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Investigation of electronic structure and half-metallic ferromagnetic behavior with large half-metallic gap in $Sr_{1-x}V_xO$

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Abstract In this study, we investigate the electronic structure and magnetic properties of V-doped rock-salt SrO as a $Sr_{1-x}V_xO$ ternary compound at concentration $x = 0.25$ by the use of first-principle calculations of density functional theory using the full potential linearized augmented plane wave method. The electronic structures of $Sr_{0.75}V_{0.25}O$ have a half-metallic character due to the metallic nature of majority-spin states and semiconducting features of minority-spin states. From results of the magnetic properties, we have found that the $Sr_{0.75}V_{0.25}O$ has a total magnetic moment of $3\,\mu_B$ and the p–d exchange coupling is ferromagnetic between V magnetic impurity and the host carriers of O atoms. The $Sr_{0.75}V_{0.25}O$ compound exhibits a wide half-metallic gap of $1.00\,eV$; this factor is a fundamental characteristic of half-metallic ferromagnetic materials for spintronics applications.

Keywords Electronic properties · p–d Exchange interaction · Magnetic moments · Half-metallic ferromagnetism

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1 Introduction

The technology of electronic and optoelectronic devices exploits the charge of electrons to store, transmit and process information, but beyond its charge, the electron possesses a magnetic moment (its spin). This characteristic is not used in classical electronics, since the charge carriers may have any spin, which gives a zero mean on the currents. The electron spin (or spintronics) approach [1] proposes to use this additional spin property of electrons in addition to their charge to control the electrons and creates spin currents in order to improve the performance of the spin storage of information [1,2]. The integration of this property (spin electronics) in semiconductor devices paves the way for a new generation of intelligent electronic or optoelectronic components for magnetic memory device applications. A revolution in spin electronics has been marked by the integration of this property in diluted magnetic semiconductors, which are promising materials for spintronics because they exhibit the stability of the ferromagnetism at temperatures higher than room temperature [3,4]. However, the expected advantage of spintronic devices with respect to the conventional electronic ones would be nonvolatility, increased data processing speed, increased transistor density and decreased power consumption [5].

Strontium oxide (SrO) belongs to the family of alkaline earth oxides, which attract considerable interest because of their applications in various technologies, ranging from

catalysis to microelectronics [6]. Several theoretical methods have been applied to investigate the structural, electronic and elastic properties of alkaline earth oxides [7–10]. SrO crystallizes in the rock-salt NaCl (B1) structure under normal conditions, and it undergoes a structural phase transition from phase B1 to B2 at a pressure of 36($\pm$4) GPa [11]. Recently, Berri et al. [12] have predicted the electronic structure and magnetic properties of Cr and Mn doped SrO for possible use in spintronics and magnetoelectronics applications. They found that $Sr_{1-x}Cr_xO$ and $Sr_{1-x}Mn_xO$ at concentrations x = 0.25 and 0.75 of Cr and Mn atoms, are half-metallic ferromagnetic with spin polarization of 100 % at Fermi level. To the best of our knowledge, there are no experimental or theoretical works on the study of electronic and magnetic properties for vanadium (V)-doped SrO.

The objective of this work is to study the electronic and ferromagnetic properties of SrO doped with vanadium (V) impurity in the NaCl (B1) structure. We investigated the half-metal ferromagnetic behavior and the spin-polarized electronic structures of $Sr_{0.75}V_{0.25}O$ in order to predict the use of this material for spintronics applications. We performed the calculations by using WIEN2K code based on the linearized augmented plane wave method (FP-LAPW) [13], where the exchange and correlation energy are treated by the generalized gradient approximation (GGA-WC) of Wu and Cohen [14].

