Superconductivity at 5.4 K in $\beta$-Bi$_2$Pd

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We investigate bulk superconductivity in a high-quality single crystal of Bi$_2$Pd ($\beta$-Bi$_2$Pd; space group: $I4/mmm$) with a superconducting transition temperature of 5.4 K, by exploring its electrical resistivity, magnetic susceptibility, and specific heat. The temperature dependence of the electrical resistivity shows convex-upward behavior at temperatures greater than 40–50 K, which can be explained using a parallel-resistor model. In addition, the temperature dependences of the upper critical magnetic field and the specific heat suggest that $\beta$-Bi$_2$Pd is a multiple-band/multiple-gap superconductor.

KEYWORDS: superconductivity, multiple superconducting gaps, $\beta$-Bi$_2$Pd, Pd-Bi alloys, electrical resistivity, parallel-resistor model, upper critical field, specific heat

Studies of alloy superconductors (SCs) were of considerable interest in the 1950s and 1960s. Matthias et al. established the empirical law that the superconducting transition temperature, $T_c$, depends on the number of valence electrons; this law is widely known as the Matthias rule. Among the Pd-Bi alloys, several superconducting materials, which were summarized in the review paper reported by Matthias et al., have been identified: $\alpha$-BiPd (monoclinic structure, space group $P2_1$) with a $T_c$ of 3.8 K; $\alpha$-Bi$_2$Pd (monoclinic structure, space group $C2/m$) with a $T_c$ of 1.73 K; $\beta$-Bi$_2$Pd (tetragonal structure, space group $I4/mmm$) with a $T_c$ of 4.25 K; and $\gamma$-phase Pd$_2$Bi$_1.5$ (hexagonal structure, space group $P6_3/mmc$) with a $T_c$ of 3.7–4 K. Among these alloys, the $\alpha$-BiPd phase has recently been investigated as a non-centrosymmetric SC. The results of studies have shown that the anisotropy of $\alpha$-BiPd is not so large and that the overall effect of the no-inversion symmetry is of minor importance with respect to the bulk properties in $\alpha$-BiPd. However, no detailed reports concerning the physical properties of the other Pd-Bi superconducting phases, other than those that have detailed their $T_c$ values and lattice parameters, have been published.

In this letter, we focus on one of the Pd-Bi alloys, $\beta$-Bi$_2$Pd, the crystal structure of which is shown in Fig. 1(a), and report the results of our investigations of a $\beta$-Bi$_2$Pd single crystal. An early study revealed that this compound showed superconductivity at temperatures less than 4.25 K. However, we found that, by improving the crystal quality, the $T_c$ of $\beta$-Bi$_2$Pd can reach 5.4 K. In addition, the temperature dependences of the upper critical magnetic field and the specific heat suggest that $\beta$-Bi$_2$Pd is a multiple-band/multiple-gap SC. While multigap superconductivity, where the gaps on different parts of the Fermi surface become different magnitudes, was proposed theoretically, the first experimental observation of the possible existence of two distinct superconducting gaps was in the tunneling measurement of Nb-doped SrTiO$_3$. The existence of multiple superconducting gaps leads to the anomalous temperature dependences of characteristics such as the specific heat, the upper critical magnetic field, and the penetration depth. After the discovery of the typical multigap SC, MgB$_2$, numerous studies on multigap superconductivity were carried out. It is now well known that there are several multigap SCs such as NbSe$_2$, Lu$_2$Fe$_2$Si$_5$, and the iron-based SCs. One of the interesting aspects of multigap SCs is the variety of pairing mechanisms. In iron-based SCs, the novel $s_\pm$-state, where a sign reversal of the gap function occurs between the hole and the electron pockets, has been proposed as a possible scenario. We demonstrate that $\beta$-Bi$_2$Pd is also a new candidate for a multigap SC, referring to the results of the specific heat and the upper critical magnetic field.

Bi$_2$Pd single crystals were grown via a melt-growth method. The starting materials were Bi grains (5N) and a Pd wire (3N). These materials, in the prescribed molar ratio of Bi:Pd = 2:1 (total: 2 g), were sealed in an evacuated quartz tube. This quartz tube was heated at 900...
°C for 24 h, successively cooled to 600 °C for 72 h, and then quenched in cold water. All of the products were characterized by powder X-ray diffraction (XRD) using Cu Kα radiation at room temperature. Magnetic susceptibility measurements were performed using a superconducting quantum interference device (SQUID) magnetometer. The electrical resistivity, ρ, was measured by the four-terminal method over the temperature range of 0.5 to 300 K under magnetic fields as strong as 3 T. The specific heat was measured by the thermal-relaxation method at temperatures as low as 2 K on a commercial apparatus (Physical Property Measurement System, Quantum Design).

