<table>
<thead>
<tr>
<th>Title</th>
<th>Hybrid density functional study of oxygen vacancies in KTaO₃ and NaTaO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Author(s)</td>
<td>Choi, Minseok; Oba, Fumiyasu; Tanaka, Isao</td>
</tr>
<tr>
<td>Citation</td>
<td>PHYSICAL REVIEW B (2011), 83(21)</td>
</tr>
<tr>
<td>Issue Date</td>
<td>2011-06</td>
</tr>
<tr>
<td>URL</td>
<td><a href="http://hdl.handle.net/2433/161786">http://hdl.handle.net/2433/161786</a></td>
</tr>
<tr>
<td>Rights</td>
<td>©2011 American Physical Society</td>
</tr>
<tr>
<td>Type</td>
<td>Journal Article</td>
</tr>
<tr>
<td>Textversion</td>
<td>publisher</td>
</tr>
</tbody>
</table>
Hybrid density functional study of oxygen vacancies in KTaO$_3$ and NaTaO$_3$

Minseok Choi$^*$ and Fumiyasu Oba$^†$

Department of Materials Science and Engineering, Kyoto University, Sakyō, Kyoto 606-8501, Japan

Isao Tanaka

Department of Materials Science and Engineering, Kyoto University, Sakyō, Kyoto 606-8501, Japan, Nanostructures Research Laboratory, Japan Fine Ceramics Center, Atsuta, Nagoya 456-8587, Japan, and Fukui Institute for Fundamental Chemistry, Kyoto University, Sakyō, Kyoto 606-8103, Japan

(Received 7 March 2011; published 10 June 2011)

Using the Heyd-Scuseria-Ernzerhof hybrid functional, we systematically study the energetics and electronic properties of oxygen vacancies in KTaO$_3$ and NaTaO$_3$. The oxygen vacancies in these systems show similar behavior. The 2+ charge state is the most stable for most positions of the Fermi level inside the band gap. The neutral and + charge states become comparable in formation energy with the 2+ charge state when the Fermi level is close to the conduction band minimum. Therefore, the oxygen vacancies are double shallow donors, which can provide carrier electrons. Two types of off-symmetric configurations, in which the two nearest tantalum atoms of the oxygen vacancies are asymmetrically located, also possibly form as metastable configurations. These metastable configurations show a striking difference in electronic structure from each other; one configuration has a delocalized characteristic as in the case of the stable configuration, while the other induces a deep, localized state in the band gap. On the basis of the predicted formation energies and electronic properties, the previous experimental and theoretical findings relevant to the oxygen vacancies are discussed.

DOI: 10.1103/PhysRevB.83.214107 PACS number(s): 61.72.J−, 61.72.Bb, 71.55.Ht

I. INTRODUCTION

KTaO$_3$ is classified as an incipient ferroelectric and its high permittivity and low dielectric loss are promising for applications in microwave device. It exhibits a large Seebeck coefficient when electrons are introduced by dopants, which is of importance to thermoelectric devices. NaTaO$_3$ is one of the candidates for high-efficient photocatalyst activating for water splitting into H$_2$ and O$_2$ under ultraviolet light irradiation. In particular, La-doped NaTaO$_3$ has shown good stability and high photocatalytic activity.

The oxygen vacancy (V$_O$) is expected to give significant influences to such optical and electrical properties of KTaO$_3$ and NaTaO$_3$, since V$_O$ is known to form with a substantial concentration in these oxides. Therefore, correct understanding of the energetics and structural and electronic properties of V$_O$ is of importance, and the state-of-the-art first-principles calculations can be useful. To date, however, only a few first-principles studies have been reported on V$_O$ in KTaO$_3$ (Ref. 7) and NaTaO$_3$ (Ref. 8) using the generalized gradient approximation (GGA), showing severe band-gap underestimation. Information on the formation energy of V$_O$ and its electronic levels is very limited, in particular for KTaO$_3$.

Likewise, V$_O$ in these oxides has been investigated by experiments, but there exists controversy about its stable charge state. V$_O^{2+}$ was suggested to be stable in $n$-type systems in a wide range of temperatures from electric conductivity measurements, whereas electron paramagnetic resonance (EPR) experiments have not clearly proven the existence of V$_O^{+}$. 10-12

In this paper, we present a systematic study of V$_O$ in KTaO$_3$ and NaTaO$_3$ using the Heyd-Scuseria-Ernzerhof (HSE06) hybrid functional. An accurate description of the energetics and electronic structure of V$_O$ is our goal, and the HSE06 hybrid functional approach is chosen because it has shown a significant improvement for describing point defects or impurities in wide band-gap semiconductors over the standard density functional approaches. Using the HSE06 functional, the lattice constants and electronic band structure of the perfect KTaO$_3$ and NaTaO$_3$ crystals are examined. Then the atomic configurations and energetics of V$_O$ in these systems are investigated. Finally, the previous experimental and theoretical findings on V$_O$ are discussed on the basis of our results.

