Ab initio study of structural properties and dynamical stability of C$_3$N$_2$
encapsulating H guest atom

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Abstract

We have investigated the structural properties and dynamical stability of C$_3$N$_2$ hosting hydrogen as a guest atom. The calculations were performed using the density functional theory (DFT) as implemented in Quantum espresso code. The generalized gradient approximation approach was used throughout the calculations presented here. We find that the guest atom leaves the lattice constant of the host almost unchanged. We, therefore, noted that C$_3$N$_2$ remains dynamically stable when a single guest atom is inserted into its cage-like structure. We also established that the guest vibrational modes are low-lying modes that lowers the acoustic bandwidth of C$_3$N$_2$.

Keywords: C$_3$N$_2$, dynamical stability, H guest atom

1. Introduction

The cage-like voids in crystal structures plays a key role in modifying the behavior of materials. The voids are the guest spots where guest atoms are inserted to form a stabilized compound or to improve material’s electrical conductivity. A good example are the C$_{60}$ and C$_{20}$ fullerenes. They have a number of very important physical and chemical properties that make them desirable for special applications. It is reported that fullerene cages can accommodate more than one guest atoms or molecules [1][2]. Using C$_{20}$ concept, Tian et. al[3] combined carbon and nitrogen to predict C$_3$N$_2$, a novel hard material. This followed other interesting works of Wang et.al [4], who reported an unexpected high-pressure stabilization of cagelike diamondoid nitrogen above 263 GPa. This findings provided a significant understanding of behavior of nitrogen related material under extreme conditions. Previous studies[5][6][7][8][9] on properties of C$_3$N$_2$, did cover the question of whether the cage have inner cavity large enough to hold any atom and whether it remains stable when it hosts a guest atom.

In the present study, atom insertion in the C$_3$N$_2$ host lattice has been performed under zero-pressure conditions. The guest atoms occupied the body-centered vacant site at (0,0,0) in the C$_3$N$_2$ host. We focused on the smallest species with atomic radius(H=0.53Å). Investigation on guest atoms with atomic radii of 1.12Å, 1.57Å, and 2.53Ådid not yield meaningful results and were therefore not considered in this work.

The paper is outlined as follows: In Section 2 we will present the details of our calculations and in Section 3 we will present our results. Finally in Section 4 we will summarize our findings and present our conclusions.

2. Computational methodology

The first step in this work was to optimize the geometry of the lattice structures and the determination of the equations of state. Therefore, the density functional theory (DFT), which has been implemented in the QUANTUM ESPRESSO code[10] was
used. Thermo_pw package\textsuperscript{[11]}, a driver of the Quantum ESPRESSO routines for the calculation of material properties was employed in the calculations of phonons based on density-functional perturbation theory\textsuperscript{[12]}. The exchange correlation functional known as Generalized gradient approximation (GGA) in the form of Perdew-Burke-Ernzerhof (PBE)\textsuperscript{[13]} and projector augmented wave (PAW) potentials\textsuperscript{[14]} were used. A plane wave cutoff energy of 40Ry, a density cutoff of 300Ry and a 6x6x6 Monkhorst-Pack\textsuperscript{[15]} grid for the electronic integrations were used throughout. Phonon frequencies were calculated on a 3x3x3 q-point grid.

3. Results and discussion

3.1. Structural properties

The initial configuration of atoms in the unit cell of the simple cubic $\text{C}_3\text{N}_2$ is shown in figure [1]. The guest atom occupied the body-centered vacant site at (0,0,0) in the $\text{C}_3\text{N}_2$ host before the structural optimization of the lattice. After the optimization, the lattice parameter of $\text{C}_3\text{N}_2$ was determined to be 5.095Å, which was in good agreement with previous studies\textsuperscript{[3, 6]}. When H atom was inserted in the $\text{C}_3\text{N}_2$ host lattice, the cage expands slightly as presented in Table 1. Such very small distortions may have very little impact on the overall structural and elastic properties. It should be noted that the cage in $\text{C}_3\text{N}_2$ is not large enough to hold atoms such as beryllium, lithium and barium, which have atomic radii of 1.12Å, 1.57Å, and 2.53Å respectively. The guest atom forces the cage to expand, just as the structure loses its dynamical stability as the lattice parameter increases significantly.

![Figure 1](image1.png)

Figure 1: (a) Unit cell of the simple cubic $\text{C}_3\text{N}_2$ with space group Pm-3m(221). The guest atoms occupied the body-centered vacant site at (0,0,0) in the $\text{C}_3\text{N}_2$ host as shown in (b).

