# Superconductivity in noncentrosymmetric BiPd

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(Received 1 April 2011; revised manuscript received 1 August 2011; published 23 August 2011)

In this work, we establish the bulk superconductivity of a high-quality single crystal of monoclinic BiPd ($\alpha$-BiPd, space group $P2_1$) below 3.8 K by studying its electrical resistivity, magnetic susceptibility, and heat capacity. We establish that it is a clean type-II superconductor with moderate electron-phonon coupling and determine its superconducting and normal state parameters. Although $\alpha$-BiPd is a noncentrosymmetric superconductor with an appreciable electronic heat capacity ($\gamma = 4$ mJ/mol $K^2$), the effect of spin-orbit splitting of the electronic bands at the Fermi level seems to be small as reflected by the absence of large anisotropy of the bulk normal and superconducting properties of $\alpha$-BiPd.

DOI: 10.1103/PhysRevB.84.064518 PACS number(s): 72.10.Fk, 72.15.Qm, 75.20.Hr, 75.30.Mb

## I. INTRODUCTION

Ever since the discovery of the noncentrosymmetric heavy fermion superconductor $CePt_3Si$,[1] there is widespread research activity to understand the nature of superconductivity in such unconventional superconductors. The term "noncentrosymmetric" characterizes the symmetry of a crystal lattice without an 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materials, the standard classification in even-parity spin-singlet and odd-parity spin-triplet superconducting phases is obsolete, because the electrons are exposed to antisymmetric spin-orbit coupling, e.g., Rashba-type of coupling,[2] which arises due to the electric field gradient in the crystal that 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 superconductor. 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 $CePt_3Si$ 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 noncentrosymmetric materials, which do not exhibit heavy fermion features, is also important since it avoids additional complication that arises due to strong f-electron correlations. Discovery of such materials also continues to increase, starting from binary carbides ($R_2C_{3-\delta}$ with R = La or Y),[6] $Cd_2Re_2O_7$,[7] $Li_2(Pd,Pt)_3B$,[8,9] $Mg_2Al_3$,[10] and the recently found $BaPtSi_3$.[11] However, many of them (except $Li_2Pt_3B$) exhibit conventional BCS-like superconductivity 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 that has conduction electrons with appreciable 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 shows bulk superconductivity below 3.8 K via, resistivity, magnetization, and heat capacity studies. Earlier reports[12,13] erroneously reported that BiPd has an orthorhombic structure that undergoes superconductivity below 3.8 K. However, detailed structural investigations[15] showed that the compound below 210°C forms in the monoclinic structure that has no inversion symmetry (space group $P2_1$). One of the important features of the structure is the presence of short Pd-Pd bonds (shorter than those present in pure Pd metal). This could result in conduction electrons with appreciable density of states at the Fermi level, which is suggested in an earlier study.[14,15]

## II. EXPERIMENTAL DETAILS

The compound BiPd undergoes polymorphic transformation from $\alpha-$BiPd (monoclinic, $P2_1$)[15] to $\beta$-BiPd (orthorhombic,$Cmc2_1$) 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 to 650°C (melting point of BiPd) in 12 h and then kept at 650°C for 12 h. Thereafter, it was slow cooled to 590°C with a rate of 1°C/h 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 from the melt was crushed into a fine powder for powder x-ray diffraction measurement using Cu K$\alpha$ radiation in a commercial diffractometer. The unit cell of the monoclinic structure ($\alpha$-BiPd, space group $P2_1$) is shown in Fig. 1. The structure consists of 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 distances (shorter than those even in pure Pd metal)

 

