Study on CePtIn$_4$ grown in a platelet-like morphology

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We present the results of our comprehensive structural investigation performed on single crystals of CePtIn$_4$ grown from In flux in a platelet-like morphology. They were found to crystallize in an orthorhombic structure having space group $Cmcm$ (no. 63) with the lattice parameters $a = 4.52175$ (15) Å, $b = 16.7777$ (5) Å, and $c = 7.3903$ (2) Å. The unit cell volume of such crystals is slightly larger than that of previously reported needle-shaped single crystals of CePtIn$_4$. This feature seems to influence the low-temperature physical properties of the compound, such as enhanced ordering temperature ($T_N = 2.3$ K versus $1.65$ K, observed before) along with a sharp drop in the electrical resistivity at $T_N$ (that was absent for the needle-like CePtIn$_4$).

Key words: Cerium compounds; Flux growth; Crystal structure; Antiferromagnetic order

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1. Introduction

Since a few decades cerium-bearing compounds have attracted much research interest due to their diverse intriguing electronic properties, such as heavy-fermion behavior, spin and valence fluctuations, non-Fermi liquid features, complex magnetic ordering, superconductivity, quantum criticality, etc. [1-3]. In recent years, extensive studies were performed on ternary cerium indides, like heavy-fermion superconductors CeCoIn$_5$ [4] and Ce$_2$PdIn$_8$ [5,6], with paramagnetic ground states, heavy-fermion systems Ce$_3$PtIn$_{11}$ [7-9] and Ce$_3$PdIn$_{11}$ [10,11], in which superconductivity coexists with long-range antiferromagnetic ordering, as well as non-superconducting antiferromagnetic or ferromagnetic Kondo lattices, such as Ce$_6$Pd$_{12}$In$_5$ [12] and Ce$_{11}$Pd$_4$In$_9$ [13], respectively.

Most recently, we reported on the formation of a novel phase in the ternary Ce-Pt-In system, namely CePtIn$_4$ [14]. Sizable needle-like single crystals of this compound were grown from In flux. They were found to crystallize with an orthorhombic crystal structure of the YNiAl$_4$-type. Measurements of their electrical transport and thermodynamic properties revealed metallic conductivity, Curie-Weiss paramagnetism due to Ce$^{3+}$ ions with well localized 4f-electrons, and antiferromagnetic order below $T_N = 1.65$ K.

Continuing our search for novel Ce-Pt-In ternaries, focused at hypothetical CePtIn$_5$, we ended up getting single crystals of the CePtIn$_4$ phase, yet with platelet-like morphology, distinctly different from that observed earlier [14]. Here, we report the results of our detailed crystallographic study of these new crystals (platelets, hereafter labeled P-type) and compare them with those of the crystals examined before (needles, labeled N-type). We also describe the low-temperature physical properties of the P-type crystals, which appeared to differ somewhat from those of the N-type ones.

2. Experimental

Single crystals of CePtIn$_4$ were synthesized using In flux method. The constituent elements (Ce-3N, Pt-4N and In-5N) were taken in the molar ratio of Ce:Pt:In = 1:1:27 and placed in an alumina crucible, which was then sealed in a quartz ampule under 0.3 atm. of argon. The ampule was first heated in a resistance furnace up to 1200 °C, kept at this temperature for 48 hours, and then cooled down to 750 °C at a rate of 150 °C/hour, maintained at this point for 10 hours, and
finally cooled down to 550 °C at a rate of 1 °C/hour. At the latter temperature, In flux was decanted using a centrifuge. The so-obtained single crystals had a form of well-developed platelets with typical dimensions $1 \times 1 \times 0.06 \text{ mm}^3$. In Figure 1, we present a photograph of the as-grown crystals. For comparison, we show in that figure also the crystals investigated in Ref. 13, which have a form of needles.

Chemical composition of the single crystals was examined by energy dispersive x-ray (EDX) analysis using a FEI scanning electron microscope equipped with an EDAX spectrometer. The results indicated that the obtained platelet-like single crystals are homogeneous and have the expected stoichiometry.

