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The force field and associated dipole force tensor in metallic systems in the tight-binding approximation

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Abstract. A self-consistent formulation for the force field and the associated dipole force tensor is presented. In the tight-binding approximation of the Hartree–Fock scheme, the variation of the total energy of the solids—up to first order in the atomic displacement—is obtained in terms of neutral quantities with respect to the frozen crystal. Improvements from our previous estimations concerning dilute substitutional and interstitial alloys are reported. Also, we present—for the first time—a derivation of the force field arising from the presence of the surface of a transition metal.

1. Introduction

The calculation of the electronic structure of defects in solids is generally restricted to frozen systems. However, the presence of a defect in a crystal modifies its total energy so that the interatomic distances are changed. This relaxation is important for the understanding of local order, magnetic and thermodynamic properties, surface reconstruction, etc. From x-ray measurements, Alefeld and Volkl (1978) have deduced the dipole force tensor in metal hydrides. The measurement of surface relaxation has been performed by low-energy electron diffusion (Sokolov *et al* 1984, Adams *et al* 1985) and by ion scattering (Gustafsson *et al* 1988).

Improvements in computing power and numerical algorithms have recently enabled more ambitious first-principles calculations to be done. We mention first the molecular dynamics method, which treats both the electronic and nuclear degrees of freedom on a common footing (Car and Parrinello 1985). Soler and Williams (1989) have recently presented a simple formula for the atomic forces in the augmented plane-wave method. Surface reconstruction has recently been studied by Ho and Bohnen (1987) and by Takeuchi *et al* (1989). The work of Ho and Bohnen uses the bulk norm-conserving pseudopotential and five Gaussian d orbitals per atom, whereas Takeuchi *et al* studied one monolayer of gold or silver on a jellium. However, up to now, no sufficiently practical formulae have been obtained for the force on the atoms, similar to those existing for the plane-wave pseudopotential method (Ihm *et al* 1979). Consequently, a variety of empirical and semiempirical schemes have been developed to describe interatomic forces in solids; Sutton *et al* (1988) have given a review of these methods in

the case of the bulk. For the surface, Ercolessi *et al* (1986) have proposed the glue model, which is similar to the embedded-atom method of Daw and Baskes (1984). Surface relaxation and reconstruction have also been studied, in the tight-binding approximation, using a Born–Mayer pair potential to mimic the ion–ion repulsion (Brocksch and Bennemann 1985, Rosato *et al* 1989).

We will now present the essential physical features of our self-consistent formulation for the forces arising from the presence of a point defect or surface in a transition metal. In this model we start with a complete orthonormalised basis set built from the atomic orbitals $|\lambda m\rangle$ of the frozen metal (λ is the site and m the symmetry). In order to describe the atomic displacements in the undisplaced basis set, we introduce, following Moraitis and Gautier (1979), a pseudopotential δw^\dagger whose matrix elements take into account the modification of the metallic levels and the hopping integrals. The variation of the total energy δE of the system, in the Hartree–Fock scheme, is given by

$$\delta E = \delta E_{\text{bs}} - \delta E_{\text{el-el}} + \delta E_{\text{ion-ion}} \quad (1.1)$$

where the band energy contribution δE_{bs} is complemented by the ion–ion interaction energy minus the ‘double-counting term’. The relaxation introduces charge transfer due to electronic rearrangement around the displaced atoms. This charge transfer contribution does not appear in the final expression for δE in the case of homogeneous dilatation of the pure metal (force theorem of McIntosh and Andersen (1980)).

Therefore, this theorem cannot be used for the study of phonons. In the scheme of Moraitis *et al* (1985), this force theorem has been generalised to the case of inhomogeneous deformation induced by point defects. Let us remark that:

- (i) the absence of charge transfer in the final expression for δE results from exact compensation between the different contributions to the total energy of the solids; it is valid up to first order in the atomic displacement u ; and
- (ii) no phenomenological form for the repulsive term is needed.

Consequently, the present self-consistent scheme for the derivation of the force field does not invoke charge neutrality, nor the Born–Mayer form for the repulsive energy (Ohta *et al* 1987).

The tight-binding (TB) approximation used here neglects, as usual, the overlap between atomic orbitals on different sites and is restricted to two-centre approximation. In this work, we assume that:

- (i) the TB orbitals are the same as those of the host for substitutional impurities and surface and those of the host plus one s orbital for the metalloid (for light interstitials); and
- (ii) the relaxed atomic orbitals are deduced from the corresponding orbitals in the frozen lattice, by a rigid displacement.

In section 2, a general expression for the variation of the total energy δE in the TB formalism is derived. In the case of point defects, the matrix elements of the perturbing potential $\Delta V(r)$ are deduced from Friedel’s sum rule. Once this has been done, expressions for δE in the case of substitutional and interstitial impurities can be obtained (Moraitis *et al* 1985, Khalifeh *et al* 1982a, b).

† In this paper δ stands for atomic relaxation whereas Δ is the perturbation induced by the impurity or the surface in the frozen lattice.

An application to the case of the surface of a transition metal has been derived for the first time. A local neutrality approximation has been used for the description of the electronic structure of the frozen surface. It is easy to prove that, up to first order in the atomic displacement, and due to cancellation between a charge-transfer term in δE_{bs} and one in $\delta E_{\text{el-el}}$, the final expression for δE depends only on neutral quantities upon relaxation.

Section 3 is devoted to the determination of the force field. For substitutional impurities, the model of Moraitis *et al* (1985) has been extended in order to take full account of the variation of the energies of the metallic levels in the expression for the dipole force tensor P (appendix 1). Let us remark that, in this scheme, the forces and P are expressed in terms of variation of the energy of the metallic levels and hopping integrals induced by the movement of neutral atoms.

A complete derivation of the force field around a light interstitial in transition metals is reported. Special attention is devoted to the derivation of P arising from the variation of the metallic and metalloid levels (appendix 2) and from the hydrogen-induced bound state (appendix 3). Finally, a derivation of the force field arising from the presence of the surface is performed.

Section 4 presents the conclusions.

2. Expression for the variation of the total energy in the tight-binding approximation

An expression for δE is obtained when the Hamiltonian H of the system can be described in a tight-binding formalism (section 2.1). Applications to the case of substitutional impurities (section 2.2), interstitial defects (section 2.3) and the surface of a transition metal (section 2.4) are reported.

