Sodium-doped superconductivity in T-carbon

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T-carbon has been proposed as a new carbon allotrope in 2011, which was successfully synthesized in recent experiments. Because of its fluffy structure, several kinds of atoms can be intercalated into T-carbon, making it a versatile candidate in various applications such as hydrogen storage, perovskite solar cells, lithium ion batteries, thermoelectrics, photocatalyst, etc. Here we show that superconductivity can appear in Na-doped T-carbon with superconducting transition temperature Tc of 11 K at ambient pressure, and Tc can be enhanced to 19 K under pressure of 14 GPa, which results from an enhancement of the electron-phonon coupling due to the shift of the phonon spectral weight to lower frequencies with the increase of pressure. The calculations on specific heat and electrical and thermal conductivities show that the normal state of the Na-doped T-carbon superconductor reveals a non-Fermi liquid behavior. The prediction of superconductivity in Na-doped T-carbon would spur great interest both experimentally and theoretically to explore novel carbon-based superconductors.

Introduction. —The observation of superconductivity in carbon materials has long been a crucial and fascinating topic in condensed matter physics and materials science, which receives much attention in recent years. Several carbon compounds were reported to be superconductors. Graphite intercalation compounds such as KC8 are known to be superconducting with very low transition temperature Tc.1 Boron-doped diamond is a bulk, type-II superconductor below the superconducting transition temperature of about 4 K.2 The discovery of fullerene C60 and C70 opens a door to explore new allotropes of carbon, which leads to subsequent flourishing explorations of carbon allotropes.3 C60 molecules can form a solid,4 which is a wide gap semiconductor with a band gap of about 2 eV, and has so large interstitial site spacings that it can accommodate intercalants. The alkali-metal5–7, alkaline earth metals8,9 and rare-earth elements10,11 intercalated C60 solids have been synthesized. The superconductivity was first discovered in K3C60 with Tc of 18 K, and then in Rb3C60 with Tc of about 30 K12,13. Since then higher Tc of 33 K14–16 at 1 bar in Cs2Rb6C60 and 40 K in Cs3C60 under pressure of 15 kbar17 were reported. In addition, low temperature superconductivity were also found in pure carbon such as single-walled carbon nanotubes18, and very recently, the magic twisted bilayer graphene19,20.

When T-carbon as a novel carbon allotrope was predicted in 201121, it has attracted much interest due to its exotic properties. Because of the large interstices between atoms in T-carbon, its density is 1.50 g/cm3, which is lower than that of graphite, diamond, etc. The low density with large interstices between atoms provides broad potential applications of T-carbon, such as hydrogen storage21, ion batteries22, etc. Due to global graphitization, T-carbon nanowires exhibit mechanical anisotropy and excellent ductility23. The mechanical properties of T-carbon can be significantly affected by the strain rate and grain size24. It was shown that T-carbon has the lowest lattice thermal conductivity among three-dimensional carbon allotropes25, and may be used as a thermal insulation material. T-carbon is a semiconductor with a direct band gap of about 5 eV. By doping elements, the band gap of T-carbon can be adjusted26,27. Moreover, the electron mobility in T-carbon is higher than that in conventional electron transport materials such as TiO2, ZnO and SnO2, implying its possible applications as a good photocatalyst and solar cells26–28. The Seebeck coefficient of T-carbon is comparable with, or even larger than that of some excellent thermoelectric materials, indicating its potential application as a thermoelectric material for energy recovery and conversion22. Nevertheless, the transport properties of T-carbon can be modified by applying strain, doping appropriate elements, or cutting into lower dimensional structures29,30. Recently, T-carbon has been successfully synthesized experimentally with a multi-walled carbon nanotube suspension in methanol by picosecond pulsed-laser irradiation31 and by plasma enhanced chemical vapor deposition32.

