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THE INFLUENCE OF LOCAL VOLUME FORCES  
ON SURFACE RELAXATION OF PURE METALS AND ALLOYS:  
APPLICATIONS TO Ni, Al, Ni<sub>3</sub>Al \*

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ABSTRACT

We present an analysis of the relative influence of the interatomic potential, lattice structure and defect symmetry on the calculated and measured distortion for the free surfaces of alloys and pure metals. In particular, the effect of using local "volume" dependent interactions is studied, as opposed to simple pair interatomic forces. The dependence of the relaxation on the lattice structure is examined by comparing pure metals with ordered alloys. A Green function method for surface relaxation is presented and used for the above analysis as well as for studying the influence of different surface symmetries. Examples based on computer simulation of Ni, Al and Ni<sub>3</sub>Al for some surface orientations are presented.

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## 1. INTRODUCTION

At present a large experimental and theoretical effort is being devoted to the study of intermetallic alloys, with special emphasis on the Ni, Al system, mainly NiAl and Ni<sub>3</sub>Al. The free surface distortion of some of those alloys has been measured by Davis and Noonan (1985) and Sondericker et al. (1985, 1986). These authors report for the (110) surface of NiAl, perpendicular distortions which oscillate in value as a function of depth and a relatively large outwards displacement of the Al atoms at the free surface (0.22 Å). For the (100) surface of Ni<sub>3</sub>Al, a slight buckling is found with a small displacement outwards of the Al atoms (0.02 ± 0.03 Å) together with a contraction of the first interplanar distance. Oscillations in the perpendicular atomic relaxations were also observed in pure Al and Ni surfaces by Sondericker et al. (1986), Nielsen et al. (1982), Anderson et al. (1984), Noonan et al. (1984) and Adams, et al. (1985). On the theoretical side, the above experimental results have been reproduced by the computer simulation calculations of Chen et al. (1986), Foiles et al. (1987), Farkas et al. (1987). Jona (1978) and Gupta (1981) showed that the above contraction of the first interplanar distance can be reproduced by those calculations if a many body interaction potential is adopted. In the above mentioned computer simulations the energy of an ensemble of N atoms is expressed as:

$$E_{tot} = U_P + U_N \quad (1)$$

where  $U_P$  is a pair interaction term and  $U_N$  depends on the local density at the atom location. This same expression (1) is the one used in the "Embedded Atom" model of Daw and Baskes (1984), in the "empirical" model of Finnis and Sinclair (1984) and in the "glue" model of Ercolessi et al. (1986a) (1986b). We shall refer hereafter to all of these potentials as "local volume dependent". Ercolessi et al. (1986a) (1986b), successfully calculated the measured surface reconstruction in Au, providing a quantitative approach to Heine and Marks' (1982) explanation of surface reconstruction as resulting by the opposition of two types of forces: a pairwise repulsion between the atoms and a multiatom electron gas attraction. Therefore, the approximation of Equation (1) for the energy has proved quite successful in the numerical simulation of surface properties both for alloys and for pure metals. Those calculations do not involve any change in the energy function at the surface except for the absence of atoms in one-half space. Also, in general, that function is adjusted only to bulk properties of the material. The purpose of this paper is to examine the relative influence of pair and local volume dependent terms in the energy on the different modes of surface relaxation, i.e., static oscillations, buckling, etc. We expect the above mentioned opposite character of the two kinds of forces not only to determine the surface restructuring but also to affect relaxation. We shall emphasize the different static distortions to be expected in alloys with respect to those in pure metals. In that sense, we will advance the basis of a lattice model for the static relaxation of the surface due to force sources. This model extends the previous ones of Gupta (1981), Jona (1978), and Allan et al. (1973), (1976) to the case of a lattice with more than one atom per unit cell. Some computer simulation results for the free surface of Ni, Al and Ni<sub>3</sub>Al are reported. These results are based on interatomic potentials of Voter et al. (1987) developed within the spirit of Daw and Baskes (1984) "Em-

bedded Atom" model. The calculated relaxations, together with previous ones reported in the literature for the same systems, are discussed based on the lattice model for the static distortion developed below. Therefore, we shall present a consistent analysis of the relative influence of the interatomic potential, lattice structure and defect symmetry on the calculated and measured distortion for the alloy and pure metal surfaces.

## 2. LATTICE DISTORTION AT THE CRYSTAL SURFACE

For the case of point defects, Flinn and Maradudin (1962) and, later, Tewary (1973) developed a Green function approach for the calculation of the lattice relaxation. An equivalent but simplified approach was reported later for the atomic relaxation at the surface of simple metals by Allan et al. (1973), (1976) and by Landman et al. (1980). A more detailed approach, which takes into account the full lattice and defect symmetry and is based on the validity of a general interatomic potential law, can be developed for the surface distortions even in the case of alloys. The physical and mathematical basis of this approach is necessary for the understanding of the general pattern of relaxation behind the computer simulation results. In this section we present the basic concepts of defect source force and lattice response.

