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Surface-induced disorder on the clean $Ni_3Al(111)$ surface

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The structure of the clean $Ni_3Al(111)$ surface has been studied using surface x-ray diffraction. Analysis of the crystal truncation rods reveals that the clean surface contains an unexpected disorder while the bulk remains ordered. This surface-induced disorder extends down to the sixth layer and it decreases gradually with depth. The surface is, on the whole, stoichiometric and the maximum deviation per layer from the ideal $3_{Ni}:1_{Al}$ composition is less than 8%. There is a very small difference (0.02 ± 0.01 Å) between the relaxations of the two different sites at the surface, and the interlayer distance between the outmost, second, and third layers is slightly reduced (0.02 ± 0.01 Å) with respect to the bulk value.

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I. INTRODUCTION

Bimetallic alloy surfaces have been widely studied due to their technological and fundamental interest. Their physical and chemical properties can be very different from those of their individual components. Phenomena such as segregation of one of the components to the surface, order-disorder transitions, or formation of surface alloy phases are common in alloys. Surface effects are principally driven by an intricate interplay between thermodynamics and kinetics.[1] One interesting effect that may arise at alloy surfaces is the surface-induced disorder (SID): a disordered phase is developed at the surface while the bulk still conserves its ordering (see, for example, Refs. 2 and 3). SID generally occurs at temperatures close to the bulk order-disorder transition temperature. There are several reviews in the literature where the experimental and theoretical results are summarized.[1,4–9]

The surfaces of fcc alloys with an $L1_2$ superlattice and A_3B composition (Au_3Cu, Cu_3Au, Cu_3Pt, Ni_3Pt, Ni_3Al,...) have been a particular focus of attention.[5] Among them, probably the most studied system is Cu_3Au. The phase diagram of this alloy presents a first-order phase transition at the critical temperature $T_c=663$ K. Interestingly, x-ray scattering experiments of the $Cu_3Au(001)$ surface, close to the critical temperature, gave evidence of surface-induced disorder[10] and an exponentially decaying oscillatory concentration profile at the surface.[2]

Ni_3Al is of special interest because of its resistance to corrosion and its applications in electronics.[11] In particular, surface energy calculations[12] predict that a minute change in the bulk Ni_3Al alloy composition from its stoichiometric value produces a transition in the segregation behavior which should be observable at the (111) surface. In a slightly aluminum-rich or stoichiometric Ni_3Al alloy, the outmost surface layer should have the ideal $3_{Ni}:1_{Al}$ stoichiometry. Instead, if the alloy is slightly nickel-rich, the surface layer should be a pure Ni overlayer.[12] In a previous low energy-electron diffraction (LEED) and Auger electron spectroscopy (AES) study,[13] it was reported that due to the preferential sputtering of Al atoms, ion sputtering yields a Ni-rich $Ni_3Al(111)$ surface. If the sample is annealed at temperatures higher than 1023 K, aluminum segregates to the surface, although an aluminum excess on the surface is not stable, and upon cooling, Al diffuses back into the bulk until the stoichiometric bulklike composition is recovered. In the same study, it was determined that the clean $Ni_3Al(111)$ surface has a small rippled relaxation with the aluminum atoms displaced outwards 0.06 ± 0.03 Å from the plane of nickel atoms, which is in turn slightly displaced inwards 0.01 ± 0.03 Å. Second and deeper interlayer distances have the bulk value.[13] Scanning tunneling microscopy (STM) images show a hexagonal array with an average interatomic distance of 4.9 ± 0.1 Å—corresponding to the Al-Al nearest-neighbor distance—and a flat surface on the nanoscopic scale with steps oriented along the [110] direction.[14,15] According to molecular-dynamics calculations,[16] at room temperature, the presence of adatoms or vacancies should not alter the ordering of the $Ni_3Al(111)$ surface.

The determination of the exact $Ni_3Al(111)$ surface composition is an open question that we investigate in this surface x-ray diffraction (SXRD) study. SXRD is a well established technique that provides structural information of surfaces and buried interfaces and which has also allowed successful determination of segregation profiles in multicomponent systems.[2,17] Here, we present a detailed atomic structure study of the $Ni_3Al(111)$ surface using a nominally $3_{Ni}:1_{Al}$ stoichiometric sample.

II. EXPERIMENT

Ni_3Al crystallizes in the Cu_3Au structure ($L1_2$-type), i.e., the atoms have a face-centered-cubic arrangement with the Al atoms at the origin and the Ni at the faces. The Ni_3Al

alloy is ordered up to the melting point.[18] The lattice constant of the stoichiometric alloy is[19] $a_{\mathrm{Ni_3Al}}=3.56$ Å. The bulk (111) layers have the stoichiometric composition with three Ni atoms and one Al atom per unit cell, packed in an *ABCABC*… sequence. In this work, the surface unit cell is described by a basis $\vec{a},\vec{b},\vec{c}$ parallel to the $[\bar{1}10]$, $[0\bar{1}1]$, and [111] bulk directions, respectively, with $|\vec{a}|=|\vec{b}|=\sqrt{2}a_{\mathrm{Ni_3Al}}$ and $|\vec{c}|=\sqrt{3}a_{\mathrm{Ni_3Al}}$. The corresponding reciprocal-lattice directions are designated as h,k,l with respect to that basis. The ideal surface cell has *P3m1* symmetry.

