Enhanced Surface Anharmonicity Observed in Vibrations on Cu(110)

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Surface anharmonicity has been measured on Cu(110) by examining the temperature dependence of surface phonons with atomic motion normal to the surface using high-resolution electron-energy-loss spectroscopy. At the Brillouin zone center $\bar{\Gamma}$ the energy of the MS_7 resonance decreases by 3.2 meV and the intrinsic width increases by 8.6 meV as the temperature increases from 21 to 766 K. Energy decrease and width increase are also observed at the Brillouin zone edge $\bar{Y}$ in the S_3 phonon. The percentage energy decrease is the same in both phonons. Direct comparison with bulk-phonon measurements shows that the anharmonicity at the surface is 4.1–4.8 times greater than in the bulk.

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The anharmonicity of vibrations in solids is well recognized, and is required to account for many macroscopic properties, including thermal expansion, volume dependence of elastic constants, finite thermal conductivity, and the asymptotic value of the specific heat at high temperatures. Anharmonicity is observed directly in phonon spectroscopies, and is responsible for the finite lifetime of phonons and the temperature dependence of phonon energies.

At a solid surface, the crystal symmetry is broken, and the anharmonicity is expected to be a factor of 2–3 greater than in the bulk.[1,2] If true, anharmonic theory may be essential to describe many surface processes involving energy transfer to and from substrate phonons, including adsorbate sticking and desorption. Vibrational lifetimes of adsorbates will also be influenced by anharmonic effects where relaxation to multiple surface phonons is important. Anharmonicity dictates the location of surface atoms, governing both the equilibrium atomic separations (thermal expansion) and the vibrational amplitudes around equilibrium (mean-square displacement, $\langle u^2 \rangle$). These are important for understanding phase transitions, diffraction intensities, and thin-film growth at surfaces.

Enhanced surface anharmonicity has been supported qualitatively by observations of a large thermal expansion on Pb(110) (Ref. 3) and on W(001).[4] Indirect evidence supporting increased anharmonicity at surfaces is also found using probes sensitive to the mean-square displacement $\langle u^2 \rangle$ of surface atoms. A $\langle u^2 \rangle$ greater than predicted by Debye-Waller theory could indicate anharmonicity, but it may also result from structural changes such as thermal roughening or vacancy creation. Thus, while an increase in $\langle u^2 \rangle$ observed in He scattering from Cu(100) (Refs. 5 and 6) has been modeled by an enhanced surface anharmonicity, thermal roughening was also considered possible.[7,8]

On Cu(110), a wide variety of surface-sensitive techniques[5,6,9–11] including He scattering, low-energy electron diffraction, low-energy ion scattering, x-ray scattering, photoemission, and inverse photoemission reveal a dramatic attenuation in measured signal above about 500 K. This decrease was first attributed to an increase in the mean-square displacement of the surface atoms $\langle u^2 \rangle$ due to surface roughening.[10] However, Zeppenfeld *et al.*[11] have since ruled out thermal roughening of this surface through an analysis of thermal-He-scattering angular profiles. They suggested that the increase in $\langle u^2 \rangle$ could instead be due to enhanced surface anharmonicity.[12]

In this Letter, we report the first direct, quantitative measurement of anharmonicity at an unreconstructed surface. We have studied phonon energies and lifetimes on the Cu(110) surface at crystal temperatures between 21 and 766 K. The temperature dependences show a distinct signature of anharmonicity. These experiments reveal a vibrational anharmonicity for motion normal to the surface which is 4–5 times greater than in bulk copper.

Vibrational measurements were made using high-resolution electron-energy-loss spectroscopy (HREELS). The spectrometer was operated with an incident electron-beam energy of 2.5 eV for $\bar{\Gamma}$ studies and 40 eV for $\bar{Y}$ to optimize the phonon cross section, and with a resolution of 3.1–3.4 meV. The crystal was aligned so the scattering plane was in the [010] direction, i.e., the rows of copper atoms on the surface were perpendicular to the scattering plane. HREELS data were acquired only during periods when the sample was not being heated. Signal averaging was employed to obtain an acceptable signal-to-noise ratio.

