Oxygen-vacancy-induced charge carrier in n-type interface of LaAlO$_3$ overlayer on SrTiO$_3$ (001): interface vs bulk doping carrier

Yun Li$^1$, S. Na Phattalung$^2$, S. Limpijumnong$^2$, and Jaejun Yu$^1$

$^1$Department of Physics and Astronomy, FPRD,
Center for Strongly Correlated Materials Research,
Seoul National University, Seoul 151-747, Korea
$^2$School of Physics, Suranaree University of Technology,
Nakhon Ratchasima 30000, Thailand

(Dated: December 24, 2009)

We investigated the role of oxygen vacancy in n-type interface of LaAlO$_3$ (LAO) overlayer on SrTiO$_3$ (STO) (001) by carrying out density-functional-theory calculations. Comparing the total energies of the configurations with one vacancy in varying locations we found that oxygen vacancies favor to appear first in LAO surface. These oxygen vacancies in the surface generate a two-dimensional distribution of carriers at the interface, resulting in band bending at the interface in STO side. Dependent on the concentration of oxygen vacancies in LAO surface, the induced carrier charge at the interface partially or completely compensates the polar electric field in LAO. Moreover, the electronic properties of oxygen vacancies in STO are also presented. Every oxygen vacancy in STO generates two electron carriers, but this carrier charge has no effect on screening polar field in LAO. Band structures at the interface dependent on the concentrations of oxygen vacancies are presented and compared with experimental results.

PACS numbers: 73.20.-r, 79.60.Jv, 77.22.Ej, 73.21.-b

I. INTRODUCTION

Since Ohtomo and Hwang reported the existence of a high mobility electron gas at the $n$-type (LaO)$^+/$(TiO)$_2$ interface between two band-gap insulators LAO and STO, many novel properties related to the electron gas at the interface, such as insulator-metal transition, superconductivity, and ferromagnetism were found. The mechanism of conductivity and the dimensionality of the induced carrier at the interface were intensively studied. In the $n$-type interface structure a polar electrical field along LAO [001] direction is arisen from the alternating stack of (LaO)$^+$ and (AlO$_2$)$^-$ charged layers. Charge reconstruction at the interface was proposed as a way to avoid diverging electrostatic potential with thick LAO, which compensates the polar electric field in LAO and induces electron gas at the interface. The densities and distributions of the induced carriers charge were measured in various experiments. Two different origins of the induced carriers charge, i.e. intrinsic and extrinsic doping, have been proposed. Intrinsic charge doping at the interface mainly happens in stoichiometrical structure without oxygen vacancy. With thick LAO overlayer the charge transfers from valence band of LAO surface to conduction band of STO at the interface, leading to a metallic interface. While extrinsic charge doping was found to be ascribed to oxygen vacancies in many experiments.

Noticeably, the conducting properties at intrinsic and extrinsic doped interfaces measured in the experiments are very different. In the ideal interface of thin LAO overlayer without oxygen vacancy the carrier densities measured by Hall effect and x-ray photoelectron spectroscopy (XPS) are even less than 0.1 electron per two-dimensional unit cell (2d.u.c.). Recent density-functional-theory (DFT) calculations showed that ionic polar distortions partially compensate polar electric field in LAO, reducing carrier density at the interface. For thin LAO overlayer the carrier charge was found in XPS experiment to distribute in a few layers of STO at the interface. Latest DFT study found that for less than 7 layers of LAO the carrier charge distributes in 3 layers of STO but for thicker LAO the carrier could accumulate in deep STO layers about 3 nm away from the interface. However, with oxygen vacancies in the interface structure the carrier densities measured in experiments vary from 0.5 to three orders of magnitude e/2-d.u.c. dependent on the oxygen pressure in preparing process. The experiment in Ref. explicitly verified that high carrier density is ascribed to high concentration of oxygen vacancies in STO substrate which were generated under lower oxygen pressure during preparing the sample.

