Distinct superconducting properties and hydrostatic pressure effects in 2D α- and β-Mo2C crystal sheets

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Abstract

Recently, 2D Mo2C, a new member of the MXene family, has attracted much attention due to the exotic superconducting properties discovered in 2D α-Mo2C. Here, not only 2D α-Mo2C but also 2D β-Mo2C crystal sheets with distinct disordered carbon distributions were successfully grown. 2D β-Mo2C shows a much stronger superconductivity than 2D α-Mo2C, and their superconductivities have different hydrostatic pressure responses. The superconducting transition temperature $T_c$ of 2D α-Mo2C shows a dome-shaped profile under pressure, implying the existence of two competing effects arising from phononic and electronic properties, while for 2D β-Mo2C, $T_c$ decreases monotonically with increasing pressure, possibly due to phonon stiffening. These results indicate that the electronic properties have a more important influence on the superconductivity in 2D α-Mo2C compared to 2D β-Mo2C. The ordered and disordered carbon distributions in 2D α-Mo2C and β-Mo2C, respectively, may be the underlying origin for their different electronic and superconducting properties.

Introduction

In the past few years, MXenes, i.e., two-dimensional transition metal carbides (2D TMCs), have received increasing attention due to their tremendous potential for electromagnetic interference shielding, energy storage, catalysis, and electronic devices1–5. As one of the most widely studied 2D TMCs, ultrathin molybdenum carbide (Mo2C) not only shows a high electronic conductivity but also exhibits exotic superconducting properties at low temperatures6. Orthorhombic α-Mo2C and hexagonal β-Mo2C are the two stable crystalline forms of the Mo2C family, but they show distinct ordered and disordered carbon atom distributions, respectively, in almost identical Mo matrices7,8. Early reports showed that the superconducting transition temperatures ($T_c$) of α-Mo2C and β-Mo2C in bulk form lie within wide ranges of 4–12.2 K and 2.4–7.2 K, respectively, due to the inconsistent sample qualities and possible impurity phases8.

Recently, Xu et al. successfully synthesized high-quality 2D α-Mo2C crystal sheets with a chemical vapor deposition (CVD) process6. This triggered the discovery of many intriguing properties in this promising 2D TMC system, including 2D superconductivity6, quantum phase transitions7,9, nonlinear optical properties10, and fantastic physics at the interfaces between α-Mo2C and other 2D materials2,11. The $T_c$ of α-Mo2C crystal sheets is as high as 3.5 K and becomes lower in thinner crystal sheets, and the superconductivity is suppressed locally at grain boundaries6,12,13. Interestingly, disorder-enhanced superconductivity in α-Mo2C sheets was observed very recently by scanning tunneling microscopy, which was attributed...
to lattice defect-enhanced disordering and strain-induced strong coupling. In addition to the interesting electronic properties, 2D Mo2C also exhibits unique structural properties. Polarized Raman spectroscopy and transmission electron microscopy studies on 2D $\alpha$-Mo2C crystal sheets revealed unique domain structures with 60° and 120° boundaries. In particular, it was found that the domain structures can be eliminated and the $\alpha$-Mo2C sheets can be transformed into $\beta$-Mo2C by electron beam irradiation. Considering the distinct ordered and disordered carbon atom distributions in $\alpha$-Mo2C and $\beta$-Mo2C, respectively, this unique structural feature should have important impacts on the superconductivity owing to the close interaction between the electronic and structural characteristics. However, there are still no reports about the superconductivity in the 2D $\beta$-Mo2C crystal sheet and its differences with 2D $\alpha$-Mo2C.

