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Theory of surface phonons in amorphous silica

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A new theoretical approach to studying surface vibrations in amorphous solids is applied to silicon dioxide. The method entails modeling the surface as a Bethe lattice with a dangling bond, and treating the two-dimensional nature of the surface and the surface topography as small perturbations. The theory successfully describes the nature and origin of the surface states, as well as their relative intensities as observed in recent infrared-reflectivity and Raman-scattering experiments. Both intrinsic surface effects and those caused by the presence of adsorbates are discussed.

I. INTRODUCTION

The current widespread interest in solid surfaces is due, in part, to the development of a number of new analytical tools adapted specifically to surface studies and distinct from those applied successfully in the past to studies of the bulk. While studies of surface vibrations have always had enormous potential for improving our understanding of the surface, the difficulty of the experiments has discouraged their use in surface analysis. Unlike surface electrons, surface phonons are extremely difficult to measure. Photons and neutrons, the probes traditionally used to detect phonons, are weakly interacting particles which tend to penetrate deeply into the material and sample its interior. Surface phonons represent a rich, untapped source of information about the surface which is just beginning to be exploited.[1]

Recently,[2,3] several experiments have been performed which overcome the problem of the inherent bulk sensitivity of the probe by substituting an extremely porous sample for an ordinary homogeneous one. A sufficiently large fraction of the atoms *inside* the sample are surface atoms that the surface phonon spectrum, superimposed on that of the bulk, may be detected using conventional spectroscopic techniques. The principal disadvantage of the approach is that the surfaces are poorly characterized in that they are irregular and disoriented as a consequence both of the preparation methods and of the amorphous nature of the substrate. Feasible surface-phonon-sensitive experiments are so rare, however, that these experiments are important despite the poor surface characterization.

Stimulated by the experimental situation, we have developed a theory of surface phonons in amorphous solids. The theory is constructed using methods recently developed for describing *bulk* amorphous solids,[4] and is based on the idea that the first- and second-nearest-neighbor environment of the surface atoms and the presence of an infinite substrate *alone* can account for the behavior of most of the surface phonons regardless of the surface topography. The theory is relatively simple, is realistic, and can be compared readily with experiment.

In this paper, we present a detailed discussion of the theory using silicon dioxide as a prototype. We have chosen silicon dioxide because of its technological importance and because of the relative abundance of experimental information on porous glass. The methods and ideas we discuss, however, are applicable to any amorphous material. The paper is organized as follows. In Sec. II, we discuss what problems are involved in constructing a theory of surface phonons in amorphous silica, what approximations are appropriate, and what we expect the theory to do. In Sec. III, we deal with the mathematical aspects of the theory. In Sec. IV we investigate the behavior of the surface predicted by the theory and compare this behavior with experiment. In Sec. V we study a chemisorption which drastically changes the surface behavior. In Sec. VI we summarize our results and discuss the accomplishments of the theory.

II. PRELIMINARY CONSIDERATIONS

The approach we follow in trying to understand a disordered silicon dioxide surface is motivated by our understanding of the effects of disorder in the bulk. In bonded solids, the two fundamental types of disorder, bond-angle fluctuations and topological disorder, disrupt the long-range order of the solid while leaving its local structure intact. As a consequence, the behavior of the amorphous and crystalline phases of bonded solids tend to be very similar locally.[5] Both kinds of disorder tend to broaden the crystal density of states somewhat and to perturb the character of states within the first few neighbors of an atom only slightly. In addition, topological disorder can introduce rings

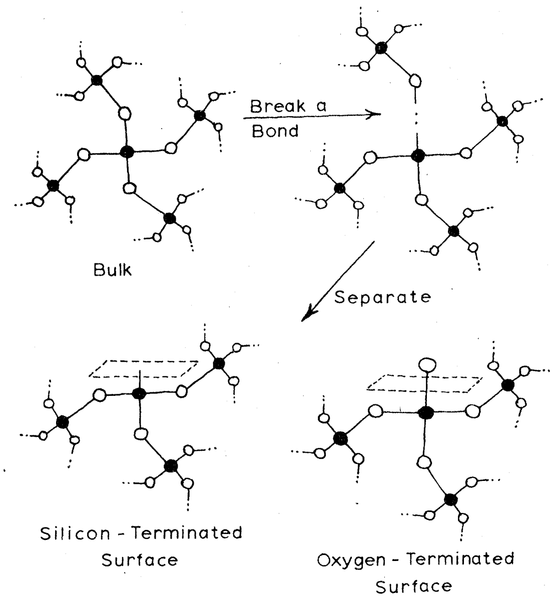

FIG. 1. Transformation of Bethe lattice from model for the bulk to model for the surface. Breaking a bond generates two fundamental kinds of surface.

of bonds of various sizes into the material whose effects can be traced to the occurrence of resonances about the rings.[5] It has recently been shown[6,7] however, that phonons in bulk amorphous silica are adequately described when the structure of the material is modeled as a Bethe lattice, a bonded network of atoms which has the same local geometry as the crystal but which has *no* rings of bonds. The Bethe lattice is effective in this function, despite the fact that it lacks the rings of bonds which any real material must have, because it is similar to the actual solid locally.

