

Supporting information

Magnetism of nanostructured hematite: From Cultural Heritage to fundamental properties

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XRD

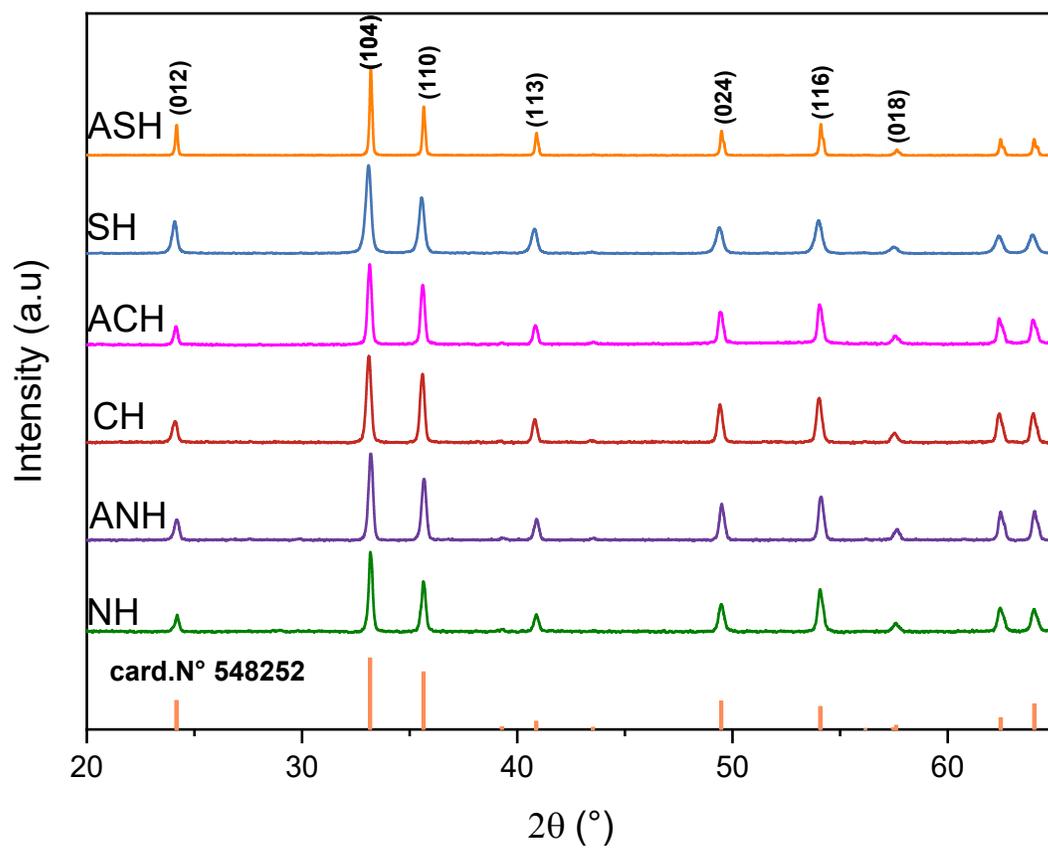
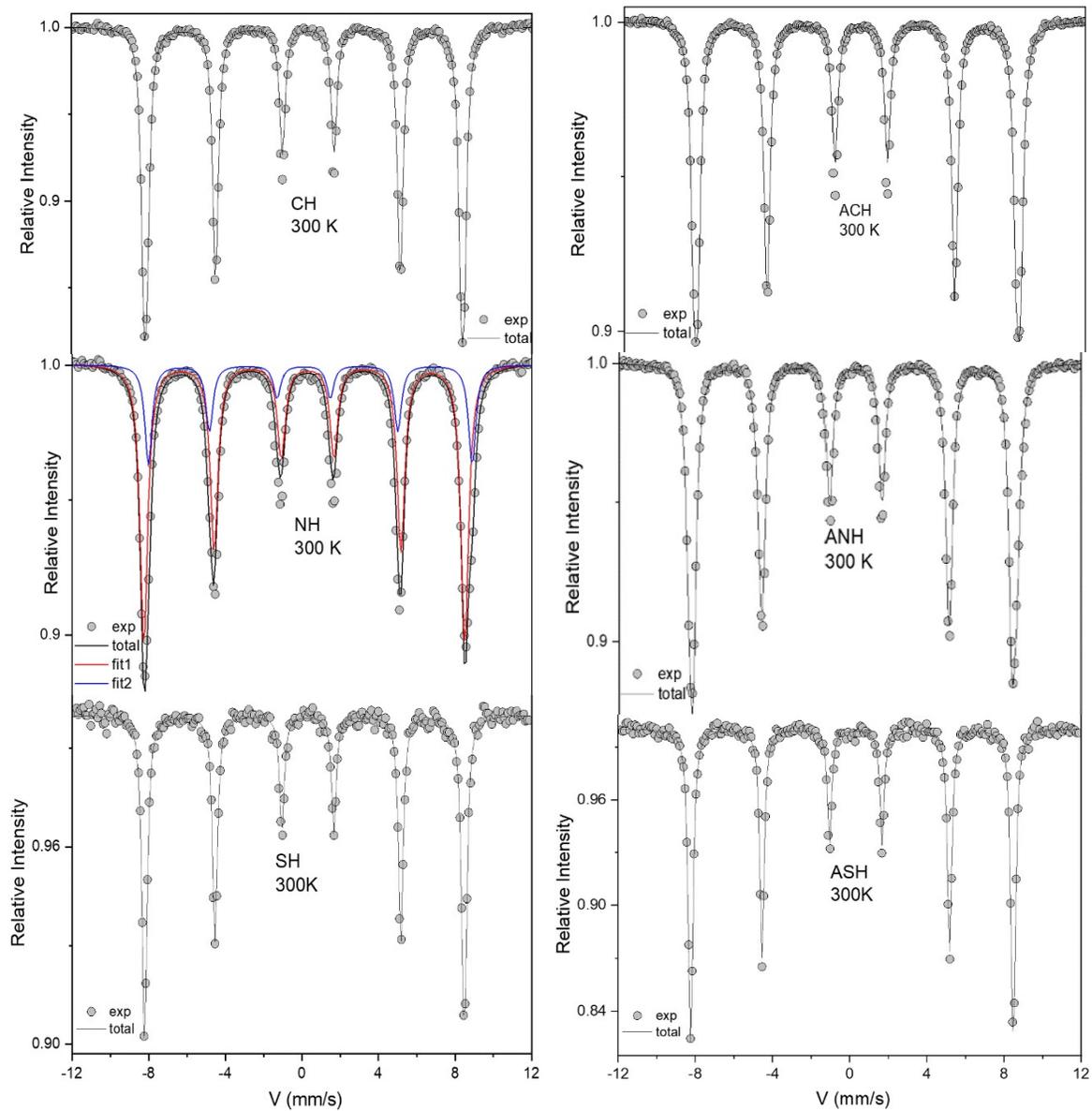


