Structural, electronic and optical characterization of bulk platinum nitrides:
a first-principles study

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We present a detailed quantum mechanical non empirical DFT investigation of the energy-optimized geometries, phase stabilities and electronic properties of bulk PtN, PtN and PtN2 in a set of twenty different crystal structures. Structural preferences for these three stoichiometries were analyzed and equilibrium structural parameters were determined. We carefully investigated the band-structure and density of states of the relatively most stable phases. Further, GW0 calculations within the random-phase approximation (RPA) to the dielectric tensor were carried out to derive their frequency-dependent optical constants of the most likely candidates for the true crystal structure. Obtained results were comprehensively compared to previous calculations and to experimental data.

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I. INTRODUCTION

Platinum is known to form simple binary compounds with other elements (e.g. PtF4, PtI2, PtO and PtS)1. However, platinum had not been known to form crystalline solid nitride, but other forms of platinum nitrides (e.g. PtN1,2, PtN2,1, (PtN)21,2 and Pt2N2) had been observed.

In January 2004, Soto3 reported the preparation of platinum thin films containing up to ~ 14 at. % nitrogen. The study concluded that platinum can form an incipient nitride phase with composition near to Pt0N. Few months later, in May 2004, Gregoryanz and co-workers1 published the discovery and characterization of solid crystalline platinum mono-nitride for the first time. The synthesis was carried out above 45 GPa and 2000 K but with complete recovery of the product at room pressure and temperature. The produced samples have a very high bulk modulus leading to important implications in high-pressure physics and technology. The 1:1 stoichiometry was assigned to the new nitride, and according to their XRD measurements, Gregoryanz et al. proposed three structures: B1, B3 and B17 (for description of the structures see sub-section II A below), all based on the Pt fcc sub-lattice. Due to some considerations, B1 and B17 were ruled out and B3 was assigned to the new product.

In addition to the well-crystallized and highly ordered regions, a common feature in the synthesized platinum nitrides is the presence of sub- or/and super-stoichiometric phases containing N or Pt vacancies and residual non-stoichiometric material distributed throughout the samples1,4.

The work of Gregoryanz et al.1 has stimulated many further theoretical studies5–7 as expected by Gregoryanz and co-workers1 themselves. However, theoretical work showed that PtN(B3) is elastically and thermodynamically unstable (see sub-section III A below). Accordingly, claiming that large errors are generally inevitable in the used experimental characterization methods6,8, and due to other paradoxical facts9 in the original experiment by Gregoryanz et al.,1 theorists questioned the chemical stoichiometry and the crystal structure of this new material and started to investigate other possibilities8–10. Moreover, the experimentally reported1 high bulk modulus of the platinum nitride has not been reproduced by any reliable calculations and its mechanism is still an unclear open problem9,10.

These investigations led to a kind of consensus that the compound does not crystallize in the proposed PtN(B3) phase4, but the true stoichiometry and the true crystal structure have become now a matter of debate6,9.

In an apparent attempt to respond to this debate, Crowhurst et al.4 managed, in 2006, to reproduce and characterize platinum nitride. Combining theory with
their own observed Raman spectrum, they came up with a conclusion to propose PtN$_2$ (C2) and rejected PtN(B3), proposed by the first platinum nitride synthesizers, and PtN$_2$ (C1), proposed in some theoretical works. Like the first proposed structures, C1$^8$ and C$_2$$^4$ structures have the fcc sub-lattice of the metal.

Despite the considerable number of the subsequent theoretical studies, the discrepancy between theory and experiment in the structural and the physical properties of this nitride is not yet satisfactorily understood. Nevertheless, many transition metals can form more than one nitride$^{11}$. Thus, it is of interest to know if platinum can form nitrides with different stoichiometries and/or crystal structures other than those proposed by the first platinum nitride synthesizers and other researchers.

In the present work, we present a comprehensive first-principles calculations of the equation of state, possible pressure-induced phase transitions, electronic and optical properties of crystalline Pt$_3$N, PtN and PtN$_2$ in a total of twenty different, previously proposed and new hypothetical structural modifications. The work partly aims to solve some of the reported discrepancies. In addition, to the best of our knowledge, there is no available experimental or theoretical optical data for the platinum nitride, and the present study may be the first one to calculate the optical spectra of platinum nitrides.

II. CALCULATION METHODS

A. Stoichiometries and Crystal Structures

The structure and stability of solids are influenced by their chemical stoichiometry$^{12}$ and the electronic structure of the outer shells of atoms is a controlling factor in proposing any crystal structure$^{13}$. Like other theoretical works (cf. Table I) we postulated various structure types that are not based on the observed fcc Pt sub-lattice. Our assignment of the following different chemical stoichiometries and crystal structures is based on the fact that many transition-metal nitrides (TMNs) are known to form more than one nitride$^{11}$. Ni, which shares the same group with Pt, and Au which shares the same period with Pt in the periodic table, are known to form Ni$_3$N and Au$_3$N nitrides. Thus, it is of interest to consider more Pt atoms in the unit cell and less symmetry structures, and to know whether platinum can form Pt$_3$N with the reported structures of these and other 3:1 TMNs. In this work, the hypothetical Pt$_3$N is studied in the following seven structures: D0$_3$ (space group Fm$ar{3}$m), A15 (space group Pm$ar{3}$m), D0$_9$ (space group Pm$ar{3}$m), L1$_2$ (space group Pm$ar{3}$m), D0$_2$ (space group Im$ar{3}$m), b-Fe$_3$N (space group P6$_{3}$mc), and RhF$_3$ (space group R3c).

The following nine structures were assigned to PtN: B1 (space group Fm$ar{3}$m), B2 (space group Pm$ar{3}$m), B3 (space group F43m), B8$_1$ (space group P6$_3$/mmc), B$_k$ (space group P6$_3$/mmc), B$_h$ (space group P6m2), B4 (space group P6$_3$mc), B17 (space group P4$_2$/mmc) and B24 (space group Fm$ar{3}$m). While C1 (space group Fm$ar{3}$m), C2 (space group Pa3), C18 (space group Pnm$ar{m}$) and CoSb$_2$ (space group P2$_1$/c) are the four structures which were proposed for PtN$_2$.

B. Electronic Relaxation Details

As implemented in the all-electron Vienna ab initio Simulation Package (VASP)$^{14-19}$, our electronic structure calculations were based on spin density functional theory (SDFT)$^{20,21}$. To solve the self-consistent Kohn-Sham (KS) equations$^{22}$

$$-rac{k^2}{2m_e} \nabla^2 + \int \frac{dr'n(r')}{|r-r'|} + V_{\text{ext}}(r)$$

$$+ V_{\text{xc}}[n(r)] \psi_{\sigma,k}^i(r) = \epsilon_{\sigma,k}^i |\psi_{\sigma,k}^i(r)|,$$

where $i$, $k$ and $\sigma$ are the band, $k$-point and spin indices, respectively, the pseudo part of the KS orbitals $\psi_{\sigma,k}^i(r)$ are expanded on plane-waves (PWs) basis. Only those PWs with kinetic energy $\frac{1}{2m_e} |k+G| < E_{\text{cut}} = 600 \text{ eV}$ were included. This always corresponds to changes in the total electronic energy and in the so-called Fermi energy $E_F$ that are less than 3 meV/atom and 0.02 eV, respectively.