2.1. General formulation for δE

The tight-binding (TB) formalism is known to give a rather good representation of the d bands of transition metals and alloys (Friedel 1969). In the TB representation, the one-electron Hamiltonian for the unrelaxed system is given by

$$H = \sum_{\lambda, m} |\lambda m\rangle \varepsilon_{\lambda}^m \langle \lambda m| + \sum_{\substack{\lambda, \mu \neq \lambda, \\ m, m'}} |\lambda m\rangle \beta_{\lambda \mu}^{mm'} |\mu m'\rangle \quad (2.1)$$

where $\varphi_{\lambda}^m(r) = \langle r | \lambda m \rangle$ represents the atomic orbital of m symmetry centred on site λ , $\beta_{\lambda \mu}^{mm'}$ are the hopping integrals and ε_{λ}^m the energy levels. In this work we assume that the TB orbitals, in the case of substitutional impurities and the surface, are the same as those of the host. In the case of light interstitials (like H, B, C, N, . . .) at site I , ε_I^m and $|Im\rangle$ are respectively the energy of the interstitial in the alloy and the metalloid orbital. Also, we suppose that the set of atomic orbitals is complete.

In the Hartree scheme, the variation of the total energy of the system is given by

$$\delta E = \delta E_{\text{bs}} - \delta E_{\text{el-el}} + \delta E_{\text{ion-ion}} \quad (2.2)$$

where δE_{bs} denote the band-structure contribution

$$\delta E_{\text{bs}} = \int^{\varepsilon_{\text{F}}} \varepsilon \delta n(\varepsilon) d\varepsilon. \quad (2.3)$$

After an integration by parts we obtain

$$\delta E_{\text{bs}} = \varepsilon_{\text{F}} \delta N(\varepsilon_{\text{F}}) - \int^{\varepsilon_{\text{F}}} \delta N(\varepsilon) d\varepsilon \quad (2.4)$$

where $\delta n(\varepsilon)$ is the variation of the density of states due to the relaxation and $\delta N(\varepsilon)$ is the number of displaced states up to energy ε relative to the relaxation

$$\delta N(\varepsilon) = -(1/\pi) \text{Im Tr log}(1 - \delta W G). \quad (2.5)$$

Here G is the unrelaxed Green function associated with H and δW is a pseudopotential defined in the basis of the undisplaced orbitals by its matrix elements (Moraitis and Gautier 1979)

$$\delta W_{\lambda\lambda}^{mm} = \delta \varepsilon_{\lambda}^m = \langle \delta \lambda m | H | \lambda m \rangle + \langle \lambda m | H | \delta \lambda m \rangle + \langle \lambda m | \delta V | \lambda m \rangle \quad (2.6a)$$

$$\delta W_{\lambda\mu}^{mm'} = \delta \beta_{\lambda\mu}^{mm'} = \langle \delta \lambda m | H | \mu m' \rangle + \langle \lambda m | H | \delta \mu m' \rangle + \langle \lambda m | \delta V | \mu m' \rangle \quad (2.6b)$$

$$\delta \varepsilon_{\lambda}^m = \delta^{\varphi} \varepsilon_{\lambda}^m + \delta^{\nu} \varepsilon_{\lambda}^m \quad (2.6c)$$

$$\delta \beta_{\lambda\mu}^{mm'} = \delta^{\varphi} \beta_{\lambda\mu}^{mm'} + \delta^{\nu} \beta_{\lambda\mu}^{mm'}. \quad (2.6d)$$

To the first order of perturbation, $\delta N(\varepsilon)$ can be expressed as

$$\delta E_{\text{bs}} = \sum_{\substack{\lambda, \mu, \\ m, m'}} \delta W_{\lambda\mu}^{mm'} N_{\mu\lambda}^{m'm} \quad (2.7a)$$

with

$$N_{\mu\lambda}^{m'm} = -\frac{1}{\pi} \text{Im} \int^{\varepsilon_{\text{F}}} G_{\mu\lambda}^{m'm}(\varepsilon) d\varepsilon. \quad (2.7b)$$

Using the relations (2.6), δE_{bs} can be decomposed into $\delta^{\varphi} E_{\text{bs}}$ and $\delta^{\nu} E_{\text{bs}}$ with

$$\delta^{\varphi} E_{\text{bs}} = \sum_{\substack{\lambda, \mu, \\ m, m'}} N_{\lambda\mu}^{mm'} \langle \delta \lambda m | H | \mu m' \rangle + \langle \lambda m | H | \delta \mu m' \rangle \quad (2.8)$$

$$\delta^{\nu} E_{\text{bs}} = \int n^{\text{el}}(r) \delta V(r) d^3r \quad (2.9)$$

with

$$n^{\text{el}}(r) = \sum_{\substack{\lambda, \mu, \\ m, m'}} N_{\lambda\mu}^{mm'} \varphi_{\lambda}^m(r) \varphi_{\mu}^{m'}(r). \quad (2.10)$$

Here $\langle r | \delta \lambda m \rangle = \delta \varphi^m(r - \lambda)$ is the modification of the atomic orbital centred on the λ site arising from the displacement of this site and $\delta V(r)$ represents the variation of the

Hartree potential induced by the relaxation. On the other hand, $\delta E_{\text{el-el}}$ and $\delta E_{\text{ion-ion}}$ are given by

$$\delta E_{\text{el-el}} = \int \delta V^{\text{el}}(r) n^{\text{el}}(r) d^3r \quad (2.11a)$$

$$\delta E_{\text{ion-ion}} = - \int \delta V^{\text{ion}}(r) n^{\text{ion}}(r) d^3r. \quad (2.11b)$$

In these expressions $\delta V^{\text{el}}(r)$ and $\delta V^{\text{ion}}(r)$ are, respectively, the electronic and ionic contributions to $\delta V(r)$, whereas $n^{\text{el}}(r)$ and $n^{\text{ion}}(r)$ represent the electronic and ionic densities for the unrelaxed alloys.

This general scheme will now be applied to three different cases:

(i) The simplest case is the dilute alloy of a transition element. For a small difference of charge ΔZ between the impurity and the matrix, a model with a perturbing potential ΔV restricted to its own cell is reliable.

(ii) The second application is related to light interstitial impurities in transition metals. Interstitials are usually located at octahedral or tetrahedral positions depending on the nature of the host. For example, hydrogen is located (Ligeon *et al* 1986) at octahedral positions in FCC transition metals and at tetrahedral positions in BCC transition metals.

(iii) Finally, investigations on the forces at the surface of a transition metal is discussed.

2.2. Transition-metal impurity in the localised perturbing potential model

The Hamiltonian in this case is given by

$$H = H^0 + \Delta V \quad (2.12)$$

where only matrix elements on the impurity site are taken into account in the determination of the phase shift. In (2.12) H^0 is the Hamiltonian of the pure metal.

