harmonic-approximation calculations and of experiments on the hydrogen-niobium system. In a subsequent paper these forces are used to evaluate the elastic interaction of hydrogen atoms in a metal.

INTRODUCTION

The harmonic approximation serves as the starting point for most theories of interstitial solid solutions. It was used by Horner and Wagner[1,2] in their treatment of the α-α' transition in hydrogen-niobium systems and has been used by others[3-6] to predict the formation of dilute ordered phases (e.g., $V_{16}O$) in metals containing the heavy-gas atoms, e.g., oxygen, nitrogen, and carbon. While the harmonic approximation appears to be adequate to the description of dilute ordered phases in metals containing heavy gases, it is inadequate to the description of ordered phases in hydrogen-metal systems since these occur at high concentrations. The reasons for this are twofold: (1) the harmonic treatment of elastic interactions does not take into account three- and four-body effects which become important when hydrogen atoms are close together as in concentrated systems, and (2) the harmonic theory does not include an adequate treatment of electronic interactions. These limitations are of little consequence for the case of dilute ordered phases of heavy-gas atoms in metals because the distance between interstitials is large enough so that electronic interactions (which are short ranged compared to elastic interactions) are unimportant and because many-body elastic interaction terms are negligible at these distances. However, in metal hydrides, where ordered phases are concentrated and hydrogen-hydrogen separations are small, electronic interactions and many-body elastic interactions are both important.[7-10] Thus the failure of the Horner and Wagner theory to predict the correct ordered phases in hydrogen-metal systems may be traced to the inadequacies of their harmonic-approximation treatment.

It is appropriate to ask which of the two inadequacies in the Horner and Wagner theory is most responsible for the theory's inability to predict the correct ordered phases at high concentrations. Our initial viewpoint on this matter was that the fault lay entirely with the crude approximation used to treat the electronic interactions. However, based on work by Futran and Hall,[10] who showed that it was impossible to find a set of pairwise electronic interactions which could predict simultaneously the disordered phases α and α' and the ordered phases β and ϵ, we have come to the view that the restriction to pairwise interactions is equally to blame.

There is both experimental and theoretical evidence for the importance of many-body interactions between hydrogen atoms in metal hydrides. Oates and Stoneham[8] used a potential-energy method to determine the relaxation energies of various configurations of H atoms in a Pd lattice. They assumed explicit forms for the pairwise Pd-H and Pd-Pd potentials as functions of atomic separations. These potentials were summed over the atomic positions of the Pd and H atoms in a particular configuration to give a total configuration-dependent energy. Rather than solve for the equilibrium displacements and interaction energies using the harmonic approximation, Oates and Stoneham used a computer simulation technique in which the total energy was minimized to give the equilibrium locations of the Pd and H atoms. With these positions known, the interaction energy for an n-body cluster of H atoms can be calculated as the relaxation energy of the n-body cluster minus the relaxation energy of n isolated H atoms. Thus, Oates and Stoneham were able to show the existence of many-body elastic interactions even in a system composed of two-body potentials. Their work must be interpreted carefully, however, since their results were sensitive to the assumptions used in the formulation of the potentials. The effect of many-body interactions on the thermodynamic properties of Pd-H has been discussed by Kuji *et al.*[7] They performed calorimetric and pressure-composition-temperature measurements on Pd-H samples in the range of the α-α' transition, and found great variations in the excess enthalpy and entropy with hydrogen concentration. They conclude that it is unlikely that pairwise interactions could cause these changes unless the interactions also varied with concentration, which is equivalent to having many-body interactions. The implications are that many-body effects may control the thermodynamic behavior of a metal hydride, at least in the case of Pd-H.

The inability of the Horner-Wagner theory to fully describe the behavior of hydrogen in metals may be traced to the limited order to which the perturbation of the metal hydride Hamiltonian is carried out. Although the expansion of the metal-metal potential is taken to second order, the hydrogen-metal and hydrogen-hydrogen potentials are expanded only to zeroth and first order, respectively. This scheme was chosen because of lack of knowledge concerning the hydrogen-metal and hydrogen-hydrogen potentials. It can be shown, however, that these terms are important at higher hydrogen concentrations. For example, Pick and Bausch[11] and others[12–14] have shown that the orthorhombic strains in β-Nb-H are due to the direct forces between hydrogen atoms which come from the first-order term in the H-H potential. The changes in elastic constants that occur during hydrogen absorption[15–18] result from second-order terms in the M-H and H-H potentials. Schober and Lottner[17] have shown that the localized vibrational modes of hydrogen in Nb, V, and Ta result from one of the second-order terms in the hydrogen-metal potential. Thus it appears that the terms neglected in the Horner-Wagner perturbation of the Hamiltonian have physical significance for the relaxations observed in metal-hydrogen systems upon ordering. This suggests that these neglected terms should be included in the Hamiltonian in order to obtain a correct description of the system's phase-change behavior at high concentrations where ordered phases occur.

Several investigators have previously developed methods that include the effects of some of the neglected second-order perturbation terms on the elastic behavior of a lattice. Dederichs *et al.*[19,20] have derived equations that show how these terms change the couplings between the lattice atoms and therefore change the elastic constants of the lattice. These new couplings will affect how the defect responds to external strains, and will change the strain field near the defect. This phenomena is known as dielastic polarization. The new coupling terms will not only change the elastic constants but will also change the elastic energy of the crystal, giving rise to "induced" interactions between defects in addition to the "permanent" elastic interactions that result from the harmonic approximation. The size of the induced interaction is significant in comparison to that of the permanent interaction. For example, Trinkhaus[21] has calculated the permanent and induced interactions for self-interstitials in Al and Cu, and finds that they are of the same order of magnitude at small defect-defect separations. Kramer[5] has applied the lattice-theory equivalent of Trinkhaus's treatment to the case of hydrogen in Nb. The resulting induced elastic interactions are about $\frac{1}{2}$ as big (with opposite sign) as the permanent elastic interactions, at small separations. From these studies it would appear that neglecting some of the expansion terms in the perturbation of the Hamiltonian (as is done in the harmonic approximation) does not give a complete accounting for the elastic energy of the crystal.

In this paper the fully harmonic lattice approximation (FHLA) to the metal hydride Hamiltonian is derived. This treatment was originally proposed by Pick and Bausch,[11] who developed it to explain the formation of orthorhombic strains in β-Nb-H, and to calculate the force-dipole tensor at high hydrogen concentrations. In this paper the elastic and electronic energy terms in the FHLA are derived, and then the forces and displacements resulting from the FHLA are evaluated. The FHLA includes all terms of the Hamiltonian expansion out to second order in the displacements. This analysis results in a differentiation between two types of forces between hydrogen atoms and metal atoms. We distinguish between direct forces, which act directly between an isolated hydrogen atom and its metal neighbors and indirect forces, which are effective forces between a hydrogen atom and its metal neighbors which arise due to the presence of neighboring hydrogen atoms. These indirect forces are responsible for the orthorhombic strains that occur in β-Nb-H and other ordered phases as was pointed out by Pick and Bausch.[11] Both the direct and indirect forces can be separated into two components: a permanent contribution which is the force exerted by a hydrogen atom on a metal atom in a lattice having the elastic properties of the pure (hydrogen-free) metal lattice and an induced contribution which corrects the permanent interactions for the fact that the coupling constants of the hydrogen-loaded lattice are different from those of the hydrogen-free lattice. In the harmonic-approximation treatment of Horner and Wagner only the permanent-direct forces are taken into account.

In paper II,[22] of this series, the FHLA will be used to evaluate the effective interaction energies between hydrogen atoms. The permanent-direct, permanent-indirect, induced-direct, and induced-indirect hydrogen-metal forces will give rise to permanent-direct, permanent-indirect, induced-direct, and induced-indirect effective elastic interactions 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[1,2–4,9] only permanent-direct interactions were considered with the exception of work by Trinkhaus[21] and Kramer[5] who performed calculations of induced-direct interactions. Our calculations of permanent-indirect and of induced interactions show that these terms make significant contribution to the elastic energy of a hydride. These many-body terms will give thermodynamic properties (e.g., critical points, phase boundaries) which are different from those which result when only pairwise interactions are considered.[23] Using the FHLA formalism the permanent and induced contributions to the direct and indirect forces and force-dipole tensors are calculated. The permanent part of the indirect forces are found to be approximately $\frac{1}{10}$ the magnitude of the permanent-direct forces, and are attractive whereas the permanent-direct forces are repulsive. The induced forces are approximately $\frac{1}{3}$ as large as the permanent forces (either direct or indirect), and are of opposite sign. From our analysis of these force terms it would appear that the permanent-indirect forces and the induced-direct and -indirect forces are approximately 40% of the magnitude of the permanent-direct forces, and that ignoring them in the energy calculation (as is done in the harmonic approximation, which uses only the permanent-direct forces) gives inaccurate results. For example, the free-surface correction derived for the FHLA is not just a second-order function of τ as it is in the harmonic approximation of Horner and Wagner,[1,2] but also includes third- and fourth-order terms.

As part of the calculations performed here, the displacements of the metal atoms surrounding a hydrogen atom (or pair of H atoms) due to the direct (and indirect) forces are determined. These displacements are compared with previous harmonic-approximation calculations of Johnston and Sholl[23] and Fukai,[24] and with experimental measurements of Behr *et al.*[25] In their calculations Johnston and Scholl used forces exerted by a hydrogen only on its nearest metal-atom neighbors, while Fukai used a Born-Mayer potential to determine forces. The present calculations use forces out to second-nearest metal neighbors that were determined from experimental force-dipole tensors. The displacements due to direct forces compare well with the previous calculations and the experimental values, and a comparison of the displacements due to direct and indirect forces indicate that $|v|^{\text{indirect}}/|v|^{\text{direct}} \sim 0.025$–$0.125$, where $|v|$ is the absolute value of the displacement.

Monte Carlo calculations on systems containing many-body interactions are extremely complex so no attempt to predict a phase diagram is made here. Instead, renormalization-group techniques can be used to reduce the complexity of the lattice of tetrahedral sites to a simpler lattice type with fewer interactions. A report on this lattice-simplification work and on phase-diagram calculations using the cluster-variation technique (which has the ability to handle many-body interactions) on the simplified lattice is planned as paper III of this series.[26]

I. THE FULLY HARMONIC LATTICE APPROXIMATION (FHLA)

A. Metal hydride Hamiltonian

In this section a perturbation expansion of the metal-hydrogen-system Hamiltonian is performed out to second order for all potentials. This is labeled the fully harmonic lattice approximation (FHLA).

Consider an ensemble of N hydrogen atoms in a bcc metal lattice containing N_L metal atoms. The atomic volume of the pure metal is $\Omega = V/N_L$, where V is the crystal's volume and the H atoms will occupy the $N_{\mathrm{H}}(=6\,N_L)$ tetrahedral interstitial sites in the metal lattice. The locations of the host lattice sites and the interstitial sites in the H-free lattice are called $\mathbf{R}^m$ and $\mathbf{Q}^a$, respectively. The interstitial sites are indicated by the letters a, b, c, and d. Metal-atom sites are indicated by the letters m and n. In the hydrogen-loaded lattice, the metal atoms and interstitial sites are displaced to new locations $\mathbf{r}^m$ and $\mathbf{q}^a$, respectively. These displacements are given by $\mathbf{v}^m = \mathbf{r}^m - \mathbf{R}^m$ for the metal atoms and $\mathbf{u}^a = \mathbf{q}^a - \mathbf{Q}^a$ for the interstitial sites. The occupation index $\tau_a = (0,1)$ defines which interstitial sites are occupied.

