Bulk superconductivity and non-trivial band topology analysis of Pb$_2$Pd

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Abstract
In this article, we report single crystal growth of superconducting binary compound Pb$_2$Pd. The crystal is well characterized through x-ray diffraction, selected area electron diffraction, transmission electron microscopy, field emission scanning electron microscopy and x-ray photoelectron spectroscopy. The bulk superconducting nature of the synthesized crystal is determined through AC susceptibility and magneto-heat capacity measurements. The specific heat jump at superconducting transition suggests Pb$_2$Pd to be a moderately coupled s-wave superconductor. The topological non-trivial character of Pb$_2$Pd is evidenced through bulk electronic band structure and $Z_2$ invariants, which are calculated under the protocols of density functional theory. Surface states spectrum of Pb$_2$Pd is also studied, which further claims Pb$_2$Pd to have topological non-trivial band structure.

Keywords: topological materials, superconductivity, x-ray photoelectron spectroscopy, magneto-heat capacity, density functional theory

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

1. Introduction
The discovery of topological insulators (TIs) has renewed the field of quantum condensed matter. Since then, a flurry of research has been carried out on the materials with symmetry protected topological states, which are characterized by non-trivial topological invariants viz. $Z_2$, $Z_4$ and the Chern numbers [1–4]. Topological materials are classified in different categories based on their band structure and the symmetry, such as TIs, topological crystalline insulators and topological semimetals (TSMs) etc [1, 5]. Moreover, TSMs are further subclassified as Dirac semimetal (DSM), Weyl semimetal (WSM) and nodal line semimetal (NLSM) [5–7]. Among them, DSMs have fourfold degenerate band crossings and WSMs have pairs of Weyl nodes, which are generated due to broken time reversal symmetry (TRS) and inversion symmetry [6]. Apart from these three categories, semimetals are classified into two other categories such high-symmetry-point semimetal and high-symmetry-line semimetal [8]. These materials show band degeneracy at high symmetry points in the bulk electronic band structure calculated without considering spin orbit coupling (SOC) [8].

TSMs with bulk superconducting properties are emerged as the materials of interest as these are regarded as the possible candidates to realize topological superconductivity [9–19]. Topological superconductors are considered as the key materials to host Majorana fermions [20, 21], while some of the p wave superconductors also show the existence of Majorana bound states inside their vortices [22, 23]. Some of the TSMs viz. PdTe$_2$ [9], PbTaSe$_2$ [10], SnTaS$_2$ [11], NbC [12], AuSn$_4$ [13], Au$_3$Pb [14] show bulk superconductivity with topological non-trivial surface states. Apart from these materials some binary compounds viz. BiPd, $\beta$-Bi$_2$Pd and Sb$_2$Pd
are also reported to have topological states with bulk superconductivity [15–17]. Theoretical calculations made on thin films of $\beta$-Bi$_2$Pd suggest the same to show topological superconductivity along with Majorana zero modes [18, 19], while this feature lacks experimental confirmation. Pb$_2$Pd is another similar compound, and its superconducting nature has been known since 1962 [24]. Pb$_2$Pd has not been much studied in the context of its topological properties, as there is only one theoretical report available in which Pb$_2$Pd is considered as a TSM [8]. Interestingly, the superconducting properties of Pb$_2$Pd have also not been explored to that extent. There are only two reports available in the literature about the superconducting properties of Pb$_2$Pd [25, 26]. The first report was on the effect of Bi substitution in Pb$_2$Pd [25] and the other one is a very recent report showing type-I superconductivity in the same [26]. It is important to study Pb$_2$Pd in the context of superconductivity and topological properties as it is supposed to be a superconducting material with topological non-trivial band structure [8, 26].

In this article, we report the synthesis of Pb$_2$Pd single crystal using solid state reaction route, this sample is well characterized through various characterization techniques. Bulk superconductivity is the key issue for superconducting topological materials, and the same with $T_c^{\text{onset}}$ at 2.86 K is confirmed in the synthesized Pb$_2$Pd crystal through AC susceptibility and magneto-heat capacity measurements. This is the first report showing magneto-heat capacity measurements for Pb$_2$Pd crystal. Further, the topological properties are studied through density functional theory (DFT) calculations and theoretical simulation of topological invariants. The obtained Z2 invariants of Pb$_2$Pd show the presence of strong topology, which is further verified by studying the surface state spectrum. It is worth mentioning here that this is the first report on such topological invariants for Pb$_2$Pd.

2. Experimental

Solid state reaction route is used to synthesize the single crystalline sample of Pb$_2$Pd. The 4 N pure powders of Pb and Pd were mixed in 2:1. The mixture was made homogenous by grinding it inside MBraun Glove Box filled with argon gas. This homogenous mixture was then pelletized and vacuum encapsulated in quartz ampoule under the pressure of $5 \times 10^{-5}$ mbar. This ampoule was heated to 900 °C at 120 °C h$^{-1}$ for 24 h. At this higher temperature Pb itself acts as flux and helps Pd to melt, despite of its higher melting point. The hold time of 24 h at 900 °C is utilized in melting the sample and to homogenize the melt. Then the sample is slowly cooled to 460 °C at 2 °C h$^{-1}$ and then kept at this temperature for 24 h. After that, the sample is quenched at 460 °C in water. The step of quenching at 460 °C is very crucial as the phase formation temperature of Pb$_2$Pd and PbPd is very close and the both phases have simultaneous existence at around 445 °C [27]. The schematic of heat treatment is shown in figure 1.

