

## Isotope Dependence of the Lifetime of the $1136\text{-cm}^{-1}$ Vibration of Oxygen in Silicon

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By simply changing the isotopes of the Si atoms that neighbor an oxygen  $O_i$  atom in crystalline silicon, the measured decay rate  $\tau$  of the asymmetric-stretch vibration ( $\nu_3 = 1136\text{ cm}^{-1}$ ) of oxygen ( $O_i$ ) in silicon changes by a factor of  $\sim 2.5$ . These data establish that  $\nu_3$  decays by creating one  $\nu_1$  symmetric-stretch, local-vibrational mode of the Si- $O_i$ -Si structure. If the residual energy ( $\nu_3 - \nu_1$ ) is less than the maximum frequency  $\nu_m$  of the host lattice, as for  $^{28}\text{Si}$ - $^{16}\text{O}$ - $^{28}\text{Si}$  in natural silicon, then it is emitted as one lattice mode, and  $\tau$  depends on the density of one-phonon states at  $\nu_3 - \nu_1$ . If  $(\nu_3 - \nu_1) > \nu_m$ , as for  $^{16}\text{O}$  in single-isotope  $^{30}\text{Si}$  silicon, two lattice modes are created in addition to  $\nu_1$ , increasing  $\tau$ . Prediction of  $\tau$  for a particular defect clearly requires a detailed knowledge of that defect.

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All excitations of a crystal lead to at least some of the energy being emitted into vibrational modes of the lattice. Here, we report on the transfer of energy from a local-vibrational mode (LVM) of an impurity, oxygen ( $O_i$ ), into the lattice of a silicon crystal. In a LVM, the atoms at the impurity vibrate at frequencies that are too high for the energy to travel through the crystal. The energy is trapped until it degrades into lower frequency modes that can be accepted by the lattice. The lifetime of the LVM is a fundamental property. For example, the diffusion of  $O_i$  through the crystal can be enhanced by optical excitation of the vibration [1], and the natural linewidth of optical transitions involving the LVM depend on the lifetime [2]. The mechanism by which an LVM decays is not immediately apparent. In some cases a "frequency gap" law works extremely well [3], and the lifetime  $\tau$  of the LVM increases exponentially with the number of lattice modes that it decays into. In other cases, significantly different decay times occur for LVMs of similar frequencies. For example, the stretch modes of hydrogen-related defects in silicon have low-temperature lifetimes of 295 ps for 2 H atoms in a divacancy [4,5], and of 4 ps for  $\text{H}_2^*$  (one H atom in a back bond from a Si-H-Si bond-centered structure) [5], even though the LVM frequencies (respectively 2072 and  $2062\text{ cm}^{-1}$ ) differ by only  $\frac{1}{2}\%$  and are considerably greater than the lattice cutoff at  $524\text{ cm}^{-1}$ . These defects have different structures, and the variation in  $\tau$  is because the

decay involves other, structure-dependent, LVMs of the defects [6]. We will show that significant differences in lifetime may occur for the same defect structure, when small changes in the frequency of the LVM are produced by isotope changes. This result unambiguously demonstrates the role of LVMs in this case, and implies that simple rules to predict the lifetimes are, in general, unreliable.

Oxygen is a key impurity in silicon grown by the Czochralski (CZ) method [7]. It is grown in as isolated interstitial atoms, with one O atom near the bond-centered position at the midpoint of two Si atoms, but displaced off the trigonal axis. The LVM frequencies may be accurately calculated by considering  $O_i$  to be a "molecule" consisting of the  $O_i$  atom plus its immediate neighbors, with a time-averaged  $D_{3d}$  point group [8]. The  $A_{2u}$   $\nu_3$  mode, in which  $O_i$  vibrates in antiphase to the two neighboring Si atoms, is infrared active (the " $1136\text{ cm}^{-1}$  line"), and is used to determine the concentration of  $O_i$  [9]. The lifetimes of the  $\nu_3$  vibration in natural silicon have been reported for  $^{16}\text{O}$  and for  $^{17}\text{O}$ , and were described as the decay of the  $\nu_3$  mode into three lattice modes [2]. The additional data presented here establish that the decay of  $\nu_3$  crucially involves creation of another LVM, resulting in the isotope dependence.

