Synthesis, characterization and physical properties of layered bismuthide PtBi$_2$

C. Q. Xu$^1$, X. Z. Xing$^2$, Xiaofeng Xu$^{1*}$, L. Q. Che$^3$, Bin Chen$^4$, Xin Lu$^3$, Jianhui Dai$^1$, Z. X. Shi$^2$

1Department of Physics and Hangzhou Key Laboratory of Quantum Matters, Hangzhou Normal University, Hangzhou 310036, China
2Department of Physics and Key Laboratory of MEMS of the Ministry of Education, Southeast University, Nanjing 211189, China
3Center for Correlated Matter and Department of Physics, Zhejiang University, Hangzhou, 310058, China and
4Department of Physics, University of Shanghai for Science & Technology, Shanghai, China

(Dated: June 3, 2016)

We report details of single crystal growth of stoichiometric bismuthide PtBi$_2$ whose structure consists of alternate stacking of Pt layer sandwiched by Bi bilayer along the c-axis. The compound crystallizes in space group P-3 with a hexagonal unit cell of $a=b=6.553\text{Å}$, $c=6.165\text{Å}$. The magnetization data show opposite sign for fields parallel and perpendicular to the Pt layers, respectively. The $T$-dependent resistivity is typical of a metal and the magnetic response shows clear two types of charge carriers and the validity of the semi-classical Kohler’s rule. Its physical properties was discussed in comparison with recently proposed topological superconductor $\beta$-PdBi$_2$.

I. INTRODUCTION

Binary bismuthide $\beta$-PdBi$_2$ has attracted much interest recently as a promising candidate of topological superconductor (TS). Topological superconductivity is a new state of matter possessing symmetry-protected superconducting pairing. The Majorana fermions are believed to exist on the surface or vortex core in such TSs, which may not only be of scientific importance, but also can lead to a wide-ranging applications in microelectronic devices and quantum computing. The centrosymmetric stoichiometric $\beta$-PdBi$_2$ ($T_c \sim 5 \text{ K}$) was claimed to be topologically nontrivial in view of the observation of the topologically-protected surface modes by spin- and angle-resolved ARPES. However, no Andreev bound states associated with Majorana fermions are detectable through point-contact spectroscopy, in sharp contrast to the cases in Cu-intercalated Bi$_2$Se$_3$ and In-doped SnTe. On the other hand, it becomes the common wisdom that spin-orbit interaction (SOI) in heavy elements is crucial for the topological states. It is therefore heuristic to ask what if we replace Pd by heavier Pt element with enhanced SOI.

In this study, we substituted Pt for Pd in PdBi$_2$ and found that this new material actually crystallizes in a distinct structure. Unlike $\beta$-PdBi$_2$ which has the tetragonal structure in an $I4/mmm$ space group, PtBi$_2$ crystallizes in space group P-3 with a hexagonal unit cell of $a=b=6.553\text{Å}$, $c=6.165\text{Å}$. It is also different from its homologue PtBi superconductor ($T_c=1 \text{ K}$) with a monoclinic unit cell. The in-plane resistivity of PtBi$_2$ shows metallic behaviors down to 2 K, the lowest temperature studied in this work. The intra-plane and inter-plane magnetization displays pronounced anisotropy, being diamagnetic with field aligned along the plane and paramagnetic when field is perpendicular to the plane. The magnetoresistance (MR) and Hall resistivity measured on the same sample both show two types of carriers and the former one scales well to the semi-classical Kohler’s rule.

II. EXPERIMENTAL

PtBi$_2$ single crystals were fabricated via a melt-growth method. The starting materials of high purity, Bi powder (4N) and Pt powder (4N), were mixed thoroughly in the prescribed molar ratio of Bi:Pt = 2:1 (2 g in total weight). All these preparations were performed in a glove box filled with protective argon gas (both H$_2$O and O$_2$ contents were limited below 0.1ppm). The mixtures were loaded and sealed in an evacuated quartz tube. This quartz tube was then heated to 700°C quickly in a sintering furnace and kept at this temperature for 48h, before being slowly cooled down to 450°C(3°C/h), and finally being quenched into cold water. Large pieces of dark-gray plate-like PtBi$_2$ single crystals of typical 7-8 mm in length were harvested.
Energy dispersive x-ray (EDX) spectrometry confirms the stoichiometric ratio of the chemical composition (32.8 : 67.2 ± 3.0% in molar percentage for Pt:Bi). The structure of crystals was characterized by powder x-ray diffraction (XRD) at room temperature using a Rigaku diffractometer with Cu Kα radiation and a graphite monochromator. Lattice parameters were obtained by Rietveld refinements. The magnetization was measured by vibrating sample magnetometry using a Quantum Design MPMS-5 system. Measurements of MR and Hall effect were performed on the same sample by changing the field polarities. Signal even in field was defined as MR and the odd component was calculated as Hall resistivity.

