Effects of surface in ε-Fe_2O_3 nanoparticles

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Maghemite γ-Fe_2O_3 and hematite α-Fe_2O_3 are the two well-known polymorphs of ferric oxide [1]. Maghemite is metastable and transforms under heating into hematite, which is thermodynamically stable. No intermediate phase is observed during the thermal treatment of powders, but for particles dispersed in silica matrices [2] or $Pd_{96}Fe_4$ alloy [3], ε-Fe_2O_3 was observed as an intermediate phase.

The crystal structure of ε-Fe_2O_3 is orthorhombic with space group P*na*2$_1$ [2], lattice parameters at 200 K, a = 5.0885 Å, b = 8.7802 Å, c = 9.4709 Å, and $\alpha = \beta = \gamma = 90°$ [4], and eight formula units per unit cell. In the structure four cation positions (Fe_1, Fe_2, Fe_3 and Fe_4 [2]) exist. One of them (Fe_4) is tetrahedrally coordinated and the other three positions are octahedrally coordinated, exhibiting various degrees of distortion. From the magnetic point of view, ε-Fe_2O_3 is a collinear ferrimagnet with magnetization parallel to a-axis or a canted antiferromagnet with Curie temperature near 490 K [5]. A random canting of the surface spins caused by competing antiferromagnetic interactions between sublattices was proposed by Coey [6] to account for the reduction of M_s in small γ-Fe_2O_3 ferrimagnetic particles.

We present here application of the core-shell model [6, 7] for Mössbauer and NMR studies of ε-Fe_2O_3 nanoparticles enriched by isotope ^{57}Fe in a silica matrix. Samples were prepared by sol-gel technique starting from molecular precursor both for ε-Fe_2O_3 and for silica [8] and they were characterized by XRD, TEM, HRTEM and DC magnetic measurement. X-ray powder diffraction pattern of ε-Fe_2O_3 was identified and α-Fe_2O_3 and β-Fe_2O_3 as other iron oxide phases present were observed. Mean coherent diffraction domain size ~27 nm was determined. Using the fit of log-normal distribution to the experimental distribution of particles, obtained from the TEM micrographs, the characteristic diameter of particles d_0 ~ 24 nm was derived. The hysteresis loops at room temperature and the dependence of magnetization after cooling in zero and non-zero magnetic field, M_{ZFC} and M_{FC}, were measured in a SQUID magnetometer. The coercivity of ~2.1 T at room temperature is observed. At external magnetic fields as high as 7 T, magnetization does not reach saturation which may be due to the magnetic structure and behaviour of the surface layer; the non-collinear arrangement of the core moments is the usually used explanation. The temperature dependence of M_{ZFC} and M_{FC} show two anomalies: a sharp change of the slope at 124 K, below which the magnetization abruptly decreases down to 100 K, and a much smaller change at 153 K, where a maximum in the magnetization is observed, agreed with the results given in [5].

Table I: Parameters of Mössbauer spectra at room temperature

	Comp.	B_{hf} **(T)**	***IS*** **(mm/s)**	ΔE_Q **(mm/s)**	ΔB_{hf} **(T)**	***RA*** **(%)**	**Orient. of moments**	ΔE_Q^{Theor} **(mm/s)**	**Cation pos.[2,4]**
ε-Fe_2O_3 core	S_1	45.3	0.42	-0.17	-	0.174	↓	-0.08	F_1 (F_{D01})
	S_2	45.0	0.38	-0.31	-	0.174	↑	-0.11	F_3 (F_{Ro})
	S_3	39.6	0.40	-0.01	-	0.174	↑	0.01	F_2 (F_{D02})
	S_4	26.2	0.23	-0.16	-	0.174	↓	-0.15	F_4 (F_T)
ε-Fe_2O_3 shell	S_5	44.1	0.42	0	5.5	0.043	random	-	-
	S_6	40.2	0.38	0	5.5	0.043	random	-	-
	S_7	35.4	0.40	0	5.5	0.043	random	-	-
	S_8	22.0	0.23	0	5.5	0.043	random	-	-
α-Fe_2O_3	S_9	51.5	0.40	-0.2	-	0.081	-	-	-
β-Fe_2O_3	D_1	-	0.40	0.72	-	0.044	-	-	-
	D_2	-	0.53	0.99	-	0.015	-	-	-

Transmission Mössbauer spectra of the ^{57}Fe nuclei in ε-Fe_2O_3 at room temperature were obtained using ^{57}Co/Rh source with constant acceleration and calibration by α–Fe at room temperature. The spectra were fitted by four sextets (S_1, S_2, S_3 and S_4) with the same intensities, four sextets (S_5, S_6, S_7 and S_8) with distribution of hyperfine field and the same intensities, one sextet S_9 and two doublets D_1 and D_2. We ascribed the sextets S_1 through S_4 to Fe in the core of ε-Fe_2O_3, the sextets S_5 – S_8 with the distribution of the hyperfine fields to Fe in the surface shell of ε-Fe_2O_3, sextet S_9 to α-Fe_2O_3 and the two doublets to β-Fe_2O_3. We supposed the same isomer shifts for the corresponding components in the shell and in the core and random canting of the shell spins in ε-Fe_2O_3, which means the average quadrupolar shifts in the shell are zero. The parameters of the Mössbauer spectra are given in Table 1.

The particular sextets from the group S_1-S_4 were assigned to cation positions Fe_1-Fe_4 with the help of the field dependence of Mössbauer spectra at temperature of 160 K and by comparison of the experimental and theoretical quadrupolar shifts. These shifts were determined by using the electric field gradient tensor calculated by the WIEN2k *ab initio* electronic structure program taking the crystal structure from of ε-Fe_2O_3 [2] and neglecting the magnetic polarization effects.

The NMR spectra of the ^{57}Fe nuclei were measured by the spin-echo method using the phase-coherent pulse spectrometer with averaging technique and the fast Fourier transformation. The measurements were performed in zero external magnetic field at liquid helium temperature. The signal-to-noise ratio was significantly improved by using the Carr-Purcell pulse sequence. The NMR spectra of the ^{57}Fe nuclei in the prepared samples consist of two signals corresponding to α-Fe_2O_3 and ε-Fe_2O_3. The NMR spectrum of in ε-Fe_2O_3 consists of two broad lines with the ratio of integral intensities equal to $Fe_4 : (Fe_1+Fe_2+Fe_3) = 1 : 3$. The splitting of the NMR spectrum for the ^{57}Fe nuclei in octahedral sites (Fe_1, Fe_2, Fe_3; 69-72 MHz) is caused by the anisotropy of the hyperfine field which points to the non-collinear orientation of the local moments.

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