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Modification of phonon spectral densities of the (001) copper surface due to copper adatoms by molecular dynamics simulation

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Abstract

Phonon spectral densities of the (001) copper surface containing copper adatoms have been calculated at various temperatures using molecular dynamics simulation. The results reveal that the presence of adatoms is manifested mainly by the appearance of new dispersionless peaks which are broadened and shifted to lower energies as the temperature increases. The existent experimental results, as well as lattice dynamics, ab initio calculations and other simulations in the case of a clean surface, are in good agreement with our predictions.

Keywords: Adatoms; Copper; Molecular dynamics simulation; Phonons; Vibrations of adsorbed atoms

Phonon density of states (DOS) and phonon spectral densities (SD) have been widely used to study the dynamical behavior of both the bulk and surfaces of metals [1–3]. The structure and the dynamics of the surfaces, roughening [4–6] and premelting [7,8] phenomena, as well as the surface disorder [9] have been the subject of numerous publications in the last decade. Among the approaches that have been used are lattice dynamical models [2], the embedded atom method (EAM) [10,11] and ab initio calculations [12], methods that are particularly well suited for the computation of the phonon dispersion curves and the SD. Lately, with the appearance of realistic potentials, the technique of molecular dynamics (MD) contributed greatly in the comprehension of many of the above mentioned topics. The models employed by MD are based either on EAM [10,13] or on the effective medium theory [14,15] or on the tight binding method (TBM) [16,17]. In addition, it has been found [15,18,19] that the presence of adatoms and/or vacancies affects drastically most of the surface effects that play a fundamental role in the behavior of the materials. While there is ample literature for the phonon DOS and for the phonon SD of surfaces [1–3,11–13], studies including adatoms on the surfaces are very scarce [19,20].

In this communication we present results showing that the copper adatoms are manifested in the phonon SD by introducing new vibrational modes or modifying the existent ones, a fact that alters significantly the dynamical behavior of the surface. New peaks are found in the longitudinal polarization at $\overline{X}$ and in

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both the longitudinal and the vertical polarization at $\overline{M}$. The results corresponding to the clean surface of copper are in good agreement with the experiment [12,21], ab initio calculations [12] and MD studies using interatomic potentials obtained by the EAM [13] (MD-EAM) or TBM [22], while those for the 4% adatom coverage show a dispersionless behavior. In addition, we find that the phonon modes are broadened and shifted to lower energies as the temperature increases.

The simulations have been carried out using standard MD in the microcanonical ensemble and a system made up of 4500 particles arranged on a fcc lattice. Periodic boundary conditions are imposed in the three space directions parallel to the [1$\bar{1}$0], [110] and [001] crystallographic axes. By fixing the dimension of the computational box at a value twice as large as the thickness of the crystal along the z-direction, an infinite slab was produced delimited by two free surfaces parallel to the (001) planes. The model is made up of 20 atomic layers parallel to the free surfaces, each containing 225 atoms. The atomic interactions derive from a potential based on the TBM in the second moment approximation [16,17] which has already yielded very good results for the bulk and the surface properties of copper [18,23]. The potential energy of an atom i, is given by:

$$E^i = \frac{A}{2}\sum_{j\neq i} e^{-p\left(\frac{r_{ij}}{d_0}-1\right)} - \xi\sqrt{\sum_{j\neq 1} e^{-2q\left(\frac{r_{ij}}{d_0}-1\right)}}, \tag{1}$$

where $r_{ij} = |\boldsymbol{r}_i - \boldsymbol{r}_j|$ is the distance between atoms i and j, $d_0 = 2.547$ Å stands for the nearest neighbor distance and the parameters $A = 0.181$ eV, $\xi = 1.243$ eV, $p = 10.68$ and $q = 2.32$ have been fitted to the cohesive energy, equilibrium condition and the elastic constants of copper, including interactions up to 5th neighbors.

The equations of motion are integrated by means of the Verlet algorithm and a time step $\delta t = 10^{-14}$ s that guarantees a total energy conservation within $\delta E/E = 10^{-5}$. Initially, 1000 time steps were used to reach thermal equilibrium. Another 1000 steps were subsequently taken to calculate averages. To increase statistical accuracy, we used nine independent trajectories produced from different initial conditions. This method has been proved [24] to be statistically more efficient than a longer trajectory since it ensures a better exploration of the phase space.