Figure 1(b) shows the XRD pattern of a Bi2Pd single crystal. Except for a few peaks that resulted from α-Bi2Pd, all of the peaks were indexed on the basis of a tetragonal lattice (no. 144, I4/mmm) with a = 3.37 Å and c = 12.96 Å. These lattice parameters are in good agreement with those reported previously.\(^2,19\)

The temperature dependence of ρ for a β-Bi2Pd single crystal is shown in Fig. 2(a). The large residual resistivity ratio [RRR, ρ(T = 300 K)/ρ(T = 6 K)] of 12 indicates the high quality of the crystal. The \(T^2\) dependence, which is defined as the temperature at which ρ begins to deviate from the normal-state behavior, and the \(T^2\) zero, which is defined as the temperature at which ρ becomes zero, were estimated to be 5.4 and 5.3 K, respectively, as shown in Fig. 2(b). These values are greater than the value of 4.25 K reported in previous papers.\(^2,19\) The temperature dependence of the magnetic susceptibility in a magnetic field of 2 Oe is shown in Fig. 2(d). This result reveals that the diamagnetic transition of β-Bi2Pd occurs at a temperature less than 5.4 K, which is in good agreement with the ρ(T) data. Here, it is interesting to note that the \(T_c\) of β-Bi2Pd reported here is almost the same as that of Pd-intercalated Bi2Te3 with a very small superconducting volume fraction (< 1%) in ref. 20, where the possibility that the topological insulator Bi2Te3 can be made into an SC by Pd intercalation between the Bi2Te3 layers is argued.

The temperature dependence of ρ for β-Bi2Pd exhibits the convex-upward characteristics at temperatures greater than 50 K; these characteristics are similar to those observed for A15 SCs.\(^21–24\) Fisk and Webb have proposed that the resistivity of A15 compounds at high temperatures saturates at a value, \(\rho_{\text{sat}}\), that corresponds to the mean free path on the order of the interatomic spacing.\(^23\) Wiesmann et al.\(^25\) developed the idea proposed by Fisk and Webb and found empirically that the ρ of A15 compounds could be described using a parallel-resistor model:

\[
\rho(T) = \left[ \frac{1}{\rho_{\text{sat}}} + \frac{1}{\rho_{\text{ideal}}(T)} \right]^{-1}, \tag{1}
\]

where \(\rho_{\text{sat}}\) is the resistivity saturated at high temperature and is independent of T, and \(\rho_{\text{ideal}}(T)\) is the “ideal” contribution according to Matthiessen’s rule, \(\rho_{\text{ideal}}(T) = \rho_{\text{ideal},0} + \rho_{\text{ideal,L}}(T)\). Here, \(\rho_{\text{ideal},0}\) is the ideal temperature-independent residual resistivity caused by impurity scattering, \(\rho_{\text{ideal,L}}(T)\) is the temperature-dependent contribution caused by thermally excited phonons and can be expressed by the Bloch-Grüneisen formula or by Wilson’s theory.\(^26,27\)

\[
\rho_{\text{ideal,L}}(T) = C_1 \left( \frac{T}{\theta_D} \right)^r \int_0^{\theta_D} \frac{x^r}{(e^x - 1)(1 - e^{-x})} dx, \tag{2}
\]

