Synthesis of Novel Transition Metal Nitrides IrN_2 and OsN_2

Andrea F. Young,[1,2] Chrystele Sanloup,[3,4] Eugene Gregoryanz,[1,5] Sandro Scandolo,[2,6]
Russell J. Hemley,[1] and Ho-kwang Mao[1]
[1]*Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Road NW, Washington D.C. 20015, USA*
[2]*CNR-INFM Democritos National Simulation Center, Trieste I-34014, Italy*
[3]*Universit Pierre et Marie Curie, case 110, 4 place Jussieu, Paris, France*
[4]*Institut de Physique du Globe de Paris, case 110, 4 place Jussieu, Paris, France*
[5]*School of Physics and Centre for Science at Extreme Conditions, University of Edinburgh, Edinburgh, EH9 3JZ, United Kingdom*
[6]*The Abdus Salam International Centre for Theoretical Physics, Trieste I-34014, Italy*
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Two new transition metal nitrides, IrN_2 and OsN_2, were synthesized at high pressures and temperatures using laser-heated diamond-anvil cell techniques. Synchrotron x-ray diffraction was used to determine the structures of novel nitrides and the equations of states of both the parent metals as well as the newly synthesized materials. The compounds have bulk moduli comparable with those of the traditional superhard materials. For IrN_2, the measured bulk modulus [$K_0 = 428(12)$ GPa] is second only to that of diamond ($K_0 = 440$ GPa). *Ab initio* calculations indicate that both compounds have a metal:nitrogen stoichiometry of 1:2 and that nitrogen intercalates in the lattice of the parent metal in the form of single-bonded N-N units.

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The design of new materials with a hardness comparable to that of diamond poses a considerable experimental challenge ([1], and references therein). Superhard solids are typically synthesized by subjecting the parent materials to extreme conditions of pressure and temperature, where structural changes are induced either by thermodynamical or by kinetic factors. If the changes are irreversible, the new phase can be recovered to ambient conditions. It is usually assumed that hardness is defined by the elastic moduli: bulk modulus, a measure of resistance to volume change by applied pressure, and shear modulus, a measure of resistance to reversible deformations upon shear stress. However, the latter is much more difficult to measure experimentally, especially for the samples synthesized at high pressures. Superhard materials are generally isotropic to prevent deformation in a preferential direction, and, since a superhard material must support the volume decrease created by applied pressure, there exists for nonmetallic materials a direct empirical relation between hardness and bulk modulus [2]. Because the bulk modulus correlates inversely with molar volume, superhard materials are traditionally expected to be compounds with short bond lengths, i.e., those made up of light elements (B, C, O, N). C_3N_4, for example, was predicted to have a bulk modulus larger than that of diamond [3]; however, no such compound has yet been synthesized, and *c*-BN remains the hardest light nitride [$K_0 = 382(3)$ GPa, $K_0' = 4.46(15)$ [4]]. An alternative approach is to search for compounds that include heavier elements but have a high coordination number. This search has recently encountered some success, with the synthesis of two transition metal nitrides with bulk moduli larger than those of their parent metal: δ-MoN [$K_0 = 345(9)$ GPa, $K_0' = 3.5(3)$] [5] and platinum nitride [$K_0 = 372(5)$ GPa, $K_0' = 4$] [6], with the bulk moduli of the parent metals being $K_0 = 267$ GPa ($K_0' = 4.5$) for molybdenum [7] and $K_0 = 274$ GPa ($K_0' = 5.2$) for platinum [8]. It is predicted that transition metal nitrides should have larger bulk moduli than their parent metal due to directional bonding introduced by nitrogen atoms in the lattice, except when such directional bonding is already present in the parent metal, e.g., W or Os [9]. These metals usually have low compressibility and have been the subject of a number of recent studies [8,10–13]. From the materials science and solid state physics perspective, the synthesis of new nitrides thus has been fueled not only by their fundamental importance in the understanding of atomic bonding but also for their potential technological applications.

Bulk osmium and iridium nitrides have not been described in the literature before. The chemistry of Ir and N_2 is limited to the search for nitrido complex molecules such as $[Ir_3N(SO_4)_6(H_2O)_3]^{4-}$ [14] in the hope of finding intermediate steps of N_2 assimilation. For Os, it is known that at ambient pressure and cryogenic temperature laser-ablated osmium atoms react with nitrogen molecules to form what is essentially osmium dinitride by the direct insertion of osmium into the dinitrogen triple bond [15]. In this Letter, we present the high-pressure/temperature synthesis of two novel transition metal nitrides: IrN_2 and OsN_2 [16]. Iridium nitride, in particular, was observed to have bulk modulus $K_0 = 428(12)$ GPa (K_0' fixed at 4), higher than that of any previously synthesized material, a milestone that may open up new paths in the search for ultrahard materials, outside the traditional B-C-O-N system.

