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# Twofold Coordinated Ground-State and Eightfold High-Pressure Phases of Heavy Transition Metal Nitrides $MN_2$ (M = Os, Ir, Ru, and Rh)

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Using ab initio evolutionary methodology for crystal structure prediction, a twofold coordinated ground-state hexagonal structure (*P*6/*mmm*, 1 f.u./cell) with peculiar double N═N bonded $N_2$ units was uncovered for $MN_2$ (M = Os, Ir, Ru, and Rh) compounds. This structure exhibits an unusual incompressibility along the *c* axis, higher than that of diamond. At much higher pressures, an eightfold coordinated tetragonal structure (*P*4/*mbm*, 2 f.u./cell) containing $MN_8$ cuboids was unraveled and possesses also orientational ultra-incompressibility. A unified phase transition diagram for these nitrides was thus derived to reveal the intriguing chemistry of nitrogen at extreme conditions. Formation energy calculations demonstrate that the ground state phase is synthesizable at low pressure (∼40 GPa) while the eightfold phase can be achieved through the phase transformation via the marcasite structure.

## 1. Introduction

Transition metal nitrides have received great attention for their potential technological applications and the understanding of fundamental physics.[1−4] The heavy transition metals of group VIII (e.g., Os, Ir, Pt, Ru, Rh, and Pd) were initially thought not to form solid nitrides for many years.[5] To a big surprise, several dinitrides of Os,[6] Ir,[6−8] Pt,[7,9] and Pd[8] have recently been synthesized at extreme conditions (approximately 50 GPa and 2000 K). These nitrides have been shown to possess ultrahigh bulk moduli (428 GPa for $IrN_2$) comparable with those of the traditional superhard materials thus exhibiting interesting mechanical properties. Extensive studies[10−18] are therefore carried out, especially on the fundamental crystal structures. By now, consensus has been reached with the aid of the experimental[6−8] and theoretical studies[10−18] that the synthesized $OsN_2$, $IrN_2$, and $PtN_2$ ($PdN_2$) adopt the marcasite, $CoSb_2$-type and pyrite structures, respectively, which are composed of $MN_6$ (M = transition metal) octahedrons.

Recently, a simple tetragonal structure (*P*4/*mbm*) was predicted to be more stable than the experimental pyrite structure for $PtN_2$ at low pressures and thus was considered as the ground state structure.[19] The existence of the tetragonal structure in $PtN_2$ naturally leads to the question of whether unknown structures exist in $OsN_2$, $IrN_2$, $RuN_2$, and $RhN_2$. Indeed, Yu et al.[16] have predicted that the $CoSb_2$-type structure in $OsN_2$ is energetically more favorable at low pressures (<15 GPa) and thus was suggested to be the ground state structure. They further suggested that the marcasite structure is the ground state of $RuN_2$ and $RhN_2$. Yu et al.'s work[16] is extremely important since the discovery of new polymorphs in these nitrides will inevitably advance our understanding of novel chemistry of nitrogen under extreme conditions. However, the proposed ground state structures are based on the knowledge of known information. There is a possibility that hitherto unknown structures are stable instead. Here, we have extensively investigated the phase

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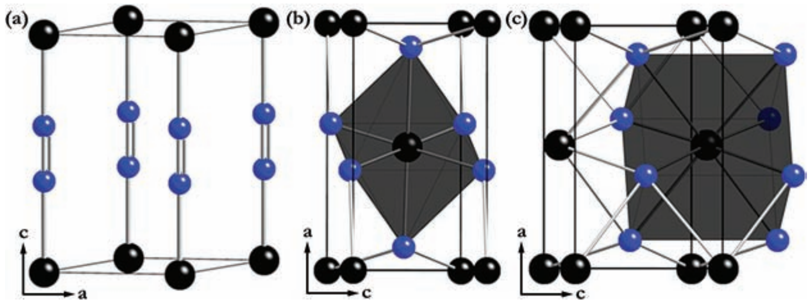

