Single crystal growth of new heavy fermion compounds CePt$_2$In$_7$ and Ce$_2$PtIn$_8$

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Abstract. We succeeded in growing single crystals of Ce$_2$PtIn$_8$ and CePt$_2$In$_7$ by In self-flux method. We performed the single crystal X-ray diffraction and determined the lattice parameters and atomic positions. We also obtained cubic-like crystals with the typical size of 1x1x1 mm$^3$, in which Ce$_2$PtIn$_8$ thin layer grows on CeIn$_3$ single crystal surface. This structure implies a peritectic growth of Ce$_2$PtIn$_8$ on most likely the CeIn$_3$(100) surface. The electrical resistivity of CePt$_2$In$_7$ shows sharp kink at the Néel temperature of 5.5 K, and exhibits the Fermi liquid behavior.

1. Introduction

The interplay between unconventional superconductivity and magnetism has been a central subject in condensed matter physics. Ce$_m$T$_n$In$_{3m+2n}$ ($m=1,2$; $m=1,2$ and T: transition metal) family is an ideal series for studying the interplay between d-wave superconductivity and magnetism at around the quantum critical point. It has a unique tetragonal crystal structure with stacking of CeIn$_3$(m) and TIn$_2$(n) layers along the [001] direction. According to the unique crystal structures, these compounds have quasi-two dimensional properties. Quasi-two dimensional CeTIn$_5$ (T: Co, Rh and Ir)(see Fig. 1(b)) exhibits superconductivity with a critical temperature $T_c = 0.4$ K in CeCoIn$_5$[1] and $T_c = 0.4$ K in CeIrIn$_5$[2] at ambient pressure and $T_c = 2.2$ K in CeRhIn$_5$ under pressure[3, 4], while pressure induced superconductivity is revealed at $T_c = 0.2$ K in three dimensional CeIn$_3$[5](see Fig. 1(a)). It is plausible to consider that the unconventional superconductivity is enhanced in reduced dimensional system.

Ce$_2$TIn$_8$ (T: Co, Rh and Ir) has a Ho$_2$CoGa$_8$ type structure (P4/mmm #123) and can be regarded as alternate stacking of double CeIn$_3$ layers and a single TIn$_2$ layer (see Fig. 1(c)). $T_c$ of Ce$_2$CoIn$_8$(0.4 K)[6] is lower than that of CeCoIn$_5$. Ce$_2$RhIn$_8$ shows an antiferromagnetic order below $T_N$ = 2.8 K, exhibits pressure induced superconductivity[7, 8]. On the other hand, Ce$_2$IrIn$_8$ remains paramagnetic[9]. Ce$_2$PdIn$_8$ and Ce$_2$PtIn$_8$ are new members of Ce$_2$TIn$_8$.
families. Ce$_2$PdIn$_8$ exhibits superconductivity with $T_c \simeq 0.7$ K and behaves deviation from the Fermi liquid behavior at ambient pressure[10].

CePt$_2$In$_7$ is a recently discovered Ce$_m$T$_n$In$_{3m+2n}$ family member[11, 12, 13]. Unlike CeTiIn$_5$ and Ce$_2$TiIn$_8$ systems, it has a body-centered tetragonal crystal structure (I4/mmm #139)[11, 14, 15]. Very recently, Klimczuk et al reported a corrected crystal structure(see Fig. 1(d))[15]. An antiferromagnetic ordering below $T_N = 5.2$ K in CePt$_2$In$_7$ is suppressed with increasing pressure, and vanishes at around the critical pressure $P_c \simeq 3.4$ GPa. Pressure induced superconductivity appears above $P > 1$ GPa, has a maximum of $T_c \simeq 2.1$ K at around $P_c$[12, 13, 16, 17, 18].

To elucidate the interplay between the unconventional superconductivity and magnetism in quasi-two dimensional systems, we made an effort to grow single crystals of CePt$_2$In$_7$ and Ce$_2$PtIn$_8$, and measured single crystal X-ray diffraction, electrical resistivity and specific heat.

