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Studium základního stavu nových intermetalických sloučenin $(RE,U)_nTlIn_{3n+2}$

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The ground-state properties of new $(RE,U)_nTIn_{3n+2}$ intermetallic compounds

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Název práce: Studium základního stavu nových intermetalických sloučenin $(RE,U)_nTIn_{3n+2}$

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Abstrakt: Vlastnosti základního stavu sloučenin s f elektrony jsou charakterizovány silnými interakcemi vedoucími k mnoha exotickým jevům. V této práci jsme se zabývali sloučeninami krystalizujícími v tetragonální soustavě typu Ho_nCoGa_{3n+2} . Připravili jsme několik nových materiálů pomocí metody růstu z indiového roztoku. Mezi nejzajímavější patří Ce_3TIn_{11} ($T = Pd, Pt$). Jejich krystalová struktura obsahuje dvě neekvivalentní polohy céru. U sloučenin pozorujeme koexistenci antiiferomagnetického uspořádání a těžkofermionové supravodivosti za normálního tlaku. Tuto koexistenci je možno popsat na základě modelu dvou tzv. mřížek Kondo-iontů. Předpokládáme, že cérové atomy v jedné z neekvivalentních poloh jsou zcela odstíněny Kondo interakcí, jejich $4f$ elektrony jeví itinerantní charakter a podílejí se na supravodivosti, zatímco cérové atomy v druhé poloze si uchovávají lokalizovaný charakter a jsou zdrojem magnetického uspořádání pomocí RKKY interakce.

Vliv krystalového pole na magnetický základní stav byl zkoumán u sloučeniny Ce_2RhIn_8 za pomoci neutronového experimentu. U_2RhIn_8 a $URhIn_5$ se uspořádávají antiiferomagneticky a narozdíl od příbuzných cérových ($4f$) systémů jsou jejich $5f$ stavy jsou zcela hybridizovány a Kondo interakce zde nehraje zásadní roli. Podobně je tomu u dalších zkoumaných sloučenin RE_2CoIn_8 ($RE = Pr, Nd, Dy$), kde pozorujeme silně lokalizované chování $4f$ elektronů. Charakter neobvyklého fázového diagramu sloučeniny Dy_2CoIn_8 je dán silným vlivem spin-orbitální a Kondo interakce.

Klíčová slova: intermetalické sloučeniny na bázi vzácných zemin a uranu, příprava monokrystalů, supravodivost a magnetismus

Title: The ground-state properties of new $(RE,U)_nTIn_{3n+2}$ intermetallic compounds

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Abstract: The ground-state properties of f -electron compounds are characterized by strong interactions which lead to a plethora of exotic states. In this thesis we focused on compounds crystallizing in the tetragonal Ho_nCoGa_{3n+2} -type structure. Several new compounds have been synthesized from In-flux; particularly enigmatic are Ce_3TIn_{11} ($T = Pd, Pt$). These compounds possess two inequivalent Ce-sites and reveal coexistence of antiferromagnetic order and heavy fermion superconductivity at ambient pressure. This coexistence can be explained in the framework of two-Kondo ion lattice model, assuming one Ce-site being completely Kondo screened with the $4f$ -electron behaving itinerant and participating in superconductivity while the second Ce-site retains its local character giving rise to magnetic order via the RKKY interaction. The influence of crystal electric field on the magnetic ground state has been investigated on the Kondo compound Ce_2RhIn_8 by means of neutron experiments. U_2RhIn_8 and $URhIn_5$ behave like transition-metal antiferromagnets, contrary to Ce($4f$)-counterparts. The $5f$ -states are entirely hybridized and Kondo interactions play no role. Neither does it in the investigated RE_2CoIn_8 ($RE = Pr, Nd, Dy$) compounds which exhibit strong localized $4f$ -electron behavior. Here, the influence of strong spin-orbit coupling on the RKKY interaction gives rise to an extraordinary magnetic phase diagram in Dy_2CoIn_8 .

Keywords: Rare-earth and Uranium Intermetallic Compounds, Single crystal growth, Superconductivity and Magnetism

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Introduction

Rare-earth (*RE*) and actinide intermetallic compounds have been surprisingly fertile in giving rise to novel ground states that have been intensively studied by the condensed-matter community. The origin of this rich variety of different ground states can be found in the diverse character of the *f*-electrons and multiple interactions the electrons are exposed to, like the long-range indirect Ruderman-Kittel-Kasuya-Yoshida (RKKY) exchange interaction, the local Kondo interaction and the crystal-electric-field effect (CEF). One can divide the research in these *f*-electron compounds into two; the interest in the magnetic structure which is determined mainly by the interplay between RKKY and CEF states and the competition between Kondo and RKKY interaction. The competition is closely connected with the observation of unusual ground states such as heavy fermion behavior, unconventional superconductivity, and even coexistence of ferromagnetism and superconductivity, generally assumed to be mutual exclusive. These phenomena have been related to the presence of a quantum critical point (QCP) – a zero temperature phase transition usually of magnetic to a non-magnetic state.

In the recent years this latter topic advanced to a driving force in research in *f*-electron compounds. The interplay of competing ground states and the appearance of unconventional superconductivity close to a QCP has been discussed in high- T_c cuprates¹, organic charge transfer salts^{2,3}, and the more recently discovered iron pnictide and chalcogenide superconductors⁴. However, it is overshadowed by material intricacies, including electronic inhomogeneity and the complexity of the phase diagrams which complicate the interpretation. The advantage of *f*-electron intermetallic compounds is that these are chemically stoichiometric materials which do not suffer from electronic and structural disorder. Moreover, the *f*-electron wave function of cerium and uranium being expanded in space is extremely sensitive to any influence of the external factors like pressure and magnetic field. Therefore, tuning towards a quantum critical point can be accomplished in a clean way.

Two different theoretical models have been proposed for QCP; a spin-density-wave (SDW) and a localized moment (LM) scenario. In the former scenario magnetism develops by the spin polarization of the Fermi surface. The second, LM model, assumes that the heavy quasiparticle is a composite bound state formed between the local magnetic moments and the conduction electrons via the Kondo effect. At the QCP where the Kondo scale goes to zero, the quasiparticle will disintegrate into its localized spin and delocalized charge degrees of freedom. While both models seem to be incompatible, recently a global phase diagram has been proposed which incorporates both scenarios. A newly introduced parameter, the dimensionality of the critical magnetic fluctuations, determines whether the SDW or the LM scenario applies. The dimensionality is by part related to the crystal structure of the compound.

In this thesis we address a broad spectrum of ground-state investigations on the $RE(U)_nT_mIn_{3n+2m}$ (T = transition metal) and $RECo_2$ compounds. Several of these compounds are newly discovered within the course of the thesis work and thus, a large part is dedicated to crystal growth. The growth from metallic solution has turned out to be an almost irreplaceable, universal way to obtain novel bulk materials presented within the thesis.

The first class of materials crystallizes in the typical tetragonal $Ho_nCo_mGa_{3n+2m}$ structure. It can be viewed as n blocks of $RE(U)In_3$ and m blocks of TIn_2 stacked along the [001] axis. The character, i.e. the electronic structure of the compound can be changed from 3D to a more 2D depending on the sequence of the respective layers. Such property allows the investigation of the parameter dimensionality. Additionally we can investigate the differences in ground-state properties with respect to $4f$ -electrons and $5f$ -electrons in otherwise identical compounds.

The investigation of the ground state of the $RECo_2$ ($RE = Ga, Dy, Er, Tm$) compounds falls into the first category of interest. The magnetic ground state is solely determined by strongly localized behavior of the $4f$ -electrons involving only the interplay between the RKKY interaction and CEF effects. In this work, the main focus lies on the single-crystal growth of these compounds.

Thesis organization

The thesis has been structured the following; chapter 1 provides the reader with a brief theoretical background concerning f -electron magnetism, Kondo behavior, quantum criticality and superconductivity. Chapter 2 gives details about the experimental techniques ranging from sample synthesis with the main emphasis placed on the solution growth method via sample characterization to the macro- and microscopic measurement techniques. The main focus of the thesis is addressed in chapter 3 presenting the crystal growth and physical properties of the new heavy fermion compounds Ce_nTIn_{3n+2} ($n = 1, 2$; $T = Pd, Pt$). Chapter 4 investigates the CEF properties of Ce_2RhIn_8 by means of neutron experiments. Synthesis and physical properties of the related uranium compounds $URhIn_5$ and U_2RhIn_8 are discussed in chapter 5. Chapter 6 presents synthesis and physical properties of the related non-Kondo RE_2CoIn_8 ($RE = Pr, Nd, Dy$) systems. Appendix A summarizes crystal structure parameters of the Ce_nTIn_{3n+2} compounds and the measurements of the electrical resistivity of Ce_3PtIn_{11} in various magnetic fields and under several hydrostatic pressures. In Appendix B, the variability and versatility of the flux growth method is demonstrated by including the results obtained on the $RECo_2$ compounds. As many compounds with different composition are discussed in the thesis we use the abbreviations based on their stoichiometries to make the reading more comfortable: 3111 is used instead of RE_3TX_{11} , 218 instead of RE_2TX_8 and 115 instead of RTX_5 .

1. Physics of f -electron systems

In this section we briefly summarize some main features of the f -electron compounds. For the basic definitions of terms regarding magnetic moment and magnetic ordering as well as for detailed derivations of presented relations, we refer the reader to literature⁵⁻¹⁰. Most of the further discussion can be found in standard literature like the series Handbook on the Physics and Chemistry of Rare Earths (Elsevier Science Publishers B.V.).

The rare-earths and the actinides show some unique properties due to the $4f$ - and $5f$ -electrons. Unlike in d -metal compounds, when a large number of rare-earth atoms are assembled to form a solid, the f -electrons in first approximation generally remain localized. They are closely bound inside the outer closed shells and therefore play a minor role in chemical bonding. Their magnetic properties closely resemble those in the free atoms with given valence. The conduction electrons themselves make only a modest contribution to the magnetic moment, but by mediating the magnetic interactions they play a crucial role in determining the characteristic magnetic properties in the solid state.

The RE and actinides exhibit a large angular momentum J and strong spin-orbit coupling. The latter lifts the J degeneracy so strongly that at room temperature usually only the lowest J multiplet is populated. The crystalline electric field is an electric field generated by the electrostatic charges and has the symmetry given by the lattice. The interaction of the CEF with the highly anisotropic charge clouds gives rise to the large magnetocrystalline anisotropies observed in the RE and actinide compounds. Moreover, in transition-metal systems this strong CEF interaction dominates over the spin-orbit interaction. In the RE series the opposite is true. In actinide compounds however, both energy scales are comparable so that neither of the above approximations are valid. It makes understanding of magnetism in the actinides difficult, because neither orbital nor CEF contributions can be neglected.

Unlike the heavier RE elements the $4f$ -electron in cerium is weakly bound despite the fact that it resides deep within the core of the atom. This is due to the relatively extended nature of the $4f$ -wave function. As a result strong correlations between the Ce $4f$ -electrons and hybridization between the $4f$ -state with those of the ligand states exist.

The $5f$ -wave function of U is extremely expanded in space. Hence, uranium compounds are extremely sensitive to any influence of the external factors like pressure, magnetic and crystal fields. Contrary to the uranium metal itself many of the U-based compounds exhibit magnetic ordering suggesting some degree of localization of the $5f$ -electrons.

1.1. Itinerant electrons vs. localized moments

The fundamental difference between localized and itinerant behavior is given in the overlap of charge distributions of neighboring atoms^{9,10}. The localized 4*f*-electrons in lanthanides lie deep inside the 5*d*6*s*-shell. As the partially filled 4*f*-shells maintain their almost free-ion character, they do not contribute to chemical bonding or conductivity. Their well-defined 4*f*-energy and undisturbed magnetic moments follow Hund's rules for free ion. The characteristic behavior for a localized moment is given by the Curie law⁵. In the case of non-interacting ions in PM state, we obtain:

$$\chi_c = \left. \frac{\partial M}{\partial B} \right|_{B=0} = \frac{C}{T} \quad (1)$$

$$C = \frac{n\mu_0\mu_{eff}^2}{3k_B}$$

Here k_B is the Boltzmann constant ($1.380\,6504(24) \cdot 10^{-23} \text{ JK}^{-1}$), μ_0 is the vacuum permeability ($4\pi \cdot 10^{-7} \text{ Hm}^{-1}$), n are magnetic moments per unit volume and C is the Curie constant. The effective moment μ_{eff} is given by

$$\mu_{eff} = g_J\mu_B\sqrt{J(J+1)} \quad (2)$$

where g_J is the Landé factor, μ_B is the Bohr magneton ($5.05078324(13) \cdot 10^{-27} \text{ JT}^{-1}$) and J is the total angular momentum which is determined by the orbital moment L and spin moment S . The PM susceptibility is positive and field-independent but it decreases with rising temperature due to the increase of thermal disorder of the magnetic moments.

On the other hand, we observe strong overlap in the case of the itinerant model typical for 3*d*-, 4*d*- and 5*d*-transition metals and partially also for actinides with 5*f*-electrons. The partially filled *d*-shells of transition metal ions which are responsible for magnetism, form very broad conduction bands. They are strongly exposed to their crystalline environment which leads to quenching of their orbital moment L . As a result, their magnetism is given mainly by the spin moment S and the spin-orbit (SO) contribution $\hat{H}_{SO}$ (see the next section).

While for the localized moment models the temperature dependence was understood at a very early stage, the development of an analogous model for itinerant electrons took some time¹⁰. The first approach performed by Pauli¹¹ was based on free electron gas. The wave functions of the valence electrons form a band with equal numbers of spins up and down. When an external field is applied, only electrons close to Fermi energy E_F change the orientation of their spins because other electron states with spins parallel to external field are already occupied. As a result, a small

surplus of one type of spins will emerge. This effect, known as Pauli-paramagnetism, is temperature-independent and given by equation

$$\chi_{par} = 2\mu_B^2 \rho(E_F) \quad (3)$$

where ρ is the density of states for the conduction band at Fermi energy E_F ⁶. The model was further developed by Mott¹², Slater^{13,14} and finally by Stoner^{15,16} who substituted discrete momentum levels by electronic bandstructure and introduced phenomenological “molecular field” model analogous to the Weiss model (see the section 1.3). The susceptibility of interacting free electron gas is given by

$$\chi_s = \frac{2\mu_B^2 \rho(E_F)}{1 - I\rho(E_F)} \quad (4)$$

where I is the Stoner exchange factor, a slowly varying atomic quantity through the periodic table. The denominator allows defining a criterion for the spontaneous onset of magnetism. For the negative denominator, the resulting negative susceptibility means that the PM state is at a total energy maximum, so that any magnetic state must have a lower total energy. According to the Stoner criterion, magnetism occurs if the inequality holds

$$I\rho(E_F) \geq 1. \quad (5)$$

As a very weak effect, Pauli paramagnetism can be covered in some materials (for example Pr_2CoIn_8 discussed in the section 6.3) by a larger PM contribution called van Vleck paramagnetism. It is a $J=0$ contribution to the second-order approximation of magnetic susceptibility and, similar to diamagnetism, it is small and temperature independent^{5,17}.

The presented free-ion and itinerant models describe only the limit cases and real materials reveal a combination of both. In the following sections phenomena connected with localized and itinerant nature of $4f$ -electrons are discussed.

1.2. Crystal electric field

The Hamiltonian $\hat{H}_0$, the residual interaction $\hat{G}$, CEF Hamiltonian $\hat{H}_{\text{CEF}}$ together with spin-orbit coupling $\hat{H}_{\text{SO}}$, form the full free-ion Hamiltonian $\hat{H}$ ^{6,17} from the independent electron approximation:

$$\hat{H} = \hat{H}_0 + \hat{G} + \hat{H}_{\text{SO}} + \hat{H}_{\text{CEF}} \quad (6)$$

The energy scales are well separated in case of lanthanides, starting from the Coulomb interaction between the f -electrons on the order of 10 eV, SO interaction, and down to CEF effects typically on the order of tens of meV (~ 100 K)¹⁸.

The CEF interaction describes the relation between $4f$ -electrons and crystal field, playing a significant role among rare earths. The crystal field represents the local environment of static electric field and is directly related to the crystal symmetry.

The perturbation can be described by the crystal field Hamiltonian⁹

$$\hat{H}_{CEF} = \sum_{L,M} B_L^M \hat{O}_L^M \quad (7)$$

where B_L^M represents CEF parameters depending on the symmetry of crystal field and $\hat{O}_L^M$ CEF operators summed over quantum numbers L and M . CEF effects decrease values of magnetic moments in RE compounds compared to the theoretical values of magnetic moments for free f -ions predicted by Hund's rules⁵.

The $(2J+1)$ -degenerated energy levels are split by CEF entirely or partially depending on the site symmetry. The splitting of the J multiplets by the CEF is of the order of 10^2 - 10^3 meV. Kramers theorem states that for odd-electron systems, so-called Kramers ions, there is a remaining twofold degeneracy forming double degenerate ground state which cannot be removed by any electric field. The entropy of such ion which has to be removed by some other mechanism is at least $S = k_B \ln 2$ at $T \rightarrow 0$.

As we are interested especially in the $Ce_n T_m In_{3n+2m}$ compounds, we will focus on Ce^{3+} in the tetragonal environment corresponding to the tetragonal $P4/mmm$ symmetry. Then, the crystal-field potential is described by the crystal-field Hamiltonian $\hat{H}_{CEF}$

$$\hat{H}_{CEF} = B_2^0 O_2^0 + B_4^0 O_4^0 + B_4^4 O_4^4 \quad (8)$$

The $J = 5/2$ ground state splits in the crystal field given by the symmetry into three Kramers doublets¹⁹ $\Gamma_7^{(2)}$, $\Gamma_7^{(1)}$ and Γ_6 :

$$\begin{aligned} 0\rangle &= \Gamma_7^{(2)} = \alpha|\pm 5/2\rangle + \beta|\mp 3/2\rangle \\ 1\rangle &= \Gamma_7^{(1)} = \beta|\pm 5/2\rangle - \alpha|\mp 3/2\rangle \\ 2\rangle &= \Gamma_6 = |\pm 1/2\rangle \end{aligned} \quad (9)$$

where $\alpha^2 + \beta^2 = 1$ are the mixing parameters.

The energy levels are determined from the positions of the peaks in the inelastic neutron spectra, while the mixing parameters are determined from the ratios of the

integrated weights of the peaks. The Kondo hybridization of the localized moments and the itinerant conduction electrons shifts the CEF excitation levels to higher energies and broadens the linewidths (Kondo effect is discussed in the section 1.4). A common calculation of susceptibility treats the CEF levels as delta functions and adds an isotropic positive molecular field contribution λ to the CEF susceptibility χ_{CEF} , which takes into account the magnetic exchange and Kondo interactions at high temperatures.

Hence the susceptibility becomes

$$\chi^{-1} = \chi_{\text{CEF}}^{-1} - \lambda \quad (10)$$

CEF interaction influences specific heat, magnetoelastic and transport properties and it is together with SO coupling $\hat{H}_{\text{SO}}$ a crucial source of magnetic anisotropy. $\hat{H}_{\text{SO}}$ is given by expression:

$$\hat{H}_{\text{SO}} = \lambda \mathbf{S} \mathbf{L} \quad (11)$$

Here, λ is the SO parameter and $\mathbf{S}$ and $\mathbf{L}$ are the spin and orbital moments, respectively. For 4f- and 5f-systems, the SO coupling dominates over CEF splitting, while for transition metal systems $\hat{H}_{\text{SO}} < \hat{H}_{\text{CEF}}$.

1.3. Exchange interactions

Exchange interactions, based on Pauli repulsion principle⁷, are a source of magnetic interactions. A long-range order occurs in the material if an exchange interaction correlating magnetic moments is stronger than their thermal fluctuations. The Heisenberg Hamiltonian^{6,9}, which describes the energy of these interactions, is given by

$$\hat{H}_{ij} = -2J_{ij} \mathbf{S}_i \mathbf{S}_j \quad (12)$$

where J_{ij} is the exchange integral and S_i, S_j are the appropriate spin quantum numbers.

In the *d*- and *p*-metals, the crucial exchange interactions are the direct exchange given by an overlap of charge distributions of magnetic ions and the super exchange given by electrons in a common non-magnetic (NM) neighbor which mediates the interaction among magnetic ions. The RKKY interaction represents a crucial indirect exchange interaction in rare-earth materials whose 4f-wave functions do not overlap. The conduction electrons and the spins interact via hyperfine interaction creating correlation energy between them. The RKKY exchange is a weak, long-range interaction which reveals an oscillatory dependence on the distance r between the

magnetic moments. Distance r determines the type of magnetic ordering - ferromagnetic (FM) for $J_{\text{RKKY}} > 0$, or antiferromagnetic (AF) for $J_{\text{RKKY}} < 0$.

In a material with strongly interacting magnetic moments a long-range magnetic ordering can be established when the cooperative energy overcomes the thermal energy below a temperature characteristic for each system⁵⁻⁸. The mean-field approximation can be applied to describe the magnetically ordered (MO) state, replacing the Heisenberg Hamiltonian by the Weiss molecular field.

Utilizing similar approach as to calculate PM susceptibility $\chi_C = C/T$ from the Curie law in PM materials (equation (1)), we obtain Curie-Weiss (C-W) law

$$\chi_{C-W} = \frac{C}{T - \theta_P} \quad (13)$$

which describes the PM behavior above an ordering temperature. Here, $\theta_P = \lambda C$ represents the Weiss temperature.

As a result, there is a plethora of magnetic structures ranging from the simple (anti)ferromagnetic and ferrimagnetic (which can be treated as uncompensated AF materials using Néel sublattice model) structures via nontrivial systems such as parimagnetic²⁰, spiral and helicoidal²¹ structures to frustrated short-range orderings (spin glass⁸). Spin-density wave (SDW)^{7,8} state can be described as a function of a nesting wave vector $\mathbf{q}$ which characterizes the modulation of magnetic moments within the structure. If the vector $\mathbf{q}$ turns out to be π/a where a is the spacing between atoms, the SDW is commensurate with the lattice and AF order results; the other magnetic structures with $\mathbf{q}'$ are called incommensurate.

1.4. Kondo problem

To introduce all the necessary terms properly, we begin this section with the description of the Fermi-gas model. A Fermi gas describes the behavior of non-interacting fermions, that is particles with half-integer spin obeying the Pauli Exclusion principle. In a solid the Fermi gas describes well the behavior of electrons if no interaction with the lattice or other electrons takes place. The heat capacity of Fermi gas is linearly dependent on temperature with Sommerfeld coefficient γ^5 which is proportional to the density of states at the Fermi level E_F and thus to the electron mass m_e . However, in real metals electron-electron interactions take place. The standard theoretical framework for describing metals is Landau–Fermi liquid (FL) theory, according to which the excitation spectrum of the metal can be adiabatically connected to that of the electron Fermi gas. Quasiparticles with effective mass replace the free electrons. An important consequence of the interactions is the formation of narrow quasiparticle bands at the E_F leading to an enhanced density of

state and accordingly large m_{eff} . The heavy fermions, f -electron compounds, can be viewed as an extreme case of Landau Fermi liquid theory⁵.

At low temperatures in RE and actinide compounds the magnetic localized f -moments strongly interacts with surrounding conduction electrons. Hereby the f -moments become effectively screened due to the formation of a singlet state with the conduction electrons, so called Kondo-singlet (see following paragraphs). The consequence of this Kondo entanglement is that the localized f -moments, charge neutral to begin with become a delocalized character (hybridize) and acquire the quantum numbers of the conduction electrons – the birth of the heavy, because the effective mass can be 1000 times the bare electron mass, quasiparticles which gave these class of materials its name (see Fig. 1).

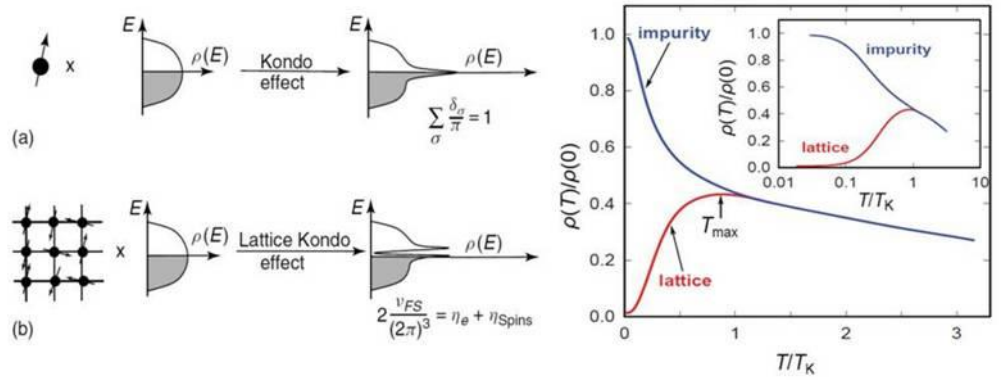


Fig. 1. (left) Evolution of the density of states (marked as $\rho(E)$ in the picture) at the Fermi level as a result of Kondo interaction for a Kondo impurity (a) and Kondo lattice (b) case (taken from Coleman²²). (right) A comparison of the associated behavior of the resistivity. For $T \gg T_K$ the temperature behavior in resistivity for the Kondo impurity and the Kondo lattice shows identical temperature dependency. Below T_{max} coherence sets in on the Kondo lattice which results in the formation of heavy-quasiparticle Bloch states.

The physics of Kondo systems and heavy fermions is usually dealt in terms of the Anderson model^{23,24}. The single impurity is taken as a starting point: if $3d$ -elements such as iron or manganese, or $4f$ - ($5f$ -) elements such as cerium, ytterbium or uranium, are dissolved as magnetic impurities in a NM host such as copper or aluminum, spin-flip scattering occurs. It generates a spin-compensating cloud of conduction electrons around the impurity²⁴. The impurity magnetic moment becomes screened, thus forming a singlet ground state resulting in a characteristic minimum and consequent increase of electrical resistivity with temperature. This unusual behavior was first explained by Kondo²⁵ in the single impurity model who assumed that a local magnetic moment with a spin $\mathbf{S}$ is coupled via an exchange interaction J with the conduction electron spin $\mathbf{s}$, i.e., $\hat{H} = J\mathbf{s}\mathbf{S}$.

Kondo's calculation was valid only at sufficiently high temperature above the so-called Kondo temperature T_K

$$T_K k_B = D e^{\frac{-1}{|JN(0)|}} \quad (14)$$

where D is a cut-off parameter and $N(0)$ is the density of states at Fermi level²⁴. T_K is the characteristic temperature in the single-channel Kondo problem below which an impurity $S = \frac{1}{2}$ magnetic spin is compensated by the surrounding conduction electrons. It represents also the energy scale limiting the validity of the Kondo results. The Kondo problem was finally solved by Wilson²⁶ who showed that the resistivity approaches a constant value as temperature goes to zero. At $T = 0$, the ground state of the impurity with spin S is found to be completely screened (compensated) by the surrounding conduction electron spins with antiferromagnetic orientation, thus forming a NM Kondo singlet. The electron screening cloud has a certain correlation length, which increases with decreasing temperature. Increasing concentration of impurities leads to their mutual interactions via conduction electrons (the RKKY interaction). This effect destroys the singlet state and the Kondo behavior disappears.

Up to now, only a single impurity (for instance in f -electron element) in a NM host was discussed. However, it is possible to increase the number of magnetic impurities up to a level where the RE ions build up a fully ordered sublattice without losing those appearances associated with the Kondo effect²⁴. In these so-called Kondo lattices, it is necessary to take into account the intersite interactions among magnetic moments and coherent scattering of the conduction electrons with the periodically arranged f -moments. This is responsible for dramatic change of $\rho(T)$: Instead of a diverging increase of resistivity at $T \rightarrow 0$, the resistivity curve of a Kondo lattice reveals a maximum²⁷ at temperature T which is roughly proportional to T_K (see Fig. 1).

The Kondo scale for a lattice of Kondo ions

$$T_K \sim \exp\left(-1/JN(0)\right) \quad (15)$$

where T_K is the Kondo temperature and $JN(0)$ represents now the hybridization. In such Kondo lattice also the RKKY interaction is present, whose scale is given by

$$T_{\text{RKKY}} \sim J^2 N(0). \quad (16)$$

The consequences of this is a competition between the Kondo effect, which suppresses the magnetic moment with decreasing temperature on each site and the RKKY interaction, which tends to give a magnetic ordering between different $4f$ -ions. This competition is demonstrated in the so-called Doniach diagram^{28,29} (see

the left part of Fig. 2). J denotes the hybridization strength here. In the limit of small J , T_{RKKY} dominates and the system orders magnetically. On the other hand, for large J , $T_K > T_{\text{RKKY}}$ and the Kondo interaction becomes robust preventing any magnetic ordering. As the result, the real Néel temperature T_N increases with increasing J first, reaches a maximum and for critical value of J_c drops to zero.

The transition at T_N is a classical second-order transition, which is observed by varying the temperature as it is driven by thermal fluctuations. However, such picture of classical phase transition has to be modified when T goes to zero at a critical value J_c because only quantum fluctuations can play a role. In contrast to a classical phase transition at nonzero temperatures, a quantum phase transition is driven by a control parameter other than temperature, e.g., external pressure, doping, or magnetic field. A formerly magnetic transition at finite temperature can be suppressed to zero, that is tuned to its quantum critical point³⁰.

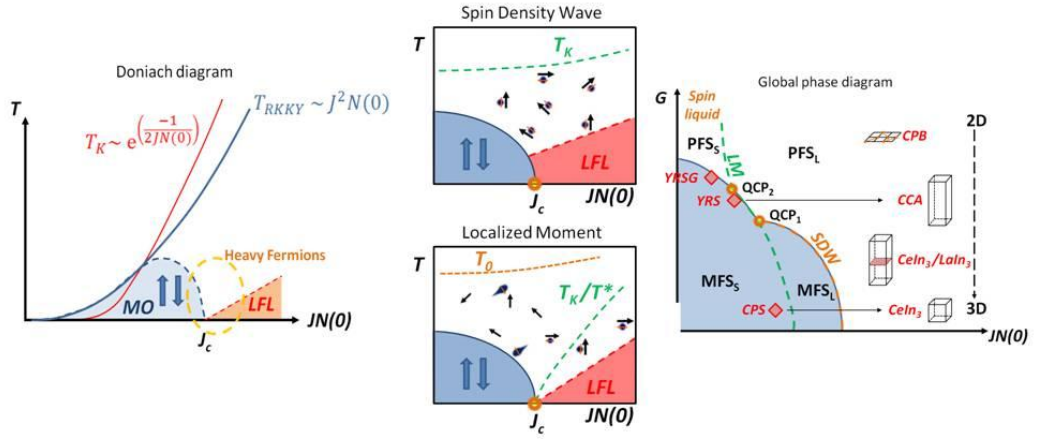


Fig. 2. Evolvement of the quantum critical phase diagram. The Doniach diagram stands as origin (MO: magnetically ordered phase; LFL: Landau Fermi Liquid phase). The SDW and LM scenario deal with the part of the Doniach phase diagram in the vicinity of the critical region. The global phase diagram unifies both scenarios. MFS_S/PFS_S (MFS_L/PFS_L): magnetic ordered/ paramagnetic small (large) Fermi surface volume. The diagram displays the combined effects of the effective Kondo coupling (on the x -axis) and the frustration, or magnetic dimensionality (on the y -axis). The compounds from the $\text{Ce}_n\text{TlIn}_{3n+2}$ group together with the artificially prepared $\text{CeIn}_3/\text{LaIn}_3$ are located in the diagram according to their layered structure which determines the structural dimensionality (the plot based on diagram from Ref.³¹).

1.5. Non-Fermi-liquid behavior and quantum criticality

Although the low-temperature properties of a large number of Kondo systems may be described successfully in terms of the Landau Fermi liquid (FL) theory, many compounds show striking deviations from the expected behavior³² (see Tab. 1), for instance linear in temperature of the electrical resistivity and logarithmic increase of the specific heat. This deviant behavior is termed non-Fermi liquid (nFL)^{24,30,33}

admitting the origin of this behavior was and still is not completely clear. Several reasons for occurrence of nFL behavior have been proposed based on multi-channel Kondo effect, disorder or a quantum critical point (for an review see Ref.³⁴). The unification of the plethora of performed experiments on the more than 50 known nFL systems using one or more of these theoretical models still lies in the future. In the following the latter will be discussed in more detail.

Tab. 1. Temperature dependencies³³ of specific heat, susceptibility and electrical resistivity for various models. The critical behavior in the SDW scenario is given only for the AF spin fluctuations ($z = 2$).

Fermi liquid		Hertz and Millis ^{35,36}		Moriya <i>et al.</i> ³⁷		Lonzarich ³⁸
		$d = 3$	$d = 2$	$d = 3$	$d = 2$	$d = 3$
C/T	$const$	$\gamma - \beta\sqrt{T}$	$\ln(T_0/T)$	$\gamma - \alpha\sqrt{T}$	$-\ln(T)$	$\gamma + \sqrt{T}$
χ	$const$	$T^{\frac{3}{2}}$	$\chi_0 - dT$	$T^{-\frac{3}{2}}$	$-\ln(T)/T$	$T^{-\frac{3}{2}}$
ρ	$\sim T^2$	$T^{\frac{3}{2}}$	T	$T^{\frac{3}{2}}$	T	$T^{\frac{3}{2}}$

The key question in the debate about quantum criticality is how the quantum critical physics in HF materials can be understood. Traditional approach uses a space-time generalization of classical “criticality”, as formulated by Hertz and Millis^{35,36}, often referred to as spin-density-wave (SDW) scenario. A new framework, evoking the breakdown of the Kondo screening in the critical region, is known as localized moment (LM) or Kondo-breakdown scenario³⁹⁻⁴². These two scenarios differ in the faith of the heavy quasiparticle upon approaching the QCP from the paramagnetic (PM) site.

The basic idea of a SDW transition³⁵⁻³⁷ is shown in Fig. 2. Below the characteristic Kondo temperature T_K the local f -moments become screened by the Kondo effect. In this region of the phase diagram the resistivity follows a $\rho \sim T^{1.5}$ or $\rho \sim T$ dependence while specific heat obeys a square root or logarithmic behavior for the AF fluctuations, respectively. When crossing the MO transition at zero temperature the Kondo singlet remains intact. The only degrees of freedom are the fluctuations of the magnetic wavevector q . The magnetic order in the close vicinity of the transition is due to the formation of a spin density wave a spatial modulation of the spins of the heavy quasiparticles of the paramagnetic phase. As a result the Fermi surface volume on both sides of the transition is large because it accounts for the conduction electrons and the delocalized f -moments. Therefore, the measurements of the Hall resistivity should reveal a continuous change of the Hall coefficient⁴³. Indeed this has been observed in $\text{Cr}_{1-x}\text{V}_x$ ⁴⁴. Other examples of heavy Fermion compounds exhibiting a SDW scenario are CePd_2Si_2 , CeIn_3 ⁴⁵ and CeCu_2Si_2 ⁴⁶.

At first sight a major difference between the SDW and LM model is apparent. Local f -moments persist down to lowest temperatures giving rise to $\rho \sim T$ and

$C/T \sim \ln T$ behavior in resistivity and specific heat, respectively. Furthermore, the Kondo singlet exists only in the paramagnetic phase³⁹. The onset of magnetic order is accompanied by the disintegration of the heavy quasiparticles in their spin (local moments) and charge (conduction electrons) constituents⁴³. The LM scenario implies the existence of an effective Kondo scale E^* (in temperature dependent measurements seen as T^*)³⁹. Below this characteristic temperature the f -moments are completely screened. At QCP this scale goes to zero and the Fermi surface volume reconfigures from a large one (in the paramagnetic phase, where the conduction electrons and the f -moments are included) to a small one (in the magnetically ordered phase accommodating only the conduction electrons).

Such dramatic scenario is reflected consequently in the physical properties. The de Haas-van Alphen experiments on CeRhIn₅ manifested a direct change of small to large Fermi surface when tuning the compound through its QCP⁴⁷. The experimental observation of the critical energy scale T^* associated with the jump in the Hall coefficient was reported for YbRh₂Si₂⁴⁸ as well as more recently in Ce₃Pd₂₀Si₆³¹.

Recent developments^{31,49-52} point to the importance of second microscopic quantity next to J , which is the degree of quantum fluctuations of the local moments, parameterized by G . Magnetic order weakens with increasing G , as it would with enhancing the hybridization strength J . These two quantities form a two-dimensional parameter space at $T = 0$ which allows constructing a tentative global phase diagram for quantum criticality in HF materials combining SDW and LM scenario as presented in Fig. 2³¹. The phase diagram contains two independent lines - one where long-range magnetic order develops (indicated by the blue line), and another where the volume of the Fermi surface jumps from small (FS_S) to large (FS_L) marked by the green dashed line. The point marked QCP₁ separates the two different types of magnetic quantum phase transition. For transitions that take place at G values above the QCP₁, the magnetic QCP will have the LM character, whereas for G values that lie below the QCP₁, the QCP will have the SDW character. Above QCP₂, the second separation point, long-range magnetic order melts under the influence of the zero-temperature spin fluctuations to form a “quantum spin-liquid state” before the Fermi surface transition takes place. Because spatial dimensionality modifies the degree of quantum fluctuations, the vertical axis can be associated with the crystal structure of the material under investigation³¹. Going from the three-dimensional (3D) cubic limit to the decoupled 2D limit means to move upwards along the vertical axis as illustrated in the figure on the example of the several materials (CeIn₃⁴⁵, Ce₃Pd₂₀Si₆ (CPS)³¹, YbRh₂Si₂ (YRS)⁵⁰, CeCu_{5.9}Au_{0.1} (CCA)⁵³ and Ce₂Pt₂Pb (CPP)⁵⁴). The recently designed thin film CeIn₃/LaIn₃ superlattices reduce the dimensionality of pure CeIn₃ towards the 2D limit by incorporating layers of non-magnetic LaIn₃. It was reported that the strength of magnetic order was drastically reduced⁵⁵.

1.6. Superconductivity

Superconductivity was discovered in 1911 by Heike Kammerlingh Onnes in mercury at 4.2 K, where the electrical resistivity abruptly disappeared⁵⁶. Except dropping of resistivity to zero, many new effects have been observed, among them so-called Meissner effect⁵⁷. Superconductors were considered to be ideal diamagnetics with $\chi = -1$ due to Meissner effect arising from persistent screening currents which flow to oppose the applied field; this magnetic flux is then expelled from the whole bulk. Following years brought a discovery of critical temperature dependence on the isotopic mass of the constituent element. This observation called isotope effect^{58,59} pointed to microscopic mechanism responsible for superconductivity and thus to the existence of the phonon-electron interaction.

A first successful microscopic theory which could explain phenomena connected with superconductivity was the BCS theory⁶⁰. A toy-model explanation of the phonon-electron interaction is based on attraction of negative electrons to the positive ions which form the crystal lattice. The ion lattice becomes deformed by the negative charge. Since the timescale is much slower than the electrons (as they are much heavier) the polarized cloud persists as the electron moves away. These inhomogeneities in the charge distribution start to attract other electrons so that they can interact via the exchange of phonons. As a result, electrons pair-up into Cooper pairs formed below the critical SC temperature T_c at distances which are long enough to overcome the electrons' repulsion. This microscopic condensation of Cooper pairs takes place in the momentum space. In real space, these correlations extend out to a distance known as the coherence length ξ which is typically much larger than the inter-particle separation. In momentum space, the correlations occur in an energy shell around Fermi surface separated from other possible electron states by a finite energy gap Δ ⁶¹. The newly created quantum state has anti-parallel spins and zero angular momentum as electrons have $\mathbf{k}$ and $-\mathbf{k}$, respectively. As a consequence, the electrons are in an isotropic s-wave pair state (spin singlet due to antisymmetry). The Cooper pair represents a new bosonic quasiparticle with integer (zero) spin underlying the Bose-Einstein statistics⁶². This is very different from a single electron which is a fermion with spin $\frac{1}{2}$.

As this thesis is not focused primarily on conventional superconductors we refer the reader for more results from the BCS theory to literature^{5,6,62} and discuss the unconventional superconductivity in the following paragraphs. By “unconventional” we mean a pair state that is not an isotropic s-wave state and where different interaction plays the crucial role (for details, see e.g. *Monthoux et al.*⁶³). The story of the HF unconventional superconductors started with the discovery of superconductivity in CeCu_2Si_2 by *F. Steglich et al.*⁶⁴. Unlike in conventional superconductors, superconductivity in HF materials has been related to the presence of magnetism. These conditions are very unfriendly for occurrence of

superconductivity according to BCS theory. No theory yet explains the emergence of this phase⁶⁵. The close relationship of superconductivity and quantum criticality is purely from experimental observation. This has lead to the idea that critical magnetic fluctuations associated with the QCP mediate superconductivity in contrast to conventional superconductors (BCS-type).

Although certainly not correct, the absence of a microscopic theory of magnetically mediated superconductivity forces the community to make use of BCS theory in order to describe the superconducting properties. We give only a brief summary of most relevant formulas applied in this thesis. Although these expressions use assumptions that are only valid for BCS superconductors (and therefore need to be critically considered for heavy fermion compounds), they are useful for the purpose of comparing different materials.

In type-II superconductors, the coherence length ξ which is a measure of pairing distance between electrons is much smaller than the penetration depth λ which is the characteristic distance of the magnetic-field penetration into a superconductor. In an applied magnetic field this leads to the formation of vortexes which can be described as lines of the magnetic field (or flux) passing through the superconducting material. The core of the vortex is into normal state.

The London penetration depth λ_L is defined as

$$\lambda_L = \sqrt{\frac{m}{\mu_0 n q^2}} \quad (17)$$

for charge carriers of mass m , number density n and charge q .

To be able to describe the behavior of SC state in external magnetic field, the terms orbital and Pauli limiting need to be explained. In the case of the orbital limiting, the kinetic energy of the Cooper pairs competes with the SC condensate energy. As the magnetic field is increased, the SC electron's kinetic energy increases as well. When it exceeds the condensate energy, a vortex state replaces the Meissner state. If Pauli paramagnetic limiting dominates, the superconductivity is destroyed as a result of a competition between the potential energy of the electrons' spins and the SC condensate energy.

The orbital limiting field $\mu_0 H_{c2}^{\text{orb}}(0)$ is a value of magnetic field where the vortex cores begin to overlap. It can be extrapolated from the field-dependent T_c to zero using the square-law fit

$$\mu_0 H_{c2}(T) = \mu_0 H_{c2}^{\text{orb}}(0) \left(1 - \left(\frac{T}{T_c}\right)^2\right). \quad (18)$$

Another approach is to obtain the orbital limiting field is called Werthamer–Helfand–Hohenberg (WHH) formula⁶⁶

$$\mu_0 H_{c2}^{orb}(0) = -0.693 \left(\frac{dH_{c2}}{dT} \right)_{T=T_c} T_c. \quad (19)$$

The superconducting coherence length $\xi(0)$ can be estimated from the Ginzburg-Landau formula for an isotropic three-dimensional superconductor

$$H_{c2}(0) = \frac{\Phi_0}{2\pi\xi^2(0)}, \quad (20)$$

where $\Phi_0 (= h/2e = 2.07 \cdot 10^{-15} \text{ Tm}^2)$, is the magnetic flux quantum. Assuming the simplification of the spherical Fermi surface for the tetragonal crystal structure, it is possible to estimate the value of the Fermi vector k_F using the expression⁶⁷

$$-\frac{dH_{c2}}{dT}(T_c) = 7.95 \cdot 10^{32} \frac{\gamma^2(T_c)T_c}{k_F^4} + 4780 \cdot \gamma(T_c)\rho_0(T_c). \quad (21)$$

With the knowledge of k_F , it is possible to evaluate the Fermi velocity using the expression

$$v_F = 6.02 \cdot 10^{-13} \frac{k_F^2}{\gamma} \quad (22)$$

derived^{67,68} from the BCS theory. The effective mass m^* is defined as the $\hbar k_F/v_F$ ratio. The superconducting coherence length ξ_{GL} can be calculated^{67,68} as

$$\xi_{GL} = 0.18 \cdot \frac{\hbar v_F}{k_B T_c}. \quad (23)$$

To complete the characterization of the superconducting transition, the quasiparticles mean free path l , the penetration depth λ_{GL} and the Ginzburg-Landau parameter κ_{GL} can be calculated according to relations presented in Ref.⁶⁹.

$$\begin{aligned} l &\sim \rho_0/k_F^2 \\ \lambda_{GL} &\sim \sqrt{\gamma}/k_F \\ \kappa_{GL} &= \lambda_{GL}/\xi_{GL} \end{aligned} \quad (24)$$

The value of the Pauli paramagnetic limiting field $\mu_0 H_{c2}^P(0)$ is a difficult quantity to determine. It can be calculated according to the BCS theory as

$$\mu_0 H_{c2}^P(T) = 1.84 \cdot T_c. \quad (25)$$

However, this approximation cannot provide reliable results for heavy fermion compounds. Having both orbital and Pauli limiting field, we can define the Maki parameter α ⁷⁰ as

$$\alpha = \sqrt{2} \cdot \frac{H_{c2}^{orb}}{H_{c2}^P}. \quad (26)$$

A very large Maki parameter ($\alpha > 1.6$) and a very clean system ($\xi \ll l$) are two critical requirements when looking for the Fulde-Ferrel-Larkin-Ovchinnikov (FFLO) state⁷¹.

1.7. The 5f-electron systems

The physical interactions which have been discussed so far are valid and necessary also for the description of the 5f-systems. However, there are several issues which are characteristic exclusively for these materials and hence, the following section is dedicated to them. Actinide series encompasses elements starting from the lightest actinium ($Z = 89$) to the heaviest lawrencium ($Z = 103$). Unlike the 4f-compounds, the behavior of 5f-electron systems cannot be described systematically due to the larger spatial extent of the 5f-wave functions⁷². The light actinides (Ac-Pu) share similarities with the 4f-systems whereas the behavior of heavier actinides (Am-Lr) resembles more the itinerant *d*-band magnetic compounds. Strong SO coupling is typical for 5f-elements. It leads to large orbital moments which are antiparallel to the spin moments in light actinides. The SO coupling stands behind the considerable hybridization of the 5f-states with the ligand states so that they can mediate strong exchange interactions. Robust magnetic anisotropy is established due to the anisotropy of the hybridization.

The 5f-electrons in the light-actinide compounds are much more delocalized compared to 4f-electrons in lanthanides and thus, they participate in chemical bonding. Consequently, a significant hybridization of the 5f- and the valence states of neighboring atoms is established. As a result, delocalized 5f-electrons form a relatively narrow 5f-band intersected by the Fermi energy and the magnetic moments are much smaller than expected for a free ion. The strength of magnetic coupling in light actinides is larger than for the 4f-moments interacting via the RKKY interaction. Significant difference between 4f- and 5f-systems can be found also in the field of magnetic excitations. Usually, the inelastic neutron scattering reveals a quasielastic response rather than CEF excitations unlike the situation in rare-earth compounds.

The increase of the 5f-overlap can be taken as a principal delocalizing mechanism of the 5f-electrons. Among the actinides, the most illustrative example of this mechanism are the uranium compounds. The spacing between uranium atoms d_{U-U} ,

which is necessary to fulfill the Stoner criterion, lies in the range of 3.4 – 3.6 Å. This critical boundary is called the Hill limit⁷³. Compounds with crystal structures where d_{U-U} is lower than the Hill limit reveal usually NM or SC ground state. For $d_{U-U} > 3.6$ Å, an (anti)ferromagnetic coupling is preferred, induced typically by the direct exchange. The crucial parameter determining the ground-state properties in compounds with $d_{U-U} > 3.6$ Å is their hybridization with ligands.

In case of transition metals, the 5*f*-wave functions overlap mainly with the *d*-states. The 5*f*-*d* hybridization leads to the onset of 5*f*-magnetism while the *d*-states are more occupied than the free *d*-elements. As a result, even magnetic transition metals can behave as non-magnetic.

In compounds with non-transition metals, it is mainly the size of ligand atoms that affects the hybridization. Compounds with larger ligands form narrow bands with high density of states and are typically magnetic (e.g., UIn₃⁷⁴), whereas those with smaller ligands are weakly paramagnetic (e.g., USi₃⁷⁵). These compounds are further discussed in the section 5.1.

The magnetic moments tend to orient perpendicular to the U-U bonding which can lead to significant uniaxial anisotropy. This is particularly observed in crystal structures where the distance to the uranium neighbor is smaller within a plane and larger interplane. The magnitude of the anisotropy, observable both in MO and PM phases, can be often estimated from the difference of the PM Curie temperatures.

2. Experimental techniques

2.1. Single-crystal growth

Crystal growth is a heterogeneous or homogeneous chemical process involving solid, liquid or gas, to form a homogeneous solid substance having three-dimensional atomic arrangement – a single crystal⁷⁶⁻⁷⁸. As the major advantage, material in a single crystal form allows the investigation of anisotropic properties in comparison to polycrystalline materials; single crystals provide also lower porosity and stress, higher purity and fewer grain boundaries. The amount of various single crystal growth methods is vast, reflecting the plethora of investigated materials within the solid state research. Following paragraphs offer a brief review of the growth methods with special attention to solution growth and on the technical equipment utilized in this work to obtain single crystals.

Commonly, the solid growth, vapor phase growth, growth from melt and solution growth are distinguished. A typical example of a solid growth process applied within this work is the annealing. The method is basically based on atomic diffusion. The vapor phase growth is particularly suitable for materials which undergo a phase transformation or melt incongruently. Specific chemical precursors are used in a

form of vapor containing the desired elements⁷⁸. After the vapor is formed, it is transported to the substrate and deposited by a condensation or chemical reaction. The growth from melt is generally the fastest method to prepare large single crystals which melt congruently (transforming from homogeneous solid to homogeneous liquid at the melting point). Czochralski method⁷⁷, one of the most popular ones, is based on the pulling of the ingot with the seed from melt. In the (floating) zone melting or in the Bridgman method, the thermal gradient is a crucial term; the differences among them are given by the shape of the crucible or its absence, respectively. The growth from solution is the most common and versatile way to produce large variety of crystals. As it is also the method which was almost solely applied for sample preparation within this work, we focus on it in more details:

Solution growth applied in solid state research uses several different types of solutions, e. g. low-temperature aqueous, superheated aqueous or high-temperature solutions (molten metal, flux). The term “flux” stands for a high temperature solvent which permits the growth to proceed at temperatures well below the melting point of the solute phase. We distinguish so-called *self-flux* method for compounds containing the solvent and *true-flux* method for compounds grown from an additional element. Nevertheless, the principle of both methods is the same: the crystal starts to form when the supersaturation of the solution is achieved, either through slow cooling, solvent evaporation or vertical temperature gradient transport. As already mentioned, the main advantage of this method is that crystals are grown below their melting temperature. It is used for materials melting incongruently (decomposing before melting or exhibiting a phase transition below the melting point). The growth can be carried out through spontaneous nucleation or crystallization on a seed. The requirements on the flux are the low melting point and vapor pressure, and a weak tendency to form stable unwanted binary phases. The flux should not attack the crucible and also ease of separation plays a considerable role^{79,80}.

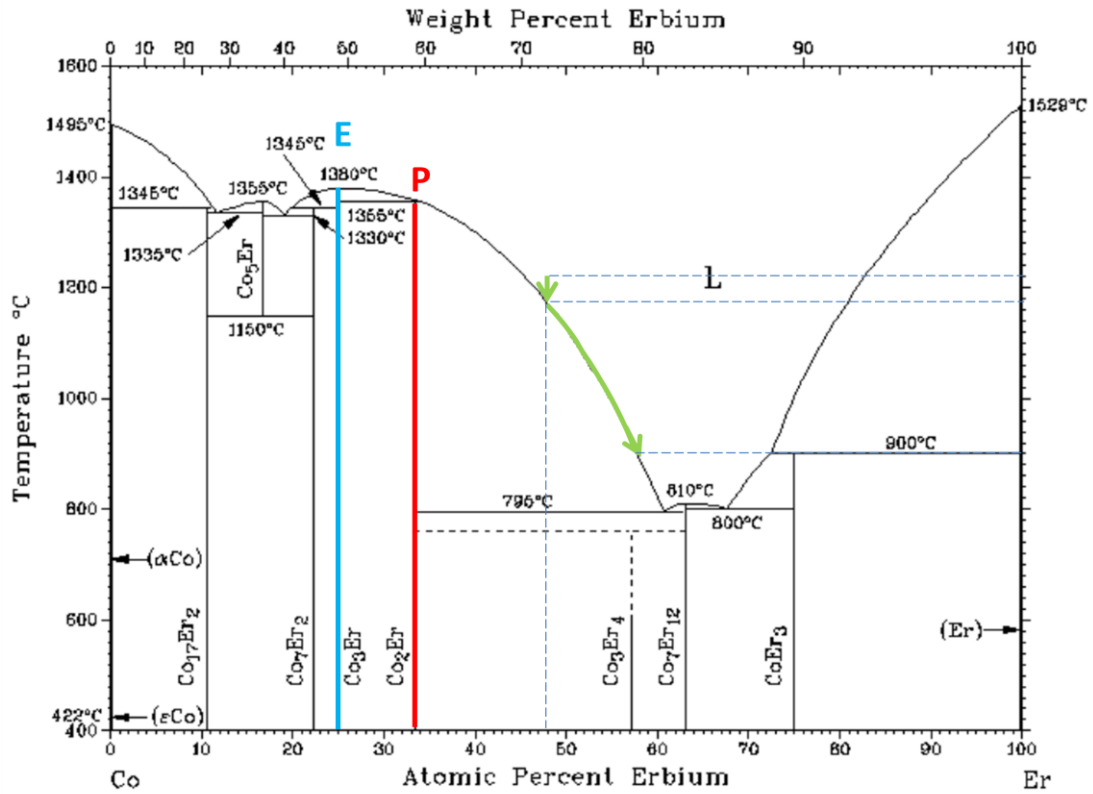


Fig. 3. Er-Co phase diagram⁸¹. The blue line marks the congruent growth of ErCo₃ from a Co-rich composition; the red line marks the incongruent growth producing the ErCo₂ phase. The green arrows depict the temperature and concentration range, in which the crystals are grown. The letter *E* marks the eutectic point (= transformation of a liquid phase into two different solid phases); *P* marks the peritectic point (= transformation of liquid and solid phase into another solid phase) of the ErCo₃ compound.

Now let us explain the principle of solution growth method. As the theory of phase diagrams and basic thermodynamic processes was discussed already in author's diploma thesis⁸², we refer to it and move directly to description of the specific case – the ErCo₂ compound - linked to this work. The growth is explained on an example of the desired ErCo₂ phase. According to the Er-Co phase diagram shown in Fig. 3, the starting Er:Co ratio should not be lower than ~ 1:2 to prevent the growth of the unwanted phase ErCo₃. After the starting composition is heated up to ~ 1200 °C; the cooling begins with a slow and constant rate. The composition reaches the solidus-liquidus line at ~ 1180 °C; now, the solution is saturated and the ErCo₂ single crystals start to grow. Solution becomes Er-richer following the solidus-liquidus line (see the green curve in Fig. 3). The system is no longer homogenous as it contains a solid phase of one stoichiometry and a liquid phase of another. The cooling is stopped at 900 °C in order to avoid the growth of spurious low-temperature binary phases.

The technical aspects of the synthesis of the cerium and other *RE* compounds including the exact steps of the preparation and necessary equipment were already

described thoroughly in author's diploma thesis; thus, we refer the reader to the literature⁸². Details of the specific parameters for the growth of phases prepared within this thesis are provided in the chapters 3-6.

Considering the flux-growth technology, laboratories of the Department of Condensed Matter Physics at MFF UK are equipped with programmable furnaces CLASIC 3013L⁸³ which enable the standard slow cooling growth and annealing treatment using ampoules from the quartz glass. Besides them, an induction heating furnace EKOHEAT developed by the Ambrell Company⁸⁴ for 50-150 kHz frequency range can be used for flux growth as well. The elements are placed first into boron nitride crucibles which are then put into molybdenum capsules; a cap is melted to a capsule to enclose it in the monoarc furnace under argon atmosphere. The capsule is then placed into a water-cooled holder and heated by the high-frequency source. Such procedure enables to perform the growth above 1200 °C, which is the temperature, when the quartz glass starts to soften already. The setup of the holder enables to rotate and move the capsule up or down slowly, similarly to the pulling head in the triarc furnace used for Czochralski growth. The frequency is proportional to the temperature. The supersaturation is enabled by the temperature gradient created by pulling the capsule slowly ($\sim$ hours to days) through the hot zone.

Recently, another furnace, utilized for the so-called “slow” Czochralski growth, has been installed in the laboratory, combining the advantages of both methods – the growth from melt and the flux growth (see Fig. 4) in order to obtain larger crystals which cannot grow congruently. The most obvious difference is the very low pulling rate which is necessary to avoid liquid inclusion incorporation. Therefore, Czochralski growth from a solution requires weeks instead of hours. The crucible is made from an ultrapure alumina instead of copper, offering a possibility to grow from indium flux which reacts easily with the copper. The diameter of the crystal can be controlled by slightly decreasing the temperature. This is done very carefully using typical temperature ramps less than 0.1 K/h. After having the desired diameter of the crystal, the temperature set point is permanently further decreased while pulling the crystal with a constant rate of about 100 $\mu\text{m/h}$ ⁸⁵.



Fig. 4. The furnace for the “slow” Czochralski growth

2.2. Characterization methods

2.2.1. X-ray diffraction

Powder diffraction

X-ray powder diffraction is a fundamental technique for structural and phase characterization which was used in this work to determine the composition of the batches of singlecrystalline samples. Both polycrystals and single crystals were pulverized into a fine powder and uniformly spread on a silicon plate. The measurement was performed on the Bruker D8 Advance diffractometer with classical Bragg-Brentano setup and the Cu K_α radiation ($\lambda = 1.5406 \text{ \AA}$). The data were analyzed using the FullProf/WinPlotr software⁸⁶ based on the Rietveld technique.

Single-crystal diffraction

To determine the crystal structure of single crystal samples, the single crystal diffraction was performed. The diffraction on selected samples glued to a glass capillary was performed using the x-ray diffractometer Gemini, equipped with the Mo lamp with graphite monochromator and Mo-Enhance collimator producing Mo K_α radiation ($\lambda = 0.7107 \text{ \AA}$), and the CCD detector Atlas. The program Superflip⁸⁷ was used for the structure solution and Jana2006⁸⁸ was used for the structure refinement. The absorption correction based on the crystal shape in combination with the empirical correction based on spherical harmonic functions was done by the data processing software CrysAlis⁸⁹.

For the verification of the lattice parameters of several single crystals, the x-ray diffractometer RIGAKU RAPID II equipped with the Mo lamp was utilized. The analysis was done by recording multiple images with a large area x-ray detector, while the single crystal was rotated in the x-ray beam. The program Rigaku CrystalClear – SM Expert 2.0⁹⁰ was used for the structure refinement.

