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Avoided crossing of vibrational modes in Ag(110) observed by He time-of-flight measurements

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The phonon spectrum of the Ag(110) surface along the $\langle 1\bar{1}0\rangle$ direction is studied by He inelastic scattering with time-of-flight detection. The Rayleigh mode and two surface vibrational resonances are described up to the surface Brillouin-zone boundary. The dispersion curves of the resonances show the avoided crossing behavior predicted but never observed for the (110) surfaces of fcc metals. Surface lattice-dynamics calculations using a simple central nearest-neighbor force-constant model are performed and found to be in close agreement with the experiment.

The study of surface vibrations is a fundamental step in understanding many processes of large interest in pure and applied physics such as adsorption-desorption of gases, gas-surface energy accommodation, surface reconstruction, and phase transitions.[1] This has led to a rapid growth in the experimental studies of surface vibrations for a wide class of single crystals[2,3] and for a few adsorbed layers.[4-6] Metal surfaces, in particular, were recently investigated with high-resolution apparatuses by inelastic He scattering[7,8] and electron energy loss spectroscopy (EELS).[4,9] These studies yield extensive data for several (111) and (100) surfaces of fcc metals. More open metal surfaces received up to now limited attention: Cu(110) was studied along the $\langle 100\rangle$ direction by inelastic He scattering[10] while Cu(110) and Ni(110) were explored by EELS measurements[11,12] at the $\bar{\Gamma}$ point.

In this paper high-resolution measurements by He time-of-flight (TOF) scattering for the Ag(110) surface along $\langle 1\bar{1}0\rangle$, yielding the dispersion curves for the surface vibrational modes, are reported. A short description of the apparatus is reported in Ref. 13. The measurements are performed with beam energies $E_b = 17.6$ and 19.0 meV, velocity spread $\Delta v/v \approx 1\%$ full width half maximum, angles of incidence θ_i ranging from 33° to 77° and scattering angles $\theta_f = 110.3° - \theta_i$. The surface, cleaned by ion bombardment, annealing, and oxygen exposure,[14] is held at room temperature during the measurements. The $\langle 1\bar{1}0\rangle$ crystal direction (x axis) and the surface normal (z axis) are set in the scattering (sagittal) plane by maximizing the specular and diffracted He intensities. The low corrugation of the surface electron density along $\langle 1\bar{1}0\rangle$ makes the elastic diffraction peaks quite small, a few parts in 10^4 of the specular peak. This, in turn, is only 1% of the direct beam due to strong out-of-plane scattering and to thermal attenuation. As a consequence, TOF spectra with quite low counting rates are measured and surface phonon creation-annihilation processes with parallel momentum exchange mostly limited to the first surface Brillouin zone (SBZ) are detected. As shown in Fig. 1, phonon annihilation processes are observed in the TOF spectra measured for $\theta_i > \theta_f$ (lower panel) while phonon creation is detected for $\theta_i < \theta_f$ (upper panel). The Rayleigh mode S_1 and two other singularities in the surface phonon spectrum indicated by MS_0 and MS_7 are resolved. The analysis of the whole set of about one hundred TOF

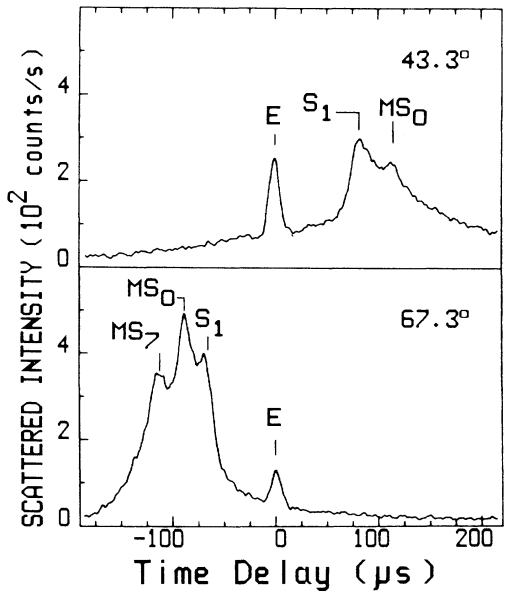

FIG. 1. He TOF spectra taken along the $\langle 1\bar{1}0\rangle$ direction of the Ag(110) surface with beam energy $E_b = 17.6$ meV and surface temperature $T_s = 300$ K. Positive time delays correspond to phonon creation. E and S_1 label the elastic incoherent peak and the Rayleigh mode, respectively, while MS_0 and MS_7 refer to the surface resonances discussed in the text. The angle of incidence is given in the upper right corner of each plot.

spectra yields the description of the surface phonon spectrum presented in Fig. 2. Q and $\hbar\omega$ are the parallel momentum and the energy of the surface phonons, respectively. The Rayleigh mode S_1 is observed with a group velocity v_g in quite good agreement with the predictions of the continuum elastic theory (dashed line).[15] No substantial decrease of v_g is observed up to the SBZ boundary. The effectiveness of the surface modes in transferring energy to the He atoms may be evaluated with the help of Fig. 3, where a few momentum loss spectra obtained from the TOF spectra are reported. It is seen that MS_7 yields counting rates decreasing with increasing Q and that MS_0 is highly effective for $Q \approx 0.4\pi/b$ where it dominates even with respect to the Rayleigh mode.

