Fully gapped superconducting state in Au$_2$Pb: A natural candidate for topological superconductor

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Abstract – We measured the ultra-low-temperature specific heat and thermal conductivity of the Au$_2$Pb single crystal, a possible three-dimensional Dirac semimetal with a superconducting transition temperature $T_c \approx 1.05$ K. The electronic specific heat can be fitted by a two-band s-wave model, which gives the gap amplitudes $\Delta_1(0)/k_BT_c = 1.41$ and $\Delta_2(0)/k_BT_c = 5.25$. From the thermal conductivity measurements, a negligible residual linear term $\kappa_0/T$ in zero field and a slow field dependence of $\kappa_0/T$ at low field are obtained. These results suggest that Au$_2$Pb has a fully gapped superconducting state in the bulk, which is a necessary condition for topological superconductors if Au$_2$Pb is indeed one.

Introduction. – In recent years, the topological materials have attracted much attention because of their novel quantum states [1–3]. Among those topological materials, the topological superconductors (TSCs) are of particular interest. The TSCs have a full gap in the bulk and Majorana fermion states on the surface [2]. The TSCs are very important since they possess potential application to topological quantum computation due to the non-Abelian statistics of Majorana fermions [4]. Experimentally, there are several routes to obtain a TSC candidate. The first one is to artificially fabricate topological insulator/superconductor heterostructures [5,6]. The second one is to dope a topological material. For example, the Cu-intercalated Bi$_2$Se$_3$ shows superconductivity below 3.8 K [7], which was considered as a TSC candidate [8–11]. The third one is to pressurize a topological material. Pressure-induced superconductivity was observed in some topological insulators, such as Bi$_2$Se$_3$ [12], Bi$_2$Te$_3$ [13], and Sb$_2$Te$_3$ [14]. Superconductivity was also found in the three-dimensional Dirac semimetal Cd$_3$As$_2$ under a tip or hydropressure [15–17]. Note that the pressure-induced superconductivity usually coincides with a change in crystal structure and the material may be no longer topological [12,17]. To further confirm that a TSC candidate is indeed a TSC, it is essential to identify the Majorana fermion states on the surface. Unfortunately, no consensus has been reached on this important issue yet [18].

Besides these routes, in some rare cases, a natural TSC candidate may exist if a stoichiometric superconductor manifests topological properties under ambient pressure. One recent example is the noncentrosymmetric superconductor PbTaSe$_2$ with $T_c = 3.72$ K [19]. Angle-resolved photoemission spectroscopy (ARPES) experiments and first-principle calculations revealed topological nodal-line semimetal states and associated surface states in PbTaSe$_2$ [20,21]. The thermal conductivity, specific heat, and London penetration depth measurements all demonstrated a fully gapped superconducting state in it [22–24], which is also required for a TSC.

More recently, it was argued that the cubic Laves phase Au$_2$Pb ($T_c \approx 1.2$ K) may be another natural TSC candidate. For example, Bi$_2$Pb$_3$Te$_6$ shows superconductivity below 3.8 K [7], which was considered as a TSC candidate [8–11]. The cubic Laves phase Au$_2$Pb ($T_c \approx 1.2$ K) may be another natural TSC candidate.

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candidate [25, 26]. Electronic band structure calculations predicted that cubic Au$_2$Pb has a bulk Dirac cone at room temperature [25]. With decreasing temperature, Au$_2$Pb undergoes structural phase transitions, and only the orthorhombic phase remains below 40 K [25, 27]. Their calculations showed that the structure transition gaps out the Dirac spectrum in the high-temperature phase, and results in a low-temperature nontrivial massive 3D Dirac phase with $Z_2 = -1$ topology [25]. In ref. [26], the first-principles calculations also point to the nontrivial topology of the orbital texture near the dominant Fermi surfaces, which suggests the possibility of topological superconductivity. To check whether Au$_2$Pb is indeed a TSC, it will be very important to determine its superconducting gap structure first.

In this letter, we investigate the superconducting gap characteristics of the Au$_2$Pb single crystal, by means of the ultra-low-temperature specific heat and thermal conductivity measurements. Our analysis shows that the electronic specific heat can be described by the two-band $s$-wave model. Furthermore, a negligible $\kappa_0/T$ in zero field and a slow field dependence of $\kappa_0/T$ at low field are revealed by the thermal conductivity measurements. These results suggest that Au$_2$Pb has a fully gapped $s$-wave superconducting state in the bulk.

