Nitride Compounds

International Edition: DOI: 10.1002/anie.201805152
German Edition: DOI: 10.1002/ange.201805152High-Pressure Synthesis of a Nitrogen-Rich Inclusion Compound $\text{ReN}_8 \cdot x\text{N}_2$ with Conjugated Polymeric Nitrogen Chains

Maxim Bykov,* Elena Bykova, Egor Koemets, Timofey Fedotenko, Georgios Aprilis, Konstantin Glazyrin, Hanns-Peter Liermann, Alena V. Ponomareva, Johan Tidholm, Ferenc Tasnádi, Igor A. Abrikosov, Natalia Dubrovinskaia, and Leonid Dubrovinsky

Abstract: A nitrogen-rich compound, $\text{ReN}_8 \cdot x\text{N}_2$, was synthesized by a direct reaction between rhenium and nitrogen at high pressure and high temperature in a laser-heated diamond anvil cell. Single-crystal X-ray diffraction revealed that the crystal structure, which is based on the ReN_8 framework, has rectangular-shaped channels that accommodate nitrogen molecules. Thus, despite a very high synthesis pressure, exceeding 100 GPa, $\text{ReN}_8 \cdot x\text{N}_2$ is an inclusion compound. The amount of trapped nitrogen (x) depends on the synthesis conditions. The polydiazenediyl chains $[-\text{N}=\text{N}-]_\infty$ that constitute the framework have not been previously observed in any compound. Ab initio calculations on $\text{ReN}_8 \cdot x\text{N}_2$ provide strong support for the experimental results and conclusions.

Rhenium–nitrogen compounds are widely studied because of their promising mechanical properties, such as high or ultra-high hardness and low compressibility.^[1] Early experimental works by Hahn and Konrad^[2] have shown that some rhenium nitrides (ReN_x) can be synthesized at ambient pressure as the direct result of the high-temperature chemical reaction between NH_4ReO_4 or ReCl_3 and NH_3 . These nitrides have the highest nitrogen content, at 0.43 ($x \leq 0.43$). An increase of the nitrogen content in nitrides may substantially raise their stiffness and hardness due to emerging covalent N–N bonds.^[3] Therefore, much effort in experimental and theoretical research has been invested in the search for nitrogen-rich rhenium–nitrogen compounds.

[*] Dr. M. Bykov, E. Koemets, T. Fedotenko, Prof. Dr. L. Dubrovinsky
Bayerisches Geoinstitute, University of Bayreuth
Universitätsstrasse 30, 95440 Bayreuth (Germany)
E-mail: maks.bykov@gmail.com

Dr. E. Bykova, Dr. K. Glazyrin, Dr. H.-P. Liermann
Photon Sciences, Deutsches Elektronen Synchrotron (DESY)
Notkestrasse 85, 22607, Hamburg (Germany)

G. Aprilis, Prof. Dr. N. Dubrovinskaia
Material Physics and Technology at Extreme Conditions
Laboratory of Crystallography, University of Bayreuth
Universitätsstrasse 30, 95440 Bayreuth (Germany)

Dr. A. V. Ponomareva
Materials Modeling and Development Laboratory
National University of Science and Technology "MISIS"
Moscow, 119049 (Russia)

J. Tidholm, Dr. F. Tasnádi, Prof. Dr. I. A. Abrikosov
Department of Physics, Chemistry and Biology (IFM)
Linköping University, Linköping SE-58183 (Sweden)

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under:
<https://doi.org/10.1002/anie.201805152>.

The emergence of the laser-heated diamond anvil cell (DAC) technique together with the development of dedicated stations at the third-generation synchrotron facilities have opened new, high-pressure routes for the synthesis of rhenium nitrides. Friedrich et al.^[1] synthesized two novel compounds: Re_3N at 13 GPa and 1700 K ($P-6m2$, $a = 2.78(1)$, $c = 7.152(4)$ Å), and Re_2N at 20(2) GPa and about 2000 K ($P6_3/mmc$, $a = 2.83(5)$, $c = 9.88(1)$ Å). Both of these compounds have exceptionally large bulk moduli exceeding 400 GPa.^[1]

