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Half-metallic behavior in non-transition metal based binary compounds *X*C (*X* = Be, Mg, Ca, Sr, Ba, and Ra): a first principles study

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We have performed FP-LAPW calculations based on the density functional theory (DFT) to study the electronic and magnetic properties of hypothetical binary compounds *X*C (*X* = Be, Mg, Ca, Sr, Ba, and Ra), assuming NaCl-type structure. The density of states (DOS) and band structures were studied to understand the electronic properties. Among the systems under investigation, SrC, BaC and RaC showed 100 % spin polarization at the Fermi energy (E_F). The total magnetic moment was found to be 2.00 μ_B, which is an integer value, as expected for half-metallic ferromagnets. The large half-metallic gaps and the location of E_F were found to be nearly independent of the lattice constants for RaC and BeC. The compound BeC is expected to be purely metallic, as E_F is passing through the uprising peak in both spins, and possess a small magnetic moment.

Alloys / Intermetallic compounds / First-principles calculations / Half metal / Spin polarization / Electronic structure

Introduction

Half-metallic ferromagnets (HMFs) are a special type of compounds, in which one spin channel presents a gap at the Fermi level, while the other one has metallic character, leading to 100 % carrier spin polarization at the Fermi level (E_F) [1]. First principles studies of half-Heusler compounds like NiMnSb and PtMnSb predicted these to be HMFs in the year 1983 [2]. After that, half-metallicity has attracted much attention in research, as compounds with such properties are prospective materials for spintronic device applications [3]. Many systems have been studied theoretically and found to be HMFs, *e.g.* ferromagnetic oxides such as CrO_2 [4] and Fe_3O_4 [5], some perovskite compounds like Sr_2FeMoO_6 and $Ba_2Fe(Re/Mo)O_6$ [6]. Ground state studies of the electronic and magnetic properties of Co_2MnAl [7] and Co_2CrSi [8] by LSDA and Co_2FeGe (LSDA+U) [9] showed half-metallic ferromagnetism. In our previous calculations many cobalt-based full Heusler compounds like Co_2TiAl [10], Co_2VAl [11], Co_2MnGe [12], Co_2MnSn [13], Co_2CrAl and Co_2CrGa [14], Co_2MnSi [15], Co_2CrSb [16], Co_2CrAs [17], and NiTbSb [18] showed half metallic behavior from first principles studies. In addition to the materials mentioned above, some more half-metallic materials (binary compounds) were recently discovered. Kusakabe *et al*. studied Ca-pnictides (CaP, CaAs, CaSb) and predicted them to be HMFs [19]. Sieberer *et al*. [20] and Volnianska *et al*. [21] found several HMFs among II-V compounds and explained the spin polarization considering the *p*-states of the anions. Recently it was found that not only transition metal based compounds are HMFs, but some binary compounds based on alkaline-earth metals (MgC, CaC, SrC, BaC) were also predicted to be good candidates for HMFs by Gao *et al*. [22]. Arif *et al*. studied Cr-doped GaAs (semiconductor) with varying lattice constant and predicted it to be a half metal [23]. Galanakis & Mavropoulos proposed a description of the formation of magnetic moments $M_t = (8\text{-}Z_t)$ (where M_t is the total magnetization and Z_t is the total number of valence electrons) in non-transition metal based binary compounds and named them d^0-ferromagnets [24]. Calculation of the electronic structure plays an

important role in determining the magnetic properties of HMFs. The study of the DOS and the band structures reveals the electronic and magnetic properties of the system.

Here we have made an attempt to explain the DOS and the band structures of the hypothetical non-transition metal based binary compounds *X*C (*X* = Be, Mg, Ca, Sr, Ba, and Ra), expecting them to be HMFs. In this paper, we have studied their ground state structural and electronic properties within the full potential linearized augmented plane wave (FP-LAPW) method. The generalized gradient approximation (GGA) [25] was used for the exchange correlation. For BeC and RaC, we arbitrarily changed the lattice constants in order to estimate hypothetical HMFs.

