

# Lattice Statics of a Hydrogen Centre in Magnesium

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In this work we consider the static perturbation of the hexagonal lattice of magnesium by one stored hydrogen atom.

Equations are given to evaluate the equilibrium positions of the ions in the disturbed crystal. The effect of the hydrogen atom is described by a so-called Kanzaki force, an additional force in the ideal lattice. The force between two ions of the ideal lattice is assumed to obey the harmonic approximation. The force constants are calculated from an effective ion-ion potential. The static Green tensor, which is the inverse of the tensor of force constants, is calculated and with its aid the equations of lattice statics are transformed. The transformed equations are solved under the assumption of a Kanzaki force acting only upon the nearest and next-nearest neighbors of the hydrogen atom at a tetrahedral interstitial site. Finally we calculate the volume change  $\Delta V$  and compare the result with the experimental value.

## § 1. The Equations of Lattice Statics

In [1] the many-body Schrödinger equation of a host crystal with stored hydrogen atoms and of a reference system (crystal without hydrogen) are decomposed adiabatically into the Schrödinger equations of the electronic, protonic and ionic subsystems. The ions and protons in the host crystal are assumed to be localized at equilibrium positions which can be obtained, according to [1], as solutions of the equations

$$\nabla_X \Delta E = 0, \quad \nabla_Y \Delta E = 0, \quad (1.1)$$

where  $\Delta E$  is the so-called storage energy

$$\Delta E = Q_{\alpha\beta\gamma}^n(Y, X) + \Delta(X).$$

In [1]  $Q_{\alpha\beta\gamma}^n$  and  $\Delta$  are defined as

$$Q_{\alpha\beta\gamma}^n(Y, X) = \frac{1}{2} \sum_{n, n'} \frac{e^2}{|Y^n - Y^{n'}|} + \sum_{n, m, i} U_i(Y^n - X^{m, i}) + \varepsilon_{\alpha}^{N+n}(Y, X) - \varepsilon_g^N(X) + H_{\alpha\beta}(Y, X) + K_{\alpha\beta\gamma}(Y, X) - K_g(X) \quad (1.2)$$

and

$$\Delta(X) = \sum_{\substack{m, i \\ m', i'}} (W_{ii'}(X^{m, i} - X^{m', i'}) - W_{ii'}(\hat{X}_R^{m, i} - \hat{X}_R^{m', i'})) + K_g(X) - K_g(\hat{X}_R) + \varepsilon_g^N(X) - \varepsilon_g^N(\hat{X}_R), \quad (1.3)$$

$Y = (Y_i^n)$  denotes the cartesian coordinates of the protons,  $X = (X_i^m)$  the cartesian coordinates of the ions,  $n = (n_1, n_2, n_3)$  and  $m = (m_1, m_2, m_3)$  are corresponding index triples according to a primitive basis  $a, b$  and  $c$ .  $\hat{X}_R$  denotes the equilibrium position of the ions in the ground state of the reference system.  $U_i$  is the proton-ion potential for ions of the  $i$ -th kind.  $W_{ii'}$  is the ion-ion potential for ions of the  $i$ -th respectively  $i'$ -th kind.  $\varepsilon_{\alpha}^{N+n}$  and  $\varepsilon_g^N$  are the energy eigenvalues of the electronic subsystem of the host lattice with hydrogen and the reference system, respectively.  $N$  denotes the number of the valence electrons and  $n$  the additional electrons of the hydrogen atoms.  $H_{\alpha\beta}$  is the vibrational energy of the protons and  $K_{\alpha\beta\gamma}$  and  $K_g$  are vibrational energies of the ions in the host lattice and the reference system, respectively.  $\alpha, \beta, \gamma$  are quantum numbers of the electronic, protonic and ionic subsystems in the host lattice,  $g$  denotes the corresponding groundstate quantum numbers of the reference system.

Vibrational energies of ions and protons are neglected in the present work. The computation of the electronic energy difference

$$\varepsilon_{\alpha}^{N+n}(Y, X) - \varepsilon_g^N(X)$$

which we use here is the topic of a special paper [2]. Equations (1.2) and (1.3) can be interpreted as follows.  $\Delta$  is the change in total energy of the crystal caused by the distortion of the lattice by the hydrogen centres and  $Q_{\alpha\beta\gamma}^n$  is the interaction of the hydrogen centres with the distorted lattice.

The equilibrium conditions (1.1) take the form

$$\nabla_Y Q_{\alpha\beta\gamma}^n(Y, X) = 0 \quad (1.4)$$

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and

$$\nabla_{\mathbf{X}} (Q_{\alpha\beta\gamma}^n(\mathbf{Y}, \mathbf{X}) + \Delta(\mathbf{X})) = 0. \quad (1.5)$$

Equation (1.4) permits, in principle, the determination of the protonic coordinates as a function of the ionic coordinates

$$\mathbf{Y} = \mathbf{Y}(\mathbf{X}).$$

This and the physical content of  $Q_{\alpha\beta\gamma}^n$  and  $\Delta$  allow the interpretation of (1.5) as a balance of two forces:

$$\mathbf{F}_{\text{latt}}(\mathbf{X}) = -\mathbf{F}_{\text{pert}}(\mathbf{X}). \quad (1.6)$$

The lattice force is defined as

$$\mathbf{F}_{\text{latt}}(\mathbf{X}) = -\nabla_{\mathbf{X}} \Delta(\mathbf{X}) \quad (1.7)$$

and the perturbation force as

$$\mathbf{F}_{\text{pert}}(\mathbf{X}) = -\nabla_{\mathbf{X}} Q_{\alpha\beta\gamma}^n(\mathbf{Y}(\mathbf{X}), \mathbf{X}). \quad (1.8)$$

The computation of the equilibrium positions of the ions using (1.6)–(1.8) will be carried out in this paper for one hydrogen centre in an ideal hcp structure. Index triples  $(m, n, k)$  refer to a primitive basis  $\mathbf{a}$ ,  $\mathbf{b}$  and  $\mathbf{c}$  chosen so that the vectors  $\mathbf{a}$  and  $\mathbf{b}$ , lying in the plane of an  $A$ -layer, enclose an angle of  $120^\circ$ .

The computations described here are applicable to magnesium, for which the value  $c/a = 1.623$  comes close to  $c/a = \sqrt{8/3} = 1.633$  of the ideal hcp structure. The reason for not taking the real hexagonal structure of magnesium as a basis for the computations is that the electronic part of the computation, not treated explicitly here, is simplified considerably by this assumption.

## § 2. Harmonic Approximation and Green Tensor

The aim of the computations in lattice statics is the determination of the new equilibrium positions

$$\tilde{\mathbf{X}} = \mathbf{R} + \mathbf{s}$$

of the ions exposed to the perturbing force.  $\mathbf{R}$  denotes the equilibrium positions in the unperturbed crystal and  $\mathbf{s}$  the deviation from it. Since  $\mathbf{s}$  is small in general, the harmonic approximation can be applied to the lattice force (1.7) and results in

$$\mathbf{F}_{\text{latt}} = -\mathcal{A} \cdot \mathbf{s} \quad \text{resp.} \quad F_i = -A_{ik}^{nm} s_k^* \quad (2.1)$$

\* Summation convention is used throughout this paper.

with the tensor of force constants

$$\mathcal{A} = (A_{ik}^{nm}) = \left( \frac{\partial^2 \Delta}{\partial X_i^n \partial X_k^m}(\mathbf{R}) \right). \quad (2.2)$$

The calculation of  $\Delta$  will be sketched briefly. For more details we refer to [3].