**Figure 1.** Crystal structures of the SH with N=N bonds (a), marcasite with $MN_6$ (M = transition metal) octahedron (b), and ST with $MN_8$ cuboid (c) phases. The M and N atoms are represented as large and small spheres, respectively.

sequences of $OsN_2$, $IrN_2$, $RuN_2$, and $RhN_2$ in a wide pressure range (0−250 GPa) by ab initio evolutionary structural predictions[20−22] unbiased by any known information. A simple hexagonal *P*6/*mmm* (denoted SH hereafter) structure with N=N bonds and an eight-coordinated simple tetragonal *P*4/*mbm* (denoted ST hereafter) structure is uncovered for all these compounds to be energetically much more preferable than any of earlier structures at low and ultrahigh pressure regimes, respectively. The two novel crystalline structures have not previously been reported in any other compounds and possess intriguing ultra-incompressibility along the *c* axis.

**Table 1.** Lattice Parameters of the SH and ST Structures[a]

| | SH | | | | ST | |
|---|---|---|---|---|---|---|
| | $OsN_2$ | $IrN_2$ | $RuN_2$ | $RhN_2$ | $OsN_2$ | $RuN_2$ |
| *P* (GPa) | 0 | 0 | 0 | 0 | 220 | 180 |
| *a* (Å) | 2.829 | 2.882 | 2.821 | 2.907 | 3.981 | 3.992 |
| *c* (Å) | 4.972 | 4.943 | 4.987 | 4.954 | 2.439 | 2.419 |
| *V* (Å$^3$) | 34.47 | 35.56 | 34.36 | 36.27 | 19.34 | 19.27 |
| *x*(Os) | | | | | 0.383 | 0.385 |
| *z*(N) | 0.384 | 0.384 | 0.385 | 0.385 | | |
| Os—N (Å) | 1.911 | 1.898 | 1.92 | 1.906 | 2.008 | 2.009 |
| N—N (Å) | 1.151 | 1.148 | 1.147 | 1.142 | 1.314 | 1.295 |

[a] Transition metals and N atoms occupy 1*a* (0,0,0) and 2*e* (0,0,*z*) positions, respectively, in the SH structure, while 2*a* (0,0,0) and 4*h* (*x*,*x*+1/2,1/2) in the ST structure.

## 2. Computational Method

The evolutionary search was done with the USPEX code.[20−22] The details of the search algorithm and its several applications have been described elsewhere.[23−29] The underlying ab initio structure relaxations were performed using density functional theory within the generalized gradient approximation,[30] as implemented in the Vienna ab initio simulation package.[31] The all-electron projector-augmented wave method[32] was adopted with a same plane-wave kinetic energy cutoff of 520 eV for all phases. The use of Monkhorst-Pack *k* points meshes of 12 × 12 × 6 for SH and 6 × 6 × 10 for ST structures were shown to give excellent convergence of the total energies, energy differences, and structural parameters. Elastic constants of the SH and ST structures were calculated by the strain−stress method[33] with denser *k* meshes of 20 × 20 × 10 and 12 × 12 × 16, respectively.

