

Calculation of Phonons on the Cu(100) Surface by the Embedded-Atom Method

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We present calculations, based on the embedded-atom method of phonon energies and polarizations on the clean Cu(100) surface. The atomic relaxations and the dynamical matrix are obtained, *without fitting to surface properties*, in one consistent calculation which is no more computationally demanding than pair potentials. Excellent agreement with experiment is obtained. We find that the force constants are qualitatively different from those obtained by fitting to two-body central-potential models, reflecting the many-body nature of the method and suggesting that fits based on central-potential models may be misleading.

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Despite their nature as an elementary excitation of a solid, surface phonons have only recently received adequately detailed attention. This is partly due to the fact that the experimental determination of surface-phonon dispersion curves throughout the surface Brillouin zone is a challenging problem. Recently, low-energy He beam scattering and high-resolution electron-energy-loss spectroscopy methods have been utilized to characterize surface phonons on a variety of metal surfaces.¹⁻⁵ Often, the experimental results are interpreted with the aid of model lattice-dynamical calculations in which the experimental phonon dispersions are reproduced by adjusting interatomic force constants. The simplest such calculations⁶ are two-body central-potential (CP) models. Although they are computationally simple, these CP models inaccurately predict that Cauchy's relation is satisfied, or else require volume-dependent energy terms, which are ambiguous at surfaces, to properly describe the elastic properties of the metal.⁷ Furthermore, they neglect many-body terms. Some of these deficiencies may be corrected by incorporating three-body angular terms; Bortolani *et al.*⁸ have had considerable success in this area. However, the basic problem with force-constant *fitting* is that more than one model can fit the data, and adding more terms can make this even worse. Ultimately, one would like to *predict* the surface modes without fitting to experimental results. First-principle techniques have been successful, with some limitations, in treating surface phonons. In "frozen-phonon" calculations⁹ the surface-phonon polarization (eigenvector) is assumed rather than calculated, and the computational complexity restricts the first-principles results to high-symmetry points of the Brillouin zone; the dispersion along symmetry lines of the Brillouin zone is then obtained by fitting force constants to the zone-edge frequencies. Self-consistent pseudopotential perturbation theory¹⁰ obtains the dispersions and polarizations throughout the zone, but is currently limited to free-electron-like metals such as Al. A predictive treatment of surface phonons in more complicated metals is the

subject of this Letter.

The embedded-atom method (EAM), which incorporates many-body interactions into the expression of the total energy, is as efficient as pair potentials, and has been shown to provide a good description of bulk-phonon modes, surfaces, defects, and liquids.¹¹ Within this method, relaxations and changes in surface force constants can be handled in one consistent framework, and phonon frequencies and polarizations in large slabs can be quickly computed at any k point. In this Letter, we will apply the EAM to the calculations of phonon dispersion curves on the Cu(100) surface. We will see that the EAM, which is fit only to bulk properties, is able to predict surface-phonon modes in excellent agreement with experiment.^{2,3}

In the EAM,¹¹ the total energy of an arbitrary arrangement of atoms is given by

$$E_{\text{tot}} = \sum_i F_i(\rho_i) + \frac{1}{2} \sum_{i,j}^{(i \neq j)} \phi_{ij}(R_{ij}). \quad (1)$$

In this expression, ρ_i is the electron density at atom i due to the remaining atoms of the system, $F_i(\rho)$ is the energy to embed atom i into the background electron density ρ , and $\phi_{ij}(R_{ij})$ is a short-ranged electrostatic interaction between atoms i and j . The embedding energy represents the interaction of an atom with the local electron gas provided by all other atoms. To make Eq. (1) of practical use, an approximation for the electron density ρ_i at atom i is provided by a linear superposition of atomic electron densities

$$\rho_i = \sum_{j(\neq i)} \rho_j^q(R_{ij}), \quad (2)$$

where $\rho_j^q(R_{ij})$ is the atomic electron density at atom i due to atom j . The functions in Eq. (1) were determined in previous work by fitting to equilibrium lattice constants, sublimation energies, elastic constants, vacancy-formation energies, and binary-alloy heats of formation.¹²

