Superconductivity in tantalum self-intercalated 4Ha-Ta1.03Se2

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Abstract
TaSe2 has several different polytypes and abundant physical properties, such as superconductivity and charge density waves (CDW), which have been investigated in the past few decades. However, there has been no report on the physical properties of the 4Ha polytype up to now. Here we report the crystal growth and discovery of superconductivity in the tantalum self-intercalated 4Ha-Ta1.03Se2 single crystal with a superconducting transition onset temperature of $T_c \approx 2.7$ K, which is the first observation of superconductivity in the 4Ha polytype of TaSe2. A slightly suppressed CDW transition is found around 106 K. A large $\mu_0H_c^2/T_c$ value of about 4.48 is found when a magnetic field is applied in the ab-plane, which probably results from the enhanced spin–orbit coupling. Special stacking faults are observed, which further enhance the anisotropy. Although the density of states at the Fermi level is lower than that of other polytypes, $T_c$ remains the same, indicating that the stack mode of the 4Ha polytype may be beneficial to superconductivity in TaSe2.

Keywords: transition metal dichalcogenide, superconductivity, charge-density waves

(Some figures may appear in colour only in the online journal)

1. Introduction

Transition metal dichalcogenides (TMDCs) are $TX_2$-type compounds ($T =$ transition metal, $X =$ S, Se, Te), which exhibit many fascinating properties, such as superconductivity [1], CDW [2], large magnetoresistance [3], and topological semimetals [4], etc. TMDCs have a layered structure, in which each layer consists of a $X – T – X$ sandwich. There are two different types of sandwich: octahedral and trigonal. The layers are coupled by van der Waals forces. Due to the different sandwich types and different stack modes, TMDCs often have many polytypes [5], such as 1T, 2Ha, 2Hb, 3R, etc. The number dictates the number of layers in one unit cell, and the capital letter represents the crystal system, i.e. $T$ is tetragonal, $H$ is hexagonal and $R$ is rhombohedral. Hexagonal TMDCs also have different types, therefore lowercase letters are used to distinguish them. In TMDCs, the modulation of the CDW state always leads to interesting phenomena. For instance, with Cu intercalation or the electric-field gating effect, the CDW transition of 1T-TiSe2 can be suppressed and superconductivity appears [6, 7]. By gate-controlled Li ion intercalation, 1T-TaS2 thin flakes undergo multiple phase transitions, including the transition from Mott insulator to superconductor [8]. In 2Ha-TaS2, pressure suppresses the CDW transition and the superconducting $T_c$ is significantly enhanced [9].

Polytype 1T-TaSe2 undergoes an incommensurate charge density wave (ICCDW) phase transition at $T_{ICDW} \approx 473$ K,
and no superconducting transition is observed [10]. With S or Te doping, superconductivity appears [11–13]. Polytype 2$H$Ta$_{1.03}$Se$_2$ also undergoes an ICCDW phase transition at $T_{C_{CCDW}} \approx 122$ K, then locks into a commensurate charge density wave (CCDW) state at $T_{C_{CCDW}} \approx 90$ K [14, 15], and finally to a superconducting state at $T_c \approx 0.14$ K [16, 17]. $T_c$ will increase with S or Te doping [18, 19], or Ni or Pd intercalations [20, 21], or under pressure [9]. Polytype 3R-TaSe$_2$ is not stable [22], but with Te, Mo or W doping, it stabilizes and superconducts at a $T_c$ of about 2 K [23]. Polytype 4$H$b-TaSe$_2$ also has two different CDW phase transitions at 410 K and 75 K respectively [24], and 6$R$-TaSe$_2$ exhibits similar behavior [25]. In 4$H$b-Ta$_{2-x}$Se$_x$(0 $\leq$ x $\leq$ 1.5) and 6$R$-Ta$_{2-x}$Se$_x$(0 $\leq$ x $\leq$ 1.6), superconductivity and CDW coexist in the whole composition range [26, 27]. Nevertheless for 4$H$a-TaSe$_2$, there have been few reports on its physical properties up to now—most likely because this polytype is difficult to synthesize.

