Ferromagnetic Spin Coupling of $2p$ Impurities in Band Insulators Stabilized by an Intersite Coulomb Interaction: Nitrogen-Doped MgO

I. Slipukhina,* Ph. Mavropoulos, S. Blügel, and M. Ležaić

Peter Grünberg Institut and Institute for Advanced Simulation, Forschungszentrum Jülich and JARA, D-52425 Jülich, Germany

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For a nitrogen dimer in insulating MgO, a ferromagnetic coupling between spin-polarized $2p$ holes is revealed by calculations based on the density functional theory amended by an on-site Coulomb interaction and corroborated by the Hubbard model. It is shown that the ferromagnetic coupling is facilitated by a T-shaped orbital arrangement of the $2p$ holes, which is in its turn controlled by an intersite Coulomb interaction due to the directionality of the p orbitals. We thus conjecture that this interaction is an important ingredient of ferromagnetism in band insulators with $2p$ dopants.

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Ferromagnetic (FM) insulators offer the potential for use as active barrier materials in novel spintronic tunneling devices. In the past years we have witnessed a new vista in engineering FM insulators not by doping nonmagnetic insulators with transition-metal ions as is traditionally accomplished in diluted magnetic semiconductors [1,2], but by doping with sp elements. The novel magnetic materials design was encouraged by unexpected experimental observations of room-temperature ferromagnetism in defective wide-gap oxide semiconductors and insulators [3–7]. This phenomenon (referred to as sp or d^0 magnetism) was associated with the partially filled p states of the intrinsic defects such as cation or anion vacancies [3,6,8] or first-row ($2p$) dopants [9].

Shortly after, numerous cation-deficient or N- and C-doped oxides and sulfides were theoretically predicted to be FM at room temperature [10–14]. Among those, MgO is distinct as it is certainly the most important barrier material for magnetic tunnel junctions. Recently, N-doped MgO films were experimentally shown to exhibit ferromagnetic properties upon thermal annealing [15].

It is commonly concluded that the FM interaction between the defects in d^0 magnets is due to partially occupied spin-polarized defect states, that are sufficiently extended to provide an exchange interaction via the double-exchange mechanism. Most likely, however, at low concentrations the impurity $2p$ electrons experience a strong on-site Coulomb repulsion U because of their spatial localization [16], leading to insulating behavior that changes the mechanism of exchange interaction and could weaken or change the sign of magnetic coupling.

Correlation effects in defect-free oxides with partially filled oxygen p shells were studied in Refs. [17–19]. The importance of electron correlations in the impurity p states was recently investigated using density functional theory (DFT) approaches amended by an on-site Coulomb repulsion [11,20] for the example of N-doped MgO. Jahn-Teller (JT)-like distortions, captured by "$+U$" [21] or self-interaction correction [22] schemes, were found to evoke an energy splitting between the occupied and unoccupied nitrogen $2p$ states, increasing the localization of a spin-polarized hole at one of the $2p$ orbitals by pushing it deeper into the band gap and thus breaking the initial symmetry of the electronic state.

In this Letter, we present new insights into the role of electron correlations in N-doped MgO by carrying out DFT calculations where strong correlations are accounted for by the generalized-gradient approximation (GGA) [23] $+U$ approach. The calculations are conceptualized on the basis of a minimal Hubbard model. We demonstrate that the symmetry breaking and the subsequent metal-insulator transition occurs even without JT distortions, and is thus electronically driven. More important, we find for the insulating state of N dimers, which are likely to be formed in the annealing process, a FM spin coupling and a T-shaped $2p$-orbital arrangement (OA). Employing a Hubbard model we show that a weak *intersite* Coulomb repulsion, that is well accounted for by the DFT, combined with the on-site Coulomb interaction is responsible for this result. While in *periodic* strongly correlated $3d$ systems the favored spin and orbital arrangement is usually well explained by the Kugel-Khomskii model [24], which does not resort to the intersite repulsion, similar arguments applied to N-N dimers in MgO yield an antiferromagnetic (AFM) coupling, in contradiction with our first-principles results. The nearest-neighbor FM interaction is not sufficient to explain the long-range FM order, but it is a necessary condition. Our aim is to shed some light on the physics driving this interaction.

