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Cross-section analysis of surface and bulk phonons by electron scattering from Cu(100)

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High-resolution electron energy-loss measurements at off-specular directions on a clean Cu(100) surface ($\bar{\Gamma}$-$\bar{X}$ direction) demonstrate the presence of both surface and bulk phonon excitations. We present what we believe to be the first detailed cross-section analysis of surface and bulk phonon excitations on the Cu(100) surface. The data are shown to be in very good agreement with calculations based on the multiple-scattering slab method. The achievement of experimental phonon intensities one to two orders of magnitude higher than previously obtained is also demonstrated.

The measurement of surface phonon dispersion on clean and adsorbate-covered surfaces by inelastic He scattering and inelastic electron scattering in the past few years has been an exciting development in surface physics. Corresponding advances in the microscopic theory of these scattering processes have also been made. In the case of high-resolution electron-energy-loss studies (EELS), detailed phonon dispersion and cross-section analysis have been made for the surface Rayleigh mode (S_4) and the higher-frequency surface mode (S_6) on the clean Ni(100) surface, as well as for adsorbate-induced modes due to oxygen and sulfur adsorption on Ni(100).[1-6] Recently, the phonon dispersion of the S_4 mode on Cu(100) has also been measured.[7] In this article, we report two new results in the study of inelastic electron scattering at relatively high impact (40–120 eV) energies from clean Cu(100) which we believe are of general importance in the field: (i) the observation and cross-section analysis of bulk phonon as well as surface phonon scattering, and (ii) the achievement of 10–60 times higher experimental phonon loss intensities than have heretofore been reported on similar systems.

The measurements are carried out in a diffusion-titanium-sublimation pumped ultrahigh-vacuum system (base pressure $\sim 5\times10^{-11}$ Torr). The Cu(100) sample is cleaned by cycles of Ar^+ bombardment and annealing to 400 °C. Auger analysis exhibits only trace amounts of carbon, and the low-energy electron diffraction (LEED) pattern is of high quality. In addition, high-sensitivity EELS analysis at low primary-beam energies (~5 eV) gives no indication of impurities. The sample is azimuthally oriented before admission to the vacuum chamber so that the scattering plane is aligned with the surface normal and the [110] direction. Subsequent photographic LEED analysis indicates a deviation from the [110] direction by $\phi = 3°$ ($\pm 2°$).

Off-specular electron-energy-loss measurements are performed with a 127° cylindrical deflection spectrometer described earlier.[8] The spectrometer employs a double-pass monochromator and single-pass analyzer. The instrument may be operated from 1–120 eV beam energy without significant loss of energy resolution or transmission. The electron optics is rigid so that the appropriate wave vector **q** in the surface Brillouin zone (BZ) is obtained at a given beam energy by polar rotation of the sample (hereafter referred to as rocking angle).

Vibrational spectra are recorded at room temperature at an energy resolution of 8 meV (64 cm^{-1}) at selected impact energies of between 40 and 120 eV. The specular elastic scattering rate ranges from $\sim 3\times10^4$ to 10^6 counts/sec depending on incident electron energy. The S_4 phonon loss peak exhibits intensities at 80 and 110 eV impact energies of ~200 counts/sec near the BZ boundary. As noted above, this intensity is many times higher than previously achieved on Ni or Cu, and this improvement is attributed to instrumental improvement in the experimental system (e.g., monochromatic current and spectrometer transmission).

The analysis of the phonon dispersion is based on a lattice-dynamical model using nearest-neighbor central

