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Direct Reaction Between Copper and Nitrogen at High Pressures and Temperatures

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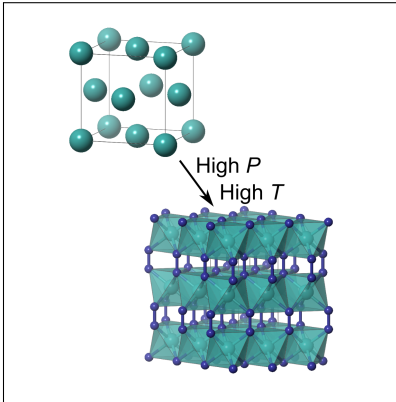
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Abstract

Transition metal nitrides have applications in a range of technological fields. Recent experiments have shown that new nitrogen-bearing compounds can be accessed through a combination of high temperatures and pressures, revealing a richer chemistry than was previously assumed. Here, we show that at pressures above 50 GPa and temperatures greater than 1500 K the elemental copper reacts with nitrogen forming copper diazenide (CuN_2). Through a combination of synchrotron X-ray diffraction and first-principles calculations we have explored the stability and electronic structure of CuN_2 . We find that the novel compound remains stable down to 25 GPa before decomposing to its constituent elements. Electronic structure calculations show that CuN_2 is metallic and exhibits partially filled N_2 antibonding orbitals, leading to an ambiguous electronic structure between $\text{Cu}^+/\text{Cu}^{2+}$. This leads to weak Cu-N bonds and the lowest bulk modulus observed for any transition metal nitride.

Graphical TOC Entry



Nitrogen is largely inert under atmospheric conditions however, it forms a large number of technologically important materials with main group elements and transition metals. Nitride compounds have been an important focus of inorganic chemistry for many decades, typically synthesised at high temperatures.¹ Recently, alternative high-pressure synthesis methods have provided highly successful for the discovery of novel materials which have been proposed as ideal candidates in a range of areas from highly non-compressible materials²⁻⁴ to explosives.^{5,6}

Solids with polymeric networks of N-N single bonds^{7,8} should act as excellent high energy density materials if suitable synthesis routes can be found. Extensive theoretical work has predicted the existence of poly-nitride species for at least sixteen metals (*e.g.* Refs⁹⁻¹⁴) and recent experiments have begun to test these predictions, uncovering intriguing structures containing polymeric nitrogen chains,¹⁵ molecular inclusion compounds,¹⁶ and pentazolate anions,^{17,18} all synthesised under high-pressure and high-temperature reaction conditions.

The platinum-group metals (Pt,² Pd,⁴ Rh,¹⁹ Os³ Ir,^{3,20} and Ru²¹) have been shown to form highly incompressible N-containing species. Although they crystallise in a range of different structures, these compounds share a number of features leading to high bulk moduli primarily N-N single bonds (≈ 1.4 Å) linking octahedrally coordinated N atoms.²² Numerous subsequent experimental and theoretical studies have continued to search for ultrahard materials amongst other transition-metal nitrides at high pressure.^{9,11,23-25}

The coinage metals (group 11: Cu, Ag, and Au) have so far shown a limited propensity to form nitrogen-bearing compounds despite intense efforts utilising an array of synthesis techniques including nitrogen-ion irradiation.²⁶⁻²⁹ Copper is known to form two nitrogen-containing compounds; copper azide (CuN_3), a highly sensitive explosive,³⁰ and copper nitride (Cu_3N) a stable semiconductor finding applications in a wide range of areas from lithium-ion battery electrodes to conductive ink and solar energy harvesting.³¹⁻³³ Under compression, the narrow band gap (0.6 eV) of Cu_3N closes by ≈ 5 GPa and no structural phase transitions are observed up to 26.7 GPa.³⁴ Silver also forms an explosive azide (AgN_3)³⁵

and attempts at forming stable gold nitrides have been limited to ion-irradiated surfaces.^{26,28}

Here, using a combination of high-pressure and high temperatures, we have explored the synthesis of novel copper-nitrogen compounds. After laser heating at 50 GPa, we observe the direct reaction between copper and nitrogen forming a previously unknown copper diazenide with stoichiometry CuN_2 . This compound is stable on decompression down to 25 GPa before decomposing to its constituent elements. Calculations show CuN_2 is a metal with a copper oxidation state lying between +1 and +2. As a result CuN_2 contains highly compressible Cu-N bonds giving mechanical properties far more in common with alkaline earth diazenides^{36–38} than other transition metal nitrides.

