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THE SURFACE RECONSTRUCTION OF Au(110):

THEORETICAL STUDY AT T = 0

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I - INTRODUCTION

The study of metal surfaces in their ground state has proceeded along two major avenues, each one parallel to a historically different development route of the study of bulk structure. One of them, disregarding the interaction between the conduction electrons and the ionic lattice, analyses the properties of the electron gas and then considers the discreteness of the ionic lattice, which is initially replaced by a uniform background, in a perturbative way using pseudopotentials (1).

The other route, the bulk bandstructure calculations, emphasizes the band structure aspects (one-electron), and includes only approximately the electron-electron interaction effects (2).

Both routes, however, imply the total theoretical inadequacy of the simplest model, used to describe the cohesion of solids, according to which the metal is composed by single entities (undeformed atoms or molecules) with a pairwise interaction. The main physical feature of a metal is the multitude of conduction electrons which, due to the smearing out of the atomic valence electron wave functions, constitutes a sort of quantum-mechanical "glue" which in no way can be parametrized in a pairwise form.

In the simple metal case, where the first route above is appropriate, second order perturbation theory (3,4) enables us to write the total energy as a large volume dependent part, plus a small term (5) which is the sum over pair of ions of the central interaction. In the case of the

transition metals, when the d electrons play the most important role, the band calculations can be used: and in a tight binding scheme, some authors (6, 7) pointed out that the main attractive part of the cohesive energy, coming just from the d electrons, is a function of two-center overlap integrals.

In spite of the absence of any theoretical foundation, the pairwise model, which arranges a center of force in every lattice position, has been up to now the only way to put forward, with no effort, many predictions, at least for the bulk metal properties.

We want now to establish the real limits of such a description stressing briefly its main shortcomings. This is done in order to show that many of them can be adjusted introducing very empirically, according to a simple idea, a new model. It gives, far from being perfect, a much more realistic description, not only for the bulk properties but also, and especially, for the observed properties of metal surfaces, without introducing any new computational difficulty.

The first misrepresentation of the pairwise model is related to the elastic behaviour of the crystal. Indeed, if such a model is used, certain relations between the elastic constants can be analytically derived. These are known as Cauchy relations and for a cubic crystal they reduce to $C_{12} = C_{44}$. It is apparent from Table I that these relations are not satisfied in real metals. The others are related to the energetics of the defects formation. The first example we want to give is the energy of the vacancy formation which in a two-body scheme always equals the cohesive

energy (Table II). The second example shows the total uselessness of using a pairwise interaction to describe any observed properties of the metal surfaces. This can be understood considering that from the results of low energy electron diffraction (LEED) experiments (8 ,9) a contraction of the distance between the outermost atomic planes is apparent. Usually, the contraction is maximum for the surface layer and rapidly disappears going into the interior ones. It is easily seen that if the interaction between crystal atoms is described by a classical, regular, two-body potential , then , when we cut the crystal, the distances between the external planes certainly increase or keep the same value if we restrict the interaction only to nearest neighbours(10). Similar arguments can be also used to convince ourselves that, in this scheme no surface reconstruction can ever be predicted.

We conclude therefore that in order to give a realistic description of the defects formation, in particular of the observed structure of real metal surfaces, we cannot disregard the presence of the conduction electrons, whose "glueing" role can in no way be simulated by using a pairwise interaction.

Both the above mentioned theories suggest that, in order to consider the electronic effects, a many-body term must be added to the interatomic two-body potential. Without entering into any particular microscopic theory, we believe that this "corrective" many-body term must be density dependent. This assumption is based on the observation that the common feature of every defect formation process, including surface, is a local change of the "atomic" arrangement in the zone where the defect has been created. Therefore the success in describing such a kind of situation seems to be related

to our capacity of distinguishing the various possible configurations of the "host" environment around the defect position. To this end, we will define, in the next chapter, a local host density, without giving it any particular microscopic interpretation, such that its value, in a given point, is just a measure of the presence, in that point, of the other single entities, up to now and later on called atoms, which are assembled in our model to form the metal. This picture becomes much more clear if we consider, for example, that in the surface reconstruction the atoms on the outermost planes rearrange themselves under the action of some driving force. In our scheme such a force is locally created by the energy variation associated to any deviation of the host density, in a given point, from its equilibrium bulk value. As a result the atoms will move in order to restore a new equilibrium situation, which, of course, will differ from the bulk one if some atoms have been wrenched from the metal. Let us stress that, in our model, the equilibrium situations are always based on the balance between the many-body forces and the two-body ones, which are not vanishing if the atoms do not find themselves on the equilibrium bulk positions.

We can summarize stating that in virtue of the new, appropriately defined energy term, host density function, every atom can choose among the various possible configurations of its neighbours the one to which the lowest value of its energy is associated.

In the next section we will clarify this idea defining our method in detail.

Part 2 is devoted to the study of the bulk properties in term of the new defined potential; after that in part 3 we will use our method to describe the metal surfaces and, with that, our theoretical, zero temperature, description of a metal is complete.

The cores of these parts emphasize how the new method, extending to a many-body form the interaction between metal atoms, fill up the main shortcomings of a description in terms of any pairwise potentials, which can be now considered just as a particular sub-class of a new defined extended one.

In order to find the limits of our model, we use it in part 4 for describing a real metal. After a bulk parametrization is done, which points out that the main lack is the absence of any angular forces, absolutely necessary in order to fit the phonon spectra of all noble and transition metals (11), we focus onto the study of the Au(110) surface. A very good agreement between our predicted stable surface structure and the experimentally observed one is then obtained.

TABLE I : ELASTIC CONSTANTS AT ROOM TEMPERATURE (10^{12} dynes /cm²)

Ref.	Metal	C ₁₁	C ₁₂	C ₄₄
12	Sodium	0.073	0.062	0.042
13	Copper	1.661	1.199	0.756
"	Silver	1.222	0.907	0.454
14	Gold	2.016	1.697	0.454
15	Alluminium	1.068	0.604	0.283
16	Vanadium	2.279	1.87	0.426
"	Niobium	2.466	1.332	0.281
"	Tantalum	2.660	1.612	0.824
"	Chromium	3.871	1.035	1.008
"	Molibdenum	4.647	1.615	1.089
"	Tungsten	5.224	2.044	1.606
17	Iron	1.519	0.862	0.762
18	Platinum	3.580	2.536	0.774
18	Iridium	5.96	2.52	2.7

Metal	E_{ν}^F (ev)	Ref	E_{coh} (eV/atom)	Ref
Niobium	2.04	19	7.57	16
Tantalum	2.9	"	8.1	16
Chromium	1.2	"	4.1	16
Molibolenum	2.24	"	6.82	16
Tungsten	3.15	"	8.9	16
Iron	1.79	20	4.28	17
Platinum	1.51	21	5.852	22
Gold	0.95	21	3.78	22
Aluminum	.76	21	3.39	22
Copper	1.14	21	3.49	22
Silver	1.08	21	2.95	22

Table II - Cohesive and vacancy formation energies for noble and transition metals.

II - THE METHOD

Let us remark that if we want to adjust the elastic constant adding to the pair-potential energy, by analogy with simple metal perturbation theory, a term dependent on the macroscopic volume of the crystal, we have to use necessarily a free surface model (23) which will be of course completely useless for describing metal surfaces.

In order to get over this handicap, we could consider the energy as a function of a certain local volume per atom (24). But in this case, any ambiguities about the definition of this volume, which will certainly arise in the calculation involving the surface, might automatically invalidate the results obtained.

It seems then justified to consider the many-body term function of the density.

In this section we only define the new model writing formally the energy of a given atom as a sum of two-body contributions plus the electronic glue considered as a general, unspecified, function of an appropriately defined host density, in such a way that using a figurative language the atoms can now feel, and weigh, the presence of their neighbours exactly as if they had a sort of 'radar' applied on them.

Since supposing a pairwise interaction between classical objects placed at the vertices of a lattice, described by a regular central potential, like Morse, Lennard-Jones, or other much more complicated parametric forms, works well in many circumstances, we thought to correct such a model by introducing in a very empirical way a local density dependent term. This term will be constructed in order to be qualitatively relevant especially where the pairwise description is meaningless. Keeping this in mind, we do the following ansatz for the total energy of a system of single units, let us call them atoms, arranged on a lattice

$$E = \sum_i U_i(\rho_i) + \frac{1}{2} \sum_{i,j} V_{ij}(R^{ij}) \quad (1.1)$$

V_{ij} is the pair potential, R^{ij} is the distance between the atoms at the sites i and j and the prime excludes the $i = j$ term in the summation.

The new term is a sum of atomic energies U_i which are functions to be determined, of the local host density ρ_i at the lattice position \underline{R}_i but without atom i .

The (1.1) is the very general starting point of our model and it could be used as a starting point of each of the previously mentioned theories (7,24) provided that we use the proper interpretation for the three quantities U_i , ρ_i , V_{ij} .

We do not lose any generality considering explicitly the various contributions to the local density :

$$\rho_i \equiv \sum_{j \neq i} n_{i,j} \quad (1.2)$$

For the sake of making easy the notation, let us consider a Bravais lattice.

In this case there is no reason to consider so many indices and the (1.1)

becomes

$$E = \sum_i U(\rho_i) + \frac{1}{2} \sum_{i,j} V(R^{ij}) \quad (1.1a)$$

Let us now do a further approximation considering $n_{i,j}$, the contribution to the host density at i coming from the unit site in j , only function of the distance R^{ij} . In other words

$$n_{i,j} \equiv n(R^{ij}) \quad (1.3)$$

So we can write

$$E = \sum_i U \left(\sum_{j \neq i} n(R^{ij}) \right) + \frac{1}{2} \sum_{i,j} V(R^{ij}) \quad (1.1b)$$

We want to emphasize that according to (1.2) a given atom in a certain sense sees the environment in which it takes place or by (1.3) it is able to count the other atoms which contribute to the host density. It seems very reasonable to expect that, defining appropriately the many-body terms U and n , the atoms can "decide" in which host structure they want to rest by lowering their energy.

Let us now define in detail the host density. First, we observe that to justify the presence in (1.1) of the classical interaction V the

atoms must be compact units: we choose for them a spherical shape. Further, we must define for each of them a "horizon" such that it can "see" all other atoms which are far from it less than such a distance, weighing them suitably. Carrying on with our figurative language, we suppose that a given atom i "feels" the presence of other atoms j in a sphere of radius R_s and the amount of this feeling is only dependent, by (1.3), on their separation R^{ij} .

Making operative these definitions and using the notation (i, R) to indicate the volume of the sphere of radius R centred on the lattice site

i we can choose in a very crude way

$$v_o n(R^{ij}) \equiv (i, R_s) \cap (j, r_o) = (j, R_s) \cap (i, r_o) \quad (1.3a)$$

r_o is obviously the radius of the atomic sphere, while $v_o = \frac{4}{3} \pi r_o^3$ is its volume. Fig. 1 elucidates this definition.

In Fig. 2 are shown the function $n(R)$ and its first and second derivatives for fixed values of the two parameters r_o and R_s . We will see later that there is no relevant dependence of the physical quantities on r_o and R_s nor quantitative one if the two parameters will vary keeping the number of neighbours felt fixed.

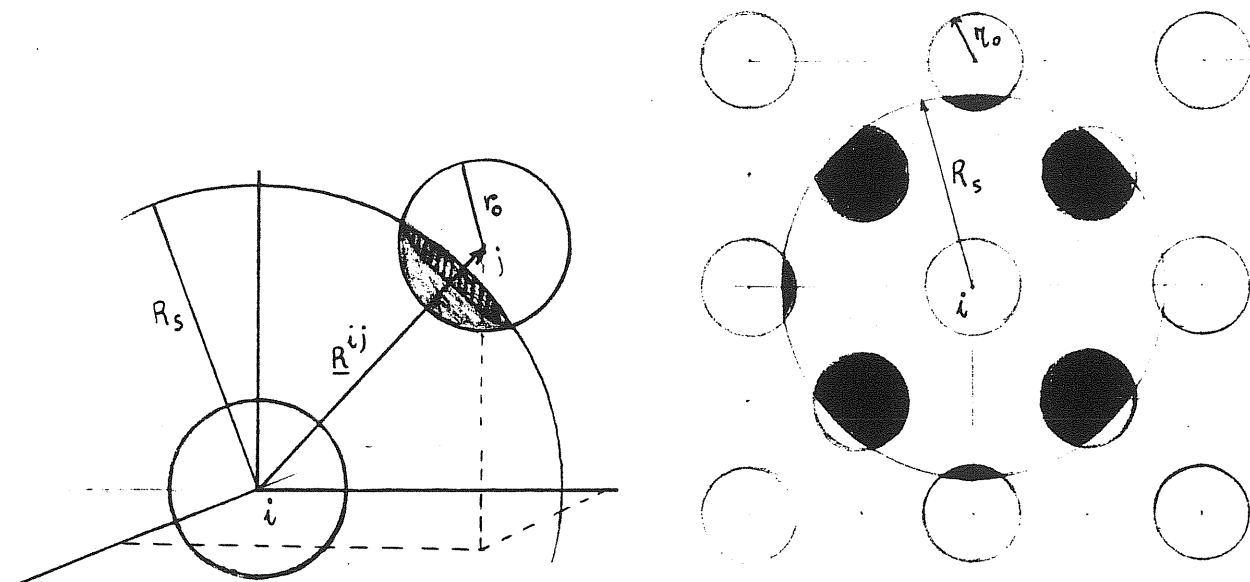


Fig. 1 a) Geometric definition of $v_0 n(|\underline{R}^i - \underline{R}^j|)$ (hatched zone)
 b) Geometric definition of the host density in the lattice site i $\rho_i = \sum_{j \in v(i)} n(R^{ij})$ hatched zone. The notation $v(h)$ denote the set of the host atoms felt by the guest atom h .

