Angular dependence of the upper critical field in the high-pressure 1T′ phase of MoTe₂

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Superconductivity in the type-II Weyl semimetal candidate MoTe₂ has attracted much attention due to the possible realization of topological superconductivity. Under applied pressure, the superconducting transition temperature is significantly enhanced, while the structural transition from the high-temperature 1T′ phase to the low-temperature 1T phase is suppressed. Hence, applying pressure allows us to investigate the dimensionality of superconductivity in 1T′-MoTe₂. We have performed a detailed study of the magnetotransport properties and upper critical field \( H_c \) of MoTe₂ under pressure. The magnetoresistance (MR) and Hall coefficient of MoTe₂ are found to decrease with increasing pressure. In addition, the Kohler’s scalings for the MR data above \(~11\) kbar show a change of exponent whereas the data at lower pressure can be well scaled with a single exponent. These results are suggestive of a Fermi-surface reconstruction when the structure changes from the 1T′ phase. The \( H_c \)-temperature phase diagram constructed at 15 kbar, with \( H \parallel ab \) and \( H \perp ab \), can be satisfactorily described by the Werthamer–Helfand–Hohenberg model with the Maki parameters \( \alpha \sim 0.77 \) and 0.45, respectively. The relatively large \( \alpha \) may stem from a small Fermi surface and a large effective mass of semimetallic MoTe₂.

The angular dependence of \( H_c \) at 15 kbar can be well fit by the Tinkham model, suggesting the two-dimensional nature of superconductivity in the high-pressure 1T′ phase.

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I. INTRODUCTION

Transition-metal dichalcogenides WTe₂ and MoTe₂ have recently been intensively studied owing to their intriguing physical properties [1]. For example, extremely large magnetoresistance (MR) has been reported in both WTe₂ [2] and MoTe₂ [3]. Further interests are generated when they are considered as candidates of type-II Weyl semimetals [4–7], which would have a pair of topologically nontrivial Weyl points at the boundary of electron and hole Fermi surfaces. A recent focus on these materials concerns their superconductivity because this opens up the possibility of finding topological superconductivity, which could stabilize exotic Majorana fermions [8]. These features are promising for the development of spintronics devices.

Both WTe₂ and MoTe₂ consist of weakly bonded (W/Mo)-Te layers stacked along the \( c \) axis. While WTe₂ crystallizes in a noncentrosymmetric orthorhombic \( T_d \) phase (space group \( Pmn2_1 \)) at ambient pressure, MoTe₂ undergoes a first-order structural transition from a centrosymmetric monoclinic 1T′ phase (space group \( P2_1/m \)) to the \( T_d \) phase at \( T_c \sim 250 \) K. At low temperature, a superconducting phase transition can additionally be observed at \( T_c \sim 0.1 \) K [9]. In contrast, superconductivity in bulk WTe₂ can only be stabilized at high pressure (\( \gtrsim 25 \) kbar) [10–12].

An interesting interplay between structural and superconducting transitions in MoTe₂ is revealed upon the application of hydrostatic pressure: \( T_c \) can be suppressed to zero at \( \sim 10 \) kbar, i.e., at high pressure, the \( T_d \) phase can be completely removed and the 1T′ phase takes over. Meanwhile, \( T_c \) is rapidly enhanced, leading to a 30-fold increase in \( T_c \) (\( \sim 4 \) K) at \( \sim 15 \) kbar [9,13–16]. A similar enhancement of \( T_c \) can also be observed in S-, Se- and Re-doped MoTe₂ as well as Te-deficient MoTe₂, but \( T_c \) is only slightly suppressed before suddenly vanishing with increasing doping or deficiency levels [13,17–19]. Therefore, pressurized MoTe₂ presents an opportunity to study the nature of the superconductivity in the 1T′ phase.

