Discovery of Superconductivity in Hard Hexagonal $\varepsilon$-NbN

Yongtao Zou1,2, Xintong Qi3, Cheng Zhang4, Shuailing Ma1, Wei Zhang5, Ying Li2, Ting Chen3, Xuebing Wang7, Zhiqiang Chen2, David Welch6,6, Pinwen Zhu1, Bingbing Liu5, Qiang Li4, Tian Cui1 & Baosheng Li2

Since the discovery of superconductivity in boron-doped diamond with a critical temperature ($T_c$) near 4 K, great interest has been attracted in hard superconductors such as transition-metal nitrides and carbides. Here we report the new discovery of superconductivity in polycrystalline hexagonal $\varepsilon$-NbN synthesized at high pressure and high temperature. Direct magnetization and electrical resistivity measurements demonstrate that the superconductivity in bulk polycrystalline hexagonal $\varepsilon$-NbN is below $\sim$11.6 K, which is significantly higher than that for boron-doped diamond. The nature of superconductivity in hexagonal $\varepsilon$-NbN and the physical mechanism for the relatively lower $T_c$ have been addressed by the weaker bonding in the Nb-N network, the co-planarity of Nb-N layer as well as its relatively weaker electron-phonon coupling, as compared with the cubic $\delta$-NbN counterpart. Moreover, the newly discovered $\varepsilon$-NbN superconductor remains stable at pressures up to $\sim$20 GPa and is significantly harder than cubic $\delta$-NbN; it is as hard as sapphire, ultra-incompressible and has a high shear rigidity of 201 GPa to rival hard/superhard material $\gamma$-B ($\sim$227 GPa). This exploration opens a new class of highly desirable materials combining the outstanding mechanical/elastic properties with superconductivity, which may be particularly attractive for its technological and engineering applications in extreme environments.

Hard superconducting materials have attracted considerable interest in materials science, condensed matter physics and solid-state chemistry since the discovery of the superconductivity in superhard boron-doped diamond with a transition temperature of $T_c \sim 4$ K1-3. For transition-metal nitrides, some of them possess very good superconductivity (e.g. 10 K for ZrN, 8.8 K for HfN, 17.3 K for $\delta$-NbN), as well as excellent mechanical properties such as low compressibility, high shear rigidity and high hardness6-16. Despite the $T_c$ for transition-metal nitrides is not very high, their remarkable mechanical properties make them good candidates of hard superconductors for specific electronic/high-field applications17 as well as potential applications in motor system, carbon-nanotube junctions and high-pressure devices16. In addition, the chemical inertness and high melting points also make these nitrides suitable for protective and wear-resistant coatings18.

It is known that rock-salt structured $\delta$-NbN possesses the highest transition temperature among transition-metal nitrides ($\sim$17 K), and has several polymorphs18-21 such as WC-type NbN, $\delta$-NbN (NiAs-type) and hexagonal $\varepsilon$-NbN ($\#194$, P6$_3$/mmc), but only cubic $\delta$-NbN has been extensively investigated12,14,18. Recent first-principles theoretical calculations of the thermodynamic properties and structural stability in NbN polymorphs22-23 (e.g. NaCl-, NiAs- and WC-type NbN) predicted that the hexagonal-structured NbN (e.g. WC- and NiAs-type) exhibited higher hardness and lower total energy than the cubic $\delta$-NbN. These results indicated that the hexagonal phases were more stable than the cubic counterpart which appeared to be the most energetically unfavorable structure or metastable phase with the rock-salt structure.

