Crystal growth and upper critical field of the noncentrosymmetric superconductor BiPd

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Abstract. The crystal growth of BiPd is reported and its magnetic phase diagram is clarified through measurements of the magnetization, resistivity, and specific heat. The bulk, thermodynamic upper critical field is roughly an order of magnitude lower than in several recent reports, and there are no noteworthy deviations from BCS s-wave expectations, again in contrast to most previous reports.

1. Introduction
Noncentrosymmetric superconductors do not possess spatial inversion symmetry, which means that parity of the superconducting wavefunction is not a meaningful concept, and singlet and triplet pairing are consequently not eigenstates. With our usual simplifying assumptions for understanding superconductivity no longer valid, a vast array of exotic physics becomes possible [1, 2]. Unfortunately, few such materials are known, many do not superconduct under ambient pressure, and single crystals have only been grown of a very few. In addition, significant spin-orbit splitting of the bands near the Fermi level is a required prerequisite for all proposed novel behaviour. As a consequence, most theoretical predictions remain unrealized.

Known to be both superconducting and noncentrosymmetric by 1953 [3] (predating BCS theory), α-BiPd was probably the first noncentrosymmetric superconductor identified as such, and crystals of the material may be readily prepared. That such materials were particularly interesting is a far more recent discovery [4], and this material is now attracting renewed attention [5-7]. Several techniques have been applied to establish whether the material exhibits nontrivial pairing, including NMR [8] and microwave susceptibility [7], turning up limited hints of unusual behaviour. The symmetry or mechanism of the pairing in this material, whether it has nodes in its gap function, and whether it exhibits mixing of singlet and triplet components have not been established. In fact, even some basic parameters of the material remain unclear.

Recent resistivity and point-contact spectroscopy measurements suggest an upper critical field $H_{c2}$ around 0.7 T [5, 6, 9], while more bulk-sensitive magnetization measurements indicate a much lower value [10]. The actual growth process, while relatively straightforward, has also not been reported in detail.

This paper details the crystal growth procedure and presents the bulk upper critical field as determined by magnetization, resistivity and specific heat measurements.
2. Experimental

Growth progressed by a modified Bridgman-Stockbarger technique, shown schematically in Fig. 1(a). Pieces of bismuth (Aldrich, 99.999%) and palladium metal (Degussa, 99.95%) in a stoichiometric ratio were loaded into a degassed quartz tube with a cone-shaped end, and sealed under a vacuum of $\sim 10^{-4}$ torr. The sealed tube was suspended vertically in a two-zone furnace, supporting a modest temperature gradient of $\approx 1.3^\circ$C/cm. The entire ampoule was heated above 850$^\circ$C — well above the congruent melting transition at 600$^\circ$C [11, 12] — and left at high temperature for four hours to fully melt and homogenize. The ampoule was cooled through the melting transition at 0.2$^\circ$C/h, corresponding to a growth rate of 1.5 mm/h. Differential thermal analysis on a test sample grown under similar conditions indicated additional apparent structural transitions at 189$^\circ$C at 245$^\circ$C, including the transition between $\alpha$-BiPd and $\beta$-BiPd [13, 14], so the ampoule was cooled through this temperature range at 0.5$^\circ$C/h before being cooled more rapidly to room temperature.

![Figure 1](image-url)

**Figure 1.** BiPd single crystal growth. (a) Schematic growth process: Molten BiPd was cooled through its melting point ($T_{mp}$) in a temperature gradient (black) while sealed in a quartz tube, leading to (b) an essentially-single-domain crystal. (c) Laue pattern of a cleaved surface.

Thanks to the cone-shaped end of the ampoule from which growth started, which rapidly selected one preferred orientation, the resulting crystal was essentially single-domain, although heavily twinned and somewhat cracked internally due to the $\alpha$–$\beta$ phase transition. As shown in Fig. 1 it cleaves readily to expose [010] faces (taking the $b$-axis as the unique monoclinic axis and $\beta > 90^\circ$). While this has been implied previously, it is worth emphasizing that the material cleaves, as this may enable a number of surface-sensitive techniques that have not been previously applied to noncentrosymmetric superconductors due to an inability to obtain suitable cleaved surfaces.