Previous high-pressure studies reported the intrinsic superconductivity in many topological materials, including Cd₃As₂ [20], TaAs [21], TaP [22], ZrTe₅ [23], HfTe₅ [24], TaIrTe₄ [25,26], and YPtBi [27–29]. In particular, the topological semimetal YPtBi has been found to be an unconventional spin-3/2 superconductor, which is beyond the value of spin in triplet superconductors [30]. In MoTe₂, the enhanced \( T_c \) at high pressure has not been envisaged in previous density-functional theory predictions [31]. This discrepancy may be due to the two-dimensional (2D) nature of the superconductivity in MoTe₂. Recently, Heikes et al. [14] suggested that applying pressure to MoTe₂ would induce the decoupling of Mo-Te layers, leading to a more-2D structure. If this high-pressure superconducting phase is quasi-2D, it would be a possible route to search for topological superconductivity [8]. Thus, it is desirable to gauge both the anisotropy of the normal

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state and the superconducting state under pressure. The case of WTe$_2$ is particularly instructive: while its crystal structure is of layered nature and hence highly two-dimensional, the electronic structure and the superconducting state (at $\sim$100 kbar) are practically isotropic. These conclusions for WTe$_2$ are drawn from quantum oscillations [32–34], angle-resolved photoemission spectroscopy (ARPES) [34,35], and angular dependence of the magnetoresistance [36] for the electronic structure, and the angular dependence of the upper critical field ($H_{c2}$) for the superconducting state [12]. In this article, we report the anisotropy of the superconductivity in the 1$T'$ phase via a measurement of $H_{c2}$ against the field angle down to 30 mK at 15 kbar.

II. EXPERIMENT

Single crystals of MoTe$_2$ were synthesized by using the NaCl-flux method, as described elsewhere [3]. Temperature-dependent electrical transport measurements were performed by a standard four-probe technique in a Bluefors dilution fridge. Hydrostatic pressure dependence was studied by using a piston-cylinder clamp cell with glycerin as the pressure-transmitting medium. The single crystals used in this study. Figure 1(a) additionally illustrates the 1$T'$ phase via a measurement of $H_{c2}$ against the field angle down to 30 mK at 15 kbar.

III. RESULTS AND DISCUSSION

Figure 1(a) shows the temperature dependence of the zero-field electrical resistivity $\rho(T)$ (solid lines) of MoTe$_2$ (S1) at ambient pressure. A pronounced anomaly in $\rho(T)$ is recorded at $T_c \approx 260$ K. This anomaly exhibits a strong hysteresis, signaling a first-order structural transition from the 1$T'$ to the $T_m$ phase, which is consistent with previous reports [3,9,13–15]. The resultant temperature-pressure phase diagram is generally consistent with previous studies [9,13–16]. In particular, zero resistance has been observed in the superconducting state at all pressures investigated [Fig. 1(c)], in contrast with several reports which covered the same pressure range [14,15].

In the established temperature-pressure phase diagram, we are able to track the pressure evolution of the electronic structure via magnetotransport. Figures 2(a) and 2(b) show the field dependence of the transverse resistivity $\rho_{xy}$ and the Hall resistivity $\rho_{yx}$ at 30 mK at different pressures, respectively. The superconducting transition can be seen in both $\rho_{xx}$ and $\rho_{xy}$ at all pressures. At low temperatures, because of the superconducting transition, $\rho_{xx}$ is zero. Therefore, $\rho_{xy}(0)$ is extrapolated from the polynomial fitting of the normal-state data. $\rho_{xy}$ is determined by first antisymmetrizing the measured voltage at positive and negative field, and converting by considering the geometry of the sample. The tiny peak at low field, which is close to the superconducting transition, might be an experimental artifact and is excluded from the analysis. Figure 2(c) shows the pressure dependence of MR [$= \Delta \rho_{xx}/\rho(0)$] at 13 T and 30 mK derived from Fig. 2(a). Figure 2(d) displays the pressure dependence of the Hall coefficient $R_H$ at 30 mK, which is extracted by fitting the $\rho_{xy}$ data in Fig. 2(b) with as the horizontal intercepts of the straight line extrapolated from the transition region [see dashed line in Fig. 1(c)]. Figure 1(d) summarizes the pressure dependence of $T_s$ and $T_c$; upon increasing pressure, $T_s$ decreases and extrapolates linearly to 0 K at 11 kbar while $T_c$ is significantly enhanced. The inset shows the superconducting transition of S2 at ambient pressure.
\[ \rho_{xy} = R_H H + \beta H^3, \] where \( \beta H^3 \) accounts for the small non-linearity in \( \rho_{xy} \). Only the normal-state data below 4 T are used for this analysis [see gray dashed line in Fig. 2(b)]. When pressure is applied, MR(13 T, 30 mK) first decreases rapidly before levelling off above \( \sim 11 \) kbar, indicating a drastic decrease of carrier mobilities. Meanwhile, a significant initial suppression of \( |R_H| (30 \text{ mK}) \) is observed, followed by a nearly constant \( |R_H| (30 \text{ mK}) \) above the same pressure \( (\sim 11 \text{ kbar}). \) \( R_H \) (30 mK) is negative for all pressures studied, indicating that electrons dominate the electronic transport, while the relative size of electron Fermi pockets increases with pressure. The relatively weak pressure dependence of \( |R_H| (30 \text{ mK}) \) and MR(13 T, 30 mK) above \( \sim 11 \) kbar is consistent with the removal of the 1\( _{ab} \) phase.