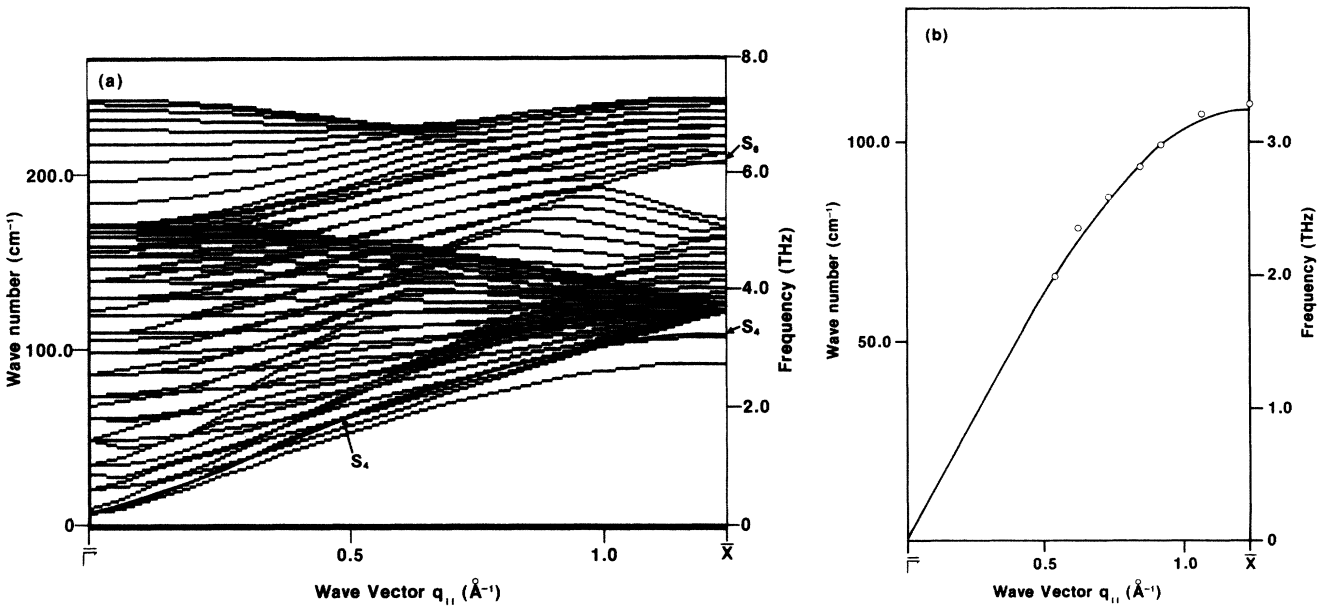

FIG. 1. (a) Calculated phonon dispersion for a 20-layer slab, using a central-force nearest-neighbor model, with $k_{12}=1.16k_B$. (b) Calculated and measured (open circles) dispersion for the S_4 surface mode.

forces.[5,6,9] A slab of 20 atomic layers is used and the surface spacings are taken from results of low-energy electron diffraction by Davis and Noonan.[10] The surface force constant k_{12} between the first and second copper layers are increased by 16% from the bulk value, i.e., $k_{12}=1.16k_B$. Figure 1(a) shows the bulk as well as surface (S_4 and S_6) phonon dispersions. The comparison between theory and experiment for the S_4 surface phonon dispersion is shown in Fig. 1(b). These results are in excellent agreement with the work of Wuttig, Franchy, and Ibach.[7]

Cross-section measurements reveal surface phonon as well as bulk phonon scattering at a number of scattering geometries. Two examples where bulk phonon scattering are measured are shown in Figs. 2 and 3, at $E=110$ eV, $q_\parallel=0.84$ Å^{-1}, and 0.62 Å^{-1}, respectively. The vertical lines are calculated differential probability $dP/d\Omega$ for the S_4 mode and for all bulk and resonance modes that have appreciable differential probability. For the electron-phonon scattering calculation, we use the rigid-ion multiple-scattering slab method which produced good agreement with experiment for surface phonon cross sections of Ni(100).[5,6,11,12] Structural and dynamical inputs for the scattering calculation are again taken from those determined by Davis and Noonan in their LEED analysis

