PAPER

Superconductivity in Topological Semimetal θ-TaN at High Pressure*

Superconductivity in Topological Semimetal θ-TaN at High Pressure *

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Recently, θ-TaN was proposed to be a topological semimetal with a new type of triply degenerate nodal points. Here, we report studies of pressure dependence of transport, Raman spectroscopy and synchrotron x-ray diffraction on θ-TaN up to 61 GPa. We find that θ-TaN becomes superconductive above 24.6 GPa with T_c at 3.1 K. The θ-TaN is of n-type carrier nature with carrier density about $1.1 \times 10^{20}/cm^3$ at 1.2 GPa and 20 K, while the carrier density increases with the pressure and saturates at about 40 GPa in the measured range. However, there is no crystal structure transition with pressure up to 39 GPa, suggesting the topological nature of the pressure induced superconductivity.

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Research on topological semimetal attracts intensive interests in recent years.[1−3] Various types of topological semimetals have been discovered, such as Dirac semimetal, Weyl semimetal and nodal line semimetal.[2] These systems are classified by the symmetry that protects the band crossing point near the Fermi energy and the effective Hamiltonian near the point.[4−6] More importantly, some of them show superconductivity by chemical doping or at pressure, which can be viewed as the candidates of topological superconductors with potential application in quantum computation and as the platform of searching the Majorana Fermions.[7−16] The main research motivations in this area are to search for new types of topological semimetals and further identify the possibility of the existence of the topological superconductivity.

A recent study proposed that θ-TaN is a topological semimetal.[1] In contrast from the previous results, this 'new fermion' state featured with triply degenerate nodal points. For an arbitrary Fermi level, the new fermion state hosts Fermi surfaces that touch each other, leading to interesting transport properties, such as a possible magnetic breakdown in the quantum oscillation experiments. The application of pressure is often effective to change the electronic structure of a compound without simultaneously introducing degree of disorder. Moreover, pressure has been confirmed as a powerful tool in searching the candidates of topological superconductors.[10−17]

The θ-TaN polycrystal samples are synthesized at 6 GPa and 1500℃. The electronic transport properties of θ-TaN at high pressure and low temperatures are investigated via the four-probe electrical conductivity method in a diamond anvil cell (DAC) made of CuBe alloy as described in previous work.[10,18] Pressure was generated by a pair of diamonds with a 300 μm diameter culet. A gasket made of T301 stainless steel was pressed from a thickness of 250 μm to 10 μm, and drilled a center hole with a diameter of 120 μm. Fine cubic boron nitride (*c*BN) powder was used to cover the gasket to protect the electrode leads insulated from the metallic gasket. The electrodes were slim Au wires with a diameter of 18 μm. A 50-μm-diameter center hole in the insulating layer was used as the sample chamber. The dimension of the sample was about 35 μm × 35 μm × 5 μm, and NaCl powder was as the pressure transmitting medium. The pressure was measured via the ruby fluorescence method at room temperature before and after each cooling.[19] The diamond anvil cell was placed inside a MagLab system to perform the experiments. The temperature was automatically controlled by a program of the MagLab system. A thermometer was mounted near the diamond in the cell to monitor the exact sample temperature. Hall coefficients were measured via the van der Pauw method. The *in-situ* high pressure angle-dispersive x-ray diffraction (ADXRD) experiments were performed using a symmetric Mao Bell DAC at Beijing Synchrotron Radiation Facility. The wavelength is 0.6199 Å. The sample in DAC is fine powder and a tiny ruby chip was regarded as the pressure marker. The two-dimensional image plate patterns obtained were converted to one-dimensional 2θ versus intensity data using the Fit2d software package.[20] The labo-