The SXRD experiment was carried out at the Surface Diffraction ID3 Beamline of the European Synchrotron Radiation Facility described elsewhere.[20] The incoming x-ray beam was generated by an undulator and monochromatized with a cryogenically cooled Si(111) double-crystal monochromator that was set to an energy of 17.19 keV. The $\mathrm{Ni_3Al}(111)$ sample (MaTeck) has a disk shape with ~10 mm diameter and ~2.5 mm thickness. The clean $\mathrm{Ni_3Al}(111)$ surface was prepared by repeated cycles of $\mathrm{Ar^+}$ sputtering (ion energy: 2 kV, $I=2$ μA) at 925 K for 45 min and subsequent annealing to 1150 K for 15—30 min. The cleanliness was checked with AES and the preparation was repeated until no traces of contaminants could be detected and until the intensity of the x-ray diffraction reflections did not increase and their width did not decrease anymore.

The structure factor of an (h,k) crystal truncation rod (CTR)[21] of the $\mathrm{Ni_3Al}(111)$ surface is[22,23]

$$h \text{ and } k=\text{even} \rightarrow F_{hk}(l) \propto 4(x_{\mathrm{Al}}f_{\mathrm{Al}}+x_{\mathrm{Ni}}f_{\mathrm{Ni}}), \qquad (1)$$

$$h \text{ or } k=\text{odd} \rightarrow F_{hk}(l) \propto S(f_{\mathrm{Al}}-f_{\mathrm{Ni}}), \qquad (2)$$

where x_{Al} and x_{Ni} are the atom fractions of aluminum and nickel in the alloy and satisfy $x_{\mathrm{Al}}+x_{\mathrm{Ni}}=1$ (for the stoichiometric $\mathrm{Ni_3Al}$ alloy, $x_{\mathrm{Al}}=\frac{1}{4}$ and $x_{\mathrm{Ni}}=\frac{3}{4}$). f_{Al} and f_{Ni} are, respectively, the atomic scattering factors of aluminum and nickel. S is the long-range-order parameter of the alloy and it is given by

$$S=\frac{4(r_{\mathrm{Al}}-x_{\mathrm{Al}})}{3}=4(r_{\mathrm{Ni}}-x_{\mathrm{Ni}}), \qquad (3)$$

with $r_{\mathrm{Al}}(r_{\mathrm{Ni}})$ being the fraction of Al (Ni) sites occupied by an Al (Ni) atom. The value of the order parameter ranges from $S=1$ (perfectly ordered and stoichiometric alloy) to $S=0$ (completely random arrangement, i.e., complete disorder). Hereafter, we shall use an order parameter S per layer to describe the order, defined in the same way. The CTRs which are independent of the degree of order [i.e., h and k are both even, Eq. (1)] are called *fundamental* CTRs (F-CTR) while those which vanish if the order disappears [i.e., h or k odd, Eq. (2)] are called *nonfundamental* CTRs (NF-CTR).[62] A sharp (1×1) LEED pattern, characteristic of an ordered surface, is observed after the preparation (see Fig. 1), which suggests the surface is ordered.

Twelve CTRs, from $l=0.5$ up to $l=5.1$ with $\Delta l=0.2$, of the clean $\mathrm{Ni_3Al}(111)$ surface were measured, which reduce to eight independent CTRs after the average: three NF-CTR—(0,1), (1,0), and (1,1); and five F-CTR—(0,2), (2,0), (2,2), (0,4), and (4,0). The integrated intensities were obtained performing rocking scans where the surface is rotated around its normal. By x-ray diffraction, we determined that the miscut was less than 0.37°. The angle of incidence was 2° and a lateral domain size of ~1000 Å was determined from the Δh width of the reflections. Correction factors were applied to the integrated intensities to convert them to structure factors.[24] The final data set comprises a total of 178 independent reflections, and an average uncertainty of 9.9% was determined by comparing symmetry-equivalent reflections.

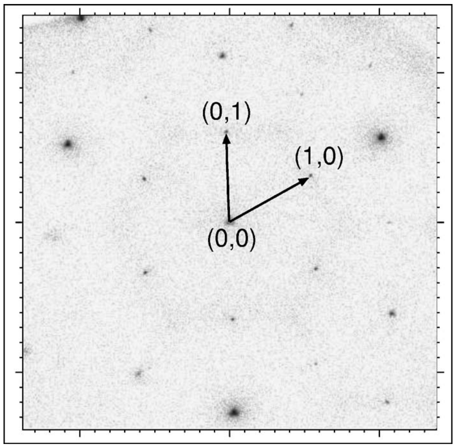

FIG. 1. LEED pattern of the clean $\mathrm{Ni_3Al}(111)$ surface ($E=92$ eV).