The vibrational energy terms have already been neglected. The ion-ion interaction  $W$  is assumed to be a Coulomb interaction between ions with positive charge  $Ze$ ,

$$W(r) = \frac{Z^2 e^2}{r},$$

where  $Z$  denotes the valence of the ions. The energy eigenvalue  $\varepsilon_g^N$  of the electronic subsystem in the reference system is assumed to be a sum of one-particle energies, computed with a one-particle model for the metal electrons in second order perturbation theory.  $\varepsilon_g^N$  then contains terms which depend on the ion coordinates and can be interpreted as indirect ion-ion interaction, and terms which are independent of the ion coordinates. Only the former ones contribute to  $\Delta$  according to the difference

$$\varepsilon_g^N(\tilde{\mathbf{X}}) - \varepsilon_g^N(\mathbf{R}).$$

In this way (1.3) reads

$$\Delta(\mathbf{X}) = \frac{1}{2} \sum_{m,n} [V(\mathbf{X}^{mn}) - V(\mathbf{R}^{mn})], \quad (2.3)$$

$$\mathbf{X}^{mn} = |\mathbf{X}^m - \mathbf{X}^n|, \quad \mathbf{R}^{mn} = |\mathbf{R}^m - \mathbf{R}^n|,$$

with an effective ion-ion interaction  $V$ .

According to [3]  $V$  takes the form

$$V(r) = \frac{Z^2 e^2}{r} + \frac{2\Omega_0}{(2\pi)^3} \int d^3q F(q) e^{-i\mathbf{q} \cdot \mathbf{r}} \quad (2.4)$$

with the energy-wavenumber characteristic

$$F(q) = -\frac{\Omega_0}{8\pi} \frac{q^2}{e^2} |\langle \mathbf{k} + \mathbf{q} | w^0 | \mathbf{k} \rangle|^2 \frac{\chi}{\varepsilon}, \quad (2.5)$$

$\Omega_0$ : volume per ion.

$\varepsilon(q) = 1 + f(q) \chi(q)$  denotes the dielectric function of the electron gas with

$$\chi(q) = \frac{1}{2\pi k_F} \left( \frac{m e^2}{\hbar^2} \right) \frac{1}{\eta^2} \left( \frac{1 - \eta^2}{2\eta} \ln \left| \frac{1 + \eta}{1 - \eta} \right| + 1 \right),$$

$$\eta = \frac{q}{2k_F}, \quad k_F = \left( \frac{3Z\pi^2}{\Omega_0} \right)^{1/3} \quad (\text{Fermi wavenumber}),$$

which includes by

$$f(q) = 1 - \frac{1}{2 + 2\alpha/\eta^2} \quad [4, 5],$$

$$\alpha = \frac{0.229}{0.458 + 0.012 r_s}, \quad r_s = \left( \frac{3}{4} \frac{\Omega_0}{\pi Z} \right)^{1/3},$$

effects of exchange and correlation. In the limit  $f(q) \rightarrow 1$   $\varepsilon$  becomes the well-known Hartree dielectric function.

Equations (2.4) and (2.5) determine  $V$  provided the unscreened electron-ion interaction  $w^0$  is known. Following Krasko and Gurskii [6] a model pseudopotential valid for simple metals is

$$w^0(r) = Z e^2 \left( \frac{\exp(-r/R_c) - 1}{r} + \frac{A_a}{R_c} \exp(-r/R_c) \right) \quad (2.6)$$

with its Fourier transform

$$\begin{aligned} \langle k+q | w^0 | k \rangle &= \frac{1}{\Omega_0} \int w^0(r) e^{-i\mathbf{q} \cdot \mathbf{r}} d^3r \\ &= \frac{4\pi Z e^2}{\Omega_0 q^2} \frac{(2A_a - 1)(qR_c)^2 - 1}{[(qR_c)^2 + 1]^2}. \end{aligned}$$

According to [6] the free parameters in (2.4)–(2.6) in case of magnesium take the values

$$\Omega_0 = 155.99 a_0^3, \quad A_a = 2.588, \quad R_c = 0.427 a_0.$$

With this  $V$  the force constants (2.2) are computed, which in the special case of (2.3) results in

$$\begin{aligned} A_{ik}^{mn} &= - \frac{(R_i^m - R_i^n)(R_k^m - R_k^n)}{(R^{mn})^2} \\ &\cdot \left( V''(R^{mn}) - \frac{V'(R^{mn})}{R^{mn}} \right) - \delta_{ik} \frac{V'(R^{mn})}{R^{mn}} \quad (m \neq n), \end{aligned} \quad (2.7)$$

$$A_{ik}^{mm} = - \sum_{n \neq m} A_{ik}^{mn}.$$

The second expression in (2.7) ensues from translational invariance of the whole crystal [7]. Figures 1 a–1 c show the potential  $V$  and its first and second derivative.

According to the harmonic approximation, (1.6) becomes

$$\mathcal{A} \mathbf{s} = \mathbf{F}_{\text{pert}}(\mathbf{s}). \quad (2.8)$$

This is a set of nonlinear equations of high dimension determining  $\mathbf{s}$ . Using the static Green tensor  $\mathcal{G}$ , defined by

$$\mathcal{G} \mathcal{A} = \mathcal{A} \mathcal{G} = \mathbf{1} \quad (2.9)$$

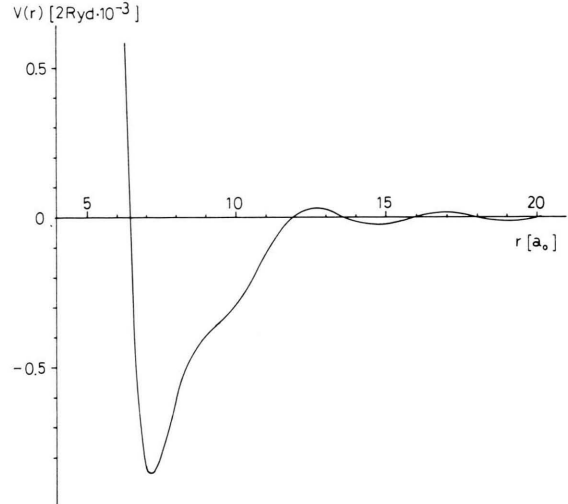


Fig. 1 a. The effective ion-ion potential in magnesium.

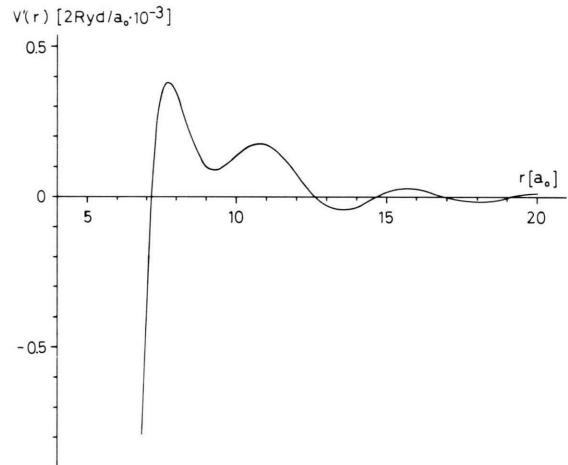


Fig. 1 b. The first derivative of the effective ion-ion potential.