**Experiments.** – Single crystals of Au$_2$Pb were grown by a self-flux method [26]. The as-grown single crystals have a plate-like shape, and the largest natural surface was determined as (111) plane at room temperature [26]. The sample for transport measurements was cut to a rectangular shape of dimensions $2.5 \times 1.0 \text{mm}^2$ in the (111) plane, with a thickness of 0.10 mm perpendicular to this natural surface. Contacts were made directly on the sample surfaces with silver paint, which were used for both resistivity and thermal conductivity measurements. The typical contact resistance is less than 100 m$\Omega$ at low temperature. The resistivity was measured in a $^4$He cryostat from 300 K to 2 K, and in a $^3$He cryostat down to 0.3 K. The thermal conductivity was measured in a dilution refrigerator, using a standard four-wire steady-state method with two RuO$_2$ chip thermometers, calibrated in situ against a reference RuO$_2$ thermometer. Magnetic fields were perpendicular to the natural surface and the heat current. Note that the natural surface is no longer the (111) plane for the low-temperature orthorhombic, distorted phase of Au$_2$Pb [25]. To ensure a homogeneous field distribution in the sample, all fields were applied at a temperature above $T_c$. The low-temperature specific heat was measured from 0.1 to 3.5 K in a physical property measurement system (PPMS, Quantum Design) equipped with a small dilution refrigerator.

**Results and discussion.** – Figure 1(a) shows the resistivity of the Au$_2$Pb single crystal in zero field. The three discontinuities at 97, 50, and 40 K are related to the structural phase transitions, as reported previously [25–27]. From the inset of fig. 1(a), the width of the resistive superconducting transition (10–90%) is 0.16 K, and the $T_c$ defined by $\rho = 0$ is 1.05 K. The $\rho(T)$ curve between 1.5 and 2.5 K is quite flat, which extrapolates to a residual resistivity $\rho_0 = 5.71 \mu\Omega\text{cm}$. Thus, the residual resistivity ratio (RRR = $\rho(295\text{K})/\rho_0$) is about 7.5.

To determine the upper critical field $H_{c2}(0)$ of Au$_2$Pb, we measured the low-temperature resistivity of the sample in various magnetic fields up to 100 mT, as shown in fig. 1(b). The temperature dependence of $H_{c2}(T)$, defined by $\rho = 0$ on the resistivity curves in fig. 1(b), is plotted in fig. 1(c). The dashed line is a guide to the eye, from which we estimate $H_{c2}(0) \approx 19.1 \text{mT}$. Fig. 1: (Color online) (a) Temperature dependence of the resistivity for the Au$_2$Pb single crystal in zero field. The arrows indicate the discontinuities related to structural phase transitions. The inset shows the superconducting transition at low temperature. (b) Low-temperature resistivity in magnetic fields up to 100 mT. (c) Temperature dependence of the upper critical field $H_{c2}(T)$, defined by $\rho = 0$. The dashed line is a guide to the eye, from which we estimate $H_{c2}(0) \approx 19.1 \text{mT}$. 

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electronic specific heat superconducting states as a function of temperature. The solid line represents the best fit to the electronic specific heat divided by temperature $T$ in the normal and superconducting states. The dash-dotted line represents the superconducting transition, the specific-heat jump $\Delta C_s/\gamma_n T_c$ is estimated to be about 1.40, which is close to the weak-coupling BCS prediction of 1.43. In ref. [25], the specific heat of Au$_2$Pb was measured down to 0.4 K. Here, we measured it down to lower temperature ($\sim 0.1$ K), which enables us to quantitatively analyze its behavior. We note that $C_v/T$ almost saturates and extrapolates to a negligible value at ultra-low temperature, yielding a residual value $\gamma_r = 0.084 \text{ mJ mol}^{-1} \text{K}^{-2}$. Taken at face value, a superconducting volume fraction $(\gamma_n-\gamma_r)/\gamma_n \approx 97\%$ is estimated. First, we simply fit $C_v/T$ in the superconducting state with the BCS $\alpha$-model, as shown in fig. 2(c). Since electronic structure calculations of Au$_2$Pb showed that there are several bands which cross the Fermi level along the $\Gamma$-$K$ line [25], there are likely more than one superconducting gaps. On the basis of a phenomenological two-gap model within the conventional BCS framework [28,29], the $T$-dependence of $C_v/T$ including the whole $T$ region below $T_c$ can also be fitted by using two BCS gaps. In this fit, the specific heat is calculated as the sum of the contributions from two bands by assuming independent BCS temperature dependence of the two $s$-wave superconducting gaps. The magnitudes of the two gaps at the $T = 0$ limit are introduced as adjustable parameters, $\alpha_1 = \Delta_1(0)/k_B T_c$ and $\alpha_2 = \Delta_2(0)/k_B T_c$, together with the quantity $\gamma_i/\gamma_n$ ($i = 1, 2$), which is the weight of the total electron density of states (EDOS) for each band. As shown in fig. 2(c), the two-band fit with $\alpha_1 = 1.41$ and $\alpha_2 = 5.25$ reproduces the specific heat very well. The superconducting gap ratio $\Delta_1(0)/\Delta_2(0) \approx 0.27$ is obtained. The weights are 8% and 92% for the two bands with the small and large gaps, respectively. This specific-heat result indicates a fully gapped superconducting state in Au$_2$Pb.

