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Spin-polarized structural, electronic and magnetic properties of diluted magnetic semiconductors $Ca_{0.75}TM_{0.25}O$ (TM = Fe, Co and Ni) in the rock salt (B1) phase

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ABSTRACT

The structural, electronic and magnetic properties of the diluted magnetic semiconductors (DMSs) $Ca_{0.75}TM_{0.25}O$ (TM = Fe, Co and Ni) were investigated in the rock salt (B1) phase using the full potential linearized augmented plan wave plus orbital (FP-L/APW+lo) method based on spin-polarized density functional theory (SDFT). The lattice constants, bulk modulii, spin-polarized band structures and total and local densities of states have been computed. We calculated the spin-exchange splitting energies ΔE^c and ΔE^v produced by Fe, Co and Ni-3d states and the results indicate that the effective potential for the minority spin is more attractive than that of the majority spin. The s–d exchange constant $N_0\ \alpha$ (conduction band) and p–d exchange constant $N_0\ \beta$ (valence band) were calculated. The magnetic moment value per Fe, Co and Ni impurity atom is found to be 3.59, 2.59 and 1.59 μB. The hybridization between Ca-p and TM-3d reduces the local magnetic moment of TM and produces small local magnetic moment on the non magnetic Ca and O sites. The Fe, Co and Ni-3d half-filled electrons have been treated as valence electrons and due to their hybridization, the ternary alloys $Ca_{0.75}TM_{0.25}O$ (TM = Fe, Co and Ni) have well defined spin-up and spin-down band structures.

KEYWORDS

Ab-initio calculation;
FP-L/APW+lo;
Diluted magnetic semiconductors;
Magnetic moment.

INTRODUCTION

The diluted magnetic semiconductors (DMSs) have been investigated due to their possibility of having magnetic properties. The II–VI alloys represent one of this family, where the II cations are randomly and partially occupied by the ferromagnetic transition metals ions TM (TM = Fe, Co and Ni). The presence of localized magnetic ions in these semiconductors leads to an exchange interaction between carriers and the magnetic TM^{+2}, resulting in extremely large Zeeman splittings of electronic levels. The Half-metallic ferromagnetic (HMF) compounds were considered as fundamental materials in spintronic devices and magnetic recording[1], and have an important interest for their use as optical limiters and non linear absorber in passive laser modulation[2,3]. The n-type II-VI DMSs were the object of vast experiment studies due to their electrical spin injection with high efficiency[4]. The development of new spintronics devices, like spin valves, spin light emitting diodes, magnetic sensors, logic devices and ultra-fast optical switches requires the finding of semiconductors with improved ferromagnetic properties. The orientation of research on DMSs was managed towards (II-Mn)VI systems[5,6]. The valence band structure enables us to predict and understand the magnetic and transport properties using the first principle calculations.

In this work, we give detailed information on the structural, band structures, total and partial density of states TDOS and PDOS and magnetic properties of $Ca_{0.75}TM_{0.25}O$ (TM = Fe, Co and Ni) semiconductors, with TM-3d treated as valence states using the full potential linearized augmented plan wave plus orbital (FP-L/APW+lo) method based on spin polarized density functional theory (SDFT). There are no experiment and theoretical data available for $Ca_{0.75}Fe_{0.25}O$, $Ca_{0.75}Co_{0.25}O$ and $Ca_{0.75}Ni_{0.25}O$ in B1 structure.

This paper is divided into three parts. In Section 2, we briefly describe the computational techniques used in this work. The most relevant results obtained for the structural, electronic and magnetic properties of $Ca_{0.75}TM_{0.25}O$ (TM = Fe, Co and Ni) are presented and discussed in Section 3. Finally, in Section 4 we summarize the main conclusions.