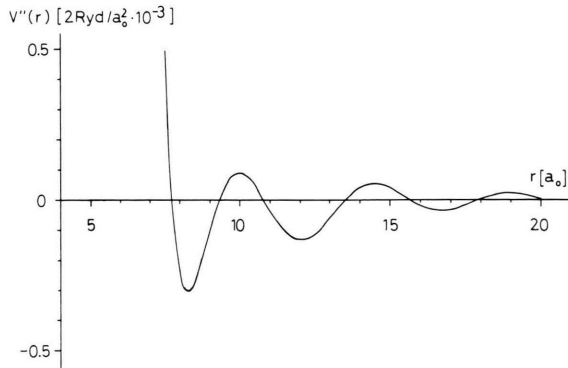


Fig. 1 c. The second derivative of the effective ion-ion potential.

and the boundary condition  $\mathcal{S} \rightarrow 0$  if  $r \rightarrow \infty$ , (2.8) becomes

$$s = \mathcal{S} \mathbf{F}_{\text{pert}}(s). \quad (2.10)$$

Because of screening effects the perturbation force depends only on the direct neighborhood and is non-vanishing only in the direct neighborhood of the perturbation centre. Equation (2.10) in contrast to (2.8) allows for solving only those equations which couple the unknown deviations of the ions of this neighborhood. Knowing the perturbation force the deviation of the other ions is given by means of the other equations of (2.10).

### § 3. Numerical Calculation of the Green Tensor

The computation of the Green tensor described in this chapter is based on the definition (2.9) in the form

$$A^{mn} G^{nl} = \delta^{ml}. \quad (3.1)$$

$A^{mn}$  and  $G^{nl}$  are  $3 \times 3$  matrices, which describe the force-deviation relations between two ions at the lattice points  $m$  and  $n$ , respectively  $n$  and  $l$ .  $\delta^{ml}$  is the  $3 \times 3$  unit matrix for  $m = l$  and  $3 \times 3$  null matrix for  $m \neq l$ . According to the summation convention one has an infinite sum of matrix products on the left side of (3.1). (3.1) can be interpreted as a set of linear equations to evaluate the components of the Green tensor.

According to the invariance of  $\mathcal{A}$  and  $\mathcal{S}$  under primitive translations of the lattice [7] one can choose  $l = 0$  and write (3.1) in the form

$$A^{0, n-m} G^{n, 0} = \delta^{m0}. \quad (3.2)$$

Because the effective ion-ion interaction and its derivatives are decreasing rapidly, a finite range  $R_{\text{eff}}$  is assumed for  $V$ , and  $V$  is set to zero for  $|\mathbf{R}^n - \mathbf{R}^m| > R_{\text{eff}}$ . Thus the summation over  $n$  in (3.2) is cut off. In our computations  $R_{\text{eff}}$  is assumed to be five lattice constants, that is,  $R_{\text{eff}} = 16.05 \text{ \AA}$  according to the lattice constant of  $a = 3.21 \text{ \AA}$  in magnesium. The assumed range includes 763 lattice points. To reduce the number of unknowns further, a partition relative to  $l = 0$  into a near and a remote area is made.

In the remote area the crystal is considered to be a continuum and therefore  $G^{n0}$  is approximated by the elastic Green's function:

$$G_{ik}^{n0} = G_{ik}(\mathbf{R}^n).$$

The elastic Green's function  $G_{ik}(\mathbf{r})$  is the solution of the elastic differential equation

$$C_{iklm} \partial_k \partial_l G_{mn}(\mathbf{r}) = -\delta_{in} \delta(\mathbf{r}) \quad (3.3)$$

with the boundary condition  $G_{ik}(\mathbf{r}) \rightarrow 0$  if  $r \rightarrow \infty$ , and can be given analytically in the hexagonal case [8]. The elastic Green's function in continuum statics is analogous to the Green tensor in lattice statics. Moreover, the boundary condition for  $\mathcal{S}$  is automatically fulfilled by the above assumption.

In the remote area the matter is described by the elastic constants  $C_{iklm}$ , in the near area by the force constants  $A_{ik}^{mn}$  respectively the effective ion-ion potential. The connection is given by the relations

$$C_{ikmn} = H_{imkn} + H_{inmk} - H_{ikmn}, \quad (3.4)$$

$$H_{ijkl} = -\frac{1}{2V_c} \sum_n A_{ij}^{nn} (R_k^n - R_k^m) (R_l^n - R_l^m)$$

with the Huang tensor  $H_{ijkl}$  [7].  $V_c$  is the volume of a primitive cell and takes the value

$$V_c = \sqrt{2} a^3$$

in an ideal hcp crystal. The following table shows the experimental elastic constants [9] used in the elastic Green's function and the elastic constants computed according to (3.4) with the force constants according to § 2. The first relation of (3.4) reads in a hexagonal lattice with the elastic constants in Voigt's notation

$$\begin{aligned} c_{11} &= H_{11,11}, \\ c_{12} &= 2H_{12,12} - H_{11,22}, \\ c_{13} &= 2H_{13,13} - H_{11,33}, \\ c_{33} &= H_{33,33}, \\ c_{44} &= H_{22,33}. \end{aligned}$$

Table 1. Elastic constants in  $10^9 \text{ N/m}^2$ .

	$c_{11}$	$c_{12}$	$c_{13}$	$c_{33}$	$c_{44}$
experimental	59.3	25.7	21.4	61.5	16.4
computed	56.25	27.41	23.08	50.69	10.27

The agreement between the description of matter by the elastic constants respectively the force constants is improved by a scaling of the potential according to

$$V_s(r) = s V(r).$$



Because of the linear dependence of the elastic constants on the potential according to (3.4) and (2.7), one gets the relation

$$(c_{kl}^{\text{comp}})_s = s (c_{kl}^{\text{comp}}).$$

We determine the scaling factor  $s$  by the condition that the quadratic deviation of the calculated from the experimental elastic constants

$$[(c_{22}^{\text{comp}})_s - c_{11}^{\text{exp}}]^2 + [(c_{12}^{\text{comp}})_s - c_{12}^{\text{exp}}]^2 + \dots + [(c_{44}^{\text{comp}})_s - c_{44}^{\text{exp}}]^2$$

has to be minimal. In this way we get

$$s = 1.098.$$

In all following computations we will use the scaled potential.

The near area is in our assumption a sphere with radius  $R_{\text{near}} = 5.242 \text{ \AA}$  around the point  $l = 0$ , which includes neighbors until 3rd order. This sphere contains 21 lattice points. One has still to determine 21  $3 \times 3$  matrices  $G^{n0}$  with a total of 186 unknowns ( $G^{00}$  is symmetric!). By means of grouptheoretical considerations [10, 11] this number can be reduced to the 16 unknowns  $G_1, G_2, \dots, G_{16}$ . The essential relation is

$$G^{m'n'} = S G^{mn} S'. \quad (3.5)$$

$m$  and  $n$  are mapped onto  $m'$  and  $n'$  by a symmetry transformation of the hexagonal space group. Using a cartesian coordinate system the transformation is given by

$$R^{m'} = (S | t) R^m = S R^m + t.$$

$S$  is an orthogonal  $3 \times 3$  matrix and  $t$  is a translation vector. Considering the symmetry operations which leave a pair  $(m, n)$  invariant or invert it, i.e.

$$(m', n') = (m, n) \quad \text{or} \quad (m', n') = (n, m),$$

(3.5) represents conditions for the matrix elements of  $G^{mn}$  (notice:  $G^{nm} = (G^{mn})'$  [7]). The procedure is applied here to one pair  $(n, 0)$  of every shell in the near area. The matrices  $G^{n0}$  of the other points on the considered shell ensue from  $G^{n0}$  by a "rotation" according to (3.5). Thus we get the following list of the matrices  $G^{n0}$  of all points in the near area with the minimal number of unknowns using a cartesian coordinate system.

