OsN$_2$: Crystal structure and electronic properties

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Osmium nitride belongs to a family of nitrides synthesized recently at high pressures from their parent elements. Here we show, based on first-principles calculations, that the crystal structure of osmium nitride is isostructural to marcasite. Excellent agreement is obtained between the authors' results and x-ray, Raman, and compressibility measurements. In the OsN$_2$ marcasite structure single-bonded N$_2$ units occupy the interstitial sites of the Os close-packed lattice, giving rise to a metallic compound. A comparison between the formation energies of OsN$_2$ and PtN$_2$ explains the similar thermodynamic conditions of formation reported experimentally for the two compounds. © *2007 American Institute of Physics.* [DOI: 10.1063/1.2430631]

A family of late transition metal nitrides has been recently synthesized starting from their constituent elements, Pt, Ir, and Os, and nitrogen.[1–3] The compounds have been obtained by subjecting the parent metal to extreme conditions of pressure and temperature, in a nitrogen embedding medium, in a diamond-anvil cell. Interest in these compounds resides in their large bulk modulus, which might suggest superhard mechanical properties. High-pressure x-ray diffraction experiments on the three compounds give bulk moduli of 372 GPa (platinum nitride),[1] 432 GPa (iridium nitride), and 358 GPa (osmium nitride), respectively.[2] Despite intense experimental and theoretical efforts over the last two years, the crystal structure of these compounds is only known in the case of platinum nitride.[4,5] X-ray diffraction measurements were able to clarify for all compounds the nature of the sublattice of the transition metal atoms, but due to the large atomic-number ratio between the metal and nitrogen, x-ray diffraction is unable to provide insight into the internal position of the nitrogen atoms nor into the stoichiometry of the compound. The metal sublattice has been reported to be face-centered cubic in the case of Pt nitride,[4] orthorhombic in Os nitride, and rhombohedral in Ir nitride.[2]

Among a number of theoretical structures proposed in the last two years for platinum nitride, *ab initio* calculations show that the crystal structure with the lowest energy is isostructural to pyrite (thus with stoichiometry Pt:N=1:2).[4,5] Calculated Raman spectra and diffraction patterns for PtN$_2$ pyrite agree very well with experiments. Nitrogen atoms in pyrite PtN$_2$ pair up to form single-bonded dinitrogen units

(N$_2$) which fill the octahedral holes of the fcc Pt sublattice.

The crystal structure of Ir and Os nitrides is not yet known. The similarity between the Raman spectra of PtN$_2$ and Ir nitride, particularly in the frequency region of the single-bonded N$_2$ stretching, suggests that Ir nitride could also be composed of dinitrogen units located in the interstitial holes of the rhombohedral Ir sublattice. The picture is, however, much less clear in the case of osmium nitride, where no Raman peaks have been observed,[2] presumably due to the metallic character of the compound.

In this work we compare the structural and mechanical data obtained from *ab initio* calculations with the experimental data of Ref. 2, and conclude that the crystal structure of Os nitride is isostructural to that of marcasite, a known polymorph of FeS$_2$ structurally similar to pyrite. Therefore, dinitrogen units similar to those found in PtN$_2$ are also present in OsN$_2$.

TABLE I. Equilibrium lattice parameters (in Å) and zero-pressure bulk modulus (in GPa) and its pressure derivative (B') obtained from fitting calculated energies over a range of volumes with a second order Birch-Murnaghan equation of state. Formation energies ΔE are relative to Os+N$_2$.

	a	b	c	B,B'	ΔE (eV)
Expt.[a]	2.714	4.910	4.102	358,4.67	⋯
Marcasite (Calc.)	2.70	4.93	4.13	359,4.28	1.15
Pyrite (Calc.)	4.85			339,3.85	2.15
Os Expt.[b]	3.03			411,4.0	⋯
Os Calc.	3.05			411,4.3	⋯

[a]Reference 2.
[b]Reference 6.

