Superconductivity at 2.5K in the new transition-metal chalcogenide Ta2PdSe5

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Received 1 July 2015, revised 27 August 2015
Accepted for publication 7 September 2015
Published 9 October 2015

Abstract
We report the synthesis and superconducting properties of a new transition-metal chalcogenide, Ta2PdSe5. Measurements of resistivity, magnetization, and specific heat reveal that Ta2PdSe5 is a bulk superconductor with Tc ≈ 2.5 K. The zero-field electronic specific heat in the superconducting state can be fitted with a two-gap BCS model. The upper critical field Hc2 shows a linear temperature dependence, and the value of Hc2(0) is much higher than the estimated Pauli limiting field Hc2P. All these results of specific heat and upper critical field suggest that Ta2PdSe5 is a multi-band superconductor.

Keywords: Transition-metal compounds, large upper critical field, multi-band superconductor

1. Introduction
For BCS superconductors with spin-singlet pairing, magnetic field destroys the superconductivity by either the orbital effect or the Pauli paramagnetic effect. The upper critical field Hc2 which reflects the pair-breaking mechanism is usually limited by the orbital effect, with the limiting field Hc2orb = Φ0/2πξ2. The Pauli paramagnetic effect becomes important when the orbital contribution is somehow suppressed or when the normal-state spin susceptibility χ(0) is enhanced due to spin–orbit coupling, resulting in the Pauli limiting field Hc2P being smaller than Hc2orb [1]. Then the spin polarization determines the upper critical field Hc2P = 1.84 Tc, within the weak-coupling BCS theory [2]. Experimentally, superconductivity with Hc2 beyond Hc2P has been observed in some low-dimensional materials, such as the organic Bechgaard salt (TMTSF)2PF6 [3], purple bronze Li2MoO4O7 [4], and iron chalcogenide β-FeSe [5]. Different theories including spin-triplet pairing, strong spin–orbit coupling, and the multi-band effect are proposed [3–5]. For practical applications, superconductors with high Hc2 are more promising for high-field applications.

Recently, a new quasi-one-dimensional (Q1D) transition-metal chalcogenide Nb2Pd0.83S8 was synthesized, in the monoclinic space group C2/m [6]. It becomes a superconductor below the transition temperature Tc ≈ 6.6 K [6]. Later, two existing compounds, Ta2PdS5 and Nb2PdSe5, with the same crystal structure [7], were also found to be superconducting below 6 K and 5.5 K, respectively [8, 9]. These three compounds display extremely high and anisotropic Hc2 [6, 8–11], suggesting a new family of exotic superconductors TcPdCh5 (T = Nb or Ta, Ch = S or Se).

The unconventional spin-triplet pairing state has been discussed based on the quasi-one-dimensionality of TcPdCh5, which may explain the unusual Hc2 [6, 8, 9]. However, this proposal is challenged by the robustness of the Hc2/Tc ratio in the Se substitution experiment in Nb2PdS5 [12]. The spin–orbit coupling was also considered as one possible origin of the high Hc2 in this family [8, 9]. This proposal is supported by the opposite substituting effect on the Hc2/Tc ratio in Nb2PdS5 [13]. The substitution of Pd by heavier Pt enhances the Hc2/Tc ratio, while lighter Ni substitution decreases it [11]. Alternatively, the multi-band effect could also give rise to their high Hc2 values [6, 8, 12, 13]. Electronic structure calculations have shown that these three compounds are multi-band superconductors with several sheets of Fermi surface [6, 8, 14]. Since the origin of the enhanced Hc2 is still not clear, finding more compounds in this family may provide us with a better understanding of their unusual Hc2/Tc.
In this paper, we report the synthesis and superconducting properties of a new transition-metal chalcogenide Ta$_2$PdSe$_5$, the fourth member of the T$_5$PdCh$_3$ family. Measurements of electrical resistivity, magnetization and specific heat confirm bulk superconductivity in this material, with $T_c \approx 2.5$ K. Both the fit of specific electronic heat and the linear temperature dependence of $H_{c2}(T)$ support multi-band superconductivity in Ta$_2$PdSe$_5$. The ratio of $H_{c2}/T_c$ is as high as 6 T K$^{-1}$, which may also be ascribed to the multi-band effect.