2 Method of calculations

In our study, we used the first-principle calculations of density functional theory [15,16] with the full potential linearized augmented plane wave (FPLAPW) method implemented in the WIEN2k package [13]. We investigated the structural, electronic and magnetic properties of strontium oxide (SrO) in a rock-salt NaCl-type (B1) structure doped with vanaduim (V) as $Sr_{0.75}V_{0.25}O$ at concentration x = 0.25. The generalized gradient approximation proposed in 2006 by Z. Wu, RE Cohen (GGA-WC) [14] was used for the exchange and correlation potential. The basic functions and potentials are extended in combinations of spherical harmonics around atomic sites, that is to say, the atomic spheres with a cutoff of l_{max} = 10, whereas the charge density was

Fourier expanded up to G_{max} = 14 (a.u.)$^{-1}$, where G_{max} is the largest vector in the Fourier expansion. The Fourier series in the interstitial region is extended in plane waves with a cutoff of $R_{MT}K_{max}$ = 9.5 (where R_{MT} is the mean radius of muffin-tin spheres). The energy cutoff was chosen as −6 Ry, which determines the separation between the valence and core states. For the sampling of the Brillouin zone, the (4 × 4 × 4) k-points of Monkhorst–Pack mesh [17,18] were used for both SrO and $Sr_{0.75}V_{0.25}O$ compounds. The self-consistent convergence of the total energy was set at 0.1 mRy.

3 Results and discussions

3.1 Structural properties

The NaCl (B1) structure of SrO strontium oxide includes two atoms, one a strontium (Sr) atom of column II and the other an oxygen (O) atom of column VI of the periodic table of the elements. The primitive cell has two atoms, one cation (Sr) and one anion (O), and each atom Sr (O) is surrounded by six O (Sr) neighboring atoms, forming an octahedron. In the conventional NaCl (B1)-type structure of SrO, the Sr atom is located at the (0, 0, 0) position and the O atom at (0.5, 0.5, 0.5) with space group ($Fm\bar{3}m$) no. 225. The Sr_3VO_4 supercell of 8 atoms is obtained by the substitution of one Sr atom by a vanadium (V) impurity. We get the $Sr_{0.75}V_{0.25}O$ cubic structure with space group ($Pm\bar{3}m$) No 221. We adjusted the variation of total energy as a function of volume by the Murnaghan equation [19] to calculate the structural parameters, such as the equilibrium lattice constants (a), bulk modules (B) and their pressure derivatives (B) of SrO and $Sr_{0.75}V_{0.25}O$ compounds. Our results are shown in Table 1 with other theoretical [12] and experimental data [11,20] for comparison purposes.

The calculated (a) and (B) parameters of SrO are very close to the experimental data [11,20]. Also, they are in good agreement with the theoretical calculations [12] found by the same GGA-WC method, though we note small deviations. The lattice constant of SrO is higher than that of $Sr_{0.75}V_{0.25}O$, implying that the ionic radius of the substi-
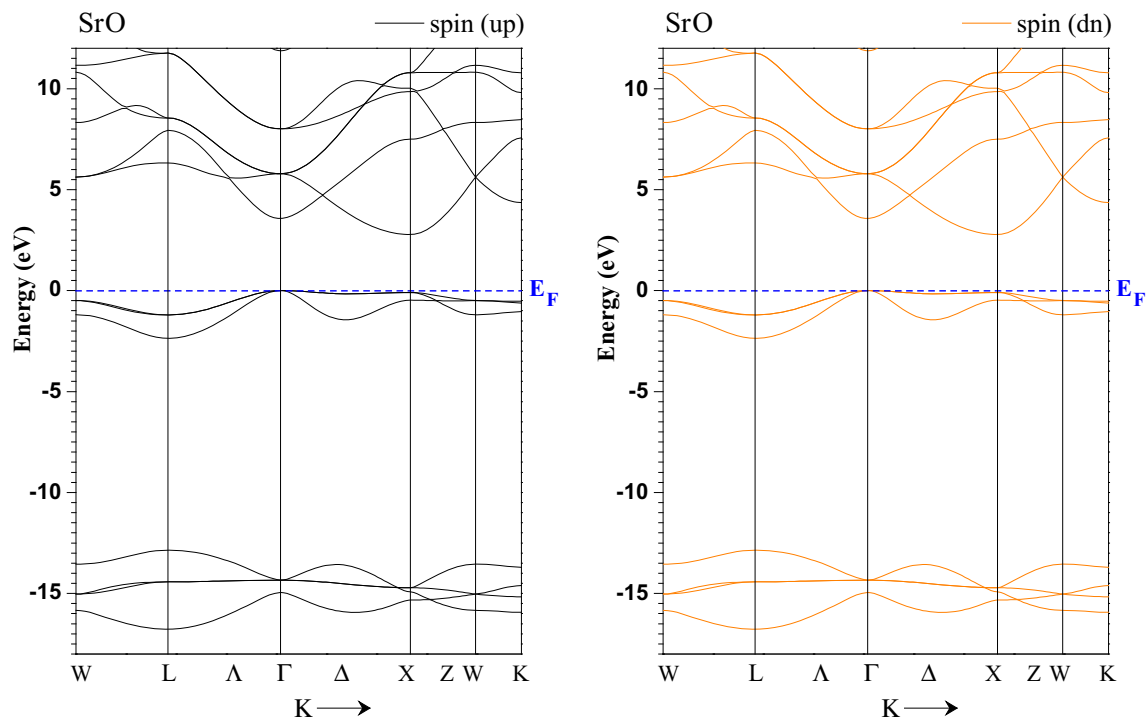
Table 1 Calculated structural parameters; lattice constant (a), bulk modulus (B), and its pressure derivative (B') for SrO and $Sr_{0.75}V_{0.25}O$

