Rippled surface structure and electronic and magnetic properties of $Ni_3Al(001)$

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Structural, electronic, and magnetic properties of $Ni_3Al(001)$ are investigated by the all-electron thin film full-potential linearized augmented plane wave method based on the local density approximation. A stable rippled surface atomic geometry is determined by atomic force and total energy calculations. The surface Ni atoms contract down to the bulk region by 4.2% of the bulk interlayer spacing while all of the other atoms including the surface Al atoms remain close to their bulk positions. The amount of rippling found by calculation (0.06 Å) is almost within experimental error (0.02 ± 0.03 Å). Charge densities, calculated work functions, and densities of states for the relaxed rippled and unrelaxed surfaces are reported. The spin polarized calculation predicts that the $Ni_3Al(001)$ surface is ''magnetically dead,'' unlike the bulk region.

I. INTRODUCTION

Low energy electron diffraction (LEED) experiments on intermetallic Ni-Al alloy surfaces have revealed rippled relaxations. Ni(Al) atoms in the NiAl(110) surface have been found to contract down (expand out) from the bulk truncated positions with a rippling of 0.22 Å (or 10.6% relative to the unrelaxed interlayer spacing).[1,2] For the $Ni_3Al(001)$ surface, there are two possible terminations: mixed Ni-Al and pure Ni compositions. It has been found in LEED experiments[3,4] and calculations[5,6] that the Ni-Al termination is more stable than the pure Ni one. The experiments also found that the first interlayer spacing d_{12} is contracted by 0.05 Å (2.8% of the bulk value 1.78 Å) and the second interlayer spacing d_{23} is bulklike; the surface Al atoms appear to be slightly displaced (0.02 ± 0.03 Å) outward with respect to the Ni atoms. It is curious that the rippling at $Ni_3Al(001)$ is much smaller than that of NiAl(110) in spite of the same composition at both surfaces.

These observations have challenged theoretical investigations in two points: (i) why is the rippling for $Ni_3Al(001)$ much smaller than that of the NiAl(110) surface? and (ii) what is the underlying mechanism for the relaxation? For the NiAl(110) surface, several theoretical/computational investigations have already been made. By use of the first principles full-potential linearized augmented plane wave (FLAPW) energy band method,[7] Lee *et al.*[8] obtained a stable surface geometry, which is in good agreement with the experimental data, and have given an explanation of the mechanism behind the relaxation in terms of charge transfer. Similar results on the relaxation of NiAl(110) have been obtained by Kang and Mele,[9] using the self-consistent pseudopotential method. Based on the embedded atom method (EAM),[10] Chen *et al.*[5] simulated the relaxation at various Ni-Al alloy surfaces. For NiAl(110), they obtained a larger rippling (0.33 Å) compared to the LEED data (0.22 Å). This trend also appeared at the $Ni_3Al(001)$ surface: the amount of rippling by the simulation (0.089 Å) is too large compared to that of experiment (0.02 ± 0.03 Å) due to the large outward relaxation of the surface Al atom. (In experiments, the Al atoms are observed to contract down slightly to the bulk region.) Similar behavior was seen in the EAM calculations by Foiles and Daw,[6] in which the Al atoms at the $Ni_3Al(001)$ surface relaxed outward by 0.06 Å. More recently, while Chulkov *et al.*[11] calculated the surface electronic structure of $Ni_3Al(001)$ by means of the linearized augmented plane wave method, they did not investigate the surface structure.

To deal with this situation, it is desirable to investigate the electronic and structural properties of $Ni_3Al(001)$ by use of a highly precise energy band method. Hence, we use the FLAPW method[7] based on the local density approximation (LDA).[12] In order to determine the stable geometry, the atomic structure is optimized with total energy and atomic force calculations.[13,14] The electronic structures, charge densities, and work functions, etc., for the relaxed rippled and unrelaxed $Ni_3Al(001)$ surfaces are calculated and discussed.

