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Metallic and Anti-metallic Properties in Strongly Covalently Bonded Energetic AlN_5 Nitride

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Dynamic and Mechanical stability:

To verify the authenticity of the structure under different pressures, mechanics and the lattice dynamics has been tested in our calculation. Judging the dynamic stability of materials, the supercell method has been used to confirm whether imaginary frequencies appear in phonon spectrum. The result of phonon spectrum has been described in Fig. S3. No imaginary frequency was found in whole Brillouin zone, which indicate that the *P*-1-AlN_5 phase at pressure of 20 GPa and *I*-42*d*-AlN_5 phase at 100 GPa are all fulfilled dynamic stability standard. We also further identified the mechanical properties of the AlN_5 structures. Therefore, the elastic constants C_{ij}, bulk modulus B, shear modulus G, Poisson ratio r and Vickers hardness H_v[1] all have been calculated and presented in Table 2. After analyzing, both *P*-1-AlN_5 and *I*-42*d* phase satisfy the criteria of mechanical stability. Especially, the modulus of *P*-1-AlN_5 phase is 719 GPa higher than diamond 442 GPa, implying that it may be a potential superhard material and has a larger volume compression resistance.[2] Furthermore, the *P*-1-AlN_5 phase has an evidently high value of C_{11} (1189 GPa) than diamond (1076 GPa), identifying its remarkable high stiffness along the *a* axis. The Poisson ratio values of *P*-1-AlN_5 (0.23) and *I*-42*d*-AlN_5 (0.26) indicate a high degree of directional covalent bonding. So, all phenomena state clearly that the two crystal phases will have relatively large hardness values. Theoretical calculation estimated hardness H_v is 15.2 GPa for *P*-1-AlN_5 phase, and *I*-42*d*-AlN_5 phase, the H_v is 31.7 GPa. To conclude, aluminum nitrides (AlN_5) exhibit not only the advantages of high energy density but also the properties of high hardness under different pressures, which can be widely used in industrial applications. The *P*1 phase under low pressures, however, with an imaginary frequency was found in the Γ-point of Brillouin zone in Fig. S4 which indicated dynamically unstable at ambient pressure from the phonon dispersion curves.

Computational Details:

The ELF was first reported by *A. D. Becke* and *K. E. Edgecombe* and derived from an earlier idea of *L. Jones* [3]. Besides, the classification of chemical bonds based on topological analysis of electron localization functions was reported by *B. Sllvl* and *A. Savin* [3, 4]. The characterization of chemical bonds in ELF is a qualitative rather than a quantitative exercise. Based on topological analysis of ELF reported by *B. Sllvl* and *A. Savin*, the formula can be written: ELF = $(1 + x^2_\sigma)^{-1}$. Where $x^2_\sigma = \mathrm{D}_\sigma / \mathrm{D}_\sigma^0$ and $\mathrm{D}_\sigma^0 = 3/5(6\pi^2)^{2/3}\rho_\sigma^{5/3}$, D_σ^0 expressed a uniform electron gas with spin-density equal to the local value of $\rho_\sigma(\mathrm{r})$. The ratio x_σ represent a dimensionless localization index calibrated with respect to the uniform-density electron gas. The feature of chemical bonds in ELF is a qualitative rather than a quantitative exercise. The ELF is useful in distinguishing the metallic, covalent and ionic bonding characters. ELF has values between 0 and 1, where 1 corresponds to perfect localization and 0.5 corresponds to electrongas-like pair probability. When the scale larger than 0.75 corresponds to the perfect localization characteristic of covalent bonds or lone pairs.

The way to judge the hybridization of nitrogen atoms is mainly through two main aspects. On the one hand, the projected DOS of nitric *s* and *p* orbits are very similar in the whole energy range, reflecting the strong orbital hybridization between N_*s* and N_*p*. In other words, in view of the electronic band structure with N_*s* and N_*p* orbital separation, the projected distributions of the N_*s* and N_*p* orbits are almost overlap, which can also reflect orbital hybridization between them. On the other hand, based on the bonding modes and space configurations of nitrogen atoms, then, we can determine the type of hybridization.

