

# Magnetism of CoO polymorphs: Density functional theory and Monte Carlo simulations

Thomas Archer, Ruairi Hanafin, and Stefano Sanvito  
*School of Physics and CRANN, Trinity College, Dublin 2, Ireland*  
 (Received 20 May 2008; published 30 July 2008)

A microscopic explanation for the room temperature ferromagnetism in diluted ZnO:Co is at present rather elusive. Although standard secondary phases can usually be ruled out, it is less clear whether regions with high Co concentration coexist with undoped portions of the film, i.e., whether some form of CoO polymorph can be responsible for the magnetic signal. Since x ray usually excludes the presence of the native rocksalt phase, the study of CoO polymorphs becomes particularly interesting. In this work we investigate theoretically the magnetism of CoO in both the wurtzite and zincblende phases. By using a combination of density functional theory with the LDA+ $U$  approximation and Monte Carlo simulations, we demonstrate that wurtzite and zincblende CoO have a complex frustrated antiferromagnetic ground state with no net magnetic moment in the bulk. Most importantly the estimated critical temperatures are well below room temperature for both cases. This suggests that bulk CoO polymorphs are not responsible for the room temperature magnetism observed for ZnO:Co, although the role of clusters with uncompensated spins or arranged in a spinodal decomposed structure still remains an open question.

DOI: [10.1103/PhysRevB.78.014431](https://doi.org/10.1103/PhysRevB.78.014431)

PACS number(s): 75.50.Pp, 75.10.Hk, 75.30.Hx, 71.20.Nr

## I. INTRODUCTION

Diluted magnetic semiconductors (DMS) (Ref. 1) are a new class of materials in which ordinary semiconductors are doped with transition metal ions, whose spins align in a ferromagnetic ground state. Their remarkable properties, in particular the interplay between ferromagnetism and free carriers, promise a generation of novel electronic devices based on the spin degree of freedom.<sup>2</sup> Unfortunately after almost a decade of research the Curie temperature ( $T_C$ ) of GaAs:Mn, the most studied among all the DMS, is still at around 170 K (Ref. 3) and it is not clear whether it will ever be possible to overcome all the limiting material issues.<sup>4</sup> It is therefore understandable that the magnetic community became excited by the announcement of room temperature ferromagnetism (RTF) in ZnO:Co.<sup>5</sup>

ZnO is transparent, conducting,<sup>6</sup> and piezoelectric.<sup>7</sup> If ferromagnetism is also demonstrated, this will be the ultimate multifunctional material. Unfortunately, in contrast to GaAs:Mn, the phenomenology associated with ZnO:Co is extremely vast and often contradictory. Several models have been proposed to explain the experimentally observed RTF including: the donor impurity band exchange,<sup>8</sup> surface mediated magnetism,<sup>9</sup> Co/oxygen vacancy pair magnetism,<sup>10</sup> and uncompensated antiferromagnetic nanoclusters.<sup>11</sup>

In general it is often difficult to exclude the presence of secondary phases, and indeed metallic Co clusters are often identified in thin films.<sup>12</sup> It is even more difficult to exclude the presence of high Co density regions. In these, the concentration of transition metals can exceed the percolation limit resulting in magnetism, as recently demonstrated for ZnTe:Cr.<sup>13</sup> This result was then extrapolated to ZnO:Co, and uncompensated spins at the surface of hypothetical CoO antiferromagnetic clusters were proposed as the source of the observed room temperature magnetism.<sup>11</sup> Therefore, as wurtzite (WZ) CoO can be considered the end member of the  $\text{Zn}_{1-x}\text{Co}_x\text{O}$  alloy, the study of its magnetic properties becomes of paramount importance. In this work we investigate the magnetic state of various CoO polymorphs, including

rocksalt (RS), zincblende (ZB), and WZ, and conclude that these phases cannot support any room temperature magnetic order in the bulk. Our results relate directly to the many bulk CoO polymorphs, which have been already experimentally synthesized but for which the magnetic characterization is still scarce. They also exclude bulk CoO as the source of magnetism in ZnO:Co, although the cluster hypothesis with uncompensated spins at the surface of the clusters remains still an open question.

