Recent Insights Into Electronic Performance, Magnetism and Exchange Splittings in the Cr-substituted CaO

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The first-principles computations of density functional theory are employed to characterize the structural properties, electronic structures, and ferromagnetism induced by Cr impurities in Ca$_{1-x}$Cr$_x$O compounds at concentrations $x = 0.25$, 0.5, and 0.75. The dynamic stability is performed by the phonon spectra calculations. The structural parameters are computed by using Wu-Cohen generalized gradient approximation, while the electronic and magnetic properties are determined by the accurate Tran–Blaha-modified Becke–Johnson exchange potential. The crystal field, direct and indirect exchange splittings were investigated to determine the origin and stability of ferromagnetic state configuration. The Ca$_{1-x}$Cr$_x$O systems have right half-metallicities, which are verified by the spin polarization of 100% and the integer values of total magnetic moments. The Ca$_{0.75}$Cr$_{0.25}$O, Ca$_{0.5}$Cr$_{0.5}$O, and Ca$_{0.25}$Cr$_{0.75}$O are half-metallic ferromagnetic with flip-gaps of 1.495, 0.888, and 0.218 eV, respectively. Therefore, the Ca$_{1-x}$Cr$_x$O materials are suitable candidates for possible applications of spin-injection in future semiconductors spintronics.

Keywords: first-principles calculations, electronic structures, ferromagnetism, exchange splittings, spintronics

INTRODUCTION

In recent years, the exploitation of new materials for technological development has become an attractive area of research for the scientific community. Spintronics is a modern field emerging from quantum electronics relating to exploration and control of the electron spin; it is currently an important research topic because the spin-based devices have interesting multifunctional characteristics such as non-volatility, data-processing speed, higher integration densities (Elilarassi and Chandrasekaran, 2017; Rai et al., 2018). In the last years, the half-metal ferromagnetic (HMF) materials have attracted considerable interest due to their wide application in spintronic devices as magnetic sensors, tunnel junctions, and spin injection sources of electrons (Özdemir and Merdan, 2019). The diluted magnetic semiconductors (DMSs) are obtained from the III–V, II–VI, or IV–VI semiconductors doped with magnetic elements, inducing changes in their structural, electronic, and magnetic properties, which are related to the concentration of magnetic impurities. These materials have received a lot of attention for scientific research because they are promising...
candidates for innovative applications in spintronics, as an example for non-volatile memories, optical switches, and magneto-optical devices (Ohno, 1998; Dietl et al., 2000; Wolf et al., 2001; Zuti et al., 2004; Sato et al., 2010; Kumar et al., 2014).

Alkaline earth chalcogenides are important materials with a wide technological application ranging from catalysis to microelectronics as well as in the area of electro- and photoluminescent devices (Hakamata et al., 2005; Speziale et al., 2006; Murtaza et al., 2014). Among these compounds, the CaX (X = O, S, Se) has a closed-shell ionic environment, crystallizing in the rock-salt NaCl-type (B1) structure at ambient conditions (Doll et al., 1996; Mishra et al., 2012). Under high pressure, they undergo a first-order structural phase transition from the NaCl-type (B1) to the CsCl-type (B2) crystal structure (Luo et al., 1994; Doll et al., 1996; Dadsetani and Doosti, 2009; Mishra et al., 2012). The CaO calcium oxide can be a potential candidate as a DMS material according to several theoretical studies (Kenmochi et al., 2004; Kemmochi et al., 2005; An Dinh et al., 2006). Kenmochi et al. (2004) have studied a new class of DMSs based on CaO without transition metals, where the substituted CaO by C and N at the oxygen sites shows room-temperature ferromagnetism with half-metallic property. The ferromagnetism in C-doped CaO is explained by the exchange coupling constants, where it is induced by the strong hybridization between 2p states of carbon and 2p states of oxygen (An Dinh et al., 2006). Further, Kenmochi et al. (2005) have found that the stability of ferromagnetic state in the C-doped CaO is originated from the Zener’s double-exchange mechanism.