COMPUTATIONAL METHOD

The calculations reported in this work are performed with a developed full potential linearized augmented plan wave plus orbital (FP-L/APW+lo) method based on spin polarized density functional theory (SDFT), as embodied in the Wien2K code[7]. The electronic exchange-correlation energy is described by the generalized gradient approximation (GGA) as parameterized by Perdew Burke and Ernzerhof (PBE)[8]. The structural parameters were determined using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) minimization technique, which provides a fast way of finding the lowest energy structure[9]. The spin-polarized calculations are carried out with both spin-up and spin-down densities. In order to simulate the ordered rock salt (B1) structures of $Ca_{075}TM_{025}O$ (TM = Fe, Co and Ni), we considered a supercell model based on eight atoms. The choice of the particular muffin-tin (MT) radii for the various atoms in the compounds shows small differences that do not affect our results. We compute the lattice constant and bulk modulus by fitting the spin-polarized total energy versus unit cell volume according to the Murnaghan's equation of state[10]. The adopted muffin-tin radii were 2.09 a.u. (Ca), 2.21 a.u. (Fe) and 1.96 a.u. (O) for $Ca_{0.75}Fe_{0.25}O$; 1.97 a.u. (Ca), 2.09 a.u. (Co) and 1.85 a.u. (O) for $Ca_{0.75}Co_{0.25}O$ and 1.99 a.u (Ca), 2.11 a.u. (Ni) and 1.87 a.u. (O) for $Ca_{0.75}Ni_{0.25}O$. Within the muffin-tin spheres, we make the expansion up to l_{max} = 10 to get the total energy eigen value convergence. On the basis of convergence tests, we are confident that 125 k points and basis functions up to R_{MT}–K_{max} = 8 (K_{max} is the plane wave cut-off) ensure an accurate and well-converged result in the irreducible wedge of the Brillouin zone. TM-3d electrons are treated as valence states. The doped compositions are totally optimized with respect to both the atomic positions and the lattice constants.

RESULTS AND DISCUSSIONS

Structural properties

We have obtained the structural parameters of $Ca_{0.75}TM_{0.25}O$ (TM = Fe, Co and Ni) by minimization of the total energy as a function of the cell volume in the rock-salt (B1) phase for the AFM states. The equilibrium lattice constant a_0 and bulk modulus B for $Ca_{0.75}TM_{0.25}O$ (TM = Fe, Co and Ni) are listed in TABLE 1. These results have been obtained by fitting the calculated total energies as a function of the volume to the Birch Murnaghan2 s equation of state[10] as shown in Figure 1. It can be seen that $Ca_{0.75}Ni_{0.25}O$ has the smaller energy, and this explains that it is more stable than $Ca_{0.75}Co_{0.25}O$ and $Ca_{0.75}Fe_{0.25}O$ respectively. There are no experiment data and theoretical calculation that have appeared in the literature for $Ca_{0.75}TM_{0.25}O$ (TM = Fe, Co and Ni). We have calculated also the lattice constant and bulk modulus for CaO parent, which are consistent with the experiment data computed by P. Pichiet et al.[11] and other theoretical result using pseudo-potential plane-waves (PP-PW) approach obtained by B. Ghebouli et al.[12].

