Molecular-dynamics theory of the temperature-dependent surface phonons of W(001)

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We study the temperature-dependent zone-boundary surface phonons across the $c(2\times2)\rightarrow1\times1$ reconstruction phase transition of the clean W(001) surface. Velocity-velocity correlations and hence the phonon spectral densities are calculated by molecular dynamics for the surface atoms of a finite-thickness (001) slab, with interatomic potentials established in a previous study of the surface statics. Our calculated $\mathbf{k}=(\frac{1}{2},\frac{1}{2})(2\pi/a)$ surface phonon spectra are dominated by three main low-frequency modes. Of these, the longitudinal and the shear horizontal modes are reconstruction related and display critical broadening and softening at the phase transition, while the third, the shear vertical mode, is basically unaffected. The reconstruction phase mode, the shear horizontal, appears to be responsible for the phase fluctuations which destroy long-range order at the transition.

I. INTRODUCTION

Some metal and semiconductor surfaces exhibit continuous reversible phase transitions even in the absence of adsorbates.[1-8] Such is the case, for example, for the (001) surface of tungsten, where the transition is from (1×1), i.e., the two-dimensional symmetry of the bulk termination at high temperature, to a $c(2\times2)$ structure starting somewhat below room temperature.[1-3] Detailed low-energy electron diffraction (LEED) symmetry and intensity analysis[9-12] indicate that at low temperature the W atoms on the surface plane are displaced periodically along the $\langle 110\rangle$ direction as shown in Fig. 1. This structural phase transition bears in many ways a resemblance to the bulk structural phase transitions in ferroelectric perovskites and dichalcogenide layered crystals.[13,14] However, the surface reconstruction is believed to be truly two dimensional in character, since only the atoms in the outermost few layers are displaced from their bulk positions with no evidence of deep-reaching fluctuations below the surface at the critical point.[15] In other words, critical fluctuations diverge only along (x,y), and not along z.[29]

Bulk structural transition in the compounds of the perovskite family such as $SrTiO_3$ have been extensively studied in the last two decades.[13] One of the attractive and important aspects of displacive structural phase transitions is the behavior of phonons across the transition, particularly phonon softening, a concept introduced by Anderson and by Cochran in the context of mean-field theory.[16] According to the soft-mode picture, the limit of stability of a crystal lattice is approached as the frequency of any mode decreases and approaches zero. Once the atoms are dispaced with the eigenvector of that particular vibration, there is no harmonic restoring force to draw them back to their original positions. Hence, they assume new equilibrium positions determined by the symmetry of this soft mode, and of magnitude controlled by the anharmonic restoring forces.

It has been clear for a long time, however, that below four dimensions large deviations from the mean-field theory do occur, both in critical behavior and in dynamics. Phonon softening remains well defined only in some systems characterized by strongly displacive behavior. In a majority of other systems some softening occurs far away from T_c, but the critical region is dominated by order-disorder behavior.[13,17,18] In such cases a large broadening occurs in the phonon density of states instead of softening. In general, any given structural transition is expected to fall somewhere between the displacive and the order-disorder limits without any sharp dividing line between the two situations. Even in a strongly displacive system, fluctuations will eventually develop

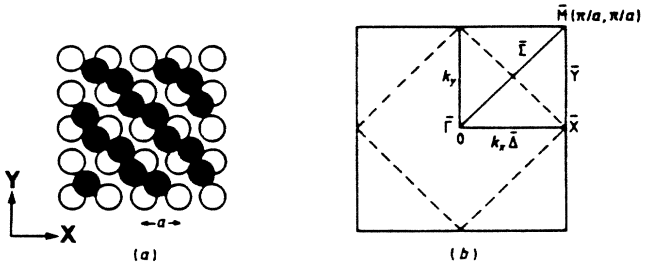

FIG. 1. (a) Geometry of the $c(2\times2)$ $\langle 110\rangle$ reconstructed clean W(001); dark circles indicate first-layer atoms, open circle, second-layer atoms. (b) First Brillouin zone of (1×1) structure (full line) and $c(2\times2)$ structure (broken line).

an order-disorder character, i.e., clusters or domains, very close to the critical point. There, the conventional soft-mode picture becomes inadequate for describing the dynamics of the system.