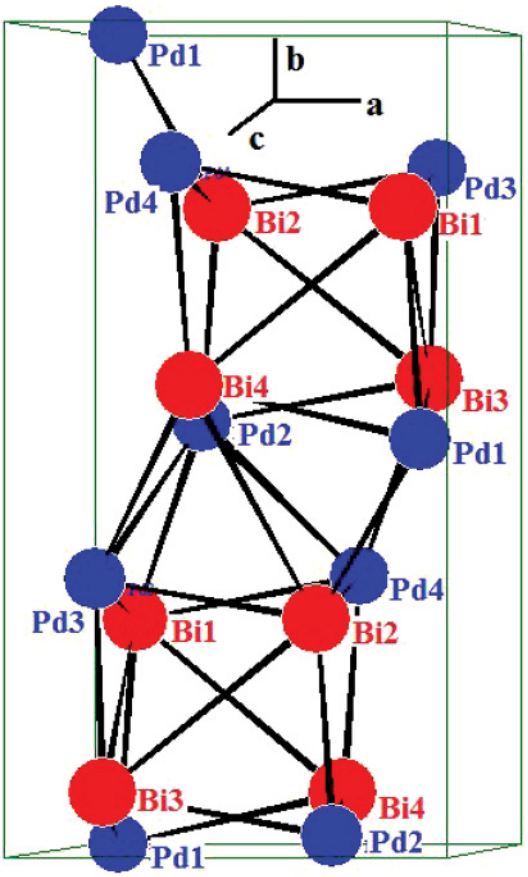


FIG. 1. (Color online) $\alpha$-BiPd has Monoclinic ($P2_1$) structure with 16 atoms in a unit cell (8 formula unit). It contains four inequivalent Bi sites and four inequivalent Pd sites. It has no inversion symmetry in its monoclinic structure. This structure is stable below 210°C.

with no inversion symmetry in the structure. The Rietveld fit[16] to the powder x-ray data is shown in Fig. 2.

The values for the lattice constants estimated from the fit are $a = 5.6284(\pm 0.0004)$ Å, $b = 10.6615(\pm 0.0004)$ Å, $c = 5.6752(\pm 0.0004)$ Å, $\alpha = \gamma = 90°$, and $\beta = 101°$. These values are in agreement with an earlier report,[15] except for the slightly higher value of $\beta$. A commercial SQUID magnetometer (MPMS 5, Quantum Design, USA) was used to measure the temperature-dependence of the magnetic susceptibility $\chi$ in a field of 5 mT for temperatures between 1.8 to 20 K to detect the superconducting transition and in a field of 0.1 T in the temperature range from 10 to 300 K. The resistivity was measured using a four-probe ac technique using a home-built setup with contacts made using silver paint on a bar-shaped sample 1 mm thick, 10 mm long, and 2 mm wide. The temperature was measured using a calibrated Si diode (Lake Shore Inc., USA) sensor. The sample resistance was measured with a LR 700 AC Bridge (Linear Research, USA) with a current of 5 mA. The absolute resistivity has an error of 2% due to errors in the estimation geometrical factors. The heat capacity was measured (with an accuracy of 1%) using a commercial setup (PPMS, Quantum Design, USA) in the temperature range from 2 to 200 K in the absence of magnetic field as well as in a field of 2 T.

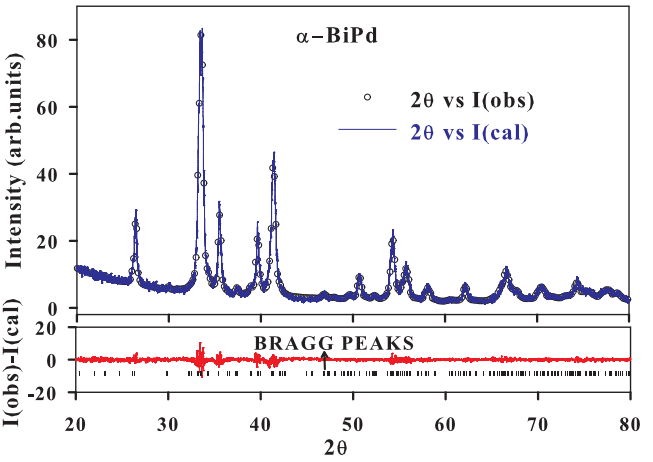


FIG. 2. (Color online) Powder x-ray diffraction data of the monoclinic ($P2_1$) $\alpha$-BiPd. The solid line is the simulated data using FullProf (Rietveld program) with the unit cell parameters obtained from Ref. 13.