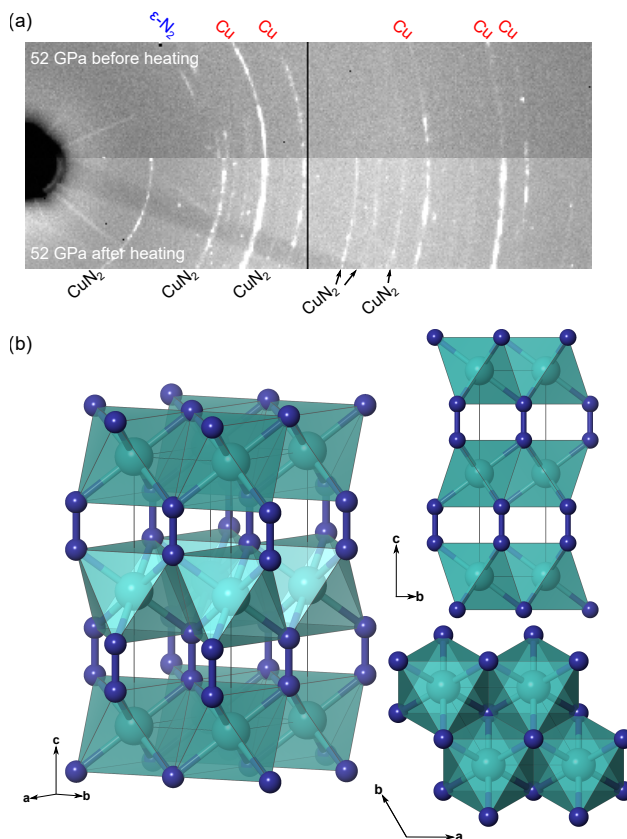


Figure 1: High pressure X-ray diffraction patterns ($\lambda = 0.3344 \text{ \AA}$) showing (a) the synthesis of CuN_2 by laser heating at 52 GPa; (b) Crystal structure of CuN_2 , Cu atoms are green, N atoms blue. Optimised structural parameters derived from DFT calculations at 52 GPa: $a = 2.741$, $c = 7.0417 \text{ \AA}$, $\text{Cu}[2a (0, 0, 0)]$, $\text{N}[4f (\frac{1}{3}, \frac{2}{3}, 0.6650)]$.

Samples of Cu powder were compressed in solid N_2 and laser heated at 10 GPa intervals

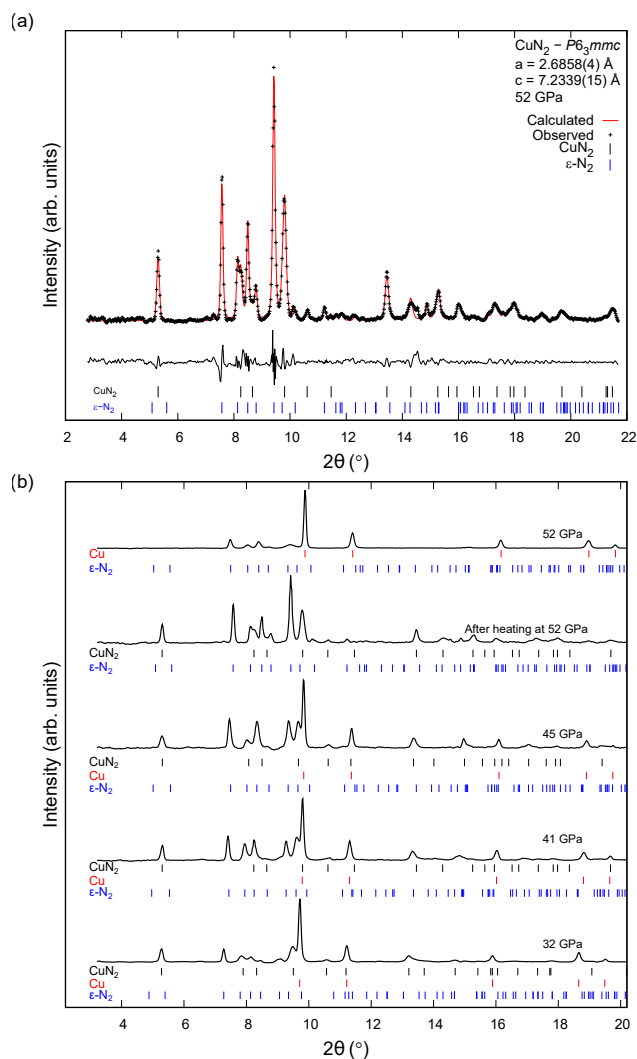


Figure 2: Representative Le Bail refinement of CuN_2 data at 52 GPa $wR_p = 0.39$ ($\lambda = 0.3344 \text{ \AA}$); (b) Synthesis and decompression of CuN_2 , tick marks indicated Bragg reflection positions for the noted phase.