For small static displacements  $\underline{u}(L)$  of an atom  $L$  or a cluster of atoms at the lattice site  $L$  of an ensemble, the energy can be expanded as a function of the displacements as:

$$E = E_{tot}^0 - \sum_L K_L^0(L) \cdot u_L(L) + 1/2 \sum_{L,L'} \Phi_{LL'}^0(L,L') u_L(L) u_{L'}(L') \quad (2)$$

where  $E_{tot}^0$  is the energy of the ensemble when every atom is located at the perfect lattice sites (for the free surface it corresponds to the energy of the unrelaxed half space).  $K_L^0(L) = -\partial E_{tot}^0 / \partial u_L(L)$  are the forces at the unrelaxed lattice site and  $\Phi^0(L,L')$  is the force constant matrix for the defect lattice:

$$\Phi^0(L,L') = \Phi(L,L') + \zeta(L,L') \quad (3)$$

In equation (3)  $\Phi(L,L') = \partial^2 E_{tot} / \partial u_L(L) \partial u_{L'}(L')$  is the force constant matrix for the perfect lattice and  $\zeta$  includes the change in force constants due to the defect. These are changed due to the loss of atomic interactions and to the eventual changes in the interaction constants.  $\zeta$  also may contain terms of order higher than second in the expansion of the energy, i.e., unharmonic distortion terms. By analogy to the approach of Kanzaki (1957) to the equivalent problem for the point defect, the Kanzaki forces  $K$  are defined to contain the effect of that change in the force constants:

$$K(L) = K^0(L) - \zeta(L,L') \cdot u(L') \quad (4)$$

The lattice relaxation can be obtained by imposing a condition of minima to the energy (2). It results in:

$$u(L) = \underline{G}^*(L,L') K^0(L') \quad (5)$$

where the Green function  $\underline{G}^*$  has been defined as the inverse of the defect lattice force constant matrix,  $\underline{G}^* = \Phi^*{}^{-1}$ . Recently, F. Garcia Moliner et al. (1984, 1986) and Levi et al. (1984) have developed a general procedure for calculating the dynamic Green function for modelling surface and interphase properties. The

above defined lattice static Green function corresponds to the zero frequency limit of their dynamic one. The only relevant approximation in their calculation is that the surface induced perturbation of the force constant matrix is taken as relatively short range. Hence, within this approach, solving Equation (5) constitutes a method for calculating surface atomic distortion alternative to the computer simulation used hereafter.

For the case of an alloy, a cluster of  $N_k$  atoms (motive) is located at lattice site  $L$ . The atomic positions associated to site  $L$  are denoted by the pair of indexes:  $(\ell, k)$ . The forces on the atoms are defined by the corresponding derivatives of the energy (2). Those forces and the atomic displacements are related to the ones in Equations (4) and (5) by the equations:

$$u(\ell, k) = u(L) + \Delta u(\ell, k) \quad (6a)$$

$$K^0(\ell, k) = K^0(L) + \Delta K^0(\ell, k) \quad (6b)$$

where the first term of the right-hand side is the symmetric, "acoustic" mode of Farkas et al. (1987):

$$u(L) = N_k^{-1} \sum_{k=1, N_k} u(\ell, k)$$

$$K^0(L) = N_k^{-1} \sum_{k=1, N_k} K^0(\ell, k)$$

The second term is the relative, antisymmetric or "optical" mode for each atom at the cell.

Minimizing the energy with respect to the atomic displacements, yields the system of coupled equations:

$$N_k \cdot K_i^0(L) = \Phi_{ij}^L(L, L') u_j(L') + \Phi_{ij}^{L, K}(L, \ell' k') \Delta u_j(\ell', k') \quad (7a)$$

$$\Delta K_i^0(\ell, k) = \Phi_{ij}^K(\ell k, \ell' k') \Delta u_j(\ell', k') + \Phi_{ij}^{L, K}(\ell k, L') u_j(L') \quad (7b)$$

where:

$$\Phi_{ij}^L(L, L') = \sum_{k, k'} \Phi_{ij}^L(\ell k, \ell' k')$$

$$\Phi_{ij}^{L, K}(L, \ell' k') = \Phi_{ij}^{L, K}(\ell' k', L) = \sum_k \Phi_{ij}^L(\ell k, \ell' k')$$

$$\Phi_{ij}^K(\ell k, \ell' k') = \Phi_{ij}^L(\ell k, \ell' k')$$

and the defect lattice force constants  $\Phi^*$  are defined like those in Equation (3) but the second derivatives are taken with respect to the relative atomic displacements within the cell. Contrary to Equation (5) these equations include the dispersive response of the lattice as defined by Kunin (1982, 1983).