The two major problems impeding a simple view of the disordered surface are the poorly defined relationship of adjacent atomic sites on the surface and the disorder of the substrate itself. Since disorder in the substrate is essentially disorder in the bulk, it follows that the substrate can be understood, like the bulk, in terms of the bonding arrangement of the atoms locally. The approach we use to overcome the remaining problem, that of intrasurface interactions, relies on the observed[8] tendency in bonded solids for the surface effects to be highly localized. The high degree of localization causes the effect of adjacent surface sites on one another to be small, and the states induced by the presence of the surface to be characteristic of an isolated site bonded to an infinite substrate. The principal approximation of our theory is that the surface sites do not interact *at all*—that the surface can be accurately modeled as *one* site, so long as the infinity of the substrate is accounted for.

The aspect of the material with which we are primarily concerned is the nature and origin of the localized surface sites. We want to know why surface states occur, how the structure of the surface affects them, and what they tell us about the surface. In order to build a theory which is tractable and at the same time capable of describing the surface states realistically, we need approximations for both the structure and the Hamiltonian of the surface which are suited to the questions we are asking.

Because of the localization of the surface states and the established[8] relative unimportance of intrasurface interactions, we need not deal initially with the effects of surface two dimensionality. To obtain a suitable structural model for the surface, therefore, we need only break a bond in the Bethe lattice. The atom with the dangling bond becomes the site, while the structure to which it is attached becomes the substrate. The bond-breaking procedure is illustrated in Fig. 1. The scission of a bond produces two fundamental types of surface, one terminating on a silicon atom, and a similar surface with an oxygen atom attached. Since native silicon dioxide surfaces are currently thought to terminate in hydroxyl groups,[9] the oxygen-terminated surface is most likely more representative of real materials. However, both kinds of surface site should be formed when a sample is broken or cut.

The Hamiltonian appropriate for the theory is the one we have used for studying the nature and origin of phonons in the bulk.[6] The Born[10] Hamiltonian assigns to every bond a potential energy of the form

$$U = \tfrac{1}{2}\alpha|\vec{x} - \vec{y}|^2 + \tfrac{1}{2}(\beta - \alpha)|(\vec{x} - \vec{y})\cdot\hat{r}|^2, \qquad (1)$$

where $\vec{x}$ and $\vec{y}$ are the displacements of the atoms at either end of the bond and $\hat{r}$ is a unit vector pointing along the bond. α and β are bond-dependent constants. The Born Hamiltonian is the simplest one which includes both bond-bending and bond-stretching forces, and it is a nearest-neighbor force law. Its primary disadvantages are that it does not properly account for the ionicity of the atoms and that it is not rotationally invariant. While neither of these problems prevents the bulk from being described qualitatively, they do introduce up to 30% inaccuracy in the frequencies of the states.[6] A more sophisticated Hamiltonian can eliminate this inaccuracy; however, the correct Hamiltonian is not known and the physically reasonable Born Hamiltonian is the simplest one which suits our purpose. It should be emphasized that the only adjustable parameters in theory are the two which characterize the Born Hamiltonian in the bulk.

III. MANIPULATING THE BETHE LATTICE

Modeling the surface as a Bethe lattice with a broken bond has the great advantage that the solution of the bulk problem is also the solution of the surface problem. Both rely on the existence of a set of transfer matrices Φ_ν, which must be calculated before the density of states of the bulk can be obtained. As has been discussed previously,[6] the transfer matrix is basically the mechanical impedance of the atom at the base of a broken-bond Bethe lattice when the restoring forces on the atom itself are artificially maintained at their bulk values. Ordinarily, removing a neighbor diminishes these restoring forces. The transfer matrix is obtained by satisfying a self-consistency relation, which is the mathematical equivalent of requiring that bonding three broken-bond Bethe lattices to a silicon atom creates a new broken-bond Bethe lattice. The transfer matrices are used to invert the dynamical matrix and produce the vibrational Green's function of the system. The imaginary part of the diagonal Green's function matrix elements are proportional to the local densities of states of the problem.