For reasons of generality the first shell of the ideal hcp lattice containing 12 lattice points is considered to be a special case of a general hexago-

nal lattice for which the first and second shell coincide, containing 6 lattice points each. The  $G^{n0}$  listed are calculated relative to the latter.

$(m, n, l)$  denotes a point of an  $A$ -layer  $(m, n, l)^*$  a point of a  $B$ -layer. In cartesian coordinates the relationship is

$$R^{m*} = R^m + (a/2, \sqrt{3}a/6, c/2)$$

with

$$R^{(m,n,l)} = (a(m-n/2), a\sqrt{3}n/2, cl).$$

## 0. Shell

$$G^{00} = \begin{pmatrix} G_1 & 0 & 0 \\ 0 & G_1 & 0 \\ 0 & 0 & G_2 \end{pmatrix}$$

## 1. Shell

$$G^{(1,0,0),0} = \begin{pmatrix} G_3 - G_6 & 0 \\ +G_6 & G_4 & 0 \\ 0 & 0 & G_5 \end{pmatrix}$$

$$G^{(1,1,0),0} = \begin{pmatrix} \frac{1}{4}(G_3 + 3G_4) & \frac{\sqrt{3}}{4}(G_3 - G_4) + G_6 & 0 \\ \frac{\sqrt{3}}{4}(G_3 - G_4) - G_6 & \frac{1}{4}(3G_3 + G_4) & 0 \\ 0 & 0 & G_5 \end{pmatrix}$$

$$G^{(0,-1,0),0} = \begin{pmatrix} \frac{1}{4}(G_3 + 3G_4) & \frac{\sqrt{3}}{4}(G_4 - G_3) + G_6 & 0 \\ \frac{\sqrt{3}}{4}(G_4 - G_3) - G_6 & \frac{1}{4}(3G_3 + G_4) & 0 \\ 0 & 0 & G_5 \end{pmatrix}$$

$$G^{(0,1,0),0} = \begin{pmatrix} \frac{1}{4}(G_3 + 3G_4) & \frac{\sqrt{3}}{4}(G_4 - G_3) - G_6 & 0 \\ \frac{\sqrt{3}}{4}(G_4 - G_3) + G_6 & \frac{1}{4}(3G_3 + G_4) & 0 \\ 0 & 0 & G_5 \end{pmatrix}$$

$$G^{(-1,-1,0),0} = \begin{pmatrix} \frac{1}{4}(G_3 + 3G_4) & \frac{\sqrt{3}}{4}(G_3 - G_4) - G_6 & 0 \\ \frac{\sqrt{3}}{4}(G_3 - G_4) + G_6 & \frac{1}{4}(3G_3 + G_4) & 0 \\ 0 & 0 & G_5 \end{pmatrix}$$

$$G^{(-1,0,0),0} = \begin{pmatrix} G_3 + G_6 & 0 \\ -G_6 & G_4 & 0 \\ 0 & 0 & G_5 \end{pmatrix}$$

## 2. Shell

$$G^{(-1,-1,0)^*,0} = \begin{pmatrix} G_7 & 0 & \\ 0 & G_8 & G_{10} \\ 0 & G_{10} & G_9 \end{pmatrix}$$

$$G^{(-1,-1,-1)^*,0} = \begin{pmatrix} G_7 & 0 & 0 \\ 0 & G_8 & -G_{10} \\ 0 & -G_{10} & G_9 \end{pmatrix}$$

$$G^{(0,0,0)^*,0} = \begin{pmatrix} \frac{1}{4}(G_7+3G_8) & \frac{\sqrt{3}}{4}(G_8-G_7) & -\frac{\sqrt{3}}{2}G_{10} \\ \frac{\sqrt{3}}{4}(G_8-G_7) & \frac{1}{4}(3G_7+G_8) & -\frac{1}{2}G_{10} \\ -\frac{\sqrt{3}}{2}G_{10} & -\frac{1}{2}G_{10} & G_9 \end{pmatrix}$$

$$G^{(0,0,-1)^*,0} = \begin{pmatrix} \frac{1}{4}(G_7+3G_8) & \frac{\sqrt{3}}{4}(G_8-G_7) & \frac{\sqrt{3}}{2}G_{10} \\ \frac{\sqrt{3}}{4}(G_8-G_7) & \frac{1}{4}(3G_7+G_8) & \frac{1}{2}G_{10} \\ \frac{\sqrt{3}}{2}G_{10} & \frac{1}{2}G_{10} & G_9 \end{pmatrix}$$

$$G^{(-1,0,0)^*,0} = \begin{pmatrix} \frac{1}{4}(G_7+3G_8) & \frac{\sqrt{3}}{4}(G_7-G_8) & \frac{\sqrt{3}}{2}G_{10} \\ \frac{\sqrt{3}}{4}(G_7-G_8) & \frac{1}{4}(3G_7+G_8) & -\frac{1}{2}G_{10} \\ \frac{\sqrt{3}}{2}G_{10} & -\frac{1}{2}G_{10} & G_9 \end{pmatrix}$$

$$G^{(-1,0,-1)^*,0} = \begin{pmatrix} \frac{1}{4}(G_7+3G_8) & \frac{\sqrt{3}}{4}(G_7-G_8) & -\frac{\sqrt{3}}{2}G_{10} \\ \frac{\sqrt{3}}{4}(G_7-G_8) & \frac{1}{4}(3G_7+G_8) & \frac{1}{2}G_{10} \\ -\frac{\sqrt{3}}{2}G_{10} & \frac{1}{2}G_{10} & G_9 \end{pmatrix}$$

## 3. Shell

$$G^{(0,1,0)^*,0} = \begin{pmatrix} G_{11} & 0 & 0 \\ 0 & G_{12} & G_{14} \\ 0 & G_{14} & G_{13} \end{pmatrix}$$

$$G^{(0,1,-1)^*,0} = \begin{pmatrix} G_{11} & 0 & 0 \\ 0 & G_{12} & -G_{14} \\ 0 & -G_{14} & G_{13} \end{pmatrix}$$

$$G^{(0,-1,0)^*,0}$$

$$= \begin{pmatrix} \frac{1}{4}(G_{11}+3G_{12}) & \frac{\sqrt{3}}{4}(G_{11}-G_{12}) & \frac{\sqrt{3}}{2}G_{14} \\ \frac{\sqrt{3}}{4}(G_{11}-G_{12}) & \frac{1}{4}(3G_{11}+G_{12}) & -\frac{1}{2}G_{14} \\ \frac{\sqrt{3}}{2}G_{14} & -\frac{1}{2}G_{14} & G_{13} \end{pmatrix}$$

