

Magnetism from $2p$ states in alkaline earth monoxides: Trends with varying N impurity concentration

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(Received 6 August 2008; revised manuscript received 6 October 2008; published 30 October 2008)

$2p$ -based magnetic moments and magnetic coupling are studied with density-functional-based methods for substitutional N in the alkaline earth monoxide series MgO, CaO, SrO, BaO. The hole is rather strongly localized near the N^{2-} ion, being somewhat more so when strong on-site interactions are included in the calculations. Strong magnetic coupling is obtained in the itinerant electron limit but decreases strongly in the localized limit in which the Coulomb repulsion within the N $2p$ shell (U) is much greater than the N $2p$ impurity bandwidth ($W \approx 0.3$ eV). We find that this limit is appropriate for realistic N concentrations. Ordering on a simple cubic sublattice may maximize the magnetic coupling due to its high directionality.

DOI: [10.1103/PhysRevB.78.134427](https://doi.org/10.1103/PhysRevB.78.134427)

PACS number(s): 71.20.-b, 75.30.Hx, 75.50.Pp, 75.30.Et

I. INTRODUCTION

After a strong research effort spent on magnetic-ion doped semiconductors as spintronics materials,¹ scientific interest has recently turned to the possibility of obtaining useful ferromagnetic (FM) order at room temperature in materials without conventional magnetic atoms with open d or f shells. Isolated defects in insulators often produce magnetic moments, which occur anytime a state in the band gap is occupied by an odd number of electrons. A common example is the p impurity in Si, where the paramagnetism of the material evolves with increased doping as the insulator-metal transition is approached. Such strictly localized states in insulators are magnetic regardless of their underlying atomic character or their degree of localization.

Elfimov *et al.*² proposed to use the cation vacancy—the charge conjugate of the conventional F-center state—in nonmagnetic oxides such as CaO (Ref. 3) as a source of magnetic moment in insulators. The resulting pair of holes, which are bound to the region for an isolated vacancy, may form a magnetic center even if it does not lie in the gap, due to the large Hund's coupling on the oxygen ions neighboring the vacancy (which can no longer be simple nonmagnetic O^{2-}). These states extend to a few atomic neighbors, with magnetic coupling resulting from direct exchange. Magnetic order becomes possible, and at concentrations of a few percent they suggested that conduction, and half-metallic ferromagnetism, might result.

The Osaka group⁴ followed by suggesting that B, C, or N substituted for O in CaO could result in local moments in the $2p$ states of the impurity ions. The coupling between moments was found, in calculations on random alloys, to be FM and half-metallic ferromagnetism was also predicted, possibly as high as room temperature. Elfimov *et al.*⁵ studied the specific case of N substituting for O in SrO, applying not only the conventional local spin-density approximation (LSDA) but also the strongly correlated form (LSDA+ U) that should be appropriate for localized magnetic states. They also obtained the possibility of half-metallic ferromagnetism at technologically relevant temperatures. Experimentally, magnetism has been observed as a surface effect in thin films of these nonmagnetic oxides.⁶

There are other examples of atomic p character giving rise to magnetism in solids. One example is the class of alkali hyperoxides [for example, RbO_2 (Refs. 7 and 8) and Rb_4O_6 (Refs. 9 and 10)]. These materials are ionic, containing the spin-half O_2^{1-} ion, and display magnetism-related properties, including unusually strong magnetostructural coupling. The SrN_2 compound, an ionic material containing the N_2^{2-} unit, is a related example,¹¹ while the SrN compound with magnetic N is predicted to be a half-metallic ferromagnet.¹² Between the bulk compounds and the (nearly) isolated magnetic impurities, another promising example has been reported. At the p -type interface between $LaAlO_3$ and $SrTiO_3$, there is (from simple electron counting) 0.5 too few electrons per interface cell to fill all of the O $2p$ states that are filled in both bulk materials. Holes must exist in the O $2p$ bands at the interface, and Pentcheva and Pickett¹³ predicted that magnetic holes arise and should order at low temperature. Subsequently, magnetic hysteresis has been observed at this interface.¹⁴

