South African Institute of Physics 57th Annual Conference (SAIP 2012), 9 – 13 July 2012, University of Pretoria, Pretoria, South Africa

First-Principles Calculations of the Structural, Electronic and Optical Properties of PdN and PdN_2

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MOTIVATIONS

* Nitrides of platinum metals (PM) group possess unusual extreme properties [1]. ➡ Potential applications.
* The **2004** discovery and characterization of crystalline PtN. ➡ Possible to synthesize other novel nitrides [2].
* In **2007**, a palladium nitride compound was successfully synthesized and argued for its PdN_2 stoichiometry and pyrite (C2) structure [3].
* Crystal structure of the synthesized phase has not been determined [4]. ➡ Search for the true structure of the synthesized phase.
* Many transition metals have more than one nitride form [5]. ➡ Search for *other* possible stoichiometries/structures of palladium nitride.
* The synthesized phase decomposes below 13 GPa [1] (Why?). ➡ Need for first-principles calculations.
* Inconsistency in the calculated properties. ➡ More sophisticated calculation methods.

[1] D. Åberg *et al.*, *Physical Review B* 82, 104116 (2010).
[2] E. Gregoryanz et. al., *Nature Materials* 3, 294 (2004).
[3] J. C. Crowhurst *et al.*, *Journal of Materials Research* 23, 1 (2008).
[4] W. Chen, J. S. Tse and J. Z. Jiang, *Journal of Physics: Condensed Matter* 22, 015404 (2010).
[5] A. F. Wells, *Structural Inorganic Chemistry*, 5th ed.,Oxford University Press (1984).

DFT CALCULATIONS DETAILS

Electronic Optimization:

Solve Kohn-Sham SDFT equations

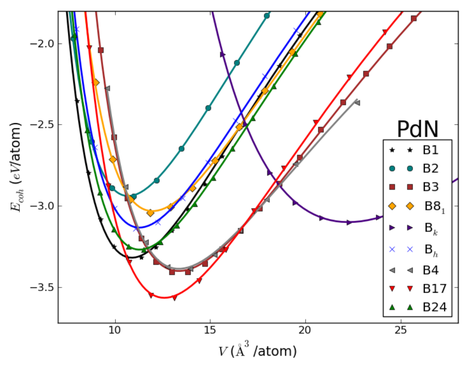
$$\left\{-\frac{\hbar}{2m_e}\nabla^2+\int d\boldsymbol{r}'\frac{n(\boldsymbol{r})}{|\boldsymbol{r}-\boldsymbol{r}'|}+V_{ext}(\boldsymbol{r})+V_{XC}^{\sigma}[\rho\uparrow,\rho\downarrow]\right\}\varphi_{nk}^{\sigma}(\boldsymbol{r})=\epsilon_{nk}^{\sigma}\,\varphi_{nk}^{\sigma}(\boldsymbol{r})$$

* Using VASP package.
* Plane waves (PWs) basis set for the expansion of the pseudo part of $\varphi^{\sigma}{}_{nk}(\mathbf{r})$.
* **Γ**-centred Monkhorst-Pack ***k*** -mesh for the first Brillouin zone (BZ) sampling.
* GGA-PBE functional for the exchange-correlation (*XC*).
* PAW method for the electron-ion interactions.

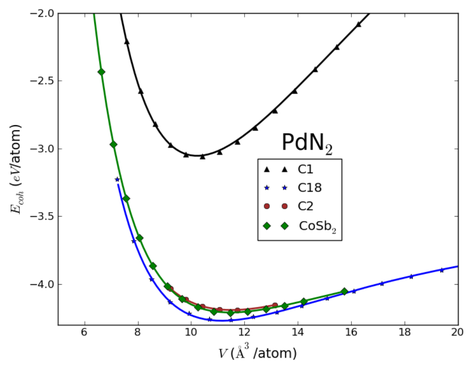
Geometry Relaxation and Equation of State (EOS):

* **PdN structures :** B1, B2, B3, $B8_1$, B_k, B_h, B4, B17 and B24.
* **PdN_2 structures:** C1, C2, C18 and $CoSb_2$.
* Relax ions until all force components are smaller than 0.01 eV/Å.
* Obtained E(V) results fitted to a Birch-Murnaghan 3rd-order EOS.
* Equilibrium cohesive energy E_0, equilibrium volume V_0 and equilibrium bulk modulus B_0 were obtained.

