

DOI: 10.1002/anie.200600431

**Mysterious Platinum Nitride\*\****Jörg von Appen, Marck-Willem Lumey, and  
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In 2004, the spectacular high-pressure synthesis of platinum nitride was communicated;<sup>[1]</sup> PtN was prepared by compressing Pt metal and N<sub>2</sub> at pressures of 45–50 GPa and temperatures above 2000 K. According to X-ray diffraction, this phase possesses a face-centered cubic (fcc) unit cell with  $a = 4.8041(2)$  Å. On the basis of Raman spectroscopy, an NaCl-type ([NaCl]; rock salt) structure was rejected, and the structure was assigned to the ZnS type ([ZnS]; zinc blende). Furthermore, an extraordinarily high bulk modulus of  $(372 \pm 5)$  GPa was determined, and analytical profiles revealed a nearly daltonide composition of PtN<sub>1-x</sub> ( $x < 0.05$ ).

The first density functional theory (DFT) investigations of PtN confirmed all of the experimental results.<sup>[2]</sup> Other research groups also verified both the structure type and the lattice parameter by using various functionals.<sup>[3,4]</sup> Nonetheless, some oddities were encountered. For example, the experimentalists found<sup>[1]</sup> that the molar volume of PtN is larger than the volume of the starting materials (Pt +  $\frac{1}{2}$  N<sub>2</sub>) at pressures above 12 GPa. This situation is paradoxical, because the reaction mixture increases its volume upon pressurization, in contradiction to Le Chatelier's principle. In addition, all of the theoretical studies mentioned above concluded that the [NaCl] structure becomes more favorable than the [ZnS] structure above 4–17.5 GPa. Another theoretical study dealing with the calculation of single-crystal elastic constants questioned the stability of PtN,<sup>[5]</sup> and suggested the alternative composition PtN<sub>2</sub>, first in a CaF<sub>2</sub>-type ([CaF<sub>2</sub>]; fluorite) structure and later in a FeS<sub>2</sub>-type ([FeS<sub>2</sub>]; pyrite) structure.<sup>[6]</sup> Indeed, the crystal structure of PtN seems to be a matter of debate.<sup>[7]</sup> Therefore, we decided to perform more comprehensive calculations and to consider other possible structure types. Moreover, we have calculated the total energies of the PtN polymorphs with respect to the energy of the elements. We also introduce the heat of formation  $\Delta H_f$  as a new theoretical aspect.

The electronic structures of PtN in the [ZnS] and [NaCl] structures were first compared to the results of the previous studies. Our findings, based on either full-potential linearized

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[\*\*] We would like to thank the supercomputing centers of the RWTH Aachen and the Research Center Jülich for having provided us with their computer resources. Financial support from the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is also gratefully acknowledged.

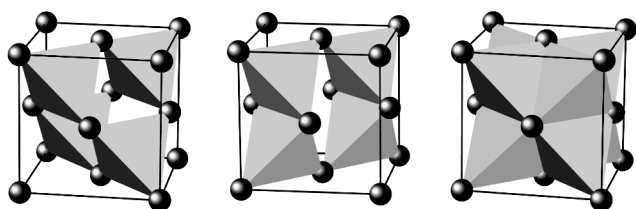
augmented plane wave (FLAPW) or pseudopotential calculations, in combination with local or gradient-corrected exchange-correlation functionals, are displayed in Table 1.

**Table 1:** Experimental data, and calculated relative energies  $\Delta E$ , lattice parameters  $a$ , bulk moduli  $B_0$ , and transition pressures  $p_T$  for PtN in the [ZnS] and [NaCl] structures. The theoretical methods, as well as the exchange-correlation functionals are indicated.

