Fe-doped CeO$_2$ DMO compound
5.1 Introduction

The rare-earth (RE) dioxides form an interesting and extensively studied series, which finds potential interest as optical materials and laser hosts. Moreover, these compounds have important applications in the catalysis and electronics industries. In particular, the design of advanced devices based upon the integration of RE oxides with silicon and other semiconductors are used for the detailed understanding of the bonding, electronic and dielectric properties of these materials. Each RE atom donates three electrons to the strongly electronegative O ions, and the remaining 4f electrons stay strongly localized at the RE site. In the lighter lanthanides, (CeO$_2$ and PrO$_2$) the f-electrons are less tightly bound, resulting in compounds that display a larger oxygen coordination number. The Ce, Pr and Tb dioxides crystallize in the cubic fluorite structure whereas the other REs form sesquioxides. Out of them, Cerium oxide (CeO$_2$), also called Ceria is an insulating high dielectric constant (k~26) transparent material. Due to the exciting properties of ceria, it have large number of applications including its use in the anodes of solid oxide fuel cells [1], catalysis [2,3], and oxygen sensors [4]. Yttrium and Gadolinium doping in cerium oxide has been shown to increase oxygen conductivity [1,5,6] for the use as an electrolyte in solid oxide fuel cells. Ceria’s importance stems from its oxygen storage capability which allows it to release oxygen under reducing conditions and to store oxygen by filling oxygen vacancies under oxidizing conditions. CeO$_2$ is non magnetic, however the formation of an oxygen vacancy is known to result in the donation of two electrons to the cerium sub-lattice [7-9] which results in weak magnetism. Thus, upon oxygen vacancy formation in CeO$_2$, two electrons are left behind, and they localize on the f-level traps of two of the neighbouring Ce atoms, changing their formal valence from Ce$^{4+}$ to Ce$^{3+}$ which takes place according to the Kröger–Vink reaction scheme [10]:

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where $O_0$ is a neutral oxygen on an oxygen lattice site, $Ce$ is a neutral cerium, $V_{O^••}$ is a doubly positively charged vacancy in an oxygen site and $Ce'$ is a singly charged cerium ($Ce^{3+}$) atom in a cerium site ($Ce^{4+}$) which gives a net negative charge of -1. The previously unoccupied f state is occupied for the $Ce^{3+}$ ions, giving the electronic configuration $Ce$-f$^1$. The reaction is reversible and allows cerium oxide to incorporate or release oxygen, a process central to the industrial use of cerium oxide [2]. Thus, the accurate theoretical description of pure and mixed $Ce^{3+}$ and $Ce^{4+}$ oxide materials is of primary importance for understanding their functioning and advancement of their practical applications. However, this is not a simple task for the researchers to simulate this since the additional electron, which is introduced on the Ce center upon reduction of $Ce^{4+}$ to $Ce^{3+}$, is a strongly correlated f electron. The proper formula for oxygen deficient cerium oxide is written $CeO_{2-\delta}$ where $0 \leq \delta < 0.5$. The cubic phase is stable over this range of oxygen deficiency [2]. Ceria is also an exciting compound because its lattice parameter is similar to that of Si which facilitates the integration of spintronic components with conventional Si-based electronic devices.

From last few years, it has been observed that the transition metal (TM) doped some RE oxides, called Dilute Magnetic Oxide (DMO) have attracted much attention to the researchers in order to find out the improved HMF and to explore the mechanism behind HMF [11-18]. A high-$T_C$ DMO created by TM-doping in $CeO_2$ is good candidate which can be used as the spin-filter layer in spin-related devices [19]. Furthermore, due to perfect compatibility of its crystal structure and parameters with that of silicon, TM-doped $CeO_2$ would be more easily integrated and thus facilitates the integration of spintronic components based on it with conventional Si-based microelectronic devices [20]. This kind of study is very useful to design new spintronics devices like spin valves, spin light emitting diodes, magnetic sensors, logic devices and ultra-fast optical switches. Moreover,
these materials are also very important for nonlinear optics [21]. In this contrast, report of ferromagnetism in undoped HfO$_2$ with oxygen vacancy by Venkatesan et al. [22] shifted research interest towards developing rare earth dilute magnetic dielectric systems. Tiwari et al. [14] observed the room temperature ferromagnetism (RTFM) in single crystal Ce$_{1-x}$Co$_x$O$_{2-\delta}$ ($x \leq 0.05$) films deposited on a LaAlO$_3$(001) substrate. Subsequently, many experimental techniques have been employed to synthesize the undoped and Co-doped CeO$_2$ compounds [15-17] and to observe the role played by the oxygen vacancies to obtain RTFM in these systems. Sharma et al. [13] synthesized the Fe-doped CeO$_2$ powder using the standard solid-state reaction method at various doping concentration of Fe ($x = 0 - 0.05 \%$) and studied the ferromagnetic properties. They found the RTFM in this powder for $x = 0.03$. Recently, Singhal et al. [18] reported the RTFM in Co-/Fe-doped and pure CeO$_2$ (including oxygen vacancy) polycrystalline samples and governed the role of oxygen vacancies and hybridization of 3d- and 2p-states of Co/Fe and O-atoms, respectively, for ferromagnetic exchange mechanism. But for pure CeO$_2$, only week ferromagnetism was established by oxygen vacancies in this study. Despite lot of efforts in experimental work for magnetic characterization of TM doped CeO$_2$ compound in powder form, there is limited data available on the same from theoretical point of view. Recently, a first principle calculation has been reported by Song et al. [20] to compute the electronic and magnetic properties of Co-doped CeO$_2$. They observed that Co-d states combined with Oxygen vacancy decide spin polarization at Fermi level ($E_F$).