Here we report successful crystal growth and superconductivity in a Ta self-intercalated 4$H$a-Ta$_{1.00}$Se$_2$ single crystal. The $T_c$ of 4$H$a-Ta$_{1.00}$Se$_2$ is about 2.7 K, which is approximately 20 times higher than that of 2$H$-Ta$_{2.0}$Se$_2$, close to the $T_c$ value reported for other doped or intercalated polytypes. We also found a phase transition around 106 K, which is analogous to the slightly suppressed CDW transition. A large $\mu_0H_{c2}/T_c$ value of about 4.48 is found when a magnetic field is applied in the $ab$ plane, which may be related to the enhanced spin–orbit coupling (SOC).

2. Experiment details

Single crystals of 4$H$a-Ta$_{1.00}$Se$_2$ were made via the vapor transport technique using iodine as the transport agent. First, Ta(99.99%) and Se(99.999%) powder were mixed with the ratio of 1.06:2, ground adequately, sealed into an evacuated quartz ampoule, heated to 800 °C and kept for 3 days. Subsequently, the mixture was reground, iodine was added at a concentration of 8.6 mg cm$^{-3}$, and it was then sealed into an evacuated quartz ampoule with a length of 16 cm. The ampoule was heated for 7 days in a two-zone furnace, where the temperature of the source zone and growth zone were fixed at 850 °C and 800 °C respectively. Finally, silver, mirror-like plate single crystals with a typical size of about 4 $\times$ 4 $\times$ 0.05 mm$^3$ were obtained. We also tried to fabricate stoichiometric 4$H$a-Ta$_{1.03}$Se$_2$ with the same method but failed. We guess that the redundant Ta atoms conduce the formation of the 4$H$a polytype.

The single crystal x-ray diffraction (XRD) data were collected by a PANalytical x-ray diffractometer (Empyrean) with Cu Kα radiation and a graphite monochromator at room temperature. The chemical compositions were determined by energy dispersive x-ray spectroscopy (EDX) with a GENESIS4000 EDAX spectrometer. High-resolution transmission electron microscope (HRTEM) images were taken at room temperature with an aberration-corrected FEI-Titan G2 80-200 ChemiSTEM. DC magnetization was measured on a magnetic property measurement system (MPMS-XL5, Quantum Design), and the ‘ultra-low field’ option was used. The specific-heat capacity was measured on a physical properties measurement system (PPMS-9, Quantum Design), using a relaxation technique. The electrical properties were measured on an Oxford Instruments-1ST cryostat with a He-3 probe.

3. Result and discussion

Figure 1 shows the EDX pattern of the single crystal. The ratio of Ta to Se is determined to be 1.03(1):2, which is an average result for multiple areas in the same single crystal. Although the starting ratio is 1.06:2, the redundant amount of Ta atoms is not all intercalated into the sample. We get similar results for several batches under the same conditions. The room temperature XRD pattern of a 4$H$a-Ta$_{1.00}$Se$_2$ single crystal is shown in the inset of figure 1, where all the reflections are (00l) peaks. The lattice constant along the $c$-axis is calculated to be 25.436 Å. Compared with the 25.180 Å of 4$H$a-Ta$_{2.0}$Se$_2$ from the literature [22], the $c$-axis is a little expanded. This should have resulted from the Ta self-intercalation, similar to the Ni- or Pd-intercalated 2$H$-TaSe$_2$ [20, 21].

The structure model is displayed in figure 2(a), and figures 2(b) and (c) show the HRTEM images of a single crystal from the zone axes [1 0 0]. The HRTEM images clearly reveal the atom arrangement mode and thus provide direct evidence of the 4$H$a polytype. Four layers constitute one unit cell. The layer stacking type can be described by using the method from the literature [5], where A(t), B(b), C(c) represent the three positions of atoms in the $ab$-plane. The capital letters correspond to the Se atoms and the lower case letters designate the Ta atoms. The same letters, no matter whether they are capital or lower case, represent the same positions in the $ab$-plane for all layers. Three letters describe one sandwich layer. Along the $c$-axis, the stacking sequence of the 4$H$a polytype is AbACbBaBCbC, just as illustrated in the left structure in figure 2(a). The HRTEM images also reveal special stacking faults in our samples as displayed in figure 2(a). Both A block and B block consist of four layers of...
the $4H_a$-TaSe$_2$ structure, but from different sections and directions as shown in figure 2(a). Our sample is randomly stacked by the A and B blocks. These stacking faults can enhance the anisotropy due to the 2D characteristic of the fragments. Moreover, the intercalated Ta atoms between two layers can clearly be observed in the locally enlarged HRTEM image, as shown in figure 2(c). It can be seen that the Ta intercalation is not microscopically homogeneous.