$$G^{(0,-1,-1)^*,0}$$

$$= \begin{pmatrix} \frac{1}{4}(G_{11}+3G_{12}) & \frac{\sqrt{3}}{4}(G_{11}-G_{12}) & -\frac{\sqrt{3}}{2}G_{14} \\ \frac{\sqrt{3}}{4}(G_{11}-G_{12}) & \frac{1}{4}(3G_{11}+G_{12}) & \frac{1}{2}G_{14} \\ -\frac{\sqrt{3}}{2}G_{14} & \frac{1}{2}G_{14} & G_{13} \end{pmatrix}$$

$$G^{(-2,-1,0)^*,0}$$

$$= \begin{pmatrix} \frac{1}{4}(G_{11}+3G_{12}) & \frac{\sqrt{3}}{4}(G_{12}-G_{11}) & -\frac{\sqrt{3}}{2}G_{14} \\ \frac{\sqrt{3}}{4}(G_{12}-G_{11}) & \frac{1}{4}(3G_{11}+G_{12}) & -\frac{1}{2}G_{14} \\ -\frac{\sqrt{3}}{2}G_{14} & -\frac{1}{2}G_{14} & G_{13} \end{pmatrix}$$

$$G^{(-2,-1,-1)^*,0}$$

$$= \begin{pmatrix} \frac{1}{4}(G_{11}+3G_{12}) & \frac{\sqrt{3}}{4}(G_{12}-G_{11}) & \frac{\sqrt{3}}{2}G_{14} \\ \frac{\sqrt{3}}{4}(G_{12}-G_{11}) & \frac{1}{4}(3G_{11}+G_{12}) & \frac{1}{2}G_{14} \\ \frac{\sqrt{3}}{2}G_{14} & \frac{1}{2}G_{14} & G_{13} \end{pmatrix}$$

## 4. Shell

$$G^{(0,0,1)^*,0} = \begin{pmatrix} G_{15} & 0 & 0 \\ 0 & G_{15} & 0 \\ 0 & 0 & G_{16} \end{pmatrix}$$

$$G^{(0,0,-1)^*,0} = \begin{pmatrix} G_{15} & 0 & 0 \\ 0 & G_{15} & 0 \\ 0 & 0 & G_{16} \end{pmatrix}$$

Equation (3.2) can now be used to get equations for the remaining unknowns choosing some  $\mathbf{m}$ 's. For every  $\mathbf{m}$  one gets nine equations for the sixteen unknowns  $G_1, \dots, G_{16}$  because (3.2) is a matrix equation.

The procedure to reduce the the number of unknowns implies that the matrices  $G^{n0}$  of the four shells are determined by certain unknowns, the 0. shell by  $G_1$  and  $G_2$ , the 1. shell by  $G_3 - G_6$ , the 2. shell by  $G_7 - G_{10}$ , the 3. shell by  $G_{11} - G_{14}$  and the 4. shell by  $G_{15} - G_{16}$ . Because the force constants are rapidly decreasing, one can expect in (3.2) the term  $n = m$  to be the main contribution in summing over  $n$ . Choosing  $m$  lying on a shell of the near area, one thus gets nine equations in which the coefficients of the unknowns of that shell compared with the others are large. This is a supposition to compute these unknowns with sufficient accuracy numerically. For this reason we chose for  $m$  one point per shell, and that according to the sequence of the shells:

$$(0, 0, 0), (1, 0, 0), (0, 0, 0)^*, (0, -1, 0)^*, (0, 0, 1).$$

We obtain 45 equations which contain exactly 7 linearly independent equations for the 7 unknowns  $G_2, G_5, G_9, G_{10}, G_{13}, G_{14}$  and  $G_{16}$ . This set of linear equations is almost decomposed from the remaining equations. Only the unknowns  $G_{10}$  and  $G_{14}$  appear in the other equations. These seven equations are unboldfaced in the following list. The other nine equations determining the 16 unknowns cannot be chosen so definitely. There are several possibilities.

The following list shows our choice of 16 linearly independent equations with regard to fulfill best the unconsidered equations. Each equation is identified by the pair of coordinate indices in (3.2).

$m$	$(i, k)$
$(0, 0, 0)$	$(1, 1), (3, 3)$
$(1, 0, 0)$	$(1, 1), (1, 2), (2, 1), (2, 2), (3, 3)$
$(0, 0, 0)^*$	$(1, 1), (1, 3), (2, 2), (3, 3)$
$(0, -1, 0)^*$	$(1, 2), (1, 3), (3, 3)$
$(0, 0, 1)$	$(1, 1), (3, 3).$

The numerical solution of this set of linear equations yields the following results (in  $m/N$ ):

$$\begin{array}{ll} G_1 = 0.272 \cdot 10^{-1} & G_9 = 0.113 \cdot 10^{-1} \\ G_2 = 0.271 \cdot 10^{-1} & G_{10} = -0.227 \cdot 10^{-2} \\ G_3 = 0.132 \cdot 10^{-1} & G_{11} = 0.478 \cdot 10^{-2} \\ G_4 = 0.775 \cdot 10^{-2} & G_{12} = 0.452 \cdot 10^{-2} \\ G_5 = 0.760 \cdot 10^{-2} & G_{13} = 0.643 \cdot 10^{-2} \\ G_6 = 0.189 \cdot 10^{-3} & G_{14} = 0.263 \cdot 10^{-3} \\ G_7 = 0.620 \cdot 10^{-2} & G_{15} = 0.562 \cdot 10^{-2} \\ G_8 = 0.998 \cdot 10^{-2} & G_{16} = 0.808 \cdot 10^{-2}. \end{array}$$

## § 4. Lattice Distortions

Treating the lattice in harmonic approximation, (2.10) connects the displacement field  $s$  of the ions and the perturbation force  $F_{\text{pert}}$  in a simple way

$$s = \mathcal{G} F_{\text{pert}}(s). \quad (4.1)$$

We have already mentioned that (4.1) has to be solved only for the vicinity of the perturbation centre.

First, we only consider the four nearest neighbors of the hydrogen interstitial. Additionally we suppose that the directions of the perturbation forces are given by the unit vectors  $n_i$  ( $i = 0, 1, 2, 3$ ), which denote the four nearest neighbors in a coordinate system with the origin at the interstitial site.

For simplicity, in this paragraph the lattice points will not be denoted by lattice indices  $(m, n, k)$  but by continuous numbering. Figure 2 shows the sites and the numbering of the nearest and next-nearest neighbors of the interstitial proton  $P$  in the hcp-structure. We assume the amount of the perturbation forces acting on the nearest neighbors to be the same. Then (4.1) turns into

$$s^k = F(s) \mathcal{G}^{ki} n_i = F(s) \tilde{G}^k \quad (k = 0, 1, 2, 3) \quad (4.2)$$

with the abbreviation  $\tilde{G}^k = \mathcal{G}^{ki} n_i$ .