In this case, δE can be written as (Moraitis *et al* 1985)

$$\begin{aligned} \delta E = \sum_{\substack{\lambda, \mu, \\ m, m'}} \Delta N_{\lambda\mu}^{mm'} \delta W_{\lambda\mu}^{0(n)mm'} - \int \delta V^{0(n)}(r) \Delta n^{\text{ion}}(r) d^3r \\ + \int \delta \Delta V^{\text{el}(n)}(r) \Delta n(r) d^3r \end{aligned} \quad (2.13)$$

where

$$\Delta N_{\lambda\mu}^{mm'} = - \frac{1}{\pi} \text{Im} \int^{\epsilon_F} \langle \lambda m | G - G^0 | \mu m' \rangle d^3r \quad (2.14)$$

and G^0 and G are the Green functions of the unrelaxed pure metal and alloy, respectively. In the above, $\delta W^{0(n)}$ represents the modification of the hopping integrals and energy levels in the host induced by the displacement of neutral atoms; $\delta V^{0(n)}$ represents the variation of the host potential upon the displacement of neutral atoms; whereas $\delta \Delta V^{\text{el}(n)}$

is the variation of the electronic perturbing potential upon the displacement of neutral atoms. Moreover,

$$\Delta n(r) = \Delta n^{\text{el}}(r) - \Delta n^{\text{ion}}(r) \quad (2.15)$$

where Δn^{el} (Δn^{ion}) represent the changes in electronic (ionic) densities of the host $n^{0,\text{el}}$ ($n^{0,\text{ion}}$) introduced by the impurity in the unrelaxed system.

2.3. Hydrogen impurity in a transition metal

The Hamiltonian in this case is given by

$$H = H^0 + |Is\rangle \varepsilon_I^s \langle Is| + \sum_{R,m} (|Rm\rangle \beta_{RI}^{ms} \langle Is| + \text{HC}) + \sum_{R,m} |Rm\rangle V_I^{mm}(R) \langle Rm|. \quad (2.16)$$

Here ε_I^s is the energy level introduced by the interstitial, at site I , β_{RI}^{ms} is the hopping integral between metallic orbital $|Rm\rangle$ and interstitial orbital $|Is\rangle$, HC is the Hermitian conjugate of the preceding term and $V_I^{mm}(R)$ is the matrix element of the perturbing potential introduced at site R by the interstitial. It has been shown that, for substitutional (Moraitis 1978) and interstitial (Khalifeh *et al* 1982a) impurities, for Hamiltonian $H = H^0 + \Delta V$,

$$\delta^v E_{\text{bs}} - \delta E_{\text{el-cl}} + \delta E_{\text{ion-ion}} = - \int \delta n^{\text{ion}}(r) \Delta V(r) d^3r \quad (2.17)$$

where $\delta n^{\text{ion}}(r)$ represents the change in ionic density of the host $n^{0,\text{ion}}(r)$ introduced by the relaxation. From equations (2.2), (2.6) and (2.17), the following expression for the variation of the total energy of the alloy is found:

$$\delta E = \delta E' + \delta^v E_{\text{bs}} \quad (2.18)$$

with

$$\delta E' = - \int \delta n^{\text{ion}}(r) \Delta V(r) d^3r \quad (2.19a)$$

$$\delta^v E_{\text{bs}} = \sum_{\substack{\lambda,\mu, \\ m,m'}} N_{\lambda\mu}^{mm'} (\langle \delta\lambda m | H | \mu m' \rangle + \langle \lambda m | H | \delta\mu m' \rangle). \quad (2.19b)$$

The summation is over metallic and hydrogen sites, and $N_{\lambda\mu}^{mm'}$ is the sum of two terms

$$N_{\lambda\mu}^{mm'} = -\frac{1}{\pi} \text{Im} \int^{\varepsilon_F} \langle \lambda m | G^I | \mu m' \rangle \quad (2.20)$$

$$\Delta N_{\lambda\mu}^{mm'} = -\frac{1}{\pi} \text{Im} \int^{\varepsilon_F} \langle \lambda m | G - G^I | \mu m' \rangle \quad (2.21)$$

where G^I is the Green function of the Hamiltonian $H^0 + |Is\rangle \varepsilon_I^s \langle Is|$.

Introducing now

$$\delta W_{\mu\lambda}^{(n)m'm} = \langle \delta\mu m' | H | \lambda m \rangle + \langle \mu m' | H | \delta\lambda m \rangle + \langle \mu m' | \delta V^{(n)} | \lambda m \rangle \quad (2.22)$$

which are the matrix elements of the pseudopotential introduced by the displacement of neutral host atoms of the alloy, this leads to

$$\delta E = \sum_{\substack{\lambda, \mu, \\ m, m'}} \Delta N_{\lambda\mu}^{mm'} (\delta W_{\mu\lambda}^{(n)m'm} - \langle \mu m' | \delta \Delta V^{(n)} | \lambda m \rangle) - \int \delta V_0^{(n)}(r) \Delta n^{\text{ion}}(r) d^3r \quad (2.23)$$

with

$$\delta V^{(n)}(r) = \delta V_0^{(n)}(r) + \delta \Delta V^{(n)}(r). \quad (2.24)$$

By taking into account the fact that

$$\Delta n^{\text{el}(n)}(r) = \sum_{\substack{\lambda, \mu, \\ m, m'}} \Delta N_{\lambda\mu}^{mm'} \varphi_{\mu}^{m'}(r) \varphi_{\lambda}^m(r) \quad (2.25)$$

we obtain the final expression

$$\begin{aligned} \delta E = \text{Tr}(\Delta N \delta W^{(n)}) - \int \Delta V^{\text{el}(n)}(r) \delta \Delta n^{(n)}(r) d^3r \\ - \int \delta V_0^{(n)}(r) \Delta n^{\text{ion}}(r) d^3r. \end{aligned} \quad (2.26)$$

2.4. Surface of a transition metal

The Hamiltonian of the system is given by

$$H = T + \sum_{\lambda} v^{\text{at}}(r - \lambda) \quad (2.27)$$

where T is the kinetic operator and $v^{\text{at}}(r - \lambda)$ is an atomic potential at site λ .

With the help of equations (2.8) and (2.9), δE_{bs} is written as

$$\delta E_{\text{bs}} = \text{Tr}(N \delta^{\varphi} W) + \int \delta V(r) n^{\text{el}}(r) d^3r. \quad (2.28)$$

If we add to this the electron–electron and ion–ion terms, given respectively by (2.11a) and (2.11b), we obtain

$$\delta E = \text{Tr}(N \delta^{\varphi} W) + \int \delta V^{\text{ion}}(r) n(r) d^3r \quad (2.29)$$

where

$$n(r) = n^{\text{el}}(r) - n^{\text{ion}}(r). \quad (2.30)$$

The first term on the right-hand side of equation (2.29) is the variation of the band-structure contribution due to the rigid displacement of the atomic orbitals. The second term expresses the modification of the interaction between the ion field and the charge density induced by the ion displacement.

3. Force field and dipole force tensor

In this section we derive the force field arising from the presence of point defects and in the case of a surface. The dipole force tensor is derived in the case of impurities only.

The α component of forces $F_\alpha(\lambda)$ acting on site λ is given by

$$F_\alpha(\lambda) = - \frac{\partial}{\partial u_\alpha(\lambda)} \delta E \quad (3.1)$$

where $u_\alpha(\lambda)$ is the α component of the displacement field. The derivative is taken for the unrelaxed positions (for the relaxed or equilibrium position, the forces vanish).

