

Structural and electronic properties of oxygen vacancies in cubic and antiferrodistortive phases of SrTiO₃

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The structural and electronic properties of oxygen vacancy (V_O) defects in cubic and antiferrodistortive (AFD) phases of bulk SrTiO₃ are investigated using results from first principles pseudopotential calculations. By systematically increasing the supercell size from 40 to 320 atoms, we show that large supercells are necessary to investigate the structural energetics of this seemingly simple defect properly. With the increase in the supercell size, the formation energy of V_O decreases by ~ 1.3 eV due to long-ranged relaxations, and the character of the defect wave function changes from a deep to a shallow level. Calculations indicate that presence of V_O decreases the relative stability of the AFD phase over the cubic phase, consistent with recent experimental results, which find a lowering of the AFD-cubic transition temperature in samples with higher V_O concentrations.

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The electronic properties of perovskite materials are heavily dominated by their oxygen content, as well as by donor- and acceptor-type impurities. Various mechanisms of self-compensation of charge (such as transition metal valence changes) due to particularly oxygen vacancies allow perovskite materials to possess a wide range of novel electronic and spin-dependent properties, such as high T_c superconductivity, or colossal magnetoresistance effect. Among the various fundamentally and technologically important oxides, SrTiO₃ is a simple structural prototype for many perovskites,¹ in which the detailed investigation of native and dopant defects can lay the theoretical groundwork that can be applied to structurally and chemically more complex perovskite materials. In addition to being an exemplary model of the basic perovskite system, SrTiO₃ displays a wide range of physical and chemical properties such as superconductivity, catalytic activity, ferroelectricity, and semiconductivity. Oxygen vacancies in SrTiO₃ are known to act as effective donors. Impurity doping and high temperature treatment in an environment where the partial pressure of O₂ can be varied, can change the material from n - to p -type and vice versa.² As such, theoretical studies of point defects, particularly oxygen vacancies, have merits of their own. Yet, only recently have first principles methods been used to study point defects in SrTiO₃.^{3–5} The aim of this paper is to present detailed first principles calculations on the structural and electronic properties of an important defect in SrTiO₃, the oxygen vacancy V_O .

At room temperature, bulk SrTiO₃ has a cubic symmetry with a 5 atom unit cell. It is well known that at lower temperatures (below ≈ 105 K), SrTiO₃ undergoes a structural phase transition to a tetragonal phase.⁶ This so-called antiferrodistortive (AFD) phase transition manifests itself by the rotation of the TiO₆ octahedra along one of the Cartesian axes (taken here to be the z axis). The sense of the rotation alternates from one 5-atom cubic unit cell to the neighboring one in all Cartesian directions, resulting in a 10-atom unit cell. Recently, *ab initio* studies of this cubic to AFD finite temperature phase transition have been performed by various

groups.⁷ In addition, the influence of defects on the critical temperature T_c of the phase transition has recently been studied experimentally.⁸ Previous theoretical studies using *ab initio* pseudopotentials with 40-atom supercells and classical interatomic potentials have hinted that the presence of oxygen vacancies could play an important role in destabilizing the cubic phase.³ It was, however, noted that *ab initio* calculations with larger supercells were needed to investigate the defect-induced long-ranged structural changes in SrTiO₃.

To gain more insight about the nature of the AFD and cubic phases of SrTiO₃ in relation to the presence of oxygen vacancies, in this paper, we examine from first principles the structural energetics and electronic structure of V_O in its (0), (+), and (2+) charge states. We show, by systematically increasing the system size, that large supercells are necessary to model this seemingly simple defect properly. In particular, the results obtained for the 320-atom supercell for the two important characteristics, (i) the deep/shallow nature of the defect state, and (ii) the relative stability of the AFD phase over the cubic phase, are completely opposite to those obtained for the 40-atom supercells. This finding is in agreement with the experimental observation that T_c of the phase transition from AFD to cubic phase decreases as the concentration of oxygen vacancies increases.