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ratory powder x-ray diffraction was performed on a Rigaku diffractometer using Cu K_α radiation generated at 40 kV and 40 mA. The data were collected at a scanning rate of 10°/min with a scanning step length of 0.01°. The electrical transport properties at ambient pressure were studied using a Quantum Design physical properties measurement system (PPMS) by the standard four-probe method. For the electronic structure, first-principles calculations based on density functional theory were carried out within a primitive cell with a $24\times24\times24$ k-point grid and 500 eV energy cutoff. Norm conservation pseudopotentials with Perdew, Burke, and Ernzerh (PBE) of exchange correlation are adopted in our calculation.[21]

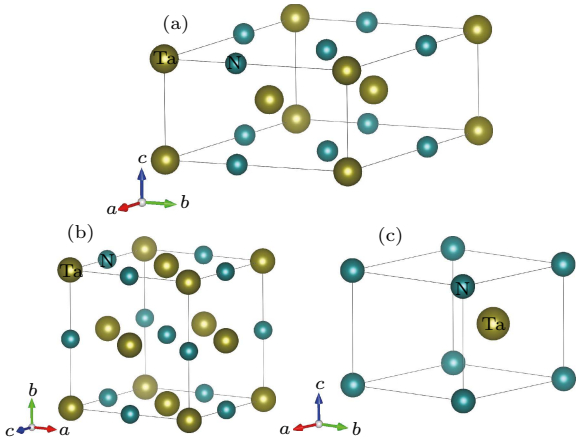

Fig. 1. Crystal structure of (a) ε-TaN, (b) δ-TaN and (c) θ-TaN.

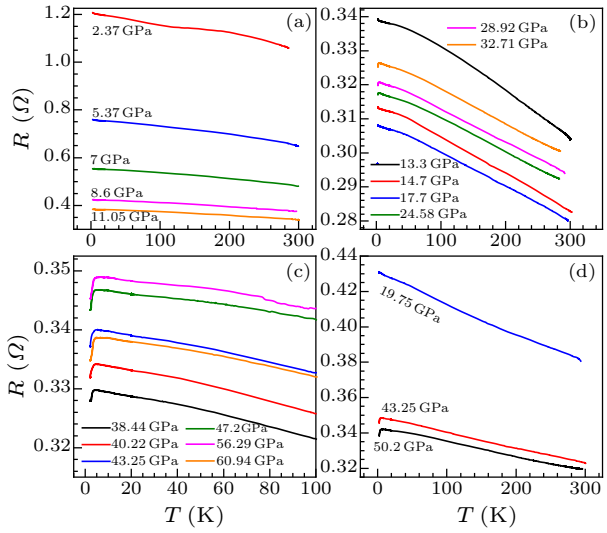

Fig. 2. Transport properties of θ-TaN at various pressures.

The ground state structure of TaN is CoSn (B35)-type, which is usually named as ε-TaN. This polymorph is hexagonal (space group $P\bar{6}2m$, see Fig. 1(a)) with $a = 5.196(4)$ Å and $c = 2.911(2)$ Å.[22] There are two polymorphs of TaN stabilized at high pressure and high pressure. One is the cubic phase δ-TaN ($Fm\bar{3}m$, B1-type structure, $a = 4.32$ Å, Fig. 1(b)). This phase can be obtained by treating the ε-TaN under different pressure and temperature conditions or ion irradiations.[23–27] The other phase θ-TaN crystallizes into WC-structure type ($P\bar{6}m2$, Fig. 1(c)), which can be fabricated at 2–10 GPa and 1073–1233 K using ε-TaN as the starting material.[28]

Figure 2 shows the evolution of resistances of θ-TaN polycrystalline as a function of temperature at various pressures. At ambient pressure, θ-TaN shows a semiconductor behavior. The resistances of θ-TaN continuously decrease with increasing pressure up to 24.6 GPa. Then, the superconductivity with T_c at about 3.1 K emerges at that point. The transition temperature T_c increases with further compression, and finally reaches a maximum of 4.68 K at about 56.3 GPa. The superconducting transition disappears upon releasing pressure, indicating that the superconducting transition is reversible. According to the previous report, superconductivity was observed in the δ phase (cubic structure) for TaN at ambient pressure with a T_c around 4.2 K,[24] but there has been no report on the θ-TaN so far. This is the first observation of superconductivity in θ-TaN to our knowledge.

