PHYSICAL REVIEW B, VOLUME 65, 125418

Structure and dynamics of atomic hydrogen on NiAl(110)

M. Konôpka and I. Štich
Center for Computational Materials Science (CCMS), Department of Physics, Slovak University of Technology (FEI STU), Ilkovičova 3, 812 19 Bratislava, Slovakia

K. Terakura
JRCAT, Angstrom Technology Partnership (ATP), 1-1-4 Higashi, Tsukuba, Ibaraki 305-0046, Japan

(Received 11 September 2001; published 13 March 2002)

Motivated by recent experiments we present an extensive theoretical study of structure and dynamics of hydrogen atomically adsorbed on the NiAl(110) surface. The study is performed in the framework of *ab initio* density-functional theory (DFT) molecular dynamics. DFT calculations indicate that at mono-layer coverage hydrogen adsorbs in slightly asymmetric positions near the Ni-Ni bridges and reduces the surface ripple present on the clean surface. At variance with recent electron energy-loss spectra (EELS) experiments which locate the hydrogen related vibrational features at anomalously low frequencies of 49.5 meV, present simulations indicate that hydrogen exhibits frequencies in the ordinary range of ~130 meV but this feature remains hidden to the EELS probe due to very weak dipole moment. The possible nature and origin of the 49.5-meV feature is discussed.

DOI: 10.1103/PhysRevB.65.125418 PACS number(s): 68.43.−h, 68.35.Ct

I. INTRODUCTION

NiAl(110) represents a prototypical alloy surface. Very clean and stable surfaces can be prepared in laboratory. The surface, composed of constituents with very different chemical properties, maintains the bulk stoichiometry. In addition, bimetallic alloys play an important role as industrial catalysts.

The clean surface has been extensively studied in the past.[1–9] Bulk NiAl has a CsCl type of structure. The (110) surface exhibits no major reconstruction, the most prominent feature being a downward contraction of (top layer) Ni atoms and an outward expansion of Al atoms. At 130 K, the interlayer spacings are changed by −3.95% (+5.45%) for the top Ni-Ni (Al-Al) distance relative to the bulk layer spacing, giving rise to a large surface ripple of 0.192 Å.[1,9] The surface vibrational structure shows an acoustic resonance at 19 meV (an in-phase motion of Ni and Al atoms) and an optical surface phonon at 27 meV (an out-of-phase motion of Ni and Al atoms).[3,5,7] These vibrational features will be sensitive to the details of atomic arrangement on the surface, such as the magnitude of the surface ripple.

Experimental studies have shown that the magnitude of the surface ripple may be controlled by adsorption of hydrogen.[8–11] A very thorough study of hydrogen adsorption induced changes of static and dynamical properties of the NiAl(110) surface exists.[8,11] The model which emerged from those studies was that hydrogen behaves as an effective potential distributed homogeneously across the surface. Consequently, increased hydrogen coverage results in monotonic changes in all properties. In particular, the surface ripple was found to smoothly reduce from 0.19 to 0.11 Å. As a consequence of this structural change the work function is reduced by 0.6 eV. Similarly, adsorption of hydrogen causes an increase of the frequency of the surface phonon from 27 to 33 meV, in line with the reduction of the surface ripple and consequent increase in the Al force constant. Experimentally, the exact hydrogen position is fairly poorly determined; the position being in the Ni-Ni bridge, 0.6–0.8 Å above the Ni row. The hydrogen induced changes in substrate dynamics were so far in line with the findings from structure and work-function studies. However, a very peculiar hydrogen dynamics was inferred from electron energy-loss spectra (EELS) measurements which deviates from this coherent simple picture. At low coverages no hydrogen-related signal could be detected. This was attributed to quantum delocalization of hydrogen along the Ni rows over this surface at low coverages. The idea that hydrogen can be delocalized over a metal surface[12] has been suggested for several systems. On NiAl(110), only well above half coverage did a measurable hydrogen induced feature start to appear at a frequency of 49.5 meV. Such a low hydrogen frequency is anomalous as on most metal surfaces EELS locates hydrogen features at much higher frequencies in the region 75–170 meV.

On the theoretical side Hammer *et al.*[10] performed a density-functional theory (DFT) study of clean and H-covered NiAl(110) surfaces. They found the clean surface to be rippled; −7% relaxation of the top Ni atoms and +4.5% relaxation of the top Al atoms. For the hydrogen-covered surface the equilibrium H position was found near the Ni-Ni bridge, 0.95 Å above the Ni row. In their study adsorption of a monolayer of hydrogen completely removed the ripple. Hence the magnitude of the ripple on the clean surface, its decrease upon hydrogen adsorption as well as the hydrogen radius are all overestimated compared to the experimental values. A hydrogen frequency perpendicular to the surface of 135 meV was found. This theoretical finding is in significant disagreement with the EELS value of 49.5 meV.