For ionic relaxation, the Brillouin zones (BZs) were sampled using $13 \times 13 \times 13 \Gamma$-centered Monkhorst-Pack meshes$^{23}$, while for the static calculations, $17 \times 17 \times 17$ meshes were used. Any increase in the density of this mesh corresponds to changes in the total energy and in Fermi energy $E_F$ that are less than 2 meV/atom and 0.02 eV, respectively.

Partial occupancies were set using the tetrahedron method with Blöchl corrections$^{24-26}$ for the static total energy and the electronic density of states (DOS) calculations; while in the ionic relaxation, the smearing method of Methfessel-Paxton (MP)$^{27}$ was used. In the latter case, the smearing width was set such that the fictitious entropy is always less than 1 meV/atom.

The Perdew, Burke and Ernzerhof (PBE)$^{28-30}$ parametrization of the generalized gradient approximation (GGA)$^{31-33}$ was employed for the exchange-correlation potentials $V_{\text{xc}}^i(r)$. VASP treats the core-valence interactions, $V_{\text{ext}}(r)$ using the projector augmented wave (PAW) method$^{19,34}$. The PAW potential explicitly treats the $2s^22p^3$ electrons of N and the $5d^{10}6s^1$ electrons of Pt as valence electrons.

In the standard mode of VASP, while fully relativistic calculations are performed for the core-electrons, only scalar kinematic effects are incorporated to treat the valence electronic structure$^{18}$. It was found that this scheme is sufficient and the spin-orbit interactions have little effect on the macro-physical properties of platinum nitride$^3$. Thus, we made no effort to consider spin-orbit coupling of the valence electrons.
The relaxation of the electronic degrees of freedom was performed using the blocked Davidson iteration scheme as implemented in VASP. The electronic self-consistent (SC) convergence was considered to be achieved when the difference in the eigenvalues and in the total energy between two successive steps are both less than $1 \times 10^{-4}$ eV.

C. Geometry Optimization and EOS

At a set of isotropically varying volumes of the unit cells, ions with internal free parameters were relaxed until all Hellmann-Feynman force components on each ion were less than $1 \times 10^{-2}$ eV/Å. Static total energy calculations (as described above) at each volume followed and the cohesive energy per atom was calculated from

$$E_{coh}^{Pt_mN_n} = \frac{E_{coh}^{solid}}{Z} - Z \times \left( mE_{atom}^{Pt} + nE_{atom}^{N} \right) \left( m+n \right).$$

(2)

Here, $Z$ is the number of Pt$_m$N$_n$ per unit cell, $E_{atom}^{Pt}$ and $E_{atom}^{N}$ are the energies of the spin-polarized non-spherical isolated Pt and N atoms, $E_{coh}^{solid}$ are the bulk cohesive energies calculated by VASP with respect to spherical non-spin-polarized reference atoms, and $m, n = 1, 2, 3$ are the stoichiometric weights.

The calculated $E_{coh}$ per atom as a function of volume $V$ per atom were fitted to a Birch-Murnaghan 3rd-order EOS

$$E(V) = E_0 + \frac{9V_0B_0}{16} \left( \left( \frac{V}{V_0} \right)^{\frac{1}{2}} - 1 \right)^3 B'_0 + \left( \left( \frac{V}{V_0} \right)^{\frac{1}{2}} - 1 \right)^2 \left( 6 - 4 \left( \frac{V}{V_0} \right)^{\frac{1}{2}} \right).$$

(3)

The four equilibrium fitting parameters: the equilibrium volume $V_0$, the equilibrium cohesive energy $E_0$, the equilibrium bulk modulus $B_0 = -V \frac{\partial P}{\partial V} |_{V = V_0}$, and its pressure derivative $B'_0 = \frac{\partial B}{\partial P} |_{P = 0} = \frac{1}{B_0} \left( V \frac{\partial}{\partial V} \left( V \frac{\partial E}{\partial V} \right) \right) |_{V = V_0}$ were determined by a least-squares method.

D. Formation Energy

In addition to $E_{coh}$, another important measure of relative stability is the so-called formation energy $E_f$. Assuming that the solid Pt$_m$N$_n$ results from the interaction between the solid Pt(fcc) metal and the gaseous N$_2$ through the chemical reaction

$$mPt_{solid} + \frac{n}{2}N_{2}^{gas} \rightarrow Pt_{m}N_{n}^{solid},$$

$E_f$ can be obtained from

$$E_f(Pt_mN_n) = E_{coh}(Pt_mN_n^{solid}) - mE_{coh}(Pt_m^{solid}) + \frac{n}{2}E_{coh}(N_2^{gas}),$$

(7)

where $m, n = 1, 2, 3$ are the stoichiometric weights and $E_{coh}(Pt_mN_n^{solid})$ is the cohesive energy per atom as obtained from Eq. 2. The ground-state cohesive energy and other equilibrium properties of the elemental platinum $E_{coh}(Pt_{solid})$ in its fcc A1 structure (space group Fm3m No. 225) are given in Table I. We found the equilibrium cohesive energy of the molecular nitrogen ($E_{coh}(N_2^{gass})$) and its N–N bond length to be $-5.196$ eV/atom and 1.113 Å. For details on how these properties were calculated, readers are referred to Ref. 43.

E. GWA Calculations and Optical Properties

Accurate quantitative description of optical properties of materials requires treatments beyond the level of DFT. One choice is to follow the method which is provided by the many-body perturbation theory (MBPT). In this approach one needs to solve a system of quasi-particle (QP) equations

$$\left\{ -\frac{\hbar^2}{2m} \nabla^2 + \int \frac{d^3r'}{|\mathbf{r} - \mathbf{r'}|} + V_{ext}(\mathbf{r}) \right\} \psi_{i,k}^{QP}(r) = \epsilon_{i,k}^{QP} \psi_{i,k}^{QP}(r).$$

(8)

In practice, one takes the wave functions $\psi_{i,k}^{QP}(r)$ from the DFT calculations. However, this technique is computationally expensive, and we had to use less dense meshes of k-points: $(10 \times 10 \times 10)$ in the case of B17 and $(12 \times 12 \times 12)$ in the case of B3. The quantity $\Sigma(r, r'; \epsilon_{i,k}^{QP})$ in Eqs. 8 above is known as self-energy. It contains all the static and dynamic exchange and correlation effects, including those neglected at the DFT-GGA level. When $\Sigma$ is written in terms of the Green’s function $G$ and the frequency-dependent screened Coulomb interaction $W$ as

$$\Sigma_{GW} = \text{Re} \int d\epsilon \, G(r, r'; \epsilon, \epsilon') W(r, r'; \epsilon),$$