The experimental data were analyzed by fitting the measured CTRs with a least-squares refinement procedure, using the ROD program written by Vlieg[25] and the extension implemented by Robach.[26] The goodness of fits was estimated using the χ^2 agreement factor.[27] A common scale factor was used for all the CTRs. The order parameter S at the surface layers has been calculated from the occupancies obtained after the refinement procedure and using Eq. (3). An individual S parameter has been considered for each layer.

The temperature factors of the structure factors have been taken in the simplest form within the harmonic approximation. $B=8\pi^2\langle u^2\rangle$ is the Debye-Waller parameter (DW) and $\langle u^2\rangle$ is the mean-square amplitude of the atomic displacements. During the analysis, a mean DW parameter of $B=0.442$ Å^2 has been used for both types of atoms in the bulk. This value was obtained by x-ray measurements[28] assuming a common DW factor for Al and Ni atoms and it corresponds to a mean-square displacement of $\sqrt{\langle u^2\rangle}=0.07$ Å.

III. RESULTS

In Fig. 2, the experimental structure factors are presented together with those calculated for an ideal bulklike terminated surface (solid line). The F-CTR data are well described by such a model, but, on the other hand, that model cannot reproduce the NF-CTR data, especially the abrupt drop in intensity between Bragg peaks observed experimentally. Furthermore, the F-CTRs can be satisfactorily fitted ($\chi^2_{\text{F-CTRs}}=1.67$) with a stoichiometric bulklike terminated model

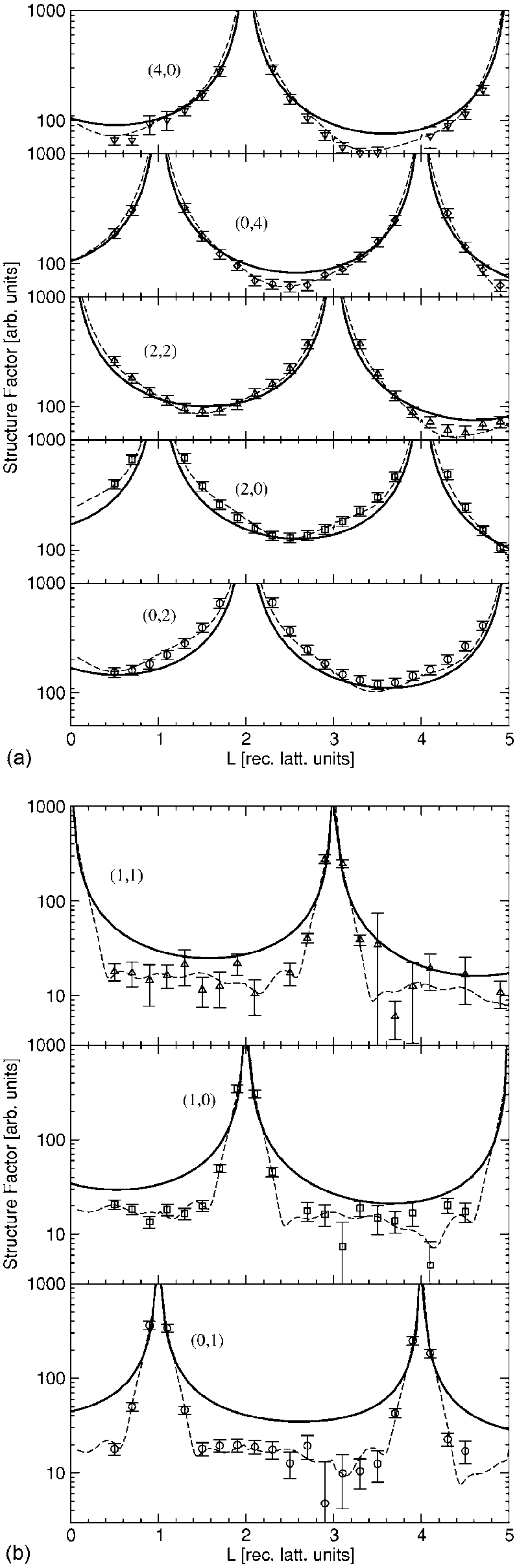

FIG. 2. Measured CTRs of the clean $Ni_3Al(111)$ surface. (a) Fundamental CTRs. (b) Nonfundamental CTRs. The continuous line corresponds to a bulklike termination. Dashed lines have been calculated with the model of Table II. The (h,k) values of each CTR are indicated in parentheses.

