First-Principles Calculation of Surface Phonons on the Al(110) Surface

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The surface-phonon dispersion curves of Al(110) have been calculated with force constants determined from first-principles self-consistent total-energy calculations. Relaxation of the surface layers produces changes in the surface force constants which have a significant influence on the surface-phonon frequencies near the zone boundary.

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Surface vibrations are involved in many processes on surfaces at ambient or elevated temperatures. A detailed knowledge of the surface-phonon spectrum is essential in studies of surface diffusion, phase transitions on clean and adsorbate-covered surfaces, and desorption processes. It is also indispensable for any quantitative studies of energy transfer and dissipation at surfaces. Furthermore, the frequencies of vibrational modes associated with adsorbed species can yield information on surface-adsorbate bonding, the geometry of the adsorption sites, and the lateral coupling between neighboring atoms or molecules on the surface.

The past few years have witnessed a rapid growth in the experimental effort to measure surface vibrations.[1-11] Development of experimental techniques in electron energy-loss spectroscopy[1-4] and inelastic He scattering[5-9] have reached such a stage of sophistication that reliable surface-phonon dispersion curves have been measured for a number of surfaces and data on many other interesting surfaces will become available in the near future. There is a need for theory to interpret these results and to provide insights into the nature of the interatomic forces at the surface.

Surface-phonon dispersion curves for crystal surfaces can be obtained by solving for the vibrational modes of a slab or semi-infinite solid. Early calculations[11] modeled the interatomic interactions by a Lennard-Jones potential. Subsequent studies[3, 12-14] use more realistic force constants deduced from the fitting of measured phonon dispersion curves in the bulk, with empirical adjustments of the surface force constants to reproduce the measured frequencies of the surface modes. However, these changes in surface constants are quite sensitive to the models adopted for fitting the bulk phonons[15] and it is important to have input from first-principles calculations to assess the magnitudes of these changes and their dependence on the surface geometry. Some progress in this direction has been reported by Eguiluz, Wallis, and Maradudin using a surface dielectric function approach.[16] An alternative approach, the "frozen-phonon" method,[17] has proven to be very successful in providing a detailed and accurate description of bulk phonons complementary to the perturbative dielectric function approach. In this paper, we have extended the frozen-phonon method to perform first-principles calculations of the surface-phonon frequencies on the Al(110) surface.

Detailed and accurate information on the equilibrium surface geometry can be obtained from precise first-principles self-consistent total-energy calculations of surfaces by the density-functional approach.[18] Recent calculations have been successful in determining the surface structures of semiconductor,[19, 20] transition-metal,[21] and simple metal[22] crystals. In a previous publication[22] (hereafter referred to as I), we determined the equilibrium positions of atomic layers on the Al(110) surface. We found a contraction of the top interlayer spacing by $(6.8 \pm 0.5)\%$, an expansion of the second interlayer spacing by $(3.5 \pm 0.5)\%$, and contraction of the third interlayer spacing by $(2.0 \pm 0.5)\%$. Our calculated interlayer separations are in agreement with results from precise LEED experiments[23] to within 0.02 Å. We also obtained the work function and surface energy for the Al(110) surface in excellent agreement with experimental values. In this paper, we have extended these calculations to evaluate interatomic force constants at the surface. Using the first-principles surface force constants we have deduced the surface-phonon dispersion curves for the Al(110) surface. Since the experimental surface-phonon spectra of the Al(110) surface have not been reported, it is hoped that this work will stimulate further experimental investigations.

