H atom in CaTiO$_3$: structure and electronic properties

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Abstract

In the present work we explore effects that an H impurity produces upon the geometry and electronic structure of the CaTiO$_3$ crystal considering cubic and orthorhombic crystallographic lattices of the material. A quantum-chemical method based on the Hartree-Fock formalism and the periodic large-unit-cell (LUC) model is used throughout the work. The analysis of outcomes shows that the interstitial H impurity binds to one of the O atoms forming the so-called O-H group. At equilibrium, the O-H distances are found to be equal to 0.89 and 1.04 Å for cubic and orthorhombic lattices respectively. Atomic displacements and relaxation energies are analyzed comparing obtained results in cubic lattice versus orthorhombic one. In the cubic phase the computed relaxation energy of vicinity of the O-H group is found to be equal to 1.1 eV and the atomic displacements generally obey the Coulomb law. So, the negatively charged O atoms move outwards the defective region by about 0.09 Å while the positively charged Ti and Ca atoms move towards the defective region by about 0.05 and 0.01 Å respectively. A similar effect is observed in the orthorhombic lattice of CaTiO$_3$ doped with an H atom. It is necessary to mention that different O positions in the orthorhombic structure are considered for the O-H bond creation. The computed relaxation energy of the atomic displacements in this structure is found to be equal to 2.3 and 2.1 eV depending on crystallographic type of the bonding O atom.

§1. Introduction

We were encouraged to make study of H-doped $CaTiO_3$ crystal by the numerous applications in which titanates are the key materials and fundamental importance of titanates. Nowadays, perovskite-type materials are the focus of scientific research due to their unusual magnetic and dielectric properties. Since the theoretical basis of the H atom behaviour in titanates has not been elucidated yet, it is important to study the equilibrium geometry of an H impurity in $CaTiO_3$ cubic and orthorhombic crystallographic lattices as well as the lattice distortion due to the impurity doping. We are also aware that the knowledge of structure and electronic properties of doped titanates can reveal interesting results and help future investigations of these complex systems. This is the main purpose of the present research.

The crystal structure of $CaTiO_3$ is not an ideal cubic perovskite but has orthorhombic distortions because the ionic radius of a Ca ion is smaller than that of Sr and Ba ions. Although the $CaTiO_3$ applications are numerous, there exist only few studies on this material due to its complicated structure. It is worth to note that $CaTiO_3$ is one of the principal components for the disposal of high-level radioactive waste materials (McCarthy 1977, Arita *et al.* 1997); it is also utilized in the construction of field devices and sensors for the study of the rheology of the interior mantles of the Earth (Li *et al.* 1996).

§2. Theoretical method

A quantum-chemical semi-empirical intermediate neglect of differential overlap (INDO) method developed specially for crystals is used in the present work. The method is based on the molecular orbital (MO) theory. Our method as implemented in the CLUSTERD computer code (Stefanovich *et al.* 1990) is based on a strict and reliable parametrization scheme (Shluger 1985). Due to its semi-empirical character and a specific parameterization scheme the computer program is not cumbersome and time-consuming in the treatment of the electronic and spatial structure of complex systems. In studies of complex materials containing point defects this method can be more

reliable than the corresponding *ab initio* techniques, especially if one studies large enough systems. This quantum-chemical computational scheme has been used with great success exploiting the so-called large unit cell (LUC) model, which is free from the limitations of different cluster approaches. The model is able of simulating real crystals, because it takes into account the property of periodicity and can incorporate point defects. Another important advantage of the method is its high precision in geometry predictions for crystals doped with point defects and impurity atoms. The method also allows one to calculate with reasonable precision the exited state of the system and give information about defect contribution into absorption and luminescence spectra of the crystal.

The numerical parameters for the $CaTiO_3$ crystal have been obtained before reproducing the most important properties of this material and also in studies of other crystals. In particular, parameters for the O 2s and 2p atomic orbitals (AOs) and the H 1s AO are taken from the work of Stefanovich *et al.* (1990), for the Ti 4s, 4p and 3d AOs from the work of Pinto and Stashans (2000), and finally for the Ca 4s and 3p AOs from the work of Erazo and Stashans (2000). As one can see we have restricted ourselves to the use of the valence basis set. The parameters utilised are given in tables 1 and 2.

