

## Surface phonons localized at step edges

P. Knipp

*Department of Physics and The James Franck Institute, The University of Chicago, Chicago, Illinois 60637*

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The surface-phonon structure of a simple model of fcc crystal dynamics is studied. The surfaces consist of wide (111) terraces separated by periodic, monatomic steps. A new class of vibrational mode is found. In addition to being localized to the surface like normal surface phonons, these modes are also localized along the step edges.

The phonon structure of the low Miller-index (MI) surfaces [i.e., the (111), (100), and (110) surfaces] has been extensively studied theoretically and experimentally. Experimental methods usually involve either electron-energy-loss spectroscopy (EELS) (Ref. 1) or thermal helium scattering.<sup>2</sup> Theoretical methods typically use ball-and-spring models whose Hamiltonian is diagonalized by standard techniques of linear algebra.<sup>3</sup> On the other hand, studies of *high*-MI surface vibrational modes have presumably been hampered by the complicated assortment of surface phonons that exists on them, in addition to other experimental and theoretical difficulties.

This Brief Report discusses numerical results that, when properly considered, show that the phonon structure of a particular type of high-MI surface is similar than previously suggested. This type consists of low-MI "terraces," several atoms wide, broken up periodically by uninked monatomic steps. Due to the large size of the (two-dimensional) unit cell, the number of surface phonons is arbitrarily large. However, they separate naturally into two classes. Not surprisingly, the first class consists of phonons of the corresponding unstepped surface, which are reflected and transmitted by the steps. The second, novel, class consists of a few surface phonons which are localized in two dimensions, rather than just one. These "step phonons" propagate freely along the step edges, but their amplitudes decay rapidly away from the steps.

The fcc(111) surface has a (triangular) close-packed top layer of atoms and exhibits a very small set of surface phonons. However, high-MI surfaces possess a considerably more complex phonon structure,<sup>4</sup> due to the large size of their unit cells. These surfaces are obtained by slicing a single crystal at an angle which is slightly different from a low-MI crystallographic plane, and are often called "vicinal" surfaces. They are easily visualized as consisting of low-MI terraces, several atomic rows wide, broken up periodically by monatomic steps. For instance, the (332) surface is oriented 10.025° from the (111) surface and consists of (111) terraces which are roughly five rows wide and separated by (11 $\bar{1}$ ) step faces.

This paper restricts itself to uninked steps, for reasons that will become apparent later. On a (111) surface, this means that the edge of the step must lie along the (1 $\bar{1}$ 0) direction, which points from one surface atom to a nearest neighbor on the surface (Fig. 1). There exist two

possible ways of constructing such a step on a (111) surface, and they correspond to either a (11 $\bar{1}$ ) or a (001) step face (Fig. 2). The MI of such a vicinal surface is of the form  $(N N N - n)$ , where  $N \gg n$ . The number of rows of atoms in the terrace equals roughly  $2|N/n|$ . If  $n > 0$ , the crystal has (11 $\bar{1}$ ) step faces, and if  $n < 0$ , it has (001) step faces.

The main difference between the phonon structures of these vicinal surfaces and of the unstepped surface lies in the shape of their (two-dimensional) Brillouin zones (BZ). Take  $\hat{x}$  in the [1 $\bar{1}$ 0] direction (i.e., along the step),  $\hat{z}$  perpendicular to the vicinal surface (i.e., almost parallel to the [111] direction), and  $\hat{y}$  perpendicular to both of these (i.e., almost parallel to the [11 $\bar{2}$ ] direction). The vicinal surfaces are periodic in both the  $\hat{x}$  and  $\hat{y}$  directions, but the period in the latter direction considerably exceeds one atomic spacing. Hence, the BZ extends only fractions of  $1 \text{ \AA}^{-1}$  in the  $\hat{Q}_y$  direction, resembling a line segment rather than a polygon (Fig. 3). Indeed, an isolated step on an otherwise flat surface would yield only one periodic translational symmetry and a one-dimensional BZ.

The analysis of phonons in the vicinity of an isolated step differs topologically from that of an unstepped surface and is considerably more difficult. It has been solved for a simple cubic (sc) lattice whose nearest neighbors are connected by springs.<sup>5</sup> The undesirable aspects of this model are that few monatomic sc lattices exist in nature, that the resultant lattice is unstable, and that it exhibits no surface phonons. It exhibits no step phonons, either. A different system, which does exhibit edge-localized phonons, is that of a crystal where two of its semi-infinite

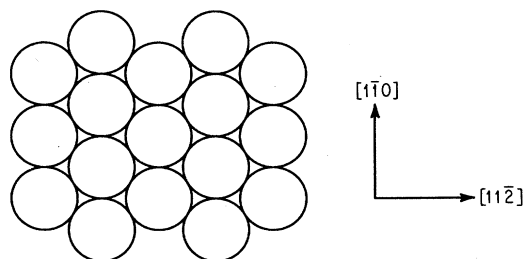


FIG. 1. fcc(111) surface atoms.