Computational details and crystal structure

A computational code (WIEN2K) [26] based on the FP-LAPW method was applied for the calculations of the structural, electronic and magnetic properties. Non-spherical contributions to the charge density and potential within the Muffin Tin (MT) spheres were considered up to $l_{max} = 10$ (the highest value of the angular momentum functions). The cut-off parameter was $R_{MT} \times K_{max} = 7$, where K_{max} is the maximum value of the reciprocal lattice vector in the plane wave expansion and R_{MT} is the smallest atomic sphere radius of all atomic spheres [27]. In the interstitial region the charge density and the potential were expanded as a Fourier series with wave vectors up to $G_{max} = 12$ a.u.$^{-1}$. The number of k-points used in the irreducible part of the Brillouin zone was 286. The Muffin Tin sphere radii (R_{MT}) used here are tabulated in Table 1. The crystal structure of the non-transition metal based binary compounds with chemical formula *X*C (*X* = Be, Mg, Ca, Sr, Ba, and Ra) was assumed to be of the NaCl type. It consists of fcc sublattices with *X* atoms at (0, 0, 0) and C atoms at (½, ½, ½) and has space group *Fm*-3*m*.

Results and discussions

Systematic calculations of the electronic and magnetic properties of binary compounds *X*C were carried out in this work. The calculated electronic structures were compared to study the effect of the different kinds of atom and valence electron concentration on the magnetic properties, and in particular on the band gap. The structural and electronic properties were calculated using GGA. Optimized lattice constants, isothermal bulk modulii and their pressure derivatives, were calculated by fitting the total energy to Murnaghan's equation of state [28]. The optimized lattice parameters were slightly smaller than previously calculated lattice parameters for the same compounds, assuming the equally cubic zinc-blende structure [22]; the difference in lattice parameters is given by $\Delta(a_o)$ in Table 2. A series of total energy calculations as a function of volume could be fitted to Murnaghan's equation of states (1) and the total energy *versus* volume per formula unit curve is shown in Fig. 1.

$$E(V) = E_0 + \left[\frac{(V_0/V)^{B_0'}}{B_0' - 1} + 1\right] - \frac{B_0 V_0}{B_0' - 1}, \quad (1)$$

where E_0 is the minimum energy at $T = 0$ K, B_0 is the bulk modulus at the equilibrium volume and B'_0 is the pressure derivative of the bulk modulus at the equilibrium volume. Pressure, $p = -\frac{dE}{dV}$, bulk modulus, $B_0 = -V\frac{\mathrm{d}p}{\mathrm{d}V} = V\frac{\mathrm{d}^2E}{\mathrm{d}V^2}$.

The results of the volume optimizations are shown in Fig. 1. The changes in the lattice constants with respect to previous results [22] are 2.82 %, 7.48 %, 7.15 %, and 7.27 % for MgC, CaC, SrC, and BaC respectively. The values of the optimized lattice parameters, bulk modulii and equilibrium energies are given in Table 2.

Spin polarization and half-metallic ferromagnetism

The electron spin polarization (*P*) at the Fermi energy (E_F) of a material is defined by equation (2) [29].

$$P = \frac{\rho\uparrow(E_F) - \rho\downarrow(E_F)}{\rho\uparrow(E_F) + \rho\downarrow(E_F)}, \quad (2)$$

where $\rho\uparrow(E_F)$ and $\rho\downarrow(E_F)$ are the spin-dependent densities of states at E_F. The arrows ↑ and ↓ indicate the majority and minority states, respectively. *P* vanishes for paramagnetic or anti-ferromagnetic materials, even below the magnetic transition temperature. It has a finite value in ferromagnetic materials below the Curie temperature [30]. The electrons at E_F are fully spin-polarized (P = 100 %) when $\rho\uparrow(E_F)$ or $\rho\downarrow(E_F)$ equals zero. In the present work, only SrC and BaC show 100 % spin polarization, whereas CaC gives 74 % and MgC 36 %. So we can predict that SrC and BaC are HMFs at their optimized lattice constants, and also CaC, since its spin polarization is close to 100 % (Table 3). According to our results, the compound MgC is purely metallic, as it shows extended DOS at E_F, $\rho\uparrow(E_F) = 1.3$ states/eV and $\rho\downarrow(E_F) = 0.60$ states/eV (Table 3). The large value of DOS is explained by the fact that E_F passes through the strongly localized C-*p* states, whereas the contribution of Mg-*p* states is very small in both spin channels, as illustrated in Fig. 2(a).

