High-frequency vibrational modes at stepped Pt(111) surfaces

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We show that vibrational modes with frequencies above the maximum in the bulk can occur at the steps of the Pt(332) or $6(111)\times(11\bar{1})$ surface, as observed by Ibach and Bruchmann, if the largest force constants are increased by ~ 30–40% at the steps. The calculations are done by applying the recursion method within clusters of thousands of atoms, with a rotationally invariant first- and second-neighbor bond-angle model for the interatomic forces.

Ibach and Bruchmann[1] have recently reported inelastic-electron-loss measurements of localized phonons at the (332) or $6(111)\times(11\bar{1})$ surface of platinum. The most interesting feature of their results is that the observed phonon loss peak occurs at a frequency of 25.4 meV, slightly higher than the maximum frequency of 24.3 meV in bulk Pt, and roughly 15% above the highest frequency peak at ~ 22 meV in the bulk density of states.[2] This is somewhat unexpected, because the usual picture is that phonon frequencies will decrease at surfaces to reflect the missing bonds. To explain higher-frequency surface vibrational modes, it is necessary to invoke relaxation accompanied by increased force constants in the surface region. Arguing by analogy to a linear chain with nearest-neighbor interactions, Ibach and Bruchmann estimated that the force constants for atoms at the steps must be increased by a factor of approximately 1.7 to explain their data.

Drawing conclusions for three dimensions from one-dimensional models is generally somewhat risky. On the other hand, high Miller index surfaces with regularly stepped structures like the fcc (332) surface are difficult to treat by either exact methods[3,4] or approximate, slab calculations[5] that rely on use of the two-dimensional transform with respect to surface wave vectors. An approach that does not vary in complexity with surface normal, i.e., one that can be programmed to deal with (hkl) surfaces in the same way as (100), (110), or (111), is the recursion method.[6] We have applied this method to large clusters of atoms to investigate vibrational modes at stepped fcc surfaces.

We use a rotationally invariant, first- and second-neighbor (1nn + 2nn) bond-angle force model like that described by Keating.[7] Scalar products of vectors are invariant under rotations, so the potential energy is expanded in powers of scalar product differences S,

$$S(n_1,n_2;n_3,n_4)=\vec{R}(n_1,n_2)\cdot\vec{R}(n_3,n_4) - \vec{R}_0(n_1,n_2)\cdot\vec{R}_0(n_3,n_4)\ , \qquad (1)$$

where $\vec{R}_0(n,n')$ is the equilibrium spacing between atoms at sites n and n', and

$$\vec{R}(n,n')=\vec{R}_0(n,n')+\vec{u}(n)-\vec{u}(n')$$

includes the displacements $\vec{u}(n)$ and $\vec{u}(n')$ away from equilibrium. The expansion is truncated at second order in the displacements to yield a harmonic phonon Hamiltonian. For the present calculations, we include squares of the following scalar product differences in the potential energy, giving an example for each: 1nn bonds—$S^2(110,0;110,0)$; 2nn bonds—$S^2(200,0;200,0)$; 1nn-1nn-1nn angles—$S^2(110,0;011,0)$; 1nn-1nn-2nn angles—$S^2(110,0;1\bar{1}0,0)$, $S^2(110,0;200,0)$. In the bulk, this five-parameter bond-angle model is equivalent to a general 1nn + 2nn Born–von Kármán model. At surfaces, however, the bond-angle model is automatically rotationally invariant, unlike a truncated Born-von Kármán model.

We generate our clusters in a way designed to eliminate boundary effects in the recursion procedure. Suppose that we want to calculate the density of states for displacements of a particular atom along a given direction, e.g., for [111] displacements of an atom at a step on an fcc (332) surface. Then level 1 of the cluster consists solely of this atom. Level 2 includes the first and second neighbors of the single atom in level 1. Level 3 comprises all first and second neighbors of the atoms in level 2 not already included in levels 1 and 2, etc. If an $N+1$ level cluster is generated, then recursion is performed at level N, before the 1nn + 2nn Hamiltonian reaches cluster

