

IS A NON-TRANSITION ELEMENT NITRIDE FERROMAGNET EVER ACHIEVABLE? INDICATION OF THE N–N PAIRING INSTABILITYWojciech GROCHALA^{a,b}^a Department of Chemistry, Warsaw University, Pasteur 1, 02093 Warsaw, Poland;
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Accepted October 11, 2006*This contribution is dedicated to the memory of Jeremy K. Burdett.*

The enthalpy of four polymorphs of CaN has been scrutinized at 0 and 100 GPa using density functional theory calculations. It is shown that structures of diamagnetic calcium diazenide (Ca₂N₂) are preferred over the cubic ferromagnetic polymorph (CaN) postulated before, both at 0 and 100 GPa.

Keywords: Main group elements; Nitrides; Ferromagnetism; Density functional calculations.

Predictions of new materials with desired properties, using methods of quantum chemistry, constitutes an important branch of modern materials science. Density functional calculations enjoy particular success, as they have an excellent quality-to-resources ratio, and they have been implemented in several packages for computations of periodic systems.

In 2004, the existence of a hypothetical non-transition element ferromagnet, CaAs, has been postulated^{1,2}. This prediction has been later expanded to its low-Z pnictide derivative³, CaN. The authors have optimized CaN in a set of NaCl-, zincblende- and wurtzite-related structures and reached conclusion that CaN is most stable in the cubic Fm-3m type. In addition, they have suggested that CaN would be ferromagnetic (due to one unpaired electron per formula unit). Similar predictions have been made for the heavier congener of CaN, notably SrN³. The authors state specifically: “CaN and SrN are ferromagnetic without d or f electrons.” “If we estimate Curie temperature based on the mean field theory, it is quite high compared with room temperature. This is very attractive in the application point of view.” “Obviously, CaN and SrN are new type ferromagnets origi-

nated from p states of nitride"³. The authors have also proposed an elaborate high-pressure route to new ferromagnet, using well-known Ca_3N_2 as a starting reagent³.

The results¹⁻³ have enjoyed positive reception⁴; unfortunately, we are suspicious about these data, from the 'textbook chemistry' point of view. A formal assignment of oxidation states in calcium nitride yields $\text{Ca}^{2+}\text{N}^{2-}$; the electronic configuration of N^{2-} in the ionic picture is $2s^22p^5$ (and in agreement with calculations for CaN^3). A first-year chemistry student asked about other species exhibiting the $2s^22p^5$ configuration immediately recalls hydroxyl radical HO^\bullet , or a fluorine atom F^\bullet . Fundamental chemistry which predominates in the behaviour of these pretty unstable species is related to their dimerization.



In the equations above all electronegative species on the left side of equation (OH, F) have one hole in their (s, p) valence orbital set.

Isoelectronic with the HO^\bullet and F^\bullet is the $\text{H}_2\text{N}^\bullet$ radical, with its 7 valence electrons; obviously, this species also readily undergoes dimerization to form hydrazine.



The process described by Eq. (1c) is favoured by 2.39–3.43 eV in enthalpy, judging from various sets of thermodynamic data for gaseous species⁵. One might naturally expect that the $\text{N}^{2-\bullet}$ species (i.e. a doubly deprotonated $\text{H}_2\text{N}^\bullet$), and its salt with Ca^{2+} , i.e. CaN , will behave in the same manner.



In this contribution, guided by chemical indications described above, we deliver the theoretical evidence that ferromagnetic CaN ('radical') is thermodynamically unstable with respect to Ca_2N_2 (calcium diazenide), and that CaN cannot be formed even at pressure as high as 100 GPa.

COMPUTATIONAL

We have used CASTEP code for all calculations⁶. Our DFT calculations utilized the Perdew–Burke–Ernzerhof correlation-exchange functional, a typical cut-off of 310 eV, a k-point grid of ca. $0.035\text{--}0.045 \text{ \AA}^{-1}$ ($9 \times 9 \times 9$ grid for primitive cell of the NaCl structure with $Z = 1$, $5 \times 5 \times 6$ grid for hexagonal cell with $Z = 6$, and $3 \times 6 \times 6$ grid for orthorhombic cell with $Z = 8$), and ultrasoft Vanderbilt pseudopotentials. The convergence criterion for energy was set to 10^{-5} eV. Spin polarization was not enforced except for ferromagnetic polymorph of CaN (NaCl type). Test calculations for $p = 0$ GPa showed that the use of primitive cell of the NaCl structure results in virtually same results as for conventional cell, both for spin-polarized and non-magnetic case.

