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Interstitial dinitrogen makes PtN₂ an insulating hard solid

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Recent synthesis of platinum nitride has provoked considerable interest on account of the compound's anomalously high bulk modulus, which is more than 30% higher than that of the parent metal. Numerous theoretical studies have since offered contradicting hypotheses on the structure and properties of this compound. Here we show, based on first-principles calculations, that the recently synthesized phase of platinum nitride has the pyrite structure. In the PtN₂ pyrite structure single-bonded N₂ units occupy the octahedral interstitial sites of the Pt close-packed lattice, giving rise to strong, directional Pt-N bonds and to an insulating character. Excellent agreement with x-ray, Raman, and compressibility measurements is obtained.

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The recent synthesis of a new platinum nitride compound¹ has generated significant interest^{2–9} for several reasons. Heavy transition metals were not previously known to form nitrides with high nitrogen content, and the formation reaction represented the first successful case of novel material synthesis under such extreme conditions (50 GPa and 2000 K). The anomalously low compressibility of the new nitride, comparable to that of c-BN, suggests that this compound might be a new super-hard material. The theoretical studies done to date diverge in their conclusions on the suggested structure, and, to our knowledge, the stoichiometry of the compound is not known exactly. The x-ray diffraction data unambiguously showed that Pt atoms form a fcc sublattice and Ref. 1 suggested zinc-blende (space group *F43m*) structure with Pt:N as 1:1 for the new compound. However, the conclusions of Ref. 1 are ambiguous because x-ray diffraction is unable to determine the positions of the nitrogen atoms due to the large Pt/N atomic mass ratio. Subsequent theoretical studies have offered a panoply of diverging opinions on the mechanical stability and bulk properties of various phases of platinum nitride, including strong confirmation of the zinc-blende structure,^{3,4} as well as the finding that this structure was not mechanically stable.² These studies proposed additional candidate structures for a platinum nitride compound, with Ref. 9 suggesting rock salt PtN (rock salt was also suggested as an alternative in the original experimental paper), while Yu and Zhang^{2,5} showed PtN₂, with fluorite structure, to be mechanically stable and have a bulk modulus comparable or slightly higher than that of the pure platinum.² In addition, recent experimental results using x-ray photoemission spectroscopy have provided evidence for an even larger nitrogen content, perhaps as high as 1:2 (Pt:N).¹⁰ Unfortunately, none of the proposed structures explains the multiple Raman active modes observed experimentally in Ref. 1. In this paper we show that the compound synthesized in Ref. 1 is PtN₂ with the pyrite structure and

that this configuration has a direct relation with the experimentally observed properties.

We will show first that according to our first-principles calculations, PtN₂ having pyrite structure is fully consistent with x-ray, Raman, and compressibility measurements of Ref. 1. Calculations¹¹ were performed within the density functional theory using a Perdew-Burke-Ernzerhoff exchange correlation functional¹² and a plane wave basis set for the electronic wave functions with a kinetic energy cutoff of 60 Ry (80 Ry for phonon calculations). A pseudopotential description of the ion-electron interaction¹³ was used, with platinum's 4*s* and 4*p* semicore states explicitly included in the valence. Brillouin zone integration was found to be converged with a uniform grid of 7×7×7 points. Structural relaxations were limited to the nitrogen positions, with platinum atoms fixed on the fcc lattice and the experimental zero-pressure lattice spacing (4.8041 Å). A preliminary search¹⁴ on the minimal unit cell containing one PtN₂ formula unit (i.e., with the rhombohedral primitive unit cell of the fcc lattice) showed that a structure with an interstitial N₂ centered in the octahedral cavity of the Pt fcc lattice, gives an energy which is lower than that of all previously proposed structures, all of which are based on atomic nitrogen centered either on the octahedral cavities (rock salt) or on the tetrahedral cavities (zinc blende and fluorite). A single interstitial N₂, however, violates the cubic symmetry of the platinum sublattice and would lead to a sizeable rhombohedral distortion, which is not observed experimentally. In this work, a deeper energy minimum is obtained by expanding our analysis to the cubic conventional cell of the fcc metal lattice. Arranging the nitrogen atoms on the eightfold sites of space group *Pā3* (see Fig. 1) minimizes the quadrupole interaction between the dinitrogen molecules, thus further reducing the energy, while preserving the observed cubic symmetry of the metal sublattice. The resulting pyrite isostructure agrees with all experimental data; indeed, a Reitveld refinement of the observed diffraction pattern using *Pā3* (Fig. 1) is indistin-