## 3. Results and Discussion

**Structural Prediction and Structural Features.** Evolutionary variable-cell simulations with one, two, three, and four formula units in the simulation cell were performed at 0−250 GPa for $MN_2$ (*M* = Os, Ir, Ru, and Rh) compounds. At 50, 100, and 150 GPa, our simulations successfully reproduced the marcasite and $CoSb_2$-type structures for $OsN_2$ and $IrN_2$, respectively, and also confirmed the marcasite structure for $RuN_2$ and $RhN_2$. Intriguingly, at 0 GPa, our structural prediction revealed a universally stable simple hexagonal structure (SH, Figure 1a) with *P*6/*mmm* symmetry for all $MN_2$ compounds. The SH structure contains the M—N—N chains along the *c* axis with very short M—N and N—N bond distances (Table 1). The N—N bond distance in $OsN_2$ is 1.15 Å, much shorter than that (1.4 Å) of the marcasite structure,[6] implying the presence of more "free-like" $N_2$ quasimolecules. It is noted that the short N—N bond distance falls in between the double N=N (1.21 Å for $N_2F_2$) and the triple N≡N bond (1.07 Å for molecular nitrogen[34]). Together with the fact that each N atom forms only two bonds (Figure 1a), a double N=N bond was thus safely derived, which is dramatically different from the single N—N bond found in the previous structures.[6−8] It is found that the Os—N bond distance (1.91 Å) is shorter than that (2.076 Å) in the marcasite structure, leading to a stronger covalent Os—N bond. Similar results and conclusions are also valid for $IrN_2$, $RuN_2$, and $RhN_2$. At 250 GPa, simulations revealed a simple tetragonal structure (ST, *P*4/*mbm*) for $OsN_2$ and $RuN_2$. This structure shares the same space group with the ground state structure of $PtN_2$[19] but adopts a different N atomic occupation (here, 4*h* site). As shown in Figure 1c, the ST structure can be regarded as a $0.5c_0$ shift of the planar $MN_4$ units along the *c*-axis of the

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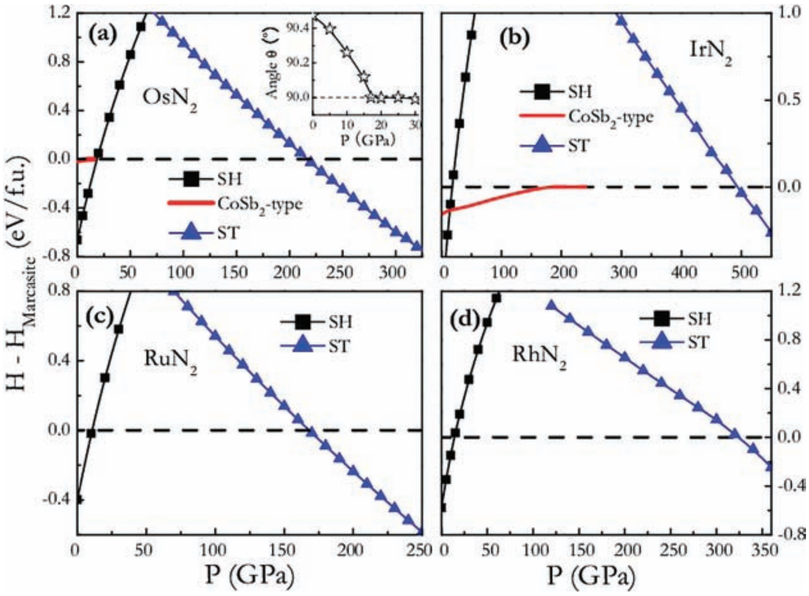

**Figure 2.** Enthalpies of earlier proposed CoSb$_2$-type, our predicted SH and ST structures relative to the marcasite structure for MN$_2$ (M = Os, Ir, Ru, and Rh) compounds. Inset in (a) represents the pressure dependence of the distortion angle (angle between [10$\bar{1}$] and [101] of the CoSb$_2$-type structure [16]) of OsN$_2$. An angle of 90° corresponds to the marcasite structure.

marcasite structure (Figure 1b). This results in an increase of the coordination number of M atom from six to eight and thus the formation of denser MN$_8$ cuboids. The M atoms site in the center of the cuboids, leading to eight identical M—N bonds, is different from the variation of the M—N bond lengths in the MN$_6$ octahedron found in the marcasite and CoSb$_2$-type structures. The N—N bond length in the ST structure is close to that in the marcasite structure, and thus the single-bonded N—N feature remains.

