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Systematic trends in the normal enhancement of the phonon anharmonicity at the surface of metals

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The temperature dependence of the Rayleigh wave frequency measured by He atom scattering for the surfaces Al(001), Al(111), and Cu(001) is compared with bulk data in order to establish the surface enhancement of phonon anharmonicity. A comparison is made also with recent HREELS data for the Cu(110) surface. In all cases the surface anharmonicity is found to be less than or at most of the order of twice the bulk anharmonicity, in agreement with recent calculations of the enhancement of the zero-point mean-square displacements.

The anharmonicity of surface phonons has been extensively studied from the theoretical point of view[1-8] due to its role in important surface properties such as thermal expansion, surface diffusion, and structural phase transitions like reconstruction, surface melting, and roughening. The reduced coordination of the atoms located at the surface plane implies a general softening of the phonon spectrum projected onto the surface plane as compared to the bulk spectrum. As a consequence the atomic mean-square displacements are larger at the surface than in the bulk, particularly for displacements normal to the surface.[1] Thus the surface atoms explore the anharmonic part of the potential more extensively than bulk atoms and larger anharmonic effects are expected at the surface. Furthermore, surface atoms are located at lattice sites with lower symmetry than at the equivalent bulk sites. The removal of the inversion symmetry, which usually exists for bulk atoms, causes cubic terms to appear in the individual surface-atom potential. The above two mechanisms—reduced coordination and broken inversion symmetry—contribute to an enhancement of the surface anharmonicity with respect to the bulk. Since they rely exclusively on the surface geometry they are expected to occur already for an ideal surface.

Additional effects are expected for a nonideal surface when, as a consequence of structural relaxation, electronic charge redistribution and a change of electron susceptibility the surface force constants are modified with respect to the bulk not only in the harmonic but also in the anharmonic parts. Ma, de Wette, and Alldredge[3] have used an elegant method to incorporate charge redistribution effects for a metal surface by modeling the corresponding electrostatic terms as simple surface Madelung forces.[9] Their calculations for Fe(110) and Cu(001) show that the surface mean-square displacements (MSD) at $T=0$ are 1.38 and 1.42 times the bulk value for the component normal to the surface, respectively. The recent molecular-dynamics (MD) simulations by Yang and Rahman[4] predict for the Cu(001) and Cu(110) surfaces almost the same MSD up to 750 K and a surface-to-bulk MSD ratio in agreement with results of Ma, de Wette, and Alldredge.[3] For bulk copper the MD simulation predicts an increase of the MSD with temperature at the approximate rate of 2.7×10^{-3} Å^2/100 K above room temperature.[4] This is about 1.75 times larger than that obtained by Ma, de Wette, and Alldredge for the bulk within the perturbative scheme.[3]

The anharmonic shift of the surface phonon energies with temperature is generally assumed[5] in a first approximation to be proportional to the harmonic energy of the corresponding oscillator, as for molecular vibrations:[10]

$$\hbar\omega(T)=\hbar\omega_0-x_e\hbar\omega_0(2n_0+1)\ , \tag{1}$$

where ω_0 is the classical harmonic phonon frequency for vanishing displacement, and $n_0=[\exp(\hbar\omega_0/kT)-1]^{-1}$ is its temperature-dependent occupation number. The anharmonicity constant

$$x_e=\beta^2\langle u^2\rangle_0=\beta^2\hbar/(2\mu\omega_0) \tag{2}$$

is proportional to the zero-point ($T=0$) vibrational mean-square displacements $\langle u^2\rangle_0$ through the square of an inverse length β which characterizes the range of the interatomic potential;[10] μ is the oscillator effective mass. For a Morse potential β is just the multiplier of the distance in the exponent. Note that the zero-point MSD $\langle u^2\rangle_0$ for a surface normal mode depends on its localization, and may not in general be identified with the first-layer MSD provided by theory.[3,4] Actually the departure of $\langle u^2\rangle_0$ from the theoretical surface MSD gives an indication of the degree of delocalization (penetration depth) of the surface mode, and, correspondingly, the surface anharmonicity enhancement.

From Eqs. (1) and (2) the temperature shift of the surface phonon frequency is directly proportional to the surface MSD. Moreover the ratio of the frequency shift for a surface phonon to that of the corresponding bulk phonon of similar symmetry and polarization is proportional to the surface-to-bulk MSD ratio, if β is the same for bulk and surface interactions. Thus the frequency shift ratio can be taken as a direct measure of the surface anharmonicity enhancement.

