VOLUME 57, NUMBER 11 PHYSICAL REVIEW LETTERS 15 SEPTEMBER 1986

Oscillatory Surface Relaxations in Ni, Al, and Their Ordered Alloys

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(Received 5 June 1986)

Results from simulations of Ni, Al, Ni_3Al, and NiAl show long-range, oscillatory surface relaxations that decay exponentially into the bulk. Pure fcc Ni and Al have oscillation periods that are close to the nearest-neighbor distance, independent of crystal face. This is shown to be due to surface smoothing and steric effects. In Ni_3Al and NiAl, the surface planes are rippled, with the Ni-Ni and Al-Al interlayer spacings oscillating 180° out of phase. Very good agreement between our results and experimentally measured atomic relaxations is obtained.

PACS numbers: 68.35.Bs, 61.55.Hg

In this Letter we present surface-relaxation simulations for a number of Ni, Al, NiAl, and Ni_3Al surfaces. Ni and Al are considered in thier face-centered cubic phases (fcc), NiAl in its ordered $B2$ phase (CsCl structure), and Ni_3Al in its ordered $L1_2$ phase (fcc with one of the four sublattices occupied by Al). The Ni-Al system is an interesting prototype for a number of reasons. The first is the large degree of current experimental interest in the surface structure of its ordered alloys.[1-3] Second, the structures of many pure Ni and Al surfaces have been investigated by LEED[4-6] and/or ion scattering.[7] Third, since the alloys contain both simple and transition metals, they provide a challenge to recent theories of surface relaxation.[8] The present simulations show the characteristic oscillatory, multilayer relaxations that have been observed previously. Detailed comparisons of our results with experimental data show good agreement for both the pure and alloy systems. Inclusion of a large number of atomic planes (>80) in the simulation reveals exponentially decaying oscillations that are still measurable many layers into the bulk. For pure Ni and Al, the oscillation period is found to be close to the nearest-neighbor distance, independent of crystal face. NiAl and Ni_3Al also show long-range, oscillatory behavior, with rippling in planes which contain both Ni and Al.

In simulating the structure of these surfaces we make use of a recent development, the embedded-atom technique due to Daw and Baskes.[9] This approach allows for a simple description of atomic interactions in the vicinity of defects such as a free surface, and has proven quite successful in a variety of applications.[10] This method is inherently of many-body character and involves two distinct terms: a local density or volume term and a pairwise term. These terms are determined by a fitting of empirical forms to experimental data. Our approach to fitting the potential used here is described in detail elsewhere[11]; we briefly summarize it here. The pairwise interaction is taken to be a Morse potential and the density function is of the form $r^6e^{-\xi r}$ (r is the radial distance and ξ is a parameter), leading to a total of five parameters with a variable cutoff length. The embedding function[9] is chosen to give exact agreement with the experimental lattice constant, cohesive energy, and bulk modulus. Concurrently, a best fit to the three elastic constants, the vacancy formation energy, and the diatomic bond length and bond energy is found by searching in the five-parameter space [while requiring $E(\mathrm{fcc}) < E(\mathrm{hcp}), E(\mathrm{bcc})$]. The rms deviations between the calculated and experimental data in the fit are 0.3% for Ni and 3.4% for Al. Without affecting the pure Ni and Al fits, a Ni-Al cross potential (Morse) is determined by our optimizing a fit to the lattice parameter and cohesive energy of NiAl and Ni_3Al, as well as to the elastic constants, stacking-fault energy, and antiphase boundary energies of Ni_3Al and to estimates of its ordering energy and vacancy-formation energy. The resultant potential is capable of describing pure Ni, pure Al, diatomic Ni_2, diatomic Al_2, Ni_3Al ($L1_2$), and NiAl ($B2$).

To determine the structure of a surface, the energy of an appropriately truncated crystal is minimized with respect to atomic coordinates via a simple gradient technique. At the end of the gradient minimization the surface energy varies by less than 0.01 mJ/m^2 (i.e., typically 1 part in 10^5) and the maximum atomic displacement does not exceed 10^{-4} Å per simulation step. The results quoted herein are obtained by use of at least eighty atomic layers and periodic boundary conditions in the plane parallel to the surface.

