Polymorphic PtBi$_2$ — candidate for topological superconductivity

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PtBi$_2$ is a polymorphic system with interesting electronic properties. Here we report optimized crystal growth and structural characterization of pyrite-type and trigonal modification of PtBi$_2$. XRD data analysis and further Rietveld refinement confirms that trigonal PtBi$_2$ crystallizes in non-centrosymmetric $P31m$ space group. Series of $\text{Pt}_1-x\text{Rh}_x\text{Bi}_2$ samples was obtained for $x = 0, 0.03, 0.35$ in the trigonal PtBi$_2$ structure. These $\text{Pt}_1-x\text{Rh}_x\text{Bi}_2$ compounds become superconducting where critical temperature increases from $T_c = 600$ mK for $x = 0$ up to $T_c = 2.7$ K for $x = 0.35$. Furthermore we calculate the electronic band structure, using the structure parameters obtained. The calculated density of states (DOS) shows a minimum for the stoichiometric compound at the Fermi level. Due to the topological properties of the electronic band structure material is a candidate for topological superconductivity.

I. INTRODUCTION

Topological materials (TM) are a new class of quantum materials, which are characterized by a non-trivial topological band structure\[1\]. After initial discovery of such properties in the family of topological insulators, many other types of TMs followed, including Dirac and Weyl types of topological semimetals (TSM), which are characterized by conduction and valence band touching at several points near the Fermi level and show linear electron dispersion near those points, which are termed Dirac and Weyl nodes respectively\[2,3\]. The presence of these points was experimentally detected by ARPES measurements as Fermi arcs\[4\]. These topological bands strongly influence charge transport properties, such as electron mobility, giant magnetoresistance and anomalous Hall effect\[5\]. Combination of non-trivial band structure with superconductivity in the same system makes it even more interesting due to possibility of realization of Majorana fermions\[6\].

In recent years PtBi$_2$ attracted a lot of attention from scientific community as one of the members of TSM family, which together with report of superconductivity in the system\[7\] makes it an attractive candidate for topological superconductivity. It crystallizes in 4 polymorphic modifications\[8\], δ, that could be formed by peritectic reaction at 660°C, which is thermodynamically stable down to 640°C. Temperature range of 420–640°C corresponds to the γ-modification\[9,10\], in between 270°C and 420°C β-modification is thermodynamically favorable with final polymorphic transition into the α-modification at the temperature around 270°C\[10,14\].

Two of these modifications, β (cubic, usually referred as pyrite-type) and γ (hexagonal, referred as trigonal below) were recently shown to exhibit interesting physical properties. Pyrite-type PtBi$_2$ shows extremely large unsaturated magnetoresistance, supersed the values demonstrated by WTe$_2$\[15\] have been proposed to host Dirac fermions\[16\]. Further multiband superconductivity with perfect electron-hole compensation under high pressure was reported\[12\]. Trigonal polymorph also shows large magnetoresistance\[13\], however, no superconductivity was reported for this modification. There are different reports on theoretical band structure of trigonal PtBi$_2$, some reports assume centrosymmetric space group $P\bar{3}$\[18,19\] while in the ref\[20\] non-centrosymmetric space group $P31m$ was assumed. Both structure variations were reported previously with the same lattice parameters: $a = 6.57\,\text{Å}$, $c = 6.16\,\text{Å}$ for $P\bar{3}$\[18,19\] and $a = 6.573\,\text{Å}$, $c = 6.167\,\text{Å}$ for $P31m$\[22\]. Trigonal modification of PtBi$_2$ was predicted to host Dirac fermions while described in space group $P\bar{3}$\[19\] or Weyl fermions and triply-degenerate point while described in $P31m$ space group due to absence of spatial inversion symmetry. This, together with the fact that predicted triply-degenerate points are near the Fermi level\[23\] makes trigonal PtBi$_2$ an interesting material for probing the properties of such fermionic excitations.

