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Magnetyczne diagramy fazowe niecentrosymetrycznych układów $CeCo_{1-x}Fe_xGe_3$ i $Ce_{1-x}Pr_xCoGe_3$ – wpływ elektronów $3d$ i $4f$

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Abstract

Strongly correlated electron systems are the subject of research in many renowned scientific centers. These materials include metallic compounds and alloys containing lanthanides or actinides. Hybridization of f-electrons with conduction electrons causes the occurrence of physical phenomena like: the heavy fermion state, fluctuating valence, quantum critical point, and heavy fermion superconductivity. The competition between RKKY and Kondo interactions is a vital factor in the appearance of the specific physical phenomena. The energies of these interactions can be controlled by external hydrostatic pressure, applying magnetic field, or by modifying the chemical composition.

The main aim of this PhD thesis was to examine the influence of the substitution of the $3d$ element on the physical properties in the $CeCo_{1-x}Fe_xGe_3$ system and the $4f$ element in the $Ce_{1-x}Pr_xCoGe_3$ series. Both of these series are based on the well-studied antiferromagnetic $CeCoGe_3$ compound. The second parent compounds of these series are: $CeFeGe_3$, characterized as a heavy fermion, and $PrCoGe_3$, a paramagnet with a low value of the electronic specific heat coefficient γ. All studied compounds and alloys were single-phase and crystallized in the non-centrosymmetric tetragonal $I4mm$ $BaNiSn_3$-type structure. Due to similar masses and ionic radii of the substituted elements, the influence of the chemical pressure is very small, and the observed evolution of the physical properties is mainly connected with changes of the electronic structure.

Polycrystalline samples of both series were prepared using the induction and arc furnaces. In this dissertation the following physical properties were examined: magnetic susceptibility, specific heat, electrical resistivity, magnetoresistance, and Seebeck coefficient. The crystal structure was verified using the X-ray diffraction method. Information on the electronic structure was collected from the X-ray photoelectron spectroscopy (XPS) experiment and supplemented by the first-principles calculations. For selected samples of the $CeCo_{1-x}Fe_xGe_3$ series the inelastic neutron scattering measurements were performed.

The $CeCo_{1-x}Fe_xGe_3$ system reveals suppression of the magnetism with the increase of the Fe concentration. This was shown in the measurements of magnetic susceptibility, specific heat, electrical resistivity, magnetoresistance and Seebeck coefficient. For concentrations of Fe $0.5 \leq x \leq 0.7$, at low temperatures, all these experimental methods indicated the possible non-Fermi liquid (NFL) behavior. Measurements of the electrical resistivity down to 500 mK confirmed the possibility of the occurrence of the quantum critical point for the stoichiometry close to that of the $CeCo_{0.4}Fe_{0.6}Ge_3$ sample. Inelastic neutron scattering measurements carried out for this alloy indicated different values of the splitting of the Ce ion ground state by crystal electric field depending on whether the region was richer in Co or in Fe. This observation might explain the variable nature of the magnetism for Fe concentration $x \leq 0.4$.

Fitting of the magnetic susceptibility results with the Curie-Weiss law and XPS measurements indicated the stable oxidation state Ce^{3+}. The electronic structure evolves near the Fermi level with the increasing Fe content. The first-principles calculations revealed that it is related to the shift of the $3d$ states towards the Fermi level. Considering magnetic phase diagram proposed within this dissertation for the $CeCo_{1-x}Fe_xGe_3$ system and referring to the Doniach diagram, we can conclude that the increase in the Fe content increases the values of $|JN(E_F)|$ and for a specific concentration we can expect an appearance of the quantum critical point.

For the $Ce_{1-x}Pr_xCoGe_3$ series, the suppression of the magnetism and Kondo interaction is observed with the growing Pr concentration, therefore this substitution causes the decrease of the $|JN(E_F)|$ values. The NFL behavior was not observed. The magnetic structure of $CeCoGe_3$ is preserved, which indicates non-interactive character of the Pr ions in the context of magnetism of the studied samples. Similarly as for previous literature reports on the $PrCoGe_3$ compound, also our XPS measurements and first-principles calculations suggest negligible contribution of Pr $4f$ electrons to the conduction band. Therefore, by studying the $Ce_{1-x}Pr_xCoGe_3$ system, the role of hybridization of f-electrons with the conduction band is exposed. The non-interactive natu-

re of the Pr $4f$ electrons might be related to the significant influence of the crystalline electric field on the physical properties in the temperature range of $10 - 30$ K.