

Family of noble metal nitrides: First principles calculations of the elastic stability

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By calculating the elastic stability using the full-potential linearized augmented plane waves (FLAPW) method, three noble metal nitrides (IrN_2 , AgN_2 , and AuN_2) were found to be stable with the fluorite structure. Together with PtN_2 , they form a new family of transition metal nitrides, where nitrogen atoms occupy all the tetrahedral interstitials of the metal sublattice, instead of larger octahedral interstitials. Using the topological analysis of charge density (atoms in molecules theory), it was shown that the stability of the new nitrides can be understood based on the simple size effect. The filling of all the small tetrahedral interstitials makes the phases difficult to compress, resulting in large bulk moduli. The frequencies of the Raman-active phonon modes were also given.

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There has been much research of transition metal nitrides, due to their importance in both fundamental science and technique applications.¹⁻⁸ Most of these works studied the nitrides of early transition metals, or the $3d$ series of late transition metals.⁹⁻¹³ The $4d$ and $5d$ series of late transition metals (Ru, Rh, Pd, Ag, Os, Ir, Pt, and Au, also known as noble metals) are generally considered not to form nitrides,^{1,2} although Ag_3N and Au_3N were reported.^{14,15} Very recently, platinum nitride were synthesized under high pressures and high temperatures¹⁶ and was shown to be of the fluorite structure (PtN_2).¹⁷

It is interesting to know whether the other noble metals can form nitrides with the fluorite structure. In the present work, we study the elastic stability of noble metal nitrides using the first-principles calculations. Three elastically stable phases (IrN_2 , AgN_2 , and AuN_2) were found. Together with PtN_2 , they form a new family of transition metal nitrides, in which the metal atoms form a face-centered cubic (FCC) lattice, while nitrogen atoms occupy all of the tetrahedral interstitial sites. Their stability of the new nitrides was shown to be attributed to a size effect.

The full-potential linearized augmented plane waves (LAPW) method^{18,19} was employed in this study. This method is one of the most accurate schemes in solving the Kohn-Sham equations in density-functional theory.²⁰ Augmented plane wave plus local orbitals (APW+lo)²¹ were used for valence states, and LAPW for the other states, with the RK_{max} of 8.0. A fully relativistic calculation was performed for core states, whereas the valence states were treated in a scalar relativistic scheme. The total Brillouin zones were sampled with 5000 k points using a modified tetrahedron method of Blöchl *et al.*²² Both the local density approximation (LDA)²³ and the generalized gradient approximation (GGA)²⁴ exchange correlation functional were employed in the present calculations. Since it is known that the LDA usually underestimates the lattice constants and overestimates the elastic constants, whereas the GGA overestimates the lattice constants and underestimates the elastic constants, we used the arithmetic average of the LDA and the GGA values as the theoretical value.

The mechanical stability of a crystal means that the strain

energy must be positive. For a cubic crystal, it implies the following restrictions:²⁵

$$c_{44} > 0, \quad c_{11} > |c_{12}|, \quad \text{and} \quad c_{11} + 2c_{12} > 0,$$

where c_{11} , c_{12} , and c_{44} are the elastic stiffness constants. In the present work, the elastic stiffness constants were obtained by fitting the total energies of the strained crystals to the third-order polynomial of the strains. Since there are three independent elastic constants for a cubic phase,²⁵ three types of strain, i.e., the volume change, and volume-conserved tetragonal and rhombohedral shear strains, were applied to the optimized structures to calculate the elastic constants. The polycrystalline shear moduli were calculated from the single crystal elastic constants based on the Voigt-Reuss-Hill averaging scheme.²⁶

In addition to PtN_2 , three other noble metal nitrides (IrN_2 , AgN_2 , and AuN_2) were found to be elastically stable with the fluorite structure. RuN_2 , RhN_2 , PdN_2 and OsN_2 were found to be either unstable or extremely soft. The calculated elastic properties of the stable nitrides are listed in Table I. Among

TABLE I. The calculated lattice parameters (in Å) and elastic constants of IrN_2 , PtN_2 , AgN_2 , and AuN_2 . All elastic constants are in GPa, except the dimensionless Poisson's ratio ν .

		a	c_{11}	c_{12}	c_{44}	B	G	E	ν
IrN_2	LDA	4.801	464	339	124	381	95	262	0.39
	GGA	4.882	391	273	115	313	88	242	0.38
	Ave.	4.842	428	306	120	347	92	253	0.38
PtN_2	LDA	4.866	532	208	122	316	137	359	0.32
	GGA	4.958	457	167	99	264	116	303	0.31
	Ave.	4.912	495	188	111	290	127	332	0.31
AgN_2	LDA	5.013	268	189	57	215	50	138	0.40
	GGA	5.141	215	138	59	164	50	136	0.37
	Ave.	5.077	242	164	58	190	50	137	0.39
AuN_2	LDA	5.035	371	183	71	246	80	216	0.36
	GGA	5.144	316	139	52	198	65	175	0.36
	Ave.	5.090	344	161	62	222	73	197	0.36

TABLE II. The sizes and charges of the atoms in the nitrides of noble metals Ir, Pt, Ag, Au, and early transition metals Ti, Zr, and Hf. The atomic radii (r in Å) of the corresponding elements are also listed for comparison. Q_M and Q_N denote the atomic charges of metal and nitrogen. V_M and V_N denote the volumes (in Å³) of metal and nitrogen atoms. The table shows GGA results.

