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# High-quality single-crystal growth and unique electronic states in cerium and uranium compounds

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## Abstract

We have grown many kinds of high-quality single crystals of cerium and uranium compounds and studied the Fermi surface properties via the de Haas–van Alphen experiments and energy band calculations. The quasi-two-dimensional electronic states are clarified in some compounds such as USb<sub>2</sub>, CeCoIn<sub>5</sub>, UPtGa<sub>5</sub> and most likely UIr. In a ferromagnet CeRh<sub>3</sub>B<sub>2</sub>, we have found unique electronic states with quasi-one-dimensional character.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

The de Haas–van Alphen (dHvA) effect is a powerful method to determine the dHvA frequency  $F$  ( $= \hbar c S_F / 2\pi e$ ) which is proportional to the cross-sectional area of the Fermi surface  $S_F$ , the cyclotron effective mass  $m_c^*$  and the Dingle temperature  $T_D$  ( $= (\hbar / 2\pi k_B) \tau^{-1}$ ), which is inversely proportional to the scattering lifetime  $\tau$  of the conduction electron [1, 2]. In strongly correlated electron systems such as the cerium and uranium compounds, the cyclotron mass is extremely enhanced via the many-body Kondo effect. Low temperatures and high magnetic fields are necessary in detecting the dHvA oscillation because the detected dHvA amplitude is, simply expressed, proportional to  $\exp\{-\alpha(m_c^*/H)(T + T_D)\}$ , where  $\alpha$  is a constant. If the conduction electron with the cyclotron mass  $m_c^* = 1 m_0$  ( $m_0$ : rest mass of an electron) is detected at  $T = 1$  K, the same dHvA amplitude should be obtained at  $T = 0.01$  K for the

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**Table 1.** Uranium compounds and their properties studied by the dHvA experiments. Para, paramagnetic state; AFQ, antiferroquadrupolar ordering; F, ferromagnetic ordering; AF, antiferromagnetic ordering.

	Method	Structure	$\gamma$ (mJ K <sup>-2</sup> mol <sup>-1</sup> )	Ordering	Moment ( $\mu_B/U$ )	Transition temperature (K)
UPd <sub>3</sub>	Cz	Hexagonal	7.6	AFQ, AF	0.01	$T_0 = 7.5, T_1 = 6.8, T_2 = 4.5$
UB <sub>2</sub>	Cz	Hexagonal	10	Para		
UB <sub>4</sub>	Cz	Tetragonal	25	Para		
UAL <sub>3</sub>	Flux	Cubic	47	Para		
USi <sub>3</sub>	Cz	Cubic	12	Para		
UC	Cz	Cubic	40	Para		
UCoGa <sub>5</sub>	Flux	Tetragonal	3	Para		
URhGa <sub>5</sub>	Flux	Tetragonal	5	Para		
UGe <sub>2</sub>	Cz	Orthorhombic	30	F	1.4	$T_C = 52$
UIr	Cz	Monoclinic	49	F	0.5	$T_C = 46$
UGa <sub>2</sub>	Cz	Hexagonal	11	F	3.0	$T_C = 124$
U <sub>3</sub> P <sub>4</sub>	CT	Cubic	90	F	1.4	$T_C = 130$
U <sub>3</sub> As <sub>4</sub>	CT	Cubic	83	F	1.8	$T_C = 200$
UGa <sub>3</sub>	Flux	Cubic	50	AF	0.6	$T_N = 67$
UIn <sub>3</sub>	Flux	Cubic	40	AF	1	$T_N = 88$
UNiGa <sub>5</sub>	Flux	Tetragonal	50	AF	0.9	$T_N = 90$
UPtGa <sub>5</sub>	Flux	Tetragonal	67	AF	0.26	$T_N = 26$
UP <sub>2</sub>	CT	Tetragonal	27	AF	2	$T_N = 204$
UAs <sub>2</sub>	CT	Tetragonal	12	AF	1.6	$T_N = 274$
USb <sub>2</sub>	Flux	Tetragonal	26	AF	1.9	$T_N = 203$
UBi <sub>2</sub>	Flux	Tetragonal	20	AF	2.1	$T_N = 181$
UPt <sub>3</sub>	Cz	Hexagonal	420	AF	0.02	$T_N = 5, T_{sc} = 0.55$
UPd <sub>2</sub> Al <sub>3</sub>	Cz	Hexagonal	150	AF	0.85	$T_N = 14.5, T_{sc} = 2.0$
URu <sub>2</sub> Si <sub>2</sub>	Cz	Tetragonal	70	AF	0.02	$T_N = 17.5, T_{sc} = 1.4$

conduction electron with a large cyclotron mass  $m_c^* = 100 m_0$ . This is realized for  $T_D = 0$  K. In other words, the low temperature of 0.01 K is meaningless in detecting the dHvA oscillation for a large  $T_D = 1$ –10 K. The low temperatures and high magnetic fields, together with a high-quality single crystal with  $T_D$  less than 1 K, are necessary to detect the dHvA oscillation for the strongly correlated electron systems.