**Phase Transformations.** Figure 2 presents the calculated enthalpies of SH, ST, and CoSb$_2$-type structures with reference to the marcasite structure. It is confirmed that the SH structure is most stable at low pressures (e.g., below 19, 15, 10, and 14 GPa for OsN$_2$, IrN$_2$, RuN$_2$, and RhN$_2$, respectively). Results further revealed that the ST structure becomes favorable above 215 GPa for OsN$_2$ and 168 GPa for RuN$_2$. Our structure prediction at 250 GPa did not reveal the ST structure for IrN$_2$ and RhN$_2$; however, the extended enthalpy calculation (Figures 2b,d) indicates that this structure exists also, but at much higher pressures above 490 GPa for IrN$_2$ and 325 GPa for RhN$_2$.

Our enthalpy calculations revealed that these nitrides follow the unified phase sequence of SH → marcasite → ST under pressure, though IrN$_2$ possesses an intermediate CoSb$_2$-type structure between SH and marcasite. The CoSb$_2$-type structure is a subgroup of the marcasite structure and can be viewed as a cell-doubling distortion of the marcasite structure. The fine structural optimization shows that the CoSb$_2$-type structure gradually transforms to the marcasite structure at 170 GPa for IrN$_2$ and 17 GPa for OsN$_2$, in good agreement with the previous study.[16] However, the CoSb$_2$-type structure in OsN$_2$ is never stable with the presence of the newly predicted SH structure since the stability field of the SH structure with respect to the marcasite structure is in the range of 0−19 GPa. For RuN$_2$ and RhN$_2$, the CoSb$_2$-type structure automatically transforms to the marcasite structure at all pressures during optimization. The earlier proposed CoSb$_2$-type structure in OsN$_2$, RuN$_2$, and RhN$_2$ is thus ruled out. The sole existence of the CoSb$_2$-type structure in IrN$_2$ is fundamental interest and could be intimately related to the largest atomic radius in the Ir element. It was previously suggested that the atomic radius is the key to describe the variation of the crystal structures in transition nitrides.[5]

**Formation Enthalpy Considerations.** The thermodynamic stability of various structural modifications as a function of pressure was investigated by calculating the formation enthalpies:

$$\Delta H = H_{MN_2} - H_M - H_{N_2}$$

It is clearly seen from Figure 3 that the marcasite structure of OsN$_2$ and CoSb$_2$-type structure of IrN$_2$ can be theoretically synthesized at pressures of above 18 and 14 GPa, respectively, which are about 32 and 36 GPa lower than the experimental pressures (~50 GPa). The large discrepancy is mainly attributed to the known large kinetic energy barrier in the formation of the nitrides. Significantly, the predicted SH structure is also found to be theoretically synthesizable at relatively lower pressure regimes of 10.5−18 GPa for OsN$_2$ and 7.5−14 GPa for IrN$_2$ (Figure 3). The narrow synthesizable pressure regions are similar to that found in the ground state structure of PtN$_2$.[19] It is expected that the SH phase in OsN$_2$ (IrN$_2$) can be experimentally synthesized at about 42.5−50 GPa (43.5−50 GPa) if one includes an additional 32 GPa (36 GPa) to conquer the formation energy barrier. Our results suggest that the ST structure is difficult to be directly synthesized. However, this structure can be obtained through phase transformation via the marcasite structure at high pressures. Taking OsN$_2$ as an illustrated case, the energy barrier for the marcasite → ST transition has been estimated. As we have described above, the formation of the ST structure follows a transition path

