Evidence for nodal superconductivity in a layered compound Ta$_4$Pd$_3$Te$_{16}$

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Abstract

We report an investigation of the London penetration depth $\Delta \lambda(T)$ on single crystals of the layered superconductor Ta$_4$Pd$_3$Te$_{16}$, where the crystal structure has quasi-one-dimensional characteristics. A linear temperature dependence of $\Delta \lambda(T)$ is observed for $T \ll T_c$, in contrast to the exponential behavior of fully gapped superconductors. This indicates the existence of line nodes in the superconducting energy gap. A detailed analysis shows that the normalized superfluid density $\rho_s(T)$, which is converted from $\Delta \lambda(T)$, can be well described by a multigap scenario, with nodes in one of the superconducting gaps, providing clear evidence for nodal superconductivity in Ta$_4$Pd$_3$Te$_{16}$.

Keywords: superconducting order parameter, London penetration depth, line nodes

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

1. Introduction

Recently the layered Pd-based ternary chalcogenides have attracted much research interest. New compounds with similar crystal structures were discovered, which opened up new opportunities to investigate the relationship between superconductivity and reduced crystal dimensionality [1–3]. Unusual superconducting properties were revealed in Ta$_2$Pd$_x$S$_5$ ($x \ll 1.0$) and Nb$_2$Pd$_{0.81}$S$_5$, where extremely large upper critical fields of $\mu_0 H_c^2(0) = 31$ T and $\mu_0 H_c^2(0) = 37$ T were observed respectively, both of which are almost twice the size of the Pauli limiting field ($H_p$) [4, 5]. These are reminiscent of the quasi-one-dimensional (Q1D) organic compounds (TMTSF)$_2$X (TMTSF = tetramethyltetraselenafulvalene, $X = PF_6$, ClO$_4$), which are believed to be unconventional superconductors [6, 7]. Moreover, subsequent specific heat measurements of Nb$_2$Pd(S$_1-x$Se$_x$) and Ta$_2$PdSe$_5$ show a slight deviation from the typical behavior of single band $s$-wave superconductors, which likely indicates multi-band superconductivity in these systems [8, 9].

A new layered Pd-based ternary compound Ta$_4$Pd$_3$Te$_{16}$ was found to exhibit superconductivity at $T_c \approx 4.6$ K [10]. It possesses a layered crystal structure as well as Q1D characteristics, with chains running along the $b$ axis. Band structure calculations for Ta$_4$Pd$_3$Te$_{16}$ reveal that its Fermi surface consists of four branches, including two one-dimensional nested sheets, a two-dimensional cylindrical sheet and a three-dimensional one, which drives this compound to be an anisotropic but three-dimensional metal [11]. This is also consistent with the results of upper critical field measurements where a moderate anisotropy of $\mu_0 H_c^2$ was observed and the coherence lengths along all three axes are much larger than the interchain distance [12]. High field measurements uncover a quasi-linear magnetoresistance without any sign of saturation up to about 50 T, as well as a violation of Kohler’s rule, indicating the existence of charge density wave fluctuations in this
compound [13], which has also been suggested from scanning tunneling spectroscopy (STS) experiments [14]. Meanwhile, there have also been various studies to characterize the superconducting order parameter, which could give the crucial information about the pairing mechanism. However, no firm conclusions have been reached on the nature of the gap structure. Evidence for nodal superconductivity came from thermal conductivity measurements, where in zero field there is a significant residual value of $\kappa(T)/T$ at zero temperature. Furthermore, there is a rapid increase of $\kappa(H)/T$ in an applied magnetic field, which is very similar to the behavior of $d$-wave superconductors [15]. This scenario is supported by electronic specific heat results, which show power law behavior at low temperatures and a non-linear field dependence of the Sommerfeld coefficient $\gamma(H)$ [12]. On the other hand, different results were obtained from STS measurements, where a BCS-like gap structure was reported by one group, whereas another report gave an indication of a highly anisotropic gap structure with gap minima or nodes [14, 16]. Therefore, due to the discrepancies between different measurements of the order parameter of $\text{Ta}_4\text{Pd}_3\text{Te}_{16}$, further measurements at lower temperatures are needed.