The aim of the present article is to study the crystal structure and physical properties of pristine PtBi$_2$ as well as PtBi$_2$ with substitution of Pt by Rh. Substitution of Pt (with outer shell configuration 5d$^9$) by Rh (4d$^8$) produces overall hole doping which should affect DOS near Fermi level. The article is constructed as follows: in the first section we report optimized methods of crystal growth of both pyrite-type and trigonal modification. For trigonal modification we study a series of crystals $\text{Pt}_1-x\text{Rh}_x\text{Bi}_2$ by means of XRD, SQUID and electrical transport measurements. Using obtained parameters of the crystal structure we find the electronic band structure for the trigonal polymorph in the framework of the DFT theory. Also we show the superconductivity in trigonal polymorph with the way of enhancing transition temperature by Rh substitution.
II. METHODS

A. Crystal growth

Single crystals of pyrite-type and trigonal PtBi$_2$ were grown via self-flux method. The optimized temperatures were chosen according to the published Pt-Bi phase diagram$^{12}$, such that crystallization happens only in the crystallization zone of chosen polymorphic modification, preventing precipitation of unwanted modifications. Small drops of flux residue were removed from the surface either mechanically or by etching in HNO$_3$ dilute solution.

**Trigonal modification:** Single crystals of trigonal PtBi$_2$ and Pt$_{1-x}$Rh$_x$Bi$_2$ were synthesized by mixing of elemental powders with molar ratio of (Pt$_{1-x}$Rh$_x$):Bi=1:4 (for $x = 0$, 0.1 and 0.3) were homogenized by grinding and placed into a Canfield crucible set$^{24}$ to facilitate flux removal on later stage. The crucible in turn was sealed inside of an evacuated quartz glass tube to prevent oxidation. The setup then was heated to 850°C, and then cooled to 420–500°C with a rate of 2°C/h, after which excess of the flux was removed by centrifugation.

**Pyrite-type modification:** Crystals of PtBi$_2$ in pyrite-type modification were obtained in likewise manner, main difference being the temperature and composition region where crystallization takes place. For growth Pt:Bi molar ratio of 1:20 was chosen. A maximum temperature of 600°C and temperature of centrifugation of 300°C has been employed for the growth.

B. Characterization of composition and structure

The composition of the as grown single crystals was determined by energy-dispersive X-ray spectroscopy (EDX), with electron beam probe (accelerating voltage 30kV, current 552pA). Structural characterization and phase purity was confirmed by means of powder X-ray diffraction using STOE powder diffractometer (2θ-ω scan, Co K$_{α1}$ or Mo K$_{α1}$ radiation, curved Ge (111) monochromator, Debye-Scherrer geometry). Rietveld refinement of the x-ray data was carried out with FullPro$^{25}$ and Jana2000$^{26}$ software packages.

C. Characterization of physical properties

Magnetization data were measured using a Quantum Design MPMS SQUID with vibrating sample magnetometer. In-plane resistivity measurements have been performed in a standard 4-probe configuration. Electrical contacts have been made with copper or silver wires glued to the sample using a conducting silver paint (Dupont 4929n). The measurements have been performed in the temperature range 2.3–300 K in a liquid $^4$He cryostat with a 3D vector magnet (6T–2T–2T).

The electronic band-structure was obtained in the framework of fully relativistic density functional theory (DFT) using the Full Potential Local Orbital band structure package (FPLO$^{27}$). The calculations were carried out within the generalized gradient approximation (GGA) of the Perdew-Burke-Ernzerhof (PBE) exchange-correlation potential$^{28}$. A k-mesh of 12x12x12 k-points in the whole Brillouin zone was employed.

III. RESULTS AND DISCUSSION

A. Composition and structure

Pyrite-type PtBi$_2$ was obtained as large, well-faceted, isometric silvery crystals up to 1 cm in diameter. As an example, one of the as-grown pyrite-type crystals is shown in Fig. 2a. Crystals of trigonal PtBi$_2$ and Pt$_{1-x}$Rh$_x$Bi$_2$ were obtained as easily cleavable silvery plates with a layered morphology in tabular hexagonal habit, which is in line with layered Van der Waals structure of the material. Acquired crystals are up to several millimeter in dimensions as shown in Fig. 2b and c.

SEM-EDX analysis of both trigonal (for SEM images see Fig. 2b and c) and pyrite-type modification

![FIG. 1. Structures of PtBi$_2$: (a) Cubic polymorph, coordination polyhedra are shown to highlight the 3D network of octahedra. (b) Trigonal polymorph, view along [100] (top) and [001] (bottom).](image)

| TABLE I. Nominal compositions and compositions according to SEM-EDX for obtained Pt$_{1-x}$Rh$_x$Bi$_2$ compounds |
|-----------------------------------------------|
| Nominal | SEM-EDX |
|---------|---------|
| cubic:  |         |
| PtBi$_2$| PtBi$_{2.00(2)}$ |
| trigonal:|         |
| PtBi$_2$| PtBi$_{2.03(4)}$ |
| Pt$_{0.97(1)}$Rh$_{0.02(1)}$Bi$_1$& |
| Pt$_{0.97(1)}$Rh$_{0.02(1)}$Bi$_1$& |
| 1K using a dilation fridge in an liquid $^4$He cryostat with a 3D vector magnet (6T–2T–2T).