where only vertical displacements and DW parameters are least squares refined, but such a model is inadequate to explain the complete data set ($\chi^2_{\mathrm{all}}=11.32$). Allowing for the presence of vacancies at the surface did not ameliorate the agreement substantially. Different roughness models were tested, but none of them could satisfactorily reproduce the experimental data. Roughness reduces the intensity of the surface diffracted signal, but it affects the intensity of all CTRs (F- and NF-CTRs) in a similar way. However, we found a more pronounced intensity decrease between Bragg peaks at the NF-CTRs which can be explained by a surface-induced disorder, i.e., by a reduction of the order parameter S [see Eqs. (1) and (2)] at the surface. The surface disorder can be produced either by chemical disorder—that is, some atoms of one type occupy the atomic sites of the other type of atom and vice versa, keeping the stoichiometry—or by segregation, since an excess of any of the alloy components implies that some sites must be occupied by the wrong kind of atom. Both models have been tested.

A model considering chemical disorder (*model 1*) yields already a very good agreement with the experimental data. The $Ni_3Al(111)$ surface layers have two types of sites: one Al site and three equivalent Ni sites. In the stoichiometric and ordered Ni_3Al phase, Al(Ni) sites are occupied only by Al(Ni) atoms, while chemical disorder (keeping the stoichiometry) arises when a percentage of each site is occupied by atoms of the other type. Chemical disorder was introduced in the model by considering that each atomic site is occupied by two types of atoms. The occupancies of all atoms are correlated such that the total occupancy at each site is equal to 1 (no vacancies) and that the ideal $3_{\mathrm{Ni}}:1_{\mathrm{Al}}$ composition is preserved. Thus, if the Al(Ni) occupancy decreases at the Al(Ni) site(s), then the same total amount of Al(Ni) is increased at the Ni(Al) sites. This can be done using only one occupancy parameter, which indicates the degree of intermixing per layer, i.e., the fraction of atoms that occupy the atomic site of the other type of atom. The initial value of the occupancy parameter was chosen to have an ideal well ordered $Ni_3Al(111)$ surface. In the fit procedure, we first started including the parameters corresponding to the first layer, and the parameters of the following layers were included progressively. The best model considering chemical disorder for the clean $Ni_3Al(111)$ surface has 13 parameters (see Table I): one common scale factor, four vertical displacements,[63] two isotropic Debye-Waller factors, and six occupancy parameters (one for each layer). The goodness of the best model is $\chi^2=1.34$ for the whole data set. The refinement of the vertical displacements of the third and inner layers did not improve the fit appreciably. Neither did the roughness parameter refinement. But, we note, disorder up to the sixth layer was necessary to attain a good fit.

A further improvement in the agreement with the experimental data ($\chi^2_{\mathrm{seg}}=1.13$) is achieved by including the possibility of segregation, i.e., the stoichiometry is not constrained to be $3_{\mathrm{Ni}}:1_{\mathrm{Al}}$ in each layer (*model 2*). Still, this is done at the expense of using more fitting parameters (see Table II). The best model considering segregation has four occupancy parameters more than the chemical disorder model and the same number of displacement and DW parameters.

TABLE I. Structural fit parameters for the best model including disorder (model 1). The entire data set has been used. $\Delta z/A_3$ indicates the out-of-plane displacement divided by the unit cell size along that direction. The vertical displacements depend on the site. B is the isotropic Debye-Waller parameter. S is the order parameter. The rippling $R_{\mathrm{Ni/Al}}$ is the difference between the vertical position of the atoms in the Al site minus the vertical position of the atoms in the Ni site. d_{ij}^{X} denotes the interlayer spacing between layers i and j for the X atom type. The values marked with $*$ have been kept fixed.

Layer	Site	$\Delta z/A_3$	B (Å^2)	S	$R_{\mathrm{Ni,Al}}$ (Å)	d_{ij} (Å)
1	Al	-0.0039_9	1.60_4	0.43_1	-0.02_1	$d_{12}^{\mathrm{Al}}=2.06_1$
	Ni	-0.0011_5				$d_{12}^{\mathrm{Ni}}=2.06_1$
2	Al	-0.0047_7	0.63_3	0.44_1	-0.02_1	$d_{23}^{\mathrm{Al}}=2.03_1$
	Ni	-0.0017_3				$d_{23}^{\mathrm{Ni}}=2.04_1$
3	Al	0^*	0.442^*	0.61_1		$d_{34}^{*}=d_{\mathrm{bulk}}$
	Ni	0^*	0.442^*			
4	Al	0^*	0.442^*	0.74_1		$d_{45}^{*}=d_{\mathrm{bulk}}$
	Ni	0^*	0.442^*			
5	Al	0^*	0.442^*	0.86_1		$d_{56}^{*}=d_{\mathrm{bulk}}$
	Ni	0^*	0.442^*			
6	Al	0^*	0.442^*	0.95_1		$d_{67}^{*}=d_{\mathrm{bulk}}$
	Ni	0^*	0.442^*			
	$\beta=0^*$		$\chi^2=1.34$			$d_{\mathrm{bulk}}=2.06$

The comparison between the experimental data and the calculated values is displayed in Fig. 2. Since the results of both fits are very close, only those of the best fit (model 2) are shown. As is clear from Tables I and II, models 1 and 2 have very similar atomic displacements, order parameters per layer, and temperature factors. The only difference between them is the stoichiometry of the outermost layers. We shall go into these details in the discussion.

