A Study of Iron Oxide Nano-particles Manufactured by Reverse Micelles

Jari í Hjøllum

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Abstract

This thesis presents a study of the implementation of the reverse micellar technique. The technique provides a tool for manufacturing iron oxide nano-particles with a high degree of control of particle size, and chemical composition. The thesis contains a report of the development process of applying the reverse micellar technique for manufacturing iron oxides. Using the technique it has been attempted to manufacture the iron oxides magnetite (Fe₃O₄), maghemite (γ -Fe₂O₃) and hematite (α -Fe₂O₃).

The manufactured samples have been studied and characterized by Mössbauer spectroscopy and by Transmission Electron Microscopy (TEM). Mössbauer is used because of its unique strength in characterizing the chemical composition of iron compounds, and TEM is used for studying the size properties of the manufactured nano-particles.

Attempts to produce hematite were not successful, but the iron compounds magnetite, maghemite and goethite (α -FeOOH) have been successfully manufactured and investigated using Mössbauer spectroscopy. Selected magnetite and maghemite samples have been investigated using TEM imaging.

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Supervisors:

Klaus Bechgaard, POL, Risø National Laboratory & Luise Theil Kuhn, Materials Research Department, Risø National Laboratory & Morten Bo Madsen, Center for Planetary Science, University of Copenhagen

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1 Preface

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3 Introduction

I have been a member of the Mars/Mössbauer group at the Ørsted Laboratory at Copenhagen University since the spring 2001. During this time I have worked much with various iron oxides, and their possible relation to the geology and history of Mars.

The Mars/Mössbauer group has primarily been working with magnetic properties experiments [9, 24, 34], in which the properties of the magnetic dust on the Martian surface have been the subject of investigation. The properties and composition of the dust rich in iron oxides may reveal much about the past of Mars.

It is known that most of the iron in the Martian rocks is Fe^{2+} , while the iron in the Martian dust is in the form of Fe^{3+} . Assuming that the dust is eroded rocky material, an oxidation of the iron has occurred. It is believed [32, 33, 40], that the dust particles on the Martian surface are composed of several much smaller particles, magnetic and nonmagnetic. The color of the dust is most similar to hematite (α -Fe₂O₃), but experiments on the NASA Mars Pathfinder mission in 1997, have revealed that the magnetization of the particles is larger than that of bulk hematite. Therefore the dust particles must contain some other magnetic material, for instance maghemite (γ -Fe₂O₃) or magnetite (Fe₃O₄).

The formation of various iron oxides in nature is very dependent on, or highly affected by the abundance of water, and therefore the investigations of the iron oxides in the Martian dust may tell a great deal about the geological history of Mars. In the hunt for life on Mars, the iron oxide dust might prove to be a very important piece in the puzzle. Recently results from the Mars Exploration Rovers showing the hydrated iron sulfate mineral called jarosite, $(K, Na, X^{+1})Fe_3(SO_4)(OH)_6$, [50] indicate that Mars has a wet past.

Iron oxides and in particular magnetic iron oxide nano-particles play an increasingly big role in science and technology in the modern world. Nano-particles are for instance used as catalysators in various chemical reactions, and the modern information technology is highly dependent on magnetic storage devices, in which magnetic nano-particles is the central storage medium.

Modern hard drives use maghemite nano-particles as storage medium, but ideally one is interested in nano-particles of other materials with a higher magnetic moment, such as magnetite, provided that it is stable, or a non-stoichiometric magnetite, which have a larger magnetic moment than maghemite.

Magnetite has great potential as a candidate for use in spintronics, microelectronic devices that function by using the spin of the electron, since it has a spin polarization of close to 100% at low temperatures. Spintronics are used in devices such as MRAM (Magnetic Random-Access Memory), and may eventually lead to the development of quantum microchips.

Recently it has been showed that it is possible to construct the basic electronic logical components, the AND, OR and NOT gates, in circuits made of magnetic material. Instead of a flowing current, the circuits function by moving domain walls which exist between magnetic domains. This opens the possibility to construct cheap logical circuits without the use of electricity.

In recent years magnetic nano-particles have played an increasing big role in medicine: It may be used as controllable carriers of medicine to a predetermined location in the body. It may in the coming years find new application as a part of cancer treatment, where a high frequency magnetic field will be applied to a tumor in which magnetic nano-particles have been injected. The high frequent movement of the magnetic particles will thereby heat the tumor locally, as well as damage the cells, both causing the tumor cells to die. Recent work has also suggested that there in some cases might be a connection between Alzheimer's disease and the content of magnetite in brain.

For my master thesis work I wanted to combine several fields of physics. I wanted my thesis to be an experimental thesis, and I wanted to continue with work relevant for Mars exploration, iron oxides and Mössbauer spectroscopy. Furthermore I wanted to work on the frontier of nano-physics.

My supervisor, Morten Bo Madsen, had the interesting idea that the magnetic properties of hematite and magnemite might become more similar as the particles become very small. I considered this idea worth investigating. Around the same time the reverse micellar technique

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[8, 12, 13] was brought to my attention by my other supervisor Luise Theil Kuhn.

The reverse micellar technique is a chemical technique in which it is utilized that soap and water in an excess of oil, will self arrange into a micro emulsion system, which consists of water droplets with a shell of soap, a micelle, within the oil bulk. Chemical reactions can therefore take place inside the micelle, which acts as a miniature test tube. The micelle size should therefore set an upper limit for the size of manufactured particles.

The technique is interesting, since it provides a unique view into the processes of iron oxidation, an area in which there still are unknown mechanisms. Furthermore the technique is potentially very useful for technological development, since it may provide a simple procedure to manufacture large quantities of well characterized mono-disperse nano-particles, which are very useful in for instance magnetic storage devices and medicine.

With the presented perspectives in mind, I decided to attempt to manufacture various magnetic iron oxide nano-particles using the reverse micellar technique, and to investigate their magnetic and size related properties.

The technique did not prove as easy to work with as first believed, and very much time (~ 600 hours) was spent working in the laboratory tuning and developing the technique. Furthermore over 100 Mössbauer spectra have been recorded during the course of this project, which makes up a considerable amount of data to be analyzed.

However, it turned out that the hard work spent in the laboratory and analyzing data was well worth the while, since I was able to get some interesting results and new discoveries, which are presented in this thesis.

Copenhagen, July 8, 2004

Jari í Hjøllum

On the Gaussian curve: Experimentalists think that it is a mathematical theorem while the mathematicians believe it to be an experimental fact. - Jules Henri Poincare (1854-1912), French mathematician.

4 Magnetism

Since we in this project will be dealing with magnetic properties of small particles, it is necessary use a little time to go through the basic concepts of magnetism and small particles.

4.1 Theory of magnetism

Magnetism describes the effect of spontaneous alignment of the magnetic moments in matter, to form an energetically favorable state which has a macroscopic magnetic moment, even in the absence of an external magnetic field. In the following I will discuss the theory of magnetism necessary for the understanding of this thesis work. This section is based on mainly based on [18, 37, 63].

Even though magnetism is a quantum mechanical effect, many of its properties can be described by Maxwell's equations. The Maxwell equations fail to explain the origin or the variation in magnetism. The origin of magnetism lies in quantum mechanics. To understand magnetism we must therefore use quantum mechanics. From electromagnetism we get an expression for the magnetism in matter

$$\vec{B} = \mu_0 (\vec{H} + \vec{M}),$$
 (4.1)

where μ_0 is the vacuum permeability, \vec{B} is the induced magnetic field, \vec{H} is the magnetic field and \vec{M} is the magnetization of the material, i.e. the density of magnetic dipole moments $\vec{\mu}$ of the electrons. $\vec{\mu}$ is in units of \hbar is given by

$$\vec{\mu} = -\mu_{\rm B}(\vec{L} + g\vec{S}),\tag{4.2}$$

where $\mu_{\rm B}$ is the Bohr magneton, \vec{L} is the orbital angular momentum, and \vec{S} is the spin momentum, and g is the electron gyromagnetic ratio [63]. Considering an atom it is clear that a filled shell has no net magnetic moment, since the sum of the orbital angular moments and the spin moments of the electrons vanish. A magnetic moment is only present if there exists an unfilled shell, *e.g.* the transition metal group and the rare earth metals, which have incompletely filled 3d and 4f shells, respectively. These metals exhibit a strong magnetic moment.

The nucleus has a magnetic moment $\vec{\mu}_n$ related to its spin \vec{I} , given by

$$\vec{\mu}_{\rm n} = g_{\rm N} \mu_{\rm N} \vec{I},\tag{4.3}$$

where the nuclear magneton, $\mu_{\rm N}$, is given by

$$\mu_{\rm N} = (m_{\rm e}/m_{\rm N})\mu_{\rm B} = (1/1836)\mu_{\rm B}, \quad g_{\rm N} \approx 1,$$
(4.4)

where $m_{\rm e}$ is the electron mass and $m_{\rm N}$ is the neutron mass.

The nuclear contribution is much smaller than the magnetic momentum related to the electrons, and is usually ignored when considering the magnetization of a crystal.

There are 3 main components in the interactions between atoms in a magnetic crystal. These are the exchange interaction, the dipole-dipole interaction, and the spin-orbit interaction. We will not make a thorough investigation of the theory, since this is done beautifully elsewhere, but make a make an overview.

We will consider the Heisenberg Hamiltonian, in which the energy of the interaction between two ions is written as

$$\hat{H}_{\text{Heisenberg}} = -2 \sum_{\langle i,j \rangle} J_e(\vec{R}_i - \vec{R}_j) \hat{S}_i \cdot \hat{S}_j = -2 \sum_{\langle i,j \rangle} J_e \hat{S}_i \cdot \hat{S}_j,$$
(4.5)

where \hat{S}_k is the spin operator of the k'th ion, consisting of either the spin angular momentum in the case of the iron-group ions, or the total angular momentum of orbital and spin angular moments in the case of the rare earth ions [63]. The $J_e(\vec{R}_i - \vec{R}_j)$ is called the exchange integral and \vec{R}_k is the position of the k'th ion. The exchange interaction is a short range interaction, and often only nearest neighbor ions are considered.

For a positive J_e , the exchange energy is minimal when the spins are aligned parallel, and for negative J_e the minimum is when the spins are aligned anti-parallel. Therefore exchange energy tends to align the spins parallel or antiparallel.

The super exchange interaction is important in some materials, and is an exchange interaction between magnetic ions carried by intermediate non-magnetic ions.

If there is an external magnetic field \hat{H} present, a Zeemann term has to be added to (4.5):

$$\hat{H}_{\text{Zeemann}} = -g\mu_{\text{B}} \sum_{j} \vec{H} \cdot \hat{S}_{j}.$$
(4.6)

The dipole-dipole Hamiltonian gives the energy involved in the interaction between the dipole magnetic moments of the ions. It is given by

$$\hat{H}_{\text{dipole}} = \frac{\mu_0}{4\pi} \sum_{i>j} \frac{1}{r_{ij}^3} \bigg(\vec{\mu}_i \cdot \vec{\mu}_j - \frac{3(\vec{r}_{ij} \cdot \vec{\mu}_i)(\vec{r}_{ij} \cdot \vec{\mu}_j)}{r_{ij}^2} \bigg), \tag{4.7}$$

where \vec{r}_{ij} is the distance vector between the two ions and $\vec{\mu}_k$ is the magnetic moment of the k'th atom.

The orbiting electron experiences a magnetic field induced by its own rotation in orbit, the so-called spin-orbit interaction. The hamiltonian is given by

$$\hat{H}_{\rm spin-orbit} = \lambda(\hat{L} \cdot \hat{S}) = \pm g\mu_{\rm B}^2 Z_{\rm eff} \langle \frac{1}{r^3} \rangle \frac{1}{2S} (\hat{L} \cdot \hat{S}), \qquad (4.8)$$

where L is the orbital angular momentum operator, λ is the spin orbit constant given in the last part of the expression. Z_{eff} is an effective charge distribution in the surrounding of the nucleus. $\langle 1/r^3 \rangle$ is an average over the electrons in the incompletely filled shells. λ is positive if the shell is less than half filled, and negative if the shell is more than half filled.

As earlier said, the exchange, the dipole-dipole and the spin orbit are the three most dominant interactions in the iron-group elements.

The effects concerning the interactions between the magnetic moments of the spins and their relative positions are the exchange interaction and the dipole-dipole interaction.

The exchange is as said to be very strong, but it is very short-ranged, since it is carried by the overlapping orbits of the electrons. The dipole-dipole is less powerful, but has longer range. The interaction between these two is further discussed in section 4.3.

The last interaction is the spin-orbit which is the only one coupling the spin and the lattice in which the ion resides. It is further discussed in section 4.2.

4.2 Anisotropy

It is easier to magnetize a crystal in some directions than others. These easy magnetization directions depend on the anisotropy of the crystal. The direction in which the magnetization requires most energy is called the hard direction of magnetization. The anisotropy energy is the energy related to turn the magnetization away from the easy magnetization direction. Anisotropy has its origin in different physical quantities. We will discus exchange energy, crystal anisotropy and shape anisotropy because these are the dominating anisotropies [18]. We will in this section use concepts introduced in section 4.1.

The **exchange energy** is due to spin-spin coupling. Exchange energy has no direct contribution to anisotropy. However the strong spin-spin coupling is linked to a certain orientation through the crystal anisotropy. Usually the exchange interaction considered is between electrons of ions that are a part of a certain crystal structure, which does not change locally. However as we might have to consider variations in oxidation of nano-particles inside a single domain, we have to consider exchange interactions which change locally, since the electrons are not part of a periodic crystal structure. This might cause unexpected change to the anisotropy.

Crystal anisotropy is due to spin-orbit coupling. For cubic crystal structures the orbital angular momentum is almost quenched. This means that the orbits are strongly fixed to the lattice and there is no net orbital magnetic moment ($\langle L \rangle = 0$). Hence the Landé factor given by [29]

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)},$$
(4.9)

which is approximately 2, where J = S + L. The spin-orbit coupling couples the spin to the lattice.

Shape anisotropy is due to dipole-dipole interaction. In an ellipsoidal (or prolate spheroid) nano-particle the dipole-dipole interaction will force the dipoles to align along the major axis of the particle. The magnetic field from a dipole is, in coordinate free form, given by [21]

$$\vec{B}_{\rm dip}(\vec{r}) = \frac{\mu_0}{4\pi} \left(-\frac{\vec{\mu}}{r^3} + \frac{3(\vec{\mu} \cdot \vec{r})\vec{r}}{r^5} \right),\tag{4.10}$$

where $\vec{\mu}$ is the dipole moment. If the dipole moments are parallel to a minor axis, there will be an overall demagnetization of the particle. The effect of this demagnetization is to align the dipole moments antiparallel. This requires the presence of a domain wall. For single domain particles this is not possible (see section 4.3). Hence the magnetic dipoles are aligned along the major axis.

4.3 Domain theory

Domains are regions in magnetic matter, where all the magnetic moments are aligned. Since these are important to the macroscopic properties of particles of magnetic matter, a discussion of domain theory is required.

Domains will act as powerful dipoles, and will therefore favor antiparallel orientation in order to minimize the magnetic field energy. This will conflict with the exchange interaction, which (for ferri/ferromagnetic materials), favors parallel spin orientations.

For a particle in which all the magnetic moments are aligned, the total dipole will generate a large external magnetic field in a large volume.

At a certain particle size the dipole-dipole interaction will become comparable to the exchange interaction (see section 4.1), meaning that the magnetic field energy will become comparable to or larger than the exchange energy, and it will be energetically favorable to split the domain into separate domains. However, the anisotropy energy will favor orientation of the spins in the easy directions of the crystal structure, and the splitting of a domain is thus a result of the competition between these three forces.

A Bloch wall is a border layer between two domains. The Bloch wall is the transition layer between two domains with non-parallel magnetic moments, where the local magnetic orientation is gradually changed.

The width of a Bloch wall is ideally independent of particle size [30], as it is determined by the exchange interaction and the anisotropy energy. However in small particles the surface affects the wall to change shape and thickness.

By division into domains, the energy in the external magnetic field is reduced. This is done on expense of an increase in the exchange energy inside a Bloch wall. The splitting into domains is thus result of the minimization of the total energy, i.e. the dipole magnetic energy and exchange energy.

Whether a particle is a multidomain or single domain particle thus is a balance between dipole and exchange energy.

The energy in a Bloch wall can be calculated from (4.5). If we treat the spins as classical vectors the exchange energy is given by [19]

$$E_{ex} = -2\sum_{\langle i,j \rangle} J_e \hat{S}_i \cdot \hat{S}_j = -2\sum_{\langle i,j \rangle} J_e |\hat{S}_i| \cdot |\hat{S}_j| \cos \phi$$
(4.11)

where ϕ is the angle between the spins. If the spins make a small angle ϕ we get

$$E_{ex} \cong -2\sum J_e |\hat{S}|^2 (1 - \phi^2/2),$$
(4.12)

which gives that in the process of changing the angle between the spins from zero to ϕ , the energy is increased by $J_e|\hat{S}|^2\phi^2$. Let $\phi = \phi_0/N$ where N is the number of atoms in a row in a Bloch wall. Then the exchange energy for a row is given by

$$E_{ex,row} = N E_{ex} = J_e |\hat{S}|^2 \phi_0^2 / N.$$
(4.13)

From this one would expect that the domain wall would become infinitely thick, filling then entire particle. However this is not the case. The reason lies in the anisotropy of the particle, which has a limiting effect on the wall thickness. While it is energetically favorable for the exchange interaction to maintain a small angle ϕ , this is not the case when considering the anisotropy. We consider a wall of thickness Na where a is the lattice constant. The anisotropy energy σ_{an} is approximately given by

$$\sigma_{an} \simeq KNa, \tag{4.14}$$

where K is the anisotropy constant.

The total energy pr unit area may be written as:

$$\sigma = \sigma_{ex} + \sigma_{an}.\tag{4.15}$$

 σ_{ex} is obtained by multiplying (4.13) by $1/a^2$. By minimizing σ with respect to N we find

$$N = \sqrt{\frac{J_e |\hat{S}|^2 \sigma_0^2}{K a^3}},$$
(4.16)

which for iron gives $N \simeq 300$ and a wall thickness of 100 nm.

When particles are sufficiently small (diameter in the range from 1 nm to 100 nm [37]), it is not energetically favorable to maintain a multi domain.

Reversal of the magnetic moment of a single domain particle by an applied field can be achieved either coherently or incoherently. Examples of incoherent magnetic moment reversal are domain rotation, fanning, curling or buckling.

For small particles the fraction S/V, where S is surface and V is volume, is very large. Therefore a large fraction of the atoms will be near the surface, and thereby lacking some neighboring atoms, giving rise to decreased exchange energy. This causes a greater susceptibility to thermal agitation of the magnetic moments.

Magnetization of a multi domain particle is done first done by reversible Bloch wall displacement, then irreversible Bloch wall displacement, and finally by domain rotation (see figure 4.1 and figure 4.2).



Figure 4.1: A typical hysteresis curve for a ferromagnetic material. Figure reproduced from [30].



Figure 4.2: Different kinds of domain magnetization. Figure reproduced from [30].

4.4 Ferromagnetism, Ferrimagnetism and Antiferromagnetism

From the (4.5) we have that the simple orientations of the ionic spins are either parallel or antiparallel. Equation (4.5) permits an infinity of other configurations, such as the helix structure [63], however, these will not be discussed further.

In the case of the parallel orientation of the ionic spins with equal magnetic moment, we have a ferromagnet. It has a spontaneous order and a macroscopic magnetic moment, up to a certain temperature, the Curie temperature, T_C , at which the order disappears.

In case of the anti-parallel orientation, or of the ionic spins not having equal magnetic moment, we have a ferrimagnet or an antiferromagnet. In the antiferromagnet the antiparallel spins cancel each other out, and the net magnetic moment is zero. In the ferrimagnet this is not the case and the material has a net magnetic moment. The ferrimagnet behaves in most cases as a ferromagnet. The temperature at which the spontaneous order disappears is called the Néel temperature, T_N , and the Curie temperature for the antiferromagnet and the ferrimagnet respectively.

The spontaneous order can disappear either through a first order transition in which the order drops to zero discontinuously, or though a second order transition in which the order drops to zero continuously, presented in figure 4.3. Since the macroscopic magnetic moment is very different for single- and multidomain particles, figure 4.3 shows the saturation magnetization when an external field is applied. The magnetization of a multidomain particle is very complex, and involves particle shape, anisotropy, chemical composition, temperature and the magnetic environment.



Figure 4.3: Schematic illustration of the saturation magnetization vs. temperature for an unspecified magnetic material. **a)** A first order/superparamagnetic transition. T_B is the blocking temperature. **b)** A second order/paramagnetic transition. T_C is the Curie temperature.

The first order transition can only occur for single domain particles. Above the blocking temperature, T_B , the material is said to be superparamagnetic, which is discussed further in section 4.5. Materials which follow the second order transition are paramagnetic above the Néel/Curie temperature.

The temperature dependence of the magnetization of nano-particles may be significantly different. There are examples of nano-particles which have a significantly different Néel/Curie temperature, than that of the bulk material [31], due to finite size effects.

Figure 4.4: Schematic representation of three types of magnetic ordering in solids (material with a crystal structure). A) Ferromagnetic, all spins are aligned. B) Antiferromagnetic, the spins in the different sublattices have antiparallel spins, and cancel each other resulting in a zero net magnetic moment. C) Ferrimagnetic, the spins in the different sublattices have antiparallel spins, but do not cancel each other, resulting in a net magnetic moment. Figure reproduced from [16].

4.5 Superparamagnetism

The dynamic single domain size is defined as the size of a single domain sized particle at which the thermal energy becomes comparable or larger than the magnetic energy. When particles become as small as or smaller than the dynamic single domain size the particles become superparamagnetic. The magnetic moment will not be locked to the crystal, and it will therefore fluctuate freely around the easy magnetization directions.

If the anisotropy of a particle is uniaxial the magnetic energy can be approximated by

$$E(\theta) = KV\sin^2\theta,\tag{4.17}$$

where K is the magnetic anisotropy constant, V is the volume of the particles and θ is the angle between the magnetization and the easy magnetization direction [23, 42]. From (4.17) we get that two arbitrary energy minima are separated by an energy barrier of height KV. From [23] we get that the probability f of the angle θ being between θ and $\theta + d\theta$ is given by the Boltzmann distribution:

$$f(\theta)d\theta = \frac{\exp(\frac{-E(\theta)}{k_{\rm B}T})\sin(\theta)d\theta}{\int_0^{\frac{\pi}{2}}\exp(\frac{-E(\theta)}{k_{\rm B}T})\sin(\theta)d\theta}.$$
(4.18)

Generally the relation between $k_{\rm B}T$, KV and the magnetic moment of the particle is:

- $k_BT \ll KV$: $f(\theta)$ is large around $\theta = 0$ and therefore the magnetic moment is fixed around the easy direction of magnetization. The sample will appear magnetic in measurements.
- $k_BT \simeq KV$: For these values the magnetic moment fluctuates around the easy directions of magnetization, and has a small probability of crossing the energy barrier. A measurement of such a sample will show a decrease in the magnetic moment, and some experimental techniques, such as Mössbauer spectroscopy might show significant line broadening, and thus decreasing resolution.
- $k_BT \ge KV$: For these values the thermal energy is high enough for the magnetic moment to have a possibility of crossing the energy barrier. This phenomenon is known as superparamagnetic relaxation, which is characterized by the relaxation time τ . τ is the mean time between two passages of the energy barrier. The relaxation time τ for a particle with uniaxial anisotropy is approximately given by the expression [43]

$$\tau = \tau_0 e^{\frac{KV}{k_B T}}; \quad KV \sim k_B T, \tag{4.19}$$

where k_B is the Boltzmann constant, V is the volume, T is the temperature and K is the anisotropy constant. From expression (4.19) we see that τ varies violently with temperature, and also is very dependent on the volume of the particle.

When the measurement time is larger than the relaxation time τ , the measuring apparatus cannot detect a permanent orientation of the magnetic moment, since the magnetic orientation of a particle does fluctatuate violently during the measuring time. The measuring apparatus will therefore reveal a very small or zero magnetic moment. This implies that detection of a permanent magnetic moment is dependent on measurement method.

