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Electronic and Magnetic Properties of Cr and V Doped CaZ (Z = S, Se)

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Abstract: Using first-principle spin-density functional computations, the structural, magnetic, and electronic properties of the Cr- and V-doped diluted magnetic semiconductors $\text{Ca}_{1-x}\text{Cr}_x\text{S}$ and $\text{Ca}_{1-x}\text{V}_x\text{Se}$ at $x = 0.25$ in the B1 (NaCl) phase are explored. Elastic constants and structural properties (lattice constants, bulk modulus, and its pressure derivative) were calculated and used to establish structure stability. Plots of the TDOS and PDOS of transition metal atom-doped CaZ at $x = 0.25$ and pure CaZ (Z = S, Se) are presented. Cr-doped CaZ (Z = S, Se) shows half-metallic character at $x = 0.25$ and is stable in ferromagnetic state, while that of V-doped CaZ compounds shows semiconductor behavior and is stable in antiferromagnetic state. Dispersion of phonons was also evaluated to check the global minima of energy in pure CaZ compounds. Curie temperature, magnetic moments, and exchange constants were also calculated for all doped systems. The current results are in excellent agreement with earlier research. Our current findings imply that CaZ doped with Cr/V (Z = S, Se) would make a promising option for spintronic applications.

Keywords: spintronics; Cr-doped CaZ (Z = S, Se); magnetic moments



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1. Introduction

Spintronics has advanced over the last two decades, and several investigations employing various ab initio methods have been carried out on DMS and DMO in an effort to identify new, more effective materials with intriguing physical characteristics, including ferromagnetic stability and high Curie temperature. These nonmagnetic DMSs are doped lightly with small amounts of magnetic impurities in the host structure. The actual development of these materials in material science is challenging because a compound must have both electronic and magnetic doping, and the interaction between electronic carriers and magnetic dopants must be thermally stable [1]. Early investigations in the field of DMS began with research on II–VI semiconductors. It was found that a modest amount of magnetic atom doping had no effect on the electrical, transport, or optical properties of the fundamental material. Instead, it introduces effects of magnetic fields in nonmagnetic materials [2]. $\text{Zn}_{1-x}\text{Mn}_x\text{Te}$ and $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ were the first II–VI semiconductor alloys that were known. These ternary alloys attracted significant interest in the scientific community as we can tune material properties of the compounds by changing their composition. The lattice constant, energy band gap, and effective mass of the carriers are all easily modifiable in II–VI compounds. Dilute magnetic semiconductor materials are high-performance materials as magnetic impurities in considerable amounts produce magnetic and cooperative phenomena such as spin–exchange interactions [3–7]. Due to the stability of their magnetic phase, the magnetic diluted industry has gained lot of interest in these types of compounds. In the year 1960, the compounds, which were Cr-doped II–VI semiconductors, were being used in a number of optical devices such as LEDs, lasers, and fluorescent displays [8]. In 2020, the electronic structure and magnetic properties of diluted $\text{Ca}_{1-x}\text{TM}_x\text{S}$ (TM = V, Cr,

and Co) in the rock salt structure at three concentrations (0.25, 0.125, and 0.0625) were proposed by Amina Aiche et al. [9] while studying the electronic structure of $\text{Ca}_{1-x}\text{Cr}_x\text{S}$ and $\text{Ca}_{1-x}\text{V}_x\text{S}$, and it was found that these compounds show half-metallic ferromagnetism behavior with 100% spin polarization at all concentrations, whereas $\text{Ca}_{1-x}\text{Co}_x\text{S}$ possessed half-metallic ferromagnetic character at 0.0625 doping concentration. Half-metallic ferromagnetism with 100% spin polarization makes these compounds attractive for potential applications in the spintronic field. Similarly, half-metallic ferromagnetic behavior of $\text{Ca}_{1-x}\text{TM}_x\text{Se}$ (TM = V, Cr, and Mn) with complete spin polarization of 100% at Fermi level was predicted by Youcef Daoudi et al. in 2021 [10]. The computed band structures and density of states indicates that these compounds are suitable candidates for possible applications in the spintronic field. On the other hand, Meryam et al. explored the new dilute magnetic semiconductor compound $\text{Ca}_{1-x}\text{Ti}_x\text{S}$ using the FP-LAPW method based on SP-DFT. Along with this, it was predicted that these compounds exhibit half-metallic ferromagnetic demenor [11]. Moreover, Hamidane et al. [12,13] reported the half-metallic ferromagnetic properties of II–VI-semiconductor-based DMS compounds such as V- and Cr-doped CaS using first-principle calculations, confirming the half-metallic ferromagnetism behavior in these compounds.

In particular, the appearance of half-metallic ferromagnetism in Ti-doped II–VI semiconductors such as $\text{Sr}_{0.75}\text{Ti}_{0.25}\text{X}$ (X = S, Se, and Te) [13], make it a favorable system for spintronic devices. While studying structural and magneto-electronic performance of $\text{Ba}_{1-x}\text{Cr}_x\text{S}$, they discovered the half-metallic characteristic with ferromagnetic state of these compounds with better magnetoelectronic performances, which makes them appropriate materials for spin-injection applications [14]. In 2021, Youcef Daoudi et al. [15] studied $\text{Ca}_{1-x}\text{TM}_x\text{Te}$ (TM = V, Cr, Mn) compounds with concentration of $x = 0.25, 0.125$, and 0.0625 . They discovered that half-metallicity of Cr-doped CaTe is due to p–d hybridization around Fermi level, and the ferromagnetic ground state of $\text{Ca}_{1-x}\text{Cr}_x\text{Te}$ could be explained by a double exchange mechanism. Further, exchange constants have a substantial role in producing half-metallicity in Cr-doped compounds and make them promising candidates for the spintronic devices.

Calcium chalcogenides are wide bandgap semiconductors [16]. These are widely used in thermo/electro/photoluminescence as well as phosphorescent and other optoelectronic materials due to their broad applications in catalysis to microelectronics and optoelectronics [17–19]. Under ambient conditions, they prefer to be crystallized in a B1-type structure [20].

Analyzing the literature thoroughly reveals that it is important to find the compounds which possess stable half-metallic ferromagnetism and high Curie temperature. This motivates us to study the V/Cr-doped CaZ (Z = S, Se) materials. In this paper, we focused on 0.25 concentration of TM dopants. We computed their structural, elastic, electrical, Curie temperature, and magnetic properties. Our paper consists of the following sections: the computational method used in the present work is described in Section 2. In Section 3, in our discussion of V/Cr-doped CaZ (Z = S, Se) compounds, we cover the ground state characteristics, electronic structure, elastic parameters, phonon dispersion, and magnetic properties. A conclusion is given in the final section.