	$\Delta E$ [eV]	$a$ [Å]	$B_0$ [GPa]	$p_T$ [GPa]
Experiment <sup>[1]</sup>		4.8041(2)	372 ± 5	
FLAPW		PBE-GGA		
[ZnS]	0	4.80	192	
[NaCl]	+0.48	4.45	232	16.5
Pseudopotentials	GGA/LDA	GGA/LDA	GGA/LDA	GGA/LDA
[ZnS]	0	4.80/4.70	190/232	
[NaCl]	+0.48/+0.36	4.50/4.41	230/288	17.6/13.3

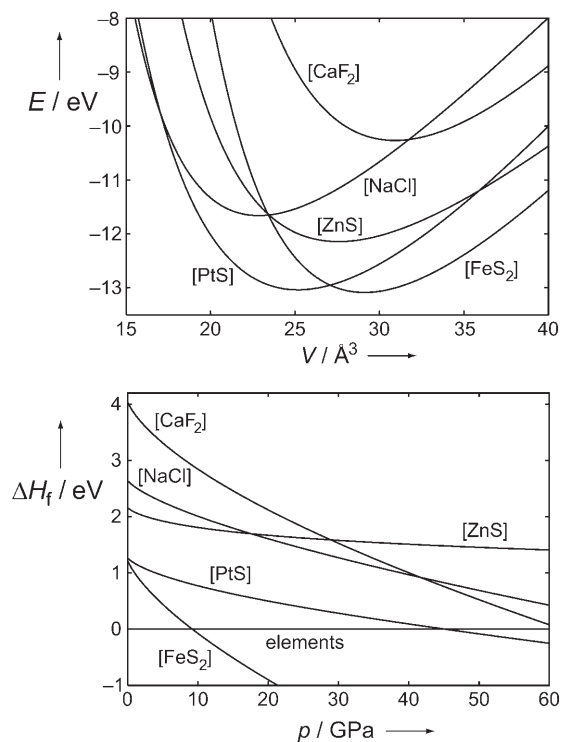
At ambient pressure, [ZnS]-PtN is more stable than [NaCl]-PtN, and seems to be thermodynamically stable at first sight; this result corresponds with previous findings.<sup>[2,3]</sup> Also in agreement with previous investigations, our high-pressure calculations predict that [ZnS]-PtN will undergo a phase transition to [NaCl]-PtN at 17.6 GPa (GGA).<sup>[2,3]</sup> It therefore seems rather unlikely that [ZnS]-PtN would be produced at an experimental pressure of 45–50 GPa, unless the phase was formed upon depressurization. Another disagreement is that the experimentally reported and extraordinarily large bulk modulus of (372 ± 5) GPa cannot be reproduced by our calculations, which give values only half as large for [ZnS]-PtN. According to our experience, such discrepancies cannot be attributed to failures of theory alone. In a next step, the calculations were expanded by including PtS-type ([PtS]; cooperite), [CaF<sub>2</sub>], and [FeS<sub>2</sub>] structures.

In [PtS]-PtN, the N atoms are tetrahedrally coordinated by Pt (as Raman spectroscopy indicated for PtN<sup>[11]</sup>); the [PtS] structure is also adopted by PtO. While in [ZnS]-PtN all of the NPt<sub>4</sub> tetrahedra are corner-sharing, in [PtS]-PtN one-dimensional chains of edge-sharing tetrahedra are interconnected by corner-sharing between tetrahedra (Figure 1). As a consequence, the Pt atoms have square-planar coordination environments in [PtS]-PtN. In [CaF<sub>2</sub>]-PtN<sub>2</sub>, each NPt<sub>4</sub> tetrahedron shares all of its edges with neighboring tetrahedra, whereas [FeS<sub>2</sub>]-PtN<sub>2</sub> (not shown) can be described as a [NaCl] structure, in which N<sub>2</sub> units occupy the Cl positions.



**Figure 1.** The [ZnS]-PtN (left), [PtS]-PtN (middle), and [CaF<sub>2</sub>]-PtN<sub>2</sub> (right) structures differ in the connectivity of the incorporated NPt<sub>4</sub> tetrahedra. The spheres represent the fcc Pt lattices.

On the basis of the total energies of the elements as a function of their volumes, the heats of formation  $\Delta H_f$  of the PtN and PtN<sub>2</sub> phases can be calculated, allowing theoretical access to thermodynamic stabilities and necessary synthesis pressures.<sup>[8]</sup> The results of these calculations are depicted in an energy–volume plot, as well as an enthalpy–pressure diagram derived from this plot (Figure 2).