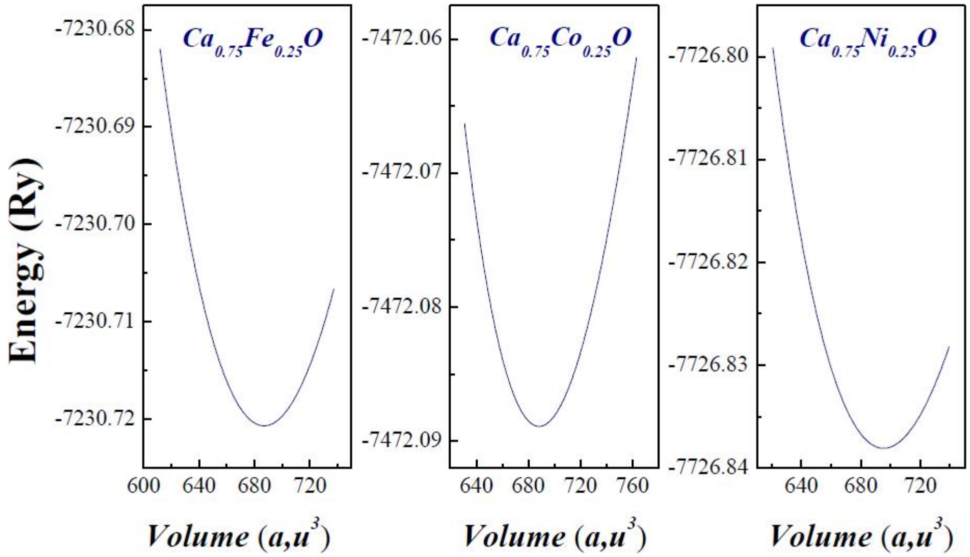

Figure 1 : The calculated spin-polarized total energy versus unit cell volume for ferromagnetic $Ca_{0.75}Fe_{0.25}O$, $Ca_{0.75}Co_{0.25}O$ and $Ca_{0.75}Ni_{0.25}O$.

TABLE 1 : The calculated structural parameters of $Ca_{0.75}Fe_{0.25}O$, $Ca_{0.75}Co_{0.25}O$, $Ca_{0.75}Ni_{0.25}O$ and CaO at equilibrium.

	Lattice constant			Bulk modulus		
	FP-PW	Expt.	Others	FP-PW	Expt.	Others
$Ca_{0.75}Fe_{0.25}O$	4.6677	-	-	121.6	-	-
$Ca_{0.75}Co_{0.25}O$	4.6707	-	-	119	-	-
$Ca_{0.75}Ni_{0.25}O$	4.6868	-	-	116.1	-	-
CaO	4.8383	4.811[11]	4.8224[12]	107.9	90.6[11]	86[12]

Electronic band structure

We use the equilibrium lattice constants to computed spin-polarized band structure of $Ca_{0.75}Fe_{0.25}O$, $Ca_{0.75}Co_{0.25}O$ and $Ca_{0.75}Ni_{0.25}O$ for spin-up (majority spins) and spin-down (minority spins) configurations along the high symmetry directions in the first Brillouin zone as are shown in Figures 2-4. For these materials, the majority spins show the semiconductor nature with R-Γ indirect band gap, while the minority spins exhibit the metallic one. In the majority spins channel around the Fermi level, there is an energy gaps of about 1.57, 1.8 and 1.89 eV for $Ca_{0.75}Fe_{0.25}O$, $Ca_{0.75}Co_{0.25}O$ and $Ca_{0.75}Ni_{0.25}O$ respectively. The half-metallic gap G_{HM} was calculated as the difference between the minimum energy point of the conduction band and the maximum energy point of the valence band near the Fermi level for both spin-up and spin-down and we take the smaller of the two values. The calculated values of G_{HM} for $Ca_{0.75}Fe_{0.25}O$, $Ca_{0.75}Co_{0.25}O$ and $Ca_{0.75}Ni_{0.25}O$ are 0.72, 0.51 and 0.42 eV respectively. The bands in the range Δ6.65 to Δ5.05 eV for $Ca_{0.75}Fe_{0.25}O$, Δ5.45 to Δ2.06 eV for $Ca_{0.75}Co_{0.25}O$ and Δ5.02 to Δ2.96 eV for $Ca_{0.75}Ni_{0.25}O$ and those near the Fermi level appear due to the Fe, Co and Ni-3d orbitals. After substitution into a cation site, the degenerate Fe, Co and Ni-3d states split into the triply degenerate p–d bonding t_{2g} states and doubly degenerate non-bonding e_g states. The triply degenerate t_{2g} and doubly degenerate eg states are separated due to the strong p–d exchange interaction between TM-3d (TM = Fe, Co and Ni) and Ca-p orbitals. We discuss only the spin-up band structures which have large number of electrons. The conduction band of the spin-up electrons is totally dominated by Ca-p state, while for the spin-down case, conduction band crosses the Fermi level leading to the HM ferromagnetism.