In the present study we present results which address this question for the surface reconstruction transition of clean W(001). In the first place, it is expected that the fluctuations will, of course, more crucially affect the dynamics in two-dimensional systems than in three-dimensional systems. Second, it is of interest to locate this phase transition somewhere between the two limits discussed above. Third, and perhaps more important, by conducting a realistic study of the temperature-dependent surface dynamics, we identify the relevant surface modes, and we single out their different behavior, corresponding to a different involvement in the phase transition. We have carried out a molecular dynamics study of all zone-boundary M-point modes $[\mathbf{k}=(\frac{1}{2},\frac{1}{2})(2\pi/a)]$ which affect the motion of the first-layer atoms of W(001), as the surface is warmed up across its reconstruction phase transition. Our results on the two "soft modes" of the reconstructed W(001) surface do, in fact, show a substantial amount of actual softening for one (the "amplitude mode"), and essentially only broadening for the other (the "phase mode"). For both modes, the mean frequency does not go all the way to zero at the transition but it is exceeded by an exploding width close enough to the transition. From this we conclude that the behavior of W(001) is mainly displacive below $0.7T_c$ and above $1.2T_c$. In between, strong order-disorder fluctuations take place. Besides the phase and amplitude (in-plane) modes, we also characterize strongly harmonic shear-vertical modes, basically unaffected by the transition. Some of these modes have recently been detected in He-scattering experiments,[19] with which we wish to make contact. Genuine $\mathbf{k}=0$ modes, including bulk modes, and a higher frequency reconstruction-related mode, recently brought out by electron energy loss,[20] were explained elsewhere[21] as mostly affecting the second atomic layer, and are not included in this study of first-layer dynamics.

We organize this paper as follows. Section II describes the method used for the present calculation. The results will be presented in Sec. III, followed by a discussion of their meaning, and by comparison with experiment.

II. METHOD

We compute the temperature-dependent surface phonon of the reconstructed W(001) surface by a slab molecular dynamics (MD) calculation. This simulation is based on the same effective lattice Hamiltonian we have previously used to study the $T=0$ lattice dynamics[15,22] and, in particular, on the detailed W-W interactions constructed for our recent study of the critical properties of this surface.[23]

The MD sample is formed by arranging 1536 particles in a six-layer bcc (001) slab with $16\times16=256$ atoms per layer to fill a square box oriented along $\langle 100\rangle$. Periodic boundary conditions are used along the x and y direction, but not along z, where the motion is free. Following Fasolino, Santoro, and Tosatti (FST),[22,15] the system is described by an effective (classical) lattice Hamiltonian where the interaction between two surface atoms, $V^S(R)$, is different from that of two bulk atoms $V^B(R)$, that is,

$$\mathcal{H}=\sum_l \frac{P_l^2}{2m}+\tfrac{1}{2}\sum_{(i,j)\neq\langle i,j\rangle} V^B(|\mathbf{R}_i-\mathbf{R}_j|) +\tfrac{1}{2}\sum_{\langle i,j\rangle} V^S(|\mathbf{R}_i-\mathbf{R}_j|)\ . \tag{2.1}$$

Here $\langle i,j\rangle$ denotes any pair of atoms at the same surface, while (i,j) denotes every other pair of atoms of the slab. The $V^B(R)$ (bulk potential) is constructed to describe the bulk lattice properties of W, including the bcc crystal structure. The interaction between two surface atoms $V^S(R)$ is supposed to be generally very different from $V^B(R)$ due to the existence of half-filled surface states.[22,24] Both $V^B(R)$ and $V^S(R)$ were constructed empirically, and chosen to be short ranged in the spirit of the "strong-coupling" charge-density-wave picture.[25] In particular, the bulk potential $V^B(R)$ includes nearest and next-nearest bulk neighbor interactions, while in the surface potential $V^S(R)$, only the interaction between nearest surface neighbors is included. The bulk and surface interactions between W atoms are shown in Figs. 2 and 3, where $V_1(R)$ and $V_2(R)$ stand for the nearest and next-nearest bulk neighbor interaction separately.[26] Note that in the present MD simulation, we impose the surface potential $V^S(R)$ only on one of the two slab surfaces, the atoms on the other surface interacting as bulk atoms. In this way, the other surface retains its ideal, bulklike structure, so that a thin six-layer-thick slab is sufficient to decouple the two (001) surfaces.