Theoretical modeling[10] appears to describe at least qualitatively the structural trend towards the decrease of the surface ripple upon hydrogen adsorption. However, it fails completely at a description of the hydrogen induced mode experimentally found at 49.5 meV. In an effort to reconcile the theoretical and experimental findings Hanbicki *et al.*[8,11] drew analogies with the behavior found for hydrogen over low-index Ni surfaces.[13] In this system a strongly anharmonic coupling parallel and perpendicular to the surface is operational. This anharmonic coupling is responsible for ~20% reduction in vibrational frequency of hydrogen, compared to the value from harmonic treatment. Hanbicki *et al.* conjectured that a similar mechanism may be behind the ~60% lowering of the H vibration on the NiAl(110) surface.

The purpose of this paper is to shed light on the peculiar structural and dynamical properties of this surface system. Our theoretical study goes well beyond the initial theoretical modeling of Hammer *et al.*[10] To elucidate the structural properties we have performed static relaxation with more layers allowed to relax (9) than in Ref. 10 (1). However, the main part of this work is the study of surface dynamics using techniques of *ab initio* (within DFT) molecular dynamics (MD). This is very important in order to understand and interpret the experimental results as well as the limitations and failures of the previous theoretical treatment.[10] It is well known that surface atoms can exhibit large anharmonicities in their motion along the surface plane. In such a case the dynamics cannot be studied using harmonic or quasiharmonic treatment, the basis of the hypothesis of Hanbicki *et al.*[8,11] The potential-energy surface of anharmonic systems is much more complicated than in a harmonic case. Static calculations and parametrization of an anharmonic system to obtain quantities of interest, such as vibrational frequencies or anharmonic shifts, may become impractical. Hence a method of choice is the *ab initio* MD.[14] Such an approach does *not* rely on harmonic approximation. In addition, the MD trajectories sample a much wider part of the underlying potential-energy surface (PES) and contain, at least in principle, the information on the entire vibrational spectrum of the model. MD in its *ab initio* version carries information also on the electronic properties which gives access to surface dipole moments which are of crucial importance for understanding the EELS spectra.[15,16]

The paper is organized as follows. The next section gives details of the simulation techniques used. The results obtained are presented in Sec. III, followed by a discussion in Sec. IV. The summary of our findings is in Sec. V.

II. MODEL AND TECHNICAL DETAILS

We have studied both clean and hydrogen covered NiAl(110) surfaces. Only a monolayer hydrogen coverage was considered in this study. We use a slab geometry five layers thick (also nine layers in the static calculations) and a primitive 1×1 surface unit cell to model the surface. For covered slabs, we consider the hydrogen overlayer adsorbed only on one side of the slab. This allows us to obtain clean-surface data from one side of such a slab and hydrogen-covered data from the other side. Nevertheless, for comparison, we have performed also independent simulations for the five-layer clean surface.

In MD simulation and in static calculations with covered slabs, all atoms were allowed to move in each direction. In the static calculation with the clean five-layer slab, relaxation of all atoms was allowed only in the direction perpendicular to the surface. Each primitive cell contains a single Ni and Al atom per layer. A consequence of the atomic arrangement used is that only infinite-wavelength surface vibrations, i.e., Γ-point phonons, can be studied. This is sufficient for the present purpose because the experimentally measured spectra[8,11] have also been collected at the Γ point and have been shown to exhibit only a minor dispersion in the surface unit cell. The height of the unit cell was taken to be 16 Å (28 Å in calculations using the nine-layer slab). Figure 1 shows the surface cell with the hydrogen atom used in the simulation along with the Cartesian axes. Our model yields a zero-temperature lattice constant of 2.870 Å. In all our calculations we use lattice parameter of 2.876 Å which includes the minor effect (+0.006 Å) of thermal expansion.[11,18] The experimental value of 2.8870 ± 0.0001 Å (Ref. 17) agrees very well with our theoretical value.

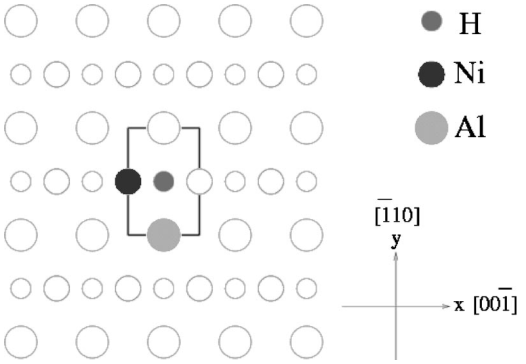

FIG. 1. Top view of the NiAl(110) surface at a monolayer hydrogen coverage. Only hydrogen atoms and atoms in the top layer are shown. The unit cell used in the simulation is in the frame, the atoms within it are filled. For simplicity, hydrogen atoms are shown exactly at the Ni-Ni bridge sites although, in reality, it is not an equilibrium position.

