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Nitrogen induced ferromagnetism in Cobalt doped BaTiO₃

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The electronic structure and magnetism of Cobalt doped BaTiO₃ (BaTi_{1-x}Co_xO₃) is investigated. Substitutional Nitrogen on an Oxygen site is found to play an important role in inducing net magnetic moments in the system. The presence of a Nitrogen atom as nearest neighbour to a Cobalt atom is crucial in producing spin splitting of both the Nitrogen and Cobalt states thereby introducing a net local magnetic moment. The introduction of Nitrogen is further found to enhance ferromagnetic interactions between Cobalt atoms. Copyright 2012 Author(s). This article is distributed under a Creative Commons Attribution 3.0 Unported License. [<http://dx.doi.org/10.1063/1.4747820>]

Over the past decade considerable interests have evolved around dilute magnetic semiconductors, as these materials seemed promising candidates for device applications. Ever since the discovery of ferromagnetism in p-type Mn-doped IV-VI,¹ III-V^{2,3} and II-VI⁴ a lot of scientific efforts were driven towards the discovery and design of multifunctional materials that combine the functionalities of both semiconductors and magnetic transition as well as rare-earth metal ions.⁵ There has also been an extensive effort to increase the Curie temperature of these systems by various means such as doping⁶ as well as to look for new candidates for high T_c ferromagnetism. Although there have been various reports of dilute magnetic semiconductors, it is only recently that experimental works have been devoted towards transitional metal doped insulators. Of particular interest have been perovskite oxides such as BaTiO₃ and SrTiO₃ which exhibit a wide range of interesting properties, by themselves, such as ferroelectricity⁷ and superconductivity.⁸

First principles calculations of transition metal doped BaTiO₃ have been previously performed by Nakayama *et al.*⁹ They reported the stabilization of a nonmagnetic state in Co doped BaTiO₃ and attributed the reason to the hybridization of the Co *d* and Oxygen *p* states. In later experimental reports,¹⁰ however, ferromagnetism in Co doped BaTiO₃ was observed. Lin *et al.* did not observe the formation of Co clusters and attributed the origin of ferromagnetism to defects such as Oxygen vacancies.

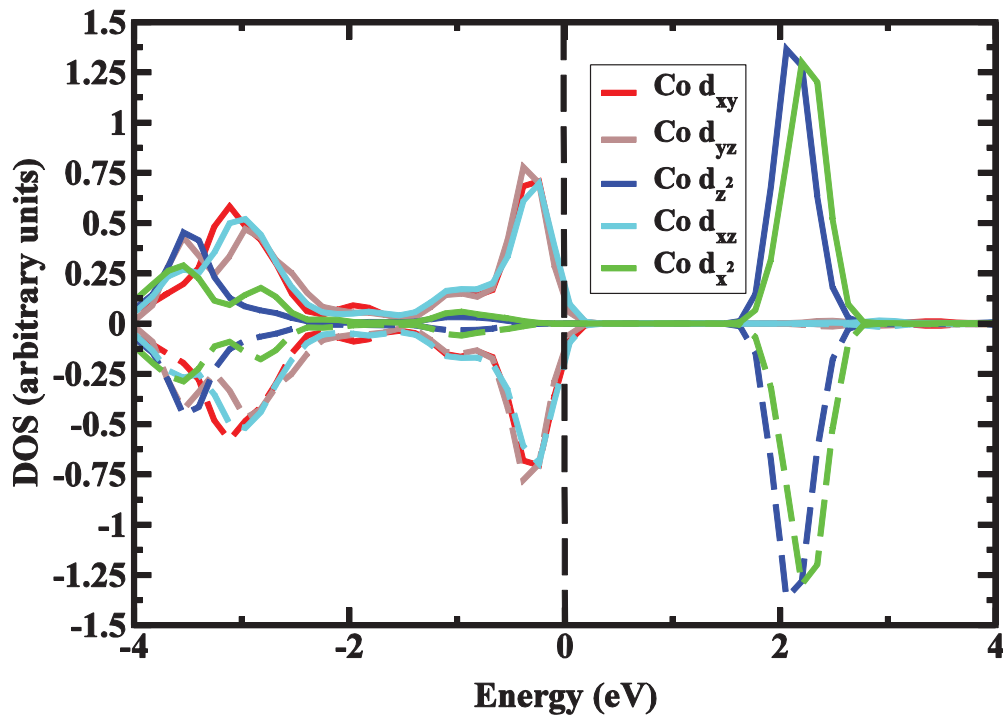
The purpose of the present work is to design Co doped BaTiO₃ in a way so as to enhance ferromagnetism in this system. We thereby propose the introduction of substitutional Nitrogen on Oxygen sites as promising candidates.

