Decay mechanism of the ν_3 865 cm^{-1} vibration of oxygen in crystalline germanium

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The ν_3 (862.5 cm^{-1}) vibration of oxygen in crystalline germanium is shown to decay into one ν_1 local mode of the oxygen center plus two lattice modes. This description predicts *increases* in the linewidths in ^{16}O-doped germanium, and *decreases* in the linewidths in ^{18}O-doped germanium, as the Ge mass in the Ge-O-Ge complex increases, in agreement with observation. The decay time is expected to vary only slightly with the isotope of oxygen, as observed, and the smallest reported linewidths are consistent with the measured decay times.

Oxygen can be present in both crystalline germanium and crystalline silicon as isolated, bond-centered interstitial atoms, with the O atom significantly off axis in the case of Ge.[1] In silicon, the asymmetric ν_3 vibrational mode occurs when the O atom moves along the $\langle 111 \rangle$ axis in antiphase with the two immediately neighboring Si atoms. It has a quantum of 1136 cm^{-1} for ^{16}O in silicon of natural isotopic abundance. The equivalent motion in germanium has 862.5 cm^{-1}, with considerable structure from the isotopes of Ge.[2,3] In both Si and Ge, the frequencies of the ν_3 modes are more than twice the maximum frequencies of the lattices (524 cm^{-1} for Si and 307 cm^{-1} for Ge). Consequently, we might expect them both to decay into three lattice modes, as was assumed initially.[4,5] However, subsequent work established that in Si of natural isotopic abundance, the primary decay channel of the ν_3 mode is into two phonons.[6] One phonon is the symmetric ν_1 local mode of the Si-O-Si complex, with an energy of 612 cm^{-1}, in which the O atom is static and the two Si atoms vibrate in antiphase. The second phonon is a lattice mode of energy $(1136-612)$ cm^{-1} $=524$ cm^{-1}. The similarity of the lattice mode and the cutoff frequency of the Si lattice results in a strong isotope dependence of the decay time of the ν_3 mode.[6]

The aim of this work is to investigate the decay of the ν_3 mode in germanium. To date, the only measurement of the decay time of the ν_3 vibration in crystalline germanium has been for ^{16}O at 10 K, giving a value of 125 ± 10 ps.[4] It was assumed that the decay was into three lattice modes. In the present work, we report the temperature dependence of the ν_3 mode in Ge. We will show that the data are best fitted if ν_3 decays into two lattice modes plus one ν_1 local mode of the Ge-O-Ge complex. This model predicts the observed opposite trends of the widths of the ν_3 bands in ^{16}O-doped and ^{18}O-doped natural-isotope germaniums as the Ge mass increases. The smallest reported linewidths are shown to be consistent with the measured decay times. We will also report that τ is almost independent of the isotope of oxygen, in contrast to the situation in silicon.[6]

Two oxygen-doped germanium crystals have been used. Both crystals have the natural isotopic abundance of Ge. One

contained ^{16}O at a concentration of 5×10^{17} cm^{-3} and the other had 6×10^{16} cm^{-3} ^{18}O and 1.5×10^{16} cm^{-3} ^{16}O, where the calibration of Litvinov *et al.*[7] has been used to convert the infrared absorption into oxygen content. The decay time measurements were performed using the Dutch free-electron laser (FELIX) at Nieuwegein in the Netherlands. FELIX delivers macropulses with a length of 4 μs at a repetition rate of 5 Hz. Each macropulse consists of a train of micropulses of duration 5 ps and 25 MHz repetition rate.[8] 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 (MCT) detector.[9] The same lifetimes were measured when substantially smaller beam power was obtained using a pulse-slicing technique to pick individual micropulses from the burst. All the data shown here were taken with the full macropulse to give better signal-to-noise ratios. Given the pulse linewidth of ~ 1 cm^{-1} and the measurement temperatures of over 10 K, the measured decay times are averaged over the different combinations of Ge isotopes.

The decay of the ν_3 vibration of O in Ge is single exponential over 2 orders of magnitude (Fig. 1). We verify the previous measurement of the lifetime for ^{16}O at low temperature of 125 ± 10 ps.[4] The temperature dependence of the decay time is shown in Fig. 2 for ^{16}O. Also shown on Fig. 2 is the decay time at low temperature for ^{18}O. In contrast to Si, there is no significant dependence of the decay time on the isotope of oxygen.

