

Nature of Surface-Phonon Anomalies in Noble Metals

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We propose a new approach to describe the many-body effects in the lattice dynamics of metals. We represent here the electron charge density in each unit cell by an expansion over the multipole moments, where the coupling of the fluctuating multipoles to ion displacements gives rise to the observed many-body effects. This model reproduces the observed surface-phonon dispersion curves and explains also their anomalous features.

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Recent He-scattering experiments have revealed some unusual features in the surface structure¹ and dynamics²⁻⁴ of metals. In particular, the gold (111) surface exhibits a solitonlike reconstruction^{1,5} and the surface-phonon dispersion curves of Cu(111) and Ag(111) show an anomalously soft resonance.³ In the case of Au(111), an extremely soft surface-acoustic branch, which lies close to the Rayleigh branch and far below the transverse bulk edge, has been reported.³ A possible reason for the observed surface-phonon anomalies is that certain effects of the electron-phonon interaction are activated or enhanced at the surface as a result of symmetry reduction. Bortolani and his co-workers^{6,7} have shown that it is possible to reproduce such anomalous phonon branches with a phenomenological force-constant model by assuming a large *ad hoc* softening of the in-plane surface force constants.

The aim of the present paper is to give an explanation for the observed surface-phonon anomalies in noble metals^{1,5} with use of a lattice-dynamical model which incorporates properly the many-body interactions. In addition, we use an approach which describes consistently the bulk and surface lattice dynamics of metals, keeping a close resemblance to the microscopic theory in the character and symmetry of its parameters.

The many-body interactions in noble metals arise mainly from *s*- and *p*-electron states, and we represent the *sp* charge density by a multipole expansion around an appropriate high-symmetry point in the unit cell, that renders the expansion rapidly convergent. In such a description, the electronic degrees of freedom are the fluctuating multipole moments, whose coupling to the ion displacements produces the observed many-body effects.

It is known from the charge-density calculations of noble metals^{8,9} that the charge density close to the ion core is predominantly of *d* character, whereas at interstitial regions it is predominantly of *sp* character. In each unit cell *l*, there exists an interstitial site \mathbf{r}_{l-} with an octahedral symmetry, where the total charge density has a minimum. We represent the conduction electron density of the *sp* states by a multipole expansion around this minimum. The modulation of a multipole centered around this site corresponds exactly to the deformation of a "coreless" particle situated at this position, which we shall, henceforth, call a pseudoparticle.¹⁰

We represent the *sp* charge density by

$$\rho_-(\mathbf{r}) = \sum_{l,\Gamma_s} c_{l\Gamma_s}^- Y_{\Gamma_s}(\mathbf{r} - \mathbf{r}_{l-}), \quad (1)$$

where the coefficient $c_{l\Gamma_s}^-$ is the multipole moment of Γ_s type belonging to the unit cell *l*. The Γ_s 's label the irreducible representations of the point group at the expansion center (e.g., O_h in our case), and the Y_{Γ_s} 's are the corresponding cubic harmonics. A similar expression can be written for the *d*-electron density $\rho_+(\mathbf{r})$, which is expanded around the ion site \mathbf{r}_{l+} . The corresponding multipole moments are labelled by $c_{l\Gamma_s}^+$. The total potential energy $U[\rho(\mathbf{r})]$ is then a functional of the charge density $\rho = \rho_- + \rho_+$. Making a Taylor expansion of the total potential energy in terms of the ion displacements $u_{l\alpha}$ and the fluctuations $\delta c_{l\Gamma_s}^\pm$ around the equilibrium configuration, we have

$$2U = [\mathbf{u} \cdot \Phi \cdot \mathbf{u} + (\mathbf{u} \cdot \mathbf{T} \cdot \delta \mathbf{c} + \text{H.c.}) + \delta \mathbf{c} \cdot \mathbf{H} \cdot \delta \mathbf{c}], \quad (2)$$

where the elements of the matrices Φ , \mathbf{T} , and \mathbf{H} are given by

$$\Phi_{\alpha\beta}^{ll'} = \partial^2 U / \partial u_{l\alpha} \partial u_{l'\beta}, \quad (3)$$