The X-ray diffraction (XRD) intensities were collected at 295 K on an Oxford Diffraction four-circle diffractometer equipped with an Atlas CCD detector using graphite-monochromatized MoK$_\alpha$ radiation ($\lambda = 0.71073$ Å). The raw data were treated with the CrysAlis Data Reduction Program (version 1.171.38.34a). The Bragg intensities were corrected for Lorentz and polarization effects. The absorption was corrected by numerical methods based on Gaussian integration over a multifaceted crystal model and empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. The crystal structure was solved by direct methods and refined by full-matrix least-squares method using SHELXS-2014 and SHELXL-2014 programs, respectively [15]. The structure was refined using anisotropic displacement parameters for each atom. Visualizations of the structure were made using Diamond 3.2k [16].

Magnetic measurements were performed in the temperature range 1.8 K – 300 K using a Quantum Design MPMS-XL SQUID magnetometer. The electrical resistivity was measured over the temperature range 1.8 K – 300 K employing standard ac four-probe technique implemented in a Quantum Design PPMS-9 platform. Specific heat measurements were carried out using relaxation method in the same PPMS system.

3. Results and Discussion

3.1. Crystal structure

The experimental details on the structure refinement of the P-type CePtIn$_4$ crystal and the main crystallographic data are gathered in Table 1. The atomic coordinates and equivalent isotropic displacement parameters are given in Table 2, while the anisotropic displacement parameters are
listed in Table 3. In general, the obtained crystal data are nearly same as those reported in Ref. [14] for the needle-like crystals of CePtIn₄. However, the refined lattice parameters are somewhat larger than those derived for the N-type crystals (with the unit cell volume smaller by about 1.6%) [14], and more similar to the values reported recently for Zn-stabilized CePtIn₄ (having the unit cell volume smaller by about 0.5% with respect to that of the P-type crystals) [17]. In the present case, In flux was used for crystal growth, so no occupational substitution of any foreign atom can occur. One should also note that all the anisotropic displacement parameters are slightly smaller for the P-type crystals than for the N-type ones. This finding suggests that all the atoms create a well-defined network. The crystal structure of the compound is shown in Figure 2, where also the coordination spheres of Ce and Pt atoms are depicted. Both atoms are basically coordinated by In atoms, with eleven and seven In neighbors, respectively (cf. Figure 2). Within the coordination sphere of the Ce atom one finds also two Pt atoms. They may play a stabilizing role in the structure. Since the unit cell dimensions of the P-type crystals are slightly larger than those of the N-type one, also the interatomic distances are somewhat longer in the former modification of CePtIn₄ (see Table 4).

3.2. Physical properties

Figure 3 shows the temperature dependence of the inverse magnetic susceptibility, \( \chi^{-1}(T) \), measured in magnetic field applied along the crystallographic b axis. Above 50K, the experimental data can be well modeled by a modified Curie-Weiss law (MCW), \( \chi(T) = \chi_0 + \frac{C}{T-\theta_p} \), where \( C \) is the Curie constant related to the effective magnetic moment as \( \mu_{\text{eff}} = \sqrt{8C} \), \( \theta_p \) stands for the paramagnetic Curie temperature, and the term \( \chi_0 \) accounts for all the temperature independent contributions, eg. Pauli susceptibility due to conduction electrons. The red solid line in Figure 2 represents fitting of MCW to the measured data yielding \( \mu_{\text{eff}} = 2.60(2) \mu_B \), \( \theta_p = -6.9(8) \) K and \( \chi_0 = 34.4(4) \times 10^4 \) emu/mol. The so-obtained value of \( \mu_{\text{eff}} \) is close to the theoretical value of 2.54 \( \mu_B \), calculated for a free Ce³⁺ ion within the Russell-Saunders coupling scenario, which in turn suggests that 4f electrons in CePtIn₄ are well localized. In turn, the negative value of \( \theta_p \) indicates antiferromagnetic (AFM) exchange interactions. Indeed, as can be inferred from the upper inset to Figure 3, the sample exhibits a pronounced maximum in \( \chi(T) \) at \( T_N = 2.3 \) K, characteristic of AFM phase transition. Remarkably, the Neel temperature of the P-type CePtIn₄ is higher than \( T_N = 1.65 \)
K determined before for the N-type modification of the compound [14] and \( T_N = 1.9 \) K reported for the Zn-containing crystals [17]. In order to confirm the AFM character of the ordered state, isothermal magnetization measurements were carried out at temperatures below and above \( T_N \). As displayed in the lower inset to Figure 3, the magnetization, \( M(H) \), taken at 1.8 K exhibits a clear deviation from linear dependency at around 1.1 T indicating a metamagnetic-like transition expected for an antiferromagnet. In strong field, \( M(H) \) tends to saturate with a substantial value of 1.35 \( \mu_B \). reached in 5 T. In contrast, the magnetization measured at \( T = 10 \) K shows a linear field dependence up to the maximum field available, thus corroborating the paramagnetic state.