III. RESULTS

The schematic view of the crystal structure of PtBi$_2$ is shown in Fig. 1. It crystallizes in a hexagonal structure with the space group P-3 (No.147). Its structure consists of alternate stacking of 2D Pt layers and bismuth bilayers along the c-axis. In one primitive unit cell, there are three Pt atoms, one being located at the corner of the polyhedron and the other two labelled as Pt(1) and Pt(2) in Fig. 1. The Bi atoms are trigonally-coordinated. The XRD pattern of PtBi$_2$ crystal is presented in Fig.2. A small trace of impurity phase, marked by the asterisks in panel (a), was detectable in the powder X-ray pattern and only (00ℓ) diffraction peaks were observed in the single-crystal X-ray, indicating good c-axis orientation of the as-grown samples. The calculated lattice parameters are $a=b=6.553\,\text{Å}$, $c=6.165\,\text{Å}$, in consistence with previous reported results.$^{14}$

Zero-field in-plane resistivity is plotted in Fig. 3. The room temperature resistivity is about 0.12 mΩcm and it is metallic down to the lowest temperature we measured (2K). The residual resistivity ratio is approximately 50 for our samples, indicative of good sample quality. The
sample is better characterized by the susceptibility measurements thereafter. Remarkably, the magnetization of the sample shows large anisotropy with respect to the field orientations. As illustrated in Fig. 3, the in-plane magnetization $\chi_{ab}$ is diamagnetic and varies little with $T$ down to 20K, below which it displays a significant upturn, whereas the inter-plane $\chi_{c}$ is paramagnetic instead and increases linearly with decreasing $T$, followed by a downward trend below 20K. The origin of these intriguing magnetization behaviors is not clear.

The magnetoresistive and Hall response of a material can open a avenue for exploring the dispersion and dynamics of the charge carriers. First, in PtBi$_2$, it is noted that the absolute value of the MR, defined as $\frac{\Delta \rho}{\rho}$, is rather large, reaching >400% at 2K in a magnetic field of 9T. This large MR implies a rather large electron mean free path, hence a long relaxation time. However, this MR is damped very fast with increasing $T$, as seen from the upper panels of Fig. 4. Second, in single-band metals, the MR at small fields is usually quadratic and the Hall resistivity varies linearly with field. However, in the two-band Drude model, on the assumption of the field-independent carrier density and relaxation time, $\frac{\Delta \rho}{\rho}(H)$ and $\rho_{xy}(H)$ can be written as:

$$\frac{\Delta \rho}{\rho} = \frac{\sigma_h \sigma_e (\sigma_h R_h - \sigma_e R_e)^2 H^2}{(\sigma_h + \sigma_e)^2 + \sigma_h^2 \sigma_e^2 (R_h + R_e)^2 H^2}$$

$$\rho_{xy}(H) = \frac{\sigma_h^2 R_h + \sigma_e^2 R_e + \sigma_h^2 \sigma_e^2 R_h R_e (R_h + R_e) H^2}{(\sigma_h + \sigma_e)^2 + \sigma_h^2 \sigma_e^2 (R_h + R_e)^2 H^2} H$$

where $\sigma_e(h)$ and $R_e(h)$ are electrical conductivity and Hall coefficient for electron (hole) band, respectively. The MR and the Hall signal for PtBi$_2$ sample are exemplified in Fig 4 at some selected temperatures. Although the individual curves can be fitted with the above two-band equations reasonably well, plotted as the red solid line in each panel, we failed to model these two transport

FIG. 4: (Color online) The magnetoresistance (upper panel) and Hall resistivity (lower panel), both measured on the same crystal with the same electrical contacts, at several selected temperatures. The red solid curves delineate the fits to two-band carrier model.
MR in PtBi

MR tends to be negligible). Moreover, the longitudinal 22T and a broad window (2K-100K. Above 100K, the pseudogap phase of the untrivial surface states, if any, await more investigations, both theoretically and experimentally.

To summarize, we synthesized the single crystals of stoichiometric bismuthide PtBi2 by a solid-state reaction method. The samples were carefully characterized by combined procedures of XRD, (magneto-)transport and susceptibility measurements. This compound shows prominent two-band transport behaviors with no clear signature from the possible surface states. However, the high-quality single crystals are now ready for prospective advanced experiments, especially for ones with more surface sensitivity.

