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# Origin of antiferromagnetism in CoO: A density functional theory study

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We have investigated the origin of antiferromagnetism of CoO in the rocksalt structure using spin-polarized density functional theory calculations. We find that in the rocksalt structure, the superexchange interaction between the occupied and unoccupied $e_g$ states plays the dominant role, which leads to an antiferromagnetic ground state, but the system also has a strong direct exchange interaction between the partially occupied minority spin $t_{2g}$ states that leads to the unusual situation that the ferromagnetic phase is more stable than most antiferromagnetic configurations. © *2010 American Institute of Physics*. [doi:10.1063/1.3402772]

Transition-metal oxides such as MnO and CoO have recently attracted much attention[1–9] not only because these materials have many unique structural, electrical, optical, and magnetic properties that are suitable for magneto-optical and magnetoelectrical applications[10,11] but also because they manifest some puzzling phenomena whose physical origins are not fully understood. For example, CoO usually adopts the rocksalt (RS) structure[12] with a space group of $Fm\bar{3}m$, in which $Co^{2+}$ ion ($d^7$) has an octahedral ($O_h$) environment. Under the $O_h$ crystal field, the Co-3$d$ states split into lower triplet $t_{2g}$ and upper doublet $e_g$. Taking into account the spin-exchange splitting, it is expected that in the spin-up channel, both the $t_{2g}$ and $e_g$ states are fully occupied, whereas in the spin-down channel the lower triply degenerate $t_{2g}$ state is 2/3 occupied and the higher doubly degenerate $e_g$ state is empty [Fig. 1(a)]. Thus, based on a general band coupling model,[13–15] one would expect that the ground state of CoO in the RS structure is ferromagnetic (FM) if the level repulsion between the partially occupied $t_{2g}$ states (direct exchange) dominates [Fig. 1(b)]. However, experimentally, it is known that CoO has a type-II antiferromagnetic (AFM-II) spin-ordering at its ground state, in which the magnetic moments on $Co^{2+}$ ions within the same (111) planes are parallel and they are antiparallel to each other between the adjacent (111) planes[16,17] [Fig. 2(b)]. The origin of such AFM ordering, however, is not clear from simple physical considerations.

In this paper, we systematically calculate the magnetic ordering preferences and electronic structure of CoO in the RS structure using the generalized-gradient approximations (GGAs) (Ref. 18) within spin-polarized density functional theory (DFT). To check the validity of our calculations for this strongly correlated system, we have also used the GGA+U approach, in which the Coulomb repulsion parameter U and the local exchange interaction parameter J are applied to describe the localized Co 3$d$ shell.

Our calculations are performed using the VIENNA *AB INITIO SIMULATION PACKAGE*.[19] Convergence with respect to the plane-wave cutoff energy (600 eV) and the Monkhorst–Pack $k$-point mesh in the Brillouin zone[20] are verified. In the GGA+U approach, all calculations are performed with $U=5.1$ eV and $J=1.0$ eV, which are consistent with the values determined by previous studies.[2,21] The calculated equilibrium lattice constant $a$ of the RS structure using GGA+U is 4.27 Å, in good agreement with experimental values of 4.26 Å.[1] For comparison, the GGA calculated lattice constants is 4.23 Å, only slightly smaller than that obtained from GGA+U.

We first discuss our calculated results using GGA. To study the underlying magnetic interactions, we have calculated the total energy of CoO in the FM, AFM-I [a spin (1×1) (001) superlattice], AFM-II, AFM-III [a spin (2×2) (201) superlattice] and AFM-IV [a spin (2×2) (002) superlattice],[22] as shown in Fig. 2. Fitting the calculated total energy to a Heisenberg model of the spin interaction $E(\sigma)=E(0)-\Sigma_{i,j}J_{i,j}\sigma_i\sigma_j$, we can also obtain the effective $n$th fcc nearest neighbor (NN) spin exchange pair interaction param-

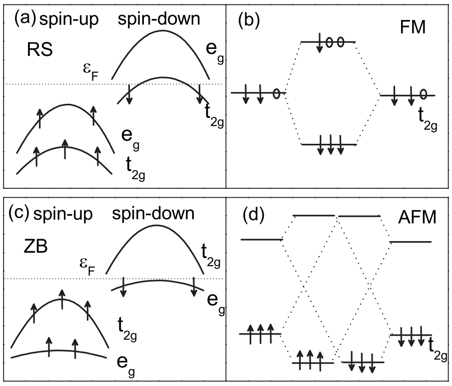

FIG. 1. Schematic plot of the occupation of the crystal field and spin exchange splitted Co $d^7$ states in (a) RS and (c) ZB structures. The energy band coupling of the partially occupied spin-down $t_{2g}$ levels in (b) favors the FM state in the RS phase and the coupling between the occupied and unoccupied $t_{2g}$ levels in (d) favor the AFM state in ZB phase. Coupling between two fully occupied or empty states does not gain energy, thus is not shown in the figure. Coupling between the occupied majority spin states and unoccupied minority spin states which favor the AFM state is also not shown.

