



Strange lifetimes of the vibrations of interstitial oxygen in SiGe alloys

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ABSTRACT

The transient-bleaching decay time of the ν_3 (1136 cm^{-1}) band of oxygen in $\text{Si}_{1-x}\text{Ge}_x$ alloys, at low temperatures, is found to increase rapidly from a few tens of picoseconds when $x = 0$, to 125 ps when x is in the range 0.011–0.066. We show that the increased decay time is caused partly by perturbations of the oxygen by the Ge, and partly by the small decrease in the frequencies of the lattice modes in the alloy. The decay time of ν_3 in crystalline germanium ($x = 1$) is also ~ 115 ps, similar to that for the dilute alloys, but it is shown to occur through a different three-phonon process.

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1. Introduction

In the last few years, there have been many studies of the lifetimes of local vibrational modes of impurities in semiconductors. To our knowledge, there are no reports of the lifetimes for local vibrational modes in semiconductor alloys. Here we report data for the local vibrational mode of oxygen in SiGe alloys. This system has been chosen in view of the huge amount of information already available on oxygen in the two extreme materials, crystalline silicon ($x = 0$) [1] and crystalline germanium ($x = 1$) [2]. We begin by reviewing the relevant data for Si:O, then present new data for the other extreme, Ge:O, and then consider SiGe alloys.

Throughout, the measurements have been made using transient bleaching (pump-probe) methods. A free-electron laser has been tuned to the energy of the local vibrational mode. The intensity of a pulse of the radiation is split into two parts, with most ($\sim 95\%$) hitting the sample in the 'pump' pulse. This pulse excites some of the optical centres and so partially depletes the ground state of the mode. The small residual fraction ($\sim 5\%$) of the pulse is again split into two components, the 'probe' and the 'reference'. The probe pulse is delayed by a variable extra path length so that it arrives after the pump pulse. The probe pulse is absorbed as it passes through the sample, the absorption depending on the population of the centres in their ground state. As the time delay increases—more of the centres relax to the ground state, and so the absorption increases—the transient-bleaching technique measures the re-population of the ground state. Finally, since the measurements are of the intensities of the

light, a correction is made for any fluctuations in intensity of the free-electron laser by measuring the intensity of a reference pulse, which has been further delayed until all the centres are in the ground state. In this work, decay times of > 10 ps were measured, Fig. 1, corresponding to a spectral spread of $\sim 0.5\text{ cm}^{-1}$ in the excitation pulses.

2. Oxygen in silicon

Most of the vibrational properties of isolated oxygen atoms can be described in terms of a Si–O–Si structure, with the O atom at a (time-averaged) bond-centred position in D_{3d} symmetry [3]. Three modes of vibration concern us. One is a low energy mode, ν_2 , in which the O atom vibrates transversely across the trigonal axis. A second, important mode, is at 1136 cm^{-1} , and is used as to determine the concentration of oxygen in silicon. In this ν_3 mode, the O atom moves along the trigonal axis, in anti-phase with the two Si atoms. Its transient-bleaching decay time depends on the isotopes of the oxygen and of the neighbouring Si atoms, with values of 4–30 ps being recorded for ^{28}Si – ^{17}O – ^{28}Si [4] to ^{30}Si – ^{16}O – ^{30}Si [5]. The reason for the isotope dependence is that the dominant decay mode when one ν_3 quantum is excited is by creating a quantum of the third localised mode, ν_1 , of energy $\sim 612\text{ cm}^{-1}$. The difference, $\nu_3 - \nu_1 \sim 524\text{ cm}^{-1}$, is close to the maximum vibrational frequency of the silicon lattice, 524.7 cm^{-1} [6], and so is in a region of rapidly changing (or even zero) density of phonon states. The precise value of $\nu_3 - \nu_1$ relative to the maximum vibrational frequency is therefore critical in determining the decay time of the ν_3 mode [5].

This analysis shows that Si:O is an example of a centre where a significant amount of the vibrational energy can be transferred to

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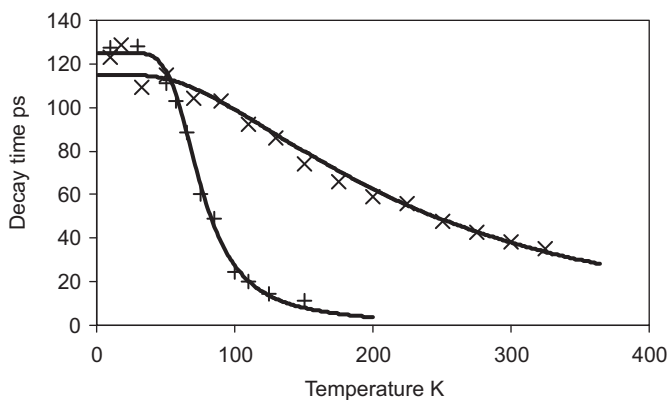


Fig. 1. Measured decay times in Ge (+) and in a $\text{Si}_{1-x}\text{Ge}_x$ alloy with $x = 0.039$ (x). The lines are calculated using Eq. (1) for Ge and Eq. (2) for SiGe.

