Electronic structure and magnetic properties of Co-doped CeO$_2$: based on first principle calculation

Electronic structure and magnetic properties of Co-doped CeO$_2$: based on first principle calculation

Y Q Song[1]**, H W Zhang**[1]**, Q H Yang**[1]**, Y L Liu**[1]**, Y X Li**[1]**, L R Shah**[2]**, H Zhu**[2] **and John Q Xiao**[2]

[1] State Key Laboratory of Electronic Films and Integrated Devices, University of Electronic Science and Technology of China, Chengdu 610054, People's Republic of China
[2] Department of Physics and Astronomy, University of Delaware, Newark, DE 19716, USA

E-mail: yuanqiangsong@gmail.com

Abstract
The electronic structure and magnetic properties of Co-doped CeO$_2$ are theoretically investigated by first principles calculations based on the density functional theory $+ U$ (DFT $+ U$) methods, using the WIEN2k package. With the presence of oxygen vacancies (V$_O$) in CeO$_2$, d and f orbits of Ce are obviously pulled closer to the Fermi level, but without spin polarization. On the other hand, in Co-doped CeO$_2$, V$_O$ defects can lead to strong ferromagnetic coupling between the nearest neighboring Co ions. Such ferromagnetic exchange coupling is mainly attributed to spin splitting of Co 3d states, via electrons trapped in V$_O$. The results provide direct evidence for the F-center mediated exchange interaction in oxide-based magnetic semiconductors.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Ceria (CeO$_2$) is a hard material with a relatively high dielectric constant ($\varepsilon = 26$) and wide band gap Ceria-based materials have been widely investigated experimentally mainly for its catalytic and electrochemical properties [1–3]. In addition, due to its perfect match in crystal lattice constant with that of a Si single crystal, CeO$_2$ has also been studied as a promising candidate to act as the crystalline insulator layer in the silicon-on-insulator structure (SOI), based on its facility to be epitaxially deposited on a Si substrate [4–6]. In fact, epitaxial growth of CeO$_2$ on Si [7] and even a Si/CeO$_2$/Si [8] stacking superlattice have been successfully fabricated as being expected to facilitate SOI devices. What is more amazing, diluted Co-doped CeO$_2$ thin films have been reported as ferromagnetic with a high Curie (T_C) temperature, well above room temperature [9]. This accomplishment has a profound implications in the two following aspects. A high-T_C diluted magnetic oxide of Co-doped CeO$_2$ is good candidate to be used as the spin-filter layer in spin-related devices [10, 11]. Furthermore, due to perfect compatibility

of its crystal structure and parameters with that of silicon, Co-doped CeO$_2$ would be more easily integrated and thus facilitate the integration of spintronic devices with advanced silicon-based microelectronic devices.

Until recently, ferromagnetism (FM) was observed in Co-doped CeO$_2$ thin films on different substrates [12, 13] fabricated by several methods including electrodeposition method. We also observed FM in Co-doped CeO$_2$ in a thin film form [14], as well as in sintered bulk and powder form [15]. It seems that FM is readily introduced into a CeO$_2$ host by diluted doping of Co ions, which is exciting but a little unexpected after the following analysis. Cerium is known for its oxygen storage capacity, i.e., it can easily take up and release oxygen under oxidizing and reducing conditions, coupling with the formation and annihilation of oxygen vacancies (V$_O$), respectively. Therefore CeO$_2$ is always partially reduced and contains a certain amount of V$_O$ [16, 17], as is also the case for Co-doped CeO$_2$ either in the thin film or bulk form referred to above. According to the F-center mechanism (an F-center consists of an electron trapped in an oxygen vacancy), there would be abundant F-centers

acting as exchange coupling centers in a Co-doped CeO$_2$ system, thus leading to a ferromagnetic coupling between diluted Co ions. The F-center mediated FM has been proposed to explain the FM in some doped oxides, but with little experimental support. For example, reducing annealing would introduce additional V$_O$ and thus an enhancement of FM, but annealing may also cause Co separation, which could also lead to an FM enhancement.