Table 1 Muffin Tin Radii (R_{MT}).

R_{MT} (a.u.)	Compounds					
	BeC	MgC	CaC	SrC	BaC	RaC
X	2.00	2.37	2.50	2.50	2.50	2.50
C	2.00	2.37	2.50	2.50	2.50	2.50

Table 2 Lattice constant, bulk modulus and equilibrium energy.

*X*C	Optimized lattice constant a_o (Å)			Bulk modulus *B* (GPa)	Equilibrium energy (Ry)
	Literature [22] [a]	Our data	$\Delta(a_o)$		
MgC	5.09	5.23	0.14 (2.82 %)	70.793	-476.640
CaC	5.75	5.32	0.43 (7.48 %)	69.439	-1436.826
SrC	6.15	5.71	0.44 (7.15 %)	59.794	-6435.714
BaC	6.49	6.02	0.47 (7.27 %)	47.459	-16354.757

[a] zinc-blende structure

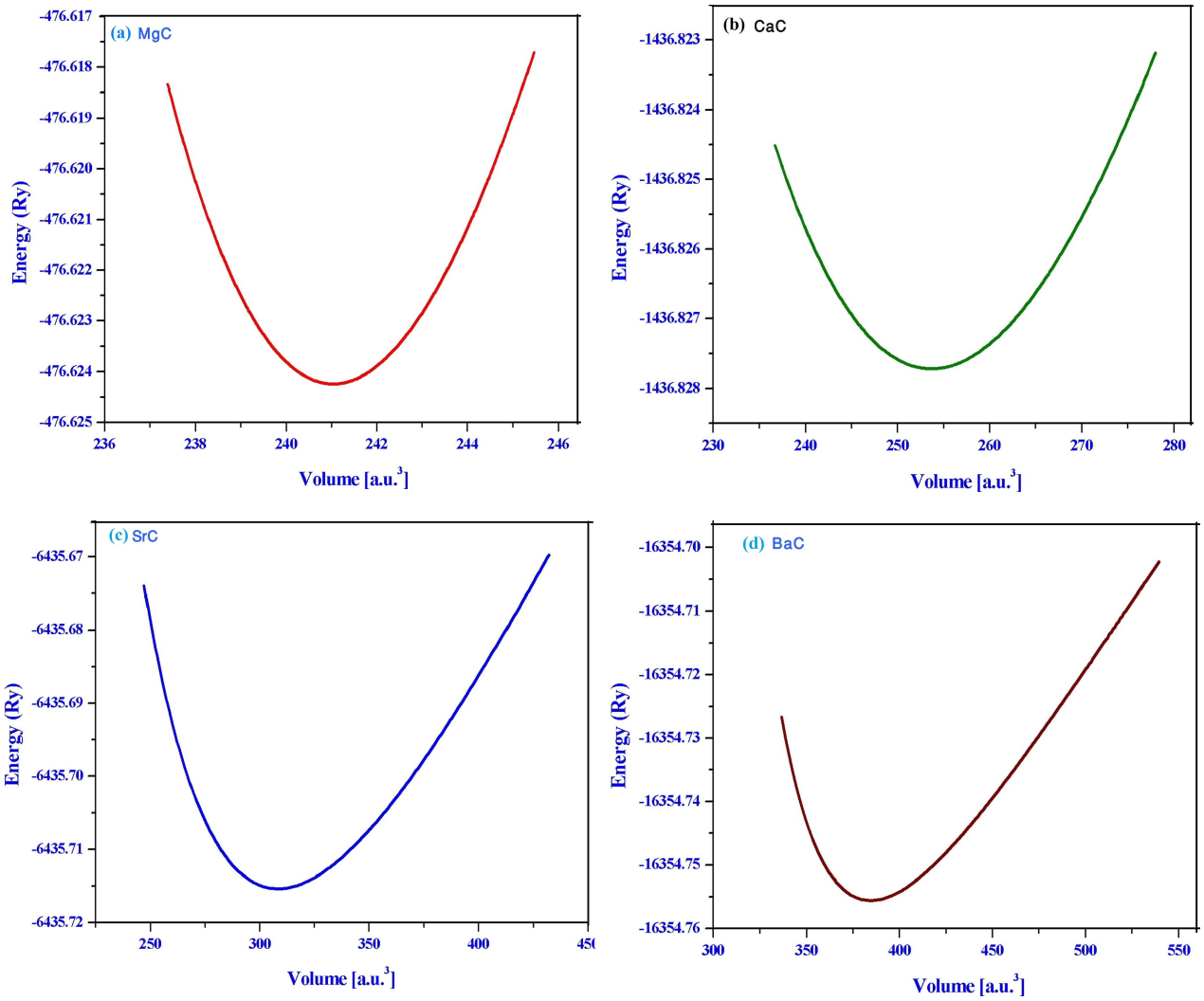

Fig. 1 Volume optimization of MgC (a), CaC (b), SrC (c), and BaC (d).

On the other hand, the corresponding DOS for SrC and BaC are 2.10 states/eV and 3.10 states/eV, respectively, in the minority channel, whereas the DOS in the majority channel is nil, which gives 100 % spin polarization at E_F (Fig. 2(c-d)). The binary compounds under investigation do not contain transition metals, thus the mechanism of the ferromagnetism is different from the concept of double exchange and *p-d* exchange or *d-d* exchange splitting, which are important in magnetic 3*d* compounds. Here the pivotal role is played by spin polarization of the *p*-states of the C atoms. Even the formation of a spin gap was found to occur in the spin-up, instead of the spin-down channel, as in the case of 3*d*-metal based compounds. As explained by Galanakis, d^0-ferromagnets are made up of *sp* hybridization, in the spin-down band the *s* and *p* orbitals of two *sp* atoms hybridize, creating bonding and anti-bonding hybrids. The bonding *sp* states are occupied, while the anti-bonding ones are empty, leading to a total of 4 occupied spin-down bands. In the spin-up band the bonding *s* state is occupied and the Fermi level crosses the bonding *p*-states, since it has less than 8 valence electrons in the unit cell [31]. The band gap is defined as the difference between the lowest energy along X symmetry in the conduction band and the highest energy along Γ symmetry in the valence band, and hence it is an indirect band gap [32]. For SrC and BaC the minority channel is metallic, whereas