To identify the phonons involved, we use the temperature dependence of the decay time. Germanium has five stable isotopes, so that 15 combinations of isotopes occur in the Ge-O-Ge local structure when the crystal is made of natural-isotope Ge, as here. For ^{16}O in Ge, ν_3 lies at $\hbar\omega_a$ $=862.5 \pm 1.5$ cm^{-1}, the spread being determined by the isotopic mixture of Ge in the Ge-O-Ge "molecule."[2] In *silicon*, the ν_3 vibration decays predominantly with the emission of one ν_1 local mode plus one or more lattice modes.[6] First, we
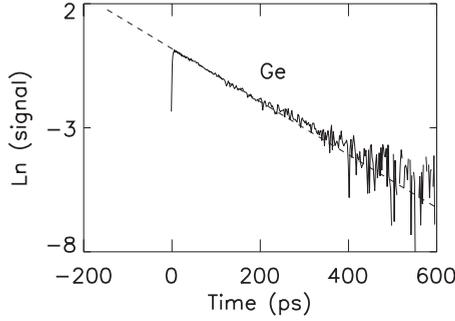
FIG. 1. The measured transient-bleaching curves at 10 K for Ge: ^{18}O. The broken line is the fit of a single-exponential decay, extrapolated to negative time for clarity. The decay time for this particular measurement was 101 ps.

will apply that model to Ge. For specific values, we will work with the isotope combination ^{70}Ge-^{16}O-^{70}Ge; the effects of changing the Ge isotopes will be discussed in detail later, but the conclusion here is independent of the isotopic combination. For ^{70}Ge-^{16}O-^{70}Ge, the asymmetric ν_3 mode has $\hbar\omega_a$=863.9 cm^{-1} (Ref. 2) and the symmetric ν_1 mode has $\hbar\omega_s$=411.2 cm^{-1}.[1] The difference $\hbar\omega_a-\hbar\omega_s$ =452.7 cm^{-1} lies well above the cutoff frequency at 307 cm^{-1} of the Ge lattice and the decay of ν_3 into ν_1 also requires the emission of (at least) two lattice phonons. If, at all temperatures, the decay process occurs through one dominant decay channel, the decay rate $1/\tau$ of the ν_3 vibration is expected to depend on temperature T as $1/\tau(T)=f(T)/\tau(0)$ where[10]

$$f(T) = \frac{[\exp(\hbar\omega_a/kT) - 1]}{\Pi_{i=1}^3[\exp(\hbar\omega_i/kT) - 1]}. \quad (1)$$

The continuous line on Fig. 2 is calculated with one of the modes, say mode 1, fixed as the ν_1 mode, $\hbar\omega_1$=411 cm^{-1}. Energy conservation requires that for any chosen $\hbar\omega_2$, the value of $\hbar\omega_3$ is $\hbar\omega_3=\hbar\omega_a-\hbar\omega_s-\hbar\omega_2$. The temperatu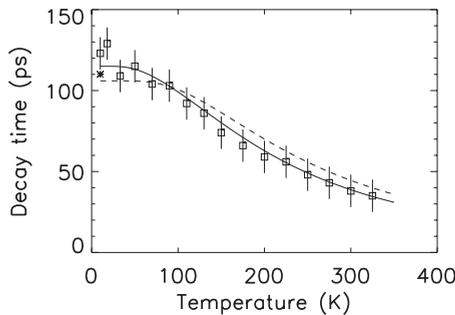re dependence of the decay time is then determined by one adjustable parameter, $\hbar\omega_2$. Fitting Eq. (1) to the data in Fig. 2 yields $\tau(0)$=115±2 ps and $\hbar\omega_2$=144 cm^{-1}. An alternative model, suggested by Sun *et al.*,[4] is that the ν_3 mode decays into three *lattice* modes. The temperature dependence is then determined by two adjustable frequencies, say $\hbar\omega_1$ and $\hbar\omega_2$. Energy conservation then gives $\hbar\omega_3=\hbar\omega_a-\hbar\omega_1-\hbar\omega_2$. The best fit is obtained when $\hbar\omega_1$ and $\hbar\omega_2$ are 307 cm^{-1} and $\hbar\omega_3$=248 cm^{-1}.

The fit obtained with the local-mode model is the better, with a squared deviation 4 times smaller than for the lattice-mode model. In both cases, the fitting process results in the lattice modes having their maximum values, so that the frequency of the remaining mode is as low as possible. The temperature dependence is predominantly determined by that one low-frequency mode. Neither of the low-frequency modes lies in a high density of states of the lattice phonons,[11] although 248 cm^{-1} is close to a resonance predicted for oxygen in germanium.[1] To determine which decay model is appropriate, we will use isotope data.