Laue method

The method is used mainly to determine the quality and orientation of the single crystals. The experiments were performed using the x-ray Laue System by Photonic Science, UK. The diffracted white beam from the single crystal sample is registered on a CCD detector with the size of $155 \times 105 \text{ mm}$. The distance of the detector from the sample was kept constant and equal to 3.9 cm.

2.2.2. Scanning electron microscope

Scanning electron microscope (SEM) images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern. The measurement within this thesis was performed on microscope Tescan Mira I LMH SEM equipped with secondary electrons (SE) detector, backscattered electrons (BSE) detector and

energy dispersive x-ray analyzer (EDX) Bruker AXS. The signals of SE result from interactions of the electron beam with atoms at or near the surface of the sample, so they provide information about surface topography. BSE are beam electrons that are reflected from the sample by elastic scattering. Because the intensity of the BSE signal is strongly related to the atomic number Z of the specimen, BSE images can provide information about the distribution of different elements in the sample. This is especially useful for samples containing elements of rather different mass, which is the case of the $RECo_2$ and uranium crystals studied within this thesis for instance. EDX allows measuring the elemental composition of the specimen by analyzing emitted x-rays characteristic of the difference in energy between the two shells. For our purposes, the EDX method is crucial, providing the point analysis and elemental mapping option. It enables to check the stoichiometry and homogeneity on the faces and the cut of selected samples.

2.2.3. Thermal analysis

This technique is used for the determination of phase diagrams and optimization of the growth without detailed knowledge of phase diagrams. Thermal analysis can also play an irreplaceable role in selecting the right crucible material for the flux or Bridgman growth⁷⁹ which predestinates this method for applications in the field of fluxed melt experiments.

The differential thermal analysis (DTA) represents a very sensitive method based on measuring the temperature difference of the sample and reference exposed to an equal heat pulse. On the other hand, the differential scanning calorimetry (DSC) determines the energy needed to compensate the temperature difference between the sample and reference. The DTA device is adapted especially to qualitative measurements (determination of transition temperature). The measurement was performed utilizing the SETSYS Evolution 24 instrument by SETARAM Instrumentation Company. The apparatus allows measuring with TG, TMA, DTA and DSC device hooked to the balance. Simultaneous TG-DTA/DSC enables measuring both the heat flow and weight changes in a material as a function of temperature or time in a controlled atmosphere. In our measurements, we used both DTA and DSC option; the data from thermogravimetry are not presented because of they do not reveal any relevant information concerning the transition temperatures. As a crucible, the standard alumina crucibles with the diameter 0.5 cm and height 1 cm were used. The onset, offset and maximum temperatures of the peaks were estimated using the SETARAM software.

2.3. Macroscopic methods

2.3.1. Magnetic measurements

The measurements of magnetization, dc and ac susceptibility were performed using the Physical Property Measurement System (PPMS) and the Magnetic Property Measurement System (MPMS) by Quantum Design Inc. and the low-temperature ($T < 30$ mK) measurements (ac susceptibility) were performed in the $^3\text{He}/^4\text{He}$ dilution refrigerator equipped with the 9 T magnet. The PPMS 9T (14T) apparatus provides measurements in the temperature range of 1.8–400 K in magnetic fields up to 9 T (14 T) while the MPMS 7T enables experiments in the temperature range of 1.8 – 400 K in magnetic fields up to 7 T. MPMS provides the extraction (dc) and the reciprocating sample option (RSO) transport. This configuration increases sensitivity for measurement and thus, it is preferred for samples providing very weak signals ($\leq 10^{-6}$ emu), typically cerium crystals with mass below 1 mg. The vibrating sample magnetometer (VSM) is utilized for measurements on PPMS. This option is preferred when the signal from the samples was sufficient ($\geq 10^{-4}$ emu), which is mainly the case of the measured non-cerium samples (RECo_2 and RE_2CoIn_8 crystals).

2.3.2. Specific heat measurements

The measurements of heat capacity were performed partially on PPMS 9T (14T) in the temperature range 0.35–300 K using ^3He option devices (1.8–300 K without the option) and in the $^3\text{He}/^4\text{He}$ dilution refrigerator in temperature range 300 mK – 400 K. The experiments were performed under vacuum conditions ($< 10^{-3}$ torr), which imply constant pressure p specific heat (C_p). The sample is placed on a corundum plate with dimensions 3×3 mm mounted on the puck with a thermometer and a heater fixed to the bottom part of the plate. To keep the sample in position and to improve the heat contact, the Apiezon-heat conductive grease is used (Apiezon N is used for temperatures below 300 K). The specific heat is measured by the relaxation method⁹¹ which is based on heating the sample by a heat pulse and consequent thermal relaxation. The decay can be described by two exponential components τ_1 and τ_2 , depending on the thermal contact between sample and the platform. The relaxation process is recorded and the value of the sample specific heat is obtained from the fit of the time dependence of temperature during the relaxation.

Specific heat is defined according to the Maxwell relation as

$$C_p = T \left(\frac{ds}{dT} \right)_p. \quad (27)$$

Therefore, the experimental knowledge of $C_p(T)$ provides a direct measure of the entropy evolution of the system.

Specific heat is, similarly to electrical resistivity, an additive quantity, i.e., it consists of contributions with various temperature dependencies^{92,93}, which become dominant in different temperature ranges.

$$C_{tot} = C_n + C_e + C_{ph} + C_{mag} + C_{Sch} \quad (28)$$

The nuclear contribution C_n plays an important role at temperatures below 0.5 K corresponding to a $\sim T^2$ dependence. Contribution C_e originating from the conduction electrons dominates roughly in the temperature range $0.5 < T < 4$ K; more precisely, the temperature region is defined by the Debye temperature θ_D discussed further. The conduction electrons are considered to be free charge carriers with a linear temperature dependence $C_e \sim \gamma T$ which is directly proportional to the density of states at the Fermi level. Experimental values of γ are extracted from a C_p/T vs. T^2 plot for $T \rightarrow 0$. The γ coefficient can be enhanced by interactions of band electrons with quasiparticles (magnons, phonons...) or magnetic correlations. A significant increase of γ is characteristic for systems with heavy electron quasiparticles in HF materials (for more details, see the section 1.4).

Lattice vibrations described by quasiparticles – phonons - give rise to a phonon contribution $C_{ph} \sim \beta T^3$. This contribution affects the specific heat dependence significantly at temperatures above $T > \theta_D/30$, i.e. it dominates at higher temperatures than the contributions C_n and C_e . The Debye temperature is related to the factor β by formula

$$\beta = \frac{12n\pi^4 k_B}{5\theta_D^3} \quad (29)$$

which is valid up to $T = \theta_D/24$. The limitation of this expression is given by its strict validity for pure elements or n atoms of equal mass.

Phonons can be divided into $3n-3$ optical branches and 3 acoustical branches where n stands for number of atoms per unit cell⁵. The high-temperature region can be described using the Dulong-Petit law $C_{ph} \rightarrow 3nk_B$ where $3n$ are 3 degrees of freedom of n atoms leading to a constant value of the phonon specific heat, independent for almost every substance. The law fails for low temperatures where it has to be replaced by a model taking into account quantum physics. Einstein and Debye models were developed to explain the low-temperature behavior of specific heat. Einstein model describes the lattice vibrations as independent vibrations of n harmonic oscillators with an equal frequency $\omega_E = h\nu_E$.

The heat capacity is given by an expression

$$C_E = 3nk_B \left(\frac{\theta_E}{T} \right)^2 \frac{e^{\frac{\theta_E}{T}}}{\left(1 - e^{\frac{\theta_E}{T}} \right)^2} \quad (30)$$

where $\theta_E = \omega_E/k_B$ is the Einstein temperature characterizing one branch. This model describes the high-temperature region and optical phonons very well but it fails when applied for temperatures lower than $\sim 0.2 \theta_E$.

The approach of the Debye model is significantly different: the material is described as a continuous elastic body, vibrating elastically in an analogy with sound vibrations. The frequencies are proportional to ck where c is the speed of vibration wave propagation and k is the size of the wave vector.

The specific heat is expressed as

$$C_D = 9nk_B \left(\frac{T}{\theta_D} \right)^3 \int_0^{\frac{\theta_D}{T}} \frac{x^4 e^x}{(e^x - 1)^2} dx. \quad (31)$$

The integral can be replaced by a fraction with polynomials

$$C_D = \frac{24.9416 + 0.05313x_D^2 + 9.85 \cdot 10^{-4}x_D^4 + 4.8 \cdot 10^{-7}x_D^6}{1 + 0.0521x_D^2 + 8.71 \cdot 10^{-4}x_D^4 + 4.56 \cdot 10^{-6}x_D^6 + 2 \cdot 10^{-8}x_D^8} \quad (32)$$

where $x_D = \theta_D/T$. Debye temperature θ_D , defined similarly as the Einstein temperature, describes one branch vibrating with the highest possible frequency $\omega_E = \hbar\nu_D$. In the real systems, θ_D can be obtained by fitting the specific heat in the whole temperature range using solely the electronic and Debye contribution assuming that the degeneracy of Debye branches is equal to the number of atoms in the unit cell.

As the Debye model mimics the specific heat in the low-temperature limit well, the low- and high-temperature region of specific heat can be described satisfactorily using both models. The fit of the high-temperature part of specific heat can be further improved by considering the thermal expansion which is not involved in the harmonic approximation. When the thermal expansion is considered, anharmonicity⁹⁴ can be involved into the specific heat description by a correction factor α . Consequently, we obtain the corrected form of the phonon contribution.

$$C_{ph} = R \left(\frac{1}{1 - \alpha_D T} C_D + \sum_{i=1}^{3N-3} \frac{1}{1 - \alpha_E T} C_E \right) \quad (33)$$

According to the last equation, there are $3n - 3 + 3n - 3 + 2 = 6n - 4$ free variables in total. This approximation leads to a very unstable system of many parameters. The degeneration of branches, which is given by the crystal symmetry, reduces the number of variables making the fitting procedure feasible.

There is a large variety of magnetic contributions C_m included in the total specific heat $C_p(T)$ ⁹². In case of the second-order transitions, a jump in C_p is expected at $T = T_{\text{ord}}$ because of the change of the dS/dT slope. T_{ord} can be experimentally determined by the equal-entropy construction criterion⁹⁵. At temperatures below T_{ord} , the temperature dependence of specific heat can be described in terms of the spin-wave theory (see *Sereni*⁹² and references therein). The theory predicts well defined relations; for ferro- and ferrimagnetic materials, $C_m \sim T^{3/2}$ (quadratic magnon dispersion $q = 2$) and for antiferromagnetic materials, $C_m \sim T^3$ (linear magnon dispersion $q = 1$). The activation energy of spin waves arises under applied magnetic field leading to an exponential increase at low temperatures associated with a gap Δ_m in the magnon spectrum.

For a FM material, we expect

$$C_m \sim T^{\pm 1/2} e^{-\Delta_m/T} \quad (34)$$

where plus holds for the magnetic field applied along the easy axis and minus for the perpendicular orientation of field, while for an AF material, we get

$$C_m \sim T^{-1/2} e^{-\Delta_m/T} \quad (35)$$

for the magnetic field applied along the easy axis; the perpendicular orientation of field renders $C_m \sim T^3$.

The CEF splitting (for more information, see the section 1.2) contributes to the magnetic part of specific heat in the PM state by the Schottky anomaly C_{Sch}

$$C_{\text{Sch}} = \frac{R}{T^2} \left(\frac{\sum_{i=0}^n \Delta_i^2 \exp\left[-\frac{\Delta_i}{T}\right]}{\sum_{i=0}^n \exp\left[-\frac{\Delta_i}{T}\right]} - \left(\frac{\sum_{i=0}^n \Delta_i \exp\left[-\frac{\Delta_i}{T}\right]}{\sum_{i=0}^n \exp\left[-\frac{\Delta_i}{T}\right]} \right)^2 \right) \quad (36)$$

where Δ_i is the energy of the i -th energy level. The magnetic entropy can be described in a high-temperature limit as

$$S_{\text{mag}} = R \ln(2J + 1). \quad (37)$$

The crystal field ground state of most cerium compounds is a doublet, which leads to the maximum theoretical value of entropy connected with magnetic phase transition equal to

$$\Delta S = R \ln 2. \quad (38)$$

Schottky anomalies are well observed when their respective characteristic energies $k_B \Delta < 20$ K.

The temperature dependence of specific heat is affected also by the Kondo effect (for more details, see the section 1.4). The formation of a virtual-bound state causes a significant increase of the density of states (observed as a strong enhancement of the γ coefficient). The height of this resonant state is inversely proportional to its width and, therefore, $\gamma \sim 1/T_K$, where T_K is the Kondo temperature. Like for Kondo impurities, $\gamma \sim 1/T_K$ is valid also in the Kondo lattice systems which are built up from a doublet ground state and the related entropy is $R \ln 2$. There are several methods of estimating T_K exactly; from the specific heat, T_K can be evaluated using a simple two-level model⁹⁶.

In this model, the magnetic entropy S is reduced from the value of $R \ln 2$ by an energy splitting of $k_B T_K$ at the Curie temperature T_C .

$$\frac{\Delta S}{R} = \ln \left[1 + \exp \left(-\frac{T_K}{T_C} \right) \right] + \frac{T_K}{T_C} \left[\frac{\exp(-T_K/T_C)}{1 + \exp(-T_K/T_C)} \right] \quad (39)$$

Various methods of estimating T_K (based on measurements of dilute impurities in an appropriate NM host material – quasi-elastic neutron scattering, estimating from the magnetic susceptibility, resistivity measurements) give different results compared to each other, but similar general trends in the evolution of T_K across the series are observed⁹⁷.

2.3.3. Electrical transport measurements

Ac transport measurement system on PPMS enables to measure electrical resistivity and Hall voltage as a function of temperature and magnetic field using a standard four-probe ac method. The measured temperature range could be extended from 0.35 to 300 K using the ^3He insert. For even lower temperatures exceeding 30 mK, the $^3\text{He}/^4\text{He}$ dilution refrigerator equipped with the 9 T magnet can be used.

The sample holders suited for PPMS enable to measure two bar-shape samples simultaneously by using two independent channels. Couples of current and voltage contacts are prepared from cooper or gold wires (thickness 0.025 mm) fixed to the sample by a conductive silver paste. Other possibility is to spot weld the wires to the sample; however, this method is not suitable for very fragile samples. Measurement

in the low-temperature region requires properly prepared contacts with electrical resistivity between them lower than $\sim 1 \Omega$. To prevent the overheating of the sample in the low-temperature region, the excitation current of ~ 0.2 mA was applied for 2-4 s during the measurement; at higher temperatures, the excitation current from 0.5 to 5 mA applied for 1-2 s was usually used.

Similar to specific heat, the electrical resistivity is an additive quantity composed from a sum of independent contributions. It is summarized in the Matthiessen's rule, which states that the charge carriers are scattered by phonons, impurities and other scattering sources (defects...).

$$\rho_{tot} = \rho_{lattice} + \rho_{impurity} + \rho_{defects} \quad (40)$$

This approximate rule is not universally valid as it assumes that the sources of scattering are independent of each other. The temperature dependencies of electrical resistivity in SCES²⁴ are discussed in the previous chapter.

2.3.4. Pressure measurements

Hydrostatic pressures p up to 3.2 GPa were generated using a hybrid two-layered CuBe/NiCrAl clamped pressure cell with highest nominal pressure of 3 GPa, which is designed to fit into the PPMS apparatus and dilution refrigerator. The interior diameter of the cell is 4 mm; the resulting specimen diameter restricted by a Teflon cap is 2.7 mm. The Daphne oil 7373, which belongs to olefin oligomers, was used as the pressure-transmitting medium⁹⁸. The manganin wire (manganin is an alloy of typically 86 % Cu, 12 % Mn, and 2 % Ni) was used to determine the pressure inside the cell according to its strong pressure-dependent resistivity

$$R(T, p) = R(T, 0)(1 + \alpha(T)p) \quad (41)$$

where $\alpha(T)$ is the pressure coefficient of the manganin resistance. Its room-temperature value (at which the changes of pressure are realized) is $\alpha(293 \text{ K}) = 2.465 \cdot 10^{-3} \text{ GPa}^{-1}$. The arrangement of two 4-wire resistivity outputs (sample and manganin) was covered by the Daphne oil and placed into the Teflon capsule. The electrical contacts between the sample and manganin inside the pressurized space and the measurement electronics were mediated by insulated Cu wires leading out of the cell through the plug. The difference Δp between the room- and the lowest measured temperature of the Daphne 7373 oil inside the used pressure cell was $\Delta p \sim 0.3 \text{ GPa}$ and remained almost constant all over the used range of pressures.

2.4. Neutron diffraction

Neutron diffraction is a very powerful tool for the investigation of microscopic properties of condensed matter. As neutrons do not carry any electric charge, they can easily penetrate into the matter. While the x-rays scatter on the electrons, the neutrons scatter directly on the atomic nuclei. As the scattering length is a random function of the atomic number, light elements like hydrogen can be easily detected. The wavelength of thermal neutrons is comparable to interatomic distances, thus suitable for investigation of the crystal structure. As the neutron has a spin $S = 1/2$, it can interact with the magnetic moments in the studied sample via the dipole-dipole interaction. The inelastic neutron scattering resolves the change in the energy of the neutron as it scatters from a sample. This effect can be used to probe a wide variety of different physical phenomena such as motion of atoms (phonons), crystal electric fields and magnetic excitations, which are then reflected in macroscopic properties (specific heat, thermal conductivity, electrical resistance). In an elastic neutron scattering event, a moment is transferred from a neutron to the sample without changing the internal state of the sample (zero energy transfer) while in the case of inelastic scattering, an excitation inside the sample is created or annihilated (see Fig. 5). Considering the experiments performed in this work, we focus only on the inelastic scattering from now on. Detailed derivations can be found in literature^{99,100}; here, we concentrate on the basic and crucial relations which are necessary for further reading.

The scattering vector is defined as $\mathbf{Q} = \mathbf{k}' - \mathbf{k}$, where $|\mathbf{k}| = 2\pi/\lambda$ is a wave vector. The magnitude of the scattering vector can be derived from wavelength λ and scattering angle 2θ as follows

$$Q = \frac{4\pi}{\lambda} \sin\theta. \quad (42)$$

If n particles are scattered per second into the angle $d\Omega$ seen by the detector under the scattering angle 2θ and into the energy interval between E' and $E' + dE'$, then the double differential cross section is defined as

$$\frac{d^2\sigma}{d\Omega dE'} = \frac{n}{j d\Omega dE'}. \quad (43)$$

Here, j refers to the incident beam flux in terms of particles per area and time.

Using the Born approximation and Fermi's Golden Rule, we can define this cross section for inelastic scattering. We allow the change of a state of a sample from α to α' (= a set of quantum numbers characterizing an eigenstate of the sample).

Since the scattering event must fulfil the energy and conservation law, we arrive at a double differential cross section.

$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{|k_f|}{|k_i|} \left(\frac{m}{2\pi\hbar^2}\right)^2 \sum_{\alpha} p_{\alpha} \sum_{\alpha'} |\langle k', \alpha' | V | k, \alpha \rangle|^2 \delta(\hbar\omega + E_{\alpha} - E_{\alpha'}) \quad (44)$$

The first summation is carried over all possible initial states α of the system, weighted with the occupation probability p_{α} . The sum over final states α' is allowed by the energy conservation. The energy transfer of the neutron to the system is denoted as $\hbar\omega$.

Dynamic structure factor $S(Q, \omega)$ is defined as

$$S(Q, \omega) = \frac{1}{2\pi N} \int_{-\infty}^{\infty} dt e^{-i\omega t} \sum_{i,j} \langle e^{iQ(r_j(t) - r_i(0))} \rangle \quad (45)$$

where $r_j(t)$ is the trajectory of an particle and N is the number of chemically identical particles. The double differential cross section is then given by:

$$\frac{d^2\sigma}{d\Omega d\omega} = Nb^2 \frac{k'}{k} S(Q, \omega) \quad (46)$$

Here, b denotes the scattering length.

Strong localization of 4f-electrons leads to a typical energy splitting below 100 meV, which is perfectly suited for thermal neutron inelastic scattering. The crystal field levels are characterized by the irreducible representations of the magnetic ion site symmetry. The intensities of corresponding lines are given by transition probabilities $\Gamma_i \rightarrow \Gamma_f^{100}$. Inelastic neutron scattering plays also an irreplaceable role in the investigation of magnon excitations. While the intensity is rising with the increasing Q for the phonon scattering, it vanishes for the magnon scattering.

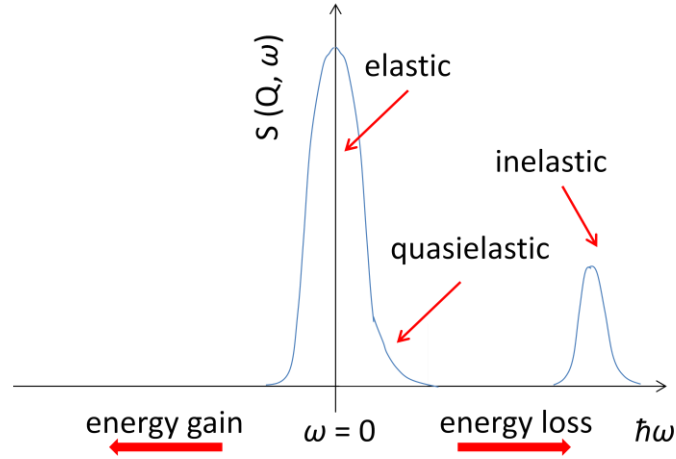


Fig. 5. The elastic, quasielastic and inelastic scattering depicted on a scheme of an energy dependence of the dynamic structure factor $S(Q, \omega)$.

Experimentally, not only of the flight direction of the scattered neutron but also its energy has to be followed. Practically, this can be accomplished using either a three-axis spectrometer, a spin-echo spectrometer or a time-of-flight spectrometer¹⁰⁰. In case of the time-of-flight spectrometer, the incident neutron energy is selected by the rotation frequency ω of the Fermi chopper and its phase delays relative to the source emission. The final energy can be computed from the time of arrival of the scattered neutron pulse at the detector. The energy can be determined simultaneously for all scattering angles and therefore, the complete Q, ω space can be measured effectively by covering a large angle with detectors. The neutron inelastic scattering experiment within this work was carried out on the time-of-flight MERLIN spectrometer¹⁰¹ at the ISIS Neutron and Muon Facility, UK. ISIS is a pulsed neutron source which is preferred in the case of time-of-flight spectrometers. The MERLIN instrument is a high count rate, direct geometry chopper spectrometer. More details can be found in the section 4.3.

2.5. Computational methods

First-principles calculations are based on the density functional theory (DFT) which describes the ground state of a many-body system, but instead of working with a system of N electrons it uses the functionals of spatially dependent electron density with 3 coordinates. Standard DFT is based on solution of the Kohn-Sham equations with the Kohn-Sham potential which includes also the exchange-correlation term. However, the exchange-correlation potential is known exactly only for the electron gas, which requires approximations to be involved. The most widely used approximation is the local-density approximation (LDA); the functional depends only on the density at the coordinate where the functional is evaluated. Generalized gradient approximation (GGA) represents a numerical approximation which takes into account the gradient of the density at the same coordinate and improves, for example, the total energies and lattice parameters of $3d$ - and $4d$ -metals. Both LDA¹⁰²

and GGA¹⁰³⁻¹⁰⁵ approximations were used within this work. Results of the first principles calculations of the RE_2CoIn_8 and U_2RhIn_8 compounds presented in this thesis were performed using methods described in Ref.¹⁰⁶. The microscopic CEF Hamiltonian in RE_2CoIn_8 was diagonalized and the eigenenergies and eigenfunctions were found. The magnetic susceptibility was calculated from the second-order perturbation theory using standard formulas. The details of the first-principles calculations of the RE_2CoIn_8 system were published in Ref.¹⁰⁷.

3. Novel $\text{Ce}_n\text{T}_m\text{In}_{3n+2m}$ compounds

In the following chapter, we focus on the ground-state properties of the novel phases Ce_2PtIn_8 and $\text{Ce}_3\text{PtIn}_{11}$ ¹⁰⁸, and of the recently reported compound $\text{Ce}_3\text{PdIn}_{11}$ ^{108,109} from the $\text{Ce}_n\text{T}_m\text{In}_{3n+2m}$ group. First, the ground-state properties of the already known related systems are introduced as well as the recent development in this field. Significant part of the chapter is devoted to description of synthesis and characterization. This is because the preparation of these materials is connected with the intergrowth of impurity phase CeIn_3 and related phases, as well as with the difficulty to determine precisely the composition of these high-stoichiometric compositions. Therefore, the differential thermal analysis was included also into the study to achieve the best possible quality of single crystals used further for the bulk measurements. The dimensions of the $\text{Ce}_3\text{TIn}_{11}$ samples enable measurement of various magnetization, thermodynamic and transport properties in applied magnetic field and/or under hydrostatic pressure.

In the Physical properties section, it is shown that $\text{Ce}_3\text{PdIn}_{11}$ and $\text{Ce}_3\text{PtIn}_{11}$ possess several unique properties among the strongly correlated systems. First of all, the compounds belong to very rare examples of centrosymmetric stoichiometric systems revealing magnetic ordering and superconductivity already at ambient pressure. Moreover, $\text{Ce}_3\text{PdIn}_{11}$ and $\text{Ce}_3\text{PtIn}_{11}$ represent new structure types which significantly enrich the spectrum of stacking compositions by representing a “missing step” between the 2D-like CeTIn_5 and the 3D CeIn_3 phases¹⁰⁸⁻¹¹⁰. Beside the novel layer-stacking sequence in $\text{Ce}_3\text{TIn}_{11}$, the structure of these materials is interesting also from the point of view of multiple inequivalent Ce-sites (i. e. sublattices) as will be shown in the section 3.2. Each Ce-site has a different crystal environment which can be described by hybridization strength between the 4*f*- and conduction electrons. The local symmetry of the inequivalent Ce-ions is different which reflects in the hybridization characterized by its own Kondo temperature T_K . Thus, the resulting ground state of the material is determined by a combination of various “ground states” corresponding to Ce sublattices¹¹¹. Different Kondo temperatures render interesting ground states as will be illustrated on a system with two independent Ce-sites. At temperature $T_{K1} > T > T_{K2}$ where T_{K1} and T_{K2} correspond to sites Ce(1) and Ce(2), the compound is in the partially screened Kondo regime which means that only the Ce(1)-ions are fully screened forming a HF state. Ce(2)-ions are screened only partially, standing behind the magnetic ground state in such system.

3.1. Introduction

The compounds with the chemical formula $\text{Ce}_n\text{T}_m\text{In}_{3n+2m}$ ($n = 1, 2$; $m = 1, 2$ and $T = \text{Co, Rh, Ir}$) have become an intensively investigated group of HF materials. These compounds are known to be on the verge of a magnetic to non-magnetic QCP

and exhibit a huge variety of interesting phenomena, such as unconventional superconductivity, nFl behavior, a possible FFLO state and coexistence of superconductivity and magnetic ordering^{112,113}. However, this family of compounds is interesting for some other reason. The general formula $Ce_nT_mIn_{3n+2m}$ possesses the $Ho_nCo_mGa_{3n+2m}$ (space group $P4/mmm$) tetragonal crystal structure and can be viewed as built of n layers of $CeIn_3$ and m layers of TIn_2 stacking along the [001] axis. For instance, in $CeTIn_5$, each $CeIn_3$ layer is separated by one TIn_2 layer. This configuration leads to a 2D-like character of the Ce sublattice. A different example is the Ce_2TIn_8 system where two $CeIn_3$ layers are separated by one TIn_2 layer. Here, the character of the dimensionality evolves from 2D to more 3D^{110,113,114}. Thus, the structural dimensionality represents, besides varying hydrostatic pressure¹¹⁵ and chemical substitution¹¹⁶, another parameter suitable for tuning the QCP. The layered structure of the $Ce_nT_mIn_{3n+2m}$ compounds makes them ideal candidates to investigate the influence of the parameter “dimensionality” with respect to quantum criticality³¹.

$CeIn_3$, $CeTIn_5$ and Ce_2TIn_8 ($T = Co, Rh, Ir$)¹¹³ are thoroughly investigated compounds, known for more than two decades. Among them, the most investigated are $CeCoIn_5$ and $CeRhIn_5$. Despite being known for a long period of time, both materials still are fruitful playgrounds for testing theoretical models and hypotheses. In the following, $CeCoIn_5$, $CeRhIn_5$ and the other most prominent examples of the $Ce_nT_mIn_{3n+2m}$ class of materials will be briefly discussed:

CeCoIn₅

$CeCoIn_5$ is an ambient pressure d -wave superconductor with the highest $T_c = 2.3$ K among the $Ce_nT_mIn_{3n+2m}$ compounds. $CeCoIn_5$ exhibits nFl behavior in the normal state suggesting the vicinity of $CeCoIn_5$ to an antiferromagnetic QCP¹¹⁷. The variation in the specific heat¹¹⁸ and thermal conductivity¹¹⁹ with fourfold symmetry for the magnetic field in the basal plane pointed to $d_{x^2-y^2}$ pairing. However, the first direct observation of the d -wave superconductivity was realized by using the Bogoliubov quasiparticle interference imaging method in the scanning tunnelling microscope¹²⁰. A superconducting energy gap with orientation of the nodes corresponding to the $d_{x^2-y^2}$ gap symmetry was observed. Recent realistic model calculations of the field-angle-resolved specific heat and thermal conductivity¹²¹ are consistent for experimental results on $CeCoIn_5$ and the parent compounds with Rh and Ir. Half a century ago, Fulde and Ferrell¹²², and Larkin and Ovchinnikov¹²³ developed theories of inhomogeneous SC states. However, many compounds have failed to reveal such a state. $CeCoIn_5$ has been attracting the attention due to its unusual SC phase diagram which made it a candidate for the FFLO state. The upper critical field H_{c2} in $CeCoIn_5$ is 11.6 T and 4.95 T for the magnetic field applied in the basal plane and along the [001] axis, respectively¹²⁴. The SC transition changes its character from a second- to a first-order one in magnetic field $H_0 \sim 10$ T and temperature $T_0 \sim 1$ K¹²⁵⁻¹²⁷. At even lower temperatures, another anomaly emerges at

$T = 0.3$ K as a second-order transition in magnetic fields close to the upper critical field H_{c2} ¹²⁸. It has been predicted that modulated triplet superconductivity occurs in singlet d -wave superconductors¹²⁹ and recently, the evidence for p -wave Cooper pair-density wave in CeCoIn₅ was reported¹³⁰ representing an example where spatially modulated superconductivity is associated with SDW order.

CeIrIn₅

CeIrIn₅ is another ambient pressure superconductor with $T_c = 0.4$ K¹¹². The susceptibility and specific heat measurements point to nFl behavior and high Sommerfeld coefficient of the normal state¹³¹. The recent doping experiments suggest that CeIrIn₅ is in proximity to an antiferromagnetic QCP, and HF superconductivity is mediated by magnetic quantum fluctuations rather than by valence fluctuations¹³². The SC temperature increases with applied pressure forming a SC dome¹³³. Field-angle-resolved specific heat and thermal conductivity revealed fourfold symmetry¹³³⁻¹³⁵ indicating $d_{x^2-y^2}$ -wave SC gap similarly to CeCoIn₅.

CeRhIn₅

CeRhIn₅ orders antiferromagnetically at $T_N = 3.8$ K¹¹² at ambient pressure in contrast to CeCoIn₅ and CeIrIn₅ and reveals a nontrivial magnetic structure for the magnetic field applied along the [100] axis^{21,114,136}. The ground state is an incommensurate antiferromagnet where $\mathbf{q} = (\frac{1}{2}, \frac{1}{2}, 0.297)$ and the magnetic moments are oriented helicoidally in the basal plane²¹; in higher magnetic fields, T_N increases and two magnetic field-induced transitions at T_1 and T_2 appear. The phase transitions divide the phase diagram into several regions¹¹⁴, which differ in magnetic structure. Between T_N and T_2 , the helicoidal ordering changes into an elliptical one. A commensurate antiferromagnetic structure with $\mathbf{q} = (\frac{1}{2}, \frac{1}{2}, \frac{1}{4})$ emerges in the high-field phase below T_1 .

While the long-range antiferromagnetic order of CeCoIn₅ and CeIrIn₅ can be established only by doping, ambient pressure antiferromagnet CeRhIn₅ becomes SC under hydrostatic pressure¹¹⁰ or by substitution^{137,138}. While increasing pressure, d -wave superconductivity appears at 0.5 GPa and as soon as the two characteristic scales T_N and T_c become equal at $p_1 \sim 1.75$ GPa, magnetism disappears and only superconductivity remains¹¹⁵. Specific heat experiments under hydrostatic pressure and magnetic field inside the SC dome reveal a line of quantum phase transitions between the SC state and the coexisting states of SC and magnetic field-induced magnetism¹¹⁵. Recent studies of electrical resistivity in hydrostatic pressure suggested that the SC state is associated with Kondo-breakdown QCP¹³⁹.

Ce₂CoIn₈

The properties of the Ce₂TIn₈ compounds are similar to those of CeTIn₅ in many ways reflecting lower anisotropy compared to the single-layered CeTIn₅. Similar to CeCoIn₅, also Ce₂CoIn₈ undergoes a SC transition, $T = 0.47$ K which is lower than

the one for CeCoIn₅ consistently with previous statement. The compound reveals nFl behavior above T_c pointing to the vicinity of the Ce₂TIn₈ system to the QCP associated with the AF correlations¹⁴⁰⁻¹⁴². Additionally, the CEF energy scheme was investigated by the temperature dependence of specific heat and the anisotropic properties of magnetic susceptibility. According to the CEF model calculations, first and second CEF states E_1 and E_2 are located at 7.9 meV and 8.8 meV above the ground state doublet, respectively¹⁴³.

Ce₂IrIn₈

Ce₂IrIn₈ stays paramagnetic down to the lowest measured temperatures and reveals a magnetic field-induced nFl behavior^{112,144}.

Ce₂RhIn₈

The Ce₂RhIn₈ compound orders antiferromagnetically at ambient pressure below $T_N = 2.8$ K¹¹². The electronic specific-heat coefficient yields 400 mJ.molCe⁻¹K⁻²¹⁴⁵. The magnetic phase diagram of Ce₂RhIn₈ at ambient pressure is reminiscent of that of CeRhIn₅¹¹⁴. The antiferromagnetic structure of Ce₂RhIn₈ can be described by the magnetic q -vector ($\frac{1}{2}$, $\frac{1}{2}$, 0) and by the deviation 38° of magnetic moments from the [001] axis¹⁴⁶. The ground state can be tuned from an AF to a SC state both by applying pressure¹⁴⁷ (Ce₂RhIn₈ becomes SC under pressure $p \sim 1.8$ GPa at $T_c = 0.9$ K¹⁴⁸) and by doping¹⁴⁹⁻¹⁵¹ suggesting presence of QCP similarly to CeRhIn₅.

Except of these well-known cerium compounds, new parent structures and compounds CePt₂In₇¹⁵², Ce₂PdIn₈¹⁵³, Ce₅Pd₂In₁₉¹⁰⁹ and Ce₃PdIn₁₁^{108,109} with $T = \text{Pd}$ or Pt have been discovered and subjected to studies of their crystal structure and physical properties:

Ce₂PdIn₈

Ce₂PdIn₈ is a HF superconductor¹⁵⁴⁻¹⁵⁸ below 0.7 K emerging out of a nFl phase. The growth of the bulk Ce₂PdIn₈ single crystals is not straightforward; the phase is obtained as a very thin layer (50 - 100 μm) growing on top of CeIn₃ single crystals¹⁵⁶⁻¹⁵⁸. Single-phase samples could be successfully isolated only by a careful mechanical separation of these phases¹⁵⁸. Studies of the polycrystalline Ce₂PdIn₈ under pressures up to 2.1 GPa showed that increasing pressure gradually suppresses T_c and pushes the system away from the nFl state¹⁵⁹. The recent studies show that the upper critical field of Ce₂PdIn₈ is almost isotropic with $H_{c2}^a = 2.0$ T and $H_{c2}^c = 2.2$ T for the magnetic field applied perpendicular and parallel to the [001] axis, respectively¹⁶⁰. Similarly to with CeCoIn₅¹²⁵, H_{c2} is strongly Pauli-limited with a large Maki parameter $\alpha = 2.9$ ¹⁶¹.

CePt₂In₇

The HF compound CePt₂In₇ is a commensurate antiferromagnet below 5.2 K¹⁶² exhibiting pressure-induced SC; there is a region of pressures $1 \leq p \leq 3$ GPa where

both phenomena coexist¹⁶³. CePt₂In₇ was presented as a new structure type (I4/*mmm*) formed by two layers of PtIn₂ and one layer of CeIn₃ connecting this compound with the Ce_{*n*}TIn_{3*n*+2} family¹⁵². Thus, it was believed to reveal stronger 2D-character than CeTIn₅ due to the doubled TIn₂ layer in the structure¹⁶². However, a recent study¹⁶⁴ revised these results by showing a different structure model which supports a strongly 3D character of the compound regarding the band structure calculations.

Ce₅Pd₂In₁₉ and Ce₃PdIn₁₁

Recently, the compounds Ce₅Pd₂In₁₉ and Ce₃PdIn₁₁ have been discovered in the Ce_{*n*}Pd_{*m*}In_{3*n*+2*m*} line¹⁰⁹, representing new structure types. They were obtained in a polycrystalline form after annealing the melt at 600 °C¹⁰⁹ together with the already known compound Ce₂PdIn₈. By recalling previous studies of isothermal sections of the Ce-Pd-In system performed at 500 °C¹⁵³, 600 °C¹⁰⁹, 750 °C¹⁶⁵ where the Ce₂PdIn₈ compound exists only in the lower two temperatures, it is most likely that these more complex structures are unstable at temperatures above ~ 750 °C. According to the magnetization and transport measurements, both of them are paramagnetic down to 2 K.

In Fig. 6, the hydrostatic pressure-temperature phase diagrams of various heavy fermion compounds from the Ce_{*n*}T_{*m*}In_{3*n*+2*m*} group are presented. Apparently, general character of all phase diagrams is similar: increasing pressure suppresses the AF order and enhances the SC temperature, forming a SC dome. The highest *T_c* is located always in the vicinity to the critical pressure for which the magnetic ordering is completely suppressed.

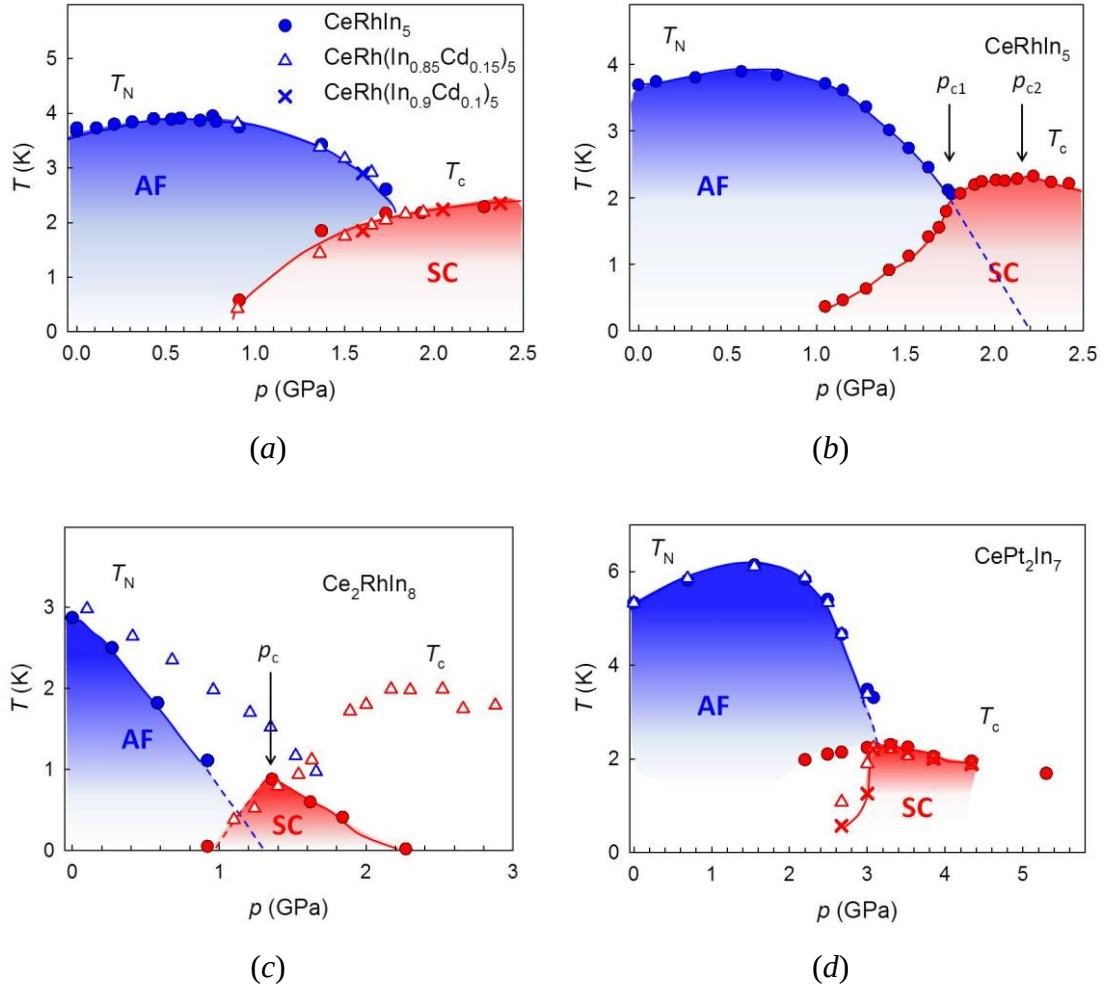


Fig. 6. The pressure-temperature phase diagrams of various Ce_nPd_mIn_{3n+2m} compounds (the data were adapted from figures shown in cited articles): (a) Cd-substituted CeCoIn₅ compared to CeRhIn₅ (the data are based on electrical resistivity and specific heat¹⁶⁶), (b) CeRhIn₅¹⁶⁷ (data determined from specific heat measurements taken from Ref.¹¹⁵), (c) Ce₂RhIn₈ (the data marked by circles were obtained by measuring In-NQR¹⁴⁸; the data denoted by triangle marks are based on electrical resistivity¹⁶⁸ and heat capacity¹⁴⁷, respectively), and (d) CePt₂In₇ (data based on electrical resistivity and heat capacity are taken from Ref.¹⁶⁹).

3.2. Synthesis and characterization

Solution growth technique turned out to be suitable for obtaining phase pure single crystals of the Ce_nTIn_{3n+2} ($n = 1, 2$, $T = \text{Co, Rh, Ir}$) systems^{110,113-115,140} of excellent quality. However, the situation in the new Pd- and Pt-based compounds is more complicated, as was already mentioned for the Ce₂PdIn₈ case¹⁵⁸. Therefore, we begin with a thorough study of the crystal growth conditions using thermal analysis in combination with detailed single-crystal characterization.

As a first step, we performed the DSC and DTA studies of the Ce-Pd-In system so that the temperature ranges for the crystal growth could be optimized according to the thermal analysis results. Consequently, single crystalline samples were grown from In self-flux. Microprobe analysis was performed using the point analysis and the elemental mapping option. The final phase identification was done by the single crystal x-ray diffraction.

3.2.1. Thermal analysis of Ce-T-In system

The samples for the DSC and DTA study were put into alumina crucibles; the total mass of each sample was ~ 100 mg. The experiment was performed under the He atmosphere and the heating/cooling rate was 10 K/min. The transition temperatures were determined as the onsets of the observed peaks in the temperature dependence of the heat flow. Ce-Pd-In batches were heated up to various temperatures between 350 °C and 1000 °C. In all performed experiments, we focused on the first thermal cycle starting with pure elements in molar ratio 2:1:25, 5:2:40 and 3:1:25. After this thermal procedure the products were carefully analyzed by the microprobe analysis. The single crystals grown during the DSC (DTA) experiment were very small. Hence, we omitted further investigation techniques such as the single crystal diffraction which could eventually disclose inclusions of other phases. Except for the microprobe, the interpretation of the data was based also on the knowledge of the Ce-In and Pd-In binary phase diagrams^{170,171}.

Some events in the studied Ce-Pd-In system were ascribed to the formation of binary phases. In order to confirm that, thermal measurements of Ce-In and Pd-In binary systems were performed using the same Ce:In and Pd:In molar ratios as in the Ce-Pd-In 2:1:25 system.

The binary Ce-In and Pd-In systems in molar composition 2:25 and 1:25, respectively, were studied by DSC (DTA) up to the temperature of 1000 °C. In Fig. 7(a), the first thermal cycle for the Ce-In system is shown. First, the heating (red curve) shows an endothermic peak at ~ 156 °C in agreement with the melting point of indium. The next peak with onset at ~ 270 °C is related to the highly exothermic reaction of Ce with In leading to the formation of solid Ce-In binary compounds. These compounds decompose in a broad temperature range at around ~ 900 °C¹⁷¹, which is manifested in a broad endothermic bump in the temperature range 800-950 °C. Upon cooling (blue curve), a peak with the onset at 900 °C is observed. The peak position is in agreement with the liquidus line reported in the Ce-In binary diagram¹⁷¹ and marks the solidification of CeIn₃; no other events were observed down to the solidification temperature of indium. In Fig. 7(b), the Pd-In binary system is shown. After the melting of indium, a broad exothermic bump with a maximum around 580 °C was found representing the formation of the Pd-In binary phases. The cooling curve shows a sharp peak at 460 °C which, consistently with the Pd-In phase

diagram¹⁷⁰, indicates the solidification of Pd_3In_7 . No other event till the solidification of indium occurs.

The ternary Ce-Pd-In system with the Ce:Pd:In molar ratio 2:1:25, 5:2:40 and 3:1:25 was studied by DSC (DTA) up to various maximum temperatures. In the upper part of Fig. 8, a heating and cooling cycle up to 750 °C is shown for the 2:1:25 concentration. The heating branch of the temperature dependence of the heat flow shows first the consumption of heat during the melting of In. It is succeeded by an exothermic event at ~ 280 °C which indicates the formation of the Ce-In binary compounds just like in the Ce-In binary system (see Fig. 7(a)). It is followed by a broad bump with maximum at ~ 600 °C, during which reactions of the Ce-In system with Pd take place. Upon cooling, an exothermic event at ~ 550 °C is observed (see the detail of Fig. 8). We ascribe this to the formation of Ce_2PdIn_8 and $\text{Ce}_3\text{PdIn}_{11}$ ternary phases. Indeed, microprobe analysis of the products confirmed the creation of both compounds with only spurious presence of CeIn_3 in the batch. As discussed previously in literature (see Refs.^{157,158}), the BSE detection does not provide any contrast to differentiate CeIn_3 and Ce_2PdIn_8 from each other.

In the lower part of Fig. 8, the thermal experiment of the Ce-Pd-In system in the 2:1:25 concentration performed up to 1000 °C is depicted. This measurement simulates some of the previous Ce_2PdIn_8 single crystal growth experiments^{155,157} and sheds light on the thermal stability of the ternary compounds. Up to 750 °C, the heating curve reproduces the previous experiments (the upper part of Fig. 8). When heated further up to the maximum temperature of 1000 °C, a broad endothermic event around 900 °C is detected. It is related to decomposition of phases formed at lower temperatures. Upon cooling, an exothermic peak at ~ 900 °C is observed. In accordance with Fig. 7, we ascribe this peak to crystallization of CeIn_3 . Below 570 °C, only small features are noticeable. With utmost probability, these peaks belong to the crystallization of the ternary phases Ce_2PdIn_8 and $\text{Ce}_3\text{PdIn}_{11}$ (see the enlarged part in Fig. 8). A sharp exothermic peak emerges at 430 °C which corresponds to the Pd_3In_7 crystallization. The presence of the Ce_2PdIn_8 , $\text{Ce}_3\text{PdIn}_{11}$, CeIn_3 and Pd_3In_7 compounds in the sample was confirmed by the microprobe analysis with a majority of the latter two. This result corroborates findings of the high temperature growth process^{155,157}.

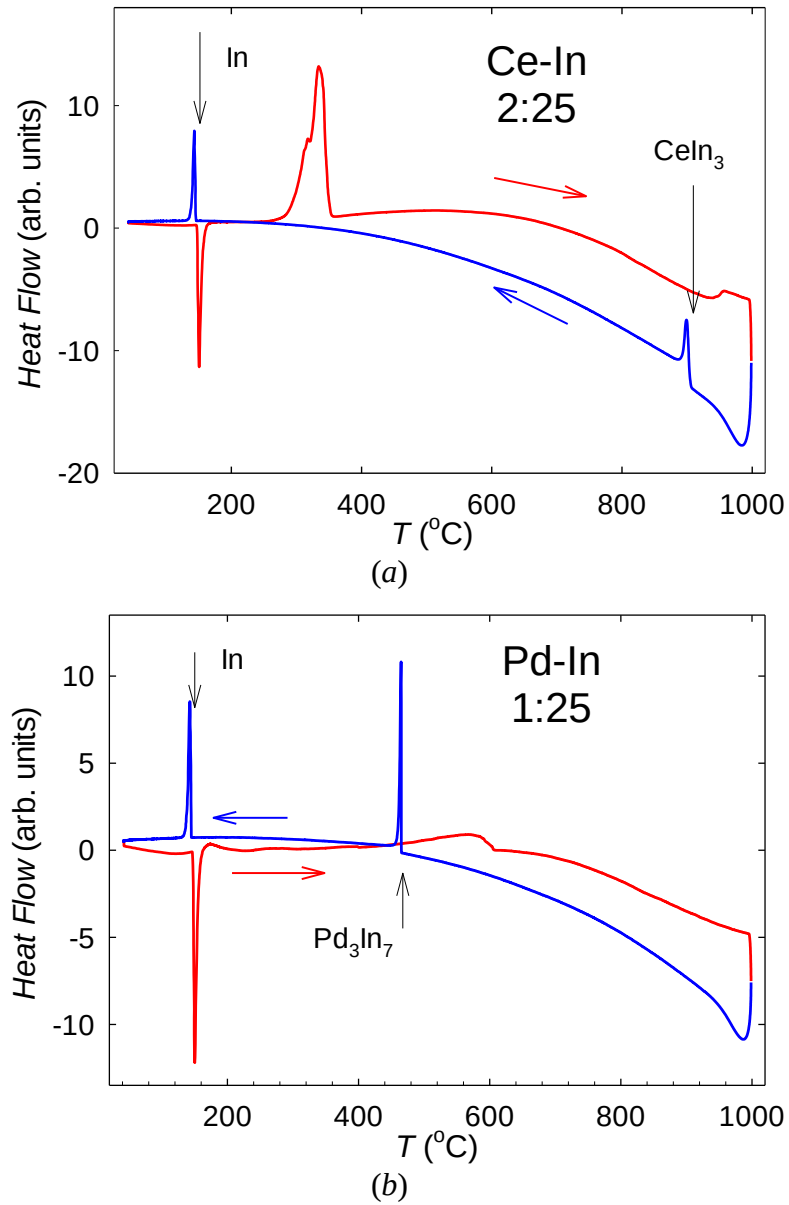


Fig. 7. Temperature dependence of the heat flow for the binary Ce-In (a) and Pd-In system (b) measured up to 1000 °C. The red and blue lines represent heating and cooling processes, respectively (also marked by red and blue arrows). While cooling, crystallization of CeIn₃ (a), Pd₃In₇ (b) and solidification of In (marked by black arrows) is detected.

Analogical experiments for slightly different compositions 5:2:40 and 3:1:25 are shown in Fig. 9(a), (b) and in Fig. 9(c), (d), respectively. They provide qualitatively similar results as for the 2:1:25 concentration. The ternary compounds crystallize at approximately similar temperatures ~ 600 °C and the CeIn₃ phase occurs only when the system is heated up to 1000 °C.

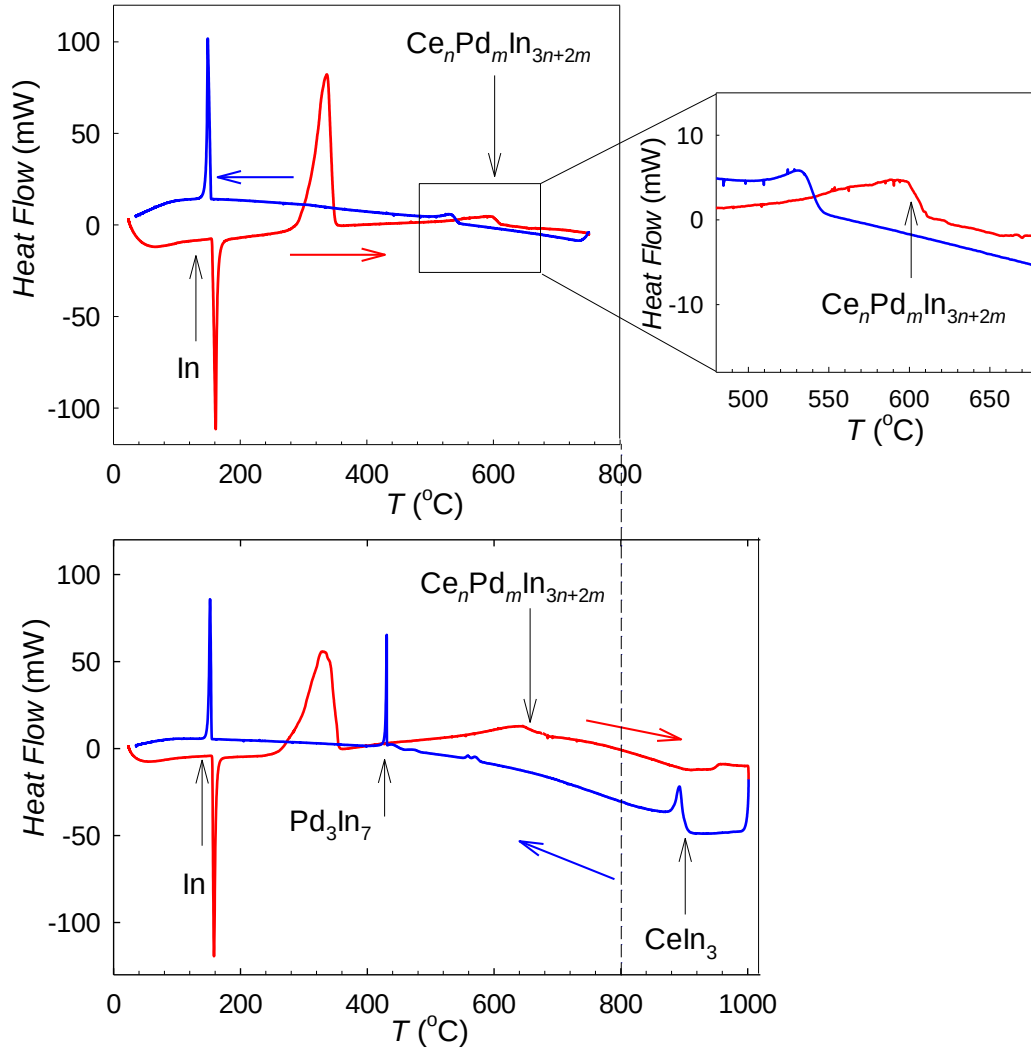


Fig. 8. Temperature dependence of the heat flow for the ternary Ce-Pd-In system in the 2:1:25 ratio measured up to 750 °C (upper part) and 1000 °C (lower part). The detail of the upper part shows the temperature region around 600 °C, where various $Ce_nT_mIn_{3n+2m}$ compounds start to decompose/crystallize. The red and blue lines represent heating and cooling processes, respectively (also marked by red and blue arrows). The black arrows point to positions of peaks connected with various thermal events.

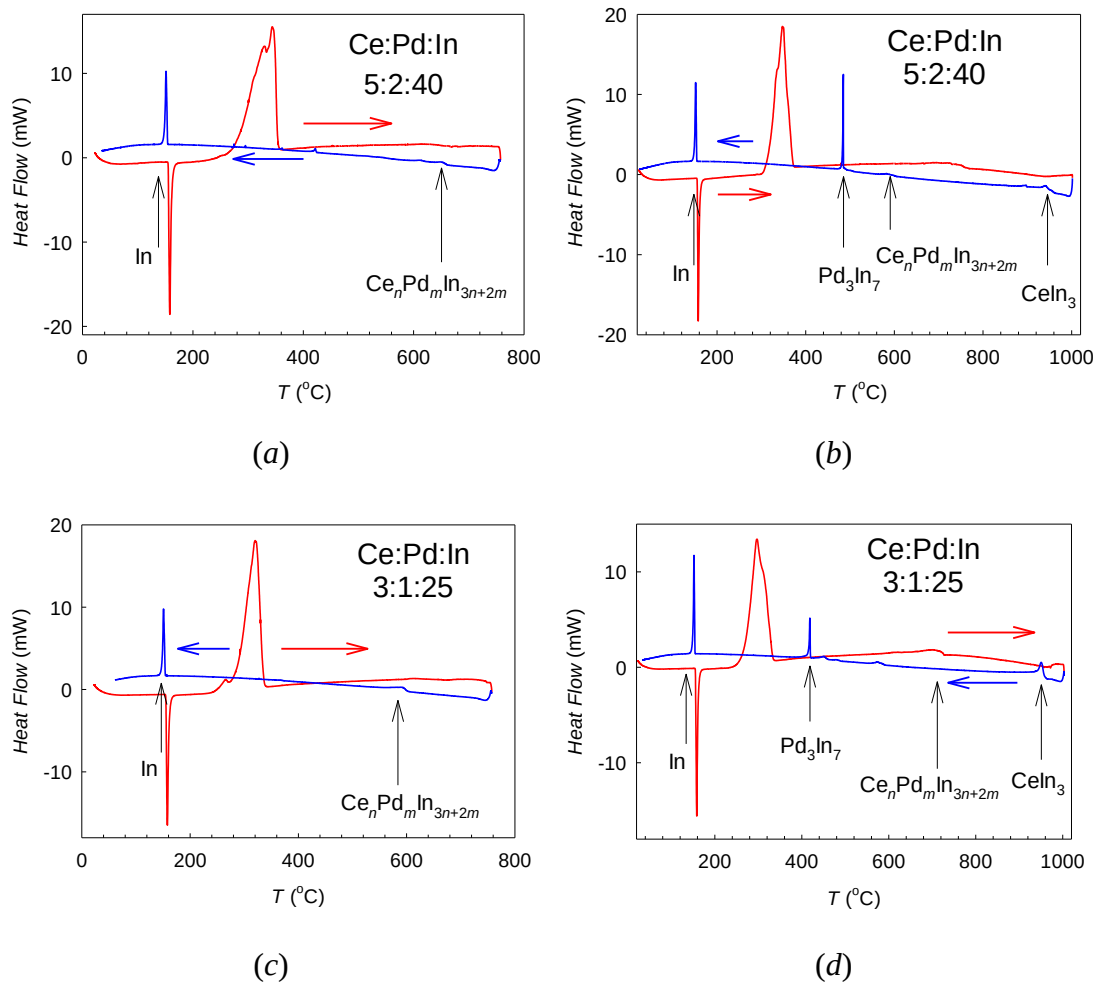


Fig. 9. Temperature dependence of the heat flow for the ternary Ce-Pd-In system in the 5:2:40 ratio measured up to 750 °C (a) and 1000 °C (b), and in the 3:1:25 ratio measured up to 750 °C (c) and 1000 °C (d). The red and blue lines represent heating and cooling processes, respectively (also marked by red and blue arrows). The black arrows point to positions of peaks connected with various thermal events.