up to 50 GPa with no observed changes in diffraction patterns with the exception of the known phase transitions in pure N₂.^{39,40} Above 52 GPa the Cu sample coupled strongly, with temperatures in excess of ~ 1500 K. Upon quenching numerous new diffraction lines appeared (Figure 1(a)), all of which could be indexed to a hexagonal unit cell [$a = 2.6759(5)$, $c = 7.235(3)$ Å, at 52 GPa], with systematic absences indicating the presence of a c -glide normal to $[1\bar{1}1]$. Attempts to solve the crystal structure were hindered by numerous overlapping reflections from ϵ -N₂, however a possible solution was found by direct methods in space group $P6_3/mmc$,⁴¹ with stoichiometry CuN₂. Rietveld refinement required excluding regions of the profile which overlapped with peaks due to ϵ -N₂ as diffraction from ϵ -N₂ took the form of quasi-single crystal diffraction peaks unsuitable for inclusion in the refinement. Due to the poor quality of the data the nitrogen-atom position was poorly defined giving a large uncertainty on the experimentally determined N-N bond distance (1.3(3) Å). However, despite extensive overlapping, unit-cell dimensions of this new phase could be extracted (Figure 2(b)) and the resulting changes in unit-cell volume with pressure (Figure 3(a)) also suggest a stoichiometry of CuN₂. To confirm our experimental structural analysis and to explore the electronic structure of CuN₂ we have performed DFT geometry optimisation calculations. We find that the structure converges to close agreement with experimentally determined unit-cell dimensions (Figure 3(b)).

The optimised structure of the novel compound CuN₂ contains octahedrally coordinated Cu atoms, in common with many transition metal-nitrogen compounds (e.g. PtN₂² and FeN₂¹⁵). These edge-sharing CuN₆ octahedra are arranged in layers in the ab -plane and are linked by N₂ anions aligned along the c -axis, with a N-N interatomic distance of 1.197 Å at 52 GPa. (Figure 1(b)). This N-N distance gives a direct insight into the nature of the electronic structure of transition metal nitrides. In cases with high metal oxidation states, the transfer of electron density from the metal results in “pernitride” anions ($[\text{N-N}]^{4-}$) which form strong M -N bonds, have high bulk moduli, and show internal N-N distances of approximately 1.4 Å, seen in the archetypal examples of PtN₂,² OsN₂³ and TiN₂.²⁴ If the metal is limited to an

oxidation state of +2, “diazenide” ($[\text{N}=\text{N}]^{2-}$) anions are formed instead. In these compounds M - N bonding is weaker, bulk moduli are lower, and the internal N - N distances are shorter, $\approx 1.2 \text{ \AA}$. This is the case for the alkaline earth metal diazenides, BaN_2 and SrN_2 .⁴² The short N - N distance in CuN_2 (1.197 \AA) would appear to suggest that, by analogy, in this compound Cu is present as Cu^{2+} and is bonded to $[\text{N}=\text{N}]^{2-}$ anions. However, a Cu^{2+} ion would be expected to display a Jahn-Teller distortion which is not consistent with proposed crystal structure. To understand this discrepancy, lattice dynamics calculations were carried out at 0 and 50 GPa, and at both pressures the $P6_3/mmc$ structure is dynamically stable and all phonons are real, indicating the absence of a driving force to distort the CuN_6 octahedra. Furthermore, geometry optimisation of a distorted structure in the orthorhombic subgroup $Cmcm$ resulted in a return to $P6_3/mmc$ symmetry within numerical accuracy.

A more detailed understanding of the electronic structure of CuN_2 is gained through the crystal orbital Hamiltonian population (COHP) analysis.^{43,44} The electronic density of states of CuN_2 is shown in Figure 4(a). This shows CuN_2 to be a metal with no clear character to the states at the Fermi level, but it is dominated by Cu - $3d$ and N - $2p$ states as expected. There is a gap at 4 eV above the Fermi level corresponding to additional unfilled N_2 $1\pi_g^*$ and $2\sigma_u^*$ states. A more quantitative picture arises from the integration of the COHP(N - N) over the energy range of these antibonding orbitals from -5 to 5 eV as seen in (Figure 4(b)). The resulting 32.5% occupancy is significantly less than the 50% expected for $[\text{N}=\text{N}]^{2-}$ anions³⁸ and, combined with the absence of a Jahn-Teller distortion, intriguingly supports an ambivalent electronic state between $[\text{N}=\text{N}]^-$ and $[\text{N}=\text{N}]^{2-}$.