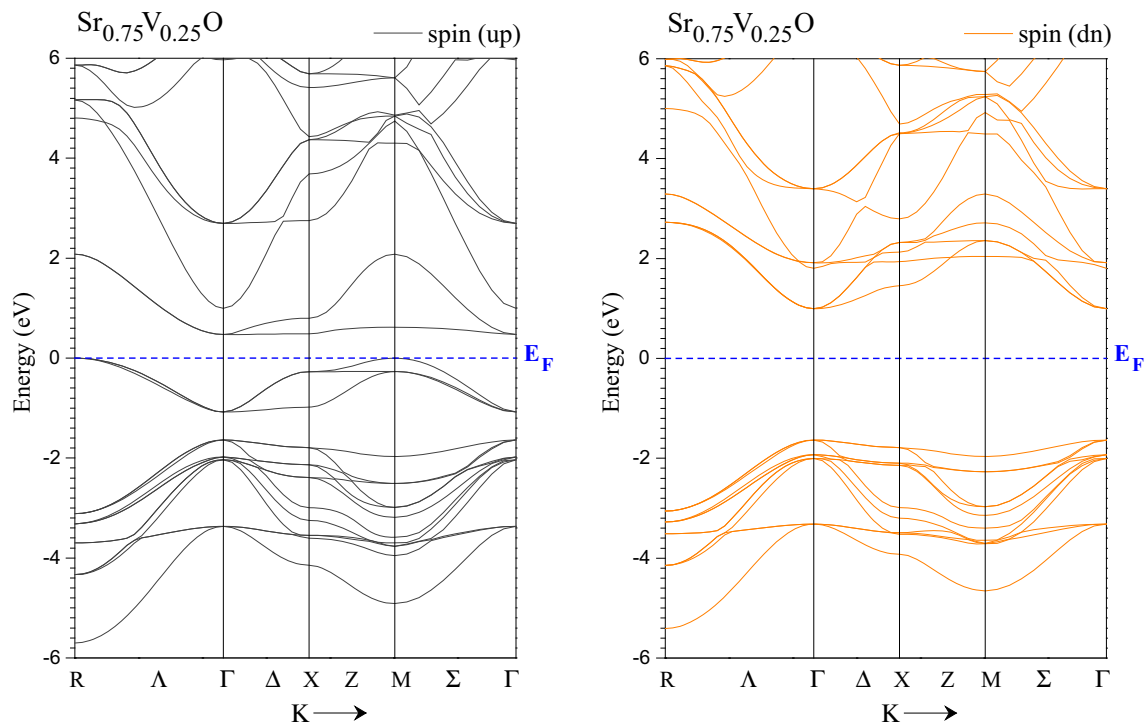| Compound	a (Å)	B (GPa)	B'
SrO	5.127, 5.21[a], 5.16[b,c]	92.66, 83.04[a], 91[c]	4.57, 4.21[a], 4.3[c]
$Sr_{0.75}V_{0.25}O$	4.979	107.86	4.58