The Hamiltonian of the hydrogen-loaded lattice is given by[1,2]

$$H = \Phi(\mathbf{r}) + \Psi(\mathbf{r},\mathbf{q},\tau) + \Gamma(\mathbf{q},\tau)\ , \tag{1}$$

where Φ is the metal-metal potential, Ψ is the metal-hydrogen potential, and Γ is the H-H potential. The FHLA consists of expanding this Hamiltonian in powers of $\mathbf{v}^m$ and $\mathbf{u}^a$ out to second order:

$$\begin{aligned} H = {} & \Phi(\mathbf{R}) + \Psi(\mathbf{R},\mathbf{Q},\tau) + \Gamma(\mathbf{Q},\tau) + \Phi^m_\mu v^m_\mu + \tfrac{1}{2}\Phi^{mn}_{\mu\nu} v^m_\mu v^n_\nu \\ & + \Psi^a_\mu(\tau) u^a_\mu + \tfrac{1}{2}\Psi^{ab}_{\mu\nu} u^a_\mu u^b_\nu + \Psi^m_\mu(\tau) v^m_\mu + \tfrac{1}{2}\Psi^{mn}_{\mu\nu} v^m_\mu v^n_\nu \\ & + \Gamma^a_\mu(\tau) u^a_\mu + \tfrac{1}{2}\Gamma^{ab}_{\mu\nu} u^a_\mu u^b_\nu + \Psi^{ma}_{\mu\nu} v^m_\mu u^a_\nu\ , \end{aligned} \tag{2}$$

where the double summation convention is assumed; e.g., $\Phi^{mn}_{\mu\nu} v^m_\mu v^n_\nu = \sum_{m,n} \sum_{\mu,\nu} \Phi^{mn}_{\mu\nu} v^m_\mu v^n_\nu$, and greek character subscripts indicate x, y, or z directions. The displacement $\mathbf{v}^m$ and $\mathbf{u}^a$ are taken here to represent the static part of the displacements only. Vibrational displacements will also occur, but these will decouple from the static displacements in the expansion because they have a time average of zero.[1] The vibrational displacements are independent of hydrogen concentration, and thus do not affect the metal hydride's phase behavior. The expansion terms in Eq. (2) are defined as

$$\begin{aligned} &\Phi^m_\mu = \partial\Phi/\partial r^m_\mu\ , \\ &\Psi^a_\mu(\tau) = \partial\Psi/\partial q^a_\mu\ , \\ &\Psi^m_\mu(\tau) = \partial\Psi/\partial r^m_\mu\ , \\ &\Gamma^a_\mu(\tau) = \partial\Gamma/\partial q^a_\mu\ , \\ &\Phi^{mn}_{\mu\nu} = \partial(\partial\Phi/\partial r^m_\mu)/\partial r^n_\nu\ , \\ &\Psi^{ab}_{\mu\nu} = \partial(\partial\Psi/\partial q^a_\mu)/\partial q^b_\nu\ , \\ &\Psi^{mn}_{\mu\nu} = \partial(\partial\Psi/\partial r^m_\mu)/\partial r^n_\nu\ , \\ &\Psi^{ma}_{\mu\nu} = \partial(\partial\Psi/\partial r^m_\mu)/\partial q^a_\nu\ , \\ &\Gamma^{ab}_{\mu\nu} = \partial(\partial\Gamma/\partial q^a_\mu)/\partial q^b_\nu\ , \end{aligned}$$

where each is evaluated at the rest positions $\mathbf{Q}^a$ and $\mathbf{R}^m$. The first partial differential quantities are the forces and the second partial differential quantities are the couplings or force constants.

The terms in Eq. (2) may be interpreted physically as follows: the Φ^m_μ is the negative of the force exerted by all metal atoms on the metal atom at m in direction μ, $\Psi^m_\mu(\tau)$ is the negative of the force exerted by all hydrogen atoms on the metal atom at m, $\Psi^a_\mu(\tau)$ is the negative of the force exerted by all the metal atoms on the H atom at a, and $\Gamma^a_\mu(\tau)$ is the negative of the force exerted by all the hydrogen atoms on the H atom at a. The forces $-\Phi^m_\mu$ and $-\Psi^a_\mu$ are identically zero since this defines the rest positions $\mathbf{R}^m$ and $\mathbf{Q}^a$, but the forces $-\Psi^m_\mu(\tau)$ and $-\Gamma^a_\mu(\tau)$ are not equal to zero since they must balance the surface forces acting on a real crystal.[11]

The couplings $\Phi^{mn}_{\mu\nu}$ are the force constants of the pure metal. The couplings $\Psi^{mn}_{\mu\nu}$ are the changes in the metal force constants due to the presence of hydrogen. The $\Psi^{ma}_{\mu\nu}$ are couplings between the metal atoms and the hydrogen atoms, and the sum $\Gamma^{ab}_{\mu\nu}+\Psi^{ab}_{\mu\nu}$ is the coupling between the hydrogen atoms in the metal matrix. The couplings have inversion symmetry; i.e., $\Phi^{nm}_{\mu\nu}=\Phi^{nm}_{\nu\mu}$, and matrix symmetry; i.e., $\Phi^{mn}_{\mu\nu}=\Phi^{nm}_{\mu\nu}$; this also applies for $\Psi^{ma}_{\mu\nu}$, $\Psi^{ab}_{\mu\nu}$, $\Gamma^{ab}_{\mu\nu}$, and $\Psi^{mn}_{\mu\nu}$.

The equilibrium FHLA Hamiltonian is found from the mechanical equilibrium conditions $\partial H/\partial v^m=\partial H/\partial u^a=0$ which gives the equilibrium values of the displacements $\mathbf{u}^a$ and $\mathbf{v}^m$. This provides a relationship between the forces and the displacements:

$$(\Phi^{mn}_{\mu\nu}+\Psi^{mn}_{\mu\nu})v^n_\nu+\Psi^{ma}_{\mu\nu}u^a_\nu=-\Psi^m_\mu(\tau)\ , \tag{3}$$

$$(\Gamma^{ab}_{\mu\nu}+\Psi^{ab}_{\mu\nu})u^b_\nu+\Psi^{am}_{\mu\nu}v^m_\nu=-\Gamma^a_\mu(\tau)\ . \tag{4}$$

When Eqs. (3) and (4) are substituted into Eq. (2), the Hamiltonian becomes

$$H=\Phi(\mathbf{R})+\Psi(\mathbf{R},\mathbf{Q},\tau)+\Gamma(\mathbf{Q},\tau)-\tfrac{1}{2}(\Phi^{mn}_{\mu\nu}+\Psi^{mn}_{\mu\nu})v^m_\mu v^n_\nu$$
$$-\tfrac{1}{2}(\Psi^{ab}_{\mu\nu}+\Gamma^{ab}_{\mu\nu})u^a_\mu u^b_\nu-\Psi^{ma}_{\mu\nu}v^m_\mu u^a_\nu\ , \tag{5}$$

which can also be written in terms of the forces and displacements,

$$H=\Phi(\mathbf{R})+\Psi(\mathbf{R},\mathbf{Q},\tau)+\Gamma(\mathbf{Q},\tau)+\tfrac{1}{2}\Psi^m_\mu(\tau)v^m_\mu$$
$$+\tfrac{1}{2}\Gamma^a_\mu(\tau)u^a_\mu\ . \tag{6}$$

This simple result for the FHLA differs from the Horner and Wagner harmonic-approximation result,

$$H=\Phi(\mathbf{R})+\Psi(\mathbf{R},\mathbf{Q},\tau)+\Gamma(\mathbf{Q},\tau)+\tfrac{1}{2}\Psi^m_\mu(\tau)v^m_\mu \tag{7}$$

in the presence of an extra term, $\frac{1}{2}\Gamma^a_\mu(\tau)u^a_\mu$. In order to transform Eq. (6) into a function of the forces only (rather than both forces and displacements) a relationship between $\mathbf{u}^m$ and $\mathbf{v}^a$ is required. This can be obtained by defining the matrix $\Lambda^{ab}_{\mu\nu}\equiv(\Psi^{ba}_{\nu\mu}+\Gamma^{ba}_{\nu\mu})^{-1}$, inverting Eq. (4) to give

$$u^a_\kappa=-\Lambda^{ab}_{\kappa\mu}\Psi^{bm}_{\mu\nu}v^m_\nu-\Lambda^{ab}_{\kappa\mu}\Gamma^b_\mu(\tau) \tag{8}$$

and then inserting Eq. (8) into (3) to obtain

$$v^m_\mu=-(\Phi^{nm}_{\nu\mu}+\Psi^{nm}_{\nu\mu}-\Psi^{na}_{\nu\alpha}\Lambda^{ab}_{\alpha\beta}\Psi^{bm}_{\beta\mu})^{-1}[\Psi^n_\nu(\tau)-\Psi^{nb}_{\nu\beta}\Lambda^{ba}_{\beta\alpha}\Gamma^a_\alpha]\ . \tag{9}$$

This may be compared with the Horner-Wagner approximation expression for v^m_μ, which is given by

$$v^m_\mu=-(\Phi^{mn}_{\mu\nu})\Psi^n_\nu(\tau)=(D^{mn}_{\mu\nu})^{-1}\Psi^n_\nu(\tau)\ , \tag{10}$$

where $D^{mn}_{\mu\nu}\equiv-(\Phi^{nm}_{\nu\mu})^{-1}$ is the static Green's function in the harmonic approximation.

A comparison of Eqs. (9) and (10) suggests the definition of a new, fully harmonic, static Green's function of the lattice

$$D^{mn}_{\mu\nu}\equiv-(\Phi^{mn}_{\nu\mu}+\Psi^{nm}_{\nu\mu}-\Psi^{na}_{\nu\alpha}\Lambda^{ab}_{\alpha\beta}\Psi^{bm}_{\beta\mu})^{-1} \tag{11}$$

which differs from the Horner and Wagner definition,[1,2] because of the inclusion of higher-order terms in the perturbation. To avoid confusion, the Horner-Wagner Green's function is denoted in this paper as $D^{0,mn}_{\mu\nu}[\equiv-(\Phi^{nm}_{\nu\mu})^{-1}]$, and will be called the Green's function of the ideal (i.e., hydrogen-free) lattice. This is because the interaction energies calculated by Horner and Wagner are calculated for the ideal lattice (i.e., the lattice with the couplings of the pure metal), while the interactions in the FHLA will be calculated for the defect (hydrogen-loaded) lattice. Insertion of Eqs. (8) and (9) into the Hamiltonian in Eq. (6) gives

$$H=\Phi(\mathbf{R})+\Psi(\mathbf{R},\mathbf{Q},\tau)+\Gamma(\mathbf{Q},\tau)$$
$$+\tfrac{1}{2}[\Psi^m_\mu(\tau)-\Psi^{ma}_{\mu\alpha}\Lambda^{ac}_{\alpha\kappa}\Gamma^c_\kappa(\tau)]$$
$$\times D^{mn}_{\mu\nu}[\Psi^n_\nu(\tau)-\Psi^{nb}_{\nu\beta}\Lambda^{bd}_{\beta\delta}\Gamma^d_\delta(\tau)]-\tfrac{1}{2}\Gamma^a_\mu(\tau)\Lambda^{ab}_{\mu\nu}\Gamma^b_\nu(\tau)\ . \tag{12}$$

It is instructive to compare the Hamiltonian of the FHLA, Eq. (12), with the Hamiltonian for the harmonic approximation,

$$H=\Phi(\mathbf{R})+\Psi(\mathbf{R},\mathbf{Q},\tau)+\Gamma(\mathbf{Q},\tau)+\tfrac{1}{2}\Psi^m_\mu(\tau)D^{0,mn}_{\mu\nu}\Psi^n_\nu(\tau)\ . \tag{13}$$

Three differences are apparent:

(1) The Green's function $D^{mn}_{\mu\nu}$ is not that of the pure lattice ($D^{0,mn}_{\mu\nu}$).

(2) There is an additional force term, $\Psi^{ma}_{\mu\alpha}\Lambda^{ac}_{\alpha\kappa}\Gamma^c_\kappa(\tau)$. This quantity is an effective force between hydrogen atoms and metal atoms caused by the presence of neighboring hydrogen atoms. Henceforth it is called the *indirect* force, to differentiate it from the *direct* H-metal forces $-\Psi^m_\mu(\tau)$ and the *direct* H-H forces $-\Gamma^a_\mu(\tau)$. The physical origin of the indirect force and its numerical evaluation will be described in the next section.

(3) An additional electronic interaction term, $-\frac{1}{2}\Gamma^a_\mu(\tau)\Lambda^{ab}_{\mu\nu}\Gamma^b_\nu(\tau)$ is present in the FHLA Hamiltonian. This term is an effective electronic interaction between hydrogen atoms, in addition to the H-H potential $\Gamma(\mathbf{Q},\tau)$. The effective electronic interaction energy serves as a correction to $\Gamma(\mathbf{Q},\tau)$ reflecting the fact that the electronic interactions should be evaluated at the sites in the loaded lattice, $\{\mathbf{q}\}$, and not at the rest sites in the unloaded lattice, $\{\mathbf{Q}\}$. These effective electronic interactions have a many-body dependence on $\{\tau_a\}$ and are important in the formation of ordered structures.[26]

B. Physical origin of the direct and indirect forces

The direct forces of the hydrogen atoms on the metal atom at m, $-\Psi^m_\mu(\tau)$, and of the hydrogen atoms on the H atom at a, $-\Gamma^a_\mu(\tau)$ can be written as sums of the individual forces exerted by the H atoms,

$$-\Psi^m_\mu(\tau)=\sum_a {}^a\psi^m_\mu \tau_a ; \quad -\Gamma^a_\mu(\tau)=\sum_c {}^c\Gamma^a_\mu \tau_c , \tag{14}$$

where ${}^a\psi^m_\mu$ is defined to be the force of a H atom at site a on a metal atom at site m, and ${}^c\Gamma^a_\mu$ is the force of a H atom at c on another hydrogen atom at a. These direct forces are shown schematically in Figs. 1(a) and 1(b). [Note that Horner and Wagner refer to $+\Psi_\mu(\tau)$ as the force of the H atoms on metal atom m whereas we define the negative of the term, i.e., $-\Psi_\mu(\tau)$ to be the force. Given their definition of the potential, their definition of $+\Psi_\mu(\tau)$ as the force is incorrect since the force should be the negative of the potential.]

