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A simple tight-binding estimate of the dipole force tensor in $\alpha$-palladium hydrides

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1. Introduction. — Johnston and Sholl [1] have recently estimated the lattice distortions and relaxation energies due to hydrogen impurities infcc and bcc transition metals using experimental results for the change in volume of the crystal due to the interstitial atom. Also Dietrich and Wagner [2] have estimated the elastic interaction between two hydrogen atoms in the incoherent phase of palladium hydrides using the experimental value of the dipole force tensor $P$. Up to now, only phenomenological pair potentials have been used for a theoretical estimation of $P$ infcc transition metals [3]. On the other hand, it has been shown recently that the tight-binding method could be a useful tool for a semi-quantitative electronic structure of sp impurities in transition metals [4]. Moreover, it has been shown that this method can give a reasonable insight into the electronic structure of hydrogen in $\alpha$-palladium hydrides [5]. The tight-binding method has also been used for an estimation of the dipole force tensor in dilute alloys of transition metals [6, 7].

Our objective is to extend this previous model [6, 7] to interstitial hydrogen in $\alpha$-palladium hydrides by using a purely tight-binding Hamiltonian for the electronic structure. The band structure of the pure transition metal is described by a spd Slater-Koster fit to first-principle calculations [8] whereas the impurity is described by an extra-orbital s. In the case of hydrogen at an octahedral position in afcc transition metal, the hopping integral between the hydrogen s and nearest metallic spd orbitals can be defined in terms of three different two centre integrals (ss, sp, and sd). A more complete description can be found in [5].

To obtain an expression for the dipole force tensor $P$ we have taken into account the effect arising from the rigid displacement of d orbitals only. Let $\beta_{ab}^{mn}$ be

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a transfer integral between two metallic atoms at sites \( \lambda \) and \( \mu \) given by:

\[
\beta_{\mu \lambda}^{m} = \langle \lambda m' \mid H \mid \mu m \rangle
\]  

(1.1)

where \( \mid \mu m \rangle \) is a d metallic orbital, \( H \) the Hamiltonian of the unrelaxed alloy, and \( H_0 \) the Hamiltonian of the unrelaxed pure metal:

\[
H = H_0 + \Delta V .
\]  

(1.2)

In the two centre approximation and for the chemical potential \( \Delta V \) discussed in [5] it can be shown that:

\[
\beta_{\mu \lambda}^{m} = \beta_{\mu \lambda}^{m} = \delta \beta_{\mu \lambda}^{m}
\]  

(1.3)

which means that the hopping integrals between the metallic sites are unaffected by the chemical potential of the impurity. If we consider now the effect of the relaxation on one site \( \lambda \) it will affect the distance \( R_{A \mu} \) between the two sites by a quantity \( u_{\lambda} \) given by:

\[
u_{\lambda} = R_{A \mu} - R_{A \mu}^{0}.
\]  

(1.4)

The resulting effect on the transfer integral is a variation \( \delta \beta_{\mu \lambda}^{m} \) defined by:

\[
\delta \beta_{\mu \lambda}^{m} = \nu_{\lambda} \cdot \nabla \beta_{\mu \lambda}^{m}(R_{A \mu}^{0})
\]  

(1.5)

\[
\delta \beta_{\mu \lambda}^{m} = \nu_{\lambda} \cdot \nabla \beta_{\mu \lambda}^{m}(R_{A \mu}^{0})
\]  

(1.6)

where the radial part of \( \beta_{\mu \lambda}^{m}(R_{A \mu}^{0}) \) is given in terms of \( \delta \beta_{\mu \lambda}^{m} \).

In section 2, we derive a general formulation for the field of forces induced on the metallic atoms by the interstitial hydrogen. Section 3 is devoted to a numerical estimate of the forces on nearest, next nearest and third nearest palladium atoms to the hydrogen impurity in terms of two parameters \( q_{\text{IND}} \) and \( q_{\text{OND}} \) which characterize the typical exponential fall-off of the sd and dd Hamiltonian matrix elements respectively. \( q_{\text{IND}} \) and \( q_{\text{OND}} \) are different but we will not differentiate between them here. Finally, section 4 presents a possible extension of this calculation for a lattice distortion.

