

Three phonon decay mode of the 1136-cm⁻¹ ν_3 vibration of oxygen in silicon

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The (1136-cm⁻¹) ν_3 vibration of oxygen in silicon is known to decay at low temperature primarily by emitting two phonons. We show here that the temperature dependence of the decay is caused by a *three*-phonon process. In both natural-isotope and single-isotope ³⁰Si, the three-phonon process is identified as the emission of one ν_1 (612 cm⁻¹) local mode, one ν_2 low-energy local mode, and one lattice mode of 524 cm⁻¹ (where the quoted values are for ¹⁶O in natural-isotope silicon). The common assumption that the decay of a vibration proceeds through one dominant process is clearly not applicable here.

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Oxygen is a key impurity in crystalline silicon.¹ It is identified and assayed by measuring a characteristic vibrational absorption line which occurs, at low-temperature ($T < 20$ K), at 1136 cm⁻¹ for ¹⁶O in natural-isotope silicon. At these low temperatures, the vibration is known to decay predominantly by the emission of two phonons.² In this Brief Report we establish that the *temperature dependence* of the decay time is caused by the emission of *three* phonons. Consequently, the simplifying assumption that is frequently used in studies of the decay of vibration, for example in Refs. 3–5, that there is only one significant decay process, is not valid here.

Oxygen atoms are incorporated predominantly as isolated, bond-centered interstitial atoms in Czochralski-grown silicon.¹ The vibrational properties of oxygen in crystalline silicon have been studied intensively, for example as in Ref. 6. The properties relevant to this work can be described in terms of a highly localized, triatomic model, consisting of the oxygen atom and its two silicon neighbors.⁷ This Si-O-Si chain has a linear configuration when time averaged,⁸ and so has four vibrational modes. The ν_3 mode (symmetry A_{2u} in the D_{3d} point group) is produced by the O atom moving along the Si-O-Si axis, in antiphase with motion of the Si atoms. This is the mode that is observed in infrared absorption at 1136 cm⁻¹. In the ν_1 mode (symmetry A_{1g}) the O atom is static and the two Si atoms move along the axis. This mode is therefore not infrared active, but it is observed in combination bands, from which the frequency of the ν_1 mode is found to be ~ 612 cm⁻¹.⁹ The final localized mode of the Si-O-Si complex is a doubly degenerate ν_2 mode, of symmetry E_{2u} , in which the O atom moves perpendicularly to the Si-O-Si axis. This anharmonic mode has a low frequency, with a first-excited state of only 29 cm⁻¹.⁸

At low temperature, the decay time of the first-excited state of the ν_3 vibration in crystalline Si depends on the isotopes of the O atom, the isotopes of the immediate Si neighbors, and the isotopes of the lattice.^{2,10} Values range from 4.5 ps for ¹⁷O in silicon of natural isotopic abundance¹⁰ to 27 ps for ¹⁶O in ³⁰Si.² The reason for this variation is that the dominant decay process of the localized ν_3 vibration (~ 1136 cm⁻¹) is by creating one localized ν_1 vibration (~ 612 cm⁻¹), leaving $\Delta\hbar\omega \sim 524$ cm⁻¹ to be dissipated in a

lattice mode.² This value is very close to the maximum frequency of the lattice, 524.6 cm⁻¹.¹¹ The precise value of $\Delta\hbar\omega$ depends on the isotopes of the O and Si atoms in the Si-O-Si complex, and since the decay rate depends on the density of phonon states at $\Delta\hbar\omega$, there is a considerable isotope-induced variation in the decay time. In a ³⁰Si crystal, $\Delta\hbar\omega$ exceeds the maximum frequency of the lattice, and the decay must involve at least three phonons, resulting in the slower decay. The three-phonon process seen in ³⁰Si can presumably also occur in natural-isotope silicon, in addition to the known two-phonon process. However, currently, we have no direct evidence on the existence of the three-phonon process in natural-isotope silicon, nor information about the phonons involved. These issues are addressed here.

The decay time measurements were made on Czochralski-grown silicon, with oxygen at the level of $(4$ to $5) \times 10^{17}$ cm⁻³, using the Dutch free-electron laser (FELIX). FELIX delivers macropulses with a length of 4 μ s at a repetition rate of 5 Hz. Each macropulse consists of a train of micropulses of duration 5 ps and 25 MHz repetition rate.¹² A transient bleaching, or balanced pump-probe, technique was used, in which the FELIX beam is split into pump, probe, and reference beams. The reference pulse travels down a 6 m arm and is then back-reflected on to the probe-pulse path, so that the probe and reference beams travel along the same optical path and are detected by the same mercury cadmium telluride detector. The same lifetimes were measured when substantially smaller beam power was obtained using a pulse-slicing technique to pick individual micropulses from the burst, and so the data used here were taken with the full macropulse, to give better signal/noise ratios.

The pump-probe decay curves were single-exponential functions with the time constants shown in Fig. 1. We know that in natural-isotope silicon, the antisymmetric ν_3 of $\hbar\omega_a = 1136.4$ cm⁻¹ can decay by emitting one ν_1 mode of 612 cm⁻¹ and a lattice mode of 524 cm⁻¹.² It is immediately apparent that these high energy modes would not produce the strong temperature dependence observed in the figure: the Boltzmann energy $k_B T = 524$ cm⁻¹ requires $T = 750$ K. Formally, these modes would lead to the decay rate $1/\tau$ changing with temperature T as $1/\tau(T) = f_2(T)/\tau(0)$ where¹³