Besides the carrier density, another issue which people have been debating extensively is the distribution of carrier charge induced by oxygen vacancy. In some sample produced in high oxygen pressure two-dimensional distributions were observed, but in others produced in low oxygen pressure obvious 3-dimensional distribution in STO were observed. These experimental hints indicated the carrier distribution is related to the concentration of oxygen vacancies in some way. Up to now, people have realized that oxygen vacancy play an important role in n-type LAO/STO interface, however the locations of oxygen vacancies and the dependence of two-dimensional and three-dimensional carrier distributions on the locations of oxygen vacancies are still not clear.

In this paper we studied the n-type interface with oxygen vacancies by using density-functional-theory (DFT) calculations. It should be noted that the interface composed of sandwich structure was also investigated in experiment but the structure of LAO overlayer on STO substrate has attracted the...
most of attentions because of its abundant conducting properties. In this paper we focused on the structure of LAO overlayers on STO. We calculated and compared the total energies of the configurations with varying locations and concentrations of oxygen vacancies. We found that the locations of oxygen vacancies are related to the concentration. From the calculations of electronic structures we also unveiled that the distribution of carriers is strongly dependent on the locations of oxygen vacancies. Based on the results from our calculations, energy band structures at the interface and localized surface conductivity were discussed.

All coordinates of atomic positions were fully relaxed with forces less than 0.02 eV/Å except for the atoms in the bottom two layers of STO, which were fixed in their bulk positions.

III. LOCATION OF OXYGEN VACANCIES OF LOW CONCENTRATION

In this paper we divide the concentrations of oxygen vacancies in the interface structure into two regions, i.e. low concentration and high concentration. In the former the concentrations of oxygen vacancies is less than or equal to 1/4 per 2-d.u.c. and the density of induced carriers is less than or equal to 0.5 electron per 2-d.u.c.. While in the latter the concentrations of oxygen vacancies is larger than 1/4 vacancy per 2-d.u.c. and the density of induced carriers is larger than 0.5 electron per 2-d.u.c.. To simulate low concentration of oxygen vacancy in the interface structure only one vacancy is involved in the supercells. While for higher concentration more vacancies are involved in the supercells. For convenient we use \( n_V \) and \( n_c \) to denote the concentration of oxygen vacancies and carrier density in 2-d.u.c., respectively.

A. Binding energies of oxygen atom

Oxygen vacancies were explicitly confirmed to exist in STO substrate of the interface structure produced under low oxygen pressure. However, up to now there has been no report about whether oxygen vacancy exits in LAO. To investigate the location of oxygen vacancy we calculated the total energies of oxygen vacancy in varying locations under various concentrations. We used \((3 \times 2)\) and \((2 \times 2)\) supercells with one vacancy as the representatives of \( n_V \) less than and equal to 1/4 per 2-d.u.c., respectively. To compare them in same plot we calculated the binding energy of one oxygen atom corresponding to the vacancy defined as:

\[
E_b = (E_V + 1/2E_{O_2}) - E_0,
\]

in which \( E_V \), \( E_{O_2} \), and \( E_0 \) are total energies of the system with oxygen vacancy, oxygen molecule and ideal system without vacancy, respectively. Figure 2 presents the binding energies of one oxygen atom corresponding to the vacancy at varying locations in \((3 \times 2)\) and \((2 \times 2)\) supercell. Oxygen atom in LAO surface has the lowest binding energy, which is far less than that in STO substrate. This indicates that oxygen vacancy is most easily formed in LAO surface rather than in STO substrate. Moreover the binding energy of oxygen atom in LAO surface decreases with the thickness of LAO. Such results are strongly related to polar electric field in LAO. In the ideal interface structure the polar field shifts the energy bands of LAO toward higher energy layer by layer, substantially raising the total energy. While oxygen vacancy in LAO dopes electron carriers at the interface, which partially or completely screen the polar field in LAO, remarkably lowering the total energy. In contrast to the vacancy in the surface, the vacancy inside LAO just screens part of polar field from the layer with the

FIG. 1: (Color online) Atomic structures of \((2 \times 2)\) supercells (a) without oxygen vacancy, and (b) with oxygen vacancy in LAO surface. Oxygen vacancy is denoted by black ball.
vacancy to the interface. Therefore corresponding configuration has higher total energy, as illustrated in Fig. 2.

