Quantum mechanical *ab initio* calculations of the structural, electronic and optical properties of bulk gold nitrides

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In the present work, the atomic and the electronic structures of Au$_3$N, AuN and AuN$_2$ are investigated using first-principles density-functional theory (DFT). We studied cohesive energy vs. volume data for a wide range of possible structures of these nitrides. Obtained data was fitted to a Birch-Murnaghan third-order equation of state (EOS) so as to identify the most likely candidates for the true crystal structure in this subset of the infinite parameter space, and to determine their equilibrium structural parameters. The analysis of the electronic properties was achieved by the calculations of the band structure and the total and partial density of states (DOS). Some possible pressure-induced structural phase transitions have been pointed out. Further, we carried out GW$_0$ calculations within the random-phase approximation (RPA) to the dielectric tensor to investigate the optical spectra of the experimentally suggested modification: Au$_3$N(D0$_9$). Obtained results are compared with experiment and with some available previous calculations.

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I. INTRODUCTION

In 2002, Šiller and co-workers$^1$ at the University of Newcastle reported direct observation of the formation of an Au$_2$N compound for the first time. Since then, single crystal and polycrystalline gold nitrides have been prepared with different methods$^{2,3}$, and many theoretical$^{4,7}$ and experimental$^{2,4,8-11}$ investigations on the structural and physical properties of gold nitride have been published. It turned out that gold nitride possesses interesting properties which may lead to potential practical applications$^{11}$.

So far, the most significant finding may be that of Šiller et al$^8$ who, in 2005, reported the production of metallic large area gold nitride films which are ~ 50% harder than pure gold films produced under similar conditions, making the gold nitride ideal for use in large-scale applications in coatings and in electronics. Moreover, the possibility of patterning gold nitride film surfaces by electron/photon beam lithography was confirmed$^{11}$.

From their experimental observations and *ab initio* calculations, Krishnamurthy *et al.*$^4$ suggested the possibility of formation of more than one gold nitride phase. Although theoretical calculations have predicted several possible structures for AuN, AuN$_2$ and Au$_3$N, none of these agrees with experiment$^2$.

To identify the most likely candidates for the true stoichiometry and the true crystal structure, we investigate the structure preference and thermodynamic stability of gold nitride in three different chemical formulas: Au$_3$N, AuN, and AuN$_2$ in 20 structural modifications. The electronic properties of the most stable candidate in each stoichiometric series, and the optical properties of a previously suggested modification: Au$_3$N(D0$_9$) are carefully studied.

II. CALCULATION DETAILS

A. Stoichiometries and Crystal Structures

Information about the considered crystal structures are given in Table I below. In this table, structures are first grouped according to the nitrogen content, starting with the stoichiometry with the lowest nitrogen content Au$_3$N, followed by the 1:1 series and ending with the nitrogen-richest AuN$_2$ 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.

The studied structural phases of Au, AuN, AuN, and AuN2. Presented are the Strukturbericht designation (symbol), the underlying Bravais lattice (BL), prototype compounds, the space group (SG), and the number of AuN formulas per unit cell (Z).

| Symbol | BL | Prototype(s) | SG | Z |
|--------|----|--------------|----|---|
| A1     | fcc | Cu           | Fm3m | 1 |
| A15    | sc  | Cr3Si        | Fm3m | 2 |
| D03    | fcc | AlFe3        | Fm3m | 1 |
| D09    | sc  | anti-ReO3 (α), Cu3N | Fm3m | 1 |
| L12    | sc  | Cu3Au        | Fm3m | 1 |
| D02    | hcc | Ca3As3 (skutterudite) | Im3 | 4 |
| c-Fe3N | hexagonal | c-Fe3N, Ni3N | P6322 | 2 |
| RbF3   | trigonal (rhomboedric) | RbF3 | R3c | 2 |
| B1     | fcc | NaCl         | Fm3m | 1 |
| B2     | sc  | CsCl         | Fm3m | 1 |
| B3     | fcc | ZaS (zincblende) | F43m | 1 |
| B61    | hexagonal | NiAs | P63/mmc | 2 |
| Bx     | hexagonal | BN | P63/mmc | 2 |
| Bn     | hexagonal | WC | P6m2 | 1 |
| B4     | hexagonal | ZnS (wurtzite) | P6m2c | 2 |
| B17    | s tetragonal | PtS (cooperite) | P42/mmc | 2 |
| B24    | fc orthorhombic | TIF | Fmmm | 1 |
| C1     | fcc | CaF2 (fluorite) | Fm3m | 1 |
| C2     | sc  | Fe3S2 (pyrite) | Pm3 | 4 |
| C18    | s orthorhombic | Fe3S2 (marcasite) | Pnmm | 2 |
| CoSb2  | s monoclinic | CoSb2 | P21/c | 4 |