It is important to note that the current computational method has already been applied to titanates, giving encouraging results. In particular, we have studied Nb and La doping in the cubic and orthorhombic phases of the $CaTiO_3$ crystal (Erazo and Stashans 2000, 2002), hole polarons and impurity centres in the $BaTiO_3$ crystal (Pinto and Stashans 2000, 2002, Stashans and Pinto 2000, Patiño and Stashans 2001a, 2001b, Stashans and Chimborazo 2002), point-defect studies in the $SrTiO_3$ crystal bulk and surface (Sánchez and Stashans 2001, Stashans 2001, Stashans *et al.* 2001) as well as modelling of PZT ceramics (Stashans *et al.* 2002).

§3. Results and discussion

3.1. *The O—H bonding*

In the case of cubic lattice the primitive unit cell of the $CaTiO_3$ crystal contains five atoms. In order to use the LUC model we have extended the primitive unit cell up to 40 atoms which is equivalent to 8 times (2 x 2 x 2) symmetric-extension. Additionally, one H atom was inserted in the middle of the LUC giving us a system consisting of 41 atoms. The LUC size was considered to be sufficient to avoid any mutual defect-defect interaction because it is known from the previous studies (Stashans and Kitamura 1996, 1997) that the H atom influence does not extend a lot in the lattice. In a similar way, keeping the symmetry properties of the pure orthorhombic crystal, we chose to use the LUC consisting of 80 atoms, which corresponds to 4 times (2 x 2 x 1) symmetric-extension of the primitive unit cell containing 20 atoms. After the insertion of an H impurity, it was obtained that 81 atoms constitute the system.

In both cases, cubic and orthorhombic lattice, we considered numerous possible positions of H atom within the crystal. So, different types of the H atom geometry optimization have been performed including the automated geometry optimization using the downhill simplex method in multidimensions (Press *et al.* 1986). As a result it was obtained in the cubic lattice that the H atom binds to one of the O atoms, O(5) atom, forming the so-called O—H group (figure 1). The impurity atom is located practically within the horizontal *x-y* plane formed by the O atoms. At equilibrium, the O—H distance is found to be equal to 0.89 Å. The computed bond length is shorter that the value of 0.97 Å in a free OH⁻ radical (Huber and Herzberg 1979). We explain the shorter bond length for the OH⁻ complex as due to the rather compact crystalline packing in the $CaTiO_3$ crystal. It is worth mentioning that recently performed first-principle pseudopotential calculations based on the local-density approximation of the H atom in the $PbTiO_3$ crystal (Park and Chadi 2000) also showed a considerable reduction in the O—H bond length in the $PbTiO_3$ crystal. This also coincides with previous studies of the H atom in $BaTiO_3$ crystal (Stashans and Chimborazo 2002) using the identical computer code utilized in the present work.

In the case of the orthorhombic lattice having the V_h^{16} (*Pbnm*) space group there are two different crystallographic positions of the O atoms. Namely, there are O atoms situated at *4c*

positions and other O atoms being located at *8d* positions (Wyckoff 1960). Therefore, in order to obtain reliable information about the O—H bonding in the orthorhombic structure, both oxygen types have to be considered.

First, we have investigated H atom binding to one of the O atoms situated at the *4c* position (figure 2). In this case the H impurity is located practically within the horizontal *x-z* plane formed by the O atoms. At equilibrium, the O—H distance is found to be equal to 1.04 Å. In the case of the O atom situated at the *8d* position (figure 3), the computed equilibrium distance is found to be equal to 1.01 Å. The impurity atom for this configuration is located within the horizontal *x-y* plane formed by the Ca and O atoms as shown in figure 3.

