Supplementary Material for "Evidence for a high-pressure isostructural transition in nitrogen"

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S-1. METHODS

High pressure was generated using a rheniums-gasket diamond anvil cell (DAC) with 100~300 μm culets. Solid nitrogen samples were successfully synthesized by compression of purity liquid and then warmed to ambient temperature for Raman and ADXRD experiments. High-pressure Raman scattering experiments were carried out using a custom-built confocal Raman spectrometry system in the back-scattering geometry excited by a solid-state laser at 532 nm. The sample pressure in Raman experiments were measured by the high-frequency edge of the diamond phonon [1, 2] and the ruby fluorescence method [3]. Considering that the ruby fluorescence scale method for the high pressure above 100 GPa cannot be read accurately, we only adopt the first-order diamond phonon [1, 2] as pressure calibration above 100 GPa. The

ADXRD experiments were collected at the 4W2 beam line of the Beijing Synchrotron Radiation Facility (BSRF, China) and the BL15U1 beam line of the Shanghai Synchrotron Radiation Facility (SSRF, China). The X-ray beam down to about $2.5\times2.5\ \mu m^2$ with 0.6199Å wavelength. The sample pressure in ADXRD experiments were measured using the high-frequency edge of the diamond phonon [1, 2], the ruby fluorescence method[3] and the equation of state (EOS) of rhenium [4]. The measured pressure error which used these methods is within 0.5 GPa (below 70 GPa). The two-dimensional diffraction patterns were analyzed with the programs Dioptas [5] and Fit2D [6], respectively. The structural refinements were performed by using software GSAS to get the lattice parameters [7].

The structures mentioned here were investigated by employing the swarm intelligence CALYPSO method [8, 9]. The total energy calculations and structure optimization were carried out using the plane wave basis, projected augmented wave (PAW) potentials, and generalized gradient approximation (GGA) with the Perdew-Burke Ernzerh (PBE) of exchange-correlation functional as implemented in the Vienna ab initio simulation package (VASP) [10-14]. The frozen-core all electron PAW potentials were used with $2S^2 2P^3$ treated as valence electrons for N. The Van der Waals density functional, namely optB86b-vdW, was adopted to treat dispersion forces. The cutoff energy (900 eV) for the expansion of the wave function into plane waves and Monkhorst-Pack [15] *k*-meshes (*k*-points density 0.02 $Å^{-1}$) are chosen to ensure that all the enthalpy calculations are well converged to better than 1 meV/atom. Using CALYPSO, we searched the

structures of nitrogen with simulation cell sizes of 1-40 formula units (f.u.) in the pressure range of 0-60 GPa. Phonon calculations were performed on the structures to determine their dynamic stability, by using a finite displacement approach as per the PHONOPY code [16, 17].

S-2. SUPPLEMENTARY DATA

	Original crystal data of Pickard's structure	Original crystal data in this work	Standardized crystal data of Pickard's structure	Standardized crystal data in this work
a/Å	2.9220	2.9183	2.9220	2.9183
b/Å	2.8910	2.8934	2.8910	2.8933
c/Å	5.5880	5.5503	4.6065	4.5919
β	132.5400	132.5177	116.6460	117.0130
V/Å^3	34.7806	34.5426	34.7806	34.5420
x	0.5678	0.0695	0.1610	0.1614
y	0.3764	0.3751	0.1236	0.1249
z	0.4534	0.4540	0.0466	0.0456

TABLE S1: The original and standardized crystal data of λ-N_2 in Ref [18] and the present work. The original data were standardized by using the Vesta software.

