diffusion via these vacancies, and since there is little or no increase in dislocation density, there is also little increase in the attenuation.

In conclusion, we have investigated the plastic deformation of bcc solid ^{4}He, and we have found its behavior to be distinctly different from that of the hcp phase. The results are consistent with a process of rapid diffusion of matter in bcc crystals, possibly via a large concentration of highly mobile vacancies, although we cannot, at this point, determine if this process is classical or quantum mechanical in nature.

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[19] There is some debate in the literature concerning the extent of the bcc phase on a P-T phase diagram (Ref. 10). Several bcc crystals were grown and slowly cooled until a sudden increase in attenuation, followed by the appearance of a new set of echoes, indicated the bcc-hcp transition. Our results for the phase boundary are in good agreement with those of Vignos and Fairbank (Ref. 8) and Grilly and Mills (Ref. 18).

Intrinsic Surface Phonons in Porous Glass

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Raman scattering and infrared reflectivity measurements have been performed on samples of porous Vycor glass. Three features in the spectra are due to intrinsic surface phonons. This identification is supported by a simple new theory for the surface.

Recently, there has been considerable interest in surfaces, particularly in their electronic properties. Very little attention has been given to surface vibrations, however, because it is virtually impossible to detect surface phonons in most samples using conventional phonon-sensitive spectroscopic techniques. A promising method[1] of overcoming this problem is to perform low-energy electron-energy-loss spectroscopy on the surface. Measurements of this kind are scarce, however, because of the extreme difficulty of the experiment. In this Letter we describe a new method for studying surface phonons. Briefly, the method involves performing conventional phonon-sensitive experiments on extremely porous samples, relying on the extensive internal surface area to counteract the inherent bulk sensitivity of the probe. Using this method, we have observed several intrinsic surface phonons in porous Vycor glass and have identified their nature and origin using a simple theory based on the cluster-Bethe-lattice method.[2]

Porous Vycor glass is a form of amorphous silicon dioxide containing a dense interconnected network of voids roughly 40 Å in diameter.[3] The voids comprise 28% of the sample volume and generate an internal surface area of about 250 m^2/g. Approximately one atom in ten is a surface atom. The glass matrix is 96% SiO_2 with the remainder chiefly B_2O_3.

The samples (Corning code No. 7930) were supplied by Corning Glass Works. They were prepared by boiling repeatedly in solutions of 30% hydrogen peroxide, rinsing in deionized distilled water, and baking at 600°C in flowing oxygen gas for about 10 h. They were cooled to room temperature in high-purity nitrogen gas and transferred in a nitrogen atmosphere to the prebaked ultrahigh-vacuum system. Data were taken at 10^{-8} Torr and room temperature.

Raman spectra were obtained with a conventional 90° geometry using the 5145-Å line of a CR52 argon-ion laser, SPEX 1401 double-grating monochromator, FW130 cooled photomultiplier tube, and photon counting techniques. The reflectivity spectra were taken using a Digilab FST-14 Fourier-transform spectrometer and normalized to the reflectance of a freshly evaporated gold mirror. The instrumental widths [full width at half-maximum (FWHM)] used were 4 cm^{-1} for the Raman and 8 cm^{-1} for the infrared.

In Fig. 1 we show the Raman spectrum and infrared reflectivity of porous Vycor glass (solid lines) as contrasted with the corresponding measurements on bulk fused silica (dashed lines). The Raman intensities of the bulk band at 440 cm^{-1} are proportional to the densities of the two samples and have been normalized to be equal. The background in the Vycor Raman trace is caused by a very broad, flat spectrum of fluorescence. The Raman spectrum of Vycor is similar to that obtained by Buechler and Turkevich.[4] The infrared spectrum of Vycor represents the first measurement performed in the intrinsic phonon region. Both the relatively small overall reflectivity peaks relative to those of fused silica are due to the reduced density of the Vycor sample.

