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High-pressure synthesis of a nitrogen-rich inclusion compound $\text{ReN}_8 \cdot x\text{N}_2$ with conjugated polymeric nitrogen chains

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Abstract: A novel nitrogen-rich compound $\text{ReN}_8 \cdot x\text{N}_2$ was synthesized in 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 the crystal structure, which is based on the ReN_8 framework having rectangular-shaped channels, which accommodate nitrogen molecules. Thus, despite the 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 $[-\text{N}=\text{N}-]_n$, which constitute the framework, have not been previously observed in any compound. *Ab-initio* calculations carried out for $\text{ReN}_8 \cdot x\text{N}_2$ provide strong support to the experimental results and conclusions.

Rhenium-nitrogen compounds are widely studied due to 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 equal to 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 both experimental and theoretical research has been invested into the search for nitrogen-rich rhenium-nitrogen compounds.

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 ~ 2000 K ($P6_3/mmc$, $a = 2.83(5)$, $c = 9.88(1)$ Å). Both of the compounds have exceptionally large bulk moduli exceeding 400 GPa.^[1]

Recently, Kawamura *et al.*^[4] have obtained ReN_2 in the solid-state high-pressure reaction between ReCl_5 and Li_3N ,^[4] and claimed it to have the MoS_2 structure type based on structure refinements using 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 works, 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 $Pmnm$ ^[12] symmetries were considered, but have not been confirmed experimentally.

Hitherto, ReN_3 with the orthorhombic symmetry $Ama2$ is a compound with the highest nitrogen content known 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, which can have similar (ReN_3 ($Imm2$)^[3]) or even higher nitrogen content, ReN_4 ($Pbca$,^[16,17] $Cmmm$ ^[17]). Nitrogen-rich compounds in metal-nitrogen systems are considered as potentially perspective high-energy density materials.^[18–21]

Obviously 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 for building a reference basis for further theoretical and experimental works. In comparison to currently, most abundant high-pressure *powder* XRD studies, single-crystal XRD in diamond anvil cells allows not only an unequivocal structure solution, but also gives 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 have 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.

$\text{ReN}_8 \cdot x\text{N}_2$ 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 and 123 GPa), and then laser heated (to 2300(200) K and 2700(200) K), in one and another experiment, respectively). Nitrogen served simultaneously as a reagent and a pressure-transmitting medium (see Experimental Section for details). Although the initial reagents were powders, the chemical reaction led to the formation of numerous good-

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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 the single-crystal data analysis.^[24–27] Further, regarding the structure solution and refinement, we will refer to the best-quality dataset collected at ~134 GPa on the sample first synthesized at 123 GPa and 2700(200)K and then further pressurized.

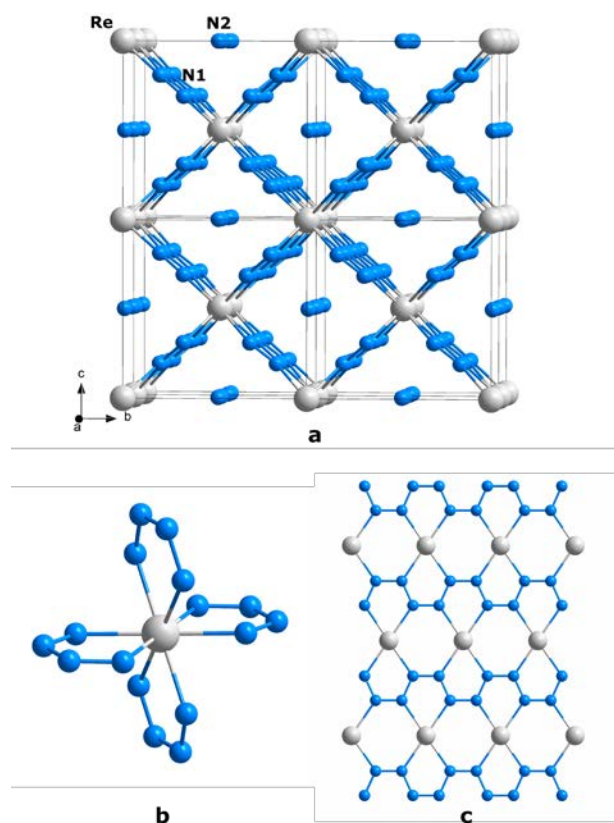


Figure 1. (a) Crystal structure of ReN₈·xN₂ at 134 GPa. Re and N1 atoms form a framework with rectangular-shaped channels, which accommodate N2 atoms. Blue and grey balls represent nitrogen and rhenium atoms, respectively. (b) Fragment of the crystal structure showing the coordination of Re atoms. Here only Re and N1 atoms are shown. (c) atoms in the lattice plane (0 1 -1). Out-of plane atoms are not shown.