the majority channel is insulating with indirect energy gaps of 1.80 eV and 1.20 eV, respectively (Table 3). The calculated energy gaps are higher than the previously obtained values of 0.83 eV for CaC, 0.81 eV for SrC, and 0.61e V for BaC [22]. |According to our results CaC is metallic as E_F is not located exactly at the middle of the gap, as shown in Fig. 3, which is in contrast with the results of Gao *et al.* [22]. It may be because our lattice constant is smaller by 7.48 % and HMF is robust to lattice constants.

We have also studied the electronic and magnetic properties of RaC and BeC by varying the lattice constants arbitrarily. The properties of RaC were found to be similar to those of SrC and BaC, but the properties of BeC revealed metallic character. Fig. 4 shows the total DOS of RaC and BeC as a function of the lattice constants. As shown in Fig. 4(a), RaC is purely metallic for a_o = 5.5 Å and the corresponding magnetic moment is 1.890 μ_B, which seems to deviate from the rule of 8, $M_t = 8–Z_t$ [24], where Z_t and M_t are the total number of valence electrons and the total magnetic moment, respectively. As we increase the lattice constant, the energy band gap becomes prominent, as a result of exchange splitting of the C-*p* states at the Fermi level. At a_o = 6.7 Å we calculated the largest energy band gap for RaC, which is around 2.00 eV and the corresponding magnetic moment is an exact integer value, 2.00 μ_B (Table 4). The magnetic moment stabilizes at ~2.00 μ_B for a lattice constant between 6.50 and 7.50 Å (Fig. 5). In the case of BeC the magnetic moment is negligibly small and gives a negative value below a_o = 4.50 Å, which indicates that this compound is a weak anti-ferromagnet.

Table 3 Energy gap and spin polarization.

*X*C	Energy gap (eV)				Spin polarization		
	E_g [22] [a]	$E_{max}(\Gamma)$	E_{min}(X)	$\Delta E = E_g$	$\rho\uparrow(E_F)$	$\rho\downarrow(E_F)$	P (%)
MgC	–	–	–	–	1.30	0.60	36
CaC	0.83	0.30	2.10	1.80	0.20	1.80	74
SrC	0.81	-0.3	1.50	1.80	0.00	2.10	100
BaC	0.61	-0.5	0.70	1.20	0.00	3.10	100

[a] zinc-blende structure

Table 4 Magnetic moments calculated for different lattice constants.

