Noncentrosymmetric superconductivity in a clean crystal of type II superconductor Bi-Pd

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Abstract. In this work, we present the bulk superconductivity of a high-quality single crystal of monoclinic BiPd (α-BiPd, space group $P\bar{2}_1$) below 3.8 K by studying its electrical resistivity, magnetic susceptibility, and heat capacity. This is the cleanest noncentrosymmetric superconductor (NCS) that display anisotropy due to spin-orbit scattering and also exhibits unusual superconducting properties due to s and p wave mixing as evidenced by the observation of Andreev bound state and multiple energy gaps via point contact measurements. In addition, Fermi surface studies suggest multiband superconductivity in this compound. Penetration depth studies and NQR investigations support mixing of s and p wave Cooper pairing in this crystal. Moreover, Muon spin rotation measurements indicate strong field dependence of the Ginzburg-Landau coefficient of this superconductor. Unusual pairing and multiband superconductivity are extremely sensitive to disorder and they can be observed only in cleanest (RRR > 170) single crystals.

1. Introduction
Ever since the discovery of the non-centrosymmetric heavy fermion superconductor CePt$_3$Si [1], there is widespread research activity to understand the nature of superconductivity in such unconventional superconductors. The term non-centrosymmetric characterizes the symmetry of a crystal lattice without inversion center. In such materials the standard classification in even-parity spin-singlet and odd-parity spin triplet superconducting phases is obsolete, because the electrons are exposed to antisymmetric spin-orbit coupling, e.g. Rashba-type of coupling [2] which arises due to electric field gradient in the crystal which has no inversion symmetry. An inherent feature is then the mixing of spin-singlet and spin-triplet Cooper pairing channels which are otherwise distinguished by parity. This mixing of pairing states is expected to cause a two-component order parameter. New forms of pairing appear giving rise to unusual temperature field dependence of the superconducting parameters. During recent years we have witnessed rapid developments on the side of experiments and synthesis of novel materials as well as in the theoretical understanding of this type of superconductors. Indeed many new materials have been found, in particular, among the heavy fermions for which unconventional Cooper pairing is expected. Exotic mixed-state phases (vortex matter) have been predicted in theory and are under experimental investigations. For example in the case of CePt$_3$Si where superconductivity occurs at ambient pressure, whereas, transition to such a state happens in UIr [3], CeRhSi$_3$[4] and CeIrSi$_3$[5] only under pressure. However, the study of superconductivity in non-centrosymmetric materials which do not exhibit heavy fermion features is also important.
since it avoids additional complication that arises due strong f-electron correlations. Discovery of such materials also continues to increase, starting from binary carbides ($R_2C_3$ with $R=La$ or Y)[6], Cd$_2$Re$_2$O$_7$[7], Li$_2$(Pd,Pt)$_3$B [8, 9], Mg$_2$Al$_3$[10] and the recently found BaPtSi$_3$[11]. However, many of them (except Li$_2$Pt$_3$B) exhibit conventional BCS-like super-conductivity due to small spin-orbit scattering. One of the common features in these compounds which show conventional superconductivity with small spin-orbit scattering is the absence of the large density of states at the Fermi level. Hence, it will be of interest to study a superconducting material which have conduction electrons with high density of states at the Fermi level (not from high f-electron correlations) but has no inversion symmetry. In this work we report our investigations in one such material, namely $\alpha$-BiPd which has no inversion symmetry in its monoclinic crystal structure (space group $P2_1$) and it shows bulk superconductivity below 3.8 K as determined from resistivity, magnetization and heat capacity studies. The unconventional nature of the superconductivity is probed also by point contact spectroscopy, NMR and penetration depth measurements.