The notation we use is the same used to discuss the bulk.[6] We again pick local coordinates for each SiO_4 tetrahedron and number the oxygen atoms 1–4. We pick a cyclic permutation σ of the four bonds and construct a 3×3 matrix S which permutes the bonds according to σ. Using S, we construct four matrices M_ν, $\nu = 1, \ldots, 4$ which describe the change of coordinates from one tetrahedron to its neighbor along the νth bond. We denote the part of the dynamical matrix connecting a silicon atom with itself by A, the part connecting the νth oxygen atom with itself by B_ν, and the part connecting these two atoms by D_ν. If we let

$$\tilde{A} = \omega^2 - A - \sum_\nu D_\nu(\omega^2 - B_\nu)^{-1} D_\nu \,, \tag{2}$$

and

$$\tilde{D}_\nu = D_\nu(\omega^2 - B_\nu)^{-1} M_\nu D_{\sigma(\nu)} \,. \tag{3}$$

The transfer matrices Φ_ν are given by

$$\Phi_\nu = \left(\tilde{A} - \sum_{\mu\neq\sigma(\nu)} \tilde{D}_\mu \Phi_\mu\right)^{-1} \tilde{D}_\nu^t \,, \tag{4}$$

and the Green's function confined to a silicon atom in the bulk by

$$G_0 = \left(\tilde{A} - \sum_\mu D_\mu \Phi_\mu\right)^{-1} . \tag{5}$$

If we define additional transfer matrices ψ_ν in the manner

$$\psi_\nu = (\omega^2 - B_\nu)^{-1}(D_\nu + M_\nu D_{\sigma(\nu)} \Phi_\nu) \,, \tag{6}$$

then we have equivalently for the Green's function confined to silicon in the bulk

$$G_0 = \left(\omega^2 - A - \sum_\nu D_\nu \psi_\nu\right)^{-1} . \tag{7}$$

To determine the analogous quantity for the silicon atom at a silicon-terminated *surface*, we first construct the reduced restoring force matrix A_0 on the surface atom

$$A_0 = -\left(\frac{m}{M}\right)^{1/2} \sum_{\nu\neq\mu} D_\nu = A + \left(\frac{m}{M}\right)^{1/2} D_\mu \,, \tag{8}$$

where m and M are the oxygen and silicon masses, respectively. μ denotes the direction of the dangling bond. We then have

$$G_0^S = \left(\omega^2 - A_0 - \sum_{\nu\neq\mu} D_\nu \psi_\nu\right)^{-1} , \tag{9}$$

for the surface Green's function submatrix.

To determine the Green's function submatrix connecting a neighbor oxygen atom with itself, we make use of the fact that the Green's function is its own transpose. If we let

$$\eta_\nu = \Phi_\nu \psi_\nu^{-1} \,, \tag{10}$$

then the Green's function confined to the oxygen neighbor in the ρth direction is given by

$$\begin{aligned} g_0^\rho &= (\omega^2 - B_\rho - M_\rho D_{\sigma(\rho)} \eta_\rho)^{-1}[1 + D_\rho(\psi_\rho G_0^S)^t] \\ &= b_\rho + \psi_\rho G_0^S \psi_\rho^t \,, \end{aligned} \tag{11}$$

where

$$b_\rho = (\omega^2 - \beta_\rho - M_\rho D_{\sigma(\rho)} \eta_\rho)^{-1} . \tag{12}$$

Similarly, the Green's function confined to the next silicon atom down is given by

$$\begin{aligned} G_0^\rho = {} & \left(\omega^2 - A - \sum_{\nu\neq\sigma(\rho)} D_\nu \psi_\nu\right)^{-1} [1 + D_{\sigma(\rho)} M^t (\eta_\rho g_0^\rho)^t] \\ & + A_\rho + \eta_\rho g_0^\rho \eta_\rho^t \,, \end{aligned} \tag{13}$$

where

$$A_\rho = \left(\omega^2 - A - \sum_{\nu\neq\sigma(\rho)} D_\nu \psi_\nu\right)^{-1} , \tag{14}$$

and so on. In this manner, the Green's function confined to a *layer* beneath the surface is generated in terms of its value on the previous layer.