We utilized the full-potential linearized augmented plane wave code FLEUR [25] in our GGA + U calculations. Relaxations were performed with an on-site Coulomb energy $U = 4.6$ eV and Hund's exchange $J = 1.2$ eV applied on the $2p$ states of O and N. The total energies were compared [26] for a set of U values that ranges between 3 and 6 eV, reported for O $2p$ states in transition-metal oxides from photoemission and Auger experiments [27], and for two values of J, 0.6 and 1.2 eV (from Hund's exchange for atomic N and O [26], we expect the physically relevant J values in a solid to fall within this range). Supercells of 64 atoms of host MgO, with a Brillouin-zone $2 \times 2 \times 2$ **k** mesh are used to study a single N impurity and N-N dimers at O sites. N-O-N "dimers" are treated in a 144-atomic supercell and sampled at the Γ point. Different OAs are introduced by initiating a specific occupation of the p orbitals of N in the GGA + U density matrix [28]. Calculations are performed for all possible types of OA at FM and AFM spin alignments (12 different spin-orbital configurations in total) for N-N and N-O-N dimers.

We first consider the case of a single N impurity, substituting O in MgO to check whether the symmetry breaking and the metal-insulator transition upon applying a finite U are driven electronically or by local lattice distortions. Figure 1(a) shows the N density of states (DOS) of the structurally unrelaxed supercell. Within the GGA, N introduces two triply degenerate states, an occupied spin-up p state in the valence band, and a partially unoccupied spin-down state at the Fermi level E_F. A single spin-polarized hole is evenly distributed among the three N p orbitals. The situation changes drastically upon applying U: the minority $2p$ state splits into a doubly degenerate occupied and a nondegenerate unoccupied level [Fig. 1(b)]. This symmetry breaking occurs even without lattice distortions, which clearly demonstrates that it is an electronically driven effect. Similar behavior was noticed for the cation vacancy in ZnO [29]. This is different from the previous reports on MgO:N [20], where the main effect of both $+U$ or self-interaction corrections resulted in symmetry breaking via a JT distortion.

Next, we examine the relative spin- and p-orbital arrangement for two substitutional N impurities in MgO. Recent local density approximation (LDA) studies [30] have shown that N-N impurity pairing in a structurally relaxed MgO supercell leads to a nonmagnetic insulating ground state with fully occupied bonding $pp\sigma$ (as well as $pp\pi$) and completely empty antibonding $pp\sigma^*$ states. However, we show that this is no longer the case in the presence of strong correlations. We consider the following relative positions of the two N atoms: (i) at the nearest-neighbor (N.N.) sites, at a distance $d_{\text{N-N}} = 2.97$ Å—a N-N dimer, (ii) connected via an O atom ($d_{\text{N-N}} = 5.83$ Å)—a N-O-N dimer, and model, correspondingly, the 1st and 2nd N.N. interaction between N atoms in the oxygen sublattice of MgO. We omit the N-Mg-N configuration from the analysis because we find the magnetic interactions to be negligibly small [31].

We define a coordinate system with the p_x and p_y orbitals pointing toward neighboring N (or O) atoms in the xy plane [Fig. 1(c)], while the p_z orbital points out of the plane, toward Mg. In the considered cases of N-N and N-O-N dimers, both N atoms are situated along the x axis; thus, the largest hopping is of the $pp\sigma$ type between neighboring p_x orbitals, while p_y and p_z orbitals are essentially nonbonding. The sign and strength of the magnetic coupling between the two spin-polarized holes is found by the total energy difference $\Delta E_{\text{AFM-FM}}$ between the AFM and FM state, calculated within GGA + U for each p-hole OA. To be able to disentangle the electronic mechanism of OA from the JT one, for the N-N dimer we performed calculations with and without structural relaxations.