The dynamics of ions was treated classically. The rationale was that hydrogen adsorbed at full coverage forms an ordered structure which, unlike at low coverages, is not likely to be affected by quantum tunneling.[8] In addition, a full understanding of the dynamics in classical approximation is a necessary prerequisite to any study including quantum fluctuations. A time step of 1 fsec was used in the integration of equations of motion. The total simulation time in the dynamical simulations was 3 psec. This simulation time was found sufficient to extract the dominant dynamical features. The system was thermostated by a Nosé-Hoover thermostat at the experimental temperature of 130 K.[8,11]

The ionic forces and energies were calculated within DFT in plane-wave pseudopotential formulation.[14,19] We use the PW91 variant of the generalized gradient approximation (GGA) for the exchange-correlation potential.[20] The Brillouin zone of the surface unit cell was sampled at a mesh of 4×4 Monkhorst-Pack k points.[21] We use a relatively large electronic smearing of 0.5 eV. Our tests show that this large value of electronic temperature has only a negligible effect on our results. Because of the presence of the localized Ni $3d$ states we make use of ultrasoft pseudopotentials.[22] This allows us to perform converged calculations with a plane-wave cutoff of 300 eV. We use the density-mixing algorithm[23] to relax the electronic degrees of freedom.

III. SIMULATION RESULTS

A. Static relaxation: Surface ripple

The dominant structural feature of the NiAl(110) surface is the ripple which, experimentally, is found to reduce significantly upon hydrogen adsorption. The static calculations have been performed on slabs with both thicknesses (cf Sec. II). We found very good agreement between results obtained from the clean five-layer slab and from the clean side of the H-covered nine-layer slab,[24] indicating that the calculation is well converged with respect to the slab thickness. Below we report results obtained from the thicker slab.

We start the relaxation from a bulk-terminated surface and let all atoms in the slab relax. We use the definition from Ref. 9 for the surface ripple,

$$|[\Delta d_{12}(\mathrm{Ni}) - \Delta d_{12}(\mathrm{Al})]|/d_0, \tag{1}$$

with $\Delta d_{ij}(X)$ being the difference between the relaxed and unrelaxed spacing of layers i and j of element X and d_0 the bulk interlayer spacing. We found the surface ripple of 0.102 Å, i.e., 4.99% of the bulk interlayer spacing. The general trend is in agreement with experiment but quantitatively our value of 4.99% is ~50% smaller than the experimentally found 9.5%. On the other hand, the value 11.5% calculated by Hammer *et al.* in their previous theoretical study[10] exceeds the experimental value. In our model, the relaxation of the first Ni-Ni (Al-Al) spacing is -3.06% (1.93%). The second interlayer ripple is also significant: 0.061 Å (3.01%), again with the Al-Al distance larger than Ni-Ni. The experiment[9] yields the value of 0.95%. For the third interlayer spacing we find a ripple of 0.021 Å (1.05%), however, now with the Al-Al distance smaller than the Ni-Ni, while the experimental value is 0.00%. All this points to the sensitivity of the magnitude of the surface ripple to the details of the theoretical model and possibly also to the experimental uncertainties involved. Note also that our theoretical results are obtained at zero temperature (except the inclusion of the effect of thermal expansion) while the experiment was done at 130 K. Experiments[1,9] show that the ripple should increase slightly with temperature.

We started the static relaxation with adsorbed hydrogen laterally positioned in the Ni-Ni bridge. We first found a relaxed structure with hydrogen at this site 0.926 Å above the top Ni rows. However, further calculations showed that this was a saddle-point structure and the true equilibrium hydrogen position is not precisely in the Ni-Ni bridge but rather in an asymmetrical (i.e., lower symmetry) position displaced by 0.326 Å from the bridge in the $\overline{1}10$ (or opposite) direction. For this true equilibrium structure, hydrogen was found 0.908 Å above the top Ni layer. The energy difference between the relaxed saddle-point structure and the equilibrium one is 0.0113 eV (131 K in temperature units, i.e., very close to the temperature in experiments in Refs. 8 and 9 and in our MD simulation). The inset of Fig. 3(b) shows a one-dimensional cut through the saddle-point PES, i.e., the dependence of the total potential-energy variation on the hydrogen y displacement from the symmetric position (all other coordinates fixed, only hydrogen is allowed to relax in the z direction). The substrate atoms are held in positions obtained from the relaxed saddle-point structure. This double-well PES will have pronounced dynamical consequences as will become apparent from our MD simulation. We have found that the top space ripple is only partially removed upon hydrogen adsorption: 0.056 Å (2.74%), with the Ni-Ni (Al-Al) distance relaxed by -2.35% (0.39%). These results agree qualitatively with the experimental values: -3.05% (2.30%) for the Ni-Ni (Al-Al) distance. We find a surprisingly good agreement with experiment in the relative decrease of the ripple upon hydrogen adsorption. Experimentally upon hydrogen adsorption the ripple decreases to 56.9% of the clean-surface value. The calculated value is 54.9%. We found a similar agreement also for the second layer ripple. Another surprising finding for the covered surface is that although the first Al-Al spacing is wider than the Ni-Ni spacing, the Ni outermost layer is positioned more outwards to vacuum than the Al-Al outermost layer. This feature arises from the corrugations of the layers[24] as follows: $\Delta d_{11}(\mathrm{Ni,Al}) = 0.014$ Å while $\Delta d_{22}(\mathrm{Ni,Al}) = 0.069$ Å.