### B. Electronic Relaxation Details

VASP code\(^{12-17}\) was used for electronic structure spin density functional theory (SDFT)\(^{18,19}\) calculations. Here, a projector augmented wave (PAW)\(^{17,20}\) description of the ion-electron interaction $V_{ext}(r)$ is implemented, where the 5$d^{10}6$s$^{1}$ electrons of Au and the 2$s^22$p$^3$ electrons of N are treated explicitly as valence electrons. While the PAW potential treats the core electrons in a fully relativistic fashion\(^{16}\), only scalar kinematic relativistic effects for these valence electrons are incorporated. Spin-orbit interactions of the valence electrons have not been considered. The Kohn-Sham (KS) equations\(^{21}\)

$$\begin{align*}
-\frac{\hbar^2}{2m_e} \nabla^2 + \int dr' \frac{n(r')}{|r-r'|} + V_{ext}(r) + V_{XC}(n(r)) \psi_{i}^{\sigma,k}(r) &= \varepsilon_i^{\sigma,k} \psi_{i}^{\sigma,k}(r),
\end{align*}$$

where $i$, $k$, and $\sigma$ are the band, $k$-point, and spin indices, receptively, are solved by expanding the pseudo part of the KS one-particle spin orbitals $\psi_{i}^{\sigma,k}(r)$ on a basis set of plane-waves (PWs). It is found that the total energy converged to $< 3$ meV/atom using cut-off energy $E_{cut} \leq 600$ eV and $\Gamma$-centered Monkhorst-Pack\(^{22}\) $17 \times 17 \times 17$ meshes for the Brillouin zones (BZs) sampling. In the ionic relaxation stage, partial occupancies were set using the smearing method of Methfessel-Paxton (MP)\(^{23}\) and Fermi surface of the metallic phases has been carefully treated, while the tetrahedron method with Böchl corrections\(^{24-26}\) was used in the static calculations. The Perdew-Burke-Ernzerhof (PBE)\(^{27-29}\) GGA\(^{30-32}\) exchange-correlation functional $V_{XC}(n(r))$ was employed.

### C. Geometry Relaxation and EOS

To optimize the geometry, those atoms which possess internal free parameters were allowed to move till all Hellmann-Feynman force components\(^{33}\) on each ion were $< 1 \times 10^{-2}$ eV/A; then static total energy calculation (as described in Subsection II B) followed. This was done at a set of isotropically varying volumes of the unit cells, and cohesive energy per atom $E_{coh}^{AuNa}$ was calculated from\(^{34,35}\)

$$E_{coh}^{AuNa} = \frac{E_{solid}^{AuNa} - Z \times (mE_{atom}^{Au} + nE_{atom}^{N})}{Z \times (m + n)}. \quad (2)$$

Here, $Z$ is the number of AuNa formulas per unit cell (as in Table I), $E_{atom}^{Au}$ and $E_{atom}^{N}$ are the energies of the spin-polarized non-spherical isolated Au and N atoms, respectively, $E_{solid}^{AuNa}$ are the bulk cohesive energies calculated by VASP with respect to spherical non spin-polarized isolated atoms, and $m, n = 1, 2$ or 3 are the stoichiometric weights.

The calculated $E_{coh}^{AuNa}$ versus volume per atom $V$ were least-squares-fitted\(^{36}\) with a 3rd-order Birch-Murnaghan equation of state (EOS)\(^{37}\)

$$E(V) = E_0 + \frac{9V_0B_0}{16} \left( \left( \frac{V}{V_0} \right)^\frac{5}{2} - 1 \right)^3 \frac{B_0}{V_0}$$

$$+ \left[ \left( \frac{V}{V_0} \right)^\frac{7}{2} - 1 \right]^2 \left[ 6 - 4 \left( \frac{V}{V_0} \right)^\frac{7}{2} \right] \right). \quad (3)$$

The fitting parameters: the equilibrium volume $V_0$, the equilibrium cohesive energy $E_0$, the equilibrium bulk modulus

$$B_0 = -\frac{V_0}{V'=V_0} \frac{\partial P}{\partial V} \bigg|_{V'=V_0} = -\frac{V_0}{V'=V_0} \frac{\partial^2 E}{\partial V^2} \bigg|_{V'=V_0}, \quad (4)$$

and its pressure derivative

$$B'_0 = \frac{\partial B}{\partial P} \bigg|_{P=0} = \frac{1}{B_0} \left( V_0 \frac{\partial}{\partial V} \left( \frac{\partial^2 E}{\partial V^2} \right) \right) \bigg|_{V=V_0}, \quad (5)$$

were then determined.
D. Formation Energy Calculations

Beside cohesive energy, another important measure of relative stability is the so-called formation energy $E_f$. Assuming the following chemical reaction between the solid Au(fcc) metal and the gaseous $N_2$

$$m \text{Au}^{\text{solid}} + \frac{n}{2} N_2^{\text{gas}} \rightarrow \text{Au}_m N_n^{\text{solid}} ,$$

$E_f$ of the solid $\text{Au}_m N_n$ can be obtained from (see Eq. 2 for definitions of the quantities):

$$E_f(\text{Au}_m N_n^{\text{solid}}) = E_{\text{coh}}(\text{Au}_m N_n^{\text{solid}}) - m E_{\text{coh}}(\text{Au}^{\text{solid}}) + \frac{n}{2} E_{\text{coh}}(N_2^{\text{gas}}) .$$

We found the equilibrium cohesive energy of the molecular nitrogen $E_{\text{coh}}(N_2^{\text{gas}})$ and its N–N bond length to be $5.196 \text{eV/atom}$ and $1.113 \text{Å}$, respectively. The ground-state cohesive energy $E_{\text{coh}}(\text{Au}^{\text{solid}})$ and other equilibrium properties of the elemental gold in its standard Al structure are given in Table II.