In this study, we have investigated the structural parameters, electronic performance, magnetism, and exchange splittings of Ca$_{1-x}$Cr$_x$O materials at various concentrations x = 0, 0.25, 0.5, and 0.75. The calculations are performed by the use of first-principle approaches of density functional theory (DFT) (Hohenberg and Kohn, 1964; Kohn and Sham, 1965) as implemented in the WIEN2k package (Blaha et al., 2001). The phonon spectra are used to verify the dynamic stability of Ca$_{1-x}$Cr$_x$O materials. The exchange and correlation potential is evaluated by the generalized gradient approximation of Wu and Cohen (GGA-WC) (Wu and Cohen, 2006), and the Tran–Blaha-modified Becke–Johnson potential (TB-mBJ) (Tran and Blaha, 2009).

**RESULTS AND DISCUSSION**

**Structural Properties**

**Crystal Structures**

The calcium oxide CaO is known as a wide-band gap II–VI semiconductor, crystallizing in rock-salt NaCl (B1) structure at ambient conditions (Doll et al., 1996; Mishra et al., 2012). The primitive unit cell of CaO contains two atoms such as the calcium (Ca) and the oxygen (O), which belong, respectively, to the main groups II and VI of the periodic table. Our study is based on the conventional NaCl structure of eight atoms of CaO such as Ca$_4$O$_4$, where the Ca is located at (0, 0, 0) position and the O atom at (0.5, 0.5, 0.5) with space group of $Fm\bar{3}m$ No. 225. The Ca$_3$CrO$_4$, Ca$_3$Cr$_2$O$_4$, and CaCr$_3$O$_4$ supercells are created by substituting one, two, and three Cr impurities at Ca sites, respectively. Consequently, we have obtained three supercells such as Ca$_{0.75}$Cr$_{0.25}$O at concentration x = 0.25, Ca$_{0.5}$Cr$_{0.5}$O at x = 0.5 and Ca$_{0.25}$Cr$_{0.75}$O at x = 0.75. The Ca$_{0.75}$Cr$_{0.25}$O and Ca$_{0.25}$Cr$_{0.75}$O have cubic lattices with space group of $Pm\bar{3}m$ No 221, while the Ca$_{0.5}$Cr$_{0.5}$O supercell has a tetragonal lattice with space group of $P4/mmm$ No. 123. We have noticed that all symmetry operations have been considered in the initialization of structures of Ca$_{1-x}$Cr$_x$O supercells for computations of different properties.

**Structural Stability**

The structural stability of the Ca$_{1-x}$Cr$_x$O compounds in the ferromagnetic rock-salt NaCl (B1) structure is verified by computing the formation energies. The formation energies ($E_{\text{form}}$) of the Ca$_{4-x}$Cr$_x$O$_4$ materials are determined using the following expression (Bai et al., 2011; Doumi et al., 2015a):
where 

\[ E_{\text{form}} = E_{\text{total}}(\text{Ca}_{4-y}\text{Cr}_y\text{O}_4) - \left( \frac{(4-y)E(\text{Ca})}{8} \right) - \left( \frac{yE(\text{Cr})}{8} \right) - \left( \frac{4E(\text{O})}{8} \right) \]  

Equation (1)

where \( E_{\text{total}}(\text{Ca}_{4-y}\text{Cr}_y\text{O}_4) \) corresponds to the minimum total energy of \( \text{Ca}_{4-y}\text{Cr}_y\text{O}_4 \) per atom, and \( E(\text{Ca}) \), \( E(\text{Cr}) \), and \( E(\text{O}) \) refer to the minimum total energies per atom of bulks Ca, Cr, and O, respectively. The \( y = 1, 2, \) and 3 are the number of substituted Cr impurities in \( \text{Ca}_{4-y}\text{Cr}_y\text{O}_4 \) supercells. We have found that the formation energies are \(-5.99\), \(-6.37\), and \(-6.76\) eV, respectively, for \( \text{Ca}_{0.75}\text{Cr}_{0.25}\text{O} \), \( \text{Ca}_{0.5}\text{Cr}_{0.5}\text{O} \), and \( \text{Ca}_{0.25}\text{Cr}_{0.75}\text{O} \). Therefore, the negative values of formation energies suggest that these compounds are thermodynamically stable in the ferromagnetic rock-salt structure.