2. Computational Details

The present calculations of $\text{Ca}_{1-x}\text{Cr}_x\text{S}$ and $\text{Ca}_{1-x}\text{V}_x\text{Se}$ at $x = 0.25$ were performed using computer code SIESTA [21]. The structural, electrical, magnetic, and elastic properties of V- and Cr-doped CaS and CaSe DMSs were calculated using DFT, and total energy calculations were performed using GGA as an XC functional [22] in the form provided by the Perdew–Burke–Ernzerhof (PBE) scheme. Ca, S, Se, Cr, and V have the pseudoelectronic configurations $3s^2 3p^6 4s^2 3d^0$, $3s^2 3p^4$, $4s^2 4p^4$, $3d^5 4s^1$, and $4s^2 3d^3$. The cutoff energy and number of k-points in the B1 structure of CaS and CaSe compounds was optimized. As a result, a plane-wave basis set with an energy cutoff of 100 Ry was employed for Brillouin zone sampling, and a $10 \times 10 \times 10$ Monkhorst–Pack [23] k-point grid was used for the B1

phase. In the B1 (NaCl) phase, Ca atoms occupy places (0.00, 0.00, 0.00), while S/Se atoms occupy positions (0.50, 0.50, 0.50). By replacing one Ca cation with one Cr/V atom, we were able to create the $\text{Ca}_{0.75}\text{T}_{0.25}\text{Z}$ ($\text{T} = \text{Cr, V}; \text{Z} = \text{S, Se}$) ternary compounds. The $\text{Ca}_{0.75}\text{T}_{0.25}\text{Z}$ ($\text{T} = \text{Cr, V}; \text{Z} = \text{S, Se}$) features an 8-atom unit cell with a cubic structure ($1 \times 1 \times 1$). In order to determine the stability of ferromagnetic states in DMSs, we calculated the energy difference between the ferromagnetic and antiferromagnetic states, i.e., $\Delta E_{\text{AFM}} - \Delta E_{\text{FM}}$. The system is stable in the FM state when the energy difference is positive; otherwise, it is in the AFM state. The Curie temperature was calculated considering the total energy difference between the FM and AFM states. Formation energy was also evaluated. Using exchange coupling constants, the magnetic characteristics of the ternary alloys $\text{Ca}_{0.75}\text{T}_{0.25}\text{Z}$ ($\text{T} = \text{Cr, V}; \text{Z} = \text{S, Se}$) were investigated. The spin-polarized calculations and geometric relaxations were found using the DZP (double-zeta plus polarization) basis set and CG (conjugate-gradient) method. This was accomplished by thorough structural optimization unless the forces were less than $0.04 \text{ eV}/\text{\AA}$.

3. Result and Discussion

3.1. Structural Properties

In proximity of the parent CaS and CaSe semiconductors' lattice parameters, the ground state optimization for $\text{Ca}_{0.75}\text{T}_{0.25}\text{Z}$ ($\text{T} = \text{V, Cr}; \text{Z} = \text{S, Se}$) compounds was performed. To start the process, the total energy of the AFM and FM states in three different configurations were established that correspond to various distances of the V- and Cr-doped CaS and CaSe compounds as shown in Table 1. Here, we set the initial V/Cr atom's location (position "0"), and positions 1, 2, and 3 of the second V/Cr atom were chosen at random. Configuration (0,1) for $\text{Ca}_{0.75}\text{V}_{0.25}\text{Z}$ represents that the initial position of the first V-doped atom is given by the "0" symbol and "1" represents the position of second V-doped atom in a unit cell of size $2 \times 2 \times 1$. Similarly, configurations (0,2), (0,3), and (0,4) represent the positions of doped transition metal atoms (V/Cr) at different positions in the unit cell. We calculated the distances dd1 and dd2 before and after relaxing for the models under consideration. It was found that the total energy differences between the AFM and FM states for $\text{Ca}_{0.75}\text{V}_{0.25}\text{Z}$ ($\text{Z} = \text{S, Se}$) and $\text{Ca}_{0.75}\text{Cr}_{0.25}\text{Z}$ ($\text{Z} = \text{S, Se}$) are negative and positive, respectively. This suggests that the Cr-doped CaZ's ferromagnetic state is more stable [24], whereas CaZ that has been doped with V remains antiferromagnetic.

Table 1. V–V and Cr–Cr distance before (dd1) and after relaxation (dd2), magnetization energy ($\Delta E = E_{\text{AFM}} - E_{\text{FM}}$).

Systems	Configuration	dd1	dd2	E_{AFM} (eV)	E_{FM} (eV)	$\Delta E = E_{\text{AFM}} - E_{\text{FM}}$ (eV)	Stable State	Tc (Curie Temperature) (K)
$\text{Ca}_{0.75}\text{V}_{0.25}\text{S}$	(0,1)	0.74	0.71	−3677.831	−3677.827	−0.031	AFM	959.3 K
	(0,2)	1.05	1.02	−3677.850	−3677.853	−0.022	AFM	680.8 K
	(0,3)	1.15	1.14	−3677.869	−3677.868	−0.019	AFM	587.9 K
$\text{Ca}_{0.75}\text{Cr}_{0.25}\text{S}$	(0,1)	0.74	0.71	−3860.632	−3860.662	0.030	FM	928.39 K
	(0,2)	1.05	1.02	−3860.455	−3860.482	0.027	FM	835.55 K
	(0,3)	1.15	1.13	−3860.701	−3860.718	0.017	FM	526.09 K
$\text{Ca}_{0.75}\text{V}_{0.25}\text{Se}$	(0,1)	4.39	4.35	−3366.987	−3366.954	−0.028	AFM	866.5 K
	(0,2)	6.21	6.19	−3366.782	−3366.761	−0.021	AFM	649.8 K
	(0,3)	7.60	7.58	−3366.685	−3366.670	−0.015	AFM	464.19 K
$\text{Ca}_{0.75}\text{Cr}_{0.25}\text{Se}$	(0,1)	4.39	4.35	−3550.696	−3550.725	0.029	FM	902.3 K
	(0,2)	6.21	6.19	−3550.489	−3550.507	0.018	FM	557.03 K
	(0,3)	7.60	7.58	−3550.790	−3550.805	0.015	FM	464.19 K

The following relation is used to determine the Curie temperature from the total energy difference ΔE :

$$T_c K_B = \frac{2 \Delta E}{3 x} \quad (1)$$

where K_B represents the Boltzmann constant and x represents the dopant concentration.

Furthermore, to establish structure stability, Murnaghan's equation was utilized to obtain the optimized value of the lattice constant A , bulk modulus B , and other elastic constants [25].

$$E(V) - E(V_0) = \frac{B_0 V}{B_0} \left[\frac{\left(\frac{V}{V_0} \right)^{B'_0}}{B'_0 - 1} \right] - \frac{B_0 V_0}{B'_0 - 1} \quad (2)$$

$$B_0 = V \frac{\partial^2 E}{\partial^2 P} \bigg|_{V = V_0} \quad (3)$$

3.1.1. Elastic Properties

In this study, the mechanical stability of binary and ternary compounds was investigated using second-order elastic constants. The structure has the space group Fm3m. C_{11} , C_{12} , and C_{44} are the only three independent elastic constants in the FCC structure. The values of the elastic constants were calculated using the following matrix [26]:

$$[C] = \begin{bmatrix} C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{12} & C_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{44} \end{bmatrix} \quad (4)$$

These three elastic constants were calculated using suitable deformations which are as below:

$$D_1 = \begin{bmatrix} 1 + \delta & 0 & 0 \\ 0 & 1 - \delta & 0 \\ 0 & 0 & \frac{1}{1 - \delta^2} \end{bmatrix}$$

$$D_2 = \begin{bmatrix} 1 + \delta & 0 & 0 \\ 0 & 1 + \delta & 0 \\ 0 & 0 & 1 + \delta \end{bmatrix} \quad (5)$$

$$D_3 = \begin{bmatrix} 1 & \delta & 0 \\ \delta & 1 & 0 \\ 0 & 0 & \frac{1}{1 - \delta^2} \end{bmatrix}$$

