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# Magnetizing Oxides by Substituting Nitrogen for Oxygen

I. S. Elfimov,[1] A. Rusydi,[2] S. I. Csiszar,[3] Z. Hu,[4] H. H. Hsieh,[5] H.-J. Lin,[5] C. T. Chen,[5] R. Liang,[1] and G. A. Sawatzky[1]

[1]*Department of Physics and Astronomy, University of British Columbia,*
*6224 Agricultural Road, Vancouver, British Columbia, Canada, V6T 1Z1*
[2]*Institut für Angewandte Physik, Universität Hamburg, Jungiusstraße 11, D-20355 Hamburg, Germany*
[3]*Chemical Physics Laboratory, Materials Science Centre, University of Groningen,*
*Nijenborgh 4, 9747 AG Groningen, The Netherlands*
[4]*II. Physikalisches Institut, Universität zu Köln, Zülpicher Straße 77, D-50937 Köln, Germany*
[5]*National Synchrotron Radiation Research Center, 101 Hsin-Ann Road, Hsinchu 30077, Taiwan*

We describe a possible pathway to new magnetic materials with no conventional magnetic elements present. The substitution of nitrogen for oxygen in simple nonmagnetic oxides leads to holes in N $2p$ states which form local magnetic moments. Because of the very large Hund's rule coupling of Nitrogen and O $2p$ electrons and the rather extended spatial extent of the wave functions these materials are predicted to be ferromagnetic metals or small band gap insulators. Experimental studies support the theoretical calculations with regard to the basic electronic structure and the formation of local magnetic moments. It remains to be seen if these materials are magnetically ordered and, if so, below what temperature.

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Since the discovery of ferromagnetism in Mn-doped GaAs [1], the study of magnetic impurities in nonmagnetic traditional semiconductors has become a major trend in the field called diluted magnetic semiconductors (DMS). Recently, it was proposed that oxide based DMS form another class of materials with promise for ferromagnetism at temperatures even higher than are currently achieved with III-V semiconductors [2]. Following this prediction, several ZnO and $TiO_2$ based systems have been reported to show ferromagnetism at room temperature if substituted with $3d$ elements [3,4].

Nevertheless, in spite of accelerated interest in these materials, the exact mechanism responsible for the observed magnetic properties continues to be strongly debated in the literature. Several studies reported strong evidence of phase separation and formation of ferromagnetic clusters suggesting a nonintrinsic behavior not suitable for technological applications. In addition, some of ZnO:Mn and Co-doped systems were reported to show only paramagnetic rather than ferromagnetic properties [5–8]. It is believed that additional hole doping is needed to stabilize the ferromagnetic ground state in such DMS [9,10]. Note that simple substitution of $Mn^{2+}$ for divalent Zn in ZnO, for example, does not generate any extra carriers in itself. This is in contrast to Mn-doped GaAs where Mn introduces one hole per substituted cation. The interaction between these holes and electrons in $3d$ impurity states is one of the critical elements in the physics of diluted magnetic semiconductors [2,11,12].

Another important factor is the strong Hund's rule coupling $J_H$ that favors a high-spin configuration on the impurity site. Note that the large splitting between occupied spin up and unoccupied spin down states in $Mn^{2+}$ impurities is only partially due to the Coulomb repulsion $U$ which

is actually strongly reduced in a solid. $J_H$, on the other hand, is hardly reduced from its atomic value of about 0.9 eV per spin pair on average for the series of $3d$ TM's [13,14]. In this context, it is worthwhile to note that strong effective Hund's rule coupling between the carriers bound to vacancies was recently proposed as another way to introduce magnetism in nonmagnetic semiconductors [15]. The origin of such strong coupling in that case is, however, in the kinetic energy and symmetry of the molecular orbitals rather than in local, on-site interactions.