$$T_{\alpha,\Gamma_s,\pm}^{ll'} = \partial^2 U / \partial u_{l\alpha} \partial c_{l'\Gamma_s}^\pm = \int d^3\mathbf{r} [\partial^2 U / \partial u_{l\alpha} \partial \rho_\pm(\mathbf{r})] Y_{\Gamma_s}(\mathbf{r} - \mathbf{r}_{l'\pm}), \quad (4)$$

and

$$H_{\Gamma_i \pm, \Gamma_j \pm}'' = \partial^2 U / \partial c_{\Gamma_i \pm} \partial c_{\Gamma_j \pm} = \int \int d^3 r d^3 r' [\partial^2 U / \partial \rho_{\pm}(\mathbf{r}) \partial \rho_{\pm}(\mathbf{r}')] Y_{\Gamma_i}(\mathbf{r} - \mathbf{r}_{i \pm}) Y_{\Gamma_j}(\mathbf{r}' - \mathbf{r}_{j \pm}). \quad (5)$$

We can now write the equations of motion for the ion displacement \mathbf{u} and for the charge-density deformation represented by the pseudovector $\delta \mathbf{c}$ in the harmonic and the adiabatic approximations¹¹ as

$$M \omega^2 \mathbf{u} = \Phi \cdot \mathbf{u} + \mathbf{T} \cdot \delta \mathbf{c}, \quad (6)$$

$$0 = \mathbf{T}^\dagger \cdot \mathbf{u} + \mathbf{H} \cdot \delta \mathbf{c}, \quad (7)$$

where M is the matrix of the ion mass. After eliminating $\delta \mathbf{c}$, we obtain

$$M \omega^2 \mathbf{u} = (\Phi - \mathbf{T} \cdot \mathbf{H}^{-1} \cdot \mathbf{T}^\dagger) \cdot \mathbf{u}. \quad (8)$$

Such a treatment is obviously an extension of both shell-¹² and bond-charge¹³ models to metallic systems. In addition, this approach represents a useful parametrization of *ab initio* methods based on the density functional theory.¹⁴ We find that with the use of this approach it is possible to provide an accurate description of both bulk and surface dynamics by considering only a few parameters. This is in contrast to the frequently used Born-von Kármán models for noble and transition metals, which require a comparatively large number of fictitious long-range force constants. Furthermore, the parameters in the present treatment have a direct physical meaning, since they are expressed in terms of functional derivatives of the total energy with respect to the partial electron densities.

The calculation of the ion-ion interaction matrix Φ for the nearest neighbors is quite straightforward, while the many-body term \mathbf{T} requires the symmetry coordinate representation of ion displacements producing the electronic deformability under consideration. In the calculation of the matrix \mathbf{H} , we neglect the interaction between neighboring pseudoparticles and retain only diagonal terms, which we determine from the translational invariance condition.

In our model, the ion-ion interaction matrix Φ is characterized by a single short-range force constant¹⁵ A_1 and the many-body term \mathbf{T} by the dipolar (K_{15}^\dagger) and quadrupolar ($K_{12}^\dagger, K_{25}^\dagger$) deformabilities. For a coreless pseudoparticle, the dipolar term actually reduces to a short-range radial force constant A_0 between the ion and the pseudoparticle. In the case of gold, we have a small contribution to the many-body interaction from the modulation of the d charge density too, in particular, from quadrupolar (Q_{12}^\dagger) and octupolar (Q_{25}^\dagger) deformabilities, which can cause virtual excitations of electrons from d to s orbitals and from $d_{x^2-y^2}$ into p_z orbitals, respectively.

The values of the parameters used in the calculation are given in Table I. They have been obtained by fitting them to the elastic constants and zone-boundary-phonon frequencies of the *bulk*. We first used this model to cal-

culate the bulk-phonon dispersion curves of Cu, Ag, and Au,¹⁶ and we obtained a good agreement with the experimental data. The main virtue of this model is that it provides a localized description for the many-body interactions, which we think is a great improvement over the standard force-constant models.

Having obtained a good fit for the bulk phonons, we subsequently used the model to calculate the surface phonons. Close to the surface layer, there is a major charge redistribution. In particular, for Cu(111), charge-density calculations indicate an increase of the sp charge per atom from $Q_b = 1.115$ electrons in the bulk to $Q_s = 1.346$ electrons at the surface.⁹ In addition, unlike the ideal (111) surface,¹⁷ the topmost layer of pseudoparticles relaxes into the underlying metallic layer.⁹ This relaxation, arising from uncompensated Coulomb forces, increases the in-plane particle-pseudoparticle attraction and leads to an effective reduction of the interionic repulsion at the surface.

