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Solution Growth and Investigation of the Single Crystals from the CePdIn System

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We report on the investigation of recently discovered heavy fermion compounds within the Ce-Pd-In system. Single crystals of $Ce_nPd_mIn_{3n+2m}$ ($n = 2, 3, 5$; $m = 1, 2$) and $Ce_4Pd_{10}In_{21}$ were synthesized from In-flux. Specific heat measurements of the multiphase $Ce_nPd_mIn_{3n+2m}$ system revealed a superconducting transition at $T_c = 0.69$ K arising from Ce_2PdIn_8 and another, magnetic transition at $T_m = 1.67$ K arising from either Ce_3PdIn_{11} or $Ce_5Pd_2In_{19}$. Low-temperature data of $Ce_4Pd_{10}In_{21}$ display ferromagnetic long-range order below 0.8 K.

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1. Introduction

The family of $Ce_nT_mIn_{3n+2m}$ ($n = 1, 2$; $m = 1$; T = transition metal) heavy fermion compounds has been heavily investigated because of being located on the verge of a quantum critical point [1]. While the heavy fermion superconductor Ce_2PdIn_8 has been thoroughly studied since the first synthesis [2, 3], the Ce_3PdIn_{11} and $Ce_5Pd_2In_{19}$ compounds were discovered only recently [4], and represent a new structure types of the series. Both structure types can be viewed as n blocks of $CeIn_3$ alternating with m blocks of $PdIn_2$ along the c -axis. The first type follows the well-known series $n = 1, 2 \dots$ and $m = 1$, while the second type consists of $n = 5$ and $m = 2$. Both compounds reveal Curie-Weiss behavior without any long range magnetic ordering down to 1.72 K. The ternary phase diagrams are poorly investigated in the In-rich regions, leaving the temperature stability of the Ce-Pd-In compounds as an open question. To shed light on their single crystal growth conditions, we have focused on refinement of the crystallization process. Magnetic transitions are well pronounced in the specific heat.

2. Experimental methods

Single crystal samples were grown from indium flux. The crucibles containing high purity elements were sealed under vacuum in quartz glass tubes and heated up quickly to maximum temperature (~ 200 °C/h), at which they were kept for several hours (8–10 h) before cooling down at a rate of 2.5 °C/h. Details of the sample preparation are provided below. The X-ray analysis was performed using powder diffractometer Bruker AXS D8 Advance. The samples were further investigated using scanning electron microscope Tescan Mira I LMH equipped with the microprobe analyser (EDX) Bruker AXS. The low-temperature part of the specific heat (0.35–2 K) was measured in PPMS 9 T using the He3 insert by *Quantum Design*.

3. Results and discussion

In order to prepare single crystals of Ce_2PdIn_8 , $Ce_5Pd_2In_{19}$ and Ce_3PdIn_{11} we have made several at-

tempts of changing the temperature of process and the composition. The stoichiometries varied from Ce:Pd:In = 3:1:25(55) and 2:1:25(55) to 1:3:25(55). Whereas the high-temperature growth of Ce_2TIn_8 compounds in the temperature region of 950–500 °C leads in general to the desired result, in case of Pd compound only thin layers (~ 50 – 100 μm) of Ce_2PdIn_8 grown on bulk $CeIn_3$ were usually obtained [5]. Moreover, two other impurity phases, Pd_3In_7 and $Ce_4Pd_{10}In_{21}$, were detected, although in minor amounts. The Ce_2PdIn_8 compound exists in the 500 °C [2] and 600 °C [4] isothermal sections of the Ce-Pd-In system while the Ce_3PdIn_{11} and $Ce_5Pd_2In_{19}$ compounds appear only in the 600 °C isothermal section [4]. These facts led us to experiments with the cooling range of 750–300 °C, which produced grains of Ce_3PdIn_{11} growing within the $Ce_5Pd_2In_{19}$ and Ce_2PdIn_8 phase. Their presence was confirmed by both powder diffraction (not shown) and EDX analysis (see left panel of Fig. 1) The quality of pure Ce_2PdIn_8 compound can be partially improved by shifting the maximum growth temperature to even lower values of around 450 °C. However, the presence of other phases cannot be avoided completely. In addition, the mass of these single crystals, grown at such low temperatures, is comparable to the mass of the Ce_2PdIn_8 fraction samples containing the $CeIn_3$ impurity, grown at high temperatures. Thus, this preparation method does not bring any significant advantage. Unfortunately, the question of preparing single-phase single crystals with dimensions comparable to other Ce_2TIn_8 compounds still remains open.

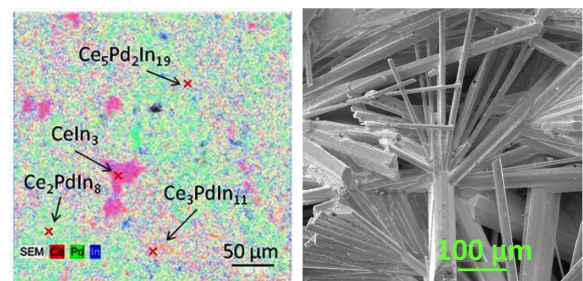


Fig. 1. EDX mapping of one of the measured samples (left); SEM image of the $Ce_4Pd_{10}In_{21}$ single crystals (right).