Magnetization measurements were performed for various field orientations in Quantum Design MPMS-7 and MPMS-XL magnetometers with the RSO option, and resistivity was measured in a Quantum Design PPMS by a standard four-wire technique — the absolute value may not be intrinsic due to possible cracking in the sample or scattering at twin boundaries, and the accuracy is limited by estimates of the sample dimensions. To confirm the bulk, thermodynamic $T_c$ and $H_{c2}$, specific heat was measured at low temperatures in a Quantum Design PPMS in zero field and for fields along the monoclinic $b$ axis.

3. Results

Magnetization in a 5 mT applied field is shown as a function of temperature in Fig. 2(a) for several field orientations, and $M(H)$ loops at 1.8 K are shown in Fig. 2(b). These data closely resemble those reported previously [6, 10]. The hysteresis loops exhibit only minor differences with field orientation, with higher onset fields for in-plane applied field. These data have not been corrected for demagnetization effects, and the crystal measured was a platelet, thin in the
Figure 2. (a) Magnetization curves in $H = 5$ mT for three field directions; (b) $M - H$ loops for the three field orientations; (c) zero-field resistivity; and (d) Crystal structure of BiPd, based on Ref.[14].

$b$ direction and irregularly shaped — the overall vertical scale may not be directly comparable, particularly when comparing in-plane and $b$-axis fields. Resistivity is presented in the same figure, but absolute values may be unreliable due to internal cracking, and the low resistivity of metallic BiPd made this measurement challenging. The residual resistivity ratio of 140 is comparable with those reported by other groups [5], as is the resistive $T_c$ of 3.8 K.

Specific heat was measured from 0.37 to 5 K in fields up to 1.5 T, to determine the bulk superconducting transitions and gain insight on the structure of the gap function; selected results are presented in Fig. 3. The curve qualitatively matches the weak-coupling BCS expectation [15] up to at least $0.5T_c$, although falling slightly below it, with a clear exponential onset implying a full gap and suggesting a relatively isotropic gap function. The data fall significant above the BCS curve on the approach to $T_c$, leading to a jump height $\Delta c_{el}/\gamma T_c$ of 1.50 (BCS: 1.43). The superconducting transition is sharp, and the extracted $T_c$ of 3.77 K agrees very well with that determined from the magnetization and resistivity measurements. Magnetic field suppresses the transition, which is completely absent above 0.4 K in a field of only 0.07 T. Fig. 3(d), depicting the data above the bulk transition $H_{c2}(T)$ for all fields, shows that there is no evidence for a second phase bulk transition which would correspond to the transition previously reported based on resistivity measurements. A polynomial fit [also shown in Fig. 3(d)] was performed to all normal-state data (up to $T^7$ because the data began deviating from standard phonon
Figure 3. (a) $c_p(T)/T$ vs. $T$ for several fields, showing the bulk superconducting transition and its suppression by field. The weak-coupling $s$-wave BCS form is included for comparison [15]. There is no transition visible above 0.4 K under 0.07 T or higher fields. (b) $c_d(T)/T$ vs. $T$. (c) The low-temperature region is fit better by assuming the $T_c$ of 3.95 K that would be predicted from the STM gap [16]; this is pursued in the paper cited. (d) All data taken above the obvious (field-dependent) bulk transition, in all fields, and all data in fields of 70 mT and above — there is no evidence to suggest an additional bulk phase transition. The apparent feature near 4 K was not reproduced in lower-temperature measurements.

$T^3$ behaviour around 3 K) to model the normal-state background. The Sommerfeld electronic specific heat coefficient $\gamma$ is a modest 4.53 mJ/molK$^2$, and the phonon $T^3$ term’s prefactor $\beta$ is 0.710 mJ/molK$^4$, corresponding to a Debye temperature of 176 K. The phonon contribution’s rapid departure from $T^3$ behaviour suggests that at least one phonon mode is rather low in energy.

Interestingly, the gap obtained from scanning tunneling spectroscopy is 0.601 meV [16], from which weak-coupling BCS theory would predict a $T_c$ of 3.95 K. If this is used instead of the actual bulk $T_c$, the data are fit significantly better below $\sim$1.8 K, as shown in Fig. 3(c). This suggests that the weak coupling approximation is not completely valid in this material. An analysis of the specific heat incorporating the known ratio of the pairing gap to $T_c$ is pursued elsewhere [16]. The otherwise strong resemblance to the BCS form and lack of any sign of nodes are striking in light of previously published results.