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FIG. 2. As grown crystals on millimeter scale: (a) pyrite-type PtBi$_2$; (b) trigonal PtBi$_2$; (c) Pt$_{0.65}$Rh$_{0.35}$Bi$_2$. SEM-BSE images: (d) PtBi$_2$; (e) Pt$_{0.65}$Rh$_{0.35}$Bi$_2$

FIG. 3. (a) Comparison of theoretically calculated powder patterns for trigonal modification of PtBi$_2$ described in $P\bar{3}$ (dashed lines) and $P31m$ space groups (solid lines); (b) Same region of experimental diffraction pattern, blue lines are guide for eyes, Bi-admixture peak is marked of PtBi$_2$ confirmed the stochiometric composition of the compounds and showed homogenic distribution of the elements along the surface. Samples with substitution show uniform rhodium incorporation into the crystal. For 10% and 30% nominal substitution level measured EDX composition is Rh$_{0.02(1)}$Pt$_{0.97(1)}$Bi$_{1.89(2)}$ and Rh$_{0.35(1)}$Pt$_{0.64(2)}$Bi$_{1.9(3)}$ respectively. Results of EDX analysis are presented in the table I. The structure of pyrite-type PtBi$_2$ was determined by powder X-ray diffraction with subsequent Rietveld analysis. X-ray powder analysis shows no secondary phases and obtained structural parameters are agreeing well with the ones published previously with $a = 16.70$.

For trigonal modification powder XRD data, from crystals ground by hand show abnormally broad diffraction peaks. This behaviour might be linked to the high ductility and ease of cleavage of the material. To obtain high quality XRD data, crystals were ground in a ball mill for 30 min, and afterwards the powder was annealed at the centrifugation temperature to relieve any internal stress caused by milling, and quenched in ambient temperature water to prevent polymorphic transformation to pyrite-type modification. Since two slightly different crystal structures for the trigonal modification were reported in the literature with same lattice parameters, our pattern was compared to the theoretically modeled one for PtBi$_2$ structures reported in ICSD. A closer look into the experimental data acquired for $2\theta$ scan in the range of 85–90°, and the same part of calculated X-Ray peaks for $P31m$ and $P\bar{3}$ models are presented in Fig. 3 for clarity. The pattern of peak intensities, while compared to experimental pattern, helps to determine structure model to be used later at the Rietveld analysis stage. To ensure that this difference cannot be explained by other factors, (e.g. strong preferred orientation of crystallites in the sample), indexing of the diffraction pattern was carried out. We can clearly describe our data in $P31m$ space group, which is in agreement with data presented for this modification in the recent report. It is worth noting that $P31m$ space group is not centrosymmetric, which makes it a theoretically proposed candidate for realization of Weyl states.

Rietveld refinement and crystal structure of trigonal PtBi$_2$ presented on Fig. 4. As initial model the structure of the PtBi$_2$ in $P31m$ space group was used, according to findings noted above. Prior to the Rietveld refinement of PtBi$_2$ secondary phases were fitted by the Le Bail method to exclude them from consideration. Lattice parameters extracted from refinement in space group $P31m$ for trigonal PtBi$_2$ compound (presented in tables III and I) are
TABLE II. Structural parameters and residual factors of Rietveld analysis

| Parameter | Composition, Pt$_{1-x}$Rh$_x$Bi$_2$, x |
|-----------|-----------------------------------|
| Wavelength (Å) | 1.78996 1.78996 |
| 2θ range (°) | 10–111.955 10–111.995 |
| Step Size (°) | 0.015 0.015 |
| Temperature (K) | 293 293 |
| Space Group | P31m (No. 157) P31m (No. 157) |
| a (Å) | 6.5731(6) 6.57696(2) |
| c (Å) | 6.1619(13) 6.14796(4) |
| $U_{\text{isotropic}}$: | |
| $U_{Pt1}$ | 0.025(1) 0.0077(5) |
| $U_{Bi1}$ | 0.052(2) 0.0164(9) |
| $U_{Bi2}$ | 0.0209(14) 0.0087(5) |
| $U_{Bi3}$ | 0.0218(10) 0.0142(5) |
| R | 0.0520 0.0226 |
| wR | 0.0725 0.0324 |
| Goodness-of-Fit | 6.68 1.92 |