If we now chemisorb an atom onto the surface, for example, an oxygen atom to form an oxygen-terminated surface, the Green's function may be propagated into the bulk exactly as before. It remains only to calculate it for the first two atoms. If we define the dynamical matrix confined to the adsorbate as B', we then construct its interaction D' with the surface silicon atom.

$$D' = -\left(\frac{m'}{M}\right)^{1/2} B' \,, \tag{15}$$

and the new restoring force matrix for the silicon atom

$$A' = A_0 - \left(\frac{m'}{M}\right)^{1/2} B' , \tag{16}$$

where m' denotes the mass of the adsorbate. We then have for the surface silicon atom

$$G_0^S = \left(\omega^2 - A' - D'(\omega^2 - B')^{-1} D' - \sum_{\nu \neq \mu} D_\nu \psi_\nu \right)^{-1} , \tag{17}$$

and for the adsorbate

$$g = (\omega^2 - B')^{-1} \{ 1 + D'[(\omega^2 - B')^{-1} D' G_0^S]^t \} . \tag{18}$$

IV. RESULTS

In Fig. 2 we show local densities of states for both a silicon-terminated and an oxygen-terminated surface. The top frame in each case refers to the surface atom, the next frame to the atom below, and so on, layer by layer into the bulk.

As we approach the silicon-terminated surface from below we see two major changes in the local density of states: a buildup of low-frequency states around 200 cm^{-1} and a sharp surface state at the upper edge of the band peaking at 450 cm^{-1}. The first effect is the consequence of the presence of acousticlike surface states. The gap from 0 to 100 cm^{-1} is a pathology of the Bethe lattice which stems from its unphysical long-range behavior. Low-frequency acoustical phonons are long-wavelength excitations which the Bethe lattice cannot describe. Short-wavelength acoustical phonons have frequencies around 100 cm^{-1} and are described correctly by the Bethe lattice. We call these vibrations acoustic*like* because the distinction between acoustical optical phonons is ill defined in a material with no periodicity. The presence of these low-frequency vibrations may also be viewed as a consequence of the reduction of the restoring forces acting on the surface silicon atom. Removing an oxygen neighbor to make the surface diminishes these forces, which causes the atom to tend to vibrate slower. The feature at 450 cm^{-1} is a genuine surface state which involves primarily vibration of the surface silicon atom. Surface relaxation increases the frequency of this state and causes it to be more distinct, particularly if it falls outside the bulk bands. Both of these effects disappear by the fourth layer into the bulk.

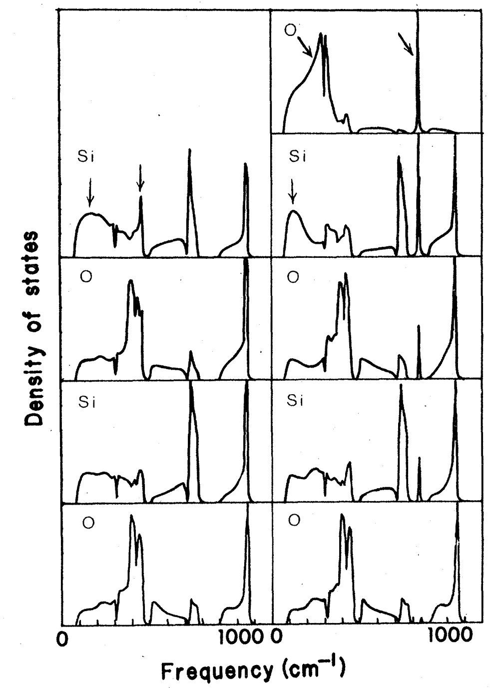

FIG. 2. Local densities of states vs frequency for silicon-terminated (left) and oxygen-terminated (right) surfaces, starting from the surface atom and proceeding layer by layer down into the bulk. The features caused by the surface are marked with arrows.

Near the oxygen-terminated surface we see three effects. Again, there is a buildup of states near 200 cm^{-1} associated with acousticlike surface vibrations. In addition, there is a sharp surface state near 850 cm^{-1} associated with bond-stretching motion of the surface oxygen atom and a band peaking at 300 cm^{-1} associated with a wagging motion of this atom. Again, the surface effects are by and large gone by the fourth atomic layer.

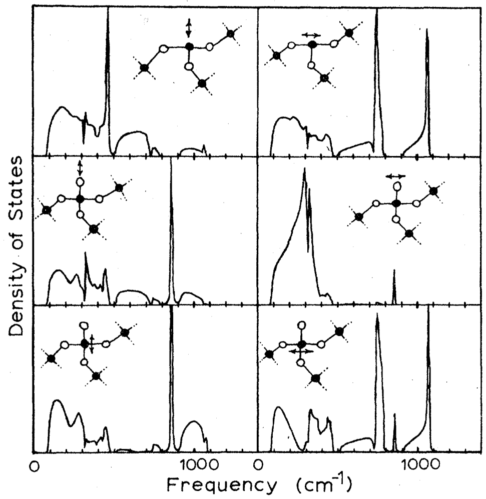

FIG. 3. Local densities of states vs frequency for silicon-terminated (top frame) and oxygen-terminated (bottom frames) surfaces broken down into components perpendicular to (left) and parallel to (right) the surface.