While facing seemingly insurmountable obstacles for experimentalists, diluted magnetic semiconductors (DMS) such as Co-doped ZnO [18, 19] and Fe-doped In$_2$O$_3$ [20] have been extensively investigated by theoretical investigations based on density functional theory (DFT), by which method the obtained results were always highly consistent with experiments. As for Ce-based compounds, however, a theoretical description has been a challenge due to the localized and extended behavior of the Ce 4f states [21]. The recently developed DFT + U calculation method, in which a Hubbard U term is added to the local density approximation (LDA) or generalized gradient approximation (GGA), yields the correct ground state description of cerium oxides compared with experimental measurements. Thus, in this work, DFT + U calculations are performed for pure CeO$_2$ and Co-doped CeO$_2$ system, aiming to address the following problems: (i) study0mg the electronic structure and magnetic property of V$_O$-included CeO$_2$, to see if V$_O$ can really lead to FM. (ii) In Co-doped CeO$_2$, what is the mechanism contributing to its FM and what is the V$_O$ effect, and does V$_O$ mediate the ferromagnetic exchange coupling between two Co ions as depicted in the F-center mechanism.

2. Details of the calculation

It is well known that Ce is a fairly heavy material, thus the Ce 4f electron states are highly localized. CeO$_2$ always displays multiple oxidation states coupling with occupied or empty 4f electron states. The energy differences between these different states is so small that SCF calculations would converge non-physically in the LDA or GGA methods. Therefore, Ce 4f states could neither totally be treated as core states or valence electrons in partially reduced CeO$_{2-\delta}$. Thus instead of the conventional DFT techniques, the calculations are performed based on DFT + U methods. The introducing of a Hubbard-U term to DFT stabilizes the electronic-structure calculations towards the physical solution, thus providing an effective way for coping with such systems.

Calculations are performed based on DFT + U by means of the full potential linearized augmented plane-wave (FP-LAPW) method within the density functional theory (DFT) framework as implemented in the WIEN2k package [22]. In DFT + U, a Hubbard U term, corresponding to the mean-field approximation of the on-site Coulomb interaction, is added to the LDA functionals. According to some references, an effective Hubbard parameter (U_{eff}) of 5.30 eV was added for the Ce 4f states, which was used in previous first principles calculations for a good description of cerium oxides [23–25]. The basis for each non-overlapping muffin-tin approximation for the crystal potential and charge density is split into core and valence subsets. CeO$_2$ has a fluorite structure with an $Fm\bar{3}m$ space group, and has four Ce atoms at $4a(0\,0\,0)$ and eight O atoms at $8c(1/4\,1/4\,1/4)$. The constant muffin-tin radius (R_{mt}) used for Ce and O are 2.20 and 1.90 au, respectively. The valence part is treated with the potential expanded into spherical harmonics (up to $l = 6$). The valence wavefunctions inside the sphere are expanded up to $l = 10$. The calculations have been tested for accuracy with respect to the number of k-points we used, and for the plane-wave expansion parameters $R_{mt}K_{max}$, where K_{max} is the plane-wave cutoff and R_{mt} is the smallest muffin-tin sphere in the structure. $R_{mt}K_{max} = 7.0$ and 104 k points in the irreducible Brillouin zone (IBZ) for CeO$_2$ ($2 \times 2 \times 2$ supercell) turns out to be sufficient for the accuracy of the results presented in this paper (0.1 mRyd for the total energy per cell).

3. Result and discussion

Although there is much literature on the calculations of CeO$_2$, and its native properties are well known experimentally, we still discuss the calculated results for pure CeO$_2$, partially to verify the validity of our calculation method for the CeO$_2$ system. The crystal structure for CeO$_2$ is shown in figure 1(a). Both spin-polarized and non spin-polarized SCF have been done, although we know CeO$_2$ is a non-magnetic oxide. As a first principle method, the lattice constants are allowed to change in a wide range around the experimental values. The bulk unit cell lattice vectors and atomic coordinates were then relaxed at a series of fixed volumes. The $E(V)$ curve obtained (figure 1(b)) was fitted using the Murnaghan equation of state, and its minimum yields the stable structure with lattice constants a and bulk modulus B_o of 5.471 Å and 176 GPa, respectively; these are comparable with the experimental values of 5.411 Å and 230 GPa [26].

