Superconductivity and band structure of layered AuSn₄

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Single crystals of the orthorhombic compound AuSn₄ have pronounced layered properties and become superconducting below T_c = 2.35 K. Here we explore the band structure and superconductivity of AuSn₄ through magnetoconductance, scanning tunneling microscopy (STM), angular resolved photoemission spectroscopy (ARPES) and density functional theory (DFT) calculations. The two lattice constants of the surface studied by ARPES and STM are very similar. In ARPES, we find anisotropic rhombic-like splitted electron Fermi surfaces around the Γ point. From STM, we observe that the superconducting density of states vanishes at the Fermi level and there is a large distribution of gap values on the Fermi surface around ∆ = 0.46 meV, which is close to ∆ = 1.76k_B T_c expected from BCS theory. We also observe superconducting features in the tunneling conductance up to temperatures about 20% larger than bulk T_c. We tentatively adscribe the increased T_c, as well as a large splitted electron band at the Fermi level identified in ARPES to structural defects close to the surface. Our results stress the relevance of defects in the electronic properties of compounds having very similar lattice parameters.

I. INTRODUCTION

Topological insulators host interesting surface states with nontrivial electronic properties, such as dissipationless charge and spin transport along surface channels [1]. The combination of superconductivity with topological insulators is expected to produce novel behavior, for instance with non-Abelian modes, thanks to the combination of edge conduction channels and the electron-hole symmetry of the superconducting state [2, 3]. However, superconductivity requires a finite density of states at the Fermi level, which can only be obtained by closing the bulk insulating gap. There exists a growing set of semimetallic systems with a finite density of states at the Fermi level that might host nontrivial topological properties [4–6]. One difficulty is that only a few are superconducting too.

Often, semimetals with potentially topological crossings in the bandstructure also present huge magnetoconductance (MR) [7–10]. Among such systems, PtSn₄ and PdSn₄ stand out because of reports connecting topological properties of the band structure with a three orders of magnitude increase in the resistance between zero field and 14 T [11–13]. In addition, the surface of PtSn₄ presents Dirac node arcs which consist of a linear dispersion extending over a portion of the Brillouin zone [14]. PtSn₄ and PdSn₄ are not superconducting, but AuSn₄ is superconducting with a critical temperature of T_c = 2.35 K [15]. In spite of the different electron count (Pt and Pd are on group 10, whereas Au is on group 11 of the periodic table), it is of interest to ask whether AuSn₄ can show anomalous properties in the band structure and superconductivity at the same time [16, 17]. A recent examination of the bulk and transport properties of single crystals of AuSn₄ provides a clear specific heat jump at the superconducting transition. The proposed magnetic field temperature phase diagram provides indications for weak antilocalization and two-dimensional superconductivity [16].

On the other hand, the recent thrust in developing lead-free solders has led to a close re-analysis of phase diagrams of Sn with other elements [18]. In the Au-Sn binary phase diagram, several intermetallic compounds form [19]. AuSn₄ is the first compound crystallizing from a Sn rich melt. It crystallizes in a melt with a concentration between 7% and 20% of Au when crossing the temperature range between 250 °C and 220 °C. This easily occurs when soldering wires to electronic appliances because many surface mounting systems finish in a Au containing surface [20–22]. The dissolution of Au and its later solidification leads to the precipitation of AuSn₄ single crystals, which migrate to the interface between the solder and the substrate and eventually participate in processes weakening the bond [21–24]. AuSn₄ indeed has an orthorhombic structure with one axis much larger than the other two and thus shows pronounced anisotropic mechanical properties [25–27]. These help producing embrittlement at critical parts of the joint.
The actual space group to which AuSn₄ belongs is yet undetermined. X-ray scattering spectra of powder samples are nearly indistinguishable between the 68 and the 41 space groups [25–27]. It is important to determine the electronic properties of AuSn₄ and how these are influenced by the anisotropic structure and near degeneracy between the two different space groups.

