Crystal growth and characterization of $RhPb_2$ and its related compounds

Nikola Subotić[1], Takashi Mochiku[2], Yoshitaka Matsushita[2], Osamu Takeuchi[1], Takanari Kashiwagi[1], Hidemi Shigekawa[1], Kazuo Kadowaki[1]

[1]University of Tsukuba, 1-1-1 Tenoudai, Tsukuba, Ibaraki 305-8573, Japan
[2]National Institute for Material Science, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan

Abstract

The physical properties of the intermetallic compound $RhPb_2$ have been unexplored in detail and are controversial so far. Two values of superconducting transition temperatures have been reported experimentally in poly-crystal samples with the *I*4/*mcm* structure. Moreover, the recent report of band calculation results showed that $RhPb_2$ with the *I*4/*mmm* structure (β-$RhPb_2$) may be a topological superconductor candidate, having a higher $T_c \approx 9.7$ K than that of the *I*4/*mcm* structure. Therefore, we grew single crystals of $RhPb_2$ and performed X-ray diffraction study and the phase stability by EPMA, and resistivity measurements to clarify this intriguing compound. Surprisingly, the resistivity measurements showed three different values of T_c (1.24 K, 2.32 K, and 6.7 K) despite the same crystal structure (*I*4/*mcm*) but different levels of Rh vacancies up to 18%, inspiring that some sort of Rh vacancy ordering may occur.

Introduction

According to the binary phase diagrams [1, 2], the intermetallic compound $RhPb_2$ grows through the peritectic reaction incongruently between 640 and 320° C, and it crystallizes in the *I*4/*mcm* structure [$CuAl_2$ (C16) structure]. The same crystal structure was observed [3], where it was shown that $RhPb_2$ becomes superconducting below 2.66 K. On the other hand, according to [4], the Pb-deficient *I*4/*mcm* structure becomes superconducting below 1.33 K. Furthermore, Zhang et al. [5] claimed that $RhPb_2$ with the *I*4/*mmm* structure (β-Pb_2Rh) may be a topological superconductor candidate, with surprisingly high superconductivity transition $T_c \approx 9.7$ K. Moreover, a recent single-crystal XRD analysis showed Rh-deficiency rather than Pb-deficiency [6].

Different values of T_c [4–6] and different space groups [5, 6] indicate that allotropes of $RhPb_2$ might exist, while the phase diagrams [2, 3] show the opposite. According to [2], the two horizontal lines at 320° C and 300° C are doubtful because such phase lines were not observed at least in our present study. Indeed, it is rare to see such two lines so close, and the meaning of 320° C is debatable [2]. The choice to perform band calculation with the

I4/mmm structure [5] instead of the *I*4/*mcm* structure is unrealistic since the *I*4/*mcm* structure of $RhPb_2$ was confirmed experimentally. On the other hand, we would like to note that allotropes of $RhSn_2$ do exist, having the *I*4/*mmm* and the *I*4/*mcm* crystal structures [2]. Since Sn and Pb are chemically similar elements, $RhPb_2$ with *I*4/*mmm* crystal structure symmetry might exist.

The present status of $RhPb_2$ can be summarized in Table 1, emphasizing the topological nature of the materials and their superconducting properties. The preparation of high-quality samples is necessary, which is an arduous task. Poor quality of the samples would make the interpretation of the experimental results difficult or often may lead to erroneous results. Besides the growth of high-quality crystals, a detailed investigation of the phase diagram is required to elucidate the topological nature of $RhPb_2$.