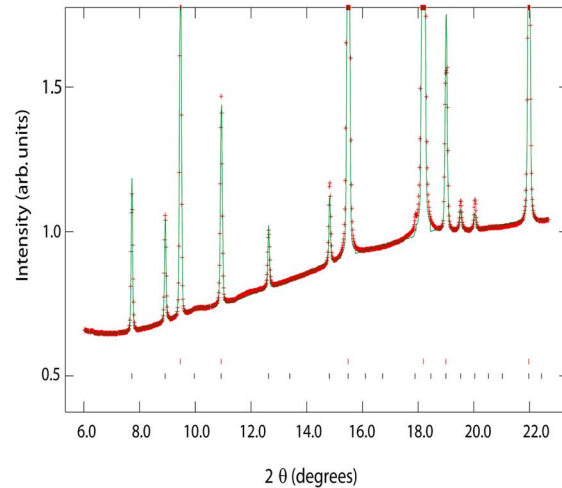
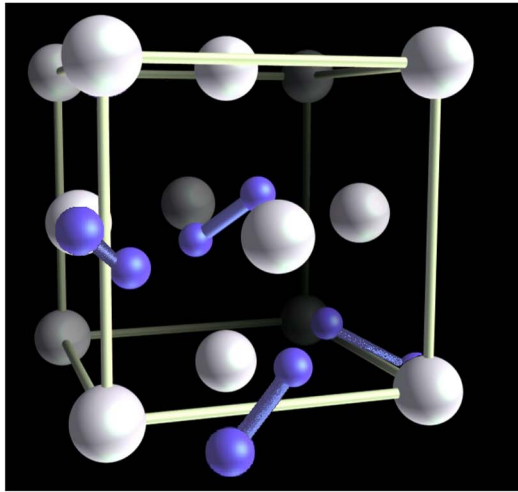


FIG. 1. (Color online) Left: Pyrite structure of PtN_2 , space group $P\bar{a}3$. Platinum atoms (white) form a face-centered cubic lattice, dinitrogen (N_2) units (grey) occupy the octahedral cavities of the Pt lattice. The calculated N-N distance at ambient pressure is 1.42 Å. Right: Rietveld fit using the $P\bar{a}3$ space group. Dark grey crosses: data at ambient pressure ($\lambda=0.3738$ Å); grey line: Rietveld fit; black ticks: PtN_2 peaks; grey ticks: Pt peaks. The most intense Pt peaks are cut off.

guishable with experimental data as compared to the originally proposed zinc-blende structure. In this structure at ambient pressure, platinum atoms are accommodated on the Wyckoff site 4a and nitrogen atoms are on the site 8c with $x=0.415$.

PtN_2 pyrite is found to have a considerably lower ground state energy than that of any other proposed structures, rendering the existence of any of these phases of PtN or PtN_2 highly unlikely. Moreover, in contrast to the structures proposed in previous reports, the pyrite phase shows not only mechanical stability, but good agreement with both bulk properties and experimentally observed Raman spectra. Our calculations (see Table I) show the pyrite structure to be 2 eV per stoichiometric unit lower in energy than the fluorite structure at ambient pressure. The comparison with 1:1 structures (zinc blende and rocksalt) is based on their respective formation energies, and shows that pyrite has energy 0.3 eV (per Pt atom) lower than that of zinc blende and 0.8 eV