We estimate this change in the Coulomb contribution to the pseudoparticle-ion force constant at the surface ΔA_c , via a phenomenological relationship to the work function W . The work function for extraction of an sp electron either from the bulk or from the surface (average initial position at the pseudoparticle center) is assumed to be proportional to the number of neighboring metal ions (n_b or n_s) and inversely proportional to the pseudoparticle-ion distance (x_b or x_s , respectively). Thus, we write

$$W = n_b e^2 / \epsilon_b x_b = n_s e^2 / \epsilon_s x_s, \quad (9)$$

where ϵ_b and ϵ_s are appropriate screening constants for the bulk and surface, respectively. The pseudoparticle-ion Coulomb force constants are analogously written as

$$A_{cb} = -\frac{2e^2 Q_b^2}{\epsilon_b x_b^3}, \quad A_{cs} = -\frac{2e^2 Q_s^2}{\epsilon_s x_s^3}, \quad (10)$$

TABLE I. Parameters used in our surface dynamical calculations of noble metals. Notice that expect for ΔA_c , values of surface parameters are the same as in the bulk.

Parameters	Cu	Ag	Au
W (eV)	4.50	4.70	4.80
x_b (Å)	1.80	2.04	2.05
Q_s ($Q_b = 1$)	1.48	1.52	1.52
$-\Delta A_c$ (10^4 erg/cm ²)	4.14	3.58	3.61
A_1 (10^4 erg/cm ²)	2.76	2.11	3.42
K_{15}^\dagger (10^4 erg/cm ²)	3.98	2.32	7.38
K_{12}^\dagger (10^4 erg/cm ²)	1.41	0.98	2.97
K_{25}^\dagger (10^4 erg/cm ²)	0.62	0.23	1.54
Q_{12}^\dagger (10^4 erg/cm ²)	0.15
Q_{25}^\dagger (10^4 erg/cm ²)	0.98

where Q_b and Q_s are the sp charge per atom in the bulk and surface, respectively. By combining Eqs. (9) and (10), we obtain an expression for the change of the Coulomb contribution at the surface as

$$\Delta A_c = -2W(Q_s^2/n_s x_s^2 - Q_b^2/n_b x_b^2). \quad (11)$$

The surface force-constant perturbation matrix is then just $\Delta A_c(x_\alpha x_\beta/x_s^2)$, where x_α and x_β are the components of x_s along the surface. We then constructed the dynamical matrix of a 35-layer slab appropriate to our model,¹¹ by incorporating this change in the Coulomb attraction term at the surface and keeping all other parameters unchanged. Using the values of Q_b and Q_s , as given in Ref. 9, and the value of W , as given in Table I, we obtain for Cu(111) $-\Delta A_c = 3.11 \times 10^4$ erg cm⁻². This value of ΔA_c gives surface resonances which are in fair agreement with the experiment. In addition, we did a best fit of the surface resonance to the experimental data and this yielded $-\Delta A_c = 4.14 \times 10^4$ erg cm⁻², which is not very different from the value calculated from Eq. (11). In the case of Ag(111), we are not able to determine ΔA_c from Eq. (11), as we do not know the values of Q_b and Q_s . So we determine ΔA_c from the best fit to the experimental surface resonance and from that we can in turn estimate the surface charge Q_s , assuming $Q_b = 1$. If we now assume that Q_s for Ag(111) and Au(111) are approximately the same, then we can estimate ΔA_c for Au(111) also, which can be used to calculate the corresponding surface resonance. It should be stressed here that, if the work function and the sp charge at the surface are known, the surface parameters are determined without any ambiguity.