For hexagonal $\varepsilon$-NbN polymorph, despite its crystal structure was ever simply referred by Terao24 and Holec et al.25, the experimental studies on hexagonal $\varepsilon$-NbN are very scarce, especially for its superconductivity and mechanical/elastic properties which have never been reported. Recently, the wide and growing interest lies in

1State Key Laboratory of Superhard Materials, College of Physics, Jilin University, Changchun, 130012, China. 2Mineral Physics Institute, State University of New York, Stony Brook, N.Y. 11794, United States. 3Department of Geosciences, State University of New York, Stony Brook, N.Y. 11794, United States. 4Condensed Matter Physics and Materials Science Department, Brookhaven National Laboratory, Upton, N.Y. 11973, United States. 5School of Science, Southwest University of Science and Technology, Mianyang, Sichuan 621010, China. 6Department of Materials Science and Engineering, State University of New York, Stony Brook, N.Y. 11794, United States. Correspondence and requests for materials should be addressed to Y.Z. (email: yongtaozou@jlu.edu.cn) or Y.L. (email: subduction6@hotmail.com)
searching for novel materials with comprehensive superconductivity and excellent mechanical/elastic properties, which makes \( \varepsilon \)-NbN a good candidate of hard superconductors for the possible use in extreme environments. Here, we report the discovery of superconductivity in bulk polycrystalline hexagonal \( \varepsilon \)-NbN, and the findings of its ultra-incompressibility, high shear rigidity and hardness.

**Results**

**Synthesis and structural stability of hexagonal \( \varepsilon \)-NbN at high pressure.** Polycrystalline hexagonal \( \varepsilon \)-NbN bulk specimens used for the current magnetization and electrical resistivity measurements were synthesized from niobium nitride starting material (Goodfellow, claimed 99% purity) at 10 GPa and 1100–1200 °C for 1.5 hour in a high-pressure multi-anvil apparatus at Stony Brook University. Details of this experimental setup were described elsewhere. As shown in Fig. 1A, the synthetic specimen is almost a pure phase of \( \varepsilon \)-NbN with the hexagonal structure (PDF: #89-4757) coexisting with a minor amount of cubic \( \delta \)-NbN. The volume fraction of cubic \( \delta \)-NbN was estimated to be ~2% from the intensity of the \( \delta \)-NbN peaks observed in synchrotron X-ray diffraction; and there is not any other phases observed within the resolution of the current X-ray diffraction, such as tetragonal NbN, octahedral NbN, and so on.

Further SEM observations revealed that the synthesized specimen was free of visible microcracks with an average grain size of about 1-2 \( \mu \)m, and exhibited an equilibrated microstructure, as shown in Fig. 1B. The corresponding composition analyses of the synthetic specimen yielded \( \text{Nb}_{0.98(2)} \text{N}_{0.96(5)} \text{O}_{0.06(4)} \) as determined by the SEM-EDX measurements, indicating that the as-synthesized specimen was almost oxygen-free \( \varepsilon \)-NbN or stoichiometric nitride within its uncertainty. The composite has also been studied by high-resolution TEM (HRTEM), which shows that the specimen possesses perfect crystalline form (Fig. 1C). The major phase was confirmed to be hexagonal \( \varepsilon \)-NbN. The up-mid inset to the HRTEM image shows the corresponding observed selected area electron diffraction (SAED) pattern along [211] axis, which can be indexed to the relevant reported structure (space group: \( P6_3/mmc \), No. 194). For further confirmation of the structure, the simulated SAED pattern
Superconductivity in bulk polycrystalline hexagonal ε-NbN. Figure 3A shows normalized magnetization for a bulk polycrystalline hexagonal ε-NbN as a function of temperature below 20 K under a magnetic field of 3 mT (or 30 Oe). Clearly, the magnetic susceptibility measurements reveal obvious diamagnetic responses at temperatures of ~11.6 K and ~17.5 K, respectively. The magnetic anomaly occurring at ~17.5 K is ascribed to the superconducting transition of NaCl-structured cubic δ-NbN, while the magnetic anomaly at ~11.6 K is related to the hexagonal ε-NbN phase. The existence of the hysteresis between the two magnetization curves for the zero-field cooling (ZFC) and field cooling (FC) modes shows that the hexagonal ε-NbN specimen is a typical type-II superconducting material.

The observed superconducting transition temperatures of \(T_C = 11.6\) K and 17.5 K for the hexagonal ε-NbN and cubic δ-NbN, have been further addressed/confirmed by the current energy-dispersive X-ray diffraction pattern which shows no phase transitions are observed throughout this experiment and the hexagonal ε-NbN remains stable at pressure up to ~20.5 GPa.