With these potentials, we have solved Newton's equations of motion by a fifth-order predictor-corrector algorithm. Other details of the MD technique are entirely standard.

Once the positions and velocities of all particles are known as a function of time, the dynamical properties of the system can be computed through the relevant correlation functions. Particularly, the surface phonon spec-

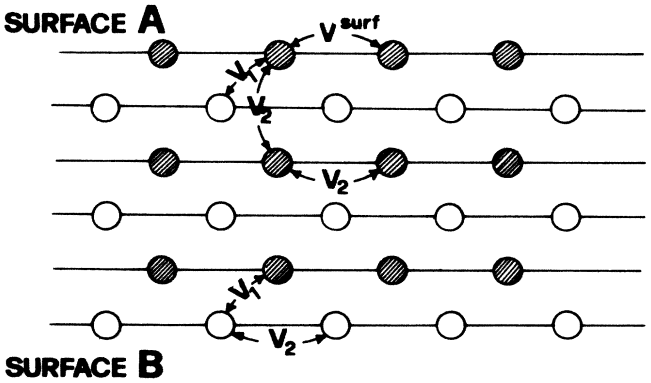

FIG. 2. Illustration of W-W interatomic interactions in a six-layer slab.

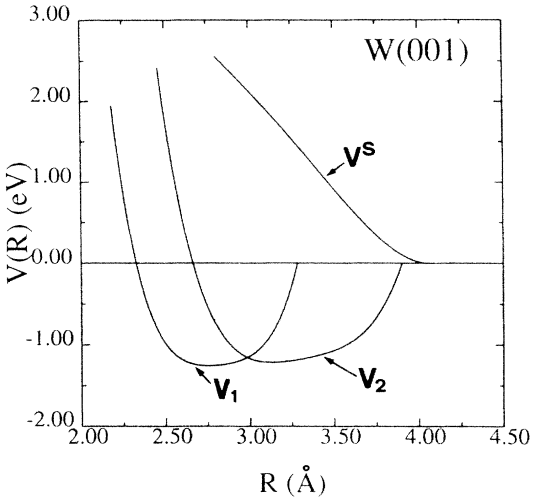

FIG. 3. MD-optimized interatomic potentials of the W(001) slab (from Ref. 23), V_1 and V_2 being the nearest- and next-nearest bulk neighbor interactions.

tral intensity of wave vector $\mathbf{k}$, polarization α is related to the first-layer velocity autocorrelation function $\langle v^\alpha(t)v^\alpha(0)\rangle$

$$g_{\alpha\alpha}(\mathbf{k},\omega)=\int_{-\infty}^{+\infty}dt\sum_n e^{i\omega t}e^{i\mathbf{k}\cdot\mathbf{R}_n}\left[\frac{\langle v_n^\alpha(t)v_0^\alpha(0)\rangle}{\langle v_n^\alpha(0)v_0^\alpha(0)\rangle}\right], \tag{2.2}$$

with

$$\langle v_n^\alpha(t)v_0^\alpha(0)\rangle=\frac{1}{MN}\sum_{m=1}^{M}\sum_{j=1}^{N}v_{n+j}^\alpha(t+\tau_m)v_n^\alpha(\tau_m), \tag{2.3}$$

where M is the number of MD steps, N is the number of first-layer particles, and v_n^α is the α component of their velocity ($n=1,\ldots,N$).