3.2. *Cubic lattice of H-doped CaTiO$_3$ crystal*

Different types of atomic relaxation was considered, which included symmetric and asymmetric atomic displacement. As a result, it was found that both symmetric and asymmetric movements reduce the total energy of the system only in the case of two specific atoms, O(1) and O(4) (figures 1 and 4). In the case of the other atoms situated within the defective region, only their symmetric displacements along some specific crystallographic directions contributed into the reduction of system's total relaxation energy. Finally, the following lattice distortion was obtained. The two H-neighbouring O atoms located in the parallel plane to the O—H bond (z-axis), O(2) and O(3) atoms, move outwards the impurity by 0.03 and 0.05 Å respectively. So, we note a augmentation of the initial inter-atomic distance from 2.58 to 2.61 Å and from 2.76 to 2.81 Å for O(2) and O(3) atom respectively. The movements of both atoms are along the <001> direction. This particular geometry relaxation contributes around 70.4% into the total relaxation energy. The other H-neighbouring O atoms, O(1) and O(4) atoms, located within the *x-y* plane opposite to each other, move towards the H atom by 0.09 and 0.19 Å. These movements are not radial forming angles of 88.18 and 76.03º respectively to the axis connecting the corresponding O atom and the H impurity. The two H-closest Ti atoms move outwards from the impurity by 0.07 Å. This corresponds to the

increasing of the initial inter-atomic distance between the H and Ti atoms equal to 1.88 Å. Finally, we have considered movements of the two nearest Ca atoms located in the same plane as the binding O atom and being situated initially at 2.14 Å from the defect. Their calculated atomic displacements were found to be equal to 0.18 and 0.31 Å and directed outwards the impurity. In this case, the movements are along the <101> and <110> directions.

The movements of positively charged defect-surrounding atoms are clearly understood if one considers the following two physical effects. First of all, the H atom is charged positively and thus due to the Coulomb interaction the Ca and Ti atoms move outwards. Secondly, insertion of the H impurity is accompanied by the creation of chemical bond between the hydrogen and one of the O atoms, O(5) atom. As a result the chemical bonds between the O(5) atom and the surrounding Ti and Ca atoms are weakened leading to the outward displacements of these atoms. The Ca and Ti atoms form two closest defect-surrounding atomic spheres. Since both spheres move outwards it also provokes the outward movement of some atoms situated in the third defect-surrounding sphere, which consists of the O atoms. In this way we can explain the outward movements of O(2) and O(3) atoms, which receive imaginary "push" from the atoms of the first two defect-closest spheres. The complete information on lattice relaxation in the cubic phase of the crystal is given in table 3. Finally, we would like to note that the atomic displacements are not radial with respect to geometric centre of the system, i.e. the O—H group. This is expected because the H insertion lowers considerably the local symmetry in the defective region of the cubic $CaTiO_3$ lattice. All atomic displacements are shown in figure 1 while the displacements along the x- and y-axes are additionally indicated in figure 4. The total relaxation energy obtained for this case is 1.1 eV.

The analysis of electronic properties shows that the H impurity is found to be an autoionised, positively charged ion and its donor level lies above the conduction-band bottom. In this positively charged state, the valence bands are fully occupied and there is no state in the bandgap. The interstitial H behaves, therefore, as a shallow donor. It is also has been observed that the impurity-closest Ca atoms practically do not change their effective charges. However, we

observe a considerable charge redistribution for the H-nearest Ti and O atoms except the O(2) atom situated rather far away from the H atom. This suggests changes in the chemical bonding within the defective region. The details of charges on atoms are shown in table 3.

3.3. *Orthorhombic lattice of H-doped CaTiO$_3$ crystal*

The atomic relaxation in the orthorhombic phase for the H-doped CaTiO$_3$ crystal was made considering both possible O positions in this structure. Similarly as in the cubic structure, different kinds of lattice distortion were considered. First, we considered the case when the O—H bonding occurs with the O atom situated at the *4c* position. For this configuration the O(3) —H bonding distance is found to be equal to 1.04 Å. The lattice distortion obeys the following pattern. The three H-closest Ca atoms move outwards the impurity by 0.30, 0.34 and 0.22 Å along the <110> direction. This corresponds to an enlargement of the initial inter-atomic distance equal to 2.46 and 2.86 Å respectively. The movements of the two H-closest Ti atoms are rather specific. One of them, Ti(1) atom, moves outwards the O—H complex by 0.27 Å, while the Ti(2) atom moves outwards the defect by only 0.09 Å despite a number of performed different symmetric and asymmetric distortions. The two H-closest O atoms move towards the defect along the <110> and <111> directions by 0.09 and 0.28 Å reducing the initial interatomic distances equal to 2.46 and 2.79 Å respectively (see figure 2). The total relaxation energy of the system is found to be equal to 2.3 eV.