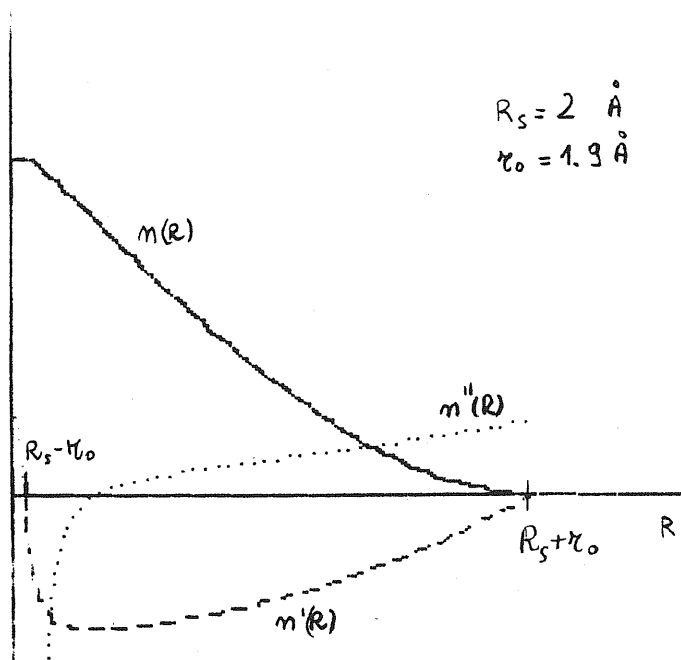


Fig. 2 $n(R)$, $n''(R) \equiv \frac{d^2 n}{dR^2}$ and $n'(R) \equiv \frac{dn}{dR}$ vs R curves.

$$n(R) = \frac{4}{v_0} \frac{\pi}{12R} \left[R^4 - 6(R_s^2 + r_0^2)R^2 + 8(R_s^3 + r_0^3)R - 3 \cdot (R_s^2 - r_0^2)^2 \right]$$

III - BULK PROPERTIES

We apply our formalism 1.1.b to an infinite lattice system and derive expressions for the physical quantities of interest which will be fitted later in order to describe a real system.

We refer here and in the following sections to a general F.C.C. structure whose lattice parameter is denoted by "a", while for the nearest neighbours distance, the symbol "d" is used (fig. 2.1). In all which follows we keep the temperature fixed to 0°K.

Table III : F.C.C. metals

metal	a(A)	metal	a(A)	metal	a(A)
		Nichel	3.52	Copper	3.61
Rhodium	3.80	Palladium	3.89	Silver	4.09
Iridium	3.84	Platinum	3.92	Gold	4.07

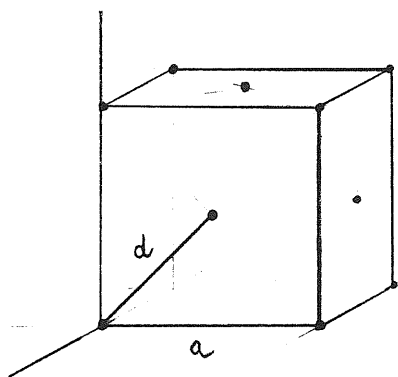


Fig. 2.1

In this section we give the general expressions for the cohesive energy and pressure. Since we consider a Bravais lattice all atoms are equivalent and, choosing to refer to a generic atom i_0 , we get for the energy required, per particle, to disassemble the crystal in its constituent parts

$$E_{coh} = - \left(\frac{1}{2} \sum_{j \neq i_0} V(R^{i_0 j}) \right) + U \left(\rho_{i_0} \right) \quad (2.1)$$

where we attribute zero energy to the situation where the atoms are infinitely far apart. In order to stress the contributions coming from the different shells of neighbours we write 2.1 in the form

$$E_{coh} = - \left(\frac{1}{2} \sum_M c_M^p V(R_M) + U \left(\sum_M c_M^p n(R_M) \right) \right) \quad (2.1a)$$

where the capital M refers to the shell of the c_M^p M^{th} neighbours which are placed on the lattice sites at a distance R_M from the origin atom. To clarify the notation we specialize the (2.1a) to second neighbour interactions

$$E_{coh} = - \frac{1}{2} \left(12 V(d) + 6 V(a) \right) - U(12 n(d) + 6 n(a)) \quad (2.1b)$$

Of course we have calculated this energy for the externally imposed lattice parameters or in other words with an external pressure applied to the

crystal. By calculating the rate of change of total energy with atomic positions we can find the pressure necessary to maintain a given volume and therefore determine the equilibrium position as those requiring zero pressure for their maintenance.

Using the symbol R_{α}^m to distinguish the component α of the position of the atom m from its equilibrium value R_{α}^m we get

$$\begin{aligned}
 P &= - \left. \frac{d\Phi}{dV} \right|_{T=0^{\circ}K} = - \frac{1}{3V} \sum_i \sum_{\alpha} R_{\alpha}^i \left. \frac{\partial \Phi}{\partial R_{\alpha}^i} \right|_{R_{\alpha}^i = R_{\alpha}^i} = \\
 &= - \frac{1}{3v_c} \sum_{l \neq 0} R^l \cdot \left[U'_0 \cdot m'(R^l) + \frac{1}{2} V'(R^l) \right] = \\
 &= - \frac{1}{3v_c} \sum_L \rho_L R_L \left[U'_0 \cdot m'(R_L) + \frac{1}{2} V'(R_L) \right] \quad (2.2)
 \end{aligned}$$

where $U'_0 = \left. \frac{dU}{d\rho} \right|_{eq}$ and $v_c = \frac{a^3}{4}$ is the volume per atom. The definition of the function Φ is apparent. We observe that E_{coh} is exactly the value of Φ per atom when they are on equilibrium lattice positions.

$$E_{coh} \equiv - \frac{1}{N} \Phi(\dots R_{\rho}^e \dots) \Big|_{R_{\rho}^e = R_{\rho}^e}$$

§ FORCES AND FORCE CONSTANTS

We know that the λ -th component of the force acting on the i -th particle is by the very general definition

$$F_{\lambda}^i \equiv - \frac{\partial \Phi}{\partial R_{\lambda}^i} = \sum_{\ell \neq i} \left[(U_i' + U_{\ell}') \cdot m'(R^{i\ell}) + V'(R^{i\ell}) \right] \frac{R_{\lambda}^{i\ell}}{R^{i\ell}} \quad (2.3)$$

where

$$U_m' \equiv \frac{dU}{d\rho_m} \Big|_{\rho_m = \sum_{\ell \neq m} n(R^{m\ell})} \quad (2.4)$$

It is understood that in the equilibrium lattice situation there is no dependence on the particle index and the U_0' symbol is used for the first derivative defined in (2.4).

We wrote F_{λ}^i in the form (2.3) to stress that the many-body term gives two contributions to the force. The first is due to the change in the density weighed by the atom i , when itself moves; the other comes out because the movement of the atom i causes a change on the density at all other sites.

We perform now the calculation of the force constants which will be useful later, when we will use them to evaluate the elastic constant and phonon dispersion. The derivation is straightforward, starting from

$$\Phi_{d\beta}^{hs} \equiv \frac{\partial^2 \Phi}{\partial R_d^h \partial R_p^s} \Big|_{R_d^l = R_d^l} = \frac{\partial}{\partial R_d^h} \left(\sum_m \sum_{n \neq m} \left[U_m^i \cdot n'(R^{mn}) + \frac{V'(R^{mn})}{2} \right] \frac{R_d^{mn}}{R^{mn}} (\delta_{m,s} - \delta_{n,s}) \right)$$

where

$$\delta_{ml} = \begin{cases} 1 & n = 1 \\ 0 & \text{otherwise} \end{cases}$$

differentiating and evaluating in the equilibrium lattice configuration

we get, giving prominence to the various contributions

$$\Phi_{d\beta}^{hs} = 2.5 + 2.6 + 2.7$$

where the first two come out from the many-body potential and read respectively

$$2.5 = \sum_m U_m^{\parallel} \sum_{l \neq m} n'(R^{ml}) \cdot \frac{R_d^{ml}}{R^{ml}} (\delta_{h,m} - \delta_{h,l}) \cdot \sum_{l' \neq m} n'(R^{ml'}) \cdot \frac{R^{ml'}}{R^{ml'}} (\delta_{s,m} - \delta_{s,l'})$$

$$2.6 = \sum_m U_0^i \sum_{l \neq m} \left[\left(n''(R^{ml}) - \frac{n'(R^{ml})}{R^{ml}} \right) \cdot \frac{R_d^{ml} R^{ml}}{(R^{ml})^2} + \frac{n'(R^{ml})}{R^{ml}} \delta_{d\beta} \right] (\delta_{h,m} - \delta_{h,l}) (\delta_{s,m} - \delta_{s,l})$$

In the end, the pairwise contribution

$$2.7 = \sum_m \sum_{l \neq m} \frac{1}{2} \cdot \left[\left(V''(R^{ml}) - \frac{V'(R^{ml})}{R^{ml}} \right) \cdot \frac{R_d^{ml} R^{ml}}{(R^{ml})^2} + \frac{V'(R^{ml})}{R^{ml}} \delta_{d\beta} \right] (\delta_{h,m} - \delta_{h,l}) (\delta_{s,m} - \delta_{s,l})$$

If we have a quick glance at the (2.6) and (2.7) we soon realize that both have the same structure. This fact suggests to consider (2.6) as being

the pairwise-like contribution to the dynamical matrix in R-space, from the density dependent term in the potential. Now we go beside that, considering 2.6 + 2.7 as given by an effective central pair-wise potential ϕ defined by

$$\phi(R) \equiv V(R) + 2U_0' n(R) \quad (2.8)$$

so

$$\Phi_{d\beta}^{hs} \equiv U_{d\beta}^{hs} + D_{d\beta}^{hs} \quad (2.9)$$

$$D_{d\beta}^{hs} = \frac{1}{2} \sum_m \sum_{l \neq m} \left[\left(\phi''(R^{me}) - \frac{\phi'(R^{me})}{R^{me}} \right) \frac{R_d^{ml} R_\beta^{mp}}{(R^{me})^2} + \frac{\phi'(R^{me})}{R^{me}} \delta_{d\beta} \right] \left(\delta_{ms} - \delta_{ls} \right) \left(\delta_{km} - \delta_{kl} \right) \quad (2.10)$$

The usefulness of such a partition is apparent if we want to distinguish the standard two-body contribution from the many-body one and if we want to emphasize all, really new, contributions we are introducing.

In what follows we will use many times this criterion. We close this section observing that the really many-body force constants given by (2.5) are of longer range than the interaction U itself. It is so because pairs of atoms, which do not interact directly, are coupled by the density induced on intermediary atoms by their movement. We can explicitly see that, limiting the range of the interactions to first neighbour and, performing the summation (2.5); the only surviving term is:

$$U_{d\beta}^{hs} = \sum_{\substack{m \neq h \\ m \neq s}} U_0'' \frac{n'(R^{ms})}{R^{ms}} \frac{n'(R^{mh})}{R^{mh}} R_\beta^{ms} R_d^{mh} \quad (2.5a)$$

from which we realize that there is a coupling between pairs of atoms h,s which have at least one common nearest-neighbour (fig. 2.2)

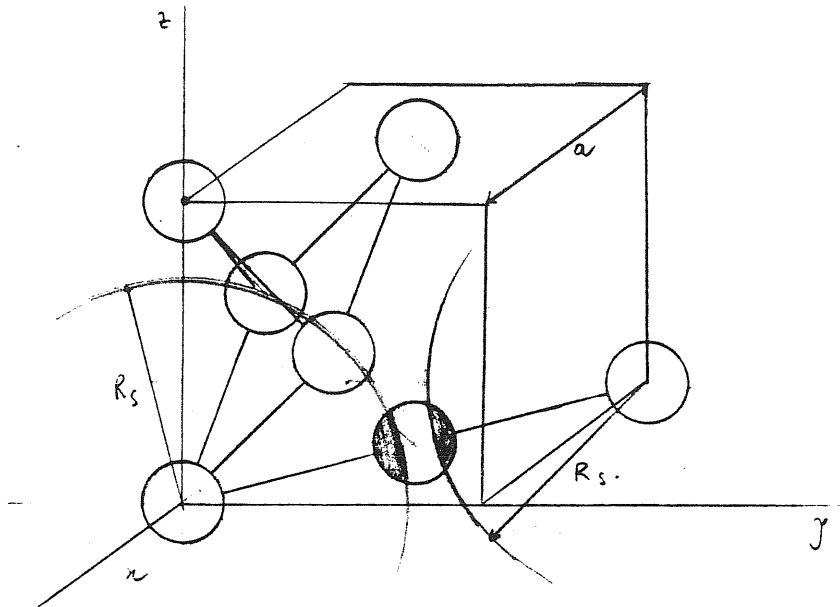


Fig. 2.2 - In a FCC lattice with interaction to first-neighbours only, the range of the many-body force constants extends up to fourth shell of neighbours.