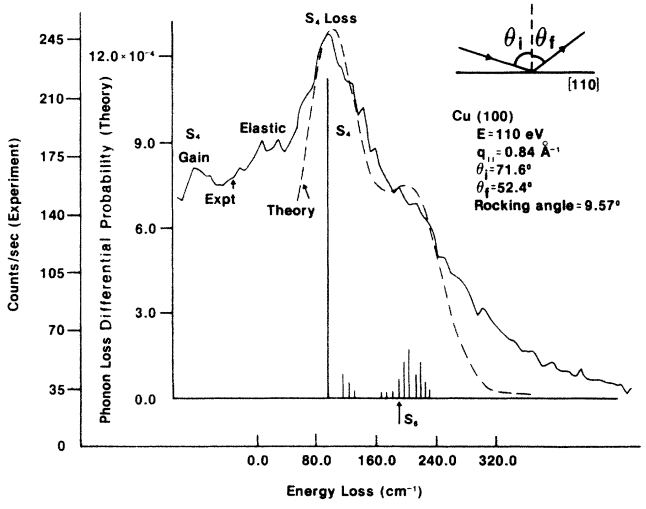

FIG. 2. Differential probability for surface and bulk phonon excitations of Cu(001): comparison between theory and experiment. The theory is done for the phonon loss case only. Estimated position of the S_6 mode is indicated in the theory. The electron energy is 110 eV, $q_\parallel=0.84$ Å^{-1}, and the rocking angle is 9.57°.

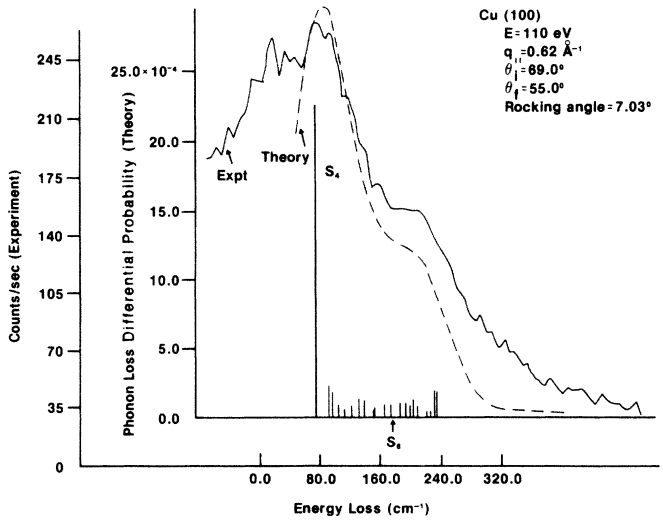

FIG. 3. Same as in Fig. 2, except for $E=110$ eV, $q_\parallel=0.62$ Å^{-1}, and rocking angle is 7.03°.

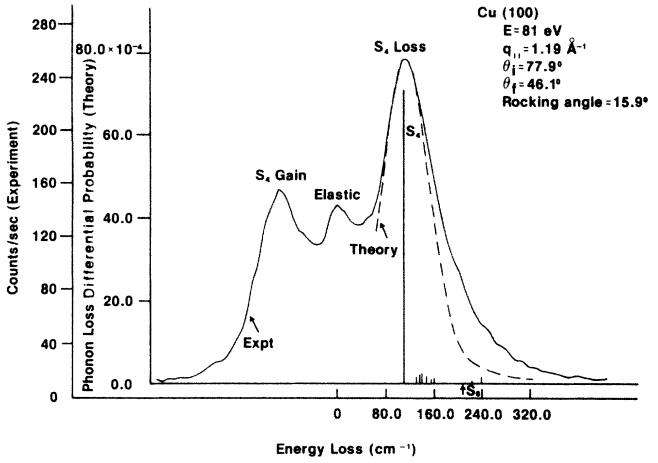

FIG. 4. Same as in Fig. 2, except for $E=81$ eV, $q_{\parallel}=1.19$ Å^{-1}, and rocking angle is 15.9°.

of Cu(001);[10] $d_{12}=1.785$ Å (i.e., a 1.1% contraction), $d_{23}=1.835$ Å (i.e., a 1.7% expansion), imaginary potential $V_I=-2.5$ eV. We use copper phase shifts from Burdick's augmented-plane-wave potential.[13] An inner potential of $V_0=9$ eV is found to provide the best agreement with the measured data. The calculation is done with an azimuthal angle $\phi=2°$ off the [110] direction. The theoretical curves in Figs. 2 and 3 are obtained by Gaussian broadening the calculated vertical lines with a full width as half maximum of 11.2 meV and superposing the resulting Gaussians.

