

Interstitial oxygen in Si and Si_{1-x}Ge_x

Shiqiang Hao, Lev Kantorovich, and Gordon Davies

Department of Physics, King's College London, Strand, London WC2R 2LS, United Kingdom

(Received 13 November 2003; revised manuscript received 12 January 2004; published 14 April 2004)

The equilibrium geometry, phonon spectra, and electronic structures of O interstitial defect in Si and Si_{1-x}Ge_x are calculated using *ab initio* plane-wave density-functional method. The effect of O, Si, and Ge isotopes on the phonon spectra is also investigated and found in good agreement with the available experimental data. Our calculations also support experimental evidence that in a Ge doped Si crystal an oxygen atom prefers to occupy a position between two Si atoms, rather than between Si and Ge atoms.

DOI: 10.1103/PhysRevB.69.155204

PACS number(s): 61.72.Ji, 63.20.Pw, 71.20.Nr

I. INTRODUCTION

Silicon and silicon-germanium (Si_{1-x}Ge_x) alloys have attracted extensive interest for applications such as microelectronic and optoelectronic devices with various unique properties. Point defects in Si or Si/Ge systems play an essential role in their properties which explains why investigation of impurities in these semiconducting materials is still a major research area. Usually the presence of light impurities results in appearance of local vibrational modes (LVM's) which are well isolated from the frequency range of the host crystal. The studies of LVM's provide precious information about the symmetry of the defects.

Oxygen plays an extremely important role in the defect engineering of silicon. On the positive side, oxygen aggregates are used to getter unwanted metals out of solid solution, but negative effects also occur, such as the formation of the well-known "thermal donors."¹

There have been many experimental and theoretical studies of the oxygen defect in Si, and its structure is rather well understood. It is now widely accepted that the oxygen interstitial occupies a bridge position between two nearest Si atoms.²⁻⁶ Total-energy calculations³⁻⁸ predict that the bond-center position with the D_{3d} symmetry is in fact a saddle point and it is slightly more energetically favorable for the oxygen atom to break the symmetry by moving away from the Si-Si bond $\langle 111 \rangle$ direction in the plane perpendicular to the bond and passing through its middle point. However, it was also found in the cluster *ab initio* density-functional calculations⁴⁻⁷ that the potential-energy surface for the oxygen atom to move around the Si-Si bond as well as across it is extremely flat with energy barriers of several meV which are much smaller than the actual precision of the calculations. This means that effectively the O interstitial (O_i) defect can be considered as *linear* with D_{3d} symmetry when the O atom occupies the middle position along the Si-Si bond; the motion of the O atom in the plane perpendicular to the Si-Si bond is highly anharmonic. In fact, the motion of the O atom in the Si lattice can be viewed as a coupling of its vibration along the direction of the bond and its rotation around it. These findings confirmed one of the first successful theoretical models for the defect² in which the combined rotational-vibrational movement of the O atom was considered. On the experimental side, the oxygen bridge configuration was identified by the position of the infrared (IR) ab-

sorption peaks,^{9,2} the magnitude of the isotopic shifts^{10,11} and the stress-induced dichroism measurements.¹²

One of the most important characteristics of the defect is its vibrational spectrum. Three fundamental low-temperature LVM's associated with the O_i defect and located at 1136, 517, and 29 cm⁻¹ were found^{10,12} (in fact, the last two are resonances). In particular, the 1136 cm⁻¹ band (the so-called ν_3 mode of the Si-O-Si molecule) is attributed to the asymmetric stretching in the linear Si-O-Si molecule, and the 517 cm⁻¹ band results from oscillations of the nearest two Si atoms to the oxygen, has E_u symmetry, and experiences almost no dependence on the oxygen mass. Recently, Hallberg *et al.*¹³ used the IR absorption method to study O_i-related vibrational bands and reported two new bands at 560 and 648 cm⁻¹. While the first band is likely to be a hot subband of the 517 cm⁻¹ band, the second band was assigned to a combination of the far-infrared 29 cm⁻¹ vibration with a band around 600 cm⁻¹ which is not directly observed in the IR experiments (but is Raman active). Pajot *et al.*⁵ studied the oxygen isotopic shifts and confirmed the existence of the IR inactive mode near 600 cm⁻¹ in which the O atom is weakly involved. In addition to that, the observed 1748 cm⁻¹ band can be explained by assuming that it corresponds to the combination of the 600 and 1136 cm⁻¹ bands.^{5,4} The existence of the 600 cm⁻¹ vibrational mode was also confirmed theoretically⁴⁻⁶ where it was found that there is a symmetric stretching mode with the vibrational frequency in the same range.

The O_i defect was also studied, both theoretically and experimentally, in germanium.^{4,6,14,15} It was found that the Ge-O-Ge model for the interstitial oxygen atom can explain most of the experimental results. However, the barrier for the O atom to cross the Ge-Ge bond within the perpendicular plane was calculated to be much larger than in the case of the oxygen in silicon (the potential-energy surface for the O rotation around the bond is still flat) so that a puckered (off-bridge) model for the molecule is more appropriate in this case. Consequently, because of a larger mass of the Ge atoms in the Ge-O-Ge molecule as compared with the Si-O-Si one, the ν_3 mode shifts to a much lower frequency 855.7 cm⁻¹. Other frequencies are also similarly affected.

There have been far fewer studies of the same defect in the Si_{1-x}Ge_x alloys, however. The effect of small germanium doping ($x < 0.0134$) on the IR absorption bands of the

Si-O-Si center was studied in Ref. 14. No evidence was found in this work of the O atom appearing close to Ge atoms, i.e., the shift of the 1136 cm^{-1} peak due to doping was found to be sufficiently small that the formation of direct Ge-O-Si or Ge-O-Ge molecules can be ruled out completely. It was, therefore, assumed that O atoms occupy bridging positions between two Si atoms as in pure silicon forming a Si-O-Si molecule. Consequently, in addition to the usual 1136 cm^{-1} band seen for the oxygen in a pure silicon, new IR adsorption peaks at 1118.5 and 1130.1 cm^{-1} were observed attributed to Si-O-Si molecules perturbed by neighboring Ge atoms at Si lattice sites. The shifted positions of other bands were ascribed to weakened anharmonic coupling between the rotational and asymmetric vibrational modes of the Si-O-Si molecule.