The $P_{\alpha\beta}$ components of the dipole force tensor are given by

$$P_{\alpha\beta} = \sum_\lambda F_\alpha(\lambda) \lambda_\beta. \quad (3.2)$$

3.1. Transition-metal impurity

It has been shown by Moraitis *et al* (1985) that δE can be well approximated by

$$\delta E \approx \sum_{\substack{\lambda, \mu, \\ m, m'}} \Delta N_{\lambda\mu}^{mm'} \delta W_{\mu\lambda}^{0(n)m'm}. \quad (3.3)$$

If we now restrict attention to the two-centre integral approximation, we find

$$F_\alpha(\lambda) = \sum_{\mu, m} \Delta N_{\mu\mu}^{mm} D_{\alpha\lambda} \varepsilon_\mu^{0(n)m} + \sum_{\substack{m, m', \\ \mu \neq \lambda}} D_{\alpha\lambda} \beta_{\lambda\mu}^{0(n)m'm} (\Delta N_{\mu\lambda}^{mm'} + \Delta N_{\lambda\mu}^{mm'}) \quad (3.4)$$

where

$$D_{\alpha\lambda} \varepsilon_\mu^{(n)m} = - \frac{\partial}{\partial u_\alpha(\lambda)} \delta \varepsilon_\mu^{(n)m} \quad (3.5a)$$

$$D_{\alpha\lambda} \beta_{\lambda\mu}^{(n)mm'} = - \frac{\partial}{\partial u_\alpha(\lambda)} \delta \beta_{\lambda\mu}^{(n)mm'}. \quad (3.5b)$$

After some manipulation the following general expression for the dipole force tensor is found (Moraitis *et al* 1985):

$$P_{\alpha\alpha} = P_{\alpha\alpha}^d + P_{\alpha\alpha}^{\text{nd}} \quad (3.6)$$

$$P_{\alpha\alpha}^d = - \sum_\mu \mu_\alpha \left(\sum_m \Delta Z^m D_{\alpha 0} \varepsilon_\mu^{0(n)m} \right) \quad (3.7a)$$

$$P_{\alpha\alpha}^{\text{nd}} = \sum_{\mu \neq 0} \sum_{m, m'} D_{\alpha 0} \beta_{0\mu}^{0(n)m'm} J_\alpha^{mm'}(\mu) \quad (3.7b)$$

where

$$\Delta Z^m = \sum_\rho \Delta N_{\rho\rho}^{mm} \quad (3.8)$$

$$J_{\alpha(\mu)}^{mm'} = \sum_\lambda \lambda_\alpha (\Delta N_{\lambda+\mu, \lambda}^{mm'} + \Delta N_{\lambda, \lambda+\mu}^{mm'}). \quad (3.9)$$

Here $\Delta Z = \sum_m \Delta Z^m$ is the difference between the electrons on the impurity atom and

those on the pure metal atom. It is well known that the atomic-like calculation of the metallic levels leads to untrustworthy results due to important effects arising from renormalised atoms (Boudeville *et al* 1983). Our purpose is therefore to express $P_{\alpha\alpha}^d$ in terms of the derivative of $\beta^{0(n)}$. The diagonal part $P_{\alpha\alpha}^d$ given by equation (3.7a), is the product of a term relative to the defect ΔZ^m times a term $\sum_{\mu} \mu_{\alpha} D_{\alpha 0} \varepsilon_{\mu}^{0(n)m}$ depending only on pure-metal quantities. Using translational invariance, we propose to express this second part in terms of the derivative of $\beta^{0(n)}$.

This can be done by starting with the fact that the displacement of a host atom does not change the total number of electrons of the system. Thus

$$\delta N^0(\varepsilon_F) = 0 \quad (3.10)$$

and $\delta N^0(\varepsilon)$ can be split into a sum of neutral and charge-transfer terms:

$$\delta N^0(\varepsilon) = \delta N^{0(n)}(\varepsilon) + \delta N^{0,ct}(\varepsilon). \quad (3.11)$$

The term $\delta N^{0(n)}(\varepsilon)$ is given by

$$\delta N^{0(n)}(\varepsilon) = \text{Tr}[(1/\pi) \text{Im } G^0 \delta W^{0(n)}]. \quad (3.12)$$

The derivative $D_{\alpha\mu} N^{0(n)}(\varepsilon_F)$ is therefore given by

$$\begin{aligned} D_{\alpha\mu} N^{0(n)}(\varepsilon_F) &= \sum_{\lambda, m} n_{\lambda\lambda}^{0mm}(\varepsilon_F) D_{\alpha\mu} \varepsilon_{\lambda}^{0(n)m} \\ &+ \sum_{\substack{\lambda, \\ m, m'}} \sum_{\nu \neq \lambda} D_{\alpha\mu} \beta_{\lambda\nu}^{0(n)mm'} n_{\nu\lambda}^{0m'm}(\varepsilon_F) \end{aligned} \quad (3.13)$$

with

$$n_{\lambda\mu}^{0mm'}(\varepsilon) = -(1/\pi) \text{Im } G_{\lambda\mu}^{0mm'}(\varepsilon). \quad (3.14)$$

As proved in appendix 1,

$$D_{\alpha\mu} N^{0(n)}(\varepsilon_F) \equiv 0. \quad (3.15)$$

By multiplying (3.13) by μ_{α} and summing over μ , it is possible to show that (appendix 1)

$$\sum_{\mu} \mu_{\alpha} D_{\alpha 0} \varepsilon_{\mu}^{(n)} = -\frac{1}{n^0(\varepsilon_F)} \sum_{\substack{\mu \neq 0, \\ m, m'}} \mu_{\alpha} D_{\alpha 0} \beta_{0\mu}^{0(n)mm'} n_{\mu 0}^{m'm}(\varepsilon_F) \quad (3.16)$$

with

$$n^0(\varepsilon_F) = \sum_m n_{00}^{0mm}(\varepsilon_F). \quad (3.17)$$

The present self-consistent scheme does not invoke local charge neutrality nor the Born–Mayer form for the repulsive energy (Ohta *et al* 1987, Sutton *et al* 1988, Finnis *et al* 1988). However, the electron density is restricted to Hartree approximation, whereas exchange–correlation potentials are developed in the case of the rigid-atom model (Finnis *et al* 1988).

