Influences of neutral oxygen vacancies and E_1' centers on α-quartz*

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Our calculations demonstrate that the concentration of neutral oxygen vacancies can affect the geometrical structrue, electronic structure, and optical properties of α-quartz. Moreover, the distribution of the neutral oxygen divacancy can also exert some influence on the properties of α-quartz. The dissimilarity and similarities are presented in the corresponding density of state (DOS) and absorption spectrum. In addition, when a higher defect concentration is involved in α-quartz, the influence of E_1' center on the geometry of α-quartz becomes more significant. However, the introduction of an E_1' center barely results in any improvement compared with the influence produced by the corresponding neutral defect.

Keywords: α-quartz, neutral oxygen vacancy, E_1' center, concentration and distribution of defects

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1. Introduction

The intrinsic point defects can markedly affect material properties.[1–5] For instance, point defects can cause the transmittance band position of multiphase zirconia film to shift[6] and enlarge the friction of carbon nanotube.[7] And the oxygen vacancies have a significant effect on the phonon mode of hexagonal $HoMnO_3$ thin film.[8] While among the point defects generated in silica (SiO_2) material,[9–12] the oxygen vacancy (V_O) is one of the most point harmful defects. It has been found that the V_O is a dominant element in the percolation of SiO_2 and is responsible for the breakdown in electric-field strength.[13–15] The V_O vacancy can increase the hole tunneling current passing through α-quartz.[16] In addition, when the number of V_O vacancies increases, the leakage current can almost exponentially rise.[17] Therefore, V_O has been extensively investigated from silica clusters[18] to solid materials.[19] In particular, a considerable amount of work has been carried out to investigate the α-quartz with deficient centers,[20,21] including the theoreticalal study by using the density functional theory (DFT).[22,23] According to the generalized gradient approximation (GGA) calculations, Kang *et al.*[24] indicated that a network of oxygen vacancies can drastically increase the gate leakage current. Furthermore, it has been found that the formation of the V_O chain is energetically feasible once the isolated V_O vacancies are created.[24] And Nadimi *et al.*[17] also reported a similar phenomenon that there is an attractive interaction between two neutral vacancies.

When the oxygen vacancy in α-quartz is exposed to radiation, the E_1' center, which appears as the E_γ' center in amorphous SiO_2, is a general generated center. Marshall *et al.*[25] observed that oxygen deficient centers can be converted into E' centers after gamma irradiation. And the center has been studied experimentally and theoretically.[12,26,27] However, there is also a controversy over the structure of the E_1' center. For example, there are several configurations provided for the E_1' center, such as $O_3 \equiv Si\cdot{}^{+}Si \equiv O_3$[18,28–30] and $O_2 = Si \cdot$ –O– $^{+}Si = O_2$.[13,31] But the universally accepted point is that the positively charged oxygen vacancy (V_O^+) is considered to be the model of E_1' center. For example, Lenahan and Dressendorfer[32] pointed out that the positive charge can be fixed at the neutral V_O, allowing the formation of the E_1' center. In the case of the stability of the E_1' center, Chadi[33] considered that the positively charged oxygen vacancy is unstable in α-quartz, but the thermodynamic stability was provided by Carbonaro *et al.*[34]

Because the above-mentioned defects have a major influence on the SiO_2 materials, a complete understanding of them can help to improve the quality. It is necessary to make a further study of the neutral V_O and E_1' center. In the present work, we focus on studying the two interior defects located within the bulk of α-quartz and not on the surface. Especially, we attempt to discuss the effects of the concentration and distribution of the two types. Although the concentration and distribution of V_O vacancies have been considered in previous works,[17,24] while the used SiO_2 layers are sandwiched between the Si structures. In this case, the effect of the concentration and distribution of V_O vacancies on the SiO_2 material has not been reported. Hence, both neutral V_O and E_1' centers are introduced into the α-quartz with a maximum number of 2 to produce an expected concentration. So two types of neutral V_O models can be distinguished as follows: a single

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V_O (1–V_O) and two V_Os (2–V_O). In the same way, the E_1' center also has two types as follows: a single E_1' (1–E_1') and two E_1's (2–E_1'). On the basis of the successful applications of the first-principles DFT,[35] which has been used to investigate the V_O[36] and neutralize supercells with charged defects,[37,38] the DFT is also applied in the calculations.