As shown in Table I, the energy $\hbar\omega_7$ of the mode MS_7 at the $\bar{\Gamma}$ point, with respect to the energy $\hbar\omega_L$ of the longitudinal bulk mode at X,[16] scales in the way observed for Cu and Ni by Stroscio, and co-workers.[11,12] Furthermore, the dispersion curves for the MS_0 and MS_7 modes present features very similar to those predicted for Ni(110) by Persson, Stroscio, and Ho.[17] These authors perform lattice dynamics calculations by using a simple model accounting only for central forces between nearest-neighbor atoms. For the Ag(110) case, similar calculations using a value suggested by Black, Shanes, and Wallis[18] for this single force constant lead to the dispersion curves shown in Fig. 2 (full lines). The calculations show that the two modes MS_0 and MS_7 originate from the avoided crossing of surface vibrational modes belonging to the same symmetry class at the surface. One of these modes is split off from a bulk sub-band and the other one is a pseudo-band-gap resonance mode. As a consequence of the avoided crossing, MS_0 and MS_7 present an interchange of polarization moving from $\bar{\Gamma}$ to $\bar{X}$. The lower branch, MS_0 is polarized in the x direction close to $\bar{\Gamma}$ and to $\bar{X}$, while it becomes z polarized in the region of the avoided crossing. As the He atoms are coupled to the phonon spectrum mainly via the z-projected vibrational amplitudes of the surface atoms,[1] the above predictions are in complete agreement with the experiment. In fact MS_0 eludes observation for $Q < 0.25\pi/b$, yields quite low counting rates for $Q > 0.75\pi/b$, and relatively high counting rates for $Q \approx 0.4\pi/b$. The experimental results shown in Fig. 3 also confirm that the upper branch MS_7 is z polarized at the $\bar{\Gamma}$ point and x polarized at the crossing.

In spite of our simple model for the lattice dynamics of Ag a rather surprising overall good agreement between the calculated and measured dispersion curves is obtained.

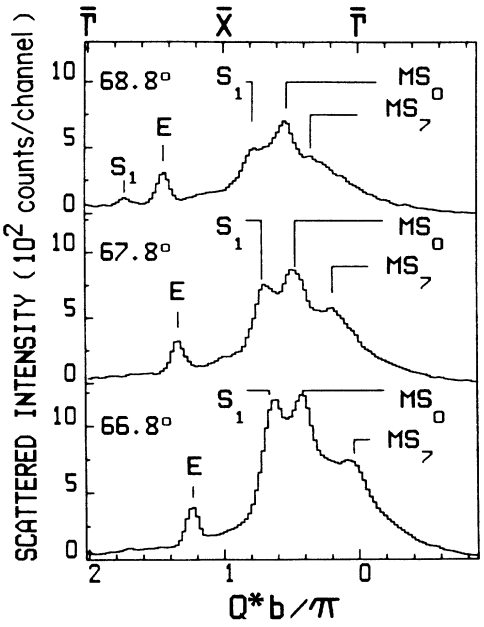

FIG. 3. Momentum loss spectra obtained from the TOF spectra detected at the angles of incidence given in the upper left corners of each plot. The peak labels, the beam energy, and the surface temperature are the same as in Fig. 1. Q^* is the phonon momentum in the extended zone.

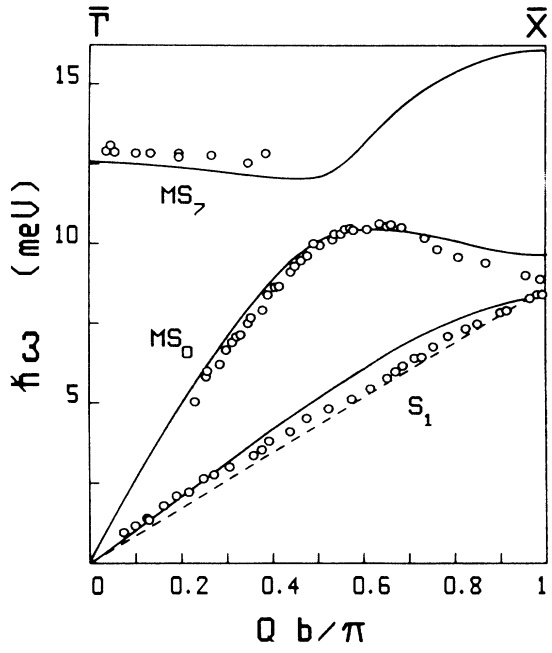

FIG. 2. Energy $\hbar\omega$ vs parallel momentum Q for the surface phonons detected for Ag(110) along $\langle 1\bar{1}0\rangle$. The surface Brillouin zone boundary corresponds to $Qb/\pi = 1$ where $b = 2.89$ Å is the nearest-neighbor distance. The dashed line shows the behavior of the Rayleigh mode as predicted by the continuum elastic theory (see Ref. 15). The full lines refer to the present lattice-dynamics calculations for the unrelaxed surface.

TABLE I. Energies of the bulk longitudinal modes at $X(\hbar\omega_L)$ and of the surface resonances MS_7 at $\bar{\Gamma}(\hbar\omega_7)$ measured in a few metals.

	Ag(110)	Cu(110)	Ni(110)
$\hbar\omega_L$ (meV)	13.7[a]	21.0[a]	26.3[a]
$\hbar\omega_7$ (meV)	12.9[b]	20[c]	24[c]

[a]Reference 16.
[b]Present work.
[c]Reference 11.

The slight discrepancies observed for the Rayleigh mode and for the MS_0 mode at the SBZ boundary may be due to the softening of the interaction between the silver atoms in the topmost layer. According to Bortolani and coworkers,[19,20] this softening originates the relaxation of the modes polarized in the surface plane and increases substantially the density of states for the sagittal modes without affecting their frequencies. For this reason a quantitative analysis of the scattering intensities for the MS_0 mode to be compared to the results by Bortolani, Franchini, and Santoro[20] appears to be highly interesting.

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