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# The interaction of hydrogen with the (110) surface of NiAl

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## Abstract

The adsorption of hydrogen onto the (110) surface of the ordered alloy NiAl is being investigated experimentally and theoretically. At this stage, the experimental and theoretical results are complementary. Experiment reveals that the dissociative adsorption of atomic hydrogen is activated and indicates that the presence of H on the surface causes dramatic changes in the atomic positions of the Ni and Al atoms. Density functional theory for a (1 × 1) H overlayer identifies the H bonding site as the Ni–Ni bridge and predicts the surface rippling on clean NiAl(110) is removed by hydrogen.

**Keywords:** Alloys; Atom–solid interactions; scattering; diffraction; Atom–solid reactions; Hydrogen; NiAl; Surface relaxation and reconstruction

## 1. Introduction

The use of multicomponent catalysts offers the opportunity to tune the activity and selectivity required in a specific chemical process by changing the components and their concentrations. An outstanding example of a direct application of this philosophy is in the employment of bimetallic catalysts used in petroleum refining processes for the production of gasoline of high antiknock quality. Indeed, this application of bimetallic catalysis in petroleum refining has been the key factor in making

feasible ‘lead-free’ gasoline. Today, virtually every reforming unit in the world employs a bimetallic catalyst system [1].

While the fundamental questions concerning reactions on multicomponent systems have not changed since the early work on reforming catalysts [1], our experimental and theoretical capabilities have greatly improved. It is now possible to determine whether interactions of a molecule with a multiple component surface are dictated by the properties of the individual constituents of the surface, or by the global properties of the system. We have chosen to study the interaction of hydrogen with the surfaces of the intermetallic alloy NiAl. This alloy is a good candidate for testing concepts associated with hydrogen adsorption on alloy surfaces for several reasons.

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First, NiAl can be grown in large single crystals of well defined stoichiometry where highly ordered surfaces can be prepared. Fig. 1 shows the bulk CsCl structure on the left and the structure of the bulk truncated low index faces on the right. Because of this experimental accessibility, the clean surfaces of NiAl have been well characterized both experimentally and theoretically. The atomic positions and concentrations [2–8], the electronic properties of both the surface and the bulk [7–11], and the surface and bulk phonon dispersions [8,12,13] are all well-known providing a good base for the study of adsorbates.

Second, this alloy is an ideal test for the theory of dissociative adsorption of molecular hydrogen. According to theory and all present experimental data on single component systems, the existence of d holes (a high d type local density of states) at the Fermi energy are essential in this process [14]. As an  $H_2$  molecule approaches a metal surface, its  $1\sigma_g$  orbital feels a Pauli repulsion from the tails of the s

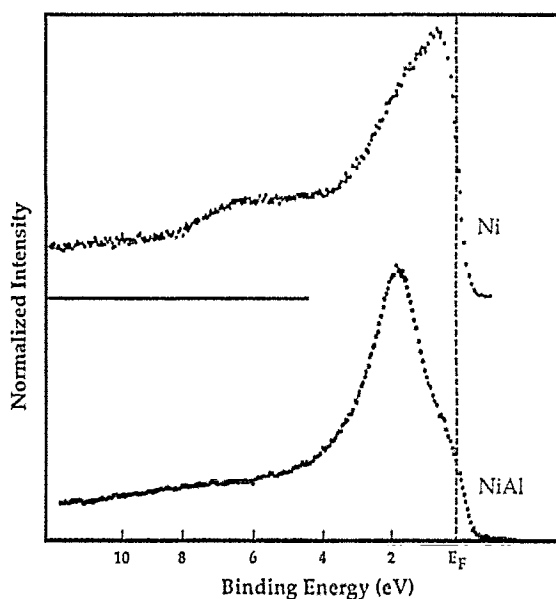


Fig. 2. The measured valence band of Ni (top) and NiAl (bottom) using X-ray photoelectron spectroscopy [11].