## II. COMPUTATIONAL DETAILS

In this work we use a combination of density functional theory (DFT) and Monte Carlo (MC) simulations to investigate both the ground state and the magnetic critical temperature  $T_C$  of CoO polymorphs. Importantly we go beyond the simple local density approximation (LDA) and use the LDA+ $U$  scheme in the Czyzyk-Sawatzky form<sup>14</sup> as implemented<sup>15</sup> in the pseudopotential code SIESTA.<sup>16</sup> As a test of our scheme we have also carried out calculations with the rotationally invariant form of the LDA+ $U$  functional proposed in Ref. 17. This yields only tiny differences in the total energy differences for the cubic phase, and it was not employed for the other polymorphs. The empirical Coulomb  $U$  and exchange  $J$  parameters are chosen to be  $U=5$  eV and  $J=1$  eV. These values reproduce the lattice constant of RS CoO in the ground state structure. Our  $U$  and  $J$  values are also in good agreement with previously determined values from constrained DFT.<sup>18</sup> In all our calculations we used norm-conserving Troullier-Martins' pseudopotentials<sup>19</sup> with nonlinear core corrections<sup>20</sup> and a real-space regular grid with a grid spacing equivalent to a plane-wave cutoff of 800 Ry. Reciprocal space integration was performed on a grid with an equivalent real-space distance of 20 Å. We relaxed all structures until the forces and pressure were smaller than 0.005 eV/Å and 5 kbar, respectively. The spin-orbit interaction is not included in our calculations, since it causes only tiny corrections to the total energy. The largest corrections are expected for the WZ structure for which electron para-

TABLE I. Summary of the calculated structural and magnetic properties for the various CoO polymorphs:  $a$ ,  $c$  (in Å), and  $u$  (fractional) are the lattice constants,  $V$  is the volume per formula unit (in Å<sup>3</sup>),  $E_0$  (in meV) is the Heisenberg energy of the paramagnetic phase,  $J_n$  (in meV) are the exchange constants, and  $T_C$  (in K) is the critical temperature calculated from the specific heat.

	$a$	$c$	$u$	$V$ (Å <sup>3</sup> )	$E_0$	$J_1$	$J_2$	$J_3$	$J_4$	$T_C$
RS	4.260	–	–	19.32	0	1.5	–12.2	–	–	210
WZ	3.244	5.203	0.416	23.71	200.6	6.1	–36.7	–0.2	–5.2	160
WZ*	3.476	4.292	0.500	22.05	120.6	0.0	–55.2	–0.8	–24	100
ZB	3.245	–	–	23.83	313.2	–5.0	0.7	0.6	–2.0	55

magnetic resonance (EPR) measurements of isolated Co ions within the ZnO lattice produce a zero-field split of  $D = 2.76 \text{ cm}^{-1}$ .<sup>21</sup>

Supercells were constructed for the RS, WZ, and ZB structures, containing 32, 48, and 36 atoms, respectively. For each polymorph 62 total energy calculations were performed for randomly assigned collinear spin configurations. We then mapped the DFT energy onto the classical Heisenberg Hamiltonian

$$H_H = E_0 - \frac{1}{2} \sum_{ij} J_{r_{ij}} \vec{S}_i \cdot \vec{S}_j, \quad (1)$$

where  $J_{r_{ij}}$  is the Heisenberg exchange constant,  $\vec{S}_i$  the classical spin associated to the  $i$ -th site ( $|\vec{S}_i| = 3/2$  for CoO), and  $E_0$  the energy of the corresponding paramagnetic phase. We prefer the simple use of collinear configurations over the more standard noncollinear scheme based on the magnetic force theorem,<sup>22</sup> since we do not possess any *a priori* information on the nature of the ground state of the various polymorphs. We then estimated the error in our computed critical temperatures by comparing the calculated Néel temperature for RS CoO with the experimental one and by transferring such an error to the other polymorphs.