In our calculations we have used the *ab initio* pseudopotential total energy method with a plane wave basis in a supercell geometry.⁹ Ultrasoft pseudopotentials with a cutoff energy of 270 eV were used in calculations for four different sizes: $2 \times 2 \times 2$, $2 \times 2 \times 4$, $4 \times 4 \times 2$, and $4 \times 4 \times 4$ supercells of 40, 80, 160, and 320 atoms, respectively. We used a $q = 2$ Monkhorst–Pack grid for all supercells. All results reported in this paper correspond to calculations performed at the experimental lattice constant of $a = 3.905$ Å. We also repeated a considerable number of the calculations at the theoretical value of 3.86 Å, and the impact of the lattice parameter on the general results was found to be negligible. We used the Ceperley–Alder parametrization within the local spin density approximation, finding that spin polarization effects are negligible for V_O in bulk SrTiO₃.

We first consider results for the 40-atom supercells. Starting from either the bulk positions or the slightly distorted random positions, we find that the system relaxes symmetrically around V_O . As was shown in previous studies of SrTiO_3 and various other ABO_3 perovskites,^{3,4} the symmetric distortions, which we will refer to as the cubic phase, are quite small. The two nearest-neighbor (nn) Ti atoms and four nn Sr atoms relax away from the vacant site by ~ 0.06 Å (neutral V_O), while the 8 nn oxygen atoms relax toward the vacant site by ~ 0.07 Å. These distortions increase in magnitude in going from the neutral to the (2+) charge state, where the distortions are found to be +0.1, +0.13, and -0.15 Å, for Sr, Ti, and O nn, respectively. The directions of the relaxations can be inferred from the electrostatic interactions of atoms with formal ionic charges of Ti^{+4} , Sr^{2+} , and O^{-2} , as was also noted for V_O in PbTiO_3 .⁴

If the atoms in the vicinity of the vacant site are given larger random distortions, the final relaxed structure for the neutral vacancy has a lower energy by 0.16 eV compared to the symmetric case presented above. The final structure is based on the AFD phase of SrTiO_3 in the sense that the same structure is obtained by starting calculations from the 40-atom bulk AFD supercell and removing one of the rotated oxygens (removing the oxygen from the O-Ti-O bond aligned in the direction of the rotation axis results in a higher energy structure). In our calculations on the 10-atom unit cell of the bulk AFD phase, we find the rotation angle to be 5.9° , in close agreement with previous results of 4.7° ⁷ and 6.9° .³ In addition, our calculated energy gain of 0.02 eV per 10-atom unit cell is close to the previously calculated values of 0.013 and 0.02 eV, respectively. All calculations using the local density or generalized gradient approximations, whether the calculations are done at the theoretical or experimental lattice constant and with or without including the additional tetragonal strain along the z direction, find the rotation angle to be 2.5 to 3 times larger than the experimental value of 2.1° , which has been attributed by Sai and Vanderbilt to possible quantum fluctuations.⁷

The distortion amplitudes as a function of the shell index around neutral V_O are plotted in the top panel of Fig. 1. The atom with the largest distortion of 0.16 Å is the oxygen atom that lies on the opposite side of the vacant site with respect to the nn Ti atom, i.e. along the V_O -Ti-O direction. The rotation angle of the particular O atom is 12° , twice as large as the theoretical bulk rotation angle of 5.9° . In addition, if the bulk AFD-cubic energy difference of 0.02 eV/cell is taken as the reference, in a defect supercell of 39 atoms and in the absence of any defect-induced electronic energy gain, one would expect the difference between cubic and AFD defect supercells to be approximately 0.08 eV. The actual calculated energy difference of 0.16 eV between the total energies of defects in cubic and AFD phases shows that not only the rotation angle, but also the stability of the AFD phase over the cubic phase is enhanced for $2 \times 2 \times 2$ supercells. Figure 2(a) shows the charge density contour plots of the defect-induced donor level in the $[001]$ plane containing V_O . The defect wave function is strongly localized on the two Ti atoms on either side of the vacant site, as was also observed in previous studies of SrTiO_3 and related perovskites.^{3,4}