The lateral displacement of the equilibrium hydrogen position by 0.326 Å from the Ni-Ni bridge is about twice that reported in Ref. 10 (0.16 Å). Also, the authors report a complete removal of the surface ripple upon hydrogen adsorption which is in disagreement with experiments and also our theoretical results. This disagreement may arise from allowing only hydrogen and the upper metallic layer to relax in the calculation in Ref. 10 (see also Sec. IV).

B. Surface dynamics

Thus far, we have demonstrated that simulation is able to reproduce at least qualitatively the structural trends found experimentally. Nevertheless, a complete picture can only come from understanding the dynamics. Experimentally, part of the changes in surface dynamics upon hydrogen adsorption can be understood in terms of reduction of magnitude of the surface ripple. However, the anomalously low hydrogen-related feature located by EELS at 49.5 meV requires more attention.

In order to extract the surface and adsorbate dynamics from our MD simulation we have applied several techniques. Pictorial insight may be gained from computer graphics animation of MD trajectories.[25] The most straightforward quantitative analysis is based on velocity correlations

$$Z(\tau) \propto \langle \mathbf{v}(\tau) \cdot \mathbf{v}(0) \rangle. \tag{2}$$

In formula (2) $\mathbf{v}(t)$ is either a $3N$-dimensional vector of velocities or a given Cartesian component; N being the number of atoms whose dynamical properties are sought. $\mathcal{Z}(\omega)$, the Fourier transform of $Z(\tau)$, gives the vibrational spectrum. Obviously, the advantage of the MD approach is that *no* harmonic approximation is involved. There are two possible limitations inherent in this type of analysis. First, very long simulations are required if features very close in energy are to be resolved. The other disadvantage is that formula (2)

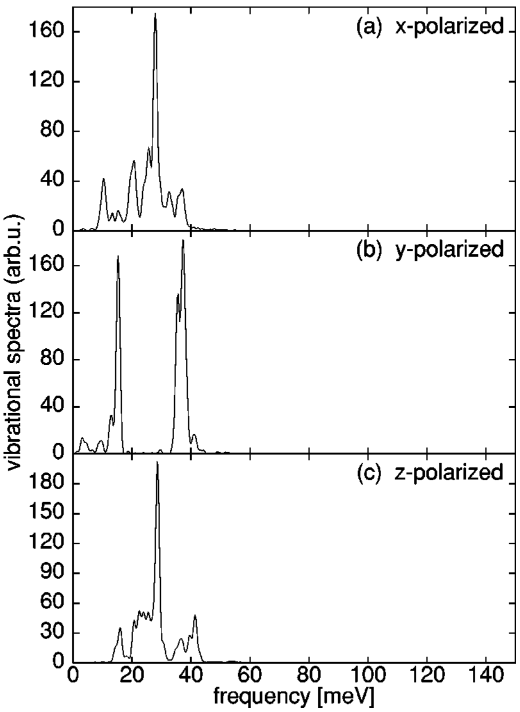

FIG. 2. Spectra of nuclei vibrations for the clean NiAl(110) surface. (a) *x* polarized, (b) *y* polarized, and (c) *z* polarized.

yields only the energy spectrum and no vibrational eigenvectors. Both limitations are alleviated by signal processing methods, such as MUSIC or its self-consistent improvement.[26,27] On the other hand, the limitation of MUSIC is its reliance on harmonic approximation. In the present study we have used the self-consistent MUSIC analysis mainly to analyze several quasiharmonic modes.

We first verify spectra obtained from the clean surface velocity autocorrelations shown in Fig. 2. In the absence of impact scattering, the EELS signal should be related to the *z* component of the dynamical dipole moment.[15] We indeed find a very close correspondence between the EELS spectra[8,11] and the *z* component of the vibrational spectra in Fig. 2(c). We find features at ∼20, 27, and ∼40 meV. The first feature corresponds to the surface resonance, experimentally found at 19 meV. Our simulation locates the surface phonon at 27 meV, identical to the experiment. The feature at 40 meV corresponds to the bulk contribution, experimentally found at 37 meV,[4] which is also present in our slab model of the surface. Note the absence of vibrations above 40 meV. Hence our model gives a description of surface dynamics of the clean surface in almost perfect agreement with the experiments. We also used the self-consistent MUSIC algorithm to extract eigenvectors of the surface phonon and surface resonance from the dynamical trajectories. For the phonon we found the surface Ni and Al atoms vibrating out of phase and for the resonance we found in-phase vibrations. These results are in a good qualitative agreement with results of Kang and Mele[3] and Mostoller *et al.*[5] Analysis of the other features, such as those found in the *y* direction, suggests that those vibrations are ordinary quasiharmonic vibrations.