In this work we perform first principles calculations to show that changes in the local chemical environment as well as the local lattice relaxation, results in the modification of the electronic structure of the Co states which in turn gives rise to a net local magnetic moment. Furthermore a ferromagnetic coupling between Co atoms is also favored in the presence of an intermediate N atom.

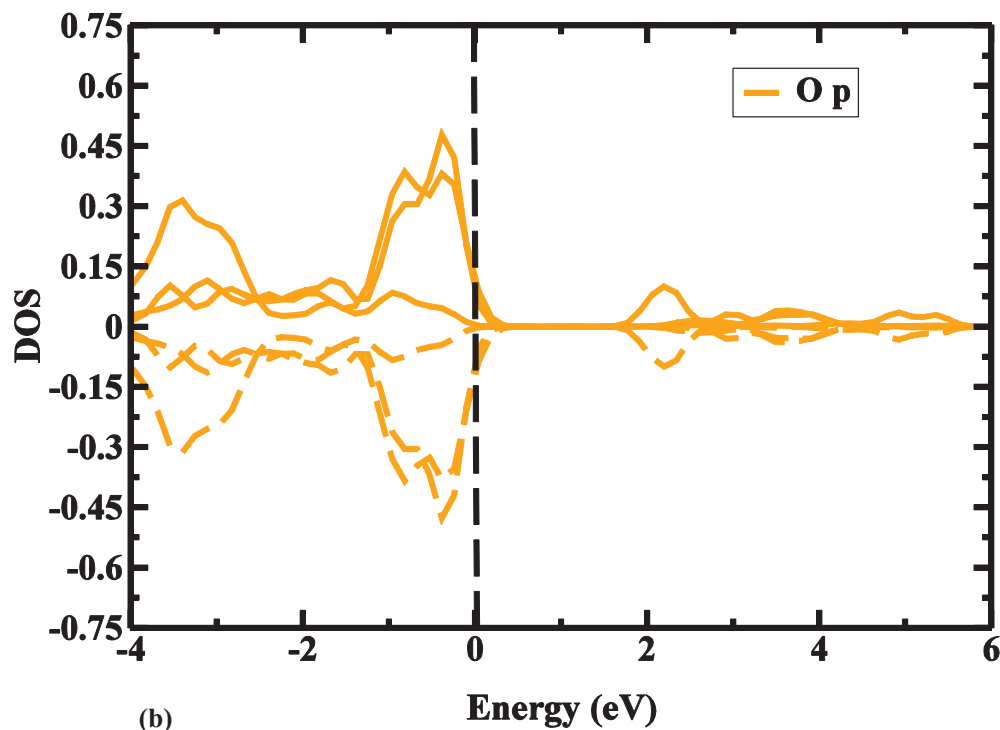
All calculations have been done using the Vienna Ab-initio Simulation Package (VASP) code.¹¹ We use projector augmented wave pseudopotentials.¹² For Ba and Ti, 5s² 5p⁶ 6s² and 3s² 3p⁶ 4s² 3d² are included as valence electrons respectively. For Co 4s² 3d⁷ have been included as valence electrons. A plane wave cut off energy of 600 eV is used and a 4x4x4 Monkhorst-Pack special k-point grid¹³ is chosen for integration over the Brillouin zone. All structural relaxations are performed keeping the lattice constant of cubic BaTiO₃ fixed, which is taken to be the experimental value of (3.995 Å). We allow the internal atomic coordinates to relax. The energies are converged to within

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(a)



(b)

FIG. 1. (a) Spin resolved DOS of Cobalt in cubic BaTiO₃. (b) Spin resolved DOS of a neighboring Oxygen atom. The Co atom is represented by the blue sphere.

