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Surface phonon dispersion on Cu(111)

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We report the first experimental determination of surface phonon dispersion on Cu(111) using high-resolution electron-energy-loss spectroscopy. The gap mode (S_2) near $\bar{M}$ in the surface Brillouin zone is measured for the first time in addition to extending earlier He scattering measurements by Toennies and collaborators of the Rayleigh and longitudinal resonance modes. Lattice-dynamical and electron-scattering analysis of these results indicate that the lateral surface force constant is softened by approximately 15% in marked contrast to earlier suggestions that a 50–70% reduction occurs on this surface.

Recent high-resolution inelastic He scattering measurements due to Toennies and co-workers[1] have raised exciting issues regarding surface phonon dispersion on the (111) surfaces of the noble metals Cu, Ag, and Au. In particular, a new longitudinal resonance (LR) detected above the Rayleigh mode (S_1) was interpreted by Bortolani *et al.*[2] in terms of a marked 50% weakening of the lateral force constants in the uppermost surface layer for Ag(111). A softening of 50% has also been suggested[1] for Cu(111) whereas a similar explanation for Au(111) requires a remarkable 70% reduction.[2] More recently, Santoro and Bortolani[3] have also proposed a 70% softening for Cu(111), again based on their analysis of the inelastic He scattering data. These results are certainly surprising in view of the close-packed nature of the (111) surfaces and the lack of significant geometric reconstruction or relaxation for Cu(111) and Ag(111), although Au(111) exhibits a type of reconstruction.[4]

The He scattering measurements noted above were restricted to the lower-frequency portion of the dispersion curves and, *importantly, did not probe the surface modes which are predicted to lie in gaps in the bulk phonon bands* near the surface Brillouin-zone (SBZ) boundaries. Such gap modes are quite sensitive, in general, to changes in the surface force constants and motivated the present high-resolution electron-energy-loss (EELS) measurements of surface phonon dispersion on Cu(111). In this Rapid Communication we report the first experimental determination of the S_2 mode frequency near $\bar{M}$ in the SBZ, for Cu(111). We have also observed the S_1 and LR modes out to $\bar{M}$, thus extending the earlier He scattering measurements to the Brillouin-zone boundary. We further identify other bulk resonances at higher frequencies for the first time.

Our most important finding, however, concerns the gap mode S_2: the 210-cm^{-1} frequency of this mode, i.e., distinctly above midgap, appears to rule out the 50–70% softening models and indeed is most consistent with an approximate 15% softening. Furthermore, we find that detailed EELS cross-section analysis, based upon multiple scattering of the electrons, is consistent with a modest (15%) softening model and satisfactorily explains the basic intensity features associated with the Rayleigh, longitudinal resonance, and gap modes. Our results thus stand in sharp contrast to the model advanced by Bortolani and co-workers which purports to explain the surface lattice dynamics of the Cu, Ag, and Au(111) surfaces in terms of dramatic intralayer force constant softening.

The EELS phonon measurements were carried out by the general methods described earlier[5] and were performed with a 127° cylindrical deflection spectrometer that employs a double-pass monochromator and single-pass analyzer.[6] The resolution of the instrument was set to 40–50 cm^{-1}. This could be maintained over a primary energy range of 1–250 eV. Owing primarily to the presence of bulk phonons, the experimental spectra exhibit peaks which always appear broader than the instrumental resolution. Nevertheless, it was found that peak positions could be reproduced to within ± 5 cm^{-1}. The Cu(111) sample was prepared by standard metallographic techniques and azimuthally oriented by x-ray analysis before introduction to the vacuum chamber for scattering along a $[\bar{1}\bar{1}2]$ azimuth. The sample was cleaned by cycles of Ar^+ bombardment and annealing to 400 °C. Auger analysis confirmed only trace amounts of carbon impurity and the low-energy electron diffraction (LEED) pattern was of high quality. All phonon measurements were carried out at room temperature.

We have carried out extensive theoretical calculations of the loss cross sections for the scattering configurations used in the experiments reported here. The calculations are performed with the methods used recently for other surfaces;[7] a multiple-scattering description is employed for the electron as it enters and exits from the crystal, and this is combined with a model of the surface lattice dynamics.[8] A complex inner potential was used in the electron scattering analysis, with a real part of 9 eV and an energy-dependent imaginary part which equaled 2.5 eV at 90 eV incident energy.