2. Experimental details

The compound BiPd undergoes polymorphic transformation from $\alpha$-BiPd (monoclinic, $P2_1$) [12, 13] to $\beta$-BiPd (orthorhombic, Cmc21) above 210°C. We have synthesized phase pure $\alpha$-BiPd which has a monoclinic structure with the space group $P2_1$ with b as its unique axis. Due to its low melting point (650°C), we have chosen to make the sample using a modified Bridgeman technique. The sample was made by control heating the individual components (Bi, 99.999% pure and Pd, 99.99% pure) in a high purity Alumina crucible with a pointed bottom which is kept in a quartz tube that is sealed under a vacuum of 10$^{-6}$ mbar. Initially the contents were heated up up to 650°C (melting point of BiPd) in 12 hrs and then kept at 650°C for 12 hrs. Thereafter it was slow cooled to 590°C with a rate of 1 °C/hr and finally the furnace was switched off. We obtained high quality poly and single crystals of few mm size with mass ranging from 10 to 50 mg. A piece of the from the melt was crushed into a fine powder for powder x-ray diffraction measurement using Cu K$_\alpha$ radiation in a commercial diffractometer which confirmed that the crystal formed $\alpha$-BiPd ($P2_1$) structure. The unit cell of this monoclinic structure is shown in Fig. 1. The structure consists four inequivalent sites for Bi and four inequivalent sites for Pd having 16 atoms in the unit cell. It also has alternate layer of Bi and Pd sheets with short Pd-Pd The values for the lattice constants estimated from the Rietveld fit [14] are $a=5.6284(\pm0.0004)$Å, $b=10.6615(\pm0.0004)$Å, $c=5.6752(\pm0.0004)$Å, $\alpha=\gamma=90$ and $\beta=101$. The resistivity, susceptibility and heat capacity measurements are performed using commercial (Quantum Design, USA) setups.

3. Results and discussions

Fig. 2(c) shows the temperature dependence of the resistivity ($\rho(T)$) from 1.5 to 300 K. NMR measurements have been done with Professor Zhang’s group (Okayama, Japan) and penetration depth studies are done in collaboration with Professo H. Yuan’s group (HangZhou, China). Fermi surface measurements are performed with Dr. Edward Yelland (St. Andrews, Scotland) and $\mu$SR measurements were done in collaboration with Professor Ted Frogan’s group (Birmingham, UK). The high quality of the sample is clearly evident from the large residual resistivity ratio ($\rho(300K)/\rho(4K)$) of 170. The inset 2(a) shows the superconducting transition below 3.8 K with a width of less than 2 mK. The inset 2(b) shows the low temperature resistivity from 4 to 30 K. The solid line is a fit to the equation,

$$\rho(T) = \rho_0 + A \times T^n$$  \hspace{1cm} (1)

The fit yields a value of 0.3 $\mu$Ω cm for $\rho_0$, $9.2 \times 10^{-5}$ $\mu$Ω cm/K$^3$ for A and n=3. This $T^3$ dependence of the resistivity is interpreted by the Wilsons theory [15] which takes into account
α-BiPd has Monoclinic (P2₁) structure with 16 atoms in a unit cell (8 formula unit). It contains four inequivalent Bi sites and four inequivalent Pd sites.[27]

Figure 1. α-BiPd has Monoclinic (P2₁) structure with 16 atoms in a unit cell (8 formula unit). It contains four inequivalent Bi sites and four inequivalent Pd sites.[27]

The Wilsons theory [15] neither considers the actual structure of the density of states of the electrons at the Fermi level nor the effect of unharmonicity of the phonon mode. But the contribution from these effects in the case of α-BiPd are small. There is yet another mechanism (parallel resistor model) suggested by Fisk and Webb [16] and later by Wisemann et al [17] which accounts for the significant deviation of the resistivity from the linear temperature dependence at high temperatures (100 K<T<300 K). This has been seen in many other compounds where
the $\rho$ value is rather high (>100 $\mu\Omega$ cm). The strong deviation from linearity and possible tendency towards saturation occur because the mean free path becomes short, of the order of few atomic spacings. When that happens, the scattering cross section will no longer be linear in the scattering perturbation. Since the dominant temperature-dependent scattering mechanism is electron-phonon interaction here, the $\rho$ will no longer be proportional to the mean square atomic displacement, which is proportional to $T$ for a harmonic potential. Instead, the resistance will rise less rapidly than linearly in $T$ and will show negative curvature ($d^2\rho/dT^2 < 0$). This behavior is also seen in our previous studies on silicides and germanides [18, 19, 20]. Wisemann et al [17] describe the $\rho(T)$ of these compounds (which is known as the parallel resistor model) where the expression of $\rho(T)$ is given by,