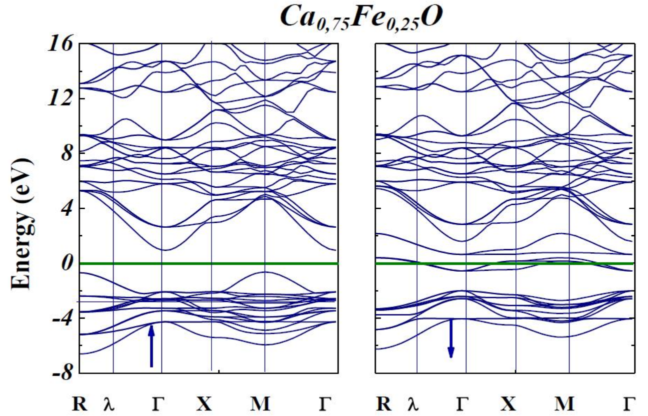

Figure 2 : Electronic band structure of ferromagnetic $Ca_{0.75}Fe_{0.25}O$ for (a) spin-up and (b) spin-down.

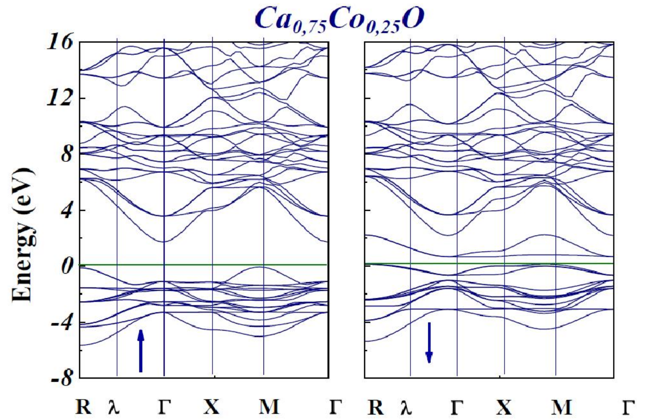

Figure 3 : Electronic band structure of ferromagnetic $Ca_{0.75}Co_{0.25}O$ for (a) spin-up and (b) spin-down.

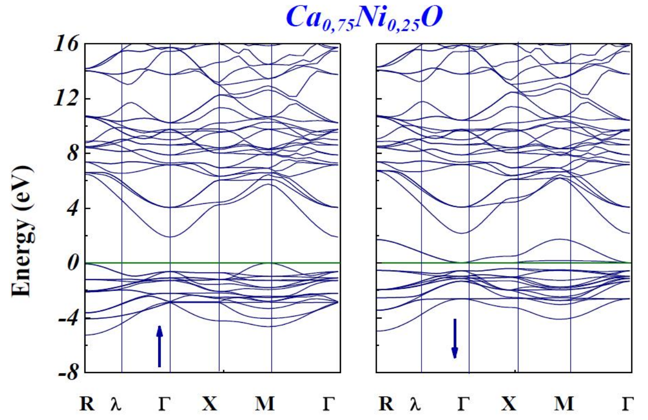

Figure 4 : Electronic band structure of ferromagnetic $Ca_{0.75}Ni_{0.25}O$ for (a) spin-up and (b) spin-down.

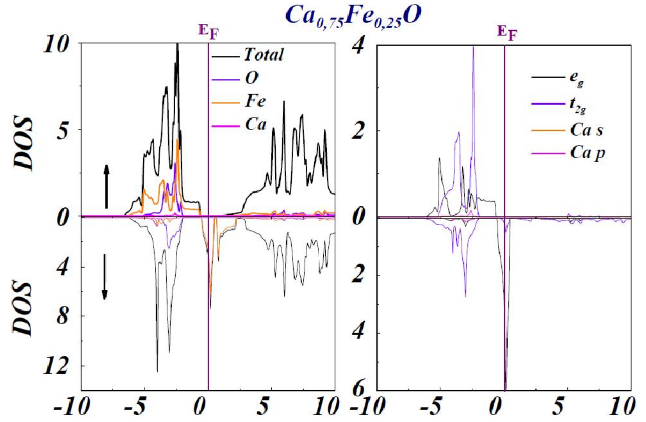

Figure 5 : Spin-dependent total and partial density of states for $Ca_{0.75}Fe_{0.25}O$ projected on three atoms.

