Electronic and Magnetic Properties of CaS$_{0.875}$M$_{0.125}$ (M = C, Si, Ge and Sn) by First Principles Theory

M Yogeswari, R Umamaheswari and G Kalpana*
Department of Physics, Anna University, Sardar Patel road, Guindy, Chennai – 600 025, INDIA

E-mail: g_kalpa@annauniv.edu, g_kalpa@yahoo.com

Abstract. The total energy, energy bands, density of states and half-metallic ferromagnetism of CaS$_{0.875}$M$_{0.125}$ (M = C, Si, Ge and Sn) have been studied using band structure calculation methods namely full potential linearized augmented plane wave (FP-LAPW) as well as tight binding linear muffin orbital (TB-LMTO) method. We find that within the generalized gradient approximation (GGA) all dopants induce half-metallic ferromagnetism in CaS, whereas in the case of local spin density approximation (LSDA) C-doping only induce half-metallicity in CaS. The calculated magnetic moment is found to be 2.00 µB per formula unit. The magnetism arises mainly from the p states of dopant atoms. The ground state properties such as lattice constant, total energy difference between non-magnetic and ferromagnetic state, total and partial magnetic moments have been calculated. Within the GGA calculation all dopants enhance the stability of ferromagnetic state.

Introduction

It is highly desirable to explore satisfactory half-metallic (HM) ferromagnetic materials for the realization of high-performance spintronic devices [1]. HM ferromagnets are materials with one of their two spin channels metallic, whereas other has a semiconductor or insulating property. It shows 100% spin polarization around the Fermi level. Since its introduction by de Groot et al. [2] in C1$\text{b}$ structure semi-Heusler alloy NiMnSb, several HM ferromagnets have been theoretically predicted such as half- and full Heusler alloys, double perovskite compounds, magnetic oxides, several zinc-blende (ZB) phase transition metal (TM) pincnides and diluted magnetic semiconductors [3]. Few of them are synthesized experimentally [4]. In this case ferromagnetism substantially arises from 3d magnetic ion impurities. Recently Gao et al. [5] have reported sp HM ferromagnetism in rock salt and ZB MS (M = Li, Na and K) using FP-LAPW method. Moreover several work reveal that non-magnetic elements like B, C, N, Mg, Ca, and Cu as dopants can produce spin polarization in some semiconducting host materials [6]. More recently, unusual HM ferromagnetism at room temperature is found in insulators such as alkaline earth oxides doped with intrinsic non-magnetic elements like B, C and N. Recently electronic structure and trends of MgO systems doped with III, IV and V main group elements for a concentration of 25% was reported using plane wave ultra soft pseudo potential method. Based on density functional theory, Liu et al [7] has studied that the C-doping in alkaline earth chalcogenides (O and S) induce half-metallic ferromagnetism. In our previous work we have investigated the electronic structure and HM ferromagnetism in calcium chalcogenides doped with B, C and N [8]. Alkaline-earth chalcogenides are important wide bandgap semiconducting materials, which can produce excitons with large binding energy. Hence they have ample technological
application in the areas of luminescent devices, catalysis, and microelectronics [9]. In this paper we study the possibility of HM ferromagnetism in calcium sulphide with 2p elements such as C, Si, Ge and Sn as dopant using full-potential linearized augmented plane wave method (FP-LAPW) and tight binding linear muffin tin orbital method (TB-LMTO). Realization of ferromagnetism in these compounds may improve the function of optical based spintronic devices.

2. Computational details

To study the electronic structure and possibility of HM ferromagnetism in CaS$_{0.875}M_{0.125}$ (M = C, Si, Ge and Sn), we have performed first principle calculations using all electron full potential-linearized augmented plane wave method based on density functional theory as implemented in Wien2k code [10]. Generalized gradient approximation of Perdew, Burke and Ernzerhof was used to treat exchange correlation potential. Relativistic effects are taken into account within the scalar approximation. We take $R_{mt}K_{max} = 8$ and the angular momentum expansion up to $l = 10$ in the muffin tins. We have used 4000 $k$-points in the first Brillouin zone. The self-consistency calculations were considered to be converged only when the total energy deviation is less than $10^{-5}$ Ry./f.u. The calculations were performed with spin polarized potentials to analyze ferromagnetic phase of compounds. To study the doping effects 2x2x2 supercell was constructed, which contains 16 atoms with fcc lattice.

Furthermore we have used tight binding linear muffin tin orbital (TB-LMTO) method [11] within local spin density approximation (LSDA) to study the possibility of HM ferromagnetism in title compound. The von Barth and Hedin parameterization has been used for exchange and correlation potential. All relativistic effects have been taken into account except spin-orbit coupling. A mesh of 12x12x12 was taken in the irreducible wedge of Brillouin Zone. The $k$ points and total energy convergence are checked. The 16 atom supercell was constructed to study the HM property in CaS$_{0.875}M_{0.125}$ (M = C, Si, Ge and Sn).