Recently, Kawamura et al.^[4] obtained ReN_2 in the solid-state high-pressure reaction between ReCl_3 and Li_3N ,^[4] and claimed it to have the MoS_2 structure type based on structure refinements using the Rietveld method for powder X-ray diffraction (XRD) data. These results were put in doubt by Wang et al.,^[5] who suggested that ReN_2 should have monoclinic $C2/m$ symmetry and transform to the tetragonal $P4/mbm$ phase above 130 GPa. In theoretical work, ReN_2 with pyrite,^[6,7] CoS_2 ,^[8] fluorite,^[6,9] NbSe_2 ,^[7,10] and many other structure types with $P4/mmm$,^[11] $P4_2/mnm$,^[12] $P4/mbm$,^[13] $P-6m2$,^[7,10] $Cmcm$,^[10] $Pbcn$,^[14] $C2/m$,^[3] and $Pmmn$ ^[12] symmetries were considered, but these have not been confirmed experimentally.

Hitherto, ReN_3 with the orthorhombic symmetry $Ama2$ has the highest known nitrogen content for the Re–N system. It was synthesized in the form of thin films by reactive magnetron sputtering.^[15] There are a number of theoretically predicted nitrogen-rich compounds, that can have similar (ReN_3 ($Immm$)^[3]) or even higher nitrogen content, ReN_4 ($Pbca$,^[16,17] $Cmmm$ ^[17]). Nitrogen-rich compounds in metal–nitrogen systems are considered potential high-energy-density materials.^[18–21]

The great interest in the Re–N system calls for more systematic investigations, which could provide unambiguous structural characterization of novel Re–N phases. Although there are several prominent examples of the synergy between powder XRD and ab initio structure prediction algorithms,^[22,23] an independent self-consistent method is required to build a reference basis for further theoretical and experimental works. In contrast to most abundant high-pressure powder XRD studies, single-crystal XRD in diamond anvil cells allows not only an unequivocal structure solution but also provides information about the chemical composition of the products of the chemical reactions occurring in laser heated DACs. In this study, we used this advantage. We synthesized a novel nitrogen-rich compound, $\text{ReN}_8 \cdot x\text{N}_2$, in a laser-heated DAC and characterized its crystal structure using high-pressure single-crystal X-ray diffraction. Our experiment is complemented with theoretical analysis of

the discovered compounds in the framework of density functional theory.

$\text{ReN}_{8.7(2)}\text{N}_2$ resulted from a direct chemical reaction between rhenium and nitrogen at high pressure and high temperature. We conducted two independent experiments in a diamond anvil cell, in which a mixture of a Re powder and N_2 was first pressurized (to 105 GPa or 123 GPa), and then laser heated (to 2300(200) K or 2700(200) K, respectively). Nitrogen served simultaneously as a reagent and a pressure-transmitting medium (see the Experimental Section for details). Although the initial reagents were powders, the chemical reaction led to the formation of numerous good-quality single-crystal domains of the new compound, so that the diffraction data from the quenched material could be treated using well-established methods of single-crystal data analysis.^[24–27] Further, regarding the structure solution and refinement, we will refer to the best-quality dataset collected at about 134 GPa on the sample first synthesized at 123 GPa and 2700(200) K and then further pressurized.

Indexing revealed a body-centered orthorhombic unit cell with the lattice parameters $a = 3.4475(7)$, $b = 6.491(11)$, and $c = 6.048(3)$ Å, and the symmetry *Immm* (Table 1). The initial

Table 1: Selected experimental and theoretical crystal structure details of $\text{ReN}_{8.7(2)}\text{N}_2$.

Experiment:	
Chemical formula	$\text{ReN}_{8.7(2)}\text{N}_2$
Pressure [GPa]	134
Space group	<i>Immm</i>
a, b, c [Å]	3.4475(7), 6.491(11), 6.048(3)
V [Å ³]	135.4(3)
Z	2
No. of measured/independent reflections	356/165
R_{int}	0.0516
Final R indexes [$I > 2\sigma(I)$]	$R1 = 0.0681$, $wR2 = 0.1607$
Final R indexes [all data]	$R1 = 0.0748$, $wR2 = 0.1693$
No. of parameters	11
Fractional atomic coordinates (x, y, z) and U_{iso} [Å ²]:	
Re	(0,0,0)
U_{iso} (Re)	0.0176(7)
N1	(−0.320(3), 0.178(3), 0.1874(16))
U_{iso} (N1)	0.0163(17)
N2	(0.336(16), 0.5, 0)
U_{iso} (N2)	0.033(15)
Occupancy (N2)	0.7(2)
Calculations:	
Pressure [GPa]	126
a, b, c [Å]	3.488, 6.465, 6.07
V [Å ³]	135.34
Re	(0,0,0)
N1	(−0.32, 0.178, 0.188)
N2	(0.34, 0.5, 0)

structure solution suggested the chemical formula ReN_8 (Figure 1) and a structure in which Re atoms occupy the $2a$ (0,0,0) site and nitrogen atoms N1 occupy the site 16° (−0.320(3), 0.178(3), 0.1874(16)). Each Re atom is a member of two mutually perpendicular almost planar