(9)

the approximation is referred to as GW approximation. The dynamically screened interaction $W$ is related to the bare interaction $v$ via

$$W(r, r'; \epsilon) = \text{Re} \int d\mathbf{r}_1 \frac{1}{\epsilon_0} (r, r_1; \epsilon) v(r_1, r'),$$

(10)

where the dielectric matrix $\epsilon$ is calculated within the random phase approximation (RPA). The QP eigenvalues

$$\epsilon_{i,k}^{QP} = \text{Re} \left( \langle \psi_{i,k}^{QP} | H_{KS} - V_{XC} + \Sigma_{GW} | \psi_{i,k}^{QP} \rangle \right).$$

(11)
are updated in the calculations of $G$, while $W$ is kept at the DFT-RPA level. This is called the $GW_0$ self-consistent routine on $G$. After the execution of the fourth iteration, $\varepsilon$ is recalculated within the RPA using the updated QP eigenvalues.\textsuperscript{46–48} It is straightforward then to calculate all the frequency-dependent optical spectra (e.g. refractive index $n(\omega)$, extinction coefficient $\kappa(\omega)$, absorption coefficient $\alpha(\omega)$, reflectivity $R(\omega)$ and transmittivity $T(\omega) = 1 - R(\omega)$) from the real $\varepsilon_{\text{re}}(\omega)$ and the imaginary $\varepsilon_{\text{im}}(\omega)$ parts of $\varepsilon_{\text{RPA}}(\omega)$.\textsuperscript{49–51}

\begin{equation}
n(\omega) = \frac{1}{\sqrt{2}} \left( \left[ \varepsilon_{\text{re}}^2(\omega) + \varepsilon_{\text{im}}^2(\omega) \right]^{\frac{1}{2}} + \varepsilon_{\text{re}}(\omega) \right)^{\frac{1}{2}} \tag{12}\end{equation}

\begin{equation}\kappa(\omega) = \frac{1}{\sqrt{2}} \left( \left[ \varepsilon_{\text{re}}^2(\omega) + \varepsilon_{\text{im}}^2(\omega) \right]^{\frac{1}{2}} - \varepsilon_{\text{re}}(\omega) \right)^{\frac{1}{2}} \tag{13}\end{equation}

\begin{equation}\alpha(\omega) = \sqrt{2} \omega \left( \left[ \varepsilon_{\text{re}}^2(\omega) + \varepsilon_{\text{im}}^2(\omega) \right]^{\frac{1}{2}} - \varepsilon_{\text{re}}(\omega) \right)^{\frac{1}{2}} \tag{14}\end{equation}

\begin{equation}R(\omega) = \frac{\left| \varepsilon_{\text{re}}(\omega) + j\varepsilon_{\text{im}}(\omega) \right|^2 - 1}{\left| \varepsilon_{\text{re}}(\omega) + j\varepsilon_{\text{im}}(\omega) \right|^2 + 1} \tag{15}\end{equation}

It may be worth to emphasize here that for more accurate optical properties (e.g. more accurate amplitudes and positions of the characteristic peaks), electron-hole excitations should be calculated by solving the so-called Bethe-Salpeter equation, the equation of motion of the two-body Green function $G_2$. The latter can be evaluated on the basis of our obtained GW one-particle Green function $G$ and QP energies.\textsuperscript{52}

\section{RESULTS AND DISCUSSION}

Cohesive energy $E_{\text{coh}}$ versus atomic volume $V_0$ equation of state (EOS) for the different phases of Pt$_3$N, PtN$_2$ and PtN are displayed graphically in Fig. 1, Fig. 2 and Fig. 3, respectively. The corresponding obtained equilibrium structural parameters and energetic and elastic properties are presented in Table I. In this table, as well as in Fig. 4, structures are first grouped according to the nitrogen content, starting with the stoichiometry with the lowest nitrogen content Pt$_3$N, followed by the 1:1 series and ending with the nitrogen-richest PtN$_2$ group. Within each series, structures are ordered according to their structural symmetry, starting from the highest symmetry (i.e. the highest space group number) to the least symmetry. Whenever possible, our results are compared with experiment and with previous calculations. In the latter case, the calculations methods and the $XC$ functionals are indicated in the Table footnotes.

To study the effect of nitridation on the elemental Pt(A1) and to easily compare the properties of these phases relative to each other, the calculated equilibrium properties are displayed relative to the corresponding ones of Pt(A1) in Fig. 4.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{(Color online.) Cohesive energy $E_{\text{coh}}$(eV/atom) versus atomic volume $V$ (Å$^3$/atom) for Pt$_3$N in seven different structural phases.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig2.png}
\caption{(Color online.) Cohesive energy $E_{\text{coh}}$(eV/atom) versus atomic volume $V$ (Å$^3$/atom) for PtN in nine different structural phases.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3.png}
\caption{(Color online.) Cohesive energy $E_{\text{coh}}$(eV/atom) versus atomic volume $V$ (Å$^3$/atom) for PtN$_2$ in four different structural phases.}
\end{figure}
Table I. The calculated (Pres.) zero-pressure properties of the platinum nitrides and the results of previous calculations (Comp.). The available experimental data are given in the last row.