With the optimized lattice constant $a = 5.471$ Å, the ground state electronic structure for pure CeO$_2$ has also been calculated and the density of states is shown in figure 2. As can be seen, all valence Ce states, including the 4f states, are empty and the system is a wide gap insulator with a measured fundamental band gap of 5.7 eV between the valence and conduction bands. The valence and conduction bands are composed of O 2p and Ce 5d states, respectively. Ce 4f states lie in the gap, forming a narrow vacant band just above the Fermi level. It also indicates totally delocalized 4f electrons in fluorite CeO$_2$ as the ground state, which is in good agreement with experiments and earlier calculations with the consideration of the 4f electron as an ordinary valence electron [27, 28]. Since there are no unpaired electrons in Ce(IV) ions, it shows no magnetic moment.

Then a V$_O$ defect is introduced for the purpose of the investigation of the effect on the magnetic properties of CeO$_2$. Considering its structure, there is only one type of V$_O$, which is situated in the center of a regular tetrahedron, surrounded by four neighboring Ce atoms as shown in figure 3(a). V$_O$ was initially generated by removing one neutral oxygen atom in the relaxed perfect lattice supercell, followed by full atomic relaxation. The lattice relaxation around the oxygen vacancy involves a small expansion of the nearest neighbor Ce ions,
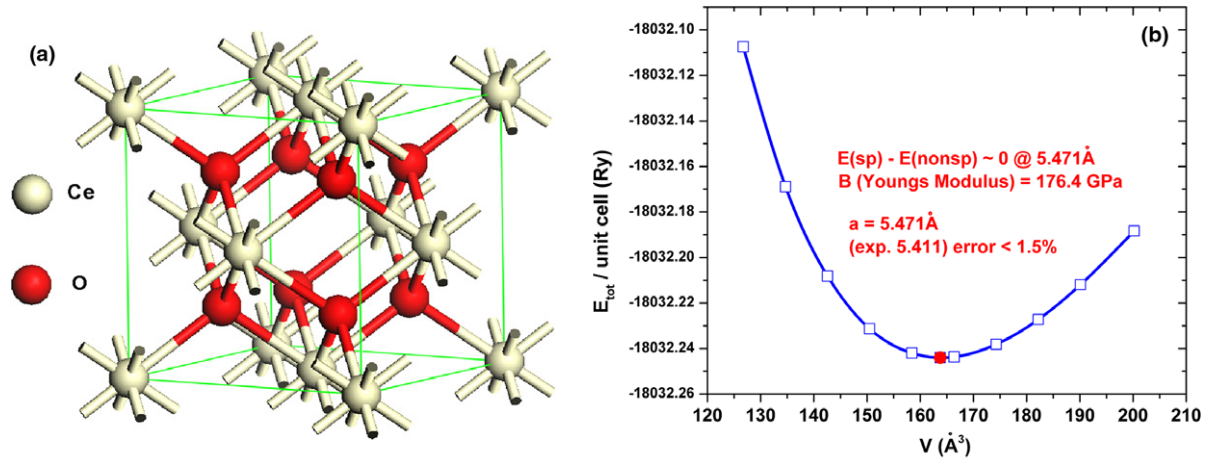
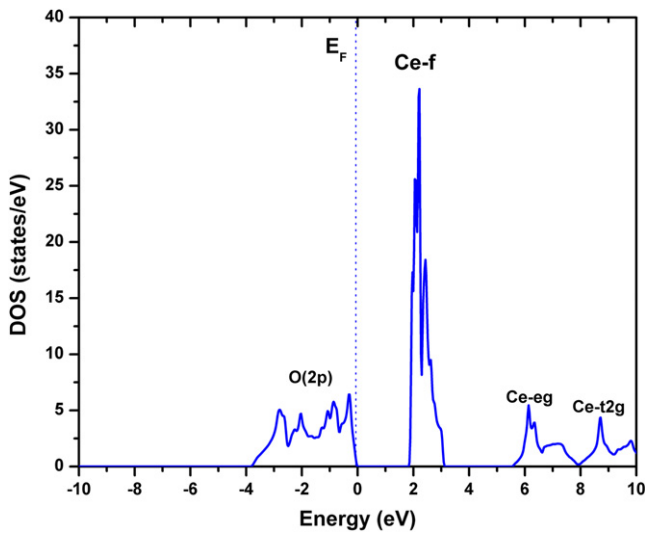**Figure 1.** (a) Crystal structure and (b) structure optimization of CeO_2.

