Single crystal growth of new heavy fermion compounds $CePt_2In_7$ and Ce_2PtIn_8

H Shishido[1,2]**, T Yoshihara**[1]**, D Nagamiya**[1]**, S Noguchi**[1,2,3]**,**
H Fujiwara[2,4] **and T Ishida**[1,2]

[1]Department of Physics and Electronics, Graduate School of Engineering, Osaka Prefecture University, Sakai, Osaka 599-8531, Japan

[2]Institute for Nanofabrication Research, Osaka Prefecture University, Sakai, Osaka 599-8531, Japan

[3]Nanoscience and Nanotechnology Research Center, Osaka Prefecture University, Sakai, Osaka, 599-8570, Japan

[4]Department of Chemistry, Graduate School of Science, Osaka Prefecture University, Sakai, Osaka 599-8531, Japan

E-mail: `shishido@pe.osakafu-u.ac.jp`

Abstract. We succeeded in growing single crystals of Ce_2PtIn_8 and $CePt_2In_7$ 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 $1\times1\times1\,mm^3$, in which Ce_2PtIn_8 thin layer grows on $CeIn_3$ single crystal surface. This structure implies a peritectic growth of Ce_2PtIn_8 on most likely the $CeIn_3$ (100) surface. The electrical resistivity of $CePt_2In_7$ 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. $Ce_mT_nIn_{3m+2n}$ (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 superconducting transition temperature $T_c = 2.3\,K$ 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_2TIn_8 (T: Co, Rh and Ir) has a Ho_2CoGa_8 type structure (P4/mmm #123) and can be regareded as alternate stacking of double $CeIn_3$ layers and a single TIn_2 layer (see Fig. 1(c)). T_c of $Ce_2CoIn_8(0.4\,K)$[6] is lower than that of $CeCoIn_5$. Ce_2RhIn_8 shows an antiferromagnetic order below $T_N = 2.8\,K$, exhibits pressure induced superconductivity[7, 8]. On the other hand, Ce_2IrIn_8 remains paramagnetic[9]. Ce_2PdIn_8 and Ce_2PtIn_8 are new members of Ce_2TIn_8
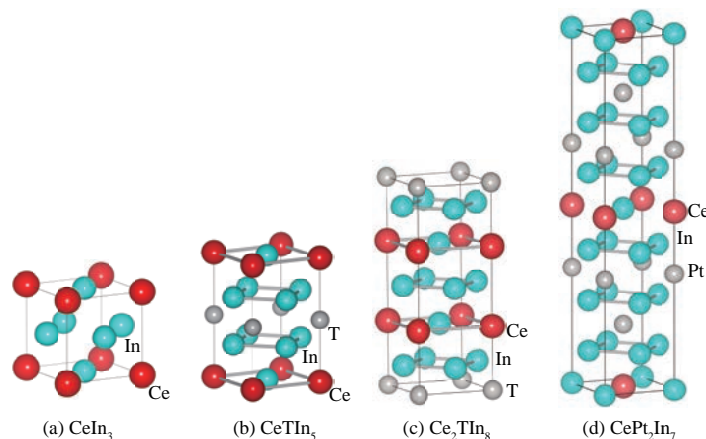
Figure 1. Crystal structures of (a)$CeIn_3$, (b)$CeTIn_5$, (c)Ce_2TIn_8 and (d)$CePt_2In_7$(T: transition metal).

families. Ce_2PdIn_8 exhibits superconductivity with $T_c \simeq 0.7\,K$ and behaves deviation from the Fermi liquid behavior at ambient pressure[10].

$CePt_2In_7$ is a recently discovered $Ce_mT_nIn_{3m+2n}$ family member[11, 12, 13]. Unlike $CeTIn_5$ and Ce_2TIn_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 $CePt_2In_7$ 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 $CePt_2In_7$ and Ce_2PtIn_8, and measured single crystal X-ray diffraction, electrical resistivity and specific heat.