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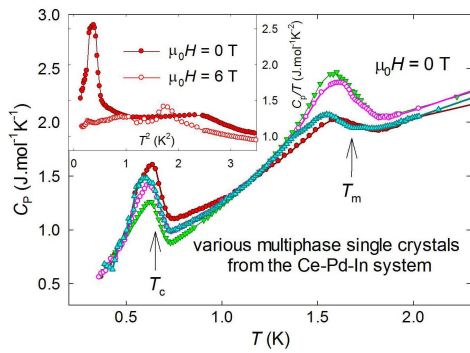


Fig. 2. Specific heat of multiphase samples in zero magnetic field. The arrows mark the superconducting transition at T_c and the magnetic transition at T_m . The inset depicts the evolution of one selected sample in higher magnetic fields.

As the next step, we measured specific heat of selected multiphase single crystals (Fig. 2). Measurement on four different samples showed a transition at $T_c = 0.67$ K, being attributed to superconductivity in Ce_2PdIn_8 [3]. The other transition, observed at $T_m = 1.67$ K, shifts to lower temperatures in applied magnetic field, indicating antiferromagnetic order at the origin of this anomaly (inset in Fig. 2). Interestingly, this peak was reported only once before [6]. More precise, the T_m -transition has never been observed in polycrystalline or pure single phase single crystals. The true nature of this transition remains unclear. Both transitions T_c and T_m are observed in all measured samples but the ratios of areas given by the superconducting and magnetic peaks vary for different samples. This effect is given by the multiphase nature of the samples. Obviously, it is not an intrinsic property of Ce_2PdIn_8 [3] but it might be coming from $\text{Ce}_3\text{PdIn}_{11}$, $\text{Ce}_5\text{Pd}_2\text{In}_{19}$ (see Fig. 1) or, although not resolved in EDX, $\text{Ce}_4\text{Pd}_{10}\text{In}_{21}$.

The $\text{Ce}_4\text{Pd}_{10}\text{In}_{21}$ phase appears as a by-product of the $\text{Ce}_n\text{PdIn}_{3n+2}$ single crystal growth together with CeIn_3 and Pd_3In_7 . The physical properties of CeIn_3 have been studied thoroughly and the single crystals of Pd_3In_7 grow always separately from other phases, thus none of these impurities provides an explanation of the transition at 1.67 K. Since the low-temperature properties of $\text{Ce}_4\text{Pd}_{10}\text{In}_{21}$ have never been reported to our knowledge, we have performed further measurements to disclose possible presence of this phase as an impurity in our samples. The needle-like (~ 2 mm) single-phase single crystals (see the right panel of Fig. 1) were grown from starting stoichiometry 1:3:55. The X-ray diffraction confirmed the $\text{Ho}_4\text{Ni}_{10}\text{Ga}_{21}$ monoclinic structure [7] and the study of lattice parameters yield $a = 23.1522$ Å, $b = 4.5514$ Å, $c = 17.2433$ Å and $\beta = 124.59^\circ$. The specific heat of three single crystals together (total mass 0.5 mg) was measured down to 0.35 K (see Fig. 3), to obtain relevant information about possible transitions in this compound. A peak is observed at $T = 0.8$ K. We attributed this to ferromagnetic ordering, as it broadens and shifts to higher temperatures with increasing magnetic field applied perpendicular to the needles. More important,

the results clearly exclude the presence of this phase in $\text{Ce}_n\text{PdIn}_{3n+2}$ multiphase samples, leaving a possibility of magnetic ordering at $T_m = 1.67$ K either in $\text{Ce}_3\text{PdIn}_{11}$ or $\text{Ce}_5\text{Pd}_2\text{In}_{19}$ compound. A simple $C/T = \gamma + \beta T^2$ fit was utilized and the Sommerfeld coefficient yields $\gamma \approx 110$ mJ mol ^{-1}Ce K $^{-2}$, qualifying $\text{Ce}_4\text{Pd}_{10}\text{In}_{21}$ as a HF compound.

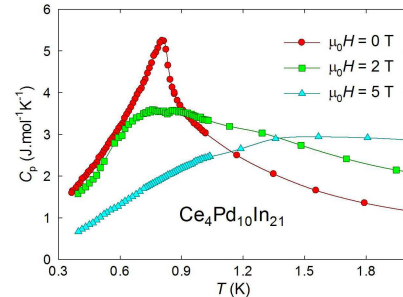


Fig. 3. Specific heat of $\text{Ce}_4\text{Pd}_{10}\text{In}_{21}$ in various magnetic fields.

4. Conclusions

A detailed study of the solution growth of the phases within the Ce-Pd-In system was performed in order to obtain single phase samples of Ce_2PdIn_8 , $\text{Ce}_3\text{PdIn}_{11}$ and $\text{Ce}_5\text{Pd}_2\text{In}_{19}$ compounds. Although the refinement of the growth parameters is still in progress, we have already suggested the explanation of the origin of the magnetic transition at $T_m = 1.67$ K, observed in Ref. [6]. The single crystals of the $\text{Ce}_4\text{Pd}_{10}\text{In}_{21}$ phase, which also appears in the Ce-Pd-In phase diagram as an impurity phase, were prepared for the first time. The bulk measurement indicates the ferromagnetic long-range order below 0.8 K.

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