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Monokryształy i nanocząstki wybranych manganitów i kobaltytów – wytwarzanie oraz właściwości magnetyczne

The subject of PhD thesis is "Single crystals and nanoparticles of selected manganites and cobaltites - preparation and magnetic properties". Examined manganites and cobaltites crystallize in the perovskite structure. They can be describe by the general formula $A_{1-x}D_xBO_3$ where A - is a lanthanide ion such as La, D - alkaline earth ion such as Ca, B - Mn ion in the case of manganites or Co ion in the case of cobaltites. The x determines the concentration of the alkaline-earth ions substituting lanthanide ions. These compounds have been studied widely in the last decade because of their colossal magnetoresistance properties. During the study a rich phase diagram of these materials was constructed. In manganites and cobaltites the magnetic ground state significantly depends on the composition. Several types of magnetic, orbital and charge ordering were observed in these materials as a result of strong competition of various types of interactions. In the case of bulk of mono- and polycrystals samples ferromagnetic (FM), antiferromagnetic (AFM), ferromagnetic metal (FMM), ferromagnetic insulator (FMI) or a spin-glass type (SG) phase was observed. When the size of the magnetic nanoparticles is reduced to few nanometres, some of their basic magnetic properties, e.g., the spontaneous magnetization, the Curie temperature, and the coercivity, are strongly influenced by the particle size and may differ significantly from the bulk properties. As the particle size decreases, the surface and interface effects become more and more important. The presence of defects, broken bonds, fluctuations in number of atomic neighbours and interatomic distances, results in topological and magnetic disorder at the surface and may cause a decrease in the magnetization value. For various manganite nanoparticles of few tens of nanometres size, a core-shell structure was proposed. In this model the inner part of the particle, i.e., the core, has the same properties as the bulk material, whereas the outer layer, namely, a shell with a width of *t*, contains most of the oxygen faults and vacancies in the crystallographic structure, leading to a magnetically dead layer. It is a quite well established that the relative shell thickness t increases with the decrease in grain size. Reducing the particle size of ferro - or ferrimagnetic below a certain critical value will lead to the single domain structure. This lead to new types of magnetic phases such as super- ferromagnetism (SFM), super spin glass (SSG) or super paramagnetic (SPM).

In the work the process of obtaining polycrystals, single crystals and nanomaterials of compounds $La_{1-x}Ca_xMnO_3$ (LCMO) and $La_{1-y}Ca_yCoO_3$ (LCCO) was described. In the case of polycrystals all steps of solid state synthesis are described. Single crystals were grown using two methods. For the crystallization LCMO electrolysis was used. The crystallization process was applied from flux Cs_2O - MoO_3. Single crystals of LCCO were obtained using the floating zone method. The nanocrystalline samples were prepared by the citrate method. Structur and composition of all samples ware characterized using X-ray powder diffraction, electron scanning microscope and transmission electron microscope.

Magnetic properties of single crystals, poly- and nanocrystalline LCMO and LCCO samples were measured with Ca concentration x = 0,05, 0,23 and 0,8 for LCMO and x = 0,08, 0,18 and 0,2 for LCCO. Particle size of nanocrystalline manganites were 15, 20, 23, 30 and 37 nm and nanocrystalline cobaltites were 8, 13, 22 and 50 nm.

It was found that the oxygen parameter is very important in LCMO samples. Oxygen parameter affects the magnetic properties as calcium concentration. Annealing in high temperature in Ar flow can change oxygen parameter. Effect of single crystals annealing on the magnetic properties was examined. To describe magnetic properties of nanocrystalline LCMO with x = 0,8 core-shell model was used with AFM core and FM shell. The FM phase was observed below T_C = 100 K. The exchange bias effect and transition from multidomian to single domain structure was observd for 20 - 23 nm nanocrystals.

It was found that FM state and effective magnetic moment of the cobalt ion are very sensitive on nanocrystalline size reduction. This effect is particularly visible in reducing particle size from 23 nm to 8 nm. It was shown that thickness of magnetic "dead" layer increase when nanoparticles size was reduced. Transition from multidomian to single domain structure was also observd for 22 nm nanocrystals. Concentration of Co ion in low-spin (LS) and intermediate-spin (IS) state was determined in temperature range 230 - 320 K based on effective magnetic moment research. It was shown that amount of cobalt ions in IS state decrease with decreasing particle size. It was found typical for super paramagnetics or spin glasses phenomena in 8 nm nanoparticles in ac magnetic susceptibility measurement.

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