Pressure-induced vibrational and electronic properties of palladium per nitride

Sanjay D. Gupta, Sanjeev K. Gupta and Prafulla K. Jha*
Department of Physics, Bhavnagar University, Bhavnagar 364002, India
*E-mail: prafullaj@yahoo.com

Abstract. We predict electronic and structural phase transition at 11GPa for crystalline PdN_2 in pyrite structure by employing first principles calculation using density functional theory implemented in Quantum Espresso code. The electronic band structure, equation of states and dynamical properties at zero as well as high pressure are calculated within the frame work of conventional GGA exchange correlation functional. We report the sharp change of the Pd-N and N-N bond length at phase transition pressure in support of isostructural phase transition driven by electronic phase transition for PdN_2 in pyrite structure. The calculated Raman frequencies near the phase transition pressure reveals the first order isostructural phase transition by the instability of longitudinal acoustical as well as optical branches, provides the mechanism for experimentally observed decomposition below 13GPa.

1. Introduction
Metallic nitrides are of great technological and fundamental importance due to extraordinary properties such as hardness, superconductivity, photoluminescence and many type of magnetism [1]. Traditional applications have taken advantage of the hard and refractory nature of many of these compounds, but numerous mere recent applications are based on their crystalline structure stability, electronic and vibrational properties [2]. Now a consensus has been reached concerning the observed crystal structure and stoichiometry i.e. one metal atom for every nitrogen dimer [1-4]. However, it was found that pyrite PdN_2 structure decomposes at pressure below ~13GPa [3-5]. Therefore, the correct stoichiometry could not be determined using electron microprobe or X-ray photoelectron spectroscopy. Until now the crystalline structure of this new synthesized palladium per nitride has not been determined. All noble metal nitrides (PtN_2, IrN_2 and OsN_2) studied to date possess uncomplicated behaviour due to significant hybridization between 5d electrons and N-2p electrons at all hydrostatic pressure [6-8]. They are recoverable to ambient conditions after synthesis at high pressure and high temperature [in the range of 60GPa and 2000K]. In contrast to these compounds, the synthesized crystalline PdN_2 at high pressure and temperature does not appear to be recoverable at ambient conditions and decomposed below 13GPa [9]. Recently, Aberg et al. [4] have argued that the equation of states (EOS) cannot be accurately described within either the local density or generalized gradient approximations for PdN_2 and only the Heyd-Scuseria-Ernzerhof exchange-correlation functional (HSE06) provides very good agreement with experimental data. Motivated with this report, we have investigated the EOS, electronic band structure phase transition and vibrational properties using conventional generalized gradient approximations and analyzed with available experimental and theoretical data. Our analysis concludes that the conventional GGA is sufficient to predict the physical properties of PdN_2 comparable to the experimental observation. We are able to observe the decomposed below 13GPa similar to experiment.

2. Computational Methodology
We have investigated structural, electronic, and lattice dynamical properties using the plane wave pseudopotential within the GGA-XC functional as parameterized by Perdew, Burke, and Ernzerhof for treating the effects of exchange correlation implemented in PWSCF package. The Brillouin zone integrations were performed using 6×6×6 Monkhorst-Pack k-point sampling for structural relaxations and the calculation of other properties. The plane-wave cutoff was set to 38Ry, and
Mathfessel-Paxton smearing with a width of 0.05eV was used to determine the eigenvalues. Atomic positions were relaxed with ionic forces converged to 0.001eV/Å. The computed equilibrium lattice constant and bulk modulus agree well with the experiment and other theoretical calculations.

3. Results and Discussion

The structure of pyrite PdN$_2$ was optimized at zero and different high pressures (11, 18 and 60GPa). The optimized structural parameters are in agreement with earlier theoretical and experimental data. The calculated electronic band structures of pyrite PdN$_2$ at zero pressure, 11GPa, 18GPa and 60GPa are presented in Figs. 1(a), 1(b), 1(c) and 1(d) respectively along with total and partial density of states. The Figs. 1(a) and 1(c) reveal a smaller direct band gap in Γ-X direction of the Brillouin zone at zero pressure as well as 18GPa. The projected density of states shown in the right panel of each figure at corresponding high pressure reveals that the valence and conduction orbital
bands are determined by N-
\(^p\) and Pd-\(d\) electron states. With the application of pressure, the Fermi energy sharply shifts towards the lower energy region suggests a transformation from insulator to metallic crystal state. Our calculated electronic band structure and density of states are very well in agreement in reported by Chen et al. \[5\] with smaller band gap at 18GPa. At higher synthesized pressure the band again closes and makes PdN\(_2\) as metallic form its insulator state as shown in Figs. 1(c) and 1(d). This electronic phase transition in pyrite crystalline PdN\(_2\) can also lead to first order isostructural transition at applied higher static pressure near the decomposition pressure. Aberg et al. \[4\] had claimed that the EOS can not accurately describe within either the LDA or GGA approximations. Our calculated EOS data is in good agreement with the theoretically calculated EOS \[4\] and experimental X-ray diffraction measurements. The anomalous behavior of EOS at 11GPa corresponds to isostructural phase transition for PdN\(_2\) pyrite crystal structure shown in Fig 2(a). Thus the electronic transition in the PdN\(_2\) pyrite crystal structure leads to the isostructural phase transition at phase transition pressure 11GPa. This is due to the fact that pressure applied, bond length increases between nitrogen dimmers and transform from N≡N to N-N single bond character and forming thermodynamically stable pyrite PdN\(_2\) crystal above 18GPa \[5\].

