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Vibrational dynamics of crystalline silicon dioxide with charged Ge impurities

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The effects of differently charged Ge impurities on the local atomic structure and lattice dynamics of α -quartz were studied. We have determined the equilibrium structures and calculated the symmetrized local density of vibrational states for the Ge-doped α -quartz. The frequencies of localized vibrations of A- and B-symmetries induced by Ge impurities were obtained. Besides, we have analyzed what contribution the vibrations of atoms located around the Ge impurities make to the localized symmetrized vibrations.

Keywords: Quartz lattice; impurities; defect structure; localized vibrations.

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1. Introduction

The object of interest of many papers¹⁻¹⁵ is low-temperature modification of silicon dioxide (α -quartz) due to its special properties. Its structure is described by either the $D_3^4 = P3_121$ (a left-handed form) or the $D_3^6 = P3_221$ (a right-handed form) space symmetry group and belongs to the trigonal crystal system. A primitive cell contains three formula units (nine atoms); a hexagonal elementary cell consists of three silicon–oxygen SiO₄-tetrahedrons.

Various properties of α -quartz at the microscopic scale are often studied by means of atomistic simulations.^{1–7} The latter employ quantum mechanics descriptions, called "first-principles" or *ab initio* methods. These approaches make it possible to distinguish two main lines. One of them includes the Hartree–Fock theory that represents the full configuration interaction, coupled cluster, etc. On the other hand, we may address the density functional theory (DFT) that allows different accuracy levels, namely, the local density approximation, the general gradient approximation or hybrid functionals.

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The atomic structure and physics of vibrations of a perfect α -quartz are well understood.^{8–12} In the case of defects, many extra phenomena can be observed, for example, anomalies in specific heat, Raman scattering spectra or infrared absorption. The microscopic origin of similar phenomena is difficult to ascertain. In particular, we need to know how the differently charged defects contribute when they break the translational symmetry of the crystal lattice. This fact requires the use of too large atomic clusters. For such systems, quantum chemical calculations involve a major computational problem, and to solve it, we should apply a classical mechanics approach describing the atom–atom interactions through interatomic potentials (called force-fields).^{13–16}

The majority of studies concerning point defects in α -quartz have been devoted to the characterization of the structure and electronic properties. Many aspects regarding their vibrational properties are not completely clarified yet. Therefore, the description of the dynamic processes in defective α -quartz is essential information about defect vibrations.

One of the simplest point defects existing in α -quartz is an isoelectronic germanium (Ge) impurity. In previous paper,¹⁷ we used the pairwise interionic potentials to model the atomic structure and lattice dynamics of α -quartz with Ge⁺⁴ impurities. However, no detailed information about charge state effect of Ge has been acquired. Moreover, it is well-known that Ge impurity is a substitute for Si and readily traps electrons to form Ge⁺³ in α -quartz.

The present paper's goal is to generalize the earlier obtained results and to thoroughly discuss how three states of Ge impurities such as Ge^{+4} , Ge^{+3} and Ge^{+2} affect the structural and vibrational properties of α -quartz.

2. Simulation Methods

The influence of the differently charged Ge impurities on the local atomic structure and vibration spectrum of α -quartz was studied within a limited-size cluster model, as described in Ref. 18. The model takes into account long-range interatomic interactions with charged defects. It divides the Ge-doped α -quartz into spherical regions: an inner region 1 and two outer regions 2 and 3, as shown in Fig. 1.

The optimization of the structures is achieved by minimizing the lattice energy. All the expressions for these calculations can be found in Ref. 19. In order to compute the symmetrized local densities of states (SLDOS) of phonons in α -quartz containing charged defects, we utilized the recursive method.^{20,21} This approach was already applied successfully.^{17,22}

As is known, the O–Si–O chemical bonds exhibit an ionic covalent character. Nevertheless, the two-body, rigid ion-type potentials are able to successfully predict relevant structural, mechanical and dynamical properties. The studies^{15,23} focus on this aspect.

Our calculations are based on the classical Born–Mayer model.¹⁵ It regards a potential V(r) as a Coulomb term and a short-range two-body exponential function Vibrational dynamics of crystalline silicon dioxide with charged Ge impurities



Fig. 1. The structural model of the Ge-doped α -quartz.

altogether. The former accounts for the long-range electrostatic interactions; the latter models, the repulsive and attractive dispersion energy between close pairs. This simple analytical potential takes advantage of a pairwise form, easy and quick to evaluate. So, the large-sized system can be simulated relatively easily. Furthermore, the potential parameterized by the van Beest–Kramer–van Santen (BKS) parameters²³ already gave some encouraging results for α -quartz.^{15,17}

The graphic dependencies of the α -quartz potentials used in this work are shown in Fig. 2. It should be noted that the Si–Si interaction has no short-range component. A cutoff radius of 8 Å is chosen for the short-range interactions.