### 3. EFFECT OF LOCAL VOLUME DEPENDENT INTERATOMIC POTENTIAL

In this Section we shall summarize some general information about the local volume dependent potentials. In Equation (1) for the energy it is assumed that the pair part can be expanded as a sum over the atom pairs at the ensemble:

$$U_p = 1/2 \sum_{M, M' \neq M} V(R_{MM'}) \quad (8)$$

where  $R_{MM'}$  is the distance between  $M$  and  $M'$  atoms - in this Section  $M = (l, k)$ . Also the local volume dependent part can be expanded as a simple sum over the atoms:

$$U_N = \sum_M f_M(\rho_M) \quad (9)$$

where  $\rho_M$  corresponds to the local density at the location of the atom  $M$ . This density is evaluated as a sum of functions dependent on the distance between the atom  $M$  and its neighbours:

$$\rho_M = \sum_{M' \neq M} \phi_{M'}(R_{MM'}) \quad (10)$$

Therefore, its value (10) is scaled with the number of neighbours per shell and the function  $\phi_{M'}$  depends on the type of neighbour  $M'$  but not on the atom  $M$  where the density is evaluated. As done by Ercolessi et al. (1986a, 1986b) in the case of only first neighbour interaction  $\phi_M$  may be normalized to unity at the neighbour distance.

The source forces  $K^0$  (Kanzaki forces for the unrelaxed lattice) in Equation (5) can be evaluated for the free surface defect. Those are obtained from the total energy of the unrelaxed semi infinite ensemble of atoms at the perfect lattice location ending at a plane free surface. By replacing (8) and (9) into (1) and deriving the energy with respect to the atom coordinates, the force on atom  $M$  is:

$$K^0(M) = - \sum_{M' \neq M} [V' + \phi'_{M'} f'_{M'} + \phi'_{M'} f'_{M'}] R_{LL'} / |R_{LL'}| \quad (11)$$

where  $V', \phi'$  stand for  $\partial(V, \phi)/\partial R_{MM'}$  and  $f'$  for  $\partial f/\partial \rho$ . At the bulk, lattice symmetry imposes the cancellation of those forces for a finite range interatomic potential. Even at the perfect lattice, equilibrium results by the cancellation between opposite pair and volume dependent forces. At the surface, some atoms miss neighbour atomic interactions. If  $M$  in Equation (11) stands for one of those atoms, the lack of the corresponding pair in the direction normal to the surface determines a net force due to non cancellation of the first term at the right-hand side of (11). Also there is a change in the local density  $\rho_M$ . This, in turn, determines the existence of a force on the surface atoms  $M$  due to the unbalanced last two terms of the right-hand side of Equation (11). However, even those atoms  $M'$  which do not lose interactions, suffer a force if they interact with surface atoms  $M$  that have reduced their local density by being at the surface. Therefore, within this local volume model, the competition between volume and pair forces is built into the source of distortion at the surface. As mentioned before, the change in Equation (3) in the force constant matrix induced by the defect is due to the loss of atomic interactions and to eventual changes in the interaction constants. These latter ones are included within the local volume dependent potential model, contrary to the case of considering only a pairwise atomic interaction which cannot consistently model a change in interaction constants at the defect core unless imposed "ad hoc". Therefore, in the local volume potentials the charge redistribution at the surface is included in the model within the spirit of the description of Heine et al. (1982) and Finnis et al. (1974). This inclusion is an important difference with the description provided by a pair interaction

model. In addition, if the lattice is modeled as in equilibrium under solely a pair potential the forces (11) must cancel even at the surface. Surface relaxation in that case results from the change in the force constant matrix due to the loss of atomic interaction at the surface and under the boundary condition of non-average crystal distortion. If a non-equilibrium pair interaction is adopted with a Cauchy pressure applied over the lattice (see Born and Huang (1966)) the source forces will be mainly determined by that pressure. In the case of a positive pressure, like in Ni, Al and Ni<sub>3</sub>Al, those forces will induce an average expansion of the first interlayer distances, in contradiction with the experimental findings.

#### 4. Ni, Al, Ni<sub>3</sub>Al SURFACE RELAXATION CALCULATION

The local volume dependent interatomic potentials used for the calculations were developed by Voter et al. (1987). Those potentials fit exactly the lattice parameter, cohesive energy and bulk modulus of the pure metals Ni and Al; while they provide an adequate fitting to elastic constants and vacancy formation energy of those metals and of Ni<sub>3</sub>Al. Also for that alloy the super lattice intrinsic stacking fault (SISF), (100) and (111) antiphase boundary energies have been fitted together with the lattice parameter and cohesive energy for that alloy and for NiAl. The corresponding functions  $V, f$  and  $\varphi_M$  defined in Equations (8) to (10) are plotted in Figure 1. In the plot for the pair part of the interactions and the density as a function of the distance the first neighbour locations for Ni, Al, NiAl and Ni<sub>3</sub>Al are shown. It can be clearly seen that at those distances, equilibrium is attained by a competition between strong pair and volume dependent interaction forces.

