Explanation of the Anomalous Peak Observed in He-Atom Scattering from Ag(111)

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The inelastic He/Ag(111) cross section has been evaluated in the one-phonon distorted-wave Born approximation. The authors use an atom-surface potential made up by a repulsive part derived from a superposition of atomic charges and by the attractive van der Waals interaction. The surface phonon density of states is evaluated within a force-constants parametrization of the bulk dynamics. By changing the surface force constants the authors are able to explain all the salient features appearing in the experimental time-of-flight spectra.

In recent years there has been an increasing interest in the problem of surface lattice dynamics in metals because of the noticeable development of experimental techniques. For acoustic long-wavelength phonons, surface Brillouin scattering[1] has given useful information on the localized surface modes as well as on the so-called mixed modes[2] embedded in the bulk continuum. These pseudo modes, or resonances, owe their existence to the presence of the surface and are an admixture of bulk and decaying waves. More recently, phonons in the entire two-dimensional Brillouin zone have been detected with electron-energy-loss spectroscopy[3] and with atomic inelastic surface scattering.[4,5]

In this paper we address the He-atom–noble-metal-surface scattering in order to explain the presence of an "anomalous" peak belong to the bulk phonon spectrum of silver, as recently observed by Doak, Harten, and Toennies[5] with the time-of-flight (TOF) technique. We show that this structure is due to a resonant mode, which can be reproduced by changing the surface interaction.

In atom-surface scattering theory the interaction potential is separated into an attractive part V_{vw} of the van der Waals type and a repulsive part V_R due to the electronic charge in the vicinity of the surface. We have previously shown[6] that the He-atom–noble-metal repulsive interaction can be written in the form

$$V_R(\vec{r}) = U_0 \sum_l \exp[-Q_c^2(\vec{R} - \vec{R}_l)^2/2]\exp[-\beta(z - z_l)], \tag{1}$$

where U_0 is derived according to the Esbjerg-Norskov procedure[7] and β is the softness parameter. For the He/Ag(111) case we found[6] $U_0 = 546$ eV, $\beta = 2.2$ Å^{-1}, and $Q_c = 0.73$ Å^{-1}. The total potential is obtained by adding to Eq. (1) the van der Waals part in the form given by Zaremba and Kohn,[8] $V_{vw} = -c_{vw}/(z - z_{vw})^3$, where $c_{vw} = 770$ meV Å^3 and $z_{vw} = 1.38$ Å. This potential accurately reproduces the He-diffraction intensities.[9]

We evaluate the scattering cross section in the one-phonon distorted-wave Born approximation.[10] This approximation is justified by the very low amplitude of the corrugation of the Ag(111) surface, as observed in diffraction measurements performed with He beams.[5,9] The cross section per unit area for an incident atom with initial momentum $(\vec{K}_i, k_{iz})$ and energy E_i, and final momentum $(\vec{K}_f, k_{fz})$ and energy E_f becomes

$$\frac{d^2R}{dE_f d\Omega_f} = \frac{2}{NM}\sum_{\vec{Q},j}\frac{(2mE_f)^{1/2}}{\omega(\vec{Q},j)|k_{iz}||k_{fz}|^2}|-i\beta e_z(\vec{Q},j) + Qe_x(\vec{Q},j)|^2\exp(-2W)\exp(-Q^2/Q_c^2)$$
$$\times |\langle\chi_{iz}|\partial V_0/\partial z|\chi_{fz}\rangle|^2 n(\omega(\vec{Q},j))\delta(\vec{K}_f - \vec{K}_i - \vec{Q})\delta(E_f - E_i - \hbar\omega(\vec{Q},j)). \tag{2}$$