3.2.2. Single crystal growth of $Ce_nT_mIn_{3n+2m}$

Single crystalline samples were grown from appropriate starting compositions of high purity elements (Ce 99.9 % further purified by solid state electrotransport (SSE)¹⁷², Pd 99.995 %, Pt 99.995 %, In 99.999 %) with total weight of 5 g placed in the high-purity alumina crucibles. Another crucible, filled with quartz wool was placed on the top of it. Based on the results from DSC (DTA) analysis, the single crystal growth was performed at temperatures below 750 °C. Therefore several growth attempts were performed in order to obtain the desired phases. The cooling rate during the growth was 1 - 3°C/h in all attempts. Thus, the kinetics of the single crystal growth process could not be fully reproduced because the cooling rate was significantly lower than in DTA (DSC). The range of the growth temperatures and starting composition together with the main growth products are summarized in Tab.

2. As can be read from the table, by decreasing the starting temperature to 750 °C, the formation of CeIn_3 was significantly suppressed and single crystals of Ce_2PdIn_8 and $\text{Ce}_3\text{PdIn}_{11}$ were found to be the majority products. The $\text{Ce}_3\text{PdIn}_{11}$ crystals were almost an order of magnitude larger (up to 20 mg) and seem to grow at higher temperatures than Ce_2PdIn_8 ; when decanting the flux at higher temperatures, better phase homogeneity of $\text{Ce}_3\text{PdIn}_{11}$ was obtained. Contrary, the low-temperature growth (starting from 450°C) favored the formation of Ce_2PdIn_8 . Still, the yield of Ce_2PdIn_8 was rather low and the crystals contained $\text{Ce}_3\text{PdIn}_{11}$ inclusions (often hidden inside the crystals). Besides the various temperature ranges we also tested the effect of starting elemental stoichiometry. The phase homogeneity of $\text{Ce}_3\text{PdIn}_{11}$ was improved by changing the growth composition from 2:1:25 to the Ce-rich composition 3:1:25 and 5:2:50. The 5:2:50 ratio suggests that $\text{Ce}_5\text{Pd}_2\text{In}_{19}$ could be eventually obtained. However, this phase was not found in any batches.

Tab. 2. Growth conditions for the $\text{Ce}_n\text{T}_m\text{In}_{3n+2m}$ compounds. The starting (decanting) temperature is marked as T_1 (T_2). In the table, the major phase is put on the first place. Only important phases are mentioned. Spurious amounts of CeIn_3 were detected in all growth batches.

T	Ce:T:In	$T_1/T_2(^{\circ}\text{C})$	Final products
Pd	2:1:25	950/350	CeIn_3 , $\text{Ce}_2\text{PdIn}_8 < 50\mu\text{m}$ layer
Pd	2:1: 25	750/300	$\text{Ce}_3\text{PdIn}_{11}$, Ce_2PdIn_8
Pd	2:1: 25	450/250	Ce_2PdIn_8 , $\text{Ce}_3\text{PdIn}_{11}$
Pd	3:1:25	750/550	$\text{Ce}_3\text{PdIn}_{11}$
Pd	5:2:40* [‡]	750/550	$\text{Ce}_3\text{PdIn}_{11}$
Pt	2: 1: 25	1000/400	CeIn_3 , $\text{Ce}_2\text{PtIn}_8 < 30 \mu\text{m}$ layer
Pt	2:1: 25* [†]	750/300	$\text{Ce}_3\text{PtIn}_{11}$, $\text{Ce}_3\text{Pt}_4\text{In}_{13}$, Ce_2PtIn_8
Pt	3:1:25* [‡]	750/550	$\text{Ce}_3\text{PtIn}_{11}$
Pt	1:2:30	1000/400	CeIn_3 , CePt_2In_7 , $\text{Ce}_3\text{Pt}_4\text{In}_{13}$
Pt	1:2:30	750/300	CePt_2In_7 , $\text{Ce}_3\text{Pt}_4\text{In}_{13}$

* Structure parameters presented in Tab. 12 were obtained on samples from these batches. A sample of Ce_2PtIn_8 on which the structure parameters were determined was used for the specific heat measurement in Fig. 13.

[‡] Samples of $\text{Ce}_3\text{TIn}_{11}$ ($T = \text{Pd}, \text{Pt}$) from these batches were used for the bulk measurements.

[†] A sample from this batch is shown in Fig. 10(c).

We have tested the growth conditions for CePt_2In_7 single crystals as reported in Ref.¹⁷³. As shown in Tab. 2, single crystals of CePt_2In_7 were obtained using the molar composition 1:2:30 and a growth temperature range of 1000-400 °C. However, more than 50% of the analyzed crystals from the batches were CeIn_3 or $\text{Ce}_3\text{Pt}_4\text{In}_{13}$ ¹⁷⁴. Lowering the growth temperature suppressed the CeIn_3 formation but did not significantly influence the CePt_2In_7 : $\text{Ce}_3\text{Pt}_4\text{In}_{13}$ yield ratio.

As already mentioned several times in this chapter, the microprobe was used to determine the composition and homogeneity of analyzed samples from both DTA (DSC) and flux-growth experiments. The elemental mapping option was mostly used to characterize the sample homogeneity and to disclose inclusions of neighboring $Ce_nT_mIn_{3n+2m}$ phases. By employing long acquisition times, the elemental mapping shows a clear contrast between the $Ce_nT_mIn_{3n+2m}$ phases (see Fig. 10(b)). However, in the sense of a quantitative composition analysis, the difference between neighboring phases such as Ce_3PdIn_{11} and $Ce_5Pd_2In_{19}$ or Ce_2PdIn_8 and $Ce_5Pd_2In_{19}$ is close to the resolution limit of 1-2 % (absolute). Fig. 10(a) shows the elemental mapping of a selected area of the sample subjected to the experiment from Fig. 9(a). The marked Ce_2PdIn_8 compound was identified by the microprobe analysis.

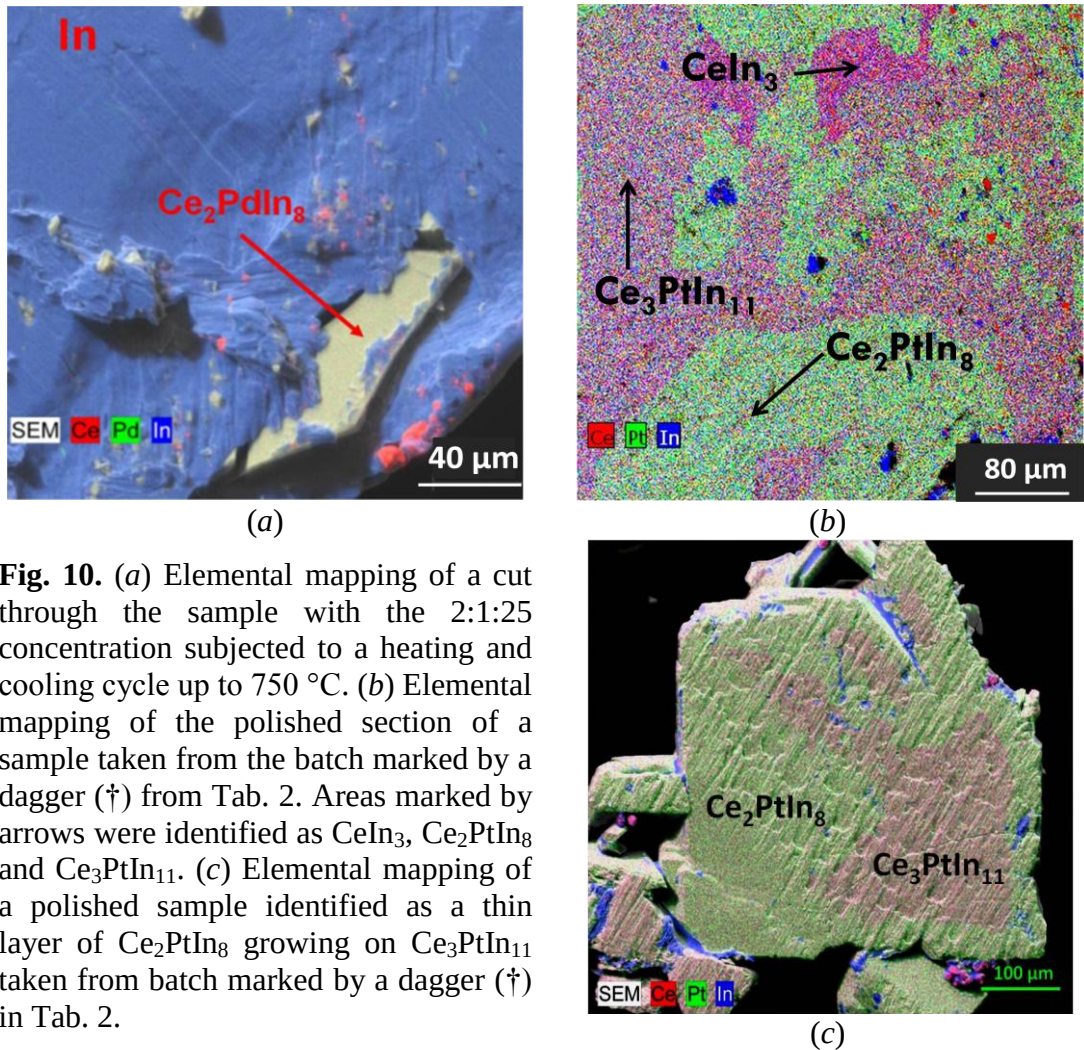


Fig. 10. (a) Elemental mapping of a cut through the sample with the 2:1:25 concentration subjected to a heating and cooling cycle up to 750 °C. (b) Elemental mapping of the polished section of a sample taken from the batch marked by a dagger (†) from Tab. 2. Areas marked by arrows were identified as $CeIn_3$, Ce_2PtIn_8 and Ce_3PtIn_{11} . (c) Elemental mapping of a polished sample identified as a thin layer of Ce_2PtIn_8 growing on Ce_3PtIn_{11} taken from batch marked by a dagger (†) in Tab. 2.

3.2.3. X-ray analysis of $Ce_nT_mIn_{3n+2m}$

Selected samples of Ce_2PdIn_8 , Ce_3PdIn_{11} , Ce_2PtIn_8 and Ce_3PtIn_{11} were subject to single crystal x-ray diffraction. The measurement was performed using the x-ray

diffractometer Gemini. The samples exhibited diffraction patterns with rather long reflection profiles due to large mosaicity. Nevertheless, they could be easily solved and refined because of the simplicity of their structure. The program Superflip was used for structure solution and Jana2006 for structure refinement; the absorption and empirical corrections were done by CrysAlis (details can be found in the section 2.2.1). The results of Ce_2PdIn_8 were in agreement with previous studies¹⁰⁹ yielding $a = 4.6881(4) \text{ \AA}$, $c = 12.2031(8) \text{ \AA}$. The $\text{Ce}_3\text{PdIn}_{11}$ structure investigation has been reported only very recently and because it was performed on single crystals isolated from polycrystalline samples¹⁰⁹, we include the analysis of this compound for comparison. The structure parameters of $\text{Ce}_3\text{PdIn}_{11}$ obtained from our study are in agreement with the reported ones. The new phases Ce_2PtIn_8 and $\text{Ce}_3\text{PtIn}_{11}$ crystallize in the Ho_2CoGa_8 - and $\text{Ce}_3\text{PdIn}_{11}$ -type structures, respectively¹⁷⁵. Basic crystallographic data are summarized in Tab. 3 and the interatomic distances are graphically shown in Fig. 11. In Appendix A, the complete structural parameters of $\text{Ce}_3\text{PdIn}_{11}$, Ce_2PtIn_8 and $\text{Ce}_3\text{PtIn}_{11}$ are presented in Tab. 12, Tab. 13 and Tab. 14, respectively. The data were obtained from samples selected from the growth batches marked in Tab. 2 by an asterisk.

Tab. 3. Basic crystallographic data for the compounds $\text{Ce}_3\text{PdIn}_{11}$, $\text{Ce}_3\text{PtIn}_{11}$ and Ce_2PtIn_8 .

Compound	$\text{Ce}_3\text{PdIn}_{11}$	$\text{Ce}_3\text{PtIn}_{11}$	Ce_2PtIn_8
Lattice parameters ($\text{\AA}$)	$a = 4.6896(11)$	$a = 4.6874(4)$	$a = 4.6898(3)$
(single-crystal data)	$c = 16.891(3)$	$c = 16.8422(12)$	$c = 12.1490(8)$
Cell volume ($\text{\AA}^3$)	371.47(14)	372.44(9)	267.21(3)
Formula weight (g.mol^{-1})	1789.74	1878.4	1393.84
Density (g.cm^{-3})	7.998	8.427	8.682

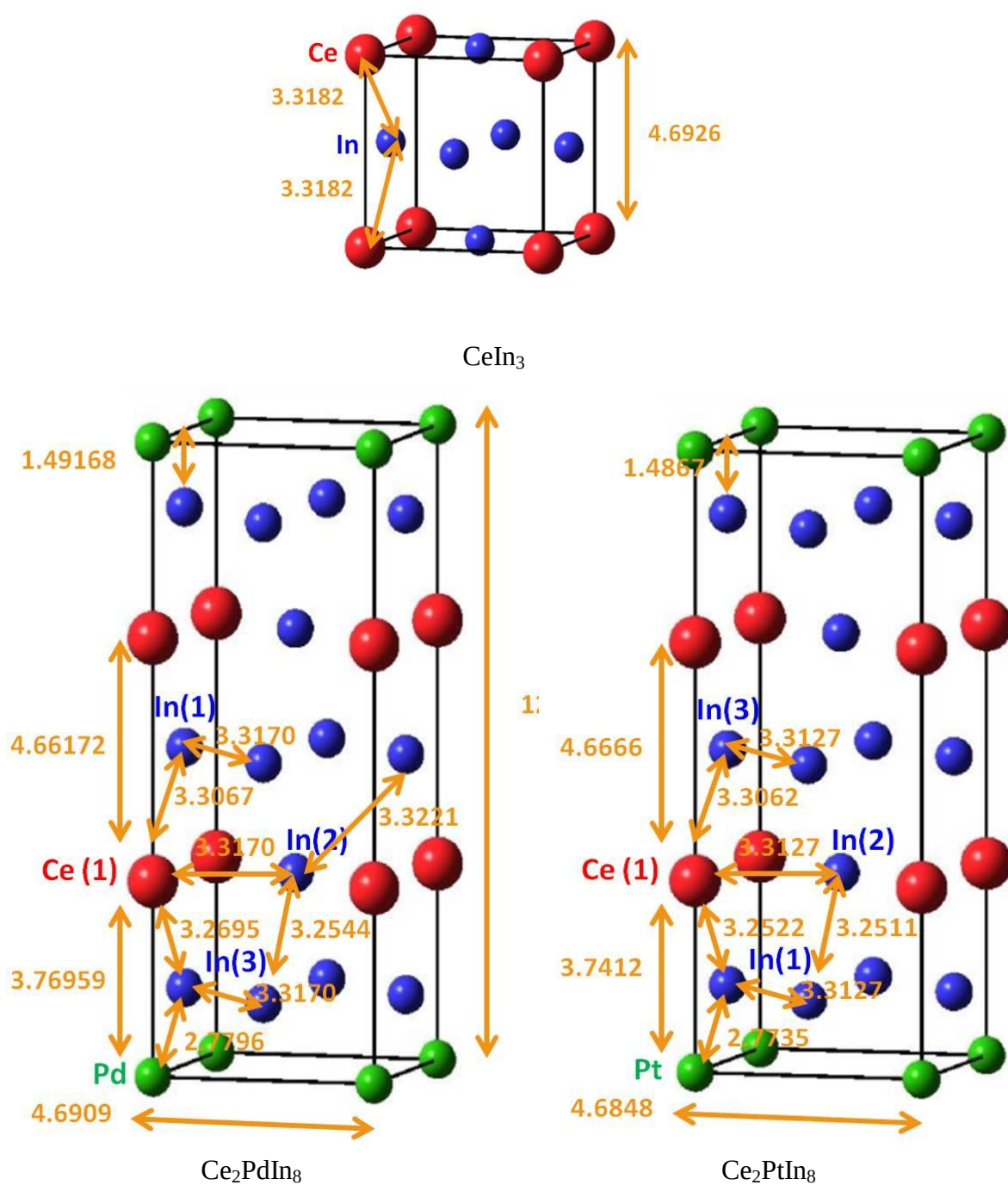


Fig. 11. The interatomic distances for CeIn₃, Ce₂PdIn₈ and Ce₂PtIn₈.

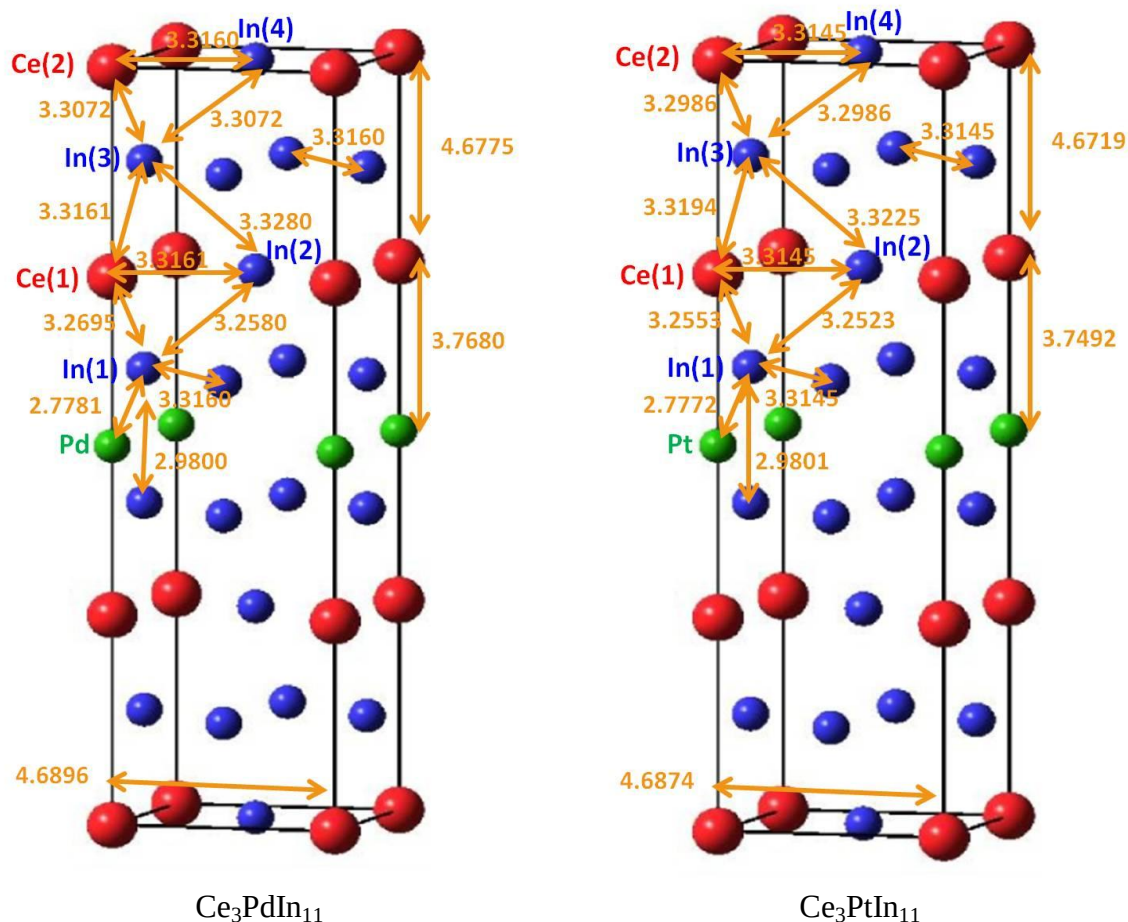


Fig. 12. The interatomic distances for $\text{Ce}_3\text{PdIn}_{11}$ and $\text{Ce}_3\text{PtIn}_{11}$.

3.3. Physical properties

The following section is divided into three parts according to the three investigated compounds. In the section 3.3.1, the low-temperature specific heat of Ce_2PtIn_8 single crystals is presented. Because this compound was not prepared in sufficient quality, only basic measurement has been performed. The second section 3.3.2 introduces the behavior of the $\text{Ce}_3\text{PdIn}_{11}$ compound at both high and low temperatures studied by means of specific heat, electrical resistivity, magnetic susceptibility and magnetization. The magnetic field- and superconducting phase diagram is composed from the obtained data. In the last part 3.3.3, the $\text{Ce}_3\text{PtIn}_{11}$ compound is characterized in an analogical way to $\text{Ce}_3\text{PdIn}_{11}$. Additionally, the high quality of the $\text{Ce}_3\text{PtIn}_{11}$ single crystals enabled to study the electrical resistivity upon applied hydrostatic pressure. Therefore, a pressure-magnetic field-temperature phase diagram could be constructed as well.

3.3.1. Ce_2PtIn_8

As was shown in the section 3.2, the preparation of single-phase single crystals of Ce_2PtIn_8 turned out to be the most challenging from all three studied cerium-based compounds. The Ce_2PtIn_8 phase was typically found as a layer growing on the $\text{Ce}_3\text{PtIn}_{11}$ bulk crystal as shown in Fig. 10(c). Nevertheless, we succeeded to separate a tiny single crystal ($m < 0.1$ mg). Its homogeneity was confirmed by the microprobe analysis and the crystal structure was characterized by the single crystal x-ray diffraction presented in Tab. 12 and Tab. 13. The synthesis conditions of the sample on which the crystal structure was determined are described in Tab. 2 in section 3.2.2. The identical single crystal was subsequently measured by means of specific heat which revealed that the compound is paramagnetic and undergoes likely a superconducting transition at $T_c = 110$ mK (see Fig. 13). The value of the transition temperature was determined as the middle of the slope marked by an arrow in the figure. Low-temperature magnetic susceptibility (not shown) was measured on a different two-phase $\text{Ce}_2\text{PtIn}_8/\text{Ce}_3\text{PtIn}_{11}$ sample resulting in observation of two step-like transitions at ~ 0.3 K and 0.1 K. The former is attributed to the superconductivity in the $\text{Ce}_3\text{PtIn}_{11}$ compound (see section 3.3.3) whereas the latter to the superconductivity in the Ce_2PtIn_8 part of the sample. The Sommerfeld coefficient γ equals $\sim 0.26 \text{ J mol}^{-1}\text{CeK}^{-2}$ determined from the linear fit $C/T = \gamma + \beta T^2$ in the temperature interval $1.5 \text{ K} < T < 3 \text{ K}$. The obtained γ coefficient corresponds well to the coefficients of parent Ce-materials, e.g. $\gamma \sim 0.24 \text{ J mol}^{-1}\text{CeK}^{-2}$ for Ce_2RhIn_8 and $\gamma \sim 0.27 \text{ J mol}^{-1}\text{CeK}^{-2}$ for Ce_2PdIn_8 ¹⁷⁶. The SC transition in Ce_2PtIn_8 reveals a jump $\Delta C_p \sim 0.015 \text{ J mol}^{-1} \text{ K}^{-1}$ at $T_c = 0.11$ K. Together with the Sommerfeld coefficient, this provides the $(\Delta C_p)_{T_c}/\gamma T_c$ ratio only about 0.53. This value is well below the value of 1.43 predicted by the BCS weak-coupling theory and it is also significantly lower than the value of 1.74 found for the parent Ce_2PdIn_8 compound¹⁵⁴. The magnitude of the ratio might be given by a broadened SC transition¹⁷⁷.

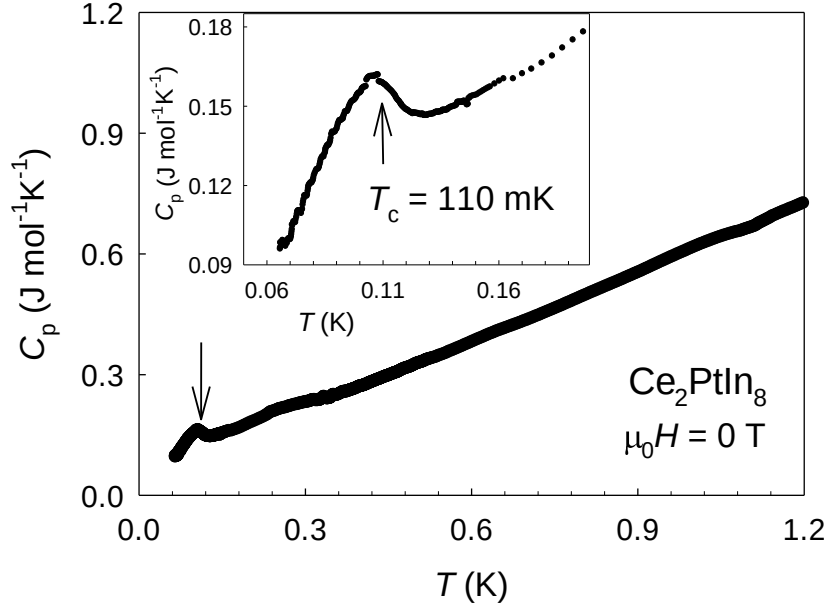


Fig. 13. The temperature dependence of the specific heat of Ce_2PtIn_8 in zero magnetic field. The inset shows the detail of the transition at $T_c = 110$ mK. The arrows mark the position of the SC transition in the main figure and in the inset.

3.3.2. $\text{Ce}_3\text{PdIn}_{11}$

Both compounds Ce_2PdIn_8 and Ce_2PtIn_8 appear to be heavy fermion superconductors. By inserting an additional CeIn_3 -layer in the structure we assume to bring the compound closer to its cubic parent CeIn_3 , meaning introducing a stronger magnetic component. Fact that now the $\text{Ce}_3\text{TIn}_{11}$ structure contains *two* inequivalent cerium sites, Ce(1) and Ce(2) in contrast to other members of the $\text{Ce}_n\text{TIn}_{3n+2}$ ($n = 1, 2$; $T = \text{Co, Rh, Ir, Pd, Pt}$) group (see Fig. 14), was already emphasized. What is new about the multiple Ce-sites particularly in this system, is that the local environments of both cerium ions are not uniquely related to $\text{Ce}_3\text{TIn}_{11}$ but exist in affiliated compounds Ce_2TIn_8 and CeIn_3 already. While the $4f$ -electrons in Ce_2PdIn_8 and Ce_2PtIn_8 are responsible for the superconducting ground state¹⁵⁴ (for Ce_2PtIn_8 see Fig. 13), CeIn_3 orders antiferromagnetically at ambient pressure¹⁷⁸. Crystallographically, Ce(1) has the Wyckoff position $2g$ with occupancy of 2 cerium atoms per unit cell and Ce(2) corresponds to the Wyckoff position $1a$ residing only 1 atom per unit cell, as mentioned in the section 3.2. Closer look on the Ce(1)-ion shows that its nearest-neighbor symmetry resembles the one of Ce(1) in the Ce_2TIn_8 compounds. The Ce(1)-ion is surrounded by one T -metal layer and one Ce-layer. On the other hand, Ce(2) is embedded in a CeIn_3 local environment.

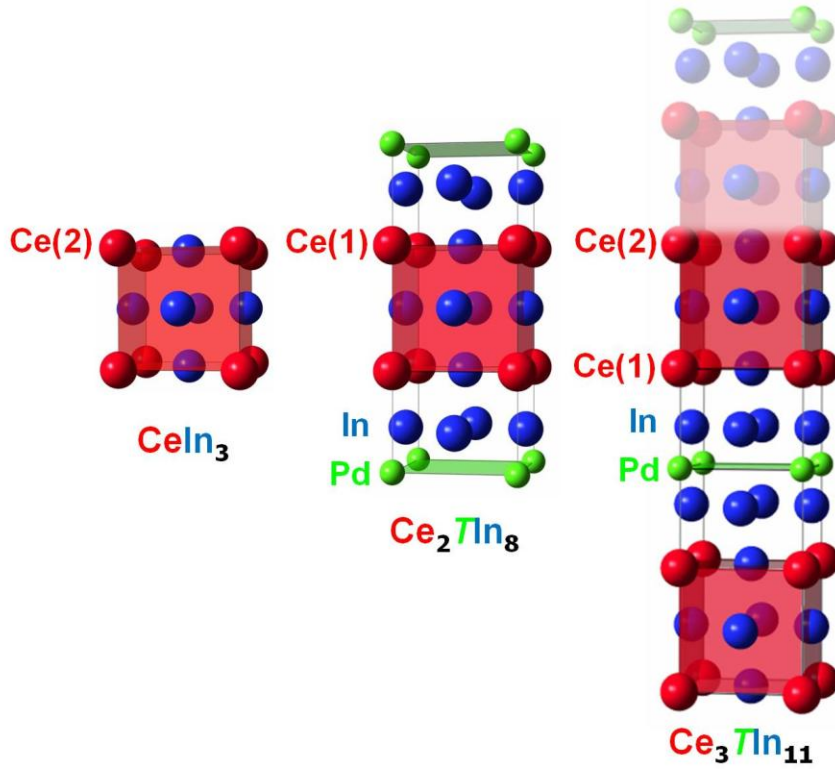


Fig. 14. The cerium sites Ce(1) and Ce(2) in the crystal structures of the CeIn_3 , Ce_2TlIn_8 and $\text{Ce}_3\text{TlIn}_{11}$ compounds. To show the local environment of the Ce(2)-ion clearly, a half of additional $\text{Ce}_3\text{TlIn}_{11}$ unit cell has been put to the $\text{Ce}_3\text{TlIn}_{11}$ unit cell along the [001] axis.

In the following paragraphs, the results of the bulk measurements will be presented together with suggestions about the role of the cerium atoms in $\text{Ce}_3\text{PdIn}_{11}$ depending on different crystallographic sites. The data were obtained on two samples which were both prepared in same conditions as given in Tab. 2 (section 3.2.2): the high-temperature (2-300 K) electrical resistivity and magnetization data were measured on the sample #1, the specific heat and the low-temperature (below 2 K) electrical resistivity data were measured on the sample #2. We start the introduction of the physical properties of this completely novel system by examining the overall temperature region using the electrical resistivity and magnetization.

The zero-field electrical resistivity of $\text{Ce}_3\text{PdIn}_{11}$ is depicted in Fig. 15 in the temperature interval from 300 K down to 2 K. The electric current j was applied in three principal crystallographic orientations [100], [110] and [001]. The $\rho(T)$ curves resemble each other strongly for all three directions, confirming rather isotropic behavior. The residual resistivity ratio (RRR) exceeds the value of 5 for $\rho_{300\text{ K}}/\rho_{2.3\text{ K}}$. It signifies a moderate quality of measured samples which can be related to their complex structure. At 300 K, the resistivity equals to $\sim 50\ \mu\Omega\text{cm}$, i.e. its magnitude is very similar to that reported previously for polycrystalline $\text{Ce}_3\text{PdIn}_{11}$ samples¹⁰⁹ and Ce_2PdIn_8 single crystals¹⁵⁴. The overall temperature dependence corresponds to Kondo systems including the related $\text{Ce}_3\text{PdIn}_{11}$ and Ce_2PdIn_8 ^{109,154}: first, the

resistivity slightly decreases on cooling from the room temperature, then it becomes almost constant, showing a shoulderlike structure at ~ 60 K, and eventually rapidly drops down at low temperatures. This structure is pronounced less than in the polycrystals of $\text{Ce}_3\text{PdIn}_{11}$ where a maximum is formed first at ~ 30 K. Such feature manifests likely a crossover from an incoherent to a coherent Kondo regime and it can be associated with the magnitude of the coherence energy in $\text{Ce}_3\text{PdIn}_{11}$. The temperature T^* , sometimes referred to as the Kondo lattice coherence temperature, is typically identified with the temperature of the maximum of such peak-like feature. The experimental data can be fitted by a simple formula according to Ref.¹⁷⁹ characteristic of dense Kondo systems:

$$\rho_{tot} = (\rho_0 + \rho_0^\infty) + c_{ph}T + c_K \ln(T) \quad (47)$$

The first term represents the residual resistivity ρ_0 and spin-disorder resistivity ρ_0^∞ (on thermally disordered magnetic moments), the second term represents the phonon contribution and the third one results from the spin-flip Kondo scattering.

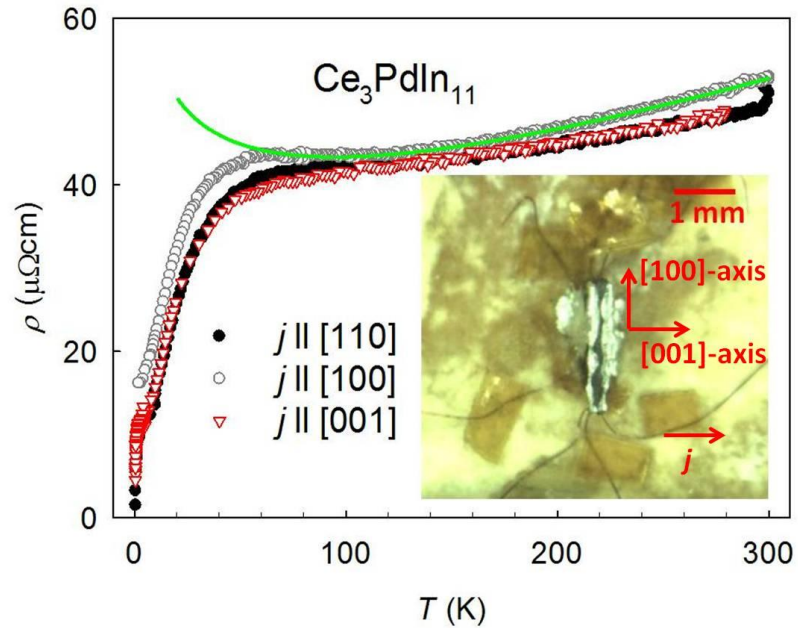


Fig. 15. Temperature dependence of the electrical resistivity of $\text{Ce}_3\text{PdIn}_{11}$ in zero magnetic field with the electric current flowing along the [001], [110] and [100] direction, respectively. The green line is a fit given by the formula (47) described in the text. The inset shows the electrical resistivity measurement of the $\text{Ce}_3\text{PdIn}_{11}$ sample oriented so that the current j flows along the [001] axis. Due to the plate-like shape of the single crystals, the wire mounting with the silver paste was much more difficult in the $j \parallel [001]$ compared to the $j \parallel [100]$ and $j \parallel [110]$ orientations. The relatively large error of the absolute values of resistivity up to 30 % is given by the small dimensions and irregular shape of the crystals.

The least-squares fit of this expression to $\rho^{[100]}$ down to 70 K yielded the following parameters: $\rho_0 + \rho_0^\infty = 76.4 \mu\Omega\text{cm}$, $c_{ph} = 0.1 \mu\Omega\text{cm/K}$ and $c_K = -9.3 \mu\Omega\text{cm}$.

The term $(\rho_0 + \rho_0^\infty)$ is somewhat lower than the value published by *Tursina et al.*¹⁰⁹ ($125 \mu\Omega\text{cm}$) which is expectable in case of single crystals compared to the polycrystalline samples. The Kondo-scattering value $-9.3 \mu\Omega\text{cm}$ is lower in absolute values than $-17.7 \mu\Omega\text{cm}$ for polycrystals¹⁰⁹ reflecting the weakly pronounced onset of coherent Kondo scattering.

To find out more about the magnetic properties of $\text{Ce}_3\text{PdIn}_{11}$, the magnetization as a function of temperature and applied magnetic field was measured. The bottom part of Fig. 16 shows the inverse dc susceptibility measured in the magnetic field of 1 T applied along both principal crystallographic orientations. The inverse susceptibility of the [001] direction of magnetic field is smaller than the one for the in-plane orientation; both curves follow the Curie-Weiss law for temperatures down to ~ 80 K. The values of paramagnetic Curie temperatures summarized in Tab. 4 in section 3.3.3 confirm the low anisotropy of this system.

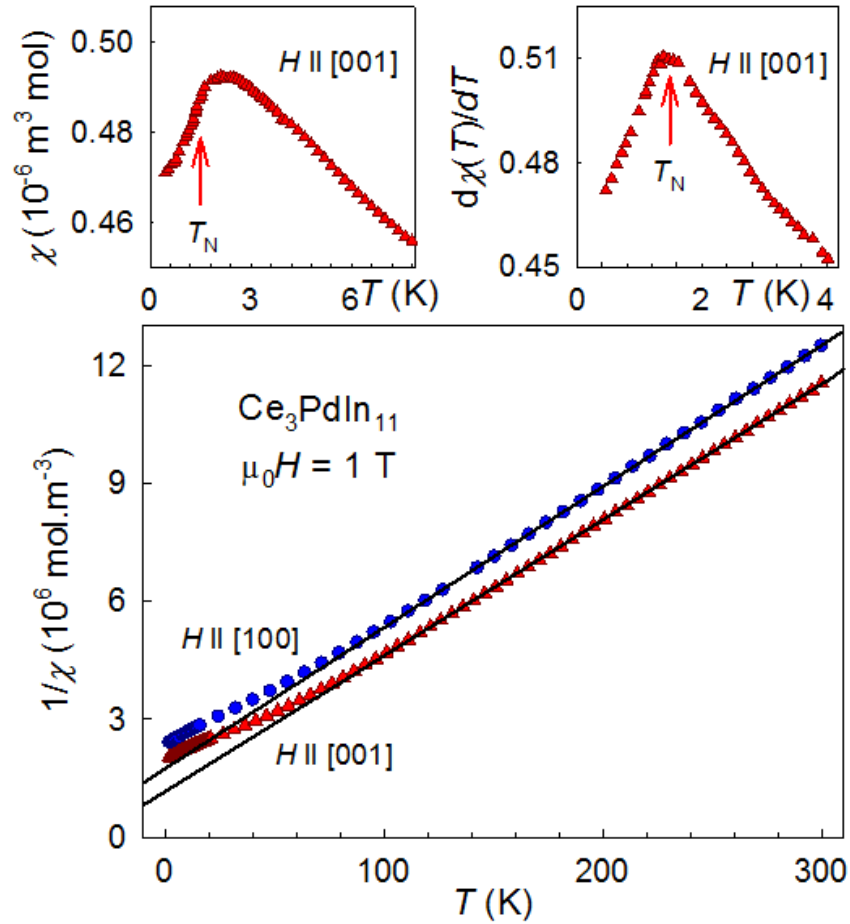


Fig. 16. The temperature dependence of the inverse magnetic susceptibility of $\text{Ce}_3\text{PdIn}_{11}$ in the 1 T magnetic field applied along the principal crystallographic directions (bottom figure). The solid lines depict the C-W law fit. The upper left figure shows the low-temperature part of the susceptibility. The upper right figure depicts the $d(\chi T)/dT$ vs T dependence. The maximum of the curve corresponds to $T_N = 1.5$ K. The arrows mark the position at T_N .

The effective moment corresponds roughly to the one expected for a free ion ($2.54 \mu_B$). According to *Hewson*¹⁸⁰, the related Kondo temperature T_K is of the order $|\theta_P|/4 \sim 11$ K.

The susceptibility $\chi^{[001]}(T)$ reveals a decrease at low temperatures as shown in the upper part of Fig. 16. The maximum at ~ 2.3 K in the curve can be probably associated with short-range antiferromagnetic correlations when approaching a magnetic phase transition. Such maximum is often observed in Ce-based systems and corresponds to results of the theory of orbitally degenerate Kondo impurities¹⁸¹.

The magnetic dependence of the magnetization depicted in Fig. 17 shows linear behavior up to 7 T in both in-plane and out-of-plane directions of applied magnetic field at 2 K. The [001] axis is the easy axis in $\text{Ce}_3\text{PdIn}_{11}$.

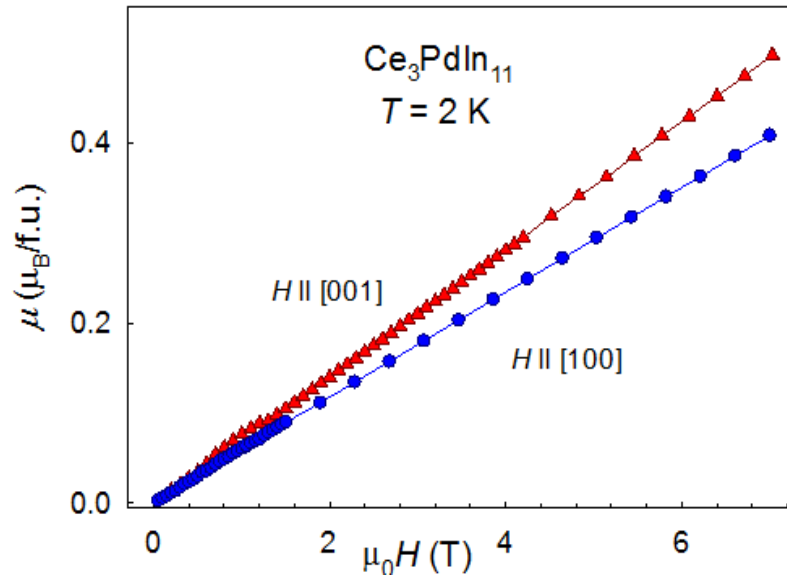


Fig. 17. The magnetization as a function of magnetic field applied along the [001] and [100] direction measured at $T = 2$ K.

To find out more about the crystal field in $\text{Ce}_3\text{PdIn}_{11}$, we have fitted the magnetic susceptibilities along both principal crystallographic axes simultaneously using a simulated annealing procedure. The parameters of a microscopic crystal-field Hamiltonian are the energy levels E_1 and E_2 and the CEF parameters B_2^0 , B_4^0 and B_4^4 . The phenomenological molecular field constant λ was included to account the magnetic exchange effects and it was fitted simultaneously for the in-plane and out-of-plane susceptibility. In the fit, the independent Ce-sites were treated as equivalent for the simplicity. In Fig. 18, a comparison of the measured inverse susceptibility of $\text{Ce}_3\text{PdIn}_{11}$ with the corresponding fitted curves is shown. The CEF parameters which characterize both curves best are summarized in Tab. 5 in section 3.3.3. The inverse susceptibility of $\text{Ce}_3\text{PdIn}_{11}$ in the high-temperature region cannot be described very well by the fit due to the simplifying presumptions. Moreover, the inset shows an interesting detail which is not observed in the measured data - a

crossing of the calculated inverse susceptibilities along the in-plane and out-of-plane direction at ~ 15 K.

The low-temperature part of the specific heat C_p and the electrical resistivity $\rho/\rho_{2.3\text{K}}$ was measured in zero magnetic field and at ambient pressure to characterize the ground-state properties of $\text{Ce}_3\text{PdIn}_{11}$. Three features can be clearly observed in Fig. 19. First, a λ -like transition appears in the specific heat at $T_1 = 1.7$ K and upon cooling, another, more pronounced transition emerges at $T_N = 1.5$ K. The phase transition temperature was estimated from the middle of the slope of the specific-heat jump. Both transitions at T_1 and T_N are difficult to follow in the corresponding electrical resistivity data, suggesting their magnetic nature; the transition at T_1 is not pronounced at all, while the transition at T_N is identified by a moderate change of slope in $\rho/\rho_{2.3\text{K}}$. As the peak at T_1 is almost immediately followed by another one at T_N we assume that the first anomaly is a transition into an incommensurate state while the transition at T_N turns the system into a commensurate AF state.

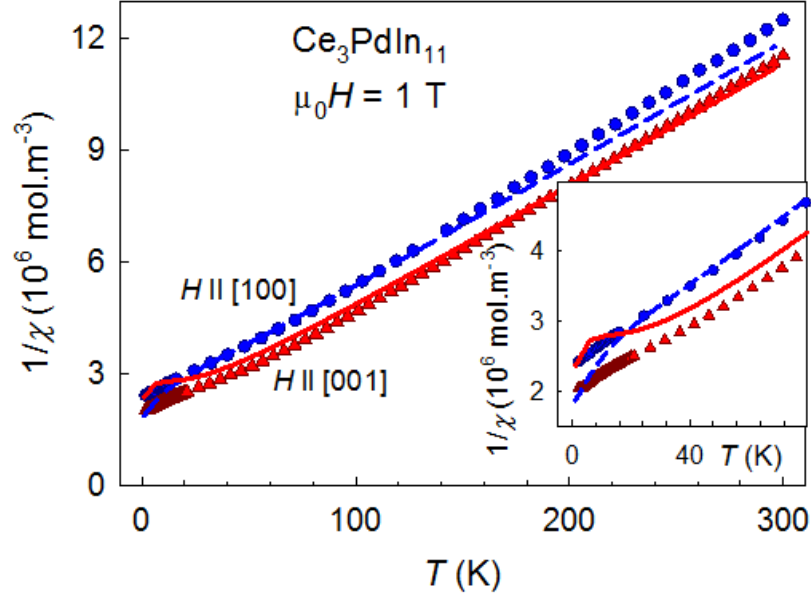


Fig. 18. The temperature dependence of the inverse magnetic susceptibility of $\text{Ce}_3\text{PdIn}_{11}$ compared to the fit with CEF parameters from Tab. 5 (red solid and blue dashed line depicts the [100] and [001] direction, respectively). The insets show the low-temperature part of the inverse magnetic susceptibility with the crossing of the fit for the [100] and [001] orientation.

Upon further cooling, we can observe another transition at $T_c = 0.42$ K. The value of T_c is defined in the middle of the increase of the peak in $C(T)$. According to the steep drop to zero in the electrical resistivity the feature marks a transition into a bulk SC state. The value of T_c is given as the middle of the slope of the drop in the resistivity curve. There is a small discrepancy in the values of SC transition temperatures obtained from the specific heat and the resistivity measurement: the specific heat yields $T_c = 0.42$ K while from the resistivity we obtain $T_c = 0.44$ K.

T_c from resistivity represents probably the first percolation path for the superconductivity, while T_c from specific heat marks the transition to the bulk superconductivity. However, these differences could be explained also in context of two independent Ce-sites as discussed later.

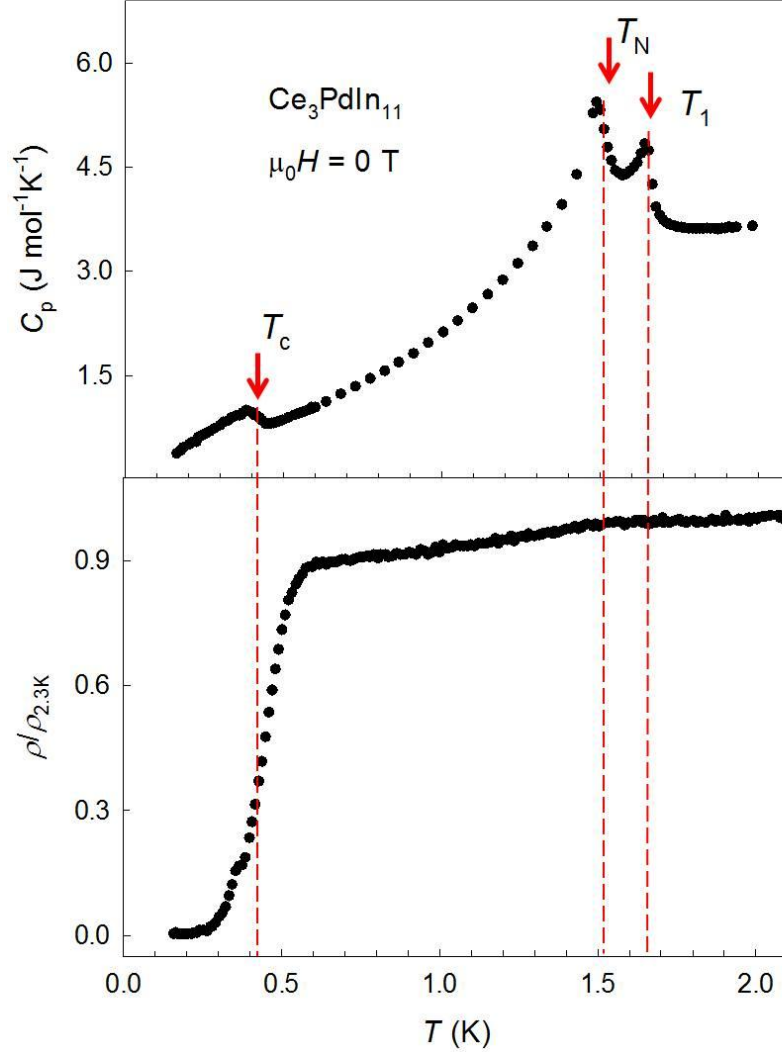


Fig. 19. The low-temperature part of specific heat and electrical resistivity of $\text{Ce}_3\text{PdIn}_{11}$ in zero magnetic field. The vertical dashed lines mark the positions of the phase transitions T_1 , T_N and T_c .

As a next step, the analysis of the specific heat was performed with respect to two inequivalent Ce-sites. The phonon term C_{ph} (Fig. 21) was subtracted from the raw C/T data which were measured up to 20 K (not shown) to allow an estimate of the magnetic entropy. The formula for the phonon subtraction is $C_{\text{el}} = C - 15 \cdot C_D$. Here C_D stands for the Debye phonon contribution calculated from the expression (32) which was fitted on the raw data and 15 is the number of atoms per formula unit. The corresponding value of Debye temperature is $\theta_D = 184$ K. The Sommerfeld coefficient γ of $\text{Ce}_3\text{PdIn}_{11}$ was determined independently from the C_{el}/T plot as the C_{el}/T ratio just above the superconducting transition and its value reaches

$0.58 \text{ J} \cdot \text{mol}^{-1} \text{CeK}^{-2}$. This procedure was chosen instead of common $C/T = \gamma + \beta T^2$ fit due to the transition temperatures of the magnetic transitions which disable a reasonable fitting in this temperature region.

Looking at the shape of the SC transition in the C/T plot in Fig. 20, one can immediately see that it is unusually broad. The broadening might be caused by the presence of two close, subsequent SC transitions; however, a natural interpretation takes into account the logarithmic contribution $C(T)/T \sim a \log(T_0/T)$ from the normal state which enhances the value of electronic specific heat $C_{\text{el}}(T)$. This contribution will be discussed later in context of different Kondo temperatures.

To be able to compare the character of the SC transition with related heavy fermion superconductors, we calculated the $(\Delta C_p)_{T_c}/\gamma T_c$ ratio. The specific-heat discontinuity $\Delta C_p \sim 0.2 \text{ J mol}^{-1} \text{ K}^{-1}$, divided by the linear term in the specific heat jump γT at $T_c = 0.42 \text{ K}$ and $\gamma = 0.58 \text{ J mol}^{-1} \text{ CeK}^{-2}$, provides the $(\Delta C_p)_{T_c}/\gamma T_c$ ratio ~ 0.82 . This value is much lower than the one of 1.43 predicted by the BCS weak-coupling theory. This might be caused by the significant broadening of the SC transition¹⁷⁷. Comparing the ratio of $\text{Ce}_3\text{PdIn}_{11}$ with the value of ~ 4.3 obtained for the well-known heavy fermion superconductor CeCoIn_5 ^{117,182}, we realize that the coupling is significantly weaker in the novel compound. From this point of view, the SC state of $\text{Ce}_3\text{PdIn}_{11}$ resembles strongly the CeIrIn_5 compound which undergoes a SC transition at $T_c = 0.4 \text{ K}$ ¹⁸² similarly to T_c in $\text{Ce}_3\text{PdIn}_{11}$, and its $(\Delta C_p)_{T_c}/\gamma T_c$ ratio equals 0.76.

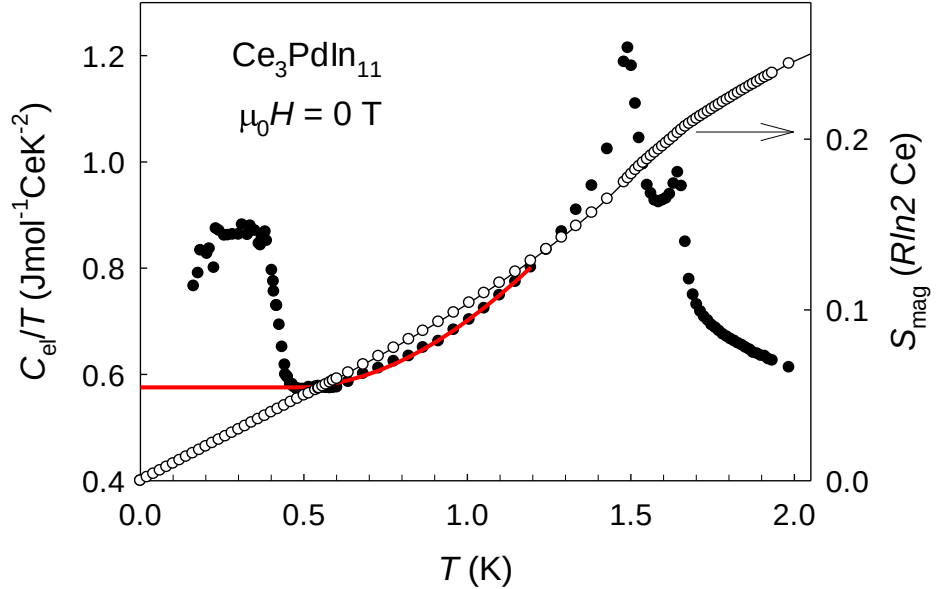


Fig. 20. The specific heat C_{el}/T vs T per cerium (closed circles) and the corresponding magnetic entropy (open symbols) of $\text{Ce}_3\text{PdIn}_{11}$. The red line represents the fit expressed by the equation below with the values of A and Δ given in the text.

In order to obtain the magnetic entropy $S_{\text{mag}}(T)$, the SC transition was cut off by extrapolating the low-temperature tail of the AF transition using a fit expression¹⁸³ (red line in Fig. 20). This expression defines the contribution of the antiferromagnetic magnons, which scatter the conduction electrons, to the specific heat

$$\frac{C_{\text{mag}}}{T} \sim A \Delta^{\frac{7}{2}} \cdot T^{\frac{1}{2}} \cdot e^{\frac{-\Delta}{T}} \cdot \left(1 + \frac{39T}{20\Delta} + \frac{51T^2}{32\Delta^2}\right), \quad (48)$$

The coefficient A in the equation (48) is related to the effective magnetic coupling between the Ce ions and Δ is the spin-wave gap. The parameters which described the fit of specific heat $C_{\text{el}}/T = \gamma + C_{\text{mag}}/T$ best in the fitting range of 0.5 – 1.2 K are $A = 0.032 \text{ J} \cdot \text{mol}^{-1} \text{Ce K}^2$ and $\Delta = 3.45 \text{ K}$. We used $\gamma = 0.58 \text{ J mol}^{-1} \text{Ce K}^{-2}$.

Below T_1 , the above described procedure with the low- T tail gives for $\text{Ce}_3\text{PdIn}_{11}$ a fraction of about $0.2 R \ln 2$ per cerium to the entropy which is probably caused by Kondo-screened ordered moments as was suggested in the case of CeRhIn_5 ¹¹⁰. Such low entropy suggests that the ordered moments are strongly Kondo-screened and hence, in analogy with the work of *Singh et al.*¹⁸⁴, we assume that $S_{\text{Ce}} = S_{\text{K}}(t)$; here, $S_{\text{K}}(t)$ is the entropy of a single ion Kondo impurity at the normalized Kondo temperature $t = T_1/T_{\text{K}}$. The entropy has been calculated using the Bethe ansatz for a spin-1/2 Kondo model⁶⁹. The procedure was performed under assumption of having only one Ce-site. Taking into account the Kondo-type interactions as the most likely mechanism for $S \sim 0.2 R \ln 2$ and $T_1 = 1.7 \text{ K}$, we would obtain the characteristic Kondo scale $T_{\text{K}} \sim 8 \text{ K}$ with respect to the values taken from the table⁶⁹. The full $R \ln 2$ entropy per cerium is recovered at $T \sim 5 \text{ K}$.

We compared this result with different approaches of calculating the Kondo temperature in order to have a basic idea of the Kondo scale in the studied material. The results are summarized in Tab. 6 in section 3.3.3. Despite the substantial simplification (neglecting two inequivalent Ce-cites), we come to relatively similar values when using the procedures by *Hewson*¹⁸⁰ and by *Desgranges and Schotte*⁶⁹ applied on magnetization and specific-heat data, respectively. Calculating T_{K} from the two-level model¹⁸¹ provides significantly lower values, suggesting that this approach generally fails due to non-negligible hybridization strength in description of the $\text{Ce}_n\text{T}_m\text{In}_{3n+2m}$ materials (as was already shown in case of Pd-substituted Ce_2RhIn_8 ¹⁷⁶).

With respect to these results, we analyse further the Kondo temperature from specific heat using the approach of *Desgranges and Schotte*⁶⁹. However, now we assume two different Ce-sublattices which do not interact with each other. As already mentioned, the studied $\text{Ce}_3\text{PdIn}_{11}$ structure implies two different Kondo temperatures T_{K} . This is because the independent cerium sites represent two local-moment sublattices which are coupled with different Kondo couplings to conduction

electrons¹¹¹. Assuming the idea of having a magnetic Ce(2)-ion and a paramagnetic Ce(1)-ion in the $\text{Ce}_3\text{PdIn}_{11}$ structure, we can consider the compounds as being in a partially-screened Kondo state with the Ce(1)-sublattice fully screened and the second Ce(2)-sublattice where local moments persist. In Fig. 21, the specific heat C/T in units of $\text{J}\cdot\text{mol}^{-1}\text{K}^{-2}$ of $\text{Ce}_3\text{PdIn}_{11}$ is plotted on a logarithmic temperature scale. The electronic contribution of specific heat C_{el} was obtained by removing the contribution from phonons C_{ph} depicted by a long-dashed line and the superconducting transition from Fig. 20 by procedures described earlier in the text. The border of the red area represents a spin-fluctuation contribution to the specific heat in the nFl form $C/T \sim \log(T_0/T)$. The temperature T_0 is the critical spin-fluctuation temperature of the value of 38 K based on the low-temperature data of Ce_2PdIn_8 (short-dashed line)^{154,179}. In this rather crude scenario, the shaded area represents the contribution from the Ce(2)-ions to the magnetic entropy S_{Ce2} and the red area represents the contribution S_{Ce1} arising from the Ce(1)-ions in the Ce_2TlIn_8 -structure block. The temperature evolution of both S_{Ce1} and S_{Ce2} is related to the right axis in Fig. 21. The entropy S_{Ce2} reaches its full value $R\cdot\ln 2$, i.e., the full entropy of the ground-state doublet of the Ce(2)-ion at ~ 8 K. The steady increase of S_{Ce2} above the magnetic transition temperature T_1 points to the overestimation of the Ce(2) contribution due to the simplicity of our model. Accordingly, the full entropy S_{Ce1} of the ground-state doublet of the Ce(1)-ion is somewhat underestimated and it is released above 20 K in both heavy fermion systems.