Since CeO$_2$ is a strongly correlated system in which Ce is heavy rare earth element and the theoretical description of Ce-f states is a challenge to the researchers due to their localization and extended behaviour. The standard density functional theory (DFT) calculations are inadequate to characterize the electronic structures of the CeO$_2$. So, the DFT + $U$ is one of effective schemes to cope with the correlation effects, in which a Hubbard $U$ term is added to the local density approximation (LDA) or generalized gradient approximation (GGA), which yields
the correct ground state description of CeO$_2$ in comparison with experiments. In order to support the experimental observations, we planned to remain focused on electronic and magnetic properties of Fe-doped CeO$_2$ and to establish the DMS characteristics for the same at Fe-concentration ($x = 0.125, 0.06$) theoretically. Due to the well known catalytic properties, CeO$_2$ easily forms stable Oxygen vacancy, so a clear connection between magnetic behavior and these vacancies is yet to be established. Thus, the other aim of this paper is to check the role played by oxygen vacancies in ferromagnetic exchange and half metallicity in Fe-doped CeO$_2$ on reducing Fe-doping. However, no such type of systematic study has been reported till date.

5.2 Details of Calculations

The calculations have been performed using FPLAPW method based on DFT [23] and is implemented in WIEN2k code [24] to study the electronic and magnetic properties of CeO$_2$ including the effect of both Fe doping and oxygen vacancy at doping concentration, $x = 0.125$ and 0.06. The XC potential was constructed using GGA+U formalism [25] in which Coulomb correction is applied to standard GGA functional within the parameterization of Perdew-Burke-Ernzerhof (PBE) [26]. The value of effective Hubbard parameter ($U_{\text{eff}}$) was taken to be 5.30 eV for the Ce-f states [27,28]. In FPLAPW calculations, the core states are treated fully relativistically whereas for the valence states, a semirelativistic calculation is performed. The plane wave cut off parameters were decided by $R_{\text{MT}}k_{\text{max}} = 8$ (where $k_{\text{max}}$ is the largest wave vector of the basis set such that $k_{\text{max}}$ controls the accuracy of the calculation) and $G_{\text{max}} = 14$ a.u.$^{-1}$ for Fourier expansion of potential in the interstitial region. The unit cell of CeO$_2$ compound crystallizes in fluorite type cubic structure (space group, Fm3m) where the Ce atom is surrounded by 8 Oxygen atoms (eight-fold coordination) shown in Fig. 5.1. The Ce atom is present at (0,0,0), O atom is at ($\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$). The present calculations
were based on the supercell approach where one Ce atom at (0,0,0) in the supercell of CeO$_2$ was replaced by Fe atom.

![Unit cell (left side) and BZ, with its IBZ, for ZB crystal structure of CeO$_2$. The symmetry \( \mathbf{k} \)-points are shown on IBZ.]