Figure 4 presents the temperature dependence of the electrical resistivity, \( \rho(T) \), of platelet-like CePtIn\(_4\) with electrical current flowing in the crystallographic \( a-c \) plane. Clearly, the compound is a metallic conductor in the entire temperature range investigated. At the onset of the AFM ordering, a sharp drop in \( \rho(T) \) is seen (see the inset to Figure 4) that occurs due to reduction in spin disorder scattering. Interestingly, no similar feature was seen before for neither for the N-type crystals nor the Zn-stabilized crystals of CePtIn\(_4\) at their respective AFM phase transitions [14,17]. The Neel temperature, defined as a maximum in the temperature derivative of the resistivity, \( \frac{d\rho}{dT}(T) \), amounts to 2.3 K, in very good agreement with the magnetic data.

Over all, the electrical behavior of P-type CePtIn\(_4\) is similar to that found before for needle-like crystals [14]. However, one should notice important differences in the data measured for the two representatives. While the residual resistivity, \( \rho_0 \), of the N-type crystal was as small as 0.1 \( \mu\Omega\)cm [14], it is about 8 \( \mu\Omega\)cm in the present case. Similarly, the resistivity observed at room temperature for the N-type crystal was only 10 \( \mu\Omega\)cm, while it amounts to about 105 \( \mu\Omega\)cm for the P-type one. In consequence, the residual resistivity ratio of the latter crystal \( \text{RRR} = 13 \) is significantly smaller than \( \text{RRR} = 100 \) reported before [14]. These striking differences might be partly attributed to strong anisotropy in the electrical behavior of single-crystalline CePtIn\(_4\), recalling that the experiment in Ref. [14] was carried out along the crystallographic \( a \) axis, whereas in the present study the resistivity was probed with current flowing in the \( a-c \) plane. Probably, however, the main factor governing the excellent electrical conductivity in the N-type crystals of CePtIn\(_4\) was ultra-high metallurgical quality of the whisker-like specimen measured.

To elucidate bulk and intrinsic nature of the AFM ordering in the P-type crystals of CePtIn\(_4\), heat capacity measurements, \( C(T) \), were performed down to 0.4 K. As shown in Figure 5, at room
temperature, the specific heat is close to the Dulong-Petit limit $3nR = 149.6$ J/(mol K), where $n$ represents the number of atoms per formula units (here $n = 6$), and $R = 8.314$ J/(mol K) is the universal gas constant. With decreasing temperature, the specific heat decreases smoothly down to $T_N = 2.3$ K, at which the AFM order sets in. A sharp $\lambda$-shaped anomaly at $T_N$ with a sizeable heat capacity jump $\Delta C = 7.6$ J/(mol K) (see the inset to Figure 5) manifests the bulk nature of the phase transition and its second-order character. Similar results were obtained before for the needle-like crystals of CePtIn$_4$ [14]. However, at odds with the previous data, $C/T(T)$ of the P-type crystals exhibits an additional broad hump like feature near 1 K (marked by vertical arrow in the inset to Figure 5), i.e. in the AFM state. This highly puzzling singularity is presently a subject of our supplementary investigations, the results of which will be reported elsewhere. From the low-temperature specific heat data, the magnetic entropy, $S(T)$, was calculated, as illustrated in the inset to Figure 5. It appeared that the entropy released by $T_N$ amounts to $S = 4.4$ J/(mol K), which is only 76% of the value $R\ln2 = 5.76$ J/(mol K) expected for magnetic ordering with a doublet ground state. This finding is also a subject of our forth-going study on the low-temperature behavior of the P-type CePtIn$_4$.