TABLE III. Refined atomic coordinates for Pt$_{1-x}$Rh$_x$Bi$_2$

| Sample   | Atom | site | x       | y       | z       |
|----------|------|------|---------|---------|---------|
| PtBi$_2$ | Pt (Pt1) | 3c  | 0.2619(5) | 0       | 0.363(13) |
|          | Bi (Bi1) | 1a  | 0       | 0       | 0       |
|          | Bi (Bi2) | 2b  | 2/3     | 1/3     | 0.155(13) |
|          | Bi (Bi3) | 3c  | 0.6144(5) | 0       | 0.630(13) |
| Pt$_{0.97}$Rh$_{0.03}$Bi$_2$ | Pt/Rh (Pt1) | 3c  | 0.2617(2) | 0       | 0.3578(6) |
|          | Bi (Bi1) | 1a  | 0       | 0       | 0.0139(6) |
|          | Bi (Bi2) | 2b  | 2/3     | 1/3     | 0.1413(6) |
|          | Bi (Bi3) | 3c  | 0.6093(2) | 0       | 0.6345(5) |

In agreement with literature. In case of the 3% substitution refinement of Rh/Pt occupational parameters from powder data is not feasible due to low Rh content, so in the refinement model the “Pt1” position was set to be fully occupied by platinum.

With the substitution of Pt by Rh we observe a slight increase in a parameter by $\Delta a \approx 0.003$ Å and a noticeable decrease of parameter $c$ by $\Delta c \approx -0.02$ Å. This effect might be another indication of solid solution formation and can be explained by compression of distorted Bi-octahedra, and, as a result, slight expansion of the Pt-Bi framework in the $ab$ plane. This lattice deformation might be a helpful tool to study Weyl point behavior, since the position of such nodes in electronic structure is quite sensitive to changes in lattice parameters.

B. Resistivity

Inset of Fig. 5 presents metallic nature of resistivity as a function of temperature in cubic PtBi$_2$ with estimated RRR=650. Fig. 5 shows the temperature dependence of the normalized in-plane resistivity $\rho/\rho_N$ of the Pt$_{1-x}$Rh$_x$Bi$_2$ crystals with $x=0$ and $x=0.35$. PtBi$_2$ presents a metallic behavior with a residual resistivity ratio (RRR) up to 32, evidencing the high purity of the sample. Pt$_{0.65}$Rh$_{0.35}$Bi$_2$ is also metallic but its RRR decreases to 2.7, due to the disorder introduced by the Rh substitution.

Measurements at very low temperature show a broad superconducting transition at 600 mK for a current of 500µA (Fig. 5). This superconducting transition disappears in the presence of a 500 mT magnetic field (Fig. 5) and we measure a critical magnetic field $B_c$ (defined as $R(Bc) = R_N/2$, $R_N$ being the resistance in the normal state) of 60 mT (Fig. 5). Further details regarding superconductivity anisotropy will be reported elsewhere. Similar transitions are observed in the Pt$_{0.65}$Rh$_{0.35}$Bi$_2$ doped crystals but with a significantly larger critical temperature of 2.75 K for a current of 0.1 mA (see Fig. 5 and inset in Fig. 5). Again, a magnetic field of 1 T aligned along the c-axis at a temperature of 1 K suppresses this superconducting transition (inset of Fig. 5). By increasing the current the transition systematically broadens (Fig. 5 for Pt$_{0.65}$Rh$_{0.35}$Bi$_2$), consistently with a pro.
FIG. 5. (a) T-dependence of the normalized resistivity $\rho/\rho_{290K}$ for trigonal PtBi$_2$ and Pt$_{0.7}$Rh$_{0.3}$Bi$_2$, inset: T-dependence of the resistivity for cubic PtBi$_2$ (b) T-dependence of $R$ for PtBi$_2$ with magnetic field $B = 0$ T and $B = 500$ mT, applied parallel to the c-axis. Inset: T-dependence of $\rho/\rho_{290K}$ for Pt$_{0.7}$Rh$_{0.3}$Bi$_2$ with magnetic field $B = 0$ T and $B = 1$ T, applied parallel to the c-axis. (c) B-dependence of $R$ for PtBi$_2$ at $T = 100$ mK. (d) Low temperature $\rho/\rho_{290K}$ vs $T$ curves for Pt$_{0.7}$Rh$_{0.3}$Bi$_2$ with different applied current from 0.1 mA to 5 mA. Inset: magnetic field dependence of $\rho/\rho_{290K}$ for Pt$_{0.7}$Rh$_{0.3}$Bi$_2$ at different $T = 2.2, 2.5$ and $2.7$ K with $I = 0.1$ mA.