In one of the preceding sections we calculated the energy as a function of the atomic position or, if we want, as a function of lattice parameters, from which mechanical properties, like Bulk modulus related to the second derivative of the energy with respect to the volume, can be deduced. However, since, in the cubic crystals, there are other two independent elastic constant, we prefer giving here another derivation and eventually use the first, together with the long wavelength limit definitions of cubic ^{elastic} constants given in fig. 2.3, just to verify the correctness of the results obtained.

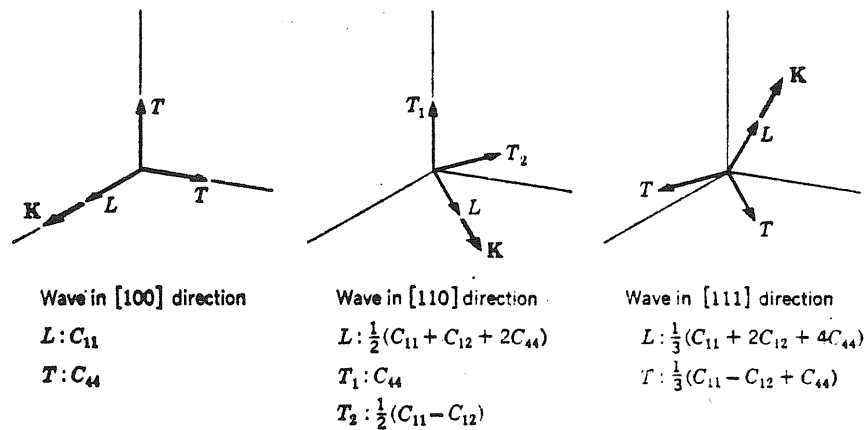


Fig. 2.3 - Effective elastic constants for the three modes of elastic waves in the principal propagation directions in a cubic crystal.

The physical content of each of the three independent elastic constants of a cubic crystal is pointed out using three kinds of deformation parameters: ν , ϵ_i , γ_i introduced by Fuchs (25).

From the fig. 2.4 we see that ν represents a homogeneous expansion or contraction of the crystal; ϵ_1 represents an expansion in the x direction and a contraction of the lattice in the y direction in such a way that the volume of the crystal is strictly conserved irrespective of the magnitude of the deformation. Analogue meaning have the parameters ϵ_2 and ϵ_3 . The deformation γ_1 also conserves the volume just tilting the y -axes in the xy plane. The definition of γ_2 and γ_3 is understood.

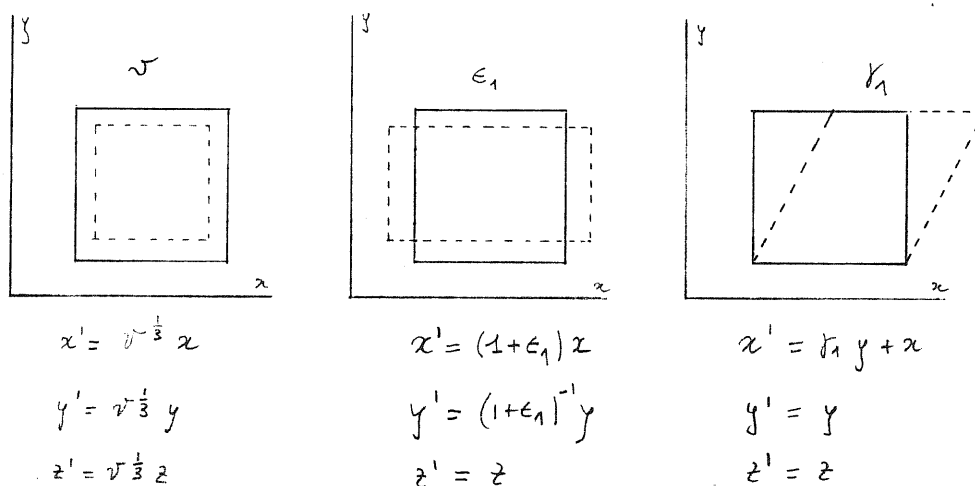


Fig. 2.4 - How the undeformed volumes (dark kind transform under $\nu, \epsilon_1, \gamma_1$, deformations (sketched line).

It is possible, starting from the very general definition of second order elastic constants (26), prove that (27):

$$\frac{\partial^2}{\partial v^2} \left(\frac{\Phi}{V} \right) = \frac{1}{3} (C_{11} + 2C_{12}) = B \quad (2.11)$$

$$\frac{\partial^2}{\partial \epsilon_1^2} \left(\frac{\Phi}{V} \right) = 2(C_{11} - C_{12}) \equiv C' \quad (2.12)$$

$$\frac{\partial^2}{\partial \delta_1^2} \left(\frac{\Phi}{V} \right) = C_{44} \quad (2.13)$$

where Φ/V , the total potential energy density (per unit of undeformed volume), can be obtained, in the very small atomic displacement limit, by a second order Taylor expansion. In this frame, using for the α -th component of the displacement $S_\alpha^m \equiv R_\alpha^m - R_\alpha^m$, of the atom m from its equilibrium position, the expression obtained extrapolating the definitions of fig. 2.4, we get

$$C_{44} = \frac{1}{V} \sum_m \sum_n \Phi_{xx}^{mn} R_y^m R_y^n \quad (2.13a)$$

$$C' = \frac{1}{V} \sum_m \sum_n \left(\Phi_{xx}^{mn} R_x^m R_x^n + \Phi_{yy}^{mn} R_y^m R_y^n + \Phi_{xy}^{mn} R_x^m R_y^n + \Phi_{yx}^{mn} R_y^m R_x^n \right) \quad (2.12a)$$

$$B = \frac{1}{9V} \sum_m \sum_l \sum_{\alpha, \beta} \Phi_{\alpha\beta}^{ml} R_\alpha^m R_\beta^l \quad (2.11a)$$

We note that to write the expressions of B, C' and C_{44} in the form 2.11a, 2.12a and 2.13a we have not made use of all symmetries which are obeyed as we could prove in a very short time, by our dynamical matrix.

Let us now use the partition for the total / matrix defined in (2.9), and the explicit expression of $U_{\alpha\beta}^{m\ell}$ and $D_{\alpha\beta}^{m\ell}$ in order to get: for the many-body contribution B_H to the bulk modulus

$$B_H \equiv \frac{1}{gV} \sum_m \sum_{\ell} \sum_{\alpha, \beta} U_{\alpha\beta}^{m\ell} R_{\alpha}^m R_{\beta}^{\ell} = \frac{1}{gV} \sum_m U_m'' \left[\sum_{i \neq m} m'(R^{m_i}) \cdot R^{m_i} \right]^2 =$$

Using the shell notation

$$B_H = \frac{1}{gV_c} U_0'' \left[\sum_H \alpha_H R_H m'(R_H) \right]^2 \quad (2.15)$$

and for the pair-wise like contribution

$$B_P = \frac{1}{gV} \sum_{\ell} \sum_m \sum_{\alpha, \beta} R_{\alpha}^{m\ell} R_{\beta}^{m\ell} \left\{ \frac{R_{\alpha}^{m\ell} R_{\beta}^{m\ell}}{(R^{m\ell})^2} \left[\phi''(R^{m\ell}) - \frac{\phi'(R^{m\ell})}{R^{m\ell}} \right] + \frac{\phi'(R^{m\ell})}{R^{m\ell}} \delta_{\alpha\beta} \right\} \quad (2.16)$$

Before writing the expressions for the two : C_{44} and C' we stress once again, that they are shear elastic constants volume conserving and then we feel that they will not present any true many-body contribution. This is the case as we can observe substituting (2.5), for real many-body force constants, into (2.13a) and (2.12a). In this last case there is a cancellation of two opposite signed equal contributions.

Therefore, using the symmetries of $D_{\alpha\beta}^{mn}$ given in (2.10), we get

$$C' = -\frac{1}{v_e} \sum_m \left(D_{\alpha\alpha}^m R_\alpha^m R_\alpha^m - D_{\alpha\beta}^m R_\alpha^m R_\beta^m \right) \quad \alpha \neq \beta \quad (2.12b)$$

$$C_{44} = -\frac{1}{2v_e} \sum_m D_{\alpha\alpha}^m R_\beta^m R_\beta^m \quad \alpha \neq \beta \quad (2.13b)$$

Finally we can measure the displacement of our interaction from a pairwise one computing the so-called Cauchy pressure

$$P_C = C_{12} - C_{44} = B - \frac{1}{6} C' - C_{44} \quad (2.17)$$

which in our case, setting the total pressure P , 2.2, equal to zero, reads,

$$P_C = B_N \quad (2.17a)$$

which fills up the first shortage of a description of a metal based on a pairwise central potential.

§ VACANCY ENERGY FORMATION

The last section of this chapter is devoted to the understanding of the mechanism of the vacancy formation. We are going to describe the energetic of such a process according to our model. Let us first recall that in the frame of a classical two-body description we get, for the energy formation of one vacancy, thought as the absence of an atom on a given lattice position o ,

$$E_{V}^F = -\frac{1}{2} \sum_{i \neq o} V(R_i^*) + \Delta E_{\text{relax}} \quad (2.18)$$

Supposing that no lattice relaxation accompanies the process, $\Delta E_{\text{relax}} = 0$, we get for the energy formation E_{V}^F the same analytical expression which we always get in this scheme, for the cohesive energy.

Let us now refer to our model. We expect that some additional term, coming from the electronic "glue", will adjust the physically wrong result (2.18). To this end we start from the definition

$$E_{V}^F = E_N^* - E_N \quad (2.19)$$

where E_N is the ground-state total energy of a system of N atoms placed on N lattice positions, and E_N^* is the energy of the excited state of the N atom system in which the N system have $N+1$ lattice positions available. Starting from a $N+1$ atom-system on $N+1$ lattice positions and supposing that the removal of a given atom, let us call it "o", does not give rise to a lattice deformation, $\Delta E_{\text{relax}} = 0$, we get

$$E_{IV}^F = -\frac{1}{2} \sum_{j \neq 0} V(R^j) + \sum_{j \neq 0} \left[U(\rho_j - m(R^j)) - U(\rho_j) \right] \quad (2.19a)$$

where by (1.2) and (1.3) $\rho_j = \sum_{l \neq j} m(R^{lj})$. Using the shell notation (2.19) is written

$$E_{IV}^F = -\frac{1}{2} \sum_{M \neq 0} \mathcal{N}_M V(R_M) + \sum_{M \neq 0} \mathcal{N}_M \left[U((\mathcal{N}_M - 1) \cdot m(R_M)) - U(\mathcal{N}_M m(R_M)) \right] \quad (2.19b)$$

in which, as usual, \mathcal{N}_M represents the number of atoms belonging to M^{th} shell of neighbours, of atom o , having radius equal to R_M .

Written in such a way the 2.19b emphasize the meaning of the new "electronic" contribution, which gives the amount of work that must be done to change the number of neighbours of all other j atoms removing the atom o . In other words, the removal of the atom o causes a change in the host density in all other lattice positions and, resuming our figurative understanding, we can say that the other atoms feel the loss of the neighbour o and rise their energy.

In the end, we just want to note that the neglected term ΔE_{relax} could be very quickly calculated by minimizing the E_{IV}^F energy with respect to the atomic positions.

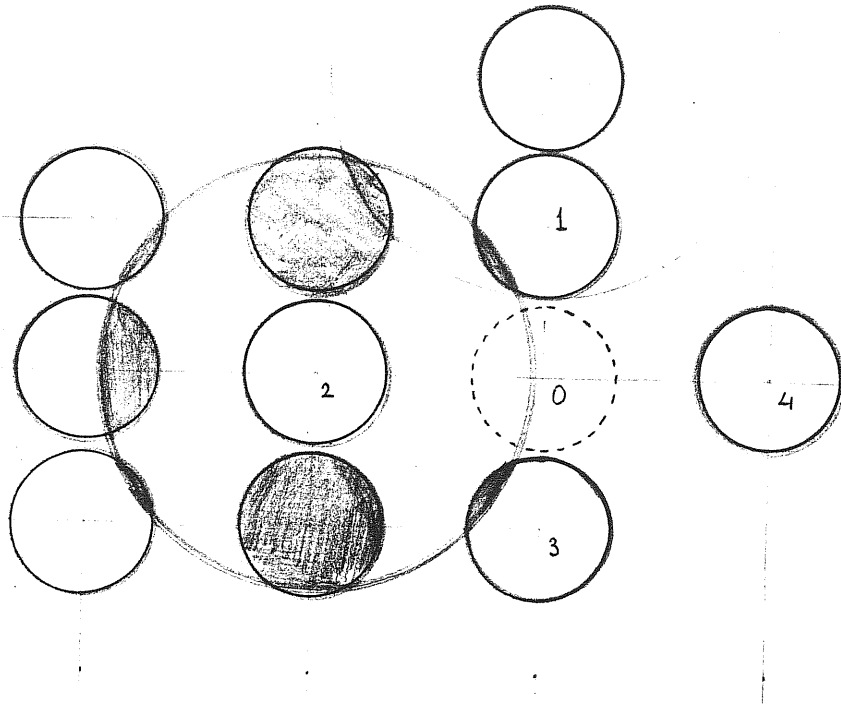


Fig. 2.5 - Two dimensional rectangular lattice. Considering only second-neighbour interaction, we have that the removal of atom 0 causes the loss of: a nearest-neighbour of atoms 1,3 and second-neighbour of atoms 2 and 4, which of course in our scheme implies a change in the host density at sites 1,2,3,4.