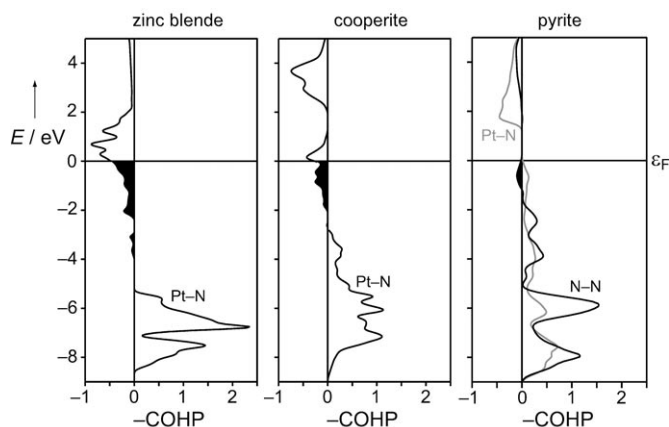
**Figure 2.** Plots of energy  $E$  as a function of volume  $V$  (per formula unit; top), and of enthalpy of formation  $\Delta H_f$  as a function of pressure  $p$  (bottom), calculated (GGA) for PtN and PtN<sub>2</sub> in different structure types.

The results for the [ZnS] and [NaCl] structures have already been discussed above. The enthalpy–pressure diagram directly shows the transition pressure at which the [NaCl] structure becomes more favorable than the [ZnS] structure for PtN. At ambient pressure, [CaF<sub>2</sub>]-PtN<sub>2</sub> is quite unstable, but it becomes more favorable than [ZnS]-PtN above approximately 30 GPa, and is more stable than the elements above approximately 60 GPa. The calculated lattice parameter of the [CaF<sub>2</sub>] structure ( $a_{\text{GGA}} = 4.98$  Å) is almost 4% larger than the experimentally reported one. The [FeS<sub>2</sub>] structure is also thermodynamically unstable at ambient conditions, but is significantly more stable than the elements above approximately 10 GPa. The theoretical lattice parameter for [FeS<sub>2</sub>]-PtN<sub>2</sub> ( $a_{\text{GGA}} = 4.89$  Å) is in good accordance with that from another calculation.<sup>[6]</sup> For our further calculations, we will not consider the possibility of a [FeS<sub>2</sub>] structure, because the experimentalists committed themselves to a 1:1 (and not 1:2) composition for platinum nitride.<sup>[1]</sup>

For the 1:1 daltonide PtN, Figure 2 reveals the puzzling finding that [ZnS]-PtN is an entirely unstable structure at any pressure. While chemists have, of course, succeeded in

synthesizing thermodynamically unstable (but kinetically stable) materials, the synthesis of PtN in a structure type of lower density (relative to that of the starting materials) is impossible to realize using high pressure. Another interesting result is that [PtS]-PtN is 0.90 eV (GGA) more stable than [ZnS]-PtN at standard pressure. To exclude systematic errors, we tried to disprove our results using other methods, but always found similar energy lowerings (0.90–1.05 eV) for [PtS]-PtN relative to [ZnS]-PtN.

These relative stabilities are also obvious from the chemical bonding in both structures, which was analyzed by calculating crystal orbital Hamilton populations (COHPs; Figure 3, left and middle). For both structures, there are deep-



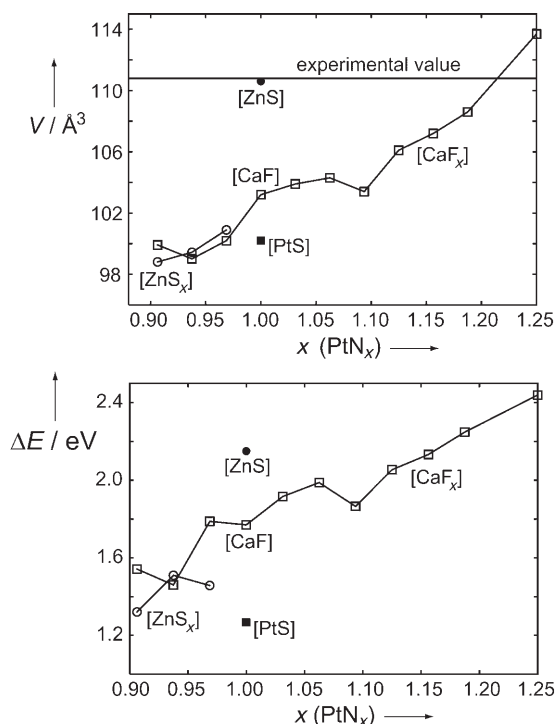
**Figure 3.** COHP analyses of the Pt–N interactions in [ZnS]-PtN (zinc blende; left) and [PtS]-PtN (cooperite; middle), and of the Pt–N and N–N interactions in [FeS<sub>2</sub>]-PtN<sub>2</sub> (pyrite; right). Occupied antibonding states are emphasized in black.