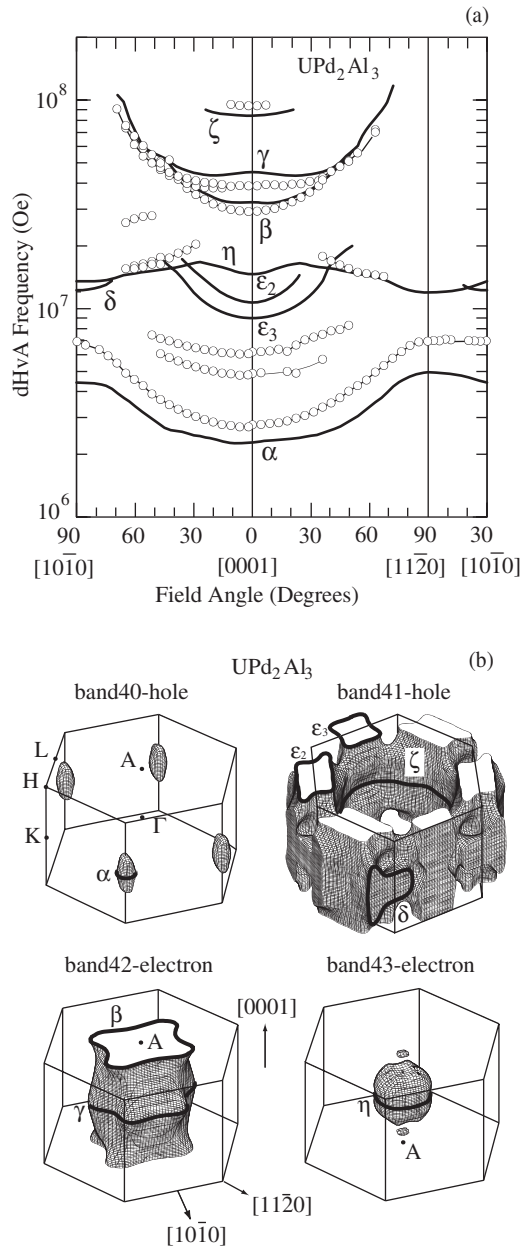
Table 1 shows the uranium compounds which we succeeded in growing by using many kinds of techniques for the crystal growth [3]. The unique electronic states of these compounds are clarified via the dHvA effect.

## 2. High-quality single-crystal growth and unique electronic states

The technique for the single-crystal growth is classified as shown in table 1, depending on the degree of the vapour pressure of the melt. If the vapour pressure is low, the Czochralski method, which is denoted as Cz in table 1, is a powerful technique to obtain a large size of single-crystal ingot. On the other hand, the flux method (flux) and the chemical transport method (CT) are utilized for those compounds (see table 1) which have high vapour pressure.

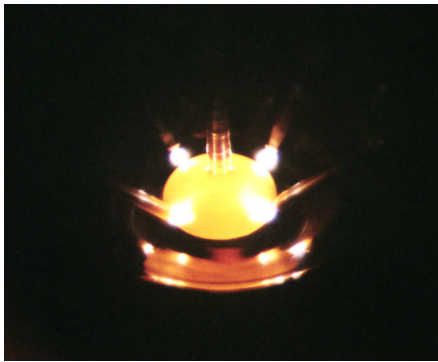
### 2.1. Czochralski method

The conduction electrons with  $100 m_0$  were detected in several compounds such as CeRu<sub>2</sub>Si<sub>2</sub> ( $m_c^* = 120 m_0$ ) [4], CeCoIn<sub>5</sub> ( $m_c^* = 87 m_0$ ) [5], UPt<sub>3</sub> ( $m_c^* = 105 m_0$ ) [6] and UPd<sub>2</sub>Al<sub>3</sub>

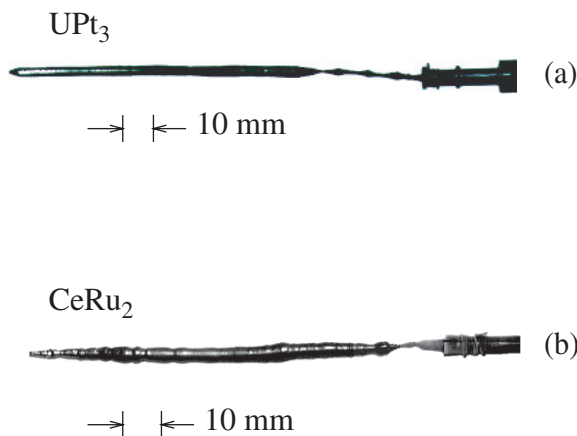


**Figure 1.** (a) Angular dependence of the dHvA frequency and (b) the corresponding Fermi surface in  $UPd_2Al_3$ .

( $m_c^* = 65 m_0$ ) [7]. In  $CeRu_2Si_2$ ,  $CeCoIn_5$  and  $UPt_3$ , a static magnetic ordering is not present, and the f-itinerant-band model is applicable for the topology of the Fermi surface, although the corresponding cyclotron mass is larger by one order of magnitude than the corresponding band mass. In  $UPd_2Al_3$  with a Néel temperature  $T_N = 14.5$  K and an ordered moment  $\mu = 0.85\mu_B/U$ , the 5f electrons possess a dual nature: the 5f electrons become itinerant and also contribute to the magnetic moment at the uranium site. Figure 1 shows the angular dependence of the dHvA frequency and the corresponding Fermi surface in  $UPd_2Al_3$ . Solid lines in figure 1(a) are the results of the spin-polarized LAPW band calculations. The



**Figure 2.** View of the single-crystal growth for  $\text{UPt}_3$  in the tetra-arc furnace.



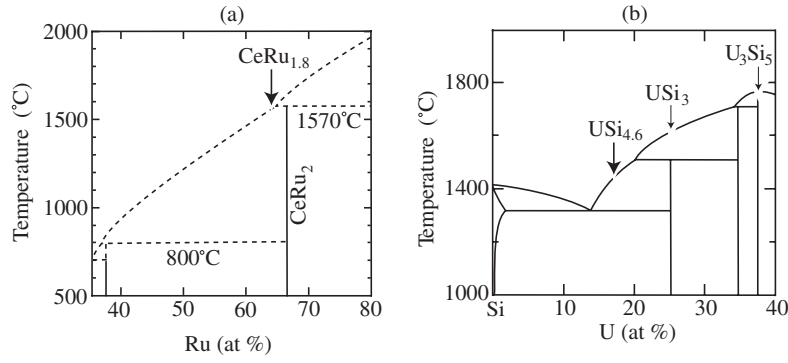
**Figure 3.** Single-crystal ingots of (a)  $\text{UPt}_3$  and (b)  $\text{CeRu}_2$ .

experimental results are in good agreement with the band calculations [7, 8]. The spin-polarized 5f-itinerant-band model is thus applicable in  $\text{UPd}_2\text{Al}_3$ . This result is important in understanding the magnetism and electronic states in the magnetically ordered uranium compounds.

