

# Atomic vibrations in alpha-quartz with silicon vacancies

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**Abstract.** A study of atomic structures and localized symmetrized vibrations in  $\alpha$ -quartz with silicon vacancies in different charge states is presented. This study is performed by computer modeling on the basis of the first-principle type potentials. The equilibrium structures are optimized by minimizing the lattice energy. The phonon symmetrized local densities of states are calculated by means of a recursion method. Moreover, frequencies of localized vibrations of A- and B-symmetries induced by silicon vacancies are determined. The results are discussed in comparative manner for the silicon vacancy in three charge states.

## 1. Introduction

Low-temperature modification of crystalline silica ( $\alpha$ -quartz) has been the object of interest of numerous experimental [1-6] and theoretical [7-12] research because it plays key role in various engineering devices. Important physical properties such as structural and vibrational ones were studied in these works. The atomic structure and the physics of vibrations in defect-free  $\alpha$ -quartz are well understood.

In the presence of point defects that violate the translational symmetry of the crystal lattice, many extra phenomena are observed: for example, diverse anomalies in spectra of the Raman scattering or infra-red absorption. The microscopic origin of similar phenomena remains unclear and their description refers to a range of difficult solvable problems. In particular, it would be helpful to know the contributions from differently charged defects in such anomalous behaviours.

At the microscopic scale, valuable information about effects of charged defects on the local atomic structure and lattice dynamics is often obtained using atomistic simulation which has become a significant method in research. This simulation can be provided by quantum-mechanical calculations called first-principles or ab initio methods. In the framework of this approach one can distinguish two main currents. There are the Hartree–Fock theory and the density functional theory used with different levels of accuracy: local density approximation, generalized-gradient approximation or hybrid functionals.

When it is necessary to use of very large atomic cluster, for instance, when modelling localized vibrations in solids containing charged defects, ab initio methods are faced with a computational demanding task. In this case, we can apply the computationally less demanding classical mechanics that describe the interactions between the atoms using interatomic potentials known as the force-field approach [13-15].

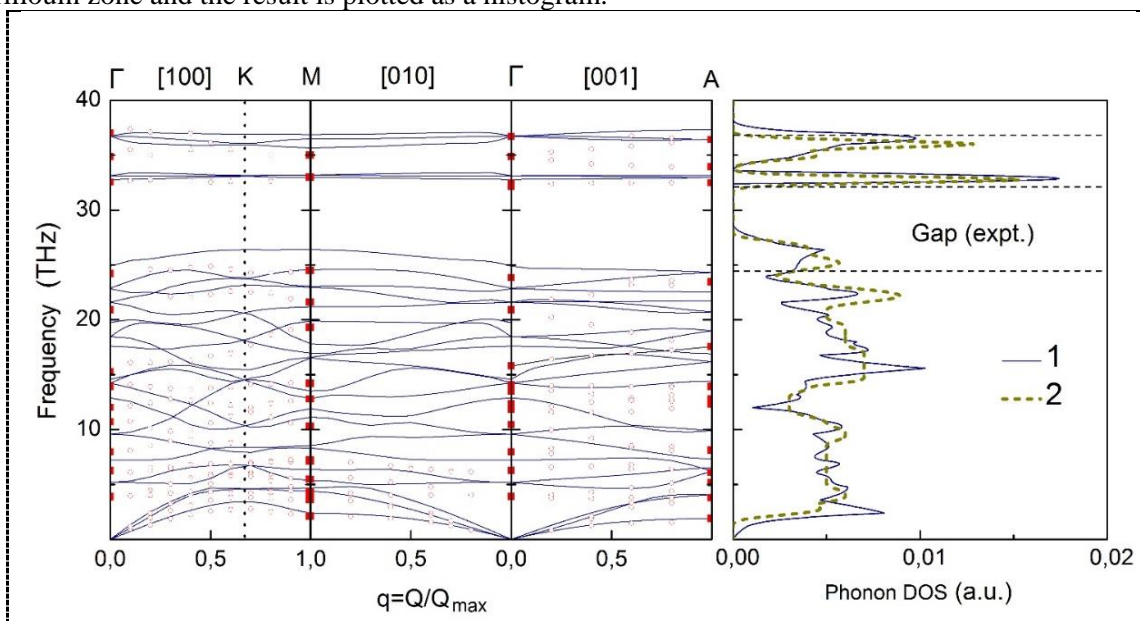
It has been shown by quantum-mechanical calculations that the local atomic structure of  $\alpha$ -quartz is strongly dependent on point defects [16,17] and their charge states [18-23]. Defects in the oxygen sublattice such as oxygen vacancies and interstitials as well as several types of impurities were examined in the above publications. Recently, we were discussing effects of the differently charged oxygen vacancies on the vibrational spectrum of  $\alpha$ -quartz [24]. It must however be admitted that the silicon vacancies which can also attend in  $\alpha$ -quartz have not received as much attention. Information