Here, we report the temperature dependence of the London penetration depth $\Delta \lambda(T)$ of single crystals of $\text{Ta}_4\text{Pd}_3\text{Te}_{16}$. A combined analysis of our $\Delta \lambda(T)$ measurements, the derived superfluid density $\rho(T)$ and the previous specific heat results show consistent evidence for multi-band superconductivity in $\text{Ta}_4\text{Pd}_3\text{Te}_{16}$ with nodes in at least one of the gaps.

2. Methods

Single crystal samples were synthesized by a self-flux method [10], and characterized using both electrical resistivity and magnetic susceptibility measurements. The temperature dependence of the resistivity was measured using the standard four-probe method from room temperature down to about 3 K, while the magnetization measurements were performed by utilizing a SQUID magnetometer (MPMS-5T) from 8 K to about 2 K with both field-cooling (FC) and zero-field-cooling (ZFC) under a small applied magnetic field of 10 Oe.

By utilizing a tunnel-diode-oscillator (TDO) based technique [17], precise measurements of London penetration depth $\Delta \lambda(T)$ were carried out in a $^3$He cryostat down to 0.45 K, and in a dilution refrigerator with a base temperature of about 0.06 K. Due to the flat needle like shape of the crystals, samples were cut into typical sizes of $(250 - 450) \times (250 - 450) \times (50 - 150) \text{ \mu m}^3$ with the plane being parallel to the chain direction. The sample was mounted on a sapphire rod so as to be inserted into the coil without any contact. The operating frequency of the TDO was about 7 MHz in the $^3$He system and 9 MHz in the dilution refrigerator, with a noise level as low as 0.1 Hz, by steadily controlling the temperature of the coil and electrical circuit independently. The sample experienced a very small ac field induced by the coil of about 20 mOe along the $c^*$ direction, which is much smaller than the lower critical field $H_{c1}$, ensuring that the sample was always in the Meissner state during the measurements. As a result, the measured frequency shift $\Delta f(T)$ can be considered to be proportional to the change of the London penetration depth in the $a^*b$ plane with $\Delta \lambda(T) = G \Delta f(T)$, where the calibration constant $G$ is solely dependent on the sample and coil geometry [18].

3. Results

The electrical resistivity $[\rho(T)]$ and magnetic susceptibility are displayed in figure 1. Metallic behavior of $\rho(T)$ is shown in the normal state, with a residual resistivity of 4.5 $\mu \Omega \text{ cm}$, just before entering the superconducting state, with zero resistivity being reached at 4.1 K. This gives rise to a large mean free path of 281 nm following the method in [19], by using a coherence length of $\xi_0 = 10 \text{ nm}$ and Sommerfeld coefficient $\gamma_n = 51.2 \text{ mJ mol}^{-1} \text{ K}^{-2}$ [12]. This calculated mean free path is much larger than the coherence length. A superconducting transition is also observed in the magnetic susceptibility measurements, with a midpoint of the transition at around 3.8 K. These results indicate that $\text{Ta}_4\text{Pd}_3\text{Te}_{16}$ is a superconductor in the clean limit.

