Pd₃Te₂: an s-wave superconductor with Pd atom coordinated by five Te atoms

X Chen¹,², J G Guo¹,³, J Deng¹,², T P Ying¹, E J Cheng¹, S Y Li¹,4 and X L Chen¹,³,6

¹ Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, PO Box 603, Beijing 100190, People’s Republic of China
² University of Chinese Academy of Sciences, Beijing, 100049, People’s Republic of China
³ Songshan Lake Materials Laboratory, Dongguan, Guangdong 523808, People’s Republic of China
⁴ State Key Laboratory of Surface Physics, Department of Physics, and Laboratory of Advanced Materials, Fudan University, Shanghai 200433, People’s Republic of China
⁵ Collaborative Innovation Center of Advanced Microstructures, Nanjing 210093, People’s Republic of China
⁶ Authors to whom correspondence should be addressed.

E-mail: jgguo@iphy.ac.cn and xlchen@iphy.ac.cn

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Abstract

We have identified a new superconductor Pd₃Te₂ based on pure phase samples. Electrical resistivity, magnetic susceptibility and specific heat measurements confirm that Pd₃Te₂ is a bulk superconductor at 2.2 K. The value of Ginzburg–Landau parameter is larger than 1/√2, suggesting type-II superconductivity. Meanwhile, the analysis of specific heat indicates that Pd₃Te₂ is a fully-gapped superconductor with electron-phonon coupling constant λ_e-p = 0.58, which features a BCS weakly coupling case. According to our theoretical calculations, the superconductivity is related to the states of hybridization of Pd d states and Te p states at the Fermi level. Our results reveal that superconductivity can occur in five coordinated palladium tellurides.

Introduction

Recently, palladium tellurides have been receiving considerable attention because of their structural diversity, superconducting and topological properties. These might be related with its unique electronic configuration (palladium has fewer electron shells being filled than its preceding elements) to some extent. For instance, Ta₄Pd₄Te₁₆ and Ta₃Pd₃Te₁₄ are quasi-one-dimension superconductors, which are composed of several different types of chains, including {PdTe₆} octahedral chains [1, 2]. Among the binary palladium tellurides, some also exhibit superconductivity [3]. Matthias showed that PdTe became a superconductor at about 2.3 K [4]. Later, it was found that the transition temperatures can be adjusted at a range of 1.8 K–4.5 K by slightly tuning the Te content in PdTe₁ₓ₋₁ [0 < x < 0.08] [5–7]. PdTe has a three dimensional (3D) structure consisting of edge-sharing octahedral coordinated polyhedral {PdTe₆}. The phase diagram of PdTe-PdTe₂ reported by Kjekshus et al confirmed that PdTe₂ is a superconductor with a Tc of 1.69 K [8]. PdTe₂ is a layered compound forming by the stacking of layers composed of {PdTe₆} octahedral as in PdTe. More recently, Noh et al reported the existence of type-II Dirac fermions in PdTe₂ by angle-resolved photoemission spectroscopy combined with ab initio band calculations [9].

Note that a common structural unit in Ta₄Pd₄Te₁₆ [1], Ta₃Pd₃Te₁₄ [2], PdTe [4] and PdTe₂ [8] is 6-coordinated {PdTe₆} octahedral. It may play a vital role in inducing superconductivity in palladium tellurides. Pd₃Te₂, however, stands out for it comprises of two types of distorted {PdTe₆} pyramids linked through edge- and corner-shared ways [10]. Besides, the topological surface states were predicted in Pd₃Te₂ [11], which increases research interest. Since Pd₃Te₂ is close to PdTe₁ₓ₋₁, PdTe₂, and Pd₃Te₁₄ in chemical compositions, it is difficult to synthesize pure phase and measure the intrinsic properties of Pd₃Te₂. Moreover, Pd₃Te₂ exists only below 780 K [12], a temperature at which Pd and Te are difficult to fully react. Up to now, no powder pure phase
of Pd₃Te₂ has been obtained. In this paper, we have prepared a single phase of Pd₃Te₂ through high-temperature (1173 K) melting and subsequent low-temperature (723 K) long-time (2 weeks) annealing treatment, which shows a superconducting transition with the s-ordination at Tₘ ≈ 2.2 K. The type II and s-wave superconductivity are confirmed by our magnetization and specific heat measurement. The derived electron-phonon coupling indicates that it belongs to a BCS-type weakly-coupled superconductor.