Furthermore, we have used the phonon spectra to demonstrate the dynamic stability of the \( \text{Ca}_{1-x}\text{Cr}_x\text{O} \) doping compounds. The diagrams of phonon frequencies at high symmetry points in the Brillouin zone of \( \text{Ca}_{0.75}\text{Cr}_{0.25}\text{O} \), \( \text{Ca}_{0.5}\text{Cr}_{0.5}\text{O} \), and \( \text{Ca}_{0.25}\text{Cr}_{0.75}\text{O} \) are shown by Figures 1–3, respectively. These figures depicted that all branches of phonons have positive frequencies, and there are no negative frequencies (Deng et al., 2019), confirming the dynamic stability of \( \text{Ca}_{0.75}\text{Cr}_{0.25}\text{O} \), \( \text{Ca}_{0.5}\text{Cr}_{0.5}\text{O} \), and \( \text{Ca}_{0.25}\text{Cr}_{0.75}\text{O} \) compounds.

**Equilibrium Structural Parameters**

The variations of total energies as a function of volumes of \( \text{Ca}_{1-x}\text{Cr}_x\text{O} \) compounds are fitted by Murnaghan (1944) equation of state to determine the equilibrium structural parameters. Table 1 summarizes the lattice constants, the bulk modules, and their first derivatives with other experimental data (Mammone et al., 1981; Kaneko et al., 1982; Richet et al., 1988) and theoretical values (Tran et al., 2007; Wu et al., 2014; Cinthia et al., 2015; Fan et al., 2015; Nejatipour and Dadsetani, 2015; Santana et al., 2016; Yang et al., 2016; Salam, 2018) computed by the generalized gradient approximation of Perdew–Burke–Ernzerhof (GGA-PBE) (Perdew et al., 1996), revised GGA of Perdew–Burke–Ernzerhof (GGA-PBEsol) (Perdew et al., 2008) and the local density approximation (LDA) (Perdew and Zunger, 1981; Perdew and Wang, 1992).

The results of lattice constants and bulk modulus of CaO are closed to theoretical values of Tran et al. (2007) and Fan et al. (2015) calculated with GGA-WC potential (Wu and Cohen, 2006). We see that there is a good agreement between our calculations and experimental results (Mammone et al., 1981; Kaneko et al., 1982; Richet et al., 1988) and theoretical value.
found by GGA-PBE sol (Perdew et al., 2008). On the other hand, the obtained values of these parameters with GGA-WC (Wu and Cohen, 2006) are better than the calculations of Tran et al. (2007), Wu et al. (2014) Cinthia et al. (2015), Nejatipour and Dadsetani (2015), Yang et al. (2016), Salam (2018), Tran et al. (2007), Fan et al. (2015), and Santana et al. (2016) found, respectively, by GGA-PBE (Perdew et al., 1996) and LDA approximation (Perdew and Zunger, 1981; Perdew and Wang, 1992). The performance of GGA-WC approximation for predicting structural parameters is due to the fourth-order gradient expansion of exchange-correlation functional (Doumi et al., 2015b; Sajjad et al., 2015). For the \( \text{Ca}_{1-x}\text{Cr}_x\text{O} \) doping compounds, the ionic radius of Cr is lower than that of Ca atom, leading to decrease in the lattice constant with increasing Cr concentration. Consequently, the bulk modulus of \( \text{Ca}_{1-x}\text{Cr}_x\text{O} \) increases with increasing concentration of Cr. The \( \text{Ca}_{1-x}\text{Cr}_x\text{O} \) doping compound becomes harder as the concentration of Cr increases.