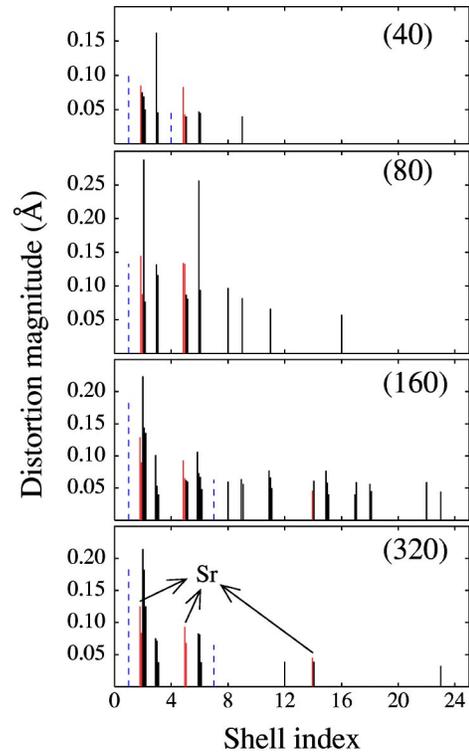


FIG. 1. Atomic relaxation magnitudes around a neutral V_O as a function of the shell index from the vacant site for 40-, 80-, 160-, and 320-atom supercell calculations. Only significant distortions ($|\Delta R| > 0.04$ Å) are displayed. For the largest supercell, there are many atoms with small displacements extending far away from the vacant site. The dashed lines (blue in the online version) represent distortions of Ti atoms, and Sr atoms (red in the online version) are shown by arrows. The rest of the distortions (black) are those of O atoms.

In going from 40 to 80 atom ($2 \times 2 \times 4$) supercells (where the supercell is doubled along the rotation axis), drastic changes are observed in the structural and electronic properties of V_O in cubic and AFD phases. As seen in the second panel of Fig. 1, much larger relaxations in the second, third, sixth, and eighth nn O sublattice as well as the first nn Sr sublattice are observed in this case. Significant relaxations ($|\Delta R| > 0.05$ Å) extend far from the vacant site up to the sixteenth shell in the oxygen sublattice, while the rotation angle of the O atom nearest the vacant site in the AFD phase decreases down to 10° . This long-ranged inward relaxation of the O sublattice cannot be accommodated in smaller cells. In the cubic phase, slightly larger relaxations compared to AFD phase (with some near 0.35 Å) due to V_O are observed, but with a slightly shorter range up to the 8th nn. The defect wave function still behaves as a deep level localized near the two nn Ti atoms. These differences between the 40 and 80 atom supercells and between the AFD and cubic phases result in a lower formation energy for V_O in the cubic phase by ~ 0.1 eV for 80 atom supercells, contrasting that observed in 40 atom supercells.

In order to understand the size dependence of the structural energetics of V_O better, next we considered $4 \times 4 \times 2$ supercells of 160 atoms, i.e., doubling the unit cells in the xy plane perpendicular to the AFD rotation axis. As seen in the

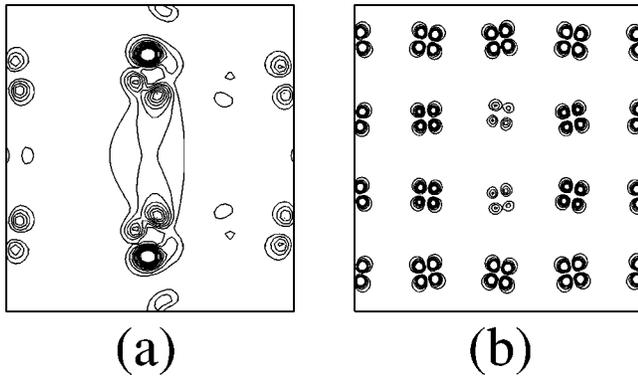


FIG. 2. Charge density contour plots for the V_O induced defect state (AFD phase) in the $[001]$ plane (perpendicular to the rotation axis) containing the defect at the center for (a) 40-atom supercell, and (b) 320-atom supercell calculations. Although drawn in squares of the same dimensions, the actual size ratio of (b) to (a) is naturally 4. 10 contour lines (maximum) are drawn in (a) increasing linearly from $15 e^-/\Omega$ to $150 e^-/\Omega$ as the Ti core is approached (Ω is the volume of the supercell). In (b), 5 contour lines (maximum) are drawn increasing linearly from $5 e^-/\Omega$ to $25 e^-/\Omega$. Notice the strong localization of the defect wave function on the nearest neighbor Ti atoms in (a), which is absent in (b).