RESULTS AND DISCUSSION

Guided by deep feeling that Ca_2N_2 must be a low-energy candidate for new representation of CaN, we have considered two structures of prototypic compounds of A_2B_2 stoichiometry, where the BB bond is present (Figs 1b, 1c). Various peroxides and acetylenides, such as Na_2O_2 and Cs_2C_2 , crystallize in these important structure types⁷. To allow direct comparison, we have also recomputed CaN in the NaCl-type (Fm-3m) structure (Fig. 1a), using the same computational accuracy as for Ca_2N_2 .

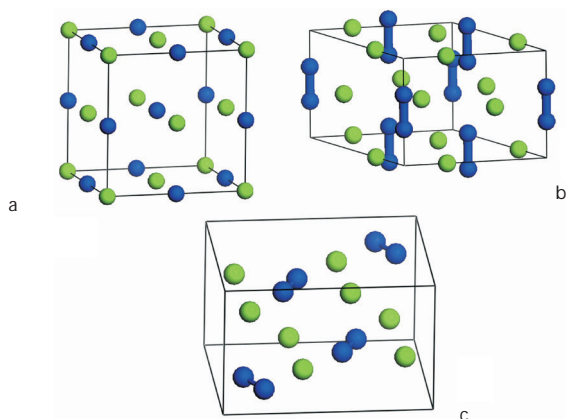


FIG. 1

The unit cells (at a pressure of 0 GPa) for three structures of CaN considered in this work. a Cubic NaCl structure (CaN may be either dia- or ferromagnetic in this structure) and two structures that might possibly be observed for Ca_2N_2 : b hexagonal and c orthorhombic. Note, single N–N bonds can be seen for b and c, Ca_2N_2 is diamagnetic

The authors¹⁻³ have neglected any structure types which allow for the N...N pairing; this is difficult to understand, especially that they have cited recent experimental results, where synthesis of diazenides of tetravalent Ir, Os and Pt has been achieved in diamond anvil cell⁸. The authors³ also mention 'Zintl phases', but since these do not guide them to Ca₂N₂ description, our surmise is that they probably use this term in another meaning than that usually adopted in solid state chemistry.

In Table I we list the optimized unit cell vectors, fractional atomic coordinates, and N-N bond lengths for the hexagonal (P62m) and orthorhombic (Pnma) polymorph of CaN considered in this work, at a pressure of 0 and 100 GPa. In Table II we show the calculated energies, *E*, enthalpies, *H*, and volumes, *V* (per one formula unit), for all polymorphs of CaN considered in this work.

TABLE I

The optimized unit cell vectors (in Å), fractional atomic coordinates and N-N bond lengths (in Å), for hexagonal and orthorhombic polymorph of CaN considered in this work. Entries are for 0 K; the results are obtained without spin polarization

P62m, 0 GPa	P62m, 100 GPa
$a = b = 6.3791; c = 4.8922$	$a = b = 5.3676; c = 4.4512$
Ca1 (0; 0.3006; 0)	Ca1 (0; 0.2763; 0)
Ca2 (0.6391; 0; 1/2)	Ca2 (0.6122; 0; 1/2)
N1 (0; 0; 0.6596)	N1 (0; 0; 0.6538)
N2 (1/3; 2/3; 0.1657)	N2 (1/3; 2/3; 0.1661)
$R(\text{N1-N1}) = 1.561$	$R(\text{N1-N1}) = 1.370$
$R(\text{N2-N2}) = 1.621$	$R(\text{N2-N2}) = 1.479$
Pnma, 0 GPa	Pnma, 100 GPa
$a = 7.8233; b = 4.9452; c = 6.8703$	$a = 7.5105; b = 4.0263; c = 4.4807$
Ca1 (0.8928; 0.25; 0.6793)	Ca1 (0.8222; 0.25; 0.9706)
N1 (0.1844; 0.25; 1.0889)	N1 (0.2694; 0.25; 0.9916)
$R(\text{N1-N1}) = 1.389$	$R(\text{N1-N1}) = 1.444$

The predicted N–N bond length varies from 1.39 via 1.56 to 1.62 Å depending on the crystal field in a given polymorph; these values may be compared with 1.46 Å for the single N–N bond of hydrazine in the solid state⁹.