lying Pt–N bonding regions arising from N 2p and Pt 5d orbitals. The instability of the two polymorphs results from the presence of antibonding Pt–N interactions (black) below the Fermi level, a scenario that nature usually tries to avoid. It is these repulsive interactions that must be counteracted by using pressure. As can easily be seen, more antibonding Pt–N levels are present near the Fermi level of [ZnS]-PtN, as expected. It must be remembered that the molar volume of [PtS]-PtN is smaller than that of [ZnS]-PtN; therefore, high pressure cannot stabilize [ZnS]-PtN. In contrast, increasing pressure stabilizes [PtS]-PtN, which is stable relative to the elements above 45 GPa, and is approximately 1.5 eV more stable than [ZnS]-PtN at this pressure. Nonetheless, the theoretical bulk modulus of 215 GPa (GGA; LDA: 240 GPa) is smaller than the experimental one. Also, the [PtS] structure is tetragonal ( $a_{\text{GGA}} = 4.20 \text{ \AA}$ ,  $c_{\text{GGA}} = 5.68 \text{ \AA}$ ) and, thus, inconsistent with the X-ray diffraction data.

Because of the problems encountered for the 1:1 phases, we searched for alternative structures with four-coordinate N atoms that, on one hand, are in harmony with the diffraction data, and on the other hand, contain the energetically advantageous structural motif of [PtS]-PtN, namely the edge-sharing NP<sub>4</sub> tetrahedra. One possibility is a structure, which we label as [CaF], in which half of the tetrahedral holes in an fcc Pt lattice are statistically occupied by N atoms. In

addition, the energy of the same model with a small excess or deficiency of N atoms (labeled [CaF<sub>x</sub>]) was calculated to examine the effect on the lattice parameters.<sup>[9]</sup> For the N-deficient phases, a model containing a selective distribution of N atoms over the tetrahedral sites that are occupied in the [ZnS] structure (labeled [ZnS<sub>x</sub>],  $x \leq 1$ ) was also examined.

Plots of the volumes and energies of the PtN<sub>x</sub> phases as a function of composition are displayed in Figure 4. As



**Figure 4.** Plots of unit-cell volumes  $V$  (top) and relative energies  $\Delta E$  (bottom) calculated (GGA) for PtN<sub>x</sub> in different structure types (see text for details), as a function of the N content  $x$ .

expected, the volumes generally increase with increasing N content (and vice versa) for both the [CaF<sub>x</sub>] and [ZnS<sub>x</sub>] structures. All volumes for the [ZnS<sub>x</sub>] ( $x \leq 1$ ) structure are much smaller than the published value for PtN. For the [CaF<sub>x</sub>] structure, an N content of  $x > 1.2$  is needed to reach the experimental volume of PtN. The phase with  $x = 1$ , [CaF]-PtN, exhibits a volume between those of the remarkably voluminous [ZnS]-PtN and the very dense [PtS]-PtN. The higher density of [PtS]-PtN is a reason for the increased stabilization of this polymorph relative to [ZnS]-PtN with increasing pressure (Figure 2, bottom).

As revealed by the plot of relative energy versus composition (Figure 4, bottom), all of the PtN<sub>x</sub> phases become less stable with increasing N content. In the region of N-deficient PtN<sub>x</sub> ( $x < 1$ ) phases, the [ZnS<sub>x</sub>] structure is generally more favorable than the [CaF<sub>x</sub>] structure. The enormous energy stabilization and volume reduction of [ZnS<sub>x</sub>]-PtN<sub>x</sub> relative to stoichiometric [ZnS]-PtN are due to the large structural distortions around the N defects. For a precise 1:1 composition, the [CaF] structure, which contains a random N distribution, is less stable than the [PtS] structure,

but more stable than the [ZnS] structure. Neither the relative energies nor the volumes of these phases match with the experimental results for PtN. In the region of N-rich PtN<sub>x</sub> ( $x > 1$ ) phases, the volumes agree with experiment, but these phases are very unstable. The most stable phases, on the other hand, have volumes that are much smaller than that measured for PtN.