$$\frac{1}{\rho(T)} = \frac{1}{\rho_1(T)} + \frac{1}{\rho_{max}},$$

where $\rho_{max}$ is the saturation resistivity which is independent of temperature and $\rho_1(T)$ is the ideal temperature-dependent resistivity. Further, the ideal resistivity is given by the following expression,

$$\rho_1(T) = \rho_0 + C_1 \left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{x^3 dx}{(1 - \exp(-x))\exp(x) - 1},$$

where $\rho_0$ is the residual resistivity and the second term is due to phonon-assisted electron scattering similar to the s-d scattering in transition metal compounds. $\theta_D$ is the Debye temperature and $C_1$ is a numerical constant. Eqn.(2) can be derived if we assume that the electron mean free path $l$ is replaced by $l + a$ ($a$ being an average interatomic spacing). Such an assumption is reasonable, since infinitely strong scattering can only reduce the electron mean free path to $a$. Chakraborty and Allen [21] have made a detailed investigation of the effect of strong electron-phonon scattering within the framework of the Boltzmann transport equation. They find that the interband scattering opens up new nonclassical channels which account for the parallel resistor model. The high temperature resistivity fit (50 K $< T$ $< 310$ K) shown in the Fig. 3(c) yields a value of 164 $\mu\Omega$ cm for $\rho_{max}$, 0.33 $\mu\Omega$ cm for $\rho_0$, 76.3 $\mu\Omega$ cm/K$^3$ for $C_p$ and 168.6 K for $\theta_D$. This value to $\theta_D$ is close to the value obtained from the heat capacity data (described later) which suggests that the parallel resistor model can successfully explain the high temperature dependence of $\rho(T)$ of $\alpha$-BiPd.

**Figure 3.** Temperature dependence of the heat capacity of the monoclinic (P2$_1$) $\alpha$-BiPd from 2 to 35 K. The insets are explained in the text. Solid line is a fit to the equation (3) described in the text.[27]

The temperature dependence of the heat-capacity ($C_p$) from 2 to 30 K of $\alpha$-BiPd is shown in Fig. 3. The inset shows the low temperature $C_p$ vs $T$ data. The jump in $C_p$ at 3.7 K ($\Delta C = 30$
mJ/mol K) clearly shows bulk superconducting ordering in this sample below this temperature. The temperature dependence of $C_p$ is fitted to the expression,

$$C_p = \gamma T + \beta T^3,$$

(3)

where $\gamma$ is due to the electronic contribution and $\beta$ is due to the lattice contribution. The value of $\Delta C_p/\gamma T_c$ is 0.2 which is significantly reduced from the BCS value of 1.43. Low values of $\Delta C_p/\gamma T_c$ have been observed before in the heat-capacity study of several superconducting compounds [22, 23]. According to these studies the reduced jump across $T_c$ could arise from extrinsic effect (such as inhomogeneity in the sample or magnetic impurities) or from intrinsic effect (such as the existence of regions which do not participate in superconductivity). In our sample of α-BiPd, we estimate the impurity content to be less than 0.1 % by volume and the sharpness of the superconducting transition also suggests good homogeneity. It is possible that the reduced jump could arise from two-band superconductivity where one band remains normal. However, detailed Fermi surface measurements are required before we can analyze the data in terms of this model. The fit to the heat capacity data using the eqn. 3 in the temperature range from 5 to 20 K yielded 41 mJ/mol K$^2$ and 0.9 mJ/mol K$^4$ for $\gamma$ and $\beta$, respectively. The $\gamma$ value has been obtained by matching the entropy of normal and superconducting state at $T_c$ as suggested by Stewart et al [24]. From the $\beta$ value of 0.9 mJ/mol K$^4$, we estimate the $\theta_D$ to be 162 K using the relation,

$$\theta_D = \left( \frac{12 \pi^4 N_A n k_B}{5 \beta} \right)^{1/3},$$

(3)

where $N_A$ is the Avogadro’s number, $n$ is the number of atoms per formula unit, and $k_B$ is the Boltzmann’s constant.

