Thermodynamic and electronic properties of ReN$_2$ polymorphs at high pressure

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The high-pressure synthesis of rhenium nitride pernitride with a crystal structure that is unusual for transition metal dinitrides and high values of hardness and bulk modulus attracted significant attention to this system. We investigate the thermodynamic and electronic properties of the $P2_1/c$ phase of ReN$_2$ and compare them with two other polytypes, the $C2/m$ and $P4/mmm$ phases, suggested in the literature. Our calculations of the formation enthalpy at zero temperature show that the former phase is the most stable of the three up to a pressure $p = 170$ GPa, followed by the stabilization of the $P4/mmm$ phase at higher pressure. The theoretical prediction is confirmed by diamond anvil cell synthesis of the $P4/mmm$ ReN$_2$ at $\approx 175$ GPa. Considering the effects of finite temperature in the quasiharmonic approximation at $p = 100$ GPa we demonstrate that the $P2_1/c$ phase has the lowest free energy of formation at least up to 1000 K. Our analysis of the pressure dependence of the electronic structure of rhenium nitride pernitride shows the presence of two electronic topological transitions around 18 GPa, when the Fermi surface changes its topology due to the appearance of an electron pocket at the high-symmetry $Y_2$ point of the Brillouin zone while the disruption of the neck takes place slightly off from the $\Gamma$-$A$ line.

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I. INTRODUCTION

The high-pressure diamond anvil cell (DAC) experiment is a successful approach to establish a wide variety of physical conditions for synthesizing materials [1–3]. However, exploring metastable phases of materials is a challenging experimental task because one has to achieve control of the small free-energy barriers separating different polymorphs. On the other hand, computational high-throughput approaches [4,5] with sophisticated structure prediction algorithms [6,7] have entered into the field to advance the materials discoveries. The launch of the Materials Genome Initiative (MGI) [8] has further accelerated this trend [9,10] and triggered the discovery of novel materials with attractive properties is to quench them to ambient conditions. The work by Bykov et al. [19] has shown that the ReN$_2$ compound in the monoclinic $P2_1/c$ phase discovered in a DAC experiment can be also synthesized in a larger amount in a large-volume press at lower pressure. This compound has a crystal structure that is unusual for transition metal dinitrides MN$_2$. It contains covalently bound dinitrogen dumbbells and discrete nitrogen atoms and represents an example of a mixed nitride-pernitride compound. Quenched to ambient pressure, rhenium nitride pernitride showed high mechanical properties, a hardness of 36.7(8) GPa, and a very high value of the bulk moduli of 428(10) GPa. The $P2_1/c$ phase was not reported in earlier experiments. Remarkably, despite numerous theoretical studies...
of the Re-N system at this composition, it was not predicted theoretically even with the use of advanced structure prediction algorithms.

Kawamura et al. [20] have reported the synthesis of ReN$_2$ at 7.7 GPa and 1473–1873 K, with a hexagonal P6$_3$/mmc (MoS$_2$ type) structure. Elastic and mechanical properties of the phase have been investigated using $T = 0$ K density functional theory (DFT) calculations [21]. In the same year, Du et al. [22], based on DFT calculations, proposed the tetragonal P4/mmmm phase of ReN$_2$ underlined by the existence of the same phase for ReB$_2$ [23]. However, static 0 K DFT calculations by Wang et al. [24] have ruled out the P4/mmmm phase as the ground state of ReN$_2$. Instead, the calculations have indicated that the monoclinic C2/m structure of ReN$_2$ is more stable at 0 K than the experimentally found P6$_3$/mmc phase. Furthermore, it has been shown that above 130 GPa the P4/mmmm phase becomes the favored phase. A computational structural search for stable and metastable rhenium nitrides up to 100 GPa pressures has been conducted [25] using a sophisticated evolutionary algorithm implemented in USPEX [6]. The study has confirmed the C2/m phase of ReN$_2$ as the ground state between 10 and 100 GPa. The P4/mmmm, Pbcm, and P6$_3$/mmc phases have been found to be metastable in the investigated pressure range.