The indirect forces can be written as sums of forces exerted not by individual hydrogen atoms but by pairs of hydrogen atoms. To simplify notation the indirect force is denoted henceforth by

$$-\Theta^m_\mu(\tau)=\Psi^{ma}_{\mu\alpha}\Lambda^{ac}_{\alpha\kappa}\Gamma^c_\kappa(\tau) , \tag{15}$$

which may be written as

$$-\Theta^m_\mu(\tau)=\sum_{a,c} {}^{ca}\theta^m_\mu \tau_a \tau_c , \tag{16}$$

where ${}^{ca}\theta^m_\mu(=-\Psi^{ma}_{\mu\alpha}\Lambda^{ac}_{\alpha\kappa}\,{}^a\Gamma^c_\kappa)$ is the indirect force exerted by a hydrogen atom at c on a metal atom at m due to the presence of a H atom at a. The physical cause of this indirect force is best understood by examining the schematic in Fig. 1(c). The couplings $\Psi^{ma}_{\mu\alpha}$ can be viewed as "springs" connecting the H atom at a to its metal neighbors, and the total coupling $\Psi^{ac}_{\alpha\kappa}+\Gamma^{ac}_{\alpha\kappa}$ as a "spring" connecting the H atoms at a and c. When hydrogen atom a exerts a direct force ${}^a\Gamma^c_\kappa$ on the H atom at c, the spring $(\Psi^{ac}_{\alpha\kappa}+\Gamma^{ac}_{\alpha\kappa}=\Lambda^{ac}_{\alpha\kappa})$ causes a to be displaced. The magnitude of this displacement is equal to $\Lambda^{ac}_{\alpha\kappa}\Gamma^c_\kappa(\tau)$. The springs $\Psi^{ma}_{\mu\alpha}$ will tend to restore a to its original position; this is equivalent to saying the displacement of a places a force on its metal neighbors. Thus the hydrogen atom at a exerts a force that displaces hydrogen atom c, which in turn causes a force on the metal atom at m.

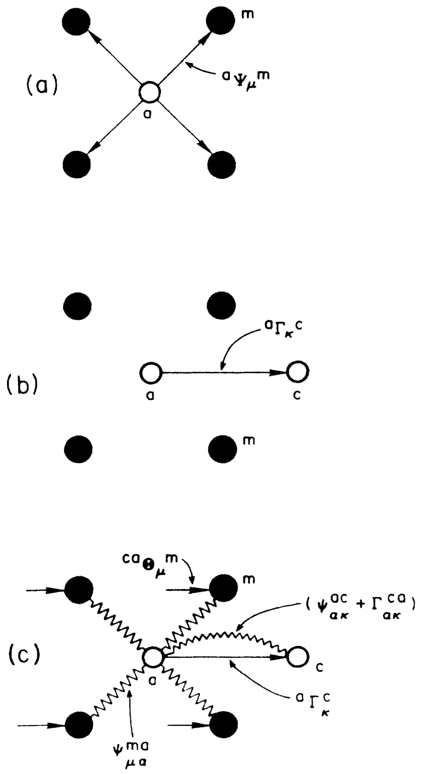

FIG. 1. Spring analogies for (a) the direct force ${}^a\Psi^m_\mu$, (b) the direct force ${}^a\Gamma^c_\kappa$, and (c) the indirect forces ${}^{ca}\Theta^m_\mu$. Large dark circles are metal atoms; small open circles are hydrogen atoms.

The indirect force ${}^{ca}\theta^m_\mu$ does not possess the same invariance properties as ${}^a\psi^m_\mu$. Although the direct force ${}^a\psi^m_\mu$ has translational invariance due to lattice symmetry, $\sum_m {}^a\psi^m_\mu=0$, the indirect force ${}^{ca}\theta^m_\mu$ does not, i.e., $\sum_m {}^{ca}\theta^m_\mu\neq 0$. However, the total of the indirect forces due to the pair (a,c) does have translational invariance, that is, $\sum_m ({}^{ca}\theta^m_\mu+{}^{ac}\theta^m_\mu)=0$, where ${}^{ca}\theta^m_\mu\neq{}^{ac}\theta^m_\mu$ [see Fig. 1(c)]. This is because the sum $\sum_m {}^{ca}\theta^m_\mu$ $(=-\sum_m \Psi^{ma}_{\mu\beta}\Lambda^{ac}_{\beta\alpha}\,{}^a\Gamma^c_\alpha)$ depends only on the direction of the force ${}^a\Gamma^c_\alpha$, and since ${}^c\Gamma^a_\alpha=-{}^a\Gamma^c_\alpha$, then $\sum_m {}^{ca}\theta^m_\mu=-\sum_m {}^{ac}\theta^m_\mu$. Because of this, the definition of $\theta^m_\mu(\tau)$ is changed to

$$-\Theta^m_\mu(\tau)=\tfrac{1}{2}\sum_{a,c} ({}^{ca}\theta^m_\mu+{}^{ac}\theta^m_\mu)\tau_a\tau_c . \tag{17}$$

In order to calculate phase diagrams and thermodynamic properties it is necessary to be able to calculate the direct and indirect forces. Since these forces are on the microscopic level and therefore cannot be measured directly, it is necessary to be able to relate them to macroscopic quantities which can be measured directly. In the next section we show how to relate the direct and indirect forces to the stresses and strains that are measured in a metal hydride.

C. Determination of direct and indirect forces from macroscopic strain measurements

In order to determine the direct and indirect forces appearing in the FHLA, one must be able to relate them to the stresses, $\sigma_{\mu\nu}$, and strains, $\epsilon_{\mu\nu}$, that are measured in a metal hydride. To do this it is necessary to get an explicit relationship for the dependence of the forces on the metal-atom displacements $\mathbf{v}^m$. This is done by eliminating $\mathbf{u}^a$ from Eq. (3) using Eq. (8) to obtain

$$(\Phi^{mn}_{\mu\nu}+\Psi^{mn}_{\mu\nu}-\Psi^{ma}_{\mu\alpha}\Lambda^{ab}_{\alpha\beta}\Psi^{bn}_{\beta\nu})v^n_\nu=-\Psi^m_\mu(\tau)-\Theta^m_\mu(\tau) , \tag{18}$$

where the $\Theta^m_\mu(\tau)$ notation for the indirect force has been inserted. If the displacements are assumed to be homogeneous (uniform throughout the lattice) then the displacements are related to the strain fields by $v^n_\nu=\epsilon_{\nu\lambda}R^n_\lambda$ (Ref. 27). This gives

$$(\Phi^{mn}_{\mu\nu}+\Psi^{mn}_{\mu\nu}-\Psi^{ma}_{\mu\alpha}\Lambda^{ab}_{\alpha\beta}\Psi^{bn}_{\beta\nu})R^n_\lambda\epsilon_{\nu\lambda}=-\Psi^m_\mu(\tau)-\Theta^m_\mu(\tau) . \tag{19}$$

Equation (19) gives the macroscopically observable strain $\epsilon_{\nu\lambda}$ in terms of the microscopic couplings and forces. It is desirable to manipulate this equation to get a relationship between stresses and strains having the form of Hooke's law. To do this we multiply Eq. (19) by R^m_ι/V and sum over repeated indices:

$$(1/V)R^m_\iota(\Phi^{mn}_{\mu\nu}+\Psi^{mn}_{\mu\nu}-\Psi^{ma}_{\mu\alpha}\Lambda^{ab}_{\alpha\beta}\Psi^{bn}_{\beta\nu})R^n_\lambda\epsilon_{\nu\lambda} = -(1/V)R^m_\iota[\Psi^m_\mu(\tau)+\Theta^m_\mu(\tau)] \,, \qquad (20)$$

thus obtaining a Hooke's law equation for the metal hydride in the FHLA. In the usual notation, Hooke's law can be written as

$$C_{\iota\mu\nu\lambda}\epsilon_{\nu\lambda}=\sigma_{\iota\mu} \,, \qquad (21)$$

where $C_{\iota\mu\nu\lambda}$ is the tensor of elastic moduli for the metal hydride,

$$C_{\iota\mu\nu\lambda}=C_{11}\delta_{\iota\mu}\delta_{\nu\lambda}+C_{44}(\delta_{\iota\nu}\delta_{\mu\lambda}+\delta_{\iota\lambda}\delta_{\mu\nu}) +(C_{11}-C_{12}-2C_{44})\delta_{\iota\mu\nu\lambda} \,, \qquad (22)$$

and $\delta_{\iota\mu}$ is the Kronecker δ function; $\delta_{\iota\mu\nu\lambda}=1$ if $\iota=\mu=\nu=\lambda$, and $=0$ otherwise. When Eq. (21) is compared to Eq. (20), it is found by analogy that

$$\sigma_{\iota\mu}=-(1/V)[R^m_\iota\Psi^m_\mu(\tau)+R^m_\iota\Theta^m_\mu(\tau)] \qquad (23)$$

and

$$C_{\iota\mu\nu\lambda}=(1/V)R^m_\iota(\Phi^{mn}_{\mu\nu}+\Psi^{mn}_{\mu\nu}-\Psi^{ma}_{\mu\alpha}\Lambda^{ab}_{\alpha\beta}\Psi^{bn}_{\beta\nu})R^n_\lambda \,. \qquad (24)$$

This may be compared with the elastic moduli obtained in the harmonic approximation (1), where the equivalent of Eq. (20) is

$$(1/V)R^m_\iota\Phi^{mn}_{\mu\nu}R^n_\lambda\epsilon_{\nu\lambda}=-(1/V)R^m_\iota\Psi^m_\mu(\tau) \,, \qquad (25)$$

leading to a harmonic-approximation stress tensor

$$\sigma^0_{\iota\mu}=-(1/V)R^m_\iota\Psi^m_\mu(\tau) \qquad (26)$$

and a harmonic-approximation tensor of elastic moduli,[24]

$$C^0_{\iota\mu\nu\lambda}=(1/V)R^m_\iota\Phi^{mn}_{\mu\nu}R^n_\lambda \,. \qquad (27)$$

Note that the tensor of elastic moduli in the harmonic approximation is given in terms of the metal-metal force constants for the pure, hydrogen-free lattice, and is therefore independent of hydrogen concentration. In contrast, the elastic moduli obtained in the FHLA are functions of hydrogen concentration due to the presence of the terms $\Psi^{mn}_{\mu\nu}-\Psi^{ma}_{\mu\alpha}\Lambda^{ab}_{\alpha\beta}\Psi^{bn}_{\beta\nu}$ since the $\Psi^{ma}_{\mu\alpha}$ and $\Lambda^{ab}_{\alpha\beta}$ will depend upon the location of the H atoms a and b, and the $\Psi^{mn}_{\mu\nu}$ will depend upon the number of H atoms near m and n. The difference in elastic moduli between the pure metal and the hydrogen-loaded metal is significant at high concentrations; e.g., at $\langle\tau\rangle\equiv N/N_{\rm H}=0.10$, values of $[C_{\iota\mu\nu\lambda}(\langle\tau\rangle=0.1)-C^0_{\iota\mu\nu\lambda}]/C^0_{\iota\mu\nu\lambda}\approx 40\%$ have been measured.[16]

Equation (23) suggests the definition of two force-dipole tensors for the FHLA, one associated with the direct force as described by Horner and Wagner and another associated with the indirect force as first proposed by Pick and Bausch.[11] This is in contrast to the harmonic approximation, where only one force-dipole tensor results. The force-dipole tensor $P_{\iota\mu}$ associated with the direct force, $\Psi^m_\mu(\tau)$, is given by

$$P_{\iota\mu}\equiv-(1/N)R^m_\iota\Psi^m_\mu(\tau)=\sum_m(R^m_\iota-Q^a_\iota)\,{}^a\psi^m_\mu \,, \qquad (28)$$

where the second equality follows from Eq. (14), the translational invariance of ${}^a\psi^m_\mu$ and $\sum_a\tau_a=N$. The direct force ${}^a\psi^m_\mu$ is taken to be a central force between a hydrogen atom and its first- and second-nearest metal neighbors,

$${}^a\psi^m_\mu=\Psi_{1,2}(R^m_\mu-Q^a_\mu) \,, \qquad (29)$$

where Ψ_1 and Ψ_2 are constants for the first and second shells, respectively. For metals in which there is more than one type of interstitial site, Eq. (28) is replaced by

$$P_{\iota\mu}=\sum_x(c_x/c)P^{(x)}_{\iota\mu} \,, \qquad (30)$$

where x refers to each type (sublattice) of site, c is the hydrogen concentration $(=N/N_L)$, and c_x is the concentration on the xth sublattice. The tetrahedral sites in a bcc lattice have tetragonal symmetry; i.e.,

$$P^{(x)}_{\iota\mu}=\begin{bmatrix} A & 0 & 0\\ 0 & B & 0\\ 0 & 0 & B\end{bmatrix} . \qquad (31)$$

With Eqs. (28) and (29), this gives for Ψ_1 and Ψ_2

$$\Psi_1=\frac{9B-2A}{4a^2},\quad \Psi_2=\frac{2A-B}{4a^2} \,. \qquad (32)$$

The force-dipole tensor associated with the indirect force is related to the term $(-1/V)R^m_\iota\Theta^m_\mu(\tau)$ in Eq. (23). The indirect force-dipole tensor is not as easy to calculate as the direct force-dipole tensor, since the individual forces ${}^{ac}\theta^m_\mu$ do not possess translational invariance as the forces ${}^a\psi^m_\mu$ do. However, by considering the total indirect force of the pair (a,c) on m, which is invariant [recall that $\sum_m({}^{ca}\theta^m_\mu+{}^{ac}\theta^m_\mu)=0$], we can define the indirect force-dipole tensor.