As shown in Fig. 3, the formation energies of (2 × 2) supercells with one vacancy in LAO surface decrease with the thickness of LAO overlayer and tend to converge for those of thickness of LAO more than 4 layers. As aforementioned, in the ideal structure the electrostatic energy induced by polar field increases with the thickness of LAO. Following electronic calculations show that for (2 × 2) supercells with one oxygen vacancy in the surface the density of doping charge at the interface is 0.5 e/2-d.u.c., which exactly compensates polar electric field. This implies that oxygen vacancy in the surface of thicker LAO overlayer eliminates more electrostatic energy than that of thinner LAO overlayer. While once the LAO overlayer exceeds 4 layers, as demonstrated in previous DFT studies, in ideal structure without vacancy the intrinsic doping charge at the interface partially screens the polar field, preventing the increasing of electrostatic energy with the thickness of LAO. Therefore, the energy difference between vacant and ideal structures does not increase with thickness of LAO. So we can predict that under same preparing condition oxygen vacancy can be formed more easily in the sample with thicker LAO film, while this tendency does not strengthen any more once LAO exceeds 4 layers. Moreover, as shown in Fig. 3 for two unitcells (2 × 2) and (3 × 2) which have the same 4 layers of LAO the lower concentration of vacancy is more stable and therefore more easily be formed. As well known, oxygen pressure is a dominant factor of the formation of oxygen vacancy in LAO/STO interface structure. In Fig. 3 at oxygen rich limit the ideal structure has the lowest formation energy. This is consistent with the experimental results that vacancy-free structures were fabricated under high oxygen pressure2,7,10,17. While in the middle or near the poor limit vacant structures have lower formation energies.

![Fig. 2](Color online) Binding energies of oxygen atom corresponding to one vacancy at varying locations in (3 × 2) supercell consisting of STO substrate and 4 LAO layers and (2 × 2) supercells consisting of STO substrate and 2 or 3 LAO layers.

![Fig. 3](Color online) Formation energies of one oxygen vacancy in LAO surface as a function of oxygen chemical potential. The thicknesses of LAO vary from 2 to 5 layers for (2 × 2) supercells, and only 4 layers of LAO for (3 × 2) supercell. Formation energy of ideal structure without vacancy is taken as zero.

To investigate dependence of the formation of oxygen vacancy in the surface on the thickness of LAO, we calculated the formation energies of one vacancy in the surface of (2 × 2) supercells consisting of 2 to 5 layers of LAO according to the formula

\[ E_f = E_V - (E_0 - \mu_O), \]

in which \( \mu_O \) is chemical potential of oxygen atom, \( E_V \), and \( E_0 \) are total energies of the system with one oxygen vacancy in the surface and ideal system without vacancy, respectively.

![Fig. 4](Color online) Formation energy of oxygen vacancy in LAO/STO interface structure.

