

Referee report on the doctoral thesis of Marie Kratochvílová, entitled:

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

This doctoral thesis concerns a comprehensive investigation of the physical properties of single crystals of the title compounds and of RECo₂ compounds with particular emphasis on novel ternary compounds of the type Ce_nT_mIn_{3n+2m} (n = 1, 2; T = Pd, Pt). These compounds display a most interesting variety of phenomena like complicated magnetic structures, non-Fermi liquid behavior and unconventional superconductivity coexisting with magnetic order, which are subjects of prime interest in present-day condensed-matter physics. The crystal structures of these new compounds can be considered as a stacking of n blocks of CeIn₃ and m blocks TIn₂ and therefore offer the possibility to study the influence of the dimensionality on the physical properties. In addition, the different structures possess inequivalent Ce sites giving rise to the occurrence of Ce ions with different ground states. The compounds Ce₃PdIn₁₁ and Ce₃PtIn₁₁ are particularly interesting because they constitute rare examples of Ce compounds in which magnetic order and superconductivity coexist. The physical properties of the prepared compounds have been determined in much detail by means of a large variety of most advanced experimental microscopic and macroscopic experimental techniques, including accurate measurements under simultaneous hydrostatic pressure and magnetic field. The experimental results are clearly presented and discussed in terms of state-of-the-art theory. The work constitutes a significant contribution to the field of research.

The study presented in the thesis has been carried out on single crystals grown by the solution growth technique. Since relevant ternary Ce-T-In phase diagrams are not available, this crystal growth was not an easy job and additional experiments like thermal-analysis (DTA/DSC) experiments have been carried out to decide about the most appropriate temperature ranges for the crystal growth. The quality of the prepared crystals has been thoroughly checked by means of X-ray diffraction and scanning electron microscopy.

It would be very much appreciated by the referee if the following comments and questions would be addressed:

Comment 1:

In Fig. 7 (Section 3.2.1), thermal-analysis results for the binaries Ce-In (2:25) and Pd-In (1:25) are presented. In Ce-In, a broad and large exothermic event occurs in the heating process around 270 C which is attributed to formation of Ce-In binary compounds which decompose at higher temperatures. The question arises which Ce-In compounds are formed because, on the basis of the phase diagram (albeit an equilibrium diagram), one would not expect anything else than CeIn₃ to be formed in a situation of excess In. Another question is whether it can be understood that a similar exothermic event is completely absent in Pd-In. In which form are the metals Ce and Pd present in the starting sample for the thermal-analysis measurement? Why have different compositions 2:25 and 1:25 been selected for Ce-In and Pd-In, respectively, and why such a large amount of excess In has been taken in both cases?

Intuitively, one would expect that, for an educated guess of the growth conditions of a crystal, the composition of the sample for thermal analysis should be rather similar to the composition of the crystal to be grown. Obviously, in case of solution growth, excess In is needed for solution and decanting purposes. In the growth results for the ternary Ce:Pt:In and Ce:Pd:In compounds, presented in Table 2, the various final products are listed, usually several for each batch. The question is whether, as one would expect, there is clear correlation between the Ce:T composition ratio of the amount of the main product of the batch and the Ce:T composition ratio of the thermal-analysis sample.

Although information from thermal analysis is limited, it seems that the Ce_2TIn_8 compounds form at a lower, but not much lower, temperature than the Ce_3TIn_{11} compounds. Because of the relatively small temperature range in which both types of compounds form, it seems important to choose rather precisely the most appropriate starting and decanting temperatures in the growth processes of these compounds. Would it be helpful in this matter to determine their melting temperatures, c.q. the decomposition temperatures?

