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# Synthetic ferromagnetic nitrides: First-principles calculations of CaN and SrN

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Encouraged by recent experimental facts of synthesizing materials which do not exist in nature, we introduce a type of ferromagnets, CaN and SrN, which have been proposed by first-principles calculations. These are half-metallic ferromagnets and they have magnetic moments of  $1\mu_B$  per chemical formula unit. Out of typical structures of binary compounds we have calculated, the rocksalt structure is the most stable form for both CaN and SrN. The majority of the magnetic moment of these compounds originates from the nitrogen sites since the  $p$  states of nitrogen are spin polarized. The mechanism of the ferromagnetism is discussed. Their formation energies have been calculated and the results show that it should be feasible to synthesize these materials. The structural stability of CaN has been confirmed by performing first-principles molecular dynamics simulations. We propose a synthesis process for CaN using the high pressure and temperature environment.

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## I. INTRODUCTION

Synthesis of substances which do not exist in nature have an enormous potential to obtain materials having excellent properties. Recent experimental reports of syntheses of PtN,<sup>1</sup> PtN<sub>2</sub>, IrN<sub>2</sub>,<sup>2</sup> PtC,<sup>3,4</sup> Hf<sub>3</sub>N<sub>4</sub>, and Zr<sub>3</sub>N<sub>4</sub> (Ref. 5) demonstrate that it is possible to synthesize materials using special experimental techniques. These materials are synthesized in the high pressure and high temperature conditions. Based on these experimental facts, theoretical calculations were performed to investigate electronic structures and elastic properties because these material are expected to be hard materials.<sup>6-12</sup>

In this study, we focus on nitride compounds and their magnetic properties, which is different from the above works. It is well known that nitrides prefer ferromagnetic (FM) states. For example, most of the rare earth nitrides become FM<sup>13</sup> and crystallize in a rocksalt (RS) structure. These facts encourage us to consider replacing the rare earth elements with Ca and Sr since their ionic radii are close to those of the rare earth ions, and from our previous results we confirmed that Ca and Sr pnictides become FM.<sup>14,15</sup> Such replacement is natural in view of the Zintl phase.<sup>16</sup> There is a probability of being able to synthesize RS-CaN and RS-SrN if appropriate experimental techniques are employed.

Many predictions of electronic and magnetic properties have been made<sup>17-20</sup> based on density functional theory (DFT)<sup>21</sup> using the local spin density approximation (LSDA) or a spin-dependent generalized gradient approximation (spin-GGA), and these predictions have been experimentally confirmed.<sup>22-27</sup> Spin-GGA calculations of electronic structures and magnetic properties of materials which consist of atoms having only  $s$  and  $p$  electrons are thought to be the most reliable and give satisfactory results.

## II. COMPUTATIONAL DETAILS

We performed first-principles calculations based on DFT using the LSDA or the spin-GGA for RS-CaN and RS-SrN by means of typical DFT codes.<sup>28,29</sup> The total energies of some structures and each magnetic state and detailed elec-

tronic structures [e.g., densities of states (DOSs) and magnetic moments] were calculated by the APW+lo method.<sup>28</sup> The value of  $R_{MT}K_{max}$  was fixed at 8.00, where  $R_{MT}$  is the minimum muffin-tin (MT) radius and  $K_{max}$  is the maximum reciprocal lattice vector. The MT radii of Ca and Sr ( $MT_{Ca(Sr)}$ ) are  $0.22a$ ,  $0.27a$ , and  $0.45a$  for the zinc-blende (ZB), RS, and CsCl structures, respectively, where  $a$  is the lattice constant. The MT radii of N ( $MT_N$ ) are set at  $0.18a$ ,  $0.221a$ , and  $0.3681a$  for the ZB, RS, and CsCl structures, respectively. For the wurtzite (WZ) structure  $MT_{Ca(Sr)}$  and  $MT_N$  are set at fixed values for each volume. The ratio of  $MT_{Ca(Sr)}$  to  $MT_N$  is 1.3:1 and the sum of both MT radii is about 95% of the nearest neighbor atomic distances. The number of the basis functions has been changed according to the  $K_{max}$  values. We have compared our results of the above conditions with those of fixed MT sphere ( $MT_{Ca}=2.5$  a.u. and  $MT_N=1.9$  a.u.), and confirmed that the change of the MT spheres does not essentially affect the results. We used an angular momentum expansion up to  $l_{max}=10$ . The energy convergence criterion was set at 0.001 mRy. Twenty  $k$  points were taken in the irreducible Brillouin zone. To confirm magnetism in the four types of structures, we performed calculations which employed ten times larger  $k$ -point sampling in the irreducible zone. By this we were able to confirm the existence of magnetic states. We used the ESPRESSO code<sup>29</sup> also to perform first-principles molecular dynamics simulations and to check the magnetism of RS-CaN. The energy cutoff of plane waves was set at 80 Ry. The  $k$ -point meshes of  $8 \times 8 \times 8$  were used for the first Brillouin zone integration.