Other parameters such as density also remained largely unchanged, indicating none of the atoms were incorporated into $\text{C}_3\text{N}_2$ host.

| Property | $\text{C}_3\text{N}_2$ | $\text{HC}_3\text{N}_2$ |
|----------|-------------------------|--------------------------|
| a        | 5.095, 5.085$^a$, 5.049$^b$ | 5.103                    |
| E0       | -446.44809638            | -447.351685595           |
| $\rho$   | 3.2159                  | 3.2129                   |

$^a$Ref.\textsuperscript{[6]} $^b$Ref.\textsuperscript{[3]}

3.2. Phonon dispersion

Our calculated dispersion curves are shown in the figure [2]. The absence of imaginary modes in the dispersion curves, clearly demonstrates that insertion of H atom in $\text{C}_3\text{N}_2$ does not interfere with dynamical stability. If we look at the two regions, i.e one below 400cm$^{-1}$ that encompasses the acoustic modes and the region of optical modes above 1200cm$^{-1}$, we observe very important information.

![Figure 2](image2.png)

Figure 2: The phonon-dispersion curves for $\text{C}_3\text{N}_2$ (left panel) and $\text{HC}_3\text{N}_2$ (right panel).

We find that H guest atom in this $\text{C}_3\text{N}_2$ host, have low-lying vibrational modes, so that their contributions to the heat capacity, the entropy, and the free energy are negligible. It is observed that the guest vibrational modes lowers the bandwidth of the acoustic range. We also note that above 1200cm$^{-1}$, the optic branches are flat, an indication that these modes do not contribute to heat transport in $\text{C}_3\text{N}_2$.

3.3. Conclusion

In summary, the structural and dynamical properties of caged-$\text{C}_3\text{N}_2$ encapsulating hydrogen atoms were studied by first-principles calculations. The voids in $\text{C}_3\text{N}_2$...
are large enough to accommodate the H atoms, hence the host remains dynamically stable after insertion of the guest atom. The phonon frequencies of the guest atom are within the acoustic range, and are expected to have little impact on the heat capacity and entropy.

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References

[1] Y. Rubin, T. Jarrosson, G.-W. Wang, M. D. Barthberger, K. Houk, G. Schick, M. Saunders, R. J. Cross, Insertion of helium and molecular hydrogen through the orifice of an open fullerene, Angewandte Chemie International Edition 40 (8) (2001) 1543–1546.

[2] R. Zhang, W. Ma, K. Han, C. Lee, A thermodynamic and kinetic study of the formation of c20 compounds encapsulating h, he and ne atoms, Theoretical Chemistry Accounts 109 (5) (2003) 278–283.

[3] F. Tian, J. Wang, Z. He, Y. Ma, L. Wang, T. Cui, C. Chen, B. Liu, G. Sou, Superhard semiconducting c3n2 compounds predicted via first-principles calculations, Physical Review B 78 (23) (2008) 235431.

[4] X. Wang, Y. Wang, M. Miao, X. Zhong, J. Lv, T. Cui, J. Li, L. Chen, C. J. Pickard, Y. Ma, Cage-like diamondoid nitrogen at high pressures, Physical review letters 109 (17) (2012) 175502.

[5] Q. Wei, M. Zhang, H. Yan, R. Li, X. Zhu, Z. Lin, R. Yao, A new superhard phase of c3n2 polymorphs, Zeitschrift für Naturforschung A 70 (12) (2015) 1001–1005.

[6] H. Chenghua, W. Feng, Z. Zhou, Ab initio study of phase stability, thermodynamic and elastic properties of c3 n2 derived from cubic c20, Physica B, Condensed Matter 407 (2012) 3398–3404.

[7] J. Du, X. Li, Theoretical investigation on two novel high-pressure orthorhombic phases of superhard c3n2, Journal of Alloys and Compounds 815 (2020) 152324.

[8] F. Yuan, L. Shi, Y. Zhang, C. Jing, Y. Wang, X. Qian, First-principles calculation of the electronic properties and external force modulation of a new tetragonal structure c3n2 crystal, Solid State Communications 338 (2021) 114455.

[9] C. Kou, X. Zhang, Y. Tian, S. Zhang, Y. Du, X. Cui, D. Zhang, M. Zhang, L. Gao, Adsorption of alkali metal atoms on predicted c3n2 sheet, Solid State Communications 334 (2021) 114367.

[10] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, et al., Quantum espresso: a modular and open-source software project for quantum simulations of materials, Journal of physics: Condensed matter 21 (39) (2009) 395502.

[11] C. Malica, A. Dal Corso, Quasi-harmonic temperature dependent elastic constants: applications to silicon, aluminum, and silver, Journal of Physics: Condensed Matter 32 (31) (2020) 315902.

[12] S. Baroni, S. De Gironcoli, A. Dal Corso, P. Giannozzi, Phonons and related crystal properties from density-functional perturbation theory, Reviews of Modern Physics 73 (2) (2001) 515.

[13] J. P. Perdew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple, Physical review letters 77 (18) (1996) 3865.

[14] P. E. Blöchl, Projector augmented-wave method, Physical review B 50 (24) (1994) 17953.

[15] H. J. Monkhorst, J. D. Pack, Special points for brillouin-zone integrations, Physical review B 13 (12) (1976) 5188.