Similar results were obtained in Ref. 16 where the IR spectrum of the interstitial oxygen in $\text{Si}_{1-x}\text{Ge}_x$ systems was investigated for a considerably larger Ge content ($0.024 < x < 0.066$). In particular, the formation of direct O-Ge bonds was not observed in the IR spectrum. It was also found that a good agreement with experiment is achieved if one assumes a random distribution of Ge atoms in the crystal. At even higher doping the IR spectrum is transformed considerably¹⁷ as nearly all interstitial oxygens have neighboring Ge atoms. Finally, recently an extensive study covering the full composition range ($0 < x < 1$) was performed in Ref. 18 using the IR and secondary ion mass spectroscopies as well as the extended x-ray fine structure method. It was found that the asymmetric stretching mode peak shifts to smaller frequencies with the increase of Ge doping, whereas the intensity of the peak decreases. At the same time, no peak was found around 855 cm^{-1} even in Ge-rich alloys, which means that no Ge-O-Ge vibration was observed. It is also pointed out in Ref. 18 on the expansion of the Si-Si bonds with increase of the Ge concentration as a possible factor which should be taken into account while analyzing the experimental IR spectra.

To the best of our knowledge, there have been no first-principles theoretical studies of the O_i defect in the Si/Ge system. Therefore, the aim of the present paper is to fill in this gap by studying the geometry, energetics, and vibrational spectrum of the O interstitial defect in a Si/Ge system in the limit of small Ge concentrations using an *ab initio* density-functional (DFT) method.

The plan of the paper is as follows. In Sec. II we briefly describe our DFT method. The O interstitial defect in the Si bulk is considered in Sec. III to verify our methodology. In addition, it serves as a convenient reference system with which the O defect in Si/Ge can be compared. The geometry, phonon, and electronic structures of the O interstitial in the Si/Ge system are presented in Sec. IV. Finally, in Sec. V we discuss our results and draw brief conclusions.

II. METHOD

We used DFT, periodic boundary conditions, and plane-wave basis set as implemented in the Vienna *ab initio* simulation package^{19–21} (VASP) to obtain the relaxed geometries, the electron density, the Kohn-Sham energies, as well as the

Hellmann-Feynman forces on atoms which are needed for the atomic relaxation and the calculations of the vibrational spectra (see below). To minimize the cost of the calculations, ultrasoft pseudopotentials^{22,23} have been used for the Si, Ge, and O atoms. Different k -point samplings have been employed depending on the system cell size. Most of the calculations reported here are based on the periodic simple cubic cell containing 64 Si atoms. Four k points in the Brillouin zone generated using the Monkhorst-Pack method with $2 \times 2 \times 2$ k -point mesh have been found sufficient for this system. When considering the O defect in this cell, only one Γ k point has been normally used. The calculations have been performed using the generalized gradient approximation.²⁴

Dynamical properties of oxygen in Si and Si/Ge have been studied using a modification of the direct (frozen-phonon) method.^{25,26} In this method, the elements of the force-constant matrix are calculated from *ab initio* forces exerted on all cell atoms when a particular cell atom is slightly displaced from its equilibrium position. As our concern in this study has been only related to the vibrational modes associated with the O defect, we used the following approach. To calculate the force-constant matrix for the Si cell with a single O atom in it, we first relax all the atomic positions until the forces exerted on atoms are less than 0.001 eV/\AA (compare, e.g., with Ref. 27). Then we identify in a cluster of atoms consisting of the oxygen and a finite number of the host Si atoms around it. The atoms of the cluster are displaced from their equilibrium positions one by one; for each configuration the *ab initio* forces and thus the corresponding contributions to the force-constant matrix are calculated. If n is the number of atoms in the cluster, this way we obtain a $3n \times 3n$ dynamical matrix which is diagonalized to give the first approximation to the local phonons. The calculation is then repeated several times by including more and more atoms into the cluster. We find that vibrational frequencies somewhere above 100 cm^{-1} converge reasonably well with the cluster size (see the following section). As expected, this method is unreliable for phonons with lower frequencies (with wavelengths larger than the cell size). These modes, if given at all by the finite cluster used, are strongly coupled to the continuum of low-frequency bulk acoustic modes (i.e., are resonances) and should show cluster size dependence. Therefore, we do not consider them in this paper, excluding the 29 cm^{-1} band in particular.

When modeling the O_i defect in the Si/Ge system, the same method is used. Note, however, that depending on the position of the Ge atom with respect to the oxygen, the choice of possible clusters can be somewhat limited since in each cluster both O and Ge atoms are to be present.

Diagonalization of the cluster dynamical matrix gives the vibration frequencies ω_λ and the corresponding eigenvectors $\mathbf{e}^{(\lambda)} = \|e_{A\alpha}^{(\lambda)}\|$. Here A is the cluster atom and $\alpha = x, y, z$ gives three Cartesian directions. The eigenvectors enable us to identify localized modes and resonances associated with the defect and/or Ge substitution. Indeed, each particular eigenvector $\mathbf{e}^{(\lambda)}$ gives the relative amplitudes of each atom in the supercell if this particular vibration λ is activated. Therefore,

by analyzing the projected phonon density of states (phonon PDOS),

$$D_A(\omega) = \sum_{\alpha} \sum_{\lambda} |e_{A\alpha}^{(\lambda)}|^2 \delta(\omega - \omega_{\lambda}), \quad (1)$$

for every atom A of interest (e.g., O atom, nearest Si or Ge atoms), one can find at which frequencies particular atoms contribute. When plotting the phonon DOS, we replace each Dirac δ function with a Gaussian of dispersion $\sigma = 10 \text{ cm}^{-1}$. This smearing procedure is necessary because our cluster method gives only a limited number of phonon modes. Using the calculated vibrational frequencies for the cells with and without the O atom, we can also calculate the quasiharmonic contribution of the defect to the vibrational entropy and the free energy of the crystal (not reported in this paper).