**IV. ELECTRONIC STRUCTURES OF OXYGEN VACANCIES OF LOW CONCENTRATION**

**A. Oxygen-vacancy state in LAO surface and induced carrier**

Above binding-energy calculations have shown that in the configurations of \( n_V = \leq 1/4 \) per 2-d.u.c. oxygen vacancy lies in LAO surface. To investigate the electronic properties of oxygen vacancy in the surface we calculated (2 × 2), (3 × 2), (3 × 3), and (4 × 4) supercells with one vacancy, respectively. As a representative of \( n_V = \leq 1/4 \) per 2-d.u.c., the electronic structure and local atomic structure of (3 × 3) supercell are presented in Fig. 4. One can see in Fig. 4 (a) and (b) that the empty state of oxygen vacancy lies a little bit below the conduction band minimum (CBM) of LAO and is localized in the surface layer. Obviously, the level of oxygen vacancy is higher than CBM of STO. Charge transfer from the state of oxygen vacancy in the surface to conduction band of STO at the interface lowers the total energy of the system. Our calculation showed that 2 electrons accumulate at the interface, i.e., \( n_c = 0.22 \) e/2-d.u.c., which is the twice of \( n_V \). The same relation between \( n_c \) and \( n_V \) were also found in other configurations of \( n_V = \leq 1/4 \) per 2-d.u.c.,
FIG. 4: (Color online) (a) Layer-projected DOS for the (3 × 3) super-cell with one oxygen vacancy in LAO surface. (b) Spacial distribution of oxygen-vacancy state in the (3 × 3) surface. (c) Side view of polar distortions of cations and anions in upper 3 layers of LAO.

B. Lattice polarization dependence on the concentration of vacancy in LAO surface

For the configurations of \( n_V < 1/4 \) per 2-d.u.c. the carrier density at the interface is less than 0.5 e/2-d.u.c. The polar electrical field in LAO overlayer is screened partly and then the potential gradient in LAO overlayer still remains. In Fig. 4(a) one can see that the valence and conduction bands shift towards higher energy layer-by-layer from the interface to the surface. The polar distortions in LAO induced by residual polar electrical field are shown in Fig. 4(c). Summarizing for configurations of \( n_V < 1/4 \) we found that with increasing the concentration of oxygen vacancy from \( (4 \times 4) \) to \( (2 \times 2) \) the density of carriers at the interface increases till 0.5e/2-d.u.c and the potential gradient and the polar distortions reduce till vanish.

For the configurations of \( n_V < 1/4 \), the thickness of LAO is another factor which affects the density of carriers at the interface. For a given concentration of oxygen vacancies, with increasing the thickness of LAO the VBM of LAO shifts upwards until it touches CBM of STO. This critical thickness of LAO, denoted as \( t_c \), is dependent on the concentration of vacancies in the surface \( n_V \). Once the thickness of LAO overlayer overruns \( t_c \), the VBM of LAO does not shift up anymore, instead, more charge transfers from valence band of LAO surface to the interface. According to the electrostatics we give an expression of carrier density \( n_c \) as a function of \( n_V \) and \( t \) (thickness of LAO overlayer)

\[
n_c = \begin{cases} 
\frac{1}{2} - \frac{A}{t - t_0} & t > t_c \\
2n_V & t \leq t_c 
\end{cases}
\]

(1)

\[
t_c = \frac{A}{1/2 - 2n_V} + t_0,
\]

(2)

where \( A=1.97 \), \( t_0=0.053 \) obtained from our previous DFT study. The scale of \( t \) and \( t_0 \) is unit-cell layer. For the configuration of \( (3 \times 3) \) with one vacancy in the surface the critical thickness equals 7 u.c in our DFT calculation and 7.1 u.c. from above formula.

Figure 5(a) presents the layer-projected DOSs of \( (2 \times 2) \) supercell with one vacancy in LAO surface. The state of vacancy in LAO surface lies a little bit below the CBM of LAO and is localized in the surface layer. Calculated density of carriers at the interface is equal to 0.5 e/2-d.u.c., which is exactly enough to completely screen the polar electric field in LAO. One can see this point from straight-aligned VBM and CBM of LAO layers in Fig. 5(a). Similar to what is shown in Fig. 4(b), oxygen vacancy in the surface induces strong tilt distortion which even extend into a few layers of STO, but average polar displacement in each LAO layer is zero. It means no net electrostatic field in LAO. For comparison Fig. 5(b) presents the layer-projected DOSs of \( (2 \times 2) \) supercell with one vacancy in STO substrate. Oxygen vacancy in STO produces a shallow energy level in the CBM of STO and generates two electron carriers. However, strong potential gradient appears in LAO overlayer because no charge transfers from the LAO surface to the interface. We can conclude that carriers generated by oxygen vacancies in STO hardly have any effect on screening the polar electric field in LAO overlayer.

