Is N-doped SrO magnetic? A first-principles view

Hua Wu

Laboratory for Computational Physical Sciences,
Surface Physics Laboratory, and Department of Physics,
Fudan University, Shanghai 200433, China
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N-doped SrO seems to be one of the model systems for $d^0$ magnetism, in which magnetism (or ideally, ferromagnetism) was ascribed to the localized N 2$p$ spins mediated by delocalized O 2$p$ holes. Here we offer a different view, using density functional calculations. We find that N-doped SrO with solely substitutional N impurities as widely assumed in the literature is unstable, and instead that a pairing state of substitutional and interstitial N impurities is significantly more stable and has a much lower formation energy than the former by 6.7 eV. The stable $(N_{\text{sub}}^- N_{\text{int}})^{2-}$ dimers behave like a charged $(N_2)^{2-}$ molecule and have each a molecular spin=1. However, their spin-polarized molecular levels lie well inside the wide band gap of SrO and thus the exchange interaction is negligibly weak. As a consequence, N-doped SrO could not be ferromagnetic but paramagnetic.

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In extensive search of magnetic semiconductors, $d^0$ ferromagnet recently draws a lot of attention. It has no magnetic transition-metal or rare-earth element present and is free of the issue of clustering of magnetic elements, which, however, has been quite often addressed for transition-metal doped semiconductors. Thus, an observed $d^0$ ferromagnetism could be intrinsic, and it is important both technologically and in the viewpoint of fundamental physics.

Very recently, a group of density functional calculations suggest that when N...
or C is doped into oxide semiconductors and insulators, the 2p hole carriers introduced by those substitutional impurities would be spin-polarized. Due to the dual character of the 2p holes—a Hund exchange as strong as in 3d transition metals and delocalization of its orbital \[12\], \(d^0\) ferromagnetism could be established for the localized N or C 2p-hole spins mediated by the delocalized O 2p holes. In this respect, those calculations using the local-density approximation (LDA) or the generalized gradient approximation (GGA) very often give a ferromagnetic and half-metallic band structure. In strong contrast, several calculations using the LDA plus Hubbard \(U\) method \[21\] or with a self-interaction correction \[22, 23\], both taking into account a correlation effect of localized electrons, show that the 2p hole state would be orbitally polarized and associated with a Jahn-Teller distortion, thus giving rise to an insulating solution with a negligibly weak magnetic coupling.

In the present Letter, using density functional calculations, we reinvestigate N-doped SrO, a recently proposed model system of the \(d^0\) ferromagnet \[12\]. We will demonstrate that a sole substitution of N for O in SrO as widely assumed in the literature is energetically highly unfavorable, and instead that a pairing state of substitutional and interstitial N dopants is much more stable. The resultant \((N_{\text{sub}}-N_{\text{int}})^2^-\) dimers carry each a molecular spin=1, and their spin-polarized levels lie well inside the wide band gap of SrO. As a result, N-doped SrO seems not to be a ferromagnetic half-metal with an atomic spin as often predicted in the literature, but a paramagnetic insulator with a molecular spin. Thus, this work suggests that much care needs to be taken when categorizing N-doped oxide semiconductors and insulators into the \(d^0\) ferromagnet.

We performed LDA calculations, using the full-potential augmented plane wave plus local orbital code (WIEN2k) \[24\]. The experimental lattice constant of 5.14 Å was used for SrO. A \(2\times2\times2\) supercell was introduced to simulate the substitutional and interstitial N impurities. The muffin-tin spheres were chosen to be 2.5 Bohr for Sr and 1.1 Bohr for O and N, the plane-wave cutoff of 12 Ry for the interstitial wave functions, and a \(5\times5\times5\) \(k\)-point mesh for integration over the Brillouin zone. Structural relaxations were carried out till the atomic force is less than 50 meV/Å. Note that our calculations using GGA gave almost the same results as LDA.

We first calculate two isolated \(N_{\text{sub}}\) impurities in the \(\text{Sr}_{32}\text{O}_{30}\text{N}_2\) supercell having the N-
FIG. 1: (Color online) Total DOS (red thin curves) and N 2p DOS (blue bold curves) calculated by LDA for a Sr$_{32}$O$_{30}$N$_2$ (2×2×2) supercell having two isolated substitutional N impurities. The upper (lower) panel shows the spin up (down) channel. Fermi level is set at zero energy. It is calculated to be a ferromagnetic half-metal having an atomic spin=1/2 carried mainly by each N$^{2-}$ impurity.

N distance of 8.9 Å. This distance is so long that this structure also mimics single N$_{sub}$ impurities. The calculation gives a half-metallic solution as reported in the literature. The obtained density of states (DOS) is shown in Fig. 1. This is because each N$_{sub}$ impurity introduces one 2$p$ hole and the strong Hund exchange makes the N 2$p$ majority-spin orbitals fully occupied and the minority-spin orbitals 2/3 filled. The sharp DOS peak at the Fermi level suggests that this structure could be unstable. The LDA calculations, due to a self-interaction error of localized electrons, overestimate electron delocalization, and thus a (long-range) ferromagnetic exchange interaction between the N$_{sub}$ impurities via the O 2$p$ is highly overestimated [21–23].

