

A Stable Half-metallic Ferromagnetic Material SrNiO₃: a Prediction from first Principles

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Abstract—Generalized gradient approximation (GGA) plus on-site Coulomb interaction corrections (GGA+*U*) method within the framework of density functional theory (DFT) is used to investigate the electronic structure of SrNiO₃. A series of on-site interaction *U* (*J* = 0.3 eV) values are employed in the calculations to investigate density of states (DOS) and local magnetic of Ni. We find that the ground state of SrNiO₃ always keeps a stable ferromagnetic state (FM), and presents half-metallic property when *U* is larger than 3.0eV. The majority spin band cross the Fermi level, showing a metallic property, while a robust band gap appears around the Fermi level in the minority spin band, showing a insulating behavior. The different behaviors of majority spin and minority spin show that the material is suitable for spin filtering. Our work provides important guidance for fabricating cubic SrNiO₃ and nickel-doped cubic oxides, experimentally.

Keywords—SrNiO₃; First principles; Ferromagnetic; Half-metallic; Density of states

I. INTRODUCTION

The ABO₃-type perovskite oxides have attracted tremendous amounts of attention because of their potential applications in future micro-electronic devices [1-3]. There have been limited studies on nickel oxide SrNiO₃ so far. Recently SrNiO₃ compounds with hexagonal space groups P63/mmc [4], and trigonal space group P321 [5] are reported. The simple cubic SrNiO₃ structure has not been fabricated so far. Considering some cubic transition-metal oxides (TMOs) such as SrMnO₃ [6], with a high symmetry, have rich magnetic property and potential applications, we wonder whether cubic SrNiO₃ have some useful properties. In cubic SrNiO₃, Ni is in Ni⁴⁺ state (3d⁶), close to half-filled state, which might bring about active performance on magnetism. Therefore we predict the properties of cubic SrNiO₃ using first-principles method. We mainly focus on four kinds of magnetic order, including FM, G-type antiferromagnetic (G-AFM), A-type antiferromagnetic (A-AFM) and C type antiferromagnetic (C-AFM). In G-AFM both the intra-plane and inter-plane (ab-plane) Ni coupling are antiferromagnetic. While in A-AFM, the intra-plane coupling is ferromagnetic and inter-plane coupling is antiferromagnetic. C-AFM means that the intra-plane coupling is antiferromagnetic while inter-plane coupling is ferromagnetic.

II. DETAILS OF CRYSTAL, MAGNETIC AND COMPUTATION

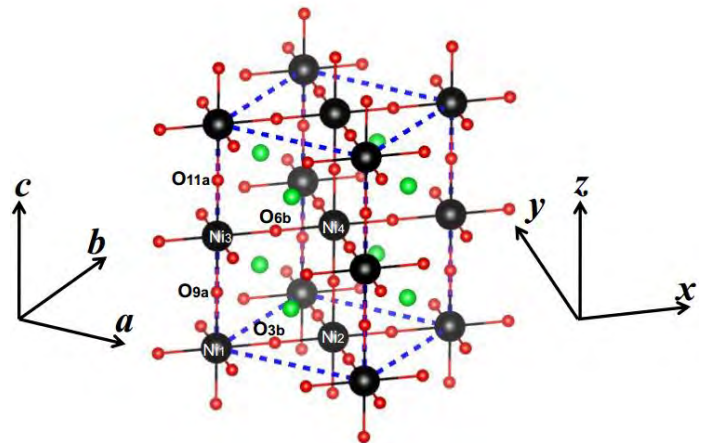


Figure 1. (Black solid line) Magnetic cell of SrNiO₃ with four formula units (f. u.). The space group is *Pm-3m*. The *abc* coordinate denotes the conventional coordinate system, based on which *xyz* coordinate is obtained by rotating 45 degree. The *x/y* direction is along Ni-O-Ni direction. O_{3b} and O_{6b} denote the *ab*-planes oxygen and O_{9a} and O_{11a} denote the apical oxygen along *z*-axis.

The initial lattice constants $a=b=c=3.85 \text{ \AA}$ are taken for cubic SrNiO₃ with a space group of *Pm-3m*. Fig. 1 shows the crystal structure within the $\sqrt{2} \times \sqrt{2} \times 2$ cell containing 20 atoms (named as Sr₁, Sr₂, Sr₃, Sr₄, Ni₁, Ni₂, Ni₃, Ni₄, O₁, O₂, O₃, O₄, O₅, O₆, O₇, O₈, O₉, O₁₀, O₁₁ and O₁₂). Based on non-spin-polarized calculations, four kinds of magnetic configurations are considered for the spin-polarized calculations. The spin combination of the Ni₁, Ni₂, Ni₃ and Ni₄ are + + + +, + - - +, + + - - and + - + - for FM, G-AFM, A-AFM and C-AFM configurations, respectively.