FIG. 5: Layer-projected DOS for the \( (2 \times 2) \) supercell (a) with one oxygen vacancy in LAO surface, and (b) with one oxygen vacancy in STO-1 layer.

V. DISTRIBUTION OF OXYGEN VACANCIES OF HIGH CONCENTRATION

A. Binding energies

We modeled the configurations of \( n_V > 1/4 \) per 2-d.u.c. by \( (2 \times 2) \) supercell with two oxygen vacancies. As we pointed out above that when \( n_V < 1/4 \) per 2-d.u.c. oxygen vacancy favors to lie in LAO surface. Considering this point in the calculations of \( (2 \times 2) \) supercell with two oxygen vacancies one is
always fixed in LAO surface and the others varies from LAO surface to STO substrate. Fig. 6 illustrates binding energies of the oxygen atom corresponds to the second vacancy. Although oxygen atom in surface still has the lowest binding energy, in contrast to the cases of \( n_V \leq 1/4 \) per 2-d.u.c. the energy differences with other configurations decrease largely. The energy difference between the configurations of the second vacancy in LAO surface and in STO substrate is about 0.2 eV, which is far less than that for the first vacancy. This implies that second vacancy has large probability to appear in STO. Following electronic structure calculations show that for the configurations of \( n_V > 1/4 \) per 2-d.u.c. the second vacancy does not contribute any energy gain by screening the electrostatic field in LAO because the first vacancy already completely screens it.

B. Electronic structure of oxygen vacancies of high concentration

Figure 7(a) presents the layer-projected DOS of \((2\times2)\) supercell with two oxygen vacancies in surface AlO\(_2\) layer. The state of vacancies is widened due to the interaction of two vacancies, and only half is occupied. Two electrons in this state transfer to the interface. Another typical configuration is shown in Fig. 7(b), in which one vacancy lies in surface AlO\(_2\) layer and the other in the (LAO-3)-AlO\(_2\) layer. The state of oxygen vacancy in LAO-3 layer extends into the surface layer and is fully occupied, while the state of oxygen vacancy in the surface layer is empty. Our calculated amount of carriers at the interface is still 2. In these two configurations the former has a metallic surface, while the latter has an insulating surface. Both dope two electron carrier at the interface, although two oxygen vacancies exist in LAO. Several other configurations with two oxygen vacancies in LAO also show the same carrier density 0.5e/2-d.u.c at the interface. This indicates that oxygen vacancies in LAO can contribute at most 0.5 electron carrier per 2-d.u.c. at the interface, and extra vacancies apart from 1/4 per 2-d.u.c. have no contribution to the conductivity at the interface. It can be understood from the sight of polar electric field in LAO. Charge transfer of 0.5 e/2-d.u.c from the LAO surface to the interface completely compensate the polar field in LAO, lowering the total energy. While Charge transfer of more than 0.5 e/2-d.u.c would set up an inverse electric field in LAO, which could raise the total energy.

Since a great amount of oxygen vacancies were found in STO substrate in the samples produced under lower oxygen pressure, the contribution of vacancies in STO to density and distribution of the carriers should be investigated. Fig. 8(a) shows the Layer-projected DOSs for the \((2\times2)\) supercell with one oxygen vacancy in LAO surface and one in STO. The carrier density is 1.0 e/2-d.u.c. in our calculation. With one more vacancy in STO, as shown in Fig. 8(b), the carrier density increases 0.5 e/2-d.u.c. more. In contrast with the upper limit
contribution of the vacancies in LAO every vacancy in STO generates two electron carriers in STO. Considering the vacancies distributing uniformly in whole STO substrate under low oxygen pressure in experiments, a 3-dimensional distribution of carriers can be formed. In respect of band structure no potential gradient appears in LAO, while valence and conduction bands of STO have evident bending at the interface.