Materials and methods

The single crystals of $RhPb_2$ were grown from the Pb-rich melt (molar ratio Rh:Pb = 1:8) in a steep temperature gradient in the infrared mirror furnace [6, 8]. Before the crystal growth, Rh and Pb were melted in an evacuated quartz tube with a flame torch to homogenize the sample. The sample was put in another quartz tube with coned-shaped bottom to promote uniform crystal growth. The quartz tube was hung in the infrared mirror furnace being attached to the upper shaft which allows rotation and vertical translation of the mounted sample. The focal point of the infrared light was at the upper part of the boule, inducing a steep temperature gradient vertically across the sample. To obtain uniform temperature horizontally, the shaft was rotated slowly (~ 10 r.p.m.). The temperature of the sample was controlled by reducing the intensity of the infrared light, not by the vertical translation of the shaft. The upper part of the boule was heated above 640° C, where the sample become completely liquid. Then, the temperature was slowly reduced with a constant rate of approximately 0.5° C/h to a temperature slightly above 320° C, then it was lowered to room temperature. Due to the steep temperature gradient and the size of the grown boule, crystals have formed both at the lower and upper parts of the grown boule. Those crystals turned out to be $RhPb_2$ by EPMA (see SI). In addition, needle-like crystals have grown in the middle part of the boule. It was evident that the needle-like crystals were not $RhPb_2$ since the crystals were soft, and the color changed due to the exposure in the air (which does not occur for $RhPb_2$), indicating higher concertation of Pb. The preliminary single-crystal XRD analysis showed that needle-like crystals may be $RhPb_4$, which crystallizes in the monoclinic *I*2/*m* space group. Detailed results of the XRD analysis can be found in the SI.

This kind of crystal formation was not observed in the previous infrared mirror furnace experiments where the size of the grown boule was smaller (the crystals have formed at the

lower part of the boule as it usually does). Initially, the crystals of $RhPb_2$ were tried to be grown with the standard muffle furnace with good temperature control. The initial molar ratio was 1:2 = Rh:Pb with various annealing temperatures. It was shown that even after 2 months of growth, no significant crystal formation was observed. Then, various concertation of Pb was tested and it turned out that a higher concentration of Pb promotes crystal growth. The various temperature gradient methods have been tried such as Bridgman, and Czochalrski, but in the end, the before mentioned method with a high concentration of Pb proved to be successful. It is interesting to note that such a crystal growth method was not reported before, and it turned out to be an ideal way how to grow or induce the formation of various phases of a single compound.

After crushing the grown boule, most of the obtained single crystals of $RhPb_2$ were investigated by EPMA, XRD, and resistivity measurements. The crushed crystals often had irregular shapes, meaning that the cleaving is rather difficult. The standard four-probe method was applied to measure the temperature dependence of resistivity. The silver paste was used to connect the voltage and current terminals. The contact resistivity was typically below 1 Ω. The EPMA measurements were performed with JEOL JXA-8500F. The voltage and probe current were at 15 kV and 5 nA, respectively. For calibration, PbS, Au, and Rh were used. The XRD measurements were conducted with two circle diffractometer Rigaku Xtal Mini II.

Results

The resistivity measurements in most cases showed one superconducting transition around 1.25 K (Fig. 1a). In other cases, the resistivity measurements releveled three superconducting transitions indicating the presence of three different phases (Fig. 1c). The transition widths of 1.25 K are smaller than the other two transitions. The corresponding $\Delta T_c/Tc$ ratios for the 1.25 K, 2.32 K, and 6.7 K transitions are 0.08, 0.21, and 0.07, respectively. The residual resistance ratio (RRR) in most cases was around 4 while the highest was around 7, which corresponds to the medium quality of the grown crystals. The residual resistance of the measured crystals ranges from 11 to 20 $\mu\Omega$ cm. The linear dependence of the resistivity at higher temperatures was observed.

The crystals, on which the resistivity measurements were performed, were cut and prepared for the EPMA measurements. The 1.25 K transition crystals showed neither Rh nor Pb deficiency within experimental error. Sample C showed its 82.58% occupancy of Rh sites. The results are shown in Table 2. The SEM photographs of crystals on which EPMA measurements were carried out are shown in Fig. 2. The COMPO images and the measurement spots on the surface of the crystals are also shown in SI.