IrN_2 and OsN_2 were both synthesized under conditions similar to those observed for the formation of PtN_2, i.e., above 50 GPa and 2000 K. For the description of the experimental technical details and the techniques used in this study, see Ref. [6], and references therein. *Ab initio* structural optimizations were carried out within the density functional theory using the Perdew-Burke-Ernserhof [17] exchange-correlation functional and the plane wave pseudopotential method. Ultrasoft pseudopotentials [18] were used with an energy cutoff for the plane wave basis set of 50 Ry. Structural searches and optimizations were performed with the QUANTUM-ESPRESSO package [19].

Electron microprobe analyses of the recovered samples gave stoichiometries ranging from 1:1 to 1:3, with statistical error much higher than in our previous study [6]. Moreover, recent theoretical results [20] and x-ray photoelectron spectroscopy data [21] have cast doubt on the reliability of microprobe measurements for noble metal nitrides, indicating a stoichiometry of 1:2 for the platinum nitride. This finding is supported by our own *ab initio* simulations for all three noble metal nitrides. It is likely that this systematic error in microprobe measurements for noble metal nitrides is due to the penetration depth of the electron beam (1 μm) being larger than the penetration depth of the nitride formation reaction. Microprobe measurements thus serve principally to establish a lower limit for nitrogen abundance and confirm the existence of stable ambient pressure phases of both Os and Ir nitrides.

For OsN_2, x-ray diffraction patterns (shown in Fig. 1, lower curve) can be indexed as orthorhombic, with $a = 2.714(2)$ Å, $b = 4.910(5)$ Å, $c = 4.102(3)$ Å at 0.1 MPa. Patterns for IrN_2 (Fig. 1, upper curve) can be indexed as hexagonal, with $a = 3.966(4)$ Å and $c = 6.958(7)$ Å at 0.1 MPa. Because of the large mass difference between nitrogen and the parent metals, nitrogen positions could not be conclusively determined by Rietveld refinement for either of the two compounds, and LeBail fits shown in Fig. 1 were therefore performed. The evolution of the volumes with pressure was fitted with a Birch-Murnaghan equation of state (Fig. 2). The zero-pressure bulk modulus K_0 of OsN_2 [$K_0 = 358(6)$ GPa with $K_0' = 4.67$] is slightly lower than that of pure Os [$K_0 = 395(5)$ GPa with K_0' fixed at 4.5 [11,13]]. For IrN_2, although the precision on the equation of state is lower due to the lower quality of the x-ray patterns, the obtained bulk modulus [$K_0 = 428(12)$ GPa with K_0' fixed at 4] is 17% higher than that for pure Ir [$K_0 = 365(5)$ GPa with K_0' fixed at 4]. Our determined equation of state of Ir falls within previously published values, $K_0 = 354(6)$ GPa with K_0' fixed at 4 [22] and $K_0 = 383(14)$ GPa with $K_0' = 3.1(0.8)$ [10].

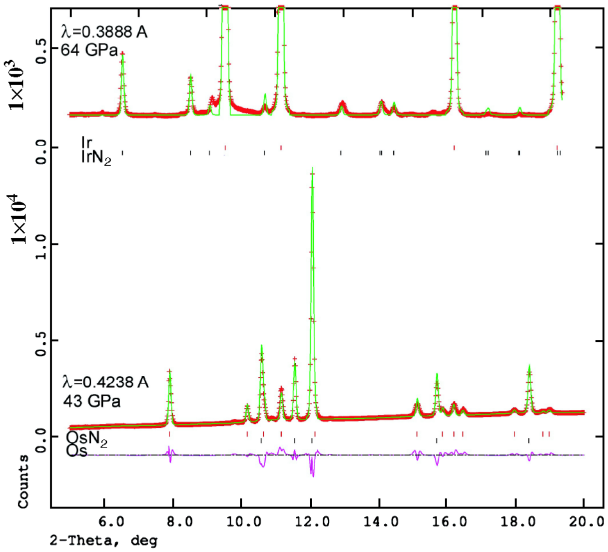

FIG. 1 (color online). X-ray diffraction patterns for the Ir + IrN_2 experiment at 64 GPa (upper curves) and of the Os + OsN_2 experiment at 43 GPa (lower curves). Gray line: LeBail refinement fit [28]; gray crosses: data; upright dashes: predicted reflections. In the case of the Ir + IrN_2 experiment, the spectrum is largely dominated by the Ir signal (ratio 1/100), which was therefore cut for clarity. Also shown is the difference curve between data and fit.