The ultra-low-temperature thermal conductivity measurement is another bulk technique to probe the superconducting gap structure [30]. In fig. 3, we present the temperature dependence of the thermal conductivity for the Au$_2$Pb single crystal in zero and magnetic fields. The thermal conductivity at very low temperature usually can be fitted to $\kappa/T = a + b T^{\alpha-1}$ [31,32], where the two terms $a T^\alpha$ and $b T^{\alpha}$ represent contributions from electrons and phonons, respectively. In order to obtain the residual linear term $\kappa_0/T$ contributed by electrons, we extrapolate $\kappa/T$ to $T = 0$ K. Because of the specular reflections of phonons at the sample surfaces, the power $\alpha$ in the second term is typically between 2 and 3 [31,32].

$\theta_D = (12 \pi^4 R Z / 5 \beta)^{1/3}$, where $R$ is the molar gas constant and $Z$ is the total number of atoms in one unit cell, the Debye temperature $\theta_D = 174$ K is estimated. Note that the Sommerfeld coefficient $\gamma_n$ and the Debye temperature $\theta_D$ obtained from our data are slightly larger than those reported previously [25,27]. From the zero-field specific-heat data, the thermodynamic critical field was determined to be 8 mT by calculating the free-energy difference between the normal and superconducting states.

Figure 2(c) displays the temperature dependence of the electron specific heat $C_v/T = C_p/T - C_{lat}/T$. At the superconducting transition, the specific-heat jump $\Delta C_s/\gamma_n T_c$ is estimated to be about 1.40, which is close to the weak-coupling BCS prediction of 1.43. In ref. [25], the specific heat of Au$_2$Pb was measured down to 0.4 K. Here, we measured it down to lower temperature ($\sim 0.1$ K), which enables us to quantitatively analyze its behavior. We note that $C_v/T$ almost saturates and extrapolates to a negligible value at ultra-low temperature, yielding a residual value $\gamma_r = 0.084 \text{ mJ mol}^{-1} \text{K}^{-2}$. Taken at face value, a superconducting volume fraction $(\gamma_n-\gamma_r)/\gamma_n \approx 97\%$ is estimated. First, we simply fit $C_v/T$ in the superconducting state with the BCS $\alpha$-model, as shown in fig. 2(c). Since electronic structure calculations of Au$_2$Pb showed that there are several bands which cross the Fermi level along the $\Gamma$-$K$ line [25], there are likely more than one superconducting gaps. On the basis of a phenomenological two-gap model within the conventional BCS framework [28,29], the $T$-dependence of $C_v/T$ including the whole $T$ region below $T_c$ can also be fitted by using two BCS gaps. In this fit, the specific heat is calculated as the sum of the contributions from two bands by assuming independent BCS temperature dependence of the two $s$-wave superconducting gaps. The magnitudes of the two gaps at the $T = 0$ limit are introduced as adjustable parameters, $\alpha_1 = \Delta_1(0)/k_B T_c$ and $\alpha_2 = \Delta_2(0)/k_B T_c$, together with the quantity $\gamma_i/\gamma_n$ ($i = 1, 2$), which is the weight of the total electron density of states (EDOS) for each band. As shown in fig. 2(c), the two-band fit with $\alpha_1 = 1.41$ and $\alpha_2 = 5.25$ reproduces the specific heat very well. The superconducting gap ratio $\Delta_1(0)/\Delta_2(0) \approx 0.27$ is obtained. The weights are 8% and 92% for the two bands with the small and large gaps, respectively. This specific-heat result indicates a fully gapped superconducting state in Au$_2$Pb.

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$\theta_D = (12 \pi^4 R Z / 5 \beta)^{1/3}$, where $R$ is the molar gas constant and $Z$ is the total number of atoms in one unit cell, the Debye temperature $\theta_D = 174$ K is estimated. Note that the Sommerfeld coefficient $\gamma_n$ and the Debye temperature $\theta_D$ obtained from our data are slightly larger than those reported previously [25,27].
In zero field, the fitting gives the residual linear term \( \kappa_0/T = -2.6 \pm 6 \mu \text{W K}^{-2} \text{cm}^{-1} \), as seen in fig. 3(a). Considering our experimental uncertainty \( \pm 5 \mu \text{W K}^{-2} \text{cm}^{-1} \), the \( \kappa_0/T \) is essentially zero. For nodeless superconductors, there are no fermionic quasiparticles to conduct heat as \( T \to 0 \), since all electrons become Cooper pairs. Therefore, there is no residual linear term \( \kappa_0/T \), as seen in conventional s-wave superconductors Nb and InBi [33,34]. However, for unconventional superconductors with nodes in the superconducting gap, the nodal quasiparticles will contribute a substantial \( \kappa_0/T \) in zero field. For example, \( \kappa_0/T = 1.41 \text{mW K}^{-2} \text{cm}^{-1} \) for the overdoped \( d \)-wave cuprate superconductor \( \text{Tl}_2\text{Ba}_2\text{CuO}_{6+\delta} \) (TI-2201), which is about 36\% of its \( \kappa_{NO}/T \) [35], and \( \kappa_0/T = 17 \text{mW K}^{-2} \text{cm}^{-1} \) for the \( p \)-wave superconductor \( \text{Sr}_2\text{RuO}_4 \), which is about 9\% of its \( \kappa_{NO}/T \) [36]. Therefore, a negligible \( \kappa_0/T \) of \( \text{Au}_2\text{Pb} \) in zero field also suggests a fully gapped superconducting state.