Here we analyze the normal state and superconducting properties of AuSn₄. We grow single crystals of AuSn₄ and characterize them using resistivity and scanning tunneling microscopy (STM). We find a linear MR with a 500\% field induced increase of the resistivity at magnetic fields of 14 T and no signs of saturation. The superconducting density of states shows well opened superconducting gap which remains above the bulk T_c. We measure its band structure using Angular Resolved Photoemission (ARPES) and find numerous electron and hole pockets and a large splitted rhombic Fermi surface.

II. EXPERIMENTS AND METHODS

Single Crystals of AuSn₄ were grown using excess Sn flux [28]. Based on the binary phase diagram data published in Ref. [29], we mixed high-purity Au (Goodfellow 99.99\%) and Sn (GoodFellow 99.995\%) with the proportion 88:12 - Sn:Au. The Au-Sn mixture was introduced in a fritted crucible set [30, 31] and sealed inside a quartz
ampoule with Ar gas. In order to fully melt the Au-Sn mixture, the ampoule was heated from room temperature to 1100°C in 12 h, then cooled to 250°C in 12 h and finally cooled to 230°C in 90 h. The ampoule remained for 48 hours at that temperature and was then extracted from the furnace. To separate the remaining liquid from the crystallized AuSn₄, we immediately placed the ampoule in a centrifuge [28]. We obtained plate like crystals with a few mm thickness. As shown in the inset of Fig. 1(a), the plates can be crucible limited and end up adopting a cryptomorphic (in this case circular/elliptical) morphology that is defined by the inner dimensions of the crucible. Powder X-ray diffraction (Cu Kα, λ = 1.54Å) on ground AuSn₄ crystals led to an orthorhombic crystalline structure with very little difference between two of the three crystalline axis. The observed a = 0.652 nm, b = 1.173 nm, c = 0.652 nm were compatible with the two reported AuSn₄ crystalline structures with little or no trace of Sn (Fig. 1(a)). These are space group No. 68, a = 0.652 nm, b = 1.173 nm, c = 0.652 nm [25] and No. 41, a = 0.652 nm, b = 0.652 nm, c = 1.173 nm [26, 27].

To measure the resistivity, we attached four gold wires using silver epoxy to a sample shaped along one of the in-plane axis. The MR was measured with the field applied perpendicular to the planar shaped samples, which is the b axis of the 68 or the c axis of the 41 space groups. In Fig. 1(b) we show the temperature dependence of the resistivity up to 300 K, from which we obtain a residual resistivity ratio of 122, twice the value found in a recent work [16]. We estimate a residual resistivity of ρ₀ ∼ 0.62 μΩ cm, which confirms the excellent quality of the samples. The superconducting transition (inset of Fig. 1(b)) provides Tₑ = 2.35 K in agreement with previous reports [15, 16].

To perform the STM measurements we use the STM and the cryogenic movable sample holder described in Ref. [32]. The resolution of the set-up is of order of 10μV, as tested measuring the tunneling density of states of Al [33, 34]. We used a tip of Au, which we cleaned and prepared following Ref. [35] on a cleaning pad of Au mounted in-situ close to the sample. We cleaved the sample below liquid Helium temperature. The sample has a layered structure and is easily cleaved giving shiny flat surfaces. These are oriented perpendicular to the long axes of the two possible orthorhombic crystalline structures. The critical magnetic field along this axis (inset of Fig. 1(b) and Ref. [16]) is of a few hundred Oe. This gives an inter-vortex distance well above 100 nm at the upper critical field, which is larger than the largest flat surfaces we could find. Thus, we did not follow the tunneling spectroscopy with the magnetic field. To render images and tunneling conductance measurements we used software described in Refs. [36, 37].