Figure 1. a) Crystal structure of $\text{ReN}_{8.7(2)}\text{N}_2$ at 134 GPa. Re and N1 atoms form a framework with rectangular-shaped channels, which accommodate N2 atoms. N blue, Re gray. b) Fragment of the crystal structure showing the coordination of Re atoms. Here only Re and N1 atoms are shown. c) Atoms in the lattice plane (0 1 −1). Out-of-plane atoms are not shown.

ReN_8 spirocycles, lying in the planes (011) and (0−11) (Figures 1 a–c). Thus, eight nitrogen atoms, which coordinate each Re atom, form a slightly distorted cube. Nitrogen atoms are connected to each other forming infinite zigzag chains running along the a -axis. Re and N1 atoms form a framework containing square-shaped channels along the a -axis with a side length of about 4.76 Å (Figure 1 a). The size of the voids is sufficiently large to accommodate nitrogen molecules. Indeed, we could detect a residual electron density (6.3 e Å^{-3}) in the channels, which allows placing another nitrogen atom N2 at the partially occupied site $4f$ ($x, \frac{1}{2}, 0$). The refined N2–N2 distance of 1.1(1) Å corresponds to the triple $\text{N}\equiv\text{N}$ bond. We could refine the structure at 134 GPa with the resultant chemical composition $\text{ReN}_{8.7(2)}\text{N}_2$. Owing to the presence of heavy Re atoms and unavoidable XRD data incompleteness imposed by the design of DAC experiments, there is considerable uncertainty in the refined occupancy of the trapped N_2 molecule. However, the presence of N_2 molecules in the voids is supported by Raman spectroscopy data (Supporting Information, Figure S4).

Additionally, we performed ab initio calculations (see the Experimental Section for details) that are in good agreement with our experimental results. In particular, the crystal

structure and unit cell parameters of $ReN_8 \cdot xN_2$ were very well reproduced (Table 1). Simulations of the different occupancies for the nitrogen molecules in the channels have shown that the ReN_8 framework becomes unstable and heavily distorted upon compression if the channels are empty. Only those frameworks in which more than a half of the N_2 positions are occupied correspond to the experimentally determined structure and the unit cell volume (see also discussion below).

The geometry of the nitrogen chains and the interatomic distances provide information about the bonding in this compound. All of the N1 atoms have planar triangular coordination, suggesting sp^2 hybridization. The N1–N1 distances are 1.24(2) and 1.30(4) Å, which are intermediate between expected double- and single-bonded N–N units at this pressure.^[20,28]

Nitrogen chains in $ReN_8 \cdot xN_2$ are therefore described as polydiazenediyl $[-N=N-]_{\infty}$, which can be derived from the molecular nitrogen $N \equiv N$ monomer and, to a certain extent, is a nitrogen analogue of polyacetylene^[29] and polythiazyl $(SN)_x$ ^[30] (Figure 2a).

