Mössbauer studies of magnetic Fe_2O_3/SiO_2 nanocomposite

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1. Introduction

- **the sol–gel process is interesting for the preparation of various products (bulk materials, films, membranes or fibres)**

- organic-inorganic hybrid materials represent
  - a creative alternative to the design of new materials
  - compounds for academic research
  - basis for the development of novel innovative industrial applications

- **these processes are based on**
  - **the copolymerisation of functional organosilanes, macromonomers and metal alkoxides**
  - **the encapsulation of organic components within sol–gel derived silica or metallic oxides**
  - **the organic functionalisation of nanofillers, nanoclays or other compounds with lamellar structures**

- **the chemical strategies** → **the development of new vectorial chemistry**

  (self-assembly, nanobuilding block approaches, integrative synthesis, coupled processes, bio-inspired strategies, etc.)

- nanoobjects able to direct the assembling of a large variety of structurally well defined blocks into complex hybrid architectures hierarchically organised in terms of structure and functions

- **open a land of promising applications in many areas:**

•optics
•electronics
•mechanics
•energy
•environment
•biology
•medicine (membranes and separation devices)
•functional smart coatings
•fuel and solar cells
•catalysts
•sensors

- **identification and crystallisation of the material must be taken into account in order to predict the final state of a sol-gel derived material**
- the application of ultrasound (sonocatalysis) to the precursors gives rise to materials, known as sonogels, with new properties
- **the effects of ultrasonic cavitation create a unique environment for sol–gel reactions leading to particular features in the resulting gels:**
  - **fine texture**
  - **homogeneous structure**
  - **high density**
- these properties determine the evolution of sonogels during further processing and the structure of the final material

➢ for successful applications a number of requirements must be met:

- sufficient mechanical strength and chemical stability,
- shaping possibilities,
- minimal association of the guest species
- control of the host-guest interactions

➢ **preparation of dense materials with closed porosity addresses some of these points, but the study of such materials is complicated**

➢ ^{57}Fe Mössbauer spectroscopy seems to be an excellent tool to investigate the iron-based nanocrystalline structures

➢ **MS is able to elucidate**

- **the nature of hyperfine interactions of the different types/sites of iron nuclei**
- **the nature of the surroundings such as type of bonding**
- **valence state**
- **number and character of the nearest neighbours**

2. Experimental

2.1 Preparation of the samples

- the selected nanocomposite samples are obtained by annealing the Fe_2O_3-SiO_2 xerogels up to 1000ºC, in air or in vacuum and N_2 atmosphere
- **two iron oxide target concentrations will be used: 20% and 30% in silica matrix**
- basically silica-based xerogels are prepared by sol-gel synthesis from TEOS in hydro-alcoholic solution, following different procedures
- **in order to obtain hybrid organic-inorganic matrix based nanocomposites, PolyVynilicAlcohol is added to the reaction mixture and Fe3+ as alcoholic solution of an inorganic salt**
- a series of samples is obtained by using sonification process during sol-gel synthesis

- **the silica polymeric sonogels syntheses are done by hydrolysis and condensation reactions carried out by subjecting the initial mixture to ultrasonic waves in an open glass container**
- ultrasonic waves (20 kHz) are generated by a high-power ultrasonic horn
- **the energy dose delivered to the system is set by the output power of the generator and the exposure time, providing an additional parameter for controlling the sol and gel properties**
- an alternative experimental setup involves an ultrasonic bath
- **in these cases a much lower ultrasonic intensity is supplied to the reactants and, consequently, the resulting samples might not possess the characteristic sonogel features**
- all the sonogel features are rather difficult to sharply define, and there is a lot of work to be done in this direction

2.2 Sample characterisations

Mössbauer spectroscopy

- **the Mössbauer spectroscopy is based on the resonance emission and absorption of the nuclear gamma-quantum by the suitable isotope :**
  - **in our case of the investigation of iron-oxide particles it is the ^{57}Fe**
- the Mössbauer spectra of our samples were acquired in the transmission mode with ^{57}Co diffused into Rh matrix as the source moving with constant acceleration
- **all spectra were measured at room temperature**
- the spectrometer is calibrated by means of a standard α–Fe foil and the isomer shift is expressed with respect to this standard at 293 K