IV. DISCUSSION

We have found two similar models that are consistent with the measured data. These models clearly demonstrate that there is a decrease of the long-range order (LRO) parameter in the outermost layers of the clean $Ni_3Al(111)$ surface (see Tables I and II and Fig. 3). This is a relatively unexpected result, since most of the previous experimental reports in the literature point toward a well-ordered $Ni_3Al(111)$ surface except STM results (see below) and a LEED study, where, inferred from the fuzziness of the LEED spots, some remanent disorder is suggested.[29] The phase diagram of bulk Ni_3Al shows that there is only one ordered phase in all the temperature range, i.e., this alloy is stable in its ordered phase up to the melting point.[30] Indeed, attempts to find an order-disorder transition in bulk Ni_3Al have been

TABLE II. Best-fit parameters for the model including disorder and segregation (model 2). The entire data set has been used. "Stoich." indicates the stoichiometry of the layer. The other parameters have already been defined in Table I. The values marked with $*$ have been kept fixed.

Layer	Site	$\Delta z/A_3$	B (Å^2)	S	Stoich.	$R_{\mathrm{Ni,Al}}$ (Å)	d_{ij} (Å)
1	Al	-0.0048_6	1.82_4	0.42_6	$3.11_3^{\mathrm{Ni}}:0.89_3^{\mathrm{Al}}$	-0.02_1	$d_{12}^{\mathrm{Al}}=2.06_1$
	Ni	-0.0018_3					$d_{12}^{\mathrm{Ni}}=2.06_1$
2	Al	-0.004_1	1.01_3	0.43_7	$3.31_4^{\mathrm{Ni}}:0.69_4^{\mathrm{Al}}$	-0.02_1	$d_{23}^{\mathrm{Al}}=2.03_1$
	Ni	-0.0009_5					$d_{23}^{\mathrm{Ni}}=2.04_1$
3	Al	0^*	0.442^*	0.59_7	$2.69_4^{\mathrm{Ni}}:1.31_4^{\mathrm{Al}}$		$d_{34}^{*}=d_{\mathrm{bulk}}$
	Ni	0^*	0.442^*				
4	Al	0^*	0.442^*	0.72_7	$2.90_3^{\mathrm{Ni}}:1.10_3^{\mathrm{Al}}$		$d_{45}^{*}=d_{\mathrm{bulk}}$
	Ni	0^*	0.442^*				
5	Al	0^*	0.442^*	0.85_1	$3_{\mathrm{Ni}}:1_{\mathrm{Al}}$		$d_{56}^{*}=d_{\mathrm{bulk}}$
	Ni	0^*	0.442^*				
6	Al	0^*	0.442^*	0.94_1	$3_{\mathrm{Ni}}:1_{\mathrm{Al}}$		$d_{67}^{*}=d_{\mathrm{bulk}}$
	Ni	0^*	0.442^*				
	$\beta=0^*$		$\chi^2=1.15$				$d_{\mathrm{bulk}}=2.055$

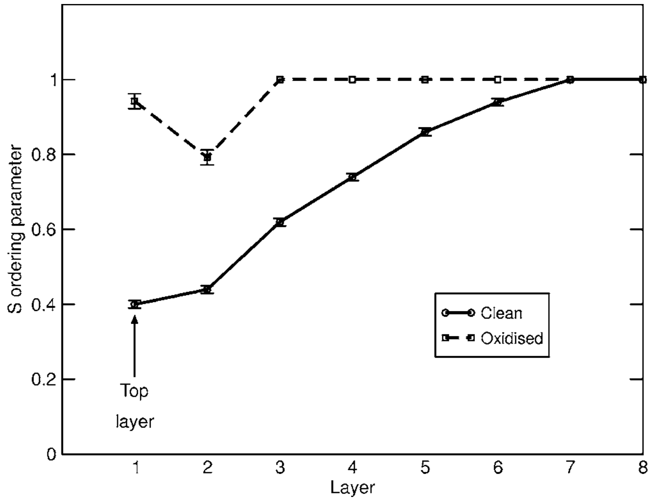

FIG. 3. *S* long-range-order parameter per layer.

unsuccessful. A small decrease of the LRO close to the melting point was found by resistometry, but diffraction experiments found no change in the LRO up to the melting point.[31] However, in those diffraction experiments, bulk Bragg reflections were measured[32,33] and therefore no information about the surface was obtained. Local disorder has been observed[34,35] near the grain boundaries in Ni_3Al and explained in terms of endothermic entropy-driven interfacial segregation.[7]