II. COMPUTATIONAL METHODS

The calculations were conducted using the projector augmented-wave method as implemented in the VASP code. The standard exchange mixing containing 25% of Hartree-Fock and 75% of the Perdew-Burke-Ernzerhof (PBE)-GGA (Ref. 25) and the screening parameter of 0.208 Å$^{-1}$ (Ref. 15) were employed in the HSE06 functional. The projector augmented-wave data sets with radial cutoffs of 1.2 Å(K), 1.2 Å(Na), 1.5 Å(Ta), and 0.8 Å(O) were used. The electronic wave functions were described using a plane wave basis set with an energy cutoff of 400 eV. A 135-atom supercell and the $\Gamma$-only $k$-point sampling were used. The atomic coordinates were relaxed until the Hellmann-Feynman force acting on each atom was reduced to less than 0.05 eV Å$^{-1}$.

In all calculations for V$_O$, the effects of spin polarization were included.

The formation energy of V$_O$ is determined by

$$\Delta E_f(V_O^{q}) = E_T(V_O^{q}) - E_T(H) + \mu_O + q(E_{VBM} + \epsilon_F),$$  \hspace{1cm} (1)

where $E_T(V_O^{q})$ is the total energy of a KTaO$_3$ or NaTaO$_3$ supercell with one V$_O$ in charge state q (0, +, and 2+), and $E_T(H)$ is the total energy of the host supercell. $\mu_O$ is the oxygen chemical potential, varying between the oxygen-rich

1098-0121/2011/83(21)/214107(6) 214107-1 ©2011 American Physical Society
limit \((\mu_O = \frac{1}{2}\mu_O(\text{molecule}))\) and the oxygen-poor limit \((\mu_Ta = \mu_Ta(\text{bulk}))\) and \(\mu_Ta + 2\mu_O = \mu_Ta(\text{bulk}))\). These equilibrium conditions are taken on the basis of previous considerations.7,8 

\(E_{VBM}\) and \(E_p\) are the valence band maximum (VBM) and the Fermi level measured from the VBM, respectively.

In order to complement the calculations using the HSE06 hybrid functional and finite-sized periodic supercells, some postcorrection processes were carried out. These were carefully applied to defect formation energies with consideration of the characteristics of single-particle states induced by \(V_O\).26–28

(i) VBM alignment was applied to charged systems using average electrostatic potentials. In the momentum-space approach with periodic supercells, the total energies of charged systems are evaluated by implicitly introducing uniform compensation-charge to keep the charge neutrality.29 This leads to an ill-defined shift of single-particle energy levels. Therefore, it is necessary to line up \(E_{VBM}\) between the host and defective supercells containing non-neutral \(V_O\). For this purpose, average electrostatic potentials in a host (defect-free) supercell and those in a bulklike environment far from \(V_O\) in defective supercells were used.

(ii) The HSE06 hybrid functional with the standard exchange mixing provides, in general, much better description of the electronic structure of semiconductors and insulators than the GGA or the local density approximation (LDA). However, the HSE06 band gaps \((E_g^{\text{HSE06}})\) of KTaO\(_3\) and NaTaO\(_3\) are still smaller compared with the experimental band gaps \((E_g^{\exp})\), as shown in Table I. Therefore, band-gap corrections must be considered to evaluate the formation energies accurately. The corrections were performed on the basis of the characteristics of \(V_O\)-induced electronic states. Since we found that \(V_O\) creates its single-particle states resonant inside the conduction band, the formation energies of \(V_O\) were extrapolated to \(E_{g}^{\exp}\) by adding \(m\Delta E_{g}\), where \(m\) and \(\Delta E_{g}\) are the number of electrons in the conduction bandlike state released from \(V_O\) \((m = 2\) for \(V_O\), and \(m = 1\) for \(V_O^+\)) and the band-gap difference, equal to \(E_{g}^{\exp} - E_{g}^{\text{HSE06}}\), respectively.