3.1. Point Contact spectroscopy measurements

From the resistivity and specific heat measurements on a similar crystal, we estimate the electronic mean free path, $l$=2.4 m at low temperatures. The quality of the crystal was also confirmed by observing de Haas-van Alphen (dHvA) oscillation. Before doing point contact measurement, the crystal surface was polished to a mirror finish. To make ballistic point contact, a mechanically cut fine tip made from 0.25mm diameter Ag wire was brought in contact with the (010) ($I_\parallel b$) and (001) ($I_\perp b$) crystal faces using a differential screw arrangement in a conventional sample-in-liquid $^3$He cryostat. I-V characteristics of the junction formed between the tip and the sample were measured at different temperature down to $T$=0.32 K using conventional 4-probe technique [28]. The dI/dV vs. V spectra was obtained by numerically differentiating the I-V curves. For all spectra reported here, the contact resistance ($R_C$) in the normal state varied in the range $R_C$~1Ω to 30Ω. The corresponding contact diameter estimated using the formula, $d = \frac{4 \pi l}{3 R_C^{1/2}} \sim 100-500$ Å, was much smaller than $l$. Therefore, all our point contact spectra are taken in ballistic limit. To further understand the nature of superconductivity, we have measured the upper critical field ($H_{C2}$) and its anisotropy along two crystallographic axes ($H_{|| b}$ and $H_{\perp b}$) by measuring ac susceptibility as function of magnetic field at different temperatures. We first concentrate on the PCAR spectra at the lowest temperature. From large statistics, we observe two kinds of PCAR spectra, corresponding to $I_\parallel b$ and $I_\perp b$ respectively. Fig. 4(a) and (b) show representative evolution with contact resistance for (dI/dV) versus V spectra for $I_\parallel b$. Figure 4(d) and (e) shows similar spectra $I_\perp b$. In both directions, the striking feature is the observation of a pronounced zero bias conductance peak (ZBCP) which coexists with more conventional gap-like features in the low $R_C$ contacts ((Fig. 4(a) and 4(d)))). In addition, for $I_\parallel b$, clear coherence peaks associated with superconducting gaps are observed around 0.1 meV and 0.4 meV respectively. For $I_\perp b$, the corresponding structures are observed at 0.4 meV and 0.8 meV respectively. Both the ZBCP and gap features disappear at the bulk $T_c$ confirming their
superconducting origin. As the contact resistance increased by gradually withdrawing the tip in both directions the ZBCP slowly vanishes and we recover spectra with only gap-like features. To quantitatively obtain the values of the superconducting energy gaps, we fit the spectra using a two-band Blonder-Thinkham-Klapwijk (BTK) model [25, 26] generalized to take into account broadening effects. Analyzing more than 50 spectra along $I_{∥}$ and $I_{\perp}$ (Fig. 4(c) and 4(f)),

![Figure 4](image_url)

**Figure 4.** PCAR spectra for different contact resistance at $T = 0.35K$: (a) and (b) $I_{∥}$ and (d) and (e) $I_{\perp}$. Solid lines (red) are fits to the modified two gap BTK model. The corresponding fits with a single gap model (black dash lines) are also shown for comparison for some of the spectra. (c), (f) Scatter plot of superconducting energy gap obtained by fitting the modified BTK model to the experimental PCAR spectra for $I_{∥}$ and $I_{\perp}$ plotted as a function of the serial number of the spectra. The bands are guides to the eye. (e) and (f) Temperature dependence of the PCAR spectra for two low $R_c$ contacts for $I_{∥}$ and $I_{\perp}$, respectively.