From the synthesis pressure, samples were decompressed to determine the stability of this newly synthesised copper diazenide. Below 25 GPa peaks due to CuN_2 disappear leaving only those from Cu and $\epsilon\text{-N}_2$. Changes in unit-cell volume with pressure were fitted with a Vinet equation of state giving a bulk modulus of $K_0(\text{CuN}_2) = 130(11)$ GPa, extremely close to that of Cu (140 GPa) and comparable to the low bulk moduli observed for the alkaline earth metal diazenides [$K_0(\text{BaN}_2) = 46$ GPa, $K_0(\text{SrN}_2) = 65$ GPa].⁴² Unsurprisingly then,

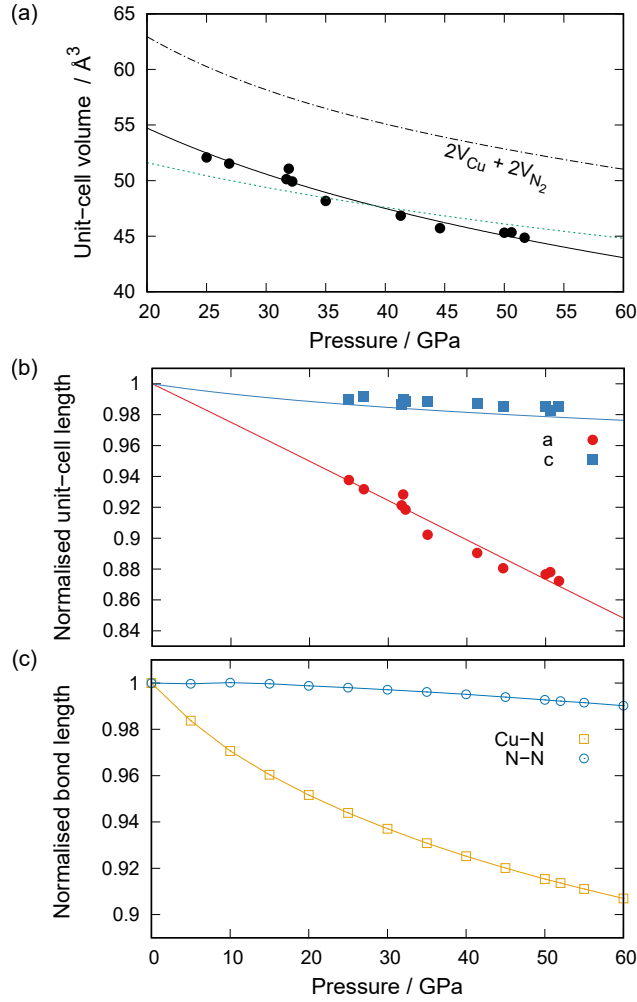


Figure 3: (a) Change in CuN₂ unit-cell volume with pressure, dashed line indicates volume of pure Cu + N₂ for comparison. Solid line indicates fitted Vinet equation of state ($V_0 = 62.3(13) \text{ \AA}^3$, $K_0 = 130(11) \text{ GPa}$, $K' = 1$), dotted line shows the unit-cell volume derived from DFT calculations; (b) Changes in normalised unit-cell lengths for CuN₂, a_0 and c_0 derived from calculations; (c) Changes in normalised bond lengths for Cu-N (yellow squares) and N-N (blue circles) with pressure.

the overall compressibility appears very similar to that calculated from the pure elements (Figure 3(a)).

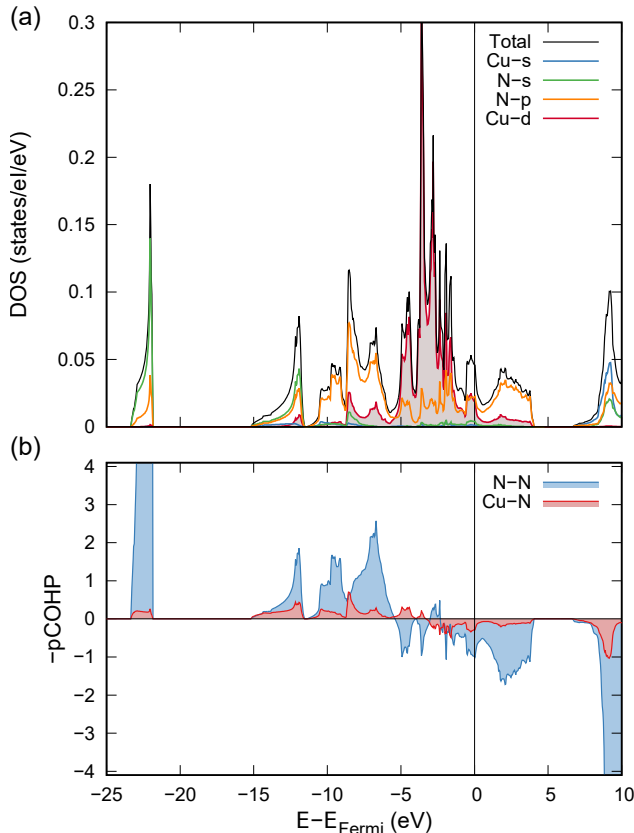


Figure 4: (a) Electronic density of states, (b) COHP analysis of CuN_2 at 50 GPa.

