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Referee report on the doctoral thesis
"Electron properties of the substituted ceriumcompounds“
by Mr. Milan Klicpera

This thesis concerns the physics of cerium based strongly correlated electron systems which attracts current interest due to the rich variety of phenomena emerging from the competition between various types of cerium on-site and cerium-cerium inter-site interactions, i.e. on-site Kondo correlations between 4f and conduction electrons as well as crystal field (CF) effects and inter-site RKKY-type interactions. These interactions involve essentially spin, orbital and charge degrees of freedom. In $CeAl_2$, and only a very few other cases, an additional distinct coupling of orbital and lattice degrees of freedom has been revealed. The focus of the present thesis is the experimental investigation of two such cerium systems, $CeCuAl_3$ and $CePd_2Al_2$, displaying excitations arising from a coupling of localized CF excitons and dispersive phonon modes. This topic is of great relevance and of high actuality for a deeper understanding of strongly correlated electron systems with multiple interacting degrees of freedom and their emerging multifunctional physical properties.

The first part of the thesis comprises three chapters with a detailed description of theoretical concepts and experimental techniques applied in this work as well as a status of preceding research. In the latter, a description of the CF exciton-phonon phenomena observed for $CeAl_2$ and $CeCuAl_3$ is provided.

The main part of the thesis is devoted to the original research which is based on an impressive variety of experimental techniques comprising material preparation and crystal growth, basic characterization by X-ray and microprobe studies, macroscopic bulk studies of physical properties such as resistivity, specific heat and magnetic measurements, and finally microscopic neutron scattering studies carried out on poly- as well as single crystalline samples using quite a number of different instruments.

New and highly relevant scientific results presented in the thesis are first of all the neutron scattering and diffraction studies of the magnetic structure of $CeCuAl_3$ presented in chapter 4.1. Resolving a complex magnetic structure of partially Kondo screened magnetic moments is a rather challenging task and preceding attempts on $CeCuAl_3$ did not yield reliable results. Combining neutron data collected in the present work at several different instruments, the antiferromagnetic order of $CeCuAl_3$ is successfully assigned to an amplitude modulated structure with in-plane orientation of the magnetic moments. This result is further discussed in a broader context of relations between parameters of the crystallographic and magnetic structures of related CeTX_3 type compounds. Another new and clearly relevant scientific result relates to the CF exciton-phonon coupling in $CeCuAl_3$ which is studied by means of macroscopic bulk techniques as well as inelastic neutron scattering on $CeCuAl_3$ and off-stoichiometric isostructural solid solutions $Ce(Cu,Al)_4$.

The second focus of the thesis is on $CePd_2Al_2$, $CePd_2Ga_2$, and their solid solutions $CePd_2(Al,Ga)_2$. Remarkable new results are again the analysis of magnetic neutron diffraction data providing insight on the magnetic structures of $CePd_2Al_2$ and $CePd_2Ga_2$, but most importantly a study of the interrelation between CF effects and the orthorhombic to tetragonal structural phase transition of these compounds as well as search for excitations related to CF-phonon coupling. The latter is confirmed for $CePd_2Al_2$. Important to mention, in particular with respect to these $CaBe_2Ge_2$ type compounds, is a significant amount of additional, successfully published, related work.

To summarise, Milan Klicpera demonstrated with this thesis his ability to perform creative scientific work. He is a very active and successful researcher and combines the ability to find appropriate research concepts, the experimental skill to obtain high-quality results and the ability to apply proper theoretical concepts for the interpretation and modelling of the experimental results and thus provided a deeper understanding to the community with his work.

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Questions:

1) In chapter 4.1.6, it is demonstrated for solid solutions $Ce(Cu,Al)_4$ that any off-stoichiometric composition away from $CeCuAl_3$ results in a marked change of the CF scheme (increase in energy of the first excited doublet). What is the role of a possibly randomized reduction of the local point symmetry of cerium ions due to substitutional disorder?

2) In chapter 4.1.4, an in-plane oriented and in-plane amplitude modulated magnetic structure is revealed for $CeCuAl_3$ and it is further demonstrated that the magnetic structure formation relates to in-plane nearest neighbour and out-of-plane next nearest neighbour Ce-Ce distances. The difference between these two parameters seems largest for $CeCuAl_3$. So, could quasi-2D dimensional frustration be responsible or at least co-responsible for the reduced entropy gain at T_N, in particular when considering the absence of a specific heat T-linear term in Fig. 4.23? What experimentally observed features would be in favour of dimensional frustration?

3) How does the expected (model calculated) entropy jump resulting from the switch of level schemes (0,8,16 to 0,1.4,16) at the structural transition of $CePd_2Al_2$ at 13 K correspond to the experimentally measured one? What is the corresponding fraction of orbital and lattice entropy changes?

4) What other experimental studies and techniques (apart from those used in course of this thesis work) could be suited to obtain new and complementary information on CF-exciton-phonon and CF to lattice couplings?