D_1 is an orthorhombic distortion that conserves volume and D_2 alters the a -lattice parameter. The distortion lattice's volume varies using D_2 , but the strained lattice's symmetry stays cubic. The energy of the volume-preserving monoclinic distortion D_3 may be computed as follows [27]:

$$E(V, \delta) = E(V_0, 0) + V_0 \left\{ (C_{11} - C_{12}) \delta^2 + O(\delta^4) \right\} \quad (6)$$

$$E(V, \delta) = E(V_0, 0) + V_0 \delta (r_1 + r_2 + r_3) + V_0 \left\{ \frac{3}{2} (C_{11} + 2 C_{12}) \delta^2 + O(\delta^4) \right\} \quad (7)$$

$$E(V, \delta) = E(V_0, 0) + V_0 (2 C_{44} \delta^2 + O(\delta^4))$$

Finally, a polynomial fitting method was used to obtain the second-order elastic constants. The three equations listed above were resolved using least square fit using

the derived elastic constants. Tables 2 and 3 show the elastic moduli results for pure and TM-doped CaS and CaSe.

Table 2. Calculated lattice constants, elastic constants, and elastic moduli of pure and TM-doped CaS.

Parameters	CaS			Ca _{0.75} V _{0.25} S	Ca _{0.75} Cr _{0.25} S
	Present	Exp.	Other Theoretical	Present	Present
a (Å)	5.72	5.689 [16]	5.717 [25] 5.598 [28] 5.721 [29]	4.778	4.463
B _{eq} (GPa)	86.24	64 [16]	57.42 [24] 115.67 [30]	64.56	63.29
B' _{eq}	4.05	4.2 [16]	3.8 [24] 4.1 [30]	3.32	3.19
C ₁₁ (GPa)	227.04	-	122.87 [24] 135 [29] 202.35 [30] 123.3 [31]	181.30	180.34
C ₁₂ (GPa)	17.24	-	32.01 [24] 31.45 [32] 23.6 [33]	19.65	18.85
C ₄₄ (GPa)	32.46	-	36.08 [24] 38 [29] 67.45 [30] 33.5 [32]	30.99	29.32

Table 3. Calculated lattice constants, elastic constants, elastic moduli, compressibility, and anisotropy for pure and TM-doped CaSe.

Parameters	CaSe			Ca _{0.75} V _{0.25} Se	Ca _{0.75} Cr _{0.25} Se
	Present	Exp.	Other. Theoretical	Present	Present
a (Å)	6.02	5.916 [16]	5.968 [24] 6.087 [29] 5.91 [31]	4.961	4.792
B _{eq} (GPa)	75.24	51 [16]	56.2 [28] 88.92 [30] 63.94 [32] 60.88 [31]	67.27	66.81
B' _{eq}	5.3	4.2 [16]	4.1 [28] 4.39 [32]	3.81	3.75
C ₁₁ (GPa)	199.55	-	155.25 [30] 135.0 [32] 120.32 [31] 104.6 [34]	156.14	160.73
C ₁₂ (GPa)	16.89	-	23.12 [28] 18 [29] 28.38 [32] 20.6 [34]	18.42	18.84
C ₄₄ (GPa)	28.58	-	29.90 [24] 31 [29] 28.5 [34]	22.70	23.52

The computed value of the lattice constant of pure CaS and CaSe was found to be comparable to experimental and other theoretical data. Tables 2 and 3 indicate that the

value of the lattice constant drops in V/Cr-doped CaS and CaSe. The reason for this is that the atomic radius of doped atoms is smaller than that of the host Ca atom. The Ca atom has an atomic radius of 231 pm, while V and Cr atoms have atomic radii of 205 pm and 128 pm, respectively. In pure CaZ systems, as well as in V and Cr-doped CaZ (Z = S, Se) systems, the values of the elastic constants C_{11} , C_{12} , and C_{44} similarly drop from S to Se.

To determine the isotropic elastic constants, three averaging approaches are implemented. In the Voigt method, uniform strain is assumed, and Russ technique is used in the event of uniform stress. Hill [35] showed that Voigt and Reuss elastic moduli are the strict upper and lower bounds, respectively. The Hill average bulk modulus may therefore be computed from the elastic moduli of Voigt and Reuss as $B_H = (B_R + B_V)/2$, where $B_V = (1/9)[(C_{11} + C_{22} + C_{33}) + 2(C_{12} + C_{23} + C_{31})]$; in addition, $B_R = [(S_{11} + S_{22} + S_{33}) + 2(S_{12} + S_{23} + S_{31})]^{-1}$; $S_{ij} (=C_{ij}^{-1})$ are the elastic compliance constants [35]. The bulk moduli of Voigt and Reuss are comparable for cubic crystal structures $C_{11} = C_{22} = C_{33}$ and $C_{12} = C_{23} = C_{31}$, $B_R = B_V = (C_{11} + 2C_{12})/3$. This property is illustrated in Tables 2 and 3, and $B_R = B_V = B_H$ for pure and doped systems. This is true only for cubic symmetry. The data also show that derived values of bulk modulus from elastic constants, $B_H = (C_{11} + 2C_{12})/3$ for all systems, are extremely near to values obtained from Mur-naghan's equation of state B_{eq} by fitting the E–V curves with a discrepancy of less than 2%. This might be substantial evidence for the correctness and reliability of the existing estimates of the elastic constants for CaS, CaSe, and $Ca_{0.75}T_{0.25}Z$ (T = V, Cr; Z = S, Se). It has been observed that the compressibility of pure and doped CaSe is greater than that of CaS. CaSe systems are therefore more compressible than pure CaS and doped CaS systems. Mechanical stability requires elastic constant limits such as $C_{11} - C_{12} > 0$, $C_{11} + 2C_{12} > 0$, $C_{11} > 0$, $C_{12} < C_{11}$, and $C_{44} > 0$ [26–38]. The evaluated elastic constants in this work satisfy all of these conditions for stable B1 structures. The cubic stability condition is also satisfied by the estimated elastic constants, i.e., $C_{12} < B < C_{11}$.

3.1.2. Phonon Dispersion Curves

We calculated the dispersion of phonons in pure CaS and CaSe semiconductors to check the global minima of energy. HF forces were used to calculate the force constants which were induced due to the displacement of atoms. The size of the supercell is utilized to determine phonon frequencies at each location of the Brillouin zone Γ , X, L, M. In the present work for the calculations of dispersion of phonons, supercell of size $(1 \times 1 \times 1)$ was considered. Phonon dynamics also helps to evaluate the macroscopic behavior of solids, e.g., thermal expansion, specific heat, etc. Furthermore, very low frequency modes can be related to a phase transition, whereas imaginary frequencies indicate that the estimated structure is inherently unstable. Figures 1 and 2 indicate that our computed phonon frequencies are positive, indicating that the structure of CaS and CaSe considered for subsequent calculations is stable.