On Cu(110), and other fcc (110) surfaces, the dominant vibration observed with HREELS at $\bar{\Gamma}$ has been identified by Stroscio *et al.*[13] as a surface resonance,

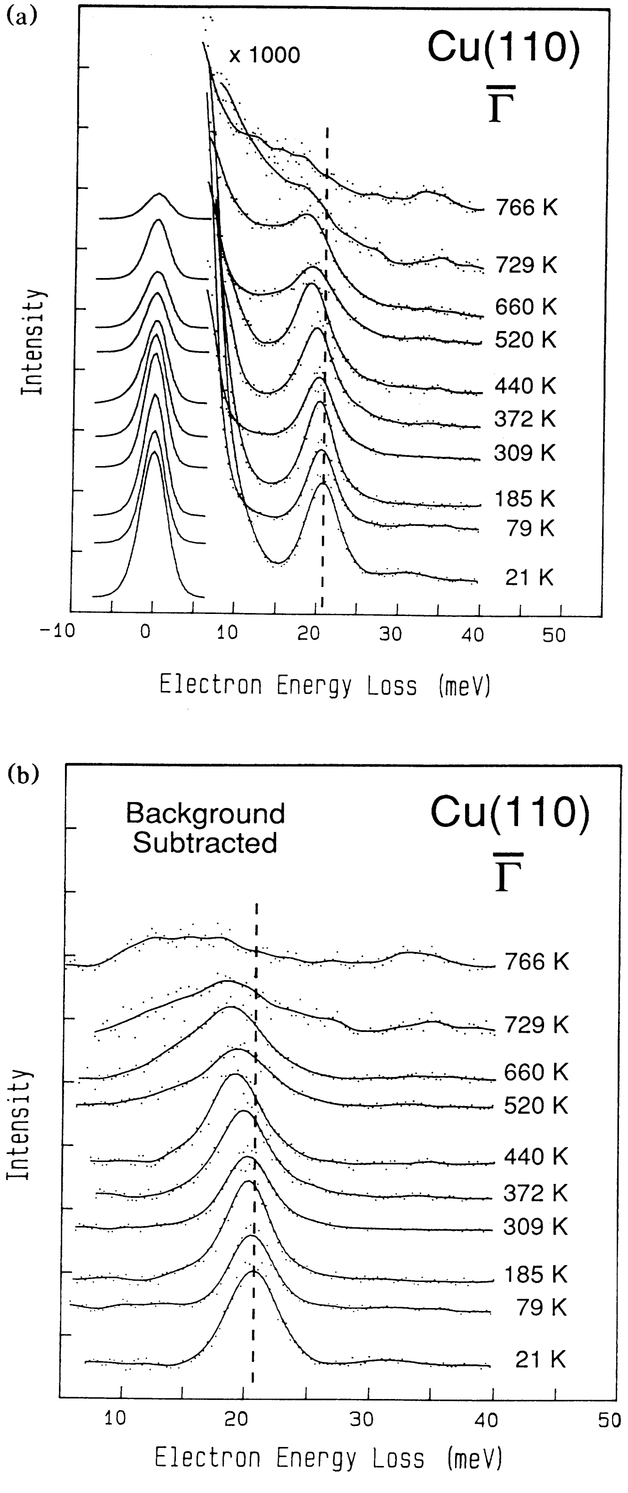

FIG. 1. (a) HREELS spectra at $\bar{\Gamma}$ for clean Cu(110) at crystal temperatures between 21 and 766 K. (b) Loss peaks with the elastic background subtracted. Spectra were obtained with an incident beam energy of 2.5 eV, and with incident and exit angles both 60° from normal. The solid lines are smooth curves drawn through the data.

designated MS_7, split off below a major peak in the density of states for the bulk longitudinal phonons propagating normal to the surface. The motion of the atoms is normal to the surface, with the entire layer of surface atoms moving together, out of phase with the second-layer atoms, in phase with the third-layer atoms, etc. Calculations indicate this phonon[14] is primarily localized in the two outermost surface layers,[15] a conclusion supported by the sensitivity of this vibration to adsorption.[16] The surface force constant most relevant for this phonon,[15] between the first and second atomic layers, is an excellent candidate for enhanced surface anharmonicity.