2. Experimental details

The polycrystalline samples of Ta$_2$PdSe$_5$ were synthesized by a conventional solid state reaction method. The starting materials of Ta(99.99%), Pd(99.99%), and Se(99.99%) powders were mixed thoroughly in the ratio of 2:1:5.5 and pressed into pellets in an argon-filled glove box. An excess of Se is necessary to compensate for the loss of Se during the reaction and then kept at this temperature for 48 hours before shutting down the furnace. This process was repeated four times, and the final samples were stable in air. X-ray diffraction (XRD) measurement was performed by using an x-ray diffractometer (D8 Advance, Bruker) with Cu Kα radiation. The dc magnetization was measured in a superconducting quantum interference device (SQUID, Quantum Design). Electrical resistivity measurements were performed in $^4$He and $^3$He cryostats, by a standard four-probe technique. The low-temperature specific heat was measured from 0.3 to 10 K in a physical property measurement system (PPMS, Quantum Design) equipped with a small dilution refrigerator.

3. Results and discussion

Figure 1 shows the powder x-ray diffraction (XRD) pattern of Ta$_2$PdSe$_5$ taken at room temperature. Most of the peaks can be well indexed to a monoclinic structure with space group C2/m. The observed XRD pattern is refined by a Rietveld method using the TOPAS Academic package, from which Ta$_2$PdSe$_5$ is recognized as the main phase, with a small amount of Pd$_4$Se$_4$ impurity, which does not display superconductivity down to 0.38 K [15]. The refined lattice parameters of Ta$_2$PdSe$_5$ are $a = 12.801(5)$ Å, $b = 3.117(1)$ Å, $c = 17.742(3)$ Å, $\alpha = \gamma = 90^\circ$, and $\beta = 106.22(2)^\circ$. A perspective view of the Ta$_2$PdSe$_5$ crystal structure along the $b$-axis direction is shown in the inset of figure 1. The one-dimensional Ta–Se chains along the $b$-axis are bridged by PdSe$_4$ squares. This compound is the fourth member of the T$_5$PdCh$_3$ ($T$ = Nb or Ta, Ch = S or Se) family.

Figure 2(a) plots the low-temperature dc magnetization of Ta$_2$PdSe$_5$ in $H = 10$ Oe, with both zero-field-cooled (ZFC) and field-cooled (FC) processes. The diamagnetic signal reveals a superconducting transition with the onset $T_c$ at about 2.6 K. Figure 2(b) shows the temperature dependence of resistivity for Ta$_2$PdSe$_5$ measured between 1.5 and 300 K. $\rho(T)$ displays metallic behavior with a residual resistivity ratio RRR = $\rho$(294 K)/$\rho$(3 K) ≈ 3.3. The inset shows the resistivity at low temperature ranging from 1 to 5 K. A clear drop of resistivity is observed, corresponding to the superconducting transition. The onset, mid-point and zero-point temperatures of the resistive transition ($T_c^{onset}$, $T_c^{mid}$ and $T_c^{zero}$) are 2.5, 2.2, and 2.0 K, respectively. The $T_c^{onset}$ is determined from the intersection of the two extrapolated lines near the transition, as seen in the inset. The $T_c^{mid}$ and $T_c^{zero}$ are defined at the temperatures where the normal-state resistivity drops by half and to zero, respectively. The width of the resistive superconducting transition $\Delta T_c$ is about 0.5 K.

Figure 3(a) plots the specific heat divided by the temperature, $C_p/T$, as a function of temperature in various magnetic fields. $C_p/T$ shows an anomaly around 2.5 K in zero field, corresponding to the superconducting transition. This anomaly shifts to lower temperatures and becomes less pronounced with increasing magnetic field, as shown in the inset. Above $T_c$, the zero-field data can be well fitted by $C_p/T = \gamma + \beta T^2 + \delta T^4$ from 3.5 to 10 K. We determine the electronic specific heat coefficient, $\gamma$, and the phononic coefficients, $\beta$, to be 10.3 mJ mol$^{-1}$ K$^{-2}$ and 3.2 mJ mol$^{-1}$ K$^{-4}$, respectively. The Debye temperature $\Theta_D = 169$ K is estimated from the equation $\beta = (12\pi^2 n k_B^2)/(5S^3)$, where $n$ is the number of atoms per formula unit.

