Lattice isotope effects on optical transitions in silicon

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We report the changes with lattice isotope of the energies of the zero-phonon lines (ZPLs) and some of the local vibrational modes (LVMs) of commonly encountered radiation-damage centers in silicon. On changing from ^{nat}Si to ^{30}Si, ZPLs of the different centers shift by +0.8 to +1.8 meV. The carbon-oxygen "C" center is taken as the primary example. For this center, the measured changes in the frequencies of the LVMs in the electronic ground state of the center agree closely with the results of density functional theory (DFT). We suggest that the LVM frequencies in the excited state can be obtained from DFT calculations of the positive charge state. The effect on the ZPL is broken into three parts. The dependence of the ZPL on the isotopically induced change in the LVMs and in the lattice volume is shown to be small compared to the effects of the electron-phonon coupling to the continuum of lattice modes. This dominant effect can be found, in principle, from the temperature dependence of the energy of the ZPL, but data can only be measured over too small a temperature range. We suggest that an estimate of the isotope effects can be derived by rescaling the appropriate data for the indirect energy gap. This simple empirical approach reproduces the measured isotope shifts of the ZPLs of the "C" and "P" centers within $\sim 10\%$, of the "I" and "T" centers within $\sim 30\%$, and within a factor of 2 for the "G" center.

I. INTRODUCTION

There is intense interest in the properties of isotopically controlled silicon.[1] Optical studies have been carried out on isotope superlattices,[2] and studies of bulk silicon have included the effect of the host isotope on the localized modes of interstitial oxygen,[3] the indirect energy gap,[4] the properties of excitons bound to shallow donors and acceptors,[5] the ionization energy of the shallow centers,[6] and the ground-state splitting[6] and isotopically induced inhomogeneous line-broadening of transitions at shallow centers.[7] In this paper we present experimental data on the effect of changing the lattice isotope on the zero-phonon lines (ZPLs) and the local vibrational modes (LVMs) of some of the *deep* radiation-induced centers in silicon. For these centers, the results add to the values in the literature for the effects of changing the carbon, hydrogen, and oxygen isotopes. A comparison with the results of *ab initio* calculations shows that the isotope effects on LVMs observed in photoluminescence (in the ground electronic state of the defect) may be calculated with high precision. However, current density functional modeling cannot predict the isotope effects on the electronic transitions of deep defects. To describe these effects, we need, first, the response of each transition to changes in volume, which is known for most of the transitions of interest. Second, we need to know the properties of the LVMs in the ground and excited electronic states; these data are not readily available for most of the transitions, the notable exception being the C-line which will be used as the primary example here. Finally, we need detailed information on the coupling of the electrons at each defect to the continuum of lattice vibrations, and this information is not available. Here we use two approaches. One is to exploit the structure of the excited states of luminescent centers in silicon, which often consist of one loosely bound charge (say an electron) orbiting an opposite, highly localized charge (a hole). For these centers we can use the (positively) charged state of the center to indicate the properties of the excited state of the neutral center. The second approach is to proceed empirically using the measured temperature dependence of the energy of the transition, which occurs through the same electron-phonon coupling as that causing the isotope shift. This approach requires data on the energy of the transition over an appreciable temperature range so that all the modes of vibration are sampled. In silicon, the luminescence from ZPLs is typically quenched by nonradiative processes at relatively low temperatures, less than ~ 100 K, and absorption measurements are made difficult by the low oscillator strengths of the transitions.[8] In contrast, data are available for the temperature dependence of the lowest indirect energy gap of silicon over a sufficient temperature range.[9] We show that the change, with isotope, of the energy gap can be described accurately with a simple parametrization of the electron-phonon coupling, plus an explicitly calculated expansion

term (Sec. III). To obtain an approximate description of the electron-phonon coupling at deep defects, we note that the vibronic band shapes of the transitions considered here all involve coupling to a continuum of acoustic and optic lattice modes. This observation suggests that we can use the temperature dependence of the energy of the ZPL to rescale the electron-phonon coupling of the energy gap, and hence predict, with no adjustable parameters, the isotope shift of the ZPL.

Taking the well-known "C" center as the primary example, we show that the lattice-isotope effects on the LVMs can be predicted accurately by density functional modeling (see Sec. V A). We show in Sec. V B that the isotope-induced shift of the ZPL may be estimated closely by using the experimental and theoretical data for the LVMs, the rescaled electron-phonon coupling, and the lattice-volume change. The analysis shows that the dominant contribution to the isotope shift comes from the coupling of the electronic states to the continuum of lattice phonons in the crystal. Consequently, although there are insufficient data for a full analysis for other defects, the shifts for other ZPLs may be predicted approximately from only the temperature dependence of the ZPL (see Sec. VI). However, we emphasize that it is not expected to be a universal rule, and for one common center it is valid only within a factor of 2 (see Sec. VI B).

We begin by describing the experimental arrangements (see Sec. II).