Among all $\mathbf{k}$ points, we have chosen in the present study to concentrate on the point $M=(\frac{1}{2},\frac{1}{2})(2\pi/a)$, believed to be crucial to the reconstruction phase transition.[24] The $T=0$ surface phonon study of Fasolino and Tosatti (FT) (Ref. 15) clearly suggests that the three M-point modes, polarized (mostly) along $x+y$ (L), $x-y$ (T), and (mostly) along z (z), which are folded into zone-center optical surface modes by the $c(2\times2)$ $\langle 110\rangle$ reconstruction at low temperatures, have a very intimate connection with the reconstruction energetics. Once folded, these three low-lying modes become $\mathbf{k}=\mathbf{0}$ modes of the reconstructed (001) surface, since then the point M is folded into $\mathbf{k}=\mathbf{0}$.

In our previous detailed study of the W(001) $c(2\times2)$ reconstruction at $T=0$, the surface distortion was found to decay exponentially into the bulk roughly like $e^{-z/\lambda}$, with $\lambda\approx1$ Å.[15,23] Therefore the first-layer amplitudes and velocities are completely representative of the two-dimensional ordering of the surface and of its dynamics. In order to extract the spectral intensities of each of the $\mathbf{k}=(\frac{1}{2},\frac{1}{2})(2\pi/a)$ modes of interest, we decompose the velocity of each surface atom $\mathbf{v}_i$ into three components according to the approximate eigenvectors of the modes, i.e.,

$$\mathbf{v}_i=v_{i\mathrm{L}}\hat{\mathbf{e}}_\mathrm{L}+v_{i\mathrm{T}}\hat{\mathbf{e}}_\mathrm{T}+v_{iz}\hat{\mathbf{e}}_z,\quad i=l,\ldots N,$$

where i runs over surface atoms, as anticipated,

$$\hat{\mathbf{e}}_\mathrm{L}=\frac{1}{\sqrt{2}}(1,1,0),$$
$$\hat{\mathbf{e}}_\mathrm{T}=\frac{1}{\sqrt{2}}(1,-1,0), \tag{2.4}$$
$$\hat{\mathbf{e}}_z=(0,0,1).$$

These vectors constitute exact symmetry directions for the eigenvectors of the unreconstructed surface, and only approximate ones for the $c(2\times2)$ reconstructed surface where in reality $\hat{\mathbf{e}}_\mathrm{L}$ has a small $\mathbf{k}=\mathbf{0}$ z admixture and $\hat{\mathbf{e}}_z$ a small $\mathbf{k}=\mathbf{0}$ L admixture. This admixture is estimated to be about 10% at $T=0$ (Ref. 15), and is expected to decrease with temperature. It will be neglected for our purposes.

According to (2.2) and (2.3), we first form the (staggered) first-layer averages

$$v^\alpha(t)=\frac{1}{N}\sum_{i=1}^{N}v_i^\alpha(t)\cos(\mathbf{k}\cdot\mathbf{R}_i^0),\quad \alpha=\mathrm{L},\mathrm{T},z, \tag{2.5}$$

where $\mathbf{R}_i^0$ denote the undistorted surface atom positions. Then the surface phonon spectral intensity

$$g_{\alpha\alpha}(\omega)=|v^\alpha(\omega)|^2/\int d\omega\,|v^\alpha(\omega)|^2$$

and the corresponding velocity autocorrelation function

$$f(t)=\langle v^\alpha(t)v^\alpha(0)\rangle/\langle v^\alpha(0)v^\alpha(0)\rangle$$

are evaluated using the fast-Fourier-transform technique.

For each temperature, after a long period of equilibration (typically about 8000 MD steps, $\Delta t=3\times10^{-15}$ sec for each step), a large number 16 384 ($=2^{14}$) of MD steps, corresponding to a time of 5×10^{-11} sec, are used for the evaluation of $v(t)$, and hence $g(\omega)$ and $f(t)$. The results of this analysis will be presented in Sec. III together with some discussion.

III. RESULTS AND DISCUSSION

Before proceeding to discuss the dynamical results, we recall from Ref. 23 the temperature behavior of the static reconstruction-related quantities such as the order parameter magnitude $\langle\rho\rangle$, phase $\langle\cos\varphi\rangle$ (defined in the standard way, as in Refs. 15, 22, and 23), and the static two-dimensional structure factors $S(\frac{1}{2},\frac{1}{2})$ and $S(\frac{1}{2},-\frac{1}{2})$ in Fig. 4. They clearly indicate the reconstruction phase transition to take place around $T_c=280$ K. In detail, the transition from the $c(2\times2)$ ordered phase to the high-temperature disordered phase was found to be driven by phase fluctuations, as is clear from the drop of $\langle\cos\varphi\rangle$.