TABLE I. Bulk modulus (in GPa), its pressure derivative (B'), and equilibrium lattice parameters (in angstroms), obtained from fitting calculated energies over a range of volumes with a second-order Birch-Murnaghan equation of state. Bold values were fixed during fitting. Formation energies ΔE are relative to $\text{Pt}+\text{N}_2$ for PtN_2 compounds, $\text{Pt}+\frac{1}{2}\text{N}_2$ for PtN compounds.

	a	B, B'	B, B'	ΔE (eV)
Exp. ^a	4.804	373, 4.00	354, 5.23	-
Pyr. (cal.)	4.848	305, 4.00	285, 5.50	1.92
Fl. (cal.)	4.939	269, 4.00	260, 4.73	3.95
ZB (cal.)	4.760	213, 4.00	217, 3.62	2.20
RS (cal.)	4.471	251, 4.00	242, 4.78	2.73
Pt exp. ^b	3.924	275, 4.78	277, 5.23	-
Pt cal.	3.966	242, 5.83	249, 5.23	-

^aReference 1.

^bReference 26.

lower than that of rocksalt. The positive sign of the formation energies in our calculations reveal, however, that PtN_2 is unstable toward dissociation into its constituent elements, at least at zero pressure. This is corroborated by experimental evidence that, below 10 GPa, PtN_2 dissociates upon mild heating. The PtN_2 pyrite structure is characterized by Pt in sixfold coordination with N, with a calculated Pt-N distance of 2.096 Å at zero pressure. Each nitrogen is fourfold coordinated to three Pt atoms and one N atom. The interstitial dinitrogen unit has a zero-pressure N-N bond length of 1.42 Å, much longer than the molecular triple bond, and consistent instead with a N-N single bond. The calculated energy versus unit-cell volume was fitted with the Birch-Murnaghan equation of state, giving an equilibrium lattice parameter that agrees with experiment to within 1% (Table 1). The bulk modulus (B) is shown to be considerably higher than that of both bulk platinum and fluorite PtN_2 , again in good agreement with experimental results. The slight overestimation of the lattice parameters and the underestimation of the calculated bulk moduli with respect to the experimental results, both for PtN_2 and for Pt, are a likely consequence of the choice of the PBE density functional.¹²

In order to check the local mechanical stability of the pyrite structure we computed its elastic constants. For crystals with cubic symmetry, application of a single strain to the lattice vectors is sufficient to determine all three independent elastic constants.¹⁵ These calculations—in addition to confirming the values of B calculated from the equations of state—also show pyrite structure PtN_2 to be mechanically stable and to have a relatively high shear modulus (Table II), an important indicator for hardness in dielectrics.¹⁶ The high G/B ratio (G being the shear modulus) or, equivalently, the low Poisson's ratio (ν) points to a high degree of covalency,¹⁷ suggesting that intercalation of the dinitrogen units into the Pt lattice induces a substantial change of the electronic structure from metallic, in bulk Pt, to covalent in PtN_2 . Our elasticity calculations for zinc-blende PtN (Table II) suggest that it is mechanically unstable, as claimed in

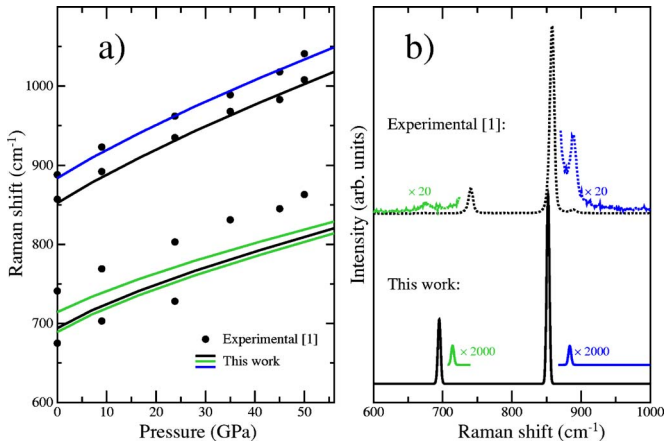


FIG. 2. (Color online) (a) Calculated and experimental (from Ref. 1) Raman frequencies as a function of pressure. An agreement within 5% in the frequency determination is typical for this kind of calculations. (b) Calculated and experimental Raman intensities. An additional calculated peak with intensity similar to the light grey peak at 710 cm⁻¹ is not shown as its frequency overlaps with the intense mode at 695 cm⁻¹.