2. Forces resulting from the presence of a hydrogen interstitial atom at an octahedral site in a fcc paramagnetic transition metal. — The aim of this section is to relate the hydrogen-metal forces \( F(\lambda) \) on palladium sites \( \lambda \) to the electronic structure of \( \alpha \)-palladium hydrides. Once this has been done, the dipole force tensor \( F \) can be obtained and compared with experimental results.

The force \( F(\lambda) \), on site \( \lambda \), induced by the defect is given by \( (x = x, y, z) \):

\[
F_{\lambda}(\lambda) = \left( -\frac{\partial \delta E}{\partial u_{\lambda}(\lambda)} \right)_{0}
\]  

(2.1)

where \( \delta E \) denotes the variation of the total energy due to the relaxation of the lattice whereas the subscript zero means that the derivative is evaluated in the unrelaxed configuration; \( u_{\lambda}(\lambda) \) is the atomic displacement. In the framework of the Hartree-Fock approximation, the change in the energy induced by the defect is given by:

\[
\delta E = \delta E_{\text{bs}} + \delta E_{\text{r}}
\]  

(2.2)

\( E_{\text{bs}} \) is the band structure term and is defined as the sum of one electron energies; \( E_{\text{r}} \) results from the electron-electron interactions which are counted twice in \( E_{\text{bs}} \) and from the ion-ion interactions. The one electron Hamiltonian in the tight-binding scheme is given by:

\[
H = \sum_{\mu m} \mid \mu m \rangle e_{\mu}^{m} \langle \mu m \mid + \sum_{v_{\mu}^{m m'}} \mid v_{\mu}^{m m'} \rangle \beta_{v_{\mu}^{m m'}}^{m} \langle \mu m' \mid
\]  

(2.3)

where \( \mid \mu m \rangle \) represents the orbital of symmetry \( m \) centred on site \( \mu \), either metallic or interstitial, \( \beta_{v_{\mu}^{m m'}}^{m} \) is the transfer integral and \( e_{\mu}^{m} \) is the energy level. The effect of the relaxation is to replace the Hamiltonian \( H \) by:

\[
\overline{H} = H + \delta V
\]  

(2.4a)

and the orbital \( \mid \lambda \rangle \) by:

\[
\overline{\mid \lambda \rangle} = \mid \lambda \rangle + \delta \mid \lambda \rangle
\]  

(2.4b)

as discussed in [6]. Using the fact that the relaxation will not modify the total number of electrons, \( \delta E_{\text{bs}} \) is obtained from the following expression:

\[
\delta E_{\text{bs}} = -\int_{E_{F}}^{E_{p}} \delta N(E) \, dE
\]  

(2.5)

where \( E_{F} \) is the Fermi energy of the pure metal and \( \delta N(E) \) is the number of states displaced by the relaxation up to energy \( E \); it can be written as:

\[
\delta N(E) = -\frac{\text{Im}}{\pi} \text{Tr} \log \left[ 1 - \delta wG(E) \right].
\]  

(2.6)

For the calculation of \( F(\lambda) \) from (2.1), it is enough to calculate the variation of the total energy of the system up to first order with respect to the displacement of one site only:

\[
\delta N(E) = \frac{\text{Im}}{\pi} \text{Tr} \delta wG(E)
\]  

(2.7)

\( G(E) \) denotes the Green function of the alloy when
\( \psi(\lambda) = 0 \) while \( \delta w \) is a pseudopotential which describes the electron scattering due to the distortion around the defect; this pseudopotential takes into account the effect of the displacement of the atomic orbitals as well as the change in the lattice potential. The matrix elements of \( \delta w \) in the basis of the undisplaced atomic orbitals are given by [6, 7, 9]:
\[
\langle \lambda \mu | \delta w | \mu' \lambda' \rangle = (1 - \delta_{\mu \mu'}) \delta_{\lambda \lambda'} + \delta_{\lambda \lambda'} \delta_{\mu \mu'} \delta_{\mu \mu'}.
\]

(2.8)

The energy shifts and the change in the transfer integrals result from the modification of the crystal potential \( \delta V \) and the basis function \( \psi_0(\mathbf{r}) \). Keeping only the terms proportional to the displacement, we obtain formally:
\[
\delta \varepsilon_{\lambda \mu} = \delta V \varepsilon_{\lambda \mu} + \delta \varepsilon_{\lambda \mu} \label{delta_lambda}
\]
\[
\delta \beta_{\lambda \mu}^{\mu'} = \delta \beta_{\lambda \mu}^{\mu'} + \delta \beta_{\lambda \mu}^{\mu'} \label{delta_beta}
\]
\[
\delta E_{bs} = \delta E_{bs} + \delta E_{bs} \label{delta_Ebs}
\]