To estimate the values of the Kondo temperatures of respective Ce-sites, we focus first on the “magnetic” Ce(2). The temperature $T_{\text{K,Ce(2)}}$ can be extracted from the value of $S_{\text{Ce2}} \sim 0.4 R\cdot\ln 2$ which is reached at T_1 . The entropy has been calculated using the Bethe ansatz for a spin-1/2 Kondo model leading to $T_{\text{K,Ce(2)}} \sim 2.2$ K with respect to the values taken from the table⁶⁹.

To extract the Kondo temperature $T_{\text{K,Ce(1)}}$ corresponding to the “paramagnetic” Ce(1)-ion, we assume that $S_{\text{K}}(t)$ scales roughly with $S_{\text{Ce1}}(T)$. As an example, we calculate $T_{\text{K,Ce(1)}}$ for two values of S_{Ce1} , $0.13 R\cdot\ln 2$ and $0.5 R\cdot\ln 2$. For these values of entropy we read from our plot $T \sim 1.5$ K and $T \sim 12$ K. Using these values of entropy and temperature, we obtain from Table 1. in Ref.⁶⁹ somewhat different “Kondo temperatures” ~ 11 K and ~ 8.1 K, respectively. The correct Kondo temperature for Ce(1) will be lower than $T < 20$ K and hence in line with the estimate from the magnetic susceptibility $T_{\text{K}} \sim 11$ K (see Tab. 6). This construction, although rather crude, supports the idea of “magnetic” Ce(2)-ions on the HF background of paramagnetic Ce(1)-ions. Further results which are in line with this scenario are discussed in the next paragraphs together with the output from the related Pt-compound.

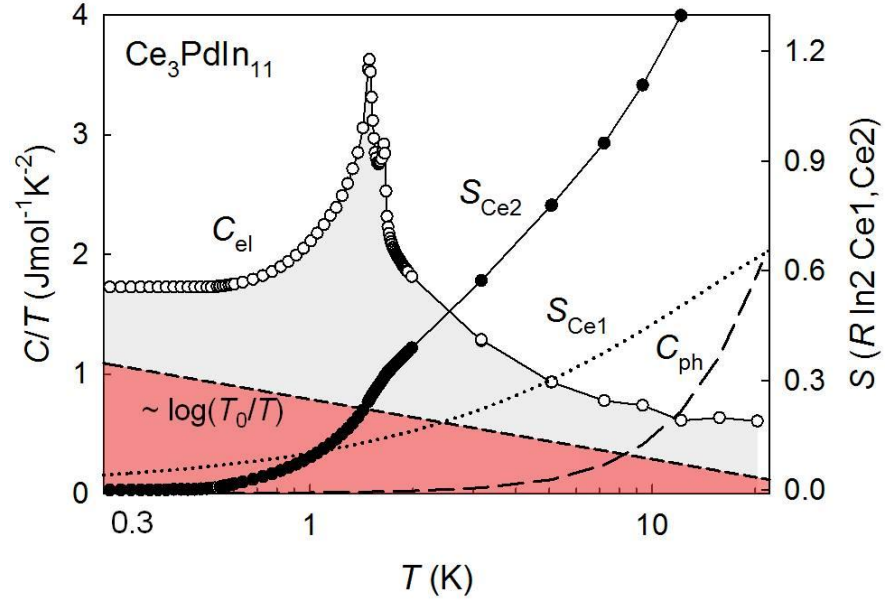


Fig. 21. Temperature dependence of the specific heat of $\text{Ce}_3\text{PdIn}_{11}$ on a logarithmic scale. The electronic part $C_{\text{el}} = C - C_{\text{ph}}$ is depicted by opened circles and the phonon part C_{ph} is marked by the long-dashed line ($C_{\text{ph}} = 15 \cdot C_{\text{D}}$ was fitted as described in the text). The short-dashed line corresponds to the spin-fluctuation contribution ($T_0 = 38$ K) of Ce_2PdIn_8 adapted from Ref.¹⁵⁴. The shaded area denotes the contribution arising from the Ce(2)-ion while the red area denotes the contribution arising from the Ce(1)-ion. The S_{Ce1} (dotted line) and S_{Ce2} (closed circles) show the entropy in units of $R \ln 2$ per Ce-ion related to Ce(1) and Ce(2), respectively.

The following section introduces two types of phase diagrams of $\text{Ce}_3\text{PdIn}_{11}$ – magnetic and superconducting.

The magnetic phase diagram

Fig. 22 shows temperature dependence of the specific heat of $\text{Ce}_3\text{PdIn}_{11}$ exposed to magnetic field applied along the [100] and [001] direction. The evolution of the transitions is particularly interesting in the $H \parallel [001]$ configuration where the field is applied presumably along the magnetic moments. The transition T_1 shifts to lower temperatures in small magnetic fields below 2.5 T while T_N remains mainly unaffected. Both transitions seem to merge at ~ 3.5 T before they split again in magnetic fields above 4 T. For even higher fields (> 5 T), the T_N transition shows a sharp λ -like anomaly. This pronounced peak contrasts with the character of the transition observed in lower fields, as is depicted by the rapid change in the color code in Fig. 23. Similar effect was observed also in the specific-heat data under applied magnetic field in CeRhIn_5 and Ce_2RhIn_8 ¹¹⁴. The shape of the peak might point to a first-order phase transition; however, any other signs of a first-order character of the AF transition were not observed experimentally.

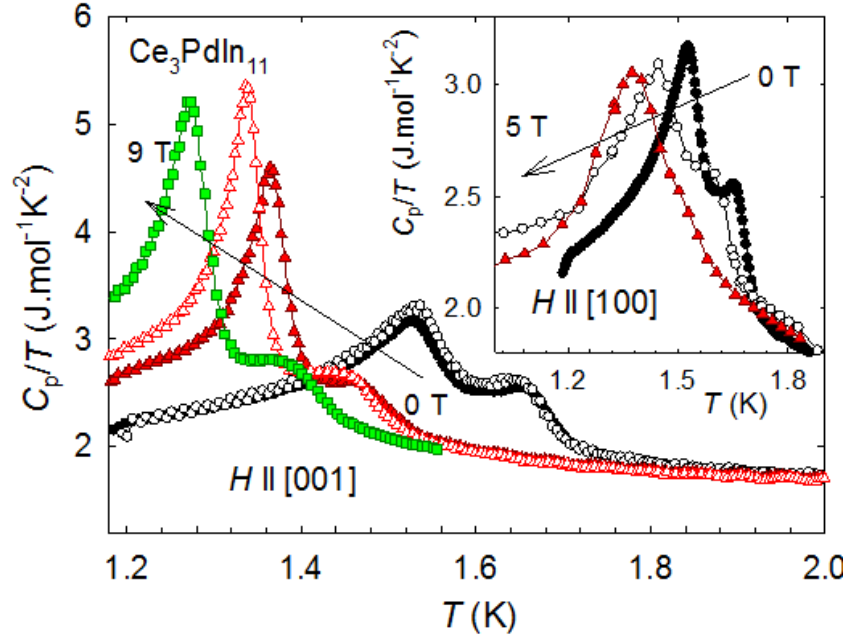


Fig. 22. The temperature dependence of the specific heat of the $\text{Ce}_3\text{PdIn}_{11}$ compound measured in various magnetic fields (from right to left: $\mu_0 H = 0, 1, 5, 7, 9$ T) applied along the [001] axis. The inset shows the monotonous decrease of T_N with increasing magnetic field applied along the [100] axis.

The behavior in the magnetic field applied along the [001] axis is summarized in the temperature–magnetic field phase diagram in Fig. 23. The diagram offers several scenarios regarding the magnetic structure below T_1 and T_N , respectively, which might be different for magnetic fields lower and higher than 3 T. The inset shows the evolution of both phase transitions when the magnetic field is applied within the basal plane. In contrast to the $H \parallel [001]$ configuration, both transitions are only weakly suppressed by the magnetic field. This type of behavior is observed for many of the structurally related compounds^{114,173} and also for the heavy fermion systems in general³⁴.

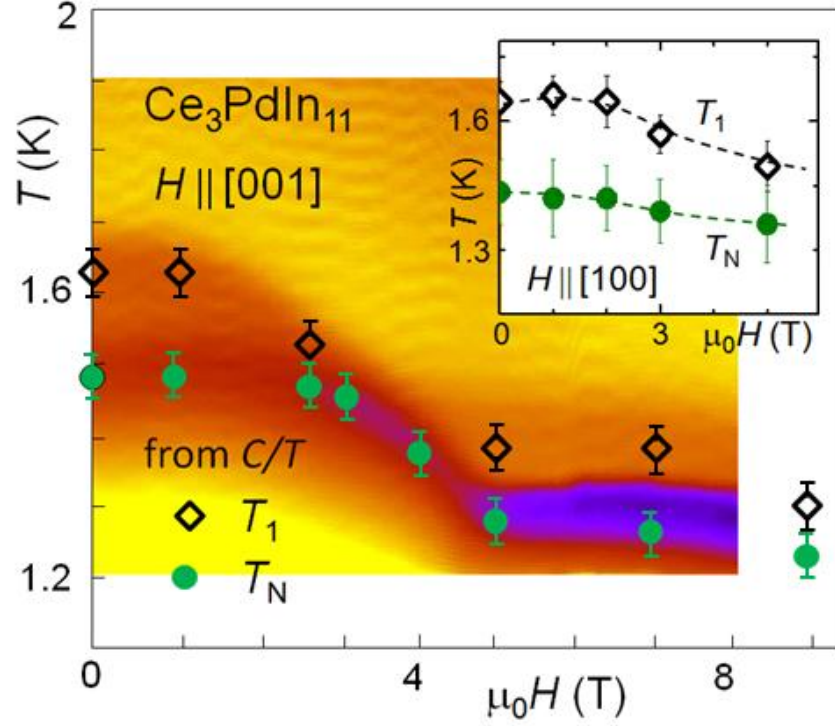


Fig. 23. The temperature–magnetic field phase diagram for $\text{Ce}_3\text{PdIn}_{11}$ mapped out by the thermal response technique (see text) in the magnetic field applied along the [001] axis. The black diamonds and green circles show T_1 and T_N , respectively, obtained from specific heat measurement. Inset depicts an analogous phase diagram for the field applied in the perpendicular [100] direction.

The diagram has been constructed by analyzing the response of the compound to thermal-heat pulses. By this method a heat pulse was applied resulting in a $\Delta T = 1$ K temperature change of the quasi-adiabatically mounted sample to the bath temperature. The consequent thermalization of the sample temperature T was monitored over the time t . The color plot shows the derivative $d(\Delta T)/dt$ as a function of the bath temperature and the magnetic field (yellow-red: small change in dT/dt ; blue-violet: large change in dT/dt).

The superconducting phase diagram

The upper critical magnetic field–temperature phase diagram for $\text{Ce}_3\text{PdIn}_{11}$ was constructed using the electrical resistivity data. The superconducting temperature T_c was determined as a middle of the slope of the transition in the resistivity curve (marked by arrows in Fig. 24). When increasing the magnetic field applied along the [001] axis, T_c is reduced as expected. The initial slope equals $\mu_0 dH_{c2}/dT(T_c) \sim -12.25$ T/K.

Extrapolation of the field-dependent T_c to zero using the square-law fit (equation (18)) yields the upper critical field $\mu_0 H_{c2}(0) \sim 2.3$ T. Using the WHH formula⁶⁶, we obtain somewhat higher values of the orbital critical field $\mu_0 H_{c2}^{\text{orb}}(0) \sim 3.7$ T from the initial slope of H_{c2} at T_c . Nevertheless, these values are significantly smaller than

those for CeRhIn₅ (at $p \sim p_c = 2.45$ GPa: $T_c = 2.2$ K, $\mu_0 H_{c2}(0) \sim 9.7$ T, $\mu_0 dH_{c2}/dT(T_c) \sim -18.4$ T/K) and CeCoIn₅ ($T_c = 0.4$ K, $\mu_0 H_{c2}(0) \sim 11.6$ T, $\mu_0 dH_{c2}/dT(T_c) \sim -24$ T/K)¹⁸⁵ as well as for Ce₂PdIn₈ (shown in Tab. 7 in section 3.3.3) which corresponds to the more 3D character of the Ce₃TlIn₁₁ crystal structure. The Pauli limiting field is $\mu_0 H_{c2}^P(0) \sim 0.8$ T according to equation (25). Assuming $\mu_0 H_{c2}^P(0) \sim \mu_0 H_{c2}(0) = 2.3$, the Maki parameter equals $\alpha \sim 2.3$. We realize that Ce₃PdIn₁₁ cannot be considered as Pauli limited, which is the case of the heavy fermion superconductors Ce₂PdIn₈¹⁶¹ and CeCoIn₅¹⁸⁶.

We have estimated the superconducting coherence length $\xi(0) = 10.84$ nm based on the Ginzburg–Landau formula (equation (20)). Inserting the values $dH_{c2}/dT(T_c) = -12.25$ T/K and $\gamma = 1.74$ J mol⁻¹K⁻² with $V_{\text{mol}} = 20.63 \cdot 10^{-5}$ m³mol⁻¹, $T_c = 0.44$ K and $\rho_0 = 9 \cdot 10^{-8}$ Ωm into equation (21), we obtain the Fermi vector $k_F \sim 0.73 \cdot 10^{10}$ m⁻¹. With this knowledge, the Fermi velocity $v_F \sim 3.83 \cdot 10^3$ m·s⁻¹ was evaluated using the equation (22). The effective mass $m^*/m_e \sim 220$ differs by two orders of magnitude from the corresponding free-electron values. The superconducting coherence length ξ_{GL} equals $\sim 12.0 \cdot 10^{-9}$ m (equation (23)).

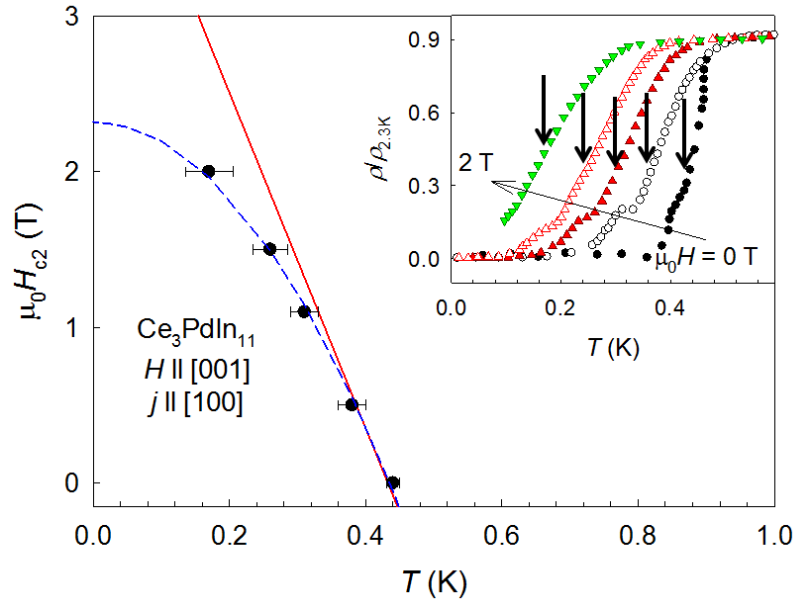


Fig. 24. The temperature dependence of the upper critical magnetic field of Ce₃PdIn₁₁ applied along the [001] axis derived from the resistivity measurements shown in the inset. The applied magnetic fields are 0, 0.5, 1.1, 1.5 and 2 T. The electric current was flowing along the [100] direction. The red solid line yields $dH_{c2}/dT(T_c) \sim -12.25$ T/K. The blue dashed line is the square-law fit to the data (see the text for details).

To complete the characterization of the superconducting transition in Ce₃PdIn₁₁ from the classical approach, the quasiparticles mean free path l , the penetration depth λ_{GL} and the Ginzburg–Landau parameter κ_{GL} were calculated according to relations (24) presented in the section 1.6.

The values of all presented parameters are summarized and compared with those for Ce_2PdIn_8 ¹⁵⁴ in Tab. 7 (section 3.3.3). The relation $l \sim 25 \text{ nm} > \xi(0) \sim 10.84 \text{ nm}$ indicates that we cannot state clearly that $\text{Ce}_3\text{PdIn}_{11}$ is a clean-limit superconductor. The parameter $\kappa_{\text{GL}} \sim 24 > 1/\sqrt{2}$ confirms that $\text{Ce}_3\text{PdIn}_{11}$ is a type-II superconductor.

To summarize the previous paragraphs, the low-temperature experiments revealed both the magnetic ordering and superconductivity in $\text{Ce}_3\text{PdIn}_{11}$. Recalling the Ce_2PdIn_8 compound reveals the SC ground state and CeIn_3 orders antiferromagnetically at ambient pressure, we can speculate that the Ce(1)-ion with the Ce_2PdIn_8 -like surrounding favors superconductivity and the magnetic order originates from the Ce(2)-site similarly to CeIn_3 . With respect to this scenario, the crystal structure of $\text{Ce}_3\text{PdIn}_{11}$ can be viewed as a sublattice structure of magnetic CeIn_3 and paramagnetic Ce_2PdIn_8 blocks alternating along the [001] axis. This structure can explain the step in the SC transition drop observed in the electrical resistivity and the different value of T_c from specific heat (see Fig. 19). We can speculate that the SC state condensates first within the paramagnetic block and the Cooper pairs can diffuse through the normal state in CeIn_3 blocks which are significantly smaller (units of Å) than the respective coherence length (hundreds of Å). With further cooling, the bulk SC state is established over the CeIn_3 layers forming the second drop to $\rho \rightarrow 0$.

3.3.3. $\text{Ce}_3\text{PtIn}_{11}$

The data were obtained on two samples which were both prepared in same conditions as given in Tab. 2 (section 3.2.2): the high-temperature (2-300 K) electrical resistivity and the specific heat were measured on the sample #1; the magnetization, the ambient-pressure low-temperature (below 2 K) electrical resistivity and the resistivity under hydrostatic pressure were measured on the sample #2. In analogy to $\text{Ce}_3\text{PdIn}_{11}$, the ground-state properties of $\text{Ce}_3\text{PtIn}_{11}$ will be introduced in the overall temperature region using the electrical resistivity and magnetization data.

The zero-field electrical resistivity of $\text{Ce}_3\text{PtIn}_{11}$ is shown in Fig. 25 in the temperature range from 2 K to 300 K with the electric current j applied in the principal crystallographic orientations [100], [110] and [001]. The character of the $\rho(T)$ curves is similar in all three directions and it reveals a relatively isotropic behavior similar to the isostructural $\text{Ce}_3\text{PdIn}_{11}$ compound. The RRR of $\text{Ce}_3\text{PtIn}_{11}$ reaches 2.5 which is the same order of magnitude as in $\text{Ce}_3\text{PdIn}_{11}$. At the room temperature, the resistivity $\rho^{[001]}$ amounts to $60 \mu\Omega\text{cm}$ which is only 30 % larger than for the other directions, and its magnitude is close to the shown for $\text{Ce}_3\text{PdIn}_{11}$. The resistivity decreases gradually down to $\sim 30 \text{ K}$ where an abrupt change of slope leads to a drop down to 2 K. No pronounced bump can be observed in the resistivity curves resembling strongly the CeRhIn_5 behavior¹⁸⁷. The least-squares fit of the equation

(47) to $\rho^{[100]}$ in the temperature range 100–300 K yielded the parameters $\rho_0 + \rho_0^\infty = 50.9 \mu\Omega\text{cm}$, $c_{\text{ph}} = 0.1 \mu\Omega\text{cm/K}$ and $c_K = -5.6 \mu\Omega\text{cm}$. The set of parameters corresponds roughly to the fitting parameters of the $\text{Ce}_3\text{PdIn}_{11}$ resistivity. No signs of a magnetic transition could be clearly distinguished down to ~ 2 K.

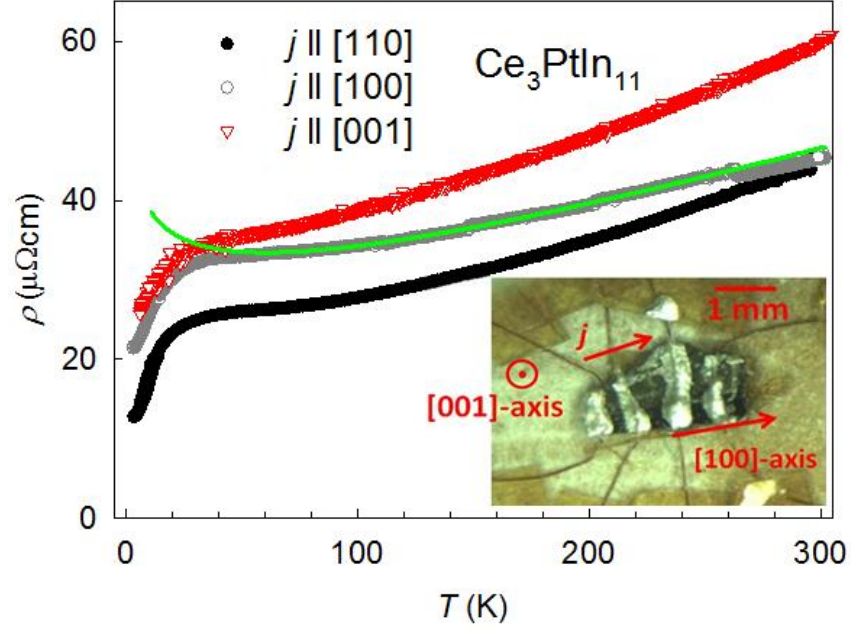


Fig. 25. Temperature dependence of the electrical resistivity of $\text{Ce}_3\text{PtIn}_{11}$ in zero magnetic field with the electric current flowing along the [001], [110] and [100] direction, respectively. The green line is a fit given by the formula (47) described in the text. The inset shows the electrical resistivity measurement of the $\text{Ce}_3\text{PtIn}_{11}$ sample oriented so that the current j flows along the [100] axis. Due to the plate-like shape of the single crystals, the wire mounting with the silver paste was much more difficult in the $j \parallel [001]$ compared to the $j \parallel [100]$ and $j \parallel [110]$ orientations. The relatively large error of the absolute values of resistivity up to 30 % is given by the small dimensions and irregular shape of the crystals.

Magnetization as a function of temperature and applied magnetic field was measured as depicted in Fig. 26. The bottom part shows the inverse magnetic susceptibility of $\text{Ce}_3\text{PtIn}_{11}$ measured in the magnetic field of 1 T applied along both principal crystallographic orientations. Similarly to the behavior of the Pd sister-compound, the inverse susceptibility of the [001] direction of magnetic field is smaller than the one for the in-plane orientation; $\chi^{-1}(T)$ departs from the Curie-Weiss law below ~ 100 K for the [001] axis, and below ~ 50 K for the [100] axis, respectively. The values of paramagnetic Curie temperatures summarized in Tab. 4 reflect the slightly enhanced anisotropy of this system compared to $\text{Ce}_3\text{PdIn}_{11}$. The effective moment is comparable to the one expected for a free ion. The Kondo temperature T_K corresponding to $\sim |\theta_P|/4 \sim 14$ K is very similar to the one obtained for $\text{Ce}_3\text{PdIn}_{11}$.

The susceptibility curve in the low magnetic field applied along the [100] axis reveals two changes of the slope at ~ 2.2 K and at ~ 2 K, respectively, and a further decrease in low temperatures, pointing to the presence of presumably antiferromagnetic phase transitions (see red arrows in the upper left part of Fig. 26). With increasing magnetic field, the lower transition is suppressed gradually, while the upper one stays almost unaffected. The upper right part of the figure shows the shift of maximum of the $\chi(T)$ curve at ~ 2.7 K (in 0.1 T) to lower temperatures with increasing magnetic field.

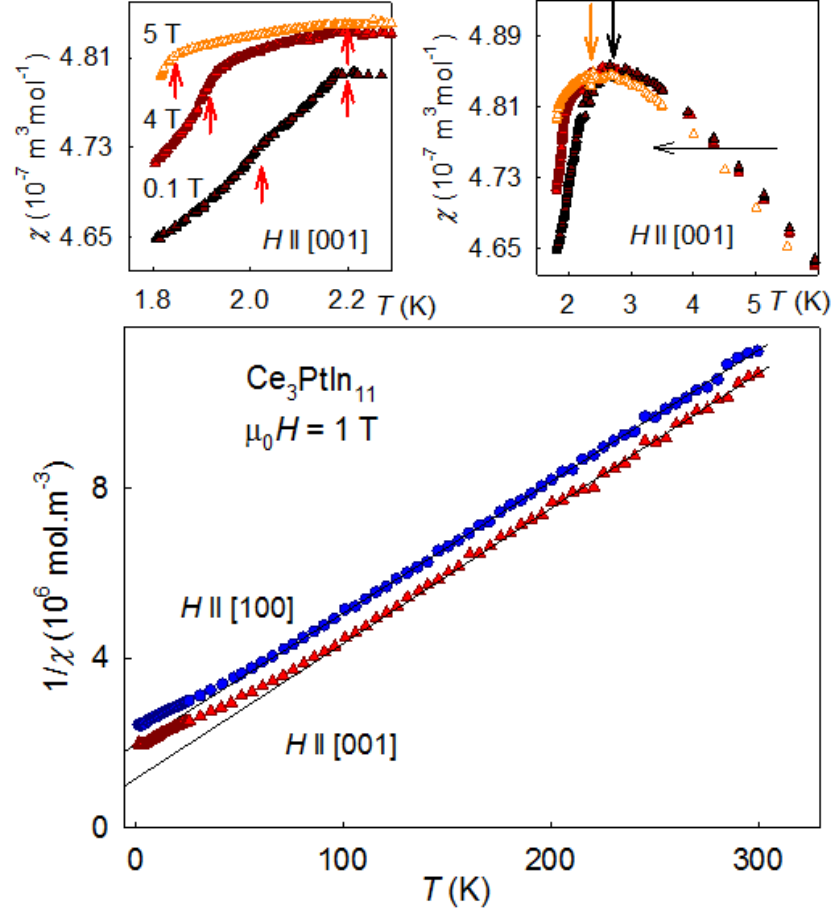


Fig. 26. The temperature dependence of the inverse magnetic susceptibility of $\text{Ce}_3\text{PtIn}_{11}$ in 1 T magnetic field applied along the principal crystallographic directions is shown in the bottom part. The solid lines depict the C-W-law fit. The upper left part shows the low-temperature part of the susceptibility in several magnetic fields applied along the [001] direction; the arrows mark the phase transitions. The upper right part shows the shift of the maxima in the $\chi(T)$ dependence (depicted by the vertical arrows) to lower temperatures with increasing magnetic field.

The linear behavior of the magnetic dependence of magnetization up to 7 T in the [001] and [100] direction of applied magnetic field measured at 1.8 K is depicted in Fig. 27. The data resembles the behavior of $\text{Ce}_3\text{PdIn}_{11}$ strongly including the easy [001] axis.

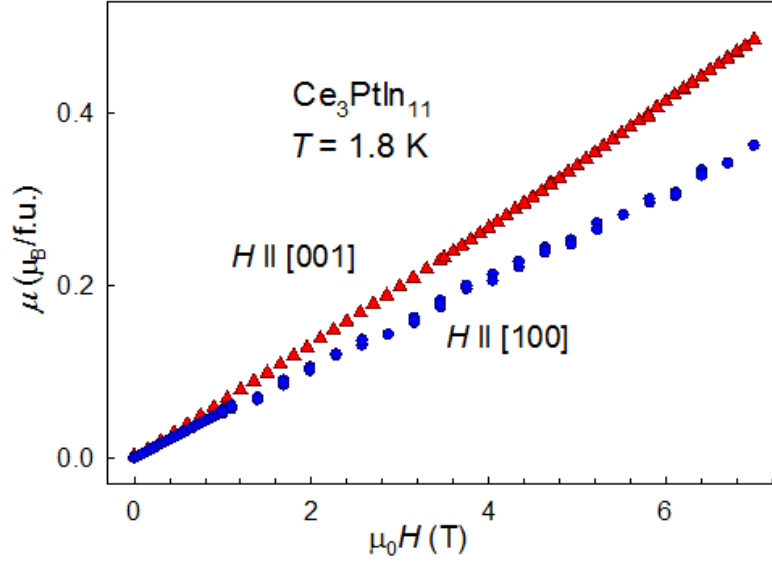


Fig. 27. The magnetization as a function of magnetic field applied along the [001] and [100] direction measured at $T = 1.8$ K.

The inverse susceptibility data of $\text{Ce}_3\text{PtIn}_{11}$ were fitted in analogy with $\text{Ce}_3\text{PdIn}_{11}$. In Fig. 28, a comparison of measured data and the corresponding fit is shown. The CEF parameters which characterize both curves best are summarized in Tab. 5. The inverse susceptibility of $\text{Ce}_3\text{PtIn}_{11}$ is described by the fit in the high-temperature region for both crystallographic directions better than in the case of $\text{Ce}_3\text{PdIn}_{11}$. However, a crossing of the calculated inverse susceptibilities along the in-plane and out-of-plane direction at ~ 15 K is observed similar to $\text{Ce}_3\text{PdIn}_{11}$ (see the inset). The fitted CEF parameters of $\text{Ce}_3\text{PdIn}_{11}$ and $\text{Ce}_3\text{PtIn}_{11}$ resemble each other strongly.

Tab. 4. The effective moment and the paramagnetic Curie temperature obtained from the C-W fit for $\text{Ce}_3T\text{In}_{11}$ ($T = \text{Pd}, \text{Pt}$) along the principal crystallographic directions.

	$\text{Ce}_3\text{PdIn}_{11}$		$\text{Ce}_3\text{PtIn}_{11}$	
	$\parallel [001]$	$\parallel [100]$	$\parallel [001]$	$\parallel [100]$
$\mu_{\text{eff}} (\mu_B/\text{f.u.})$	2.48	2.43	2.58	2.62
$\theta_p (\text{K})$	-34	-49	-36	-63

Tab. 5. CEF parameters B_l^m , CEF energies $E_{1,2}$ and the molecular field λ for $\text{Ce}_3T\text{In}_{11}$ ($T = \text{Pd}, \text{Pt}$). The units of all quantities are in meV except λ which is in mol/emu.

	$\text{Ce}_3\text{PdIn}_{11}$	$\text{Ce}_3\text{PtIn}_{11}$
B_2^0	-0.170	-0.167
B_4^0	0.019	0.020
B_4^4	-0.114	-0.114
E_1	6.7	6.7
E_2	8.9	9.0
λ	-22	-16

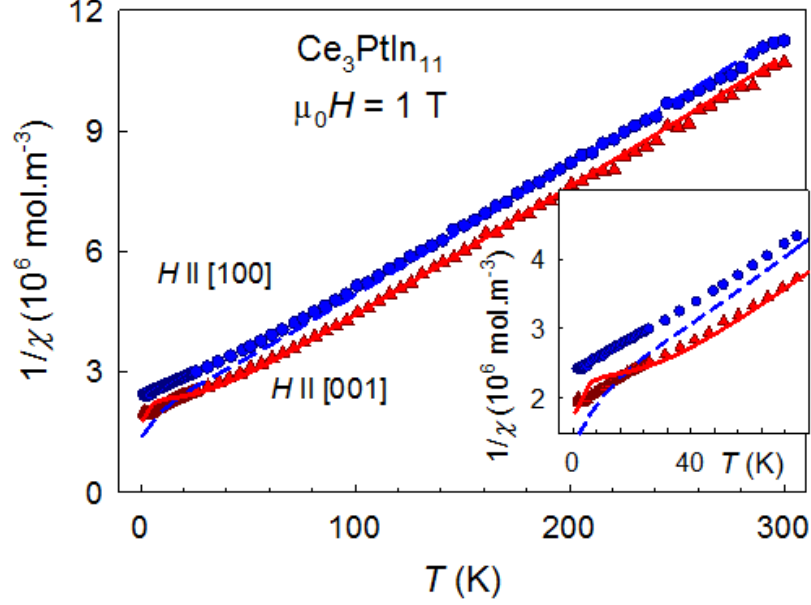


Fig. 28. The temperature dependence of the inverse magnetic susceptibility of $\text{Ce}_3\text{PtIn}_{11}$ compared to the fit with CEF parameters from Tab. 5 (red solid and blue dashed line depicts the [100] and [001] direction, respectively). The insets show the low-temperature part of the inverse magnetic susceptibility with the crossing of the fit for the [100] and [001] orientation.

We can now compare the CEF parameters of $\text{Ce}_3\text{TIn}_{11}$ ($T = \text{Pd}, \text{Pt}$) and the related Ce_2RhIn_8 and CeRhIn_5 compounds. While the first excited level $E_1 \sim 80$ K is the same as in $\text{Ce}_n\text{RhIn}_{3n+2}$ ($n = 1, 2$), the second level $E_2 \sim 104$ K is lower by $\sim 50\%$ compared to $E_2 \sim 220$ K in Ce_2RhIn_8 and by $\sim 36\%$ compared to $E_2 \sim 290$ K in CeRhIn_5 ¹⁹ (for Ce_2RhIn_8 , see section 4.3.). One can immediately see that the energy of the second excitation E_2 decreases with increasing the 3D character of the crystal structure. Similar result can be obtained for the parameters B_2^0 which decrease when going from CeRhIn_5 over Ce_2RhIn_8 to $\text{Ce}_3\text{TIn}_{11}$. The fitted values are somewhat lower than those for $\text{Ce}_n\text{RhIn}_{3n+2}$ ($n = 1, 2$), which is in line with our observation that the CEF parameters obtained from the analysis of the magnetic susceptibility tend to be slightly underestimated. Nevertheless, it is necessary to keep in mind that the compared compounds contain various transition metals which would lead to further differences. Detailed analysis of the CEF spectra of $\text{Ce}_n\text{TIn}_{3n+2}$ can be found in the section 4.3.

The low-temperature part of the specific heat C_p and the electrical resistivity $\rho/\rho_{2.3\text{K}}$ was measured in zero magnetic field and at ambient pressure as shown in Fig. 29. Interestingly, the behavior of $\text{Ce}_3\text{PdIn}_{11}$ and $\text{Ce}_3\text{PtIn}_{11}$ resembles each other strongly. Similar to $\text{Ce}_3\text{PdIn}_{11}$, three features in specific heat can be clearly observed. A λ -like transition appears in the specific heat at $T_1 = 2.2$ K, followed by another transition at $T_N = 2.0$ K, which is more pronounced in line with $\text{Ce}_3\text{PdIn}_{11}$ data. The observation of two phase transitions in $\text{Ce}_3\text{PtIn}_{11}$ confirms our previous results from the magnetic susceptibility. Both transitions at T_1 and T_N are identified by a moderate

change of slope in $\rho/\rho_{2.3K}$. With respect to similar character of $\text{Ce}_3\text{PdIn}_{11}$ data, we ascribe the first anomaly to a transition into an incommensurate state and the second one to a transition into a commensurate AF state.

Upon further cooling, we can observe another transition at $T_c = 0.32$ K in the specific heat of $\text{Ce}_3\text{PtIn}_{11}$. The value of T_c from specific heat is defined in the middle of the slope of the increasing peak. According to the steep drop in the electrical resistivity the feature marks a transition into a bulk SC state. The value of T_c from resistivity is given as the middle of the drop. Similar to $\text{Ce}_3\text{PdIn}_{11}$, there is a small discrepancy in the values of SC transition temperatures from different experiments; the resistivity provides $T_c = 0.36$ K instead of $T_c = 0.32$ K from the specific heat. The possible explanation was suggested in the section 3.3.2 discussing $\text{Ce}_3\text{PdIn}_{11}$.

The resistivity data of $\text{Ce}_3\text{PtIn}_{11}$ below T_N can be described using the spin-gap relation¹⁸⁸ which is represented by a red line in Fig. 29

$$\rho(T) = \rho_0 + AT^2 + DT(1 + 2T/\Delta)\exp(-\Delta/T) \quad (49)$$

where ρ_0 is the residual resistivity, A is the electron-electron scattering coefficient arising from an additional Landau-Fermi-liquid contribution, D is the electron-magnon and spin-disorder scattering coefficient and Δ is the magnon-energy gap. The fit yielded the values: $\rho_0 = 0.6 \mu\Omega\text{cm}$, $A = 0.59 \mu\Omega\text{cm K}^{-2}$, $D = 24.4 \mu\Omega\text{cm K}^{-1}$ and $\Delta = 7.78$ K which is in the order of magnitude of T_N .

Following the procedure for $\text{Ce}_3\text{PdIn}_{11}$, we analyze the specific heat with respect to two independent Ce-sites by subtracting the phonon term C_{ph} from the raw C/T data (see Fig. 31) which were measured up to 30 K. The formula for the phonon subtraction is again $C_{el} = C - 15 \cdot C_D$. The Debye temperature $\theta_D = 182$ K is very similar to the one for $\text{Ce}_3\text{PdIn}_{11}$. The Sommerfeld coefficient $\gamma = 0.40 \cdot \text{J mol}^{-1}\text{CeK}^{-2}$ was determined independently from the C_{el}/T plot as the C_{el}/T ratio just above the superconducting transition. The value of the γ coefficient of both compounds is somewhat higher than those of the parent heavy fermion materials $\text{Ce}_n\text{TIn}_{3n+2}$ ($n = 1, 2$; $T = \text{Rh, Ir}$)^{110,112,114}. This difference might reflect also different fitting procedures.

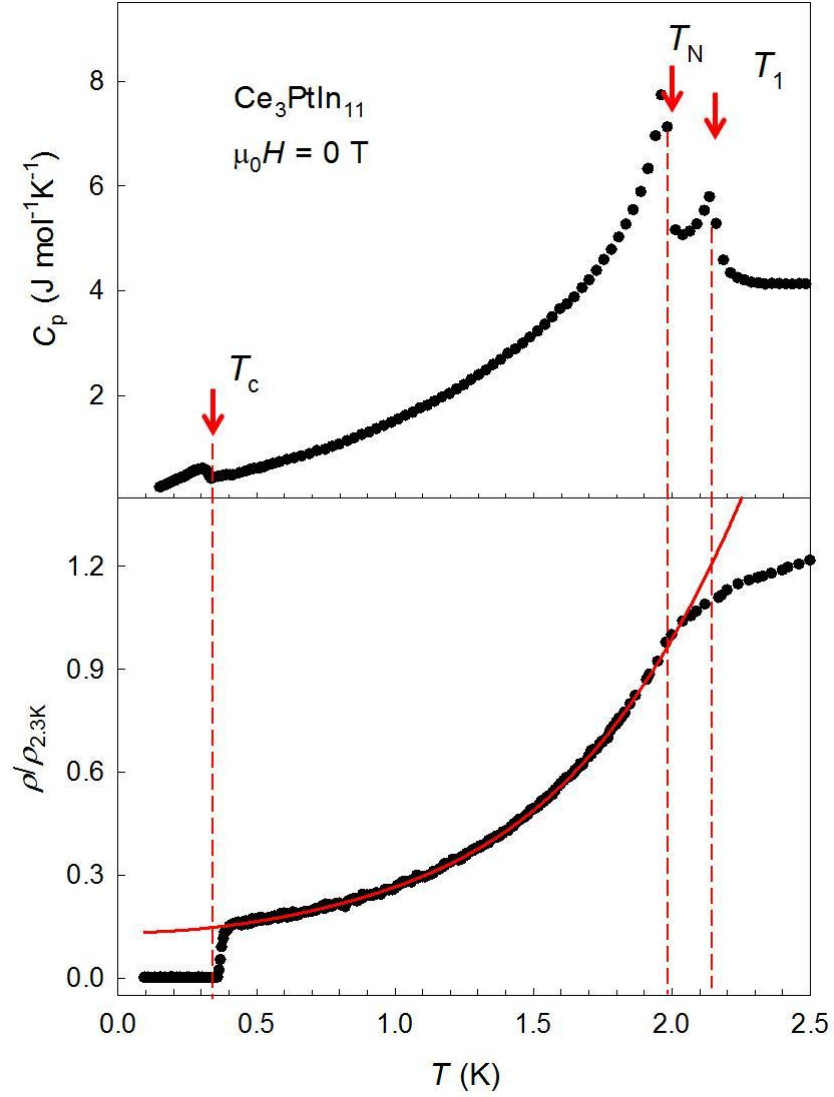


Fig. 29. The low-temperature part of specific heat and electrical resistivity of $\text{Ce}_3\text{PtIn}_{11}$ in zero magnetic field. The vertical dashed lines mark the positions of the phase transitions T_1 , T_N and T_c . The red solid line is the spin-gap fit to the data (see the text for more details).

Having both the coefficient A from the quadratic term in the resistivity spin-gap fit and the respective Sommerfeld coefficient γ of $\text{Ce}_3\text{PtIn}_{11}$, we can determine the Kadowaki-Woods ratio¹⁸⁹ A/γ^2 . However, in our case we observe a deviation $\sim 3.7 \cdot 10^{-6} \mu\Omega\text{cm}(\text{molK/mJ})^2$ from the predicted value of $1.0 \cdot 10^{-5} \mu\Omega\text{cm}(\text{molK/mJ})^2$ for Fermi-liquid materials. Such difference can be treated in the context of the „grand Kadowaki-Woods relation“¹⁹⁰, which is A/γ^2 normalized by $\frac{1}{2} N(N-1)$. For isolated atoms, N is defined as $2J + 1$, with J the total angular momentum and in solids, N varies due to the competition between the CEF splitting Δ and the Kondo temperature T_K ¹⁹⁰. For $N = 2$, the relation corresponds to classical Kadowaki-Woods ratio, consistent with the situation $T_K < \Delta$, which results in the low degeneracy of $N = 2$ ¹⁹⁰. Thus, gathered data on a broad range of heavy fermion compounds suggest that the A/γ^2

ratios are not specific to materials, but are commonly scaled by degeneracy. Applying this normalized relation on $\text{Ce}_3\text{PtIn}_{11}$, we obtain $N \sim 3$. This value does not depart significantly from the "classical" A/γ^2 relation pointing to a moderate increase of the Kondo effect.

The transition in $\text{Ce}_3\text{PtIn}_{11}$ reveals a jump $\Delta C_p/T_c \sim 0.53 \text{ J mol}^{-1} \text{ K}^{-2}$ at $T_c = 0.32 \text{ K}$. Using the coefficient $\gamma = 0.40 \text{ J mol}^{-1} \text{ Ce K}^{-2}$, the $(\Delta C_p)_{T_c}/\gamma T_c$ ratio ~ 1.33 is obtained. While the ratio in $\text{Ce}_3\text{PdIn}_{11}$ does not exceed 1, the character of the SC transition in the Pt-compound resembles more the conventional behavior described by the BCS theory.

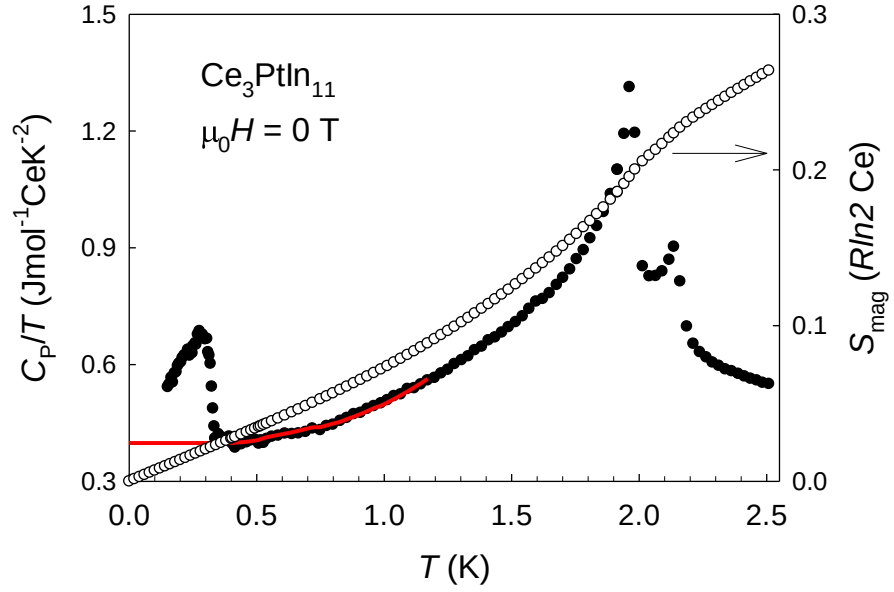


Fig. 30. The specific heat C_{el}/T vs T per cerium (closed circles) and the corresponding magnetic entropy (open symbols) of $\text{Ce}_3\text{PtIn}_{11}$. The red line represents the fit expressed by the equation above with the values of A and Δ given in the text.

In the following paragraphs, we calculate the magnetic entropy and the corresponding Kondo temperatures $T_{K,Ce(1)}$ and $T_{K,Ce(2)}$ in line with the specific-heat data treatment in $\text{Ce}_3\text{PdIn}_{11}$ (for details see the section 3.3.2). The same procedure and assumptions are adapted. The SC transition was cut off by extrapolating the low-temperature tail of the AF transition (red line in Fig. 30). The parameters used to fit the specific heat $C_{el}/T = \gamma + C_{mag}/T$ in the temperature range of 0.4 – 1.2 K are $A = 0.0101 \text{ J mol}^{-1} \text{ Ce K}^2$ and $\Delta = 15.18 \text{ K}$ (equation (48)). The Sommerfeld coefficient $\gamma = 0.40 \text{ J mol}^{-1} \text{ Ce K}^{-2}$ was not refined. Below T_1 , the above described procedure gives for $\text{Ce}_3\text{PtIn}_{11}$ an entropy fraction of about $0.2 \cdot R \ln 2$ per cerium, similarly to $\text{Ce}_3\text{PdIn}_{11}$. Thus, we can also assume that the Kondo-type interactions play a dominant role and simplify the calculation by accepting $S_{Ce2} = S_K(t)$. Again, we take into account only one inequivalent Ce-site first. With respect to $T_1 = 2.2 \text{ K}$ and to the table⁶⁹, we obtain the characteristic Kondo scale $T_K \sim 10 \text{ K}$. The full $R \ln 2$ entropy per cerium is recovered at $T \sim 5 \text{ K}$ similarly to $\text{Ce}_3\text{PdIn}_{11}$. To verify the

procedure of T_K estimation, several other approaches were performed as summarized in Tab. 6. Relatively similar values of T_K are obtained by different methods^{69,180} (applied on magnetization and specific-heat data) as was already shown in the case of $\text{Ce}_3\text{PdIn}_{11}$. Calculating T_K from the two-level model¹⁸¹ provides significantly lower values for both $\text{Ce}_3\text{TIn}_{11}$ compounds.

Tab. 6. Comparison of Kondo temperatures of the $\text{Ce}_3\text{TIn}_{11}$ systems ($T = \text{Pd}, \text{Pt}$) obtained by different procedures.

	T_K of $\text{Ce}_3\text{PdIn}_{11}$ [K]	T_K of $\text{Ce}_3\text{PtIn}_{11}$ [K]
<i>Hewson</i> ¹⁸⁰	11	14
<i>Rajan</i> ¹⁸¹	1.5	1.9
<i>Desgranges and Schotte</i> ⁶⁹	8	10

We analyse the Kondo temperatures assuming now two inequivalent Ce-sites from specific heat. The similar approach as in $\text{Ce}_3\text{PdIn}_{11}$ is applied (see Fig. 21). The electronic contribution of specific heat C_{el} was obtained by removing the contribution from phonons C_{ph} (depicted by a long-dashed line) and the superconducting transition by procedures described earlier in the text. The spin-fluctuation contribution $C/T \sim \log(T_0/T)$ (marked by red area in the plot) was taken entirely from the $\text{Ce}_3\text{PdIn}_{11}$ analysis to be able to provide comparable results. We accepted this simplification considering the crudeness of the overall analysis. The temperature evolution of both S_{Ce1} and S_{Ce2} is related to the right axis in Fig. 31. The entropy S_{Ce2} reaches its full value $R \ln 2$ at ~ 9 K. The increase of S_{Ce2} above the magnetic transition temperature T_1 is a sign of the overestimation of the Ce(2) contribution. Accordingly, the full entropy S_{Ce1} of the ground-state doublet of the Ce(1)-ion is somewhat underestimated and it is released above 20 K, in analogy with the results from $\text{Ce}_3\text{PdIn}_{11}$.

Similarly to the procedure applied in $\text{Ce}_3\text{PdIn}_{11}$, the temperature $T_{K,\text{Ce}(2)}$ corresponding to the “magnetic” Ce(2)-ion was calculated using the Bethe ansatz. The value of $T_{K,\text{Ce}(2)} \sim 2.8$ K was obtained with respect to the values taken from the table⁶⁹. To extract the Kondo temperature $T_{K,\text{Ce}(1)}$, we assume that $S_K(t)$ scales roughly with $S_{\text{Ce1}}(T)$. Identical approach as in the Pd sister-compound gives us “Kondo temperatures” ~ 13.5 K and ~ 9 K for the same values of entropy. Thus, the correct Kondo temperature $T_{K,\text{Ce}(1)}$ for $\text{Ce}_3\text{PtIn}_{11}$ does not exceed 20 K, either. Moreover, it is slightly higher than in $\text{Ce}_3\text{PdIn}_{11}$ which is consistent with the trend in T_K estimated from the magnetic susceptibility.

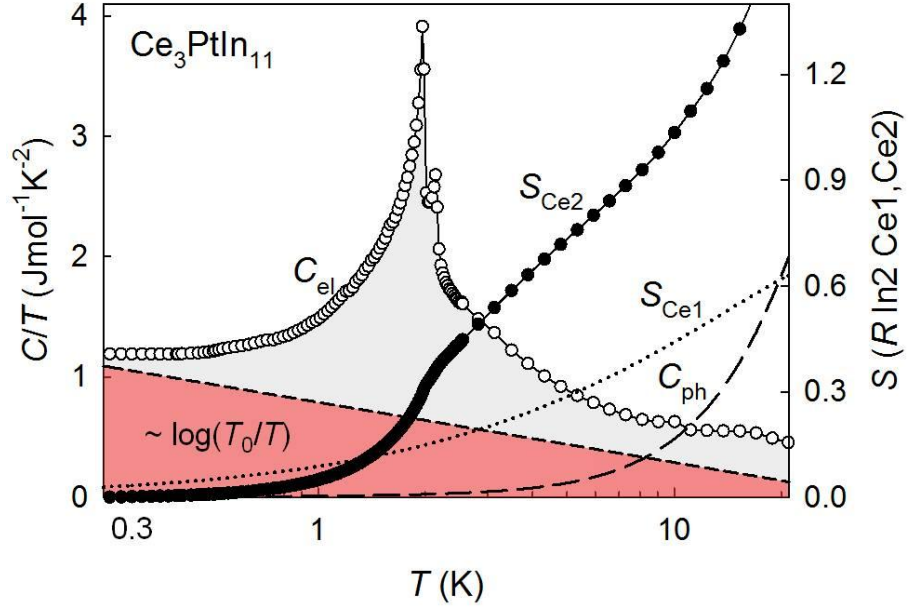


Fig. 31. Temperature dependence of C/T of $\text{Ce}_3\text{PtIn}_{11}$ on a logarithmic scale. The electronic part $C_{\text{el}} = C - C_{\text{ph}}$ is depicted by opened circles and the phonon part C_{ph} is marked by the long-dashed line ($C_{\text{ph}} = 15 C_{\text{D}}$ was fitted as described in the text). The short-dashed line corresponds to the spin-fluctuation contribution ($T_0 = 38$ K) of Ce_2PdIn_8 adapted from Ref.¹⁵⁴. The shaded area denotes the contribution arising from the Ce(2)-ion while the red area denotes the contribution arising from the Ce(1)-ion. The S_{Ce1} (dotted line) and S_{Ce2} (closed circles) show the entropy in units of $R \ln 2$ per Ce-ion related to Ce(1) and Ce(2), respectively.

The following section is divided into three parts, each discussing different type of phase diagrams of $\text{Ce}_3\text{PtIn}_{11}$ – magnetic, superconducting and under hydrostatic pressure.

The magnetic phase diagram

Analogically to the Pd sister-compound, the temperature dependence of specific heat of $\text{Ce}_3\text{PtIn}_{11}$ was measured under various magnetic fields applied along the [100] and [001] directions and the corresponding temperature–magnetic field phase diagram was constructed. Fig. 32 and Fig. 33 show that the behavior of both compounds resembles each other strongly in both principal crystallographic directions. This can be illustrated by merging of both magnetic transitions at ~ 3.5 T and the sharp λ -like shape of the magnetic transition at T_{N} above 5 T. The transition at T_1 remains completely untouched when the magnetic field is applied in the $H \parallel [100]$ configuration. Hence, its response is even weaker than in $\text{Ce}_3\text{PdIn}_{11}$.

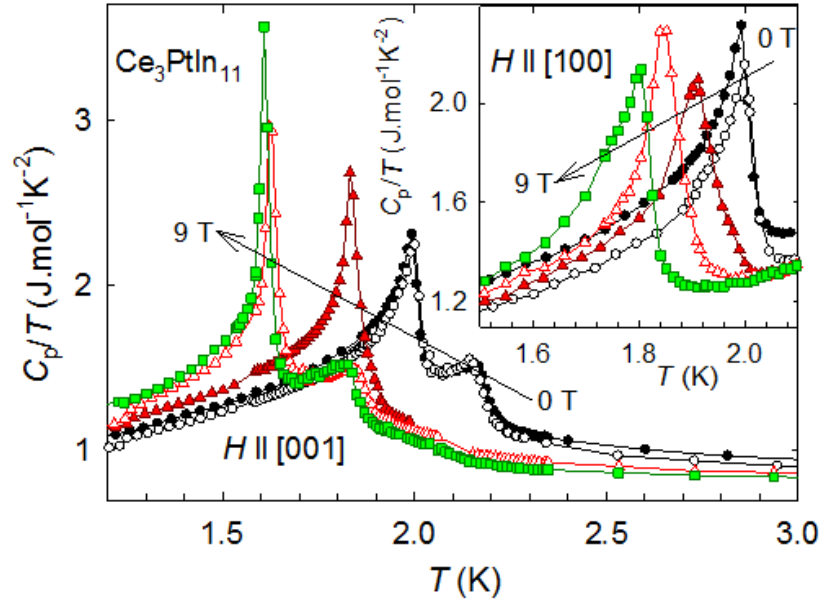


Fig. 32. The temperature dependence of specific heat of the $\text{Ce}_3\text{PtIn}_{11}$ compound measured in various magnetic fields (from right to left: $\mu_0 H = 0, 1, 5, 7, 9$ T) applied along the [001] axis. The inset shows the monotonous decrease of T_N with increasing magnetic field applied along the [100] axis.

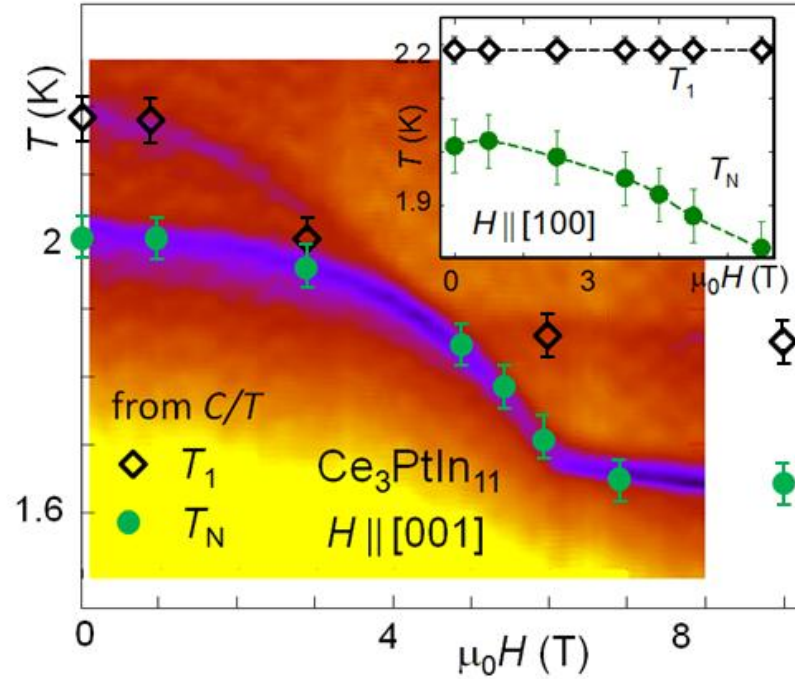


Fig. 33. The temperature–magnetic field phase diagram for $\text{Ce}_3\text{PtIn}_{11}$ mapped out by the thermal response technique (see text) in the magnetic field applied along the [001] axis. The black diamonds and green circles show T_1 and T_N , respectively, obtained from the specific-heat measurement. Inset depicts an analogous phase diagram for the field applied in the perpendicular [100] direction.

The superconducting phase diagram

The upper critical magnetic field–temperature phase diagram for $\text{Ce}_3\text{PtIn}_{11}$ was constructed using the resistivity data. The superconducting temperature T_c was determined as the middle of the slope of the drop (marked by an arrow in the figure). When increasing the magnetic field applied along the [001] axis, T_c is reduced as expected. The initial slope equals $\mu_0 dH_{c2}/dT(T_c) \sim -8.04$ T/K as shown in Fig. 34.

Extrapolation of the field dependent T_c to zero using the square-law fit (equation (18)) yields the orbital upper critical field $\mu_0 H_{c2}(0) \sim 1.4$ T. Using the WHH formula, we obtain a slightly higher value $\mu_0 H_{c2}^{\text{orb}}(0) \sim 2.0$ T from the initial slope of H_{c2} at T_c . Similarly to $\text{Ce}_3\text{PdIn}_{11}$, the calculated value is significantly smaller than those for CeRhIn_5 (at $p \sim p_c = 2.45$ GPa: $T_c = 2.2$ K, $\mu_0 H_{c2}(0) \sim 9.7$ T, $\mu_0 dH_{c2}/dT(T_c) \sim -18.4$ T/K) and CeCoIn_5 ($T_c = 0.4$ K, $\mu_0 H_{c2}(0) \sim 11.6$ T, $\mu_0 dH_{c2}/dT(T_c) \sim -24$ T/K)¹⁸⁵ as well as for Ce_2PdIn_8 (shown in Tab. 7). The relation from BCS theory (equation (25)) provides the value of the Pauli limiting field $\mu_0 H_{c2}^{\text{P}}(0) \sim 0.66$ T which is significantly lower than the orbital field $\mu_0 H_{c2}^{\text{orb}}(0) = 2$ T. Assuming $\mu_0 H_{c2}^{\text{P}}(0) \sim \mu_0 H_{c2}(0) = 1.4$ T, we obtain the Maki parameter $\alpha \sim 2$. In line with results from $\text{Ce}_3\text{PdIn}_{11}$, $\text{Ce}_3\text{PtIn}_{11}$ cannot be considered as Pauli limited.