The effective Hamiltonian  $H_H$  was then used in our MC simulations to determine the ground state and  $T_C$ . In the case of WZ CoO we also included a uniaxial anisotropy term setting a hard axis along the WZ  $c$  axis, with the value for the zero-field split taken from EPR measurements  $D = 2.76 \text{ cm}^{-1}$ .<sup>21</sup> Thus the final Hamiltonian used for the MC simulations is

$$H_H = E_0 - \frac{1}{2} \sum_{ij} J_{r_{ij}} \vec{S}_i \cdot \vec{S}_j + \sum_i D (\vec{S}_i \cdot \hat{n})^2, \quad (2)$$

where  $\hat{n}$  is a unit vector along the WZ  $c$  axis. Spins were reoriented using the standard Metropolis algorithm. The acceptance probability of a new state is 1 if the new configuration has a lower energy. Otherwise it is given by the Boltzmann distribution  $e^{-\Delta E/k_B T}$ ,<sup>23</sup> where  $\Delta E$  is the energy difference between the old and the new configurations. Each system was first equilibrated at a given temperature, then the specific heat and Binder cumulants were calculated over several million MC steps. These were used to extract  $T_C$ . Simulations were performed with lattices containing 512 and 1000 Co atoms with periodic boundary conditions.

### III. ROCKSALT COBALT OXIDE

We begin our analysis by investigating RS CoO, since both its structure and magnetic properties are experimentally very well established. This represents a good test for our computational scheme, and it will also give us the opportunity of estimating its likely uncertainty. RS CoO is a type-II antiferromagnet (AFII) below the Néel temperature  $T_N = 287 \text{ K}$ . In this magnetic configuration ferromagnetic planes align antiferromagnetically along the [111] direction.<sup>24</sup> Our calculated lattice parameters are reported in Table I and agree by construction with previously published experimental data.<sup>25</sup> The calculated densities of states (DOS) are shown in Fig. 1. The valence band is a hybrid band formed from the O- $p$  and the Co- $d$  orbitals, while the conduction band is of purely  $d$  in character. This places the material on the Zaanen-Sawatzky-Allen<sup>26</sup> diagram between charge transfer and Mott-Hubbard insulators, as reported by several other calculations.<sup>18</sup> The Mulliken populations for the Co- $d$  orbitals return a magnetic moment of  $2.77 \mu_B$  with no contributions from O, in good agreement with the 2+ oxidation state.

The exchange constants  $J_n$  are presented next (Table I). We find that the first and second nearest-neighbor constants  $J_1$  and  $J_2$  are sufficient to reproduce the DFT total energies with a standard deviation of less than 3 meV/Co. This corresponds to about 3% of the total magnetic energy of the

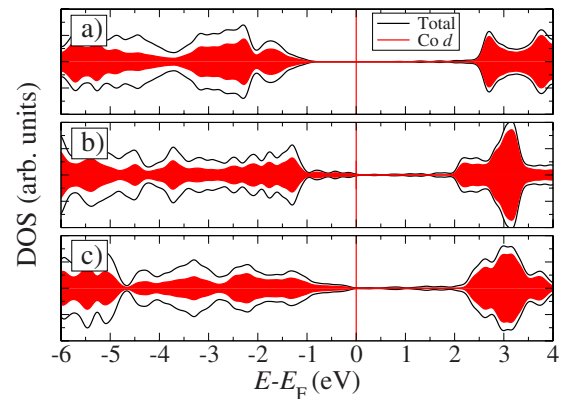


FIG. 1. (Color online) Projected densities of states for (a) rock-salt, (b) wurtzite, and (c) zinc blende CoO. The antiferromagnetic configurations used are type-II for the RS phase,  $c$ -type for WZ and antiferromagnetic with alternating ferromagnetic planes along the [100] direction for the ZB.

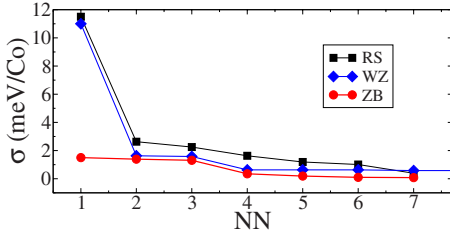


FIG. 2. (Color online) Standard deviation  $\sigma$  for the fit of the calculated DFT total energies onto the Heisenberg Hamiltonian as a function of the number of nearest neighbors (NN) included in the model.

AFII structure (see Fig. 2). The MC calculated specific heat,  $C$ , as a function of temperature, is presented in Fig. 3. A clear peak is observed, indicating that the Néel temperature is  $T_N \sim 210$  K. This also agrees with the value calculated by using the Binder cumulants and scaling theory, but it is 30% lower than the experimental  $T_N = 287$  K.<sup>24</sup> Considering the various approximations introduced in our scheme, such as collinearity and the possible errors originating from the exchange and correlation functional, we regard this value as satisfactory. Moreover, since 2+ oxidation state for Co is also observed for the WZ and ZB polymorphs, one can expect a similar underestimation of  $T_C$  ( $\sim 30\%$ ).

