Vacancy distribution in maghemite

E. Sváb[1], Gy. Mészáros[1], Z. Somogyvári[1], K. Krezhov[2], I. Sajó[3], F. Bourée[4] , I. Dézsi[5], Cs. Fetzer[5] and Á. Gombkötő[5]

[1]*Research Institute for Solid State Physics and Optics, 1525 Budapest, POB 49, Hungary*
[2]*Institute for Nuclear Research and Nuclear Energy, 72 Tzarigradsko Chaussee, 1784 Sofia, Bulgaria*
[3]*Institute of Chemistry, 1525 Budapest, POB 17, Hungary*
[4]*Laboratoire Léon Brillouin , CEA/Saclay, 91191 Gif-sur-Yvette, France*
[5]*Research Institute for Particle and Nuclear Physics, 1525 Budapest POB 49, Hungary*

Keywords: maghemite, nanosize, vacancy

Maghemite (γ-Fe_2O_3) serves as the subject of many recent studies on nanomagnetism. However, there have been only few attempts to correlate its microstructure with the size/shape of the grains.

The structure of γ-Fe_2O_3 is closely related to that of magnetite (Fe_3O_4, inverse spinel, s.g. *Fd-3m*), but the network of iron atoms is partially depleted containing only ferric ions. The vacancies are dominantly distributed on the octahedral sites, and their basic ordering can be described in s.g $P4_332$. Eventually, a more complex ordering has been observed, and s.g. $P4_12_12$ was found to identify the lattice symmetry [1], but the detailed structural description has not yet been provided.

We have undertaken a systematic study for the quantitative analysis of maghemite with different shape/size grains, focusing our interest on vacancy distribution. Samples of needle shaped (240nm×30nm), and spherical (17nm and 28nm) grains were prepared by soft chemistry. In order to verify the only presence of Fe^{3+}, charge state Mössbauer measurements were performed. The spectra showed six characteristic lines indicating the lack of Fe^{2+} cations and supported the γ-Fe_2O_3 structure.

Neutron- and X-ray diffraction patterns measured on acicular maghemite have shown several sharp extra peaks in addition to the basic spinel reflections, while such type of extra peaks were not observed for the two other samples.

For the needle shaped γ-Fe_2O_3 sample - from multiprofile Rietveld analysis -we have concluded, that the ordering of vacancies results in the formation of an approximately tripled unit cell with space group $P4_12_12$ even at this small particle size. For the spherical grain sized samples the best fit was obtained by a model, based on random vacancy distribution on the octahedral cation sites. Preliminary results of this work have been reported in [2,3].

The work was supported by OTKA-T42495 and T32096, and BG-NFSR-F1202.

[1] N. Shmakov, G.N.Kryukova, S.V. Tsibula, A.I. Chuvilin, L.P. Solovyeva, J. Appl. Cryst. 28, 141-145 (1995)

[2] Z. Somogyvári, E. Sváb, Gy. Mészáros, K. Krezhov, I. Nedkov, I. Sajó, F. Bourée, Applied Physics A74 [Suppl.], S1077-S1079 (2002)

[3] Z. Somogyvári, E.Sváb, Gy. Mészáros, K. Krezhov, P. Konstantinov, T. Ungár, J. Gubicza, Materials Science Forum 378- 381, 771-776 (2001)