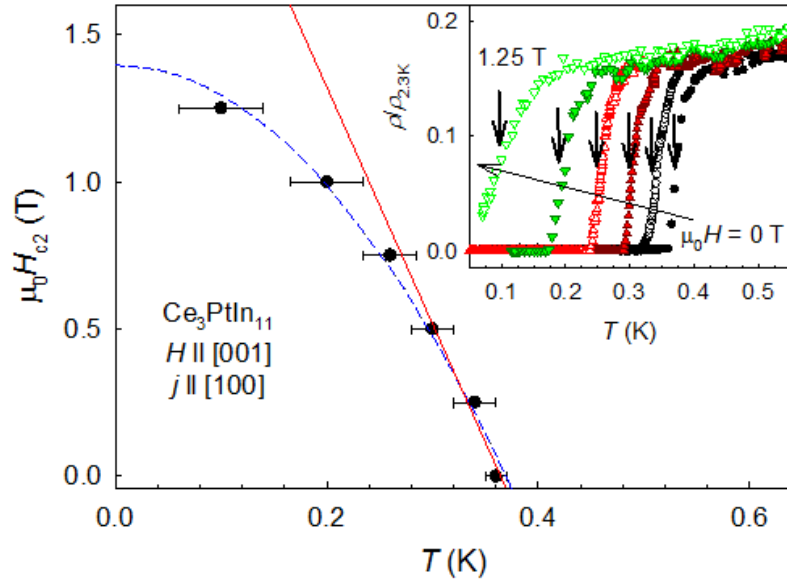


Fig. 34. The temperature dependence of the upper critical magnetic field of $\text{Ce}_3\text{PtIn}_{11}$ applied along the [001] axis derived from the resistivity measurements shown in the inset. The applied magnetic fields are 0, 0.25, 0.5, 0.75, 1 and 1.25 T. The electric current flows along the [100] direction. The red solid line yields -8.04 T/K. The blue dashed line is the square-law fit to the data (see the text for details).

From the Ginzburg–Landau formula (equation (20)) the superconducting coherence length $\xi(0) = 8.66$ nm was estimated. Inserting the value $\mu_0 dH_{c2}/dT(T_c) = -8.04$ T/K and $\gamma = 1.19$ J mol⁻¹K⁻² with $V_{\text{mol}} = 51.8 \cdot 10^{-5}$ m³mol⁻¹,

$T_c = 0.36$ K and $\rho_0 = 4.6 \cdot 10^{-7}$ Ωm into equation (21), we obtain the Fermi vector $k_F \sim 0.47 \cdot 10^{10} \text{ m}^{-1}$ and consequently the Fermi velocity $v_F \sim 5.88 \cdot 10^3 \text{ m} \cdot \text{s}^{-1}$ using the equation (22). The effective mass $m^*/m_e \sim 93$ differs by two orders of magnitude from the corresponding free-electron values. The superconducting coherence length $\xi_{GL} \sim 22.5 \cdot 10^{-9} \text{ m}$ was calculated from equation (23).

To complete the characterization of the superconducting transition in $\text{Ce}_3\text{PtIn}_{11}$ from the classical approach, the quasiparticles mean free path l , the penetration depth λ_{GL} and the Ginzburg-Landau parameter κ_{GL} were calculated according to relations presented in the section 1.6. The values of all presented parameters are summarized and compared with those for $\text{Ce}_3\text{PdIn}_{11}$ and Ce_2PdIn_8 ¹⁵⁴ in Tab. 7. The relation $l \sim 12 \text{ nm} > \xi(0) \sim 8.66 \text{ nm}$ indicates that $\text{Ce}_3\text{PtIn}_{11}$ cannot be identified as a clean-limit superconductor, similarly to $\text{Ce}_3\text{PdIn}_{11}$. The parameter $\kappa_{GL} \sim 10 > 1/\sqrt{2}$ confirms that $\text{Ce}_3\text{PtIn}_{11}$ is a type-II superconductor.

Tab. 7. Comparison of the main thermodynamic parameters of $\text{Ce}_3\text{PdIn}_{11}$, $\text{Ce}_3\text{PtIn}_{11}$ and Ce_2PdIn_8 ^{154,161} (except k_F and v_F ¹⁵⁵) derived from the BCS theory using equations from Ref.^{67,68}.

	$\text{Ce}_3\text{PdIn}_{11}$	$\text{Ce}_3\text{PtIn}_{11}$	Ce_2PdIn_8
T_c [K]	0.44	0.36	0.7
$-\mu_0 dH_{c2}/dT(T_c)$ [T/K]	12.25	8.04	13.5
$\mu_0 H_{c2}(0)$ [T] – square-law	2.3	1.4	2.32
$\mu_0 H_{c2}^{\text{orb}}(0)$ [T] - WHH	3.7	2	6.8
$\xi(0)$ [nm]	10.84	8.66	4.9
k_F [10^{10} m^{-1}]	0.73	0.47	0.92^{155}
v_F [$\text{km} \cdot \text{s}^{-1}$]	3.83	5.88	4.15^{155}
m^* [m_e]	220	93	193
ξ_{GL} [nm]	12.0	22.5	11.5
l [nm]	25	12	27
λ_{GL} [nm]	284	229	422
κ_{GL}	24	10	37

The hydrostatic-pressure phase diagram

In the parent heavy fermion compounds^{115,147,163} the application of hydrostatic pressure reduces the temperature of magnetic ordering transition while the superconductivity is enhanced, forming a SC dome in the phase diagram. Our measurements reveal a very similar result and hereby confirm an unconventional nature of the SC state mediated by magnetic fluctuations. The data were collected from the specific heat at ambient pressure and from the low-temperature resistivity measurements at hydrostatic pressures. Due to the higher quality of the $\text{Ce}_3\text{PtIn}_{11}$ sample which manifests itself by clearly pronounced transitions, the pressure measurements have been performed preferably on this compound. The electric

current j was oriented along the [001] direction in all measurements under hydrostatic pressure.

The temperature dependence of the electrical resistivity for selected values of hydrostatic pressure is shown in Fig. 35. The data were obtained in a tiny magnetic field of $\mu_0 H = 0.04$ T in order to suppress the SC transition of indium (~ 3 K at ambient pressure). Both magnetic transitions T_N and T_1 in $\text{Ce}_3\text{PtIn}_{11}$ shift towards lower temperatures with increasing pressure; the incommensurate antiferromagnetic state (IMO) appears to be rather sensitive to the volume changes as it disappears completely above $p \sim 0.6$ GPa. Thus, only the commensurate magnetic state (MO) is observed for higher pressures. The SC temperature T_c is almost constant up to 0.7 GPa; interestingly, the dT_c/dp slope changes above this pressure and T_c starts to grow steeper up to ~ 1.1 GPa where $T_N \approx T_c \sim 0.7$ K. The value ~ 0.7 GPa coincides roughly with the highest pressure, where the magnetic transition at T_1 can be observed. The values of T_N and T_c become equal at the critical pressure $p_{c1} = 1.1 \pm 0.03$ GPa. In CeRhIn_5 , the critical pressure p_{c1} reaches 1.75 GPa and the comparable phase diagram of CeIn_3 ¹⁷⁸ reveals $p_{c1} \sim 2.65$ GPa. The critical pressure p_{c2} where the MO is fully suppressed and only the SC state survives is estimated using the T - p phase diagram of CeRhIn_5 . Extrapolation of the pressure dependence of T_N in CeRhIn_5 in the absence of the SC state yields $T_N = 0$ at $p_{c2} \sim 2.25$ GPa¹¹⁵. Thus, we tentatively draw an analogical conclusion for $\text{Ce}_3\text{PtIn}_{11}$ obtaining the value of critical pressure $p_{c2} = 1.2 \pm 0.05$ GPa. The critical pressure p_{c2} corresponds to the maximum of the SC dome at $T_c = 0.69$ K. Further increase of hydrostatic pressure causes a gradual suppression of T_c down to 0.21 K in 2.3 GPa which is the highest value of the hydrostatic pressure applied in the experiment. Assuming analogical behavior as in the phase diagram of CeRhIn_5 ¹¹⁵, the superconductivity disappears approximately at ~ 2.5 GPa. The zero field temperature-hydrostatic pressure phase diagram is shown in Fig. 37.

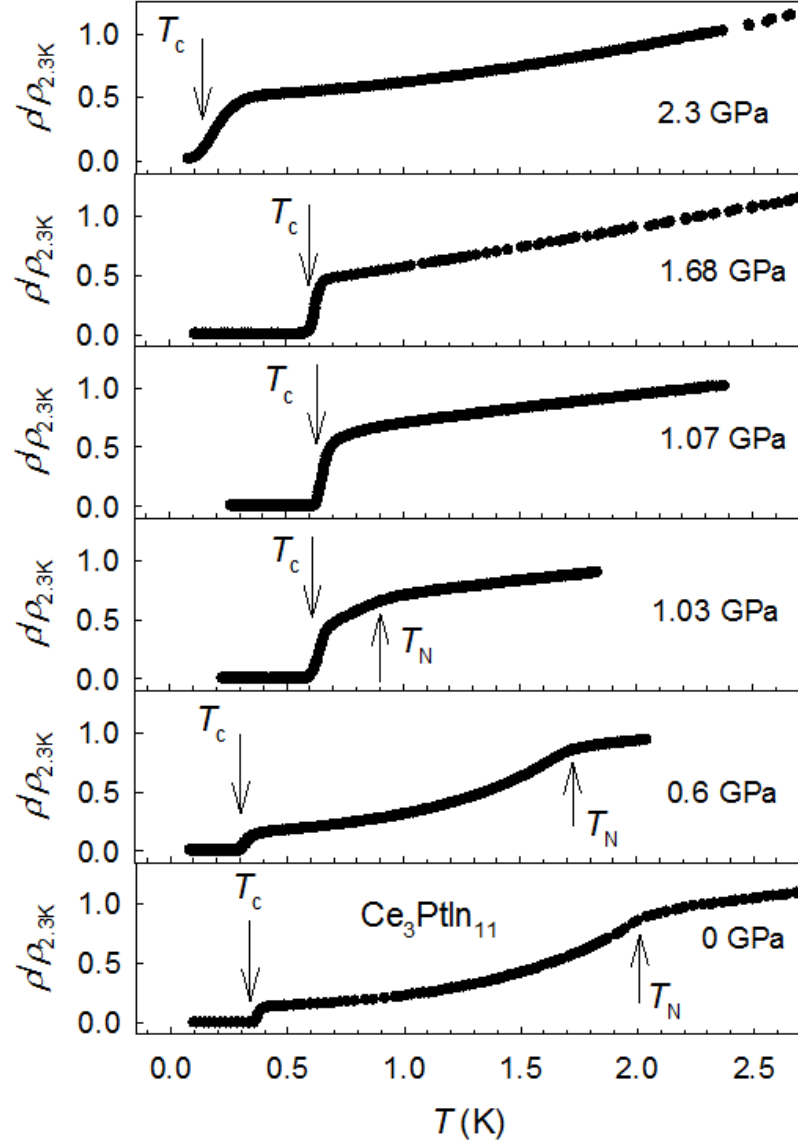


Fig. 35. The low-temperature evolution of the normalized electrical resistivity $\rho/\rho_{2.3K}$ of $\text{Ce}_3\text{PtIn}_{11}$ under various hydrostatic pressures. The arrows mark the transition temperatures at T_N and T_c .

The power-law temperature dependence of electrical resistivity at low temperatures was studied in pressures above ~ 1 GPa. Fig. 36 gathers together the T^n -dependent resistivity curves for pressures 1.07, 1.3, 1.68 and 2.3 GPa and the corresponding linear fits. One can see that for the hydrostatic pressure of 1.07 GPa, the coefficient $n = 0.8$ is lower than 1 which is a value commonly understood as a sign of nFl behavior. Interestingly, the same coefficient ($n = 0.85$) for 1.3 GPa in $\text{Ce}_3\text{PtIn}_{11}$ was observed in CeRhIn_5 ¹⁹¹ and in the Pd-substituted CeRhIn_5 ¹⁹² for $p = 2.25$ GPa. These values of pressures correspond roughly in all pressure-temperature phase diagrams to the maximum of the SC dome. The coefficient reaches 1 first for 1.68 GPa, where the transition temperature T_c decreases already. At even higher pressures, the Fermi-liquid behavior with $n = 2$ is finally

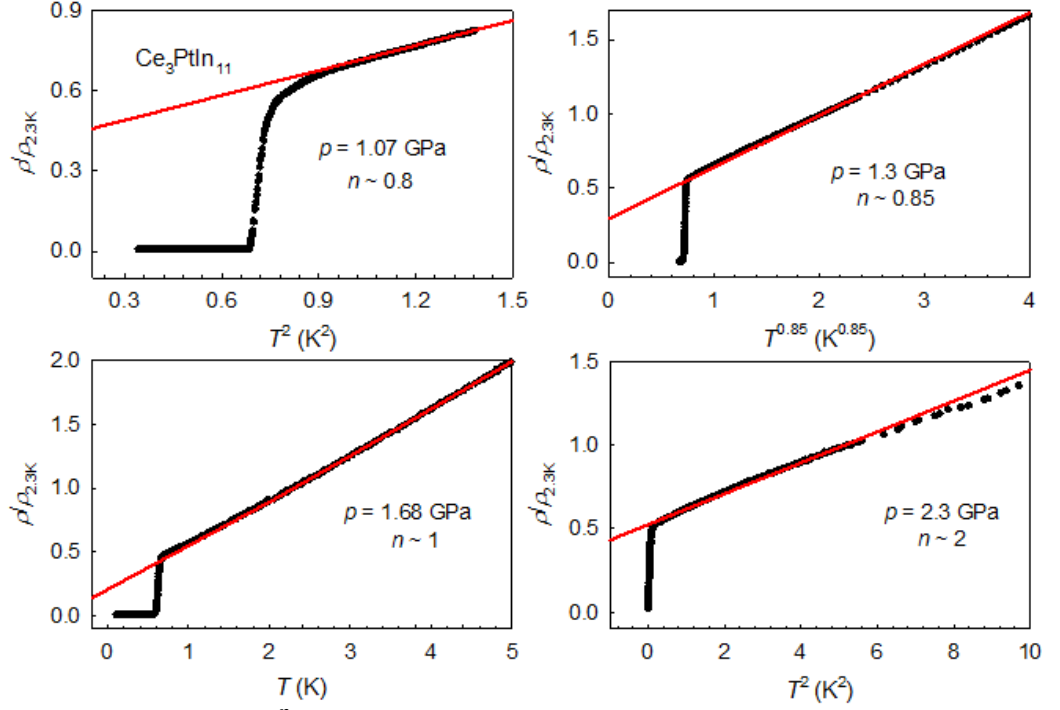


Fig. 36. The power-law T^n dependence of the normalized electrical resistivity $\rho/\rho_{2.3K}$ in hydrostatic pressures from 1.07 to 2.3 GPa with the corresponding n coefficients from 0.8 to 2. The linear fits (red lines) to the resistivity curves depict the nFI behavior above T_c .

restored. The nFI and FI regions are depicted in the temperature-pressure phase diagram in Fig. 37.

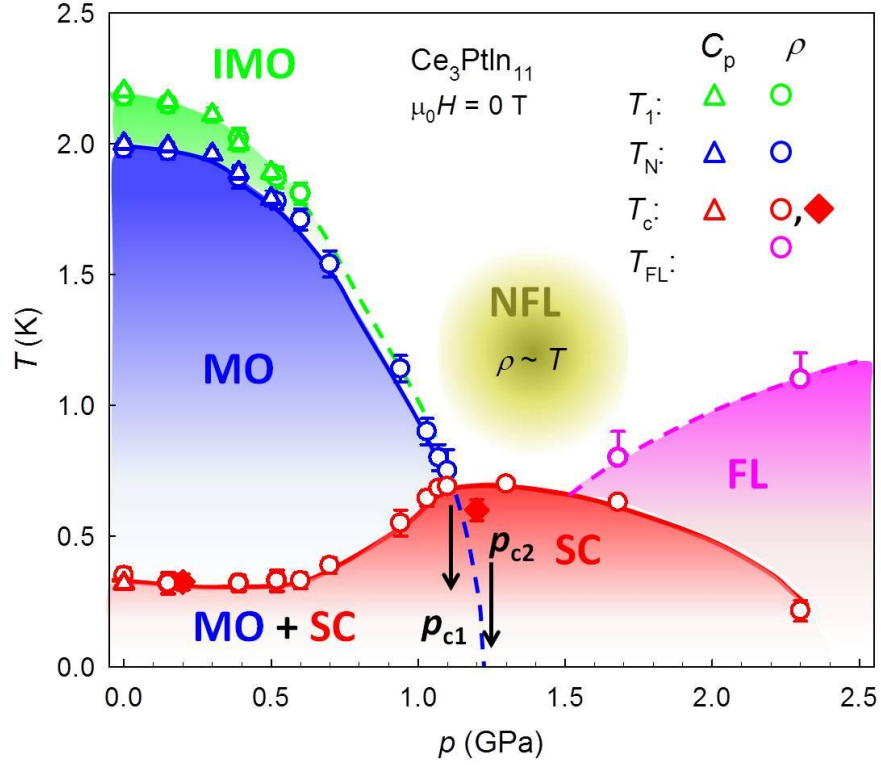


Fig. 37. The temperature-pressure phase diagram in zero field. The data marked by triangles are taken from the heat capacity whereas those marked by circles are obtained from the resistivity (both on sample #2). The data marked by the red diamond represent resistivity data obtained on sample #1. IMO marks the presumably incommensurate magnetic order (green region); MO the commensurate order (blue) and SC the superconductivity (red); nFl marks the region (yellow) where an approx. linear T -dependence of resistivity was observed and FL marks the region (pink) where the square T -dependence is restored. The arrows mark the critical pressures p_{c1} and p_{c2} . The green dashed line suggests pressure evolution of T_1 and the blue dashed line depicts the suggested pressure evolution of the T_N based on the T - p phase diagram of CeRhIn_5 ¹¹⁵.

Fig. 38 shows the temperature dependence of $\mu_0 H_{c2}$ for different pressures up to 2.3 GPa in the [001] direction of the applied magnetic field. The data were fitted using the square law to extract the pressure dependence of the upper critical field as shown in the inset. Parallel, the theoretical values of H_{orb} calculated using the WHH formula are depicted in the plot. At ~ 0.5 GPa we observe a steep increase up to the maximum value at 1.3 GPa. For even higher pressures, $H_{c2}(0)$ and H_{orb} decrease monotonically. This anomaly points to an increase of the robustness of antiferromagnetic fluctuations and shows that the pressure pushes the system to the vicinity of a QCP.

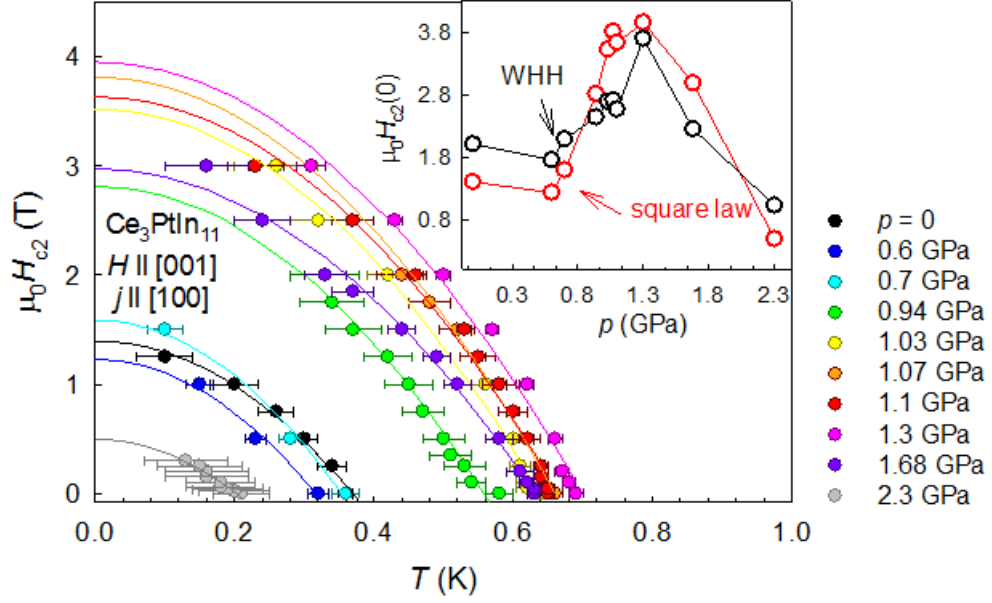


Fig. 38. The upper critical magnetic field of $\text{Ce}_3\text{PtIn}_{11}$ along the [100] axis measured at various hydrostatic pressures. The lines are square-law fits to the data. The pressure evolution of the upper critical field obtained from the square-law fit (red) and the theoretical orbital field H_{orb} calculated from the WHH formula (black) is shown in the inset. The lines are guides to eyes.

To summarize the effect of both hydrostatic pressure and magnetic field on the transition temperatures of $\text{Ce}_3\text{PtIn}_{11}$, a 3D temperature-hydrostatic pressure-magnetic field (T - p - $\mu_0 H$) phase diagram was constructed (see Fig. 39(a)). In analogy with the 3D diagram for CeRhIn_5 ¹¹⁵, we can adopt the concept of a tetracritical point (TCP). The region of coexistence of both MO and SC phase is located in the low-field region in a broad range of pressures from zero to ~ 1.1 GPa. The MO to magnetically disordered (MD) boundary is obtained by the extrapolation $T_N \rightarrow 0$ shown in the T - p phase diagrams in various magnetic fields (see Fig. 68 in Appendix A). The hydrostatic pressure, for which the MO phase is induced in the increasing magnetic field, is almost constant, meeting the upper critical field line H_{c2} at $p_{c2} \sim 1.2$ GPa, at a TCP according to Ref.¹¹⁵. The red star located in the $T = 0$ plane marks the position of TCP where the yellow dashed line (depicting the pressure evolution of H_{c2}) and the green dashed line cross. At the tetracritical point, four “different phases” meet – the SC, MO, MD phase and the phase revealing coexistence of SC and MO. Here, the line separating a phase of MO and SC coexistence from a purely SC phase terminates. Also, the transition line between MO and MD phases for $H > H_{c2}$ starts at TCP. In contrast to the phase diagram of CeRhIn_5 ¹¹⁵, the boundary between the MO and MD phase seems to be almost pressure-independent both below and above H_{c2} .

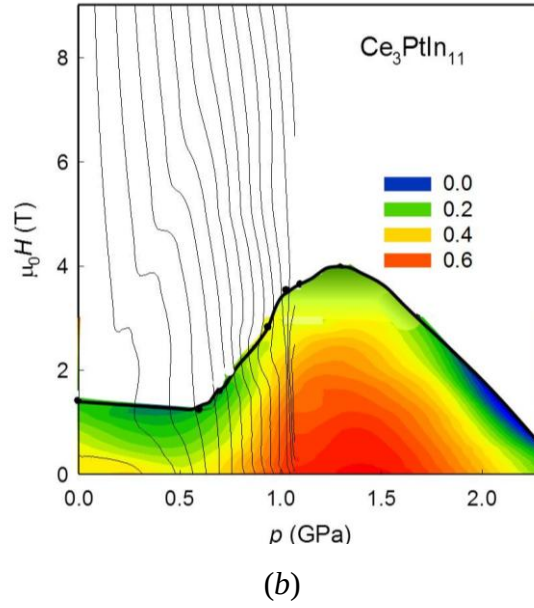
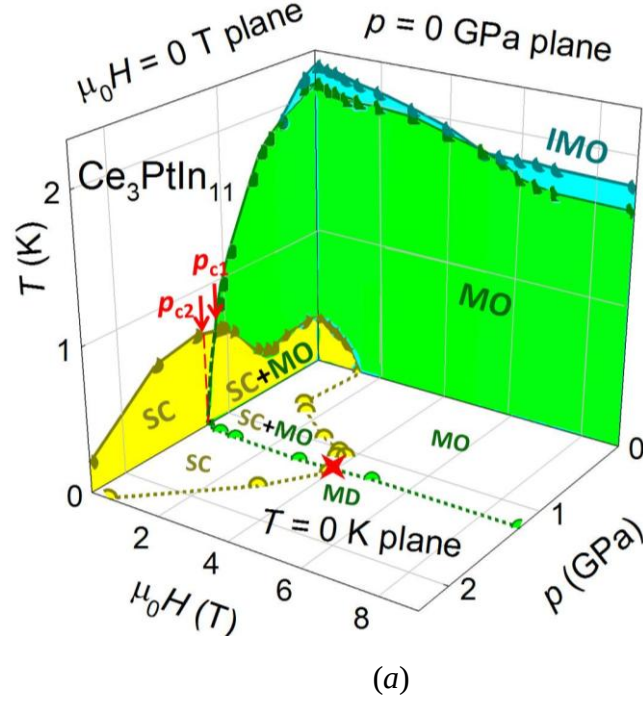


Fig. 39. (a) The temperature-hydrostatic pressure-magnetic field phase diagram of $\text{Ce}_3\text{PtIn}_{11}$. The evolution of T_1 , T_N and T_c is depicted in the T - μ_0H plane at ambient pressure and in the T - p plane in zero field. The p - μ_0H plane is depicted at $T = 0$ where the data points for $T_c = 0$ were obtained as the upper critical fields H_{c2} from Fig. 38 and the data points for $T_N = 0$ were obtained using the extrapolation shown in the T - p phase diagrams from Fig. 68. The dashed lines are a guide to the eye. Abbreviations IMO, MO and SC are used analogically to Fig. 37; MD means magnetically disordered. The vertical arrows mark the critical pressures p_{c1} and p_{c2} . The red star marks a tetracritical point where the H_{c2} line and the MO to MD boundary cross. (b) The plot displays the values of T_c (spectral colors) and T_N (contours) in a 2D projection into the μ_0H - p plane. The black line depicts the border given by the upper critical field as shown in the inset of Fig. 38. The magnetic transition at T_1 is omitted for simplicity.

Another view on the evolution of the transition temperatures is provided in Fig. 39(b) where $T_N(\mu_0 H, p)$ and $T_c(\mu_0 H, p)$ are projected on the $\mu_0 H$ - p plane in the corresponding contour lines and spectral colors, respectively. The magnetic phase below T_1 is avoided in the plot for better clarity. From the shape of the black contours it is evident, that the steep decrease in T_N observed around 4 T at ambient pressure is smeared out with increasing pressure. The superconducting state becomes more robust with increasing pressure up to ~ 1.2 GPa where the maximum of the SC dome is formed as depicted by the red color.

3.4. Discussion

The results from the combined measurement under hydrostatic pressure and magnetic field suggest that the SC state can only fully develop first at ~ 0.7 GPa. Such interpretation raises question whether this scenario could assume two regions with different nature of superconductivity, an “ambient-pressure” and a “pressure-induced” SC phase with crossover at steep increase of T_c and H_{c2} , as shown in Fig. 39(a). While the increasing pressure seems to suppress the “ambient-pressure” superconductivity, the other one gets more robust and this effect is even more pronounced in nonzero magnetic fields. One might speculate about the relationship between these two SC phases and the role of two crystallographically inequivalent Ce-sites. As already mentioned, the CeIn_3 compound reveals a maximum in pressure-induced T_c in the vicinity of QCP¹⁷⁸. Extrapolating the pressure behavior of the 4*f*-electrons in CeIn_3 to $\text{Ce}_3\text{PtIn}_{11}$, the emergence of the “pressure-induced” superconductivity can be ascribed to the Ce(2)-ion. The pressure evolution of the “ambient-pressure” superconductivity resembles the behavior of Ce_2PdIn_8 in pressure which is represented by the Ce(1)-ion.

The presence of two inequivalent cerium sites in the layered crystal structure of $\text{Ce}_3\text{TIn}_{11}$ is unique among related systems and stands behind their complex ground-state properties. According to the simple idea with the different Ce-site environments in the CeIn_3 and Ce_2TIn_8 structures presented in section 3.3.2, we suggested the Ce(1)In₃-layer is responsible for superconductivity while the Ce(2)In₃-layer is linked to the magnetic ordering. This scenario was further supported by the performed entropy analysis. The electronic structure is composed according to this picture of two local-moment Kondo sublattices revealing distinct Kondo scales¹¹¹. The Ce(1)-site behaves itinerant as it is involved in the heavy fermion behavior and superconductivity. In contrast, the Ce(2)-site maintains its localized character. This is in agreement with the two-Kondo ion lattice model¹¹¹ where the Ce(1)-site is completely Kondo screened while the Ce(2)-site is a source of the long-range magnetic order. With respect to this model, we speculate that the observed pressure-induced quantum critical point might be of a local-moment type.

Another aspect which supports the previous analysis focuses on the sublattice structure of CeTIn_5 and CeIn_3 . We introduce the modified c^*/a ratio in the crystal structure as shown in Fig. 40(a). Here, c^* is the distance between the Ce(1)-ions separated by the TIn_2 layer. Thus, the c^*/a ratio is equivalent to the c/a ratio in the CeTIn_5 compounds. The T_c vs c^*/a diagram in Fig. 40(b) gathers together the known ambient-pressure superconductors from the CeTIn_5 ($T = \text{Co}, \text{Rh}, \text{Ir}$) group and the $\text{Ce}_3\text{TIn}_{11}$ ($T = \text{Pd}, \text{Pt}$) compounds. The dependence of T_c on the c/a ratio is almost linear for CeTIn_5 with the exception of $\text{CeCo}_{0.5}\text{Ir}_{0.5}\text{In}_5$ (data taken from Ref.¹¹⁶). The $\text{Ce}_n\text{TIn}_{3n+2}$ compounds ($n = 1, 2$; $T = \text{Pd}, \text{Pt}$) reveal, surprisingly, a very similar linear dependence of T_c on the modified c^*/a ratio, in line with the concept above.

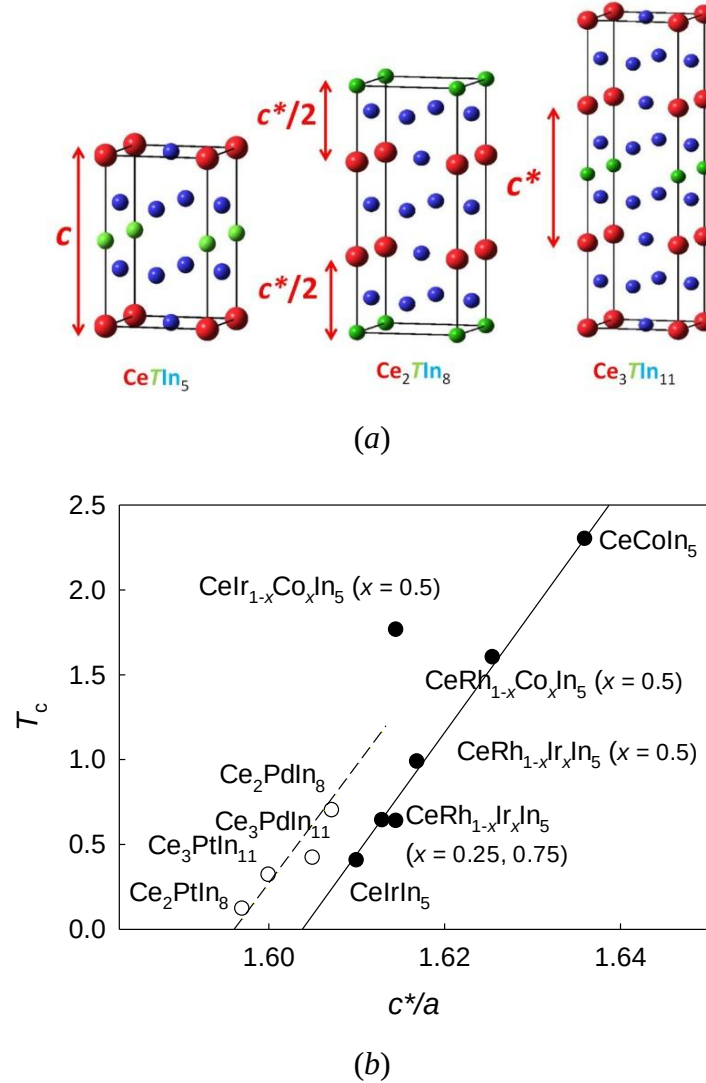


Fig. 40. (a) The structures of CeTIn_5 , Ce_2TIn_8 and $\text{Ce}_3\text{TIn}_{11}$ with the c^* -parameter. (b) The T_c vs. c^*/a diagram. The known superconductors from the CeTIn_5 ($T = \text{Co}, \text{Rh}, \text{Ir}$) group are depicted by the full points and the novel Pd- and Pt-compounds discussed in this chapter are marked by empty points. The lines are guides to the eye.

The sketched scenario of two independent Ce-sites responsible for magnetism and superconductivity separately could not be proved without any microscopic

experiment. Nevertheless, there are known several examples of cerium-based materials with more inequivalent Ce-sites which are a source of very complex ground state. One example is the $\text{Ce}_3\text{Pd}_{20}\text{Si}_6$ compound³¹ where it is speculated that two crystallographically inequivalent cerium sites are responsible for the antiferromagnetic and quadrupolar order. Another case is the CeRuSn showing a sequence of polymorphic transitions with increasing number of the independent cerium sites¹⁹³. The character of the structure of the artificially grown $\text{CeIn}_3/\text{LaIn}_3$ layers⁵⁵ makes them an utmost 2D-dimensional representative of the $\text{Ce}_n\text{T}_m\text{In}_{3n+2m}$ family.

3.5. Summary

A detailed study of the novel cerium heavy fermion systems Ce_2PtIn_8 , $\text{Ce}_3\text{PdIn}_{11}$ and $\text{Ce}_3\text{PtIn}_{11}$ was performed. Based on a comprehensive thermal analysis (DTA and DSC), the optimal growth parameters for these materials have been found and directly applied in the In self-flux synthesis. Despite many efforts, we were not able to prepare single-phase single crystals of Ce_2PtIn_8 with dimensions larger than $\sim 100 \mu\text{m}$. The specific heat showed that the superconducting state of this compound is established below $T_c \sim 110 \text{ mK}$.

On the other hand, the single-phase single crystals of $\text{Ce}_3\text{PdIn}_{11}$ and $\text{Ce}_3\text{PtIn}_{11}$ exceeded sufficient mass suitable for the majority of bulk measurements. The performed experiments show that both systems are very similar from many aspects.

The electrical resistivity and magnetic susceptibility point to relatively low anisotropy of both systems in the 2-300 K temperature range. Focusing on the low-temperature region, we come to the most intriguing observation which is the coexistence of ambient-pressure heavy fermion superconductivity and magnetic ordering. $\text{Ce}_3\text{PdIn}_{11}$ ($\text{Ce}_3\text{PtIn}_{11}$) exhibits two successive magnetic transitions at $T_1 = 1.7 \text{ K}$ ($T_1 = 2.2 \text{ K}$) and $T_N = 1.5 \text{ K}$ ($T_N = 2.0 \text{ K}$), presumably into incommensurate and commensurate antiferromagnetic states. While the magnetic field applied along the [100] axis has only a moderate effect on both magnetic transitions; unusual behavior is observed in magnetic field along the [001] axis. Both magnetic transitions merge at 4 T and split again in higher magnetic fields.

Upon cooling, a superconducting state is established below $T_c = 0.42 \text{ K}$ in $\text{Ce}_3\text{PdIn}_{11}$ and below $T_c = 0.32 \text{ K}$ in $\text{Ce}_3\text{PtIn}_{11}$. The thorough analysis of the SC state in terms of the BCS theory provides results comparable to other heavy fermion superconductors, such as Ce_2PdIn_8 or CeCu_2Si_2 ¹⁵⁴.

The application of the hydrostatic pressure in $\text{Ce}_3\text{PtIn}_{11}$ enhances the temperature T_c forming a SC dome characteristic for related cerium systems. The magnetic order below T_1 is sensitive to applied pressure as it is not detected above $\sim 0.6 \text{ GPa}$. The values of T_N and T_c become equal at the critical pressure $p_{c1} = 1.1 \pm 0.03 \text{ GPa}$. The

maximum of the SC dome coincides with the complete suppression of T_N at the critical pressure $p_{c2} = 1.2 \pm 0.05$ GPa. At this pressure the nFI behavior is detected as the system is driven into the vicinity of QCP which might be of a local-moment type.

We suggest how these complex physical properties of $\text{Ce}_3\text{TlIn}_{11}$ can be explained by different local environments of the two inequivalent cerium atoms. With respect to the two-Kondo ion lattice model¹¹¹ we assume that the Ce(1)-site is completely Kondo screened participating in superconductivity while the Ce(2)-site is localized being a source of the long-range magnetic order. Hence, the compounds fulfill as the first ones the conditions given in the theoretical work of *Benlagra et al.*¹¹¹.

To sum up the previous paragraphs, $\text{Ce}_3\text{PdIn}_{11}$ and $\text{Ce}_3\text{PtIn}_{11}$ represent very rare cerium systems which reveal both magnetic order and heavy fermion superconductivity at ambient pressure already. The other two known systems are the CeCu_2Si_2 ⁶⁴ and the noncentrosymmetric CePt_3Si ¹⁹⁴ compounds.

This fact predetermines them as ideal candidates within the heavy fermion compounds to investigate these phenomena using a broad range of measurement methods. In the near future, number of experiments is planned. Further work is underway to reveal more of the superconducting properties of Ce_2PtIn_8 using a combination of experimental methods (focused ion beam for microfabrication, lithography). The attention will be focused on the pressure experiments on $\text{Ce}_3\text{PdIn}_{11}$ which has been somewhat in the shadow of its Pt sister-compound so far. The anisotropy of the upper critical field $H_{c2}(0)$ in the [100] and [001] direction is necessary to be analyzed to shed the light on the superconducting properties of both systems. Of very high importance are the neutron experiments to investigate the magnetic structure and further measurements including ARPES, STM and μSR which can reveal the role of the inequivalent Ce-sites in the ground-state properties of $\text{Ce}_3\text{TlIn}_{11}$.

4. Ce₂RhIn₈

The following chapter focuses on the inelastic neutron scattering (INS) experiment of the well-known Ce₂RhIn₈ compound. While the crystal-electron field (CEF) of the CeTIn₅ compounds has been thoroughly investigated, it was not studied so far in the Ce_nTIn_{3n+2} compounds with $n = 2$. Recently, the importance of understanding the role of various low-temperature energy scales in forming the ground state was discussed in the work of *Willers et al.*¹⁹⁵. Interestingly, the magnetic structures of CeRhIn₅ and Ce₂RhIn₈ are strikingly different although the overall behavior of both systems under various conditions (applied magnetic field along both principal crystallographic axes, hydrostatic pressure) is very similar. The connection between the crystal-field interaction and the magnetic ground state in these systems motivated us to investigate the CEF energy scale of Ce₂RhIn₈ by means of an inelastic neutron measurement.

4.1. Introduction

The Ce₂RhIn₈ topic is closely related to the previous chapter which summarizes the physical properties of the prototypical Ce_nTIn_{3n+2} compounds ($T = \text{Co, Rh, Ir}$; $n = 1, 2$)¹¹³ as well as on the new Ce_nT_mIn_{3n+2m} systems ($T = \text{Pd, Pt}$; $n = 3, 5$; $m = 1, 2$)^{108,109}. For general information about this class of compounds, see the section 3.1; the following paragraphs focus on the crystal field of these materials.

To understand how the competing RKKY, Kondo and CEF energy scales determine the bulk properties of the Ce_nT_mIn_{3n+2m} compounds, the knowledge of CEF parameters is of high importance. It has been argued that the symmetry anisotropy of certain wave functions may give rise to the f -conduction electron hybridization and in some cases may produce spin fluctuations which are more favorable to the formation of the SC ground state¹⁹⁶. As was already shown, these materials have been investigated thoroughly in the last years using various experimental tools; however, studies of the CEF scheme by the inelastic neutron scattering have been performed only on the CeTIn₅ ($T = \text{Co, Rh, Ir}$) compounds^{19,197}. Experimental results indicate that the CEF level splitting in all three materials is similar, exhibiting two magnetic ground-state excitations at about 5–7 and 24–30 meV, respectively^{19,197}. The CEF scheme can be thought of as being derived from the cubic parent compound CeIn₃ in which an excited quartet at $E = 0.12$ meV splits into two doublets by the lower symmetry of the tetragonal environment. In all studied systems, the CEF excitations are considerably broadened due to Kondo hybridization¹⁹⁷. It was found that the hybridization increases starting from Rh via Ir to Co transition metal and simultaneously the 5/2) contribution decreases so that CeRhIn₅ has the flattest 4 f orbital¹⁹. A correlation between the f -conduction electron hybridization and the temperature T_c indicates that significant hybridization is required to establish a SC state¹⁹⁷.

A comparative CEF-scheme study of the Ce_2TIn_8 compounds represents a missing part in the systematic investigation of the $\text{CeTIn}_5 \rightarrow \text{Ce}_2\text{TIn}_8 \rightarrow \text{CeIn}_3$ series. Several attempts to elucidate the CEF splitting in the Ce_2TIn_8 series have been performed, based upon bulk measurements (thermal expansion⁹⁷, magnetization¹⁴⁵) but there are discrepancies in the reported results. It was proposed that the crystal field of Ce_2RhIn_8 consists of $\Gamma_7^{(2)}$, $\Gamma_7^{(1)}$ and Γ_6 levels with energies $E = 0, 6.12 \text{ meV}$ (71 K) and 16.80 meV (195 K), respectively⁹⁷. The mixing parameter $\alpha = 0.85$ and molecular field interaction $\lambda = -30 \text{ emu/mol}$ were predicted. An analysis of susceptibility measurements¹⁴⁵ suggested somewhat lower values $E = 0, 1.21 \text{ meV}$ (14 K) and 12.84 meV (149 K), with the mixing parameter $\alpha = 0.997$ and molecular field interaction $\lambda = -49.5 \text{ emu/mol}$.

Recently, a correlation between ground-state properties and the CEF ground-state wave functions has been observed in the CeTIn_5 systems¹⁹⁵. It was suggested that the shape of the cerium wave function - expressed through the parameter α^2 - can distinguish SC from non-SC compounds. According to this scenario, once the purely SC region of the phase diagram has been reached, α^2 does not change any more and the a/c ratio seemingly tunes T_c . The a/c ratio by itself cannot be used to predict whether or not a compound becomes superconducting. In other words, the anisotropic hybridization plays an important role in description of the ground state of the cerium systems.

To clarify the role of CEF excitations and to resolve the uncertainties from the indirect experiments we performed an INS experiment on the Ce_2RhIn_8 compound. The magnetic contribution was obtained by subtracting the data of the non-magnetic La_2RhIn_8 compound. The experimental data were additionally compared to the calculations of the magnetization based on our CEF parameters including the Kondo effect in an *ad hoc* manner¹⁹⁷.

4.2. Synthesis and INS experimental setup

The high-quality single crystals of Ce_2RhIn_8 and La_2RhIn_8 were prepared using the In-flux growth method^{176,198}. Microprobe analysis confirmed the sample composition and homogeneity. Powder x-ray diffraction measurements were performed to verify the phase homogeneity: Lattice parameters of $a = 4.665(1) \text{ \AA}$, $c = 12.241(6) \text{ \AA}$ and $a = 4.696(2) \text{ \AA}$, $c = 12.343(9) \text{ \AA}$ were obtained for Ce_2RhIn_8 and La_2RhIn_8 , respectively. Both sets of lattice parameters are in good agreement with the previously published values^{176,198}. No impurity peaks except those of indium were detected in the diffraction pattern of Ce_2RhIn_8 and La_2RhIn_8 . Thus, the samples for the neutron experiment were carefully cleaned from residual indium by HCl acid before they were crushed into a fine powder for the measurement. The total mass of Ce_2RhIn_8 and La_2RhIn_8 was 6.40 g and 7.88 g, respectively. Because of an enormous absorption of In and Rh, a special sample setup was used; the powder was

homogeneously distributed into three stripe-shaped envelopes made from alumina foil to maintain the uniform sample thickness. The stripes were then wrapped around a cylindrical sample holder.

The neutron-scattering function $S(\mathbf{Q}, \omega)$ was measured on the direct geometry chopper spectrometer MERLIN at the neutron spallation source ISIS with incoming energies E_i of 15, 30 and 60 meV and counting times ranging from 3 to 24 h. During the performed experiment, a closed-cycle refrigerator with He-exchange gas was used providing temperatures ranging from 1.5 K to 300 K. The Ce_2RhIn_8 sample was measured at 7 and 75 K; to help identify the NM scattering in Ce_2RhIn_8 , the La_2RhIn_8 compound was measured at 7 K. All data were normalized in absolute units by measuring a standard vanadium sample with identical conditions. The Lorentzian line shape convoluted with instrument resolution function was used. The instrument resolution parameters were estimated from measurement of vanadium.

4.3. Results and discussion

Color-coded plots of the INS intensity $S(\mathbf{Q}, \omega)$ in absolute units of $\text{mb} \cdot \text{sr}^{-1} \text{meV}^{-1} \text{f.u.}^{-1}$ for $E_i = 60$ meV are shown in Fig. 41. The scattering of Ce_2RhIn_8 and La_2RhIn_8 at 7 K is shown in Fig. 41(a) and (b), respectively. Extra intensity extending in two regions - from 5 to 10 meV and from 15 to 20 meV - can be identified at low $\mathbf{Q}$ ($2\text{-}3 \text{ \AA}^{-1}$) in the Ce_2RhIn_8 plot compared to La_2RhIn_8 . This is an evidence for a magnetic contribution to the total scattering as the scattering for La_2RhIn_8 is low at these energy transfers, apart from the high- $\mathbf{Q}$ region. The magnetic scattering can still be identified in the plot for Ce_2RhIn_8 at 75 K (Fig. 41(c)) with reduced intensity, showing similar character as at low temperatures.

The cuts of the INS intensity $S(\mathbf{Q}, \omega)$ in absolute units of $\text{mb} \cdot \text{sr}^{-1} \text{meV}^{-1} \text{f.u.}^{-1}$ for $E_i = 30$ and 60 meV are shown in Fig. 42(a) and (b), respectively. They were made by integrating across low ($0\text{-}3 \text{ \AA}^{-1}$) values of $\mathbf{Q}$ in the main figures and corresponding high ($5\text{-}10 \text{ \AA}^{-1}$) $\mathbf{Q}$'s shown in the insets. The low- $\mathbf{Q}$ scattering of Ce_2RhIn_8 is significantly greater than the scattering of La_2RhIn_8 in the energy transfer range from 5 to 25 meV as shown in Fig. 42(a). On the other hand, the behavior of La_2RhIn_8 exceeds the one of Ce_2RhIn_8 in the same energy range of the high- $\mathbf{Q}$ scattering. The character of the low- and high- $\mathbf{Q}$ scattering is preserved also for $E_i = 60$ meV for the energy transfer range up to almost 30 meV (see Fig. 42(b)). Such observation points to the magnetic contribution to the low- $\mathbf{Q}$ scattering which is not present at high $\mathbf{Q}$'s. The magnetic scattering plays an important role in the low- $\mathbf{Q}$ scattering because the magnetic intensity is proportional to the square of the magnetic form factor $F^2(\mathbf{Q})$. $F^2(\mathbf{Q})$ reaches maximum values for zero moment transfer and is negligible for $\sim Q > 5 \text{ \AA}^{-1}$. At high momentum transfers where the behavior of both materials is similar, the phonon scattering dominates, increasing as a square.

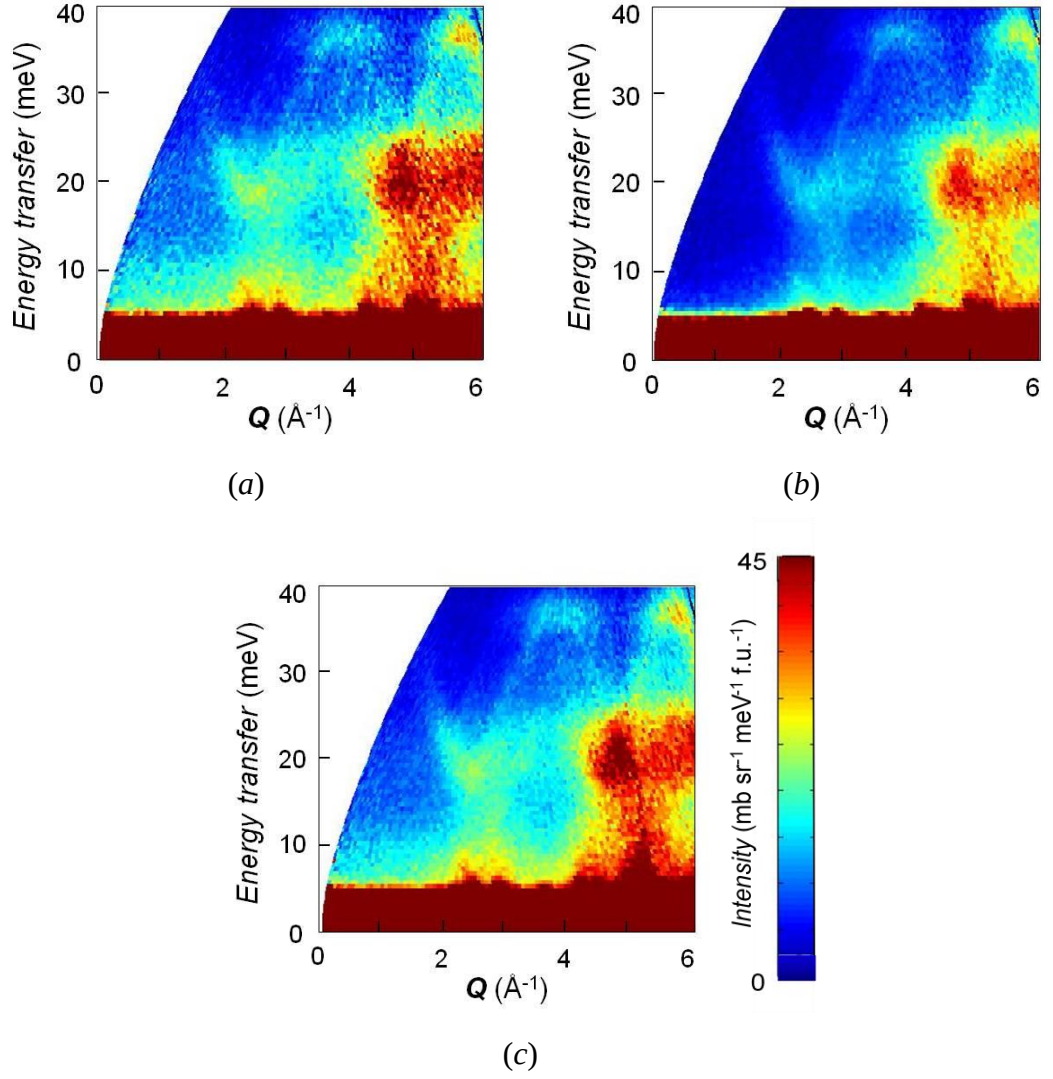
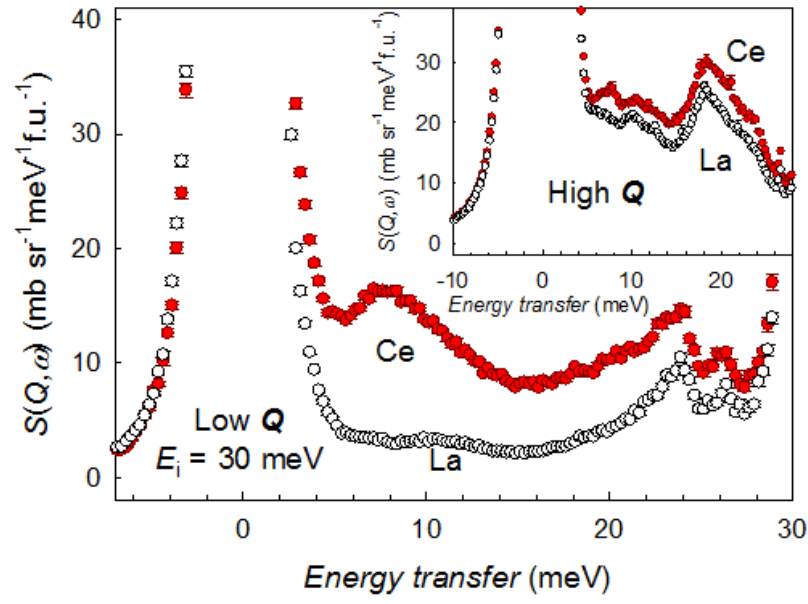
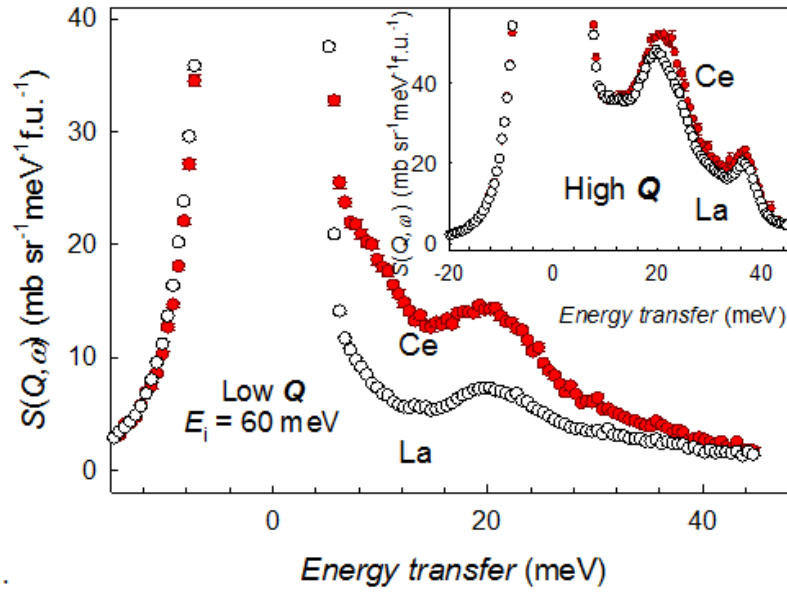


Fig. 41. Color-coded plots of the INS intensity with $E_i = 60$ meV for (a) Ce₂RhIn₈ at 7 K, (b) La₂RhIn₈ at 7 K and (c) Ce₂RhIn₈ at 75 K.

The magnetic contribution $S_{\text{mag}}(\mathbf{Q}, \omega)$ to the total scattering was obtained at low Q 's ($0-3^\circ \text{\AA}^{-1}$) by subtracting the phonon scattering. We used data of the phonon reference compound La₂RhIn₈, which was then directly subtracted from the data of Ce₂RhIn₈ to estimate the magnetic scattering. The magnetic scattering at 7 K and 75 K was fitted simultaneously to get a unique value of the CEF parameters. All values obtained from the fitting procedure including the crystal-field parameters B_2^0 , B_4^0 and B_4^4 are summarized in Tab. 8.



(a)



(b)

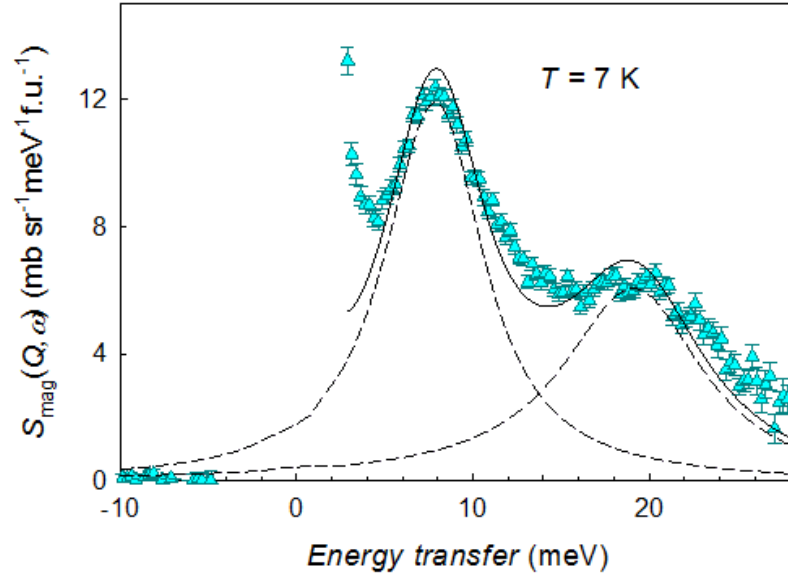
Fig. 42. Low Q cuts of $S(Q, \omega)$ for Ce_2RhIn_8 and La_2RhIn_8 at 7 K with incident energies of (a) 30 meV and (b) 60 meV, with the corresponding high Q cuts shown in the insets. The low Q cuts were integrated from $0\text{--}3^\circ\text{\AA}^{-1}$ while the high Q cuts were integrated from $5\text{--}10^\circ\text{\AA}^{-1}$.

The magnetic scattering of Ce_2RhIn_8 measured at 7 K is displayed in Fig. 43(a) for $E_i = 30$ meV. As the experimental temperature is well above the ordering temperature $T_N = 2.8$ K of Ce_2RhIn_8 , no magnetic response from the magnon density of states could be expected. The compound exhibits two magnetic ground-state

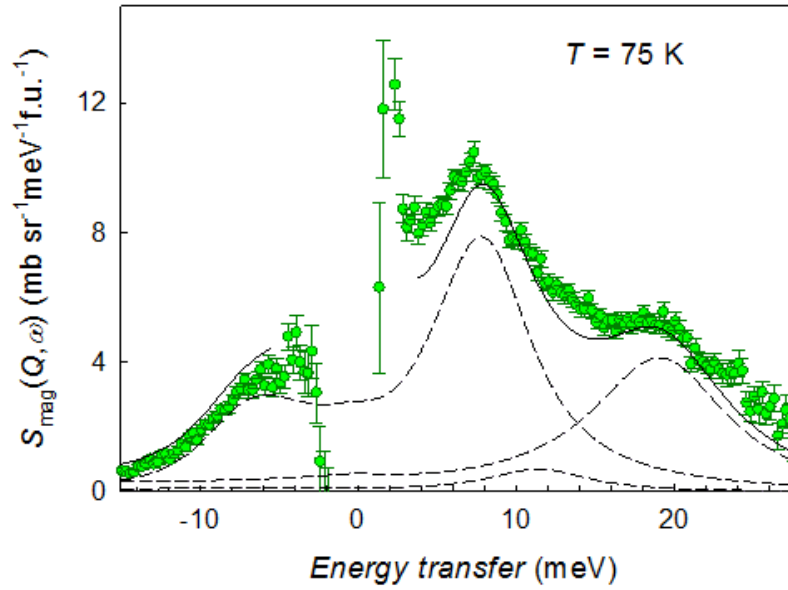
excitations E_1 and E_2 at (7.85 ± 0.27) and (19.12 ± 0.16) meV with half-widths at half maximum of (3.1 ± 0.2) and (4.7 ± 0.4) meV, respectively. The same set of data was taken at $T = 75$ K (see Fig. 43(b)) where a transition from the first $|1\rangle$ to the second $|2\rangle$ excited state at $E_2 - E_1$ could be expected. Indeed, another, significantly weaker peak has been resolved at (11.4 ± 0.4) meV with a half-width at half maximum of (3.8 ± 0.5) meV. The set of CEF parameters gives the mixing parameters $\alpha = 0.997$ and $\beta = 0.073$ for the ground state $|0\rangle = \Gamma_7^2$ (from the equation (9) describing the Kramers doublets). The mixing parameter α from the INS experiment resembles the value obtained from magnetization measurements¹⁴⁵ which predicted almost pure $|\pm 5/2\rangle$ ground state.