\( \delta E_{bs} \) is the variation of the band structure energy resulting from the potential modification, \( \delta V \):
\[
\delta E_{bs} = \int \delta V(r) n^k(r) d^3r \label{delta_Ebs}
\]
with
\[
n^k(r) = \sum_{\mu \mu'} \psi_{\mu}(r) \psi_{\mu'}(r) N_{\mu \mu}^{\mu'} \label{n_k}
\]
and
\[
N_{\mu \mu}^{\mu'} = - \frac{1}{\pi} \int_{E_F}^{E_F} G_{\mu \mu}^{\mu'}(E) dE \label{N_mm}
\]

\( \delta E_{bs} \) expresses the contribution of \( \delta \psi_0(\mathbf{r}) \); it is written as:
\[
\delta E_{bs} = \delta a_1 - \delta a_2 \label{delta_Ebs}
\]

where \( \Delta N \) denotes the variation due to the interstitial impurity when \( \psi(\lambda) = 0 \). The prime in the summation means that the sum is restricted to lattice sites only.

Following [10] closely, it can be shown that \( \delta E \) can be reasonably approximated by:
\[
\delta E \simeq \text{Tr} [\delta w^{(n)} \Delta N] \label{delta_E}
\]

(2.23)

where \( \delta w^{(n)} \) is expressed in terms of neutral quantities (\( \delta \beta^{\mu \mu'} \), \( \delta \varepsilon_{\lambda \mu} \)), so that partial cancellations between \( \delta E_{bs} \) and \( \delta E_t \) allow us to avoid the self-consistent calculation of the charge transfer introduced by the atomic displacements. In what follows we will suppress the exponent (n) so that \( \delta E \) can be written explicitly in the following form:
\[
\delta E = \sum_{\mu \mu'} \Delta N_{\mu \mu}^{\mu'} \delta \varepsilon_{\mu \mu'} + \sum_{\mu \mu'} \Delta N_{\mu \mu}^{\mu'} \delta \beta_{\mu \mu'} + \Delta N_{\mu \mu}^{\mu'} \delta \beta_{\mu \mu'} + \sum_{\mu \mu'} (\Delta N_{\mu \mu}^{\mu'} \delta \beta_{\mu \mu'} + \Delta N_{\mu \mu}^{\mu'} \delta \beta_{\mu \mu'}) \label{delta_E}
\]
where \( I \) is the interstitial site. Let us define the following quantities:

\[
X^m_{\nu} = \sum_{\nu m'} G^{0mm'}_{\nu m} \rho^{mm'}_{\nu m} \\
\Delta_{I\nu}^m(E) = \sum_{\nu m'} \beta^{mm'}_{\nu I} X^m_{\nu} \\
\rho^{m'm'}_{\nu m} = \frac{\rho^{mm'}_{\nu I} \rho^{mm'}_{\nu I}}{E - E_{I\nu} - \Delta_{I\nu}^m(E)}
\]

where \( t \) is the usual \( t \) matrix relative to the point defect, \( E_{I\nu} \) is the interstitial hydrogen level at site \( I \) and \( \beta^{mm'}_{\nu I} \) is the hopping integral between the hydrogen s orbital at site \( I \) and metallic orbital of symmetry \( m \) at site \( \nu \). In terms of the definitions appearing in equations (2.25), (2.26) and (2.27) we obtain:

\[
\Delta N_{I\nu}^m = - \frac{1}{\pi} \int E_F \frac{dE}{E - E_{I\nu} - \Delta_{I\nu}^m} \\
\Delta N_{I\nu}^{mm'} = - \frac{1}{\pi} \int E_F \frac{X^m_{\nu} X^{m'}_{\nu}}{E - E_{I\nu} - \Delta_{I\nu}^m} \\
\Delta N_{\mu\nu}^{mm'} = - \frac{1}{\pi} \int E_F \sum_{m''} G^{0mm'}_{\mu \nu} \rho^{m'm''}_{\nu I} G^{0mm''}_{\mu I} dE
\]

where \( G^0 \) is the Green function relative to the pure, unrelaxed host. The matrix elements \( \rho^{m'm'}_{\nu I} \) are calculated for each \( m' \) and \( m'' \) up to first nearest neighbours. It is shown that, due to high anisotropy of the hopping integrals \( \beta^{mm'}_{\nu I} \), a considerable number of these matrix elements is equal to zero.