E. GWA Calculations

In order to obtain quantitatively accurate optical spectra of $\text{Au}_3 N(D0_h)$, one must go beyond the level of DFT. A practical method is the so-called GW method. In this technique, which is provided by many-body perturbation theory (MBPT), a system of quasi-particle (QP) equations

$$\left\{-\frac{\hbar^2}{2m} \nabla^2 + \int dr' \frac{n(r')}{|r-r'|} + V_{\text{ext}}(r) \right\} \psi_{i,k}^{\text{QP}}(r) + \int dr' \Sigma(r,r';\epsilon_{i,k}) \psi_{i,k}^{\text{QP}}(r') = \epsilon_{i,k}^{\text{QP}} \psi_{i,k}^{\text{QP}}(r)$$

is to be solved; where wave functions $\psi_{i,k}^{\text{QP}}(r)$ are taken from the DFT calculations. However, this approach is computationally demanding, and one had to use less dense meshes of $k$-points, $10 \times 10 \times 10$, while keeping $E_{\text{cut}}$ at 600 eV.

The so-called self-energy $\Sigma(r,r';\epsilon_{i,k})$ in Eqs. 8 above, is a quantity that contains all the static and dynamic exchange and correlation effects, including those neglected in the DFT-GGA reference system. Writing $\Sigma$ in terms of the Green’s function $G$ and the frequency-dependent screened Coulomb interaction $W$ as

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

gives rise to the term GW approximation (GWA). $W$ and the bare Coulomb interaction $v$ are related via

$$W(r, r'; \epsilon) = j \int dr r^{-1} \langle r, r; \epsilon | v(r, r') \rangle ,$$

where the dielectric Cartesian tensor $\varepsilon$ (in this case is diagonal and isotropic because of the cubic nature of $\text{Au}_3 N(D0_h)$) is calculated within the random phase approximation (RPA).

Following the so-called $GW_0$ routine, the QP eigenvalues

$$\epsilon_{i,k}^{\text{QP}} = \text{Re} \left( \langle \psi_{i,k}^{\text{QP}} | H_{\text{KS}} - V_{\text{XC}} + \Sigma_{GW_0} \psi_{i,k}^{\text{QP}} \rangle \right)$$

were updated four times in the calculations of $G$, while $W$ was kept at the DFT-RPA level. Using the updated QP eigenvalues, $\varepsilon$ was recalculated after the execution of the last iteration.

F. Optical Spectra Calculations

Assuming orientation of the $\text{Au}_3 N(D0_h)$ crystal surface parallel to the optical axis, it is straightforward then to derive all the desired frequency-dependent optical spectra (e. g. reflectivity $R(\omega)$, refractive index $n(\omega)$, energy-loss $L(\omega)$ and absorption coefficient $\alpha(\omega)$) from the real $\varepsilon_{\text{re}}(\omega)$ and the imaginary $\varepsilon_{\text{im}}(\omega)$ parts of $\varepsilon_{\text{RPA}}(\omega)$.

$$R(\omega) = \left| \frac{\varepsilon_{\text{re}}(\omega) + j \varepsilon_{\text{im}}(\omega)}{\varepsilon_{\text{re}}(\omega) + j \varepsilon_{\text{im}}(\omega)} \right|^2 - \frac{1}{\varepsilon_{\text{im}}(\omega)}$$

$$n(\omega) = \frac{1}{\sqrt{2}} \left( \frac{\varepsilon_{\text{re}}(\omega) + \varepsilon_{\text{im}}^2(\omega)}{\varepsilon_{\text{re}}(\omega) + \varepsilon_{\text{im}}^2(\omega)} \right)^{1/2} + \varepsilon_{\text{re}}(\omega)$$

$$L(\omega) = \frac{\varepsilon_{\text{im}}(\omega)}{\varepsilon_{\text{re}}^2(\omega) + \varepsilon_{\text{im}}^2(\omega)}$$

$$\alpha(\omega) = \sqrt{2} \omega \left( \frac{\varepsilon_{\text{re}}^2(\omega) + \varepsilon_{\text{im}}^2(\omega)}{\varepsilon_{\text{re}}^2(\omega) + \varepsilon_{\text{im}}^2(\omega)} \right)^{1/2}$$

It should be emphasized here that to obtain more accurate optical spectra (that is, more accurate positions and amplitudes of the characteristic peaks), one should solve the so-called Bethe-Salper equation, the equation of motion of the two-body Green function $G_2$, in order to obtain the electron-hole excitations. However, $G_2$ can be evaluated on the basis of our obtained $GW_0$ one-particle Green function $G$ and QP eigenvalues.