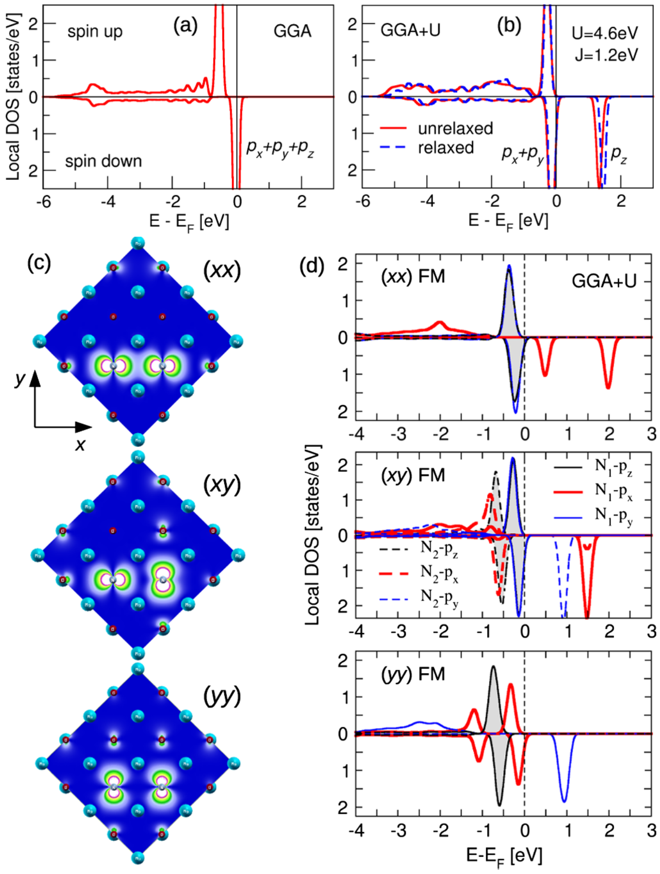

FIG. 1 (color online). Spin- and orbital-resolved DOS for a single N in MgO calculated in GGA (a) and GGA + U (b). (c) Minority p holes spin-density distribution in the xy plane around the N-N dimer, with (xx), T-shaped (xy), and (yy) OA. Big blue, small red, and light gray spheres denote Mg, O, and N, respectively. (d) Spin- and orbital-resolved DOS of the N atom 1 (2) [solid (dashed) lines] of the N-N dimer for the depicted OAs, with FM spin alignment. Thick red, thin blue, and black lines with gray background depict the p_x, p_y, and p_z orbitals, respectively.

The results are summarized in Table I. For each OA the spin configuration (FM or AFM) with the lowest energy is shown. Clearly, there are substantial energy differences between different types of OA. Comparing the N-N and N-O-N dimers, the rapid decrease of $\Delta E_{\text{AFM-FM}}$ with the N-N distance confirms previous studies [31]. Importantly, for both dimers the FM T-shaped OA [(xy) or (xz)] is of the lowest energy, moreover, for any choice of U and J parameters (see Supplemental Material [26]).

TABLE I. The GGA + U total energies ΔE relative to the lowest-energy state and exchange interaction $\Delta E_{\mathrm{AFM-FM}}$ both in meV/supercell, calculated for different OA for N-N and N-O-N dimers in MgO. Positive (negative) $\Delta E_{\mathrm{AFM-FM}}$ corresponds to FM (AFM) coupling.

	N-N		N-N, relaxed		N-O-N	
OA	ΔE	$\Delta E_{\mathrm{AFM-FM}}$	ΔE	$\Delta E_{\mathrm{AFM-FM}}$	ΔE	$\Delta E_{\mathrm{AFM-FM}}$
(xx)	156	−129	99	−189	35	−8
(xy)	4	26	0	34	7	2
(xz)	0	24	13	31	0	2
(yz)	185	1	258	1	19	0
(yy)	192	2	280	1	28	0
(zz)	198	5	294	3.6	12	0

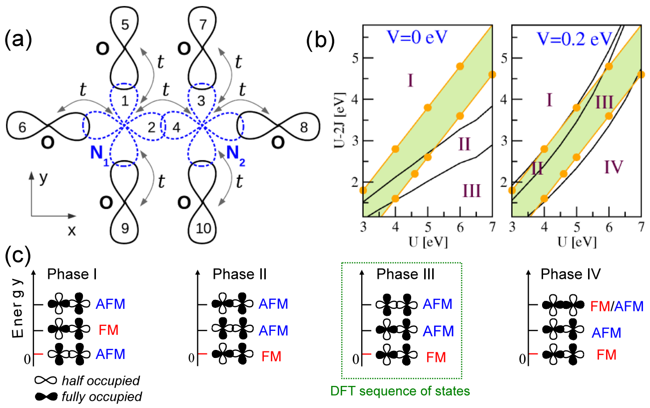

FIG. 2 (color online). (a) A schematic view of the cluster of p orbitals used in the model Hamiltonian (1). The dashed blue line depicts p_x and p_y orbitals of the N.N. nitrogen atoms (N_1 and N_2), while the solid black line depicts the corresponding orbitals of the O atoms. The possible hopping processes t between two orbitals on neighboring sites are also shown. (b) The $(U - 2J)$ vs U phase diagram of the model for $V = 0$ and $V = 0.2$ eV. Orange circles denote the U and J values, considered in our *ab initio* calculations [26], outlining the physically relevant area (in green). (c) The phases I, II, III, and IV, corresponding to different sequences of several orbitally arranged states in the order of energetic stability.