In order to generate 6.25 \%/12.5 \% Fe-doping in CeO$_2$, a tetragonal supercell, (2×2×1)/(2×1×1) has been constructed. The super cell of Ce$_{1-x}$Fe$_x$O$_2$ at $x = 0.125$ and 0.06 with and without $V_O$ are shown in Fig 5.2-5.5. Additionally, the effect of oxygen vacancy is taken into account by keeping one O-site vacant in respective supercell. The radius of muffin-tin (MT) spheres ($R_{MT}$) for Ce, Fe and O atom were chosen to be 2.3, 2.0 and 1.6 a.u., respectively, ensuring nearly touching spheres and minimizing the interstitial space. The energy convergence criterion was set to $10^{-4}$ Ry and the charge convergences were also monitored along with it. The $\mathbf{k}$-space integration has been carried out using the modified tetrahedron method [29] with 30/63 $\mathbf{k}$-points in the irreducible Brillouin zone (IBZ) for 6.25 \%/12.5 \% doping. All these parameters are sufficient to guarantee accuracy in results.
Fig. 5.2  
(2×1×1) Supercell for crystal structure of Ce$_{1-x}$Fe$_x$O$_2$ without V$_O$ at $x = 0.125$.

Fig. 5.3  
(2×1×1) Supercell for crystal structure of Ce$_{1-x}$Fe$_x$O$_2$ with V$_O$ at $x = 0.125$. 
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**Fig. 5.4** (2×2×1) Supercell for crystal structure of Ce\(_{1-x}\)Fe\(_x\)O\(_2\) without V\(_O\) at x = 0.06.

**Fig. 5.5** (2×2×1) Supercell for crystal structure of Ce\(_{1-x}\)Fe\(_x\)O\(_2\) with V\(_O\) at x = 0.06.
The important concept of half metallicity for spintronics was first presented by de Groot [30] predicting its existence in half Heusler compounds. The model suggests that the density of states (DOS) exhibits a gap for minority electrons. Thus these materials are supposed to be 100% spin polarized at $E_F$. It is useful to define the electron spin polarization ($P$) of a material at $E_F$, although it is difficult to be measured [31], as

$$P = \frac{N_\uparrow(E_F) - N_\downarrow(E_F)}{N_\uparrow(E_F) + N_\downarrow(E_F)}$$  \hspace{1cm} (1)

where $N_\uparrow(E_F)$ and $N_\downarrow(E_F)$ are the spin dependent DOS at $E_F$ for majority and minority spins, respectively. $P$ vanishes for paramagnetic materials and also for anti-ferromagnetic materials even below the magnetic transition temperature. However, it has a finite value in ferromagnetic or ferrimagnetic materials below the Curie temperature. The electrons at $E_F$ are fully spin polarized ($|P|=1$) when either $N_\uparrow(E_F)$ or $N_\downarrow(E_F)$ equals zero.

5.3. Result and discussion

The host semiconductor Ceria is a wide band gap semiconductor in its pure form. Further, it acts as an oxygen vacancy reservoir and has a tendency to store and release oxygen. When oxygen vacancy ($V_O$) is taken into account, it shows weak magnetism rather than semiconducting behavior. The unique features of CeO$_2$ justify its candidature in formation of efficient DMO compounds. We have summarized, from the literature, some important ground state properties of pure CeO$_2$ semiconductor in Table 5.1 for the overview of experimental studies performed for CeO$_2$ semiconductor which is used as host materials to make DMO by Fe-doping.
Table 5.1: List of experimental crystallographic and ground state properties of CeO₂ compound.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Experimental Crystal structure</th>
<th>Ground state Characterization</th>
<th>Experimental band gap (eV)</th>
<th>Characterization techniques</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO₂</td>
<td>C1</td>
<td>Semiconducting</td>
<td>6.00</td>
<td>x-ray photoelectron spectroscopy (XPS)</td>
</tr>
<tr>
<td>CeO₂+V₀</td>
<td>C1</td>
<td>Weak ferromagnetic</td>
<td>-</td>
<td>SQUID magnetometry, x-ray diffraction and XPS</td>
</tr>
</tbody>
</table>

5.3.1 Ground state properties

The structural optimizations for nonmagnetic-CeO₂, ferromagnetic Fe-doped CeO₂ with and without oxygen vacancy (V₀) at x = 0.125 and 0.06 as depicted in Fig. 5.6, have been performed in the neighbourhood of experimental lattice parameters [13] of pure CeO₂ semiconductor. The equilibrium values of optimized lattice parameters are listed in Table 5.2. A good agreement in equilibrium lattice parameters of pure CeO₂ (5.460 Å) w.r.t. experiment (5.41 Å) [13] validates the computed results. An increment in these parameters has been observed on decreasing the doping concentration from 0.125 to 0.06 in Fe-doped CeO₂ without V₀ but the presence of oxygen vacancies proposes the opposite trend and reduces the parameters from 5.498 Å to 5.449 Å on this concentration.
change. The optimized parameters have been used to carry out the detailed analysis of ground state properties of studied compounds.

