#### Mössbauer Spectroscopy Applied to Iron(III) Oxides In-Field and/or Low Temperature Measurements

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### Outline

- 1. Low Temperature Mössbauer Spectroscopy of Hematite  $(\alpha Fe_2O_3)$
- 2. Low Temperature Mössbauer Spectroscopy of β-Fe<sub>2</sub>O<sub>3</sub>
- 3. In-Field and Low Temperature Mössbauer Spectroscopy of Maghemite (Υ-Fe<sub>2</sub>O<sub>3</sub>)
  - (i) Maghemite in Bulk
  - (ii) Nanoparticles of Maghemite

# α-Fe<sub>2</sub>O<sub>3</sub> (Hematite)



It has a rhombohedrally centered hexagonal structure of the corundum type with a close-packed oxygen lattice in which 2/3 of octahedral sides are occupied by Fe(III) ions.

Space group:  $R\overline{3}c$ 

Figure 1. Crystal packing in the structure of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, the view onto (001). Fe, shaded circles; O, white circles.



# Hematite

- Recording the Mössbauer spectra in a wide range of temperatures allows one to study and register the magnetic transition temperatures:
- a) transitions related to the loss of magnetic ordering ( $T_N$  and  $T_B$ ), reflected by a sextet to a doublet change in spectra
- b) transitions related to changes in magnetic ordering from AF to WF states at  $T_{_{M}}$ , manifested by a change in the parameters of magnetic splitting and the quadrupole shift at  $T_{_{M}}$ .

#### Hematite

Both magnetically nonequivalent phases can be probed separately, in contrast to magnetic measurements where mainly the WF phase is observed.



**Figure 2.** Mössbauer spectrum of the pure synthetic hematite at 260 K, showing the coexistence of both the AF and WF phases.

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### Hematite

The hyperfine parameters at RT:  $IS_{Fe} = 0.37 \text{ mm/s}, \epsilon = -0.21 \text{ mm/s}, B = 51.7 \text{ T}$ 

At  $T_{M}$  **B** decreases by 0.8 T

The quadrupole shift parameter  $\varepsilon$  changes even more markedly(!)

The  $\varepsilon$  depends on the canting angle  $\varphi$  of the spins with respect to the EFG ( $E_{Q}$ ) axis, given by  $\varepsilon = \Delta E_{Q} (3 \cos^{2} \varphi - 1)/2$  and yields values with **opposite sign** for AF ( $\varphi = 0^{\circ}$ ) and WF ( $\varphi = 90^{\circ}$ )

In this way both magnetically nonequivalent phases can be probed separately

Hematite is thermally the most stable polymorph of iron(III) oxides undergoing a thermal reduction to magnetite (Fe, $\Phi_{\mu}$ ) at temperatures above 1200°C



**Figure 4.** Crystal packing in the structure of  $\beta$ -Fe<sub>2</sub>O<sub>3</sub>, the view onto (110). Fe, shaded circles; O, white circles.

It has a bcc "bixbyite" structure with  $Ia\overline{3}$ space group and 2 nonequivalent octahedral sites of Fe(III) in crystal lattice. The cubic unit cell contains 32 Fe(III) ions, 24 of which have a C<sub>2</sub> symmetry (d position) and 8 a C<sub>3</sub> symmetry (b position).

Figure 5. Schematic representation of nonequivalent sites of Fe in the structure of  $\beta$ -Fe<sub>2</sub>O<sub>3</sub>.

 $C_2$ 

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Fe<sup>3+</sup>- b site

 $Fe^{3+}$ - d site

 $\beta$ -Fe<sub>2</sub>O<sub>3</sub>

#### At RT $\beta$ -Fe<sub>2</sub>O<sub>3</sub> is PM, T<sub>N</sub> $\approx$ (100-119K)



#### $\beta$ -Fe<sub>2</sub>O<sub>3</sub>

The Mössbauer spectra consist of 2 subspectra, the relative intensities of which are in ratio 3 to 1, in accordance with the ratio of Fe(III) in the nonequivalent octahedral positions (d/b = 24/8).

At RT the parameters of MS are:  $IS_{Fe} = 0.37$  mm/s and QS = 0.69 mm/s for *d* position  $IS_{Fe} = 0.37$  mm/s and QS = 0.90 mm/s for *b* position

**But**, the difficulty in distinguishing between nonequivalent cation positions could lead to the fitting of the RT spectrum by one doublet with  $IS_{Fe}$ =0.37 mm/s and QS = 0.75 mm/s.

#### At low temp-res (below 110K, in magnetically ordered state) nonequivalent sites are better distinguished than at room temperature.



Methods of preparations:

1. This polymorph was prepared on various substrates in the form of a thin film at 300°C in the atmosphere of  $O_2$  using the chemical vapor deposition method when an organometallic compound was used as a precursor material, most frequently iron(III) acetylacetonate.

2. Isolation from a reaction mixture during a thermally induced solid-state reaction between NaCl and  $Fe_2(SO_4)_3$  in air.

 $\beta$ -Fe<sub>2</sub>O<sub>3</sub> is thermally **metastable** and at temperatures around 500°C is transformed into hematite.

# **Υ-Fe<sub>2</sub>O<sub>2</sub>(Maghemite)**



**Figure 7.** Crystal packing in the structure of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, the view onto (100). Fe, shaded circles; O, white circles.