For the  $\tilde{G}^k$  we get the following representation:

$$\begin{aligned} \tilde{G}^0 &= \mathcal{G}^{00} n_0 + \mathcal{G}^{01} n_1 + \mathcal{G}^{02} n_2 + \mathcal{G}^{03} n_3 \\ \tilde{G}^1 &= \mathcal{G}^{10} n_0 + \mathcal{G}^{11} n_1 + \mathcal{G}^{12} n_2 + \mathcal{G}^{13} n_3 \\ &= (\mathcal{G}^{01})^t n_0 + \mathcal{G}^{00} n_1 + \mathcal{G}^{07} n_2 + \mathcal{G}^{08} n_3 \\ \tilde{G}^2 &= \mathcal{G}^{20} n_0 + \mathcal{G}^{21} n_1 + \mathcal{G}^{22} n_2 + \mathcal{G}^{23} n_3 \\ &= (\mathcal{G}^{02})^t n_0 + (\mathcal{G}^{07})^t n_1 + \mathcal{G}^{00} n_2 + \mathcal{G}^{06} n_3 \\ \tilde{G}^3 &= \mathcal{G}^{30} n_0 + \mathcal{G}^{31} n_1 + \mathcal{G}^{32} n_2 + \mathcal{G}^{33} n_3 \\ &= (\mathcal{G}^{03})^t n_0 + (\mathcal{G}^{08})^t n_1 + (\mathcal{G}^{06})^t n_2 + \mathcal{G}^{00} n_3. \end{aligned}$$

By means of the properties  $G^{mn} = G^{0, n-m}$  and  $G_{ik}^{mn} = G_{ki}^{nm} = (G_{ik}^{nm})^t$  the unknown Green-matrices in the expressions for the  $\tilde{G}^k$  are led back to the matrices  $\mathcal{G}^{0k}$  from § 3.

Inserting the computed components of the Green matrices in the relations for  $\tilde{G}^k$ , we get the numerical values (in units of  $10^{-3} m/N$ )

$$\begin{aligned} \tilde{G}^0 &= (-7.505, -4.333, -2.833), \\ \tilde{G}^1 &= (7.505, -4.333, -2.833), \\ \tilde{G}^2 &= (0, 8.666, -2.833), \\ \tilde{G}^3 &= (0, 0, 9.379), \end{aligned}$$

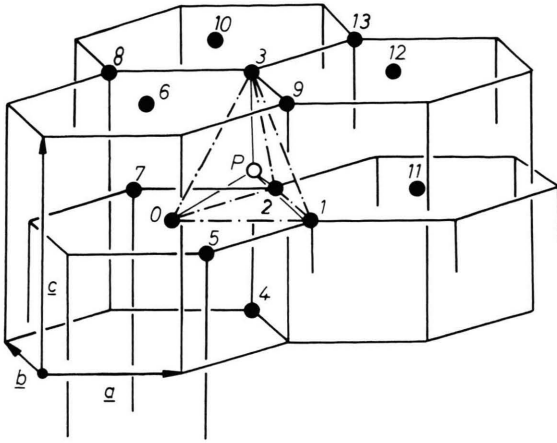


Fig. 2. Nearest (0–3) and next-nearest (4–13) neighbours of the proton at a tetrahedral site in the hcp-structure.

$$\text{and } |\tilde{\mathbf{G}}^k| = 9.117 \quad \text{for } k = 0, 1, 2, \\ |\tilde{\mathbf{G}}^3| = 9.379.$$

The vectors  $\tilde{\mathbf{G}}^k$  and the unit vectors  $\mathbf{n}^k$  are collinear, apart from small deviations [ $\angle(\tilde{\mathbf{G}}^k, \mathbf{n}^k) \approx 1^\circ$ ]. This is in agreement with the assumption of radial displacements.

In this case the perturbation forces can easily be computed by (1.8):

$$\mathbf{F}_{\text{pert}}^k = - \left[ \frac{d}{ds} \left( \frac{2e^2}{d_0 + s} + \frac{1}{4} \lambda(s) \right) \right] \mathbf{n}^k = F_0 \mathbf{n}^k, \quad (4.3)$$

where  $F_0 = |\mathbf{F}_{\text{pert}}^k|$  and where  $d_0$  is the distance between proton and a nearest neighbor in the undistorted, host lattice. Besides we will neglect the vibrational energies  $K_{\alpha\beta\gamma}(\mathbf{Y}, \mathbf{X})$  in (4.3), and it is made use of the relation [1]

$$\varepsilon_{\alpha}^{N+1}(\tilde{\mathbf{Y}}, \tilde{\mathbf{X}}) - \varepsilon_{\alpha}^N(\tilde{\mathbf{X}}) = \omega(\tilde{\mathbf{Y}}, \tilde{\mathbf{X}}) \\ = \lambda(\tilde{\mathbf{Y}}, \tilde{\mathbf{X}}) + T_r[V_H(\mathbf{x}, \tilde{\mathbf{Y}}) S_0(\mathbf{x}, \mathbf{x})].$$

In (1.8) we introduce the pure Coulomb interaction for the proton-ion-interaction.

The electronic energy difference  $\lambda(\mathbf{Y}, \mathbf{X})$  is multiplied by a factor 1/4, because in the calculation of  $\lambda(\mathbf{Y}, \mathbf{X})$  all four nearest neighbors are displaced by the same amount and we suppose that each of these neighbors delivers the same contribution to  $\lambda$ .

All simplifications made here reduce the set of (4.2) to a single nonlinear equation for the displacement  $s_0 = |\mathbf{s}^k|$  of the nearest neighbors:

$$s_0 = |\tilde{\mathbf{G}}^0| F_0(s_0) = |\tilde{\mathbf{G}}^0| \left[ \frac{2e^2}{(d_0 + s_0)^2} - \frac{1}{4} \frac{d}{ds_0} \lambda(s_0) \right]. \quad (4.4)$$

Maichle [2] calculated  $\lambda(s_0)$  in the intervall  $-0.25 a_0 \leq s_0 \leq 0.25 a_0$  ( $a_0$  is the Bohr radius  $a_0 = 0.529177 \text{ \AA}$ ).

The numerical values of  $\lambda(s_0)$  will be approximated by polynomials of fourth order in parts of the whole displacement intervall. A solution of (4.4) is found in the intervall

$$0.07 a_0 \leq s_0 \leq 0.09 a_0.$$

We choose numerical values of  $\lambda(s_0)$  for the displacements  $s_{0,n} = (0.07 + n \cdot 0.005) a_0$  ( $n = 0, 1, 2, 3, 4$ ). Then we get for  $\lambda(s_0)$  the polynomial

$$\lambda(s_0) = 396.13515 s_0^4 - 97.98091 s_0^3 \\ + 10.758542 s_0^2 + 0.41889347 s_0 - 0.1571295$$

[ $\lambda(s_0)$  in Ryd,  $s_0$  in atomic units].

Because of the difference in  $|\tilde{\mathbf{G}}^3|$  and  $|\tilde{\mathbf{G}}^k|$  we solve the analogous equation for the displacements  $s_0$  of the ion  $k = 3$ . The obtained displacements and perturbation forces are:

$$s_0 = 0.0794 a_0 \quad \text{for } k = 0, 1, 2 \\ F_0 = 4.61 \cdot 10^{-10} \text{ N}$$

$$s_0 = 0.0796 a_0 \quad \text{for } k = 3. \\ F_0 = 4.49 \cdot 10^{-10} \text{ N}$$

This result confirms the assumption that the forces and displacements of all four neighbors are the same.

In a next step we also consider the next-nearest neighbors of the interstitial hydrogen. Actually the tetrahedral interstitial in a hcp-lattice has only one next-nearest neighbor at a distance  $d = 3.276 \text{ \AA}$ . Then nine neighbors follow at a distance  $d_1 = 3.764 \text{ \AA}$ . For simplicity, all these ten host ions are regarded as next-nearest neighbors. In this case the system (4.1) consists of  $14 \cdot 3$  nonlinear equations. We reduce this system with the following three assumptions to two equations for the displacements  $s_0$  and  $s_1$  of the nearest and next-nearest neighbors.