Figure 2. Calculated total DOS of pure CeO_2.

with displacements in the range of 0.01–0.02 Å. It is typical for the F-center type defects already studied in cubic ionic oxides such as MgO [29]. Both the AFM and FM spin polarizations are carried out. However, the final convergence yields an AFM ground state. The calculated density of states (DOS) is shown in figure 3(b). Comparing it with that of defectless CeO_2, the d and f states shift down towards the Fermi level, and part of the f states even cross E_f. By inspecting the partial DOS, an occupation of the 4f states by almost one electron is found, which gives rise to a magnetic moment of about $1.0\mu_B$ per Ce ion neighboring with V_O. It is understandable by considering that, when the neutral oxygen atom is taken from the structure, it will give back two electrons, and part of them would refill the Ce 4f and 5d orbits of the Ce ions, contributing to the magnetic moments.

To support this statement we have taken a closer look at the bonding situation by comparing the charge-density distribution for CeO_2, with and without V_O, since the existence of real hybridization between the states of Ce and O should lead to covalent bonds between these atoms. In order to check out

the influence of V_O on the charge distribution, the $CeO_2(110)$ plane containing six O atoms and two neighboring Ce atoms is selected. Total charge-density distributions of the (110) plane without and with one V_O is plotted in figures 4(a) and (b), respectively. It is clearly seen from figure 4(a), that cerium oxide without V_O is characterized by a nearly spherical charge-density distribution around the Ce and O ions and a low charge density in the interstitial region. Charge-density spheres around the Ce and O ions almost overlap with each other forming a typical charge-density bridge between two neighboring Ce and O ions. However, with a V_O introduced into CeO_2, the radius of the charge density around Ce and O ions is obviously reduced, leading to a relative departure of the Ce and O ions as shown in figure 4(b). It seems that with a neutral O atom picked off from CeO_2 unit, the two electrons given back from the O ions totally return to the Ce ions and fill in the Ce 4f and 5d orbits.

However, even if there are unpaired electrons in a V_O containing CeO_2 unit, the overall magnetic moment per cell is found to be zero with AFM spin ordering, which is a little unexpected. We believe this is due to the small exchange splitting, since the density of states at the Fermi level is very small. This study indicates that, with the introduction of V_O, 4f states become more localized with partial occupation, but it is not enough for V_O alone to spin polarize the neighboring unpaired electrons.

After clarification of the V_O effect, we turn to the Co-doped CeO_2 system to investigate the FM originating mechanism. Cobalt-doped CeO_2 is also investigated based on a $2 \times 2 \times 2$ supercell. In CeO_2, one O atom is bonded to four neighboring Ce atoms to form a normal tetrahedron as shown in figure 3(a). Co ions are placed to substitute the two neighboring Ce cations with a V_O between the dopants. FM/AFM calculations are performed for the configurations both with and without V_O.