In Fig. 3 we have broken the surface local den-

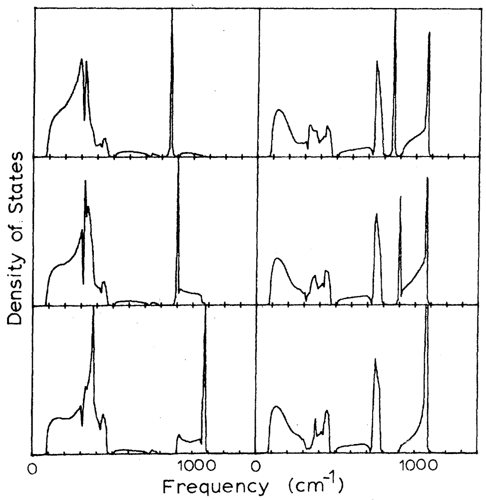

FIG. 4. Local densities of states vs frequency for oxygen-terminated surface with successively stronger relaxations. The surface oxygen local density of states is on the left, and that of the silicon atom below it is on the right. The Si-O force constants are multiplied respectively by 1.0 (top), 1.25 (middle), and 1.45 (bottom).

sities of states down into components parallel and perpendicular the surface, in order to show the extent to which the surface states are directed. We find that the surface state at 450 cm^{-1} is a motion of the surface silicon atom normal to the surface. The stretching and wagging peaks of the oxygen-terminated surface are appropriately normal and parallel to the surface, respectively, with a small amount of mixing due to the asymmetry of the SiO_4 unit caused by the silicon neighbors. The low-frequency surface states are in both kinds of surface fairly isotropic. It is interesting that the wagging state at 300 cm^{-1} involves *reduced* motion of the silicon atom immediately below the surface oxygen atom, an effect which is partially responsible for the large infrared activity of the state.

When the surface atoms are allowed to relax, we find generally that the surface states do not change substantially in character, but tend to increase in frequency. The effect of relaxing the Si-O bond at an oxygen-terminated surface is shown in Fig. 4. As the Si-O force constants at the surface are increased, the very low-frequency local densities of states remain relatively unchanged, as do the bulklike features, while the stretching and wagging features move steadily upward.

One other atomic configuration which might occur in actual silica surfaces is that of two oxygen atoms dangling into the vacuum. In Fig. 5, we show the first two local densities of states associated with such a surface. Both the stretching and wagging peaks split slightly into doublets, the stretching more so than the wagging because it couples more strongly to the silicon atom immediately below. However, the most pronounced effect is the introduction of a sharp surface state at about 100 cm^{-1} which corresponds to motion of the surface SiO_2 unity as a whole against the rest of the sub-

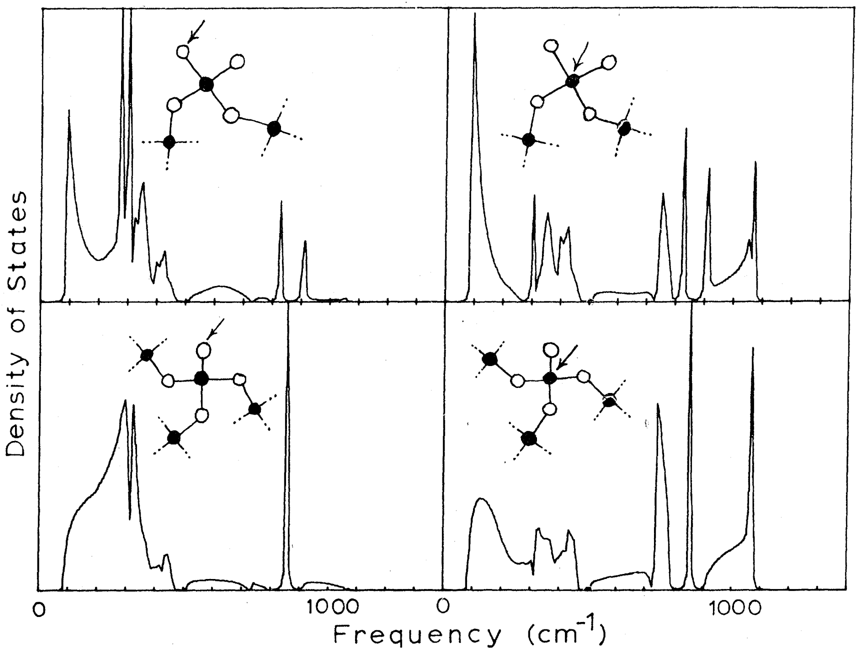

FIG. 5. Comparison of surface terminated with two oxygen atoms with one terminated with only one oxygen atom.