Figure 1 shows the phonon at $\bar{\Gamma}$ on Cu(110) for crystal temperatures between 21 and 766 K. The elastic intensity decreases rapidly at higher temperatures, consistent with the decreases observed in other spectroscopies as mentioned earlier. The phonon loss peak also changes rapidly at the higher temperatures, decreasing in energy and intensity, and increasing in width. Above ~750 K the peak has broadened sufficiently to make distinction from the background difficult. Effects are most accurately observed in Fig. 1(b), where the background from the elastic tail has been removed. At 21 K the phonon peak is centered at 20.65 ± 0.2 meV and has an intrinsic width (assuming Gaussian distributions for the elastic and loss peaks) of 2.1 ± 0.7 meV. The estimated errors increase with temperature as the peak intensity decreases and width increases.

By fitting the elastic and loss peaks with Gaussians, the phonon energy (difference in elastic and loss energies) and the intrinsic phonon width (Gaussian deconvolution of the elastic from the loss width) have been obtained. The phonon energies and intrinsic widths be-

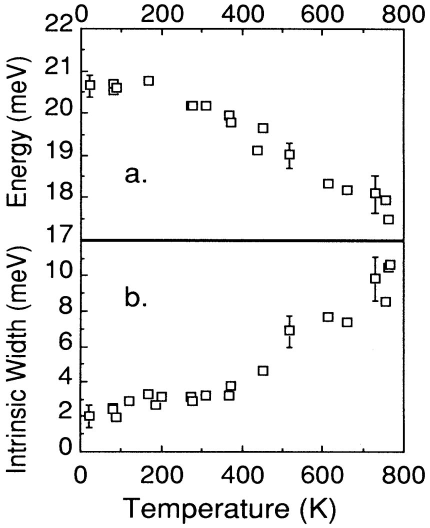

FIG. 2. (a) Energy and (b) intrinsic width for the phonon at $\bar{\Gamma}$. Experimental points, represented by squares, were obtained by assuming a Gaussian line shape.

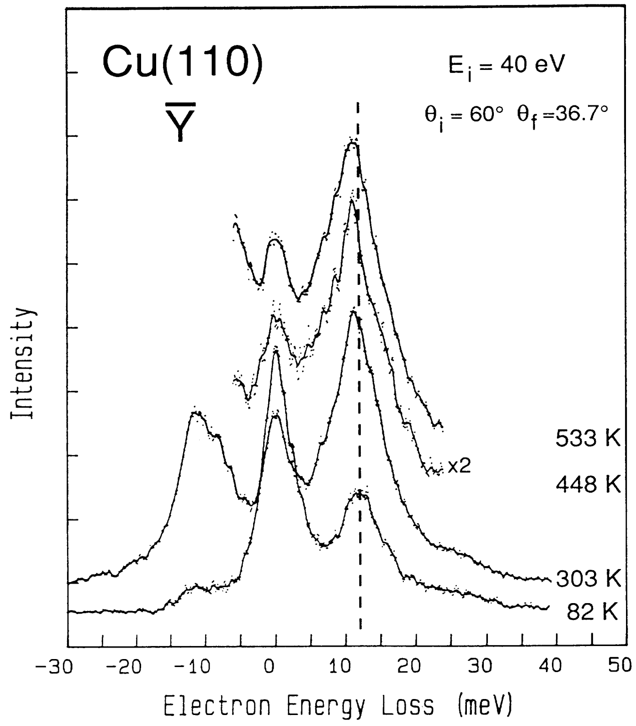

FIG. 3. HREELS spectra at $\bar{Y}$ for clean Cu(110) at crystal temperatures between 82 and 533 K. The elastic peak is surrounded by peaks corresponding to S_3 phonon gains and losses. Solid lines are curves through the data.

tween 21 and 766 K (from the data in Fig. 1 and other spectra) are plotted in Figs. 2(a) and 2(b). Below 200 K, the phonon energy and width show little change with temperature. Above ~300 K, the temperature dependence is nearly linear, with the slope of the phonon energy equal to −0.0050 meV/K. The width of the peak increases with a slope of 0.011 meV/K. Over the complete temperature range examined, the phonon energy decreases by 3.2 meV while the intrinsic width increases by 8.6 meV.