For the configuration without V_O, the lower calculated energy of the AFM exchange interaction indicates a predomination of AFM spin ordering, suggesting a strong super-exchange between two Co ions via the intermediate O ions. However, the presence of the intervening V_O makes
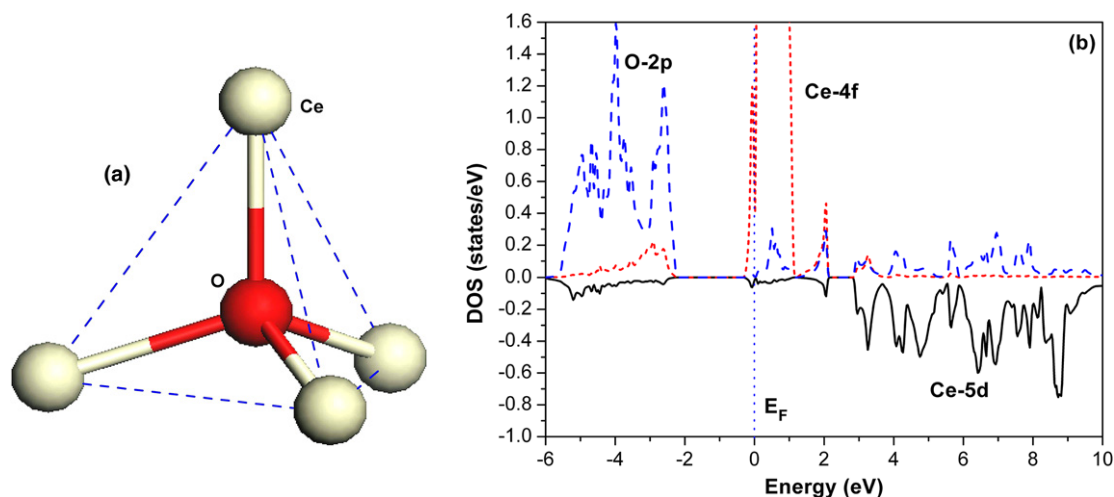
Figure 3. (a) The geometry around an oxygen vacancy, the central O atom is included for clarity and (b) the partial DOS of the V_O included-CeO_2.
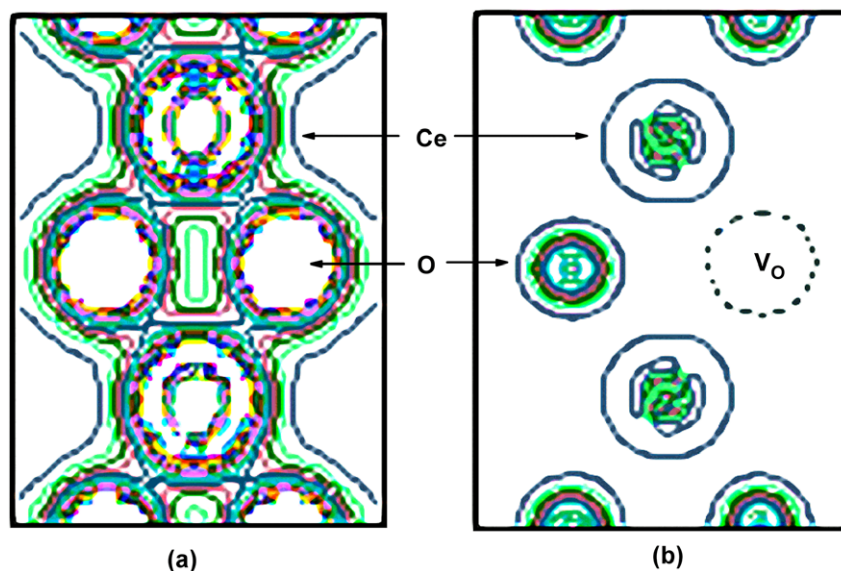

Figure 4. Total charge-density distributions of (a) intact $CeO_2(110)$ plane and (b) V_O-included structure.

an FM ordering more stable than AFM ordering according to energy variation. The spin-polarized DOS of the V_O-included configuration is shown in figure 5. It is clearly that the total DOS are spin polarized, with the spin polarization mainly contributed by the Co 3d orbits. It can be seen that Ce 4f states revert to an energy above the Fermi level, while Co 3d orbits are obviously spin splitting instead. All the spin up states of Co ion states are filled, and the spin down of the 3d e_g states are partially filled, with empty spin down t_{2g} states. Considering the Co $3d^7$ configuration of the Co^{2+} ion, it would contribute $3\mu_B$ per Co in principle. However, as can be seen from figure 5, a slight admixture of Co 3d character into the O 2p valence band can be observed, which would lead to some spin degeneracy and thus a reduced moment contribution. In fact, one Co ion in the configuration contributes $2.523\mu_B$ according to the calculation.