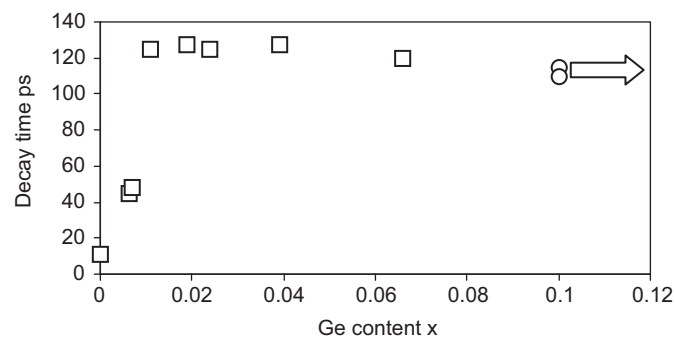


Fig. 2. Measured decay times at low temperature (~ 10 K) for the ν_3 line in $\text{Si}_{1-x}\text{Ge}_x$ alloys as a function of the alloy composition x . The values for Ge, $x = 1$, (shown by circles) are schematically included at $x = 0.1$. For the Ge data, the higher point is for ^{16}O , and the lower for ^{18}O . The uncertainty is about $\pm 8\%$.

a lower energy local mode—other examples are some of the Si:H centres—where involving a second local vibrational mode can reduce the decay time by two orders of magnitude compared to other Si:H centres [7].

The two-phonon decay involves high energy phonons of 524 and 612 cm^{-1} and so is only weakly temperature dependent. In addition to this dominant decay mode, a second decay channel occurs with a time at low temperature of 27 ps. It is this slower channel that determines the temperature dependence. The probability of emitting three phonons of frequency ω_1 , ω_2 and ω_3 depend on the product $(1+n_1)(1+n_2)(1+n_3)$ where n is the Bose–Einstein population term $n = 1/[\exp(\hbar\omega/kT) - 1]$. However, it is possible to re-populate the ν_3 mode by absorbing three phonons, with a probability depending on $n_1n_2n_3$. Consequently, with increasing temperature, the decay rate $1/\tau$ increases at a rate given by the difference [8]

$$1/\tau = [(1+n_1)(1+n_2)(1+n_3) - n_1n_2n_3]/\tau_0 \quad (1)$$

Here τ_0 is the decay time at 0 K. The fit to the data is excellent, Fig. 1, with values for the three phonons of 612, 489 and 35 cm^{-1} . The first value has been fixed at the ν_1 frequency, and since energy must be conserved, there is only an adjustable frequency. The value of 35 cm^{-1} is close to the ν_2 frequency, giving the appealing model that the ν_3 local mode can decay into ν_1 and ν_2 local modes, plus one lattice phonon.

3. Oxygen in germanium

There is one published measurement of the transient bleaching time for Ge:O [4], showing that at low temperature, Ge: ^{16}O decays with a time of 125 ± 10 ps. We have confirmed that measurement, extended the temperature range, and found that the decay time is independent of the isotope of oxygen (Fig. 2). The ν_3 mode of, Ge: ^{16}O has an energy of 862 cm^{-1} , and the ν_1 mode has 412 cm^{-1} . Again, it is reasonable to expect that the decay of the ν_3 mode will involve the ν_1 mode, since both are highly localised on the Ge–O–Ge ‘molecule’. But in contrast to Si:O in Ge the difference $\nu_3 - \nu_1$ considerably exceeds the maximum lattice frequency (307 cm^{-1}), and so two lattice modes must also be emitted. The total three-phonon process is expected by the ‘frequency-gap rule’ [7] to be slower than the two-phonon process in Si:O, as is observed [5]. Another consequence of the larger value of $\nu_3 - \nu_1$ is that the decay time is independent of the isotopes of oxygen or germanium. For example, when the oxygen isotope is changed to ^{18}O , ν_3 in Ge:O is reduced to 819 cm^{-1} [4], ν_1 to 401 cm^{-1} [9], and the difference $\nu_3 - \nu_1$ is still sufficiently above the maximum lattice frequency

that the decay time is unchanged, as reported in Fig. 2. The simplest description of the temperature dependence of the ν_3 mode is to assume that only ν_1 and two lattice modes are involved in the decay. The decay rate is then fitted using Eq. (1), resulting in an excellent fit, Fig. 1.

Oxygen in germanium is evidently a good example of a system in which there is one well-defined decay process, in this case involving three phonons. The temperature dependence, the isotope-invariance, and the relatively long decay time, compared to Si:O, are all consistent with this simple picture.

