Thermodynamic ground states of platinum metal nitrides

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The thermodynamic stabilities of various phases of the nitrides of the platinum metal elements are systematically studied using density functional theory. It is shown that for the nitrides of Rh, Pd, Ir and Pt two new crystal structures, in which the metal ions occupy simple tetragonal lattice sites, have lower formation enthalpies at ambient conditions than any previously proposed structures. The region of stability with respect to those structures extends to 17 GPa for PtN₂. Calculations show that the PtN₂ simple tetragonal structures at this pressure are thermodynamically stable also with respect to phase separation. The fact that the local density and generalized gradient approximations predict different values of the absolute formation enthalpies as well different relative stabilities between simple tetragonal and the pyrite or marcasite structures are further discussed.

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Until recently none of the Platinum-Metal (PM) elements (Pt, Ir, Os, Ru, Rh, Pd) were known to form stable compounds with nitrogen. Several such compounds have now been synthesized primarily under high static pressure and temperature (in the range of 60 GPa and 2000 K respectively). These include nitrides of Pt [2, 3], Ir [3, 4], Os [4] and Pd [5]. Except for PdN₂, all these compounds have been shown to be at least metastable at ambient conditions. The resulting crystal structures have been investigated by several groups both experimentally and theoretically [2–8], and by now consensus has been reached concerning the observed crystal structures and stoichiometry (one metal atom for every nitrogen dimer). PtN₂ and PdN₂ are formed in the pyrite crystal structure, a cubic phase with the metal atoms occupying fcc sites. The nitrogen dimers are centered around the fcc octahedral interstitial sites, oriented in all the four possible ⟨111⟩ directions, such that all the nearest neighbor dimers make an angle of 70.53° with each other. A rotation of dimers such that two pairs point in the [111] and [111] direction, respectively, results in the marcasite structure, the predicted ground state phase of RuN₂, RhN₂ and OsN₂ [7]. A small lattice distortion of marcasite then yields the monoclinic baddeleyite (CoSb₂) structure found in IrN₂ [5, 7].

The low-pressure phase diagrams of these systems are still not well understood. In particular their degree of thermodynamic stability has only been addressed briefly [3], where it was proposed that the Pt-N compound is only metastable at low pressures. In this work, we address this issue by calculating the formation enthalpies of all the PM nitrides as a function of pressure. We also report the discovery of two new low-energy crystal structures that at low pressures are thermodynamically more stable than any of the crystal phases that have up to now been synthesized experimentally or calculated from theory. To our knowledge, these new crystalline phases have not previously been observed in any other compound.

In spite of the apparent differences in the overall symmetries of the pyrite, marcasite and baddeleyite structures, they all belong to the same class of crystal structures. They can be obtained by placing the PM atoms on an fcc lattice and the center of ⟨111⟩-oriented nitrogen dimers on the octahedral interstitial sites of this lattice and allowing for atomic relaxations. For each nitrogen dimer there are four possible orientations, and thus for crystals with the periodicity of the fcc unit...
cell having four distinct PM-N\(_2\) units, there are nine different crystal structures, two of which are the pyrite and marcasite phases. Note that as mentioned above, the baddeleyite structure is merely a distorted marcasite structure.

Geometrically each individual crystal structure in this class can be distinguished by the projections of its dimers centered at 0.5a\(\hat{x}\), 0.5a\(\hat{y}\), 0.5a\(\hat{z}\) and 0.5a (\(x + \hat{y} + \hat{z}\)) onto a (111)-plane. The dimer projections and space groups of the resulting crystal phases are displayed in the top panel of Fig. 1. For reference, structures (3) and (8) correspond to marcasite and pyrite, respectively. To assess their theoretical equation-of-state we have performed density functional theory calculations using projector augmented-waves as implemented in the Vienna ab-initio simulation package [9]. Both atomic position relaxations and cell shape relaxations were performed. In fact, only structures (8) and (9) maintained cubic symmetry after relaxation, while the others showed deviations of various magnitude. The resulting LDA energy vs volume curves for PdN\(_2\) are shown as the solid lines in the lower panel of Fig. 1. As expected, amongst these structures, pyrite and marcasite have the lowest energies in the low-pressure region.