Finally, we obtain:

\[
\Delta N_{\mu\nu}^{mm'} = - \frac{1}{\pi} \int E_F \frac{X^m_{\nu} X^{m'}_{\nu}}{E - E_{I\nu} - \Delta_{I\nu}^m(E)} dE.
\]

The component \( \alpha \) of the force acting on the matrix atom sitting at the \( \lambda \) site is then given by:

\[
F_{\alpha}(\lambda) = F_{\alpha}^0(\lambda) + F_{\alpha}^1(\lambda)
\]

where

\[
F_{\alpha}^0(\lambda) = \sum_{\mu \nu} \Delta N_{\mu\nu}^{mm'} D_{\alpha\lambda} \delta e^m_{\mu} + \sum_{\mu \nu} \Delta N_{\mu\nu}^{mm'} D_{\alpha\lambda} \delta \beta^{mm'}_{\mu \nu}
\]

\[
F_{\alpha}(\lambda) = \Delta N_{I\nu}^m D_{\alpha\lambda} \delta e^m_{\nu} + \sum_{\mu \nu} \Delta N_{I\nu}^{mm'} D_{\alpha\lambda} \delta \beta^{mm'}_{\mu \nu} + \Delta N_{I\nu}^{mm'} D_{\alpha\lambda} \delta \beta_{\mu \nu}
\]

with the notations

\[
D_{\alpha\lambda} \delta e^m_{\nu} = - \frac{\partial}{\partial u_{\alpha\lambda}(\lambda)} \delta e^m_{\nu} \\
D_{\alpha\lambda} \delta \beta^{mm'}_{\mu \nu} = - \frac{\partial}{\partial u_{\alpha\lambda}(\lambda)} \delta \beta^{mm'}_{\mu \nu}
\]

Once the forces on sites \( \lambda \) have been obtained a component \( P_{\mu \alpha} \) of the dipole force tensor is given by:

\[
P_{\mu \alpha} = P_{\mu \alpha}^0 + P_{\mu \alpha}^1
\]

where \( P_{\mu \alpha}^0 \) is relative to \( F_{\alpha}^0(\lambda) \) and \( P_{\mu \alpha}^1(\lambda) \) to \( F_{\alpha}^1(\lambda) \).

3. Numerical estimation of the forces and of the dipole force tensor in \( \alpha \)-palladium hydrides. —

\( F_{\alpha}^0(\lambda) \) and \( F_{\alpha}^1(\lambda) \), defined by equations (2.33) and (2.34) are the sums of a diagonal term (containing \( \delta e^m_{\nu} \)) and a non-diagonal part (containing \( \delta \beta^{mm'}_{\mu \nu} \)):

\[
F_{\alpha}^0(\lambda) = F_{\alpha}^{OD}(\lambda) + F_{\alpha}^{OND}(\lambda)
\]

\[
F_{\alpha}^1(\lambda) = F_{\alpha}^{ID}(\lambda) + F_{\alpha}^{IND}(\lambda)
\]

In order to estimate \( F_{\alpha}^0(\lambda) \) we replace \( \beta^{mm'}_{\nu I} \) by \( \beta^{0mm'}_{\nu I} \) as discussed in the introduction and the term \( e^m_{\nu} \) by \( e^m_{\nu} \) [11]:

\[
\delta \beta^{mm'}_{\mu \nu} = \delta \beta_{\nu I}^{0mm'} \\
\delta e^m_{\nu} = \delta e^m_{\nu}
\]
where the superscript 0 means that these quantities are relative to the unrelaxed pure metal. $F(\lambda)$ will now be expressed in terms of known quantities which are the two centre integrals relative to the Slater-Koster fit of the band structure of pure palladium to a first-principle band structure calculation [8] and the hopping integrals between the hydrogen s orbital and the metallic d level of Pd [5, 11].

Moreover, it can be shown that the dipole force tensor relative to $F_{\text{IND}}(\lambda)$ and defined by:

$$
P_{\text{IND}}^{ss} = \sum_{m} \rho_{m} D_{m} \delta \xi_{m}^{0m}$$

is zero. The fact that $H^{0}$, the Hamiltonian of pure Pd will be unchanged by a lattice translation implies the following expression:

$$
P_{\text{IND}}^{ss} = \sum_{m} \rho_{m} D_{m} \delta \xi_{m}^{0m}$$

Table I. — Values in eV of a dipole force tensor component $P_{ss}(\alpha = x, y$ or $z)$ as a function of the parameter $q$.