## III. RESULTS AND DISCUSSION

### A. Resistivity studies

Figure 3(c) shows the temperature dependence of the resistivity along the (010) direction [$\rho(T)$] from 1.5 to 300 K. The high quality of the sample is clearly evident from the large residual resistivity ratio ($\rho_{300\,\mathrm{K}}/\rho_{4\,\mathrm{K}}$) of 160. The inset of Fig. 3(a) shows the superconducting transition below 3.8 K with a width of 10 mK. The inset of Fig. 3(b) shows the low-temperature resistivity from 4 to 30 K. The solid line is a fit to the equation

$$\rho(T) = \rho_0 + AT^n. \tag{1}$$

The fit yields a value of $(0.3 \pm 0.003)$ $\mu\Omega$ cm for $\rho_0$, $(9.2 \pm 0.1) \times 10^{-5}\,\mu\Omega$ cm/K$^3$ for A, and $n = 3 \pm 0.05$. This $T^3$ dependence of the resistivity is interpreted by the Wilson's theory,[17] which takes into account the interband *s-d* phonon-induced scattering within the Debye approximation. However, the same theory predicts a linear temperature dependence for

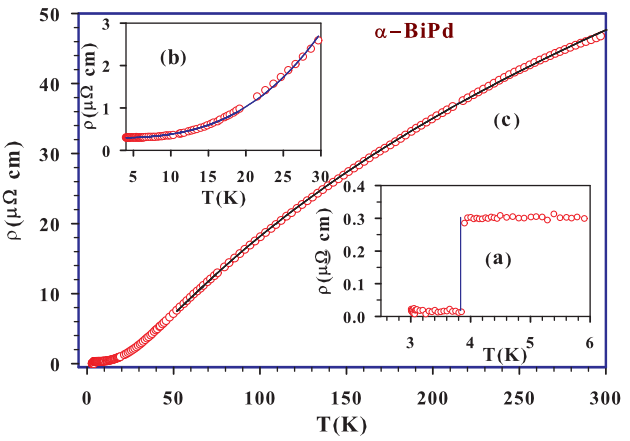


FIG. 3. (Color online) Temperature dependence of the electrical resistivity long the (010) direction of the monoclinic ($P2_1$) $\alpha$-BiPd. Insets a and b are described in the text. The solid lines are fits to the equations described in the text.

the resistivity at higher temperatures ($T \geqslant \theta_D$, where $\theta_D$ is the Debye temperature), which is not observed in $\alpha$-BiPd [see Fig. 3(c)]. Wilson's theory 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 $\alpha$-BiPd are small. There is yet another mechanism (parallel resistor model) suggested by Fisk and Webb[18] and later by Wisemann *et al.*,[19] which accounts for the significant deviation of the resistivity from the linear temperature dependence at high temperatures ($100\,\mathrm{K} < T < 300\,\mathrm{K}$). This has been seen in many other compounds where the $\rho$ value is rather high ($\approx 100\,\mu\Omega\,\mathrm{cm}$). The strong deviation from linearity and possible tendency toward 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.[20–22]

Wisemann *et al.*[19] describe the $\rho(T)$ of these compounds (which is known as the parallel resistor model) where the expression of $\rho(T)$ is given by

$$\frac{1}{\rho(T)} = \frac{1}{\rho_1(T)} + \frac{1}{\rho_{\max}}, \tag{2}$$

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:

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

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. Equation (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[23] 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* that account for the parallel resistor model. The high temperature resistivity fit ($50\,K < T < 310\,K$) shown in Fig. 3(c) yields a value of $(164 \pm 4)\ \mu\Omega$ cm for $\rho_{\max}$, $(0.33 \pm 0.05)\ \mu\Omega$ cm for $\rho_0$, $(76.3 \pm 2)\ \mu\Omega\ \mathrm{cm/K^3}$ for $C_p$, and $(168.6 \pm 3)$ 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. It is interesting to note that the anisotropy in the resistivity is not large[37] (in comparison with respect to the resistivity along a axis) even though the sample has no inversion symmetry.