EOS & RELATIVE STABILITIES



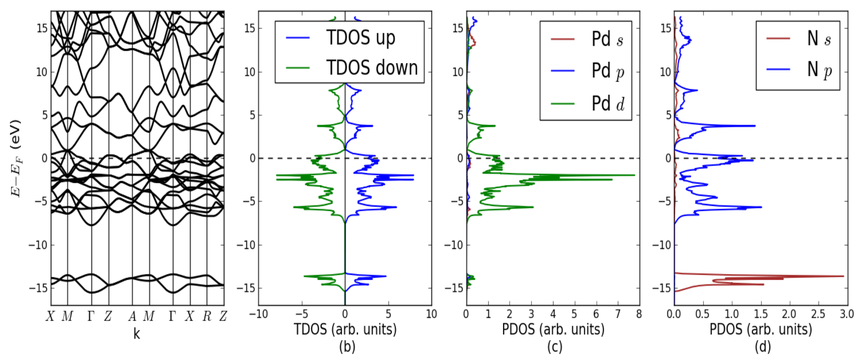
(a)



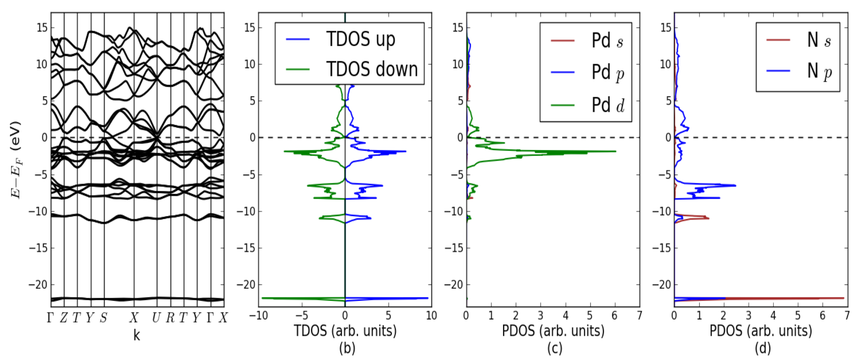
(b)

Figure 1: DFT calculated cohesive energy E_{coh}(eV/atom) versus atomic volume V(Å^3/atom): **(a)** For PdN in nine different structures. The most stable structure (B17) was theoretically predicted to be the ground state of the synthesized PtN. **(b)** For PdN_2 in four different structures. Both C18 and $CoSb_2$ are energetically more stable than C2!

ELECTRONIC PROPERTIES



(I)



(II)

Figure 2: DFT calculated electronic properties of the most stable phases: **(I)** PdN (B17), and **(II)** PdN_2(C18). In each subfigure: (a) band structure along the high-symmetry **k**-points; (b) spin-projected total density of states (TDOS); (c) partial density of states (PDOS) of Pd(s; p; d) orbitals; and (d) PDOS of N(s; p) orbitals. Both phases show metallic feature at **0** GPa and **0** K. The very low DFT-TDOS around E_F for PdN_2(C18) may open under pressure or if a hybrid *XC* functional is used.

EQUILIBRIUM PROPERTIES

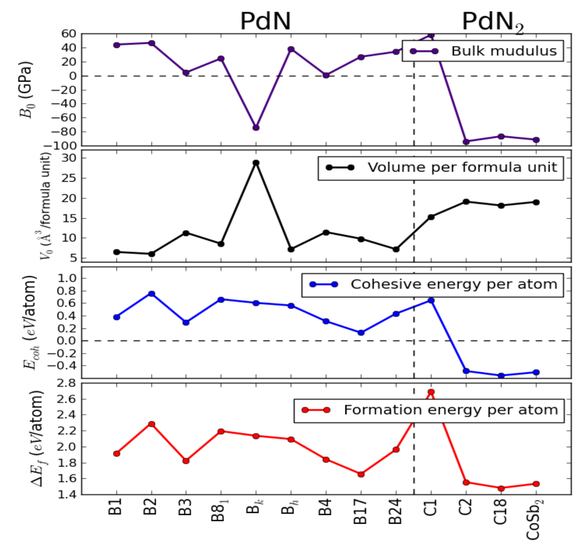


Figure 3: DFT calculated equilibrium properties of the 13 studied phases of palladium nitrides. All quantities are given relative to the fcc crystalline palladium: B_0 = *163.5* GPa, V_0 = *15.47 Å^3/atom*, E_{coh} = *-3.706 eV/atom*. Notice the large increase in the separation between ions of the metal sub-lattice in all structures. This is a common behavior of all PM nitrides [1].

GW CALCULATIONS AND OPTICAL PROPERTIES

* Start from KS eigenfunctions and eigenvalues, use many-body perturbation theory (MBPT) and solve the quasi-particle (QP) equations:

$$\left\{-\frac{\hbar}{2m}\nabla^2+\int d\boldsymbol{r}'\frac{n(\boldsymbol{r})}{|\boldsymbol{r}-\boldsymbol{r}'|}+V_{ext}(\boldsymbol{r})\right\}\varphi_{nk}^{QP}(\boldsymbol{r})+\int d\boldsymbol{r}'\,\Sigma\left(\boldsymbol{r},\boldsymbol{r}';\epsilon_{nk}^{QP}\right)\varphi_{nk}^{QP}(\boldsymbol{r}')=\epsilon_{nk}^{QP}\,\varphi_{nk}^{QP}(\boldsymbol{r})$$