#### IV. WURTZITE COBALT OXIDE

We now consider the WZ phase. Since this is the same lattice structure of ZnO, WZ CoO is the most likely candidate as secondary phase in ZnO:Co. Although WZ CoO was first grown in the early 1960s (Ref. 27) and can now be synthesized by several groups,<sup>28–30</sup> relatively little is known about its electronic and magnetic properties. Risbud *et al.*<sup>28</sup> found no ferromagnetism, but confirmed the presence of rather strong magnetic coupling between the Co ions. DFT-LDA calculations by the same authors indicate that the ferromagnetic state has lower energy than the nonmagnetic one, although it is not necessarily the ground state. In fact a later study by Han *et al.*<sup>31</sup> demonstrated that the ferromagnetic ground state is higher in energy than a magnetic configura-

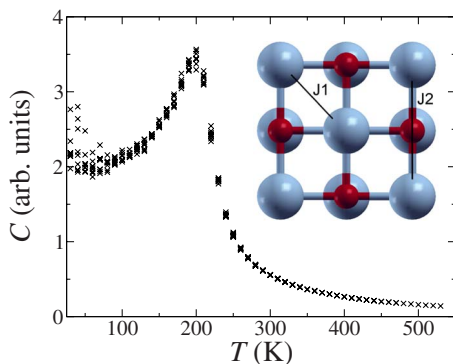


FIG. 3. (Color online) Monte Carlo calculated specific heat for cubic CoO. Note a rather sharp peak at  $T \sim 210$  K that we associate with the Néel temperature  $T_N$ . In the inset we present the RS CoO cell and indicate the various  $J$  constants.

tion in which ferromagnetic  $a, b$  planes align antiferromagnetically along the WZ  $c$  axis ( $c$ -type antiferromagnetic). Whether or not this is the ground state is unknown.

For the calculations of the WZ phase we use the experimental lattice parameters measured by Risbud *et al.*<sup>28</sup> ( $a = 3.244$  Å,  $c = 5.203$  Å, and  $u = 0.416$ ), which give a small pressure (18 kbar) and forces ( $< 0.005$  eV/Å). The calculated paramagnetic energy per formula unit  $E_0$  is 200.6 meV higher than that of the RS structure. This is obtained at a considerably larger volume (19.32 Å<sup>3</sup> for RS, 23.71 Å<sup>3</sup> for WZ), suggesting that the WZ polymorph will not form at equilibrium in the bulk. However, these are not large energy differences and one expects that the WZ phase can indeed be stabilized in thin films or when alloying with ZnO.

Interestingly the structure proposed by Risbud *et al.*<sup>28</sup> does not appear to be a stable phase in DFT. Conjugate gradient relaxation moves the oxygen atoms along the  $c$  axis so that they lie in the same plane as Co ( $u \rightarrow 0.5$ ). For such a distorted phase (denoted as WZ\*)  $E_0$  is 80 meV lower than that of the experimental WZ phase and thus only 120 meV higher than that of the RS. WZ\* has a volume slightly smaller than that of undistorted WZ, although still substantially larger than that of the naturally occurring RS. Interestingly the  $c$  axis in WZ\* is considerably compressed, and the  $a$  and  $b$  axes are expanded with respect to the WZ phase. This distortion lowers the cell volume and increases the Co-O coordination number from 4 to 5. Since such a highly distorted phase has never been observed experimentally, we believe it may merely be an intermediary state in the transition from WZ to RS. This is supported by experimental evidence that the WZ polymorph is metastable and reverts back to the RS when annealed.<sup>29</sup> Interestingly this fivefold coordinated structure has been previously predicted by DFT calculations for MgO,<sup>32</sup> when forced into a WZ crystal phase. Notably the energy difference between the RS and the WZ phases in the case of CoO is considerably lower than in the case of MgO, explaining why WZ CoO was synthesized, while WZ MgO was not.