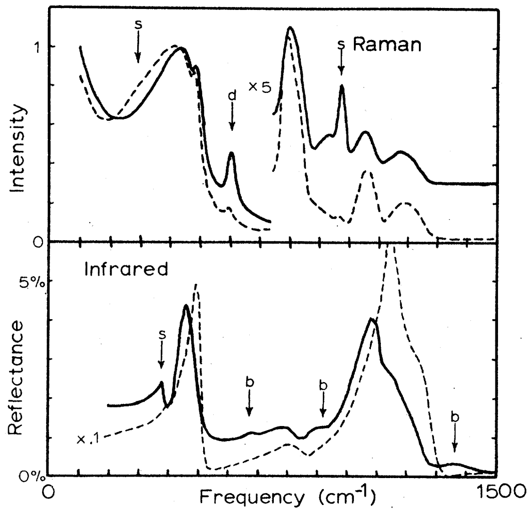

FIG. 6. Experimental infrared and Raman spectra of porous Vycor glass (solid lines) and bulk fused silica (dashed lines). The surface-induced features marked *b* are due to the presence of Boron impurities, those marked *s* are due to surface phonons, and the one marked *d* to a defect mode.

strate.

Some of the changes induced by the presence of the surface in the theory have been observed in experiment.[2,3] In Fig. 6 we show Raman and infrared reflectivity measurements performed by Murray *et al.*[3] on samples of porous Vycor glass. Porous Vycor is a spongelike form of amorphous silicon dioxide containing 28% voids roughly 40 Å in diameter. This material has surface-to-volume ratio sufficiently large that these measurements are sensitive to the surface phonons. The features in these spectra which are characteristic of the *porous* material we have marked with arrows. Those marked with *b* have been identified conclusively as being due to boron impurities in the Vycor.[3,11] Those marked *s* are due to surface phonons characteristic of a simple oxygen-terminated surface. The one marked *d* has properties consistent with what one would expect for a *silicon*-terminated surface state. We identify the peak at 980 cm^{-1} in the Raman spectrum as the oxygen-stretching vibration, the peak at 380 cm^{-1} in the infrared as the oxygen-wagging vibration, and the buildup of Raman intensity below 100 cm^{-1} at the expense of intensity at 250 cm^{-1} as a signature of the acousticlike surface states. All of the features in the theory appear at slightly higher frequencies in the experiment because of the increase of the interatomic forces at the surface caused by relaxation.

The peak at 980 cm^{-1} has been thought for some time[9] to be the stretching vibration of an hydroxyl group bound to a silicon atom. The other identifications, however, are new ones based in part on calculations we have performed to determine the theoretical *intensities* of the peaks. The model we have constructed explains why the stretching peak is visible only in the Raman effect, why the wagging peak is visible only in the infrared, and why the acousticlike surface states alter the Raman spectrum the way they do. None of these effects can be explained in terms of symmetry, and only one can be explained trivially in terms of the bonding arrangement.

To calculate an approximate infrared spectrum, we perform the sum[6]

$$\chi_{\mathrm{phonons}} \propto \mathrm{Im}\left(\sum_{ij} \vec{q}_i \overleftrightarrow{G}_{ij} \vec{q}_i\right), \tag{19}$$

where G_{ij} is the Green's function submatrix connecting atoms i and j and q_i is the change on the ith atom. Following Kleinman and Spitzer,[12] we let q_i be a tensor whose value depends on the configuration of bonds around the atom. If $\vec{r}_\mu$ is the unit vector pointing away from the atom along the μth bond, then the effective charge tensor is given by

$$\overleftrightarrow{q} = \alpha I + \beta \sum_\mu \vec{r}_\mu \otimes \vec{r}_\mu , \tag{20}$$

where α and β are constants fitted to the infrared activity of the bulk. Because the surface atom is missing a bond, its effective charge can be different by this mechanism than that of a similar atom in the bulk. We treat the oxygen atom at an oxygen-terminated surface as though it were unbonded on one side, even though in practice it is bonded to a hydrogen atom. The approximation that it is unbonded is appropriate in this case because the O-H bond is essentially rigid at these low frequencies.