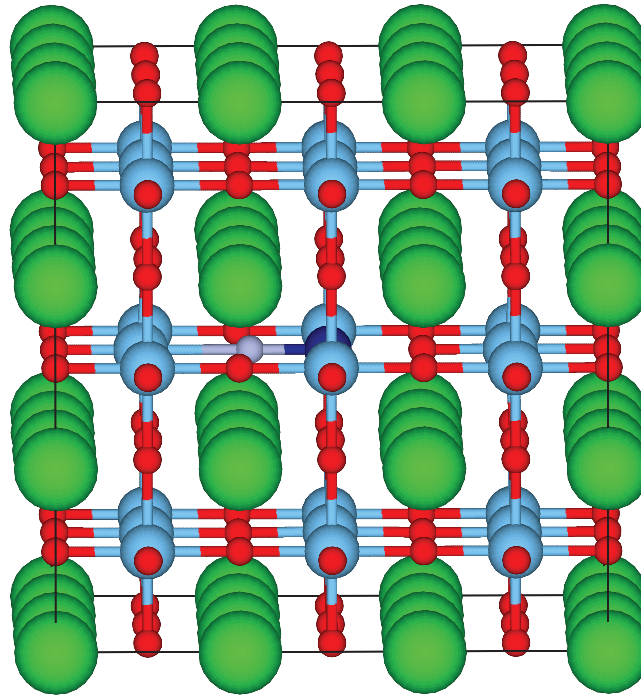


FIG. 2. Supercell structure of a Nitrogen as nearest neighbor to Cobalt in BaTiO_3 . The Nitrogen atom is represented by the grey sphere.

10^{-6} eV/cell. All forces are converged to within 0.004 eV/Å. In order to model $\text{BaTi}_{1-x}\text{Co}_x\text{O}_3$ we choose a $3 \times 3 \times 3$ cubic supercell of BaTiO_3 where the Co atom is substituted on a Ti site.

In order to study correlation effects of d electrons on Co, we add an onsite Colomn correlation parameter, U , on the d electrons. Here we employ the LSDA+ U formalism as introduced by Dudarev *et al.*¹⁴ For Co atom the U parameter is chosen according to Reference 15 where this parameter has been extracted from photoemission data of Co metal. An effective U ($U-J$) value of 4 eV has been used for all the calculations.

We first study the electronic structure of a single Co atom doped in a 135 atom supercell of BTO. This corresponds to a Co concentration of 3.7%. We find that Co maintains a cubic symmetry with all the octahedrally coordinated Oxygen atoms sitting at equal distances from the Co atom. In Fig. 1(a) we show the spin resolved orbital projected density of states (DOS) of Co. Triply degenerate t_{2g} and doubly degenerate e_g orbitals are seen which is to be expected and the system is metallic. There is no spin splitting and the system is found to be non-magnetic. We also find that the O p's hybridize with the Co d states in agreement to previous work⁹ (Fig. 1(b)).

We then introduce a second Co atom in order to study the magnetic interaction between two Co atoms. We introduce the second Co atom as first and second nearest neighbors in order to study the magnetic interaction as a function of distance between the Co atoms. For each Co-Co inter atomic distance we compare the energies between a ferromagnetic and an anti-ferromagnetic configuration. We find that in the absence of any defect the nearest neighbor Co atoms move slightly close to each other by an amount 0.05 Å compared to the ideal structure. Furthermore the the antiferromagnetic configuration is found to be favored over the ferromagnetic configuration by an amount of 0.16 eV. This is in accordance with the Goodenough-Kanamori-Anderson rule¹⁸⁻²⁰ where a superexchange antiferromagnetic interaction takes place for a 180° cation-anion-cation bridge when a virtual electron transfer takes place between two half-filled (or empty orbitals). As second nearest neighbors the Co atoms show negligible interaction as both the ferromagnetic and antiferromagnetic configurations are found to be almost degenerate. This suggests the presence of

