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Pressure-induced superconductivity in topological semimetal NbAs$_2$

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Topological superconductivity with Majorana bound states, which are critical to implement nonabelian quantum computation, may be realized in three-dimensional semimetals with nontrivial topological feature, when superconducting transition occurs in the bulk. Here, we report pressure-induced superconductivity in a transition-metal dipnictide NbAs$_2$. The emergence of superconductivity is not accompanied by any structural phase transition up to the maximum experimental pressure of 29.8 GPa, as supported by pressure-dependent synchrotron X-ray diffraction and Raman spectroscopy. Intriguingly, the Raman study reveals rapid phonon mode hardening and broadening above 10 GPa, in coincident with the superconducting transition. Using first-principle calculations, we determine Fermi surface change induced by pressure, which steadily increases the density of states without breaking the electron–hole compensation. Noticeably, the main hole pocket of NbAs$_2$ encloses one time-reversal-invariant momenta of the monoclinic lattice, suggesting NbAs$_2$ as a candidate of topological superconductors.

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INTRODUCTION
There have been various proposals in search of quasiparticle excitations of Majorana fermions (MFs) in solids, which are the subject of both fundamental research and error-tolerant topological quantum computing. Superconductor–topological insulator (TI) heterostructures turn the surface Dirac fermions of topological insulators (TIs) into p-wave-like Cooper pairs. Majorana zero modes by this superconducting proximity effect may also create MFs in semiconducting nanowires with strong spin–orbital coupling or in ferromagnetic atomic chains. Alternatively, chiral Majorana edge states are expected in two-dimensional (2D) chiral topological superconductors, consisting of a topological insulator in proximity to an s-wave superconductor. It is intriguing that superconducting phase transitions are widely observed in many topological materials when high pressure is applied, such as type II Weyl semimetals of MoTe$_2$ and WTe$_2$, Dirac semimetals of Cd$_3$As$_2$ and ZrTe$_5$, and topological insulators of Bi$_2$Se$_3$, Bi$_2$Te$_3$ and Sb$_2$Te$_3$. Recently tip-induced superconductivity (SC) has attracted much attention because it could offer a new platform to study topological superconductors. Charge carrier doping is the another effective method to induce SC in topological insulators such as in Cu$_3$Bi$_2$Se$_3$ and Sr$_3$Bi$_2$Se$_3$. The experimental observations strongly suggest the feasibility to realize TSC in novel topological materials with nontrivial topological features. However, before the emergence of SC, most of these topological compounds undergo structural phase transitions, which usually change the topological states. Very recently, transition-metal dipnictides of the MPn$_2$ family, where M represents Mo, Nb, or Ta atom, and Pn is As or Sb atom, respectively, generate a wide interest as a new prototype of topological semimetals with extremely large magnetoresistance (XMR). When spin–orbital coupling is included, the band anticrossing in MPn$_2$ between the $d_{xy}$ and $M - d_{x^2-y^2}$ orbitals along the $I-L-I'$ direction are fully gapped, resulting in weak topological insulator invariants of $Z_2 = [0:111]$. Another interesting point in the MPn$_2$ family is that magnetic field could induce Weyl points. With its monoclinic lattice (Space group No. 12), which is normally stable under very high pressure, it is tempting to study the physical properties of MPn$_2$ under high pressure.

In this work, we report pressure-dependent transport measurement and structure evolution in NbAs$_2$, using the diamond-anvil cell (DAC) technique to continuously tune the electronic structure. Superconducting transition has been successfully observed at 12.8 GPa with a critical temperature ($T_c$) of 2.63 K. Further increase in pressure gradually suppresses $T_c$, which disappears completely at 27.9 GPa when bad metal (BM) behavior dominates below the helium temperature. Using high-pressure X-ray diffraction (XRD) and Raman scattering, we confirm that there is no structural phase transition up to the maximum experimental pressure of 29.8 GPa, which implies that the topological state maybe remain undisturbed under high pressure. Intriguingly, the electron-hole compensation in NbAs$_2$ changes little even in the superconducting region, as suggested by first-principle calculations, although...
the electron–hole compensation under pressure is not so perfect. Instead, the dwindling of XMR and the emergence of SC are characterized by continuous Fermi surface change and gradual growth in density of state. Our results thus indicate the coexistence of XMR and SC. The growing density of states is usually beneficial to the occurrence of SC. Moreover, the Cooper pair formation in NbAs$_2$ may also be correlated to the enhanced electron–phonon coupling under high pressure, since the Raman studies reveal significant phonon mode hardening and broadening above 10 GPa. It is noteworthy that, in the SC region, the main hole pocket of NbAs$_2$ encloses the time-reversal-invariant (TRI) momenta $M$. These suggest NbAs$_2$ as a candidate of TRI topological superconductors.