For instance Mössbauer spectroscopy (section 5) may see a sample as being magnetic, whereas a Hall probe might see it as being superparamagnetic. The explanation is that the measurement time for these two detectors is widely different, about $\sim 10^{-9}$ s and $\sim 10^{-4}$ s respectively.

In order to destroy the superparamagnetism of the particle, and make it magnetic, one has to ensure that the thermal energy is lower than the magnetic energy. This is done either by lowering the thermal energy of the particle by cooling, or by increasing the magnetic energy of the particle by applying an external magnetic field.

4.6 Canting

In bulk material the proportion of atoms that are located at or very near (2-3 crystal planes) the surface is negligible, and hence measurement yield will be due to bulk atoms.

In nano-particles a large fraction of the atoms are placed at or close to the surface, which gives the nano-particles gives some special properties. The periodic border conditions are not valid in nano-particles since a surface atom does not have neighbors in all directions. The surface atoms may therefore have a significant influence on the magnetic order in nano-particles and can not be neglected.

Canting is one of the major surface atom effects. Due to the imbalance in surrounding magnetic ions, the surface ion will not follow the magnetic direction of the bulk ions, but will instead be orientated in a more energetically favorable direction. The direction will be dictated by the dipoledipole and exchange interactions and the anisotropy energy.

5 Mössbauer spectroscopy

The force of Mössbauer spectroscopy is its ability to see the local magnetic environment at the nucleus. In contrast, other experiments such as hysteresis curve measurements measure the macroscopic response to an applied field. As mentioned earlier the external field can be very different for single- and multidomain particles, and is can be difficult to investigate local magnetic environments and interactions. Due to its force in the area, Mössbauer spectroscopy is used to study these magnetic interactions.

Since a vast majority of the sample analysis is done with Mössbauer spectroscopy, we will in this section go through the theory, application and analysis methods. The following sections are based in part on [35, 42].

5.1 The Mössbauer effect

Mössbauer spectroscopy would not be very useful without the presence of the Mössbauer effect. The force of Mössbauer spectroscopy is its ability to measure very small deviations in the magnetic field, quadrupole field felt by the nucleus of the ⁵⁷Fe atoms, reflecting its chemical environment.

The Mössbauer effect was discovered in 1958 by Rudolf L. Mössbauer. Prior to the discovery of the effect, the emission and absorption of nuclear gamma radiation was treated in a classical way, and the energy and momentum conservation was considered for a free nucleus.

We consider the emission of a gamma ray from a nucleus at rest. The emission is associated with recoil of the nucleus to conserve momentum. The energy of the gamma ray is thus

$$E_{\gamma} = E_0 - E_R,\tag{5.1}$$

where E_0 is the difference between the excited state of the nucleus and the ground state and E_R is the recoil energy.

The recoil energy is given as

$$E_R = \frac{p^2}{2M} = \frac{E_{\gamma}^2}{2Mc^2},$$
(5.2)

where p is the momentum of the gamma photon equal to the recoil momentum of the nucleus. M is the mass of the nucleus. In case of an absorption there is an equal energy loss to the absorbing nucleus.

Resonant gamma ray emission can only occur if the cross section of the emission and absorption lines overlap. In order to find whether resonant gamma ray emission will occur, the recoil energy of the gamma photon must be compared with the line width Γ of the emission line. The line width is related to the mean lifetime of the excited state as

$$\Gamma \tau = \hbar. \tag{5.3}$$

When gamma rays are emitted by free nuclei (e.g. in a gas) which move isotropically in thermal motion, the width of the emission line will be further broadened by the Doppler effect. The Doppler broadening at the temperature, T, is given by

$$D \cong 2\sqrt{k_B T E_R},\tag{5.4}$$

where k_B is the Boltzmann constant.

The typical line width, Γ , is of the order 10^{-8} eV for $\tau \approx 100 \text{ ns}$. Since E_R is of the order 10^{-4} eV to 10^{-2} eV , and the emission and absorption lines are separated by $2E_R$, resonance is very unlikely to occur since $E_R \gg \Gamma$. The Doppler broadening is typically of the order 10^{-3} eV . Thus even with the Doppler broadening, resonance is very unlikely to occur, since the cross section between the emission and absorption lines becomes very small (see figure 5.1).

What Mössbauer discovered in 1958, was that when the emitting and absorbing nuclei are bound in a solid, a certain fraction of the emissions may occur with negligible energy loss due to recoil. This can be explained by the fact that the recoil energy is absorbed by the crystal as a whole. If we consider (5.2) and replace the mass M of the nucleus with the mass of the entire crystal, we see that the recoil energy in becomes very small. This is however not the full picture, and we have to consider the quantum-mechanical aspects of an atom embedded in a crystal. There are three cases to be considered:

- If the free-atom recoil energy, E_R , is larger than the binding energy of the atom in the crystal, then the emitting atom will be displaced from its position in the crystal lattice, and the situation is similar to the situation of the free atom. This will typically occur when the gamma ray energy is of the order of 1 MeV. The nuclear gamma resonance will not occur in this case.
- If E_R is smaller than the binding energy, but larger than the characteristic phonon energy defined in terms of the Debye energy (ω_D) or Einstein energy (ω_E) , the atom will remain at its position in the lattice, but will dissipate the recoil energy by creating phonons in the lattice. This will typically occur when the gamma ray energy is of the order of several 100 keV. The energy of the emitted photon will be smaller than the resonance energy by $n\omega_D$ or $n\omega_E$, and nuclear gamma resonance will not occur in this case
- If E_R is smaller than the phonon energy, we have a new situation, since the solid as a quantum system can not be excited in any way. There is not enough energy to either displace the atom or to create a phonon. The recoil momentum has to be absorbed by the solid as a whole, in order for momentum to be conserved, and the atom will behave as if rigidly bound in the solid. From equation (5.2) we see that the recoil energy becomes negligible as compared with Γ in (5.3). This may occur for gamma ray emissions of the order 10-150 keV. When this occurs in both the emitting and absorbing matter, the conditions for nuclear gamma ray resonance are fulfilled, and a large resonance is observed. This recoil-free emission and absorption of nuclear gamma radiation is called the Mössbauer effect.

5.2 f-factor

The probability for the Mössbauer effect to occur is given by the f-factor. Neglecting multi-phonon processes in the 3rd case above $(E_R \ll \hbar \omega_E)$, the f-factor is given by

$$f = 1 - \frac{E_R}{\hbar\omega_E}$$
, $E_R = \frac{E_{\gamma}^2}{2Mc^2} = \frac{p^2}{2M} = \frac{\hbar^2\kappa^2}{2M}$, (5.5)

where κ is the magnitude of the wave vector. This gives

$$f = 1 - \frac{\hbar^2 \kappa^2}{2\hbar\omega_E M}.$$
(5.6)

A general expression for the f-factor is given by the Debye-Waller (W) factor:

$$f = \exp(-2W) = \exp(\frac{-4\pi^2 \langle x^2 \rangle}{\lambda^2}) = \exp(-\kappa^2 \langle x^2 \rangle), \tag{5.7}$$

where

$$\kappa = \frac{2\pi}{\lambda} = \frac{E_{\gamma}}{\hbar c},\tag{5.8}$$

where λ is the wavelength for the gamma photon and $\langle x^2 \rangle$ is the component of the mean square amplitude of the emitting nucleus in the direction of the emitted gamma ray. From (5.7) we see that the f-factor is highly dependent on the ratio between $\langle x^2 \rangle$ and λ^2 . In gasses and viscous fluids the $\langle x^2 \rangle$ is not limited, which is why the Mössbauer effect is not seen here.

Using the Debye model of lattice dynamics, the dependence of the Mössbauer effect of temperature is given by

$$f = \exp\left(-\frac{6E_R}{k_B\Theta_D}\left(\frac{1}{4} + \frac{T^2}{\Theta_D^2}\int_0^{\Theta_D/T}\frac{xdx}{e^x - 1}\right)\right) = \exp(-2W),$$
(5.9)

where Θ_D is the Debye temperature, T is the temperature, $x = \hbar \omega / k_B T$. The Debye temperature for iron is 470 K [20].

At low temperatures $(T \ll \Theta_D) f$ is given by

$$f = \exp\left(-\frac{E_R}{k_B\Theta_D}\left(\frac{3}{2} + \frac{\pi^2 T^2}{\Theta_D^2}\right)\right),\tag{5.10}$$

which at $T = 0 \,\mathrm{K}$ is reduced to

$$f = \exp\left(-\frac{3E_R}{2k_B\Theta_D}\right).$$
(5.11)

At high temperatures $(T \gg \Theta_D/2)$ is given by

$$f = \exp\left(-\frac{6E_RT}{k_B\Theta_D^2}\right).$$
(5.12)

The last expression is only valid in the range where the Debye model is valid.



Figure 5.1: Conditions for the occurrence of the nuclear gamma resonance for free nuclei. (a): When $\Gamma < 2E_R$. (b): When thermally broadened lines partially overlap. Figure reproduced from [35].

5.3 Line shape and resolution

As seen from (5.3), the recoil-free gamma radiation emitted from the source has a Heisenberg width Γ_s at half height. The distribution of energies around E_{γ} is given by the Breit-Wigner formula, resulting in a Lorentzian line shape

$$w(E) = \frac{(\Gamma_s/2)^2}{(E - E_\gamma)^2 + (\Gamma_s/2)^2},$$
(5.13)

where w(E) is amplitude as function of energy E. The cross section for resonance absorption is given by

$$\sigma(E) = \sigma_0 \frac{(\Gamma_a/2)^2}{(E - E_\gamma)^2 + (\Gamma_a/2)^2},$$
(5.14)

where Γ_a is the absorption line width. In a resonance experiment, the emission line is moved over the absorption line, resulting in an observed resonance line given by [35]

$$\sigma_{exp}(E) = \int_{-\infty}^{\infty} w(e)\sigma(E-e)de.$$
(5.15)

If we consider a thin absorber, we can neglect secondary emission and absorption, and (5.15) can be simplified to

$$\sigma_{exp}(E) = \sigma_0 \frac{(\Gamma_s + \Gamma_a)^2 / 4}{(E - E_\gamma)^2 + (\Gamma_s + \Gamma_a)^2 / 4}.$$
(5.16)

If $\Gamma_a \cong \Gamma_s \cong \Gamma$ we get:

$$\sigma_{exp}(E) = \sigma_0 \frac{\Gamma^2}{(E - E_\gamma)^2 + \Gamma^2}.$$
(5.17)

The energy resolution of the Mössbauer effect is defined by

$$\Delta E/E_{\gamma} = \Gamma/E_{\gamma},\tag{5.18}$$

and is of the order $10^{-12} - 10^{-15}$ depending on Mössbauer isotope. This very high resolution makes Mössbauer spectroscopy a very powerful tool for studying hyperfine interactions.

The maximum resonance absorption occurs when the source energy, E_{γ}^s , and the absorber energy, E_{γ}^a , coincide. Should this not be the case naturally it is possible to alter these values by moving either (usually the source) with respect to the other, thus taking advantage of the Doppler effect. The change of energy due to the Doppler effect is given by

$$\Delta E = \frac{v}{c} E_{\gamma},\tag{5.19}$$

where v is the velocity of the source.

5.4 ⁵⁷Fe Mössbauer spectroscopy

In this project only iron and iron-oxides are of interest, and therefore only Fe Mössbauer isotopes will be discussed. The naturally occurring isotopes of Fe are: ⁵⁴Fe, ⁵⁶Fe, ⁵⁷Fe, ⁵⁸Fe.

⁵⁴Fe, ⁵⁶Fe and ⁵⁸Fe have a nuclear spin of I = 0 in the ground state, and hence do not interact with a magnetic field. Therefore these isotopes can not reveal any information about the magnetic environment (see the sections 5.5, 5.6). However ⁵⁷Fe has a spin $I = \frac{1}{2}$ in the ground state and will therefore interact with a magnetic field, and can reveal information on the magnetic environment.

We will be dealing with transitions between $I = \frac{3}{2}$ and $I = \frac{1}{2}$ states of ⁵⁷Fe. These energy levels differ by the characteristic energy 14.41 keV. Due to hyperfine magnetic interaction, the energy levels split into 4 and 2 levels respectively. From the selection rules of quantum mechanics, we see that there exist only 6 possible transitions ($\Delta I = \pm 1$; $\Delta m = \pm 1, 0$). Other transitions would violate conservation of angular momentum.

If we consider the case where an external magnetic field is applied, the magnetic moment of the nucleus will be oriented along the applied field. If the external field is oriented parallel to the direction of the incoming photon, the transitions with $\Delta m = 0$ do not involve a change in angular momentum, and since the photon carries the angular momentum $\pm h$, these transitions are not allowed. The other 4 transitions are allowed, since they involve a change in angular momentum of h. If the applied field is oriented perpendicular to the direction of the incoming photon all transitions are allowed.

The six absorption lines are connected to the transitions as follows from table 5.1 and figure 5.2.

In the case where the magnetic field at the nucleus forms an arbitrary angle θ with the incoming photon, the relative transition probabilities, are given by the expression in table 5.1. The relative line intensities are also given for a random orientation of the magnetic field at the nuclei in an absorber.



Figure 5.2: Left: The 6 allowed transitions for ⁵⁷Fe. Right: The corresponding Mössbauer spectrum. Reproduced from [42].

5.5 Hyperfine interaction

A nucleus with a magnetic moment will interact with a magnetic field. A nucleus with quantum number I > 0 carries a magnetic dipole moment $\vec{\mu}$. Thus it will interact with a magnetic field at the nucleus. The interaction energy between $\vec{\mu}$ and a magnetic field, \vec{B} , is given by

$$E = -\vec{\mu} \cdot \vec{B}.\tag{5.20}$$

The magnetic interaction splits the nuclear energy into 2I + 1 equispaced sublevels. The energy of each m-level is given by [23]

$$E_m = -g_n \beta_n m B, \tag{5.21}$$

where g_n is the nuclear Landé factor, β_n is the nuclear magneton, and m is the m-quantum number. This interaction is however only a small perturbation on the energy gap, hence the name hyperfine interaction. This can be illustrated by the following calculation

$$\Delta E_m = E_{I,m=\frac{3}{2},\frac{3}{2}} - E_{I,m=\frac{1}{2},\frac{1}{2}} = -\beta_n B(g_e \frac{3}{2} - g_g \frac{1}{2}) = 2.56 \cdot 10^{-7} \, eV, \tag{5.22}$$

where B is the magnetic field, and we have used the value for the hyperfine field of bulk iron (33.02 T). This value is to be compared with the transition energy of 14.41 keV.

The magnetic field at the nucleus, \vec{B} , in (5.20) can be generalized to

$$\vec{B} = \vec{B}_{ext} + \vec{B}_{L} + \vec{B}_{D} + \vec{B}_{C},$$
 (5.23)

where the contributions are:

#	$ I;m\rangle$	\mapsto	$ I;m\rangle$	Angular dependence	Relative intensities
1	$ \frac{1}{2}; -\frac{1}{2}\rangle$	\mapsto	$ \frac{3}{2}; -\frac{3}{2}\rangle$	$9/4(1+\cos^2\theta)$	3
2	$\left \frac{\overline{1}}{2};-\frac{\overline{1}}{2}\right\rangle$	\mapsto	$ \frac{3}{2}; -\frac{1}{2}\rangle$	$3\sin^2\theta$	2
3	$\left \frac{\overline{1}}{2};-\frac{\overline{1}}{2}\right\rangle$	\mapsto	$ \frac{3}{2};+\frac{1}{2}\rangle$	$3/4(1+\cos^2\theta)$	1
4	$\left \frac{\overline{1}}{2};+\frac{\overline{1}}{2}\right\rangle$	\mapsto	$\left \frac{\overline{3}}{2};-\frac{\overline{1}}{2}\right\rangle$	$3/4(1+\cos^2\theta)$	1
5	$\left \frac{\overline{1}}{2};+\frac{\overline{1}}{2}\right\rangle$	\mapsto	$ \frac{3}{2};+\frac{1}{2}\rangle$	$3\sin^2\theta$	2
6	$\left \frac{1}{2};+\frac{1}{2}\right\rangle$	\mapsto	$ \frac{3}{2};+\frac{3}{2}\rangle$	$9/4(1+\cos^2\theta)$	3

Table 5.1: The six allowed transitions and the corresponding absorption lines, with the relative transition probabilities and line intensities. θ is the angle between the magnetic field and the gamma photon direction. Reproduced in part from [42].

- \vec{B}_{ext} is the external magnetic field,
- $\vec{B}_{\rm L}$ is the magnetic field arising from the orbital motion of the electrons,
- $\vec{B}_{\rm D}$ is the contribution from the magnetic moment of the spins of the electrons,
- $\vec{B}_{\rm C}$ is the contribution of the electron spin-density at the nucleus arising from the s-electrons.

 \vec{B}_C is often, by far, the largest contribution. It may be expressed by the Fermi contact term as

$$\vec{B}_{C} = 16\frac{\pi}{3}\mu_{\rm B} \left\langle \sum (|\Psi_{s}^{\uparrow}(0)|^{2} - |\Psi_{s}^{\downarrow}(0)|^{2}) \right\rangle, \tag{5.24}$$

where $\mu_{\rm B}$ is the Bohr magneton and $|\Psi_s^{\uparrow}(0)|^2$ and $|\Psi_s^{\downarrow}(0)|^2$ are the spin-up and spin-down densities for s-electrons at the nucleus. The summation is taken over all s-electrons.

5.6 Electric quadrupole interaction

Nuclear states with spin $I > \frac{1}{2}$ will have a non-spherical charge distribution, and hence give rise to a quadrupole moment at the nucleus. The shift of the energy levels can be derived as follows [42, (7.1)].

The charge deformation can be described by

$$eQ = \int \rho_n(\vec{r}) \cdot r^2 (3\cos^2\theta - 1)d\tau, \qquad (5.25)$$

where Q is the electric quadrupole moment, +e is the charge of a proton and $\rho_n(\vec{r})$ is the nuclear charge density in the volume element $d\tau$ at the distance r from the center of the nucleus and at an angle θ to the nuclear spin quantization axis.

The electric quadrupole energy depends on the electric field gradient (EFG) at the nucleus. This results in a 3×3 tensor [42, (7.2-3)]

$$EFG = \nabla E = -\nabla^2 V$$
, where $V_{ij} = \frac{\partial^2 V}{\partial i \partial j}$, (5.26)

where i, j = x, y, z. If it is assumed that the order of differentiation is interchangeable, then the EFG tensor will be symmetric. Hence it can be diagonalized. Further the Laplacian (5.26) requires a traceless tensor ($\sum V_{ii} = 0$). It is therefore necessary to define the EFG by two independent properties η and V_{zz} :

$$\eta = \frac{V_{xx} - V_{yy}}{V_{zz}}.$$
(5.27)

If the axis are arranged such that $|V_{zz}| \ge |V_{xx}| \ge |V_{yy}|$, then $0 \le \eta \le 1$. The tensor can be considered to be representing two contributions:

- 1. A *lattice contribution* arising from the charges of neighboring ions which surround the Mössbauer atom in a non-cubic lattice.
- 2. A valence electron contribution arising from an anisotropic electron distribution in the valence shell of the Mössbauer atom.

The total contribution to the quadrupole tensor can, to a good approximation, be represented by [42]

$$V_{zz} = (1 - \gamma_{\infty})(|V_{zz}|)_{\text{slat}} + (1 - R)(|V_{zz}|)_{\text{val}}, \qquad (5.28)$$

and

$$\eta = \frac{1}{V_{zz}} (1 - \gamma_{\infty}) (|V_{zz}|)_{\text{lat}} \eta_{\text{lat}} + (1 - R) (|V_{zz}|)_{\text{val}} \eta_{\text{val}},$$
(5.29)

where γ_{∞} and R are the so called Sternheimer shielding factors [42]. For Fe-atoms $1-\gamma_{\infty}$ is approximately 10, whereas 1-R is of the order of 0.65-0.75. The energy levels are shifted according to the equation [42, (7.13)]

$$E_Q = \frac{eQV_{zz}}{4I \cdot (2I-1)} (3m^2 - I(I+1))\sqrt{(1+\frac{\eta^2}{3})},$$
(5.30)

where *m* is the m-quantum number. The ground state of Fe does not split since it has a spin of $I = \frac{1}{2}$ and therefore no quadrupole moment. The first excited state has spin $\frac{3}{2}$ and will split into two components, $m = \pm \frac{3}{2}$ and $m = \pm \frac{1}{2}$ (figure 5.3).



Figure 5.3: The quadrupole splitting of 57 Fe and the effects in Mössbauer spectroscopy. Figure reproduced from [42].

In the case of no magnetic field (hyperfine field, see section 5.5) at the nucleus, but only an electric field gradient, the relative intensities of the two lines in the quadrupole split spectrum depend on the direction of the principal axes relative to the gamma photon direction. For an axially symmetric EFG ($\eta = 0$), the angular dependencies are given in table 5.2.

m>	\mapsto	m>	Angular dependence
$ \pm 3/2>$	\mapsto	$ \pm 1/2>$	$1 + \cos^2 \theta$
$ \pm 1/2>$	\mapsto	$ \pm 1/2 >$	$5/3 - \cos^2 \theta$

Table 5.2: Angular dependencies of ${}^{57}Fe$ Mössbauer transitions for the axially symmetric EFG tensor. Reproduced from [42].

5.7 The isomer shift

The isomer shift arises from electric interaction between the nucleus and the s-electrons, since only the s-electrons have a non-zero probability of being in the vicinity of the nucleus. From [42] we get

$$\delta E = \int_0^\infty -e|\Psi(r)|^2 (V' - V) 4\pi r^2 dr, \qquad (5.31)$$

where

$$V = \frac{Ze}{4\pi\epsilon_0 r}, \quad (r > 0), \tag{5.32}$$



Figure 5.4: The isomer shift of ⁵⁷Fe and its effect in Mössbauer spectroscopy. The electric monopole interaction shifts the levels without lifting the energy levels. Figure from [42].

is the electrostatic potential for a nuclear point charge Ze at a distance r, while V' is the potential for a nucleus of finite size. V' is given by

$$V' = \frac{Ze}{4\pi\epsilon_0 R} (\frac{3}{2} - \frac{r^2}{2R^2}), \quad (r \le R),$$
(5.33)

$$V' = \frac{Ze}{4\pi\epsilon_0 r}, \quad (r \ge R).$$
(5.34)

Insertion into (5.31) gives:

$$\delta E = \frac{1}{10\epsilon_0} Z e^2 R^2 \Psi(0)^2. \tag{5.35}$$

The nucleus has different radii in the ground state, R_g , and excited state, R_e . This yields an energy difference of $\Delta E = \delta E_e - \delta E_g$. Furthermore the source and absorber usually have different chemical environments, so $|\Psi_a(0)|^2 \neq |\Psi_s(0)|^2$. Summing these components, we get the total expression for the isomer shift

$$\delta = \frac{Ze^2}{10\epsilon_0} (R_e^2 - R_g^2) (|\Psi_a(0)|^2 - |\Psi_s(0)|^2), \qquad (5.36)$$

visualized by figure 5.4.

5.8 Zeemann effect

If the atom is subjected to an external magnetic field we have a situation which is similar to that of the hyperfine interaction. The only difference lies in the origin of the magnetic field. However the result is essentially the same. The interaction energy between $\vec{\mu}$ and the magnetic field is given by (5.20).

Ferromagnetic materials have a simple response to an applied magnetic field, and the hyperfine field will be increased or decreased, depending on the angle between the magnetic moment of the ion and the applied field.

Antiferromagnetic and ferrimagnetic materials have a somewhat different response. These materials have multiple sublattices magnetically oriented in different directions. Depending on the angle of the applied magnetic field, it will be source of an increase or decrease of the magnetic field at the nucleus, thus shifting the hyperfine field of the different sublattices in opposite directions.

5.9 Accumulated effects

We have hitherto only dealt with four physical effects relevant to Mössbauer spectroscopy in a quantitatively manner, however the bigger picture is yet to be given. As reference we use the Mössbauer spectrum of α -Fe, i.e. Fe atoms in a pure iron crystal.