2. Experimental method

Single crystals of CePt$_2$In$_7$ and Ce$_2$PtIn$_8$ were grown by In self-flux method. Starting materials were 99.9 % pure (3N) Ce, 3N-Pt and 4N-In. These materials with composition of Ce:Pt:In = 1:1.24:8.33(CePt$_2$In$_7$) and 2:1:10(Ce$_2$PtIn$_8$) were inserted in alumina crucibles and sealed in quartz tubes under a partial pressure of argon gas. These tubes were heated up to 1050 °C and slowly cooled down to 400 °C by spending 700 hours. Figure 2 shows the scanning electron microscope (SEM) images of (a) CePt$_2$In$_7$ and (b) Ce$_2$PtIn$_8$, respectively. We obtained platelet crystals, reflecting the layered crystal structure. The typical size of CePt$_2$In$_7$ is 2-3 times larger than that of Ce$_2$PtIn$_8$, as shown in Fig. 2. Single crystals of CeIn$_3$, Ce$_6$Pt$_{11}$In$_{14}$ and Ce$_3$Pt$_4$In$_{13}$
Table 1. The structure parameters for Ce$_2$PtIn$_8$.

| Crystal system     | Tetragonal |
|-------------------|------------|
| Space group       | $P4/mmm$   |
| Unit cell dimensions | $a = 4.710(2)$ Å  |
|                   | $c = 12.218(4)$ Å  |
| Unit cell volume  | $271.3(2)$ Å$^3$ |
| $Z$ value         | 1          |
| $R$, $R_w$        | 0.0894, 0.0898 |

| Atom   | $x$  | $y$  | $z$  |
|--------|------|------|------|
| Ce(2g) | 0    | 0    | 0.3079(3) |
| Pt(1a) | 0    | 0    | 0    |
| In(4i) | 0    | 0.5  | 0.1215(3) |
| In(2e) | 0    | 0.5  | 0.5  |
| In(2h) | 0.5  | 0.5  | 0.3074(4) |

Table 2. The structure parameters for CePt$_2$In$_7$.

| Crystal system     | Tetragonal |
|-------------------|------------|
| Space group       | $I4/mmm$   |
| Unit cell dimensions | $a = 4.6182(3)$ Å  |
|                   | $c = 21.682(2)$ Å  |
| Unit cell volume  | $462.45(6)$ Å$^3$ |
| $Z$ value         | 2          |
| $R$, $R_w$        | 0.0722, 0.0797 |

| Atom   | $x$  | $y$  | $z$  |
|--------|------|------|------|
| Ce(2b) | 0    | 0    | 0.5  |
| Pt(4e) | 0    | 0    | 0.3256(1) |
| In(2a) | 0    | 0    | 0    |
| In(4d) | 0    | 0.5  | 0.25 |
| In(8g) | 0    | 0.5  | 0.1081(2) |

were also found to grow together with CePt$_2$In$_7$ and Ce$_2$PtIn$_8$ in the same batch, as reported previously by Kratochvilova et al. [19]. The composition of the crystal was investigated by energy dispersive X-ray (EDX) spectroscopy. The single crystal X-ray diffraction performed using a Rigaku IP diffractometer. The electrical resistivity was measured by conventional four-probe method. The specific heat measurement was done using a Quantum Design PPMS system.

3. Results and discussion

The crystal structure of Ce$_2$PtIn$_8$ and CePt$_2$In$_7$ were determined by the single crystal X-ray diffraction method. The structure parameters presented in table 1 for Ce$_2$PtIn$_8$ and table 2 for CePt$_2$In$_7$ are in agreement with the previous reports [15, 19].

We also obtained a few large cubic-like crystals with the typical size of about $1\times1\times1$ mm$^3$. We confirmed that the surface of the crystals is Ce$_2$PtIn$_8$ using by EDX and X-ray diffraction. The six surface planes of a cubic-like crystal are, however, (001) plane of Ce$_2$PtIn$_8$, according

![Figure 3](image.png)

**Figure 3.** (a)The scanning electron microscope images of the cut surface of a cubic-like crystal stacked with the energy dispersive X-ray mapping images for Ce(red), Pt(green) and In(blue). As shown by arrows, inside CeIn$_3$ is covered by thin Ce$_2$PtIn$_8$ layers, where Ce$_3$Pt$_4$In$_{13}$ contamination was seen in the area around right bottom side. Individual mapping images are shown in (b) Ce, (c) Pt and (d) In, respectively.
Figure 4. Temperature dependence of the electrical resistivity in CePt$_2$In$_7$ in zero magnetic field. $T_N$ is shown by the arrow in panel (b). Inset of panel (a) shows a photograph of the sample. $T^2$ dependence of the resistivity can be seen in inset of panel (b).

to X-ray diffraction results. To investigate the internal constitution of the crystal, we cut the crystal and observed the cut surface by a SEM and EDX.