## III. RESULTS AND DISCUSSION

In Figs. 1(a) and 1(b), the total energies of CaN and SrN are plotted as functions of volume per chemical formula unit. We have chosen the RS structure along with the other typical structures of binary compounds, namely, ZB, WZ, and CsCl structures. The lowest energy structure is the RS structure, while the WZ structure is the second lowest. The WZ structure was optimized with respect to both  $c/a$  and the internal parameter. We checked the stabilities against tetragonal dis-

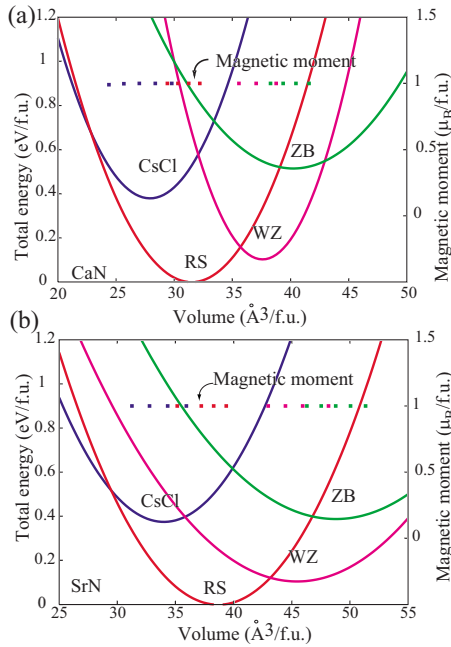


FIG. 1. (Color online) Total energies and magnetic moments of (a) CaN and (b) SrN are plotted as functions of volume. The origin of the total energy has been shifted to the energy minimum point of the rocksalt structure. The magnetic moment per chemical formula unit is shown on the right vertical axis.

tortion for the RS and CsCl structures and confirmed the stability. In addition, we confirmed the stability of the cubic structure of the RS-CaN by the first-principles molecular dynamics simulations described below. In the ZB-type structure, on the contrary, tetragonal distortion reduces the total energy of the ZB structure, which is similar to CaAs in the ZB structure.<sup>15</sup> Among tetragonal distortions,  $c/a=1.0$  is located at the maximum energy point and  $c/a=0.6$  is at the minimum energy point. The energy difference between the maximum and the minimum points is about 0.13 eV/f.u. for CaN and 0.06 eV/f.u. for SrN, respectively.

All of the four structures used in the calculations for CaN and SrN are of half metal as well as FM in spite of not containing any transition or rare earth metals. In other words, CaN and SrN are FM without having any  $d$  or  $f$  electrons. The magnetic moments are plotted in Figs. 1(a) and 1(b). The calculated magnetic moments for both CaN and SrN are  $1\mu_B$ , which is evidence of their half metallicity. The DOSs of RS-CaN are shown in Fig. 2. The total DOS indicates completely spin-polarized electronic states at the Fermi level.

All of these CaN and SrN are half metallic, and hence the magnetic moment is independent of the volume in the range

TABLE I. The magnetic moment of CaN. In units of  $\mu_B$ .