about the influence of charge states of these defects on the atomic structure and vibrational spectrum of  $\alpha$ -quartz has not been acquired. A few publications have been devoted to silicon vacancies [21-23]. The purpose of this paper is to investigate and to thoroughly discuss the effects of differently charged silicon vacancies  $V_{\text{Si}}^{-4}$ ,  $V_{\text{Si}}^{-2}$  and  $V_{\text{Si}}^0$  on the atomic structure and vibrational spectrum of  $\alpha$ -quartz.

## 2. Computational methods

The simulation is based on force-field approach and the numerical methods of the present work are precisely those used in our previous paper on oxygen vacancies [24]. In order to model the structures and the vibrations in quartz with defects in different charged states we used two-body potentials of the classical Born-Mayer model. The potentials with parameters [25] were chosen to describe the interactions between ions. The reliability of this simple model was verified by comparing available experimental data with calculated values for structural, elastic and dynamical properties of pure  $\alpha$ -quartz. For example, Figure 1 depicts the dispersion curves in three highly symmetric directions of the Brillouin zone and the density of states (DOS) of phonons. The frequency distribution is determined by solving the Fourier transform of the dynamic matrix for randomly selected wave vectors of the first Brillouin zone and the result is plotted as a histogram.



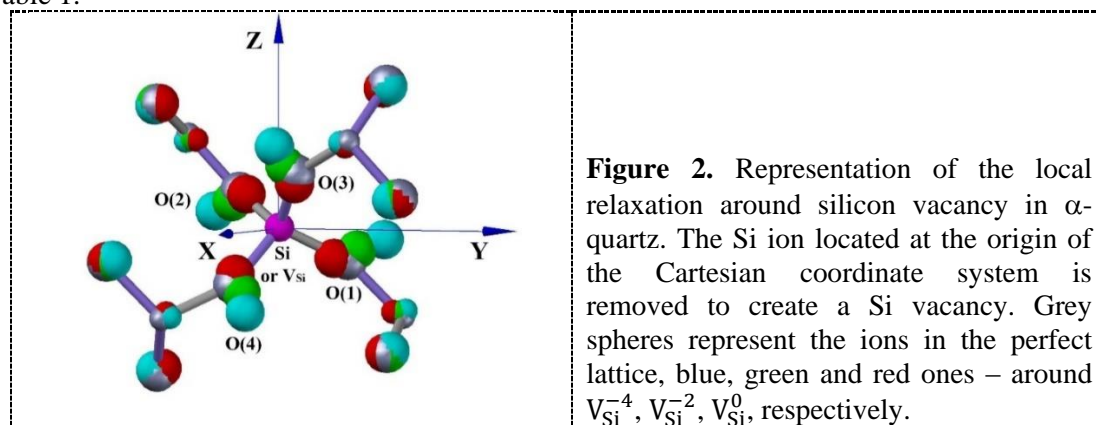
**Figure 1.** (Left panel) Phonon dispersion in  $\alpha$ -quartz along the main symmetry directions. Squares are observed values [3], open circles – [4-6]. (Right panel) Calculated phonon DOS: using chosen point of the Brillouin zone (curve 1), by a recursive method (curve 2).

The formation of silicon vacancies is accompanied by a geometrical distortion of the crystal lattice. The structural optimization was performed using the process of minimizing the lattice energy. All the expressions that are needed for these calculations are presented in detail in [26]. The effect of the silicon vacancies on the vibration spectrum of  $\alpha$ -quartz was evaluated by analyzing the local symmetrized densities of states (LSDOS) of phonons in defect-free and defective quartz. The recursion method based on the Lanczos algorithm [27] with the initial vector of a given symmetry is used to calculate the phonon LSDOS. The projection operator method is used to find the symmetry coordinates, which determine this initial vector. The LSDOS is expressed by the imaginary part of the diagonal element of the Green's function matrix, which is written by the easily calculated continued fraction.

A cluster of 4000 ions is sufficient to construct the total phonon DOS and in this case the Lanczos technique is used for 10 levels of recursion. The calculation result is plotted in Figure 1. The comparison of the curves obtained by different methods shows a reasonable agreement.