Since sample A contained only one T_c the sample may be homogenous and without vacancies. The other two samples show that the vacancies of Rh may not be distributed homogenously since three different values of T_c were observed. For sample C, if it is assumed that the various values of T_c are due to the variation of Rh vacancies, the 6.61 K transition may be due to the 82.58% occupancy of the Rh sites because the 2.39 K transition is negligible, and the 1.26 K is due to the non-deficient structure. Therefore, the remaining 2.32 K transition is probably due to 96.39% occupancy of the Rh sites.

Discussion and conclusion

The topological superconductor candidate, $RhPb_2$ has been investigated experimentally. The medium-quality crystals were grown by a slow-cooling process in a steep temperature gradient infrared furnace. Besides $RhPb_2$, $RhPb_4$ single crystals were found to exist newly. Its preliminary crystal structure has been determined for the first time to be monoclinic $I2/m$ [a = 6.853(4) Å, b = 5.958(6)Å, c = 13.157(3) Å, β = 98.451(2)°].

The EPMA and XRD measurements indicated that the 1.26 K transition is due to the nondeficient structure, not the Pb-deficient structure reported by [4]. Therefore, the Pb-deficient structure might not occur. The 2.32 K transition may be due to the slight Rh-deficient crystals (around 96%), which may correspond to samples found in Ref. [3]. The situation regarding the 6.7 K transition is more difficult to interpret. It may be due to the even more Rh-deficient crystals (around 18%) according to the EPMA and XRD measurements. If this is true, the question is, under what conditions do such structures form. It would be a unique opportunity to investigate how T_c, lattice constants, topology, and other properties do depend on Rh-deficiency. XRD measurements of 18% and 4% (samples C and B) Rh-deficient crystals will be conducted in the near future to confirm if those crystals belong to the tetragonal $I4/mcm$ space group.

Another possibility is that the 6.7 K transition is due to the presence of Pb or $RhPb_4$. It is unlikely that the 6.7 K is due to the presence of Pb since its T_c is 7.1 K. Grown crystals of $RhPb_4$ could be measured with SQUID or a similar technique to determine the T_c. If the T_c is different from 6.7 K, then it is quite certain that the 6.7 K transition is due to the Rh-deficient structure. To confirm whether $RhPb_4$ belongs to the $I2/m$ space group, analysis of better quality crystals is required. It would be quite interesting to perform the band calculation and inspect the topological properties of $RhPb_4$.

The presence of $RhPb_2$ at both ends of the boule and $RhPb_4$ in the middle of the grown boule indicate that there is a considerable temperature difference across the grown boule due to the steep temperature gradient and the size of the boule. As it turned out, this method is favorable for the formation of various phases since a 6.7 K transition was observed for the first time,

besides the 2.3 K and 1.23 K reported in previous studies [3, 4]. The next step is to separate those phases to prove if the Rh-deficiency does influence the superconducting properties of $RhPb_2$. The high concertation of Pb may lead to the Rh-deficiency on the one hand. On the other hand, crystals of Au_2Pb and $AuPb_2$ grown under similar conditions do not exhibit deficiency indicating that the deficiency in $RhPb_2$ is due to the nature of the material itself rather than the growth method. To determine if the Pb-rich part of the phase diagram yields Rh-deficiency structures, in the future, ratios near 1:2 will be explored in detail.

XRD measurements did not show that the structure of grown crystals of $RhPb_2$ is a tetragonal $I4/mmm$. The reason might be that β-Pb_2Rh is a metastable state. Even without $I4/mmm$ space group, the known binary phase diagrams Pb-Rh are incomplete. Therefore, a detailed investigation of the phase diagram is required. Annealing of grown crystals at various temperatures could be also quite useful in determining the desired conditions and improving the quality of the grown crystals.

