

Half-metallic ferromagnetism in zinc-blende CaC, SrC, and BaC from first principles

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(Received 15 November 2006; revised manuscript received 26 March 2007; published 25 May 2007)

Using the first-principles full-potential linearized augmented plane-wave method based on density functional theory, we have investigated the electronic structure and magnetism of hypothetical MC ($M=\text{Mg, Ca, Sr, and Ba}$) compounds with the zinc-blende (ZB) crystal structure. It is shown that ZB CaC, SrC, and BaC are half-metallic ferromagnets with large half-metallic gaps (up to 0.83 eV). The half metallicity is found to be robust with respect to the lattice compression and is maintained up to the lattice-constant contraction of 14%, 13%, and 9% for CaC, SrC, and BaC, respectively. The exchange interactions in these compounds are studied using the augmented spherical wave method in conjunction with the frozen-magnon approach. The Curie temperature is estimated within both the mean field approximation and the random phase approximation. The predicted Curie temperatures of all three half-metallic compounds considerably exceed the room temperature. The large half-metallic gaps, the robustness of the half metallicity with respect to the lattice contraction, and the high Curie temperatures make these systems interesting candidates for applications in spintronic devices. The absence of the transition-metal atoms makes these compounds important model systems for the study of the origin and properties of the half-metallic ferromagnetism of s - p electron systems.

DOI: [10.1103/PhysRevB.75.174442](https://doi.org/10.1103/PhysRevB.75.174442)

PACS number(s): 75.90.+w, 71.20.Dg

I. INTRODUCTION

Half-metallic (HM) ferromagnets, where one of the two spin channels is metallic while the other has an energy gap around the Fermi energy, attract increasing research interest as potential materials for spintronic device applications, in particular as a source of spin-polarized carriers injected into semiconductors. Since the first prediction in 1983 by de Groot *et al.*¹ of HM ferromagnetism in the half-Heusler compounds NiMnSb and PtMnSb, many further systems have been found to be HM ferromagnets, e.g., ferromagnetic oxides such as CrO₂ (Ref. 2) and Fe₃O₄,³ diluted magnetic semiconductors such as Mn-doped GaN (Ref. 4) and Cu-doped ZnO,⁵ and some perovskite compounds.⁶ Recently, binary transition-metal pnictides^{7–11} and chalcogenides^{8,12} with zinc-blende (ZB) structure have been investigated intensively by means of first-principles calculations, and it was predicted that many compounds of this class are HM ferromagnets. Although the ground-state crystal structure of these compounds is of the NiAs type,^{7,9} ZB CrAs,¹³ CrSb,¹⁴ and MnAs (Ref. 15) films have been grown successfully on appropriate III-V semiconductor substrates using molecular-beam epitaxy. Also, some of the hypothetical wurtzite transition-metal pnictides and chalcogenides^{16,17} were found to be robust HM ferromagnets.

In 2004, Kusakabe *et al.*¹⁸ predicted that ZB Ca pnictides (i.e., CaP, CaAs, and CaSb) belong to the class of HM ferromagnets. Very recently, Sieberer *et al.*¹⁹ and Volnianska *et al.*²⁰ found HM ferromagnetism in many II-V ZB compounds. These compounds do not contain transition-metal atoms and therefore the mechanism of the ferromagnetism is different from both the double exchange and the p - d exchange that are important in magnetic $3d$ compounds. Here the crucial role is played by the spin polarization of the p states of anions. The HM ferromagnetism makes these sys-

tems attractive not only as materials for possible applications but also as model objects for the study of new mechanisms of formation of ferromagnetism.