CZ-grown samples of silicon of natural isotopic abundance and of optically characterized [10,11], single-

isotope  $^{30}\text{Si}$  (mean mass number 29.98) have been used. They contained  $9 \times 10^{17} \text{ cm}^{-3}$   $^{16}\text{O}$  oxygen. Decay-time measurements have been made by the transient-bleaching method [12], using 5 ps pulses of radiation from a free-electron laser. The decay times of the bleaching were invariant over 15 dB of attenuation in the pulse beam's intensity. In this limit the decay time accurately measures the time for the population in the ground state to recover. Measurement temperatures between 5 and 100 K were obtained by using a helium flow cryostat.

The decay times measured at 10 K are listed in Table I. Our value of 11 ps for  $^{28}\text{Si}$ - $^{16}\text{O}$ - $^{28}\text{Si}$  agrees with that of Sun *et al.* [2]. They also reported a decay time of 4 ps for  $^{28}\text{Si}$ - $^{17}\text{O}$ - $^{28}\text{Si}$ . They noted that the lifetimes are qualitatively consistent with the  $\nu_3$  mode decaying into three lattice modes since the density of three-phonon states is 1.3 times larger for  $\nu_3$  of  $^{17}\text{O}$  than for  $^{16}\text{O}$ . However, we report that the measured decay time in natural silicon of  $\nu_3$  for  $^{29}\text{Si}$ - $^{16}\text{O}$ - $^{28}\text{Si}$  is 19 ps, and for  $^{30}\text{Si}$ - $^{16}\text{O}$ - $^{28}\text{Si}$  is 27 ps. The increased decay time, by 50%, occurs despite the  $\nu_3$  vibration moving to a *higher* density of three-phonon lattice states. In single-isotope  $^{30}\text{Si}$ ,  $\nu_3 = 1129 \text{ cm}^{-1}$ , placing it at almost the same level on its three-phonon density of states curve as the  $1136 \text{ cm}^{-1}$  vibration in natural silicon, but the decay time is 2.5 times longer.

The sensitivity of the lifetime to the isotopic composition of the nearest neighbors is readily explained if the decay occurs through the creation of one quantum of the  $\nu_1$  LVM plus one or two lattice phonons of total frequency  $\nu_3 - \nu_1$ . The frequencies of the relevant modes for the different isotopes are listed in Table I. In the  $\nu_1$  mode, an  $A_{1g}$  mode in the  $D_{3d}$  point group, the two Si neighbors to O vibrate in antiphase along the trigonal axis, and the O atom

is static (strictly, for Si atoms of equal mass). This LVM is therefore independent of the isotope of O. It is infrared inactive, but appears in combination modes [8,13], giving the frequency for  $^{28}\text{Si}$ -O- $^{28}\text{Si}$  as  $\nu_1 \sim 612 \text{ cm}^{-1}$  [14]. Figure 1 shows the density of lattice phonons [16], with the frequencies scaled by a factor of 1.02 to modify to low temperature, and, for  $^{30}\text{Si}$ , also scaled to allow for the heavier atoms. (The isotope dependence of the volume has insignificant effects [17].) The vertical lines show  $\Delta\nu = \nu_3 - \nu_1$  for the different isotope combinations, labeled by the measured decay times given in Table I. When  $\Delta\nu$  falls *outside* the one-phonon spectrum, as for  $^{30}\text{Si}$ - $^{16}\text{O}$ - $^{28}\text{Si}$  and single-isotope  $^{30}\text{Si}$ , the measured decay time  $\tau_m$  increases to 27 ps, Fig. 1 and Table I. Then,  $\Delta\nu$  falls in similar values of the two-phonon density of states, Fig. 1, and also of the three-phonon density of states (not shown). The decay could then occur through emission of one  $\nu_1$  LVM plus 2 or 3 lattice phonons, and the frequency gap law will favor the LVM-plus-two-phonon process. When  $\Delta\nu$  is *inside* the one-phonon spectrum,  $\tau_m$  decreases with increasing density of states, as expected. This rule also applies (broken line in Fig. 1) for  $^{28}\text{Si}$ - $^{18}\text{O}$ - $^{28}\text{Si}$ , where  $\nu_3 = 1085 \text{ cm}^{-1}$ ,  $\Delta\nu = 473 \text{ cm}^{-1}$ , and taking  $\tau_m \sim 11$  ps from its reported linewidth [13]. Inspection of the data shows no such clear correlation of  $\tau_m$  with the isotope data if the transverse mode is used instead of  $\nu_1$ .