### Electronic Properties

#### Band Structures and Half-Metallicity

We have used the predicted structural parameters to characterize the electronic structures and the half-metallicity in \( \text{Ca}_{1-x}\text{Cr}_x\text{O} \) compounds. The TB-mBJ potential is used to determine the electronic structures and accurate band gaps of \( \text{Ca}_{1-x}\text{Cr}_x\text{O} \) compounds at concentration \( x = 0, 0.25, 0.5, \) and 0.75. The band structures of \( \text{CaO}, \text{Ca}_{0.75}\text{Cr}_{0.25}\text{O}, \text{Ca}_{0.5}\text{Cr}_{0.5}\text{O}, \) and \( \text{Ca}_{0.25}\text{Cr}_{0.75}\text{O} \) are shown, respectively, by the Figures 4–7.

According to Figure 4, the CaO is a semiconductor because both majority and minority spins revealed the analogous band structures with indirect gaps. The CaO has an indirect gap\( E_{\text{ind}} \) between the valence bands maximum and conduction bands minimum situated, respectively, at \( \Gamma \) and X high symmetry points. Figures 5–7 demonstrate that the \( \text{Ca}_{1-x}\text{Cr}_x\text{O} \) for all concentrations are metallic and semiconductors, respectively, for majority- and minority-spin bands. Consequently, the \( \text{Ca}_{1-x}\text{Cr}_x\text{O} \) doping materials are half-metallic ferromagnets. The metallic character is due to localized partially filled 3d-Cr states of majority spins around Fermi level \( E_F \), which interact with carriers of valence states of host semiconductor. For minority spins, the \( \text{Ca}_{1-x}\text{Cr}_x\text{O} \) doping systems keep a semiconductor behavior as CaO compound because the 3d-Cr empty minority-spin states arise in the bottom of conduction band minimum at \( \Gamma \) high symmetry point far than \( E_F \). Thus, the gap nature shifted from indirect band gap for CaO to direct gap for \( \text{Ca}_{1-x}\text{Cr}_x\text{O} \) doping systems.

The minority spins of \( \text{Ca}_{1-x}\text{Cr}_x\text{O} \) systems are characterized by direct wide-band gaps called half-metallic ferromagnetic (HMF) gaps located at the \( \Gamma \) high symmetry point. The minimal energies that separate the Fermi level (zero eV), and the conduction band minimums determine the half-metallic (HM) gaps. Table 2 shows the computed band gaps such as the direct HMF gaps

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**Table 1** | Computed structural parameters such as lattice constants \( a \), bulk modules \( B \), and their pressure derivatives \( B' \) for \( \text{Ca}_{1-x}\text{Cr}_x\text{O} \) materials at concentrations \( x = 0, 0.25, 0.5, \) and 0.75 with other experimental and theoretical data.