Experimental

Polycrystalline samples of Pd₃Te₂ were synthesized via the melting high purity palladium powder (99.99% Alfa Aesar) and tellurium powder (99.9999% Alfa Aesar). The powders of Pd and Te were weighted in the ratio of 3:2, thoroughly ground and pelleted. The pellet was packed into a corundum crucible, and sealed it into a quartz tube under vacuum, which was heated in a box furnace to 1173 K and held at this temperature for 30 h. Then the mixtures were ground to powder and were annealed in corundum crucibles for 2 weeks at about 723 K, which is to reduce the amount of PdTe as much as possible.

Powder x-ray diffraction (PXRD) patterns of the obtained sample were collected at room temperature using a Panalytical diffractometer with Cu Kα (λ = 1.5408 Å) radiation. Rietveld refinement of the PXRD patterns was performed using Fullprof software suites [13]. Microstructures of the Pd₃Te₂ were examined using a scanning electron microscope (SEM). The chemical composition was determined by Energy Dispersive Spectrum (EDS) based on the average of five sets of data. The electrical resistivity (ρ), Hall effect and specific heat capacity (Cp) were measured through the standard four-wire method and the thermal relaxation method using the thermal property measurement system with a He3 insert (PPMS, Quantum Design). The magnetic properties were characterized using a vibrating sample magnetometer (PPMS, Quantum Design). First principles calculations were performed with the Vienna ab-initio simulation package (VASP) [14, 15]. We adopted the generalized gradient approximation (GGA) in the form of the Perdew-Burke-Ernzerhof (PBE) exchange-correlation potentials. The projector augmented-wave (PAW) pseudopotential [17] was used with a plane-wave energy cutoff 600 eV. A Monkhorst-Pack [18] k-mesh of 14 × 14 × 6 was used for sampling the first Brillouin zone in the self-consistent calculation and 27 × 27 × 13 for the density of states. Spin-orbital coupling effect was considered in the calculations. The lattice constants and atomic coordinates used in the calculations were derived from the experimental results.

Results and discussion

SEM images of small Pd₃Te₂ crystals are shown in supplementary figure S1 is available online at stacks.iop.org/JPCO/3/095008/mmedia. The chemical composition was determined as atomic ratio Pd:Te = 3:2 within the measurement precision (±1% depending on the elements), confirming that the crystals is the stoichiometric Pd₃Te₂. The lattice parameters can be indexed as a = 7.8994(2) Å, b = 12.6851(3) Å, c = 8.58551(1) Å and V = 386.305(2) Å³. Figure 1 displays the Rietveld refinement of PXRD pattern of Pd₃Te₂ powder sample. The observed reflections of main phase Pd₃Te₂ obey the extinction conditions for space group Amam (No. 63). A two-phase Rietveld refinement [19] with initial structural prototype Pd₃Te₂ [10] and PdTe converges well as R_p = 4.41%, R_w = 6.34% and χ² = 5.49. The mass fraction for main phase Pd₃Te₂ and PdTe are 99% and 1%, respectively. Besides, the refined crystallographic parameters of Pd₃Te₂ are shown in table 1. The crystal structure of Pd₃Te₂ is shown in figure 2(a), which contains four formula units (f.u.) with 20 atoms in a unit cell. The structure of Pd₃Te₂ is 3D structure comprising of two types of edge- and corner-shared {PdTe₃} pyramids. Figures 2(b) and (c) show that the pyramid 1 includes four Pd(1)-Te(1) (2.79 Å) bonds and one Pd(1)-Te(2) (2.64 Å) bond, and oblique pyramid 2 has two Pd(2)-Te(1) (2.87 Å) bonds and three Pd(2)-Te(2) (2.70 Å) bonds. Figure 2(d) shows the crystal structure of PdTe stacked with edge-shared octahedra. The single octahedral unit is shown in figure 2(e), which has six identical Pd-Te bonds of 2.77 Å.