IV - SURFACE PROPERTIES

§ SURFACE ENERGY

We know that the Surface Energy $\tilde{\sigma}_{(\alpha)}$ by definition is the work required per unit area of the new surface formed to split the infinite crystal in two, along the plane " (α) ". We take the two fragments into which the crystal is split to be identical. Then, denoting the energy of each fragment by E_f and by E the energy of the whole crystal, we get

$$\tilde{\sigma}_{\alpha} \equiv \frac{1}{A_{\alpha}} [2E_f - E] \quad (3.1)$$

where A_{α} denotes the area of the new exposed face on each fragment. Specializing the (3.1) to our case we get

$$\tilde{\sigma}_{\alpha} = -\frac{1}{d_{\alpha}} \left\{ \frac{1}{2} \sum_i \sum_{\ell} V(R_{i\ell}) + \sum_i \left[U(p_i) - U\left(p_i - \sum_{\ell} m_{\ell} R_{i\ell}\right) \right] \right\} \quad (3.1a)$$

where the summation on i includes all atoms which contribute, losing their neighbours ℓ , to the formation of a portion, of area d_{α} , of the surface on one fragment. The additional many-body contribution has exactly the same meaning as expressed in the last section of the previous chapter and reflects the change in energy due to a modification in the host atomic density, in every lattice site in one fragment, caused by the loss of all neighbours which belong to the other fragment. It is understood that limiting the interactions only to atoms included in a certain shell of neighbours the summation of i in (3.1a) covers a finite number of atoms and becomes of practical utility

allowing us to ideally subdivide the fragment in a bulk and surface zone.

Let us now try to understand if this new term in (3.1a) gets over the misrepresentations, mentioned at the very beginning, of any pairwise descriptions. First we must observe that in a two-body interaction scheme only the first term in the right hand survives. Then, if we consider only first neighbour interaction, the surface energy has its minimum value when all atoms occupy the sites of a perfect semi-infinite lattice. Therefore no relaxation, change of the distance between planes parallel to the surface area, nor reconstruction, change of the lattice structure of the outermost lattice planes, will be predicted.

On the other side, in order to form the surface, supposing to cut the crystal in two parts along a plane, we have to remove all right or left neighbours of every surface atom. In this situation the host density differs from its equilibrium bulk value, in which every atom "sees" its \mathcal{N}_1^p first-neighbour arranged exactly on the \mathcal{N}_1^p nearest neighbour lattice positions. This change gives rise to a driving force which will move the atoms in order to reduce the generating host density variation. But the displacement of the atoms from their positions can make active also the two-body forces; then, the final stable structure will be given by the balance of both processes.

In order to be practical, we now apply our formalism to the study of a real metal surface. We consider a noble metal for which a pairwise description, apart from its well-outlined misrepresentations, is not completely meaningless.

We devote our attention mainly to the Au(110) surface because it presents both reconstruction and relaxation processes (28), and up to now no theoretical prediction is able to justify the experimental observations.

Before doing so, a bulk parametrization is necessary in order to define correctly the many-body term and prove that in our scheme it is possible to describe all the main observed bulk properties (cohesive energy, energy of vacancy formation, elastic constants, ...) except that the phonons spectra cannot be fitted since no angular force is present (8). Then we focus on the surface structure. We show the agreement between the experimental results (29) and our predicted ones. This is done by choosing some proposed (30) surface structure models and by minimizing the energy with respect to the variation of atomic positions. Among the various models checked, we show that the Au(110) stable surface is a relaxed (1x2) missing row one.

§ BULK PARAMETRIZATION

a) Elastic constants and phonon spectra fittings

The set of three equations for the bulk modulus (2.15+2.16) and the other two elastic constants (2.12b and 2.13b) together with the equilibrium condition 2.2

$$P = -\frac{1}{3V_0} \sum_M \mathcal{N}_M R_M \phi'_M = 0$$

can be solved to give the values of all the first and second derivatives of the effective two-body potential ϕ'_L, ϕ''_L at the various equilibrium shell radii $R_L (L = 1, \dots)$ together with the equilibrium second derivative of U_0'' of the many-body function.

In order to be practical we decided, for the moment, to limit the interactions only to the second shell of neighbours. Then we can solve the set of the first four equations and get the value of the five parameters $\phi'_1, \phi'_2, \phi''_1, \phi''_2, U_0''$ (one of them is externally fixed). Using those values, we find the phonon dispersion curves shown in fig. 4.1.

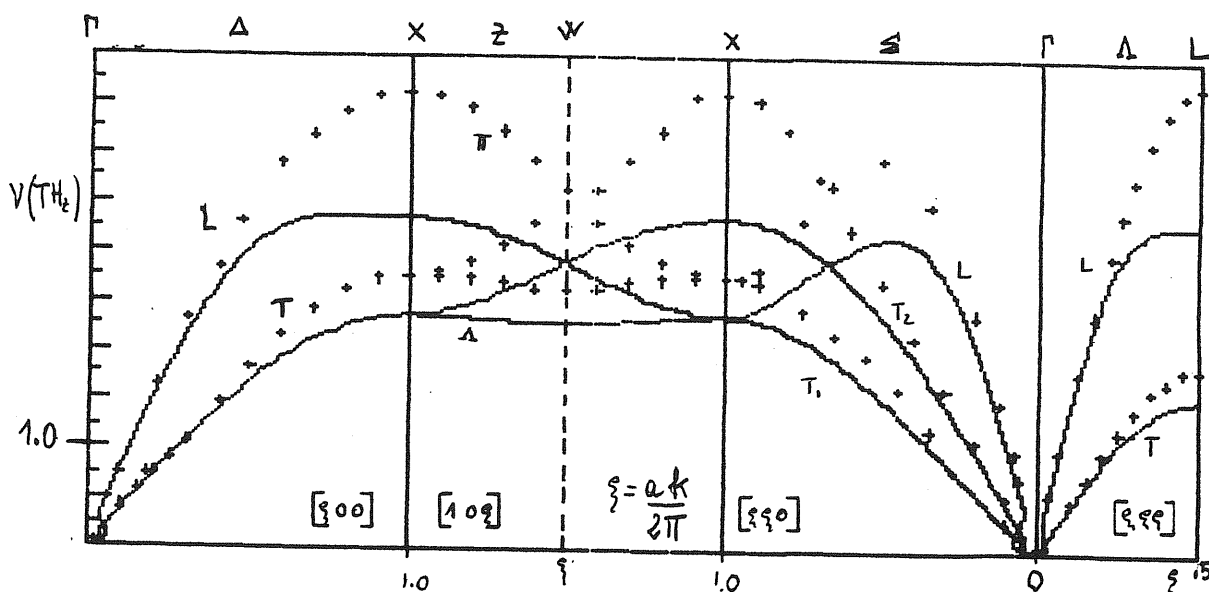


Fig. 4.1: The phonon spectrum obtained using second-neighbour interactions.

The three elastic constants are fitted. The experimental points (cross) are taken from: J.W. Lynn et al. Phys. Rev. B. 8 (1973) p. 3493.

Let us now consider that the only interacting atoms are nearest-neighbours. The unknowns are now ϕ_1' (which is fixed to be zero by the $P = 0$ relation) ϕ_1'' and U_0'' . Therefore, renouncing to fit one elastic constant (C_{12}) but not the Cauchy pressure we can solve the system and get the phonon spectra shown in fig. 4.2

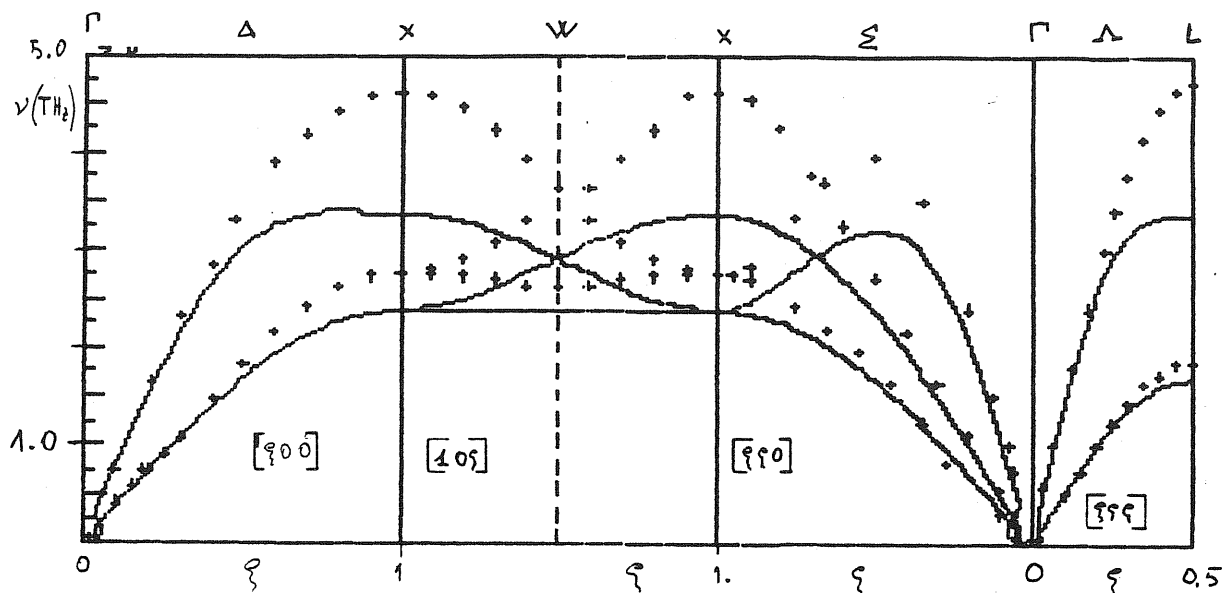


Fig. 4.2: Phonon spectrum obtained using first-neighbour interactions.

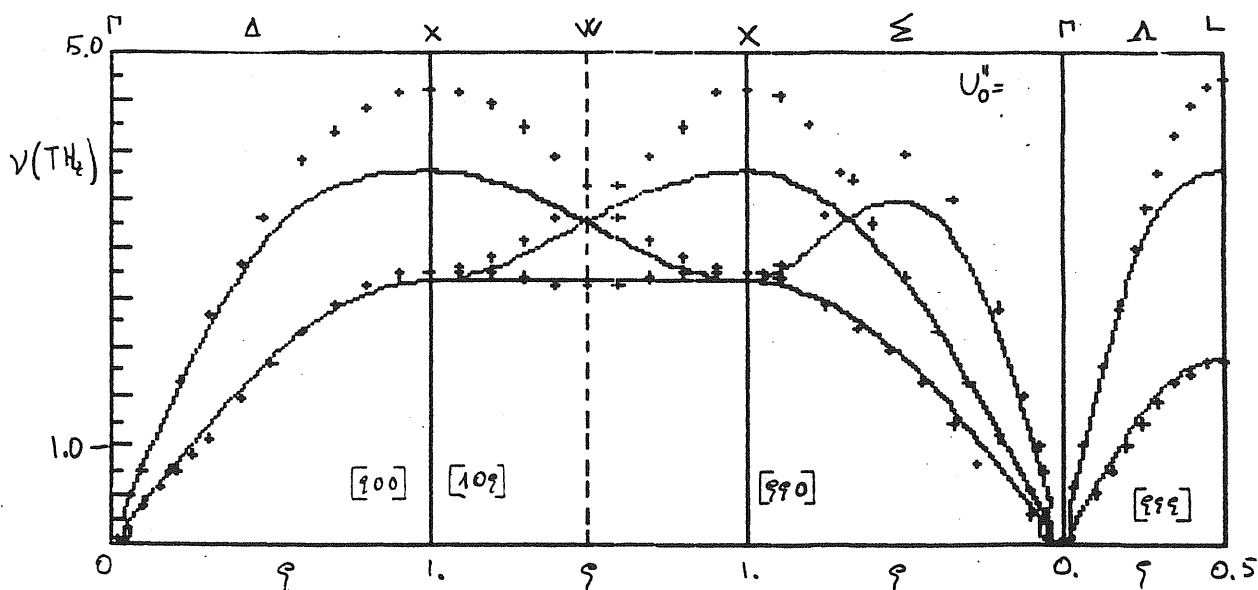


Fig. 4.3: Phonon spectrum obtained using first neighbour interactions and doing a best fitting.

Another possibility is to perform a best fitting. In fig. 4.3 we also show in this case the phonon spectrum.

Fig. 4.4. shows the effect on the phonon spectrum of changing the parameter U_0'' .