II. EXPERIMENTAL DETAILS

The Si sample used in this work was isotopically enriched Czochralski ^{30}Si with abundances ^{28}Si (0.67%), ^{29}Si (0.59%), and ^{30}Si (98.74%), giving a mean mass number of $\bar{M}(^{30}\text{Si}) = 29.98$. The sample contained substitutional carbon at a concentration of $[\text{C}] \approx 10^{17}$ cm^{-3}, interstitial oxygen at $[\text{O}] = 8.8 \times 10^{17}$ cm^{-3}, and substitutional boron at $[\text{B}] = 5.5 \times 10^{16}$ cm^{-3}. Measurements were made on the sample as-grown. It was then irradiated with 1.5 meV electrons to a dose of 10^{17} cm^{-2} at nominal room temperature on a water-cooled copper block, and spectra were taken at stages of annealing up to 900°C, when the damage was fully removed.

All the photoluminescence (PL) data reported here were collected with the samples mounted in a strain-free manner and either immersed in liquid helium at 4.2 K, or held in a helium drip-feed cryostat for variable-temperature measurements with a temperature-sensitive diode in close thermal contact. Temperatures are believed to be accurate to ±1 K. Spectra were collected using a Bomem DA8 Fourier transform spectrometer fitted with a KBr beam splitter and a North-Coast fast-response Ge diode detector cooled to 77 K. The PL was generated by the 514.5 nm line of an Ar$^+$ laser with an output power of ~300 mW, about half of which was delivered at the sample.

III. INDIRECT ENERGY GAP

The electron-phonon coupling of a defect center can be found from the temperature dependence of the energy of its
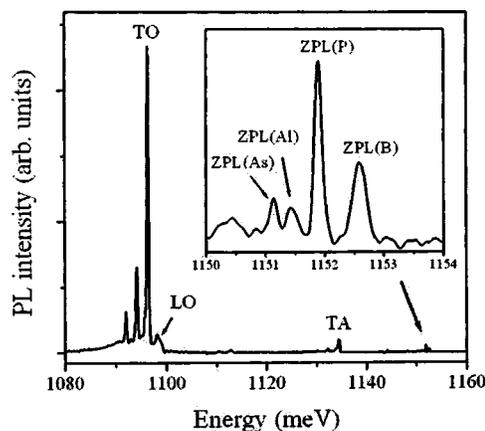

FIG. 1. Photoluminescence from Czochralski-grown isotopically enriched ^{30}Si. The ZPL region is expanded in the inset. TA, LO, and TO label the wave-vector conserving phonon sidebands which are predominantly created by the boron. The spectra are not corrected for the spectrometer response.

ZPL. However, as noted in Sec. I, it is not possible to make the measurements over a sufficient range of temperature that all the relevant phonon states are sampled. We therefore begin by considering the lowest indirect energy gap, for which there are sufficient data.[9] In the next section we use our PL spectra to find the isotope shift of the energy gap. In Sec. III B, the electron-phonon coupling is extracted by fitting the published temperature-dependence data, and we show that this coupling then predicts an isotope effect very close to that observed.

A. Measured isotope effect

The near band-edge photoluminescence spectrum is dominated by lines associated with excitons bound to shallow impurities in the as-grown ^{30}Si sample (see Fig. 1). Boron produces the ZPL at 1152.57(4) meV plus the broader lines at 1134.49(2), ~1098, and 1096.36(2) meV, which are the corresponding phonon sidebands with wave-vector conserving transverse-acoustic, longitudinal-optic, and transverse-optic phonons, respectively. The presence of the 1151.88(2), 1151.4(1), and 1151.14(5) meV lines indicates that the samples also contain phosphorus (P), aluminum (Al), and arsenic (As). The energies of the B, P, and Al ZPLs as measured under the same conditions in samples of natural-isotope Czochralski silicon with similar oxygen concentrations as the ^{30}Si sample are given in Table I. Each ZPL in ^{30}Si is shifted to higher energies compared to those in natural silicon, $^{\text{nat}}$Si, by 1.94(3) meV. A suitable sample doped with As was not available, but comparison via the standard float-zone (fz) values listed in Table I indicates the same isotopic shift.

It is known that the ionization energies of the phosphorus donor and the boron acceptor in ^{30}Si are ~0.09 and ~0.04 meV higher in energy than in $^{\text{nat}}$Si.[10] The binding energy E_b of the excitons is about 10% of the ionization energy (Haynes rule), so that the isotope-induced change in E_b is negligible in the present measurements. Consequently,

TABLE I. Measured energies of the ZPLs in photolumines- cence. The ZPL energies of ^{nat}Si are measured from CZ ^{nat}Si samples containing [O] $=9\times10^{17}$ cm^{-3}.