As previously mentioned the **Zeemann effect** and the **hyperfine interaction** both have the same effect on the energy levels, which is to is split the existing energy levels into 2I+1 energy sublevels. The magnitude of the splitting depends on the magnetic field:

$$E_{\text{split}} = \vec{\mu} \cdot (\vec{B}_{\text{hyperfine}} + \vec{B}_{\text{Zeemann}}). \tag{5.37}$$

The **isomer shift** is responsible for shifting the energy levels. It will shift all the absorption lines by an equal amount. The **electric quadrupole interaction** is responsible for increasing the energy of the $|\frac{3}{2}; \pm \frac{3}{2} >$ states and decreasing the energy of the $|\frac{3}{2}; \pm \frac{1}{2} >$ states according to (5.30), if V_{zz} is positive. If V_{zz} is negative the effects are opposite. After inserting into (5.30) we get

$$E_Q(m = \pm \frac{3}{2}) = C(-3),$$
 (5.38)

$$E_Q(m = \pm \frac{1}{2}) = C(\pm 3),$$
 (5.39)

where

$$C = \frac{eQV_{zz}\sqrt{1+\frac{\eta^2}{3}}}{4I(2I-1)}.$$
(5.40)

This results in an increment of the energy of transitions 1 and 6, thereby moving these absorption lines to the right. The energy of the other transitions is lowered and the absorption lines move left. This is, however, only valid when the principal component V_{zz} of the EFG tensor is parallel to the magnetic field.

When the principal component forms an angle, θ , with the axis of the magnetic field, and the EFG is axially symmetric, and $E_Q \ll E_m$ the combined energies are given by:

$$E_{Q,M} = -g_n \beta_n m B + (-1)^{(|m| + \frac{1}{2})} \frac{e Q V_{zz}}{8} (2\cos^2 \theta - 1).$$
(5.41)



Figure 5.5: A typical Mössbauer spectrum (here α -Fe) with a well developed sextet.

5.10 Second order Doppler shift

When considering spectra at different temperatures, we need to take into account the second order Doppler shift. Equation (5.19) is only valid when considering non-relativistic velocities. However the velocities of the atoms due to lattice vibrations are typically $10^3 \,\mathrm{m/s}$, and this is enough to influence the Mössbauer spectrum.

To calculate the magnitude of the second order Doppler shift, we have to consider the relativistic expression for radiation emitted by a moving nucleus, which is given by

$$E(v) = E_0 \left(1 + \frac{v}{c} \right) \left(1 - \frac{v^2}{c^2} \right)^{1/2},$$
(5.42)

where v is the velocity of the nucleus. Since the frequency of the lattice vibrations is of the order of $10^{13} Hz$, and thereby much faster than the characteristic time for nuclear decay, it is necessary to average the velocity to obtain:

$$E(v) = E_0 \left(1 + \frac{v}{c} \right) \left(1 - \frac{\langle v^2 \rangle}{2c^2} \right)$$
(5.43)

using $\sqrt{1+x} = 1 + x/2 - x^2/8 + \dots$. Thus the energy is shifted by

$$\delta E = -E_0 \left(\frac{\langle v^2 \rangle}{2c^2}\right),\tag{5.44}$$

which implies that (5.43) can be written as

$$E(v) = E_0 \left(1 + \frac{v}{c} \right) + \delta E.$$
(5.45)

If we assume that the atoms can be described as harmonic oscillators, and U is the internal energy per unit mass associated with the atoms, we get

$$\frac{1}{2}M_{\rm c}U = \frac{1}{2}M_{\rm c}\langle v^2\rangle,\tag{5.46}$$

where M_c is the mass of the crystal. Combining (5.44) and (5.46) we get:

$$\frac{\delta E}{E_0} = -\frac{U}{2c^2} \tag{5.47}$$

which when differentiated with respect to temperature yields

$$\frac{\partial}{\partial T}\frac{\delta E}{E_0} = -\frac{C_{\rm p}}{2c^2},\tag{5.48}$$

where $C_{\rm p}$ is the heat capacity at constant pressure. This can be transformed into:

$$\delta E = \int \frac{-E_0 C_p}{2c^2} \,\partial T. \tag{5.49}$$

For iron at high temperatures $(T \gg \Theta_D)$, the absorption lines are shifted about -0.07 mm/s per 100 K, due to the second order Doppler shift.

5.11 Paramagnetism and superparamagnetism

A paramagnetic transition (se section 4.4) is a second order transition, and is in Mössbauer spectroscopy seen as a continually decreasing hyperfine field with rising temperature. The lines of the well developed sextet will gradually overlap, and eventually paramagnetism is seen as a collapse into a singlet or doublet at a specific temperature, the Curie/Néel temperature.

If a sample is completely superparamagnetic, it is as paramagnetism seen as a singlet or a doublet. The difference between superparamagnetism and paramagnetism is the path to and

from the ordered state (see section 4.5). Superparamagnetism is a first order transition, and has therefore a non-continuous path to a collapse of the ordered state.

Opposed to paramagnetism the magnetic order does not disappear at a specific temperature, but rather over a range of temperatures. This behavior is caused by the nature of superparamagnetism, involving the single domain magnetic particle, which has a thermal energy competing with the anisotropy energy of the particle.

When relaxation time τ is larger than the time resolution for Mössbauer spectroscopy by an order of magnitude or more, the components will be well resolved. The time resolution for Mössbauer spectroscopy is ~ 10⁻⁹ s (τ_l in table H.2).

When the τ becomes comparable to the time resolution, the orientation of the magnetic field at the nucleus of particle flips during measurement, and the variation in hyperfine field is thus smeared and an average value is observed.

If, on the other hand, τ is smaller than the time resolution by an order of magnitude or more, the components are completely collapsed.

In practice a sample always contains particles with a certain size distribution. Close to the blocking temperature T_B some particles will be superparamagnetic, and will be seen as a singlet/doublet. Other particles will be magnetic and seen as a sextet.

When cooling a superparamagnetic sample, the spectrum will initially show a singlet/doublet. As one reaches the range of blocking temperatures described above, the spectrum will suddenly show an additional sextet with relative sharp lines. The area of the sextet will over a short range of temperatures become larger and larger, and the area of the singlet/doublet correspondingly smaller and smaller. The continuous variation of hyperfine field from zero to saturation magnetization seen in paramagnetism does not occur. If compensating for the variation in the f-factor the total area is constant.



Figure 5.6: Schematic illustration of the connection between particle sizes and the superparamagnetic relaxation and the influence on Mössbauer spectra. As a comparison the development of paramagnetism and the resulting Mössbauer spectra as a function temperature is shown.

In order to detect the energy difference between the non-degenerate states (showing magnetic splitting), and then degenerate states (not showing magnetic splitting), a certain measuring time

is necessary according to the Heisenberg uncertainty relation:

$$\tau \cdot |E_m| \ge \hbar. \tag{5.50}$$

The energy difference is given by (5.22), and using this formula, the energy splitting is calculated by

$$|\Delta E_{(i,j)}| = |\Delta E_i| + |\Delta E_j| = 2|\Delta E_i|, \qquad (5.51)$$

where (i, j) = (1, 6), (2, 5), (3, 4). Applied to the line pairs (1, 6), (2, 5), (3, 4) then energy splitting is calculated:

$$|\Delta E_{(1,6)}| = -2(\beta_n B(g_e \frac{3}{2} - g_g \frac{1}{2})) = \beta_n B \cdot g_{16} = \beta_n B \cdot 0.491858,$$
(5.52)

$$|\Delta E_{(2,5)}| = -2(\beta_n B(g_e \frac{1}{2} - g_g \frac{1}{2})) = \beta_n B \cdot g_{25} = \beta_n B \cdot 0.284758,$$
(5.53)

$$|\Delta E_{(3,4)}| = -2(\beta_n B(g_e \frac{-1}{2} - g_g \frac{1}{2})) = \beta_n B \cdot g_{34} = \beta_n B \cdot 0.077658,$$
(5.54)

where $g_g = 0.181208$ and $g_e = -0.10355$ are the g-factors for the ground state and the excited state respectively, values from [42]. From (5.50) the corresponding relaxation times are obtained, using a B-field of 33.02 T (bulk iron):

$$\tau_{(1,6)} = 1.286 \cdot 10^{-9} s \tag{5.55}$$

$$\tau_{(2,5)} = 2.221 \cdot 10^{-9} s \tag{5.56}$$

$$\tau_{(3,4)} = 8.138 \cdot 10^{-9} \, s \tag{5.57}$$

From Heisenberg relation (5.50), a line is only resolved if the following relation is fulfilled:

$$\tau > \tau(i,j) \tag{5.58}$$

Since $\tau_{(1,6)} < \tau_{(2,5)} < \tau_{(3,4)}$, the lines 3 and 4 will collapse first when τ is decreased, followed by 2 and 5, and finally 1 and 6.

5.12 Interaction effects

Small magnetic particles may interact with other nearby particles. The interaction depends on the nature and composition of the considered samples.

There are two main types of interaction that have to be considered, dipole-dipole interaction and exchange interaction.

The **dipole-dipole interaction** is relevant if the individual particles are not well separated, for instance by a non-magnetic material. The particles will in this case respond to the magnetic field from the neighboring particles.

The **exchange interaction** is relevant if the particles are so closely packed (touching), that the electron orbitals of the atoms overlap. We have a situation where the dipole-dipole interaction is powerful, with a weak exchange interaction.

Interaction will be negligible if temperature is very low or if the absorption lines are well defined. However if the temperature is high, close to the Néel/Curie or blocking temperature, the interaction effects are relevant.

Particles of a ferri/ferromagnetic material will mainly be affected by the dipole-dipole interaction, since exchange effects are short ranged, and the interface between the particles, in which exchange interaction is effective, will be relatively small. The dipole-dipole interaction will act as an applied field on the particles, and the Mössbauer spectrum will neither show superparamagnetic or paramagnetic behavior. Although the thermal energy of the particles will be larger than the anisotropy energy, they will also be affected by a magnetic field from the neighboring particles. This results in a corrected expression for the anisotropy energy given by

$$E = -\vec{\mu} \cdot \vec{B} + KV \sin^2 \theta \tag{5.59}$$

The corrected anisotropy energy is larger than the original expression (4.17), and the particles will thus be less willing to flip. We have in (5.59) assumed that the effect behaves like an external field; however this is not entirely the case. The magnetic field from every particle in the population will influence the neighboring particles, which thereby composes a chaotic system. Qualitatively it causes a drag in the flipping, illustrated in figure 5.7.

The situation where the inter-particle dipole-dipole interaction dominates the exchange interaction situation is called a superferromagnet [46], since the ferromagnetic microcrystals have a long range interaction.

The theory and derivation of the related expressions of superferromagnetism is somewhat complex, and it will only be cited here. It is derived beautifully in [46].

A superferromagnetic material will be superparamagnetic above the transition temperature, T_p , and superferromagnetic down to the blocking temperature. T_p can be derived from

$$T_p = K_{ex} M_0^2(T_p) / 3k_B, (5.60)$$

where K_{ex} is a measure of the interaction force of the magnetic moments of neighboring particles, and it comes from the expressions of anisotropy:

$$E_{i} = -\sum_{j} K_{ex}^{i,j} \vec{M}_{i} \cdot \vec{M}_{j} + K_{i} V_{i} \sin^{2} \theta, \qquad (5.61)$$

$$K_{ex} = \sum_{j} K_{ex}^{i,j}, \qquad (5.62)$$

where M_k is the magnetization of the k'th crystallite. When K_{ex} increases, T_p approaches the Curie/Néel temperature. $M_0(T_p)$ is the absolute magnetization of the crystallite, often assumed to be equal to the magnetization of the bulk material.



Figure 5.7: Schematic illustration of the connection between particle interaction and Mössbauer spectra.

Antiferromagnetic particles will have no macroscopic field, and the exchange interaction will hence be the only effect relevant. The antiferromagnetic particles will experience a drag in their superparamagnetic flipping, since the volume felt by the particles is larger than when isolated, due to exchange interaction.

The situation with the inter-particle exchange interaction is called a super-spin-glass [46], since the microcrystals have a spin glass behavior carried by inter-particle exchange interaction. Above the transition temperature the system is superparamagnetic, and below it behaves like a spin glass.

Spectra showing either of the interaction effects will show a very broad singlet/doublet with broad steps to both sides. The steps are due to particles that behave magnetic, and therefore displaying hyperfine fields close to of bulk material. The broad slope consists of a distribution of hyperfine fields, ranging from zero to saturation magnetization. This distribution is due to the particles that fluctuate but not flip entirely. The particles with zero hyperfine field are superparamagnetic.

5.13 Experimental setup

During the work on this thesis, we have used Mössbauer spectrometric setups at both DTU^1 and $\emptyset L^2$. These differ in some small details, which will not be mentioned further here. We will explain the setup at $\emptyset L$ which has been used the most. The apparatus consists of 3 parts:

- 1. The drive unit with a velocity transducer containing the radioactive source.
- 2. The MCA^3 .
- 3. Detector and SCA^4 .



Figure 5.8: Schematic overview of the Mössbauer apparatus setup. Slightly modified from [42, fig. 13.1]

5.13.1 Source

We have a photon source that emits γ -photons with an energy of 14.41 keV. A small portion of the photons will be absorbed by the ⁵⁷Fe-nuclei, and then remitted in an arbitrary direction. If a detector is placed behind the sample, a small decrease is observed in the number of photons at the energies corresponding to the allowed transitions.

As source we use ⁵⁷Co which has a lifetime of 270 days. It decays to ⁵⁷Fe^{**} $(I = \frac{5}{2})$, which again in 90% of the cases decays to an intermediate state of ⁵⁷Fe^{*} $(I = \frac{3}{2})$ and 10% to ⁵⁷Fe $(I = \frac{1}{2})$. When ⁵⁷Fe^{*} decays to ⁵⁷Fe it emits a γ -photon of 14.41 keV (see figure 5.9).

5.13.2 Drive unit

The energy of the photon emitted when the 57 Fe^{*} atom decays to 57 Fe, is approximately 14.4 keV. In Mössbauer spectroscopy we are concerned with the small variation around this energy. The source is mounted at the end of a rod that is attached to two electro magnets. The energy variation is obtained by oscillating the radioactive source with a constant acceleration in each direction, taking advantage of the Doppler effect. One of the electro magnets is feed appropriate

¹Technical University of Denmark, Department of Physics. The measurements were performed by Helge Rasmussen.

⁴Single channel analyzer



Figure 5.9: The Decay of ⁵⁷Co to ⁵⁷Fe. Figure reproduced from [42].

voltage; this results in an oscillating motion of the rod. The current induced in the others coil is proportional to the velocity of the rod. This current is used in an electric feedback system, and ensures that the velocity is precisely controlled [42]. A typical maximum velocity of the source is $\sim 10 \text{ mm/s}$.

5.13.3 Detector and SCA

The detector is a proportional current counting device, which, when detecting a pulse supplies a current proportional to the energy of the pulse. It is similar to a Geiger-Müller (G-M) detector. However when the G-M detector detects radiation, the incoming radiation starts a total electron avalanche, which results in a very high current peek. Following each pulse a G-M detector has a "dead"-time in which it is insensitive to radiation. In contrast, the electron avalanche inside the detector used for Mössbauer is controlled, and thus results in a controlled current peek reflecting the energy of the incoming photon. The difference between the detectors is also reflected by the different gasses inside.

When the detector registers the incoming photons it sends a pulse to the pre-amplifier, which again sends it to the amplifier. The amplifier is connected to a SCA. The controlled current peak allows an energy filtering by the SCA, filtering out peaks that are not caused by a 14.41 keV transition. The filtering energy window is set prior to each measurement. The filtering resolution is limited by the detector to approximately 0.1 keV, and is far from accurate enough to resolve the energy differences that are measured using Mössbauer spectroscopy.

The SCA is connected to a MCA, which in turn is coupled to a computer. Often the SCA and MCA are combined into a single component inside a computer.

5.13.4 MCA

The role of the MCA is to sort the incoming photons into channels according to their energy, which is determined by the velocity of the source when the photon was detected. Each channel registers the number of photons received within a specified energy interval. Often a 512 or 1024 channel MCA is used [40].

The velocity is non-relativistic so the energy perturbation can be derived from (5.19)

$$\Delta E = E_0 \frac{v}{c}, \quad E_0 = 14.41 \,\text{keV}, \tag{5.63}$$

where v is the velocity of the source and c is the velocity of light in vacuum. Inserting into (5.63), one gets $\Delta E = 4.8 \cdot 10^{-10}$ keV for v = 10 mm/s, which is far from the resolution of the detector.

To sort the pulses the MCA has to receive data from both the SCA and the drive unit. By reading the velocity of the source when a pulse is received, the MCA calculates which channel count should be increased.

The accumulated data can be transferred from the MCA to a computer for processing. Typical time span for a Mössbauer experiment is 4 hours to 2 weeks depending on how thick the sample is, how radioactive the source is, the geometry of the system and finally the desired measuring uncertainty.

6 Iron oxides

The purpose of this project is to manufacture iron oxides, in particular hematite (α -Fe₂O₃), maghemite (γ -Fe₂O₃) and magnetite (Fe₃O₄), therefore we will go through the properties of the most common iron oxides. We will discuss different properties, such as color and various phases and transitions, but it should be kept in mind that these are properties of bulk material, and that some, if not all of these properties change, on the nano-scale. For instance, when approaching the nano-particle regime, particles may become single domain particles, and various exotic magnetic phenomena might occur. Parts of the following are based on [17, 37, 61]. Values for superparamagnetic behavior are based on [17], and are assumed to be based on Mössbauer measurements.



Figure 6.1: A schematic illustration of the pathways of formation of various common iron oxides. Figure reproduced from [7, 23].

6.1 Magnetite

Magnetite (Fe₃O₄, [Fe³⁺[Fe²⁺Fe³⁺]O₄]) is common in nature. It has the lowest oxidation level of the stable iron oxides, and may, under certain conditions be oxidized further to maghemite or hematite, although it is easier oxidized into maghemite, since they have the same crystal structure. It is a ferrimagnet and has a Curie temperature of 850 K. Magnetite has a saturation magnetization of 92-100 Am²kg⁻¹ at 300 K.

It is an inverse spinel, with the cations sited at tetrahedral (A) sites, and octahedral (B) sites (see figure 6.2). The ions at the tetrahedral sites are Fe^{3+} , and at the octahedral sites both Fe^{2+} and Fe^{3+} . The inverse spinel structure has the formula $B[AB]O_4$ compared to the spinel structure which has the formula $A[B_2]O_4$, indicating that half the trivalent ions (Fe³⁺) swap places with the divalent ions.

Name	Formula	Magnetic	Crystal structure	T_C/T_N (K)
Magnetite	Fe_3O_4	Ferrimagnetic	cubic, inv. spinel	850
Maghemite	γ -Fe ₂ O ₃	Ferrimagnetic	cubic, spinel	$\sim\!\!820\text{-}986$
Hematite $> 260 \mathrm{K}$	α -Fe ₂ O ₃	Weak ferromagnet,	hexagonal, corundum	965
		canted antiferromagnet		
Hematite ${<}260{\rm K}$		Antiferromagnetic		
Goethite	α -FeOOH	Antiferromagnetic	orthorhombic, diaspore	400
Lepidocrocite	γ -FeOOH	Antiferromagnetic	orthorhombic	400
Akaganéite	β -FeOOH	Antiferromagnetic	cubic, bcc	290
Feroxyhyte	δ' -FeOOH,		hexagonal	
	δ -FeOOH	Ferrimagnetic	hexagonal	$\sim\!\!440\text{-}460$

Table 6.1: Crystallographic and magnetic properties of selected iron oxides. Further properties are listed in table G.2. Values from [17, 62]



Figure 6.2: A schematic of the spinel structure. The small white spheres represent the iron ions at tetrahedral sites, the small dark spheres represent the iron ions at octahedral sites and the large light spheres represent the oxygen ions. The spin direction of the ions for magnetite (an inverse spinel) are indicated by arrows. Figure reproduced in part from [1, 17].

The spin formula of magnetite is $\downarrow \text{Fe}^{3+} \uparrow \text{Fe}^{2+}]O_4$. The main type of interaction is an antiferromagnetic coupling via the Fe_A-O-Fe_B bonds, which is stronger than the coupling on the octahedral sites.

Magnetite is a soft magnetic material due to its cubic crystal structure and the easy magnetization axis, which are the 8 [111] cube diagonals.

On the octahedral sites there is a thermally delocalized electron around the Fe^{2+} and Fe^{3+} ions. The loose electron shifting between the two iron ions causes several of the special properties of magnetite, such as its high conductivity. The shifting electron is also seen in Mössbauer spectroscopy, where the Fe^{2+} and Fe^{3+} on the B-sites can not be distinguished, and are collectively seen as $Fe^{2.5+}$. The black color of magnetite is also caused by the delocalized electron, which is able to absorb photons continuously within a broad frequency range in the visible spectrum.

The delocalized electron state can exist down to the Verwey transition at 118 K, at which an ordered arrangement of the Fe²⁺ and Fe³⁺ ions at the octahedral sites is obtained.

Synthesis of magnetite in aqueous systems at temperatures less than 373 K can produce rounded, cubic or octahedral crystals. When Fe²⁺ is excess of OH⁻ spherical particles are produced, whereas cubic particles are produced when OH⁻ is in excess and pH is around 12 [17].

6.2 Maghemite

Maghemite (γ -Fe₂O₃) is also common in nature. Maghemite has a cubic unit cell, and it is a spinel structure. The crystal structure is similar to that of magnetite, and a broad range of intermediate phases with different degrees of oxygen content exist. It is a ferrimagnet, with an estimated Curie temperature between 820 K and 986 K. At 713 K it is transformed into hematite, causing the uncertainty concerning the Curie temperature. Maghemite has a saturation magnetization of 60-80 Am²kg⁻¹ at 300 K.

The magnetic structure of magnemite is due to the similar crystal structure very similar to magnetite. It consists of two sublattices corresponding to Fe ions located at tetrahedral and octahedral sites. The spins are parallel within the sublattices, but the spins of the two sublattices are antiparallel.

Maghemite is as magnetite a soft magnetic material due to its cubic crystal structure and the easy magnetization axis, which are the 8 [111] cube diagonals.

The structural spin formula for maghemite is $(\downarrow \text{Fe}^{3+})[\uparrow \text{Fe}^{3+}, \uparrow \text{Fe}^{3+}_{2/3}, \Box_{1/3}]O_4$, where \Box indicates a vacancy. A sixth of the octahedral iron sites are therefore vacant. A spinel structure with no vacancies is displayed in figure 6.2 for illustration. The vacancies are caused by the balancing of cations to anions, and the vacancies may themselves form arrangements within the spinel, affecting the properties of the maghemite sample.

Maghemite is formed mostly formed by oxidation of magnetite, or lepidocrocite (see figure 6.1). The color is black or dark red-brown.

6.3 Goethite



Figure 6.3: The crystal structure of goethite. The large white spheres represent the oxygen ions, the small light gray spheres represent the hydrogen ions and the medium sized dark gray spheres represent the iron ions. Figure reproduced in part from [17].

Goethite (α -FeOOH) is common, and occurs in various parts of nature. The crystal structure of goethite is orthorhombic, and it is a diaspore structure.

Goethite is one of the thermodynamically most stable iron oxides and is therefore the first oxide to form. It can also be the end result of an iron oxide transformation from for instance lepidocrocite. In massive crystals goethite is dark brown or black, whereas it is yellow in nanoparticle form.

It is antiferromagnetic, with the spins orientated along the c-axis. The spins are arranged in alternate chains of octahedra. The strongest exchange interaction is between corner sharing octahedra. Superexchange interaction between edge sharing octahedra are weak due to the lower bond angle involved.

It has a Néel temperature of 400 K, unless the particle size is small (less than 15-20 nm), where it becomes superparamagnetic at room temperature. If the particles are less than 8 nm, goethite can be superparamagnetic down to 77 K, depending on measuring method (see section 4.5). Goethite is reported to have a saturation magnetization of 0.01-1 $\text{Am}^2\text{kg}^{-1}$ at 300 K [17].

Goethite is formed by either by oxidation direct oxidation from Fe^{3+} , or through formation of ferrihydrite at high pH values (see figure 6.1).

6.4 Lepidocrocite

Lepidocrocite (γ -FeOOH) is not as common as goethite. It is an oxidation product of Fe²⁺ and is found in soil and various biological organisms. It has an orthorhombic unit cell containing four formula units. It is dark orange. Usually it is the end product in the formation process, but can be transformed into goethite. It is an antiferromagnet, and has a Néel temperature of 77 K.

It is formed through complete oxidation of green rust at pH 5-7 (see figure 6.1).