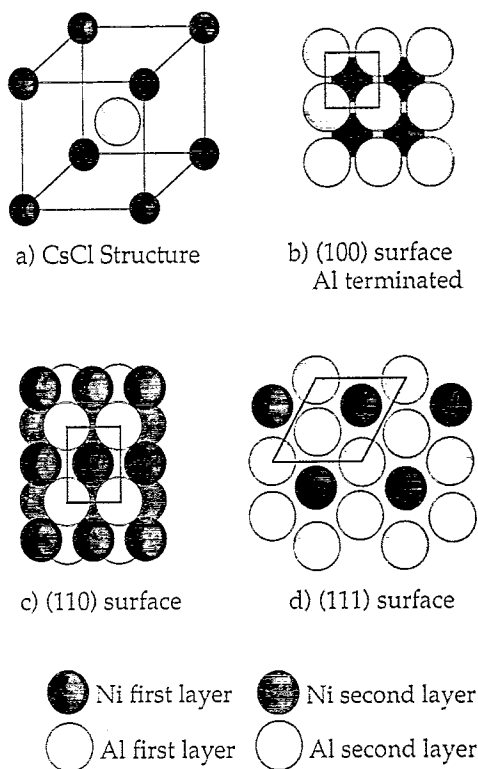


Fig. 1. Drawings of the NiAl structure for the bulk (a) and the three lowest index faces (b,c,d). The surface structures are shown with perfect bulk truncation.

electrons in the metal. If the metal has d holes, an s electron can be promoted to the d band reducing the Pauli repulsion, and thereby reducing the subsequent energy barrier. As expected, transition metals, like Ni, readily dissociate and adsorb hydrogen, while for noble or simple metals, like Cu or Al,  $H_2$  dissociation is an activated process [15]. In NiAl, the bonding is due to a strong hybridization of the Ni d and the Al p electrons which gives rise to a narrow Al(p)–Ni(d) band centered 2 eV below the Fermi level [9]. Therefore, unlike pure Ni, NiAl has a low density of d holes near the Fermi energy. Fig. 2 shows the measured density of states of both Ni and NiAl [11]. From this and the comparison to theory [9], it is apparent that the electronic properties of this alloy are more like those of a noble metal than those of a transition metal.

This paper describes the progress of a joint experimental and theoretical program aimed at understanding the interaction of hydrogen with alloy surfaces. We have started with the (110) face of NiAl as a first step in the study of the adsorption behavior of hydrogen on alloy surfaces. This face is terminated by 50% Ni and 50% Al (Fig. 1c) with the rows of Al atoms expanded out toward the vacuum and the rows of Ni atoms contracted toward the bulk resulting in a

rippled surface. In the end, we hope to have a detailed picture of the dissociation, bonding, surface modifications, diffusion, and recombination of hydrogen on the surface of a multicomponent system. At present, the experimental data and theoretical calculations are complementary in that the experiment has focused on the activated dissociation of hydrogen and the theory, using density functional theory together with the local density approximation (LDA) for the exchange–correlation functional, has investigated the resulting bonding and structure induced by the adsorption of atomic hydrogen. The next steps are to use the generalized gradient approximation extension to LDA to examine the activation barrier theoretically [16] and to do structural and vibrational determinations experimentally so that direct comparisons can be made.

## 2. Experiment

### 2.1. Experimental details

The experimental work done on this surface was performed in an ultrahigh vacuum chamber operating at a base pressure of  $1.0 \times 10^{-10}$  Torr. The sample was cleaned at regular intervals by sputtering with 1 keV neon ions for 20 min and subsequent annealing to 1125 K for 10 min. Sample cleanliness was verified with high-resolution electron energy loss spectroscopy (HREELS) and the presence of a sharp  $(1 \times 1)$  low-energy electron diffraction (LEED) pattern.

Both molecular and atomic hydrogen were dosed with the sample at 115 K. Atomic hydrogen was prepared via a hot tungsten filament at the end of a stainless steel tube through which the hydrogen was flowed. The sample was placed 3 cm in front of the tungsten filament for dosing. Because of the unknown efficiency of the filament, the exposure of atomic hydrogen is reported as arbitrary units of exposure (E), whose value is recorded as the Langmuir exposure based on the background pressure. Information on the amount of adsorbed hydrogen was obtained qualitatively from thermal desorption spectroscopy (TDS) and quantitatively from nuclear reaction analysis (NRA). Modifications of the surface symmetry were monitored with LEED.