Rigaku Miniflex II table top x-ray diffractometer (XRD) equipped with Cu-K$_\alpha$ (1.5406 Å) was used for phase purity characterization of synthesized Pb$_2$Pd single crystal. Surface morphology and elemental composition were analyzed using MIRA II LMH TESCAN made field emission scanning electron microscope (FESEM) equipped energy dispersive x-ray (EDX) detector, JEOL/JEM-F200 with one view CMOS camera (4 K × 4 K) transmission electron microscope (TEM) is used to get side angle electron diffraction (SAED) pattern and to visualize atomic planes. X-ray photoelectron spectroscopy was performed by using X-ray photoelectron spectrometer (XPS) (Model: K-Alpha-KAN9954133, Thermo Scientific) with monochromated and micro-focused Al K$_\alpha$ radiation (1486.6 eV). The spectrometer has been designed with a dualbeam flood source to provide a charge compensation option and calibration is confirmed by the position of C 1s line at the binding energy value of 284.8 eV. The working pressure was maintained <6 × 10$^{-8}$ mbar. The scans for Pb 4f and Pd 3d were recorded with the step size of 0.1 eV. AC susceptibility and heat capacity measurements were carried out using Quantum Design Physical Property Measurement System (QD-PPMS) in temperature range from 5 K to 2 K. Full-Prof software and VESTA software were used for Rietveld refinement and the unit cell construction respectively.

To study and understand the topological properties of synthesized Pb$_2$Pd crystal, the first principle simulations have been carried out and Z2-invariants are also calculated to categorize the topology present in the system. For this, DFT based on first principle calculations is executed in QUANTUM ESPRESSO [28, 29] to obtain the bulk electronic band structure and density of states (DOS). For the calculations, atomic positions of primitive unit cell of Pb$_2$Pd are considered. The Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation is used to account for the electronic exchange and correlation. The wave functions are expanded in a plane wave with Gaussian smearing of the width 0.01 on a Monkhorst–Pack $k$-grid of $8 \times 8 \times 8$. The electronic bands are calculated with and without inclusion of SOC. For band structure calculated without-SOC, we used standard solid-state pseudo-potential library. For with-SOC band calculations, we used...
the PSEUDOJO library, which incorporates full relativistic approximations. For the convergence of self-consistent calculation cutoff is set to $1.2 \times 10^{-9}$ Ry and charge cut-off is set to 320 Ry and wave function cut-off 45 Ry is used. For calculation of ZZ invariants, DFT generated Bloch wave function is wannierized using the WANNIER90 software [30]. The WANNIER90 uses the Wannier functions which are the representation of bloch wave functions in real space [31, 32]. Out of 108 Bloch wave-functions, 44 are wannierized and disentanglement calculation converges with threshold limit $10^{-10}$. The band structure is reproduced in the energy range $E_F \pm 2$ eV by selecting projectors p orbitals of Pb and d orbitals of Pd atoms with the whole Brillouin zone sampled on a dense $8 \times 8 \times 8$ K-mesh. The band structure is again obtained using the maximally localized Wannier function (MLWF) and it is verified by the band structure generated through first principle method. An effective tight-binding (TB) model for Pb,Pd crystal was obtained using MLWFs after wannierization of block wavefunction. This effective TB model is further processed and applied in WANNIER-TOOLS [33]. The whole Brillouin zone is sampled on a $8 \times 8 \times 8$ K-mesh, for all calculations. The states of ZZ-invariants are determined by the evolution of Wannier charge centers (WCCs) in Brillouin zone planes, which are sampled on a much denser grid of $61 \times 61 \times 21$. Further, the surface spectral function is calculated using the iterative surface Green’s function method [34, 35] along the plane (011).

3. Result and discussion

Figure 2 represents the Rietveld refinement results of powder XRD (PXRD) pattern of synthesized PbPd single crystal. The synthesized PbPd crystal crystallizes in tetragonal structure with $I4/mcm$ space group. All peaks of PXRD pattern are well fitted with the phase parameters and confirms that the synthesized crystal is phase pure. The quality of refinement is determined through $\chi^2$ value which is found to be 4.95, which is reasonably good. The constituent elements viz. Pb and Pd occupies the atomic positions viz. (0.165,0.665,0) and (0,0,0.25) in a tetragonal unit cell. The Rietveld refined lattice parameters are $a = b = 6.863(5)$ Å, $c = 5.840(5)$ Å and $\alpha = \beta = \gamma = 90^\circ$. All these parameters are in good agreement with previous report on the same compound [26]. The unit cell parameters along with the refinement parameters are listed in table 1. The inset of figure 2 represents the VESTA drawn unit cell of synthesized PbPd crystal. Crystallographic information file (CIF) generated from Rietveld refinement is used to draw the unit cell. The synthesized crystal is shown to have a body-centered tetragonal unit cell with Pd atoms at the body center.

Figure 3(a) shows SAED pattern of synthesized PbPd single crystal. SEAD pattern was taken on powdered sample. Spots from (002), (004) and (220) are encircled in figure 3(a). Crystalline nature of synthesized PbPd crystal is evident from TEM image, shown in figure 3(b). Figure 3(b) shows that the atomic planes are stacked in a regular manner along a specific growth direction. The calculated interplanar spacing between the atomic planes as shown in TEM image is found to be 2.94 Å, which corresponds to the interplanar spacing of (002) planes. Stacking of atomic planes in (002) plane direction as revealed by TEM image, suggests that the crystal of PbPd is grown in (001) direction, it is also consistent with previous report [26]. To get more insight about crystalline nature of synthesized PbPd, surface morphology is visualized through FESEM image. Figure 3(c) shows the FESEM image of the synthesized PbPd single crystal. The FESEM image is showing terrace type morphology which represents layer by layer growth of the sample. No grain is visible in the FESEM image which also confirms the single crystalline nature of the synthesized crystal. Elemental composition is determined through EDX analysis and the as shown in figure 3(d). The EDX spectra shows the presence of constituent elements viz. Pb and Pd. No impurity element is detected in EDX spectra, which shows the purity of the synthesized crystal. Elemental composition is shown in the inset of figure 3(d), both the elements are found to be in near stoichiometric ratio.