The Czochralski method was useful in growing the single crystals of  $\text{UPd}_2\text{Al}_3$  as well as  $\text{CeRu}_2\text{Si}_2$  and  $\text{UPt}_3$ . Figures 2 and 3(a) show a view of the crystal growth in a tetra-arc furnace and a single-crystal  $\text{UPt}_3$  ingot, respectively. It is noted that there is no contamination between the melt of  $\text{UPt}_3$  and the water-cooled Cu hearth. In particular,  $\text{UPt}_3$  is a congruent compound with the highest melting temperature  $T_m = 1700^\circ\text{C}$  in a binary U–Pt phase diagram, meaning that other binary compounds such as  $\text{UPt}_6$ ,  $\text{UPt}_2$  and  $\text{UPt}$  are not included in  $\text{UPt}_3$ . Moreover, a low vapour pressure of  $\text{UPt}_3$  is a good condition for the crystal growth by using the Czochralski technique in the tetra-arc furnace. This method was also applied to the crystal growth for  $\text{UPd}_2\text{Al}_3$  and  $\text{CeRu}_2\text{Si}_2$ .

Furthermore, a single-crystal ingot of  $\text{UPt}_3$  was annealed under high vacuum of  $10^{-10}$  Torr via the electrotransport method. The degas effect for impurity gases immersed in the  $\text{UPt}_3$  ingot during the crystal growth was very effective in elevating the sample quality. It was clarified by the chemical analysis for a uranium ingot that an Fe impurity of 40 ppm in the starting uranium ingot was reduced to less than 2 ppm via the electrotransport method [9]. This annealing method was also applied to iron, where superconductivity  $T_{sc} = 1$  K was observed under pressure of about 30 GPa [10].

High-quality single crystals were grown in  $\text{CeRu}_2\text{Si}_2$ ,  $\text{UPt}_3$  and  $\text{UPd}_2\text{Al}_3$ . For example, the residual resistivity  $\rho_0$  and the residual resistivity ratio  $\rho_{RT}/\rho_0$  ( $\rho_{RT}$ : the resistivity at



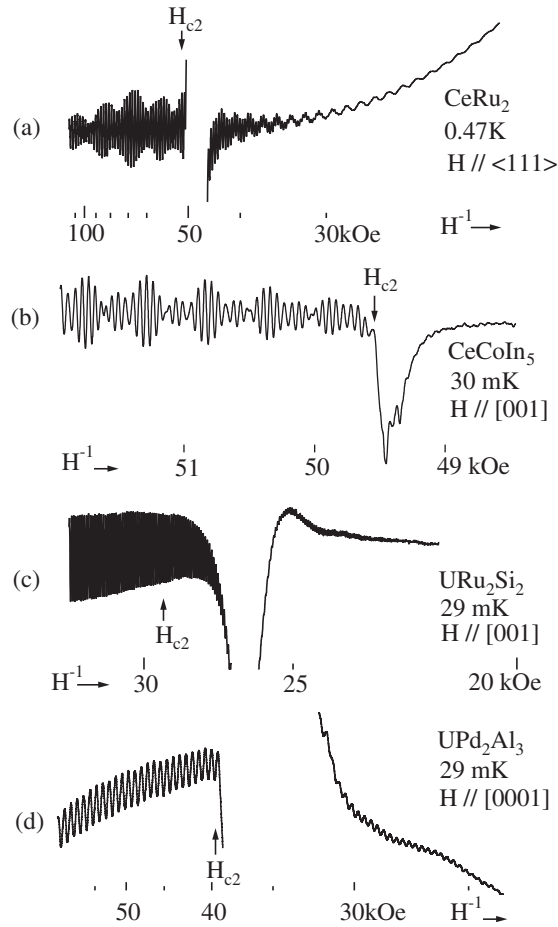
**Figure 4.** Binary phase diagrams of (a) CeRu<sub>2</sub> and (b) USi<sub>3</sub>.

room temperature) are 0.25  $\mu\Omega$  cm and 490 in CeRu<sub>2</sub>Si<sub>2</sub>, 0.18  $\mu\Omega$  cm and 680 in UPt<sub>3</sub> and 1.40  $\mu\Omega$  cm and 104 in UPd<sub>2</sub>Al<sub>3</sub>. In the dHvA experiments, we can estimate the mean free path  $l$  for a circular Fermi surface from the following relations:  $S_F = \pi k_F^2$ ,  $\hbar k_F = m_c^* v_F$ ,  $T_D = (\hbar/2\pi k_B)\tau^{-1}$  and  $l = v_F \tau$ , where  $k_F$  is the caliper length of  $S_F$  and  $v_F$  is the Fermi velocity. For example,  $l = 1200$  Å in UPt<sub>3</sub> is larger by one order than the coherence length  $\xi = 120$  Å in superconductivity. For this high-quality single crystal of UPt<sub>3</sub>, the NMR Knight shift experiments were done, clarifying that the superconductivity is of odd parity [11].

The Czochralski method was also applied to the incongruent compounds such as CeRu<sub>2</sub> and USi<sub>3</sub>. Figure 4 is the binary phase diagram of CeRu<sub>2</sub> and USi<sub>3</sub>. For these compounds, we prepared the off-stoichiometric starting materials of CeRu<sub>1.8</sub> and USi<sub>4.6</sub> in the tetra-arc furnace. Large single-crystal ingots 3–4 mm in diameter and 60 mm in length for CeRu<sub>2</sub> and USi<sub>3</sub> were grown, as shown in figure 3(b) for CeRu<sub>2</sub>. Annealing of the electrotransport method was also applied to the ingot, reaching the residual resistivity  $\rho_0 = 0.6$   $\mu\Omega$  cm and the residual resistivity ratio 270 in CeRu<sub>2</sub>. A very unique dHvA oscillation was detected for the present sample of CeRu<sub>2</sub> [12], as shown in figure 5(a). The dHvA oscillation was observed far below  $H_{c2} = 52$  kOe, down to a low field of 18 kOe or 0.3  $H_{c2}$ .