third panel of Fig. 1, distortion amplitudes change considerably with respect to 40 and 80 atom supercells. Particularly, the two nn Ti atoms as well as the two Ti atoms above them in the Ti- V_O -Ti direction (7th shell) relax considerably. The relaxations are quite long-ranged, involving significant distortions in the Sr atoms in the 14th shell and O sublattice as far away as the 23rd shell. This long-ranged relaxation pattern results in V_O formation energies dropping significantly by ~ 0.8 eV, and the relative stability of V_O in AFD and cubic phases gets reversed again with V_O vacancies in the AFD being more favorable by 0.15 eV. In addition, the defect now behaves more like a shallow level, as evidenced from the spread of the defect wave function over almost the entire supercell in the xy plane, as well as the close proximity of the defect-induced level in the eigenvalue spectrum to the conduction band minimum.

From the lessons learned in 80 and 160 atom supercells, we therefore conclude that at least a $4 \times 4 \times 4$ supercell of 320 atoms is needed to describe the structural energetics of a single V_O in SrTiO_3 accurately. The bottom panel of Fig. 1 shows the significant distortion amplitudes ($|\Delta R| > 0.04 \text{ \AA}$) due to an oxygen vacancy in a 320-atom SrTiO_3 supercell. Extending the supercell in both the xy plane and along the z axis results in some of the significant distortions averaging out. Hence, although 160-atom supercell seems to have a longer-ranged pattern, and some of the distortions in 80-atom supercells are larger compared to the largest supercell, the actual pattern of the relaxations for 320-atom supercells is relatively complex with many small distortions, not shown in Fig. 1, contributing to the pattern. In addition to the long-ranged relaxations in the O sublattice, the distortions in the Ti and Sr sublattices are significant (especially Ti atoms along the Ti- V_O -Ti direction and Sr planes sandwiched between them) making it necessary to use such a large super-

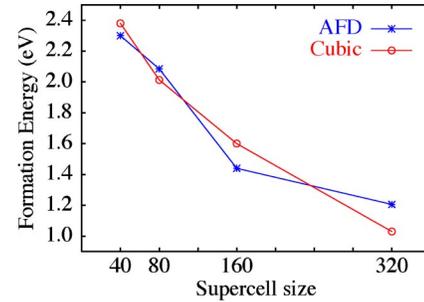


FIG. 3. Formation energy (in eV) for V_O in cubic (circles) and AFD (stars) phases of SrTiO_3 at $\mu_O = \frac{1}{2}\mu_{O_2} - 4.5$ eV as a function of the number of atoms in the bulk supercell.

cell. The charge density contour plots displayed in Fig. 2 for the defect level show the striking contrast between the results for 40- and 320-atom supercells. The defect wave function is spread over the entire supercell and actually has a much smaller localization on the two Ti atoms nearest the vacancy compared to other Ti atoms. In addition, the V_O formation energy drops further compared to 160-atom supercells and makes the V_O in the cubic structure even more stable than that in the AFD phase by a considerable 0.2 eV. A natural question to ask at this point is whether convergence has actually been reached for 320-atom supercells. While a straightforward way of checking this would be to go a larger (such as $6 \times 6 \times 6$) supercell, such a calculation is computationally very demanding. A careful examination of the relaxation patterns of the 80- and 160-atom in comparison to 40-atom supercells shows that as the boundaries of the larger cells are approached, the relaxation amplitudes become very small. Hence, we believe that as long as four unit cells in each direction are included in the supercell, the results for structural energetics of V_O in SrTiO_3 will be converged.

The formation energy of an oxygen vacancy $\Omega_{V_O}(q)$ in charge state q can be written in terms of the supercell total energy $E(q)$, the chemical potentials μ_i and the number n_i of the constituent atoms as¹⁰

$$\Omega_{V_O}(q) = E(q) - n_{\text{Sr}}\mu_{\text{Sr}} - n_{\text{Ti}}\mu_{\text{Ti}} - n_{\text{O}}\mu_{\text{O}} + q(\mu_e + \epsilon_v + \overline{\Delta V}) + E_{\text{mp}}(q), \quad (1)$$