Chemical states of the constituent elements of PbPd are analyzed through XPS spectra. XPS peak of C 1s is taken

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**Table 1. Parameters obtained from Rietveld refinement.**

| Cell parameters | Refinement parameters |
|-----------------|-----------------------|
| Cell type: tetragonal | $\chi^2 = 5.09$ |
| Space group: $I4/mcm$ | $R_p = 7.58$ |
| Lattice parameters: $a = b = 6.863(5)$ Å, $c = 5.840(5)$ Å and $\alpha = \beta = \gamma = 90^\circ$ | $R_{wp} = 9.68$ |
| Cell volume: 275.068 Å$^3$ | $R_{exp} = 4.29$ |
| Density: 12.577 g cm$^{-3}$ | — |
| Atomic coordinates: | — |
| Pb (0.1643,0.6643,0) | |
| Pd (0,0,0.25) | |
Figure 3. (a) SAED pattern of synthesized Pb₂Pd crystal (b) TEM image of Pb₂Pd crystal showing stacking of (002) planes. (c) FESEM image of surface morphology of synthesized Pb₂Pd crystal (d) EDX spectra of Pb₂Pd crystal in which inset is showing the atomic percentage of the constituent elements.

Figure 4. XPS spectra of synthesized Pb₂Pd crystal in (a) Pb 4f region (b) Pd 3d region. as the reference to calibrate all XPS peaks. Figures 4(a) and (b) show XPS spectra of synthesized Pb₂Pd crystal in Pb 4f and Pd 3d regions respectively. These spectra are fitted with Gaussian distribution function. The XPS spectra in Pb 4f region is deconvoluted in four peaks viz. P1, P2, P3 and P4. Peaks P1 and P3 correspond to spin-orbit doublet of Pb 4f viz.
Table 2. XPS peaks position and FWHM of constituent elements of synthesized Pb₂Pd single crystal.

| Element | Spin–orbit doublet | Binding energy (eV) | FWHM (eV) |
|---------|-------------------|---------------------|------------|
| Pb      | 4f_5/2            | 138.55 ± 0.005      | 1.6 ± 0.02 |
|         | 4f_7/2            | 143.42 ± 0.001      | 1.6 ± 0.01 |
| Pd      | 3d_3/2            | 335.85 ± 0.009      | 0.7 ± 0.08 |
|         | 3d_5/2            | 341.15 ± 0.012      | 0.6 ± 0.07 |

Pb 4f_5/2 and Pb 4f_7/2. These peaks occurred due to core levels of Pb\(^{2+}\) cations and the corresponding binding energies are found to be 138.55 eV and 143.42 eV for Pb 4f_5/2 and Pb 4f_7/2 respectively. These values are shifted from the binding energy values for metallic Pb [36], this shift in binding energies is occurred due to bonding with Pd atoms. This suggests strong covalent bonding between Pb and Pd. The remaining peaks viz. P2 and P4 corresponds to Pb\(^{2+}\) cations resulting from PbO formation. These peaks occurred due to surface oxidation of the synthesized sample due to air exposure. The peaks of Pb\(^{2+}\) ions generated due to PbO formations is less pronounced in comparison to that observed due to Pb\(^{2+}\) cations of synthesized Pb₂Pd crystal. The energy separation between the spin orbit doublets of Pb is found to be 4.87 eV, which is very close to the standard value (4.86 eV) [36]. Figure 4(b) shows the XPS spectra in Pd 3d regions, which consists of XPS peaks due to spin orbit doublet of Pd 3d core levels viz. Pd 3d_3/2 and Pd 3d_5/2. The peaks of spin orbit doublets viz. Pd 3d_3/2 and Pd 3d_5/2 are observed at 335.85 eV and 341.16 eV respectively. These values are slightly shifted from the standard value due to bonding of Pd with Pb atoms [36]. The energy separation of these peaks is found to be 5.31 eV which is very close to the standard value (5.26 eV) [36]. These XPS results suggest that the valency of Pb atoms in Pb₂Pd is +2. All XPS peaks for spin orbit doublet of constituent elements viz. Pb and Pd along with their respective full width at half maxima (FWHM) are listed in table 2.

Figure 5 shows the results of AC susceptibility measurements carried out at different AC magnetic field viz. 3 Oe, 5 Oe, 7 Oe, 9 Oe and 11 Oe. During the whole AC magnetization measurement, the frequency of the AC field was set at 333 Hz and the background DC field was made stable to 0 Oe. Real part of AC magnetic susceptibility (\(\chi''\)) is shown in the lower plot while the imaginary part (\(\chi'\)) of the same is shown in upper one. Both the real and imaginary parts of the magnetic susceptibility show presence of bulk superconductivity in the synthesized Pb₂Pd crystal. The onset superconducting transition temperature (\(T_{\text{onset}}\)) is found to be 2.9 K. Generally, AC susceptibility measurements give the hint about the granularity of the sample. For a granular superconductor, \(T_c\) tends to shift to lower temperature with increasing the amplitude of the AC field. This effect occurs due to the intergranular coupling of superconductors. The shift of \(T_c\) with respect to the change in AC field amplitude determines the strength of intergranular coupling [37]. Here, \(T_c\) remains constant when the amplitude of the AC field is increased. This suggests that grains are absent due to which intergranular \(T_c\) could be evolved. This also determines the crystalline character of the synthesized Pb₂Pd crystal. For quantitative analysis of superconducting properties through AC magnetization measurements, it is important to consider the demagnetization factor of measured sample. Demagnetization factor depends on the shape of the sample, and for a perfectly cylindrical sample its value is accounted to be 1. Here due to crystalline nature of the sample, measurements have been carried out on a mechanically cleaved rectangular flake. For a rectangular superconducting sample, demagnetization factor can be calculated by the following formula as suggested in ref. [38]:

\[
N = 1 - \frac{1}{1 + \frac{4\pi a^2}{b}}
\]

(1)

where \(a\) and \(b\) are dimensions of the sample in perpendicular to applied field and parallel to the applied field, and these are 3.1 mm and 0.21 mm respectively. The other parameter \(q\) is shape dependent parameter and for a rectangular sample it is determined by the following formula

\[
q = \frac{\pi}{4} + 0.64 \tanh \left[ \frac{0.64 b}{a} \ln \left(1.7 + 1.2 \times \frac{a}{b}\right)\right].
\]

(2)

The value of \(q\) is found to be 0.866 and the corresponding value of demagnetization factor is found to be \(N = 0.927\). Demagnetization factor is used to determine effective AC susceptibility by using the relation \(\chi_{\text{eff}} = \frac{\chi_m}{1 + qN}\), where \(\chi_m\) is measured AC susceptibility. The synthesized Pb₂Pd crystal is found to show a superconducting volume fraction about 42%, which is quite low as compared to the standard value for a perfect bulk superconductor. This low volume fraction is observed due to air exposure. Pb₂Pd single crystal is prone to surface oxidation, this is also observed in XPS measurements.
Heat capacity measurements are the most reliable method to determine bulk superconductivity in a superconducting sample. Heat capacity measurements are carried out on synthesized Pb₂Pd crystals at different magnetic fields viz. 0 Oe, 20 Oe, 30 Oe and 50 Oe. Heat capacity divided by $T$ i.e. $C/T$ is plotted against the temperature and the same is shown in the inset of figure 6(a). A clear heat capacity jump is visible with $T_c$ onset at 2.86 K. This confirms the presence of bulk superconductivity in the synthesized Pb₂Pd single crystal. The heat capacity of a material is mainly contributed by two terms; first one is electronic term ($C_{el}$) and the other is phonon term ($C_{ph}$). These are described by the following equation

$$\frac{C}{T} = \gamma_n + \beta_n T^2$$

or

$$C = \gamma_n T + \beta_n T^3.\quad (3)$$

In the above equation the first term $\gamma_n T$ represents electronic contribution to heat capacity and the second term $\beta_n T^3$ phonon contribution to heat capacity. The coefficient associated with these terms can be determined by linearly fitting the $C/T$ vs $T^2$ plot with equation (3). The figure 6(a) represents a linearly fitted $C/T$ vs $T^2$ plot of synthesized Pb₂Pd single crystal. The coefficient of $C_{el}$ i.e. $\gamma_n$ is known as the Sommerfeld coefficient and it is found to be $5.72 \pm 0.34 \text{ mJ mol}^{-1} \text{K}^{-2}$. The other constant term $\beta_n$ is found to be $3.18 \pm 0.02 \text{ mJ mol}^{-1} \text{K}^{-4}$. The value of $\gamma_n$ is used to determine the DOS at Fermi level [$D_c(E_F)$] using the formula,

$$\gamma_n = \pi^2 k_B^2 D_c(E_F) / 3.\quad (4)$$
Here, \( k_B \) is Boltzmann constant. The obtained value of \( D_1(E_F) \) is 2.35 states eV\(^{-1}\) f.u.\(^{-1}\). The coefficient associated with phonon contribution term i.e. \( \beta_n \) is related to Debye temperature with the following formula

\[
\theta_D = \left( \frac{12\pi^4 n R}{5\beta_n} \right)^{1/3}.
\]

Here \( R = 8.314 \text{ J mol}^{-1} \text{ K}^{-2} \), \( n = 3 \) (for Pb\(_2\)Pd). The obtained value of \( \theta_D \) is 122 ± 1 K. Now the values of \( \theta_D \) and \( T_c \) are used to determine the electron phonon coupling constant \( \lambda_{e-ph} \) using the McMillan formula \([39]\) given below

\[
\lambda_{e-ph} = \frac{1.04 + \mu^* \ln \left( \theta_D/1.45T_c \right)}{(1 - 0.62\mu^*) \ln \left( \theta_D/1.45T_c \right) - 1.04}.
\]

Here, the value of \( \mu^* \) is taken to be 0.13 as taken in \([26]\) and it is known as the screened repulsive Coulomb potential. \( \mu^* \) can be assigned any value between 0 and 0.2 for superconductors with \( T_c \) below 20 K \([39]\). The empirical value of \( \mu^* \) suggested in \([39]\) is 0.13, which is taken in present study. The similar value of \( \mu^* \) is taken for other Pb based heavy intermetallic superconductors \([40]\). The obtained value of \( \lambda_{e-ph} \) is 0.70 and it is higher than the usual values that are obtained for weakly coupled superconductors. This suggests moderate coupling in synthesized Pb\(_2\)Pd single crystal. The obtained value of \( \lambda_{e-ph} \) is verified through theoretical studies in later part of this article.