The $\mathbf{k}=(\frac{1}{2},\frac{1}{2})(2\pi/a)$ surface phonon spectral density $g(\omega)$ for the three chosen polarizations, and the corresponding velocity autocorrelation $f(t)$ calculated in this work are presented in Figs. 5–10 for temperatures ranging from $T=100$ to 1000 K. Each polarization is clearly dominated by one single mode, both at very low and at very high temperatures. We call the (mean) frequency

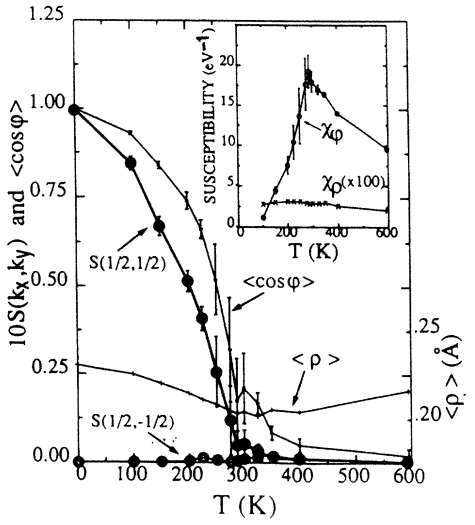

FIG. 4. Temperature-dependent static properties of the W(001) surface reconstruction phase transition.

of these modes ω_L, ω_T, and ω_z, with obvious reference to their longitudinal, shear-horizontal, and shear-vertical polarizations. The real-time correlation functions qualitatively indicate a rather harmonic behavior for ω_z, an extremely anharmonic behavior for ω_T, and a somewhat intermediate behavior for ω_L, already at low temperatures. Their Fourier transforms, presented in Figs. 8, 9, and 10 are more instructive, specifically:

(1) At low temperature, the shear-vertical and longitudinal spectra consist of a well-defined peak, centered at $\omega_L=10$ meV, $\omega_z=9$ meV. These two frequencies are close to those found at $T=0$ by Fasolino and Tosatti,[15] i.e., $\omega_L^{(0)}=10.3$ meV, $\omega_z^{(0)}=9.2$ meV. The small deviation is caused both by the approximate evaluation of the distortion magnitude in Ref. 15, and by a small thermal shift between 0 and 100 K. The shear-horizontal spectrum seems to exhibit a double peak. However, this apparent splitting turns out to be an artifact caused by the small slab thickness. The apparent splitting changes if we go, say, from six to seven layers as exemplified in Fig. 11. This shows that in reality, the mode ω_T of Fig. 9 is just a single broad peak, which must be understood as the envelope of all the split peaks. If ideally we could increase indefinitely the number of layers, these peaks

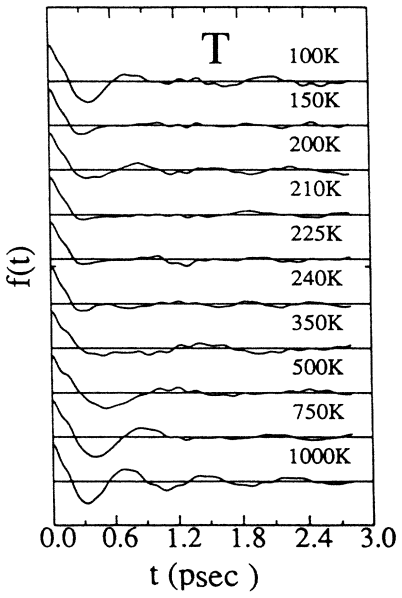

FIG. 6. Temperature-dependent real-time velocity-velocity autocorrelation functions of the shear-horizontal (T) modes.