| Comp. | a(Å) | b(Å) | c(Å) | α(°) | V0(Å³/atom) | E90(eV/atom) | B0(GPa) | B'0 | E(0)(eV/atom) |
|-------|------|------|------|------|-------------|--------------|---------|-----|----------------|
| Pt    | 3.978| 15.74| −5.451| 242.999 | 5.486 | 281.8, 281º | 5.184 | 5.215 | 293.84, 5.238 |
| A1    | 3.924| 15.076| −5.84| 273.3, 281º | 5.184 | 5.215 | 293.84, 5.238 |
| Comp. | 3.909, 3.890, 3.981 | 3.907, 3.960 | −7.53, 3.74, 305.5, 320.8, 238 | 249, 242, 244, 218.44 | 5.16, 5.307, 5.258 | 5.23, 5.83, 5.28 |
| PLN  | 4.924 | 14.92 | −3.79 | 194.136 | 5.16 | 1.268 | 1.268 |
| B1    | 4.54 | 11.41 | −4.85 | 102.839 | 5.241 | 0.829 | 0.829 |
| Comp. | 4.924 | 14.92 | −3.79 | 194.136 | 5.16 | 1.268 | 1.268 |
| B2    | 4.54 | 11.41 | −4.85 | 102.839 | 5.241 | 0.829 | 0.829 |
| Comp. | 4.924 | 14.92 | −3.79 | 194.136 | 5.16 | 1.268 | 1.268 |
| B3    | 4.721, 4.825, 4.779 | 4.7095, 4.814 | −3.74, 190.58, 3.91, 194 | 244, 219, 213 | 4.09, 1.1 | 0.95 | 0.95 |
| Comp. | 4.682, 4.786, 4.769 | 4.809, 4.70, 4.699 | −3.74, 190.58, 3.91, 194 | 244, 219, 213 | 4.09, 1.1 | 0.95 | 0.95 |
| B4    | 4.54 | 11.41 | −4.85 | 102.839 | 5.241 | 0.829 | 0.829 |
| Comp. | 4.924 | 14.92 | −3.79 | 194.136 | 5.16 | 1.268 | 1.268 |
| B17   | 4.54 | 11.41 | −4.85 | 102.839 | 5.241 | 0.829 | 0.829 |
| Comp. | 4.924 | 14.92 | −3.79 | 194.136 | 5.16 | 1.268 | 1.268 |
| C1    | 4.942, 5.005, 4.957 | 4.866, 4.958, 4.939 | −3.918, 263.295 | 4.74, 1.367 | 1.367 | 1.367 |
| Comp. | 4.924, 4.957 | 4.866, 4.958, 4.939 | −3.918, 263.295 | 4.74, 1.367 | 1.367 | 1.367 |
| C2    | 4.924 | 11.41 | −4.85 | 102.839 | 5.241 | 0.829 | 0.829 |
| Comp. | 4.924 | 11.41 | −4.85 | 102.839 | 5.241 | 0.829 | 0.829 |
| C18   | 4.924 | 11.41 | −4.85 | 102.839 | 5.241 | 0.829 | 0.829 |
| Comp. | 4.924 | 11.41 | −4.85 | 102.839 | 5.241 | 0.829 | 0.829 |

**Table Note:**

- **Pt:** Using the projector augmented wave (PAW) method within LDA.
- **B1:** Using the full-potential linearized augmented plane wave (LAPW) method within GGA.
- **B2:** Using the semi-empirical estimate based on the calculation of the slope of the shock velocity.
- **B3:** Using the full-potential linearized augmented plane wave (LAPW) method within GGA.
- **B4:** Using the full-potential linearized augmented plane wave (LAPW) method within GGA.
- **B17:** Using the full-potential linearized augmented plane wave (LAPW) method within GGA.
- **C1:** Using the full-potential linearized augmented plane wave (LAPW) method within GGA.
- **C2:** Using the full-potential linearized augmented plane wave (LAPW) method within GGA.
- **C18:** Using the full-potential linearized augmented plane wave (LAPW) method within GGA.
- **CoSb:** Using the full-potential linearized augmented plane wave (LAPW) method within GGA.

**Notes:**

- Ref. 53: This is an average of 23 experimental values, at room temperature.
- Ref. 54: Coesite cohesive energies are given at 0 K and 1 atm = 0.0001 GPa; while bulk moduli are at room temperature.
- Ref. 25: in 55; at room temperature.
- Ref. 8: See Refs. [8]–[11] in 55.
- Ref. 56: Using the full-potential linearized augmented plane waves (LAPW) method within LDA.
- Ref. 57: Using the projector augmented wave (PAW) method within LDA.
- Ref. 58: Using the semi-empirical method in which the experimental static P – V data are fitted to an EOS form. The given values are estimated at ~298 K.
- Ref. 59: Using the semi-empirical method in which the experimental static P – V data are fitted to an EOS form. The given values are estimated at ~298 K.
FIG. 4. (Color online.) Calculated equilibrium properties of the twenty studied phases of platinum nitrides. All quantities are given relative to the corresponding ones of the fcc crystalline elemental platinum given in the first row of Table I.
A. EOS and Relative Stabilities

Fig. 1 reveals that Pt₃N in its least symmetric phase, the trigonal (rhombohedral) structure of RhF₃, is the most favorable phase in this series. However, after ∼15.9 Å³/atom the EOS of Pt₃N(RhF₃) is almost identical with the EOS of Pt₃N in the simple cubic structure of the anti-ReO₃ (D₀₉). They share a minimum at ∼(17.4 Å³/atom, −4.56 eV). Very close to this point, at ∼(17.23 Å³/atom, −4.59 eV), the EOS of Pt₃N(D₀₂) has a kink due to a change in the positions of some Pt ions.

The EOS of Pt₃N(Fe₃N) has two minima located at (14.11 Å³/atom, −4.697 eV) and (18.26 Å³/atom, −4.679 eV). Thus, the two minima are very close in energy but, due to the difference in V₀, they correspond to bulk moduli of 222.7 GP and 169.0 GP, respectively. The Pt ions are in the 6q Wyckoff positions: (x, 0, 0), (0, x, 0), (−x, x, 0), (−x, −x, 0), (−x, 0, 1/2), (0, −x, 1/2) and (x, x, 1/2). Upon ion relaxation of Pt₃N(Fe₃N), atomic positions change from x ∼ 1/3 to x = 1/2 causing the sudden change in the potential surface (at ∼16.83 Å³/atom) as the bulk Pt₃N(Fe₃N) being decompressed (Fig. 1). It may be worth mentioning here that Ag₃N(Fe₃N) and Cu₃N(Fe₃N) were found to behave in a similar manner.

Hence, one of the two minima in the EOS of Pt₃N(RhF₃) is shared with the minimum of the EOS of Pt₃N(D₀₉) and the other is shared with one of the two minima of Pt₃N(Fe₃N).

The crossings of the less stable D₀₉, L1₂ and A15 EOS curves with the more stable D₀₂ EOS at the left side of their equilibria indicates that D₀₂ would not survive under pressure and that possible pressure-induced phase transitions from the latter phase to the former ones may occur.

Fig. 4 shows that the Pt₃N most stable phases may energetically compete with the PtN and PtN₂ most stable ones. However, from the foregoing discussion, it seems that Pt₃N would not have a simple potential surface.

Using the full potential augmented plane wave plus local orbitals (APW+lo) method within GGA(PBE), the energy-volume EOS’s for B₁, B₂, B₃ and B₄ have been studied by the authors of Ref. 59. Some of their obtained equilibrium properties are included and referred to in Table I. Within the considered parameter sub-space, our obtained EOS’s (Fig. 2), relative stabilities, and equilibrium structural parameters and mechanical properties (Table I) are in excellent agreement with their findings. However, relaxing the c/a parameter, they obtained an additional EOS which lies below all the other considered ones, but its equilibrium B₀ is significantly smaller.

From Fig. 2, it is evident that PtN(B₁₇) is the energetically most stable phase in the PtN series. The difference in the equilibrium $E_{coh}$ between PtN(B₁₇) and the next (less) stable phase, PtN(B₃), is about 0.5 eV (Table I). This difference was found by other researchers to be 0.9−1.05 eV. The crossings of the EOS curve of B₁₇ with some of those of less stability at the left side of their equilibrium reveals possible pressure-induces phase transitions. To closely investigate these transitions, we plot the corresponding relations between enthalpy $H = E(V) + PV$ and the imposed external pressure P. Possible transitions and the pressures at which they occur are carefully depicted. A point where two $H(P)$ curves (of two modifications with the same chemical stoichiometry) meet represents a phase transition from the phase with the higher $H$ to the one with the lower $H$.