The relaxation in the surface region is calculated by means of a numerical procedure based on DEVIL, the computer simulation program developed at Harwell by Norgett et al. (1972). The program is based on a conjugate gradient method for finding the minimum of the energy (1) for a given ensemble of atoms. DEVIL allows to generate a lattice with up to six atoms per lattice site. The lattice coordinate axis are taken in accordance with the type of surface to be simulated. Denoting by  $\hat{z}$  the direction normal to the surface, periodic boundary conditions are used in the directions perpendicular to  $\hat{z}$ . That is the location  $S$  of an atom  $M$  outside the relaxed region is uniquely related to an atom  $M^0$ , within it, by the translation:

$$S(M) = S(M^0) + m\Delta x\hat{x} + n\Delta y\hat{y} \quad (12a)$$

where  $n$  and  $m$  are integers and  $\Delta x, \Delta y$  are the periodicity lengths. This implies for the displacements:

$$u(M) = u(M^0) \quad (12b)$$

Therefore, the free surface is determined by a simple square lattice in the  $xy$  plane and is semi-infinite in the  $\hat{z}$  direction. The conditions (12b) mean that the square planar lattice cannot be distorted:

$$\sum_{M=1, N_S} u(M) \cdot \hat{x} = \sum_{M=1, N_S} u(M) \cdot \hat{y} = 0 \quad (13)$$

where  $N_S$  are the atoms located in the relaxed region. (If (13) were not satisfied the displacements (12b) would depend on  $n$  and  $m$  in (12a)).

## 5. CALCULATION RESULTS

Chen et al. (1986, 1987), Foiles et al. (1987), and Farkas et al. (1987) have calculated some free surface distortions for Ni, Al, NiAl and Ni<sub>3</sub>Al by using local volume dependent interatomic potentials. For the sake of completeness we shall briefly review their main results. For the alloy NiAl a contraction was found for the (110) surface 50/50 NiAl termination and for the (111) pure Ni termination. On the other side the (100) surface either with 50/50 NiAl or pure Ni termination expanded. Also an expansion was predicted for the (111) surface in that alloy. Chen et al. (1987) explain these results as a consequence of the relative size of the Ni and Al atoms. This determines Al to be under compression in the alloys, while the Ni atoms are under tension but smaller compared with the Al straining. The calculations for Ni<sub>3</sub>Al generally show a small displacement of the first atomic layer but always a rippling effect, with the Al atoms outwards with respect to the Ni ones. Finally, Farkas et al. (1987) show in their study of (111) planar defects in Ni<sub>3</sub>Al, relaxations oscillatory in directions parallel to the defect plane. Here, we shall report some simulations of the (100), (111) and (120) free surfaces of Ni, Al and Ni<sub>3</sub>Al. These were done by allowing for the relaxation of more than 100 planes parallel to the surface, Farkas et al. (1987). The results will be analyzed within the theory developed in Section 2.

The (100), (111) and (120) free surface configurations of the pure metals and of Ni<sub>3</sub>Al are shown in Figure 2. Arrows proportional to the Kanzaki forces at the unrelaxed configuration and evaluated through Equation (11) are plotted in that Figure. For the pure metals, those forces are perpendicular to the (100) and (111) surfaces, while they have a shear component parallel to the (120) surface. These

shear forces must satisfy the same equilibrium condition (13) than the atomic displacements. One can see also that the perpendicular forces change sign as a function of the distance from the surface. While the existence of opposite signs in the shear forces is a consequence of the surface symmetry, this change in the sign of the perpendicular forces results from the competition between the pair and the local volume dependent part of the potential. As discussed in Section 3 the surface determines some pair interaction plus volume dependent forces to remain unbalanced for the outmost external atoms while the change in the local density of those same atoms determines density dependent forces to appear over deeper ones. For the alloy, even in the case of the (100) surface, there is an internal straining of the lattice cell by force micromoments. For the (100) surface those micromoments are perpendicular to the surface and may give rise to rippling. For the (111) surface the internal straining and micromoments may be either perpendicular to the surface or within a 120° rotation symmetry around a normal axis that contains an Al atom at the surface. For the (120) surface, the axis normal to the surface is not a symmetry axis of the unit cell; the resulting Kanzaki forces straining is, therefore, more complex. Those forces for the unrelaxed lattice are schematically shown in Figure 2.

We summarize in Table 1 the relaxation of the first layers calculated for the (100) surface of the pure metals and the two possible terminations of the Ni<sub>3</sub>Al alloy, as well as the predicted rippling. These results agree with those obtained by Chen et al. (1986) based on the same interatomic potential but using a somewhat different relaxation procedure. Also Foiles et al. (1987) calculated a similar relaxation pattern; they report for the 50/50 termination of the alloy an outwards displacement of the Al atom of 0.06 Å, smaller than ours. Both calculated values

are much larger than the experimental ones of Sondericker et al. (1985, 1986). In addition, the average outer layers distance contraction calculated by us is 10 times smaller than the measured one. However, this disagreement is also a consequence of the large outwards relaxation of the Al atoms predicted by the simulation; i.e., the Ni atoms relax inwards 0.05 Å, agreeing with the experimental value ( $0.05 \pm 0.03$  Å).