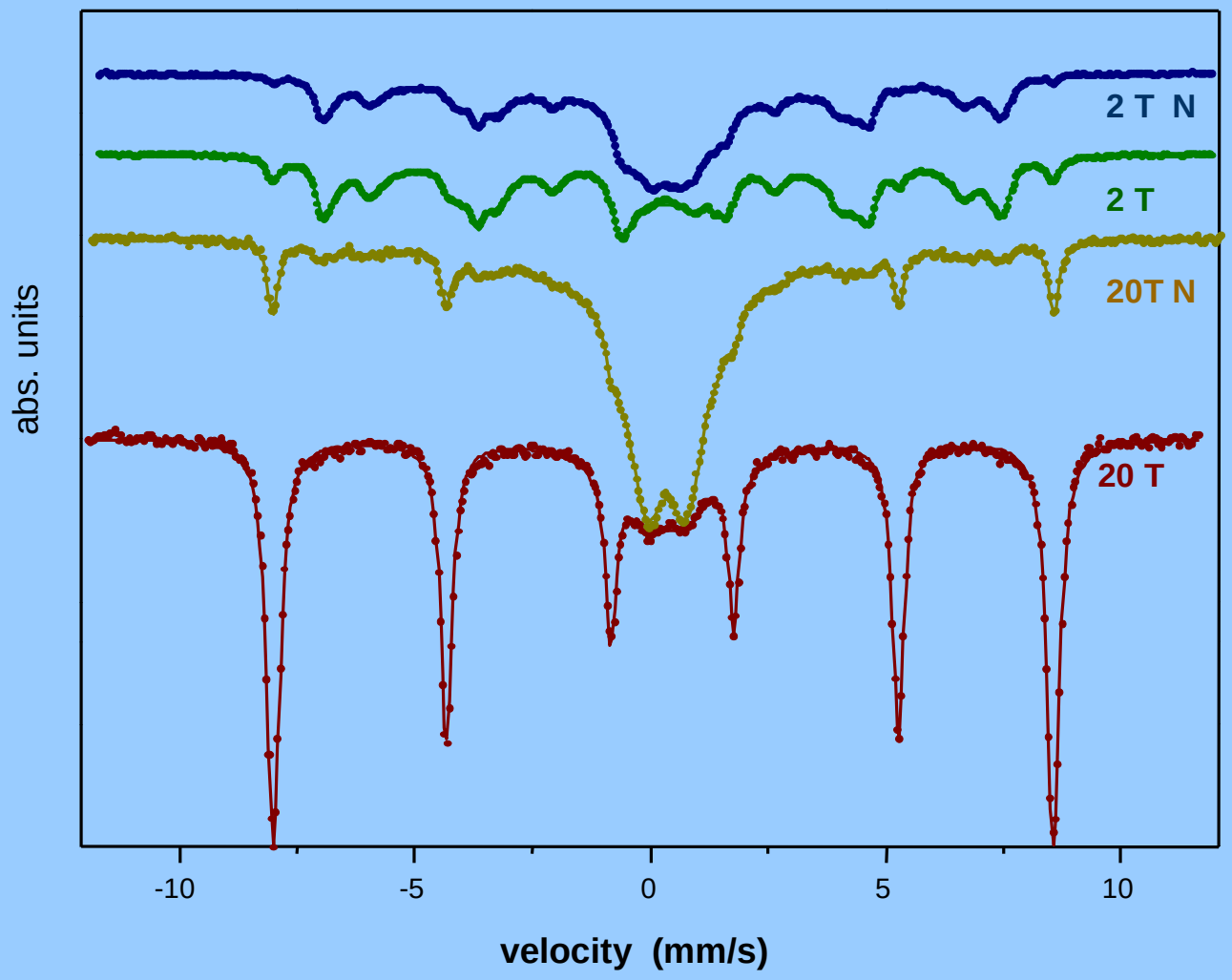
Question: **Better when we measure by low temperature???**

It is new part of my next research!!!

3. Results and Discussion

- **the spectra were fitted with the help of the NORMOS program**
- the spectra consisted of 1- 4 sextets and a doublet and/or singlet
- **three sextets were ascribed to 4 various sites of iron in ε-Fe_2O_3**
- one sextet (with hyperfine field of about 51.5 T) belongs to hematite
- **for one of the sample 2 sextets corresponding to magnetite were found**
- singlet and/or doublet were ascribed to the present paramagnetic Fe ions