Closer analysis shows the majority of this compression is taken up by the a and b axes, by 52 GPa the a axis decreases by 12.8 % ($-0.392(5)$ Å) relative to the calculated ambient pressure value as compared to the far more rigid c axis which decreases by just 0.65 % ($-0.047(3)$ Å) over the same pressure range (Figure 3(b)). The origin of this anisotropic behaviour lies in the contrasting strengths of Cu-N and N-N bonding, as shown in Figure 3(c). As would be expected for a strongly-bonded diazenide anion, N=N distance reduces by less than 1% up to 60 GPa, almost an order of magnitude more resilient than the Cu-N bonds which compress by -9.3% . The presence of highly compressible M -N bond and the resulting low bulk modulus again marks CuN_2 as being far more similar to the alkaline earth diazenides rather than other transition metal nitrides. This is the logical conclusion to the

trend observed across the first-row transition metal nitrides MN_2 , as the N_2 anion shows greater molecular character, M - N bonds weaken and bulk moduli reduce: $K_0(\text{TiN}_2) = 382(3)$ GPa,²⁴ $K_0(\text{FeN}_2) = 344(13)$ GPa,²⁵ $K_0(\text{CoN}_2) = 216(18)$ GPa⁴⁵ and $K_0(\text{CuN}_2) = 130(11)$ GPa.

In conclusion, we have utilised *in situ* laser heating combined with high pressures to perform the first direct reaction between elemental nitrogen and a coinage metal to form a novel copper diazenide (CuN_2) compound. The structure was determined by a combination of powder X-ray diffraction and DFT calculations. Surprisingly for a transition metal nitride, CuN_2 is highly compressible due to the presence of extremely weak Cu- N bonds. The origins of this surprising behaviour lie in the limited electron transfer between Cu and N_2 . Electronic structure analysis indicates partially-filled antibonding orbitals on the N_2 anions which combined with the absence of a Jahn-Teller distortion, suggests an electronic structure between $\text{Cu}^+[\text{N}=\text{N}]^-$ and $\text{Cu}^{2+}[\text{N}=\text{N}]^{2-}$. This compound remains stable down to 25 GPa before decomposing to its constituent elements.

High purity copper powder (99.8%, 1.6 μm particle size) from Alfa Aesar was placed into diamond-anvil cells (DAC) and subsequently loaded with high purity nitrogen gas (99.9%) at 0.17 GPa. Loading of nitrogen was confirmed by the observation of the nitrogen vibrational mode using a custom-built micro-focused Raman system.⁴⁶ Rhenium gaskets were used to form the sample chamber in all experimental runs with diamond-anvil culets ranging from 200 to 300 μm .

The Cu-sample was heated *in-situ* from both sides uniaxially by directly coupling to an yttrium-aluminium-garnet (YAG) laser with wave-length $\lambda = 1064$ nm. Angle-dispersive X-ray diffraction data were collected at beamline 13-IDD (GSECARS) at APS, USA.⁴⁷ The diffraction from 0.3344 Å wavelength X-rays was recorded using a Pilatus 1M image-plate detector. Two-dimensional image-plate data were integrated with *DIOPTAS* to yield intensity *vs.* 2θ plots.⁴⁸ Diffraction patterns were indexed with *CONOGRAPH*,⁴⁹ Le Bail and Rietveld refinement was carried out in *Jana2006*.⁵⁰⁻⁵²

Total energy calculations were carried out within the framework of density functional theory (DFT) in conjunction with the projector-augmented wave method and a plane wave basis, as implemented in the VASP code.^{53,54} We used the PBE exchange-correlation functional⁵⁵ and included the Cu $3p$, $4s$, and $3d$ and N $2s$ and $2p$ electrons in the valence space. Brillouin zone sampling was done on regular k -point grids with linear densities of $50 / \text{\AA}^{-1}$, the plane wave cutoff energy was 1000 eV. Structures were optimised over a sequence of pressures until remaining forces on the atoms were smaller than $1 \text{ meV}/\text{\AA}$. Partial DOS and COHP analysis carried out using LOBSTER.⁵⁶