[a] Theoretical values from Ref. [12]
[b] Experimental value from Ref. [11]
[c] Experimental values from Ref. [20]

Fig. 1 Band structures of majority spin (*up*) and minority spin (*dn*) for SrO. The Fermi level is set to zero (*horizontal dotted line*)

Fig. 2 Band structures of majority spin (*up*) and minority spin (*dn*) for $Sr_{0.75}V_{0.25}O$. The Fermi level is set to zero (*horizontal dotted line*)

tuted (V) atom is lower than that of Sr. The bulk modulus of $Sr_{0.75}V_{0.25}O$ is higher than that of SrO, meaning that the SrO is easily compressible compared to the $Sr_{0.75}V_{0.25}O$ compound. For the structural parameters of $Sr_{0.75}V_{0.25}O$, there are no experimental or theoretical results to compare with our calculations.

Table 2 Calculated half-metallic ferromagnetic gap (G_{HMF}) and half-metallic gap (G_{HM}) of minority-spin band for $Sr_{0.75}V_{0.25}O$ and indirect band gap $E^{\Gamma X}$ for SrO

| Compound	G_{HMF} (eV)	G_{HM} (eV)	$E^{\Gamma X}$ (eV)
$Sr_{0.75}V_{0.25}O$	2.63	1.00	
SrO			2.78, 3.335[a], 5.71[b]

[a] Theoretical value from Ref. [25]
[b] Experimental value from Ref. [26]

3.2 Electronic structure with half-metallic property

In this section, we used the computed theoretical values of lattice constants to determine the electronic structures of SrO and the $Sr_{0.75}V_{0.25}O$ compound. The spin-polarized band structures of SrO and $Sr_{0.75}V_{0.25}O$ compounds for special high symmetry points in the Brillouin zone are represented, respectively, by Figs. 1 and 2. Figure 1 shows that the majority-spin and minority-spin bands of SrO are symmetric with respect to the semiconducting feature. In contrast, the Fig. 2 of band structures of $Sr_{0.75}V_{0.25}O$ revealed a metallic character for majority spin and sa emiconducting nature for minority spin around the Fermi level (E_F). Consequently, the $Sr_{0.75}V_{0.25}O$ is a half-metallic ferromagnet with a magnetic spin polarization of 100 % at E_F.

Moreover, SrO shows an indirect band gap ($E^{\Gamma X}$) between the Γ and X high symmetry points. The strong p–d exchange interaction between the $3d$ (V) and p (O) states creates a half-metal (HM) ferromagnetic (F) gap (G_{HMF}) and an HM gap (G_H) in $Sr_{0.75}V_{0.25}O$. The HM gap (spin-flip gap) is determined to be the minimum energy with respect to the Fermi level of majority (minority) spin between the lowest energy of conduction bands and the absolute value of highest energy of valence bands [21–24]. However, the HM gap (spin-flip gap) of the $Sr_{0.75}V_{0.25}O$ compound is situated between the Fermi level and the conduction band maximum, which equals 1 eV. Therefore, in this case the HM gap describes the minimal energy band gap for spin excitation to create an electron in the minority-spin conduction bands.