WZ CoO shows a similar electronic structure to that of RS with considerable O- $p$ /Co- $d$  hybridization in the valence band (Fig. 1). In this case the Mulliken populations of the Co  $d$  orbitals are found to be 4.76 and 2.12 for the majority and minority spins, respectively. The oxygen atoms carry no magnetic moment so a total Mulliken magnetic moment of  $2.64 \mu_B$  is observed, consistent with the 2+ valence state. In the case of WZ CoO (both WZ and WZ\*) four  $J$  constants are sufficient to yield a standard deviation of less than 1 meV/Co (see Fig. 2).

The dominant interaction in WZ CoO is a strong nearest-neighbor antiferromagnetic coupling in the  $\{001\}$  planes, leading to a Néel frustrated state, in which adjacent spins in the planar triangular lattice are rotated by  $120^\circ$  with respect to each other. Along the  $c$  axis the interaction is ferromagnetic between nearest-neighbor planes and antiferromagnetic between second nearest neighbor, resulting in an overall ferromagnetic coupling between the  $\{001\}$  planes.  $C(T)$  for WZ CoO is presented in Fig. 4, from which we can estimate a critical temperature of about 160 K. A similar analysis for the WZ\* phase gives  $T_C = 100$  K. Assuming that the error found for the RS phase is transferable to WZ CoO, we obtain criti-

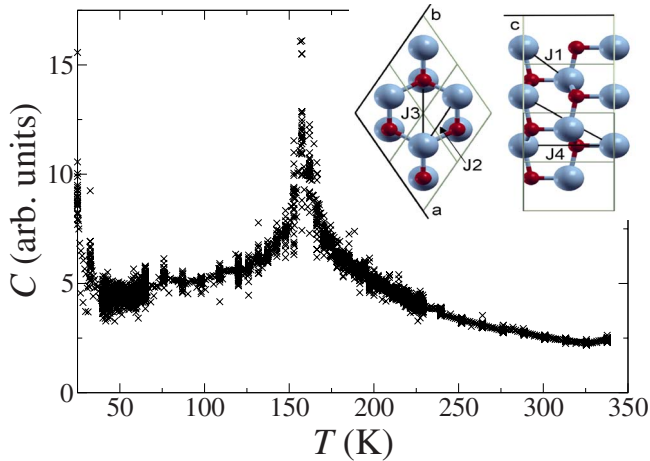


FIG. 4. (Color online) Monte Carlo calculated specific heat for wurtzite CoO. Note a rather sharp peak at  $T \sim 160$  K that we associate with the magnetic critical temperature. In the inset we present the WZ CoO cell and indicate the various  $J$  constants.

cal temperatures in the range of 100–200 K. These are well below room temperature and suggest that bulk WZ CoO cannot be responsible for the room temperature magnetic signal often found in ZnO:Co.

## V. ZINC BLENDE COBALT OXIDE

Finally we consider ZB CoO. This has been discovered experimentally during the synthesis of WZ CoO that is indeed always accompanied by the formation of the ZB phase.<sup>28</sup> The ZB structure is now structurally characterized,<sup>33</sup> although no information is available about its magnetic state. For the purpose of comparing the atomic and electronic structures, we set the spin configuration of the ZB cell to have ferromagnetic planes arranged in an antiferromagnetic stack along the  $[100]$  direction. Our relaxed structure has a lattice parameter of 3.245 Å, which compares well with the experimental value of 3.230 Å.<sup>33</sup> Similar to the other polymorphs, ZB CoO shows a strong O- $p$ /Co- $d$  hybridization in the valence band (Fig. 1), and the Mulliken magnetic moment is around  $3 \mu_B$  ( $2.74 \mu_B$  with a Co  $d$  Mulliken occupation of 4.77 and 2.03 for the majority and minority spins, respectively). The ZB phase is found to be the least stable phase among all the CoO polymorphs studied, with  $E_0 = 313.2$  meV. At equilibrium the volume is essentially identical to that of WZ, and the energy difference between the ZB and WZ phases is small, supporting the experimentally observed coexistence of the WZ and ZB phases.<sup>28</sup>

The first four  $J_s$  already describe accurately the total magnetic energy of the ZB phase with a standard deviation of less than 1 meV/Co. We find that in the case of ZB CoO the