VI. DISCUSSION

A. Band diagrams

According to above calculated electronic structures we plot schematic band diagrams of the interface. Since oxygen vacancies in STO do not cause the band bending at the interface, only the band structure with various concentrations of oxygen vacancies in LAO are plotted. Fig. 9 presents the band structures of oxygen vacancies in or near LAO surface. At the interface in STO side strong band bending happens in all configurations. The reason is that net positive-charged LAO overlayer, produced by electrons transfer from LAO surface to STO, generates an attractive potential to electrons in STO, lowering the potential at the interface in STO side. In Fig. 9 (a) \( n_V < 1/4 \) per 2-d.u.c. and \( n_v < 0.5 \) e/2-d.u.c.. The polar electrical in LAO is partially screened and the residual field results in bands sloping in LAO. In Fig. 9 (b) \( n_V = 1/4 \) per 2-d.u.c. and \( n_v = 0.5 \) e/2-d.u.c.. The polar field is completely screened, leading to flat bands in LAO. In contrast with \( n_V < 1/4 \) per 2-d.u.c. in the case of \( n_V = 1/4 \) per 2-d.u.c. more charge transfers from the surface to the interface, leading to larger band bending at the interface in STO side. In Fig. 9 (c) \( n_V > 1/4 \) per 2-d.u.c. but still \( n_v = 0.5 \) e/2-d.u.c.. The band structure is the same as the case of \( n_V = 1/4 \) but the surface is metallic. In Fig. 9 (d) vacancies are in surface and the layer below surface and the surface is insulating. In previous XPS experiment a flat valence band was observed. According to above analysis one can easily realize that such a band structure is arisen from the oxygen vacancies of \( n_V = 1/4 \) per 2-d.u.c. in LAO surface.

B. Charge carriers distribution: 2-dimensional or 3-dimensional

To clarify the distribution of the carriers induced by oxygen vacancy we carried out the calculations of electronic structure for \((\text{LAO})_3/(\text{STO})_{17}\times(2 \times 1)\) supercell by employing 17 STO layer. With one oxygen vacancy in LAO surface the integrated carrier density in STO is 0.5 e/2-d.u.c.. While the carriers in STO consist of two separate components, as illustrated in Fig. 10 (a). The interface component contains the main part of carriers, and the extended part with a broad peak locates near the 14th layer, i.e., about 5 nm, from the interface. The potential profile in the STO side illustrated in Fig. 9 resembles the case of the inversion layer in metal-oxide-semiconductor field-effect transistor and semiconductor heterostructure. Within this triangle-like potential, the carriers in the lowest bound state which can be approximately described by the Airy function accumulate at a few nm away from the interface. However, the interface state is originated from different mechanism. To understand the nature of two different components of the carriers, we plotted the charge density of the induced carrier in the STO side in Fig. 10 (b). The interface component consists mostly of the Ti \( d_{xy} \) orbitals, but the extended component has contributions from all the Ti \( t_{2g} \) orbitals, i.e., \( d_{xy}, d_{yz}, \) and \( d_{zx} \) states. The character at the interface stems from a strong compressive distortion of the TiO\(_6\) octahedron at the interface, which produces a strong tetragonal field, lowering of the \( d_{xy} \) state. Similar character of carriers was found in the ideal interface of LAO/STO without vacancy, and the mechanism was detailedly analyzed in our previous work.

From Fig. 10 one can see that most of carriers accumulate at the interface in four layers of STO although there is extended state. Such a two-dimensional distribution of carriers induced by oxygen vacancy in LAO surface is consistent.
with the two-dimensional electron gas measured in LAO/STO samples produced under higher oxygen pressure.\textsuperscript{10} While under low oxygen pressure vacancies can be formed uniformly in STO besides LAO surface. As well known, oxygen vacancies in STO generate a shallow level in conduction band and Fermi level lies in the CBM of STO. Considering band-bending at the interface the carriers first fill in the potential valley at the interface and then in STO inside. This implies that large amount of oxygen vacancies in LAO/STO system would generate a three-dimensional distribution of carriers in STO but with higher carrier density near the interface. Above picture about carrier distribution was measured in previous experiment by using conducting atomic force microscopy (AFM), in which the carrier density was found to decays exponential near the interface and extends a few $\mu$m in STO.\textsuperscript{10}