4. Oxygen in silicon–germanium

There are no published data for the transient-bleaching decay time of oxygen in SiGe alloys. At low temperature we find three surprising results:

- at low temperature, the decay time increases very rapidly with Ge content, Fig. 2, so that already at 1% Ge, the decay time is 125 ± 15 ps, very similar to that of Ge:O;
- however, the decay time in SiGe has a distinctly different dependence on temperature compared to that in Ge, Fig. 1; and
- the decay time is independent of the wavelength of the excitation in the alloy-broadened ν_3 absorption band.

First, we take the temperature dependence, Fig. 1. It is not possible to fit the data using a two- or a three-phonon process in the form of Eq. (1). The simplest explanation is that at low temperature, the decay is controlled by the emission of three phonons of sufficiently high energy that they do not contribute significantly to the temperature dependence. To obtain a fast decrease in decay time near 60 K, we assume that another decay mode is important, involving four phonons, with one of the phonons being absorbed from the lattice. The temperature dependence of this four-phonon process is predominantly determined by the product $(1+n_4)(1+n_5)(1+n_6)n_7$. Here, the first three terms describe the emission of three phonons, and the final term is the population of the phonon states to be absorbed; again n is the Bose–Einstein population term. With these assumptions, the total decay rate is then given by a three-phonon process, as in Eq. (1), which we have assumed to be almost constant at a rate r , and the four phonon term. The decay rate is then

$$1/\tau = [r + (1+n_4)(1+n_5)(1+n_6)n_7]/\tau_0 \quad (2)$$

where τ_0 is the decay time at 0K. The fit is then excellent, with values for the three emitted phonons of 612, 446 and 351 cm^{-1} , and 273 cm^{-1} for the absorbed phonon. The temperature dependence illustrates that the decay of ν_3 in SiGe is very different from that in Ge, and the long decay times show that the decay modes are completely different from those in Si.

To understand the differences, we first consider the perturbations of the oxygen vibration by the Ge atoms in the dilute alloys.

5. Perturbations of the ν_3 mode by germanium

It has long been known that in dilute alloys, $x < 0.03$, the 1136 cm^{-1} line that is seen at low temperatures in Si divides into three distinct lines, labelled O-I, O-II and O-III [10–12]. O-I occurs very close to 1136 cm^{-1} , O-II is at $\sim 8\text{ cm}^{-1}$ lower energy, and O-III at $\sim 16\text{ cm}^{-1}$ below O-I. The precise values depend on the Ge content, but in our sample of highest Ge, $x = 0.066$, the frequency of the O-III line is only perturbed by 1.4% from 1136 cm^{-1} , the perturbations to the energies are small. The lines are generally assigned as follows. O-III is produced when one Ge atom is in the second-neighbour position to the O atom, giving a configuration like Si–O–Si–Ge. The less-perturbed O-II has the configuration Si–O–Si–Si–Ge, with one Ge atom in the third-neighbour position. The sharpest peak (O-I) at the high energy side is similar to the 1136 cm^{-1} line of Si:O, with no Ge atoms in the second or third neighbour positions. The three lines are broadened by the random distribution of Ge atoms that are more distant from the O atom. There are no reports of the ' 1136 cm^{-1} ' band in SiGe alloys with a Ge atom in the first neighbour position, in agreement with predictions that the formation energy for a Ge atom in the immediate neighbour configuration, Si–O–Ge, is 0.7 eV higher than for O-I, O-II and O-III [13].

Evidently, the fast two- and three-phonon processes that occur in Si are quenched at the configurations found in the SiGe alloys, even though the first-order perturbations to their energies are small. However, one significant change in the absorption is that there is no coupling of the ν_3 and ν_2 modes in the O-II and O-III configurations. The effect of this is seen in the bandshape at 77 K. In Si, multiple structure occurs on the low energy side of the 1136 cm^{-1} line. It is well known that this structure is caused by population of the low energy ν_2 mode, and (crucially) that the coupling of ν_2 and ν_3 results in significant differences in energy of the ν_2 levels when the ν_3 mode is excited. The loss of that structure in the SiGe alloys is caused by the rapid quenching of the coupling at the Ge content increases. Measurements on the intensity of the combination band seen at $\nu_3 + \nu_2 = 1205\text{ cm}^{-1}$, also demonstrate that the coupling between ν_3 and ν_2 is effectively quenched to zero at the O-II and O-III configurations. Reduced coupling of ν_3 and ν_2 has been reported in SiGe alloys with small Ge contents by Yamada-Kaneta [12] and also in crystalline silicon under hydrostatic stress [14]. Its importance here is that the three-phonon process found in Si with a low temperature decay time of $\sim 27\text{ ps}$, and which requires coupling of the ν_3 and ν_2 modes, becomes forbidden in SiGe alloys for the O-II and O-III configurations.