It is interesting to realize that the lowest energy configuration for two holes in $2p$ orbitals of oxygen or nitrogen is a spin triplet ($^3P$) configuration and the energy required to reach the first exited, spin singlet $^1D$, is 1.47 eV in the case of atomic O [16]. Note that the Hartree-Fock value of $J_H$ for $3d$ electrons in Cu, for example, is 1.45 eV [13]. This demonstrates that there is no reason why a system with holes in anion $p$ bands could not be magnetic provided the band width is not too large.

Auger spectroscopy studies of simple oxides show that $F^0$ integral for two holes in an O $2p$ orbital is 4–7 eV [17,18]. In the case of $Cu_2O$ the $F^2$ integral is found to be 6 eV that corresponds to 1.2 eV for $J_H$ [19,20].

In spite of such striking similarities, there are several important difference between TM $3d$ orbitals and oxygen $2p$ in oxides. First the oxygen $2p$ bands are usually full in ionic oxides leaving no room for unpaired spins. Even in the hole doped cuprates the density of O holes is small so that the effect of this Hund's rule coupling will be rather small. An interesting exception is $CrO_2$ in which oxygen based bands cross the Fermi energy and indeed there is unpaired spin density in O [21]. Secondly the much larger spatial extend of the O $2p$ orbitals which could facilitate longer range exchange interactions. Note that $d$-$d$ hopping

integrals ($t_{dd}$) scale as the inverse of the fifth power of interatomic distance whereas $t_{pp} \sim 1/r^2$ [22]. The consequence of this is twofold. First the larger spatial extend will cause large bandwidths which will compete with the tendency towards ferromagnetism. Larger lattice constants as in SrO can compensate for this. Secondly, the larger hopping integrals will cause more delocalization over neighboring atoms resulting in longer range exchange interactions. The first is unfavorable but the second favorable. To get a win-win situation in which both effects favor ferromagnetism we suggested the use of N substitution for O. $N^{2-}$ has one less electron and because of the lower binding energy the N $2p$ states will be closer to the chemical potential than the O $2p$ states, forming a relatively narrow impurity band with one hole per N situated just above the chemical potential. We note that such a substitution has recently been discussed in the context of ferromagnetism in Mn-doped ZnO, for example, where it is used to increase the ferromagnetic coupling between Mn impurities [9,10]. In the present Letter we present theoretical arguments combined with some experimental support that substitution of nitrogen for oxygen in simple band insulators such as SrO is, in itself, sufficient to produce DMS. This reveals a whole class of new materials whose magnetic properties are determined solely by the interaction between the carriers in $p$ rather than $d$ or $f$ atomic shells.

SrO has the rock salt crystal structure with a lattice constant of 5.16 Å. It is a nonmagnetic band insulator with a forbidden gap of 5.3 eV. The LDA-calculated gap is 3.9 eV. In contrast to TM in III-V semiconductors, nitrogen substitution in oxides can be substantially higher provided that one uses molecular beam epitaxy (MBE) methods to introduce N [23]. It is, therefore, interesting to investigate the effect of high Nitrogen concentration on the properties of $SrO_{1-x}N_x$.

Figure 1 shows the total and N $2p$ partial density of states calculated for 25% nitrogen substitution with computer code TB-LMTO [24] within the local spin density approximation (LSDA). As in the case of low N concentration, LSDA predicts a ferromagnetic metallic ground state. However, it is well known that LSDA usually fails to describe strongly correlated systems adequately. In order to account for correlation effects we performed a LSDA + $U$ calculation [25] with $U^{N2p} = U^{O2p} = 4.6$ eV, and $J_H^{N2p} = J_H^{O2p} = 1.2$ eV. The $\sqrt{2} \times \sqrt{2} \times 2$ supercell con-