What is more interesting, FM exchange interaction via V_O can also expand to an indirect range, e.g., two cell parameters ($2a$) between two Co ions with V_O between them as sketched in figure 6, as well as a Co–V_O–Co direct interaction. In the $2a$-spaced configurations as shown in figure 6, each Co ion contributes about $2.5\mu_B$/atom for both types of V_O configuration, as labeled in figure 6, with no obvious diminishing of the magnetic moments as compared with that of Co–V_O–Co direct interaction. The detailed calculation results for these two configurations are listed in table 1. It can be predicted that long range FM ordering can be established by a relatively small fraction of V_O density, which is consistent with the ease of obtaining FM in the Co:CeO_2 system [30–32].

In conclusion, V_O induced FM in Co-doped CeO_2 was studied by performing first principles calculations. The results indicate that V_O leads to spin ordering by an F-center mediated exchange interaction in such a candidate. What is more interesting is that this interaction range can expand to a wide range, of at least two unit cells. Thus it can reasonably be
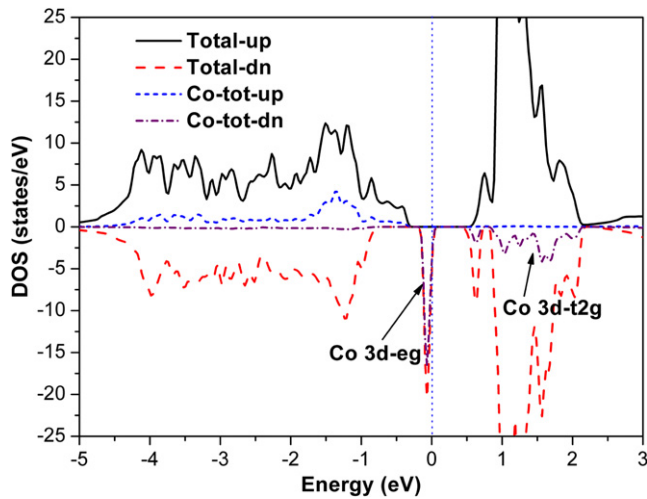
Figure 5. The corresponding spin-polarized DOS of the Co–V_O–Co configuration in the $(2 \times 2 \times 2)$ supercell.
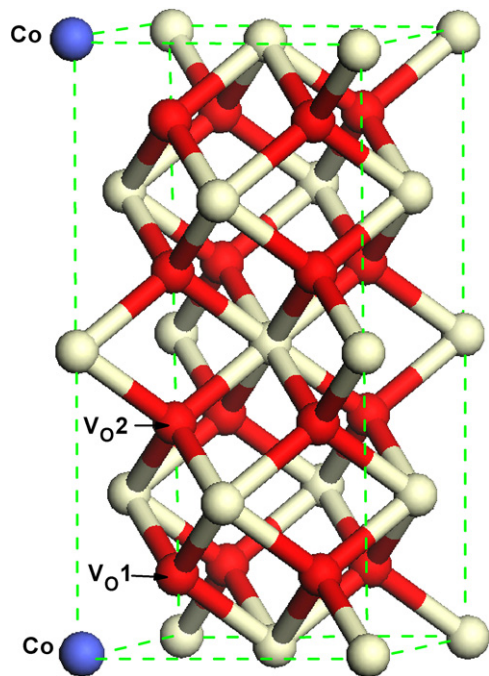
Figure 6. Two configurations of V_O in $2a$-spaced Co-doped CeO_2 structure as labeled. The structure is subtracted from the CeO_2 $(2 \times 2 \times 2)$ supercell for clarity.

Table 1. Detailed moments contributions in the two V_O-configurations shown in figure 6.

	M			
V_O	μ_B/Co	μ_B/Ce	μ_B/O	μ_B (interstice)
V_O1	2.505	0.004	0.355	0.056
V_O2	2.511	0.450	0.168	0.246

predicted that long range ferromagnetic ordering can easily be established with a relatively small V_O density in the Co:CeO_2 system, as reported in recent experiments.

