

## Mechanochemical activation of magnetite nanoparticles

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### Abstract

Using Mössbauer spectroscopy as a function of ball milling time, it was found that nanomagnetite behaves differently than magnetite during mechanochemical activation. The phase sequence is determined by the original particle size of the powder. Magnetite suffers a phase transformation to hematite, while nanomagnetite ( $d = 19$  nm) gives rise to superparamagnetism as effect of prolonged milling.

### Introduction

Magnetite ( $\text{Fe}_3\text{O}_4$ ) is an oxide with the inverse spinel structure, which has one  $\text{Fe}^{3+}$  ion on the tetrahedral (A) site and two Fe ions, with a total valence of 5+, on the octahedral [B] site.

Because of the technological importance of the iron oxides and hydroxides, the preparation and properties of these materials have been thoroughly investigated over the years. Some effects of milling magnetite have been studied, focusing on the reduction of  $\text{Fe}_3\text{O}_4$  through displacement reactions [1–8].

In this paper we emphasize the comparative behavior of magnetite and nanomagnetite during mechanochemical activation. To identify the phases and inequivalent sites occurring in the ball-milled products, we utilize transmission Mössbauer spectroscopy. Our results demonstrate the crucial role played by the particle size in determining the kinetics of the mechanochemical activation process.

### Experimental

Magnetite powder, prepared by the hydrothermal method, having an average particle diameter

$\langle d \rangle = 1.07 \mu\text{m}$  was milled in a sealed hardened steel vial with six stainless steel balls (type 440, four of 6.25 mm in diameter and two of 12.5 mm in diameter) in a SPEX 8000 mixer/mill for various periods of time.

Nanomagnetite, purchased from NanoTek had an average particle diameter ( $d$ ) = 19 nm. It was subjected to high-energy ball milling for the same time periods used for magnetite processing.

Mössbauer spectroscopy was used in transmission geometry with a  $^{57}\text{Co}(\text{Rh})$  source. Least squares fitting of the spectra was performed using the NORMOSITE program.

### Results and discussion

Figure 1 shows the transmission Mössbauer spectrum of original magnetite. It could be resolved by considering two Zeeman sextets (Table 1), corresponding to the two magnetic sublattices present in the sample. The tetrahedral (A) site is represented by a sextet with a magnetic hyperfine splitting of 49.22 T and the octahedral [B] site is described by a six-line pattern having a splitting of 46.20 T. Lowering of the hyperfine magnetic field value of the second sublattice is related to the

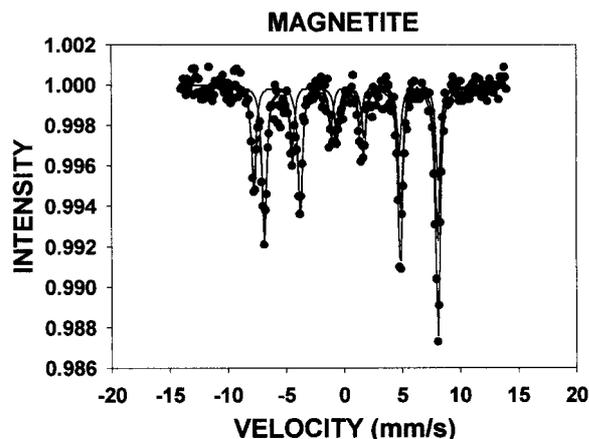


Figure 1. Transmission Mössbauer spectrum of original magnetite.

Table 1. The fitted Mössbauer parameters (hyperfine fields of various subspectra and relative areas) for magnetite and nanomagnetite as functions of milling time. SPM designates the superparamagnetic fraction in the samples

Sample	Milling time (h)	$H_{\text{hf}}$ (T)	$A_{\text{rel}}$ (%)
Magnetite	0	49.22	38.2
		46.20	61.7
	17	48.92	26.8
		45.18	53.8
		33.02	10.7
		51.66	7.3
SPM	1.4		
40	51.90	100.0	
Nanomagnetite	0	49.83	71.1
		46.78	28.9
	17	49.00	44.0
		46.00	33.1
		43.00	22.9
	40	49.00	25.0
		46.00	60.0
SPM		15.0	

presence of  $\text{Fe}^{2+}$  ions at the [B] sites. The site populations are 38.3% and 61.7%, respectively. These values are close to 1:2 and indicate a high degree of stoichiometry of the initial material. The error margins are 0.5 T and 0.5%, respectively.