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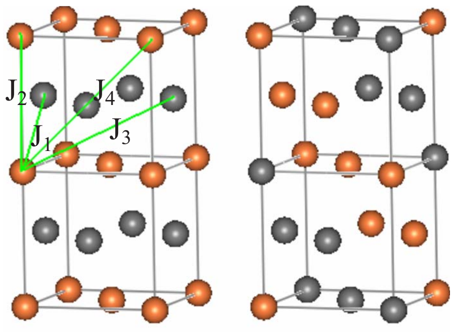
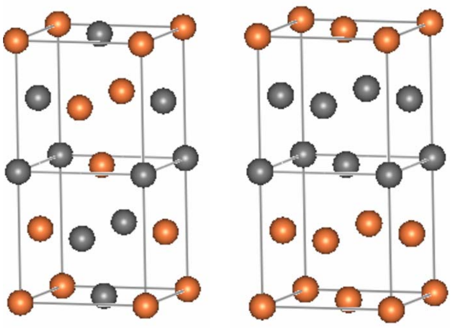


**(a) AFM-I** **(b) AFM-II**



**(c) AFM-III** **(d) AFM-IV**

FIG. 2. (Color online) Spin configurations of Co ion in AFM-I, -II, -III, and -IV states in both RS and ZB phases. Orange and gray balls denote the spin-up and spin-down Co atoms, respectively. For clarity, the anions are not shown. Green lines indicate one of the $n$th($n=1-4$) fcc NNs of the Co atom at the origin.

eters $J_n$ for ($n=1-4$). For the RS phase calculated at $a=4.23$ Å, we find the AFM-II phase has the lowest energy (Table I), in agreement with experiment. However, we also find that the FM phase has lower energy than the other three AFM spin configurations. The fitted exchange interaction parameters (Table II) show that although the next NN magnetic interaction $J_2$ is AFM and dominant, as in many magnetic semiconductors in the RS structure,[22] the NN interaction parameter $J_1$ is also large but FM. This unusual behavior indicates that there is a strong competition between the NN FM interaction caused by the partial occupation of the minority $t_{2g}$ states that has charge toward the (110) direction [Fig. 1(b)] and the next NN AFM interaction caused by the level repulsion between the occupied majority $e_g$ and unoccupied minority $e_g$ states, which have charge directed toward the (100) ligand $O^{2-}$ ions (not shown). The coupling between the occupied majority $t_{2g}$ and partially occupied minority $t_{2g}$ states [similar to that described in Fig. 1(d)] also helps the stabilization of the AFM phase. The anion mediated coupling between $e_g$ states is usually very weak and often neglected in zinc-blende (ZB) systems because there is no direct coupling between the cations in the ZB phase but it is strengthened in the RS phase due to the octahedral bonding networks.

TABLE I. Summary of the calculated magnetic moment $\mu$ (in $\mu_B$) and energy difference between FM and AFM (in eV per f.u.) using GGA and GGA+U for the RS and ZB phases of CoO, respectively.

| | | Magnetic moment | | $\Delta E_{\text{AFM-FM}}$ | |
|---|---|---|---|---|---|
| | | GGA | GGA+U | GGA | GGA+U |
| RS | FM | 2.60 | 2.77 | 0.0 | 0.0 |
| | AFM-I | 2.31 | 2.76 | 0.129 | 0.250 |
| | AFM-II | 2.41 | 2.67 | −0.153 | −0.119 |
| | AFM-III | 2.38 | 2.74 | 0.069 | 0.088 |
| | AFM-IV | 2.44 | 2.72 | 0.015 | 0.085 |
| ZB | FM | 2.40 | 2.73 | −0.253 | 0.073 |
| | AFM-I | 2.12 | 2.66 | −0.307 | −0.003 |
| | AFM-II | 2.20 | 2.67 | −0.306 | 0.010 |
| | AFM-III | 2.10 | 2.65 | −0.348 | −0.009 |
| | AFM-IV | 2.23 | 2.68 | −0.288 | 0.026 |

TABLE II. Calculated spin exchange interaction parameters $\{J_n\}$ (in meV) within GGA and GGA+U for RS and GGA+U for ZB phases of CoO, respectively.

