

## Pressure tuning of localized and extended vibrational modes in Si:O

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Interstitial oxygen in silicon (Si:O) is a model system for the study of vibrational modes in semiconductors. Hydrostatic pressure has been used to probe the vibrational properties of this defect. In this paper, the results of infrared (IR) spectroscopy experiments on Si:<sup>16</sup>O and Si:<sup>18</sup>O are reviewed. As pressure is applied, the oxygen atom buckles outward. This structural change results in a qualitative change in low-frequency vibrational motion in the [111] plane, as the system transforms from a harmonic oscillator to a rotor. A particularly interesting phenomenon occurs when the Si:<sup>18</sup>O local vibrational mode (LVM) approaches the two-phonon continuum. First, the LVM exhibits an avoided crossing with certain combination modes of the defect. Second, when the LVM enters the two-phonon continuum, the linewidth abruptly broadens, due to a decrease in the lifetime.

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### 1 Introduction

Local vibrational modes (LVMs) are vibrational modes of defects in solids that are localized in real space and frequency space [1]. If the vibrational frequency of an impurity in a semiconductor lies above the maximum phonon frequency, then the mode can only decay via the emission of two or more phonons. In the harmonic approximation, such modes would live forever. Anharmonic coupling between LVMs and lattice phonons results in finite lifetimes, which are typically seen indirectly as linewidth broadening. Recent experiments involving high pressures [2] and ultrafast spectroscopy [3] have provided new information about the coupling between LVMs and extended lattice phonons.

In this paper, high-pressure experiments involving the infrared (IR) spectroscopy of interstitial oxygen in silicon (Si:O) are reviewed. Interested readers are directed to the papers of McCluskey and Haller [4] and Hsu, McCluskey, and Lindstrom [5], which describe the experiments and theoretical modelling in detail. In addition, a review of LVMs in semiconductors, including Si:O, is given in Ref. [6].

In our studies, we have investigated oxygen in silicon as a model “laboratory” for the study of local-extended mode interactions. In addition to the fundamental science, oxygen is one of the most omnipresent and technologically important impurities found in Czochralski-grown silicon [7]. In as-grown crystals, oxygen occurs principally as an interstitial defect. The oxygen atom is bound to two nearest-neighbor silicon atoms and is found in the bond-centered position. When pressure is applied, the Si–O–Si quasimolecule buckles [4]. As the oxygen atom moves outward (Fig. 1), the motion in the [111] plane transforms from vibrational to rotational.

The LVMs of interstitial oxygen have been measured extensively over the past half century, and have been successfully modeled by a range of theoretical methods [6]. The antisymmetric *stretch* mode has a frequency of 1136 cm<sup>-1</sup> and corresponds to the oscillation of an <sup>16</sup>O atom along the [111] direction. The

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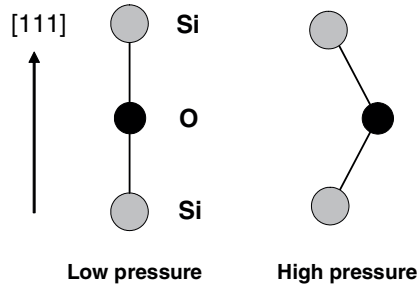


Fig. 1 Buckling of the Si:O defect under pressure.

*transverse* mode has a very low frequency ( $30\text{ cm}^{-1}$ ) and corresponds to the oscillation of the oxygen atom in the [111] plane. The *resonant* mode of  $^{16}\text{O}$  has a frequency of  $517\text{ cm}^{-1}$ , and it involves the transverse motion of the neighboring silicon atoms. Unlike the stretch mode, the resonant mode is extended spatially, with many neighboring silicon atoms participating in the vibration.

Using hydrostatic pressure and IR spectroscopy, we brought the stretch mode of  $^{18}\text{O}$  in silicon into resonance with a second harmonic of the  $^{18}\text{O}$  resonant mode [5]. The resonant interaction results in an avoided crossing between the modes. In addition to this anti-crossing behavior, the linewidth abruptly increases, due to a dramatic decrease in lifetime as the LVM enters the two-phonon continuum. A model of the interaction between these modes produced excellent agreement with the experimentally observed frequencies and linewidths.