we observed that the dominant feature is a gap, $\Delta_1 = 0.40 \pm 0.1$ meV present along both directions. For $I_{||}$, in about 50% of the spectra we can clearly resolve a smaller gap, $\Delta_2 = 0.1 \pm 0.05$ meV with $\omega \sim 0.2-0.6$. On the other hand in 50% of the spectra along $I_{\perp}$, we can clearly resolve a
larger gap $\Delta_3 = 0.80.15$ meV with $\omega \sim 0.1 - 0.35$. We did not obtain any spectra showing the three gaps simultaneously in the same spectra. The large variation in $\omega$ and the dispersion in gap values arise from surface roughness which limits our inability to precisely inject current along the desired direction. The temperature variation of the superconducting energy gaps are obtained by analyzing the temperature dependence of two point contacts along the two directions with large $R_c$ (Fig. 5(a) and 5(c)), where the ZBCP is suppressed. The temperature dependence of $\Delta_1, \Delta_2$ and $\Delta_3$ obtained from a fit of these spectra with the generalized BTK model are shown in Figures 5(b) and 5(d). One can see that $\Delta_1$ has similar temperature variation for both I||b and I⊥b and closes at $T_C$, suggesting that this gap originates from an isotropic s-wave order parameter. The small gap $\Delta_2$ observed for I||b on the hand decreases rapidly at low temperatures and forms a tail towards $T_C$ as expected for a multiband superconductor. We now focus on the origin of the ZBCP in the low resistance spectra. Since ZBCP can arise from several origins it is important to analyze the observed ZBCP in BiPd critically. First, we look for extrinsic origins of the ZBCP that are not associated with genuine spectroscopic features. It has been shown that in the case where the point contact is not purely in the ballistic limit, ZBCP can arise from the current reaching the critical current ($I_C$) of the point contact. However, in our case such a possibility can be trivially ruled out for two reasons. First, as we have shown before our contact is well in the ballistic limit even after considering error associated with our determination of contact diameter from $R_S$. More importantly, the conductance spectra at currents larger than $I_C$
cannot contain any spectroscopic information. In our case however, we observe clear signatures of the superconducting energy gap at bias voltages much larger than voltage range where the ZBCP appears. Other origins of ZBCP include (i) magnetic scattering (ii) proximity induced pair tunneling (PIPT) and (iii) Andreev bound state (ABS) when the superconductor has an unconventional symmetry. Magnetic scattering and PIPT can be ruled out since in the former ZBCP should split under the application of magnetic field and in the latter the ZBCP should get suppressed at small fields of the order of 0.1 T. None of these is observed in our measurements. We therefore conclude the ZBCP-s observed here are manifestations of ABS originating from an unconventional component of the order parameter in this material. Further confirmation of the ABS origin of the ZBCP comes from its evolution with contact size. Since the mean size of the ABS is of the order of the dirty limit coherence length ($\xi_0$), the ZBCP originating from ABS gradually disappears as the contact diameter becomes smaller than $\xi_0$. We can see that for both directions of injection currents the ZBCP gradually disappears as $d \leq \xi_0$. We therefore conclude that the ZBCP in BiPd originates from the ABS resulting from an unconventional pairing for which the phase varies on the Fermi surface. While in principle $\Delta_1$, $\Delta_2$ and $\Delta_3$ could also arise from a multiband scenario containing three different bands, this is a very unlikely possibility for the following reasons. First, a simple multiband scenario consisting of multiple s-wave gap functions on different Fermi sheets cannot explain the existence of the pronounced ZBCP that we observe in our data. Secondly, we do not observe $\Delta_2$ and $\Delta_3$ simultaneously in any of our spectra despite the surface roughness that produces a significant scatter in their individual for both directions of injection current. It is therefore unlikely that these two gaps arise from two different gap functions on different Fermi sheets. Therefore, $\Delta_2$ and $\Delta_3$ are likely to be associated with a strongly anisotropic gap function ($\Delta$) for which the observed gap values are different for the two different directions of current injection.