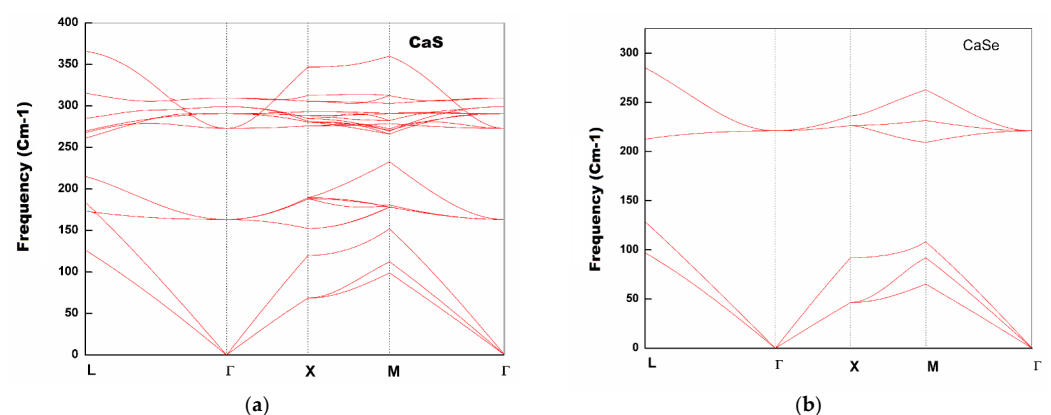


Figure 1. (a): Phonon dispersion curves for CaS and (b) CaSe semiconductor [39].

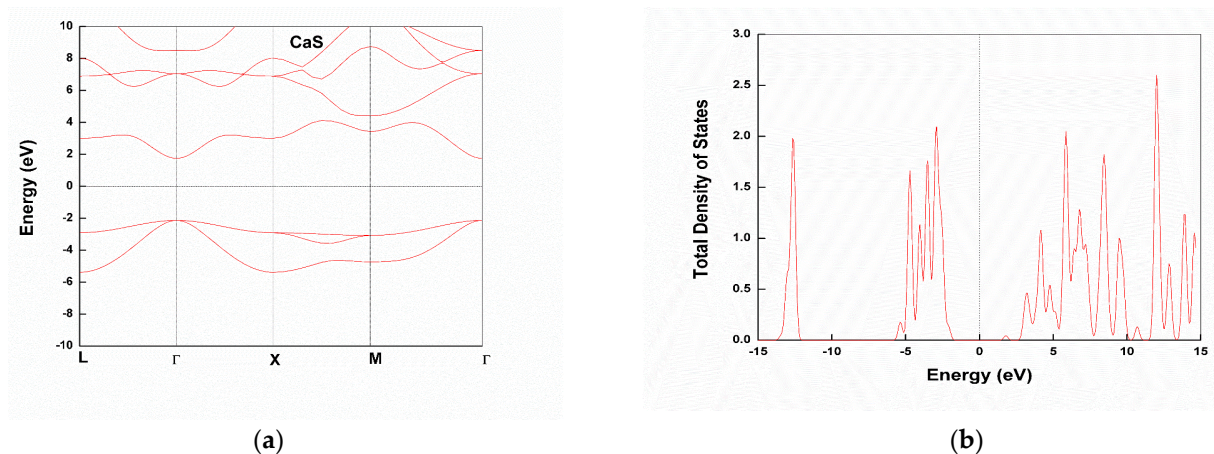


Figure 2. (a) Electronic band structures and (b) total density of states of CaS [22,40].

3.2. Electronic Structure

We performed simulations to determine the electrical and magnetic characteristics of pure and V/Cr-doped CaS and CaSe compounds after confirming structure stability. Understanding electronic band structure is tremendously important for spintronics. Using an optimum lattice parameter, the electronic band structures and total density of states of pure and doped materials were investigated. As shown in Figures 2 and 3, we first calculated the band structures and total density of states of pure CaS and CaSe semiconductors along various symmetry lines in the Brillouin zone. The horizontal line in band structure and the vertical line in TDOS at $E = 0$ eV represent the Fermi level. The investigation of band structures reveals that the conduction band minima (CBM) and valence band maxima (VBM) for both substances, CaS and CaSe, are located at the Γ point. We found that CaS and CaSe have 3.84 eV direct band gaps and 3.27 eV in the B1 phase at ambient pressure, respectively, which agrees with other theoretical predictions listed in Table 3.

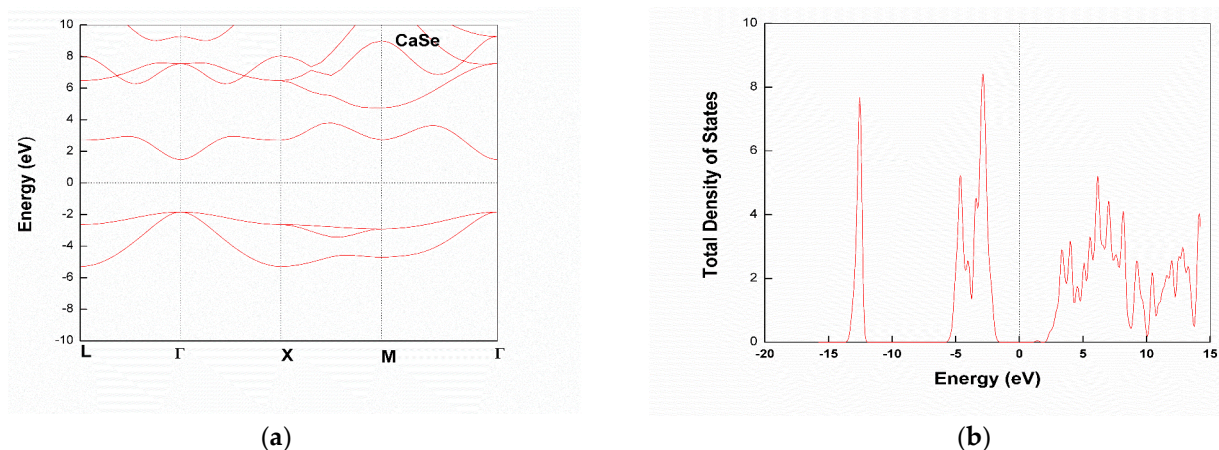


Figure 3. (a) Electronic band structures and (b) total density of states of CaSe [40].

Furthermore, the total and partial density of states, as well as the spin-polarized band structures, of V/Cr-doped CaS and CaSe semiconductors at $x = 0.25$ in B1 phase were also determined. Spin-polarized band structures with TDOS Cr-doped CaS and CaSe diluted magnetic semiconductors are shown in Figures 4 and 5, respectively, and V-doped CaS and CaSe DMSs in B1 phase for spin-up and spin-down states, with high symmetry directions in the Brillouin zone, are shown in Figures 6 and 7. The forbidden gap in the majority spin channel (MAC) is shown in Figures 4 and 5 to be completely filled with impurity atom energy levels, suggesting that the studied compound exhibits a metallic character in the MAC. These impurity energy levels are generated by Cr-3d states, which generate

a significant number of electron traps. As a result, they significantly improve electrical conductivity and optical characteristics of CaS semiconductors. In contrast, the conduction band minima and valence band maxima of a minority spin channel (MNC) are both found at the Γ K-point. As a result, these compounds exhibit semiconductor behavior in the minority channel. As a result, at $x = 0.25$, Cr-doped CaS and CaSe compounds exhibit half-metallic behavior in the B1 phase. The bottom energy of the minority (dominant) spin conduction band is subtracted from the Fermi level to determine the half-metallic band gap. Table 3 shows the predicted half-metallic gaps of minority spin channels (GHM) of Cr-doped CaS and CaSe. The total density of states (TDOS) of $\text{Ca}_{0.75}\text{Cr}_{0.25}\text{S}$ and $\text{Ca}_{0.75}\text{Cr}_{0.25}\text{Se}$ alloys are also useful in establishing the band state character. The maximum of the valence band crosses the Fermi energy level in the majority channel, as seen by the total density of states in Figures 4 and 5, but the maximum of the valence band remains below the Fermi energy level and the bottom of the conduction band remains above the Fermi energy level in the minority spin state, implying that Cr-doped CaS and CaSe in the spin-up state exhibit metallic behavior and in the spin-down state exhibit semiconductor behavior.