where \(C_1\) is a numerical constant, \(\theta_D\) is the Debye temperature, and the values of the exponent r are 3 and 5 for Wilson’s theory and the Bloch-Grüneisen formula, respectively. The data for ρ from 300 to 75 K were fitted to eq. (1), and the fitted result is shown in Fig. 2(a) as the solid curve. For \(\rho_{\text{ideal,L}}(T)\), we found that a better fit for ρ(T) in β-Bi2Pd is given by Wilson’s expression [specific...
ically, \( r = 3 \) in eq. (2)], which takes into account the interband electron-phonon Umklapp scattering between a low-mass s-band and a heavy-mass d-band.\(^{27}\) The best-fitted result yields the values of 134 K for \( \theta_D \), 241 \( \mu \)Kcm for \( \rho_{\text{heat}} \), 9.63 \( \mu \)Kcm for \( \rho_{\text{ideal,0}} \), and 63.3 \( \mu \)Kcm\(^{-3}\) for \( C_1 \). The value of \( \theta_D \) is very close to that obtained from the specific heat measurement, as will be discussed later. These results show that the parallel-resistor model explains the \( \rho(T) \) behavior of \( \beta\)-Bi\(_2\)Pd well at high temperatures. In contrast, notable deviations between the experimental data and the parallel-resistor model are observed at low temperatures. In Fig. 2(c), \( \rho \) is plotted as a function of \( T^2 \) at low temperatures, which shows that the resistivity is proportional to \( T^2 \) at temperatures less than 25 K. A similar crossover from the \( T^2 \) behavior to the saturated behavior upon heating has been observed in A15 compounds such as Nb\(_3\)Sn\(^{21,28}\) and in \( \beta\)-pyrochlore oxides, AOs\(_2\)O\(_6\) (\( A = \text{K}, \text{Rb}, \text{Cs} \)).\(^{29}\) Some mechanisms of the \( T^2 \)-dependence of \( \rho(T) \) have been proposed.\(^{30-35}\) However, the origin of the \( T^2 \)-dependence of \( \rho \) in \( \beta\)-Bi\(_2\)Pd cannot be specified solely from the results presented in this letter; further studies are needed.

Next, the specific heat divided by temperature, \( C/T \), at \( \mu_0 H = 0 \) (red squares) and 0.6 T (black circles) is plotted in the inset of Fig. 2(c) as a function of \( T^2 \). \( C/T \) at \( \mu_0 H = 0.6 \) T, where superconductivity is fully suppressed above 2 K, was fitted to the expression

\[
C = \gamma_n T + \beta_n T^3 + \alpha_n T^5, \tag{3}
\]

where \( \gamma_n T \) is the electronic term, \( C_e \), and \( \beta_n T^3 + \alpha_n T^5 \) represents the phonon contribution. From the fitting with eq. (3), which is shown in the inset of Fig. 2(c) as the blue solid curve, we obtained the parameters \( \gamma_n = 12 \text{ mJmol}^{-1} \text{K}^{-2} \), \( \beta_n = 2.3 \text{ mJmol}^{-1} \text{K}^{-4} \), and \( \alpha_n = 0.02 \text{ mJmol}^{-1} \text{K}^{-6} \). The existence of the \( T^5 \) term in the normal-state specific heat suggests a complex phonon density of states. From this value of \( \beta_n \), \( \theta_D \) was estimated to be 136 K using the relation \( \theta_D = (12\pi^4 N k_B / 5 \hbar) ^ {1/3} \),\(^{26}\) where \( N \) is the number of atoms, and \( k_B \) is the Boltzmann constant. This value of \( \theta_D \) is similar to that obtained from the analysis of the \( \rho(T) \) data using eq. (1), as previously mentioned. The temperature dependence of normalized electronic specific heat at \( \mu_0 H = 0 \) T, which is estimated using the above parameters, is shown in Fig. 2(e). A clear jump appeared in \( C_e / \gamma T \) at a temperature of 5.0 K. This value is slightly lower than the \( T_c \) estimated from the temperature dependences of \( \rho \) and \( \chi \). The magnitude of the jump at \( T = T_c \), \( \Delta C \), is 40 mJmol\(^{-1} \text{K}^{-1} \), and the value of the normalized specific-heat jump, \( \Delta C / \gamma_n T_c \), is 0.82. This value is smaller than that expected in the simple BCS weak-coupling limit, i.e., 1.43. In addition, \( C_e \) of \( \beta\)-Bi\(_2\)Pd below \( T_c \) shows a peculiar temperature dependence. That is, there is a plateau at approximately 3 K. One might conclude that this plateau results from some impurity phases, for example, amorphous Bi or Bi-Pd alloys other than \( \beta\)-Bi\(_2\)Pd. However, there is no anomaly in \( \chi (T) \) at \( T \sim 3 \) K. Thus, it is unlikely that the origin of this plateau in the normalized electronic specific heat is an impurity phase. These features, that is, the small jump at \( T_c \) and the plateau at approximately 3 K, in \( C(T) \) of \( \beta\)-Bi\(_2\)Pd are familiar in the multigap SCs.\(^{7,8,36}\) In the case of an SC with a single gap, the entropy, \( S \), and \( C \) are described as follows:\(^{37}\)

\[
\frac{S}{\gamma_n T_c} = -\frac{6}{\pi^2 k_B T_c} \int_0^\infty \left[ f \ln f + (1 - f) \ln (1 - f) \right] \, df, \tag{4}
\]