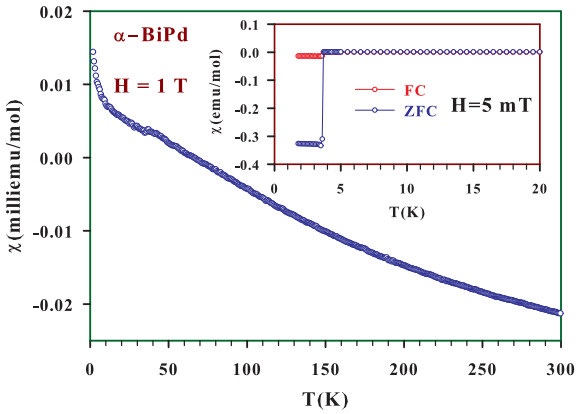


FIG. 4. (Color online) Temperature dependence of the magnetic susceptibility along the (010) direction of the monoclinic ($P2_1$) $\alpha$-BiPd in 1 T. The inset shows the temperature dependence of the susceptibility in a field of 5 mT in the zero-field-cooled (ZFC) and field-cooled (FC) states.

### B. Magnetic susceptibility studies

The temperature dependence of the magnetic susceptibility [$\chi(T)$] of $\alpha$-BiPd is shown in Fig. 4. The inset shows the low-temperature susceptibility (010 direction) data in 5 mT, which reveals the diamagnetic transition of $\alpha$-BiPd below 3.8 K that is in agreement with the resistivity data. The inset also shows the zero-field-cooled and field-cooled susceptibility data, which elucidates low but significant pinning of the vortices in this compound. The high temperature $\chi$ data of $\alpha$-BiPd in its normal state is diamagnetic and its value ranges from $(-2.2 \pm 0.02) \times 10^{-5}$ emu/mol at 300 K to $(1.4 \pm 0.01) \times 10^{-5}$ emu/mol at 1.8 K. The diamagnetic susceptibility at 300 K is indeed surprising given that the value of the Sommerfeld coefficient [$\gamma = (4 \pm 0.1)$ mJ/mole $\mathrm{K^2}$] is appreciable. We believe that the observed diamagnetism in $\alpha$-BiPd is due to the large core diamagnetism of Bi. In general, the observed value of the susceptibility can be written as

$$\chi_{\mathrm{obs}} = \chi_{\mathrm{core}} + \chi_{\mathrm{Landau}} + \chi_{\mathrm{Pauli}}, \tag{4}$$

where $\chi_{\mathrm{core}}$ is the core diamagnetism, $\chi_{\mathrm{Landau}}$ is the Landau diamagnetism, and $\chi_{\mathrm{Pauli}}$ is the Pauli paramagnetism. Equation (4) can be rewritten as

$$\chi_{\mathrm{obs}} - \chi_{\mathrm{core}} = \chi_{\mathrm{Pauli}} \left[1 - \left(\frac{1}{3}\right)\left(\frac{m}{m_b}\right)\right]. \tag{5}$$

Here, $\chi_{\mathrm{Pauli}} = N_A \mu_B^2 S N(E_F)$, where $N_A$ is the Avogadro number, $\mu_B$ is the Bohr magneton, $S$ is the Stoner factor, $N(E_F)$ is the density of states at the Fermi level, $m$ is the free electron mass, and $m_b$ is the band mass. The estimated value of $\chi_{\mathrm{Pauli}}$ is $1.3 \times 10^{-4}$ emu/mol. If one assumes the core diamagnetic susceptibility of Bi as $-5 \times 10^{-5}$ emu/mol and that of Pd as $0.2 \times 10^{-6}$ emu/mol, we get a value $-5.02 \times 10^{-5}$ emu/mol as the total contribution to the core diamagnetism in $\alpha$-BiPd. From this we calculate the Stoner enhancement factor S as 3. A weak-temperature dependence of $\chi(T)$ could arise due to two reasons. One of them could be the presence of magnetic

