Crystal Growth and Magnetic Properties of New Ce-T-In and Pr-T-In Compounds (T = Rh, Pd): Sythesis and Characterization of a New Ambient-pressure Superconductor Ce_2PdIn_8

K. Uhlířová, J. Prokleška, V. Sechovský

Charles University Prague, Faculty of Mathematics and Physics, Prague, Czech Republic.

Abstract. New single crystals of R_2PdIn_8 (R = Pr, Ce) and R2RhIn8 compounds have been synthesized by solution growth from In flux and studied with respect to structure and electronic properties. Pr_2RhIn_8 exhibits van Vleck paramagnetism and strong magnetocrystalline anisotropy attributed to a crystal-field effect on the Pr^{3+} ion. Ce_2PdIn_8 compound is paramagnetic down to 0.7 K, superconductivity below 0.7 K has been found. The Sommerfeld coefficient γ = 700–800 mJ/mol^{-1}K^{-2} links this compound with the heavy-fermion family.

Introduction

In the Ce-based compounds, the interaction of the Ce ions with the conduction electrons often leads to a large enhancement of the effective electron mass and these are called the heavy-fermion (HF) compounds. They exhibit attractive electronic properties, such as strongly enhanced para-magnetism, non-Fermi liquid behavior, interplay between magnetism and superconductivity (SC), etc.

In the last decade, the Ce_nTIn_{3n+2} series of compounds, where n = 1 or 2 and T = Co, Rh,Ir, attracted attention. These compounds form quasi-two-dimensional tetragonal system with the $CeIn_3$ units and TIn_2 layers alternating along the c-axis. All of them perform the HF behavior combined with superconductivity. While $CeCoIn_5$, $CeIrIn_5$ and Ce_2CoIn_8 [*Chen*, 2002; *Movshovich*, 2001; *Kim*, 2004; *Hedo*, 2004] are ambient-pressure superconductors, $CeRhIn_5$ and Ce_2RhIn_8 are tuned to SC by applying pressure or doping [*Nicklas*, 2003; *Hegger*, 2000; *Ferreira*, 2008; *Yang*, 2008]. Recently, coexistence of antiferromagnetism (AF) and SC in Ce_2PdIn_8 has been reported [*Kaczorowski*, 2009].

Following our research of the PrTIn$_5$ compounds revealing indications of the quadrupolar ordered state [*Uhlirova*, 2008], we commenced a study of the Pr_2TIn_8 structural variants. In this paper we report on single-crystal preparation and the crystal structure of these Pr compounds and magnetic properties of Pr_2RhIn_8. Since the preparation of R_2PdIn_8 was found to be rather complicated, details of sample preparation as a key part of a successful experiment revealing intrinsic electronic properties. First results of electrical-resistivity, ac-susceptibility and specific-heat measurements are presented.

Experimental

We have prepared single crystals of Ce_2TIn_8 and Pr_2TIn_8 compounds listed in Table 1. The solution growth technique from a ternary In-rich flux [*Uhlirova*, 2008] was used. Pure elements were placed into an alumina crucible with a large amount of In metal, resulting in the total atomic composition $R_2TIn_{25\text{-}35}$ and sealed in a silica tube under high vacuum. Then the system was heated up to 950 °C and slowly (4 °C/h) cooled down to 400 °C. After the thermal process the remaining indium was centrifuged through the quartz-wool stopper.

Heat capacity (C_p), electrical resistivity (ρ), magnetization (M) and ac susceptibility (χ_{ac}) were measured with the Quantum Design PPMS and MPMS apparatuses, The χ_{ac} at low temperatures (0.35 < T <2.5 K) was measured using the custom made extension to PPMS allowing to measure χ_{ac} using the ACMS option with the 3He insert (including the ACMS preamplifier) [*Prokleska*, 2009].