The field dependence of \( \kappa_0/T \) can give more information about the superconducting gap structure [30]. Between \( H = 0 \) and 17 mT, we fit all the curves and obtain the \( \kappa_0/T \) for each magnetic field, as shown in fig. 3(b). The normalized \( \kappa_0/T \) of \( \text{Au}_2\text{Pb} \) as a function of \( H/H_{c2} \) is plotted in fig. 4. For comparison, the data of the clean \( s \)-wave superconductor Nb [33], the dirty \( s \)-wave superconducting alloy InBi [34], the multiband \( s \)-wave superconductor \( \text{NbSe}_2 \) [37], and an overdoped \( d \)-wave cuprate superconductor TI-2201 [35], are also plotted. For a clean \( s \)-wave superconductor with a single gap, \( \kappa_0(H)/T \) should grow exponentially with the field, as observed in Nb [33]. While for the s-wave InBi in the dirty limit, the curve is exponential at low \( H \), crossing over to a roughly linear behavior closer to \( H_{c2} \) [34]. In the case of \( \text{NbSe}_2 \), the distinct \( \kappa_0(H)/T \) behavior was well explained by multiple superconducting gaps with different magnitudes [37].

In fig. 4, the field dependence of \( \kappa_0(H)/T \) for \( \text{Au}_2\text{Pb} \) grows slightly faster than that of the dirty s-wave superconductor InBi. Note that the internal field is actually...
larger than the applied field when considering the demagnetization factor [38]. This effect is more significant at low fields, thus the $k_0(H)/T$ of Au$_2$Pb may be close to that of InBi. Since we do not know enough parameters, such as the Fermi velocity, to estimate the mean free path of the carriers in Au$_2$Pb, we cannot judge whether it is in the clean or dirty limit. In case that it is in the clean limit, such a $k_0(H)/T$ behavior may result from multiple superconducting gaps. As we mentioned earlier, electronic structure calculations of Au$_2$Pb showed that there are several bands [25]. Analysis of electronic specific heat also reveals two superconducting gaps with the amplitudes $\Delta_0(0)/k_BT_c = 1.41$ and $\Delta_2(0)/k_BT_c = 5.25$, respectively. Note that the weight of the small gap is low (8%), which may be the reason why the $k_0(H)/T$ of Au$_2$Pb grows much slower than that of NbSe$_2$.

So far, PbTaSe$_2$ and Au$_2$Pb are the only two natural TSC candidates. Our results demonstrate that Au$_2$Pb has a similar fully gapped superconducting state to PbTaSe$_2$. A full superconducting gap is a necessary condition for TSCs, but is also the criterion for a conventional s-wave superconductor. To judge which the case is, it is essential to know their topological properties. While the topological band structure and surface states have been verified in PbTaSe$_2$, detailed ARPES experiments on Au$_2$Pb are highly desired. Note that recent scanning tunneling microscopy (STM) experiments on PbTaSe$_2$ observed a full superconducting gap in zero field, and the zero-energy bound states at superconducting vortex cores in magnetic field [39]. However, the thermal broadening at $T = 0.26K$ makes it impossible to discriminate the ordinary Caroli-de Gennes Matricon (CdGM) bound states and Majorana bound states [39]. Therefore, more STM experiments, such as spin-polarized STM [6], are needed to determine whether these two natural TSC candidates are TSCs or conventional s-wave superconductors.

Summary. – In summary, the superconducting gap structure of Au$_2$Pb has been studied by the ultra-low-temperature specific heat and thermal conductivity experiments. The analysis of the electronic specific heat suggests two s-wave superconducting gaps with the amplitudes $\Delta_1(0)/k_BT_c = 1.41$ and $\Delta_2(0)/k_BT_c = 5.25$. Furthermore, a negligible $\kappa_0/T$ in zero field and the field dependence of $\kappa_0/T$ also suggest nodeless superconducting gaps. These results indicate that the natural TSC candidate Au$_2$Pb has a fully gapped superconducting state in the bulk.

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