6.5 Akaganéite

Akaganéite (β -FeOOH) occurs rarely in nature. It is found in Cl-rich environments. The crystal structure is body centered cubic (bcc), and contains low levels of Cl or F ions. The color is brown to bright yellow. It is an antiferromagnet and has a Néel temperature of 290 K. It forms an aqueous media by direct precipitation from soluble Fe³⁺ species. A threshold level of chlorite fluoride ions must be present for Akaganéite to form.

6.6 Feroxyhyte

Feroxyhyte (δ' -FeOOH) exists in nature, but is not common, and is often found as nano-crystals. It has a hexagonal crystal structure. There exists a related synthetic material, δ -FeOOH, with slightly different unit cell parameters. The natural and synthetic materials differ in the arrangements of cations. The natural compound is a disordered form of the synthetic compound. The natural form contains two formula units per unit cell, whereas the synthetic contains one formula unit per unit cell.

Synthetic δ -FeOOH is ferrimagnetic, with an estimated Néel temperature of 440-460 K. Due to poor crystallinity and small particle size the natural feroxyhyte is superparamagnetic at room temperature [17].

The color of feroxyhyte is dark reddish-brown.

6.7 Ferrihydrite

Ferrihydrite ($Fe_2O_3 \cdot 0.5H_2O$) is very common in nature and hematite may be formed by further oxidation. It is a very poorly ordered form of iron oxide hydroxide and is often considered amorphous. It is speromagnetic and the magnetic ordering of ferrihydrite takes place over a relative broad range of temperatures from 25 K to 115 K. At room temperature it is often superparamagnetic [17].

It forms in the same way as the FeOOH phases, but under conditions where the formation of these is prevented, by rapid hydrolysis of a Fe^{3+} salt solution or by oxidation of a Fe^{2+} salt solution.

Ferrihydrite is dark reddish brown, a bit lighter than feroxyhyte. However due to its poor order, the color may vary, depending on crystal structure and particle size.

6.8 Hematite

In nature the most common iron oxide is hematite $(\alpha - \text{Fe}_2O_3)$, which is known to most people as "common rust". Hematite has a corundum crystal structure with a hexagonal unit cell. It is considered the highest natural oxidation state of iron (all the iron is Fe^{3+}), although maghemite has all its iron in the same oxidation state. Hematite is energetically favorable, due to an energetically favorable crystal structure.

In temperatures ranging from 0 K to 260 K it is antiferromagnetic, and above 260 K it is a weak ferromagnet/canted antiferromagnet. The transition at 260 K is called the Morin transition. The Curie temperature is 965 K. Hematite has a saturation magnetization of $0.3 \text{ Am}^2 \text{kg}^{-1}$ at 300 K.

At the basal plane hematite consists of two interpenetrating antiferromagnetic sublattices Below the Morin temperature the spins, which are orientated along the c-axis, are exactly antiparallel



Figure 6.4: The structure of hematite (α -Fe₂O₃). Only the iron ions are displayed, represented by the small gray spheres. The arrows indicate the spin direction in the ferromagnetic state (above the Morin transition). Below the Morin transition the spins reorientate to the c-axis plane, resulting in an antiferromagnetic structure. Figure reproduced from [39].

and hematite is antiferromagnetic. At the Morin temperature the spins reorientate and form an angle of 0.1° , and hematite is weakly ferromagnetic along the c-axis.

The Fe spins are antiferromagnetically coupled along the c-axis through the octahedrahdral faces, and are thereby separated by an O^{2-} triplet. Weak superexchange interaction takes places between these Fe³⁺ ions. The Fe spins are ferromagnetically coupled to Fe spins which lie of the c-axis.

Particles smaller than 8 nm exhibit superparamagnetism at room temperature [17].

Hematite forms from ferrihydrite in aqueous media by combined dehydration and reorganization. It can also be formed by thermal decomposition of other iron oxide and hydroxide compounds.

The color of hematite may vary quite extensively in small particles, from bright red-brown to dark brown depending on particle size. Bulk hematite is gray or black.

7 Sample preparation

Crystallite size, distribution of particle sizes, and particle interactions have a major impact on the magnetic properties of the nano crystalline samples. Therefore an ideal synthesis technique must provide superior control over these parameters. Through the history of nano-scale material manufacturing a variety of methods such as gas condensation, chemical precipitation, aerosol reactions, and self-assembly processes, have been used.

Fabrication of particles in water-oil microemulsions (reverse micelles or inverse micelles) offers great control over particle size, shape and size distribution [12, 13, 55], and is therefore an increasingly popular method of preparing nano-particles. There are, however, some difficulties involved in the manufacturing process.

The samples investigated in this thesis are manufactured using the reverse micellar technique. We will in the following go through the theory behind the reverse micellar technique and later go through our application of, and experiments with the technique.

Parts of the following are based on [12, 13, 55].

7.1 Reverse micelles

Surfactants get their name from the acronym "surface acting agent". They are used to affect surface tension along interfaces. The surfactant molecule consists of a long hydrocarbon chain and a hydrophilic group. The hydrophilic group typically comes in the form of a ionic group such as a sulphate (SO_4^{2-}) or quaternary amine⁵ forming either anionic or cationic surfactants, respectively. Non-ionic surfactants having either ethers or alcohol functional groups are also common. The combination of polar and non-polar groups allows the surfactants to solubilize water in a water-oil-emulsion.

An interesting phenomenon in a water-oil-surfactant system is the presence of self-assembled arrays of surfactants called micelles. At certain ratios the mixture of oil, water and surfactants form a clear, seemingly one-phase system, as found by Winsor in 1953 [11]. Such a system called a micelle or microemulsion solution contains small droplets of one liquid dispersed within the other, with a self-assembled layer of surfactant molecules along the interface between the two phases.

Micelles were originally characterized with a bulk aqueous phase where the hydrophobic carbon chains were turned inward to stabilize the oil phase. Later reverse micelles where characterized, where the conditions were reversed, such that the bulk phase was oil, and the hydrophilic head groups turned inward to stabilize the water phase. The conditions under which the micelles exist are very specific, and dictated by the molar ratio of oil, water and surfactant.

If the ratio of water to surfactant changes greatly, the micelle solution becomes unstable and forms a traditional emulsion solution [13].

Reverse micelles can form both in the presence and absence of water, however in the absence of water they are very small. When water is added, it is readily solubilized into the polar area of the micelles forming a water pool. The water pool is characterized by ω , the molar water to surfactant ratio:

$$\omega = \frac{[\mathrm{H}_2\mathrm{O}]}{[\mathrm{S}]}.\tag{7.1}$$

The spherical nature of the surfactant aggregates in the reverse micelles is a response to a thermodynamically driven process. It represents a need for the surfactant to reach an energetically favorable packing configuration at the interface between the water phase and the oil phase. The packing configuration depends highly on the molecular geometry of the surfactant.

 $^{^{5}}$ From www.slb.com: "A cationic amine salt in which the nitrogen atom has four groups bonded to it and carries a positive charge."


Figure 7.1: The phase diagram of the three solution components: surfactant, water, oil. The areas near the lowest corners are regions which are characterized by spherical micelles. Moving out of these regions there are regions of rod-like microemulsions. Rod-like microemulsions are mainly due to excess surfactant. The lower region between water and oil is a characteristic microemulsion region. The large white area covers regions with various water/surfactant/oil configurations not relevant here. Figure reproduced from [13].

If we assume that the water-in-oil droplets are spherical, the radius of the water sphere is given by

$$R = 3\frac{V}{A},\tag{7.2}$$

where R is the radius of the droplet, V is the volume and A is the surface area. If we furthermore assume that the volume is filled with water molecules and the surfactant molecules determine the surface area, then the water pool radius can be expressed as

$$R_w = 3 \frac{V_{\rm aq}[{\rm H_2O}]}{\sigma[{\rm S}]} = 3 \frac{V_{\rm aq}}{\sigma} \omega, \qquad (7.3)$$

where R_w is the radius of the water pool, V_{aq} is the volume of a water molecule and σ is the area per polar head group of surfactant. Various experiments have confirmed the linear variation of the water pool radius with the water content.

When a reactant is dissolved in the water phase e.g. into the droplet, it could affect the overall size of the droplet and the factor ω . There are four cases (figure 7.2):

- A) If the solute is located on the outside of the micelle in the bulk oil phase, then the overall water to surfactant ratio is unchanged. There should therefore be no change in the size of the water pool.
- **B)** The addition of the solute into the water pool increases the overall volume while keeping the overall surface area constant, resulting in an increase of the observed size of the water pool, and fewer but larger micelles.
- **C)** The addition of the solute bound to the interface layer increases the surface area, while keeping the overall volume. This results in a reduction of the water pool, and more numerous and smaller micelles.

D) The addition of the solute induces a formation of small aggregates surrounding the solute. This would produce two sizes of micelles. The surface would be reduced as surfactant is used in aggregates about the solute, resulting in an increase of the water pool.



Figure 7.2: The possible four cases in which the surfactant, water, and oil can coexist. The interior of the micelles consists of water, and the bulk of oil. The fluffy circles indicate the surfactant, and the black indicates the reactant. Figure reproduced from [13].

Studies involving small angle X-ray scattering and neutron scattering have been used to determine which of the presented cases is the most likely. These studies have shown that the most likely case is B or C. When the reactants are ionic, the case tends to be B due to the high polarity of the water. In the case of non-ionic reactants, such as proteins the case is likely to be C since their low polarity stabilizes them at the interface.

Micelles are subject to Brownian motion due to their small size. They collide continuously with other micelles. This eventually causes the content of a micelle to be distributed over the entire micelle population. During long measuring times the micelles appear as static rigid shells and studies indicate that the particles size is proportional with ω [13].

7.2 Iron oxide chemistry

We are attempting to manipulate and control the oxidation of iron ions, and therefore a brief summary of the chemistry will be given. Theoretically the oxidation of iron is dictated by the pH of the aqueous solution, and the electrochemical potential of the solution. The electrochemical potential is determined by the amount of dissolved oxygen in the system and the presence of other oxidizing agents.

A diagram of these variables is called a Pourbaix diagram. Two Pourbaix diagrams for the iron oxygen system are presented in figure 7.3.



Figure 7.3: Two Pourbaix (E-pH) diagrams for the Fe-O aqueous system. Calculated using the computer program "HSC chemistry" [15]. Top: 298 K. Bottom: 373 K.

The chemical reactions when dissolving the iron salts in water are:

$$\operatorname{FeSO}_4 \cdot 7\operatorname{H}_2O \rightarrow \operatorname{Fe}^{2+} + \operatorname{SO}_4^{2-} + 7\operatorname{H}_2O,$$
 (7.4)

$$\operatorname{FeCl}_2 \cdot 6\operatorname{H}_2O \rightarrow \operatorname{Fe}^{2+}2\operatorname{Cl}^- + 6\operatorname{H}_2O.$$
 (7.5)

When ammonia is added to water it dissociates water:

$$\mathrm{H}_{2}\mathrm{O} + \mathrm{N}\mathrm{H}_{3} \to \mathrm{O}\mathrm{H}^{-} + \mathrm{N}\mathrm{H}_{4}^{+}. \tag{7.6}$$

The chemical reactions inside a micelle are given below. The reaction towards magnetite is

$$3Fe^{2+} + 6OH^{-} + \frac{1}{2}O_2 \rightarrow Fe_3O_4(s) + 3H_2O,$$
 (7.7)

which may react further to form maghemite:

$$2Fe_3O_4(s) + \frac{1}{2}O_2 \to 3\gamma - Fe_2O_3(s).$$
 (7.8)

A direct reaction to maghemite is also possible:

$$2Fe^{2+} + 4OH^{-} + \frac{1}{2}O_2 \rightarrow \gamma - Fe_2O_3(s) + 2H_2O.$$
 (7.9)



Figure 7.4: Chemical representations of two surfactants used in the sample manufacturing. Left: AOT (dioctylsulfosuccinate sodium salt). Right: CTAB (cetyltrimethylammonium bromide). The lines indicate bonds, unmarked corners are carbon, hydrogen is not marked. Figure reproduced from [13].

7.3 Manufacturing strategy

As surfactants, the two well-known surfactants AOT (dioctylsulfosuccinate sodium salt, $C_{20}H_{37}NaO_7S$) and CTAB (cetyltrimethylammonium bromide, $C_{19}H_{42}BrN$), were chosen. These are shown in figure 7.4.

Iso-octane (2,2,4-trimethylpentane) is used as solvent for the AOT systems. When AOT is dissolved in iso-octane micelles form with sizes ranging from 5 to 60 nm, depending on ω .

As salts are dissolved within the micelle the maximum micelle size drops to 35 nm when using 0.1 M Fe^{2+} and 15 nm when using 1 M Fe^{2+} .

When using CTAB as surfactant, n-octane is used as solvent. Unlike AOT, CTAB has a very large extended hydration sphere, which greatly reduces the environment inside the micelle in which the reactions can be carried out. To reduce the hydration sphere and increase the stability of the micelle solution, a co-surfactant of n-butanol is used.

The size of the micelles of both surfactant systems display the same linear dependence of the water to surfactant ratio as dictated by ω [13].

When the reactants and counterions such as ammonia (NH_3) have been added, and the solutions has been allowed to react for a period of time, the solvents, surfactants and residual counterions have to be removed. This is done by washing the solution repeatedly with acetone (C_3H_6O) , methanol (CH₃OH), ethanol (C₂H₅OH), water and chloroform (CHCl₃), and filtering out the particles. The filtering can be done with magnetic separation, centrifugation or precipitation. It can be very difficult to wash out all the surfactant, and it is common, even after several repeated washes, that the remaining material contains a significant amount of surfactant.

Since the reverse micelle technique was completely unknown to us when this project was started, we decided to start with something simple and well documented. We decided to attempt to synthesize magnetite since it should be simpler to synthesize than maghemite and hematite [13]. As references to the technique we used mainly [13, 14, 51, 55].

Due to little experience, we decided to make a few random attempts in which we varied parameters as surfactant (AOT or CTAB), water-to-surfactant ration, ω , washing method (methanol, water, ethanol), and reactants (FeCl₂, FeSO₄). After the preliminary analysis we investigated the results, to determine a strategy for future synthesis.

The samples manufactured where numbered JH001 and up if they were potentially interesting.

7.4 Preliminary experiments

During our first attempts we had quite a lot of difficulty reproducing the results presented to us in literature. There reasons were: The technique was unknown to us and therefore we made several beginner errors, furthermore some of the references were somewhat unspecific.

We made experiments manufacturing the samples JH001 to JH016 without getting any trace of magnetite. Some samples investigated with Mössbauer spectroscopy had resemblance with pyrite (FeS₂), other with lepidocrocite (γ -FeOOH), and again others were difficult to identify all together.

Eventually we had assistance from Dr. Everett E. Carpenter (see references). Dr. Carpenter was so kind to pay us a visit at Risø, and to help us manufacture some samples. During his stay, we were able to manufacture some promising samples. The samples produced in cooperation with Dr. Carpenter were JH017 to JH041.

In the following the manufacturing procedure will be outlined, and various tips and tricks learned along the way will be mentioned.

The AOT/iso-octane system has received most of the focus, and we have devoted a vast majority of the time to develop it, and we will therefore start by describing the AOT/iso-octane system.

The CTAB/n-butanol/octane and the CTAB/chloroform systems, have received limited focus and we will therefore discuss these briefly. Furthermore, these systems have common features with the AOT system, which do not need to be described repeatedly.

7.5 The AOT system

AOT ($C_{20}H_{37}NaO_7S$) is an extensively studied surfactant, well-known to chemistry, and studied for several decades [5, 12], and therefore it is a good choice as a surfactant.

This section describes the end-manufacturing process, which has been developed during the course of this project. In the development phase a wide range of parameters have been adjusted.

Since our goal was to manufacture magnetite (Fe₃O₄), which has iron ions in oxidation states Fe^{2+} and Fe^{3+} it is essential to start the synthesis with Fe^{2+} ions, which at an appropriate time can be further oxidized. To achieve this, an iron salt, in our case $FeSO_4$ was dissolved in water at room temperature. To avoid oxidation at this stage, a droplet of concentrated sulphuric acid is added, which lowers the pH value. If the pH is not lowered, the dissolved iron salt, which has a light greenish color, will become bright yellow. Since Fe^{2+} is green, and Fe^{3+} is yellow, it is clear that the iron has been oxidized. Fe^{2+} is soluble in water, whereas Fe^{3+} is not, and the precipitation forms aggregates which are incompatible with the micellar technique. The pH value of the iron salt solution has at this stage been measured to 3. The low pH is due to the added acid.

Some experiments were performed using the yellow iron salt solution without added acid (pH=6), and these were unsuccessful.

The next stage is to prepare the AOT/iso-octane solution. Usually we created a stock solution with a known concentration. The amount of iron salt solution to AOT solution is essential to particle size, since it determines the ratio ω . However there is an unknown factor: Solid AOT has a tendency to absorb water vapor, which makes the exact amount of water uncertain and thereby the ω factor difficult to calculate. To evaporate water from the AOT, it is subjected to vacuum. This decreases the amount of water, but does not solve the problem entirely. We have thus been forced to accept a certain content of water in the AOT.

After the creation of the iron salt solution, another AOT solution with the same ω has to be manufactured, only replacing the iron salt part with a base, such as an ammonia solution.

To control the oxidation process, it is essential to control the amount of present oxygen, and therefore we have sonicated all solutions in an argon atmosphere.

Eventually the solutions are mixed while stirring in a beaker containing argon. The solution is allowed to stir, in some cases, overnight or longer to facilitate particle formation and oxidation.

According to theory [12, 15] the pH value of the solution is important at this point, since it determines which iron oxide is being formed. Two calculated Pourbaix diagrams are shown in figure 7.3.

According to [12] pH should usually be 8.4 ± 0.5 for magnetite to form. We have however found that the best samples are produced when the pH value is around 11, and samples with a final pH value of 10 are significantly less magnetic. The pH value is determined by the concentration of the base in the base micellar solution.

Comparison of our results with our reference [12], and considering the Pourbaix diagrams (see figure 7.3), indicates that we have had a lower electrochemical potential during our reactions. In other words our reactions have been performed in an other area of the Pourbaix landscape, than those of our references.

We have used ammonia as base in our synthesis. The pK_A value of ammonia is 9.25 [20, p. 8-44], which means that at the equivalence point of ammonia in water, defined by

$$\frac{[\rm NH_3]}{[\rm NH_4^+]} = 1, \tag{7.10}$$

the pH value of the solution is 9.25 at 298 K, as can be seen from

$$pH = pK_A + \log\left(\frac{[A^-]}{[A]}\right) = pK_A + \log\left(\frac{[NH_3]}{[NH_4^+]}\right).$$
(7.11)

The equivalence point is close to some of the pH values aimed for in synthesis (see figure 7.5[left]). As can be read from figure 7.5[right], this will be in a region where the pH of the solution will be extremely sensitive to a very small change in base concentration. A pH value in this region will therefore be extremely difficult to achieve, and ideally an other base or a buffered solution with a different equivalence point should be found, but ammonia has the advantages that it is a simple and well characterized base. Furthermore our reference [13, 14] has used ammonia successfully.

The calculated pH graph in figure 7.5, has been calculated using the formula below which is valid for weak bases [58]

$$[OH^{-}] = \frac{2c_{B}}{1 + \sqrt{1 + 4c_{B}/K_{B}}},$$
(7.12)

where c_B is the formal concentration of the base and K_B is the base dissociation constant for the reaction

$$AOH \rightleftharpoons A^+ + OH^-, \tag{7.13}$$

defined as

$$K_{\rm B} = \frac{[{\rm OH}^-][{\rm A}^+]}{[{\rm AOH}]}.$$
 (7.14)

The pH value is calculated from (7.12) as

$$pH = 14 - pOH = 14 - (-\log([OH^{-}])).$$
(7.15)



Figure 7.5: Left: A schematic illustration of the equality point of ammonia on the buffer graph. The axes are not to scale. Right: A calculated pH - conc. graph for ammonia.

It has been found that it is very important during the formation process to ensure that the solution is sealed, and is not exposed to atmosphere, since this causes loss of control of the oxygen in the solution.

During formation the color and the color changes of the synthesis liquid provide information on the development of the synthesis. The color also provides information on the yield of the synthesis, and whether it is successful. Furthermore the sample may be subjected to an applied magnetic field, to investigate if the synthesis responds to a magnetic field. However, often it is sufficient to investigate whether material sticks to the stirring magnet.

7.5.1 Potential problems

Applying the synthesis, there are several hidden hurdles that have to be considered. Not all are common, but those mentioned have all been encountered during our work with developing the procedure.

It is very important that the pH value is correct at all stages in the synthesis. During the early stages of synthesis, we were unable to dissolve the iron salt correctly in the water (the solution became yellow), and the Mössbauer spectra of the synthesis yield had features resembling pyrite, which is not in accordance with literature [12, 13, 14].

Later the solution of iron salt could be facilitated using acid in relatively large amounts, which lead us to suspect the AOT of being contaminated with sulphur, yielding the iron salt solution basic.

The shape, and in particular the surface to volume ratio of the beakers used in the synthesis, seem to be important. The best results have been achieved using tall sealable measuring glasses (see figure 7.6).

Even though care is taken in using clean chemicals, and the appropriate amount of acid, experience shows that there is a certain amount of un-dissolved material, making the solution unclear. This is suspected of causing unpredictable results, and should be filtered out by centrifugation.

7.6 Hematite manufacturing

From the yield of the AOT/iso-octane synthesis we have attempted to manufacture hematite. This was done by using the yield of a copy of JH032 (named JH032a), which was heated in decalin. Heating magnetite/maghemite may facilitate transformation into hematite (section 6.8). A schematic of the experimental setup is shown in figure 7.7.



Figure 7.6: A schematic of the experimental setup, using AOT surfactant in sealable measuring glasses.



Figure 7.7: A schematic overview of the experimental setup for manufacturing hematite (JH032a). Iso-octane, water, AOT are boiled of and are condensed inside the condensation tube, and collected in the waste beaker. The remainder consists of decalin and iron oxide.

Direct transformation from maghemite to hematite occurs in dry state around 643-873 K [17], depending on origin and foreign ion content. However there are examples of maghemite transforming into hematite in hydrothermal conditions around 423-453 K [17].

In the setup we added decalin to the AOT/iso-octane/iron-oxide solution. Decalin has a boiling point of 458 K at room temperature and atmospheric pressure. The solution is heated to approximately 380 K. At about 353 K iso-octane and water start to boil off, and at 388 K iso-octane and AOT start to boil off. The remains are a solution of the manufactured iron-oxide and decalin. This was heated to \sim 423 K and the temperature kept constant for some time. The decalin is washed of with chloroform, water and finally acetone.

The setup is shown in figure 7.7. The silicone oil provides homogeneous heating of the round glass. The thermometer allows us to monitor the temperature and thereby progress. In the right part of the figure a condensation tube with cold water circulating inside is shown. The liquid boiled off will condensate on the inside of the condensation tube, and will be collected in the waste container.

7.7 The CTAB system

CTAB ($C_{19}H_{42}BrN$) is a well known surfactant in chemistry, and it is, along with AOT, a good choice for inverse micelles. Due to its long hydrophobic hydrocarbon chain, it is well suited for forming small micelles. It is not as easily dissolved in octane as AOT is in iso-octane, and therefore the solvent used is a mixture of n-butanol, and octane. n-butanol as mentioned furthermore decreases the size of the hydration sphere.

As iron salt we both used iron(II)sulphate ($FeSO_4$), and iron(II)chloride ($FeCl_2$), which were dissolved in water.

The iron(II)sulphate salt is dissolved in water, approx. 0.6 g in 2 ml of water, and mixed with a CTAB/n-butanol/octane solution. The CTAB solution consists approximately of 6 g of CTAB mixed with 5 g n-butanol and 22 g octane. The solution is then sonicated to remove oxygen in the solution.

Opposed to the AOT system, the base is not added in a separate solution, but as concentrated ammonia solution (14.5 M).

After mixing the solutions, the particle forming process seemed to be fast, since material stuck to the magnetic stirring magnet after 5-10 minutes.

The surface to volume ratio of the synthesis liquid seemed important, since there was a significant difference in the yielded iron oxide, depending on which glass we used for the synthesis.

