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journal homepage: www.elsevier.com/locate/jmmmEffects of S and N doping on the structural, magnetic and electronic properties of rutile CrO₂You Xie^{a,b,*}, An-Ning Zhou^b, Kai-Gang Sun^a, Ya-Ting Zhang^b, Yi-Ping Huo^c,
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ABSTRACT

Magnetic and electronic properties of S- and N-doped CrO₂ are studied by using the first-principle projector augmented wave potential within the generalized gradient approximation. The optimized lattice constants for CrO₂ agree well with the previous work. With increasing S doping (N doping), the lattice constants of CrO_{2-x}S_x (CrO_{2-x}N_x) (x=0.5, 1 and 1.5) all increase (decrease). While these compounds remain the tetragonal structure. CrO_{1.5}S_{0.5}, CrO_{1.5}N_{0.5} and CrON compounds remain the half-metallicity, while the band gap is determined by different factors. It is also found that the change of the total magnetic moment with equivalent atom S doping in CrO₂ compound is small except for x=1.

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1. Introduction

Increased interest in the field of magnetoelectronics or spin electronics during the last decade has intensified research on the so-called half-metallic ferromagnetic materials [1–6], a material that is a metal for one spin channel and an insulator for the other. Their characterization has attracted great attention, since a fully spin-polarized ferromagnetic material can be very useful for fabricating spin batteries and ideal magnetic tunnel junctions used in spintronics applications [7–9]. These offer opportunities for a new generation of devices combining standard microelectronic with spin-dependent effects such as nonvolatile magnetic random access memories and magnetic sensors [10]. This in turn has led to the study of composites of ferromagnetic and ferroelectric materials, which can exhibit properties superior to a single-phase compound [11].

A potential candidate for spintronic applications is CrO₂, which is a well established half-metallic ferromagnet ($T_C \sim 400$ K) [12–15]. Since its early discovery, several works were devoted to its physical properties [16,17]. In pure CrO₂, Cr atoms appear to have a single +4 valence state and a magnetic moment of 2 μ_B . However, the electronic properties of CrO₂ are still not fully understood. For instance, the resistivity between 10 and 300 K is usually described

in terms of an excitation gap [18,19], while a clear connection with an electronic or spin gap excitation cannot be made. Also, different results have been reported with respect to the Hall effect. Recent theoretical works suggested that self-doping generates the maxed valence state of Cr atoms and oxygen-mediated the double exchange interaction [20,21]. Insight into the electronic properties can also be obtained through doping studies. Chetry et al. investigated the electronic and magnetic structure of CrO₂-RuO₂ interfaces [22]. The relatively good matching between the majority of the energy bands of CrO₂ and both RuO₂ channels in the (100), (110), and (001) directions was found. For (100) interfaces, they find a small induced Ru moment oriented opposite to that of the Cr moments. While the large negative moment that forms when a Ru ion substitutes for a Cr ion. Williams et al. also suggested that the Cr-doped rutile-phase material remained FM and half-metallic even for high concentrations in V_{1-x}Cr_xO₂ [23]. Recently, Ren et al. revealed the tuning of magnetic transition and associated reversible magnetocaloric effect in CrO_{2-x}F_x by manipulating the doping levels [24]. At x=0.12, the magnetic transition occurs at room temperature, with magnetic-entropy changes of around 4 J kg⁻¹ K⁻¹ and relative cooling power of 388 J kg⁻¹ at magnetic-field changes from 0 to 50 kOe. The reversibility was verified by negligible thermal and magnetic hysteresis, as well as the positive slope at Arrott plots. Up to now, the equivalent valence atom S doping in CrO₂ compound has not been reported. So, it is interesting to investigate the effects of the S doping on magnetic and electronic properties of CrO₂ compound.

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In this paper, we study systematically the effects of S- and N-doped on the structural, magnetic and electronic properties of CrO_2 by using the first-principle projector augmented wave (PAW) potential within the generalized gradient approximation (GGA). The paper is organized as follows. In Section 2, the computational method is described. In Section 3, the optimized lattice constants, formation energy, electric structure and magnetic properties are discussed. Finally in Section 4, we summarize our results and conclusions.

2. Computational method

The calculations are performed using the Vienna *ab initio* simulation package (VASP) based on the density function theory (DFT) [25–28]. The electron–ionic core interaction is represented by the projector augmented wave (PAW) potentials [29] which are more accurate than the ultra-soft pseudopotentials. To treat electron exchange and correlation, we chose the Perdew–Burke–Ernzerhof (PBE) [30] formulation of the generalized gradient approximation (GGA). A conjugate-gradient algorithm is used to relax the ions into their ground states, and the energies and the forces on each ion are converged within 1.0×10^{-4} eV/ion and 0.01 eV/Å, respectively. The cutoff energy for the plane-waves is chosen to be 400 eV. A $5 \times 5 \times 9$ Monkhorst–Pack grid for k -point sampling is adopted for Brillouin zone integration, together with a Gaussian smearing broadening of 0.2 eV.