The coordination geometry of the ReN_8 network recalls metal tetrazadiene complexes with planar MN_4 metallacycles.^[31] Such compounds are successfully stabilized at ambient conditions by substituting hydrogen atoms of tetrazadiene with organic groups, whereas neither tetrazadiene nor its organic derivatives have been isolated. In the classical approach, the ligands are generated in situ from organic azides or diazonium cations, and, following the discovery of $Fe(MeNNNNMe)(CO)_3$ by Doedens,^[32] an extensive range of transition metal tetrazadiene complexes have been synthesized.^[31] There are several ways for a single tetrazadiene group to coordinate to a metal atom: η^4 ; N-1,N-4-bridging; and N-1,N-4 metallocyclic, which is the most common geometry.^[31] Owing to the delocalized π systems in such complexes, derivatives of tetrazadiene are non-innocent ligands with two canonical forms: tetrazene-1,4-diyl ($M^{(n+2)+}/RN^--N=N-N-R$) and tetrazadiene ($M^{n+}/RN=N-N-NR$). The distinction between these two forms is usually made based on crystallographic information about the N–N bond lengths. Similarly, two coordination geometries exist for $ReN_8 \cdot xN_2$ (I and II in Figure 2b). The main difference between them is, in fact, the *cis* or *trans* configuration of the polydiazenediyl chains. For the *cis* form (I), the $N_{\alpha}-N_{\beta}$ distances are expected to be longer than the $N_{\alpha}-N_{\alpha}$ and $N_{\beta}-N_{\beta}$ distances (see Figure 2b for the notation of N atoms). For compounds in the *trans* form (II), the reverse is expected, that is, the $N_{\alpha}-N_{\beta}$ distances should be shorter. In $ReN_8 \cdot xN_2$, $N_{\beta}-N_{\beta}$ and $N_{\alpha}-N_{\alpha}$ distances are slightly shorter than $N_{\alpha}-N_{\beta}$ (1.25(2) vs. 1.30(3) Å). The difference is not considerable because of the conjugation within the nitrogen chain with a preference for form I. The calculated charge density maps (Figure 2c) also show that there is only a very slight increase

Figure 2. a) The polydiazenediyl $[-N=N-]_{\infty}$ chain. b) Coordination of Re atoms by nitrogen atoms of one polydiazenediyl chain. c) Calculated charge density maps for nitrogen chains in the (011) plane. d) Nitrogen molecules in the (001) plane in $ReN_8 \cdot N_2$. e) Calculated electronic density of states for $ReN_8 \cdot N_2$. ($V = 135.3 \text{ \AA}^3$). f) Calculated phonon

in the electron density between $N_\alpha-N_\alpha$, $N_\beta-N_\beta$ compared to $N_\alpha-N_\beta$ bonds, therefore, the bonding picture is adequately described by Scheme III (Figure 2b). In the ionic consideration, each Re atom gives four of its seven valence electrons to four N_4 units. Thus, each N_4 unit accommodates 2 electrons and has 22 valence electrons in total: four N–N σ bond pairs (8e), four dative N→Re bonds (8e), and six π -delocalized electrons with an effective N–N bond order of 1.25. Re, therefore, should have a formal oxidation state +4. A delocalized π -system should give rise to metallic conductivity in $\text{ReN}_8 \cdot x\text{N}_2$, and this conclusion is supported by theoretical calculations (Figure 2e).

To the best of our knowledge, $\text{ReN}_8 \cdot x\text{N}_2$ is the first synthetic compound that contains polydiazenediyl chains. Chains of a similar type were recently predicted in CaN_4 ^[33] (η^4 -coordination together with metallocyclic coordination ■ ok? ■■■), MgN_4 ,^[18,34] HfN_{10} ,^[35] and in some hydrogen-nitrogen compounds.^[36] Interestingly, the structure of HfN_{10} as predicted^[35] is similar to the crystal structure of $\text{ReN}_8 \cdot x\text{N}_2$. Recently, we reported a novel compound FeN_4 containing polymeric nitrogen chains of a different type. These chains consist of sp^2 - and sp^3 -hybridized nitrogen atoms forming catena-poly[tetraz-1-ene-1,4-diyl] chains.^[37]

Next, we studied the compressional behavior of $\text{ReN}_8 \cdot x\text{N}_2$, which was first synthesized at 106 GPa (synthesis 1), and then gradually decompressed by releasing pressure in the diamond anvil cell. X-ray diffraction was measured at a few pressure points down to 22.5 GPa. Because of a substantial deterioration of the crystal quality below 90 GPa, we did not perform crystal structure refinements, but indexed the diffraction patterns and obtained the unit cell parameters. The pressure dependence of the unit cell volume of $\text{ReN}_8 \cdot x\text{N}_2$ (synthesis 1) could be described by the third-order Birch–Murnaghan equation of state with $V_0 = 179.9 \text{ \AA}^3$, $K_0 = 286(16) \text{ GPa}$, $K'_0 = 2.7(2)$. We could not preserve the sample below 22.5 GPa. However, this compound can potentially be recovered at ambient pressure. This possibility is predicted by the calculated phonon dispersions (Figure 2f), which show the dynamical stability of $\text{ReN}_8 \cdot \text{N}_2$ for the entire pressure range (from volume $138 \text{ \AA}^3$ to $180 \text{ \AA}^3$).