III. RESULTS

Cohesive energy $E_{\text{coh}}$ versus atomic volume $V_0$ equation of state (EOS) for the considered modifications of $\text{Au}_3 N$, $\text{AuN}$ and $\text{Au}_3 N_2$ are displayed graphically in Figs. 1, 2 and 3, respectively. The corresponding calculated equilibrium structural, energetic and mechanical properties of these twenty phases and of $\text{Au}(1)$ are presented in Table II. Modifications in this table are ordered in the same way as in Table I. 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.
TABLE II. Calculated and experimental zero-pressure properties of Au(A1) and of the twenty studied phases of AuN, AuN and AuN²: Lattice constants [a(Å), b(Å), c(Å), α(°) and β(°)], equilibrium atomic volume V₀(Å³/atom), bulk modulus B₀(GPa) and its pressure derivative B₀', and formation energy E₂(eV/atom). The presented data are of the current work (Pres.), experimentally reported (Expt.) and of previous calculations (Comp.).

| Structure | Pres. | a(A) | b(A) | c(A) | α(°) | β(°) | V₀(A³/atom) | Ecoh(eV/atom) | B₀(GPa) | B₀' | E₂(eV/atom) |
|-----------|-------|------|------|------|------|------|-------------|--------------|---------|-----|-------------|
| Au        |       |      |      |      |      |      |             |              |         |     |             |
| A1        | 4.174 | 18.18|       |      |      |      | -2.982      | 135.363      | 5.926   |     |             |
| Exp.      |       |      |      |      |      |      |             |              | -3.81b  |      |             |
| Comp.     |       |      |      |      |      |      |             |              | 173.2b  | 6.29d|             |
| D0₁       | 6.368 |      |      |      |      |      | -2.238      | 133.110      | 5.656   |     | 1.297       |
| A15       | 5.124 |      |      |      |      |      | -2.084      | 121.792      | 5.645   |     | 1.451       |
| D0₂       | 4.336 |      |      |      |      |      | -2.695      | 95.370       | 5.518   |     | 0.840       |
| Comp.     |       |      |      |      |      |      |             |              |         |     |             |
| Li₂       | 4.017 |      |      |      |      |      | -2.254      | 135.621      | 5.686   |     | 1.281       |
| D0₃       | 8.672 |      |      |      |      |      | -2.695      | 95.692       | 5.551   |     | 0.840       |
| c-Fe₇N   | 5.473 |      |      |      |      |      | -2.546      | 253.363      | 5.551   |     | 0.989       |
| RhF₉      | 6.075 |      |      |      |      |      | -2.694      | 95.859       | 5.534   |     | 0.841       |
| AuN       |       |      |      |      |      |      |             |              |         |     |             |
| B1        | 4.670 |      |      |      |      |      | 12.73       | 170.385      | 5.178   |     | 1.678       |
| B2        | 2.912 |      |      |      |      |      | 12.35       | 170.874      | 5.269   |     | 2.035       |
| B3        | 4.989 |      |      |      |      |      | 15.52       | 126.414      | 5.119   |     | 1.711       |
| B₈        | 3.600 |      |      |      |      |      | 14.05       | 151.504      | 5.271   |     | 1.945       |
| B₉        | 3.508 |      |      |      |      |      | 24.86       | 73.343       | 5.126   |     | 1.772       |
| B₁₀       | 3.138 |      |      |      |      |      | 13.96       | 163.369      | 5.285   |     | 1.866       |
| B₁₁       | 3.526 |      |      |      |      |      | 15.54       | 20.842       | 5.711   |     | 1.707       |
| B₁₇       | 3.119 |      |      |      |      |      | 13.74       | 170.760      | 5.334   |     | 0.984       |
| B₂₄       | 4.380 |      |      |      |      |      | 13.08       | 161.383      | 5.092   |     | 1.714       |
| C₁        | 5.162 |      |      |      |      |      | 11.46       | 195.138      | 4.890   |     | 2.124       |
| Comp.     |       |      |      |      |      |      |             |              | 246a    |      |             |
| C₂        | 5.471 |      |      |      |      |      | 14.69       | 26.129       | 7.643   |     | 0.816       |
| Comp.     |       |      |      |      |      |      |             |              | 198a    |      |             |
| C₁₈       | 3.467 |      |      |      |      |      | 14.59       | 27.178       | 7.609   |     | 0.836       |
| Comp.     |       |      |      |      |      |      |             |              | 126a    |      |             |
| CoSb₂ₜ    | 6.219 |      |      |      |      |      | 10.679      | 151.225      | 15.67   |     | 0.791       |
| Comp.     |       |      |      |      |      |      |             |              | 11.430  |      |             |