Here $\vec{Q}$ is the phonon lateral momentum in the extended zone scheme. N is the number of atoms per unit surface area, M the atomic mass, $n(\omega)$ the Bose occupation number, $\exp(-2W)$ the Debye-Waller factor, $\omega(\vec{Q},j)$ the phonon frequency of the jth mode with lateral momentum $\vec{Q}$, and $\vec{e}(\vec{Q},j)$ the polarization vector of the surface atoms. In the matrix elements appearing in Eq. (2) the eigenfunctions χ of the laterally averaged total potential V_0 (Ref. 10) are determined numerically with the Numerov procedure. These matrix elements are decaying functions of $\vec{Q}$. We want to stress the importance in the scattering cross section of the cutoff factor $\exp(-Q^2/Q_c^2)$. This factor explains why for metals umklapp process-

es (Q beyond the first zone) are not observed, while in alkali halides it is impossible to detect excitations up to the second zone.[11] In fact, we found[6] that for metals Q_c^2 is typically 0.14 a.u.$^{-2}$ while in alkali halides (LiF) $Q_c^2 \simeq 0.5$ a.u.$^{-2}$.

The eigenvectors $\vec{e}(\vec{Q}, j)$ and eigenvalues $\omega(\vec{Q}, j)$ for the Ag(111) surface have been evaluated for a slab of 69 (111) atomic planes, within a force-constant parametrization of the bulk lattice dynamics. Central and angular forces have been included up to second neighbors, to account for the effects due to the inhomogeneity of the electron gas. The details of the calculation are given elsewhere.[12] In our model the surface interactions are determined by the nearest-neighbor radial force constant β_1^S, the angular force constant δ_1^S, and the tangential force constant α_1^S. In a previous paper,[13] by using surface force constants equal to those of the bulk, we were able to explain the position and the decay of the Rayleigh-wave (RW) peak as a function of Q. On the contrary, in the bulk region we did not obtain any significant structure, in complete disagreement with the presence of a well defined peak in the experimental data.[5] In the present paper, by varying the nearest-neighbor surface force constants around the bulk values[14] (hereafter labeled by a superscript B), we give an explanation of this structure.

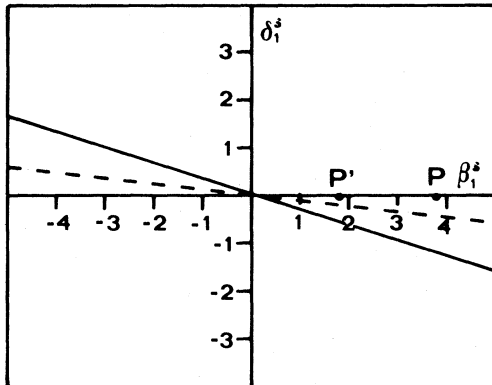Let us consider the stability problem of the (111) surface. The first modes which become

soft as a result of variations of the surface force constants belong to the M point of the surface Brillouin zone. In Fig. 1 the surface stability diagram at fixed α_1^S is shown. As one can see a small lowering of δ_1^S makes the surface unstable against M shear horizontal (SH) modes, while the frequency of the sagittal M mode does not change appreciably. In fact, for surface atoms the angular force constant δ_1^S is mainly related to SH modes. Also the lowering of α_1^S produces the same instability. The diagram of Fig. 1 is a useful guide for changing the force constants. In particular, a significant lowering of the longitudinal modes can be achieved by reducing the radial force constant β_1^S, keeping $\alpha_1^S = \alpha_1^B$ and $\delta_1^S = \delta_1^B$. We have found that a reduction of β_1^S of 30% is sufficient to produce a resonance below the longitudinal threshold. For $\beta_1^S = 0.48 \beta_1^B$ (point P' in Fig. 1) we obtain the best fit to the experimental TOF data,[5] for both the position and the intensity of the resonance. In Fig. 2 the sagittal phonons of the Ag(111) surface are drawn. There is a clear evidence of a resonance located between the transverse and the longitudinal thresholds.