	^{30}Si (meV)	^{nat}Si (meV)	Isotopic shift (meV)	FZ (meV)[a]
ZPL(B)	1152.57(4)	1150.64(2)	1.93(4)	1150.73
ZPL(P)	1151.88(2)	1149.95(1)	1.93(2)	1149.93
ZPL(Al)	1151.4(1)	1149.48(2)	1.95(10)	1149.57
ZPL(As)	1151.14(5)	⋯	⋯	1149.18

[a]Reference 35.

the change, with isotopic mass, in energy of the photons emitted from the bound excitons equals the change in energy ΔE_g of the indirect energy gap from ^{nat}Si to ^{30}Si

$$\Delta E_g = +1.94 \pm 0.03 \text{ meV}, \qquad (1)$$

similar to the value of $+1.98(\pm0.01)$ meV reported in Ref. 4. The energy change (in meV) normalized to the fractional change in mass is very similar for Si, $\Delta E_g = 28\Delta M/\bar{M}$, and for Ge, $\Delta E_g = 26\Delta M/\bar{M}$.[11] The quanta of the wave-vector conserving phonons change according to the virtual crystal approximation, at this level of accuracy, for the TA and TO phonons,[4] and also for the LO phonon.

B. Fit to the data

We first summarize the mechanism by which the indirect gap energy $E_g(M,T)$ changes with isotopic mass M and temperature T. The change is the sum of two effects

$$\Delta E_g(M,T) = \Delta E_g^V(M,T) + \Delta E_g^{EP}(M,T), \qquad (2)$$

where $\Delta E_g^V(M,T)$ and $\Delta E_g^{EP}(M,T)$ are the contributions from the lattice volume change and the electron-phonon interac- tion, respectively. The temperature dependence of the energy gap of ^{nat}Si is known over the range 0–800 K.[9] The highest temperatures ensure that the modes of highest energy are sampled (66 meV $\equiv$ 760 K). The shift, in meV, at a tempera- ture T, in K, is given accurately by the Varshni equation[9] $\Delta E_g(T) = -0.35T^2/(T+430)$.

The volume term is

$$\Delta E_g^V(M,T) = \Xi \Delta V/V, \qquad (3)$$

where $\Xi = +1380$ meV is the deformation potential for the lowest indirect energy gap;[12] an expansion of the lattice *in- creases* the energy gap. If the isotope mass is constant but T increases, the change in volume is

$$\Delta V/V = 3\int_0^T dT\alpha(T), \qquad (4)$$

where α is the coefficient of linear expansion which has been tabulated numerically below 300 K (Ref. 13) and can be fit- ted above 300 K by[14]
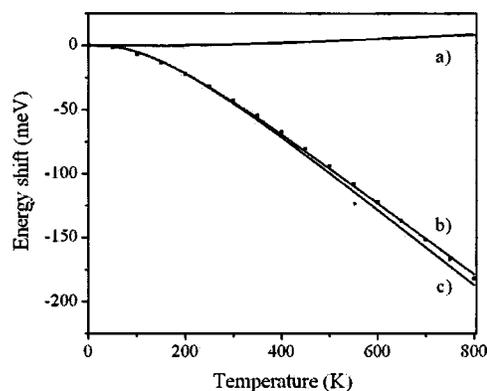

FIG. 2. Points show representative data for the temperature de- pendence of the indirect energy gap (Ref. 9). Line (a) is the contri- bution from the shift caused by lattice expansion. Line (c) is the shift term ΔE_g^{EP}, calculated from Eq. (7), and scaled so that the total shift [line (b)] has a best fit to the datum points.

$$\alpha(T) = (3.275\{1 - \exp[-5.88 \times 10^{-3}(T-124)]\}$$
$$+ 5.548 \times 10^{-4}T) \times 10^{-6} \text{ K}^{-1}. \qquad (5)$$

The contribution of this term to the measured temperature dependence of the energy gap is shown in Fig. 2.

The change in energy gap produced by the electron- phonon term $\Delta E_g^{EP}(T)$ derives from the perturbation of the zero-phonon states describing the top of the valence band and the bottom of the conduction band as a result of the phonon displacements. The effect depends on the mean square displacement $\langle Q^2 \rangle$ in each vibrational mode, and for a harmonic oscillator of frequency ω

$$\langle Q^2 \rangle = \frac{\hbar}{2M\omega}[1 + 2n(\omega)], \qquad (6)$$

where $n(\omega) = 1/[\exp(\hbar\omega/kT) - 1]$ is the phonon occupation number. The electron-phonon term must be integrated over all the phonon states, defined by their wave vectors and fre- quencies. The contribution from the different states varies both with the phonon branch and with the frequency within that branch.[15,16] Nevertheless, we show that a very close ap- proximation to the data is achieved simply by integrating over all frequencies, from $\omega = 0$ to the maximum frequency ω_m

$$\Delta E_g^{EP}(M,T) = \int_0^{\omega_m} d\omega f(\omega)[1 + 2n(\omega)], \qquad (7)$$

where $f(\omega)d\omega$ determines the contribution from all the modes of frequencies between ω and $\omega + d\omega$. We can expect that in general phonons of shorter wavelength will produce greater electron-phonon coupling, and so we represent $f(\omega)$ by the density of phonon states $g(\omega)$ of silicon[17] multiplied by a frequency-dependent term. The relation $f(\omega) \propto \omega^p g(\omega)$ works well for diamond when $p=1$.[18] For ^{nat}Si, the change in energy gap with temperature, after removing the volume ex- pansion term, is fitted accurately with $p=0.5$ (see Fig. 2).