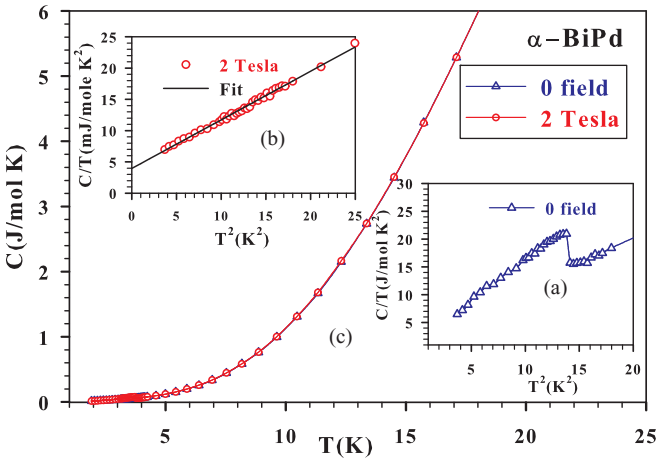


FIG. 5. (Color online) (c) The temperature dependence of the heat capacity of the monoclinic ($P2_1$) $\alpha$-BiPd from 1.9 to 20 K. The insets (a and b) are plots of $C_p/T$ vs $T^2$ in 0 and in applied field of 2 T, respectively. The lines in a and c are guides to the eye. Solid line in the b is a fit to Eq. (6), described in the text.

impurities at the 100 ppm level in the compound. This could account for the observed small temperature dependence of the $\chi(T)$. However, we believe that impurity concentration of this amount either in Bi or in Pd is unlikely (given that the limit of the impurities both in Bi and Pd elements imposed by the manufacturer is $\leqslant$10 ppm). The second reason could be the temperature variation of the density of states at the Fermi level, which results in a temperature-dependent Pauli spin susceptibility as seen in some of the A-15 compounds. Knight-shift measurements would be useful to resolve this issue. The anisotropy in the susceptibility is also not large, as in the case of the resistivity.

### C. Heat capacity studies

The temperature dependence of the heat-capacity ($C_p$) from 1.9 to 20 K of $\alpha$-BiPd is shown in Fig. 5(c). The insets (a and b) show the low temperature $C_p/T$ vs $T^2$ data in 0 field and in an applied field of 2 T, respectively. The jump in $C_p/T$ at 3.7 K ($\Delta C \approx 18$ mJ/mol K) in the inset (a) clearly shows bulk superconducting ordering in this sample below this temperature. The temperature dependence of $C_p$ is fitted to the expression

$$\frac{C_p}{T} = \gamma + \beta T^2, \tag{6}$$

where $\gamma$ is due to the electronic contribution and $\beta$ is due to the lattice contribution. The superconductivity is suppressed by a magnetic field of 2 T and the data is fitted to Eq. (6), which is displayed as a solid line in inset (b). The fit to the heat capacity data using Eq. (6) in the temperature range from 1.9 to 5 K yielded (4 $\pm$ 0.1) mJ/mol K$^2$ and (0.8 $\pm$ 0.01) mJ/mol K$^4$ for $\gamma$ and $\beta$, respectively. The value of the ratio $\Delta C_p/\gamma T_c$ is 1.2 which is slightly lower than 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.[24,25] 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 $\alpha$-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. Moreover, two-band nature of the superconductivity can be established via point contact/STM studies which are in progress. From the $\beta$ value of (0.8 $\pm$ 0.01) mJ/mol K$^4$, we estimate the $\theta_D$ to be (169 $\pm$ 1) K using the relation