The recent MD studies of anharmonicity for aluminum[11] and copper[4] surfaces suggest that anharmonicity can be fairly well described by only a single effective parameter, i.e., by an approximately constant x_e. For example, the four surface modes S_1, S_2, S_3, and S_5 at the $\overline{Y}$ point of Cu(110) show in the MD simulation approximately the same absolute decrease with temperature

($x_{e,s}$ =0.0160, 0.0144, 0.0169, and 0.0183, respectively),[4] independently of their frequencies (which range from 6.8 to 18.6 meV at 150 K).[4] This is actually consistent with Eq. (1), which gives at sufficiently high temperature an absolute shift $\Delta(\hbar\omega) \simeq -2x_e\Delta(kT)$.

Recent experimental studies on the thermal expansion of Pb(110) (Ref. 12) and W(001) (Ref. 13) and on the surface Debye-Waller factor of copper and nickel surfaces,[14–16] and related theoretical studies[4,17–19] suggest large enhancements of surface anharmonicity. Such arguments seem to be corroborated by a recent study of Baddorf and Plummer,[20] who directly measured the temperature dependence of the 20-meV surface resonance in Cu(110) by means of high-resolution electron-energy-loss spectroscopy (HREELS). The resonance frequency was found to decrease from 20.65±0.2 meV at 21 K to 17.5 meV at 766 K. This led the authors to the conclusion that surface anharmonicity, at least for this resonance, is 4–5 times larger than for bulk phonons of equivalent symmetry [either L or T_1 at (011), or T at (100), all having the same displacement pattern]. This result seems to contradict the above expectations based on the surface enhancement of the MSD, because the calculations of Ma, de Wette, and Alldredge[3] as well as the recent MD simulations[4,11] predict surface-to-bulk MSD ratios less than two.[4]

In this paper we collect some recent helium-atom scattering (HAS) data on the surface phonon frequency shift with temperature for the smooth copper and aluminum surfaces and compare them with the frequency shifts of the equivalent bulk phonons. It appears that the observed surface anharmonicity enhancement never exceeds the general theoretical predictions.[3,4] We also show that the HREELS data on Cu(110),[20] if compared to a careful analysis of the bulk data, are in fact quite consistent with a normal anharmonicity enhancement. The values of x_e for the surface phonons are given in Table I together with the corresponding bulk values.

The HAS data for Al(001) at the $\bar{X}$ point and for Al(111) at the $\bar{M}$ point[11] are shown in Fig. 1. The fitted values of x_e are compared in Table I with the theoretical

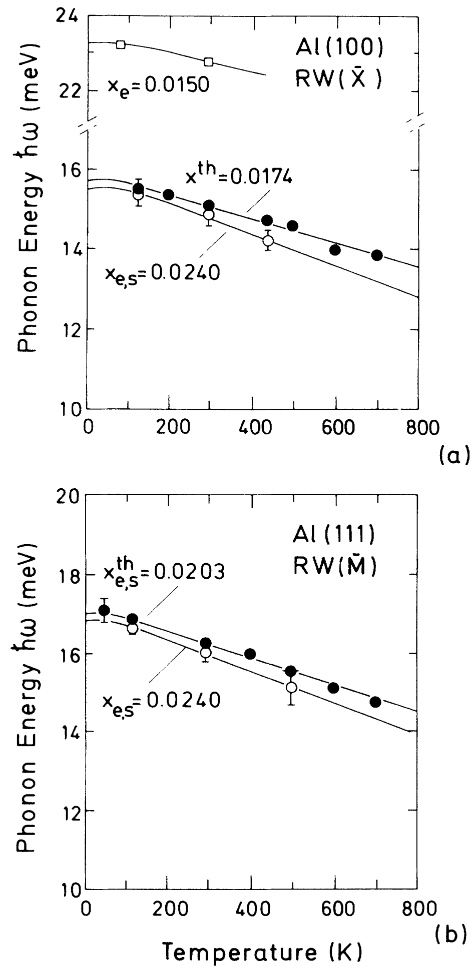

FIG. 1. The Rayleigh wave frequency in Al(001) (a) and Al(111) (b) at the zone boundary points $\bar{X}$ and $\bar{M}$, respectively, as a function of temperature: the open circles are the experimental results and the closed circles are the results of a molecular-dynamics simulation (from Ref. 11). The squares show the neutron data for the bulk (Ref. 21). The solid curves are fits based on Eq. (1).

TABLE I. Anharmonicity constants for surface phonons [Rayleigh waves for Al and Cu(001), $\bar{\Gamma}$-point resonance and $S_3(\bar{Y})$ mode for Cu(110)] and for the equivalent bulk transverse modes at symmetry points, and surface anharmonicity enhancement for different metal surfaces.