We comment in more detail on our model of the surface lattice dynamics. We used the nearest-neighbor central force model, with force constant chosen to provide a best

fit to the measured phonon dispersion curves, as determined by a least-squares analysis. This gave a value of 2.49×10^4 dyn/cm for the bulk force constant. While this procedure fails to fit the elastic constants which control the dispersion curves at long wavelengths, it provides a very adequate fit to the bulk dispersion curves throughout the Brillouin zone, in the regime of wave vectors accessible to neutrons. We find no evidence of the role of surface stress when we fit the electron-scattering data reported here[9] (the frequency of the Rayleigh mode at $\bar{M}$ is sensitive to the presence of surface stress), so we do not include its influence. Our only adjustable parameter is the force constant k_s which couples atoms within the surface.

Jayanthi, Bilz, Kress, and Benedek[10] have recently proposed a microscopic model for the lattice dynamics of the noble metals based on many-body interactions. If k_0 is the bulk force constant, we find the choice $k_s=0.7k_0$ provides a good fit to the picture of the surface lattice dynamics of Cu(111) which emerges from their analysis, as judged by the frequency of the gap mode at $\bar{M}$, the dispersion curves of the Rayleigh wave, and longitudinal resonance along the line $\bar{\Gamma}$–$\bar{M}$, and also the spectral densities for surface atom motions normal to, and in the two directions parallel to, the surface at $\bar{M}$. We have also employed the eigenvectors generated by this model to calculate the electron-energy-loss cross sections at various impact energies for exciting modes at $\bar{M}$, and save for small details we find excellent agreement with the nearest-neighbor central force model, with the choice $k_s=0.7k_0$.

In Fig. 1 we report a comparison between theory and experiment for EELS scattering cross sections at three different primary beam energies of 110, 150, and 175 eV for momentum transfer corresponding to $\bar{M}$. In the case of 110 eV the spectrum is dominated by the Rayleigh mode S_1, although weaker contributions from the LR, S_2, and bulk modes are discernible. At 150 eV major contributions come instead from the LR ($\sim$150 cm^{-1}) and other resonant bulk modes $\sim$230 cm.$^{-1}$ Finally, at 175 eV the spectrum is clearly dominated by the S_1 and S_2 modes. Thus the strong energy dependence of the EELS cross section allows the separation of all of the major surface phonon and resonance features in spite of the rather low resolution of the technique. The 175 eV spectrum is particularly interesting in this regard since we can accurately determine the position of the gap mode S_2 by using the gain and loss peaks and a Gaussian-fitting procedure. We note that the S_1 mode dispersion may be determined by the 110-eV data, and hence the only free parameters in the 175-eV fit pertain to S_2. At 150 eV, a similar procedure can be used to determine the center of the LR. We note that both the S_2 and LR modes are of primarily longitudinal polarization whereas the S_1 mode is primarily shear vertical. Further, the LR is actually a collection of bulk modes of approximately 20 cm^{-1} width.

In Fig. 1 we show the comparison of three softening models corresponding to $k_s=0.5$, 0.7, and $0.85k_0$ using the theory outlined above. It is clear from these and other comparisons that the 50% softening model does not provide a good description of the data. Furthermore, the 15% softening model provides a better description of the S_2 mode position than the 30% model, as well as providing an

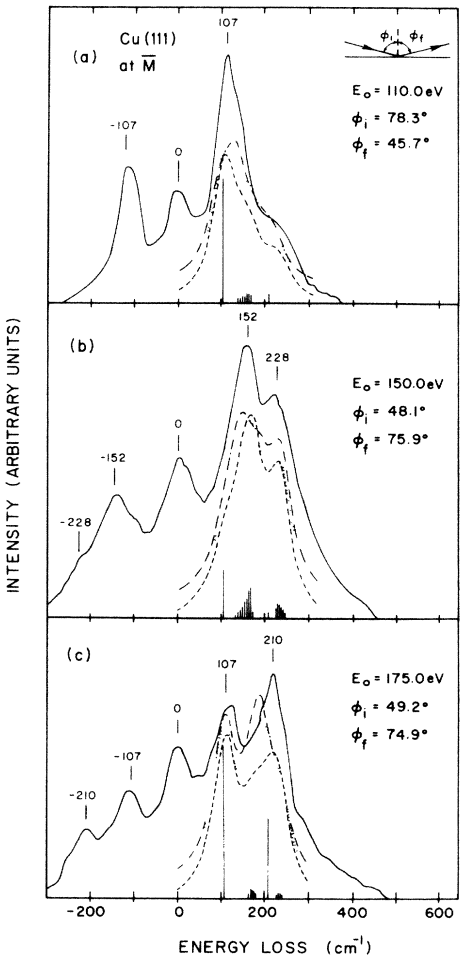

FIG. 1. High-resolution EELS measurements for Cu(111) at $\bar{M}$ in the surface Brillouin zone are shown for (a) 110 eV, (b) 150 eV, and (c) 175 eV primary beam energies. The theoretical calculations are shown for 15% (dashed), 30% (dotted), and 50% (dashed-dotted) softening models of the intralayer surface force constant. Only the loss side of the data is compared to the calculation. The histrograms at the bottom of each panel depict individual mode scattering strengths for the 15% softening model.

