Referee report on the PhD thesis of Mgr. Jan Fikáček

Physical phenomena in ytterbium- and cerium-based compounds

Mgr. Jan Fikáček studied magnetic and related electronic properties of three new or not properly studied ternary intermetallic compounds of f-electron elements, Ce and Yb. Such materials exhibit, as a rule, very large anisotropy of magnetic and other physical properties. For this reason, high-quality single crystals are needed for collection of reliable quantitative data. The compounds selected for the study are CeRuSn, YbPt₂Si₂ and Yb₂Pt₃S₅. The work deals first of all with rather sophisticated preparation of single crystals by different methods. Then the crystals were studied using magnetization, specific heat, X-ray diffraction, thermal-expansion and electrical-resistivity measurements including application of high external pressure.

Mgr. Jan Fikáček focused his main research efforts on investigation of unusual appearance of several polymorphic phases of equiatomic ternary intermetallic compound CeRuSn. This material is characterized by specific valence states of each of the inequivalent Ce lattice sites. To enable measurements of intrinsic properties he has developed reliable technology for reproducible preparation and characterization of CeRuSn single crystals. His single crystals are the only high quality CeRuSn single crystals available in the world. By careful single crystal XRD analysis he has demonstrated how different Ce valence states relate to different Ce-Ru interatomic distances. In his work he has proposed that the largest Ce-Ru distance allows for the magnetic Ce³⁺ valence state, whereas the short Ce-Ru distances lead to non-magnetic Ce³⁺-Ce⁴⁺ mixed valence or the tetravalent state.

The experiments with CeRuSn single crystals were performed in great detail in two temperature ranges:

- 1) 120-350 K, where he studied anomalies of several physical properties associated with polymorphic transitions from one phase to another for which the microscopic explanation lies in variations of the valence of Ce ions in different crystallographic positions.
- 2) low-temperatures (< 10 K) related to stable antiferromagnetic arrangement of moments of one third of Ce ions which are trivalent, which agrees with the proposed model.

By these results Mgr. Jan Fikáček contributed significantly to the understanding of the microscopic nature of a number of anomalous phenomena in this compound. His publications on CeRuSn in Physical Review B and Journal of Physics: Condensed Matter are therefore positively cited in publications from foreign institutions focused on the physics of CeRuSn.

Very interesting are also the results showing the effect of external pressure on the critical parameters of CeRuSn and magnetism and magnetoresistance behavior associated with metamagnetic transitions at temperatures below 1 K. These results are valuable in the dissertation and are subject of upcoming publications.

In addition to the main part on CeRuSn, the dissertation also presents the results on YbPt₂Si₂ and Yb₂Pt₃S₅. Yb₂Pt₃S₅ was discovered by the author and YbPt₂Si₂ which is representative of a wide isostructural series of f-metal intermetallics was studied on single crystals for the first time. Both compounds are paramagnetic.

The thesis consists of 111 pages. It has Introduction, description of experimental methods used in the work, 3 chapters with original results, Summary, Appendix and List of references. It contains 62 figures, 11 tables and 73 references. After the Introduction, the author gives a theoretical background of the phenomena considered in the original part of the thesis (Chapter 1). The chapter provides an adequate introduction for further interpretation of the obtained results. The experimental techniques and details of measurements are described in Chapter 2. The main part of the thesis is formed by Chapters 3 (CeRuSn), 4 (YbPt₂Si₂) and 5 (Yb₂Pt₃S₅), containing the original results.

After critical reading of the thesis, I have several remarks and questions to the author. Most of them are connected with Part 3.4.1., magnetization of CeRuSn, and are related to each other.

- 1. Magnetization was measured up to 14 T. After the low-field metamagnetic transitions, the magnetization curves along the a and b axes do not practically tend to approach the highest curve along the c axis. This reflects very large magnetic anisotropy. One can expect additional field-induced transitions along the a and b axes in higher fields. Did you check such a possibility or do you plan to check it?
- 2. Moreover, even along the c axis which you consider as the easy axis, one can expect an additional transition. The obtained in 14 T practically saturated value 0.7 μ_B is very important in the work because it is compared with single-ion moment of Ce^{3+} 2.1 μ_B . From their ratio, a conclusion about concentration of Ce^{3+} states in the compound is made. But it is valid if the state at 14 T is forced collinear ferromagnetic. If it is still non-collinear, which is possible in such a complicated crystal, the magnetic moment and, consequently, concentration of Ce^{3+} states, is underestimated. Even if the state is already collinear ferromagnetic, one cannot exclude the appearance of an additional transition along the c axis. In this case it will

reflect field-induced change of the valence from non-magnetic 4+ to magnetic 3+ for the

major part of Ce ions. So, again, did you check such a possibility or do you plan to check it?

3. Did you measure magnetization within the (ac) plane between the a and c axes? I can

treat the values of magnetization above the metamagnetic transitions as projections of the

magnetic moment on the main axes. In such a case, it can be calculated that the easy

magnetization direction deviates by 35 degrees from the c axis and the magnetic moment is

 $0.85 \mu_B$, noticeably larger than along the c axis, which leads to a correction of the

concentration of 3+ states.

I have found some misprints and other minor errors in the thesis but their number does

not exceed an acceptable level. Examples: a) Page 77, second line of second paragraph. It is

written "The samples from growths PS1 and PS2 contained a non-negligible amount of YbAs

in their bottom parts most probably originating from contamination of alumina crucibles". I

hope there should be YbAl, not YbAs? b) List of references is not formatted in the same style

(initials before or after surnames, with and without titles of articles).

In conclusion, the work represents an extensive experimental study with many

interesting results. I think that the author, Mgr. Jan Fikáček, satisfies the requirements of the

PhD degree.

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