The simulations of the surface with adatoms were performed for a concentration of 4% on each face of the slab. This coverage was chosen so as to guarantee reasonable statistics and at the same time exclude possible interaction between the adsorbates. Simulations at 80, 300, 500 and 800 K were performed to deduce the temperature dependence of the various quantities. The density of the system is adjusted, at each temperature, by using the value of the lattice constant that results to zero pressure for the bulk system. The DOS were calculated using fast Fourier transform of the velocity autocorrelation function. SD's were calculated for a given polarization ($p = x$, y, z) and a specific k vector in the surface plane, by Fourier transforming the following autocorrelation function [25]:

$$A^p(k,t) = \frac{\langle v_k^p(0)\, v_k^p(t)\rangle}{\sum_p \langle v_k^p(0)\, v_k^p(0)\rangle} \tag{2}$$

with

$$v_k^p(t) = \sum_i v_i^p(t) e^{-iK\cdot R_i(t)}, \tag{3}$$

where $\boldsymbol{R}_i(t)$ and $v_i(t)$ stand for the particle position and velocity at time t respectively (the sum is over all surface atoms and the averages in Eq. (2) denote time averages).

In practice we use the following procedure:

Let a function $f(t)$ be decomposed as:

$$f(t) = \sum_k a_k e^{i\omega_k} \tag{4}$$

and let

$$F(\omega,T) = \int_0^T f(t) e^{-i\omega t} dt = \sum_k a_k \frac{e^{i(\omega_k-\omega)T}-1}{i(\omega_k-\omega)} \tag{5}$$

be its finite Fourier transform. Then by inspection one has:

$$\frac{F(\omega,T)}{T} = \begin{cases} a_k & \text{for } \omega \to \omega_k \\ O\left(\frac{1}{T}\right) & \text{otherwise,} \end{cases} \tag{6}$$

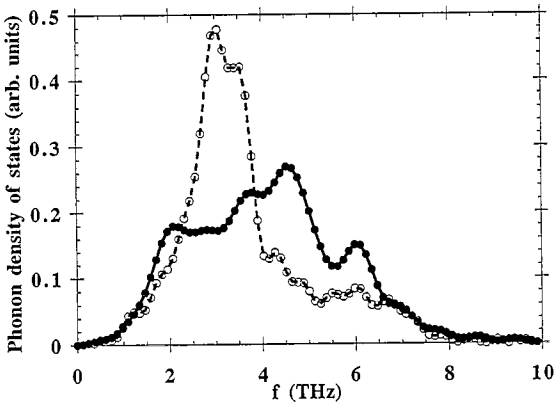

Fig. 1. Phonon density of states of Cu(001) surface at 300 K. Solid line: in plane, along the [110] direction; dashed line: normal to the surface.

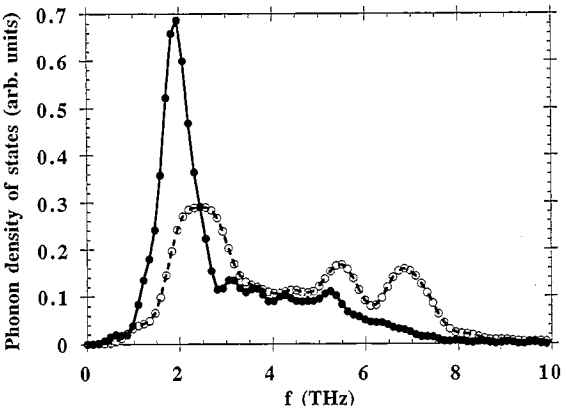

Fig. 2. Phonon density of states of 4% copper adatoms on the Cu(001) face at 300 K. Solid line: parallel to the surface, along the [110] direction; dashed line: normal to the surface.

and hence for large T one has both a location for the eigen-frequencies ω_k and an estimator for the corresponding amplitudes a_k.

The DOS for the clean surface (001) at $T = 300$ K is presented in Fig. 1. Solid and dashed lines correspond to the parallel to the surface ([110]) and to the normal to the surface direction. These results are in good agreement with the method of generating coefficients of lattice Green's functions [1] or the continued fraction technique [3]. Along the [110] direction we observe in the lower frequency range the existence of a peak around 2 THz, corresponding to the shear horizontal polarization S_1 ($\overline{X}$ point at the end of the surface Brillouin zone along [110] direction). In the intermediate frequency region the structure is similar to that of the bulk, while for higher frequencies the existing peak, situated around 6 THz corresponding to the longitudinal polarization S_6 ($\overline{X}$ point), is shifted towards lower frequencies. Concerning the normal to the surface phonon spectrum, two peaks are found at 3.0 and 3.7 THz. The first one is due to localized surface modes vertically polarized and corresponding to S_4 at $\overline{X}$, while the next one is due to S_1 at $\overline{M}$ ([100] direction).