Figure 3(a) exhibits a SEM image stacked with EDX mapping images for Ce(red), Pt(green) and In(blue) of the cut crystal. Individual mapping images are shown in (b) Ce, (c) Pt and (d) In, respectively. Ce$_2$PtIn$_8$ thin layer grows on the surface of CeIn$_3$. It also contains Ce$_3$Pt$_4$In$_{13}$ as a minor phase(see Fig. 3(a) and (c)). This internal constitution implies a peritectic growth of the crystals. We consider that a single crystal of CeIn$_3$ is formed upon cooling, then Ce$_2$PtIn$_8$ grows epitaxially on most likely the CeIn$_3$ (100) planes. Note that the a-axis lattice constant of Ce$_2$PtIn$_8$ is almost the same with that of CeIn$_3$, therefore, (100) surface of CeIn$_3$ is suitable for the epitaxial growth of Ce$_2$PtIn$_8$.

We obtained relatively large single crystals of CePt$_2$In$_7$ without containing minor phases, in sharp contrast with the Ce$_2$PtIn$_8$ case. We measured the temperature dependence of the electrical resistivity $\rho$ in CePt$_2$In$_7$. The inset of Fig. 4(a) displays a photograph of the sample used for the measurement. The resistivity decreases with decreasing temperature, and has a shoulder corresponding to the Kondo effect at around 70 K, as shown in Fig. 4(a). A kink-

Figure 5. Temperature dependence of the specific heat $C/T$ of the cubic-like crystals in zero magnetic field. The Néel temperature of CeIn$_3$ $T_{N_{\text{CeIn}_3}}$, $T_N$ and $T_m$ are shown by arrow. The inset shows the magnetic phase diagram of $T_N$ and $T_m$. 


like anomaly at \( T_N = 5.5\, \text{K} \), shown in the Fig.4(b), is due to the antiferromagnetic ordering of CePt\textsubscript{2}In\textsubscript{7}. It is in good agreement with previous reports\cite{12, 13, 16, 17, 18}. No anomaly appears at around 10 K, coming from the Néel temperature of CeIn\textsubscript{3}. This assures that our CePt\textsubscript{2}In\textsubscript{7} sample has no contamination of CeIn\textsubscript{3} in marked contrast with features appeared in the cubic-like crystals of Fig. 3. The residual resistivity \( \rho_0 \) and residual resistivity ratio are 0.38 \( \mu \Omega \cdot \text{cm} \) and 90, respectively, indicating that our sample is of high quality. The temperature dependence of \( \rho \) below 2.5 K is well fitted by the Fermi liquid relation of \( \rho = \rho_0 + AT^2 (A = 3.2 \times 10^{-2} \mu \Omega \cdot \text{cm/K}^2) \), as represented in the inset of Fig.4(b), where \( A \) is related to the Sommerfeld coefficient \( \gamma \) as the Kadowaki-Woods relationship: \( A/\gamma^2 \simeq 1 \times 10^{-5} \mu \Omega \cdot \text{cm (mJ/K-mol)}^{-2} \). \( \gamma \) \( \simeq 57 \) mJ/K\textsuperscript{2}\textperiodcentered mol thus estimated is almost the same with previously reported ones\cite{12, 14}.

Figure 5 (a) shows the temperature dependence of the specific heat \( C/T \) for the cubic-like crystal with the mass of 7.62 mg, which is already shown in Fig. 3. A large specific heat jump at \( T_N^{\text{CeIn}_3} = 10 \) K corresponds to the antiferromagnetic ordering of CeIn\textsubscript{3}. It is consistent with the EDX mapping analysis shown in Fig. 3. Addition to this apparent jump at 10 K, finite jumps appear at \( T_N \simeq 2.1 \) K and \( T_m \simeq 2.0 \) K, as displayed in Fig. 5 (b). We measured \( C/T \) under various magnetic fields up to 9 T. \( T_N \) is almost independent of magnetic field up to 9 T, whereas \( T_m \) is gradually suppressed at higher fields, as shown in the inset of Fig. 5 (b). We point out that Ce\textsubscript{3}Pt\textsubscript{In\textsubscript{11}} shows magnetic orderings at almost the same temperatures with \( T_N \) and \( T_m \)\cite{19}. Therefore, we argue that these phase transitions likely correspond to magnetic orderings of Ce\textsubscript{3}Pt\textsubscript{In\textsubscript{11}} contained as the minor phase in the cubic-like crystals.