Figure 2 represents the transmission Mössbauer spectrum of magnetite after 17 h of mechanochemical activation by high-energy ball milling. The spectrum could be resolved by considering four sextets and a quadrupole-split doublet. The sextets with the hyper-

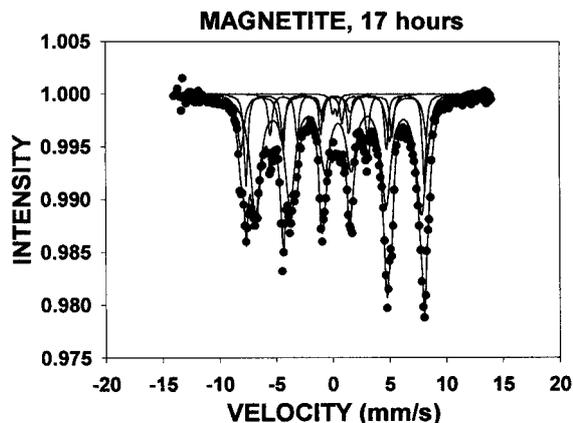


Figure 2. Transmission Mössbauer spectrum of magnetite after 17 hours of ball milling.

fine magnetic fields of 48.92 and 45.18 T correspond to the tetrahedral (A) and octahedral [B] sublattices, respectively. However, their relative populations of 26.8% and 53.8% indicate that the processed material exhibits nonstoichiometry as effect of milling. The presence of  $\alpha\text{-Fe}$  as an intermediate product is supported by the appearance of the sextet with a hyperfine magnetic splitting of 33.02 T and a relative abundance of 10.7%. This phase could originate in the steel present in the balls and vial. The main transformation, however, is represented by the appearance of hematite, which has a magnetic hyperfine field of 51.66 T and occurred in the proportion of 7.3%. This indicates that the mainstream transformation of magnetite to hematite [7] starts to take place. The quadrupole doublet with a splitting of 0.15 mm/s and a relative abundance of 1.4% corresponds to superparamagnetic particles, formed in bulk magnetite due to ball milling.

It can be seen in Figure 3 that the entire Mössbauer spectrum after 40 h of milling time can be described by a sextet with a hyperfine magnetic field of 51.9 T, corresponding to hematite. Consequently, the conversion of magnetite to hematite is complete after 40 h of mechanochemical activation.

Figure 4 represents, to our best knowledge, the first observation of the Mössbauer spectrum of nanomagnetite. It was argued by many whether the two magnetic sublattices are still resolved at the nanoscale. Our results indicate that the two magnetic sublattices are still present in nanomagnetite, with hyperfine magnetic fields of 49.83 and 46.78 T. However, the corresponding populations are 71.1% and 28.9% for

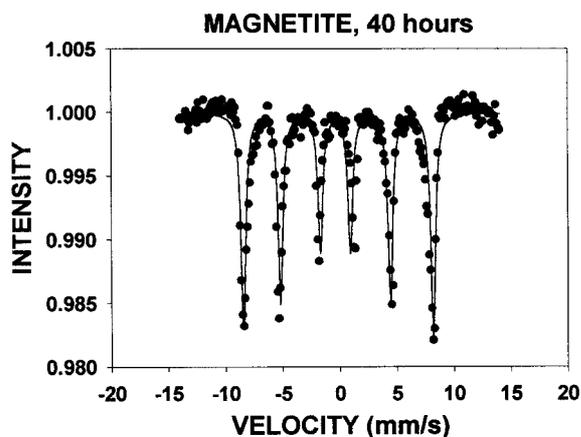


Figure 3. Transmission Mössbauer spectrum of magnetite after 40 hours of ball milling.

