This is the accepted manuscript made available via CHORUS. The article has been published as:

Anisotropic angular magnetoresistance and Fermi surface topology of the candidate novel topological metal \( \text{Pd}_3\text{Pb} \)
N. J. Ghimire, Mojammel A. Khan, A. S. Botana, J. S. Jiang, and J. F. Mitchell
Phys. Rev. Materials 2, 081201 — Published 20 August 2018
DOI: 10.1103/PhysRevMaterials.2.081201
Anisotropic angular magnetoresistance and Fermi surface topology of the candidate novel topological metal Pd₃Pb

N. J. Ghimire,* Mojammel A. Khan, A. S. Botana, J. S. Jiang, and J. F. Mitchell

Materials Science Division, Argonne National Laboratory,
9700 South Cass Avenue, Argonne, Illinois 60439, United States

(Dated: June 21, 2018)

Abstract

The recent realization of topological electronic states such as Dirac and Weyl fermions in real materials and their potential for future energy and electronics applications has motivated interest in the study of new forms of topological behavior embodied through new materials. Pd₃Pb is one such candidate predicted recently to host unique topological features, including a dispersionless band near the Fermi level and triple nodal points hosting Dirac fermions and open Fermi arcs. Here, we report the crystal growth and electric transport properties of Pd₃Pb. Our low field magnetoresistance measurements indicate an anisotropic Fermi surface. We found that Pd₃Pb manifests a large transverse magnetoresistance, which reaches 650 % at 1.8 K and 14 T, and pronounced Shubnikov-de Haas (SdH) oscillations. Preliminary analysis of the field dependence of the SdH oscillations points to the likelihood of nontrivial Berry phase in Pd₃Pb. Further studies in high field limit are desirable to extend the realization of the topological properties of the predicted novel fermions in this material.
I. INTRODUCTION

Materials in condensed matter have recently been testbeds for several exotic particles, predicted but never realized, in high energy physics. The examples are skyrmions observed in magnetic textures,$^1$ Weyl fermions in the low energy electronic excitations of Weyl semimetals,$^{2,3}$ and Majorana fermions$^4$ in topological superconductors. These discoveries have not only allowed access to the fundamental physics of the rare particles but also driven large interest in the application of such exotic states to future technologies such as spin based electronics and quantum computation. The exceptional properties of Dirac and Weyl semimetals include large magnetoresistance,$^{5-7}$ high mobility,$^{5-8}$ and the chiral anomaly.$^9,10$ Discoveries of topological states in materials have largely benefited from the precision of the electronic structure calculations in these weakly correlated systems. It has further led to the prediction of other novel topological phases having no counterpart in high energy physics.$^{11,12}$ DFT calculations along this line have recently predicted a unique fermionic state in the cubic compound Pd$_3$Pb with an unusual flat band near the Fermi level.$^{13}$ Without spin-orbit coupling, calculations reveal that this compound hosts a combination of triple nodal points and three-dimensional nodal rings giving rise to topological surface states. Spin-orbit coupling leads to anticrossings of the nearly degenerate bands that give rise to ten fourfold degenerate Dirac points. In addition, it lowers the flat band towards the Fermi level, giving rise to a peculiar fermi surface depicted in Figs. 1(d) and (e).

Here we report the magnetotransport properties of Pd$_3$Pb, where we have found large magnetoresistance, large mobility, semimetallic behavior and enhanced quantum oscillations as compared to those expected for a normal metal. The transverse magnetoresistance at 1.8 K and 14 T reaches 650 % and remains unsaturated. The angular dependent transverse magnetoresistance is anisotropic and shows a four-fold symmetry. Analysis of the Shubnikov-de Haas (SdH) oscillations indicates the possible topological character in terms of non-trivial $\pi$ Berry phase. Taken together, these transport properties reveal features that are common to several known topological materials and make Pd$_3$Pb a candidate material to host unconventional fermions.
II. EXPERIMENTAL AND CALCULATIONS DETAILS

Single crystals of Pd$_3$Pb were synthesized by the self-flux method. Pd pieces and Pb shot were loaded in a 2 mL aluminum oxide crucible in a molar ratio of 3:1. The crucible was then sealed in a fused silica ampoule under vacuum. The sealed ampoule was heated to 1175°C over 10 hours, homogenized at 1175°C for 12 hours, and then cooled to 900°C over 150 hours. Once the furnace reached 900°C, the excess flux was decanted from the crystals using a centrifuge. Well faceted cubic crystals as large as 3 mm $\times$ 3 mm $\times$ 2 mm were obtained. An optical image of a single crystal is shown in Fig. 1(b).

