Predicted novel metallic metastable phases of polymeric nitrogen at high pressures

Xiaoli Wang\textsuperscript{1,2}, Fubo Tian\textsuperscript{1}, Lin Wang\textsuperscript{1,3}, Xilian Jin\textsuperscript{1}, Defang Duan\textsuperscript{1}, Xiaoli Huang\textsuperscript{1}, Bingbing Liu\textsuperscript{1} and Tian Cui\textsuperscript{1,4}

\textsuperscript{1} State Key Laboratory of Superhard Materials, College of Physics, Jilin University, Changchun 130012, People’s Republic of China
\textsuperscript{2} Institute of Condensed Matter Physics, Linyi University, Linyi 276005, People’s Republic of China
\textsuperscript{3} HPSynC, Carnegie Institution of Washington, 9700 South Cass Avenue, Argonne, IL 60439, USA
E-mail: cuitian@jlu.edu.cn

New Journal of Physics 15 (2013) 013010 (9pp)
Received 17 July 2012
Published 9 January 2013
Online at http://www.njp.org/
doi:10.1088/1367-2630/15/1/013010

Abstract. Two new metallic polymeric structures of nitrogen, \textit{Pnnm} and \textit{Cccm}, are found by means of the first-principles density functional theory and a random structure-searching method. Firstly, it is shown that the transition behavior of nitrogen from insulator to metal starts at a pressure of approximately 460 GPa at 0 K. The \textit{Pnnm} phase becomes energetically favorable with respect to \textit{cubic gauche} at 363 GPa, and then transforms to the \textit{Cccm} structure at 884 GPa. Electron–phonon coupling calculations suggest that the \textit{Pnnm} crystal possesses superconductivity. The stability of these two phases is also explored, showing for the first time that they are stable structures of nitrogen exhibiting metallic properties.

\textsuperscript{4} Author to whom any correspondence should be addressed.

Content from this work may be used under the terms of the Creative Commons Attribution-NonCommercial-ShareAlike 3.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.
1. Introduction

The pressure-induced transformation of molecular crystals into nonmolecular states, which is expected to be accompanied by a decrease in the band gap and eventually metallization, has attracted a lot of interest. Pressure-induced metallization has been observed in many systems, especially in some elemental solids, such as sulfur [1], oxygen [2–3] and iodine [4] etc, which are very important for understanding and researching metallic hydrogen. Nitrogen, one of the most important elements, is also expected to become a metallic state when compression is sufficiently strong. However, metallic nitrogen at high pressure has still not been found. It is well known that molecular nitrogen transforms to polymeric nitrogen at high pressure, which becomes a high energy density material. Plenty of polymeric nitrogen structures have been proposed and studied [5, 6]. Nevertheless, only cubic gauche (cg) has been successfully synthesized experimentally [7]; none of the other structures theoretically proposed have been obtained experimentally. We explored all of the polymeric phases of nitrogen, and found that they were all insulators. Recently, a molecular dynamics study demonstrated a new metastable metallic structure, cis–trans chain (ch) [8]. However, its enthalpy was significantly higher than that of cg at pressures above 15 GPa. Another metallic phase, Cmcm, was also predicted [9]. This phase was the first dynamically stable (40–240 GPa) metallic nitrogen, but its enthalpy was also much higher. By analogy with high-pressure solid phases, the existence of liquid nitrogen was suggested as well. Recently, Donadio et al explored the melting line of nitrogen at high pressure, and found the transformation in liquid accompanied by the insulator-to-metal transition [10]. The metallization and metallic solid nitrogen phase at high pressure is still the subject of heated debate.

In this paper, two new metallic polymeric nitrogen structures with Pnmm and Cccm symmetries are revealed by means of the first-principles density functional theory (DFT) and a random structure-searching method. The stability of the two new phases and possible phase transitions from cg to Pnmm and Cccm are discussed. Furthermore, various physical properties including the electronic properties and electron–phonon coupling (EPC) of the metallic phases suggest that Pnmm nitrogen possesses superconductivity at high pressure.

2. Theoretical method and computational details

All calculations reported in this paper were based on the first-principles plane-wave pseudo-potential DFT. The structure relaxations and Hellmann–Feynman forces were performed with the CASTEP code [11]. The Quantum-ESPRESSO package was employed to study
the Fermi surface and EPC [12]. The ultrasoft pseudo-potential was used, and the exchange and correlation effects were described using the generalized gradient approximation, Perdew–Burke–Ernzerhof [13]. The electron wave functions and the electron density were expanded by the plane-wave basis sets with an energy cutoff of 500 eV, which demonstrated an excellent convergence of the total energies and structural parameters.