Initially we tuned the n-butanol/octane system using miniature test tubes. However the sample JH029 was manufactured in a beaker glass and became brown after a while, not reproducing the tuning synthesis. On the other hand, the synthesis of JH030 was performed in a measuring glass with much less surface. JH030 reproduced the trial results, yielding a lot of magnetic particles, easily pulled on with a permanent magnet.

The figures 7.8 and 7.9 show very clearly the different beakers used in the experiments. The log book entries for these experiments are found in section C.2 and section C.3.



Figure 7.8: Left: A schematic overview of the experimental setup using a beaker glass. Right: Image of the synthesis of JH029.

A sample manufacturing attempt was performed using iron chloride and chloroform $(CHCl_3)$ as surfactant. To maintain a saturated chloroform atmosphere and to prevent oxygen contamination this was done using an experimental setup with a sealed chloroform saturated atmosphere. The setup is schematically shown in figure 7.10.

7.8 Washing and filtering

There are three main purposes with washing the synthesis yield:

1. To wash out the surfactants and solvents, and thereby to destroy the reverse micelles. If the reaction is not finished it will be terminated by the washing, since it will disrupt the water to surfactant ratio, causing it to fall outside the micellar domain, thereby destroying the micelles.



Figure 7.9: Left: A schematic overview of the experimental setup using a measuring glass. Right: Image of the synthesis of JH030.



Figure 7.10: A schematic overview of the experimental setup used for manufacturing JH041.

- 2. To filter the manufactured particles, both in terms of size and size distribution, and in terms of magnetic properties of the material. This allows a further control of the synthesis yield. It is important, since the synthesis in some cases will result in a broad range of sizes and different kinds of oxides. The methods applied are magnetic and centrifugal filtering, as well as precipitation.
- 3. To concentrate the manufactured material in such a way that it is possible to make measurements on it.

The washing has been performed using a separation funnel (see figure 7.11). The reaction solution is mixed with the washing chemicals and shaken to mix the components. After some time the washing solution is filtered by either magnetically filtering, centrifugally filtering or phase filtering. Which filtering technique is used, depends on various factors such as: Washing progress, washing, chemicals, planned oxide species.

The three filtering techniques used:

- Magnetic filtering takes advantage of the macroscopic moment of the iron oxide particles. The synthesis solution containing the suspended particles is subjected to a magnetic field during washing. The magnetic particles are extracted from the fluid, while the fluid is changed. Depending on the various circumstances such as magnetic field strength, field gradient, fluid viscosity, and the magnetic moment of the particles, some particles will not be caught by the magnet, and are therefore wasted. This filtering technique is of course useless if the particles do not have magnetic moment.
- **Centrifugal filtering** takes advantage of the density difference between the particles and the liquid, in which they are suspended. The liquid solution is centrifuged, and the precipitated particles are collected. Depending on the particle size and fluid viscosity, the centrifugation may be unable to filter out all particles, missing the smallest.



Figure 7.11: A schematic overview of the washing and magnetic filtering setup using a separation funnel.

Phase filtering is mainly used for filtering out various solvents, and takes advantage of the phase separation of different fluids, such as iso-octane and methanol. After the solution has been shaken inside the separation funnel, it is allowed to separate into phases, which are easily separated using the funnel. Usually the iron oxide material is only suspended within one of the phases.

There are several issues that have to be taken into account when washing. The most important is an undesired transformation/oxidation of the particles.

For instance we have during our work encountered several examples of magnetite experiments that have showed all signs of being very successful, e.g. being black, very magnetic and having the right behavior during reactions.

During washing some of these samples changed color within minutes to reddish/brown, and the particles became less magnetic. Even after we discovered this, and were very careful in keeping the solutions under argon, this could happen. The only plausible explanation is that the particles oxidize very fast, even though they are kept in an atmosphere with low oxygen content.

This is however not surprising, since it is a well know phenomena that nano-particles oxidize very rapidly due to the large surface to volume ratio. Especially iron is known to have a very fast surface oxidation.

To minimize the oxygen content several precautions were taken:

- Iron salt dissolved in water and ammonia were sonicated in an argon atmosphere to remove gasses, in particular oxygen, from the solutions.
- The surfactant/solvent solution was sonicated in argon atmosphere.
- The reverse micellar solutions containing iron salt and ammonia respectively were sonicated in argon atmosphere.
- The mixing of the micellar solutions was performed in a tall measuring glass filled with argon.
- After mixing the solution was sealed with argon during formation of the iron oxides.

- Washing and magnet filtering was performed in a sealed separation funnel filled with argon.
- Manufactured powder samples were stored in a sealed container with argon atmosphere.

7.9 Post synthesis oxidation

It is our experience that the particles have a strong tendency to change color, and thereby, most likely, to be oxidized. If the purpose is to manufacture an iron oxide that is not fully oxidized, or not in thermal equilibrium with the surroundings, the sample has to be well protected, and if at all possible, subjected to investigations as soon after manufacturing as possible.

The oxidation may also occur while washing, and even when the particles are still inside the micelles, so care has to be taken.

8 Transmission electron microscopy

Transmission electron microscopy (TEM) is a very powerful method for imaging very small features in solid materials. It can under favorable circumstances show features as small as $\sim 1-10$ Å.

Since we have investigated some of the manufactured samples using TEM, we will in this section briefly go through the basics of TEM. This section is based in part on [56].



Figure 8.1: A schematic illustration of the interior of a transmission electron microscope. The illustration is based on [56, fig. 2.2].

An illustration of a TEM is displayed in figure 8.1. A TEM in principle works like a classical light microscope, but it uses electrons instead of photons. The electrons are emitted by the electron gun on top of the column, which is kept at high vacuum. The electrons are accelerated through the acceleration tube. After the acceleration the electrons pass through the illumination lenses and are incident on a sample. After passing through the sample the electrons pass through the objective lens which enlarges the image. Thereafter the image is formed by image forming lenses. The image is viewed on a florescent screen, and the image is recorded either on a photographic film or on a CCD (Charge-Coupled Devices) chip.

8.1 The electron gun

There are two types of electron guns, the thermionic emission type and the field emission type. The prior type has been used in conventional transmission electron microscopes for a long time, and uses a cathode which has been heated to utilize electron emission. The electrons are collected by a Wehelt electrode before being accelerated.

The latter type is a newer invention, in which a field emission gun (FEG) can generate electrons in higher brightness and higher coherence. There are two types of FEG's, the cold FEG and the thermal FEG.

The cold FEG the cathode has room temperature, and the electrons are thorn loose by a large potential difference. It has an advantage of a small energy spread of (0.3-0.5 eV).

The thermal FEG uses a heated cathode (1600-1800 K) which when subjected to a large electric field emits electrons. It has an advantage of less maintenance requirements, and smaller emission noise than the cold FEG. However it has a disadvantage of having a larger energy spread (0.6-0.8 eV), than the cold FEG.

8.2 Acceleration tube and illumination lens system

A device generating a high voltage is used to accelerate the electrons. The electrons are accelerated through the acceleration tube which utilizes the high voltage device. Variations in the high voltage should be kept to a minimum since it causes defocusing of the electron microscope images.

After the acceleration tube the electrons pass through the deflection system which is used for beam alignment, tilting, shifting, scanning and etc. This is done by using two deflection coils, of which the angle and intermediate distance can be varied to achieve the desired effect.

The illumination lens system is used for focusing the electron beam in an appropriate fashion depending on the investigation method and purpose.

8.3 Sample holder

The sample to be investigated is placed in the sample holder which is then introduced into the microscope column, in such a fashion that the electron beam is incident on the sample. Often the sample holder is capable of tilting the sample on two axes, making the sample visible from different angles. Due to the transmission principle the sample has to be thin ~1000 Å.

8.4 Image-forming lens system

The image is formed when the electrons pass through the objective lens, which is the first stage lens. The image quality of the TEM is determined mainly by the performance of the objective lens. The image-forming lens system, which consists of several lenses, forms an image of the specimen by forming and magnifying the electron beam through two to four stages.

8.5 Viewing chamber and camera chamber

The formed image is viewed on a florescent screen in the viewing chamber. The florescent screen is viewed through a lead-glass window, to shield the observer from x-ray radiation.

When an image is about to be recorded the fluorescent screen is flipped up, to allow the electron bream to enter the camera chamber, where an image recording apparatus is localized. The image is recorded either by a photographic film or a charge-coupled device (CCD-chip).

8.6 Application

The TEM apparatus has a wide range of applications. It is possible to use the TEM as a common microscope for direct image-making. Furthermore it is possible to produce light/dark images, phase images, diffraction images and holograms just to mention some.

8.7 Measurements

For measurements we have used the TEM at the Ørsted Laboratory and the TEM at the Materials Research department at Risø National Laboratory. The used sample substrate is composed of amorphous carbon film, which fulfills the thickness requirements.

The TEM at the Ørsted Laboratory has a LaB_6 thermionic electron gun, and runs with an acceleration potential of 200kV. At the Ørsted Laboratory we have investigated the samples with magnifications of 3.4k, 4.4k, 27.5k, 38k, 44k, 50k and 390k.

The TEM at Risø is a thermal FEG, and runs with an acceleration potential of 300 kV, At Risø we have investigated the samples with magnifications of 250k, 400k and 600k.

9 Sample analysis

9.1 Introduction

This chapter contains the analysis of the measurements on the samples manufactured using the reverse micellar technique. I present here a short overview.

The analysis of the iron oxide particles produced by the reverse micellar technique reveals that we have successfully tuned the technique to manufacture the iron oxides goethite, maghemite, and non-stoichiometric magnetite up to high degree of stoichiometry. Using analysis of TEM images we are able to confirm the dependence of particle size of the micellar solution ω . We have not been successful in manufacturing hematite by using the reverse micellar technique.

The chapter starts with the considerations o the sample selection in section 9.2. Before commencing the actual sample analysis I will go through some details regarding the use of the two analysis techniques used; Mössbauer spectra analysis and TEM image analysis, in sections 9.3 and 9.4.

In the sections 9.5 to 9.12 I present the analysis of the selected samples (the remaining results can be found in appendices A and B.

I am presenting the main conclusions of the analysis in section 9.13.

9.2 Sample selection

From the successfully manufactured samples during the work with the reverse micellar technique, we have chosen the most interesting samples for analysis: JH030, JH032, JH032a, JH036, JH037T, JH041, JH046, JH047, JH048, JH050 and JH053.

The chosen samples will all be analyzed, but since the analysis material is very extensive only the most interesting will be presented in this chapter, and the rest samples are presented in appendix A.

To provide an overview of the successfully manufactured samples these are presented in table 9.1, with their manufacturing parameters. A transcript of the logbook entry for each sample is provided in appendix C. Furthermore an overview of the analysis results is found in table 9.62 in section 9.13.

The sorting of interesting samples has been done in several steps. The first indications of the properties of a sample are visible during synthesis, as color changes and color reveal information on the oxidation step of the iron. During washing the response of the material to the filtering magnet provides information on the magnetic properties of the particles.

After drying of the samples, the assessment of the criteria was repeated, and the most promising samples were selected for Mössbauer spectroscopy investigations.

Liquid specimens were collected from promising samples during the washing process at various stages, and frozen in liquid nitrogen to protect them from further oxidation. Some of these have been investigated further through Mössbauer spectroscopy and TEM.

Mössbauer spectra of liquid samples will contain a high degree of background noise. The noise is due to the large thickness (1-5 mm) of the sample holder containing the liquid sample, which results in large scattering of the gamma photons.

Furthermore the liquid samples often contain relatively little amounts of iron oxide material, which results in a very low absorption.

The samples selected for analysis in this section are:

JH030 which consists of goethite.

JH032 which contains non-stoichiometric magnetite.

JH032a which is an attempt to manufacture hematite.

JH037 which contains maghemite manufactured using AOT and iso-octane.

JH041 which contains maghemite manufactured using CTAB and chloroform.

- **JH046** which contains non-stoichiometric magnetite, and consists of a powder and a liquid sample from which a particle distribution has been extracted.
- **JH048** which consists of maghemite.
- **JH053** which contains magnetite close to being stoichiometric. It has been investigated extensively, and comparison with JH046 provides evidence that particle size control is possible.

Sample	Surfactant	Solvent	Metal	Metal salt	Surfactant	ω	section
name			salt	conc.	conc.		
JH030	CTAB	n-butanol, octane	$FeSO_4$	$1.15\mathrm{M}$	$0.48\mathrm{M}$	9.04	9.5
JH032	AOT	iso-octane	$FeSO_4$	$0.75\mathrm{M}$	$0.49\mathrm{M}$	12.49	9.6
JH032a	AOT	iso-octane	$FeSO_4$	$0.75\mathrm{M}$	$0.49\mathrm{M}$	12.49	9.7
JH036	AOT	iso-octane	$FeSO_4$	$0.74\mathrm{M}$	$0.49\mathrm{M}$	12.59	A.1
JH037	AOT	iso-octane	$FeSO_4$	$0.74\mathrm{M}$	$0.54\mathrm{M}$	11.42	9.8
JH041	CTAB	chloroform	FeCl_2	$1.27\mathrm{M}$	$0.33\mathrm{M}$	3.37	9.9
JH046	AOT	iso-octane	$FeSO_4$	$0.75\mathrm{M}$	$0.55\mathrm{M}$	11.22	9.10
JH047	AOT	iso-octane	$FeSO_4$	$0.70\mathrm{M}$	$0.55\mathrm{M}$	4.76	A.2
JH048	AOT	iso-octane	$FeSO_4$	$0.75\mathrm{M}$	$0.53\mathrm{M}$	11.64	9.11
JH050	AOT	iso-octane	$FeSO_4$	$0.74\mathrm{M}$	$0.53\mathrm{M}$	17.46	A.3
JH053	AOT	iso-octane	$FeSO_4$	$0.82\mathrm{M}$	$0.53\mathrm{M}$	5.95	9.12

Table 9.1: The main manufacturing parameters of the selected samples.

9.3 Mössbauer analysis

For fitting the Mössbauer spectra I have mainly used the computer program Fit;0) [25]. The fitting program is supplied with two fitting algorithms, random-walk and amoebe, which both have been used. The measure of "goodness" of a fit to the data is provided in the variable χ^2 which is defined as

$$\chi^2 = \frac{1}{\Omega} \sum_{i=1}^{N} (d_i - f_i)^2, \qquad (9.1)$$

where N is the number of data channels, d_i is the i'th data channel and f_i is the value of the fitting model at the position of the i'th data channel. Ω is a scaling factor related to the conversion from counting numbers to relative scale. As can be deduced from the definition of χ^2 , the fitting algorithms are least squares fitting algorithms. I will through the analysis provide the value of χ^2 for each fit, but of course the values are not comparable among the different spectra unless they are similar in absorption level and noise level.

The fitted spectra which are displayed in analysis will contain all fitting components (singlets, doublets and sextets), as well as the sum and the difference. In special cases the sum is omitted for the sake of clarity.

The fit parameters of the fitted spectra are presented in tables. However, because of limited space only the most significant parameters, isomer shift, quadrupole shift, quadrupole split, the asymmetry parameter b, magnetic hyperfine field and absolute and relative area will be provided in these tables. Intensity and width of the individual peaks will not be provided since these are of less interest.

When displaying sextet components there will often be a ratio displayed next to the line shape e.g. "(3:2:1)", which means that this components has been fitted with an area ratio of 3:2:1:1:2:3 between the individual absorption lines of the sextet. Furthermore "S-L" is short for "Split-Lorentz" (see table 9.2).

The line shapes used in the Mössbauer analysis and the properties of these are presented in table 9.2.

Name	Formula	Area	Parameter
Lorentz	$L_{Lor}(v) = I_0 \left(1 + \left(\frac{2(v-v_0)}{W}\right)^2 \right)^{-1}$	$A_{Lor} = \frac{I_0 W \pi}{2}$	-
Gauss	$L_{Gau}(v) = I_0 \exp\left(-\left(\frac{2(v-v_0)}{W}\right)^2\right)$	$A_{Gau} = \frac{I_0 W \sqrt{\pi}}{2}$	-
Split-Lorentz	$L_{S-L}(v) = \begin{cases} L_{Lor}(W_1) &, v < v_0 \\ L_{Lor}(W_2) &, v \ge v_0 \end{cases}$	$A_{S-L} = \frac{1}{2} \sum_{i=1}^{2} A_{Lor}(W_i)$	$b \equiv \frac{W_1}{W_2} - 1$ $W_1 \ge W_2$

Table 9.2: Line shapes used for Mössbauer analysis. Reproduced from [23].

9.4 TEM image analysis

As mentioned earlier some of the samples have been investigated using Transmission Electron Microscopy (TEM). The TEM images have been used for particle size measurements, as well as the lattice distance has been measured for some samples. All image measurements have been done using imaging software.

The particle sizes were measured in different ways depending on the apparent shape of the particles. For particles to qualify for the statistics, several requirements had to be met. The particles had to have a well defined visible border and the particles had to have a shape for which an area could be calculated easily. These requirements were applied to get "good" statistics. Furthermore the particles were classified as being rectangular, trapezoidal, irregular, hexagonal or semi-hexagonal, for use in particle size calculations.

A few particles did not fulfill the shape requirements. These particles have been neglected, since it does not cause deterioration of the statistics.



Figure 9.1: Schematic of particle shapes found in TEM images. The lines indicate how the size measurement lines have been drawn. **a)** Rectangular particles. **b)** Trapezoidal particles. **c)** Hexagonal and semi-hexagonal particles. **d)** Irregular particles.

The particles have been divided into two main groups, regular and irregular. The particle size is measured differently for each group. In figure 9.1 different encountered particles shapes are presented.

The particles seen in the TEM images are two-dimensional projections of the true particle shape. The regular particles, which appear parallelogram, trapezoidal or hexagonal shaped may in fact be octahedra oriented in various ways. As can be seen in figure 9.2, an octahedra can appear like these shapes depending of the orientation of it. The fact that magnetite forms octahedral crystals, makes this worth keeping in mind.



Figure 9.2: An octahedral crystal, here magnetite, in various orientations. Constructed using an applet on webmineral.com [62].

However, there is no way to determine the true particle shape, so a simple approach has been used in calculating the size of the particles.

Size measurements were performed by drawing two lines $(x_1, y_1)_i \rightarrow (x_2, y_2)_i$ and calculating the length of the line by the following formula (Pythagoras' formula):

$$d = ((x_2 - x_1)^2 + (y_2 - y_1)^2)^{\frac{1}{2}}.$$
(9.2)

The size measurement lines of the rectangular and trapezoidal particles (case a) and b) i figure 9.1) were drawn from corner to opposite corner, and the approximate area is calculated from

$$A = \left(\frac{d_1}{\sqrt{2}}\right) \cdot \left(\frac{d_2}{\sqrt{2}}\right) = \frac{1}{2}d_1 \cdot d_2, \tag{9.3}$$

assuming that the particle was not far from being a square, which was true in most of the cases.

The irregular particles (case d) in figure 9.1) were all ellipsoidal- or rectangular-like, and their size was measured by drawing lines from edge to opposite edge at an angle of $\sim 90^{\circ}$ between the two lines.

The size of a hexagonal particle (case c) in figure 9.1) has been calculated using the same method as used with the irregular particles. Due to the uncertainty of the measuring method (poor image contrast), and the small misfit using this method, this simple method has been chosen in competition with the correct calculation for determining the area of a hexagonal particle.

The approximate area of the irregular and hexagonal particles was calculated by

$$A = d_1 \cdot d_2. \tag{9.4}$$

When an approximate area has been found, a measure of the mean particle edge length d can be calculated by:

$$d = \sqrt{A} \,. \tag{9.5}$$

9.5 JH030

The sample JH030 was manufactured using n-but and and octane as solvent, CTAB as surfactant and FeSO₄ as iron salt. It has an ω of 9.04. It is the only sample manufactured using these conditions.

After manufacturing the sample, it was characterized as being light brown and magnetic. The magnetic properties were examined by subjecting the sample to a magnetic field from a permanent magnet, and observing the response of the sample material.



Figure 9.3: Mössbauer spectra as a function of temperature of the sample JH030.

The Mössbauer spectra of JH030 in figure 9.3 show a significant increase in the hyperfine field from 295 K to 80 K. This is a feature that is typical of goethite (α -FeOOH) [46]. The table values for the Mössbauer parameters of goethite can be found in table G.1.

It is also clear from the broad range in values of magnetic hyperfine field that there is substantial particle-particle interaction particularly visible in the 295 K spectrum. These interactions prevent some of the particles from exhibiting fast superparamagnetic relaxation, resulting in a spectrum with a broad distribution of hyperfine fields.

Assuming the sextet to be goethite, I have fitted the 295 K spectrum with goethite, and considering the small particle interaction I have allowed the hyperfine field to be slightly smaller than the hyperfine field of bulk goethite. Furthermore I have chosen the line shape of the sextet to be Split-Lorentz, with a free asymmetry parameter, also due to interaction. I have fitted the doublet feature in the center of the spectrum with a doublet, which is allowed to vary freely. Based on the observation that the isomer shift of the fitted doublet is the same as for the sextet, I deduce that the sample consists of ordered and superparamagnetic goethite. The fit parameters are presented in table 9.3 and the fit in figure 9.4.

I have fitted the 80 K spectrum with a sextet with the parameter values of bulk goethite, and the depression between line 3 and 4 with a doublet. Of the preset parameters of the goethite sextet I have only allowed the hyperfine field to vary, and for the doublet only the variation in the isomer shift is restricted. The fit matches goethite quite well. The hyperfine field is slightly smaller than the value for bulk goethite, but is well within acceptable bounds, considering that we are dealing with nano-particles.



Figure 9.4: Left: The fitted Mössbauer spectra of JH030 at 295 K. Right: The fitted Mössbauer spectra of JH030 at 80 K.

Name	Lineshape	B_{HF}	E_Q	δ	b	Area	Area
		Т	$\mathrm{mm/s}$	$\mathrm{mm/s}$		%mm/s	%
Goethite	S-L(3:2:1)	35.1	-0.13	0.37	1.91	11.0	73.9
Doublet 1	Lorentz		0.76	0.38	-	3.9	26.1

Table 9.3: The parameters in fitting JH030 at 295 K with goethite. The hyperfine field was allowed to vary. $\chi^2 = 0.02088$

Name	Lineshape	B_{HF}	E_Q	δ	b	Area	Area
		Т	$\mathrm{mm/s}$	$\mathrm{mm/s}$		$\rm \%mm/s$	%
Goethite	S-L(3:2:1)	49.8	-0.13	0.48	0.92	21.7	74.7
Doublet 1	Lorentz	-	1.59	0.48	-	7.4	25.3

Table 9.4: The parameters in fitting JH030 at 80 K with goethite. $\chi^2 = 0.33556$.

Goethite often forms needle shaped particles, which produce texture effects in Mössbauer spectra. The lines 2 and 5 in the spectrum are larger than the lines in the fit model, which may be a result of texture in the material. Therefore this is an additional support for the goethite model. The resulting fit is presented in table 9.4 and in figure 9.4.

The 20 K spectrum shows very fine absorption lines of a sextet, and I have fitted it with only one goethite sextet. I have not allowed the preset parameters to vary during fitting. The resulting fit is presented in table 9.5 and in figure 9.5.

Considering the analysis results, the Mössbauer spectra strongly indicates goethite. The initial analysis properties showed magnetic response, which does not comply well with goethite which is an antiferromagnet. However, sufficiently small antiferromagnetic particles often have a magnetic moment due to uncompensated spins at the surface. The magnetic moment is proportional to d^{-1} , where d is the diameter of the particle [45]. In very small (~4 nm) antiferromagnetic particles there also may exists a thermoinduced magnetization [45]. So, my conclusion of the analysis



Figure 9.5: The fitted Mössbauer spectra of JH030 at 20 K.

Name	Lineshape	B_{HF}	E_Q	δ	b	Area	Area
		Т	$\mathrm{mm/s}$	$\rm mm/s$		%mm/s	%
Goethite	S-L(3:2:1)	50.6	-0.13	0.48	1.40	25.5	100

Table 9.5: The parameters in fitting JH030 at 20 K. $\chi^2 = 0.53135$.

of sample JH030 is that the manufactured material is indeed goethite. Due to lack of samples to compare with, it is difficult to give an estimate of the particle size, but a rough estimate from ω and the spectra would be $\sim 10-25$ nm.