For the Ge-doped α -quartz, the potential parameters of the Ge–O interaction are presented in Ref. 17. The above paper deals with an empirical fitting procedure for deriving them. In this case, the potential has the same shape as in the Born– Mayer model including the Coulomb interactions. Figure 2 represents the potential energy corresponding to the Ge–O interaction. The effective charge value of +2.4 is supposed to be neutral with respect to the Ge⁺⁴ impurity in the α -quartz lattice, because the effective ionic charges for Si and O are determined to be +2.4 and -1.2 in the BKS potential.²³ These charges are considered necessary for better accounting of α -quartz bond covalency. The model with formal ionic charges ($q_{si} =$ +4, $q_o = -2$) reproduces the observed structural, elastic and vibrational behavior of the worse crystal. Effective charges localized on Ge⁺³ and Ge⁺² ions are negative with respect to the crystal lattice, have fractional values and are equal to +1.8 and +1.2, respectively. A. N. Kislov



Fig. 2. The pair potentials of interionic interactions.

3. Results and Discussion

To construct the static equilibrium structure of SiO₂:Ge, we first optimized the structure of a perfect α -quartz crystal as in our previous work.¹⁷ The local relaxation occurred around the Ge⁺⁴ ion is shown schematically in Fig. 3. The values obtained for distances between some ions in the Ge-doped α -quartz are summarized in Table 1 (the notations O(1), O(2), O(3), O(4) refer to the labels as in Fig. 3).

In the Ge⁺⁴-doped α -quartz, the simulated Ge–O bond length is 1.638 Å for O(1) (or O(2)) ion and 1.649 Å for O(3) (or O(4)) ion. These data are found to



Fig. 3. (Color online) The structural fragments of SiO_2 :Ge around the Ge⁺⁴ impurity. Gray circles indicate the ions before the lattice relaxation, red circles — after the relaxation.

	Charge of Ge impurity		
Ion–Ion	+2.4	+1.8	+1.2
$\overline{\text{Ge-}[O(1) \text{ or } O(2)]}$	1.638	1.714	1.806
Ge-[O(3) or O(4)]	1.649	1.730	1.827
O(1) - O(2)	2.774	2.896	3.047
O(3) - O(4)	2.704	2.820	2.962

Table 1. Distances (Å) between some ions in SiO_2 :Ge.

be larger than the calculated Si–O bond lengths for perfect α -quartz, but a few less than the Ge–O bond lengths for α -quartz like GeO₂. In α -quartz, the Si–O bond lengths are 1.598 (1.605) Å for two oxygen ions O(1) and O(2) and 1.606 (1.614) Å for the other two O(3) and O(4), where the numbers in parentheses are experimental values.⁸ In α -quartz-like GeO₂, the calculated Ge–O distance is 1.650 Å for the O(1) (or O(2)) ion, as Ref. 17 shows; the experimental value is 1.737 Å, given in Ref. 24. Our results are in agreement with the first-principles cluster model calculations,²⁵ where it is pointed out that the substitution of Si atom by Ge one causes an average Ge–O distance to be about 0.1 Å longer than the Si–O bond.

The analysis of interatomic interactions can explain the nature of structural deformations in the vicinity of the Ge ion. Being inserted into the lattice, the Ge^{+4} impurity diminishes the energy of the short-range interactions between the Ge impurity and the nearest O-ions. The attraction of these pairs weakens as well. This circumstance appears to cause an increase in distance between the Ge^{+4} impurity and the oxygen ions.

The results demonstrate that the lattice relaxation behavior strongly depends on the charge state of the Ge impurity. After replacing one of the Si^{+4} ions by the Ge^{+3} ion, the Ge–O or O–O distance between the nearest neighboring ions increases, see Table 1. The DFT calculations for germanium-doped silica also indicate that Ge–O bonds are elongated by about 0.2 Å.²⁶ In the event of substituting the Ge⁺² ion for the Si^{+4} ion, the distance between the neighbors increases even more.

The next important point was to model the phonon SLDOS for both perfect and defective α -quartz crystals. For this purpose, we wrote the Fourier transform of the lattice Green's function of the dynamical matrix in real space. For calculating the phonon SLDOS, we resorted to the Lanczos algorithm²⁷ using an appropriate symmetry vector as starting.

We have calculated the phonon SLDOS projected onto the region containing five ions: SiO_4 (or GeO_4), which is associated with the 15-dimensional atomic displacement space. The Si (or Ge) ion executes one A-symmetry mode and two modes symmetrized by the representation B. Both ions O(1) and O(2) or O(3) and O(4) accomplish two A-vibrations and one B-vibration. The A-symmetry vibrations of O ions are made up of one symmetric bending mode and one symmetric stretching mode, the B-symmetry vibration is an asymmetric stretching mode. In Fig. 4, we show the directions of the motion of A-type vibrations.

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Fig. 4. A-symmetry motions of the GeO₄ unit. The X-axis is the C_2 -axis of rotation through 180° .