3.2. NMR/NQR measurements

For NMR/NQR measurements [29], the samples were crushed into powders. The $T_C$ at zero and a finite magnetic field $H$ was determined by measuring the ac susceptibility using the in situ NMR/NQR coil. A standard phase-coherent pulsed NMR spectrometer was used to collect data. Measurements below 1.4K were carried out in a $^3$He/$^4$He dilution refrigerator. Figure 6 shows the $^{209}$Bi ($I=9/2$) NQR spectra of BiPd measured at $T = 4.2$ K. Four transition lines centered at 12.4, 14.3, 21.4, and 28.8 MHz are observed, which correspond to the transitions between the adjacent levels ($\pm 1/2 \leftrightarrow \pm 3/2$), ($\pm 3/2 \leftrightarrow \pm 5/2$), ($\pm 5/2 \leftrightarrow \pm 7/2$) and ($\pm 7/2 \leftrightarrow \pm 9/2$), respectively. The NQR frequency $\nu_Q = 7.31$ MHz and the asymmetry parameter $\eta = 0.35$. Figure 7 shows the temperature dependence of $1/T_1$ of $^{209}$Bi, which was measured at the $4\nu_Q$ ($\pm 7/2 \leftrightarrow \pm 9/2$) transition. In the normal state above $T_C$, $1/T_1$ varies in proportion to $T$, as seen in conventional superconductors. The $1/T_1$ is enhanced just below $T_C$ over its normal-state value, forming a suppressed, broad coherence peak. The result also indicates an isotropic superconducting gap dominating in $\alpha$-BiPd. The solid curve below $T_C$ shown in Fig. 7 is a calculation with $2\Delta = 2.7k_BT_C$ and $\tau = 7$. The parameter $2\Delta$ is slightly smaller than the BCS value of 3.5 $k_BT_C$. However, a second superconducting gap was reported to appear below 2 K from other measurements (point contact, penetration depth and Muon spin resonance) is not present here. We believe this could due to the disorder effects present in powdered sample. In BiPd, although all atoms break the inversion symmetry along all direction, $Pd$ probably makes the main contribution to the bands near the Fermi level, so that the ASOC is small. Indeed, the band splitting at the Fermi level was calculated to be around 80 meV, which is smaller than the value of Li$_2$Pt$_3$B. Nonetheless, we found a clear correlation between the band splitting caused by the asymmetric spin orbit coupling (ASOC) and the height of the coherence peak. Figure 7 shows the $1/T_1$ normalized by its value at $T_C$ against the reduced temperature for LaBiPt and $\alpha$-BiPd. Generally, the height of the coherence peak can be affected by many factors such as the anisotropy of superconducting
gap, impurity scattering, and phonon scattering. However, it is possible when a spin-triplet component is induced, the corresponding gap component will have nodes. As a result, the observed height of the coherence peak will be suppressed. Knight shift measurements could suggest whether there exists substantial component of the spin-triplet state in α-BiPd.

3.3. Penetration depth measurements
Temperature dependence of the penetration depth was precisely measured [30] by utilizing a tunnel diode oscillator mounted on a $^3$He cryostat or a $^3$He/$^4$He dilution refrigerator. The operating frequency of this oscillator is 7 MHz with a frequency resolution as low as 0.05 Hz, which corresponds to a resolution of penetration depth of 0.1 Å. The penetration depth change is proportional to the shift of the TDO frequency, i.e., $\Delta \lambda(T) = G \Delta f(T)$, where the $G$ factor is solely determined by the sample geometry. Figure 8(c) shows the changes of the in-plane $[\lambda_{ac}(T)]$
Figure 8. Schematic drawing of magnetic penetration for (a) the isotropic ac plane and (b) the anisotropic ab plane, respectively. A small ac magnetic field $H$ is generated perpendicular to the sample planes. The shade denotes the field-penetrating area. (c) The in-plane ($\Delta \lambda_{ac}$) and out-of-plane ($\Delta \lambda_b$) penetration depth at low temperatures for several BiPd crystals. The G factors are 3.0 Å/Hz and 5.8 Å/Hz for samples A1 and A2, respectively. The inset shows $\lambda_{ac}(T)$ of sample A1 over a wide temperature range.[30]

and out-of-plane [$\lambda_b(T)$] penetration depth for BiPd. For each field orientation, several samples were measured and the data are highly reproducible. We note that the samples were cut either along or perpendicular to the b axis. Within the ac plane, the samples are randomly aligned and the good reproducibility of $\lambda_{ac}(T)$ for samples A1 and A2 indeed suggests an isotropic behavior of the in-plane penetration depth. However, the penetration depth shows distinctly anisotropic behavior for $H//b$ and $H\perp b$. The in-plane penetration depth $\lambda_{ac}(T)$ is flattened for $T<1$ K, showing exponential-type temperature dependence below 1.75 K. On the other hand, the out-of-plane penetration depth $\lambda_b(T)$ grows much faster with temperature. The inset of Fig. 8(c) plots $\lambda_{ac}(T)$ of sample A1 over a broad temperature region, where the sharp drop marks a superconducting transition at $T_c = 3.7$ K, which is a value that is close to that estimated from the electrical resistivity and magnetization. In order to analyze the gap symmetry, we take samples A1 ($H//b$) and B1 ($H\perp b$) as examples and fit their low-temperature penetration depth with various models. Figure 9 shows the temperature dependence of the penetration depth $\lambda_{ac}(T)$ and $\lambda_b(T)$. The penetration depth at zero temperature, $\lambda(0)$, can be estimated by $\lambda(0)E1.06*10^{10}/\xi\gamma^{1/2}T_C$, where $\xi$ and $\gamma$ represent the coherence length and the specific-heat Sommerfeld coefficient, respectively. By taking the values of $\xi^\perp = 32$ nm, $\xi^\parallel = 23$ nm, and $\gamma = 4$.

