Conventional magnetism occurs in systems which contain transition metals or rare earth ions with partially filled $d$ or $f$ shells. It is theoretically predicted that compounds of groups IIA and IVA with IV and V, in some structural phases, are ferromagnetic half-metals which made them new candidates for spintronics applications. Employing density functional theory (DFT) we investigate magnetism in binary compounds CaN and CaAs. Regarding the prediction of analogous magnetic materials and experimental results of CaAs synthesis, we have considered two cubic structures: rocksalt (RS) and zincblende (ZB), and four hexagonal structures: NiAs, wurtzite (WZ), anti-NiAs, and NaO. The calculated results show that CaN in cubic, NiAs, and wurtzite structures, and CaAs only in zincblende phase have ferromagnetic ground states with a magnetic moment of $1 \mu_B$. Electronic structure analysis of these materials indicates that magnetism originates from anion $p$ states. Existence of flat $p$ bands and consequently high density of states at the Fermi level of magnetic structures gives rise to Stoner spin splitting and spontaneous ferromagnetism.

I. INTRODUCTION

Half-metallic ferromagnetism, which involves metallic conductivity only in one spin channel, has played a significant role in spintronics. Its first-principles introduction by de Groot et al. [1] raised enthusiasm among the community to explore this property within materials. For them, several reports have been published regarding the prediction and/or observation of a half-metallic electronic structure in different materials including metallic oxides [2–8], full and half Heusler alloys [4–7], and diluted magnetic semiconductors [8–10]. In spite of several half-metallic compounds appeared in the literature, the search for novel ferromagnetic half-metals is an active research area. In this context, a significant attention is attracted to the transition metal pnictides and chalcogenides with zincblende (ZB) structure [11–15]. Although, many of transition metal compounds exhibit half-metallic property in the ZB structure, these materials crystallize in a different crystal structure including hexagonal NiAs or orthorhombic structures; hence realization of their half-metallic behavior requires special requirement for synthesis of metastable ZB structure. It is claimed that the ZB structure MnAs [10], CrAs [17], and CrSb [18] have been successfully synthesized in the form of thin films.

In 2004 Kusakabe et al. [19] showed that calcium pnictides in the ZB structure, in absence of any transition metal element, exhibit half-metal ferromagnetism. These compounds expose an unconventional type of ferromagnetism where the spin polarization is induced by ionicity and a slight hybridization of anion $p$ orbitals and $d$ states. Later on, Sieberer et al. [20] and Volnianska et al. [21] studied ferromagnetism in the binary compounds of $1^A/II^A, V$ elements in tetrahedrally and octahedrally coordinated structures. They argued that half-metallic ferromagnetism originates from the flat band magnetism of holes and may occur in more structures including RS and NiAs. It was explained that large cell volume, high ionicity and a slight hybridization of anion $p$ orbitals and induced $d$ states around the Fermi level effectively enhance formation of ferromagnetic (FM) state in the system.

Our specific aims in this work is to apply accurate first-principles electronic calculations to investigate magnetic properties and structural stability of two members of binary $p$ magnetic compounds (CaN and CaAs) in six different structures. In section III we will discuss structural and magnetic properties of CaN and CaAs. Electronic structures of these two compounds are described in section IV.

II. COMPUTATIONAL METHOD

We performed first-principles calculations based on density functional theory (DFT) using pseudopotential technique and spin-dependent generalized gradient approximation (GGA) in the scheme of Perdew, Burke, and Ernzerhof by means of QUANTUM ESPRESSO package [22]. The relativistic effects are taken into account in the scalar limit, neglecting the spin-orbit coupling which is expected to be small in light atoms like Ca, N, and As. Using conventional GGA calculations of electronic and magnetic properties of materials which do not consist of atoms with inner $d$ or $f$ electrons are thought to be accurate and give reliable results. We used ultrasoft pseudopotentials [24], a kinetic energy cut off of 35 Ryd for the plane wave expansion of Kohn-Sham orbitals, and a kinetic energy cut off of 400 Ry for the Fourier expansion of electron density. The Brillouin-zone integra-
TABLE I: Computed spin polarization energies $\Delta E_{FM,NM}^{FM,NM}$ (meV/\text{fu}), lattice parameters (\AA), and bulk moduli (GPa) for CaN and CaAs in six studied structures. For hexagonal structures, the lattice parameter $c/a$ is given below the first lattice parameter.

|                  | RS | ZB | NiAs | WZ | AsNi | NaO |
|------------------|----|----|------|----|------|-----|
| $\Delta E_{FM,NM}^{FM,NM}$ |    |    |      |    |      |     |
| CaN              | -102 | -214 | -177 | -124 | 0 | 0 |
| CaAs             | 0 | -110 | 0 | 0 | 0 | 0 |