The surface-phonon dispersion curves obtained by the diagonalization of the slab dynamical matrix are shown in Fig. 1. The lowest surface-localized branch is the Rayleigh wave (S_1), which has polarization in the sagittal plane. The next higher mode, appearing below the edge of the surface-projected acoustic bulk-phonon band, is an acoustic shear-horizontal mode. This mode is not observed in He-scattering experiments.³ Similarly, some of the surface gap modes (e.g., S_3) have also not yet been detected experimentally. The vertically shaded areas within the surface-projected bulk bands represent the dispersion of the quasilongitudinal surface resonance, S_6 . This is the anomalous mode we referred to in the introduction. The agreement of this mode with the experimental data is reasonably good. We find that this mode appears because of the surface charge redistribution, which increases the Coulomb attraction term at the surface. This implies an effective reduction of the ion-ion repulsion at the surface, which results in an anomalous softening of the quasilongitudinal surface-resonance mode. However, in the case of Au, the perturbation of the Coulomb term at the surface, although comparable to that of Cu and Ag, is not sufficient to produce such a soft resonance. This is because the repulsive term A_1 in

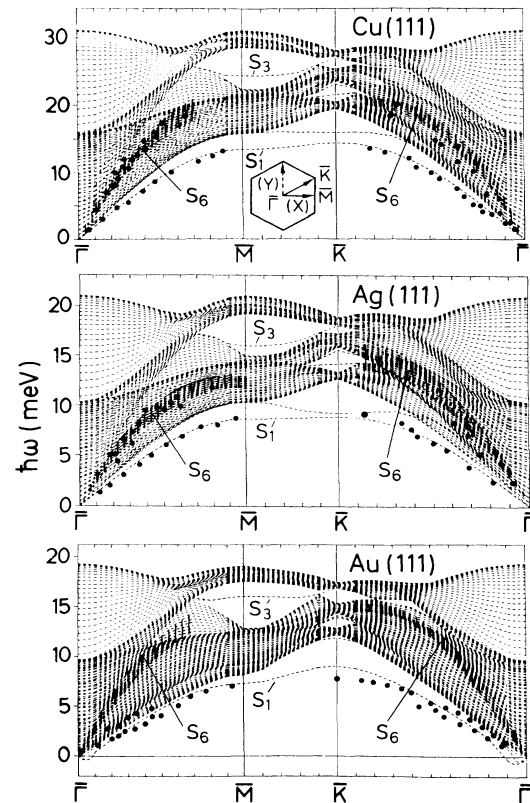


FIG. 1. Calculated surface-phonon dispersion curves of Cu(111), Ag(111), and Au(111). S_1 , S_3 , and S_6 represent the Rayleigh wave, the gap mode, and the surface resonance, respectively. The spectral width of the surface-resonance mode S_6 is indicated by the lengths of the vertical bars. In a small region close to $\bar{\Gamma}$, we find for Au(111) a lattice instability, i.e., some of the phonon frequencies of the S_1 branch become imaginary (represented in the figure as negative ordinate values). Experimental points are depicted by filled circles and, for the sake of clarity of the figure, not all experimental points are given.

Au is much larger than the corresponding values for Cu and Ag (see Table I). We find that this is one essential difference between Au(111) and the (111) surfaces of Cu and Ag. In addition, for the (111) surface of gold, we find a lattice instability, i.e., some of the phonon frequencies become imaginary for wave vector $\bar{q} \approx (2\pi/a) \times (0.1, 0)$. This finding is consistent with the recent diffraction experiments on reconstruction of the Au(111) surface.^{4,5} We point out that the appearance of the surface instability as well as the absence of the anomalously soft resonance in Au(111) are not related to the additional deformabilities (Q_{12}^+ , Q_{25}^-) in the bulk dynamics of gold. The instability occurs even when these additional terms are neglected. Finally, we attribute the observed doubling or splitting of the S_1 branch in Au(111) to the anisotropy induced by the reconstruction.

In summary, we have proposed a new approach to treat the many-body interactions in the lattice dynamics of noble metals. These interactions arise from the coupling of the electronic deformations to the ion displacement. Our description provides a local representation of many-body forces. In addition, the parameters used in the model have a clear microscopic meaning and may be determined from *ab initio* calculation. Finally, we find that the large softening of the quasilongitudinal resonance in Cu(111) and Ag(111) is due to the increased Coulomb attraction at the surface. Furthermore, we find an instability for the Au(111) surface, reminiscent of the observed surface reconstruction.

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¹⁷By ideal surface we mean the geometrical termination of the bulk with no relaxation of either the pseudoparticle or the metallic layer.