a Ref. 31. This is an average of 40 experimental values, at 20 °C, with a deviation: ±0.0002 Å.
b Ref. 52. Cohesive energies are given at 0 K and 1 atm = 0.00010(GPa); while bulk moduli are given at room temperature.
c Ref. 25 in 33. at room temperature.
d Ref. 55. LAPW-TB.
e Ref. 54. LAPW-LDA.
ô Ref. 55. PAW-LDA.
ô Ref. 55. PAW-PW91.
ô Ref. 53: using the so-called method of transition metal pseudopotential theory; a modified form of a method proposed by Wills and Harrison to represent the effective interatomic interaction.
ô Ref. 53: using a semi-empirical estimate based on the calculation of the slope of the shock velocity vs. particle velocity curves obtained from the dynamic high-pressure experiments. The given values are estimated at ~ 298 K.
f Ref. 53: using a semi-empirical method in which the experimental static P − V data are fitted to an EOS form where B₀ and B₀' are adjustable parameters. The given values are estimated at ~ 298 K.
g Ref. 55: using Vanderbilt USPPs within GGA(PBE). B₀'s were calculated from the elastic constants. E₀coh(N₄⁰^solid) was used in Eq. 7 instead of E₀coh(N₄⁰^gas).
h Ref. 5: Using the full-potential linearized augmented plane waves (LAPW) method within LDA.
i Ref. 5: Using the full-potential linearized augmented plane waves (LAPW) method within GGA(PBE).
and, as mentioned above, we undertook (see Ref. 58), and we traced back this behavior to the structural relationships between these three phases (For more details, see Ref. 35 and references therein). As can readily be seen from Fig. 4 and Table II, these structural relations have manifested themselves in all the presented structural, energetic and mechanical properties, giving rise to almost identical values. Therefore, one may conclude that, if one phase is synthesizable, the three phases may co-exist during the Au3N synthesis process.

Noting that Cu, Ag and Au share the same group in the periodic table of elements, it may be worth to mention here that D09 structure is known to be the structure of the synthesized Cu3N59-61 and, as mentioned above, we found it to be the most stable structure of Ag3N58.

Assuming that it is the most likely stoichiometry, Krishnamurthy et al.4 undertook ab initio pseudopotential calculations on Au3N and studied all the Au3N structures in Table I. Although they found D09 to be the most stable modification in this sub-parameter space, yet, they identified a triclinic crystal structure with 0.25 eV/atom lower energy than the D09. Krishnamurthy and co-workers determined the triclinic phase to be metallic. It must be mentioned here that all the 3:1 structures we have investigated in the present study were taken mainly from the work of Krishnamurthy et al.4. However, Krishnamurthy et. al. gave only the lattice vectors of their triclinic structure, but no basis vectors were given. So, we were not able to properly place the atoms inside the cell they gave. Allowing them to relax, ions keep moving over the potential surface with no sign of a local minimum, and the structure seems to be very soft!

The odd behavior of the EOS curve of Au3N(Rhf3) with the existence of two minima (Fig. 1) reveals that the first minimum (the one with higher $E_{coh}$) is a metastable local minimum on the potential surface that cannot be maintained as the material is decompressed. The potential barrier, represented by the sudden drop of the Au3N(Rhf3) curve, at $\sim 18.4$ eV/atom is due to the change of positions of those metal ions which possess in-
FIG. 4. (Color online.) Calculated equilibrium properties of the twenty studied phases of gold nitrides. All quantities are given relative to the corresponding ones of the fcc crystalline elemental gold given in the first row of Table II.

cernal degrees of freedom.

Concerning the AuN series, it is evident from Fig. 2 that the simple tetragonal structure of cooperite (B17) would be the energetically most stable structure, with 0.694 eV/atom less than B1. This B17 structure was theoretically predicted to be the ground-state structure of CuN\textsuperscript{35}, AgN\textsuperscript{58} and PtN\textsuperscript{62,63}.

Kanoun and Said\textsuperscript{6} studied the $E(V)$ EOS for AuN in the B1, B2, B3 and B4 structures. Within this parameter sub-space, the relative stabilities they arrived at agree in general with ours. However, they predicted that B3 is always more stable than B4, while Fig. 2 shows that B4 is preferred against B3 only at low pressures.

In the AuN\textsubscript{2} series, the least symmetric simple CoSb\textsubscript{2} monoclinic structure is found to be the most stable (Fig. 3). This agrees with the conclusion of Ref. 7, where it is suggested that AuN\textsubscript{2} may be synthesized at extreme conditions (higher pressure and temperature) and/or it
that less stable phases tend to pre-
visualize these values rel-
shows that a transition from D0
unit cell, is visualized in the same subwindow.

may have other Au:N stoichiometric ratios than 1:2.

B. Pressure-induced phase transitions

Enthalpy-pressure relations of Au$_3$N for five considered structures are displayed in Fig. 5. A point at which enthalpies $H = E_{coh}(V) + PV$ of two structures are equal defines the transition pressure $P_t$, where transition from the phase with higher enthalpy to the phase with lower enthalpy may occur.