A decay may involve more than one independent decay channel, in which case the measured decay time  $\tau_m$  is related to the component decay times  $\tau_i$  by  $1/\tau_m = \sum_i 1/\tau_i$ . All the  $\Delta\nu$  values lie at similar values of the two-phonon density of states, Fig. 1, and so the decay of  $\nu_3$  into one  $\nu_1$  plus two lattice modes will have similar decay times. We suggest that this channel has a decay

TABLE I. Vibrations of  $\text{O}_i$  in silicon, and the isotope dependence of  $\nu_1$  and  $\nu_3$ . The second column lists the local isotopic structure, for example, as 28-17-28 for  $^{28}\text{Si}$ - $^{17}\text{O}$ - $^{28}\text{Si}$ . The data for  $^{30}\text{Si}$ - $^{16}\text{O}$ - $^{30}\text{Si}$  are for single isotope  $^{30}\text{Si}$ . The measured (10 K) and calculated (present work) frequencies of the vibrations are listed in the third and fourth columns. The differences  $\nu_3 - \nu_1$  are in the fifth column. The measured decay times at low temperature are in the sixth column, and values in square brackets give the decay time of the process involving  $\nu_1$  plus one lattice phonon, using a competing three-phonon decay time of 27 ps. The seventh column lists the calculated (present work) decay time. References cite the frequency  $\nu$  or decay time  $\tau$ .

Label	Species	Frequency ( $\text{cm}^{-1}$ )		$\nu_3 - \nu_1 \text{ cm}^{-1}$	Lifetime (ps)		Reference
		Exp.	Theory		Exp.	Theory	
$\nu_2$	28-16-28	29.3					$\nu$ : [8]
Transverse	28-16-28	517.8					$\nu$ : [13]
$\nu_1$	28-16-28	612	641				$\nu$ : [14]
$\nu_3$	28-16-28	1136.4	1187	524	11 [19]	10	$\tau$ : [2]
$\nu_1$	28-17-28	612	641				
$\nu_3$	28-17-28	1109.5	1158	497	4 [4.7]	7	$\tau$ : [2]
$\nu_1$	29-16-28	608					$\nu$ : [14]
$\nu_3$	29-16-28	1134.4	1185	526	19 [64]	15	$\tau$ : this work
$\nu_1$	30-16-28	602	630				$\nu$ : [14]
$\nu_3$	30-16-28	1132.7	1183	530	27 [ $\infty$ ]	22	$\tau$ : this work
$\nu_1$	30-16-30	594					$\nu$ : [15]
$\nu_3$	30-16-30	1129.1		535	27 [ $\infty$ ]		$\tau$ : this work

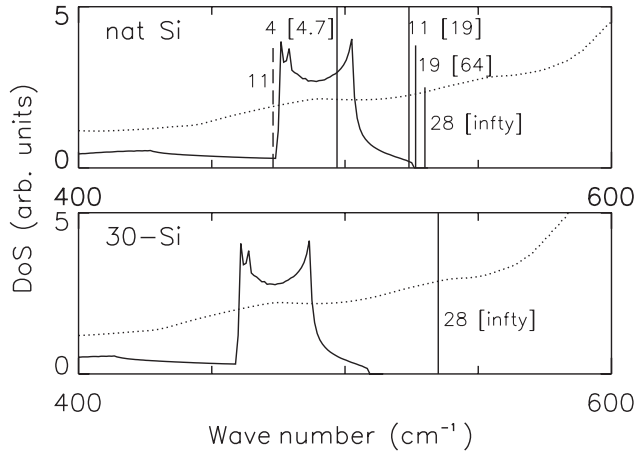


FIG. 1. The solid curves shows the one-phonon density of states, and the dotted lines the two-phonon densities, for natural silicon (upper panel) and for single-isotope  $^{30}\text{Si}$  (lower panel). The vertical lines show the differences  $\Delta\nu = \nu_3 - \nu_1$  for the isotope combinations, identified by the decay times shown in Table I. The broken line is for  $^{28}\text{Si}-^{18}\text{O}-^{28}\text{Si}$ ,  $\tau_m = 11$  ps,  $\Delta\nu = 473$   $\text{cm}^{-1}$ ; see text.