| Material              | \( a \) (Å) | \( B \) (GPa) | \( B' \) | Method                                      | Method References                  | References              |
|-----------------------|-------------|---------------|----------|---------------------------------------------|------------------------------------|-------------------------|
| This work             |             |               |          | Generalized gradient approximation of Wu and Cohen (GGA-WC) |                                    |                         |
| \( \text{CaO} \)      | 4.772       | 113.15        | 4.44     |                                             |                                    |                         |
| \( \text{Ca}_{0.75}\text{Cr}_{0.25}\text{O} \) | 4.860       | 126.40        | 4.63     |                                             |                                    |                         |
| \( \text{Ca}_{0.5}\text{Cr}_{0.5}\text{O} \)      | 4.549       | 128.91        | 3.63     |                                             |                                    |                         |
| \( \text{Ca}_{0.25}\text{Cr}_{0.75}\text{O} \)      | 4.415       | 133.23        | 3.75     |                                             |                                    |                         |
| Other calculations   |             |               |          |                                            |                                    |                         |
| \( \text{CaO} \)      | 4.812       | 111           | 4.2      | Experimental                                 |                                    | Kaneko et al., 1982     |
| \( \text{CaO} \)      | 4.8105      | 115           | 4.1      | Experimental                                 |                                    | Richet et al., 1988     |
| \( \text{CaO} \)      | 4.777       | 116           |          | GGA-WC                                      |                                    | Mammone et al., 1981    |
| \( \text{CaO} \)      | 4.841       | 105           |          | Generalized gradient approximation of Perdew–Burke–Ernzerhof (GGA-PBE) |                                    | Tran et al., 2007       |
| \( \text{CaO} \)      | 4.81        | GGA-PBE       |          |                                            |                                    | Fan et al., 2015        |
| \( \text{CaO} \)      | 4.857       | GGA-PBE       |          |                                            |                                    | Wu et al., 2014         |
| \( \text{CaO} \)      | 4.843       | 107           | 4.2      | GGA-PBE                                      |                                    | Cinthia et al., 2015    |
| \( \text{CaO} \)      | 4.843       | GGA-PBE       |          |                                            |                                    | Nejatipour and Dadsetani, 2015 |
| \( \text{CaO} \)      | 4.834       | GGA-PBE       |          |                                            |                                    | Yang et al., 2016       |
| \( \text{CaO} \)      | 4.836       | 102.3         | 4.17     | GGA-PBE                                      |                                    | Salam, 2018             |
| \( \text{CaO} \)      | 4.77        | Revised GGA of Perdew–Burke–Ernzerhof (GGA-PBEsol)  |          |                                            |                                    | Fan et al., 2015        |
| \( \text{CaO} \)      | 4.719       | 129           |          | Local density approximation (LDA)           |                                    | Tran et al., 2007       |
| \( \text{CaO} \)      | 4.71        | LDA           |          |                                            |                                    | Fan et al., 2015        |
| \( \text{CaO} \)      | 4.734       | 119.54        | 4.23     | LDA                                         |                                    | Santana et al., 2016    |
FIGURE 4 | Band structures of CaO. (A) Majority spins (\(\uparrow\)) and (B) minority spins (\(\downarrow\)). The Fermi level is set to zero (horizontal dotted line).

FIGURE 5 | Band structures of Ca\(_{0.75}\)Cr\(_{0.25}\)O. (A) Majority spins (\(\uparrow\)) and (B) minority spins (\(\downarrow\)). The Fermi level is set to zero (horizontal dotted line).

\(E_{\text{HMF}}\) and HM gaps \(E_{\text{HM}}\) of Ca\(_{0.75}\)Cr\(_{0.25}\)O, Ca\(_{0.5}\)Cr\(_{0.5}\)O, and Ca\(_{0.25}\)Cr\(_{0.75}\)O, and the indirect gap \(E_{\text{\Gamma X}}\) of CaO with other theoretical (Fan et al., 2015; Nejatipour and Dadsetani, 2015; Yang et al., 2016; Tran and Blaha, 2017; Salam, 2018) and experimental data (Whited et al., 1973). The result of wide-indirect gap of 5.392 eV of CaO is in good agreement with recent calculated value of 5.35 eV of Tran and Blaha (2017) study using the same TB-mBJ potential (Becke and Johnson, 2006; Tran and Blaha, 2009), and it is better than the values ranging from 3.437 to 3.67 eV of Fan et al. (2015), Nejatipour and Dadsetani (2015), Yang et al. (2016), Tran and Blaha (2017), Salam (2018) found by the LDA (Perdew and Zunger, 1981; Perdew and Wang, 1992), GGA-WC (Wu and Cohen, 2006), GGA-PBE (Perdew et al., 1996), and GGA-PBEsol exchange potentials (Perdew et al., 2008). The TB-mBJ provides accurate gap for CaO because it is known for its performance in the calculation of electronic structures of insulators and semiconductors with respect to LDA and all forms of GGA approximations (Bhattacharjee and
FIGURE 6 | Band structures of Ca$_{0.5}$Cr$_{0.5}$O. (A) Majority spins (up) and (B) minority spins (dn). The Fermi level is set to zero (horizontal dotted line).

FIGURE 7 | Band structures of Ca$_{0.25}$Cr$_{0.75}$O. (A) Majority spins (up) and (B) minority spins (dn). The Fermi level is set to zero (horizontal dotted line).

