Potential super-hard Osmium di-nitride with fluorite structure: First-principles calculations

Chang-Zeng Fan, Song-Yan Zeng
Department of Material Science and Engineering, Harbin Institute of Technology, Harbin 150001, China

Li-Xin Li, Ri-Ping Liu, Wen-Kui Wang
Key Laboratory of Metastable Material Science and Technology, Yanshan University, Qinhuangdao 066004, China

Ping Zhang
Institute of Applied Physics and Computational Mathematics, Beijing 100088, China

Yu-Gui Yao
Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, China

We have performed systematic first-principles calculations on di-carbide, -nitride, -oxide and -boride of platinum and osmium with the fluorite structure. It is found that only PtN$_2$, OsN$_2$ and OsO$_2$ are mechanically stable. In particular OsN$_2$ has the highest bulk modulus of 360.7 GPa. Both the band structure and density of states show that the new phase of OsN$_2$ is metallic. The high bulk modulus is owing to the strong covalent bonding between Os 5$d$ and N 2$p$ states and the dense packed fluorite structure.

PACS numbers: 81.05.Zx, 62.20.Dc, 71.20.Be, 61.66.Fn

The search for novel hard materials compared to or even harder than diamond, which has the highest measured hardness of 96 GPa$^4$ and bulk modulus of 443 GPa$^4$ has a long history and has stimulated a variety of great achievements in high-pressure research$^{3,4,5,6}$. Consequently, many new superhard materials have been prepared by high-pressure technique, especially after the laser-heated diamond-anvil cells (DACs) was invented. In general two groups of materials are powerful candidates for super-hard materials: (i) strong covalent compounds formed by light elements, such as polymorph of C$_3$N$_4^7$, B$_6$O$_8^8$ and c-BC$_2$N$_3^9$ (ii) Partially covalent heavy transition metal boride, carbide, nitride and oxide. RuO$_2^{10}$ and OsB$_2^{11}$ are such examples. Theoretically, the nature of hardness has been extensively investigated and many new models have been proposed$^{1,2,3,12,13,14,15,16}$. For the strong covalent materials, hardness can be directly derived$^{13,14,15,16}$ while for some metallic transition metal-based super-hard materials, it is acknowledged that bulk modulus or shear modulus can measure the hardness in an indirect way$^{12,17}$. That is, materials with high bulk or shear modulus are likely to be hard materials.

In the present paper, we focused on the bulk modulus, mechanical and energetic stability of osmium di-nitride (OsN$_2$) with CaF$_2$ structure$^{18}$ by calculating the elastic constants within the density functional based electronic structure method$^{19}$. For the first time we report that the proposed OsN$_2$ compound has very high value of bulk modulus (360.7 GPa) which is even higher than that of OsO$_2$ with the same structure (347.5 GPa) and is comparable with that of orthorhombic OsB$_2$ (365-395 GPa$^{11}$). All first-principles calculations were performed with the CASTEP code$^{20}$. The ultrasoft pseudopotential (USPP)$^{21}$ was employed to describe the interaction between ions and electrons. Both the local-density approximation (LDA)$^{22}$ and the generalized gradient approximation (GGA)$^{23}$ were used to describe the exchange and correlation potentials. For the Brillouin-zone sampling, the Monkhorst-Pack (MP) scheme with a grid of 0.03 Å$^{-1}$ was adopted$^{24}$ The plane-wave cutoff energy is chosen to be 550 eV for LDA and 500 eV for GGA calculations. For the self-consistent field iterations, the convergence was assumed when (i) the total energy difference between the last two cycles was less than 1×10$^{-6}$ eV/atom; (ii) the maximal force on each atom was below 0.006 eV Å$^{-1}$, and (iii) the maximal atomic displacement was below 2×10$^{-4}$ Å. We have tested that with even more strict parameters the total energy can be converged within 0.002 eV/atom for all the systems studied. After getting the equilibrium geometry configuration, we applied the so-called “stress-strain” method to obtain the elastic constants in that the stress can be easily obtained within the density functional based electronic structure method$^{26}$. The “stress-strain” relation can be described as

$$ (\sigma_1, \sigma_2, \sigma_3, \sigma_4, \sigma_5, \sigma_6) = C(\varepsilon_1, \varepsilon_2, \varepsilon_3, \varepsilon_4, \varepsilon_5, \varepsilon_6)^T. \quad (1) $$