This result has recently been confirmed in an experiment at the Danish technical University where the manufacturing process of this sample was copied, and the sample analyzed using Mössbauer spectroscopy.

9.6 JH032

The sample JH032 was manufactured using iso-octane as solvent, AOT as surfactant and FeSO₄ as iron salt. It has an ω of 12.49. It is a result of the tuning of the AOT system, and the first to be successful.

During washing and filtering, the sample became divided into two different samples. A part of the material agglomerated on the bottom of the test tubes, and was extracted. Assuming that these particles were the larger particles in the sample I named it JH032L (L for large particles). A part of the samples did not precipitate, and was extracted from the waste. Assuming that these particles were small, I named the sample JH032S (S for small particles). After drying the sample was characterized as being black and having a very strong response to a magnetic field. The sample was has been examined using Mössbauer spectroscopy with and without an applied magnetic field.

9.6.1 JH032S



Figure 9.6: Mössbauer spectra as a function of temperature of the sample JH032S.

The 295 K spectrum shows clear signs of both particle interaction and of superparamagnetism. The spectrum has a very broad doublet, with indications of a sextet. The indications are however so weak that I have chosen not to fit the spectrum.

The 200 K spectrum contains a sextet with broad absorption lines which show signs of asymmetry, somewhat similar to those of magnetite. I have fitted this component with two sextets for magnetite. Furthermore I have inserted a doublet to compensate for the well resolved doublet in the spectrum. The resulting fit is presented in table 9.6 and figure 9.7.

The fit did not reveal a good match with magnetite, since the neither isomer shifts or hyperfine fields seemed to match the bulk values well. The hyperfine field value can be explained by nano-particle effects, whereas this can not explain the isomer shift values. A possible explanation



Figure 9.7: The fitted Mössbauer spectra of JH032S. Left: 200 K. Right: 80 K.

is that the iron phase in question is a form of defect or non-stoichiometric magnetite, close to magnemite. However, the found values of the isomer shift lie between the values of the A and B sextet of magnetite. I find it therefore likely that the obtained values are due to the fitting procedure which has shifted the values towards the mean value during fittings.

Name	Lineshape	B_{HF}	E_Q	δ	b	Area	Area
		Т	$\mathrm{mm/s}$	$\rm mm/s$		$\rm \% mm/s$	%
Sextet 1	S-L(3:2:1)	46.5	0.00	0.46	0.14	1.32	17.9
Sextet 2	S-L(3:2:1)	42.4	0.00	0.57	1.42	4.39	59.6
Doublet 1	Lorentz	-	0.66	0.43	-	1.65	22.5

Table 9.6: The fitted spectrum of JH032S at 200 K. $\chi^2 = 0.00837$.

The 80 K spectrum shows a nice sextet with some small imperfections. However, these imperfections are so significant, that I have fitted the spectrum with two sextets. The imperfections include features such as lines 1 and 2 being broader and shallower than lines 6 and 5 respectively. The slopes and tops between these lines are not symmetric either.

The fit parameters are presented in table 9.7 and the fitted spectrum in figure 9.7.

Name	Lineshape	B_{HF}	E_Q	δ	b	Area	Area
		Т	$\mathrm{mm/s}$	$\mathrm{mm/s}$		$\rm \% mm/s$	%
Sextet 1	S-L(3:2:1)	49.6	0.00	0.65	1.55	4.53	67.0
Sextet 2	S-L(3:2:1)	49.5	-0.03	0.38	0.06	2.22	33.0

Table 9.7: The fitted spectrum of JH032S at 80 K. $\chi^2 = 0.00385$.

The 20 K spectrum shows much sharper absorption lines, however it also reveals some surprising features. The features consist of the unknown component between lines 3 and 4, and the small bumps on the inner slopes of lines 1 and 2. These features resemble those of magnetite [48], and are marked in the spectrum in figure 9.8.

The spectrum has been fitted in the same manner, and using the same assumptions as in fitting the 80 K spectrum. The fit parameters are presented in table 9.8 and the fitted spectrum in figure 9.8.

The 295 K and the 200 K spectra both bear some resemblance with spectra of maghemite nano-particles (~6 nm) [9], which have been manufactured by thermally decomposing nontronite (Na_{0.3}Fe₂³⁺(Si, Al)₄O₁₀(OH)₂ · n(H₂O)) (950°C, 20 min in air). The most probable magnetic hyperfine field of these particles is 47 T, and the average value is 41 T, furthermore a significant portion of the particles exhibit superparamagnetism.

Comparison with Mössbauer spectra in [9, 41, 44, 52, 59] leads me to the conclusion that the iron oxide in question is probably very non-stoichiometric magnetite close to maghemite. Non-stoichiometric magnetite has the formula $Fe_{3-x}O_4$, 0 < x < 1/3. If x = 1/3 the iron oxide has become maghemite.

The explanation for the appearance of the magnetite features in the 20 K spectrum is probably that it is well below the Verwey transition. The Verwey temperature, which is 118 K for stoichiometric magnetite, drops significantly for non-stoichiometric magnetite [3, 4].

From comparison with the spectra in [52], where the non-stoichiometric spectrum with the largest value of the x parameter has a value of x = 0.09, it is my estimate that $x \simeq 0.2$ in this sample.



Figure 9.8: The fitted Mössbauer spectra of JH032S at 20 K.

Name	Lineshape	B_{HF}	E_Q	δ	b	Area	Area
		Т	$\mathrm{mm/s}$	$\mathrm{mm/s}$		$\rm \%mm/s$	%
Sextet 1	S-L(3:2:1)	50.8	-0.08	0.37	0.26	3.26	40.2
Sextet 2	S-L(3:2:1)	51.4	0.03	0.63	0.55	4.85	59.8

Table 9.8: The fitted spectrum of JH032S at 20 K. $\chi^2 = 0.01024$.

Name	Lineshape	B_{HF}	E_Q	δ	b	Area	Area
		Т	$\mathrm{mm/s}$	$\mathrm{mm/s}$		$\rm \%mm/s$	%
Sextet 1	S-L(3:4:1)	48.6	-0.02	0.38	0.36	3.70	59.3
Sextet 2	S-L(3:4:1)	47.4	-0.02	0.79	1.38	2.54	40.7

Table 9.9: The fitted spectrum of JH032S at 200 K and 0.5 T \perp . $\chi^2 = 0.01327$.

In order to investigate the sample further a spectrum has been recorded at 200 K with an external magnetic field of 0.5 T applied perpendicular to the gamma ray direction. This spectrum



Figure 9.9: Mössbauer spectra of the sample JH032S at 200 K, without and with an external applied perpendicular magnetic field.



Figure 9.10: The fitted Mössbauer spectrum of JH032S at 200 K with an applied perpendicular field of 0.5 T.

is presented in figure 9.9.

The 200 K 0 T spectrum has been analyzed earlier, and the fit is located in table 9.6. The 0.5 T spectrum shows a clear and strong response to the applied field, when compared to the 0 T spectrum. The 0 T spectrum shows what may be interpreted as a considerable particle-particle interaction, displayed as a very broad distribution of hyperfine fields. Broadening is caused by dynamic effects, but the magnetic order is restored by the external field [26]. The order imposed by the applied magnetic field reveals a pinning of the atomic and nuclear magnetic moments. The ordering confirms the hypothesis of particle-particle interaction as causing the broadening, and further confirms that the particles have a significant macroscopic magnetic moment, and hence must be ferro/ferrimagnetic.

The spectrum with applied magnetic field exhibits the same asymmetry as the spectrum with no applied magnetic field. The lines are narrower and it is now clear that line 1 consists of more than one component.

I have fitted the spectrum with two sextets to compensate for the asymmetries of the spectrum. The fit of the 0.5 T spectrum is presented in table 9.9 and in figure 9.10.

Considering the misfit on the fitted 0.5 T spectrum, I suspect a non-linearity in the spectrum setup, indicated by a skewness in the background level in the left side of the spectrum. However, the signs are not unambiguous, and I have therefore chosen to ignore it, since it does not change the result of the fit.

9.6.2 JH032L



Figure 9.11: Mössbauer spectra as a function of temperature of the sample JH032L.

The 295 K spectrum (figure 9.11) displays significant particle-particle interaction, by exhibiting a broad distribution of hyperfine fields, with clear signs of dominating sextets. The spectrum is somewhat asymmetric, indicating several iron ion sites. Due to the broad slopes I have chosen not to fit the spectrum.

The 250 K spectrum shows a fairly well developed sextet, which yet shows distinct signs of particle-particle interaction, and of being in the process of ordering. The sextets show clear signs of asymmetry across the center, signs that resemble those of magnetite. The clearest sign is that the lines 1 and 2 are broader than lines 6 and 5 respectively. I have therefore fitted the spectrum



Figure 9.12: The fitted Mössbauer spectra of JH032L. Left: 250 K. Right: 200 K.

with two sextets, shown in table 9.10, with a quadrupole shift of zero. The fitted spectrum is displayed in figure 9.12.

Name	Lineshape	B_{HF}	E_Q	δ	b	Area	Area
		Т	$\mathrm{mm/s}$	$\rm mm/s$		$\rm \% mm/s$	%
Sextet 1	S-L(3:2:1)	46.5	0.00^{*}	0.42	1.57	24.8	31.5
Sextet 2	S-L(3:2:1)	40.3	0.00^{*}	0.52	3.71	53.8	68.5

Table 9.10: The fitted spectrum of JH032L at 250 K. * indicates that this parameter has been locked during fitting. $\chi^2 = 0.11284$.

The 200 K has the same characteristics as the 250 K spectrum, but it has a significantly higher degree of magnetic order. I have used the same fitting approach as used when fitting the 250 K spectrum. The resulting fit is presented in table 9.11 and figure 9.12.

Name	Lineshape	B_{HF}	E_Q	δ	b	Area	Area
		Т	$\mathrm{mm/s}$	$\mathrm{mm/s}$		$\rm \%mm/s$	%
Sextet 1	S-L(3:2:1)	47.8	0.00^{*}	0.37	1.16	22.4	27.3
Sextet 2	S-L(3:2:1)	46.4	0.00^{*}	0.60	3.34	59.8	72.7

Table 9.11: The fitted spectrum of JH032L at 200 K. * indicates that this parameter has been locked during fitting. $\chi^2 = 0.14025$.

The 140 K spectrum show several interesting features. The asymmetry across the center has disappeared all together, and the lines are pairwise symmetric. However, the lines 2 and 5 are deeper and narrower than the lines 1 and 6. This indicates an existence of at least two sextets still overlapping at lines 2 and 5 but not overlapping in the same manner at lines 1 and 6. The fit is shown in table-form and graphic-form in table 9.12 and figure 9.13 respectively.

Assuming the non-stoichiometric magnetite model, the 80 K shows the expected next step in the development of the spectrum during cooling. The lines 1 and 2 become increasingly narrower, and the lines 5 and 6 become increasingly wider. This change of width is of course counteracted by the amplitude of the peaks which change in the opposite direction. The slopes of the individual absorption lines have at this point almost become symmetric, indicating that the temperature



Figure 9.13: The fitted Mössbauer spectra of JH032L. Left: 140K. Right: 80K.

Name	Lineshape	B_{HF}	E_Q	δ	b	Area	Area
		Т	$\mathrm{mm/s}$	$\mathrm{mm/s}$		$\rm \% mm/s$	%
Sextet 1	S-L(3:2:1)	49.3	0.00^{*}	0.41	0.91	34.4	39.6
Sextet 2	S-L(3:2:1)	48.2	0.00^{*}	0.62	1.99	52.4	60.4

Table 9.12: The fitted spectrum of JH032L at 140 K. * indicates that this parameter has been locked during fitting. $\chi^2 = 0.26529$.

is approaching the point where particle-particle interaction effects are close to negligible. The asymmetry that is left is more pronounced for the lines 5 and 6. To keep consistency, I have fitted the spectrum with two sextets. The result of the fitting process is presented in table 9.13 and figure 9.13.



Figure 9.14: The fitted Mössbauer spectra of JH032L. Left: 20 K. Right: 295 K and 1.4 T.

At 20 K all the interaction effects are invisible, since there are no more thermal excitations to make them visible, and the absorption lines are now pure Lorentzian. The development of the asymmetry described above continues, and lines 1 and 2 are at this point narrower than 5 and

Name	Lineshape	B_{HF}	E_Q	δ	b	Area	Area
		Т	$\mathrm{mm/s}$	$\mathrm{mm/s}$		$\rm \% mm/s$	%
Sextet 1	S-L(3:2:1)	50.7	0.03	0.48	0.33	47.9	51.9
Sextet 2	S-L(3:2:1)	48.8	-0.13	0.54	0.75	44.4	48.1

Table 9.13: The fitted spectrum of JH032L at 80 K. $\chi^2 = 0.49422$.

6. The spectrum show clear non-maghemite signs, marked by arrows in figure 9.14, which will indicate that it is probably non-stoichiometric magnetite. I have fitted the spectrum with two sextets, which is sufficient. The result of the fit is shown in table 9.14 and figure 9.14.

Name	Lineshape	B_{HF}	E_Q	δ	b	Area	Area
		Т	$\mathrm{mm/s}$	$\mathrm{mm/s}$		$\rm \% mm/s$	%
Sextet 1	Lorentz(3:2:1)	51.4	0.00	0.57	-	58.7	65.7
Sextet 2	Lorentz(3:2:1)	50.5	-0.05	0.35	-	30.7	34.3

Table 9.14: The fitted spectrum of JH032L at 20 K. $\chi^2\!=\!0.98806$.



Figure 9.15: Mössbauer spectra of the sample JH032L at 295K, without and with an applied external perpendicular magnetic field.

Name	Lineshape	B_{HF}	E_Q	δ	b	Area	Area
		Т	$\mathrm{mm/s}$	$\mathrm{mm/s}$		$\rm \% mm/s$	%
Sextet 1	S-L(3:4:1)	48.7	0.00^{*}	0.25	1.63	21.9	46.2
Sextet 2	S-L(3:4:1)	47.8	0.00^{*}	0.56	3.20	25.5	53.8

Table 9.15: The fitted spectrum of JH032L at 295 K and 1.4 T. * indicates that this parameter has been locked during fitting. $\chi^2 = 0.13702$.

To investigate the sample further and to confirm the non-stoichiometric magnetite model, a spectrum has been recorded at 295 K with an applied field of 1.4 T perpendicular to the gamma ray direction. For comparison, the spectra obtained with applied field and with no applied field, are displayed in figure 9.15.

The spectrum reveals a significant ordering of the sextets, implying a pinning of the atomic and nuclear magnetic moments. The iron oxide is hereby confirmed to be ferro/ferrimagnetic.

The applied magnetic field accentuates the asymmetries between the lines 1 and 2, and 5 and 6, which must be caused by more than one component. This supports the non-stoichiometric model, which I consider very likely.

I have fitted the spectrum with two sextets, to account for the asymmetries. The fitted spectrum is presented in figure 9.14, and the fit parameters are displayed in table 9.15.

My estimate of the value of the x parameter in $\text{Fe}_{3-x}O_4$, 0 < x < 1/3, is like that of JH032S, set to 0.2.

9.6.3 Conclusion

To conclude the analysis of the sample JH032 quite a few threads have to be gathered. A thorough analysis of the sample's two subsamples independently lead me to the same conclusion, namely that the sample is mainly composed of non-stoichiometric magnetite, close to maghemite in overall oxidation state. My estimate to the stoichiometry-parameter, x, is for JH032S and JH032L estimated to 0.2 ± 0.05 .

From ω and the Mössbauer spectra I roughly estimate the particle size to be ~25-35 nm.

9.7 JH032a

As previously mentioned this sample is a result of an attempt to manufacture hematite, by heating material from a copy of the sample JH032 for a couple of hours (2-3 hours). It has an ω of 12.49.

After manufacturing the sample was characterized as: Dark brown, magnetic, possibly hematite. The sample has been examined using Mössbauer spectroscopy, and the obtained spectra are show in figure 9.16.



Figure 9.16: Mössbauer spectra as a function of temperature of the sample JH032a.

The 295 K Mössbauer spectrum in figure 9.16 shows only a narrow doublet with no signs of a magnetically ordered component. I have therefore fitted it with a doublet with no constraints. The resulting fit is presented in table 9.16 and figure 9.17.



Figure 9.17: The fitted Mössbauer spectra of JH032a. Left: 295 K. Right: 80 K.

Name	Lineshape	B_{HF}	E_Q	δ	b	Area	Area	
		Т	$\mathrm{mm/s}$	$\mathrm{mm/s}$		$\rm \%mm/s$	%	
Doublet 1	Lorentz	-	0.72	0.39	-	33.57	100	

Table 9.16: The fitted spectrum of JH032a at 295 K. $\chi^2 = 0.48453$.

The 80 K spectrum in figure 9.16 shows a broad absorption line, in which the left slope is steeper than the right slope. The absorption line has features at the bottom, which indicate that it may be composed of multiple components. Furthermore the right slope has an indication of a plateau approximately halfway up (marked in figure 9.17). This feature resembles superparamagnetic magnetite [40].

I have fitted the spectrum with two doublets to compensate for the two components with different isomer shifts in magnetite. I have not restricted the components during fitting. The fitted spectrum is presented in figure 9.17 and the fit parameters are presented in table 9.17.

Name	Lineshape	B_{HF}	E_Q	δ	b	Area	Area
		Т	$\mathrm{mm/s}$	$\mathrm{mm/s}$		$\rm \% mm/s$	%
Doublet 1	Lorentz	-	1.32	0.91	-	19.45	40.84
Doublet 2	Lorentz	-	1.27	0.21	-	28.18	59.16

Table 9.17: The fitted spectrum of JH032a at 80 K. $\chi^2 = 0.56299$.



Figure 9.18: The fitted Mössbauer spectra of JH032a at 20 K.

The 20 K spectrum in figure 9.16 shows a very broad absorption peak with broad slopes, and signs of at least one sextet component. The features of the spectrum are symmetric, which indicates a single phase material.

The spectrum is a typical spectrum of a material with interaction among the particles. A material showing such particle interaction at such a low temperature, contains very small particles. At low temperatures particle interaction is usually more significant compared to thermal excitations than at higher temperatures. This indicates that the particle interaction is weak, either due to relatively large inter-particle distances, or a small magnitude of the interaction forces. The weak particle interaction could be caused by inter-particle exchange interaction, such as of a super-spin-glass, or possibly the presence of surfactant molecules.

I have fitted the spectrum with a doublet to compensate for the broad peak, and a Split-Lorentzian sextet with a large b parameter to account for the broad slopes. The obtained fit is

Name	Lineshape	B_{HF}	E_Q	δ	b	Area	Area
		Т	$\mathrm{mm/s}$	$\mathrm{mm/s}$		$\rm \%mm/s$	%
Sextet 2	S-L(3:2:1)	47.3	0.04	0.52	7.25	42.7	63.7
Doublet 2	Lorentz	-	1.17	0.50	-	24.3	36.3

shown in table 9.18 and figure 9.18. The fit components have practically the same isomer shift, supporting the assumption that the sample consists of a single iron oxide phase.

Table 9.18: The fitted spectrum of JH032a at 20 K. $\chi^2 = 0.18575$.

From the fit data of the 20 K spectrum it is difficult to determine which iron oxide we are dealing with, since there are several candidates matching the found values. The quadrupole shift is close to 0 mm/s indicating a cubic crystal structure. Hematite has a quadrupole shift of 0.49 mm/s at 4.2 K and can be ruled out as an option. Matching the remaining values are only maghemite and feroxyhyte. Since we have not seen feroxyhyte in any other sample, it is highly likely that the manufactured material is well crystallized but ultrafine sized maghemite.

From ω and the Mössbauer spectra I roughly estimate the particle size to be ~10-20 nm.

The purpose of manufacturing this sample was to manufacture hematite. Considering the found sample composition, it has to be discussed whether hematite can be manufactured by heating in the experimental setup used for manufacturing of this sample. From the diagram of formation in figure 6.1, the three ways of hematite formation are by aggregation from ferrihydrite, by dehydration from goethite and by heating maghemite. The treatment which the material has been exposed to (heating to 150° C) could only have resulted in hematite if the original material consisted of goethite.

The original material was a copy of JH032, which I have concluded to consist of non-stoichiometric magnetite. Therefore it is likely that the original material of this sample also consisted of non-stoichiometric magnetite. From figure 6.1 we see that formation of maghemite is possible by oxidation and heating (200-250°C) of magnetite. Since the material consists of nano-particles, the temperature required may be lower, possibly as low as 150°C which we have used in the sample preparation.

It is therefore my conclusion that the manufacturing procedure used for manufacturing hematite can only yield hematite if the original material is goethite. However, it is well suited for formation of well-separated nano-particle maghemite.

9.8 JH037T

The sample JH037 was manufactured using iso-octane as solvent, AOT as surfactant and FeSO₄ as iron salt. It has an ω of 11.42.

The sample had a very powerful and interesting magnetic response during manufacturing, in that it formed small "tadpoles" of magnetic material which was attracted to the magnet, and assumed an orientation parallel to the magnetic field lines.

The bottom part of the sample did separate during centrifuging, while the top part did not. The bottom part has not been investigated further, since it has not been considered as interesting. It was after manufacturing characterized as: Brown, magnetic, probably large particles.

The top part was stored in liquid form and named JH037T. The characteristics of the liquid sample JH037T after manufacturing was: Magnetic, probably large particles. Before the sample was investigated with Mössbauer spectroscopy, it was dried. The recorded spectra are presented in figure 9.19.



Figure 9.19: Mössbauer spectra as a function of temperature of the sample JH037T.

The 295 K spectrum shows a fine doublet, and I have thus fitted it with a doublet with freely

Name	Lineshape	B_{HF}	E_Q	δ	b	Area	Area
		Т	$\mathrm{mm/s}$	$\mathrm{mm/s}$		$\rm \% mm/s$	%
Doublet 1	Lorentz	-	0.68	0.39	-	22.0	100

Table 9.19: The fitting parameters of JH037T at 295 K. $\chi^2 = 0.05543$.

varying parameters. The result of the fitting procedure is presented in table 9.19 and figure 9.20.

Name	Lineshape	B_{HF}	E_Q	δ	b	Area	Area
		Т	$\mathrm{mm/s}$	$\mathrm{mm/s}$		$\rm \%mm/s$	%
Sextet 1	S-(3:2:1)	48.8	-0.03	0.58	1.83	8.17	23.1
Doublet 1	Lorentz	-	0.79	0.50	-	27.1	76.9

Table 9.20: The fitting parameters of JH037T at 78 K. $\chi^2 = 0.06507$.

In the 78 K spectrum a sextet is starting to emerge, and I have therefore fitted the spectrum with a broad sextet and a free doublet. The doublet could possibly have been fitted using two doublets to account for the slight asymmetry, but I have chosen not to do this, since the improvement of the fit is negligible. The resulting fit is found in table 9.20 and figure 9.20.

Name	Lineshape	B_{HF}	E_Q	δ	b	Area	Area
		Т	$\mathrm{mm/s}$	$\mathrm{mm/s}$		$\rm \%mm/s$	%
Sextet 1	S-L(3:2:1)	48.8	-0.14	0.51	1.37	7.00	17.7
Doublet 1	Lorentz	-	0.28	0.52	-	32.1	81.4
Doublet 2	Lorentz	-	0.49	0.16	-	0.34	0.9

Table 9.21: The fitting parameters of JH037T at 60 K. $\chi^2 = 0.05004$.

The 60 K spectrum has much of the same properties as the previous spectrum, but it has a clearer sextet component. The sextet has very broad lines and shows signs of particle-particle interaction. I have fitted it with a sextet. The doublet has become broader and I have fitted it with two doublets to account for the features of the doublet. The second doublet is, however very small. The fit is presented in table 9.21 and figure 9.21.

An interesting result of the fits of 78 K and 60 K spectra is that the sextet component appears to diminish at the lower temperature. Assuming that the sextet is composed of a partly phase, this can not be accurate, and must be due to the nature of the fitting algorithm.

At 40 K the doublet has been completely split into an emerging sextet. The line width of the new sextet is, however, still very broad, and the transition to an ordered sextet is not yet complete. I have fitted the spectrum with two sextets with large line widths and Split-Lorentz parameters. The found fit values are found in table 9.22 and figure 9.21.