In the present paper we investigate the thermodynamic stability of the P2$_1$/c phase with respect to the competing tetragonal P4/mmmm and C2/m monoclinic phases in the pressure range between 0 and 180 GPa. We use first-principles electronic structure calculations and a quasiharmonic approximation for the lattice dynamics and establish that the former is indeed thermodynamically more stable than the two other polymorphs at pressures up to $\approx 170$ GPa. At higher pressures the calculations predict the stabilization of the P4/mmmm phase. As this phase was not reported in earlier experiments, we carry out the high-pressure synthesis of ReN$_2$ in a diamond anvil cell at $\approx 175$ GPa. The theoretical prediction is verified by a characterization of the synthesized sample, which confirms the stabilization of the P4/mmmm ReN$_2$. Moreover, we calculate electronic properties of the P2$_1$/c phase and show the presence of two electronic topological transitions at $\approx 18$ GPa.

TABLE I. The size of the structural models and the applied sampling of the Brillouin zone to calculate formation enthalpy and the phonon dispersions.

| Structure  | Supercell | k-point mesh | Supercell | k-point mesh |
|------------|-----------|--------------|-----------|--------------|
| cg-N       | (1 x 1 x 1) | (23 x 23 x 23) | (4 x 4 x 4) | (5 x 5 x 5) |
| hcp Re     | (1 x 1 x 1) | (15 x 15 x 15) | (5 x 5 x 5) | (5 x 5 x 5) |
| P4/mmmm ReN$_2$ | (1 x 1 x 1) | (19 x 19 x 19) | (3 x 3 x 3) | (5 x 5 x 5) |
| C2/m ReN$_2$ | (1 x 1 x 1) | (9 x 21 x 7) | (4 x 4 x 2) | (5 x 5 x 5) |
| P2$_1$/c ReN$_2$ | (1 x 1 x 1) | (24 x 14 x 18) | (3 x 2 x 3) | (3 x 3 x 3) |

DENSITY. Fermi surfaces have been calculated and visualized using XCRYSDEN [30] and VESTA [31]. The free energies of formation have been calculated within the quasiharmonic approximation using PHONOPY [32] combined with force calculations performed with VASP [33–36]. In all VASP calculations the energy cutoff was set to 700 eV. Table I lists the supercell sizes and the applied sampling of the Brillouin zone in the VASP calculations. To underline the agreement of our simulations by QE and VASP, we have compared the stress tensor elements of the three different phases at around 100 GPa with unrelaxed atomic positions in the unit cells using the supercell sizes and k-point samplings from Table I. The deviations are less than 4 GPa. The largest error, $\Delta\%$, has been observed for $\sigma_{yy}$ in the case of comparing the P2$_1$/c and C2/m phases. In the enthalpy calculations the hcp phase of rhenium [37] and the cubic gauche phase of nitrogen (which is stable up to $\approx 150$ GPa) have been used as the end-member states [38].

III. EXPERIMENTS

A piece of Re metal was placed in a sample chamber of a BX90 diamond anvil cell [39] equipped with Boehler-Almax type diamonds (40-μm culet diameters). Nitrogen served as a pressure-transmitting medium and as a reagent [40]. The DAC was compressed up to a target pressure of $\approx 175$ GPa and laser heated using double-sided laser-heating systems installed at the Bayerisches Geoinstitut (BGI, Bayreuth, Germany) [41]. The sample was studied by means of powder and single-crystal x-ray diffraction at the synchrotron beamline ID11 of the ESRF using a monochromatic x-ray beam focused to $\approx 0.3 \times 0.3 \mu m^2$. For the single-crystal XRD measurements the sample was rotated around the vertical $\omega$ axis in a range $\pm 38^\circ$. The diffraction images were collected with an angular step $\Delta\omega = 0.5^\circ$ and an exposure time of 10 s/frame. For analysis of the single-crystal diffraction data (indexing, data integration, frame scaling, and absorption correction) we used the CRYSTALISPRO software package. To calibrate an instrumental model in the CRYSTALISPRO software, i.e., the sample-to-detector distance, detector origin, offsets of goniometer angles, and rotation of both the x-ray beam and the detector around the instrument axis, we used a single crystal of orthoenstatite (Mg$_{91.93}$Fe$_{0.06}$Si$_{93.93}$Al$_{0.05}$)O$_{16}$, Pnca space group, $a = 8.8117(2)$, $b = 5.1832(10)$, and $c = 18.2391(3)$ Å. The structure was solved based on the single-crystal XRD data using the SHELXT structure solution program [42] by intrinsic phasing and refined using the OLEX2 program [43]. Pressure was determined based on the equation of state of
TABLE II. Space group numbers and the lattice parameters of the investigated ReN\textsubscript{2} phases at $T = 0$ K and $p = 0$ GPa.