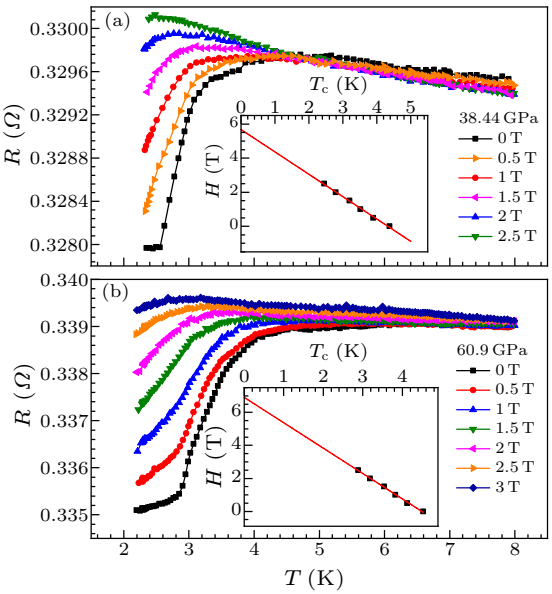

Fig. 3. Temperature dependence of superconducting transition for θ-TaN in different magnetic fields at (a) 38.4 GPa and (b) 60.9 GPa. The insets show the upper critical field H_{c2}.

To determine whether the resistance drop is indeed a superconducting transition, we measured the temperature dependence of resistance at various external magnetic fields. Figure 3 shows that T_c decreases with increasing the applied magnetic field H perpendicular to the ab-plane of the θ-TaN at 60.9 GPa, indicating that the transition is superconductivity indeed. The inset shows the magnetic field H evolution as a function of T_c at 38.4 GPa and 60.9 GPa, respectively. Although it is limited by the temperature range we measured, one can see an apparently linear temperature dependence of H. With a linear fit to the data,

the upper critical fields $H_{c2}(0)$ are estimated to be about 5.67 T and 6.91 T, respectively. Moreover, we notice that all the H_{c2} show linear temperature dependence behavior, which is similar to that observed in Bi_2Se_3,[11] $Cu_xBi_2Se_3$[14,28] and Au_2Pb,[29] indicating an unconventional superconducting state.

The Hall resistance as a function of applied pressure at 20 K shows a linear behavior with a negative slope, indicating that the carrier is n-type over the entire pressure range measured (n is for electron concentration). The pressure dependent carrier density at 20 K is shown in Fig. 4(b). At 1.2 GPa, the carrier density is about $1.1 \times 10^{20}/\text{cm}^3$. It increases with the pressure, and reaches about $2.6 \times 10^{20}/\text{cm}^3$ at 43.3 GPa. When the pressure further increases, the carrier density remains constant and stabilized around $2.7\times10^{20}/\text{cm}^3$. This behavior is similar to that observed for the pressure-dependent superconducting transition temperature (Fig. 4(a)).

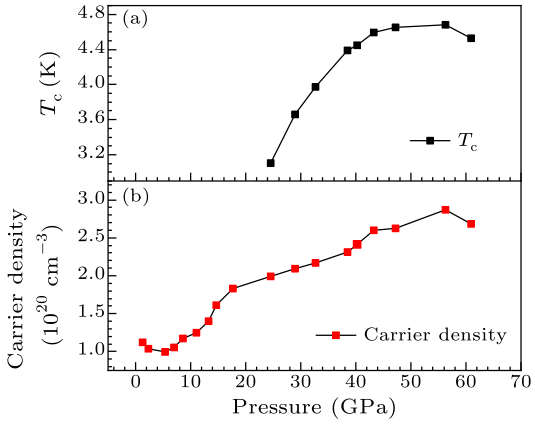

Fig. 4. (a) Pressure dependence of superconductive transition temperature T_c of θ-TaN. (b) Pressure dependence of carrier density at temperature of 20 K of θ-TaN.