For the cubic crystal, there are only three non-zero independent symmetry elements ($c_{11}$, $c_{12}$ and $c_{44}$). Applying two kinds of strains ($\varepsilon_1$ and $\varepsilon_4$) along the crystallographic directions shown in Fig. 1(a)-(b), respectively, can give...
TABLE I: The calculated equilibrium lattice parameters $a$ (Å), elastic constants $c_{ij}$ (GPa), bulk modulus $B$ (GPa), polycrystalline shear modulus $G$ (GPa), Young’s modulus $E$ (GPa), and Poisson’s ratio $\nu$ of typical pure crystals

|       | $a$   | $c_{11}$ | $c_{33}$ | $c_{44}$ | $c_{13}$ | $c_{12}$ | $B$   | $G$   | $E$   | $\nu$ |
|-------|-------|----------|----------|----------|----------|----------|-------|-------|-------|-------|
| Diamond | LDA   | 3.525    | 1105.8   | 607.3    | 140.5    | 462.3    | 545.0 | 1173.8| 0.08  |
|        | GGA   | 3.566    | 1053.3   | 569.1    | 119.5    | 430.7    | 518.0 | 1109.3| 0.07  |
|        | Ave.  | 3.546    | 1079.6   | 588.2    | 130.0    | 446.5    | 531.5 | 1141.6| 0.08  |
|        | Expt. | 3.567$^a$|          |          |          |          | 443$^b$|       |       |       |
| Pt (fcc) | LDA   | 3.921(3.890$^c$) | 391.1    | 82.3     | 279.0    | 316.4(320$^c$) | 69.2  | 193.5 | 0.40  |
|        | GGA   | 3.998(3.967$^c$) | 307.9    | 65.7     | 232.9    | 257.9(238$^c$) | 51.6  | 145.1 | 0.41  |
|        | Ave.  | 3.960(3.928$^c$) | 349.5    | 74.0     | 256.0    | 287.2(279$^c$) | 60.4  | 169.3 | 0.41  |
|        | Expt. | 3.924$^d$  |          |          |          |          | 276$^e$|       |       |       |
| Os (fcc) | LDA   | 3.798(3.814$^f$) | 686.9    | 361.3    | 323.1    | 444.4(441.3$^f$) | 271.6 | 676.9 | 0.25  |
|        | GGA   | 3.851(3.851$^f$) | 614.7    | 328.0    | 282.5    | 393.2(392.9$^f$) | 247.1 | 612.9 | 0.24  |
|        | Ave.  | 3.824(3.841$^f$) | 650.8    | 344.7    | 302.8    | 418.8(417.1$^f$) | 259.4 | 644.9 | 0.25  |
| Os (hcp) | LDA   | 2.712     | 808.7    | 888.6    | 271.2    | 264.7    | 243.7 | 449.0 |       |       |
|        | GGA   | 2.750(2.746$^g$) | 730.1    | 798.3    | 246.9    | 230.5    | 209.8 | 398.9 |       |       |
|        | Ave.  | 2.731     | 1538.8   | 843.5    | 259.1    | 247.6    | 226.8 | 424.0 |       |       |
|        | Expt. | 2.7313$^h$ |          |          |          |          | 395$^i$,462$^j$|       |       |       |

$^a$Reference 12. $^b$Reference 2. $^c$Reference 26, 37. $^d$Reference 34. $^e$Reference 35. $^f$Reference 28. $^g$Reference 33. $^h$Reference 29.

FIG. 1: (Color online) The schematic of strain types: (a)$\varepsilon_1$; (b)$\varepsilon_4$; (c)$\varepsilon_3$

stresses relating to these three elastic coefficients, yielding an efficient method for obtaining elastic constants for the cubic system. For the hexagonal crystal, there are five independent symmetry elements ($c_{12}$, $c_{13}$, $c_{33}$ and $c_{44}$). In order to obtain the additional components $c_{13}$ and $c_{33}$, another strain $[\varepsilon_4$, see Fig. 1(c)] is needed. For each strain, in our practical calculations, its value is varied from -0.003 to +0.003 with a step of 0.0012, then each of three elastic constants takes the arithmetic average value of the six steps. The bulk modulus is obtained from the elastic constants by the relation $B=(c_{11}+2c_{12})/3$.