A detailed set of results for the computer simulation of (111) planar defects in Ni<sub>3</sub>Al have been reported by Farkas et al. (1987); those have been obtained by using the same interatomic potential and relaxation program used here. In that work we have already separated the symmetric, "acoustic", contribution to the atomic displacements from the antisymmetric, "optical", one. The first results mainly from the relaxation of the body forces induced by the above discussed Kanzaki forces, while the second is mainly due to the internal straining induced by the micromoments of those same forces over the atomic cells. As shown in Figure 2, body forces are, in this case, perpendicular to the surface and their main effect is to contract the first interlayer distance. The micromoments induce the rippling of the outermost layer, with the Al atoms outwards with respect to the Ni ones. Also, oscillations parallel to the free surface appear. Those have the allowed symmetry of 120° around the Al atom and are mainly located in the first and second layer below the surface, Figure 3. Therefore, the internal straining results in a consistent outwards relaxation of the Al atoms at the outermost layer while their nearest neighbour Ni atoms, in the same atomic plane move outwards from the Al atoms located at the second plane. The Ni atoms at the second plane displace by trying to compensate the density change due to the large outwards

displacement of the Al. The displacements are consistent with the symmetry restrictions above mentioned.

As a final set of results we report in Figure 4 the atomic relaxation perpendicular to the (120) surfaces. It can be seen that, except for the scale, the pure Ni and Al relaxations are identical. For both terminations of the Ni<sub>3</sub>Al, by performing an average over the Ni and Al atom relaxations at the same (120) plane, an oscillatory pattern appears very similar to the one in the pure metals. This pattern is, therefore, a consequence of the surface symmetry. However, for the alloy, micromoments have a strong effect and they impose, on the one hand, the relaxation of the Al atoms outwards with respect to the Ni ones at the outermost layer and, on the other, affect the pattern of the average relaxations plotted here. For example we see in the Figure that, in the case of a mixed Ni-Al termination, the plane interspace 2-3 contracts, while it expands in the pure metals. In the case of pure Ni termination it expands even more. This difference is due to the fact that for the mixed termination case, the third atomic layer contains Al atoms which want to displace outwards with respect to that layer. The opposite happens for the pure Ni termination, where now the Al atoms are located at the second layer and none is at the first and third ones. In our calculation, Al seems to impose severe internal strainings. Another way of visualizing the importance of the micromoments with respect to the body forces is by showing those strainings at different atomic tetrahedra in the surface. In figure 3, we have joined with a dotted line the change in the interplanar distances due to the atoms 1,3,6,8 and the one of 2,4,1',3' (see Figure 2 for the numbering). It can be seen that the first of those tetrahedra, where Al is at the free surface, is less strained than the second one, which contains an inside Al atom. Also, displacements



parallel to the surface, if allowed by symmetry, can be important in relaxing internal micromoments, even for the pure metals, within those atomic cells. We have found in our calculation displacements parallel to the (120) surface of up to 0.015 Å in Ni, 0.038 Å in Al and 0.055 Å in Ni<sub>3</sub>Al. For the pure metals the main displacement takes place at the third layer, while for the alloy it does so at the outermost layer.

## 6. SUMMARY AND DISCUSSION

In this paper we have studied some of the physical causes of the atomic displacements from the perfect lattice sites at the free surfaces of metals and alloys, mainly pure Ni, Al, and Ni<sub>3</sub>Al. In Section 2, we have established the basis of a force discontinuity model for calculating lattice surface relaxation. Within that model, the displacement of the surface atoms from their perfect lattice positions was treated as the response to a set of Kanzaki forces, defined also in that Section. In Section 3 some effects of using local volume dependent potentials for the calculations were described. Surface distortion predicted by using those potentials were compared with those resulting from a simple pair interaction model. It was found that, for the systems studied, the latter model is unable to reproduce even the measured contraction of some surfaces. In Section 4, we have shown the influence of the surface and lattice symmetry on the possible distortion modes of the free surface when restructuring is not allowed. In Section 5, we reported some computer simulations of the static configuration of free surfaces in Ni, Al and Ni<sub>3</sub>Al. The interatomic potential deduced by Voter et al. (1987) was used for the calculations. There, it was shown that very symmetric surfaces, like (100) and (111) in fcc, allow only for perpendicular, however oscillatory, relaxation in the

pure metal. In addition, for the alloy, rippling was calculated, in agreement (although somewhat larger in value) with the experiments. For the (111) surface oscillatory relaxations parallel to the surface were reported by Farkas et al. (1987). We emphasized that this relaxation can be understood in the same manner as the rippling, as due to straining of the tetrahedra formed by the motive in Ni<sub>3</sub>Al. Finally for the (120) surface, less symmetric than the previous ones, oscillatory distortions parallel to the surface were found even for pure metals. Also the local straining of different lattice cells located at the same distance from the (120) surface was shown. We shall now discuss the consistency of the above results.

We shall first discuss the origin of the perpendicular relaxation at the surface and the connection between the calculated outer layer contraction and oscillations with the assumptions of the model. We have shown in Section 3 that if a pair interaction potential is assumed for the calculation, a perpendicular expansion will be predicted for Ni, Al and Ni<sub>3</sub>Al surfaces, in disagreement with the experimental findings. On physical grounds, the surface contraction occurs when the atoms at the surface, located at the perfect lattice site, try to regain their local bulk density, strongly depleted by the absence of neighbours. However, this relaxation implies that some inner atoms suffer an increase in their local density due to the now nearer ones located at the immediate neighbourhood of the surface. Therefore, the system gains energy if those atoms compensate the induced increment in their local density by relaxing outwards from their inner neighbours. As the distortion is propagated into inner layers, this density compensation tendency changes sign and it is intrinsically oscillatory, hence the oscillations in the relaxation. If the system is to be modelled by means of interatomic forces, the