In conclusion, the Pb-rich binary phase diagram of the Pb-Rh system was studied. According to the presently available binary phase diagrams [1, 2], several kinds of single crystals can be grown from the appropriate combi- nation of Pb and Rh. Most of their physical properties turn out to be unexplored, for example, different values of T_c of the intermetallic compound $RhPb_2$. This unexpected result encourages further investigation of $RhPb_2$ as a topological superconductor candidate. It certainly requires better quality of single crystals of $RhPb_2$. In addition, the relation between its corresponding Rh-deficient structures and the physical properties must be understood clearly, elucidating the complex nature of the binary phase diagram Pb-Rh. The results from ARPES and STM measurements should be indispensable for understanding the topological properties of $RhPb_2$ and the related compounds. Furthermore, magnetoresistance measurements could also provide important information about the Fermi surface to reveal the topological nature of $RhPb_2$. Such measurements will be conducted in the near future.

Supplementary Information

The online version contains supplementary material available at https://doi.org/10.1557/s43580-022-00292-5.

Data availability

The data that supports the above-presented results are available from the corresponding author upon reasonable request.

Declarations

Conflict of interest

On behalf of all authors, the corresponding author states that there is no conflict of interest.

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Table 1. Current situation of $RhPb_2$. The *I*4/*mcm* structure might have topological properties.

References	[3]	[4]	[5]	[6]
Compound	Rh Pb_2	Rh $Pb_{1.9}$	β-$RhPb_2$	$Rh_{0.95}Pb_2$
Sample type	Poly-crystal	Poly-crystal	Band calculation	Single-crystal
Space group	I4/mcm	I4/mcm	I4/mmm	I4/mcm
T_c	2.66 K	1.33 K	9.7 K	–
Topology	Z_2 (1;1,1,1) [7] Dirac, Weyl semimetal, topological superconductor?	–	Topological superconductor	–

Table 2. The occupancy of the Pb and Rh sites.

Sample	Rh (%)	Pb (%)	Measured T_c (K)
A $Rh_{0.993}Pb_{2.007}$	99.3	100	1.25
B $Rh_{0.963}Pb_{2.037}$	96.3	100	1.24
			2.32
			6.7
C $Rh_{0.825}Pb_{2.125}$	82.5	100	1.26
			2.39
			6.61

The almost non-deficient structure (sample A) showed one transition temperature only, while sample C revealed even more Rh-deficiency compared to [6] with three different T_c. In the table are shown the averaged values assuming that the Pb sites are fully occupied. The atomic percentage of the measured spots along with the COMPO photograph of the samples is shown in the SI