The phonon SLDOS projected onto A-symmetry displacements of the Si ion in perfect α -quartz and the Ge⁺⁴ ion in SiO₂:Ge are presented in Fig. 5(a). As can be seen, the Ge⁺⁴ ion contributes to shifting the low- and middle bands of the phonon densities to the low-frequency part of the spectrum. Such a redistribution of the phonon SLDOS can be explained by weakening the effective interaction between the Ge⁺⁴ and its surrounding ions as compared to the Si-host lattice interaction in perfect α -quartz. The SLDOSs of the defective and perfect crystals clearly differ in peaks. In the first case, they correspond to the localized vibrations induced by the Ge impurities.

According to Fig. 5(a), the Ge⁺⁴ impurity is responsible for four resonant A-symmetry vibrations at the frequencies of 2.0, 5.6, 14.8 and 16.4 THz, which are related with the movement of Ge⁺⁴ ion. Besides the resonant vibrations, the Ge⁺⁴ impurity also induces one gap B-symmetry vibration at the frequency of 30.4 THz, see Table 2. The oxygen ions make a contribution in this gap vibration. Furthermore, O ions can participate in two resonant A-symmetry vibrations of 16.4 and 34.0 THz.

Our calculations show that the other germanium defects: Ge^{+3} and Ge^{+2} also induce resonant vibrations and one gap vibration at frequencies of 31.2 and 31.6 THz, respectively. These gap vibrations are associated with the *A*- and *B*-symmetry motion of oxygen ions. The frequencies of localized symmetrized vibrations in SiO₂:Ge induced by the Ge impurities are listed in Table 2.

For example, Fig. 5(b) displays the phonon SLDOS projected onto *B*-symmetry displacements of the O(3)- and O(4)-ions in α -quartz with Ge⁺⁴, Ge⁺³ and Ge⁺² impurities. The redistribution of the density of states is observed in the middle-frequency and forbidden bands. The middle band of the phonon SLDOS shifts toward the low-frequency spectrum range. The peak in the forbidden band is displaced rightward, to the higher frequencies when changing the charge state of Ge from +4 to +2.



Fig. 5. Phonon SLDOS: (a) projected onto A-symmetry displacements of Si ions in perfect α quartz (curve 1) and Ge⁺⁴ ion in SiO₂:Ge (curve 2), (b) projected onto B-symmetry displacements of O(3) and O(4) ions in α -quartz with Ge⁺⁴ ion (curve 1), Ge⁺³ ion (curve 2) and Ge⁺² ion (curve 3). The arrows indicate the localized vibrations that involve Ge⁺⁴ ion. The vertical dotted lines indicate the boundaries of the spectrum parts of the perfect α -quartz found from experiment.¹⁰

	Ion	Vibration symmetry		
Ge charge		A	В	
+2.4	$\begin{array}{c} {\rm Ge} \\ {\rm O}(1),{\rm O}(2) \\ {\rm O}(3),{\rm O}(4) \end{array}$	$\begin{array}{c} 2.0,\ 5.6,\ 14.8,\ 16.4\\ 16.4,\ 34.0\\ 15.2,\ 34.0\end{array}$	$2.0, 3.2, 8.4, 12.8 \\30.4 \\16.0, 30.4$	
+1.8	$\begin{array}{c} {\rm Ge} \\ {\rm O}(1),{\rm O}(2) \\ {\rm O}(3),{\rm O}(4) \end{array}$	2.4, 5.6, 13.6 15.6, 31.2, 33.6 14.8, 31.2, 33.6	$3.6, 8.0, 11.2 \\31.2 \\14.8, 31.2$	
+1.2	$\begin{array}{c} {\rm Ge} \\ {\rm O}(1),{\rm O}(2) \\ {\rm O}(3),{\rm O}(4) \end{array}$	2.8, 5.6, 12.8 14.8, 31.6, 33.2 13.6, 31.6, 33.2	$2.8, 6.8, 11.2 \\31.6 \\14.0, 31.6$	

Table 2. Frequencies (THz) of localized vibrations induced by Ge impurity.

The O(3) and O(4) ions contribute to causing one resonant *B*-symmetry vibration and one gap *B*-symmetry vibration. Their frequency values depend on the charge state of Ge impurity (see Table 2). The change of Ge charge from +2.4 to +1.2 leads to a decrease in the resonant mode frequency, while the gap mode frequency demonstrates a slight increase.

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4. Conclusions

In this work, the simulation methods to investigate how different charged states of Ge impurities affect the atomic structure and vibrational properties of α -quartz were used. It turns out that the change in charge states of the Ge impurities leads to strong deformation of the crystal structure. Besides, the phonon density dramatically changes as well. The values of the localized vibration frequencies are also dependent on the charge state of the Ge impurities. The calculations make it possible to predict the appearance of a gap vibration caused by the Ge impurities. The recursive method used allows estimating the contribution of the ion motion to the localized vibrations induced by the differently charged Ge ions.

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