RaC			BeC	
Lattice constant (Å)	Energy gap E_g (eV)	Magnetic moment (μ_B)	Lattice constant (Å)	Magnetic moment (μ_B)
5.50	0.00	1.890	4.00	-0.045
6.00	0.70	1.980	4.50	-0.001
6.50	1.60	2.000	4.75	0.000
6.70	2.00	2.000	5.00	0.015
7.00	1.90	2.000	5.50	0.633
7.50	1.70	2.010	6.00	1.744

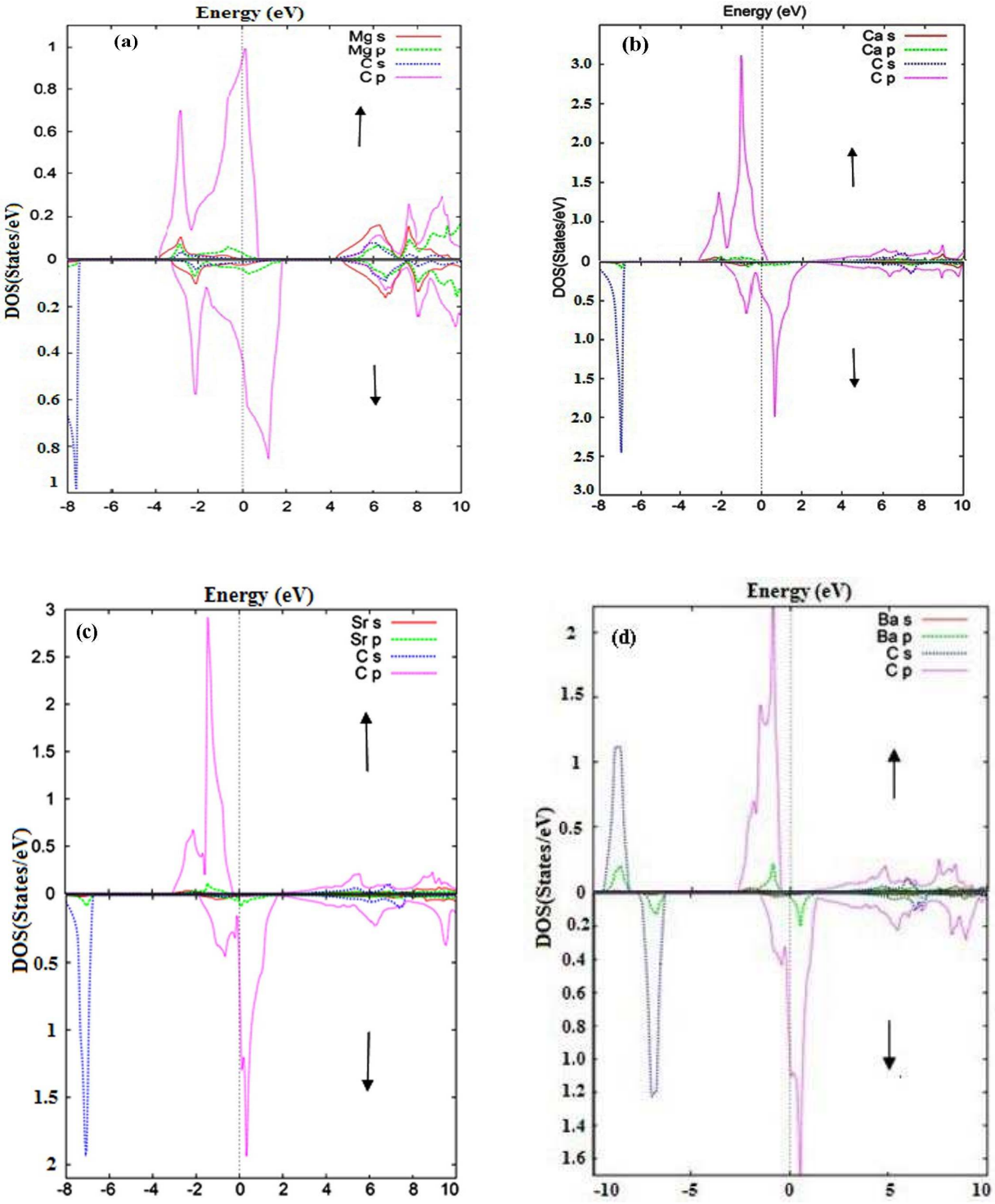

Fig. 2 Partial DOS of MgC (a), CaC (b), SrC (c), and BaC (d).