In natural-isotope germanium doped with ^{16}O, the width of the ν_3 absorption line is observed to increase with increasing Ge mass in the Ge-O-Ge complex.[12] Recent measurements by Pajot for the combinations ^{70}Ge-^{16}O-^{70}Ge and for ^{76}Ge-^{16}O-^{74}Ge gave widths at 1.6 K of ∼0.030 and ∼0.045 cm^{-1}, respectively.[13] The frequencies of the ν_3 modes for these two structures are, respectively, 863.9 and 861.4 cm^{-1}.[5] If the ν_3 mode decays into three lattice modes, we need to compare these values to the three-phonon density of states. The three-phonon density of states is shown in Fig. 3, calculated using convolution integrals from the 300 K one-phonon density of states[11] with allowance for the 2% increase in phonon frequencies at low temperature. A vertical line on the figure indicates the position of the ^{16}O 863.9 cm^{-1} frequency. The three-phonon densities of states are the same to ±1% at 861.4 and 863.9 cm^{-1}. Given the similarity in the densities of states and the weak selection rules for three-phonon processes, the decay times would be expected to be very similar, in contradiction to experiment. If the ν_3 mode decays into one ν_1 mode and two lattice modes, we need to compare the difference in frequencies $\hbar\omega_a-\hbar\omega_s$ of ν_3 and ν_1 to the two-phonon density of states. The ν_1

FIG. 2. Squares show the lifetime τ of the ν_3 vibration of Ge: ^{16}O as a function of temperature. The continuous line is the best fit of Eq. (1) for the local-mode case with $\hbar\omega_1=\hbar\omega_s$=411 cm^{-1} and two adjustable parameters $\tau(0)$=115±10 ps and $\hbar\omega_2$=144 cm^{-1}. The broken line is the best fit for the three-lattice mode case with three adjustable parameters, giving $\tau(0)$=106 ps, $\hbar\omega_1$=307 cm^{-1}, and $\hbar\omega_2$=307 cm^{-1}. Star shows the decay time for ^{18}O, 110±10 ps.
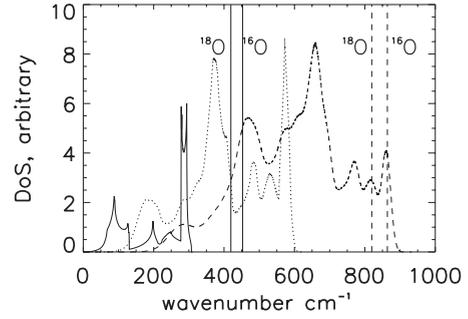

FIG. 3. The density of phonon states is shown by the solid line (Ref. 11). The densities of states for two phonons and three phonons are shown, respectively, by dotted and broken lines, arbitrarily scaled for clarity. The broken vertical lines at 863.9 and 819.6 cm^{-1} indicate the frequencies of the ν_3 modes for ^{16}O and ^{18}O and the solid vertical lines at 452.7 and 419.4 cm^{-1} are for the differences in frequencies, $\nu_3-\nu_1$. The values plotted are for ^{70}Ge-O-^{70}Ge.

mode is more sensitive to the isotope of Ge than is the ν_3 mode, where the motion is dominated by the O atom. The differences of $\hbar\omega_a - \hbar\omega_s$ are, respectively, 452.7 and 457.8 cm^{-1} for ^{70}Ge-^{16}O-^{70}Ge and ^{76}Ge-^{16}O-^{74}Ge.[1] The line at 452.7 cm^{-1} on Fig. 3 lies on an increasing part of the two-phonon density of states leading to the peak near 480 cm^{-1} produced by the combination of acoustic (200 cm^{-1}) and optic modes. The total two-phonon density of states increases by 13% between 452.7 cm^{-1} for ^{70}Ge-^{16}O-^{70}Ge and 457.8 cm^{-1} for ^{76}Ge-^{16}O-^{74}Ge, implying a shorter decay time and a larger linewidth with increasing Ge mass, qualitatively as observed. There is poor quantitative agreement between the observed 50% increase and the 13% change expected from the two-phonon density of states, possibly implying the importance of phonon selection rules in the decay. Nevertheless, the local-mode model predicts a significant change, in contrast to the lattice-mode model.