The shape of the data in Figs. 2(a) and 2(b) is a signature of an anharmonic potential. Quite generally anharmonic potentials result in a region of little change in phonon energy or width at low temperatures, followed by a roughly linear decrease (increase) in the vibrational energy (width). This functional form is found in anharmonic systems ranging from bulk phonons[17] to the vibration of a molecule in an anharmonic potential on a surface.[18] Although typical for anharmonic potentials, this form is not consistent with surface roughening, contamination, or harmonic potentials.

Although Fig. 1 shows only the region of the surface phonon, vibrational spectra were recorded up to 80 meV. No surface contamination was observed below 700 K. Above 700 K, a few percent of a monolayer of sulfur is observed as a vibrational peak at 36 meV (Fig. 1). The impact of sulfur on the phonon has been examined previously,[16] and a coverage this small appears to have little significance.

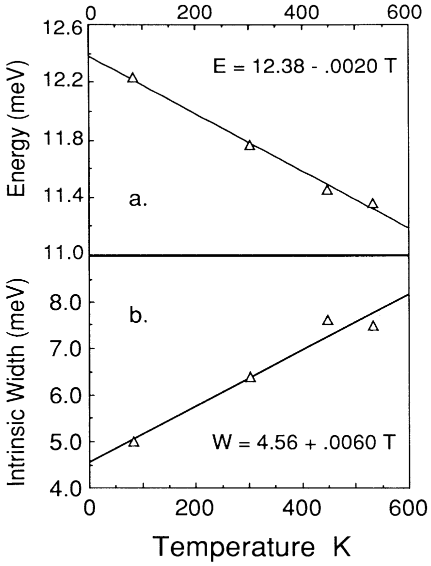

FIG. 4. (a) Energy and (b) intrinsic width for the phonon at $\bar{Y}$. A linear least-squares fit is shown as a solid line.

To confirm the generality of anharmonicity in vibrations normal to the Cu(110) surface, measurements were made of the transverse-acoustic phonon (S_3) at $\bar{Y}$ at several temperatures. This phonon has been identified on Cu(110) using inelastic helium scattering,[19] and involves coordinated motion of [1$\bar{1}$0] surface rows normal to the surface, with adacent rows out of phase. A survey of beam energies revealed that this phonon dominated HREELS spectra for a 40-eV beam incident 60° from the crystal normal.

HREELS spectra for the S_3 phonon at $\bar{Y}$ at several temperatures are displayed in Fig. 3. Because scattering conditions for $\bar{Y}$ are far from specular, elastic intensities are much smaller than at $\bar{\Gamma}$, and phonon loss intensities were only a few counts per second. Nevertheless, a clear temperature dependence in the loss energy and width is observed, with energy decreasing and width increasing as the temperature is raised. The observed phonon energy and intrinsic width (after background subtraction) are plotted in Figs. 4(a) and 4(b) along with linear least-squares fits. Insufficient data are available at $\bar{Y}$ to compare to the functional form observed at $\bar{\Gamma}$; however, over the temperature range shared by the two data sets, the energies of both phonons show the same percentage decrease.

The magnitude of the changes in the surface phonon energy and width indicate the surface anharmonicity is greater than the bulk anharmonicity of copper. The best evidence for enhanced surface anharmonicity comes from direct comparison with bulk-phonon energies. Although no bulk phonon shares the symmetry of the S_3 phonon at $\bar{Y}$, a direct comparison can be made between the temperature dependence of the surface phonon at $\bar{\Gamma}$ and its bulk counterpart, the longitudinal phonon propagating in the (110) direction at the Brillouin-zone boundary. Both surface and bulk phonons have the same symmetry and nearly the same energy (20.2 vs 21.0 meV at 300 K).[13] The temperature dependence of the bulk phonon has been measured by two independent groups using neutron scattering. Nicklow *et al.*[20] found a 0.16-meV decrease in the bulk-phonon energy between 49 and 298 K. Between these temperatures the surface phonon decreased 0.76 meV, a factor of 4.8 times greater. Larose and Brockhouse measured the bulk phonons in a higher temperature range, and between 296 and 673 K found an energy decrease of 0.52 meV.[21] In this temperature range, the surface phonon decreased 2.15 meV, 4.1 times greater than observed in the bulk.

