Theory of Inelastic Electron Vibrational Spectroscopy of W(001) at Finite Temperature

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The temperature-dependent dipole-active phonons of the clean $c(2\times2)$ W(001) surface, across the reconstruction phase transition at $T_c \simeq 250$ K, are studied by molecular dynamics. Our calculated inelastic electron rate shows a reconstruction-related low-temperature peak, corresponding to a mostly second-layer surface phonon of high frequency. This mode disappears above T_c, because of fluctuations of the distortion phase angle, and provides a new explanation of the recent electron-energy-loss spectroscopy data of Woods and Erskine.

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The $c(2\times2)$ reconstruction of W(001) has attracted much interest[1] because of its electronic motivation,[2] of its displacive nature,[3] and of its continuous reversible two-dimensional phase transition[4] near room temperature. In direct analogy with the classic studies of continuous displacive three-dimensional transitions,[5] one is led to inquire on the nature of the phonons in this surface, and particularly on their behavior with temperature, across the phase transition. While experimental electron-energy loss-spectroscopy (EELS),[6] and inelastic He-scattering data,[7] are becoming available, theoretical studies of surface dynamics[8-12] are still confined at $T=0$. The main reason is, of course, that temperature-dependent dynamics is difficult, unless one can resort to a direct simulation study, based on a reliable potential.

In this Letter we report results of a molecular-dynamics (MD) simulation, possibly the first of this type, aimed at calculating the $k=0$ surface phonon spectral function at finite temperature, and particularly across the reconstruction phase transition of W(001). Our results elucidate the existence of one main dipole-active reconstruction-related mode and its destruction by critical phase fluctuations. Moreover, they explain naturally in terms of single phonons the EELS spectra of Woods and Erskine,[6] which had recently led to speculative proposals involving second harmonics or double losses.[9]

Our simulation is based on an n-layer slab (usually $n=6$, but checks have also been run with $n=5,7$), each layer consisting of $16\times16=256$ W atoms with in-plane (x,y) periodic boundary conditions, and free z motion. This size was found satisfactory in recent parallel studies of the static properties of this system.[13] We take here the same well-tested effective Hamiltonian, based on the concept that two neighboring surface atoms have a very different interaction potential than two bulk atoms.[8,10,11] First- and second-neighbor bulk pairwise potentials and also the surface potential have the form of anharmonic wells, i.e., $V^{(i)}(r)=\sum_{l=0}^{4} c_l^{(i)} x^l$, where $x=(r/r_0^{(i)}-1)$ ($r_0^{(i)}$ is the equilibrium distance) and $c_l^{(i)}$ are constants, which differ for bulk first neighbors ($i=1$), second neighbors ($i=2$), or surface ($i=s$). We have used $r_0^{(1)}=2.7366$ Å, $c_0^{(1)}=-1.25$ eV, $c_1^{(1)}=-0.2247$ eV, $c_2^{(1)}=17.2252$ eV, $c_3^{(1)}=-116.4571$ eV, $c_4^{(1)}=936.1500$ eV; $r_0^{(2)}=3.16$ Å, $c_0^{(2)}=-1.21$ eV, $c_1^{(2)}=0.2996$ eV, $c_2^{(2)}=16.4263$ eV, $c_3^{(2)}=-131.4771$ eV, $c_4^{(2)}=624.1000$ eV; $r_0^{(s)}=3.16$ Å, $c_0^{(s)}=1.758$ eV, $c_1^{(s)}=-7.4892$ eV, $c_2^{(s)}=-4.6932$ eV, $c_3^{(s)}=6.2576$ eV, $c_4^{(s)}=93.6150$ eV, as in our earlier work.[10,11,13] Our slabs are asymmetric in the sense that the surface potential is used only on one side, and the other side remains bulklike, to simulate a bulk termination. At low temperature, our surface lattice undergoes a spontaneous $c(2\times2)$ $\langle 110\rangle$ distortion, of amplitude $\simeq 0.22$ Å, accompanied by an energy gain of $\simeq 30$ meV/atom.[10,13] Details of the MD simulation form the subject of a longer report.[13] The essence of it is that the $c(2\times2)$ reconstruction is stable until about 250 K, where it makes a transition to a disordered phase. The nature of this disorder consists mainly in a loss of coherence of the in-plane distortion phase angle.