### 3. Results and Discussion

We began our investigation with the construct of static equilibrium structures of the  $\alpha$ -quartz with Si vacancies in different charge states. The local configurations in the vicinity of  $V_{\text{Si}}^{-4}$ ,  $V_{\text{Si}}^{-2}$  and  $V_{\text{Si}}^0$  vacancies are shown in Figure 2. The distances between some ions in relaxed configurations are given in Table 1.



**Table 1.** Interionic distances ( $\text{\AA}$ ) in  $\alpha$ -quartz with Si vacancies.

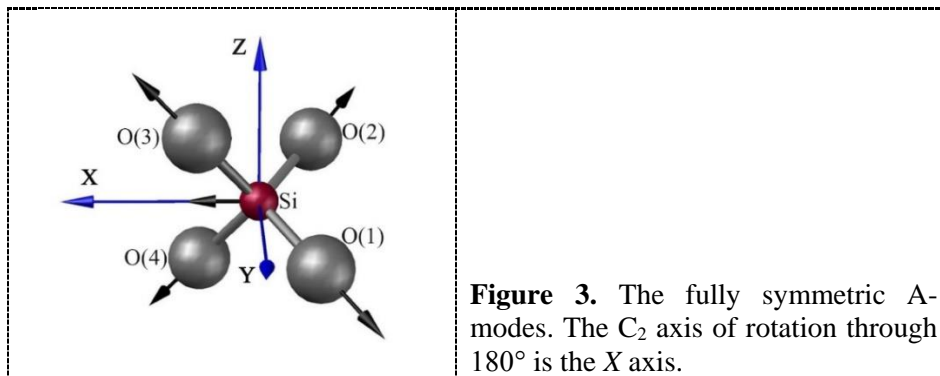
	Charge state of vacancy		
	-4	-2	0
$V_{\text{Si}}\text{--}[\text{O}(1) \text{ or } \text{O}(2)]$	2.201	1.713	1.363
$V_{\text{Si}}\text{--}[\text{O}(3) \text{ or } \text{O}(4)]$	2.080	1.658	1.353
O(1)–O(2)	3.657	2.835	2.266
O(3)–O(4)	3.426	2.740	2.235
Si–[O(1) or O(2)]	1.544	1.549	1.613
Si–[O(3) or O(4)]	1.540	1.551	1.609

A negatively charged vacancy  $V_{\text{Si}}^{-4}$  is produced by removing a silicon ion. The character of the lattice distortions near this defect correlates with the fact that it has an excess negative charge with respect to the crystal lattice. The distances between vacancy  $V_{\text{Si}}^{-4}$  and nearest oxygen ions are found to be larger than the Si–O bond lengths in defect-free  $\alpha$ -quartz, in which the Si–O distances are determined to be 1.598 (1.605)  $\text{\AA}$  for two oxygen ions and 1.606 (1.614)  $\text{\AA}$  for the other two oxygen ions, where the numbers in parentheses are the experimental data [2].

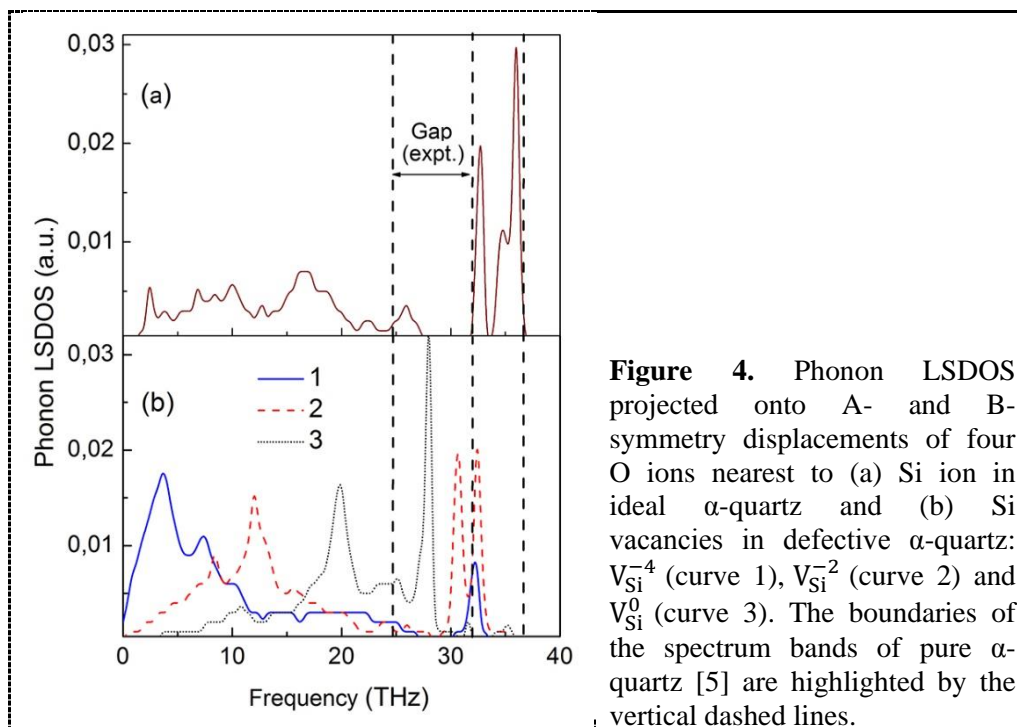
For a neutral  $V_{\text{Si}}^0$  vacancy, the situation is different. This defect can be formed when extra holes are trapped on nearest-neighbors of the negatively charged Si vacancy. The interaction energy between the neutral silicon vacancy and nearest oxygen ions is increased. This circumstance leads to strengthen an attraction in these pairs and to decrease distances between Si vacancy and O ions.