The ARPES experiments were performed using tunable vacuum ultraviolet (VUV) laser ARPES spectrometry.
ter that consists of a Scienta DA30 electron analyzer, picosecond Ti:Sapphire oscillator and fourth-harmonic generator [38]. Data from the laser based ARPES were collected with 6.7 eV photon energy. Angular resolution was set at ≈ 0.1° and 1°, along and perpendicular to the direction of the analyzer slit respectively, and the energy resolution was set at 2 meV. The VUV laser beam was set to vertical polarization, i.e. along \( k_y \) direction. The diameter of the photon beam on the sample was ≈ 15μm. Samples were cleaved in-situ at a base pressure lower than 2.2×10^{-11} Torr usually producing very flat, mirror-like surfaces, similar to those obtained in the STM studies. Results were obtained at a temperature of 10.5 K and were reproduced on several different single crystals.

We carried out DFT calculations of the bulk electronic band structure as implemented in the Quantum ESPRESSO package [39]. We used the generalized gradient approximation (GGA) and the Perdew–Burke–Ernzerhof (PBE) functional to describe the exchange-correlation energy [40]. To fully optimize the structure, we selected standard solid-state US pseudopotentials from the Materials Cloud database [41] and sampled the Brillouin zone by a fine \( \Gamma \)-centered \( 8 \times 8 \times 8 \) k-point Monkhorst–Pack mesh [42]. The ground state and electronic structure of the material were calculated including spin orbit coupling (SOC) by taking fully relativistic norm-conserving pseudopotentials from the Pseudo-Dojo database [43]. We sampled the Brillouin zone by a \( \Gamma \)-centered \( 10 \times 10 \times 10 \) k-point Monkhorst–Pack mesh [42]. The electronic wave functions were expanded with well-converged kinetic energy cut-offs for the wave functions and charge density of 80 Ry and 640 Ry respectively. Dispersion corrections were considered by applying semi-empirical Grimme-D3 corrections [44]. The structure was fully optimized using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm [45] until the forces on each atom were smaller than 1·10^{-3} Ry/au and the energy difference between two consecutive relaxation steps was less than 1·10^{-4} Ry. We obtained the lattice parameters mentioned above, \( a = 0.652 \) nm, \( b = 1.173 \) nm, \( c = 0.652 \) nm, compatible with X-ray scattering data.

To obtain the surface band structures of AuSn₄ in the space groups 41 and 68, we constructed maximally localized Wannier functions (MLWFs) [46, 47] in the Wannier 90 code. The bulk band structures including SOC were calculated using VASP [48, 49] with the lattice constants obtained from X-ray scattering [25, 27]. We reproduced the bulk band structure in the range \( E_F ± 1 \) eV by selecting the Au s,d and Sn s,p orbitals as projectors. We then calculated the surface spectral functions of semi-infinite surfaces using the surface Green’s function method [50, 51], as implemented in Wannier tools [52].

III. RESULTS

A. Magnetoresistance.

In Fig. 2(a) we show the MR \( (\text{MR} = \frac{\Delta \rho(H,T)}{\rho(0,T)}) \) as a function of the magnetic field up to 14 T at different temperatures between 2.5 K and 100 K. The MR increases by more than 500% between 0 T and 14 T at 2.5 K. In the inset of Fig. 2(a) we provide the MR at small magnetic fields. We do not observe the dip found in a similar magnetic field range in Ref. [16], but instead a smooth increase with the magnetic field.

The MR changes as a function of temperature. At temperatures below 20 K we observe a slight downward curvature below about 2 T. Above 2 T, we observe a linear increase up to 14 T without any sign for saturation. Above 20 K we observe that the MR is significantly reduced and the magnetic field dependence approaches the quadratic behavior observed in simple metals for the whole field range. We provide Kohler’s plot in Figure 2(b). This compares the temperature dependence of the resistivity \( \rho(H = 0,T) \) with the MR, by normalizing the magnetic field to \( \rho(H = 0,T) \). We see that Kohler’s scaling roughly holds, as curves at all temperatures are quite close to each other. Nevertheless, we also observe that the downward curvature below 20 K and the quadratic behavior at high temperatures produce visible deviations from Kohler’s rule.