(iii) The formation energy of a defect is dependent upon supercell size owing to spurious interactions between defect and its periodic images. For charged defects in ionic crystals, electrostatic interactions are dominant in many cases, as pointed out by Leslie and Gillan30 and by Makov and Payne.31 It has been reported that such a cell-size dependence can be affected by characteristics of defect-induced electronic states and also by elastic interactions.16,32–35 In this case, a simple use of the Makov-Payne correction scheme31 cannot be justified. One practical way to reduce uncertainty arising from the cell-size dependence is to use the correction terms obtained by fitting formation energies calculated using supercells with various sizes to an appropriate formula. However, the HSE06 calculations need too high computational costs to follow this scheme. Instead, one can predict the cell-size dependence on the basis of the GGA or LDA results. For NaTaO\(_3\), our previous GGA study found that the formation energies of \(V_O^+, V_O^{2+}\), and \(V_O^{3+}\) decrease as the supercell size increases, and such a trend is almost identical for all the charge states.8 As a consequence, thermodynamical transition levels obtained using a 135-atom cell are unchanged for a larger supercell containing 625 atoms, and \(V_O^{2+}\) is the most stable for most Fermi level position in the band gap. Similar tendencies have been reported on \(V_O\) in other semiconducting oxides such as SrTiO\(_3\) (Ref. 36) and TiO\(_2\).18 The formation energies of \(V_O\) in KTaO\(_3\) and NaTaO\(_3\) by the HSE06 calculations are likely to have the same trend as those by the GGA,8 since the HSE06 calculations show single-particle electronic structures similar to the GGA results for \(V_O^+, V_O^{2+}\), and \(V_O^{3+}\), as described in Sec. III. Therefore, our discussion and conclusions are unlikely to be altered by the supercell size.

### III. RESULTS AND DISCUSSION

Figure 1 shows the electronic band structures of pure KTaO\(_3\) and NaTaO\(_3\) obtained using the HSE06 and PBE-GGA functionals. The computed lattice constants and band gaps are summarized in Table I. As expected, the HSE06 band gaps are larger and much closer to the experimental data than the PBE-GGA values. Band dispersions near the band gap of the KTaO\(_3\) and NaTaO\(_3\) resemble each other. Also in each system, the band dispersions of the HSE06 and PBE-GGA results are quite similar. In all the cases, the conduction band minimum (CBM) and VBM are located at the \(\Gamma\)- and \(R\)-points, respectively. The HSE06 hybrid functional also reproduces the lattice constants very accurately, while the PBE-GGA overestimates by nearly 1%.

Moving to \(V_O\) in KTaO\(_3\) and NaTaO\(_3\), the atomic configurations of \(V_O\) are systematically explored. Our calculations indicate that the formation of \(V_O\) leads to the nearest Ta atoms relaxed equally and outwardly from their ideal positions in the perfect system. As a result, \(V_O\) possesses the atomic configuration with \(D_{4h}\) point-group symmetry, whose principal rotation axis is along the Ta–\(V_O–Ta\) chain, as depicted in Figs. 2(a) and 2(b). Table II shows the calculated interatomic distance between \(V_O\) and its nearest two Ta atoms \((d_{V_O–Ta})\). The three charge states exhibit nearly the same atomic configurations, which is attributed to the delocalized characteristic of \(V_O\) in single-particle electronic structure as discussed later.

The formation energies of \(V_O\) in KTaO\(_3\) and NaTaO\(_3\) as a function of the Fermi level are illustrated in Fig. 3. The \(2+\) charged \(V_O\) is the most stable in most of the Fermi level positions inside the band gap. This indicates that \(V_O\) is a double shallow donor in both systems and releases two electrons. At the oxygen-rich limit, the formation energies of \(V_O\) are as high as \(\sim 6\) eV. However, under the oxygen-poor limit, the

| Table I. Lattice constant, \(a\) (Å), and electronic band gap, \(E_g\) (eV). HSE06, GGA, and \(\exp\) in superscript denote the HSE06, PBE-GGA, and experimental values, respectively. Experimental data are collected from Refs. 7 and 8 and references therein. |
|-----------------|-----------------|
|                 | KTaO\(_3\)      | NaTaO\(_3\)      |
| \(a^{\text{HSE06}}\) | 3.995           | 3.947           |
| \(a^{\text{GGA}}\) | 4.027           | 3.976           |
| \(a^{\exp}\)     | 3.988           | 3.929           |
| \(E_{g}^{\text{HSE06}}\) | 3.40           | 3.60           |
| \(E_{g}^{\text{GGA}}\) | 2.06           | 2.22           |
| \(E_{g}^{\exp}\) | 3.7            | 4.1            |
HYBRID DENSITY FUNCTIONAL STUDY OF OXYGEN... PHYSICAL REVIEW B 83, 214107 (2011)