Here we will analyze the magnetism and magnetic coupling in alkaline earth monoxides doped with N in more detail. Substitution of O by N in an insulating host presents a clear platform for local moments, and the basic picture is simple. Besides changing the potential locally, the substitution of O by N removes one electron giving a $N^{-2} 2p^5$ ion, and thereby introduces a hole that is necessarily magnetic (being spin-uncompensated). Ferromagnetism may result if the magnetic coupling has the right character and is sufficiently robust. Within the series MgO, CaO, SrO, and BaO the unit cell volume varies by a factor of 2.3 and the band gap varies by over a factor of 1.8; see Table I. By introducing dopant nitrogen atoms in ordered supercells with concentrations of one N atom per 8, 16, and 32 O atoms, we are able to model impurity concentrations of 12.5%, 6%, and 3%, respectively. The goal here is to understand the electronic structure and magnetic character of the substitutional N impurity, to study dopant interactions for the various concentrations, and to analyze the magnetic properties by calculating the conditions for maximizing the coupling. We have not considered the case of an inhomogeneous distribution of dopants, which is known to play a crucial role in determining

TABLE I. Experimental lattice parameters (Ref. 15) and band gap (Ref. 16) of the corresponding monoxides under study.

Compound	Lattice parameter (Å)	Band gap (eV)
MgO	4.12	7.2
CaO	4.81	6.2
SrO	5.16	5.3
BaO	5.52	4.0

the magnetic transition temperature in diluted magnetic semiconductors.^{17,18}

These monoxides under study crystallize in a rocksalt structure. Upon increasing the lattice parameter by introducing a bigger cation, there should be a tendency for the N hole state to become more *localized*. However, the band gap narrows in proceeding from the smallest to largest (7.2 eV for MgO, 4.0 eV for BaO), a trend that should cause a corresponding increase in the tendency toward *delocalization* of the impurity state. It is important to determine how these effects compete. Another distinction is that the lowest conduction states in CaO, SrO, and BaO are *d* states, while MgO is very different in this regard (Mg *s*, O *3s*, *3p*). The hole state will be formed from valence orbitals, however, so the impact both of the magnitude of the band gap and the character of the conduction band must be calculated.

Table II summarizes the nearest-neighbor (NN) distances in the different compounds for the various concentrations considered. As the concentration changes, the coordination of the impurities varies, as is provided in the table.

II. COMPUTATIONAL DETAILS

Electronic structure calculations were performed within density-functional theory¹⁹ using WIEN2K,²⁰ which utilizes an augmented plane wave plus local orbitals (APW+lo) (Ref. 21) method to solve the Kohn-Sham equations. This method uses an all-electron, full-potential scheme that makes no

TABLE II. Nearest-neighbor distances and number of nearest neighbors for the impurity at various concentrations and monoxides under study.

Compound	Concentration	NN distance (Å) (No. of neighbors)
MgO	1/8	6.0 (12)
MgO	1/16	6.0 (4)
MgO	1/32	8.4 (6)
CaO	1/16	6.8 (4)
SrO	1/8	7.3 (12)
SrO	1/16	7.3 (4)
SrO	1/32	10.3 (6)
BaO	1/8	7.8 (12)
BaO	1/16	7.8 (4)
BaO	1/32	11.0 (6)

shape approximation to the potential or the electron density. The exchange-correlation potential utilized was the Wu-Cohen version of the generalized gradient approximation (GGA) (Ref. 22) and strong correlation effects were introduced by means of the LSDA+*U* scheme²³ including an on-site effective *U* for the O and N *p* states. We have used option nldau=1 in WIEN2K, i.e., the so-called “fully localized limit,” using an effective $U_{\text{eff}}=U-J$, *J* being the on-site Hund’s rule coupling constant, taken as *J*=0. The justification of utilizing the LSDA+*U* scheme comes from spectroscopic measurements in oxides, which estimate large values of *U* (5–7 eV) for the *p* states.²⁴ This has been shown to be crucial in understanding the interfacial electronic structure of transition metal oxides, where magnetic moments can localize in the O atoms.¹³ All the calculations were converged with respect to all the parameters used, to the precision necessary to support them ($R_{\text{mt}}, K_{\text{max}}=6$, *k* mesh up to $6 \times 6 \times 6$).