Since Al(110) is one of the best-studied metallic surfaces, we begin by comparing simulation results with existing data. In Table I we list the percentage changes in interlayer spacing ($\Delta d_{n,n+1}$) determined by two different LEED studies[4,6] along with the results of the present simulations and the theoretical work of Barnett, Landman, and Cleveland.[8] Our results are in reasonable agreement with both the LEED data and the theoretical results. All the results show clear oscillatory behavior in $\Delta d_{n,n+1}$ with increasing layer depth, except for the results of Noonan and Davis[6] (see Δd_{45}).

TABLE I. A comparison of the percentage changes in the interlayer spacings near the relaxed Al (110) surface.

$\Delta d_{n,n+1}$	Present simulation	LEED (Ref. 4)	LEED (Ref. 6)	Theory (Ref. 8)
Δd_{12}	−10.36	−8.6 ±0.8	−8.5 ±1.0	−10
Δd_{23}	+3.23	+5.0 ±1.1	+5.5 ±1.1	+4
Δd_{34}	−2.58	−1.6 ±1.2	+2.2 ±1.3	−3
Δd_{45}	+1.58	+0.1 ±1.3	+1.6 ±1.6	· · ·
Δd_{56}	−0.41	· · ·	· · ·	· · ·

A simulation of Ni(110) yields $\Delta d_{12} = -4.9\%$, $\Delta d_{23} = +0.57\%$, and $\Delta d_{34} = -0.86\%$. This is to be compared with recent high-energy ion scattering[7] (HEIS) and LEED[5] data which yield $\Delta d_{12} = (-4.8 \pm 1.7)\%$, $\Delta d_{23} = (+2.4 \pm 1.2)\%$, and $\Delta d_{12} = (-8.7 \pm 0.5)\%$, $\Delta d_{23} = (+3.0 \pm 0.6)\%$, $\Delta d_{34} = (-0.5 \pm 0.7)\%$, respectively. While Δd_{12} is in good agreement with the HEIS data, there is a discrepancy in Δd_{23}, which we cannot currently account for. While simulations of many other Ni and Al surfaces were performed, detailed comparisons were not made either because of the unavailability of experimental data allowing relaxation of at least two interlayer spacings or because of substantial variation in the reported $\Delta d_{n,n+1}$.

The (110), (210), (310), (320), (410), and (520) surfaces of Ni and Al each reveal oscillatory, multilayer relaxations. [The (111) and (100) relaxation amplitudes were much smaller and will not be discussed here.] The amplitudes of the oscillations depend on both the material and the surface under consideration. However, the period of the oscillation appears to be nearly independent of crystal face. This is made clear in Fig. 1 where we plot $\Delta d_{n,n+1}$ versus depth for the (110), (210), (310), and (320) surfaces of Al. Although the number of atoms per period varies from surface to surface, this period remains close to the nearest-neighbor distance ($= 2^{-1/2}a$, where a is the lattice constant). All of these phenomena are also observed in Ni.

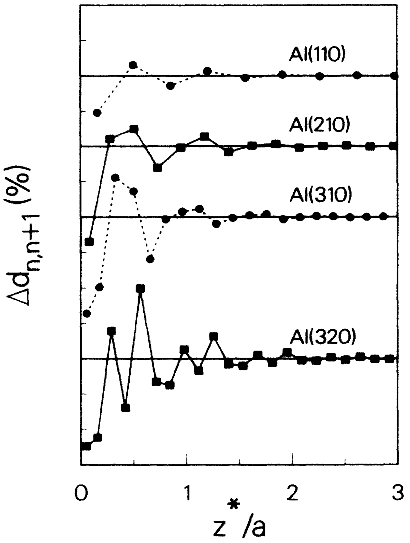

FIG. 1. Surface relaxations of the pure Al (110), (210), (310), and (320) surfaces as functions of depth. The depth is measured in units of z^*/a, where a is the lattice constant and z^* is the midpoint between the atoms on layer n and $n+1$. Each tick mark on the vertical axis corresponds to 10%.