Structure	RS	ZB	CsCl	WZ
Total	1.000	1.000	1.000	1.000
Ca	0.038	0.038	0.033	0.024
N	0.794	0.787	0.822	0.590
Interstitial	0.168	0.175	0.145	0.386

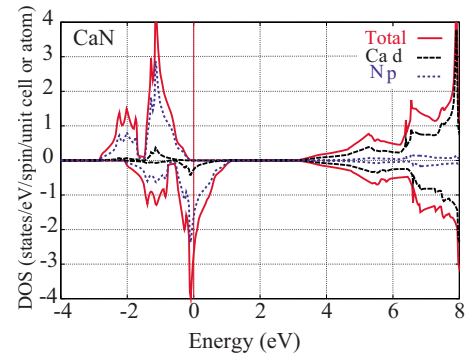


FIG. 2. (Color online) The DOSs of RS-CaN. The partial DOS is calculated within the muffin-tin sphere used in the band calculations.

we calculated as shown in Fig. 1, while the magnetic moments of Ca(P,As,Sb) and Sr(P,As,Sb) depend on lattice constants or volumes as well as on structure.<sup>15</sup> The partial DOSs indicate that the main component at the Fermi level consists of  $p$  states of N. As expected, the majority of the magnetic moment resides on the N atom as shown in Table I. The magnetic moment at the Ca or Sr sites is quite small being less than that of the interstitial region.

We show in Fig. 3 the differences in the total energies for the FM, antiferromagnetic (AFM), and nonmagnetic (NM) states for RS-CaN using four times larger unit cell than the primitive cell. The symmetry of this unit cell takes tetragonal symmetry and antiferromagnetic ordering of spins is taken between the nearest neighbor layers perpendicular to  $z$  axis. The energy difference between the FM and AFM states for RS-CaN is more than 0.05 eV/f.u., while that for RS-SrN is about 0.028 eV/f.u.

We discuss the origin of ferromagnetism of CaN. From the calculated charge distribution of RS-CaN the number of charges in the interstitial region is estimated to be about two. By counting the number of charges in each MT sphere most of the charges in the interstitial region come from the Ca atom in spite of the larger MT sphere of the Ca atom than that of the N atom.

Based on the above result, we have calculated fcc N with two additional electrons as another hypothetical model sys-

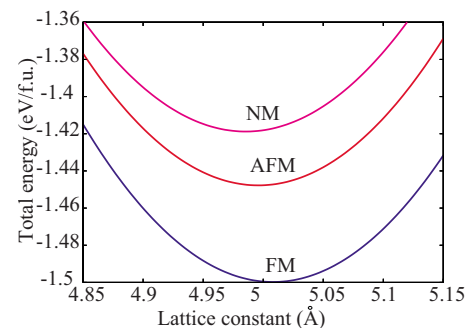


FIG. 3. (Color online) Total energies as functions of the lattice constant are compared for the ferromagnetic (FM), antiferromagnetic (AFM), and nonmagnetic (NM) states of CaN, where RS structure is assumed.

tem. In this calculation uniform background charges are added to satisfy charge neutrality. It is confirmed that the band structure near the Fermi level of the fcc N is very similar to that of CaN. This fcc N system becomes FM, not AFM. The magnetic moment is  $1\mu_B$ /f.u. The results of the CaN can deny a possibility of ferrimagnetism between the spins of Ca and N atom due to the quite small magnetic moment of the Ca atom and the result of fcc N. We consider that the essence of the magnetic properties of RS-CaN is extracted in the fcc N.

We note that we have studied a hypothetical model crystal which is obtained by removing Ca atom from the RS-CaN lattice and the electrons consisting of  $p$  orbitals align their spins in the same direction. It is considered that this result is equal to align the spins in the same direction by Hund coupling and the local spin moment is  $3\mu_B$  per N atom in this calculation.

If we assume a reduced symmetry of the fcc as we calculated RS-CaN, then we can calculate the AFM state between the nearest neighbor layers. The FM state takes lower energy than the AFM. The energy differences between FM and AFM states at the equilibrium lattice constant of RS-CaN (5.02 Å) and RS-SrN (5.37 Å) are 0.115 eV per N atom and 0.114 eV per N atom, respectively.

It is considered that a role of Ca atom is to provide two electrons for fcc N. The lattice constants of RS-CaN and the other structures are governed by its ionic potential. The equilibrium lattice constants of CaN in our calculated structures are appropriate for the localization of wave functions. With decreasing lattice constant the magnetic moment decreases and finally vanishes. However, from the fact that the spins hardly exist on Ca atom and the band dispersion of fcc N is essentially similar to CaN, it is not considered that Ca atom directly contributes to the electronic structure of CaN.