The crystal structure of the compound was verified by Rietveld refinement\textsuperscript{14} of powder x-ray diffraction pattern collected on pulverized single crystals at room temperature using a PANalytical X’Pert Pro diffractometer. The Rietveld refinement was carried out using FULLPROF software\textsuperscript{15} and is shown in Fig. 1(c). The chemical composition of the single crystals was studied using a scanning electron microscope (SEM) with an energy dispersive x-ray spectrometer (EDS). The atomic percentages of Pd and Pb were found to be 76.09:23.91 (3.18:1), respectively, which are within the expected uncertainty for the standard-less measurements of the composition Pd:Pb = 3:1.

Electrical resistivity measurements were made on an oriented crystal in a Quantum Design Physical Property Measurement System (PPMS) down to 1.8 K and in magnetic fields up to 14 T. A four wire configuration with 25 $\mu$m gold wire and Epotek H20E silver epoxy were used for the resistivity and magnetoresistance measurements. The Hall effect was measured in a Hall bar geometry. Longitudinal (transverse) voltages were symmetrized (antisymmetrized) about H = 0 T, to account for any small misalignment of the voltage leads.

The electronic structure calculations to obtain the Fermi surface were performed within density functional theory using the all-electron, full potential code WIEN2K\textsuperscript{16} based on the augmented plane wave plus local orbitals (APW + lo) basis set.\textsuperscript{17} The Perdew-Burke-Ernzerhof version of the generalized gradient approximation was used as the exchange-correlation functional.\textsuperscript{18} Spin-orbit coupling (SOC) effects were included in a second variational procedure.\textsuperscript{19} All calculations were fully converged with respect to all the parameters used. In particular, $R_mK_{max} = 8.0$, a dense $k$ mesh of $40 \times 40 \times 40$, and muffin-tin radii of 2.5 a.u. for Pd and Pb were chosen.
III. RESULTS AND DISCUSSION

Pd$_3$Pb is reported$^{20}$ to crystallize in a face centered cubic structure (space group Pm$\bar{3}$m) having a Pd$_6$ octahedron, as depicted in Fig. 1a. We used the reported structure for the Rietveld refinement of the room temperature powder x-ray diffraction pattern, which is shown in Fig. 1(c). Lattice parameter obtained from the fit is $a = 4.034(8)$, which is in good agreement with previously reported values.$^{13,20–22}$

The zero field resistivity between 1.8 and 300 K measured on three samples (S1, S2, and S3) of Pd$_3$Pb single crystals is shown in Fig. 2(a). The current was applied along the crystallographic $a$-axis. Although the resistivity of S1 is slightly larger than S2 and S3, the normalized resistivity $[\rho(T)/\rho(300\,\text{K})]$ of all three samples coincide, as shown in the inset to Fig. 2(a), suggesting that the difference in S1 is due to a geometric factor. The resistivity decreases with decreasing temperature down to 15 K and levels off below this. Hall effect and transverse magnetoresistance shown in Figs. 2(b-d) were measured on S1. All other measurements were carried out on S2. Fig. 2(b) shows the temperature dependence of the resistivity of Pd$_3$Pb measured in transverse magnetic fields of 0, 9 and 14 T applied along the crystallographic $c$-axis. The effect of the magnetic field becomes significant at lower temperatures. The resistivity starts increasing below 70 K at 14 T and 50 K at 9 T. In both fields, the resistivity saturates below 15 K.