The charge density $\rho(\mathbf{r})$ of every cell has been analyzed using the LEV00 package²⁸ by plotting the density along lines and in planes cutting through the cell. Additional insight into the density distribution in every system, and in particular a possible charge transfer between atoms, has been gained by calculating the charge in spheres of different radii centered on various atoms (cf. Ref. 29). Electronic total and projected DOS has been calculated from the Kohn-Sham eigenstates using the method of tetrahedra.^{30,31}

Formation energies of the O interstitial were calculated using^{4,3}

$$E_f(\text{O}) = E_D - \sum_i n_i \mu_i. \quad (2)$$

Here E_D is the total energy of the supercell containing the defect and composed of n_i atoms of species i whose chemical potential is μ_i . The chemical potential μ_{Si} of Si is simply the energy per atom in the bulk phase. It was calculated as $\mu_{\text{Si}} = -5.427 \text{ eV}$ using the fcc cell with 128 Si atoms and a sufficient number of k points. To calculate the chemical potential μ_{O} of an oxygen atom, we considered^{3,4} the α -quartz crystal. There are three Si and six O atoms in the unit cell of the α quartz. Therefore, the O chemical potential is $\mu_{\text{O}} = \frac{1}{6}(E_{3\text{SiO}_2} - 3\mu_{\text{Si}}) = -9.19 \text{ eV}$.

III. INTERSTITIAL OXYGEN IN SILICON BULK

A. Equilibrium structure

The geometrical characteristics and formation energies of the relaxed linear structure of the D_{3d} symmetry [see Fig. 1(b)] calculated using supercells containing 32, 54, 64, and 128 Si atoms are shown in Table I. By taking the O atom away from the Si-Si bond direction within the plane perpendicular to it and allowing all atoms to relax again, we obtained in each case the C_{1h} symmetry structure [Fig. 1(a)] with slightly lower total energy. The parameters of this structure for every supercell are also shown in Table I. Three points follow from these results. First, our results for the O_i defect are in a good agreement with the previous DFT calculations.⁴ Formation energies are slightly smaller than in Ref. 4 which we think is due to differences in the particular

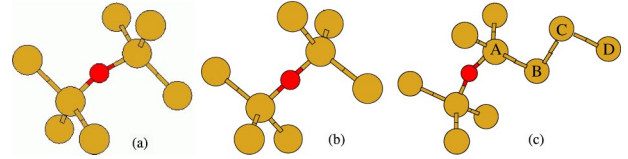


FIG. 1. Different configurations for interstitial oxygen (small circle) in Si and Si_{1-x}Ge_x systems. (a) C_{1h} and (b) D_{3d} configurations in Ge-free silicon, and (c) a puckered configuration for systems with a Ge atom in positions marked A, B, C, and D (systems A, B, C, and D, respectively).

implementations of the DFT method used. Second, the intermediate size 64 atom cell is sufficient for the O defect calculations; note, however, that it has not completely converged with respect to the defect formation energy since on doubling the cell to 128 atoms, E_f is 0.4 eV lower. All our subsequent calculations have been done using the 64 atom cell. Third and most important, the difference between the D_{3d} and the lower symmetry C_{1h} structures is found to be extremely small. To explore this point even further, we have taken the O atom away from the C_{1h} symmetry and allowed all atoms to relax. The resulting C_1 symmetry structure has only 1.03 meV lower energy than the C_{1h} structure, 157° Si-O-Si angle, and 1.62 Å Si-O distance. Thus, our calculations, in complete agreement with the previous theoretical studies,^{2,4-6} clearly demonstrate that the potential-energy surface for the O atom around the linear configuration is extremely flat with very small barriers between different shallow energy minima. This point is also reinforced in our calculations of the phonon structure which showed the existence of one or two imaginary vibrational frequencies for every geometry studied.

The distribution of the electron density in the Si-O-Si system is shown in Fig. 2(a). The covalent bonding between the two Si atoms of the Si-O-Si molecule and the O is clearly visible. The two electrons (one from each of the two Si atoms) which used to form the Si-Si bond in the O-free system participate now in the covalent bonding with the O atom

TABLE I. Si-O distance, Si-O-Si angle, and formation energy in the relaxed structures of C_{1h} and D_{3d} symmetries found for the three cell sizes considered here.

Cell (k points)	Property	C_{1h}	D_{3d}	C_{1h} (Ref. 4)
bcc 32 (14)	$E_f(\text{O})$ (eV)	1.68	1.69	1.83
	Si-O (Å)	1.613	1.604	
	Si-O-Si (deg)	161.0	180	
fcc 54 (4)	$E_f(\text{O})$ (eV)	1.63	1.69	
	Si-O (Å)	1.628	1.598	
	Si-O-Si (deg)	146.4	180	
sc 64 (4)	$E_f(\text{O})$ (eV)	1.55	1.56	1.81
	Si-O (Å)	1.619	1.605	1.62
	Si-O-Si (deg)	157.1	180	157
fcc 128 (4)	$E_f(\text{O})$ (eV)	1.15	1.16	1.38
	Si-O (Å)	1.619	1.605	
	Si-O-Si (deg)	161.8	180	

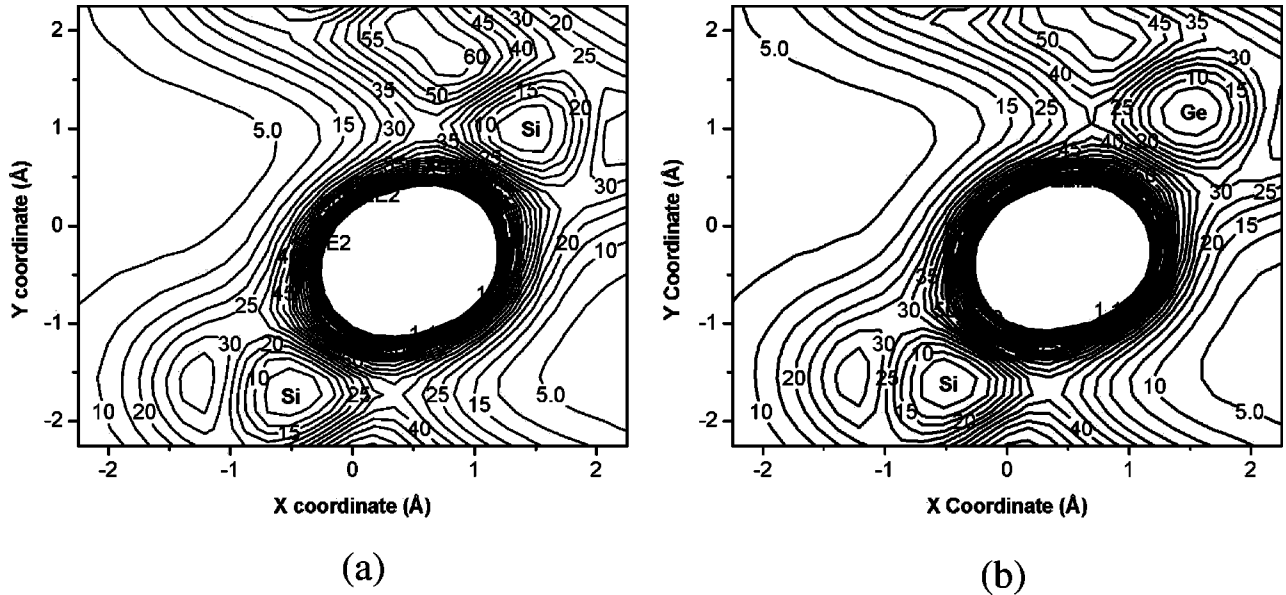


FIG. 2. The electron charge densities of the linear Si-O-Si (a) and Si-O-Ge (b) systems.