These findings motivated us to continue the study of binary compounds with the ZB structure, searching for further HM ferromagnets that do not contain $3d$ atoms. In this paper, we systematically investigate the electronic structure and magnetism of the hypothetical zinc-blende (ZB) MC compounds ($M=\text{Mg, Ca, Sr, and Ba}$) by using the first-principles full-potential linearized augmented plane-wave (FPLAPW) method. We predict that ZB CaC, SrC, and BaC are HM ferromagnets with an integer magnetic moment of $2.00\mu_B$. We show that the HM gaps of ZB CaC, SrC, and BaC are large (up to 0.83 eV for CaC) and the half metallicity is robust against lattice compression (up to 14% decrease of the lattice parameter for CaC). Note that an interesting case of ferromagnetism originating in the spin splitting of the anion p states has been discussed in our previous work on organic magnets.²¹

Wide application of HM ferromagnets in devices is possible only for materials with the Curie temperature substantially exceeding room temperature. We apply the augmented spherical wave (ASW) method in conjunction with the frozen-magnon approach to study interatomic exchange interactions that are used to estimate the Curie temperature within both the mean field approximation (MFA) and the random phase approximation (RPA). The three HM compounds studied in the paper have been found to satisfy the condition of high Curie temperature.

II. COMPUTATIONAL METHOD

The geometry optimization and electronic structure calculations for ZB MC are carried out using the FPLAPW

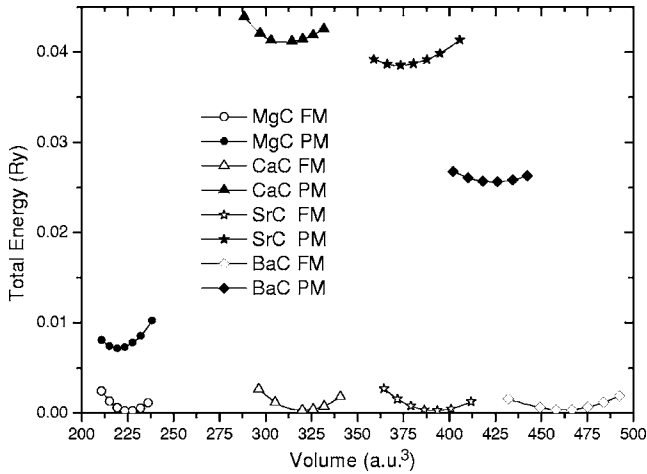


FIG. 1. Total energy as a function of the volume per formula unit for the paramagnetic (PM) and ferromagnetic (FM) states of ZB MC ($M=\text{Mg, Ca, Sr, and Ba}$).

method implemented in the WIEN2K package.²² The generalized gradient approximation (GGA) in the scheme of Perdew, Burke, and Ernzerhof²³ (PBE) is used for the exchange-correlation functional, and the relativistic effects are taken into account in the scalar approximation. The spin-orbit coupling has small effect on the ferromagnetism of the systems and is not taken into account. We take $R_{\text{mt}}K_{\text{max}}$ equal to 8.0 and make the expansion up to $l=10$ in the muffin tins. The radii R_{mt} of the muffin tins are chosen to be approximately proportional to the corresponding ionic radii and as large as possible under the condition that the spheres do not overlap. We use 3000 k points in the first Brillouin zone. Self-consistency is considered to be achieved when the total-energy difference between succeeding iterations is less than 10^{-5} Ry per formula unit.

To estimate the Curie temperatures we map the systems on the Heisenberg Hamiltonian. For the calculations of the Heisenberg exchange parameters we employ the augmented spherical wave method²⁴ in conjunction with the frozen-magnon approach.^{25,26} The exchange-correlation potential is chosen in the generalized gradient approximation.²⁷ A dense Brillouin zone sampling $30 \times 30 \times 30$ is used. We use the mean field approximation and the random phase approximation²⁶ to evaluate the Curie temperature. The MFA and RPA have been earlier successfully applied to estimate the Curie temperature for many HM ferromagnets.^{28–30} We refer the reader to Refs. 28–30 for all details of the calculational schemes for the exchange parameters and Curie temperatures.

III. RESULTS AND DISCUSSION

A. Total energy and electronic structure

We first calculate the total energy as a function of the volume per formula unit for the ferromagnetic and paramagnetic states of four ZB MC compounds (Fig. 1). We find that for all systems the ferromagnetic phases have lower energies than the paramagnetic phases. Table I presents the calculated

TABLE I. Predicted equilibrium lattice constant (a), HM gap (E_g), total magnetic moment per formula unit (μ_{tot}), M ($M=\text{Mg, Ca, Sr, and Ba}$) magnetic moment (μ_M), C magnetic moment (μ_C), and magnetic moment in the interstitial region (μ_{in}).