The lattice and elastic constants of diamond, pure platinum, hexagonal and cubic pure osmium were calculated to verify the reliability of the present calculations. It is well known that LDA usually underestimated the lattice constants and overestimated the elastic constants, while GGA overestimates the lattice constants and underestimates the elastic constants. For this reason we adopted to use the average of the LDA and GGA results as our theoretical estimates. As shown in Table I, the theoretical average lattice constant and bulk modulus of diamond are 3.546 Å and 446.5 GPa, which agree well with the experimental values of 3.567 Å and 443 GPa, with an error of 0.59% and 0.79%, respectively. For the cubic osmium and cubic platinum, the theoretical bulk modulus values (Pt: 287.2 GPa, Os: 418.8 GPa) are also in accordance with previous theoretical results (Pt: 279 GPa, Os: 417.1 GPa). Based on above-mentioned accordance, therefore, we believe that the plane-wave ultrasoft pseudopotential (PW-PP) method we employed is reliable in investigating the mechanical properties of osmium and platinum compounds.

Now we turn to fully study OsN$_2$ with fluorite structure. The results of lattice constant, elastic constants, and bulk modulus of OsN$_2$ are listed in Table II. For comparison, we have in addition given a calculation on platinum dinitride (PtN$_2$) and osmium dioxide (OsO$_2$), and the results are also listed in Table II. Given the elastic constants and bulk modulus, the shear modulus $G$ and the Young’s modulus $E$ can be deduced as follows: $G=(c_{11}-c_{12}+2c_{44})/4$, $E=9B(G/3B+G)$ and $\nu=E/(2G)-1$. These quantities are also shown in Table II.

The key criteria for mechanical stability of a crystal is that the strain energy must be positive, which means in a hexagonal crystal that the elastic constants should
satisfy the following inequalities,

$$c_{44} > 0, c_{11} > |c_{12}|, (c_{11} + c_{12})c_{33} > 2c_{13}^2,$$  \hspace{1cm} (2)

while for a cubic crystal,

$$c_{44} > 0, c_{11} > |c_{12}|, c_{11} + 2c_{12} > 0. \hspace{1cm} (3)$$

It is straightforward to verify from Table I that the elastic constants of the hexagonal osmium satisfy formula (2), implying the stability of hcp Os, which is consistent with the experimental observation. In the same manner, from our calculation results in Table I, one can find that PtN$_2$, OsN$_2$ and OsO$_2$ with fluorite structure are also mechanically stable since their elastic constants fit well in formula (3). The stability of these three crystals can also be confirmed by providing the Poisson’s ratio, whose value is usually between -1 and 0.5, corresponding to the lower and upper limit where the materials do not change their shapes. Note that the present result of bulk modulus of PtN$_2$ is 295.2 GPa. The previous FLAPW (full-potential linearized augmented plane waves) calculation gives 290 GPa$^{26}$ Remarkably, the two approaches agree well, suggesting again the reliability of PW-PP method in exploring the structural properties of transition metal compounds. On the other hand, we obtained the bulk modulus of OsO$_2$ to be 347.5 GPa, which is ~13% smaller than that obtained from full-potential linear muffin-tin orbital (FP-LMTO) method$^{35,36}$ This difference may come from different density functional based electronic structure method. It reveals in Table I that OsN$_2$ has the highest bulk modulus of 360.7 GPa in our series of calculations, this value of OsN$_2$ is much higher than that of other noble metal di-nitride (347 GPa for IrN$_2$, 190 GPa for AgN$_2$, and 222 GPa for AuN$_2$). The shear modulus of OsN$_2$ is calculated to be 103.4 GPa, comparable with that of PtN$_2$ (104.6 GPa) as shown in Table I, but much smaller than those of diamond (531.5 GPa) and OsO$_2$ (237.1 GPa). Thus compared to diamond or OsO$_2$, OsN$_2$ cannot withstand the shear stress to a large extent. It is interesting to point out that OsN$_2$ was implicitly referred in Ref.$^{37}$ to be unstable or has a little bulk modulus. This inconsistency may come from the intrinsic technique flaws in WIEN2K code for obtaining the elastic constants, in which the implanted rhombohedral distortion is not volume-conservative. When applying a non-volume-conservative strain, the expression $\phi_{\text{elast}} = \frac{1}{2}c_{ij}\varepsilon_i\varepsilon_j$ for elastic energy is no longer accurate, resulting in unexpected results in some special cases$^{38}$.