In this paper, by means of the first-principles calculations, we report that the Na-doped T-carbon is a superconductor with Tc of 11 K at ambient pressure, and Tc can reach about 19 K at pressure of 14 GPa. The increase of Tc under pressure for the Na-doped T-carbon was revealed from an enhancement of the electron-phonon coupling due to the shift of the phonon spectral weight to lower frequencies. The superconductivity was induced by the electron-phonon interaction through Bardeen-Cooper-Schrieffer (BCS) mechanism.

Calculation method. —Our first-principles calculations were based on the density-functional theory (DFT) as implemented in the QUANTUM-ESPRESSO package33, using the projector augmented wave method34. The generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof35 realization was adopted for the exchange-correlation functional. To warrant an en-
ergy convergence of less than 1 meV per atom, the plane-wave kinetic-energy cutoff was set as 80 Ry and the energy cutoff for charge density was set as 1000 Ry. The structural optimization was performed until the forces on atoms were less than 1 meV/Å. An unshifted Brillouin zone (BZ) k-point mesh of $24 \times 24 \times 24$ was utilized for electronic charge density calculations. The phonon modes are computed within density-functional perturbation theory\textsuperscript{36} on a $6 \times 6 \times 6$ $q$ mesh. The electronic transport properties were calculated with the package BoltzTraP\textsuperscript{17}.

Structure and stability. —T-carbon possesses face-centered cubic lattice with the space group of $Fd\bar{3}m$ (No.227). Each unit cell contains two tetrahedrons with eight carbon atoms, and the lattice constant is about 7.52 Å. The three unit vectors are $\vec{a} = (l/2)(0,1,1)$, $\vec{b} = (l/2)(1,0,1)$, and $\vec{c} = (l/2)(1,1,0)$, and carbon atoms occupy the Wyckoff position 4\textit{a} with $x \sim 0.0706$. The Na-doped T-carbon possesses a half-Heusler structure with the space group of $F43m$ (No.216), and Na atoms occupy the Wyckoff position 4\textit{a}(0.5; 0; 0) and carbon atoms occupy the Wyckoff positions 16\textit{e}(0.92954; 0.57046; 0.42954) or 16\textit{e}(0.32066; 0.17934; 0.32066), as shown in Fig. 1(a). The optimized lattice constant of Na-doped T-carbon is about 7.5794 Å, which is slightly larger than that of T-carbon.

To provide more information for the experimental identification, we simulated the x-ray diffraction (XRD) spectra of Na-doped T-carbon with wavelength 1.54 Å. The results are presented in Fig. 2(a). The XRD spectra peaks appear at the angles $2\theta = 20.3^\circ$ of (111), 23.5$^\circ$ of (200), 33.4$^\circ$ of (220), 39.4$^\circ$ of (311), 63.8$^\circ$ of (511), 73.9$^\circ$ of (531) and 75.2$^\circ$ of (600). The simulated infrared (IR) and Raman vibrational modes with corresponding frequencies are presented in Figs. 2(b) and (c), respectively. The IR spectra show two peaks at 77 cm$^{-1}$ (2.31 THz) and 996 cm$^{-1}$ (29.90 THz). The Raman spectra exhibit well-marked peaks at 477, 996, 1361 and 1574 cm$^{-1}$. These attainable features may be useful for future experimental identification of Na-doped T-carbon.

Electronic properties. —The electronic structures and density of states (DOS) of Na-doped T-carbon are given in Fig. 3(a). The Na-doped T-carbon is metallic with a dispersive band cross the Fermi level. The bands around the Fermi energy are dominated by the $s$ and $p$ orbitals of C atoms and $s$ orbital of Na atom. Without inclusion of spin-orbit coupling (SOC), there is a triple degenerate point at $\Gamma$ point near Fermi level. With including of SOC, the triple degenerate point at $\Gamma$ point turns into four-fold degenerate point because each band is doubly degenerate that is cased by the symmetries. Moreover, around the degenerate point, the bands have quadratic dispersion along all directions. Such point is qualified as a quadratic contact point\textsuperscript{38}, which can be transformed into a variety topological phases, and has unconventional features in the Landau spectrum under strong magnetic field\textsuperscript{38}. The Fermi surface of Na-doped T-carbon was plotted in Fig. 1(b). It is a corner-truncated tetrakaideca-