Compound	a (Å)	E_g (eV)	μ_{tot} (μ_B)	μ_M (μ_B)	μ_C (μ_B)	μ_{in} (μ_B)
MgC	5.09		1.72	0.09	1.23	0.40
CaC	5.75	0.83	2.00	0.15	1.52	0.33
SrC	6.15	0.81	2.00	0.12	1.61	0.27
BaC	6.49	0.61	2.00	0.12	1.56	0.32

equilibrium lattice constants for the ferromagnetic phase that are determined by fitting the total energy as a function of volume to the Murnaghan equation of state.³¹

The spin-polarized band structures of ferromagnetic MgC, CaC, SrC, and BaC at equilibrium lattice constants are shown in Fig. 2. For MgC, both the majority-spin and the minority-spin electrons exhibit metallic character. For CaC, SrC, and BaC, the minority-spin channel is metallic whereas in the majority-spin channel there is an energy gap around the Fermi level of about 3.25, 2.48, and 2.01 eV for CaC, SrC, and BaC, respectively. Therefore, these three systems are HM ferromagnets. The HM gap,^{7,10,12} which is determined as the minimum between the lowest energy of majority- (minority-)spin conduction bands with respect to the Fermi level and the absolute values of the highest energy of the majority- (minority-)spin valence bands, is 0.83, 0.81, and 0.61 eV, respectively, for CaC, SrC, and BaC. These gaps are comparable with the large HM gaps of CrTe (0.88 eV), CrSe (0.61 eV),¹² and CrSb (0.77 eV).⁷ Note that in the half-metallic ZB transition-metal pnictides and chalcogenides, the majority-spin channel is metallic, while there is a semiconducting gap in the minority-spin channel, which is opposite to the properties of the MC half-metallic systems (Fig. 2). The metallic character of the minority-spin channel and semiconducting character of the majority-spin channel is similar to the HM ferromagnetism of ZB MnC.^{28,32}

The calculated total magnetic moment for ZB CaC, SrC, and BaC per formula unit is $2.00\mu_B$. An integer value of the magnetic moment is a characteristic feature of HM ferromagnets. The total magnetic moment contains three contributions one each from the alkaline-earth atom, the C atom, and the interstitial region (Table I). The main contribution comes from the C atom, whereas the moments of the cations are small. The moments of C and cation atoms are parallel to each other, which is different from the transition-metal pnictides and chalcogenides, but similar to ZB CaAs.^{18,19} The mechanism of the parallel alignment between the anion and the cation magnetic moments has been explained in Ref. 19 on the basis of a model of covalent polarization.

In the following we concentrate the discussion on the properties of ZB CaC. The corresponding properties of SrC and BaC are similar to the properties of CaC. Figure 3 shows the calculated spin-resolved total and partial densities of states (DOSs) of ZB CaC at its equilibrium lattice constant. Comparing the DOSs with the band structure (Fig. 2), we see that the lowest three bands of majority-spin electrons are