From the $H(P)$ diagrams (not shown here) we found that PtN(B₁₇) would transform to PtN(B₁, B₂, B₆ or B₂₄) at ∼ 93 GPa, ∼ 143 GPa, ∼ 193 GPa or ∼ 123 GPa, respectively.

It may be worth to mention here a few points about this B₁₇ structure: (i) It was theoretically predicted to be the ground-state structure of Cu₃N⁴³, Ag₃N⁵¹, AuN⁶² and PdN⁶³. (ii) The same foregoing phase PtN-PtN structural pressure-induced transitions have been predicted for PdN, but at relatively smaller pressures in the range (25.8 ∼ 62.1 GPa)⁶³. (iii) B₁₇ is the structure of PtS⁶⁴ and PtO⁹. (iv) It was found by other authors to be a possible ground state for PtN⁹. (v) The B₁₇ structure has an fcc Pt sub-lattice (as the synthesized platinum nitride), but it is tetragonal and the sub-lattice are highly distorted ($c/a ≈ 3$ versus $c/a = \sqrt{2}$ for ideal fcc), and probably because of this distortion it was rejected by the platinum nitride synthesizers. (vi) Fig. 5 that B₁₇ is energetically favorable over B₁ and B₃ at all pressures.

Nevertheless, PtN(B₁₇) was found to be elastically unstable¹⁰. Assuming 1:1 stoichiometry, the first platinum nitride synthesizers assigned the B₃ structure for their product¹. However, it was shown in the same work that PtN(B₃) should break down or transform at pressures above 12 GPa. In agreement with this experimental prediction, Fig. 5 shows that PtN(B₃) would not survive at pressures above 19 GPa where the B₃→B₁ phase transition occurs. Other theoretical works also predicted that B₁ becomes more favorable than B₃ structure above 13.3 GPa⁹, ∼ 15 GPa⁷, 16.5 GPa⁹, and 17.6 GPa⁹.

Therefore, we support Ref. ⁹ on the judgment that, unless the PtN(B₃) was formed upon depressurization, its production at 45−50 GPa³ is questioned. Further, first-principles calculations showed that PtN(B₃) is elastically unstable⁵,⁶,⁸, and that it may distort spontaneously to a tetragonal lattice to lower the energy⁸.

In the PtN₂ series, we can see from Table I and from Fig. 4 that PtN₂ in the simple orthorhombic structure of Fe₃S marcasite (C₁₈) is the most stable phase, while the face-centered cubic structure of CaF₂ fluorite (C₁) is significantly the least favorable structure. Yet, Fig. 5 reveals that the latter PtN₂(C₁) is more favorable than the proposed PtN(B₁, B₃ and B₁₇) at pressures above
and from Fig.
I arrived at an astonishing result: the experimentally
and Ag
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obtained an
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reveal

try to optimize the lattice parameters ratios (see Table
modifications. While we sticked to the original C18
three considered PtN modifications (B1, B3 and B17), and the
four considered PtN3 structures in the present work (C1, C2, C18 and CoSb2). The arrows indicate the pressures at which
curves cross each other. From these curves, it is clear that PtN2(C18), followed by
PtN2(C2), are the most energetically favorable phases at all
pressure. At pressures above 10 GPa, PtN2(CoSb2)
has lower enthalpy than the rest of the modifications, including
PtN(B17) and PtN2(C1). At pressures higher
than 8 GPa, PtN(B17) becomes more favorable than
Pt3N(Rhf3), but the former never competes behind
52 GPa when PtN2(C1) becomes more favorable. How-
ever, Pt3N(Rhf3) is more stable than PtN(B3) at all
pressures. In summary, Fig. 5 reveals that even if a PtN
phase has been observed (at pressures around 50 GPa),
this phase must be unstable toward phase decomposition
into solid constituents Pt and PtN2 (see also Ref. 7)
or into Pt and Pt3N. However, the series of the possible
phase transitions must be carefully investigated.

![Graph](image.png)

FIG. 5. (Color online.) Enthalpy $H$ vs. pressure $P$ equation
of state (EOS) for the most favorable Pt3N phase (Rhf3), the
three proposed PtN modifications (B1, B3 and B17), and the
four considered PtN3 structures in the present work (C1, C2,
C18 and CoSb2). The arrows indicate the pressures at which
curves cross each other.

4 GPa, 14 GPa and 52 GPa, respectively. Others found
PtN2(C1) to be more favorable than PtN(B3) at
pressures above 30 GPa.

In contrast to our enthalpy-pressure EOS’s in Fig.
Chen, Tse and Jiang60 obtained an $H(P)$ curve
for C18 which lies always above the curve for C2 and
coincides with the one of CoSb2. They concluded that
C2 is the most stable structure among these three
modifications. While we sticked to the original C18
relative dimensions, it seems that Chen, Tse and Jiang
tried to optimize the lattice parameters ratios (see Table
I). However, the $c : a : b$ ratio they obtained is very
close to our $a : b : c$ ratio, and the difference in $V_0$ is
less than 0.03 Å$^3$/atom.65 Another difference is the
atomic electronic configuration of Pt 5d$^6$6s$^2$ they used.
Nevertheless, they agreed with us that in the 0 – 60 GPa
pressure range, no transition between these three phases
occurs.

Comparing the relative stability of the three most sta-
bile compositions, we find from Table I and from Fig.
that PtN2(C18) is the most favorable, followed by
Pt3N(Rhf3), and the least stable phase is PtN(B17).
However, the differences in their equilibrium $E_{coh}$ lies
within a narrow range of 0.036 eV. Relative to their par-
etal material, all phases have higher $E_{coh}$, i.e. they are less
bound than Pt(A1). Hence, we found, as other theoretical
works8, that platinum nitride can be stabilized in
stoichiometries and structures other than that proposed
by the first synthesizers1.

In Ref. 9, the energy-volume EOS for B1, B3, B17,
C1, and C2 have been studied using DFT-GGA. Within
this parameter sub-space, our obtained EOS’s (Figs. 2,
3 and 4) are in excellent agreement with the findings of
9. From the relative enthalpy-pressure diagrams66, Ref.
9 arrived at an astonishing result: the experimentally
proposed PtN(B3) is an entirely unstable structure at
any pressure.