As a second possibility we have considered the case when the O—H bonding occurs with the O atom situated at the *8d* position. For this configuration the O(3) —H bonding distance is found to be equal to 1.01 Å. The lattice relaxation for this configuration is as follows. The three H-closest Ca atoms move outwards from the impurity by 0.09, 0.18 and 0.37 Å each one along the <101> directions, which is 0.87, 1.83, and 3.5% of the corresponding initial distance equal to 2.63, 2.59 and 2.28 Å respectively. The two H-closest Ti atoms also move outwards from the impurity by 0.09 and 0.37 Å, which represent 1.53, and 2.3% of the corresponding initial distance equal to 1.91 and 1.92 Å. These movements are along the <111> directions. The six H-closest O atoms move

toward the defect by around 0.09 Å, while the seventh closest O atom displaces toward the impurity by 0.37 Å. It is worth to be mentioned that the relaxations of all O—H group-closest atoms are according to the Coulomb's law. The total relaxation energy for this configuration is found to be equal to 2.1 eV.

The electronic density analysis for the orthorhombic structure shows somewhat different pattern from that observed in the cubic lattice. In particular, there is not only charge redistribution between the Ti and O atoms but also some noticeable changes on atomic charges for the Ca atoms. However, the Ti atoms hold forth a tendency to become less positive, while the O atoms tend to be less negative thus the general tendency of covalency increasing within the defective region is preserved. A detailed information on atomic charges in the orthorhombic H-doped $CaTiO_3$ crystal is given in tables 4 and 5.

According to our outcomes the total energy of system containing O—H group with the O atom at the *4c* position is 0.57 eV lower compared to the configuration when the interstitial H atom binds to oxygen situated at the *8d* position. Due to a small energy difference between the both configurations one can conclude that both configurations are stable enough and can occur in the $CaTiO_3$ crystal.

§4. Conclusions

We have studied H-doping in cubic and orthorhombic lattices of $CaTiO_3$ crystal using a quantum-chemical method developed for crystal computations. The outcomes reveal that atomic displacements are along the known crystallographic directions in both cubic and orthorhombic structure and reduce considerably the total energy of the systems. We can conclude that generally atomic relaxation occurs due to the Coulomb electrostatic interaction, although in some cases the changes in chemical bonding produced because of the O—H formation influence the corresponding atomic movements.

The O—H bond length is found to be equal to 0.89 Å in the cubic lattice of the crystal. This is somewhat shorter than in a free OH⁻ complex and is in an agreement with previous theoretical studies in similar structures of the $PbTiO_3$ (Park and Chadi 2000) and $BaTiO_3$ crystals (Stashans and Chimborazo 2002). The obtained results in the lower symmetry orthorhombic lattice, 1.04 and 1.01 Å, for the bonding O atom at the *4c* and *8d* positions are considerably different pointing out to the fundamental differences at the crystallographic level between two structures. The obtained atomic relaxation energies, 1.1 eV for the cubic and 2.3 and 2.1 eV for the orthorhombic lattices respectively also imply considerable differences between the two lattices.

References

Arita, Y., Nagarajan, K., Ohashi, T., and Matsui, T., 1997, *J. nucl. Mater.*, **247**, 94.

Erazo, F. and Stashans, A., 2000, *Phil. Mag.* B, **80**, 1499; 2002, *Int. J. quant. Chem.*, **87**, 225.

Huber, K. P., and Herzberg, G., 1979, *Molecular Spectra and Molecular Structure.*

Constants   of Diatomic Molecules (New York: Van Nostrand).

Li, P., Karato, S. I., and Wang, Z., 1996, *Phys. Earth Planetary Interiors*, **95**, 19.

