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Interaction between localized and extended modes of oxygen in silicon

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Abstract

The interaction between localized and extended vibrational modes in solids is of central importance in understanding how local vibrational modes (LVMs) decay into phonons. In this study, we have investigated interstitial oxygen (O_i) in silicon as a model 'laboratory' for such local-extended mode interactions. Using hydrostatic pressure and infrared spectroscopy, we brought the stretch mode of $^{18}O_i$ in silicon into resonance with a second harmonic of the $^{18}O_i$ resonant mode. The resonant interaction results in an avoided crossing between the modes. In addition to this anti-crossing behaviour, the line width 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 line widths.

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The mechanisms by which local vibrational modes (LVMs) decay into lattice phonons are largely unknown. Recent ultrafast pump-probe experiments have succeeded in measuring vibrational lifetimes of hydrogen and oxygen in silicon, shedding light on this problem [1–3]. In the frequency domain, Fourier transform infrared (FTIR) spectroscopy has been used to investigate resonant interactions between vibrational modes of hydrogen in semiconductors [4,5]. With FTIR or Raman spectroscopy, vibrational lifetimes can be inferred from the line widths of the peaks, although inhomogenous broadening necessarily affects these results. Hydrostatic pressure is an excellent means for tuning interactions between vibrational modes [6].

In this paper, we review recent work [7] in which we used hydrostatic pressure to induce a resonant interaction between extended and localized vibrational modes of interstitial oxygen in silicon. In addition, the results of first-principles calculations are presented to illustrate the 'localized' versus 'extended' character of these modes. The interaction between localized and extended modes is important because it can provide information about the first steps in the decay of a LVM into lattice phonons.

Over the past half century, the LVMs of interstitial oxygen have been measured and

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modelled extensively, [8–13] making Si:O a model system for the study of vibrational dynamics. The antisymmetric *stretch* mode has a frequency of $1136\,cm^{-1}$ and corresponds to the oscillation of an $^{16}O_i$ atom along the [1 1 1] direction [14]. The *transverse* mode at $29\,cm^{-1}$ corresponds to movement of the oxygen atom in the [1 1 1] plane [15]. The *resonant* mode of $^{16}O_i$ has a frequency of $517\,cm^{-1}$ [16], and it involves the transverse motion of the neighbouring silicon atoms. Unlike the stretch mode, the resonant mode is extended spatially, with many neighbouring silicon atoms participating in the vibration.

A custom piston-cylinder diamond-anvil cell (DAC) [17] was used in our high-resolution vacuum FTIR spectrometer (Bomem DA8). An off-axis parabolic mirror efficiently focuses a collimated IR beam onto the sample. A Ge:Cu photoconducting detector [17] is placed in close proximity to the sample, so that a large fraction of the transmitted IR light is collected. The DAC was placed in a Janis STVP continuous-flow liquid-helium cryostat with wedged ZnSe windows, and maintained at a temperature of 8 K. Between measurements, the DAC was removed from the cryostat and warmed up to room temperature. The pressure was then adjusted and the DAC placed back in the cryostat.

Fig. 1 shows IR absorption spectra of the $^{18}O_i$ stretch mode. Near atmospheric pressure, four distinct peaks are observed [8]. The highest-energy peak (I) corresponds to a transition from the ground state to the stretch-mode excited state. The two smaller peaks correspond to the same transition, but with the $^{18}O_i$ atom bound to combinations of less abundant Si isotopes. The lowest energy peak (II) corresponds to a transition from a thermally populated transverse mode to a stretch-plus-transverse mode. At high pressures, the frequencies of the two transitions (I and II) become nearly degenerate, as shown in the case of Si:$^{16}O_i$. However, the peak at high pressure is very broad, which is evidence of a significant decrease in lifetime. This abrupt decrease in lifetime is a result of the LVM frequency entering the two-phonon continuum at a pressure of 4 GPa.

The full-width at half-maximum (FWHM) for peak I is plotted as a function of pressure (Fig. 2). FWHM values are plotted for peaks above and below the avoided crossing, as explained further. Whereas the width of the $^{16}O_i$ peak remains fairly constant over the entire pressure range, the $^{18}O_i$ peak broadens at 4 GPa. For pressures greater than 4 GPa, the stretch mode lies within the two-phonon density of states. Assuming the local density of states is roughly flat for frequencies below the resonant mode [18], the line width should increase when the mode enters the two-phonon continuum [19], in agreement with the experimental observation.

