Referee report on the doctoral thesis of Jana Vejpravova, entitled:

"Impurities in rare earth metallic systems: from super-purified metals to heavy-fermion superconductors".

In this doctoral thesis, an impressive amount of highly interesting research is reported on well chosen materials that are manifestations of the intriguing physics of rare-earth metals and rare-earth-based compounds.

The thesis starts with a general, but quite profound, theoretical introduction into the physics of the materials involved in the study presented in the thesis. After this, an overview is given of the variety of methods used in the preparation and characterization of the samples, usually in poly- or single-crystalline form. To this end, the Department of Condensed Matter Physics (DCMP) is state-of-the-art equipped with mono- and tri-arc furnaces, a splat-cooling apparatus and equipment for X-ray diffraction. It is well known that the physical properties of rare-earth metals may strongly be influenced by impurities. Therefore, purification of rare-earth metals is one of the important issues that are addressed in the present thesis. At DCMP a new-generation apparatus for solid-state electrotransport (SSE) is operational in which interstitial impurities like hydrogen, carbon, nitrogen and oxygen can be removed. In the thesis, the SSE treatment of the rare-earth metals Ce, Tb and Er is presented and discussed

The materials that have been investigated in the thesis are $CePt_3X$ compounds and their derivatives, and compounds of the type Ce-Ru-Si. The experimental results are presented and discussed in the context of, separately presented, results available in literature.

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

<u>Comment 1:</u>
In the SSE treatment of rare-earth metals, the purification is limited to interstitial impurities. In the thesis, it is mentioned that SSE treatment of the starting materials is sometimes beneficial for the stabilization of compounds during the growth of an ingot (pages 155, 191). Is this the main advantage of the SSE treatment of the starting rare-earth metals? Or are also examples known of impurities, that can be removed by SSE, that have undesired influence on the physical properties of the rare-earth metals or on the rare-earth compounds to be prepared?

<u>Comment 2:</u>
The inelastic-neutron-scattering experiments performed on $CePt_3Si$ by Metoki et al. [285] show peaks at 1 meV and 24 meV from which it is concluded that the six-fold degenerate 4f-levels are split into three doublets, a ground state with first and second excited levels at 1 meV (~ 10 K) and 24 meV (~ 240 K). This result is largely, and also fundamentally, different from the level scheme proposed in the thesis (p. 193), that has been derived from the Schottky contribution to the specific heat and that consists of a ground-state singlet with a higher singlet at 11 K and two higher doublets at 80 K and 160 K. The

latter level scheme seems to violate Kramers' theorem which, as mentioned on p. 25, states that a doublet is the lowest possible degeneracy in a system with an odd number of electrons. The same apparent violation of Kramers' theorem concerns the level scheme for $CePt_3B$ (p. 159) that is proposed consist of a ground-state singlet with a higher singlet at 5 K and two higher doublets at 80 K and 120 K. Does a proper fit to the Schottky contribution of these two compounds particularly require that the two lowest levels are singlets and rule out a doublet as ground state? What does a fit with Metoki's level scheme look like?

Comment 3:
Figure 8.4a shows that the two anomalies at 7 K (T_N) and at 5 K (T_C) in the specific heat of an as-cast $CePt_3B$ sample turn into one anomaly at 6 K (T_N) after annealing, suggesting that annealing is needed for obtaining single-phase material. Is this conclusion correct? Qualitatively consistent with the result on the as-cast sample, the measurements in applied magnetic fields on the unannealed sample D/2, shown in Fig 8.6a, also exhibit two anomalies, a λ-type anomaly at 7.8 K (T_N) and a shoulder at about 6 K (T_C). The field dependence of the specific heat is intriguing, showing a distinct enhancement of the λ-type anomaly at 2 T. Can this originate from the opposite effects of the applied field on the T_C- and T_N?
The negative magnetic entropy in all applied fields (Fig. 8.7b) indicates that, except at very low fields, the ordering in $CePt_3B$ is predominantly ferromagnetic. This seems very similar to the situation for Tb (p. 88).

Comment 4:
In Fig. 9.2b it is shown what the corrected specific heat of $Ce_{35}Ru_{58}Si_7$ (sample S6) looks like if the huge peak at 6 K is attributed to Ce-oxide. After this correction, a broad maximum remains which casts doubts on the otherwise seemingly very realistic assumption of the presence of Ce-oxide. Have experimental results on Ce-oxide been used in this subtraction? Is it possible to estimate whether the amount of Ce-oxide established in the correction is realistic? Have the measurements presented in Fig. 9.2c been pursued to above 6 K to study the field dependence of the anomaly in some detail? In view of the composition of sample S6, as listed in Table 9.2, assignment of the peak at 6 K to an off-stoichiometric $CeRu_2Si_2$ phase seems less realistic.

Comment 5:
The referee agrees with the conclusion in Chapter 10 that study of the effect of dimensionality on phenomena in strongly-correlated-electron systems will be of large interest. What is precisely meant with the stagnancy in the SCES-related research and how will this fundamentally be solved by extending the research to the nanoregime?

In conclusion, the interesting experimental results presented by Jana Vejpravova in this doctoral thesis and the theoretical interpretation that she has given, clearly demonstrate that she is able to carry out scientific research in an independent way.