From Eq. (6), in the limit $T \to 0$, the electron-phonon con- tribution produces an isotopic change in proportion to $1/\sqrt{M}$.
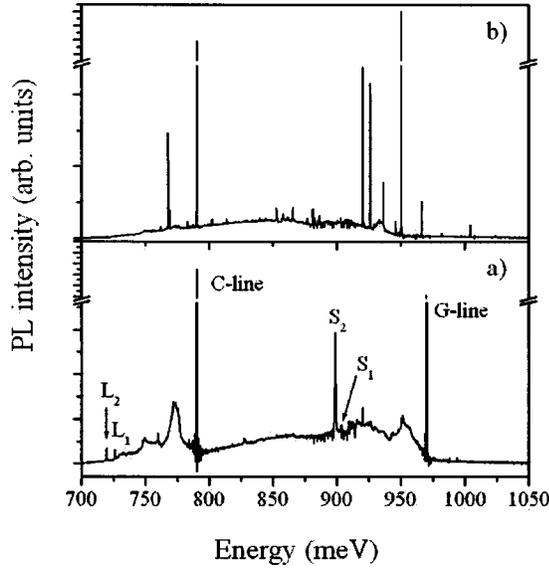
FIG. 3. Photoluminescence from electron-irradiated ^{30}Si (a) before and (b) after annealing at 400°C for 30 min. L_1 and L_2 are the LVMs of the C-line with quanta 64.0 and 70.6 meV; S_1 and S_2 are the LVMs of the G-line with quanta 66.4 and 71.3 meV, respectively. The sharp absorption lines at about 900 meV are due to atmospheric absorption. The spectra are not corrected for the spectrometer response.

All the modes of vibration have the same fractional change with mass. From Eq. (7), the shift from ^{nat}Si to ^{30}Si is

$$\Delta E_g^{EP}(M,0) = \frac{1}{2}\left(\sqrt{\frac{28.1}{29.98}} - 1\right)\int_0^{\omega_m} d\omega f(\omega) = +2.09 \text{ meV}.$$

(8)

In addition, there is an effect from the isotopically induced volume change as the mass increases. The volume change[19] is $\Delta V/V = -1.32(1) \times 10^{-4}$, giving $\Delta E_g^V(M) = -0.18$ meV. The sum of the two isotopically induced shifts is then closely in agreement with the measured value in Eq. (1)

$$\Delta E_g = \Delta E_g^V + \Delta E_g^{EP} = 2.09 - 0.18 = 1.91 \text{ meV}.$$

(9)

We have shown that a simple parametrization of the electron-phonon term by a power law allows the temperature dependence of the energy gap to be fitted closely, and hence its isotope dependence to be calculated.

IV. DATA FOR RADIATION-INDUCED DEFECTS

After electron irradiation, the PL spectrum of the ^{30}Si sample is dominated by the PL bands of the "C" and "G" centers. Subsequent annealing destroys these bands, creating others. The range of PL defects available is illustrated by Fig. 3. The measured isotope shifts from ^{nat}Si to ^{30}Si for the ZPL are listed in Table II. We will focus particularly on the "C" center, and data for its local mode quanta are listed in Table III.

TABLE II. Zero-phonon energies of deep centers in ^{30}Si and ^{nat}Si.

	^{30}Si (meV)	^{nat}Si (meV)	Measured shift (meV)
P-line	767.95(5)	767.15(3)	0.80(6)
C-line	790.41(2)	789.57(2)	0.84(3)
H-line	926.55(5)	925.63(3)	0.92(6)
T-line	936.88(2)	935.11(5)	1.77(5)
F-line	950.81(2)	949.85(3)	0.96(3)
I-line	966.73(5)	964.96(5)	1.77(7)
G-line	970.34(2)	969.41(3)	0.93(3)

V. "C" AND "P" CENTERS

The "C" center, ZPL at 789 meV, has been very well investigated by experiments and theory and most of the necessary data are available. It is created when one interstitial carbon atom migrates to, and is trapped at, one interstitial oxygen atom,[8] resulting in a monoclinic I (C_{1h}) center.[20] The optical properties of the center are, in fact, close to those for a tetragonal center, with the major axis along a cube axis of the crystal.[21] The "P" center is a very close analog of the "C" center: The ZPL has moved slightly to 767 meV, but the symmetries of the centers[22] and the deformation potentials of the ZPLs are the same,[20,22,23] and the vibronic sideband and local modes are very similar,[24] as is the excited-state structure.[25] Within uncertainties, the zero-phonon shifts induced by changing the silicon isotope are also the same (see Table II). We therefore concentrate on the "C" center. Information on the LVMs in the ground electronic state is available from midinfrared absorption measurements[26] and from PL measurements.[27] These vibrational modes may also be predicted by density functional modeling.[28] Some data on the LVMs in the excited electronic state have been obtained from photoluminescence excitation (PLE) spectra.[27] Since the electronic states involved in the "C" transition are orbitally nondegenerate, only those modes transforming as the totally symmetric representation are strongly observed in the PL and PLE spectra.