2. Experimental method

Single crystals of $CePt_2In_7$ and Ce_2PtIn_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($CePt_2In_7$) and 2:1:10(Ce_2PtIn_8) were inserted in alumina crucibles and sealed in quartz tubes under a partial pressure of argon gas. These tubes were heated up to $1050\,^\circ C$ and slowly cooled down to $400\,^\circ C$ by spending 700 hours. Figure 2 shows the scanning electron microscope (SEM) images of (a) $CePt_2In_7$ and (b) Ce_2PtIn_8, respectively. We obtained platelet crystals, reflecting the layered crystal structure. The typical size of $CePt_2In_7$ is 2-3 times larger than that of Ce_2PtIn_8, as shown in Fig. 2. Single crystals of $CeIn_3$, $Ce_6Pt_{11}In_{14}$ and $Ce_3Pt_4In_{13}$
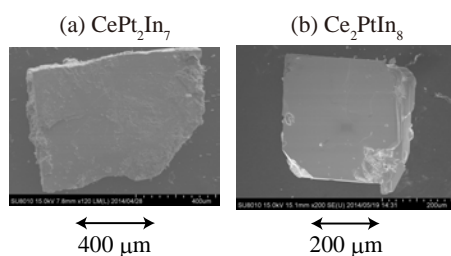
Figure 2. The scanning electron microscope images of single crystals (a)$CePt_2In_7$ and (b)Ce_2PtIn_8, respectively.

Table 1. The structure parameters for Ce_2PtIn_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 $CePt_2In_7$.

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 $CePt_2In_7$ and Ce_2PtIn_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 disscussion

The crystal structure of Ce_2PtIn_8 and $CePt_2In_7$ were determined by the single crystal X-ray diffraction method. The structure parameters presented in table 1 for Ce_2PtIn_8 and table 2 for $CePt_2In_7$ are in agreement with the previous reports[15, 19].

We also obtained a few large cubic-like crystals with the typical size of about $1 \times 1 \times 1$ mm^3. We confirmed that the surface of the crystals is Ce_2PtIn_8 using by EDX and X-ray diffraction. The six surface planes of a cubic-like crystal are, however, (001) plane of Ce_2PtIn_8, according
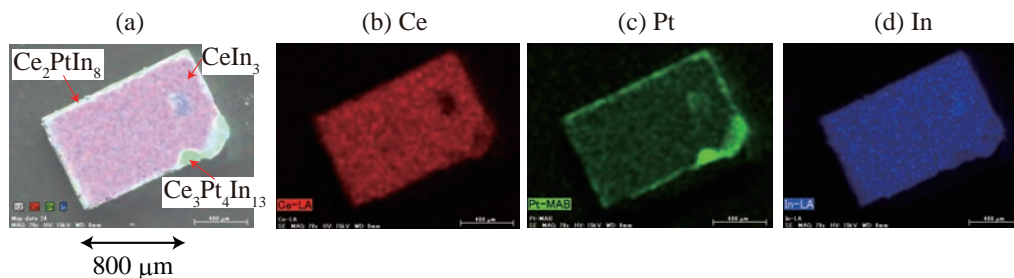
Figure 3. (a)The scanning electron microscope images of the cut surface of a cubic-like crystal stacked with the energy dispersive X-ray mapping images for Ce(red), Pt(green) and In(blue). As shown by arrows, inside $CeIn_3$ is covered by thin Ce_2PtIn_8 layers, where $Ce_3Pt_4In_{13}$ contamination was seen in the area around right bottom side. Individual mapping images are shown in (b) Ce, (c) Pt and (d) In, respectively.
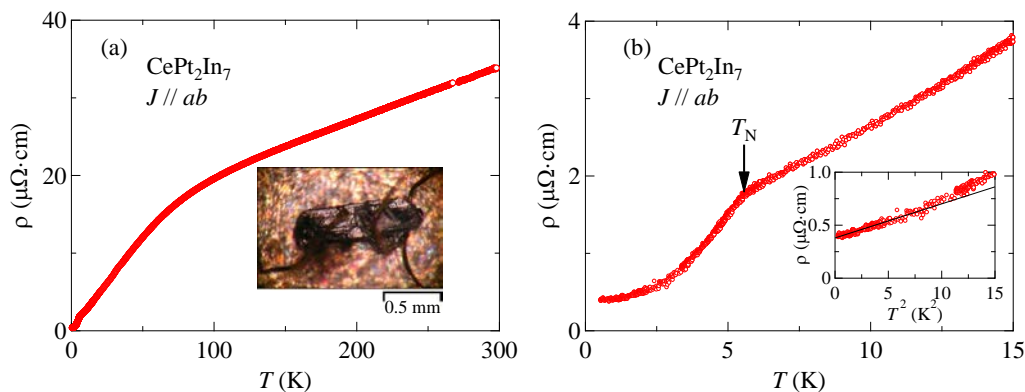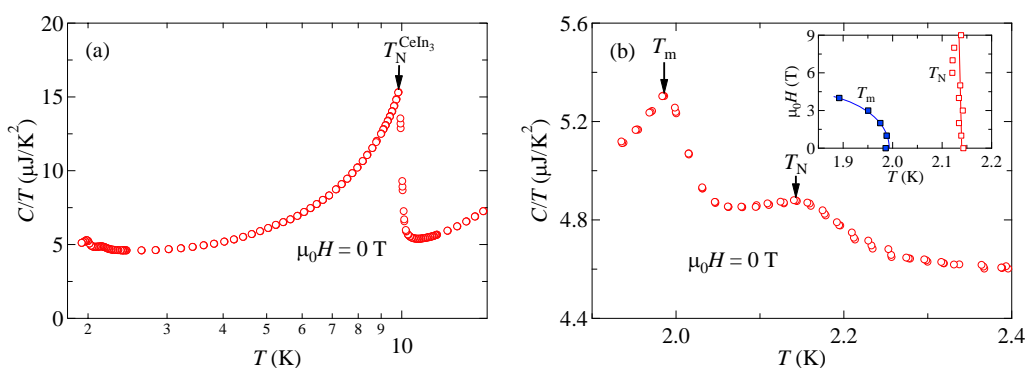
Figure 4. Temperature dependence of the electrical resistivity in $CePt_2In_7$ in zero magnetic field. T_N is shown by the arrow in panel (b). Inset of panel (a) shows a photograph of the sample. T^2 dependence of the resistivity can be seen in inset of panel (b).