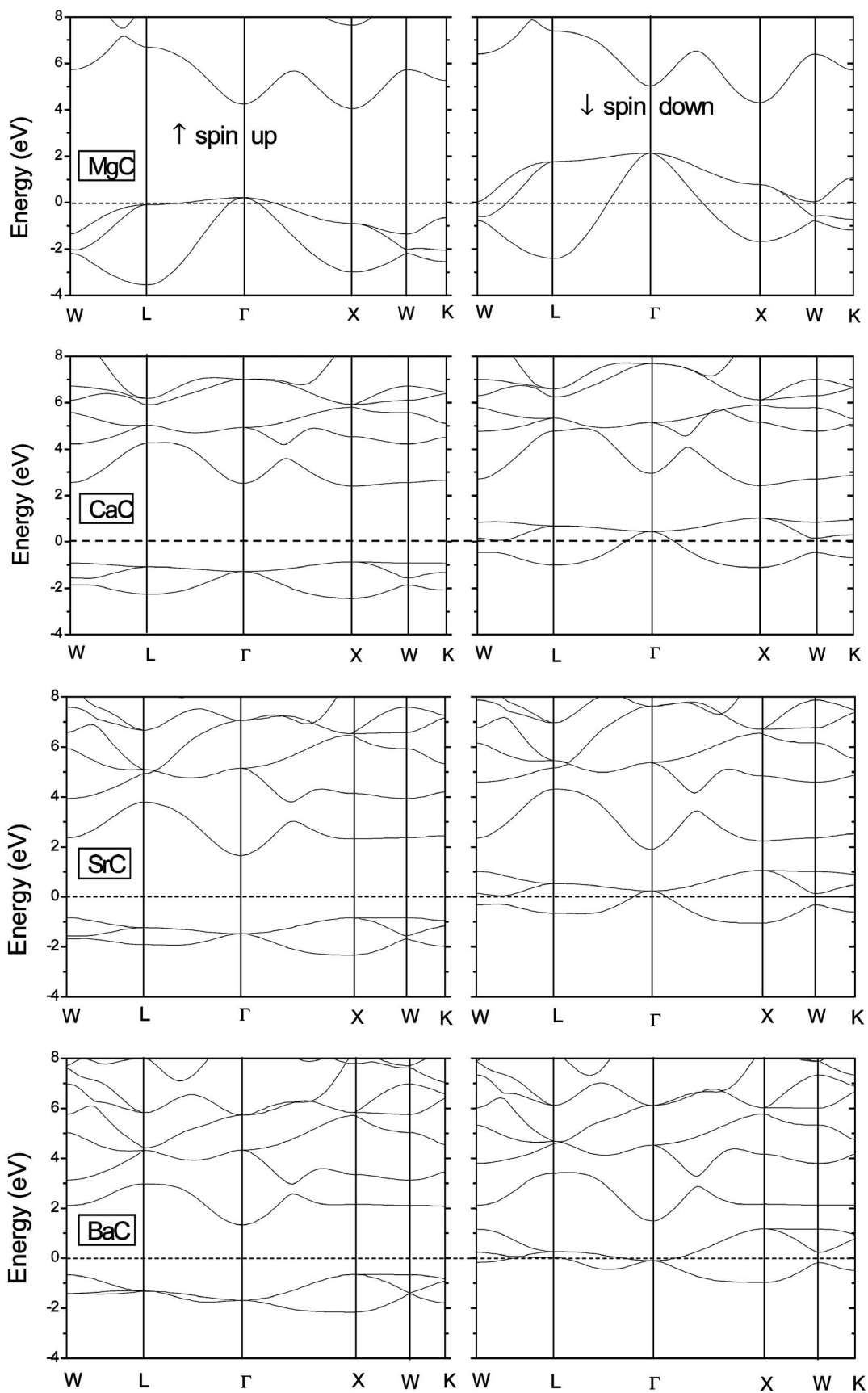


FIG. 2. Spin-polarized band structure of ZB MC (M =Mg, Ca, Sr, and Ba) at their predicted equilibrium lattice constants. The horizontal dashed line indicates the Fermi level at 0 eV.

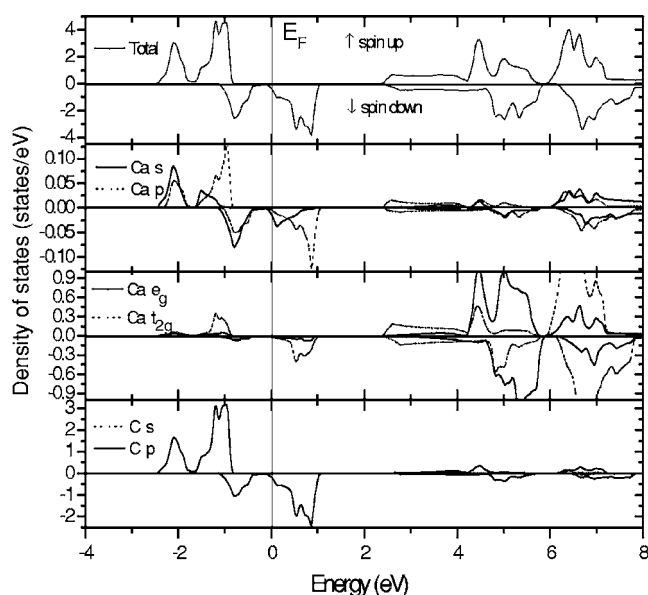


FIG. 3. Spin-dependent total and partial DOSs of ZB CaC at its predicted equilibrium lattice constant.