Now, the electronic heat capacity (\( C_{el} \)) is calculated by subtracting the phonon term from the total heat capacity. The normalized electronic heat capacity is plotted against \( T/T_c \) and is shown in figure 6(b). This is used to determine the magnitude of heat capacity jump i.e. \( \Delta C_{el}/\gamma_nT_c \), which is found to be 1.83. This value is higher than the bardeen-cooper-schrieffer (BCS) weak coupling limit which is 1.43. This also suggests that the synthesized Pb\(_2\)Pd is a moderately coupled superconductor, which agrees with the obtained value of \( \lambda_{e-ph} \). Normalized electronic heat capacity also gives the information about the superconductivity of the sample, whether it is a conventional superconductor or an unconventional superconductor. Also, it is used to determine the value of the parameter \( \alpha = 2\Delta(0)/k_BT_c \). For this, the normalized specific heat data is fitted with the s wave equation and it is found to be well fitted with the same, showing Pb\(_2\)Pb to be a bulk superconductor with conventional s-wave pairing. The obtained value of \( \alpha \) from the fitted plot is 5.68, which is also higher than the BCS value for weakly coupled superconductors. The corresponding value of superconductivity energy gap at absolute zero \( \Delta(0) \) is found to be 0.70 meV. All above discussed parameters suggest that synthesized Pb\(_2\)Pd single crystal is a moderately coupled superconductor with conventional s-wave pairing; these results are in agreement with the previous report on the same compound \([26]\). The parameters obtained from heat capacity measurements are listed in table 3.

Figure 6(c) shows the results of heat capacity vs \( T \) measurements at different field viz. 0 Oe, 20 Oe, 30 Oe and 50 Oe. In this plot, \( C/T \) is plotted against \( T \) to visualize the heat capacity jump more clearly. These measurements give the value of \( T_c^{onset} \) to be 2.86 K, 2.75 K, 2.66 K and 2.40 K at 0 Oe, 20 Oe, 30 Oe and 50 Oe respectively. It can be clearly seen that the \( T_c \) is decreasing with increasing field. Critical field is plotted against the temperature and fitted with the following equation:

\[
H_c(T) = H_c(0) \times \left( 1 - \frac{T^2}{T_c^2} \right)
\]

where \( T_c \) is taken to be 2.86 K. The fitted plot is shown in inset of figure 6(c), this fitted plot gives the value of critical field at absolute zero, \( H_c(0) \) to be 260 Oe, which is comparable to that was obtained in previous report \([26]\). The value of \( H_c(0) \) is verified through magnitude of heat capacity jump. Sommerfeld coefficient and heat capacity jump are related to \( H_c(0) \) through the following formula \([41, 42]\).

\[
\Delta C = \frac{4H_c(0)^2}{\mu_0T_c^3} = 1.43\gamma_nT_c.
\]

Here, \( \Delta C \) and \( \gamma_n \) are taken in per unit volume. The molar volume of Pb\(_2\)Pd is found to be \( 4.14 \times 10^{-5}\text{ m}^3\text{ mole}^{-1} \) and the magnitude of heat capacity jump, \( \Delta C/T_c^3 \) is taken to be 1.83. The obtained value of \( H_c(0) \) is found to be 249 Oe, which is nearly equal to 260 Oe as obtained from the fitted plot.

Moreover, \( C_{el}(T) \) is determined at the various applied fields. \( C_{el}(T) \) is plotted against \( T \) and is shown in figure 6(d). This gives the value of \( \gamma \) at different fields at \( T = 2 \) K. The values of \( \gamma \) are normalized with \( \gamma_n \) and are plotted against the applied field. This gives the important information regarding the low energy excitations which exists in the proximity the Abrikosov vortex line. In conventional superconductors, these low energy excitations take place inside the vortex cores in normal states having the radius which are proportional to penetration depth (\( \xi \)). For this, specific heat in superconducting state is proportional to vortex density and linearly depends on magnetic field giving \( \gamma(H) \propto H^1/2 \). Meanwhile, in case of superconductors having nodes in energy gap, the DOS are found in the neighborhood of gap nodes. Due to this, the low energy excitations occur outside the vortex core and the specific heat is found to show square root dependence on magnetic field given as \( \gamma(H) \propto H^{1/2} \), this is known as Volovik effect \([44]\). In the present case, \( \gamma(H) \) is found to have a linear relationship with the applied field as shown in inset of figure 6(d). This also confirms that the observed bulk superconductivity in synthesized Pb\(_2\)Pd single crystal is conventional superconductivity.

| Parameter          | Obtained value |
|--------------------|----------------|
| \( T_c^{onset} \)  | 2.86 K         |
| \( \gamma_n \)     | 5.72 ± 0.34 mJ mol\(^{-1}\) K\(^{-2}\) |
| \( \beta_n \)      | 3.18 ± 0.02 mJ mol\(^{-1}\) K\(^{-4}\) |
| \( D_1(E_F) \)     | 2.35           |
| \( \theta_D \)     | 122 ± 1 K      |
| \( \lambda_{e-ph} \)| 0.70          |
| \( \Delta C_{el}/\gamma_nT_c \)| 1.83         |
| \( \alpha = 2\Delta(0)/k_BT_c \) | 5.68          |
| \( \Delta(0) \)    | 0.70 meV       |