From Figs. 2 and 3, we see that a significant amount of bulk phonon scattering comes from modes which resonate with the S_6 surface phonon as the latter merges into the bulk band.[14] Since the incident electron has a very short mean free path (~4 Å), only those phonons that have appreciable displacement amplitudes in the top two or three atomic layers can have measurable electron cross sections. However, having a large surface displacement amplitude is

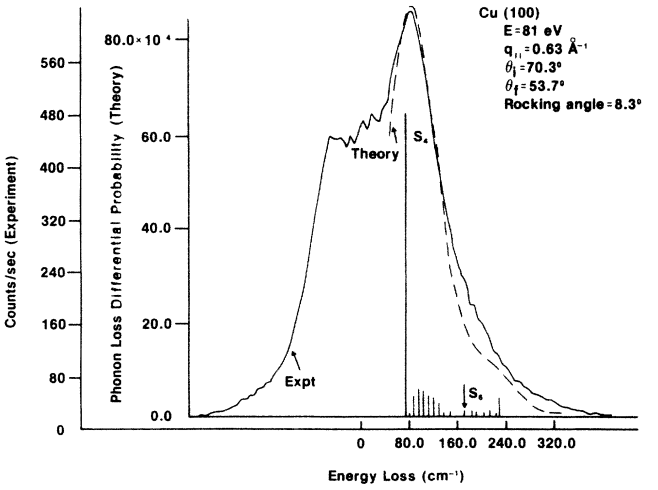

FIG. 5. Same as in Fig. 2, except for $E=81$ eV, $q_{\parallel}=0.63$ Å^{-1}, and rocking angle is 8.3°.

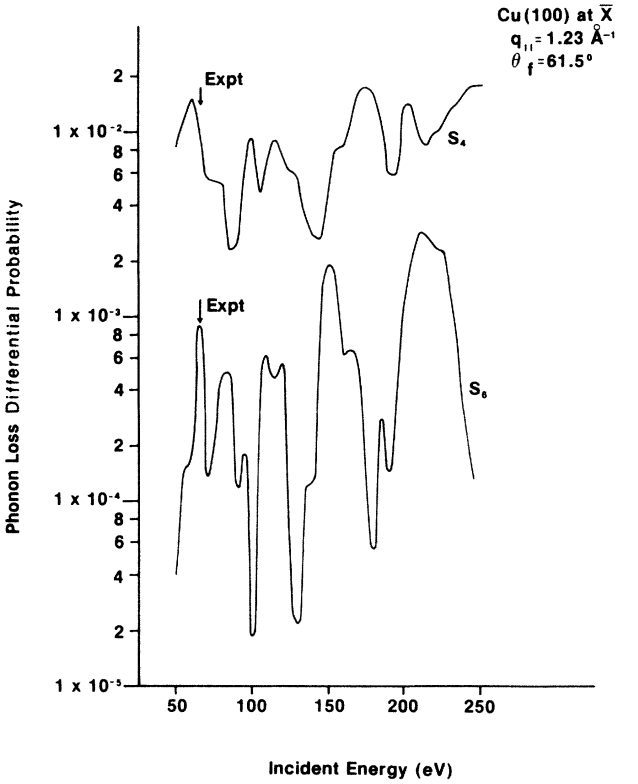

FIG. 6. Energy dependence of S_4 and S_6 differential probability, calculated for $q_{\parallel}=1.23$ Å^{-1}, $\theta_f=61.5°$.

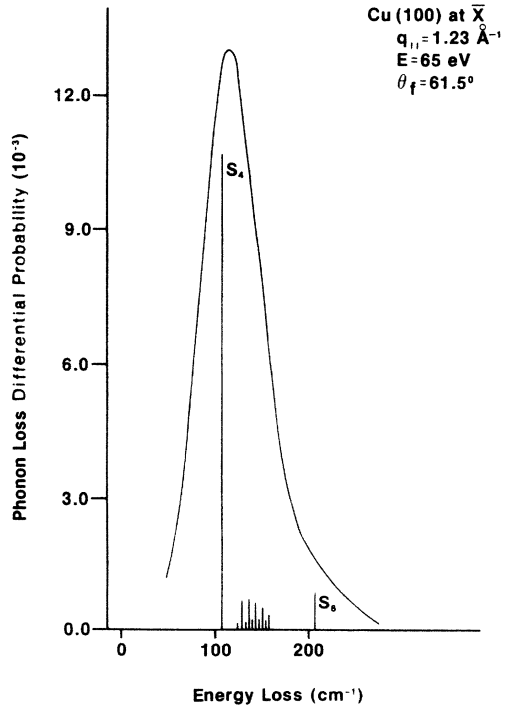

FIG. 7. Calculated differential probability for surface and bulk phonon modes of Cu(100) at $E=65$ eV, $q_{\parallel}=1.23$ Å^{-1}, and $\theta_f=61.5°$.