B. Scanning tunneling microscopy.

We show in Fig. 3(a) the two orthorhombic crystal structures of AuSn₄ (space groups 41, left and 68, right, notice that the long axis and the in-plane lattice constants are equal). In Fig. 3(b-e) we show several STM images found in different fields of view and in different cool downs. We find flat surfaces separated by steps whose height is an integer or half integer number of the b-axis lattice constant of the 68 structure and the c-axis lattice constant of the 41 structure (Fig. 3(f)). Inside the planes we find atomic size features (Fig. 3(g)). These can be associated to the Au in-plane sublattice (black dashed circles in Fig. 3(g)) found in both structures (Fig. 3(a)), suggesting that the Au sublattice provides a cleaving plane. This agrees with previous work on PtSn₄, which found a Pt sublattice at the surface [53].

The tunneling conductance vs bias voltage obtained at different positions is shown in Fig. 3(h). We observe a well opened superconducting gap and pronounced quasiparticle peaks. We show the temperature dependence of the tunneling conductance in Fig. 4(a). The superconducting gap value is reduced when increasing temperature, but remains finite above the \( T_c \) found in the resistive transition. To obtain the superconducting density of states \( N(E) \) as a function of temperature, we deconvolute \( N(E) \) from the tunneling conductance \( \sigma(V) \), follow-
ing Refs. [36, 54–57]. \(\sigma(V)\) is related to \(N(E)\) through 
\[\sigma(V) = \int dE N(E) \frac{\partial f(E - eV)}{\partial E},\]
where \(E\) is the energy, and \(f(E)\) the Fermi function. We seek at each temperature the \(N(E)\) that best fits the experiment, showing the corresponding \(\sigma(V)\) at each temperature as a black line in Fig. 4(a). We show \(N(E)\) in Fig. 4(b). We can reproduce \(N(E)\) at the lowest temperatures by assuming a \(s\)-wave BCS density of states built from a distribution of gap values \(\Delta_i\), 
\[N(E) \propto \sum_i \gamma_i \sqrt{E^2 - \Delta_i^2}.\]
This provides a Gaussian shaped \(\gamma_i(\Delta_i)\), shown in the inset of Fig. 4(c). The maximum of this distribution is located at 0.46 meV, which gives \(\Delta(T = 0K) \approx 1.8k_BTc\) close to the BCS expectation of \(\Delta_{BCS}(T = 0K) = 1.76k_BTc\). We show in Fig. 4(c) \(\Delta(T)\). We find that it follows the BCS prediction for the temperature dependence of the superconducting gap, except that the tunneling conductance is gapped above \(Tc\) obtained from resistivity.

In Fig. 4(d) we show the data at the lowest temperature in a logarithmic scale as magenta points. Calculated \(\sigma(V)\) and the density of states are shown as, respectively, black and blue lines. We see that \(N(E)\) is far from the expectations from most simple \(s\)-wave BCS theory. Instead of the sharp quasiparticle peaks and zero states within the gap we observe smeared quasiparticle peaks and \(U\)-shaped behavior at low energies. The shape of \(N(E)\) at low energies follows a quadratic dependence, \(N(E) \propto E^2\) for \(E \to 0\) (blue dashed line in Fig. 4(d)).

C. Angular Resolved Photoemission (ARPES).

In Fig. 5(a) we show the photoemission intensity at the Fermi surface and the energy dispersion relation along cuts made through relevant parts of the Fermi surface in Fig. 5(b-f). Crystals are cleaved similarly as in STM, so that data are obtained at the same surface plane. That is, the plane of the sample shown in the inset of Fig. 1(a), which is the \(a-b\) plane of the 41 plane group or the \(a-c\) plane of the 68 space group. We first notice a Fermi surface with a rhombic shape around the center of the Brillouin zone \(\Gamma\). We can identify two rhombic structures with different Fermi wave vectors \(k_F\), suggesting a splitted band. There are a few additional pockets at the sides along \(k_x\). One is located around \(k_y = 0\) and another one at a finite \(k_y\). The general structure of the Fermi surface, elongated along the \(k_x\) axis, is in agreement with an orthorhombic crystal structure.