Figure 3 shows the Kohler plots at 5.8, 11, 15, and 17 kbar, respectively. MR against \( H/\rho(0) \) is plotted, where \( \rho(0) \) is the zero-field resistivity at a fixed temperature [37]. At 5.8 kbar, the data at different temperatures collapse onto a single curve which is nearly quadratic in field, indicating that Kohler’s rule is obeyed. The observation of the Kohler’s rule has also been demonstrated at ambient pressure [38]. However, at 15 and 17 kbar, Kohler’s scalings are less satisfied and, when plotted on log-log scales, a slope change is detected. The slope change is also noticeable at 11 kbar [Fig. 3(b)], although the feature is much weaker. This indicates a change in the field exponent and is reminiscent of the case of LaSb [39], in which a similar change of exponent is noticeable in the Kohler plot at ambient pressure. In LaSb, this behavior is attributed to the different mobilities associated with different electron Fermi pockets. Thus, if the change of the field exponent detected in MoTe\textsubscript{2} at \( \geq 11 \) kbar is similarly rooted on the details of Fermiology, the Fermi surfaces could be different from those at \( < 11 \) kbar. This is consistent with the pressure evolution of \( |R_H| (30 \text{ mK})| \)

\[ H^{\text{orb}}(0) = -0.693 T_c \frac{dH_{c2}}{dT} \bigg|_{T=T_c}. \]

The initial slope \( (dH_{c2}/dT)_{T=T_c} \) is \(-0.26 \) T/K and \(-0.12 \) T/K for \( H \parallel ab \) and \( H \perp ab \), respectively. Thus, \( H^{\text{orb}}(0) \) are estimated as 0.65 and 0.29 T, respectively, which are larger than the experimental data at the 0 K limit \( [H_{c2}(0)] \). The suppression of \( H_{c2}(0) \) is more pronounced with \( H \parallel ab \), and this suppression can be described by the Maki parameter \( \alpha \). The WHH formula with a finite \( \alpha \) is used to fit \( H_{c2}(T) \), as displayed in Fig. 4, and the values of \( \alpha \) are 0.77 for the \( H \parallel ab \) direction and 0.45 for the \( H \perp ab \) direction.

The Maki parameter \( \alpha \) can be written as

\[ \alpha = \sqrt{2H^{\text{orb}}(0)/H_F(0)} \sim \frac{m^*\Delta(0)}{E_F}, \]
where $H_{F}(0)$ and $\Delta(0)$ are the Pauli-limiting upper critical field and the magnitude of the superconducting gap at the zero-temperature limit, respectively, and $E_F$ is the Fermi energy. Thus, $\alpha$ describes the relative strength of the orbital and spin-paramagnetic (Zeeman) effects. For a conventional metal, $E_F$ is $\sim 1$ eV while $\Delta(0)$ is $\sim 1$ meV, $\alpha$ is usually much smaller than 1. Therefore, the value of $\alpha = 0.77$ is unexpected, indicating a non-negligible spin-paramagnetic contribution to the pair breaking. As stipulated in Eq. (2), an enhanced spin-paramagnetic contribution can come from a small Fermi surface, a large effective mass, or a large $\Delta(0)$. Since $T_c$ is low in this system, $\Delta(0)$ alone cannot drive the enhancement of $\alpha$. However, the importance of electron-electron correlations has recently been highlighted [47,48]. Together with the semimetallic nature of MoTe$_2$, the enhancement of $\alpha$ can probably be traced back to the low $E_F$ and high $m^*$. Another possible scenario is that the suppression of $H_{c2}$ could be attributed by the multiband effect with large tunneling between the valleys in Dirac and Weyl semimetals, according to the recent calculation [49].

