Localized adatom vibrations in Si clusters

J. L. Feldman and Efthimios Kaxiras*
Complex Systems Theory Branch, Naval Research Laboratory, Washington, D.C. 20375

X.-P. Li
Department of Physics, University of Illinois, Urbana, Illinois 61801
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We present results for the vibrational spectra of models for Si clusters. Our calculations are based on the Stillinger-Weber phenomenological potential. We find that in a 33-atom model cluster there exist localized "adatom" vibrations that are similar in character to modes of the 7×7 reconstructed Si(111) crystalline surface. The unique character of the localized adatom modes would serve as a stringent test of the cluster geometry through Raman experiments.

The chemical reactivity of Si clusters with ammonia has been observed to depend critically on the size of the cluster: certain sizes, known as "magic numbers," have chemical reactivity much lower than their immediate neighbors.[1] This can be interpreted as an indication of uncommon structural stability for the magic-number clusters. With the realization that the surface-to-volume ratio is very large (close to 1) for small clusters, Kaxiras has developed models for two of the magic-number clusters, containing 33 and 45 atoms.[2] Both models are based on the premise that close similarity of the cluster geometry to the stable reconstructions of the Si(111) surface can lead to structural stability and reduced chemical reactivity. Experiments performed under different conditions and using different reactive agents (ethylene and oxygen) failed to reveal "magic-number" behavior.[3] This has led to some controversy on whether magic numbers exist. Reactivity exeriments give only *indirect* information on the cluster structure. One possible way to resolve this controversy is through probes that unambiguously relate experimental measurements to the *structure* of a cluster. Here we propose such a test based on the vibrational properties of one of the models of Ref. 2.

Electron-energy-loss-spectroscopy (EELS) experiments have revealed high-frequency split-off and mid-frequency modes which were attributed to localized adatom vibrations on the 7×7 reconstruction of Si(111).[4] This finding is particularly interesting, because the split-off modes are quite distinct from the rest of the vibrational spectrum of Si. The model for the 33-atom cluster proposed in Ref. 2 embodies features very similar to the adatom geometry which gives rise to the split-off modes in Si(111)7×7. For this reason we study the vibrational spectrum of this model and provide an understanding of the similarities and differences between cluster and crystalline surface modes. We use the Stillinger-Weber[5] (SW) interatomic potential to solve the dynamical matrix (this choice will be justified below). We have taken the overall structure of the cluster to be fixed by the conjecture of Ref. 2, but then relaxed the coordinates with the SW potential to obtain a properly optimized geometry for the vibrational calculation. This step is essential because a geometry that is not fully relaxed with the specific force field used in the vibrational calculation would give rise to spurious imaginary frequency modes.

The SW potential has been discussed in detail and has been used extensively in the literature. Suffice it to say that it consists of two- and three-body parts, it was chosen to describe the bulk structural and melting properties of Si, and gives the diamond crystal as the minimum energy structure.[5] We recognize that the SW potential does not yield the correct surface reconstruction of Si(111) by virtue of calculations for different possible geometries.[6] However, the same calculations on the surface *vibrational* properties using the SW and another classical potential[6] give very similar results, which are qualitatively in good agreement with experiment. This suggests that the choice of the potential is not crucial for the vibrational properties we seek.

As far as experimental measurements of cluster vibrational properties are concerned, special Raman techniques[7] applied to Ge clusters have shown an overall shift of the cluster frequency spectrum toward lower frequencies in relation to the spectra of either amorphous or crystalline structures. These Raman measurements did not reveal specific spectral features, such as the adatom mode in Si(111)7×7. It is possible that these features exist but were not detected, because many different cluster sizes were present in the sample.[7] On the other hand, these features may only be present in Si clusters but not in Ge clusters.

Let us briefly review the vibrational and structural characteristics of the Si(111)7×7 surface. As mentioned above, EELS experiments[4] reveal a high-frequency mode at 570 cm^{-1} which is about 10% higher than the highest bulk mode in crystalline or amorphous Si. A mid-frequency mode was also seen in EELS experiments, with a broadened peak at about 220 cm^{-1} In a separate measurement of a pseudo-1×1 surface which may consist of 5×5, 7×7, and 9×9 structural units, a high-frequency