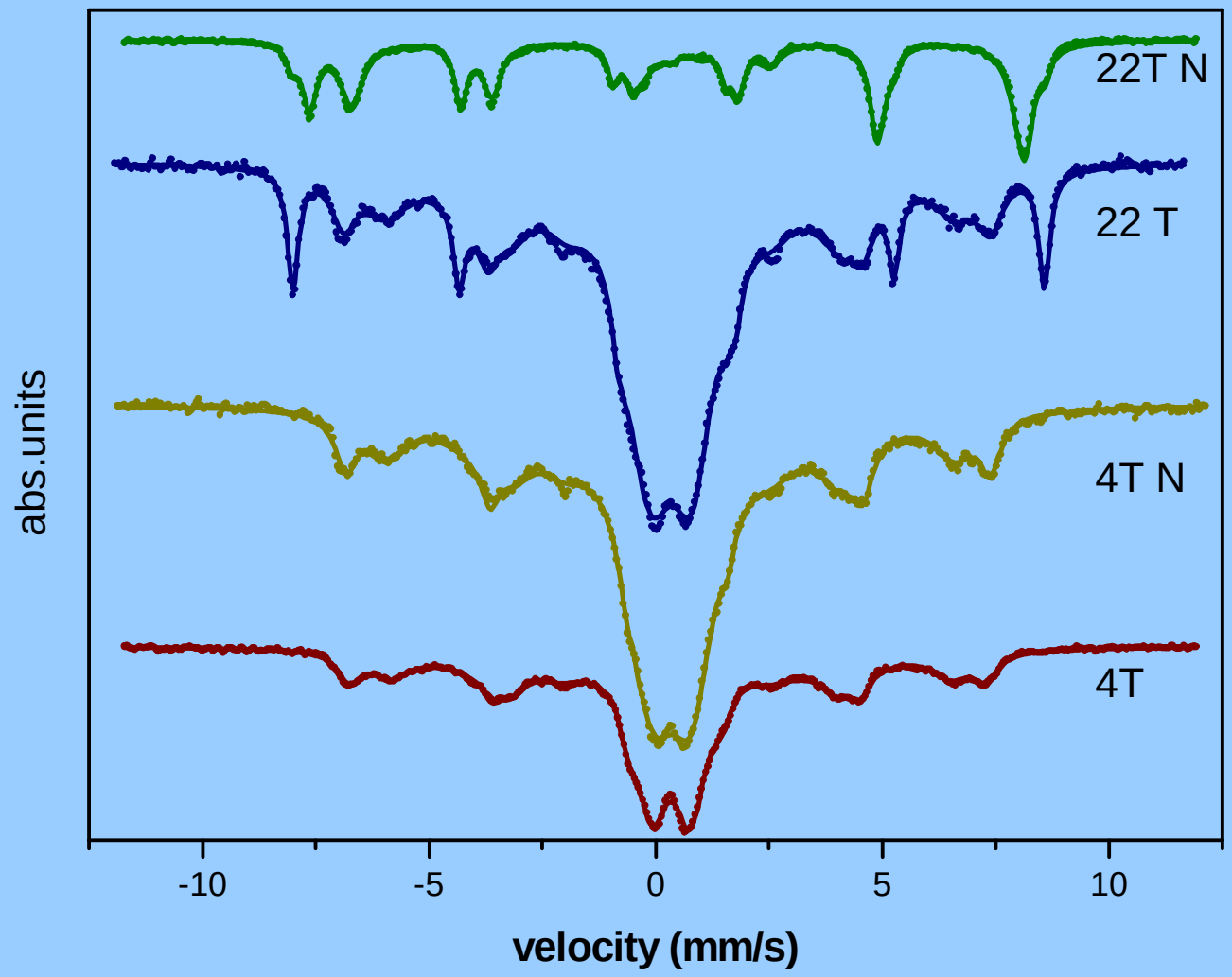
30% Fe_2O_3



30% Fe_2O_3

Sample	Hematite		ε-Fe_2O_3						PM
	B_{hf} [T]	rel. area [%]	45 T (2 positions)		39 T		26 T		rel.area [%]
			B_{hf} [T]	rel.area [%]	B_{hf} [T]	rel.area [%]	B_{hf} [T]	rel.area [%]	
2T 1000°C	51.4	6.1	44.5	25.3	39.0	28.5	25.7	21.5	18.6
20T 1000°C	51.5	75.3							24.7
2T N 1000°C	51.4	1.1	44.6	16.6	39.1	21.3	25.5	17.3	43.7
20T N 1000°C	51.6	9.7	44.7	4.4	39.6	4.0	17.0*	30.9	51.0

20 % Fe_2O_3



20% Fe_2O_3

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	B_{hf} [T]	rel. area [%]	45 T (2 positions)		39 T		26 T		Rel.area [%]
			B_{hf} [T]	rel.area [%]	B_{hf} [T]	rel.area [%]	B_{hf} [T]	rel.area [%]	
4T 1000°C			43.6	12.4	38.4	18.0	25.2	29.1	40.5
22T 1000°C	51.5	10.9	44.3	10.4	39.05	15.6	24.3	17.9	45.2
4T N 1000°C			44.2	10.3	38.9	18.0	24.5	21.8	49.9
	Hematite		**Magnetite**						**PM**
	B_{hf} [T]	rel.area [%]	B_{hf} [T]	rel.area [%]	B_{hf} [T]	rel.area [%]			
22T N 1000°C	51.6	6.9	49.1	30.9	45.8	48.5			13.6

4. Conclusions

- ✓ all the samples with 30 % Fe_2O_3 contained **hematite**
- ✓ the annealing in N_2 atmosphere causes the increase of the relative area belonging to **the paramagnetic state**
- ✓ we were able to only distinguish 3 various positions of iron **in ε-Fe_2O_3**
- ✓ relative areas of the 4 (or 3 in our case) various positions of Fe in ε-Fe_2O_3 **are not according** to literature data
- ✓ the transformation to ε-Fe_2O_3 was **not yet finished** in our range of annealing temperatures and Fe oxide concentrations
- ✓ our conditions of preparations (Fe-oxide concentration, sonification power, temperatures and atmospheres of annealing) do not allow to produce nanocomposite systems only containing **ε-Fe_2O_3 oxide phase**

This is only part of the research!

Acknowledgements

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Thank you for your attention