The dHvA oscillations are usually observed in the normal state under high-field conditions as mentioned above. This phenomenon was, however, observed even in the superconducting mixed state of CeRu<sub>2</sub> as well as CeCoIn<sub>5</sub>, URu<sub>2</sub>Si<sub>2</sub> and UPd<sub>2</sub>Al<sub>3</sub> [5, 7, 13], as shown in figure 5. The main Fermi surface named  $\alpha_i$  in CeCoIn<sub>5</sub> was detected in magnetic fields close to  $H_{c2}$ . Surprisingly, a small Fermi surface in CeRu<sub>2</sub>, URu<sub>2</sub>Si<sub>2</sub> and UPd<sub>2</sub>Al<sub>3</sub> was detected in low fields down to  $H/H_{c2} = 0.3$ –0.5. It is questionable whether the small Fermi surface has a superconducting energy gap in magnetic fields far below  $H_{c2}$ . This might indicate the growth of a pair-breaking effect far below  $H_{c2}$  for the small Fermi surface. More importantly, there is a possibility that the superconducting state for the small Fermi surface is changed into a normal state far below  $H_{c2}$ .

In the case of a ferromagnet UIr with a Curie temperature  $T_C = 46$  K, the binary phase diagram is extremely complicated. Nevertheless, we succeeded in growing a high-quality single crystal with the residual resistivity 0.5  $\mu\Omega$  cm and the residual resistivity ratio 200 [14]. Recently we observed superconductivity in a critical pressure region [15]. The Curie temperature  $T_C = 46$  K is reduced to zero at 1.7 GPa but another magnetic ordering with a ferromagnetic component along the [10 $\bar{1}$ ] direction appears above 1.9 GPa. The magnetic ordering temperature in the second magnetic phase also becomes zero around 2.6–2.7 GPa, where superconductivity sets in below 0.14 K. In the paramagnetic state above 2.9 GPa, superconductivity disappears completely.

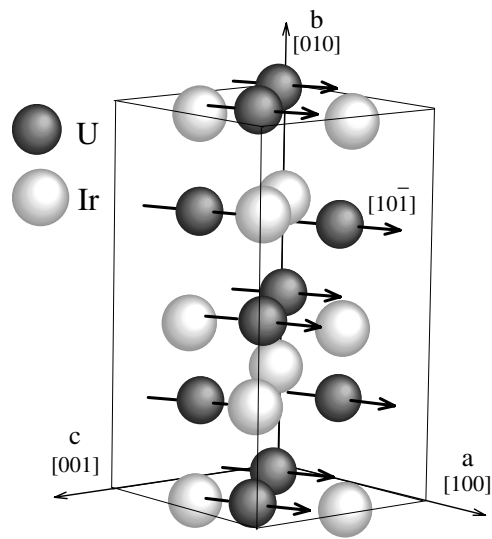


**Figure 5.** dHvA oscillations in the superconducting mixed states of CeRu<sub>2</sub>, CeCoIn<sub>5</sub>, UPd<sub>2</sub>Al<sub>3</sub> and URu<sub>2</sub>Si<sub>2</sub>.

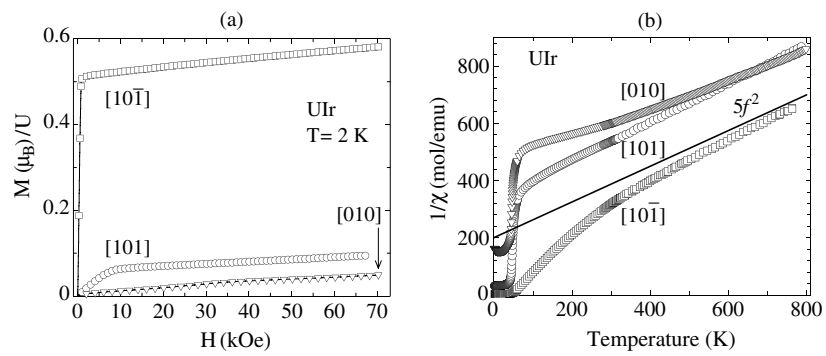
It is noted that the present superconductivity is unique because the crystal structure is of the monoclinic PbBi type, which lacks inversion symmetry (space group  $P2_1$ ,  $a = 5.62 \text{ \AA}$ ,  $b = 10.59 \text{ \AA}$ ,  $c = 5.60 \text{ \AA}$ ,  $\beta = 98.9^\circ$ ), as shown in figure 6. The magnetic moment of  $0.5\mu_B/U$  is oriented along  $[10\bar{1}]$ , as shown in figures 6 and 7(a) [16]. The other directions correspond to the hard axes in magnetization, indicating an Ising-like magnetization. This compound indicates the Curie–Weiss law with effective moments of  $5f^2$  or  $5f^3$  configuration at high temperatures,  $3.6\mu_B/U$ , as shown in figure 7(b). The saturation moment of  $0.5\mu_B/U$  is, however, small, most likely indicating  $5f$ -itinerant-band magnetism, similar to UGe<sub>2</sub> [17].

Figure 8 shows the angular dependence of the dHvA frequency in UIr. The dHvA branches are detected along the  $[010]$  direction ( $b$ -axis), reflecting the crystal structure. Namely, the crystal structure is elongated along the  $b$ -axis, which brings about a flat Brillouin zone along the  $b$ -axis, most likely producing cylindrical but highly corrugated Fermi surfaces along the  $b$ -axis. The cyclotron mass is relatively large, ranging from 10 to  $30 m_0$ , consistent with the electronic specific heat coefficient  $\gamma = 49 \text{ mJ K}^{-2} \text{ mol}^{-1}$ .