In addition to their attractive high temperature properties, Ni-Al alloys also have interesting magnetic properties which are very sensitive to their structures. Experiments have shown that bulk Ni_3Al is weakly ferromagnetic[15] with a small magnetic moment of $0.07\mu_B$ per Ni atom.[16] By a FLAPW calculation, it was confirmed that bulk Ni_3Al is weakly ferromagnetic, but the calculated Ni magnetic moments ($0.093\mu_B$,[17] $0.20\mu_B$,[18] and[19] $0.15\mu_B$) are higher than

TABLE I. The z position of atoms and the amount of relaxation with respect to the bulk position, Δz, of a relaxed nine-layer $Ni_3Al(001)$ slab for the spin-polarized case in units of Å.

Position	Atom type	z	Δz
S	Ni	6.900	−0.060
	Al	6.960	0
$S-1$	Ni	5.232	+0.012
$S-2$	Ni	3.491	+0.011
	Al	3.481	0
$S-3$	Ni	1.740	0
C	Ni	0.000	0
	Al	0.000	0

TABLE II. Angular momentum decomposed electronic valence charge in the muffin-tin sphere and magnetic moments in μ_B of a nine-layer $Ni_3Al(001)$ film for the unrelaxed and relaxed geometries.

Layer	Atom type	s	p	d	Total	Magnetic moment
			Unrelaxed			
S	Ni	0.40	0.32	8.36	9.09	0.00
	Al	0.65	0.61	0.13	1.42	
$S-1$	Ni	0.45	0.45	8.31	9.24	0.00
$S-2$	Ni	0.45	0.46	8.30	9.24	0.01
	Al	0.62	0.73	0.20	1.59	
$S-3$	Ni	0.45	0.46	8.30	9.24	0.01
C	Ni	0.45	0.46	8.30	9.24	0.01
	Al	0.63	0.72	0.20	1.59	
			Relaxed			
S	Ni	0.41	0.34	8.36	9.13	0.01
	Al	0.66	0.62	0.13	1.43	
$S-1$	Ni	0.45	0.46	8.31	9.26	0.06
$S-2$	Ni	0.45	0.46	8.30	9.24	0.13
	Al	0.62	0.72	0.20	1.59	
$S-3$	Ni	0.45	0.46	8.30	9.24	0.16
C	Ni	0.45	0.46	8.30	9.24	0.18
	Al	0.63	0.72	0.20	1.59	

the experimental value. Hence, another purpose of the present study is to investigate the magnetic properties of the $Ni_3Al(001)$ surface. We calculate charge and spin densities, layer-by-layer magnetic moments, and densities of states in the $Ni_3Al(001)$ film, and discuss the fine features of the surface magnetism of $Ni_3Al(001)$.

In Sec. II, we briefly describe our model and the method used. The results on the surface geometry of $Ni_3Al(001)$ and the electronic and magnetic properties are presented in Sec. III, as are discussions on the mechanism behind the surface rippling. A brief summary is given in Sec. IV.

II. MODEL AND METHODOLOGY

To investigate the surface properties, we approximated the $Ni_3Al(001)$ surface by a single slab consisting of nine layers. For the surface layer, we chose the composite Ni-Al surface, which has been shown to have lower energy than that of the 100% Ni surface, by both experiments[3,4] and calculations.[5,6] Since the calculated surface relaxations are known to depend very sensitively on the lattice constants[20] and LDA calculations usually result in smaller lattice constants, we determined the bulk lattice constant using the FLAPW method[7] so as to have an internally consistent bulk/thin film description. The Kohn-Sham equations incorporating the Hedin-Lundqvist exchange-correlation potential[21] are solved self-consistently.[7] The theoretical lattice constant determined by the LDA is $a_0=3.48$ Å, which is smaller than the experimental value[4] (3.56 Å) by 2.5%. It is expected that generalized gradient approximation[22] calculations would improve the agreement with experiment.