3. Results and discussion

A set of initial nitrogen structures including molecular structures and the candidate polymeric structures were designed, then the nitrogen atoms were moved away from their equilibrium positions. After renormalizing the volume to a reasonable value and relaxing the system to minimum enthalpy at a given pressure, a new structure, $Pnnm$, was formed. The dynamic stability of this phase was explored and the imaginary frequency appeared near the $S$ point at 800 GPa. Based on the eigenvectors of this softened mode, the original $Pnnm$ was distorted to find the appropriate atomic displacements. Another new phase, $Cccm$, was obtained following full geometry optimization from the distorted structure. These two structures with $Pnnm$ and $Cccm$ symmetries are more energetically stable than $cg$ at high pressures.

The new $Pnnm$ nitrogen is orthorhombic (space group $Pnnm$) with $a = 6.0767$ Å, $b = 2.3885$ Å, and $c = 2.0807$ Å at 450 GPa. There are eight atoms per unit cell with two equivalent crystallographic sites, which are at 4g (0.8579, 0.7321, 0) and 4g (0.3532, 0.0858, 0) positions. The $Cccm$ nitrogen is orthorhombic (space group $Cccm$) with $a = 5.7513$ Å, $b = 2.1398$ Å, and $c = 1.9785$ Å at 890 GPa. There are also eight atoms per unit cell but with one inequivalent crystallographic site, which is at 8f (0.3621, 0.1789, 0) position. They are all layered structures, which consist of zigzag chain units. The neighboring zigzag chains are connected by single bonds. The N–N single bonds in the zigzag unit form a highly symmetrical three dimensional framework. As far as we know, these two structures have not been reported previously. The crystal structure of $Pnnm$ is shown in figure 1. Analysis results of electron localization functions (ELF) (figure 1(b)) suggest that all the N atoms are sp$^3$ hybridized with lone pair lobes pointing opposite to the pyramid. The lone pairs are arranged in such a way that their lobes are avoiding each other.

The stabilities of all the candidate structures have been explored extensively in our previous work [14]. Some competitive structures, $cg$, $Cmcm$, $A7$, $Pba2$, were selected and the enthalpies...
Figure 2. Enthalpy curves (relative to cg) as a function of pressure for Pnnm, Cccm, Cmcm, cw, Pba2 and A7.

difference (relative to cg) together with Pnnm and Cccm are presented in figure 2. It is clear that cg nitrogen is the most stable below 174 GPa among these structures, which is consistent with previous calculations [14–18]. Pnnm and Cccm are more stable than Cmcm and cw in the whole pressure range studied. The Pnnm phase has lower enthalpy than the cg phase above 363 GPa, and then transforms to a Cccm structure at 884 GPa. Pnnm has a unique bonding configuration: the three nearest-neighbor N–N distances are not equal. Because of this, its calculated packing efficiency of 35.59% is higher than that of the polymeric N structures: Cmcm (29.45%) and cg (32.24%). This suggests that the unique bonding packing of Pnnm will be more thermodynamically stable. Compared with Pba2 structures, it is noteworthy that Pnnm and Cccm are metastable structures from the viewpoint of enthalpy. As we know, the metastable phase can be formed from suitable precursors with high chemical potential if the activation barriers between the metastable phases and more stable phases are sufficiently high. As the precursors fall into the energy range, they can be trapped in a metastable structure [19]. It suggests that the metastable phases we proposed could be created by using appropriate conditions and techniques.

The mechanical stability of crystal structures could provide a useful insight into the stability of materials that require the strain energy to be positive and the whole set of elastic constant $C_{ij}$ to satisfy the Born–Huang criterion [20]. For an orthorhombic crystal, the independent elastic stiffness tensor consists of nine components: $C_{11}$, $C_{22}$, $C_{33}$, $C_{44}$, $C_{55}$, $C_{66}$, $C_{12}$, $C_{13}$ and $C_{23}$. The mechanical stability criteria are given by $C_{11} > 0$, $C_{22} > 0$, $C_{33} > 0$, $C_{44} > 0$, $C_{55} > 0$, $C_{66} > 0$, $(C_{11} + C_{22} - 2C_{12}) > 0$, $(C_{11} + C_{33} - 2C_{13}) > 0$, $(C_{22} + C_{33} - 2C_{23}) > 0$, $(C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23})) > 0$ [21]. To evaluate the mechanical stability of these two new phases, elastic constants were calculated and are listed in table 1. The elastic constants of the two structures satisfy the mechanical stability criteria, indicating that these two structures are mechanically stable. The elastic constants at other pressures were also explored, and the results suggest that the Pnnm phase is mechanically stable in the range of 300–900 GPa, while Cccm is mechanically stable above 800 GPa. The phase Pnnm, rather than Cccm, is mechanically stable at ambient conditions. Phonon calculations also...
Table 1. Elastic constants $C_{ij}$ (GPa) of $Pnnm$ and $Cccm$ crystals calculated at 400 and 890 GPa, respectively.