3.2. Hydrogen impurity at site I in a transition metal

In this section we will restrict attention, for the derivation of the dipole force tensor, to the following Hamiltonian:

$$H = H^0 + |Is\rangle\epsilon_I^s\langle Is| + \sum_{R,m} (|Rm\rangle\beta_{Ri}^{ms}\langle Is| + \text{HC}). \quad (3.18)$$

It has been shown (Khalifeh *et al* 1982b) that the effect of $V_I^{mm}(R)$ present in equation (2.16) does not modify the results quantitatively. We restrict attention also, for δE , as in Khalifeh *et al* (1982a, b), to the first term in equation (2.26). In this case the α component of the force acting on site $\lambda \neq I$ is given by

$$F_\alpha(\lambda) = F_\alpha^0(\lambda) + F_\alpha^I(\lambda) \quad (3.19)$$

with

$$F_\alpha^0(\lambda) = \sum_{\rho,m}' \Delta N_{\rho\rho}^{mm} D_{\alpha\lambda} \epsilon_\rho^{(n)m} + \sum_{\substack{\mu,\rho \neq \mu, \\ m,m'}}' \Delta N_{\rho\mu}^{mm'} D_{\alpha\lambda} \beta_{\mu\rho}^{(n)m'm} \quad (3.20a)$$

and

$$F_\alpha^I(\lambda) = \Delta N_{II}^{ss} D_{\alpha\lambda} \epsilon_I^{(n)s} + \sum_{\mu,m}' \Delta N_{I\mu}^{sm} D_{\alpha\lambda} \beta_{\mu I}^{(n)ms} + \sum_{\mu,m}' \Delta N_{\mu I}^{ms} D_{\alpha\lambda} \beta_{I\mu}^{(n)sm}. \quad (3.20b)$$

The prime means that the summation is restricted to metallic atoms only. The corresponding α component of the dipole force tensor is given by

$$P_{\alpha\alpha}^I = \sum_\lambda \lambda_\alpha F_\alpha^I(\lambda) \quad (3.21)$$

whereas $P_{\alpha\alpha}^0$ is the sum of two terms

$$P_{\alpha\alpha}^{0,d} = \sum_{\rho,m}' \Delta N_{\rho\rho}^{mm} \sum_\lambda \lambda_\alpha D_{\alpha\lambda} \epsilon_\rho^{(n)m} \quad (3.22a)$$

$$P_{\alpha\alpha}^{0,nd} = \sum_{\substack{\lambda,\rho \neq \lambda, \\ m,m'}}' \lambda_\alpha (\Delta N_{\rho\lambda}^{mm'} D_{\alpha\lambda} \beta_{\lambda\rho}^{(n)m'm} + \Delta N_{\lambda\rho}^{mm'} D_{\alpha\lambda} \beta_{\rho\lambda}^{(n)m'm}). \quad (3.22b)$$

$P_{\alpha\alpha}^{0,d}$ can also be written (appendix 2)

$$P_{\alpha\alpha}^{0,d} = \sum_\rho \rho_\alpha \frac{1}{\pi} \text{Im} \sum_{\substack{\nu,\gamma, \\ m',m''}} \int^{\epsilon_F} d\epsilon t_{\nu\gamma}^{m'm''} \frac{d}{d\epsilon} G_{\gamma\nu}^{0m'm'}(\epsilon) D_{\alpha 0} \epsilon_\rho^{(n)m} \quad (3.22c)$$

where t is the T matrix of the impurity (Demangeat *et al* 1978).

In the work of Khalifeh *et al* (1982a, b), the derivation of P was performed in a model of local neutrality in the frozen alloy, where no bound states were present. In order to extend the approach to a more realistic model, we have to take into account, explicitly, the presence of these bound states. As shown by Khalifeh and Demangeat (1983), in the presence of a bound state, a charge transfer from metal to hydrogen appears in the frozen lattice and this has to be taken into account in a correct derivation of P . The influence of the bound state shows up in the derivation of $\Delta N_{\lambda\rho}^{mm'}$. In appendix 3 we have derived expressions for these terms in the presence of a bound state.

Jena *et al* (1985) have derived lattice relaxation around hydrogen in a BCC transition metal, in the effective-medium approximation. In their approach the d states are approximated by a homogeneous density of states, whereas in the present scheme the d states are obtained in a tight-binding approximation, which is more realistic (Friedel 1969).

3.3. Forces at the surface of a transition metal

Up to now only phenomenological models have been used for the determination of the force field at the surface. These models neglect arbitrarily the charge-transfer contribution in the band-structure term whereas the repulsive term is approximated through a Born–Mayer form (Luo and Legrand 1988).

In this section we derive, from equation (2.29) for the variation of the total energy δE of the system, an expression for the force field induced by the surface.

Let us first develop the trace present in (2.29):

$$\delta E = \sum_{\lambda, m} \delta \varphi \varepsilon_{\lambda}^m N_{\lambda\lambda}^{mm} + \sum_{\substack{\lambda, \mu \neq \lambda, \\ m, m'}} \delta \varphi \beta_{\lambda\mu}^{mm'} N_{\mu\lambda}^{m'm} \quad (3.23a)$$

with

$$N_{\mu\lambda}^{m'm} = -\frac{1}{\pi} \text{Im} \int^{\varepsilon_F} \langle \mu m' | G | \lambda m \rangle d\varepsilon \quad (3.23b)$$

where G is the Green function related to the Hamiltonian H of section 2.4.

The α component of the force $F'_{\alpha}(\rho)$ acting on site ρ is given by

$$F'_{\alpha}(\rho) = \sum_{\lambda, m} D_{\alpha\rho}^{\varphi} \varepsilon_{\lambda}^m N_{\lambda\lambda}^{mm} + \sum_{\substack{\lambda, \mu \neq \lambda, \\ m, m'}} D_{\alpha\rho}^{\varphi} \beta_{\lambda\mu}^{mm'} N_{\mu\lambda}^{m'm}. \quad (3.24)$$

Let us now discuss the first term on the right-hand side of (3.24),

$$D_{\alpha\rho}^{\varphi} \varepsilon_{\lambda}^m = \delta_{\lambda\rho} \int \nabla_{\alpha} \varphi^m(r - \lambda) H \varphi^m(r - \lambda) d^3r + \text{HC}. \quad (3.25)$$

Using the expression for H given by (2.27), we obtain

$$\begin{aligned} D_{\alpha\rho}^{\varphi} \varepsilon_{\lambda}^m &= \delta_{\lambda\rho} \int \nabla_{\alpha} \varphi^m(r - \lambda) h^{\text{at}}(\lambda) \varphi^m(r - \lambda) d^3r + \delta_{\lambda\rho} \int \nabla_{\alpha} \varphi^m(r - \lambda) \\ &\times \sum_{\lambda' \neq \lambda} v^{\text{at}}(r - \lambda') \varphi^m(r - \lambda) d^3r + \text{HC}. \end{aligned} \quad (3.26)$$

The first integral is zero because $(\nabla_{\alpha} \varphi) \varphi$ is an odd function. After some manipulation, the following expression for (3.26) is obtained:

$$D_{\alpha\rho}^{\varphi} \varepsilon_{\lambda}^m = -\delta_{\lambda\rho} \nabla_{\rho\alpha} \Delta V_{\rho}^m. \quad (3.27)$$

Let us remark that ΔV_{ρ}^m , the modification of the crystal-field integral induced by the surface, can be obtained through a self-consistent calculation of the local density of state $n_{\rho}^m(E)$ in the local neutrality approximation method for the frozen layer (Dreyssé 1984). If ΔV_{ρ}^m is independent of m , then the first term of $F'_{\alpha}(\rho)$ is

$$-Z \nabla_{\rho\alpha} \Delta V_{\rho}$$

where Z is the valency of the metal.