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References

- (1) Höhn, P.; Niewa, R. In *Handbook of Solid State Chemistry*; Dronskowski, R., Kikkawa, S., Stein, A., Eds.; Wiley-VCH, 2017; Chapter 7, pp 251–361.
- (2) Gregoryanz, E.; Sanloup, C.; Somayazulu, M.; Badro, J.; Fiquet, G.; Mao, H.-k.; Hemley, R. J. Synthesis and Characterization of a Binary Noble Metal Nitride. *Nature Materials* **2004**, *3*, 294–297.
- (3) Young, A. F.; Sanloup, C.; Gregoryanz, E.; Scandolo, S.; Hemley, R. J.; Mao, H. K. Synthesis of Novel Transition Metal Nitrides IrN₂ and OsN₂. *Physical Review Letters* **2006**, *96*, 155501.
- (4) Crowhurst, J. C.; Crowhurst, J. C.; Goncharov, A. F.; Sadigh, B.; Evans, C. L.; Morrall, P. G.; Ferreira, J. L.; Nelson, A. J. Synthesis and Characterization of the Nitrides of Platinum and Iridium. *Science* **2006**, *311*, 1275–1278.
- (5) Pickard, C. J.; Needs, R. J. High-Pressure Phases of Nitrogen. *Physical Review Letters* **2009**, *125702*, 1–4.
- (6) Li, Y. C.; Qi, C.; Li, S. H.; Zhang, H. J.; Sun, C. H.; Yu, Y. Z.; Pang, S. P. 1,1'-Azobis-1,2,3-triazole: A high-nitrogen compound with stable N₈ Structure and Photochromism. *Journal of the American Chemical Society* **2010**, *132*, 12172–12173.
- (7) Eremets, M. I.; Gavriluk, A. G.; Trojan, I. A.; Dzivenko, D. A.; Boehler, R. Single-bonded cubic form of nitrogen. *Nature Materials* **2004**, *3*, 558–563.
- (8) Gregoryanz, E.; Goncharov, A. F.; Sanloup, C.; Somayazulu, M.; Mao, H.-k.; Hemley, R. J. High P-T transformations of nitrogen to 170 GPa. *The Journal of Chemical Physics* **2007**, *126*, 184505.
- (9) Aydin, S.; Ciftci, Y. O.; Tatar, A. Superhard transition metal tetranitrides: XN₄ (X = Re, Os, W). *Journal of Materials Research* **2012**, *27*, 1705–1715.

- (10) Prasad, D. L.; Ashcroft, N. W.; Hoffmann, R. Evolving structural diversity and metallicity in compressed lithium azide. *Journal of Physical Chemistry C* **2013**, *117*, 20838–20846.
- (11) Zhao, Z.; Bao, K.; Li, D.; Duan, D.; Tian, F.; Jin, X.; Chen, C.; Huang, X.; Liu, B.; Cui, T. Nitrogen concentration driving the hardness of rhenium nitrides. *Scientific Reports* **2014**, *4*, 4797.
- (12) Zhu, S.; Peng, F.; Liu, H.; Majumdar, A.; Gao, T.; Yao, Y. Stable Calcium Nitrides at Ambient and High Pressures. *Inorganic Chemistry* **2016**, *55*, 7550–7555.
- (13) Zhang, J.; Oganov, A. R.; Li, X.; Niu, H. Pressure-stabilized hafnium nitrides and their properties. *Physical Review B* **2017**, *95*, 020103.
- (14) Kvashnin, A. G.; Oganov, A. R.; Samtsevich, A. I.; Allahyari, Z. Computational Search for Novel Hard Chromium-Based Materials. *Journal of Physical Chemistry Letters* **2017**, *8*, 755–764.
- (15) Bykov, M.; Bykova, E.; Aprilis, G.; Glazyrin, K.; Koemets, E.; Chuvashova, I.; Kuppenko, I.; McCammon, C.; Mezouar, M.; Prakapenka, V. et al. Fe-N system at high pressure reveals a compound featuring polymeric nitrogen chains. *Nature Communications* **2018**, *9*, 2756.
- (16) Bykov, M.; Bykova, E.; Koemets, E.; Fedotenko, T.; Aprilis, G.; Glazyrin, K.; Liermann, H. P.; Ponomareva, A. V.; Tidholm, J.; Tasnádi, F. et al. High-Pressure Synthesis of a Nitrogen-Rich Inclusion Compound $\text{ReN}_8 \cdot x\text{N}_2$ with Conjugated Polymeric Nitrogen Chains. *Angewandte Chemie - International Edition* **2018**, *57*, 9048–9053.
- (17) Laniel, D.; Weck, G.; Loubeyre, P. Direct Reaction of Nitrogen and Lithium up to 75 GPa : Synthesis of the Li_3N , LiN , LiN_2 , and LiN_5 Compounds. *Inorganic Chemistry* **2018**, *57*, 10685–10693.