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the electrical resistivity transition (i.e. the resistivity drops to 50% of that at 11.6 K) is about 11.1 K. The transition width is as small as ∼1 K, suggesting that the bulk polycrystalline hexagonal ε-NbN (nominal) specimen owns high quality and the homogeneous nature of the crystals.

Anisotropic behavior and mechanical/elastic properties of hexagonal ε-NbN. Niobium nitride polymorphs are attractive also due to their excellent mechanical/elastic properties (elastic behavior) besides their superconductivity, so understanding their hardness, elastic behavior, especially the Young’s modulus (E) and shear modulus (G), are of great importance for technological and engineering applications. Compressibility measurements upon compression revealed a significant degree of anisotropy in the elastic behavior of hexagonal ε-NbN, where ε-NbN is more compressible along the a-axis direction, while stiffer along the c-axis. The least-squares fit of the lattice constants as a function of pressure yields d(a/a0)/dP = −0.00096(1) GPa⁻¹ and d(c/c0)/dP = −0.00077(2) GPa⁻¹, as shown in Fig. 4. For comparison, our theoretical first-principles calculations of the pressure-dependent lattice constants are also displayed here, agreeing well with our experimental data, especially for the compressibility of c-axis.

Hardness measurements were performed on the synthesized polycrystalline hexagonal ε-NbN by means of the Vickers indentation method using a pyramidal diamond indenter. The loading force of the hardness tester is adjusted from 2.94 to 9.8 N (0.49, 0.98, 1.98, 2.94, 4.9 and 9.8 N loads). The dwelling time was fixed at 15 s. At each applied load, five indentations were performed. Under a certain applied load of P, the hardness (HV) was determined by HV = 1854.4P/d², where d is the arithmetic mean of the two diagonals of the indent in micrometers. The average HV values were 29.7 ± 1.0, 26.0 ± 1.3, 24.0 ± 0.7, 21.9 ± 1.0 and 21.5 ± 0.6 GPa under a load of 0.49, 0.98, 1.98, 2.94, 4.9 and 9.8 N, respectively. The results show that the hardness appears to increase with a decrease under various loading forces. The average measured Vickers hardness HV for polycrystalline hexagonal ε-NbN under different loads are shown in Fig. 5A. Clearly, the hexagonal ε-NbN exhibits a Vickers hardness of 22~30 GPa, which is significantly harder than the high-pressure synthesized polycrystalline ReB₂ (17~19 GPa) as reported by Qin et al. and is almost as hard as sapphire Al₂O₃. Figure 5B shows a summary
of the Vickers hardness of $\varepsilon$-NbN as a function of applied load, compared with the previous study on rock-salt structured cubic NbN, HfN and ZrN, showing that the hexagonal-structured $\varepsilon$-NbN is consistently harder than cubic NbN (17–20 GPa), HfN (15.5–19.1 GPa) and ZrN (11.8–16.9 GPa) under various loading forces ranging from 0 to 9.8 N, respectively.4

It is widely accepted that bulk and/or shear moduli can reflect the hardness in an indirect way.27,35 To further explore the correlations between the elastic modulus ($B$, $G$, $E$) and other physical properties, we have performed in situ ultrasonic measurements on hexagonal $\varepsilon$-NbN at high pressure. The experimental procedure in details can be seen elsewhere.26–31 The high-pressure elasticity and sound velocities of hexagonal $\varepsilon$-NbN are out of the current scope of this paper and will be published elsewhere.28 The ambient-condition bulk and shear moduli derived from the acoustic measurements on $\varepsilon$-NbN yielded $B_{0}\approx373\pm1$ (2 GPa) and $G_{0}=237\pm1$ (1 GPa).36 Clearly, hexagonal $\varepsilon$-NbN exhibits a remarkable incompressibility, which is as incompressible/stiff as superhard material cBN ($\sim381$ GPa).24 The shear rigidity of $\varepsilon$-NbN ($\sim201$ (1) GPa) rivals that for superhard $\gamma$-B ($\sim227$ GPa)37, which is well consistent with the theoretical shear modulus/rigidity of $G_{0}=199$ GPa by our first-principles calculations. According to our experimentally obtained bulk ($B_{0}$) and shear ($G_{0}$) moduli, the Young’s modulus ($E$) is derived to be $510\pm1$ GPa by applying the equation $E=9B_{0}G_{0}/(3B_{0}+G_{0})$, which surpasses that of superhard $\beta$-$\text{B}_4\text{C}$ composite (501 GPa)38, and can be comparable to that of polycrystalline cBN (587 GPa)39, indicating that the hexagonal $\varepsilon$-NbN will also be a good candidate for mechanical applications.