![Graph showing total energy versus lattice parameters](image)

**Fig. 5.6** Total energy versus lattice parameters of Ce$_{1-x}$Fe$_x$O$_2$ ($x = 0.06$ and $0.125$) DMS compound with and without V$_O$. The solid lines show a polynomial fit for determining the optimized lattice constants. $E_{\text{equi}}$ corresponds to equilibrium energy at optimized lattice constant.

### 5.3.1.1 Density of states (DOS) and HM character

The total density of states (TDOS) of Ce$_{1-x}$Fe$_x$O$_2$ ($x = 0.125$ and $0.06$) with and without V$_O$ are presented in Fig. 5.7-5.8. A general observation from the Fig.
is that the ground state properties of bulk CeO$_2$ compound have been modified significantly due to the substitution of Fe-dopant at the cation (Ce) site with/without V$_O$. The new states have been produced at Fermi level (E$_F$) which accounts for the magnetism on the doping. For deep analysis in the observed DOS, the muffin-tin projected partial DOS (PDOS) for parent CeO$_2$, Fe-doped CeO$_2$ with and without V$_O$ are shown in Fig. 5.9.

**Table 5.2:** Optimized lattice parameters, calculated HM gaps, total DOS of majority and minority spin (i.e. $N_\uparrow$ (E$_F$) and $N_\downarrow$ (E$_F$) ), and spin polarization (P) at E$_F$ of Ce$_{1-x}$Fe$_x$O$_2$ (x = 0.125 and 0.06) DMS compounds with and without V$_O$.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Doping Conc. (x)</th>
<th>a(Å)</th>
<th>$\Delta$E$_{HM}$ (eV)</th>
<th>$N_\uparrow$ (E$_F$)</th>
<th>$N_\downarrow$ (E$_F$)</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce$<em>{0.875}$Fe$</em>{0.125}$O$_2$</td>
<td>0.125</td>
<td>5.436</td>
<td>0.077</td>
<td>5.943</td>
<td>0.000</td>
<td>1</td>
</tr>
<tr>
<td>Ce$<em>{0.94}$Fe$</em>{0.06}$O$_2$</td>
<td>0.06</td>
<td>5.452</td>
<td>0.120</td>
<td>7.817</td>
<td>0.000</td>
<td>1</td>
</tr>
<tr>
<td>Ce$<em>{0.875}$Fe$</em>{0.125}$O$_2$ + V$_O$</td>
<td>0.125</td>
<td>5.498</td>
<td>0.560</td>
<td>0</td>
<td>3.464</td>
<td>-1</td>
</tr>
<tr>
<td>Ce$<em>{0.94}$Fe$</em>{0.06}$O$_2$ + V$_O$</td>
<td>0.06</td>
<td>5.449</td>
<td>0.675</td>
<td>0</td>
<td>5.086</td>
<td>-1</td>
</tr>
</tbody>
</table>

As the partial contributions towards total DOS in studied compound at both dopant concentrations are almost alike, thus we have explored the spin dependent partial DOS (PDOS) of the compound at x = 0.06 only as a representative.

The analysis of TDOS and PDOS of studied compound in three cases is presented separately as under:

**(i) Pure CeO$_2$:** Although, the native properties of CeO$_2$ are well known experimentally, but we still discuss the spin polarized TDOS of pure CeO$_2$ compound, shown in Fig. 5.7(a), in order to compare the change in the various electronic states on Fe-doping in CeO$_2$ with/without V$_O$. The O-p states are
extended up to top of the valence band (VB) and reaches $E_F$. The conduction band (CB) is mainly composed of Ce-d and f-states.

![Graph showing calculated total DOS of Ce$_{1-x}$Fe$_x$O$_2$ DMS compound (x = 0.125) with and without V$_O$. The total DOS of CeO$_2$ semiconductor is also shown for comparison.](image)

**Fig. 5.7** Calculated total DOS of Ce$_{1-x}$Fe$_x$O$_2$ DMS compound (x = 0.125) with and without V$_O$. The total DOS of CeO$_2$ semiconductor is also shown for comparison.