Fig. 3 shows a plot of the frequencies of the observed peaks for both $^{16}O_i$ and $^{18}O_i$ as a

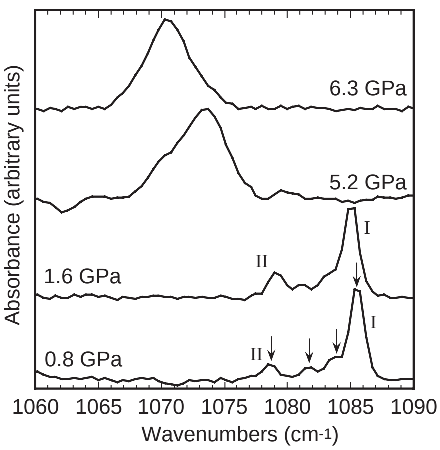

Fig. 1. IR spectra of Si:^{18}O under pressure.

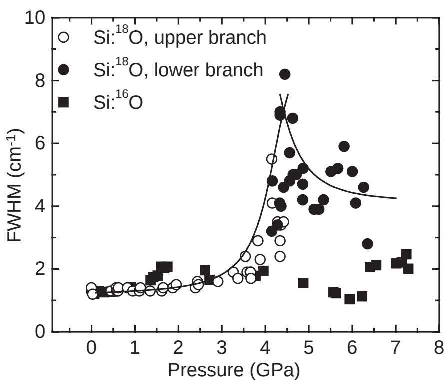

Fig. 2. Plot of Si:O stretch-mode FWHMs as a function of pressure.

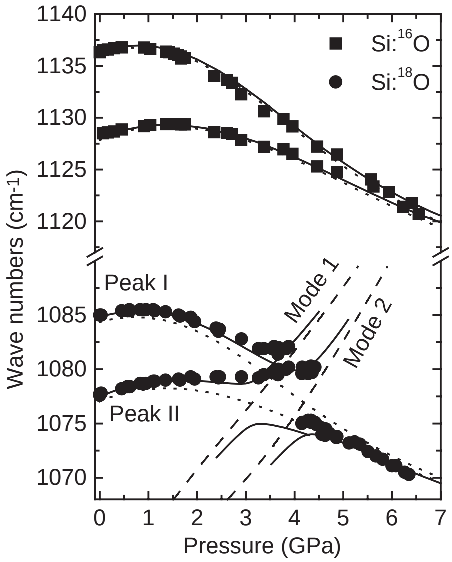

Fig. 3. Plot of Si:O stretch-mode frequencies as a function of pressure.

function of pressure. The dotted and solid lines are frequencies generated by the theoretical model, as discussed in Ref. [7]. The peaks associated with Si:$^{16}O_i$ show a smooth, continuous shift with pressure. However, for the Si:$^{18}O_i$ peaks, there is an avoided crossing around 4 GPa. This anticrossing behaviour is the result of a resonant interaction between the $^{18}O_i$ stretch mode and modes involving the second harmonic of the 517 cm^{-1} resonant mode. 'Mode 1' is the combination of the second-harmonic resonant mode and a second-hamonic transverse mode. 'Mode 2' is the combination of the second-harmonic resonant mode and the fundamental transverse mode. Both of these modes are *spatially extended*, in contrast to the stretch mode. At the anti-crossing pressures, the eigenstate of the system is not a stretch mode or resonant mode, but rather a linear combination of these modes.

To illustrate the localized versus extended nature of these modes, first-principles calculations were performed on a $Si_{44}H_{30}O$ cluster, using the commercially available software *Gaussian98* [20]. Density-functional theory was used with the Becke 3-parameter method [21] and the 3-21G basis set. The stretch (A_{2u}) and resonant (E_u, doubly degenerate) modes were calculated to be 1216 and 482 cm^{-1}, respectively, in fair agreement with the experimental values of 1136 and 517 cm^{-1}. In Fig. 4, the normal modes of the stretch and resonant modes are shown, where the bar charts indicate the magnitudes of the atomic displacements. It can be seen that the stretch mode is strongly localized, whereas the transverse mode involves significant motion of all the atoms in the cluster. Hence, a transition from a stretch mode to a second-harmonic resonant mode would substantially delocalize the vibrational mode. Such a transition is the first step on the downhill journey that an LVM takes as it eventually becomes a collection of lattice phonons; i.e., heat.