- (18) Steele, B. A.; Stavrou, E.; Crowhurst, J. C.; Zaug, J. M.; Prakapenka, V. B.; Oleynik, I. I. High-Pressure Synthesis of a Pentazolate Salt. *Chemistry of Materials* **2017**, *29*, 735–741.
- (19) Niwa, K.; Dzivenko, D.; Suzuki, K.; Riedel, R.; Troyan, I.; Eremets, M.; Hasegawa, M. High Pressure Synthesis of Marcasite-Type Rhodium Pernitride. *Inorganic Chemistry* **2013**, *53*, 697–699.
- (20) Crowhurst, J. C.; Goncharov, A. F.; Sadigh, B.; Zaug, J.; Aberg, D.; Meng, Y.; Prakapenka, V. B. Synthesis and characterization of nitrides of iridium and palladium. *Journal of Materials Research* **2008**, *23*, 1–5.
- (21) Niwa, K.; Suzuki, K.; Muto, S.; Tatsumi, K.; Soda, K.; Kikegawa, T.; Hasegawa, M. Discovery of the Last Remaining Binary Platinum-Group Pernitride. *Chemistry - A European Journal* **2014**, *20*, 13885–13888.
- (22) Liu, Z.; Gall, D.; Khare, S. Electronic and bonding analysis of hardness in pyrite-type transition-metal pernitrides. *Physical Review B* **2014**, *90*, 134102.
- (23) Wessel, M.; Dronskowski, R. A New Phase in the Binary Iron Nitrogen System ? - The Prediction of Iron Pernitride, FeN₂. *Chemistry - A European Journal* **2011**, *17*, 2598–2603.
- (24) Bhadram, V. S.; Kim, D. Y.; Strobel, T. A. High-Pressure Synthesis and Characterization of Incompressible Titanium Pernitride. *Chemistry of Materials* **2016**, *28*, 1616–1620.
- (25) Laniel, D.; Dewaele, A.; Garbarino, G. High Pressure and High Temperature Synthesis of the Iron Pernitride FeN₂. *Inorganic Chemistry* **2018**, acs.inorgchem.7b03272.
- (26) Krishnamurthy, S.; Montalti, M.; Wardle, M.; Shaw, M.; Briddon, P.; Svensson, K.;

- Hunt, M.; Šiller, L. Nitrogen ion irradiation of Au (110): Photoemission spectroscopy and possible crystal structures of gold nitride. *Physical Review B* **2004**, *70*, 045414.
- (27) Tibbetts, G. G.; Burkstrand, J. M.; Tracy, J. C. Electronic properties of adsorbed layers of nitrogen, oxygen, and sulfur on copper (100). *Physical Review B* **1977**, *15*, 3652–3660.
- (28) Siller, L.; Hunt, M. R. C.; Brown, J. W.; Coquel, J. M.; Rudolf, P. Nitrogen ion irradiation of Au(110): formation of gold nitride. *Surface Science* **2002**, *513*, 78–82.
- (29) Lancaster, G. M.; Rabalais, J. W. Chemical Reactions of N^{2+} Ion Beams with First-Row Transition Metals. *The Journal of Physical Chemistry* **1979**, *83*, 209–212.
- (30) Liu, X.; George, J.; Maintz, S.; Dronskowski, R. β - CuN_3 : The overlooked ground-state polymorph of copper azide with heterographene-like layers. *Angewandte Chemie - International Edition* **2015**, *54*, 1954–1959.
- (31) Wang, J.; Li, F.; Liu, X.; Zhou, H.; Shao, X.; Qu, Y.; Zhao, M. Cu_3N and its analogs: a new class of electrodes for lithium ion batteries. *Journal of Materials Chemistry A: Materials for energy and sustainability* **2017**, *5*, 8762–8768.
- (32) Nakamura, T.; Hayashi, H.; Hanaoka, T. A.; Ebina, T. Preparation of copper nitride (Cu_3N) nanoparticles in long-chain alcohols at 130–200° C and nitridation mechanism. *Inorganic Chemistry* **2014**, *53*, 710–715.
- (33) Zakutayev, A.; Caskey, C. M.; Fioretti, A. N.; Ginley, D. S.; Vidal, J.; Stevanovic, V.; Tea, E.; Lany, S. Defect tolerant semiconductors for solar energy conversion. *Journal of Physical Chemistry Letters* **2014**, *5*, 1117–1125.
- (34) Kuzmin, A.; Anspoks, A.; Kalinko, A.; Timoshenko, J.; Nataf, L.; Baudelet, F.; Irifune, T. Origin of Pressure-Induced Metallization in Cu_3N : An X-ray Absorption Spectroscopy Study. *Physica Status Solidi (B)* **2018**, *1800073*.