filled. These bands are formed mainly by the C p states with a small contribution from the Ca t_{2g} states. For the minority-spin channel, the lowest three bands also originate mainly from the C p states with a small contribution from the Ca t_{2g} states, but in this case the Fermi level crosses the bands. The two bands around 5 eV for both majority- and minority-spin channels correspond to the Ca e_g states, and the three higher bands around 7 eV in both spin channels are mainly of Ca t_{2g} character.

B. The nature of the ferromagnetism

It is instructive to compare the mechanism of ferromagnetism in ZB CaC with the corresponding mechanism for transition-metal pnictides and chalcogenides with ZB crystal structure. In the ZB structure, the cations are in a tetrahedral environment. This leads to the splitting of the $3d$ states into a doublet with e_g symmetry and a triplet with t_{2g} symmetry. The e_g states are lower in energy than the t_{2g} states. The splitting of the $3d$ states is obtained for Ca $3d$ states (Fig. 3). Since, however, the e_g and t_{2g} states are not occupied and lie, respectively, at about 5 and 7 eV above the Fermi level, this splitting does not play an important role in CaC. The magnetic moment of CaC originates mainly from the p electrons of the C atom (Table I). The C p states are strongly spin split and are situated close to the Fermi level, resulting in the partial occupation of the spin-down states (Fig. 3). There are six valence electrons in CaC (Ca, $4s^2$, and C, $2s^2 2p^2$); two of them occupy the low-energy C s states (about 7 eV below the Fermi level, not shown in Fig. 3), and the remaining four electrons occupy mainly the C p states. The three isolated spin-up bands of predominantly C p character are completely filled (Figs. 2 and 3). The remaining one electron leads to the partial occupation of the corresponding spin-down bands. The main contribution to the magnetic moment, $1.52\mu_B$, comes from the C p states (Table I). The contribu-

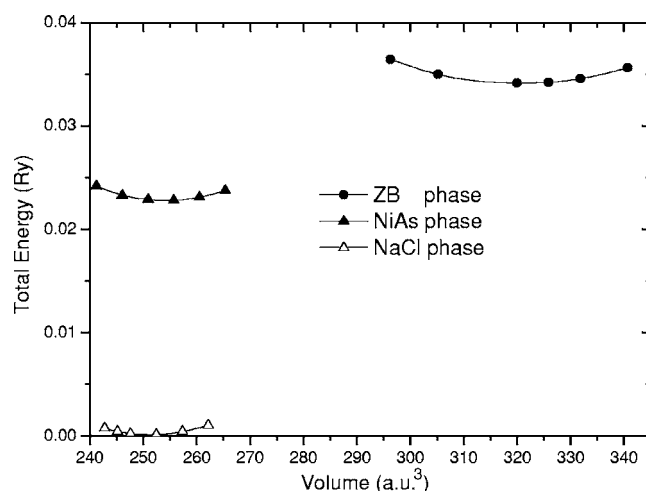


FIG. 4. Total energy as a function of volume per formula unit for CaC in the ZB, NiAs, and NaCl phases with ferromagnetic states.

tion of the Ca atom to the total moment is small and results from the hybridization between the C p and the Ca t_{2g} states. A considerable contribution to the magnetic moment comes from the interstitial region ($0.33\mu_B$).

In ZB transition-metal pnictides and chalcogenides, the anion p states are completely filled and the magnetic moment is formed mainly by the transition-metal $3d$ electrons. In this case the half metallicity originates from the $p-d$ hybridization governed by the ZB symmetry and leading to the bonding-antibonding splitting (see Refs. 7, 8, and 10).