The result of the hypothetical fcc N lattice implies that there is an expected FM interaction between N atoms. At least it is difficult to explain this result without spin alignment originated from Hund coupling. Since the lattice is the fcc and the  $p$  bands are triply degenerated, the situation in the case of RS-CaN is the same as that of fcc N. It is considered that each site is  $5/6$  filled by electrons. This is the same as  $1/6$  filled by holes. We can consider an analogy between these results and the discussion of Slater *et al.*<sup>30</sup> or Kanamori<sup>31</sup> because these theories are correct when the number of electrons or holes on each site is quite lower than unity. The degeneracy of the band depends on the symmetry of the system. Once RS-CaN is formed, the RS structure is kept within our calculation as described later. The FM state is the resultant property of RS-CaN. In the case of CsCl and WZ, they have degenerated bands. The mechanism of ferromagnetism of CsCl and WZ-CaN is considered the same as that of RS-CaN. It is considered that these systems are completely  $p$ -electron ferromagnets.

We further confirmed the structural stability of CaN having the RS structure by using first-principles molecular dynamics simulations. The simulations have been performed starting from the cubic unit cell, which contains eight atoms and is four times larger than the primitive cell, as the starting cell. We have not assumed any space group for the atomic positions, that is, we assume  $P1$  space group. We have per-

formed two types of molecular dynamics simulations: (1) a first-principles damped dynamics simulation using a variable cell, and (2) a first-principles constant-pressure and temperature molecular dynamics simulation using the Parrinello-Rahman method, where we have used the velocity scaling method to control the temperature. The purpose of simulation (1) is to confirm whether the RS structure is at least metastable with respect to changes in the internal atomic positions and in the shape of the unit cell, while the purpose of simulation (2) is to confirm the stability of the RS structure at finite temperature and ambient pressure. From the simulation (1) we have confirmed that atomic forces become negligibly small (less than  $1.0 \times 10^{-4}$  Ry/a.u.) and that atomic positions in the RS structure are at least metastable. From simulation (2) we have confirmed that the RS structure is stable at ambient pressure and finite temperatures (130, 210, and 800 K). These results support the possibility that CaN having the RS structure would be stable once it can be synthesized.

We have estimated the formation energy defined by  $E_{\text{formation}} = E_{\text{tot}} - (E_{\text{Ca(Sr)}} + E_{\text{N}_2}/2)$  for the RS, ZB, WZ, and CsCl structures.  $E_{\text{Ca(Sr)}}$  is the total energy of the bulk Ca (Sr) per atom at ambient pressure which we have evaluated using the fcc structure.  $E_{\text{N}_2}$  denotes the total energy of an isolated N<sub>2</sub> molecule. The energy of the molecule is evaluated using a large unit cell ( $a=18$  Å, for an fcc cell containing one molecule). The calculated formation energies are -11.2 eV (RS), -10.7 eV (ZB), -11.1 eV (WZ), and -10.8 eV (CsCl) for CaN, and -10.8 eV (RS), -10.5 eV (ZB), -10.8 eV (WZ), and -10.5 eV (CsCl) for SrN, respectively. These results suggest that CaN and SrN having the four structures investigated will not decompose once they have been formed. In these structures, the formation energy of the RS is lower than that of the other structures for both CaN and SrN.

We now proceed to propose ideas for how CaN and SrN can be synthesized in the laboratory. In this paper, we only consider RS-CaN. Firstly, we enumerate known experimental facts. Under normal conditions, Ca and N usually form Ca<sub>3</sub>N<sub>2</sub> in the  $Ia\bar{3}(\alpha\text{-Ca}_3\text{N}_2)$  structure. This structure is transformed to  $\beta\text{-Ca}_3\text{N}_2$  whose structure is  $P\bar{3}m1$ ,<sup>32</sup> when the temperature is increased. The transition temperature does not seem to be determined experimentally. We compare volumes of both phases at ambient pressure. The volume of  $\beta\text{-Ca}_3\text{N}_2$  is smaller than that of  $\alpha\text{-Ca}_3\text{N}_2$ .<sup>32</sup> It is considered that  $\beta\text{-Ca}_3\text{N}_2$  is a high pressure phase of  $\alpha\text{-Ca}_3\text{N}_2$  as well as high temperature phase.