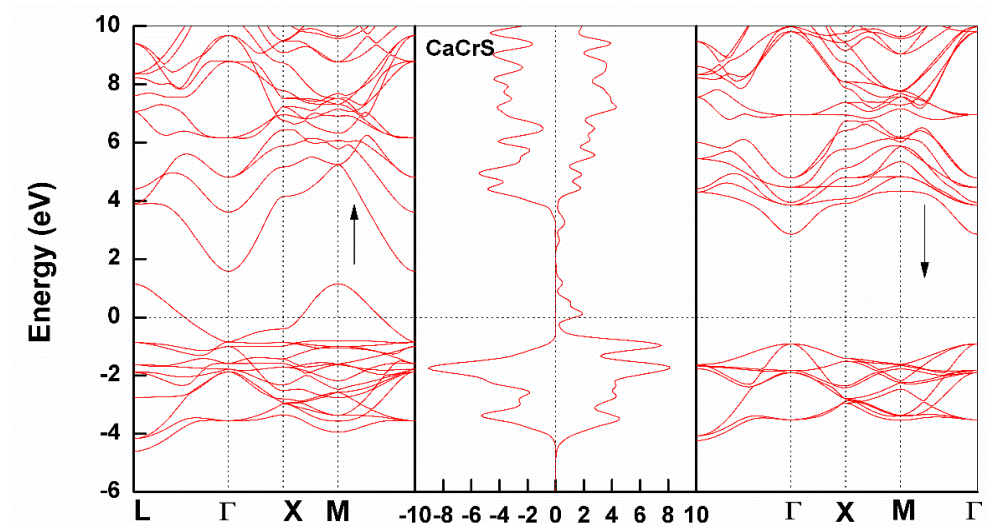


Figure 4. Spin-polarized band structure of $\text{Ca}_{0.75}\text{Cr}_{0.25}\text{S}$.

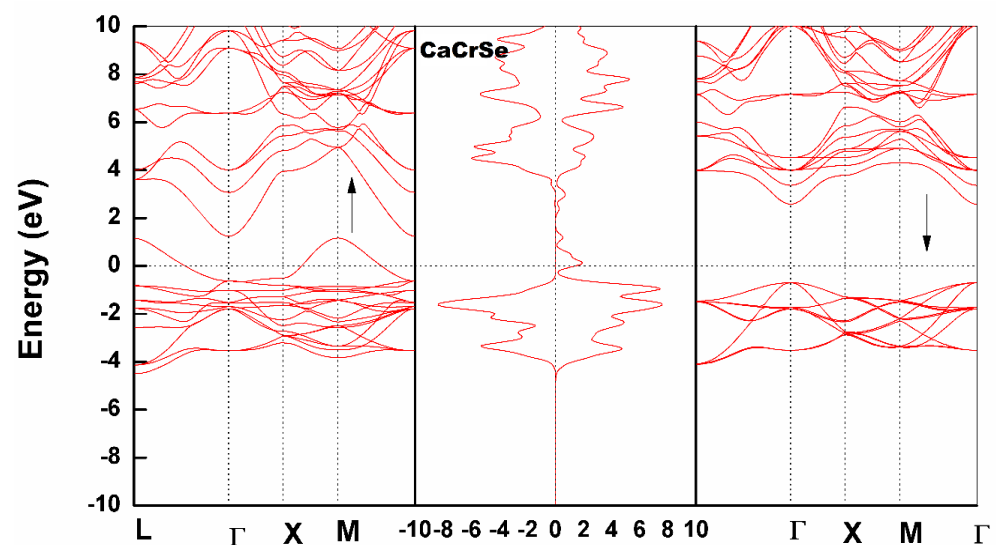


Figure 5. Spin-up and spin-down band structure of $\text{Ca}_{0.75}\text{Cr}_{0.25}\text{Se}$.

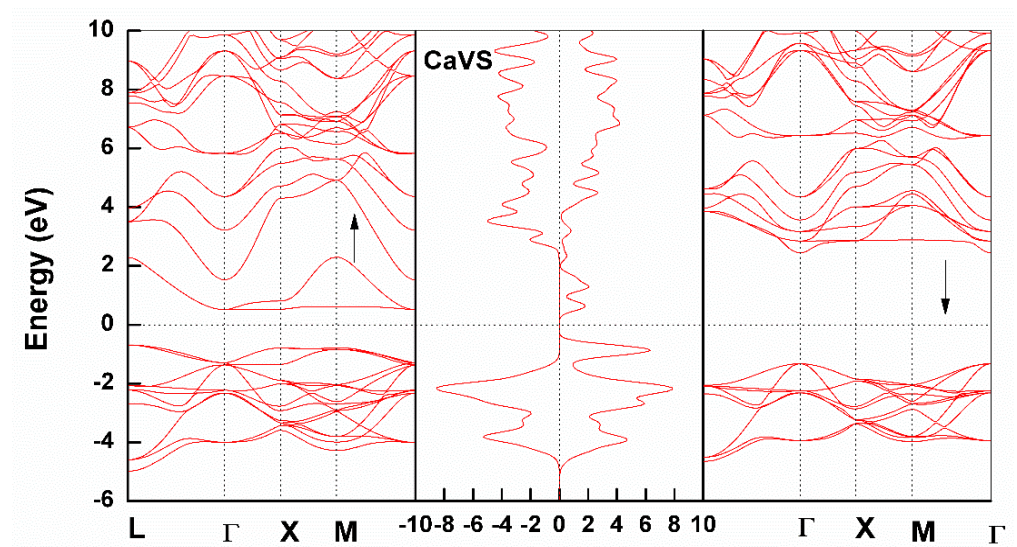


Figure 6. Spin- up and Spin – down band structure of $\text{Ca}_{0.75}\text{V}_{0.25}\text{S}$.