In order to determine the internal positions of the nitrogen atoms and confirm the 1:2 stoichiometry of the nitrides, we have performed *ab initio* structural optimizations for both IrN_2 and OsN_2 by tentatively fixing the metal lattice parameters and positions to the experimentally determined values and considering a variety of different nitrogen starting positions.

In the case of iridium nitride, we started by considering one-formula-unit structures with either one or two nitrogen atoms. The lowest energy structure was found to contain two nitrogen atoms per unit cell, closely paired to form an interstitial single-bonded dinitrogen unit, with a bond length of ~1.3 Å. It has been recently shown by us [23] that dinitrogen units are responsible for the very intense Raman signal observed in PtN_2 [6]. Strong Raman modes at similar frequencies are reported also for IrN_2 (see Fig. 3), which we therefore attribute to dinitrogen units inserted into the Ir lattice. However, the internal positions

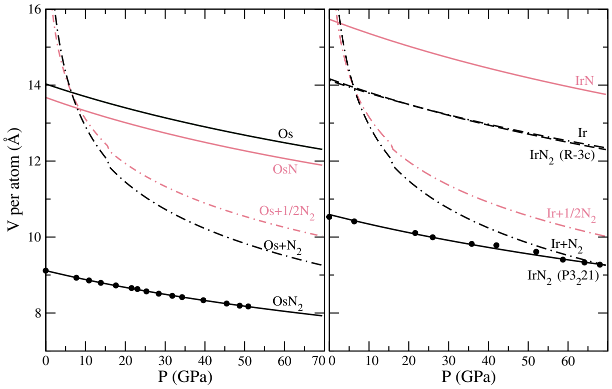

FIG. 2 (color online). Equation of state of Ir, Os, IrN, OsN, IrN_2, and OsN_2. Volume per atom for the observed metal nitrides compared with the volume of the reactants (one atom of metal + N_2) at room temperature. Solid circles: Experimental data points. Note that the equation of state of Ir is undistinguishable at this scale with that of IrN_2 if indexed with $R\bar{3}c$ large cell.

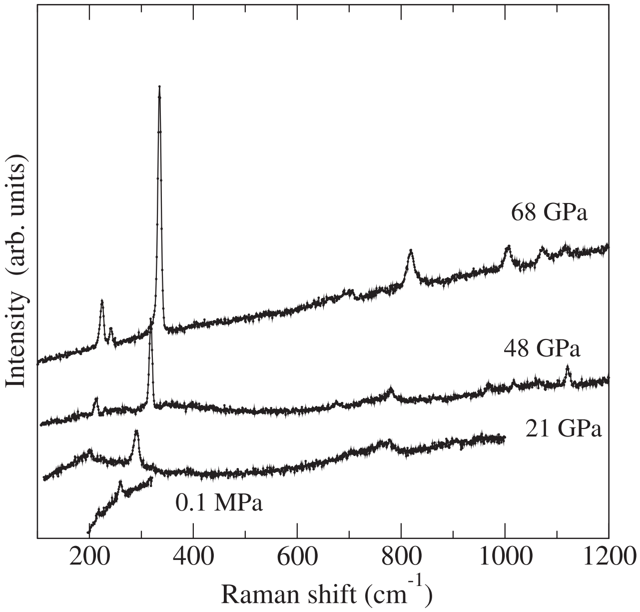

FIG. 3. Representative Raman spectra of IrN_2 under pressure.

of the optimal one-formula-unit IrN_2 structure were not consistent with the symmetry requirements imposed by the x-ray pattern. We thus extended the search to structures with 1:2 stoichiometry, but containing more than one formula unit, and found two space groups which show good, but not complete, agreement with experimentally observed parameters. The first is a primitive hexagonal cell $P3_221$, for which we obtain, fixing the lattice parameters to the experimental values, a structural minimum with iridium atoms on site 3a ($x = 0.353$) and nitrogen atoms on site 6c ($x = -0.200$, $y = -0.769$, $z = -0.137$). A subsequent optimization of the lattice parameters, however, leads again to a significant distortion in this structure from the experimental parameters. Also, we note that, due to its odd number of electrons per unit cell, IrN_2 structures containing an odd number of formula units must be metallic and are, therefore, not compatible with the observed strong first order Raman activity. Subsequent searches on IrN_2 were restricted to an even number of formula units, as an attempt to fulfill the requirement of nonmetallicity, and to structures with threefold symmetry, as observed in the x-ray diffraction data. Such reasoning produced a rhombohedral structure with cell parameters doubled with respect to the $P3_221$ hexagonal cell, which can be indexed as $R\bar{3}c$, with iridium atoms on site 6d and nitrogen atoms on site 12f (rhombohedral settings). With the deletion of axial nitrogen atoms, this structure shows good agreement with x-ray diffraction data with the exception of two low-2θ peaks predicted by this space group which were not observed. Despite good agreement with equilibrium volume and lattice parameters, this structure is predicted to have a very low bulk modulus and a larger volume per atom compared to the $P3_221$ structure (Fig. 2). The calculated and measured volumes and bulk moduli are summarized in Table I, together with calculated energies of formations for both space groups. Depending on the structure, the N-N distance in IrN_2 varied from ~1.25 to ~1.35 Å.