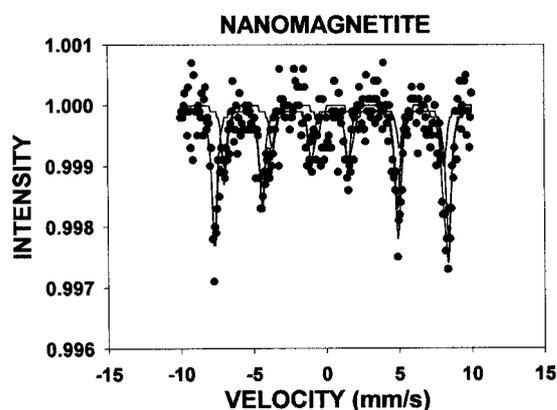


Figure 4. Transmission Mössbauer spectrum of nanomagnetite.

the (A) and [B] sites, respectively, indicating that the octahedral sublattice is less populated than in bulk magnetite. The most striking feature is the reduction of the resonant area under the spectrum from 0.037 mm/s (normalized to the background) for magnetite to 0.009 mm/s for nanomagnetite, indicating a considerable decrease in the recoil-free fraction for the case of nanoparticles.

Let us now follow the behavior of magnetite nanoparticles under mechanochemical activation. Figure 5 shows the Mössbauer spectrum of nanomagnetite after 17 h of ball milling. Unlike bulk magnetite powder, the spectrum consists of three sextets, with magnetic hyperfine fields of 49.00, 46.00 and 43.00 T. These values correspond to the tetrahedral (A) sites

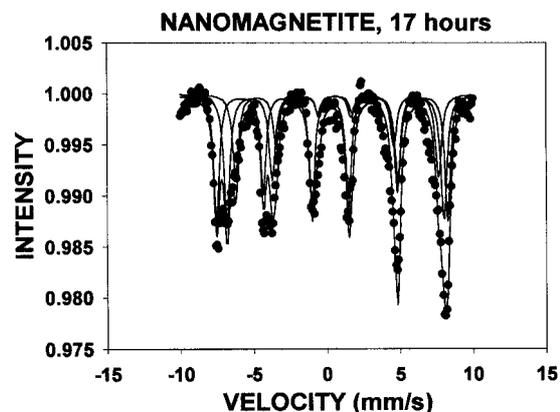


Figure 5. Transmission Mössbauer spectrum of nanomagnetite after 17 hours of ball milling.

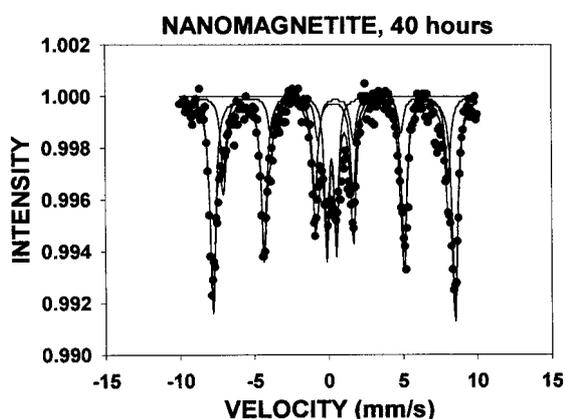


Figure 6. Transmission Mössbauer spectrum of nanomagnetite after 40 hours of ball milling.

(occupied 44.0%), the octahedral [B] sites (with a population of 33.1%) and respectively, the grain boundary phase, which was produced due to milling.

It can be seen in Figure 6 that the Mössbauer spectrum after 40 h of ball milling consists of the two magnetic sublattices (A) and [B] with fields of 49.00 and 46.00 T, respectively, and a quadrupole split doublet, with a splitting of 0.65 mm/s and a relative abundance of 15%. This doublet corresponds to superparamagnetic particles formed in the processed material. We propose that the grain boundary phase, characteristic to nanoparticles, decays under prolonged milling to form the superparamagnetic particles. Their relative abundance is considerably higher than in the case of bulk magnetite transformation.

### Conclusions

Magnetite and nanomagnetite behave differently under ball milling. These differences originate in particle size effects. Magnetite is transformed to hematite under prolonged milling, while nanomagnetite is characterized by the occurrence of superparamagnetism in the milled system.

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