4. Conclusion

In summary, we have grown platelet-like single crystals of CePtIn$_4$, which were established within the experimental accuracy to possess the same chemical composition and the same orthorhombic crystal structure as the needle-like crystals of the compound, which were investigated by us before [14]. Comparing the crystal data of the P-type and N-type crystals one finds out that the crystallographic unit cell of the former is about 1.6 % larger than that of the latter.

Alike N-type CePtIn$_4$, its P-type variant shows Curie-Weiss paramagnetism due to the presence of fairly stable Ce$^{3+}$ ions and orders antiferromagnetically at low temperatures. However, the Neel temperature of the platelet-like crystals ($T_N = 2.3$ K) is distinctly higher than that of the needles ($T_N = 1.65$ K). We anticipate that this difference may reflect the effect of chemical pressure, and can be rationalized in terms of the Doniach phase diagram, invoking dissimilar hybridization strength between 4f electronic states of cerium and electronic orbitals of neighboring atoms, mostly p-states of indium. Further experimental studies of single-crystalline CePtIn$_4$ with both platelet-like and needle-like morphologies as well as electronic band structure calculations are presently
underway to shed more light on the actual microscopic origin of the discrepancies in their low-temperature physical properties.

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Supplementary information

Further details on the present structural study can be obtained from the Fachinformationzentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (http://www.fiz-karlsruhe.de/), quoting the depository number CCDC 1907453.

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Table 1. Crystal data and structure refinement details for P-type CePtIn$_4$.

| Property                        | Value                          |
|---------------------------------|--------------------------------|
| **Crystal system**              | orthorhomic                    |
| **Space group**                 | Cmcm                           |
| $a$, $b$, $c$ (Å)               | 4.52175 (15), 16.7777 (5), 7.3903 (2) |
| $V$ (Å$^3$)                     | 560.66 (3)                     |
| $Z$                             | 4                              |
| $\mu$ (mm$^{-1}$)               | 48.81                          |
| Crystal size (mm)               | 0.08 × 0.05 × 0.03             |
| **Data collection**             |                                 |
| $T_{\text{min}}$, $T_{\text{max}}$ | 0.122, 0.299                   |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 8428, 418, 415 |
| $R_{\text{int}}$                | 0.026                          |
| $(\sin \theta/\lambda)_{\text{max}}$ (Å$^{-1}$) | 0.666                          |
| **Refinement**                  |                                 |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.010, 0.019, 1.31             |
| No. of reflections/param.       | 418/24                         |
| $\Delta \rho_{\text{max}}$, $\Delta \rho_{\text{min}}$ (e Å$^{-3}$) | 0.63, −0.78                  |
Table 2. Atomic coordinates and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for the crystal structure of P-type CePtIn$_4$. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

|       | X    | y     | z     | $U(\text{eq})$ |
|-------|------|-------|-------|----------------|
| Ce(1) | 0    | 0.1233(1) | 0.25 | 11(1)         |
| Pt(1) | 0    | 0.2253(1) | 0.75 | 9(1)          |
| In(1) | 0    | 0.5    | 0.5   | 14(1)         |
| In(2) | 0    | 0.0669(1) | 0.75 | 13(1)         |
| In(3) | 0    | 0.3169(1) | 0.4506(1) | 9(1) |