Equilibrium lattice parameters

|                  | CaN | CaAs |
|------------------|-----|------|
| $a$              | 5.00 | 6.00 |
| $c$              | 5.45 | 6.73 |
| $b$              | 3.39 | 3.88 |
| $a/c$            | 1.88 | 2.10 |
| $b/c$            | 1.18 | 2.22 |
| $b/a$            | 1.34 | 2.16 |
| $c/a$            | 0.77 | 0.75 |

Bulk modulus

|                  | CaN | CaAs |
|------------------|-----|------|
| $B$              | 78.4 | 40.9 |
| $B$              | 55.4 | 24.9 |
| $B$              | 79.8 | 39.3 |
| $B$              | 62.3 | 30.5 |
| $B$              | 86.9 | 41.4 |
| $B$              | 92.1 | 49.4 |

tions were performed using a Monkhorst-Pack mesh of $12 \times 12 \times 12$ k points for cubic structures and equivalent meshes for hexagonal structures. Atomic relaxation of the structures with internal parameters was accurately performed to achieve residual forces less than 0.01 mRy/Bohr and energy accuracy of better than 0.001 mRy/\text{fu} (formula unit).

III. STRUCTURAL AND MAGNETIC PROPERTIES

In this work, we take into account six different structures for binary CaN and CaAs compounds: ZB, wurtzite (WZ), rock-salt (RS), hexagonal NiAs, hexagonal anti-NiAs (AsNi), and NaO structures. The tetracoordinated cubic ZB structure is important because several binary compound exhibit half-metallic ferromagnetism in this structure. The fact that many binary semiconductors crystallize in the ZB structure increases the importance of study of this structure for binary half-metals, because these half-metals are expected to be ideal ferromagnetic sources for spin injection into semiconductors. Also the tetracoordinated WZ structure is the hexagonal analogous of the cubic ZB structure and hence is included in our study. The significant electronegativity differences in Ca-N (2.0 Pauling) and Ca-As (1.0 Pauling) pairs shows the significant contribution of ionic bonding in CaN and CaAs and hence these compounds may favor a higher coordination atomic arrangement to reduce their total energy. Therefore, the hexacoordinated cubic RS structure is also considered in this work. Recently Liu et al. have claimed that they have grown a layer of RS-CaN on Cu(0 0 1) by means of a new unclear self-assembly mechanism. Since some of magnetic transition metal pnictides (II$^{TM}$-V compounds) crystallize in the hexagonal NiAs structure, both NiAs and AsNi (anti-NiAs) structures were considered for CaN and CaAs. The natural crystal structure of CaAs seems to be a NaO type lattice, which is derived from the AsNi structure, by a 30$^\circ$ rotation clockwise around the z axis, followed by a shift of [0, 0, 0.25] in the z direction, and finally an increase of the $a$ and $b$ cell parameters by a factor of $\sqrt{3}$.

The difference between the minimized total energies of the FM and non-magnetic (NM) states, $\Delta E_{FM,NM}^{FM,NM}$, of CaN and CaAs in all considered structures are presented in table I. To find the minimized total energies, we have optimized lattice constants of all structures and atomic positions of the low symmetry NaO structure. The negative values indicate more stability of the FM phase. It is seen that CaN has a FM ground state and non-vanishing magnetic moment in the RS, ZB, NiAs, and WZ structures while the FM behavior of CaAs is limited to the only ZB structure. Both compounds are NM in the NaO phase. Regardless of the crystal structure, in all magnetic ground states, the total magnetic moment per chemical formula unit is 1 $\mu_B$. In contrast to the transition metal pnictides, the small cation spin moment in the magnetic structures of CaN and CaAs is parallel to anion moment which may be explained by the model of covalent polarization. Furthermore, table II lists the equilibrium lattice parameter and bulk modulus for both compounds. It is generally seen that magnetic structures, compared with the nonmagnetic systems, have higher volume and lower bulk modulus. As it was mentioned in the introduction, a large cell volume enhances spin polarization of binary $p$ magnetic materials.
The calculated total energies in different volumes for CaN and CaAs are plotted in figure 1. According to the figure, the structures with hexacoordinated anions are energetically more favorable. These structures have smaller cell volumes and higher bulk moduli, indicating that their bonds are stronger due to the smaller interaction distances. The ZB structure has the highest total energy and the experimentally observed structure for CaAs, NaO, with a difference of about 0.1 Ry/fu is the most favorable one for both compounds. The calculated equilibrium lattice constants of NaO structure for CaAs are 14.93 and 11.15 Bohr for a and c, respectively, which is in good agreement with the experimentally found values of 14.85 and 11.19 Bohr. The comparison of the ZB and WZ structures shows that the hexagonal arrangement gives rise to lower energy for both compounds.