Fig. 5 shows that a transition from D0$_0$ phase to the Fe$_3$N phase would take place at a very low pressure $\sim 6.3$ GPa; and it is clear that the D0$_0$ phase is favourable only at low pressures below $\sim 6.3$ GPa, while the Fe$_3$N hexagonal structure of Ni$_3$N is favoured at higher pressures. Fig. 5 also reveals that L1$_2$ and D0$_3$ phases may co-exist over a wide range of pressure and that they are both favoured over D0$_9$ phase at pressures higher than $\sim 20$ GPa, while A15 would be favoured over D0$_9$ only at pressures higher than $\sim 33$ GPa.

C. Volume per Atom and Lattice Parameters

The numerical values of the equilibrium lattice parameters and the corresponding volume per atom $V_0$ for the twenty modifications are presented in Table II. The middle sub-window of Fig. 4 depicts the $V_0$ values relative to Au(A1). To measure the average of the Au–Au bond length in the silver nitride, the equilibrium average volume per Au atom ($V_{Au}^{0}$), which is simply the ratio of the volume the unit cell to the number of Au atoms in that unit cell, is visualized in the same subwindow.

From the $V_0$ curve in Fig. 4, we can see that, all AuN and AuN$_2$ modifications, except the open AuN(B$_k$) phase, decrease $V_0$; while the Au$_{35}$N phases tend, on average, not to change the number density of the parent Au(A1). The metal-metal bond length, as represented by the volume per metal atom $V_{Au}^{0}$, increases (on average) in the direction of increasing nitrogen content and decreasing structural symmetry.

Both trends in $V_0$ and in $\Delta V_{Au}^{0}$ were found to be true for copper$^{35}$, silver$^{58}$ and platinum$^{63}$ nitrides. The trend in $\Delta V_{Au}^{0}$, however, reveals the fact that in all these nitrides, the introduced N ions displace apart the ions of the host lattice causing longer metal-metal bonds than in the elemental parent metal. This cannot be seen directly from the $V_0$ values depicted in the same figure.

D. Bulk Modulus and its Pressure Derivative

The numerical values of the equilibrium bulk moduli and their pressure derivatives for the twenty modifications are presented in Table II. The second from top and the top sub-windows of Fig. 4 visualize these values relative to Au(A1).

In the Au$_3$N series, one can see from the second top subfigure of Fig. 4 that less stable phases tend to preserve the $B_0$ value of their parent Au(A1), while the most stable phases (D0$_9$, D0$_2$ and RhF$_3$) posses lower $B_0$ values.

Except B$_k$, AuN modifications and AuN$_2$(C1) tend, on average, to increase the $B_0$ value of their parent Au(A1), with the highest $B_0$ value possessed by the most stable AuN phase: B17.

The last least symmetric structures AuN$_2$(C2, C18 and CoSb$_2$) possess the lowest $B_0$ values among the 20 studied modifications. The $B_0$ values of AuN$_2$’s have the same trend as their corresponding $E_{coh}$’s and opposite trend as their corresponding $V_0^{Au}$’s.

From the top subfigure of Fig. 4 one can see that upon application of external pressure, all Au$_{35}$N and AuN phases and C1 phase tend to lower their $B_0$. The last AuN$_2$ three modifications, however, are more sensitive to external pressure, and their bulk moduli tend to increase under pressure.

E. Thermodynamic Stability

The numerical values of the calculated formation energy $E_t$ (Table II) and their graphical representation (Fig. 4) show clearly that all the twenty obtained $E_t$ values are positive. This, in principle, means that all these phases are thermodynamically unstable (endothermic). However, it is common that one obtains positive DFT-calculated $E_t$ for (even the experimentally synthesized) transition-metal nitrides. Moreover, the zero-pressure zero-temperature DFT calculations have to be corrected for the conditions of formation of these nitrides. Another source of this apparent shortcoming stems from the PBE-GGA underestimation of the cohesion in N$_2$. We have discussed this point further in Ref. 35. Nevertheless, formation energies in the present work are used
as a measure of the relative thermodynamic stabilities of the phases under consideration. That is, the lower the formation energy, the lower the tendency to dissociate back into the constituent components Au and N$_2$.

Fig. 4 shows that, relative to each other and within each series, the formation energy $E_f$ (defined by Eqs. 6 and 7) of the studied phases has the same trend as the cohesive energy$^{64}$. That is, all phases have the same relative stabilities in the $E_f$ space as in the $E_{coh}$ space. This trend was found to be true for the nitrides of Cu$^{65}$ and Ag$^{58}$ as well. However, while Au$_3$N phases tend to have comparable $E_{coh}$ as the AuN phases, all Au$_3$N modifications have a lower $E_f$ than the AuN ones, except B17. In fact, Fig. 4 indicates that it may be relatively hard to form a 1:1 gold nitride other than B17. Moreover, it is apparent that the tendency of AuN$_2$(C2,C18 and CoSb$_2$) phases to decompose back to Au and N$_2$ is comparable with that of Au$_3$N(D0$_9$, D0$_{10}$ and RhF$_3$).