The indirect force-dipole tensor associated with H-H pairs (a,c) is denoted by $\Pi_{\iota\mu}$ to distinguish it from the direct force-dipole tensor $P_{\iota\mu}$. It is defined by

$$\Pi_{\iota\mu}\equiv-(N_L/N^2)R^m_\iota\Theta^m_\mu(\tau) =(N_L/2N^2)\sum_{a,c}\sum_m[R^m_\iota-\tfrac{1}{2}(Q^a_\iota+Q^c_\iota)] \times({}^{ac}\theta^m_\mu+{}^{ca}\theta^m_\mu)\tau_a\tau_c \,, \qquad (33)$$

where $\frac{1}{2}(Q^a_\iota+Q^c_\iota)$ is the center of mass of the pair (a,c). The right-hand side of Eq. (33) cannot be reduced to a simple function of c as in Eq. (28) because the forces ${}^{ac}\theta^m_\mu$ will depend upon the distance between the H atoms a and c and their orientations with respect to the metal lattice. Thus, if there are several types of pairs (a,c), where each type has a specific separation and orientation, then each type will have an indirect force-dipole tensor associated with it. The total indirect force-dipole tensor will then be a weighted average of the indirect force-dipole tensors of each type of pair, with the weights being determined according to the population of the individual types of pairs. (The situation here is reminiscent of the case of interstitial dumbbells, which are pairs of metal atoms that occupy interstitial sites in a metal lattice. The force-dipole tensor of a dumbbell will depend on its orientation with respect to the lattice.[19]) A few of the many possible orientations and separations of H-H pairs in a bcc lattice are shown in Fig. 2. For a completely disordered distribution of hydro-

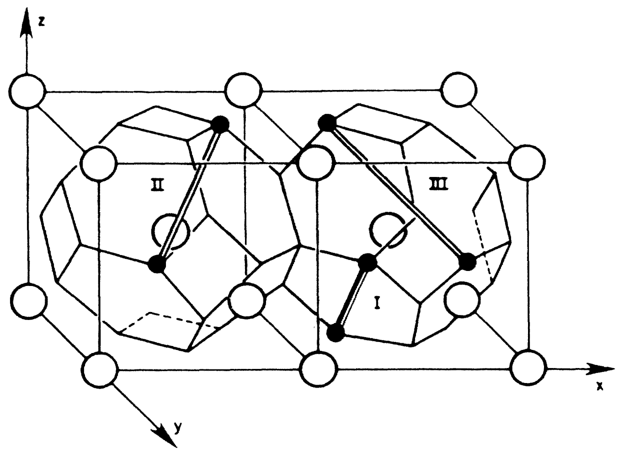

FIG. 2. Possible orientations and separations of pairs of H atoms in a bcc lattice. Orientation I corresponds to $4(Q^c-Q_a)/a=(0,2,2)$; orientation II corresponds to $(2,-2,2)$; and orientation III corresponds to $(2,2,-2)$. These pairs occur in the β phase of Nb-H.

gen atoms, we can substitute $\sum_a \tau_a=N$ and $\tau_c=\langle\tau_c\rangle=N/N_{\mathrm{H}}$, so that the average force-dipole tensor becomes

$$\Pi_{\iota\mu}=(N_L/2N_H)\sum_c\sum_m[R_\iota^m-\tfrac{1}{2}(Q_\iota^c+Q_\iota^a)]({}^{ac}\theta_\mu^m+{}^{ca}\theta_\mu^m)\ , \tag{34}$$

where $\sum_c$ is a summation over all interstitial sites around a.

Although one can calculate $\Pi_{\iota\mu}$ from experimental strain data, there are too many possible types of H-H pairs to permit each ${}^{ac}\theta_\mu^m$ to be determined separately. Some restrictions must be placed on the types of pairs to be considered. Because we are interested in the high-concentration region of the phase diagram, we will consider only those pairs that occur in the β phase of Nb-H (see Fig. 2). In the β phase the indirect forces will cause orthorhombic (noncubic) distortions of the metal lattice. This allows one to calculate ${}^{ca}\theta_\mu^m$ from the off-diagonal elements of the stress tensor $\sigma_{\iota\mu}$. We shall further restrict the types of H-H pairs considered to be nearest neighbors $[4(\mathbf{Q}^a-\mathbf{Q}^b)/a=(0,2,2)]$ and next-nearest neighbors $[4(\mathbf{Q}^a-\mathbf{Q}^b)/a=(2,-2,2)$ or $(2,2,-2)]$ in the lattice formed by the β phase. This will give only two different indirect forces to be determined from the strain data. If we denote the type of H-H pair by the index k, where k is the number of the shell of interstitial sites that c is in with respect to a, then we can replace the sum over c in Eq. (34) with a sum over k. The H atoms at sites a and c may be on different sublattices, in which case the values of k will depend upon the sublattices that a and c are on. If a is on the xth sublattice and c is on the yth sublattice, then Eq. (34) is replaced by

$$\Pi_{\iota\mu}=\sum_{x,y}\Pi_{\iota\mu}^{(x,y)}c_x c_y/c^2\ , \tag{35}$$

where $\Pi_{\iota\mu}^{(x,y)}$ is the indirect force-dipole tensor for the xth and yth sublattices

$$\begin{aligned}\Pi_{\iota\mu}^{(x,y)}&=\sum_k {}^k\Pi_{\iota\mu}^{(x,y)}\\&=(N_L/N_{\mathrm{H}}^y)\sum_c{}^{(y)}\sum_m[R_\iota^m-\tfrac{1}{2}(Q_\iota^c+Q_\iota^a)]\\&\qquad\times({}^{ac}\theta_\mu^m+{}^{ca}\theta_\mu^m)\ .\end{aligned} \tag{36}$$

Here N_{H}^y is the number of interstitial sites on the yth sublattice (for tetrahedral sites, $N_{\mathrm{H}}^y=N_L$), and the notation $\sum_c{}^{(y)}$ indicates a summation over all interstitial sites c on the yth sublattice that surround site a, which is on the xth sublattice.

Our ultimate goal in evaluating $\Pi_{\iota\mu}$ is to be able to calculate ${}^{ac}\theta_\mu^m$, and this requires a knowledge of the couplings $\Psi_{\mu\beta}^{mb}$ and $\Psi_{\alpha\beta}^{ab}+\Gamma_{\alpha\beta}^{ab}=(\Lambda_{\beta\alpha}^{ba})^{-1}$ because we want to know how ${}^{ac}\theta_\mu^m$ depends on $\mathbf{Q}^c-\mathbf{Q}^a$ [see Eqs. (15) and (16)]. The customary approach would be to model them as springlike couplings,[17,20] but the experimental evidence indicates that these couplings should be considered as being "rigid" or nonspringlike. Schober and Lottner[17] calculated $\Psi_{\mu\beta}^{mb}$ for nearest-neighbor hydrogen and metal-atom pairs by fitting them to the high-frequency (>20 T Hz) vibrational modes of H in Nb, Ta, and V. They found these coupling constants to be much larger than the metal-metal coupling constants. At low frequencies, in the range of the acoustic modes of the metal atoms, these springs would be too stiff to stretch. Instead, the tetrahedron formed by the H atom and its four nearest-metal neighbors would move as a single unit, or a rigid body. A similar situation exists for the couplings $\Psi_{\alpha\beta}^{ab}+\Gamma_{\alpha\beta}^{ab}=\Lambda_{\beta\alpha}^{ba}$. Burkel *et al.*[28] found intermediate frequency vibrational modes in highly concentrated α-Nb-D which they attributed to the stretching of the spring between adjacent Nb$_4$D tetrahedra, the springs associated with the $\Psi_{\alpha\beta}^{ab}+\Gamma_{\alpha\beta}^{ab}$ couplings. At lower frequencies this spring would also be too stiff to stretch. From these experimental observations it is concluded that the couplings $\Psi_{\alpha\beta}^{ab}+\Gamma_{\alpha\beta}^{ab}$ and $\Psi_{\mu\alpha}^{ma}$ are not springs, but instead are rigid.

If the M_4-H tetrahedron moves as a rigid body, then translational invariance (see Ref. 24) requires that $\sum_m \Psi_{\mu\kappa}^{mc}+\Psi_{\mu\kappa}^{ca}+\Gamma_{\mu\kappa}^{ca}=0$ or

$$\sum_m \Psi_{\mu\kappa}^{mc}(\Psi_{\mu\kappa}^{ca}+\Gamma_{\mu\kappa}^{ca})^{-1}+1=0\ , \tag{37}$$

which can also be written as

$$-\sum_m \Psi_{\mu\kappa}^{mc}\Lambda_{\kappa\alpha}^{ca}=\delta_{\mu\alpha}\ . \tag{38}$$

This gives for indirect force

$$\sum_m {}^{ac}\theta_\mu^m\equiv-\sum_m \Psi_{\mu\kappa}^{mc}\Lambda_{\kappa\alpha}^{ca}\,{}^c\Gamma_\alpha^a={}^c\Gamma_\mu^a\ , \tag{39}$$

or

$${}^{ac}\theta_\mu^m=\tfrac{1}{4}\,{}^c\Gamma_\mu^a \tag{40}$$

if m is a nearest neighbor of c. The assumption of a rigid structure is therefore equivalent to saying that the sum of the indirect forces over the metal atoms exactly balances the direct H-H force. With this result the indirect force-dipole tensor [Eq. (36)] can be written

$$\begin{aligned}\Pi_{\iota\mu}^{(x,y)} &= \tfrac{1}{2}\sum_{c}^{(y)}\sum_{m}[R_\iota^m-\tfrac{1}{2}(Q_\iota^c+Q_\iota^a)]({}^{ac}\theta_\mu^m+{}^{ca}\theta_\mu^m)\\ &= \tfrac{1}{2}\sum_{c}^{(y)}\sum_{m}[(R_\iota^m-Q_\iota^c)+\tfrac{1}{2}(Q_\iota^c-Q_\iota^a)]({}^{ac}\theta_\mu^m)+\tfrac{1}{2}\sum_{c}^{(y)}\sum_{m}[(R_\iota^m-Q_\iota^a)+\tfrac{1}{2}(Q_\iota^a-Q_\iota^c)]({}^{ca}\theta_\mu^m)\\ &= \tfrac{1}{2}\sum_{c}^{(y)}\sum_{m}(R_\iota^m-Q_\iota^c){}^{ac}\theta_\mu^m-\tfrac{1}{4}\sum_{c}^{(y)}(Q_\iota^a-Q_\iota^c)\left[\sum_{m}{}^{ac}\theta_\mu^m\right]\\ &\quad+\tfrac{1}{2}\sum_{c}^{(y)}\sum_{m}(R_\iota^m-Q_\iota^a){}^{ca}\theta_\mu^m-\tfrac{1}{4}\sum_{c}^{(y)}(Q_\iota^c-Q_\iota^a)\left[\sum_{m}{}^{ca}\theta_\mu^m\right]. \end{aligned} \tag{41}$$

The first term vanishes because of the inversion symmetry of $\Psi_{\mu\kappa}^{ma}$ in ${}^{ac}\theta_\mu^m=-\Psi_{\mu\kappa}^{mc}\Lambda_{\kappa\alpha}^{ca}{}^{c}\Gamma_\alpha^a$,

$$\left[\sum_{m}(R_\iota^m-Q_\iota^c)\Psi_{\mu\kappa}^{mc}\right]\Lambda_{\kappa\alpha}^{ca}{}^{c}\Gamma_\alpha^a=(0)\Lambda_{\kappa\alpha}^{ca}{}^{c}\Gamma_\alpha^a\,, \tag{42}$$

while the third term vanishes because $\sum_c {}^{ca}\theta_\mu^m=0$. The second and fourth terms are equal because $\sum_m {}^{ca}\theta_\mu^m=-\sum_m {}^{ca}\theta_\mu^m$. The final result is

$$\Pi_{\iota\mu}^{(x,y)}=-\tfrac{1}{2}\sum_{c}^{(y)}(Q_\iota^a-Q_\iota^c){}^{c}\Gamma_\mu^a\,, \tag{43}$$

where we have used the result of Eq. (40).