As shown in figure 2, the temperature dependence of the London penetration depth shift $\Delta \lambda(T)$ for various single crystals was measured from 8 K down to 0.06 K, which exhibit similar reproducible behavior. A clear superconducting transition is observed in $\Delta \lambda(T)$, with $T_c = 3.9$ K determined from the endpoint of the transition, which was used in the subsequent calculations. We note that in both the resistivity and TDO based measurements, there is an onset of superconductivity at higher temperatures of around 6 K, whereas the endpoints of the transitions are close to the $T_c$ values in the specific heat and dc magnetic susceptibility. Since the resistivity and frequency shift are much more sensitive to non-bulk superconductivity, these results suggest that there is the onset of filamentary superconductivity with a small volume fraction.
at higher temperatures, above the sharp onset of bulk superconductivity in the rest of the sample. The main panel displays the enlargement of the low temperature behavior of $\Delta \lambda(T)$, where a quasilinear temperature dependence is observed from 1.4 K down to about 0.2 K, below which a small downturn in $\Delta \lambda(T)$ is observed. The temperature dependence of $\Delta \lambda(T)$ at $T \ll T_c$ is usually related to the low energy excitations, which is determined by the superconducting gap structure. In the case of nodeless weakly coupled $s$-wave superconductors, $\Delta \lambda(T)$ regularly exhibits an exponential decrease below around $T_c/3$, due to the absence of low energy excitations. Whereas in other materials, such as the cuprate and heavy fermion superconductors where there are often nodes in the gap, a power law temperature dependence of $\Delta \lambda(T)$ is usually observed and in particular, when $\Delta \lambda(T) \sim T$ at low temperatures, there is a strong indication of line nodes [20, 21]. Therefore, the clear observation of linear behavior at low temperatures in the penetration depth measurements is evidence against fully-gapped superconductivity in Ta$_4$Pd$_3$Te$_{16}$, and suggests that the superconducting gap has line nodes. We note that the small downturn below 0.2 K is consistently observed in different samples, including when the sample is polished to avoid any extrinsic effect from the as-grown surface (lower inset of figure 2). The overall size of the downturn of the signal is only around 0.04% of the overall frequency shift from above $T_c$ and therefore this may correspond to the presence of a very small impurity phase, which is not likely to significantly affect the measurements at higher temperatures.

To get further insight into the superconducting pairing symmetry of Ta$_4$Pd$_3$Te$_{16}$, the normalized superfluid density $\rho_s(T)$, calculated using $\rho_s(T) = \lambda^2(T)/\lambda^2(T_c)$ with $\lambda(T) = \lambda(0) + \Delta \lambda(T)$, is plotted in figure 3(a). The value of $\lambda(0)$ was derived from solving $\mu_0 H_{c1} = (\Phi_0/4\pi \lambda)(\ln(\lambda/\xi) + 0.5)$, where $\Phi_0$ is the magnetic flux quantum. By using the parameters $\mu_0 H_{c2}(0) = 3.3$ T and $\mu_0 H_{c1}(0) = 2.99$ mT [12], the value of $\lambda(0) = 492$ nm was estimated. The inset of figure 3(a) also shows $\rho_s(T)$ for a change in $\lambda(0)$ of $\pm \sim 20\%$ and the data show similar behavior. The temperature dependence of $\rho_s(T)$ solely depends on its Fermi surface and superconducting gap structure. For a given gap function $\Delta_k$, the normalized superfluid density $\rho_s(T)$ was calculated using:

$$\rho_s(T) = 1 + 2 \left\langle \int_{\Delta_k} \frac{E dE}{\sqrt{E^2 - \Delta_k^2}} \frac{\partial f}{\partial E} \right\rangle_{FS}$$

where $f(E,T) = [1 + \exp(E/T)]^{-1}$ is the Fermi distribution function with the Boltzmann constant defined as $k_B = 1$, and $\langle \ldots \rangle_{FS}$ denotes the integration over a cylindrical Fermi surface. The superconducting gap function is given by $\Delta_k(T) = \Delta(0)g_k(\phi)$. Here, $g_k(\phi)$ is a dimensionless function that determines the angular dependence of the gap and $\phi$ is the azimuthal angle. $\Delta_k(T)$ describes the temperature dependence of the gap, which is approximated by:

$$\Delta_k(T) = \Delta(0)\tanh \left\{ 1.82[1.018(T_c/T - 1)]^{0.51} \right\},$$

where the parameter which characterizes the zero temperature gap magnitude $\Delta(0)$ is the only adjustable parameter [22].

Several forms of $g_k(\phi)$ were used to fit the experimental data, as displayed in figure 3(a). Firstly, a single band $s$-wave model with $g_k(\phi) = 1$ fails to describe the data at low temperatures, although the high temperature part above 0.7$T_c$ is fitted quite well. When the superconducting gap is

Figure 2. Low temperature behavior of the London penetration depth $\Delta \lambda(T)$ for three single crystals of Ta$_4$Pd$_3$Te$_{16}$. The solid red line shows the linear decrease of $\Delta \lambda(T)$ below around 1.4 K. The upper inset shows the temperature dependence of $\Delta \lambda(T)$ up to above $T_c$. The lower inset shows a comparison between the low temperature behavior of an unpolished sample (#1) and a sample where the surface was polished (#4), normalized by the respective values at 1.8 K.