making it effectively O^{2-} . Other three electrons of the two Si atoms are engaged in the covalent bonding with the surrounding Si atoms as in the O-free system, so that the density on the two Si atoms nearest to the O atom remains largely unaffected. The calculated electron DOS shown in Fig. 3 does not show any states in the gap between the valence and conduction band, although some considerable changes within the occupied band due to the O defect are clearly visible.

B. Vibrational properties

The vibrational frequencies of the O defect have been calculated using the modified direct method described above. We find that, apart from the single lowest phonon mode which decrease steadily with the increase in the cluster size, all other frequencies converge reasonably well. In all subse-

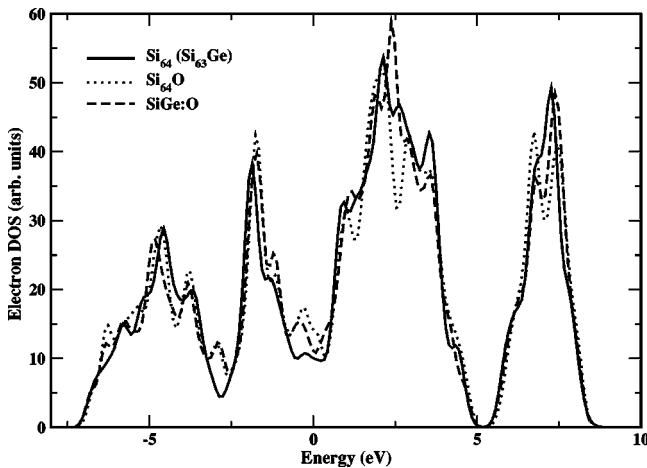


FIG. 3. Electron DOS for the O-containing systems. Note that the energy gap between the valence band (VB) and conduction band (CB) is reduced due to the smearing procedure used (Sec. II).

quent calculations of the phonon frequencies to be described in the following a cluster containing 26 Si atoms has been found sufficient.

Comparing the phonon DOS of the cell with and without the O atom, we find a number of features due to the O defect. These appear as peaks and resonances in the projected DOS shown in Fig. 4: the modes around 140 , 260 , and 1107 cm^{-1} (the first two are resonances and the last one is a local mode) involve the oscillation of the O atom, while the 160 , 526 , and 599 cm^{-1} modes (two resonances and a local mode split off the bulk band, respectively) are associated with the symmetric oscillations of the two Si atoms of the Si-O-Si molecule with almost no O participation (there is some contribution from the O atom to the 160 cm^{-1} peak). A more detailed analysis of the symmetry of each mode showed that the 526 , 599 , and 1107 cm^{-1} oscillations correspond to the well-known 517 , 600 , and 1136 cm^{-1} bands, respectively. Note that the resonance around 140 cm^{-1} has been predicted be-

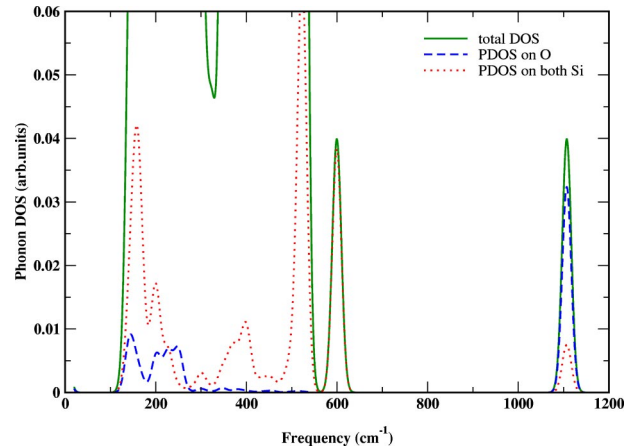


FIG. 4. Total and projected phonon DOS for the D_{3d} symmetry O defect in silicon.

TABLE II. Some of the LVM's (cm⁻¹) and their downward isotopic shifts.

	This work	Observed ^a	From Refs. 4 and 3
²⁸ Si- ¹⁶ O- ²⁸ Si	1107.2, 599.6, 526.2	1136.4, 618, 517.8	1184, 519, 619 ⁴ 1098, 630 ³
³⁰ Si- ¹⁶ O- ²⁸ Si	3.6, 10.2, 0.2	3.7, 9.5,	4, 10, 1 ⁴
³⁰ Si- ¹⁶ O- ³⁰ Si	7.1, 19.6, 4.4		
²⁸ Si- ¹⁸ O- ²⁸ Si	51.1, 0, 0	51.4, 0, 0.0	55, 0, 0 ⁴ 50, 2 ³
³⁰ Si- ¹⁸ O- ²⁸ Si	54.8, 10.2, 0.3	55.2	58, 10, 1 ⁴
³⁰ Si- ¹⁸ O- ³⁰ Si	58.5, 19.5, 4.5		
⁷² Ge- ¹⁶ O- ²⁸ Si	28.1, 73.5, 3.4		

^aFrom Ref. 5, except for the 618 cm⁻¹ band which is from Ref. 13.

fore in Ref. 3, while the one around 260 cm⁻¹ also clearly related to the O defect, as far as we are aware, has never been reported before. Our frequencies are in close agreement with those observed, which demonstrates that the cluster model used in our calculations is adequate. Note, however, that the 140 cm⁻¹ mode still shows a weak cluster size dependence. As our interest here is in the effect of the Ge atoms on the O defect, these drawbacks of our model are not important since the same cluster model will be used for Si/Ge systems as well.

