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Abstract

Development of structure and magnetism in ferrite nanoparticles studied during growth by high-resolution x-ray spectroscopy

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At the beginning of the 21st century, humanity achieved spectacular successes associated with the use of nanotechnology, especially in the fields of electronics and biotechnology. Unfortunately, the precision and control over procedures in these fields have not yet translated into all branches of nanotechnology. The development of techniques is limited due to, among other things, alterations of the characteristics of materials known for a macro scale, high costs and demands for advanced research techniques, and undesirable effects at the borders between phases. Some of these phenomena can be harnessed to provide the main advantages of nanoscale technology. Magnetic particles are a fitting example, as their magnetic moments can be thermally agitated by thermal fluctuations that occur frequently below a particular size, leading to the disappearance of coercivity and high susceptibility, without losses during magnetization reorientation (superparamagnetism). Similarly to non-magnetic nanoparticles, their surface can be functionalized to serve as a catalyst or for the transport of other substances, however they can also be steered with the use of an external magnetic field with relative ease. Additionally, such particles can be heated by interaction with an external field, which is used in magnetic hyperthermia therapy, or act as a contrast agent in magnetic resonance imaging, thus increasing their potential in targeting and destroying cancer tissue. In some applications it is important to reduce the size as much as possible, but this also worsens the magnetic properties of the particles. Below a size of a few nanometers, the ordering of internal magnetic moments can completely disappear.

The presented thesis addresses the issue of limiting size for the disappearance of superparamagnetism in nanoparticles and discovering its causes through research conducted on the products of the synthesis of magnetite and cobalt ferrite nanoparticles. The study also related to the problems of reaction kinetics, changes during storage of the samples, measurements of particles size and measurements of magnetic properties.

In this work, resonant inelastic X-ray spectroscopy in conjunction with magnetic circular dichroism (RIXS-MCD) is proposed for a comprehensive study of the structure and magnetism of magnetic nanoparticles. In 1s2p RIXS-MCD technique for transition metals, emission in the vicinity of Kα emission lines upon excitation on the K edge is studied. The use of high-energy photons allows for the examination of the selected metal in the volume of the entire nanoparticle, which may be suspended in any system transparent to X-rays. The strong MCD effect allows to study the magnetism of the selected metal. This technique has proven effective for research performed on small amounts of materials, solutions, nanostructures, and composites. In this work, as a challenging example of RIXS-MCD application for magnetic nanoparticles, the *in-situ* study of ongoing synthesis of magnetic nanoparticles was chosen.

Studying particles has the advantage that they do not undergo modification over time between the synthesis and examination through processes such as aging, contact with the environment, or due to sample preparation in accordance with requirements of *ex-situ* examination techniques. The synchrotron research was paired with laboratory techniques, mainly allowing for the determination of particles size distribution (TEM, SAXS), magnetic properties (VSM, Mössbauer spectroscopy) and an analytical method allowing for deconvolution of spectra into main components and their concentrations (MCR-ALS).

The conducted RIXS-MCD synchrotron experiments and *ex-situ* studies allowed for a comprehensive analysis of the development of structure and magnetism in growing nanoparticles. The synthesis begins with the formation of clusters with impaired structure compared to perfect magnetite, with an overabundance of iron ions in the octahedral sites. The produced nanoparticles initially exhibit deficiency in local ordering, mainly in tetrahedral sites, with developed long-range ordering characteristic for the spinel. With the proposed model of magnetism growth, it was assessed that within magnetite nanoparticles the magnetic ordering appears abruptly upon crossing limiting size of about 4.5 nm. It was associated with the increasing occupation of tetrahedral sites characteristic of magnetite by iron ions. Magnetite nanoparticles do not display coercivity, even at cryogenic temperatures.

The produced ferrite cobalt was proven to be non-stoichiometric and has a disrupted atomic structure, but the disappearance of magnetism in particles larger than fractions of nanometer has been ruled out. The nanoparticles have high coercivity, exceeding 0.25 T at a temperature of 80 K. The growth of magnetism is limited mainly by the rate of spinel structure formation, which is twice as fast as in magnetite synthesis, despite

the use of the same iron precursor. The addition of cobalt causes acceleration of both cluster and entire long-range structure formation. Both cobalt and iron incorporate into the structure at the same rate. Iron is partially reduced, but the particles are stable over time. The rapid transformation from the molecular precursor to the spinel structure results in faster nanoparticle formation, leading to smaller sizes of individual particles.

The presented results prove that high-resolution X-ray spectroscopy is a valuable and efficient tool for fundamental study of synthesis and structure and magnetism development, which can be useful in designing of nanoparticles with desired properties and minimizing their size while maintaining strong superparamagnetism.