The force ${}^{c}\Gamma_\mu^a$ is assumed here to be a central force

$${}^{c}\Gamma_\mu^a=\Gamma_{1,2}(Q_\mu^a-Q_\mu^c)\,, \tag{44}$$

where Γ_1 is associated with the nearest-neighbor pairs $[4(\mathbf{Q}^a-\mathbf{Q}^c)/a=(0,2,2,)$ and $(0,-2,-2)]$ and Γ_2 is associated with next-nearest neighbors $[4(\mathbf{Q}^a-\mathbf{Q}^c)/a=(2,-2,2)$, $(-2,-2,2)$, $(2,2,-2)$, and $(-2,2,2)]$ in the β phase of Nb-H. The central forces Γ_1 and Γ_2 for the β phase of Nb-H can be determined from the measured values of the indirect force-dipole tensor, as was first shown by Pesch *et al.*:[13]

$$\Pi_{\iota\mu}^{(x,y)}=\begin{bmatrix}0&0&0\\0&H_1&H_1\\0&H_1&H_1\end{bmatrix}+\begin{bmatrix}H_2&0&0\\0&H_2&-H_2\\0&-H_2&H_2\end{bmatrix}, \tag{45}$$

where the first term in large parentheses is for nearest-neighbor pairs, and the second term is for next-nearest neighbors. The constants Γ_1 and Γ_2 are determined from the tensor components H_1 and H_2 by substituting Eq. (44) into Eq. (43), inserting the values of $\mathbf{Q}^a-\mathbf{Q}^c$ for the different pairs and then equating the resulting tensors with the ones in Eq. (45). This gives

$$\Gamma_1=-4H_1/a^2,\quad \Gamma_2=-2H_2/a^2\,. \tag{46}$$

To determine the constants Ψ_1, Ψ_2, Γ_1, and Γ_2, we take a somewhat similar approach to that used in Refs. 11–14. The force-dipole tensors are calculated from the experimental stress-strain data in the following fashion. The macroscopic stress can be written in terms of the force-dipole tensors by substituting Eqs. (28), (30), (33), and (36) into Eq. (23) to get

$$\sigma_{\iota\mu}=\sum_{x}(c_x/\Omega)\left[P_{\iota\mu}^{(x)}+\sum_{y}c_y\Pi_{\iota\mu}^{(x,y)}\right]. \tag{47}$$

Equations (47) and (21) give us the information necessary to calculate the force-dipole tensors from the experimental strain data and elastic moduli. To do this, Eqs. (31) and (45) are substituted into Eq. (47), and the resulting different tensor elements of $\sigma_{\iota\mu}$ (i.e., $\sigma_{11},\sigma_{12},\sigma_{22}$, etc.) are equated with the experimentally measured values for tensor elements of the product $C_{\iota\mu\nu\lambda}\epsilon_{\nu\lambda}$ in Eq. (21). This procedure gives the following relations between the components of the force-dipole tensors and the experimental strain data:[13]

$$\begin{aligned}&c(A+H_2c)=\Omega(\epsilon_{11}C_{11}+2\epsilon_{33}C_{12})\,,\\ &c[B+(H_1+H_2)c]=\Omega[\epsilon_{11}C_{11}+\epsilon_{33}(C_{11}+C_{12})]\,,\\ &(H_1-H_2)c^2=2\Omega C_{44}\epsilon_{12}=\gamma^{\beta}\Omega c_{44}\,,\end{aligned} \tag{48}$$

where $\gamma^{\beta}(\equiv 2\epsilon_{12})$ is the angle in radians of the orthorhombic distortion[11] in the β phase. The elastic constants C_{11}, C_{12}, and C_{44}, the components of the strain tensor ϵ_{11} and ϵ_{33}, and the volume Ω are evaluated at the concentration, c. There are not enough relationships in Eq. (48) to determine A, B, H_1, and H_2 separately. Pick and Bausch[11] chose $H_2=0$ and were then able to determine A, B, and H from the data, while Mair *et al.*[14] set $A=B$ and then solved for H_1 and H_2. In this paper we can determine A, B, H, and H_2 separately by using additional information from the indirect force-dipole tensor associated with other ordered phases besides β-Nb-H. For example, the ϵ phase of the Nb-H system, having the stoichiometry Nb_4H_3, would give

$$\tfrac{1}{6}(4H_1-5H_2)c^2=\gamma^{\epsilon}\Omega C_{44}\,, \tag{49}$$

where H_1 and H_2 are the same quantities as in Eq. (48), but $\gamma^{\epsilon}\neq\gamma^{\beta}$. Equation (49) differs from the last line in Eq. (48) due to the different number of nearest and next-nearest H-H pairs in the ϵ and β phases of Nb-H. In the β phase, each hydrogen atom has two nearest H neighbors and four next-nearest H neighbors. In the ϵ phase the number of nearest and next-nearest neighbors of a hydrogen atom will depend on its location in the superlattice on the average, however, each H atom has $\frac{4}{3}$ of a nearest H neighbor and $\frac{10}{3}$ of a next-nearest H neighbor, thus, the equivalent of Eq. (45) for the ϵ phase is

TABLE I. Lattice expansion, elastic properties, and coupling constants for Nb-H.

Phase →	β (Ref.)	ϵ (Ref.)
c	0.75	0.75
γ (deg)	0.526 (14)	0.774 (13)
C_{11} (10^{12} dyn/cm^2)	2.52 (18)	2.58 (18)
C_{12} (10^{12} dyn/cm^2)	1.49 (18)	1.64 (18)
C_{44} (10^{12} dyn/cm^2)	0.451 (18)	0.489 (18)
Ω (10^{-24} cm^3)	20.03 (11)	20.03 (11)
ϵ_{11}/c	0.0398 (13)	0.0398 (13)
ϵ_{33}/c	0.0351 (13)	0.0351 (13)
A (10^{-12} erg)	5.82 (This work)	5.82 (This work)
B (10^{-12} erg)	5.70 (This work)	5.70 (This work)
H_1 (10^{-12} erg)	−0.563 (This work)	−0.563 (This work)
H_2 (10^{-12} erg)	−0.711 (This work)	−0.711 (This work)

$$\Pi_{\mu\mu}^{(x,y)} = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 4H_1/6 & 4H_1/6 \\ 0 & 4H_1/6 & 4H_1/6 \end{bmatrix} + \begin{bmatrix} 5H_2/6 & 0 & 0 \\ 0 & 5H_2/6 & -5H_2/6 \\ 0 & -5H_2/6 & 5H_2/6 \end{bmatrix} . \tag{50}$$

With Eq. (49) used to evaluate data in the ϵ phase (at the ϵ-phase concentration), and Eq. (48) used to evaluate data in the β phase, the values for H_1, H_2, A, and B can be determined. The calculated values for the tensor components, along with the experimental data used to calculate them, are given in Table I.

D. Metal-atom displacements

In this section the metal-atom displacements are calculated and compared with results from other theories and from experiment. The metal-atom displacements may be broken down into contributions from the direct and indirect forces. The direct displacement ${}^{a}w_\mu^m$ of metal atom m due to H atom a acting via direct force ${}^{a}\psi_\mu^m$ and the indirect displacement ${}^{ac}s_\mu^m$ of metal atom m due to the pair (a,c) acting via the indirect force ${}^{ac}\theta_\mu^m + {}^{ca}\theta_\mu^m$ are defined to be

$${}^{a}w_\mu^m \equiv -D_{\mu\nu}^{0,mn}({}^{a}\psi_\nu^n) , \tag{51}$$

$${}^{(a,c)}s_\mu^m \equiv -D_{\mu\nu}^{0,mn}({}^{ca}\Theta_\nu^n + {}^{ac}\Theta_\nu^m) , \tag{52}$$

so that the total displacement of metal atom m is

$$v_\mu^{0,m} = \sum_a ({}^{a}w_\mu^m + \sum_c {}^{(a,c)}s_\mu^m \tau_c)\tau_a . \tag{53}$$

The superscript 0 on the v indicates that these displacements are the so-called permanent displacements which are the displacements that would result if the forces were acting in the ideal lattice (the lattice whose couplings are those of the hydrogen-free metal, i.e., $D = D^0$). (The concepts of permanent and induced displacements, forces, etc., will be amplified in Sec. II A).

Equations (51)–(53) are used to calculate the direct and indirect displacements for the various metal neighbors surrounding each defect. The direct forces ${}^{a}\psi_\mu^m$ are determined from the direct force-dipole tensor and Eqs. (29) and (32) while the indirect forces ${}^{ac}\Theta_\mu^m$ are determined from the indirect force-dipole tensor and Eqs. (39), (44), and (46). Values for the force-dipole tensors are given in Table I. The Green's function $D_{\mu\nu}^{0,mn}$ was evaluated using the formulas and programs described in Ref. 9.

In Table II the calculated (direct) displacements (denoted by $\mathbf{v}$) of the first and second neighboring metal atoms surrounding an isolated H atom are given in the first row, along with the calculated results of Johnston and Sholl[23] (second row) and the calculated results of Fukai[24] (third row). The differences between the values calculated here and calculated values from the other sources can be attributed in part to differences in the calculation methods. Johnston and Sholl used a force model that included only forces exerted by the hydrogen atoms on their nearest metal-atom neighbors, while Fukai used a force model based upon a Born-Mayer potential. In the present case, however, we have used a nearest- and next-nearest-neighbor force model, and have empirically fitted these forces to the force-dipole tensors. These calculated values of $|\mathbf{v}|$ ($|\mathbf{v}|$ = absolute value of $\mathbf{v}$) should be compared with the experimental measurements of Behr *et al.*,[25] who found $|\mathbf{v}| = 0.1$ Å for nearest neighbors. The direct displacements calculated here for the isolated H atom are comparable to the displacements obtained from previous calculations and the experimental value, although there are some differences which may be attributed in part to the variation in the value of the force-dipole tensor used in each calculation.

The fourth and fifth rows of Table II show the calculated indirect displacements of metal atoms due to the H-H pairs (a,c) with $\mathbf{Q}^a = (0,0,0)$ and $4\mathbf{Q}^c/a = (0,-2,2)$ and $(2,-2,2)$. If the center of mass of the defect is denoted by $\mathbf{Q}^D$ [where $\mathbf{Q}^D = \mathbf{Q}^a$ for the isolated hydrogen atom and $\mathbf{Q}^D = \frac{1}{2}(\mathbf{Q}^a + \mathbf{Q}^c)$ for the H-H pair] then $4(\mathbf{R}^m - \mathbf{Q}^D)/a$ gives the distance from the defect to the metal neighbor at $\mathbf{R}^m$. Included in Table II is the value of the direct force-dipole tensor used to determine the forces in each calculation. The displacements of the metal atoms caused by the indirect forces of the H-H pairs

TABLE II. Calculated displacements of metal neighbors around H defects in Nb.

			Direct forces			
$(\mathbf{R}^m-\mathbf{Q}^D)$[a] $(a/4)$	TrP $(10^{-12}$ erg)	v_x	v_y $(a/100)$	v_z	$\lvert v \rvert$ (Å)	Ref.
(1,0,2)	17.21	1.10	0	2.29	0.084	This work
(3,0,2)		0.44	0	0.23	0.016	
(1,0,2)	16.02	0.72	0	1.69	0.061	22
(3,0,2)		0.94	0	0.31	0.033	
(1,0,2)	16.66	1.40	0	3.20	0.115	23
(3,0,2)		0.15	0	0.0	0.005	
		Experimental value $\lvert v \rvert^{\text{expt}}=0.1$ Å (Ref. 24)				

				Indirect forces		
$(\mathbf{Q}^c-\mathbf{Q}^a)$ $(a/4)$	$(\mathbf{R}^m-\mathbf{Q}^D)$[a] $(a/4)$	TrP $(10^{-12}$ erg)	v_x	v_y $(a/100)$	v_z	$\lvert v \rvert$ (Å)
(0,−2,2)	(1,−1,1)	−1.12	0.046	−0.026	0.026	0.002
	(1,−1,−3)		0.004	0.22	−0.21	0.10
(2,−2,2)	(0,1,1)	−1.07	0	0.031	0.031	0.0015
	(0,−1,−3)		0.14	−0.13	0.10	0.0072
	(2,−1,−1)		0.08	−0.14	0.11	0.0063
	(2,−1,−3)		0.16	−0.16	0.16	0.0092

[a] Q^d is the center of mass of the defect. For explanation, see text.

are an order of magnitude smaller than those caused by the direct forces of an isolated H atom ($\lvert v \rvert^{\text{indirect}}/\lvert v \rvert^{\text{direct}} \sim 0.025$–$0.125$). There is also an order-of-magnitude difference between the displacements of the nearest and next-nearest metal neighbors around the isolated H atom ($\lvert v \rvert^{\text{nearest}}/\lvert v \rvert^{\text{next-nearest}} \sim 5$).