C. Comparison with other crystal structures

Studies on HM ferromagnets of binary ZB transition-metal pnictides and chalcogenides^{7-10,12} as well as ZB II-V compounds¹⁹ have shown that the ZB structure does not have the lowest total energy compared to other crystal lattices. The ZB films can, however, be fabricated on appropriate ZB semiconductor substrates.¹³⁻¹⁵ We have a similar situation in the case of MC compounds studied in this paper. We performed calculations for the NiAs and NaCl structures of CaC, SrC, and BaC, and found that the NaCl structure is energetically more stable than the NiAs and ZB structures. This is different from VTe, where the NiAs structure is the most stable.³³ Figure 4 shows the total energy as a function of volume per formula unit of ferromagnetic CaC in the ZB, NiAs, and NaCl phases. The calculated total-energy differences per formula unit between the ZB phase and the NaCl (NiAs) phase are 0.46 (0.15), 0.38 (0.10), and 0.36 (0.12) eV for CaC, SrC, and BaC, respectively. Although the ZB structure does not have the lowest energy, we consider as feasible the epitaxial growth of ZB MC films on the proper substrate of a ZB semiconductor. Note that, for example, ZB CrSb and CrAs have been realized in the form of thin epitaxial films though the energies of the ZB phases of these compounds are 1 and 0.9 eV higher than the energies of the corresponding NiAs phase.^{7,13,14}

Since the lattice parameter of an epitaxially grown film depends on the lattice parameter of the substrate, it is impor-

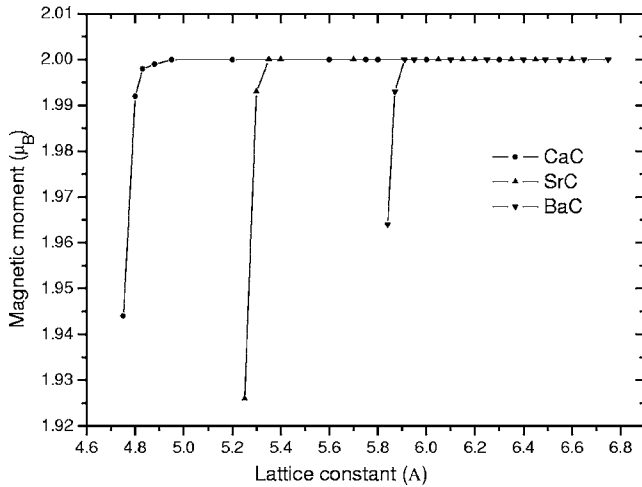


FIG. 5. Magnetic moment (units of μ_B) as a function of the lattice constant (\AA) per formula unit for ZB CaC, SrC, and BaC.

tant to study the robustness of the half metallicity with respect to variation of the interatomic distances. Figure 5 shows the total magnetic moment per formula unit for ZB CaC, SrC, and BaC as a function of the lattice constant. The total magnetic moments remain integer until the lattice constants are compressed to the critical values of 4.95, 5.35, and 5.91 \AA for CaC, SrC, and BaC, respectively. Therefore, the half metallicity of ZB CaC, SrC, and BaC is maintained up to contraction of the lattice parameter of 14%, 13%, and 9%, respectively. The lattice constants of ZB semiconductors that can be used as a substrate for growing the ZB *MC* films vary in a broad interval: GaAs (5.65 \AA), ZnSe (5.67 \AA), GaSb (6.10 \AA), ZnTe (6.10 \AA), InSb (6.48 \AA), CdTe (6.48 \AA),³⁴ and correlate well with the equilibrium parameters of ZB CaC (5.75 \AA), SrC (6.15 \AA), and BaC (6.49 \AA). This relation between interatomic distances confirms the feasibility of epitaxial growth of ZB *MC* films on the corresponding semiconductor substrates.

We have also performed calculations for several further binary *MX* ($M=\text{Ca, Sr, and Ba}$; $X=\text{Si and Ge}$) compounds in the ZB structure. The general picture is similar to that for the *MC* compounds discussed above.³⁵ No improvement of the half-metallic characteristics compared to the *MC* systems is obtained.

D. Exchange interactions and Curie temperature

In addition to high spin polarization of the states at the Fermi level, an important further condition for spintronics materials is a high Curie temperature. Only systems with the Curie temperature exceeding substantially room temperature can be considered for wide device applications. To estimate the Curie temperatures for half-metallic CaC, SrC, and BaC with the ZB structure, we first apply the ASW method in conjunction with the frozen-magnon approach to calculate the interatomic exchange interactions. These calculations are performed for equilibrium lattice constants. The computed carbon-carbon exchange parameters are presented in Table II. The *C-M* ($M=\text{Ca, Sr, Ba}$) exchange interactions are very

TABLE II. Calculated carbon-carbon exchange parameters and Curie temperatures within the MFA and RPA. J_i ($i=1,2,3,4$) represents the exchange parameters from the first to the fourth nearest neighborhood.