In addition, the superconductivity can be significantly modulated by a basic thermodynamic variable, the hydrostatic pressure ($P$). A higher $dT_c/dP$ of a superconductor implies that a suitable chemical substitution or epitaxial strain at ambient pressure may be utilized to achieve an enhanced $T_c$. In particular, research on the superconducting properties under high pressures may help uncover the superconducting mechanism by revealing the impacts of different competing orders in superconducting materials. For instance, in simple metal superconductors with s or p orbital electronic conduction, such as Al, In, Sn, and Pb, a ubiquitous reduction in $T_c$ was observed due to stiffening of lattice vibration spectra under pressure, suggesting the importance of phononic properties for the superconductivity. For some transition metals with d orbital electronic conduction, such as Tl and Re, the pressure-modulated Fermi surface topology is important for the nonmonotonic pressure dependence of $T_c$, reflecting the critical role and complexity of their electronic properties. For unconventional superconductors, such as high-temperature cuprate superconductors, $T_c$ often shows a dome-like pressure dependence due to the complex and strongly correlated electronic effects. However, there is still no research devoted to the pressure effects on the superconductivities of $\alpha$-Mo2C and $\beta$-Mo2C thus far. Pressure studies may shed light on the understanding of the superconductivities in Mo2C of these two structures with different carbon atom distributions.

In this work, the crystal structures and superconductivities of 2D $\alpha$-Mo2C and $\beta$-Mo2C sheets were systematically studied. By investigating the electronic transport and superconducting properties under hydrostatic pressures, it was discovered that their $T_c$ upper critical fields ($H_{c2}$), pressure responses of the superconductivity, and transport behaviors in normal states are quite different. These different electronic properties may be highly related to the different carbon atom distributions in the $\alpha$-Mo2C and $\beta$-Mo2C sheets.

Materials and methods

Sample preparation

CVD with a Cu/Mo bilayer substrate was used to grow 2D Mo2C crystal sheets. Different from our previous report, the formations of rectangular-shaped $\alpha$-Mo2C sheets and hexagonal-shaped $\beta$-Mo2C sheets in the same batch were achieved by using a higher flow rate of methane of ~0.6 sccm. The Mo2C sheet crystals were transferred onto TEM grids for structural characterizations and 10 mm × 10 mm SiO2 (300 nm)/Si substrates for transport measurements.

Characterizations

The structures were investigated by high angle angular dark field (HAADF)-scanning transmission electron microscopy (STEM) and corresponding selected area electron diffraction (SAED) by TEM with a spherical aberration corrector (Talos F200X). The sample thicknesses were measured by an atomic force microscope (Oxford MFP-3D Infinity). Electron-beam lithography (JEOL JBX-6300FS) and a lift-off process were used to prepare Ti/Au (10/90 nm) electrodes, and e-beam irradiation at 100 kV and 10 nA was performed in the electron-beam lithography equipment. A Quantum Design Physical Property Measurement System (QD PPMS 9 T) with an HPC-33 piston-type pressure cell (Daphne 7373 oil as the pressure transmitting medium) was used to perform the resistance measurements at different magnetic fields under various pressures. The superconducting transition temperature of Sn was used to calibrate the magnitude of the pressure.

Results and discussion

Structural characteristics of 2D $\alpha$-Mo2C and $\beta$-Mo2C crystal sheets

As reported previously, 2D $\alpha$-Mo2C crystals grown by CVD at a low flow rate of methane mainly have 6 kinds of regular shapes (hexagons, rectangles, triangles, etc.), indicating a typical characteristic of good crystallization. In contrast, the 2D Mo2C sheets used in our study were grown by CVD with a high flow rate of methane and were mostly rectangular and hexagonal, with lateral sizes of 10–20 μm and thicknesses (d) of 5–30 nm. The thicknesses of the sheets were measured by atomic force microscopy, and representative images are shown in Supplementary Fig. S1. The superconducting properties of Mo2C crystal sheets are highly stable under ambient conditions due to their excellent thermal and chemical stabilities.