Figure S1. X-ray powder diffraction patterns of all the samples; the observed reflexes fulfil the hematite crystalline phase.

Hyperfine Structure

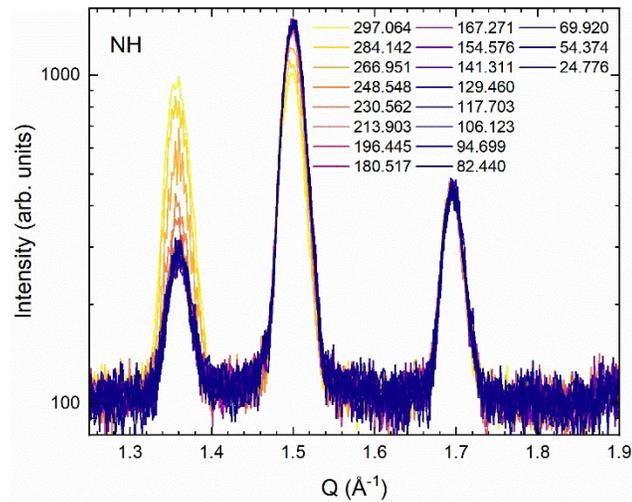
Hyperfine parameters extracted at 300 K, the spectra of SH and CH samples (Figure S2, Table S1) show similar results. Spectrum of both samples has been fitted with one sextet corresponding to Fe^{3+} cations in octahedral site, this spectrum was fitted with hyperfine value $B_{\text{hyp}}=51.03$ T. It was found that the isomer shift (IS) and the quadrupole shift (QS) were 0.38 mm s^{-1} and -0.20 mm s^{-1} respectively, which is in correspondence with the reported values of weak ferromagnetic (WF) hematite above T_M ^{1,10}. A similar result was also obtained for the SH sample. Conversely, the spectrum at 300 K for the NH sample was fitted with two sextets with hyperfine values of 51.72 T and 52.17 T. The first sub spectrum with $B_{\text{hyp}}=51.72$ T presents the quadrupole shift value $QS = -0.164 \text{ mm s}^{-1}$ and the isomer shift value $IS=0.37 \text{ mm s}^{-1}$ (close to the reported stoichiometric hematite values¹¹), whereas for the sub spectrum fitted with $B_{\text{hyp}}=52.17$ T, the IS and the QS are higher in comparison with the stoichiometric hematite crystalline structure. Indeed, the two different sextets are an indication of the existence of two different environments within the sample. In the nanoscale, the ratio of surface to volume is higher than that in bulk, which strongly affects the magnetic behavior of the material. The negative and the positive values of QS may suggest that there are two magnetic phases, the negative value is relative to the weak ferromagnetic phase corresponding to hematite crystalline structure arising from the Fe^{3+} cations coming from the inner core and the positive value is relative to the non-stoichiometric hematite coming from the cations of the outer surface. After thermal treatment, all the samples show one sextet corresponding to the hematite structure.



FigureS2. Mössbauer spectra in zero magnetic field, recorded at 300K for all the samples before and after annealing.

TableS1: Data extracted from the fit of the Mössbauer spectra at 300K. Isomer shift (δ), quadrupole splitting (QS), hyperfine magnetic field (B_{hyp}) and relative percentage area of the components.

Sample	$\delta(mm.s^{-1})$	$2\varepsilon(mm.s^{-1})$	$B_{hyp}(T)$	%
CH	0.38	-0.204	51.03	
NH	0.37	-0.164	51.72	75
	0.42	0.347	52.17	25
SH	0.38	-0.18	50.6	
ACH	0.38	-0.194	51.83	
ANH	0.38	-0.139	51.70	
ASH	0.38	-0.202	51.7	



FigureS3. NPD-MR data for the NH sample collected on cooling and evidencing the magnetic transition occurring around 220 K; the intensity scale is plotted using a logarithmic scale to better highlight the small, but sizeable contribution of the magnetic peak at $\sim 1.35 \text{ \AA}^{-1}$.