II. ELASTIC BEHAVIOR OF THE HYDROGEN-LOADED LATTICE

A. The transition matrix method

Before one can determine the displacement fields or elastic energy of the hydrogen-loaded lattice, one must be able to evaluate the static Green's function of the loaded lattice. In the FHLA this Green's function cannot be determined exactly since the couplings between the metal atoms will vary due to the presence of hydrogen. (In contrast, the Green's function used in the harmonic approximation is calculated for the unloaded lattice.) To overcome this problem the transition matrix method[5,20,27,29] is used as an approximation to calculate the Green's function in the FHLA. In this section the transition matrix method is reviewed, and the equations for determining the metal-atom displacements using the transition matrix are derived.

From Eq. (9) the displacement v_μ^m can be written

$$v_\mu^m = D_{\mu\nu}^{mn}[\Psi_\nu^n(\tau)+\Theta_\nu^n(\tau)] \,, \tag{54}$$

where

$$D_{\mu\nu}^{mn} = (\Phi_{\nu\mu}^{nm}+\Psi_{\nu\mu}^{nm}-\Psi_{\nu\alpha}^{na}\Lambda_{\alpha\beta}^{ab}\Psi_{\beta\mu}^{bm})^{-1} \tag{55}$$

is the static Green's function of the defect (hydrogen-loaded) lattice. The complicated couplings in $D_{\mu\nu}^{mn}$ prevent one from performing a Fourier transformation to obtain $D_{\mu\nu}^{(\mathrm{q})}$ as was done by Horner and Wagner for $D_{\mu\nu}^{0,mn}$ because $D_{\mu\nu}^{mn}$ will now depend on the locations of both m and n, and a and b. In general, $D_{\mu\nu}^{mn}$ will be different for each configuration of hydrogen atoms. To obtain $D_{\mu\nu}^{mn}$ would require the inversion of the full matrix of force constants $(\Phi_{\nu\mu}^{nm}+\Psi_{\nu\mu}^{nm}-\Psi_{\nu\alpha}^{na}\Lambda_{\alpha\beta}^{ab}\Psi_{\beta\mu}^{bm})$ which has the dimensions $3N_L \times 3N_L$.

Instead of trying to invert such a large matrix, we use an approximation to get $D_{\mu\nu}^{mn}$. We assume that the lattice can be separated into two regions: the defect space [the area immediately around the H atoms (defects) where the couplings have changed]; and the undisturbed space, where the couplings are those of the pure metal $\Phi_{\mu\nu}^{mn}$ (Refs. 5, 27, and 30). In the defect space the metal atoms respond locally to displacements with effective couplings $\Phi_{\mu\nu}^{mn}+\widetilde{\Psi}_{\mu\nu}^{mn}$, where $\widetilde{\Psi}_{\mu\nu}^{mn}=(\Psi_{\mu\nu}^{mn}-\Psi_{\mu\alpha}^{mn}\Lambda_{\alpha\beta}^{ab}\Psi_{\beta\nu}^{bn})$. The Green's function for the undisturbed space will be $D_{\mu\nu}^{0,mn}$, which can be calculated by the Fourier-transform method as in Horner and Wagner. To get the Green's function for the defect space one need only invert $\Phi_{\mu\nu}^{mn}+\widetilde{\Psi}_{\mu\nu}^{mn}$ for those metal atoms m and n in the defect space. In general, the couplings $\widetilde{\Psi}_{\mu\nu}^{mn}$ will affect only the nearest neighbors of the defect. The advantage here is that the defect space will have a much smaller dimensionality than the total space, since it includes only the nearest neighbors of the defect.

If we consider only the defect space, then $D_{\mu\nu}^{mn}$ can be written in matrix notation (where the superscripts mn have been dropped for convenience),

$$\begin{aligned} \underline{D} &= -(\underline{\Phi}+\underline{\widetilde{\Psi}})^{-1} \\ &= -[(\underline{1}+\underline{\widetilde{\Psi}}\,\underline{\Phi}^{-1})\underline{\Phi}^{-1}]^{-1} \\ &= -\underline{\Phi}^{-1}(\underline{1}+\underline{\widetilde{\Psi}}\,\underline{\Phi}^{-1})^{-1} \\ &= \underline{D}^{0}(\underline{1}-\underline{\widetilde{\Psi}}\,\underline{D}^{0})^{-1} \,, \end{aligned} \tag{56}$$

where $\underline{D}^0 = -(\underline{\Phi})^{-1}$. The matrices $\underline{D}$, $\underline{D}^0$, $\underline{\Phi}$, and $\underline{\widetilde{\Psi}}$ have dimensionality $3N_D \times 3N_D$, where N_D is the number of metal atoms in the defect space. Equation (52) can also be shown to equal

$$\underline{D} = (\underline{1} - \underline{D}^0 \underline{\widetilde{\Psi}})^{-1} \underline{D}^0 \,, \tag{57}$$

a result that will be used at a subsequent point. The expression for D in Eq. (56) can be expanded in powers of the perturbation $\widetilde{\Psi}$:

$$\underline{D} \cong \underline{D}^0 + \underline{D}^0 \underline{\widetilde{\Psi}} (\underline{1} - \underline{D}^0 \underline{\widetilde{\Psi}})^{-1} \underline{D}^0 \cong \underline{D}^0 + \underline{D}^0 \underline{t}\, \underline{D}^0 \,. \tag{58}$$

Equation (58) defines the transition matrix, $\underline{t} = \underline{\widetilde{\Psi}} (\underline{1} - \underline{D}^0 \underline{\widetilde{\Psi}})^{-1}$, also called the "$t$ matrix," which acts as a bridge between the properties of the pure lattice and those of the defect lattice. It has the same matrix properties as $\underline{\Phi}$ and $\underline{\Psi}$, i.e., $t_{\mu\nu}^{mn} = t_{\nu\mu}^{mn} = t_{\nu\mu}^{nm}$. The total t matrix is assumed to be the sum of the coupling changes for each isolated hydrogen atom, or

$$t_{\mu\nu}^{mn} = \sum_b {}^b t_{\mu\nu}^{mn} \tau_b \,. \tag{59}$$

Here we have assumed that there are no additional coupling changes due to pairs of atoms, as did Kramer,[5] i.e., that the term $\Psi_{\mu\alpha}^{ma} \Lambda_{\alpha\beta}^{ab} \Psi_{\beta\nu}^{bn}$ in Eq. (55) contributes a negligible amount to $\widetilde{\Psi}_{\nu\mu}^{mn}$.

Because the potential $\Psi(\mathbf{R},\mathbf{Q},\tau)$ between the hydrogen atoms and the metal atoms is unknown, it is not possible to calculate $\underline{\widetilde{\Psi}}$ (and thus $\underline{t}$) from first principles. It is therefore necessary to be able to relate the t matrix to some macroscopic quantity which can be measured experimentally. This quantity is called the dielastic polarizability,[24,27,28] $\alpha_{\iota\mu\kappa\lambda}$, and it is determined from the change in elastic properties that occurs when hydrogen is absorbed into a metal. The relationship between the elastic constants and the t matrix is found by substituting Born's approximation ($\underline{t} \simeq \underline{\widetilde{\Psi}}$) (Ref. 27) into Eq. (24):

$$\begin{aligned} C_{\iota\mu\nu\lambda} &\simeq (1/V) R_\iota^m (\Phi_{\mu\nu}^{mn} + t_{\mu\nu}^{mn}) R_\lambda^n \\ &\simeq C_{\iota\mu\nu\lambda}^0 + (1/V) R_\iota^m t_{\mu\nu}^{mn} R_\lambda^n \,, \end{aligned} \tag{60}$$

where $C_{\iota\mu\kappa\lambda}^0$ is given by Eq. (27). The second term contains the dielastic polarizability, $\alpha_{\iota\mu\nu\lambda}$ which is given by Eqs. (5) and (20):

$$\begin{aligned} (1/V) R_\iota^m t_{\mu\nu}^{mn} R_\lambda^n &= (N/V) R_\iota^m \, {}^b t_{\mu\nu}^{mn} R_\lambda^n \\ &\equiv -\sum_x (c_x/\Omega) \alpha_{\iota\mu\nu\lambda}^{(x)} \,, \end{aligned} \tag{61}$$

where

$$\alpha_{\iota\mu\nu\lambda}^{(x)} \equiv -R_\iota^m \, {}^b t_{\mu\nu}^{mn} R_\lambda^n \tag{62}$$

for an isolated defect at site b on the xth sublattice. The notation $\sum_x$ indicates a summation over all possible sublattices. Thus, Eq. (60) becomes

$$C_{\iota\mu\nu\lambda} = C_{\iota\mu\nu\lambda}^0 - (1/\Omega) \sum_x \alpha_{\iota\mu\nu\lambda}^{(x)} c_x \,. \tag{63}$$

The dielastic polarizability is seen to be a fourth-order tensor having the same tensor symmetry as $C_{\iota\mu\kappa\lambda}^0$.

Schober and Lottner[17] have calculated the components of the t matrix by fitting $\alpha_{\iota\mu\nu\lambda}$ to the experimentally observed changes in $C_{\iota\mu\nu\lambda}$ with hydrogen concentration. They chose a model that had couplings $\Psi_{\mu\nu}^{mn}$ between the four nearest-neighboring metal atoms around a tetrahedral site in a bcc lattice. The matrix $\underline{\widetilde{\Psi}}$ for their model has a 12×12 dimensionality, which makes it difficult to perform the inversion of $\underline{1} - \underline{D}^0 \underline{\widetilde{\Psi}}$ to get t. To avoid this problem, Schober and Lottner used group-theoretical partitioning to reduce the large matrix to several smaller matrices which can be manipulated more easily. The irreducible representation for the Schober-Lottner model and the elements of the t matrix have been used in our calculation of the induced forces, and of the elastic interaction energy that is described in the next paper.

In theories involving the t matrix, it is natural to introduce the concepts of permanent and induced displacements, forces, and interactions.[5,30,31] The permanent and induced displacements arise in the following manner. Consider the metal-atom displacements as given by Eq. (54). In the defect space, the $\mathbf{v}$ are given by

$$\mathbf{v} = \underline{D}(\mathbf{\Psi} + \mathbf{\Theta}) = \underline{D}^0(\mathbf{\Psi} + \mathbf{\Theta}) + \underline{D}^0 \underline{t}\, \underline{D}^0 (\mathbf{\Psi} + \mathbf{\Theta}) = \mathbf{v}^0 + \mathbf{v}^I \,, \tag{64}$$

where

$$\mathbf{v}^0 = \underline{D}^0 (\mathbf{\Psi} + \mathbf{\Theta})$$

and

$$\mathbf{v}^I = \underline{D}^0 \underline{t}\, \underline{D}^0 (\mathbf{\Psi} + \mathbf{\Theta}) \,.$$

The $\mathbf{v}^0$ are called permanent displacements, and are the displacements that would result if the forces were acting in the ideal lattice (the lattice in which the couplings are those of the hydrogen free metal; i.e., $\underline{D} = \underline{D}^0$). The $\mathbf{v}^I$ are called induced displacements, and are corrections to $\mathbf{v}^0$ that arise due to changes in lattice couplings caused by the defect. Both the permanent and induced displacements can be broken down into contributions from the direct and indirect forces acting in the defect space. The direct-permanent displacements ${}^a w_\mu^m$ of metal atom m due to H atom a acting via direct force ${}^a \psi_\mu^m$, and indirect-permanent displacements ${}^{ac} s_\mu^m$ of metal atom m due to the pair (a,c) acting via the indirect force ${}^{ac}\Theta_\mu^m + {}^{ca}\Theta_\mu^m$ have already been defined in Eqs. (51) and (52).

The induced displacements have not been calculated here, since the formalism using the induced forces does not require them. Beyond this, it would be pointless to calculate the induced displacements, since they cannot be compared with anything measurable. One might naively think that the sum of the calculated permanent and induced displacements would give the actual microscopic displacements in the real lattice, but this would be incorrect, since the t-matrix method is an approximation that is best at the macroscopic level. The actual displacements could only be obtained by calculating the full Green's function [without the approximation of Eq. (58)] for the full lattice, (not just the defect space) and using this to solve Eq. (54).