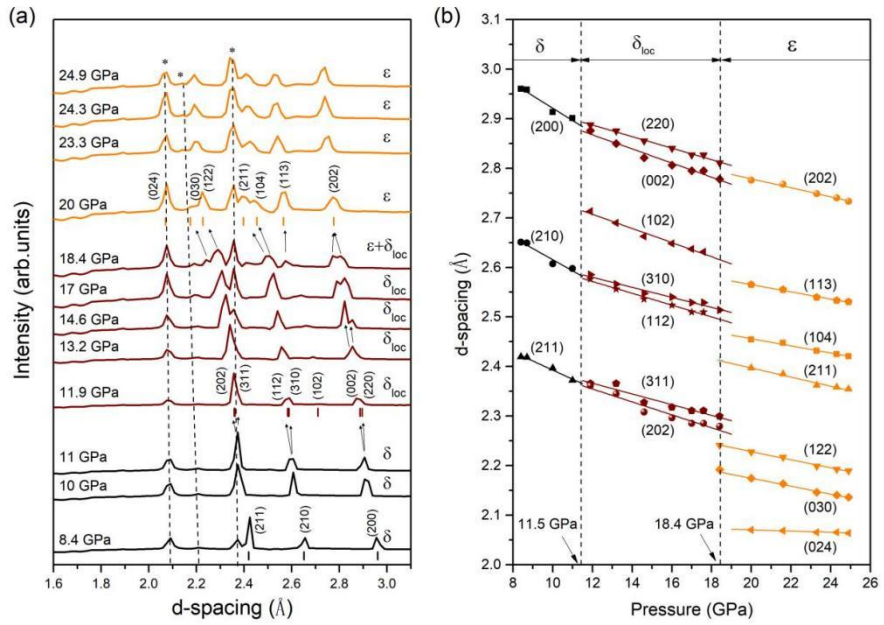

FIG.S1: (a) Integrated x-ray diffraction patterns of ordinary nitrogen phases collected at room temperature from 8.4 to 24.9 GPa at Beijing Synchrotron Radiation Facility (BSRF, China) with an X-ray wavelength of 0.6199 Å. The black dashed lines indicate the three diffraction lines of Re gasket, also identified at 24.9 GPa by black asterisks, which could be followed with pressure. Vertical bars indicated the *d* spacing positions. Nitrogen from 8.4 GPa to 11 GPa was identified as the δ-N_2 phase. The onset of the δ_{loc}-N_2 phase occurs at 11.5 GPa. The phase transition from δ_{loc} to ε occurs at 18.4 GPa. (b) The *d* spacings of the δ, δ_{loc}, and ε phases are presented as a function of pressure. The black dashed lines indicate the pressure boundary between these phases.

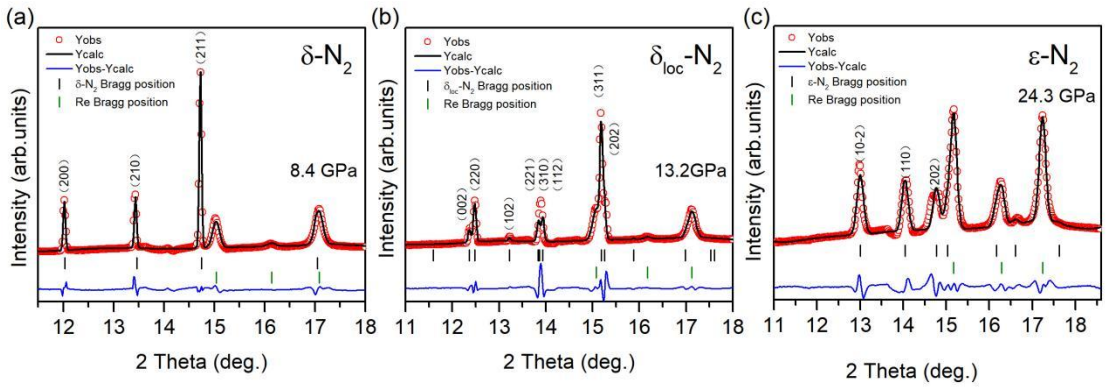

FIG. S2: Representative diffraction data and Rietveld-refined patterns of δ-N_2, δ_{loc}-N_2, and ε-N_2 at 8.4 GPa, 13.2 GPa, and 24.3 GPa, respectively. (a) The refinement results of δ-N_2 at 8.4 GPa: $a=b=c$=5.9139 Å, R_{wp}=2.97%, R_p=1.89%. (b) The refinement results of δ_{loc}-N_2 at 13.2 GPa: $a=b$=8.1360 Å, c=5.7014 Å, R_{wp}=4.01%, R_p=1.84%. (c) The refinement results of ε-N_2 at 24.3 GPa: $a=b$=7.4349 Å, c=10.4038 Å, R_{wp}=5.70%, R_p=6.90%.