Secondly, we enumerate results of first-principles calculations. We neglect the effect of entropy as the first step since it is difficult to obtain entropy, and investigate enthalpy. The enthalpy is plotted as functions of pressure in Fig. 4. We show the enthalpy of  $\beta\text{-Ca}_3\text{N}_2$  and that of the sum of the two resultant substances,  $2\text{CaN} + \text{Ca}$ . We assume the structures of Ca as an fcc, bcc, or sc. As the pressure is increased, the structure of Ca is transformed from the fcc into bcc (at 20 GPa) and into sc (at 32 GPa) according to high pressure experiments.<sup>33</sup> The enthalpy of  $2\text{CaN} + \text{Ca(sc)}$  becomes lower than that of  $\beta\text{-Ca}_3\text{N}_2$  at about 50 GPa. The volume of the  $\beta\text{-Ca}_3\text{N}_2$  has been optimized at each pressure. At zero

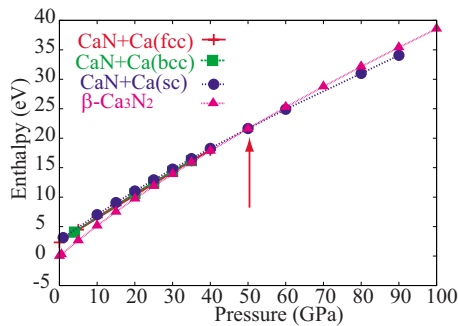


FIG. 4. (Color online) The enthalpy of  $\beta$ - $\text{Ca}_3\text{N}_2$  and the sum,  $2\text{CaN}+\text{Ca}$ , as functions of pressure. Three types of structure of Ca are assumed and plotted.

pressure we have confirmed that the volume of  $\beta$ - $\text{Ca}_3\text{N}_2$  is smaller than that of  $\alpha$ - $\text{Ca}_3\text{N}_2$ . From the experimental data and the results of our calculation, we expect the  $\beta$ - $\text{Ca}_3\text{N}_2$  as the high pressure phase as well as high temperature phase.

If we take the effect of entropy and temperature into account, then the transition pressure may shift to the high pressure side because the entropy of  $\beta$ - $\text{Ca}_3\text{N}_2$  may be considered larger than that of  $2\text{CaN}+\text{Ca}$  and the effect of  $-TS$  for  $\beta$ - $\text{Ca}_3\text{N}_2$  is also larger than that of  $2\text{CaN}+\text{Ca}$ , so that the crossing point shifts to the high pressure side. Based on the calculations of the formation energy of RS-CaN and the constant pressure and temperature first-principles molecular dynamics simulation,  $2\text{CaN}+\text{Ca}(\text{sc})$  should not decompose once it has been formed. This result strongly suggests that  $\beta$ - $\text{Ca}_3\text{N}_2$  is transformed into RS-CaN with sc Ca.

Based on the experimental facts and our calculated results, a possible method and processes suggest by themselves. It is high pressure and high temperature synthesis. One of the scenarios for the hopeful synthesis of the RS-CaN is the following: Firstly, heat  $\alpha$ - $\text{Ca}_3\text{N}_2$  until it is transformed

into  $\beta$ - $\text{Ca}_3\text{N}_2$  and then compress it using a pressure higher than 50 GPa until the reaction  $\beta$ - $\text{Ca}_3\text{N}_2 \rightarrow 2\text{CaN}+\text{Ca}$  occurs. After that, cool the product and decompress it to ambient pressure.

From the experimental point of view, we might consider  $\beta$ - $\text{Ca}_3\text{N}_2+\text{N}_2 \rightarrow 6\text{CaN}$  reaction. In this process  $\text{N}_2$  will be liquid and is used to compress  $\alpha$ - $\text{Ca}_3\text{N}_2$  hydrostatically. We have not checked the influence of pressure for that process yet.

#### IV. CONCLUSION

In conclusion, we have proposed and investigated nitrides, ferromagnetic CaN, and SrN. These are half-metallic ferromagnets as a result of the polarization of  $p$  orbitals of N. The mechanism of ferromagnetism has been discussed. The important points are the degeneracy and the localization of  $p$  orbitals. The roles of Ca atom are to provide two electrons for fcc N system and form the appropriate atomic configuration to possess the above conditions. The process for synthesizing RS-CaN using a high pressure is proposed based on the results of the first-principles calculations. The development of experimental techniques may allow us to synthesize such materials.

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