FIG. 1. (a) The cubic crystalline structure of Na-doped T-carbon NaC$_8$ with Na atoms (green color) occupying the Wyckoff position 4\textit{a}. (b) The Fermi surface of Na-doped T-carbon.

FIG. 2. (a) The simulated x-ray diffraction (XRD) spectra, (b) infrared (IR) spectra and (c) Raman spectra of Na-doped T-carbon. The X-ray with wavelength of 1.54 Å is used.
hedron with an “electronic” structure. The Fermi surface possesses the same symmetry as the crystalline structure of Na-doped T-carbon.

Superconductivity. — As the Na-doped T-carbon is a metal with an electronic Fermi surface, superconductivity may be induced by phonon-mediated electron pairing. We now focus on the phonon properties and the electro-phonon coupling (EPC) of this structure. Figure 4(a) shows the phonon spectra along high-symmetry path of L-Γ-X-W-K-Γ for the Na-doped T-carbon. No imaginary frequency mode of phonons is found, indicating that the compound is dynamically stable. It is instructive to note that there exists a wide direct band gap (9 THz) of phonons between the frequency 21-30 THz at Γ point. From the animation of phonon modes, we find that the main contribution to the low-frequency modes of the acoustic branches below 2 THz is from the vibrations of C and Na atoms in (111) plane. The vibrations of Na atoms only locate at low-frequency with a peak of phonon density of states (PhDOS) at about 2 THz. According to Migdal-Eliashberg theory\textsuperscript{39,40}, the EPC parameter $\lambda_{qv}$ can be calculated by

$$
\lambda_{qv} = \frac{\gamma_{qv}}{\pi h N(E_F) \omega_{qv}^2},
$$

where $\gamma_{qv}$ is the phonon linewidth, $\omega_{qv}$ is the phonon frequency, and $N(E_F)$ is the electronic density of states at the Fermi level. $\gamma_{qv}$ can be estimated by

$$
\gamma_{qv} = \frac{2\pi \omega_{qv}}{\Omega_{BZ}} \sum |g'_{kn,k+qm}|^2 \delta(\epsilon_{kn} - \epsilon_F) \delta(\epsilon_{k+qm} - \epsilon_F),
$$

where $\Omega_{BZ}$ is the volume of BZ, $\epsilon_{kn}$ and $\epsilon_{k+qm}$ denote the Kohn-Sham energy, and $g'_{kn,k+qm}$ represents the EPC matrix element, which describes the probability amplitude for the scattering of an electron with a transfer of crystal momentum $q$ and can be obtained self-consistently by the linear response theory\textsuperscript{41}. The Eliashberg electron-phonon spectral function $\alpha^2 F(\omega)$, and the cumulative frequency-dependent EPC $\lambda(\omega)$ of Na-doped T-carbon at ambient pressure.
lated by
\[ \alpha^2 F(\omega) = \frac{1}{2\pi N(E_F)} \sum_{q\nu} \gamma_{q\nu} \delta(\omega - \omega_{q\nu}), \] (3)

and
\[ \lambda(\omega) = 2 \int_0^\omega \frac{\alpha^2 F(\omega)}{\omega} d\omega, \] (4)

respectively.