3. Results and discussions

See Fig. 1(a), CrO_2 has a rutile structure ($P4_2/mnm$) with 2-formula-unit supercell (2 Cr atoms and 4 O atoms). With S (N) substituting O, $\text{CrO}_{1.5}\text{S}_{0.5}$ ($\text{CrO}_{1.5}\text{N}_{0.5}$), CrOS (CrON) and $\text{CrO}_{0.5}\text{S}_{1.5}$ ($\text{CrO}_{0.5}\text{N}_{1.5}$) compounds are got. As an example, here we only show the structures of $\text{CrO}_{1.5}\text{S}_{0.5}$, CrOS and $\text{CrO}_{0.5}\text{S}_{1.5}$ in Fig. 1 (b), (c) and (d), respectively. After completely relaxing, the structures of these compounds are optimized and the lattice constants are listed in Table 1. The optimized lattice constants of $a=b=4.454$ Å and $c=2.923$ Å for CrO_2 agree well with the previous work of $a=b=4.421$ Å and $c=2.916$ Å, respectively [31]. With increasing S-doped, the all of the lattice constants increase. The different case occurs in CrO_2 compound with N-doped, the

lattice constants of c decrease with increasing N-doped, while the volume increases. The reason may be the atomic radius of 1.48 Å for S atom is slightly larger than that of 1.40 Å and 1.46 Å for O and N atoms, but the electronegativity of 2.58 for S is smaller than that of 3.44 and 3.04 for O and N atoms, respectively. We also calculate the distance lengths between Cr and O, Cr and S, as well as the distance lengths between Cr and N atoms. It can be seen that the Cr–O bonds ($d_{\text{Cr1-O}}$ and $d_{\text{Cr2-O}}$) are obviously smaller than the Cr–S bonds ($d_{\text{Cr1-S}}$ and $d_{\text{Cr2-S}}$) for the S-doped CrO_2 . But for N doping case, the Cr–O bonds ($d_{\text{Cr1-O}}$ and $d_{\text{Cr2-O}}$) are equal to the Cr–N bonds ($d_{\text{Cr1-N}}$ and $d_{\text{Cr2-N}}$) except for $d_{\text{Cr2-N}}$ in $\text{CrO}_{0.5}\text{N}_{1.5}$ compound. With increasing both S- and N-doped, the compound maintains the tetragonal structure.

The stability of the defective CrO_2 compound is investigated, which can be deduced from the value of the formation energy. The defect formation energy E_f is calculated by

$$E_f = E_{\text{def}} - E_{\text{id}} - \sum n_i \mu_i \quad (1)$$

Where E_{def} and E_{id} represent the total energies of the compound with and without defect, respectively. The energy difference added or removed is represented by the last term $\sum n_i \mu_i$. For the case of the substituting defect, n_i is the number of atom transferred ($n_i = +1$ for the added atom and $n_i = -1$ for the removed atom) and μ_i is the chemical potential of these atoms in their stable solid or gas phase. As also listed in the last column of Table 1, we can see that with increasing S doping, the formation energy of the defective CrO_2 decreases. That is to say, the impurity S facilitates stabilizing the structure. The formation energies of CrOS and $\text{CrO}_{0.5}\text{S}_{1.5}$ are negative values, suggesting the possibility of spontaneous formation of these kinds of the defective compounds. The same situations occur in $\text{CrO}_{2-x}\text{N}_x$ ($x=0, 0.5, 1$ and 1.5) compounds. While the positive value of the formation energy for $\text{CrO}_{1.5}\text{S}_{0.5}$ implies the formation processes of this defect is endothermic.

Next, we further focus our attention on the electronic structure of $\text{CrO}_{2-x}\text{S}_x$ and $\text{CrO}_{2-x}\text{N}_x$ ($x=0, 0.5, 1$ and 1.5) compounds. Fig. 2 shows the total density of states (DOS) of $\text{CrO}_{2-x}\text{S}_x$ with (a) $x=0$, (b) $x=0.5$, (c) $x=1$ and (d) $x=1.5$. The black (red) line represents the up-spin (down-spin) channel. The Fermi level E_f is set at zero energy and indicated by vertical green line. From Fig. 2(a), we can see that there is a positive spin-splitting between up-spin and down-spin channels around the Fermi level E_f . Especially, the up-

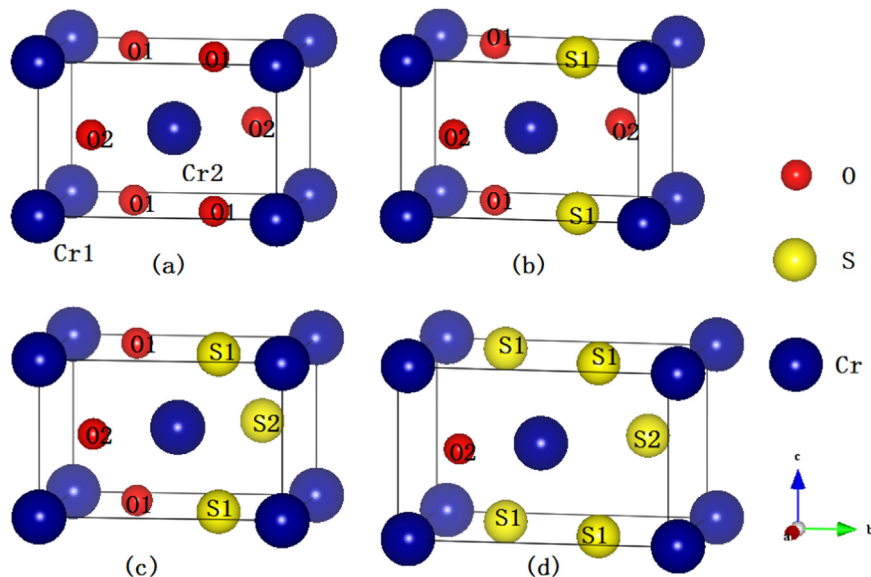


Fig. 1. Crystal structures of $\text{CrO}_{2-x}\text{S}_x$ ($x=0, 0.5, 1, 1.5$) compounds. (a), (b), (c) and (d) represent CrO_2 , $\text{CrO}_{1.5}\text{S}_{0.5}$, CrOS and $\text{CrO}_{0.5}\text{S}_{1.5}$, respectively.

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