Our calculations were performed by use of the first-principles pseudopotential approach within the local-density–functional formalism. The only approximations made in these calculations are the local-density approximation for treating the exchange-correlation energy of the electrons,[18] the frozen-core approximation, and the Born-Oppenheimer approximation.[24] The norm-conserving pseudopotential[25] used in our calculations has been used in previous investigations of the structural properties and phonon frequencies of bulk Al with excellent results.[26] We followed the same procedures as described in paper I: The calculations were performed for a periodic geometry with slabs fifteen layers thick separated by five layers of vacuum. (We have found in paper I that for this surface of Al, a slab of thirteen to fifteen layers thick is necessary to obtain convergence.) The electronic wave functions were expanded with plane waves up to a cutoff energy of 8.5 Ry and plane waves up to 12.0 Ry were included via second-order perturbation. Brillouin-zone sums were made with a sampling grid of 35 points in the irreducible part of the surface Brillouin zone (SBZ) (see inset in Fig. 1.) The reader is referred to paper I for further calculational details and various convergence tests.

To calculate the surface force constants, we start with the zero-force geometry determined previously and displace the surface layer of atoms by small distances in the x ([-110]), y ([001]), and z ([110]) directions. The self-consistent electronic structures for each of the off-equilibrium geometries are calculated and the forces exerted on the atomic layers in the slab evaluated by use of the Hellmann-Feynman theorem.[27] From this we obtained the interplanar force constants coupling the surface with the subsurface layers. We find that the interlayer couplings at the (110) surface are dominated by those to the first- and second-neighboring layers which are roughly 10 times larger than the coupling to more distant layers.[28]

Surface force constants responsible for intralayer coupling are determined from calculations in which the periodicity parallel to the surface is modified. Calculations were performed for distortions of the top layer with displacements corresponding to the zone-boundary wave vectors $\bar{X}$ and $\bar{Y}$ in the SBZ. For both wave vectors, calculations were performed for displacements of the surface atoms in the x, y, and z directions. These calculations require a unit cell twice the size of the undistorted surface.[29] Sampling grids are chosen such that they correspond to 35 points in the undistorted SBZ. From our calculations we obtained first-principles intralayer and interlayer force constants for displacements of the surface layer in the x, y, and z directions at the $\bar{\Gamma}$, $\bar{X}$, and $\bar{Y}$ points in the SBZ. The couplings among the inner layers can be obtained in a similar manner, but in the present paper we have assumed that they are unchanged from the bulk values. Although expected to be small, calculations are in progress to check the changes in subsurface force constants and their effects on surface-phonon frequencies.

Using the calculated force constants, we can construct the dynamical matrix and obtain the eigenmodes at $\bar{X}$ and $\bar{Y}$ for an arbitrarily thick slab (51 layers were used in the present calculations). Table I summarizes our results for the frequencies and the corresponding displacements of the atoms in the surface layer for the surface modes at $\bar{X}$ and $\bar{Y}$. Also listed are the results obtained when all force constants are kept at the bulk values. At both $\bar{X}$ and $\bar{Y}$, the differences caused by use of the surface force constants are biggest for the shear modes with displacements in the surface plane. Because of symmetry requirements, these modes have zero displacement at the second layer and the first layer couples weakly to the third layer through a shear force. Thus these modes are highly localized on the top layer. The frequency of this mode is raised by ~1.5 THz at $\bar{X}$ and ~1.0 THz at $\bar{Y}$ above the frequency obtained with bulk force constants. The physical origin of the general stiffening of the surface vibrations is the inward relaxation of the surface layer which produces a buildup of charge between the surface atoms and its neighbors.[22] In the most extreme case, this can lead to an increase of the surface force constants by as much as 85%.

In order to extend our results to other parts of the SBZ, we fitted our first-principles intralayer and interlayer force constants using a central-force Born–von Kármán model. In the present calculations, we used the results of Gilat and Nicklow[30] for the bulk force constants. The force constants coupling the surface atoms to atoms in the surface, second, and third layers were modified. Figure 1(a) shows the surface-phonon dispersion curves obtained from such a model along symmetry directions in the SBZ. The shaded regions in the background show the projected bulk phonon

TABLE I. Calculated frequencies and surface atomic displacements for surface modes of the relaxed Al(110) surface. x denotes the [-110] direction, y the [001] direction, and z the [110] direction which is perpendicular to the surface. The subscript 2 on the mode label indicates displacements for atoms on the second layer, the atomic displacements of the surface atoms being zero by symmetry. Also shown are the results obtained when modifications of the surface force constants are neglected.