gressive suppression of the superconducting phase (the not-well-defined geometry of the sample did not allow a reliable estimation of the critical current). As expected for the superconducting state, the superconductivity is weakened by increasing the temperature and the critical field decreases accordingly. In the inset of Fig. 5d the field-dependence of $\rho/\rho_{290K}$ is also presented: with increasing the temperature, the critical field, required to suppress the superconducting phase, diminishes as expected.

C. Magnetization

Magnetization measurements in the temperature range of $T = 1.8$–$300$ K in 0.5 T field show diamagnetic behavior for both parent and Rh-substituted compounds with a Curie tail region at low temperatures, perhaps due to some paramagnetic impurities. Fig. 6 presents the temperature dependent volume susceptibility ($\chi_{\text{vol}}$) for the Pt$_{0.65}$Rh$_{0.35}$Bi$_2$ compound. $\chi_{\text{vol}}$ was deduced from the measured magnetization vs temperature dependence and has not been corrected for demagnetization effects. The sharp onset of the superconducting transition starts at $T_c \approx 3$ K. However, the saturation is not seen down to 1.8 K, probably due to temperature limitations of the device. Observed $T_c$ is in line with the $T_c$ estimated from resistivity measurements.

D. Electronic band structure calculation

Fig. 7d shows electronic density of states (DOS). The density of states (DOS) shows a minimum for the stoichiometric compound at the Fermi level. Close to the Fermi level, only 6p Bi and 5d Pt states are present. The orbital projected band structure is presented at Fig. 7a and correspondent Fermi surface is shown in Fig. 7c. The colormap in the figure shows the velocity of the corresponding groups of electrons at the Fermi level. The obtained band structure agrees with one reported earlier. The substitution of Pt by Rh leads to hole doping and enhancement of the DOS at the Fermi level. The rise of superconducting critical temperature with Rh doping
IV. CONCLUSION

In summary, we have successfully grown single crystals of both trigonal and pyrite-type polymorphic modifications of PtBi$_2$, as well as trigonal Pt$_{1-x}$Rh$_x$Bi$_2$ for $x=0.03, 0.35$ via self-flux technique. As grown crystals were carefully characterized by SEM/EDX and powder X-ray diffraction. Further, we have successfully grown the single crystals of Rh-doped PtBi$_2$ in trigonal modification, which also shows Pt$_{1-x}$Rh$_x$Bi$_2$ solid solution formation. Structural characterization demonstrates that crystal structure is preserved up to at least $x = 0.35$. For $x = 0.35$ compound as measured superconducting transition temperature is 2.7K from both resistivity as well as from susceptibility measurements, which is in line with DOS shift near the Fermi level according to calculations. Our findings together with data published previously make PtBi$_2$-family of materials a strong candidate for topological superconductivity. The effect of the substitution on the non-trivial band structure of the compound has to be further investigated by revisiting electronic structure measurements by ARPES.

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VI. DATA AVAILABILITY

The datasets analyzed during the current study are available from the corresponding authors upon reasonable request.

VII. AUTHOR CONTRIBUTION

Single crystal growth and characterization experiments were performed by GS, IK, BRP, BB and SA. The resistivity measurements from 300K to 1.8K were performed and analyzed by SS, FC and CH. Low temperature resistivity measurements were performed and analyzed by AV, VL, RG and JD. Electronic band structure calculations were performed by DVE. GS and SA wrote the manuscript with input from all co-authors. The overall project was led by GS, BB and SA.

VIII. COMPETING INTERESTS

Authors declare no competing financial or non-financial interests.

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FIG. 7. (a) Orbital decomposed band structure of trigonal PtBi$_2$, showing the contribution of 5d Pt and 6p Bi orbitals. (b) Total DOS for trigonal PtBi$_2$ and partial contribution of Pt and Bi orbitals and DOS in Pt$_{0.97}$Rh$_{0.03}$Bi$_2$. (c) Fermi surface of trigonal PtBi$_2$. 

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