**Discussion**

**Mechanism of superconductivity in hexagonal $\varepsilon$-NbN.** It is well known that the rock-salt structured transition-metal nitrides (e.g. ZrN, NbN, HfN) and the rhombohedral $\beta$-ZrNCl ($\sim13$ K) and $\beta$-HfNCl ($\sim26$ K) compounds show good superconductivity.40,41 The structures of cubic $\delta$-NbN, hexagonal $\varepsilon$-NbN and rhombohedral $\beta$-ZrNCl along $a$ axis are shown in Fig. 6. In the hexagonal-structured $\varepsilon$-NbN, each N atom is surrounded by six Nb atoms and there are six N atoms around the Nb atoms (Fig. 6B). The rhombohedral $\beta$-ZrNCl can be considered to be composed of alternate stacking of honeycomb ZrN bilayers sliced from a ZrN crystal of the hexagonal structure and sandwiched by chloride layers, as shown in Fig. 6B,C. Therefore, the Nb-N layer in hexagonal-structured $\varepsilon$-NbN, as shown in Fig. 6B, is considered a critical component to stabilizing its superconductivity.

To gain insight into the mechanism of superconductivity in hexagonal $\varepsilon$-NbN against those for the rock-salt structured nitrides as well as rhombohedral $\beta$-ZrNCl, their crystal structures (Fig. 6) and their structural parameters have been further investigated. The lattice constants, average bond length, bond angle and superconducting transition temperatures ($T_c$) of niobium nitrides derived from our first-principles calculations and magnetic/electrical measurements are summarized in Table 1, in comparison with those of cubic ZrN and $\beta$-ZrNCl superconductors.40,41 Our theoretical calculations show that the average bond length of Nb-N for hexagonal $\varepsilon$-NbN (2.2219 Å) is longer than those of the NaCl-structured NbN (2.2077 Å) and rhombohedral $\beta$-ZrNCl (2.2127 Å), but shorter than that of cubic ZrN (2.2890 Å). As shown in Fig. 6, the average bond angle (N-Nb-N) for the distorted NbN$_6$ (trigonal prismatic coordination) of $\varepsilon$-NbN is $\sim82.25^\circ$, and the layered hexagonal-structured $\varepsilon$-NbN is almost coplanar against the NaCl-structured NbN/ZrN with the bond angle of $90^\circ$. Therefore, the weaker bonding in the Nb-N network and the co-planarity may be the reason for the relatively lower $T_c$ of $\varepsilon$-NbN ($\sim11.6$ K) compared with the cubic $\delta$-NbN counterpart ($\sim17.5$ K). This correlation is further supported by the rock-salt...
structured ZrN and rhombohedral \( \beta \)-ZrNCl superconductors (Table 1), where a stronger bonding of Zr-N in \( \beta \)-ZrNCl (2.2127 Å) results in a higher \( T_C \) (\( \sim 13.0 \) K), in comparison with the NaCl-structured ZrN (2.2890 Å, 10.7 K). On the other hand, the shorter average bond length of N-N (2.9728 Å) for \( \varepsilon \)-NbN together with the lower total energy, compared with \( \delta \)-NbN (N-N: 3.2122 Å), indicated that the hexagonal \( \varepsilon \)-NbN is more stable than the cubic counterpart.