| Structure | Space group | Lattice parameters (Å) |
|-----------|-------------|------------------------|
| $P_{21}/c$ | 14 (monoclinic) | $a = 3.630$, $b = 6.432$, $c = 4.977$, $\beta = 111.511^\circ$ |
| $C_{2m}$ | 12 (monoclinic) | $a = 6.800$, $b = 2.824$, $c = 9.336$, $\beta = 142.35^\circ$ |
| $P_{4}/mbm$ | 127 (tetragonal) | $a = b = 4.376$, $c = 2.650$ |

Re. The refined unit cell volume of Re, 22.50(4) Å, may correspond to pressures of 172.5 GPa \[37\], 177 GPa \[44\], or even 206 GPa \[45\].

IV. RESULTS

Figure 1 shows three polymorphs of ReN\textsubscript{2} considered in this study: $P_{21}/c$, $C_{2m}$, and $P_{4}/mbm$. The large sized spheres represent the rhenium atoms, while the small ones the nitrogen atoms or dumbbells. The discrete nitrogen atoms are denoted by N\textsubscript{1}. If a nitrogen atom binds to another one and they form a dumbbell, then both nitrogen atoms are labeled by N\textsubscript{2}. The $P_{4}/mbm$ structure contains only nitrogen dumbbells, while the two monoclinic structures have both types of nitrogen. Table II summarizes the optimized structural parameters obtained at $T = 0$ K and $p = 0$ GPa.

In Fig. 2(a) we present the calculated formation enthalpy differences ($\Delta H$) for the $P_{21}/c$ and $P_{4}/mbm$ phases in the pressure interval from 0 to 180 GPa relative to the values obtained for the $C_{2m}$ phase. The relevance of spin-orbit coupling (SOC) effects on the formation energy differences between the $P_{21}/c$ and $C_{2m}$ phases at 0 GPa can be ruled out by the electronic band structures calculated without SOC—see Materials Project \[12\] IDs mp-1077354 and mp-1019055.

The figure shows that the recently synthesized $P_{21}/c$ phase is the most stable of the three up to $\approx 170$ GPa at $T = 0$ K. Above this pressure the tetragonal phase is favored over the two monoclinic structures. Another interesting observation is that the $P_{21}/c$ phase is favored over the $C_{2m}$ monoclinic phase in the whole pressure range. The dynamical stability at 0 GPa has been proven for all three phases earlier \[19,25,46\]. The effect of temperature on the relative stability of the three phases is analyzed in Fig. 2(b). The figure shows the Gibbs free energy of formation of the $P_{21}/c$, $C_{2m}$, and $P_{4}/mbm$ phases at 100 GPa within the quasiharmonic approximation up to 1000 K. The dashed vertical line is used to make a correspondence between (a) and (b)—see text.
TABLE III. Data collection, refinement, and crystal structure data for the \textit{P}4/\textit{mbm} polymorph of Re\textsubscript{N}2.

| Crystal data                                      | ReN\textsubscript{2} |
|--------------------------------------------------|----------------------|
| **Chemical formula**                             | \textit{P}4/\textit{mbm} |
| **Mr**                                           | 214.22               |
| **Crystal system, space group**                  | Tetragonal           |
| **Pressure**                                     | 175(10) GPa          |
| **a, c (Å)**                                     | 4.0013(12), 2.442(2) |
| **Volume**                                       | 39.10(4)             |
| **Z**                                            | 2                    |
| **Radiation type**                               | Synchrotron          |
| **μ (mm\textsuperscript{-1})**                   | 0.3092 Å             |
| **Crystal size (mm × mm × mm)**                  | 0.001 × 0.001 × 0.001|
| **Data collection**                              | Multiscan            |
| **Diffra"ctometer**                             | CRYSLALIS PRO        |
| **Absorption correction**                        | Empirical absorption correction using spherical harmonics implemented in SCALE3 ABSPACK scaling algorithm. |
| **\(T_{\text{min}}, T_{\text{max}}\)**          | 0.3165, 1.000        |
| **No. of measured, independent, and observed \([I > 2\sigma(I)]\) reflections** | 0.3165, 1.000        |
| **\(\bar{R}_{\text{int}}\)**                   | 0.060                |
| **(\(\sin \Theta / \lambda\))_{\text{max}} (Å\textsuperscript{-1})** | 0.936               |
| **Refinement**                                   | 0.043, 0.107, 1.02   |
| **No. of reflections**                           | 59                   |
| **No. of parameters**                            | 6                    |
| **Crystal structure**                            | Re, N                |
| **Wyckoff site**                                 | 2b, 4g               |
| **Coordinates**                                  | (0, 0, 0.5), [0.618(9), 0.118(9), 0] |