The computations are carried out by plane-wave pseudopotential method within density functional theory framework. The projector augmented wave (PAW) [7, 8] method, implemented in the Vienna *ab initio* simulation package (VASP) [9] is employed. For the exchange correlation potential we adopt generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof form [10]. The on-site Coulomb correlation corrections

approaches of rotationally invariant LSDA+ U method according to Liechtenstein [11] is employed. GGA + U

method is used to deal with the Ni 3d electrons for a better

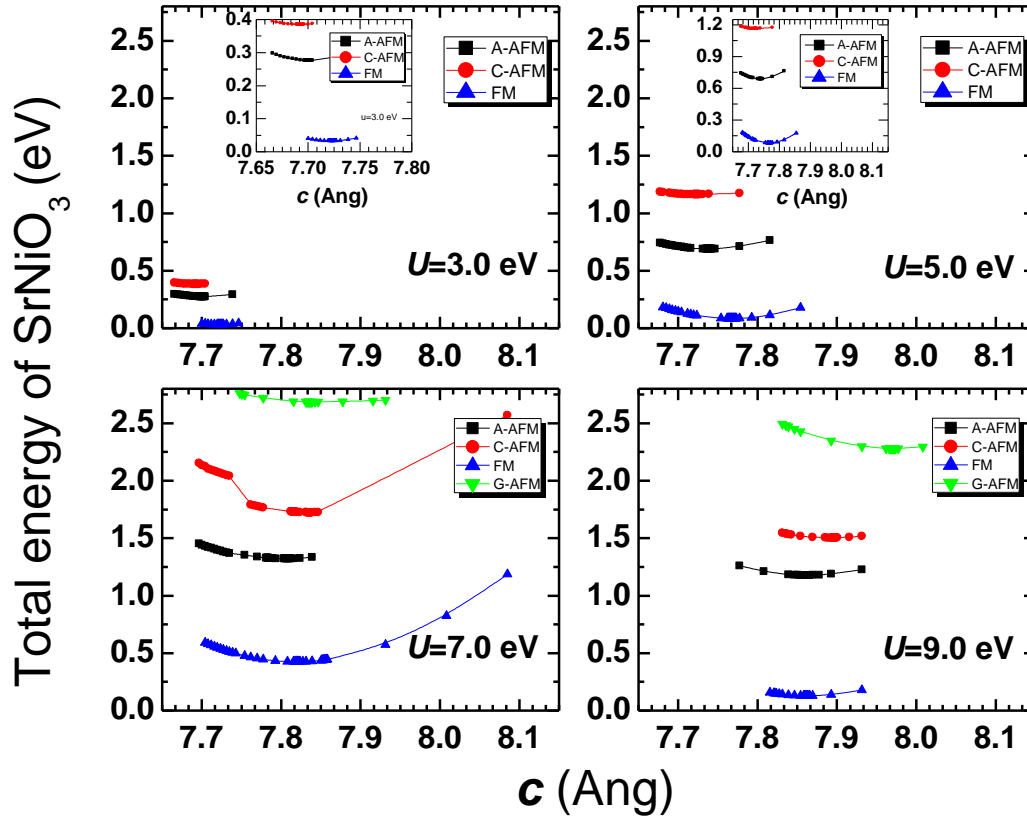


Figure 2. Total energy of four kinds of magnetic phase for U at 3.0 eV, 5.0 eV, 7.0 eV and 9.0 eV, respectively.

description of the electronic structure of SrNiO₃. A k mesh of $8 \times 8 \times 6$ is used with a plane-wave cutoff energy of 500 eV. In the present paper, we fix $J=0.3$ eV and set U as 3.0 eV, 4.0 eV, 5.0 eV, 7.0 eV, 9.0 eV, 11.0 eV, respectively.

III. RESULTS AND DISCUSSIONS

A. The total energies of SrNiO₃ for different magnetic configurations from GGA+ U calculations

The total energy calculations for different magnetic configurations (i.e. FM, G-AFM, A-AFM and C-AFM) from GGA+ U method are performed. The total energies for different magnetic configurations at $U=3.0$ eV, 5.0 eV, 7.0 eV and 9.0 eV are shown in Fig. 2, representatively.