Furthermore, the electronic structure and chemical bonding of OsN$_2$ with fluorite structure are studied by calculating its total charge density, Mulliken population,
and density of state (DOS). In Fig. 2, we plot the total electron density in a (110) plane which cut through both the Os and N sites. The bonding behavior of OsN₂ can be effectively revealed by analyzing the charge density data in real space ρ(r) at three types crystalline symmetry points, as indicated by filled circles, open squares, and open circles in Fig. 2. We found that the charge density of these three kinds points are about 0.8, 0.3 and 0 e Å⁻³ respectively. Thus the charge density maximum lies between Os and N atoms, indicating formation of strong covalent bonding between them. Combining the fact that each N atom occupies the tetrahedral interstitial formed by four Os atoms around it, it is not difficult to understand that OsN₂ has a low compressibility. Table III shows bond Mulliken population analysis of OsN₂, OsO₂ and PtN₂. NM1 and NM2 denote the first and second non-metal atoms, and M denotes the metal atom.

| Atomic (e) | Bond (e) |
|-----------|----------|
| NM1       | NM2      | M        | NM1-M    | NM2-M    | NM1-NM2 |
| OsN₂      | -0.54    | -0.54    | 1.09     | 1.25     | 1.25     | -0.7    |
| OsO₂      | -0.55    | -0.55    | 1.10     | 0.98     | 0.98     | -0.45   |
| PtN₂      | -0.45    | -0.45    | 0.9      | 1.08     | 1.08     | -0.34   |

III reveals that OsN₂ has a low compressibility. Table III also lists the Mulliken atomic population analysis results, from which we can see the total charge transfer from Os to N is 1.10, resulting Os in +1.10 charge state and N -0.55 charge state. Therefore, the chemical bonding between Os and N has some character of ionicity. It shows in Table III that the transferred charge in OsN₂ is almost the same as that in OsO₂, and is more than that in PtN₂. Thus we can make a conclusion that the charge transfer effect is more influenced by the metal atom rather than the non-metal atom. It is interesting to note that the mechanical properties of OsN₂ are also very similar to OsO₂ rather than PtN₂, as revealed in our above discussions.

The partial DOS is shown in Fig. 3, no energy gap near Fermi level is seen, indicating the metallic nature of OsN₂. At the Fermi level the total DOS is 1.88 states/eV formula units. It reveals that from -18 to -12 eV the states are mainly N (2s) states with a small contribution from Os (5d and 6p). The states above -9 eV mainly come from Os 5d and N 2p orbitals.

It was recently demonstrated in both theory and experiment that the synthesized platinum nitride crystallized in pyrite structure. The pyrite structure (space group number 205), which was also observed in the silica recently, is cubic with 12 atoms per primitive cell. For pyrite PtN₂, both the four Pt atoms and the midpoints of the four nitrogen pairs arrange in fcc positions and result in NaCl-type arrangement. In addition, each pair of nitrogen atoms aligns along one of the (111) directions. Besides the lattice constant a, the position (u, u, u) of N is the only free structural parameter of pyrite PtN₂. Inspired by these advances, we have also performed a series of ab initio total energy calculations to find if OsN₂ favors the intriguing pyrite structure as platinum nitride does. Figure 4(a) gives the the energy of OsN₂ with the internal parameter u varied from 0.23 to 0.40. The plot reveals that fluorite OsN₂ lies at a local minimum, indicating its metastable nature. The location of lowest total energy is at 0.3614 for GGA calculations, corresponding to the lattice constant of 4.9246 Å of the pyrite structure. The bond length of nitrogen pairs in pyrite OsN₂ is found to be 1.365 Å, even smaller than that of pyrite PtN₂ (1.51 Å). The separation of nitrogen pairs in the pyrite OsN₂ and PtN₂ is nearly the same as that of a single-bonded cubic-gauche structure of N observed recently, which means that the nitrogen pairs probably consist some characteristics of covalent bonding. The calculated formation energies of pyrite and fluorite OsN₂ at ambient pressure are 0.69 eV and 1.10 eV (per formula unit), which are smaller than those of pyrite PtN₂ (0.72eV) and fluorite PtN₂ (3.5eV) respectively. Figure 4(b) plots the enthalpy versus pressure for the fluorite and pyrite structures. In the overall range of external pressure that we have studied, the enthalpy of pyrite OsN₂ is always lower than that of fluorite OsN₂, implying that no first-order phase transition might occur at zero-temperature between these two structures. In addition, the elastic constants of pyrite OsN₂ and PtN₂ are also calculated and listed in Table II, wherein the results for PtN₂ show good agreement with those of experimental and other available theoretical results. The calculated elastic constants of pyrite OsN₂ satisfy formula. Therefore, it is also a mechanically stable crystal structure though its bulk modulus is about 10% lower than...
Practically, systematic calculations were performed on di-