III. RESULTS

We begin by studying the local electronic structure of a N $2p^5$ impurity in MgO. Comparing a nonmagnetic solution for the N atom and a solution with $1 \mu_B/\text{N}$ (a local moment formation in the N site), the total energy difference favors the magnetic solution by more than 100 meV/N, a value that is nearly independent of the concentration of impurities. The introduction of a value of $U_{\text{eff}}=5$ eV produces a further stabilization of the magnetic solution with respect to the nonmagnetic one (the energy difference rises above 300 meV/N).

A. Effect of atomic relaxation

Substitutional N in these monoxides will break the symmetry and may lead to some local distortion of the otherwise perfectly octahedral environment of the cation. To determine the importance of atomic relaxation we performed structural minimization for $\text{MgO}_{1-x}\text{N}_x$, with $x=1/16$. If sufficiently localized, the hole might occupy a p_z orbital ($l_z=0$), leading to an elongation of the N-Mg distance along the *z* axis, or it could be $p_x \pm ip_y$ ($l_z = \pm 1$) that is unoccupied, leading to an elongation of the N-Mg distance in the plane perpendicular to the *z* axis. The symmetric LSDA solution shares the hole among the *p* orbitals equally. We have performed a structural optimization within GGA (i.e., without including strong correlation effects) which leads to an electron density describing the hole in the N atom being symmetric. The result is that Mg-N distances get modified only slightly, becoming elongated by less than 0.5%. Also, using the LSDA+*U* scheme for doing the structure optimization, the hole located in a p_z state leads to an elongation of about 3% of the Mg-N distance along the *z* axis. We have found that these small differences have little effect on the trends we study, either the localization of the magnetic moment or the magnetic coupling, hence we have neglected relaxation in the results that follow.

B. Electronic and magnetic trends

We have treated the N concentrations listed in Table II. For each concentration, we have assumed that the N impuri-

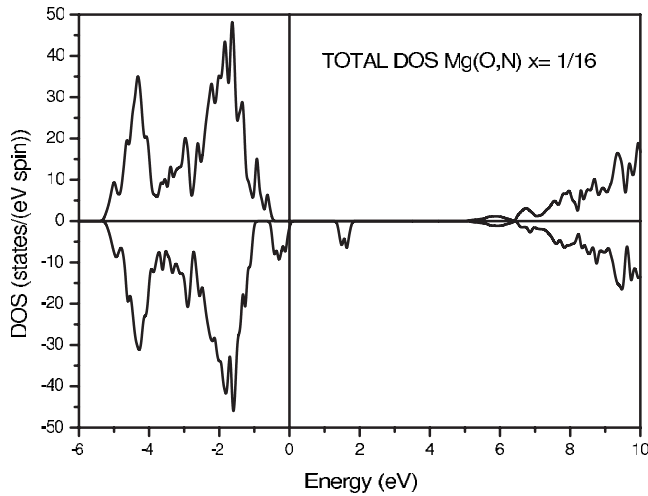


FIG. 1. Total density of states for ferromagnetically aligned $\text{MgO}_{1-x}\text{N}_x$ with $x=1/16 \approx 6\%$, calculated with the LSDA+ U method including spin-orbit effects using $U=5.5$ eV for the 2p states of both N and O. The majority DOS is plotted upward; the minority is plotted downward.

ties are as regularly distributed as possible (their separation is maximized). As mentioned above, one can imagine how the physics can change from MgO to BaO as the size of the cation, and the volume, increases. On one hand, greater delocalization is permitted as the band gap is reduced (by a factor of 2 experimentally, by a factor of 3 from our calculations for the doped compounds with $U_{\text{eff}}=5.5$ eV). On the other hand, for a given concentration of impurities, the NN distance becomes larger for the larger volume compounds. The former could encourage an easier propagation of the magnetic coupling throughout the crystal, while the latter would imply a smaller magnetic interaction if the size of the defect state remains the same.