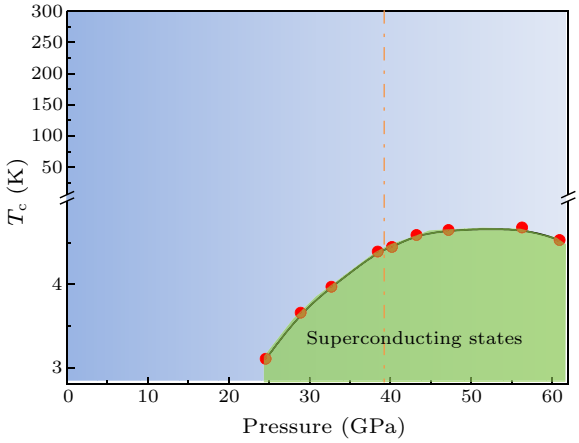

Fig. 5. Phase diagram of θ-TaN as a function of pressure up to 60.9 GPa.

Selected angle resolved x-ray diffraction patterns at high pressure indicate that the main Bragg peaks of the θ-TaN phase sustained up to the highest pressure in the experiment; i.e., 39 GPa (see Fig. S1). This implies that there is no structure phase transition in the measured pressure range.

Figure 5 shows global phase diagram of θ-TaN as a function of pressure up to 60.9 GPa. There is apparently a region of constant T_c from 43.3 to 61 GPa. Such a phase diagram is very similar to that of 3D topological insulator Bi_2Se_3, which also shows a nearly constant T_c from 30 to 50 GPa after an initial increase of T_c starting from 12 GPa.[11] A constant T_c over such a large pressure range is highly anomalous. Usually, it is considered that the unique pressure evolution of T_c and the linear temperature dependence of H_{c2} are two evidences for unconventional superconductivity in Bi_2Se_3. The experimental results suggest that θ-TaN is likely an unconventional superconductor generated by high pressure.

To check the electronic structure, the first-principles calculation with spin-orbital coupling is performed. The results are shown in Fig. S2, in which triple band crossing point preservers up to 28 GPa. The band structure is not significantly modified at high pressure; i.e., the compound keeps the topological structure at high pressure. Based on both the experimental results and the DFT calculation, we suggest that θ-TaN may be a candidate of topological superconductor.

In summary, we have successfully synthesized the WC-type hexagonal θ-TaN by high pressure. The superconductivity is observed at 24.6 GPa and the superconducting transition temperature T_c increases with the pressure with a maximum of 4.68 K at 56.3 GPa. Hall coefficient measurement indicates that the carrier is n-type. High pressure x-ray diffraction indicates that there is no crystal structure transition at room temperature with pressure up to 39 GPa. The DFT calculation also indicates that the triple-band crossing point maintains to high pressure. Our result provides a new platform to investigate the interplay between superconductivity and topological state.

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Supplementary Material: Superconductivity in Topological Semimetal θ-TaN at High Pressure*