$$\theta_D = \left(\frac{12\pi^4 N_A n k_B}{5\beta}\right)^{1/3}, \tag{7}$$

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

#### 1. Upper critical field studies

The estimation of the upper critical field ($H_{c2}$) value at a given temperature has been made by measuring the resistance of the sample under a given magnetic field. The transition temperature in a given field is defined as the temperature that corresponds to the midpoint of the resistance jump. The temperature dependence of $H_{c2}$ oriented along the (010) direction is shown in Fig. 6. It is well known that in nonmagnetic superconductors, the magnetic field interacts with the conduction electrons basically through two different mechanisms. Both lead to pair breaking and eventually destroys the superconductivity at a given field, which is known as the critical field. One of these mechanisms arises due to the interaction of the field with the orbital motion of the electrons (orbital pair breaking) and the other is due to the interaction of the field with the electronic spin (Pauli paramagnetic limiting effects). Orbital pair breaking is the dominant mechanism at low fields and at very high fields; Pauli paramagnetic effect limits the upper critical field.

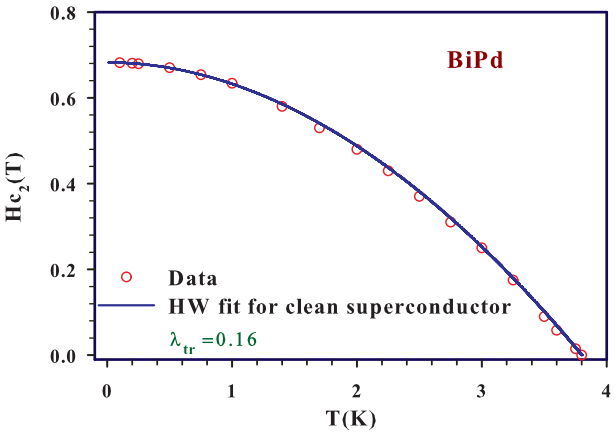


FIG. 6. (Color online) Temperature dependence of the upper critical field [$H_{c_2}(T)$] of $\alpha$-BiPd oriented along the (010) direction. The estimation was made using both resistivity and magnetization measurements as described in the text.

We have fitted the temperature dependence of $H_{c2}$ to the theory of clean type-II superconductor,[28,29] which can be written as

$$ln\left(\frac{1}{t}\right) = \sum_{\nu=-\infty}^{\nu=\infty}\left\{\frac{1}{|2\nu+1|} - \left[|2\nu+1| + \frac{h/3t}{|2\nu+1|\,t+\lambda_{tr}}\right]^{-1}\right\}, \quad (8)$$

where $h$ is the reduced critical field [$h = 2eHc2(\frac{v_F}{2\pi T_c})^2$] and $\lambda_{tr}$ is the reduced mean collision frequency ($\lambda_{tr} = \frac{1}{2\pi T_c \tau}$) in the usual notation. We obtain a value of $(0.16 \pm 0.006)$ for $\lambda_{tr}$, 0.7 T for $H_{c_2}(0)$, and 3 kOe/K for $dH_{c2}/dT$ near $T_c$. The value of the Pauli paramagnetic limiting field ($H_{\text{Pauli}} = 1.84 \times T_c$ in (tesla)) for $\alpha$-BiPd is very large (7.05 T) compared to the estimated value of the upper critical field at 0 K. From the GLAG[30–32] theory, we get the value of the upper critical field at 0 K as,

$$H_{c_2}(0) = 0.72(dH_{c_2}/dT)T_c. \quad (9)$$

From this Eq. (9) we get a value of 0.8 T for $H_{c_2}(0)$, which is marginally larger than the extrapolated experimental value of $H_{c_2}$. However, assuming the clean limit for the type-II superconductor, one can also estimate the $dH_{c2}/dT$ using the relation

$$dH_{c_2}/dT = 9.5510^{24}\gamma^2 T_c[n^{2/3}(S/S_F)]^{-2}(inOe/K), \quad (10)$$