The force-constant tensor \mathbf{K}_{ij} can be obtained in a

straightforward way from Eqs. (1) and (2). The result is

$$\mathbf{K}_{ij} = \partial^2 E_{\text{tot}} / \partial \mathbf{R}_i \partial \mathbf{R}_j = -\mathbf{A}_{ij} + F_{i'}(\rho_{i'}) \rho_{j'}^a(\mathbf{R}_{ij}) \hat{\mathbf{r}}_{ji} \mathbf{g}_i + F_{j''}(\rho_{j''}) \mathbf{g}_j \rho_{i''}^a(\mathbf{R}_{ij}) \hat{\mathbf{r}}_{ij} + \sum_{k(\neq i,j)} F_{k''}(\rho_{k''}) \rho_{j''}^a(\mathbf{R}_{jk}) \rho_{i''}^a(\mathbf{R}_{ij}) \hat{\mathbf{r}}_{jk} \hat{\mathbf{r}}_{ik}, \tag{3a}$$

where

$$\mathbf{A}_{ij} = \psi_{ij} \hat{\mathbf{r}}_{ij} \hat{\mathbf{r}}_{ij} + \psi_{ij'}(1 - \hat{\mathbf{r}}_{ij} \hat{\mathbf{r}}_{ij}) / R_{ij}, \tag{3b}$$

$$\psi_{ij}(\mathbf{R}_{ij}) = F_{i'}(\rho_{i'}) \rho_{j'}^a(\mathbf{R}_{ij}) + F_{j''}(\rho_{j''}) \rho_{i''}^a(\mathbf{R}_{ij}) + \phi_{ij}(\mathbf{R}_{ij}), \quad \mathbf{g}_i = \sum_{j(\neq i)} \rho_{j'}^a(\mathbf{R}_{ij}) \hat{\mathbf{r}}_{ij}.$$

Here the unit vector $\hat{\mathbf{r}}_{ij} = (\mathbf{R}_i - \mathbf{R}_j) / R_{ij}$ points from atom j to atom i . The dynamical matrix¹³ for the system, which yields the squared phonon frequencies and polarizations upon diagonalization, is constructed from \mathbf{K} .

The tensor \mathbf{A}_{ij} represents the contribution to \mathbf{K}_{ij} from the environment-dependent effective pair potential ψ_{ij} . The other terms in \mathbf{K}_{ij} include environment-dependent many-body contributions.¹¹ The environmental dependence of ψ_{ij} is contained in the first derivatives of the embedding functions, $F_{i'}(\rho_{i'})$ and $F_{j''}(\rho_{j''})$, which are determined by the charge density of atoms i and j . The environmental dependence of the many-body terms comes from the gradients of the charge densities at atoms i and j as measured by the quantities \mathbf{g}_i and \mathbf{g}_j . The charge density and its gradient will necessarily be different at the surface than in the bulk, thereby modifying the force constants and leading to shorter bond lengths and deeper potential wells at the surface. *The interlayer relaxations and force-constant changes are thus obtained in one consistent calculation.*

In Fig. 1, we show the calculated and measured¹⁴ bulk phonons of fcc Cu along several symmetry lines. As can be seen from Fig. 1, good agreement between theory and experiment is found throughout the Brillouin zone. Because the semiempirical EAM functions were fitted to the experimental elastic constants, we are assured of a good fit for small wave vector q . Small discrepancies at the zone boundaries are found for the longitudinal mode

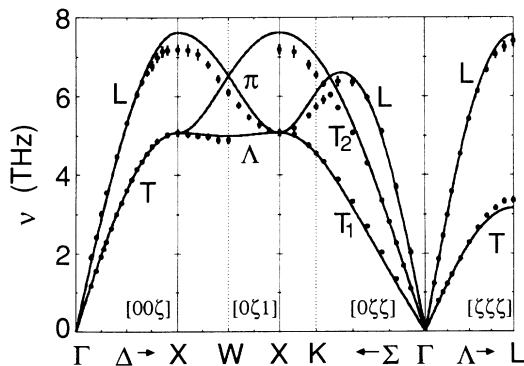


FIG. 1. Calculated and measured bulk-phonon frequencies of fcc Cu. The experimental points, taken from Ref. 14, are the solid circles with error bars.

(L) at $q = (001)$, the transverse mode (T_2) at $q = (001)$, and the transverse mode (T) at $q = (111)$. These discrepancies are reasonable given the fact that no fitting to the zone-edge phonons has been done. Since we have not exactly reproduced the bulk-phonon spectrum, the most important quantity we will compare to experiment is the shift of the surface frequency from the bulk bands.