The energy dependence of the band structure is shown in Figs. 5(b-f) as cuts through different relevant directions, shown by red dashed lines in Fig. 5(a). Let us start by the pocket located at the left of Fig. 5(a) (cut 1), at a large \(k_x = 0.65\pi/a\), shown in Fig. 5(b). The pocket at \(k_y = 0\) corresponds to a set of bands with a hole-like dispersion and crossing bands with electron like dispersion. The electron like bands have their bottoms around 0.3 eV below the Fermi level, while at least one of the hole bands has the top very close to the Fermi level. There are also bands close to the Fermi level at \(k_y \approx -0.5\pi/T\).

When moving towards the center of the Brillouin zone (cut 2 in Fig. 5(a), shown in Fig. 5(c)), we observe around \(k_y = 0\) that the hole-like dispersion is lost and there are just electron-like bands. These provide the rhombic Fermi surface structures. At the position of cut 2, there is just one electron-like band. At \(k_y = -0.4\pi/T\) we observe that there is a set of hole like bands with its top close to the Fermi level which produces a high density of states, and the pocket shown at the bottom of cut 2 in Fig. 5(a). When moving further towards the center of the Brillouin zone (cut 3 in Fig. 5(a), shown in Fig. 5(d)), we observe qualitatively the same behavior, although the electron like bands around \(k_y = 0\) are more developed and have

**FIG. 4.** In (a) we show tunneling conductance vs bias voltage curves as a function of temperature as colored lines (vertically shifted for clarity). Black lines are the fits obtained from convoluting the density of states vs energy \(N(E)\) curves shown in (b) with the derivative of the Fermi function at each temperature. In (c) we show the temperature dependence of the superconducting gap, normalized to its value at 0 K, \(\Delta_0 = 0.46\) meV, obtained by following the position of the maximum in the energy derivative of \(N(E)\) (shown in (b)). The color of each point follows the color code of (a,b). The black line is the expression from s-wave BCS theory using the bulk critical temperature \(Tc = 2.35\) K. In (d) we show the tunneling conductance (magenta points) taken at 100 mK in a log-log scale. We also show the density of states \(N(E)\) as a blue line. The convolution between the density of states \(N(E)\) and the tunneling conductance is shown as a black line. The dashed blue line provides a \(N(E) \propto E^2\).
FIG. 5. (a) ARPES intensity in the plane of AuSn$_4$ close to the Fermi level (the color scale goes from white, low intensity, to blue, high intensity). The directions of the cuts displayed in subsequent panels are shown by red dashed lines. (b-f) Energy dependence of the photoemission intensity along the cuts shown by red lines in (a). We use for simplicity in this figure $a$ and $b$ to show the directions which are parallel to the surface of the sample, which are the $a$-$b$ directions of the 41 space group or the $c$-$a$ directions of the 68 space group.

moved below the Fermi level, increasing the size of the Fermi surface cut.

In cut 4 (of Fig. 5(a)), made at $k_x = 0$ and shown in Fig. 5(e), the whole band structure just shows the dispersion of the rhombic elongated Fermi surface. We observe two electron-like bands which become indistinguishable at their bottom, located at about 0.3 meV below the Fermi level. Cut 5 (Fig. 5(f)) shows the same splitting along the diagonal of the Brillouin zone.