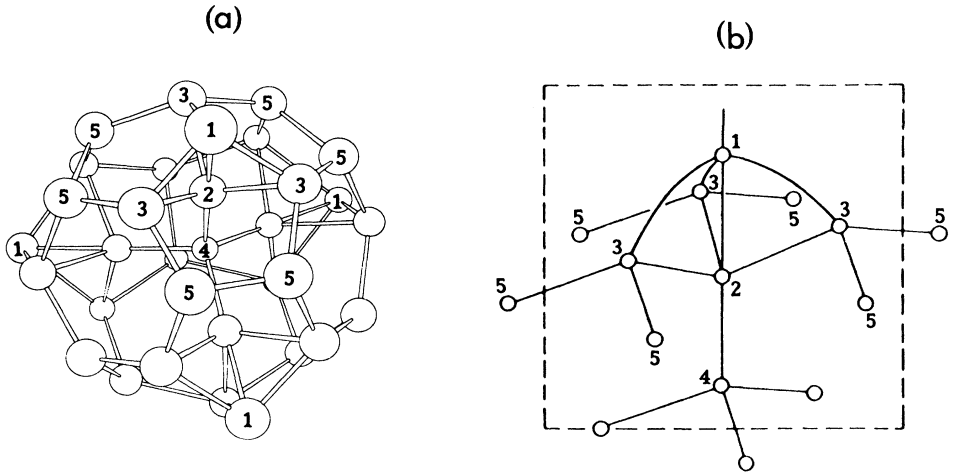

FIG. 1. (a) Perspective view of the 33-atom Si cluster. Inequivalent atoms are labeled 1–5. The labeling scheme is chosen to illustrate similarities with the crystalline surface geometry. (b) Schematic representation of a section of the Si(111)7×7 surface reconstruction, containing one adatom and its immediate neighbors. This figure is reproduced here for the convenience of the reader from Ref. 4.

feature at 555 cm^{-1} was observed instead. Both first-principles electronic structure calculations and SW classical potential calculations have been employed to support the interpretation of the split-off modes on the 7×7 surface as localized primarily at the adatom sites. These modes involve the motion of an unusually strongly bonded complex of Si atoms (hence the high frequency). The first-principles calculation was based on a finite cluster geometry which represents the local structure of the adatom in the 7×7 reconstruction, and displacements were restricted to the adatom and its immediate neighbors.[4] The classical potential calculation[6] considered the entire 7×7 unit cell of the Takayanagi[8] structure, and yielded a single split-off frequency and a mid-range frequency, both associated with large adatom motion. In the surface unit cell of the latter calculation there exist twelve adatoms and the degeneracy of the split-off modes is equal to the number of adatoms. Hence, there is an average of one high-frequency mode per adatom.

We turn next to a brief comparison of the Si(111)7×7 surface structure with the 33-atom model of Ref. 2. In this model there are four adatoms labeled 1 [see Fig. 1(a)]. Each adatom is coordinated to another atom (labeled 2), which is closer to the central atom (labeled 4), and to three other atoms (labeled 3) which are related by symmetry. Atoms 1, 2, and 4 are colinear, making atom 2 fivefold coordinated. Similarly, each adatom of the crystal surface is colinear, along a vector normal to the surface, with two other atoms [see Fig. 1(b)]. However, in the crystalline case, the innermost atoms (equivalent to atom 4 in the cluster) corresponding to different adatoms are distinct. In that sense the adatoms on the crystalline surface are almost isolated from each other, giving rise to the 12-fold degeneracy of localized split-off adatom modes. The comparison of interatomic distances obtained with the SW potential to those obtained with first-principles local-density-functional (LDF) calculations for the 33-atom cluster,[2] and with tight-binding (TB) calculations for the Si(111)7×7 surface,[9] is given in Table I. Most interatomic distances determined with the SW potential are within about 0.2 Å of the corresponding LDF and TB results. The only exception is the adatom distance to its fivefold-coordinated neighbor which is given less accurately by the SW calculation (see Table I). This

TABLE I. Interatomic distances in Å for different pairs of atoms. The labels correspond to those used in Fig. 1. In the 7×7 surface model there exist four types of adatoms, which have slightly different bonds (two sets of numbers are included for the pairs 1-2 and 1-3 of the surface geometry, giving the extrema of the adatom bond lengths).

		Pair					
		1-2	2-4	5-5	1-3	3-5	2-3
Cluster	SW	2.945	2.207	2.389	2.782	2.419	2.386
	LDF[a]	2.342	2.188	2.306	2.503	2.345	2.384
Surface	SW[b]	3.01,3.02			2.67,2.77		
	TB[c]	2.46,2.48		2.429	2.46,2.48		

[a] Reference 2.
[b] Reference 6.
[c] Reference 9.

