Superconductivity in Ce₃PdIn₁₁ single crystals – intrinsic phenomenon or parasitic effect?

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Abstract. Single crystals of the compound Ce₃PdIn₁₁ that belongs to a large family of superconducting cerium indides with the general formula CeₘTₙIn₃m+2n (T stands for d-electron transition metal) were grown from indium flux and characterized by means of low-temperature specific heat and electrical resistivity measurements. The collected data revealed significant sample-dependent divergence in their magnetic and superconducting properties which raises the question of whether these two cooperative phenomena are intrinsic properties of Ce₃PdIn₁₁.

1. Introduction
In recent years, cerium-based indides have been intensively studied due to their very interesting physical properties, especially including heavy-fermion superconductivity and its coexistence with long-range magnetic ordering (see e.g. Refs.[1, 2, 3]). An example of such material is Ce₃PdIn₁₁ that belongs to a group of ternaries with the general formula CeₘTₙIn₃m+2n (T = Co, Rh, Ir, Pd, Pt), which includes also the well-known phases CeTIn₅ and Ce₂TIn₈. The Ce₃PdIn₁₁ indide crystallizes with a tetragonal crystal structure (space group P4/mmm, no. 123) that hosts two crystallographically inequivalent Ce sites in the unit cell [4]. The compound was characterized as a heavy-fermion antiferromagnet with two consecutive magnetic transitions at $T_{N₁} = 1.67$ K and $T_{N₂} = 1.53$ K and a large value of the Sommerfeld coefficient [5, 6]. Remarkably, Ce₃PdIn₁₁ becomes superconducting below $T_c = 0.42$ K [5, 6], which suggests that long-range magnetic order and heavy-fermion superconductivity may coexists in this material at low temperatures. Thus, these unique physical properties make Ce₃PdIn₁₁ an attractive platform for studying mutual relationship between antiferromagnetism and superconductivity at ambient pressure.

Earlier bulk-properties studies postulated that the antiferromagnetic ordering in Ce₃PdIn₁₁ is associated with one of the Ce sublattices, while the other one is responsible for heavy-fermion behavior and superconductivity [5]. In order to verify this conjecture, more advanced measurements, such as neutron diffraction or muon spin rotation spectroscopy, must be performed. For this purpose, we made numerous attempts to synthesize large and high quality single crystals of this material. Unexpectedly, by performing basic characterization of the obtained crystals, we observed significant differences in their low-temperature properties. Here, we present a comparative study of the collected data.
2. Experimental details

Single crystals of Ce$_3$PdIn$_{11}$ were grown out of indium flux, in a manner reported by Kratochvílová et al. [5, 7]. This technique yielded single crystals with dimensions up to 1 x 1 x 0.5 mm$^3$. Although most of excessive flux was centrifuged, some residuals of indium were found on the surface of crystals. Hence, individual crystals were additionally cleaned by manual dipping in isopropyl alcohol and scraping indium residues with the use of wooden toothpick (diluted hydrochloric acid, typically used to remove remaining indium flux, was found to attack also crystals of Ce$_3$PdIn$_{11}$).

The so-prepared samples were characterized by means of specific heat measurements performed in the temperature range from 0.35 K up to 20 K using a standard time-relaxation method [8] implemented in a commercial Quantum Design PPMS platform equipped with a $^3$He cryostat. The same equipment was utilized to perform electrical resistivity measurements by means of conventional ac four-probe technique.

3. Results and discussion

![Figure 1](image)

**Figure 1.** (a) Temperature dependencies of the specific heat measured on four different individual single crystals of Ce$_3$PdIn$_{11}$ (for clarity, the data for each sample was shifted vertically). The positions of both magnetic phase transitions $T_{N1}$ and $T_{N2}$ are marked by dashed lines and the position of superconducting phase transition $T_c$ is indicated by dotted line. (b) Temperature variation of the electrical resistivity of sample 4. Arrows mark the critical temperatures $T_{c1}$ and $T_{c2}$ of two superconducting phases and the temperatures of two magnetic transitions $T_{N1}$ and $T_{N2}$.