Another way to solve the problems with respect to the existence of platinum nitride is to simply ignore the experimental chemical analysis. In contrast to PtN, which is unstable over the entire pressure range in the [ZnS] structure and below 45 GPa in the [PtS] structure, the 1:2 phase [FeS<sub>2</sub>]-PtN<sub>2</sub> is stable above 10 GPa (Figure 2, bottom) and has a molar volume that is smaller than that of the elements, thereby fulfilling Le Chatelier's principle. Indeed, a fascinating experimental report on the synthesis and characterization of [FeS<sub>2</sub>]-PtN<sub>2</sub>,<sup>[10]</sup> with a lattice constant of  $a = 4.8 \text{ \AA}$ , came to our attention during the revision of our manuscript (March 3, 2006). This result resolves all of the discrepancies between theory and experiment<sup>[1]</sup> mentioned above, by refuting the experiment. The stability of the [FeS<sub>2</sub>] structure can, again, be explained through a COHP analysis of the Pt–N and N–N bonds (Figure 3, right). The Pt–N interactions, which were antibonding near the Fermi level in the PtN structures, are now bonding over the entire region below the Fermi level. Instead, antibonding N–N quasimolecular states are now located just below the Fermi level. Their occupation enlarges the N≡N triple bond of 1.10 Å to a double bond of 1.42 Å (experimental: 1.41 Å<sup>[10]</sup>). Thus, the very large bulk modulus of 265 GPa (GGA; LDA: 334 GPa) calculated for PtN<sub>2</sub> is immediately understandable, because of the high molecular stiffness of the negatively charged N<sub>2</sub> molecule whose antibonding  $\pi^*$  states have been partially filled. We note that similar diazenide (or pernitride) anions have been found experimentally in SrN<sub>2</sub><sup>[11]</sup> and BaN<sub>2</sub><sup>[12]</sup> which were also synthesized under high pressure. Therefore, the reported "platinum nitride" PtN<sub>2</sub><sup>[10]</sup> would be better described as platinum diazenide (or pernitride).

In summary, there has been no convincing evidence for the synthesis of platinum nitride, PtN, to date. However, platinum diazenide, PtN<sub>2</sub>, has been prepared recently, and its properties are in excellent agreement with theory. Nonetheless, PtN may be accessible by incorporating atomic N into an fcc Pt lattice at pressures above 45 GPa. We predict that the equilibrium phase of PtN will crystallize in the [PtS] structure, but that [PtS]-PtN will be thermodynamically unstable with respect to decomposition into PtN<sub>2</sub> and Pt. Thus, the synthesis would have to exploit the potential kinetic stability of PtN, which is a true challenge for experimentalists. Despite the low X-ray scattering contribution of the N atoms relative to the Pt atoms, the tetragonal [PtS]-PtN will be easy to detect, even using powder methods.

## Theoretical Methodology

The first-principles electronic-structure calculations were performed using the Vienna ab initio simulation package,<sup>[13,14]</sup> with plane-wave basis sets and ultrasoft pseudopotentials. We also used the FLAPW method<sup>[15]</sup> and carried out tight-binding linear muffin-tin orbital

atomic-sphere approximation (TB-LMTO-ASA) calculations.<sup>[16–20]</sup> Chemical bonds were analyzed using the COHP technique.<sup>[21]</sup> Electronic energies were calculated by DFT, using a cut-off energy of 500 eV. Exchange-correlation contributions were treated both in the local-density approximation (LDA),<sup>[22–24]</sup> as well as in the generalized-gradient approximation (GGA).<sup>[25]</sup>

Received: February 1, 2006

Revised: April 18, 2006

Published online: May 31, 2006

**Keywords:** density functional calculations · diazenides · high-pressure phases · nitrides · platinum nitride

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