The phonon spectra as well as the phonon density of states (PhDOS), the Eliashberg electron-phonon spectral function \( \alpha^2 F(\omega) \), and the cumulative frequency-dependent EPC \( \lambda(\omega) \) are presented in Fig. 4(b). From the PhDOS, one can observe a peak of phonon density of states from Na atoms at the low frequency. It is noted that the low-frequency phonons (below 10 THz) account for 67% of the total EPC (\( \lambda = \lambda(\infty) = 0.63 \)), while the phonons below 20 THz contribute 92% to the total EPC. The main parts of the PhDOS and \( \alpha^2 F(\omega) \) are also distributed in this region, while the phonons in high-frequency region contribute little to the EPC strength.

Utilizing our calculated \( \alpha^2 F(\omega) \) and \( \lambda(\omega) \) together with a typical value of the effective screened Coulomb repulsion constant \( \mu^* = 0.1 \), we calculate the logarithmic average frequency \( \omega_{\text{log}} \) by
\[ \omega_{\text{log}} = \exp\left[ \frac{2}{\lambda} \int_0^\infty \frac{d\omega}{\omega} \alpha^2 F(\omega) \log \omega \right]. \] (5)

The superconducting transition temperature \( T_c \) can be obtained by
\[ T_c = \frac{\omega_{\text{log}}}{1.2} \exp\left[ -\frac{1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)} \right]. \] (6)

The relative parameters of \( N(E_F) \), \( \omega_{\text{log}} \), \( \lambda \), and \( T_c \) for Na-doped T-carbon are listed in Table I. \( T_c \) of 10.9 K was obtained for Na-doped T-carbon at ambient pressure.

**Transport properties.** —The electronic specific heat of Na-doped T-carbon in normal state as a function of temperature is calculated, as presented in Fig. 5(a). It is found that at low temperature (\( T<15 \) K), the specific heat \( C(T) \sim T^3 \) (upper inset), at 15 K<\( T<50 \) K, \( C(T) \sim T^2 \) (lower inset), and at \( T>50 \) K, \( C(T) \sim T \). From Fig. 5(b), it is noted that the Lorenz number \( L \) (\( L = \kappa/\sigma T \)) at low-temperature (<50 K) is not a constant, violating the Wiedemann-Franz law. The low-temperature behavior of specific heat and electrical and thermal conductivities indicates that the normal state of Na-doped T-carbon superconductor reveals a non-Fermi liquid behavior, implying that the electron correlation play an essential role in this system. Our results on specific heat are consistent with the previous studies in superconducting Vanadium\(^{42}\).

**Pressure effect.** —To study the effect of pressure on superconducting transition temperature \( T_c \) for Na-doped T-carbon superconductor, we calculated several low-pressure cases (below 14 GPa) and the results are

\[ P(\text{GPa}) \quad N(E_F) \quad V(\text{Å}^3) \quad \omega_{\text{log}}(\text{K}) \quad \lambda \quad T_c(\text{K}) \]

\begin{tabular}{cccccc}
0 & 0.85 & 108.85 & 413.2 & 0.63 & 10.9 \\
3 & 0.83 & 106.81 & 389.8 & 0.67 & 12.1 \\
5 & 0.82 & 105.54 & 369.8 & 0.70 & 12.9 \\
7 & 0.82 & 104.35 & 348.0 & 0.74 & 13.8 \\
10 & 0.80 & 102.67 & 297.2 & 0.86 & 16.0 \\
12 & 0.79 & 101.61 & 254.4 & 0.98 & 17.2 \\
14 & 0.79 & 100.60 & 181.0 & 1.36 & 18.7 \\
\end{tabular}