Ref. 2, but our difference between c_{11} and c_{12} for that particular configuration is too small to allow us to make conclusive statements about stability within the approximations used. However, our calculations show conclusively that zinc blende as well as rocksalt and fluorite structures are in poor agreement with the bulk properties reported in Ref. 1 (Table I).

The calculated zone-center vibrational modes of PtN₂ pyrite, as determined using density-functional perturbation theory,¹⁸ show good agreement with experimentally observed Raman spectra. Calculated and experimental Raman frequencies over a range of pressures are compared in Fig. 2(a). Calculations show the existence of two almost degenerate modes giving rise to a Raman peak around 700 cm⁻¹ [Fig. 2(a)] which was reported but not shown in Ref. 1 and originally attributed to a nonstoichiometry of the samples. The

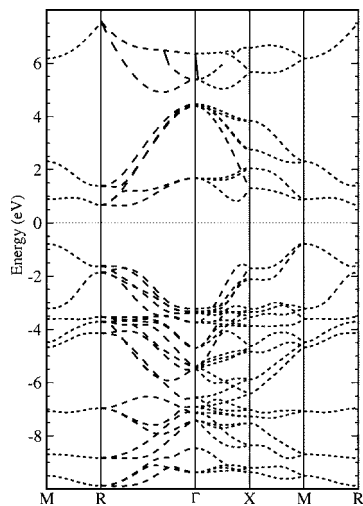


FIG. 3. Electronic bands of Pyrite PtN₂ at ambient pressure along high symmetry directions. Filled states have negative energies.

TABLE II. Elastic constants and elastic moduli (in GPa) for a variety of proposed PtN and PtN₂ phases, calculated in the limit of infinitesimal strain (E is the Young's modulus, other quantities are defined in the text). Mechanical stability for cubic crystals is expressed in the following conditions on the elastic constants Ref. 25: $c_{44} > 0$, $c_{11} > |c_{12}|$, and $B = \frac{c_{11} + 2c_{12}}{3} > 0$.

	c_{11}	c_{12}	c_{44}	B	G	E	ν
Pyrite	696	83	136	288	221	528	0.19
Fluorite	473	160	115	264	136	348	0.28
Zinc-Blende	197	200	22	199	10	30	0.48
Rock-Salt	266	221	36	236	30	86	0.44

calculated Raman intensities¹⁹ [Fig. 2(b)] show the presence of two intense peaks, in good agreement with the experimental results, and of three weak modes, two of which are seen in the experimental spectra. It is interesting to note that all Raman active phonon modes of PtN₂ pyrite, although calculated using the full cell, arise only from the displacements of the nitrogen atoms, and do not have Pt components. In fact their frequencies are in fair agreement with those predicted²⁰

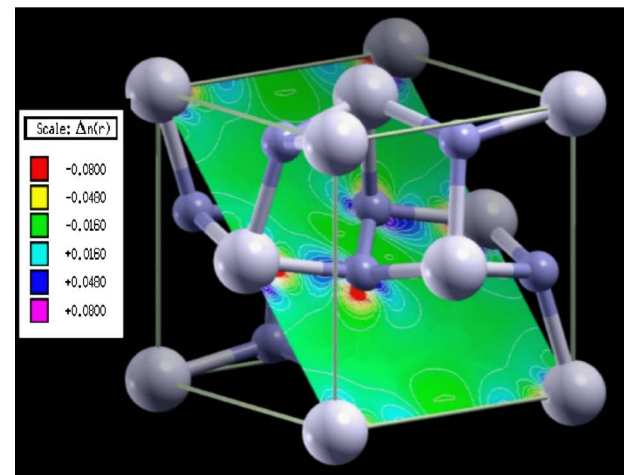
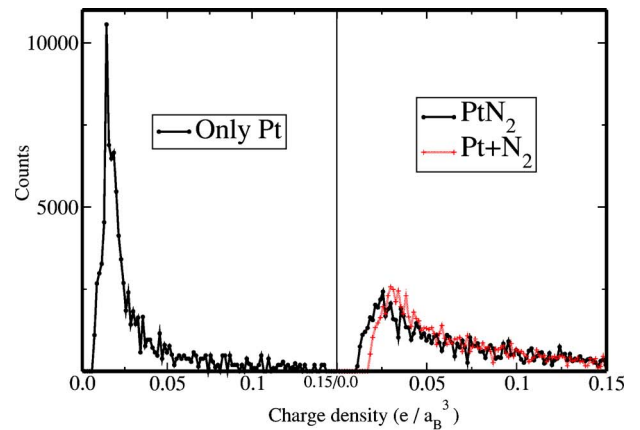