McCarthy, G. J., 1977, *Nucl. Technol.*, **32**, 92.

Park, C. H., and Chadi, D. J., 2000, *Phys. Rev. Lett.*, **84**, 4717.

Patiño, E. and Stashans, A., 2001a, *Ferroelectrics*, **256**, 189; 2001b, *Comput. Mater. Sci.*, **22**, 137.

Pinto, H., and Stashans, A., 2000, *Comput. Mater. Sci.*, **17**, 73; 2002, *Phys. Rev.* B, **65**, 134304.

Press, W. H., Flannery, B. P., Teukolsky, S. A., and Vetterling, T., *Numerical Recipes: The Art of Scientific Computing* (Cambridge University Press).

Sánchez, P., and Stashans, A., 2001, *Phil. Mag.* B, **81**, 1963.

Shluger, A., 1985, *Theor. chim. Acta*, **66**, 355.

Stashans, A., 2001, *Mater. Chem. Phys.*, **68**, 124.

Stashans, A., and Chimborazo, J., 2002, *Phil. Mag.* B, **82**, 1145.

Stashans, A., Erazo, F., Ortiz, J., and Valverde, P., 2001, *Phil. Mag.* B, **81**, 1977.

Stashans, A., and Kitamura, M., 1996, *Solid St. Commun.*, **99**, 583; 1997, *J. Phys. Chem. Solids*, **58**, 777.

Stashans, A., and Pinto, H., 2000, *Int. J. quant. Chem.*, **79**, 358.

Stashans, A., Zambrano, C., Sánchez, A., and Prócel, L. M., 2002, *Int. J. quant. Chem.*, **87**, 145.

Stefanovich, E. V., Shidlovskaya, E. K., Shluger, A. L., and Zakharov, M. A.,

1990, *Phys. Stat. sol. (b)*, **160**, 529.

Wyckoff, R. W. G., 1960, *Crystal Structures* (New York: Interscience).

Table 1. Semiempirical parameter sets used in the present work: ζ, E_{neg}, P^0 and β.

Atom	AO	ζ (au)	E_{neg} (eV)	P^0 (electrons)	β (eV)
Ca	4s	1.48	14.0	0.15	-0.4
	3p	2.80	42.5	2.00	-3.0
Ti	4s	1.4	3.7	0.65	-0.5
	4p	1.1	-15.0	0.04	-0.5
	3d	1.93	7.2	0.55	-9.0
O	2s	2.27	4.5	1.974	-16.0
	2p	1.86	-12.6	1.96	-16.0
H	1s	1.2	4.0	0.8	-2.0

Table 2. Two-centre parameters $\alpha_{\mu B}$ (au^{-1}) where $\mu \in$ A.

A	$\alpha_{\mu B}$ (au^{-1})			
	B=Ca	B=Ti	B=O	B=H
Ca	0.15	0.55	0.18	0.00
Ti	0.07	0.13	0.38	0.00
O	0.57	0.10	0.15	0.23
H	0.20	0.00	0.42	0.33

Table 3. Displacements d of atoms in the defective region of the cubic

CaTiO$_3$ crystal and charges on atoms in the defective region: perfect crystal,

Q_1; doped crystal without lattice relaxation, Q_2; equilibrium configuration

of the doped crystal, Q_3. Atomic numeration corresponds to that given

in figures 1 and 4.

Atom	d	Q_1	Q_2	Q_3
	(Å)	(units of e)	(units of e)	(units of e)
Ca(1)	0.31	1.89	1.88	1.89
Ca(2)	0.18	1.89	1.88	1.88
Ti(1)	0.05	1.55	1.75	1.76
Ti(2)	0.13	1.86	1.80	1.91
O(1)	0.09	-1.32	-1.37	-1.34
O(2)	0.03	-1.32	-1.34	-1.32
O(3)	0.05	-1.32	-1.33	-1.33
O(4)	0.19	-1.34	-1.36	-1.30
O(5)	—	-1.30	-1.24	-1.19
H(1)	—	—	0.44	0.41

Table 4. The orthorhombic H-doped $CaTiO_3$ with the bonding O atom at the *4c* position. Displacements *d* of atoms in the defective region and charges on atoms: perfect crystal, Q_1; equilibrium configuration of the doped crystal, Q_2. Atomic numeration corresponds to that given in figure 2.