	Surface		Bulk		
	Point	$x_{e,s}$	Point	x_e	$x_{e,s}/x_e$
Al(001)[a]	$\bar{X}$	0.0240 (0.0174)	$(\frac{1}{2}\frac{1}{2}0)$	0.0150	1.61
Al(111)[a]	$\bar{M}$	0.0240 (0.0203)	(100)		
Cu(001)[b]	$\bar{X}$	0.0175	$(\frac{1}{2}\frac{1}{2}0)$	0.0138	1.28
	$\bar{M}/2$	0.0139	$(\frac{1}{2}00)$	0.0115	1.20
Cu(110)[c]	$\bar{\Gamma}$	0.0295	(100)	0.0133	2.21
	$\bar{Y}$	0.0116 (0.0114)	$(\frac{1}{2}00)$	0.0115	1.01

[a] Surface data: HAS (Ref. 11); bulk data: neutrons (Ref. 21); in parentheses: theoretical MD values (Ref. 11).

[b] Surface data: HAS (Ref. 22); bulk data: neutrons (Refs. 23–28).

[c] Surface data: HREELS (Ref. 20); bulk data: neutrons (Refs. 23–28); in parentheses: theoretical MD value over the range 150–600 K; a larger value of 0.0169 is fitted over the entire range 150–900 K of the MD simulation (Ref. 4).

MD values (in parentheses) and the bulk neutron data of Stedman and Nilsson[21] in Table I. The HAS data for Cu(001) are derived from the temperature shift of the Rayleigh wave (RW) frequency at the $\bar{X}$ point and at $\bar{M}/2$, which denotes one-half of the $\bar{\Gamma}\bar{M}$ wave vector (Fig. 2, Ref. 22). The surface data are compared in Table I with the experimental frequency shift of the bulk T_1 mode at the equivalent $(\frac{1}{2}\frac{1}{2}0)$ and $(\frac{1}{2}00)$ points, respectively, as determined from neutron-scattering data.[23,24]

The present He-scattering data indicate that the measured enhancement of surface anharmonicity, expressed by $x_{e,s}/x_e$ (last column of Table I), is comparable to the MSD ratio $\langle u_{sz}^2\rangle_0/\langle u_z^2\rangle_0$ at $T=0$ as calculated by Ma, de Wette, and Alldredge.[3] For Cu(001), where a direct comparison is possible, the measured enhancements at the points $\bar{X}$ (28%) and $\bar{M}/2$ (20%) are both smaller than the predicted surface MSD enhancement at $T=0$ (42%). From this comparison we can also evaluate the degree of localization of the surface phonons in question. With increasing participation of the second layer in the normal-mode motion the normal-mode MSD approaches the bulk MSD because the zero-point MSD of the second layer of Cu(001) turns out to be only 2% larger than the bulk MSD.[3] Thus we argue that the RW displacement in the second layer is already appreciable at $\bar{X}$ and comparable to that of the topmost layer at $\bar{M}/2$.

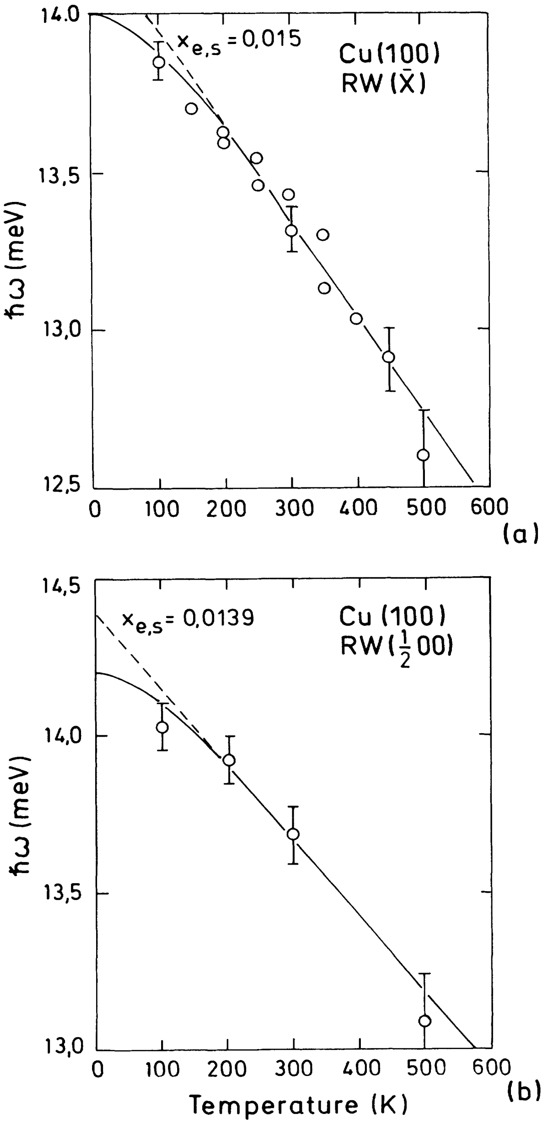

FIG. 2. The Rayleigh wave frequency in Cu(001) at the points $\bar{X}=(\frac{1}{2}\frac{1}{2}0)$ (a) and $\bar{M}/2=(\frac{1}{2}00)$ (b) as a function of temperature (from Ref. 22). The solid curves are fits based on Eq. (1).