Figure 9. Temperature dependence of the (a) in-plane and (b) out-of-plane penetration depth for BiPd (symbols). The lines represent the fits of experimental data to various models.[30]
mJ/mol K² from the earlier study [27], we obtain \( \lambda_0(0) = 163 \) nm and \( \lambda_{ac}(0) \) E ratio depth \( \lambda(T) \) to the BCS model as well as the power-law behaviors. According to the isotropic BCS model in the local limit, the penetration depth can be approximated by the expression at \( T < T_C \):

\[
\Delta \lambda(T)/\lambda_0 = \sqrt{ \pi / 2 } \Delta(0)/k_B T \exp(-\Delta_0/k_B T)
\]

where \( \Delta_0 \) is the superconducting energy gap at \( T=0 \) K. The BCS model can describe \( \lambda_{ac}(T) \) with \( \Delta(0) = 1.62 k_B T_C \) (0.52 meV) [see Fig. 9(a)], but gives a poor fit to \( \lambda_0(T) \) in the same temperature range [see Fig. 9(b)]. It is noted that, in the low temperature limit, \( \lambda_0(T) \) can be reasonably fitted by the BCS model with a small gap of 1.2 \( k_B T_C \) (0.38 meV). Furthermore, the power-law behavior of \( \lambda(T) \sim T^n \) with \( n = 1 \) and 2 fails to illustrate the experimental data too, excluding nodal superconductivity for BiPd. Instead, \( \lambda_0(T) \) can be reasonably fitted by \( \lambda_0(T) \sim T^3 \) at low temperatures. These experimental facts indicate a complex gap structure for BiPd, showing a possible scenario of multiband superconductivity with anisotropic gaps. In the following, we further elucidate this feature by analyzing the superfluid density of \( \alpha \)-BiPd. From the temperature dependence of the London penetration depth in two orthogonal field orientations for \( \alpha \)-BiPd, anisotropic superconductivity is observed in the penetration depth and its corresponding superfluid density. For \( T < T_C \), the in-plane penetration depth \( \lambda_{ac}(T) \) shows BCS-type exponential behavior, while the out-of-plane penetration depth \( \lambda_0(T) \) follows power-law-like temperature dependence. Detailed analysis of the superfluid density \( \rho_s(T) \) suggests anisotropic two-band superconductivity for \( \alpha \)-BiPd. As a possible scenario, these experimental results can be interpreted in terms of the mixed pairing states in NCS SCs, shedding light on superconductivity without inversion symmetry.

3.4. Muon spin rotation and small angle neutron scattering measurements
The outcome of the TF-\( \mu \)SR experiments are really interesting and suggesting BiPd to be a multiband superconductor, consisting of at least two superconducting components with very different energy gaps and hence critical field. We are also finding indication for low-\( T_C \) type-II intermediate mixed state at low fields and temperatures, but conventional type II high-\( T_C \) superconductivity at high fields in NCS BiPd. Fig. 10 shows the measurements of the TF-\( \mu \)SR depolarization rates at 200 G, a field well below \( H_c2 \) showed a crossover from short (\( \lambda=2000 \) Å) to long (\( \lambda=11,500 \)Å) relaxation times between 2 and 3 K, well below \( T_C \) (3.8 K) along with a 15/17 component with a small non-precessing component. This indicates the presence of at least two components with very different critical fields. Both TF-\( \mu \)SR and SANS measurements have shown the presence of an intermediate mixed state below 220 G, due to long range attraction and short range repulsion of vortices. This results in a phase separated mixture of vortex lattice and Meissner regions. Clearly TF-\( \mu \)SR suggest multiple superconductivity gaps. Efforts are being made to observe spontaneous magnetization signal which will confirm the presence of unconventional pairing of Cooper pairs in \( \alpha \)-BiPd.