Atom	*d* (Å)	Q_1 (units of *e*)	Q_2 (units of *e*)
Ca (1)	0.30	1.87	1.87
Ca(2)	0.34	1.31	1.71
Ca(3)	0.22	1.87	1.86
Ti(1)	0.28	2.10	1.89
Ti(2)	0.09	2.10	1.88
O(1)	0.28	-1.22	-1.08
O(2)	0.19	-1.18	-1.19
O(3)	—	-1.21	-1.23
H(1)	—	—	0.47

Table 5. The orthorhombic H-doped $CaTiO_3$ with the bonding O atom at the *8d* position. Displacements d of atoms in the defective region and charges on atoms: perfect crystal, Q_1; equilibrium configuration of the doped crystal, Q_2. Atomic numeration corresponds to that given in figure 3.

Atom	d	Q_1	Q_2
	(Å)	(units of e)	(units of e)
Ca(1)	0.09	1.87	1.87
Ca(2)	0.18	1.87	1.86
Ca(3)	0.37	1.31	1.70
Ti(1)	0.09	2.24	2.11
Ti(2)	0.37	2.10	1.93
O(1)	0.37	-1.21	-1.15
O(2)	0.07	-1.22	-1.12
O(3)	0.09	-1.18	-1.16
O(4)	0.09	-1.18	-1.21
O(5)	0.09	-1.21	-1.11
O(6)	0.09	-1.50	-1.50
O(7)	0.09	-1.18	-1.17
O(8)	—	-1.50	-1.43
H(1)	—	—	0.48

