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Surface effects in α-Fe_2O_3 nanoparticles studied by ILEEMS and TMS

C. Van Cromphaut · V. G. de Resende · E. De Grave · R. E. Vandenberghe

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Abstract To understand the particular properties of thin α-Fe_2O_3 films, hematite nanoparticles with sizes between 20 and 140 nm have been examined by integral low-energy electron Mössbauer spectroscopy (ILEEMS) and transmission Mössbauer spectroscopy (TMS) at room temperature and 80 K. By comparing the results of both Mössbauer variants, surface effects of the Morin transition are studied. The results clearly indicate that the Morin transition takes place at higher temperature in the interior of the particles as compared to the outer layers. It is found that the lowering of the Morin transition is much stronger at the surface of smaller particles.

Keywords Mössbauer spectroscopy · ILEEMS · Hematite · Surface effect

1 Introduction

The magnetic properties of small hematite particles, and particularly the Morin transition, have been studied extensively [1–3]. It is generally accepted that the behavior of the Morin transition, i.e., the phase transition from an antiferromagnetic (AF) to a weakly ferromagnetic (WF) state in α-Fe_2O_3, is largely influenced by the particle size, next to foreign-element substitution. Comparison of the Morin transition temperature with the particle characteristics showed that smaller grain size lowers the temperature at which the Morin transition takes place [1]. De Grave et al. [4, 5] proved by integral low-energy electron Mössbauer spectroscopy (ILEEMS) that the local spin-flip of the Morin transition in small hematite particles obtained from goethite (few hundreds of nanometers long axis) differs at the surface Fe species from those in the bulk of the particles. The WF contribution in the surface significantly exceeds the WF contribution in the bulk at a given temperature in the

C. Van Cromphaut · V. G. de Resende · E. De Grave (✉) · R. E. Vandenberghe
Department of Subatomic and Radiation Physics, University of Ghent, 9000 Gent, Belgium
e-mail: eddy.degrave@ugent.be

transition region. This is being explained by a significant lowering of the Morin transition in the surface layers of small-particle hematites.

Recently, thin α-Fe_2O_3 films of ~100 nm thick have been studied by ILEEMS (unpublished results). The films have grain sizes which are larger than 20 nm, nevertheless some of them exhibit a weakly ferromagnetic phase at all temperatures between 140 K and 330 K. Remarkably the hyperfine field distributions for these films extracted from the ILEEMS spectra consistently show two maxima, implying the co-existence of two distinct magnetic phases. Others of about ~400 nm thick, however, show the presence of both a weakly ferromagnetic and an antiferromagnetic phase for all temperatures between 140 K and 330 K.

The objective of this study is to determine whether the special behavior of the Morin transition in the films could be related to surface effects or if they are intrinsically related to thin film properties. If the properties were surface related, similar properties should be found at the surface of particles with similar grain size. For that purpose less defectuous α-Fe_2O_3 nanoparticles with sizes between 20 and 140 nm obtained from decomposition of lepidocrocite, have been measured by ILEEMS and compared with transmission Mössbauer spectroscopy (TMS). In ILEEMS electrons with very low energy (<15 eV) are detected, making it more sensitive to the first 20 nm of the sample surface (see [4] and references therein).

2 Experimental

Six well characterized small-sized hematite samples obtained from decomposition of lepidocrocite [6] were used in this study. Mössbauer spectra (MS) at room temperature (RT) and 80 K were collected with a spectrometer operating in constant acceleration mode with triangular reference signal. $^{57}Co(Rh)$ source was used. ILEEMS spectra were collected in a vacuum chamber using a channeltron with a bias voltage of 146 V. The measurements were run several days until a background of at least 1.5×10^5 counts per channel was reached. Isomer shifts are referenced with respect to α-Fe at room temperature.

3 Results and discussion

The small-sized hematite particles were characterized by X-ray diffraction (XRD) and BET specific surface area measurements [2]. The results are summarized in Table 1.