High-resolution STEM was utilized to characterize the crystal structures of the Mo2C sheets. Figure 1a, b shows
bright-field TEM images of the Mo$_2$C crystal sheets of rectangular and hexagonal shapes, respectively, and Fig. 1c, d shows the corresponding SAED patterns. It can be seen that the rectangular- and hexagonal-shaped Mo$_2$C sheets have different crystal lattice symmetries. The rectangular-shaped sheets of Mo$_2$C are of the $\alpha$-phase with an orthorhombic structure. As for the hexagonal-shaped sheets, they are of the $\beta$-phase with a hexagonal structure. Moreover, the $\alpha$-Mo$_2$C sheet grows along the [100] direction, while the $\beta$-Mo$_2$C sheet grows along the [0001] direction, perpendicular to their surfaces. As highlighted by the yellow circles in the SAED pattern shown in Fig. 1c, superlattice diffraction spots are observed for the $\alpha$-Mo$_2$C sheets. This feature has been proven to result from the ordered distribution of carbon atoms, which attract each other in the Mo octahedrons, leading to a regular distortion of the hexagonal close-packed Mo lattice.$^{7,8,24}$ In contrast, there is no Mo lattice distortion in the $\beta$-Mo$_2$C sheets because the disordered distribution of carbon atoms mutually offsets the interactions.$^7$ It is worth mentioning that the $\alpha$-Mo$_2$C sheets can be transformed into $\beta$-Mo$_2$C by the electron beam irradiation-induced order-disorder transition.$^7$ In other words, $\beta$-Mo$_2$C is a disordered counterpart of the ordered $\alpha$-Mo$_2$C phase at high temperature.$^{25}$

Figure 1e, f shows atomic-resolution HAADF-STEM images of $\alpha$-Mo$_2$C and $\beta$-Mo$_2$C sheets, respectively. As seen from the magnified images shown in the insets of Fig. 1e, f, there exist extra Mo lattice points (denoted by the green spheres) located at the centers of Mo hexagons, which is due to the stacking faults in the growth direction.$^{26}$ In addition, it can be seen that the Mo atoms in the $\alpha$-Mo$_2$C (along the [100] zone axis) and $\beta$-Mo$_2$C (along the [0001] zone axis) sheets have very similar atomic configurations. Actually, $\alpha$-Mo$_2$C and $\beta$-Mo$_2$C are closely crystallographically related, namely, $a_\alpha = c_\beta$, $b_\alpha = 2b_\beta$, and $c_\alpha = \sqrt{3}a_\beta$, as illustrated in Fig. 1g. Therefore, considering the almost identical Mo lattices, the main structural difference between $\alpha$-Mo$_2$C and $\beta$-Mo$_2$C sheets is the different distributions of carbon atoms.

Another interesting feature is the presence of diagonal domain boundaries in hexagonal $\beta$-Mo$_2$C sheets, as
shown in Fig. 1b. An atomic-resolution HAADF-STEM image near the boundary is shown in Fig. 1f, and the domain boundary is highlighted by the yellow dashed line. Interestingly, the lattice remains unchanged on the two sides of the boundary. The SAED patterns in each domain area are also studied (Supplementary Fig. S2), and the same SAED patterns in all areas indicate that the crystal structure is uniform throughout the whole crystal. It should be noted that diagonal domain boundaries have also been observed in hexagonal-shaped orthorhombic $\alpha$-Mo$_2$C crystal sheets, but the lattice of the adjacent domain areas rotates by 60° in plane, which results in different SAED patterns in the neighboring domains$^{15,24}$. Moreover, the fringe contrast at the domain boundary in Fig. 1f indicates that there exists a translational strain of the Mo lattice at the domain boundary of $\beta$-Mo$_2$C sheets, which is also different from the feature of $\alpha$-Mo$_2$C sheets$^{15,24}$.