The second term on the right-hand side of (3.24) can be written as

$$D_{\alpha\rho}^{\varphi}\beta_{\lambda\mu}^{mm'} = \delta_{\lambda\rho}D_{\alpha 0}^{\varphi}\beta_{0,\mu-\rho}^{mm'} + \delta\mu\rho D_{\alpha 0}^{\varphi}\beta_{\lambda-\rho,0}^{mm'}. \quad (3.28)$$

The last term of the second member of equation (2.29) is now discussed. In this expression,

$$\delta V^{\text{ion}}(r) = \sum_{\mu} \delta v^{\text{ion}}(r - \mu) \quad (3.29)$$

$$n^{\text{el}}(r) = \sum_{\lambda,m} N_{\lambda\lambda}^{mm} [\varphi^m(r - \lambda)]^2 \quad (3.30a)$$

$$n^{\text{ion}}(r) = \sum_{\lambda} Z_{\lambda}^{\text{p}} \delta(r - \lambda) - \sum_{\substack{\lambda,n, \\ l,m}} Z^{nlm} [\varphi_c^{nlm}(r - \lambda)]^2 \quad (3.30b)$$

where Z_{λ}^{p} is the number of protons of the atom at site λ , Z_{λ}^{nlm} is the number of electrons in the atomic nl shell of component m and $\varphi_c^{nlm}(r - \lambda)$ are the corresponding atomic orbitals of the core. In the point-charge approximation, we get

$$F_{\alpha}^n(\rho) = Z \sum_{\substack{\lambda \neq \rho, \\ m}} N_{\lambda\lambda}^{mm} \int \frac{r_{\alpha}}{r^3} [\varphi^m(r - (\lambda - \rho))]^2 d^3r - Z^2 \sum_{\lambda \neq \rho} \frac{(\lambda - \rho)_{\alpha}}{|\lambda - \rho|^3}. \quad (3.31)$$

Using Fourier transformation, we obtain after some developments

$$F_{\alpha}^n(\rho) = -i \frac{\Omega}{8\pi^3} \int q_{\alpha} v(q) d^3q \left(\sum_{\lambda \neq \rho, m} e^{-iq(\lambda - \rho)} N_{\lambda\lambda}^{mm} - Z \sum_{\lambda \neq \rho} e^{-iq(\lambda - \rho)} \right). \quad (3.32)$$

By definition, $\sum_m N_{\lambda\lambda}^{mm} = Z$, and finally

$$F_{\alpha}^n(\rho) = 0 \quad \text{for } \rho \rightarrow +\infty. \quad (3.33)$$

The long-range Coulomb terms have been eliminated without invoking local charge neutrality at the relaxed surface. This is an improvement over methods assuming local charge neutrality on each atom (Luo and Legrand 1988) and a Born–Mayer form for the repulsive energy. We have to say, once again, that relaxation does induce charge transfer. While this charge transfer is rather localised, in the case of impurities it does not induce long-range Coulomb terms; this is not the case for surfaces. Therefore, the neglect of charge transfer in this last case is unrealistic.

4. Conclusions and outlook

We have presented a self-consistent derivation, in the tight-binding formalism, of the force field around defects in metals. While in the case of a point defect (substitutional or interstitial) we can define and estimate an expression for the dipole force tensor, in the case of the surface we have to restrict attention to the force field. Up to now this general scheme has been applied, with some simplifications, to the case of substitutional (Moraitis *et al* 1985) and interstitial (Khalifeh *et al* 1982a, b, Mokrani *et al* 1989) impurities in transition metals.

We will now discuss the approximations appearing in those previous calculations.

In the case of substitutional impurities in transition metals (Moraitis *et al* 1985), only the non-diagonal part $P_{\alpha\alpha}^{0,\text{nd}}$ of the dipole force tensor was estimated using a simple

s-band model. The numerical results exhibit the trend expected from Vegard's law. However, deviations from this law are observed experimentally. We expect that this may be related to the diagonal part $P_{\alpha\alpha}^{0,d}$. Here we propose a way to obtain $P_{\alpha\alpha}^{0,d}$ in terms of the derivatives of the hopping integrals between neutral atoms (see appendix 1).

In the case of light interstitial impurities in transition metals, a calculation has been performed for hydrogen, at octahedral position, in a FCC transition metal. Unfortunately, this calculation was performed within the framework of an oversimplified model (Khan *et al* 1980) of the electronic structure of the alloy. For the frozen alloy, the local neutrality criterion used in this model could not explain the presence of a bound state in this alloy. A better model was therefore built (Khalifeh and Demangeat 1983) and charge transfer (from Pd to H) together with the presence of a bound state below the conduction band was obtained. More recently (Moraitis *et al* 1984a), this charge-transfer effect was taken into account for the derivation of P . The effect of the bound state (as shown explicitly in appendix 3) was only taken into account in the case of H in V and Nb (Mokrani *et al* 1989).

The formalism developed for the determination of the force field in bulk transition-metal alloy is extended to the case of a metallic surface. Our self-consistent scheme leads to a simple expression for the forces without invoking local charge neutrality induced by the relaxation nor a phenomenological repulsive pair interaction.

Moreover, we will present in a forthcoming publication (Moraitis and Demangeat 1990) a derivation of the force constants of the pure transition metal and their substitutional alloy in the Christensen (1984) scheme. In these formulae, due to exact cancellation, charge transfer induced from the atomic movement does not appear, contrary to the case already presented by Moraitis *et al* (1984b).

Appendix 1

The purpose of this appendix is to relate the quantity $\sum_{\mu} \mu_{\alpha} D_{\alpha 0} \epsilon_{\mu}^{0(n)m}$ that appears in $P_{\alpha\alpha}^d$ (cf equation (3.7a)) in terms of the derivatives of the hopping integrals. For simplicity, we drop the superscripts 0 and (n) in the following.

This proof is in two steps: the first is to show that $D_{\alpha\mu} N(\epsilon_F) = 0$; the second is to use this relation in order to express $P_{\alpha\alpha}^d$ in terms of $D_{\alpha\lambda} \beta_{\lambda\mu}^{nm'}$.