Three characteristic vibrational modes together with their downward isotopic shifts are shown in Table II. The asymmetric stretching mode at 1107 cm⁻¹ is shifted by 51.1 cm⁻¹ with the ¹⁸O atom in good agreement with the experimental result of 51.4 cm⁻¹. A good agreement with the observed isotopic shifts has been found in other cases as well. For instance, the calculated 3.6 cm⁻¹ shift for the ³⁰Si-¹⁶O-²⁸Si system is also in excellent agreement with the observed value of 3.7 cm⁻¹. The 599 and 526 cm⁻¹ modes originate from a symmetrical vibration of the two Si atoms of the Si₂O molecule with a negligible contribution from the O atom and are thus practically unaffected by the ¹⁶O → ¹⁸O change. The isotope shifts due to change of the masses of the two Si atoms agree well with other theoretical calculations.^{3,4}

IV. INTERSTITIAL OXYGEN IN Si_{1-x}Ge_x

A. Energetics and geometry

To study the oxygen defect in the Si_{1-x}Ge_x system, we considered the same 64 Si atom cells as above in which one Si atom was substituted by a Ge atom (this corresponds to the value of $x = \frac{1}{64} \approx 0.016$) and then all atoms of the Si₆₃Ge cell were allowed to relax to their equilibrium positions. The Si and Ge atoms are nearly identical from the chemical point of view, the latter one having slightly larger atomic radius. Nevertheless, we find very little atomic relaxation in the system around the Ge atom and a negligible change in the electronic DOS. For instance, the Si-Ge bond length and the Si-Ge-Si angle, $\alpha_{\text{Si-Ge-Si}}$, were found to be 2.39 Å and 109.47°, respectively, which are very close to the values 2.36 Å and $\alpha_{\text{Si-Si-Si}} = 109.47^\circ$ found for the perfect Si system.

Then we have introduced a single O atom to the Si₆₃Ge cell. Four Si₆₃GeO systems have been considered in which the O atom was positioned [see Fig. 1(c)]: system *A*, nearest to the Ge atom, i.e., forming a Si-O-Ge molecule; system *B*, in the second sphere, i.e., nearest to the Si-O-Si molecule; system *C*, in the third sphere; and system *D*, in the fourth sphere. In every case all atoms were allowed to relax to their mechanical equilibrium. Both linear and puckered configurations of the Si-O-X molecule were considered. Formation energy of the O defect,

$$E'_f(\text{O}) = E_{\text{Si}_{63}\text{OGe}} - (E_{\text{Si}_{63}\text{Ge}} + \mu_{\text{O}}), \quad (3)$$

which is calculated with respect to the Si₆₃Ge cell, together with the geometric characteristics of the Si-O-X molecule ($X = \text{Ge}$ for system *A* and $X = \text{Si}$ for other three systems) are shown in Table III.

As in the case of the O defect in silicon discussed in the preceding section, we found that from the point of view of the total energies the linear geometry is in each case a saddle point and the puckered configurations are more energetically favorable. The energy barriers between two opposite puckered geometries calculated at the linear configuration for cases *B*, *C*, and *D* are comparable to that found for the O in silicon. The formation energies for these configurations and geometry parameters are similar to each other and are also very close to those for the O in silicon (cf. Table I). Thus, if the Ge atom does not appear as the nearest neighbor of the O atom, the O defect can be viewed as the Si-O-Si molecule

TABLE III. The formation energy, $E'_f(\text{O})$, and geometry of the O interstitial defect in the Si/Ge systems.

System	$E'_f(\text{O})$ (eV)	Si-O (Ge-O) (Å)	Angle (deg)
<i>A</i> (puckered)	2.25	1.61 (1.80)	144.6
<i>A</i> (linear)	2.37	1.58 (1.76)	180
<i>B</i> (puckered)	1.48	1.62	157.6
<i>B</i> (linear)	1.49	1.60, 1.61	170.4
<i>C</i> (puckered)	1.51	1.62	157.9
<i>C</i> (linear)	1.52	1.60, 1.61	174.8
<i>D</i> (puckered)	1.50	1.62	153.6
<i>D</i> (linear)	1.51	1.61, 1.61	176.4

which is only slightly perturbed by the Ge atom in the neighboring spheres. This is in agreement with the previous studies.¹⁴

The situation is rather different, however, if the Ge atom is positioned next to the oxygen (system *A* in Table III). In this case a Si-O-Ge molecule is formed with the linear geometry to be 0.12 eV higher in energy than the puckered one. This is consistent with the results for the O defect in germanium⁶ where it was found that the energy difference between the puckered and linear configurations of the Ge-O-Ge molecule is noticeably larger than that for the O in silicon. Then, as expected, we also find that the Si-O-Ge molecule is no longer symmetrical. For example, in the puckered geometry the Si-O bond length is by nearly 0.2 Å shorter than the O-Ge distance and the Si-O-Ge angle is by more than 10° smaller. This is mainly due to a larger size of the Ge atom. Most importantly, the energy of the O defect with the Ge atom in the first sphere (system *A*) was found to be at least 0.7 eV less energetically favorable than for the other three systems in which the Ge atom is located further away from the oxygen. Thus, we conclude that the O atom does not prefer to form a direct chemical bonding with the Ge atom.

The electron DOS for the Si-O-Ge system (system *A*) is shown in Fig. 3 where some redistribution of the electron states within the valence band is clearly visible. However, there are no states in the gap similar to the O in silicon. The difference in the electronic DOS for the two systems is due to some atomic relaxation in and around the Si-O-Ge molecule caused by a larger Ge atom. This latter point can also be seen in the electron density for the Si-O-Ge system which is compared to that of the Si-O-Si system in Fig. 2. The two charge densities look very similar. However, the Si-O-Ge molecule has a slightly larger size which induces a local mechanical strain in the surrounding lattice. This strain is larger than that induced by a single Ge atom in the pure silicon lattice which explains why the Si-O-Ge system is less energetically favorable than any of the Si-O-Si systems with the Ge atom in their neighborhood.