Transverse magnetoresistance, defined as TMR = $100 \times [\rho_{xx}(\mu_0 H) - \rho_{xx}(\mu_0 H = 0)]/\rho_{xx}(\mu_0 H = 0)$ with H $\perp$ I measured in the magnetic field up to 9 T, is presented in Fig. 2(c). The TMR shows a quadratic behavior over the entire temperature range. At room temperature and 9 T, there is a small TMR of about 10 %. It increases with decreasing temperature and reaches over 360 % at 1.8 K and 9 T and 650 % at 14 T [Fig. 4(a)] and remains unsaturated.

Figure 2(d) shows the Hall resistivity as a function of magnetic field between $\pm$9 T at different temperatures. The Hall resistivity is defined as $\rho_{yx} = (V_y/I_x)t$, where $t$ is the thickness of the sample, and $V_y$ is the transverse voltage in the presence of a magnetic field applied along $c$-axis with current $I_x$ along the crystallographic $a$-axis. At high temperatures, the sign of the Hall resistivity is positive with respect to the applied magnetic field. Below 50 K, the sign of the Hall resistivity remains positive at magnetic field up to 3 T, but becomes negative at higher fields, indicating a multi-band effect, which is consistent with the calculated Fermi surface that shows the presence of multiple electron and hole pockets,
[see Figs. 1(d) and (e)]. To analyze our data, we adopt a two-band model given in Equations (1 and 2) with one electron- and one hole- band, that has been used to describe several multi-band compounds.\textsuperscript{23–25}

\begin{align*}
\rho_{xx}(B) &= \frac{1}{e} \left( \frac{n_h \mu_h + n_e \mu_e}{(n_h \mu_h + n_e \mu_e)^2} + (n_h - n_e)^2 \mu_h^2 \mu_e^2 B^2 \right), \\
\rho_{yx}(B) &= \frac{B}{e} \left( \frac{n_h \mu_h^2 - n_e \mu_e^2}{(n_h \mu_h + n_e \mu_e)^2} + (n_h - n_e)^2 \mu_h^2 \mu_e^2 B^2 \right),
\end{align*}

Equation (1)

Here, B = \mu_0 H, n_h and n_e are hole and electron concentration, and \mu_h, and \mu_e are hole and electron mobility, respectively. An attempt to fit this two-band model to \rho_{xx} and \rho_{yx} measured at 1.8 K failed to give a unique solution. Using the constraints\textsuperscript{26}: 1) Eqn. (1) must reproduce \rho_{xx}(\mu_0 H=0) and 2) in high field limit, \rho_{yx} \sim \frac{B}{e} \frac{1}{(n_e - n_h)}, a fit to \rho_{yx} in Eqn. (2) [as shown in Fig. 2(d)] yields \( n_h = 1.52 \times 10^{20}/cm^3, n_e = 4.32 \times 10^{20}/cm^3, \mu_h = 2.3 \times 10^3 \) cm\(^2\)/Vs, and \( \mu_e = 1.2 \times 10^3 \) cm\(^2\)/Vs.