The zero-field electronic specific heat $C_e/T$ obtained by subtracting the lattice terms from $C_p$ is depicted in figure 3(b). The bulk nature of the superconductivity in Ta$_2$PdSe$_5$ is confirmed by the significant jump of $C_e/T$. In order to get more information about the superconducting gap, we fit $C_e/T$.
in the superconducting state with the BCS α-model $C_e = C_0 \exp(-\Delta/k_B T)$, where $\Delta$ is the size of the superconducting gap. It is found that the one-gap model with $\alpha = 0.44$ cannot describe the experimental data well, while the two-gap model with $\alpha_1 = 0.56$ and $\alpha_2 = 2.08$ gives the best fit [16]. The superconducting gap ratio $\Delta_1/\Delta_2 \simeq 3.7$ is obtained. This result is consistent with the band structure calculation of $T_{2PdCh_5}$ [6, 8, 14]. Taking spin–orbit coupling into account, the calculated Fermi surface of $T_{2PdSe_5}$ consists of a large hole sheet and two electron sheets (a large two-dimensional cylinder around the zone center and small closed sections on the zone faces), and the superconductivity is likely to be dominated by the two larger sheets [14].

To estimate the coupling strength of $T_{2PdSe_5}$, the normalized specific heat jump $\Delta C_e/\gamma T_c$ is estimated to be about 0.83. This value is smaller than that expected for weak-coupling BCS superconductors ($\Delta C_e/\gamma T_c = 1.43$), which could be another indication of multi-band superconductivity in $T_{2PdSe_5}$ [17]. Note that a similar value of $\Delta C_e/\gamma T_c = 0.9$ was also reported for the sister compound, $Nb_2PdS_5$ [12, 18].

Figure 2. (a) Low-temperature dc magnetization of $Ta_2PdSe_5$ measured with both field-cooled (FC) and zero-field-cooled (ZFC) processes. The superconducting transition is observed at about 2.6 K. (b) Temperature dependence of the resistivity $\rho(T)$. The inset shows the superconducting transition at low temperature, with different definitions of the transition temperature $T_c$.
dependence of $H_{c2}(T)$ and the abnormally high $H_{c2}(0)/T_c$ are common features of $T_2$PdCh$_5$ [6, 8, 9].

In figure 4(b), a linear fit of the $H_{c2}^{\text{outset}}(T)$ data near $T_c$ provides the initial slope $|dH_{c2}/dT|_{T_c} = 4.17$ T K$^{-1}$. For one-band BCS superconductors, the orbital limiting field $H_{c2}^{\text{orb}}(0)$ is commonly derived from this slope, and Werthamer–Helfand–Hohenberg (WHH) theory predicts $H_{c2}^{\text{orb}}(0) = -0.69|dH_{c2}/dT|_{T_c} T_c$ in the dirty limit and $H_{c2}^{\text{orb}}(0) = -0.73|dH_{c2}/dT|_{T_c} T_c$ in the clean limit. For $T_2$PdSe$_5$, the Ginzburg–Landau coherence length $\xi_0 = 65.8$ Å is calculated by using $\xi_0 = [\Phi_0/(2\pi H_{c2}(0))]^{1/2}$. The electron mean free path $l \approx 24$ Å is roughly estimated from $\rho_0$ and $\gamma$ [8]. Since $l < \xi_0$, $T_2$PdSe$_5$ is close to dirty limit. Therefore, the orbital limit based on the one-band WHH formula gives $H_{c2}^{\text{orb}}(0) = -0.69|dH_{c2}/dT|_{T_c} T_c = 7.28$ T. This value is higher than the expected weak coupling Pauli limiting field $H_{c2}^{\text{P}}(0) = 1.84T_c = 4.6$ T in the case of spin-singlet pairing, but still far below the measured $H_{c2}(0)$ value. Such an abnormal $H_{c2}(0)$ cannot be understood in terms of one-band Ginzburg–Landau theory.