The point about only small perturbation of the O defect due to the Ge substitution for systems *B*, *C*, and *D* can also be illustrated by the following simple calculation. The total formation energy of the O defect in those systems,

$$E'_f(\text{O, Ge}) = (E_{\text{Si}_{63}\text{OGe}} + \mu_{\text{Si}}) - (E_{\text{Si}_{64}} + \mu_{\text{Ge}} + \mu_{\text{O}}), \quad (4)$$

can formally be written as a sum of the formation energies of the oxygen defect in the Si/Ge system, Eq. (3), and the energy

$$E_s(\text{Ge}) = (E_{\text{Si}_{63}\text{Ge}} + \mu_{\text{Si}}) - (E_{\text{Si}_{64}} + \mu_{\text{Ge}}) \quad (5)$$

required to substitute a single Si atom with a Ge atom in the O-free system. If these two defects, namely, the O interstitial and the Ge substitution, are independent of each other, then the formation energy of oxygen, $E'_f(\text{O})$, in the Si/Ge system should be very close to the formation energy $E_f(\text{O})$ in the Ge-free system reported in Table I. Using from our calculations the available total energies of all the systems featured in the above formula (here the choice of μ_{Ge} is not impor-

tant; it was taken as the energy of a single Ge atom), we find that $E'_f(\text{O})$ is equal to 1.48, 1.51, and 1.50 eV for systems *B*, *C*, and *D*, respectively. The linear geometry of the Si-O-Si molecule was used in each case. One can see that in cases *C* and *D* the oxygen formation energy is extremely close to the value of 1.56 eV for the Ge-free system. In the case of system *B* the discrepancy is slightly larger since in this case the influence of the Ge atom on the structure of the Si-O-Si molecule immediately next to it is obviously not negligible.

Similarly one can compare the substitution energy $E_s(\text{Ge}) = -0.057$ eV, Eq. (5), in the O-free system with that calculated for systems with the O atom using

$$E'_s(\text{Ge}) = (E_{\text{Si}_{63}\text{OGe}} + \mu_{\text{Si}}) - (E_{\text{Si}_{64}\text{O}} + \mu_{\text{Ge}}). \quad (6)$$

The substitution energies $E'_s(\text{Ge})$ obtained for systems *B*, *C*, and *D* are -0.073 , -0.046 , and -0.052 eV, respectively. Again, in the cases *C* and *D* these are close to the energy $E_s(\text{Ge}) = -0.057$ eV, whereas the difference in substitution energies between system *B* and the O-free system is somewhat more significant.

B. Vibrational properties

To investigate how the Ge doping perturbs the vibrational properties of the O defect in silicon, we have calculated the phonon PDOS for the Si_{63}Ge cell without and with an oxygen atom; in the latter case all four positions of the O with respect to the Ge atom have been considered (systems *A* to *D*). We found only a very little change in the phonon DOS for the oxygen-free system due to Ge substitution. A heavier Ge atom introduces a small resonance at around 120 cm^{-1} as well as some insignificant features in the middle of the silicon phonon continuum. The phonon total and projected DOS for the system with an oxygen atom positioned next to the Ge (system *A*) and in the third coordination sphere (system *C*) are shown in Fig. 5. The phonon DOS for the Si_{63}GeO system *D* is very similar to that for system *C*, while the DOS for system *B* (not shown) is intermediate to those for systems *A* and *C*.

First of all, we note that the DOS for system *C* (and thus for system *D* as well) is very similar to that for the Si-O-Si Ge-free system shown in Fig. 4 and discussed earlier. This is consistent with our earlier conclusion based merely on energetic arguments that these systems can be treated as consisting of independent Si-O-Si molecule and a Ge substitution defect. Consider now the phonon DOS for the Si-O-Ge system (system *A*). Three significant differences can be noticed if compared with the phonon DOS of the Si-O-Si system (Fig. 4). First, the peak at 1107 cm^{-1} has moved to much lower frequency 962 cm^{-1} ; second, the contribution of the Ge atom into this peak is much less significant than that of the Si; third, the 599 cm^{-1} peak which was split off from the top of the phonon continuum in the Ge-free system has become a resonance in the case of system *A*.

To understand these effects, we considered the vibrational spectrum of the O defect in the silicon system in which one of the Si atoms was given the mass of the heavier Ge atom. We kept the force-constant matrix as well as the atomic ge-

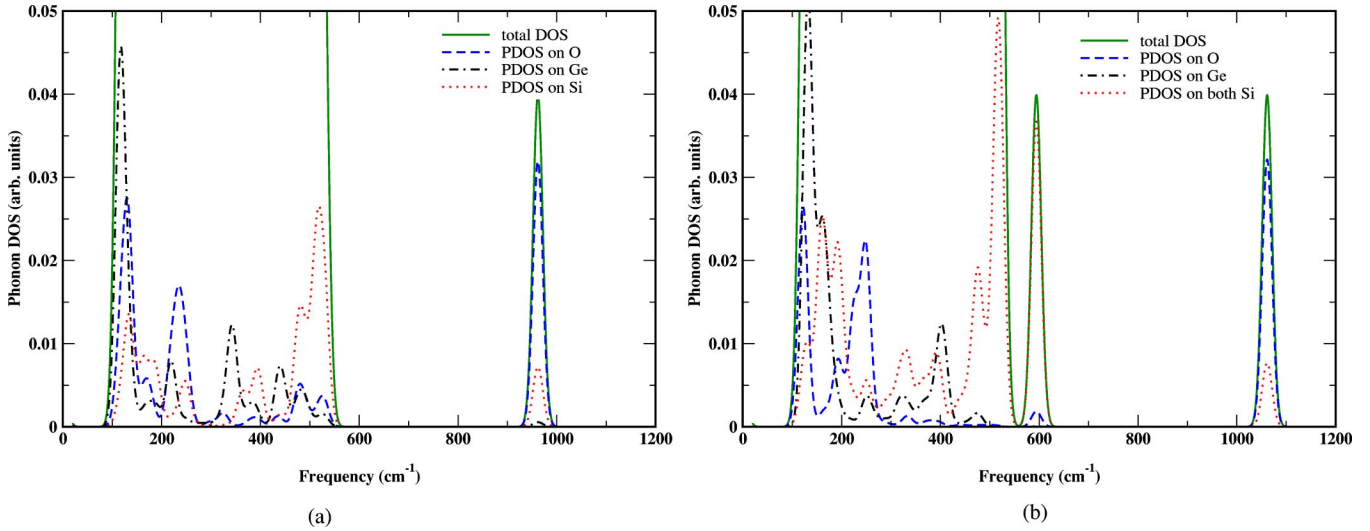


FIG. 5. Total and projected phonon DOS of two Si₆₃GeO systems with the Ge atom (a) in the first (system A) and (b) the third (system C) coordination spheres with respect to the O atom. A linear geometry of the Si-O-X molecules ($X = \text{Ge}, \text{Si}$) was used in each case.