* Use Hedin's *GW approximation* to the self-energy **Σ**.
* Calculate the dielectric tensor ε(ω) within the random phase approximation (RPA) to obtain the screened Coulomb interaction *W*.
* Follow the GW_0 self-consistent routine on the Green's function *G* of the many-electron system.
* Derive optical constants from the real and the imaginary parts of the updated $\varepsilon_{RPA}(\omega)$**:**

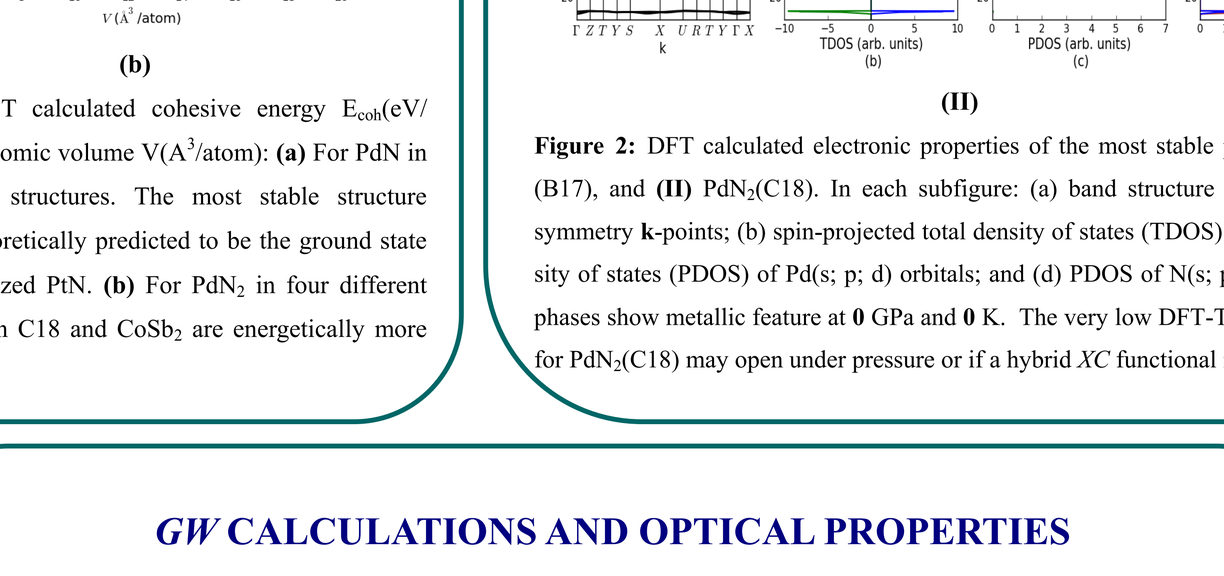


Figure 4: The real and the imaginary parts of the frequency-dependent dielectric function and the corresponding derived optical constants of PdN(B24). Absorption coefficient shows that this high-pressure competing phase [Fig. 5(b)] is metallic.

PRESSURE-INDUCED PHASE TRANSITIONS

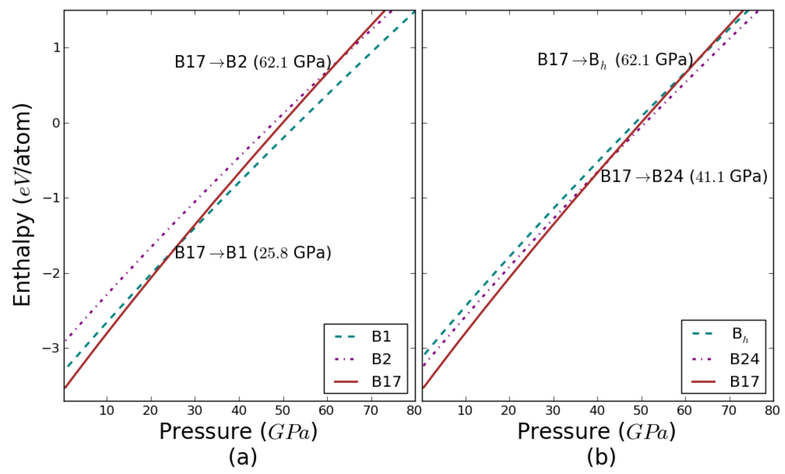


Figure 5: Enthalpy-pressure relations for some PdN phases in the phase transition pressure regions, revealing four possible transitions from B17 to (a) B1, B2, (b) B_h and B24. In this parameter sub-space, B17 is preferred below 25 GPa, while B24 is favoured at pressures above 41 GPa.

CONCLUSION

We have successfully employed *ab initio* DFT calculations to investigate the structural and electronic properties of some possible stoichiometries and crystal structures of the recently discovered palladium nitride. From the study of the equation of state (EOS), we identified the energetically most stable phases and determined their equilibrium structural parameters. Electronic properties were investigated by calculating the band-structure and the total and partial density of states (DOS). The more sophisticated GW approach was invoked to investigate excitation energies and optical properties of this promising material.