In conclusion, we have observed the first direct, quantifiable measure of enhanced surface anharmonicity on an unreconstructed surface by tracking the decrease in energy and increase in width of a surface phonon on Cu(110) between 21 and 766 K. For vibrational motion normal to the surface, the surface anharmonicity is 4.1–4.8 times greater than for similar motion in the bulk. The changes in the phonon can be semiquantitatively fitted by a simple model based on an anharmonic potential. The model assumes the changes are brought about by thermal occupation of vibrational levels of different energy. What is needed at this stage is a more complete theoretical calculation at finite temperatures as has been done for bulk vibrations.[17]

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[1] S. K. S. Ma, F. W. De Wette, and G. P. Alldredge, Surf. Sci. **78**, 598 (1978).

[2] C. S. Jayanthi and E. Tosatti, Phys. Rev. B **31**, 3456 (1985).

[3] J. W. M. Frenken, F. Huussen, and J. F. van der Veen, Phys. Rev. Lett. **58**, 401 (1987).

[4] J. Kirschner and R. Feder, Surf. Sci. **104**, 448 (1981).

[5] G. Armand and J. R. Manson, Phys. Rev. Lett. **53**, 1112 (1984).

[6] D. Gorse and J. Lapujoulade, Surf. Sci. **162**, 847 (1985).

[7] C. S. Jayanthi, G. Armand, and J. R. Manson, Surf. Sci. Lett. **154**, L247 (1985).

[8] G. Armand, D. Gorse, J. Lapujoulade, and J. R. Manson, Europhys. Lett. **3**, 1113 (1987).

[9] S. Thevuthasan and W. N. Unertl (to be published); Th. Fauster, R. Schneider, H. Dürr, G. Engelmann, and E. Taglauer, Surf. Sci. **189/190**, 610 (1987); R. S. Williams, P. S. Wehner, J. Störh, and D. A. Shirley, Phys. Rev. Lett. **39**, 302 (1977).

[10] S. G. J. Mochrie, Phys. Rev. Lett. **59**, 304 (1987).

[11] P. Zeppenfeld, K. Kern, R. David, and G. Comsa, Phys. Rev. Lett. **62**, 63 (1989).

[12] G. Armand and P. Zeppenfeld, Phys. Rev. B **40**, 5936 (1989).

[13] J. A. Stroscio, M. Persson, S. R. Bare, and W. Ho, Phys. Rev. Lett. **54**, 1428 (1985).

[14] For clarity, we disregard the distinction between a surface resonance and phonon, justified in this case by the high degree of surface localization.

[15] M. Persson, J. A. Stroscio, and W. Ho, Phys. Scr. **36**, 548 (1987).

[16] A. P. Baddorf, J. M. Mundenar, and E. W. Plummer, J. Electron Spectrosc. Relat. Phenom. **38**, 219 (1986).

[17] C. Z. Wang, C. T. Chan, and K. M. Ho, Phys. Rev. B **40**, 3390 (1989).

[18] Z. Y. Zhang, Phys. Lett. A **143**, 413 (1990); D. C. Langreth and M. Persson (to be published).

[19] P. Zeppenfeld, K. Kern, R. David, K. Kuhnke, and G. Comsa, Phys. Rev. B **38**, 12329 (1988).

[20] R. M. Nicklow, G. Gilat, H. G. Smith, L. J. Raubenheimer, and M. K. Wilkinson, Phys. Rev. **164**, 922 (1967).

[21] A. Larose and B. N. Brockhouse, Can. J. Phys. **54**, 1990 (1976).