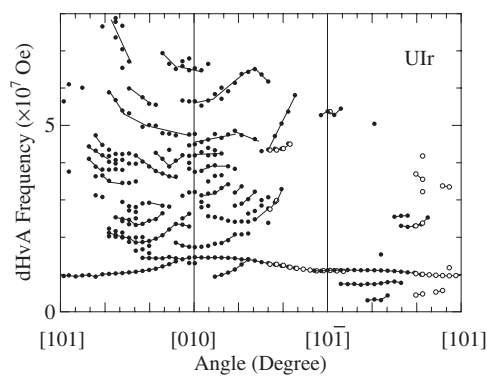
The tetra-arc furnace is useful for the crystal growth of compounds with a high-temperature melting point  $T_m \simeq 2000^\circ\text{C}$ . We succeeded in growing high-melting-point compounds such as UC ( $T_m = 2630^\circ\text{C}$ ), UB<sub>2</sub> ( $T_m = 2385^\circ\text{C}$ ), UB<sub>4</sub> ( $T_m = 2495^\circ\text{C}$ ) and CeRh<sub>3</sub>B<sub>2</sub>, where the melting point of CeRh<sub>3</sub>B<sub>2</sub> is unknown but is estimated to be above  $2000^\circ\text{C}$ . Among these



**Figure 6.** Crystal structure of UIr. The magnetic moment is directed along  $[10\bar{1}]$ .

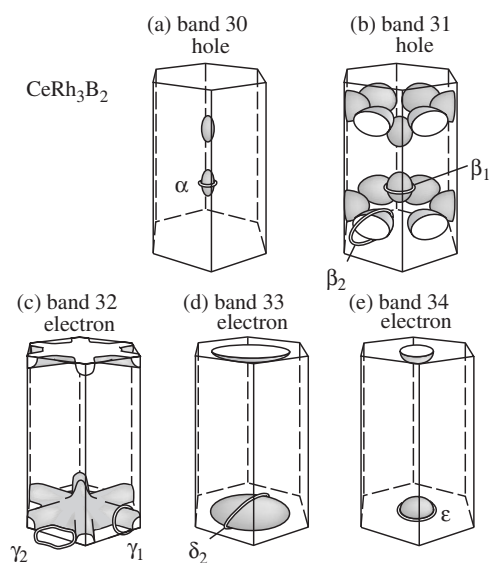


**Figure 7.** (a) Magnetization and (b) the temperature dependence of the inverse magnetic susceptibility in UIr.



**Figure 8.** Angular dependence of the dHvA frequency in UIr.





**Figure 9.** Fermi surfaces with a quasi-one-dimensional character in  $\text{CeRh}_3\text{B}_2$ .

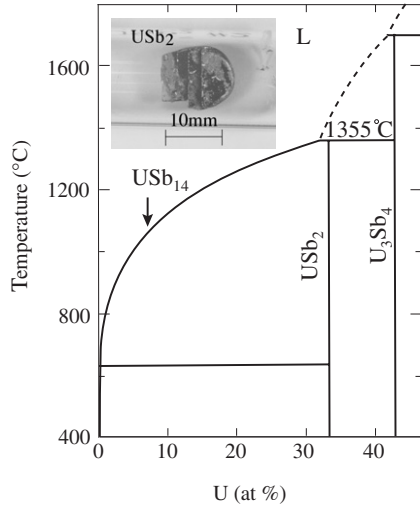
compounds,  $\text{CeRh}_3\text{B}_2$  is a unique compound with the highest Curie temperature  $T_C = 120$  K in the cerium compounds. Surprisingly, the Curie temperature  $T_C = 120$  K is far above  $T_C = 91$  K in  $\text{GdRh}_3\text{B}_2$ . This means  $T_C = 120$  K in  $\text{CeRh}_3\text{B}_2$  is higher by two orders of magnitude than the magnetic ordering temperature expected from the de Gennes factor scaling. An ordered magnetic moment of  $0.4 \mu_B/\text{Ce}$ , which is oriented along the  $[10\bar{1}0]$  direction of the hexagonal structure, is small compared to the usual value of about  $1 \mu_B/\text{Ce}$ .

We have carried out the dHvA experiments on a ferromagnet  $\text{CeRh}_3\text{B}_2$  and a non-4f reference compound  $\text{LaRh}_3\text{B}_2$  [18]. The dHvA data of  $\text{LaRh}_3\text{B}_2$  are well explained by the results of energy band calculations. Flat Fermi surfaces are realized in  $\text{LaRh}_3\text{B}_2$ . This is because the lattice constant along the  $c$ -axis ( $[0001]$  direction) is very short, which enhances the quasi-one-dimensional (1D) conductivity along the  $c$ -axis. The topology of the Fermi surfaces in  $\text{CeRh}_3\text{B}_2$  is found to be experimentally very similar to that of  $\text{LaRh}_3\text{B}_2$ , possessing wavy but flat Fermi surfaces in the basal plane, as shown in figure 9, which was obtained experimentally on the basis of the Fermi surface of  $\text{LaRh}_3\text{B}_2$ . The observation of quasi-1D electronic states in these two compounds is the first case in the rare earth compounds.

## 2.2. Flux method

The flux method is also a useful technique for a high-vapour-pressure case of the melt. In particular, the compounds containing Zn, Cd, Al, Ga, In, Sn, Pb, Sb and Bi metals are grown as single crystals by the so-called self-flux method. Figure 10 shows the U–Sb binary phase diagram. Starting materials with  $\text{USb}_{14}$  were set in a crucible, as shown by an arrow in figure 10. The temperature was heated up to  $1050^\circ\text{C}$  and cooled down to  $600^\circ\text{C}$  with a rate of  $0.5^\circ\text{C h}^{-1}$ . Many pieces of single crystals of  $10 \times 10 \times 5 \text{ mm}^3$  were grown, as shown in the inset. Excess antimony was removed by using a centrifuge.