D. Density Functional Theory calculations.

To analyze the band structure of AuSn$_4$ further we performed DFT calculations using the 68 and 41 space groups. We present general aspects of the band structure of bulk AuSn$_4$ in Fig. 6(a). We show the results for the 68 space group. However, the differences of the band structures obtained within 41 and 68 space groups are minor. The orbital resolved density of states is shown in Fig. 6(b). We see that the Fermi surface is predominantly of Sn 5p character, with some Sn 5s contribution. The five Fermi surface sheets are shown in Fig. 6(d-h). We see that there is one sheet with set of intricate pockets at the corners of the Brillouin zone (Fig. 6(d)). Furthermore, there is another sheet which is large and covers most of the Brillouin zone and has large open orbits (Fig. 6(e)). There is also a sheet which consists of a 3D pocket centered in the Brillouin zone and quasi 2D pockets at the corners of the Brillouin zone (Fig. 6(f)). Another similar sheet with slightly smaller pockets is shown in Fig. 6(g). Finally, there are small closed pockets at the center of the Brillouin zone, shown in Fig. 6(h).

We can try to compare these results with the ARPES data of Fig. 5. The two rhombic bands could be a combination of the projection towards the surface plane of the Fermi surfaces shown in Fig. 6(f,g). However, the calculated band structures are very complex and it is difficult to compare quantitatively with the experiment.

We thus calculated the surface band structures. Here we find differences among the 68 and 41 space groups. We show the result of the calculation for the 68 space group in Fig. 7(a). For the 41 space group, the result is in Fig. 7(d,g). As 41 is non-centrosymmetric we provide the results of the projection to the two inequivalent top and bottom $a$-$b$ surfaces. We identify a rhombic shape around the center of the Brillouin zone which is in-plane asymmetric for both structures. Some details of the surrounding features are slightly different. For example, there are pockets around the diagonals of the plane which are more elliptical like in the calculation for the 41 space group. But, generally, there are signatures of enhanced density of states at the Fermi level around the rhombic structure.

It is interesting to focus on the cuts 2 and 4 of ARPES data (Fig. 5(c,e)) and compare these with the equivalent cuts in DFT for the 68 space group (Fig. 7(b,c)) and for the 41 space group Fig. 7(d,e,g,h). We see from these cuts that the calculations show electron bands of a similar size as the experiment. These electron bands form a rhombic structure, which is similar to the rhombic Fermi surface seen in ARPES. At the sides of it, calculations show hole like bands and numerous band crossings. ARPES also shows numerous band crossings, although a precise identification remains difficult. The density of states around $\Gamma$ is negligible in ARPES, which is compatible with the 68 and top 41 surfaces. We do not identify clearly the splitting found in ARPES, Fig. 5(e), nor the joining of the splitted bands near its bottom, in the calculations.

IV. DISCUSSION AND CONCLUSIONS

Our results show that the MR of AuSn$_4$ is large, but considerably smaller than the MR of PtSn$_4$ and PdSn$_4$[11–13]. Other than a slight downward curvature below 2T, AuSn$_4$ shows a linear and non-saturating behavior of the MR, in contrast to a quadratic-like MR observed in PtSn$_4$ and PdSn$_4$. A simple two-band model with near electron-hole compensation, successfully used previously in PtSn$_4$ and PdSn$_4$, see Refs. [11–13], cannot fit the MR of AuSn$_4$. The inset of
A charge density wave would lead to a feature in the temperature dependence of the resistivity, which we do not observe. Distributed current paths are unlikely, given the extremely small value of the residual resistance. Thus, the large and complex multiband Fermi surface and the presence of several open orbits in different sheets likely leads to the observed MR.

In particular, our calculations show that the AuSn$_4$ Fermi surface is different from the Fermi surface obtained in PtSn$_4$. The latter is formed by three small pockets and only one large Fermi surface sheet [11, 14, 74], whereas the calculated Fermi surface of AuSn$_4$ is formed by four large and one small sheets. In PtSn$_4$, the surface band structure around the X point (PtSn$_4$ crystallizes in the 68 space group) presents a sharp band with two Dirac features which are gapped when moving across the X point. This leads to nodes formed by the crossing point of the Dirac dispersion around the X point. Here we observe sharp features in ARPES, but the features observed in the calculations do not show neatly defined surface states.