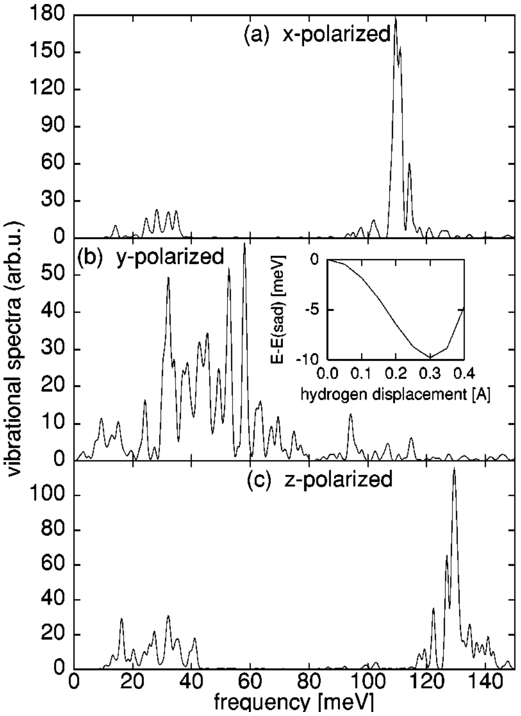

FIG. 3. Spectra of nuclei vibrations for the hydrogen covered NiAl(110) surface. (a) *x* component, (b) *y* component, and (c) *z* component. The inset shows the total potential-energy variation vs hydrogen *y* displacement from the symmetric Ni-Ni bridge site with all other atoms fixed and the hydrogen *z* coordinate relaxed.

We now turn to the analysis of vibrational spectra of the hydrogen-covered surface shown in Fig. 3. In the *z*-polarized spectra we see substrate related features at frequencies <40 meV and the hydrogen induced features above. The peak at ∼20 meV corresponds to surface resonance. The feature at 33 meV corresponds to the surface phonon whose frequency increased upon hydrogen adsorption by 6 meV in excellent agreement with experiment.[9,11] Notice also the presence of the features at 27 and 40 meV. They emanate from the bottom surface of our slab (which is not hydrogen covered) and from the bulk, respectively. We conclude that thus far the hydrogen induced changes of the vibrational features from our model correlate very well with the EELS spectra and with what is expected from reduction of the surface ripple upon hydrogen adsorption. The most striking feature is the hydrogen normal mode which in our model appears at 130 meV. This frequency is very close to the value of 135 meV found also by Hammer *et al.*[10] in harmonic approximation. Hence these results indicate that the harmonic approximation does *not* have an overly strong effect on the high-frequency mode. Note also that this mode *is* in the usual range of frequencies (75–170 meV) expected for normal vibrations of hydrogen on metals surfaces. These results provide a strong indication that the origin of the discrepancy between the experimental and theoretical hydrogen induced frequency is *not* rooted in the strong in- and out-of-plane anharmonic coupling as suggested by Hanbicki *et al.*[8,11]

The *x*-polarized spectra display peaks below 40 meV corresponding to substrate modes. The high-frequency peak at

110 meV corresponds to the in-plane hydrogen normal mode polarized in the *x* direction. The relatively large frequency 110 meV implies that the potential minimum in this direction is correspondingly narrow. The mode can be considered as approximately harmonic with slight anharmonic splitting arising from coupling with the large-amplitude *y*-polarized in-plane motion (see below).

A look at Fig. 3(b) reveals a rich vibrational behavior in the *y* direction. Analysis of MD trajectories[25] indicates that a prominent feature of the hydrogen dynamics is a large-amplitude strongly anharmonic oscillation in the *y* direction (along aluminum rows; cf. Fig. 1). The main feature is a multiple peak structure in the frequency region 30–60 meV. How can we interpret this behavior? Some of these peaks correspond to usual quasiharmonic surface vibrations. However, some of them arise from strong anharmonicities. A special feature is the saddle point in the symmetric hydrogen position (in the Ni-Ni bridge) and the resulting double-well PES discussed already in Sec. III A. The consequence of this is a strong anharmonicity for the in-plane motion along the aluminum rows. Part of the rich structure of the vibrational spectrum in Fig. 3(b) is artificial and can be traced back to the presence of two different surfaces in our slab model of the surface [compare with Fig. 2(b)]. We also speculate that some of the peaks in Fig. 3(b), such as those in the region 60–80 meV, correspond to nonlinear oscillations at sum frequencies of ordinary (i.e., quasiharmonic) phonons.