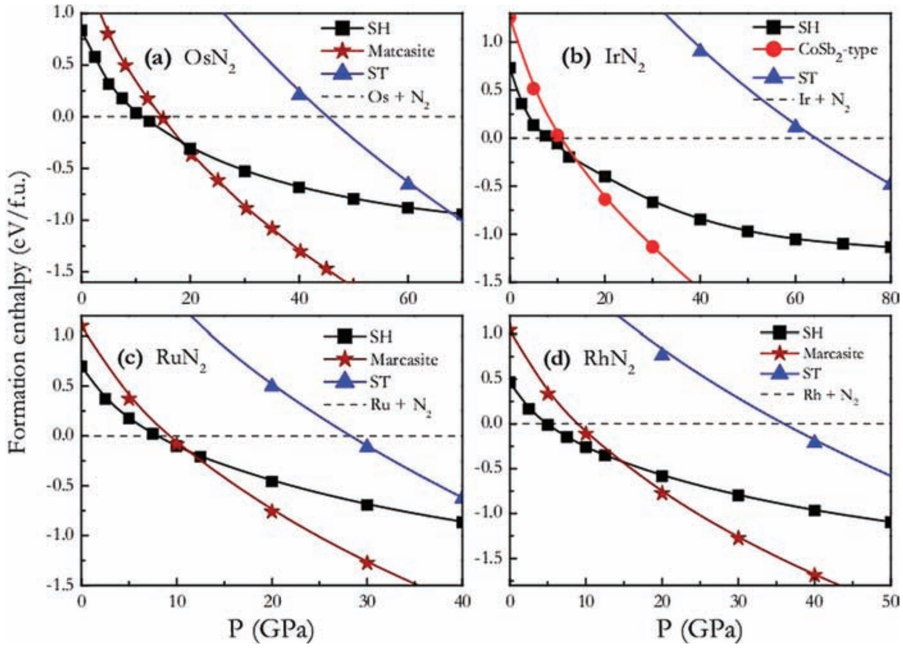

**Figure 3.** Formation enthalpies of OsN$_2$ (a), IrN$_2$ (b), RuN$_2$ (c), and RhN$_2$ (d) as a function of pressure for marcasite, CoSb$_2$-type and the predicted SH and ST structures.

that the planar MN$_4$ units shift 0.5$c_0$ along the *c*-axis of the marcasite structure. The total energy for a series of atomic displacements along this transition path at the transition pressure (215 GPa) was calculated to derive an energy barrier of 0.76 eV/f.u. This indicates that a much larger pressure is needed to conquer this energy barrier for the formation of the ST structure. As a rough estimate from Figure 2a, an extra 105 GPa can compensate the 0.76 eV barrier and thus the experimental synthesis of the ST structure is expected to be at 320 GPa. We note that this transition pressure is an upper limit since (i) one cannot rule out other possible transition paths, which might be much more favorable with much lower energy barrier, and (ii) we perform the calculation at zero temperature, while high temperature could efficiently lower the energy barrier. Furthermore, we have firmly demonstrated that RuN$_2$ and RhN$_2$ can be experimentally synthesized. Future experimental syntheses are thus greatly demanded.

**Mechanical Properties.** To check the structural stabilities of the predicted SH and ST polymorphs, the elastic constants (Table 2) and phonon dispersions (not shown) were calculated for these nitrides. The results show that the SH structure is both mechanically and dynamically stable at all pressures while the ST structure is only stable within its pressure stability field. Interestingly, we found an extremely large $C_{33}$ value in the SH structure for all nitrides, reflecting the high incompressibility along the *c* axis. The highest $C_{33}$ value of 1403 GPa obtained in OsN$_2$ is much larger than the largest component $C_{22}$ (913−939 GPa[10,14]) of the marcasite structure and even ~300 GPa larger than that of diamond ($C_{33}$ = 1079 GPa[35]). The large $C_{33}$ could be well understood by the strong covalent Os—N and N═N bonds along *c* axis. Since there exists only one-dimensional bonds, the elastic constant components along other directions are much smaller, leading to an overall small bulk moduli of MN$_2$ (Table 2). It is also found that the ST structure possesses unusually large $C_{11}$ and $C_{33}$ at high pressures, indicating the orientationally ultra-incompressible nature of these materials. These results suggest excellent mechanical properties and the possibly technological applications of the studied nitrides.