RESULTS AND DISCUSSION

Pressure-dependent structure analysis

The structure evolution of NbAs$_2$ under pressure is determined by synchrotron radiation-based high-pressure XRD and Raman spectroscopy, as shown in Fig. 1. The XRD data are refined using the Rietveld method, and the Bragg peaks are well indexed by the space group $C2/m$ for both the 0.6 and 25.3 GPa data (See Supplementary Fig. S1). Within 30 GPa, the pressure-induced lattice changes are reversible. In Fig. 1a, we show the XRD results of NbAs$_2$ when the DAC is slowly decompressed from 29.8 to 0.3 GPa. The data are essentially identical to the bottom curve of 0.6 GPa. In Fig. 1b, the high pressure dependent unit-cell volumes can be fitted by the third-order Birch–Murnaghan equation of state, and no distinct drop of the unit-cell volume is observed with the increase of pressure, which suggests stability of this structure. The monoclinic lattice is also manifested in pressure-dependent Raman scattering measurements, showing six fingerprinting peaks between 180 and 350 cm$^{-1}$, namely $A_{2g}$, $A_{3g}$, $B_{3g}$, $A_{4g}$, $A_{5g}$, and $A_{6g}$ respectively (see Fig. 1c). It is intriguing that Raman spectroscopy shows distinctive enhancement of $A_{2g}$, $A_{3g}$, $B_{3g}$, $A_{4g}$, and $A_{5g}$ above 10 GPa, when the data are normalized by the $A_{2g}$ peak intensity. The distinct broadening in $A_{2g}$, $A_{4g}$ and $A_{5g}$, which could be an indication of stronger electron–phonon coupling or pressure-enhanced defect scattering, is also discernable above 10 GPa.

Resistivity measurements

Figure 2a, b summarize the resistance vs. temperature ($R$–$T$) characteristics of NbAs$_2$ at various pressures from 0.5 to 27.9 GPa. Below 9.8 GPa, NbAs$_2$ shows typical metallic behavior, which is characterized by monotonic increase in resistance with increasing temperature, and exhibits a lower residual-resistivity-ratio with enhancement of pressure. The trend is reversed at 9.8 GPa, when the whole $R$–$T$ curve is upshifted by $-0.03 \Omega$ compared to 6.1 GPa. SC with a transition temperature of 2.63 K emerges at 12.8 GPa, but the resistance does not drop to zero even at 1.8 K (Fig. 2a). Further increase in pressure surprisingly starts to suppress $T_c$, although the SC transition becomes sharper, and zero-resistance behavior is observed at 16 GPa. Noticeably, the zero-resistance transition is accompanied by a positive resistance kink, which is very sharp and only extends within a temperature range of 0.2 K. Subsequently, the superconducting transition is gradually suppressed when the positive resistance kink becomes broader and its onset shifts to lower $T$. Above 23 GPa, the positive-resistance kink completely dominates.

In previous studies, the emergence of SC is generally accompanied with a suppression of the XMR effect in topological semimetals. There are different interpretations in the XMR suppression mechanism. Cai et al. suggest that pressure weakens the electron–hole compensation in WTe$_2$ by gradually decreasing the hole carrier population. In situ pressure-dependent Hall measurements by Kang et al. indeed observe the change from a positive sign to negative sign in the Hall coefficients, suggesting increasing population of the electron carriers and decreasing hole carriers density. Moreover, Pan et al. report that the SC transition is induced by rapid increase in the density of states at the Fermi surface, as a result of the compression of the...
unit cell, while the difference between hole pockets and electron pockets is enhanced with increasing pressure.