The temperature dependence of electrical resistivity (ρ) for Pd₃Te₂ is shown in figure 4(a). Below 300 K, ρ(T) shows a metallic behavior with a linear dependence above 50 K. The high resistivity ratio (ρ₁₀₀/ρ₀) ~ 18) suggests that Pd₃Te₂ is a good metal. The linear-dependence of Hall voltage against magnetic field (H) (see figure 3(a)) suggests that the Hall coefficient (R_H) is nearly independent of H. In figure 3(b), the positive value of R_H over the entire temperature range (1.8–240 K) suggests that the conducting carriers are dominated by holes. This result reveals that its carrier type is opposite to those of PdTe and PdTe₂ [20, 21]. With increasing temperature, R_H increases slowly, and then the carriers concentration and carriers mobility decreases gradually, see figures 3(b)–(d). The carrier concentration is estimated to be n = 6 × 10²² cm⁻³ at 240 K by n = 1/eR_H of the simple one-band model. Below 30 K, the R_H decreases with lowering temperature to a minimum value of 4.4 × 10¹⁵ cm⁻³, corresponding to n = 1.4 × 10¹⁴ cm⁻³ at 2 K.
A superconducting transition ($T_{c}\text{onset}$) is observed at 2.5 K and $T_{c}\text{zero}$ = 2.2 K as shown in figure S2(a). There is no significant change in other temperature ranges, suggesting that the content of the residual of PdTe superconductivity phase is very small. Figure 4(b) shows the magneto-resistivity perpendicular to the applied magnetic field up to 450 Oe. With increasing magnetic field, the $T_{c}$ decreases at the rate of ~2 K/kOe. Based on the 90% of $T_{c}\text{onset}$, we estimated the upper critical fields [$H_{c2}(0)$] are 1253 Oe and 809 Oe by Werthamer-Helfand-Hohenberg (WHH) equation and Ginzburg-Landau (GL) equation, respectively, see figure 4(c). According to the equation of $H_{c2}(0) = \Phi_0/2\pi\xi_0^2$, where $\Phi_0 = 2.0678 \times 10^9$ Oe Å$^2$ [22], we can get the superconducting coherence length $\xi_0 = 513$ (638) Å. The magnetic susceptibility is measured to further confirm the superconductivity of Pd$_3$Te$_2$. The magnetization is recorded in both zero field cooled (ZFC) and field cooled (FC) modes for Pd$_3$Te$_2$ under $H = 10$ Oe, which is shown in figure 4(d). Below 2.2 K, the susceptibility changes into negative value for both ZFC and FC curves. The $4\pi\chi_{ZFC}$ is about 60% at 1.8 K, because of demagnetizing field inside the material, indicating bulk superconductivity. We determined that the superconductivity of 2.2 K should come from the main phase of Pd$_3$Te$_2$ rather than PdTe, because the mass fraction of PdTe is very small as our refined results. At the same time, we also found a weak superconducting transition (about 1%) at 4.5 K as shown in the figure S2(b), which is consistent with the report of superconductivity of PdTe in the literature [7, 20]. Figure 4(e) shows the isothermal magnetization curves recorded from 1.8 K to 2.2 K in the superconducting state. As the magnetic field increase from zero, the absolute value of magnetization linearly decreases up to $H_{c1}$ and then slowly increases. We are able to obtain $H_{c1}$ at each temperature, and the estimation of $\mu_0H_{c2}(0)$, 150 Oe (92 Oe), has been estimated from the WHH (GL) equation as shown in figure 4(f). The thermodynamic critical field $H_{c}(0)$ can be acquired as the arithmetic mean of the $H_{c2}(0)$ and $H_{c1}(0)$ at 0 K, i.e. $H_{c}(0) = [H_{c2}(0)+H_{c1}(0)]^{1/2}$, and the resultant value is 434 (273) Oe. The GL

![Figure 1. Rietveld refinement of powder x-ray diffraction of Pd$_3$Te$_2$. Result of the Rietveld refinement shows good convergence ($R_{wp} = 6.34\%, R_p = 4.41\%$).](image-url)
Figure 2. Crystallographic structure of Pd₃Te₂ and PdTe. (a) Crystal structure of Pd₃Te₂, PdTe₅ pyramid 1 and oblique pyramid 2 are shown in the (b) and (c), respectively. (d) Crystal structure of PdTe. PdTe₆ octahedral unit of the PdTe is shown in the (e).

Figure 3. Hall effect of Pd₃Te₂. (a) Hall resistance up to µ₀H = 9 T at various temperatures from 2 K-240 K for polycrystalline Pd₃Te₂. (b) Temperature dependence of Hall coefficient R_H(T) at µ₀H = 9 T. (c) Temperature dependence of apparent carrier concentration n_H(T) obtained from the single-band model. (d) Derived carrier mobility µ₀(T) as a function of temperature.
parameter $\kappa$ is estimated to be 2.04 (2.10) by $H_{c2}(0) = 2^{1/2}\kappa H_s(0)$, significantly larger than 1/2, indicating a type-II superconductivity. Besides, the penetration depth $\lambda(0)$ is found to be 1047 (1340) Å from $\lambda(0) = \kappa \xi(0)$, which is larger than 786 Å of PdTe [20].