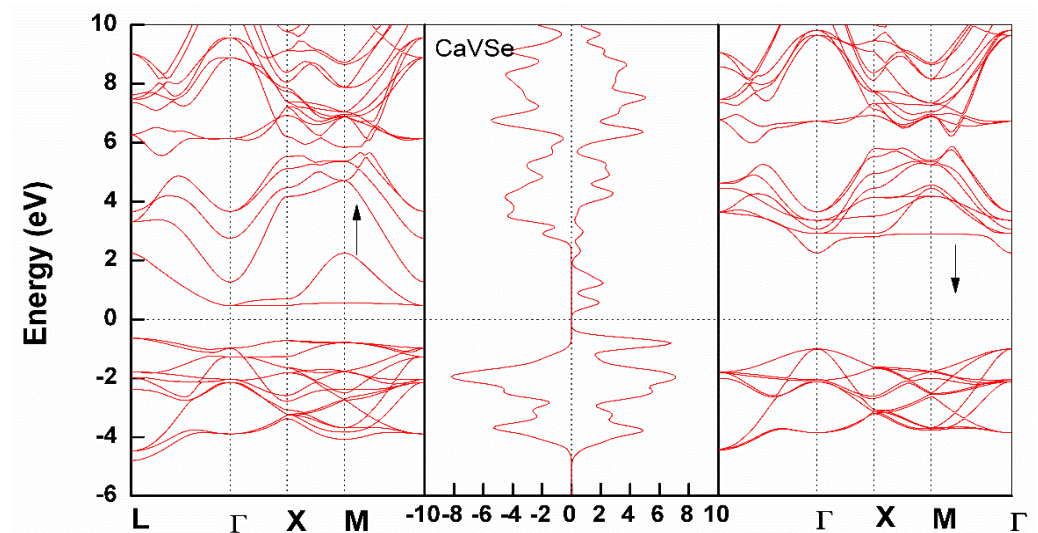


Figure 7. Spin- up and spin-down band structure of $\text{Ca}_{0.75}\text{V}_{0.25}\text{Se}$.

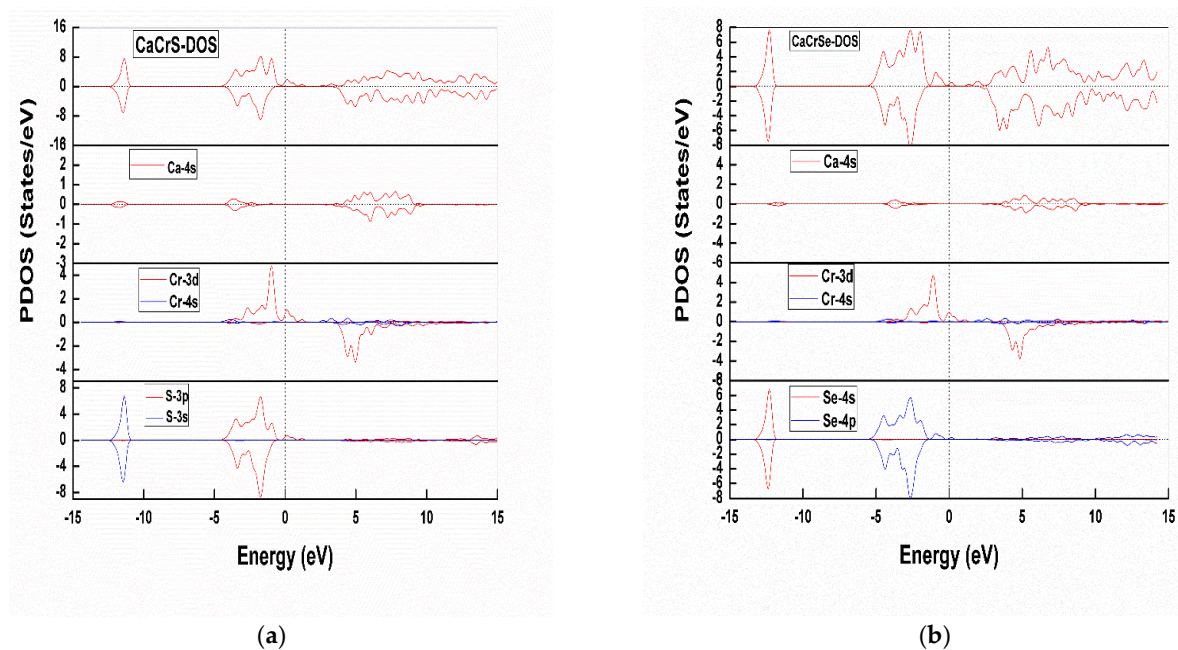
Figures 6 and 7 show that in $\text{Ca}_{0.75}\text{V}_{0.25}\text{S}$ and $\text{Ca}_{0.75}\text{V}_{0.25}\text{Se}$, valence band maxima and conduction band minima in MAC and MNC both lie at the K-point Γ , indicating that direct band gaps exist in V-doped CaS and CaSe compounds at Γ point and both DMSs exhibit semiconductor behavior. Table 4 shows the computed spin-up and spin-down band gaps of $\text{Ca}_{0.75}\text{V}_{0.25}\text{S}$ and $\text{Ca}_{0.75}\text{V}_{0.25}\text{Se}$ diluted magnetic semiconductors at $x = 0.25$. Total density of states (TDOS) $\text{Ca}_{0.75}\text{V}_{0.25}\text{S}$ and $\text{Ca}_{0.75}\text{V}_{0.25}\text{Se}$ are also useful in demonstrating the semiconductor behavior of these alloys. Total density states shown in Figures 6 and 7 show that in V-doped CaS and CaSe, in spin-up and spin-down states no electronic energy state occurs at Fermi energy level. CaVS and CaVSe DMSs exhibit semiconductor behavior in the B1 phase at $x = 0.25$.

Partial Density of States

The partial density of states for $\text{Ca}_{1-x}\text{Cr}_x\text{S}$ and $\text{Ca}_{1-x}\text{Cr}_x\text{Se}$ at $x = 0.25$ in B1 phase is depicted in Figure 8 and the overall density of states was decomposed into s-, p-, and d-orbital contributions to perform a qualitative investigation of each set of energy bands of $\text{Ca}_{1-x}\text{Cr}_x\text{S}$ and $\text{Ca}_{1-x}\text{Cr}_x\text{Se}$.

Table 4. Spin-up and spin-down and half-metallic band gaps of V/Cr-doped CaZ (Z = S, Se).

Compound	Spin-Up Band Gap E_g (eV)	Spin-Down Band Gap E_g (eV)	Other's Calculations	Nature	Half-Metallic Band Gap G_{HM} (eV)
CaS	3.84	-	3.969 [31], 4.086 [27]	Semiconductor	-
CaSe	3.26	-	3.491 [27], 3.451 [31]	Semiconductor	-
Ca _{0.75} Cr _{0.25} S	0.439	3.75	-	Half-Metallic	2.811
Ca _{0.75} Cr _{0.25} Se	0.081	3.28	-	Half-Metallic	2.577
Ca _{0.75} V _{0.25} S	1.374	3.76	-	Semiconductor	-
Ca _{0.75} V _{0.25} Se	1.44	3.19	-	Semiconductor	-

**Figure 8.** (a) Partial density of states of Ca_{0.75}Cr_{0.25}S and (b) Ca_{0.75}Cr_{0.25}Se.

In S and Se, valence electrons are s- and p-state electrons. The remaining electrons, on the other hand, are considered to be part of the core. Figure 8 indicates that the 3s states of S, with a tiny contribution from 4s states of Ca, of the valence band are in the lowest section in Ca_{0.75}Cr_{0.25}S.