These Ce-f empty states lie just above the $E_F$, forming a narrow vacant band due to its strong localization character. Our calculations predict a band gap between the O-p and Ce-d states of 5.80 eV which is in better agreement than previous theoretical values [20,32] w.r.t. experiment [33,34]. The observed band gap characterizes it in the category of wide band gap semiconductors.
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(ii) Fe-doped CeO$_2$: Fe-doping in CeO$_2$ can be constructed by replacing one Ce atom with Fe in a suitable supercell as per need of the doping level. This substituted Fe atom induces spin-polarization in the neighbouring Ce and O atoms. The calculated TDOS for Ce$_{1-x}$Fe$_x$O$_2$ \((x = 0.125)\) is shown in Fig. 5.7(b). The splitting of minority DOS in vicinity of $E_F$ is clearly visible which endows the 100 % spin polarization \((P = 1)\) with a band gap in this spin channel and half metallic (HM) characteristics.

![Graph showing DOS with and without Vo](image)

**Fig. 5.8** Calculated total DOS of Ce$_{1-x}$Fe$_x$O$_2$ DMS compound \((x = 0.06)\) with and without $V_O$.

The resultant spin polarization opens the route for spin conduction useful for spintronic devices. A true HM ferromagnet is governed by a non zero HM gap
instead of band gap in any spin channel [35,36]. This HM gap (ΔEHM) is defined as the minimum value out of (EF − E\text{v}^{\text{top}}) or (E\text{c}^{\text{bot}} − EF), where E\text{v}^{\text{top}} and E\text{c}^{\text{bot}} represent the energy corresponding to top of VB and bottom of CB, respectively. The values of HM gap in Ce\text{1-x}Fe\text{x}O\text{2} (x = 0.125 and 0.06) as listed in Table 5.2, show an increase on reducing x which is direct consequence of stronger hybridization of O-p states and Fe-d states for lower doping (Fig 5.8(b)). On doping, the O-p states in VB are blue shifted and cross EF, thereby deciding the occupation of EF in majority spin. Further, Ce-f states are red shifted due to reduced interaction of these with O-p states as compared to that in pure CeO\text{2}. The DOS in VB and CB in the vicinity of EF are attributed to Fe-d states with an admixture of O-p states in both, majority and minority spin channels. The Ce-d states lie deeper in both, VB and CB and hence do not decide the formation of band gap or HM gap. In the majority spin, the states at EF exhibit a mixed character of O-p states with Fe-d states which are most important to induce HMF in these compounds. The bottom of the CB is mainly contributed by the Fe-d states in minority spin channel only, whereas a band of Ce-f states contribute equally for both spin channels. The hybridization of O-p states with Fe-d states in the vicinity of EF resulting in a gap in minority spin channel. This hybridization is stronger for lower doping which results large spacing between bonding and antibonding states.

(iii) Fe-doped CeO\text{2} including V\text{O}: Finally, we turn to Ce\text{1-x}Fe\text{x}O\text{2} including V\text{O} in order to investigate role of V\text{O} to decide the magnetism. Due to well known catalytic property, the presence of V\text{O} cannot be ignored in Fe-doped CeO\text{2} DMO compound. The inclusion of V\text{O} actually in the calculations can serve as authentic simulated data for realistic comparison with experiments in future. The spin polarized TDOS of Ce\text{1-x}Fe\text{x}O\text{2} (x = 0.125/0.06) including V\text{O} are shown in Fig. 5.7(c)/5.8(c).
Again, the DMO system come out to be fully spin polarized ($P = -1$) but in majority spin channel. The formation of an oxygen vacancy creates two electrons to the Ce sub-lattice [37,38] which remains localized on the f-level traps of two neighbouring Ce and/or Fe-atoms. In this way, the formal valence of these atoms gets altered from tetrahedral to trivalent. The calculated PDOS of Fe-doped CeO$_2$ with V$_O$ shown in Fig. 5.9(c) indicates that the oxygen vacancies pull the Ce-d and f states closer to $E_F$ as compared to doped and undoped CeO$_2$ without V$_O$, and some part of Ce-f states in CB even cross $E_F$.

**Fig. 5.9** Calculated total and partial DOS of Ce$_{1-x}$Fe$_x$O$_2$ ($x = 0.06$) compound with and without V$_O$. Spin polarized DOS of CeO$_2$ semiconductor is also shown for exhaustive analysis.
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The oxygen vacancy in the system tries to create zero band gap \([13,18]\) but due to the interaction of O-p states with Fe-d states and Ce-f states, the HM gap predominates in majority spin with partial occupation of \(E_F\) by Ce-f states and Fe-\(e_g\) states (doubly degenerated d-states) in minority spin channel.