In Fig. 2 we present the phonon DOS of 4% copper adatoms on the Cu(001) face at 300 K. The structure of this phonon density of states is completely different from that appearing in Fig. 1. This result, in agreement with previous calculations [19], shows the different character of the vibrational properties of the copper adatoms on that surface. Along the [110] direction, parallel to the surface (solid line), a pronounced peak at 2 THz emerges, suggesting weaker interactions from those existing between surface atoms. The DOS at the normal direction shows three peaks, in excellent agreement with lattice dy-

Table 1
Comparison of the surface phonon modes of Cu(001) surface at the symmetry points $\overline{X}$ and $\overline{M}$ found by the present work and in the existent literature (frequencies are in THz)

Symmetry points	Modes	Ab initio [12]	EAM [11]	MD (EAM) [13] MD (TBM) [22]	Experimental work	Present work
$\overline{X}$	S_1	2.3	2.09	1.91 [13]	–	1.95
	S_4	3.1	2.99	2.91 [13] 2.56 [22]	3.24 [21]	2.95
	S_6	6.2	6.08	5.77 [13]	6.10 [12]	6.10
$\overline{M}$	S_1	4.3	3.97	3.88 [13] 3.41 [22]	4.05 [21]	3.80
	L_1	5.0	–	5.10 [13]	–	5.05

namics calculations [19]: the first one is situated at 2.44 THz and it is broader and shifted towards lower frequencies comparing with the main surface peak (3.0 THz in Fig. 1) and the other two at 5.5 and 6.8 THz. This shift is very important because it denotes

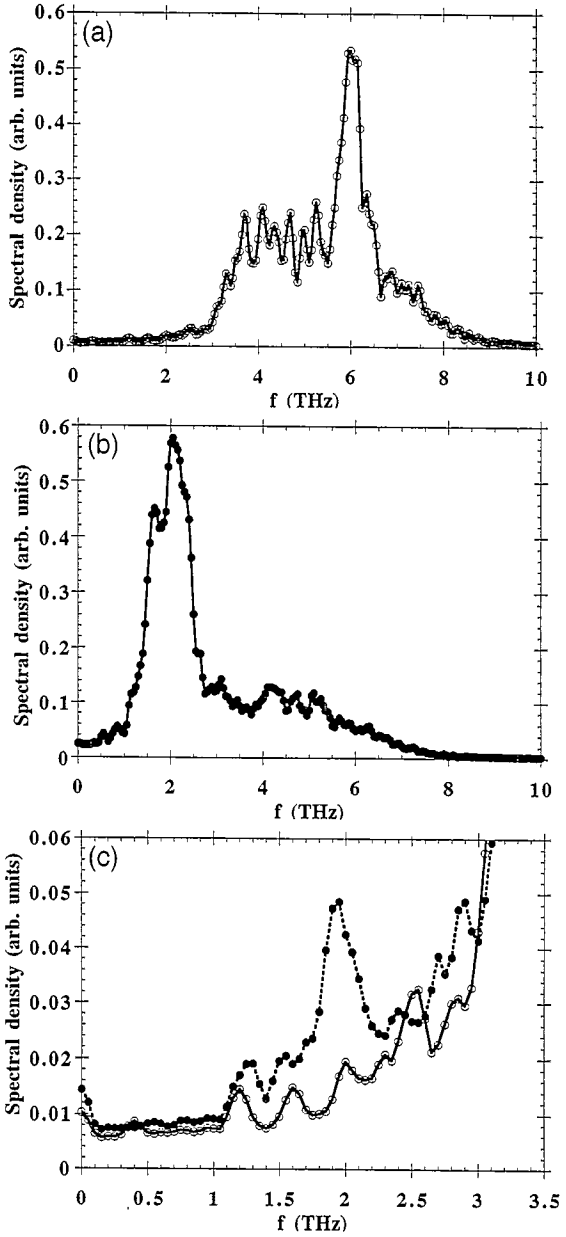

Fig. 3. Spectral density of phonon states at 300 K at $\overline{X}$ (longitudinal polarization). (a) Clean surface of Cu(001). (b) 4% copper adatoms on Cu(001) face. (c) Zoom of (a) around 2 THz; solid line: Cu(001) clean surface; dashed line: Cu(001) with 4% copper adatoms.