Moreover, the half-metallic gap or flip-gap is an interesting performance for exploring the spin-injection for a half-metallic material in spintronics. The Ca$_{0.75}$Cr$_{0.25}$O, Ca$_{0.5}$Cr$_{0.5}$O, and Ca$_{0.25}$Cr$_{0.75}$O compounds have the HM gaps of 1.495, 0.888, and 0.218 eV, respectively, situated between the conduction bands minimum (CBM) and $E_F$. The CBM moves toward $E_F$ due to widening of 3d-Cr empty states at the bottom of conduction band, and hence, the HM gap decreases from Ca$_{0.75}$Cr$_{0.25}$O, Ca$_{0.5}$Cr$_{0.5}$O, to Ca$_{0.25}$Cr$_{0.75}$O. The HM gap behavior is maintained for different concentrations, meaning that the Ca$_{1-x}$Cr$_x$O doping systems are right half-metallic materials.

Densities of States and Spin Polarization

In order to understand the origin of half-metallic feature induced by the substituting effect of Cr, we have plotted the total and partial densities of states (DOS) of Cr, Ca, and O atoms of Ca$_{1-x}$Cr$_x$O compounds. Figures 8–10 show, respectively, the DOS of Ca$_{0.75}$Cr$_{0.25}$O, Ca$_{0.5}$Cr$_{0.5}$O, and Ca$_{0.25}$Cr$_{0.75}$O. We
TABLE 2 | Computed band gaps such as indirect band gap (E_F) for CaO, half-metallic ferromagnetic (HMF) gaps (E_{HMF}), and half-metallic (HM) gaps (E_{HM}) of minority-spin bands for Ca_{1-x}Cr_{x}O at concentrations x = 0.25, 0.5, and 0.75 with other theoretical and experimental data.

| Material               | E_{HMF} (eV) | E_{HM} (eV) | E_{F} (eV) | Method                |
|------------------------|--------------|-------------|------------|-----------------------|
| This work              |              |             |            |                       |
| CaO                    | 5.392        |             |            | Tran–Blaha-modified   |
| Ca_{0.75}Cr_{0.25}O    | 5.242        | 1.495       |            | Becke–Johnson potential (TB-mBJ) |
| Ca_{0.5}Cr_{0.5}O      | 5.142        | 0.888       |            | TB-mBJ                |
| Ca_{0.25}Cr_{0.75}O    | 5.195        | 0.218       |            | TB-mBJ                |
| Other calculations     |              |             |            |                       |
| CaO                    | 3.53         |             |            | GGA-WC                |
| CaO                    | 3.647        |             |            | GGA-PBE               |
| CaO                    | 3.669        |             |            | GGA-PBE               |
| CaO                    | 3.65         |             |            | GGA-PBE               |
| CaO                    | 3.658        |             |            | GGA-PBE               |
| CaO                    | 3.67         |             |            | GGA-PBE               |
| CaO                    | 3.518        |             |            | GGA-PBEsol            |
| CaO                    | 3.437        |             |            | LDA                   |
| CaO                    | 3.49         |             |            | LDA                   |
| CaO                    | 5.35         |             |            | TB-mBJ                |
| CaO                    | 7.00         |             |            | Experimental          |

Magnetic Properties

Magnetic Moments

The spin-polarized electronic structures show an asymmetric character, indicating that the Ca_{1-x}Cr_{x}O compounds are magnetic in nature. The magnetism is induced by the magnetic spins arising from the localized 3d-Cr majority-spin states around E_F. The Cr impurity contributes two electrons to host carriers of valence bands, resulting in Cr^{2+} ion. Thus, the 3d-Cr states become partially filled with four electrons. Therefore, the magnetism is originated from the four itinerant electrons of Cr^{12} ions in Ca_{1-x}Cr_{x}O doping materials.