The direct- and indirect-induced displacements can be treated in the same manner as the direct- and indirect-permanent displacements but it turns out to be more convenient to use the t matrix to define direct- and indirect-induced forces. The usefulness of the induced-force concept will be apparent from the following discussion. In the ideal lattice the permanent forces cause the permanent displacements. The permanent forces also act in the real lattice, but because of the changes in the metal-metal couplings the displacements caused by the permanent forces will not be the same as the displacements they cause in the ideal lattice. The induced forces are defined as effective forces that, when acting in unison with the permanent forces in the ideal lattice, cause the same displacements in the ideal lattice as the permanent forces acting alone in the real lattice. In this way the induced forces can be thought of as additional Kanzaki forces. Recall that Kanzaki forces are effective forces acting in the undisturbed lattice that cause the same displacements as the real forces acting in the real lattice. It can be seen that the term $\underline{t}\,\underline{D}^0(\boldsymbol{\Psi}+\boldsymbol{\Theta}) = \underline{t}\,\mathbf{v}^0$ in Eq. (64) has the units of force; it is therefore called the total induced force to distinguish it from the total permanent force $\boldsymbol{\Psi}+\boldsymbol{\Theta}$. We define the direct-induced force $\boldsymbol{\Psi}^I$ as

$$\boldsymbol{\Psi}^I=\underline{t}\,\underline{D}^0\boldsymbol{\Psi} \tag{65}$$

and the indirect-induced force $\boldsymbol{\Theta}^I$as

$$\boldsymbol{\Theta}^I=\underline{t}\,\underline{D}^0\boldsymbol{\Theta} \ . \tag{66}$$

The total induced force on metal atom m (in the usual notation) can be written as

$$\begin{aligned}\Psi_\mu^{I,m}(\tau)+\Theta_\mu^{I,m}(\tau)&=t_{\mu\nu}^{mn}D_{\nu\lambda}^{0,nl}[\Psi_\lambda^l(\tau)+\Theta_\lambda^l(\tau)]\\&=t_{\mu\nu}^{mn}v_\mu^{0,n} \ .\end{aligned} \tag{67}$$

The induced forces $\Psi_\mu^{I,m}(\tau)$ and $\Theta_\mu^{I,m}(\tau)$ will have a hydrogen-concentration dependence determined by the concentration dependences of $t_{\mu\nu}^{mn}$ and $v_\nu^{0,n}$. To keep the nomenclature consistent in the rest of this paper, the forces $\Psi_\mu^m(\tau)$ and $\Theta_\mu^m(\tau)$ referred to previously are henceforth called permanent forces, and their force-dipole tensors, given by Eqs. (28) and (43), are called permanent force-dipole tensors.

The direct- and indirect-induced forces can be given an explicit dependence on τ_a in the following way. By substituting Eqs. (14), (17), (51), (52), and (59) into Eqs. (65) and (66) the induced forces on the metal atom at m in the μ direction can be written as

$$\begin{aligned}\Psi_\mu^{I,m}(\tau)&=-\sum_{a,b}{}^b\psi_\mu^{I,m}\tau_a\tau_b \ ,\\\Theta_\mu^{I,m}(\tau)&=-\sum_{a,b,c}{}^b\theta_\mu^{I,m}\tau_a\tau_b\tau_c \ ,\end{aligned} \tag{68}$$

where the direct-induced force ${}^b\psi_\mu^{I,m}$ and the indirect-induced force ${}^b\theta_\mu^{I,m}$ are defined as

$${}^b\psi_\mu^{I,m}={}^bt_{\mu\nu}^{mn}\,{}^aw_\nu^n$$

and (69)

$${}^b\theta_\mu^{I,m}={}^bt_{\mu\nu}^{mn}\,{}^{(c,a)}s_\nu^n \ .$$

The force ${}^b\psi_\mu^{I,m}$ is the direct-induced force of b on m (caused by the displacement field of a) in the μ direction, while ${}^b\theta_\mu^{I,m}$ is the indirect-induced force of b on m [caused by the displacement field of the pair (a,c)] in the μ direction. From these induced forces we can define induced force-dipole tensors for the hydrogen atom at site b as

$$\begin{aligned}{}^bP_{\iota\mu}^{I,(a)}&\equiv\sum_m R_\iota^m\,{}^b\psi_\mu^{I,m}=\sum_m R_\iota^m\,{}^bt_{\mu\nu}^{mn}\,{}^aw_\nu^n \ ,\\{}^b\Pi_{\iota\mu}^{I,(a,c)}&\equiv\sum_m R_\iota^m\,{}^b\theta_\mu^{I,m}=\sum_m R_\iota^m\,{}^bt_{\mu\nu}^{mn}\,{}^{(a,c)}s_\nu^n \ .\end{aligned} \tag{70}$$

The superscripts (a) or (a,c) appear on the induced force-dipole tensors because these tensors will have different values depending on the location of site a or sites a and c and the location of site b. The induced forces possess translational invariance $\sum_m {}^b\psi_\mu^{I,m}=0$, just as the permanent forces do; therefore

$$\begin{aligned}{}^bP_{\iota\mu}^{I,(a)}&=\sum_m (R_\iota^m-Q_\iota^b)\,{}^b\psi_\mu^{I,m} \ ,\\{}^b\Pi_{\iota\mu}^{I,(a,c)}&=\sum_m (R_\iota^m-Q_\iota^b)\,{}^b\theta_\mu^{I,m} \ .\end{aligned} \tag{71}$$

Using Eq. (69), the direct and indirect forces of H in Nb have been calculated for different H-M and H-H separations. These are listed in Table III, for the case in which sites a and b in Eq. (69) are the same, along with the permanent-direct and permanent-indirect forces. The induced contributions are about one third the size of the permanent contribution, and are of opposite sign. The significance of the induced forces will be addressed in the discussion at the end of the paper.

B. The induced stress

In this section, we introduce the induced stress, which is that part of the macroscopic stress which results from the microscopic induced forces. Values for the induced stress, and in particular for the force-dipole tensor associated with the induced stress (the induced force-dipole tensor), will be necessary for paper II of this series, in which we calculate the elastic energy of the finite lattice and the so-called free-surface correction. The concept of the induced stress may be motivated by considering how the coupling changes caused by the hydrogen atoms will affect the elastic energy of a metal hydride. On a macroscopic level, this energy is

$$H_{\text{elast}}=\tfrac{1}{2}\sigma_{\iota\mu}\epsilon_{\iota\mu} \ , \tag{72}$$

where $\sigma_{\iota\mu}$ is the permanent stress and $\epsilon_{\iota\mu}$ is the strain in the defect (nonideal) lattice. The difficulty in evaluating Eq. (72) is due to the fact that $\epsilon_{\iota\mu}$ will have both induced and permanent contributions, and cannot be easily determined. It is more convenient to instead define an induced stress,[30,31] which when acting together with the permanent stress in the ideal lattice gives the same strain $\epsilon_{\iota\mu}$ in the ideal lattice as would occur in the defect (hydrogen-loaded) lattice:

$$\epsilon_{\iota\mu}=S_{\iota\mu\nu\lambda}\sigma_{\nu\lambda}=S^0_{\iota\mu\nu\lambda}(\sigma_{\nu\lambda}+\sigma_{\nu\lambda}^{\text{induced}}) \ , \tag{73}$$

where $\sigma_{\nu\lambda}^{\text{induced}}$ is the induced stress. The induced stress will be the result of the microscopic induced forces, which

TABLE III. Comparison of the permanent and induced components of the direct and indirect forces.

		Direct, permanent ${}^{a}\psi^{m}$ (10^{-4} dyn)	Direct, induced ${}^{a}\psi^{I,m}$ (10^{-4} dyn)
$(R^m-Q^a)4/a$			
(1,0,2)		(0.7244,0,1.448)	(−0.2858,0,−0.5602)
(1,0,−2)		(0.7244,0,−1.448)	(−0.2858,0,0.5602)
(−1,−2,0)		(−0.7244,−1.448,0)	(0.2858,0.5602,0)
(−1,2,0)		(−0.7244,1.448,0)	(0.2858,−0.5602,0)
$(\mathbf{R}^m-\mathbf{Q}^a)4/a$	$(\mathbf{Q}^c-\mathbf{Q}^a)4/a$	Indirect, permanent ${}^{ca}\theta^{m}$ (10^{-6} dyn)	Indirect, induced ${}^{a}\theta^{I,m}$ (10^{-6} dyn)
(1,0,2)	(0,−2,2)	(0,−8.22,−8.22)	(−0.9602,−0.6094,−1.304)
(1,0,−2)		(0,−8.22,−8.22)	(−1.014,0.4106,0.1503)
(−1,−2,0)		(0,−8.22,−8.22)	(1.014,0.1503,0.4106)
(−1,2,0)		(0,−8.22,−8.22)	(0.9602,−1.304,−6094)
(1,0,2)	(−2,2,−2)	(−20.8,+20.8,−20.8)	(−0.4424,0.1480,−1.002)
(1,0,−2)		(−20.8,+20.8,−20.8)	(−0.1511,0.1517,0.3720)
(−1,−2,0)		(−20.8,+20.8,−20.8)	(−0.0990,0.5452,−0.1234)
(−1,2,0)		(−20.8,+20.8,−20.8)	(0.6924,−0.8449,0.7536)

have been described before as Kanzaki forces,[27] in addition to the Kanzaki forces that cause the permanent displacements.

In this section we will derive the relationship between the induced stress and the dielastic polarizability, and the relationship between the induced stress and the induced force-dipole tensors. In order to obtain an expression for the induced stress, we separate the force-displacement expression [Eq. (18)] written here in matrix notation:

$$(\underline{\Phi}+\tilde{\underline{\Psi}})\mathbf{v}=-\boldsymbol{\Psi}-\boldsymbol{\Theta}\ , \tag{74}$$

into terms associated with $\underline{\Phi}$ and terms associated with $\boldsymbol{\Psi}$,

$$\underline{\Phi}\mathbf{v}+\tilde{\underline{\Psi}}\,\underline{D}(\boldsymbol{\Psi}+\boldsymbol{\Theta})=-\boldsymbol{\Psi}-\boldsymbol{\Theta}\ , \tag{75}$$

where we have used $\mathbf{v}=\underline{D}(\Psi+\Theta)$ as in Eq. (64). The product $\tilde{\underline{\Psi}}\,\underline{D}$ can be written in terms of $\underline{t}$ using Eqs. (56), (57), and (58),

$$\begin{aligned}\tilde{\underline{\Psi}}\,\underline{D}&=\tilde{\underline{\Psi}}\,\underline{D}^{0}(\underline{1}-\tilde{\underline{\Psi}}\,\underline{D}^{0})^{-1}\\&=\tilde{\underline{\Psi}}(\underline{1}-\underline{D}^{0}\tilde{\underline{\Psi}})^{-1}\underline{D}^{0}=\underline{t}\,\underline{D}^{0}\ .\end{aligned} \tag{76}$$

[The relationship $\underline{D}^{0}(\underline{1}-\tilde{\underline{\Psi}}\,\underline{D}^{0})^{-1}=(\underline{1}-\underline{D}^{0}\tilde{\underline{\Psi}})^{-1}\underline{D}^{0}$ holds because of the equivalent derivations of Eqs. (56) and (57).] Substituting Eq. (76) into Eq. (75) and using the definition $\mathbf{v}^0=\underline{D}^{0}(\boldsymbol{\Psi}+\boldsymbol{\Theta})$ we recover

$$\underline{\Phi}\mathbf{v}+\underline{t}\mathbf{v}^0=-\boldsymbol{\Psi}-\boldsymbol{\Theta}\ . \tag{77}$$

With subscripts and superscripts included, Eq. (77) becomes

$$\Phi^{mn}_{\mu\nu}v^{n}_{\nu}+t^{mn}_{\mu\nu}v^{0,n}_{\nu}=-\Psi^{m}_{\mu}(\tau)-\Theta^{m}_{\mu}(\tau)\ . \tag{78}$$

By assuming homogeneous distortions $v^n_\nu=\epsilon_{\nu\lambda}R^n_\lambda$ and $v^{0,n}_\nu=\epsilon^0_{\nu\lambda}R^n_\lambda$, Eq. (78) becomes

$$\Phi^{mn}_{\mu\nu}\epsilon_{\nu\lambda}R^{n}_{\lambda}+t^{mn}_{\mu\nu}\epsilon^{0}_{\nu\lambda}R^{n}_{\lambda}=-\Psi^{m}_{\mu}(\tau)-\Theta^{m}_{\mu}(\tau) \tag{79}$$

which, when multiplied by (R^m_ι/V) results in

$$\begin{aligned}(1/V)R^{m}_{\iota}\Phi^{mn}_{\mu\nu}R^{n}_{\lambda}\epsilon_{\nu\lambda}+(1/V)R^{m}_{\iota}t^{mn}_{\mu\nu}R^{n}_{\lambda}\epsilon^{0}_{\nu\lambda}\\=-(1/V)[R^{m}_{\iota}\Psi^{m}_{\mu}(\tau)+R^{m}_{\iota}\Theta^{m}_{\mu}(\tau)]\ .\end{aligned} \tag{80}$$