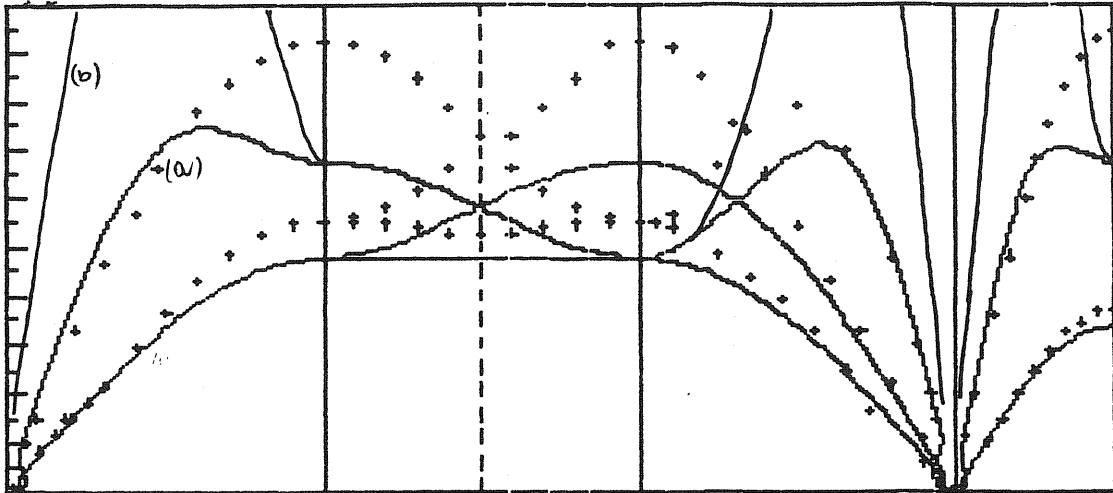
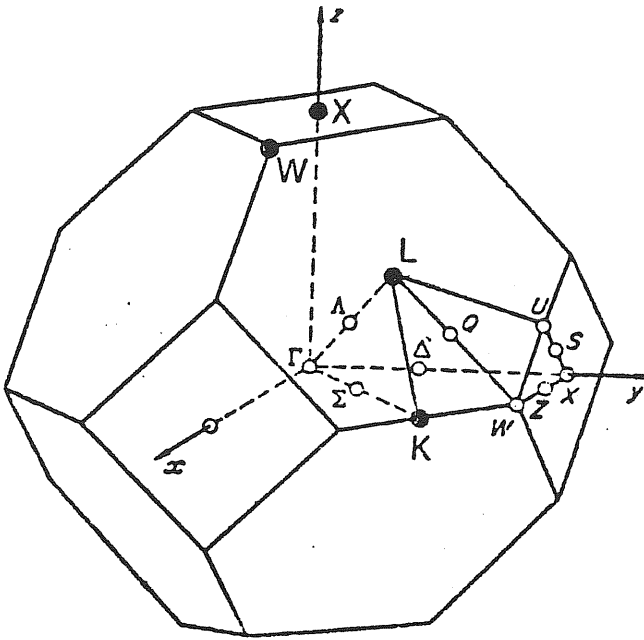


Fig. 4.4: The phonon spectra obtained using two different values of U_0'' :
a) $U_0'' \cong 10$; b) $U_0'' \gg 10$. The transverse frequencies are not changed by varying U_0'' .

From all these figures we observe that the transverse frequencies do not depend on the real many-body term or in other words they are completely determined by the effective two-body potential. It seems to be so because in a transverse mode our local host density is not modulated and then no restoring force is created.

The other peculiarity of the phonon dispersion curves shown is that the frequency values to Brillouin zone (Fig. 4.5) boundaries depends

only on the effective pairwise potential.



$$X = \left(0, 0, \frac{2\pi}{a}\right), \quad L = \left(\frac{\pi}{a}, \frac{\pi}{a}, \frac{\pi}{a}\right)$$

$$W = \left(\frac{\pi}{a}, 0, \frac{2\pi}{a}\right), \quad K = \left(\frac{3\pi}{2a}, \frac{3\pi}{2a}, 0\right)$$

Fig. 4.5: Brillouin Zone for the F.C.C. lattice.

In order to understand this fact we can consider a very simple situation as, for example, a linear chain, or a square lattice, with nearest-neighbour interaction.

In this case, it can be quickly proved that in a longitudinal mode the real many-body force constants are non zero only for atoms situated on alternated parallel planes (orthogonal to the wavevector) - or in the linear chain case, it introduces a "spring" just between second neighbour atoms - which have a fixed distance for a boundary zone value of the wavevector.

The last spectra are relative to the situation in which $U_0'' = 0$ (no real many-body term), with an effective two body interaction between first neighbours and to the case in which, with $U_0'' \neq 0$, a best fitting is done extending the interactions to the second shell of neighbours.

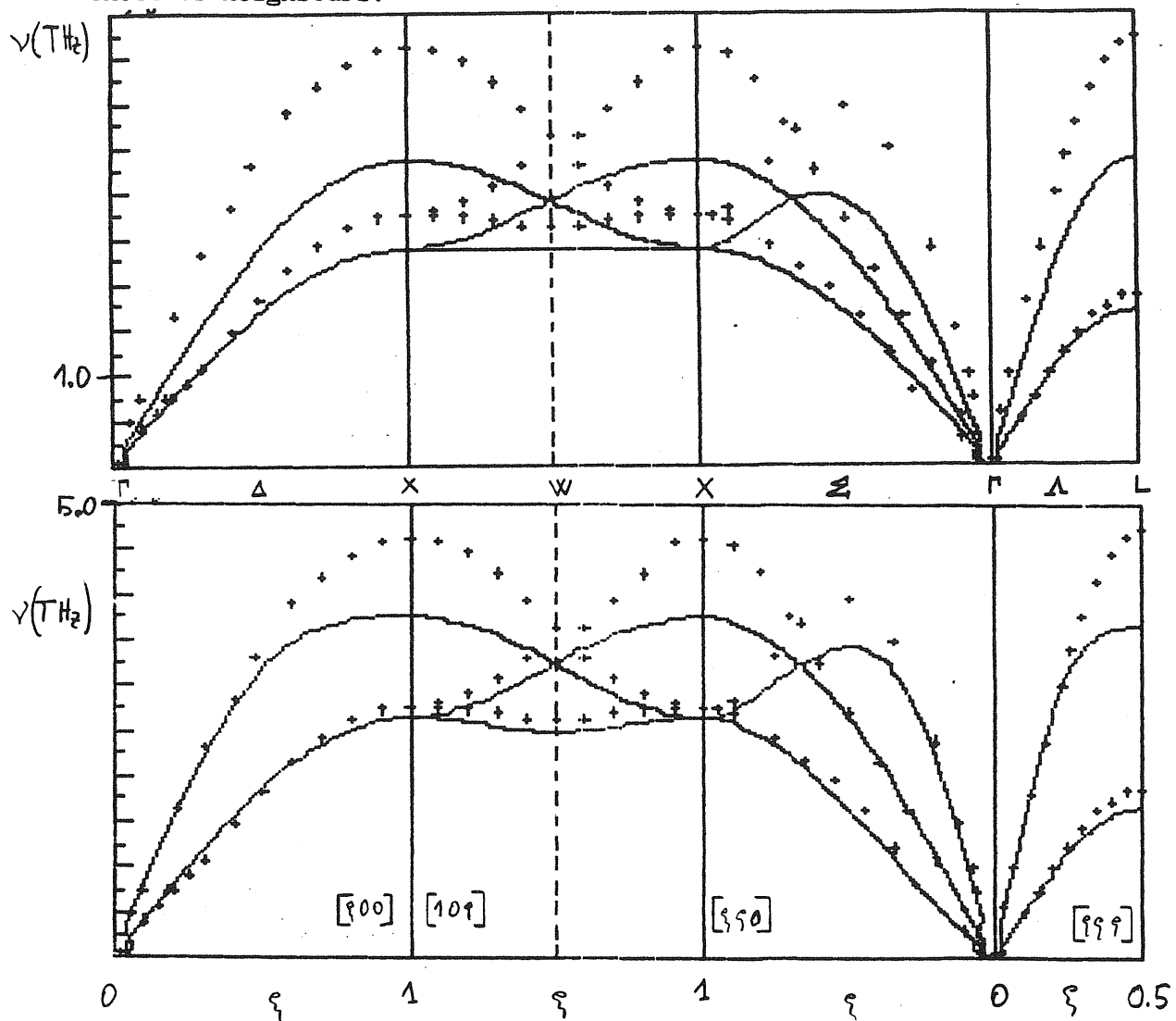


Fig.	ϕ_1'	ϕ_1''	ϕ_2'	ϕ_2''	U_0''	C_{11}	C_{12}	C_{44}
4.1	-0.0141	1.843	.02	-1.325	4.422	2.016	1.697	0.454
4.2	0.	1.848	0.	0.	3.491	2.016	1.697	0.454
4.3	0.	2.32	0.	0.	3.116	2.016	1.697	.565
4.4	0.	1.848	0.	0.	8.	3.15	1.697	.454
	0.	1.848	0.	0.	0.	.908	.454	.454
	-0.0141	2.295	.02	-2.56	4.422	2.116	1.808	.565

$$\frac{R_S}{H_0} = \frac{2.}{1.9} = 1.0526$$

Table - Values of the parameters used in order to obtain the various phonons spectra shown in figures indicated in column 1. The elastic constants are in 10^{12} dyn/cm².

b) Cohesive, surface and vacancy formation energies

Considering only nearest neighbour interactions

$$E_{coh} = - \left[\frac{1}{2} n_1 V_1 + U(n_1 m_1) \right] \quad (3.1)$$

$$E_{V}^F = - \frac{1}{2} n_1 V_1 + n_1 \left[U((n_1 - 1) \cdot m_1) - U(n_1 m_1) \right] \quad (3.2)$$

$$\sigma_{\alpha} = - \frac{1}{a_{\alpha}} \left\{ \frac{1}{2} \sum_i N_i^{\alpha,1} V_1 + \sum_i \left[U(n_1 m_1) - U((n_1 - N_i^{\alpha,1}) \cdot m_1) \right] \right\} \quad (3.3)$$

in which $V_1 \equiv V(R_1)$, $n_1 \equiv n(R_1)$, m_1 is the number of nearest neighbours

(12 in a F.C.C. lattice). In the σ_{α} expression $N_i^{\alpha,1}$ is the number

of first neighbours lost by the atom i when the surface is created cutting

the crystal along the plane α . In order to be practical, we choose the

atomic (111) plane to fit the experimental surface energy value. In this

way the three equations become

$$E_{coh} = -6 V_1 - U_0 \quad (3.1a)$$

$$E_{V}^F = -6 V_1 + 12 \left[U(11 \cdot m_1) - U_0 \right] \quad (3.2a)$$

$$\sigma_{111} = - \frac{1}{\frac{\sqrt{3}}{2} d^2} \left[\frac{3}{2} V_1 + U_0 - U(9 m_1) \right] \quad (3.3a)$$

where as usual we have considered $U_0 \equiv U(\rho_0)$ and $\rho_0 \equiv 12 \cdot m_1$

In order to understand the 3.3a we must consider that just one surface atom, loosing three of its twelve nearest neighbours, contributes to the formation of an area $\frac{\sqrt{3}}{2} a^2$ of (111) surface (Fig. 4.8)

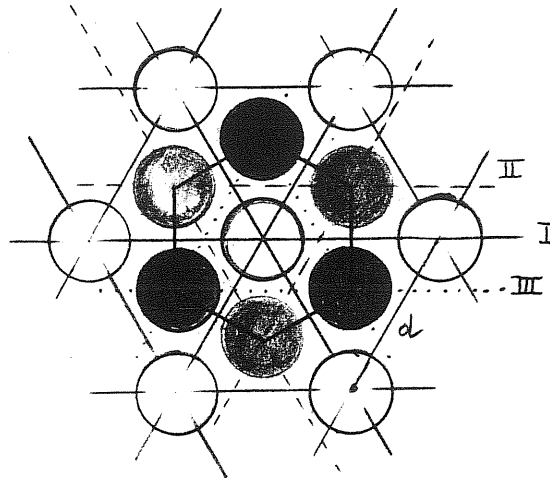


Fig. 4.8. In the small exagon of area $\frac{\sqrt{3}}{2} d \cdot a$ there is one surface atom \bigcirc , one second layer atom \odot , and a third layer one \bullet . The only atom which has neighbours is the surface one.

Fixing V_1 we can solve the three equations with respect to U_0 , $U(9n_1)$ and $U(11n_1)$. In fig. 4.9 are shown the U versus ρ curves for different choices of V_1 using a spline interpolation, which is modified in order to fix externally the first and second derivative: $U'_0 \equiv \left. \frac{dU}{d\rho} \right|_{\rho=\rho_0}$, $U''_0 = \left. \frac{d^2U}{d\rho^2} \right|_{\rho=\rho_0}$

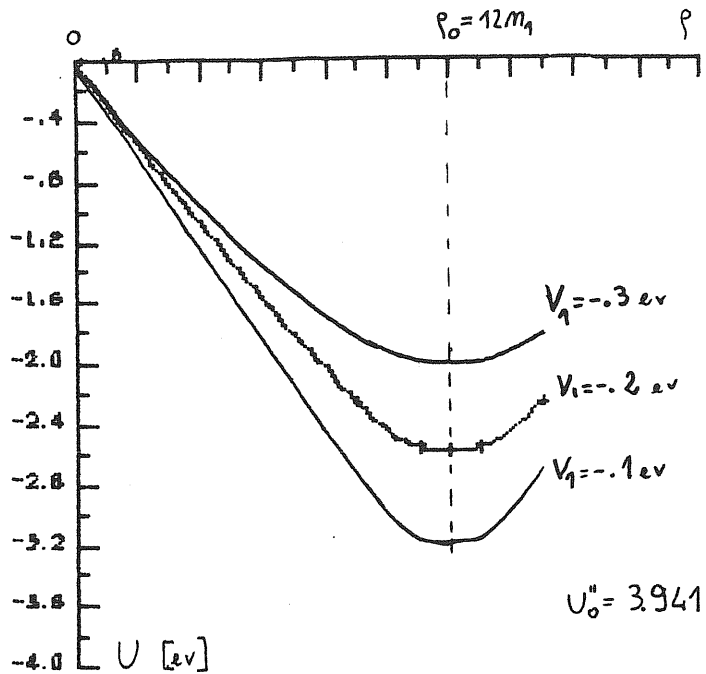


Fig. 4.9

In order to make the calculation as simple as possible, we decide to fix $U'_0 = 0$ in such a way that the equilibrium condition 2.2, in general satisfied by the balance of two opposite non zero pressure components, is now automatically verified if the atoms are arranged at a distance univocally determined by the two body potential, on the sites of a lattice whose coordination number is fixed by the ratio $\frac{\rho_0}{m_1}$.