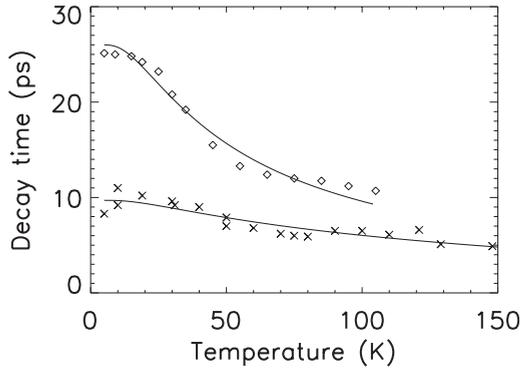


FIG. 1. Crosses show measured data for the pump-probe decay time of the ν_3 vibration of ^{16}O in natural-isotope silicon. The diamonds show the data reported previously for single-isotope ^{30}Si . The estimated uncertainties are ± 1 ps. The lines are calculated as described in the text.

$$f_2(T) = \frac{\exp(\hbar\omega_a/kT) - 1}{\prod_{i=1}^2 [\exp(\hbar\omega_i/kT) - 1]}. \quad (1)$$

The other decay channel is by the emission of three phonons, which were undefined in Ref. 2. The total decay rate is then

$$\frac{1}{\tau(T)} = \left[f_2(T) + \frac{c}{1+c} f_3(T) \right] \frac{1}{\tau(0)}, \quad (2)$$

where c is the relative weight of the three-phonon and two-phonon processes, to be discussed below, and the three-phonon process contributes

$$f_3(T) = \left[\frac{\exp(\hbar\omega_a/kT) - 1}{\prod_{j=1}^3 [\exp(\hbar\omega_j/kT) - 1]} \right]. \quad (3)$$

The two-phonon process is already defined, with $\hbar\omega_1=612$ cm^{-1} and $\hbar\omega_2=524$ cm^{-1} .² We will also assume that the ν_1 local mode takes part in the three-phonon process and let $\hbar\omega_j=612$ cm^{-1} for $j=1$. To conserve energy, $\hbar\omega_a=\sum\hbar\omega_j$, and so there is only one phonon frequency to adjust in making the fit. In addition, c is variable. The least-squares fit to the data requires the three-phonon process to have $\hbar\omega_2=489$ cm^{-1} , and therefore $\hbar\omega_3=35$ cm^{-1} . We note the involvement of this very low-energy mode, which is the origin of the strong temperature dependence, and suggest that it is the low-energy ν_2 mode. The emission of a ν_2 mode requires the ν_3 and ν_2 modes to be coupled, and the coupling is known to occur from the presence of the $(\nu_3+\nu_2)$ combination bands in absorption spectra.⁷

The decay rate is the sum of the two- and three-phonon processes, $1/\tau=1/\tau_2+1/\tau_3$, and as $T\rightarrow 0$, $\tau_2/\tau_3\rightarrow c$. The least-squares fit yields $c=0.66$. Since the observed decay time as $T\rightarrow 0$ is $\tau=10.7\pm 1$ ps, the decay time of the three-phonon process is derived to be $\tau_3=27\pm 2.5$ ps. The same

value was measured for the total decay time in single-isotope ^{30}Si , where a three-phonon process is necessary.²

The data reported previously in Ref. 2 for the decay of ν_3 in single-isotope ^{30}Si are included in the figure. These data were misunderstood in the original publication and will now be reinterpreted.¹⁴ In single-isotope ^{30}Si , the antisymmetric ν_3 occurs at $\hbar\omega_a=1129.1$ cm^{-1} , and the symmetric ν_1 at $\hbar\omega_s=594$ cm^{-1} . The difference $\hbar\omega_a-\hbar\omega_s=535$ cm^{-1} lies above the maximum lattice frequency for ^{30}Si of 506 cm^{-1} . The two-phonon decay process seen in natural-isotope silicon cannot occur. Assuming that there is one dominant three-phonon decay channel, the decay rate of the ν_3 vibration is simply $1/\tau=f_3(T)/\tau(0)$, with the appropriate phonons. Again we assume that one mode, say mode number 1, is the ν_1 local mode, so $\hbar\omega_1=594$ cm^{-1} . Then for any chosen $\hbar\omega_2$, the energy of the third phonon is fixed to conserve energy, and the temperature dependence is determined by only one adjustable phonon energy. Fitting Eq. (3) to the data in Fig. 1 gives $\tau(0)=26\pm 2$ ps and $\hbar\omega_2=503\pm 10$ cm^{-1} , and so predicts $\hbar\omega_3\sim 32$ cm^{-1} , closely equal to the energy of the ν_2 local modes, as in natural-isotope silicon. A lattice mode of 503 ± 10 cm^{-1} in ^{30}Si would have a value of 520 ± 10 cm^{-1} in natural-isotope silicon, equal to the value of 524 cm^{-1} observed in the two-phonon decay process in natural-abundance silicon.²

To summarize, the decay time of 10.7 ± 1 ps observed at low T for ^{16}O in natural silicon is the result of two decay channels, the emission of two phonons, and the emission of three phonons. In this work we have identified the phonons involved in the three-phonon as the ν_1 and ν_2 local modes and an energy-conserving lattice mode, producing a decay time of 27 ± 2.5 ps as $T\rightarrow 0$. The decay time of the two-phonon process as $T\rightarrow 0$ is therefore 17.8 ± 1.7 ps. Qualitatively, the involvement of two local modes in a three-phonon process is consistent with the decay time being relatively rapid compared to many three-phonon processes,⁴ and only 50% slower than the two-phonon process. We have shown that it is the three-phonon process that predominantly determines the temperature dependence of the decay time. The usual assumption that a decay occurs through one dominant mechanism is clearly not valid here. In single-isotope ^{30}Si , where the two-phonon process is forbidden, we have reanalyzed the data and have identified the phonons involved in the three-phonon process; they are the same (isotopically shifted) phonons as occur in the three-phonon decay process in natural-isotope silicon.

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