**Hydrostatic pressure responses of the superconductivities in 2D $\alpha$-Mo$_2$C and $\beta$-Mo$_2$C crystal sheets**

With the distinct structural features, it will be interesting to study the transport property differences between the $\alpha$-Mo$_2$C and $\beta$-Mo$_2$C sheets by tuning a thermodynamic variable—pressure. Figure 2a, b shows the temperature dependences of the sheet resistances ($R_s$) for a 23.7-nm-thick $\alpha$-Mo$_2$C sheet (labeled $\alpha$-1) and a 13.3-nm-thick $\beta$-Mo$_2$C sheet (labeled $\beta$-1) at various hydrostatic pressures. $R_s$ is defined by $R_s = \rho/d = RW/L$, where $W$ is the width and $L$ is the length. Obviously different pressure effects on $T_c$ were observed for $\alpha$-Mo$_2$C and $\beta$-Mo$_2$C sheets, as the pressure dependences of $T_c$ in Fig. 2c, d show. Here, the top and bottom lines of the error bars are the onset temperature $T_{c\text{onset}}$ and zero resistance temperature $T_{c\text{zero}}$, respectively, and $T_{c\text{onset}}$, $T_c$, and $T_{c\text{zero}}$ are defined by the resistance dropping to 90%, 50%, and 0.1% of the normal state resistance, respectively$^{27,28}$. For $\alpha$-Mo$_2$C sheets, $T_c$ first increases and then decreases with increasing pressure, presenting a dome-like shape. For $\beta$-Mo$_2$C sheets with $T_c$ higher than that of $\alpha$-Mo$_2$C sheets, a monotonic reduction in $T_c$ under pressure with $dT_c/dP = -0.12 \text{ K GPa}^{-1}$ was obtained for $\beta$-1. Similar measurements were also performed for a 25.1-nm-thick $\alpha$-Mo$_2$C sample (labeled $\alpha$-2) and a 7.1-nm-thick $\beta$-Mo$_2$C sample (labeled $\beta$-2, $dT_c/dP = -0.10 \text{ K GPa}^{-1}$), and consistent pressure effects were observed (Supplementary Fig. S3). In addition, we noted that the resistivity transitions in some of the samples, such as $\alpha$-1 (Fig. 2a) and $\beta$-2 (Fig. S3b), show pronounced shoulders, which may be due to sample inhomogeneity$^{29}$ (such as domain boundaries$^{24}$) and/or electrode contact quality.

Here, the hydrostatic pressure effect on the superconductivity of Mo$_2$C can be discussed in the BCS framework$^{30,31}$. Typically, the hydrostatic pressure
dependences of $T_c$ for BCS superconductors can be analyzed in terms of McMillan theory as follows\cite{32}:

$$T_c = \frac{\Theta_D}{1.45} \exp\left\{ -\frac{1.04(1+\lambda)}{\lambda - \mu^* (1+0.62\lambda)} \right\}. \quad (1)$$

Here, $\Theta_D$ is the Debye temperature, $\lambda$ is the electron-phonon coupling parameter, and the Coulomb pseudopotential $\mu^*$ is equal to 0.1 and is insensitive to pressure.\cite{21,33,34} Equation (1) has successfully described the pressure-manipulated $T_c$ in many systems, including elemental superconductors\cite{19}, transition-metal nitrides\cite{35}, MgB$_2$, LaH$_{10}$, etc.\cite{37,38}. Based on Eq. (1), the following relationship can be obtained by the logarithmic volume derivative:\cite{33}

$$\frac{d\ln T_c}{d\ln V} = -B \frac{d\ln T_c}{dP} = -\gamma + \Lambda \left( \frac{d\ln \eta}{d\ln V} + 2\gamma \right), \quad (2)$$