It was suggested [11,20] that the introduction of U would reduce the magnetic coupling in d^0 magnets. However, a precise physical value of the parameter U is not known. To check the persistence of the magnetic coupling, we repeated the calculations for the N-N dimer, varying U in the range between 0 and 6 eV (neglecting atomic relaxations), with $J/U = 0.26$. At $U = J = 0$, the system is half-metallic and ferromagnetic with $\Delta E_{\mathrm{AFM-FM}} = 265$ meV. However, at $U > 2$ eV, it becomes insulating and the interaction through the double-exchange mechanism is no longer possible. Thus, the magnetic coupling is much weaker and we expect AFM coupling due to the kinetic exchange interaction. Instead, the orbital arrangement sets in and despite the insulating state, the interaction between the spin-1/2 holes remains FM with a total magnetic spin moment of $2\mu_B$. In the following, we provide a qualitative understanding of this unexpected finding.

In the first step we show that kinetic exchange alone favors an AFM ground state. We consider a minimal multi-orbital Hubbard model that describes the system of strongly correlated open-shell $2p$ electrons in terms of the kinetic energy t of spin-conserving hoppings between orbitals of the largest overlap [N.N. $pp\sigma$ orbitals, see Fig. 2(a)], the on-site Coulomb repulsion energy U, and the interorbital exchange (Hund's rule) coupling J [see also Eq. (1)].

For a given OA, the favored magnetic interaction is determined by the hopping of the electrons within the N-N dimer. A substantial magnetic coupling occurs only for those OAs that allow hopping between the two p_x orbitals of the N dimer, where at least one of these orbitals is half-filled: the (xx) and the T-shaped (xy) and (xz) OAs (see Table I). The relative coupling strength can be qualitatively understood by considering that each spin-conserving hopping t into half-filled orbitals lowers the energy by $t^2/(U - J)$ (in 2nd order perturbation theory) if the intermediate virtual atomic state satisfies Hund's rule for one of the atoms, and t^2/U otherwise. In the (xx) OA, this gives $E_{\mathrm{AFM}} = -2t^2/U$, $E_{\mathrm{FM}} = 0$, i.e., an AFM ground state (the factor 2 arises because there is one half-filled orbital per atom participating in the hopping). In the T-shaped OA there is only one half-filled orbital participating; then we have $E_{\mathrm{AFM}} = -t^2/U$, $E_{\mathrm{FM}} = -t^2/(U - J)$, i.e., a FM ground state.

Among all possible types of OA, the T-shaped and AFM (xx) states are the ones that have the lowest energy, because these are the only ones that allow hopping between the N atoms. The hopping between O and N atoms provides a smaller total energy gain, because of (i) the separation between the on-site energy levels of O and N, that differ by 0.5–1 eV, and (ii) the delocalization of the O states that form an itinerant band. From the previous discussion, it follows that among the two OAs, the AFM (xx) one should be lower in energy by $2t^2/U - t^2/(U - J)$ as long as $J < U/2$. Thus, the arguments of the kinetic exchange interaction favor the AFM (xx) state, contradicting our DFT finding of a FM T-shaped ground state.