We measured the specific heat ($C_p$) of Pd$_3$Te$_2$ from 2 K to 200 K, which is plotted in figure 5(a). The enlarged image of $C_p/T$ is shown in figure S2(c) from 0.2 K to 5 K, and the specific heat of samples 2 shows a slight jump at 4.3 K, which comes from the PdTe impurity. The experimental data cannot be well fitted by single Debye model. So we use an equation that includes the contribution of Einstein model to fit the data. The solid blue line is the fitting curve from the sum of Einstein and Debye model contributions,

$$C_p = a \times 9 N R \left( \frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_E} dx \frac{x^4 e^x}{(e^x - 1)^2} + (1 - a) \times 3 n R \left( \frac{\Theta_E}{T} \right)^2 \frac{e^x}{(e^x - 1)^2},$$

Figure 5. Temperature dependence of specific heat for Pd$_3$Te$_2$. (a) Heat capacity ($C_p$) as a function of temperature, the blue line is the fitting curve as the equation in the text. The horizontal dashed line represents the Dulong–Petit limit. The inset is $C_p/T$ versus $T^2$, in which the red straight line represents the fit with the formula $C_p/T = \gamma + \beta T^2$ for the normal-state data from 0.2 to 3 K. (b) Electronic specific heat divided by temperature $C_e/T$ in the superconducting state, where $C_e = C - \beta T^2$, and blue line in (b) is the theoretical curves calculated as the BCS model.
Here, $a$ is 0.90, $R$ the gas constant, $\Theta_D$ Debye temperature and $\Theta_E$ Einstein temperature. Fitting the data against the above equation yields $\Theta_D = 217.2$ K and $\Theta_E = 63.8$ K. The inset of figure 5(a) shows the plot of $C_p/T$ versus $T^2$. A sharp superconducting transition occurs at $T_c \sim 2.2$ K, in accordance with the transport data presented above. In the normal-state, the $C_p$ curve is well fitted by $C_p/T = \gamma + \beta T^2 + \delta T^4$ from 3–10 K, where the first and the second term correspond to the normal-state electronic and phonon contribution, respectively. A linear fit to $C_p/T$ versus $T^2$ above $T_c$ gives the value of the Sommerfeld coefficient $\gamma = 9.67$ mJ mol$^{-1}$ K$^{-2}$, $\beta = 1.40$ mJ mol$^{-1}$ K$^{-4}$ and $\delta = 0.03$ mJ mol$^{-1}$ K$^{-6}$. Using the value of $\beta$, the $\Theta_D$ can be calculated from the following expression [23]:

$$\Theta_D = \frac{12 \pi^4 R}{5 \beta}$$

where $\tau = 5$ is the number of atoms per formula unit in Pd$_3$Te$_2$. We can obtain to the value of $\Theta_D = 191$ K, which is close to the value of PdTe (203 K) [17]. By extrapolating the data in the superconducting state at zero field down to 0 K, we find a residual value $\gamma_0 \approx 3.69$ mJ mol$^{-1}$ K$^{-2}$, indicating a contribution by a non-superconducting fraction in volume of about 38%. We suggest that the superconductivity depends sensitively on the stoichiometric ratio of Pd and Te. So, it is safe to conclude that the superconducting-state Sommerfeld coefficient ($\gamma_n$) for the present sample is 5.98 mJ mol$^{-1}$ K$^{-2}$.

Using the value of $\Theta_D$ (191 K), the electron-phonon coupling is estimated by the McMillan’s formula [24]:

$$\lambda_{e-p} = \frac{1.04 + \mu^* \ln \left( \frac{\Theta_D}{1.45 T_c} \right)}{(1 - 0.62 \mu^*) \ln \left( \frac{\Theta_D}{1.45 T_c} \right) - 1.04}$$

If the Coulomb parameter $\mu^*$ is 0.13. The calculated $\lambda_{e-p}$ is 0.58, indicating a weak coupling state.