- The perturbation forces which act on the nearest and next-nearest neighbors amount to  $F_0$  and  $F_1$ , respectively.
- The directions of the perturbation forces are given by the unit vectors  $\mathbf{n}^i$ .
- The displacements of the neighboring ions are radial
 
$$\mathbf{s}^k = |\mathbf{s}^k| \mathbf{n}^k = s^k \mathbf{n}^k, \\ |\mathbf{s}^k| = s_0 \text{ for all nearest and } |\mathbf{s}^k| = s_1 \text{ for all next-nearest neighbors.}$$

With these assumptions we transform (4.1) as follows:

$$\begin{aligned} \mathbf{s}^k &= \sum_{i=0} \mathcal{G}^{ki} \mathbf{F}_{\text{pert}}^i \stackrel{\text{b)}}{=} \sum_{i=0} \mathcal{G}^{ki} |\mathbf{F}_{\text{pert}}^i| \mathbf{n}^i \stackrel{\text{a)}}{=} \\ &= F_0 \sum_{i=0}^3 \mathcal{G}^{ki} \mathbf{n}^i + F_1 \sum_{i=4}^{13} \mathcal{G}^{ki} \mathbf{n}^i \\ &=: F_0 \tilde{\mathbf{G}}_n^k + F_1 \tilde{\mathbf{G}}_{nn}^k \quad (k = 0, 1, \dots, 13). \end{aligned} \quad (4.5)$$

The indices n and nn point to the contributions of the nearest and next-nearest neighbors.

Because all nearest, respectively all next-nearest neighbors are treated equally, the system (4.5) is reduced to the two equations for  $s_0$  and  $s_1$

$$\begin{aligned} s_0 &= (F_0^2 |\tilde{\mathbf{G}}_n^0|^2 + 2 F_0 F_1 |\tilde{\mathbf{G}}_n^0| |\tilde{\mathbf{G}}_{nn}^0| \cos \gamma_0 \\ &\quad + F_1^2 |\tilde{\mathbf{G}}_{nn}^0|^2)^{1/2}, \\ s_1 &= (F_0^2 |\tilde{\mathbf{G}}_n^5|^2 + 2 F_0 F_1 |\tilde{\mathbf{G}}_n^5| |\tilde{\mathbf{G}}_{nn}^5| \cos \gamma_5 \\ &\quad + F_1^2 |\tilde{\mathbf{G}}_{nn}^5|^2)^{1/2}. \end{aligned} \quad (4.6)$$

From (4.5) we choose the equations for  $k = 0$  and  $k = 5$ .  $\gamma_0$  and  $\gamma_5$  are the angles between  $\tilde{\mathbf{G}}_n^0$  and  $\tilde{\mathbf{G}}_{nn}^0$  and between  $\tilde{\mathbf{G}}_n^5$  and  $\tilde{\mathbf{G}}_{nn}^5$ , respectively. For the values  $\tilde{\mathbf{G}}_n^0$ ,  $\tilde{\mathbf{G}}_{nn}^0$ ,  $\tilde{\mathbf{G}}_n^5$ ,  $\tilde{\mathbf{G}}_{nn}^5$ ,  $\cos \gamma_0$  and  $\gamma_5$  we get

$$\begin{aligned} \tilde{\mathbf{G}}_n^0 &= \begin{pmatrix} -0.00724 \\ -0.00418 \\ -0.0028 \end{pmatrix}, \quad |\tilde{\mathbf{G}}_n^0| = 0.0088165, \\ \tilde{\mathbf{G}}_{nn}^0 &= \begin{pmatrix} 0.0022836 \\ 0.0013182 \\ 0.01517 \end{pmatrix}, \quad |\tilde{\mathbf{G}}_{nn}^0| = 0.015397, \\ \cos \gamma_0 &= -0.47503, \\ \tilde{\mathbf{G}}_n^5 &= \begin{pmatrix} 0 \\ 0.0010845 \\ -0.000362 \end{pmatrix}, \quad |\tilde{\mathbf{G}}_n^5| = 0.0011434, \end{aligned}$$

$$\begin{aligned} \tilde{\mathbf{G}}_{nn}^5 &= \begin{pmatrix} 0 \\ -0.012745 \\ 0.011832 \end{pmatrix}, \quad |\tilde{\mathbf{G}}_{nn}^5| = 0.01739, \\ \cos \gamma_5 &= -0.91065, \end{aligned}$$

[all values in m/N].

In the calculation of  $\tilde{\mathbf{G}}_n^5$  and  $\tilde{\mathbf{G}}_{nn}^5$  Green-matrices are needed which are not in the discrete part of the Greentensor  $\mathcal{G}$ . For these matrices we use the fundamental integral from Kröner [8].

The perturbation forces  $F_0$  and  $F_1$  we obtain as in the case where only the nearest neighbors are considered. For computing  $F_1$  the new distance  $d_1$  and the contributions of ten additional neighbors to the energy difference  $\lambda(s_0, s_1)$  have to be taken into account.

$\lambda(s_0, s_1)$  is calculated for radial displacements  $s_0$  and  $s_1$ . Then the forces  $F_0$  and  $F_1$  are obtained from (1.8):

$$\begin{aligned} F_0 &= -\frac{\partial}{\partial s_0} \left[ \frac{2e^2}{d_0 + s_0} + \frac{1}{4} \lambda(s_0, s_1) \right] \\ &= \frac{2e^2}{(d_0 + s_0)^2} - \frac{1}{4} \frac{\partial}{\partial s_0} \lambda(s_0, s_1), \\ F_1 &= -\frac{\partial}{\partial s_1} \left[ \frac{2e^2}{d_1 + s_1} + \frac{1}{10} \lambda(s_0, s_1) \right] \\ &= \frac{2e^2}{(d_1 + s_1)^2} - \frac{1}{10} \frac{\partial}{\partial s_1} \lambda(s_0, s_1). \end{aligned}$$

To get an analytical expression for  $\lambda(s_0, s_1)$ , which reproduces the numerical values with a satisfactory accuracy, the interpolation formula of Lagrange is used. On a small intervall  $[s_{0,0}, s_{0,m}] \times [s_{1,0}, s_{1,n}]$ ,  $\lambda(s_0, s_1)$  is accordingly given by the Lagrange polynomial

$$\lambda(s_0, s_1) = \sum_{i=0}^m \sum_{k=0}^n L_i^{(1)}(s_0) L_k^{(2)}(s_1) f_{ik}$$

with the abbreviation

$$L_i^{(1)}(s_0) = \frac{(s_0 - s_{0,0}) \cdots (s_0 - s_{0,i-1}) (s_0 - s_{0,i+1}) \cdots (s_0 - s_{0,m})}{(s_{0,i} - s_{0,0}) \cdots (s_{0,i} - s_{0,i-1}) (s_{0,i} - s_{0,i+1}) \cdots (s_{0,i} - s_{0,m})}$$

$[L_k^{(2)}(s_1)]$  is of the same form].

$f_{ik}$  are the values  $\lambda(s_0, s_1)$  for the displacement

$$(s_{0,i}, s_{1,k}) \in [s_{0,0}, s_{0,m}] \times [s_{1,0}, s_{1,n}] \quad f_{ik} = \lambda(s_{0,i}, s_{1,k}).$$

In the derivatives of  $\lambda(s_0, s_1)$  needed to calculate the forces  $F_0$  and  $F_1$ , the derivatives  $L_i^{(1)'}(s_0)$  and  $L_k^{(2)'}(s_1)$  appear.