The above arguments clarify that the frequency of the 130-meV mode should not be lowered to ~50 meV due to strongly anharmonic behavior. However, we still have not produced any argument for why the EELS experiment does not detect the high-frequency mode or, vice versa, why our simulation does not yield any frequency in the ~50-meV region of perpendicular vibrations [Fig. 3(b)]. We believe that the 130-meV feature is a genuine mode which remains hidden to the EELS probe, the reason being that only those vibrations with sufficiently large dynamic dipoles can be detected. In other words, if we restrict ourselves to dipole scattering, an EELS signal in the specular direction corresponds to dipole oscillations, rather than to oscillations of nuclei. Therefore a more appropriate quantity to compare with the EELS experiment is the frequency spectrum of the time-dependent surface dipole, i.e., the Fourier transform of a dipole correlation function of the type

$$D(\tau)\propto\langle d_z(\tau)d_z(0)\rangle, \tag{3}$$

with d_z being the *z* component of the time-dependent surface dipole moment. The main practical problem with applying formula (3) is how to define and compute the surface dipole moment. Often, this quantity is approximated by just the adsorbate dipole moment.[16] In general, such an approach is unsatisfactory. First, it is impossible to separate the adsorbate atom from the surface and, second, the experimental EELS signal exhibits peaks arising from both surface atoms and adsorbates. Hence we include all top layer metallic atoms and the adsorbate atoms to compute the dipole. Admittedly, this is an *ad hoc* choice but it certainly includes all main surface vibrations. We define the *z* component of the surface dipole as

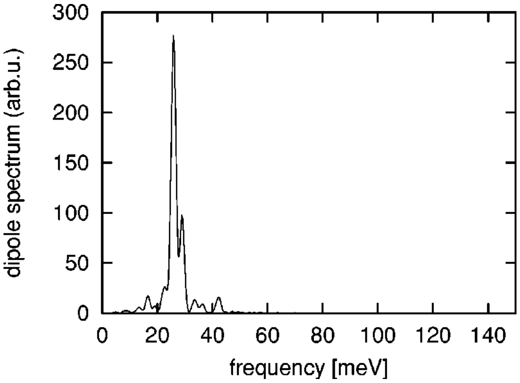

FIG. 4. Spectrum of dipole vibrations of the clean NiAl(110) surface.

$$d_z=\int_{\text{surf}}\rho(\mathbf{r})zd^3r+\sum_{I=1}^{N}Q_IZ_I, \tag{4}$$

where $\rho(\mathbf{r})$ is the (valence) electronic charge density, Q_I the effective charge of the Ith nucleus (pseudopotentials are used in our simulations), and Z_I is the *z* coordinate of the Ith nucleus and I runs over all nuclei in the volume of the surface region. The surface dipole (4) is easily calculated from an *ab initio* MD as the electronic charge densities $\rho(\mathbf{r})$ as well as ionic positions Z_I are naturally generated in the simulation. The surface region (integration volume) must contain zero total charge. In the case of a time-dependent problem it is not possible to maintain the charge neutrality within a fixed integration boundary. Therefore we make a slight adjustment of the bottom boundary of the integration volume to maintain the charge neutrality at each time step. From the dipole $d_z(t)$ we subtract the permanent dipole moment. We then calculate the spectrum of its oscillations from an autocorrelation of the type (3).

The dipole spectra for the clean surface and hydrogen-covered surface are shown in Figs. 4 and 5, respectively. Generally, these curves show good agreement with the experimental EELS results,[8,11] except for the absence of the 49.5-meV feature in our curves. The prominent features of these curves are the peaks from surface phonons at 27 and 33 meV in excellent agreement with EELS. The other prominent

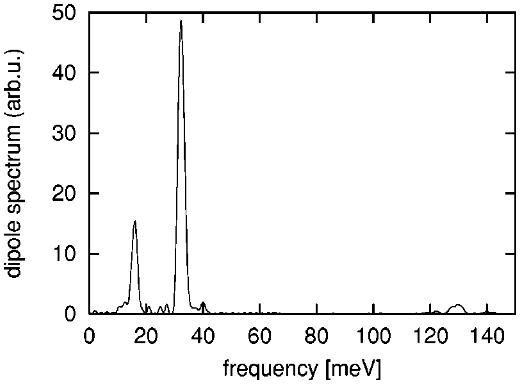

FIG. 5. Spectrum of dipole vibrations of the hydrogen covered NiAl(110) surface.

feature is a significant decrease of the intensity of the peak corresponding to the hydrogen mode at 130 meV in the dipole spectrum. This gives important hints as to why this peak remains hidden to the EELS probe.