In Figure 3 we show polar plots of magnetoresistance of Pd\(_3\)Pb measured at the external magnetic field of 9 T in two different configurations - transverse configuration [TC - Fig. 3(a)] and transverse-to-longitudinal configuration [TLC - Fig. 3(c)]. Sketches showing the direction of current and axis of rotation with respect to the crystal and the hole pockets in the Fermi surface are depicted in Figs. 3(c) and (d). In TC mode, current (I) is applied along the crystallographic \( a \)-axis and magnetic field (H) is applied along the \( c \)-axis. The crystal is rotated about the axis parallel to I such that H always remains perpendicular to I. In TLC measurements, current still remains along the \( a \)-axis, but the crystal is rotated about an axis perpendicular to both H and I, so that the angle between I and H changes between 0 and 360\(^\circ\), as shown in the right panel of Fig. 3(d). The angular magnetoresistance presented in the polar plots is the relative change in the resistivity as a function of angle, normalized to the minimum resistivity - i.e., resistivity at 45\(^\circ\) in TC and resistivity at 90\(^\circ\) in TLC mode of measurement. A four-fold (two-fold) symmetry is observed in the TC (TLC) measurement. The mobility of the carriers in the plane perpendicular to the direction of the magnetic field dictates the response of the charge carriers to the applied magnetic field. In TC measurement, the magnetoresistance becomes maximum each time when the magnetic field is along a crystallographic axis, which suggests that in this configuration the charge carriers move in the minimum cyclotron orbit and hence the four-fold symmetry in the angular magnetoresistance indicates the anisotropy in the Fermi surface.\textsuperscript{27,28}
To explore the further details of the effect of the Fermi surface on the transport properties, we carried out measurements up to the magnetic field of 14 T. Magnetoresistance at 1.8 K in the TLC geometry at several angles between I and H is depicted in Fig. 4(a). The anisotropy between transverse (0°) and longitudinal (90°) magnetoresistance at 14 T is 22.5. Shubnikov-de Haas (SdH) oscillations are observed in the magnetoresistance measurements above 7 T. The oscillations are clearly visible in the longitudinal measurement, as depicted in Fig. 4(b). However upon subtraction of a non oscillatory background \( <\rho_{xx}> \) (a third order polynomial fit to \( \rho_{xx} \)) the SdH oscillations \( \Delta \rho_{xx} = \rho_{xx} - <\rho_{xx}> \) are visible at all measured angles [Fig. 4(c)]. The amplitude of the SdH oscillations is larger in the transverse MR than in the LMR. The SdH oscillations at other angles are much weaker. Figure 4(d) shows the frequencies of the SdH oscillations obtained by Fast Fourier Transform (FFT) of \( \Delta \rho_{xx} \) as a function of \( 1/\mu_0 H \). The SdH oscillations in transverse mode show several frequencies, with a frequency at 126 T (\( F_\alpha \)) being prominent. Higher harmonics of this frequency, labelled \( F_{2\alpha} \) and \( F_{3\alpha} \), are also visible. \( F_\alpha \) and its harmonics are also observed clearly in the longitudinal mode.

As the SdH oscillations in longitudinal configuration show fewer frequencies than in transverse configuration, we analyzed the SdH oscillations obtained in the longitudinal magnetoresistance measurements in detail. The results are depicted in Fig. 5. Longitudinal SdH oscillations \( \Delta \rho_{xx} \) as a function of \( 1/\mu_0 H \) measured at various temperatures between 1.8 and 20 K are shown in Fig. 5(a). The amplitude of the SdH oscillations decreases with increasing temperature or decreasing magnetic field. The FFT spectrum of the SdH oscillations shown in Fig. 5(b) reveals one prominent primary frequency \( F_\alpha = 126 \) T and its second and third harmonics \( F_{2\alpha} = 252 \) T and \( 3\alpha = 378 \) T, respectively. In addition, there are two other weaker frequencies at 238 and 364 T. While \( F_\alpha \) survives up to 20 K, these two frequencies disappear quickly with increasing temperature, and are completely suppressed at 5 K. According to the Lifshitz-Onsager relation, the SdH oscillation frequency, \( F \), is proportional to the extremal cross-sectional area \( S_F \) of the Fermi surface, i.e.

\[
F = \frac{\hbar}{2\pi e} S_F
\]  

(3)

For Pd\(_3\)Pb, \( S_F \) is 0.012 Å\(^{-2}\). This cross-sectional area occupies only 0.5 % of the whole area of the Brillouin zone in the \( k_x - k_y \) plane corresponding to the lattice constant \( a = 4.034 \) Å. Supposing a circular cross-section, it gives the Fermi momentum \( k_F = \sqrt{\frac{2S_F}{\pi}} = 0.062 \) Å.
The decay amplitude of the SdH oscillations with temperature and magnetic field is described by the Lifshitz-Kosevich (LK) formula:\textsuperscript{29,30}

\[
A(T, B) \propto e^{-\frac{2\pi^2 k_B T_D}{k_B T}} \frac{2\pi^2 k_B T}{\hbar \omega_c} \sinh \left( \frac{2\pi^2 k_B T}{\hbar \omega_c} \right),
\]