It can also be seen from Table II that hexagonal Ca₂N₂ significantly outperforms cubic CaN in enthalpy at 0 GPa; the enthalpy gain associated with dimerization reaches –0.56 eV per one formula unit, much less than for hydrazine itself (< –2.4 eV). The orthorhombic type is less preferred at 0 GPa than the hexagonal one, yet still more stable (by 0.27 eV) than the cubic type.

TABLE II

The calculated energies, *E*, enthalpies, *H*, and volumes, *V*, per one formula unit, for three polymorphs of CaN considered in this work. Features for a pressure of 0 and 100 GPa are marked with appropriate subscripts (0 or 100). Entries are for 0 K. SP stands for 'spin polarization', FM for 'ferromagnetic'

Polymorph	Fm3m, no SP	Fm3m, FM	P62m, no SP	Pnma, no SP
<i>p</i> ₀ , GPa	–0.0079	–0.0010	–0.0107	+0.0327
<i>E</i> ₀ , eV	–1276.455	–1276.572	–1277.139	–1276.848
<i>H</i> ₀ , eV	–1276.470	–1276.582	–1277.139	–1276.853
<i>V</i> ₀ , Å	30.900	31.339	28.734	33.225
<i>p</i> ₁₀₀ , GPa	100.0361	100.0033	99.9915	100.0098
<i>E</i> ₁₀₀ , eV	–1274.092	–1274.100	–1274.936	–1274.583
<i>H</i> ₁₀₀ , eV	–1261.895	–1261.886	–1263.382	–1264.013
<i>V</i> ₁₀₀ , Å	19.554	19.587	18.510	16.937

Importantly, the calculated volume of one formula unit (CaN) at 0 GPa is smaller for hexagonal and orthorhombic polymorphs than for the cubic ones; the difference reaches as much as ~8% (hexagonal Ca₂N₂ vs ferromagnetic CaN), which suggests that ferromagnetic CaN would be even less preferred at increased pressure. Obviously, this conclusion would be valid only if compressibilities of all polymorphs of CaN were very close to each other. Since this might not be the case, we have actually optimized all four polymorphs of CaN at an external pressure of 100 GPa. The calculations indicate that it is orthorhombic Ca₂N₂ which is most stable at 100 GPa; it is

stabilized by over 2.1 eV with respect to cubic CaN. In conclusion, cubic CaN would not be achievable via high pressure synthesis, followed by rapid quenching.

SUMMARY AND PROSPECT

Our calculations clearly indicate the energy preference of structures with the N–N bond, in agreement with the Zintl–Klemm concept. This seems to be the most fundamental obstacle to achieve ferromagnetic CaN; this result also puts in question any other predictions of the related compounds supposedly ferromagnetic without a transition element. Of course, it is impossible to test all possible structure types which might be adopted by Ca_2N_2 and related compounds at ambient and at elevated pressure. However, if more stable polymorphs are found in any future studies, the formation of ferromagnetic CaN will meet even bigger problems.

One cannot generate main-group radicals with impunity; this always comes with a large energy bill, even in solids. Albeit physics of ‘main group ferromagnets’ is certainly very exciting – we feel that there must be some room left for chemistry as well¹⁰. The task is very challenging; investigations are worth pursuing rather for different compositions, particularly those which include much softer atoms, such as As.

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9. As a referee correctly reminds us, the N–N separation is pretty long for the hexagonal polymorph at 0 GPa; this might suggest that the [N₂] unit is significantly reduced for this form. Interestingly, the N–N distance for the orthorhombic form slightly increases upon compression, which might be connected with the increasing Ca→N charge transfer and enhanced ionicity. Unfortunately, the MS DFT package does not allow for the COOP analysis.
10. When this manuscript was shown to Prof. R. Hommann (Cornell, U.S.A.), he commented on the prediction of FM CaN: “It is good to have crazy ideas, even if they come out of unnecessary ignorance”, and he agreed to be quoted here.