Uranium dipnictides  $\text{UX}_2$  (X: Bi, Sb, As and P) crystallize in the tetragonal structure of anti- $\text{Cu}_2\text{Sb}$  type ( $D_{4h}^7$  of  $P4/nmm$ ). They order antiferromagnetically. The magnetic moments of uranium ions are aligned ferromagnetically in the (001) planes, which are stacked along the  $[001]$  direction in an antiferromagnetic ( $\uparrow\downarrow$ ) sequence in  $\text{UBi}_2$ . In the case of  $\text{USb}_2$ ,  $\text{UAs}_2$  and  $\text{UP}_2$ , this sequence is ( $\uparrow\downarrow\downarrow\uparrow$ ). It is worth mentioning here that the magnetic unit cell of  $\text{USb}_2$ ,



**Figure 10.** U–Sb binary phase diagram. The inset shows the  $\text{USb}_2$  single crystal.

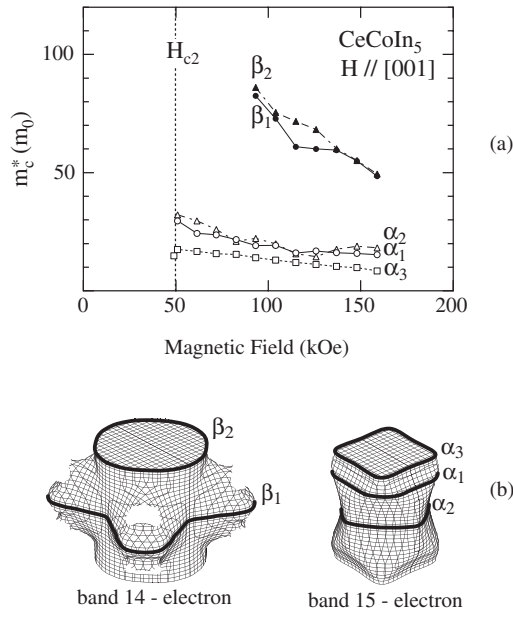
$\text{UAs}_2$  and  $\text{UP}_2$  is doubled with respect to the chemical unit cell along [001], which brings about a flat magnetic Brillouin zone.

We have studied the Fermi surface properties from the dHvA experiments. The Fermi surface of  $\text{UBi}_2$  is found to consist of one spherical hole Fermi surface and two cylindrical electron Fermi surfaces. For  $\text{USb}_2$  with  $T_N = 203$  K, we observed a quasi-two-dimensional Fermi surface [19]. Namely, each Fermi surface in  $\text{UBi}_2$  splits into two cylindrical Fermi surfaces in  $\text{USb}_2$ , which are well explained by the band-folding procedure in a flat magnetic Brillouin zone. The quasi-2D character of these Fermi surfaces is mainly due to the conduction electrons in the U plane, including the 5f electrons, because the cyclotron masses of compensated electron and hole carriers are moderately large, ranging from 2.0 to 6.0  $m_0$ .

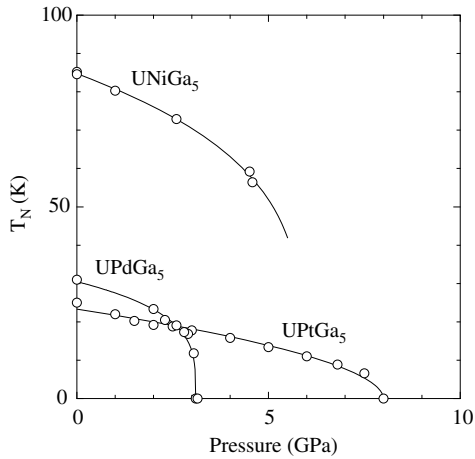
Quasi-2D Fermi surfaces were observed in  $\text{CeAgSb}_2$  [20],  $\text{CeTIn}_5$  (T: Co, Rh, Ir) [21],  $\text{UTGa}_5$  (T: Fe, Ni, Pt) [21, 22] and  $\text{CePtX}$  (X: P, As) [23] compounds. Among them,  $\text{CeCoIn}_5$  with the tetragonal structure is typical in the Fermi surface properties.  $\text{CeTIn}_5$ ,  $\text{UTGa}_5$  and  $\text{PuTGa}_5$  (T: transition metal) crystallize in the same tetragonal crystal structure. In  $\text{CeTIn}_5$ , uniaxially distorted  $\text{AuCu}_3$ -type layers of  $\text{CeIn}_3$  and the  $\text{TIn}_2$  layers are stacked sequentially along the [001] direction (*c*-axis). The d electrons in the T atom hybridize with the 5p electrons of In in  $\text{CeTIn}_5$ , which results in a small density of states around the Fermi energy. This means that there are very few conduction electrons in the  $\text{TIn}_2$  layer and hence the Fermi surface mainly consists of two kinds of cylindrical Fermi surfaces.

Figure 11 shows the field dependence of the cyclotron mass for branches  $\alpha_i$  and  $\beta_i$  and their cylindrical Fermi surfaces. Both Fermi surfaces are mainly of 4f-electron character. Branch  $\beta_i$  (band 14-electron Fermi surface) is expected to possess a cyclotron mass of 100  $m_0$  at low fields, while branch  $\alpha_i$  possesses the cyclotron mass of 15–30  $m_0$ . It has been pointed out theoretically that the magnetically mediated pairing is more robust for the nearly antiferromagnetic system (for example, a spin-singlet  $d_{x^2-y^2}$  state) than for the ferromagnetic one (a spin-triplet p-wave state) and is more favourable in the quasi-two-dimensional than three-dimensional systems [24].