From Fig. 2, one can see that among the four magnetic configurations, FM state gives the lowest total energy, no matter what kind of U value is taken. In the case of $U=3.0$ eV and $U=5.0$ eV, G-AFM solution cannot be obtained and they are absent in Fig. 2. To clearly show the trend of total energy with the lattice constant c , we add two insets (with a smaller energy scale) into the upper figures. When U is larger than 5 eV, the energy difference between FM and AFM becomes larger. Therefore, the FM ground state of SrNiO₃ is quite robust upon all of the U values employed in our calculations. Our results suggest that FM configuration has more chances to form, if one fabricates cubic SrNiO₃ experimentally.

B. Electronic and magnetic structure from GGA+ U calculations for FM.

From A., we've learned FM is the ground state.

Therefore, we will carry on detailed analysis on FM SrNiO₃. TABLE I. presents the magnetic moment of Ni₁ at FM state. The Ni₂, Ni₃ and Ni₄ have the same magnetic moments and therefore they are not shown. The evolution of the magnetic moments with increasing U is also shown in Fig. 3. One can see that the magnetic moment increases with U , which portends spin polarization of Ni becomes stronger and stronger. The 3d⁶ electrons in Ni⁴⁺ valence state can split into e_g (twofold degenerate) and t_{2g} (threefold degeneracy) in cubic symmetry. At high spin state,

TABLE I. THE MAGNETIC MOMENT (μ_B) OF Ni IN FM SrNiO₃ WITH U FROM 1.0 (eV) TO 11.0 (eV).

	Magnetic moment(μ_B)					
U (eV)	3.0	4.0	5.0	7.0	9.0	11.0
Ni	0.855	1.029	1.170	1.407	1.569	1.689

electron configuration consist of five spin-up electrons and one spin-down electron. As a consequence, the magnetic moment is $4\mu_B$. However, the maximum magnetic moment from TABLE I. is $1.689\mu_B (<4\mu_B)$, which means $Ni^{4+} 3d^6$ is not likely to be at high-spin state.

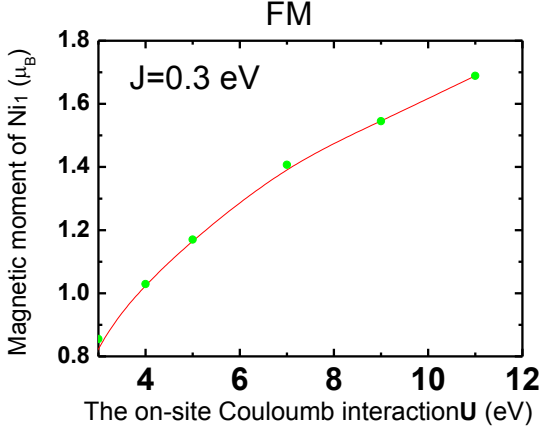


Figure 3. The magnetic moment as a function of on-site Coulomb interaction U (for J being fixed at 0.3 eV).