At 20 K the spectrum is totally split and it shows clear signs of being composed of multiple sextets. These signs are clearest in a strange narrowing near the peak of line 1 and 6 (marked in figure 9.22), and in very broad absorption lines. I have therefore fitted the spectrum with two sextets, of which the fit parameters are presented in table 9.23 and the fitted spectrum in figure 9.22.

The 14 K spectrum is quite similar to the 20 K spectrum, but the indications that the absorption lines have to be fitted with several sextets is even more evident. The broadening of lines 2 and 5 (marked in figure 9.22) clearly indicate at least two separate components. I have fitted



Figure 9.20: The fitted Mössbauer spectra of JH037T. Left: 295 K. Right: 78 K.

Name	Lineshape	B_{HF}	E_Q	δ	b	Area	Area
		Т	$\mathrm{mm/s}$	$\mathrm{mm/s}$		$\rm \%mm/s$	%
Sextet 1	S-L(3:2:1)	49.8	-0.01	0.51	1.67	14.9	35.8
Sextet 2	S-L(3:2:1)	38.7	-0.10	0.52	2.33	26.7	64.2

Table 9.22: The fitting parameters of JH037T at 40 K. $\chi^2 = 0.06835$.



Figure 9.21: The fitted Mössbauer spectra of JH037T. Left: 60 K. Right: 40 K.

the spectrum two sextets with free parameters, and the result is found in table 9.24 and figure 9.22.

Name	Lineshape	B_{HF}	E_Q	δ	b	Area	Area
		Т	$\mathrm{mm/s}$	$\mathrm{mm/s}$		$\rm \% mm/s$	%
Sextet 1	S-L(3:2:1)	47.3	-0.02	0.51	0.55	30.0	76.9
Sextet 2	S-L(3:2:1)	51.5	0.00	0.53	0.59	9.0	23.1

Table 9.23: The fitting parameters of JH037T at 20 K. $\chi^2 = 0.06733$.
Name	Lineshape	B_{HF}	E_Q	δ	b	Area	Area
		Т	$\mathrm{mm/s}$	$\mathrm{mm/s}$		$\rm \%mm/s$	%
Sextet 1	S-L(3:2:1)	47.4	-0.05	0.52	0.10	26.9	66.8
Sextet 2	S-L(3:2:1)	51.5	-0.01	0.51	0.87	13.4	33.2

Table 9.24: The fitting parameters of JH037T at 14 K. $\chi^2 = 0.07626$.



Figure 9.22: The fitted Mössbauer spectra of JH037T. The dotted lines represent the misfit. Left: 20 K. The arrows indicate the strange narrowing of line 1 and 6. Right: 14 K. The broadening of lines 2 and 5 are marked by arrows.

To identify the composition we have to look at the entire spectrum series. There are several interesting observations that can be made. The ordering of the spectrum from 78 K to 20 K is a superparamagnetic ordering, from which we can conclude that the mineral has a Curie/Néel temperature higher than 78 K, assuming that the sample only consists of one phase. The quadrupole shift of the sextets is around 0 mm/s, indicating that the crystal structure is cubic. The isomer shift found from fitting the sextets at low temperatures reveals a value of approximately 0.5 mm/s.

The precipitated part of the same sample showed, shortly (a few days) after synthesis, response to a magnetic field. Assuming that the precipitated part consisted of large particles, the sample is likely composed of either ferro- or ferrimagnetic material.

The low temperature spectra show sextets with hyperfine fields between approximately 47 T and 52 T. Since the other parameters are virtually identical, I can reasonably assume that we are observing the effects of particle-particle interaction, causing a distribution in the hyperfine fields.

Usually interaction effects are difficult to see at low temperatures, since all parameters usually converge if there is only one mineral or iron oxide species. This implies that the particles are small. Alternatively there can be either more than one mineral - or one mineral that also at low temperatures has a broad distribution of magnetic hyperfine fields, i.e. many different individual sites for iron atoms.

However, in this case it is likely that the sample is composed of a single iron oxide phase, with sizes distributed within a certain range. This also explains the gradual transition from doublet to sextet, since the relaxation time is depends exponentially on particle volume (4.19). From the fitted spectrum we can conclude that the sample contains an iron oxide with a bulk hyperfine field of at least 51.5 T at 14 K.

From these considerations we have to consider feroxyhyte, goethite, maghemite, and possibly magnetite. However goethite and feroxyhyte can be ruled out, since the sextet with the larger hyperfine field has a larger value than that of these at 4.2 K. Magnetite can be ruled out, since the spectrum is relatively simple and does not show signs of asymmetry. On the other hand maghemite fits relatively well with the observed features, and it is my conclusion that the sample consists of maghemite, possibly with a lot of crystal defects (vacancies, strain, etc.).

From ω and the Mössbauer spectra I roughly estimate the particle size to be ${\sim}15\text{-}20\,\mathrm{nm}.$

9.9 JH041

The sample JH041 was manufactured using chloroform as solvent, CTAB as surfactant and FeCl₂ as iron salt. It has an ω of 3.37.

The sample JH041 is interesting since it is the only sample manufactured under an sealed chloroform saturated atmosphere, and using chloroform as surfactant (see section 7.7 and figure 7.10). The surfactant used in the manufacturing process was CTAB. A detailed log of the manufacturing process can be found in table C.7. After drying the sample was characterized as: Black and very magnetic.

Mössbauer measurements have been done on this sample using two different experimental setups, and therefore there are two different 295 K spectra in this section.



Figure 9.23: Mössbauer spectra as a function of temperature of the sample JH041.

The 295 K spectrum is difficult to fit, but several observations can be made. There is a superparamagnetic doublet component, with broad slopes. The doublet reveals paramagnetism or superparamagnetism, but the slopes reveal a high degree of small particle interaction effects, which act as a restriction on the oscillation of the magnetic moment of the particles (fast superparamagnetic relaxation), preventing them from becoming completely superparamagnetic. The slope has faint signs of sextets. To further analyze this sample we have to examine the spectra obtained at other temperatures. I have chosen to examine the 14 K spectrum first, and work my way up.

Name	Lineshape	B_{HF}	E_Q	δ	b	Area	Area
		Т	$\mathrm{mm/s}$	$\mathrm{mm/s}$		%mm/s	%
Sextet 1	Lorentz(3:2:1)	51.3	0.00^{*}	0.70	-	10.7	65.0
Sextet 2	Lorentz(3:2:1)	51.1	0.00^{*}	0.23	-	5.7	35.0

Table 9.25: The fitted spectrum of JH041 at 14 K. * indicates that this parameter has been locked during fitting. $\chi^2 = 0.02683$.

The 14 K spectrum contains a regular sextet component, with slight asymmetries between the two sides, very much resembling that of the maghemite spectra in [59, fig. 2]. Therefore I have chosen to fit the spectrum with two sextets to compensate for the asymmetries. To fit maghemite



Figure 9.24: The fitted Mössbauer spectra of JH041. Left: 14 K. Right: 80 K.

with two sextets is actually the correct approach, since maghemite, just as magnetite, has iron in two sites, tetrahedral and octahedral. In maghemite the sextets overlap in such a manner, with only slightly different isomer shifts, that it usually is impossible to distinguish between them. However, several sources in literature [44, 59] report an asymmetry at low temperature. The 14 K spectrum has therefore been fitted as maghemite, and the parameters are presented in table 9.25 and figure 9.24. While fitting, I have not allowed the quadrupole shift of the sextets to vary, since maghemite is a cubic structure and therefore has a quadrupole shift of zero.

Name	Lineshape	B_{HF}	E_Q	δ	b	Area	Area
		Т	$\mathrm{mm/s}$	$\rm mm/s$		%mm/s	%
Sextet 1	Lorentz(3:2:1)	48.9	0.00^{*}	0.31	-	5.7	33.8
Sextet 2	Lorentz(3:2:1)	48.9	0.00^{*}	0.65	-	11.2	66.2

Table 9.26: The fitted spectrum of JH041 at 80 K. * indicates that this parameter has been locked during fitting. $\chi^2 = 0.05037$.

The 80 K spectrum shows a well developed sextet. Following the path of fitting the 14 K spectrum with maghemite, I have attempted to fit this spectrum with maghemite. As seen from the fit in table 9.26 and figure 9.24, the match is quite good. Hyperfine field is a bit low, but this is not unusual in nano-particles. The low hyperfine field is caused mainly by the large amount of surface atoms in nano-particles. The isomer shift is also slightly off, but well within acceptable limits.

Close study of the 80 K and the 14 K spectra reveal that there appears to be a quadrupole shift in the spectrum. To investigate this the spectra have been fitted with the quadrupole parameter of the sextets free. The spectra have been fitted with point of origin in the previous fits of the spectra. Fitting reveals that the sextets have a quadrupole shift of between -0.05 mm/s and -0.12 mm/s, which does not comply well with the maghemite model. The fits are presented in table 9.27, table 9.28 and figure 9.25.

Returning to the 295 K spectrum and following the same path as used in the two previous spectra, I have attempted to fit the spectrum using the same model. The spectrum was fitted with two doublets to account for the weak asymmetry of the doublet and a magnetite sextet for the slope, giving a very good match.

The line shape of the sextet is Split-Lorentz with an asymmetry large parameter to account for the broad slope.



Figure 9.25: The fitted Mössbauer spectra of JH041 with the quadrupole shift allowed to vary freely. Left: 80 K. Right: 14 K.

Name	Lineshape	B_{HF}	E_Q	δ	b	Area	Area
		Т	$\mathrm{mm/s}$	$\rm mm/s$		$\rm \%mm/s$	%
Sextet 1	Lorentz	48.9	-0.05	0.34	-	6.4	37.8
Sextet 2	Lorentz	48.9	-0.09	0.64	-	10.5	62.2

Table 9.27: The fitted spectrum of JH041 at 80 K with the quadrupole shift allowed to vary. $\chi^2 = 0.04752$.

Name	Lineshape	B_{HF}	E_Q	δ	b	Area	Area
		Т	m mm/s	m mm/s		$\rm \%mm/s$	%
Sextet 1	Lorentz	51.3	-0.06	0.72	-	9.7	59.3
Sextet 2	Lorentz	51.1	-0.12	0.26	-	6.7	40.7

Table 9.28: The fitted spectrum of JH041 at 14 K with the quadrupole shift allowed to vary. $\chi^2 = 0.02235$.



Figure 9.26: The fitted Mössbauer spectra of JH041 at 295 K.

I have not allowed the preset parameters, except the hyperfine field, of the maghemite sextet to

Name	Lineshape	B_{HF}	E_Q	δ	b	Area	Area
		Т	$\mathrm{mm/s}$	$\mathrm{mm/s}$		%mm/s	%
Doublet 2	Lorentz(3:2:1)	-	0.09	0.38	-	6.55	42.6
Maghemite	S-L(3:2:1)	47.1	0.01^{*}	0.32	31.2	8.84	57.4

Table 9.29: The fitted spectrum of JH041 at 295 K. * indicates that this parameter has been locked during fitting. $\chi^2 = 0.05013$.

vary during the fit. It is hard to get a reasonable fit, but considering the spectrum and the other spectra in the series, I have accepted the maghemite model for this spectrum too. The resulting fit is presented in table 9.29 and figure 9.26.



Figure 9.27: Mössbauer spectra at 295 K without and with an applied magnetic field of the sample JH041.

To investigate the sample further a spectrum has been obtained in which the sample was subjected to a 1.4 T magnetic field applied perpendicular to the gamma ray direction.

The spectra without and with applied B-field are displayed in figure 9.27.

The first spectrum is very similar to that in figure 9.23 and in table 9.29, and without further analysis the fit will be presented in table 9.30 and figure 9.28. The difference between this spectrum and the previous 295 K, 0 T spectrum, is that they have been recorded in different experimental setups.

Name	Lineshape	B_{HF}	E_Q	δ	b	Area	Area
		Т	m mm/s	$\mathrm{mm/s}$		$\rm \%mm/s$	%
Maghemite	S-L(3:2:1)	46.0	0.01^{*}	0.32	12.7	18.6	49.3
Doublet 2	Lorentz	-	-0.734	0.44	-	19.1	50.7

Table 9.30: The fitted spectrum of JH041 at 295 K. and 0 T. * indicates that this parameter has been locked during fitting. $\chi^2 = 0.11796$.

A comparison of the 1.4 T spectrum to the 0 T spectrum shows a magnetic splitting of the components, which is due to the applied magnetic field.

The 1.4 T spectrum consists of an asymmetric sextet with an area ratio of the lines of 3:4:1. Furthermore there is a depression between line 3 and 4. I have fitted the spectrum with two sextets and a doublet. I have not allowed the quadrupole shift of the sextets to vary. The resulting fit is



Figure 9.28: The fitted Mössbauer spectra of JH041 at 295 K with applied magnetic fields. Left: 0 T. Right: 1.4 T.

presented in table 9.31 and figure 9.28.

Name	Lineshape	B_{HF}	E_Q	δ	b	Area	Area
		Т	$\mathrm{mm/s}$	$\rm mm/s$		%mm/s	%
Sextet 1	S-L(3:4:1)	48.1	0.00^{*}	0.36	0.81	14.7	41.2
Sextet 2	S-L(3:4:1)	43.7	0.00^{*}	0.45	1.02	15.5	43.5
Doublet 1	Lorentz	-	1.04	0.51	-	5.5	15.3

Table 9.31: The fitted spectrum of JH041 at 295 K. and 1.4 T. * indicates that this parameter has been locked during fitting. $\chi^2 = 0.05310$.

To finalize the analysis of JH041, I will draw some conclusions. The sample contains particles that isolated would be superparamagnetic, but are packed so closed that there is significant interaction. The sample is magnetically ordered by an applied magnetic field, and the particles are therefore ferro- or ferrimagnetic.

There is an observed quadrupole shift different from zero. However the found values are so small that the crystal structure is likely cubic.

The iron ions in the sample have at least two different environments, since it is necessary to fit several spectra, and most importantly, the spectrum with the applied field using two different sextets.

The non-zero quadrupole shift value points towards goethite, but goethite can be eliminated since the sample showed a powerful response to a magnetic field and since the found hyperfine field is larger than that of goethite.

Considering the hyperfine field and isomer shift used in the fit, the most likely iron oxides are maghemite and magnetite. My assumption to fit the spectra using a maghemite model is likely correct, since there is not enough difference between the parameters of the sextets, and thus not enough difference between the environments of the iron ion sites for the oxide to be magnetite. I therefore conclude that the sample is composed mainly of nano-particle maghemite.

Due to lack of samples to compare with, it is difficult to give an estimate of the particle size, but a rough estimate from ω and the spectra would be ~15-20 nm.

9.10 JH046

The sample JH046 was manufactured using iso-octane as solvent, AOT as surfactant and FeSO₄ as iron salt. It has an ω of 11.22.

The sample has during manufacturing been split into a liquid sample and a powder sample. This was done since we wanted to investigate differences in oxidation between powder samples and samples stored in frozen liquid using Mössbauer spectroscopy, i.e. to investigate whether the powder samples were further oxidized when drying. Furthermore we wanted to investigate the particles using TEM, in order to determine particle size and size distribution. This section has therefore been divided into three subsections. A detailed log of the manufacturing process can be found in table C.8.

The powder sample was just after manufacturing characterized as: Consisting of brown-black **very** magnetic lumps.

9.10.1 JH046 powder

The powder sample has been investigated using Mössbauer spectroscopy. The Mössbauer spectra obtained at different temperatures are presented in figure 9.29.



Figure 9.29: Mössbauer spectra as a function of temperature of the sample JH046 Powder.

Name	Lineshape	B_{HF}	E_Q	δ	b	Area	Area
		Т	$\mathrm{mm/s}$	$\rm mm/s$		%mm/s	%
Magnetite A	Lorentz(3:2:1)	49.1	-0.01*	0.36	-	9.22	47.3
Magnetite B	Lorentz(3:2:1)	46.0	0.00^{*}	0.72	-	4.58	23.5
Doublet 1	Lorentz	-	0.54	0.40	-	3.12	16.0
Doublet 2	Lorentz	-	1.07	0.43	-	2.59	13.3

Table 9.32: The fitted spectrum of JH046 powder at 80 K. * indicates that this parameter has been locked during fitting. $\chi^2 = 0.03651$.

The 295 K spectrum has features that resemble non-stoichiometric magnetite (marked in figure



Figure 9.30: The fitted Mössbauer spectra of JH046 powder. Left: 295 K. The magnetite features are marked by arrows. Right: 80 K.

(9.30) [52]. However, at lower temperature (20 K) the spectrum has small features that are similar to those of maghemite [44].

The maghemite signs are primarily the narrowness of line 1 compared to line 6 at low temperature. However, since only small signs point in the direction of maghemite, I have chosen to fit the spectrum with a model of non-stoichiometric magnetite.

I have fitted the 295 K spectrum with two sextets for magnetite. Magnetite is at room temperature usually fitted with two sextets, for the A and B sites respectively. Magnetite has a cubic crystal structure and has therefore a quadrupole shift of 0 mm/s. During fitting I have only restricted the variation of the quadrupole shift. The quadrupole shift has been restricted to prevent the fitting algorithms from finding non-physical values.

The 295 K spectrum furthermore shows a distinct doublet which is slightly asymmetric. I have fitted the doublet feature with two doublets. The parameters of found the fit are presented in table 9.32 and figure 9.30. The fit parameters match the table values of magnetite very well (see section G.1). From the area ratio of the two magnetite components it is possible to calculate how much of the iron is in the oxidation states Fe^{3+} and $Fe^{2.5+}$, which in stoichiometric magnetite are sited at the tetrahedral (A) and octahedral (B) sites respectively. Thereby it is possible to calculate how stoichiometric the magnetite is. The ratio of Fe^{3+} to $Fe^{2.5+}$ for stoichiometric magnetite is 1:2. In this sample it has been found to be:

$$\frac{[\mathrm{Fe}^{3+}]}{[\mathrm{Fe}^{3+}]} = \frac{47.3}{23.5} \simeq 2. \tag{9.6}$$

Since I have fitted the 295 K spectrum with the two magnetite sextets, the 80 K has also been fitted with two sextets. The parameters are quite different, but it is also known that the Mössbauer spectrum of magnetite is quite complicated below the Verwey transition (at around 118 K) with at least 5 sextets [42].

I have chosen to fit this spectrum with 2 sextets, since a 5 sextet spectrum is very difficult to fit and does not improve the accuracy. Furthermore a two sextet fit is sufficient to observe the Verwey transition. The result of the fitting process is presented in table 9.33 and figure 9.30.

The 20 K spectrum shows only small signs of the doublet component present in the 295 K and 80 K spectra. Following the path laid out in the analysis of the two previous spectra, I have chosen

Name	Lineshape	B_{HF}	E_Q	δ	b	Area	Area
		Т	$\mathrm{mm/s}$	$\mathrm{mm/s}$		%mm/s	%
Sextet 1	Lorentz(3:2:1)	51.0	0.00^{*}	0.44	-	5.23	39.8
Sextet 2	Lorentz(3:2:1)	51.0	0.00^{*}	0.54	-	3.77	28.7
Doublet 1	Lorentz	-	0.84	0.62	-	1.42	10.8
Doublet 2	Lorentz	-	0.76	0.34	-	2.72	20.7

Table 9.33: The fitted spectrum of JH046 powder at 80 K. * indicates that this parameter has been locked during fitting. $\chi^2 = 0.02441$.

to fit the 20 K spectrum with two sextets, sextet 1 and sextet 2, to compensate for the magnetite component. I have fitted the component which is split at 20 K with sextet 3. A feature between line 3 and 4 of the spectrum, possibly paramagnetic, is fitted with two doublets. During fitting I have constrained the magnetite components to the same area ratio as in the two previous spectra. The resulting fit is presented in table 9.34 and figure 9.31.



Figure 9.31: The fitted Mössbauer spectra of JH046 powder at 20 K. The spectrum is enlarged to improve readability.

9.10.2 JH046 liquid

The liquid sample of JH046 has been investigated using Mössbauer spectroscopy, and the recorded spectrum is presented in 9.32.

Liquid samples are as previously mentioned very noisy with little absorption. Therefore this spectrum has not been easily fitted.

The spectrum shows similar features to that of the 20 K powder spectrum. These features include a depression on the inner slope of the lines 1 and 2 (marked in figure 9.32) compared to their counter parts 5 and 6. I have therefore assumed that there is little difference between the iron oxides of the two samples, although the liquid sample has been protected through freezing in liquid nitrogen and the powder sample has been stored in a closed plastic container at room temperature.

With this assumption and using the fit of the 20 K powder spectrum as a point of origin and inspiration, I have fitted the 20 K spectrum of the liquid sample with two sextets to compensate for

Name	Lineshape	B_{HF}	E_Q	δ	b	Area	Area
		Т	$\mathrm{mm/s}$	$\mathrm{mm/s}$		%mm/s	%
Sextet 1	Lorentz(3:2:1)	50.6	0.00^{*}	0.45	-	9.26	39.1
Sextet 2	Lorentz(3:2:1)	52.5	0.00^{*}	0.54	-	6.46	27.2
Sextet 3	Lorentz(3:2:1)	46.2	-0.21	0.81	-	5.37	22.7
Doublet 1	Lorentz	-	1.63	0.91	-	0.93	3.9
Doublet 2	Lorentz	-	1.54	0.10	-	1.70	7.1

Table 9.34: The fitted spectrum of JH046 powder at 20 K. * indicates that this parameter has been locked during fitting. $\chi^2 = 0.05205$.



Figure 9.32: Left: The 20 K Mössbauer spectrum of the sample JH046 liquid. Right: The fitted Mössbauer spectrum of the sample JH046 liquid at 20 K. The fit parameters can be found in table 9.35.

the magnetic component in the powder spectrum at room temperature. Furthermore I have used a sextet to compensate for the component which in the powder spectrum splits at low temperatures.

I have fitted the large absorption around 0 mm/s with a singlet and a doublet. The doublet has the role of the doublets in the powder spectrum, although it has a significantly smaller quadrupole split, and an intermediate isomer shift compared to those of the powder spectrum. The singlet component can not be directly compared to any component in the powder spectrum, although it is likely that it is composed of a superparamagnetic component along with a part of one of the doublets in the powder spectrum. The fitted spectrum is presented in figure 9.32, and the fit parameters in table 9.35.

Name	Lineshape	B_{HF}	E_Q	δ	b	Area	Area
		Т	$\mathrm{mm/s}$	$\mathrm{mm/s}$		%mm/s	%
Sextet 1	Lorentz(3:2:1)	50.8	0.00^{*}	0.49	-	0.48	30.8
Sextet 2	Lorentz(3:2:1)	50.0	0.00^{*}	0.51	-	0.49	31.6
Sextet 3	Lorentz(3:2:1)	39.0	-0.47	0.35	-	0.26	16.9
Singlet 1	Lorentz	-	-	-0.12	-	0.07	4.7
Doublet 1	Lorentz	-	0.59	0.20	-	0.24	16.0

The liquid spectrum supports the assumption that the sample is composed of magnetite.

Table 9.35: The fitted spectrum of JH046 liquid at 20 K. * indicates that this parameter has been locked during fitting. $\chi^2 = 0.00138$.

9.10.3 TEM image analysis

The sample has been investigated with TEM. The TEM investigations were made on the same material that the liquid sample is composed of. The TEM images were made at $\mathcal{O}L^6$. The material used for TEM had not been protected by freezing, however this should be of no consequence since exposure to air, and a further non-violent oxidation, will not change the crystal structure of the particles.



Figure 9.33: TEM image of JH046 at 27.5k magnification. The bar is 100 nm.

I have extracted a particle size distribution from the images for each of the magnifications 27.5 k and 390 k, and the result is presented in table 9.36 and figure 9.35. I have calculated the size distribution of the particles using the method described in section 9.4.

The particle size distribution is quite wide, and not as narrow as I expected when considering the theory and the chemistry on which it is based. The distribution does deviate significantly from a normal distribution. This, however, may be due to several factors. The magnetic separation which was used will most likely collect large particles more efficiently than the small particles, since larger particles have a larger magnetic moment, and relatively less surface. The smaller particles may also be less visible in TEM images, since they provide less contrast.

Theoretical calculations [5], show that the distribution of radius of the micelles in the water/AOT/isooctane is close to normal.

Magnification	Ν	$ar{d}$	q	σ
		nm	nm	nm
27.5k	158	28.4	25.9	10.3
390k	12	27.9	29.3	12.9

Table 9.36: Size distribution data measured from TEM images of sample JH046L. \bar{d} is mean particle size, q is the median and σ is the standard deviation.