As N atom has a high electronegativity and the 2$p$ hole state of the N$_{sub}$ impurities in SrO would be unstable, the N$_{sub}$ impurities could prefer a pairing. We therefore calculate the pairing state, assuming two N$_{sub}$ impurities sitting on two nearest neighboring O sites (with the distance of about 3.6 Å). After a structural relaxation, the pairing state is found to have a lower energy than the above isolated impurity state by 170 meV and the two N$_{sub}$ impurities move closer by only 0.12 Å (each N$_{sub}$ impurity displaces from the ideal O vacancy site by 0.06 Å). Obviously, this is not a true pairing state, in view of the small energy gain.
(in terms of a chemical bonding energy) and the long N-N distance (of 3.5 Å). The obtained solution is still a ferromagnetic half-metal with spin=1/2 for each N\textsubscript{sub} impurity (not shown here). If that were a true pairing state, the solution would be a nonmagnetic insulator having closed molecular orbitals of the \((N\textsubscript{sub}-N\textsubscript{sub})^4^-\) dimers (cf. Fig. 2(c), with two more electrons filling up the \(pp\pi^*\) antibonding state, and leaving only the highest-level \(pp\sigma^*\) antibonding state unoccupied). But if the N\textsubscript{sub} impurities formed a dimer and thus strongly displaced from the ideal O vacancy sites, there would be a huge energy cost associated with the large lattice deformation. This would prevent the N\textsubscript{sub} impurities forming the dimers.

So far, the stability of the solely substitutional N impurities in SrO has been a remaining issue. As SrO has a large lattice spacing, interstitial N impurities \(N\textsubscript{int}\) are also possible, in addition to the widely assumed N\textsubscript{sub} impurities. As a result, a N\textsubscript{sub}-N\textsubscript{int} pairing state could be a right way to enhance the stability of N-doped SrO. This is indeed the case, as supported by the following calculations.

We then calculate the \(Sr_{32}O_{31}N_2\) supercell having one N\textsubscript{sub} impurity and one N\textsubscript{int} impurity nearby. After a full structural relaxation, the N\textsubscript{sub} impurity displaces from the ideal O vacancy site, and the initialized N\textsubscript{sub}-N\textsubscript{int} pair becomes a \((N_2)^2^-\) dimer, which symmetrically straddles the O vacancy site along a body diagonal of the cubic supercell, see Fig. 2(b). The resultant dimer has a short bondlength of 1.25 Å and thus gains a lot of energy due to the strong chemical bonding. Taking the free O\textsubscript{2} molecules as a reservoir, we compare the total energy of the supercells \(Sr_{32}O_{30}N_2\) (plus 1/2 O\textsubscript{2}) and \(Sr_{32}O_{31}N_2\). We find that the latter having the \((N_2)^2^-\) dimer has a much lower formation energy than the former by 6.7 eV. Thus the stability of N-doped SrO is indeed significantly enhanced via the dimerization of the N\textsubscript{sub}-N\textsubscript{int} impurities, compared to the sole N\textsubscript{sub} impurities widely assumed in the literature. The molecular level diagram of the \((N_2)^2^-\) dimer is schematically plotted in Fig. 2(c). The \(pp\pi^*\) antibonding state is half filled and thus the \((N_2)^2^-\) dimer has a molecular spin=1 like the gas-phase O\textsubscript{2} molecules. A similar molecular magnetism was studied in our previous work \[8\] and addressed in a recent review article \[9\]. Note, however, that the spin-split \(pp\pi^*\) level lies well inside the wide band gap of SrO (albeit the experimental gap of 5.3 eV is underestimated to be 3.5 eV by LDA), see the insulating solution shown in Fig. 2(a). As a consequence, the exchange interaction between those magnetic dimers, if
any, would be superexchange like and tiny. This is indeed supported by our calculations which show that an antiferromagnetic state has ‘lower’ energy than a ferromagnetic state by only 1 meV. Those calculations were performed for a Sr$_{32}$O$_{30}$N$_4$ supercell, which has two (N$_2$)$_2^-$ dimers symmetrically straddling the corner and body-center oxygen vacancy sites, respectively, along a body diagonal of the 2×2×2 supercell. The inter-dimer distance (from one center to the other center) is 8.9 Å. The intra-dimer N-N distance remains to be 1.25 Å after a full atomic relaxation. Taking the computational accuracy into account, we could propose that practically there is no magnetic coupling between those magnetic dimers. Thus,
N-doped SrO would be a paramagnetic insulator.