For COHP formula [5]:

$$\sum_{\mathbf{j}} f_j \varepsilon_j \, \delta(\varepsilon_j - \varepsilon) = \sum_j f_j \sum_{R'L'} \sum_{RL} u_{RLj}{}^{*} H_{RL,\,R'L'} \, u_{R'L'j} \, \delta(\varepsilon_j - \varepsilon)$$

$$= \sum_{R'L'} \sum_{RL} H_{RL,\,R'L'} \sum_{\mathrm{j}} f_j u_{RLj}{}^{*} H_{RL,\,R'L'} \, u_{R'L'j} \, \delta(\varepsilon_j - \varepsilon)$$

$$= \sum_{R'L'} \sum_{RL} H_{RL,\,R'L'} N_{RL,\,R'L'}(\varepsilon)$$

$$= \sum_{R'L'} \sum_{RL} COHP_{RL,\,R'L'}(\varepsilon)$$

Where j present the band index, whereas R specifies the atomic site and L is a shortened notation for the angular momentum quantum numbers L = lm. Note that $\sum_{RL}$ stands for a double sum running first over all atoms R within the primitive unit cell and second overall atomic orbitals L centered on R. Thus, the distribution of all one-particle energies has been rewritten into a sum of pair contributions, which we call crystal orbital Hamilton populations (COHP).

Table 1. The unit-cell parameters and atomic positions of the *P*-1-AlN_5 and *I*-42*d*-AlN_5 phases at 20 GPa and 100 GPa, respectively.

Structures	**Lattice parameters (Å)**	**Atomic coordinates (fractional)**	**Sites**
	a= 3.66	N1 (0.51 0.77 0.66)	2*i*
P-1	b= 4.41	N3 (0.88 0.77 0.66)	2*i*
P= 20 GPa	c= 6.72	N5 (0.85 0.52 0.29)	2*i*
	α= 85.02	N7 (0.49 0.53 0.30)	2*i*
	β= 81.98	N9 (0.33 0.00 0.00)	2*i*
	γ= 66.28	Al1 (0.01 0.89 0.23)	2*i*
	a= 5.19		
I-42*d*	b= 5.19	N1 (-0.32 0.63 0.65)	16*e*
P = 100	c= 5.14	N9 (0.00 0.50 0.25)	4*b*
	α= 90.00	Al1 (0.00 -0.00 0.50)	4*a*
	β= 90.00		
	γ= 90.00		

The distances (in Å) of two adjacent nitrogen atoms in AlN_5 structures: Referring to previous theoretical studies,[1] we generally believe that the bond length of single bond is 1.45 Å, double bond is 1.25 Å, and triple bond is 1.10 Å at ambient conditions. Besides, For calibration, the N − N single bond distance in *cg*-N is 1.31 Å at 200 GPa. These values were used to guide assignment of nitrogen − nitrogen bonds in order to rationalize the local structural environments using VSEPR theory.