### 2.2. Results

Exposure to  $H_2$  at both 115 and 300 K resulted in no adsorbed hydrogen as judged by thermal desorption, LEED, and vibrational spectra. Atomic hydrogen does adsorb to this surface, therefore *dissociative adsorption of molecular hydrogen is an activated process on the rippled NiAl(110) surface*. Subsequent experimental and theoretical evidence that will be presented shows that the presence of the atomic H on the surface causes a restructuring of the NiAl(110) surface. It is possible, therefore, that the potential energy surface for dissociation of the incoming H is different from the potential energy surface for recombination and dissociation [17].

At low exposures of atomic hydrogen, there is a single desorption peak at 300 K which decreases in temperature with increasing coverage. As shown in Fig. 3, the desorption temperature for  $H_2$  from NiAl(110) is closer to the desorption temperature for  $H_2$  from Cu than it is from either Ni or Al. The desorption order and the desorption energy can be extracted from the data using a modified Arrhenius plot [18]. At the lowest coverages, this analysis yields a desorption energy of  $0.54 \pm 0.03$  eV with second-order kinetics. As the coverage is increased, both the desorption energy and the order of kinetics decrease until, by an exposure of 10 E, the desorp-

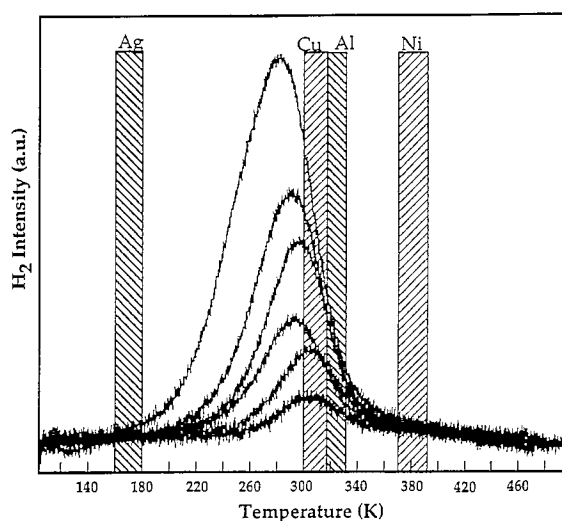


Fig. 3. Thermal desorption spectra of  $H_2$  from NiAl(110) as a function of H coverage. Overlaid on the data are the temperatures at which  $H_2$  desorbs from Ag, Cu, Al, and Ni.

tion energy is  $0.35 \pm 0.04$  eV and the order of kinetics approaches one. A second desorption peak developing at a slightly lower temperature, not well resolved in thermal desorption, could be responsible for this apparent change in kinetics. Contamination at the higher coverages could also be a problem.

At low exposures of atomic hydrogen, the LEED pattern remains a strong  $(1 \times 1)$ . In the exposure range of 10 to 20 E, a very weak  $c(2 \times 2)$  LEED

pattern is observable which is shown in Fig. 4a. The  $I$ - $V$  characteristics of the  $(1, 0)$  and  $(0, 1)$  spots in this  $c(2 \times 2)$  regime are different from the clean surface, with the peaks shifted to higher energy by as much as 7 eV (Fig. 4b). Qualitatively, an upward shift in energy is consistent with a reduction of the ripple in the surface [19], but a quantitative comparison of the data shown in Fig. 4b with unpublished  $I$ - $V$  curves for a nonrippled  $(110)$  surface is not very