2. Calculation method

The periodic supercell applied in our investigation contains 72 atoms, which are obtained by $2a \times 2b \times 2c$ superlattice. The lattice parameters[39] of the used primitive cell are $a = b = 4.913$ Å, $c = 5.4052$ Å, $\alpha = \beta = 90°$, and $\gamma = 120°$. The space group of the primitive cell is $P3_121$, and there are three formula units per cell, that is to say, there are three Si atoms and six O atoms. The primitive cell in the supercell is shown by a dotted line in Fig. 1(a). According to Ref. [19], the neutral V_O is created by removing the O atom from its lattice site in the intact crystal. With the purpose of producing a concentration of defects, one and two oxygen atoms are removed to establish 1–V_O and 2–V_O defects, respectively. So we have the vacancy concentration of 1.4% and 2.8%, respectively. To investigate the distribution of defects, a larger 8-membered (i.e. 8 Si–O–Si bonds) ring is chosen to vary the position of the V_O. Therefore, the two oxygen vacancies are separated by different numbers of Si–O–Si bonds (0, 1, 2, or 3 Si–O–Si bonds). For convenience, the model of two adjacent V_Os (separated by 0 Si–O–Si bond) is denoted as $2a$–V_O, and the oxygen divacancy separated by 1, 2, or 3 Si–O–Si bonds are represented by $2b_1$–V_O, $2b_2$–V_O, and $2b_3$–V_O, respectively.

To build the model with the E_1' center, a net positive charge is appended to one of the two Si atoms neighboring the neutral vacancy. Like the neutral oxygen divacancy, the two E_1' centers can also be separated by 0, 1, 2, or 3 Si–O–Si bonds, and the types are identified as $2a$–E_1', $2b_1$–E_1', $2b_2$–E_1', and $2b_3$–E_1' respectively. The positive charge can be arbitrarily assigned to one of the two neighboring Si atoms; thus, two models for each E_1' center can be constructed. Consequently, we investigate the effects caused by changing the location of the positive charge.

With the formation of the oxygen divacancy, two pairs of adjoining Si atoms (marked as Si_1, Si_2, Si_3, and Si_4) remain with the two V_Os. In addition, Si_2 and Si_3 are adjacent to each other, and Si_1 and Si_4 are at the ends. The introduction of a positive charge into the system with the 2–V_O center results in the model with one V_O and one E_1'. If the positive charge is fixed on the Si_2 or Si_3 atom, the type of defect is denoted as 1–E_1'(I), and when the positive charge lies on the Si_1 or Si_4 atom, the defect is marked as 1–E_1'(I). As for the model with two E_1's, two positive charges are applied to the two V_Os. The 2–E_1'(II) defect is defined as two positive charges lying on Si_2 and Si_3. The 2–E_1'(II) defect is defined as two positive charges locateed at Si_1 and Si_3, or Si_2 and Si_4. When the charges are located at Si_1 and Si_4, the defect is denoted as 2–E_1'(III).

The relaxation of the related structures is performed at zero pressure by using the GGA–PBE and ultrasoft pseudopotentials.[40] All of the calculations are carried out by using the CASTEP software.[41] In the relaxation process, the total energy convergence accuracy is set to be 2.0×10^{-5} eV/atom and the maximum force acting on atom is 0.05 eV/Å. Additionally, the volume and cell shape are also relaxed, except for the atomic positions. The $4 \times 4 \times 4$ Monkhorst–Pack k-point grid is used for the Brillouin zone integration. The maximum energy cutoff value for plane wave expansion is 340.0 eV. The optimized configurations of α-quartz with neutral V_Os can be distinguished in Fig. 1.

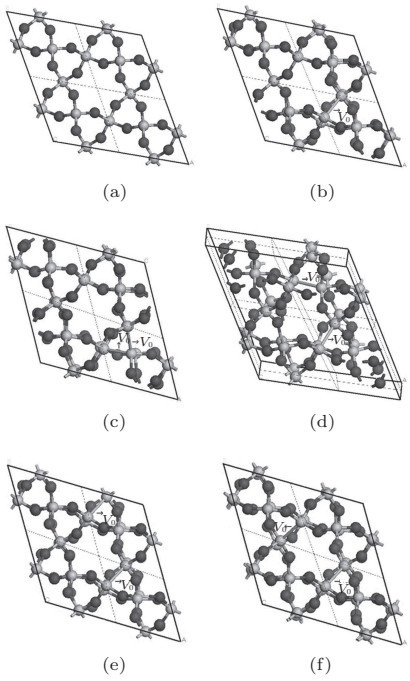


Fig. 1. Configurations of α-quartz with different types of neutral V_O: (a) without defect, (b) 1–V_O, (c) $2a$–V_O, (d) $2b_1$–V_O, (e) $2b_2$–V_O, and (f) $2b_3$–V_O. The gray and black spheres represent Si and O atoms, respectively.