A1.1. Proof of $D_{\alpha\mu} N(\epsilon_F) = 0$, for pure metal

Starting with equation (3.13),

$$D_{\alpha\mu} N(\epsilon_F) = \sum_{\lambda, m} n_{00}^{mm}(\epsilon_F) D_{\alpha\mu} \epsilon_{\lambda}^m + \sum_{\substack{\lambda, \nu, \\ m, m'}} D_{\alpha\mu} \beta_{\lambda\nu}^{mm'} n_{\nu\lambda}^{m'm}(\epsilon_F) \quad (\text{A1.1})$$

we will first prove that the second term on the right-hand side is zero. Indeed,

$$\begin{aligned} \sum_{\substack{\lambda, \nu, \\ m, m'}} D_{\alpha\mu} \beta_{\lambda\nu}^{mm'} n_{\nu\lambda}^{m'm}(\epsilon_F) &= \sum_{\substack{\nu, \\ m, m'}} D_{\alpha 0} \beta_{0, \nu-\mu}^{mm'} n_{\nu-\mu, 0}^{m'm}(\epsilon_F) \\ &+ \sum_{\substack{\lambda, \\ m, m'}} D_{\alpha 0} \delta \beta_{\lambda-\mu, 0}^{mm'} n_{0, \lambda-\mu}^{m'm}(\epsilon_F) \end{aligned} \quad (\text{A1.2})$$

where we have taken into account the fact that the perfect lattice is translationally invariant.

The fact that, in the case of d orbitals, (i) $\beta_{0\rho}^{mm'}$ is an even function of ρ and its gradient is an odd function, and (ii) $n_{0,-\rho}^{m'm}(\epsilon_F) = n_{0,\rho}^{m'm}(\epsilon_F)$, leads to

$$\sum_{\rho} n_{0,-\rho}^{m'm}(\epsilon_F) D_{\alpha 0} \beta_{0\rho}^{mm'} = 0 \quad (\text{A1.3})$$

so that

$$\sum_{\substack{\lambda, \nu, \\ m, m'}} D_{\alpha\mu} \beta_{\lambda\nu}^{mm'} n_{\nu\lambda}^{m'm}(\epsilon_F) = 0. \quad (\text{A1.4})$$

Also, we will prove that the first term on the right-hand side of equation (A1.1) is equal to zero. Indeed,

$$D_{\alpha\mu} \epsilon_{\lambda}^m = \int \varphi_m^2(r - \lambda) \nabla_{\alpha} v(r - \mu) d^3r. \quad (\text{A1.5})$$

Because $\nabla_{\alpha} v(r)$ is an odd function, we obtain immediately

$$\int \varphi_m^2(r - \rho) \nabla_{\alpha} v(r) d^3r = - \int \varphi_m^2(r + \rho) \nabla_{\alpha} v(r) d^3r \quad (\text{A1.6})$$

so that

$$\sum_{\lambda} D_{\alpha\mu} \epsilon_{\lambda}^m = 0 \quad \text{for all } m. \quad (\text{A1.7})$$

From equations (A1.4) and (A1.7) we obtain

$$D_{\alpha\mu} N(\epsilon_F) = 0. \quad (\text{A1.8})$$

A1.2. A relation between $\sum_{\mu} \mu ({}_{\alpha} D_{\alpha 0} \epsilon_{\mu}^m)$ and the derivative of the β s

Let us multiply the right-hand side terms of (A1.1) by μ_{α} and sum over

$$\sum_{\lambda, m} n_{00}^{mm}(\epsilon_F) \sum_{\mu} \mu_{\alpha} D_{\alpha\mu} \epsilon_{\lambda}^m + \sum_{\substack{\lambda, \gamma, \\ m, m'}} \mu_{\alpha} D_{\alpha\mu} \beta_{\lambda\gamma}^{mm'} n_{\gamma\lambda}^{m'm}(\epsilon_F) = 0. \quad (\text{A1.9})$$

It can be shown that

$$\sum_{\lambda, \mu} \mu_{\alpha} D_{\alpha\mu} \epsilon_{\lambda}^m = -N \sum_{\rho} \rho_{\alpha} D_{\alpha 0} \epsilon_{\rho}^m. \quad (\text{A1.10})$$

We examine now the second term of (A1.9):

$$\begin{aligned} \sum_{\lambda, \gamma \neq \lambda} \sum_{\mu} \mu_{\alpha} D_{\alpha\mu} \beta_{\lambda\gamma}^{mm'} n_{\gamma\lambda}^{m'm}(\epsilon_F) &= \sum_{\lambda, \gamma \neq \lambda} \lambda_{\alpha} D_{\alpha 0} \beta_{0, \gamma - \lambda}^{mm'} n_{\gamma - \lambda, 0}^{m'm}(\epsilon_F) \\ &+ \sum_{\lambda, \gamma \neq \lambda} \gamma_{\alpha} D_{\alpha 0} \beta_{\lambda - \gamma, 0}^{mm'} n_{0, \lambda - \gamma}^{m'm}(\epsilon_F). \end{aligned} \quad (\text{A1.11})$$

The first term on the right-hand side can be written as

$$- \sum_{\lambda, \gamma \neq \lambda} (\gamma - \lambda)_{\alpha} D_{\alpha 0} \beta_{0, \gamma - \lambda}^{mm'} n_{\gamma - \lambda, 0}^{m'm}(\epsilon_F) + \sum_{\lambda, \gamma \neq \lambda} \gamma_{\alpha} D_{\alpha 0} \beta_{0, \gamma - \lambda}^{mm'} n_{\gamma - \lambda, 0}^{m'm}(\epsilon_F). \quad (\text{A1.12})$$

The last term of (A1.11) cancels with the last term of (A1.12), so that

$$\sum_{\lambda, \gamma \neq \lambda} \sum_{\mu} \mu_{\alpha} D_{\alpha\mu} \beta_{\lambda\gamma}^{mm'} n_{\gamma\lambda}^{m'm}(\epsilon_F) = -N \sum_{\rho \neq 0} \rho_{\alpha} D_{\alpha 0} \rho_{0, \rho}^{mm'} n_{\rho, 0}^{m'm}(\epsilon_F). \quad (\text{A1.13})$$

If we assume that ϵ_{ρ}^m is independent of m , we find

$$\sum_{\rho} \rho_{\alpha} D_{\alpha 0} \epsilon_{\rho} = - \frac{1}{n(\epsilon_F)} \sum_{\substack{\rho \neq 0, \\ m, m'}} \rho_{\alpha} D_{\alpha 0} \beta_{0\rho}^{mm'} n_{\rho 0}^{m'm}(\epsilon_F). \quad (\text{A1.14})$$

Appendix 2

In this appendix we derive a simple expression for $P_{\alpha\alpha}^{0,d}$ (equation (3.22a)) in the case of a light interstitial in a transition metal:

$$P_{\alpha\alpha}^{0,d} = \sum'_{\rho,m} \Delta N_{\rho\rho}^{mm} \sum_{\lambda} \lambda_{\alpha} D_{\alpha\lambda} \epsilon_{\rho}^{(n)m}. \tag{A2.1}$$

In the following, we will for simplicity suppress the superscript (n). In this case,

$$\epsilon_{\rho}^m = \epsilon_{\rho}^{\varphi m} + \epsilon_{\rho}^{vm} \tag{A2.2}$$

$$\delta^{\varphi} \epsilon_{\rho}^m = \int \delta\varphi_{\rho}^m H^0 \varphi_{\rho}^m d^3r + \int \varphi_{\rho}^m H^0 \delta\varphi_{\rho}^m d^3r. \tag{A2.3}$$

We will first show that the contribution of this term to $P_{\alpha\alpha}^{0,d}$ is zero. The first term of (A2.3) is given by

$$\delta^{\varphi} \epsilon_{\rho}^m = -\mathbf{u}_{\rho} \int \nabla\varphi^m(r-\rho) H^0 \varphi^m(r-\rho) d^3r \tag{A2.4}$$

where H^0 is the Hamiltonian of the pure metal.