\[
\frac{C}{\gamma_n T_c} = \left( \frac{d (S/\gamma_n T_c)}{dT} \right) T_c. \tag{5}
\]

where \( f = \left[ \exp (E/k_B T) + 1 \right]^{-1} \). The energy of quasi particles is given by \( E = [\epsilon^2 + \Delta^2 (t)]^{0.5} \), where \( \epsilon \) is the energy of the normal electrons relative to the Fermi surface and \( \Delta (t) = \Delta_0 \delta (t) \) is the temperature dependence of the gap energy. Here, \( \delta (t) \) is the normalized BCS gap at the reduced temperature, \( t = T/T_c \).\(^{38}\) For the analysis of the data for \( \beta\)-Bi\(_2\)Pd, we use the two-band, two-gap model, where the total specific heat is considered as the sum of the contributions of each band calculated independently according to eq. (5), as in the cases of MgB\(_2\) and Lu\(_2\)Fe\(_2\)Si\(_5\).\(^{7,8}\) Each band is characterized by the Sommerfeld coefficient, \( \gamma_n \), with \( \gamma_1 + \gamma_2 = \gamma_n \). We calculate the specific heat by this two-gap model using three parameters of two gaps \( (\Delta_1, \Delta_2) \) and the relative weights \( (\gamma_1/\gamma_n \equiv x, \gamma_2/\gamma_n \equiv 1 - x) \), and one of the calculated results is shown as the dashed curve in Fig. 2(c). The curve calculated using the two-gap model is in agreement with the experimental data, at least above 2 K, which suggests that \( \beta\)-Bi\(_2\)Pd is a multigap SC. In this analysis, however, there is still some uncertainty and it is difficult to determine only one set of three parameters for lack of experimental data of \( C \) at temperatures less than 2 K. A more detailed analysis requires data at lower temperatures, and such measurements are currently in progress.

The effect of a magnetic field on \( \rho \) is shown in Fig. 3(a). The \( T_c \) decreases almost linearly with increasing magnetic field. The upper critical field, \( \mu_0 H_{c2} \), which is defined as the field in which \( \rho \) becomes half the value of the normal-state resistance, is plotted in Fig. 3(b) as a function of temperature. The upper critical field extrapolated to \( T = 0 \) K, namely, \( \mu_0 H_{c2}(0) \), is estimated to be \( 1.13 \pm 0.05 \text{ T} (H_{c2}^{ab}(0)) \) and \( 0.73 \pm 0.05 \text{ T} (H_{c2}^{ab}(0)) \) for magnetic fields parallel and perpendicular to the ab-plane, respectively. These results give Ginzburg-Landau coherence lengths of \( \xi_{ab}(0) \sim 212 \pm 8 \text{ Å} \) and \( \xi_{c}(0) \sim 137 \pm 2 \text{ Å} \), using \( \mu_0 H_{c2}^{ab}(0) = \Phi_0 / 2\pi \xi_{ab}(0) \xi_{ab}(0) \) and \( H_{c2}^{ab}(0) = \Phi_0 / 2\pi \xi_{ab}(0)^2 \), where \( \Phi_0 = 2\pi h / 2e = 2.07 \times 10^{-15} \text{ Tm}^2 \) is the magnetic flux quantum. The anisotropy parameter, \( \Gamma \), which is defined as \( \Gamma = H_{c2}^{ab}(0) / H_{c2}^{ab}(0) \), is found to be 1.6. It should be noted that the temperature dependence of \( \mu_0 H_{c2} \) in \( \beta\)-Bi\(_2\)Pd reveals a positive curvature close to \( T_c \), which becomes negative at temperatures less than approximately 3 K, as shown in Fig. 3(b). These temperature dependences have also appeared in other multigap SCs, such as MgB\(_2\),\(^{10,39}\) LaFeAs(O,F),\(^{12,40}\) and SrPtAs.\(^{41}\) In addition, in some theoretical papers, this temperature dependence of \( \mu_0 H_{c2} \) has been explained on the basis of multiple superconducting gaps.\(^{42-44}\) This result
In conclusion, we observed bulk superconductivity with a $T_c$ of 5.4 K in $\beta$-Bi$_2$Pd by investigating the electrical resistivity, the magnetic susceptibility, and the specific heat. The value of $T_c$ reported in this letter is higher by approximately 1.2 K than those reported in previous papers and is the highest among the Pd-Bi alloy systems. In addition, the temperature dependences of the upper critical field and the specific heat suggest that $\beta$-Bi$_2$Pd is a multigap superconductor.

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