We also observe that superconductivity presents an ample distribution of gap values over the Fermi surface, going down to values very close to zero energy. This suggests that there are portions of the Fermi surface with a very small superconducting gap. The experimentally obtained density of states has a quadratic energy dependence at low energies inside the gap. It is useful to discuss the possibility of a gap structure with symmetry imposed nodes. There are eight irreducible representations of the superconducting order parameter in the orthorhombic lattice, four even $A^g$, $B^g$, $B^u$ and four odd representations $A^u$, $B^u$, $B^g$ and $B^g$, which lead respectively to singlet and triplet superconducting states [75–77]. $B^g$, $B^g$, $B^u$ and $B^g$ representations have two perpendicular line nodes and $B^u$, $B^u$, $B^u$ have point nodes [75]. In most simple terms, we can expect a $N(E) \propto E$ for line nodes and a superlinear dependence for point nodes. This connects our finding of $N(E) \propto E^2$ to the triplet representations $B^u$, $B^u$, and $B^u$. However, there are no evidences for ferromagnetic correlations that could
favor triplet pairing in AuSn₄. Thus, we conclude that the low energy behavior of the density of states is rather connected with a superconducting order parameter having the full symmetry of the lattice (A₁g). The obtained wide distribution of values of the superconducting gap can then be connected with widely differing values of the superconducting gap over the Fermi surface.

It is interesting to discuss the superconducting correlations we find above T_c. Previous work also showed different T_c’s in thin films of AuSn₄ [78]. These were subsequently associated to the presence of a superstructure in crystals obtained from a stoichiometric cooling from the melt [25, 26, 79]. However, subsequent investigations of the binary phase diagram showed that cooling from a stoichiometric composition cannot lead to pure crystals, because AuSn₄ forms out of a peritectic reaction [29]. At this point, it is useful to compare the crystal structures of AuSn₄, PtSn₄ and PdSn₄, the latter two belonging unmistakably to the 68 space group. The orthorhombic crystal structure has been determined, finding a = 0.643 nm, b = 1.135 nm and c = 0.638 nm for PtSn₄ [80], a = 0.644 nm, b = 1.145 nm and c = 0.639 nm for PdSn₄ [81], but a = 0.652 nm, b = 1.173 nm and c = 0.652 nm for AuSn₄ (assuming the 68 space group) [25]. Thus, the values of a and c are much closer to each other in AuSn₄ than in the other two compounds, making the presence of stacking faults and of domains with rotated in-plane orientations considerably more likely [26, 27]. Contrary to crystals of PtSn₄ and PdSn₄, crystals of AuSn₄ have a plate-like shape and are extremely easy to cleave and very brittle. The Debye temperatures are of 304 K, 255 K and 238 K in PtSn₄, PdSn₄ and AuSn₄ respectively [82], suggesting that AuSn₄ is softer than PtSn₄ and PdSn₄. Furthermore, the thermal expansion is larger along the c-axis in PtSn₄ and PdSn₄ than in the a-b plane, but not in AuSn₄, where the in-plane thermal expansion is larger than the c-axis thermal expansion [26]. Taken together, we can see that the properties of AuSn₄ are easily modified by stress or stacking faults.

The presence of stacking faults close to the surface might also explain the splitting found in ARPES for the electron bands (Fig. 5), which is absent in the tunneling conductance well above the bulk T_c, i.e. up to 2.8 K, as compared to the 2.35 K obtained in resistivity (Fig. 4(c)). In summary, we have characterized superconducting and normal phase properties of the layered compound AuSn₄. We find a large MR, but do not find the huge MR of PtSn₄ and PdSn₄. This can be ascribed to the intricate shape of the Fermi surface. We determine the band structure from ARPES and find several elongated bands crossing the Fermi level, with electron as well as hole character. We observe a band splitting, which we tentatively ascribe, together with an increase in T_c at the surface, to the crystalline defects due to the occurrence of two very similar lattice constants.

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