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**Table 3.** Parameters obtained from heat capacity measurements.
To determine topological non-trivial character of synthesized Pb$_2$Pd crystal, bulk electronic band structure and DOS are calculated using DFT protocols. The band structure calculation is performed using the cell parameters obtained from the Rietveld refinement. Both the SOC and without SOC protocols are executed in calculations as these are applied in Quantum Espresso with PBE exchange-correlation functional [28, 29]. The $k$-path which is followed for calculations is determined from the SeeK-path: the $k$-pathfinder and visualizer [45], which eventually suggests that the $k$-path to be $Z \rightarrow \Gamma \rightarrow M \rightarrow X \rightarrow \Gamma \rightarrow N \rightarrow P \rightarrow X$ is an optimized path. Figure 7(a) depicts this particular $k$-path, as it is marked in the first Brillouin zone. The DFT calculated bulk electronic band structure is shown as the left-hand side image of figure 7(b) while the DOS are shown in the right one. The calculated DOS and bulk electronic band structure indicates that the bands near Fermi level have major contributions from the d-orbitals of Pd and p-orbitals of Pb atoms. There are four bands, which cross Fermi level, confirming metallic/semi-metallic behavior of the crystal. The Fermi surfaces corresponding to these four bands are calculated using WANNIER TOOLS and plotted in XCRYSDEN [46], the same are shown in figure 7(a). The DOS at Fermi level are found to be 2.74 states eV$^{-1}$ per primitive unit cell, and there are two formula units of Pb$_2$Pd in its primitive unit cell, so there will be 1.37 states eV$^{-1}$ f.u.$^{-1}$. The difference between the theoretical and experimental values of DOS at Fermi level hints towards moderate coupling of electrons and phonons. Theoretically calculated value of DOS at Fermi level is used to determine theoretical Sommerfeld coefficient $\gamma_b$, which is found to be 3.34 mJ mole$^{-1}$ K$^{-2}$. The calculated DOS is determined from the SeeK-path: the $k$-pathfinder and visualizer [45], which eventually suggests that the $k$-path to be $Z \rightarrow \Gamma \rightarrow M \rightarrow X \rightarrow \Gamma \rightarrow N \rightarrow P \rightarrow X$ is an optimized path.

Moreover, bands are found to show line degeneracy which is eventually lifted when SOC parameters are included in the calculations. This indicates the effectiveness of SOC in the studied Pb$_2$Pd system. Particularly, along the path $N \rightarrow P$, the bands near Fermi level are doubly degenerate forming nodal lines. Interestingly, when SOC parameters are included in calculation, the line degeneracy has been lifted except from a few points where double degeneracy remains intact. The region showing the bands along path $N \rightarrow P$, is shaded in figure 7(b). The zoomed view of the shaded region is shown in figure 7(c). Nodal lines are clearly visible in figure 7(c) and the line degeneracy is found to be removed when SOC parameters are considered. Figure 8(a) shows (011) plane in the first Brillouin zone, for which gap energy dispersion has been calculated. The gap energy dispersion is shown in figure 8(b), in which the image in the left panel shows without SOC dispersion and the right panel shows the same with inclusion of SOC parameters. Without SOC dispersion, closed-loop line degeneracy can be seen but when SOC is included, all line degeneracy seems to be lifted. Therefore, Pb$_2$Pd is not a NLSTM. However, along the high symmetry path $\Gamma \rightarrow M$ and $M \rightarrow X \rightarrow \Gamma$ in the bulk electronic band structure in figure 7(b), we find that there exists a type-II Dirac cone like band structure, where degeneracy is lifted when SOC parameters are included. The presence of Dirac points along the high symmetry lines in with SOC bands suggest that Pb$_2$Pd can be classified as a high symmetry line semimetal which is also in agreement with the previous report [8], which is a catalogue of all possible topological materials.

Further, we calculated the surface state spectrum using the iterative Green’s function implemented in Wannier Tools. The surface card is set to be plane (011), and the calculation was done by taking 101 slices of one reciprocal vector. The plane (011) is shown in figure 8(a), and in that plane, the path taken for surface state spectrum calculation is $M \rightarrow X \rightarrow M$. Figure 8(c) shows the obtained spectrum, where a possible Dirac cone is observable at $X$ point near energy $-1.0$ eV. A similar Dirac cone of type-II is observable very close to Fermi energy towards high symmetry point $M$ but not at the high symmetry point. Both the surface state spectrum and bulk electronic band structure indicates that the studied Pb$_2$Pd crystal is a topological material.

It is important to characterize the topology present in a topological material in terms of a topological invariant. These topological invariants depend on the symmetry preserved by the material. The observed splitting of bands with inclusion...
of SOC parameters in bulk electronic band structure, suggests that the system respects the TRS and these kinds of topological systems are characterized in terms of $Z_2$-invariants \[49\]. Here, we follow the Soulyanov–Vanderbilt \[49\] method of WCCs, calculated from MLWFs to calculate $Z_2$ invariants. The WCCs are the pseudo charge points, which are the locations of extremum probability points distribution of MLWFs, maximum probability point regarded as negative charge and
Figure 8. (a) The (011) plane is shown with the path marked for surface spectrum calculation. (b) The image shows the gap energy dispersion contours in (011) plane, left shows without SOC and right one shows for with SOC case. (c) This shows the surface state spectrum, Dirac cone is observable at X point near energy $-1.0\,\text{eV}$. A similar Dirac cone of type-II is observable very close to Fermi energy towards high symmetry point $M$.