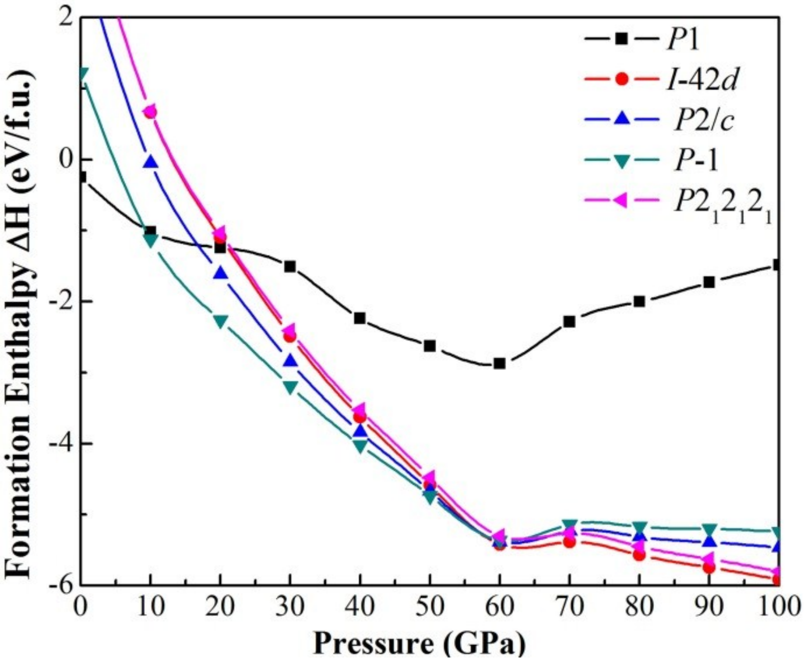

Fig. S1. Enthalpy curves of candidate structures in AlN_5 nitride as a function of pressure.

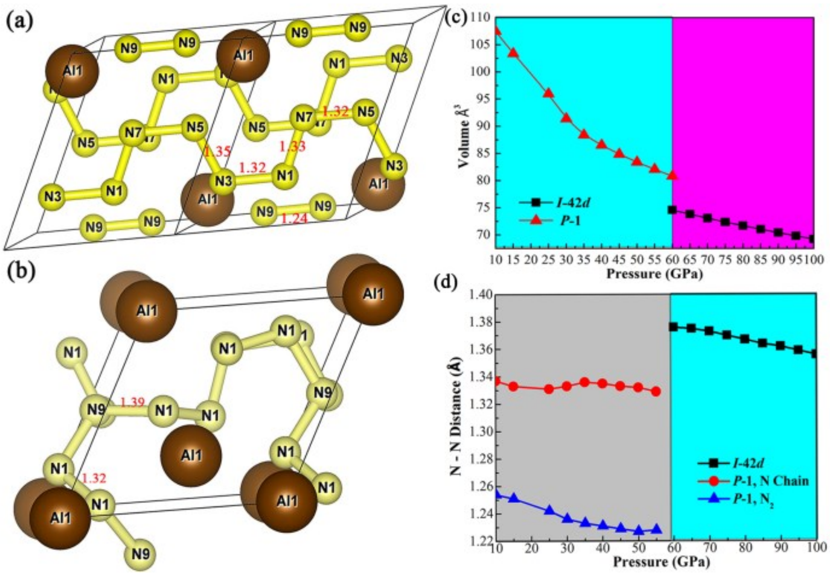

Fig. S2. The distances (in Å) of two adjacent atoms present in (a) *P*-1-AlN_5 phase at 20 GPa and (b) *I*-42*d*-AlN_5 phase at 100 GPa, respectively. (c) Lattice volume and (d) N-N distances curves of *P*-1 and *I*-42*d* structures as a function of pressure.

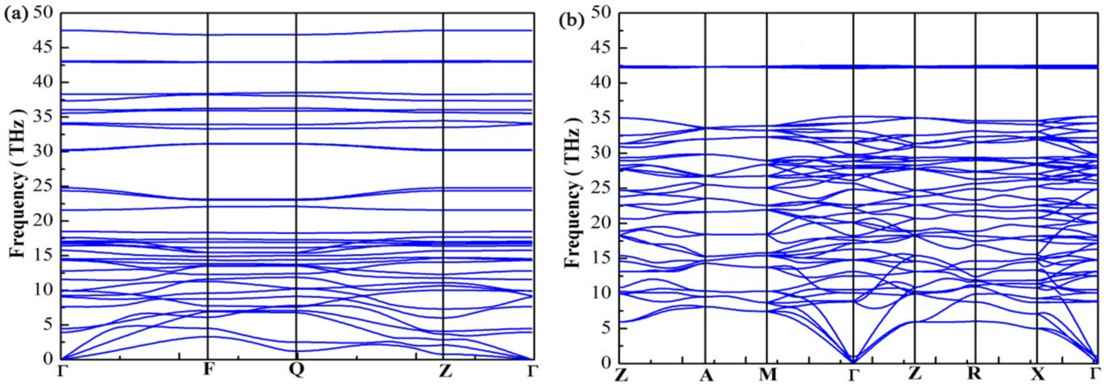

Fig. S3. Phonon dispersion curves for the (a) *P*-1-AlN_5 phase at pressure of 20 GPa. (b) *I*-42*d*-AlN_5 phase at 100 GPa.