## 2 Experimental approach

Hydrostatic pressures were generated with either piston-cylinder or Merrill–Bassett diamond-anvil cells with type IIA diamonds, which are transparent in the IR spectral range of interest. Czochralski-grown silicon samples, with oxygen concentrations of approximately  $10^{18}\text{ cm}^{-3}$ , were used for the Si: $^{16}\text{O}$  studies. The natural abundances of oxygen isotopes are as follows:  $^{16}\text{O} = 99.762\%$ ,  $^{17}\text{O} = 0.038\%$ , and  $^{18}\text{O} = 0.2\%$ . For the Si: $^{18}\text{O}$  studies, samples with isotopically enriched oxygen-18 were used.

Samples were polished to thicknesses of  $\sim 50\text{ }\mu\text{m}$  and placed in a  $340\text{ }\mu\text{m}$  hole drilled in a pre-indented, stainless steel gasket. Liquid nitrogen was used as the pressure-transmitting fluid. The liquid nitrogen contained trace quantities of  $\text{CO}_2$ , which gave rise to IR absorption peaks near  $2350\text{ cm}^{-1}$ . The frequency of that mode is very sensitive to pressure [8], so it was used as an *in situ* pressure calibration. The diamond-anvil cell was placed in a Janis cryostat with wedged, IR-transparent windows (ZnSe). The sample temperature was maintained at 8 K during the measurements. A low-noise, Ge:Cu detector was placed directly behind the cell [9].

## 3 Transverse-stretch coupling

As mentioned in the Introduction, the stretch mode of  $^{16}\text{O}$  has a frequency of  $1136\text{ cm}^{-1}$ . This value is the energy difference between the ground ( $N = 0$ ) and excited ( $N = 1$ ) states of the stretch mode, where the transverse mode is in its ground state ( $l = 0$ ). This transition is labelled I (Fig. 2). At nonzero tempera-

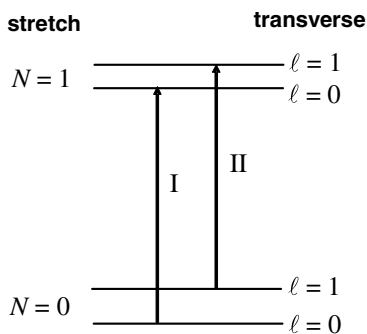


Fig. 2 Energy-level diagram of stretch and transverse vibrational modes in Si:O.

tures, however, it is possible that the transverse mode may be excited. One can then have a transition from the ( $N = 0, l = 1$ ) state to the ( $N = 1, l = 1$ ) state. This transition is labelled II (Fig. 2). Although additional transitions are possible, in the present work we focussed on I and II only. These transitions give rise to strong IR absorption peaks, which we observed as a function of pressure.

In the absence of anharmonic coupling between the transverse and stretch modes, peaks I and II would have the same frequency. Since there *is* coupling, however, the frequencies are slightly different, with peak II on the low-frequency side of peak I. In other words, the transverse motion of the oxygen atom effectively softens the spring constant, thereby reducing the stretch-mode frequency.

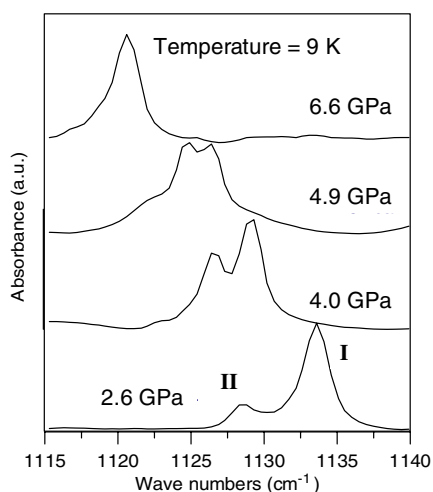
#### 4 The effect of pressure

The effect of hydrostatic pressure on the IR absorption peaks I and II, for Si: $^{16}\text{O}$ , is shown in Fig. 3. For sufficiently high pressures, the frequencies decrease. Furthermore, the splitting between peaks I and II decreases until the peaks effectively merge. These observations may be explained by the buckling model. As pressure is applied, the bonds in the Si crystal are compressed. For small pressures, the molecule is essentially linear (Fig. 1). For large pressures, however, the oxygen buckles in a transverse direction. Quantum mechanically, this means that at zero pressure, the mean position of the oxygen atom is at the bond centre, whereas for large pressures the mean position is off-centre (Fig. 4). The buckling model, which was proposed to explain the pressure-dependent experiments, was subsequently verified by *ab initio* calculations [10].