To closely study the non-zero pressure stoichiometric
and structural preferences, we displayed in Fig. 5 the
enthalpy $H$ vs. pressure $P$ equation of states (EOS) for
the most favorable Pt3N phase (Rhf3), the three pre-
viously proposed PtN modifications (B1, B3 and B17),
and the four considered PtN3 structures in the present
work (C1, C2, C18 and CoSb2). The arrows indicate
the pressures at which curves cross each other. From
these curves, it is clear that PtN2(C18), followed by
PtN2(C2), are the most energetically favorable phases at
all pressure. At pressures above 10 GPa, PtN2(CoSb2)
has lower enthalpy than the rest of the modifications, including
PtN(B17) and PtN2(C1). At pressures higher
than 8 GPa, PtN(B17) becomes more favorable than
Pt3N(Rhf3), but the former never competes behind
52 GPa when PtN2(C1) becomes more favorable. How-
ever, Pt3N(Rhf3) is more stable than PtN(B3) at all
pressures. In summary, Fig. 5 reveals that even if a PtN
phase has been observed (at pressures around 50 GPa),
this phase must be unstable toward phase decomposition
into solid constituents Pt and PtN2 (see also Ref. 7)
or into Pt and Pt3N. However, the series of the possible
phase transitions must be carefully investigated.

B. Volume per Atom and Lattice Parameters

The obtained equilibrium volume per atom $V_0$, i.e. the
inverse of the number density, for all the considered mod-
ifications are numerically presented in Table I and graphi-
cally depicted relative to the Pt(A1) in Fig. 4. On aver-
age, Pt3N phases tend not to change the number density of
the host parent Pt(A1); PtN phases tend to slightly
increase it; while the PtN2 increase it significantly.

It is also evident from Fig. 4 that in crossing the board-
ers between the Pt3N and PtN and between the PtN and
PtN2 islands, i.e. in increasing the N content, $V_0$ tends
to decrease while the volume per Pt atom $V_{0^{Pt}}$, a measure
of the average Pt–Pt bond length, tends to increase. The
latter finding has been found to be true for the nitrides
of Cu43 and Ag61 as well.

C. Bulk Modulus and its Pressure Derivative

With only a few exceptions, Fig. 4 and Table I reveal
that nitridation of Pt apparently tends to reduce its bulk
modulus. Relative to each other, the twenty $B_0$’s show no
clear trend. The most energetically favorable PtN phase,
B17, has 42 GPa higher bulk modulus than the proposed
PtN(B3).

As we mentioned somewhere else67, $B_0$ is far more sen-
titive to any change in volume than the change in $E_{coh}$.
The case of PtN(B2) is a clear example, in which the
slight decrease in $V_0$ overcomes the significant increase in
Given that all the considered phases have higher $E_{\text{coh}}$ than Pt(A1), the foregoing argument fails to explain the decrease in $B_0$ in the case of the structures which have lower $V_0$ than their parent Pt(A1) and have lower $E_{\text{coh}}$ than the extreme case PtN(B2). However, if one replaces $V_0$ in the argument above with $V_0^{\text{Pt}}$, the contradiction can be lifted. Therefore, we believe that the mechanical properties in these nitrides may be dominated by the effect of the Pt-Pt bond length more than the simple number density.

Although the GGA calculated $B_0$ values in the present and previous works (Table I) are far smaller than the reported experimental value, our obtained bulk modulus for PtN$_2$(C1) is 20 GPa higher than that of Pt(A1). This is exactly the measured value for Pt after the PtN formation took place. The observation was considered by Gregoryanz et al. as an indication that some N is dissolved in Pt$^1$. Recalling that the $B_0$ of the produced platinum nitride is $\sim 100$ GPa than that of Pt(A1)$^3$, our GGA-obtained $B_0$ for PtN$_2$(C1) is $\sim 80$ GPa less than the experimental value$^{68}$.

It may be worth to notice from Table I that the lattice parameter $a$ of PtN$_2$(C1) is 0.13 Å higher than that of PtN(B3); yet the $B_0$ of the former is $\sim 70$ GPa higher than the latter. This difference in $B_0$ can be attributed to the fact that in B3, N atoms occupy only half of the tetrahedral interstitial sites of the Pt sub-lattice, while in C1, the four remaining tetrahedral interstitial sites are filled with N atoms$^{8,9,69}$. This filling significantly reduces the compressibility but slightly increases the volume of the unit cell. This fact can also be seen readily as a consequence of the difference in the average volume per atom in the two cases (Table I).

The pressure derivative of the bulk modulus, $B'_0$, measures the sensitivity of $B_0$ to any external pressure. The top subfigure in Fig. 4 reveals that the bulk modulus of Pt$_3$N(Fe$_3$N) and PtN$_2$(C2, C18 and CoSb$_2$) increase upon application of external pressure. Pt$_3$N(D$_0$) is very sensitive and its $B_0$ will increase significantly under an infinitesimal excess of pressure. Pt$_3$N(L1$_2$ and RhF$_3$) tend to be inert; while Pt$_3$N(D$_0$$_3$, A15 and D$_0$$_9$), PtN$_2$(C1) and all PtN phases tend to decrease their bulk modulus upon application of external pressure. Although $B'_0$ is a measurable quantity$^{55}$, we couldn’t find any experimental value to test our obtained values against.

### D. Formation Energies

From Fig. 4 and Table I, it is evident that formation energy $E_f$ has the same trend as the cohesive energy $E_{\text{coh}}$. If $E_f$ is taken as a measure of synthesized, then the relatively most favorable Pt$_3$N phases have the same synthesized as the most favorable PtN and PtN$_2$.

A positive value of $E_f$ means, in principle, that, at the temperature and pressure at which $E_f$ is calculated, the phase is thermodynamically unstable (endothermic) and have a tendency to decompose into its constituent components. In our case, this observation is corroborated by the experimental fact that the synthesis of the platinum nitrides was achieved only at high temperature and temperature$^{6,60}$.

Using different methods, other researchers$^{4,6,60}$ obtained positive (zero-pressure and zero-temperature) formation energies for some PtN and/or PtN$_2$ phases. Some of their values are included in Table I with indication to the methods of calculations.

The obtained relative difference in $E_f$ for PtN$_2$(C1) and PtN$_2$(C2) is in good agreement with Ref. 4. However, the differences in our and their obtained $E_f$ values can be attributed to three factors: First, the difference in the obtained lattice parameter (see Table I). Second, the value of our calculated equilibrium free parameter $u$ is 0.417 while Ref. 4 obtained 0.415$^{70}$. Third, and the most significant source of difference, the experimental value of $E_{\text{coh}}(N_2^{\text{gas}})$ in Eq. 7 was used by Ref. 4, while we calculated it as described in sub-section IID.

It may be worth mentioning here that a negative theoretical value of $E_f = -0.4 \ eV/\text{atom}$ was obtained for PtN$_2$(C2) at $P = 50 \ \text{GPa}$, showing excellent agreement with experiment$^4$. Moreover, Young et al.$^9$ claimed that PtN$_2$ dissociates upon mild heating below $P = 10 \ \text{GPa}$.

