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Electronic structure of $3d$-transition-metal monoxides: surface and bulk-point-defects

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Abstract

We discuss exchange coupling constants of a Heisenberg model in NiO and NiO(001), obtained with *ab initio* SIC-LSD method. In addition, using the same approach, we study vacancy induced half-metallicity in NiO and MnO.

Transition-metal (TM) oxides are potential candidates for spintronics applications, as they might give rise to high spin-polarisation [1]. For engineering spintronics devices it is crucial to know the electronic and magnetic structure of these materials at the quantum-mechanical level. Also, characterization of properties at an atomic level is important for experimental interpretation or providing parameters for theoretical investigations.

Due to strong correlations within the TM-d-electron states, local spin density (LSD) approximation to density-functional theory (DFT) is not able to yield an adequate description of these materials. Self-interaction corrected (SIC)-LSD, on the other hand, provides reasonable electronic structure of these materials [2,3].

Here we report on an application of SIC-LSD, in the supercell implementation, to study magnetic interactions in NiO and NiO (001) [4]. In addition, we discuss the effect of low concentration of cation vacancies on the magnetic properties of such TM oxides as MnO and NiO [5].

The magnetic interactions in bulk TM oxides can be represented by an isotropic Heisenberg model with finite range interaction of localised classical spin moments residing on the TM-sites:

$$H = - \sum_{ij}^{nn,nnn} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j, \qquad (1)$$

including only nearest- (nn) and next nearest-neighbour (nnn) interactions (exchange coupling constants J_1^b and J_2^2). To extract the exchange constants we map the *ab initio* SIC-LSD total energies of different magnetic configurations onto the Heisenberg-model. For bulk NiO, SIC-LSD gives coupling constants of $J_1^b = 1.8\text{meV}$ and $J_2^b = -11\text{meV}$ which are in accord with the experimental values of $J_1^b = 0.7\text{meV}$ and $J_2^b = -9.5\text{meV}$

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[6], respectively. For the (001) surface of NiO, we distinguish between coupling within the layers ($J_\perp$) and coupling between the layers ($J_\parallel$). Applying the same approach, we have obtained for the coupling in the surface layer a decrease of 10%, with respect to the bulk, whereas for the coupling from the surface layer into the deeper lying layers an increase of 20-30% has been found. The other coupling constants are essentially unaffected, i.e., they are similar to the bulk values. Our results compare well with cluster calculations [7].

Recently, it has been shown that cation vacancies in diamagnetic oxides with rocksalt-structure can induce half-metallic behaviour [8]. Here we show that introducing cation vacancies into magnetic oxides, NiO and MnO, also leads to half-metallic behaviour. Our calculations for 3.125% of vacancies, introduced onto one spin sublattice (realizing $Mn_{0.97}O$ and $Ni_{0.97}O$), give half-metallic behaviour for both antiferromagnetic (AF2) and ferromagnetic (FM) orders. Table 1 shows the to-

Table 1
Total magnetic moments of the supercell with and without vacancy. IS and HM denote insulating and half-metallic states, respectively.

	m^{total} in μ_B	state
MnO AF2 *bulk*	0	IS
AF2 with vacancy	3	HM
NiO AF2 *bulk*	0	IS
AF2 with vacancy	0	HM

tal spin magnetic moments of MnO and NiO without and with vacancies as calculated in the SIC-LSD supercell (consisting of 32 formula units) approach. In all the cases we obtain integer total magnetic moments. Most interestingly, a cation vacancy embedded into AF2-ordered NiO, gives total spin magnetic moment of zero, *i.e.,* this system is a half-metallic antiferromagnet [9]. The moments given in Table 1 imply that the spin polarization of neighbouring atoms, induced by vacancy creation, gives rise to a compensating integer moment of $2\mu_B$, which in case of NiO in the AF2 ordering, makes the total spin moment exactly zero μ_B.

A more detailed look at the distribution of moments around the vacancy for the case of MnO (the findings for NiO are similar) is displayed in Fig. 1.
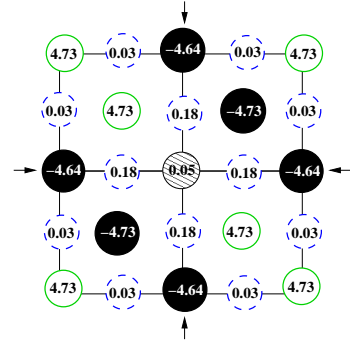

Fig. 1. Spin magnetic moments in the atomic spheres surrounding vacancy in the (100) plane of MnO. The underlying pattern of the supercell is AF2 (oxygen are shown with dashed circles, large black (filled) and white circles mark the underlying AF2 pattern, a cation vacancy is depicted in the center by a shaded circle). The respective moments of the ideal bulk structure are $m_{Mn}^{AF2} = \pm 4.73\mu_B$ and $m_O^{AF2} = 0\mu_B$ in our calculations. Small arrows indicate the positions of next nearest neighbours to the impurity.

As can be seen in the case of an underlying AF2 ordering, the oxygens around the vacancy exhibit a moment of $0.18\mu_B$ (in the bulk the oxygens are frustrated in the AF2 ordering and have no moment). In doing so they preserve the AF2 pattern which has been destroyed by taking out the Mn atom from the position occupied by the vacancy.

To conclude we note, that the induced half-metallicity of TM oxides survives a local 10% inward relaxation of the neighbouring oxygen atoms, but is lost when doubling the vacancy concentration.

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