<table>
<thead>
<tr>
<th>$q$ in atomic units</th>
<th>$P_{ss}$ (eV) theoretical value</th>
<th>$P_{ss}$ (eV) experimental value [16]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.30</td>
<td>3.2</td>
<td>3.5</td>
</tr>
<tr>
<td>0.35</td>
<td>3.7</td>
<td></td>
</tr>
<tr>
<td>0.40</td>
<td>4.3</td>
<td></td>
</tr>
</tbody>
</table>

The number of external electrons brought by the interstitial ($Z = 1$) is equal to the variation of the displaced states:

$$
Z = \Delta N_{m}^{ss} + \sum_{m} \Delta N_{m}^{mm}.
$$

As discussed in [5], $\Delta N_{m}^{ss} = 1$ so that (3.4) is found equal to zero. We are left with $F_{\text{IND}}(\lambda)$ which is given in terms of the electronic structure of the unrelaxed alloy and $\delta \beta_{\mu \nu}^{0m}$ with $m$ and $\nu$ relative to d orbitals only. It is easily shown that [12]:

$$
F_{\text{IND}}(\lambda_{s}) = \frac{\text{Im}}{\pi} \int_{0}^{\infty} \frac{dE}{E} \sqrt{2 \beta_{\mu \nu}^{0m}} \left\{ G^{0}(\lambda_{s}) + 2 G^{0}(4) - 4 G^{0}(5) \right\} \frac{E - E_{1} - \Delta_{n}^{m}(E)}{E}
$$

where $G^{0}(\Gamma_{1})$, $G^{0}(4)$ and $G^{0}(5)$ are respectively intrasite and intersite matrix elements of the Green function $G^{0}$ (see [11] for detail) and $q_{\text{IND}}^{0}$ is the parameter entering in the exponential variation of $\delta \sigma$ with distance. Let us remark that the derivative of the angular part of $\beta_{\mu \nu}^{0m}$ is zero.

We are still left with two parameters $q_{\text{IND}}^{0}$ (in the definition of $P_{ss}^{0}$) and $q_{\text{IND}}^{0}$ (in the definition of $F_{\text{IND}}(\lambda_{s})$). For convenience we will make the following approximation:

$$
q_{\text{IND}}^{0} = q_{\text{IND}}^{0} = q.
$$

However, recent calculations in the case of Ni-H bonds have shown [15] that $q_{\text{IND}}^{0}$ is much bigger than $q_{\text{IND}}^{0}$; this probably remains true in the case of Pd-H.
and should be taken into account in an improved model. Once the value of \( q \) is obtained (Table I) by comparison with the experimental value [16], the forces \( F(\lambda) \) on palladium atom \( \lambda \) are known and reported in Table II. For nearest and next nearest neighbours they are in qualitative agreement with the calculation of Johnston and Sholl [1].

Table II. — Forces (in \( 10^{-4} \) dyn.) from an interstitial hydrogen at an octahedral site in palladium. The \( a \) component (\( a = x, y, z \)) of the forces \( F(\lambda) \) are reported up to third nearest neighbour \( \lambda_3 \) to the hydrogen impurity. \( a \) is the lattice parameter.

<table>
<thead>
<tr>
<th>( \lambda_1 = \frac{a}{2}(0, 0, 1) )</th>
<th>( \lambda_2 = \frac{a}{2}(1, 1, 1) )</th>
<th>( \lambda_3 = \frac{a}{2}(0, 2, 1) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( F_a(\lambda_1) ) ( F_a(\lambda_2) ) ( F_a(\lambda_3) )</td>
<td>( F_a(\lambda_1) ) ( F_a(\lambda_2) ) ( F_a(\lambda_3) )</td>
<td>( F_a(\lambda_1) ) ( F_a(\lambda_2) ) ( F_a(\lambda_3) )</td>
</tr>
<tr>
<td>0.0</td>
<td>0.037</td>
<td>0.012</td>
</tr>
<tr>
<td>0.0</td>
<td>-0.012</td>
<td>-0.012</td>
</tr>
<tr>
<td>0.045</td>
<td>0.025</td>
<td></td>
</tr>
</tbody>
</table>

