Self-Consistent-Screening Calculation of Surface-Phonon Dispersion Curves at the (110) Surface of Aluminum

A. G. Eguiluz
Department of Physics, Montana State University, Bozeman, Montana 59717

and

A. A. Maradudin and R. F. Wallis
Department of Physics, University of California at Irvine, Irvine, California 92717

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We have calculated the dynamical matrix for an aluminum slab bounded by a pair of (110) surfaces using a self-consistent implementation of pseudopotential perturbation theory. The screening response of the conduction electrons to the field of the ions is obtained within the local-density approximation of density-functional theory. Both relaxed and unrelaxed geometries are treated. We present numerical results for the dispersion curves of surface phonons. Comparison is made with recent theoretical and experimental results.

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The majority of the existing calculations of surface-phonon properties are based on force-constant models, in which the atomic force constants in the interior of the crystal are generally obtained from bulk-phonon dispersion curves. The force constants coupling atoms in the outer atomic planes are usually modified[1] in order to reproduce the experimental data. However, for a given physical system there is a built in ambiguity in a force-constant model: More than one model can explain the same data.[1,2]

These attributes of the force-constant model approach have prompted us to carry out microscopic calculations of surface-phonon dispersion curves in simple, i.e., *sp*-bonded, metals on the basis of a self-consistent pseudopotential perturbation theory.[3] In this Letter we report results for the case of Al(110), a surface which has recently received attention, both experimentally[4,5] and theoretically.[6-8]

The approach used in the present work differs significantly from previous calculations of this type. In the pseudopotential perturbation-theoretic calculations of Calandra and co-workers for alkali-metal surfaces,[9] the ground state and response properties of the electronic subsystem were calculated with the infinite-barrier model for the electron wave functions. The present work is based on the self-consistent evaluation of the electron wave functions and screening response of the conduction electrons by the use of the local-density approximation (LDA) of density-functional theory. The limitations of an infinite-barrier-model–based screening calculation[10] are in fact illustrated by the results of Calandra and co-workers.[9] These authors find that exchange and correlation (XC) effects, which are absence from the infinite-barrier model ground state, must be introduced in the response calculation in order to stabilize the surface-phonon spectrum for the case of, e.g., potassium (001). Moreover, it has been shown recently that a surface screening calculation that does not treat the response problem self-consistently with the ground-state problem leads to a violation of some surface sum rules.[11] Clearly, then, XC should be treated self-consistently, as we do. The present approach also differs from that of Ho and Bohnen.[8] These authors evaluated a few interlayer and intralayer force constants at the surface of Al(110) by creating appropriate high-symmetry distortions of the outermost atomic layer. The distortion energy was obtained via a pseudopotential-based total-energy calculation. With this procedure, values of the phonon frequencies at the $\bar{X}$ and $\bar{Y}$ points in the surface Brillouin zone (SBZ) were obtained. A force-constant scheme was then fitted to these frequencies in order to obtain dispersion curves along symmetry lines in the SBZ. By contrast, our method (as does that of Ref. 9) yields *all* the *interatomic* force constants of a metal slab.

The solution of the central problem in our approach, namely the screening of the ion cores by the conduction electrons, requires the knowledge of the density response function for interacting electrons, $\chi(\mathbf{xx}')$. In density-functional theory $\chi(\mathbf{xx}')$ satisfies an integral equation of the form[12,13]

$$\chi=\chi^{(0)}+\chi^{(0)}V\chi, \qquad (1)$$

where $\chi^{(0)}(xx')$ is the density response function for noninteracting electrons, which is obtained from the knowledge of the LDA electron wave functions and energy eigenvalues,[13] and $V(\mathbf{x}_1\mathbf{x}_2)$ is the full electron-electron interaction. In LDA $V(\mathbf{x}_1\mathbf{x}_2)$ consists of the bare Coulomb interaction plus the local interaction $\delta(\mathbf{x}_1-\mathbf{x}_2)dV_{\mathrm{XC}}(\mathbf{x}_1)/dn_0(\mathbf{x}_1)$, where $V_{\mathrm{XC}}(\mathbf{x})$ is the XC contribution to the effective potential in the LDA ground state, and $n_0(\mathbf{x})$ is the ground-state electron density.[12,13]

For the case of *sp*-bonded metals, where the pseudopo-

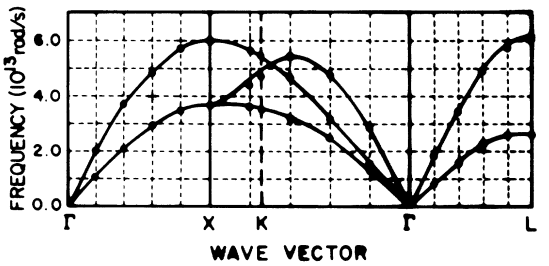

FIG. 1. Calculated phonon dispersion relations for bulk aluminum. The points represent the experimental data (neutron scattering) quoted in Ref. 15.