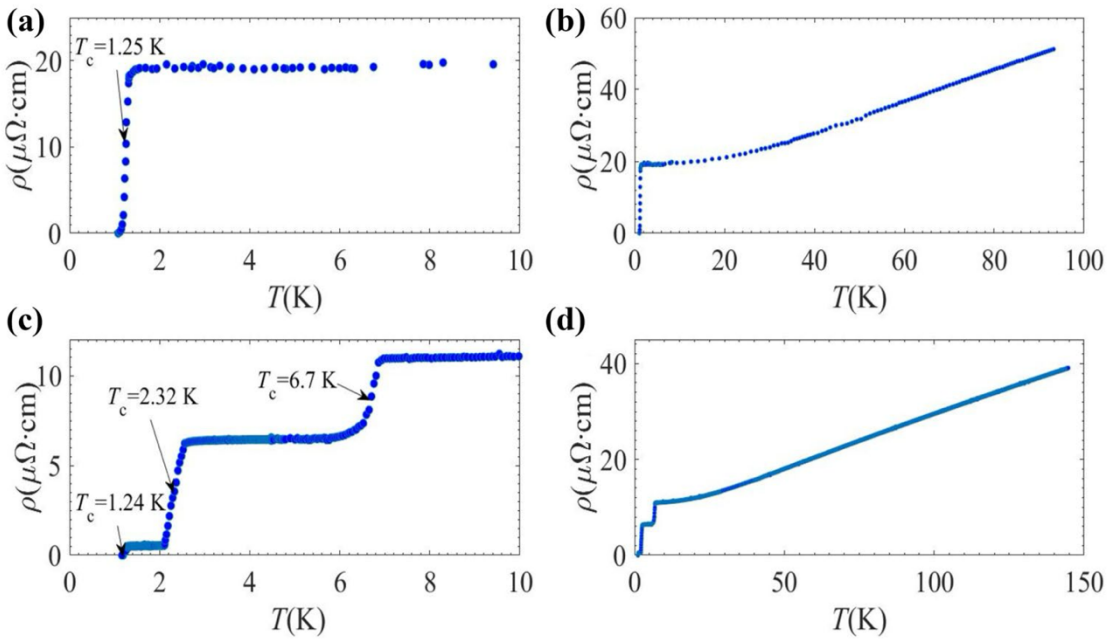

Fig. 1 a. Resistivity plot of $Rh_{0.993}Pb_{2.007}$ up to 10 K. The residual resistance of ≈ 19 $\mu\Omega$·cm is not so high while the room temperature resistivity is 142.4 $\mu\Omega$ cm. The transition width is ΔT_c=0.1 K. The photograph of the measured crystal is shown in SI. **b** The resistivity plot of $Rh_{0.993}Pb_{2.007}$ up to 100 K. Linear dependence is obvious, indicating the metallic behavior of $RhPb_2$. **c** The resistivity plot of sample $Rh_{0.963}Pb_{2.037}$ up to 10 K. Three transitions can be observed. The transition width of 1.24 K transition is significantly narrower (0.1 K) compared to the higher temperature transition width (0.5 K). The residual resistance is lower compared to sample $Rh_{0.993}Pb_{2.007}$. The room temperature resistance is 70.15 $\mu\Omega$ cm which corresponds to the RRR being around 6. The measured single crystal is shown in the SI. **d** The resistivity plot of sample $Rh_{0.993}Pb_{2.007}$ up to 150 K. The linear dependence is obvious, same as the previous sample, indicating the metallic behavior of $RhPb_2$.

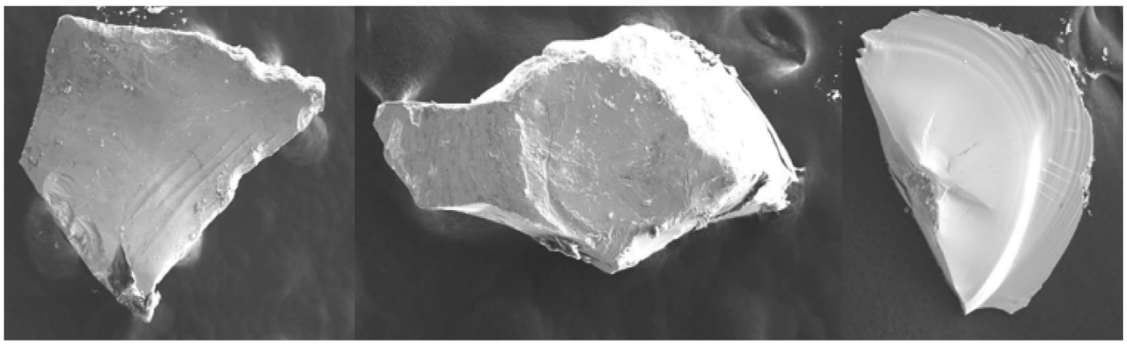

Fig. 2. SEM photographs of $Rh_{0.993}Pb_{2.007}$, $Rh0_{.963}Pb_{2.037}$, and $Rh_{0.825}Pb_{2.125}$, respectively (from left to right), on which the EPMA measurements were done. The size of $Rh_{0.993}Pb_{2.007}$ is roughly $600 \times 600\ \mu m^2$, $Rh_{0.963}Pb_{2.037}$ around $300 \times 200\ \mu m^2$, and $Rh_{0.825}Pb_{2.125}$ approximately $100 \times 100\ \mu m^2$.