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_2PtIn_8 thin layer grows on the surface of $CeIn_3$. It also contains $Ce_3Pt_4In_{13}$ 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_2PtIn_8 grows epitaxially on most likely the $CeIn_3$ (100) planes. Note that the a-axis lattice constant of Ce_2PtIn_8 is almost the same with that of $CeIn_3$, therefore, (100) surface of $CeIn_3$ is suitable for the epitaxial growth of Ce_2PtIn_8.

We obtained relatively large single crystals of $CePt_2In_7$ without containing minor phases, in sharp contrast with the Ce_2PtIn_8 case. We measured the temperature dependence of the electrical resistivity ρ in $CePt_2In_7$. 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 $CeIn_3$ $T_N^{CeIn_3}$, 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 $T_N = 5.5$ K, shown in the Fig.4(b), is due to the antiferromagnetic ordering of $CePt_2In_7$. It is in good agreement with previous reports[12, 13, 16, 17, 18]. No anomaly appears at around 10 K, coming from the Néel temperature of $CeIn_3$. This assures that our $CePt_2In_7$ sample has no contamination of $CeIn_3$ in marked contrast with features appeared in the cubic-like crystals of Fig. 3. The residual resistivity ρ_0 and residual resistivity ratio are $0.38\,\mu\Omega\cdot$cm and 90, respectively, indicating that our sample is of high quality. The temperature dependence of ρ below 2.5 K is well fitted by the Fermi liquid relation of $\rho = \rho_0 + AT^2 (A = 3.2\times10^{-2}\,\mu\Omega\cdot$cm/K^2), as represented in the inset of Fig.4(b), where A is related to the Sommerfeld coefficient γ as the Kadowaki-Woods relationship : $A/\gamma^2 \simeq 1\times10^{-5}\,\mu\Omega\cdot$cm (mJ/K$\cdot$mol)$^{-2}$. $\gamma \simeq 57\,$mJ/K$^2\cdot$mol thus estimated is almost the same with previously reported ones[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 $T_N^{CeIn_3} = 10$ K corresponds to the antiferromagnetic ordering of $CeIn_3$. 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_3PtIn_{11} shows magnetic orderings at almost the same temperatures with T_N and T_m[19]. Therefore, we argue that these phase transitions likely correspond to magnetic orderings of Ce_3PtIn_{11} contained as the minor phase in the cubic-like crystals.

4. Summary

We were successful in growing single crystals of $CePt_2In_7$ and Ce_2PtIn_8 using the In self-flux method. The crystal structures of Ce_2PtIn_8 and $CePt_2In_7$ were confirmed by the single crystal X-ray diffraction method. $CePt_2In_7$ orders antiferromagnetically at temperatures below $T_N = 5.5$ K. We obtained relatively large crystals with complex internal constitution, which consists of inner $CeIn_3$, surface thin Ce_2PtIn_8 and contaminations such as $Ce_3Pt_4In_{13}$ and Ce_3PtIn_{11}. It implies a peritectic growth of Ce_2PtIn_8 on most likely the $CeIn_3$ (100) surface.

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, Seropegin 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 : Baue E D, Lee H O, Sidorov V A, Kurita N, Gofryk K, Zhu J -X, Ronning F, Movshovich R, Thompson J D, and Park T 2010 *Phys. Rev. B* **81** 180507(R)

[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, Müchler 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