FIG. 1. (Color online) Band structure of KTaO₃ (top) and NaTaO₃ (bottom). Solid (red) and dash-dotted (black) curves denote the HSE06 and PBE-GGA results, respectively. The VBM is set to zero in each case.

formation energies become lower by 3.97 eV, corresponding to half the formation energy of TaO₂. This amount of change is close to that of the previous GGA results.⁷,⁸ It leads to the formation energies of V₂⁺, the Fermi level at the CBM, ΔE^CBM(V₂⁺) = 2.08 and 1.63 eV for KTaO₃ and NaTaO₃, respectively. Hence, V₀ is likely to form under oxygen-poor conditions and may contribute to the physical properties such as the n-type conductivity in KTaO₃ and NaTaO₃. In the single-particle electronic structure, hydrogenic effective-mass states are found in the neutral charge state, indicating that V₀ is regarded as V₂⁺ with weakly bound or unbound two electrons. Similarly, V⁺ corresponds to V₂⁺ that has a weakly bound or unbound electron. These features are compatible with the formation-energy diagram shown in Fig. 3, indicating nearly the same formation energies for V₀, V⁺, and V₂⁺ when the Fermi level lies near the CBM.

FIG. 2. (Color online) Atomic configurations of neutral V₀ in KTaO₃ and NaTaO₃. Top and bottom panels show the stable (D₄₈) and metastable V₀-I (C₄ᵥ) configurations, which are illustrated on the Ta–O plane including V₀. The principal rotation axis of the D₄₈ and C₄ᵥ point-group symmetry is along the Ta–V₀–Ta chain.

FIG. 3. (Color online) Formation energies of V₀ in KTaO₃ (left) and NaTaO₃ (right) as a function of the Fermi level. Top and bottom panels indicate the formation energies at the oxygen-rich and oxygen-poor limits, respectively. The slope corresponds to the charge state as defined by Eq. (1). Note that in these systems the 2+ charge state is stable for most positions of the Fermi level in the band gap.

TABLE II. Atomic distance between V₀ and the nearest Ta atoms in Å units. D₄₈-I (C₄ᵥ), and II (C₄ᵥ) denote the stable V₀, metastable V₀-I, and metastable V₀-II configurations, respectively. Ideal denotes the interatomic distance between O atom and its nearest Ta atoms in the perfect-crystal cell.

<table>
<thead>
<tr>
<th></th>
<th>KTaO₃</th>
<th>NaTaO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>D₄₈</td>
<td>I (C₄ᵥ)</td>
</tr>
<tr>
<td>Ideal</td>
<td>2.00</td>
<td></td>
</tr>
<tr>
<td>V₀</td>
<td>2.18</td>
<td>1.80, 2.56</td>
</tr>
<tr>
<td>V⁺</td>
<td>2.19</td>
<td>1.80, 2.56</td>
</tr>
<tr>
<td>V₂⁺</td>
<td>2.19</td>
<td>1.80, 2.56</td>
</tr>
</tbody>
</table>

TABLE II. Atomic distance between V₀ and the nearest Ta atoms in Å units. D₄₈-I (C₄ᵥ), and II (C₄ᵥ) denote the stable V₀, metastable V₀-I, and metastable V₀-II configurations, respectively. Ideal denotes the interatomic distance between O atom and its nearest Ta atoms in the perfect-crystal cell.

<table>
<thead>
<tr>
<th></th>
<th>KTaO₃</th>
<th>NaTaO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>D₄₈</td>
<td>I (C₄ᵥ)</td>
</tr>
<tr>
<td>Ideal</td>
<td>2.00</td>
<td></td>
</tr>
<tr>
<td>V₀</td>
<td>2.18</td>
<td>1.80, 2.56</td>
</tr>
<tr>
<td>V⁺</td>
<td>2.19</td>
<td>1.80, 2.56</td>
</tr>
<tr>
<td>V₂⁺</td>
<td>2.19</td>
<td>1.80, 2.56</td>
</tr>
</tbody>
</table>