Because defects can modify electronic states and then affect optical properties. Thus, the density of state (DOS) is calculated to describe how the defects influence the electronic properties. To characterize the optical property, the absorption coefficient is calculated, which can be obtained by the complex dielectric function $\varepsilon(\omega)$ ($\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$). The absorption spectrum is described by the following equation:[42]

$$I(\omega) = \sqrt{2}\omega \left[\sqrt{\left[\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)\right]} - \varepsilon_1(\omega) \right]^{1/2},$$

where ω is the frequency of light, and $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ are the real and imaginary parts of the complex dielectric constants, respectively.

3. Results and discussion

3.1. Structures

The calculated lattice parameters of the perfect α-quartz supercell are $a = b = 10.0795$ Å, $c = 10.9558$ Å, $\alpha =$

89.5366°, $\beta = 90.4634°$, and $\gamma = 120.835°$. Compared with the experimental values, the GGA values have the deviation within 2.6% for the lattice parameters. As for the cell volume, the result obtained by GGA approximation is about 5.7% larger than the experimental data. Additionally, for the Si–O bond length in the intact α-quartz, our setting predicts lengths in a range of 1.618 Å–1.630 Å compared with the experimental value of 1.61 Å.[43] Meanwhile, the previous calculations give the values of 1.623 Å–1.631 Å.[13,15]

When the oxygen vacancy (1–V_O) is introduced into α-quartz, the Si–Si bond length at the vacancy is 2.463 Å, which is similar to the previous results of 2.50 Å[44] and 2.44 Å.[15] It is also consistent with the observed Si–Si separation at the relaxed oxygen vacancy $\sim$ 2.50 Å.[45] At the same time, the range of the Si–O bond lengths surrounding the vacancy extends to 1.633 Å–1.642 Å. Table 1 gives the structural parameters of the oxygen vacancies, when the α-quartz has a higher V_O concentration (oxygen divacancy), there is a further expansion in the Si–Si length compared with the length in the crystal with 1–V_O, except for $2b_2$–V_O (2.424 Å and 2.423 Å), which can be found in Table 1. Especially, with the defect of $2a$–V_O, the atomic structure of the vacancies is quite different from the others', and the Si–O bonds are severely distorted. But the atomic structures of the two vacancies are similar to each other, as well as the other types of 2–V_O. For the type of $2b_3$–V_O, the two vacancies share the same atomic structure in the Si–Si and Si–O bonds. Moreover, our calculated Si–Si bond length, 2.467 Å, is close to the reported value of 2.46 Å.[15]

Table 1. Structural parameters of the oxygen vacancies for the configurations with oxygen divacancy, and the length bond is given in unit Å.

	$D_{Si_1-Si_2}$	D_{Si_1-O}	D_{Si_2-O}	$D_{Si_3-Si_4}$	D_{Si_3-O}	D_{Si_4-O}
$2a$–V_O	2.518	1.643	1.656	2.520		1.644
$2b_1$–V_O	2.467	1.632	1.644	2.501	1.641	1.636
$2b_2$–V_O	2.424	1.640	1.639	2.423	1.639	1.640
$2b_3$–V_O	2.467	1.638	1.636	2.467	1.636	1.638

$D_{Si_1-Si_2}$ is the length of Si_1–Si_2 bond, and $D_{Si_3-Si_4}$ is the Si_3–Si_4 bond length. At the same time, D_{Si_1-O}, D_{Si_3-O}, D_{Si_3-O}, and D_{Si_4-O} represent the average lengths of Si_1–O, Si_2–O, Si_3–O, and Si_4–O respectively.