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Figure 1. A schematic diagram describing the H equilibrium position in the cubic structure of the CaTiO$_3$ crystal. White circles indicate O atoms located in the middle of vertical and horizontal planes. Grey and black circles show Ca and Ti atoms respectively. The impurity H atom is located just above the plane formed by O(1), O(2), O(3) and O(5) atoms. The arrows point out the direction of atomic displacements due to the O—H complex formation.
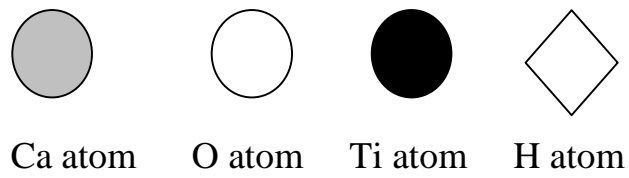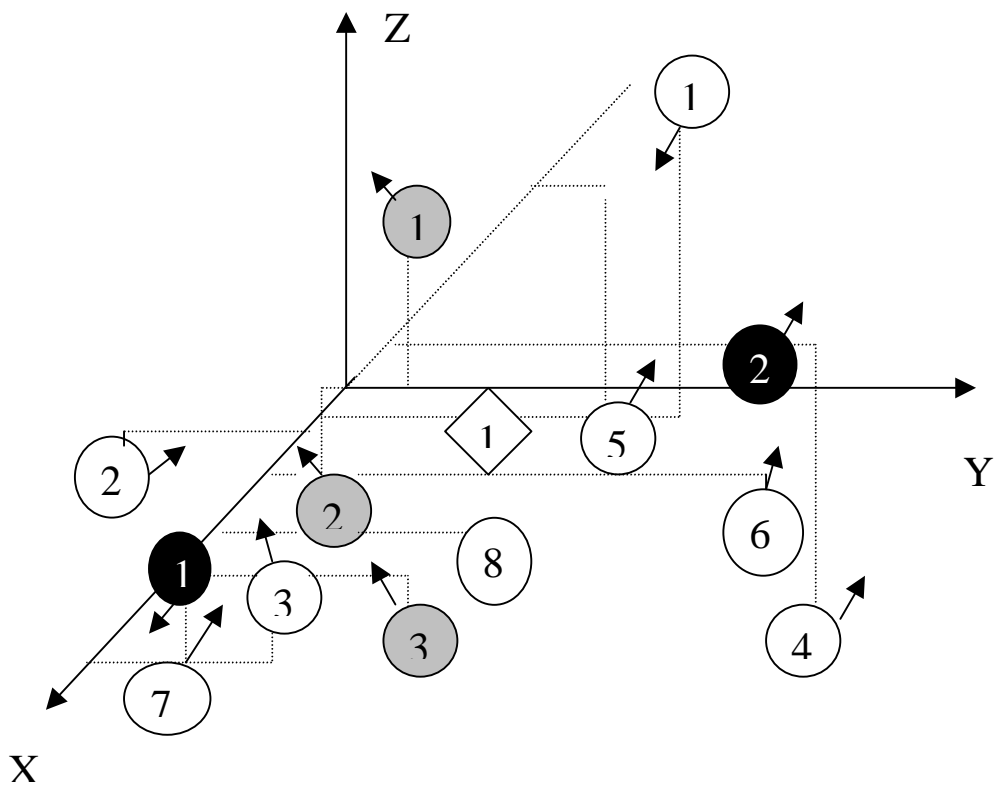
Figure 2. The O—H binding in the orthorhombic lattice if the involved O atom is at *4c* position. The arrows show defect-outward and inward displacements of the O—H-surrounding atoms. The component of atomic displacements along the vertical z-axis is considerably larger compared to the same variable obtained in the cubic phase.
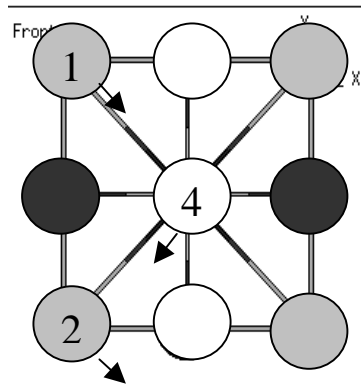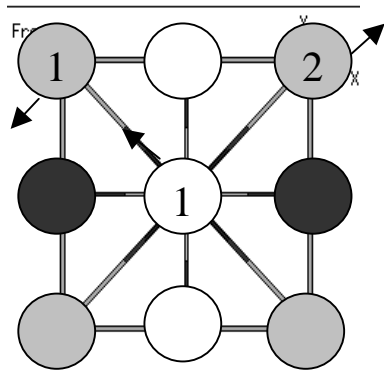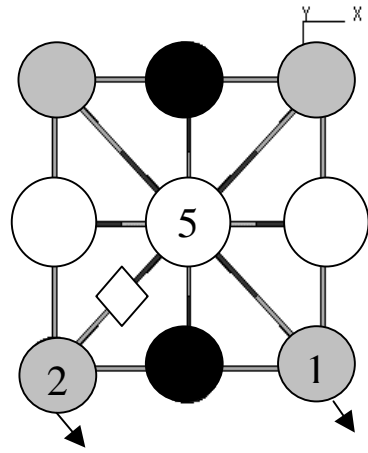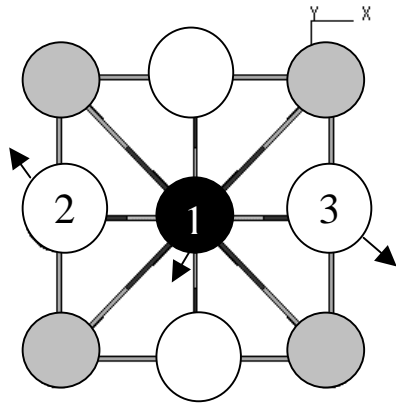
Figure 3. The O—H binding in the orthorhombic lattice if the involved O atom is at *8d* position. The arrows show defect-outward and inward displacements of the O—H-surrounding atoms.

Figure 4. Lattice relaxation in the cubic phase of the defective region along the x- and y-axes. The arrows show defect-   outward and inward displacements of the O—H-closest atoms. The component of atomic displacements along the x-axis is considerably larger than those along other directions.
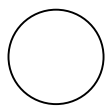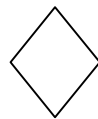
Z

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Ca atom   O atom   Ti atom   H atom

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