At each temperature, a suitable number of canonical MD steps, usually no fewer than 6000 (one step $=3\times10^{-15}$ sec) is allowed for equilibration. Following this, a total of $2^{14}=16348$ steps are used for evaluation of the average

$$W(t)=\frac{\langle[\dot z_1(t)-\dot z_2(t)][\dot z_1(0)-\dot z_2(0)]\rangle}{\langle[\dot z_1(0)-\dot z_2(0)]^2\rangle}, \qquad (1)$$

where $\dot z_1(t)$ is the average z velocity component of all first-layer atoms at time t, and $\dot z_2(t)$ that of second-layer atoms. The theory of EELS vibrational scattering was given by Evans and Mills.[14] Based on that, a simple argument suggests that the Fourier transform of $W(t)$ should be roughly proportional, within a factor ω^2, to the dipole EELS cross section for $k=0$. In essence, the mean instantaneous modulation of the first-second layer spacing is assumed to be proportional to the oscillating macroscopic dipole moment capable of scattering the electron.[14]

At $T=0$, where MD is meaningless, we can calculate $W(\omega)$ directly from harmonic slab lattice dynamics

(LD), in the equivalent form

$$W_0(\omega)=g(\omega)\left[\int_0^\infty g(\omega)\,d\omega\right]^{-1}, \tag{2}$$

where

$$g(\omega)=\omega^2\sum_{\lambda,i=1,2}[u_1^{iz}(k=0,\lambda)-u_2^{iz}(k=0,\lambda)]^2\delta_{\omega,\omega_{k\lambda}}, \tag{3}$$

where u_l^{iz} denotes the (normalized) eigenvector z component of the atom i on layer l of branch $(k\lambda)$ of frequency $\omega_{k\lambda}$. The slab LD calculations for the present model of W(001) are standard and described in full detail in Ref. 10. Figure 1(b) presents our MD results for $W(\omega)$ [from Eq. (1)] as a function of temperature. For comparison, Fig. 1(a) shows the $T=0$, LD results [Eq. (2)] for a thin and a thick slab. We identify three main frequency ranges: low frequencies ($\omega<14$ meV), bulk frequencies ($14<\omega<29$ meV), and high frequencies ($\omega>29$ meV). Our MD-calculated EELS spectra exhibit (A) a low-frequency peak at $\omega\simeq 10$ meV, of intensity growing with temperature, (B) several strong peaks in the bulk range, the intensity shifting from one to the other with temperature, (C) a high-frequency peak at $\omega\simeq 31$ meV whose intensity decreases with temperature.

Peak A is an artifact due to the free-slab geometry. In fact, the three main $T=0$, $k=0$ [really at $k=(\frac{1}{2},\frac{1}{2})2\pi/a$, folded into $k=0$ by the $c(2\times2)$ reconstruction], low-frequency surface phonons are, with the present potential,[10] a mostly shear vertical $\omega_z=9.2$ meV, a mostly in-plane longitudinal $\omega_l=10.3$ meV, and a shear horizontal $\omega_t=4.7$ meV. Of these, only ω_l should give rise to a tiny modulation of $\dot{z}_1-\dot{z}_2$, practically invisible on this scale (as is indeed the case in the LD results). We have checked that peak A is due instead to "spilling out" of ω_2 mediated by a long-wavelength oscillation of the unsupported slab. Introductions of an artificial support, such as a rigid bottom layer, removes this peak.

The series of B peaks is instead genuine. However, only their "envelope" is meaningful, while their precise number and position is determined by the chosen slab. This was checked directly by either reducing ($n=5$) or increasing ($n=7$) the MD slab thickness (results not shown). The LD results of Fig. 1(a) clearly demonstrate the same point, i.e., that the individual peaks of a thin slab are an artifact, but their envelope is meaningful and close to that of a thick slab. To make the comparison between MD and LD results more direct, LD results are shown both for the $T=0$ equilibrium values of the distortion $\langle\rho\rangle$ and distortion-related extra relaxation h ($\langle\rho\rangle=0.225$ Å and $h=0.028$ Å) and for the average values of the same quantities at $T=100$ K ($\langle\rho\rangle=0.2$ Å and $h=0.02$ Å). The overall feature B represents the surface dipole scattering produced by bulk modes. It is not very weak, and should be fully observable. However, it is neither very eventful, nor very reconstruction related (from LD, the unreconstructed surface has a similar broad feature B, its intensity dropping at $\simeq 21$ meV rather than $\simeq 24$ meV, i.e., 3 meV narrower; see Fig. 2).