The explanation in the case of BeC is similar to that of MgC for a lattice constant of and above a_o = 5.00 Å, since both of them are metallic in the fcc structure and exhibit no gap at the Fermi level. We have noticed that an increase of the lattice constant increases the magnetic moments, thus retaining the ferromagnetic character, as shown in Fig. 5 for BeC.

Magnetic properties

Information regarding the partial and total magnetic moments calculated for the compounds under investigation is summarized in Table 5. In the case of CaC the calculated total magnetic moment is close to an integer value, as expected for half-metallic systems.

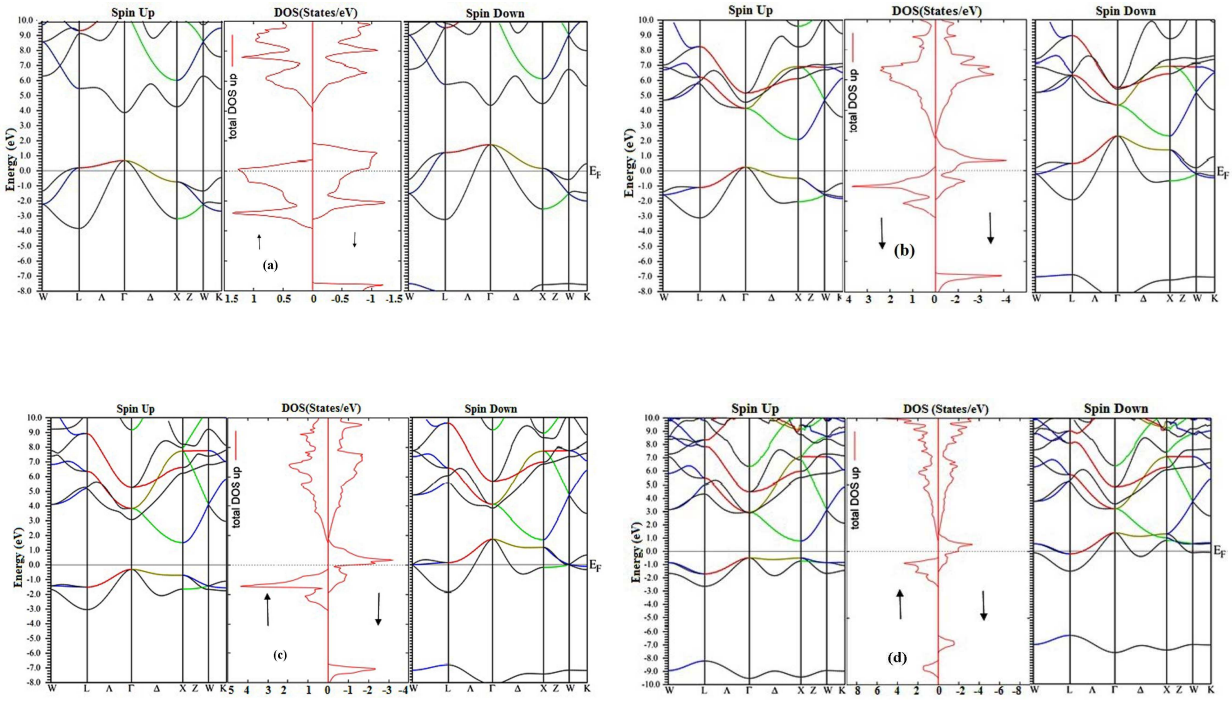

Fig. 3 Band structures of MgC (a), CaC (b), SrC (c), and BaC (d).

Table 5 Total and partial magnetic moments.