Tab. 8. Crystal-field parameters B_l^m , crystal-field energies $E_{1,2}$, inelastic half-widths Γ_{in} at 7 K and 75 K and the mixing parameter α for Ce_2RhIn_8 compared to CeRhIn_5 and Ce_2CoIn_8 ^{19,143}. The units of all quantities (except for α , which is unitless and λ , which is in mol/emu) are in meV.

	Ce_2RhIn_8	CeRhIn_5 ¹⁹	Ce_2CoIn_8 ¹⁴³
B_2^0	-0.607 ± 0.034	-0.928	0.026
B_4^0	0.0446 ± 0.0020	0.052	0.013
B_4^4	0.131 ± 0.008	0.128	0.156
E_1	7.85 ± 0.27	7.0 ± 0.5	7.9
E_2	19.12 ± 0.16	24.7 ± 0.1	8.8
Γ_{in}^1	3.1 ± 0.2 @ 7 K	1.6 ± 0.5 @ 5 K	-
Γ_{in}^2	4.7 ± 0.4 @ 7 K	1.8 ± 0.5 @ 5 K	-
Γ_{in}^1 @ 75 K	3.6 ± 0.2	2.5 ± 0.5	-
Γ_{in}^2 @ 75 K	5.1 ± 0.5	-	-
α	0.997	0.62	0.812
λ_{ab}	-28	-	-90
λ_c	-16	-	-53



(a)



(b)

Fig. 43. Magnetic scattering of Ce_2RhIn_8 at 7 K (a) and 75 K (b) for $E_i = 30$ meV and low $\mathbf{Q}$'s. The solid line presents the final fit which is a sum of individual fits depicted by dashed lines.

The values of E_1 and E_2 from the microscopic experiment are somewhat higher than the results predicted for Ce_2RhIn_8 from the indirect methods^{97,145}, especially compared to the susceptibility measurements¹⁴⁵. On the other hand, the calculated¹⁴⁵ and experimentally obtained CEF parameters resemble each other quantitatively well. Thus, our measurement showed that the values of the CEF energies and parameters determined by the indirect methods are qualitatively correct although they might be slightly underestimated.

The quantity α^2 determines the out-of-plane anisotropy where the bigger α^2 corresponds to a more oblate $4f$ -orbital (for $\alpha^2 > 1/6$)¹⁹⁵. From our measurement it is evident that the $4f$ -orbital in Ce_2RhIn_8 has almost a donut shape. The predicted value for Ce_2CoIn_8 ¹⁴³ is lower reaching 0.812 which suggests a more prolate $4f$ orbital. This trend corresponds to the behavior in the 115 compounds, where the obtained mixing parameter $\alpha = 0.62$ for CeRhIn_5 is also higher than $\alpha = 0.36$ for CeCoIn_5 ¹⁹.

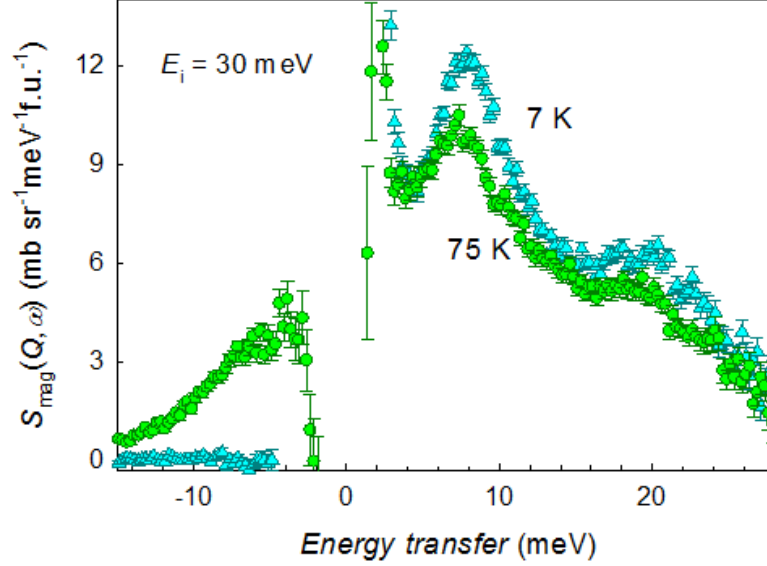


Fig. 44. The magnetic scattering of Ce_2RhIn_8 at 7 and 75 K for $E_i = 30$ meV, estimated by subtracting the phonon scattering from the La-compound.

$S_{\text{mag}}(\mathbf{Q}, \omega)$ for temperatures 7 and 75 K is displayed in Fig. 44 for $E_i = 30$ meV. Even for this relatively small temperature difference one can clearly see that the magnetic excitations at E_1 and E_2 shift to higher values of energy transfer with decreasing temperature and they become also more pronounced. The quasielastic response caused by larger population of states can be observed at 75 K on the neutron energy-gain side.

The magnetization measurements (see Fig. 45) were performed on MPMS 7T and they were compared to susceptibility curves (red lines) calculated by the home-made program based on Fortran. The program uses the CEF parameters obtained from the neutron scattering experiment and the phenomenological molecular field constant λ which is included to account for magnetic exchange effects. The value of $\lambda = -22$ mol/emu fitted simultaneously for the in-plane χ_{ab} and out-of-plane χ_c susceptibility corresponds well to $\lambda = -30$ mol/emu obtained from the thermal expansion measurements⁹⁷. For $T_N = 2.8$ K and $C_{J=5/2} = 0.807$ emu $\cdot$ K⁻¹mol⁻¹, the value $\lambda = -22$ mol/emu corresponds to „high-temperature“ Kondo temperature $T_K \sim 15$ K according to the expression $(T_K + T_N)/C_J$ ^{97,197}. This value is close to $T_K \sim 21$ K obtained from the analysis of thermal expansion experiment⁹⁷ and coincides also with the value $T_K \sim 12$ K estimated using relation $T_K \sim |\theta_p|/4$ from Hewson¹⁸⁰. Here, θ_p is the paramagnetic Curie temperature from the Curie-Weiss-law

fit. The calculated susceptibility deviates from the data below ~ 150 K in the [001] direction; the experimental data is much better described along the [100] axis, where the calculated curve departs at ~ 30 K. Such difference might be a sign of the presence of Kondo interactions or spin fluctuations¹⁴³. The exchange anisotropy can be taken into account by separate fitting of the [100] and [001] direction providing contributions $\lambda_c = -16$ mol/emu and $\lambda_{ab} = -28$ mol/emu. However, these numbers might be only fitting parameters mimicking phenomenologically the microscopic description of the susceptibility affected by the Kondo interactions. Nevertheless, the values of λ_c and λ_{ab} reveal significantly lower anisotropy compared to those calculated for Ce_2CoIn_8 ¹⁴³.

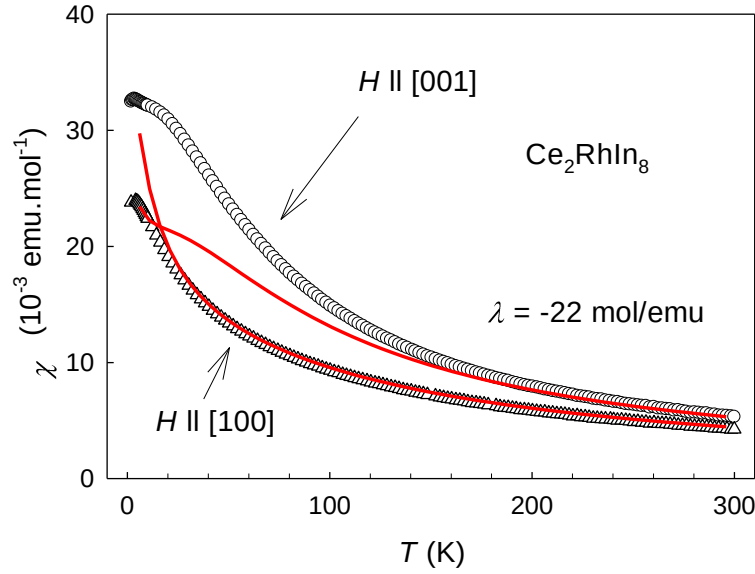


Fig. 45. Magnetic susceptibility in $H \parallel [100]$ (triangles) and $H \parallel [001]$ (circles) direction of Ce_2RhIn_8 , compared to the curves calculated using the CEF parameters from Tab. 8 with a molecular field of $\lambda = -22$ mol/emu (red lines).

Let us now examine in detail the CEF schemes across the CeRhIn_5 - Ce_2RhIn_8 - CeIn_3 series taking into account fact that the data on Ce_2RhIn_8 are significantly better pronounced compared to CeTIn_5 ^{19,197} due to better flux and resolution. The overall character of the $S_{\text{mag}}(\mathbf{Q}, \omega)$ scattering of Ce_2RhIn_8 resembles that of parent 115 compounds^{19,197}. The energy E_1 of the first excited state $|1\rangle$ corresponding to ~ 90 K is comparable in both 115 and 218 systems. In case of the isotropic cubic CeIn_3 compound, one excited level at 11.6 meV¹⁹⁹ is observed. This value is close to the first excited level at E_1 in the ternary analogs. The energy splitting between the ground state and the second energetic level $|2\rangle$ corresponding to ~ 230 K increases by about 20 % when going from Ce_2RhIn_8 to the more anisotropic CeRhIn_5 (~ 290 K). Thus, this direct measurement confirms previous results obtained from the thermal expansion⁹⁷. A similar trend was observed in the isostructural antiferromagnetic non-Kondo systems $\text{Nd}_n\text{T}_m\text{In}_{3n+2m}$ systems ($T = \text{Rh, Ir}$; $n = 1, 2$)²⁰⁰. The obtained crystal-field parameter B_2^0 is also smaller than that of CeRhIn_5 ¹⁹.

Interestingly, the ratios $B_2^0(115)/B_2^0(218) \sim 1.45$ and $E_2(115)/E_2(218) \sim 1.26$ roughly scale with the $T_N(115)/T_N(218)$ ratio ~ 1.36 . Such trend supports the idea that there is a tight relationship among crystal structure, the stacking composition, the CEF energy scale, spin fluctuations and the heavy-fermion superconductivity²⁰¹.

We have shown that the character of the CEF level scheme of Ce_2RhIn_8 is very similar to CeRhIn_5 with respect to the scaling. Both compounds resemble each other strongly also in other aspects like the evolution of the magnetic ground states under hydrostatic pressure (see the T - p phase diagrams in Fig. 6) and in external magnetic field¹¹⁴. This is in sharp contrast with respect to the magnetic structures of CeRhIn_5 and Ce_2RhIn_8 which are very different. While CeRhIn_5 reveals an incommensurate $(\frac{1}{2}, \frac{1}{2}, 0.297)$ structure with the magnetic moments oriented helicoidally in the basal plane in zero magnetic field¹³⁶, Ce_2RhIn_8 has a commensurate $(\frac{1}{2}, \frac{1}{2}, 0)$ structure with the moments pointing in 52° out of the basal plane¹⁴⁶. The only different parameter we obtained by the analysis of the INS data is the mixing parameter α which is much higher for Ce_2RhIn_8 . As mentioned above, the parameter α^2 is associated with out-of-plane anisotropy. According to the first-principle calculations by Shim *et al.*²⁰², anisotropic hybridization was predicted in the form where the out-of-plane hybridization of Ce ions with the In ions is stronger than the one with the in-plane ions. The crystal structure of CeRhIn_5 has two inequivalent In positions, one in-plane with respect to Ce positions and one out-of-plane. In the work of Willers *et al.*¹⁹⁵ it was suggested that the α^2 out-of-plane anisotropy is the most important despite nearly identical Ce–In bond lengths. Thus, the interaction of the transition metal and the out-of-plane indium ions plays an important role in minimization of the total electronic energy. This has a strong impact on the nature of the ground state within the $\text{Ce}_n\text{TIn}_{3n+2}$ family¹⁹⁵. The difference of the out-of-plane anisotropies represented by the quantity α^2 stands behind the very oblate $4f$ orbital in Ce_2RhIn_8 and a more cubic-like shaped $4f$ orbital in CeRhIn_5 . This difference suggests a possible impact on the nature of magnetic structures of Ce_2RhIn_8 and CeRhIn_5 .

4.4. Summary

We have determined the CEF level scheme of Ce_2RhIn_8 as the first 218 system from the $\text{Ce}_n\text{TIn}_{3n+2}$ group of compounds by means of inelastic neutron scattering. Generally, our results are coherent with previous works dedicated to the 115 compounds^{19,197} as we have observed two magnetic ground-state excitations E_1 and E_2 at 7.85 and 19.12 meV. Ce_2RhIn_8 which is closer to the cubic 3D arrangement of CeIn_3 than to the more anisotropic CeRhIn_5 reveals lower energy E_2 of the second excited state $|2\rangle$ than CeRhIn_5 . The obtained CEF parameters B_2^0 , the energy levels E_2 and the phase transition temperatures T_N scale for the $\text{Ce}_n\text{RhIn}_{3n+2}$ ($n = 1, 2$) compounds which corresponds to the assumption that the ground state of these materials is controlled by the structural dimensionality. Comparison to the CEF

energy scheme of Ce_2RhIn_8 calculated using thermal expansion⁹⁷ and magnetic susceptibility measurements¹⁴⁵ points to qualitatively good agreement with the inelastic experiment. The resulting CEF parameters provide reasonable fits to the magnetic susceptibility and the Kondo temperature $T_K \sim 15$ K corresponds well to the values estimated using various approaches.

The ground-state wave function in Ce_2RhIn_8 is almost a pure $\pm 5/2$ state with $\alpha = 0.997$. A more significant $\mp 3/2$ admixture into the $\pm 5/2$ ground state was found in their 115 analogs^{19,197}. Therefore, the out-of-plane anisotropy defined by the parameter α^2 is different from the one in CeRhIn_5 as the $4f$ -orbital of Ce_2RhIn_8 has almost a donut-like shape. This simplified picture might be linked to the different character of magnetic structures in Ce_2RhIn_8 and CeRhIn_5 taking into account the anisotropic hybridization.

5. U_nRhIn_{3n+2} ($n = 1, 2$)

The investigation of the heavy fermion $Ce_nT_mIn_{3n+2m}$ compounds, which is the crucial topic of this manuscript, stands behind the study of uranium materials presented in the following chapter. Our aim was to determine the consequences of replacing the cerium atom which establishes the localized $4f$ magnetism by uranium with delocalized $5f$ -electrons and enhanced hybridization by preserving the identical layered structure. We focus mainly on the novel compounds U_2RhIn_8 and $URhIn_5$ which are prepared using the indium self-flux method. The compounds were subjected to magnetization, thermodynamic and transport experiments (at ambient and hydrostatic pressure) with stress on measurements along the principal crystallographic axes in order to study the magnetic anisotropy. In contrast to their Kondo analogs with cerium, both uranium compounds order magnetically at temperatures which are two orders of magnitude higher and the magnetic order is very robust against the external magnetic field. Different evolution of the ground-state properties in U_nRhIn_{3n+2} and Ce_nRhIn_{3n+2} ($n = 1, 2$) according to the n parameter will be discussed.

5.1. Introduction

Magnetism of uranium compounds is discussed thoroughly in the section 1.7; in the following paragraphs, the properties of uranium compounds related to U_2RhIn_8 are reviewed. Considering the UX_3 ($X = p$ -metal) materials, the size of the p -atom plays a crucial role in determining the ground-state properties of the material. In the case of smaller X -ions (Si, Ge), the p -wave function decays slower at the U-site, resulting in strong $5f$ - p hybridization which leads to an absence of magnetic ordering (UGe_3 , USi_3)^{75,203,204} while larger X -ions (In, Pb, Tl) cause the hybridization to be weaker resulting in a magnetic ground state (UIn_3 , UPb_3 , UTl_3)^{74,203,205}. Large d_{U-U} exceeding 4.6 Å, a weak $5f$ -ligand hybridization and the AF ground state is characteristic for the cubic UIn_3 compound.

The U_nTX_{3n+2} ($n = 1, 2$; $T =$ transition metal; $X = In, Ga$)²⁰⁶⁻²¹⁰ compounds adopt the layered Ho_nCoGa_{3n+2} -type structure which consists of n UX_3 layers alternating with a TX_2 layer along the [001] direction in the tetragonal lattice. The compounds are isostructural to the thoroughly investigated Kondo Ce_nTIn_{3n+2} systems¹¹³ known for their outstanding physical properties described in details in the section 3.1.

For $n = 1$, there exist numerous uranium compounds with Ga element - $UNiGa_5$, $UPdGa_5$ and $UPtGa_5$ which are itinerant antiferromagnets with ordering temperatures $T_N = 86$ K, 30 K and 26 K, respectively. The propagation vector $\mathbf{k} = (1/2, 1/2, 1/2)$ for $UNiGa_5$ and $\mathbf{k} = (0, 0, 1/2)$ for $UPdGa_5$ and $UPtGa_5$ were found²¹¹⁻²¹³. On the other hand, the $UFeGa_5$, $UCoGa_5$, $URhGa_5$ and $UIrGa_5$ compounds are paramagnetic²¹⁴. So far, there have been only two compounds U_2FeGa_8 and U_2RhGa_8

with the 218 stoichiometry reported. They are both Pauli paramagnets with relatively large Sommerfeld coefficients $\gamma = 52 \text{ mJmol}^{-1}\text{K}^{-2}$ and $\gamma = 43 \text{ mJmol}^{-1}\text{K}^{-2}$, respectively²⁰⁶.

For $X = \text{In}$ the URhIn_5 compound²¹⁰ has been known among structurally related compounds so far. Because of its larger ionic radius, In occupies the X site in the 115 compounds with larger unit cell volume, while uranium with its small ionic radius forms stable structures only when $X = \text{Ga}$ ²¹⁴. The unit cell volume of URhIn_5 is 26 % larger than that of URhGa_5 and hence the $5f$ electrons possess a more localized character. In contrast to its nonmagnetic analog ThRhIn_5 , URhIn_5 orders antiferromagnetically below $T_N = 98 \text{ K}$ ²¹⁰. Magnetization measurements revealed huge magnetocrystalline anisotropy and an extremely large negative paramagnetic Curie temperature with effective magnetic moment corresponding to a localized uranium ion. A crossover from a high-temperature localized to a low-temperature itinerant character occurs around $T \sim 150 \text{ K}$ where the magnetic susceptibility and electrical resistivity reveal a marked anomaly. Increasing hydrostatic pressure supports the robustness of the antiferromagnetic phase.

Since the U_2RhIn_8 compound has not been reported yet, we focused on the crystal structure study followed by an investigation of magnetic, transport and thermodynamic properties with respect to applied magnetic field and hydrostatic pressure. We prepared also the single crystals of URhIn_5 and UIn_3 for a comparative study of the evolution of the ground-state properties on the structural dimensionality.

5.2. Synthesis and characterization

Single crystals of UIn_3 , URhIn_5 and U_2RhIn_8 have been prepared using the In self-flux method. High-quality elements U (purified by SSE), Rh (3N5) and In (5N) were used. The starting compositions of $\text{U}:\text{In} = 1:10$, $\text{U}:\text{Rh}:\text{In} = 1:1:25$ and $\text{U}:\text{Rh}:\text{In} = 2:1:25$ were placed into high-purity alumina crucibles in order to obtain UIn_3 , URhIn_5 and U_2RhIn_8 , respectively. The crucibles were further sealed under vacuum in quartz glass tubes. The ampoules were then heated up to 950°C , kept at this temperature for 10 h to let the mixture homogenize properly and consequently cooled down slowly ($\sim 3^\circ\text{C/h}$) to 600°C in 120 h. At this temperature the single crystals were decanted. The chosen temperature range and starting stoichiometries were based on the previous experience with the growth of cerium analogs $\text{Ce}_n\text{RhIn}_{3n+2}$. After decanting, plate-like single crystals of U_2RhIn_8 (URhIn_5) with typical dimensions of $1 \times 0.5 \times 0.3 \text{ mm}^3$ ($1 \times 1 \times 0.5 \text{ mm}^3$) were obtained. In case of UIn_3 , however, our attempts led to the growth of single crystals of typical mass $\sim 0.1 \text{ mg}$. The single crystal of UIn_3 ($2 \times 2 \times 2 \text{ mm}^3$) suitable for bulk measurements was obtained as a by-product of the URhIn_5 synthesis. Except the growth of the Rh-compounds, we performed several attempts to prepare isostructural single crystals with other transition metals such as Mn, Fe, Co, Ni, Ru, Pd, Ir and Pt; identical growth

procedure led to synthesis of binary T -In compounds only with the exception of palladium. In this case, we succeeded in preparation of U_2PdIn_8 single crystals; however their dimensions $< 50 \mu\text{m}$ prevented us from performing any further bulk experiments. Nevertheless, this material might be a suitable candidate for future experiments with microfabrication using the focused ion beam (FIB) technology in SEM. We have also tried to prepare uranium ternary compounds with Sn and Pb on the X -site; these attempts resulted in growth of UX_3 binary phases.

Tab. 9. Atomic coordinates and equivalent isotropic displacement parameters ($\text{\AA}^2$) for the compounds URhIn_5 and U_2RhIn_8 .

Atom	Wyckoff position	x	y	z	U_{eq}
URhIn_5 ($a = 4.6210(5) \text{\AA}$, $c = 7.4231(7) \text{\AA}$)					
U1	$2a$	0	0	0	0.0123(4)
Rh1	$1b$	1	0	0.5	0.0156(7)
In1	$4i$	0.5	0	0.30179(11)	0.0159(5)
In2	$1c$	0.5	0.5	0	0.0173(5)
U_2RhIn_8 ($a = 4.6056(6) \text{\AA}$, $c = 11.9911(15) \text{\AA}$)					
U1	$2g$	0.5	0.5	0.30883(7)	0.0093(3)
Rh1	$1a$	0.5	-0.5	0	0.0104(3)
In1	$2e$	0.5	0	0.5	0.0131(3)
In2	$4i$	0.5	0	0.12263(11)	0.0138(4)
In3	$2h$	0	0	0.30916(14)	0.0149(4)

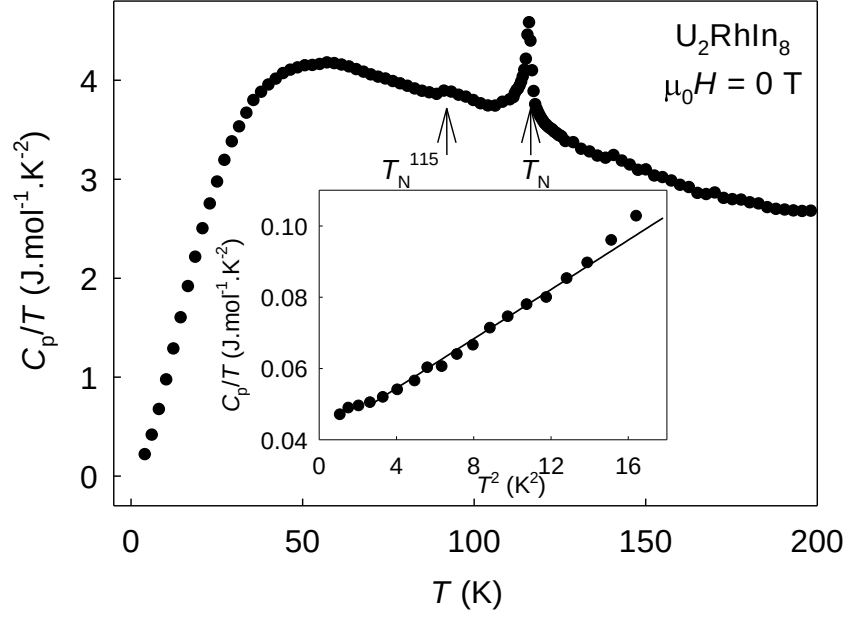
Homogeneity and chemical composition of the UIn_3 , URhIn_5 and U_2RhIn_8 single crystals were confirmed by the EDX point and mapping analysis. The lattice parameter of UIn_3 was determined by the RIGAKU diffractometer as $a = 4.600 \text{\AA}$ which is in agreement with the literature data⁷⁴. The crystal structure of URhIn_5 and U_2RhIn_8 was determined by the single crystal x-ray diffraction using the x-ray diffractometer Gemini and the obtained diffraction patterns were refined by software Jana2006. The diffraction confirmed the Ho_2CoGa_8 - (HoCoGa_5)-type structure for U_2RhIn_8 (URhIn_5). In Tab. 9 the lattice parameters, atomic coordinates and the equivalent isotropic displacement parameters U_{eq} are summarized.

5.3. Physical properties and theoretical calculations

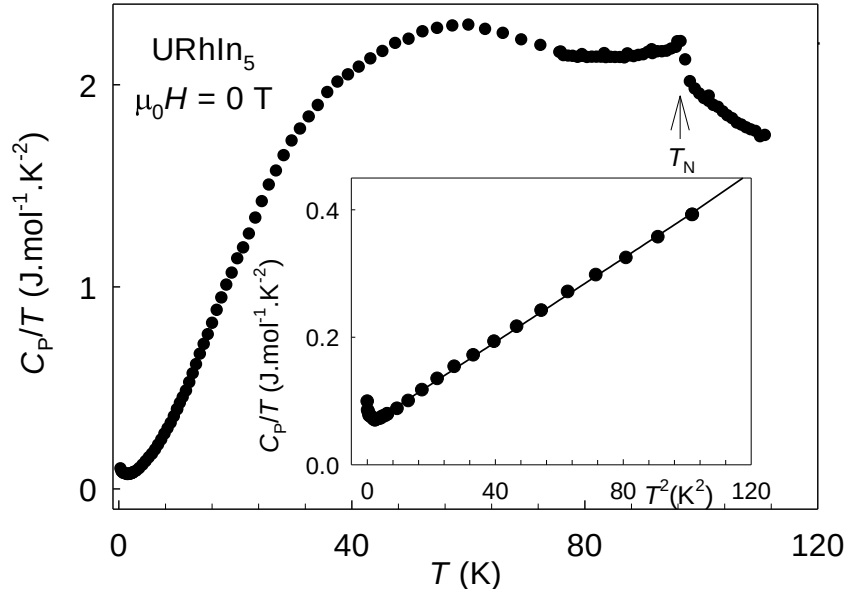
The results of bulk measurements presented in the following paragraphs are performed on one single crystal of U_2RhIn_8 and URhIn_5 , respectively.

The temperature dependence of the specific heat $C(T)/T$ of U_2RhIn_8 and URhIn_5 is presented in Fig. 46. A clear lambda-type anomaly at $T_N = 117 \text{ K}$ and $T_N = 98 \text{ K}$, respectively, indicates a second-order phase transition into an antiferromagnetic state (the AF nature of the ground state is confirmed by measurements in magnetic field

shown later). The specific heat of URhIn₅ is in line with the previously published data²¹⁰. Another small anomaly (marked as T_N^{115} in the figure) arising likely from a tiny amount of URhIn₅ is detectable at $T \sim 100$ K in the specific heat of U₂RhIn₈.



(a)



(b)

Fig. 46. The temperature dependence of specific heat in the zero magnetic field for U₂RhIn₈ (a) and URhIn₅ (b), respectively. The insets show the low-temperature part of specific heat with the linear $C/T = \gamma + \beta T^2$ fit.

At temperatures < 0.5 K, an upturn in the C/T data in URhIn₅ is observed, which might be a sign of a nuclear Zeeman contribution C_n arising from the In nuclei. The electronic contribution to the specific heat determined from the $C/T = \gamma + \beta T^2$ fit

provides the Sommerfeld coefficient $\gamma = 47 \text{ mJmol}^{-1}\text{U K}^{-2}$ for U_2RhIn_8 and $\gamma = 61 \text{ mJmol}^{-1}\text{U K}^{-2}$ for URhIn_5 , respectively (in the fit interval $1 \text{ K} < T < 10 \text{ K}$). The β coefficient for U_2RhIn_8 yields $3.4 \text{ mJ mol}^{-1}\text{U K}^{-4}$ corresponding to the Debye temperature $\theta_D = 150 \text{ K}$ and similar values ($3.3 \text{ mJ mol}^{-1}\text{U K}^{-4}$, $\theta_D = 165 \text{ K}$) were obtained also for URhIn_5 in agreement with literature²¹⁰. As the ordering temperatures of all compounds from the UIn_3 - URhIn_5 - U_2RhIn_8 row are known by now, we can examine closer the relation between the crystal structure and T_N . By plotting the Néel temperatures vs. the c/a ratio as shown in Fig. 47 we realize that T_N increases linearly with the increasing c/a .

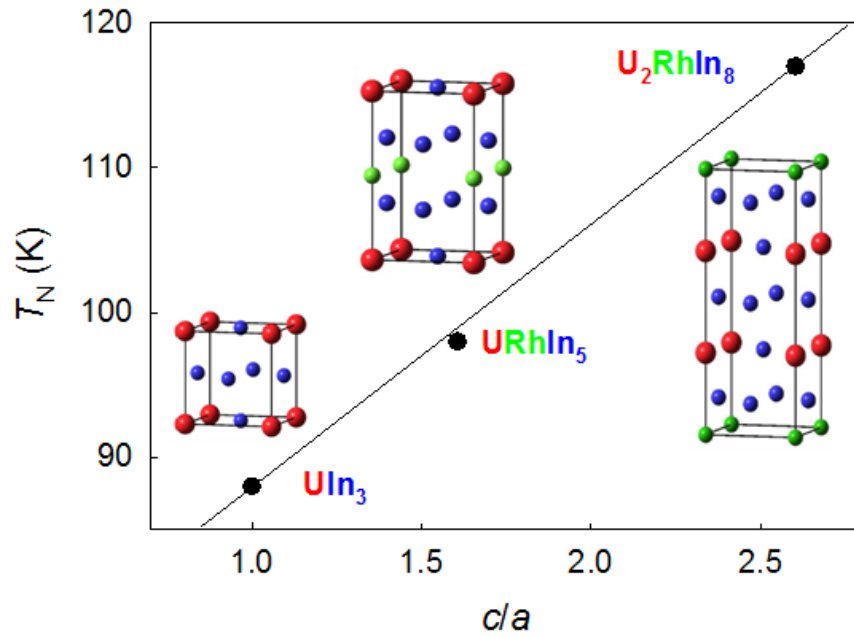


Fig. 47. The T_N vs. c/a diagram accompanied by the tetragonal structures of the UIn_3 , URhIn_5 and U_2RhIn_8 compounds.

The behavior of novel uranium compounds was further investigated in an external magnetic field. U_2RhIn_8 is almost unaffected (within experimental uncertainty) by the magnetic field of 9 T applied along the $[001]$ axis compared to the zero-field data (see Fig. 48(a)); an equivalent response to the magnetic field is observed in URhIn_5 shown in Fig. 48(b). The antiferromagnetic order seems to be robust also in the perpendicular direction of applied magnetic field (within the basal plane) for both materials (not shown).

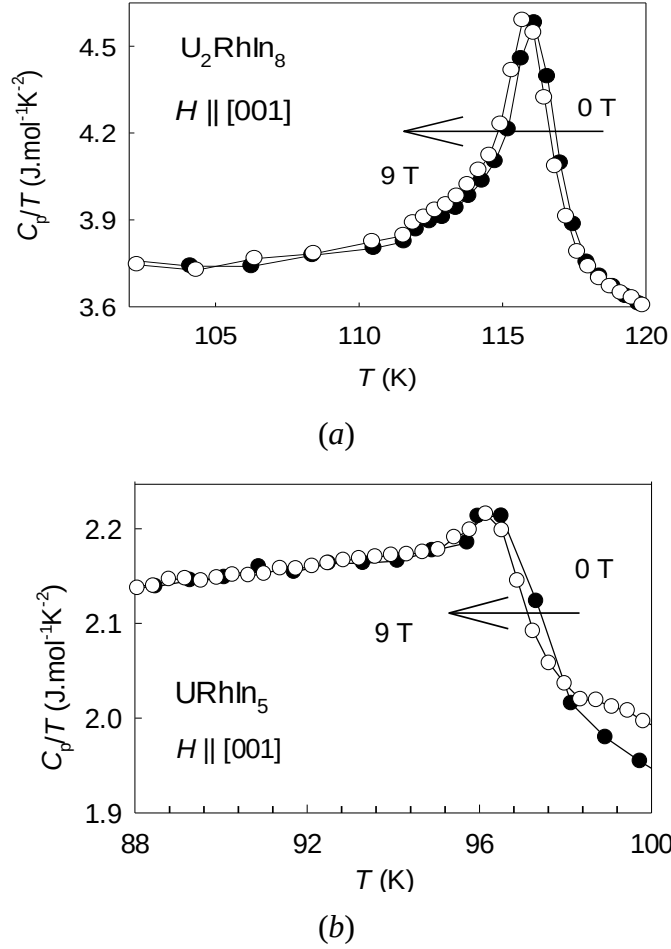
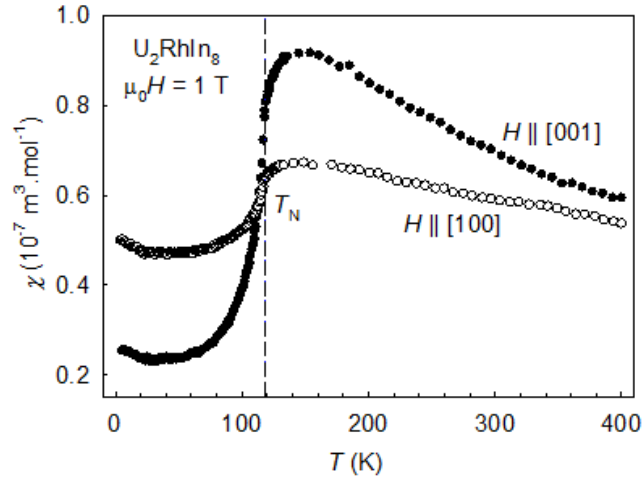
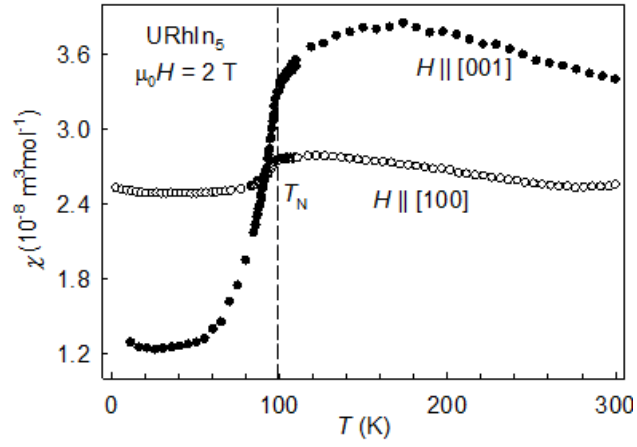


Fig. 48. The effect of magnetic field applied along the $[001]$ -axis is shown on the detail of magnetic transition in U_2RhIn_8 (a) and URhIn_5 (b).

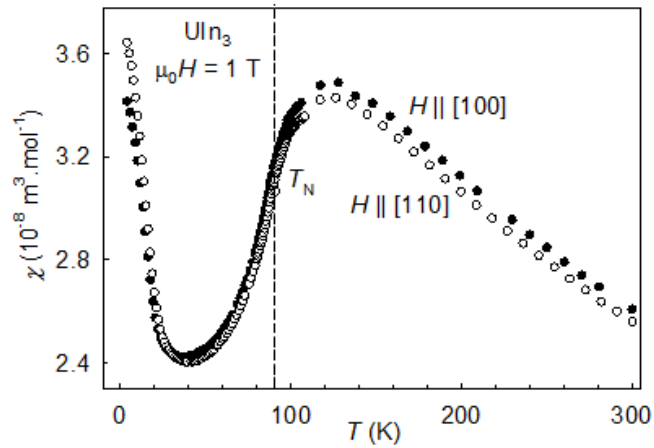
Fig. 49 summarizes the temperature dependence of the magnetic susceptibility in magnetic field oriented along the $[100]$ and $[001]$ directions in the case of URhIn_5 and U_2RhIn_8 and along the $[110]$ and $[100]$ directions in the case of UIn_3 . The susceptibility of the ternary compounds reveals significant magnetocrystalline anisotropy resembling the behavior of URhIn_5 ²¹⁰. The magnetic susceptibility increases in all compounds with decreasing temperature and this increase is much more pronounced for the $[001]$ direction in the ternary compounds. The PM susceptibility is not linearly temperature-dependent in both ternary compounds and thus it cannot be described by the C-W law. The formal application of the C-W law leads to extremely high values of the θ_p temperatures in order of 100 K, especially in the $[100]$ direction. This is the result of a very weak temperature dependence of the magnetic susceptibility which might be caused by a partially itinerant nature of both materials. In many uranium compounds (UPtGa_5 , UPt_3 , UPd_2Al_3 and URu_2Si_2 ²¹⁵) the linear behavior is recovered above 400 K suggesting a crossover of the $5f$ -electrons from a low-temperature itinerant to a high-temperature localized nature.



(a)



(b)



(c)

Fig. 49. The temperature dependence of magnetic susceptibility for both principal crystallographic directions in U_2RhIn_8 (a), URhIn_5 (b) and UIn_3 (c). The black dashed lines mark the position of T_N determined from the specific-heat measurements.

The maximum in the magnetic susceptibility is reached at $T_{\max} = 150$ K for U_2RhIn_8 , at $T_{\max} = 160$ K for URhIn_5 and at $T_{\max} = 130$ K for UIn_3 (consistently with literature⁷⁴). The observed maximum is probably due to antiferromagnetic correlations when approaching T_N . Interestingly, the temperatures $T_{\max}$ for both studied ternary compounds are the highest among uranium compounds up to our knowledge (UPd_2Al_3 : $T_{\max} = 30$ K; URu_2Si_2 : $T_{\max} = 60$ K²¹⁵). By further cooling, the materials enter the antiferromagnetic state; the values of the Néel temperatures are determined as the maxima of the $T \cdot d(\chi(T))/dT$ curve as proposed by Fisher²¹⁶. The susceptibility of the ternary compounds drops rapidly below T_N ; the decrease is steeper in the [001] direction than in the [100] direction, indicating the magnetic moments are aligned along the [001] axis below T_N which is the easy axis. The susceptibility curve saturates at ~ 20 K and starts to increase slightly again below ~ 10 K.

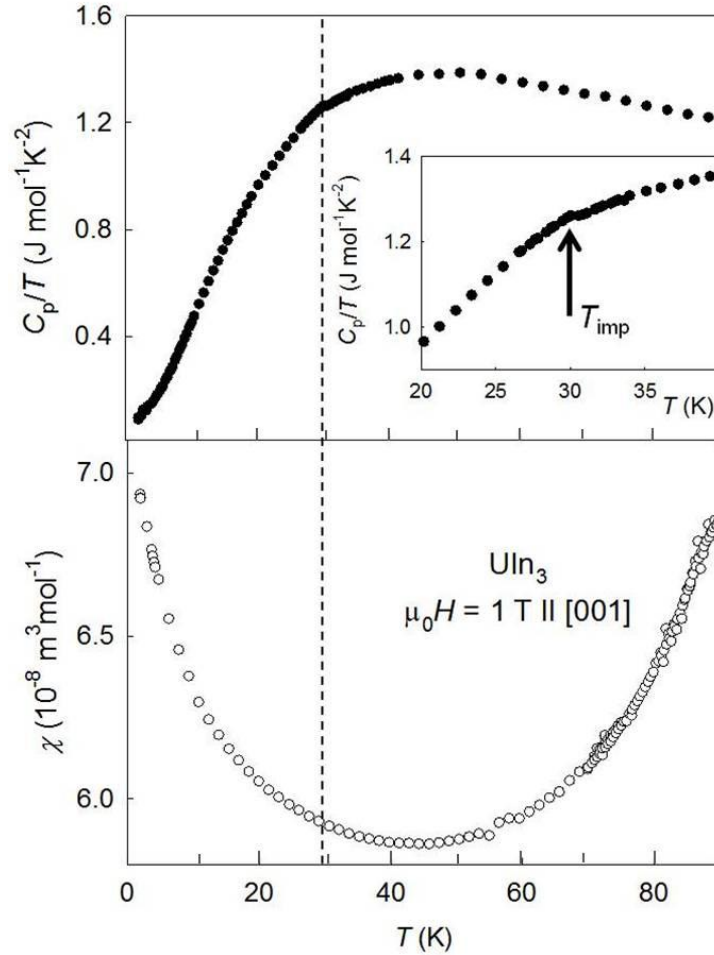
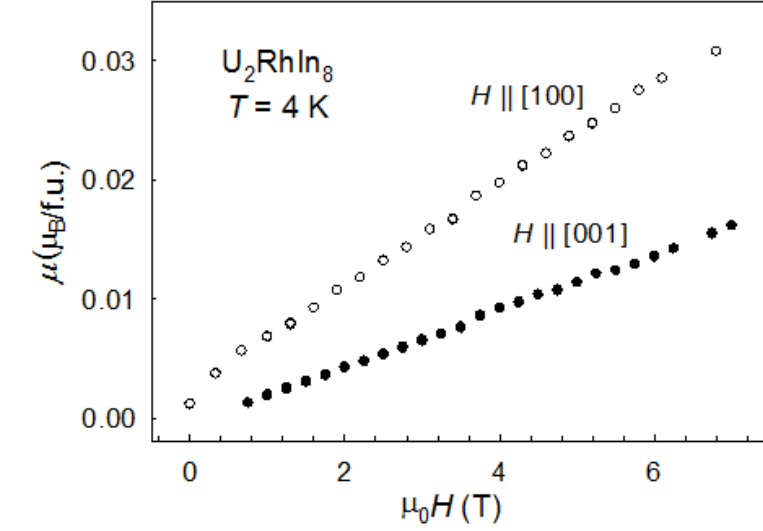


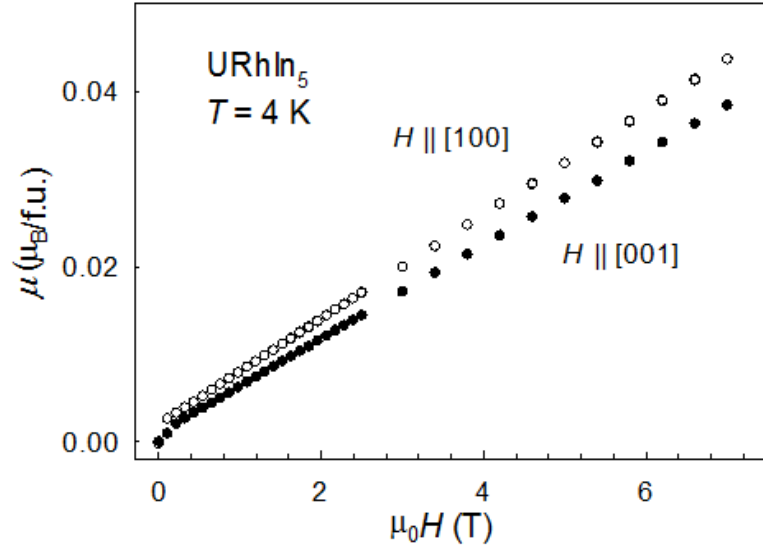
Fig. 50. The comparison of the specific heat and magnetic susceptibility data of UIn_3 . The dashed line and the arrow at T_{imp} mark the position of the possible transition temperature of the impurity phase within the UIn_3 sample.

In case of UIn_3 , the low-temperature upturn of the susceptibility is much more pronounced compared to the ternary compounds and also to previous results⁷⁴. It is

probably caused by a considerable amount of PM impurities. However, the magnitude of the increase of the susceptibility is different for the [100] and [001] direction; thus the origin might be also intrinsic. To shed the light on this increase, we measured the specific heat and compared it with the magnetic susceptibility as shown in Fig. 50. A tiny bump in C/T at ~ 30 K is observed (see the inset of Fig. 50). It coincides roughly with the onset of the steep increase in χ . Thus, it might be a sign of a transition temperature T_{imp} of an impurity binary phase which was not detected by the microprobe.



(a)



(b)

Fig. 51. The magnetization of U_2RhIn_8 (a) and URhIn_5 (b) as a function of magnetic field applied along the principal crystallographic directions at 4 K.

The magnetic-field dependence of magnetization of U_2RhIn_8 measured at $T = 4$ K for the magnetic field oriented along the [001] and [100] direction is shown in Fig. 51(a). Both magnetization curves reveal linear character up to 7 T; the [100] axis is the easy axis of magnetization, being almost twice higher than the magnetization in the other direction. The magnetization data for URhIn_5 depicted in Fig. 51(b) show relatively low anisotropy between both directions compared to U_2RhIn_8 . Such difference in anisotropy might be given by an unstable mounting of the sample while measuring in applied magnetic field.

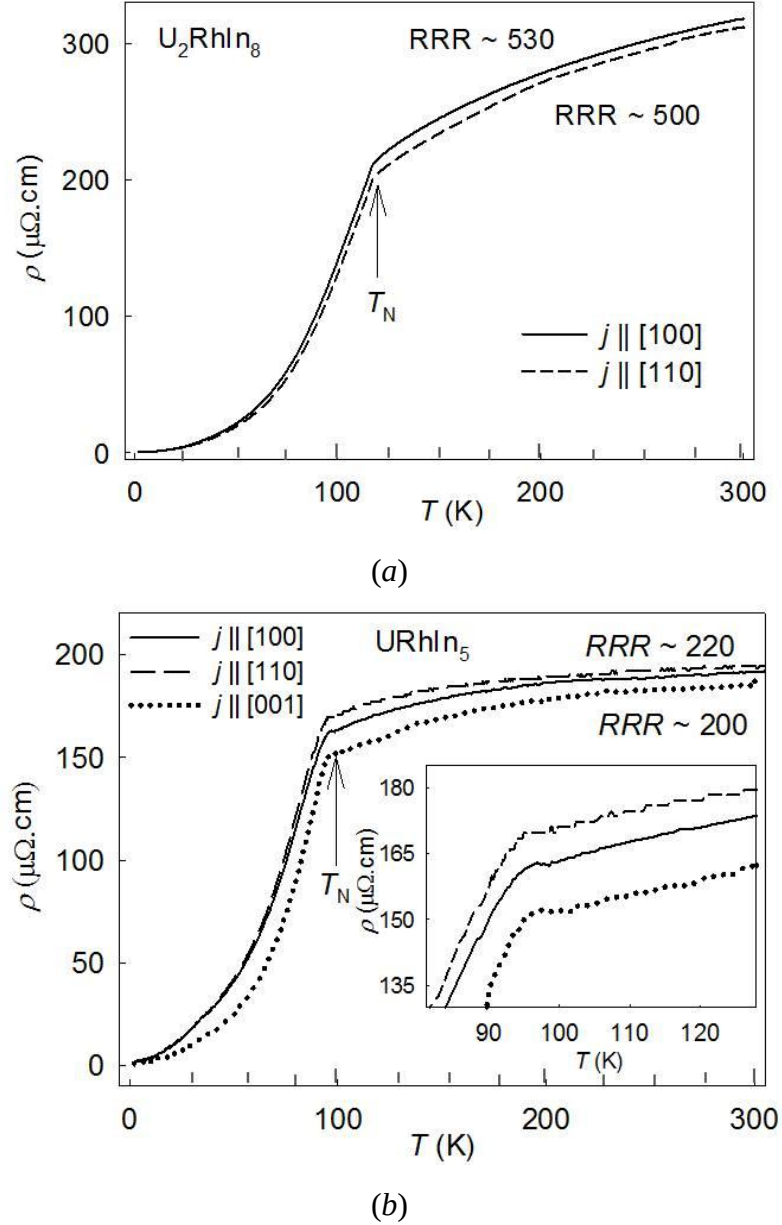


Fig. 52. The electrical resistivity of U_2RhIn_8 as a function of temperature for the electric current applied along the [100] and [110] directions (a). The temperature dependence of the electrical resistivity of URhIn_5 for current applied along the [100], [110] and [001] directions (b). The arrows mark the onset of the antiferromagnetic

transition obtained from specific heat. The inset in (b) shows the transition into the AF state in detail.

The easy axis in URhIn₅ is the [100] axis similarly to U₂RhIn₈. In low magnetic fields (< 0.4 T), the character of the magnetization curves in both compounds is not linear any more which is caused likely by the low signal received from the measured samples.

Using a relation $k_B T_{\max} = \mu_B H_c$ ²¹⁷, where $T_{\max} = 150$ K defines the position of the maximum of the magnetic susceptibility, and H_c is the critical magnetic field of a metamagnetic transition, the value of $H_c = 220$ T is obtained for U₂RhIn₈. This extremely large value of magnetic field explains the absence of a metamagnetic transition in our experimental data.

Fig. 52 shows the temperature dependence of the electrical resistivity of U₂RhIn₈ and URhIn₅ for electric current j applied along principal crystallographic directions. The URhIn₅ sample was measured additionally along the [001] direction which was not feasible in case of U₂RhIn₈ crystals due to small dimensions of the single crystals in this orientation. The room-temperature in-plane resistivity of U₂RhIn₈ in Fig. 52(a) yields 320 $\mu\Omega\text{cm}$. The residual resistivity ratio exceeds 500 confirming very high quality of the sample. The electrical resistivity decreases monotonically down to ~ 117 K. Here, a tiny kink is observed, a sign of a second-order phase transition and gap formation at the Fermi surface. With further cooling, the resistivity decreases rapidly with decreasing temperature. The low-temperature part of the electrical resistivity ($T < 30$ K) is described well by the equation (49). For both crystallographic directions, we obtain similar values of parameters $\rho_0 = 0.56 \mu\Omega\text{cm}$, $A = 0.006 \mu\Omega\text{cmK}^{-2}$, $D = 1.1 \mu\Omega\text{cm K}^{-1}$ and $\Delta = 118$ K.

The room-temperature resistivity of URhIn₅ with the electric current applied in-plane equals 180 $\mu\Omega\text{cm}$ and is only slightly lower for the out-of-plane electric current exceeding 170 $\mu\Omega\text{cm}$ (see Fig. 52(b)) in accordance with published data²¹⁰. The high quality of measured sample is proven by the high RRR ~ 200 . The data manifest a clear anomaly at $T_N = 98$ K. Entering the AF state, the resistivity drops down rapidly in all directions. Applying the fitting formula (48), the low-temperature resistivity data provide results $\rho_0 = 1 \mu\Omega\text{cm}$, $A = 0.013 \mu\Omega\text{cmK}^{-2}$, $D = 0.35 \mu\Omega\text{cm K}^{-1}$ and $\Delta = 82$ K for the [100] and [110] direction, respectively. Significantly higher energy of the gap $\Delta = 119$ K was obtained from the fit of the [001] resistivity curve reflecting the pronounced magnetocrystalline anisotropy.

As the quadratic term A from the temperature dependence of electrical resistivity and the linear term γ from the temperature dependence of the specific heat were already obtained, the Kadowaki-Woods¹⁸⁹ A/γ^2 ratio can be calculated. We get $2.7 \cdot 10^{-6} \mu\Omega\text{cm}(\text{molK/mJ})^2$ for U₂RhIn₈ and $3.6 \cdot 10^{-6} \mu\Omega\text{cm}(\text{molK/mJ})^2$ for URhIn₅. According to the work of Tsujii *et al.*, who generalized the Kadowaki-Woods ratio using a normalizing term shown in equation (3)¹⁹⁰, we obtain $N \sim 3-4$. These values

are lower than those in the common heavy fermion systems corresponding to the expected value of $N = 2$. However, the definition of N in uranium compounds is ambiguous, as the $5f$ electrons have larger spatial extent compared to the localized $4f$ electrons¹⁹⁰.

To investigate the effect of hydrostatic pressure on the transition temperature T_N , we measured the temperature dependence of electrical resistivity of U_2RhIn_8 up to ~ 3.2 GPa. According to the pressure-temperature phase diagram (see Fig. 53), the value of T_N increases from 117 K (ambient pressure) to 128 K (3.2 GPa) with the rate of 5.4 ± 0.9 K·GPa⁻¹ corresponding well to the pressure evolution of T_N in $URhIn_5$ ²¹⁰. The inset in Fig. 53 shows the temperature dependence of the electrical resistivity in the vicinity of the AF transition for electric current applied along the $[100]$ direction at ambient pressure and at 3.2 GPa. The positive pressure dependence of T_N can be explained by the spin-fluctuation theory of an itinerant $5f$ electron system together with the Hubbard model^{218,219}. According to this scenario, the hybridization between the $5f$ - and conduction electrons increases when the hydrostatic pressure is applied. As a result, the exchange coupling J among U ions becomes more robust. However, this effect competes with the decrease of the $5f$ magnetic moment at the uranium sites which tends to suppress the T_N .

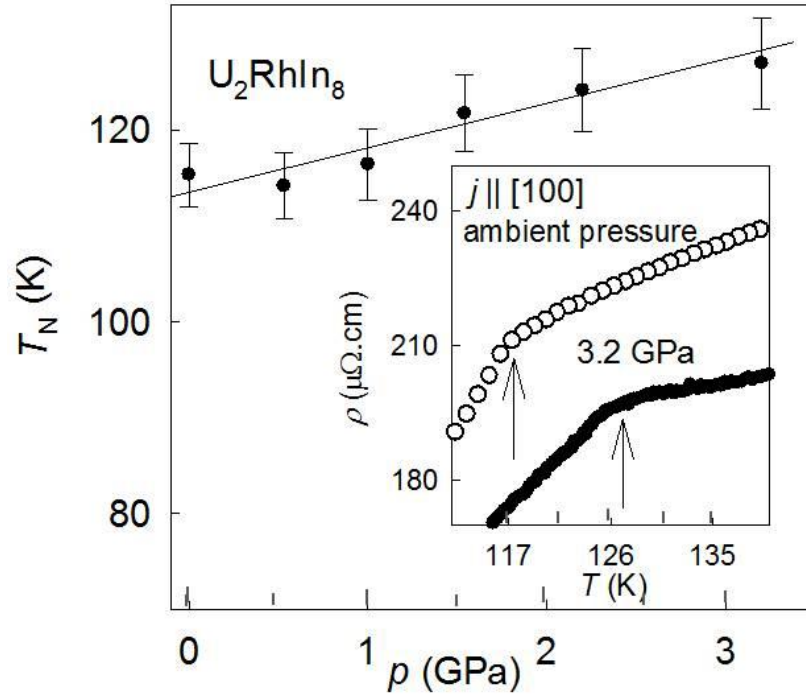


Fig. 53. T - p phase diagram of U_2RhIn_8 . The detail of the resistivity curve near T_N for electric current applied along the $[100]$ direction at ambient pressure and at 3.2 GPa is shown in the inset. Arrows mark the AF transition.

Theoretical methods based on DFT were applied to shed the light on the formation of magnetic moments in U_2RhIn_8 . The electronic structure and magnetic moments were calculated using the latest version of APW+lo WIEN2k code²²⁰. The

5*f*-electrons form the Bloch states with non-integer occupation number. The SO coupling was included due to presence of strong magnetocrystalline anisotropy using the second-order variational step²²¹. The calculations were ferromagnetic for the sake of simplicity, since there is no information about the character of the AF ground state. The spin-polarized local spin-density approximation (LSDA) splits the spin-up and spin-down bands with spin magnetic moment at uranium site $2.17 \mu_B$. The calculated spin magnetic moment at uranium site decreases to $M_S = 1.744 \mu_B$ and the orbital magnetic moment $M_L = -2.418 \mu_B$ is antiparallel. As the magnetic moments located at rhodium and indium sites are both smaller than $0.1 \mu_B$, the obtained total uranium magnetic moment is $|M_{\text{tot}}| = 0.674 \mu_B$. However, from comparison with URhIn₅, larger total uranium moment $|M_{\text{tot}}| \sim 1.6 \mu_B$ is expected. Thus the correlated movement of 5*f* electrons cannot be neglected and the usage of LSDA+U method²²⁰ is necessary. Spin magnetic moment $M_S = 1.738 \mu_B$ and orbital magnetic moment $M_L = -3.3 \mu_B$ were found providing the total magnetic moment $|M_{\text{tot}}| = 1.592 \mu_B$ for medium effective $U = 1.3$ eV. Although such calculation loses the first-principle character on this level, the heuristically derived values of effective U allows us to obtain valuable results. Microscopic experiment is needed to confirm this value; nevertheless, similar approach applied on URhIn₅ provides the total magnetic moment $|M_{\text{tot}}| = 1.618 \mu_B$ for the effective $U = 1.5$ eV which is very close to the experimental value $\mu = 1.65 \pm 0.11 \mu_B/\text{U}$ obtained from the recent neutron diffraction experiment²²².

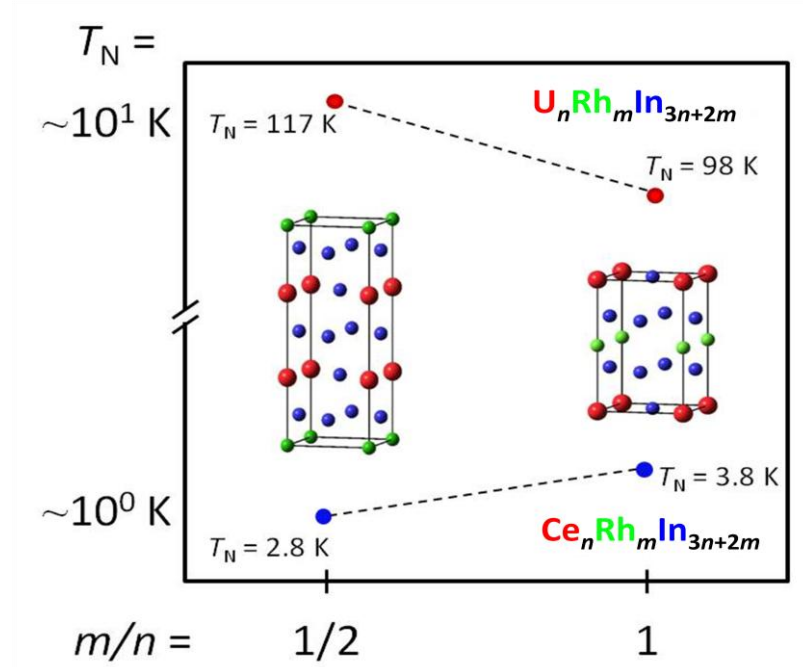


Fig. 54. The T_N vs. m/n diagram depicting the relationship of the crystal structure and magnetism of the U-based and Ce-based layered structures. The points are accompanied by the tetragonal structures of the U(Ce)RhIn₅ and U(Ce)₂RhIn₈ compounds. Dashed lines are a guide to the eye.