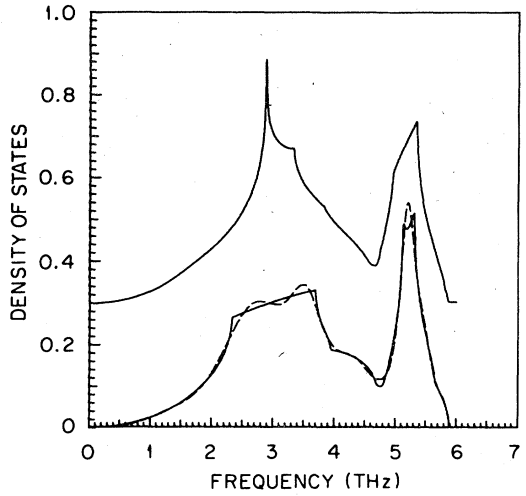

FIG. 1. Phonon densities of states for bulk Pt calculated by the Gilat-Raubenheimer (GR) and recursion methods: top—GR, six-neighbor force model of Ref. 2; bottom—GR (full line) and recursion (dashed line) results for the 1nn + 2nn force model fitted to the 90 K data in Ref. 2. All densities of states shown here and in Fig. 3 are normalized to integrate to unity.

boundary atoms in level $N+1$ that are the only atoms in the cluster with missing neighbors.

The first step in the calculations was to fit the 1nn + 2nn force model to the neutron scattering data of Dutton *et al.*[2] Reasonably good agreement with the measured dispersion curves was obtained, although forces of longer range are needed to fit all details of the spectrum. Figure 1 compares the bulk Pt density of states calculated by the Gilat-Raubenheimer method[8] for our 1nn + 2nn force model with the results of the six-neighbor model of Ref. 2. The details of the curves are somewhat different, but the major spectral features appear in the same places.

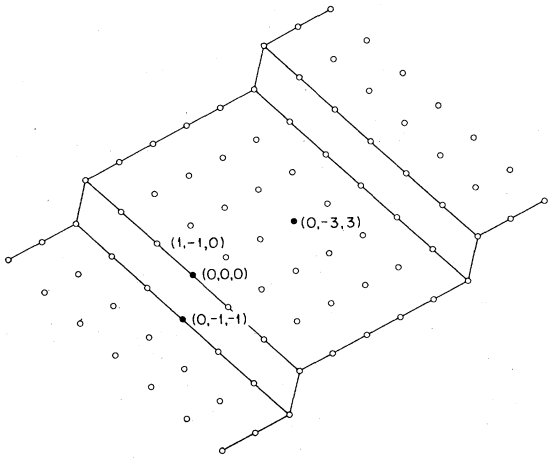

FIG. 2. Fcc (332) or $6(111)\times(11\bar{1})$ surface.

Figure 1 also shows level-9 recursion results, calculated within a level-10 cluster of 4579 atoms, for the 1nn + 2nn force model. These compare very well with the corresponding Gilat-Raubenheimer results.

For a surface as complex as the fcc (332) surface of a transition metal, it is difficult to argue what relaxation will occur and how the force constants will