It is an inverse spinel with a cubic unit cell, space group  $P4_{1}32$ . It contains, as in  $Fe_{3}O_{4}$ , cations in tetrahedral A and octahedral B positions, but there are vacancies  $(\Box)$ , usually in octahedral positions, to compensate for the increased positive charge. Stoichiometry can be formally described by the formula:  $Fe^{A}(Fe_{5/3} \square_{1/3})^{B}O_{4}$ 



Fe3+ - B site

Figure 8. Schematic representation of nonequivalent sites of Fe in the structure of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>.

# Maghemite

It is typical ferrimagnetic material

The RT Mössbauer spectrum forms a "slightly asymmetric" sextet

 $IS_{Fe} = 0.34 \text{ mm/s}, \epsilon = 0 \text{ mm/s}, B = 50.0 \text{ T}$ 



# Maghemite (bulk)





Despite the distribution of ferric ions over two magnetically disparate sublattices, the spectrum displays **only one** broadened sextet that is observable at all temperatures attainable below the RT.

There is **no** clear evidence that the final spectrum is composed of 2 subspectra as the lines confining from the tetrahedral and octahedral positions strongly overlap.

At room temp-re:

A-site:  $B_{hf}$ =50.0 T,  $\delta$ =0.25 mm/s,  $\epsilon_0$ =0

B-site:  $B_{hf}$ =50.5 T, δ=0.35 mm/s, ε<sub>Q</sub>=0

At low temperature the spectrum asymmetry increases as the lines 1,2,3 become progressively more intense than the lines 4,5,6.

### Maghemite

When the temperature is lowered, it is possible, depending on the crystallinity of the measured sample, to achieve a somewhat better resolution of the two non-equivalent positions, but **the only way** how to sufficiently separate the lines is **to apply a strong external magnetic field**.

# Maghemite (bulk)



The A and B site fields make parallel or antiparallel alignment with respect to the applied field and the resultant fields differ significantly.

The relative areas of the six lines are given by 3:x:1:1:x:3 where  $x = 4 \frac{\sin^2\theta}{(1 + \cos^2\theta)}$  with  $\theta$  being the angle between the magnetic hyperfine field and the gamma ray direction.

Lines 2 and 5 vanish when the spins are completely aligned with the external field.

The outermost lines are splitted.

The ratio of subspectra areas  $A_{B}/A_{A} = 5/3$ 

## Nanocrystalline Maghemite



Nanoparticles of 4.6 nm in diameter

Distorted coordination symmetry at the surface of small maghemite particles can produce a sizeable quadrupole shift ( $\varepsilon_0 \neq 0$ ).

The thermal evolution of the MS is characterized by a quadrupole doublet and a slightly perturbed sextet that coexist together in various proportions.

The area of each component is proportional to the number of iron atoms being either in a non-blocked or blocked state.

# Nanocrystalline maghemite in-field





With decreasing crystallinity of maghemite the spins do not align perfectly but exhibit canting (lines 2 and 5). This behavior suggests that directions of atomic moments are disordered due to spin frustration.

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# Nanocrystalline maghemite

#### T = 7K H = 6T



The average canting angle decreases as the size of the particles increases. Based on the core-shell model, it have been calculated the thickness of a canted surface to be equal to  $(0.35 \pm 0.05)$  nm



The schematic representation of the spherical particle with canted magnetic moment in the surface layer. The white arrow represents the arrangement of magnetic moments in the core of the particle and black arrows do- in the surface layer of the particle.

#### The effective field at the nucleus of the iron atom



where  $A_{i,j}$  is the intensity of the line *i* or *j* (*i*,*j* =1,6; 2,5;3,4)

The intensities of the lines are in the ratio 3:x:1:1:x:3

 $x = 4 \sin^2 \varphi / (1 + \cos^2 \varphi) \qquad \varphi = \arcsin \sqrt{\frac{6r}{4 + 3r}}$ where  $r = A_{2,5} / A_{1,6}$  $\varphi = \arccos \sqrt{\frac{4 - s}{4 + s}}$  $s = A_{2,5} / A_{3,4}$ 

#### Nanomaghemite

#### T=5K, H=4T



It was prepared 2 samples of identically and uniformly sized spherical particles with an average diameter of 3.5 nm.

As a consequence of the various degree of the internal structural disorder: dissimilar magnetic properties.

The relative areas of the lines 2 and 5 were found to be larger for the poorly ordered samples.

# Maghemite

 $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> is thermally unstable and is transformed to hematite at higher temperatures. The temperature and mechanism of the structural transformation are dependent on experimental conditions and particularly on the size of maghemite particles. For well-developed crystals of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> the temperature of transformation has been determined at 400°C and a direct transformation mechanism to  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> is expected.

In the case of very small particles, a notably higher transformation temperature was noticed with  $\epsilon$ -Fe<sub>2</sub>O<sub>3</sub> being an intermediate of the structural transformation  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>  $\rightarrow \alpha$ -Fe<sub>2</sub>O<sub>3</sub>

### Conclusions

The application of in-field and/or low temperature Mössbauer Spectroscopy is a powerful tool for the investigating the structural and magnetic properties of Fe(III) oxides.

Among them, nanomaghemite, which represents a ke material of modern nanotechnologies.