There is a minor contribution of 3p states of S in the top section of the valence band, which is near the Fermi level. Cr-3d states play a key role in the upper area of the valence band, but in the spin-up condition, these are near the Fermi surface. In the spin-down situation, these states are a few electron volts below the Fermi surface. Ca-4s states dominate the bottom of the conduction band, with a tiny contribution from S-3s states in the spin-up condition and Ca-4s and Cr-3d states in the spin-down situation. The energy difference between the spin-up and spin-down peaks due to effective Cr-3d states is characterized as the spin-exchange splitting energy. The lowest half of the valence band in Cd_{0.75}Mn_{0.25}Se is attributable to Ca-4s states with a tiny contribution from Se-4s states, whereas the upper part of the valence band is filled with Ca-4s, Se-4p, and Cr-3d states. Cr-3d states are present around the Fermi level in spin-up states, but a few eV below the Fermi level in spin-down states. In the conduction band, which lies above the Fermi surface, the bottom of the conduction band is occupied with Ca 4s and Se-4p states for spin-up states, and Cr-3d and Ca-4s states for spin-down states.

Furthermore, substitution of a transition metal atom on the semiconductor's cation site degenerates the 3d atomic levels of Cr atom in Ca_{0.75}Cr_{0.25}S and Ca_{0.75}Cr_{0.25}Se, degenerating into three degenerate t_{2g} states and two doubly degenerate e_{2g} states, as illustrated

in Figure 9. These states are separated by tetrahedral crystal field splitting caused by the Ca cation and the S/Se anion. In general, both the e_g and t_{2g} states are in the valence band for majority spin. In these systems, a percentage of t_{2g} states in majority spin states cross the Fermi level, whereas it is completely in conduction in minority spin states. It can also be noticed that the Fermi level only crosses the peak in one direction, suggesting that $\text{Ca}_{0.75}\text{Cr}_{0.25}\text{S}$ and $\text{Ca}_{0.75}\text{Cr}_{0.25}\text{Se}$ are half-metallic in nature.

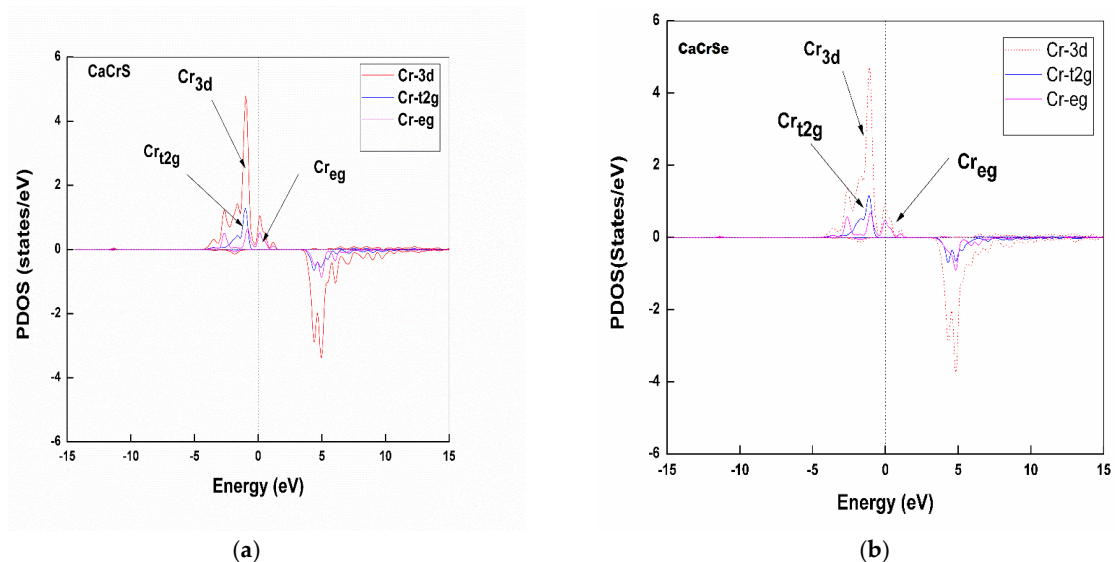


Figure 9. Partial density of states of Cr-3d states in (a) CaCrS and (b) CaCrSe.

Figure 10 shows that in $\text{Ca}_{0.75}\text{V}_{0.25}\text{Se}$, Ca-4s states, with a small contribution from S-3s states, dominate the bottom portion of the valence band, while Ca 4s and S-3p levels at the Fermi surface control the upper portion of the valence band. For spin-up states, V-3d states can be observed in the upper section of the valence band. For spin-up states, they are close to the Fermi surface, while for spin-down states, they are a few electron volts below the Fermi surface. In the spin-up situation, Ca 4s states dominate the bottom of the conduction band above the Fermi surface, whereas in the spin-down situation, Ca 4s and V-3d states dominate.

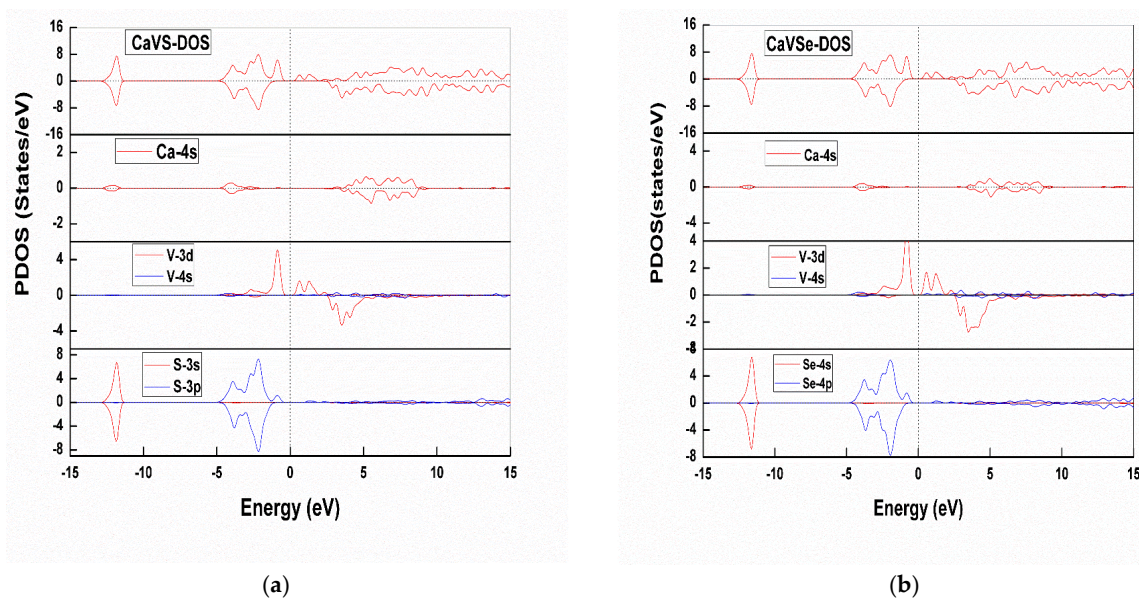


Figure 10. (a) Partial density of states of $\text{Ca}_{0.75}\text{V}_{0.25}\text{S}$ and (b) $\text{Ca}_{0.75}\text{V}_{0.25}\text{Se}$.