Total and partial density of states

The local density of states (LDOS) plots for $Ca_{0.75}Fe_{0.25}O$, $Ca_{0.75}Co_{0.25}O$ and $Ca_{0.75}Ni_{0.25}O$ as it displayed in Figures 5-7 shows that the valence band is constituted to three zones. The lower part of the valence band located between —6.3 to -4.98 eV, -5.25 to -3.48 eV and -5 to -3.03 eV for $Ca_{0.75}Fe_{0.25}O$, $Ca_{0.75}Co_{0.25}O$ and $Ca_{0.75}Ni_{0.25}O$ is occupied by Fe, Co and Ni-3d states in both the spin cases. The zone extended between -4.98 to -2.06 eV, -3.48 to -1.16 eV and -3.03 to -0.7 eV, where the electronic density contribution is mainly due to the TM (TM = Fe, Co, Ni) mixed with O atoms. It is seen that the upper part of the valence band has TM-3d character that is different for majority-spin and minority-spin around the Fermi level. The results of DOS show that these compounds exhibit HM behavior, which is semiconducting for the majority-spin and metallic for the minority-spin. The ferromagnetism is induced due to the exchange-splitting of O-2p and TM-3d hybridized bands. For all the doped systems under study, the spin-up d bands are occupied in all TM (TM = Fe, Co, Ni), whereas in the spin-down, the Ni-3d states are only occupied. This trend is generally observed in most of the magnetic semiconductors[13,14]. On the other hand for the spin down case, the upper part of the valence band is mainly occupied by the TM-3d (TM = Fe, Co, Ni) states and they are a few electron volts below the Fermi level, while above the Fermi level, the bottom of the conduction band is also dominated by TM-3d states. We have also calculated the spin-exchange-splitting energy $\Delta_x(d)$, which is defined as the separation between the corresponding majority-spin and minority-spin peaks. The $\Delta_x(d)$ values are 2.58, 1.56 and 0.61 eV for $Ca_{0.75}Fe_{0.25}O$, $Ca_{0.75}Co_{0.25}O$ and $Ca_{0.75}Ni_{0.25}O$ respectively.

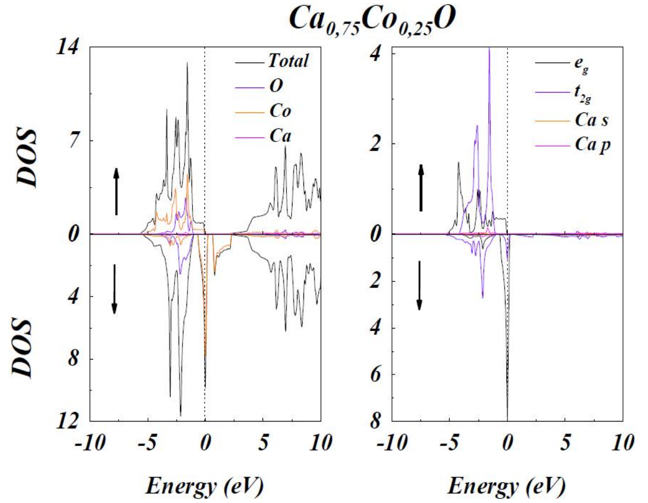

Figure 6 : Spin-dependent total and partial density of states for $Ca_{0.75}Co_{0.25}O$ projected on three atoms.