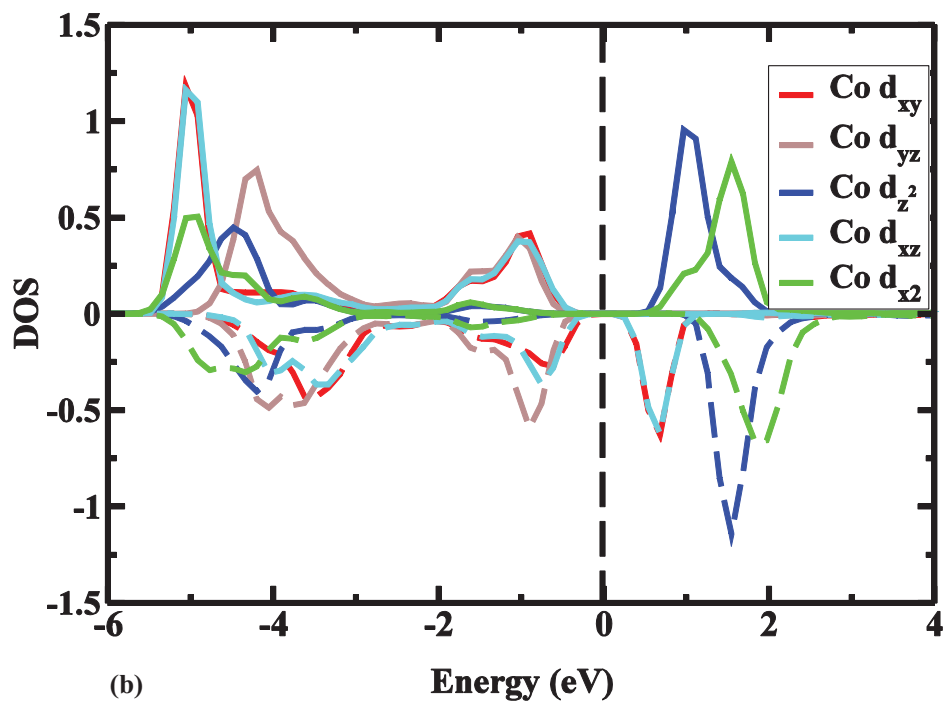
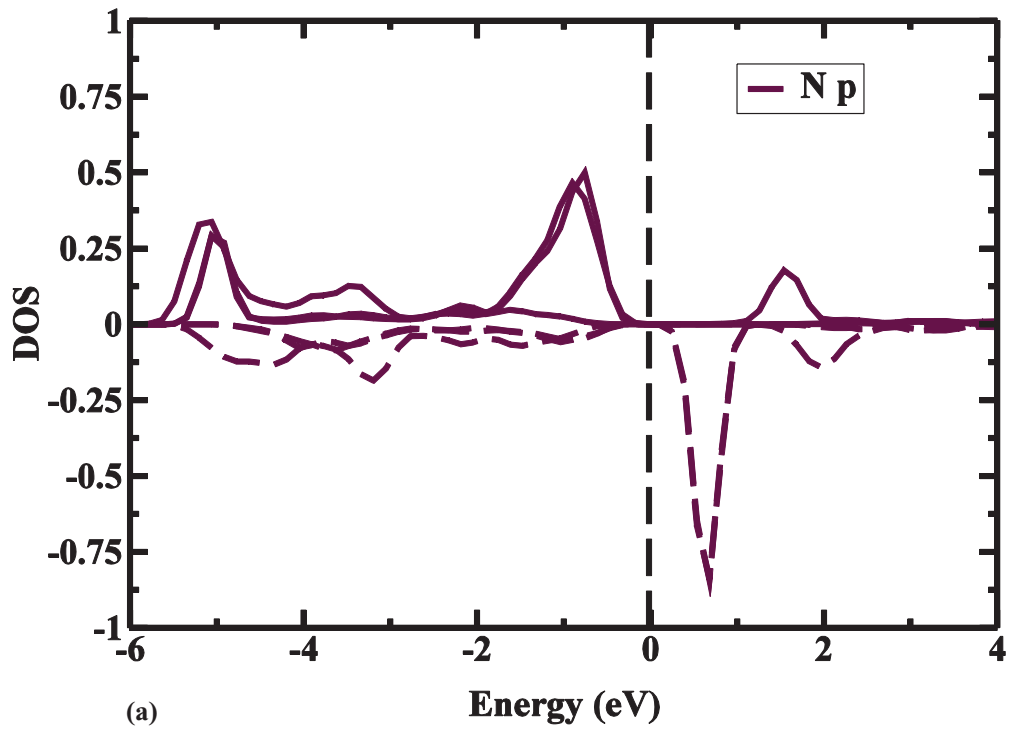


FIG. 3. (a) Spin resolved DOS of Nitrogen. (b) Spin resolved DOS of the adjacent Co atom.

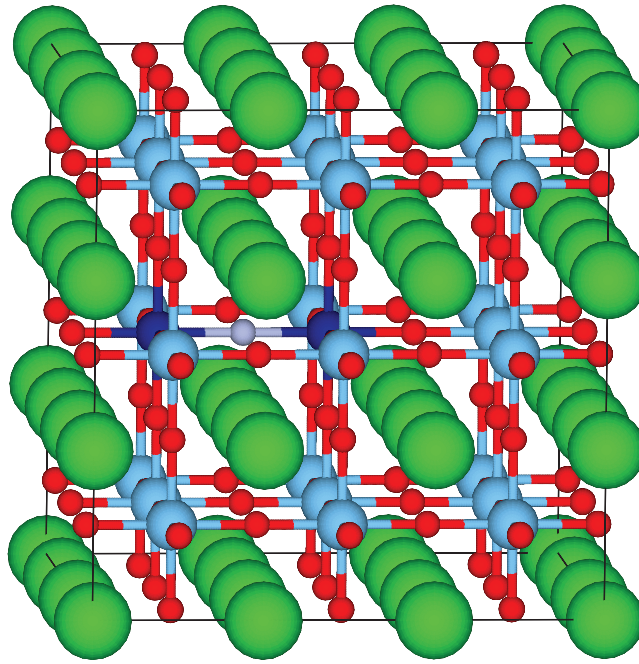


FIG. 4. Supercell structure of two Co atoms as nearest neighbors with N being the mediating anion.