We started from an unrelaxed interlayer spacing with half of the calculated bulk lattice constant. The equilibrium surface geometry was then optimized by total energy and atomic force calculations which allow automatic structure optimization.[14] We assumed that we had found a fully relaxed structure when the force on each atom was less than 1 mRy/a.u. and the position did not change by more than 3×10^{-3} a.u.

The muffin-tin (MT) radii of Al and Ni atoms are set to 1.20 Å. Inside each muffin-tin sphere, charge (spin) densities and potentials are expanded in lattice harmonics with angular momentum up to $l=8$. The core electrons, including the $3p$ states of Ni, are treated fully relativistically and the valence electrons derived from the atomic $3d$, $4s$, and $4p$ orbitals are treated semirelativistically,[23] by dropping the spin-orbit term but keeping all the other relativistic terms in the Hamiltonian. Within the irreducible wedge of the two-dimensional Brillouin zone, eigenvalues and eigenvectors are calculated for 18 special k points. Self-consistency was assumed when the rms difference between the input and output charge (spin) densities was less than 2×10^{-4} electrons/(a.u.).[3]

III. RESULTS

The rippled geometry determined by total energy and force calculations for the Ni_3Al nine-layer slab is given in Table I for the spin-polarized case. We have also performed the calculations for the paramagnetic system, but there were no meaningful differences from those of the spin-polarized system. From this table, we find that all the atoms remain almost at their bulk positions except for the surface Ni atoms, which are relaxed into the bulk region by 0.06 Å. The amount of rippling is therefore 0.06 Å, which is almost within experimental error, and the contraction of the interlayer spacing (Δd_{12}) between Ni surface and subsurface is -4.2% (0.072 Å), which is 50% larger than the experimental value (-2.8%).

The overall features of our results are closer to the experiments than those obtained with the EAM calculations of Chen *et al.*[5] and Foiles and Daw,[6] which showed considerable outward relaxation of the surface Al atoms (Chen *et al.*, 0.039 Å; Foiles and Daw, 0.06 Å). The wrong tendency for the Al relaxation in their calculations is considered to be caused by an intrinsic defect of the EAM, namely, the use of parametrized potentials deduced from the bulk results, which is considered to overestimate the repulsive potential at the surface.

We have also performed similar calculations using the experimental lattice constant (3.56 Å). Although the amount of rippling at the surface layer is found to be similar to that obtained with the theoretical lattice constant, the calculated surface relaxation showed large discrepancies with experiment and also with those obtained with the theoretical lattice constant: Both surface Ni and Al atoms contracted considerably into the bulk regions (Ni by -19.2%, Al by -15.6%). The other atoms, including atoms in the $(S-3)$ layers, also contracted down into the bulk region—which is inconsistent with experiment. This result demonstrates that one should be careful in choosing the lattice constant to get consistent results in the LDA calculation.

Having established the rippled geometry for the $Ni_3Al(001)$ surface, we now focus on the possible mecha-