To summarize, using LDA electronic structure calculations, we cast a doubt on the suitability of handling N-doped SrO as a model system of the $d^0$ ferromagnet. Our calculations show that the solely substitutional N impurities in SrO, widely assumed in the literature, are unstable. The corresponding ferromagnetic half-metallic solution with atomic $2p$ hole states could thus be an artifact. Instead, we find that a $\text{N}_{\text{sub}}-\text{N}_{\text{int}}$ pairing state, with $(\text{N}_2)^{2-}$ dimers each straddling an oxygen vacancy site symmetrically, is much more stable. Although those $(\text{N}_2)^{2-}$ dimers have each a molecular spin=1, their magnetically active levels lie well inside the wide band gap of SrO and thus the superexchange interaction between those magnetic dimers is negligibly weak. As a consequence, N-doped SrO could not a ferromagnetic half-metal with an atomic spin, but a paramagnetic insulator with a molecular spin. As the atomic $2p$ hole state has quite often been used to predict the $d^0$ ferromagnetism in the N or C doped oxide semiconductors and insulators, the present study provides a warning message against such predictions.

[1] T. Dietl, Nat. Mater. 9, 965 (2010).
[2] J. M. D. Coey, Solid State Sci. 7, 660 (2005).
[3] C. D. Pemmaraju and S. Sanvito, Phys. Rev. Lett. 94, 217205 (2005).
[4] A. Zunger, S. Lany, and H. Raebiger, Physics 3, 53 (2010).
[5] H. Pan, J. B. Yi, L. Shen, R. Q. Wu, J. H. Yang, J. Y. Lin, Y. P. Feng, J. Ding, L. H. Van, and J. H. Yin, Phys. Rev. Lett. 99, 127201 (2007).
[6] S. Zhou, Q. Xu, K. Potzger, G. Talut, R. Grötzschel, J. Fassbender, M. Vinnichenko, J. Grenzer, M. Helm, H. Hochmuth, M. Lorenz, M. Grundmann, and H. Schmidt, Appl. Phys. Lett. 93, 232507 (2008).
[7] J. A. Chan, S. Lany, and A. Zunger, Phys. Rev. Lett. 103, 016404 (2009).
[8] H. Wu, A. Stroppa, S. Sakong, S. Picozzi, M. Scheffler, and P. Kratzer, Phys. Rev. Lett. 105, 267203 (2010).
[9] O. Volnianska and P. Boguslawski, J. Phys.: Condens. Matter 22, 073202 (2010).
[10] Yu Liu, Gang Wang, Shunchong Wang, Jianhui Yang, Liang Chen, Xiubo Qin, Bo Song, Baoyi Wang, and Xiaolong Chen, Phys. Rev. Lett. 106, 087205 (2011).
[11] K. Kenmochi, M. Seike, K. Sato, A. Yanase, and H. Katayama-Yoshida, Jpn. J. Appl. Phys. 43, L934 (2004).
[12] I. S. Elfimov, A. Rusydi, S. I. Csiszar, Z. Hu, H. H. Hsieh, H.-J. Lin, C. T. Chen, R. Liang, and G. A. Sawatzky, Phys. Rev. Lett. 98, 137202 (2007).
[13] L. Shen, R. Q. Wu, H. Pan, G. W. Peng, M. Yang, Z. D. Sha, and Y. P. Feng, Phys. Rev. B 78, 073306 (2008).
[14] Haowei Peng, H. J. Xiang, S.-H. Wei, Shu-Shen Li, Jian-Bai Xia, and Jingbo Li, Phys. Rev. Lett. 102, 017201 (2009).
[15] Xiangyang Peng and Rajeev Ahuja, Appl. Phys. Lett. 94, 102504 (2009).
[16] S. W. Fan, K. L. Yao, and Z. L. Liu, Appl. Phys. Lett. 94, 152506 (2009).
[17] P. Mavropoulos, M. Ležaić, and S. Blügel, Phys. Rev. B 80, 184403 (2009).
[18] N. Kapila, V. K. Jindal, and H. Sharma, J. Phys.: Condens. Matter 23, 446006 (2011).
[19] Q. J. Wang, J. B. Wang, X. L. Zhong, Q. H. Tan, and Y. C. Zhou, Europhys. Lett. 95, 47010 (2011).
[20] I. Slipukhina, P. Mavropoulos, S. Blügel, and M. Ležaić, Phys. Rev. Lett. 107, 137203 (2011).
[21] V. Pardo and W. E. Pickett, Phys. Rev. B 78, 134427 (2008).
[22] A. Droghetti, C. D. Pemmaraju, and S. Sanvito, Phys. Rev. B 78, 140404(R) (2008).
[23] A. Droghetti and S. Sanvito, Appl. Phys. Lett. 94, 252505 (2009).
[24] P. Blaha, K. Schwarz, G. Madsen, D. Kvasnicka, and J. Luitz, WIEN2k, 2001. ISBN 3-9501031-1-2.