Results and discussion

The compounds with T = Rh and Ir formed plate like crystals of a size 5×5×2 mm^3 and the c-axis perpendicular to the plate. In case of T = Pd, we obtained a multiphase product, mainly cuboids-shaped single crystals of RIn_3 covered by very thin layer (50–100 μm) of R_2PdIn_8. The rest of Pd formed a cubic phase Pd_3In_7 (a = 9.436 Å). Thence we assumed that R_2PdIn_8 grows in a narrow

concentration region and therefore, we used the Pd-richer composition to suppress the initial growth of RIn_3. $RPd_{2-3}In_{35}$ has been found as the best composition, though still some $CeIn_3$ remained down in well-defined regions. For the higher Pd concentration, $CePd_3In_6$ starts to grow, which makes the separation of Ce_2PdIn_8 more complicated. The boundary between Ce_2PdIn_8 and $CeIn_3$ was very well defined. Since Ce_2PdIn_8 have a very similar lattice parameter a = 4.695 Å with the cubic $CeIn_3$ (a = 4.689 Å), there is no surprise that the layer of Ce_2PdIn_8 is single-crystalline with the *c*-axis perpendicular to the surface. The crystals of Ce_2PdIn_8 were cut from the $CeIn_3$, polished and checked by EDX analysis to be sure there is no more $CeIn_3$ left. Small amount of indium, which we were not able to remove, was present on the surfaces. The powder X-ray patterns obtained on crushed single crystals show that all selected crystals had the tetragonal Ho_2CoGa_8 structure type, the lattice parameters are listed in Table 1. Although we tried to grow the crystals from a broad concentration range of Ce a Pd, the growth and isolation of the 115 stoichiometry with Pd has not been very successful yet.

Table 1. Lattice parameters of prepared compounds with tetragonal Ho_2CoGa_8-type structure.

Compound	a (Å)	c (Å)
Pr_2RhIn_8	4.652	12.21
Pr_2IrIn_8	4.662	12.17
Pr_2PdIn_8	4.678	12.18
Ce_2RhIn_8	4.667	12.24
Ce_2PdIn_8	4.695	12.21

Pr_2RhIn_8

Pr_2RhIn_8 has been found paramagnetic in the whole measured temperature range. In Figure 1 one can see that the temperature dependence of the reciprocal susceptibility ($1/\chi$) is linear with temperature above 100 K, i.e. the χ (=*M*/*H*) vs. *T* dependence of the susceptibility follows the Curie-Weiss law with values of effective moment μ_{eff} and paramagnetic Curie temperature Θ_p listed in Table 2. The values in brackets are results presented on $PrRhIn_5$. The μ_{eff} values are close to the effective moment calculated for the Pr^{3+} free ion (3.58 μ_B), the difference in the Θ_p values for *B*||*a* and *B*||*c*, respectively, reflect the magnetocrystalline anisotropy. Below ≈ 80 K, $1/\chi$ vs. *T* departs the Curie-Weiss behavior due to the crystal field (CF) effect on the Pr^{3+} ion. Also the low-temperature magnetization is strongly anisotropic (see Figure 2); the magnetization along the *c*-axis is about 3.5-times higher than in the *a*-axis. The magnetocrystlline anisotropy is lower than in the one of $PrRhIn_5$ which is in agreament with the fact that R_nTIn_{3n+2} structures become less 2D-like with increasing *n*.

Table 2. Effective moment μ_{eff} and paramagnetic Curie temperature Θ_p of Pr_2RhIn_8 and $PrRhIn_5$ (in brackets).

	B||*a*	B||*c*
μ_{eff} (μ_B/f.u.)	3.6 (3.72)	3.5 (3.67)
Θ_p (K)	-42 (-86)	16 (28)

Ce_2PdIn_8

Few Ce_2PdIn_8 single crystals have been extracted from the two-phase $CeIn_3$+Ce_2PdIn_8 samples. The presence of $CeIn_3$ impurity in the crystal was tested by tracing the ac susceptibility and specific heat or resistivity anomaly around 10 K where $CeIn_3$ undergoes a phase transition to the AF ordering [*Vandiepe*, 1971].