NbAs$_2$ is a well-compensated semimetal at ambient pressure. When high pressure is applied, XMR at 8T is effectively suppressed from 5.16 at 0.5 GPa to 0.08 at 14.6 GPa, as shown in Fig. 2c. The dwindling of XMR as a function of pressure can be explained well by pressure-induced decrease in the average mobility $\mu$, using the power-law relation of MR $\sim (B)^{l}$. Using logarithmic scale (see the inset of Fig. 2c), it is clear that the XMR curves at different pressures have nearly the same linear slope ($l = 1.43$), which is a simple measure of the electron–hole compensation accuracy, and the electron–hole compensation here is not so perfect. By fitting the experimental data to the aforementioned equation, we found that $\mu$ decreases quasi-linearly as a function of pressure, and only shows a slight upward curvature as entering the SC region above 10 GPa (see Fig. 2d). Our results thus imply that a distinct phase boundary does not exist between SC and XMR, and the mechanism of SC in NbAs$_2$ may be different compared to other topological semimetals.

The positive resistance kinks, which become broader and shift to lower temperature as a function of pressure ($P$), may be rooted in different mechanisms, such as superconductor to metal transition in disordered system, a probable foreshadow of p-wave SC in superconductor–ferromagnet nanowires structure, or highly anisotropic superconducting gap, but should not be the same as the semiconductor-like behavior in LaO$_{0.5}$F$_{0.5}$BiSe$_2$. When external magnetic field ($B$) is applied, $T_c$ monotonically shifts to lower temperatures and the positive resistance kinks gradually become predominant. As shown in Fig. 3a, it is surprising that the superconducting transition at 16 GPa is completely suppressed at 1000 Oe. This may be due to the predominant resistivity upturn, which pushes $T_c$ to below 1.8 K. Nevertheless, with the available experimental data, we can define an empirical critical $T_c$ by those points at which $R$ is 90% of the normal state, as seen in the inset of Fig. 3b. In Fig. 3b, the deduced $T_c$ can be well fitted by the Werthamer–Helfand–Hohenberg (WHH) model, which yields critical temperature $T_c^{WHH} = -0.69 T_c \times dH_c/dT |_{T=T_c} = 2288$ Oe.

Interestingly, by plotting the pressure-dependent $R$ at different $T$ (4.5, 100, 200, and 300 K, respectively) in Fig. 3c, we are able to clearly see an anomaly at 12.8 GPa, which corresponds to the emergence of SC. However, there is no structural phase transition up to 29.8 GPa, so the origin of this behavior needs further investigation. By including the characteristic parameters of XMR, $T_c^{p}$ as a function of pressure, we can draw the $P$–$T$ phase diagram for NbAs$_2$. As summarized in Fig. 3e, high pressure suppresses the XMR effect (the blue region) by reducing the average mobility $\mu$. The emergence of SC may be related to the enhancement of density of states, and calculated density of states increase as a function of pressure, as seen in Fig. 3d. Nonetheless, there is a significant overlap between the XMR (the blue region) and SC region (the magenta region) when SC emerges at 12.8 GPa. Such a coexistence of XMR and SC is in contrast to the other cases like WTe$_2$ where XMR is significantly suppressed as entering the SC state under high pressure. Above 16 GPa, there is a probable phase competition between SC and the BM transition (the green region), which maybe lead to the vanishing of $T_c$ at 27.9 GPa.
Electronic structures under pressure

To get insights into the aforementioned experimental results, we have studied the pressure-dependent electronic structure of NbAs$_2$ using density-functional theory (DFT) calculations, which adopt the experimental lattice parameters determined by XRD. Figure 4 displays the DFT calculations at ambient pressure, 15.6, and 22.7 GPa, respectively. In excellent agreement with the XMR measurements, the DFT results confirm that pressure simultaneously increases electron and hole populations in NbAs$_2$, which is displayed in Fig. 4d–f where the electron pockets (magenta) and hole pockets (blue) all enlarge with increasing pressure. This is not surprising since the monoclinic lattice is retained under high pressure. Equally important, the steady growth in charge carrier does not show any anomaly, neither in density of states in Fig. 3d nor in Fermi surface topology, in the vicinity of 12.8 GPa when SC starts to emerge. According to the proposed theory by Fu et al.,$^{26}$ time-reversal-invariant topological SC in a centrosymmetry system requires odd-parity spin pairing and an Fermi surface enclosing an odd number of TRIM points. Although the pairing symmetry is not explicitly known, the latter condition is well satisfied in NbAs$_2$. As shown in Fig. 4, the main hole pocket of NbAs$_2$ enlarges under pressure, centering the TRIM point of M. In addition, the electronic specific-heat coefficient of $\gamma = 0.45$ mJ/mol/K$^2$ is observed from the specific heat measurements (see Fig. S3 in Supplementary Materials), suggesting weak electronic correlation in NbAs$_2$ at ambient pressure. With increasing pressure, the sudden hardening and broadening phonon modes may start to play a critical role in the emergence of SC, and the phonon-mediated pairing maybe have an odd-parity symmetry in NbAs$_2$ if there is a singular behavior of the electron–phonon interaction at long wavelength.$^{47,48}$ In addition, no structural transition is observed as entering the superconducting states with increasing pressure and thus the topological surface state should remain undisturbed at high pressure, which suggests the possibility of topologically superconducting surface states in NbAs$_2$ because of superconducting proximity effect.$^3$ Therefore, NbAs$_2$ with time-reversal and inversion symmetries may be a candidate for topological superconductor. It is necessary to be checked by further experiments.