Table 3. Anisotropic displacement parameters ($\text{Å}^2 \times 10^3$) of the atoms in the crystal structure of P-type CePtIn$_4$. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^*U_{11} + \ldots + 2hk a^* b^* U_{12} ]$.

|       | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|-------|----------|----------|----------|----------|----------|----------|
| Ce(1) | 8(1)     | 9(1)     | 15(1)    | 0        | 0        | 0        |
| Pt(1) | 7(1)     | 9(1)     | 10(1)    | 0        | 0        | 0        |
| In(1) | 13(1)    | 10(1)    | 20(1)    | 0(1)     | 0        | 0        |
| In(2) | 12(1)    | 9(1)     | 18(1)    | 0        | 0        | 0        |
| In(3) | 8(1)     | 11(1)    | 8(1)     | 0(1)     | 0        | 0        |
Table 4. Interatomic distances [Å] in the unit cell of P-type CePtIn₄.

|  |  |  |
|---|---|---|
| Ce(1) | 1 In(2) | 3.1912(5) |
|  | 4 In(3) | 3.3188(2) |
|  | 2 Pt(1) | 3.4013(3) |
|  | 2 In(3) | 3.5713(4) |
|  | 4 In(1) | 3.5780(2) |
|  | 2 In(2) | 3.8141(1) |
| Pt(1) | 1 In(2) | 2.6564(5) |
|  | 2 In(3) | 2.6944(3) |
|  | 4 In(3) | 2.79473(19) |
|  | 2 Ce(1) | 3.4013(3) |
| In(1) | 2 In(3) | 3.0933(3) |
|  | 4 In(2) | 3.12833(17) |
|  | 4 Ce(1) | 3.5780(2) |
| In(2) | 1 Pt(1) | 2.6564(5) |
|  | 4 In(1) | 3.12834(17) |
|  | 1 Ce(1) | 3.1913(5) |
|  | 4 In(3) | 3.3326(4) |
|  | 2 Ce(1) | 3.8141(1) |
| In(3) | 1 Pt(1) | 2.6944(3) |
|  | 2 Pt(1) | 2.79474(19) |
|  | 1 In(3) | 2.9651(6) |
|  | 2 In(3) | 3.2690(4) |
|  | 2 Ce(1) | 3.3188(2) |
|  | 2 In(2) | 3.3327(4) |
|  | 1 Ce(1) | 3.5713(4) |
Figure captions

Figure 1. Photograph of as-grown N-type and P-type single crystals of CePtIn$_4$ taken under optical microscope on a millimeter grid.

Figure 2. (a) Schematic view of the crystallographic unit cell of P-type CePtIn$_4$ projected on the $b$-$c$ plane. (b) Coordination spheres of the Ce and Pt atoms.

Figure 3. Temperature dependence of the reciprocal magnetic susceptibility of P-type CePtIn$_4$ measured in a magnetic field of 0.3 T applied along the crystallographic $b$ axis. The solid red line represents least-squares fit of modified Curie-Weiss law to the experimental data above 50 K. Upper inset: low-temperature variation of the magnetic susceptibility taken in $\mu_0 H = 0.1$ T parallel to the $b$ axis. Lower inset: field dependencies of the magnetization measured at $T = 1.8$ K (ordered state) and 10 K (paramagnetic state) in magnetic field along the $b$ axis.

Figure 4. Temperature dependence of the electrical resistivity of P-type CePtIn$_4$ measured with electric current flowing within the crystallographic $a$-$c$ plane. Inset: low-temperature resistivity data and temperature derivative of the electrical resistivity in the region of antiferromagnetic phase transition.

Figure 5. Temperature dependence of the specific heat of P-type CePtIn$_4$. Inset: low-temperature data plotted as specific heat over temperature ratio and magnetic entropy in the region of antiferromagnetic phase transition.
Figure 1.
Figure 2.
Figure 3.
Figure 4.

CePtIn$_4$

$i \parallel ac$

$\rho$ (\(\mu\Omega\text{ cm}\))

$T$ (K)

$\frac{\delta \rho}{\delta T}$ (arb. unit)
Figure 5.