The ternary compounds U_nTX_{3n+2} with $T = \text{Rh}$ and $X = \text{In}$ represent the first system which offers the possibility to study the effect of stacking composition on the magnetism of uranium layered structures. Within the group of isostructural uranium compounds, they form the widest structural series $\text{UIn}_3 \rightarrow \text{U}_2\text{RhIn}_8 \rightarrow \text{URhIn}_5$. In the other cases, either only the cubic compound (USn_3 , UPb_3 ²²³) or the cubic compound (UGa_3 ²²⁴) together with its 115 (or 218) parent system ($T = \text{Fe, Co, Ni, Pd, Ir, Pt}$ ^{206,208,225-227}) are known. In contrast to the $U_nT\text{In}_{3n+2}$ compounds, the Ga-based compounds with $T = \text{Fe, Rh}$ and $n = 1, 2$ are paramagnetic. In order to study the effect of the layer stacking on magnetic ordering, a T_N vs. m/n diagram ($m = 1$) was constructed (see Fig. 54). The temperature T_N decreases with increasing m/n ratio. This behavior is in contrast to the cerium analogs $\text{Ce}_nT_m\text{In}_{3n+2m}$ where the T_N increases monotonically with increasing m/n ratio. Opposite trends in cerium and uranium compounds are connected with different energy scales determining the ground-state properties. While the microscopic interactions in the Ce-based compounds are determined mostly by the competition of the RKKY interaction and Kondo effect at very low temperatures, the ground state of the uranium compounds is affected significantly by the 5f-ligand hybridization with the ordering temperature at least an order of magnitude higher.

5.4. Summary

Single crystals of UIn_3 , URhIn_5 and of the novel U_2RhIn_8 phase were synthesized by the In self-flux method and studied by means of magnetization, thermodynamic and transport measurements both in ambient conditions and under hydrostatic pressure. The behavior of U_2RhIn_8 strongly resembles that of the related URhIn_5 compound. The U_2RhIn_8 compound adopts the Ho_2CoGa_8 -type structure with lattice parameters $a = 4.6056(6) \text{ \AA}$ and $c = 11.9911(15) \text{ \AA}$. In contrast to the paramagnetic sister compound U_2RhGa_8 , U_2RhIn_8 orders antiferromagnetically at $T_N = 117 \text{ K}$ with a slightly enhanced Sommerfeld coefficient $\gamma = 47 \text{ mJmol}^{-1}\text{U K}^{-2}$. The transition temperature is the highest among the parent uranium compounds (UIn_3 and URhIn_5 order at $T_N = 88 \text{ K}$ and 98 K , respectively^{209,210}). The high quality of the studied ternary compounds URhIn_5 and U_2RhIn_8 was confirmed by an electrical resistivity measurement which revealed RRR exceeding 200 and 500, respectively. The temperature dependence of the magnetic susceptibility of URhIn_5 and U_2RhIn_8 reveals strong magnetic anisotropy and suggests that both systems undergo an itinerant-localized crossover at high temperatures above 400 K, similar to other uranium-based compounds (UPd_2Al_3 , URu_2Si_2 ²¹⁵), including UPtGa_5 ²¹⁵ from the same group of compounds. Magnetic field leaves the value of Néel temperature for both URhIn_5 and U_2RhIn_8 unaffected up to 9 T. The application of hydrostatic pressure supports the robustness of the antiferromagnetic ordering in both ternary compounds with similar pressure coefficients²¹⁰. The first-principles calculations

provided reasonable estimate of the total magnetic moment on the uranium site in U_2RhIn_8 .

Successful synthesis of U_2RhIn_8 provides an opportunity to study the evolution of the ground-state properties on the crystal structure and structural dimensionality in this class of materials. The Néel temperature in the uranium compounds is more than one order of magnitude higher than in the cerium compounds¹¹⁴ and reveals a monotonic decrease with respect to the m/n ratio in contrast to $\text{Ce}_n\text{RhIn}_{3n+2}$, reflecting different driving microscopic mechanisms.

6. RE_2CoIn_8 ($RE = Pr, Nd, Dy$)

Generally, investigation of the “non-Kondo” materials enables to understand better the 4*f*-electron magnetism where the Kondo interactions do not play a crucial role and the ground state is purely magnetic in contrast to the related cerium compounds. The first-principles study of the RE_2CoIn_8 compounds¹⁰⁶ motivated the investigation of these not well studied lanthanide systems. We focused on the Pr_2CoIn_8 , Nd_2CoIn_8 and Dy_2CoIn_8 compounds which have been prepared only in the polycrystalline form so far. The crystal growth parameters were refined so that the single crystals could be successfully prepared. Their anisotropic properties were determined by means of magnetization measurements and compared to the theoretical predictions. Besides this primary task, the behavior in the applied magnetic field was studied by the specific heat in order to reveal the magnetic phases and subsequently to compose magnetic phase diagrams. While most of the known RE_nTIn_{3n+2} compounds reveal very similar phase diagrams, Dy_2CoIn_8 represents an exception by showing an additional magnetic phase in the zero magnetic field already.

6.1. Introduction

Since the discovery of the pressure-induced superconductivity in $CeIn_3$ emerging at the antiferromagnetic QCP¹⁷⁸, the attention of the condensed-matter community has been drawn to the structurally related Ce_nTIn_{3n+2} compounds. Since the quantum critical AF fluctuations have been suggested as mediating the unconventional superconductivity in these cerium-based materials²²⁸ (for more details about the Ce_nTIn_{3n+2} compounds see the section 3.1), the interest has turned soon also to the non-Kondo counterparts. Due to a great variation in selecting the transition and the RE metal, this group of materials represents one of the most complex systems to tune both magnetism and superconductivity. These compounds are suitable for investigation of solely 4*f*-electron magnetic properties where the RKKY and CEF interactions play a dominant role. The research activities discovered numerous compounds revealing a plethora of physical properties from antiferromagnetic ($RE = Nd-Tm$ except Eu and Pm) and “van Vleck” paramagnetic ($RE = Pr$) to “Pauli paramagnetic” ($RE = La, Y, Lu$) ground states. From the broad variety of magnetic phenomena, one should mention at least the large magnetoresistance observed in Tb_2CoIn_8 ²²⁹ and the often observed multiple metamagnetic transitions from an AF ground state to a “magnetic field-forced FM state” (as illustrated in the magnetic phase diagrams of RE_2RhIn_8 ²³⁰⁻²³² and $RERhIn_5$ ²³³ compounds). Although many compounds from the RE_nTIn_{3n+2} family have been studied on single crystals obtained by the solution growth method^{230,234-240}, the RE_2CoIn_8 compounds have been investigated only on polycrystals so far²²⁹. The recent theoretical study of the

electronic structure of selected compounds ($RE = Y, Pr, Nd, Dy$)¹⁰⁶ motivated us to perform experiments on single crystals.

We refined successfully the crystal-growth parameters and obtained single crystals of Pr_2CoIn_8 , Nd_2CoIn_8 and Dy_2CoIn_8 . The evolution of anisotropic magnetic properties was investigated by means of magnetization and specific heat measurements. To support the interpretation of the experimental results, we fitted the magnetic susceptibility along both principal crystallographic axes simultaneously using a simulated annealing procedure to find the parameters of a microscopic crystal-field Hamiltonian. The magnetic susceptibility from first-principles calculations of the electronic properties and the CEF parameters from literature¹⁰⁶ were derived. Finally, the results of the calculations and the experimental data were compared.

6.2. Synthesis and characterization

Single crystals of RE_2CoIn_8 ($RE = Pr, Nd, Dy$) were prepared by the solution growth method from indium flux. A series of crystal-growth experiments revealed the necessity to reduce the grow temperatures similarly to Ref.¹⁴⁰ and to increase slightly the amount of the RE metal above the value given by the stoichiometric formula to avoid the growth of $RECoIn_5$ analogs. The elements with starting composition $RE:Co:In = 2.2:1:50$ were put into high-purity alumina crucibles, sealed under high vacuum and heated up to 700 °C for a period of 3 h and kept at this temperature for 10 h for proper homogenization. The samples were then slowly cooled down (4 °C/h) to 300 °C where the remaining indium solution was centrifuged. In this way, plate-shaped single crystals were prepared as shown in Fig. 55. The largest dimension exceeded 0.5 – 1 mm with the [001] axis oriented perpendicular to the plate and the typical mass was ~ 1 mg. Attempts to prepare single crystals of parent compounds with other RE elements were not successful, mainly due to the intergrowth of the corresponding $RECo_2$ binary phases.

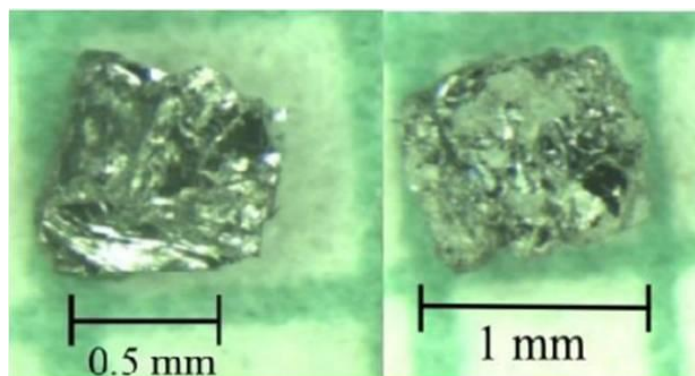


Fig. 55. Single crystals of RE_2CoIn_8 obtained from In flux.

The homogeneity and phase composition of the samples used for further bulk measurements was confirmed by the microprobe analysis. The crystal structure was investigated on powdered single crystals using a Bruker D8 Advance diffractometer. The tetragonal Ho_2CoGa_8 -type crystal structure was confirmed for all three compounds studied in this chapter. The determined unit-cell parameters listed in Tab. 10 are in a good agreement with the polycrystalline data²²⁹.

Tab. 10. The unit-cell parameters determined by x-ray powder diffraction on powdered single crystals of the RE_2CoIn_8 ($\text{RE} = \text{Pr}, \text{Nd}, \text{Dy}$) compounds.

	a (Å)	c (Å)
Pr_2CoIn_8	4.629 ± 0.3	12.214 ± 0.9
Nd_2CoIn_8	4.613 ± 0.7	12.181 ± 0.9
Dy_2CoIn_8	4.556 ± 0.3	12.015 ± 0.6

6.3. Physical properties and theoretical calculations

The magnetization and specific heat measurements presented in the following section are performed on an identical single crystal of Pr_2CoIn_8 , Nd_2CoIn_8 and Dy_2CoIn_8 , respectively.

Pr_2CoIn_8

To confirm the paramagnetic ground state of Pr_2CoIn_8 , the specific heat was measured as shown in the form of a C/T vs. T plot in Fig. 56. The $C/T(T)$ curve reveals no anomaly over the entire range of temperatures which would indicate some magnetic phase transition. The C/T vs. T^2 plot shown in the inset of Fig. 56 is linear at temperatures lower than 10 K and yields the electronic specific-heat coefficient $\gamma = 32 \text{ mJ mol}^{-1} \text{ K}^{-2}$.

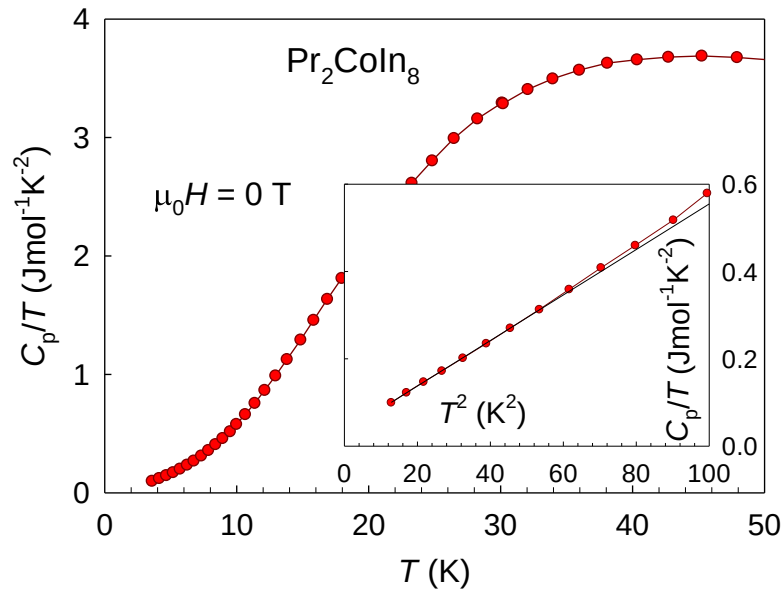


Fig. 56. Temperature dependence of the specific heat of Pr_2CoIn_8 . In the inset the linear fit $C/T = \gamma + \beta T^2$ is displayed.

Magnetic susceptibility data collected on the Pr_2CoIn_8 single crystal are presented in Fig. 57. The temperature dependence of the inverse susceptibility is linear at temperatures above ~ 150 K, exhibiting the C-W-law behavior of a system with localized magnetic moments in the PM region. The obtained PM Curie temperatures θ_p for the two principal crystallographic directions are considerably closer (-5 and 18 K for the [100] and [001] axis, respectively) than for PrCoIn_5 (-43 and 19 K) which indicates a weaker anisotropy in the Pr_2CoIn_8 system. Upon cooling below 150 K, the $1/\chi(T)$ dependence deviates gradually above the C-W-law line extrapolated from high temperatures. The susceptibility becomes almost temperature-independent below 30 K for both directions of the magnetic field, i.e. along the [100] and [001] axis. Similar to PrCoIn_5 , temperature-independent van Vleck paramagnetism is observed at low temperatures. It is caused by the lack of population of the CEF levels the above the ground-state singlet of the Pr^{3+} ion. In PrCoIn_5 , the [001]-axis susceptibility at the lowest temperature is five times larger than the [100]-axis susceptibility²³⁸. In Pr_2CoIn_8 we find the [001]-axis susceptibility higher by factor of ~ 3 reflecting the lower anisotropy of 218 compounds with respect to the crystal structure (see Fig. 57). The $M(H)$ dependence shown in Fig. 58 is linear as expected. The ratio between the [001]- and [100]-axis susceptibility is maintained in applied fields up to 7 T.

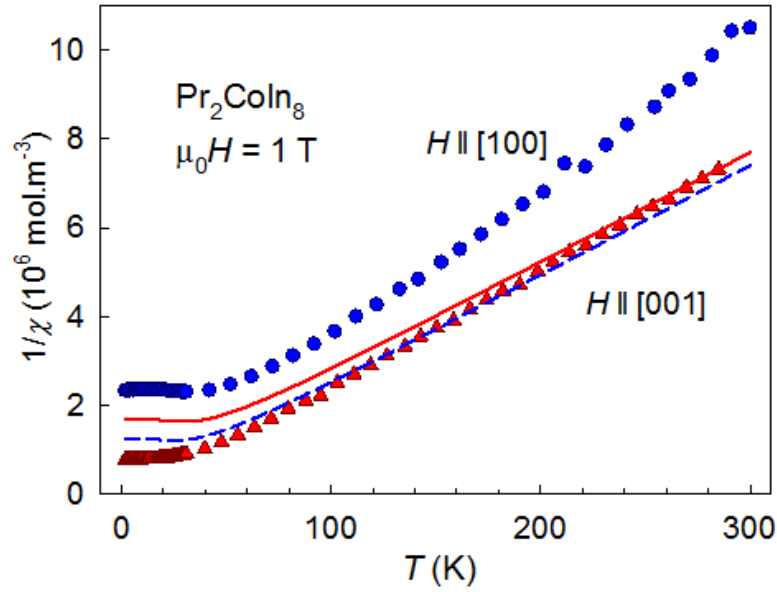


Fig. 57. Temperature dependence of the inverse susceptibility of Pr_2CoIn_8 measured in a magnetic field applied along the [100] axis (●) and the [001] axis (▲), and calculated¹⁰⁶ (solid and dashed lines with corresponding color).

The susceptibility calculated using the CEF parameters¹⁰⁶ reveals significantly smaller anisotropy than the measured one. Moreover, the [100] axis in the calculated $1/\chi(T)$ curves is the easy axis which contradicts the experimental results. Fitting of experimental data in order to obtain the CEF parameters provides unsatisfactory

results. Similarly, the CEF parameters based on a fit of polycrystalline data²²⁹ do not describe the single-crystal data well. However, this can be partially ascribed to the fact that the CEF Hamiltonian for an orthorhombic structure has been considered instead of a tetragonal one²²⁹. Comparing the experimental and calculated susceptibility, one should keep in mind that the magnetocrystalline anisotropy in the actual material might be driven also by anisotropic hybridization of Pr 4*f*-electron states with valence states of Co and In ligands. Such hybridization is not included in the model of CEF calculations and thus, it offers a possibility to explain the difference between the experimental and calculated data.

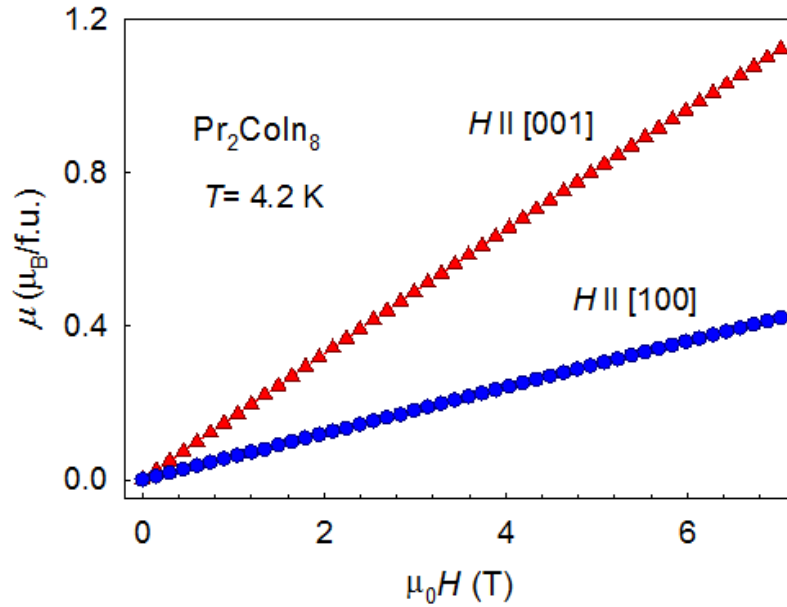


Fig. 58. Magnetic isotherms of Pr_2CoIn_8 measured at 4.2 K in the magnetic field applied along the [100] axis (●) and the [001] axis (▲).

Nd_2CoIn_8

The Nd_2CoIn_8 compound orders antiferromagnetically at ~ 10 K according to the previous study on a polycrystalline material²²⁹. In agreement with the literature, the temperature dependence of the specific heat (C_p/T vs. T plot in Fig. 59) measured in zero magnetic field exhibits a clear λ -type anomaly pointing to a transition from PM to AF phase at $T_N = 9.6$ K (determined by the equal-entropy construction). The transition is sensitive to magnetic field applied along the [001] axis. It is getting gradually diminished and shifted to lower temperatures with increasing magnetic field to vanish in fields above 9 T.

An additional anomaly appears at lower temperatures (at $T_1 \sim 3$ K in 6 T) developing with varying magnetic field applied along the [001] axis into a second-order transition. It is most probably reflecting an order-to-order magnetic phase transition. The transition at T_N is suppressed by the increasing magnetic field gradually. Both transitions are suppressed in magnetic fields above 8 T. The obtained value of the Sommerfeld coefficient $\gamma = 50 \text{ mJ mol}^{-1} \text{ K}^{-2}$ is slightly larger compared

to Pr_2CoIn_8 implying the increasing robustness of the electron–phonon interaction in Nd_2CoIn_8 .

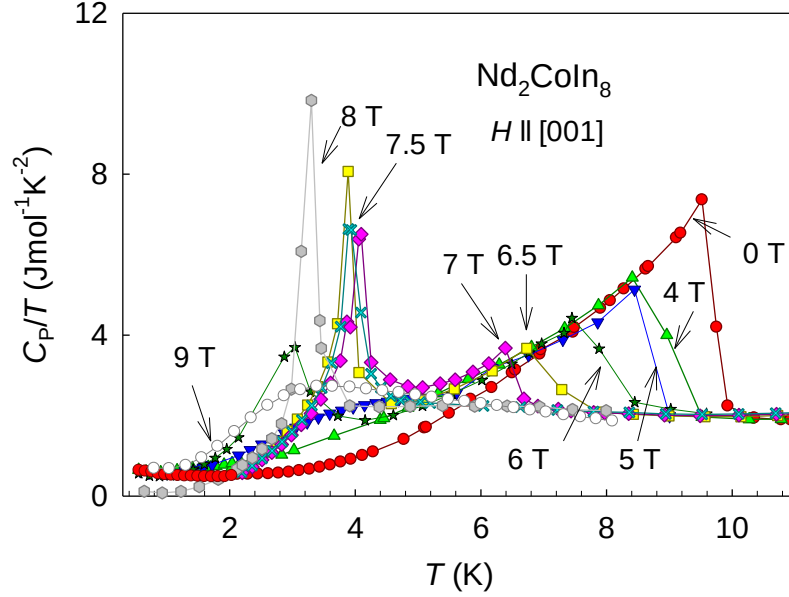


Fig. 59. Temperature dependence of the specific heat of Nd_2CoIn_8 without in zero field and in several magnetic fields (the values are shown in the figure) applied along the [001] axis.

The maximum in the temperature dependence of the magnetic susceptibility of Nd_2CoIn_8 (see Fig. 60(a)) indicates a transition from PM to AF phase. As has been shown by *Fisher*²¹⁶, the correct value of T_N can be derived from susceptibility data as the temperature at which the product $(T \cdot d(\chi(T))/dT)$ has a maximum. This maximum is located at $T = 9.6$ K in a good agreement with the specific heat. The temperature dependence of the inverse susceptibility along the [100] and [001] axis at temperatures above 150 K (Fig. 60(b)) is linear, satisfying the C-W law. The values of the PM Curie temperature θ_p of 8 K and 13 K for the field applied along the [001] and [100] axis, respectively, are rather close and indicate weak anisotropy of this compound in the PM region. Similar to the case of the praseodymium compounds, both the low-temperature and the PM susceptibility curves of Nd_2CoIn_8 reveal weaker anisotropy than NdCoIn_5 ²³⁸.

The susceptibility of Nd_2CoIn_8 calculated using the CEF parameters¹⁰⁶ reveals much weaker anisotropy than the measured data (see Fig. 60(b)). The calculated curves are parallel in the temperature range from 50 to 300 K. The [100]-axis susceptibility is higher than the [001]-axis susceptibility which again disagrees with the experimental results. The predicted susceptibilities exhibit also an intersection of the [100]- and [001]-axis data below 50 K (see the inset in Fig. 60(b)), so that the low-temperature magnetic anisotropy is described correctly by the calculations. Similar to Pr_2CoIn_8 , the anisotropy of the magnetic properties of Nd_2CoIn_8 may be

influenced considerably by the 4*f*-ligand hybridization, which could explain the difference between the measured and the calculated data.

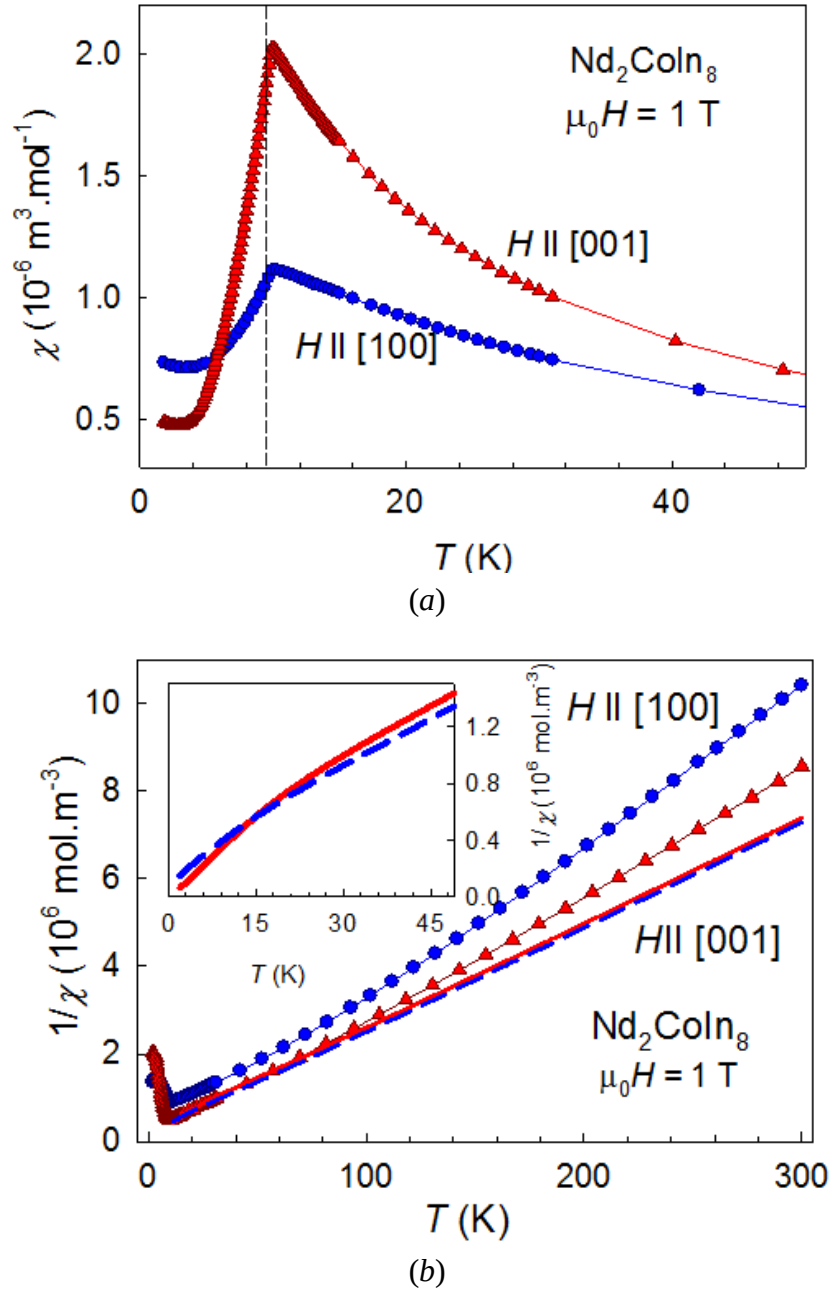


Fig. 60. (a) Temperature dependence of the magnetic susceptibility of Nd_2CoIn_8 measured in a magnetic field applied along the [100] axis (●) and the [001] axis (▲). The dashed line marks the transition temperature. (b) Temperature dependence of the inverse susceptibility of Nd_2CoIn_8 measured in magnetic field applied along the [100] axis (●) and the [001] axis (▲), and calculated¹⁰⁶ (the solid and dashed line are of corresponding color). The inset depicts a low-temperature detail of (b).

The magnetic isotherm measured at $T = 2.5 \text{ K}$ (see Fig. 61) reveals two metamagnetic transitions at 6.2 and 8.2 T for the magnetic field applied along the [001] axis. The magnetization steps are equal and show almost negligible hysteresis.

This type of magnetic isotherm is similar to the one observed in the RE_2TIn_8 or $REIn_5$ compounds where the [001] axis is the easy magnetic axis like in Nd_2CoIn_8 ^{230,241,242}. The magnetic moment observed in the maximum field of the experiment (14 T) equals $5.0 \mu_B/\text{f.u.}$ whereas the expected saturated moment of two free Nd^{3+} ions amounts $6.54 \mu_B$. Despite the fact that the measured magnetization curve of Nd_2CoIn_8 is not yet fully saturated, the discrepancy between the measured a theoretical value is considerable. The reduced value of the measured moment can be ascribed to the CEF influence on the Nd^{3+} ion moment in analogy to several RE_2RhIn_8 compounds²³⁰. In contrast to the behavior observed when the magnetic field is applied along the [001] axis, no metamagnetic transition is found for the field applied within the basal plane. The measured weak PM response is characteristic for the hard-magnetization direction at strong uniaxial magnetocrystalline anisotropy. However, a clear upturn from the linear evolution is observed above 8 T, similar to what has been observed for Nd_2RhIn_8 . A high-field magnetization measurement on Nd_2RhIn_8 reveals upward curvature of the [100]-axis magnetization with increasing field above 15 T²⁴¹. This reflects moment rotation to the hard-magnetization axis and can be generally discussed in terms of anisotropy constants.

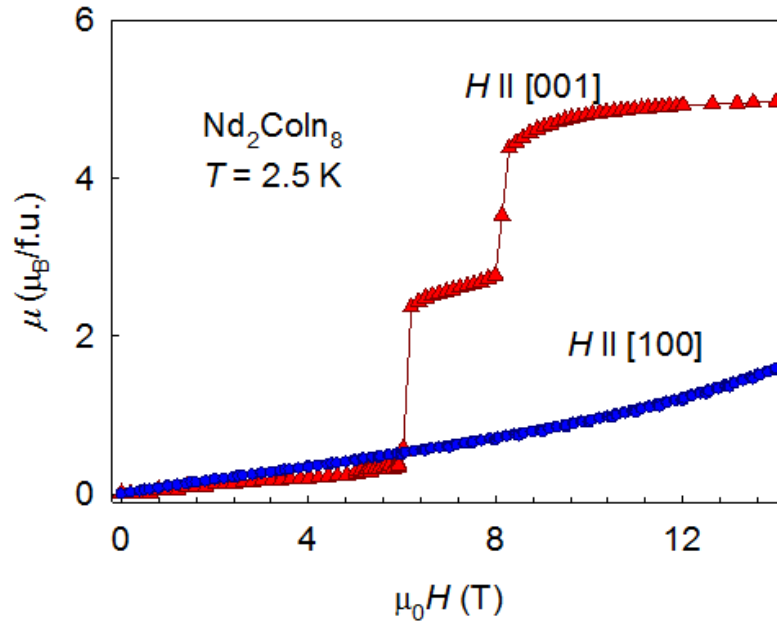


Fig. 61. Magnetic isotherms of Nd_2CoIn_8 measured at 2.5 K in a magnetic field applied along the [100] axis (●) and the [001] axis (▲).

As the magnetization data of Nd_2CoIn_8 remind strongly the magnetic behavior of many other RE_nRhIn_{3n+2} compounds, we have constructed a magnetic field-temperature diagram as shown in Fig. 62. The temperatures of the steps in the $M(H)$ curves measured at different temperatures, and the $M(T)$ and $C_p/T(T)$ dependencies measured in different magnetic fields were used to compose the diagram. Both magnetization and specific-heat data are in good agreement. In analogy to previously published diagrams^{230,242}, we depict the low-magnetic field

region within the ordered phase as AF1 and the high-magnetic field region as AF2. The resulting phase diagram corresponds to RE_nRhIn_{3n+2} phase diagrams showing analogical phase boundaries and suggesting similar magnetic properties.

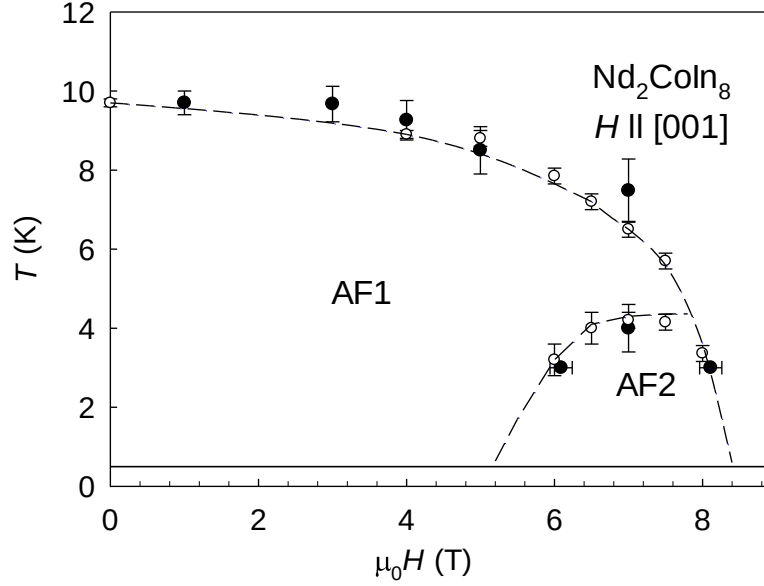


Fig. 62. The temperature-magnetic field phase diagram of Nd_2CoIn_8 for magnetic fields applied along the [001] axis. The MO phases are marked as AF1 and AF2. Data were determined from the specific heat (white circles) and magnetization measurements (black circles). The lines are drawn to guide the eye.

Dy_2CoIn_8

The temperature dependence of the specific heat of Dy_2CoIn_8 (see Fig. 63) shows sharp peaks at 16.2 K and 4.6 K, respectively. The first transition indicates the presence of a phase transition to a low-temperature antiferromagnetic state while the latter one is likely connected with an order-to-order transition. Applying the equal-entropy construction on the two anomalies, the transitions at $T_N = 16.7$ K and $T_1 = 5$ K have been determined in agreement with literature²²⁹.

The peak at T_N is gradually suppressed and shifted to lower temperatures by applying magnetic field along the [001] axis while the other transition becomes simultaneously enhanced and moves to higher temperatures. Both transitions merge at $T_m = 10.5$ K in the field $\mu_0 H_m = 7$ T which is related probably to the onset of a ferromagnetic ordering prevailing in the material in high magnetic fields and at low temperatures.

The evolution of the two specific-heat anomalies with the magnetic field applied within the basal plane is qualitatively different from the scenario with field applied along the [001] axis. While T_N is less affected by the increasing magnetic field, the transition at T_1 is rapidly suppressed and it is not observed in magnetic fields higher than 3 T. However, increasing magnetic field induces another magnetic transition

above 8 T which leads to merging of the AF transition and the magnetic field-induced transition in magnetic field $\mu_0 H_m = 12$ T at $T_m = 12.2$ K.

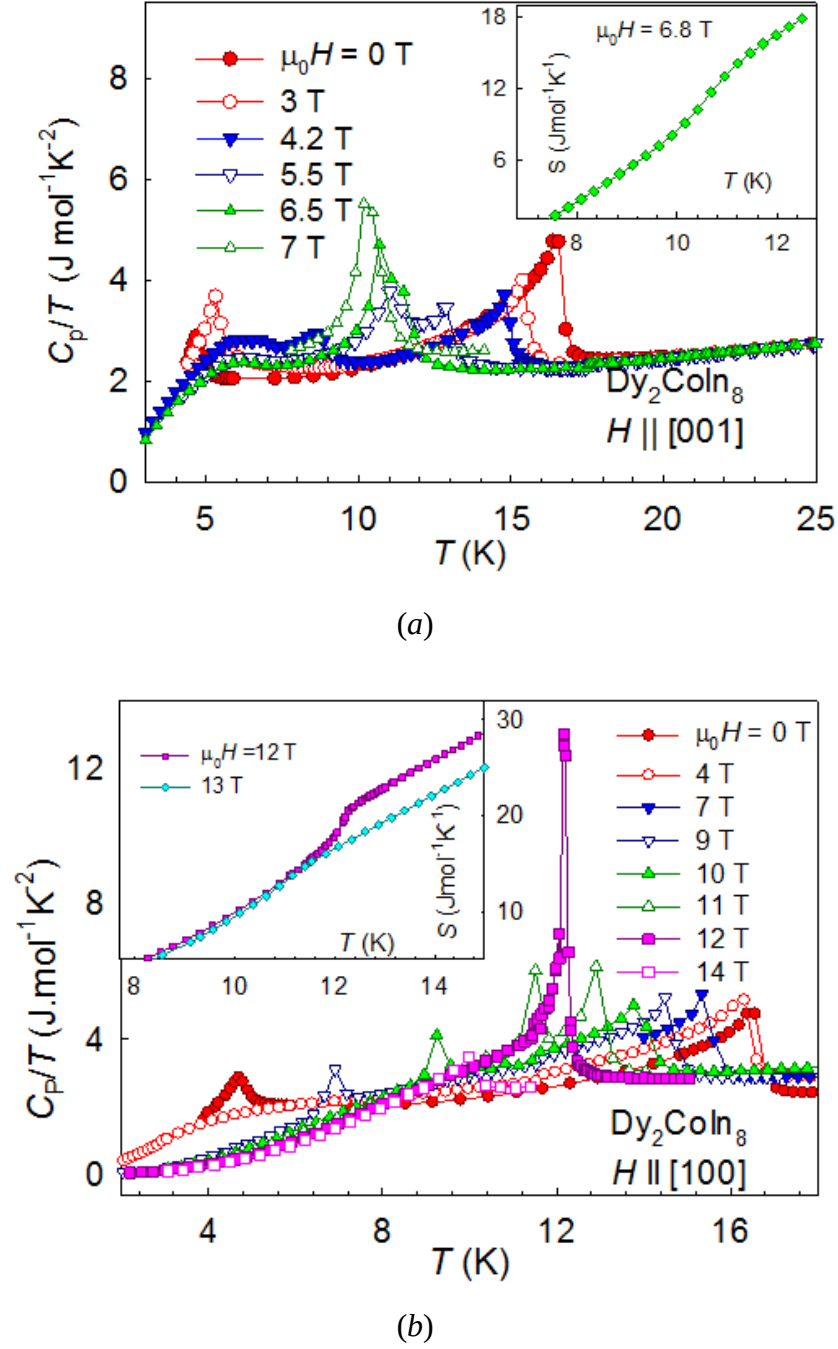


Fig. 63. The evolution of the specific heat measured in various magnetic fields oriented along the [001] axis (a) and the [100] axis (b). The insets show the temperature dependence of total entropy in magnetic field H_m and at temperature T_m where the field-induced transition and the AF transition merge.

The transitions at T_m , H_m for the magnetic field along the [001] axis and for the basal-plane field, respectively, have apparently different character. In the basal-plane field, while there is a smeared entropy change observable in the [001]-axis field at the critical value of $\mu_0 H_m = 6.8$ T, a significant step is clearly visible on the entropy

curve measured in magnetic field $\mu_0 H_m = 12$ T applied within the basal plane. Id, the specific-heat anomaly is very sharp indicating a first order-like transition whereas the typical λ -type anomaly manifests likely the second-order transition for the magnetic field applied along the [001] axis.

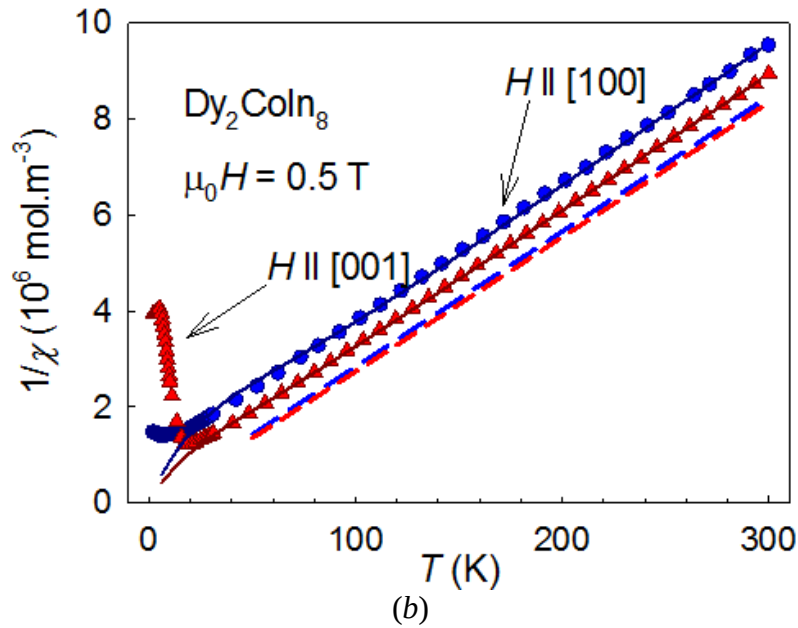
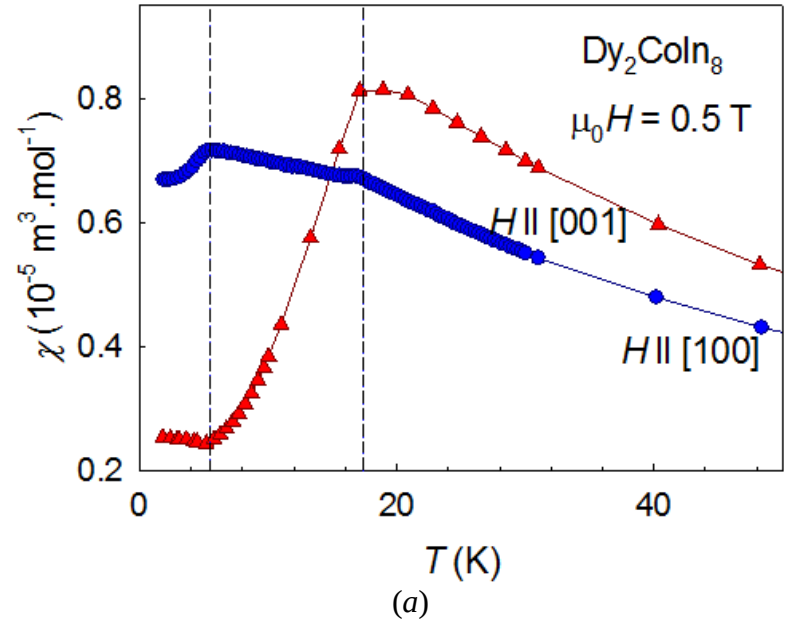


Fig. 64. (a) Temperature dependence of the magnetic susceptibility of Dy_2CoIn_8 in a magnetic field of 0.5 T applied along the [100] axis (●) and the [001] axis (▲). The dashed lines mark the transition temperatures. (b) Temperature dependence of the inverse susceptibility of Dy_2CoIn_8 measured in a magnetic field applied along the [100] axis (●) and the [001] axis (▲), and calculated¹⁰⁶ (dashed lines of corresponding colors). The CEF fit of experimental data is depicted by full lines of corresponding colors.

This observation is illustrated in the insets of Fig. 63(a) and (b) showing the S – T plot determined by integrating the total heat capacity. The temperature dependence of the magnetic susceptibility of Dy_2CoIn_8 (see Fig. 64(a)) shows also two distinct anomalies: the maximum at ~ 17 K (data taken at a field of 0.5 T), pronounced for the [001] axis and much less pronounced for the [100] axis and an anomaly at $T_1 = 5$ K, observed as a maximum for the magnetic field along the [100] axis (minimum for the [001] axis). The two temperatures agree well with the characteristic temperatures derived from the specific heat presented above.

The $1/\chi(T)$ dependence of Dy_2CoIn_8 measured in magnetic field perpendicular and parallel to the [001] axis is depicted in Fig. 64(b). The fit to the C-W law in the PM region from 50 to 300 K reveals a small difference in θ_p temperatures along the [001] and [100] axis (-17 K and -33 K, respectively) indicating weak anisotropy, which is also typical for other $\text{Dy}_n\text{TIn}_{3n+2}$ compounds^{230,243}.

Tab. 11. The CEF parameters obtained from the first-principles calculations¹⁰⁶ and from fitting of the experimental susceptibility in the temperature range 20–300 K.

	From first-principles ¹⁰⁶	From fitting experimental data
B_2^0 [meV]	$-0.54 \cdot 10^{-2}$	-0.26
B_4^0 [meV]	$0.29 \cdot 10^{-4}$	0.01
B_4^4 [meV]	$0.48 \cdot 10^{-3}$	0.03
B_6^0 [meV]	$0.31 \cdot 10^{-6}$	$-3.57 \cdot 10^{-5}$
B_6^4 [meV]	$-0.97 \cdot 10^{-5}$	$-0.44 \cdot 10^{-3}$

The results of first-principles calculations show that the scenario in Dy_2CoIn_8 is qualitatively different from the Pr_2CoIn_8 and Nd_2CoIn_8 compounds. The Dy 4*f*-wave functions are localized and shielded by Dy 5-*s* and 5*p*-wave functions much more than in the case of Pr and Nd; thus, the hybridization contribution becomes negligible and the calculated first-principles susceptibility is in a reasonable agreement with our singlecrystalline data. Also, the CEF fit of our data describes well the PM regime along the [100] and [001] axis. The fitted CEF parameters correspond qualitatively to the calculated ones as the signs of the dominant parameters B_2^0 , B_4^0 and B_4^4 are identical. Both sets of parameters are listed in Tab. 11 and the calculated and fitted susceptibilities are depicted in Fig. 64(b). For the parent compound Dy_2CoGa_8 , comparable values of the CEF parameters were obtained from fitting the inverse susceptibility²⁴⁰.

Similar to Nd_2CoIn_8 , the magnetization of Dy_2CoIn_8 measured at 2.5 K with the field applied along the [001] axis reveals two equal-step metamagnetic transitions, at 3.7 T and 8.6 T (see Fig. 65). With increasing temperature, the transition at 8.6 T shifts to lower fields (red arrow) and both transitions become gradually smeared. The magnetic isotherm at 25 K is linear indicating that the material is in a paramagnetic regime (see the inset of Fig. 65). The highest magnetization measured in 14 T reaches only 75 % of the saturation value of two free Dy^{3+} ions which can be attributed to the effect of the crystal field²³⁰. In contrast to many other $RE_n\text{TIn}_{3n+2}$

compounds, also the magnetic isotherm measured in a magnetic field applied within the basal plane reveals a metamagnetic transition at a relatively low field of 8.5 T. With increasing temperature, this transition shifts to higher fields (blue arrow), i. e. opposite to the effect observed for the direction perpendicular to the basal plane, which excludes any possibility of a projection from this orientation.

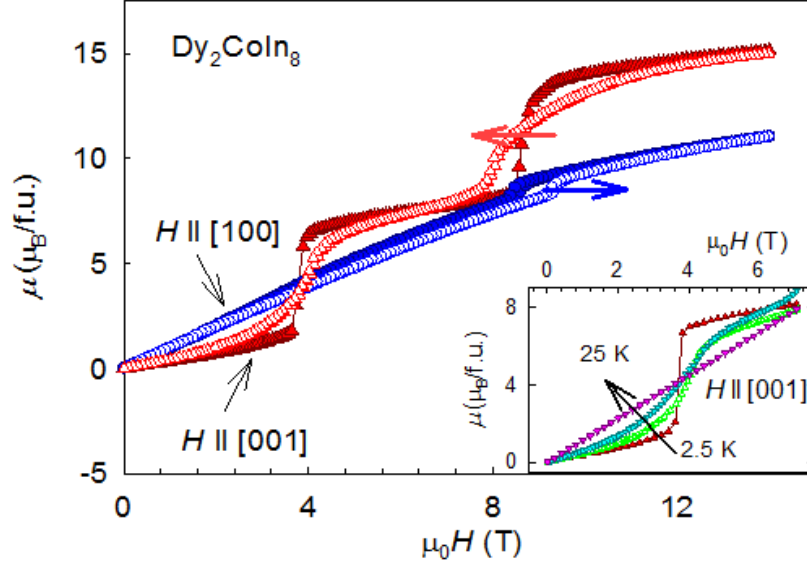


Fig. 65. Magnetic isotherms of Dy_2CoIn_8 measured at 2.5 K (filled symbols) and 8 K (open symbols) in magnetic field applied along the [100] axis (●) and the [001] axis (▲). The red and blue arrow marks the direction of the shift of transition caused by the increasing temperature. The evolution of the magnetization curves at temperatures below and above the MO state for $H \parallel [001]$ is depicted in the inset.

As the Dy_2CoIn_8 compound reveals a nontrivial evolution of its ground state in the magnetic field, we propose the possible temperature-magnetic field phase diagram for both principal crystallographic orientations (see Fig. 66) based on results discussed above. The phase transition temperatures obtained from the $C_p/T(T)$ dependencies are in good agreement with magnetization data. The diagram for the [001] orientation of magnetic field consists of three regions of MO phases. It resembles partially the diagrams of related $RE_n\text{RhIn}_{3n+2}$ compounds^{230,242}; however, our notation cannot be linked automatically to the already used one as no microscopic investigation has been performed so far on the Co-compounds. The region below T_N is characterized by an antiferromagnetic ordering labeled AF1. Further cooling causes the reorientation of magnetic moments and another, probably antiferromagnetic phase AF3 is established below T_1 . Finally, the increase of magnetic field induces phase AF2. For the perpendicular orientation along the [100] axis, the magnetic phase will be probably different, thus it is marked as AF'2. The phases AF2 and AF'2 might be analogous to the high-field AF2^{Rh} phase^{230,242}; however the nature of the AF1^{Rh} phase cannot be easily attributed to either the AF1 or AF3 without microscopic investigation. Nevertheless, the character of the AF1

and AF3 phases points to different configurations of the antiferromagnetic order present in the AF1^{Rh} phase. An analogy of the AF1 phase can be found in the phase diagram of the Ho₂RhIn₈ compound which shows two transitions in zero magnetic field in a very narrow temperature region²³².

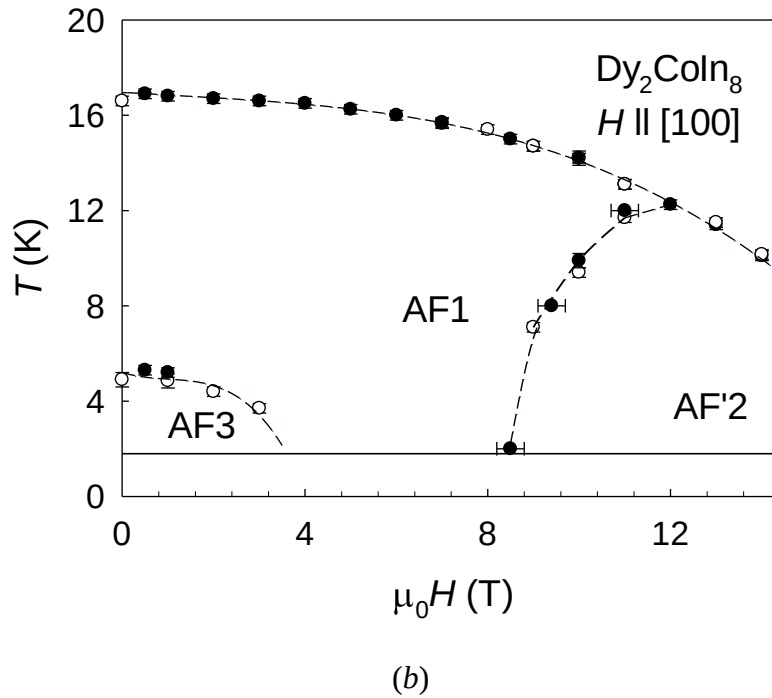
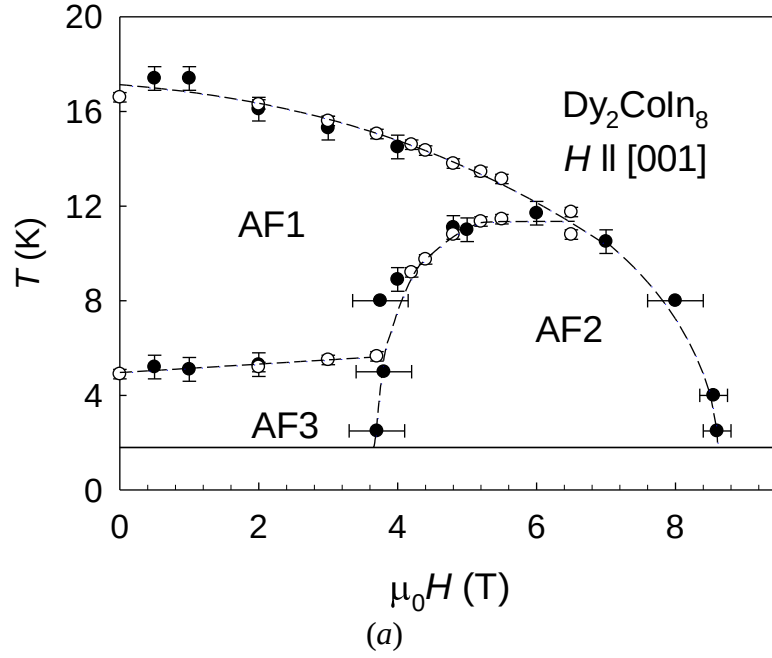


Fig. 66. Temperature-magnetic field phase diagrams of Dy₂CoIn₈ for both principal crystallographic orientations. The MO phases for $H \parallel [001]$ (a) and $H \parallel [100]$ (b) are marked as AF1, AF2 and AF3 and AF1, AF'2 and AF3, respectively. Data were determined from specific heat (white circles) and magnetization measurements (black circles). The lines are drawn to guide the eye.

In line with the limited temperature and magnetic-field range, the presence of an incommensurate magnetic structure precursor in Ho_2RhIn_8 was confirmed by neutron experiments, turning rapidly into the commensurate ordering while cooling down. On the other hand, the AF1 phase in Dy_2CoIn_8 extends over much broader region of temperatures and magnetic fields, compared to Ho_2RhIn_8 , thus forming a stable magnetic ordering. However, the example of a stable, incommensurate ordering observed in the parent CeRhIn_5 compound supports the idea of an incommensurate arrangement of the AF1 phase¹³⁶. Dy_2CoIn_8 represents a unique case among the $RE_2\text{TIn}_8$ and $RE\text{TIn}_5$ compounds which show usually a single magnetic phase in zero magnetic field. Therefore, the determination of corresponding magnetic structure by neutron diffraction is highly desirable for this system.

6.4. Summary

Single crystals of Pr_2CoIn_8 , Nd_2CoIn_8 and Dy_2CoIn_8 have been prepared successfully for the first time and their anisotropic magnetic properties have been investigated both experimentally and theoretically by fitting the susceptibility data to CEF Hamiltonian and comparing with the results of first-principles calculations. It has been shown that the anisotropy of the magnetic properties decreases when moving from the $RE\text{CoIn}_5$ to $RE_2\text{CoIn}_8$ compounds, i.e. with increasing 3D character of the structural dimensionality. The van Vleck paramagnetism in Pr_2CoIn_8 has been confirmed. Nd_2CoIn_8 and Dy_2CoIn_8 order antiferromagnetically below $T_N = 9.6$ and 16.7 K, respectively. Both Nd_2CoIn_8 and Dy_2CoIn_8 undergo two metamagnetic transitions similarly to many other $RE_n\text{TIn}_{3n+2}$ compounds. However, Dy_2CoIn_8 shows an additional magnetic phase in zero magnetic field and a metamagnetic transition along the hard-magnetization axis. Thus, the magnetic phase diagram of Dy_2CoIn_8 is exceptional among the non-cerium $RE_n\text{TIn}_{3n+2}$ compounds, resembling somewhat the diagram of Ho_2RhIn_8 . The first-principles calculations described satisfactorily only the anisotropic properties of Dy_2CoIn_8 , pointing to a low hybridization contribution among the rare earth and the In and Co ligands, respectively.

The present results contribute to understanding of the variety of complex magnetic ordering in the $RE_n\text{TIn}_{3n+2}$ compounds. They show that the behavior of these non-Kondo analogs of the famous unconventional $\text{Ce}_n\text{CoIn}_{3n+2}$ superconductors is rather universal across the series of isostructural compounds containing various lanthanide and *T*-metal components. Determination of the magnetic structures of Nd_2CoIn_8 and Dy_2CoIn_8 will be a task for the future neutron-diffraction studies.

7. General conclusions

The thesis summarizes the investigation of different groups of materials which are linked together by their tetragonal crystal structure with the chemical formula $RE(U)_nTIn_{3n+2}$ ($n = 1, 2, 3$; RE = rare earth; T = transition metal). Thanks to the layered character of the structure, these materials represent a fruitful playground for studying the interplay between their crystal structure and physical properties. The studied compounds reveal a broad spectrum of ground states ranging from rather complicated magnetic structures over the non-Fermi-liquid behavior to the unconventional superconductivity and its coexistence with magnetic ordering.

With respect to the previous work based on Pd substitutions in the Ce_nRhIn_{3n+2} compounds^{82,192}, we have focused our attention on novel phases with $T = Pd$ and Pt . These compounds are isostructural with different layer stacking reminiscent of the artificially prepared $CeIn_3/LaIn_3$ superlattices⁵⁵. Hence they represent a suitable system providing a unique opportunity to test the effect of varying stacking composition (and thus structural dimensionality) on the quantum criticality. Ce_3PdIn_{11} (Ce_3PtIn_{11}) single crystals exhibit two successive transitions at $T_1 = 1.7$ K ($T_1 = 2.2$ K) and at $T_N = 1.5$ K ($T_N = 2.0$ K) into a presumably incommensurate and commensurate antiferromagnetic states, respectively. Applying magnetic field within the basal plane gradually suppresses T_N and leaves the other transition almost untouched. Contrary, in the perpendicular orientation, both transitions are gradually suppressed; they merge at 4 T and split again in higher fields. Ambient-pressure superconductivity emerges at $T_c = 0.42$ K ($T_c = 0.32$ K). In the case of Ce_3PtIn_{11} , the hydrostatic pressure up to ~ 2.3 GPa was applied. Both magnetic order and superconductivity are observed in a broad range of hydrostatic pressures. We found that the pressure pushes the Ce_3PtIn_{11} system towards the quantum critical point, which might be of a local-moment type. A superconducting dome with the maximum at $T_c^{\max} = 0.69$ K at ~ 1.2 GPa is formed in the vicinity of this QCP. The combined application of magnetic field and hydrostatic pressure in Ce_3PtIn_{11} points to a possible presence of two different SC phases. In contrast to the other well-known Ce_nTIn_{3n+2} materials, the crystal structure of Ce_3TIn_{11} contains two crystallographically independent cerium sites. The performed experiments suggest that the local environment of these cerium atoms determines the global physical properties. We have shown that these properties can originate from distinct different Kondo scales related to the inequivalent Ce-sites. In this sense Ce_3TIn_{11} is a unique realization of a two-Kondo lattice model discussed by *Benlagra et al.*¹¹¹ showing a new variant of a coexistence of superconductivity and magnetism.

Except the novel cerium-based materials, we studied also the prototypical representative of the Ce_nTIn_{3n+2} materials - the antiferromagnetic Ce_2RhIn_8 compound. We performed the so far missing study of the CEF-level scheme by means of inelastic neutron scattering. The experiment revealed that the ratios of the

obtained CEF parameters B_2^0 , the energy levels E_2 and the phase transition temperatures T_N for Ce_2RhIn_8 and CeRhIn_5 , respectively, are very similar. Such observation is in line with the assumption that the energy scales in these materials are controlled by the structural dimensionality. A more significant $\mp 3/2$ admixture into the $\pm 5/2$ ground state was found compared to the related CeRhIn_5 compound which might contribute to better understanding the character of their magnetic structures.

The $\text{U}_n\text{RhIn}_{3n+2}$ systems were studied as the only representatives of a 5f-electron system in this thesis. They order antiferromagnetically at temperatures significantly higher than their cerium analogs and reveal a strong magnetic anisotropy. The transition temperature T_N decreases in these novel materials with increasing m/n ratio in opposite to $\text{Ce}_n\text{RhIn}_{3n+2}$ demonstrating different energy scales which determine their ground-state properties.