ometry in all these calculations as for the Ge-free system. Since chemically Si and Ge atoms are very similar, this way one can approximately simulate all four systems from *A* to *D* depending on which Si atom (with respect to the oxygen) was given the Ge mass. We call these “fake” Ge systems. The phonon DOS for the O in the Ge-free system as well as for the fake and real system *A* are compared in Fig. 6. One can clearly see that the 1107 cm⁻¹ phonon peak moved towards lower frequencies in the case of the fake system *A*; at the same time, the peak near 599 cm⁻¹ moved to lower frequencies and became a resonance. A similar analysis has been made for systems *B*, *C*, and *D*. We find that there is a very little difference between the phonon DOS for the fake and real systems *B*, *C*, and *D*. Thus, we conclude that the phonon spectra of the O defect in the Si/Ge system, except for the 1107 cm⁻¹ peak of system *A*, can be explained almost entirely by the different mass of the Ge atom. The 1107 cm⁻¹ mode is found to be also sensitive to the change in the chemical bonding of the O atom to its two neighbors caused by the Ge substitution.

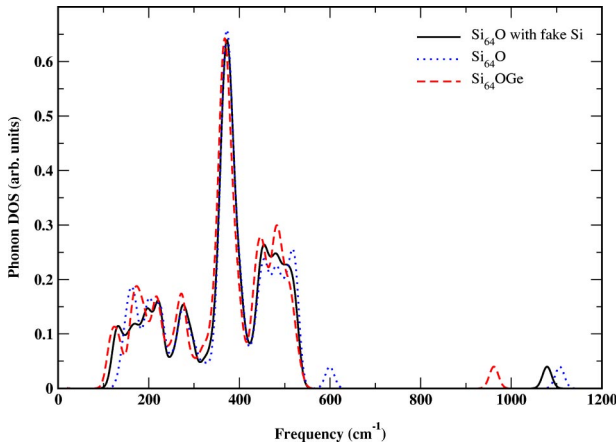


FIG. 6. Comparison of the total DOS for Si₆₄O (Ge-free), fake, and real systems *A*.

The isotopic effects based on the phonon calculations of the Si₆₃GeO unit cell with linear geometries of the Si-O-X molecules are listed in Table IV. In all cases the Si isotope corresponds to Si atom directly bonded to the oxygen. Different Ge isotopes play a very small effect on the highest frequency of the peak near 1061 cm⁻¹. This is to be expected for systems *B* and *C* in which the Ge atom is not directly bound to the O. In the case of system *A* this is consistent with the fact, mentioned earlier, that the Ge contribution into this particular vibration is small. The effect of the Ge mass on all other frequencies is also insignificant. On the other hand, the mass of the O atom significantly affects the vibrational frequencies which is in line with our results for the Ge-free system, Table II. Since the O atom prefers not to have the Ge atom in the first sphere, we can conclude that, at least for small Ge concentrations in which the effect of the lattice expansion due to Ge substitution is not significant, one should not expect any significant shifts in the phonon spectrum due to different Ge isotopes; on the other hand, the peaks due to O isotopes also should not depend on the Ge concentration.

TABLE IV. Calculated LVM's (cm⁻¹) for systems *A*, *B*, and *C* with ²⁸Si, ¹⁶O, and ⁷²Ge and their corresponding isotopic shifts (see text).

Isotopes	System A	System B	System C
²⁸ Si, ¹⁶ O, ⁷² Ge	961.7	1046.3, 594.6	1061.5, 594.3
²⁸ Si, ¹⁶ O, ⁷⁰ Ge	-0.2	0, -0.02	0, 0
²⁸ Si, ¹⁶ O, ⁷⁴ Ge	0.18	0, 0.01	0, 0
²⁸ Si, ¹⁸ O, ⁷² Ge	43.6	48.4, 1.7	48.6, 1.5
²⁸ Si, ¹⁸ O, ⁷⁰ Ge	43.4	48.4, 1.7	48.6, 1.5
²⁸ Si, ¹⁸ O, ⁷⁴ Ge	43.8	48.4, 1.7	48.6, 1.5
³⁰ Si, ¹⁶ O, ⁷⁰ Ge	5.5	3.1, 9.5	3.3, 10.0
³⁰ Si, ¹⁶ O, ⁷⁴ Ge	5.9	3.1, 9.5	3.3, 10.0
³⁰ Si, ¹⁸ O, ⁷⁰ Ge	49.6	51.6, 11.2	52.1, 11.5
³⁰ Si, ¹⁸ O, ⁷⁴ Ge	50.0	51.6, 11.2	52.1, 11.5

V. DISCUSSION AND CONCLUSION

In this paper we report first-principles DFT calculations of the O interstitial defect in pure Si and Si/Ge systems. In both cases we studied geometry, energetics, as well as vibrational properties of the defect.

Chemically, the O atom establishes a strong covalent bonding with the two Si atoms which donate an electron each to form the Si-O-X molecule, where X is either Si or Ge. Our calculations for the oxygen defect in silicon agree reasonably well with the existing experimental data and previous calculations. In particular, we confirm a highly peculiar anharmonic character of this defect which can be considered as a vibration of the oxygen atom along the Si-Si direction coupled to its rotation around the same axis. Therefore, our calculations agree with the conclusion made in Ref. 5 that this defect should be treated as linear rather than puckered. This is in spite of the fact that the linear configuration does not correspond to the global energy minimum of the system.

Using a simple finite cluster approach whereby a finite number of atoms in the periodic supercell are considered explicitly, we calculated the phonon spectrum of the O in silicon system. In particular, we show that the vibrational spectrum contains two local vibrations, asymmetric and symmetric stretching modes around 1107 cm^{-1} and 599 cm^{-1} , respectively. Although the first mode has been known for a long time, the latter one has only been suggested rather recently⁵ since it is IR inactive. In addition to these local discrete modes, we have also found some resonances which are attributed to the O defect. The resonances around 140 and 526 cm^{-1} have been reported before in Ref. 3 and Refs. 12, 10, 6, 5, and 4, respectively; at the same time, the low-frequency resonance around 260 cm^{-1} , as far as we are aware, has not been reported previously. One has to have in mind, however, that low-frequency resonances might be difficult to observe experimentally since they may be masked by the bulk phonons in the same frequency range. We have also calculated isotope shifts which agree well with the available data.