IV. DISCUSSION

In the first part of Sec. III we have demonstrated the ability of the DFT and slab model of the surface to reproduce the experimental structural trend, namely the reduction of the surface ripple upon hydrogen adsorption. The calculated relative decrease of the surface ripple upon hydrogen adsorption is found to be in excellent agreement with experiments.[9] However, our absolute values differ from the experimental ones typically by 50%. This may be due, in part, to the technical parameters used in our simulations, such as k points, GGA functional, etc., and possibly also due to experimental uncertainties. In Ref. 9 experimental results of several authors are compared, obtained with various techniques. For example, at 300 K, the first Ni-Ni interlayer distance relaxation varies from -2.8% to -7.0% relative to the bulk value. Our results differ significantly from those in Ref. 10 because these authors allowed only the top metallic layer (and the hydrogen overlayer) to relax. We believe that this is why they obtain a complete hydrogen-induced removal of the surface ripple in contradiction with experiments.[9] Recently Hǿjrup Hansen *et al.* performed static DFT relaxation[28] of the clean NiAl(110) surface using a slab model of 13 layers with the first two layers allowed to relax. They report data on the movement of the layers with respect to the bulk-terminated geometry. From their results the relaxations of the top Ni-Ni and Al-Al distances and the surface ripple according to definition 1 can be calculated. The values are -3.6% (3.4%) for the Ni-Ni (Al-Al) spacing. The resulting ripple is 7.0%. This agrees well with our result of 4.99% (see Sec. III A). As an additional check we have performed a calculation of a clean slab with only two layers allowed to relax (other parameters were the same as for the covered slab). In this case the results are even closer (ripple of 5.60%) to that of Ref. 28. The small difference between the ripple of Ref. 28 and our value of 5.60% may arise mainly from different k-point samplings, cell heights, and pseudopotentials. The comparison of our two results (all and only two layers relaxed) shows that more than two layers must by relaxed to obtain a quantitatively correct value of the ripple.

The *ab initio* MD yields substrate related dynamical features for both clean and hydrogen-covered NiAl(110) surface in good agreement with experiments, the only discrepancy being the different frequency of the hydrogen mode in the experiment (49.5 meV) and theory (130 meV). This is a huge difference which, if true, would indicate a serious failure of the DFT and/or Born-Oppenheimer (BO) approximation to model the hydrogen-metal surface interactions. Hanbicki *et al.*[8,11] explain the difference by strongly anharmonic in- and out-of plane coupling. This hypothesis was, in part, motivated by the theoretical work of Hammer *et al.*[10] who used the harmonic approximation with a similar result (135 meV) to ours. For the BO electronic surface, this can safely be excluded as the reason for the discrepancy as our MD results, free of any harmonic approximation, yield a frequency only marginally lower. As a matter of fact, Fourier and MUSIC analysis indicate that this mode *is* harmonic to a good approximation. We have presented a compelling evidence that the most probable reason why EELS is missing this mode is that it is not dipole active.

What is then the reason for the discrepancy? We consider a number of possible scenarios. (i) classical treatment of hydrogen dynamics; (ii) failure of DFT and/or BO approximation; (iii) presence of subsurface hydrogen, contaminants or surface roughness; (iv) presence of impact scattering in the EELS experiment. (i) could cause the difference if the quantum delocalization could introduce the strong anharmonic coupling. At full coverage, hydrogen appears to be localized near the equilibrium positions and hence such an additional strong anharmonic coupling appears unlikely. Moreover, we have found very strongly anharmonic in-plane vibrations in our model which showed no tendency to lower significantly the frequency of the harmonic high-frequency mode. (ii) could indeed cause the massive discrepancy if the BO DFT PES's were completely wrong. While this certainly cannot be completely ruled out, the fact that so many other features correlate well with the experiments makes such a scenario improbable. It would be tempting to contemplate the presence of subsurface hydrogen. However, the authors of the experimental work[8,11] exclude this possibility. From the present study, the presence of impact scattering in the EELS experiment appears as the most probable reason for appearance of the 49.5-meV feature in the EELS spectra. Our simulation identified strong in-plane vibrations in this frequency region. This, in fact, is one of the most prominent dynamical features.[25] This in-plane hydrogen motion along the Al rows naturally arises on the NiAl(110) phase but is absent on other phases, such as the (111) (Ref. 8) or other materials lacking the surface ripple.

Finally, we should at least qualitatively answer the question what is the relation between the dipole spectra of Figs. 4, and 5 and the EELS signal. The frequency dependence of EELS signal in dipole-scattering case is[15]

$$I_{\text{loss}}=K\frac{1}{\omega}(e^{*})^{2}, \tag{5}$$

where K is a constant and e^{*} is dynamic dipole which is proportional to dipole matrix element (ME). This dipole ME corresponds to vibrational transition caused by an EELS electron. Because we employ the classical description of nuclei in our simulations, we do not have any direct information about the ME. In classical physics, the EELS electron would cause a change Δd_0 of an amplitude d_0 of the dipole vibrations. We know that there is proportionality between Δd_0 and d_0. Therefore we can qualitatively assume that peaks in the spectrum shown in Figs. 4 and 5 would correspond to peaks in the EELS signal. We have not included the factor $1/\omega$ to our dipole spectra in Figs. 4 and 5. This correction would make the 130-meV feature even less pronounced.

V. CONCLUSIONS

We have presented an extensive *ab initio* study of static and dynamic properties of clean and hydrogen covered NiAl(110) surfaces. The present study was stimulated by experimental work[8,11] which represents probably the most thorough and comprehensive studies of hydrogen interaction with an alloy surface.

Using the DFT and slab model we have been able to account for most experimental findings. In particular, our model qualitatively correctly describes the reduction of the surface ripple of the NiAl(110) upon hydrogen adsorption.