A. Local vibrational modes

Two strong LVMs are seen with quanta 65.7 and 72.9 meV in ^{nat}Si. In ^{30}Si their quanta are changed by -1.7 and -2.3 meV, respectively. The shifts expected if the modes only involved Si atoms would be -2.2 and -2.4 meV (see Table III). Evidently, the modes predominantly involve Si atoms, in agreement with the very small shifts on carbon- and oxygen-isotope substitution.[23] The frequencies and their shifts in ^{30}Si have been calculated for the neutral charge state of the "C" center using a supercell density functional code (AIMPRO). Further details have been reported elsewhere.[28] For isotope shifts, the secular equation has been solved twice using different masses of the Si atoms in the supercell. The calculated quanta nearest to the measured 65.7 and 72.9 meV modes are 67.5 and 73.6 meV, respectively. Their symmetry is totally symmetric, as required for their appearance in the vibronic band, and they predominantly involve the motion of

TABLE III. Measured and calculated host-isotopic shifts of the local vibrational modes (LVM) for the C-center. Measured data are given from photoluminescence (PL) measurements and mid-infrared absorption (Ref. 28) (vibrations in the ground electronic state) and from photoluminescence excitation (PLE) (Ref. 27). The LVM frequencies are calculated in the approximation that only Si atoms are involved in the vibration, and by *ab initio* density functional calculations for the C-center in the neutral charge state. Values $\hbar\omega_e$ are from density functional calculations for the positive charge state of the C center. The final column gives the symmetry of the vibration as calculated, in the C_{1h} point group.

Label	Experiments				Si-only	*Ab initio* calculation			Symmetry
	^{nat}Si PL meV (cm^{-1})	^{nat}Si PLE meV (cm^{-1})	^{30}Si PL meV (cm^{-1})	$\Delta\hbar\omega$ ^{30}Si$-^{nat}$Si meV (cm^{-1})	$\Delta\hbar\omega$ ^{30}Si$-^{nat}$Si meV (cm^{-1})	$\hbar\omega$ ^{nat}Si meV (cm^{-1})	$\Delta\hbar\omega$ ^{30}Si$-^{nat}$Si meV (cm^{-1})	$\hbar\omega_e$ ^{nat}Si meV (cm^{-1})	
					−2.2 (−17.5)	67.5 (544.2)	−2.28 (−18.4)	66.1 (533)	B
L1	65.7 (530)	63.6 (511)	64.0 (516)	−1.7 (−14)	−2.2 (−17.5)	67.5 (545)	−1.76 (−14.2)	66.3 (535)	A
	68.2 (550)				−2.2 (−17.9)	69.0 (556)	−2.29 (−18.5)	67.9 (548)	B
L2	72.9 (588)	69.8 (563)	70.6 (569)	−2.3 (−19)	−2.4 (−19)	73.6 (593)	−2.2 (−17.4)	71.5 (577)	A
	92.1 (743)				−3.03 (−24.4)	94.2 (759.6)	−0.50 (−4.2)	92.7 (748)	A
L3	107.4 (866)				−3.50 (−28.1)	108.6 (876)	−1.0 (−8.1)	102.5 (827)	A
L4	138.4 (1116)				−4.5 (−36.6)	141 (1138)	−0.62 (−5.0)	134.9 (1088)	A

the silicon atoms near the defect core. The predicted isotope shifts are in close agreement with our measured data (see Table III). [Note that the assignment of 67.5 to the 65.7 meV mode differs from an earlier assignment of it to a B mode.[28] This incorrect assignment followed after comparing the calculated frequencies with the large ^{18}O-shift (5.2 cm^{-1}) associated with the measured 529.6 cm^{-1} line. However, when the defect contains ^{18}O, a crossover is predicted to occur for the two lowest energy modes.]

Having established confidence in the calculations for the observable quanta of 65.7 and 72.9 meV lines, we list in Table III the calculated Si-isotope shifts for the remaining modes given as 67.5, 69.0, 94.2, 108.6, and 141 meV.

B. "C" zero-phonon line

The change in energy of the "C" zero-phonon line from ^{nat}Si to ^{30}Si is by $+0.84\pm0.03$ meV. Some contributions to the isotope shift of the "C" ZPL can be calculated explicitly.

First, since the rate of change in energy of the "C" line with volume is $\Xi_C = +900$ meV,[21] with an uncertainty probably on the order of 20%, the isotope-induced volume contraction changes the "C" line energy by $\Delta E_C^V \sim -0.12\pm0.02$ meV.