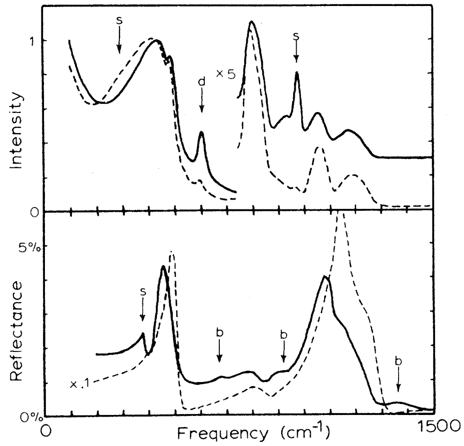

FIG. 1. Experimental spectra of porous Vycor (solid line) and vitreous silica (dashed line). Top, Raman intensities normalized to 1 at 440 cm^{-1}; bottom, absolute infrared-reflectance measurements. Typical error bars are comparable to the line thickness for the traces with the exception of the low-frequency (< 450 cm^{-1}) region in the reflectance measurements, where they are ± 0.3%. Arrows designate important changes in the spectra as discussed in the text.

In Fig. 1 we have marked with arrows seven features in the Vycor spectra which distinguish them from the corresponding spectra of fused silica. The three of these labeled *b* in Fig. 1, occurring at 670, 930, and 1380 cm^{-1}, have been observed previously in borosilicate glasses[5] and are directly attributable to the presence of boron impurities. The peak labeled *d*, occurring at 606 cm^{-1} in the Raman spectrum, is presently believed to be a defect mode.[6] The features labeled *s* we believe to be due to surface phonons. We find they do not appear in the Raman spectra of either preleached or condensed Vycor glass. The peak at 980 cm^{-1} in the Raman spectrum is associated with the Si-O stretching vibration of a surface hydroxyl group bonded to a silicon atom.[7] It is presently accepted[8] that silicon dioxide surfaces terminate in a layer of hydroxyl groups. The peak in the reflectivity at 380 cm^{-1} is due to the wagging vibration of this surface hydroxyl group. The shift of Raman intensity to very low frequencies near 300 cm^{-1} is due to a band of surface acousticlike vibrations.

Our identification of stretching and wagging vibrations in these spectra tacitly assumes the validity of a model for the surface in which the surface hydroxyl group is bonded to a massive, structureless object. While this point of view is approximately valid, there are three important aspects of the experimental results which cannot be explained in terms of such a model. First, the simple model assumes no other moleculelike vibrations of this kind, for example, vibration of the Si-OH unit against the rest of the substrate, exist. These vibrations are absent in the experiment and this indicates that there is an identifiable property of the surface which is forbidding them. Second, the stretching and wagging peaks are relatively narrow. In light of the composition of the substrate, it is not clear that these vibrations should be localized to the surface at all, nor is it clear that their frequencies should be sufficiently well defined for them to be observed in the experiment as peaks. Third, it is hard to understand why the oxygen-stretching peak is invisible in the infrared. Since the solid is amorphous, there is no symmetry, and thus no selection rule preventing a Raman-active vibration from being infrared active as well. One might argue that the infrared matrix element of the stretching mode is small; yet the peak at 380 cm^{-1}, which is almost certainly the wagging vibration, interacts with the *same* matrix element as the stretching mode in the elementary model, basically the charge on the hydroxyl group. It would appear, therefore, that we are observing not an hydroxyl group vibrating against a massive object, but rather a complicated cooperative vibration of the surface as a whole.

It has recently been shown[9] that phonons in bulk amorphous silicon dioxide are reasonably well described by a model in which the interactions are approximated by a nearest-neighbor Born force law and the structure is approximated by a Bethe lattice. A Bethe lattice is an infinite, bonded network of atoms which contains no rings of bonds and is an ideal model for the substrate in these experiments. By bonding the Bethe lattice to a surface atom, we can simulate the effect of the substrate on this atom while simultaneously taking into account the disorder of the material.[9] The principal disadvantage of the approach is that the force law with which the Bethe lattice is constructed is very primitive and incapable of providing the exact frequencies of the surface states. However, the loss of precision is counterbalanced by the gain of simplicity and the qualitative picture with which we interpret the experiments is correct. We should emphasize that there are no adjustable parameters in the theory.