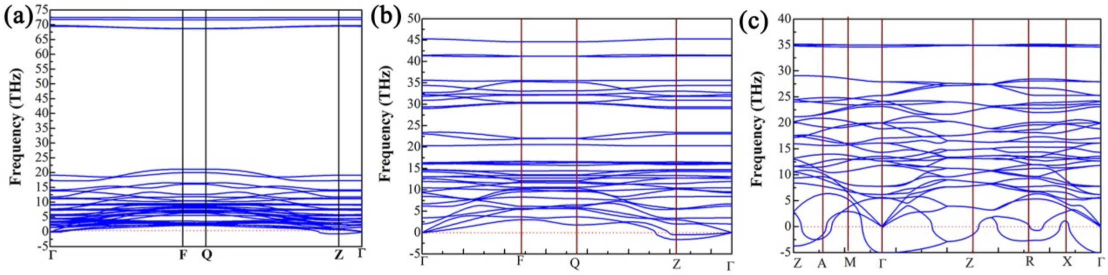

Fig. S4. Phonon dispersion curves for (a) the *P*1-AlN_5 phase at 0 GPa, (b) the *P*-1-AlN_5 phase at 0 GPa (c) the *I*-42*d*-AlN_5 phase at 0 GPa

Table 2. The calculated elastic constants C_{ij} (GPa) and bulk moduli B_0 (GPa), G_0 (GPa), r (G/B) as well as equilibrium H_V (GPa) together with available diamond data and other computational results.

	C_{11}	C_{12}	C_{13}	C_{15}	C_{22}	C_{23}	C_{33}	C_{35}	C_{44}	C_{46}	C_{55}	C_{66}	B_0	G_0	r	H_v
P-1	1095	936	532	-	498	143	236	77	655	-8	773	159	232	133	0.23	15.2
I-42*d*	1189	405	497				1371		429			422	719	408	0.26	31.7
Diamond[6]	1055	119							564				431			96

The Born–Huang criterion for *P*-1-AlN_5 phase:

$C_{11} > 0$, $C_{22} > 0$, $C_{33} > 0$, $C_{44} > 0$, $C_{55} > 0$, $C_{66} > 0$, $C_{11} + C_{22} + C_{33} + 2*(C_{12} + C_{13} + C_{23}) > 0$, $C_{33}*C_{55} - C_{35}*C_{35} > 0$, $C_{44}*C_{66} - C_{46}*C_{46} > 0$, $C_{22} + C_{33} - 2*C_{23} > 0$

The Born–Huang criterion for I-42d-AlN_5 phase:

$C_{11} > 0$, $C_{33} > 0$, $C_{44} > 0$, $C_{66} > 0$, $(C_{11} - C_{12}) > 0$, $(C_{11} + C_{33} - 2*C_{13}) > 0$, $[2*(C_{11} + C_{12}) + C_{33} + 4*C_{13}] > 0$

Thus, the proposal structures all satisfy Born–Huang criterion, representing the stability of the mechanical property.

S5. Schrodinger equation for the model of one-dimensional particle in a box:

$$-\frac{\hbar^2}{2m}\frac{d^2}{dl^2}\varphi = E\varphi \qquad (1)$$

Its general solution is $E_{(n)} = \frac{n^2\,(2\pi\hbar)^2}{8ml^2}$ and $n = 1, 2, 3, 4......$ (2)

When π electrons pairs are localized in two deep potential wells, the energy is:

$$E_{(I)} = \frac{2\times 2\,(2\pi\hbar)^2}{8ml^2} = 4E_1,\ \left[E_1 = \frac{(2\pi\hbar)^2}{8ml^2}\right] \qquad (3)$$

When π electrons pairs are delocalized in a deep potential well, the energy is:

$$E_{(II)} = \frac{2\,(2\pi\hbar)^2 + 2\times 2^2\,(2\pi\hbar)^2}{8m(3l)^2} = \frac{10}{9}E_1 \qquad (4)$$

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