Second, the LVMs are negligibly populated at low temperature, and so make no contribution to the temperature dependence of the ZPL. However, their zero-point motion does contribute to the isotope shift, since the ZPL involves the difference in zero-point energies, $\frac{1}{2}(\hbar\omega_e - \hbar\omega_g)$, for each

mode in the excited and ground electronic states. This contribution to the ZPL shift on going from ^{nat}Si to ^{30}Si is then

$$\Delta E_C^{LM} = \frac{1}{2}\sum_i (\hbar\omega_{ei}^{30} - \hbar\omega_{gi}^{30} - \hbar\omega_{ei}^{nat} + \hbar\omega_{gi}^{nat}), \quad (10)$$

where the sum is over all the modes. In this expression, we know each $\hbar\omega_{gi}^{nat}$ from experiments and density functional calculations, which have been substantiated in Sec. V A. Similarly, the values of all the $\hbar\omega_{gi}^{30}$ are known from the calculations. However, experimental values are only available for two LVMs in the excited electronic state.[27] We note that the excited state of the "C" center consists of a deep hole with an electron orbiting in effective mass states.[23] The presence of the electron in these states is unlikely to affect the vibrational properties of the core of the center, just as there are no vibrational sidebands of the electronic transitions at the P donor. The vibrational properties of the excited state of the neutral "C" center are therefore expected to be like those of the ground state of the positively charged "C" center. These values have been calculated for ^{nat}Si (see Table III). The values in ^{30}Si are simply obtained by scaling, $\hbar\omega_{ei}^{30} = \hbar\omega_{ei}^{nat}\hbar\omega_{gi}^{30}/\hbar\omega_{gi}^{nat}$. Then Eq. (10) gives $\Delta E_C^{LM} = +0.14$ meV.

An alternative method of estimating ΔE_C^{LM} is to note that for each mode, the frequency in the ground and excited states changes with isotope in the ratio $\sqrt{m_{i,nat}/m_{i,30}}$, where m_i is the effective mass of the mode. The ratio is given by the change in frequency in the ground state when the isotope is changed, and the frequency change has either been measured

in PL or is known with confidence from the density functional calculations (see Table III). Consequently, the LVMs induce an isotope shift of the ZPL by

$$\Delta E_C^{\text{LM}} = \frac{1}{2} \sum_i \left(\sqrt{m_{i,\text{nat}}/m_{i,30}} - 1 \right)(\hbar\omega_{ei} - \hbar\omega_{gi}), \quad (11)$$

where the sum is over each LVM. For the totally symmetric modes, $\hbar\omega_{ei}$ can be measured from the vibronic band observed in optical absorption, and $\hbar\omega_{gi}$ for the same modes can be found from the PL spectrum. Wagner *et al.*[27] have shown that both the 65.7 and 72.5 meV modes soften by 2 to 3 meV (about -3.5%) in the excited electronic state (see Table III). On isotope substitution, these modes therefore move the ZPL by $+0.03$ and $+0.04$ meV, respectively. We assume, in the absence of other data, that similar shifts occur from the two low-energy B modes (Table III). The high-frequency A modes are predominantly C- and O-related. Assuming the same -3.5% change between ω_e and ω_g for each of these modes, Eq. (11) predicts that each will give an isotope shift to the ZPL of $+0.01$ to $+0.02$ meV. The total contribution from the 7 LVMs listed in Table III is $\Delta E_C^{\text{LM}} \sim +0.18$ meV, in close agreement with our previous estimate. We will use the mean, $\Delta E_C^{\text{LM}} \sim +0.16 \pm 0.02$ meV.

Finally, the "C" vibronic band consists of the broad spectrum of the lattice modes, as well as the LVMs (Fig. 3). We will assume that the coupling of the electrons to the lattice phonons is very similar to that of the indirect energy gap. Then, we can take the measured data for the temperature dependence of the energy of the "C" line, remove the lattice expansion contribution, and scale the remainder to the electron-phonon coupling term in the indirect energy gap. The "C" line has a very low oscillator strength[8,29] making absorption measurements difficult, and in PL it is thermally quenched, restricting measurements to $T < 80$ K.[23] The measured shift between 0 and 80 K is -1.52 ± 0.08 meV (see Fig. 4). In this temperature range, the crystal is contracting with increasing temperature, giving a shift of -0.04 meV. The electron-phonon coupling therefore produces a shift of -1.48 ± 0.08 meV, compared to -4.3 meV for the energy gap at the same T. The contribution from the electron-phonon term to the isotope shift is then a fraction $\sim 1.52/4.3$ of that for the indirect gap, giving a lattice-mode contribution for the "C" line of $\Delta E_C^{\text{EP}} = +0.72 \pm 0.04$ meV. The total predicted shift is then $\Delta E_C^{V} + \Delta E_C^{\text{LM}} + \Delta E_C^{\text{EP}} = +0.76 \pm 0.05$ meV compared to the measured $+0.84 \pm 0.03$ meV. There is agreement within the uncertainties, and a difference of about 10% in the central values.