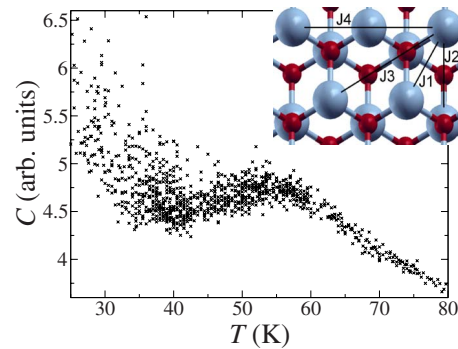


FIG. 5. (Color online) Monte Carlo calculated specific heat for zincblende CoO. Note a rather diffused peak at  $T \sim 55$  K that we associate with the magnetic critical temperature. In the inset we present the ZB CoO cell and indicate the various  $J$  constants.

first nearest-neighbor interaction is by far the largest and accounts for most of the magnetic energy. This however is considerably lower than the dominant  $J$  for both the WZ and the RS phases, and one expects a considerably lower critical temperature. This is confirmed by our MC simulations (Fig. 5), which give us  $T_C = 55$  K. Importantly  $J_1$  is antiferromagnetic leading to three-dimensional frustration, evident in the rather diffused peak in  $C(T)$ .

## VI. CONCLUSIONS

In conclusion a combination of DFT and Monte Carlo methods has been used to calculate the thermodynamic properties of CoO polymorphs in their bulk phases. The scheme was tested first for the RS phase and then applied to both the WZ and ZB structures. Interestingly the ground state of the three polymorphs is rather different. RS CoO has a type-II antiferromagnetic structure, WZ CoO is a two-dimensional frustrated system, and ZB CoO is a three-dimensional frustrated system. In addition a second WZ structure was identified. Crucially, despite these differences, all the polymorphs show critical temperature considerably below room temperature. Although our results are for the bulk phases we expect them to be applicable to the central atoms of a cluster. Therefore bulk CoO clusters in any crystalline phase cannot be the explanation for the experimentally observed room temperature magnetism of diluted ZnO:Co. Whether this can originate from uncompensated spins at the surface of those clusters however cannot be ruled out.

This work is sponsored by Science Foundation of Ireland (07/IN.1/1945). We thank TCHPC and ICHEC for providing computational support.