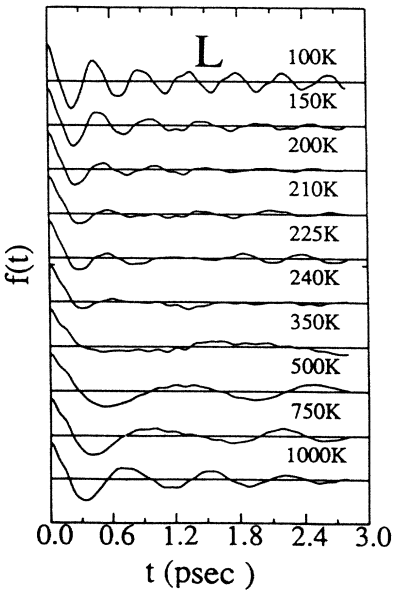

FIG. 5. Temperature-dependent real-time velocity-velocity autocorrelation functions of the in-plane longitudinal (L) modes.

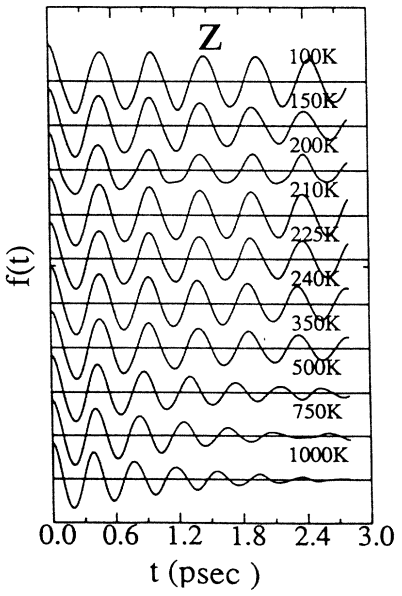

FIG. 7. Temperature-dependent real-time velocity-velocity autocorrelation functions of the shear-vertical (z) modes.

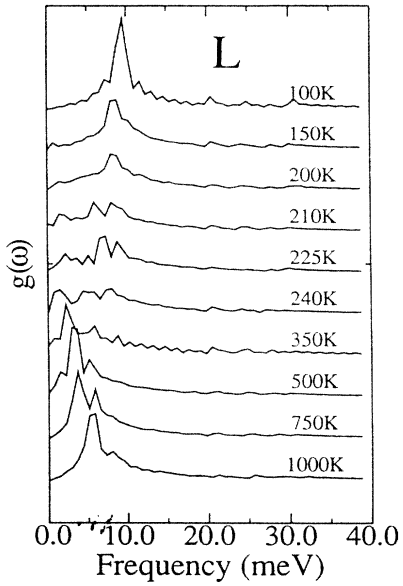

FIG. 8. Temperature-dependent phonon spectral density of the in-plane longitudinal (L) modes. The softening and broading behavior of the mode ω_L is clearly visible.

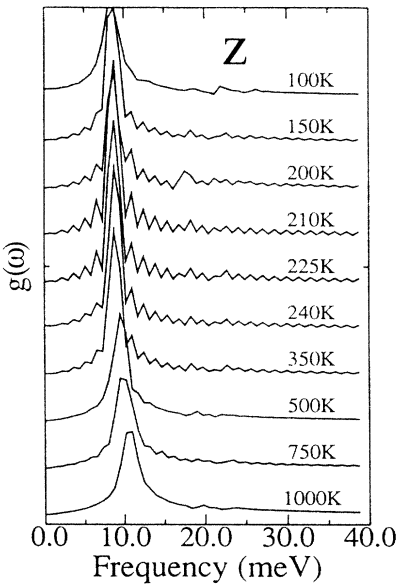

FIG. 10. Temperature-dependent phonon spectral density of the shear-vertical (z) modes. The main ω_z peak is very little affected by the reconstruction transition.

would become denser and denser and eventually merge with the envelope. In conclusion, we extract a very broad envelope for ω_T centered at $\omega_T \sim 5$ meV. Again, this frequency agrees closely with the $T=0$ value $\omega_T^{(0)}=4.7$ meV of Ref. 15.

(2) As the transition temperature $T_c \sim 280$ K is approached, the longitudinal mode ω_L softens considerably, and becomes anharmonic as well. The shear-horizontal mode ω_T broadens much more than softening, and is totally ill defined between 200 and 300 K. In contrast, the vertical mode ω_z remains harmonic all the way across the phase transition.