phases at 100 GPa up to 1000 K. The dashed vertical line in Figs. 2(a) and 2(b) is used to establish the correspondence between the zero-temperature static calculations (triangles) and calculations including the effects of the lattice dynamics, e.g., the zero-point motion (circles). One sees that the relative order of the three phases is not changed by temperature, though the formation energy differences become slightly smaller with increasing temperature. In Fig. 2(b) along the dashed line the energy differences between the values marked by a triangle and a sphere shows the effect of the zero-point energies of the lattice vibrations for each of the phases.

The characterization of the high-pressure synthesized sample has shown that at \(\approx 175\) GPa Re\textsubscript{N}2 indeed crystallizes in the tetragonal space group (\textit{P}4/\textit{mbm}, No. 127) with Re and N occupying Wyckoff sites 2b and 4g, respectively. See Table III and the Crystallographic Information File (CIF) in the Supplemental Material [47] for details. Figure 3 shows the x-ray reflections corresponding to the \((hk\bar{2})\) reciprocal lattice plane of the \textit{P}4/\textit{mbm} phase. Re atoms are coordinated by eight nitrogen atoms forming Re\textsubscript{N}8 rectangular prisms. These prisms are stacked along the \(c\) axis (short edge of the rectangular prism) sharing faces and forming infinite columns. The columns also share common edges and additionally interconnected via N-N bonds as shown in Fig. 1(d). The refined N-N distance of 1.34 Å is close to the expected value of a single N-N bond at this pressure [48], suggesting that nitrogen forms a pernitride anion [N-N]\textsuperscript{4-}, while Re has an oxidation state +4.
To understand the electronic properties of ReN$_2$ polytopes at 0 GPa we have calculated the electronic structure of all three phases. The calculated total and partial density of states (DOS) are shown in Figs. 4(a)–4(c). For each phase the first panel shows the total DOS curves including the total rhenium 5$d$ partial DOS as shaded curves. One should note here that the tetragonal polymorph has half as many atoms as the other two, therefore double the DOS is plotted. The second panel compares the nitrogen 2$p$ partial DOS for the different types (N$_1$ and N$_2$) nitrogens. In comparison, the total DOS of the three structures show different characteristics at the Fermi level. One observes nearly semimetallic behavior for $P_{2_1/c}$ and significantly more typical metallic behavior for the two competing phases. For the $P_{2_1/c}$ phase the calculations predict a low DOS value at the Fermi energy. In the case of $C_{2/m}$, one sees instead a peak close to the Fermi energy, though the Fermi level is located in a valley between the two peaks. This could indicate a smaller contribution from the one-electron energy to the structural stability of the $C_{2/m}$ phase relative to the $P_{2_1/c}$ phase. In comparison, for $P_{4/mmb}$ one observes a finite value of the total DOS with a plateau in a vicinity of the Fermi energy. It also indicates a smaller contribution from the one-electron term to the structural stability of the phase. For each of the polymorphs, one notes significant
hybridization between the Re 5d and N 2p orbitals. However, the strongly distorted trigonal prismatic local environments of the Re atoms do not allow any deeper analysis of the Re 5d orbitals using crystal field theory.