The nature of the oscillatory surface oscillations, their decay into the bulk, and the size of the period may be explained in terms of (i) surface smoothing and (ii) steric interactions. These concepts are made more clear in Fig. 2 where we show the atomic structure of an Al (310) surface and the displacements of the atoms due to surface relaxation. The uppermost atoms along a surface ledge (atoms 1 and 2) move down (towards the bulk) and have the largest displacement amplitudes. Atom 3, which is near the lower portion of the ledge, moves up. These atomic displacements clearly result in surface smoothing. The tendency toward surface smoothing was first suggested by Finnis and Heine[12] on the basis of a simple electrostatic model.

Beginning with atom 4, steric effects become more important. Although surface smoothing would make atom 4 move up, atom 1′ pushes it down and over. Atom 5 is pushed down by atom 1′ (and atom 2′). Similarly, atoms 6, 7, and 8 are pushed (pulled) by the atoms most directly above them. Such displacements of the atoms below the surface layer due to the atoms above naturally lead to periodicity in the direction per-

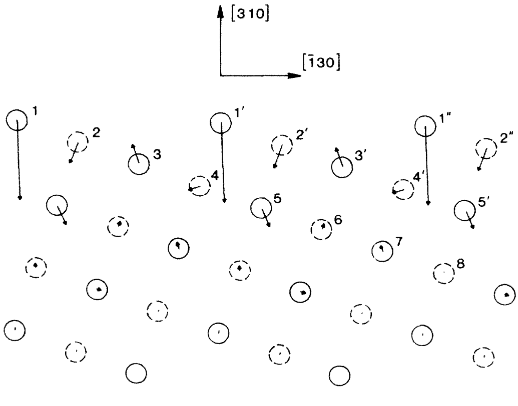

FIG. 2. Relaxation of the Al (310) surface. The circles represent unrelaxed (truncated bulk) atomic positions (dotted atoms lie in a plane $\frac{1}{2}a$ below the other atoms). The vectors show the relaxation motions of the atoms, magnified 10 times.

pendicular to the surface. Thus, atom 5 begins a new pseudoperiod. For fcc $(lm0)$ surfaces (as shown in Fig. 1), the number of atoms in a pseudoperiod is simply the number of unique atoms in a period along the surface in the $[\bar{m}l0]$ direction. Note that the number of atoms in the pseudoperiod is usually less than the number of atoms in the true period normal to the surface [e.g., 4 vs 10 for (310)]. Since the vertical distance between atom 1′ and the atom nearly below it (atom 5 in this case) that starts the new pseudoperiod can only fall within a narrow range [between 1 and $2^{-1/2} \approx 0.707$ nearest-neighbor distances, corresponding to the (110) and (100) fcc surfaces, respectively], the period of the oscillations will also fall within this small range. For surfaces with more than one step per period [e.g., the (320) surface], extra oscillations occur within each period. The predicted range of period sizes is in agreement with those found in Fig. 1 and in recent experiments.[13]

The amplitudes of the oscillations shown in Fig. 1 decay exponentially into the bulk. The surface smoothing and steric interactions discussed above can also be used to explain this exponential decay. Since atoms near the tops of surface ledges move down and those near the bottoms of the ledges move up, we may model the surface relaxation as an infinite array of parallel lines of force along the surface, directed alternately into and out of the bulk. A simple elastic analysis of this model shows that the strains decay exponentially into the bulk.[14]

For ordered alloys, surfaces with the same index are not neccesarily identical. For example, layers parallel to the (110) and (100) surfaces of Ni_3Al alternate between 100% Ni and a 50-50 Ni-Al composition. For the (100) surface of Ni_3Al we find that the 50% Ni surface is more stable, in agreement with Auger-electron spectroscopy.[2] Recent LEED data[2] show $\Delta d_{12}(\mathrm{Ni}) = -2.8\%$ compared with -2.73% from our simulation. The first layer was found to ripple (Al out, Ni in) by 0.02 ± 0.03 Å in the LEED study and by 0.088 Å in the simulation. $Ni_3Al(111)$ has only one termination (75% Ni). LEED results[2] suggest $\Delta d_{12}(\mathrm{Ni}) = -0.48\%$, $\Delta d_{12}(\mathrm{Al}) = +2.4\%$, and a Ni-Al surface rippling of 0.06 Å (Al out, Ni in). For comparison, the present simulation study yields $\Delta d_{12}(\mathrm{Ni}) = -0.33\%$, $\Delta d_{12}(\mathrm{Al}) = +3.18\%$, and a Ni-Al surface rippling of 0.07 Å. For the Ni_3Al (110) surface, the agreement with preliminary LEED results[2] is not as good. Experimentally, the (110) surface terminates with the 50-50 composition with, surprisingly, both the Ni and Al atoms closer to the pure Ni second layer (by 11.9% and 10.7%, respectively), whereas we find a 3.0% contraction for Ni and a 1.5% expansion for Al.