where $V$ is the sample volume and $B$ is the bulk modulus parameter. $\eta = N(E_F) / (T^2)$ is the product of the Fermi-level density of states $N(E_F)$ with the average squared electronic matrix element $(T^2)$. $\gamma = -d\ln(\omega) / d\ln V$ is the Grüneisen parameter, $\omega$ is the mean phonon frequency, and $\Lambda = 1.04 \times [1 + 0.38\mu^* (\lambda - \mu^* (1+0.62\lambda))]^{-2}$. It can be seen that Eq. (2) contains the electron-phonon coupling, the density of states at the Fermi level, and the energy scale of the phonon excitations (Debye frequency). The terms $\gamma = -d\ln(\omega) / d\ln V$ and $d\ln \eta / d\ln V$ represent the variations in the lattice and electronic characteristics with volume, respectively. It has been noted that the electronic term $d\ln \eta / d\ln V$ typically equals $-1$ for simple metal superconductors ($s$ or $p$ orbital electrons) and $-3$ to $-4$ for transition metal superconductors ($d$ orbital electrons).\cite{21,33}. For Mo$_2$C, $N(E_F)$ is mainly contributed by the 4$d$ orbitals of the molybdenum atoms.\cite{40} According to Eq. (2), the negative electronic term $d\ln \eta / d\ln V$ tends to enhance $T_c$ under pressure.\cite{21} However, for most BCS superconductors, the effect from the pressure-induced phonon stiffening (i.e., $\gamma > 0$) overcomes the effect related to the change in electronic properties, which leads to a ubiquitous decrease in $T_c$.\cite{21}

For $\beta$-Mo$_2$C sheets, the negative $dT_c / dP = -0.12$ K GPa$^{-1}$ means a positive $-B d\ln T_c / dP$ on the left side of Eq. (2). Using $T_c = 4.33$ K at ambient pressure, $\Theta_D = 590$ K, and $\mu^* = 0.1$, we obtained $\lambda = 0.46$ and $\Delta = 4.46$ from Eq. (1). The electron–phonon coupling parameter $\lambda = 0.46$ is in agreement with the value $\lambda = 0.5$ obtained from first-principles density-functional theory calculations.\cite{30} Inserting these values, $dT_c / dP = -0.12$ K GPa$^{-1}$, $d\ln \eta / d\ln V = -3$ to $-4$, and $B = 290$ GPa$^{-1}$ into Eq. (2), we obtain $\gamma = 2.7$ to 3.3. The large and positive $\gamma$ suggests significant stiffening of the lattice vibration spectrum under pressure, which results in the reduction in $T_c$ in $\beta$-Mo$_2$C sheets.

For $\alpha$-Mo$_2$C sheets, $T_c$ first increases under low pressures and then decreases with further increases in pressure, leading to a distinct dome-like pressure dependence of $T_c$, which is obviously different from the decrease in $T_c$ in $\beta$-Mo$_2$C sheets. Typically, an increase in $T_c$ with pressure for a BCS superconductor occurs when the effect of the variation arising from the electronic characteristics with pressure overcomes the pressure-induced phonon stiffening effect. For example, in some BCS superconductors (e.g., Lu, Nb$_2$Ge, and NbSe$_2$), owing to the pressure-induced complex variation in electronic properties, $T_c$ initially increases under low pressures.\cite{21,42,43} Similarly, for $\alpha$-Mo$_2$C sheets, the increase in $T_c$ under low pressures may also be because of the complex variation in electronic properties overcomes the phonon stiffening. For the decrease in $T_c$ under high pressures, the phonon stiffening effect may overcome the electronic effect, similar to that in $\beta$-Mo$_2$C sheets. In other words, the distinct pressure responses of the superconductivities in $\alpha$- and $\beta$-Mo$_2$C suggest their different electronic and phononic properties under pressure.

Upper critical fields $H_{c2}$ of 2D $\alpha$-Mo$_2$C and $\beta$-Mo$_2$C crystal sheets