Using Vanderbilt USPPs within GGA(PBE), Chen, Tse and Jiang$^7$ calculated $E_f$ of C2,C18 and CoSb$_2$ phases. Their results are included in Table II for comparison. Although they got positive results, as expected, the differences between our obtained values and theirs can be traced back to the fact that they used $E_{coh}(N_2^\text{solid})$ in Eq. 7 instead of $E_{coh}(N_2^\text{gas})$. Moreover, the smaller the difference between our obtained values and their obtained equilibrium lattice parameters, the smaller the difference in $E_f$.

Unfortunately, no experimental values of $E_f$ for the synthesized gold nitride phases are available.

**F. Electronic Properties**

In this subsection, the DFT calculated electronic structure for the most energetically stable phases are shown graphically. In each case, presented information include (a) spin-projected total density of states (TDOS); (b) partial density of states (PDOS) of Au($s, p, d$) orbitals in Au$_3$N; (c) PDOS of N($s, p$) orbitals in Au$_3$N, and (d) band structure along the high-symmetry $k$-points.

Beside D0$_9$ (Fig. 6), the equilibrium electronic structure of its two competing phases: D0$_2$ and RhF$_3$, are presented in Figs. 7 and 8, respectively. This is because the foregoing similarity in their EOS’s may reflect in their electronic properties.

Krishnamurthy et al.$^4$ predicted Au$_3$N(D0$_9$) to be an indirect band-gap semiconductor, but they did not give a value. Fig. 6 shows that it is indeed a semiconductor with an $(R – X)$ indirect DFT band gap of 0.139 eV GGA value. According to the fact that the produced gold nitrides are metallic, the D0$_9$ structure may not be the true candidate for the most likely stoichiometry, Au$_3$N.

Fig. 7 shows that Au$_3$N(D0$_9$) has its CBM at $(H, 0.065 \text{ eV})$, and its VBM is at $(H, -0.073 \text{ eV})$, resulting in a direct energy band gap at $H$: $E_g = 0.139 \text{ eV}$. This is exactly equal to $E_g$ of Au$_3$N(D0$_9$).

The Fermi surface $E_F$ in Au$_3$N(RhF$_3$) crosses the valence band at $\Gamma$ and the phase seems to have a poor metallic character, since there is only a very narrow width of energy of the unoccupied states above $E_F$ and around $\Gamma$.

A common feature in these three Au$_3$N phases, there is an Au($d$)-N($p$) mixture in the range $\sim -8.8 - E_F$ which becomes stronger around $-4.45 \text{ eV}$.

Although it might not be clear on the graph, Fig. 9(a) shows that AuN(B17) is a DFT(GGA) indirect band gap semiconductor. With its valence band maximum (VBM) at $(X, -0.012)$ and its conduction band minimum (CBM) very close to $E_F$ at $(M, 0.001 \text{ eV})$, AuN(B17) possesses a very narrow band gap of width: $E_g = 0.013 \text{ eV}$.

This insulating feature is in contrast to PdN$^{66}$, PtN$^{63}$, CuN$^{35}$ and AgN$^{58}$ which were all found to be metallic in this B17 structure.

With the Fermi surface crossing many partly occupied bands, it is evident from Fig. 10 that AuN$_2$(CoSb$_2$) is a metal.

**G. Optical Properties**

Within a frequency range that includes the optical region (i.e. the visible spectrum: $[(390 ~ 750 \text{ nm}) \equiv (3.183 ~ 1.655 \text{ eV})]$), Fig. 11 displays the real and the imaginary parts of the frequency-dependent dielectric function $\varepsilon_{RPA}(\omega)$ of Au$_3$N(D0$_9$) and the corresponding derived optical constants (Eqs. 12 – 15).

From the absorption coefficient $\alpha(\omega)$ spectrum, it can be seen that Au$_3$N(D0$_9$) starts absorbing photons with $\sim 0.9 \text{ eV}$ energy. Hence, it is clear that $GW_0$ calculations give a band gap of $\sim 0.9 \text{ eV}$, which is a significant improvement to the obtained DFT-GGA value. Therefore, our presented $\alpha(\omega)$ spectrum confirms that Au$_3$N(D0$_9$) would be a true semiconductor and that D0$_9$ cannot be the true structure of the most likely Au$_3$N stoichiometry.

**IV. CONCLUDING REMARKS**

We have successfully applied first-principles calculation methods to investigate the structural, stability, electronic and optical properties of Au$_3$N, AuN and AuN$_2$. Within the accuracy of the employed methods, the obtained structural parameters, EOS, $B_0$, $B'_0$ and electronic properties show acceptable agreement with some of the available previous calculations.

Among the studied modifications, we determined metallic (RhF$_3$ and CoSb$_2$) and semiconducting (D0$_9$ and B17) phases.

According to the fact that the produced gold nitride phases are metallic, our DFT-GGA and GW calculations confirmed that D0$_9$ structure cannot be the true candi-
date for the Au$_3$N stoichiometry that has been suggested by experimentalists.