The (110) surface of NiAl has recently been studied by LEED[1] and medium-energy ion scattering[3] (MEIS). The surface relaxations reported in the LEED study (the MEIS data are in close agreement) are $\Delta d_{12}(\mathrm{Ni}) = -6.0\%$ and $\Delta d_{12}(\mathrm{Al}) = +4.6\%$. The LEED data were analyzed[1] in terms of a model in which the second atomic layer was held rigid, and the values of $\Delta d_{12}(\mathrm{Ni})$ and $\Delta d_{12}(\mathrm{Al})$ were optimized to obtain the best fit to the experimental spectra. To compare to this LEED data, we measure Δd_{12} with respect to the midplane of the rippled second layer, leading to $\Delta d_{12}(\mathrm{Ni}) = -6.61\%$ and $\Delta d_{12}(\mathrm{Al}) = +9.58\%$. While the Δd_{12} value for the relaxation of the first layer Ni is in close agreement with the experimental data, the agreement with the Al relaxation is too large by a factor of 2 (0.1 Å). This deviation may be due to the limitation of the single-layer LEED analysis. Note that the magnitude of the surface rippling is in good agreement with the experimental data (i.e., 0.33 Å for the simulation and 0.22 Å for the LEED study).

Figure 3 shows $\Delta d_{n,n+1}$ for both the Ni-Ni and Al-Al interlayer spacings, to a depth of ten layers, for the simulation of the NiAl (110) surface. The most striking feature is the pronounced oscillation in the sign of $\Delta d_{n,n+1}$. The oscillations have periods of twice the interlayer spacing and Ni and Al are precisely out of phase. In addition, the magnitudes of the surface relaxations of the Ni and Al atoms are nearly identical, compared with the pure metals in which the Al relaxation exceeds that of Ni by a factor of 2. These simulations provide the first evidence that the rippling of the near-surface planes in alloys is long range and oscillatory. The magnitudes of the Ni and Al layer oscillation amplitudes decay nearly exponentially, with a decay length of approximately $1.5a$.

Although we find that the decay of the oscillation amplitude is approximately exponential, the magnitude of the deviations in interlayer spacing can be large many layers below the surface. This point is particularly important in regard to the extraction of $\Delta d_{n,n+1}$

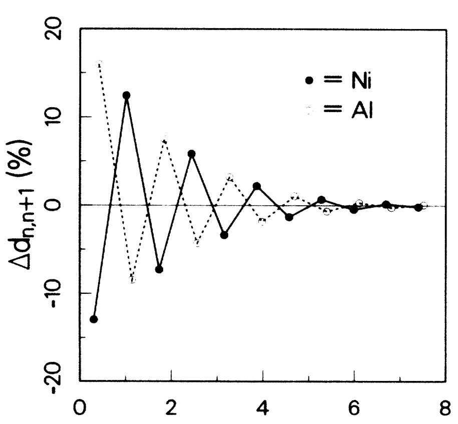

FIG. 3. Surface relaxation vs depth for NiAl(110). The percentage deviation from the perfect-crystal interlayer spacings are given separately for the Ni and Al atoms.

from experimental data, since these analyses usually allow relaxation of three or fewer layers. Nonetheless, the overall agreement between the simulation results and the experimental data is surprisingly good.

The authors gratefully acknowledge useful discussions on unpublished results with W. R. Graham, F. Jona, D. Sondericker, P. M. Marcus, S. Foiles, and M. S. Daw. This work was supported by the Energy Conversion and Utilization Technologies (ECUT) Program of the U.S. Department of Energy.

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