	IrN ₂	PtN ₂	AgN ₂	AuN ₂	TiN ₂	ZrN ₂	HfN ₂	TiN
r (Ref. 27)	1.36	1.39	1.44	1.44	1.45	1.59	1.56	1.45
Q_M	1.50	1.28	1.04	1.08	2.00	2.36	2.40	1.74
Q_N	-0.75	-0.64	-0.52	-0.54	-1.00	-1.18	-1.20	-1.74
V_M	11.83	12.57	12.34	13.99	7.40	10.47	10.36	8.01
V_N	8.62	8.94	10.81	10.01	11.14	12.63	12.35	11.27
V_N/V_M	0.73	0.71	0.88	0.72	1.51	1.21	1.19	1.41

all the new nitrides, IrN₂ has the highest bulk modulus (347 GPa), and PtN₂ has the highest shear modulus (127 GPa). As expected from the properties of the corresponding elements, AgN₂ and AuN₂ are softer in both bulk and shear moduli.

The four nitrides form a new family of transition metal nitrides, where nitrogen atoms occupying the tetrahedral interstitials of the metal sublattice. It is well known that the most popular structure for transition metal nitrides is not the fluorite structure, but the rock-salt (NaCl) structure,²⁷ in which N atoms occupy all the four octahedral sites of the FCC metal lattice. Typical examples are early transition metal nitrides TiN, ZrN, and HfN. This is surprising considering the atomic radii of Ir, Pt, Ag, and Au are smaller than those of Ti, Zr, and Hf, and the tetrahedral interstitials are much smaller than the octahedral ones. Here we calculated the topological properties of the nitrides on the basis of Bader's quantum theory of "atoms in molecules" (AIM),²⁸⁻³⁰ and found that the stability of the fluorite-structured nitrides can be attributed to the small ratios of the volumes of the N atoms to those of the metal atoms in the noble metal nitrides.

In the AIM theory, an atom is defined as a region containing a single nucleus, with the flux in the gradient vector field of the electron density $\rho(\mathbf{r})$ vanishing at its surface, i.e.,

$$\nabla\rho(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) = 0,$$

where $\mathbf{n}(\mathbf{r})$ is the exterior normal vector to the surface of the region. Once the atomic basins are determined atomic properties of each atom can be obtained by integration of corresponding property densities over the basin of the atom, and each atom makes an additive contribution to the value of the property of the total system. The electron population in atom Ω , for example, is given as

$$N(\Omega) = \int_{\Omega} \rho(\mathbf{r}) d\mathbf{r}.$$

Based on the topology of electron density, the AIM theory provides vigorous definitions for atoms in molecules/crystals and the bonds that link the atoms, and thus transform the qualitative concepts into a quantitative description.

We calculated the volumes of the atoms in the nitrides of Ir, Pt, Ag, Au, and those of Ti, Zr, Hf for comparison. For titanium nitride, both the stable rock-salt structure (TiN) and the hypothetical fluorite structure (TiN₂) were considered to check if the atomic volume depends much on the crystal structure. The calculation results are given in Table II. We use the atomic volume ratio V_N/V_M to represent the relative size of the N atoms to the metal atoms. Table II shows that the ratios V_N/V_M for the titanium nitrides are around 1.5 and do not depend much on the crystal structure. As seen from Table II, the ratios V_N/V_M for the noble metal nitrides are nearly only half those for the titanium nitrides. This can be attributed to the fact that less charge is transferred from the noble metal atoms to N atoms, giving a smaller size of the latter. Since the size of the N atoms relative to the metal atoms in the noble metal nitrides is small, it should be more stable for the N atoms to occupy small tetrahedral sites, in-

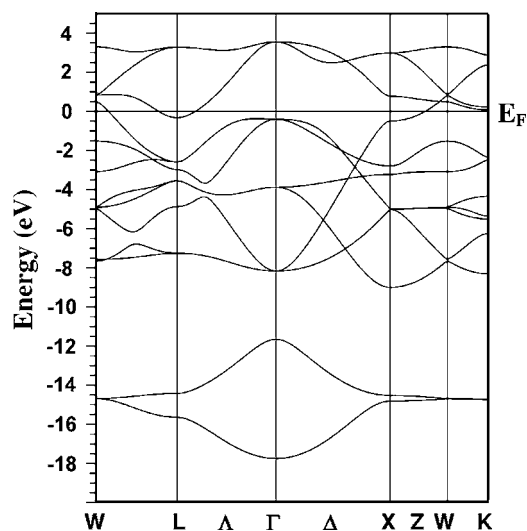


FIG. 1. Calculated band structure of PtN₂.

TABLE III. Electron density (ρ in eÅ⁻³), eigenvalues of Hessian and Laplacian (λ_i , $\nabla^2\rho$ in eÅ⁻⁵) of ρ , and the ratio $|\lambda_1|/\lambda_3$ at the critical points of PtN₂. The table shows GGA results.