Peak C is far more interesting. It is present and strongest at $T=0$ [Figs. 1(a) and 2 (curve a)] and is

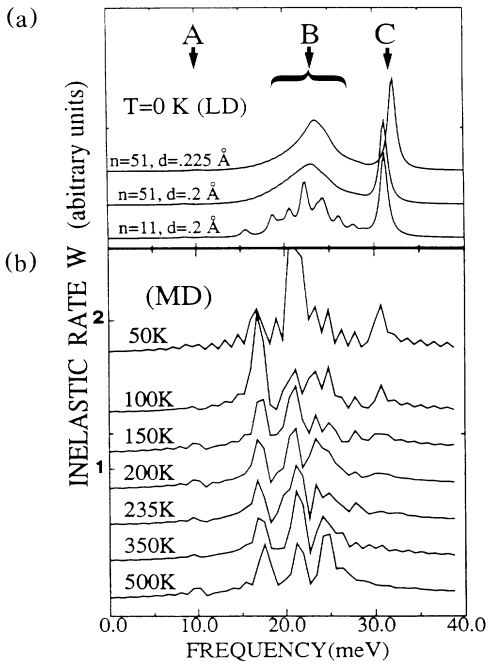

FIG. 1. Dimensionless inelastic rates due to $k=0$ modes of the W(001) surface: (a) from lattice dynamics [Eq. (2)] and (b) from molecular dynamics [Eq. (1)]. The peak structures in region B are an artifact due to small slab thickness (see text). Peak C reflects mode L_1 of the $c(2\times2)$ reconstruction.

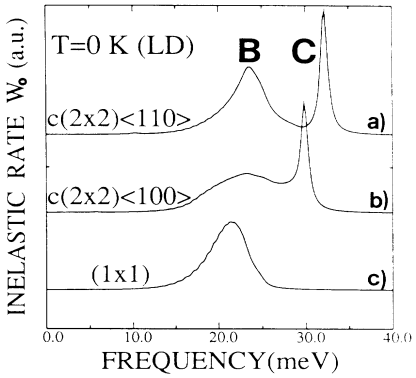

FIG. 2. Calculated rates for three different states of the W(001) surface: (curve a) ⟨100⟩ reconstruction, (curve b) ⟨100⟩ reconstruction, and (curve c) no reconstruction. The broad bulk peak B is only marginally affected, while the second-layer peak C shifts strongly from curve a to curve b and disappears in curve c.

not altered by a rigid bottom layer. It is entirely due to reconstruction, and it disappears if the corresponding distortion is removed [Fig. 2 (curve c)]. Finally, its intensity falls rapidly with increasing temperature, and is already hard to detect at 235 K, where with our potential the W(001) surface is starting to switch from $c(2\times2)$ order to disorder.[13] We have already noted and described in our extensive lattice-dynamical study[10] one surface phonon, called L_1, giving rise to this peak. It has the same sagittal symmetry as ω_l described above. Its eigenvector mixes 60% in-plane longitudinal motion, of nominal wave vector $\mathbf{k}=(\frac{1}{2},\frac{1}{2})2\pi/a$, with a 40% vertical $k=0$ component (which is the only one that makes it dipole active and visible in EELS). This mixture is made possible by the reconstruction, which folds the M-point longitudinal mode into $k=0$, and also lowers the symmetry, causing in-plane and vertical displacements to mix. One curious feature of this surface mode L_1 is that it moves the *second* atomic layer by a factor about 3.5 more than the first layer.[10]

The notion of surface modes which localize successively on the first, second, third, and deeper layers is well established.[15] For a Lennard-Jones crystal, for example, the first-layer mode has the lowest frequency, the second is higher, the third is even higher, and so on. All these frequencies lie *below* the largest bulk frequency of same (k_x,k_y). However, this ordering of the frequencies, as well as the necessity that they lie below the bulk limit, is easily upset if the surface forces are or masses are substantially altered.[16]

In our model of W(001) the surface forces are so very different from the bulk forces as to cause reconstruction. The pushing up in frequency of L_1 can be traced to a reconstruction-related stiffening of the first-second-layer force constants. Essentially, first-layer atoms can only realize the $c(2\times2)\langle110\rangle$ Debe-King distortion by climbing over second-layer atoms. While some of the related strain is relieved by a substantial outward relaxation of the entire first layer ($h=0.028$ Å in our model), the residual compression, and the related increase of spring constants relative to the bulk, are sufficient to give rise to this somewhat atypical mode, exactly as suggested by Woods and Erskine.[6] We find, in fact, that the radial force constants between one atom in the second layer and the atom on the surface which climbs on it is increased at $T=0$ by $\simeq40\%$. Further support to this picture is obtained if the $c(2\times2)$ $\langle110\rangle$ distortion is arbitrarily phase rotated by 45°, to give rise to a $c(2\times2)$ $\langle100\rangle$ reconstruction [which is typical of H/W(001) for coverage above 0.11 [17]]. In this new distortion, there is no more climbing on the second-layer atoms in this case, and the L_1 mode should soften. Figure 2 (curve b) indeed shows that its frequency has fallen to become very close to the bulk edge (29 meV in our parametrization) as expected. We note, incidentally, that such a bulk-edge peak is not characteristic of the ideal surface [which yields a spectrum such as Fig. 2 (curve c), quite similar to the surface spectrum of Black, Laks, and Mills[18]], so that its appearance on the H-covered surface[6] cannot be used to identify it as "ideal."