The opposite dependence on the Ge mass is observed in natural-isotope germanium doped with ^{18}O. Here, the width of the ν_3 absorption line for the ^{70}Ge-^{18}O-^{70}Ge structure is observed to be greater than the linewidth for ^{76}Ge-^{18}O-^{74}Ge.[5] A reanalysis by Pajot for the combinations ^{70}Ge-^{18}O-^{70}Ge and for ^{76}Ge-^{18}O-^{74}Ge gave widths at 6 K of $\sim$0.06 and $\sim$0.05 cm^{-1}, respectively: the change is small but real.[13] The frequencies of the ν_3 mode for these two structures are, respectively, 819.6 and 816.9 cm^{-1}.[5] A vertical line on Fig. 3 indicates the position of the ^{18}O 819.6 cm^{-1} frequency. There is a negligible, less than ±1%, change in the three-phonon density of states between 819.6 and 816.9 cm^{-1}. For the local-mode model, we again compare the difference in frequencies $\hbar\omega_a - \hbar\omega_s$ of ν_3 and ν_1 to the two-phonon density of states. Coutinho *et al.*[14] calculated that the ν_1 mode is reduced in frequency by 11 cm^{-1} for ^{18}O compared to ^{16}O (when the same isotopes of Ge are considered). The value of $\hbar\omega_a - \hbar\omega_s = 419.4$ cm^{-1} is indicated on Fig. 3. The frequency of the ν_1 mode is known from experiment to decrease by 7.7 cm^{-1} between ^{70}Ge-^{16}O-^{70}Ge and ^{76}Ge-^{16}O-^{74}Ge and we would expect that the shift would be very similar between ^{70}Ge-^{18}O-^{70}Ge and ^{76}Ge-^{18}O-^{74}Ge, as confirmed by calculation.[14] Consequently, $\hbar\omega_a - \hbar\omega_s$ is 5.0 cm^{-1} smaller for the ^{70}Ge-^{18}O-^{70}Ge structure than for ^{76}Ge-^{18}O-^{74}Ge. These values lie on a rapidly changing part of the two-phonon density of states (Fig. 3) and the density for ^{70}Ge-^{18}O-^{70}Ge is 50% higher than for ^{76}Ge-^{18}O-^{74}Ge, qualitatively in agreement with the $\sim$20% larger linewidth. Again, qualitative agreement is obtained if ν_3 decays into the local ν_1 mode, plus two lattice modes, but not if the decay is into three lattice modes.

In this discussion, we have assumed that the linewidth is determined primarily by the decay time. We have seen that our measurement of the decay time is an average over the different isotope combinations. It is also an average over the fine structure resulting from thermal population of the low-energy rotational modes of the O atom. Averaging over the

fine structure is expected to have little effect since the dipole moment of the ν_3 mode is almost independent of the low-energy rotational mode. The average over the isotopes gives the minimum average width Γ of the absorption lines. Using $\Gamma = 1/2\pi c\tau$, with $\tau = 115$ ps, the calculated width is $\Gamma = 0.046$ cm^{-1}, closely in agreement with the high-resolution experimental measurements quoted above for ^{16}O and ^{18}O.

We noted that, in contrast to silicon, there is little dependence of τ on the isotope of oxygen: the decay time for Ge:^{18}O is 110 ± 10 ps, possibly slightly shorter than the 115 ± 10 ps for ^{16}O (Fig. 2). A shorter decay time would be qualitatively consistent with the larger linewidths reported above for ^{18}O. The three-phonon density of states is $\sim$35% higher at ν_3 for ^{16}O than for ^{18}O (Fig. 3), suggesting that the decay times for ^{16}O and ^{18}O would be significantly different if the decay was into three lattice modes. In contrast, the differences $\hbar\omega_a - \hbar\omega_s$ lie in very similar densities of two-phonon states, consistent with the observed very similar decay times. However, this argument raises a question we cannot answer: the value for ^{18}O lies on the tail of the combination of two optic modes, while the value for ^{16}O is in a region where the combination of one high-frequency acoustic mode and one optic mode is becoming significant. Surprisingly, the specific modes do not seem to be important here.

Finally, the decay of the ν_3 mode of Ge:O into three phonons results, qualitatively, in τ being 1 order of magnitude larger than the value of 11 ps observed in Si. This qualitative result is consistent with recent discussions of the frequency-gap law, where the decay time increased by about 1 order of magnitude for each additional phonon that had to be emitted.[15] In order for one of the phonons to be the ν_1 local mode, the ν_3 and ν_1 modes must be coupled. Independent evidence for the coupling of ν_3 and ν_1 is well known from the observation of the $\nu_3 + \nu_1$ combination band at 1270 cm^{-1} (from which the frequencies quoted above of the ν_1 mode are found[1]).

To summarize, data are consistent with the ν_3 vibration of oxygen in germanium decaying by the creation of three phonons, one of which is the ν_1 local mode and with $\tau \sim 115$ ps at low temperature. This model is consistent with the increase in linewidth in Ge-^{16}O-Ge as the Ge mass increases and with the opposite trend in Ge-^{18}O-Ge. The value of τ is consistent with the magnitude of the observed linewidths of the absorption lines at low temperature.

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