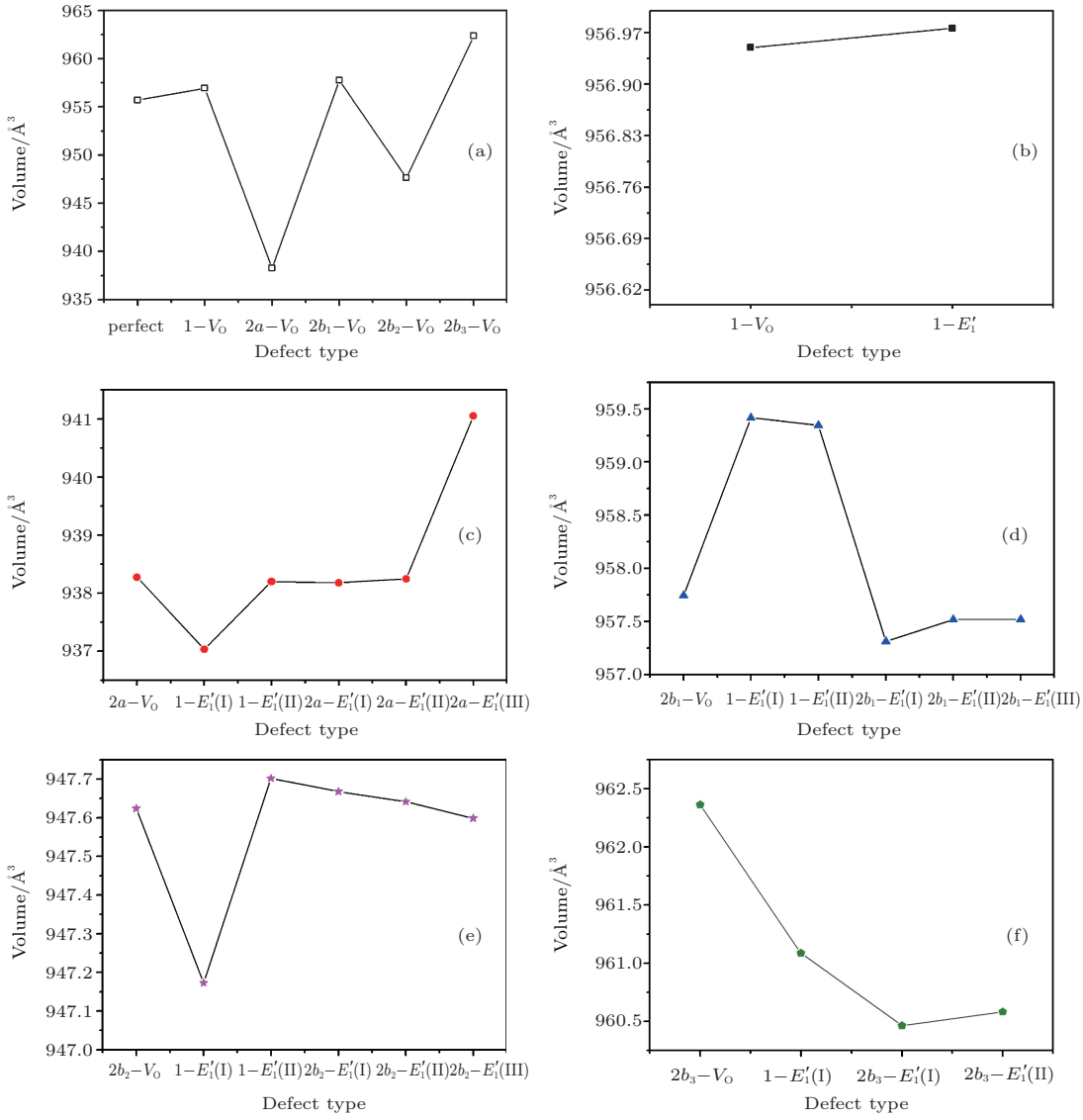


Fig. 2. (color online) Calculated volumes of α-quartz with various defects: (a) neutral V_O(s), (b) 1–V_O, and E_1' center, (c) $2a$–V_O and E_1' center, (d) $2b_1$–V_O and E_1' center, (e) $2b_2$–V_O and E_1' center, and (f) $2b_3$–V_O and E_1' center.

The volumes of α-quartz structures with various defects are listed in Fig. 2. 1–V_O enlarges the geometry of α-quartz with a value of 1.264 Å^3 as shown in Fig. 2(a). However, different types of 2–V_O result in different volumes and geometries. $2b_1$–V_O and $2b_3$–V_O lead to a further expansion in the volume. Whereas the volume becomes smaller than the perfect crystal size, when the structure with $2a$–V_O or $2b_2$–V_O. It indicates that the distribution of the two vacancies can affect the geometry of α-quartz.