Let us observe that a sufficient condition for the $U'_0 = 0$ condition is to choose a U function symmetric with respect to ρ_0 . This will be our choice in order to avoid undesired temperature dependent effects (31) in future calculations. With the constraints: $U'_0 = 0$, U''_0 fixed by the Cauchy pressure and choosing V_1 in order to reproduce the right melting temperature (31) we get the U vs. ρ curve displayed in fig. 4.10 which will be always used, together with the central potential shown in fig. 4.11, in what follows. The pairwise potential

is a modified version, appropriate to gold, of an empirical one, constructed point by point in order to reproduce the thermal properties of Cu (31).

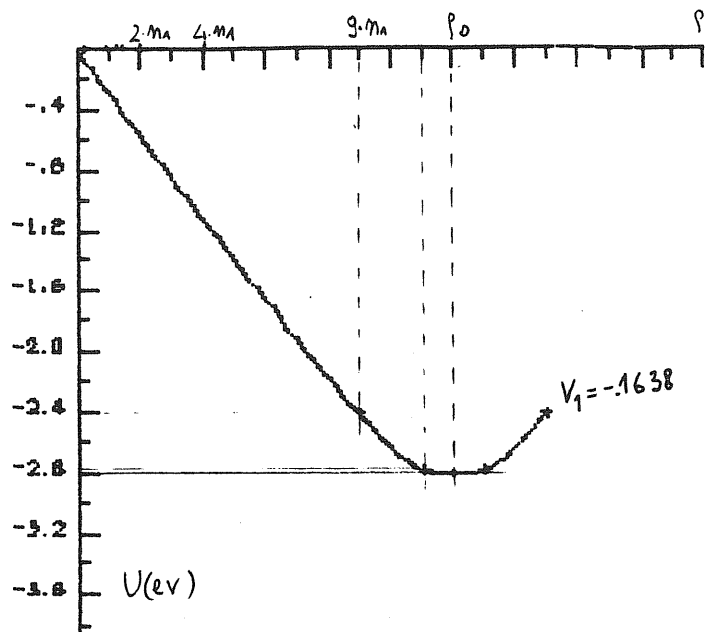


Fig. 4.10

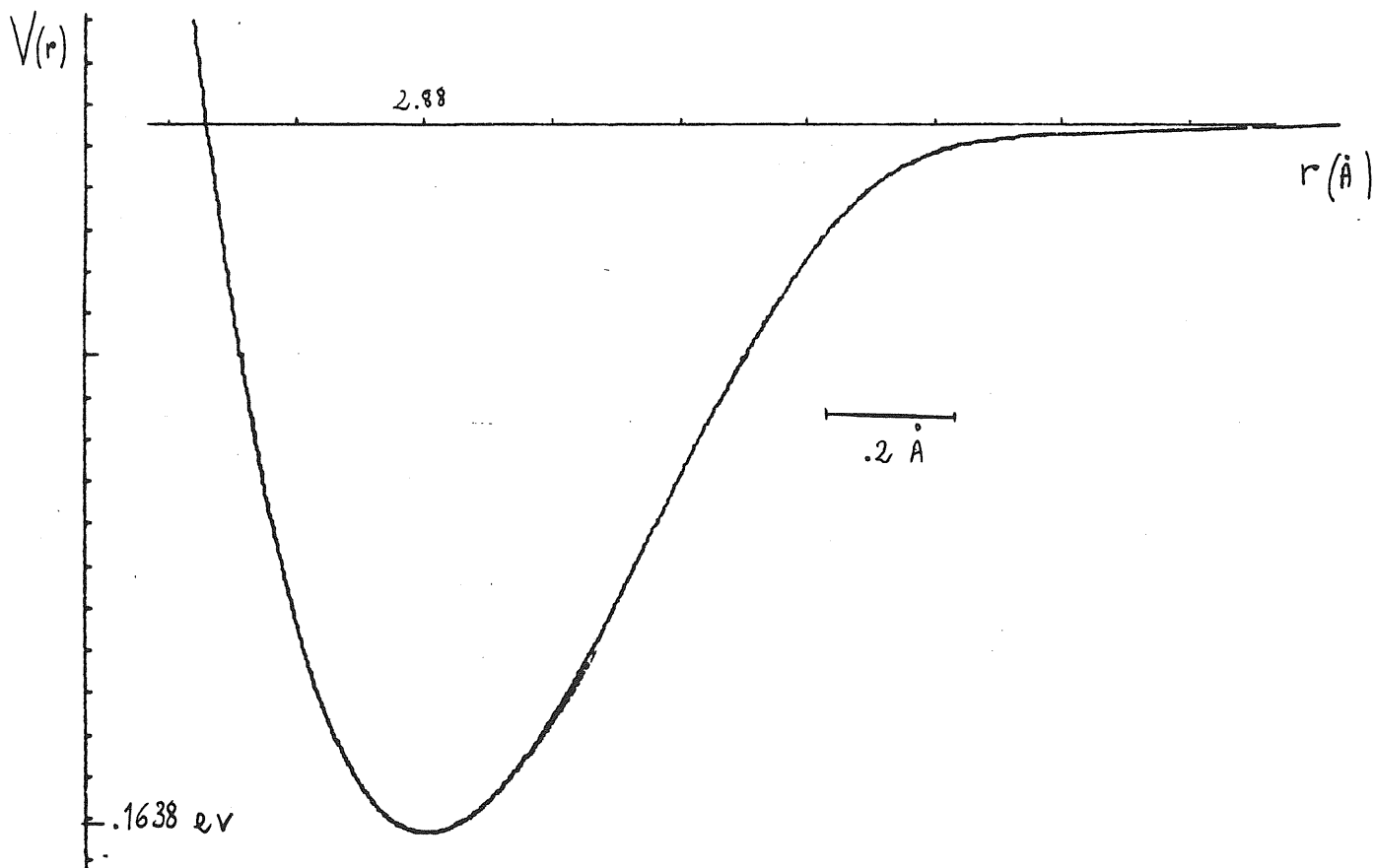


Fig. 4.11

§ Au(110) SURFACE: Experimental facts

There is a considerable quantity of experimental results showing that the Au(110) surface has a reconstructed structure of the 1×2 type. Among the various models proposed, we consider only those which seem to be favoured by a large number of experiments. They are the "Missing row" and the "saw tooth" models. The difference between them are shown in fig. 4.12 from which their different symmetries appear.

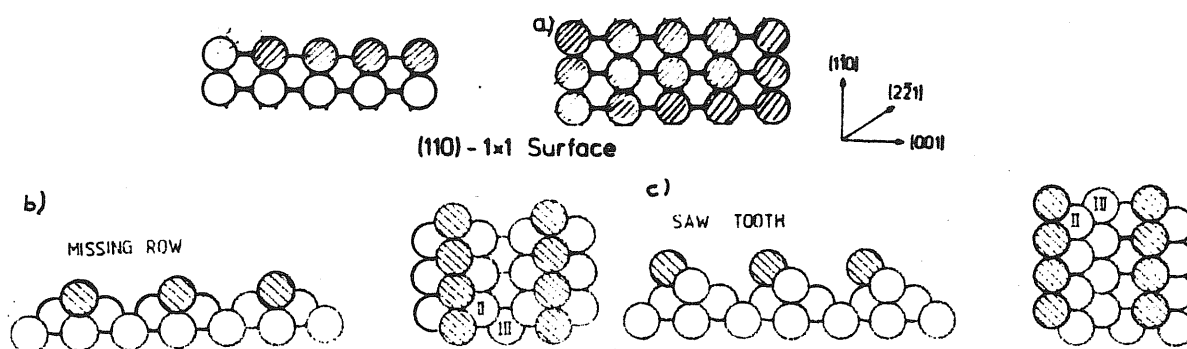
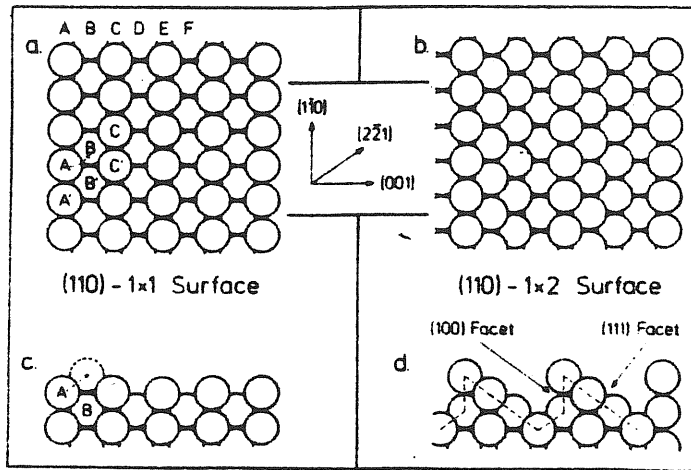


Fig. 4.12 Side and frontview of the: a) flat (110) surface; reconstructed: b) missing row; c) saw tooth.

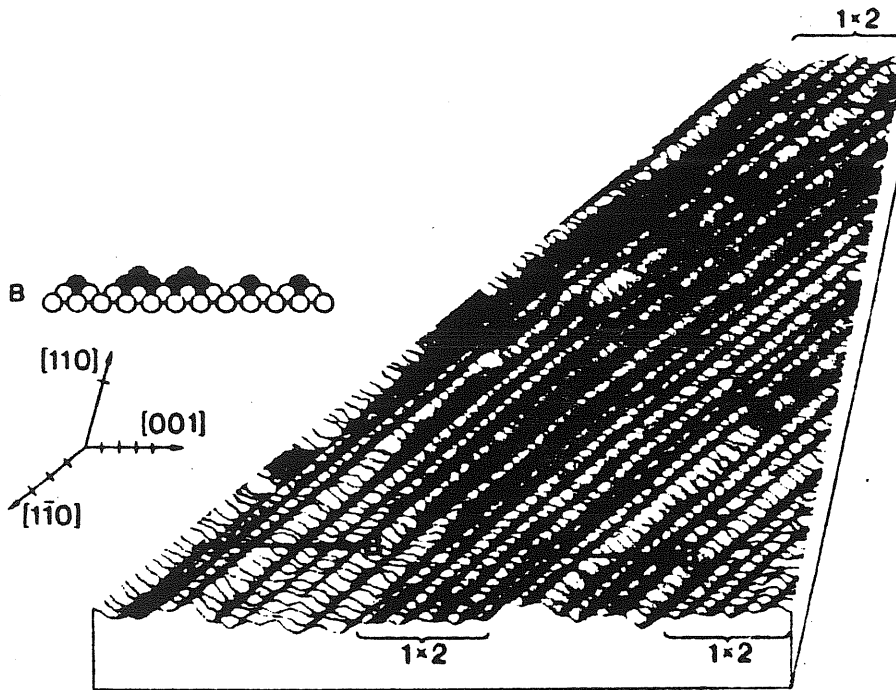
An inherent difficulty of the missing row model, which motivated the introduction of the saw tooth model, is the surface mass transport: atoms must move over several hundred Å to produce such a kind of reconstruction starting from their position on the flat ordered surface. In the saw tooth model, as can be seen in fig. 4.13-1, the atoms will move only on a distance of 2.8 Å. (32).



Structure model of a (110) surface: (a) and (b) top view; (c) and (d) side view of surface profile.

Fig. 4.13-1

In fig. 4.13-2 we show the Au(110) surface as appears in a Scanning Tunneling Microscopy experiment(29).



Original recordings of an STM picture, showing 1×2 reconstructed ribbons interrupted by monolayer steps and 1×3 channels. The skewed directions of the $[1\bar{1}0]$ and $[11\bar{0}]$ axes are determined by thermal drift and crystal misalignment respectively. Divisions on all axes correspond to 5 Å. The disorder structure at B is repeated at B₁. The inset envisages a possible transition from the structure at A to that at B by shifting rows along the $[1\bar{1}0]$ direction.

Fig. 4.13-2

From this, we can see that the basic driving mechanism for the reconstruction is the (111) faceted nature of the Au(110) surface. In particular (111) facets with two free rows generate the 1x2 reconstruction.

This feature, we will prove, is very well understood in our scheme since the glue is such that the surface atoms want to change their coordination in the least possible way: we have that the stablest surfaces are the most closely packed ones.

§ Au(110) SURFACE: theoretical results

Let us write the surface energy expressions for the Au(100) and Au(110) flat, unrelaxed, surface energies

$$\sigma_{100} = -\frac{1}{d^2} \left[2V_1 + U_0 - U(8 \cdot n_1) \right]$$

$$\sigma_{110} = -\frac{1}{a \cdot d} \left[3V_1 + 2U_0 - U(11n_1) - U(7n_2) \right]$$

From the table we see that, as expected, the minimum work is required to form the (111) surface

SURFACE	UNIT CELL AREA	SURFACE ENERGY (eV/Å ²)
Flat Au(111)	$a \cdot d \cdot \sqrt{\frac{3}{2}}$	$\frac{1}{ad} \cdot 0.5221$
Flat Au(110)	$a \cdot d$	$\frac{1}{ad} \cdot 1.3984$
Flat Au(100)	$d \cdot d$	$\frac{1}{d^2} \cdot 1.3573$

Coming now to the Au(110) surface, a numerical minimization of the γ_{110} energy relative to the three structural models considered show for this surface a relaxed missing row type reconstruction (fig. 4.14).