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). Initial structure solution suggested the chemical formula ReN₈ (Figure 1) and the structure, in which Re atoms occupy the 2a (0,0,0) site, and nitrogen atoms N1 – the site 16o (-0.320(3), 0.178(3), 0.1874(16)). Each Re atom is a member of two mutually perpendicular almost planar ReN₈ spirocycles, laying in the planes (011) and (0-11) (Figure 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 the side length of ~4.76 Å (Figure 1a). The size of the voids is sufficiently large to accommodate nitrogen molecules. Indeed, we indeed could detect a residual electron density (6.3 e/Å³) 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 N≡N bond. We could refine the structure at 134 GPa with the resultant chemical composition ReN₈·0.7(2)N₂. It should be noticed that due to the

presence of heavy Re atoms and unavoidable XRD data incompleteness imposed by design of DAC experiments, there is a considerable uncertainty in the refined occupancy of the trapped N₂ molecule.

Additionally, we have performed *ab initio* calculations (see Experimental Section for details), which are in good agreement with our experimental results. In particular, the crystal structure, and the unit cell parameters of ReN₈·xN₂ were very well reproduced (Table 1). Simulations of the different occupancies for the nitrogen molecules in the channels have shown that the ReN₈ framework becomes unstable and heavily distorted on compression, if the channels are empty. Only those frameworks, in which more than a half of the N2 positions are occupied, correspond to the experimentally determined structure and the unit cell volume (see also discussion below).

Table 1. Selected experimental and theoretical crystal structure details of ReN₈·xN₂.

Experiment:	
Chemical formula	ReN ₈ ·0.7(2)N ₂
Pressure, GPa	134
Space group	<i>Immm</i>
<i>a, b, c</i> , Å	3.4475(7), 6.491(11), 6.048(3)
<i>V</i> , Å ³	135.4(3)
<i>Z</i>	2
No. of measured / independent reflections	356, 165
<i>R</i> _{int}	0.0516
Final <i>R</i> indexes [$ \geq 2\sigma(I)$]	<i>R</i> ₁ = 0.0681, <i>wR</i> ₂ = 0.1607
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0748, <i>wR</i> ₂ = 0.1693
No. of parameters	11
<i>Fractional atomic coordinates (x,y,z) and U_{iso} (Å²)</i>	
Re	(0,0,0)
<i>U_{iso}</i> (Re)	0.0176(7)
N1	(-0.320(3), 0.178(3), 0.1874(16))
<i>U_{iso}</i> (N1)	0.0163(17)
N2	(0.336(16), 0.5, 0)
<i>U_{iso}</i> (N2)	0.033(15)
Occupancy (N2)	0.7(2)
Calculations:	
Pressure, GPa	126
<i>a, b, c</i> , Å	3.488, 6.465, 6.07
<i>V</i> , Å ³	135.34
Re	(0,0,0)
N1	(-0.32, 0.178, 0.188)
N2	(0.34,0.5,0)