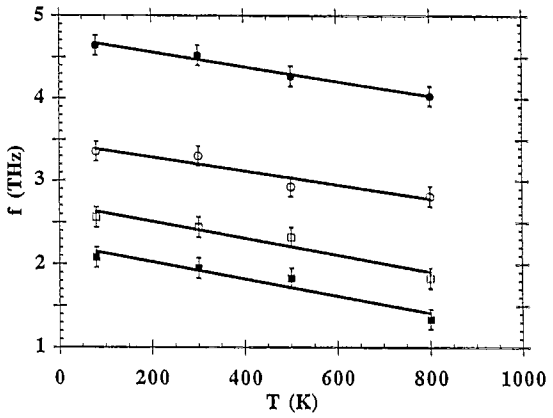

Fig. 4. Temperature dependence of some dominant phonon modes of the clean surface (circles) and the adatoms (squares); filled and open symbols correspond respectively to the parallel and normal to the surface direction.

a rather strong coupling between the adatoms and the surface atoms [19]. These conclusions are compatible with the calculations of the mean square displacements of adatoms; indeed, in the parallel to the surface direction we find values about twice the values in the normal direction [26].

For a more detailed study we decided to calculate the SD's for some particular k vectors. In Fig. 3a we present the SD of the clean surface (001) along the [110] direction at the point $\overline{X}$ for the longitudinal polarization. We observe a pronounced peak at 6.1 THz corresponding to the S_6 mode, in agreement with experimental results [12], ab initio computations [12] and MD simulations using EAM potentials [13].

In Table 1, we present the positions of the modes we find, along with others reported in the literature. We remark that our results compare well with ab initio and EAM calculations as well as with experiments, suggesting that the model we used in conjunction with the MD simulation can give reliable information concerning the vibrational properties of surfaces. We note that since we studied the first layer atoms, modes mainly due to second layer vibrations (the S_2 mode at $\overline{X}$ and $\overline{M}$) are not shown. In addition, our simulations predict the L_1 mode at $\overline{M}$, in excellent agreement with ab initio calculations [12] and MD-EAM simulations [13], while the force constant model [2] or the EAM fail [11] to reproduce this mode. It is worth to be noted that despite the

different models used, the MD simulations (MD-EAM and the present study) give practically the same values.

Fig. 3b shows the SD of the adatoms calculated under the same conditions as in Fig. 3a. We chose this case because the pronounced peaks (6.1 THz for the clean surface and 2 THz for the adatoms) are completely separated. It is interesting to look at the SD calculated for the surface with adatoms, from where we remark that the whole spectrum has practically the same structure with the SD of the clean surface for all frequencies except for a small new peak appearing at 2 THz, which is shown in Fig. 3c magnified.

At $\overline{M}$ and for the longitudinal polarization, a similar additional peak appears at the same frequency, while for the vertical polarization two new modes are found at 5.5 and 6.8 THz. Thus, the presence of adatoms on that surface changes the SD, causing additional peaks with dispersionless character. Indeed, the DOS of adatoms, Fig. 2, is of the same structure as their spectral density, Fig. 3b. We verified that these additional peaks are well reproduced for all the equivalent directions and that the statistics confirm the localization of the peaks. For other $\boldsymbol{k}$ vectors, the additional peaks due to the adatoms are generally situated near the main peaks of the clean surface and it is therefore difficult to distinguish their contribution to the SD of the surface with adatoms.

In order to deduce the temperature dependence of these peaks, we performed simulations at four different temperatures 80, 300, 500 and 800 K The main result is a broadening and a shift towards lower energies of both the clean surface peaks and the peaks due to the adatoms. Similar features are also found [13] by the MD-EAM for the case of a clean surface. In Fig. 4 we present the following phonon DOS modes at the indicated directions versus temperature: (a) the 4.5 THz mode (parallel to the clean surface – filled circles), (b) the 3 THz mode (normal to the clean surface – open circles) (c) the 2 THz adatom mode (parallel to the surface – filled squares) and (d) the 2.44 THz adatom mode (normal to the surface direction – open squares). A practically identical linear dependence for all these modes is observed within the error bars referring to the frequency step of 0.12 THz used.

Since the surface phonon spectrum modifications due to the presence of adatoms yields important information about the interactions between surface and adsorbate atoms, it would be of great interest to extend the present investigation to the study of second layer atomic vibrations, various adsorbates and coverages and to experimentally verify these new findings by suitable methods such as electron-energy-loss-spectroscopy or thermal helium beam scattering.

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