Figure 3. (a) The temperature dependence of the normalized superfluid density $\rho_s(T)$ for sample #1 of Ta$_4$Pd$_3$Te$_{16}$ using $\lambda(0) = 492$ nm. The lines show the results from fitting various models. The inset shows $\rho_s(T)$ for two different values of $\lambda(0)$. The dashed lines show fits for the two different $\lambda(0)$ using the same $d$-wave model described in the text. The bottom panels show the angular dependence of the amplitudes of the two gaps at zero temperature from the fitted (b) $s + es$ and (c) $s + d$ models, where the solid dots represent the nodal directions.
nodeless, $\rho_s(T)$ is always expected to flatten at $T \ll T_c$, but no such saturation is observed in the experimental data and $\rho_s(T)$ continues to increase with decreasing temperature. The observation of a linear temperature dependence of $\Delta\lambda(T)$ and $\rho_s(T)$ provides evidence for the existence of line nodes in the superconducting energy gap, as in the case of the $d$-wave superconductivity of the cuprates. Consequently, a $d$-wave model with $g_1(\phi) = \cos 2\phi$ was fitted, which can successfully describe $\rho_s(T)$ at low temperatures but significantly deviates in the high temperature region. Although the derived $\rho_s(T)$ data will be affected by uncertainties in both the calibration constant $G$ and $\lambda(0)$, as displayed in the inset, upon changing $\lambda(0)$ by $\pm \sim 20\%$, the $d$-wave model is still unable to account for the data.

Due to the presence of multiple Fermi surface sheets from theoretical calculations [11], we also fitted various two-band models. In a phenomenological two-band model, the total superfluid density $\rho(T)$ can be obtained from a linear combination of two components:

$$\rho(T) = \alpha \rho_s^0(\Delta_1^0, T) + (1 - \alpha) \rho_d^0(\Delta_2^0, T),$$  \hspace{1cm} (3)

where $\Delta_i^0 (i = 1, 2)$ represent the superconducting gap functions of the two components and $\alpha$ is the relative weight for $\rho_s^0$. Since a linear temperature dependence of $\rho_s(T)$ is clearly observed at $T \ll T_c$, which cannot be reproduced by a calculation with two isotropic nodeless gaps, both $s + es$ and $s + d$ models were fitted to the experimental data. In the $s + es$ model there is one isotropic gap and an anisotropic $s$-wave (es) gap, with a gap angular dependence given by $g_1(\phi) = 1 + r \cos 2\phi$, where $r$ characterizes the gap anisotropy [12, 16, 23]. It can be seen that the energy gap is always nodeless for $r < 1$, while for $r > 1$, it goes to zero along $\phi = 0.5\arccos(-1/r)$, where the accidental nodes are located. We note that a single band anisotropic $s$-wave model was previously reported to be unable to account for the specific heat data [12]. On the other hand the $s + d$ model has an isotropic $s$-wave gap as well as a $d$-wave gap, and this model was also applied in the analysis of STS and specific heat data, where the nodal $d$-wave component was one possibility for explaining the deviation from isotropic, fully-gapped behavior [12, 16]. As shown in figure 3(a), both models can well fit the experimental data across the whole temperature range. For the $s + es$ model, the fitting parameters are $\Delta_s(0) = 2.36T_c$, $\Delta_es(0) = 1.25T_c$ and $r = 1.9$, with a weighting of $\alpha = 0.3$ for the isotropic $s$-wave component. For the $s + d$ model, the fitted values are $\Delta_s(0) = 2.9T_c$, $\Delta_d(0) = 2.67T_c$ and $\alpha = 0.6$. The angular dependence of the gap structures for the fitted models are displayed in figures 3(b) and (c), where the value of $r = 1.9$ indicates that for the $s + es$ model, there are nodes in the anisotropic gap. It should be noted that the linear temperature dependence of $\rho_s(T)$ at low temperatures cannot be reproduced by an $s + es$ model with $r < 1$, where both superconducting gaps are fully open. In that case, due to a nodeless superconducting gap structure, $\Delta\lambda(T)$ and the derived $\rho_s(T)$ always become flat below a certain temperature depending on the value of the gap magnitude, whereas no such saturation is observed in the measurements, even down to $0.06\, \text{K} \sim (0.015T_c)$. In addition, the $s + es$ and $s + d$ models were also fitted to the previously reported electronic specific heat data from [12], as displayed in figure 4. The entropy $S$ in the superconducting state can be expressed as [24]:

$$S = -\frac{3\gamma}{\pi^3} \int_0^{2\pi} \int_0^{\infty} [f \ln f + (1 - f) \ln (1 - f)] d\epsilon d\phi,$$  \hspace{1cm} (4)

where $\epsilon = \sqrt{E^2 - \Delta_k^2(T)}$, and $\Delta_k(T)$ follows the same expression used in the superfluid density analysis. In the superconducting state, the superconducting electronic specific heat is derived from $C_e = T dS/dT$. Both the $s + es$ and $s + d$ models can well describe the data, taking into account a residual contribution to $C_e/T$ of $0.02 \, \text{mJ mol}^{-1} \, \text{K}^{-2}$. The fitted parameters are $\Delta_s(0) = 2.1T_c$, $\Delta_es(0) = 1.16T_c$, $\alpha = 0.53$ and $r = 2.0$ for the $s + es$ model and $\Delta_s(0) = 2.85T_c$, $\Delta_d(0) = 2.05T_c$, and $\alpha = 0.48$ for the $s + d$ model. Since the specific heat is sensitive to excitations along all directions but $\rho_s(T)$ only probes directions perpendicular to the applied field, this may account for the small differences between the fitting parameters from the two techniques.

Therefore, both the two-band $s + es$ and $s + d$ models can reasonably account for the penetration depth and specific heat data. However, even though the $d$-wave model did not give a good fit to our experimental data, due to the complex Fermi surface in this compound [11], $d$-wave superconductivity also cannot be excluded. As such, it is difficult to distinguish between these different scenarios for nodal superconductivity on the basis of our measurements. The primary result of our present study is the linear behavior of $\Delta\lambda(T)$ at low temperatures, which strongly suggests the existence of line nodes in the gap structure. In the case of the $s + d$ model, the $s$-wave and $d$-wave instabilities will generally be expected to have different transition temperatures and therefore a split...
superconducting transition would be anticipated [25]. It has also been noted that the nodal superconducting gap structure is expected to be more robust in $d$-wave superconductors than in the extended $s$-wave cases, where the accidental nodes can be easily lifted by disorder [26]. Therefore, it maybe helpful to study samples where random defects are introduced, for example by electron irradiation. On the other hand, theoretical calculations indicate that there are complex anisotropic Fermi sheets in $\text{Ta}_4\text{Pd}_3\text{Te}_{16}$, and suggest that the system is far away from a magnetic instability [11]. In that sense, the complex Fermi surface maybe play an important role in leading to the anisotropic interactions which give rise to nodes.

4. Conclusion

To summarize, we have precisely measured the temperature dependence of the change of the London penetration depth $\Delta \lambda(T)$ for the newly discovered layered superconductor $\text{Ta}_4\text{Pd}_3\text{Te}_{16}$ using a TDO method. Linear behavior of $\Delta \lambda(T)$ is clearly observed at low temperatures, as well as in the corresponding superfluid density $\rho_s(T)$, which can be successfully described in terms of either a phenomenological two-band $s + \delta s$ or $s + d$ model, in line with our reanalysis of the previous specific heat results. Our findings show a distinct discrepancy from the behavior of fully-gapped superconductors and provide strong evidence for nodal superconductivity in $\text{Ta}_4\text{Pd}_3\text{Te}_{16}$.

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