Structural properties of magnetic nanoparticles

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The basic magnetic properties of nanoparticles have been intensively studied and the influence of the small (nano) size on the magnetic properties is generally well understood. However, the magnetic properties of mixed-oxide nanoparticles depend on the size of particles not only directly, but also indirectly, through the influence of the small size on the structure of nanoparticles.

It is known that the structure of nanoparticles is more flexible compared to the "bulk" structure. Usually, it adapts to the small size and the large surface-to-volume ratio resulting in distribution of atoms over different lattice sites that is significantly different to that of the bulk material. Additionally, defects are usually present in the structure of the nanoparticles.

Different aspects of the deviations in the structure of nanoparticles from the ideal "bulk" state will be discussed in the cases of two structural types of magnetic nanoparticles: spinel ferrites ($ZnFe_2O_4$, $Mn_{0.5}Zn_{0.5}Fe_2O_4$, $CoFe_2O_4$) and hexagonal ferrite (hexaferrite, $BaFe_{12}O_{19}$).

In the spinels, the deviation of the nanoparticles crystal structure from the bulk situation expresses itself mainly with different distribution of the constituting cations over two different lattice sites existing in the structure (tetrahedrally coordinated A sites and octahedrally coordinated B sites). In the case of hexaferrites, the exchange of two cations, Ba and Fe over different lattice positions is not likely. A hexaferrites' crystal structure can be described as a stacking sequence of two basic blocks, a spinel block S, containing Fe cations, and the block R, containing Fe and Ba cations. Here, the adaptation of the crystal structure to the small nanoparticle size by the change in the stacking of the two structural blocks is expected.

The flexibility in the nanoparticles crystal structure results in a flexibility of the nanoparticles' chemical composition, allowing large compositional deviations from the bulk stoichiometry without losing the single-phase structure. Depending on the method used for their synthesis, the nanoparticles also differ in the state of their crystallinity.

The small spinel ferrite nanoparticles of controlled sizes could be relatively simply prepared already at low temperatures. In this work, two methods were used: a co-precipitation in reversed microemulsions and a thermal decomposition of the corresponding oleates. In contrary to spinel ferrites, relatively high temperatures are needed for the formation of hexaferrites making their controlled synthesis in the form of the small nanoparticles relatively difficult. Special hydrothermal methods were used for their synthesis in this work.

The structure of the nanoparticles has been studied using X-ray diffractometry (XRD), high-resolution electron microscopy (HREM) coupled with energy-dispersive X-ray spectroscopy (EDX), and X-ray absorption spectroscopy (EXAFS, XANES) measured at E4 beamline of synchrotron radiation laboratory HASYLAB at DESY, Hamburg (project II-04-065 EC) under EU Contract RII3-CT-2004-506008 (IA-SFS).

Figure 1: HREM image of the hexaferrite nanoparticle.