This behavior of the modes has several implications.

(a) The surface reconstruction transition of W(001) involves mainly in-plane fluctuations. This is consistent with both $T=0$ studies, and $T>0$ equilibrium properties, as obtained from our extensive MD simulations.[23]

(b) Both ω_L and ω_T are heavily involved in the transition. However, the "driving" phase mode ω_T is broadened so much to be essentially destroyed in the

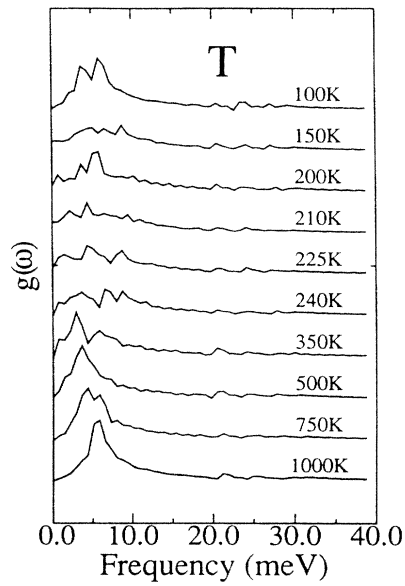

FIG. 9. Temperature-dependent phonon spectral density of the shear-horizontal (T) modes. The envelope of the low-frequency structures is identified with the broad mode ω_T.

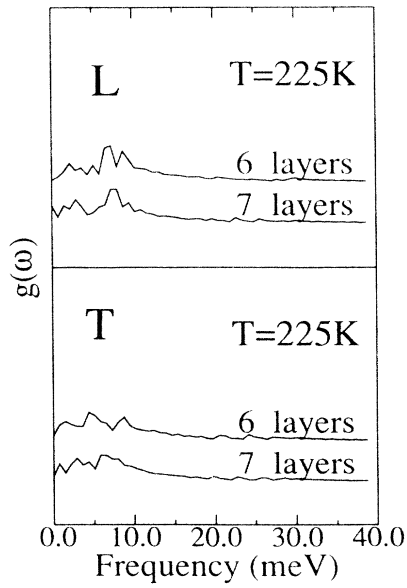

FIG. 11. Comparison of the phonon spectral densities obtained from six- and seven-layer slabs. The apparent peak splitting changes from six to seven layers; the envelope remains similar.

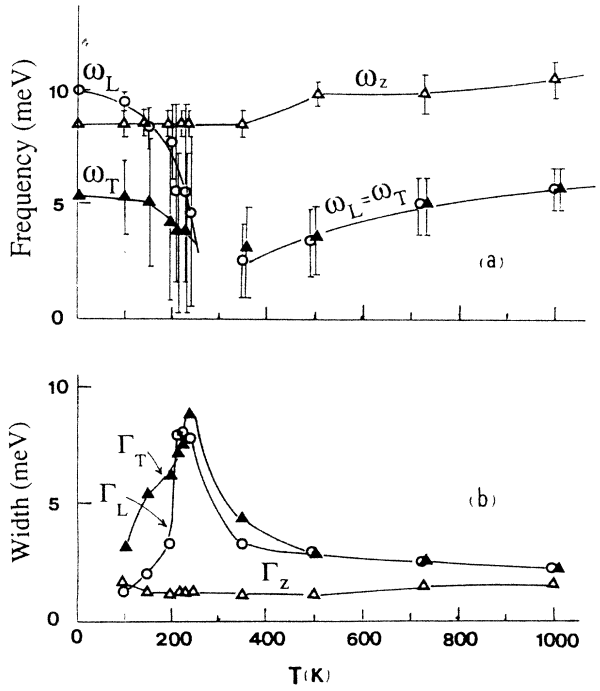

FIG. 12. Peak positions (a) and peak widths (b) of the three low-frequency surface modes of W(001) as a function of temperature.

process, while the "driven" amplitude mode ω_L is strongly softened, and broadens only nearer T_c.