The ILEEMS and TMS at 80 K of a few powders are shown in Fig. 1 and the corresponding Mössbauer parameters are summarized in Table 2. The spectra have been analyzed using discrete, symmetrical components with Lorentzian line shapes. Each sextet is adjusted with two line width parameters, i.e. the line width of the inner lines and a line-width increment and the peak-area ratios were constrained to 3:2:1:1:2:3. At RT the spectra consist of one sextet that could be attributed to weakly ferromagnetic hematite. At 80 K a second sextet sometimes appears that corresponds to the antiferromagnetic phase of hematite. If so, the sextets are imposed to have equal line width and isomer shift.

Table 1 Results from XRD and BET of the samples as reported by Vandenberghe et al. [2]

Sample name	Lattice parameter *a* (nm)	Lattice parameter *c* (nm)	MCL_{104} (nm)	MCL_{110} (nm)	S_{HLZ} (m^2/g)
HL121	0.50344	1.3745	110	140	7.9
HL65	0.50340	1.3754	120	140	8.2
HL86	0.50314	1.3746	35	50	26.2
HL147	0.50323	1.3747	30	40	32.9
HLB2	0.50300	1.3753	20	30	32.6

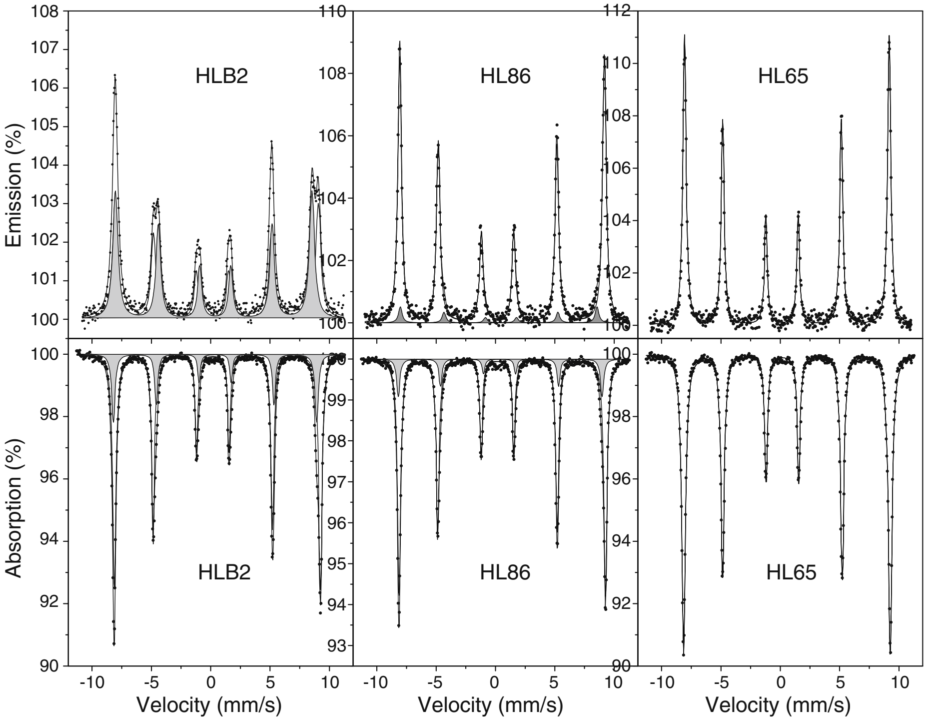

Fig. 1 ILEEMS (*top*) and TMS (*bottom*) at 80 K of small hematite particles HLB2 (30 nm), HL86 (50 nm) and HL65 (140 nm); weakly (*filled grey*) and antiferromagnetic (*not filled*) contributions can be distinguished

Because the AF contribution at 80 K of the ILEEMS spectra is higher than for the TMS it is clearly the Morin transition is shifted downwards in the surface as compared to the bulk, similarly to what has been found in the goethite-derived samples [5]. Also the values of the quadrupole shifts are higher at the surface of the particles. For the smallest particles, it becomes even positive for the WF phase. From these measurements, it can be seen that when the particles become smaller, the decrease of the Morin transition at the surface will go faster compared to the bulk. In small particles, the surface effect which makes that the surface Morin transition decreases will be larger.