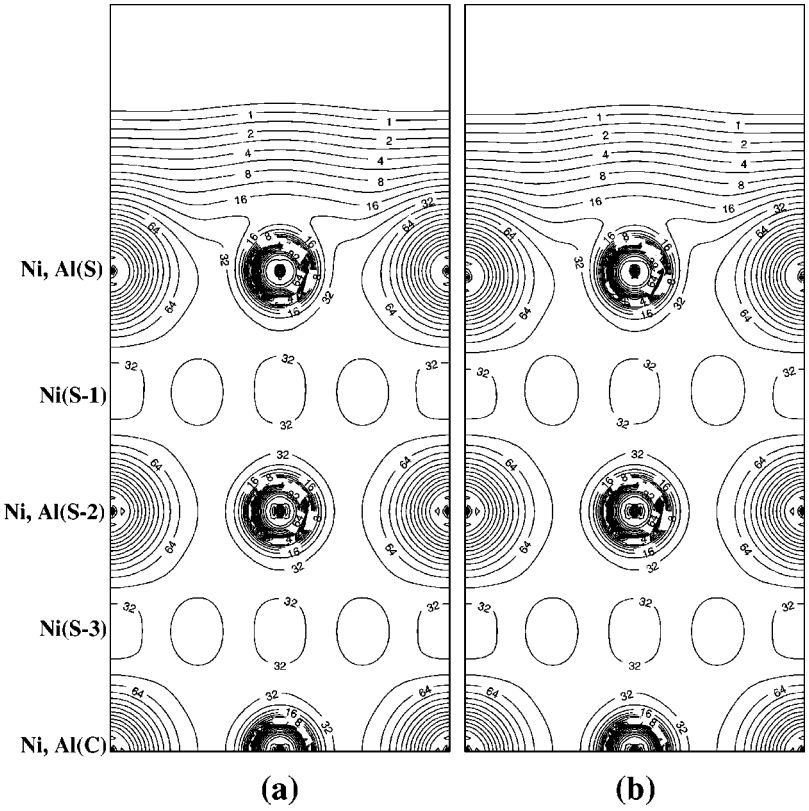

FIG. 1. Valence electronic charge density contour plots for (a) the unrelaxed and (b) the relaxed $Ni_3Al(001)$ surface geometries (with Δd_{Ni} −3.4% and Δd_{Al} 0.0%) on the (110) plane normal to the surface in units of $10^{-4}e/(\text{a.u.})^3$. Successive contour lines differ by a factor of $\sqrt{2}$.

nism behind the rippled relaxation, following the discussions for transition metal surfaces by Pettifor[24] and Fu *et al.*[25] In transition metals, the bulk lattice constant represents a balance of the inward force of localized *d* bonds and the homogeneous outward pressure of the *s*,*p* electrons. As the surface is created, the bulk equilibrium is destroyed. The *d*-*d* bonding between surface and subsurface atoms is enhanced and so the surface atoms contract down to the bulk region. For $Ni_3Al(001)$, the Ni atoms at the surface layer contract down as a result of the increased *d*-*d* bonding with the Ni atoms in the subsurface layer, which consists of all Ni atoms. The small contraction actually found theoretically and experimentally may well be the result of an opposite effect: the tendency to contract may be diminished by the more localized *d* electrons in the surface Ni atoms compared to bulk, as we can see from Table II, in which the number of valence electrons in each MT sphere is given for the relaxed and unrelaxed structures.

As for other metal surfaces, there is a spilling out of electrons into the vacuum region. The spill-out charge (mostly *s*,*p*-like) serves to alleviate the sudden discontinuity in creating a surface.[26] The electron charge density distribution in the vacuum region then becomes smooth and flat, as shown in Fig. 1. These spill-out electrons give an outward pressure to the surface Ni and Al atoms. However, the outward relaxation of the surface Al atoms is reduced by the more localized nature of the *s*,*p* electrons in surface Al atoms compared to other Al atoms, and this makes the surface Al atoms remain at the ideal bulk terminated position. This mechanism for the relaxation of the $Ni_3Al(001)$ surface, originating from the balance of inward *d*-*d* bonding and outward *s*,*p* pressure, is different from the NiAl(110) surface case, which has a large amount of rippling mainly caused by charge transfer. The calculated work function decreases from 5.01 eV for the unrelaxed surface to 4.97 eV for the rippled one. Note that this value of the work function is smaller than that (5.18 eV) of the NiAl(110) surface,[8] which has more open space into which the *s*,*p* electrons can spill.