The Raman intensity is similarly approximated by[6]

$$\text{Intensity} \propto \mathrm{Im}\left(\sum_{ij} (\nabla\alpha_i) G_{ij} (\nabla\alpha_j)\right), \tag{21}$$

where $\nabla\alpha_i$ denotes the derivative of the polarizability of the material with respect to displacement of the ith atom. For $\nabla\alpha_i$ we again follow Kleinman and Spitzer[12] and adopt a mechanism in which the polarizability increases when bonds are compressed. If $\vec{r}_\mu$ denotes the unit vector pointing away from the atom along the μth bond, then

$$\nabla\alpha \propto \sum_\mu \vec{r}_\mu . \tag{22}$$

By this mechanism the silicon atoms are invisible in the Raman effect in the bulk because the bond unit vectors sum to zero. However, at a silicon-terminated surface, the surface silicon atom does

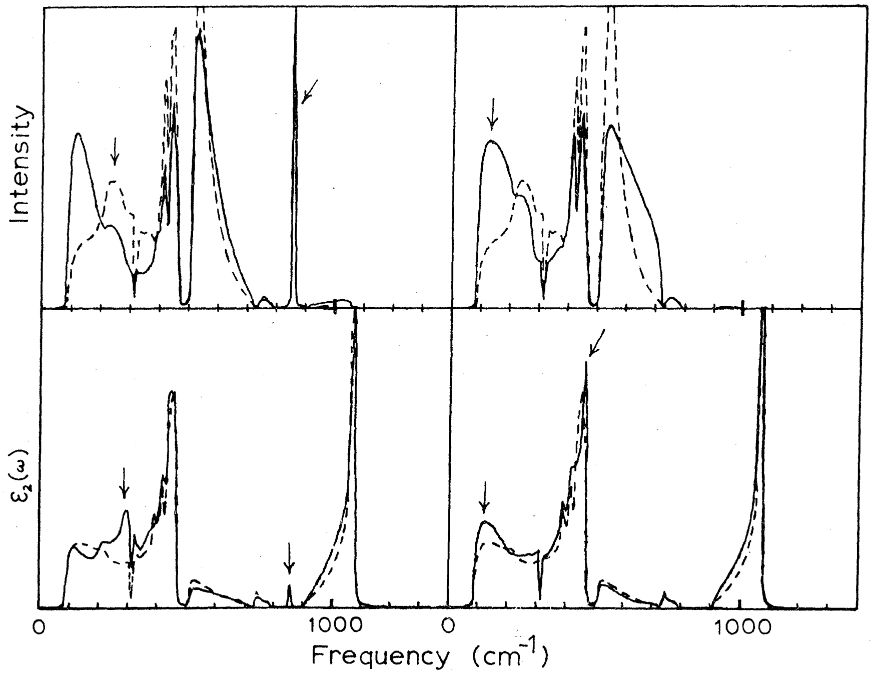

FIG. 7. Approximate Raman (top) and infrared (bottom) spectra calculated for an oxygen-terminated (left) and a silicon-terminated (right) surface. The dashed lines refer to the same calculation performed for a five-atom cluster in the bulk. Arrows indicate surface-induced features.

interact.

Using these mechanisms, we have calculated approximate infrared and Raman spectra for both a silicon-terminated and an oxygen-terminated surface. These are compared with identical calculations performed for the bulk in Fig. 7. As with the bulk,[6] we restrict the sums (19) and (21) to a small cluster of atoms at the surface, the size of which is limited by the extent to which the Bethe lattice structure approximates that of the actual solid. Because the surface states are confined to the first few atomic layers, we found it suitable to restrict the sums to an SiO_4 unit, except in the case of the silicon-terminated surface, where an SiO_3 unit was used. Each spectrum has been renormalized by the number of atoms in the cluster, so that its integral, weighted by ω, is 1.

In the theoretical Raman spectra, we see that both kinds of surface tend to increase the very low frequency signal associated with the acousticlike vibrations. The oxygen-stretching peak is pronounced in the spectrum of the oxygen-terminated surface, while the wagging peak is not. This is easily understood from the point of view that only the stretching vibration compresses the bond. However, the wagging peak is additionally suppressed by the tendency of the silicon atom immediately below it to sit still at 300 cm^{-1}. The surface state at 450 cm^{-1} in the silicon-terminated surface is *not* enhanced in the Raman effect. For this reason we believe that silicon-terminated surfaces do not produce the peak labeled *d* in the experimental Raman spectrum. However, we believe the two are intimately related. Since the surface site is in our model identical to a broken-bond defect, the Raman calculation indicates that a silicon atom with a dangling bond is probably not the cause of the peak, as has been proposed.[13] If two such defects are bonded together to form a Si-Si defect, however, there arises a defect state near the proper frequency which *derives* from this surface state. The Raman scattering from this defect could be quite large if the polarizability derivative of the Si-Si bond were sufficiently large, and the state would be invisible in the infrared because of symmetry.