- <sup>1</sup>T. Dietl, H. Ohno, F. Matsukura, J. Cibert, and D. Ferrand, *Science* **287**, 1019 (2000).
- <sup>2</sup>S. A. Wolf, D. D. Awschalom, R. A. Buhrman, J. M. Daughton, S. von Molnár, M. L. Roukes, A. Y. Chitchekanova, and D. M. Treger, *Science* **294**, 1488 (2001).
- <sup>3</sup>T. Jungwirth *et al.*, *Phys. Rev. B* **72**, 165204 (2005).
- <sup>4</sup>A. H. MacDonald, P. Schiffer, and N. Samarth, *Nat. Mater.* **4**, 195 (2005).
- <sup>5</sup>K. Ueda, H. Tabata, and T. Kawai, *Appl. Phys. Lett.* **79**, 988 (2001).
- <sup>6</sup>Special issue on Transparent Conducting Oxides, edited by D. S. Ginley and C. Bright, *MRS Bull.* **25**, 15 (2000).
- <sup>7</sup>V. E. Wood and A. E. Austin, *Magnetolectric Interaction Phenomena in Crystals* (Gordon and Breach, London, 1975).
- <sup>8</sup>J. M. D. Coey, M. Venkatesan, and C. B. Fitzgerald, *Nat. Mater.* **4**, 173 (2005).
- <sup>9</sup>A. Quesada, M. A. García, M. Andrés, A. Hernando, J. F. Fernández, A. C. Caballero, M. S. Martín-González, and F. Briñones, *J. Appl. Phys.* **100**, 113909 (2006).
- <sup>10</sup>C. D. Pemmaraju, R. Hanafin, T. Archer, H. B. Braun, and S. Sanvito, arXiv:0801.4945v1, *Phys. Rev. B* (to be published).
- <sup>11</sup>T. Dietl, T. Andrearczyk, A. Lipińska, M. Kiecana, M. Tay, and Y. Wu, *Phys. Rev. B* **76**, 155312 (2007).
- <sup>12</sup>J. M. D. Coey, *Curr. Opin. Solid State Mater. Sci.* **10**, 83 (2006).
- <sup>13</sup>S. Kuroda, N. Nishizawa, K. Takita, M. Mitome, Y. Bando, K. Osuch, and T. Dietl, *Nat. Mater.* **6**, 440 (2007).
- <sup>14</sup>M. T. Czyzyk and G. A. Sawatzky, *Phys. Rev. B* **49**, 14211 (1994).
- <sup>15</sup>M. Wierzbowska, D. Sánchez-Portal, and S. Sanvito, *Phys. Rev. B* **70**, 235209 (2004).
- <sup>16</sup>J. M. Soler, E. Artacho, J. D. Gale, A. García, J. Junquera, P. Ordejón, and D. Sánchez-Portal, *J. Phys.: Condens. Matter* **14**, 2745 (2002).
- <sup>17</sup>S. L. Dudarev, G. A. Botton, S. Y. Savrasov, C. J. Humphreys, and A. P. Sutton, *Phys. Rev. B* **57**, 1505 (1998).
- <sup>18</sup>W. E. Pickett, S. C. Erwin, and E. C. Ethridge, *Phys. Rev. B* **58**, 1201 (1998).
- <sup>19</sup>N. Troullier and J. L. Martins, *Phys. Rev. B* **43**, 8861 (1991).
- <sup>20</sup>J. Zhu, X. W. Wang, and S. G. Louie, *Phys. Rev. B* **45**, 8887 (1992).
- <sup>21</sup>P. Sati, R. Hayn, R. Kuzian, S. Régnier, S. Schäfer, A. Stepanov, C. Morhain, C. Deparis, M. Lüigt, M. Goiran, and Z. Golacki, *Phys. Rev. Lett.* **96**, 017203 (2006).
- <sup>22</sup>M. Pajda, J. Kudrnovsky, I. Turek, V. Drchal, and P. Bruno, *Phys. Rev. B* **64**, 174402 (2001).
- <sup>23</sup>D. P. Landau and K. Binder, *A Guide to Monte Carlo Simulations in Statistical Physics* (Cambridge University Press, Cambridge, 2000).
- <sup>24</sup>F. B. Lewis and N. H. Saunders, *J. Phys. C* **6**, 2525 (1973).
- <sup>25</sup>W. B. Pearson, *A Handbook of Lattice Spacings and Structures of Metals and Alloys* (Pergamon, New York, 1958).
- <sup>26</sup>J. Zaanen, G. A. Sawatzky, and J. W. Allen, *Phys. Rev. Lett.* **55**, 418 (1985).
- <sup>27</sup>M. J. Redman and E. G. Steward, *Nature (London)* **193**, 867 (1962).
- <sup>28</sup>A. S. Risbud, L. P. Snedeker, M. M. Elcombe, A. K. Cheetham, and R. Seshardi, *Chem. Mater.* **17**, 834 (2005).
- <sup>29</sup>J. F. Liu, S. Yin, H. P. Wu, Y. W. Zeng, X. R. Hu, Y. W. Wang, G. L. Lv, and J. Z. Jiang, *J. Phys. Chem. B* **110**, 21588 (2006).
- <sup>30</sup>R. W. Grimes and K. P. Lagerlöf, *J. Am. Ceram. Soc.* **74**, 270 (1991); J. F. Liu, S. Yin, H. P. Wu, Y. W. Zeng, X. R. Hu, Y. W. Wang, G. L. Lv, and J. Z. Jiang, *J. Phys. Chem. B* **110**, 21588 (2006); K. An, N. Lee, J. Park, S. C. Kim, Y. Hwang, J.-G. Park, J.-Y. Kim, J.-H. Park, M. J. Han, J. Yu, and T. Hyeon, *J. Am. Chem. Soc.* **128**, 9753 (2006).
- <sup>31</sup>M. J. Han and J. Yu, *J. Korean Phys. Soc.* **48**, 1496 (2006).
- <sup>32</sup>S. Limpijumnonng and W. R. L. Lambrecht, *Phys. Rev. B* **63**, 104103 (2001).
- <sup>33</sup>L. P. Snedeker, A. S. Risbud, O. Masala, J. Ping, and R. Seshadri, *Solid State Sci.* **7**, 1500 (2005).