$\bar{X}$			$\bar{Y}$		
Frequency (THz)			Frequency (THz)		
Relaxed	Unrelaxed	Mode	Relaxed	Unrelaxed	Mode
4.1	4.2	x	1.9	2.1	y
4.2	3.7	z	3.4	3.2	z
5.5	3.9	y	3.6	2.5	x
6.0	⋯	z	6.0	5.9	y
6.3	⋯	y_2			
7.7	7.8	x			
⋯	8.4	z			

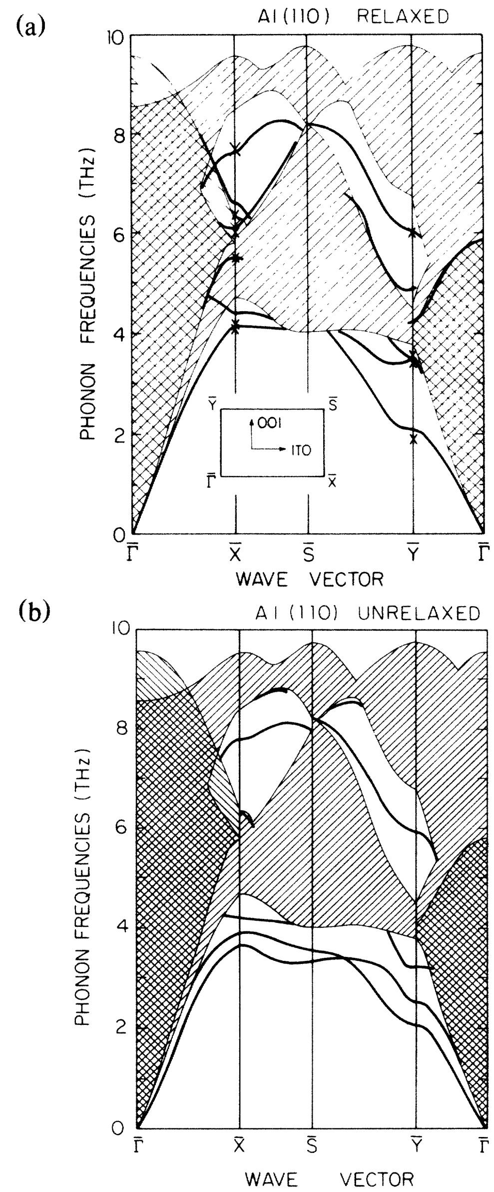

FIG. 1. (a) Calculated surface-phonon dispersion curves along symmetry directions of the SBZ. The shaded regions indicate the projection of the bulk phonon dispersion curves onto the SBZ. Different shadings indicate phonons with different symmetries. The inset shows the surface Brillouin zone. (b) Surface-phonon dispersion curves obtained with bulk force constants.

spectrum. The thick solid lines indicate surface modes obtained from a 51-layer slab calculation. The crosses indicate the positions of surface modes at $\bar{X}$ and $\bar{Y}$ obtained from first-principles interlayer and intralayer force constants without resorting to the central-force model. For comparison, we show in Fig. 1(b) the results obtained with all force constants kept at the bulk values. In some regions of the SBZ (especially near $\bar{S}$) modifications of surface constants lead to qualitative changes in the surface-phonon dispersion curves.

In conclusion, we have shown that first-principles calculations of total energy and forces on surfaces, in addition to giving detailed information about the surface geometry, also provide theoretical surface force constants which can be used in calculations of surface-phonon dispersion curves and in future model simulations of various surface kinetic processes.

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[28] Additional calculations have been performed for movement of the inner layers (in the z direction) to calculate bulk interplanar force constants from which we can deduce the dispersion curve of the longitudinal mode in the [110] direction. Our calculated results are within 5% of the measured dispersion curve.

[29] Solution of the Schrödinger equation in this case involves the diagonalization of matrices with sizes $\sim 1800 \times 1800$.

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