where the ϵ_v is the energy of the valence band maximum (VBM), μ_e is the electron chemical potential referenced to VBM, and $E_{\text{mp}}(q)$ is the multipole correction due to the compensating background charge, which is quite negligible in SrTiO_3 due to its large dielectric constant. The correction $\overline{\Delta V}$ due to VBM alignment for charged defects is less than 0.01 eV for 320-atom cells, while it can be as large as 0.2 eV for 40-atom supercells. The V_O formation energy depends on the individual chemical potentials, which obey $\mu_{\text{Sr}} + \mu_{\text{Ti}} + 3\mu_{\text{O}} = \mu_{\text{SrTiO}_3, \text{bulk}}$. From total energy calculations on bulk SrTiO_3 , Sr, Ti, SrO, TiO_2 , and molecular oxygen, we find that μ_{O} spans a wide range of ~ 6 eV below its molecular value. Figure 3 shows the formation energy of a neutral V_O as a function of size at $\mu_{\text{O}} = \frac{1}{2}\mu_{\text{O}_2} - 4.5$ eV, corresponding to the Sr and Ti-rich end of the stoichiometry. The strong

dependence of Ω_{V_O} on the system size is evident as the formation energies drop by ~ 1.1 to 1.38 eV for the AFD and cubic phases in going from 40- to 320-atom supercells. The lower formation energy of V_O in the cubic phase can be interpreted as oxygen vacancies having a destabilizing effect at low temperatures for the AFD phase, not the cubic phase. This is in agreement with a recent experimental study by Hünnefeld *et al.*,⁸ who have found that the T_c for the cubic to AFD phase transition drops from 105 K to near 98 K for samples with higher (approximately two orders of magnitude) V_O concentrations. Comparison of the charge density plots and atomic distortions near the vacant site for both cubic and AFD phases shows that in the presence of V_O , the local atomic structures and charge densities are quite similar. In a sense, the energy gain of the AFD phase over the cubic phase by the rotation of the TiO_6 octahedra along a particular direction is locally replicated by an oxygen vacancy in the cubic phase while still maintaining a D_{4h} symmetry. Hence the cubic phase becomes more competitive with the AFD phase in lowering the T_c .

Figure 4 shows the formation energies of (+) and (2+) charge states of V_O relative to the neutral defect in cubic $SrTiO_3$ as a function of the electron chemical potential μ_e . For a wide band gap (3.2 eV) material like $SrTiO_3$, we believe that it would be misleading to extend the electron chemical potential beyond our LDA theoretical value of 2.3 eV without GW corrections and shifting ionization levels via projections onto valence and conduction states.¹⁰ As seen in Fig. 4, (2+) is the lowest energy charge state for almost the entire range of μ_e , switching directly to (0) for the highly n -type material with a negative U behavior. This behavior is observed in spite of the spin polarization, which lowers the energy for the (+) charge state by about 0.1 eV. We also note that in our calculations repeated with LSDA, we con-

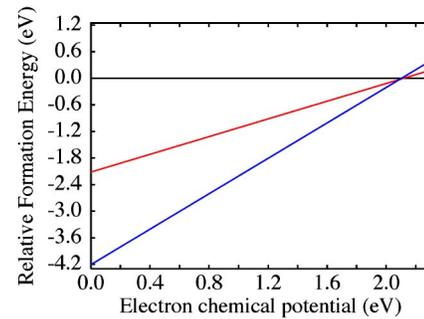


FIG. 4. Formation energy of (+) (slope of 1) and (2+) (slope of 2) charge states of V_O relative to neutral defect as a function of μ_e in the cubic phase from calculations on the 320-atom bulk supercell. The single (0/2+) ionization level at 2.1 eV indicates a negative U behavior.

sistently did not find a spin-polarized ground state for the neutral charge state, as suggested by Astala and Bristowe in their 40-atom supercell calculations.³

In summary, we have performed a detailed investigation of the structural and electronic properties of neutral and charged oxygen vacancy defects in bulk $SrTiO_3$ from first principles. We find rather unexpectedly that large supercells are necessary to investigate the structural energetics of this seemingly simple defect accurately. We have shown that the relative stability of the AFD phase over the cubic phase of $SrTiO_3$ decreases considerably in the presence of oxygen vacancies, which is in agreement with recent experimental results that find a lowering of the T_c for the AFD phase transition in samples with higher V_O concentrations.

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