The transitions obtained from magnetization, resistivity and specific heat measurements taken in a variety of applied magnetic fields may be combined into an $H - T$ phase diagram, shown in Fig. 4. The sparse data below 1.8 K do not allow a reliable estimate of $H_{cd}(0)$,
but it is clearly inconsistent with the previously-reported $H_{c2}(0)$ of 0.7 T ($H \parallel b$) and 1.2 T ($H \perp b$) from resistivity and point-contact spectroscopy \[5, 9\]. Indeed, it would appear to be a full order of magnitude lower, and more consistent with values of 92 $|H \parallel (010)|$ and 138 mT $|H \parallel (100)|$ reported based on magnetization measurements \[10\], although even those values are likely incompatible with these data. The slight upward curvature observed near $T_c$ and apparent linear dependence at intermediate temperatures would be unusual for an ordinary BCS superconductor, but are commonly observed in multi-band systems. BiPd’s large number of valence electrons, low symmetry, and potential band splitting due to spin-orbit coupling make it exceedingly likely that this system has multiple bands crossing the Fermi level.

The zero-field electronic specific heat $c_{el}$ may be integrated to obtain the thermodynamic critical field $H_c$, using

$$\frac{\mu_0 H_c^2}{2} = -\frac{\gamma T_c^2}{2} + \int_0^{T_c} c_{el} dT$$

in appropriately chosen volume units. The resulting thermodynamic $H_c$ of 41 mT, combined with the $H_{c2}^{\parallel}(0)$ of roughly 80 mT for $H \parallel b$ obtained by scanning tunneling microscopy \[16\] and consistent with the higher-temperature data reported here, would indicate a $\kappa_{GL}^{\parallel} \approx 1.4$ for this field orientation. This would make the superconductivity weakly Type-II. If the $ac$-plane coherence length $\xi_{ac}$ can be assumed to be isotropic, as the magnetization would suggest, then the $\xi_{ac}(0)$ extracted from $H_{c2}(0)$ is 64 nm. If the same assumption is extended to the penetration depth, $\lambda_{ac}(0) = 89$ nm, although such an assumption is not well justified at this stage. It is worth noting that this penetration depth is very far from the value assumed in recent microwave work \[7\]. If one further assumes that the factor of $\sim 1.2$ anisotropy seen in the magnetization-derived transition in Fig. II continues to zero temperature, $H_{c2}^{\perp}(0)$ would be 96 mT, $\kappa_{GL}^{\perp}$ would take a slightly stronger Type-II value of 1.67, $\xi_{b}(0)$ would be 53 nm, and $\lambda_{b}(0)$ would be 107 nm. Obtaining these values required several very significant assumptions, and they will require confirmation, either by extending measurements of $H_{c2}^{\perp}$ to low temperature, or through independent measurements of the coherence length and penetration depth, perhaps from muon spin rotation.
4. Conclusion

The data presented here in characterizing BiPd show no evidence of any significant deviation from weak-coupling BCS superconductivity. $H_{c2}(T)$ exhibits upward curvature suggestive of multi-band superconductivity, which would be wholly unsurprising in this material, and the specific heat suggests that BiPd is not fully in the weak-coupling limit, but there is no evidence for nodes. The upper critical field is found to be significantly lower than reported previously based on resistivity and point-contact measurements. Possible reasons for this include differences in stoichiometry: a significant Bi deficiency has been shown to lower $T_c$ and the residual resistivity ratio [6] and both metrics indicate the crystals in question to be of similar quality, but it’s conceivable that minor deviations from the ideal stoichiometry could have significant effects on a nodal gap. Samples could also differ in twin domain size. If the twins are small compared to the coherence length, conceivably the material may no longer appear noncentrosymmetric to the superconducting carriers. It is perhaps most likely that the higher $H_{c2}$ values benefit from thin limit physics, with filamentary superconductivity occurring along extended defects such as grain or twin boundaries. It is also possibly worth noting that in Sr$_2$RuO$_4$, widely thought to be a chiral $p$-wave superconductor, the superconducting onset temperature can double at boundaries with Ru metal inclusions [17], and there is some evidence that this boundary may nucleate one component of the multi-component order parameter. Twin boundaries may exhibit analogous physics in BiPd. To resolve the apparent contradiction in upper critical fields, it would be desirable to apply bulk probes to crystals known to have a high $H_{c2}$, and to use local probes to check for (and characterize) remnant superconductivity above $H_{c2}$ at twin boundaries.

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