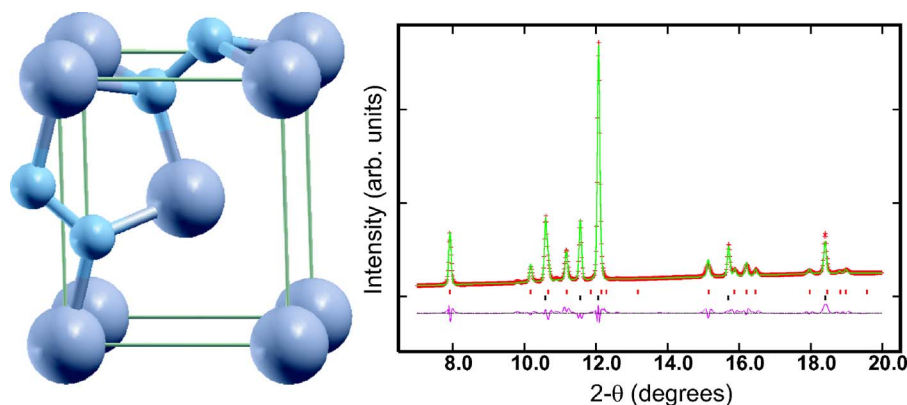a)Electronic mail: amontoya@sissa.it

FIG. 1. (Color online) Marcasite structure of OsN_2, space group *Pnnm*. Osmium atoms (gray) form an orthorhombic lattice, and dinitrogen (N_2) units (light blue) occupy the cavities of the Os lattice. The calculated $N-N$ distance at ambient pressure is 1.427 Å. The Rietveld fit using the *Pnnm* space group is in excellent agreement with experiments, red crosses: data at ambient pressure (λ =0.4237 Å); green line: Rietveld fit; black ticks: OsN_2 peaks; red ticks: Os peaks. The most intense Os peaks are cut off.

Calculations[7] were performed within density functional theory using a Perdew-Burke-Ernzerhoff exchange correlation functional[8] and a plane wave basis set for the electronic wave functions with a kinetic energy cutoff of 70 Ry. A pseudopotential description of the ion-electron interaction[9] was used, with osmium's $5s$ and $5p$ semicore electrons included in the valence. Brillouin zone integration was found to be converged with a uniform grid of $9 \times 9 \times 9$ points (corresponding to 205 points in the irreducible zone of the marcasite structure).

The marcasite structure has the space group *Pnnm*, with osmium atoms on the Wyckoff sites $2a$ [(0,0,0) and $(1/2,1/2,1/2)$] and nitrogen atoms on the site $4g$ [(x,y)], with two internal parameters x and y. Structural relaxations were thus performed by relaxing the nitrogen positions, while osmium atoms are fixed by symmetry. The calculated properties (equilibrium volume, lattice parameters, and bulk modulus) of OsN_2 marcasite are reported in Table I and agree very well with experiment. The calculated nitrogen internal parameters at 0 GPa are $x=0.127\,51$ and $y=0.403\,86$. A Rietveld refinement (Fig. 1) of the observed diffraction pattern using the *Pnnm* space group shows that the marcasite structure is fully consistent with the x-ray data.

The theoretical formation energy of marcasite OsN_2, calculated as a difference between the *ab initio* total energies of OsN_2 and those of Os metal and molecular N_2 in the ϵ structure at zero pressure, is found to be positive (1.15 eV), indicating that the compound is in principle thermodynamically unstable towards decomposition into its constituent elements, at zero pressure. It is interesting to remark that the formation energy of PtN_2 was also found to be positive, but larger than the one found here for OsN_2.[4] This indicates a lower propensity to dissociate back into the constituent elements in the case of OsN_2, with respect to PtN_2, which is consistent with the experimental observation that much larger quantities of OsN_2 than PtN_2 have been found in the samples recovered at ambient pressure. From the calculated energies as a function of volume, at $T=0$ K, we extracted the pressure dependence of the enthalpies shown in Fig. 2.