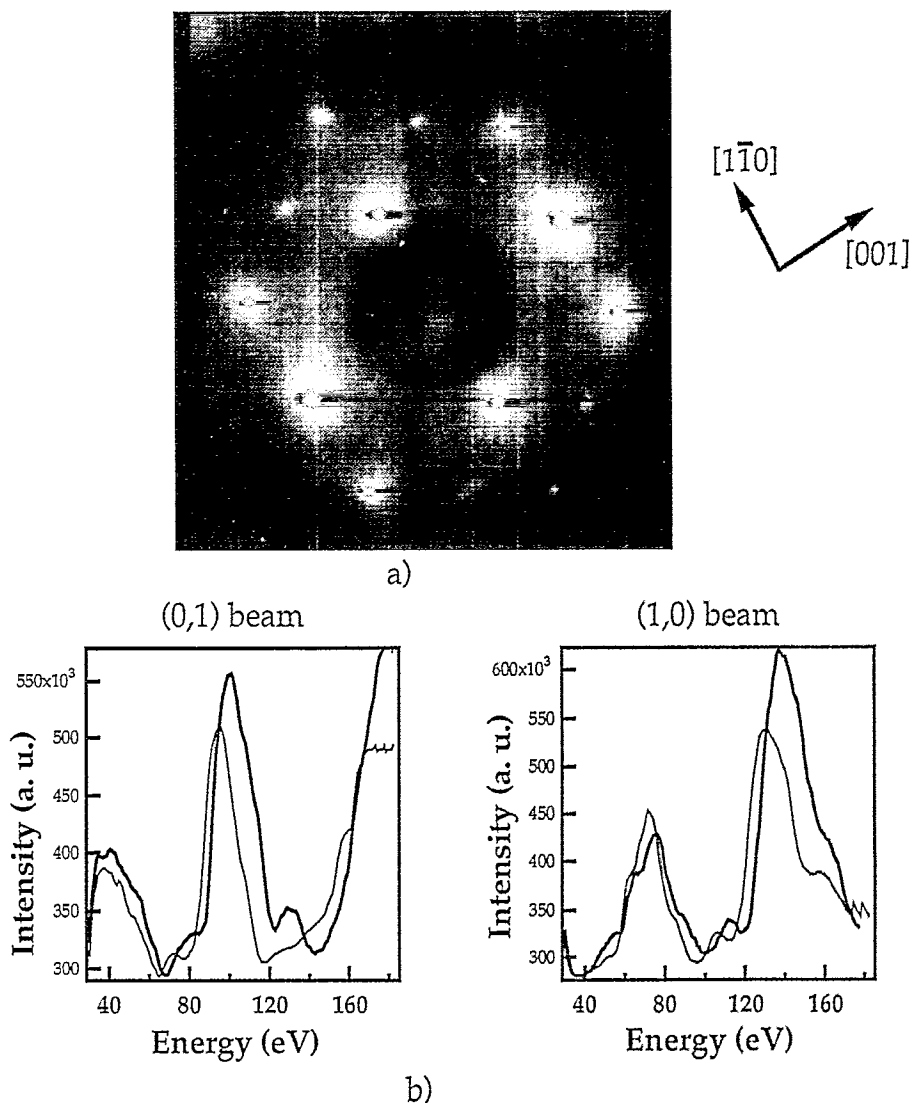


Fig. 4. (a) LEED pattern showing the H-induced  $c(2 \times 2)$  structure. The beam voltage was 63 eV and the H exposure 15 E. (b) The change in the  $(0, 1)$  and  $(1, 0)$  beams with this exposure to hydrogen. The heavy lines are for the H-covered surface.

good [20]. Above this coverage region, the LEED pattern returns to a  $(1 \times 1)$  but with a slightly higher background.

A preliminary investigation of the absolute coverage of hydrogen has been performed. NRA indicates that, in the dose regime yielding a  $c(2 \times 2)$  LEED pattern, the surface is covered by approximately  $1/2$  monolayer (ML) of hydrogen. That is to say there is one hydrogen atom per two surface unit cells. Additionally, coverage measurement at larger doses suggest that the saturation coverage is 1 ML.