In summary, we study the high-pressure-induced SC in topological semimetal NbAs$_2$, which shows a superconducting transition temperature of 2.63 K at 12.8 GPa. Unlike previously reported topological semimetals, no structural phase transition occurs near the superconducting region, which is supported both by the high-pressure synchrotron XRD and Raman data. Raman spectroscopy, resistance and specific heat data all suggest the critical importance of electron-phonon interactions on the SC pairing in NbAs$_2$, which may be a candidate of time-reversal-invariant topological superconductor with odd spin paring parity.

Strikingly, the SC phase emerges with a nearly invariable electron-hole compensation and shows no anomaly in the density of states in the vicinity of the critical pressure of 12.8 GPa. Our results illustrate that high-pressure induced SC may be more complex in physical origins than the prevailing explanations, and the monoclinic family of MPn$_2$ may provide a platform to test various theoretical proposals and to search for topological SC.
Methods

Samples and experimental technique

Single crystals of NbAs$_2$ were grown by means of a vapor transport technique. High pressure was generated by a screw-pressure-type DAC consisting of nonmagnetic Cu-Be alloy and two diamonds with the culet of 300 μm diameter. A T301 stainless-steel gasket with a 280 μm diameter hole was used for different runs of high-pressure resistance measurement by the standard four-probe method. The single crystal was placed in the hole and a mixture of fine cubic boron nitride powder with epoxy was compressed firmly to insulate the electrodes from the gasket. Pressure medium was daphne 7373 oil and some ruby powder was applied to demarcate the pressure by the ruby fluorescence method at room temperature. High-pressure synchrotron powder XRD ($\lambda = 0.4246$ Å) was performed at room temperature at the beamline 16 BM-D, High Pressure Collaborative Access Team (HPCAT).

DFT calculations

The electron structure calculations were performed with the Vienna ab initio simulation package by the method of the projector augmented wave and the generalized gradient approximation in order to introduce the exchange-correlation potential. Spin-orbit coupling has been included using the second variation perturbation method. In addition, the plane-wave cutoff energy is setting about 500 eV and $21 \times 21 \times 13$ k-points sampling is performed based on the Monkhorst-Pack scheme. The total energy is ensured to be converged within $10^{-6}$ eV. We use the structure parameters of high-pressure synchrotron XRD to relax the structure with the tolerance of 0.01 eV/Å.

Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Author contributions

Y.P. Li synthesized and characterized the single crystals, C. An, Y.H. Zhou, and Z.R. Yang conducted the high-pressure transport measurements. Y. Zhou, C. An, and R.R. Zhang carried out the Raman experiments. X.L. Chen and C.Y. Park performed the high-pressure synchrotron X-ray diffraction experiments. C.Q. Hua and Y.H. Lu did the DFT calculations. Y.P. Li, C.Q. Hua, Y.H. Lu, Z.R. Yang, Y. Zheng, and Z.A. Xu wrote the paper. All the authors analyzed the data and discussed the results. Y.P. Li, C. An, and C.Q. Hua were co-first authors to this work. Z.R. Yang and Z.A. Xu co-supervised the project.

Additional information

Supplementary information accompanies the paper on the npj Quantum Materials website (https://doi.org/10.1038/s41535-018-0132-1).

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