We can briefly analyze the effect of the E_1' center on the geometry of α-quartz in Figs. 2(b)–2(f). From Fig. 2(b), we find that the E_1' center can hardly change the volume of α-quartz with 1–V_O. When there are two point defects, the number of E_1' centers makes some differences, so does the position of the positive charge. It indicates that when α-quartz involves a higher defect concentration, the effect of E_1' center on the α-quartz geometry will become significant.

3.2. Density of states

3.2.1. Neutral oxygen vacancy

Figure 3 shows the calculated DOSs for the α-quartz with and without neutral oxygen vacancies. We can know that the band gap of the perfect α-quartz is 5.67 eV, which is smaller than the experimental values of 8.29 eV–9.55 eV[46] and 8.9 eV.[47] But it is similar to the calculated values of 5.8 eV[15] and 5.7 eV.[16] As shown in Fig. 3, there are four distinct bands (three bands in the valence band and one band in the conduction band) in the DOS curve of the perfect α-quartz, and the highest occupied state (the maximum of valence band) is located near the Fermi level. Upon formation of the V_O, the locations of the four bands evidently shift compared with those in the case of the intact crystal. Almost all of the bands move toward the lower energy level as described by Zhang *et al.*[15] In particular, the movement of the band in the conduction band results in the reduction of the band gap. Meanwhile, the peaks also decrease with the formation of V_O. However, there is agreement in the positions of the DOS bands for the defective α-quartz, except for the model with $2a$–V_O. When the α-quartz has two adjacent V_Os, further movement occurs in all bands, especially in the DOSs in the conduction band. As a result, the band gap becomes narrower than those of other structures. The changes in the DOSs may be a result of the redistribution of the two electron charges that remains after the O atom has moved to the two neighboring Si atoms.

In the valence band, each of the calculated DOSs is lower than that of the undefected α-quartz. Moreover, the DOS bands (in the valence band) continually decrease as the number of defects increases. However, the DOSs for the models with 2–V_O centers are higher than those with 1–V_O at the edge of conduction band, except for the model with the $2b_2$–V_O center. In addition, we find that different types of 2–V_O centers exhibit minimal differences in the DOS of the valence band, and the $2b_2$–V_O center exhibits a noticeable decrease. The similarity in the DOSs is also present in $2b_1$–V_O and $2b_3$–V_O as their curves almost completely overlap. The variations observed in the calculated DOSs are attributed to the electrons activated at various levels. On the basis of these results, we infer that the concentration and distribution of vacancies can sufficiently affect the electronic structure.

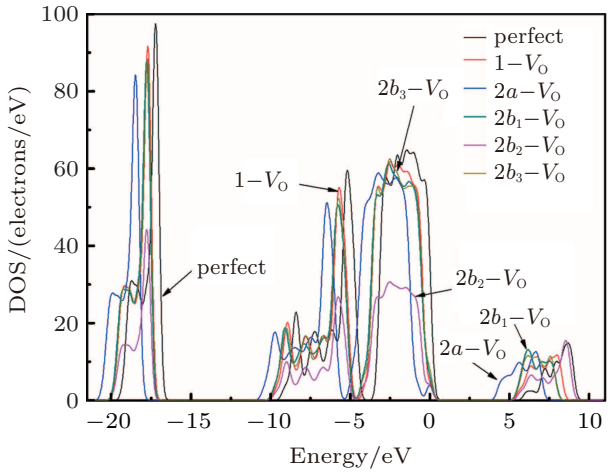


Fig. 3. (color online) The calculated DOSs for α-quartz without and with neutral oxygen vacancy/vacancies.

3.2.2. E_1' center

The DOSs of structures with E_1' centers are also calculated. The results are shown in Fig. 4. DOSs for the models with 1–E_1' and 1–V_O are in excellent agreement as illustrated in Fig. 4(a). It means that neither shifting a single V_O defect into the E_1' center nor catching a hole or losing an electron (one of the Si atoms at the V_O) will affect the electronic structure.