### 3. Theory

#### 3.1. Theoretical details

The theoretical study of clean and hydrogen-covered NiAl(110) is done using density functional theory. The electronic wave functions are expanded in a plane wave basis with a kinetic energy up to 50 Ry. The surface is modeled by a five-layer slab, the surfaces of adjacent slabs are separated by 12 Å of vacuum. 32 special  $k$ -points are included in the entire first surface Brillouin zone corresponding to the  $(1 \times 1)$  surface unit cell. The Ni and Al atoms are described by norm-conserving pseudopotentials of the Troullier–Martins [21] and Bachelet–Hamann–Schlüter [22] type respectively. H is described by the bare Coulomb potential of the proton. The one-electron non-relativistic Schrödinger equation is solved by means of alternating direct minimization steps [23] and subspace rotations [24]. The  $k$ -summation is stabilized by employing a Fermi broadening with  $k_B T_{\text{el}} = 0.1$  eV. The LDA [25] is used for the exchange and correlation. The theoretical lattice constant and bulk modulus of the NiAl crystal are determined to be 2.845 Å and 175 GPa in good agreement with the experimental values, 2.887 Å and 158 GPa [26,27]. Note that zero-point vibrations are not taken into account in the theoretical values. All slab calculations are done at the theoretically determined lattice constant.

#### 3.2. Results

The energy of formation for the unrelaxed (110) surface is 2.0 J/m<sup>2</sup> (1.44 eV per  $(1 \times 1)$  unit cell).

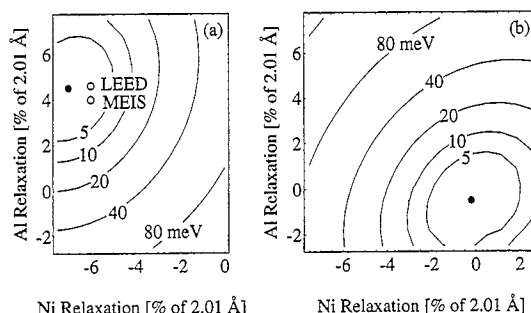


Fig. 5. The potential energy per  $(1 \times 1)$  unit cell for: (a) The clean NiAl(110) surface and; (b) the 1 ML  $(1 \times 1)$  H-covered NiAl(110) surface. The potential energy is calculated as a function of the relaxation (in percent of the unrelaxed interlayer distance) of the Ni and Al atoms in the surface layer. The closed circles mark the equilibrium relaxations (at which point the potential energy is set equal to zero). The open circles indicate experimentally determined relaxations of the clean NiAl(110) surface (LEED: Ref. [2] and MEIS: Ref. [4]).

Allowing the Ni and Al atoms in the surface layer to move away from their bulk-truncated positions leads to a sizable reduction in the surface energy of 0.13 J/m<sup>2</sup> (0.09 eV per  $(1 \times 1)$  unit cell).

Fig. 5a shows a contour plot of the change in the total energy as a function of the vertical positions of the Ni and Al atoms in the surface layer with atoms in underlying layers kept at their bulk-truncated positions. The equilibrium Ni and Al relaxations are  $-7\%$  (inwards) and  $+4.5\%$  (outwards) of the unrelaxed interlayer separation respectively. Also indicated in Fig. 5a are the results of LEED and MEIS experimental studies [2,4]. The agreement is seen to be quite good.

Turning to the H-covered NiAl(110) surface, the present results of the modeling of a 1 ML  $(1 \times 1)$  H overlayer are described. The experimentally observed H-induced  $c(2 \times 2)$  structure will be the subject of future work. The structure of the  $(1 \times 1)$  H-covered NiAl(110) surface is determined from calculations involving the full relaxation of the surface NiAl layer and the  $(1 \times 1)$  H overlayer. The lateral position of the H within the surface unit cell is varied to ensure that the global minimum – the equilibrium structure – is found. 1 ML of  $(1 \times 1)$  H leads to H bonded slightly asymmetrically in the Ni–Ni bridges. The H sits 0.95 Å above the Ni row tilted 0.16 Å in the  $[1\bar{1}0]$  direction, away from the plane containing the Ni atoms and the  $[110]$  surface