We have shown that for the "C" line, the dominant contribution to the isotope shift comes from the electron-phonon interaction. The size of the interaction can be scaled from the temperature dependence of the indirect energy gap. The effects of the LVMs and the volume change are relatively small. The very close similarity of the "P" center to the "C" center (see Sec. V) results in an equally good fit to the measured isotope shift.
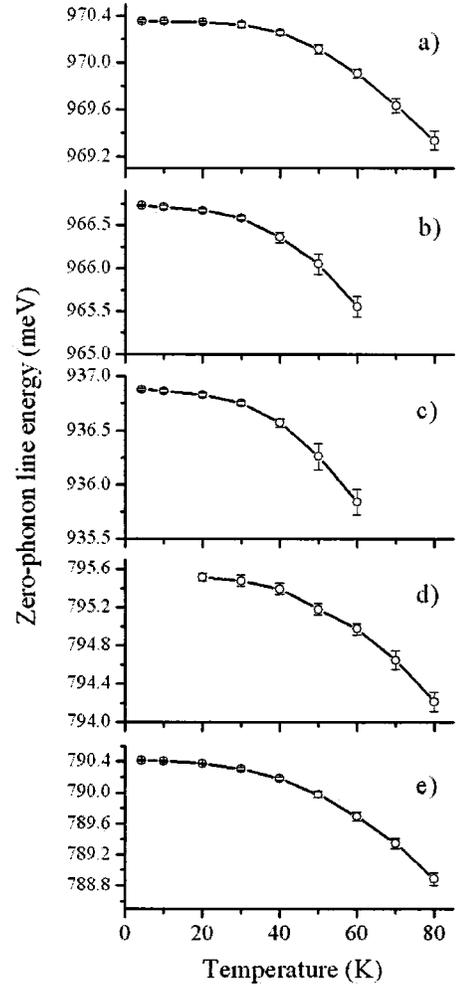

FIG. 4. Temperature dependence of (a) the "G" line, (b) the "I" line (c) the "T" line, (d) the "C" line (from an excited state of the "C" center), and (e) the "C" line. All data are measured using ^{30}Si.

VI. OTHER CENTERS

A. "I" and "T" centers

The "T" center (ZPL at 935.1 meV) and "I" center (965.0 meV) are produced when electron-irradiated silicon is annealed at $\sim 450 \degree$C. From studies of isotopically doped silicon, the "T" center has been shown to contain (at least) two inequivalent carbon atoms and one hydrogen atom.[30] Similarly, the "I" center shows evidence for two inequivalent C atoms and one hydrogen atom, and oxygen is also possibly implicated since the center has only been detected in oxygen-rich silicon.[31] A close parallel has been drawn between the two centers:[31] the ZPL energies is similar, the LVM quanta are identical within 2%, and the effect of stress and magnetic fields on the ZPLs is similar.[31,32] Both centers have C_{1h} symmetry and in both cases the centers have a primary axis close to $\langle 001 \rangle$. The excited states of both centers consist of a tightly bound electron and a shallow hole. The excited state structure, and the response to stress and magnetic field perturbations, can be modeled by assuming that the hole is in a weakly bound valence-band state, and that it orbits the center in an axial field equivalent to an internal stress along the

TABLE IV. Measured and calculated host-isotopic shifts of LVMs for the "G" center. Measured data are given from photoluminescence (PL) measurements and absorption (Ref. 34). The LVM frequencies are calculated in the virtual crystal approximation and would be valid if only Si atoms were involved in the vibration, and by *ab initio* density functional calculations for the "G" center in the neutral charge state. The final column gives the symmetry of the vibration as calculated in the C_{1h} point group.

Label	Experiments				Si-only	*Ab initio* calculation		Symmetry
	^{nat}Si	^{nat}Si	^{30}Si	$\Delta\hbar\omega$	$\Delta\hbar\omega$	$\hbar\omega$	$\Delta\hbar\omega$	
	PL	abs	PL	^{30}Si$-^{nat}$Si	^{30}Si$-^{nat}$Si	^{nat}Si	^{30}Si$-^{nat}$Si	
	meV	meV	meV	meV	meV	meV	meV	
	(cm^{-1})	(cm^{-1})	(cm^{-1})	(cm^{-1})	(cm^{-1})	(cm^{-1})	(cm^{-1})	
S1	67.4		66.4	−0.9	−2.2	68.15	−0.87	A
	(544)		(536)	(−7.0)	(−18)	(549.7)	(−7.0)	
					−2.2	68.19	−0.84	B
					(−18)	(550.0)	(−6.8)	
S2	71.9	70.2	71.3	−0.6	−2.3	71.96	−0.62	A
	(580)	(566)	(575)	(−5.0)	(−19)	(580.4)	(−5.0)	
					−2.5	79.53	−0.61	B
					(−20)	(641.5)	(−4.9)	
					−2.9	89.68	−0.51	A
					(−23)	(723.4)	(−4.1)	
					−3.3	104.25	−0.87	A
					(−27)	(840.9)	(−7.0)	

⟨001⟩ axis of 85 MPa for I[31] and 75 MPa for "T" (calculated using the data of Ref. 32). The same data give the deformation potentials as $\Xi_I = 120$ meV and $\Xi_T = -1200$ meV, and again we will assume a 20% uncertainty.