Type	ρ	λ_1	λ_2	λ_3	$\nabla^2\rho$	$ \lambda_1 /\lambda_3$
BCP	0.75	-3.35	-3.35	10.51	3.80	0.32
RCP	0.25	-0.90	0.64	3.56	3.30	0.25
CCP	0.02	0.10	0.10	0.10	0.30	1.00

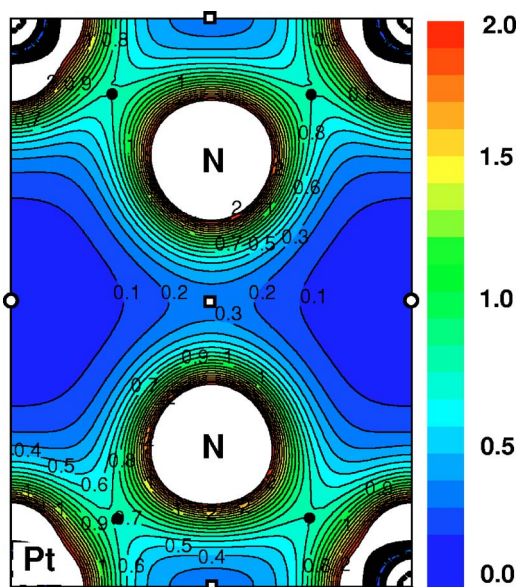


FIG. 2. (Color online) The electron density at the (110) plane of PtN_2 . The bonding, ring, and cage critical points are labeled with filled circles, open squares, and open circles, respectively.

stead of the large octahedral sites, just as observed in the present work. The filling of all the tetrahedral sites is accompanied by short metal-nitrogen bond lengths, and makes the phases difficult to compress, resulting in large bulk moduli.

As an example of the new nitride family, the electronic structure of PtN_2 at zero pressure was calculated. The band structure is shown in Fig. 1. No energy gap is seen, indicating a metallic nature of the platinum nitride. The states between -18 and -12 eV are mainly composed of $\text{N}(2s)$ states. The states above -9 eV are mainly composed of $\text{Pt}(5d)$ states (t_{2g} and e_g) and $\text{N}(2p)$ states.

In order to quantitatively describe the bonding in PtN_2 , the topology of charge density was analyzed in detail.^{28–30} Table III lists the electron density ρ , its curvatures λ_i , and Laplacian $\nabla^2\rho$, at the critical points, where the electron density gradient vanishes. Figure 2 shows the valence electron density in a (110) plane, where the critical points are labeled. BCP, RCP, and CCP denote the bonding, ring, and cage critical points, respectively, as discussed in the following. Between Pt and N lies the bonding critical point (BCP), where the two curvatures (λ_1, λ_2) in the directions perpendicular to the bonding axis are negative, leaving charge accumulation to the bond. At the intersection of Pt—Pt and N—N interlines lies a ring critical point (RCP), where only the curvature in the direction perpendicular to the plane expanded by the Pt—Pt and N—N interlines is negative. The center of

TABLE IV. The calculated Raman frequencies of the fluorite structured noble metal nitrides. The table shows LDA results.

	IrN_2	PtN_2	AgN_2	AuN_2
ω (cm^{-1})	605	628	377	437
γ	1.65	1.68	2.12	1.88

the octahedra formed by Pt atoms is the charge density minimum of the system, with the positive curvatures in all directions. It is a cage critical point (CCP).

Considering that the Raman spectroscopy is frequently used for phase identification in high-pressure synthesis methods, the frequencies of the Raman-active phonon modes were calculated. The fluorite structured transition metal nitrides have an $Fm\bar{3}m$ space group with nitrogen atoms occupying the $8c$ position. They have only one Raman-active phonon mode, which has T_{2g} symmetry and involve the motion of nitrogen atoms around each metal atom in opposite directions along $\langle 111 \rangle$. The frequencies of the phonon mode were calculated using the frozen-mode method.³¹ The frequencies at different volumes were calculated, based on which the mode Grüneisen parameters $\gamma = -\partial \ln \omega / \partial \ln V$ were obtained. In Table IV the phonon frequencies at zero pressure and the mode Grüneisen parameters are listed.

It is noted that the calculated Raman frequency of PtN_2 is different from the strong peaks in Fig. 1 of Ref. 16. However, a closer examination of the figure reveals a weak peak at 675 cm^{-1} , which is close to the present calculations. The origin of the strong peaks is not clear and further investigations are needed.

In conclusion, a new family of late transition metal nitrides is predicted from first-principles calculations. Four nitrides, IrN_2 , PtN_2 , AgN_2 and AuN_2 , were shown to be mechanically stable with the fluorite structure. The stability of the nitrides can be understood from simple geometrical considerations. Among the four nitrides, platinum nitride has recently been synthesized under high pressures and temperatures, and the phase sustained in ambient conditions. It is expected that the other nitrides predicted in the present work can also be synthesized in forms of bulk or thin film under suitable conditions.

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