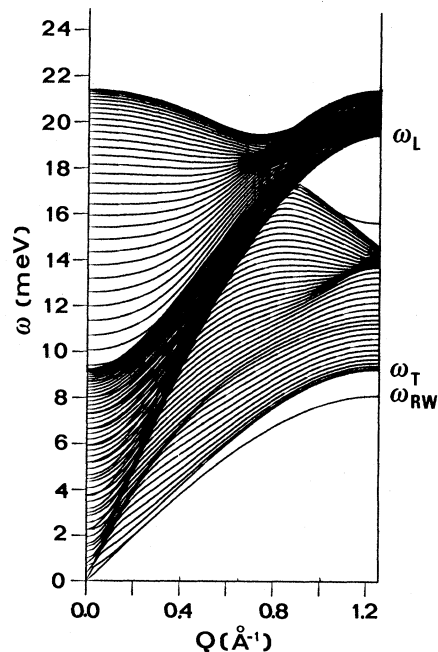The density of states along the kinematical curves for a given scattering geometry is pre-

FIG. 1. Stability diagram of the Ag(111) surface as a function of the nearest-neighbor surface force constants (in THz^2) β_1^S and δ_1^S at fixed $\alpha_1^S = \alpha_1^B$. P is for $\beta_1^S = \beta_1^B$ and $\delta_1^S = \delta_1^B$. P' is for $\beta_1^S = 0.48\beta_1^B$ and $\delta_1^S = \delta_1^B$. The region below the continuous line refers to surface force constants producing an instability of the M phonon polarized in the sagittal plane with mainly longitudinal character. The dashed line corresponds to the instability of the M SH phonon.

FIG. 2. Surface phonons for Ag(111) relative to the point P' of Fig. 1. ω_{RW}, RW dispersion curve. ω_T and ω_L, dispersion curves for bulk transverse and longitudinal thresholds.
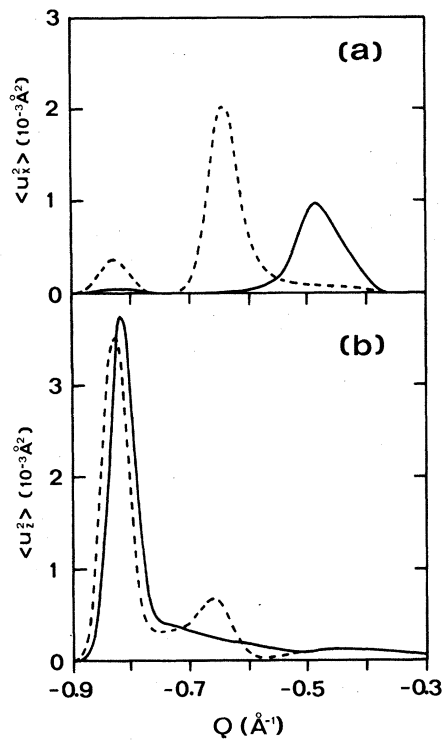
FIG. 3. Mean-square-displacement components along the kinematical curve for $\theta_i = 55°$. Continuous lines, ideal surface (P in Fig. 1). Dashed lines, modified force constants (P' in Fig. 1). (a) Longitudinal component; (b) normal component.
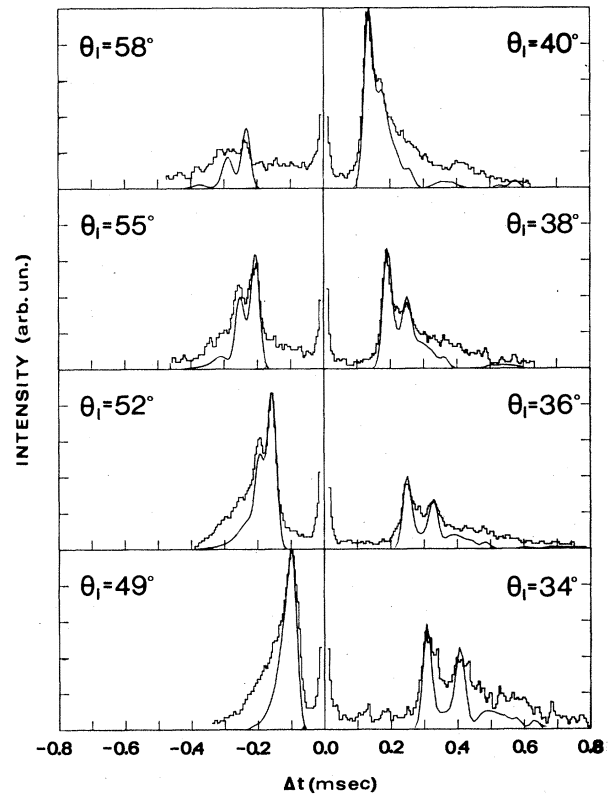