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Figure S1

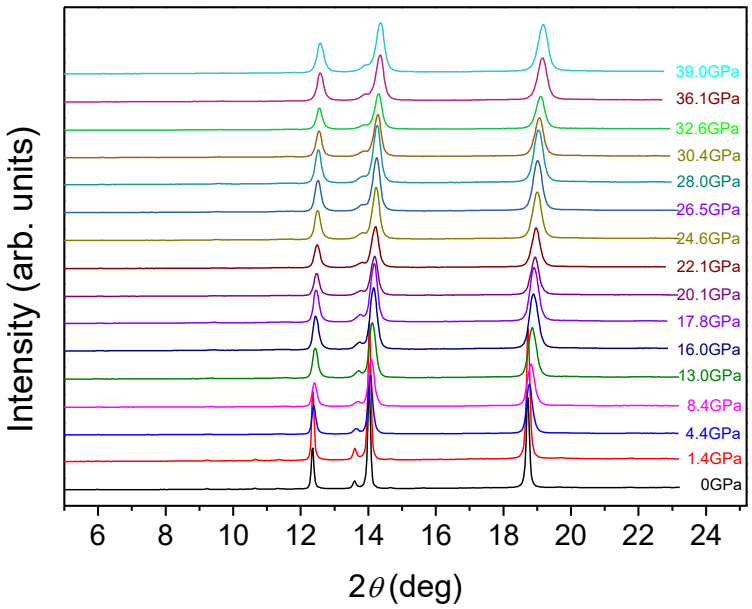

Fig. S1. Synchrotron X-ray diffraction patterns at selected pressures.

Figure S2

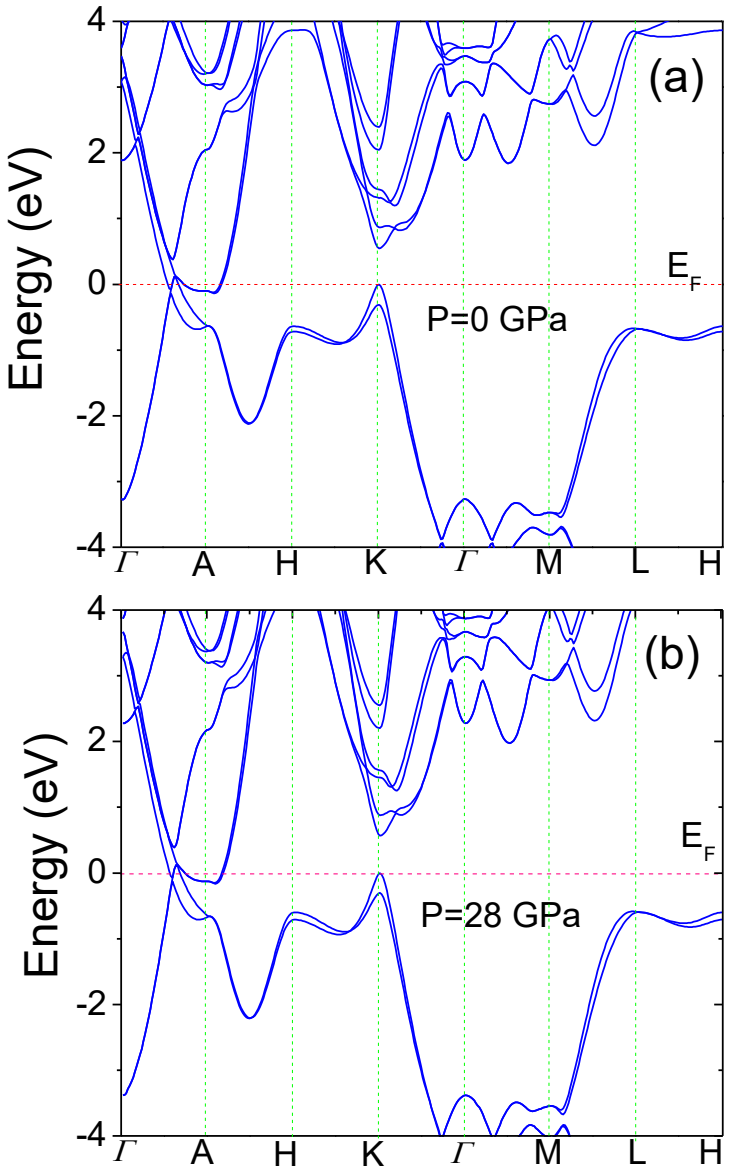

Fig. S2. DFT calculations of band structure θ-TaN (a) at ambient pressure and (b) at 28 GPa.