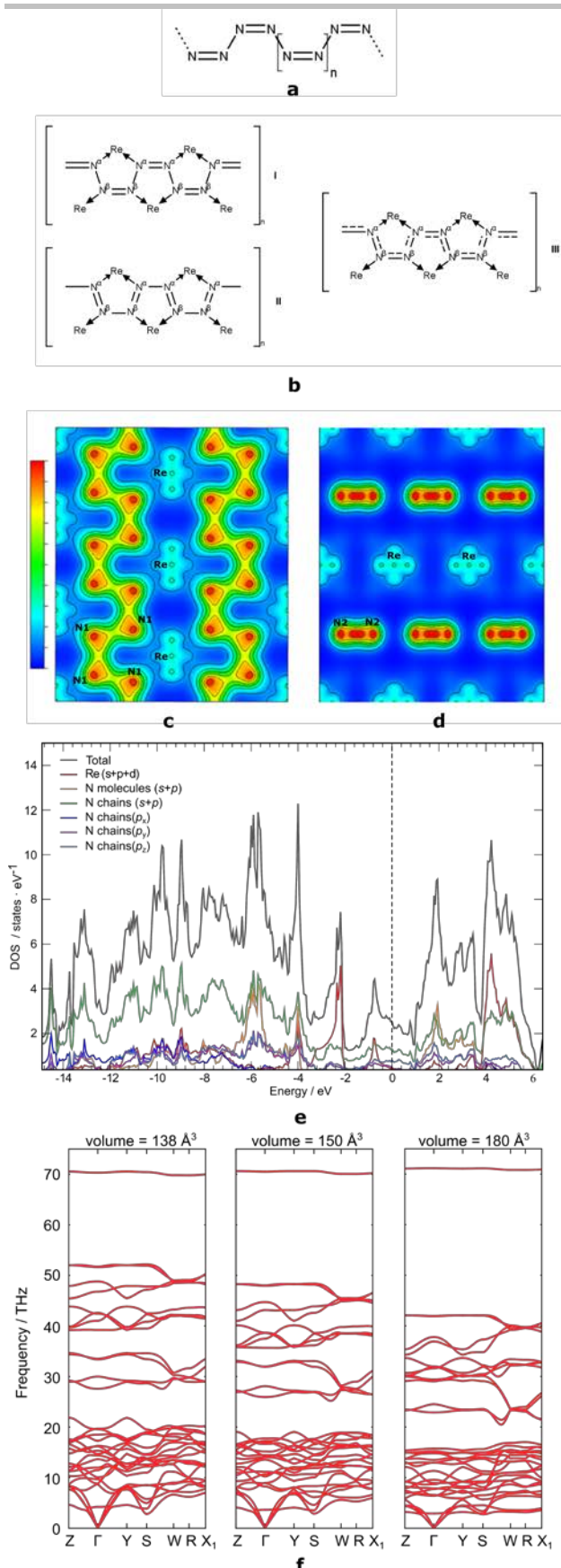


Figure 2. (a) Scheme of the polydiazenediyl $[-N=N-]_{\infty}$ chain; (b) coordination of Re atoms by nitrogen atoms of one polydiazenediyl chain. (c) Calculated charge density maps for nitrogen chains in the (011) plane; and (d) nitrogen molecules in the (001) plane in $ReN_8 \cdot N_2$ (e) Calculated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

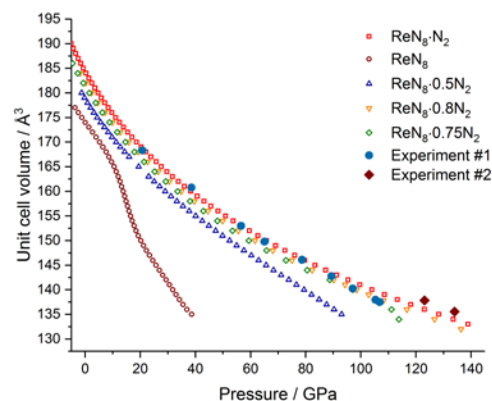


Figure 3. Calculated (open symbols) and experimental (filled symbols) pressure dependence of the unit cell volume of $ReN_8 \cdot xN_2$.

Geometry of the nitrogen chains and interatomic distances provide us information about the bonding scheme in this compound. All N1 atoms have planar triangular coordination suggesting their sp^2 hybridization. The N1-N1 distances have lengths of 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 in accord with the description 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).

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, while neither tetrazadiene itself nor its organic derivatives have ever been isolated. In the classical approach, the ligands can be 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 how a single tetrazadiene group can coordinate a metal atom: η^4 ; N-1,N-4-bridging; and N-1,N-4 metalocyclic, which is the most common.^[31] Due 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 the crystallographic information about the N-N bond lengths. Similarly, two ways of coordination exist for $ReN_8 \cdot xN_2$ (I and II in Figure 2b). The main difference between them is, in fact, *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, i.e., 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 the form I. The calculated charge density maps (Figure 2c) also show that there is only a very slight increase in

the electron density between N_{α} - N_{α} , N_{β} - N_{β} compared to N_{α} - N_{β} bonds, therefore, the bonding picture could be adequately described by the scheme III (Figure 2b). In the ionic consideration, each Re atom gives four out 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 $N \rightarrow Re$ 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. Delocalized π -system should give rise to the metallic conductivity of $ReN_8 \cdot xN_2$, and this conclusion is also supported by theoretical calculations (Figure 2e). Metallic nature of the compound makes Raman spectroscopy, which is often employed for the analysis of N-N bonding in nitrides, not useful here.

To the best of our knowledge, $ReN_8 \cdot xN_2$ is the first synthetic compound, which contains polydiazenediyl chains. Chains of the similar type were recently predicted in CaN_4 ^[33] (η^4 -coordination together with metallocyclic one), 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 $ReN_8 \cdot xN_2$. Recently we reported a novel compound FeN_4 containing polymeric nitrogen chains of a different type. These chains consist of both sp^2 and sp^3 - hybridized nitrogen atoms forming catena-poly[tetraz-1-ene-1,4-diyl] chains.^[37]

Next, we have also studied the compressional behavior of $ReN_8 \cdot xN_2$, 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 $ReN_8 \cdot xN_2$ (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, potentially this compound could be recovered at ambient pressure. This argument is predicted by the calculated phonon dispersions (Figure 2f), which show dynamical stability of $ReN_8 \cdot N_2$ for the entire pressure range (from volume 138 \AA^3 to 180 \AA^3).