There appear to be no published data for the temperature dependence of the lines: The shifts up to 60 K are -1.1 ± 0.15 meV (see Fig. 4). There is a negligible contribution from the thermal expansion, which is only $\Delta V/V = -7 \times 10^{-6}$. At 60 K, the electron-phonon part of the shift for the energy gap is -2.54 meV. The isotope effect therefore scales as $1.1/2.54$ of the electron-phonon contribution to the isotope shift of the energy gap, giving shifts of $+0.91 \pm 0.13$ meV for both "T" and "I" centers. The volume change caused by the change in isotope shifts the T-line by $+0.16 \pm 0.03$ meV. The LVMs of the "T" center have been listed by Safonov *et al.*[30] as measured in luminescence. There are no data for the LVMs in the excited state, and so we assume that the modes soften by 3.5% as for the C-line. We find that the modes[30] L2 (65.9 meV) and L3 (70.4 meV) change in energy by half the values expected if the effective mass was entirely that of silicon, and assuming that ratio applies to all the LVMs, they contribute ∼0.22±0.05 meV to the ZPL isotope shift. The sum of the effects for the "T" line gives a predicted shift of ∼1.3±0.2 meV, the central value being 25% different from the measured 1.77±0.05 meV.

For the "I" line, LVM values for the ground state are listed in Ref. 31 and are similar to those of the "T" center. The measured temperature dependence of the ZPL is -1.25 ± 0.2 meV to 60 K (see Fig. 4). The measured deformation potential for the "I" line is essentially zero,[31] but since it enters in two opposing ways in the calculation, the predicted isotope shift for the "I" line is again 1.3±0.2 meV,

compared to the measured value of 1.77±0.07 meV.

B. "G" center

The "G" center, with its zero-phonon line at 969.45 meV, is one of the structural forms (the "B" form) adopted by an interstitial carbon atom and a substitutional carbon atom.[33] In contrast to all the other centers discussed here, there is no evidence that the excited state of the optical transition involves a loosely bound particle. We cannot, therefore, calculate the frequencies of the excited state using a charged state.

The deformation potential of the "G" ZPL is $\Xi = +800 \pm 200$ meV (Ref. 34) and so the shift of the "G" line from the isotopically induced volume change is -0.11 ± 0.03 meV. Table IV shows the measured host-isotopic shifts of the 67.4 meV (544 cm^{-1}) and 71.9 meV (580 cm^{-1}) LVMs of the "G" line, together with the LVM frequencies calculated *ab initio* for the neutral ground state "B-form" "G" center. We see that these modes are only weakly affected by the host isotopes and that these effects are considerably weaker than those measured previously for the carbon isotope.[34] Hence, all the modes are largely localized on the C atoms and there are no stress induced modes, like those found in the "C" center. The excellent agreement between the measured and calculated host-isotope shifts gives us further confidence in the current model of the "G" center. There are only data for one LVM in the excited electronic state, the 71.9 meV mode, which is reduced by mode softening to 70.2 meV,[34] a change of -2.4%. Assuming that all the LVMs change by between this amount and the -3.5% observed at the C center, the contribution to the isotope shift is ∼+0.07±0.01 meV. To calculate the contribution due to

coupling with the continuum of lattice phonons, we again use the measured temperature dependence of the zero-phonon line, of -1.0 ± 0.1 meV to 80 K (see Fig. 4). The thermal change in the lattice contributes -0.04 ± 0.01 meV, and scaling the difference (-0.96 ± 0.1 meV) to the energy gap gives an isotope contribution of $+0.3\pm0.05$ meV. The total predicted shift is then $\sim0.5\pm0.05$ meV, about half of the measured value. The simple rescaling rule is clearly not universal. We have noted that the LVMs are more dependent on the impurity atoms than the LVMs of the "C" center. We also note that the shape of the temperature-dependence plot (see Fig. 4) is different from those of the other lines, with proportionally less change in energy up to 30 K. Despite the similar vibronic bandshapes of the "C" and "G" centers, there are evidently significant differences in their electron-phonon coupling.

VII. SUMMARY

We have reported some of the effects of changing the silicon isotopes on the commonly observed centers in irradiated silicon. For the centers discussed here, we now have some knowledge of the effects of changing the silicon, carbon, hydrogen, and oxygen isotopes. Where experimental and density functional theoretical data exist, they are in good agreement for the changes in the frequencies of the LVMs in the electronic ground states of the centers. We have reported the changes in energy of the ZPLs of the centers. The contribution from the change with isotope of the lattice volume has been calculated explicitly. The effect of the LVMs has been estimated by combining experimental data and density functional theory. Both of these contributions have been shown to be small, for the centers discussed here, compared to the effect of the coupling of the electronic states to the continuum of lattice modes. To calculate this dominant effect we have used the temperature dependence of the zero-phonon energy, and since this dependence cannot be measured over a sufficiently large temperature range, we have rescaled the appropriate data for the indirect energy gap. We have shown that for the "C" and "P" centers the rescaling produces the correct isotope shift within $\sim10\%$, and for the "T" and "I" centers it is correct within 30%. However, such a simple approach cannot be expected to apply to all centers, and for the "G" center the result is only correct within a factor of 2. The work is another demonstration of the need to be able to model the excited states of defects in materials.

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