Here we note the superconducting transition temperature  $T_{sc}$ .  $\text{PuCoGa}_5$  is a superconductor with a large  $T_{sc}$  value of 18.5 K and a relatively large  $\gamma$  value of  $\gamma = 77 \text{ mJ K}^{-2} \text{ mol}^{-1}$  [25]. This  $\gamma$  value is smaller by one order of magnitude than that of  $\text{CeCoIn}_5$ . Therefore a relatively large band width, together with two dimensionality, probably enhances the superconducting



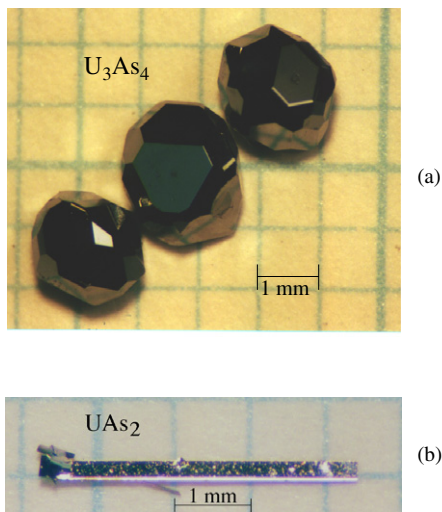
**Figure 11.** (a) Field dependence of the cyclotron mass for branches  $\alpha_i$  and  $\beta_i$  and (b) the corresponding main cylindrical Fermi surfaces in CeCoIn<sub>5</sub>.



**Figure 12.** Pressure dependence of the Néel temperature for UNiGa<sub>5</sub>, UPdGa<sub>5</sub> and UPtGa<sub>5</sub>.

transition temperature in PuCoGa<sub>5</sub>. It is interesting to note the  $T_{sc}$  values:  $T_{sc} = 0.22$  K in CeIn<sub>3</sub> under 2.7 GPa with a three-dimensional Fermi surface, 2.3 K in CeCoIn<sub>5</sub> and 18.5 K in PuCoGa<sub>5</sub>. The correlation of  $T_{sc}$  with the band width can be extended to a large  $T_{sc}$  value of high- $T_{sc}$  cuprates, where the itinerant 3d electrons in the CuO<sub>2</sub> plane are responsible for superconductivity. We also note the electronic states of UCoGa<sub>5</sub>. It is a Pauli paramagnet and possesses small closed Fermi surfaces, indicating a semimetal [21]. This is a reason why superconductivity is not realized in UCoGa<sub>5</sub>.

There is, however, a possibility of pressure-induced superconductivity in antiferromagnets UTGa<sub>5</sub> (T: Ni, Pd and Pt). For example, Fermi surfaces of UPtGa<sub>5</sub> are quasi-two-dimensional. Four kinds of cylindrical Fermi surfaces with 10–24 $m_0$  were observed in the dHvA experiments [22]. Figure 12 shows the pressure dependence of the Néel temperature for UNiGa<sub>5</sub> (a Néel temperature  $T_N = 86$  K, an ordered moment  $\mu = 0.90\mu_B/U$ ), UPdGa<sub>5</sub>



**Figure 13.** Single crystals of (a)  $U_3As_4$  and (b)  $UAs_2$ .

( $T_N = 31$  K,  $\mu = 0.33 \mu_B/U$ ) and  $UPtGa_5$  ( $T_N = 26$  K,  $\mu = 0.26\mu_B/U$ ). The Néel temperature decreases with increasing pressure and becomes zero at a critical pressure  $P_c = 6$ – $7$  GPa in  $UNiGa_5$ ,  $P_c = 3$  GPa in  $UPdGa_5$  and  $P_c = 8$  GPa in  $UPtGa_5$ . We are now searching for superconductivity around  $P_c$  for these compounds.

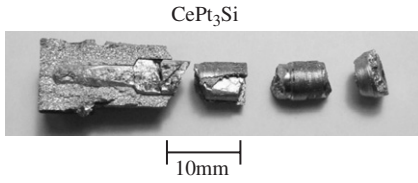
### 2.3. Chemical transport method with iodine

In the extremely-high-vapour-pressure case of the melt, a chemical transport method using iodine vapour is useful for the compounds containing P, As, S, Se and Te elements. Figure 13 shows a photograph of  $U_3As_4$  and  $UAs_2$  single crystals. The stoichiometric amounts of U and As in  $U_3As_4$  were sealed together with  $3 \text{ mg cm}^{-3}$  iodine in an evacuated quartz ampoule. The ampoule was gradually heated and retained at  $950^\circ\text{C}$  for four days until pre-reaction of U with As was completed. Then the ampoule was placed in the temperature gradient with a hot region at  $925^\circ\text{C}$  and a hotter region at  $975^\circ\text{C}$  for two weeks. Many but small single crystals were grown on the wall of the ampoule.

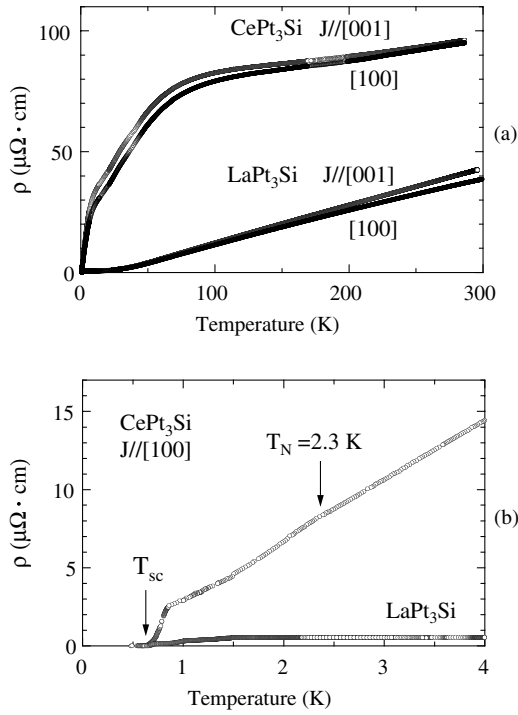
The dHvA experiments were done for  $U_3As_4$  as well as  $U_3P_4$  [26]. The cyclotron effective mass of the detected Fermi surfaces is large, ranging from 5 to  $70 m_0$ . High-pressure experiments using a diamond anvil cell were also done for  $U_3P_4$  [27]. The Curie temperature  $T_C = 138$  K decreases with increasing pressure and becomes zero at  $P_c = 5$  GPa. The coefficient  $A$  of the resistivity  $\rho = \rho_0 + AT^2$  becomes maximum at  $P_c$ :  $A = 0.05 \mu\Omega \text{ cm K}^{-2}$  at ambient pressure and  $0.92 \mu\Omega \text{ cm K}^{-2}$  at 5 GPa. Superconductivity was, however, not observed in this compound down to 0.1 K. It is noted that the crystal structure ( $T_d^6$  or  $I\bar{4}3d$ ) lacks inversion symmetry.