Compound	Magnetic moment (μ_B)					
	Literature [22] [a]			Our data		
	X	C	Total	*X*	C	Total
MgC	0.09	1.23	1.72	0.045	0.766	0.946
CaC	0.15	1.52	2.00	0.154	1.539	1.962
SrC	0.12	1.61	2.00	0.106	1.549	2.000
BaC	0.12	1.56	2.00	0.120	1.492	2.000

[a] zinc-blende structure

The calculated magnetic moments are in good agreement with previous results [22], except for MgC, which shows a huge deviation of almost 45 %. In all cases the C atoms contribute much more to the total magnetic moment than the *X* atoms. There are six valence electrons in *X*C; for BaC (Ba: $6s^2$ and C: $2s^22p^2$) the C-*s* states occupy the low-energy region below -5 eV and the C-*p* states are predominant at the Fermi level (Fig. 2(d)). The main contribution to the magnetic moment comes from the C-*p* states. The contribution of the *X* atoms to the total magnetic moment is small, and is the result of the hybridization of C-*p* and *X*-*s* states. The two sharp peaks in the spin-up and spin-down channels above -5 eV in Fig. 4 come from exchange splitting of C-*s* states, and around the Fermi level exchange splitting appears due to C-*p* states. As a result of these two exchange splittings of C-*s* and C-*p* states, the partial magnetic moment of the C atom is larger than that of Ra. To predict half-metal ferromagnetism for a binary compound, the total magnetic moment has to be an integer value following the rule of 8, $M_t = 8–Z_t$ [24]. For example, for BaC (Ba: $6s^2$ and C: $2s^22p^2$); the total number of valence electrons is 2+2+2 = 6, then $M_t = 8–6 = 2.00$ μ_B. In our work we found that the total magnetic moment is 2.00 μ_B for BaC, thus we can predict this compound to be a HMF. Similar explanations may follow for other binary compounds.