IV. ELECTRONIC STRUCTURE

In this section, the detailed investigation of the electronic structure of all considered crystal structures is presented, and the essence of ferromagnetism in these materials is discussed by analyzing their electronic structure. According to a previous study [21], in agreement with ours, for Ca pnictides (CaN, CaP, CaAs, CaSb) in the ZB phase, the energy of spin polarization is the largest for CaN and decreases with the increase in atomic number of the anion, and almost vanishes for CaSb. Therefore, anions should have an important contribution in governing magnetization in these compounds. For better understanding, we calculated free atom energies in the spin unpolarized and polarized states and found that the spin polarization energy of a free N atom (-3.32 eV) is significantly higher than a free As atom (-1.58 eV). This observation may explain stability of FM state in more structures for CaN, compared with CaAs.

In Fig 2, the spin resolved total density of states (DOS) of the systems are presented. It is seen that the crystal field splitting between bonding and antibonding states is more pronounced in the tetra coordinated ZB and WZ structures, compared with other systems. The magnetic structures including NiAs, WZ, ZB, and RS structure of CaN and ZB structure of CaAs obviously exhibit half-metallic property, as in their majority spin channel there is an energy gap around the Fermi level while their minority spin bands cut the Fermi level. This is different from the half-metallic transition metal pnictides and chalcogenides, where their majority spin channel is metallic and the half-metallic gap appears in their minority spin channel. The spin flip gap, the distance between the majority valence band maximum and the Fermi level, measures the minimum required energy for creating a majority spin carrier at the top of the majority valence band. Hence, systems with larger spin flip gap are expected to be better source of fully spin polarized current. Among the studied systems, the largest spin flip gap (0.8 eV) is observed in the ZB-CaN.

It has been argued [29] that the half-metallicity in the ZB structure is mainly caused by the local bonding environment. These alkaline pnictides involve seven valence electrons per formula unit. Since the anion s states are the lowest energy valence states, they must be occupied by two electrons, and the rest five electron occupy the anion p states which can accommodate six electrons. Because of spin splitting, the majority p states lie lower in energy than the minority p states, so the majority spin p bands are fulfilled by three electrons and the minority spin p bands are partially filled. As a result of the hole
The inter-metallic CaN and CaAs compounds are made of a strong cationic metal and weak anionic elements, which are known as the Zintle phase. The Zintle phases stand somewhere in-between metallic and ionic compounds. In Zintle phases anions do not reach the stable octet state as isolated species, and hence they need additional bonds to become more stable. Therefore, in these compounds the anion atoms usually connect covalently together and form dimers. Formation of anion dimers in the Zintle phases, electronically balances the system and leads to closed-shell compounds, i.e. the number of electrons provided by the constituting elements equals the number of electrons needed for covalent bonding in the structure.

The spin-dependent band structures along high symmetry lines in the Brillouin zone for the best half-metallic structure (ZB) and the most stable structure (NaO) are given in Fig 3. We know that the anion p states are localized around the nuclei and hence the valence bands are flat and low dispersed. The anion atoms and according to DOS profiles the hybridization between the anion p states and the Ca d states is weak. reflecting the weak polarized-covalent bonds of the anions p orbitals and Ca d states.

V. CONCLUSION

Conventional magnetism occurs in systems which contain transition metals or rare earth ions with partially filled d or f shells. Recent experimental and/or theoretical observations of magnetism in systems with no valence d or f electron challenge our classical understanding of magnetism. It is theoretically predicted that compounds of groups IA and IIA with IV and V, in some structural phases are ferromagnetic half-metals which made them new candidates for spintronics applications. Employing density functional theory (DFT) we investigate magnetism in binary compounds CaN and CaAs. Regarding the structure of analogous magnetic materials and experimental results of CaAs synthesis, we have considered two cubic structures: rocksalt (RS) and zinc-blende (ZB), and four hexagonal structures: NiAs, wurtzite (WZ), anti-NiAs, and NaO. The calculated results show that CaN in cubic, NiAs, and wurtzite phases, and CaAs only in zincblende phase have ferromagnetic ground states with a magnetic moment of 1 \( \mu_B \). Electronic structure analysis of these materials indicates that magnetism originates from anion p states. Existence of flat p bands and consequently high density of states at the Fermi level of magnetic structures gives rise to Stoner spin splitting and spontaneous ferromagnetism. Larger hybridization will be strengthened and the valence bands characterized by p states are expanded which would reduce the spin flip gap. When the lattice constants are compressed to smaller than the critical value, the expanded majority p-character bands would cut the Fermi level and the half-metallicity is destroyed.
exchange interaction in $2p$ orbitals of nitrogen respect to $4p$ orbitals of arsenic causes that CaN has more structures with ferromagnetic ground state than CaAs. Slight hybridization with calcium $d$ states increase density of $p$ states at the Fermi level and enhance ferromagnetism in the system.