The magnetization and magnetic susceptibility of the Ce_2PdIn_8 crystal were measured in magnetic field applied along the *a*-axis only (**Figure 3**). The temperature dependence of the susceptibility above ≈ 80 K can be fitted with a modified Curie-Weiss law:

$$\chi = \frac{C}{T - \Theta_p} + \chi_0 ,$$

where $C = N\mu_{eff}^2/3k_B$ .The fitted value of effective moment μ_{eff} = 2.8 μ_B/Ce^{3+} is somewhat higher than

the Ce^{3+} free-ion value, Θ_p = –60 K, $\chi_0 = 4 \cdot 10^{-8}$ m^3/mol. The susceptibility reaches its maximum at T^{χ}_{max} = (21±2) K, this maximum is a rough estimation of T^*, the nonuniversal characteristic scale temperature [*Nakatsuji*, 2002] which is a border between single ion screening and collective hybridization that produces coherent behavior below T^* [*Yang*, 2008]. No sign of magnetic phase transition to magnetically ordered phase has been found down to lowest temperatures.

Figure 4 presents the temperature dependence of resistivity, the resistivity has a maximum at T_{max} = 25 K, which is of the same magnitude as reported for $CeRhIn_5$ [*Ferreira*, 2008; *Hegger*, 2000; *Yang*, 2008]. The temperature T_{max} could be another estimation of T^* [*Yang*, 2008] and is in agreement with the one given by the susceptibility measurements. Below 0.6 K a transition to the super-conducting state was detected, see inset of Figure 5. The transition was found to be very sensitive to sample composition and homogeneity as presented in Figure 6, where are specific heat data of all three samples b-d identified in Figure 1. Each sample has different T_c, more than one transition are visible. One of the reason can be presence of different polytypic phases, which were observed in case of Ce_2RhIn_8 [*Moshopoulou*, 2006]. *Polytypism* is the phenomenon of the existence of an element or compound in two or more layer-like crystal structures that differ in layer stacking sequences [*Bailey*, 1977].

Conclusion

The synthesis of R_2PdIn_8 was found to be rather complicated since the phase tends to grow on RIn_3 in a thin single crystalline plan-parallel layer. The transition-plane between the two phases is extremely well defined, which is due to the matching values of their lattice parameter *a*. The improvement of the crystal growth as well as the search for the related 115 compound is still point of our interest.

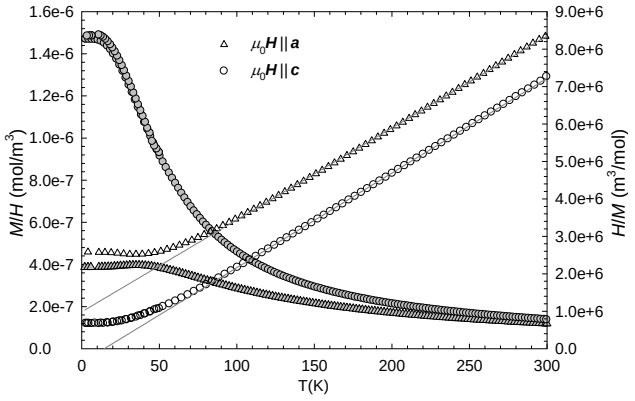

Figure 1. The χ vs. T and $1/\chi$ vs. T plots Pr_2RhIn_8 in $B\|a$ and $B\|c$. The lines are the Curie-Weiss fits.

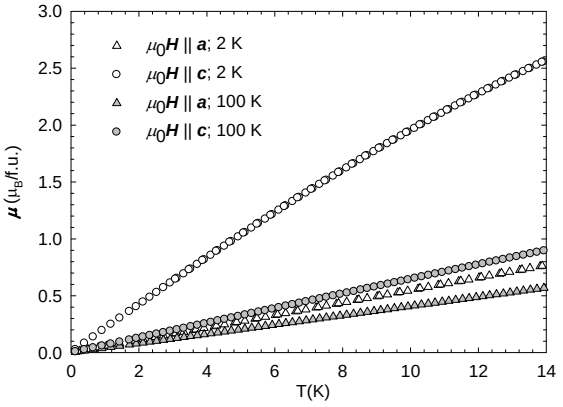

Figure 2. Magnetization curves of Pr_2RhIn_8 measured at 2 K and 100 K in in $B\|a$ and $B\|c$.