sisted of 16 Sr, 12 O, and 4 N atoms and was used to account for possible orbital ordering of charge-compensating holes. Nitrogen was introduced to form a simple cubic superstructure in the original fcc O sublattice. In LDA + $U$ $SrO_{0.75}N_{0.25}$ is a semiconductor for $U > 3.3$ eV and for $U = 4.6$ eV it exhibits an energy gap of 0.7 eV in the ferromagnetic spin arrangement (Fig. 1) and 1.1 eV in the antiferromagnetic one. The magnetic moment calculated within the N muffin-tin sphere is $0.9\mu_B$ in all cases. The total magnetic moment per supercell in the ferromagnetic calculation is $4\mu_B$. The orbital degeneracy is lifted via the mechanism of orbital ordering much as in the $3d$ transition metal oxides. The orbital ordering is actually frustrated if nitrogen is distributed over the lattice in the periodic fashion such as in a simple cubic superstructure. One possible hole-density configuration, which corresponds to the calculated ferromagnetic density of states, is shown in the inset of Fig. 1. We also note that, similar to manganites, spin and orbital degrees of freedom in these materials are strongly correlated, which influences drastically the low energy properties. Although, ferromagnetic and A-type antiferromagnetic solutions are nearly degenerate (the total energy difference between former and latter is 1 meV), the $G$-type of order is 0.19 eV higher in energy due to a transition from antiferro to ferro orbital ordering. This, of course is very sensitive to lattice spacing, crystal structure distortion, and morphology of the actual material. It is, therefore, really important to address these issues from an experimental point of view.

To demonstrate the difference in the spatial extend of the induced spin density between transition metal and ligand substitutions we compare first principle density functional calculations of 0.9% Mn and N substituted in SrO. As in the case of 25% N substitution, these calculations were performed for a simple cubic impurity superlattice. Within the bounds of the LSDA + $U$ approach, both systems are magnetic and insulating with the moment of 5 and $1\mu_B$ per supercell, respectively. We note that our LSDA calculations based on the supercell approximation agree with the coherent potential approximation results [26]. The LSDA + $U$ calculations of Mn-doped SrO were performed with $U^{Mn3d} = 2.34$ eV and $J_H^{Mn3d} = 0.89$ eV [13]. The values of $U$ and $J$ for O $2p$ were 4.6 and 1.2 eV, respectively. As one can see from Fig. 2, the spin density due to Mn is highly concentrated around the first nearest oxygen
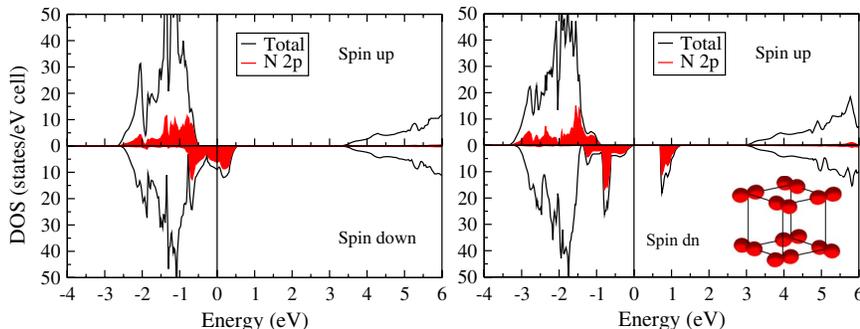


FIG. 1 (color online). Ferromagnetic total and N $2p$ partial densities of states calculated in LSDA (left panel) and LSDA + $U$ (right panel) for 25% N substitution. The LSDA + $U$ density of states is calculated with $U^{N2p} = U^{O2p} = 4.6$ eV and $J_H^{N2p} = J_H^{O2p} = 1.2$ eV. The zero of energy is at Fermi energy.
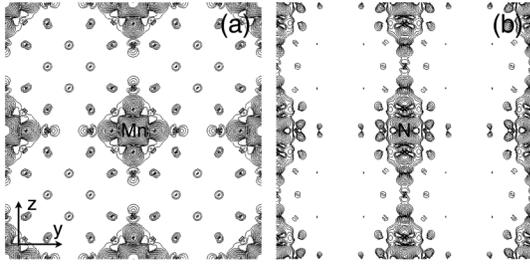
FIG. 2.   LSDA + $U$ spin density calculated for 0.9% Mn (a) and nitrogen (b) substitution in SrO with $U^{N2p} = U^{O2p} = 4.6$ eV, $J_H^{N2p} = J_H^{O2p} = 1.2$ eV, $U^{Mn3d} = 2.34$ eV, and $J_H^{Mn3d} = 0.89$ eV. Shown is a cut in the (100) plane of $6 \times 6$ super cell. Note that the charge-compensating hole resides in the N $p_z$ orbital. Lattice sites are not shown for clarity.

neighbors whereas for nitrogen it is spread out over several neighboring shells and it is rather directional. This, of course, directly follows from the spatial and angular dependences of the hopping parameters for $2p$ in comparison to $3d$ orbitals.