above process seems to require the inclusion of many body interactions in the model. The quasi analytical models of Allan et al. (1973, 1976) and Landman et al. (1980) for the surface relaxation have also obtained oscillatory variations of the interplanar distance as a function of the distance from the surface and, in some cases, a contraction in the first of those distances. Within a simplified description of those models, Allan et al. (1973, 1976) included two quadratic terms in the energy expansion as a function of the interplane separation, one proportional to the product of neighbour interplanar distances ( $\alpha d_{n,n+1} d_{n+1,n+2}$ ) and a second quadratic in those distances ( $\beta (d_{n,n+1})^2$ ;  $\alpha, \beta > 0$ ). It is easy to show that for a first neighbour pair interaction potential only this last term will appear; while for a longer range one the sign of  $\alpha$  in the first term of that energy expansion will be determined by the curvature of the potential at neighbours beyond the first. If either only one of the above terms appears in the energy expansion, or they are of opposite sign, no oscillations in the relaxation will be predicted by those simplified models.

With respect to the influence of the surface symmetry and lattice structure on the relaxation; we found, as said above, for the most symmetric surfaces, like (100) or (111), displacements only in the direction perpendicular to the surface plane. For less symmetric ones, (120), parallel displacements are also obtained. Those must satisfy the condition (13). Therefore the distortions are oscillatory and, generally, of shear type. However, their calculated magnitude is not negligible. For the case of alloys, the possibility of straining the alloy cell adds new degrees of freedom to those available for relaxation at the same orientation of the free surface. We have seen that, as a consequence of that straining, rippling appears at the surface, with the Al atoms outwards from the Ni whenever present

at the outer plane of the Ni<sub>3</sub>Al alloy. Also oscillatory local density changes are found, even for high symmetry surfaces, like the (111). Their appearance is consistent with the existence of rippling at the outer atomic layer. The internal straining of each atomic cell in the alloy depends on the cell location with respect to the surface and that of the Al atom. In the (120) surface, we have obtained a larger straining for those cells with an inner Al than for those where Al is at the outer atomic layer. We can describe the effect of surface straining by the Al, including the rippling, as the surface relaxing internal lattice strains or, equivalently, as a surface induced distortion in the electron density which, in turn, results into an atomic distortion. Within the inherent empirical character of the interatomic potentials, the surface distortion can be taken as a potential fitting parameter. The fitting can be obtained through Equation (7), where the atomic displacements are taken as the measured ones. This fitting will mainly affect first and second derivatives of the interaction and it will give information about internal straining at the unit cell. This kind of information is not generally available in the properties used for fitting the interatomic potentials, except when the phonon optical modes are fitted.

We conclude that, in spite of the large success attained by using simple pair potentials for the calculation of the distortion due to lattice defects, for the case of the free surface, those potentials are not only unable to reproduce some experimental results but, in addition, do not seem to contain some of the physical features more relevant to the surface distortion. The main one being that the competition in a crystal between the pair atomic interaction forces with multi-atom ones cannot be neglected. For the free surface, which is a large topological discontinuity, not only restructuring, as discussed by Heine et al. (1982), but also

its relaxation seems to be determined by that competition. We have tried in this paper to show the validity of that assessment. We have also stressed the effect of surface symmetry and lattice structure on the relaxation.

As a final point in the discussion we want to refer to our result that, for an alloy, the dispersive character of the lattice and its influence on the relaxation cannot be neglected, even in the elastic limit. The internal straining of the atomic cell seems to be an important mechanism of energy relaxation. This will affect the atomic displacements at the defect core and its interaction with other sources of distortion.

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## FIGURE CAPTIONS

FIGURE 1: Interatomic potential functions for Ni, Al and Ni/Al alloys, Voter et al. (1987). Full and dotted lines correspond to a set of energy functions related among themselves by the relations discussed in the text.

FIGURE 2: Sketch of (100), (111) and (120) surfaces. 2a, 2c, 2e: pure metals. 2b, 2d, 2f: Ni<sub>3</sub>Al alloy. Shaded circles stand for Al atoms and the arrows for the "unrelaxed" lattice Kanzaki forces (not to scale).

FIGURE 3: Atomic displacements of the first two layers of a (111) surface in Ni<sub>3</sub>Al. The arrows showing the displacement are in units of lattice distance multiplied by 50.

FIGURE 4: Relative change of interplanar distance perpendicular to (120) surface. For the Ni<sub>3</sub>Al two terminations are shown. The full line for Ni<sub>3</sub>Al corresponds to the average (120) plane displacement, the dots stand for the relative change in the distance of an atom in the plane  $n$  to the displaced  $(n + 1)$  plane.