The linear temperature dependence of $H_{c2}(T)$ was previously observed in the two-band superconductor MgB$_2$ [19–21], and explained by Gurevich based on the dirty two-gap Usadel equations [22, 23]. Unlike one-gap theory in which $H_{c2}(T)$ has a downward curvature, $H_{c2}(T)$ of a dirty two-gap superconductor can show linear dependence or even upward curvature, depending on the intraband diffusion ratio caused by strong impurity scattering [22, 23]. Moreover, the inter-band scattering can make the $H_{c2}(0)$ significantly higher than that estimated from one-gap theory [24]. Therefore, we ascribe the linear temperature dependence of $H_{c2}(T)$ and the abnormally high $H_{c2}(0)/T_c$ observed in $T_2$PdCh$_5$ family to the multi-band effect. However, one may not ignore the effect of spin–orbit coupling, since large spin–orbit scattering due to Pd deficiency in these compounds can suppress the paramagnetic pair breaking, thus enhancing the limit of the upper critical field [9]. From the perspective of applications, $T_2$PdSe$_5$ and the related chalcogenides provide a new family of materials exhibiting high $H_{c2}$, which makes them candidate materials for high-field applications.

![Figure 4](image)

**Figure 4.** (a) Low-temperature resistivity $\rho(T)$ of Ta$_2$PdSe$_5$ in various magnetic fields up to 14 T. (b) Reduced temperature $T/T_c$ dependence of the upper critical field $H_{c2}(T)$. The data points of $H_{c2}^{\text{outset}}$, $H_{c2}^{\text{mid}}$ and $H_{c2}^{\text{zero}}$ are extracted from each $\rho(T)$ curve in (a) according to the definitions of $T_{c2}^{\text{outset}}$, $T_{c2}^{\text{mid}}$ and $T_{c2}^{\text{zero}}$, respectively.

| $T_c$ (K) | $\gamma$ (mJ mol$^{-1}$ K$^{-2}$) | $H_{c2}^{\text{outset}}(0)$ (T) | $H_{c2}^{\text{outset}}(0)/T_c$ (T K$^{-1}$) |
|-----------|-------------------------------|--------------------------------|----------------------------------------|
| Nb$_2$PdS$_5$ | 6.6 | 15 | 37 | 5.6 |
| Nb$_2$PdSe$_5$ | 5.0 | 12.8 | 35 | 5.9 |
| Ta$_2$PdS$_5$ | 5.4 | 27.6 | 31 | 5.7 |
| Ta$_2$PdSe$_5$ | 2.5 | 10.3 | 15.5 | 6.2 |

$H_{c2}^{\text{outset}}(T)$ curve to zero temperature. The corresponding ratio of $H_{c2}(0)/T_c$ comes out to be 6 T K$^{-1}$. In table 1, we list the $T_c$, $\gamma$, $H_{c2}(0)$, and $H_{c2}(0)/T_c$ for all four members of the $T_2$PdCh$_5$ family [6, 8, 9]. Both the linear temperature dependence of $H_{c2}$ indicate multi-band superconductivity in $T_2$PdSe$_5$.

Note added: Stimulated by the preprint of this work (arXiv:1412.6983), the electronic structure and related properties of $T_2$PdSe$_5$ were theoretically obtained from density functional calculations [25]. The Fermi surface has two

4. Summary

In summary, a new transition-metal chalcogenide compound $T_2$PdSe$_5$ was first synthesized. Measurements of resistivity, magnetization and specific heat revealed that $T_2$PdSe$_5$ is a superconducting material with $T_c \approx 2.5$ K. This compound displays a remarkably high upper critical field $H_{c2}(0)$ relative to its superconducting transition temperature $T_c$. Both the fit of electronic specific heat and the linear temperature dependence of $H_{c2}$ indicate multi-band superconductivity in $T_2$PdSe$_5$. 

4.1. Note added: Stimulated by the preprint of this work (arXiv:1412.6983), the electronic structure and related properties of $T_2$PdSe$_5$ were theoretically obtained from density functional calculations [25]. The Fermi surface has two...
disconnected sheets [25], which are consistent with our experimental results.

Acknowledgments

This work is supported by the Natural Science Foundation of China, the Ministry of Science and Technology of China (National Basic Research Program No: 2012CB821402 and 2015CB921401), China Postdoctoral Science Foundation No: 2014M560288, Program for Professor of Special Appointment (Eastern Scholar) at Shanghai Institutions of Higher Learning, and STCSM of China (No. 15XD1500200).

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