respectively. Hence, V₀ is likely to form under oxygen-poor conditions and may contribute to the physical properties such as the n-type conductivity in KTaO₃ and NaTaO₃. In the single-particle electronic structure, hydrogenic effective-mass states are found in the neutral charge state, indicating that V₀ is regarded as V₂⁺ with weakly bound or unbound two electrons. Similarly, V⁺ corresponds to V₂⁺ that has a weakly bound or unbound electron. These features are compatible with the formation-energy diagram shown in Fig. 3, indicating nearly the same formation energies for V₀, V⁺, and V₂⁺ when the Fermi level lies near the CBM.
are the cross-sections of isosurfaces at panels (a) and (b) correspond to localized in-gap states are not found in the minority spin component. Panels (c) and (d) show $V^-$ by conditions that are far from thermal equilibrium and/or considered for the atomic configuration of $V^-$ atomic distortion near perovskite oxides. Here we examine the effects of local configuration with a lower symmetry, $V$ for the neutral charge state, there exist the states at 0.26 and 0.83 eV below the CBM. The shallower state in each system is characterized $D$ with composition of Sr is an unintentionally incorporated metal impurity in $V$ and local polar nanoregions and relaxorlike ferroelectricity have recently been found in bulk and thin films of SrTiO$_3$ and local polar nanoregions and relaxorlike ferroelectricity have been observed in nominally pure KTaO$_3$ samples and Ta$_4^{2+}$-V$^{2+}$ or Ta$_4^{4+}$-$V^{2+}$-$O^{2-}$-$Me_I^{4+}$ centers were proposed to explain them, where $Me_I$ is an unintentionally incorporated metal impurity in the given samples. Within these paramagnetic centers, a Ta atom and a metal impurity capture electrons released from the nearest $V_0$, leading to the inversion symmetry breaking and thereby to the local dipole moment. However, $V^+$ is unlikely to form under Ti-rich conditions. By analogy, we propose that Ta antisite defects, that is, a Ta atom off-centered from the K site, are also considerable sources of the polar microregions. In fact, it has been reported that $extrinsic$ A-site dopants such as Li can create the local polar clusters through after specific post-treatments. Note that the total energies of $V_0$-I and $V_0$-II are, in fact, lower than that of the stable $V_0$. However, we found that the asymmetric relaxation to break the cubic symmetry, as occurring for $V_0$-I and $V_0$-II in $C_{4v}$ symmetry, also lowers the total energy of the perfect crystal cell for both KTaO$_3$ and NaTaO$_3$. The distorted perfect crystal is therefore used for the evaluation of the formation energies of $V_0$-I and $V_0$-II to compensate the energy gain associated with the asymmetric relaxation. It is also noteworthy that $V_0$-I, whose $|\psi_n|^2$ is similar to that of the stable $V_0$, has a lower energy than $V_0$-II showing localized $|\psi_n|^2$ characteristics. This supports our conclusion that $V_0$ acts as a shallow double donor.

Next, we discuss the physical properties relevant to $V_0$ for each system on the basis of our results:

(i) KTaO$_3$. Through the temperature-dependence measurements of electric conductivity, the ionization energy of $V_0^+$ in KTaO$_3$ was suggested to be 0.1–0.2 eV. Laguta and co-workers reported through thermally stimulated conductivity measurements that the concentrations of shallow-electron traps, assigned as $V_0^0$ or $V_0^{\ddagger}$ states, are $10^{11}$–$10^{13}$ cm$^{-3}$, but the EPR could not detect $V_0$ in the same samples. They attributed no such EPR signal to (i) a lower concentration of $V_0$ than the EPR sensitivity ($10^{15}$–$10^{16}$ cm$^{-3}$), (ii) a large radius of $V_0$-induced states at the traps, and/or (iii) the coupling of many of $V_0$ with a metal impurity, leading to deeper electron traps. As predicted by our calculations, the double shallow donor nature of $V_0$ can be an actual cause of no EPR signal.

The local polar microregions have been observed in nominally pure KTaO$_3$ samples and Ta$_4^{2+}$-V$^{2+}$ or Ta$_4^{4+}$-$V^{2+}$-$O^{2-}$-$Me_I^{4+}$ centers were proposed to explain them, where $Me_I$ is an unintentionally incorporated metal impurity in the given samples. Within these paramagnetic centers, a Ta atom and a metal impurity capture electrons released from the nearest $V_0$, leading to the inversion symmetry breaking and thereby to the local dipole moment. However, $V^+$ is unlikely to form under Ti-rich conditions. By analogy, we propose that Ta antisite defects, that is, a Ta atom off-centered from the K site, are also considerable sources of the polar microregions. In fact, it has been reported that $extrinsic$ A-site dopants such as Li can create the local polar clusters through
a large off-centering ($\sim$1 Å) from the K site and thereby produce the relaxorlike ferroelectric state.\textsuperscript{46,47} In the same sense, Ta antisite defects are expected to play roles as intrinsic off-centered A-site dopants.