3. Results and discussions

3.1 Total energy and stability calculations

Total energy calculations are performed for binary host compound CaS, from which the equilibrium lattice constant was calculated. The calculated lattice constants are slightly overestimated by FP-LAPW and underestimated in TB-LMTO as compared with experimental value. Before doing the electronic and magnetic calculations, full atomic position and volume optimization was performed for CaS$_{0.875}M_{0.125}$ (M = C, Si, Ge and Sn). In order to determine the equilibrium lattice constant for doped systems, the total energies were calculated as a function of reduced volume for both non-magnetic and magnetic states and fitted into Murangaun equation of state. The predicted lattice constant, total energy difference ($\Delta E = E_{NM} - E_{FM}$) are tabulated for both methods namely FP-LAPW and TB-LMTO (Table 1). The lattice constant of the doped systems decreases with size of the dopant, since bigger the radius of the dopant, the larger the lattice constant. The calculated total energy difference ($\Delta E = E_{NM} - E_{FM}$) between the nonmagnetic and ferromagnetic states are positive (Table 1) except for CaS$_{0.875}$Ge$_{0.125}$ and CaS$_{0.875}$Sn$_{0.125}$, it shows that the ferromagnetic state is more stable than non-magnetic state. The total energy difference increases as atomic size of the dopant decreases. This is due to; when size of the dopant atom decreases the overlap with neighbouring atom decreases and the valence band become very narrow.

3.2 Electronic band structure and magnetic properties

The spin dependent band structure of CaS$_{0.875}M_{0.125}$ (M = C, Si, Ge and Sn) compounds were calculated at their equilibrium lattice constant along the selected high symmetry directions. The electronic band structure profile is same for all compounds, so for illustration, electronic band structure of CaS$_{0.875}$Si$_{0.125}$ calculated by FP-LAPW is shown in figure 1. From figure 1, in the majority...
Table 1. Calculated equilibrium lattice constant ‘a’ (Å) for both nonmagnetic (NM) and ferromagnetic (FM) phases, total energy difference $\Delta E$ (meV/cell) and total magnetic moment ($\mu_B$) of CaS$_{0.875}$M$_{0.125}$ (M = C, Si, Ge and Sn).

| Compounds      | ‘a’ (Å) | $\Delta E$ (meV/cell) | Total magnetic moment ($\mu_B$) |
|----------------|---------|-----------------------|---------------------------------|
|                | FP-LAPW | TB-LMTO               | FP-LAPW | TB-LMTO | FP-LAPW | TB-LMTO |
| CaS$_{0.875}$C$_{0.125}$ | 5.681   | 5.679                 | 5.558   | 5.568   | 538     | 424      | 2.00    | 2.00    |
| CaS$_{0.875}$Si$_{0.125}$ | 5.772   | 5.769                 | 5.636   | 5.639   | 223     | 73       | 2.00    | 1.87    |
| CaS$_{0.875}$Ge$_{0.125}$ | 5.778   | 5.774                 | 5.642   | 5.641   | 157     | -42      | 2.00    | 1.69    |
| CaS$_{0.875}$Sn$_{0.125}$ | 5.834   | 5.831                 | 5.688   | 5.671   | 135     | -36      | 2.00    | 1.30    |

Figure 1. Band structure of (a) majority and (b) minority spin states of CaS$_{0.875}$Si$_{0.125}$ using FP-LAPW method (GGA scheme).

Spin system 2p state of impurity atom is completely filled, so it substantially lies within the valence band by keeping semiconducting behaviour. While the minority 2p spin states (spin-down) has partially filled band, therefore it crosses the Fermi level and exhibit a metallic behaviour. It indicates that these materials are true half-metallic. The three bands nearer to the Fermi level are mainly from the 2p states of dopant (Si) atom. Spin polarized calculation based on FP-LAPW shows that substitution of C, Si, Ge and Sn at the anion site of CaS gives rise to total magnetic moment of 2.00 $\mu_B$ per formula unit. Whereas in TB-LMTO spin polarized calculation C- doping induce magnetism and exhibit half-metallicity, but Si-, Ge- and Sn- doping do not exhibit half-metallicity.

Figure 2. Spin polarized (a) GGA and (b) LSDA density of sates for CaS$_{0.875}$Si$_{0.125}$ at their equilibrium lattice constant. Fermi level is set to zero.
3.3 Density of states calculations

The dopant induced spin polarization in the host electrons is characterized by its density of states (DOS). The spin polarized DOS of CaS$_{0.875}$M$_{0.125}$ (M = C, Si, Ge and Sn) was calculated and for illustration the LSDA and GGA spin polarized total DOS of CaS$_{0.875}$Si$_{0.125}$ is shown in figure 2. In the minority spin channel in both approximations the spin-polarized DOS shows a metallic character. In the majority spin channel, there is a gap around the Fermi level in GGA DOS so it behaves like half-metallic ferromagnet. In the case of LSDA calculation it slightly crosses the Fermi level. Here it behaves like ferromagnet. Here the ferromagnetism mainly comes from 3p states of dopant. Replacement of anion by partially filled valence p shell elements introduce hole into the valence band. So these spin-polarized holes may mediate the ferromagnetic coupling through strong p-p interaction in these compounds.

4. Conclusion

To summarize, the possibility of magnetization in CaS with the presence of nonmagnetic sp impurities such as C, Si, Ge and Sn were studied based on both FP-LAPW and TB-LMTO-ASA method within the density functional study. Both LSDA and GGA lattice constant are follow the same trend. However, the exchange-correlation functions act differently on the orbital and from this the results about their half-metallic state and their ferromagnetism differ. Our calculation based on FP-LAPW illustrates that all dopants (C, Si, Ge and Sn) induce a total magnetic moment of 2.00 $\mu_B$ per f.u. on behalf of spin polarized p states of dopants in the bandgap. Our studies based on TB-LMTO indicate that C only can induce half-metallic ferromagnetic state in calcium chalcogenide. The strong p-p interaction between chalcogenide and impurity atom may be responsible for forming ferromagnetic coupling.

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