Then we have calculated the phonon LSDOS projected onto ion displacements of  $\text{SiO}_4$  unit. Si ion (Si vacancy) is on the site with point symmetry  $C_2$ . The oxygen ions are involved in two vibrations of A-symmetry and one vibration of B-symmetry. The A-type vibrations consist of one symmetric bending mode and one symmetric stretching mode, the B-type vibration is an asymmetric stretching mode. As an example, Figure 3 illustrates the directions of the motions for A-symmetry vibrations.

The phonon LSDOS projected onto A- and B-type displacements of four O ions nearest to Si ion in ideal  $\alpha$ -quartz and differently charged Si vacancies in defective  $\alpha$ -quartz are shown in Figure 4. According to obtained results, symmetric- and asymmetric-stretch vibrations are mostly present in the high-frequency spectrum band, symmetric bending is responsible for the low-frequency and the medium-frequency bands.



For neutral Si vacancies, the high-band of the phonon LSDOS is shifted to the low-frequency part of the spectrum and the low- and middle bands are shifted to the high-frequency part. There is the large peak in the band gap. These changes may be explained the following. The short-range repulsive interaction is decreased, but the Coulomb interaction remains the same as in the perfect  $\alpha$ -quartz. Thus



**Table 2.** Frequency (THz) of vacancy-induced defect vibrations in  $\alpha$ -quartz with Si vacancies.

Vacancy charge state	Ions	Vibration symmetry	
		A	B
-4	O(1) and O(2)	3.6, 32.4	3.6, 32.4
	O(3) and O(4)	3.6, 7.6, 10.4, 32.4	3.6, 7.6, 10.4, 32.4
-2	O(1) and O(2)	8.4, 12.0, 30.8	30.8
	O(3) and O(4)	8.4, 12.0, 15.6, 30.8	8.4, 12.0, 30.8
0	O(1) and O(2)	20.0, 28.0	25.0
	O(3) and O(4)	10.8, 20.0, 25.0, 28.0	25.0, 28.0

the effective interaction of O ions making the bending movement becomes greater. Consequently, the phonon density located lower than 20 THz shifts to the high-frequency part of the spectrum. The effective interaction of oxygen ions doing stretching movement diminishes and the phonon LSDOS located higher than 30 THz shifts to the low-frequency zone.

The Si vacancies are responsible for resonant vibrations. These defects also induce one gap vibration. The oxygen ions contribute to causing this gap vibration. The frequencies of the vibrations depend on the charge state of Si vacancies. The frequencies of localized symmetrized vibrations induced by Si vacancies are given in Table 2.

#### 4. Conclusion

We investigate the influence of silicon vacancies in three charge states on the structure and the phonon spectrum of  $\alpha$ -SiO<sub>2</sub> using first-principle potentials. We predict frequencies of localized vibrations induced by differently charged Si vacancies. Our study indicates that the structural and vibrational properties of  $\alpha$ -quartz depend substantially on the charge state of the defect. It demonstrates that the Si vacancies can strongly affect the static lattice deformation and the phonon DOS by changing the charge state. The obtained results can be applied to the interpretation of the vibrational spectra that are measured experimentally by means of IR absorption and Raman spectroscopy.

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