From experiment, *ab initio* calculations of Krishna-murthy *et al.*$^4$, and from the present work, one may conclude that if Au$_3$N is the true stoichiometry, it must have a metallic character only at low crystal symmetries: i.e. RhF$_3$ (present work) or a triclinic (Ref. 4). However, the better hardness -compared to pure gold- of the synthesized phases remains a mystery and may be a property of gold nitride at low dimensions only.

The low symmetry AuN$_2$ phases have far lower cohesive energy than all Au$_3$N, have comparable formation energy with the most favorable Au$_3$N modifications, and their bulk moduli become higher under pressure.

**FIG. 6.** (Color online.) DFT calculated electronic structure for Au$_3$N in the D0$_9$ structure: (a) spin-projected total density of states (TDOS); (b) partial density of states (PDOS) of Au($s,p,d$) orbitals in Au$_3$N; (c) PDOS of N($s,p$) orbitals in Au$_3$N, and (d) band structure along the high-symmetry $k$-points which are labeled according to Ref. [65]. Their coordinates w.r.t. the reciprocal lattice basis vectors are: $M(0.5,0.5,0.0)$, $\Gamma(0.0,0.0,0.0)$, $X(0.0,0.5,0.0)$, $R(0.5,0.5,0.5)$.

**FIG. 7.** (Color online.) DFT calculated electronic structure for Au$_3$N in the D0$_2$ structure: (a) spin-projected total density of states (TDOS); (b) partial density of states (PDOS) of Au($s,p,d$) orbitals in Au$_3$N; (c) PDOS of N($s,p$) orbitals in Au$_3$N, and (d) band structure along the high-symmetry $k$-points which are labeled according to Ref. [65]. Their coordinates w.r.t. the reciprocal lattice basis vectors are: $\Gamma(0.0,0.0,0.0)$, $N(0.0,0.0,0.5)$, $P(0.25,0.25,0.25)$, $H(0.5,-,0.5)$.

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FIG. 8. (Color online.) DFT calculated electronic structure for Au$_{14}$N in the RhF$_3$ structure: (a) spin-projected total density of states (TDOS); (b) partial density of states (PDOS) of Au($s,p,d$) orbitals in Au$_{14}$N; (c) PDOS of N($s,p$) orbitals in Au$_{14}$N, and (d) band structure along the high-symmetry $k$-points which are labeled according to Ref. [65]. Their coordinates w.r.t. the reciprocal lattice basis vectors are: $F(0.5,0.5,0.0)$, $Q(0.375,0.625,0.0)$, $B(0.5,0.75,0.25)$, $Z(0.5,0.5,0.5)$, $\Gamma(0.0,0.0,0.0)$, $L(0.0,0.5,0.0)$, $Y(0.25,0.5,0.25)$, $\Sigma(0.0,0.5,0.5)$.

FIG. 9. (Color online.) DFT calculated electronic structure for AuN in the B17 structure: (a) spin-projected total density of states (TDOS); (b) partial density of states (PDOS) of Au($s,p,d$) orbitals in AuN; (c) PDOS of N($s,p$) orbitals in AuN, and (d) band structure along the high-symmetry $k$-points which are labeled according to Ref. [65]. Their coordinates w.r.t. the reciprocal lattice basis vectors are: $X(0.0,0.5,0.0)$, $M(0.5,0.5,0.0)$, $\Gamma(0.0,0.0,0.0)$, $Z(0.0,0.0,0.0)$, $A(0.5,0.5,0.5)$, $R(0.0,0.5,0.5)$.

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FIG. 10. (Color online.) DFT calculated electronic structure for AuN₂ in the CoSb₂ structure: (a) spin-projected total density of states (TDOS); (b) partial density of states (PDOS) of Au(s, p, d) orbitals in AuN₂; (c) PDOS of N(s, p) orbitals in AuN₂, and (d) band structure along the high-symmetry k-points which are labeled according to Ref. [65]. Their coordinates w.r.t. the reciprocal lattice basis vectors are: Γ(0, 0, 0, 0), X(0, 0, 0, 0), S(−5, 0, 0, 0), Y(−5, 0, 0, 0), Z(0, 0, 0, 0, 0.5), U(0, 0, 0, 0.5), R(−5, 0, 0, 0.5), T(−5, 0, 0, 0.5).

FIG. 11. (Color online.) Normal-incidence frequency-dependent optical spectra of Au₃N(D0₅) obtained using Eqs. 12–15 and GW₀ eigenvalues.

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$V (\text{Å}^3 / \text{atom})$

$E_{\text{coh}} (\text{eV/atom})$

**Au$_3$N**

- A15
- D0$_3$
- L1$_2$
- Fe$_3$N
- D0$_9$
\[ E_{\text{coh}} (\text{eV/atom}) \]

\[ V (\text{\AA}^3 \text{/atom}) \]

Graph showing the cohesive energy \( E_{\text{coh}} \) as a function of volume \( V \) for different materials with various markers and lines.