with least (zero) probability point are regarded as positive charge. Exchange of these charge centers in different $k$-planes define trivial and non-trivial topology. The evolution of WCC take place in the six-planes in the Brillouin zone, namely $k_1$, $k_2$, $k_3 = 0$ and $k_1$, $k_2$, $k_3 = 0.5$. The calculated $\mathbb{Z}_2$ invariants for the Pb$_2$Pd crystal in the mentioned six planes are
The topological Z2 index is represented by four parameters as $(v_0; v_1, v_2, v_3)$, where $v_0$ represents the strong index and $v_1, v_2, v_3$ represent the weak index. The weak index is the values of Z2 numbers for $k_i = 0.5$ planes ($i = x, y$ and $z$). The strong index may have some redundancy as the strong index is given by Z2 value for all three planes $k_i = 0(i = x, y$ and $z)$ and Z2 value may not be the same for all three planes. Here, we find that for all three planes, $v_0 = 1$, indicate a topologically non-trivial state and strong topology present in the system. Here the weak index has no redundancy, and thus Z2 index is $(1;000)$ for the studied PbPd system. The same Z2 index is reported for Bi$_2$Te$_3$, which is considered as a strong topological material [50]. Recently, another group [48] has reported the same non-trivial Z2 index $v_0 = 1$ using a different method—evaluating the band parity at high symmetric time reversal invariant momenta points $\Gamma$ and $M$ [51]. Thus, on the basis of theoretical calculations, it can be concluded that PbPd has strong non-trivial band topology.

4. Conclusion

Summarily, we have presented detailed analysis of bulk superconductivity and non-trivial topological properties of self-flux grown PbPd single crystal. PbPd is characterized for the first time characterized through TEM and XPS techniques in this article. Pb is found to be Pb$^{2+}$ state in PbPd. The synthesized PbPd crystal is found to be a bulk superconductor with $T_c^{\text{onset}}$ at 2.86 K. The calculated parameters viz. electron phonon coupling constant $\lambda_{e-ph}$, $\Delta_C$ and $\Gamma_T$ confirm that PbPd is a moderately coupled s wave superconductor. Conventional superconductivity is also confirmed through magnetic field dependence of the Sommerfeld coefficient in its superconducting state. The calculated bulk electronic band structure gives the glimpses of band inversion with including SOC parameters and suggest PbPd to be a possible topological material with bulk superconductivity. Topological properties of PbPd are also confirmed by calculating Z2 invariants and surface states spectrum, which suggest the presence of strong topology in PbPd. This is the first report on calculation of topological invariants for PbPd. This report strongly represents PbPd material as a possible material to realize topological superconductivity.

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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Conflict of interest

Authors have no conflict of interest.

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References

[1] Hasan M Z and Kane C L 2010 Colloquium: topological insulators Rev. Mod. Phys. 82 3045
[2] Qi X-L. and Zhang S-C 2011 Topological insulators and superconductors Rev. Mod. Phys. 83 1057
[3] Moore J E and Balents L 2007 Topological invariants of time-reversal-invariant band structures Phys. Rev. B 75 121306(R)
[4] Roy R 2009 Topological phases and the quantum spin Hall effect in three dimensions Phys. Rev. B 79 195322
[5] Burkov A A 2016 Topological semimetals Nat. Mater. 15 1145
[6] Armitage N P, Mele E J and Vishwanath A 2018 Weyl and Dirac semimetals in three-dimensional solids Rev. Mod. Phys. 90 015001
[7] Fang C, Weng H, Dai X and Fang Z 2016 Topological nodal line semimetals Chin. Phys. B 25 117106
[8] Zhang T, Jiang Y, Song Z, Huang H, He Y, Fang Z, Weng H and Fang C 2019 Catalogue of topological electronic materials Nature 566 475
[9] Leng H, Orain J-C, Amato A, Huang Y K and de Visser A 2019 Type-I superconductivity in the Dirac semimetal PdTe$_2$, probing by $\mu$SR Phys. Rev. B 100 224501
[10] Bian G et al 2016 Topological nodal-line fermions in spin-orbit metal PbTaSe$_2$ Nat. Commun. 7 10556
[11] Chen W, Liu L, Yang W, Chen D, Liu Z, Huang Y, Zhang T, Zhang H, Liu Z and Shen D W 2021 Evidence of topological nodal lines and surface states in the centrosymmetric superconductor SnTaS$_2$ Phys. Rev. B 103 035133
[12] Karn N K, Sharma M M, Sharma P, Gjuraj G, Patnaik S and Awana V P S 2021 Superconductivity with topological non-trivial surface states in NbC Supercond. Nov. Magn. 34 2717
[13] Shen D, Kuo C N, Yang T W, Chen I N, Lue C S and Wang L M 2020 Two-dimensional superconductivity and magneto-transport from topological surface states in AuSn$_4$ semimetal Commun. Mater. 1 56
[14] Xing Y et al 2016 Superconductivity in topologically nontrivial material Au:Pb npj Quantum Mater. 1 16005
[15] Khan M A, Graf D E, Vechter I, Browne D A, DiTusa J F, Adam Phelan W and Young D P 2019 Quantum oscillations and a nontrivial Berry phase in the non-centrosymmetric
topological superconductor candidate BiPd Phys. Rev. B 99 020507(R)

[16] Iwaya K, Kohsaka Y, Okawa K, Machida T, Bahramy M S, Hanaguri T and Sasagawa T 2017 Full-gap superconductivity in spin-polarised surface states of topological semimetal β-PdBi$_2$ Nat. Commun. 8 976

[17] Kumar N et al 2020 Signatures of sixfold degenerate exotic fermions in a superconducting metal PdBi$_2$ Adv. Mater. 32 1906046

[18] Tu X H, Liu P F, Yin W, Zhang J R, Zhang P and Wang B T 2022 Topological superconductivity in Rashba spin-orbital coupling suppressed monolayer β–Bi$_2$Pd Mater. Today Phys. 24 100674