It should be mentioned that for $ReN_8 \cdot xN_2$ synthesized at 123 GPa (synthesis #2), the unit cell volumes are systematically larger than those of $ReN_8 \cdot xN_2$ synthesized in experiment #1 (Figure 3a). This might be related to the different amount of nitrogen trapped in the channels. Indeed, the results of theoretical calculations (Figure 3b) show that the unit cell volume increases with the increase of the amount of nitrogen molecules inside the channels. Interestingly, the quantity of trapped nitrogen may also influence the mechanism of compression of $ReN_8 \cdot xN_2$. 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, in this work we have synthesized a novel rhenium-nitrogen compound, in which the amount of nitrogen is highest in the Re-N system. Along with metal polyazides^[38], $ReN_8 \cdot xN_2$ belongs to inorganic compounds with the highest nitrogen content known so far. The synthesis of $ReN_8 \cdot xN_2$ is a unique example of a formation of a complex porous framework in a direct reaction between two elements, in which one of the

reagents plays, in addition, a role of a guest molecule essential for the stability of the synthesized compound. These results contribute to the exploration of large variety of polymeric nitrogen forms and of the role of the binding metal in chemical bonding between nitrogen atoms. Full understanding of these phenomena definitely require further joint systematic efforts from the theoretical and experimental communities.

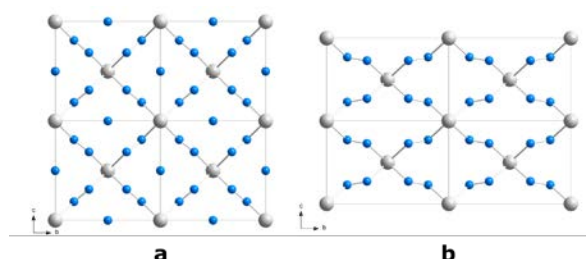


Figure 4. Calculated structures of $ReN_8 \cdot N_2$ (a) and ReN_8 (without trapped nitrogen molecules) (b) having the same unit cell volume (138 \AA^3).

Experimental Section

Synthesis

We have performed two series of experiments. In both of them a powder of Re was placed inside a $60 \mu\text{m}$ hole in a Re gasket, preindented to the thickness of about $22 \mu\text{m}$. 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 $\sim 105 \text{ GPa}$ and laser-heated up to $2300(200) \text{ K}$ (synthesis #1), while the second sample was compressed up to $\sim 123 \text{ GPa}$ and then laser-heated up to $2700(150) \text{ K}$ (synthesis #2).

X-ray diffraction studies

The reaction products were studied by means of single-crystal X-ray diffraction on the synchrotron beamline P02.2 at DESY, Hamburg, Germany ($\lambda \sim 0.29 \text{ \AA}$, Perkin Elmer 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 in the range from -38° to $+38^\circ$ ω . We determined pressure using the equations of state of Re.^[40] Diffraction data analysis (peak search, unit cell finding, data integration, frame scaling etc.) was performed with CrysAlis^{Pro} software. Detailed information about the treatment of the multigrain dataset is provided in the supplementary 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).

Calculations

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 $ReN_8 \cdot xN_2$ properties were carried out using 22-atoms ($x=0$ and 1), 42-atoms ($x=3/4$) and 64-atoms periodic ($x=5/6$) cells. The sampling for Brillouin zone integrations is 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 to be equal to 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. The 0 K harmonic phonon calculations were done using the finite displacement approach implemented into the PHONOPY.^[48] Converged phonon dispersions were achieved using a (3x3x3) supercell with 297 atoms and 5x5x5 Monkhorst-Pack^[49] k-point sampling.

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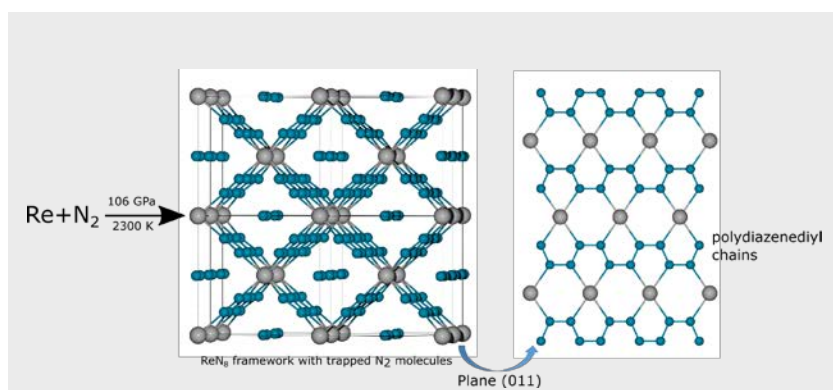
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Entry for the Table of Contents

COMMUNICATION



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High-pressure synthesis of a nitrogen-rich inclusion compound ReN₈·xN₂ with conjugated polymeric nitrogen chains