Table 2 Hyperfine parameters of sample HLB2, HL147, HL65, HL85 and HL121 measured by TMS and ILEEMS at RT and 80 K

Sample	T(K)	AF				WF			
		H_{hf}	δ	$2\varepsilon_Q$	RA[a]	H_{hf}	δ	$2\varepsilon_Q$	RA[a]
TMS									
HLB2	RT	–	–	–	–	509	0.37	−0.21	100
HL147	RT	–	–	–	–	508	0.37	−0.21	100
HL86	RT	–	–	–	–	511	0.37	−0.22	100
HL65	RT	–	–	–	–	516	0.36	−0.23	100
HL121	RT	–	–	–	–	515	0.37	−0.20	100
HLB2	80K	538	0.48	0.39	78	531	0.48	−0.06	22
HL147	80K	538	0.47	0.35	82	530	0.47	−0.06	18
HL86	80K	539	0.48	0.40	86	533	0.48	0.05	14
HL65	80K	540	0.48	0.38	100	–	–	–	–
HL121	80K	540	0.46	0.36	95	534	0.46	−0.02	5
ILEEMS									
HLB2	RT	–	–	–	–	507	0.38	−0.21	100
HL147	RT	–	–	–	–	507	0.37	−0.23	100
HL86	RT	–	–	–	–	510	0.37	−0.21	100
HL65	RT	–	–	–	–	512	0.37	−0.22	100
HL121	RT	–	–	–	–	514	0.37	−0.22	100
HLB2	80K	532	0.43	0.35	48	513	0.43	0.13	52
HL147	80K	536	0.47	0.43	75	525	0.47	0.07	25
HL86	80K	535	0.47	0.38	94	514	0.47	−0.19	6
HL65	80K	535	0.46	0.41	100	–	–	–	–
HL121	80K	538	0.47	0.42	96	534[b]	0.47	−0.02[b]	4

The values of isomer shifts are with reference to metallic iron at RT. Relative spectral areas (RA values)

H_{hf} hyperfine field (kOe), $2\varepsilon_Q$ quadrupole shifts (mm/s), δ isomer shifts (mm/s)

[a]Fractional spectral area of total spectrum, approximating the fraction of Fe species in respective sites

[b]Parameter values were kept fixed during iteration

[c]Line with of the inner line

The surface hyperfine field of the AF and WF phase is always lower than the bulk one. It is well documented that surface iron nuclei exhibit a smaller hyperfine field as compared to the bulk [7]. The difference in hyperfine field seems not to have any relation with the particle size. For the smallest particles (HLB2), it can be noted that the AF phases at the surface is very large (∼52.5%), meaning that the Morin transition has lowered significantly. Also the difference in surface and bulk hyperfine field becomes large, especially for the WF phase (∼18 kOe). These particles have a size which is very close to 20 nm. It is well-known that for particles smaller than 20 nm the Morin transition does not appear anymore. These measurements suggest that the origin of the latter effect starts at the surface of the particles, and can be attributed to surface effects.

4 Conclusions

Small hematite particles have been measured by ILEEMS to determine the behavior of the Morin transition at the surface. The measurements were compared to the results of TMS and confirmed the result from previous studies that the Morin transition is lowered at the surface. This decrease of the transition temperature is observed to be the strongest for very small particles (~25 nm). There is no relation found between the surface Morin transition of small hematite particles and the recent effects found in thin hematite films, indicating that the latter effects cannot be ascribed to surface properties of the films.

At this moment positron annihilation measurements are planned to observe the defect structure of the particles in order to find a relationship with the observed effects.

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