Table 2 summarize our calculations of the indirect band gap ($E^{\Gamma X}$) of SrO, HMF gap (G_{HMF}) and HM gap (G_H) of minority spin of $Sr_{0.75}V_{0.25}O$ with other theoretical [25] and experimental data [26]. The analysis of these gaps show that the computed value of band gap ($E^{\Gamma X}$) for SrO is significant compared to theoretical value [25], with the generalized gradient approximation (GGA-PBE) of J.P. Perdew et al., [27]. The difference between them is due to the GGA-PBE mishaps in the calculation of the lattice parameter. It is noted that the valence band maximum and conduction band minimum of spin-down of $Sr_{0.75}V_{0.25}O$ are located at the Γ haut symmetry point, implying that this compound is characterized by a direct HMF gap. On the other hand, the $Sr_{0.75}V_{0.25}O$
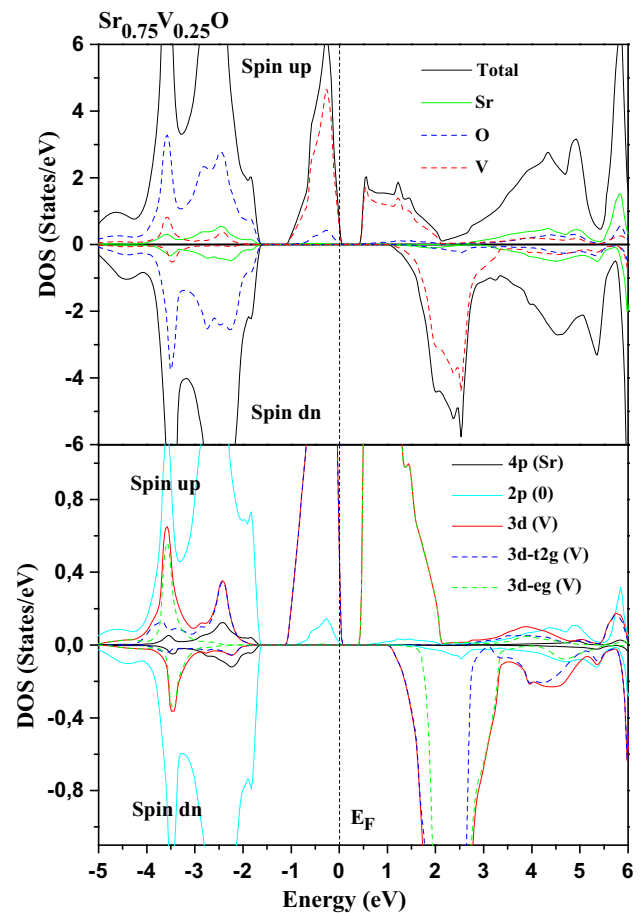
Fig. 3 Spin-polarized total and partial densities of states of $Sr_{0.75}V_{0.25}O$. The Fermi level is set to zero (*vertical dotted line*)

reveals a large HM gap of 1.00 eV. Therefore, $Sr_{0.75}V_{0.25}O$ can be considered a good candidate for possible spintronics applications.

The total (T) and partial (P) electron densities of states of $Sr_{0.75}V_{0.25}O$ are shown in Fig. 3. The PDOS of $Sr_{0.75}V_{0.25}O$ depicted that the $3d$ (V) levels mainly dominate the non-bonding and anti-bonding levels of the majority-spin valence band and the bottom of the minority-spin conduction band. Also, the bonding in the valence levels of two spin channels in the range of −4 to −1.7 is mostly formed by p (O) states, with admixture of small contributions of $3d$ (V) and p (Sr) states. Fig. 3 shows that TDOS of majority-spin states (MAS) are metallic, but minority-spin states (MIS) reveal a gap. For PDOS of MAS, a large hybridization between the $3d$ states of (V) and p of (O) dominates the Fermi level (E_F), which is partially occupied by electrons, whereas the MIS are unoccupied (equal to zero) at E_F. Therefore, the $Sr_{0.75}V_{0.25}O$ is a half-metallic ferromagnet. Besides, in $Sr_{0.75}V_{0.25}O$ the V atom is substituted at the cationic site of Sr, where the six oxygen (O) ions surround a vanadium (V) atom and form an octahedral crystal field. Under the effect of this field, the $3d$ (V) shells are