For $\text{ReN}_8 \cdot x\text{N}_2$ synthesized at 123 GPa (synthesis 2), the unit cell volumes are systematically larger than those of $\text{ReN}_8 \cdot x\text{N}_2$ synthesized in synthesis 1 ■ ok? ■■■ (Figure 3a). This might be related to the different amounts of nitrogen trapped in the channels. Indeed, the results of theoretical calculations (Figure 3b) show that the unit cell volume increases with the amount of nitrogen molecules inside the channels. Interestingly, the quantity of trapped nitrogen may also influence the mechanism of compression of $\text{ReN}_8 \cdot x\text{N}_2$. According to the theory (Figure 4), under compression, the channels, which are fully occupied, maintain their rectangular shape, but they tend to collapse with the negative linear compressibility of the b -axis, if the amount of N_2 is too small (Figure 4).

In summary, we have synthesized a novel rhenium-nitrogen compound with the highest amount of nitrogen in the Re–N system. Along with metal polyazides,^[38] $\text{ReN}_8 \cdot x\text{N}_2$ belongs to inorganic compounds with the highest nitrogen content known to date. The synthesis of $\text{ReN}_8 \cdot x\text{N}_2$ is a unique

Figure 3. Calculated (open symbols) and experimental pressure dependence (filled symbols) of the unit cell volume of $\text{ReN}_8 \cdot x\text{N}_2$.

Figure 4. Calculated structures of a) $\text{ReN}_8 \cdot \text{N}_2$ and b) ReN_8 (without trapped nitrogen molecules) having the same unit cell volume ($138 \text{ \AA}^3$).

example of the formation of a complex porous framework in a direct reaction between two elements, in which one of the reagents plays, in addition, the role of a guest molecule essential for the stability of the synthesized compound. These results contribute to the exploration of a large variety of polymeric nitrogen forms and of the role of the binding metal in chemical bonding between nitrogen atoms. A full understanding of these phenomena definitely requires further joint systematic efforts from the theoretical and experimental communities.

Experimental Section

Two series of experiments were performed. In both series, a powder of Re was placed inside a $60 \mu\text{m}$ hole in a Re gasket pre-indented to a thickness of approximately $22 \mu\text{m}$. The sample chamber was loaded with nitrogen, which served as a pressure-transmitting medium. We used BX90 diamond anvil cells equipped with Boehler-Almax type diamonds (culet diameter of $120 \mu\text{m}$). The first sample was compressed up to about 105 GPa and laser-heated up to 2300(200) K (synthesis 1), whereas the second sample was compressed up to about 123 GPa and then laser-heated up to 2700(150) K (synthesis 2).

The reaction products were studied by means of single-crystal X-ray diffraction on the synchrotron beamline P02.2 at DESY, Hamburg, Germany ($\lambda \approx 0.29 \text{ \AA}$, PerkinElmer XRD1621 flat panel detector).^[39] At each pressure step, we collected the X-ray diffraction images upon continuous rotation of the cell from -20° to $+20^\circ$ ω . At selected pressure points, we collected the data with a narrow 0.5° scanning step from -38° to $+38^\circ$ ω . We determined the pressure using

the equation of state of Re.^[40] Diffraction data analysis (peak search, unit cell finding, data integration, frame scaling) was performed with CrysAlis^{Pro} software. Detailed information about the treatment of the multigrain dataset is provided in the Supporting Information. The crystal structures were solved and refined against single-crystal diffraction data using computer programs JANA2006^[41] and OLEX2.^[42] Further details of the crystal structure investigation(s) may be obtained from FIZ Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, on quoting the deposition number CSD-434024).

The ab initio calculations were performed using the supercell technique and all electron projector-augmented-wave (PAW) method^[43] as implemented in the VASP code.^[44–46] We used the generalized gradient approximation with the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional.^[47] The simulations of ReN₈·xN₂ properties were carried out using 22-atom ($x=0$ and 1), 42-atom ($x=3/4$), and 64-atom periodic ($x=5/6$) cells. The sampling for Brillouin zone integrations was performed using the gamma scheme with $11 \times 11 \times 11$, $6 \times 12 \times 12$, and $4 \times 12 \times 12$ k-point grids for $x=0$ (and 1), $x=1/3$, $x=5/6$, respectively. The energy cutoff for the plane waves included in the expansion of wave functions was set to 700 eV. The convergence criterion for the electronic subsystem was chosen as 10^{-5} eV for two subsequent iterations, and the ionic relaxation loop within the conjugated gradient method was stopped when forces became of the order of 10^{-4} eV Å⁻¹. The 0 K harmonic phonon calculations were performed using the finite displacement approach implemented into PHONOPY.^[48] Converged phonon dispersions were achieved using a $(3 \times 3 \times 3)$ supercell with 297 atoms and $5 \times 5 \times 5$ Monkhorst-Pack^[49] k-point sampling.