We first consider the $U_{\text{eff}}=5.5$ eV electronic structure for a particular case, MgO with $x=1/16 \sim 6\%$, where the density of states (DOS) for separate spin directions is shown in Fig. 1. For the minority spin, the narrow hole band lies in the gap and has a full bandwidth of $W \approx 0.3$ eV. The other two N 2p minority states are occupied and lie above the O 2p bands. The separation of filled and unfilled minority N states is 2 eV, the Hund's exchange being about 0.6 eV in the occupied N p states. The conduction bands show no appreciable spin splitting. When we include spin-orbit coupling, the hole occupies the p_x - $i p_y$ state, $l_z=-1$ orbital, satisfying Hund's rule.

To display the trends across the series, it is sufficient to look only at the minority DOS, which is plotted for each compound in Fig. 2. The band gap reduction through the series Mg \rightarrow Ba is evident. The O 2p bandwidth is much larger for MgO but this has little effect on the defect state, except perhaps contributing a small additional broadening. In spite of this large band gap variation, and the change in the volume (hence the near neighbor distance) the position of the unoccupied hole state changes rather little, staying 2 ± 0.5 eV above the highest occupied state. The variation that does occur is nonmonotonic and may be due to the conduction bands that fall in energy through the series. For BaO, the narrowest band gap member, the N hole band merges into the bottom of the conduction Ba d bands.

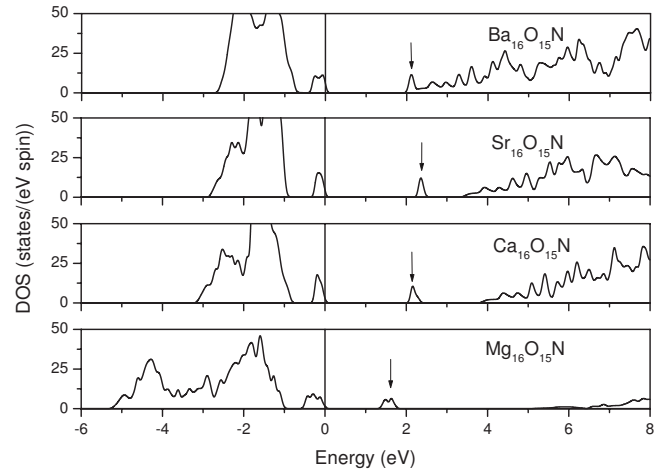


FIG. 2. Total density of states of the various monoxides under study for FM alignment, calculated with the LSDA+ U method for $U=5.5$ eV. Only the minority spin channel is shown, since it illustrates all the important features: O 2p bandwidth, narrowing of the band gap, and the position of the hole state at 2–2.5 eV above the valence-band maximum.

Because the intra-atomic Coulomb interaction strength U is at least a few eV, these systems are in the regime $U/W \gg 1$ (W being the N 2p hole bandwidth) so hopping of the holes will be inhibited, giving insulating behavior. This is the limit in which the LSDA+ U method works well. For values of U bigger than ~ 1 eV, the material is insulating whereas for smaller values (i.e., in LSDA or GGA), the N hole band intersects the upper valence bands and the band structure becomes metallic (or half-metallic).

C. Sign, strength, and character of magnetic coupling

Since the N ions form a strong local magnetic moment, the next question is whether they couple ferromagnetically and what the strength of the magnetic interaction is. We have performed calculations on both FM and antiferromagnetic (AF) alignments to obtain the coupling between nearest-neighbor N moments, for the different concentrations and monoxides under study. We have estimated the Curie temperature by using the mean-field expression from a Heisenberg model of the type $H = -\sum J_{ij} S_i S_j$, with $S = 1/2$ (the sum is over pairs),

$$T_c = [2zS(S+1)J/3k_B], \quad (1)$$

where z is the number of nearest neighbors and J is the exchange constant. This procedure is known to overestimate transition temperatures,^{25,26} by up to a factor of 2. Our results are worthwhile for studying trends across the series and predicting the conditions for strong coupling.