STM images[14] of the $Ni_3Al(111)$ surface are consistent with our findings. A recent study by Jurczyszyn *et al.* evidences that STM only images the aluminum atoms of the $Ni_3Al(111)$ surface while the nickel atoms remain invisible.[36] STM images[14,36,37] show an absence of long range order in the aluminum sublattice. Larger-scale images obtained by Addepalli and co-workers[15] may also indicate some lack of order on the surface. Surface segregation and SID are common in metallic alloys. Close to an order-disorder phase transition, a disordered surface and an ordered bulk may be expected because at the surface the symmetry is broken and there are missing neighbor atoms. These phenomena are not strictly restrained to the top layer and SID can be extended several layers into the solid.[3,10] However, our measurements have been made at room temperature, that is, well below the melting point of the Ni_3Al alloy [$T_m = 1633$ K (Ref. 30)] and also much lower than the temperature ($T_s = 900$ K) at which exchange type mechanisms between Al atoms and Ni atoms become significant and can induce some local disorder at the surface.[16]

We have found two possible models for the decrease of LRO at the surface layers: either it is a consequence of chemical disorder or an oscillatory concentration profile (see Fig. 4). In both models, the decrease in the order parameter *S* per layer is the same within the experimental error (Fig. 3). The two models only differ in the stoichiometry of the layers and the other parameters are very similar. In model 1, the ideal bulk stoichiometry is maintained in each layer. In model 2, the outermost two layers are slightly nickel-rich, and the third and fourth layers have a small increase in the aluminum concentration with respect to the stoichiometric value. The bulk stoichiometry is recovered after the fifth layer. The LRO increases progressively from the surface into the bulk and it is totally recovered after the seventh layer. It is noteworthy that, within the experimental error, there is no overall deviation from the ideal bulk stoichiometry in the outermost four layers (see Table II), i.e., there is no net excess of any of the alloy components at the $Ni_3Al(111)$ surface. Since the information depth of AES is ~5–10 Å, both models are in agreement with a previous AES experimental report[13] where the $Ni_3Al(111)$ surface was found to be stoichiometric after the sputtering and annealing procedure. The differences in the agreement factors are small and consequently, from the goodness of fits alone, neither model is favored. However, the main factor contributing to the decrease of the LRO is the chemical disorder. Segregation alone, being small, accounts only for a fraction of the decrease of the order parameter *S*.

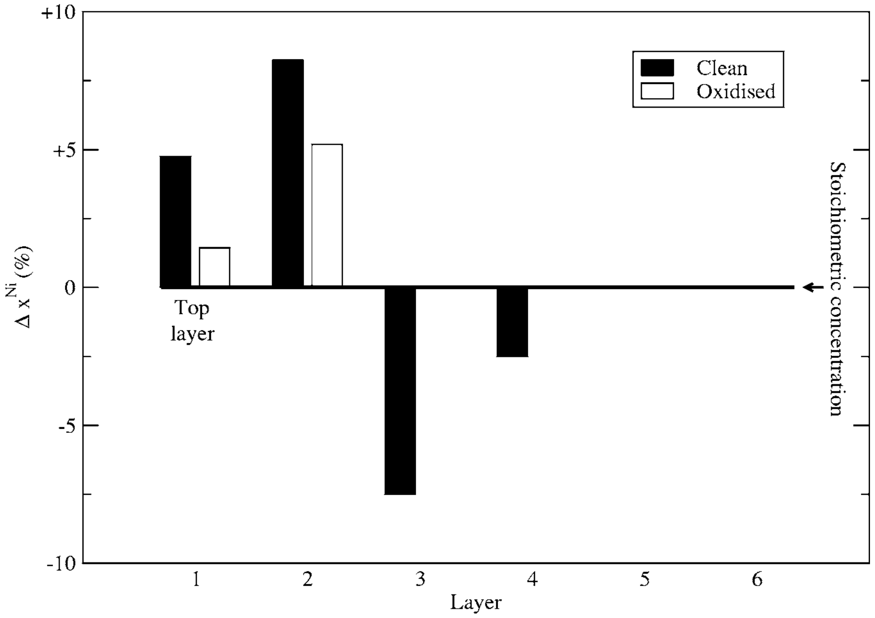

FIG. 4. Ni layer concentration profile at the clean (black bars) and oxidized (open bars) $Ni_3Al(111)$ surface. Δx_i^{Ni} is the excess of the Ni concentration with respect to the average bulk value.