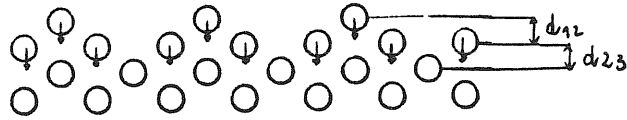


Fig. 4.14

For each of the analysed models, we write the appropriate surface energy expression considering the contributions, coming from all the atoms on the outermost planes, to the formation of a surface area having a fixed projection on a flat (110) plane, fig. 4.15. Then we check the minima varying the distance between the outermost planes.

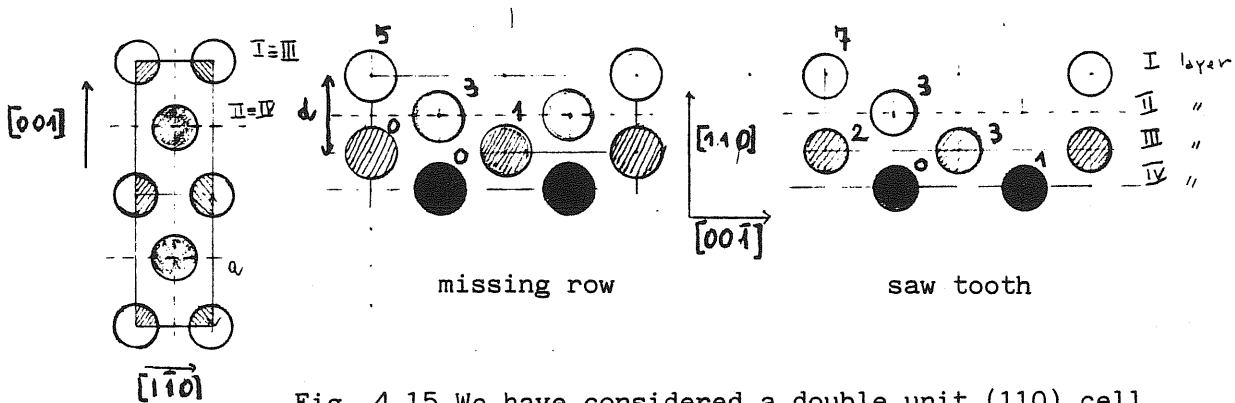


Fig. 4.15. We have considered a double unit (110) cell because of the asymmetry of the saw tooth model. The numbers on the atoms indicate the neighbours lost by that atom.

MODEL	UNRELAXED SURFACE ENERGY PER UNIT CELL	RELAXED SURFACE ENERGY PER UNIT CELL	$\frac{\Delta d_{12}}{d_{12}}$	$\frac{\Delta d_{23}}{d_{23}}$
FLAT	1.3984 (ev)	1.0716 (ev)	-25%	+ 2%
MISSING ROW	1.3806 (ev)	1.0322 (ev)	-19%	- 6%
SAW TOOTH	1.8381 (ev)	1.5668 (ev)	-13%	-12%

Table VI

Our results, shown in Table VI and in fig. 4.16 agree with those predicted in ref.(33) and with the experimental observation of ref.(28)

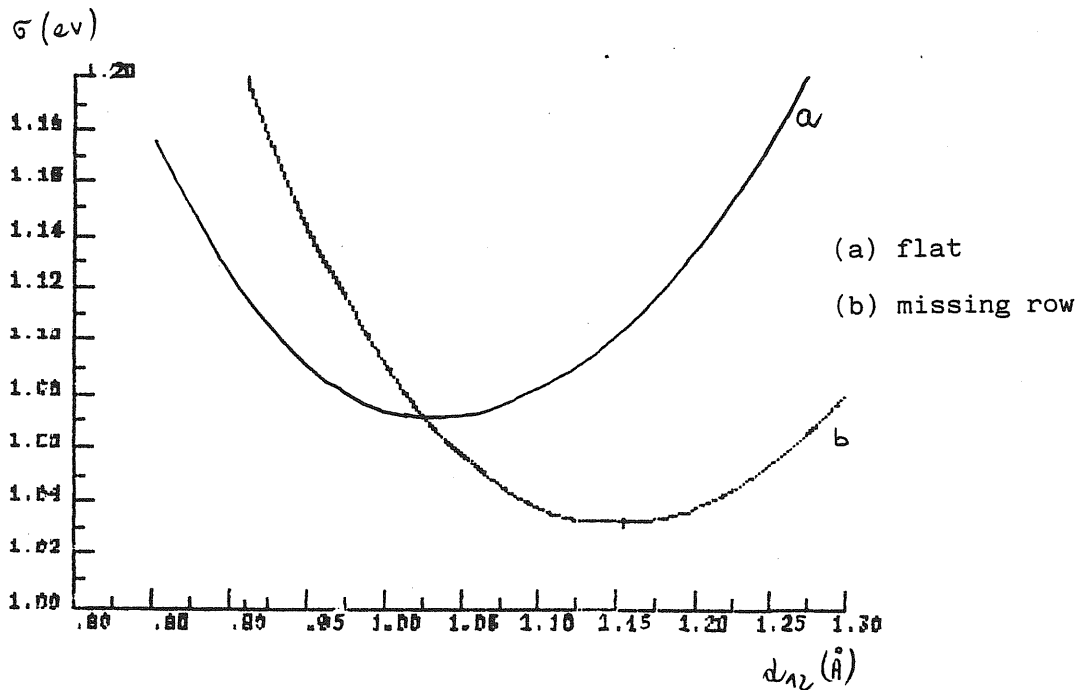


Fig. 4.16-1: The three surface energy curves are obtained using for each one the value of separation of the second and third layer d_{23} to which the values shown in Table VI correspond:
(a) $d_{23} = 1.4741(\text{Å})$, (b) $d_{23} = 1.3441(\text{Å})$

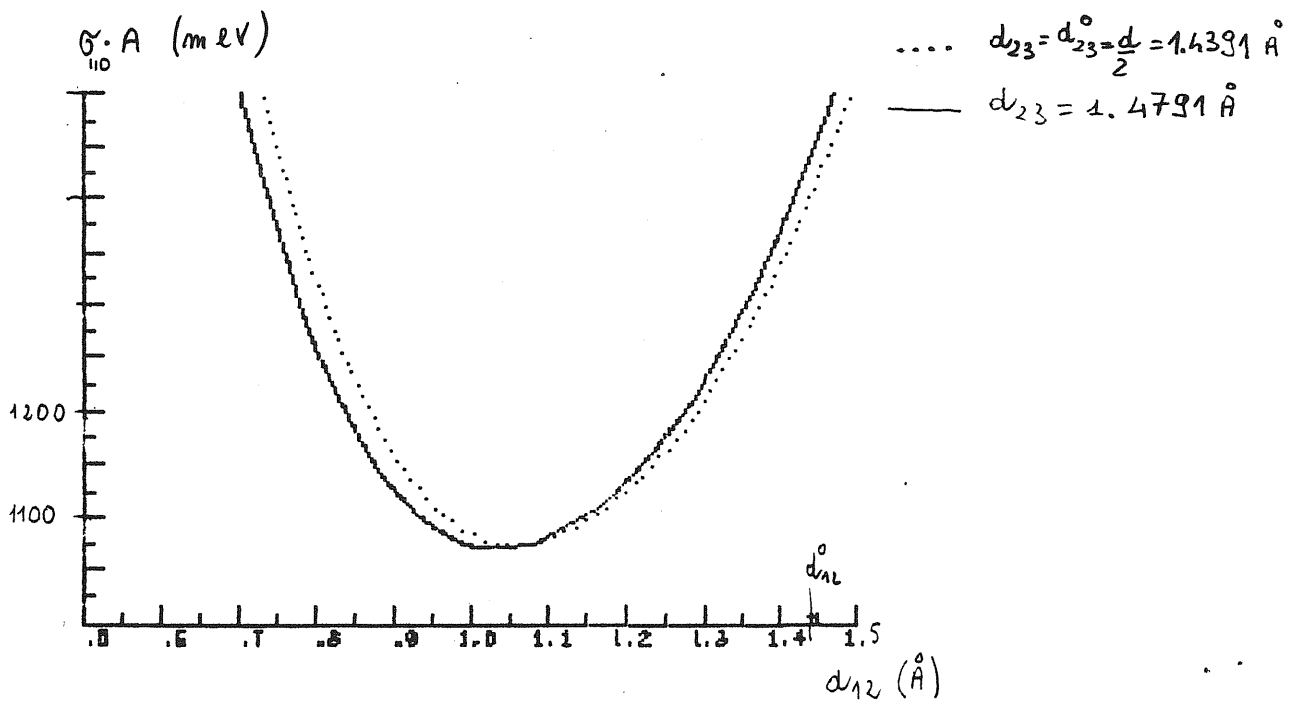
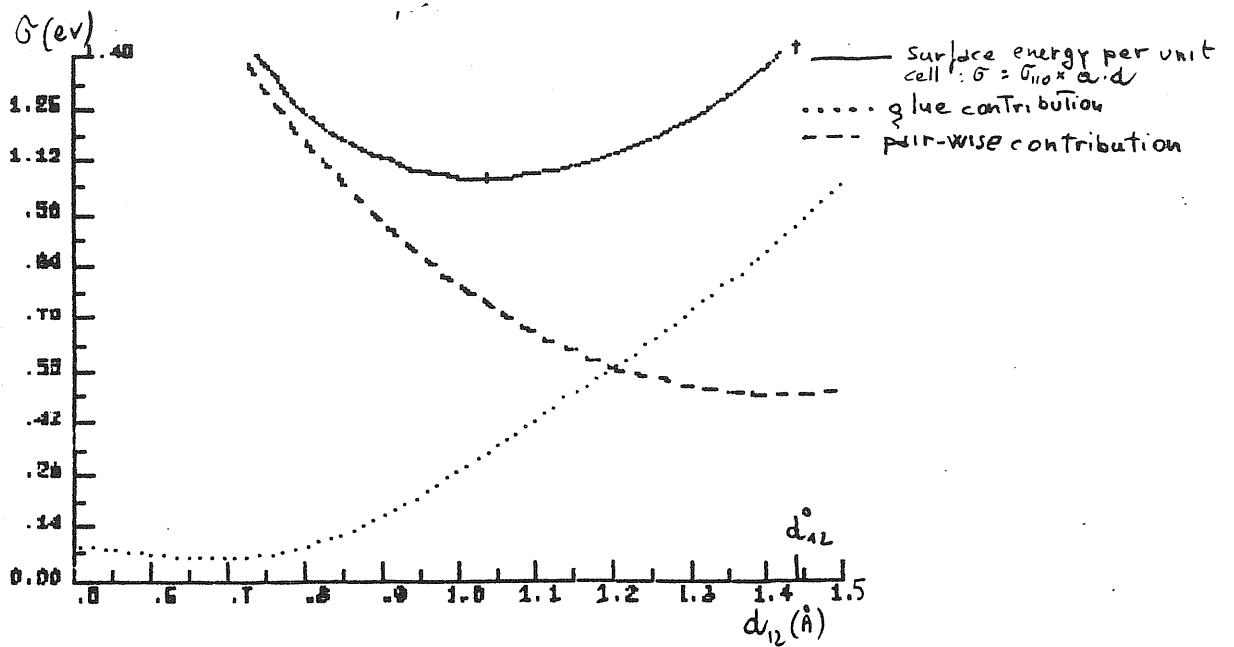


Fig. 4.16-2

Figures 4.16-2, 4.16-3, 4.16-4 show, for each one of the three models, flat, missing row and saw tooth:

- the many-body (dotted line) and two-body (full line) contributions to the surface energy;
- two surface energy vs. d_{12} curves for d_{23} as in 4.15 (full line) and $d_{23} = d_{23}^0 = d/2$ (dotted line).