where, \( k_B \) is the Boltzmann constant, \( B = \mu_0 H \), \( T_D \) is the Dingle temperature, \( \omega_c = \frac{eB}{m^*} \) is the cyclotron frequency, and \( m^* \) is the effective mass. The obtained value of \( m^* \) from the temperature-dependent SdH oscillations in the field of 12.56 T is 0.21\( m_e \), where \( m_e \) is the bare electron mass [Fig. 5(c)]. The Fermi energy estimated using the experimentally obtained effective mass (\( m^* \)), and the Fermi radius (\( k_F \)) using the relation \( E_F = \hbar^2 k_F^2 / 2m^* \), gives a value of 70 meV.

In order to further analyze the SdH oscillations of \( \rho_{xx} \), we use the following expression for a 3D system:\textsuperscript{24,30}

\[
\frac{\Delta \rho_{xx}}{< \rho_{xx} >} = A(T, B) \cos \left[ 2\pi \left( \frac{F}{B} - \gamma + \delta \right) \right],
\]

where \( < \rho_{xx} > \) is the non-oscillatory part of \( \rho_{xx} \), \( F \) is the frequency of oscillation, \( \gamma \) is the Onsager phase, and \( \delta \) is an additional phase shift taking a value between \( \pm 1/8 \) depending on the curvature of the Fermi surface topology.\textsuperscript{24,30,31} The Onsager phase is given by \( \gamma = 1/2 - \varphi_B / 2\pi \), where \( \varphi_B \) is the Berry phase. In a topologically trivial band with a parabolic dispersion, \( \varphi_B = 0 \). Thus \( \gamma \) takes a value of 1/2. In case of a Dirac system, \( \varphi_B = \pi \) and hence \( \gamma = 0 \). To check the topological feature of the \( \alpha \) pocket, we plot the Landau fan diagram in Fig. 5(d) by assigning the peaks (valleys) of \( \Delta \rho_{xx} \) to \( n (n+1/2) \) Landau level (LL) indices. A linear extrapolation of \( n \) vs \( 1/B \) gives the intercept \( (\gamma - \delta) \). We find the intercept to be -0.03, which falls between \(-1/8\) and \(1/8\), suggesting the likelihood of a nontrivial \( \pi \) Berry phase in Pd\(_3\)Pb. The slope obtained form the fit is 125.4 T that corresponds to the frequency of the oscillation (126 T). We emphasize that this result should be treated with caution for two reasons. First, the lowest LL obtained is \( n = 9 \), which is far from the quantum limit and confirmation by measurement in higher magnetic fields will be required to verify this hypothesis. Second, in the superconducting magnets there can be small shift between the recorded magnetic fields measured as a magnet current and the actual magnetic fields at the sample. It is possible that such a discrepancy can influence the interpretation of a Berry phase contribution.
IV. CONCLUSION

In summary, we have grown single crystals of the proposed novel topological metal Pd$_3$Pb using a self flux method. It shows electrical transport properties similar to those observed in several (topological) semimetals, but with a reduced magnitude. Pd$_3$Pb displays a large transverse magnetoresistance that reaches 650% at 1.8 K and 14 T. SdH oscillations are obtained at relatively low field i.e. above 7 T. Preliminary analysis of SdH oscillations point towards the likelihood of a non-trivial $\pi$ Berry phase as expected in a Dirac system. Our low field measurements thus establishes Pd$_3$Pb as a candidate material with possible novel fermionic state. At the moment, it is not clear whether these properties are due to the predicted topological features - Dirac points and Fermi arcs. Further transport measurements in high magnetic field and spectroscopic techniques such as ARPES may shed light on this issue.

V. ACKNOWLEDGEMENTS

This work was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Science and Engineering Division. The authors thank insightful discussion with Anand Bhattacharya, and Filip Ronning. The EDS measurements were performed at the Center for Nanoscale materials in the Electron Microscopy Center, which was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357. We acknowledge the computing resources provided on Blues, a high-performance computing cluster operated by Argonne’s Laboratory Computing Resource Center.