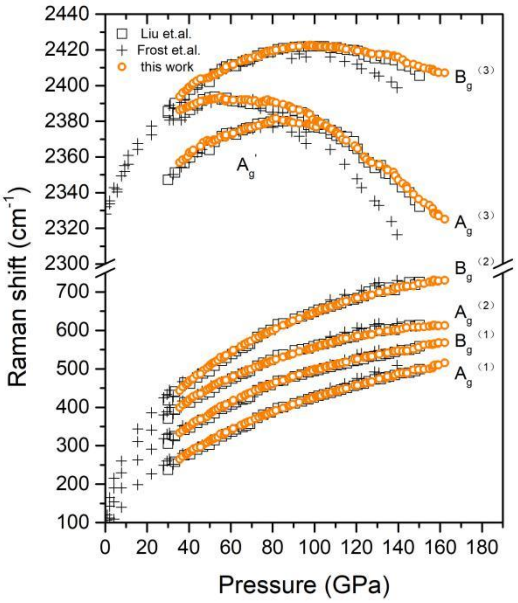

FIG. S3: The experimental Raman peaks of λ-N_2 at various pressures at room temperature in comparison with the data in the literature [19, 20]. The orange circles are the present data. The hollow squares and vertical crosses represent experimental data in the literature [19, 20].

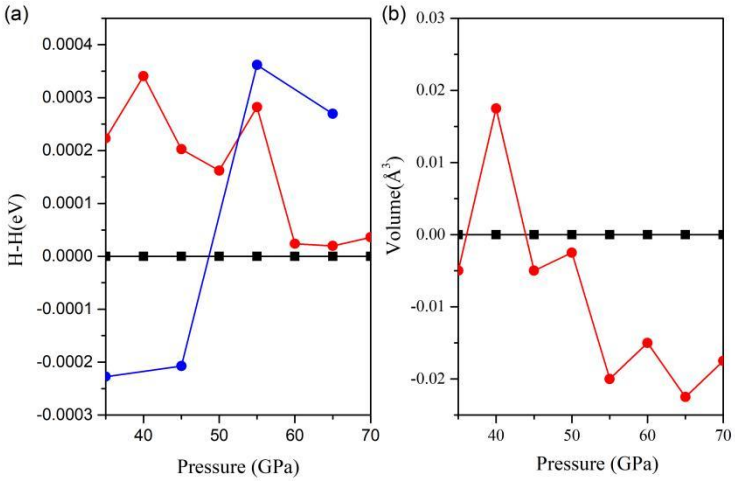

FIG. S4: (a) Enthalpy difference and (b) volume difference curves of the λ-N_2 around 50 GPa. The square and circles represent the data of Pickard's structure and the present structure, respectively. The red circles represent the calculated enthalpy without taking the zeor-point energy, and blue circles are the calculated data taking consideration of the zero-point energy.

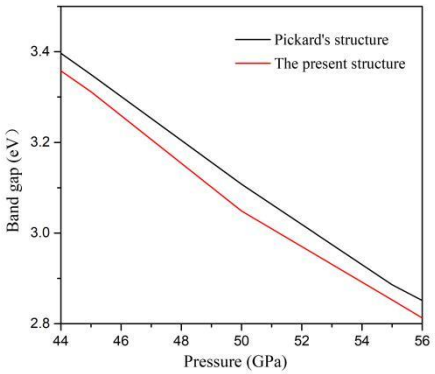

FIG. S5: The band gap of λ-N_2 with the two structures as a function of pressure.