This gives a macroscopic stress-strain relationship in terms of microscopic quantities. By substituting Eqs. (23), (27), (59), and (61) into Eq. (80), one gets the Hooke's law relation for the defect lattice in which the elastic constants of the ideal lattice (those of the pure metal) are used:

$$C^{0}_{\iota\mu\nu\lambda}\epsilon_{\nu\lambda}-(1/\Omega)\sum_{x}\alpha^{(x)}_{\iota\mu\nu\lambda}\epsilon^{0}_{\nu\lambda}c_x=\sigma_{\iota\mu}$$

or (81)

$$C^{0}_{\iota\mu\nu\lambda}\epsilon_{\nu\lambda}-\sigma^{\text{induced}}_{\iota\mu}=\sigma_{\iota\mu}\ ,$$

where $\sigma_{\iota\mu}$ is the permanent stress and

$$\sigma^{\text{induced}}_{\iota\mu}=(1/V)R^{m}_{\iota}t^{mn}_{\mu\nu}R^{m}_{\lambda}\epsilon^{0}_{\nu\lambda}\equiv(1/\Omega)\sum_{x}\alpha^{(x)}_{\iota\mu\nu\lambda}\epsilon^{0}_{\nu\lambda}c_x \tag{82}$$

is the induced stress. From Eq. (81) it can be seen that the coupling changes caused by the defects are equivalent to an additional stress $\sigma^{\text{induced}}_{\iota\mu}$, acting in the pure metal (ideal lattice) to give the same strain fields as in the real lattice. The induced stress can be thought of as being caused by the induced forces $\Psi^{I,m}_{\mu}(\tau)$ and $\Theta^{I,m}_{\mu}(\tau)$, just as the permanent forces $\Psi^{m}_{\mu}(\tau)$ and $\Theta^{m}_{\mu}(\tau)$ cause the permanent stress $\sigma_{\iota\mu}$. To get the induced stress in terms of the induced force-dipole tensors requires a relationship between the induced stress and the induced forces. The relationship between $\sigma^{\text{induced}}_{\iota\mu}$ and $\Psi^{I,m}_{\mu}(\tau)$ and $\Theta^{I,m}_{\mu}(\tau)$ can be derived in the same way that Eq. (81) was derived, except that we first substitute Eq. (67) into Eq. (78) to get

$$\Phi^{mn}_{\mu\nu}v^{n}_{\nu}=-\Psi^{I,m}_{\mu}(\tau)-\Theta^{I,m}_{\mu}(\tau)-\Psi^{m}_{\mu}(\tau)-\Theta^{m}_{\mu}(\tau)\ . \tag{83}$$

Equation (83) states that the permanent and induced forces, acting in the ideal lattice (with force constants

$\Theta^{mn}_{\mu\nu}$), causes the displacements v^n_ν which are the same as the v^n_ν that occur in the real lattice. By assuming homogeneous distortions, $v^n_\nu=\epsilon_{\nu\lambda}R^n_\lambda$, and multiplying to the left by (R^m_ι/V), Eq. (83) becomes

$$(1/V)R^m_\iota\Phi^{mn}_{\mu\nu}R^n_\lambda\epsilon_{\nu\lambda}+(1/V)[R^m_\iota\Psi^{I,m}_\mu(\tau)+R^m_\iota\Theta^{I,m}_\mu(\tau)] \\ =-(1/V)[R^m_\iota\Psi^m_\mu(\tau)+R^m_\iota\Theta^m_\mu(\tau)]\ . \qquad (84)$$

Comparison of Eq. (84) with Eq. (80) gives

$$(1/V)R^m_\iota t^{mn}_{\mu\nu}R^n_\lambda\epsilon_{\nu\lambda}=(1/V)[R^m_\iota\Psi^{I,m}_\mu(\tau)+R^m_\iota\Theta^{I,m}_\mu(\tau)]\ , \qquad (85)$$

which with the aid of Eqs. (61) and (82) can be written

$$\sigma^{\text{induced}}_{\iota\mu}=-(1/V)[R^m_\iota\Psi^{I,m}_\mu(\tau)+R^m_\iota\Theta^{I,m}_\mu(\tau)]\ . \qquad (86)$$

When Eqs. (68) and (71) are substituted into (86), we find

$$\sigma^{\text{induced}}_{\iota\mu}=(1/V)\sum_{a,b}\left[{}^bP^{I,(a)}_{\iota\mu}+\sum_c {}^b\Pi^{I,(a,c)}_{\iota\mu}\tau_c\right]\tau_a\tau_b\ . \qquad (87)$$

For a homogeneous distribution of H atoms the average concentration can be substituted for τ_a, τ_b, and τ_c. If we take site a to be on the zth sublattice, c to be on the yth sublattice, and b to be on the xth sublattice, then Eq. (87) becomes

$$\sigma^{\text{induced}}_{\iota\mu}=(1/\Omega)\sum_{x,z}\left[\sum_a({}^bP^{I,(a)}_{\iota\mu}+\sum_y\left[\sum_c {}^b\Pi^{I,(a,c)}_{\iota\mu}\right]c_y\right]c_xc_z\ . \qquad (88)$$

A comparison of Eq. (88) with Eq. (47) shows that $\sigma^{\text{induced}}_{\iota\mu}$ is one order higher in c than the permanent stress, $\sigma_{\iota\mu}$. Thus, the concentration dependence of $\sigma^{\text{induced}}_{\iota\mu}$ has been found, as well as its relationship to the induced force-dipole tensors.

The evaluation of $\sigma^{\text{induced}}_{\iota\mu}$ requires the values of all the induced force-dipole tensors ${}^bP^{I,a}_{\iota\mu}$ and ${}^b\Pi^{I,(a,c)}_{\iota\mu}$ as defined by Eqs. (70) and (71). The induced force-dipole tensors are functions of the relative locations of a, b, and c, but they appear in the expression for $\sigma^{\text{induced}}_{\iota\mu}$ [Eq. (88)] as $\sum_a {}^bP^{I,a}_{\iota\mu}$ and $\sum_{a,c} {}^b\Pi^{I,(a,c)}_{\iota\mu}$. These sums depend only on the location of site b (and therefore only upon the sublattice that b occupies). From these sums we can define two new induced force-dipole tensors

$$P^{I,(x)}_{\iota\mu}=(1/N^y_{\mathrm{H}})\sum_a {}^bP^{I,a}_{\iota\mu}\ , \\ \Pi^{I,(x)}_{\iota\mu}=(1/N^y_{\mathrm{H}})\sum_{a,c} {}^b\Pi^{I,(a,c)}_{\iota\mu}=\sum_k {}^k\Pi^{I,(x,y)}_{\iota\mu}\ , \qquad (89)$$

where we sum over only those sites a on the yth sublattice and those sites b on the xth sublattice. To evaluate the sums in Eq. (89) would be a lengthy operation; however, we can make use of the inversion symmetry of $t^{mn}_{\mu\nu}$ to evaluate the sums approximately. If Eqs. (69) and (71) are substituted into Eq. (89) the result is

$$P^{I,(x)}_{\iota\mu}=(1/N^y_{\mathrm{H}})\sum_a\sum_m(R^m_\iota-Q^b_\iota)\,{}^bt^{mn}_{\mu\nu}\,{}^aw^n_\nu\ , \\ {}^k\Pi^{I,(x)}_{\iota\mu}=(1/N^y_{\mathrm{H}})\sum_a\sum_m(R^m_\iota-Q^b_\iota)\,{}^bt^{mn(c,a)}_{\mu\nu}s^n_\nu\ . \qquad (90)$$

The evaluation of $P^{I,(x)}_{\iota\mu}$ is considered first. If homogeneous distortions are assumed, then ${}^aw^n_\nu=-\epsilon_{\nu\lambda}(R^n_\lambda-Q^a_\lambda)/N^y_{\mathrm{H}}$, and $P^{I,(x)}_{\iota\mu}$ becomes

$$P^{I,(x)}_{\iota\mu}=(-1/N^y_{\mathrm{H}})\sum_a\sum_m(R^m_\iota-Q^b_\iota)\,{}^bt^{mn}_{\mu\nu}\epsilon_{\nu\lambda}(R^n_\lambda-Q^a_\lambda)/N^y_{\mathrm{H}}\ . \qquad (91)$$

It can then be separated into two parts,

TABLE IV. Direct and indirect permanent and induced force dipole tensors for Nb-H.

	Permanent	Induced
Direct	$P^{(x)}_{\iota\mu}$ =(5.82,0,0)	$P^{I(x)}_{\iota\mu}$ =(−0.978,0,0)
	=(0,5.70,0)	=(0,−1.917,0)
	=(5.82,0,5.70)	=(0,0,−1.917)
Indirect	${}^k\Pi^{(x)}_{\iota\mu}$=(−0.563,0,0)	${}^k\Pi^{I(x)}_{\iota\mu}$=(0.0675,0,0)
$k=1$,	=(0,−0.563,−0.563)	=(0,0.0961,0.0349)
$\mathbf{Q}^c-\mathbf{Q}^a=\frac{(0,2,2)a}{4}$	=(0,−0.563,−0.563)	=(0,0.0349,0.0961)
Indirect	${}^k\Pi^{(x)}_{\iota\mu}$=(−0.356,0.356,−0.356)	${}^k\Pi^{I(x)}_{\iota\mu}$=(0.0203,−0.0071,0.0071)
$k=2$,	=(0.356,−0.356,0.356)	=(−0.0071,0.0472,−0.0149)
$\mathbf{Q}^c-\mathbf{Q}^a=\frac{(2,-2,2)a}{4}$	=(−0.356,0.356,−0.356)	=(0.0071,−0.0149,0.0472)
Indirect	${}^k\Pi^{(x)}_{\iota\mu}$=(−0.356,−0.356,0.356)	${}^k\Pi^{I(x)}_{\iota\mu}$=(0.0203,0.0071,−0.0071)
$k=2$,	=(−0.356,−0.356,−0.356)	=(0.0071,0.0472,−0.0149)
$\mathbf{Q}^c-\mathbf{Q}^a=\frac{(2,2,-2)a}{4}$	=(0.356,0.356,−0.356)	=(−0.0071,−0.0149,0.0472)

All tensors are in units of 10^{12} ergs.

$$P_{\iota\mu}^{I,(x)} = (-1/N_{\mathrm{H}}^{\nu}) \sum_{a} \sum_{m} (R_{\iota}^{m} - Q_{\iota}^{b})\, {}^{b}t_{\mu\nu}^{mn} \epsilon_{\nu\lambda} (R_{\lambda}^{n} - Q_{\lambda}^{b})/N_{\mathrm{H}}^{\nu}$$
$$+ (-1/N_{\mathrm{H}}^{\nu}) \sum_{m} (R_{\iota}^{m} - Q_{\iota}^{b})\, {}^{b}t_{\mu\nu}^{mn} \epsilon_{\nu\lambda}$$
$$\times \sum_{a} (Q_{\lambda}^{b} - Q_{\lambda}^{a})/N_{\mathrm{H}}^{\nu} \,. \tag{92}$$

The second term will vanish because lattice symmetry requires that for every site a there must be a site a' such that $Q_{\lambda}^{b} - Q_{\lambda}^{a} = -(Q_{\lambda}^{b} - Q_{\lambda}^{a'})$. This result allows us to write

$$P_{\iota\mu}^{I,(x)} = (1/N_{\mathrm{H}}^{\nu}) \sum_{a} \sum_{m} (R_{\iota}^{m} - Q_{\iota}^{b})\, {}^{b}t_{\mu\nu}\, {}^{b}w_{\nu}^{n}$$
$$= \sum_{m} (R_{\iota}^{m} - Q_{\iota}^{b})\, {}^{b}t_{\mu\nu}^{mn}\, {}^{b}w_{\nu}^{n} \,, \tag{93}$$

which can be evaluated easily with the t matrix. If the same treatment is used for ${}^{k}\Pi_{\iota\mu}^{I,(x)}$, we find that

$${}^{k}\Pi_{\iota\mu}^{I,(x)} = \sum_{m} (R_{\iota}^{m} - Q_{\iota}^{b})\, {}^{b}t_{\mu\nu}^{mn}\, {}^{(b,d)}s_{\nu}^{n} \tag{94}$$

which is also easy to evaluate with the t matrix. The values of $P_{\iota\mu}^{I,(x)}$ and ${}^{k}\Pi_{\iota\mu}^{I,(x)}$ (for $k =$ nearest and next-nearest H-H pairs) are given in Table IV.

DISCUSSION

From a comparison of the forces listed in Table III (or, equivalently, from a comparison of the force-dipole tensors in Tables I and IV), it can be seen that the induced components of the direct and indirect forces make a substantial contribution to the "total" force. Because the permanent and induced contributions are of opposite sign, the total force is smaller than the permanent contribution alone. Thus, in the FHLA, the lattice forces which include permanent-direct, permanent-indirect, induced-direct, and induced-indirect forces are smaller than those in the harmonic approximation, which include only permanent-direct forces. The smaller lattice forces calculated in the FHLA can be expected to give smaller elastic energies than those calculated in the harmonic approximation. This is desirable since the critical temperature of the α-α' phase transition for Nb-H can be shown to be proportional to the elastic energy at the critical point (26) and the critical point temperature estimated for the H-Nb system by Horner and Wagner using the harmonic approximation is too high.[2,9] Similarly, harmonic-approximation values for T_c for order-disorder transitions are too big.[3-5] A lower (less negative) value for the elastic energy should give a lower value for the critical temperature which would be more in line with that observed experimentally.

In paper II of this series of papers, the elastic interaction energies will be calculated in the FHLA and compared with harmonic-approximation values.

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