- (35) Schmidt, C. L.; Dinnebier, R.; Wedig, U.; Jansen, M. Crystal structure and chemical bonding of the high-temperature phase of AgN_3 . *Inorganic Chemistry* **2007**, *46*, 907–916.
- (36) Vajenine, G. V.; Auffermann, G.; Prots, Y.; Schnelle, W.; Kremer, R. K.; Simon, A.; Kniep, R. Preparation, Crystal Structure, and Properties of Barium Pernitride, BaN_2 . *Inorganic Chemistry* **2001**, *40*, 4866–4870.
- (37) Auffermann, G.; Prots, Y.; Kniep, R. SrN and SrN_2 : Diazenides by Synthesis under High N_2 -pressure. *Angewandte Chemie - International Edition* **2001**, *40*, 547–549.
- (38) Schneider, S. B.; Seibald, M.; Deringer, V. L.; Stoffel, R. P.; Frankovsky, R.; Gina, M.; Laqua, H.; Duppel, V.; Jeschke, G.; Dronskowski, R. et al. High-Pressure Synthesis and Characterization of $\text{Li}_2\text{Ca}_3[\text{N}_2]_3$ an Uncommon Metallic Diazenide with $[\text{N}_2]^{2-}$ Ions. *Journal of the American Chemical Society* **2013**, *135*, 16668–16679.
- (39) Hanfland, M.; Lorenzen, M.; Wassilew-Reul, C.; Zontone, F. Structures of Molecular Nitrogen at High Pressures. *the Review of High Pressure Science and Technology* **1998**, *7*, 787–789.
- (40) Stinton, G.; Loa, I.; Lundegaard, L.; McMahon, M. The crystal structures of δ and δ^* nitrogen. *The Journal of Chemical Physics* **2009**, *131*, 104511.
- (41) Altomare, A.; Cuocci, C.; Giacovazzo, C.; Moliterni, A.; Rizzi, R.; Corriero, N.; Falicchio, A. EXPO2013: a kit of tools for phasing crystal structures from powder data. *Journal of Applied Crystallography* **2013**, *46*, 1231–1235.
- (42) Wessel, M.; Dronskowski, R. Nature of N-N Bonding within High-Pressure Noble-Metal Pernitrides and the Prediction of Lanthanum Pernitride. *Journal of the American Chemical Society* **2010**, *132*, 2421–2429.

- (43) Dronskowski, R.; Bloechl, P. E. Crystal orbital Hamilton populations (COHP): energy-resolved visualization of chemical bonding in solids based on density-functional calculations. *The Journal of Physical Chemistry* **1993**, *97*, 8617–8624.
- (44) Maintz, S.; Deringer, V. L.; TchougrÃeff, A. L.; Dronskowski, R. Analytic projection from plane-wave and PAW wavefunctions and application to chemical-bonding analysis in solids. *Journal of Computational Chemistry* **2013**, *34*, 2557–2567.
- (45) Niwa, K.; Terabe, T.; Kato, D.; Takayama, S.; Kato, M.; Soda, K.; Hasegawa, M. Highly Coordinated Iron and Cobalt Nitrides Synthesized at High Pressures and High Temperatures. *Inorganic Chemistry* **2017**, *56*, 6410–6418.
- (46) Dalladay-Simpson, P.; Howie, R. T.; Gregoryanz, E. Evidence for a new phase of dense hydrogen above 325 gigapascals. *Nature* **2016**, *529*, 63–67.
- (47) Shen, G.; Prakapenka, V. B.; Eng, P. J.; Rivers, M. L.; Sutton, S. R. Facilities for high-pressure research with the diamond anvil cell at GSECARS. *Journal of Synchrotron Radiation* **2005**, *12*, 642–649.
- (48) Prescher, C.; Prakapenka, V. B. DIOPTAS: a program for reduction of two-dimensional X-ray diffraction data and data exploration. *High Pressure Research* **2015**, *35*, 223–230.
- (49) Oishi-Tomiyasu, R. Robust powder auto-indexing using many peaks. *Journal of Applied Crystallography* **2014**, *47*, 593–598.
- (50) Le Bail, A.; Duroy, H.; Fourquet, J. Ab-initio structure determination of LiSbWO₆ by X-ray powder diffraction. *Material Research Bulletin* **1988**, *23*, 447–452.
- (51) Rietveld, H. M. A profile refinement method for nuclear and magnetic structures. *Journal of Applied Crystallography* **1969**, *2*, 65–71.
- (52) Petříček, V.; Dušek, M.; Palatinus, L. Crystallographic computing system JANA2006:

- general features. *Zeitschrift für Kristallographie-Crystalline Materials* **2014**, *229*, 345–352.
- (53) Kresse, G.; Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Physical Review B* **1996**, *54*, 11169.
- (54) Kresse, G.; Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Physical Review B* **1999**, *59*, 1758–1775.
- (55) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized gradient approximation made simple. *Physical review letters* **1996**, *77*, 3865.
- (56) Maintz, S.; Deringer, V. L.; Tchougréeff, A. L.; Dronskowski, R. LOBSTER: A tool to extract chemical bonding from plane-wave based DFT. *Journal of computational chemistry* **2016**, *37*, 1030–1035.