In order to model an oxygen interstitial defect in a Si/Ge alloy system, we substituted a Si atom in the 64 atom supercell by Ge and then placed an oxygen atom at four possible

positions with respect to the oxygen. These calculations correspond to a rather low concentration of Ge atoms in the alloy $\text{Si}_{1-x}\text{Ge}_x$ ($x \approx 0.016$). Our main conclusions coming from the calculations can be summarized as follows. First, the O atom finds it energetically more preferable to stay away from the Ge atom: the likelihood of finding O atoms making a direct chemical bond with Ge atoms (at least at small Ge concentrations) is small. Therefore, O atoms are most likely to form Si-O-Si molecules similar to those formed in pure silicon; these molecules may, however, have Ge atoms in their neighborhood. This conclusion is in good agreement with the available experimental data.^{14,16,18} Second, the effect of the Ge atoms on the geometry and vibrational properties of the Si-O-Si molecules is not very significant, apart from the case when a Ge atom is positioned next to the molecules which results in $\approx 40\text{ cm}^{-1}$ downward shift of the asymmetric stretching mode. Third, at higher Ge concentrations one has also to consider a possibility of Si-O-Ge molecules (and Ge-O-Ge molecules at even higher concentrations). We find that the vibrational spectrum of the Si-O-Ge molecule in silicon, geometry of which is intermediate to that of the Si-O-Si and Ge-O-Ge molecules, is considerably deformed in comparison with the vibrational properties of the O defect in pure silicon. In particular, we find that the 1107 cm^{-1} peak moves considerably downwards, while the 599 cm^{-1} local mode becomes a resonance. The downward shift of the asymmetric stretching mode with an increase of the Ge concentration was observed in Ref. 18.

The study reported in this paper is rather limited since it corresponds to only very small concentrations of Ge atoms in silicon. We plan to consider several Ge atoms around an O defect in the near future. We think it is also important to understand the diffusion properties of the O defect in the $\text{Si}_{1-x}\text{Ge}_x$ alloys.

ACKNOWLEDGMENTS

S.H. would like to acknowledge the financial support from EPSRC (Grant No. GR/R24561/01). We would also like to thank A. Mainwood for a number of valuable discussions.

¹H. Bender and J. Vanhellefont, *Materials, Properties and Preparation*, Handbook on Semiconductors Vol. 3B (North-Holland, Amsterdam, 1994), Chap. 22, pp. 1637–1753.

²H. Yamada-Kaneta, C. Kaneta, and T. Ogawa, *Phys. Rev. B* **42**, 9650 (1990).

³M. Pesola, J. vonBoehm, T. Mattila, and R.M. Nieminen, *Phys. Rev. B* **60**, 11 449 (1999).

⁴J. Coutinho, R. Jones, P.R. Briddon, and S. Oberg, *Phys. Rev. B* **62**, 10 824 (2000).

⁵B. Pajot, E. Artacho, C.A.J. Ammerlaan, and J.M. Spaeth, *J. Phys.: Condens. Matter* **7**, 7077 (1995).

⁶E. Artacho *et al.*, *Phys. Rev. B* **56**, 3820 (1997).

⁷R. Jones, S. Oberg, and A. Umerski, *Mater. Sci. Forum* **83-87**, 551 (1991).

⁸J. Plans, G. Diaz, E. Martinez, and F. Yndurain, *Phys. Rev. B* **35**, 788 (1987).

⁹T. Yamada-Kaneta, C. Kaneta, T. Ogawa, and K. Wada, *Mater. Sci. Forum* **38-41**, 637 (1989).

¹⁰D.R. Bosomworth, W. Hayes, A.R.L. Spray, and G.D. Watkins, *Proc. R. Soc. London, Ser. A* **317**, 133 (1970).

¹¹B. Pajot and B. Cales, *Mater. Res. Soc. Symp. Proc. No. 59* (Materials Research Society, Pittsburgh, 1986), p. 39.

¹²J. Corbett, R. McDonald, and G. Watkins, *J. Phys. Chem. Solids* **25**, 873 (1964).

¹³T. Hallberg, L.I. Murin, J.L. Lindstrom, and V.P. Markevich, *J. Appl. Phys.* **84**, 2466 (1998).

¹⁴H. Yamada-Kaneta, C. Kaneta, and T. Ogawa, *Phys. Rev. B* **47**, 9338 (1993).

- ¹⁵B. Pajot, P. Clauws, J.L. Lindström, and E. Artacho, Phys. Rev. B **62**, 10 165 (2000).
- ¹⁶D. Wauters and P. Clauws, Mater. Sci. Forum **258-263**, 103 (1997).
- ¹⁷L.I. Khirunen, Yu.V. Pomozev, M.G. Sosnin, N.V. Abrosimov, M. Höhne, and W. Schröder, Physica B **273-274**, 305 (1999).
- ¹⁸I. Yonenaga, M. Nonaka, and N. Fukata, Physica B **308-310**, 539 (2001).
- ¹⁹G. Kresse and J. Hafner, Phys. Rev. B **47**, 558 (1993).
- ²⁰G. Kresse and J. Furthmüller, Comput. Mater. Sci. **6**, 15 (1996).
- ²¹G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11 169 (1996).
- ²²G. Kresse and J. Hafner, J. Phys.: Condens. Matter **6**, 8245 (1994).
- ²³D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).
- ²⁴J.P. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Pederson, D.J. Singh, and C. Fiolhais, Phys. Rev. B **46**, 6671 (1992).
- ²⁵K. Parlinski, Z.Q. Li, and Y. Kawazoe, Phys. Rev. Lett. **78**, 4063 (1997).
- ²⁶G. Kresse, J. Furthmüller, and J. Hafner, Europhys. Lett. **32**, 729 (1995).
- ²⁷Y.J. Lee, M. Pesola, J. von Boehm, and R.M. Nieminen, Phys. Rev. B **66**, 075219 (2002).
- ²⁸L.N. Kantorovich, <http://www.cmmmp.ucl.ac.uk/~lev/codes/lev00/index.html> [user-friendly package for DFT codes CASTEP/VASP/SIESTA (1996-2004)].
- ²⁹L.N. Kantorovich, J. Holender, and M.J. Gillan, Surf. Sci. **343**, 221 (1995).
- ³⁰G. Lehmann and M. Taut, Phys. Status Solidi **54**, 469 (1972).
- ³¹O. Jepsen and O.K. Andersen, Solid State Commun. **9**, 1763 (1971).