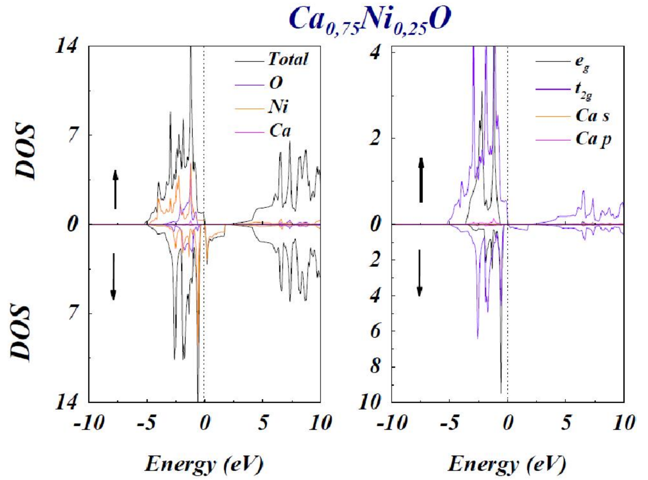

Figure 7 : Spin-dependent total and partial density of states for $Ca_{0.75}Ni_{0.25}O$ projected on three atoms.

Magnetic properties

(a) Magnetic moment

The study of the half-metallicity robustness with respect to the variation of lattice constant under pressure is interesting for spintronic device applications. Figure 8 shows the total magnetic moment of $Ca_{0.75}TM_{0.25}O$ (TM = Fe, Co and Ni) per TM atom as a function of the lattice constant. We can observe that the total magnetic moment for all TM cases remains integer with the compression of the lattice constant with respect to the equilibrium values until they are compressed to the critical values of 4.33 Å for $Ca_{0.75}Fe_{0.25}O$ and 4.57 Å for $Ca_{0.75}Co_{0.25}O$ and $Ca_{0.75}Ni_{0.25}O$. The half-metallicity of $Ca_{0.75}Fe_{0.25}O$, $Ca_{0.75}Co_{0.25}O$ and $Ca_{0.75}Ni_{0.25}O$ is maintained up to the reduction of the lattice constant by 7.2 %, 2.1 % and 2.4 %, respectively. So the half-metallicity of $Ca_{0.75}Fe_{0.25}O$ is most robust among all TM cases. The calculated results for total and local magnetic moments for DMSs $Ca_{0.75}Fe_{0.25}O$, $Ca_{0.75}Co_{0.25}O$ and $Ca_{0.75}Ni_{0.25}O$ using the muffin-tim spheres as well as in the interstitial sites are listed in TABLE 2. It can be seen that the total magnetic moments are mainly from the TM (Fe, Co and Ni) atoms with a very little contributions of Ca and O atoms. The magnetic moments of TM and O are parallel to each other, which mean that the magnetic moment of O comes from the spin delocalization of TM. The sign of the magnetic moment on Ca is opposite to that on TM, which means that the valence-band carriers having manly Ca-p character interact antiferromagnetically with TM spin. The occupied TM-3d states require the production of permanent local magnetic moment in these materials and it decreases in going from Fe to Co and Ni. The large magnetic moment and the robustness of the half-metallicity with respect to lattice compression make these systems promising candidates in spintronic devices for spin injection.

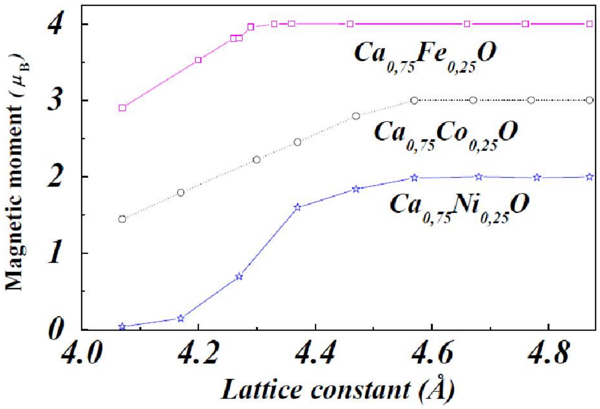

Figure 8 : The total magnetic moment as a function of the lattice constant for ferromagnetic $Ca_{0.75}Fe_{0.25}O$, $Ca_{0.75}Co_{0.25}O$ and $Ca_{0.75}Ni_{0.25}O$.