C. Localized surface conductivity

Another finding in our calculations which we like to emphasize is the surface conductivity in the system of LAO/STO. As shown in Fig. [7(a), oxygen vacancies of more than 1/4 per 2-d.u.c. generated a metallic surface. In contrast to nearly uniform distribution of the carriers at the interface, the carriers in the surface is relatively localized. In the case of Fig. [7(a), the states of two close vacancies overlap. A part of electrons in the states transfer to the interface and the left form localized surface carriers. This localized surface carriers may be responsible for the few-nanometer-size conducting islands in the surface of LAO/STO found in recent experiment.\textsuperscript{9}

VII. SUMMARY

We investigated the n-type LAO overlayer on STO(001) substrate with oxygen vacancies by using DFT calculation. We found that oxygen vacancies favor to appear first in LAO surface, which generate a two-dimensional carriers at the interface. The density of carriers induced by vacancies in LAO surface has an upper limit 0.5 e/2-d.u.c. For the concentration of vacancies in LAO surface less than 1/4 per 2-d.u.c., the density of induced carriers at the interface is less than 0.5 e/2-d.u.c. and the energy bands in LAO slope up from interface to surface. While for that of equal to or more than 1/4 per 2-d.u.c. the density of induced carriers is equal to 0.5 e/2-d.u.c. and no slope of the energy bands occurs in LAO. We found that for the case of the concentration of oxygen vacancies more than 1/4 per 2-d.u.c. the surface presents metallicity. We also investigated the role of oxygen vacancy in STO. We found that every oxygen vacancy in STO generates two electron carrier, but this carrier charge has no effect on screening the polar electric field in LAO. We predict that when a large amount of oxygen vacancies present in LAO/STO system the carriers in STO show a three-dimensional distribution with higher density at the interface.

Acknowledgments

This work was supported by BK21 and KOSEF through the ARP (R17-2008-033-01000-0). We also acknowledge the support from KISTI under the Supercomputing Application Support Program.
R. Pentcheva and W. E. Pickett, Phys. Rev. B, 74, 035112 (2006).
22 R. Pentcheva and W. E. Pickett, Phys. Rev. B, 78, 205106 (2008).
23 S. Ishibashi, and K. Terakura, J. Phys. Soc. Jpn. 77, 104706 (2008).
24 J. Lee and A. A. Demkov, Phys. Rev. B, 78, 193104(2008).
25 M.S. Park, S.H. Rhim, and A.J. Freeman, Phys. Rev. B 74, 205416 (2006).
26 W. C. Lee* and A. H. MacDonald, Phys. Rev. B 76, 075339 (2007).
27 G. Kresse, and J. Furthmüller, Phys. Rev. B 54, 11169 (1996).
28 Y. Wang, J.P. Perdew, Phys. Rev. B 44, 13298 (1991).
29 P.E. Blöchl, Phys. Rev. B 50, 17953 (1994).
30 G. Kresse, and D. Joubert, Phys. Rev. B 59, 1758 (1999).
31 G. Makov and M.C. Payne, Phys. Rev. B 51, 4014 (1995).
32 K. Uchida and S. Tsuneyuki, Phys. Rev. B 68, 174107 (2003).
33 K. Janicka, J. P. Velev, and E. Y. Tsymbal, Phys. Rev. Lett. 102, 106803 (2009).
34 S. Gemming and G. Seifert, Acta Mater. 54, 4299 (2006).
35 S. M. Nakhmanson, K. M. Rabe, and D. Vanderbilt, Appl. Phys. Lett. 87, 102906 (2005).
36 J. H. Lee, J. Yu, and U. Waghmare, J. Appl. Phys. 105, 016104 (2009).
37 M. Stengel and N. A. Spaldin, Nature 443, 679 (2006).
38 T. Ando, A. B. Fowler, and F. Stern, Rev. Mod. Phys. 54, 437 (1982).