| | Methods | $J_1$ | $J_2$ | $J_3$ | $J_4$ |
|---|---|---|---|---|---|
| RS | GGA | 7.41 | −20.81 | 0.33 | 1.78 |
| RS | GGA+U | 8.00 | −25.54 | 3.81 | 0.07 |
| ZB | GGA+U | −4.56 | −0.50 | −0.09 | −0.34 |

Although the GGA calculated magnetic ordering is consistent with experimental observations, there is some important disagreement between the theory and experiment. Figure 3(a) shows the GGA calculated total (black), Co $t_{2g}$ (red, dark gray) and $e_g$ (green, light gray) electronic density of states (DOS) for CoO in RS phase. We see that all the calculated RS phases are metals but it is known experimentally that CoO is a semiconductor with a charge-transfer insulating band gap.[23] Moreover, we find that in the GGA calculation the calculated total energy of the ground-state ZB phase (Table I) is lower in energy than the ground-state RS AFM-II phase. To trace this discrepancy, we notice that in the GGA calculation the calculated energy separation between the occupied and unoccupied Co $d$ states is underestimated. This underestimation of the separation between occupied and unoccupied states overestimates the AFM coupling in both phases but is more significant for the delocalized $t_{2g}$ state in

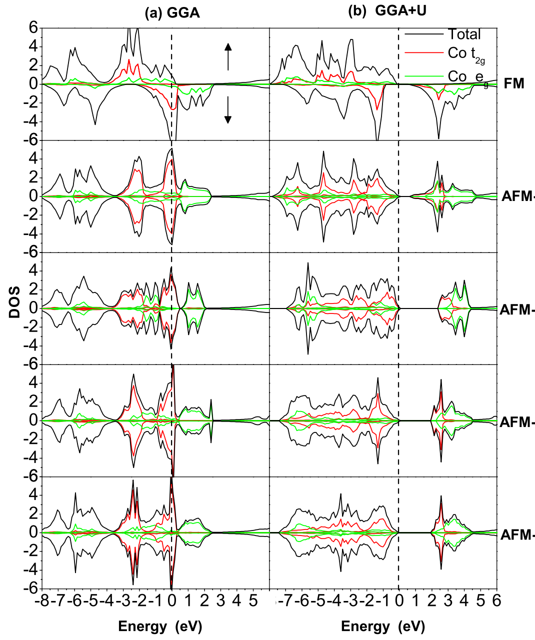


FIG. 3. (Color online) Total (black) and Co $t_{2g}$ (red, dark gray) and $e_g$ (green, light gray) projected DOS for RS CoO with the FM, AFM-I, -II, -III, and -IV spin configurations, respectively. The plots on the left-hand-side is calculated with GGA, whereas the one on the right-hand-side is calculated by GGA+U. The Fermi energy is at zero energy.

the ZB phase (Fig. 1), thus erroneously predicting the ZB AFM phase to be the global ground-state.

To correct for the GGA error, we have performed further GGA+U calculations, with the calculated DOS shown in Fig. 3(b). Indeed, we find that after the correction, CoO in the RS phase becomes a charge transfer insulator. The occupied electronic configuration can be written as $[(t_{2g}\uparrow)^3(e_g\uparrow)^2(t_{2g}\downarrow)^2]$. This results in a magnetic moment close to 3 $\mu_B$ per Co (Table I), as expected. The AFM-II phase has the lowest total energy, which is consistent with the fact that it also has the largest band gap as shown in Fig. 3(b). The fact that in both GGA and GGA+U calculations the magnetic phase stability is unchanged (Table I) indicates that AFM-II ordering is indeed stabilized by the AFM superexchange interaction between the occupied majority and unoccupied minority $e_g$ states.

To test the validity of our calculation, we have also studied the stability of CoO in the ZB phase. It has been shown experimentally that metastable ZB CoO with space group $F\bar{4}3m$ can be formed,[24] in which the $Co^{2+}$ ion ($d^7$) is in a tetrahedral ($T_d$) environment. Under the $T_d$ crystal field, the Co 3*d* states split into lower $e_g$ and upper $t_{2g}$ states, opposite to the order in the RS structure. Taking spin exchange splitting into account, it leads to the full occupation of all the majority spin states and minority spin $e_g$ state,[15] whereas the minority spin $t_{2g}$ state is unfilled [Fig. 1(c)]. Thus, based on a general band coupling model,[13–15] one would expect that the ground state spin-ordering of CoO in the ZB structure is AFM due to the superexchange interaction between occupied and unoccupied $t_{2g}$ states [Fig. 1(d)].