Obviously, a qualitative description of the relative stability of spin and orbitally arranged states in N-doped MgO requests an extension of the minimal Hubbard model beyond the conventional electron hopping t and *on-site* Coulomb repulsion U. The N-N dimer breaks the cubic symmetry of the MgO lattice. Considering the directional nature of the $2p$ orbitals, this leads to an orbital-dependent intersite Coulomb repulsion that is well accounted for within the GGA/LDA . In terms of the Hubbard model it is expressed by an additional effective intersite Coulomb repulsion energy V between N.N. $pp\sigma$ orbitals of N-N and N-O pairs. To capture this effect by such an extended

Hubbard model we study an impurity cluster of 2 N and 6 N.N. O atoms [Fig. 2(a)], with 1 (2) p orbital on each O (N) site that form N.N. $pp\sigma$ orbitals. Thus, we restrict ourselves to 10 p orbitals that can be occupied by 18 electrons and 2 holes of spins ↑ and ↓. The Hamiltonian for such a system can be written as

$$\begin{aligned} H = \sum_{m,s}\epsilon_m n_{ms} - t\sum_{\langle m,m'\rangle}\sum_{s}[c^\dagger_{ms}c_{m's} + \text{H.c.}] + U\sum_{m} n_{m\uparrow}n_{m\downarrow} \\ + V\sum_{\langle m,m'\rangle} n_m n_{m'} + (U' - J)\sum_{\langle\langle m,m'\rangle\rangle,s} n_{ms}n_{m's} \\ + U'\sum_{\langle\langle m,m'\rangle\rangle,s} n_{ms}n_{m'-s}. \qquad (1) \end{aligned}$$

Here $\langle m, m'\rangle$ indicates the pair of N.N. orbitals of $pp\sigma$ overlap, ϵ_m denotes the energy level, $c^\dagger_{ms}$ (c_{ms}) creates (annihilates) a particle of spin $s = \uparrow, \downarrow$ of orbital m, while n_{ms}, $n_m = n_{m\uparrow} + n_{m\downarrow}$ are the spin number and number operators, respectively. Since we have two orbitals at the N atoms, U' accounts for the *interorbital* on-site Coulomb interaction; $\langle\langle m, m'\rangle\rangle$ stands for the two on-site orbital pairs (1,2) and (3,4). We neglect on-site spin-flip and pair-hopping terms as they are nonzero only for the states with an empty and a fully occupied orbital at the same site, which turned out to be of much higher energy. The matrix elements of (1) are evaluated in the 18-electron-state basis (190 basis functions in total). The eigenvalues of the model are obtained numerically by exactly diagonalizing (1) for a given set of parameters. We impose the relations $U > U' > J > 0$, $U' = U - 2J$ (for a derivation see the Supplemental Material [26]) and we take $t = 0.75$ eV [extracted from the splitting of the DOS on Fig. 1(d)]. As the p levels of N atoms are higher in energy than those of O, we take $\epsilon_m = 0.5$ eV for N and zero for O. The p_z orbitals which are omitted from the model are considered to be always filled and have only an effect of a constant shift on the on-site energies ϵ_m.

Figure 2(b) shows a $(U - 2J)$ vs U phase diagram, resulting from Hamiltonian (1) for $V = 0$ and $V = 0.2$ eV. The black lines denote the boundaries between the phases I, II, III, and IV, corresponding to different sequences of energetic stability of OAs [see Fig. 2(c)]. We find that the FM (xy) state is the lowest-energy one for the phases II, III and IV. However, for almost all U and J values, the AFM (xx) state (phase I) is the ground state if $V = 0$, contradicting our *ab initio* results [26]. Moreover, at $V = 0$ the sequence of DFT states from Table I (phase III) is not reproduced. In contrast, at finite V the whole sequence of DFT states is reproduced for a wide range of physically relevant values of U and J. Hence, the intersite Coulomb interaction V, which defines the repulsion of electrons on N.N. p orbitals directed toward each other, is crucial for stabilizing the FM state in doped insulators with partially occupied p orbitals like MgO:N.

In summary, we have shown that the physics of spin-polarized holes of N-doped MgO is largely determined by p-electron correlation effects. For a single impurity, the splitting of the N $2p$ states at finite U is mainly an electronic effect, enhanced by the lattice distortions. Moreover, the p-electron correlations lead to a spin and orbital arrangement of the $2p$-hole states of the N-N dimer, resulting in a FM coupling between T-shaped orbitally arranged spin-polarized p holes. The FM state is realized at reasonable values of U and J, if an intersite Coulomb repulsion V is accounted for. Considering the small value of $V \approx 0.2$ eV necessary to drive the phase transition from an AFM to a FM ground state, and the fact that the directional nature of the p orbitals controls the strength of the intersite Coulomb repulsion, we conjecture that our finding affects all oxides where magnetism is due to p electrons or defects in the p-electron systems.

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*Corresponding author.
i.slipukhina@fz-juelich.de

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