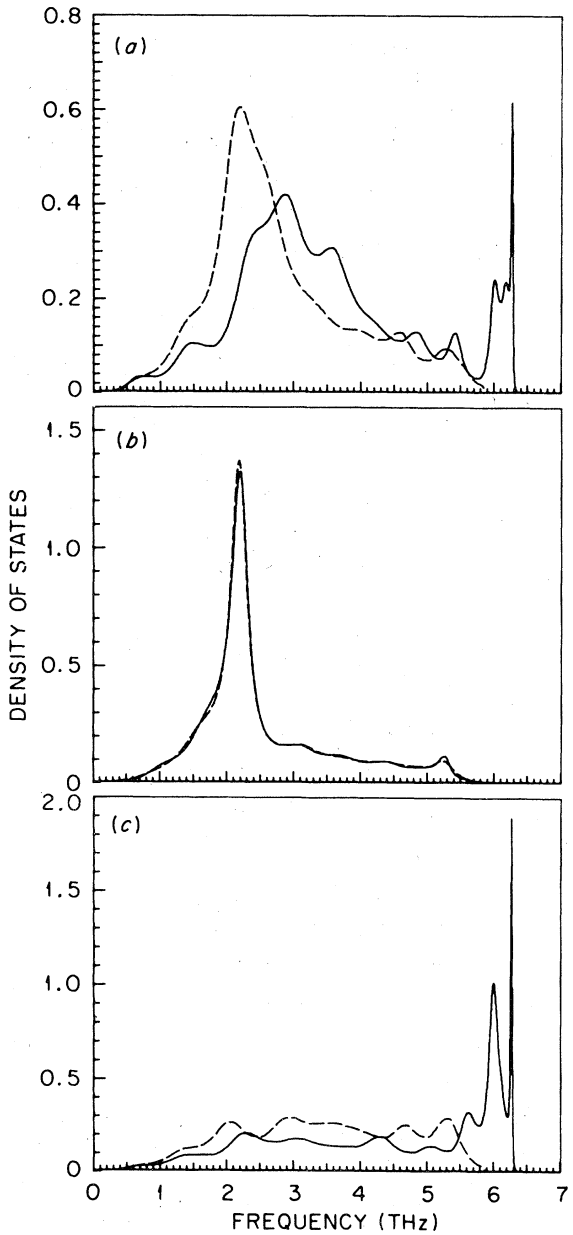

FIG. 3. Normalized densities of states for [111] vibrations at the Pt(332) surface. (a), (b), and (c) give results for edge, terrace, and corner atoms, respectively; full lines are for 1nn bond-stretching force constant increases of 15000 dynes/cm at the steps as described in the text, dashed lines for no force-constant changes.

change. We have therefore adopted a pragmatic viewpoint, focused our attention on the step edges, and set out to illustrate the magnitude of the changes needed to produce high-frequency step modes like those observed. Specifically, we allow changes only in the 1nn bond-stretching force constants for atoms at the top and bottom of the step edges, and no attempt is made to include relaxation to new equilibrium spacings $\vec{R}_0(n,n')$ near the surface.

Figure 2 shows the surface we are dealing with. The atoms at (0,0,0), (0,-1,-1), and (0,-3,3) will be referred to as edge, corner, and terrace atoms, respectively. Any atom that does not occupy a site on a surface step will be called a bulk atom.

Figure 3 compares densities of states for edge, terrace, and corner atoms for vibrations along the [111] direction, the normal to the steps. To obtain these results, recursion was performed at level 11 in level-12 clusters of 4099, 4313, and 4468 atoms, respectively. The dashed curves are those obtained with no changes in the forces at the surface except for the absence of interactions involving missing neighbors. The solid curves were calculated by assuming that all 1nn bond-stretching force constants for edge-corner, edge-bulk, and corner-bulk atom pairs were increased by about 35%, that is, by 15000 dynes/cm from the value of 41 500 in the bulk.

Figure 3 shows that no high-frequency modes occur for edge, corner, or terrace atoms in the absence of force-constant changes, although the [111] densities of states for the three atoms are quite different from one another and from the bulk results. With 1nn forces at the steps increased by $\sim 35\%$ as specified, high-frequency peaks appear for both edge and corner atoms, while essentially no change is seen in the terrace atom density of states. In fact, the results shown for the terrace atom are virtually the same as those for Pt(111) vibrations along [111] with no force-constant changes. The pronounced high-frequency structure for edge and corner atoms extends from about the top of the bulk spectrum at 24.4 meV to about 26.1 meV (5.9–6.3 THz; 1 THz=4.135 meV). The electron-loss peak observed by Ibach and Bruchmann[1] fell at 25.4 meV (6.15 THz); this was considerably broader than the calculated results in Fig. 3, but most of the experimental width appears to have been instrumental.

In the results shown for edge and corner atoms with increased forces, the high-frequency modes are nearly split off above the bulk spectrum. The one-band recursion procedure we have used gives only semiquantitative accuracy for such cases. Thus, while the overall shape of the solid curves in Figs. 3(a) and (c) is reliable, the fine structure does vary with changes in such computational parameters as the recursion level. This does not affect our conclusions; the variations in the calculated results are small with respect to the experimental resolution.

Other sets of force-constant changes at the steps yield high-frequency modes for vibrations along the step-normal direction. These can be distinguished from one another by the structure they give for [111] vibrations and by their effects for other atoms and vibrational directions. All that we have tested require substantial (30–40%) increases in the force-model parameters at the steps, but not of the magnitude (70%) inferred by Ibach and Bruchmann from one-dimensional arguments. We have also performed calculations for another stepped surface similar to the (332) or $6(111)\times(1\bar{1}1)$, namely, the (755) or $6(111)\times(100)$ and found similar results.

For these illustrative calculations, we have only considered changes in the 1nn bond-stretching force constants for atoms at the step edges and corners, because this provides a relatively simple model with few parameters that concentrates on the regions where the largest perturbations are expected. However, other force-constant changes no doubt occur at these surfaces, and we intend to explore more general phenomenological models to investigate the effects of such other changes.

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