|       | $C_{11}$ | $C_{22}$ | $C_{33}$ | $C_{44}$ | $C_{55}$ | $C_{66}$ | $C_{12}$ | $C_{13}$ | $C_{23}$ |
|-------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| $Pnnm$ | 2826     | 1779     | 3338     | 1394     | 479      | 207      | 778      | 755      | 1332     |
| $Cccm$ | 3553     | 4682     | 4323     | 1191     | 2204     | 998      | 1899     | 2248     | 1581     |

Figure 3. The phonon dispersion curves for (a) $Pnnm$ at 400 GPa, and (b) $Cccm$ at 890 GPa, respectively. The Fermi surface of $Pnnm$ at (c) 460 GPa and (d) 600 GPa.

give a criterion for crystal stability. Therefore, the phonon dispersion curves for the $Pnnm$ and $Cccm$ phases at selected pressures were calculated and the results are shown in figures 3(a) and (b). The absence of imaginary frequency modes indicates that these two structures are dynamically stable. However, both phases are not dynamically stable at ambient conditions. The unit cell of each structure contains eight atoms, giving 24 phonon branches. The group theory analysis shows that the 24 vibrational modes of $Pnnm$ at the zone center have the irreducible representations $\Gamma_{pnnm} = 2(A_R^R + 2B_{1g}^R + B_{1u}^R + B_{2g}^R + 2B_{2u}^R + B_{3g}^R + 2B_{3u}^R)$, $\Gamma_{cccm} = 2A_g^R + 2B_{1g}^R + B_{1u}^R + B_{2g}^R + 2B_{2u}^R + B_{3g}^R + 2B_{3u}^R$. The Raman active modes are labeled as superscript R, and the infrared active modes are labeled with superscript I. Both infrared and Raman frequencies of the two structures (zone-center phonons in figures 3 (a) and (b)) will provide useful information for future experiments to identify the two phases as in the case of the $cg$ structure.

To sum up, the new structures $Pnnm$ and $Cccm$ are mechanically and dynamically stable phases. Comparing with $Pba2$, $Pnnm$ and $Cccm$ are metastable phases due to their higher enthalpies. However, from a phase transformation point of view, the low pressure phase could directly transform into a high pressure phase when the pressure increases very quickly and the atoms do not have enough time to respond. Therefore, the metallic $Pnnm$ phase we found
could be obtained by quickly compressing \(cg\) up to 363 GPa. Take \(Y_2O_3\) as an example: shock compression (pressure increased very fast) can stabilize the monoclinic structure, which is a metastable phase at high pressure. However, this phase could not be observed in static high pressure experiments [22, 23]. In addition, the nano-size effect provides us with another way to stabilize the metastable phase at ambient conditions. For example, \(\alpha-Al_2O_3\), a metastable phase that can only be found at high temperatures in bulk materials, can be obtained at ambient conditions by reducing its grain size to \(\sim 10\) nm [24].

As we know, stable metallic nitrogen has not been found as yet. To explore the metallic properties of nitrogen, we have further calculated the band structures and density of states of the molecular phases (\(\alpha, \beta\) and \(\gamma\) phases) at low pressure (0–100 GPa) and the polymeric phases including \(cg, bp, Pba2\) and \(P2_12_12_1\) at the pressure range from 100 to 600 GPa. Our results indicate that all the structures are insulators. It means that no metallic structure appears in existing proposed dynamically stable structures of nitrogen at pressures lower than 600 GPa. Recently, another two metallic structures, \(ch\) [8] and \(Cmcm\) [9], were proposed, but their enthalpies are much higher than \(cg\), which indicates that they are energetically unfavorable [9]. Here, we explored the metallic properties of the two new phases. The calculated electronic band structures of the \(Pnnm\) phase at 460 GPa and the band gaps as a function of pressure for \(Pnnm, bp, cg, Pba2\) and \(P2_12_12_1\) are shown in figures 4(a) and (b). The results (figure 4(a)) clearly show the Fermi level cross the energy bands, indicating that polymeric nitrogen with the \(Pnnm\) structure will transform into metallic crystal at 460 GPa. Compared with the above results, the band gaps of the competitive structures \(Pnnm, bp, cg, Pba2\) and \(P2_12_12_1\) are calculated as a function of the pressure present in figure 4(b). The results show that the band gaps of \(bp, Pba2\) and \(P2_12_12_1\) changed little as the pressure increased. The metallic properties are not apparent, although the band gap of \(cg\) decreased rapidly as the pressure increased up to 600 GPa. However, the band gap of \(Pnnm\) disappears at 460 GPa, indicating its metallization, and is consistent with the observation from figure 4(a) that the Fermi level crosses the energy band, indicating that the