TABLE I

(100) surface relaxation  
in units "per thousand" of interplanar separation.

| $\Delta d_{n,n-1}$ | Ni          | Al  | Ni <sub>3</sub> Al |               | Ni/Al term. |               |
|--------------------|-------------|-----|--------------------|---------------|-------------|---------------|
|                    |             |     | Ni term.           | $z$ Al-Ni [Å] | Ni/Al term. | $z$ Al-Ni [Å] |
| $\Delta d_{1,2}$   | -10         | -29 | $\cong 0^*$        | --            | -3          | 0.09          |
| $\Delta d_{2,3}$   | -5          | -8  | -4                 | 0.01          | -4          | --            |
| $\Delta d_{3,4}$   | $\cong 0^*$ | 1   | $\cong 0^*$        | --            | $\cong 0^*$ | 0.00          |

$z$  Al-Ni: separation between Al and Ni atoms at the  $n$ th plane below the surface.

\*: absolute value smaller than 0.5 per thousand.

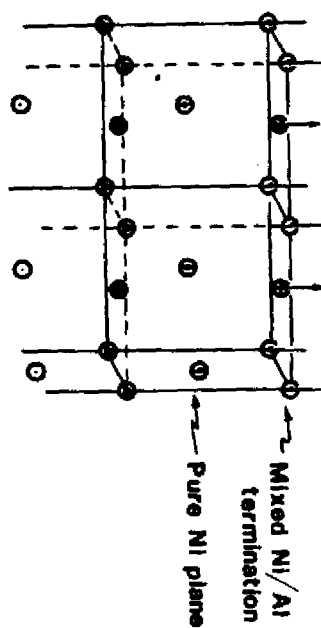


FIG. 2b. Ni<sub>3</sub>Al  
⊙: Al ○: Ni

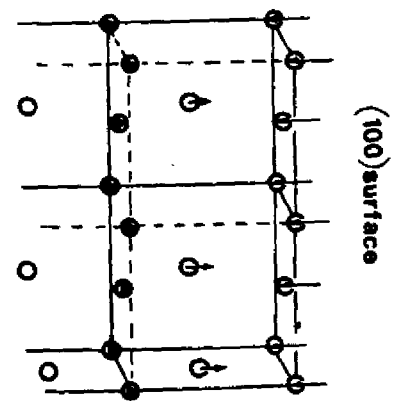


FIG. 2a. Ni, Al

-24-

-25-

(III) surface

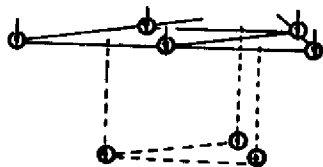


Fig. 2c. Ni, Al

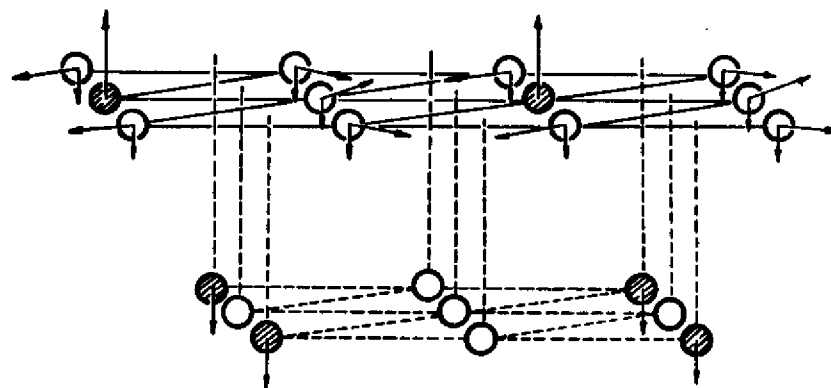


fig. 2d Ni<sub>3</sub>Al

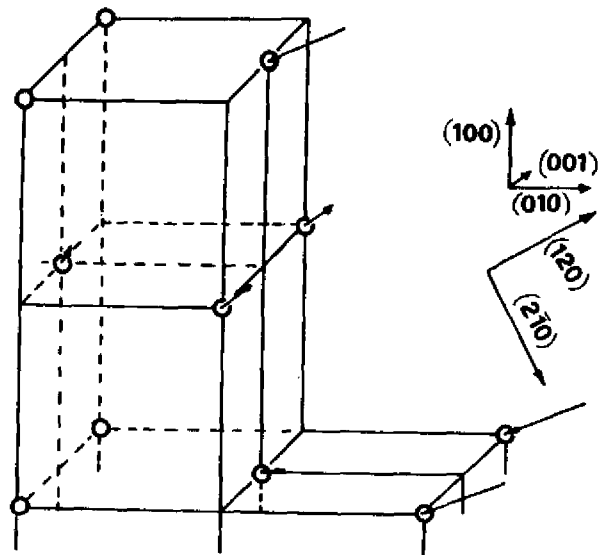


Fig. 2e)