On the experimental side we tried first to prepare $SrO_{1-x}N_x$ by solid-state chemistry methods using powders of SrN and SrO but found in the end only phase separated materials or Sr nitroxides. However, the MBE results mentioned above suggest that the lower temperatures used in MBE growth together with the fact that only surface, and not bulk, diffusion is needed for layer-by-layer growth results in metastable materials with substitutional N. We note that this may be of general importance in other new systems such as phosphorous substituted sulfides, etc.

Films were grown epitaxial on MgO (100) single crystal under ultrahigh vacuum (UHV) conditions [27]. In order to produce films of high quality we use MBE. Reflection high energy diffraction (RHEED) was used to monitor the growth process. The periodic oscillations observed in the specular spot intensity of the high-energy electron beam reflected from the film surface are evidence for a layer-by-layer type of growth. Films with various concentrations of N were grown using NO gas as an oxidizing agent. We note that these samples are very hydroscopic and if not protected will deteriorate rapidly if exposed to air. The structure of the films was proven to be the same as the substrate (fcc), although (due to a large lattice mismatch) after several layers, having a different in-plane lattice constant then the substrate. This in-plane lattice constant turned out to be also dependent on N concentration, namely, increasing with increasing N content. Good low energy electron diffraction (LEED) images also confirm the high quality of the films. A more detailed description of the growth will be given elsewhere.

The composition of the films was checked by *in situ* measurements of x-ray photoemission spectroscopy (XPS). In Fig. 3 we show XPS spectra taken at room temperature on samples with 0%, 18%, and 25% nitrogen. In agreement with the results of band structure calculations, the N $2p$ peak is found to be about 2 eV lower in binding energy
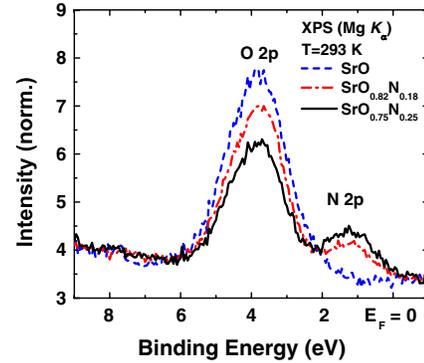


FIG. 3 (color online).   Room temperature XPS valence band spectra of $SrO_{1-x}N_x$ films. The zero of binding energy is at the Fermi level of copper. The SrO spectrum is shifted towards the low binding energy by 1.4 eV to match the energy of the O $2s$ core level in SrO and $SrO_{1-x}N_x$.

relative to the position of O $2p$ peak. The relative change in intensity of these two peaks upon doping strongly indicates that the growth process is indeed a process of substitution. This is also supported by RHEED and LEED data.