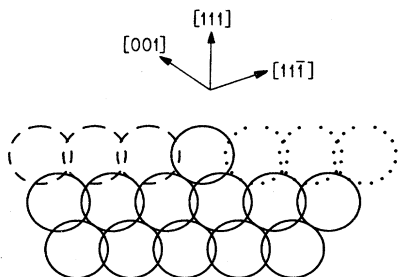


FIG. 2. Side view of a fcc(111) surface, with the  $[1\bar{1}0]$  direction pointing out of the page. Removing the dotted atoms (circles) creates a  $(11\bar{1})$  step face, whereas removing the dashed atoms creates a  $(001)$  step face.

surfaces meet at an angle to form an edge. Using elastic theory, the existence of a long-wavelength edge phonon has been proven.<sup>6</sup> However, for a surface with a monatomic step, no such long-wavelength step phonon exists. There still exists the possibility of step phonons existing at larger wave vectors ( $\bar{Q} \neq \bar{\Gamma}$ ), near the BZ boundary. This possibility depends on whether or not the step, viewed as a defect, is "strong" enough to localize a vibrational mode.<sup>7</sup>

This introduction to the theoretical aspects of step phonons uses a very basic model of lattice dynamics, consisting of atoms connected to nearest neighbors by linear springs. For this simple model, the spring constant and the crystalline geometry in the vicinity of terraces and steps are assumed to remain unchanged from their bulk values. The model has only one free parameter and works fairly well for a sizable class of monatomic fcc crystals at predicting the characteristics (i.e., frequency, polarization, and amplitude) of phonons, both in the bulk<sup>8</sup> and on the surface.<sup>9</sup> The harmonic approximation causes the quantum and classical results to coincide. Reference 4 performs the calculation for many vicinal surfaces, and much of the "data" to be discussed can be taken directly from that extensive numerical work. For this report, the method of calculation was a Green's-function technique,<sup>10</sup> slightly different from the "slab" method used in Refs. 3 and 4. The widths of the terraces were increased until the step-phonon characteristics stabilized, usually after the terraces were only a few atoms

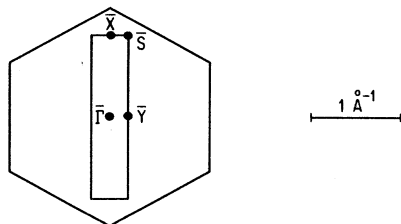


FIG. 3. BZ for fcc(111) and (332) surfaces. The scale is appropriate for Pt.

wide. Since no step phonons exist at the origin of the BZ and since surface phonons tend to become more prevalent at BZ boundaries, the calculations were performed at the point  $\bar{Q} = \bar{X}$ . At this point in the BZ, the atoms oscillate  $180^\circ$  out of phase with their nearest neighbors in the  $\hat{x}$  direction. The magnitude of  $\bar{X}$  is inversely proportional to the periodicity along the edge, which is the reason why this paper restricts itself to uninked steps.

In addition to one band of bulk phonons and one band of "ordinary" surface phonons, three step phonons appear for either type of step. The squared amplitudes of the row vibrations decay rapidly away from the steps, in both the  $\hat{y}$  and  $\hat{z}$  directions. This behavior is depicted for one of the step phonons in Fig. 4(a) and contrasts with that of bulk phonons and ordinary surface phonons, typical examples of which are depicted in Figs. 4(b) and 4(c). The polarizations of the step phonons change from row to row, but one step phonon is strictly longitudinal and the other two are strictly transverse (and perpendicular to each other) at the step edge, where the amplitudes are maximum. The characteristics of the edge phonons are summarized in Table I. The nomenclature introduced for the edge phonons is analogous to that coined for surface phonons in Ref. 3. In units of  $\sqrt{k/m}$ , where  $k$  is the spring constant and  $m$  is the atomic mass, the bulk frequency band is  $\sqrt{2} \leq \omega \leq 2\sqrt{2}$  and the (substantially narrower) surface phonon band is  $1.227 < \omega < 1.241$ . The frequency of  $E_1$  is below both bands and  $E_2$  is within the band gap. The longitudinal mode  $ME_3$  (where ME denotes mixed-edge phonon) is degenerate with the bulk band, so technically it is not a truly localized step phonon. Instead, it is a finite-lived "step resonance" whose