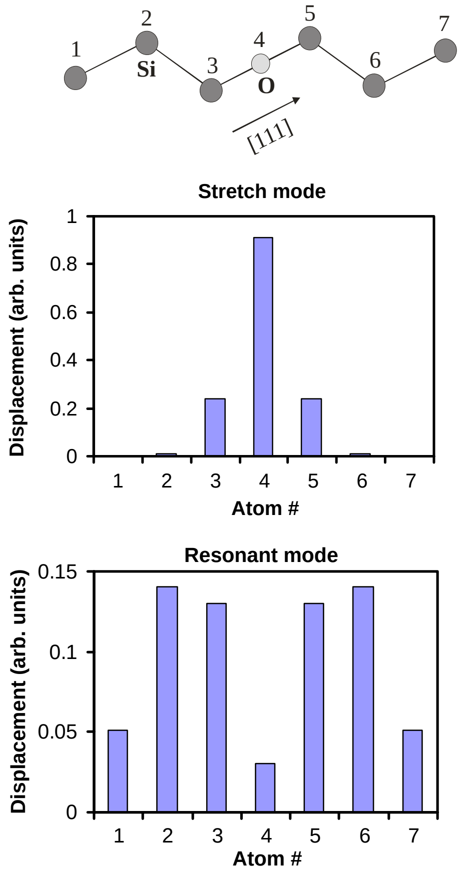

Fig. 4. Calculated displacements for the stretch and resonant modes of Si:O. The numbering of the atoms is shown in the top figure. The bar charts show the magnitudes of the normal-mode displacements for the two vibrational modes.

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References

[1] M. Budde, G. Lüpke, C. Parks Cheney, N.H. Tolk, L.C. Feldman, Phys. Rev. Lett. 85 (2000) 1452.
[2] M. Budde, G. Lüpke, E. Chen, X. Zhang, N.H. Tolk, L.C. Feldman, E. Tarhan, A.K. Ramdas, M. Stavola, Phys. Rev. Lett. 87 (2001) 145501.
[3] G. Lüpke, X. Zhang, B. Sun, A. Fraser, N.H. Tolk, L.C. Feldman, Phys. Rev. Lett. 88 (2002) 135501.
[4] J.-F. Zheng, M. Stavola, Phys. Rev. Lett. 76 (1996) 1154.
[5] M.D. McCluskey, E.E. Haller, W. Walukiewicz, P. Becla, Solid State Commun. 106 (1998) 587.
[6] M.D. McCluskey, J. Appl. Phys. 87 (2000) 3593.
[7] L. Hsu, M.D. McCluskey, J.L. Lindstrom, Phys. Rev. Lett. 90 (2003) 095505.
[8] B. Pajot, in: F. Shimura (Ed.), Semiconductors and Semimetals, Vol. 42, Academic Press, New York, 1994, pp. 191–249.
[9] R. Jones, A. Umerski, S. Öberg, Phys. Rev. B 45 (1992) 11321.
[10] H. Yamada-Kaneta, C. Kaneta, T. Ogawa, Phys. Rev. B 42 (1990) 9650.
[11] H. Yamada-Kaneta, Physica B 308–310 (2001) 309.
[12] J. Coutinho, R. Jones, P.R. Briddon, S. Öberg, Phys. Rev. B 62 (2000) 10824.
[13] T. Hallberg, L.I. Murin, J.L. Lindström, V.P. Markevich, J. Appl. Phys. 84 (1998) 2466.
[14] H.J. Hrostowski, R.H. Kaiser, Phys. Rev. 107 (1957) 966.
[15] D.R. Bosomworth, W. Hayes, A.R.L. Spray, G.D. Watkins, Proc. Phys. Soc. London A 317 (1970) 133.
[16] M. Stavola, Appl. Phys. Lett. 44 (1984) 514.
[17] Haller-Beeman and Associates (www.haller-beeman.com).
[18] E. Artacho, A. Lizón-Nordström, F. Ynduráin, Phys. Rev. B 51 (1995) 7862.
[19] R.C. Newman, et al., Mater. Sci. Forum 258–263 (1997) 1.
[20] M.J. Frisch, et al., Gaussian 98, Revision A.9, Gaussian, Inc., Pittsburgh, Pennsylvania, 1998.
[21] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.