**Table 2.** Calculated Elastic Constants and Bulk Moduli of the SH and ST Structures

| | SH | | | | ST | | | |
|---|---|---|---|---|---|---|---|---|
| | OsN$_2$ | IrN$_2$ | RuN$_2$ | RhN$_2$ | OsN$_2$ | | RuN$_2$ | |
| $P$ | 0 | 0 | 0 | 0 | 0 | 220 | 0 | 180 |
| $C_{11}$ | 279 | 197 | 213 | 129 | 644 | 1987 | 533 | 1736 |
| $C_{33}$ | 1403 | 1384 | 1176 | 1085 | 754 | 2162 | 584 | 1785 |
| $C_{44}$ | 47 | 37 | 37 | 25 | −43 | 396 | −45 | 345 |
| $C_{66}$ | | | | | 216 | 548 | 231 | 515 |
| $C_{12}$ | 95 | 64 | 71 | 50 | 262 | 817 | 324 | 745 |
| $C_{13}$ | 20 | 26 | 12 | 12 | 154 | 854 | 118 | 689 |
| $B_0$ | 169 | 123 | 129 | 84 | | | | |

**Electronic Properties.** The electronic band structures were studied to reveal the electronic properties. Here, we only represent the results of OsN$_2$ in Figure 4 as an illustrative case. The band structures of all three phases in OsN$_2$ reveal clear metallic characters with large dispersion bands crossing the Fermi level ($E_F$). The partial densities of states (DOS) of the SH and ST phases of OsN$_2$ were also studied to make sense of the bonding properties. As shown in Figure 5, the DOS profile of the SH phase (Figure 5a) was separated into two main parts by a deep minimum valley about 5 eV below the $E_F$. The lower and upper parts are mainly originated from N 2p and Os 5d orbitals, respectively. The separated energy regions of Os and N DOSs are mainly due to the existence of the double N═N bonds. It is evidenced from Figure 5b that the DOS of the ST phase has a quite different pattern. Both Os 5d and N 2p orbitals are more spread, resulting in a significant overlap in the wide energy region (−15−0 eV) to form the strong covalent Os—N bonds.

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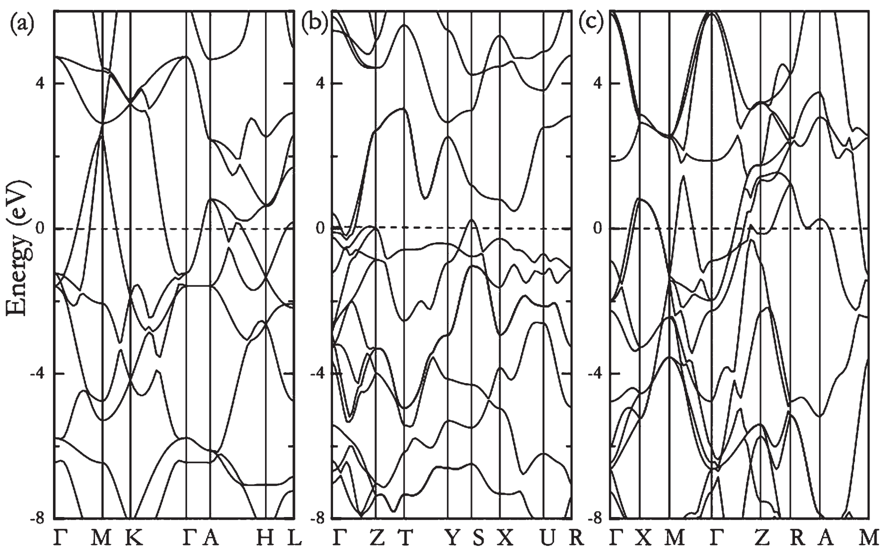

**Figure 4.** Electronic band structures of $OsN_2$ within the SH phase at 0 GPa (a), the marcasite phase at 20 GPa (b), and the ST phase at 250 GPa (c). The horizontal dashed lines represent the Fermi level.