where $\gamma$ is the electronic heat capacity coefficient (ergs/cm$^3$K$^2$), $n$ is the conduction electron density in units of cm$^{-3}$, and $S/S_F$ is the ratio of the area of the Fermi surface to that of a free electron gas of density $n$. Substituting the values of $\gamma$, $n$, and assuming a simple model of spherical Fermi surface ($S/S_F = 1$), we get a value 0.45 kOe/K, which is much smaller than the value (3 kOe/K) obtained from the experiment. The reason for this large discrepancy cannot be ascertained at this moment, though similar anomalies in the value of $dH_{c2}/dT$ have been reported in earlier studies.[33,34] In those earlier reports, they have studied strong-coupled superconductors that have complex phonon spectra. In that case, utilizing the theory to analyze is not strictly valid, as the theory assumes electron interact via weak-coupling BCS-type interaction potential and have spherical Fermi surface. Alternatively, one can assume the Eq. (10) holds good for $\alpha$-BiPd and estimate $[n^{2/3}(S/S_F)]$ as $1.75 \times 10^{14}$ using the experimental value of 3 kOe/K for $dH_{c_2}/dT$ near $T_c$.

### D. Estimation of normal and superconducting states parameters

Using the values of $\theta_D$ and $T_c$, we can estimate the electron-phonon scattering parameter, $\lambda$, from McMillan's theory,[35] where $\lambda$ is given by

$$\lambda = \frac{1.04 + \mu^* ln(\theta_D/1.45T_c)}{(1-0.62\mu^*)ln(\theta_D/1.45T_c) - 1.04}. \quad (11)$$

Assuming $\mu^* = 0.1$, we find the value of $\lambda$ to be 0.7, which puts $\alpha$-BiPd as an intermediate coupling superconductor. On the basis of purely thermodynamical arguments, the thermodynamic critical field at $T = 0$ K [$H_c(0)$] can be determined by integrating the entropy difference between the superconducting and normal states. From our experimental heat capacity data, we obtain the value of 700 Oe for $H_c(0)$.[26] One can also calculate the thermodynamical critical field $H_c(0)$ from the expression[27]

$$H_c(0) = 4.23\gamma^{1/2}T_c, \quad (12)$$

where $\gamma$ is the heat capacity coefficient (erg/cm$^3$ K$^2$). This gives a value of $H_c(0)$ as 650 Oe. We can also estimate the Ginzburg-Landau coherence length $\xi_{GL}$ at $T = 0$ K from the relation,

$$\xi_{GL}(0) = 5.8710^{-17}(\gamma T_c)^{-1}[n^{2/3}(S/S_F)]. \quad (13)$$

We get a value of 170 Å for $\xi_{GL}(0)$. One can also estimate $\kappa_{GL}(0)$ as 7.6 [since $\kappa_{GL}(0) = \frac{H_{c_2}(0)}{\sqrt{2}H_c(0)}$]. From the value of $\xi_{GL}(0) = 170$ Å, we get a value of 1292 Å for the Ginzburg-Landau penetration depth at 0 K [$\lambda_{GL}(0)$]. The lower critical value can be determined by using the relation

$$H_{c1}(0) = \frac{H_c(0)ln[\kappa_{GL}(0)]}{2^{1/2}\kappa_{GL}(0)}, \quad (14)$$

which yields a value of 123 Oe for the lower critical field at 0 K. This value of $H_{c1}(0)$ is in agreement with the recent magnetization measurements on the same sample. The enhanced density of states can be calculated using the relation

$$N^*(E_F) = 0.2121\gamma/N, \quad (15)$$

where $N$ is the number of atoms per formula unit and $\gamma$ is expressed in mJ/mol K$^2$. The value of $N^*(E_F)$ is 0.42 states/(eV atom spin-direction) and the value of the bare density of states $N(E_F) = N^*(E_F)/(1+\lambda) = 0.25$ states/(eV atom spin-direction).