Figure 2. (a) The structure of the $4H_a$ polytype and the illustration for the special stacking faults in our samples. The purple letters in the left structure illustrate the stacking sequence of the $4H_a$ polytype. The right structure of $4H_a$-TaSe$_2$ is rotated 180° along the c-axis. (b) An HRTEM image of a $4H_a$-Ta$_{1.03}$Se$_2$ single crystal from the zone axes [100]. (c) A locally enlarged HRTEM image; the red arrows point out some of the intercalated Ta atoms.

Figure 3. (a) The temperature dependent in-plane resistivity of $4H_a$-Ta$_{1.03}$Se$_2$ for 1.5 K–300 K. Inset: the derivative of resistivity of $4H_a$-Ta$_{1.03}$Se$_2$. (b) The temperature dependence of dc magnetic susceptibility for $4H_a$-Ta$_{1.03}$Se$_2$ ($H//ab$, $H = 1$ Oe). ZFC and FC denote zero-field cooling and field cooling. Inset: the field dependence of the initial part of the magnetization curve ($H//ab$, $T = 2$ K).

Figure 3(a) displays the temperature dependence of in-plane electrical resistivity for $4H_a$-Ta$_{1.03}$Se$_2$ single crystals. The sample was cut to a size of about $4 \times 1 \times 0.05$ mm$^3$ for the resistivity measurement. Similar to other polytypes, $4H_a$-Ta$_{1.03}$Se$_2$ are metallic in their normal state. Around 106 K, a slope change appears. This change can be better observed in the derivative of the resistivity curve, as shown in the inset. Below 106 K, there is a sudden increase in the derivative of the
resistivity curve. This slope change is analogous to the case in other TMDCs and is usually attributed to the CDW transitions [21]. The superconducting transition temperature onset $T_c$ is about 2.7 K, with a narrow transition width of about 0.2 K. For other polytypes, when doping or intercalating, $T_c$ is always in the range 2 K–4 K. Although the 4Ha polytype has a disparate stacking pattern, the superconducting transition temperature remains similar to the others. Figure 3(b) shows the results of the magnetic measurements. The inset shows the field dependence of the initial part of the magnetization curve at 2 K with the magnetic field applied parallel to the long direction in the $ab$-plane. The lower critical field ($H_{c1}$) is estimated to be about 3 Oe. Thus we measured the temperature dependence of dc magnetic susceptibility under a magnetic field of 1 Oe applied in the $ab$-plane. This was measured for both zero-field cooling (ZFC) and field cooling (FC). The $T_c$ determined from magnetic susceptibility is 2.7 K, which is close to the onset temperature derived from the resistivity transition. The estimated superconducting shielding volume fraction is about 42.2% at 2 K. As mentioned above, the Ta intercalation is not microscopically homogeneous, therefore we conjecture that the intercalation concentration is important for the occurrence of superconductivity—i.e. only the area with enough intercalated Ta atoms will show superconductivity.

Figures 4(a) and (b) display the temperature dependence of in-plane electrical resistivity under different magnetic fields of 4Ha-Ta$_{1.03}$Se$_2$ with the field applied parallel to the $c$-axis and in the $ab$-plane respectively. For both field directions, the resistivity curves shift parallel down towards the low temperature with increasing fields. This behavior is different from the intercalated 2H-TaSe$_2$, whose resistive transition broadens when the magnetic field is applied out of the $ab$-plane [21]. We summarize the temperature-dependent upper critical field ($H_{c2}$) determined by $T_{\text{onset}}$ (90% of normal state resistivity) in figure 4(c). In both directions, the $H_{c2}$ data can be well fitted by the Ginzberg–Landau equation [28]:

$$H_{c2}(T) = H_{c2}(0) \left( \frac{1 - T^2}{1 + T^2} \right)$$

(1)