We subtracted the phonon contribution from the $C_p$ and plotted the temperature-dependent electronic specific heat ($C_e$) over T from 0.2 K to 3.0 K in figure 5(b). The value for the jump, $\Delta C_e/\gamma_0 T_c$, is 1.82 in the electronic specific heat at $T_c$, which is higher than the BCS value (1.43) for superconductors in the weak-coupling limit. Such inconsistency in coupling state may come from an imprecise subtraction of the electronic contribution. Other Pd-Te superconductors are also reported to the BCS weak coupling state, like PdTe (1.33) [7], Pd$_x$Te$_{2-y}$ (1.52) [25], Ta$_x$Pd$_{3-y}$Te$_{16}$ (1.4) [1] and Ta$_x$Pd$_3$Te$_{14}$ (1.35) [2]. The $C_e/T$ data (below 1/3 $T_c$) can be fitted by the expression from the BCS theory $C_e/T \propto e^{-\Delta/\sqrt{4\pi T}}$ [23, 26]. The yielded $\Delta(0) = 0.176$ meV. The good agreement between the measured data (green symbols) and the BCS fitting (blue line) provides evidence for an s-wave isotropic superconducting gap. Furthermore, the fitting yields $\Delta(0)/k_B T_c = 1.12$, which is also lower than the value of 1.76 for BCS theory.

The band structure, projected density of states and Fermi surface of Pd$_3$Te$_2$ are shown in figure 6. The calculations were firstly checked for convergence, we choose 600 eV for cutoff energy and k-pacing 0.02 Å$^{-1}$ (k-mesh of $14 \times 14 \times 6$), as shown in figure S3. We have calculated band structures with spin-orbital coupling. There are four bands crossing the Fermi level ($E_F$) along the high symmetry paths as shown in figure 6(a), the corresponding total and projected densities of states are shown in figure 6(b). The finite value of DOS at $E_F$ is consistent with the metallic behavior in $\rho(T)$. The bands crossing $E_F$ are composed of hybridized states of Pd $d$ and Te $p$ orbitals. The each $d$-orbital contributions of Pd at the $E_F$ are almost equal, around 0.5/eV per primitive cell, while the each $p$-orbital of Te contributes $\sim$0.4/eV per primitive cell. The total DOS at $E_F$ is $N(E_F) = 5.61$/eV per primitive cell (2 formula units), corresponding to a value of electronic heat coefficient $\gamma_0 = 6.59$ mJ mol$^{-1}$ K$^{-2}$. According to the equation $\gamma_n = \gamma_0(1 + \lambda_{e-p} (\text{mJ/mole} K^2))$, we can obtain value...
with 5-coordination in palladium tellurides system.

Table 2. Superconducting properties of Pd$_3$Te$_2$.

| $T_c$ K | $H_{c2}(0)$ Oe | $\xi_0$ Å | $H_{c1}(0)$ Oe | $H_{c2}(0)$ Oe | $\kappa$ | $\lambda(0)$ Å | $\Theta_D$ K | $\gamma_n$ mJ/mol K$^2$ | $\lambda_{c-p}$ | $\Delta(0)/k_BT_c$ |
|--------|----------------|-----------|----------------|----------------|-------|---------------|------------|----------------|--------------|----------------|
| 2.2    | 1253           | 531       | (WHH)          | (WHH)          | 150   | 434           | (WHH)      | 2.04           | 1047         | 191           | 5.98          | 0.58          | 1.12          |
|        | 809            | 638       | (GL)           | (GL)           | 92    | 273           | (GL)       | 2.10           | 1340         |              |               |               |

$\gamma_n = 10.41$ mJ mol$^{-1}$ K$^2$, which is higher than the experimental value of 5.98 mJ mol$^{-1}$ K$^2$, because of non-superconducting phase of Pd$_3$Te$_2$ sample. The Fermi surface of Pd$_3$Te$_2$ has three-dimensional feature with rather complicated geometry, as shown in figure 6(c). The origin of superconductivity is dependent on Pd $d$ states and Te $p$ states at $E_F$, irrelevant to atomic coordination in palladium tellurides system. All of the superconducting properties of Pd$_3$Te$_2$ are listed in table 2.

Conclusion

In summary, we have investigated and studied the superconducting properties of polycrystalline Pd$_3$Te$_2$. The electrical resistivity, magnetic susceptibility and specific heat confirm that the $T_c$ of Pd$_3$Te$_2$ is 2.2 K. Further analysis of the experimental data indicates that Pd$_3$Te$_2$ is a type-II superconductor. The value of $\lambda_{c-p}$ suggests that the Pd$_3$Te$_2$ is a BCS-type weakly-coupled superconductor. Our discovery reveals a new superconductor with 5-coordination in palladium tellurides system.

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ORCID iDs

X Chen https://orcid.org/0000-0003-3477-2204
J G Guo https://orcid.org/0000-0003-3880-3012
X L Chen https://orcid.org/0000-0001-8455-2117

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