The stability and the composition of a surface are largely influenced by a complex interplay between interatomic interaction, bulk, surface and interface energies, and atomic radii, which can result in lattice constant differences. In this case, strain/stress energy is a crucial parameter in the stability of the phase formed.[38] However, for $Ni_3Al(111)$, we have not found any indication of lattice mismatch between the disordered surface phase and the bulk substrate. Regarding the composition of well-ordered alloy surfaces, it has been reported that small deviations from the ideal stoichiometry in the bulk or in the subsurface region may drastically affect the surface composition.[12,39] The ordering tendency of the alloy makes less favorable the presence of Ni-antisite defects in the bulk and consequently defects should segregate to the surface. Although our Ni_3Al sample is nominally stoichiometric, we cannot rule out a very small concentration deviation from stoichiometry. Regarding the theoretical study by Ruban,[12] we observe that model 1 would be in partial agreement with those predictions if the sample were either stoichiometric or Al-rich, but model 2 would be in conflict in any case since Ruban predicts either a pure Ni overlayer or a bulklike topmost layer.[12] The increment in nickel in the outermost layer is probably induced by the ordering tendency of the alloy. In fact, if only the surface energies of Al and Ni are considered and the ordering tendency of the alloy and the possibility of surface strain/stress is ignored, due to its lower surface energy, an Al-rich surface would be more stable.[40]

The determination of the exact amount of disorder at a surface is a very delicate problem. Atoms at a surface can have larger anharmonic vibrations than in the bulk that can influence the SXRD structure analysis.[41] Indeed, vibrational anisotropy and disorder could have similar effects in the diffracted intensities, as it has been indicated for different metal surfaces.[41–43] We have checked the influence of the temperature parameters in the structural analysis by making use of many different combinations of them. All models used predict a surface disorder. The best two models have similar values of the DW parameters. The thermal vibrations are larger at the surface and their amplitude decreases progressively to the bulk value. There are several reasons that support the validity of the values obtained for the order parameter S. First, an identical value within the errors is obtained for the two models presented here. Second, the same value for the ordering parameter is obtained when an individual DW factor is utilized for each type of atom but the agreement is not improved. And third, the temperature factors affect the intensities of all the CTRs and we have observed a decrease in intensity only in the NF-CTRs, which strongly suggests that it is principally due to disorder and not to thermal vibrations.

It is clear that the preparation method may affect the final surface composition. Argon ion sputtering produces a Ni-rich $Ni_3Al(111)$ surface due to preferential sputtering of Al atoms.[13] The preferential sputtering, for the Ni_3Al alloy and in the 0.5-1 keV energy range, depends strongly on the argon ion energy.[44] Final surface compositions depending on the annealing temperature after sputtering have been reported[45,46] for other alloy surfaces such as $Ni_{90}Al_{10}(111)$ and $Ni_3Pt(111)$. Although in this study and in the LEED/AES experiment by Sondericker *et al.*[13] very similar annealing temperatures have been used, the temperature effect cannot be disregarded completely. Neither can the argon ion energy dependence be ruled out because our sample was cleaned by argon ion bombardment at 2 keV (see Sec. II) while Sondericker *et al.* used lower-energy ions (375 eV). This difference can result in a very different composition profile[44] and longer annealing times might be necessary to recover the bulklike composition at the surface. Still, as we have determined in this study, the deviation from stoichiometry at the $Ni_3Al(111)$ surface is, if any, minimal. For that reason, we believe the annealing times we have employed were long enough, and consequently the disorder is most probably intrinsic to the surface rather than due to the preparation method.

The ordering at the $Ni_3Al(111)$ surface is dramatically modified after oxidation. We exposed the $Ni_3Al(111)$ sample to 100 Langmuir of oxygen ($P_{O_2} \sim 5 \times 10^{-8}$ mbar) at 1050 K, followed by a slow cooling down. After this procedure, a thin aluminum oxide film is formed which yields a sharp and complex LEED pattern.[23,47,48] The structural features of the oxide film and of the interface between the film and the $Ni_3Al(111)$ substrate are reported elsewhere.[23,49] Here, we will only point out the main features regarding the ordering at the interface. Oxidation alters the ordering at the interface (see Figs. 3 and 4). The oxide covered $Ni_3Al(111)$ substrate is much better ordered than the clean $Ni_3Al(111)$ surface. The outermost layer is marginally Ni-rich ($\sim 1.5\%$) and the Ni excess in the second layer is slightly higher ($\sim 5\%$). Accordingly, the net excess of Ni at the surface is small ($\sim 6\%$). The slight depletion of aluminum in the two outermost layers of the $Ni_3Al(111)$ substrate is probably produced by the segregation of aluminum to the oxide overlayer. During oxidation of Ni_3Al at low oxygen pressures, only aluminum oxide is formed,[50] although the existence of nickel-oxygen interaction has also been proposed.[48] Very recent STM images where the $Ni_3Al(111)$ substrate is imaged through the thin aluminum oxide film give evidence that the order of the oxide covered $Ni_3Al(111)$ interface is much higher than the clean surface.[37] These results suggest that the decrease of the LRO at the clean surface may be due to the reduced coordination of the atoms at the surface. We do not rule out that a disordered state may be formed at high temperatures and frozen in during the cooling down to room temperature. Unfortunately, it was not possible to control or change the cooling rate precisely during our experiment. We are preparing a new setup in which the sample heating/cooling rate can be controlled. In forthcoming experiments, the dependence of the order/disorder with the temperature and the possible existence of an order/disorder phase transition will be investigated. Notwithstanding, we remark that the $Ni_3Al(111)$ surface presents a different order/disorder behavior than the Ni_3Al bulk. The disorder at the $Ni_3Al(111)$ surface is clearly another example of SID.