adequate description of the LR feature. The sensitive dependence of the S_2 mode on the force constant k_s is shown in Fig. 2. The value of $k_s=0.85k_0$ is in excellent agreement with the experimental determination of $210(\pm5)$ cm^{-1} for this mode and provides very strong evidence against the 50–70% softening models proposed earlier.[1,3] We emphasize that these conclusions are made within the context of the lattice dynamical models discussed above; nevertheless, any definitive model must be consistent with the determination of the gap-mode frequency presented herein.

A summary of the experimental phonon dispersion compared to the 15% softening model is given in Fig. 3. We emphasize that the dispersion of the S_1 and LR resonance modes obtained in our experiments are in excellent agreement with the He scattering data,[1] although the latter for the LR was reported only to $q_\parallel\simeq1$ Å^{-1},

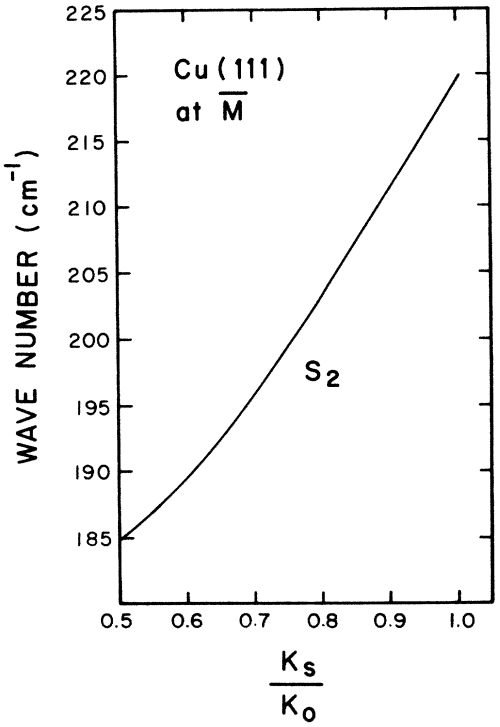

FIG. 2. Calculated dependence of the S_2 (gap) mode frequency on the value of the intralayer surface force constant.

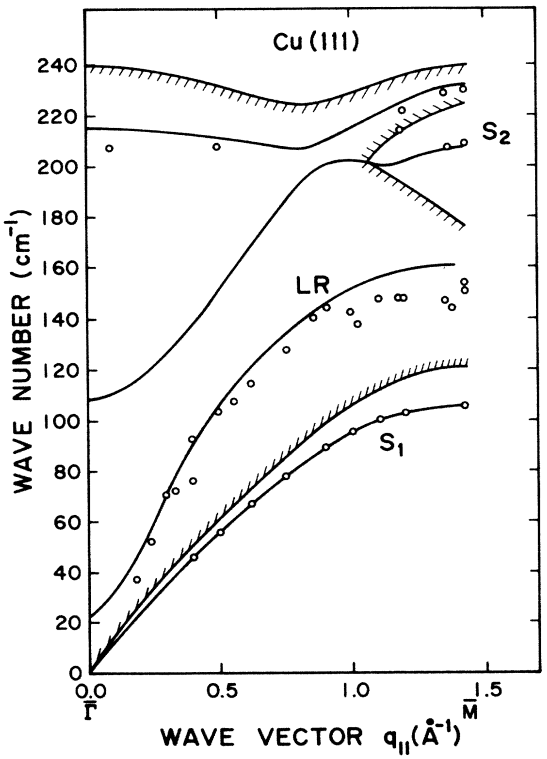

FIG. 3. Experimental and theoretical (15% softening model) dispersion curves for surface and resonance modes on Cu(111). The experimental data are indicated by open circles and the calculation by solid line. The bulk mode boundaries are shown as cross-hatched curves.

presumably due to reduced intensity near the zone boundary. As shown in Fig. 3, the present EELS data extend these measurements to $\bar{M}$ as well as providing the S_2 mode and another bulk resonance mode ~ 230 cm^{-1}. These results demonstrate the crucial role played by zone-boundary gap modes such as S_2 in elucidating the nature of the surface lattice dynamics of these materials.

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