To further understand the different superconducting characteristics of $\alpha$-Mo$_2$C and $\beta$-Mo$_2$C sheets, their upper critical fields $H_{c2}(T)$ (defined by the resistance dropping to 90% of the normal state resistance\cite{28}) were studied under various pressures. Based on the temperature-dependent resistances measured in various perpendicular magnetic fields under different pressures (Supplementary Fig. S4), the upper critical fields $H_{c2}(T)$ of $\alpha$-Mo$_2$C (sample $\alpha$-1) and $\beta$-Mo$_2$C (sample $\beta$-1) sheets are shown in Fig. 3a. For 2D superconducting systems, $H_{c2}(T)$ can be well fitted by the following relationship:\cite{44,45}

$$H_{c2}(T) = H_{c2}(0)(1 - T / T_{c,\text{onset}})^{1+\alpha}, \quad (3)$$

where $H_{c2}(0)$ and $\alpha$ are the fitting parameters, and $\alpha \sim 0.34$ and $\alpha \sim 0.04$ are obtained for $\alpha$-1 and $\beta$-1, respectively. Figure 3b shows the pressure dependences of $H_{c2}(0)$ for $\alpha$-1 and $\beta$-1 sheets with distinct nonmonotonic and monotonic curvatures, respectively. At ambient pressure, the $H_{c2}(0)$ for $\alpha$-Mo$_2$C sheets is 0.34 T, comparable with earlier reports,\cite{6,13} while the $H_{c2}(0)$ of 5.55 T for $\beta$-Mo$_2$C...
sheets is ~16 times that for α-Mo2C sheets. The initial slopes \(d H_{c2}/dT\) for the α-Mo2C and β-Mo2C sheets are −0.06 and −1.11, respectively, and they are almost independent of pressure. Moreover, similar measurements were also performed for the \(H_{c2}(T)\) in α-Mo2C (sample α-3, \(d = 18.9\) nm) and β-Mo2C (sample β-3, \(d = 15.6\) nm) sheets in parallel magnetic fields, and much larger \(H_{c2}(0)\) in parallel magnetic fields than that in perpendicular magnetic fields can be observed, as expected for 2D superconductor systems (Supplementary Fig. S6).

The α-Mo2C sheet with an ordered carbon atom distribution was considered to be a clean superconductor\(^6\), while for β-Mo2C, it should be treated as a dirty superconductor system due to its disordered carbon atom distribution. Typically, for a dirty superconductor, \(H_{c2}\) is highly related to the mean free path \(l\) and the coherence length \(\xi\) as follows\(^46\):

\[
H_{c2}(0) \approx \Phi_0/2\pi \xi l \propto 3 \times 10^4 T_c/v_F l,
\]

where \(\Phi_0\) is the magnetic flux quantum and \(v_F\) is the Fermi velocity. The product \(v_F l\) is proportional to the electron diffusion coefficient, and a smaller \(v_F l\) typically indicates stronger disorder\(^47,48\). According to Eq. (4), the \(H_{c2}\) of β-Mo2C should be proportional to its \(T_c\) and inversely proportional to \(v_F l\). Therefore, the dramatic enhancement of the \(H_{c2}\) in β-Mo2C can be due to its higher \(T_c\) and smaller \(v_F l\) induced by the disordered carbon atom distribution. From the above discussions, it can be seen that the significant differences between α-Mo2C and β-Mo2C sheets should be related to the electronic structure differences, which are affected by the ordered and disordered carbon distributions. The detailed contributions of the ordered and disordered carbon atom distributions to the electronic structures of Mo2C require further theoretical studies in the future.

Relationships among the thickness, residual resistivity ratio, and superconductivity of samples

For 2D sheets, the sample thickness generally has a significant influence on the electronic transport properties\(^49,50\). It is thus interesting to study the effects of thickness on the superconductivities of α-Mo2C and β-Mo2C sheets. Figure 4a, b shows the superconducting transitions of representative α-Mo2C and β-Mo2C crystal sheets with different sheet thicknesses, respectively. It can be seen that the values of \(T_c\) decrease with decreasing thickness for both α-Mo2C and β-Mo2C crystal sheets. Figure 4a, b shows that the superconducting transitions of representative α-Mo2C and β-Mo2C crystal sheets with different sheet thicknesses, respectively. It can be seen that the values of \(T_c\) decrease with decreasing thickness for both α-Mo2C and β-Mo2C crystal sheets. Typically, in many superconducting systems, \(T_c\) is maximum \((T_{c-max})\) in the bulk sample and gradually decreases with decreasing sample thickness, and when the thickness is below a certain level \((d_c)\), the sample will no longer be in the superconducting state\(^51,52\). Based on the Ginzburg-
Landau equations, Simonin proposed a relationship between $T_c$ and the thickness as follows:

$$T_c = T_{c,\text{max}}(1 - d_c/d).$$  \hspace{1cm} (5)