3.5. Fermi surface studies
Fermi surface and quasiparticle masses have been determined using quantum oscillations observed both in the electrical resistivity (the Shubnikov-de Haas (SdH) effect) and in the [32] magnetic torque (the de Haas-van Alphen (dHvA) effect). dHvA effect in BiPd has been studied using a piezoresistive cantilever to measure magnetic torque. Electrical resistivity of a second crystal from the same grain as the dHvA crystal has been measured and found to have a residual resistance ratio \( R(300 \) K)/\( R(1 \) K)=170; which indicates high sample quality. Torque and transport measurements were made at temperatures 20mK <\( T <10 \)K in a dilution fridge with a 15/17 T magnet. For the rotation study the angle \( \theta \) between the crystal b-axis and the applied field B was varied. The rotation axis was parallel to (101) so that \( \theta = 90 \) corresponds to B// (101). A clear signal contains quantum oscillations even at 10 K and by 1 K many frequencies are observed in \( \alpha \)-BiPd. Similar oscillations have also been observed in magnetic torque oscillation. Due to the high quality single crystals of BiPd (RRR=170) clear quantum
oscillation in the magnetic torque and the electrical resistivity has been observed even up to 10 K, which allowed successful construction of the Fermi surface of the noncentrosymmetric superconductor BiPd. These measurements revealed that α-BiPd is a high carrier density, three dimensional metal with a complex Fermi surface of many separate sheets and six spin-orbit split pair bands are crossing the Fermi level. Calculation of density functional theory to determine Fermi Surface is also in good agreement with the measured one and comparison with the specific heat measured at low temperature indicates a fairly low but appreciable renormalization ~2 which is consistent with light quasiparticle masses in the range ~0.8–1.5 electron masses deduced from the quantum oscillation measurements. The crystal structure is densely packed with nearest neighbour distances: Pd-Bi 2.74 Å, Pd-Pd 2.84 Å, Bi-Bi 3.31 Å and a density larger than either elemental Bi or Pd. The spatial distribution of states at EF is: 45% (22%) inside the Bi (Pd) atomic spheres, and a significant remainder, 33% in the interstitial volume reflecting the dense crystal structure and large overlaps. The symmetry of states at EF within the atomic spheres is predominantly Bi-p and Pd-d with small contributions 20% from Bi-s and Pd-p. The calculated DOS N(E_F) = 1.0 states μ−1eV−1 gives a bare value for the low temperature T-linear term of the specific heat c_0 = 2.3 mJ/ mol K^2 compared to the measured value = 4 mJ/ mol K^2, implying a renormalization of 2. This is consistent with typical values of the mass enhancement m^*/m_0 deduced for individual extremal FS orbits. The Fermi surface calculated without spin-orbit results from 6 bands crossing E_F and is compensated, enclosing equal volumes of electrons and holes (1.21 of each). With spin-orbit included, 6 spin-orbit split pairs of bands are involved. The lowest lying 2 pairs (bands 241-244) have similar dispersion throughout the BZ and give rise to 4 concentric zone-corner-centered ellipsoidal Fermi surfaces enclosing holes (Fig. 10c). Pair 245-

**Figure 10.** Gaussian TF μSR depolarisation rates in single crystal BiPd versus temperature at applied fields of 200 G and 500 G. right) Gaussian TF μSR depolarisation rates in polycrystal BiPd versus temperature.[31]
4. Conclusion

We have established multiple superconducting energy gaps in high quality single crystal of α-BiPd using various techniques. It appears that even a small presence of disorder seems to wipe out unconventional pairing and multiple energy gaps [33]. Moreover, the upper critical field estimated from transport measurements seems to be an order of magnitude (0.7 T along b-axis) larger as compared to the one estimated from dc magnetization and heat capacity studies (∼ 0.06T along b). The reason for this behavior could either due to large reversible region (pin free) in the vortex state or due to twin boundaries as suggested by a recent work [34]. More puzzling is the absence of multiple gaps in the STM measurements on Bi deficient BiPd crystals [34, 35]. The STM measurements also show Dirac surface states in the normal state of α-BiPd which is confirmed by ARPES data [36]. Clearly both normal and superconducting state properties of α-BiPd are unusual and warrant more investigations.
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