Consider now the paramagnetic layer-by-layer density of states (LDOS) associated with each atom type for the relaxed geometry presented in Fig. 2. The LDOS for the spin-polarized case, which is not presented here, is almost the same as the paramagnetic one since the spin splitting is neg-

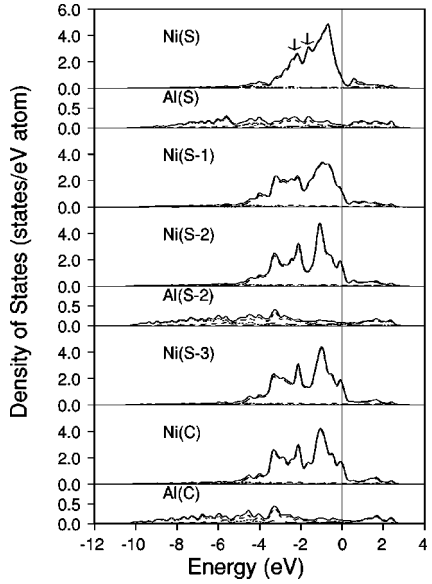

FIG. 2. Paramagnetic partial density of states associated with each atom type for relaxed $Ni_3Al(001)$ surface in units of states/eV atom. Dotted lines indicate *d* states and broken lines represent *s* (· · · ·) and *p* (—·—·—·—) states.

ligible as will be discussed below. The shape of the LDOS for the center (C), ($S-3$), and ($S-2$) layers is almost the same, but that for the ($S-1$) layer becomes blurred, which is a result of the reduced interlayer spacing due to relaxation. We find that the peaks in the DOS of surface Ni atoms (mostly contributed by d electrons), indicated by arrows, are located in the same energy regions as those of surface Al atoms (mostly contributed by p electrons). This suggests a stronger p-d hybridization between Al and Ni atoms in the surface layer than in the other layers.

We first discuss the magnetic properties by use of the paramagnetic DOS. From Stoner theory, an examination of the paramagnetic DOS at E_F for each atom type allows one to predict possible magnetic instabilities. If we compare the DOS at E_F of Ni atoms in each layer given in Fig. 2, we see that the value decreases by one-half on going from the center layer to the surface layer. Considering that the Stoner factor of bulk Ni_3Al is slightly greater than 1,[27] it is expected that the surface Ni is not magnetic at the $Ni_3Al(001)$ surface.

The above argument is confirmed by the spin-polarized calculations. The results of the calculated magnetic moments for the relaxed and unrelaxed $Ni_3Al(001)$ are summarized in the last column of Table II. The magnetic moments of the Ni atom for the relaxed (unrelaxed) system decreases from $0.18\mu_B$ ($0.01\ \mu_B$) for the center layer to $\sim 0.01\mu_B$ ($0.00\mu_B$) for the surface layer, which indicates that the $Ni_3Al(001)$ surface is essentially paramagnetic. The reason is that the increased hybridization between s,p electrons (mainly spilled-out p electrons in the surface layer) of Al and d electrons of Ni in the surface region screens the d-d interaction between Ni atoms. We note that the magnetic moments for the relaxed geometry are larger than those for the unrelaxed one. This is due to the increased d-d interactions between Ni atoms in the relaxed geometry.

IV. SUMMARY

The structural, electronic, and magnetic properties of $Ni_3Al(001)$ have been investigated by the self-consistent all-electron full-potential linearized augmented plane wave method. The stable rippled geometry, determined by total energy and atomic force calculations, results from the fact that the surface Ni atoms contract into the bulk region by 0.06 Å while the other atoms remain at their bulk positions. The calculated value of rippling for the spin-polarized case (3.4%,0.06 Å) is almost within experimental error (0.02 ± 0.03 Å). The underlying mechanism for the relaxation is explained by the balance of inward d-d bonding and outward pressure by s,p electrons.

The value of the paramagnetic DOS at E_F implies that the Stoner factor for the surface Ni atom is less than 1, and hence that the $Ni_3Al(001)$ surface is not magnetic. The spin-polarized calculation confirms this fact: the magnetic moment of the surface Ni atom for relaxed geometry is negligible ($\sim 0.01\mu_B$) while that of the center layer is $0.18\mu_B$. The magnetically dead surface of $Ni_3Al(001)$ is explained by the fact that the enhanced s,p,d hybridization in the surface region caused by the spilled-out s,p electrons from the surface Al atoms weakens the d-d interaction between Ni atoms.

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