tential can be expected to be weak, one can use the solution to Eq. (1) obtained recently^{13} for an *electron gas* confined self-consistently in the direction normal to the surface on both sides of a jellium slab, as the basis for a perturbative formulation. Let us call $V_1(\mathbf{x})$ the difference between the potential due to the discrete array of pseudoions and that due to the jellium (care must be exercised in defining this difference^7). Carrying out a coupling-constant integration over the Hamiltonian $\lambda V_1(\mathbf{x})$ $(0 \le \lambda \le 1)$, we obtain for the ground-state energy $E_{\text{g.s.}}$ of the conduction electrons to second order in V_1

$$E_{\text{g.s.}} = E_{\text{g.s.}}^{(0)} + \int d^3x\, n_0(\mathbf{x}) V_1(\mathbf{x}) + \tfrac{1}{2}\int d^3x \int d^3x'\, V_1(\mathbf{x}) \chi(\mathbf{x}\mathbf{x}') V_1(\mathbf{x}'), \qquad (2)$$

where $E_{\text{g.s.}}^{(0)}$ and χ are respectively the electronic ground-state energy and the solution to Eq. (1), for $V_1 = 0$. Differentiating Eq. (2) twice with respect to the displacements of the ions from their equilibrium positions gives the electronic contribution to the atomic force constants. From these the electronic contribution to the dynamical matrix of the slab is obtained. This must be added to the contribution from the direct ion-ion force constants (obtained with Ewald summation techniques).

The above procedure was implemented first for bulk aluminum, with use of the local form of the Heine-Abarenkov pseudopotential. Its two parameters (core radius r_c and well depth u_c) were determined by our requiring that^{14} (i) the total bulk energy be a minimum for the experimental value of the lattice constant, and (ii) the average of the squares of the bulk phonon frequencies over the Brillouin zone agree with the value extracted from neutron-scattering data.^{15,16} Condition (i) is of importance for the consistency of the surface relaxation calculation. Condition (ii) sets the overall scale for the vibrational problem. In Fig. 1 we show the dispersion curves obtained for bulk phonons propagating along symmetry directions in the Brillouin zone. Overall agreement with the neutron data is excellent. The elastic moduli obtained from the long-wavelength limit of the theoretical dispersion curves are (in units of 10^{11} dynes/cm^2; the experimental values are in parentheses) $C_{11} = 10.23$ (10.68), $C_{12} = 6.07$ (6.07), and $C_{44} = 3.62$ (2.82). The discrepancy between theory and experiment for C_{44} is presumably due to the neglect of higher-order terms in the pseudopotential in $E_{\text{g.s.}}$. We note that although the bulk force constants obtained from Eq. (2) are central, the calculated elastic moduli violate the Cauchy relation $C_{12} = C_{44}$, in qualitative agreement with experiment. That central-force pair interactions in metals can yield elastic moduli such that $C_{12} \neq C_{44}$ has been shown by Brovman, Kagan, and Kholas^{17} to be a consequence of the dependence of the electronic polarizability on the electron density.

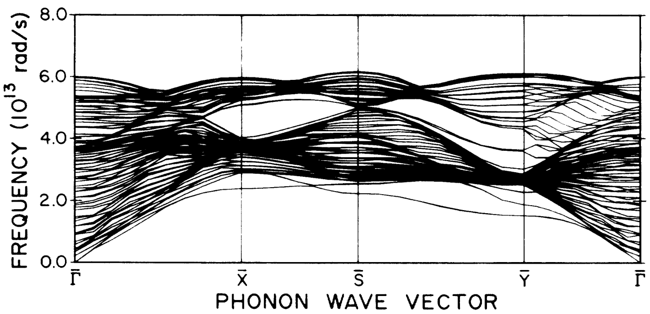

FIG. 2. Calculated surface-phonon dispersion relations along symmetry directions in the SBZ for an *unrelaxed* 27-layer aluminum slab bounded by a pair of (110) surfaces.

In Fig. 2 we show the results of a calculation of the phonon spectrum for a 27-layer ideal, unrelaxed slab bounded by a pair of (110) surfaces. (The zone-boundary frequencies are independent of the slab thickness for slabs thicker than about 23 atomic layers.) We emphasize that the surface calculation has no adjustable parameters; it has been carried out from first principles, according to the outline given above, with the values of r_c and u_c that were used in the evaluation of the bulk dispersion curves.

The presence of surface modes below and in the gaps of the surface-projected bulk branches is clearly seen in Fig. 2. In fact, the overall nature of the surface-phonon spectrum is qualitatively similar to the results obtained by Allen, Alldredge, and de Wetts^{18} in their seminal work on surface phonons for model fcc crystals with

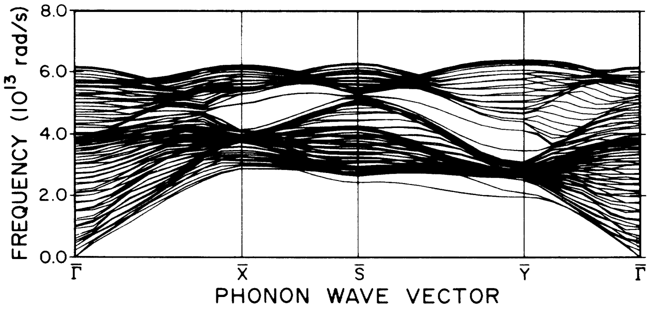

FIG. 3. Same as Fig. 2, but for a *relaxed* crystal.