References

[1] Steele B C H 1984 *Solid State Ion.* **12** 391
[2] Mogensen M, Sammes N M and Tompsett G A 2000 *Solid State Ion.* **129** 63
[3] Tye L, Elmasry N A, Chikyow T, McLarty P and Bedairet S 1994 *Appl. Phys. Lett.* **65** 3081
[4] Yoshimoto M, Nagata H, Tsukahara T and Koinuma H 1990 *Japan. J. Appl. Phys.* **29** L1199
[5] Inoue T, Yamamoto Y, Koyama S, Suzuki S and Ueda Y 1990 *Appl. Phys. Lett.* **56** 1332
[6] Sundaram K B, Wahid P F and Siskk P J 1992 *Thin Solid Films* **221** 13
[7] Huang D D, Qin F G, Yao Z Y, Ren Z Z, Lin L Y, Gao W B and Ren Q Y 1995 *Appl. Phys. Lett.* **67** 3724
[8] Jones J T, Croke E T, Garland C M, Marsh Q J and McGill T C 1998 *J. Vac. Sci. Technol.* B **16** 2686
[9] Tiwari A, Bhosle V M, Ramachandran S, Sudhakar N, Narayan J, Budak S and Gupta A 2006 *Appl. Phys. Lett.* **88** 142511
[10] Moodera J S, Hao X, Gibson A G and Meservey R 1988 *Phys. Rev. Lett.* **61** 637
[11] Worledge D C and Geballe T H 2000 *J. Appl. Phys.* **88** 5277
[12] Vodungbo B, Zheng Y, Vidal F, Demaille D, Etgens V H and Mosca D H 2007 *Appl. Phys. Lett.* **90** 062510
[13] Fernandes V, Klein J J, Mattoso N, Mosca D H, Silveira E, Ribeiro E, Schreiner W H, Varalda J and Oliveira A J A 2007 *Phys. Rev.* B **75** 121304(R)
[14] Song Y Q, Zhang H W, Wen Q Y, Zhu H and Xiao J Q 2007 *J. Appl. Phys.* **102** 043912
[15] Wen Q Y, Zhang H W, Song Y Q, Yang Q H, Zhu H and Xiao J Q 2007 *J. Phys.: Condens. Matter* **19** 246205
[16] Trovarelli A 1996 *Catal. Rev.-Sci. Eng.* **38** 439
[17] Vinokurov I, Zonn Z and Ioffe V 1968 *Sov. Phys.—Solid State* **9** 2659
[18] Sluiter M H F, Kawazoe Y, Sharma P, Inoue A, Raju A R, Rout C and Waghmare U V 2005 *Phys. Rev. Lett.* **94** 187204
[19] Chanier T, Sargolzaei M, Opahle I, Hayn R and Koepernik K 2006 *Phys. Rev.* B **73** 134418
[20] Hu S J, Yan S S, Lin X L, Yao X X, Chen Y X, Liu G L and Mei L M 2007 *Appl. Phys. Lett.* **91** 262514
[21] Wuilloud E, Delley B, Schneider W D and Baer Y 1984 *Phys. Rev. Lett.* **53** 202
[22] Perdew J P, Burke K and Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865
[23] Fabris S, de Gironcoli S, Baroni S, Vicario G and Balducci G 2005 *Phys. Rev.* B **72** 237102
[24] Da Silva J L F, Ganduglia-Pirovano M V, Sauer J, Bayer V and Kresse G 2007 *Phys. Rev.* B **75** 045121
[25] Da Silva J L F 2007 *Phys. Rev.* B **76** 193108
[26] Duclos S J, Vohra Y K, Ruoff A L, Jayaraman A and Espinosa G P 1988 *Phys. Rev.* B **38** 7755
[27] Koelling D D, Boring A M and Wood J H 1983 *Solid State Commun.* **47** 227
[28] Adachi G and Imanaka N 1998 *Chem. Rev.* **98** 1479
[29] Kantorovich L N, Holender J M and Gillan M J 1997 *Surf. Sci.* **343** 221
[30] Tiwari A, Bhosle V M, Ramachandran S, Sudhakar N, Narayan J, Budak S and Gupta A 2006 *Appl. Phys. Lett.* **88** 142511
[31] Fernandes V, Klein J J, Mattoso N, Mosca D H, Silveira E, Ribeiro E, Schreiner W H, Varalda J and de Oliveira A J 2007 *Phys. Rev.* B **75** 121304(R)
[32] Vodungbo B, Zheng Y, Vidal F, Demaille D, Etgens V H and Mosca D H 2007 *Appl. Phys. Lett.* **90** 062510