Some minor differences emerge in the two bands near the Fermi level (in the conduction band and at the edge of valence band), when the $2a$–V_O center is introduced into the α-quartz as shown in Fig. 4(b). However, the differences from the other valence bands are undetected. The undetected differences imply that the E_1' center can hardly affect the major of DOS, but the E_1' center has a great influence on the DOSs near the Fermi level. Furthermore, it suggests that the effect of catching a hole or losing an electron (an arbitrary Si atom in the V_O center) is almost negligible, and the electronic excitation can easily happen. Similar phenomena also appear in the other systems as shown in Figs. 4(c)–4(e). We can conclude that for the configuration with one or two E_1' centers, the behavior of the DOS is qualitatively similar to that of α-quartz with corresponding 2–V_O center.

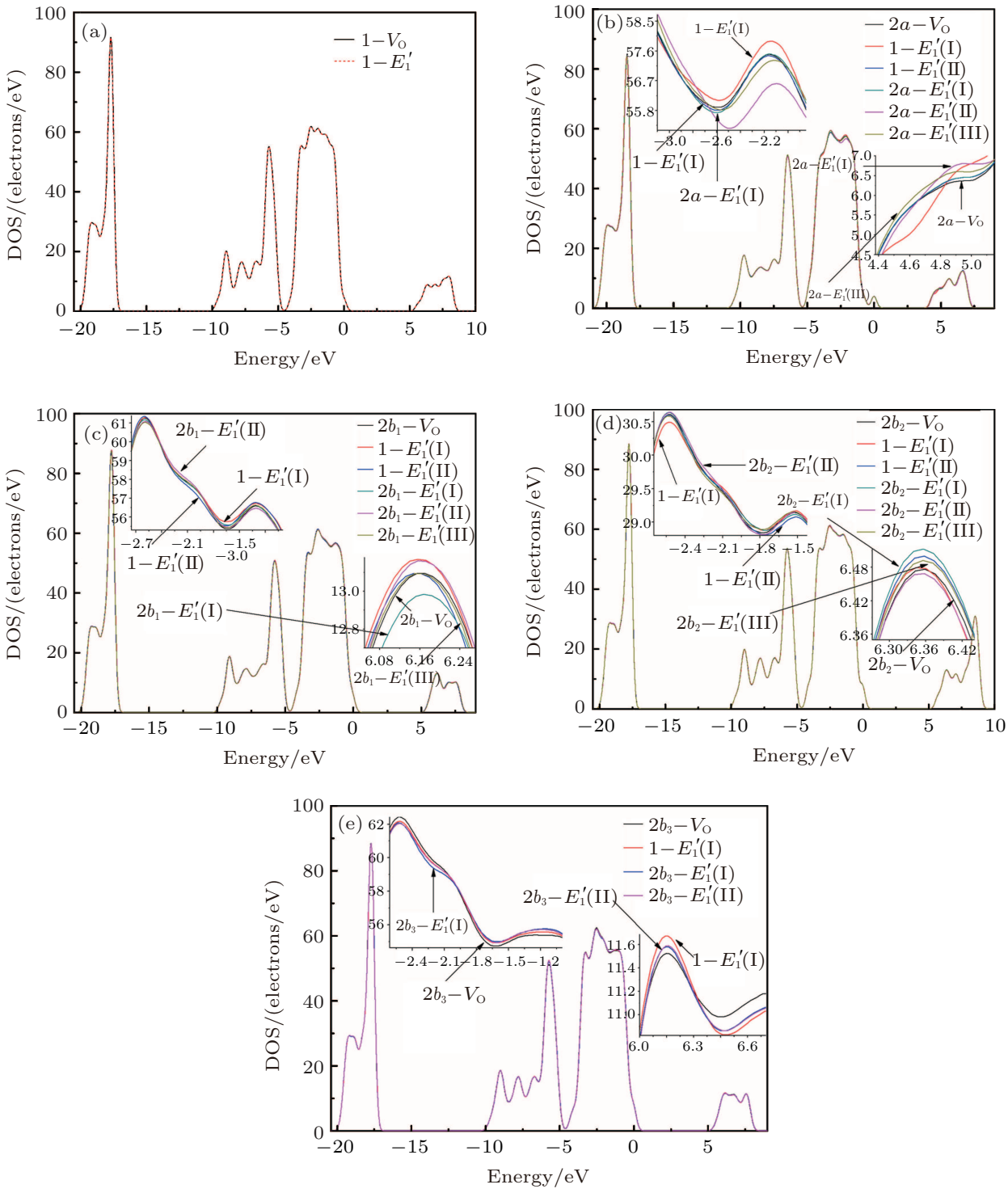


Fig. 4. (color online) DOSs of different configurations with E_1' center(s): (a) 1–V_O, (b) 2a–V_O, (c) 2b_1–V_O, (d) 2b_2–V_O, and (e) 2b_3–V_O.