Figure 4c shows the evolution of $T_c$ as a function of the inverse of the thickness ($1/d$), and the experimental results can be fitted very well by Eq. (5) with $T_{c,\text{max}} = 4.03$ K and $d_c = 3.3$ nm (7 unit cells) for α-Mo$_2$C sheets and $T_{c,\text{max}} = 5.67$ K and $d_c = 2.8$ nm (6 unit cells) for β-Mo$_2$C sheets. The $T_{c,\text{max}}$ values of α- and β-Mo$_2$C fall in the ranges of their bulk $T_c$ of 4 K-12.2 K and 2.4 K-7.2 K, respectively, and the Mo$_2$C sheets may no longer be in a superconducting state when the sample thicknesses are below 6~7 unit cells. Furthermore, the $T_c$ of β-Mo$_2$C sheets is ~1.6 K higher than that of α-Mo$_2$C sheets with similar thicknesses. The higher $T_c$ of β-Mo$_2$C than that of α-Mo$_2$C may be due to the enhanced electron-phonon coupling related to the disordered carbon distribution in β-Mo$_2$C as well as the higher Debye temperature of β-Mo$_2$C (~590 K) than that of α-Mo$_2$C (~580 K). To further illustrate the role of the carbon distribution in Mo$_2$C, e-beam irradiation was used to produce varying degrees of disorder in the carbon distribution, and the order-disorder transition from α-Mo$_2$C to β-Mo$_2$C results in increases in $T_c$ and the sheet resistance (Supplementary Figs. S7 and S8), consistent with Fig. 4.

According to the BCS superconducting mechanism, a stronger electron-phonon coupling, related to the intrinsic phononic and electronic properties, will lead to a higher $T_c$, which can be reflected by the normal state properties. For example, in elemental superconductors, a relatively strong electron-phonon coupling often results in a relatively poor electronic conduction, and disorder-enhanced electron-phonon coupling accompanied by an increase in resistivity was also observed in other superconductors, such as Mo$_3$Ge. Thus, it will be interesting to study the normal state transport behaviors of α-Mo$_2$C and β-Mo$_2$C sheets. Figure 5a shows the temperature dependence of the normalized resistance $R_s/R_{s,300K}$ of representative α-Mo$_2$C (d = 23.2 nm) and β-Mo$_2$C (d = 21.8 nm) sheets from 1.9 K to 300 K. A faster decrease in the normal-state resistance with decreasing temperature was observed in the α-Mo$_2$C sheets, which indicates a stronger metallicity in the α-Mo$_2$C.

To obtain a more comprehensive assessment of the normal state properties of α-Mo$_2$C and β-Mo$_2$C sheets, the thickness dependences of their residual resistance ratio ($RRR = R_{s,300K}/R_{s,6K}$) and sheet resistance at 10 K ($R_{s,10K}$) are shown in Fig. 5b, c, respectively. Compared with α-Mo$_2$C sheets, β-Mo$_2$C shows a much smaller $RRR$ and a much higher $R_{s,10K}$. In particular, the thickness-dependent trends for $RRR$ and $R_{s,10K}$ are obviously
different between $\alpha$-Mo$_2$C and $\beta$-Mo$_2$C sheets. A thicker $\alpha$-Mo$_2$C sheet possesses a higher RRR and a smaller $R_s$ at 10K, while a thicker $\beta$-Mo$_2$C sheet has a lower RRR and a larger $R_s$ at 10K. A larger $R_s$ means less electronic scattering, which will lead to a better electrical conductivity, namely, a smaller sheet resistance\(^{56}\). The electronic scattering in 2D sheet or film mainly results from two aspects: surface and/or interface scattering and intrinsic lattice scattering. In $\alpha$-Mo$_2$C sheets, the intrinsic lattice scattering is relatively weak due to the ordered carbon atom distributions, and the surface scattering is dominant. Thus, for $\alpha$-Mo$_2$C sheets, the importance of the surface scattering declines for thicker samples, which leads to an overall lower electronic scattering, a higher RRR, and a smaller sheet resistance. For $\beta$-Mo$_2$C sheets, the disordered carbon atom distributions will result in strong intrinsic lattice scattering. As a result, the overall stronger lattice scattering in a thicker $\beta$-Mo$_2$C sheet will lead to a smaller RRR and a larger sheet resistance.