Table III shows how the magnetic coupling between N moments varies both with the concentration and the different compound considered. The data presented in the table were obtained for a calculation without considering strong correlation effects ($U=0$), but including spin-orbit effects, and also using the Wu-Cohen GGA functional. The effect of introducing U is to reduce the magnetic coupling, because it

TABLE III. Strength of the magnetic coupling converted into Curie temperature of the corresponding monoxides under study obtained from a LSDA calculation (including spin-orbit effects) and a GGA (Wu-Cohen) calculation ($U=0$).

Compound	Concentration	T_c (K)	
		(LSDA+SO)	(GGA)
MgO	1/8	330	320
MgO	1/16	400	400
MgO	1/32	5	70
CaO	1/16	72	83
SrO	1/8	82	66
SrO	1/16	31	41
SrO	1/32	250	98
BaO	1/8	32	31
BaO	1/16	11	13
BaO	1/32	280	230

further localizes the moments. In fact, using a range of values of U up to 8 eV, we find that, for BaO and SrO, the introduction of U as small as 1.5 eV leads to magnetic coupling too small to determine reliably from supercell energy differences (from our calculations it is not possible to estimate transition temperatures below 4 K). A small magnetic coupling has also been observed treating correlations by self-interaction correction (SIC) methods for MgO doped with N.²⁷ The hole states no longer overlap directly, and the materials are insulating with no means to transfer magnetic coupling except classical dipolar coupling. For MgO at the higher concentrations ($x=1/8$ and $x=1/16$), the magnetic coupling is much higher than for the other compounds, because of the much smaller lattice parameter, and the introduction of U reduces the size of the interaction but does not bring T_c to zero.

Putting all these LSDA data together, we can make a plot of how the magnetic interaction strength J varies in these compounds with respect to the NN distance, neglecting all the differences between the various compounds we are considering. The result can be seen in Fig. 3, which shows an exponential-like decay in the strength of the magnetic coupling as the N impurity atoms are separated. There is, remarkably, an upturn for NN distances above 10 Å, with values close to room temperature for BaO and SrO for a concentration around $x \sim 3\%$. For this supercell, the magnetic impurities are located on a simple cubic sublattice at lattice constant $2a$. Elfimov *et al.*⁵ have shown that the electronic coupling between N impurities in SrO is highly directional, with strong coupling along the crystalline axes (large effective p_x - p_x coupling along the x axis, for example). This opens the possibility of reaching high temperature FM at attainable concentrations of N dopant in the limit $U \sim W$.

A double-exchange-like microscopic mechanism seems to be the best explanation of the FM coupling in these monoxides in the GGA limit, when the Fermi level lies within the impurity band. Double exchange is normally associated with carriers coupled to a background of moments, with kinetic energy favored by alignment of the moments. Electronic structure-wise, the added kinetic energy shows up as an in-

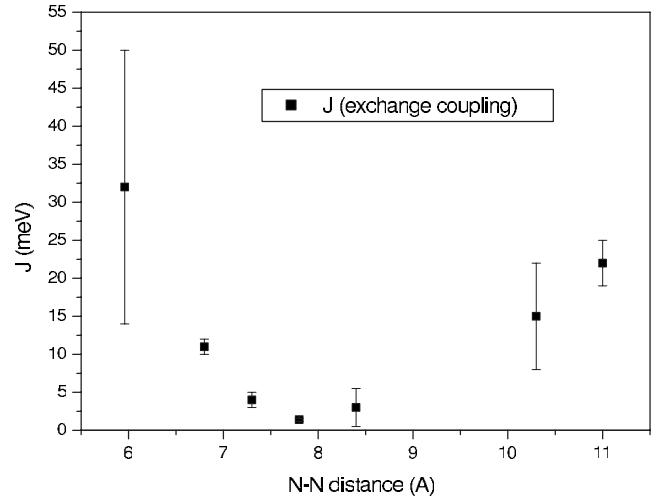


FIG. 3. Exchange coupling strength with respect to the NN distance, considering all the LSDA data from the various compounds together. “Error” bars simply denote the range of values that were calculated for the same near neighbor distance; see Table II.