**FIG. 5.** (a) Temperature dependence of electronic specific heat \( C \) in the normal state of Na-doped T-carbon superconductor. The upper and lower insets are the enlarged parts of the specific heat at different temperature ranges. (b) Temperature dependent Lorenz number \( L \) (\( L = \kappa/\sigma T \)). The inset exhibits the temperature dependent electrical (\( \sigma \)) and thermal (\( \kappa \)) conductivities over the relaxation time (\( \tau \)).
listed in Table I. With the increase of the pressure, the cumulative EPC \( \lambda \) increases, while the Eliashberg electron-phonon spectral function \( \alpha^2 F(\omega) \) decreases, and they together lead to the increase of \( T_c \). The pressure dependent of \( T_c \) is presented in Fig. 6(a). The pressure (volume) dependent transition temperature takes the following form:

\[
\frac{d\ln T_c}{d\ln V} = -\frac{d\ln T_c}{dP} = -\gamma + \Delta \left\{ \frac{d\ln \eta}{d\ln V} + 2\gamma \right\},
\]

where \( B \) is the bulk modulus (\( \sim 178 \) GPa), \( \gamma \equiv -\frac{d\ln \langle \omega \rangle}{d\ln V} \) is the Gr"{u}neisen parameter, \( \eta \equiv \langle \langle E_f \rangle \rangle / \langle \langle I^2 \rangle \rangle \) is the Hopfield parameter\(^{44} \) with \( \langle \langle I^2 \rangle \rangle \) the square of the electron-phonon matrix element averaged over the Fermi surface, and \( \Delta \equiv 1.04\lambda(1+0.38\mu')[\lambda\mu'(1+0.62\lambda)]^{-2} \). Due to the value of the first term on the right smaller than the second\(^{45} \), the sign of the pressure derivative \( dT_c/dP \) is determined by the relative magnitude of the two terms in curly brackets. The Gr"{u}neisen parameter \( \gamma \) can be directly obtained from Table I, and the Hopfield term can be determined by Eq. (7). These results are shown in Fig. 6. It can be seen that our calculated results are perfectly agreement with Eq. (7). From Fig. 6(a), we can obtain \( d\ln T_c/d\ln V = -6.94 \) based on \( B \) and \( d\ln T_c/dP(=0.039) \), where the Gr"{u}neisen parameter \( \gamma < 0 \) and Hopfield term \( d\ln \eta/d\ln V > 0 \) [Fig. 6(b)], the latter originates from the slightly decrease of electronic density of states \( N(E_f) \) under pressure as given in Table I. Therefore, we may see that the calculated increase in \( T_c \) with pressure for Na-doped T-carbon results from an enhancement of the electron-phonon coupling \( \lambda \) due to the shift of the phonon spectrum to lower frequencies. By analogy to alkali-doped fullerides\(^{46} \), the Na-doped T-carbon should be also a \( s\)-wave superconductor owing to its highly symmetric electronic type Fermi surface.

In terms of pressure dependent \( T_c \), the Na-doped T-carbon is different from the doped fullerenes \( A_3C_{60} \) (A=K, Rb, Cs), where the transition temperature decreases under pressure\(^{15,17,47–49} \). The rapid decrease of \( T_c \) under pressure in doped fullerenes \( A_3C_{60} \) is due to the sharp decrease of electronic density of states \( N(E_f) \) under pressure because of the rapid increase of the width of the conduction band as \( C_{60} \) molecules are pressed together.

**Summary.** —In this work, we show that the Na-doped T-carbon is a phonon-mediated superconductor accord with the BCS mechanism. The superconducting transition temperature \( T_c \) is estimated to be 11 K under ambient pressure, and can be reached to 19 K at the pressure of 14 GPa. The increase of \( T_c \) under pressure was unveiled from the enhancement of the electron-phonon coupling owing to the shift of the phonon spectrum to lower frequencies. The increased behavior of superconducting transition temperature of Na-doped T-carbon under pressure is in contrast to the \( A_3C_{60} \) superconductors, where the \( T_c \) decreases under pressure because of the sharp decrease of electronic density of states \( N(E_f) \) under pressure. The low-temperature behavior of specific heat (\( \sim T^3 \)) and electrical and thermal conductivities indicates that the normal state of Na-doped T-carbon superconductor reveals a non-Fermi liquid behavior, implying that the electron correlations play role in this system. Our result makes T-carbon more fascinate as a new carbon allotrope to design new functional materials.

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