that of fluorite OsN₂.

In conclusion, the OsN₂ with fluorite structure is first
reported to be mechanically stable and have a very high
bulk modulus of 360.7 GPa by the first-principles calcula-
tions. The electronic and chemical bonding properties
have been investigated, indicating that the bonding is a
mixture of covalent and ionic components. It is found
that the electronic properties of OsN₂ is very similar to
that of PtN₂ with the same structure. As a pyrite-type
PtN₂ and a orthorhombic-type OsN₂ have been very re-
cently synthesized under high pressure and high temper-
ature conditions, we expect that the OsN₂ as well as
PtN₂ with fluorite structure may be experimentally
prepared in the future.

We are also grateful to Dr. R. Yu for useful discus-
sions and the two anonymous referees for fruitful sugges-
tions. This work is supported by NSFC Nos. 10404035,
10534030, 50325103, and 10544004.

1. D. M. Teter, MRS Bull. 23, 22 (1998).
2. C. Kittel, Introduction to Solid State Physics, 8th edition
(Wiley, New York, 1996).
3. A. Y. Liu, and M. L. Cohen, Science 245, 841 (1989).
4. R. A. Andrews, Inter. J. Refract. Meta. & Hard Mater.
19, 447 (2001).
5. V. V. Brazhkin, A. G. Lyapin, and R. J. Hemley, Phil.
Mag. A 82, 231 (2002).
6. P. F. Mcmillan, Nat. Mater. 3, 184108 (2003).
7. G. -M. Rignanese, J. -C. Charlier, and X. Gonze, Phys.
Rev. B 73, 015501 (2006).
8. D. W. He, Y. S. Zhao, L. Daemen, J. Qian, T. D. Shen,
and T. W. Zerda, Appl. Phys. Lett. 82, 643 (2002).
9. Z. C. Pan, H. Sun, and C. F. Chen, Phys. Rev. B 70,
174115 (2004).
10. K. Benyahia, Z. Nabi, A. Tadjer, and A. Khalfi, Physica.
B 339, 1 (2003).
11. R. W. Cumberland, M. B. Weinberger, J. J. Gilman, S. M.
Clark, S. H. Tolbert, and R. B. Caner, J. Am. Chem. Soc.
127, 7264 (2005).
12. M. I. Petrescu, Diam. Relat. Mater. 13, 1848 (2004).
13. F. M. Gao, J. L. He, E. D. Wu, S. M. Liu, D. L. Yu, D.
C. Li, S. Y. Zhang, and Y. J. Tian, Phys. Rev. Lett. 91,
015502 (2003).
14. J. L. He, E. D. Wu, H. T. Wang, R. P. Liu, and Y. J. Tian,
Phys. Rev. Lett. 94, 015504 (2005).
15. A. Šimůnek, and J. Vackář, Phys. Rev. Lett. 96, 085501
(2006).
16. F. M. Gao, Phys. Rev. B 73, 132104 (2006).
17. M. Mattesini, R. Ahuja, and B. Johansson, Phys. Rev. B
68, 184108 (2003).
18. Practically, systematic calculations were performed on di-
carbide, -nitride, -oxide and -boride of platinum and os-
mium with the fluorite structure respectively, but only
found that PtN₂, OsN₂ and OsO₂ are mechanically sta-
able. The unstable phases are not shown here.
19. P. Hohenberg, W. Kohn, Phys.Rev. 136, B864 (1964); W.
Kohn, L. J. Sham, Phys. Rev. 140, A1133 (1965).
20. M. D. Segall, P. L. D. Linda, M. J. Probert, C. J. Pickard,