5.3.1.2 Magnetic properties

The Fe-doping in CeO\(_2\) induces a net magnetic moment of \(\sim 4.0\ \mu_B\) in all cases which shows an important role of Fe-d states. Further, the integer values of total moments for all compounds confirm the HM characteristics of these. The total and atom resolved magnetic moments of Fe-doped CeO\(_2\) with and without V\(_O\) at both doping concentration are listed in Table 5.3.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Doping Conc. (x)</th>
<th>(M_{Ce}) ((\mu_B))</th>
<th>(M_{Fe}) ((\mu_B))</th>
<th>(M_o) ((\mu_B))</th>
<th>(M_{int}) ((\mu_B))</th>
<th>(M_{tot}) ((\mu_B))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce(<em>{0.875})Fe(</em>{0.125})O(_2)</td>
<td>0.125</td>
<td>0.007</td>
<td>3.902</td>
<td>-0.004</td>
<td>0.099</td>
<td>4.000</td>
</tr>
<tr>
<td>Ce(<em>{0.94})Fe(</em>{0.06})O(_2)</td>
<td>0.06</td>
<td>0.018</td>
<td>3.90</td>
<td>-0.008</td>
<td>0.108</td>
<td>3.959</td>
</tr>
<tr>
<td>Ce(<em>{0.875})Fe(</em>{0.125})O(_2) + V(_O)</td>
<td>0.125</td>
<td>-0.167</td>
<td>3.855</td>
<td>0.034</td>
<td>-0.135</td>
<td>3.999</td>
</tr>
<tr>
<td>Ce(<em>{0.94})Fe(</em>{0.06})O(_2) + V(_O)</td>
<td>0.06</td>
<td>-0.193</td>
<td>4.047</td>
<td>0.102</td>
<td>-0.280</td>
<td>3.999</td>
</tr>
</tbody>
</table>

The major contributions in total moments come only from Fe-atoms. The emergence of ferromagnetism in Fe-doped CeO\(_2\) without V\(_O\) can be explained by Zener's double exchange mechanism for ferromagnetism (FM) as in other DMS \([39]\) compounds. In the present case, the d states of dopant hybridize strongly with p-states of neighboring anions, then these anions get spin polarized and can couple
ferromagnetically to Fe-dopant, resulting in an indirect FM coupling. This is so called p-d hybridization mechanism.

On the other hand, the magnetism in \( \text{Ce}_{1-x}\text{Fe}_x\text{O}_2 \) \((x = 0.125 \text{ and } 0.06)\) with \( V_O \) originates in a different manner. This spin polarization at \( E_F \) in majority spin channel is due the existence of exchange interaction between the trivalent Fe ions and the carriers captured by \( V_O \). This means that spins of the localized defects \( (V_O) \) align with the nearby Fe ions, activating the long-range ferromagnetic interactions. Moreover, due to the presence of \( V_O \), Fe ions retain the trivalent state and Ce ions are also reduced to the trivalent \( (\text{Ce}^{3+}) \) state from its tetravalent \( (\text{Ce}^{4+}) \) state. Therefore, both the \( \text{Fe}^{3+} \) and \( \text{Ce}^{3+} \) electron spins contribute to ferromagnetic ordering. This additional exchange interaction between the spins of the unpaired \( 4f^1 \) electrons in \( \text{Ce}^{3+} \) state is responsible for the observed enhanced ferromagnetism. This type of interaction is known as F-center exchange coupling [15,17,40].

### 5.4. Conclusions

A full potential treatment of electronic and magnetic properties of Fe-doped \( \text{CeO}_2 \) DMO compounds at dopant concentration, \( x = 0.125 \) and \( 0.06 \) is presented. The half metallicity remains intact on reducing the dopant concentrations with a HM gap in minority/majority spin channel in all compounds with/without \( V_O \). This property makes these compounds suitable for practical spintronic devices. Moreover, the existence of HM gap is a striking feature of studied DMS compound. The HM gap decreases on reducing the dilute limit in all studied compounds. The HM gap in minority spin for Fe-doped \( \text{CeO}_2 \) without \( V_O \) is a fingerprint of the Fe-d and O-p interaction and the emergence of ferromagnetism can be explained by Zener's double exchange mechanism for ferromagnetism as in DMS. On the other hand, interactions between O-p, Fe-d and Ce-f are accountable for the HMF in the majority spin channel for Fe-doped \( \text{CeO}_2 \) with \( V_O \). The total magnetic moment of studied compound with and without \( V_O \) is mainly governed.
by Fe-atom due to the presence of energetic Fe-d states. We believed that this study will serve as a groundbreaking step in the development of new spintronic devices.

References:


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