In Fig. 2 we show the results of a numerical calculation performed for two types of surface as modeled by the Bethe lattice. The left column refers to a silicon-terminated surface, the right column to the same surface with an oxygen atom (hydroxyl group) bonded onto it. Plotted against frequency are local densities of states, starting with the surface atom and proceeding layer-by-layer down into the bulk.

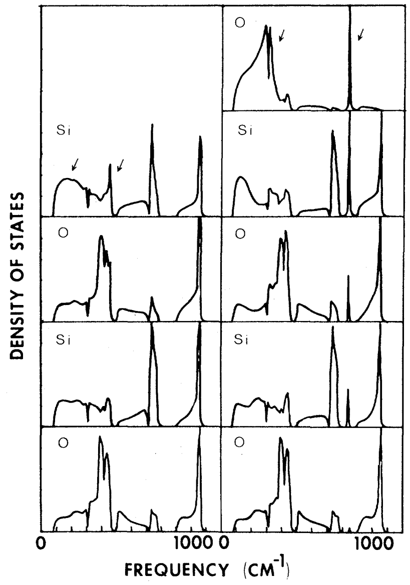

FIG. 2. Theoretical local densities of states vs frequency for silicon-terminated (left) and oxygen-terminated (right) surfaces, starting from the surface atom (top) and proceeding layer-by-layer into the bulk. The arrows indicate surface-induced features.

Near the silicon-terminated surface we see two effects. As we proceed toward the surface there is an increase in the low-frequency density of states around 100 cm^{-1} and the appearance of a sharp surface state at the upper edge of the band peaking at 450 cm^{-1}. The former corresponds to the presence of acousticlike surface phonons and the latter corresponds to motion of the surface silicon atom normal to the plane of the surface.

Near the oxygen-terminated surface we find three effects. There is the sharp surface state at 850 cm^{-1} associated with bond-stretching motion of the surface oxygen atom, there is a low-frequency band of surface states peaking at 300 cm^{-1} associated with the wagging motion of the surface oxygen atom, and again there is an enhancement of the low-frequency density of states.

The theory thus yields four surface-induced features: an oxygen-stretching state at high frequency, a siliconlike state at intermediate frequency, an oxygen-wagging state at low frequency, and a general migration of states to lower energies near and below 200 cm^{-1}. Note that the surface-induced features in the theory have the same relative positions as the features marked *s* and *d* in the experimental spectra.

In order to determine how the four surface-induced features in the theory should manifest themselves in the experiments, we have calculated approximate infrared and Raman spectra using a cluster technique that is described elsewhere.[9] Briefly, the method involves allowing the Bethe lattice surface to interact with the radiation only through the surface atom and its first- and second-nearest neighbors. This calculation is very crude, but it tells us quickly whether or not the surface states are infrared or Raman active. The mechanism by which the radiation interacts with the solid is in each case the one appropriate for quartz.[9] For the infrared calculation, we assign Kleinman and Spitzer's[10] tensor effective charges to the atoms, while in the Raman calculation we assume that the polarizability of the material increases when bonds are compressed.

When such a calculation is performed for the silicon-terminated surface, it is found that the siliconlike surface state, which nearly coincides with the peak labeled *d* in Fig. 1, is very infrared active and hardly Raman active at all. For this reason, we believe that this peak is *not* due to the presence of silicon-terminated surfaces, but to a increased number of structural defects in the glass. It has been suggested[6] that the defect responsible for this peak is a silicon atom with a dangling bond. Since the silicon-terminated surface we have constructed is similar in many respects to a dangling-bond defect, our calculations also suggest that this peak is not a dangling-bond defect either. We have found, however, that a state at nearly the same frequency arises when two dangling-bond defects are bonded together to form a Si-Si defect. This state would have the correct Raman and infrared intensities since it is approximately symmetric under inversion.