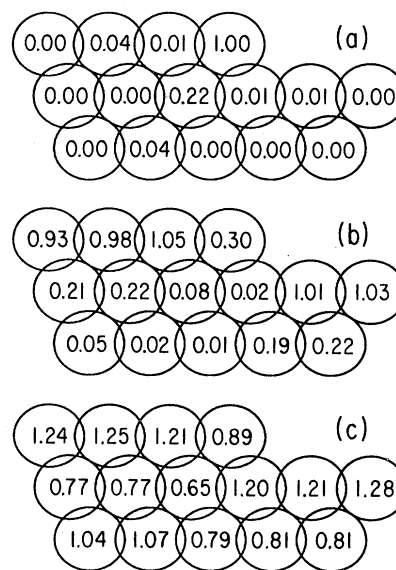


FIG. 4. Squared amplitude of vibration for rows of a (111) surface in the vicinity of a  $(11\bar{1})$  step face, for (a)  $E_1$  step phonon, (b) surface phonon, and (c) bulk phonon. The normalization is different for (a), (b), and (c), so the values should not be compared.

TABLE I. Step-phonon characteristics. The squared amplitude is normalized to unity.

Step face	Mode	Frequency [ $\times(k/m)^{1/2}$ ]	Polarization ( $T$ or $L$ )	Squared amplitude at step edge
(11 $\bar{1}$ )	$E_1$	1.21	[110] transverse	0.74
(11 $\bar{1}$ )	$E_2$	1.29	[001] transverse	0.77
(11 $\bar{1}$ )	$ME_3$	2.35	[1 $\bar{1}$ 0] longitudinal	0.57
(001)	$E_1$	1.10	[110] transverse	0.58
(001)	$E_2$	1.28	[001] transverse	0.77
(001)	$ME_3$	2.38	[1 $\bar{1}$ 0] longitudinal	0.36

lifetime exceeds the inverse of its frequency by more than 2 orders of magnitude.

A full study of the phonon structure in the vicinity of a step will be reported later. This will include dispersion relations for the step phonons throughout the (one-dimensional) BZ and the dependence of their characteristics on realistic force-constants deviations in the vicinity of terraces and steps. As stated earlier, edge-localized modes are not expected to survive in the neighborhood of  $\bar{\Gamma}$ . Instead, they will become degenerate with surface and/or bulk phonons, radiate away their amplitude into the terraces and/or the bulk, respectively, and become step resonances. A study will also be made of the step-phonon structure on a surface with (100) terraces. Preliminary investigation of the data in Refs. 4 and 11 does not reveal any such modes for the unrelaxed step on a (100) surface, when evaluated at any of the high symmetry points of the BZ.

This author is aware of only two inelastic scattering experiments that have been performed on vicinal surfaces.<sup>12,13</sup> Both were EELS experiments, were performed at  $\bar{\Gamma}$  (i.e., at specular reflection), and demonstrated evidence for vibrational modes localized (at least temporarily) at the step edge. To agree with theory, both results required a modification of the force constants in the vicinity of the step edge, a not unexpected result. The first experiment, on Pt(332), detected a mode at 205  $\text{cm}^{-1}$ , considerably higher than the maximum bulk-phonon frequency, at 190  $\text{cm}^{-1}$ . This is surprising, considering that

Rayleigh's theorem predicts that surface (and step) -phonon frequencies should fall *below* corresponding bulk-phonon frequencies.<sup>7</sup> Also, no such high-frequency modes have been seen on the Pt(111) surface. An explanation was later provided which required the use of substantially stiffened force constants in the neighborhood of a step edge.<sup>14</sup> *Ab initio* calculations of step relaxation have provided theoretical support to this model of stiffened force constants for Pt(332).<sup>15</sup> The second experiment, on TiC(310), detected a phonon whose frequency fell below that predicted for the surface phonons. By a process of elimination, the mode was determined to be localized to the step edge. To agree with theory, the force constants near the step edge had to be decreased, thereby contrasting with the Pt(332) results.

In conclusion, I report the existence and characteristics of edge-localized vibrational modes for the simplest model of fcc surface lattice dynamics. Two recent EELS observations of such step phonons proved to be sensitive to force-constant changes near edges. It appears that for Pt (a metal) the atoms "tighten" near a step, whereas for TiC (an ionic insulator) the atoms "loosen" near a step.

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