To analyze the nearly semimetallic DOS of the $P_{2\frac{1}{1}}/c$ phase we have calculated the electronic band structure in the Brillouin zone parallel to the $\Gamma$-A and $\Gamma$-$Y_2$ paths (see the inset figure of the Brillouin zone in Fig. 5). Figure 5(a) shows the band structures at ambient pressure while Fig. 5(b) shows it for 23 GPa. One observes that the unoccupied band at $Y_2$ and the occupied band along the $\Gamma$-A line could be responsible for the semimetallic behavior at $p = 0$ GPa. However, there are small electron pockets along the lines in the $\Gamma$-A-E-Z plane (not shown) which are responsible for the finite DOS at the Fermi energy. Interestingly, with increasing pressure [Fig. 5(b)] the band at $Y_2$ passes the Fermi energy. Besides this, one sees that the band along the $\Gamma$-A path crosses the Fermi energy, but not in the $\Gamma$-A-$Y_2$ plane, where the valence band just touches the Fermi energy. Accordingly, one expects that the Fermi surface consists of a simple hole pocket around the $\Gamma$-A line at low pressures, while at higher pressure an additional electron pocket is expected around the $Y_2$ point in the Brillouin zone. Thus, an electronic topological transition (ETT), that is the change of the Fermi surface topology [49], should be observed with increased pressure.

To investigate the topology of the Fermi surface and to calculate the pressure at which ETT occurs, we have increased the accuracy of the calculations by increasing the density of $k$ points in the electronic structure calculations. We have selected the $k$-point sampling ($26 \times 14 \times 20$) which provides sufficient resolution for the study of the ETT and its influence on the materials properties. Figure 6 shows the Fermi surface of the $P_{2\frac{1}{1}}/c$ phase of ReN$_2$ at 0 and 23 GPa. The figure underlines the appearance of the additional electron pocket around $Y_2$ with increasing pressure. Importantly, one sees the second ETT associated with a disruption of the neck between the two shifts of the Fermi surface slightly off from the $\Gamma$-A line. The ETT is connected to the band which touches the Fermi energy along this line at $p = 0$ GPa (Fig. 6) and shifts below it with increasing pressure [Fig. 6(b)]. Based on the chosen 1 GPa pressure grid the calculations have shown that the two ETTs occur at 18 $\pm$ 0.5 GPa.

Experimental identification of the pressure-induced ETT is a nontrivial task, as exemplified by the cases of Zn [50–53], Os [54–58], and Fe [59]. The point is that the thermodynamic potential and its first derivatives are not affected by an ETT, the second derivatives may show weak square-root shaped peculiarities, while strong peculiarities are observed only for the third derivatives of the thermodynamic potential, leading to a classification of ETTs as the so-called “21$^2$” order phase transitions. Indeed, Fig. 7 shows that, as expected, the pressure dependence of the lattice parameters ratios $c/a$ and $b/a$ obtained in highly converged calculations at $T = 0$ K does not show any peculiarities. However, as pointed out in Ref. [59], the ETT should lead to peculiarities of the thermal expansion, and it can show up in the lattice parameter ratios measured at finite temperatures due to anisotropy of the thermal expansion. The effect was indeed observed experimentally in hcp Fe [59] and Os [58]. Interestingly, comparing the calculated zero-temperature lattice parameter ratios in Fig. 7 with the
properties of the room-temperature experiment of Ref. [19], we observe good agreement between the two data sets. But the experimental information at pressures around 18 GPa is, unfortunately, missing. Therefore, careful examination of the lattice parameters of the $P2_1/c$ phase of ReN$_2$ can be used to investigate the effect of the predicted ETT on the properties of this compound.

V. CONCLUSIONS

We have investigated the thermodynamic and electronic properties of the $P2_1/c$ phase of ReN$_2$ in comparison with previously suggested, competing phases. Our density functional theory calculations at $T = 0$ K have shown that the $P2_1/c$ phase is the most stable polymorph of the three studied modifications of the compound up to $\approx 170$ GPa. Above this pressure the tetragonal $P4/mmb$ becomes more stable. This calculation is supported by the experiment. Using the quasiharmonic approximation we have shown that the $P2_1/c$ phase is also a stable phase up to 1000 K at $p = 100$ GPa. Moreover, our electronic structure calculations have shown that two nearly coexisting electronic topological transitions occur in the $P2_1/c$ phase of ReN$_2$ with increasing pressure. We propose additional experiments that should verify the theoretically predicted ETT.

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