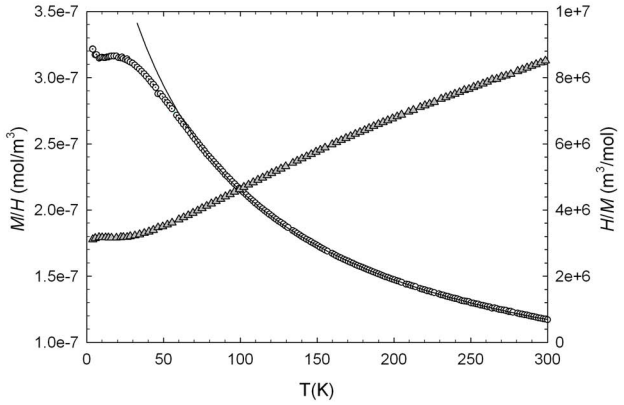

Figure 3. The χ vs. T and $1/\chi$ vs. T plots for Ce_2PdIn_8 in $B\|a$. The line is the modified Curie-Weiss fit.

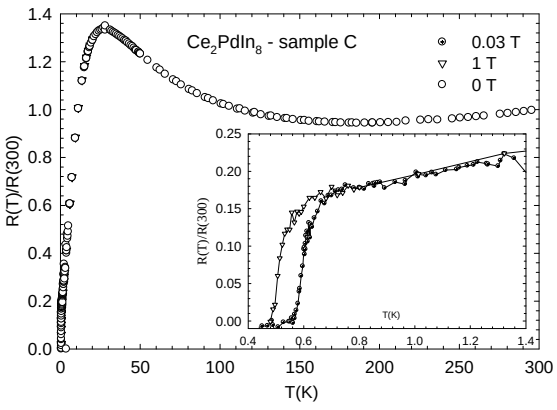

Figure 4. Electrical resistivity of sample C.

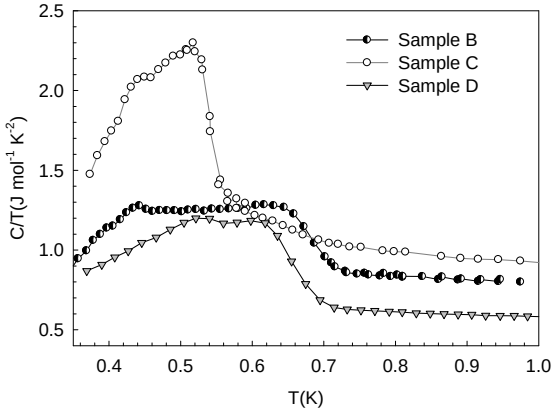

Figure 5. The low-temperature heat capacity of three samples identified as Ce_2PdIn_8.

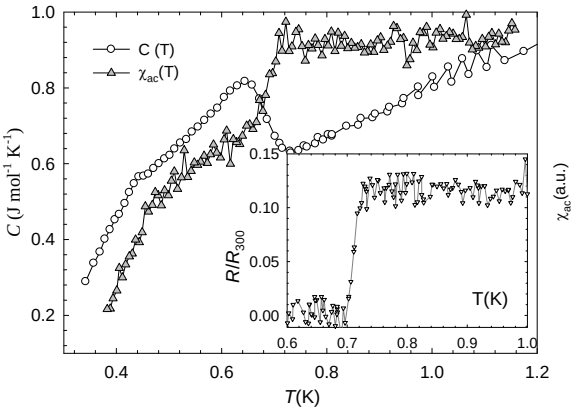

Figure 6. Comparison of the heat capacity, resistivity and ac susceptibility measurements of sample B. Two SC transition are evident on the eat capacity and ac susceptibility data.

The paramagnetic Pr_2RhIn_8 exhibits strong magnetocrystalline anisotropy caused by the crystal field interaction with the orbital moment. The anisotropy is clearly evident from the large difference of the values of Θ_p determined from the high-temperature Curie-Weiss susceptibility along *a*- and *c*-axis and the anisotropic magnetization curves at low temperatures. As the structure of Pr_2RhIn_8 is more 3D-like than in case of $PrRhIn_5$, the anisotropy is weaker.

The Ce_2PdIn_8 compound was found to be a heavy-fermion superconductor with the critical temperature $T_c \approx 0.7$ K, which is strongly dependent on sample composition. Because we found three relatively well defined (sharp) transitions we expect an existence of more polytypic phases which cannot be detected by microprobe analysis and standard powder X-ray diffraction method. The superconductivity is expected to be the second order type typical for this family of compounds.

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