Acknowledgements

Parts of this research were carried out at the beamline P02.2 at DESY, a member of the Helmholtz Association (HGF). N.D. thanks the German Research Foundation (Deutsche Forschungsgemeinschaft, DFG, projects no. DU 954-8/1 and DU 954-11/1) and the Federal Ministry of Education and Research, Germany (BMBF, grant no. 5K16WC1) for financial support. L.D. acknowledges DFG funding through projects the CarboPaT Research Unit FOR2125 and the Research Unit FOR 2440—Matter under Planetary Interior Conditions. Theoretical analysis of structural properties was supported by the Ministry of Education and Science of the Russian Federation (Grant No. 14.Y26.31.0005). Simulations of the electronic structure were supported by the Ministry of Education and Science of the Russian Federation in the framework of Increase Competitiveness Program of NUST “MISIS” (No K2-2017-080) implemented by a governmental decree dated 16 March 2013, No 211. Financial support from the Swedish Research Council (VR) through Grant No. 2015-04391, the Swedish Government Strategic Research Area in Materials Science on Functional Materials at Linköping University (Faculty Grant SFOMatLiU No. 2009 00971), and the VINN Excellence Center *Functional Nanoscale Materials* (FunMat-2) Grant 2016–05156 is gratefully acknowledged.

Conflict of interest

The authors declare no conflict of interest.

Keywords: high-energy-density materials · high-pressure chemistry · nitrides · polymeric nitrogen · X-ray diffraction