creased bandwidth compared to antialignment. Indeed for the GGA calculations and for small values of U , the system is (half) metallic and the double exchange picture as conventionally interpreted makes sense. As U is increased beyond ~ 1 eV, a gap appears, and in the large U regime the coupling is certain to be via direct exchange. However, as shown in Fig. 4, the coupling strength (as reflected in T_c in this figure) does not appear to undergo any discontinuity at the metal-insulator transition. The coupling (and T_c) does, however, decrease rapidly as the value of U is increased. Having band states at the Fermi level leads also to a larger FM coupling.

In Fig. 4 we illustrate more explicitly how the effect of U reduces the Curie temperature. Strong correlation effects produce a stronger localization of the magnetic moments, i.e., their effects extend to fewer neighbors. The reduced overlap leads to a corresponding reduction in the magnetic interac-

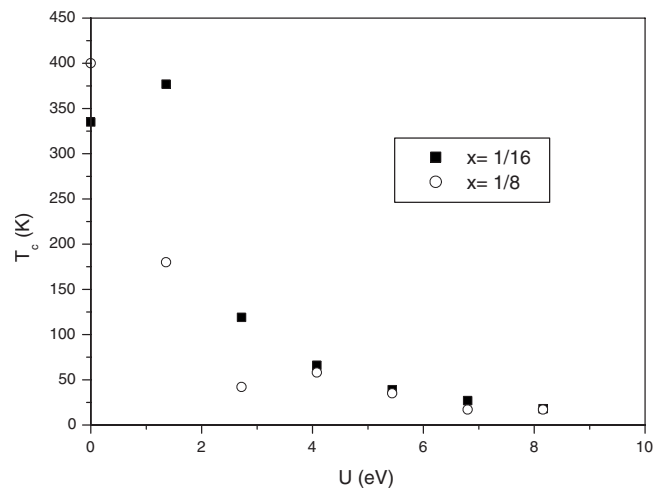


FIG. 4. Strength of the magnetic coupling in MgO obtained from a LSDA+ U calculation (including spin-orbit coupling) with various values of U calculated in terms of the Curie temperature.

tion. Hence, in the limit $U \gg W$, where this system resides for the concentrations we study, the magnetic coupling will not be strong.

IV. SUMMARY

In this paper we have studied the formation of local moments when substitutional N impurities are introduced in alkaline earth monoxides. We have calculated the coupling for a variety of concentrations, paying particular attention to the effect of Hubbard repulsion U (since $U > W$ for these systems, where W is the impurity bandwidth). The local moments that form, mainly confined to the N atoms and their nearest neighbors, would lead to room-temperature ferromagnetism in the itinerant electron limit via a double-exchange-like exchange coupling within the impurity band. However, in the more realistic localized electron limit $U \gg W$ the coupling must be due to direct exchange (local im-

purity state overlap) and becomes drastically reduced. Interestingly, the crossover between the double-exchange coupling and the direct exchange as the interaction strength is increased does not lead to any discernible anomaly in magnetic coupling strength at the metal-insulator transition. Finally, we confirm that the impurity state is highly anisotropic, and as a result magnetic coupling is enhanced by ordering of the magnetic N impurities on a periodic (simple cubic) sublattice.

ACKNOWLEDGMENTS

We have benefited from discussion on this topic with S. S. P. Parkin and G. A. Sawatzky. This project was supported by the DOE under Grant No. DE-FG02-04ER46111 and through interactions with the Predictive Capability for Strongly Correlated Systems team of the Computational Materials Science Network. V.P. acknowledges financial support from Xunta de Galicia (Human Resources Program).

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