4. Conclusion. — Using a tight-binding method we have deduced, for the first time, the dipole force tensor in terms of the electronic structure of hydrogen at an octahedral position in a palladium host. Our calculation relies only on one parameter \( q \) (once the electronic structure is known) and comparison with experimental result gives a reasonable value for \( q \). During the calculation we have expressed the forces on first, second and third palladium neighbours to hydrogen in terms of \( q \). Once \( q \) is obtained, from comparison of \( P \) with experimental result, the forces \( F(\lambda) \) on palladium atom \( \lambda \) are known. It is clear, from lattice statics [17] that the atomic displacements \( u(\lambda) \) can be deduced from \( F(\lambda) \) through the relation \( (a, \rho = x, y, z) : \)

\[
u_a(\lambda) = \sum_{\mu} G_{a\mu}^{L} F_{\mu}(\rho) \tag{4.1}\]

where \( \lambda, \mu \) are lattices sites and \( G^L \) is the static Green function which is given in terms of the force constants of the alloy. \( G^L \) is formally given in terms of \( G^{0L} \), the host lattice Green function and perturbation due to the hydrogen defect [18]. \( G^L \) can be related to \( G^{0L} \) if we introduce an auxiliary function \( G^{UL} \). \( G^{UL} \) is the lattice Green function of the system hydrogen-metal with zero coupling between the two components.

Concerning \( G^{0L} \) it should be obtained from the electronic structure of the host. It can be obtained through the long wavelength limit of the phonon Green function [19] or more directly by an estimation of the elastic constants [20, 21]. This remain even now a rather formidable task and will be discussed in more detail in a future publication.

Appendix A. — Some elements about the determination of the forces acting on nearest palladium atoms to the hydrogen impurity. — As discussed in the text, we are left with the non-diagonal part of the forces \( F^{OND}(\lambda) \) due to the fact that the dipole force tensor with respect to the diagonal part is zero:

\[
F^{OND}(\lambda) = \sum_{\mu \neq \lambda} \{ \Delta N_{\mu\lambda}^{mm'} D_{\mu\lambda} \delta \beta_{0mn}^{m'm'} + \\
+ \Delta N_{\mu\lambda}^{mm'} D_{\mu\lambda} \delta \beta_{0mn}^{m'm'} \}. \tag{A.1}\]

As shown by equations (3.7-3.8) the derivative \( D_{\mu\lambda} \) splits the expression of the forces into two terms, one depending on the parameter, \( q^{OND} \), entering in the exponential, the other depending on the derivative of the angular part of \( \beta \). This calculation is trivial but lengthy and leads to cumbersome expressions for the forces [22]. They depend, in our approximation, on the hopping integral \( sd\sigma \) between the hydrogen impurity and its nearest neighbour palladium atoms, on the \( dd \) hopping integrals \( dd\sigma \), \( dd\pi \), \( dd\delta \) and on the matrix elements \( G^{0}(T, 1), G^{0}(4), G^{0}(5), G^{0}(6) \) of the Green function \( G^{0} = [E - H^{0}]^{-1} \) between \( d \) orbitals. The definition of these matrix elements of \( G^{0} \) can be found in [11].

Let \( I = (0, 0, 0) \) be the location of the interstitial hydrogen at an octahedral site. The force acting on the nearest \( Pd \) atom \( \lambda_1 = \frac{a}{2}(0, 0, 1) \) has the following components:

\[
F^{OND}_{x}(\lambda_1) = 0 \tag{A.2}
F^{OND}_{y}(\lambda_1) = 0
F^{OND}_{z}(\lambda_1) \neq 0.
\]

The components of the force acting on the next nearest neighbour palladium atoms are found equal whereas the component of the force on third nearest neighbour \( \lambda_3 = \frac{a}{2}(0, 2, 1) \) are:

\[
F^{OND}_{x}(\lambda_3) = 0 \tag{A.3}
F^{OND}_{y}(\lambda_3) \neq 0
F^{OND}_{z}(\lambda_3) \neq 0.
\]

No relation has been found between the \( y \) and the \( z \) component of the force. The force acting on \( \lambda_4 = \frac{a}{2}(3, 1, 1) \) is zero and results from the fact that we have retained in our calculations only matrix elements of \( H \) up to first nearest neighbours.
References