Compound	J_1 (mRy)	J_2 (mRy)	J_3 (mRy)	J_4 (mRy)	T_C^{MFA} (K)	T_C^{RPA} (K)
CaC	0.906	-0.020	-0.020	-0.026	1051	735
SrC	0.776	-0.056	-0.010	-0.008	910	652
BaC	0.548	-0.108	0.005	0.008	643	471

weak and are not presented. As seen from Table II, the leading interaction is a large ferromagnetic coupling between the nearest C atoms. In CaC, this coupling is the strongest of the three compounds and is about twice the corresponding coupling in BaC. A similar situation is found in the ZB half-metallic compounds containing *3d* transition-metal atoms.²⁸

The calculated exchange parameters are used to estimate the Curie temperature of the systems within both the MFA and the RPA (Table II). The values of the Curie temperature reflect the properties of the exchange interactions discussed above. For all three systems and for both theoretical schemes (MFA and RPA), the calculated Curie temperatures are substantially higher than room temperature. The MFA always gives a value of the Curie temperature that is larger than the corresponding RPA value, and usually overestimates the experimental Curie temperature. As shown in Refs. 29 and 36, this relation reflects the property that the MFA expression for the Curie temperature corresponds to an equal weighting of the low- and high-energy spin-wave excitations. A better weighting of the magnetic excitations is provided by the RPA, where lower-energy excitations make a larger contribution. Therefore, the RPA is expected to provide a better estimation of the Curie temperature.

Finally, we point out that the calculations reported in this paper are based on the GGA for the exchange-correlation potential. Recent studies of Heusler compounds containing *3d* atoms have shown that taking account of electronic correlations beyond the GGA or local density approximation (LDA) can be important. For instance, the application of the LDA + dynamic mean field theory³⁷ (DMFT) scheme to NiMnSb,³⁸ CrAs,³⁹ and other cases⁴⁰ changes the electronic structure significantly since nonquasiparticle states show up in the gap region. Chioncel *et al.*⁴¹ found that VAs in the ZB structure is a ferromagnetic semiconductor within the GGA scheme but a ferromagnetic half metal within the LDA + DMFT scheme. For the HM ferromagnets CaC, SrC, and BaC studied in this paper, the effect of correlations might be expected to be less important since the magnetic properties are governed by *p* electrons which experience fewer correlations than *d* electrons. Still, LDA + DMFT study of half-metallic ferromagnets without transition-metal elements remains an interesting theoretical problem for future research.

IV. CONCLUSIONS

In summary, we have used the FPLAPW method based on density functional theory to investigate the electronic struc-

ture and ferromagnetism of the hypothetical ZB MC ($M = \text{Mg, Ca, Sr, and Ba}$). HM ferromagnetism is predicted for ZB CaC, SrC, and BaC. These systems have large HM gaps (up to 0.83 eV) and their half metallicities can be maintained for lattice constants compression up to 14%, 13%, and 9%, respectively, for CaC, SrC, and BaC. The MFA and RPA are used to estimate the Curie temperatures of CaC, SrC, and BaC. For all three HM compounds and for both theoretical schemes (MFA and RPA), the calculated Curie temperatures are considerably higher than room temperature. The large HM gaps, the robust stability of the half metallicity with respect to the lattice contraction, the small mismatch of lattice constants between the predicted HM compounds and

some zinc-blende semiconductors, and the high Curie temperatures make CaC, SrC, and BaC promising candidates for successful spintronics applications. We hope that the present work will stimulate experimental efforts toward fabrication and study of ZB MC films.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China under Grants No. 10574048 and No. 20490210. This work was also supported by the China 973 plan under Grant No. 2006CB921605. We also acknowledge valuable discussions with Y. S. Zhang, L. Zhu, and Y. L. Li.

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