FIG. 4. (Color online) Up: Histogram of charge densities for bulk Pt (left), for PtN₂ (down, black), and for Pt+N₂ (right, grey). Down: Cut of the charge density difference (compound-individual atoms) showing charge displacement.

and later observed²¹ for single-bonded nitrogen in its polymeric phase.

Finally, the calculated electronic band structure of pyrite PtN₂ at zero pressure, reported in Fig. 3, shows a clear insulating character. Band gaps are typically underestimated within density-functional theory, so the calculated indirect band gap of about 1.5 eV could correspond to a true gap of 2–3 eV, which would make PtN₂ an interesting candidate for optical applications.²² The insulating character is consistent with the covalent nature of bonding revealed by the low Poisson's ratio.

All the evidence presented so far strongly indicates that the new compound has a $P\bar{a}3$ structure with interstitial single-bonded N₂ units, hence making it desirable to find an explanation for how this structure can in effect be responsible for the hardness and insulating properties of this compound. Insertion of atomic nitrogen into transition metals is known to lead to an increase in directional bonding and therefore to an increase of mechanical strength. Grossman *et al.*²³ have shown that such changes are more dramatic for early transition metals, due to the fact that the flat density distribution of the elemental phase is more heavily altered by the insertion of interstitial nitrogen atoms. Late (heavier) transition metals have a more corrugated density distributions in their elemental phases, and therefore should not increase their hardness in the nitride phases, as shown in Ref. 23 for the rock-salt phases. A histogram of the density distribution for pyrite PtN₂ (Fig. 4) shows however that insertion of dinitrogen in Pt causes a fourfold reduction of the histogram peak, which is qualitatively comparable to the reduction observed in Ref. 23 for light transition metals, indicating that directional bonding with dinitrogen interstitials is stronger than with atomic nitrogen. Moreover, a comparison

of the density histogram of PtN₂ with that obtained by summing the densities of Pt and N₂ calculated separately but at the same lattice positions, shows that, in the compound, the charge density reaches a lower minimum value than that obtained for the sum of the Pt and N₂ densities. This is also clear from Fig. 4, where a two-dimensional cut of such charge difference is shown. Besides a noticeable rehybridization of the Pt semicore orbitals, the figure also shows that, in the PtN₂ compound, charge flows from interstitial low-density regions to bonding regions of higher density, which is again consistent with covalency. The presence of interstitial dinitrogen units is crucial to explain the insulating character of pyrite PtN₂, since all platinum nitride structures proposed so far contain interstitial nitrogen in the atomic form and have been reported to be conducting.

In conclusion, in Ref. 1 platinum nitrite was observed as a result of the reaction of a molecular nitrogen fluid with Pt metal at high pressure and temperature ($P \sim 45$ GPa and $T \sim 2000$ K). Here, we show that this compound is PtN₂ having a pyrite structure consisting of interstitial single-bonded N₂ units incorporated in the octahedral cavities of a fcc Pt sublattice. This incorporation implies a change of bonding for N₂ from triple to single, a transition that molecular nitrogen is known to undergo during amorphization at higher pressures and low temperatures.²⁴ We therefore argue that pressure-induced changes in the bonding character of nitrogen are key to understand the synthesis of PtN₂.

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