In the theoretical infrared spectrum, we see a strong enhancement of the oxygen-wagging vibration and a complementary reduction of the stretching peak. If the surface oxygen atom were considered by itself, both of these vibrations would be infrared active. The cooperative motion of the substrate atoms, however, in conjunction with the particular effective charge tensors used, causes the stretching peak to be suppressed. The silicon-terminated surface has little effect on the infrared spectrum. There is a slight enhancement of ϵ_2 near the surface state at 450 cm^{-1}, but the enhancement is probably too small to be observed in experiment. The enhancement of the low-frequency surface states in the infrared is again a cluster effect.

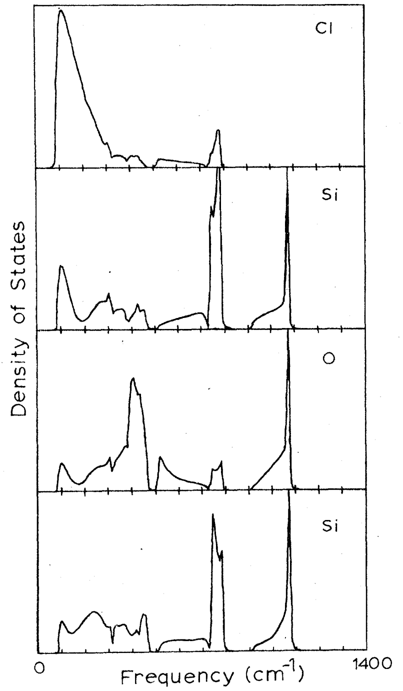

FIG. 8. Local densities of states versus frequency for a chlorinated silica surface starting from the surface atom (top) and proceeding layer by layer down into the bulk.

V. CHLORINE CHEMISORPTION

Since we have found the model to be completely consistent with existing experimental information about silicon dioxide surface, we may use it to investigate the effects of chemical impurities on the surface. In Fig. 8 we show the result of bonding a chlorine atom onto a silicon-terminated surface, the situation which is thought[14] to prevail when porous glass is chlorinated. The force constants connecting the chlorine atom to the surface silicon atom are taken to be the same as those connecting oxygen to silicon. The force constants are a little too large, the bending constant more so than the stretching constant, but the amount is not significant, especially in light of relaxation effects. As with an oxygen-terminated surface, we see stretching and wagging states of the surface atom. However, because of the greater mass of the chlorine atom, the mixing of these states into the bulk bands is very pronounced. The wagging vibration is now found to have merged into the acousticlike bands and to be *no longer distinguishable* from them. The stretching vibration moves downward only as far as the top of the siliconlike bands at 750 cm^{-1}, and becomes very siliconlike. This calculation indicates that the adsorbate rather than the substrate, is tending to remain stationary. The stretching vibration is no longer an adsorbate motion but one of the silicon atom underneath it. This explains why the vibration is stuck at the top of the silicon-like bands at 750 cm^{-1}. *Increase of the adsorbate mass cannot move the stretching vibration below these bands.* Of course, if the bonding is weakened, this state will soften and eventually become the 450-cm^{-1} surface state of the silicon-terminated surface. However, we believe a fully chlorinated surface should show up in Vycor glass as an augmentation of the 800-cm^{-1} bulk band in the Raman effect, perhaps a similar effect in the infrared, and a complete disappearance of the 980- and 380-cm^{-1} hydroxyl-induced surface states.

VI. SUMMARY

We have presented a theory of surface phonons in amorphous silicon dioxide based on the use of the Bethe lattice as a model for the structure of the amorphous material. The theory treats the surface as an isolated atomic site which is bonded to the Bethe lattice everywhere the site ordinarily bonds to the substrate. The theory is motivated by the observed tendency in bonded solids for the two-dimensional nature of the surface to be less important, in most respects, than the bonding arrangement near the surface and the infinity of the substrate. We have constructed our model using a simple nearest-neighbor Hamiltonian containing two parameters which are fit to the bulk. We have used it successfully to interpret and clarify infrared and Raman scattering experiments performed on samples of porous Vycor glass. We have also predicted the effects on the Raman and infrared spectra of chlorinating the glass.

The most important accomplishment of the theory is the demonstration that the potentially complicated surface of an amorphous solid can be understood almost completely in terms of the bonding on and near a surface site. We have isolated the various effects of the substrate, identified the most important one, namely, the substrate's infinity, and found a way of including it in the model so that the important *local* effects can be identified. Since the tendency of the surface states to be localized at the surface is a property of all bonded solids, crystal and amorphous, the theory and the simplifications inherent in it are also applicable to crystal surfaces. Accordingly, the methods discussed in this paper can be applied to an enormous variety of materials. We feel that the approach holds great promise for clarifying some of the fundamental problems of surface physics.

ACKNOWLEDGMENTS

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