![Figure 2(a). Equation of state as obtained from GGA-XC.](image)

![Figure 2(b). Bond length between palladium and nitrogen as function of pressure.](image)

![Figure 2(c). Bond length of nitrogen dimmers as a function of pressure.](image)

We have obtained Pd-N and N-N bond length up to 15GPa by optimized at each pressure and shown in Figs. 2(b) and 2(c) respectively. The Figs. 2(b) and 2(c) clearly indicates sharp deep and rise in bond length near phase transition pressure (11GPa) between Pd-N and N-N bonding in nitrogen dimmer respectively. Thus the electronic phase transition leads to an exponential increase in free carrier concentration as well screening effect causes and anomalous behavior of the bond length. Thus the volume dependence bond length foreshadows of peculiar properties of this compound near the phase transition pressure. The palladium per nitride with pyrite structure is very soft and elastically stable at 0GPa, though thermodynamically unstable, become energetically favourable at high pressure but the lattice dynamical calculations reveal that the pyrite PdN\(_2\) is dynamically stable at ambient and 60GPa \[4\]. The zone centre phonon frequencies 1042.9 cm\(^{-1}\) and 1118.7 cm\(^{-1}\) of A\(_g\) and T\(_g\) modes particularly at 60GPa, which are the Raman active phonons agree well with the experimental Raman data. The pressure variation of Raman active modes shows a linear variation; however, at higher pressure the optical frequencies decrease and acoustic frequencies increases \[2-3\]. From Fig. 3(b) shows that almost all the zone centre phonon branches behaves anomalously at calculated electronic phase transition provides clear support in the decomposition of PdN\(_2\) pyrite structure at 11GPa and predict the quenching of crystal structure from high pressure to ambient pressure can be possible to recover crystalline pyrite PdN\(_2\) in ambient pressure.
4. Conclusion
In conclusion, we have investigated structural electronic and phonon properties for PdN\textsubscript{2} in pyrite crystal structure up to 60GPa using first principles calculations. Our results show first time that all calculated properties reproduced accurately and consistent, with available experimental data calculated by GGA-XC functional. The electronic phase transition from insulator to metallic state, multivalued EOS, drastic change in Bond length of Pd-N and N-N, and dynamical instability as well as anomalous behavior of zone centre phonon frequencies at 11GPa clearly suggest that PdN\textsubscript{2} pyrite crystal structure decomposes at 11GPa sharply. The mechanical and dynamical stability clearly shows the PdN\textsubscript{2} pyrite crystal structure can be recovered in high crystalline form at ambient pressure.

Acknowledgements
The financial support from the Department of Science and Technology, Govt. of India, New Delhi and Department of Atomic Energy, Govt. of India, Mumbai is highly appreciated for this work.

References
[1] Toth L 1971 Transition metal carbides and Nitrides (New York: Academic Press)
[2] Samsonov G V and Vinittski I M, 1976 Handbook of Refractory Compounds (Metallurgiya, Moscow; IFZ/Plenum, New York, 1980)
[3] Aberg D, Sadigh B, Crowhurst J and Goncharov A F 2008 Phys. Rev. Lett 100 095501
[4] Aberg D, Erhart P, Crowhurst J, Zaug J M, Goncharov A F and Sadigh B 2010 Phys. Rev. B 82 104116
[5] Chen W, Tse J S and Jiang J Z 2010 J. Phys.: Condens. Matter 22 015404
[6] Crowhurst J C, et al. 2006 Science 311 1275
[7] Yu R, Zhan Q and Zhang X F 2006 Appl. Phys. Lett. 88 051913
[8] Young A F, Montoya J A, Lazzeri C, Lazzeri M, Gregorzyan E and Scandolo S 2006 Phys. Rev. B 73 153102
[9] Soto G 2004 Mater. Lett. 58 2178
[10] Nye J F 1985 Physical Properties of crystals (Oxford: Oxford University press)