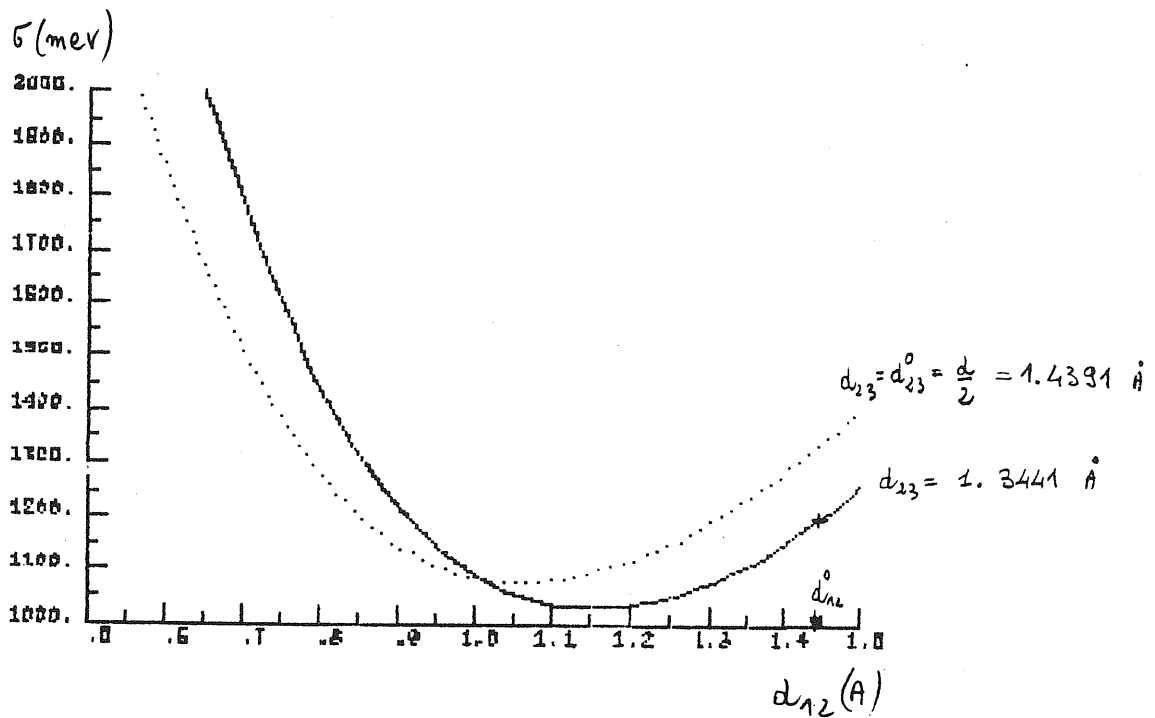
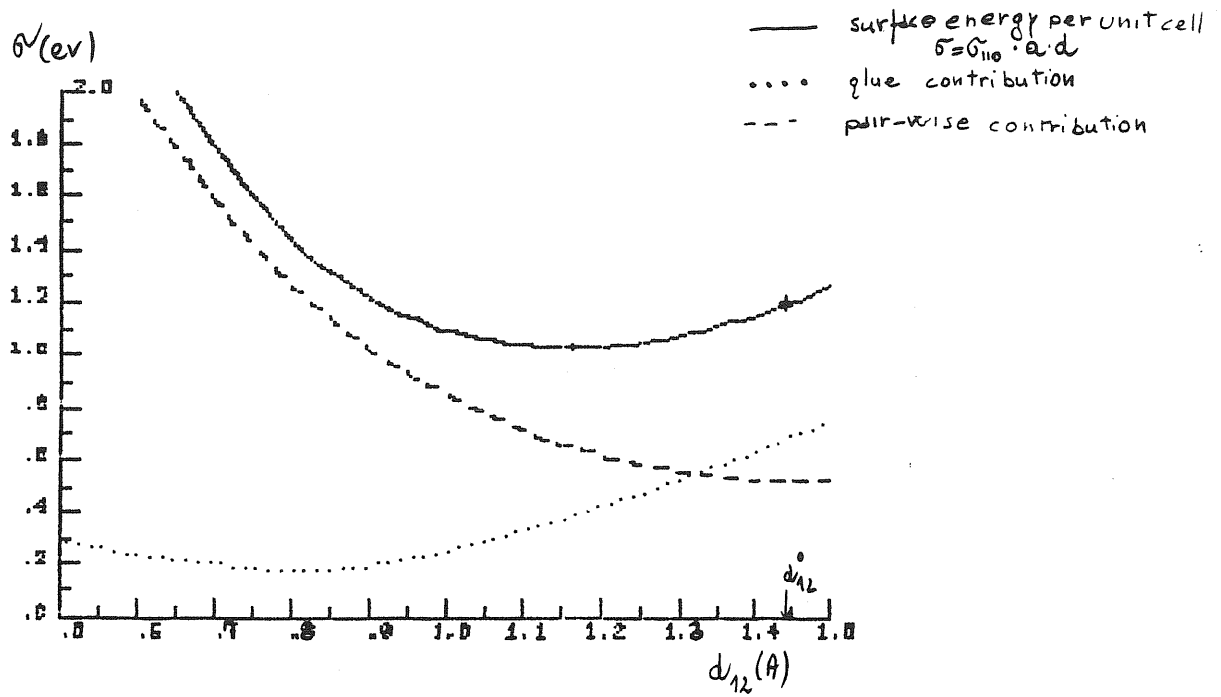


Fig. 4.16-3 : missing row

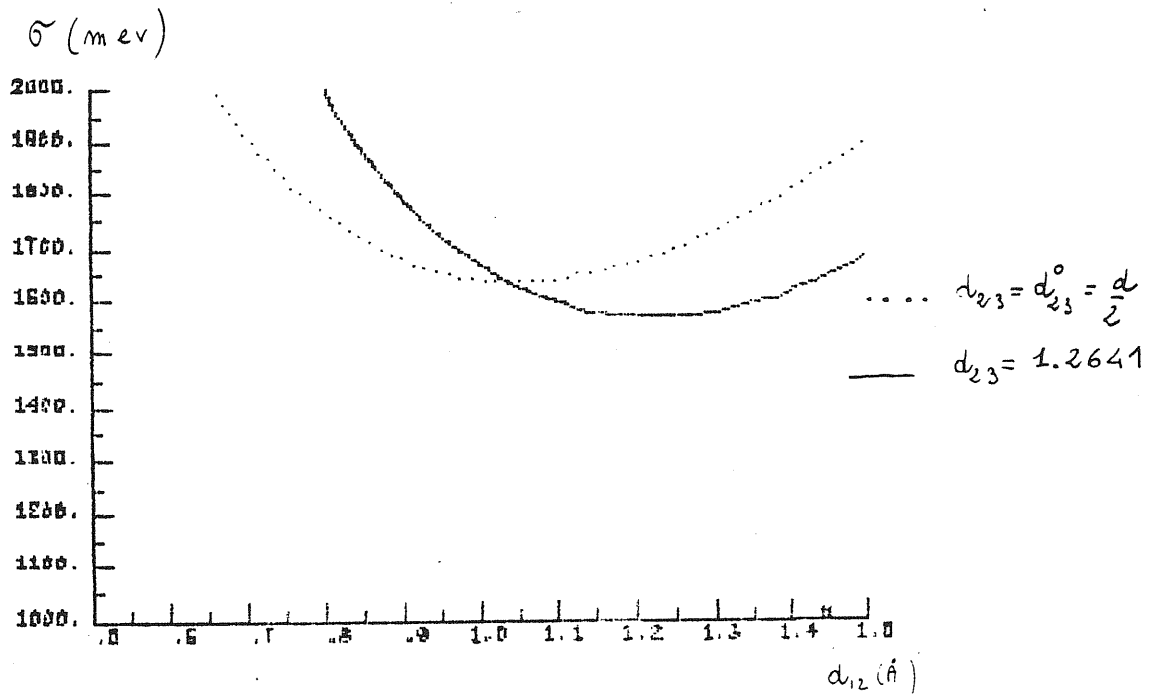
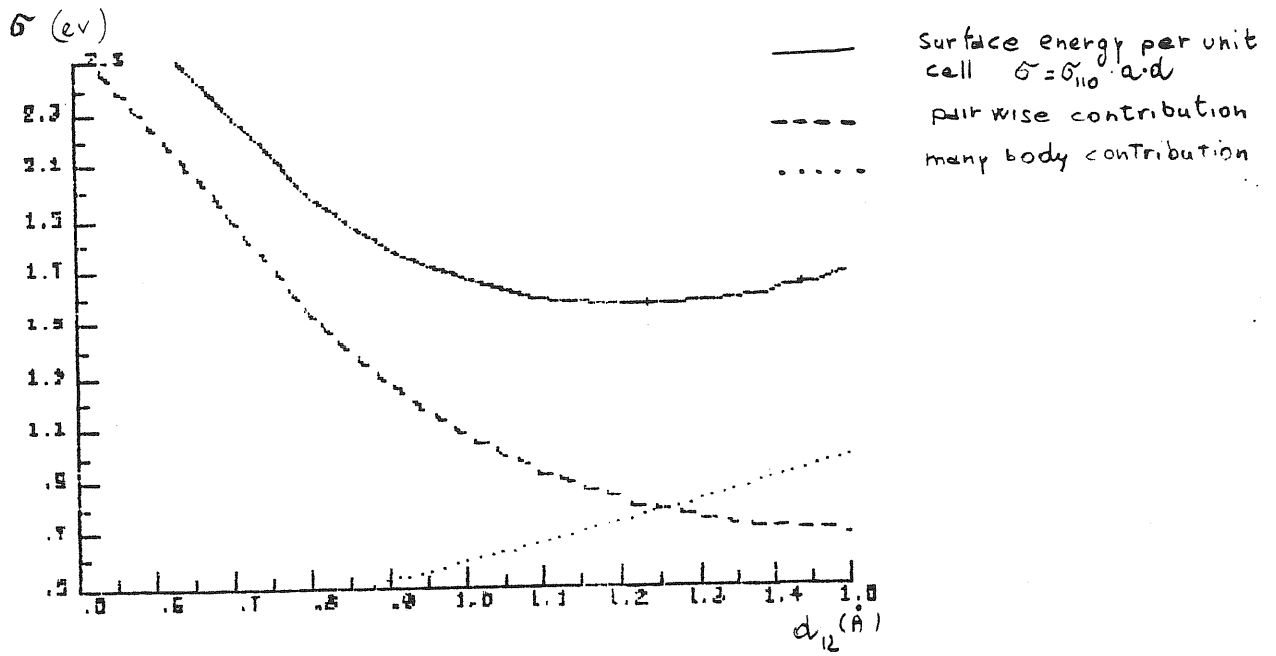
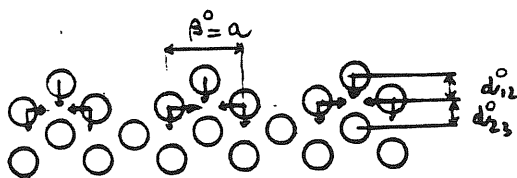


Fig. 4.16-4 :

From the parts a of these three figures we see that the effect of the two-body forces of keeping fixed the atomic distances at their equilibrium bulk values wrangles the atomic tendency, due to the many body forces, of moving in higher host density regions. The effect of contracting the second and third layer distance on the surface energy curves are shown in parts b.

We have also checked a missing row in which a new parameter is introduced in order to take into account a possible horizontal displacement of the second layer atom. The model is displayed in fig. 4.17 in which the related results are also shown.



$$\beta = a - 0.12 \text{ \AA}$$

$$d_{12}^0 - d_{12} = 0.27 \text{ \AA}$$

$$d_{23}^0 - d_{23} = 0.085 \text{ \AA}$$

Fig. 4.17: The minimum value of the surface energy $\sigma = 1.0442 \text{ (eV)}$ is found in correspondence to a contraction of the separation between first and second layer and between second and third layer (-13%, -5%) and a horizontal displacement of second layer atoms.

VI - CONCLUSIONS AND OUTLOOK

We have introduced in a very empirical way a new many-body potential based on the observation that the common feature of any defect promotion process, including surfaces, is the change in the atomic presence in the place where the defect has been formed. The new many-body potential has been then defined, to be just a function of an appropriate host density, in order to make the atoms "sensitive" to every change in the surrounding environment. Formally, this has been done writing the density function energy as a sum of atomic terms

$$\sum_m U(\rho_m) = \sum_m U\left(\sum_{l \neq m} n_{lm}\right)$$

in which the various contributions n_{lm} to the host density ρ_m , in the lattice site m , coming from the atoms placed at l , are explicitly written above.

Many physical interpretations of our model are possible. The only example we want to give is to consider ρ_i as the local electronic charge density at site i constructed by a rigid superposition of atomic densities n . This assumption is based on a theorem (35, 37) which proves that the energy of an atom, let us call it impurity, in a host system, like a lattice environment, is a unique functional of the host electron density. This statement is to be distinguished from the Hoemberg-Kohn theorem (38) which shows that the total energy of the system is a unique functional of the total electron density. In the simplest approximation

(36), the energy of the impurity plus its screening cloud, treated as a unit, called quasiautom, is just a function of the electron density of the host, without the impurity, at the site where the quasiautom is to be placed.

Let us note that our new many-body term, if the function U is just a constant, reduces to the usual two-body potential: this up to now has been the only way to get many qualitative pieces of information, with no effort, at least for what concerns the bulk properties.

However, we have proved that if the U function is not a constant a new kind of interaction, a real many-body one, is then introduced; as a result, when we apply our formalism - in which the many-body effects combine with the explicitly considered two-body effects - to the study of a real metal, the elastic constant as well as the surface and vacancy formation energies can now all be fitted, without introducing any new computational task.

The poor agreement between our predicted gold phonon frequencies and the experimental ones seems to be the main misrepresentation of our model. This confirms the absence, in our scheme, of any angular forces which are essential to fit the phonon spectra of both noble and transition metals.

For what concerns the surfaces we predict a relaxed and missing row reconstructed Au(110) surface, in good agreement with the experimental results.

In order to fix further limits of our model, we have planned to apply it to the study of the other noble metal surfaces. A first application will be the study of the Ir(110) and Pt(110) which shows the same structure of Au(110) surface. Another probing test could be given by the description of copper: indeed, in spite of the fact that it frequently presents features analogous to gold, its surfaces do not show any reconstruction.

After that, we are planning to study the properties of lead in order to describe its solid-liquid transition which raises many open and interesting theoretical questions (39).

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