(ii) NaTaO$_3$. To our knowledge, there is only one computational study reported dealing with the structural and electronic properties of V$_0$ as well as other native defects in NaTaO$_3$.$^9$ This study was conducted using the PBE-GGA functional, and showed that V$_0$\textsuperscript{2+} is thermodynamically the most stable for most positions of the Fermi level inside the band gap. This finding on V$_0$ is the same as what the present HSE06 calculations figure out. In other words, both studies suggest that V$_0$ acts as a double shallow donor in NaTaO$_3$, providing carrier electrons. Even at the oxygen-rich limit, where V$_0$ is energetically unfavorable in general, the HSE06 formation energy of V$_0$ is largely negative when the Fermi level is located near the VBM [see Fig. 3(b)]. Such a negative $\Delta E_f$ implies that making $p$-type NaTaO$_3$ is difficult under thermal equilibrium because of the spontaneous formation of V$_0$\textsuperscript{2+} and hence carrier compensation. No EPR measurement has been reported about V$_0$ in NaTaO$_3$.

In connection with the theoretical approach, one thing is noteworthy. As mentioned above, our HSE06 calculations in conjunction with the band-gap correction yielded a $\Delta E_f^{\text{CBM}(V_0^{2+})}$ value of 5.60 eV at the oxygen-rich limit. In the previous GGA study, $\Delta E_f^{\text{CBM}(V_0^+)}$ at the oxygen-rich limit is 8.46 eV after the band-gap correction. With the PBE-GGA, the band gap was underestimated by $\Delta E_g$ = 1.83 eV, and $\Delta E_f^{\text{CBM}(V_0^+)}$ was raised by 3.66 eV via the band-gap correction based on the rigid upward shift of the CBM.$^8$ If the correction is not applied to the PBE-GGA and HSE06 results, $\Delta E_f^{\text{CBM}(V_0^{2+})}$ are different by $\sim$0.2 eV. This points out that the CBM-shift-only scheme in conjunction with the GGA or LDA, showing severe band-gap underestimation, significantly overestimates defect formation energies relative to the HSE06 values. This can be partly attributed to the different absolute VBM position obtained by respective functionals. Similar findings have been recently reported on other oxides such as ZnO (Refs. 16, 17, and 48), TiO$_2$ (Ref. 18), and In$_2$O$_3$.\textsuperscript{19}

IV. SUMMARY

The HSE06 hybrid functional calculations have been performed to study V$_0$ in two perovskite tantalates, KTaO$_3$ and NaTaO$_3$. Their bulk properties such as the lattice constant and band gap are well reproduced using the HSE06 hybrid functional, and the calculated values are much closer to experimental data than those obtained by the GGA. The formation energies and single-particle electronic structures of V$_0$ in KTaO$_3$ and NaTaO$_3$ indicate that V$_0$ prefers to have $D_{4h}$ symmetric atomic configuration and is a double shallow donor, which can provide carrier electrons for the $n$-type conductivity in both systems. Two other configurations, V$_0$-I and V$_0$-II, are also found through the symmetry breaking of atomic configurations near V$_0$. These configurations possess the same point-group symmetry of $C_{4v}$ but have very different single-particle electronic structures from each other. V$_0$-II shows electron-localized states in the band gap, while V$_0$-I does not. However, these asymmetric configurations are less stable than the $D_{4h}$ configuration, and thereby are unlikely to form in KTaO$_3$ and NaTaO$_3$ under thermal equilibrium. This explains no observations of V$_0^+$ in the EPR measurements and indicates that the high ionization energies assigned to V$_0$ in electric conductivity measurements may not be responsible for V$_0$ but for other defects, complexes, or impurities.

ACKNOWLEDGMENTS

This work was supported by Grants-in-Aid for Scientific Research (A), Young Scientists (B), Scientific Research on Priority Areas (Grant No. 474), and a Global COE Program from the Ministry of Education, Culture, Sports, Science, and Technology of Japan.
\[ \text{MINSEOK CHOI, FUMIYASU OBA, AND ISAO TANAKA} \]

**PHYSICAL REVIEW B** \textbf{83}, 214107 (2011)