We have not yet explained the loss of the two-phonon process for all the configurations, nor the quenching of the 27 ps process for the O-I configuration. To understand the increased lifetime, we evidently need to look outside the Si–O–Si 'molecule'.

6. Perturbations of the lattice modes

The energy in the ν_3 mode must eventually be emitted into the lattice, and so the 'lattice' frequencies of the alloy are important.

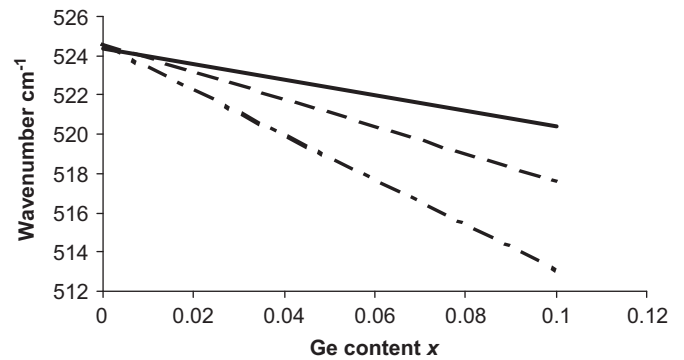


Fig. 3. The solid line shows the value of $\nu_3 - \nu_1$ in $\text{Si}_{1-x}\text{Ge}_x$ alloys as a function of the alloy composition x . This energy must be emitted into lattice modes. The broken line is the trend of the measured data for the highest Raman frequency [15]. The chain line is the change in the maximum frequency using the mean fractional shift rate from the two-phonon absorption bands in $\text{Si}_{1-x}\text{Ge}_x$.

However, which vibrational frequencies should be used is not clear at present. When Ge atoms are included in silicon, the maximum frequency of vibration of the lattice is reduced from 524 cm^{-1} at $x = 0$ to 307 cm^{-1} at $x = 1$. In Fig. 3 we estimate the changes in the maximum frequency. The broken line shows the trend from Ref. [15] for the Raman Si–Si vibration, which emphasises the local Si–Si bonds. To use more general modes, we have measured the energies of the clearly defined features in the two-phonon absorption spectrum of the alloys. The chain line shows the mean rate of the fractional change in frequency, $\Delta\omega/\omega = -0.22x$. The virtual crystal approximation (not shown) would predict a much faster decrease at the rate of about $-400x\text{ cm}^{-1}$. In contrast, the ν_3 and ν_1 modes are little changed in our range of x , $x < 0.066$. From fits to the bandshapes, we measure $d\nu_3/dx = -40\text{ cm}^{-1}$. The ν_1 mode is infra-red inactive, but the combination band $\nu_3 + \nu_1$ is weakly observable, and the frequency of the ν_1 mode appears to be independent of x , as predicted [13]. We recall from Section 2 that in Si:O, the residual energy $\nu_3 - \nu_1$ is emitted as lattice phonons, leading to the critical dependence of the decay time on the frequencies. If $\nu_3 - \nu_1$ is less than the maximum lattice frequency ν_{max} , then only one lattice mode needs to be emitted, but if $\nu_3 - \nu_1 > \nu_{\text{max}}$ then two lattice modes must be created, increasing the decay time. When $x = 0$ we expect $\nu_3 - \nu_1$ to lie in the one-phonon continuum of the crystal (Section 2). Taking the long-range one-phonon continuum to be represented best by the changes in the two-phonon absorption spectrum, $\nu_3 - \nu_1$ emerges from the one-phonon continuum at $x \sim 0.0026$. For larger values of x , a three-phonon process would be required for the decay, resulting in lengthened decay times. The values appear to be qualitatively consistent with the plot in Fig. 2.

7. Summary

We have presented the first data for the transient-bleaching decay time of the ν_3 band of oxygen in SiGe alloys, and as part of the study have extended the data for oxygen in crystalline silicon and germanium. In contrast to Si:O, where the decay is critically dependent on the exact frequencies of the ν_3 and ν_1 modes, the decay process for Ge:O involves three phonons, is independent of the isotope of oxygen, and has a simple temperature dependence that is consistent with the three-phonon decay. In SiGe alloys, even with only 1% of Ge, the decay time is equal to that in Ge, and is independent of excitation into the O-I, O-II or O-III bands produced by different levels of perturbation of the oxygen. For O-I, the energies of the ν_3 and ν_1 modes are little changed by the

random distribution of Ge, but the lattice modes are reduced in energy sufficiently to convert the two-phonon decay of Si:O into a three phonon decay, lengthening the decay time. For O-II and O-III the three phonon process found in Si is quenched by the reduction in the coupling of the ν_3 and ν_1 modes.

Detailed molecular modelling will be required to understand why the O-II and O-III configurations do not decay by two-phonon emission.

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