We have investigated the anisotropy and magnetic phase diagrams of the RE_2CoIn_8 ($\text{RE} = \text{Pr}, \text{Nd}, \text{Dy}$) single crystals. Our results were compared with the theoretical calculations and provided a good agreement in the case of Dy_2CoIn_8 ; for the other systems, the 4f-ligand hybridization which was not included in the model of CEF calculations plays a significant role. From all known non-cerium $\text{RE}_n\text{TIn}_{3n+2}$ ($T = \text{Co}, \text{Rh}, \text{Ir}$) systems, the results from the study of the Dy_2CoIn_8 compound should be pointed out. Its rather complex magnetic phase diagram containing three different magnetic phases is different from most of the related non-cerium materials and hence requires further, microscopic investigation by means of neutron diffraction.

The major experimental issue discussed in the work is the single-crystal growth as most of the studied materials were prepared as completely novel phases or synthesized for the first time in a single-crystal form. The Appendix B devoted to the RECo_2 compounds is an example of a successful application of the solution growth method demonstrating its main advantages.

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List of abbreviations

APW	Augmented plane wave
AF	Antiferromagnetism, antiferromagnet, antiferromagnetic
BCS	Bardeen, Cooper, Schrieffer
BSE	Backscattered electrons
CEF	Crystal electric field
C-W	Curie-Weiss law
DFT	Density functional theory
DSC	Differential scanning calorimetry
DTA	Differential thermal analysis
EDX	Electron dispersive x-ray (detector, analysis)
Fl	Fermi-liquid
FM	Ferromagnetism, ferromagnet, ferromagnetic
FFLO	Fulde-Ferrel-Larkin-Ovchinnikov
GGA	Generalized gradient approximation
HF	Heavy fermion
IMO	Incommensurately magnetically ordered
INS	Inelastic neutron scattering
LDA	Local density approximation
LM	Local moment
lo	Local orbitals
LSDA	Local spin-density approximation
MO	Magnetically ordered
nFl	Non-Fermi-liquid
NM	Non-magnetic
PM	Paramagnetic
QCP	Quantum critical point
RE	Rare earth
RKKY	Ruderman-Kittel-Kasuya-Yoshida interaction
RRR	Residual resistivity ratio
SC	Superconducting
SCES	Strongly correlated electron systems
SE	Secondary electrons
SEM	Scanning electron microscope (microscopy)
SDW	Spin-density wave
SDW	Spin-density wave
SO	Spin-orbit
SQUID	Superconducting Quantum Interference Device
SSE	Solid state electrotransport
T_C	Curie temperature
T_N	Néel temperature

T_c	Superconducting temperature
TCP	tetracritical point
WHH	Werthamer–Helfand–Hohenberg
2D, 3D	two-dimensional, three-dimensional
μ SR	muon-spin rotation/relaxation

Appendix A

In this section, the complete crystallographic data of the crystal structures of $\text{Ce}_3\text{PdIn}_{11}$, $\text{Ce}_3\text{PtIn}_{11}$ and Ce_2PtIn_8 are summarized in Tab. 12, Tab. 13 and Tab. 14. In Fig. 67(a–j), the temperature evolution of the normalized electrical resistivity of $\text{Ce}_3\text{PtIn}_{11}$ in various hydrostatic pressures and magnetic fields applied along the [001] axis is shown. The Néel temperature was estimated from the change of the slope in the $\rho(T)$ curves; the superconducting temperature is given as the middle of the slope (marked by an arrow) of the drop in the resistivity curve. The hydrostatic pressure in the figures is the low-temperature value given by subtracting the value of 0.3 GPa from the pressure measured at the room temperature (for details, see the section 2.3.4). The temperature-pressure-magnetic field diagrams in Fig. 68 presented in the section 3.3.2 are based on the values of T_c and T_N obtained from these data.

Tab. 12. Crystallographic data for the compounds $\text{Ce}_3\text{PdIn}_{11}$, $\text{Ce}_3\text{PtIn}_{11}$ and Ce_2PtIn_8 .

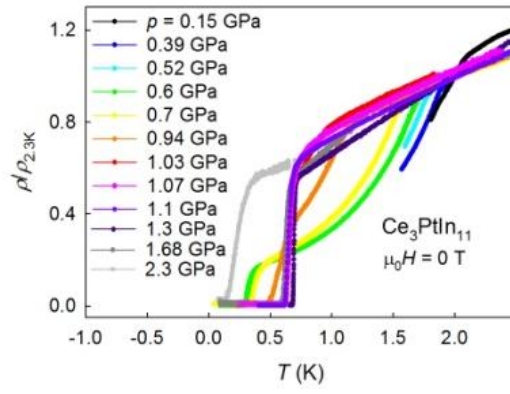
Compound	$\text{Ce}_3\text{PdIn}_{11}$	$\text{Ce}_3\text{PtIn}_{11}$	Ce_2PtIn_8
Lattice parameters (Å)	$a = 4.6896(11)$	$a = 4.6874(4)$	$a = 4.6898(3)$
(single-crystal data)	$c = 16.891(3)$	$c = 16.8422(12)$	$c = 12.1490(8)$
Cell volume (Å ³)	371.47(14)	372.44(9)	267.21(3)
Formula weight (g.mol ⁻¹)	1789.74	1878.4	1393.84
Density (g.cm ⁻³)	7.998	8.427	8.682
$\mu(\text{mm}^{-1})$	26.81	35.14	38.29
Crystal size (mm)	0.3 x 0.11 x 0.08	0.83 x 0.55 x 0.30	0.28 x 0.17 x 0.11
Reflections measured, independent, independent with $I > 3\sigma$, R_{int}	1510, 348, 269, 0.058	5150, 361, 348, 0.107	3814, 261, 255, 0.047
$R(F^2 > 3\sigma), wR(F^2), S$	0.054, 0.132, 1.63	0.037, 0.104, 1.65	0.022, 0.076, 1.53
No of parameters, No of restraints	22, 0	22, 0	17, 0
Weighting scheme		$w = 1/[\sigma^2(I) + 0.0016I^2]$	
Extinction coefficient	110(20)	390(40)	100(17)
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (eÅ ⁻³)	6.87, -5.58	5.76, -5.32	1.32, -2.10

Tab. 13. Atomic coordinates and equivalent isotropic displacement parameters ($\text{\AA}^2$) for the compounds $\text{Ce}_3\text{PdIn}_{11}$, $\text{Ce}_3\text{PtIn}_{11}$ and Ce_2PtIn_8 .

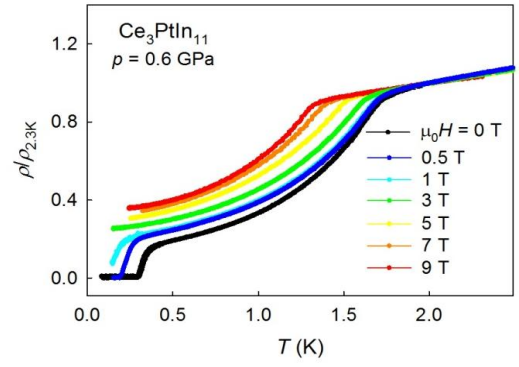
Atom	Wyckoff position	x	y	z	U_{eq}
$\text{Ce}_3\text{PdIn}_{11}$					
Ce1	2g	0	0	0.27683(8)	0.0123(4)
Ce2	1a	0	0	0	0.0133(5)
Pd1	1b	0	0	0.5	0.0156(7)
In1	4i	0.5	0	0.41180(8)	0.0159(5)
In2	2h	0.5	0.5	0.27797(11)	0.0173(5)
In3	4i	0.5	0	0.13805(8)	0.0186(5)
In4	1c	0.5	0.5	0	0.0177(7)
$\text{Ce}_3\text{PtIn}_{11}$					
Ce1	2g	0	0	0.27755(5)	0.0093(3)
Ce2	1a	0	0	0	0.0096(4)
Pt1	1b	0	0	0.5	0.0104(3)
In1	4i	0.5	0	0.41167(6)	0.0131(3)
In2	2h	0.5	0.5	0.27784(7)	0.0138(4)
In3	4i	0.5	0	0.13792(5)	0.0149(4)
In4	1c	0.5	0.5	0	0.0136(5)
Ce_2PtIn_8					
Ce	2g	0	0	0.30795(7)	0.0068(3)
Pt1	1a	0	0	0	0.0085(2)
In1	4i	0	0.5	0.12241(8)	0.0109(3)
In2	2e	0	0.5	0.5	0.0121(4)
In3	2h	0.5	0.5	0.3072(6)	0.0117(3)

Tab. 14. Interatomic distances in $\text{Ce}_3\text{PdIn}_{11}$, $\text{Ce}_3\text{PtIn}_{11}$ and Ce_2PtIn_8 .

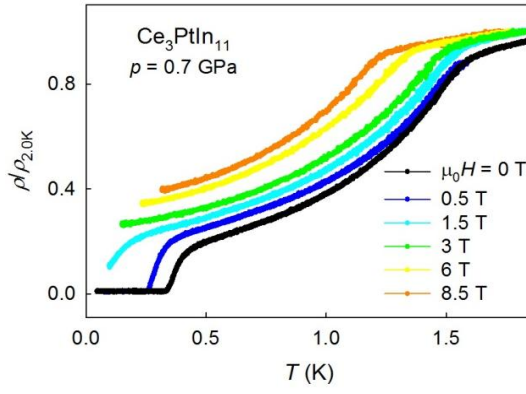
$\text{Ce}_3\text{PdIn}_{11}$			$\text{Ce}_3\text{PtIn}_{11}$			Ce_2PtIn_8		
Atom	To atom	d ($\text{\AA}$)	Atom	To atom	d ($\text{\AA}$)	Atom	To atom	d ($\text{\AA}$)
Ce1	In1	3.2704	Ce1	In1	3.2551	Ce1	In1	3.2501
	In2	3.3161		In2	3.3145		In2	3.3054
	In3	3.3156		In3	3.3200		In3	3.3127
Ce2	In3	3.3069	Ce2	In3	3.2998	In1	In1	3.3127
	In4	3.3160		In4	3.3145		In1	2.9730
In1	In1	3.3160	In1	In1	3.3145		In1	2.9730
	In1	2.9800		In1	2.9755		In3	3.2442
	In2	3.2570		In2	3.2516		Pt1	2.7743
In2	Pd1	2.7780	Pt1	Pt1	2.7760		In2	3.3127
	In3	3.3291		In3	3.3235		In3	3.3114
	In3	3.3160		In3	3.3145			
In3	In4	3.3069	In4	In4	3.2998			



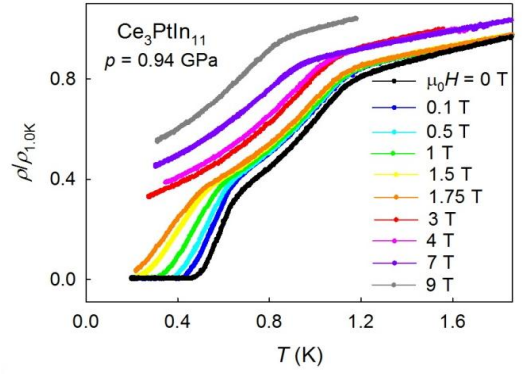
(a)



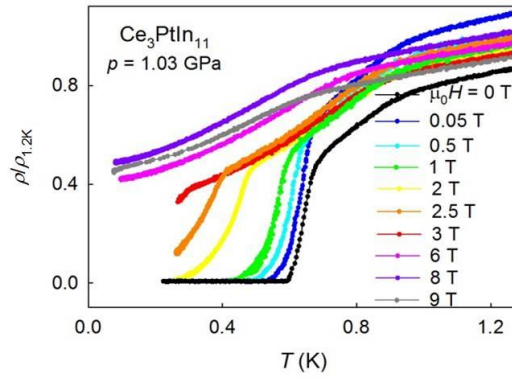
(b)



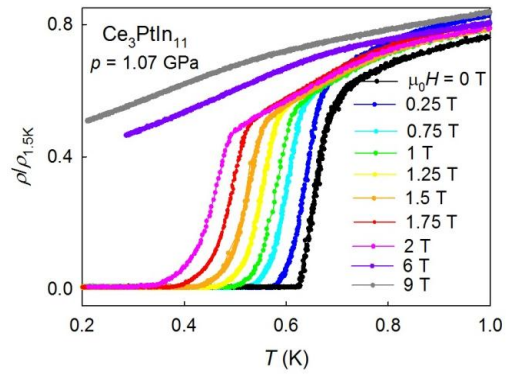
(c)



(d)

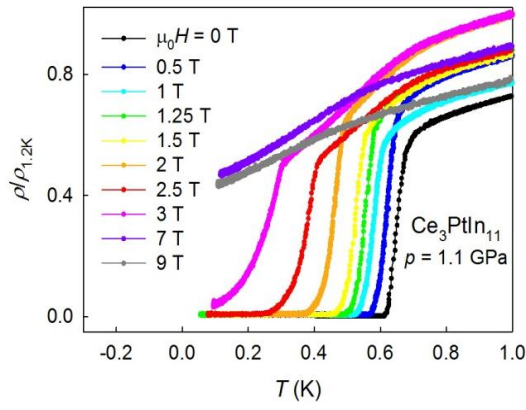


(e)

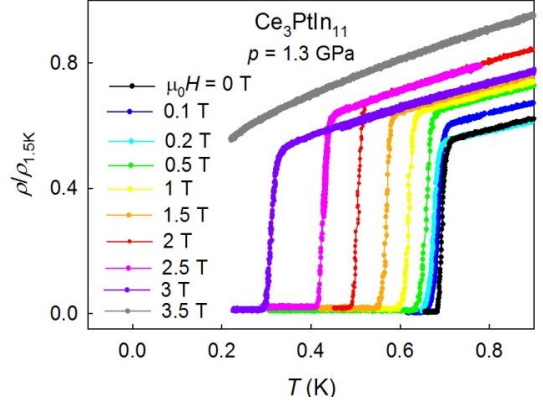


(f)

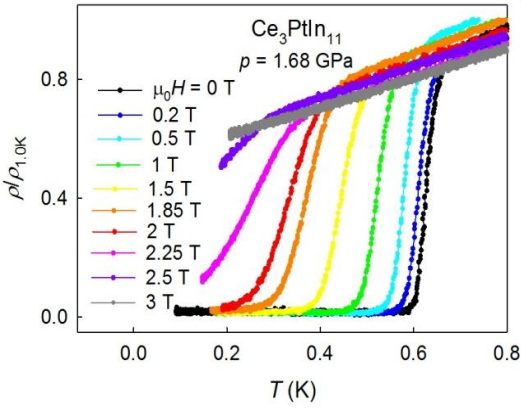
Figure continues on the next page.



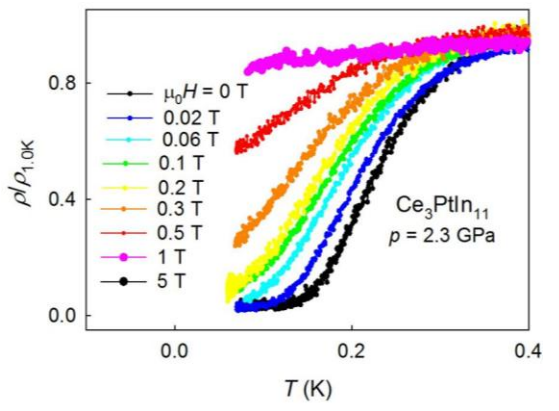
(g)



(h)



(i)



(j)

Fig. 67. The low-temperature evolution of the normalized electrical resistivity ρ of $\text{Ce}_3\text{PtIn}_{11}$ in ambient pressure (a) and under hydrostatic pressures of (b) 0.60 GPa, (c) 0.70 GPa, (d) 0.94 GPa, (e) 1.03 GPa, (f) 1.07 GPa, (g) 1.10 GPa, (h) 1.30 GPa, (j) 1.68 GPa and (j) 2.30 GPa in various magnetic fields applied along the [001] axis.

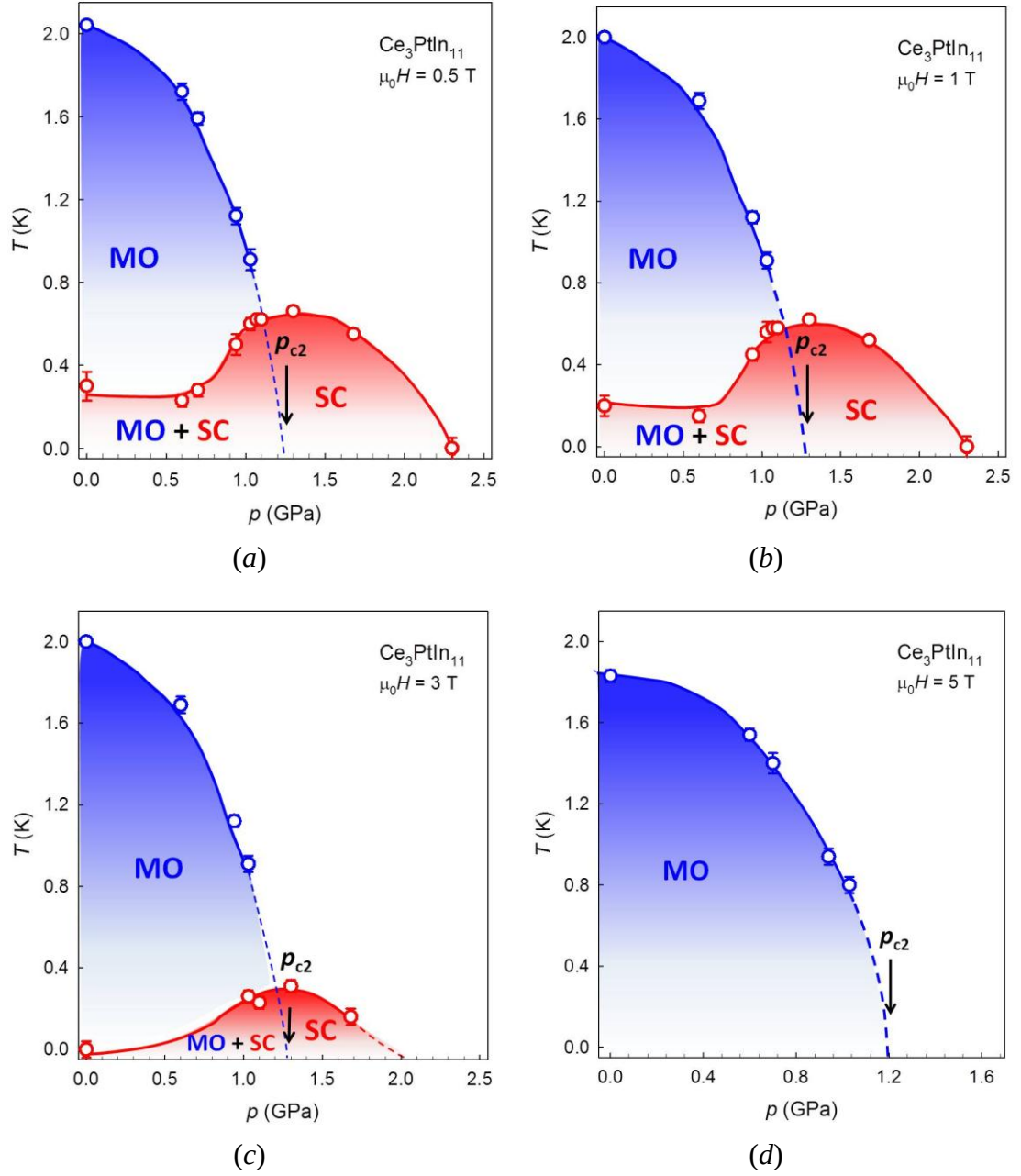


Fig. 68. The temperature-hydrostatic pressure phase diagrams of $\text{Ce}_3\text{PtIn}_{11}$ in magnetic fields of (a) 0.5 T, (b) 1 T, (c) 3 T and (d) 5 T. The ambient pressure data points are taken from the heat capacity experiments whereas those under hydrostatic pressure are obtained from the electrical resistivity. In analogy with Fig. 37, MO depicts the commensurate magnetic order and SC the superconductivity. The arrows mark the positions of the critical pressure p_{c2} . The green and brown dashed lines depict the suggested pressure evolution of the critical temperatures based on the T - p phase diagram in Fig. 37.

Appendix B

***RECo₂* (*RE* = Gd, Dy, Ho, Er, Tm) compounds**

The magnetic properties of the well-known *RECo₂* compounds discussed in this section are determined by the interplay of the cobalt 3*d* electrons and lanthanide 4*f* electrons. The following chapter is located in Appendix due to two reasons; first, the crystal structure of *RECo₂* is cubic in contrast to the layered tetragonal structure of the previously studied materials; secondly and more importantly, the focus of this part is primarily the crystal growth refinement, not the investigation of novel ground-state properties. Similarly to previous chapters, also here, the single-crystal synthesis is based on the solution growth method which represents, however, an unusual approach in this class of materials. The method was chosen to determine both advantages and disadvantages with respect to the single-crystal quality for various rare earths. The quality of the crystals was tested by the bulk measurements (magnetization, specific heat, ac magnetic susceptibility). The advantages of the flux growth method in the context of possible applications of the *RECo₂* single crystals for further experiments are discussed in the summary.

Introduction

For more than 30 years, the *RECo₂* compounds have been attracting the attention of solid-state community due to several reasons: They represent a suitable material for testing simple theoretical models of the itinerant 3*d*-electron magnetism and the coexistence of the itinerant and the well-localized 4*f* electrons. These models can be used for description of systems revealing a larger variety of magnetic interactions²⁴⁴.

RECo₂ compounds crystallize in the very stable cubic Laves *MgCu₂*-type (C15) structure²⁴⁵ with *RE* atoms localized in the diamond lattice and Co atoms forming four tetrahedra within one unit cell. According to the Stoner criterion, the existence of cobalt magnetic moment is given by the local magnetic field which is determined by the surrounding *RE*-ion neighbors. The local magnetic field can be enhanced by reaching the temperature where the *RE* moments order magnetically. The hybridization of the Co 3*d* electrons and the 4*f* electrons plays a crucial role in determining the ground-state properties of the magnetic *RECo₂* compounds. *RE* and Co ions form two FM sublattices. In this work, we focused on the compounds with the heavy *RE* elements (Gd-Er), which are ferrimagnetic with the sublattices oriented antiparallel to each other. *RECo₂* compounds where *RE* = Dy, Ho, Er reveal a first-order phase transition²⁴⁶ caused by the itinerant metamagnetism of the Co sublattice. At *T_C*, the exchange field of the ordered 4*f* moments in these compounds causes an abrupt increase of the Co magnetic moment. The first-order phase transition can be changed into a second-order one by chemical doping, application of

external magnetic field or hydrostatic pressure. The other magnetic $RECo_2$ compounds reveal a second-order transition at ambient pressure.

Recently, a new type of magnetic ordering – parimagnetism - was reported in the $ErCo_2$ compound²⁴⁷. Parimagnetism is described as a short-range antiparallel coupling between magnetization of Co clusters and RE magnetic moments. Small angle neutron scattering (SANS) revealed the presence of short-range correlation among the Co moments forming cobalt magnetic clusters. Their dimension corresponds roughly to the size of the unit cell of $ErCo_2$ and it decreases with increasing temperature²⁴⁷. The system keeps its antiparallel orientation towards the Er sublattice in the temperature range between the so-called flipping temperature T_f and T_C . The presence of cobalt magnetic moment was observed using the x-ray magnetic circular dichroism (XMCD) and it can be detected also by the ac susceptibility measurement in zero or very small magnetic fields²⁴⁷. Parimagnetism was predicted and observed later also in $HoCo_2$ and $TmCo_2$ ^{248,249}. It was proposed that this phenomenon corresponds to a Griffith phase-like behavior²⁴⁹ because of a strong FM coupling between dilute Co-rich regions which might give rise to a new collective magnetic ordering between these regions in the PM regime²⁵⁰. However, further studies revealed significant differences between polycrystalline samples and single crystals²⁰ pointing to the absence of parimagnetism in the singlecrystalline form of these compounds.

The series of $RECo_2$ compounds and their substitutions have been intensively studied mainly by means of the magnetocaloric effect studied on polycrystalline samples^{251,252}, and magnetization²⁵³⁻²⁵⁵, magnetoresistance²⁵⁶ and magnetoelasticity²⁵⁷ studied on single crystals. The single crystals are traditionally synthesized by the Czochralski pulling method^{255,257} or by the Bridgman method^{253,256}. Generally, these methods can produce crystals of mass suitable for a broad range of experiments including e.g. neutron diffraction. However, they deal with certain complications, such as the intergrowth of $RECo_3$ impurity phases in a form of thin layers covering the bulk $RECo_2$ phase²⁵⁸. The single crystals reveal transitions from the PM to the FM state in a broad region of temperatures ($31\text{ K} < T_C < 38\text{ K}$ for $ErCo_2$ ²⁵⁸; $4\text{ K} < T_C < 7\text{ K}$ for $TmCo_2$ ²⁵⁴) depending on the starting stoichiometries, crystal-growth conditions and the subsequent thermal treatment. Besides, in the case of the as-cast $ErCo_2$ single crystals, the order of the phase transition is sample-dependent²⁵⁸. As the $RECo_2$ materials are incongruently melting with the exception of $ErCo_2$ (as is shown on the example of the Er-Co binary phase diagram in the section 2.1), the synthesis from molten metal solution could be naturally favored.

Thus, as an alternative, we have performed a series of crystal-growth experiments from the RE -Co flux ($RE = Gd, Dy, Ho, Er, Tm$) with the effort to avoid at least some of the above mentioned complications. Moreover, this crystal-growth method

represents an advantage for single-crystal experiments which focus on the anisotropic properties along the [100], [110] and [111] directions^{253,255,256,259} as the synthesis provides natural habit of crystals simplifying the preparation of samples. Further motivation for this work is connected with the method called electron magnetic circular dichroism (EMCD)²⁵⁹. The experiment with the detection of the EMCD signal from $4f$ electrons was suggested to be performed on $RECo_2$ single crystals²⁶⁰.

Synthesis

Single crystals of $RECo_2$ ($RE = Gd, Dy, Ho, Er, Tm$) were prepared by the solution growth method from $RE-Co$ melt with an excess of RE metal. The range of the growth temperatures and starting compositions together with the main growth products are summarized in Tab. 15. Appropriate starting element compositions were derived from the binary phase diagrams. Generally, $RE-Co$ binary phase diagrams ($RE =$ heavy rare earths Gd, Dy, Ho, Er) resemble each other strongly, revealing only small changes in order of $\sim 5\%$ in the optimal $RE:Co$ ratio and the temperature range for obtaining the respective $RECo_2$ compound. The corresponding liquidus-solidus line is shifted to higher temperatures systematically when increasing the atomic number of the RE metal. In case of Er , the liquidus-solidus line is shifted to the highest temperatures (the binary phase diagram for Tm and Co is not known), which led us to the usage of the molybdenum capsules in the induction-heating furnace instead of the quartz glass ampoules. The elements were put into the boron nitride (PBN) crucibles (except the $Er-Co$ and $Tm-Co$ samples which were put additionally into a molybdenum capsule, for details see the section 2.1). The usual alumina crucible cannot be used in this case as it reacts with the RE metals in such high concentration of RE (RE metal forms $\sim 60\%$ of the total mass of the batch compared to $\sim 10\%$ in Ce_nTIn_{3n+2}). The samples were sealed under ~ 0.3 of argon atmosphere to prevent the deformation of the quartz glass at high temperatures exceeding $1200\text{ }^{\circ}C$. The ampoules were heated up to the starting temperature T_1 and kept at this temperature for 10 h for proper homogenization. The samples were then slowly cooled down ($1-2\text{ }^{\circ}C/h$) to T_2 where the remaining solution was centrifuged. In this way, octahedra-shaped single crystals and their fragments of typical maximum dimensions $\sim 1-3\text{ mm}$ and mass $\sim 1-10\text{ mg}$ were obtained. In case of the $ErCo_2$ and $TmCo_2$ compounds, another procedure was selected due to the high growth temperature and unknown phase diagram. The starting amount of the Er and Co elements corresponding to the “solution growth” ratio was placed into the induction-heating furnace and heated up to $\sim 1360\text{ }^{\circ}C$ which corresponds to 280 V (frequency 121 kHz). Then the capsule was pushed through the heating zone with the translation rate of 1 mm/h . After 5 days, the capsule left the heating zone completely and could be opened to analyze the crystals. For the $TmCo_2$ compound, both approaches – the solution growth and the Bridgman method – were performed. The capsule was

heated up to ~ 1410 °C (melting temperature of TmCo_2 is 1350 °C according to the DTA measurements²⁶¹) and pushed through the heating zone with the translation rate of 2.5 mm/h.

Analyzing the results summarized in Tab. 15, one can see that the Ho- and Dy-phases grow easily producing no impurity phases. In general, lowering the growth temperatures and increasing the amount of cobalt at the expense of the *RE* metal improved the quality and increased slightly the dimensions of the single crystals.

Tab. 15. Growth conditions for the RECo_2 compounds. The starting (decanting) temperature is marked as T_1 (T_2). In the table, the major phase is put on the first place.

<i>RE</i>	<i>RE:Co</i>	T_1/T_2 (°C)	Final products
Gd	0.5:0.5	1200/950/850*	Gd_2Co_3 , Gd_3Co_2
	0.43:0.57§	1100/800	GdCo_2 , < 5% of Gd_3Co_2 , Gd_2Co_3
Dy	0.45:0.55	1100/850	$\text{DyCo}_2 \sim 0.5$ mm; < 5% of DyCo_3
	0.42:0.58§	1150/800	$\text{DyCo}_2 > 0.5$ mm; < 5% of DyCo_3
Ho	0.52:0.48§	1100/900	$\text{HoCo}_2 > 0.5$ mm
Er	0.48:0.52§	1360/25	$\text{ErCo}_2 \sim 0.5$ mm
Tm	0.5:0.5	1190/950	TmCo_2 , Tm_2Co_3 , Tm_3Co_2
	0.42:58 [†] §	1150/910	TmCo_2 , $\sim 10\%$ of Tm_3Co_2
	1.01:2 [§]	1410/25	TmCo_2 , <5% of Tm_3Co_2

* The ampoule was heated up to 1200 °C, quickly cooled down (in 3 h) to 950 °C and finally slowly cooled down (1-2 °C/h) to 850 °C.

§ Single crystals from these batches were further characterized by bulk measurements.

[†] The sample from this batch is shown in Fig. 69(a).

Characterization and physical properties

As this chapter is focused primarily on the refinement of the solution growth and characterization of the RECo_2 single crystals prepared via solution growth, we decided to merge the results from characterization and physical properties into one section.

As the rare-earth and Co atoms differ significantly in their mass, the RECo_2 phases can be easily recognized from unwanted binary compounds with different stoichiometry by BSE (see Fig. 69(a)). In case of TmCo_2 and DyCo_2 , a small amount of impurities (~ 5 %) was present as shown in Tab. 15 and Fig. 69(a); in all the other compounds, we were able to avoid spurious phases completely according to the microprobe analysis.

The cubic MgCu_2 -type (Fd-3m) crystal structure of powdered single crystals was confirmed using a Bruker D8 Advance diffractometer. Additionally, the lattice parameters of single crystals used for further experiments were verified by the single crystal x-ray diffraction on RIGAKU diffractometer. The determined unit cell parameters listed in Tab. 16 are in a good agreement with the published polycrystalline data.

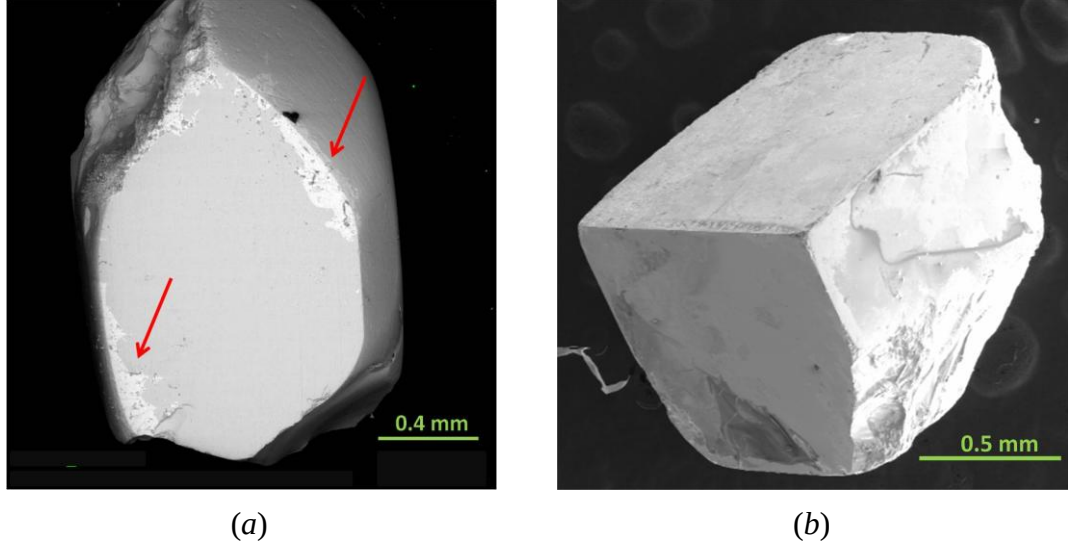


Fig. 69. (a) BSE image of a TmCo_2 single crystal with a Tm_3Co_2 impurity (brighter than the major phase) marked by the red arrows. (b) SEM image of a polished GdCo_2 single crystal used for cutting a lamella by FIB.

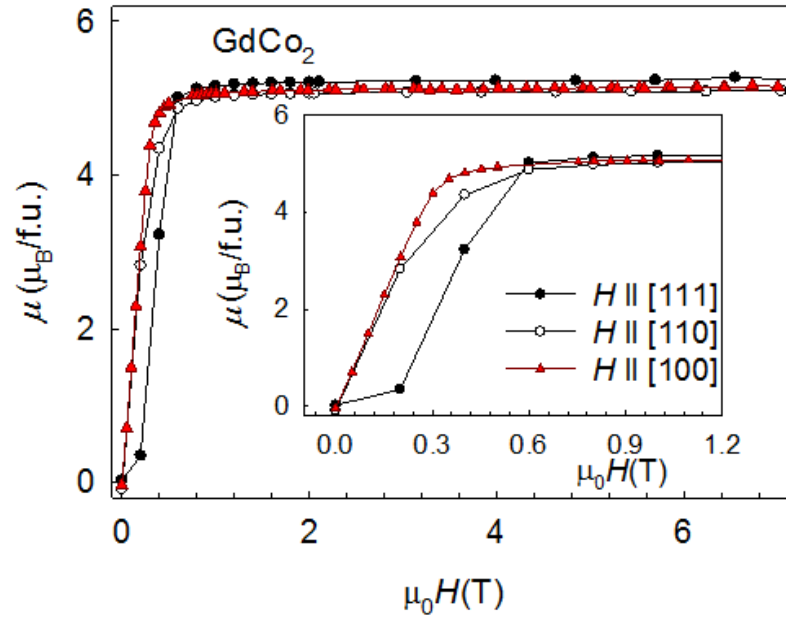
Tab. 16. The unit-cell parameters of RECo_2 ($\text{RE} = \text{Gd}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}$) determined by single crystal x-ray diffraction and the corresponding T_C obtained from the measurement compared to T_C (on single crystals) from literature. The easy axis is given to complete the overview of the physical properties of RECo_2 .

RE	a (Å)	T_C (K)	T_C (K) from literature	easy axis
Gd	7.264 ± 0.013	-	400^{262}	[100]
Dy	7.191 ± 0.008	143	136^{255}	[100]
Ho	7.166 ± 0.010	82	78^{257}	[100] above T_r , [110] below T_r
Er	7.152 ± 0.009	33	32^{256}	[111]
Tm	7.148 ± 0.015	~ 4	$4 < T_C < 7^{254}$	[111]

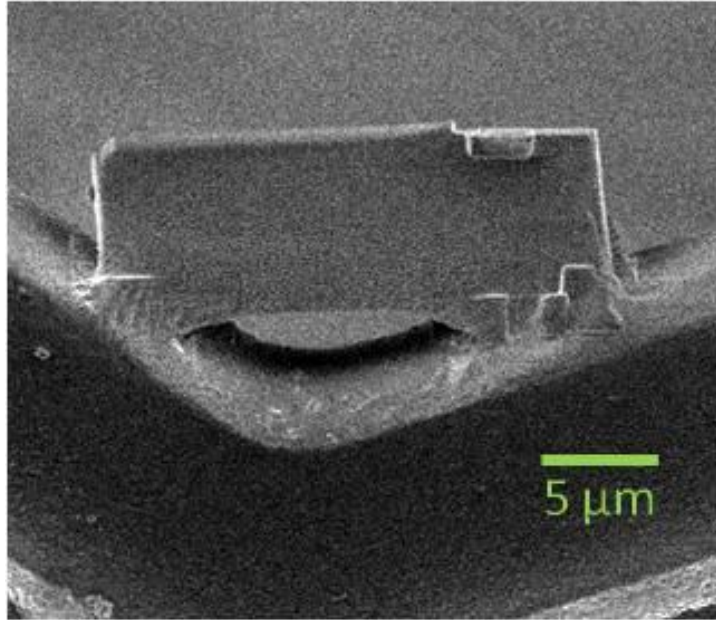
The samples were oriented using Laue method and consequently cut and/or polished to plates or cubes with dimensions $\sim 0.2\text{-}1 \text{ mm}^3$ (see Fig. 69(b)) so that they could be measured in various directions with respect to magnetic field ([100], [110], [111]).

As a next step, selected single crystals of GdCo_2 , DyCo_2 , HoCo_2 , ErCo_2 and TmCo_2 were investigated using specific heat, ac susceptibility and/or magnetization. To summarize the general results: the phase transitions in specific heat of HoCo_2 and ErCo_2 revealed clearly the first-order character. No anomaly, which could be associated with the paramagnetic transition, was found in any of the ac susceptibility

measurements confirming the previously published results²⁰. The values of saturated magnetization are lower than those expected for corresponding RE^{3+} ion which can be partially explained by taking into account the Co magnetic moments oriented antiparallel to the rare-earth moments in $RECo_2$ systems²⁶³. The remaining difference is given presumably by the CEF effects.



(a)



(b)

Fig. 70. The magnetization of $GdCo_2$ as a function of magnetic field for the principal crystallographic directions [100], [110] and [111]; the inset shows the detail of the magnetization curves in low magnetic fields (a). SEM image of a lamella cut from the $GdCo_2$ single crystal attached to the grid, by T. Thersleff (b).

GdCo₂

As the T_C exceeds 400 K, the magnetization measurements could be performed already in the ordered state only. Within the experimental accuracy, magnetization anisotropy measured along the [100], [110] and [111] axis (see Fig. 70(a)) is negligible being in line with literature²⁵³. The [100] axis is the easy axis and the spontaneous magnetization yields $5.2 \mu_B/\text{f.u.}$ at $T = 2 \text{ K}$ which is very close to the published value²⁵³. The saturated value for Gd^{3+} -ion is $7 \mu_B$; the difference is given by the Co moments $2.0 \pm 0.4 \mu_B$ per GdCo_2 which align antiparallel to the Gd moment²⁶³. Fig. 70(b) shows the SEM image of the lamella of $\sim 50 \text{ nm}$ thickness cut from the oriented GdCo_2 single crystal using the FIB technology. The lamella was used as a testing sample for successful detection of the EMCD signal from the $4f$ electrons²⁶⁰.

DyCo₂

Specific heat measured in various magnetic fields is shown in Fig. 71. The transition peak at $T_C = 143 \text{ K}$ is somewhat less pronounced than the one measured for polycrystalline sample²⁶⁴ unlike most of the other RECo_2 single crystals. With increasing magnetic field applied along the easy [100] axis, the transition temperature increases and the transition peak is smeared out gradually.

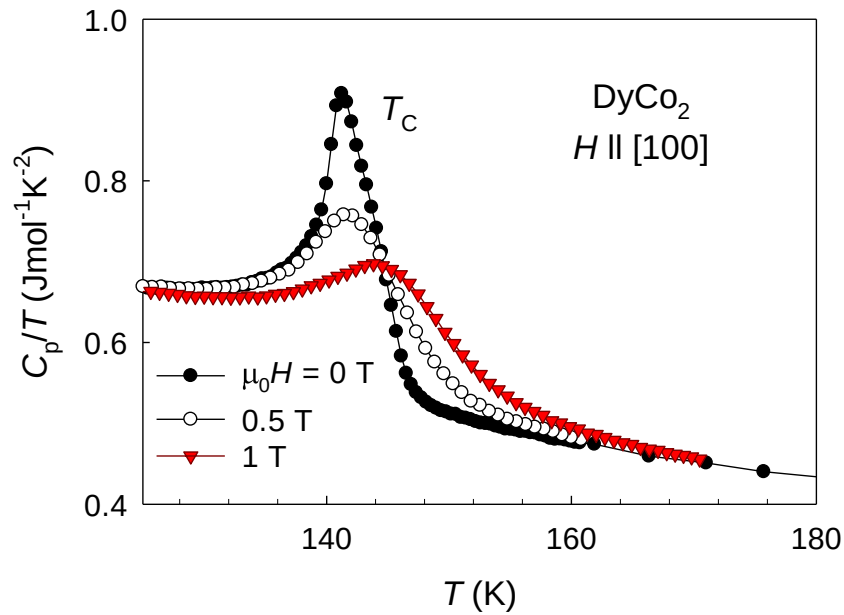


Fig. 71. The temperature dependence of specific heat of DyCo_2 for various magnetic fields oriented along the easy axis.

Measurements of the ac magnetic susceptibility (Fig. 72(a)) did not reveal any anomaly above T_C which could be ascribed to the presence of a paramagnetic transition in contrast to the results obtained on the polycrystalline samples^{20,249}. The [100] axis is the easy axis as shown in Fig. 72(b). The spontaneous magnetization in

the [100] direction yields $8.80 \mu_B/\text{f.u.}$ at $\mu_0 H = 5.5 \text{ T}$ which resembles previous results²⁵⁵. The suppression of the experimental value compared to the saturation value for Dy^{3+} -ion ($gJ = 10 \mu_B$) is given mainly by the Co magnetic moments which orient antiparallel to the RE moments²⁶³ and presumably by the CEF effects. In contrast to literature²⁵⁵, the magnetization along the [111] axis tends to saturate at values close to the magnetization along the [110] direction.

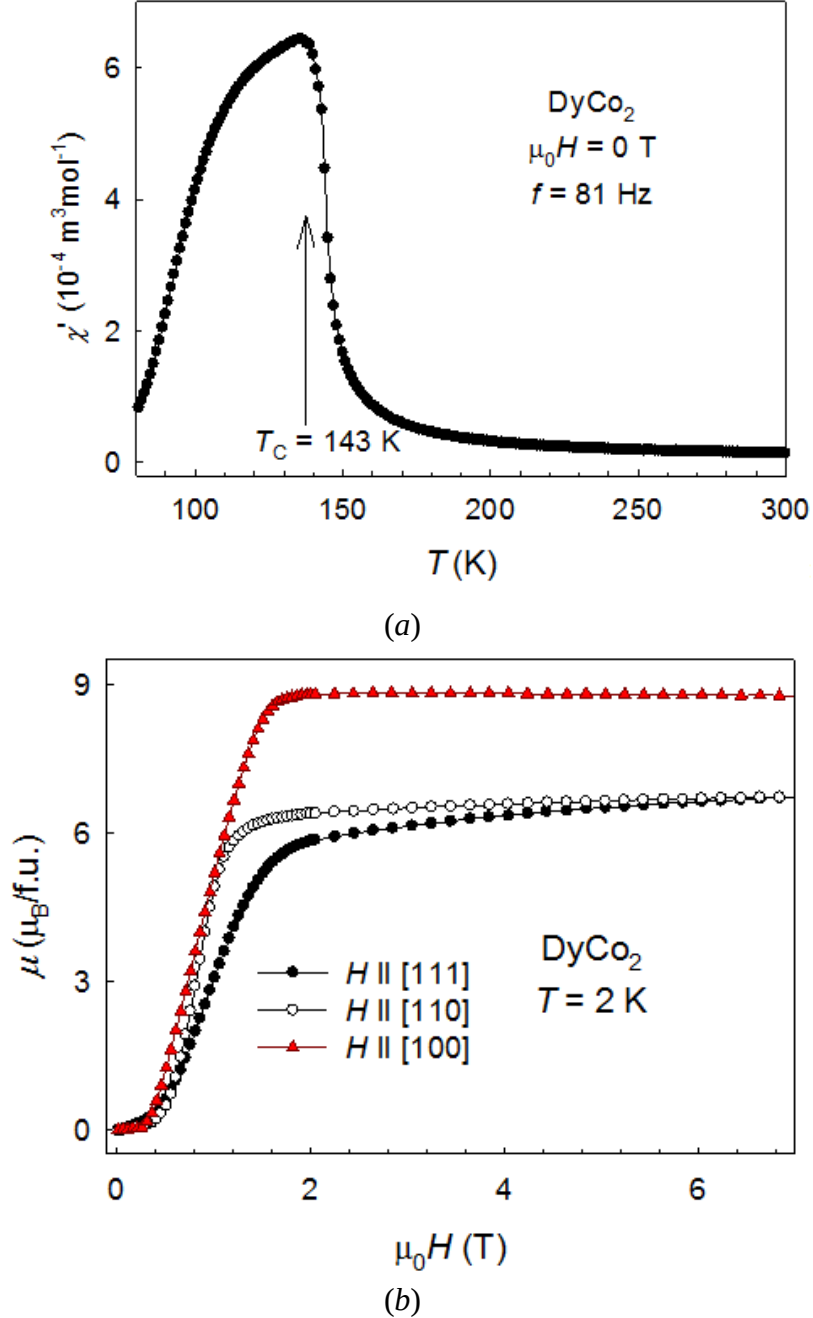


Fig. 72. The temperature dependence of the real part of the ac magnetic susceptibility $\chi'(T)$ of DyCo_2 for $f = 81 \text{ Hz}$ in the zero magnetic field (a). The magnetization of DyCo_2 as a function of magnetic field for principal crystallographic directions [100], [110] and [111] at $T = 2 \text{ K}$ (b).

This is probably caused by rotation of the sample inside the holder due to the large magnetic moments of Dy in increasing magnetic field; the stabilization of the sample position in certain directions was limited with respect to the shape of the crystals.

HoCo₂

Specific heat measurement in the zero magnetic field revealed that the HoCo₂ single crystal undergoes a first-order transition at $T_C = 82$ K which is followed by another transition at the reorientation temperature $T_R = 14.4$ K as shown in Fig. 73.

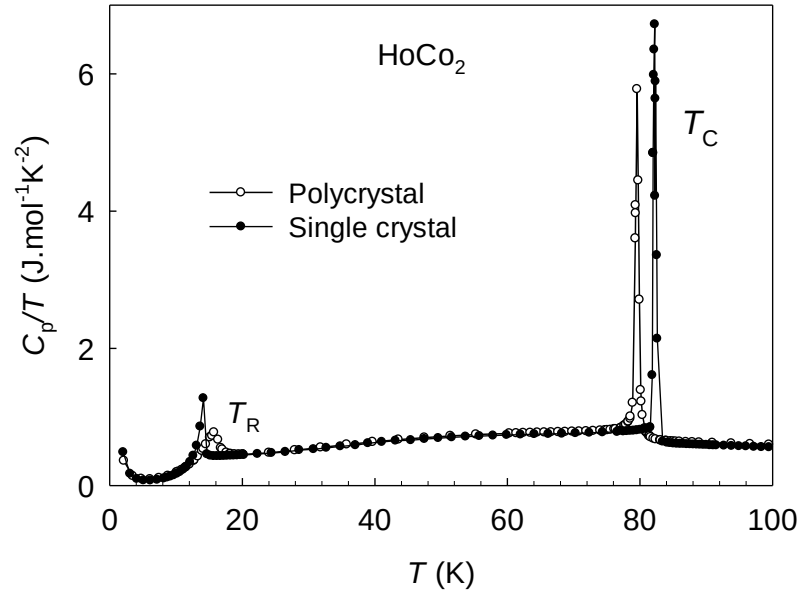


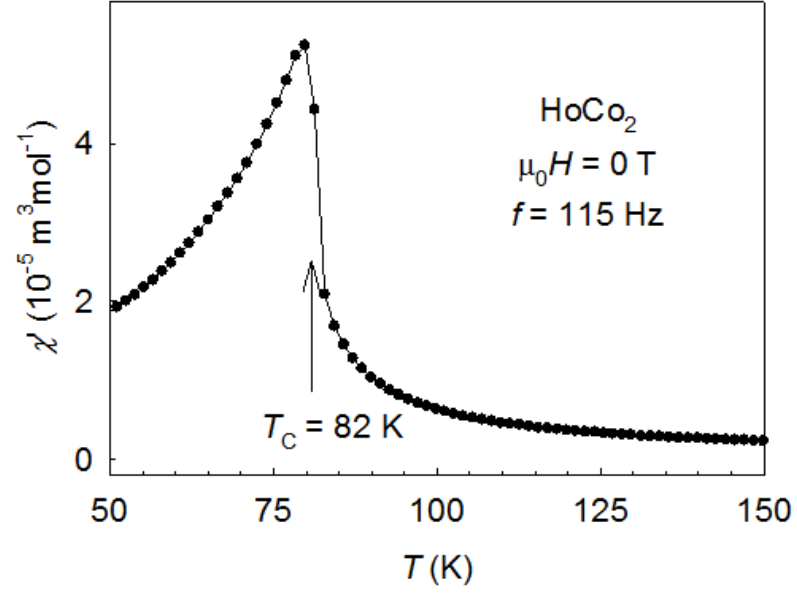
Fig. 73. The temperature dependence of specific heat in the zero magnetic field of the HoCo₂ single crystal and of a polycrystalline sample.

Below T_C and above T_R , the [100] axis is the easy axis; below T_R , the magnetic moments align in the [110] direction²⁶⁵. Measurements of the ac magnetic susceptibility (Fig. 74(a)) did not reveal any presence of paramagnetic transition above T_C similarly to the results obtained from the polycrystalline samples^{20,249}. The metamagnetic transition in the $M(H)$ data shown in Fig. 74(b) corresponds to the presence of transition at T_C . The spontaneous magnetization yields $8.4 \mu_B/\text{f.u.}$ at $T = 15$ K which confirms previous results²⁵³. The difference between the experimental and the saturation value for the Ho³⁺-ion ($gJ = 10 \mu_B$) is given by the Co magnetic moments of $1.0 \pm 0.2 \mu_B$ which orient antiparallel to the RE moments²⁶³.

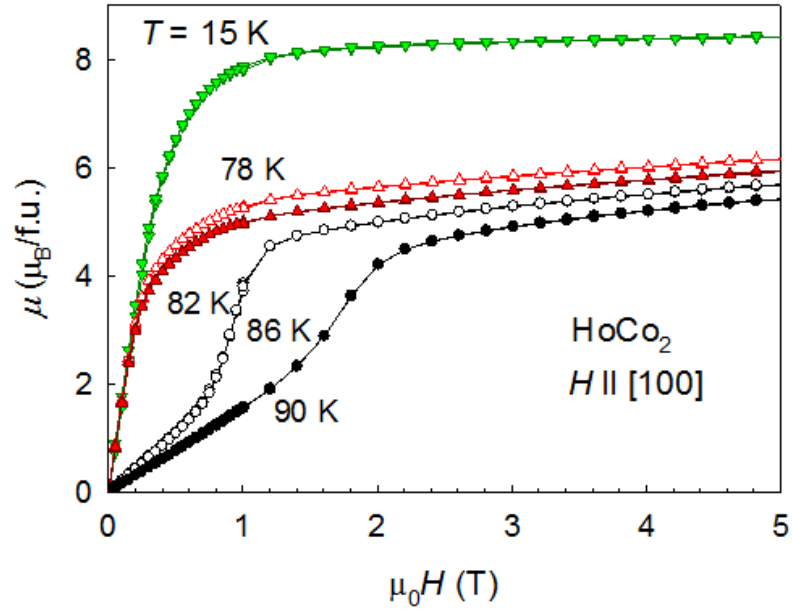
ErCo₂

The temperature dependence of the specific heat of the ErCo₂ single crystal was measured in various magnetic fields applied along the [111] direction which is the easy axis²⁵⁶. The first-order transition in the as-cast sample is clearly observed at

$T_C = 33$ K (see Fig. 75) in contrast to the Czochralski-grown samples²⁵⁸. With increasing magnetic field applied along the easy axis, the transition temperature gradually increases and changes its character to a second-order one.



(a)



(b)

Fig. 74. The temperature dependence of the real part of the ac magnetic susceptibility $\chi'(T)$ of the HoCo_2 single crystal for $f = 115$ Hz in the zero magnetic field (a); the magnetization of the HoCo_2 single crystal as a function of magnetic field oriented along the $[100]$ axis for temperatures above and below T_C (b).

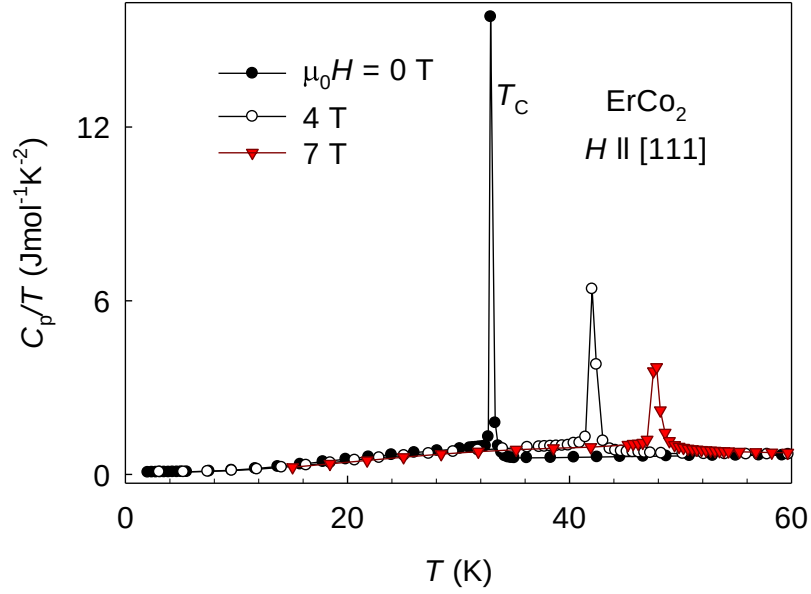


Fig. 75. The temperature dependence of the specific heat of the ErCo₂ single crystal measured in various magnetic fields applied along the [111] axis.

TmCo₂

Similar to the DyCo₂ single crystals and unlike the other flux-grown RECo₂ single crystals, the magnetic phase transition of the TmCo₂ single crystal does not reveal a sharp transition, although the Laue and microprobe analysis revealed high quality of the single crystal. Instead of the first-order character of the transition, a broad bump at $T_C \sim 4$ K was observed in the specific-heat curve, as shown in Fig. 76.

The specific-heat data are different also from the data obtained on polycrystalline material where clearly a first-order transition was observed²⁶¹. Therefore, our attention was focused on the Bridgman method using the induction-heating furnace. The specific heat of single crystals prepared by this method shows similar character of transition; however, the transition temperature is shifted to somewhat higher value $T_C \sim 5.5$ K. Similar to other RECo₂ single crystals, no anomaly reflecting a paramagnetic transition was observed in the ac susceptibility data (not shown).

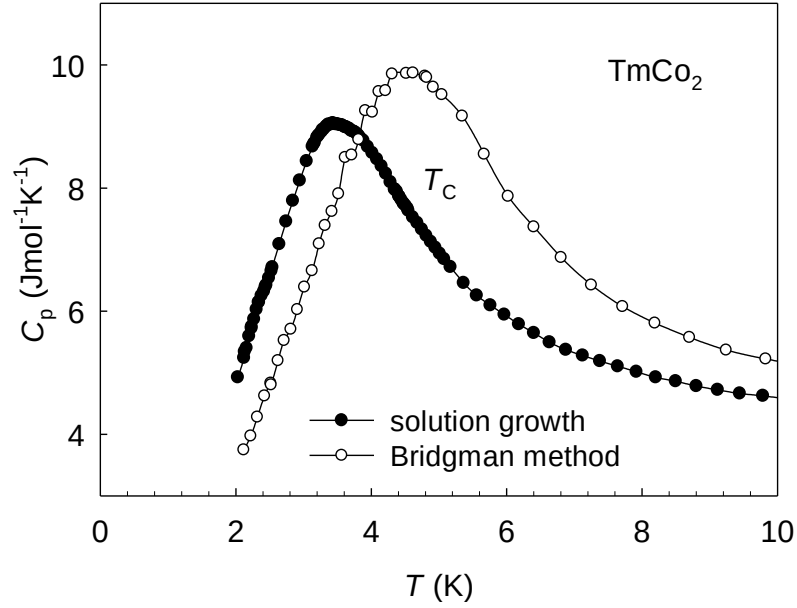


Fig. 76. The broad bump around T_C on the specific heat curve in the zero magnetic field of the TmCo_2 single crystal prepared from the Tm-Co flux and from the Bridgman method.

Summary

Generally, the anisotropic single-crystal bulk properties of RECo_2 ($\text{RE} = \text{Gd}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}$) compounds were not completely described yet although these materials have been studied for many decades^{253,254}. The growth from melt, which is traditionally used for their synthesis, faces several challenges such as intergrowth of foreign phases and sample-dependent properties^{254,258,261}. In the recent years²⁴⁸, new questions regarding the presence of the paramagnetic transition in poly- and single crystals have been discussed intensively. Moreover, the RECo_2 single crystals were suggested as candidates for an EMCD²⁵⁹ experiment using a transmission electron microscope in order to observe the signal from $4f$ electrons. All these facts motivated us to find an efficient way how to produce high-quality single crystals of these materials. As a result, single crystals of RECo_2 ($\text{RE} = \text{Gd}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}$) were prepared from RE-Co flux for the first time and their anisotropic physical properties were determined by means of magnetization and thermodynamic measurements. We have shown that the solution growth represents an alternative method to produce high-quality single crystals of RECo_2 compounds. Compared to samples prepared from melt, the flux growth of the RECo_2 single crystals (with the exception of ErCo_2 and TmCo_2) provides several advantages, such as lower amount of impurities, constant T_C independent on the parameters of the growth procedure and also other advantages which are typical for this method in general (see section 2.1). ErCo_2 and TmCo_2 turned out to be the most challenging systems within the RECo_2 family regarding the quality of the single crystals. However, first growth experiments

presented here reveal useful hints for the future attempts. The paramagnetic phase was not observed in any of the ac susceptibility measurements in accordance with literature²⁰. The single crystals of GdCo₂ and DyCo₂ were prepared via flux growth in order to be used for a specific experiment – performed for the very first time - a detection of the EMCD signal (performed by T. Thersleff, K. Leifer and J. Rusz at Uppsala University)²⁶⁰. The lamella of ~ 50 nm thickness cut from the oriented GdCo₂ single crystal using the FIB technology turned out to be suitable testing sample for a successful detection of the EMCD signal from 4f electrons. Future analogous experiments on DyCo₂ are in progress.

Thus, we can conclude that despite of many years of studying the *RE*Co₂ systems, it is still possible to contribute to this topic and to use these materials as a useful playground for testing new measurement techniques.