From the DOS of majority spins, one can see that the non-bonding states of minority spins enclosing low-lying t_{2g} states arising from the localized 3d-Cr majority-spin states around E_F. The Cr impurity contributes two electrons to host carriers of valence bands, resulting in Cr^{2+} ion. Thus, the 3d-Cr states become partially filled with four electrons. Therefore, the magnetism is originated from the four itinerant electrons of Cr^{12} ions in Ca_{1-x}Cr_{x}O doping materials.

The calculated total and partial magnetic moments of Ca, Cr, and O atoms and in the interstitial sites for Ca_{0.75}Cr_{0.25}O, Ca_{0.5}Cr_{0.5}O, and Ca_{0.25}Cr_{0.75}O are given in Table 3. The total magnetic moment per Cr atom is an integer number of 4 \mu_B. It is a typical feature of half-metallic materials (Wang et al., 2017; Zhang et al., 2017). All compounds have negative partial magnetic moments for O atoms, revealing that carriers of host valence bands enclosing p-O states interact anti-ferromagnetically with 3d-Cr states. Besides, the positive partial magnetic moments of Cr and Ca atoms describe the ferromagnetic interaction between Cr and Ca magnetic spins.
Exchange Splitting Mechanisms

The ferromagnetism is created from the localized electrons of $t_{2g}$ and $e_{2g}$ of 3d-Cr states mediated by holes, where the empty holes of $e_{g}$ states occur at the top of valence band and generate an acceptor hole type carrier hybridizing with carriers of host valence band (Doumi et al., 2013). The degenerate 3d-Cr into $t_{2g}$ and $e_{2g}$ is due to crystal field generated from the electrostatic environment of surrounding oxygen (O) ions, where the 3d-Cr majority-spin levels contain four unpaired electrons (Noor et al., 2018). According to the Hund's rule, this kind of process mediates magnetism in Ca$_{1-x}$Cr$_x$O materials (Yaqoob et al., 2019). It is understood that both exchange splitting of 3d-Cr states and
crystal field take part in the contribution of ferromagnetism in Ca$_{1-x}$Cr$_x$O doping materials.

The magnitude of crystal field energy ($\Delta E_{CF}$) is defined as a difference between $E_{eg}$ and $E_{t2g}$ energies of $e_g$ and $t_{2g}$ states ($\Delta E_{CF} = E_{eg} - E_{t2g}$). The direct exchange splitting energy $\Delta_x(d) = d \downarrow - d \uparrow$ is determined from the separation between the empty d-Cr ($d \downarrow$) minority-spin and occupied d-Cr ($d \uparrow$) majority-spin peaks. Another factor is used to determine the magnitude of ferromagnetism such as the indirect $\Delta_x(pd) = E^\downarrow_v - E^\uparrow_v$ exchange splitting resulted from the energy difference.
between $E_\uparrow$ and $E_\downarrow$ valence band maximums of minority- and majority-spin channels, respectively.

The values of $\Delta_{CF}$, $\Delta_d(d)$, and $\Delta_{pd}$ exchange splitting are shown in Table 4. The obtained values of ($\Delta_{CF}$ and $\Delta_d(d)$) are (1.71 and 4.98 eV), (2.97 and 4.90 eV), and (1.74 and 5.17 eV), revealing that the direct exchange splittings are more dominated compared to the crystal field splittings. Therefore, the ferromagnetism state is mainly favored by the contribution of direct exchange splitting mechanism than that of crystal field (Amin et al., 2018). Besides, the partial magnetic moment of Cr increases from 3.652 $\mu_B$ for Ca$_0.75$Cr$_0.25$O, 7.203 $\mu_B$ for Ca$_0.5$Cr$_0.5$O, to 10.541 $\mu_B$ for Ca$_0.25$Cr$_0.75$O with decreasing
Δn(pd), meaning that magnetic moment of Cr is directly related to the indirect exchange splitting. On the other hand, the attraction nature of spin-polarized electrons is measured from the indirect exchange splitting (Verma et al., 2011; Mahmood et al., 2016, 2018). The indirect exchange splittings Δx(pd) have negative values because the valence band maximums of minority-spins are situated at lower energies with respect to the valence band maximums of majority-spins. This means that the minority-spins have more attractive (negative) potential than that of majority-spins, leading to perfectly localized magnetic states. Consequently, the ferromagnetism is preferred in the Ca1-xCrxO compounds. In the DMS based on III–V and II–VI semiconductors doped with transition metals, when the d states of magnetic dopants are partially occupied (Sato and Katayama-Yoshida, 2002; Sato et al., 2003a,b), the stability of ferromagnetism is described by the double-exchange mechanism (Akai, 1998). According to this rule, the anti-bonding states of partially filled 3d-Cr atoms associated with double-exchange mechanism stabilize the ferromagnetic state configuration in Ca1-xCrxO.