(c) The two broad longitudinal and shear-horizontal spectra become very similar at the transition, where full (time-averaged) C_{4v} symmetry is recovered, and remain coincident thereafter.

(d) By further heating well above T_c, the twofold-degenerate mode $\omega_L=\omega_T$ "stiffens up" gradually again, and gives rise to a clear "motionally narrowed" single peak for $T>350$ K.

The overall behavior of surface mode frequencies, and of their half-widths (extracted somewhat empirically from the envelope of Figs. 8–10) is condensed on Fig. 12, which summarizes our findings. Below 200 K, in the pre-critical temperature regime, our main result is a rapid broadening of the phase mode ω_T. This behavior can be clearly related to the strongly anharmonic $\cos^2(2\varphi)$ "sine-Gordon" effective Landau-Ginzburg potential which controls the phase fluctuations, as described in detail in Ref. 15. In other words, while the distortion amplitude $\langle\rho\rangle$ is only mildly renormalized, the phase of the distortion $\langle\cos\varphi\rangle$ begins to fluctuate with more and more frequent large local excursions from $\langle 11\rangle$ to $\langle 10\rangle$ local behavior.

In the critical region, $200<T<350$ K, gradual phase averaging takes place, with fully order-disorder behavior, as indicated by the large diffusive widths Γ_L and Γ_T.

Finally, quasiharmonic surface modes are restored in the post-critical region $T>350$ K, where $\omega_L=\omega_T$ begin "hardening" again, as expected in the displacive picture.[13]

The present results[30] find a direct experimental confirmation by comparison with the very recent inelastic He-scattering data of Ernst, Hulpke, and Toennies.[19] Since the shear-horizontal mode ω_T does not have a vertical component, it is not directly visible with that technique. Conversely, it is expected that the two other modes, namely ω_L and ω_z, which are sagittal and have a vertical component, (the first is small, the second large) should be observable. Indeed, Ernst *et al.*[19] observe two sagittal modes along the ΓM direction (although their intensity fades out close to point M). Of those, the highest (ω_1) is practically T independent, while ω_2 softens considerably on cooling from 450 K down to 280 K. We thus suggest the identification of ω_1 with our shear-vertical mode ω_z and ω_2 with our amplitude mode ω_L (more precisely, with their connecting modes along the line ΓM). While any attempt at more quantitative comparison will have to await a fully k-resolved calculation, we regard the present contact between the present theory and these data as quite encouraging. Confirmation of the partial softening behavior of ω_L is particularly gratifying, and provides strong support for our overall picture of the dynamics. It would be very interesting if the remaining part of the present results, i.e., the low-temperature behavior of ω_L and the successive high-temperature narrowing and hardening of both ω_L and ω_T could be also tested experimentally.

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[26]The need for separate potentials for bulk first and second neighbors arises from the necessity to avoid unphysical effects at the surface, such as the vertical hopping of surface atoms between (roughly equivalent) first- and second-neighbor positions relative to the second layer. The present potentials V_B have also been carefully checked, through a Parrinello-Rahman–type simulation [M. Parrinello and A. Rahman, Phys. Rev. Lett. **45**, 1196 (1980)] to yield a stable bcc bulk structure, with correct thermal properties.
[27]A related discussion of the statics, based on more qualitative models, has already been given by L. D. Roelofs, G. Y. Hu, and S. C. Ying [Phys. Rev. B **28**, 6369 (1983)], A. Yoshimori, T. Inaoka, and T. Sugibayashi [J. Electron. Spectrosc. **38**, 197 (1986)] L. D. Roelofs [Surf. Sci. **178**, 235 (1986)], and by L. D. Roelofs and J. F. Wendelken [Phys. Rev. B **34**, 3319 (1986)].
[28]E. Tosatti, Solid State Commun. **25**, 637 (1978).
[29]Possible exceptions could, however, arise, for example, in the incommensurate surface phases involving acoustical mode coupling, of the type recently proposed by two of us [A. Fasolino and E. Tosatti, Surf. Sci. **178**, 483 (1986)].
[30]These results are part of C. Z. Wang's Ph.D. thesis, International School for Advanced Studies, Trieste, 1986 (unpublished).