The geometrical features of our best models (Tables I and II) are in fair agreement with the values reported in the literature. Sondericker, Jona, and Marcus[13] reported that the Al atoms are 0.06 ± 0.03 Å above the plane of Ni atoms, which is in turn displaced 0.01 ± 0.03 Å inwards. In the LEED analysis of Sondericker *et al.*, second and deeper interlayer spacings were maintained at their bulk values.[13] In our analysis, the possibility of relaxations in the second and deeper layers have been considered. The outermost two layers are slightly shifted inwards—the mean positions of the Al and Ni sites of the first and second layers are relaxed, respectively, -0.02 ± 0.01 Å and -0.04 ± 0.01 Å—and the third and deeper layers remain at their ideal positions. Atoms at Al sites have a slightly lower position than atoms at Ni sites. However, we note that, due to disorder and segregation, there are many antisite atoms, and therefore the values of the rippling of this work and that of Sondericker *et al.*[13] cannot be compared directly. Considering the way the vertical displacement parameters were introduced in the models to simulate the disorder (see note 63), the values in this study correspond to an average of the rippling. Thus, the actual rippling at the $Ni_3Al(111)$ surface may be larger. In any case, it can be concluded that the relaxations at the $Ni_3Al(111)$ surface are very small.

It is interesting to compare the results of the $Ni_3Al(111)$ surface with those of the extensively studied NiAl(110) surface. This surface has also, ideally, the bulk stoichiometry, but there are conflicting experimental results. In a SXRD experiment,[17,23] some chemical disorder (less than 4%) and a rippled surface in qualitative agreement with previously reported results[51–55] were found. Indeed, STM images of the clean NiAl(110) show a well-ordered surface.[56] On the other hand, in another SXRD investigation,[57] a much larger rippling and a defective surface were determined. The defects consist of Al vacancies in the outermost four layers, Ni vacancies in the outermost layer, and 15% of Ni atoms on bridge sites, indicating a considerable disorder in the Ni sublattice at the surface. The disagreement between the different results obtained for the NiAl(110) surface may also be due to variations in the stoichiometry of the samples. In principle, the lower enthalpy of formation of NiAl ($\Delta H_{Ni_3Al}=-41$ kJ/mol and $\Delta H_{NiAl}=-59$ kJ/mol, respectively[19]) makes this phase much more stable and, accordingly, disorder in the bulk is hindered to a greater extent than in Ni_3Al. However, the stronger ordering tendency may also induce to a greater extent the segregation of defects to the surface.[39] Even new phases may develop due to the symmetry breaking at the surface, as found for the $Ni_{90}Al_{10}(110)$ surface.[40]

Other (111) surfaces of alloys isomorphous to Ni_3Al show very different behaviors. $Cu_3Au(111)$ has the stoichiometric composition, but after annealing at 723 K and cooling down, the surface is disordered. The ordering can be regained after a long annealing at 573 K for 20 h.[58] The $Cu_3Pt(111)$ surface can be prepared in an ordered or disordered state, depending on the annealing temperature, as it was revealed by LEED experiments.[59,60] The $Pt_3Sn(111)$ surface is ordered and has the bulk stoichiometry. The first layer is rippled, with the Sn atoms being 0.21 Å above the Pt atoms.[61] These differences are not fully understood yet, although there is a strong suggestion that at least some of the results may be related to deviations from the ideal stoichiometry.[58] To explain these effects, systematic studies of alloys with a well defined stoichiometry, going from the Al-rich to the Ni side, would be advisable and also temperature-dependent measurements to determine if there is a first- or second-order order/disorder transition at the surface.

V. SUMMARY

The atomic structure of the $Ni_3Al(111)$ surface has been investigated by surface x-ray diffraction. The atomic relaxations are in fair agreement with previous LEED results, but there is a large SID at the outermost surface layers. The ordering increases progressively with depth. The disorder has been explained in terms of chemical disorder at the surface and the possibility of segregation has also been considered, although the surface is stoichiometric overall. The possible implications of the preparation method or the exact sample composition in the final surface structure have been discussed. The SID is most probably intrinsic to the $Ni_3Al(111)$ surface and caused by segregation or a small off-stoichiometry of the bulk composition. These results are in disagreement with the theoretical predictions of Ref. 12.

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[63] The vertical displacements were assigned according to the atomic sites in an ordered $Ni_3Al(111)$ surface. Thus, a nickel atom which is in an aluminum site has the same displacement parameter as an aluminum atom which is in the aluminum site. Conversely, an aluminum atom in a nickel site has the same displacement parameter as a nickel atom in a nickel site.