**Figure 4.** (a) The calculated band structure for the phase of \(Pnnm\) at 460 GPa. (b) Band gaps calculated as a function of pressure for \(Pnnm, bp, cg, Pba2\) and \(P2_12_12_1\).
new phase, \textit{Pnnm}, is metallic nitrogen. The Mulliken population analysis was also performed on the \textit{Pnnm} structure. The population of the bonds is 0.48 for the longer bond and 1.16 for the shorter bond at 400 GPa, and 0.49 for the longer bond and 1.15 for the shorter bond at 500 GPa, respectively. Regarding the atomic populations, it was found that the electrons transfer from s-orbitals to d-orbitals as the pressure increases. These two factors result in metallization of \textit{Pnnm} at high pressure. As the pressure increases up to 884 GPa, the metallic \textit{Pnnm} phase transforms to the \textit{Cccm} phase, which is also a metallic phase. The reason for metallization is that the compression and the consequent shortening of the bond length widen both valence and conduction bands, and therefore tend to reduce the gap.

The Fermi surface and the perspectives were further computed to investigate the metallic properties of \textit{Pnnm} as shown in figures 3(c) and (d). The Fermi surface of the second band forms small rubies and is shown in blue. The Fermi surface for the third band is denoted by a red interior and the fourth band is denoted by a green exterior and forms petals. At high pressure, the Fermi surface for the fifth band is shown alone for greater clarity. This indicates that the new metal phase will allow better conductivity. As we know, the fifth group elements in the periodic table are not superconductors at ambient conditions. Nevertheless, P [25], As [26], Sb [27] and Bi [28] would become superconducting under pressure. Pressure-induced superconductivity has been developed for these elements. Although nitrogen is the simplest element in this group, there have been no reports about its superconductive properties to date. From our calculations above, the \textit{Pnnm} phase we proposed will transform to metal at high pressure, so it is desirable to investigate the possibility of superconductivity in nitrogen in the \textit{Pnnm} phase. As seen from the band structure in figure 4(a), the electronic bands along the \textit{G–Z} direction are quite steep. Moreover, a flat band was observed along the \textit{Y–S–X} directions. These electronic features apparently satisfy the ‘steep band–flat band’ scenario, which has been suggested to be a favorable condition for the occurrence of superconductivity [29]. Figure 5 demonstrates the Eliashberg phonon spectral function, \( \alpha^2 F(\omega) \), and the integrated \( \lambda(\omega) \), as a function of frequency at 600 GPa. The EPC parameter, \( \lambda \), was increased from 0.100
to 0.236 with increasing pressure from 500 to 600 GPa. The $T_c$ can be estimated from the Allen–Dynes modified McMillan equation \[ T_c = \frac{\omega_\text{log}}{\lambda} \exp\left[\frac{-0.04(1+\lambda)}{\lambda - \mu^* (1+0.62\lambda)}\right], \] which has been found to be highly accurate for many materials with $\lambda < 1.5$, where $\omega_\text{log}$ is the logarithmic average frequency calculated directly from the phonon spectrum. The Coulomb pseudo potential $\mu^*$ is often taken as 0.1 for most metals. For the $Pnnm$ phase at 500 and 600 GPa, the calculated $\omega_\text{log}$ are 954.231 and 733.504 K, respectively. Using $\mu^*$ of 0.1, the estimated $T_c$ is 0.21 mK at 500 GPa and increases to 0.089 K at 600 GPa. The estimated $T_c$ is smaller than those of other nitrides [31], suggesting that nitrogen is not a good superconductor. However, it is noteworthy that nitrogen will transform to a superconductor at high pressure. A more accurate theoretical method or future experiments are needed to investigate the superconductivity of polymeric nitrogen.

4. Conclusions

In summary, two new mechanically and dynamically stable metallic phases ($Pnnm$ and $Ccmm$) were predicted through $ab initio$ calculations. The results indicate that polymeric nitrogen with a $Pnnm$ structure possesses excellent metallic properties, which are important for understanding the simple element N. EPC calculations suggest that $Pnnm$ would be a superconductor at high pressure. We hope that this study will stimulate the search for new metallic nitrogen.