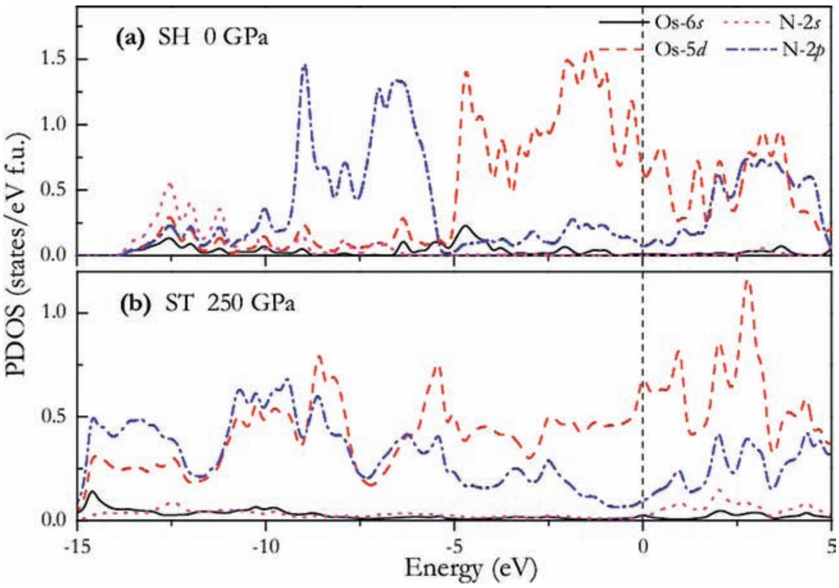

**Figure 5.** Calculated partial density of states (DOS) of the SH (a) and ST (b) phases of $OsN_2$ at 0 and 250 GPa, respectively. Vertical dashed lines indicate the Fermi energy.

**Superconductivity Prediction.** Metallic compounds containing light elements have attracted considerable attention for decades because of their potential superconducting properties. Recent first-principles study proposed that the marcasite phase of $OsN_2$ might be a superconductor with $T_c \approx 1$ K, which originates from the stretching of covalently bonded $N_2$ units embedded in the transition metal matrix.[36] It is seen from Figure 4 that there are more bands crossing the $E_F$ in the SH and ST structures than those in the marcasite structure, resulting in particularly richer and more complex Fermi surfaces of the SH and ST structures. This provides the possibly stronger electron–phonon coupling necessary for superconductivity.[37] Additionally, one-dimensional-like bands are also found in the SH phase by evidence of a nearly flat band along $\Gamma - A$ at around 1.8 eV below the $E_F$ (Figure 4a). The simultaneous occurrence of flat and steep bands near the $E_F$ has been suggested as favorable conditions for enhancing electron pairing, which is essential to superconducting behavior.[38] Previous study has confirmed that transition temperature of the marcasite structure of $OsN_2$ is enhanced with the increased phonon frequencies associated with the N—N modes by a hole doping.[36] Note that the predicted SH structure has stronger N═N bonds, thus leading to much higher phonon frequency. Therefore, it has a high possibility that these nitrides with the SH and ST structures are superconducting. The current finding will inevitably stimulate extensive experimental works on synthesizing these technologically important materials.

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## 4. Conclusion

In summary, a hexagonal $P6/mmm$ structure is unraveled to be the universal ground state structure for all $MN_2$ (M = Os, Ir, Ru, Rh) compounds at low pressures, which is energetically much superior to the earlier structures. In this structure, the diatomic $N_2$ unit is for the first time found to possess double-bonded N=N character in the transition metal nitrides. The $P6/mmm$ structure has short and strong covalent M—N and N=N bonds, resulting in an unusual high incompressibility along the $c$ axis. We have demonstrated that the $P6/mmm$ phase is synthesizable at rather low and readily attainable pressures (~40 GPa). In addition, another new tetragonal $P4/mbm$ structure is found to be stable at higher pressures for all these nitrides and can be obtained through the phase transformation via the marcasite structure. The predicted unified phase diagram of SH → marcasite → ST upon compression is of fundamental interest in view of the distinct chemistry changes. The transition follows the elevated two, six, and eight coordination numbers. Intuitionally, this might be as expected under pressure but reveals rich bonding capability of both heavy transition metals and nitrogen. This finding will inevitably stimulate extensive experimental works on synthesizing these technologically important materials.

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