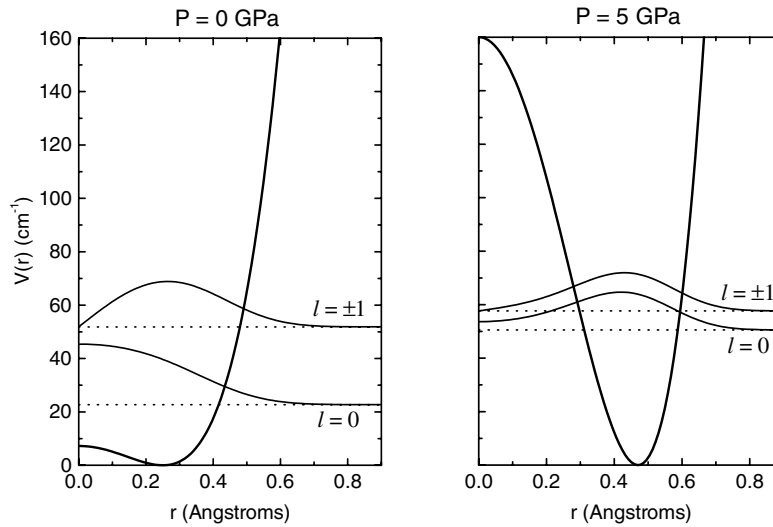
As shown in Fig. 4, at zero pressure, the  $l = 0$  and  $l = \pm 1$  modes resemble simple-harmonic-oscillator wavefunctions. As pressure is applied, the  $l = 0$  wavefunction is pushed outward. For large pressures, the  $l = 0$  and  $l = \pm 1$  wavefunctions look nearly identical. The fact that these wavefunctions are very similar leads to a decrease in the transverse–stretch coupling, and hence a reduction in the energy difference between peaks I and II.

IR spectra for Si: $^{18}\text{O}$ , at several different pressures, are shown in Fig. 5. Initially, the pressure-dependent behaviour is similar to that of Si: $^{16}\text{O}$  – the peaks move to lower frequency and merge. At pressures near 4 GPa, however, something strange happens. A new peak appears at the low-frequency side of the stretch-mode peak. The intensity of this peak grows, and the other peak diminishes. For pressures above 4.6 GPa, only one peak is observed, and it is substantially broadened.

The frequencies of the peaks in Si: $^{16}\text{O}$  and Si: $^{18}\text{O}$  as a function of pressure are shown in Fig. 6. Clearly, there is an avoided crossing for Si: $^{18}\text{O}$  but not for Si: $^{16}\text{O}$ . To explain this phenomenon, a model was proposed in which the stretch mode coupled to a *combination* of several low-frequency modes. These combination modes are denoted ‘Mode 1’ and ‘Mode 2’, and they both involve the second harmonic of the  $517\text{ cm}^{-1}$  resonant mode ( $2 \times 517\text{ cm}^{-1} = 1034\text{ cm}^{-1}$ ). Mode 1 is the combination of a sec-



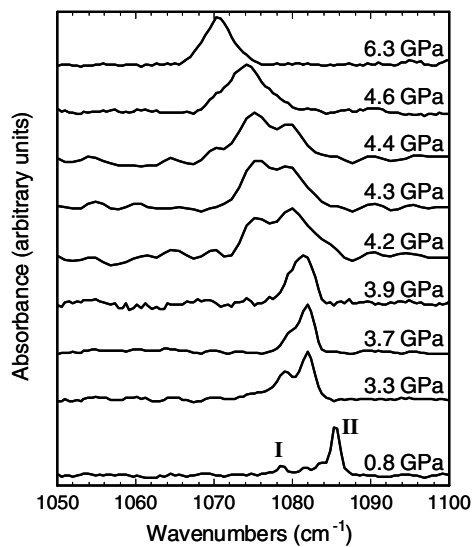
**Fig. 3** IR spectra of Si: $^{16}\text{O}$  for several different pressures. At large pressures, peaks I and II merge.