P. J. Hasnip, S. J. Clark, and M. C. Payne, J. Phys.: Con-
dens. Matter 14, 2717 (2002).
21. D. Vanderbilt, Phys. Rev. B 44, 7892 (1990). For the
GGA calculations, the pseudopotential generated by us-
using the related Perdew- Burke-Ernzerhof type of exchange-
correlation functions should be used.
22. D. M. Ceperley, and B. J. Alder, Phys. Rev. Lett. 45, 566
(1980).
23. J. P. Perdew, K. Burke, and W. Ernzerhof, Phys. Rev.
Lett. 77, 3865 (1996).
24. H. J. Monkhorst, and J. D. Pack, Phys. Rev. B 13, 5188
(1976).
25. O. H. Nielsen, and R. M. Martin,Phys. Rev. B 32, 3792
(1985).
26. R. Yu, and X. F. Zhang, Appl. Phys. Lett. 86, 121913
(2005).
27. C. Stampfl, W. Mannstadt, R. Asahi, and A. J. Freeman,
Phys. Rev. B 63, 155106 (2001).
28. B. R. Sahu, and Leonard Kleinman, Phys. Rev. B 72,
113106 (2005).
29. H. Cynn, J. E. Klepeis, C. S. Yoo, and D. A. Young,
Phys. Rev. Lett. 88, 135701 (2002).
30. L. Fast, J. M. Wills, B. Johansson, and O. Eriksson,
Phys. Rev. B 51, 17431 (1995).
31. J. C. Zheng, Phys. Rev. B 72, 052105 (2005).
32. F. Occelli, D. L. Farber, J. Badro, C. M. Aracne, D. M.
Teter, M. Hanfland, B. Canny, and B.Couzinnet, Phys. Rev.
Lett. 93, 095502 (2004).
33. T. Kenichi, Phys. Rev. B 70, 012101 (2004).
34. J. F. Nye, Physical Properties of Crystals (Oxford Univer-
sity Press, Oxford, 1985).
35. U. Lundin, L. Fast, L. Nordstrom, B. Johansson, J. M.
Wills, and O. Eriksson, Phys. Rev. B 57, 4979 (1998).
36. H. W. Hugosson, G. E. Grechnev, R. Ahuja, U. Helm-
sisson, L. Su, and O. Eriksson, Phys. Rev. B 66, 174111
(2002).
37. R. Yu, and X. F. Zhang, Phys. Rev. B 72, 054103 (2005).
38. R. Yu, Private communication.
39. E. Gregoryanz, C. Sanleup, M. Somayazulu, J. Badro, G.
Fliquet, H.K. Mao, and R. J. Hemley, Nat. Mater. 3, 294
(2004).
40 Y. Kuwayama, K. Hirose, N. Sata, and Y. Ohish, Science 309, 923 (2005).
41 R. Yu, Q. Zhang, and X. F. Zhang, Appl. Phys. Lett. 88, 051913 (2006).
42 J. C. Crowhurst, A. F. Goncharov, B. Sadigh, C. L. Evans, P. G. Morrall, J. L. Ferreira, and A. J. Nelson, Science 311, 1275 (2006).
43 A. F. Young, J. A. Montoya, C. Sanloup, M. Lazzeri, E. Gregoryanz, and S. Scandolo, Phys. Rev. B 73, 153102 (2006).
44 M. I. Eremets, A. G. Gavriluk, I. A. Trojan, D. A. Dzivenko, and R. Boehler, Nat. Mater. 13, 558 (2004).
45 T. Zhang, S. Zhang, Q. Chen, and L. M. Peng, Phys. Rev. B 73, 094105 (2006).
46 A. F. Young, C. Sanloup, E. Gregoryanz, S. Scandolo, R. J. Hemiey, and H. K. Mao, Phys. Rev. Lett. 96 155501 (2006).
47 W. B. Pearson, A Handbook of Lattice Spacing and Structures of Metals and Alloys, (Pergamon, New York, 1958).
48 E. A. Brandes, Smithells Metal Reference Book, 6th ed. (Butterworth, London, 1983).