If we take into account the fact that (by symmetry)

$$\int \nabla\varphi^m(r) v^{at}(r) \varphi^m(r) d^3r = 0$$

then

$$D_{\alpha\lambda}^{\varphi} \epsilon_{\rho}^m = \delta_{\lambda\rho} \int \nabla_{\alpha} \varphi^m(r) \sum_{\mu \neq 0} v^{at}(r-\mu) \varphi^m(r) d^3r \tag{A2.5}$$

where μ is a lattice vector. Now $P_{\alpha\alpha}^{0,d}$ can be written as

$$P_{\alpha\alpha}^{0,d} = \sum'_{\rho,m} \Delta N_{\rho\rho}^{mm} \sum_{\lambda} \lambda_{\alpha} \delta_{\lambda\rho} D_{\alpha 0}^{\varphi} \epsilon_{\rho}^m. \tag{A2.6}$$

If we can neglect the m dependence of ϵ_{ρ}^m , it appears that the φ component of $P_{\alpha\alpha}^{0,d}$ is zero.

It is trivial to see that

$$D_{\alpha\lambda}^v \epsilon_{\rho}^m = D_{\alpha 0}^v \epsilon_{\rho-\lambda}^m \tag{A2.7}$$

where

$$D_{\alpha\lambda}^v \epsilon_{\rho}^m = \int \varphi^m(r-\rho) \nabla_{\alpha} v^{at}(r-\lambda) \varphi^m(r-\rho) d^3r. \tag{A2.8}$$

In the second member of (A2.8) we translate all the quantities by λ , so that we obtain

$$\int \varphi^m(r-(\rho-\lambda)) \nabla_{\alpha} v^{at}(r) \varphi^m(r-(\rho-\lambda)) d^3r.$$

This is exactly $D_{\alpha 0}^v \epsilon_{\rho-\lambda}^m$. Therefore $P_{\alpha\alpha}^{0,d}$ depends only on the derivative of the potential, so that it is now given by (ρ is a lattice vector)

$$P_{\alpha\alpha}^{0,d} = \sum'_{\rho,m} \sum_{\lambda} \lambda_{\alpha} \Delta N_{\lambda+\rho, \lambda+\rho}^{mm} D_{\alpha 0}^v \epsilon_{\rho}. \tag{A2.9}$$

We will now express this sum in terms of the matrix elements of the Green function $G^l(\epsilon)$ and of the t matrix t . Finally, after some manipulations,

$$P_{\alpha\alpha}^{0,d} = \sum'_{\rho} \rho_{\alpha} \frac{1}{\pi} \text{Im} \sum_{\substack{\gamma, \nu, \\ m', m''}} \int^{\epsilon_F} t_{\nu\gamma}^{m'm''} \frac{d}{d\epsilon} G_{\gamma\nu}^{0m'm'}(\epsilon) d\epsilon D_{\alpha 0}^v \epsilon_{\rho}. \tag{A2.10}$$

Appendix 3

The effect of the bound state, present in the case of interstitial alloys, on the determination of $\Delta N_{\lambda\rho}^{mm'}$ (section 3.2), is given by

$$\Delta N_{\lambda\rho}^{mm'} = -\frac{1}{\pi} \text{Im} \int^{\epsilon_F} dE \langle \lambda m | G - G^0 | \rho m' \rangle. \quad (\text{A3.1})$$

Here, we restrict attention to the bound state, so that the integration is from $-\infty$ to ϵ_{bs} (the bottom of the conduction band).

The wavefunction $|\psi_n\rangle$ of the alloy is given by

$$|\psi_n\rangle = A_I^s(n) |Is\rangle + \sum'_{\mu,m} A_{\mu}^m(n) |\mu m\rangle. \quad (\text{A3.2})$$

Using the fact that we have only one bound state ϵ_{bs} (Khalifeh and Demangeat 1983), we obtain straightforwardly

$$\Delta N_{\lambda\rho}^{mm'}(\text{bs}) = A_{\lambda}^m(\epsilon_{\text{bs}}) A_{\rho}^{m'}(\epsilon_{\text{bs}}). \quad (\text{A3.3})$$

In order to get an expression for the A s, we start with the fact that $\langle \psi_n | \psi_n \rangle = 1$ and that the Schrödinger equation can be written (by taking into account that $H = H^I + V$ and $G^I = (\epsilon - H^I)^{-1}$) as

$$|\psi_n\rangle = G^I V |\psi_n\rangle \quad (\text{A3.4})$$

so that

$$\sum'_{\lambda,m'} |A_{\lambda}^{m'}(n)|^2 = -|A_I^s(n)|^2 \frac{d}{d\epsilon} \Delta_{II}^{ss}(\epsilon) \quad (\text{A3.5})$$

with

$$\Delta_{II}^{ss}(\epsilon) = \sum_{\substack{\lambda,m' \\ \nu,m}} \beta_{I\nu}^{sm} G_{\nu\lambda}^{0mm'} \beta_{\lambda I}^{m's} \quad (\text{A3.6})$$

where the derivative is taken at the bound-state energy ϵ_{bs} .

Then ΔN defined by (A.3) is written in the following final form:

$$\Delta N_{\lambda\rho}^{mm'}(\text{bs}) = \frac{1}{1 - d\Delta_{II}^{ss}(\epsilon)/d\epsilon} \sum'_{\mu,m'} G_{\lambda\mu}^{0mm''} \beta_{\mu I}^{m's} \sum'_{\mu',m'''} G_{\rho\mu'}^{0m'm'''} \beta_{\mu' I}^{m''s} \quad (\text{A3.7a})$$

$$\Delta N_{\lambda I}^{ms} = \frac{1}{1 - d\Delta_{II}^{ss}/d\epsilon} \sum_{\mu,m'} G_{\lambda\mu}^{0mm'} \beta_{\mu I}^{m's}. \quad (\text{A3.7b})$$

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