The above results constitute a very precise prediction for a high-resolution EELS vibrational experiment as a function of temperature. Using EELS, Woods and Erskine[6] have recently discovered on clean W(001) a reconstruction-related peak around 36 meV. This is in many ways an exciting result, as it is among the first clear evidences of the effect of reconstruction on surface dynamics. The peak is present at 77 K, it disappears at room temperature, and it has not been convincingly explained. Reinecke and Ying[9] have recently suggested an explanation in terms of a second harmonic, or double absorption of the shear vertical mode ω_z. Our results provide instead strong support for a new identification of the 36-meV peak with our peak C, which is placed at 31 meV without any adjustable parameters, and which behaves similarly with temperature.

By contrast, the alternative explanations do not seem viable. The mode ω_z is not even dipole active, and cannot lead to double absorption. Second harmonics, i.e., simultaneous creation of two ω_z phonons, is in principle possible. The intensity of this anharmonic process, however, should increase, rather than decrease, with temperature. In fact, the mode ω_z at $\mathbf{k}=(\frac{1}{2},\frac{1}{2})2\pi/a$ is not particularly reconstruction related,[7,10,11] and two such modes have quite naturally $k=0$, independently of reconstruction. Moreover, we estimate this process at $\simeq20$ meV, that is, in region B. Hence, second harmonics fails to explain the observed behavior of peak C.

It is interesting to pursue, before closing, the detailed reason why the intensity of peak C falls off so fast with temperature. We believe that the explanation lies in the strong fluctuations of the phase ϕ of the two-dimensional distortion order parameter[2,10,13] $\rho\exp(i\phi)$. The phase susceptibility

$$\chi_\phi=(k_BT)^{-1}(\langle\cos^2\phi\rangle-\langle\cos\phi\rangle^2),$$

also calculated by MD,[13] grows very fast, even before the decrease in the $(\frac{1}{2},\frac{1}{2})$ structure-factor intensity becomes substantial. This means that the two $c(2\times2)$ distortions, the $\langle110\rangle$ ($\phi=0$), and the $\langle100\rangle$ ($\phi=\pi/4$), become closer and closer in free energy, and begin to mix locally with one another (probably in the form of time-dependent $\langle100\rangle$ domains becoming increasingly common in spite of the overall $\langle110\rangle$ character). In turn, the phase fluctuations can produce a larger broadening of the phonon L_1 even before they lead to complete disorder, simply because the L_1 frequencies in the $\langle110\rangle$ and $\langle100\rangle$ phases are so different. To check this, we compare in Fig. 3 the inverse phase susceptibility χ_ϕ^{-1} with the integrated relative intensity of the peak C versus temperature. The simultaneous fall of both quantities with tem-

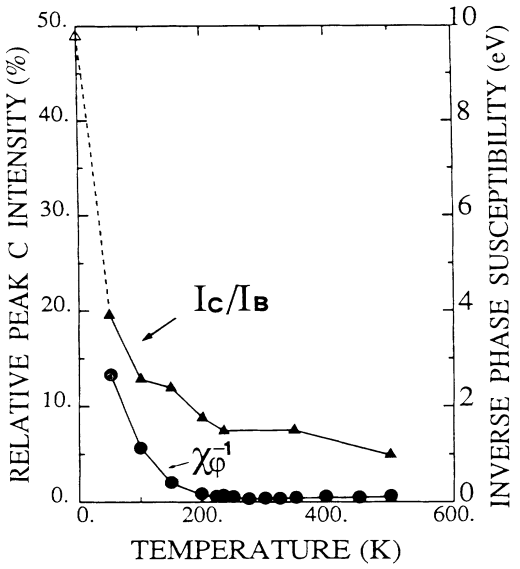

FIG. 3. Comparison of the relative integrated intensities of peaks C and B with the inverse phase susceptibility, as a function of temperature.

perature supports the above viewpoint. We conclude by proposing, in turn, that a detailed study of the 36-meV peak intensity should provide direct experimental insight into these phase fluctuations.

In summary, we have reported a study, carried out mostly by molecular dynamics, of the temperature-dependent surface dynamics of reconstructed W(001), as it would appear through inelastic vibrational spectroscopy. We have found that an unusual reconstruction-related second-layer surface phonon plays a major role in this spectrum. The corresponding peak is identified and explained in existing EELS spectra for the clean W(001). The temperature dependence of this peak appears to monitor directly the strong phase fluctuations of this surface.

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