normal, with a H–Ni distance of 1.72 Å. This tilting away from the symmetric Ni–Ni bridge position is associated with an energy gain of a few meV, and will therefore be neglected below. Associated with the 1 ML ( $1 \times 1$ ) H overlayer is a pronounced change in the Ni and Al relaxations. This is investigated in Fig. 5b, where the potential energy of the 1 ML ( $1 \times 1$ ) H-covered surface is given as a function of the surface layer Ni and Al relaxations. All of the Ni and Al positions are held at the bulk-truncated positions with only the surface atoms being allowed to relax, and the H is fixed laterally in the Ni–Ni bridge, with full relaxation of the H height above the surface included. Fig. 5b clearly shows that the presence of the H removes the rippled relaxation of the clean NiAl(110) surface presented in Fig. 5a. For single component metal surfaces, Baddorf et al. [28] have concluded from LEED  $I$ - $V$  data that H removes the interplanar contraction on Cu(110) and Feibelman and Hamann [29] have shown theoretically that atomic H will bring the first interlayer spacing in Rh(100) back to the bulk-truncated value. However, no experiment or theory exists for a rippled or multicomponent surface.

### 3.3. Discussion

The nature of the rippled relaxation of the clean NiAl(110) surface is discussed thoroughly by Kang and Mele [30]. The volume of bulk NiAl comes about through a competition between Ni(d)–Al(p) hybridization and the kinetic energy of the delocalized Al sp electrons. The former drives the bulk towards a small volume while the latter drives it towards a large volume. The two forces are in balance in the bulk at the equilibrium volume, but the truncation of the bulk, creating the (110) surface, disturbs this balance. A Ni (Al) atom positioned in the surface layer loses 2 out of the 8 nearest neighbor Al(Ni) atoms that it has in bulk. This reduces the Ni(d)–Al(p) hybridization and, consequently, the energy gain associated with hybridization. If the entire first layer, composed of 50% Ni and 50% Al, relaxes inward, decreasing the nearest neighbor distance, the hybridization energy lost because of the reduction in the number of neighbors at the surface can be regained. At the same time, however, the electron charge in the region between the first and second

layers would be compressed (to first order not allowing the electronic wavefunctions to adapt to the atomic relaxation, simply scaling them in the interlayer region). This leads to an energy increase through the kinetic energy term and thus counteracts the inward relaxation. The hybridized Ni(d)–Al(p) states have the majority of their weight of the Ni sites due to the very strong and localized attractive potential at the Ni. This means that, although the Ni and Al surface atoms have lost the same number of neighbors, more hybridization energy will be gained by an inward relaxation of the Ni atoms than by the Al atoms. This is the origin of the rippling at the surface. Because of the asymmetry in the spatial weight of the hybridized states, only the surface Ni atoms relax inward. The surface Al atoms relax outward to allow a release of the compressed electron charge between the otherwise inwardly relaxed first and second layer. The outward relaxation of the surface Al atoms by 4.5% relative to their truncated positions (11.5% relative to the relaxed Ni position) only increases the Ni–Al distance within the rippled surface layer by 0.5% while the inwards relaxation of the Ni by 7% leads to a 5% decrease in the Ni–Al distance from the first to the second layer. Consequently, the relaxation of the Al does not reduce the hybridization dramatically but does reduce the kinetic energy.

The balance of the competing effects is altered when hydrogen is adsorbed. As mentioned, the adatoms bridge the Ni atoms along the [001] direction of the surface. The H s electron bonds strongly to the Ni d electrons and in part makes up for the Al neighbors lost by the Ni due to the formation of the surface. The small hydrogen atom is free to move perpendicularly to the surface and thereby adapt to precisely that amount of hybridization that is desired by the surface Ni atoms. This is energetically more favorable than relaxing the Ni atom inward as relaxation is associated with the compression of the interlayer electronic charge as discussed for the clean NiAl(110) surface. Therefore, upon adsorption of the H in the Ni–Ni bridge positions, no Ni relaxation occurs, and as a consequence, the Al atoms need not relax outward to release any compression of the interlayer electron charge. The result of adsorbing H on the NiAl(110) is therefore to remove the rippled relaxation.

#### 4. Summary

The chemical properties of NiAl(110) are dictated by the alloy electronic properties. There is an activation energy barrier for the dissociative adsorption of molecular hydrogen onto the rippled NiAl(110) surface, and the desorption behavior of atomic hydrogen does not resemble desorption from either Ni or Al. The theoretical investigation of the 1 ML ( $1 \times 1$ ) H overlayer predicts that the H bonds in the Ni–Ni bridge and removes the rippled relaxation seen on the clean surface.

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