where $T = T/T_c$ is the reduced temperature. From this fit we can deduce $\mu_0 H_{c2}(0) = 1.51$ T and $\mu_0 H_{c2}^{ab}(0) = 12.09$ T. The Pauli paramagnetic limit for the upper critical field is $\mu_0 H_P = 1.84 T_c = 4.96$ T. $H_{c2}^{FM}(0)$ is about 2.44H$_P$, where $\mu_0 H_{c2}^{FM}(0)/T_c = 4.48$. For 2H-TaSe$_2$, $H_{c2}$ is much smaller than the Pauli paramagnetic limit for both directions, and $\mu_0 H_{c2}^{FM}(0)/T_c = 0.03$ only [17]. However, for the Pd intercalated 2H-Pd$_{0.09}$TaSe$_2$, $\mu_0 H_{c2}^{FM}(0)/T_c = 3.75$ [21], which is just slightly lower than the value in this work. Such a large value of $\mu_0 H_{c2}^{FM}(0)/T_c$ was also found in the quasi-one-dimensional Nb$_2$PdS$_4$, where the value is 3 [29], and in Pt, Ir or Ru-doped Nb$_2$PdS$_4$ where $\mu_0 H_{c2}(0)/T_c$ increases due to the additional SOC effect [30, 31]. We speculate that in TaSe$_2$, extra Ta atoms may resemble the effect to increase the SOC, hence leading to large upper critical fields. The anisotropy factor $\gamma = H_{c2}^{FM}(0)/H_{c2}(0) \approx 8$, which is larger than the value of about 3–4 for 2H polytypes [17, 21]. As mentioned above,
the special stacking faults may also contribute to such large anisotropy.

Figure 4(d) shows the temperature dependence of the specific-heat $C(T)$ for $4Ha$-$Ta_{1.03}$Se$_2$ from 1.8 K to 200 K. No distinct specific-heat jump is observed for the CDW transition around 106 K. Combining it with the minimum in the derivative curvature of resistivity, we can conclude that the CDW transition has been severely suppressed by Ta self-intercalation in $4Ha$-$Ta_{1.01}$Se$_2$. This phenomenon is similar to $2H$-Ni$_{0.02}$TaSe$_2$ [20], where there is an anomaly in temperature-dependent resistivity but not in the specific-heat. Moreover, similar to $2H$-Ni$_{0.02}$TaSe$_2$, there is no obvious specific-heat jump around $T_c$, which may be due to the low volume fractions of magnetic shielding. The $C/T$ versus $T^2$ curve is displayed in the inset of figure 4(d). The data can be estimated by the McMillan equation [32]:

$$\lambda_{e-ph} = \frac{\mu^* \ln(\frac{\rho_n}{1.132\Theta_D}) + 1.04}{\ln(\frac{\rho_n}{1.132\Theta_D})(1 - 0.62\mu^*) - 1.04}$$

where $\mu^*$ is the Coulomb pseudopotential and is often set to 0.15 as the empirical value. From the estimation we get $\lambda_{e-ph} = 0.69$. This value is less than the minimum value of 1 for strong coupling, which suggests it is still in an intermediate coupling range. The density of states at the Fermi level $N(E_F)$ can be calculated by the equation:

$$N(E_F) = \frac{3\gamma}{\pi^2 k_B^2 (1 + \lambda_{e-ph})}$$

$N(E_F)$ is close to that of undoped $2H$-TaSe$_2$ which is 1.51 state eV$^{-1}$ f.u.$^{-1}$, but lower than those of other doped or intercalated TaSe$_2$ which are about 2 state eV$^{-1}$ f.u.$^{-1}$ [21]. In general, a high $N(E_F)$ is in favor of superconductivity. In spite of having a low $N(E_F)$, $4Ha$-$Ta_{1.03}$Se$_2$ also has a $T_c$ which is comparable to other doped or intercalated TaSe$_2$, indicating that the stacking mode of $4Ha$ may be more in favor of superconductivity than other polytypes.

4. Conclusion

In summary, we discover superconductivity with an onset $T_c$ of 2.7 K in the Ta self-intercalated $4Ha$-$Ta_{1.01}$Se$_2$. A suppressed CDW transition is observed around 106 K. A kind of special stacking fault is revealed, which may increase the anisotropy. The $\mu_0H_{c2}(0)/T_c = 4.48$ is larger than other polytypes, and the estimated $H_{c2}(0)$ is 2.44 times the Pauli paramagnetic limit, which may result from an enhanced SOC. $\lambda_{e-ph} = 0.69$, indicating that it is still in the intermediate coupling range. On the other hand, $N(E_F)$ is only 1.53 state eV$^{-1}$ f.u.$^{-1}$, which is smaller than that of other doped or intercalated TaSe$_2$, although the $T_c$ is almost the same. This work indicates that the stack mode of the $4Ha$ polytype is of benefit to superconductivity and $H_{c2}$ for TaSe$_2$, and superconductivity can even be enhanced if $N(E_F)$ is increased.

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