For phonon-mediated superconductivity, \( T_C \) is given by McMillan’s formula

\[
T_C = \frac{\Theta_D}{1.45 \exp \left( \frac{-1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)} \right)},
\]

where \( \Theta_D \) is the Debye temperature, \( \mu^* \) is the Coulomb pseudopotential or electron-electron interaction constant and \( \lambda \) is the electron-phonon coupling. Based on the obtained elastic bulk and shear moduli together with the ambient-condition density \( \rho = 8.30(2) \) g/cm\(^3\) of hexagonal \( \varepsilon \)-NbN as derived from our ultrasonic measurements\(^{28}\), the Debye temperature \( \Theta_D \) is determined to be \( \sim 738 \) K from the equation described as

\[
\Theta = \frac{h}{k_B} \left( \frac{N}{M} \right)^{1/3} \left( \frac{\rho}{M^2} \right)^{1/3} \left( \frac{1}{3} \right)^{1/3} \left( \frac{1}{2} \right)^{1/3} \left( \frac{1}{2} \right)^{1/3},
\]

which is significantly larger than the theoretical result of \( \Theta_D = 629 \) K for cubic \( \delta \)-NbN\(^{43}\), and is double the previously experimental value of \( \sim 363 \) K (ref. 11). Using the obtained values of \( \Theta_D = 738 \) K, \( T_C = 11.6 \) K, and a well-accepted Coulomb parameter \( \mu^* = 0.1-0.13 \) for transition-metal nitrides\(^3\), we estimate the electron-phonon coupling \( \lambda = 0.57-0.63 \) for \( \varepsilon \)-NbN is significantly weaker than those (\( \lambda = 0.87 \) and 0.906) for cubic \( \delta \)-NbN counterpart\(^8,9\).

Figure 6. Comparison of the atomic structures of cubic \( \delta \)-NbN (A), hexagonal \( \varepsilon \)-NbN (B) and rhombohedral \( \beta \)-ZrNCl (C) along a axis. The corresponding single unit cell is displayed in solid line. Blue, red, and green spheres stand for Zr/Nb, N and Cl atoms, respectively.

| Compounds       | hexagonal \( \varepsilon \)-NbN | \( \delta \)-NbN | cubic ZrN | \( \beta \)-ZrNCl |
|-----------------|-------------------------------|-----------------|-----------|-----------------|
| Lattice constant (Å) |                               |                 |           |                 |
| \( a \)         | 2.9722                        | 4.4154          | 4.576     | 3.606           |
| \( c \)         | 11.2891                       | 4.4154          | 4.576     | 27.67           |
| Bond length (Å) |                               |                 |           |                 |
| M-N             | 2.2219                        | 2.2077          | 2.2890    | 2.2127          |
| N-N             | 2.9728                        | 3.1222          |           | 2.9728          |
| Bond angle (°)  |                               |                 |           |                 |
| N-M-N           | 82.3°                         | 90°             | 90°       | 115.9°          |
| \( T_C \) (K)   | 11.6                          | 17.5            | 10.7      | 13.0            |
| Ref.            | This study                    | This study      | Ref. 40   | Ref. 40,41      |

Table 1. Structural parameters and superconducting transition temperatures (\( T_C \)) of transition-metal nitrides.
It is clearly seen from the McMillan's formula that the effects of $\lambda$ (as the exponential term) on the $T_c$ is much more significant than $\Theta_D$ (as the linear term), which can shed light on the relatively smaller $T_c = 11.6\, K$, compared with $T_c = 17\, K$ for $\delta$-NbN. The relatively small value of $\lambda$ for $\varepsilon$-NbN can be understood qualitatively from the relation of $\lambda = N(0)\langle\hbar\omega\rangle^2/M$ (Ref. 42), where $N(0)$ is the density of electronic states at the Fermi energy, $\langle\hbar\omega\rangle$ is the average square of the electron-phonon matrix element, $M$ is the ionic mass and $\langle\hbar\omega\rangle$ is a characteristic phonon frequency averaged over the phonon spectrum having $\langle\hbar\omega\rangle = 0.58\hbar\omega_p$ (Ref. 42). Although the ionic mass of $\varepsilon$-NbN is similar to that of $\delta$-NbN, its stronger covalent bonds in $\varepsilon$-NbN imply a smaller $\langle\hbar\omega\rangle$, compared to those for $\delta$-NbN. These results have been further confirmed by experimentally measured $\Theta_D = 629\, K$ for $\varepsilon$-NbN, which is larger than the $\Theta_D = 570\, K$ for $\delta$-NbN.