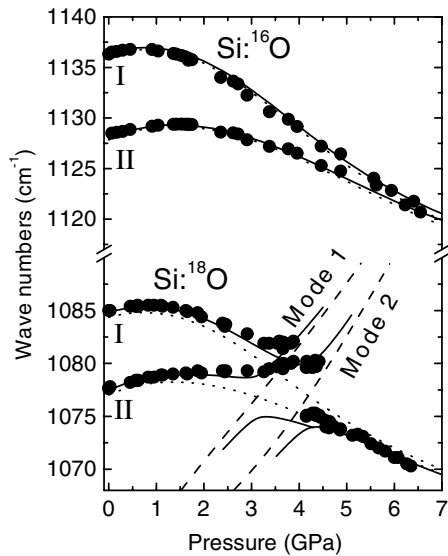
**Fig. 4** Potential energy surface of interstitial oxygen, as a function of radial distance ( $r$ ), for two different pressures. The  $l = 0$  and  $l = \pm 1$  wavefunctions are shown, and the dashed lines indicate the energy levels.

ond-harmonic resonant mode and the second-harmonic ( $l = 2$ ) transverse mode. Mode 2 is the combination of a second-harmonic resonant mode and the fundamental ( $l = 1$ ) transverse mode. The pressure dependencies were obtained by adding twice the pressure shift of the Raman phonon [11] to the calculated pressure shift of the transverse mode. As discussed in Ref. [4], the symmetries of these modes are such that Mode 1 interacts with Peak II whereas Mode 2 interacts with Peak I. These interactions produce the avoided crossings, shown by the solid lines in Fig. 6. Si:<sup>16</sup>O does not exhibit this behaviour because the <sup>16</sup>O stretch mode is much higher in frequency than Mode 1 and 2, so the interaction is much less.

The broadening of the peak at large pressures is explained by the fact that, for pressures greater than 4 GPa, the <sup>18</sup>O stretch mode finds itself within the two-phonon density of states. The additional decay channels made available by two-phonon processes decreases the LVM lifetime, resulting in a significant broadening of the line. The <sup>16</sup>O stretch mode, in contrast, remains above the two-phonon density of states



**Fig. 5** IR spectra of Si:<sup>18</sup>O under pressure.



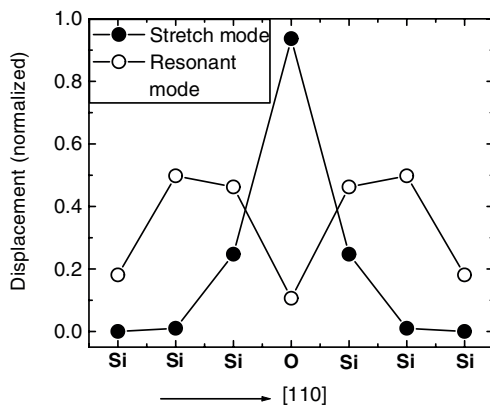
**Fig. 6** Frequencies of the stretch-mode peaks I and II in Si:<sup>16</sup>O and Si:<sup>18</sup>O under pressure. The dashed lines are fits to a model that does not include coupling between the stretch modes and the combination modes (Mode 1 and Mode 2). The solid lines are fits to the model that includes this coupling.

for all pressures, and therefore does not exhibit broadening. Similar phenomena have been observed with intrinsic Raman phonons in ZnO [12]. To our knowledge, the present work is the first report of a pressure-induced lifetime reduction of a *local* vibrational mode.

## 5 Localized versus extended modes

As mentioned in the Introduction, the stretch mode is *localized*, whereas the resonant mode is *extended*. Therefore, the coupling between the stretch mode and resonant mode enables the stretch mode to become delocalized. Eventually, the energy of the stretch mode will be deposited entirely into the acoustic-phonon bath, heating up the crystal.

In order to quantify the localized versus extended character of Si:O vibrational modes, we performed first-principles calculations on a 76-atom cluster, using the software package *Gaussian98* [13]. Details of this calculation are given in Ref. [14]. The magnitudes of the normal-mode displacements are shown for the O atom and neighbouring Si atoms, for the stretch mode and resonant mode (Fig. 7). For the stretch mode, it is clear that the vibrational motion is localized to the oxygen atom and its two neighbouring silicon atoms. For the resonant mode, however, all the silicon atoms participate in the vibrational motion.



**Fig. 7** Displacements of atoms, along the [110] “zig zag”, for the stretch mode and the resonant mode.

## 6 Conclusions

In summary, the application of hydrostatic pressure causes significant changes in the structure and vibrational character of interstitial oxygen in silicon. Under pressure, the oxygen buckles outward, and its vibrational motion in the [111] plane goes from vibrational to rotational. In Si:<sup>18</sup>O, the oxygen LVM is in resonance with a spatially extended mode, at a pressure of 4 GPa. This resonant interaction results in an avoided crossing of the modes. For larger pressures, the <sup>18</sup>O LVM is significantly broadened, due to the fact that its frequency lies within the two-phonon continuum.

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