The expression for  $L_i^{(1)'}(s_0)$  is

$$L_i^{(1)'}(s_0) = \sum_{p=0}^m \frac{(s_0 - s_{0,0}) \cdots (s_0 - s_{0,i-1}) (s_0 - s_{0,i+1}) \cdots (\widehat{s_0 - s_{0,p}}) \cdots (s_0 - s_{0,m})}{(s_{0,i} - s_{0,0}) \cdots (s_{0,i} - s_{0,i-1}) (s_{0,i} - s_{0,i+1}) \cdots (s_{0,i} - s_{0,m})}$$



[“ $\wedge$ ” excludes the appropriate factor from the product].

We sum to  $m=n=4$ , i.e.  $\lambda(s_0, s_1)$  is approximated with a polynomial of fourth order in  $s_0$  and  $s_1$ .

Now the equations (4.6) are solved numerically. The result is a repulsion of the nearest neighbors and an attraction of the next-nearest neighbors towards the interstitial hydrogen.

$$F_0 = 5.4743 \cdot 10^{-10} \text{ N}, \quad s_0 = 0.09575 a_0, \\ F_1 = -0.3055 \cdot 10^{-10} \text{ N}, \quad s_1 = -0.02138 a_0.$$

[Negativity denotes attractive forces respectively displacements towards the proton.]

Inserting this result in (4.5) for  $k=0$  and  $k=5$ , we find that the displacements  $s^0$  and  $s^5$  are not radial as supposed. In a first approach we take this into consideration by solving (4.5) with the new proton-ion distances (not  $d_0 + s_0$ , but

$$\sqrt{d_0^2 + 2 d_0 s_0 \cos[\angle(\mathbf{n}_0, \mathbf{s}^0)] + s_0^2}$$

for the nearest and analogously for the next-nearest neighbors). The angle  $\angle(\mathbf{n}_0, \mathbf{s}^0)$  is computed with the results above. This procedure is repeated till the results do not change. In the electronic computation we neglect the deviation from the radial displacements.

After three steps of iteration we obtain the following result:

$$F_0 = 5.4926 \cdot 10^{-10} \text{ N}, \quad F_1 = -0.331 \cdot 10^{-10} \text{ N}, \\ s_0 = 0.09646 a_0, \quad s_1 = -0.02223 a_0, \\ \cos[\angle(\mathbf{n}_0, \mathbf{s}^0)] = 0.9975, \quad \cos[\angle(\mathbf{n}_5, \mathbf{s}^5)] = -0.7643.$$

## § 5. Volume Change $\Delta V$

The displacement field  $\mathbf{s}$ , produced after introducing a point defect in a metallic crystal, alters the volume of the crystal by an amount  $\Delta V$ . From [7] we have an expression for  $\Delta V$ :

$$\Delta V = \int d\mathbf{r} \operatorname{tr} \{\epsilon\} = \operatorname{tr} \{SP\} = S_{ii, mn} P_{mn}. \quad (5.1)$$

$S$  is the tensor of the elastic coefficients. It is the inverse of the elastic moduli  $C$ .  $P_{ik}$  are the components of the double force tensor  $P$ .

Because perturbation forces act, according to our assumption, only on the ions  $k=0, \dots, 13$ ,  $P$  takes the form [7]

$$P_{sk} = \sum_{j=0}^{13} X_s^j F_k^j.$$

$X_s^j$  and  $F_k^j$  are the cartesian components of the ion sites  $\mathbf{R}^j$  and the perturbation forces  $\mathbf{F}_{\text{pert}}^j$ .

With the assumptions made above,  $P$  has the representation

$$P_{sk} = F_0 \sum_{j=0}^3 X_s^j n_k^j + F_1 \sum_{j=4}^{13} X_s^j n_k^j =: P_{sk}^{(n)} + P_{sk}^{(nn)}.$$

The portions  $P_{sk}^{(n)}$  of the nearest and  $P_{sk}^{(nn)}$  of the next-nearest neighbors in the double force tensor are separately specified:

$$P_{11}^{(n)} = P_{22}^{(n)} = P_{33}^{(n)} = a \frac{\sqrt{6}}{3} F_0 \quad (a = \text{lattice constant}),$$

$$P_{sk}^{(n)} = 0, \quad \text{when } s \neq k,$$

$$P_{11}^{(nn)} = P_{22}^{(nn)} = \frac{10}{11} a \sqrt{22} F_1,$$

$$P_{33}^{(nn)} = a \left( \frac{5}{12} \sqrt{6} + \frac{19}{44} \sqrt{22} \right) F_1,$$

$$P_{sk}^{(nn)} = 0, \quad \text{when } s \neq k.$$

For the diagonal double force tensor  $P$  (5.1) turns into

$$\Delta V = S_{11} P_{11} + S_{12} P_{22} + S_{13} P_{33} + S_{22} P_{22} + S_{23} P_{33} \\ + S_{21} P_{11} + S_{31} P_{11} + S_{32} P_{22} + S_{33} P_{33}, \quad (5.2)$$

where Voigt's notation is used for  $S$ .

The elastic coefficients can be expressed by the elastic moduli  $C_{ik}$

$$S_{11} = \frac{1}{2} \left[ \frac{1}{C_{11} - C_{12}} + \frac{C_{33}}{C_c} \right],$$

$$S_{12} = -\frac{1}{2} \left[ \frac{1}{C_{11} - C_{12}} - \frac{C_{33}}{C_c} \right],$$

$$S_{12} = \frac{-C_{13}}{C_c}, \quad S_{33} = \frac{C_{11} + C_{12}}{C_c},$$

and

$$C_c = (C_{11} + C_{12}) C_{33} - 2 C_{13}^2.$$

With the experimental values in Table 1 for  $C_{ik}$  we obtain the following elastic coefficients [in  $10^{-10} \text{ m}^2/\text{N}$ ]

$$S_{11} = 0.22013, \quad S_{12} = -0.07749, \\ S_{13} = -0.0496388, \quad S_{33} = 0.1971435.$$

In a hexagonal lattice hold the relations

$$S_{11} = S_{22} \quad \text{and} \quad S_{23} = S_{13}.$$

According to (5.2),  $\Delta V$  is now written in the form

$$\Delta V = 2 P_{11}^{(n)} (S_{11} + S_{12} + 2 S_{13} + \frac{1}{2} S_{33}) \\ + 2 P_{11}^{(nn)} (S_{11} + S_{12} + S_{13}) + P_{33}^{(nn)} (2 S_{13} + S_{33})$$

or, expressed in numerical values

$$\Delta V \approx (0,744 F_0 + 3,5028 F_1) \text{ \AA}^3,$$

$$F_0 \text{ and } F_1 \text{ in } 10^{-10} \text{ N.}$$

For the two examined cases we obtain the volume change  $\Delta V$  as

i) only nearest neighbors considered:

$$\Delta V = 3,43 \text{ \AA}^3,$$

ii) nearest and  $n - n$  neighbors considered:

$$\Delta V = 2,93 \text{ \AA}^3.$$

The experimental value for the volume change  $\Delta V$  for all metal hydrides is close to  $2,9 \text{ \AA}^3$  (Peisl in [12]).

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