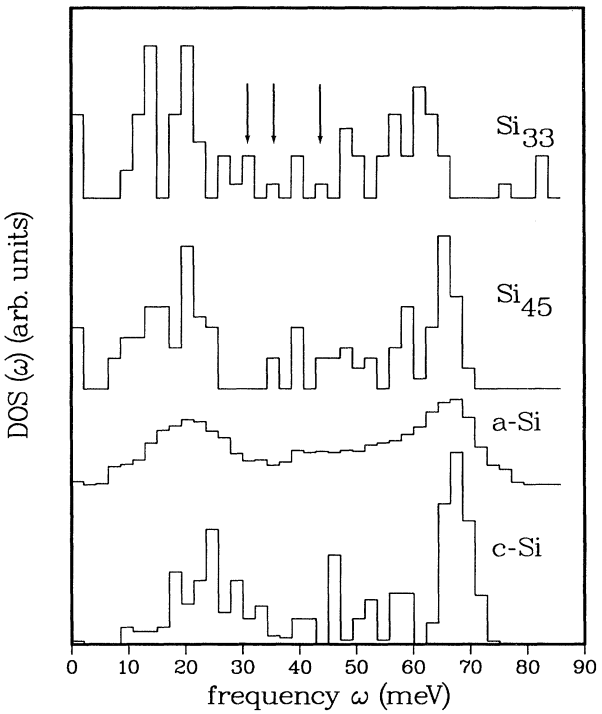

FIG. 2. The total density of states (DOS) of the Si 33-atom cluster, as a function of frequency. DOS for a model of a 45-atom Si cluster (from Ref. 2), a model of the amorphous structure (*a*-Si, from Ref. 10), and the diamond crystal (*c*-Si) are also included for comparison. The arrows indicate adatom-related acoustic modes.

is true both for the cluster and the surface geometries.

The frequency spectrum of the 33-atom cluster is given in Fig. 2. This spectrum is compared with SW-based spectra for crystalline Si (*c*-Si), an amorphous structural model (*a*-Si) (Ref. 10), and a model for the Si 45-atom cluster, also proposed by Kaxiras,[2] which corresponds to the (2×1) reconstruction of Si(111). The high-frequency split-off modes are characteristic of the 33-atom cluster and of the Si(111)7×7 surface,[6] but are not encountered in any of the other cases shown in Fig. 2.

In the cluster spectrum there are *two* distinct split-off frequencies. These correspond to a nondegenerate (symmetric) mode at 614 cm^{-1} (ω_1=76.2 meV) and a triply degenerate set at higher frequency, 665 cm^{-1} (ω_2=82.6 meV). Since there are four adatoms in the cluster there is an average of one split-off mode per adatom, just as in the case of the crystalline surface. The normalized eigenvectors, **e**, for these modes are given in Table II. We present only one of the three basis vectors for the triply degenerate modes and we give the eigenvector components for the colinear atoms (1, 2, and 4) and for two of the nonequivalent neighboring atoms (3 and 5). The largest displacements in these modes correspond to the three colinear atoms 1, 2, and 4. For both modes atom 2 (the middle atom in the linear chain) moves *against* the other two atoms (see Table II). The unusually high frequency of the split-off modes is the result of this motion and the high coordination of atom 2. In addition to the split-off modes there are also primarily "adatom" acousticlike modes (shown by arrows in Fig. 2), as observed in the case of the crystalline surface.[6] These were identified as adatom modes by an analysis of partial densities of states projected on different atomic sites, following the method of Ref. 6.

The calculated frequency of the cluster split-off modes is somewhat higher than the EELS measurement for the Si(111)7×7 surface. This can be attributed to the approximate nature of the SW potential used here. The split-off modes of Si(111)7×7 obtained with the SW potential were also found to be higher than the experimental values. The average split-off mode in the cluster ($0.25\omega_1+0.75\omega_2$=81 meV) is very close to the SW-calculated split-off mode for Si(111)7×7 (79 meV, see Ref. 6). However, it was pointed out in Ref. 2 that the bond between atoms 1 and 2 in the 33-atom cluster is stronger than the equivalent bond in a surface geometry, although we suspect the SW potential cannot reproduce such subtle differences in bonding. Based on this observation, we expect the split-off modes of the cluster to be actually *higher* in frequency than the corresponding modes of Si(111)7×7.

In summary we have obtained the vibrational frequency spectra for a model of a Si cluster containing 33 atoms. We find localized modes, associated with the motion of adatoms, similar in character to those of the 7×7 reconstructed Si(111) surface. There is a splitting of the adatom modes in the cluster, since these modes are now closely coupled to one another due to the difference

TABLE II. Polarization vectors for the symmetric (ω_1) and one of the triply degenerate (ω_2) high-frequency split-off modes of the 33-atom cluster. The projections on representative atoms are given. Atom labels are partially defined in Fig. 1. The *z* axis is along the atoms 1-2-4 direction.

	ω_1=76.2 meV (614 cm^{-1})			ω_2=82.6 meV (665 cm^{-1})		
Atom	e_x	e_y	e_z	e_x	e_y	e_z
4	0	0	0	−0.477	+0.004	−0.132
2	0	0	+0.353	+0.022	0	+0.168
1	0	0	−0.264	+0.002	0	−0.081
3	−0.133	0	+0.022	−0.053	0	+0.006
5	−0.016	−0.002	−0.004	−0.006	0	−0.001

in structure between the crystalline surface and the cluster model: In the cluster all adatoms are second neighbors to the *same* central atom, whereas on the crystalline surface adatoms are isolated from one another. The existence of high-frequency split-off modes in the 33-atom cluster could be tested by precise Raman experiments of the type reported for Ge clusters.[7] This would serve as a stringent test of the proposed cluster model.

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*Also at Sachs/Freeman Associates Inc., Landover, MD 20785.

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