Fig. 1(a) displays the low-temperature dependencies of the specific heat $C_p(T)$ of Ce$_3$PdIn$_{11}$ measured on four different single-crystalline samples, labeled 1 to 4. Importantly, each sample was proven to be free from contamination by antiferromagnetic CeIn$_3$ ($T_N = 10$ K) that is a plausible impurity in the Ce$_m$T$_n$In$_{3m+2n}$ systems [5, 6, 9, 10]. As can be inferred from the figure, notable differences were found in the $C_p(T)$ data of different crystals. While for sample 1 a distinct jump occurs at the critical temperature $T_c = 0.47$ K, no similar anomaly is seen for sample 4. In turn, two consecutive features related to the magnetic phase transitions at $T_{N1} = 1.63$ K and $T_{N2} = 1.47$ K can be distinguished for sample 4 and sample 3, while for sample 2 they are negligibly small and entirely absent for sample 1. It should be noted that the values of $T_{N1}$ and $T_{N2}$ are very close to those reported before [5, 6]. Another important observation is that the relative ratio of the specific heat magnitude at $T_{N1}$ and $T_c$ is different for each of the samples studied. In general, the following rule is obeyed: the larger $C_p(T)$ anomalies related to
the antiferromagnetic ordering at $T_{N1}$ and $T_{N2}$, the smaller specific heat jump associated with the superconducting phase transition. Since heat capacity is an additive quantity, this finding can be most straightforwardly explained by considering the presence of two independent phases in the crystals investigated. One of them plausibly represents antiferromagnetic Ce$_3$PdIn$_{11}$, while the other one, of unclear origin, would be responsible for the superconductivity. In such a scenario, sample 1 and sample 4 constitute pure (or almost pure) superconducting and antiferromagnetic phases, respectively, whereas samples 2 and 3 contain a mixture of both phases in different proportion.

Although no bulk superconductivity was identified in the $C_p(T)$ data of sample 4, the electrical resistivity $\rho(T)$ of this sample exhibits two clear drops, likely due to superconducting phase transitions (see Fig. 1(b)). Remarkably, the anomaly at $T_{c1} = 0.67$ K matches almost perfectly with the onset of superconductivity in Ce$_2$PdIn$_8$ [9, 10]. The absence of a corresponding anomaly in the heat capacity suggests that this feature may be caused by a minor contamination of sample 4 by the latter phase. The other drop in $\rho(T)$ is broader and occurs at about $T_{c2} = 0.46$ K that is the position of the specific heat jump due to the superconductivity in samples 1–3. However, due to the lack of similar anomaly in $C_p(T)$ of sample 4 also this feature can be attributed to the presence of impurity phase rather than to intrinsic property of Ce$_3$PdIn$_{11}$. In this context it is also worth noting that down to 0.35 K, the electrical resistivity of sample 4 did not reach zero value. This finding is another indication that only small fraction of the measured specimen became superconducting below $T_{c2}$.

4. Conclusion
Our low-temperature measurements of the heat capacity of single-crystalline Ce$_3$PdIn$_{11}$ revealed a behavior that appeared strongly sample-dependent. While some of the crystals were found to exhibit properties consistent with the data reported in the literature [5, 6], some others behaved quite differently. Quantitative analysis of the $C_p(T)$ and $\rho(T)$ curves measured for individual crystals leads us to hypothesize that the superconductivity and the antiferromagnetic order observed in the samples of Ce$_3$PdIn$_{11}$ may actually originate from two distinct phases. Their differentiation in individual crystals can be very challenging because of complex phase equilibria near the ideal chemical composition Ce$_3$PdIn$_{11}$, and the formation of other ternaries with similar stoichiometry and closely related crystal structures [4]. As a result, crystals with stacking faults (or other structural defects) can be grown in a single batch that ostensibly represent the same material, but may harbor distinctly different electronic ground states.

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