### E. Electronic Properties

The DFT obtained band diagrams $E(k)$ and spin-projected total and partial densities of states (DOS) of the most stable modifications: Pt$_3$N(Rhf$_3$), PtN(B3 and B17), and PtN$_2$(C18) are displayed in Figs. 6, 7, 8 and 9, respectively. Spin-projected total density of states (TDOS) are shown in sub-figure (b) in each case. Because in these four considered cases electrons occupy the spin-up and the spin-down bands equally, it was sufficient only to display spin-up DOS and spin-up band diagrams. Displaying the energy bands along densely sampled high-symmetry strings of $k$-points allows us to extract information about the electronic structure of these phases. Moreover, to investigate the details of the orbital character of the bands, the Pt($s,p,d$) and N($s,p$) resolved DOS’s are plotted at the same energy scale.

With The Fermi surface crossing the partly occupied bands, it is clear from Figs. 6, 7, and 8 that Pt$_3$N(Rhf$_3$) PtN(B3) and PtN(B17) are metals.

The TDOS of Fig. 9(b) reveal that PtN$_2$(C18) is a semiconductor with (Fig. 9(a)) its valence band maximum (VBM) at ($Y$, −0.091 eV) and its conduction band minimum (CBM) at ($Y$, 0.044 eV), resulting in a narrow direct energy band gap $E_g = 0.135 \ eV$ of width. Below this fundamental gap there are three bands: the deep one at $\sim −20.5 \ eV$ consists mainly of the N(2$s$) states. Its high DOS and sharp feature correspond to its little and slow energy variation in the $k$–space. The second band
FIG. 6. (Color online.) DFT calculated electronic structure for Pt$_3$N in the RhF$_3$ structure: (a) band structure along the high-symmetry $k$-points which are labeled according to Ref. [71]. Their coordinates w.r.t. the reciprocal lattice basis vectors are: $F(0.5, 0.5, 0.0)$, $Q(0.375, 0.625, 0.0)$, $B(0.5, 0.75, 0.25)$, $Z(0.5, 0.5, 0.5)$, $\Gamma(0.0, 0.0, 0.0)$, $L(0.0, 0.5, 0.0)$, $Y(0.25, 0.5, -0.25)$, $\Sigma(0.0, 0.5, -0.5)$; (b) spin-projected total density of states (TDOS); (c) partial density of states (PDOS) of Pt($s, p, d$) orbitals in Pt$_3$N; and (d) PDOS of N($s, p$) orbitals in Pt$_3$N.

FIG. 7. (Color online.) DFT calculated electronic structure for PtN in the B3 structure: (a) band structure along the high-symmetry $k$-points which are labeled according to Ref. [71]. Their coordinates w.r.t. the reciprocal lattice basis vectors are: $\Gamma(0.0, 0.0, 0.0)$, $X(0.0, 0.5, 0.0)$, $W(0.75, 0.25, 0.5)$, $L(0.5, 0.5, 0.5)$, $K(0.750, 0.375, 0.375)$, $U(0.625, 0.250, 0.625)$; (b) spin-projected total density of states (TDOS); (c) partial density of states (PDOS) of Pt($s, p, d$) orbitals in PtN; and (d) PDOS of N($s, p$) orbitals in PtN.

*a The coordinates of the W point is not as the same as in Ref. [71], but they are equivalent. Also, the coordinates of U and K are not given in Ref. [71]. The coordinates of U, K and the equivalent W were created by means of XCrystalDen!*

FIG. 8. (Color online.) DFT calculated electronic structure for PtN in the B17 structure: (a) band structure along the high-symmetry $k$-points which are labeled according to Ref. [71]. Their coordinates w.r.t. the reciprocal lattice basis vectors are: $X(0.0, 0.5, 0.0)$, $M(0.5, 0.5, 0.0)$, $\Gamma(0.0, 0.0, 0.0)$, $Z(0.0, 0.0, 0.5)$, $A(0.5, 0.5, 0.5)$, $R(0.0, 0.5, 0.5)$; (b) spin-projected total density of states (TDOS); (c) partial density of states (PDOS) of Pt($s, p, d$) orbitals in PtN; and (d) PDOS of N($s, p$) orbitals in PtN.
is relatively narrow (~ 2.2 eV of width) with low density and 

staining mainly from a mixture of the N states with 

Pt(d) states. The superposition Pt(d) and N(p) states 

in the region from −10.314 eV to −0.091 eV below the 

fundamental gap constitutes the third band with highly 

structured, intense and narrow series of peaks. Our 

obtained TDOS and PDOS show excellent agreement with Ref. 60 where also PtN(C18) was predicted to be a 

semiconductor, but band diagrams and \( E_g \) value are not 

given.

It may be worth mentioning here that PtN(B1)\(^1\) and 

PtN(B4)\(^59\) were found to be metallic, PtN(C1) was 

found to be a poor metal\(^8\), PtN(C18)(CoSb)\(^60\) was found to 

be a semiconductor, and an indirect band gap between 

1.2 eV\(^60\) and 1.5 eV\(^8\) has been obtained for PtN(C2).

F. Optical Properties

\(GW\) calculations were carried out for the PtN(B3) and 

PtN(B17) metallic phases at their equilibrium. Figs. 10 

and 11 display the obtained real and imaginary parts of 

the frequency-dependent dielectric function \(\varepsilon_{\text{RPA}}(\omega)\) of 

these two phases and the corresponding derived optical 

spectra (Eqs. 12–15). In each sub-figure, the optical re-

gion \([\sim (3.183 - 1.655)\ eV \equiv (390 - 750)\ nm]\) is shaded.

The non-vanishing absorption coefficient \(\alpha(\omega)\) in 

the whole range for both phases confirms their metallic 

character. As it should be the case, refraction \(n(\omega)\) and 

extinction \(k(\omega)\) coefficients behave as the real \(\varepsilon_{\text{re}}(\omega)\) and 

the imaginary \(\varepsilon_{\text{im}}(\omega)\) dielectric functions, respectively.

As one can see from sub-figure 10(d), close to the edge 

of the optical region at \(\sim (1.762\ eV = 703.768\ nm)\) 

PtN(B3) is 50% reflector and 50% transmitter. From 

\(\sim (2.071\ eV = 598.579\ nm)\) to the UV region, PtN(B3) is 

only \(~ 40%\) reflecting but \(~ 60%\) transmitting. However, more 

of the transmitted portion in this region will be 

absorbed as the photon energy increases. This fact can 

be readily noticed if one compares sub-figures 10(c) and 

10(d).

PtN(B17), as can be seen from sub-figure 11(d), is a very 

good reflector in the whole region until 

\(\sim (3.000\ eV = 413.281\ nm)\) where it equally reflects and 

transmits the violet light. However, less of the transmit-

ted portion in the optical region will be absorbed as the 

photon wavelength decreases. This fact can be readily 

observed in sub-figures 11(c).