3.3. Absorption spectrum

3.3.1. Neutral oxygen vacancy

The absorption spectra for the related configurations with neutral V_O(s) are displayed in Fig. 5. Notably, the absorption intensity, as well as the frequency where the peaks occur, decreases upon formation of the V_O. Simultaneously, the optical absorption band widens compared with the shape of absorption spectrum curve for the perfect α-quartz. The changes indicate that the introduction of V_O can remarkably influence the optical property of α-quartz. Once the two V_Os appear, the absorption intensities are further reduced, except for the 2b_2–V_O type. The decrease observed in the absorption coefficient shows that the concentration of defects can affect the optical property of α-quartz. However, the absorption band widths of configurations with single V_O and some types of 2–V_O are still similar.

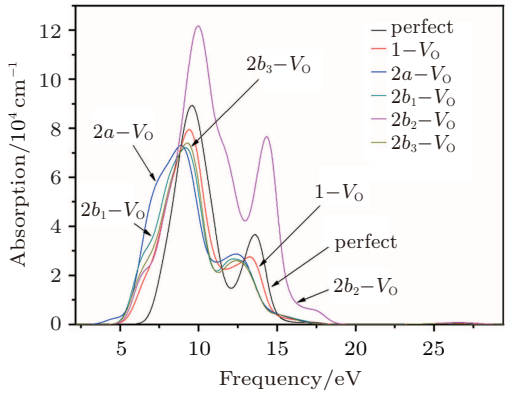


Fig. 5. (color online) Absorption spectra for the α-quartz without and with neutral oxygen vacancy/vacancies.

It should be emphasized that the influence of $2b_2$–V_O on the absorption spectrum is profoundly different from those of the other types of defects. The $2b_2$–V_O center results in a maximum absorption intensity that is considerably higher than those of other configurations, and the positions of the two peaks are at the lower energies. In addition, we can also notice that the $2b_2$–V_O leads to the widest optical absorption band among the defective configurations. However, the lineshapes of the absorption spectrum for $2b_1$–V_O and $2b_3$–V_O are similar to each other, which is similar to the case of the corresponding DOSs. The dissimilarities and similarities reveal that the distribution of vacancies becomes more significant.

3.3.2. E_1' center

According to Fig. 6, the absorption spectrum for α-quartz with E_1' centers is similar to that from the model with the corresponding V_O, just like the case of DOSs. And the absorption spectra are very close, including the absorption peaks and the frequencies where the peaks take place. Especially, the two absorption lines for α-quartz with 1–E_1' and 1–V_O coincide with each other as shown in Fig. 6(a). From Figs. 6(b)–6(e), some differences can be seen in the absorption spectra, when there are two defects in α-quartz. However, the differences are minor enough. It suggests that shifting the neutral V_O into the E_1' center will make very little effect on the optical properties of α-quartz.