Table 3 Calculated total and local magnetic moments (in Bohr magneton μ_B) within the muffin-tin spheres and in the interstitial sites for $Sr_{0.75}V_{0.25}O$

Compound	Total (μ_B)	V (μ_B)	Sr (μ_B)	O (μ_B)	Interstitial (μ_B)
$Sr_{0.75}V_{0.25}O$	3	2.481	0.011	−0.0007	0.511

separated into two groups; the t_{2g} (d_{xy}, d_{xz} et $d_{yz}t$) threefold and twofold e_g (d_{x^2} and $d_{x^2-y^2}$) symmetry states. However, the Fig. 3 exhibits that the high-lying e_g levels lie above the low-lying t_{2g} levels [24,28] due to octahedral neighboring created by the vanadium (V) atoms. K. Sato et al. [3,29] have explained the origin of ferromagnetism in doped magnetic semiconductors by the partially occupied anti-bonding states associated with double exchange mechanism. For our $Sr_{0.75}V_{0.25}O$ material, the strong hybridization between the partially filled $3d - e_g$ (V) and the p (0) levels stabilizes the ferromagnetic configuration related to the double exchange mechanism [30].

3.3 Magnetic properties

Our results of total and local magnetic moments in the muffin-tin spheres and in the interstitial sites of the V, Sr and O atoms of $Sr_{0.75}V_{0.25}O$ compound are shown in Table 3. The electronic configuration of the vanadium (V) element in the $Sr_{0.75}V_{0.25}O$ compound is (^{23}V): [Ar] $3d^34s^2$. In addition, the vanadium (V) atom is substituted at the cationic site of Sr in $Sr_{0.75}V_{0.25}O$, which contributes two electrons to the valence band containing p (O) states. Consequently, the $3d$ (V) spin-up levels are partially occupied by three (3) electrons; these states generate a total magnetic moment equal to 3 μ_B (μ_B is the Bohr magnetron). Thus the total magnetic moment of $Sr_{0.75}V_{0.25}O$ of 3 μ_B originates from the local magnetic moment of $3d$ states of the vanadium (V) ion. This partial magnetic moment is reduced to 2.481 μ_B, which is less than its free space value of 3 μ_B due to the effect of $p-d$ exchange interaction between p (O) and d (V) levels. Both half-metallic behavior and integral total magnetic moment of 3 μ_B confirm that $Sr_{0.75}V_{0.25}O$ is accurately a half-metallic ferromagnet. The major contribution of the total moment is localized on the vanadium atom, and owing to the p–d exchange interaction, smaller contributions of magnetic moments are induced at the other Sr, O and interstitial sites. The negative magnetic moment of oxygen explains the anti-ferromagnetic interaction between the magnetic spins of V and O atoms, while the ferromagnetic interaction is initialized between the magnetic spins of V and Sr atoms.

4 Conclusion

In summary, we have used the first-principle calculations of the full-potential linearized augmented-plane wave method within density functional theory to determine the structural parameters, electronic structures and magnetic properties of $Sr_{0.75}V_{0.25}O$. We have found that the lattice constant of SrO is higher compared to $Sr_{0.75}V_{0.25}O$ owing to differences in the ionic radii between Sr and V atoms, and hence SrO is easily compressible compared to $Sr_{0.75}V_{0.25}O$. The $Sr_{0.75}V_{0.25}O$ exhibits a half-metallic (HM) ferromagnetic character with half-metallic ferromagnetic gap of 2.78 eV. In addition, the $Sr_{0.75}V_{0.25}O$ reveals an integral total magnetic moment of Bohr magneton of 3 μ_B with a wide half-metallic gap of 1.00 eV. Therefore, we suggest that $Sr_{0.75}V_{0.25}O$ is a perfect half-metallic ferromagnet, and a usable candidate for spin injection in spintronics applications.

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