Structural optimizations for the osmium-nitrogen compounds were less exhaustive than for IrN_2 but also suggest a 1 : 2 Os:N stoichiometry and similar dinitrogen units, as no phase could be stabilized at 1:1 stoichiometry with an equilibrium volume within 20% of that observed experimentally. The N-N distance is found to be ~1.4 Å, similar to PtN_2 but slightly larger than those calculated for the IrN_2 structures. The presence of dinitrogen configurations in OsN_2 would suggest an intense Raman signal also in this compound, which is instead found to display no Raman activity. We infer that the lack of Raman activity for OsN_2 may be on account of its metallicity.

Further insights into the stoichiometry of the new compounds can be gained by considering that a necessary thermodynamic condition for the pressure-induced reaction leading to the nitrides is that the volume of the products be smaller than that of the parent phases. The measured volume per atom (Fig. 2) of OsN_2 is always smaller than that of the initial reactants ($Os + N_2$). In contrast, the volume per atom in the case of 1:1 stoichiometry is smaller only below ~10 GPa, i.e., well below the observed reaction pressure. The 1:1 stoichiometry can thus be ruled out for osmium nitride. Similar considerations for iridium nitride rule out a 1:1 stoichiometry also for this compound but indicate that the $R\bar{3}c$ phase of IrN_2 should also be ruled out.

The relative intensity of the x-ray diffraction peaks of the nitride with respect to its parent metal is a good measure of nitride abundance, as Ir and Os (and Pt) have similar atomic form factors. Judging by the intensity ratio between osmium nitride and osmium (about 1:3), OsN_2 is synthesized in much larger quantities than IrN_2 or PtN_2. Although the intensity of the PtN_2 signal varied on different runs, an average intensity ratio between nitride and metal of about 1:10 was observed, while IrN_2 had a signal that was even weaker (1:100) (Fig. 1).

Finally, it is interesting to note that the conditions of pressure and temperature required for the formation of the noble metal nitrides PtN_2, IrN_2, and OsN_2 are nearly identical. This raises interesting questions about the

TABLE I. The calculated and measured volumes per IrN_2 unit and bulk moduli and calculated energies of formations of the proposed structures. Formation energies are relative to the $Ir + N_2$ compound.

Ir-N_2	$P3_221$		$R\bar{3}c$	
	Expt.	Theory	Expt.	Theory
Energy (eV)	···	2.89	···	2.39
K_0(GPa)	428(12)	260	428(12)	155
Volume (Å^3)	31.6(0.1)	29.4	31.6(0.1)[a]	25.8

[a] In the case of $R\bar{3}c$, the volume corresponds to 1/8 of the unit cell volume.

mechanisms of the reaction and the role of the reactant phases. If the reactions were driven by thermodynamics, the position of the transition lines in the P-T space would be determined by the relative enthalpy of the reactant and product phases. Relative enthalpies would then need to behave very similarly for the three nitrides in order to explain the identical conditions of formation. Alternatively, the synthesis may take place within the domain of thermodynamic stability of the products but driven by changes in the kinetics of the reaction. A fit of the melting curve of nitrogen measured up to 18 GPa in Ref. [24], with both Simon-type [25] and Kechin-type [26] melting equations [27], gives 1500–1750 K for the liquid-solid transition temperature at 50 GPa, which is below the reaction temperature (~1800 K). Accordingly, nitrogen is likely to be in the fluid state at the conditions of synthesis, which could accelerate the reactions.

In summary, this discovery opens the door to a new chemistry of nitrogen under extreme conditions with great promise for both a new understanding of the phase diagram of nitrogen at extreme conditions as well as the design of materials with interesting and useful properties, strengthening the hope of finding potentially hard high-pressure phases outside the B-C-O-N system, i.e., with large volumes per atom but high coordination.

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