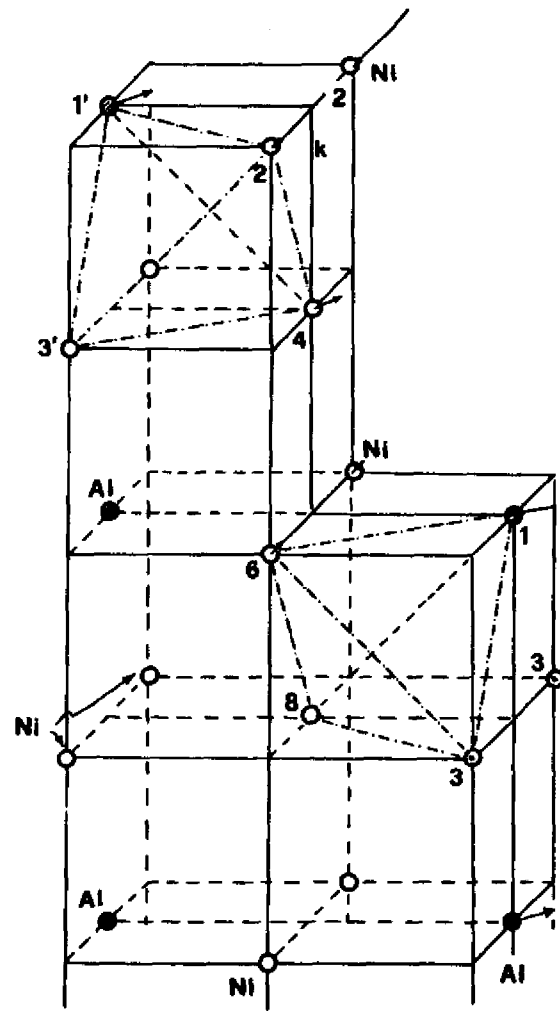


Fig. 2f)

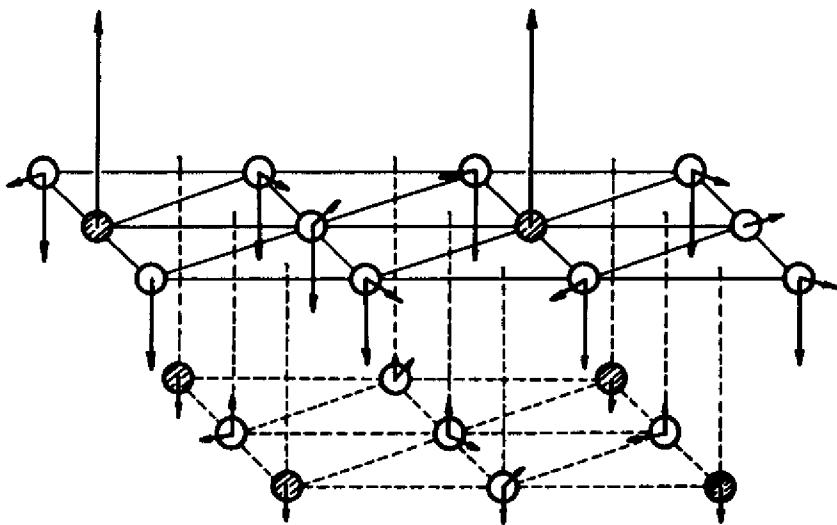


fig. 3

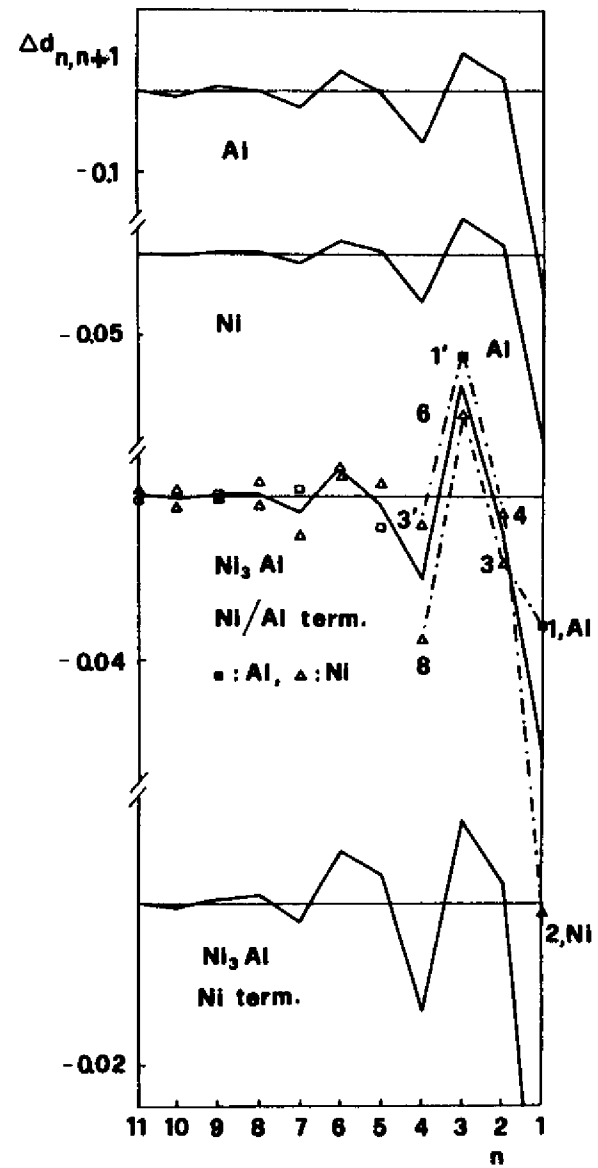


Fig. 4