* corresponding author; nghimire@anl.gov, nepnjg@gmail.com


24 Y. Luo, N. J. Ghimire, M. Wartenbe, H. Choi, M. Neupane, R. D. McDonald, E. D. Bauer,


30 H. Murakawa, M. S. Bahramy, M. Tokunaga, Y. Kohama, C. Bell, Y. Kaneko, N. Nagaosa,

FIG. 1.  

a) Crystal structure of Pd$_3$Pb in the cubic space group Pm$\bar{3}$m with lattice constant $a = 4.034$ Å. 
b) Optical image of single crystal of Pd$_3$Pb on a 1 mm × 1 mm grid. 
c) Rietveld refinement of a laboratory x-ray powder pattern of Pd$_3$Pb collected at room temperature. 
d) GGA+SOC band structure of Pd$_3$Pb. 
e) GGA+SOC Fermi surface of Pd$_3$Pb. The Fermi surface consists of narrow cylindrical hole pockets (related to the flat band near $E_F$) that cross at $\Gamma$ and spherical electron pockets centered at $R$ and surrounded by smaller elliptical hole pockets. Ten Dirac points appear between the sphere and the cylindrical hole pockets (see details of the corresponding band structure in Ref.$^{13}$).
FIG. 2.  a) Temperature dependent resistivity of three Pd$_3$Pb single crystals in zero external magnetic field. Inset shows that $\rho(T)/\rho(300K)$ vs $T$ for all three samples coincide. b) Temperature dependent resistivity of Pd$_3$Pb in 0, 9 and 14 T with H || c-axis and I || a-axis. c) Transverse magnetoresistance of Pd$_3$Pb at temperatures indicated. d) Hall resistivity of Pd$_3$Pb with H || c-axis and I || a-axis.
FIG. 3. a) Polar plot of angular magnetoresistance of Pd₃Pb measured at 1.8 K and 9 T in transverse configuration (TC). Here, $\Delta \rho_\theta = \rho_\theta - \rho_{45^\circ}$. b) Sketch of the transverse configuration (TC) measurement showing the direction of current, magnetic field and the rotation axis. In this case, I is always normal to H. c) Polar plot of angular magnetoresistance of Pd₃Pb measured at 1.8 K and 9 T in transverse-to-longitudinal configuration (TLC). Here, $\Delta \rho_\theta = \rho_\theta - \rho_{90^\circ}$. d) Sketch of the transverse-to-longitudinal configuration (TLC) measurement showing the direction of current, magnetic field and the rotation axis. Diagram in the top right corner shows relationship between I and H with the rotation angle $\theta$. When $\theta = 0$, I $\perp$ H, when $\theta = 90^\circ$, I $\parallel$ H.
FIG. 4. a) Magnetoresistance of Pd$_3$Pb at selected angles in the TLC configuration at 1.8 K. Inset shows the relationship between I and H with the rotation angle $\theta$. When $\theta = 0$, I $\perp$ H, when $\theta = 90^\circ$, I $\parallel$ H. b) Longitudinal magnetoresistance (MR at 90$^\circ$) of Pd$_3$Pb at 1.8 K. c) SdH oscillations of Pd$_3$Pb between 7 and 14 T at specified angles between I and H. Here, $\Delta \rho_{xx} = \rho_{xx} - <\rho_{xx}>$. d) FFT amplitude of the SdH oscillations presented in panel (c). The FFT spectra are shifted for clarity. The dashed lines are guide to the frequency $F_\alpha$, $F_{2\alpha}$, and $F_{3\alpha}$. 
FIG. 5.  

a) SdH oscillations of the longitudinal magnetoresistance of Pd$_3$Pb between 7 and 14 T at specified temperatures. Here, $\Delta \rho_{xx} = \rho_{xx} - \langle \rho_{xx} \rangle$. b) FFT amplitude of the SdH oscillations in panel (a). c) Normalized amplitude of SdH peaks at the magnetic field of 12.56 T as a function of T. The solid line is the fit to Lifshitz-Kosevich formula. d) Landau fan diagram.