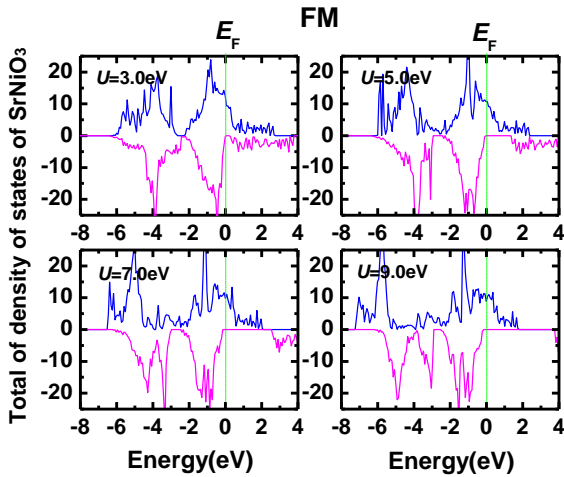
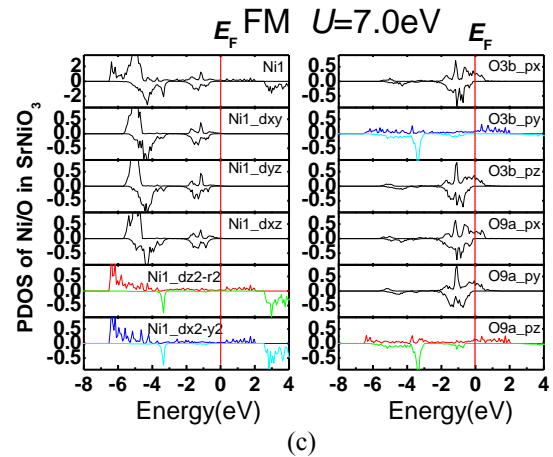
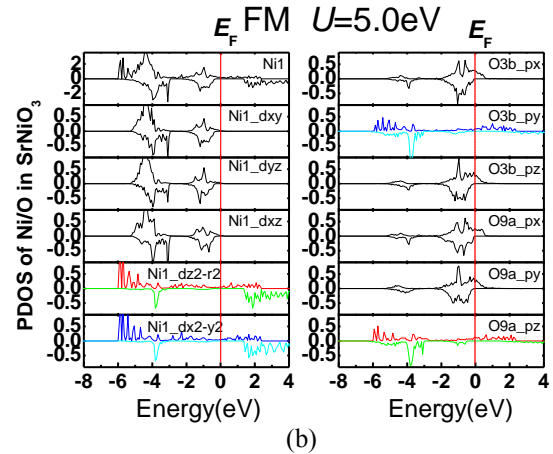
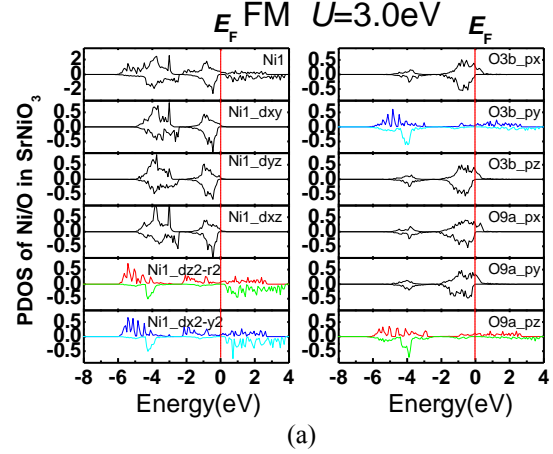


Figure 4. Total density of states (TDOS) of FM $SrNiO_3$ for U at 3.0 eV, 5.0 eV, 7.0 and 9.0 eV.

Fig. 4 shows the total density of states (TDOS) of FM $SrNiO_3$ from GGA+ U ($U=3.0$ eV, 5.0 eV, 7.0 eV and 9.0 eV). The main features of the TDOS is that the majority spin (i.e. spin-up) cross the fermi level, while a big band gap appear around E_F in the minority spin (i.e. spin-down) band. This is the characteristic of half-metallic property. We will explore the origin of the half-metallicity in the following.

Fig. 5 shows partial density of states (PDOS) of Ni $3d$ and O $2p$ from GGA+ U ($U=3.0$ eV, 5.0 eV, 7.0 eV and 9.0 eV). Twofold degenerate e_g levels include dz^2-r^2 and dx^2-y^2 and Three-fold degenerate t_{2g} levels include dxy , dyz and dxz . Spin polarization is negligible in t_{2g} orbitals, which is in agreement with the non-high-spin state of Ni^{4+} . On the contrary, the spin polarization of e_g orbits is very robust over the whole range of U employed in this article. The hybridization between Ni $3d_{3z^2-r^2}$ orbital and O $2p_z$ are so strong that noticeable magnetic behavior can be observed in O atom. The hybridization between Ni $3d_{x^2-y^2}$

y^2 orbital and O $2p_y$, also contribute a lot to the formation of magnetism of O atom. It is amazing that half-metallic property is mainly from O $2p$, not Ni $3d$. This can be understood according to a mechanism similar to the double exchange mechanism. The Ni^{4+} has a positive magnetic moment and one spin-up electron hop from the



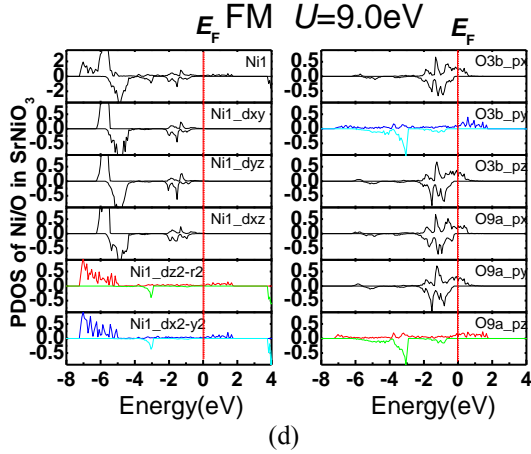


Figure 5. (a), (b), (c) and (d) show the PDOS of Ni $3d$ and $2p$ of O_{3b} and O_{9a} for U at 3.0 eV, 5.0eV, 7.0eV and 9.0eV (O_{3b} denotes the *ab*-plane O and O_{9a} denotes out-of-plane O). The majority is shown as positive and the minority spin as negative.