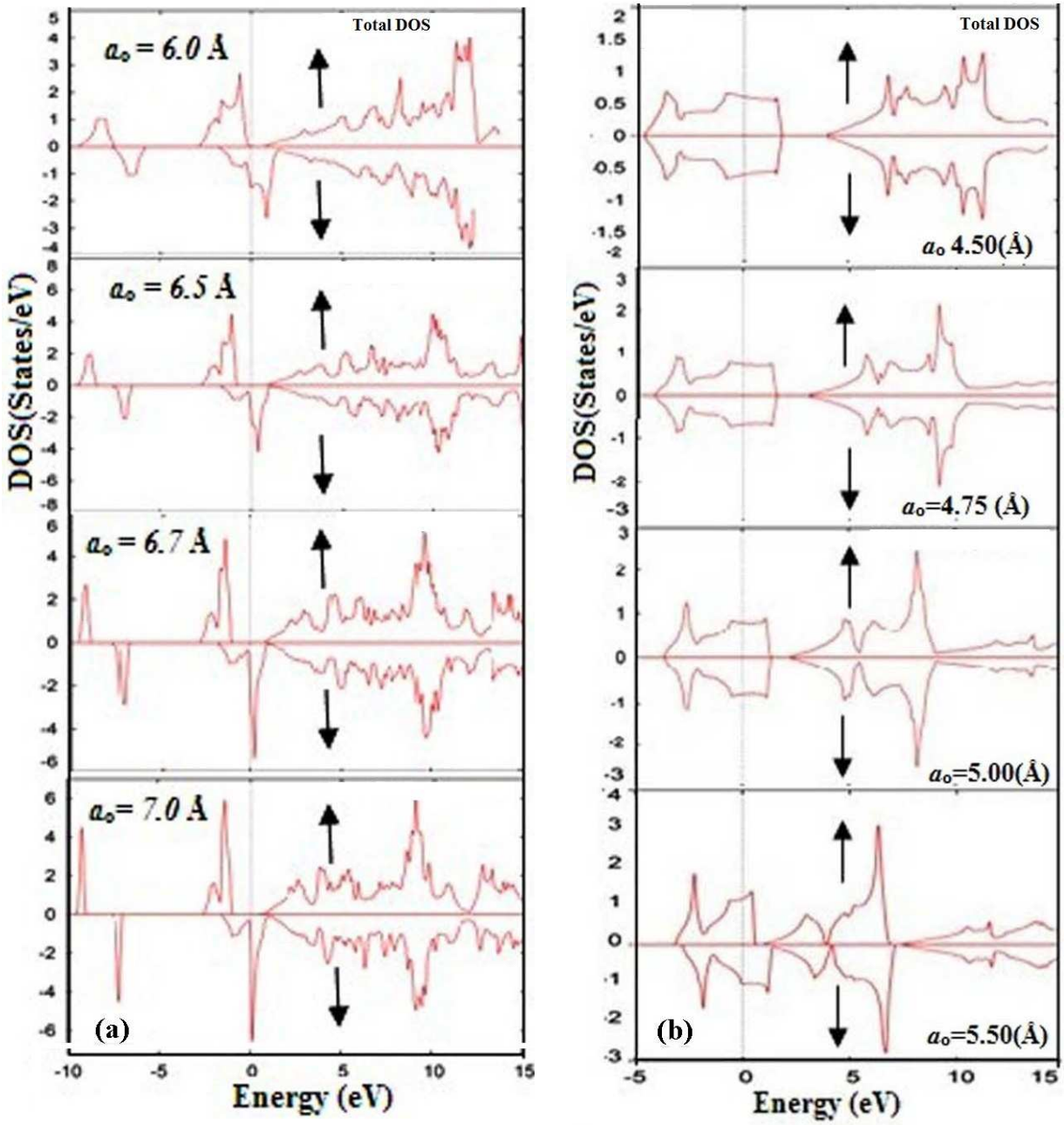

Fig. 4 Calculated total DOS of RaC (a) and BeC (b) with the variation of lattice constants.

Conclusion

HMFs are a special type of compounds, which has aroused interest in the field of spintronics and magneto-electronics, due the large spin-polarization of the electrons at the Fermi level. In this work, we have investigated the electronic and magnetic properties of non-transition metal based binary compounds *X*C (*X* = Be, Mg, Ca, Sr, Ba, and Ra). The calculations were based on the first-principles FP-LAPW method. We found that MgC and BeC are expected to be metallic while CaC, SrC, BaC, and RaC may exhibit half-metallicity with stable ferromagnetic ground states. The calculated total magnetic moment was found to be 2.00 μ_B per formula unit, which obeys the Slater-Pauling rule, $M_t = 8–Z_t$, and the HM gaps about 1.80 eV (CaC), 1.80 eV (SrC) and 1.20 eV (BaC). Among all these compounds RaC exhibits the largest HM gap: about 2.0 eV at a_o = 6.7 Å. HMFs with low magnetic moments have attracted interest in recent years as they can be promising candidates for spintronic applications due to their high value of spin polarization, low stray field and small energy loss in spintronic devices.

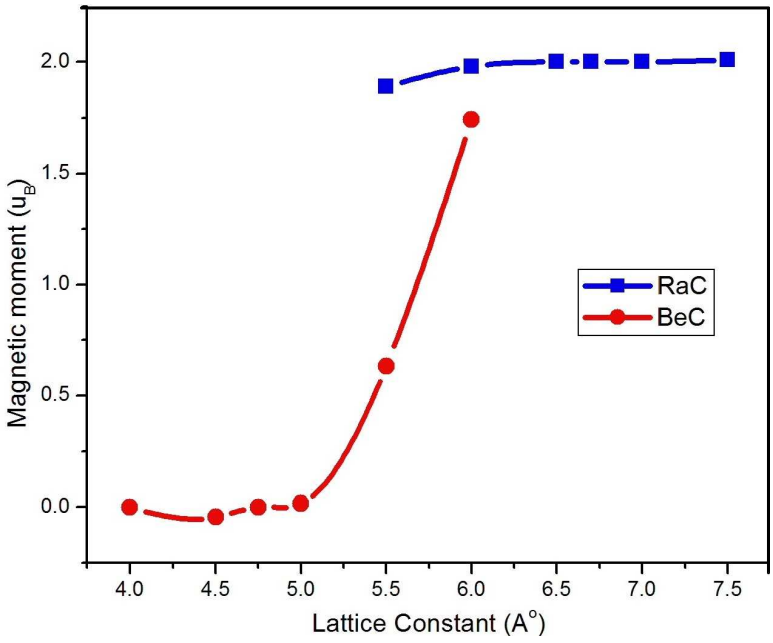

Fig. 6 Calculated magnetic moments of RaC and BeC with the variation of lattice constants.

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