Besides the nine structures mentioned above, we also show in Fig. 1 the corresponding curves for two additional structures (dashed lines). These are obtained by a continuous transformation from structure (2) by translating every other (001) plane in the [100] direction (corresponding to a zone-boundary phonon mode). By allowing the lattice to relax by a tetragonal distortion in the [001] direction, the metal ions become arranged in a simple tetragonal (ST) lattice. During this transformation the nitrogen dimers that initially were oriented in the \(\langle 111\rangle\) directions collapse into the (001) planes and now point in the \(\langle 100\rangle\) and \(\langle 001\rangle\) directions. In this way, a new class of crystal structures is created where metal nitride layers are stacked in different sequences. Each layer is composed of metal ions occupying square lattice sites and face-centered nitrogen dimers pointing along the edges of the squares and always being perpendicular to the four nearest-neighbor dimers. Fig. 2 illustrates two particularly high-symmetry structures in this class with AA and AB stacking that have lower energies than any previously proposed crystal structure for most PM nitrides at ambient conditions. The first structure, hereafter denoted ST\(_{AA}\), is simple tetragonal and belongs to space group 127 (P4/mmm). The metal ions occupy the 2\(a\) Wyckoff positions and the nitrogen atoms are located at the 4\(g\) positions. The second structure, ST\(_{AB}\), is monoclinic and belongs to space group 12 (P2\(_1\)/m). The metal ions occupy the 4\(e\) sites and the nitrogen atoms are located at the 4\(h\) and 4\(i\) positions.

As is clearly seen in Fig. 1 the ST structures at low pressures are significantly lower in energy than both the pyrite and marcasite structures. Also, their equilibrium volumes are shifted towards larger volumes and the bulk moduli are smaller. Both LDA and GGA calculations yield small but finite densities-of-states at the Fermi level for the ST structures [11]. However, it is well-known that these approximations often underestimate band gaps and e.g. predict Ge to be a metal. Hence, it is quite possible that the ST phases can be insulators with small band gaps.

The high-pressure PM-nitride synthesis results from the past few years have established the extent of (meta-)stability of many of these compounds. Since they have not been observed in nature, it is reasonable to rule out that they are thermodynamically stable with respect to phase separation at ambient pressure and temperature conditions. Based on experiments it is known that they are certainly stable at pressures above 50 GPa, and that PtN\(_2\) (pyrite), IrN\(_2\) (baddeleyite) and OsN\(_2\) (marcasite), are at least metastable at zero pressure.

There is however no real understanding either of the relative stabilities among the compounds or of their their degree of metastability at low-pressure conditions. These are very important issues for the synthesis and potential application of these materials. As it is yet difficult to assess their equilibrium phase diagrams experimentally we have performed extensive first principles calculations of the thermodynamic stabilities of the six PMN\(_2\) compounds as a function of pressure.

The thermodynamic stability of any PMN\(_2\) compound with respect to the separate phases as a function of pressure, is quantified in terms of the formation enthalpy:

\[
\Delta H = H_{\text{PMN}_2} - H_{\text{PM}} - H_{\text{N}_2}
\]

Under experimental conditions, nitrogen is molecular in its solid phase. At ambient pressure, it crystallizes into a hexagonal phase only at low temperatures and exhibits a polymorphic phase diagram undergoing several structural transformations upon increasing pressure. It is thus quite difficult to perform accurate free energy calculations for this system. Therefore, the most reliable way of estimating the enthalpy of this system as a function of pressure is to split it into contributions from the dimer energy and the cohesive energy:

\[
H_{\text{N}_2} = E_{\text{dimer}} + \Delta H_{\text{coh}}
\]

where we note that the dominant contribution to \(H_{\text{N}_2}\) at ambient conditions is due to the bonding energy of the dimer, which can easily be calculated from first principles. We estimate the enthalpy of cohesion by calculating it for the hexagonal phase at zero temperature and pressure within LDA/GGA and extract the change with pressure using the experimental equation-of-state data [12].

Fig. 3 shows the calculated formation enthalpies within the LDA. For clarity, we consider here only the most important phases; pyrite, baddeleyite, marcasite and the two ST struc-
The formation enthalpies for RuN$_2$, RhN$_2$, PdN$_2$, OsN$_2$, IrN$_2$, and PtN$_2$ are plotted as a function of pressure in Fig. 3. The figure illustrates the stability of the various crystal structures: pyrite, marcasite/baddeleyite (MB), and the two simple tetragonal (ST) structures. The LDA calculations show that the ST structures are favored at lower pressures for the compounds formed with the group IX and X platinum metals, while the group VIII nitrides form in the marcasite/baddeleyite (MB) structure at all pressures. The range of stability of the ST structures versus pyrite and MB is consistently pushed towards lower pressures for the group IX nitrides as compared with the group X nitrides.

According to the LDA, the ST structures for PdN$_2$ and PtN$_2$ are stable up to 13 GPa, while for IrN$_2$ and RhN$_2$ they are only stable at very low pressures. The high pressure crystal structure of the group X nitrides is that of pyrite, while for all the earlier PM nitrides, the MB structures are the only structures observed at higher pressures.

The same trend is observed in the GGA-calculations, displayed in Fig. 4, except that the relative stabilities of the ST structures are more pronounced as they constitute the low-enthalpy phases up to 20 GPa for PdN$_2$ and PtN$_2$ and up to 10 GPa for RhN$_2$ and IrN$_2$.