According to the best of our knowledge, there is no 

available experimental optical spectra for the platinum 

nitride. However, from their visual appearance, all the 
synthesized platinum nitride samples look very shiny and 
darker than their parent platinum in reflected light and 
totally opaque in transmitted light. These features 
suggest that PtN is either a poor metal or a semiconductor 
with a small band gap\(^1\).

From Figs. 11 and 8, the above mentioned properties 

are strongly met by PtN(B17), but purely seen (Figs. 10 

and 7) in PtN(B3), as discussed above. Unfortunately, 

we did not carry out optical calculations for PtN\(_2\)(C1 or 

C2).

G. PtN versus PtN\(_2\)

Using our own obtained results in the present work as 

well as the findings of other researchers, below we make 
a comparison between the PtN modifications (supported 

by the experimentalists) and the PtN\(_2\) phases (supported 

by the theoreticians):

- Given that GGA calculated lattice parameters are 

usually overestimated\(^72-74\), the obtained values of 

the \(a\) lattice parameter for PtN\(_2\)(C1 and C2) are 

the closest ones to the experimental value (to within 3 % and 2 \%, respectively), while the PtN 

phases are in poor agreement with experiment, as 

can be seen in Table I.

- First-principles studies of transition metals nitrides 

show that the \(B_0\)'s of the elemental metals are 
generally enhanced by nitridation\(^175\). Compared 
to experiment, Table I and Fig. 4 reveal that this trend is met by PtN\(_2\)(C1), while PtN(B3) has 
50 GPa lower than Pt(A1).

- Like the first synthesized sample and the proposed 

PtN(B3) modification\(^1\), PtN\(_2\)(C1\(^8\) and C2\(^4\) have 

fcc sub-lattice of Pt.

- PtN\(_2\)( C1\(^8\), C2\(^6, 60\), C18\(^60\) and CoSb\(_2\)\(^60\)) have 

all been found to be elastically stable, while 

PtN(B3\(^5, 6, 8, 10\) and B17\(^10\)) were found to be elas-

tically unstable.

- Formation and cohesive energies of PtN\(_2\)(C2, C18 

and CoSb\(_2\)) are lower than that of PtN(B3) [Table 

I and Fig. 4].

- In excellent agreement with experiment, the calculated 

formation energy of PtN\(_2\)(C2) at \(P = 50\ GPa\) 

was calculated to be negative\(^4\), while calculations 

found PtN(B3) to be thermodynamically unstable 
at all pressures\(^9\).

- The experimentally obtained Raman spectrum of the 

reproduced platinum nitride\(^4\) matches closely 

that of pyrite (FeS\(_2\)), i.e. in the C2 structure, 

but does not match the PtN(B3) spectrum that 

expected from group theory\(^4\).

- The theoretically calculated\(^6, 60\) Raman spectrum 

for PtN\(_2\)(C2) shows good agreement with the first 

experimentally obtained one\(^1\).

- In agreement with the experimental observation 

and the visual appearance of the first produced 

platinum nitrides\(^1\), PtN\(_2\)(C1) was found to be a
FIG. 9. (Color online.) DFT calculated electronic structure for PtN$_2$ in the C18 structure: (a) band structure along the high-symmetry $k$-points which are labeled according to Ref. [71]. Their coordinates w.r.t. the reciprocal lattice basis vectors are: $\Gamma(0,0,0,0), X(0,0,0.5,0.0), S(-0.5,0.5,0.0), Y(-0.5,0.0,0.0), Z(0.0,0.0,0.5), U(0.0,0.5,0.5), R(-0.5,0.5,0.5), T(-0.5,0.0,0.5)$; (b) spin-projected total density of states (TDOS); (c) partial density of states (PDOS) of Pt($s,p,d$) orbitals in PtN$_2$; and (d) PDOS of N($s,p$) orbitals in PtN$_2$.

FIG. 10. (Color online.) The GW calculated frequency-dependent optical spectra of PtN(B3): (a) the real $\varepsilon_{re}(\omega)$ and the imaginary $\varepsilon_{im}(\omega)$ parts of the dielectric function $\varepsilon_{BPA}(\omega)$; (b) refraction $n(\omega)$ and extinction $\kappa(\omega)$ coefficients; (c) absorption coefficient $\alpha(\omega)$; and (d) reflectivity $R(\omega)$ and transmittivity $T(\omega)$. The shaded window highlights the optical region.

FIG. 11. (Color online.) The GW calculated frequency-dependent optical spectra of PtN(B17): (a) the real $\varepsilon_{re}(\omega)$ and the imaginary $\varepsilon_{im}(\omega)$ parts of the dielectric function $\varepsilon_{BPA}(\omega)$; (b) refraction $n(\omega)$ and extinction $\kappa(\omega)$ coefficients; (c) absorption coefficient $\alpha(\omega)$; and (d) reflectivity $R(\omega)$ and transmittivity $T(\omega)$. The shaded window highlights the optical region.
poor metal\textsuperscript{8}, and we found PtN\textsubscript{2}(C18) to be a semiconductor with a small band gap.

Hence, in contrast to the proposed PtN modifications, PtN\textsubscript{2} phases possess many similar properties as the synthesized phase\textsuperscript{76}.

IV. CONCLUSIONS

In summary, we presented a systematic series of first-principles calculations of the energy-optimized geometries, phase stabilities and electronic and optical properties of bulk Pt\textsubscript{2}N, PtN and PtN\textsubscript{2} in twenty different crystal structures. Comprehensive comparison with experiment and with previous calculations has been made, and excellent agreement has been achieved. We found that both the lowest energy and the highest bulk modulus phases belong to the PtN\textsubscript{2} series and not to the PtN family. Moreover, the calculated electronic and optical properties of the PtN\textsubscript{2} phases show stronger consistency with experiment than the claimed PtN(B3) phase. In the present work, we have investigated a wider parameter sub-space than previous calculations, and to the best of our knowledge, the present work is the first to propose and to study the physical properties of Pt\textsubscript{2}N, as well as the first to theoretically calculate the optical spectra of this new material. However, optical properties of PtN\textsubscript{2}(C1 and C2) have not been investigated, and we strongly recommend optical calculations for these phases and obtained results should be tested against experiment. Moreover, experimentalists should provide the community with more data.

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Surprisingly, Chen, Tse and Jiang got exactly the same $V_0$ values for C2 and C18 within both GGA and LDA; but the average values they gave are different! Thus, we suspect the equal $V_0$ values they gave for C2 and C18 in both GGA and LDA (see Table 1 in that article); and it may be a typo.

These are $H(P)$ diagrams but relative to their elemental constituents.

Recall that we only consider values relative to Pt(A1) to eliminate systematic errors.

Fixing the lattice parameter at the experimental value $a = 4.8041$ Å, Ref. 6 relaxed the N ions and obtained the same value $u = 0.415$.

Such an observation was arrived at by other authors for the PtN(C1). Here we are making more comprehensive comparison.