Using the same EAM functions as in the bulk calculations, we have calculated the phonon modes for 28-layer slabs of Cu with (100) faces; both ideal and relaxed 1×1 surfaces were considered. (With the EAM we can easily do much thicker slabs; 28 layers are more than required to converge the edges of the bulk-band continuum.) The changes in interlayer spacing for the relaxed surface were found to be $\Delta_{12} = -0.026 \text{ \AA}$ and $\Delta_{23} = -0.006 \text{ \AA}$.¹² Experimentally,¹⁵ $\Delta_{12} = -0.02 \pm 0.01 \text{ \AA}$ and $\Delta_{23} = +0.03 \pm 0.01 \text{ \AA}$.

The calculated phonon modes for the relaxed surface are given in Fig. 2 and are compared to experiment in Fig. 3. In Fig. 2, we see several surface-related vibrational modes, $S_1, S_4, S_6,$ and S_7 , appearing in bulk gaps or split off from the bulk-band edges. The Rayleigh

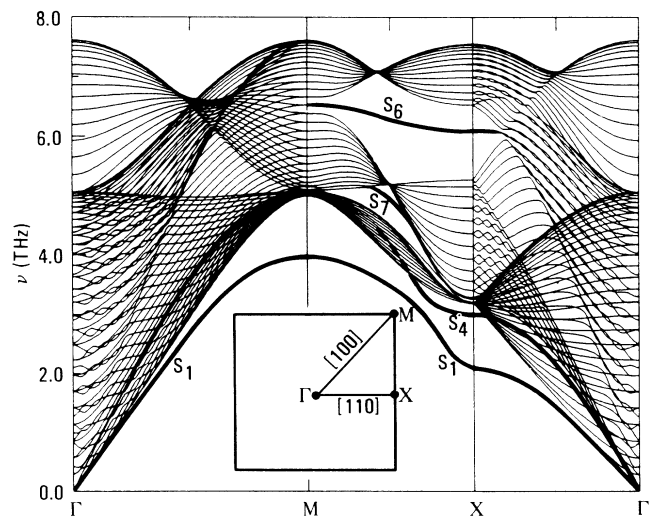


FIG. 2. Calculated phonon frequencies for a 28-layer Cu slab with (001) faces. Surface modes are indicated by bold lines.

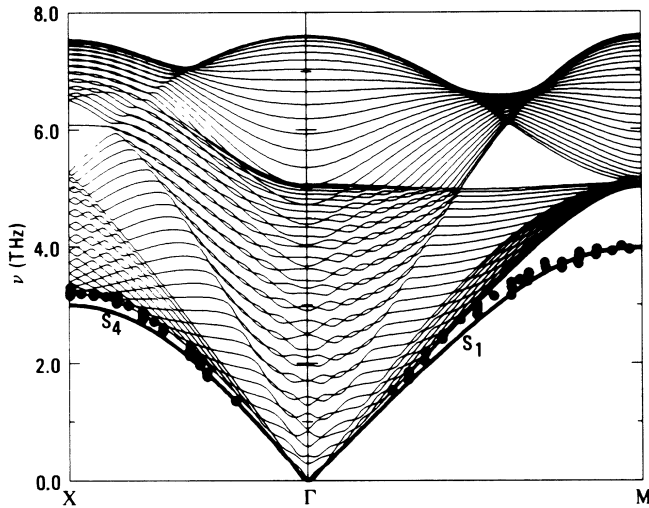


FIG. 3. Comparison of experimental and theoretical phonon frequencies. Only modes of even symmetry are shown. The experimental points, taken from Refs. 2 and 3, are the solid circles.

modes S_1 along ΓM and S_4 along ΓX have been measured by high-resolution electron-energy-loss spectroscopy, and as can be seen in Fig. 3 are in excellent agreement with the calculated surface modes. In the scattering geometry used, the S_1 mode along ΓX is not observed because it is polarized perpendicular to the sagittal plane. The S_6 mode has not been observed on Cu(100), but on the Ni(100) surface⁴ it was found to have a much smaller cross section for detection than the S_4 surface mode. Like the S_6 mode, the S_7 surface mode has yet to be experimentally identified on this surface.

Table I summarizes the results for the frequency of the surface-related vibrational modes at X and M for the ideal and relaxed 1×1 surfaces. The split-off frequency, $\Delta\nu_{so}$, is given by the difference in frequency between the bulk edge and the surface mode at the corresponding symmetry point. The effect of interlayer relaxation on the S_1 surface mode is to increase the frequency by 0.12 THz at M and 0.15 THz at X . With these frequency shifts, $\Delta\nu_{so}$ is within 0.05 THz of the experimental value.