Using GGA+U, we find the calculated lattice constant $a$ for the ZB structures is 4.61 Å, in good agreement with experimental values of 4.55 Å.[24] For the ZB phase calculated at $a=4.61$ Å, the electronic configuration of the occupied states can be written as $[(e_g\uparrow)^2(t_{2g}\uparrow)^3(e_g\downarrow)^2]$. This also leads to a magnetic moment close to 3 $\mu_B$ per Co. We find that, unlike the RS phase, in the ZB phase the AFM states always have lower energy than the FM state. In the ZB phase, AFM-III ordering is the ground state because the AFM phase is stabilized by the anion-mediated AFM coupling of the occupied majority and unoccupied minority $t_{2g}$ states, which have the charge density points toward (110) and equivalent directions, thus gives the dominant NN AFM interaction $J_1$ and a relatively large fourth neighbor interaction, as observed in other ZB magnetic semiconductors.[22] More importantly, we find that after the Coulomb U correction, the RS AFM-II phase has a total energy that is 110 meV lower than the ZB AFM-III phase, in agreement with the experimental observation that the ground state of CoO is the RS AFM-II phase.

In summary, using spin-polarized DFT, we have investigated the origin of the spin-ordering in CoO in the RS, as well as ZB structures. We find that unlike in the ZB structure, where AFM ordering is always more stable than FM ordering, in the RS structure the superexchange interaction between the occupied and unoccupied $e_g$ states plays the dominant role, which leads to the AFM-II ground state, in agreement with experiment. However, the system also has a strong direct exchange interaction between the partially occupied minority spin $t_{2g}$ states, and subsequently, it has the unusual situation that the FM phase is more stable than most of the AFM configurations.

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[1] M. J. Redman and E. G. Steward, Nature (London) **193**, 867 (1962).
[2] T. Archer, R. Hanafin, and S. Sanvito, Phys. Rev. B **78**, 014431 (2008).
[3] J. Zaanen, G. A. Sawatzky, and J. W. Allen, Phys. Rev. Lett. **55**, 418 (1985).
[4] W. A. Harrison, Phys. Rev. B **76**, 054417 (2007).
[5] B. H. Miller and E. Dan Dahlberga, Appl. Phys. Lett. **69**, 3932 (1996).
[6] E. Shipton, K. Chan, T. Hauet, O. Hellwig, and E. E. Fullerton, Appl. Phys. Lett. **95**, 132509 (2009).
[7] W. Zhang, K. Koepernik, M. Richter, and H. Eschrig, Phys. Rev. B **79**, 155123 (2009).
[8] E. Engel and R. N. Schmid, Phys. Rev. Lett. **103**, 036404 (2009).
[9] C. Rödl, F. Fuchs, J. Furthmüller, and F. Bechstedt, Phys. Rev. B **79**, 235114 (2009).
[10] S. Jin, Th. Tiefel, M. McCormarck, R. Fastnacht, and R. Rchen, Science **264**, 413 (1994).
[11] A. J. Millis, Nature (London) **392**, 147 (1998).
[12] C. G. Shull, W. A. Strauser, and O. Wollan, Phys. Rev. **83**, 333 (1951).
[13] G. M. Dalpian, S.-H. Wei, X. G. Gong, A. J. R. da Silva, and A. Fazzio, Solid State Commun. **138**, 353 (2006).
[14] J. M. D. Coey, M. Venkatesan, and C. B. Fitzgerald, Nature Mater. **4**, 173 (2005).
[15] A. Walsh, J. L. F. Da Silva, and S.-H. Wei, Phys. Rev. Lett. **100**, 256401 (2008).
[16] W. L. Roth, Phys. Rev. **110**, 1333 (1958).
[17] U. D. Wdowik and K. Parlinski, Phys. Rev. B **75**, 104306 (2007).
[18] J. P. Perdew and Y. Wang, Phys. Rev. B **33**, 8800 (1986).
[19] G. Kresse and J. Hafner, Phys. Rev. B **47**, R558 (1993); **48**, 13115 (1993).
[20] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).
[21] W. E. Pickett, S. C. Erwin, and E. C. Ethridge, Phys. Rev. B **58**, 1201 (1998).
[22] S.-H. Wei and A. Zunger, Phys. Rev. B **48**, 6111 (1993).
[23] Z.-X. Shen, J. W. Allen, P. A. P. Lindberg, D. S. Dessau, B. O. Wells, A. Borg, W. Ellis, J. S. Kang, S.-J. Oh, I. Lindau, and W. E. Spicer, Phys. Rev. B **42**, 1817 (1990).
[24] Y. C. Sui, Y. Zhao, J. Zhang, S. Jaswal, X. Z. Li, and D. J. Sellmyer, IEEE Trans. Magn. **43**, 3115 (2007).