only a necessary condition, because the electron cross section is a sensitive function of the scattering geometry. We illustrate this by Figs. 4 and 5, wherein neither the surface mode S_6 nor any of the bulk modes have large enough cross sections to be measured. These results also point to the importance of microscopic calculations. The surface phonon S_4 has a cross section generally large enough to be detected at most scattering geometries. On the other hand, the surface phonon S_6 and bulk modes have smaller cross sections and can only be seen at particular scattering geometries. For example, the recent measurement of Wuttig *et al.*[7] at $\bar{X}$ on Cu(001) did not see these modes. We have calculated the cross sections of S_4 and S_6 at the scattering geometry given by experiment[7] as a function of the incident energy. The results are shown in Fig. 6. We see that at $E = 65$ eV, where the experiment was done, the S_6 mode has a much smaller cross section than that of the S_4 mode. Even including bulk modes and with Gaussian broadening, the resulting curve still shows no sign of the S_6 mode (see Fig. 7). This result is in good agreement with the data presented by Wuttig *et al.*[7] The microscopic calculations thus serve two important functions: (i) they can identify scattering geometries, wherein the S_6 or bulk modes are detectable, and (ii) perhaps more importantly, at geometries where the S_6 or bulk modes are detected, the calculations help identify the contribution from each mode to the measured cross section.

In summary, we have shown that both surface and bulk phonon excitations are observed for Cu(001). At $\mathbf{q}_\parallel$ points, where the S_6 mode has merged into the bulk band, phonon modes in resonance with the S_6 phonon contribute significant amounts to the observed cross section. Through instrumental improvement, the new spectrometer yields a phonon intensity about 10–60 times large than those previously reported.

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[1]See, for example, *Electron Energy Loss Spectroscopy and Surface Vibrations,* edited by H. Ibach and D. L. Mills (Academic, San Francisco, 1982).

[2]S. Lehwald, J. M. Szeftel, H. Ibach, T. S. Rahman, and D. L. Mills, Phys. Rev. Lett. **50**, 518 (1983).

[3]J. M. Szeftel, S. Lehwald, H. Ibach, T. S. Rahman, J. E. Black, and D. L. Mills, Phys. Rev. Lett. **51**, 268 (1983).

[4]S. Lehwald, M. Rocca, H. Ibach, and T. S. Rahman, Phys. Rev. B **31**, 3477 (1983).

[5]M. L. Xu, B. M. Hall, S. Y. Tong, M. Rocca, H. Ibach, S. Lehwald, and J. E. Black, Phys. Rev. Lett. **54**, 1171 (1985).

[6]M. Rocca, H. Ibach, S. Lehwald, M. L. Xu, B. M. Hall, S. Y. Tong, in *The Structure of Surfaces,* edited by M. A. Van Hove and S. Y. Tong (Springer, Heidelberg, 1985).

[7]M. Wuttig, R. Franchy, and H. Ibach, Solid State Commun. **57**, 445 (1986).

[8]L. L. Kesmodel, J. Vac. Sci. Technol. A **1**, 1456 (1983).

[9]J. E. Black, D. A. Campbell, and R. F. Wallis, Surf. Sci. **105**, 629 (1981).

[10]H. L. Davis and J. R. Noonan, Surf. Sci. **126**, 245 (1983).

[11]S. Y. Tong, C. H. Li, and D. L. Mills, Phys. Rev. Lett. **44**, 407 (1980).

[12]C. H. Li, S. Y. Tong, and D. L. Mills, Phys. Rev. B **21**, 3057 (1980).

[13]G. A. Burdick, Phys. Rev. **129**, 138 (1963).

[14]Resonance modes are discussed in, for example, T. S. Rahman, J. E. Black, and D. L. Mills, Phys. Rev. B **27**, 4059 (1983).