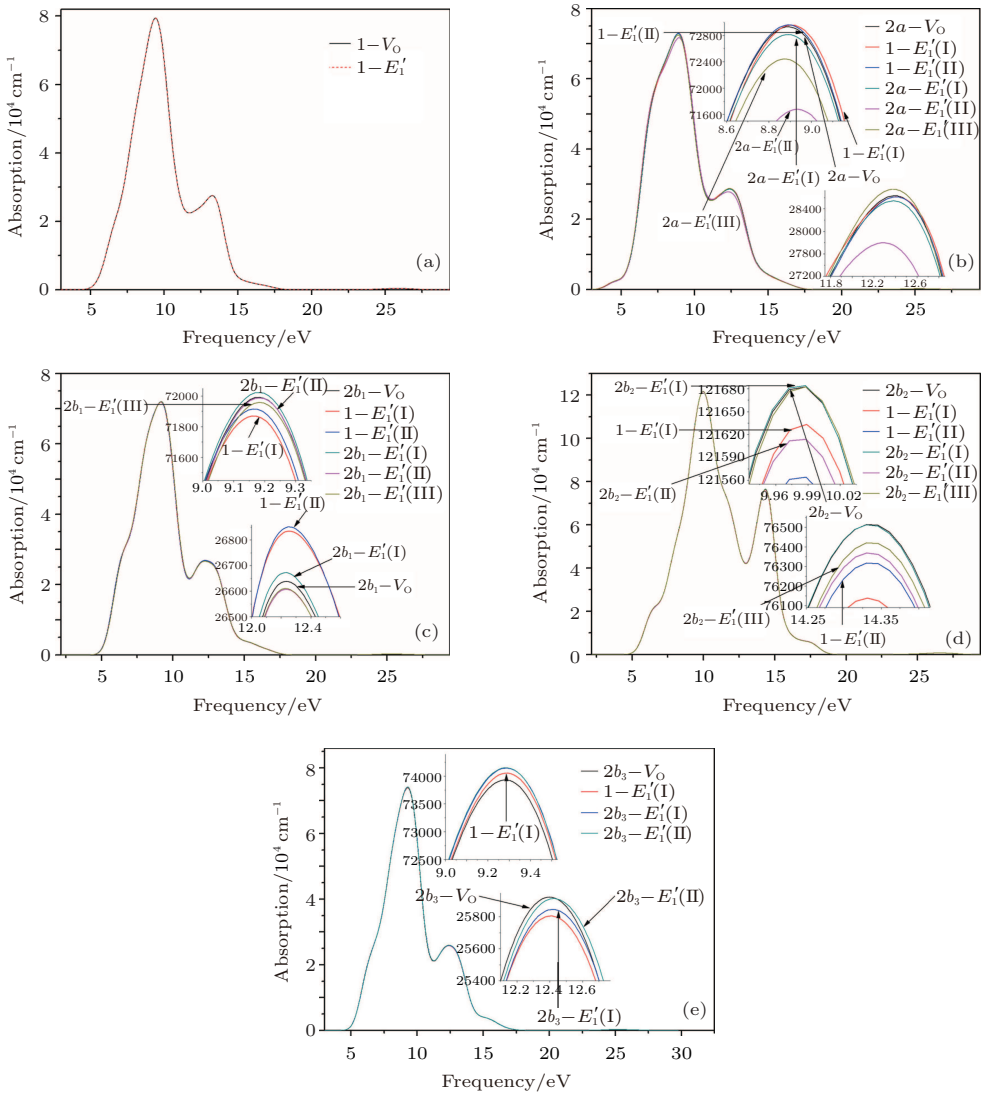


Fig. 6. (color online) Absorption spectra for the α-quartz with E_1' centers: (a) 1–V_O, (b) $2a$–V_O, (c) $2b_1$–V_O, (d) $2b_2$–V_O, and (e) $2b_3$–V_O.

4. Summary and conclusions

According to the calculations, the number of neutral V_Os, as well as the type of 2–V_O ($2a$–V_O, $2b_1$–V_O, $2b_2$–V_O, and $2b_3$–V_O), can affect the geometrical structrue of α-quartz. The presence of E_1' center does not significantly change the volume of α-quartz with 1–V_O. However, when the higher defect concentration is involved in α-quartz, the influence of E_1' center becomes more significant.

There are evident variations in the positions of the four bands of the DOSs upon the formation of the V_O center, almost all of them move toward the lower energy level. The movement of the band in the conduction band results in the reduction of the band gap. In addition, different types of 2–V_O centers can lead to some differences in DOS, and the $2b_2$–V_O center results in a noticeable decrease. However, a similarity is also present as the curves of the DOSs for $2b_1$–V_O and $2b_3$–V_O almost completely overlap. The above descriptions suggest that the concentration and distribution of oxygen vacancies can cause changes in the electronic structure of α-quartz. At the same time, the similarity, which is observed in the DOSs between the configurations with E_1' center(s) and the corresponding 2–V_O center, indicates that the presence of E_1' center can hardly affect the electronic structure.

Our calculations also show that the optical absorption band widens with the formation of the V_O, and the absorption intensity becomes lower than that of the undefected α-quartz. The changes indicate that the introduction of V_O can remarkably influence the optical properties of α-quartz. When the 2–V_O center appears in the α-quartz, the dissimilarites and similarities are also reflected in the absorption spectra, similar to the case of DOSs. The results reveal that the concentration and distribution of neutral oxygen vacancies can influence the electronic structures and optical property of α-quartz.

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