### 2.4. Bridgman method

The Bridgman method is useful in the same high-vapour-pressure case of the melt, and also for the incongruent compounds. For example, in the case of a new heavy-fermion superconductor  $CePt_3Si$ , the Czochralski and Bi- and Sn-flux methods were not useful in growing a single crystal because this compound is an incongruent compound. The Bridgman and/or mineralization methods were applied to it. The starting materials were arc-melted, sealed in a Mo crucible. The crucible was heated up to  $1450^\circ\text{C}$  and cooled down gradually.



**Figure 14.** Cross-section of the single-crystal ingot of CePt<sub>3</sub>Si in a Mo crucible.



**Figure 15.** Temperature dependence of the electrical resistivity in CePt<sub>3</sub>Si and LaPt<sub>3</sub>Si.

Figure 14 shows the cross-section of a single-crystal ingot of CePt<sub>3</sub>Si in the Mo crucible. We show in figure 15 the temperature dependence of the electrical resistivity in CePt<sub>3</sub>Si and LaPt<sub>3</sub>Si single crystals. The electrical resistivity for  $J \parallel [100]$  and  $[001]$  is almost the same, indicating the 3D electronic states in CePt<sub>3</sub>Si and LaPt<sub>3</sub>Si. Both compounds become superconductive below 0.6–0.7 K.

CePt<sub>3</sub>Si is unique, possessing a few characteristics [28]. Superconductivity is realized in the long-range antiferromagnetic ordering. The Néel temperature is 2.2 K, while the superconducting transition temperature is 0.75 K. Both transitions were observed clearly in the specific heat measurement. The electronic specific heat coefficient  $\gamma$  is large, 300–400 mJ K<sup>-2</sup> mol<sup>-1</sup>. Moreover, CePt<sub>3</sub>Si lacks a centre of symmetry in the tetragonal structure ( $P4mm$ ). The existence of inversion symmetry in the crystal structure is believed to be a favourable factor for superconductivity. The absence of superconductivity in, for example, a ferromagnet MnSi [29] or U<sub>3</sub>P<sub>4</sub> mentioned above has been tentatively attributed to a lack of inversion symmetry. Theoretical considerations are needed to clarify the relation between superconductivity and lack of inversion symmetry for CePt<sub>3</sub>Si and also UIr.

### 3. Concluding remarks

We have presented the unique electronic states, focusing on the quasi-2D electronic states, which are closely related to the crystal structure elongated along the *c*-axis in the tetragonal or hexagonal structures. It was clarified experimentally and theoretically that the superconducting transition temperature in the quasi-2D compounds, for example  $T_{sc} = 2.3$  K in CeCoIn<sub>5</sub>, is enhanced compared to that in the 3D compounds, 0.2 K in CeIn<sub>3</sub> under 2.7 GPa. The quasi-2D electronic states are also found to be formed by the flat magnetic Brillouin zone as in USb<sub>2</sub>.

In the magnetically ordered uranium compounds, the 5f electrons contribute to the volume of the Fermi surface and also to the magnetic moment of the uranium site, possessing a dual nature. We presented that the Fermi surface in UPd<sub>2</sub>Al<sub>3</sub> is well explained by the spin-polarized 5f-itinerant-band model. This model is also applicable to an antiferromagnet UPtGa<sub>5</sub>, but not applicable to all the magnetically ordered uranium compounds. For example, the dHvA data of a ferromagnet UGa<sub>2</sub> ( $T_C = 124$  K, a saturation moment  $3.0 \mu_B/U$ ) are explained by neither the spin-polarized 5f-itinerant-band model nor the 5f-localized-band model [30]. It is noted that the 5f-localized-band model is applicable to the dHvA data of an antiferroquadrupolar compound, UPd<sub>3</sub> [31], where the 5f electrons are clarified to be localized from the neutron scattering experiment. On the other hand, the conventional 5f-itinerant-band model is well applicable to the non-magnetic uranium compounds including UPt<sub>3</sub>. For the magnetically ordered uranium compounds, it is furthermore needed to study the Fermi surface property experimentally and theoretically.

In the non-magnetic cerium compounds including CeRu<sub>2</sub>Si<sub>2</sub> and CeCoIn<sub>5</sub>, it is also clarified that the dHvA data are well explained by the 4f-itinerant-band model. On the other hand, the 4f electron in the magnetically ordered cerium compounds does not contribute to the volume of the Fermi surface but to the magnetic moment at the cerium site. In an antiferromagnet CeRh<sub>2</sub>Si<sub>2</sub>, the nature of the 4f electron was tuned by pressure and it was clarified via the dHvA experiment and the energy band calculation that a discontinuous change of the Fermi surface from 4f localized to itinerant occurs at a critical pressure  $P_c \simeq 1.06$  GPa, implying a first-order phase transition [32]. It is now needed to clarify the Fermi surface property of a new heavy-fermion superconductor CePt<sub>3</sub>Si. In CePt<sub>3</sub>Si, together with UIr, many experimental and theoretical studies are needed to clarify superconductivity without space inversion symmetry.

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