A consistent feature observed in the phase diagrams is that the marcasite or baddeleyite structures are lower in energy for the group VIII PM nitrides and the pyrite and ST structures are lowered in energy for the group IX and X PM nitrides.

The formation enthalpies reported in Fig. 3 also contain information on the absolute thermodynamic stability of these compounds. According to the LDA all but OsN$_2$ exhibit at least one stable phase with respect to the separate phases at ambient conditions. In fact, the lowest enthalpy phases for all considered PM-nitrides but OsN$_2$ are predicted to be stable at all pressures. This is in contrast to the results from the GGA, which predict that the compounds are stable at 12 GPa for RuN$_2$, 20 GPa for OsN$_2$, around 15 GPa for RhN$_2$, IrN$_2$ and PtN$_2$ and 25 GPa for PdN$_2$.

In summary, we find from Fig. 3 the remarkable result that according to the LDA two novel crystal structures, never observed before, constitute the ground state phases of the group IX and X PM nitrides. PtN$_2$ is the most stable among all these compounds, with a cohesive energy of about 0.3 eV/f.u. In contrast, GGA predicts all the PM nitrides to phase separate at ambient conditions. For example, the PtN$_2$ ST phases are unbound within GGA by 0.6 eV/f.u. at zero pressure. They become thermodynamically stable at about 15 GPa. Upon further investigation of Figs. 3 and 4 we find that the difference between GGA and LDA enthalpies mainly stems from a rigid upward shift of the GGA curves by about 1.2 eV/f.u. This is not a surprising result as it is well known that LDA usually predicts larger cohesive energies and smaller lattice constants for solids than GGA. To compare with other nitrides, we find in the literature LDA formation energies of zinc-blende GaN, InN, AlN compounds that are 0.4 - 0.6 eV/f.u. lower than the corresponding values from GGA [13]. This is less than half the difference found for the PM nitrides in this work. We attribute this to the presence of the nitrogen dimers. To prove this point, we calculated the formation energy of PtN in the zinc-blende structure and found that the LDA prediction is smaller than the GGA by about 0.4 eV/f.u.

Hence, the difference between the LDA and GGA cohesive energies of the PM nitrides is consistent with previous literature. As discussed above, this difference has important ram-

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**FIG. 3:** LDA Formation enthalpies per formula unit of a) RuN$_2$, b) RhN$_2$, c) PdN$_2$, d) OsN$_2$, e) IrN$_2$ and f) PtN$_2$ as a function of pressure for marcasite or baddeleyite (MB), pyrite and the two simple tetragonal structures.
ifications for the low-pressure phase stability of these compounds. Generally, GGA is expected to provide better cohesive energies and equilibrium volumes than LDA. This is true for the zinc-blende nitrides (GaN, AlN, InN) mentioned above. However, in the case of PM nitrides, LDA seems to slightly outperform GGA with regards to lattice constants. For example, LDA predicts the lattice constant of PtN$_2$ to be 4.80 Å, in perfect agreement with experiment, as compared with the GGA lattice constant of 4.88 Å [3]. Nevertheless, for the cohesive energies we believe that the GGA provides the most accurate values.

When comparing with experiments we find that the calculated formation pressures are less than half the observed synthesis pressures. For example, the measured synthesis pressure for the nitrides of Pt and Ir is approximately 50 GPa [2, 3], and 58 GPa for palladium nitride [5], while the calculated formation pressures within GGA for the same systems are 17, 15 and 27 GPa respectively. At the experimental synthesis pressures, GGA predicts formation enthalpies of -1.4, -1.1 and -1.4 eV/f.u., respectively for these systems. We attribute this discrepancy to the presence of large kinetic barriers to the formation of PM nitrides when synthesized in the diamond anvil cell. The latter may be associated with for example a strain due to lattice mismatch between the compound and the parent metal on which it is grown. The existence of large energy barriers to the formation of nitrides is well known in the synthesis literature. For example, according to GGA, GaN has a formation enthalpy of -1.7 eV/f.u. at zero pressure [13] but it requires a synthesis pressure of 2 GPa [14].

In conclusion, the LDA clearly overestimates the stability of the PM nitrides. The GGA also predicts the transition pressures to be far below the experimental values. These results are however consistent with the large kinetic barriers found for zinc-blende nitrides. The only compound that exhibit a thermodynamically stable ST-phase is PtN$_2$. The combination of large barriers to formation and small region of stability make the synthesis of these phases in the diamond anvil cell difficult. However, as we indicated earlier, these structures can be obtained through martensitic transformations from marcasite or pyrite structures. Hence careful experimental work at pressures in the window of stability of the ST structures may be required to produce these phases. Furthermore, since the associated Raman spectra are probably weak another primary in-situ diagnostic may be required such as x-ray diffraction.

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