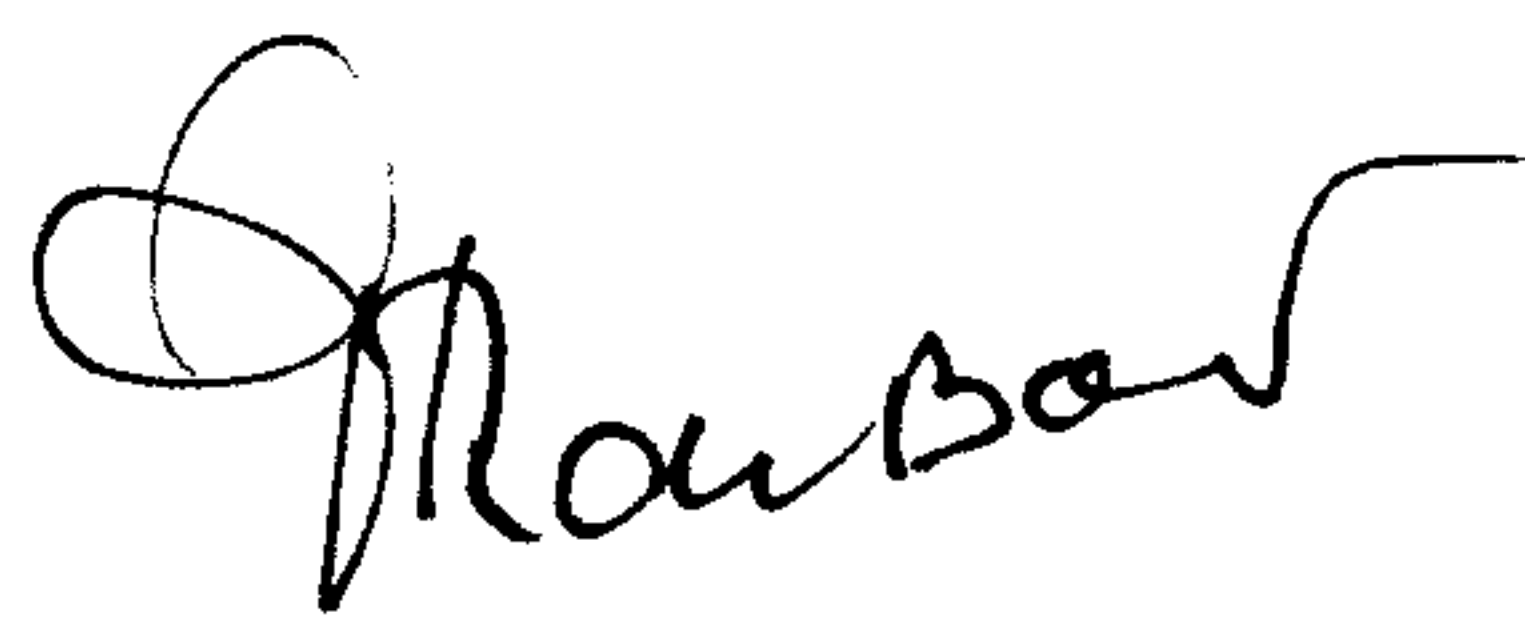
Comment 2:

In Fig. 18, results are presented of a CEF description of the temperature dependence of the susceptibility of Ce_3PdIn_{11} along the [100] and the [001] direction. The fit to the experimental data is very bad which is attributed to the simplifying assumption that the two Ce sites in this compound are equivalent. Despite the very bad fit, it is specified on p. 55 as an interesting detail that, in contrast to the measured susceptibility curves, the calculated susceptibilities for the two directions are crossing. In which respect is this crossing interesting? Is it more than a simply demonstration that the CEF calculations are not realistic?

Comment 3:

On p. 166, it is mentioned that the magnetic phase transition in the $TmCo_2$ crystal does not reveal a sharp peak in the specific heat although Laue and microprobe analysis have pointed out that the single crystal is of high quality. If broadening of a magnetic phase transition originates from insufficient quality of crystal, what kind of shortcomings of the quality should one think of and are these potential shortcomings all traceable with the analysis techniques used? If, like in the case of $TmCo_2$, there does not seem to be a lack of quality, which physics may be behind the broadening?

In conclusion, the interesting experimental work presented by Marie Kratochvílová in her doctoral thesis and the given theoretical interpretation, clearly demonstrate that she is able to carry out scientific research in an independent way. Marie Kratochvílová satisfies the requirements of the PhD degree.



F.R. de Boer

Amsterdam, 6 August 2015