Upon application of pressure the formation energy of OsN_2 marcasite decreases and eventually vanishes at 23 GPa [Fig. 2(a)] above which the compound becomes more stable than its constituents, at least at low temperature. This is consistent with the experimental finding that the compound can be synthesized only when pressure reaches 50 GPa. We also notice that the enthalpy of a hypothetical OsN_2 compound with the pyrite structure is significantly higher than that of OsN_2 marcasite at all calculated pressures (up to 200 GPa).

A more appropriate comparison of the theoretical predictions with the reported conditions for the synthesis of the compound (50 GPa, 2000 K) would require a calculation of its finite-temperature Gibbs free energy of formation, which is beyond the scope of this work. We remark, however, that at the conditions of synthesis, nitrogen is likely to be in the liquid state. An extrapolation of the melting curve of nitrogen measured up to 18 GPa,[10] in fact, gives 1500–1750 K for the melting temperature at 50 GPa,[2] which is below the reaction temperature. Assuming that differences between the vibrational contributions to the free energy are negligible for the solid phases and using for the excess free energy of the liquid the empirical expression derived by Kroll based on thermochemical data,[11] we obtain at 50 GPa a reaction temperature of 2100 K, in good agreement with the experimental value. We thus conclude that the synthesis of the compound is likely to occur at, or close to, the thermodynamic boundary.

In an attempt to rationalize the experimental observation that the synthesis conditions of the three nitrides are nearly
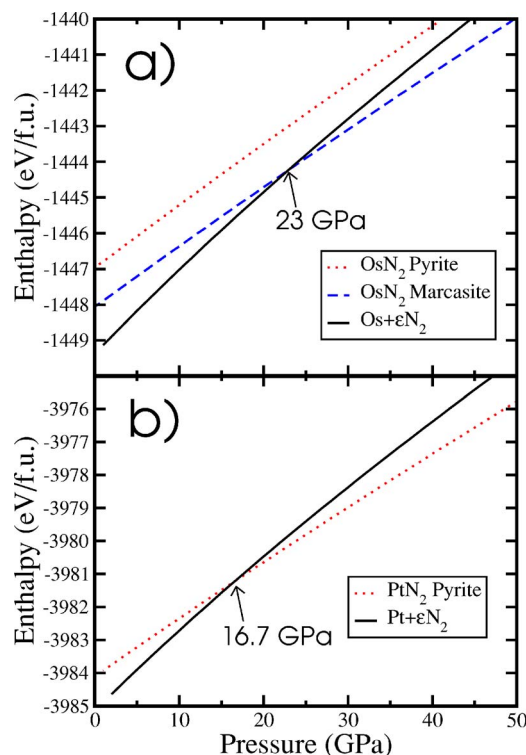

FIG. 2. (Color online) (a) Enthalpy vs pressure for OsN_2 pyrite, OsN_2 marcasite, and their constituents at $T=0$. (b) Same as in (a) for PtN_2 pyrite.
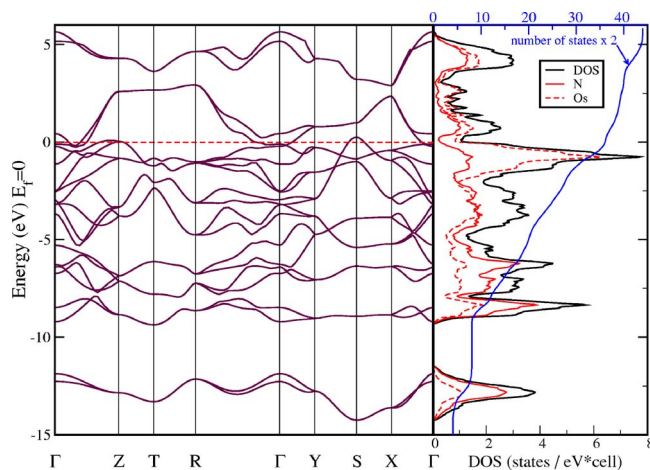
FIG. 3. (Color online) Electronic bands of marcasite OsN_2 at ambient pressure along high symmetry lines together with the corresponding density of states and its projection onto the constituent atoms. The Fermi energy is set to zero.