lifetime of  $\sim 27$  ps, as observed for  $^{30}\text{Si}-^{16}\text{O}-^{28}\text{Si}$  and in single-isotope  $^{30}\text{Si}$ . Consequently, the decay time  $\tau_\nu$  of the channel involving one  $\nu_1$  mode plus one lattice mode is  $\tau_\nu = (1/\tau_m - 1/27)^{-1}$ , where the times are in picoseconds. This correction changes  $\tau_m = 11$  ps into  $\tau_\nu = 19$  ps, and the other values listed in parentheses in Table I and on Fig. 1. These corrected values look very plausible compared to the one-phonon density of states.

To verify the model and identify the nature of the receiving modes, we performed first-principles calculations. Our results are based on the SIESTA [18,19] implementation of molecular-dynamics (MD) simulations in 64 host-atom periodic supercells. Accurate vibrational lifetimes for various H-related LVMs in Si have been obtained with supercells of this size [6]. Norm-conserving pseudopotentials in the Kleinman-Bylander form [20] are used to remove the core regions from the calculations. The valence regions are treated self-consistently within local density-functional theory with the exchange-correlation potential of Ceperley-Alder [21] parametrized by Perdew-Zunger [22]. The basis sets for the valence states (double-zeta in the present work) are linear combinations of numerical atomic orbitals of the Sankey type [23,24]. The charge density is projected on a real-space grid with equivalent cutoffs of 150 Ry to calculate the exchange-correlation and Hartree potentials.

The calculated LVMs are given in Table I. The eigenvectors of the dynamical matrices are used to prepare the supercell in thermal equilibrium at the desired temperature and set the initial excitation of the LVM  $\nu_3$  with initial kinetic energy  $\frac{3}{2}\hbar\omega$ , as described in Ref. [6]. In order to calculate the lifetime at the temperature  $T$ , several MD calculations are performed for each isotope combination:

five for the shorter-lived LVMs ( $^{28}\text{Si}-^{17}\text{O}-^{28}\text{Si}$  and  $^{28}\text{Si}-^{16}\text{O}-^{28}\text{Si}$ ) and three for the longer-lived ones ( $^{29}\text{Si}-^{16}\text{O}-^{28}\text{Si}$  and  $^{30}\text{Si}-^{16}\text{O}-^{28}\text{Si}$ ). For each isotope, the energy in the  $\nu_3$  mode, averaged over the different runs at  $T = 200$  K, is fit to an exponential. The resulting calculated lifetimes, column 7 of Table I, are close to the measured values and change correctly with isotope.

Figure 2 shows a single example of the decay of the  $\nu_3$  mode of  $^{28}\text{Si}-^{16}\text{O}-^{28}\text{Si}$  in order to illustrate the decay process. As  $\nu_3$  decays, the energies increase in the  $\nu_1$  mode and in an optic mode at  $524$   $\text{cm}^{-1}$ . In all our simulations,  $\nu_1$  is a receiving mode for all the isotope combinations. The longer decays involve  $\nu_1$  and more than one lattice mode. Since the receiving lattice modes themselves have very short lifetimes, they decay while still absorbing energy from the LVM, and so are difficult to identify when plotting the energies of all the modes in the supercell.

Figure 3 reports the temperature dependence of the decay rate of  $\nu_3$ , using single-isotope  $^{30}\text{Si}$  to avoid complications from detecting different combinations of isotopes. It is usually possible to identify the phonons involved in the decay process by measuring the  $T$  dependence of the decay rate. A simple fit to the data is obtained by noting that transient-bleaching measurements give the relaxation time of the *ground* state of the optical transition, and that the low-energy  $\nu_2$  mode is usually in thermal equilibrium with the ground state. The higher levels of the  $\nu_2$  vibration, which are rapidly occupied as  $T$  increases, approximate to two-dimensional harmonic vibrations [25] of quantum  $\hbar\omega = 49$   $\text{cm}^{-1}$ , independent of the Si mass [13]. The pump pulse partially empties the ground state, destroying the thermal equilibrium. We assume that repopulation of the ground state from the  $\nu_2$  manifold occurs at a rate that is proportional to the fraction of unoccupied