Furthermore, the relationships between the $T_c$ and RRR of $\alpha$-Mo$_2$C and $\beta$-Mo$_2$C sheets plotted in Fig. 5d show different variation trends, and $\beta$-Mo$_2$C has a higher $T_c$ with a smaller RRR, in contrast to $\alpha$-Mo$_2$C. It is worth mentioning that a higher $T_c$ usually accompanies a higher RRR due to the less scattering and higher sample quality\(^{49,56}\), which is the case for $\alpha$-Mo$_2$C sheets. In contrast, a higher $T_c$ with a lower RRR was observed in the $\beta$-Mo$_2$C sheets. Considering the almost identical Mo lattices in $\alpha$-Mo$_2$C and $\beta$-Mo$_2$C, it can be concluded that although the disordered distribution of carbon atoms increases the electronic scattering, it may promote the electron-phonon coupling and is beneficial for higher $T_c$, similar to Mo$_3$Ge\(^{55}\).

**Conclusions**

In summary, the $\alpha$- and $\beta$-phases of Mo$_2$C sheet crystals with rectangular and hexagonal shapes, respectively, were successfully grown by the CVD technique. It was found that the intriguing superconductivities in Mo$_2$C sheets of $\alpha$- and $\beta$-phases have different hydrostatic pressure responses. Similar to conventional superconductors, $\beta$-Mo$_2$C sheets have a monotonic decrease in $T_c$ under pressure due to the increase in the average vibration frequency of phonons, while the $T_c$ of $\alpha$-Mo$_2$C sheets shows a dome-shaped profile under pressure, which suggests the more critical role of the electronic properties in $\alpha$-Mo$_2$C sheets. The $\beta$-Mo$_2$C sheets not only possess a higher $T_c$ but also have a much larger $H_C$ (an order of magnitude larger than that of the $\alpha$-Mo$_2$C sheets), which may be related to a stronger electron-phonon coupling strength as well as a smaller $\nu_{el}$. Furthermore, the thickness-dependent $T_c$, RRR, and normal-state resistances were analyzed for $\alpha$-Mo$_2$C and $\beta$-Mo$_2$C sheets, and the distinct thickness-dependent trends in the normal state can be explained by the stronger lattice scattering in $\beta$-Mo$_2$C sheets. The distinct superconducting and normal-state electronic properties in $\alpha$-Mo$_2$C and $\beta$-Mo$_2$C sheets should be related to their ordered and disordered carbon atom distributions, respectively. Our study provides a deep understanding of the superconductivity in $\alpha$-Mo$_2$C sheets and lays the groundwork for future research into $\beta$-Mo$_2$C sheets, and the results may have great implications in the study of MXenes and superconductivity.

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C.X. prepared the samples in the lab led by W.C.R. and H.M.C. X.L., Y.J.F., and C. M. performed the measurements. X.G.L., Y.W.Y., and W.C.R. designed and supervised the experiments. Y.J.F., X.L., W.C.R., Y.W.Y., and X.G.L. wrote the manuscript. All the authors contributed to the refinement of the manuscript. Y. J.F., C.X., and X.L. contributed equally.

**Conflict of interest**

The authors declare that they have no conflict of interest.

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