Crystal field theory states that when V transition metal ions replace the cationic sites of CaZ (Z = S/Se), the tetrahedral crystal field created by the S/Se ion splits the fivefold degenerate 3D states of the transition metal ions into three high-lying t_{2g} (d_{xy} , d_{yz} , d_{zx}) and two low-lying ($d_{x^2-y^2}$, d_{z^2}) symmetries, as shown in Figure 11. $\text{Ca}_{0.75}\text{V}_{0.25}\text{S}$ and $\text{Ca}_{0.75}\text{V}_{0.25}\text{Se}$ are found to be semiconductors in nature since the Fermi level does not pass any peak in either direction.

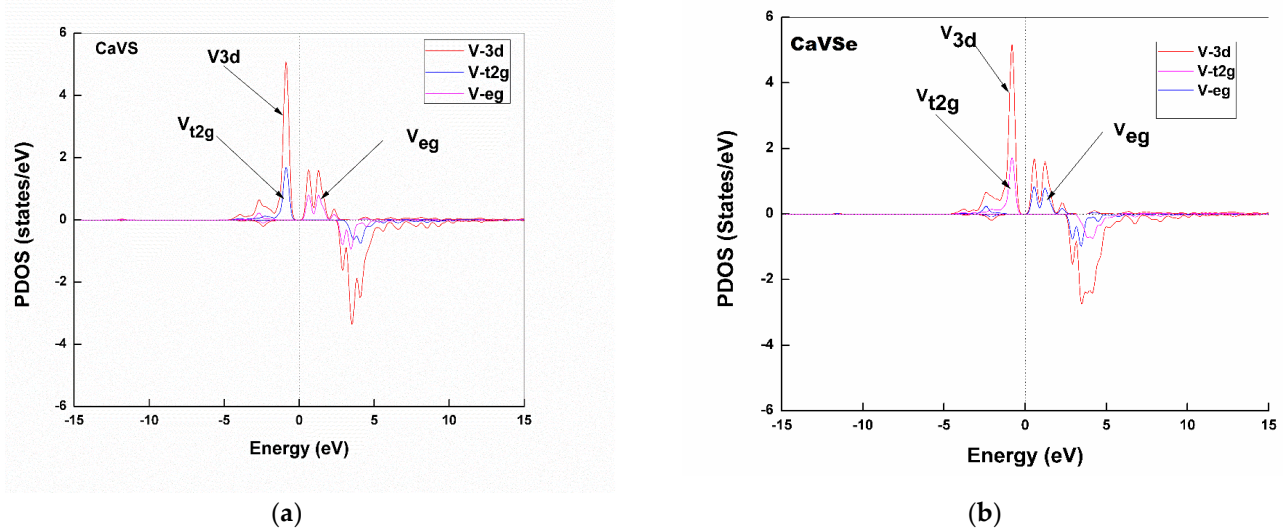


Figure 11. Partial density of states of V-3d states in (a) CaVS and (b) CaVSe.

3.3. Magnetic Properties

The magnetic characteristics of V/Cr-doped CaZ (Z = S, Se) DMSs were studied using exchange constants. We evaluated $N_0\alpha$ and $N_0\beta$ exchange constants. The s–d exchange constant is $N_0\alpha$, while the p–d exchange constant is $N_0\beta$. The cation concentration is N_0 . The interaction between V/Cr spin and conduction electron carriers is shown by $N_0\alpha$ (s–d exchange constant), whereas the interaction between V/Cr spin and holes is defined by $N_0\beta$ (s–d exchange constant). Valence and conduction band edge splitting are important in the exchange and splitting process. These exchange constants can also be evaluated experimentally using spin split exciton bands and optical-magneto absorption experiments [41]. Total magnetic moments, local magnetic moments, exchange constants, and valence and conduction band edge splitting are all determined in Table 5. The following formulas were used to determine exchange constants [42]:

$$N_0\alpha = \frac{\Delta E_c}{x\langle S \rangle}, N_0\beta = \frac{\Delta E_v}{x\langle S \rangle} \quad (8)$$

where ΔE_c and ΔE_v are band edge splitting of conduction band minima (CBM) and valence band maxima (VBM), x is the concentration of V/Cr atom, and $\langle S \rangle$ is one half of the magnetization per V/Cr ion.

The total magnetic moment of 3d electrons inside the Cr sphere in CaCrS and CaCrSe is 4.00 μ_B , while the total magnetic moment of 3d electrons within the V sphere in CaVS and CaVSe is 3.00 μ_B , as shown in Table 5. DMSs create permanent local magnetic moments due to partly filled Cr 3d/V-3d levels. Other fascinating features of DMSs result from exchange interactions between magnetic ions and electrons or holes near the band boundaries [42–47]. On nonmagnetic Ca, S, and Se atoms, a Cr/V atom induces a local magnetic moment. The magnetic moments of Ca, S, and Se atoms are all negative, suggesting that their magnetic moments are antiparallel. The magnetic moments of S/Se and Ca atoms are also the result of Cr/V and Cs S/Se orbital hybridization.

Table 5. Calculated values of band edge splitting of CBM and VBM, exchange constants, and total and local magnetic moments.

Parameter	Ca _{0.75} Cr _{0.25} S	Ca _{0.75} Cr _{0.25} Se	Ca _{0.75} V _{0.25} S	Ca _{0.75} V _{0.25} Se
ΔE_C (eV)	1.25	1.33	2.00	1.75
ΔE_V (eV)	−2.06	−1.87	−0.38	−0.25
$N_0\alpha$	2.50	2.65	5.34	4.66
$N_0\beta$	4.12	3.74	1.01	0.66
M (μ_B)	4.0	4.0	3.00	3.00
m_{Ca} (μ_B)	−0.054	−0.045	−0.03	−0.027
m_S (μ_B)	−0.567	-	−0.265	−
m_{Se} (μ_B)	-	−0.638	-	−0.301
m_{Cr} (μ_B)	4.61	4.70	-	-
m_V (μ_B)	-	-	3.294	3.33

4. Conclusions

The structural, vibrational, elastic, electronic, and magnetic characteristics, as well as the Curie temperature, of pure and transition metal atoms V/Cr-doped CaS and CaSe semiconductors were investigated using density functional theory. Our calculated phonon frequencies for CaS and CaSe semiconductors are positive in nature which shows that compounds are dynamically stable. It is found that Cr-doped CaS and CaSe DMSs are ferromagnetically more stable than in the antiferromagnetic state, whereas Ca_{0.75}V_{0.25}S and Ca_{0.25}V_{0.75}Se compounds are stable in the antiferromagnetic state. It was also established that the Fermi level crosses the peak in just one direction in Cr-doped CaS and CaSe DMSs, which implies that Ca_{0.75}Cr_{0.25}S and Ca_{0.25}Cr_{0.75}Se compounds show half-metallic behavior. On the other hand, V-doped CaS and CaSe show semiconductor behavior, where the Fermi level does not cross any peak. Double exchange in the ferromagnetic phase is the mechanism responsible for its stability in Ca_{0.75}Cr_{0.25}S and Ca_{0.25}Cr_{0.75}Se, while the super exchange coupling is responsible for the stability of the antiferromagnetic state in Ca_{0.75}V_{0.25}S and Ca_{0.25}V_{0.75}Se. We also evaluated the Curie temperatures for V/Cr-doped CaS and CaSe at different positions of the dopant atoms, and distance was also evaluated before and after the optimization. At ambient pressure, the elastic constants of pure and doped systems in B1 phase were computed. The estimated elastic constant values indicate that these compounds are mechanically stable.

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