FIG. 4. (Color online) Density of electronic states and its integral for (a) OsN_2 marcasite, (b) OsN_2 pyrite, and (c) PtN_2 pyrite. The Fermi energy is set to zero.

identical,[2] we report in Fig. 2(b) the enthalpy of formation for pyrite PtN_2 (a similar comparison with Ir nitride is not possible as its structure is not yet known). Interestingly, even though the zero-temperature calculated transition pressure is slightly lower than the one found for OsN_2, the zero-temperature formation energy of PtN_2 at 50 GPa is very similar to that of OsN_2 (~-1.3 eV). Under the assumption discussed above that finite-temperature corrections to the free energy can be approximated by simply considering the excess free energy of liquid nitrogen, then it appears that the thermodynamical boundaries for the high-temperature synthesis of OsN_2 and PtN_2 are likely to be very close, in agreement with the experimental findings.

We finally comment on the electronic structure of OsN_2 marcasite. Our band structure calculations (Fig. 3) show that, contrary to PtN_2 which is known to be an insulator,[4] OsN_2 marcasite has a metallic character, which is in agreement with the experimentally observed absence of first-order Raman peaks for this compound. Os belongs, like Pt, to the last row of the transition metal series and has two electrons less than Pt, so an insulating character would be compatible with electron counting arguments. In order to understand why OsN_2 is a metal it is interesting to consider a hypothetical OsN_2 compound with the pyrite structure. In a simplified picture in which the density of electronic states (DOS) only depends on the crystal structure and not on the electron filling, the electronic structure of pyrite OsN_2 can be obtained from that of pyrite PtN_2 by removing eight electrons (the unit cell of pyrite contains 4 f.u.), which corresponds to the Fermi level indicated by the red line in Fig. 4(c), which would imply a metallic character also for this hypothetical compound. The *ab initio* DOS of OsN_2 pyrite [Fig. 4(b)] confirms that the reasoning is correct. The gap at a filling of 80 electrons/cell (eight electrons above the Fermi level) is still present, and the Fermi level lies in a region of finite density of states. However, the OsN_2 pyrite DOS has a very high density of states at the Fermi level, which is typically
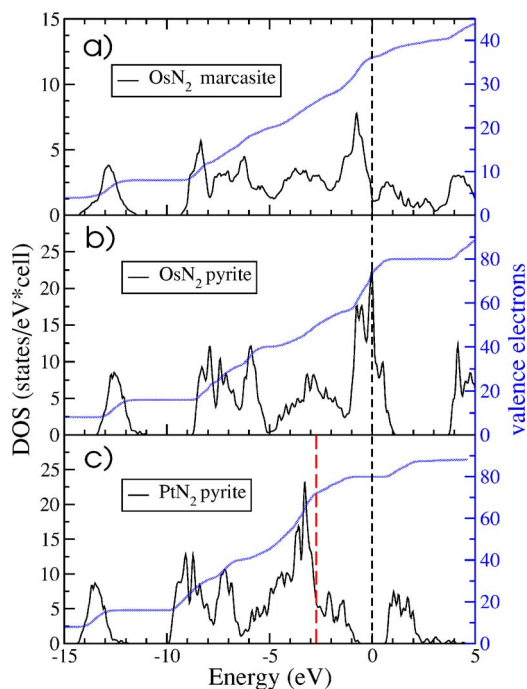
associated with an instability of the electronic structure, leading either to magnetism or to structural distorsions. The marcasite structure, with its simple structural connection to pyrite, can be seen as a way for the system to relieve the electronic instability found in the pyrite structure. OsN_2 marcasite [Fig. 4(a)] shows, in fact, a much lower density of states at the Fermi level, which explains its lower energy with respect to OsN_2 pyrite.

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