[1] R. A. de Groot, F. M. Mueller, P. G. v. Engen, and K. H. J. Buschow, Phys. Rev. Lett. 50, 2024 (1983).
[2] F. J. Jedema, A. T. Filip, and B. J. van Wees, Nature 410, 345 (2001).
[3] S. P. Lewis, P. B. Allen, and T. Sasaki, Phys. Rev. B 55, 10253 (1997).
[4] C. Borca, T. Komesu, H.-K. Jeong, P. Dowben, D. Ristoiu, C. Hordequin, J. Pierre, and J. Nozières, Applied Physics Letters 77, 88 (2000), cited By (since 1996) 38.
[5] T. Ambrose, J. Krebs, and G. Prinz, Applied Physics Letters 76, 3280 (2000), cited By (since 1996) 0.
[6] I. Galanakis, P. Dederichs, and N. Papanikolaou, Physical Review B - Condensed Matter and Materials Physics 66, 1744291 (2002), cited By (since 1996) 0.
[7] S. Fujii, S. Sugimura, Ishida, and S. Asano, Journal of Physics: Condensed Matter 2, 8583 (1990).
[8] H. Akai, Phys. Rev. Lett. 81, 3002 (1998).
[9] T. Ogawa, M. Shirai, N. Suzuki, and I. Kitagawa, Journal of Magnetism and Magnetic Materials 196197, 428 (1999), ISSN 0304-8853.
[10] K. Yao, G. Gao, Z. Liu, L. Zhu, and Y. Li, Physica B: Condensed Matter 366, 62 (2005), ISSN 0921-4526.
[11] B. Sanyal, L. Bergqvist, and O. Eriksson, Phys. Rev. B 68, 054417 (2003).
[12] K. Yao, G. Gao, Z. Liu, and L. Zhu, Solid State Communications 133, 301 (2005), ISSN 0038-1098.
[13] I. Galanakis and P. Mavropoulos, Phys. Rev. B 67, 104417 (2003).
[14] W.-H. Xie, Y.-Q. Xu, B.-G. Liu, and D. G. Pettifor, Phys. Rev. Lett. 91, 037204 (2003).
[15] Y.-Q. Xu, B.-G. Liu, and D. G. Pettifor, Phys. Rev. B 66, 184435 (2002).
[16] T. Kim, H. Jeon, T. Kang, J. Lee, H.S. nad Lee, and S. Jin, Applied Physics Letters 88, 1 (2006), cited By (since 1996) 34.
[17] M. Mizuguchi, H. Akinaga, T. Manago, M. Ono, K. nad Oshima, M. Shirai, M. Yuri, H. Lin, H. Hsieh, and C. Chen, Journal of Applied Physics 91, 7917 (2002), cited By (since 1996) 63.
[18] J. Zhao, F. Matsukura, K. Takamura, E. Abe, D. Chiba, and H. Ohno, Applied Physics Letters 79, 2776 (2001), cited By (since 1996) 134.
[19] K. Kusakabe, M. Geshi, H. Tsukamoto, and N. Suzuki, Journal of Physics: Condensed Matter 16, S5639 (2004).
[20] M. Sieberer, J. Redinger, S. Khmelevskiy, and P. Mohn, Phys. Rev. B 73, 024404 (2006).
[21] O. Volnianska and P. Boguslawski, Phys. Rev. B 75, 224418 (2007).
[22] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996), URL http://link.aps.org/doi/10.1103/PhysRevLett.77.3865.
[23] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, et al., Journal of Physics: Condensed Matter 21, 395502 (19pp) (2009), URL http://www.quantum-espresso.org.
[24] G. Kresse and D. Joubert, Phys. Rev. B 59, 1758 (1999), URL http://link.aps.org/doi/10.1103/PhysRevB.59.1758.
[25] M. Winter, Webelements periodic table of the elements, https://www.webelements.com.
[26] X. Liu, B. Lu, T. Imori, K. Nakatsuji, and F. Komori, Surface Science 602, 1844 (2008), ISSN 0039-6028.
[27] A. Iandelli and E. Franceschi, Journal of the Less Common Metals 30, 211 (1973), ISSN 0022-5088.
[28] J. R. Lalanne and R. Boisgard, Electronic Structure and Chemical Bonding (World Scientific, 1996).
[29] M. Geshi, K. Kusakabe, H. Tsukamoto, and N. Suzuki (2004), 0402641.