The magnitudes of valence and conduction band edge splitting are measured by the two sp-d exchange constants N0α and N0β. The N0α parameter determines the s-d exchange interaction between the s carriers of conduction bands and d-Cr levels, while the N0β describes the p-d exchange coupling between the p states of carriers of valence bands and d-Cr levels. We have used the mean field theory (Sanvito et al., 2001; Raebiger et al., 2004) to calculate the exchange constants of Ca1-xCrxO compounds given by the following relations.

\[
N_{0\alpha} = \frac{\Delta E_{c}}{x(s)} \quad (3)
\]

\[
N_{0\beta} = \frac{\Delta E_{c}}{x(s)} \quad (4)
\]

The \(\Delta E_{c} = E_{c}^{\uparrow} - E_{c}^{\downarrow}\) and \(\Delta E_{v} = E_{v}^{\uparrow} - E_{v}^{\downarrow}\) difference energies correspond, respectively, to the valence band-edge and conduction band-edge spin-splittings at \(\Gamma\) high symmetry point. The \(s\) and \(x\) are the half total magnetic moment per Cr and the concentration of Cr, respectively (Sanvito et al., 2001). The calculated \(\Delta E_{v}, \Delta E_{c}, N_{0\alpha}\), and \(N_{0\beta}\) are summarized in Table 5. Yaqoob et al. (2019) have predicted that the negative values of \(N_{0\alpha}\) and \(N_{0\beta}\) are due to the quantum confinement effect or structural symmetry changes that modify the coupling of different states. For Ca1-xCrxO materials, the negative values of \(N_{0\alpha}\) and \(N_{0\beta}\) describe the anti-ferromagnetic coupling between the valence and conduction bands and the 3d states of magnetic Cr atoms.

### CONCLUSIONS

We have characterized the structural properties, the spin-polarized electronic structures, and ferromagnetic performance induced by the Cr impurities in Ca1-xCrxO compounds at concentrations \(x = 0, 0.25, 0.5, \) and 0.75. The Ca1-xCrxO doping materials are dynamically stable due to their positive phonon frequencies. The structural parameters and indirect gap of CaO are very significant with respect to the recent calculations found by GGA-WC and TB-mBJ. For Ca1-xCrxO, the lattice constant decreases with increasing Cr concentration, leading to the increase in bulk modulus, where the sizes of the ionic radii of Ca and Cr atoms are the factors determining these changes. The Ca1-xCrxO systems have a half-metallic ferromagnetic feature, where the ferromagnetism is favored by the large contribution of direct exchange splitting than that of the crystal field. The analysis of magnetic properties shows that both double-exchange and p-d exchange mechanisms participate to stabilize ferromagnetic state configuration. The half-metallic ferromagnets Ca1-xCrxO compounds maintain a half-metal gap feature for all concentrations with spin polarization of 100%, making them suitable spin-injection candidates for possible exploration in spintronics.

### DATA AVAILABILITY STATEMENT

All datasets presented in this study are included in the article/supplementary material.

### AUTHOR CONTRIBUTIONS

With the submission of this manuscript, all authors declare that the manuscript is original. All authors of this research contributed equally to the work. The manuscript is original, and all authors declare that the manuscript is original.
paper have contributed to this manuscript. All authors of this paper have read and approved the final version submitted. The contents of this manuscript have not been copyrighted or published previously. The contents of this manuscript are not now under consideration for publication elsewhere.

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