extrinsic sources, in the form of defects, to make Co doped BaTiO_3 a promising candidate for room temperature ferromagnets.

In this work we propose that a N atom (which acts as a *p*-type dopant) substituted on an O site, as a nearest neighbor atom to Co, plays an important role in enhancing ferromagnetism in $\text{BaTi}_{1-x}\text{Co}_x\text{O}_3$. However, it must first be verified that N would indeed be energetically favorable to be present nearest to Co rather than far away. In order to check this we compare the formation energy of a supercell with a Nitrogen atom sitting nearest to a Co atom, which we call E_{near} and that sitting far away, which we call E_{far} . The formation energy is computed using the Zhang-Northrup formalism as described in.¹⁶ It is obtained from the following equation:

$$\Delta E = [E_{\text{BaTi}_{1-x}\text{Co}_x\text{O}_{3-y}\text{N}_y} - E_{\text{BaTi}_{1-x}\text{Co}_x\text{O}_3}] - \mu_{\text{N}} + \mu_{\text{O}}$$

where the first two terms within the square bracket represents the difference in total energies between the supercell containing Nitrogen and that without it. Since Nitrogen is substituted on an Oxygen site one also needs the chemical potential of Nitrogen and Oxygen (μ_{N} and μ_{O} respectively) chosen as references. Here we choose these values as half of N_2 and O_2 molecules respectively.¹⁷ Upon plugging in all the values in the above equation we obtain $E_{\text{near}} = 2.785$ eV and $E_{\text{far}} = 4.225$ eV. Hence the formation energy gets significantly lowered when the Nitrogen atom sits as a nearest neighbor to Co. This suggests that upon doping $\text{BaTi}_{1-x}\text{Co}_x\text{O}_3$ with Nitrogen, the Nitrogen atom will be more likely to be found closer to the Cobalt atom thus enabling it to introduce important magnetic effects in the system.

The relaxation effect and the electronic structure of N doped $\text{BaTi}_{1-x}\text{Co}_x\text{O}_3$ is now analysed. Upon relaxing the structure it is found that the N atom moves closer towards the Co atom (Fig. 2) and hence the Co-N bond length now decreases to 1.7\AA compared to the ideal Co-O bond length of 1.99\AA . In Figs. 3(a) and 3(b) we present the orbital resolved DOS plots of N and Co atom. Contrary to the O atom there is a clear spin splitting of the N spin up and spin down states resulting in a net magnetic moment of $1\mu_{\text{B}}$. Due to the change in its chemical environment and also due to the breaking of its octahedral symmetry there is also a spin splitting in the Co states. This results in a magnetic moment of $0.8\mu_{\text{B}}$ on the Co atom. The presence of Nitrogen plays an important role as it suggests that even in a very dilute limit of Co concentration one may obtain a net local magnetic moment moment of about $2\mu_{\text{B}}/\text{Co}$ atom in the system. Upon placing the Nitrogen atom far away

from Cobalt we find the system goes back to the non-magnetic state with no net magnetic moments being induced on either Nitrogen or Cobalt. We further introduce another Co atom in order to check the magnetic interaction between them in the presence of a N atom as seen in Fig. 4. We find that the ferromagnetic configuration is now favored by as much as 0.5 eV to the antiferromagnetic interaction, in the presence of N. This suggests that a p-type dopant in Co doped BaTiO₃ can indeed induce ferromagnetism in the system.

In conclusion, we have performed first principles calculation of Co doped BaTiO₃ and find that Nitrogen doping can play a significant role in making it a promising candidate for room temperature ferromagnetism. While in the absence of N the nonmagnetic state is stabilized in the cubic phase of BaTiO₃, inclusion of N induces important changes in its local symmetry as well as shortening the Co-N bond length by 0.3 Å compared to the ideal structure. This brings about spin splitting of its electronic states which in turn results in stabilizing a net local magnetic moment. The presence of N also brings about ferromagnetic interaction between the Co atoms.

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