First-principles calculations show that the superconducting and mechanical properties for transition-metal nitrides/carbonitrides are closely related to their electronic properties. For a good understanding of the mechanical/superconducting properties of $\varepsilon$-NbN, electronic properties of the total densities of states (TDOS) and partial densities of states (PDOS) for hexagonal $\varepsilon$-NbN at ambient pressure have been calculated, in comparison with those for cubic $\delta$-NbN counterpart (see Supplementary Materials: Fig. S1). Both hexagonal $\varepsilon$-NbN and cubic $\delta$-NbN show similar bonding features with a finite DOS at the Fermi level ($E_F$), originating mostly from the 4$d$ electrons of Nb and 2$p$ electrons of N and agree well with our electrical measurements that $\varepsilon$-NbN is a metallic electrical conductor at ambient conditions. Clearly, there is a strong hybridization between Nb 4$d$ and N 2$p$ states in $\varepsilon$-NbN as revealed by the appearance of "pseudogap" just below and/or above the Fermi level, indicating the covalent and/or ionic bonding between Nb and N atoms (Fig. S1(A)). When comparing with the electronic structures of hexagonal $\varepsilon$-NbN and cubic $\delta$-NbN, we note that there is a small peak dominated by the Nb- $d$ orbital at about $-0.68\, eV$ in the DOS for $\varepsilon$-NbN (Fig. S1(A,B)). The appearance of this peak with low energy indicates a stronger bonding arising from the metal $d$ orbitals in $\varepsilon$-NbN as compared to $\delta$-NbN, resulting in an enhancement of the elastic/mechanical strength of $\varepsilon$-NbN. Fig. S1(A) shows that the TDOS around the Fermi level ($E_F$) lies in a dip for $\varepsilon$-NbN, whereas the density of states increases monotonically at $E_F$ for $\delta$-NbN (Fig. S1(B)). This agrees well with the result from the total-energy calculations that the hexagonal $\varepsilon$-NbN is more stable than the cubic counterpart.

As reported by Oya et al.47, tetragonal phases $\gamma$-NbN$_3$ and Nb$_2$N$_4$ with long-range-ordered arrangement of vacancies exhibited superconductivity, whereas the hexagonal NbN and Nb$_2$N didn't show superconductivity at temperatures down to 1.77 K. For the mechanism of superconductivity in transition-metal nitrides, it is suggested that the continuous promotion of $s$, $p$ electrons to the $d$ shell in all solids under pressure is one of the factors which will induce superconductivity. As seen from Fig. S1, the contribution of the 4$d$-state is larger than those of the $5s$ and $5p$ states. The larger contribution of 4$d$ state electrons clearly shows the possibility of superconductivity in hexagonal-structured NbN at ambient pressure.