FIG. 4. TOF spectra for He/Ag(111) for $E_i = 17.5$ meV. The histograms are the experimental data of Ref. 5. The calculated curves refer to the point P' of Fig. 1 and are normalized to the RW experimental peaks.

sented in Fig. 3, for both the sets P and P' of force constants. Figure 3(b) refers to the component of the phonon displacement field normal to the surface. The RW gives rise to the most prominent structure of the spectrum. The ideal calculation with $\beta_1^S = \beta_1^B$ does not present any additional structure. The modified force-constant calculation shows a new small peak due to the resonance; however, the modification of the RW peak is negligible. This explains why the RW TOF peak is not affected by the value of β_1^S, at least in the range $\beta_1^S/\beta_1^B = 0.5$–$1.0$. The longitudinal spectrum of Fig. 3(a) shows more clearly the nature of the resonant mode. The continuous line for $\beta_1^S = \beta_1^B$ exhibits a broad peak corresponding to the longitudinal threshold; when β_1^S is lowered this peak shifts considerably to higher values of $|Q|$ and consequently to lower values of ω, because of the kinematical condition.[11] Although for $\beta_1^S = \beta_1^B$ a longitudinal peak is already present in the density of states, such a structure almost disappears in the calculated TOF spectra because of cross-section effects in Eq. (2). A

comparison between Figs. 3(a) and 3(b) shows that the new resonant mode has mainly longitudinal character and originates from bulk modes lying just above the longitudinal phonon edge. The localization of the longitudinal resonant mode is increased by lowering β_1^S because in this case the mode is embedded in a bulk continuum with prevailing transverse polarization.

The TOF spectra evaluated with Eqs. (1) and (2) are presented in Fig. 4 for different scattering angles. The highest peak always refers to annihilation ($\theta_i > 45°$) or creation ($\theta_i < 45°$) of a RW. When θ_i is close to $45°$ (specular reflection) the spectra are dominated by the exchange of the Rayleigh phonon, even if for $\theta_i = 40°$ the pseudo mode in the bulk region is already resolved, both in the experimental and in the calculated spectra. Away from the specular reflection the two peaks become comparable. The calculated TOF spectra accurately reproduce the experimental line shapes. Notice that also the behavior of the

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scattering intensity versus the scattering angle θ_i is in agreement with the experimental data.[13] The structureless background present in the spectra is typical of multiphonon events. The shape of the calculated TOF spectra depends strongly on the repulsive cutoff potential and also on the van der Waals interaction. These terms modulate the phonon displacement field in Eq. (2) and are essential in order to reproduce correctly the relative intensities of the RW and of the resonance.

In conclusion, we have shown that the "anomalous" peak observed in the atom-scattering spectra of silver is a pseudo mode of longitudinal character. The appearance of this resonance is due to the lowering of the nearest-neighbor radial force constant in the surface plane. By considering the softness of the potential, through the cutoff factor, and the attractive van der Waals interaction we are also able to explain the decay of the scattering intensities as a function of the momentum transfer Q.

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[13]V. Bortolani, A. Franchini, F. Nizzoli, G. Santoro, G. Benedek, V. Celli, and N. Garcia, Solid State Commun. 12, 1045 (1983).

[14]Bulk force constants (in THz^2). First nearest neighbors: $\alpha_1{}^B = -0.019$, $\beta_1{}^B = 3.796$, $\delta_1{}^B = -0.058$. Second nearest neighbors: $\alpha_2{}^B = 0.019$, $\beta_2{}^B = 0.088$, $\delta_2{}^B = 0.147$.