The parameters are calculated using the Ginzburg-Landau theory for clean type-II superconductors. To verify the self consistency of our approach, we have estimated the mean free path ($l$) of our sample using the expression,

$$l = 1.2710^4[\rho n^{2/3}(S/S_F)]^{-1}, \quad (16)$$

where $n$ is the conduction electron density in units of cm$^{-3}$ and $S/S_F$ is the ratio of the area of the Fermi surface to that of a free electron gas of density n. Substituting the value of $[n^{2/3}(S/S_F)]$ obtained earlier, one gets $l$ as 2422 nm. One can also calculate the value of the BCS coherence length from the expression,

$$\xi_0 = 7.9510^{-17}[n^{2/3(S/S_F)}](\gamma T_c)^{-1}, \quad (17)$$

where $\gamma$ is expressed in ergs/cm$^3$ K$^2$. The value of $\xi_0$ was found to be 23 nm, which is much lower than $l$, which implies $\alpha$-BiPd is a clean type-II superconductor. Moreover, we get the value of 0.008 for $\lambda_{tr}$ using the equation $\lambda_{tr} = \frac{0.882\xi_0}{l}$, which is much smaller than the value of 0.16 obtained from the HW fit Eq. (9) earlier. Such a discrepency is not uncommon due to the assumption that that the sample has a spherical Fermi surface and the uncertainty in the estimation of the Fermi velocity $v_F$.

### E. Conclusion

Noncentrosymmetry (NCS) introduces an electrical field gradient in the crystal, which creates a Rashba-type anti-symmetric spin-orbit coupling.[2] An inherent feature is then

TABLE I. Normal and superconducting state properties of a single crystal $\alpha$-BiPd.

| $\rho_{300\,K}$ $\mu\Omega$-cm | $\rho_{4.2\,K}$ $\mu\Omega$-cm | $\gamma$ mJ/mol-K$^2$ | $\theta_D$ K | $H_{c2}(0)$ T | $H_{c1}(0)$ T | $dH_{c2}/dT$ T/K | $\kappa_{GL}(0)$ | $\lambda$ | $\xi_0$[a] nm | l* nm |
|---|---|---|---|---|---|---|---|---|---|---|
| 130 | 0.3 | 4 | 169 | 0.8 | 0.012 | 0.3 | 7.6 | 0.7 | 23 | 2422 |

[a]Order of magnitude estimates, since spherical Fermi surface is assumed in the calculations.

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. Such a behavior is observed in heavy fermion compounds like $CePt_3Si$,[1] $CeRhSi_3$,[4] $CeIrSi_3$,[5] and UIr.[3] Apart from heavy fermion properties, the occurrence of superconductivity in materials without inversion symmetry deserves its own merit. Therefore, we aim to find NCS superconducting materials without strong correlations among $d$ or $f$ electrons. This may set the stage for reliable electronic structure calculations, proving the splitting of bands due to missing inversion symmetry. Previous examples of superconductors without strong electron correlation, where, however, NCS was not a central issue of investigation, are binary $R_2C_3$ with R = La or Y[6] or $Cd_2Re_2O_7$ with $T_c = 1$ K.[7] More recently, the solid solution $Li_2Pd$,$Pt_3B$ was demonstrated to show superconductivity.[8] While $Li_2Pd_3B$ is accounted for in terms of a conventional BCS-like superconductor, $Li_2Pt_3B$ refers to unconventionality,[9] presumably due to a very large spin-orbit coupling. A recent study on $Li_2Pd_xPt_{3-x}B$ by muon-spin rotation and specific heat, however, suggests that the whole series comprises single-gap $s$-wave superconductivity.[36]

As far as $\alpha$-BiPd is concerned, it is classified as a type II superconductor in the clean limit (see Table I) with not a large anisotropy in the values of the upper critical field.[37] However, the present bulk measurements cannot establish the presence or absence of nodes of the superconducting energy gaps on the Fermi surface. They cannot also ascertain the mixing of the spin singlet or triplet pairing. One needs microscopic measurements such as NMR or STM to resolve this issue. As far as present studies are concerned, the overall effect of the noninversion symmetry seems to be of minor importance (no significant anisotropy) for the bulk properties. In this respect, $\alpha$-BiPd seems to be in line with conclusions drawn for $Li_2Pd_3B$ and $BaPtSi_3$.[11] In addition to microscopic measurements, band structure calculations of $\alpha$-BiPd are important, and they are in progress.


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