- [1] A. Friedrich, B. Winkler, L. Bayarjargal, W. Morgenroth, E. A. Juarez-Arellano, V. Milman, K. Refson, M. Kunz, K. Chen, *Phys. Rev. Lett.* **2010**, *105*, 251910.
- [2] H. Hahn, A. Konrad, *Z. Anorg. Allg. Chem.* **1951**, *264*, 174–180.
- [3] Z. Zhao, K. Bao, D. Li, D. Duan, F. Tian, X. Jin, C. Chen, X. Huang, B. Liu, T. Cui, *Sci. Rep.* **2014**, *4*, 4797.
- [4] F. Kawamura, H. Yusa, T. Taniguchi, *Appl. Phys. Lett.* **2012**, *100*, 2–5.
- [5] Y. Wang, T. Yao, J.-L. Yao, J. Zhang, H. Gou, *Phys. Chem. Chem. Phys.* **2013**, *15*, 183–187.
- [6] S. K. R. Patil, N. S. Mangale, S. V. Khare, S. Marsillac, *Thin Solid Films* **2008**, *517*, 824–827.
- [7] G. Soto, *Comput. Mater. Sci.* **2012**, *61*, 1–5.
- [8] P. Kroll, *Key Eng. Mater.* **2009**, *403*, 77–80.
- [9] J. Zhou, Z. Sun, R. Ahuja, *J. Alloys Compd.* **2009**, *472*, 425–428.
- [10] I. R. Shein, A. N. Enyashin, A. L. Ivanovskii, *Phys. Solid State* **2013**, *55*, 1821–1825.
- [11] X. P. Du, Y. X. Wang, V. C. Lo, *Phys. Lett. A* **2010**, *374*, 2569–2574.
- [12] E. Zhao, Z. Wu, *Comput. Mater. Sci.* **2008**, *44*, 531–535.
- [13] H. Yan, M. Zhang, Q. Wei, P. Guo, *J. Alloys Compd.* **2013**, *581*, 508–514.
- [14] Y. Li, Z. Zeng, *Chem. Phys. Lett.* **2009**, *474*, 93–96.
- [15] G. Soto, H. Tiznado, W. de la Cruz, A. Reyes, *J. Mater.* **2014**, *2014*, 1–9.
- [16] S. Aydin, Y. O. Ciftci, A. Tatar, *J. Mater. Res.* **2012**, *27*, 1705–1715.
- [17] W.-J. Zhao, H.-B. Xu, Y.-X. Wang, *Chin. Phys. B* **2010**, *19*, 16201.
- [18] S. Yu, B. Huang, Q. Zeng, A. R. Oganov, L. Zhang, G. Frapper, *J. Phys. Chem. C* **2017**, *121*, 11037–11046.
- [19] A. G. Kvashnin, A. R. Oganov, A. I. Samtsevich, Z. Allahyari, *J. Phys. Chem. Lett.* **2017**, *8*, 755–764.
- [20] M. I. Erements, A. G. Gavriluk, I. A. Trojan, D. A. Dzivenko, R. Boehler, *Nat. Mater.* **2004**, *3*, 558–563.
- [21] D. Tomasino, M. Kim, J. Smith, C. S. Yoo, *Phys. Rev. Lett.* **2014**, *113*, 1–5.
- [22] W. Zhang, A. R. Oganov, A. F. Goncharov, Q. Zhu, S. E. Boulfelfel, A. O. Lyakhov, E. Stavrou, M. Somayazulu, V. B. Prakapenka, Z. Konopkova, *Science* **2013**, *342*, 1502–1505.
- [23] A. Dewaele, N. Worth, C. J. Pickard, R. J. Needs, S. Pascarelli, O. Mathon, M. Mezouar, T. Irifune, *Nat. Chem.* **2016**, *8*, 784–790.
- [24] E. Bykova, *Single-Crystal X-Ray Diffraction at Extreme Conditions in Mineral Physics and Material Sciences*, University of Bayreuth, **2015**.
- [25] V. Cerantola, E. Bykova, I. Kuppenko, M. Merlini, L. Ismailova, C. McCammon, M. Bykov, A. I. Chumakov, S. Petitgirard, I. Kantor, et al., *Nat. Commun.* **2017**, *8*, 15960.
- [26] B. Lavina, Y. Meng, *Sci. Adv.* **2015**, *1*, e1400260.
- [27] E. Bykova, L. Dubrovinsky, N. Dubrovinskaya, M. Bykov, C. McCammon, S. V. V. Ovsyannikov, H.-P.-P. Liermann, I. Kuppenko, A. I. Chumakov, R. Rüffer, et al., *Nat. Commun.* **2016**, *7*, 10661.
- [28] G. V. Vajenine, G. Auffermann, Y. Prots, W. Schnelle, R. K. Kremer, A. Simon, R. Kniep, *Inorg. Chem.* **2001**, *40*, 4866–4870.
- [29] A. J. Heeger, *Rev. Mod. Phys.* **2001**, *73*, 681–700.
- [30] M. M. Labes, P. Love, L. F. Nichols, *Chem. Rev.* **1979**, *79*, 1–15.
- [31] D. S. Moore, S. D. Robinson, *Adv. Inorg. Chem.* **1986**, *30*, 1–68.
- [32] R. J. Doedens, *Chem. Commun.* **1968**, 1271–1272.
- [33] S. Zhu, F. Peng, H. Liu, A. Majumdar, T. Gao, Y. Yao, *Inorg. Chem.* **2016**, *55*, 7550–7555.

- [34] S. Wei, D. Li, Z. Liu, X. Li, F. Tian, D. Duan, B. Liu, T. Cui, *Phys. Chem. Chem. Phys.* **2017**, *19*, 9246–9252.
- [35] J. Zhang, A. R. Oganov, X. Li, H. Niu, *Phys. Rev. B* **2017**, *95*, 20103.
- [36] G.-R. Qian, H. Niu, C.-H. Hu, A. R. Oganov, Q. Zeng, H.-Y. Zhou, *Sci. Rep.* **2016**, *6*, 25947.
- [37] M. Bykov, E. Bykova, G. Aprilis, K. Glazyrin, E. Koemets, I. Chuvashova, I. Kuppenko, C. McCammon, M. Mezouar, V. Prakapenka, et al., *Nat. Commun.* **2018**. ■ ■ citation incomplete: DOI? ■ ■
- [38] R. Haiges, J. a. Boatz, R. Bau, S. Schneider, T. Schroer, M. Yousufuddin, K. O. Christe, *Angew. Chem. Int. Ed.* **2005**, *44*, 1860–1865; *Angew. Chem.* **2005**, *117*, 1894–1899.
- [39] H.-P. Liermann, Z. Konôpková, W. Morgenroth, K. Glazyrin, J. Bednarčík, E. E. McBride, S. Petitgirard, J. T. Delitz, M. Wendt, Y. Bican, et al., *J. Synchrotron Radiat.* **2015**, *22*, 908–924.
- [40] C. S. Zha, W. A. Bassett, S. H. Shim, *Rev. Sci. Instrum.* **2004**, *75*, 2409–2418.
- [41] V. Petricek, M. Dusek, L. Palatinus, *Z. Kristallogr.* **2014**, *229*, 345–352.
- [42] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339–341.
- [43] P. E. Blöchl, *Phys. Rev. B* **1994**, *50*, 17953–17979.
- [44] G. Kresse, J. Furthmüller, *Comput. Mater. Sci.* **1996**, *6*, 15–50.
- [45] G. Kresse, J. Furthmüller, *Phys. Rev. B* **1996**, *54*, 11169–11186.
- [46] G. Kresse, D. Joubert, *Phys. Rev. B* **1999**, *59*, 1758–1775.
- [47] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.
- [48] A. Togo, I. Tanaka, *Scr. Mater.* **2015**, *108*, 1–5.
- [49] H. J. Monkhorst, J. D. Pack, *Phys. Rev. B* **1976**, *13*, 5188–5192.