In summary, we have discovered the superconductivity at $\sim 11.6\, K$ in bulk polycrystalline hexagonal $\varepsilon$-NbN, which was synthesized at high pressure and high temperature in a high-pressure multi-anvil apparatus. The weaker bonding in the Nb-N network and the co-planarity may be the reason for the relatively lower $T_c(\sim 11.6\, K)$ compared with the cubic $\delta$-NbN counterpart ($\sim 17.5\, K$). Our theoretical calculations reveal that the contribution of the 4$d$-state is larger than those of the $5s$ and $5p$ states, and the relatively larger contribution of 4$d$ state electrons may be responsible for the superconductivity in hexagonal $\varepsilon$-NbN. In addition, the hexagonal $\varepsilon$-NbN was found to exhibit excellent mechanical properties, which is as hard as sapphire $A_1O_3$ (21–23 GPa) and possessed a remarkable incompressibility (as stiff as superhard $\beta$BN of $\sim 381\, GPa$). The shear rigidity of $\varepsilon$-NbN ($\sim 201(1)\, GPa$) rivals that for superhard $\gamma$-B ($\sim 227\, GPa$)12, and the Young's modulus ($\sim 510(1)\, GPa$) is surpassing for $\beta$-B$_2$O$_3$ composite (501 GPa). Our theoretical calculations indicate that the hexagonal $\varepsilon$-NbN is more stable than the cubic $\delta$-NbN, and the stronger bonding arising from the metal $d$ orbitals in $\varepsilon$-NbN compared to $\delta$-NbN results in an enhancement of the elastic/mechanical strength of $\varepsilon$-NbN. This study opens a new window for the design of desirable materials with the combination of excellent mechanical properties and superconductivity, which may be particularly attractive for its technological and engineering applications in extreme conditions.

**Methods**

**Magnetization and electrical resistivity measurements on polycrystalline hexagonal $\varepsilon$-NbN.** Magnetization measurements of the high-pressure synthesized bulk polycrystalline hexagonal $\varepsilon$-NbN were performed in a Superconducting Quantum Interference Device (SQUID) based magnetometer (MPMS, Quantum Design). Electrical resistivity measurements on hexagonal $\varepsilon$-NbN were conducted in a Physical Property Measurement System (PPMS, Quantum Design) using the standard four-probe method.

**In situ X-ray diffraction study of hexagonal $\varepsilon$-NbN at high pressure.** High-pressure synchrotron X-ray experiments using diamond-anvil cell (DAC) techniques were performed at the X17C beamline of National Synchrotron Light Source, Brookhaven National Laboratory. Stainless T301 steel plates with an initial thickness of 250 μm were used as gaskets. The $\varepsilon$-NbN powder, a tiny ruby ball, and the methanol-ethanol pressure medium (1:1) were loaded into the hole in the gasket. The experimental cell-pressure was determined by the pressure-induced fluorescence shift of ruby49. The incident synchrotron radiation beam was monochromatized to a wavelength of 0.4072 Å. The collected two-dimensional X-ray diffraction patterns were analyzed by integrating 2D images as a function of 2θ using the program Fit2D to obtain conventional, one-dimensional profiles.

**First-principles calculations.** Our first-principles calculations were performed with the CASTEP code, based on density functional theory (DFT) using Vanderbilt-type ultrasoft pseudopotentials and a plane-wave expansion of the wave functions. The local density approximation (LDA) and generalized gradient approximation (GGA) in the scheme of Perdew-Burke-Ernzerhof (PBE) were employed for determination of the exchange and correlation potentials for electron-electron interactions. The Brodyen-Fletcher-Goldfarb-Shanno
optimization method was applied to search for the ground states of \(\varepsilon\)-NbN. For the Brillouin-zone sampling, the Monkhorst-Pack scheme was adopted. To confirm the convergence of our calculations, we have carefully analyzed the dependences of the total energy on the cutoff energy and the \(k\) points with a cutoff energy of 600 eV in the electronic property calculations. All these parameters have been tested using special \(k\) points generated with 10×10×2. One-electron valence states are expanded on a basis of plane waves with a cutoff energy of 600 eV in the electronic property calculations. All these parameters have been tested to be sufficient for the convergence.

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Author Contributions

Y.Z. and B.L. designed this work. Y.Z., C.Z., Q.L., D.W., B.B.L., T.C. and B.L. analyzed the data and wrote this manuscript. Y.Z., S.M., X.Q., X.W., Y.L., W.Z., Z.C., P.Z., B.B.L., T.C. and B.L. conducted in situ ultrasonic measurements, synchrotron X-ray diffraction experiments, hardness measurements, theoretical calculations, HRTEM-SAED and SEM-EDX analyses. C.Z. and Q.L. performed superconductivity characterization by magnetization and transport measurements. All the authors contributed to discussion on the results for this manuscript.

Additional Information

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