In Fig. 3, we show the results of performing this calculation for an oxygen-terminated surface. If we compare Figs. 1 and 3, we see immediately that the oxygen-stretching peak is correctly suppressed in the theoretical infrared spectrum, as is the oxygen-wagging peak in the Raman effect. We also see in the theory the enhancement of the low-frequency states observed in the experimental Raman spectrum. This latter effect shows that the disorder in the sample is relaxing the $k = 0$ selection rule[11] and allowing relatively high-frequency "acoustic" phonons to be observed in the Raman effect. The oxygen-wagging state is not seen in the Raman effect because only vibrations which compress bonds are visible. The oxygen-stretching peak is invisible in the infrared because the sympathetic motion of the substrate atoms on and near the surface causes the dipole moment of the *entire state* to be small. Other factors which are important in the effect are the particular effective charges appropriate for silicon dioxide and the tendency of the oxygen-wagging state to mix strongly with the bulk states. This latter effect causes the oxygen-wagging state to appear inordinately large in the infrared.

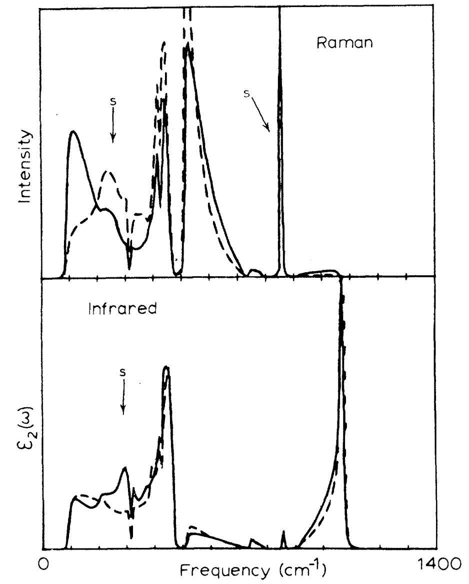

FIG. 3. Theoretical Raman and infrared spectra for an oxygen-terminated surface (solid line) and bulk (dashed line). The features indicated by arrows are surface derived.

The study of a very porous sample has enabled us to observe intrinsic surface phonons. The approach we have followed is applicable to virtually any porous material, and for this reason we believe it to have great potential for elucidating the nature of surfaces.

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Soft-Mode Behavior in the Phonon Dispersion of YS

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We have measured the phonon dispersion of the superconducting transition-metal chalcogenide YS by inelastic neutron scattering. The longitudinal branches exhibit well-defined soft-mode regions that closely resemble those found in the structural and electronic analogs NbC and TiN. In contrast, no softening is observed in the transverse-acoustic branches. The experimental dispersion curves are well reproduced by calculations based on a double-shell model.

The discovery[1] of anomalies in the phonon dispersion of superconducting transition-metal (TM) carbides of group Vb has instigated both intensive theoretical efforts[2-4] to elucidate their origin and a search for the occurrence of similar anomalies in related compounds. The correlation between soft-mode behavior and high-temperature superconductivity in NbC and TaC has been investigated[3,4] by theories aiming at a microscopic description of the electron-phonon exchange interaction. Recently, soft-mode regions have been observed[5] in the acoustic branches of the phonon dispersion of TiN. This finding indicates that the rigid-band picture is appropriate for the electronic band structure of TM carbides and nitrides with nine valence electrons per molecule.

The monochalcogenides of the TM's of group IIIb are related in many of their physical properties to the IVb nitrides and Vb carbides. Just like these, they crystallize in the rock-salt structure and possess 9 valence electrons per molecule. They are also superconducting; however, their transition temperatures are generally lower than those of the carbides and nitrides.

In view of the established correlation between superconductivity and phonon anomalies in these compounds, the question arose whether the phonon spectra of the IIIb chalcogenides should exhibit soft-mode regions—as suggested by the rigid-band model—or whether the decrease of their T_c's should be associated with the disappearance of the phonon anomalies.

In this Letter we report on measurements of the phonon dispersion relations of YS. We have found that phonon anomalies exist in the longitudinal acoustic branches, similar to those observed in the IVb nitrides and Vb carbides, whereas they are completely absent in the transverse acoustic branches. Thus our results provide a sensitive test for the validity both of model theo-