The S_1 mode corresponds to motion of the surface atoms in the surface plane (shear horizontal) at X and normal to the surface plane (shear vertical) at M . At both symmetry points the second-layer atom remains at rest. The S_4 surface mode is particularly insensitive to interlayer relaxation, while the S_6 mode changes by about the same amount as the S_1 mode, 0.11 THz. The split-off frequency of the S_4 surface mode is also within 0.05 THz of the experimental value. Our results indicate that, on the average, the surface vibrational modes on the Cu(100) surface change by 0.1 THz upon interlayer relaxation.

The force-constant tensor, \mathbf{K} , predicted by the EAM is qualitatively different than that of a CP model. As an illustration of this difference, let us consider the force constants for neighbors along the [011] crystallographic direction in a fcc (100) plane for a bulk and a surface layer. With x (the surface normal), y , and z defined as [100], [010], and [001], respectively, and rows and columns of the force-constant tensor in xyz order, the CP expression is

$$\mathbf{K} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & -f/2 & -f/2 \\ 0 & -f/2 & -f/2 \end{pmatrix}$$

for both the bulk and the unrelaxed (100) surface. Here f is the only free parameter, and is allowed in the fitting process to be different for each pair of atoms near the surface. By contrast, the elements of this force-constant tensor in the EAM have the following relations:

$$\mathbf{K} = \begin{pmatrix} \gamma & 0 & 0 \\ 0 & -\alpha & -\beta \\ 0 & -\beta & -\alpha \end{pmatrix}$$

for the bulk and

$$\mathbf{K} = \begin{pmatrix} \gamma' & \eta & \eta \\ -\eta & -\alpha' & -\beta' \\ -\eta & -\beta' & -\alpha' \end{pmatrix}$$

for the unrelaxed (100) surface. The terms α , β , γ , and η are not fit; they are determined by the atomic positions and the EAM functions. The terms α and β include the effective pair interaction described by \mathbf{A} in Eq. (3b); β

TABLE I. Zone-edge phonon frequencies.

		Frequency (THz) at M			Frequency (THz) at X		
		Ideal	Relaxed	Expt. ^a	Ideal	Relaxed	Expt. ^a
S_1	ν	3.85	3.97	4.05	1.94	2.09	
	$\Delta\nu_{so}$	1.15	1.03	1.08	1.23	1.08	
S_4	ν				3.01	2.99	3.24
	$\Delta\nu_{so}$				0.17	0.18	0.13
S_6	ν	6.49	6.51		5.97	6.08	
	$\Delta\nu_{so}$				0.51	0.39	

^aReferences 2 and 3. No error bars were reported.

and γ include three-body terms which are mediated by atoms in layers above and below the ones in question. When the bulk is truncated, the plane above is removed and both two- and three-body terms are necessarily modified. In addition, interactions denoted by η become important; these are strictly three-body terms arising from the charge-density gradient at the surface. The magnitudes of γ and η , zero in the CP model, are typically 10% of α and β in the EAM. *The surface of this tensor is made considerably richer by the inclusion of many-body terms; fitting the surface phonons with the more constrained form of the CP model may therefore be misleading.* Our conclusions are consistent with the pseudopotential perturbation theory work¹⁰ for Al(110), which also finds that the gradient of the electron-density profile at the surface, and three-body interactions at the surface which are neither central nor pairwise, make important contributions to the dynamical matrix.

We find that both the intralayer and interlayer force constants for surface-layer atoms change by about 15% relative to the bulk. The modifications of the force constants at the surface can be viewed in a two-step process. First, the bulk is truncated to create the unrelaxed (100) surface. This process causes the intralayer and interlayer force constants to change from their bulk values by 15% and 5%, respectively. In the second step, the bulk terminated surface is allowed to relax. The dominant effect of this step is to modify the intralayer and interlayer force constants by 1% and 10%, respectively. The overall changes in the force constants due to both processes result in a 15% softening of the intralayer force constants and a 15% stiffening of the force constants between the surface- and second-layer atom.

In summary, we have shown that the EAM can provide a consistent description of the surface relaxations and phonon modes without fitting to any experimental surface data. The calculated and measured surface modes are in excellent agreement. The analysis of the force-constant tensor shows that changes in both intralayer and interlayer forces are important, and that some important elements of the tensor cannot be obtained in a central-potential model. The calculated phonon modes on the (100) surfaces of Ni, Pd, Ag, Pt, and Au show features similar to the Cu phonons reported here. Work to study the phonons on the (110) and (111) surfaces of these metals is in progress.¹⁶

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