We now assess the anisotropy of the superconductivity in the $1T'$ phase via a full angular dependence of the upper critical field $H_{c2}(\theta)$ at selected temperatures between 30 mK ($0.008T_c$) and 2.2 K ($0.61T_c$), as illustrated in Fig. 5(a). The definition of the angle $\theta$ is shown in Fig. 5(c), where $\theta = 0^\circ$ ($90^\circ$) corresponds to $H \parallel ab$ ($H \perp ab$). At all temperatures studied, $H_{c2}(\theta)$ exhibits a distinct cusp around $H \parallel ab$, which can be well described by the Tinkham model for 2D superconductivity [50]:

$$\left[ \frac{H_{c2}(\theta)\sin(\theta)}{H_{c2}(90^\circ)} \right]^2 + \left[ \frac{H_{c2}(\theta)\cos(\theta)}{H_{c2}(90^\circ)} \right]^2 = 1. \quad (3)$$

Figure 5(b) compares the 2D Tinkham model and the three-dimensional (3D) anisotropic mass Ginzburg–Landau (G-L) model. The 3D anisotropic mass G-L model clearly fails to capture the cusp at $0^\circ$. Therefore, the superconductivity in $1T'$ MoTe$_2$ is identified to be two-dimensional. This is in sharp contrast with the case of WTe$_2$ at 98.5 kbar, in which $H_{c2}(\theta)$ can be described by the 3D anisotropic mass G-L model [12].

Despite the success of the Tinkham model in describing $H_{c2}(\theta)$, the anisotropy factor $\gamma = H_{c2}(0^\circ)/H_{c2}(90^\circ)$ is 2.1, which is rather low (inset of Fig. 4) and only slightly larger than the $\gamma$ of 1.7 established in WTe$_2$ [12]. Furthermore, the in-plane and out-of-plane coherence lengths at the zero-temperature limit, $\xi_\parallel$ and $\xi_\perp$, respectively, can be extracted from the $H_{c2}$ data, giving $\xi_\parallel = 35.6$ nm and $\xi_\perp = 17.8$ nm. The value of $\xi_\perp$ is much larger than the interlayer distance, which is surprising considering the 2D nature of the superconductivity. In fact, the present case is reminiscent of CaAlSi, a superconductor with a MgB$_2$-like structure. In CaAlSi, $H_{c2}(\theta)$ also follows the Tinkham model with a rather low anisotropy factor [51]. There, $\xi_\perp$ is also larger than the thickness of the normal layer, and $\gamma$ ranges from $\sim 2$ (similar to the present study) at 0.5$T_c$ to $\sim 3.5$ at $\sim 0.9T_c$. The large out-of-plane coherence length for a 2D superconductor remains a puzzle and has to be reconciled in the future.

**IV. CONCLUSIONS**

In summary, we have constructed the temperature-pressure phase diagram of MoTe$_2$ and investigated the anisotropy of superconductivity of the high-pressure $1T'$ phase at 15 kbar. The first-order structural phase transition temperature $T_c$ (from the high-temperature $1T'$ phase to the low-temperature $T_d$ phase)
is suppressed with applied pressure and vanishes at \(~11\) kbar, while the superconducting transition temperature \(T_c\) is significantly enhanced. With the application of pressure, the magnetoresistance (MR) and Hall coefficient decrease and saturate to low values at \(>11\) kbar. The Kohler scaling can well describe the MR data at all pressures. Meanwhile, a change of exponent is observed at high pressure, suggestive of a Fermi-surface reconstruction. Thus, the temperature-pressure phase diagram, together with the magnetotransport measurements, support the conclusion that the superconductivity at \(>11\) kbar is in the 1\(T'\) phase. Using the Werthamer–Helfand–Hohenberg model with the inclusion of the Maki parameter \(\alpha\), the temperature dependence of the upper critical field \(H_{c2}\) at 15 kbar, obtained at \(H \parallel ab\) and \(H \perp ab\), can be nicely described with \(\alpha = 0.77\) for \(H \parallel ab\) and \(\alpha = 0.45\) for \(H \perp ab\). These surprisingly large \(\alpha\) indicate the presence of the spin-paramagnetic effect. This behavior may be related to the low Fermi energy in the semimetallic 1\(T'\)-MoTe\(_2\), and the large effective mass due to the non-negligible electron-electron correlation. Finally, the angular dependence of \(H_{c2}\) can be described by the Tinkham model over a wide temperature range, indicating that the dimensionality of the superconducting state in the high-pressure 1\(T'\) phase is two-dimensional in nature.

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