Ni^{4+} to the neighboring O. This demands the O has a negative spin so that they obey the Pauli exclusion principle. The second step is the spin-up electron continues to hop to another Ni and thus the hopping between neighboring Ni atoms is realized through the medium O atom. This is in agreement with the negative magnetic moments of O atoms.

Half-metallic (HM) materials have promising applications in electronics. They can be used as spin-injector materials [12] in spintronic devices [13]. Our work suggests a new method to prepare a robust half-metallic material, which can be obtained by using a cubic substrate (like the cubic $SrTiO_3$ and $SrMnO_3$ etc) or in a cubic circumstance of perovskite.

IV. CONCLUSIONS

A series of on-site Coulomb interaction U (J is fixed at 0.3 eV) are employed in GGA+ U calculations to explore the properties of cubic $SrNiO_3$. FM is found to be the ground state over a large range of U employed. A robust half-metallic property is obtained from all of the GGA+ U calculations with a series of U values. The promising half-metallic $SrNiO_3$ to be verified by experimental work.

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REFERENCES

- [1] Ma C L, Yang Z Q and Picozzi S. “*Ab initio* electronic and magnetic structure in $La_{0.66}Sr_{0.33}MnO_3$: Strain and correlation effects”. *Journal of physics: Condensed*, 2006, 18(32): 7717–7728.
- [2] Chen J M, Lee J M and Huang S W, et al. “Intra- and intersite electronic excitations in multiferroic $TbMnO_3$ probed by resonant inelastic X-ray scattering”. *PHYSICAL REVIEW B*, 2010, 82(9): 094442.
- [3] Miura K, Azuma M, Funakubo H. “Electronic and structural properties of ABO_3 : Role of the B-O coulomb repulsions for ferroelectricity”. *Materials*, 2011, 4(1): 1–338.
- [4] M. Zinkevich. “Constitution of the Sr–Ni–O system”. *Journal of Solid State Chemistry*, 178 2005, 178: 2818–2824.
- [5] Ewelina Ksepko. “Perovskite-type $Sr(Mn_{1-x}Ni_x)O_3$ materials and their chemical-looping oxygen transfer properties”. *International Journal of Hydrogen Energy*, 2014, 39: 812–8137.
- [6] Xing-Yuan Chen, Wei-ling Zhu and Shi-Yuan Lin, et al. “Theoretical study of magnetic phase transitions of cubic $SrMnO_3$ under physical and chemical pressures”. *Computational Materials Science*, 2014, 83: 394–397.
- [7] P. E. Blöchl. “Projector augmented-wave method”. *PHYSICAL REVIEW B*, 1994, 50: 17953–17979.
- [8] G. Kresse and D. Joubert. “From ultrasoft pseudopotentials to the projector augmented-wave method”. *PHYSICAL REVIEW B*, 1999, 59: 1758–1775.
- [9] G. Kresse and J. “Furthmüller. Efficient iterative schemes for *ab initio* total-energy calculations using a plane-wave basis set”. *PHYSICAL REVIEW B*, 1996, 54: 11169–11186.
- [10] J. P. Perdew, K. Burke and M. Ernzerhof. “Generalized Gradient Approximation Made Simple”. *Physical Review Letters*, 1996, 77: 3865-3868.
- [11] A. I. Liechtenstein, V. I. Anisimov and J. Zaanen. “Density-functional theory and strong interactions: Orbital ordering in Mott-Hubbard insulators”. *PHYSICAL REVIEW B*, 1995, 52 : R5467-R5470.
- [12] Zhi-Yuan Chen, in Xu and G.Y. Gao. “Half-metallic ferromagnetism with low magnetic moment in zinc-blende $TiBi$ from first-principles calculations”. *Journal of Magnetism and Magnetic Materials*, 2013,347: 14–17.
- [13] M. Yogeswari and G. Kalpana. “Electronic structure and half-metallic ferromagnetism in (C, Si, Ge and Sn) doped alkaline-earth sulfides: A first principles approach”. *Journal of Alloys and Compounds*, 2013, 573: 83–89.