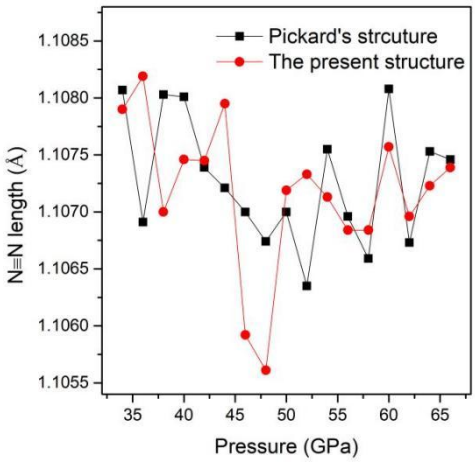

FIG. S6: The N≡N bonding length of λ-N_2 with the two different structures as a function of pressure.

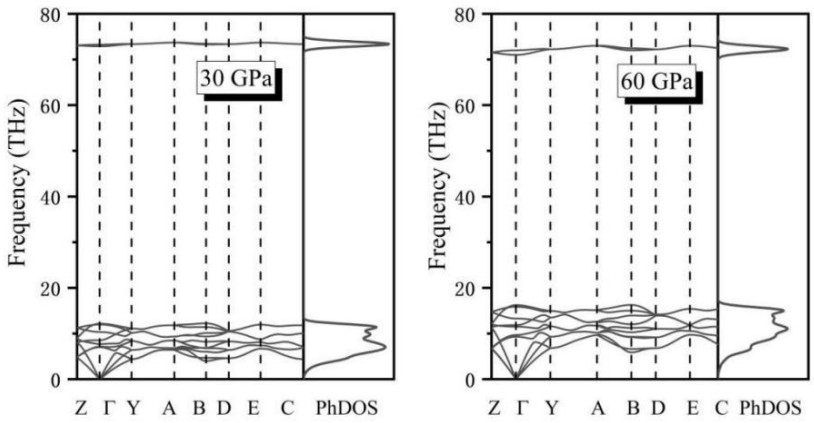

FIG. S7: Phonon dispersion and phonon DOS curves for λ-N_2 with our structure at 30 and 60 GPa, respectively.

1. Akahama Y and Kawamura H 2004 *J. Appl. Phys.* **96** 3748

2. Akahama Y and Kawamura H 2010 *J. Phys. Conf. Ser.* **215** 012195

3. Mao H K, Xu J and Bell P M 1986 *J. Geophys. Res.* **91** 4673

4. Zha C-S, Bassett W A and Shim S-H 2004 *Rev. Sci. Instrum.* **75** 2409

5. Prescher C and Prakapenka V B 2015 *High Pressure Res.* **35** 223

6. Hammersley A P, Svensson S O, Hanfland M, Fitch A N and Hausermann D 1996 *High Pressure Res.* **14** 235

7. Toby B H 2001 *J. Appl. Crystallogr.* **34** 210

8. Lv J, Wang Y, Zhu L and Ma Y 2011 *Phys. Rev. Lett.* **106** 015503

9. Wang Y, Lv J, Zhu L and Ma Y 2010 *Phys. Rev. B* **82** 094116

10. Kresse G and Furthmüller J 1996 *Phys. Rev. B* **54** 11169

11. Kresse G and Joubert D 1999 *Phys. Rev. B* **59** 1758

12. Dong W, Kresse G, Furthmüller J and Hafner 1996 J *Phys. Rev. B* **54** 2157

13. Blochl P E 1994 *Phys. Rev. B* **50** 17953

14. Perdew J P, Burke K and Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865

15. Monkhorst H J and Pack J D 1976 *Phys. Rev. B* **13** 5188

16. Togo A, Oba F and Tanaka I 2008 *Phys. Rev. B* **78** 134106

17. The force constants matrix is determined by VASP. Convergence test gave the use of a $3 \times 3 \times 2$ supercell

18. Pickard C J and Needs R J 2009 *Phys. Rev. Lett.* **102** 125702

19. Frost M, Howie R T, Dalladay-Simpson P, Goncharov A F and Gregoryanz E 2016 *Phys. Rev. B* **93** 024113

20. Liu S, Pu M, Tang Q Q, Zhang F, Wu B B and Lei L 2020 *Solid State Commun*. **310** 113843