Acknowledgments

The authors would like to thank C. M. J. Andrew, A. F. Bangura for stimulating discussions. This work is sponsored by the National Key Basic Research Program of China (Grant No. 2014CB648400), and by National Natural Science Foundation of China (Grant No. 11474080, U1432135, 11611140101). X.X. would also like to acknowledge the financial support from the Distinguished Young Scientist Funds of Zhejiang Province (LR14A040001) and an open program from Wuhan National High Magnetic Field Center (2015KF15).

1 Y. Imai, F. Nabeshima, T. Yoshinaka, K. Miyatani, R. Kondo, S. Komiyai, I. Tsukada, and A. Maeda, J. Phys. Soc. Jpn. 81, 113708 (2012).
2 K. Zhao, B. Lv, Y. Xue, X. Zhu, L. Deng, Z. Wu, C. W. Chu, Phys. Rev. B 92, 174404 (2015).
3 E. Herrera, et al., Phys. Rev. B 92, 054507 (2015).
4 M. Sakano, K. Okawa, M. Kanou, H. Sanjo, T. Okuda, T. Sasagawa, K. Ishizaka, Nat. Comm. 6, 8595 (2015).
5 J. Kačmarčík, et al., Phys. Rev. B 93, 144502 (2016).
6 L.Q. Che, T. Le, Xiaofeng Xu, Xin Lu, To appear in Phys.
Rev. B.

7 M.Z. Hasan, C.L. Kane, Rev. Mod. Phys. **82**, 3045 (2010).
8 Y.S. Hor, A.J. Williams, J.G. Checkelsky, P. Roushan, J. Seo, Q. Xu, H.W. Zandbergen, A. Yazdani, N.P. Ong, and R.J. Cava, Phys. Rev. Lett. **104**, 057001 (2010).
9 Liang Fu, C. L. Kane, Phys. Rev. B. **76**, 045302 (2007).
10 Liang Fu, C. L. Kane, E. J. Mele, Phys. Rev. Lett. **98**, 106803 (2007).
11 M. Kriener, K. Segawa, Z. Ren, S. Sasaki, and Y. Ando, Phys. Rev. Lett. **106**, 127004 (2011).
12 S. Sasaki, M. Kriener, K. Segawa, K. Yada, Y. Tanaka, M. Sato, and Y. Ando, Phys. Rev. Lett. **107**, 217001 (2011).
13 M. Novak, S. Sasaki, M. Kriener, K. Segawa, and Y. Ando, Phys. Rev. B **88**, 140502 (2013).
14 E. M. Savitskii, V. V. Baron, Yu. V. Efimov, M. I. Bychkova, L. F. Myzenkova, *Superconducting Materials* (Springer 1973).
15 B.T. Matthias, Phys. Rev. **92**, 874 (1953).
16 M. Kohler, Ann. Phys. **32**, 211 (1938).
17 N. Luo, and G. H. Miley Physica C **371**, 259 (2002).
18 P. Li, F. F. Balakirev, and R. L. Greene, Phys. Rev. Lett. **99**, 047003 (2007).
19 F. Rullier-Albenque, D. Colson, A. Forget, H. Alloul, Phys. Rev. Lett. **103**, 057001 (2009).
20 P. M. C. Rourke, A. F. Bangura, A. Proust, J. Levallois, N. Doiron-Leyraud, D. LeBoeuf, L. Taillefer, S. Adachi, M. L. Sutherland, and N. E. Hussey Phys. Rev. B **82**, 020514(R) (2010).
21 F. Rullier-Albenque, D. Colson, A. Forget, H. Alloul, Phys. Rev. Lett. **109**, 187005 (2012).
22 M.K. Chan, M.J. Veit, C.J. Dorow, Y. Ge, Y. Li, W. Tabis, Y. Tang, X. Zhao, N. Barisic and M. Greven, Phys. Rev. Lett. **113**, 177005 (2014).
23 A. Narduzzo, A. Enayati-Rad, S. Horii, N.E. Hussey Phys. Rev. Lett. **98**, 146601 (2007).
24 X. Xu, et al., J. Phys.: Condens. Matter **27**, 335701 (2015).
25 A. Narayanan, M.D. Watson, S.F. Blake, N. Bruyant, L. Drigo, Y.L. Chen, D. Prabhakaran, B. Yan, C. Felser, T. Kong, P.C. Canfield, A.I. Coldea, Phys. Rev. Lett. **114**, 117201 (2015).
26 A.A. Abrikosov Phys. Rev. B **58**, 2788 (1998).
27 D.X. Qu, Y.S. Hor, J. Xiong, R.J. Cava, N.P. Ong, Science **329**, 821 (2010).
28 N.E. Alkseevskii, Yu. P. Gaikov, EKSP. TEOR. FIZ **25**, 383 (1953).