[19] Liu P-F, Jingyu L, Xin-Hai T, Yin H, Baisheng S, Zhang J, Singh D J and Wang B-T 2020 Prediction of superconductivity and topological aspects in single-layer β–Bi$_2$Pd Phys. Rev. B 102 155406

[20] Leijnse M and Flensberg K 2012 Introduction to topological superconductivity and Majorana fermions Semicond. Sci. Technol. 27 124003

[21] Sato M and Fujimoto S 2016 Majorana fermions and topology in superconductors J. Phys. Soc. Japan 85 072001

[22] Phong V T, Walet N R and Guinea F 2016 Majorana zero modes in a two-dimensional p-wave superconductor Phys. Rev. B 96 060505(R)

[23] Wilczek F 2009 Majorana returns Nat. Phys. 5 614–8

[24] Gendron M F and Jones R E 1962 Superconductivity in the CuAl$_2$ (C16) crystal class J. Phys. Chem. Solids 23 405

[25] Miao W and Tang K 2019 Bi substitution effect on superconductivity of novel Pb$_3$Pd alloy Phys. C. 565 1355158

[26] Motla K, Kataria A, Sharma S, Bearc J, Pula M, Nugent M and Singh R P 2021 Type-I superconductivity in single-crystal Pb$_2$Pd Phys. Rev. B 103 184506

[27] Ghosh G 1999 Thermodynamic modeling of the palladium-lead-tin system Metall. Mater. Trans. A 30 5

[28] Giannozzi P et al 2009 QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials J. Phys.: Condens. Matter 21 395502

[29] Giannozzi P et al 2017 Advanced capabilities for materials modelling with QUANTUM ESPRESSO J. Phys.: Condens. Matter 29 465901

[30] Mostofi A A, Yates J R, Pizzi G, Lee Y S, Souza I, Vanderbilt D and Marzari N 2014 An updated version of wannier90: a tool for obtaining maximally-localised Wannier functions Comput. Phys. Commun. 185 2309

[31] Wannier G H 1937 The structure of electronic excitation levels in insulating crystals Phys. Rev. 52 191

[32] Wannier G H 1962 Dynamics of band electrons in electric and magnetic fields Rev. Mod. Phys. 34 645

[33] Wu Q S, Zhang S N, Song H-F, Troyer M and Soluyanov A A 2018 WannierTools: an open-source software package for novel topological materials Comput. Phys. Commun. 224 405

[34] Sancho M P L, Sancho J M L and Rubio J 1984 Quick iterative scheme for the calculation of transfer matrices: application to Mo (100) J. Phys. F 14 1205

[35] Sancho M P L, Sancho J M L, Sancho J M L and Rubio J 1985 Highly convergent schemes for the calculation of bulk and surface Green functions J. Phys. F 15 851

[36] Moulder J F, Stickle W F, Sobol P E and Bomben K D 1992 Handbook of X-Ray Photoelectron Spectroscopy (Eden Prairie: Flying Cloud Drive)

[37] Rani P, Jha R and Awana V P S 2013 AC susceptibility study of superconducting YBa$_2$Cu$_2$O$_7$:Ag$_x$ bulk composites (x=0.0–0.20): the role of intra and inter granular coupling J. Supercond. Nov. Magn. 26 2347

[38] Brandt E H 1999 Irreversible magnetization of pin-free type-II superconductors Phys. Rev. B 60 11939

[39] McMillan W L 1968 Transition temperature of strong-coupled superconductors Phys. Rev. 167 331

[40] Kong T, Görnicka K, Gołęb B, Klimczuk T and Cava R J 2018 J. Phys. Soc. Japan 87 074711

[41] Salis M V, Huang Y K and de Visser A 2021 Heat capacity of superconducting YBa$_2$Cu$_2$O$_7$:Ag$_x$ bulk composites (x=0.0–0.20): the role of intra and inter granular coupling J. Supercond. Nov. Magn. 26 2347

[42] Poole C P, Farach H A, Creswick R J and Prozorov R 2007 Phys. Rev. B 103 104502

[43] Poole C P, Farach H A, Creswick R J and Prozorov R 2007 Superconductivity 2nd edn (Amsterdam: Elsevier)

[44] Caroli C, de Gennes P G and Matricon J 1964 Bound fermion states on a vortex line in a type II superconductor Phys. Lett. 9 307

[45] Volovik G E 1993 Superconductivity with lines of GAP nodes: density of states in the vortex JETP Lett. 58 469

[46] Hinuma Y, Pizzi G, Kumagai Y, Oba F and Tanaka I 2017 Band structure diagram paths based on crystallography Comput. Mater. Sci. 128 140

[47] Kokalj A 2003 Computer graphics and graphical user interfaces as tools in simulations of matter at the atomic scale Comput. Mater. Sci. 28 155

[48] Bezotonsny P I et al 2019 Electronic band structure and superconducting properties of SnAs Phys. Rev. B 100 184514

[49] Chamorro J R et al 2022 Anomalous residual surface conductivity in a superconductor with strong spin-orbit coupling (arXiv:2112.10840)

[50] Soluyanov A A and Vanderbilt D 2011 Wannier representation of Z$_2$ topological insulators Phys. Rev. B 83 035108

[51] Rauch T, Flieger M, Henk J, Mertig I and Ernst A 2014 Dual topological character of chalcogenides: theory for Bi$_2$Te$_3$ Phys. Rev. Lett. 112 016802

[52] Fu L and Kane C L 2007 Topological insulators with inversion symmetry Phys. Rev. B 76 045302