4. Summary

We were successful in growing single crystals of CePt\textsubscript{2}In\textsubscript{7} and Ce\textsubscript{2}Pt\textsubscript{In\textsubscript{8}} using the In self-flux method. The crystal structures of Ce\textsubscript{2}Pt\textsubscript{In\textsubscript{8}} and CePt\textsubscript{2}In\textsubscript{7} were confirmed by the single crystal X-ray diffraction method. CePt\textsubscript{2}In\textsubscript{7} orders antiferromagnetically at temperatures below \( T_N = 5.5 \) K. We obtained relatively large crystals with complex internal constitution, which consists of inner CeIn\textsubscript{3}, surface thin Ce\textsubscript{2}Pt\textsubscript{In\textsubscript{8}} and contaminations such as Ce\textsubscript{3}Pt\textsubscript{4}In\textsubscript{13} and Ce\textsubscript{3}Pt\textsubscript{In\textsubscript{11}}. It implies a peritectic growth of Ce\textsubscript{2}Pt\textsubscript{In\textsubscript{8}} on most likely the CeIn\textsubscript{3} (100) surface.

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References

[1] Petrovic C, Pagliuso P G, Hundley M F, Movshovich R, Sarrao J L, Thompson J D, Fisk Z, and Monthoux P 2001 J. Phys.: Condens. Matter 13 L337.
[2] Petrovic C, Movshovich R, Jaime M, Pagliuso P G, Hundley M F, Sarrao J L, Fisk Z, and Thompson J D 2001 Europhys. Lett. 53 354.
[3] Hegger H, Petrovic C, Moshopoulou E G, Hundley M F, Sarrao J L, Fisk Z, and Thompson J D 2000 Phys. Rev. Lett. 84 4986.
[4] Muramatsu T, Tateiwa N, Kobayashi T C, Shimizu K, Amaya K, Aoki D, Shishido H, Haga Y, and Ōnuki Y 2001 J. Phys. Soc. Jpn. 70 3362.
[5] Mathur N D, Grosche F M, Julian S R, Walker I R, Freye D M, Haselwimmer R K W, and Lonzarich G G 1998 Nature 394 39.
[6] Chen G, Ohara S, Hedo M, Uwatoko Y, Saito K, Sorai M, and Sakamoto I 2002 J. Phys. Soc. Jpn. 71 2836.
[7] Bao W, Pagliuso P G, Sarrao J L, Thompson J D, and Fisk Z 2001 Phys. Rev. B 64 020401.
[8] Nicklas M, Sidorov V A, Borges H A, Pagliuso P G, Petrovic C, Fisk Z, Sarrao J L, and Thompson J D 2003 Phys. Rev. B 67 020506(R).
[9] Thompson J D, Movshovich R, Fisk Z, Bouquet F, Curro N J, Fisher R A, Hammel P C, Hegger H, Hundley M F, Jaime M, Pagliuso P G, Petrovic C, Phillips N E, and Sarrao J L 2001 J. Mag. Mag. Mater. 226-230 5.
[10] Kaczorowski D, Pikul A P, Gnida D, and Tran V H 2009 Phys. Rev. Lett. 103 027003.
[11] Kurenbaeva Z, Murashova E, Serogepin Y, Noel H, and, Tursina A 2008 Intermetallics 16 979.
[12] Bauer E D, Sidorov V A, Lee H, Kurita N, Ronning F, Movshovich R, and Thompson J D 2010 J. Phys.: Conf. Ser. 200 012011

[13] apRoberts-Warren N, Dioguardi A P, Shockley A C, Lin C H, Crocker J, Klavins P, and Curro N J 2010 Phys. Rev. B 81 180403

[14] Tobash P H, Ronning F, Thompson J D, Scott B L, Moll P J W, Batlogg B, and Bauer E D 2012 J. Phys.: Condens. Matter 24 015601

[15] Klimczuk T, Walter O, Mückler L, Krizan J W, Kinnart F, and Cava R J 2014 J. Phys.: Condens. Matter 26 402201

[16] Sakai H, Tokunaga Y, Kambe S, Lee H-O, Sidorov V A, Tobash P H, Ronning F, Bauer E D, and Thompson J D 2011 Phys. Rev. B 83 140408

[17] Sidorov V A, Lu X, Park T, Lee H, Tobash P H, Baumbach R E, Ronning F, Bauer E D, and Thompson J D 2013 Phys. Rev. B 88 020503(R)

[18] Sakai H, Tokunaga Y, Kambe S, Ronning F, Bauer E D, and Thompson J D 2014 Phys. Rev. Lett. 112 206401

[19] Kratochvilova M, Dusek M, Uhlirova K, Rudajevova A, Prokleska J, Vondrackova B, Custers J, and Sechovsky V 2014 J. Cryst. Growth 397 47