Our *ab initio* MD simulations describe the dynamics of the clean surface as well as the changes of the dynamics upon hydrogen adsorption in a good agreement with the experiments. They also strongly suggest that hydrogen on the NiAl(110) surface vibrates at the frequency of 130 meV (perpendicular to the surface), i.e., in the range of frequencies expected for hydrogen adsorbed on a metal surface. However, the corresponding dynamic dipole is estimated to be too weak to be detected with EELS. We expect that the strongly anharmonic hydrogen motion parallel to the surface [Fig. 3(b)] can give the origin to the weak EELS signal at 49.5 meV. We speculate that the impact scattering may give rise to this experimentally observed feature.

ACKNOWLEDGMENTS

We thank A. Hanbicki and E. Plummer for providing us with their experimental results. A part of the calculations was performed on the JRCAT supercomputer system. This work was partly supported by the New Energy and Industrial Technology Development Organization (NEDO).

---

[1] H.L. Davis and J.R. Noonan, Phys. Rev. Lett. **54**, 566 (1988).

[2] M.H. Kang and E.J. Mele, Phys. Rev. B **36**, 7371 (1987).

[3] M.H. Kang and E.J. Mele, in *The Structure of Surfaces II*, edited by J.F. van der Veen and M.A. van Hove (Springer, Berlin, 1987), p. 160.

[4] S.-C. Lui, M.H. Kang, E.J. Mele, E.W. Plummer, and D.M. Zehner, Phys. Rev. B **39**, 13 149 (1989).

[5] M. Mostoller, R.M. Nicklow, D.M. Zehner, S.-C. Lui, J.M. Mundenar, and E.W. Plummer, Phys. Rev. B **40**, 2856 (1989).

[6] S.-C. Lui, J.W. Davenport, E.W. Plummer, D.M. Zehner, and G.W. Fernando, Phys. Rev. B **42**, 1582 (1990).

[7] M. Wuttig, W. Hoffmann, E. Preuss, R. Franchy, H. Ibach, Y. Chen, M.L. Xu, and S.Y. Tong, Phys. Rev. B **42**, 5443 (1990).

[8] A.T. Hanbicki, Ph.D. thesis, University of Pennsylvania, 1997.

[9] A.T. Hanbicki, H.L. Davis, A.P. Baddorf, D.B. Poker, and E.W. Plummer, Surf. Sci. **365**, L639 (1996).

[10] A.T. Hanbicki, A.P. Baddorf, E.W. Plummer, B. Hammer, and M. Scheffler, Surf. Sci. **331-333**, 811 (1995).

[11] A. Hanbicki, P.J. Rous, and E.W. Plummer (unpublished).

[12] K. Christmann, R.J. Behm, G. Ertl, M.A. van Hove, and W.H. Weinberg, J. Chem. Phys. **70**, 4168 (1979).

[13] M.J. Puska, R.M. Nieminen, M. Manninen, B. Chakraborty, S. Holloway, and J.K. Nǿrskov, Phys. Rev. Lett. **51**, 1081 (1983).

[14] See, for instance, M.C. Payne, M.P. Teter, D.C. Allan, T.A. Arias, and J.D. Joannopoulos, Rev. Mod. Phys. **64**, 1045 (1992).

[15] H. Ibach, Surf. Sci. **66**, 56 (1977).

[16] B.N.J. Persson, Surf. Sci. **92**, 265 (1980).

[17] A. Taylor and N.J. Doyle, J. Appl. Crystallogr. **5**, 201 (1972).

[18] D.B. Miracle, Acta Metall. Mater. **41**, 649 (1993).

[19] We used a CASTEP 4.2 (academic version) suite of programs, licensed under the UKCP-MSI Agreement, 1999; for the theory behind this code see Refs. 14, 22, and 23.

[20] J.P. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Pederson, D.J. Singh, and C. Fiolhais, Phys. Rev. B **46**, 6671 (1992).

[21] H.J. Monkhorst and J.D. Pack, Phys. Rev. B **13**, 5188 (1976).

[22] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).

[23] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11 169 (1996); D.R. Bowler and M.J. Gillan, Chem. Phys. Lett. **325**, 473 (2000).

[24] The results of the convergence tests using the different thicknesses of the slab model may be downloaded from: http://www.ccms.elf.stuba.sk

[25] Computer graphics animation of our simulation results may be downloaded from: http://www.ccms.elf.stuba.sk. In this graphical presentation the 1×1 simulation surface cell is periodically replicated to a 3×3 surface cell.

[26] J. Kohanoff, Comput. Mater. Sci. **2**, 221 (1994).

[27] I. Štich, J. Kohanoff, and K. Terakura, Phys. Rev. B **54**, 2642 (1996).

[28] K. Hǿjrup Hansen, J. Gottschalck, L. Petersen, B. Hammer, E. Lægsgaard, F. Besenbacher, and I. Stensgaard, Phys. Rev. B **63**, 115421 (2001).