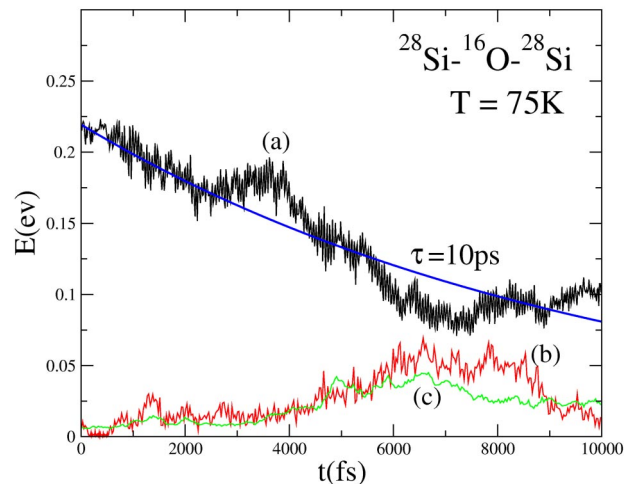


FIG. 2 (color online). Calculated energies of the three most active modes in the decay of  $\nu_3$ , labeled (a). The curves labeled (b) and (c) are  $\nu_1$  and an optic phonon at  $524$   $\text{cm}^{-1}$ , respectively. The 10 ps lifetime shown is the average of five MD runs (see text).

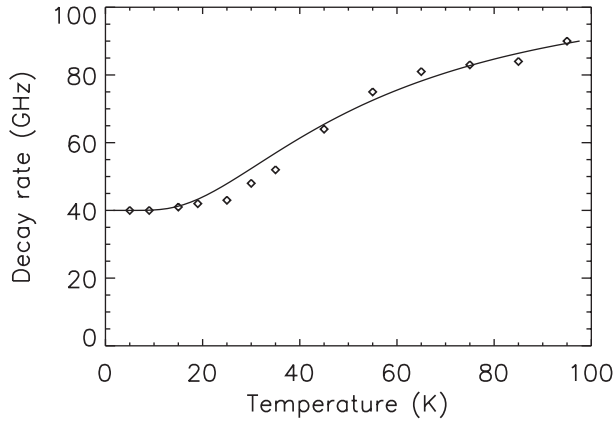


FIG. 3. The decay rate of the  $\nu_3$  transient signal in  $^{30}\text{Si}$  as a function of  $T$ : points are measured data, the line is Eq. (1).

ground states [the term in brackets  $\{$  in Eq. (1)]. Then

$$\frac{1}{\tau(T)} = \frac{1}{\tau(0)} + s\{1 - [1 - \exp(-\hbar\omega/kT)]^2\}. \quad (1)$$

The one adjustable parameter is given as  $s \sim 70$  GHz, corresponding physically to a decay time,  $1/s$ , of  $\sim 20$  oscillations in the (effective)  $49 \text{ cm}^{-1}$  modes. Since relaxation from the  $\nu_2$  states dominates the measured  $T$  dependence, it contains no accessible information about the assumed  $\nu_1$ ,  $\Delta\nu$  process. However, the  $\nu_2$  modes have negligible effects on the measurements at 10 K.

We have reported experimental data showing that the decay time  $\tau$  of the  $\nu_3$  mode is sensitive to the isotopes of the Si atoms that neighbor the  $\text{O}_i$ . These results, and data for  $^{17}\text{O}_i$  and  $^{18}\text{O}_i$ , establish that  $\nu_3$  decays by creating one  $\nu_1$  LVM phonon. The remaining energy,  $\Delta\nu = \nu_3 - \nu_1$ , is emitted as one or more lattice modes, and rapidly degrades into many lattice modes, Fig. 2. The sensitivity of  $\tau$  arises from the location of  $\Delta\nu$  relative to the density of one-phonon states, Fig. 1. Consequently, small modifications of the same defect can result in significant changes in  $\tau$ . Prediction of  $\tau$  for a particular defect requires a detailed knowledge of that defect.

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