X-ray absorption spectroscopy (XAS) measurements performed on the NSRRC Dragon beam line in Taiwan confirm our XPS results. This experiment was carried out with the incident beam polarization parallel to the sample surface (001 surface of MgO and $SrO_{1-x}N_x$). In Fig. 4 we show XAS spectra taken in the total electron yield mode at the nitrogen and oxygen $K$ edges. The strong prepeak at the N $K$ edge strongly supports the existence of N $2p$ holes. The presence of a weaker O preedge structure supports the
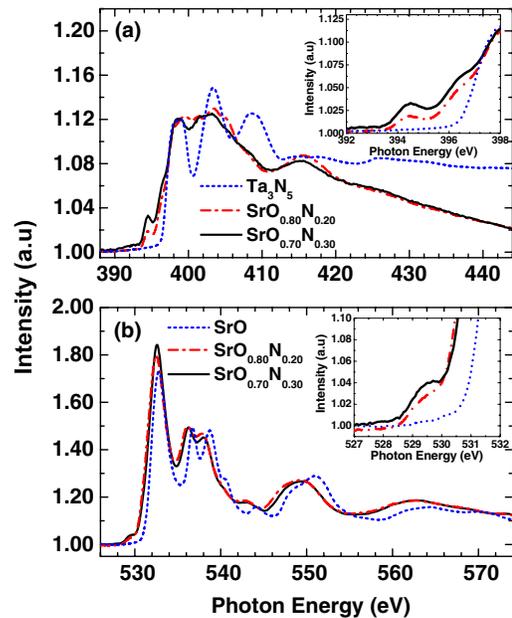


FIG. 4 (color online).   Room temperature x-ray absorption spectra with $E \perp c$ of $SrO_{1-x}N_x$ films, taken in the total electron yield mode at the nitrogen (a) and oxygen (b) $K$ edges. Note the preedge structure at 394.5 eV in (a) and 529.25 eV in (b).
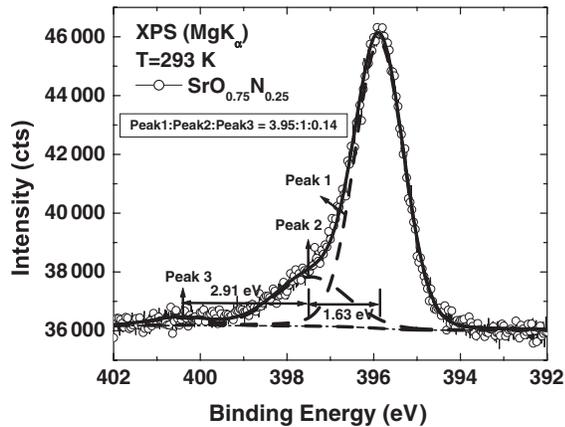
FIG. 5. Room temperature N 1$s$ core-level XPS spectra of $SrO_{1-x}N_x$ film with $x0.25$. The three peak structure is due to a local spin 1/2 moment.

suggestion of delocalization of the N 2$p$ hole states onto neighboring O. Note that neither $Ta_3N_5$ nor SrO has such a feature in their $K$ edge spectra.

Nitrogen 1$s$ core-level XPS was used to examine the degree of charge and spin localization. If charge-compensating holes reside primarily in the nitrogen 2$p$ orbitals, the spectra of $SrO_{1-x}N_x$ films should be similar to one found in gas phase NO with a double peak structure, due to the exchange coupling of the unpaired 2$p$ spin with the core hole. In the absence of all other interactions, the intensity ratio between a triplet (lower binding energy) and singlet (higher binding energy) peak should be 3:1. Of course, in the real material this is often not the case and it is rather common that the experimental ratio is large [28]. We find that in the $SrO_{0.75}N_{0.25}$ sample the ratio is 4:1 (Fig. 5). The observed energy separation between singlet and triplet peaks is 1.6 eV. This is consistent with 1.5 eV found in NO which has a spin of 1/2 localized mainly on N. We note that the high-binding-energy satellite peak (peak 3 in Fig. 5) originates from the shake-off energy loss processes involving band gap transitions and its energy position agrees with band gap of SrO.

The electrical resistivity measurements of the films have been performed *in situ* using gold contacts. The contacts were evaporated on the substrate and material was grown on top. The resistivity of highly doped $SrO_{0.75}N_{0.25}$ films was found to be in the range of 0.1 Ohm cm which is typical for small gap semiconductors or bad metals.

In conclusion, our experimental and theoretical results show that substitution of nitrogen for oxygen in simple nonmagnetic and insulating oxides results in a dramatic change of the electronic and perhaps also magnetic properties. This opens a possible path to new classes of magnetic semiconductors whose properties are solely determined by the interactions between the holes in ligand $p$ orbitals.

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