Manuscript received: May 3, 2018

Accepted manuscript online: May 18, 2018

Version of record online: ■ ■ ■ ■, ■ ■ ■ ■

Communications

Nitride Compounds

M. Bykov,* E. Bykova, E. Koemets,
T. Fedotenko, G. Aprilis, K. Glazyrin,
H.-P. Liermann, A. V. Ponomareva,
J. Tidholm, F. Tasnádi, I. A. Abrikosov,
N. Dubrovinskaia,
L. Dubrovinsky ———— ■■■■-■■■■

High-Pressure Synthesis of a Nitrogen-
Rich Inclusion Compound $\text{ReN}_8 \cdot x\text{N}_2$ with
Conjugated Polymeric Nitrogen Chains

A nitrogen-rich compound, $\text{ReN}_8 \cdot x\text{N}_2$, was synthesized by a direct reaction between rhenium and nitrogen at high pressure and temperature. The crystal structure has rectangular-shaped channels that accommodate nitrogen molecules. The amount of trapped nitrogen (x) depends on the synthesis conditions. The polydiazenediyl chains $[-\text{N}=\text{N}-]_\infty$ that constitute the framework have not been previously observed in any compound. ■
■ ok? ■ ■

Nitride

M. Bykov,* E. Bykova, E. Koemets,
T. Fedotenko, G. Aprilis, K. Glazyrin,
H.-P. Liermann, A. V. Ponomareva,
J. Tidholm, F. Tasnádi, I. A. Abrikosov,
N. Dubrovinskaia,
L. Dubrovinsky ———— ■■■■-■■■■

High-Pressure Synthesis of a Nitrogen-
Rich Inclusion Compound $\text{ReN}_8 \cdot x\text{N}_2$ with
Conjugated Polymeric Nitrogen Chains

Die stickstoffreiche Substanz $\text{ReN}_8 \cdot x\text{N}_2$ wurde durch direkte Umsetzung von Rhenium mit Stickstoff bei hohen Drücken und Temperaturen synthetisiert. Die Kristallstruktur zeigt rechteckige Kanäle, in denen variable Mengen an Stickstoffmolekülen eingelagert sind; x hängt von den Synthesebedingungen ab. Die das Gerüst bildenden Polydiazendiyl-Ketten $[-\text{N}=\text{N}-]_\infty$ wurden bislang noch nicht beschrieben.

Please check that the ORCID identifiers listed below are correct. We encourage all authors to provide an ORCID identifier for each coauthor. ORCID is a registry that provides researchers with a unique digital identifier. Some funding agencies recommend or even require the inclusion of ORCID IDs in all published articles, and authors should consult their funding agency guidelines for details. Registration is easy and free; for further information, see <http://orcid.org/>.

Dr. Maxim Bykov <http://orcid.org/0000-0003-0248-1728>

Dr. Elena Bykova

Egor Koemets

Timofey Fedotenko

Georgios Aprilis

Dr. Konstantin Glazyrin

Dr. Hanns-Peter Liermann

Dr. Alena V. Ponomareva

Johan Tidholm

Dr. Ferenc Tasnádi

Prof. Dr. Igor A. Abrikosov

Prof. Dr. Natalia Dubrovinskaia

Prof. Dr. Leonid Dubrovinsky