Acknowledgments

This work was supported by the National Basic Research Program of China (grant number 2011CB808200), Program for Chang Jiang Scholars and Innovative Research Team in University (grant number IRT1132), the National Natural Science Foundation of China (grant numbers 51032001, 11074090, 11147007, 11004072, 10979001, 51025206, 11104102, 11174102), Program for New Century Excellent Talents in University (NCET, 2010), Graduate Innovation Fund of Jilin University (20121035). Parts of calculations were performed in the High Performance Computing Center (HPCC) of Jilin University.

References

[1] Luo H, Desgreniers S, Vohra Y K and Ruoff A L 1991 Phys. Rev. Lett. 67 2998
[2] Desgreniers S, Vohra Y K and Ruoff A L 1990 J. Phys. Chem. 94 1117
[3] Akahama Y C, Kawamura H, Häusermann D, Hanfland M and Shimomura O 1995 Phys. Rev. Lett. 74 4690
[4] Riggleman B M and Drickamer H G 1963 J. Chem. Phys. 138 2721
[5] Zahariev F, Hu A, Hooper J, Zhang F and Woo T 2005 Phys. Rev. B 72 214108
[6] Zahariev F, Hooper J, Alavi S, Zhang F and Woo T K 2007 Phys. Rev. B 75 140101
[7] Eremets M I, Gavriliiuk A G, Trojan I A, Dziwenko D A and Boehler R 2004 Nature Mater. 3 558
[8] Alemany M M G and Martins J L 2003 Phys. Rev. B 68 024110
[9] Mattson W D, Sanchez-Portal D, Chiesa S and Martin R M 2004 Phys. Rev. Lett. 93 125501
[10] Davide D, Spanu L, Duchemin I, Gygi F and Galli G 2010 Phys. Rev. B 82 020102(R)
[11] Segall M D, Lindan P L D, Probert M J, Pickard C J, Hasnip P J, Clark S J and Payne M C 2002 J. Phys.: Condens. Matter 14 2717
[12] Goncharenko I, Eremets M I, Hanfland M, Tse J S, Amboage M, Yao Y and Trojan I A 2008 Phys. Rev. Lett. 100 045504

New Journal of Physics 15 (2013) 013010 (http://www.njp.org/)
[13] Perdew J P, Burke K and Ernzerhof M 1996 Phys. Rev. Lett. 77 3865
[14] Wang X L, Tian F B, Wang L C, Cui T, Liu B B and Zou G T 2010 J. Chem. Phys. 132 024502
[15] Wang X L, He Z, Ma Y M, Cui T, Liu Z M, Liu B B, Li J F and Zou G T 2007 J. Phys.: Condens. Matter 19 425226
[16] Kotakoski J and Albe K 2008 Phys. Rev. B 77 144109
[17] Ma Y M, Oganov A R, Li Z W, Xie Y and Kotakoski J 2009 Phys. Rev. Lett. 102 065501
[18] Wang X L, Wang Y C, Miao M S, Zhong X, Lv J, Cui T, Li J F, Chen L, Pickard C J and Ma Y M 2012 Phys. Rev. Lett. 109 175502
[19] Bridgman P W 1955 Sci. Am. 193 42
[20] Born M and Huang K 1956 Dynamical Theory of Crystal Lattices (Oxford: Clarendon)
[21] Watt J P 1979 J. Appl. Phys. 50 6290
[22] Wang L, Pan Y, Ding Y, Yang W, Mao W L, Sinogeikin S V, Meng Y, Shen G and Mao H K 2009 Appl. Phys. Lett. 94 061921
[23] Atou T, Kusaba K, Fukuoka K, Kikuchi M and Syono Y 1990 J. Solid State Chem. 89 378
[24] Li J G and Sun X D 2000 Acta Mater. 48 3103
[25] Shirotani I, Kawamura H, Tsuji K, Tsuburaya K, Shimomura O and Tachikawa K B 1988 Chem. Soc. Japan 61 211
[26] Chen A L, Lewis S P, Su Z P, Yu P Y and Cohen M L 1992 Phys. Rev. B 46 5523
[27] Wittig J 1984 Mater. Res. Soc. Symp. Proc. 22 17
[28] Il’ina M A 1972 Sov. Phys.—JETP 34 1263
[29] Simon A 1997 Angew. Chem. Int. Edn Engl. 36 1788
[30] Allen P B and Dynes R C 1975 Phys. Rev. B 12 905
[31] Chen X J et al 2005 Proc. Natl Acad. Sci. USA 102 3198