In Table I we also include the recent HREELS data of Baddorf and Plummer for Cu(110).[20] We have reexamined their comparison of the surface temperature shift at the $\bar{\Gamma}$ point with the shift in the equivalent neutron data for the (001)L bulk mode.[23–28] As shown in Fig. 3, the frequency shift of the bulk mode over the temperature interval 0–800 K is 1.4 meV versus 3.1 meV for the surface resonance, and this gives a surface-to-bulk ratio of 2.21. A value of 2.46 is obtained if the bulk fit is made on the actual (011)L frequencies (horizontal arrow)[24] rather than on the more reliable interpolated values (closed circles).[24] This ratio is only about one-half of that reported by Baddorf and Plummer, the discrepancy being due to the fact these authors apparently compared their surface frequency shift to bulk frequency shifts evaluated from only two selected bulk points rather than to the whole set of available bulk phonon data.[23–28] Still a surface anharmonicity enhancement of 2.21 (2.46) should be regarded as a large, though not anomalous effect, and could be peculiar of an open surface with large relaxation such as Cu(110).[4]

Baddorf and Plummer were also able to measure the

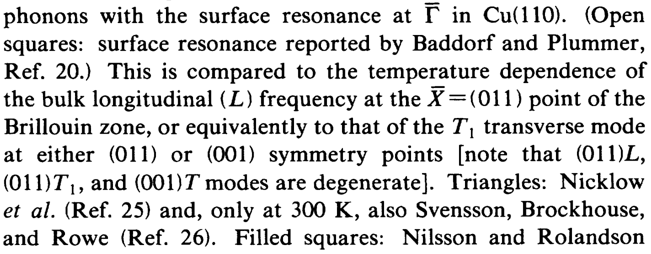

FIG. 3. Comparison of the temperature dependence of bulk phonons with the surface resonance at $\bar{\Gamma}$ in Cu(110). (Open squares: surface resonance reported by Baddorf and Plummer, Ref. 20.) This is compared to the temperature dependence of the bulk longitudinal (L) frequency at the $\bar{X}=(011)$ point of the Brillouin zone, or equivalently to that of the T_1 transverse mode at either (011) or (001) symmetry points [note that (011)L, (011)T_1, and (001)T modes are degenerate]. Triangles: Nicklow *et al.* (Ref. 25) and, only at 300 K, also Svensson, Brockhouse, and Rowe (Ref. 26). Filled squares: Nilsson and Rolandson (Ref. 27). Closed circles: Larose and Brockhouse (Ref. 24). For 673, 973, and 1336 K we chose the data as obtained from the interpolating curves drawn by Larose and Brockhouse in Fig. 7 of their paper for the shifts with respect to room-temperature data of the T_1 mode along the (011) direction. The horizontal arrows indicate the actual (011)L mode frequencies at the above temperatures. Downward triangles: Miller and Brockhouse (Ref. 28). Solid curves are fits based on Eq. (1).

temperature dependence of the S_3 mode frequency at $\bar{Y}$. Surprisingly the value of $x_{e,s}$ fitted to these data is equal to that of the corresponding bulk mode (Table I, last row), which indicates that for the surface mode S_3 at the $\bar{Y}$ point of Cu(110) there is no resonance enhancement at all. In some respect this result is even more unexpected than that for the $\bar{\Gamma}$-point resonance, but is in close agreement with the MD simulation by Yang and Rahman[4] over the same temperature range of 150–500 K. It should be noted, however, that this MD calculation predicts large deviations from linearity, with practically no decrease up to 300 K and an increasing slope at higher temperatures, in disagreement with the HREELS data which show a good linearity. The average MD slope over the entire range 150–900 K is 0.0169.

The present analysis of the experimental data for surfaces which are usually considered as well behaved, in combination with the theoretical study of Ma, de Wette, and Alldredge,[3] provides guidelines for a normal enhancement of surface anharmonicity. HAS data on other metal surfaces such as W(001),[29] TaSe$_2$(0001),[30] and Fe(110) (Ref. 31) show important anomalies in the temperature dependence of the Rayleigh wave frequency, associated with either surface reconstruction, a charge density wave state, or magnetization, respectively. In systems where a strong electron-phonon interaction at the Fermi level is in competition with the phonon-phonon (anharmonic) coupling, the temperature dependence of the phonon frequencies may be rather complex, and the ordinary anharmonic effect can hardly be divided out. Qualitative information on the normal anharmonic behavior of surface phonons is thus conceptually useful in the analysis of surface phase transitions by means of surface phonon spectroscopy.

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