Lennard-Jones interatomic interactions.

In Fig. 3 we show the phonon dispersion curves in the presence of multilayer relaxation.[7] The values obtained for the percentage change of the first three interplanar spacings are $\Delta_{12}=-5.4$, $\Delta_{23}=+0.8$, and $\Delta_{34}=-2.6$, where a negative (positive) value denotes a contraction (expansion). The main effect of the relaxation process is to raise the frequencies of the surface modes.[19]

For both the relaxed and unrelaxed crystals we find that the *xx* and *yy* elements of the dynamical matrix are reduced substantially for the outermost plane in relation to their values for the inner planes, a result favoring the creation of surface modes. For the case of the *zz* element, the smallest value is obtained for the *second* atomic plane. This also favors the creation of surface modes.

An important feature of our results is that for an atom in the outermost layer there is a large contribution to the total dynamical matrix from the first-order term in Eq. (2). The physical origin of this contribution to the dynamical matrix is the large gradient of the electron density profile at the surface. In addition we have that at the surface, unlike in the bulk, the term of second order in Eq. (2) gives rise to interatomic interactions which include contributions that are neither central nor pairwise. For a given pair of surface atoms the surface acts as a third body, by virtue of the breaking of the translational symmetry normal to it which is built into the surface-screening response function χ.

In Table I we compare the values of the frequencies of the surface phonons measured by Toennies and Wöll[5] at the $\bar{X}$ and $\bar{Y}$ points in the SBZ with the corresponding theoretical values obtained in the present work, and by Ho and Bohnen.[8] We have that (i) at the X point both theoretical values are close to the measured surface-phonon frequency when the calculation is done for the unrelaxed surface, but not for the relaxed one; (ii) at the $\bar{Y}$ point the same conclusion applies for the lower-frequency mode. On the other hand, our calculated value of the frequency of the higher surface mode agrees very well with experiment, in the presence of relaxation.

TABLE I. Comparison of the values of the energies of the surface phonons measured by Toennies and Wöll for Al(110) at the $\bar{X}$ and $\bar{Y}$ points in the SBZ with the theoretical values obtained in this work and by Ho and Bohnen. (Energies are in millielectronvolts.)

	$\bar{X}$		$\bar{Y}$	
	Unrelaxed	Relaxed	Unrelaxed	Relaxed
Present work	15.8	19.0	10.0	13.0
			12.4	13.8
Ho-Bohnen[a]	15.3	17.4	8.7	7.9
			13.2	14.1
Toennies and Wöll[b]		14.8		9.3
				13.5

[a] Reference 8.

[b] Reference 5.

Toennies and Wöll[5] have argued that the quantitative disagreement between the value of the surface phonon frequency measured at $\bar{X}$ and the theoretical value of Ho and Bohnen[8] is possibly due to systematic errors in the theory (they question, e.g., the validity of LDA in the surface-phonon calculation, also used in the present work). While this may turn out to be the case, we would like to point out that another possible reason for the disagreement between the measured values of the surface phonon at $\bar{X}$ and the theoretical values obtained by Ho and Bohnen[8] and in our work may be the poor quality of the Al(110) surface used in the experiments,[5] which contains a high density of defects and steps, the latter having a mean separation of $\simeq 15$ Å. Toennies and Wöll argue that at $\bar{X}$ the surface phonon frequency is insensitive to the coupling of a surface atom to its two first neighbors in the surface plane, which would then make the quality of the surface unimportant. However, a numerical test based on changing this coupling[20] shows that the opposite is true: The frequency of the surface phonon at $\bar{X}$ does depend sensitively on the coupling of a surface atom to one of its neighbors in the surface plane.

The pseudopotential perturbative approach is limited to free-electron-like metals. In evaluating the force constants for non-free-electron-like metals, the effects of the electron-ion potential must be incorporated into the response function $\chi(\mathbf{x},\mathbf{x}')$, which remains the key element of the theory.

In conclusion, we have presented a calculation of surface-phonon dispersion for Al(110) whose salient features are these: (i) The underlying bulk calculation gives dispersion curves which agree very well with experiment along symmetry lines, (ii) the surface calculation has no adjustable parameters, (iii) both relaxed and unrelaxed geometries are treated on the same footing, and (iv) the full set of interatomic force constants *for the slab* has been implicitly obtained in the evaluation of the dynamical matrix. To the extent that pseudopotential perturbation theory may remain valid for the surface vibrational problem, our results show that the net restoring force on an atom in the outermost layer is *not* in the nature of a sum over pair potentials. This force includes significant effects due to the surface electronic environment (large gradient in the electron density profile), and to the surface screening process (through which, for a given pair of atoms, the surface plays the role of a third body).

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