(b) Exchange coupling

The significant parameters which are computed from the magnetic properties of DMSs are the s–d exchange constant $N_0\alpha$ and the p–d exchange constant $N_0\beta$, where N_0 denotes the concentration of cation. $N_0\alpha$

describes the exchange interaction between the conduction electron carriers and the TM spin, whereas $N_0\beta$ is due to the exchange interaction between the holes and the TM-3d states. From the conduction and valence band edges, the exchange constants can be calculated as given in Ref.[15] $N_0\alpha = \frac{\Delta E^C}{x(S)}$ and $N_0\beta = \frac{\Delta E^{\nu}}{x(S)}$.

where ΔE^c and ΔE^{ν} are the respective band edge splitting of the conduction band minima at Γ point and valence band maxima at the M point, x is the concentration of TM and (S) is one-half of the magnetization per TM atom. The calculated values of ΔE^c, ΔE^{ν}, $N_0\alpha$ and $N_0\beta$ of ferromagnetic $Ca_{0.75}Fe_{0.25}O$, $Ca_{0.75}Co_{0.25}O$ and $Ca_{0.75}Ni_{0.25}O$ are listed in TABLE 3. There is no experiment and theoretical data for these parameters were available to compare them with our results. We find that $N_0\alpha$ is much smaller than $N_0\beta$ for all materials, this indicates that the interaction between the cation s and the TM-3d states at the conduction band minimum is much weaker than the p–d interaction at the valence band maximum and this result proves the ferromagnetic behavior of these alloys.

TABLE 2 : The calculated total magnetic moment M^{tot} (μ_B) and local magnetic moment m (μ_B) of several sites for $Ca_{0.75}Fe_{0.25}O$, $Ca_{0.75}Co_{0.25}O$ and $Ca_{0.75}Ni_{0.25}O$.

	$Ca_{0.75}$Fe0.25O	$Ca_{0.75}Co_{0.25}O$	$Ca_{0.75}Ni_{0.25}O$
M^{tot}	4.0025	3.0023	1.9999
m^{Ni}	-	-	1.5946
m^{Co}	-	2.5927	-
m^{Fe}	3.59	-	-
m^{Ca}	-0.0065	-0.0033	-0.0030
m^{O}	0.1295	0.1376	0.1359
m^{int}	0.047	0.0085	0.0072

TABLE 3 : The calculated conduction and valence band-edge spin-splittings E^c and ΔE^v and exchange constants for $Ca_{0.75}Fe_{0.25}O$, $Ca_{0.75}Co_{0.25}O$ and $Ca_{0.75}Ni_{0.25}O$.

	ΔE^c	ΔE^v	$N_0\ \alpha$	$N_0\ \beta$
$Ca_{0.75}Fe_{0.25}O$	-4.624	0.081	-6.165	0.108
$Ca_{0.75}Co_{0.25}O$	-5.513	-0.579	-6.300	-0.661
$Ca_{0.75}Ni_{0.25}O$	-6.451	-0.758	-6.451	-0.758

CONCLUSION

This paper reports a systematic study of structural, spin-polarized electronic and magnetic properties of the ferromagnetic $Ca_{0.75}TM_{0.25}O$ (TM = Fe, Co and Ni) in the rock salt (B1) phase. The energy band structure and density of states clearly exhibit the HM ferromagnets with the ferromagnetic state is more favorable than the antiferromagnetic one. The ferromagnetism is induced by the exchange-splitting of O-2p and TM-3d hybridized bands. The examination of the local densities of states allowed us to determine the exchange splittings parameters produced by TM-3d (TM = Fe, Co and Ni) states and to conclude that the effective potential for the minority spin is more attractive than that for the majority spin. The coupling between TM-t2g state and Ca-t2p state with each other is strong. The total magnetic moment arises mainly from the Fe, Co and Ni atom with a small contribution from the Ca and O sites and it was reduced by the p–d hybridization. The half-metallicity of $Ca_{0.75}TM_{0.25}O$ (TM = Fe, Co and Ni) is found to be robust with respect to the lattice constant compression and was maintained up to 7.2 %, 2.1 % and 2.4 % respectively.

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