⁶Using the Ørsted Laboratory TEM, operated by Erik Johnson.



Figure 9.34: TEM image of JH046 at 390k magnification. The bar is 20 nm.

The size distributions have been extracted from the TEM images, in which only a two dimensional projection of the particles is seen. Many particles have shapes close to quadratic, which is why we have chosen to assume this as the common shape of the projection.

If we consider the statistics, the mean value of the two data collections is relatively close, and the true mean is most likely identical. The difference of σ is largely due to the difference in N, in the two populations. σ is calculated by the formula [57]

$$\sigma = \sqrt{\frac{1}{N-1} \sum (x_i - \bar{x})^2},$$
(9.7)

which implies that σ will be smaller for larger populations, provided that the populations are similar.

However, before we can threat the particles as quadratic, we have to investigate if this assumption is reasonable. I have therefore investigated if the particles are rectangular, and if so "how" rectangular the particles are. The investigation can not be performed using the diagonal measurements, from which the particle distribution has been produced, since the diagonals are equal for a rectangle. I have therefore made an additional measurement, in which the distance from edge to edge (z_1, z_2) at an angle of 90° has been measured for 30 particles. I have defined a measure of the relative deviation from the quadratic form as

$$e = \frac{z_1 - z_2}{\frac{(z_1 + z_2)}{2}}.$$
(9.8)

For illustration the data is displayed in two graphs in figure 9.36. The left graph displays the distribution of e, with the theoretical normal distribution curve for comparison. The mean value and the σ of the normal distribution are those extracted from the measured data. However, since the order of z_1 and z_2 is random, so is the sign of e, and to get a better picture of e, the right graph in figure 9.36, displays |e|. The normal distribution in this graph has a mean of 0, and a σ which has been constructed from the added datasets |e| and -|e|. From the data and taking into account the limited resolution and contrast of the TEM images, I conclude that the particles are quadratic.



Figure 9.35: Left: Particle size distribution of JH046 as determined at 27.5k magnification. The theoretical normal distribution with the same mean and standard deviation is displayed for comparison. Right: Particle size distribution of JH046 as determined at 390k magnification. The theoretical normal distribution with the same mean and standard deviation is displayed for comparison.



Figure 9.36: Left: Distribution of e for JH046 as determined at 27.5 k magnification. The theoretical normal distribution with the same mean and standard deviation is displayed for comparison. **Right:** Distribution of |e| for JH046 as determined at 27.5 k magnification. The theoretical normal distribution with mean of 0 and the same standard deviation is displayed for comparison.

The e distribution, however, does not provide information on the angles of the corners of the "quadrates", and it therefore has to be investigated if the particles are parallelogram-shaped, with right angles or not.

If the particle edge corners have right angles the diagonals d_1 , d_2 have equal lengths, but if angles are not right the diagonals are not of equal length. I have defined a measure f of the deviation from the right angle corner model as

$$f = \frac{d_1 - d_2}{\frac{(d_1 + d_2)}{2}}.$$
(9.9)

For this investigation the diagonals used in the size distribution can be used, and additional measurements were not necessary.

The resulting distribution is given in figure 9.37. Similar to the e distribution, the left graph show the distribution of f with a normal distribution for comparison, and the right graph shows |f|with a normal distribution. From the data we see that there is some variation in f, which indicates some asymmetry in the particle shapes. How much is due to uncertainty in measurements, and how much is due to true deviation from the quadratic form, is hard to tell, but after careful



Figure 9.37: Left: Distribution of f for JH046 as determined at 27.5 k magnification. The theoretical normal distribution with the same mean and standard deviation is displayed for comparison. Right: Distribution of |f| for JH046 as determined at 27.5 k magnification. The theoretical normal distribution with mean of 0 and the same standard deviation is displayed for comparison.

considerations, I have arrived at the conclusion that the particles are octahedra (see figure 9.2), and that a large portion of the deviations from the quadratic form in the images, is due to the randomness in particle orientation with respect to the electron beam.

However, I believe that a portion of the deviations seen in the investigations are due to deviations from the perfect octahedral form in some particles.

A question that has to be raised is why do we see all the particles as close to quadratic, and none as hexagons? Is it possible that the particles all are oriented in the same direction? While the TEM images are acquired, the sample is located inside a homogeneous magnetic field of approximately 1 T. It may be that the particles are oriented by the external magnetic field. To asses if this is possible I will in the following give an estimate of the forces on the particle. As calculation example I will use a cubic single domain magnetite crystal, with a 20 nm edge length. The calculations are based on [2, 28, 54]

The saturation magnetization of magnetite is $\sigma_{s,magnetite} = 90 \text{ Am}^2/\text{kg}$ and the density $\rho = 5.21 \text{ g/cm}^3$. We first calculate the mass of the magnetite particle:

$$m = \rho \cdot V = 5.21 \,\mathrm{g/cm^3} \cdot (20 \cdot 10^{-9} \mathrm{m})^3 = 4.17 \cdot 10^{-20} \,\mathrm{kg}.$$
 (9.10)

The magnetic moment of a 20 nm nano-particle is then given by:

$$\mu = \sigma_{s,\text{magnetite}} \cdot m = 3.75 \cdot 10^{-18} \text{Am}^2.$$
(9.11)

The expression for torque on a magnetic moment in a magnetic field is

$$\tau = \vec{\mu} \times \vec{B},\tag{9.12}$$

and the expression for mechanical torque is

$$\tau = \vec{r} \times \vec{F} \tag{9.13}$$

If we assume the magnetic moment is oriented perpendicular to the magnetic field and the magnetic field acts on it to orient it parallel, and that the total mass of the particle is placed at the end of the moment vector, the two above expressions can be combined to

$$F = \frac{\mu \cdot B}{r} = \frac{3.75 \cdot 10^{-18} \,\mathrm{Am^2} \cdot 1 \,\mathrm{T}}{20 \cdot 10^{-9} \,\mathrm{m}} = 1.9 \cdot 10^{-10} \,\mathrm{N},\tag{9.14}$$

which is a rough estimate of the magnetic force acting on the particle.

However, the particles are probably surrounded by surfactant, which will cause friction. The viscosity of the fluid is important, but difficult to calculate. Firstly viscosity of a fluid changes with temperature, and since the temperature of the sample inside the TEM is unknown, this provides the first unknown. Second it has been observed several times, that the electron beam of the TEM decomposes the surfactant, leaving an unknown substance. Third, the fluid properties are fundamentally different at nano-scale, since the van der Waal forces are important and might cause the greatest friction. Considering these facts I have chosen not to attempt calculate the fluid friction on the particles.

Besides fluid friction we have to consider the dipole field from the neighboring particles. The magnetic field from a magnetic dipole at a distance \vec{r} is

$$\vec{B}(\vec{r}) = \frac{\mu_0}{4\pi} \left(-\frac{\vec{\mu}}{r^3} + \frac{3(\vec{\mu} \cdot \vec{r})\vec{r}}{r^5} \right),\tag{9.15}$$

where $\vec{\mu}$ is the magnetic moment. If $\vec{B} || \vec{r}$ and the above values are inserted the equation gives

$$\vec{B}_{||}(r=20\,nm) = -0.047\,\mathrm{T}\cdot\vec{u}_{\vec{\mu}||\vec{r}},\tag{9.16}$$

where \vec{u} is a unit vector. If $\vec{B} \perp \vec{r}$ the field is

$$\vec{B}_{\perp}(r = 20 \, nm) = 0.094 \,\mathrm{T} \cdot \vec{u}_{\vec{\mu} \perp \vec{r}}.$$
(9.17)

If r = 40 nm the equations give:

$$\vec{B}_{||}(r = 40 \, nm) = -0.0059 \,\mathrm{T} \cdot \vec{u}_{\vec{\mu}||\vec{r}},\tag{9.18}$$

$$\vec{B}_{\perp}(r=40\,nm) = 0.011\,\mathrm{T} \cdot \vec{u}_{\vec{\mu}\perp\vec{r}}.$$
(9.19)

From these calculations we see that it is only if the particles are close packed the magnetic dipole field is significant compared to the applied field of 1 T.

The fluid friction forces might be larger, but considering the force on a 20 nm magnetic particle, I do not find it unlikely that the magnetic field is powerful enough to turn the magnetic particles.

As the torque caused by the magnetic field is given by the cross product between the particle magnetic moment and the magnetic field, it becomes small when the angle between field and the moment become small, which may explain why not all particles are seen as perfect squares.

However, there is another possible explanation. The applied magnetic field might cause the magnetic orientation of the particles in the sample to turn, without turning the particle itself. This will cause the magnetic moments of the particles to be oriented in the same direction, which will cause them to be attracted to each other, and possibly form clusters or chains. Close packed particles will likely be oriented in the same direction to minimize the magnetic energy, and are therefore seen as having the same shape.

A search for clusters and in the TEM images reveals many structures that appear to be chains of particles. Some of the found structures have been marked in figure 9.33.

9.10.4 Conclusion

To conclude the investigation of the sample JH046, there are three threads to be merged. The Mössbauer investigations of the powder sample strongly indicate that the sample is composed of non-stoichiometric magnetite, and although the liquid sample is somewhat more inconclusive, it too indicates non-stoichiometric magnetite. It would be bold to conclude magnetite on the Mössbauer investigations of the liquid sample alone, since the identification of the iron oxide phase is made difficult by the noisiness of the spectrum, and complex nature of magnetite at low temperatures.

However, the liquid sample provides an option to investigate the manufactured material with little particle-particle interaction, and it supports the findings from the analysis of the powder sample. The fact that the liquid sample appears to have clearer magnetite sign supports my assumption that the liquid sample is less oxidized than the powder sample. The liquid sample magnetite sextets have a lower hyperfine field than the powder sample at 20 K. However, this is most likely due to the content of smaller particles liquid sample, compared to the powder sample.

From the findings in the Mössbauer spectra analysis, it is my conclusion that the sample is composed of non-stoichiometric magnetite.

The TEM images confirm the small particle size, expected from the literature [13] and partly confirmed by the analysis of the Mössbauer spectra.

Although I have measured the particle size, I have for consistency estimated the particle size from ω and the Mössbauer spectra to be \sim 20-30 nm.

9.11 JH048

The sample JH048 was manufactured using iso-octane as solvent, AOT as surfactant and FeSO₄ as iron salt. It has an ω of 11.64.

After manufacturing and washing the sample was divided into to two samples, JH048 powder (JH048P) which was dried and sealed for measuring using Mössbauer spectroscopy, and JH048 liquid (JH048L) which in liquid form was sealed and frozen in liquid nitrogen for measuring using Mössbauer spectroscopy and TEM imaging.

Storing the sample in nitrogen protects the sample from further oxidization, making a study of the particles prior to washing possible. Such a liquid sample is also ideal for TEM investigation, since it has particles suspended in the liquid.

When preparing the sample for TEM investigation it could not be avoided that the sample would be exposed to oxygen, but this was accepted after some considerations. Experience [36] shows that nano-particles are unlikely to change crystal structure during a post-formation oxidation. Since TEM only reveals particle size and crystal parameters, and considering that maghemite and magnetite have indistinguishable⁷ crystal parameters, this was accepted, since we assumed that the samples consisted of these oxides. A detailed log of the manufacturing process can be found in section C.11.

The powder sample was characterized just after manufacturing as consisting of fine very magnetic powder, with a grey-brown color.

9.11.1 JH048 powder



Figure 9.38: Mössbauer spectra as a function of temperature of the sample JH048 powder.

The 295 K spectrum shows only one significant feature, namely the slightly asymmetric doublet peak with an isomer shift around 0.5 mm/s. I have fitted spectrum with only one doublet since fitting with two doublets did not give a better fit. The fit parameters are presented in table 9.37 and the fitted spectrum in figure 9.39.

 $^{^7\}mathrm{At}$ the resolution of the TEM's at HCØ and Risø.



Figure 9.39: The fitted Mössbauer spectra of JH048 powder. Left: 295 K. Right: 80 K.

Name	Lineshape	B_{HF}	E_Q	δ	b	Area	Area
		Т	$\mathrm{mm/s}$	$\mathrm{mm/s}$		$\rm \%mm/s$	%
Doublet 1	Lorentzian	-	0.70	0.39	-	17.0	100.0

Table 9.37: The parameters in fitting JH048 powder at 295 K with one doublet. $\chi^2 = 0.03206$.

The 80 K spectrum has three main features, the doublet in the middle, the broad slopes to both sides and on top of these the trace of a broad sextet. From the 295 K spectrum it remained to be determined whether the doublet was due to paramagnetism or superparamagnetism, but the broad slopes in the 80 K spectrum are clear signs of superparamagnetism. The broad slopes are caused by dynamic effects which are due to particle interaction, which isolated would be superparamagnetic. We can however not rule out that the sample contains a component which is paramagnetic at 295 K and is ordered at 80 K. The doublet might still partly consist of a paramagnetic component, but I find it unlikely since the 20 K spectrum does not show signs of more than one component.

Considering these arguments I have fitted the superparamagnetic component with a doublet and the broad slopes with a sextet with broad lines and large b parameter values. The fit parameters are presented in table 9.38 and figure 9.39.

The 20 K spectrum shows a sextet which exhibits significant particle interaction effects. The peaks have broader slopes inwards than outwards. There is no visible quadrupole shift, ruling out any non-cubic crystal structure. The 1st peak is narrower and has a larger intensity than peak 6, which is one of the characteristics of maghemite at this temperature. However, bulk maghemite has a hyperfine field of 52.6 T at low temperatures (see table G.1), which is significantly higher than the highest occurring in the spectrum.

I have chosen to fit the spectrum with two models, a low temperature magnetite/maghemite model and a goethite model. The arguments for the magnetite/maghemite model are that I expected to get maghemite or magnetite, and that the spectrum resembles these quite well. The

Name	Lineshape	B_{HF}	E_Q	δ	b	Area	Area
		Т	$\mathrm{mm/s}$	$\mathrm{mm/s}$		$\rm \% mm/s$	%
Doublet 1	Lorentz	-	0.90	0.51	-	6.1	24.7
Sextet 1	S-L(3:2:1)	44.0	0.01	0.51	5.53	18.63	75.3

Table 9.38: The parameters in fitting JH048 powder at 80 K. $\chi^2 = 0.02022$.



Figure 9.40: The fitted Mössbauer spectra of JH048 powder. The dotted lines at the top of the spectrum is the misfit (the difference between the data and the fit), which is displayed for comparison of the two spectra. Left: At 20 K, fitted with two sextets. Right: At 20 K, fitted with table values of goethite.

Name	Lineshape	B_{HF}	E_Q	δ	b	Area	Area
		Т	$\mathrm{mm/s}$	$\mathrm{mm/s}$		$\rm \% mm/s$	%
Sextet 1	S-L(3:2:1)	48.2	0.00^{*}	0.48	0.73	15.5	69.2
Sextet 2	S-L(3:2:1)	51.1	0.00^{*}	0.52	0.42	6.9	30.8

Table 9.39: The parameters in fitting JH048 powder at 20 K with two sextets. * indicates that this parameter has been locked during fitting. $\chi^2 = 0.03489$.

argument for using the goethite model is that the spectrum parameters also resemble the table values for goethite and values in the literature [46] quite well. Goethite does have a quadrupole shit of -0.13 mm/s, but since this is relatively low it might be overlooked.

According to literature [42] the Verwey transition of magnetite introduces a complex low temperature spectrum since the thermally delocalized electron is now localized. The complex spectrum contains at least 5 sextets [42], which is too complex to fit.

Maghemite has as magnetite two iron ion sites, A and B. These sites produce two similar sextets, which mainly differ by their different isomer shifts, typically $\sim 0.33 \text{ mm/s}$ and $\sim 0.42 \text{ mm/s}$ for the tetrahedral and octahedral sites respectively. The area ratio of the maghemite sextets is 3:5 for the tetrahedral and octahedral sites respectively [40].

Considering these facts I have attempted to fit the spectrum with two components, one for the A sites and one for the B sites of magnetite/maghemite. I have constrained the components of the fit to having a quadrupole shift of 0, and having parameters close to magnetite at room temperature. The hyperfine field, the isomer shift and the parameter b were allowed to vary. The resulting fit is presented in table 9.39 and figure 9.40.

As the second alternative I fitted the spectrum with the goethite parameters at 4.2 K. Only the parameter b was allowed to vary. The resulting fit is presented in table 9.40 and figure 9.40.

Name	Lineshape	B_{HF}	E_Q	δ	b	Area	Area
		Т	$\mathrm{mm/s}$	$\rm mm/s$		$\rm \%mm/s$	%
Goethite	S-L(3:2:1)	50.6^{*}	-0.13*	0.48^{*}	1.60	22.4	100.0

Table 9.40: The parameters in fitting JH048 powder at 20 K with goethite. * indicates that this parameter has been locked during fitting. $\chi^2 = 0.07411$.

It is possible for antiferromagnetic nano-particles to have a magnetic moment due to compensated surface spins. However, the sample material showed a significant magnetic moment during washing, which makes it unlikely that the sample consists of goethite.

Therefore the fit with two sextets is considered to be the better model. Low temperature magnetite usually shows more complex features, than the spectrum in focus, which points to maghemite.

9.11.2 JH048 liquid

The JH048 liquid Mössbauer spectra presented in figure 9.41 have been obtained at DTU. The sample was contained in a 5 mm thick sample holder during both storage and measurements.



Figure 9.41: Mössbauer spectra as a function of temperature of the sample JH048 liquid.

The spectrum at 80 K shows a very dominate, broad sloped and asymmetric doublet around 0 mm/s, with vague indications of sextet components. The spectrum has a low absorption and much noise, and therefore error-bars (not displayed) are large.

I have fitted the central doublet with two doublets to compensate for the asymmetry. The broad slope is as earlier mentioned due to interaction effects, and I have fitted this component with a Gaussian singlet. In order to make the fit more correct, I have chosen to add a sextet with broad lines. The sextet has broad lines since it is unclear from the spectrum whether the spectrum has one or several overlapping sextets. The found fit parameters are presented in table 9.41 and in figure 9.42.

Name	Lineshape	B_{HF}	E_Q	δ	b	Area	Area
		Т	$\mathrm{mm/s}$	$\mathrm{mm/s}$		$\rm \% mm/s$	%
Doublet 1	Lorentz	-	0.96	0.47	-	0.28	7.4
Singlet 1	Gauss	-	-	0.40	-	1.16	31.1
Doublet 2	Lorentz	-	0.76	0.49	-	1.17	31.5
Sextet 1	Lorentz(3:2:1)	44.4	-0.25	0.60	-	1.11	30.0

Table 9.41: The parameters in fitting JH048 liquid at 80 K. $\chi^2 = 0.00557$.

The spectrum at 20 K shows several interesting features. It has a well developed sextet, which has the same asymmetry of the lines 1 and 6 as JH048 powder at 20 K. I have fitted the sextet



Figure 9.42: The fitted Mössbauer spectra of JH048 liquid. Left: 80 K. Right: 20 K.

with two sextets, and I have chosen not to allow the quadrupole shift to vary to ensure that the fitting algorithm does find physically meaningful values.

Furthermore the spectrum contains there several minor components around 0 mm/s. Since the spectrum has a low absorption, I have chosen to fit these components as simple as possible with a singlet and a doublet. The fit parameters are presented in table 9.42 and figure 9.42.

Name	Lineshape	B_{HF}	E_Q	δ	b	Area	Area
		Т	$\mathrm{mm/s}$	$\rm mm/s$		$\rm \%mm/s$	%
Sextet 1	Lorentz(3:2:1)	49.3	0.00^{*}	0.49	-	1.96	40.8
Sextet 2	Lorentz(3:2:1)	46.0	0.00^{*}	0.48	-	2.48	51.8
Singlet 1	Lorentz	-	-	-0.14	-	0.26	5.4
Doublet 1	Lorentz	-	0.49	0.20	-	0.10	2.0

Table 9.42: The parameters in fitting JH048 liquid at 20 K. * indicates that this parameter has been locked during fitting. $\chi^2 = 0.00813$.

9.11.3 TEM image analysis

TEM images were made from the sample JH048 liquid. The particles were found to have spherical shape, which was surprising. However, the number of particles found was also surprisingly low, since only 6 particles were found. Extensive analysis revealed that the particles were composed of carbon nano-onion particles. These are not relevant for the project, and I will not deal further with them in the project. However, the analysis is presented in appendix F.

9.11.4 Conclusion

I was unable to obtain TEM images of the iron oxide particles, which means that we do not have particle size data on the sample JH048.

The Mössbauer measurements of the sample indicate that the sample is composed of maghemite. Although I have fitted the 20 K powder spectrum with goethite, it can be ruled out, since the hyperfine field of the sextet in the spectrum is larger than the hyperfine field of goethite at 4 K, which is clearly visible from the misfit in the spectrum.

The powder spectra show a quite symmetric component, with only small asymmetries, which rules out magnetite. Line 1 is narrower that line 6 at low temperature, which does not rule out maghemite. Furthermore none of the characteristics of magnetite below the Verwey transition are visible. My conclusion is therefore that the powder sample consists of maghemite.

From ω and the Mössbauer powder spectra I roughly estimate the particle size to be ~15-25 nm. The liquid sample is not as symmetric at the powder sample, and the hyperfine values found at 20 K are lower than those in the powder spectrum. This is most likely due to smaller particles in the liquid sample. However, the liquid sample shows small signs similar to those of magnetite. It is therefore my conclusion that the liquid sample consists of nearly stoichiometric maghemite particles, probably smaller than those of the powder sample.

9.12 JH053

The sample JH053 was manufactured using iso-octane as solvent, AOT as surfactant and FeSO₄ as iron salt. It has an ω of 5.95.

The sample has during manufacturing been divided into 3 sub-samples, with potentially different properties. JH053A is a liquid sample taken from the synthesis liquid before washing and exposure to atmospheric air. JH053D is a liquid sample taken after washing, just before drying, and JH053E is the dried powder sample. The liquid samples were frozen in liquid nitrogen, and the powder sample was dried using vacuum and then sealed in an Argon atmosphere.

The samples were only exposed to atmospheric air very briefly, before being frozen or sealed in Argon. The powder sample was further only exposed to air when it was transferred to the Mössbauer spectroscopy apparatus. The Mössbauer measurements of the powder sample were commenced within 6 hours after the sample had been removed from vacuum.

Since the sample consists of three subsamples, and since these have been examined extensively, this section is somewhat large.

9.12.1 JH053A



Figure 9.43: Mössbauer spectra as a function of temperature of the sample JH053A.

The spectra of the liquid sample JH053A (figure 9.43) are very noisy, and thus difficult to analyze in detail. There are however some distinct features.

The 80 K spectrum consists of a doublet, in which the left slope is steeper than the right slope. Furthermore the right slope has indications of a plateau approximately 1/3 up the slope (marked in figure 9.44). Both are features of magnetite, and therefore I have fitted the spectrum with a model of superparamagnetic magnetite [40, 43, 47, 48, 49].

Superparamagnetic magnetite consists of two doublets. In the magnetically ordered state above the Verwey transition magnetite consists of two sextets with different isomer shifts and hyperfine fields. The isomer shift is not affected by the magnetic environment. The spectrum also show vague signs of sextets, but I have chosen to neglect these in the fit due to the noise in the spectrum. The fit parameters are presented in table 9.43 and figure 9.44.

The spectrum at 20 K shows mainly the same features as the 80 K spectrum. However, the plateau on the right slope is not as distinct. There is a broad feature in the spectrum around 1.5-2.5 mm/s, which I have been unable account for, marked with an arrow in the figure 9.44. Due to the poor resolution of the spectrum we have had to consider if the feature is due to noise. However the 80 K spectrum has indications of a similar feature, and therefore we can not write it



Figure 9.44: The fitted Mössbauer spectra of JH053A liquid. Left: 80 K. The plateau on the right slope is marked. Right: 20 K.

Name	Lineshape	B_{HF}	E_Q	δ	b	Area	Area
		Т	$\mathrm{mm/s}$	$\mathrm{mm/s}$		%mm/s	%
Doublet 1	Lorentz		1.24	0.65	-	0.21	30.3
Doublet 2	Lorentz		0.54	0.23	-	0.49	69.7

Table 9.43:	The param	eters in	fitting	JH053A	at 80 K.	$\chi^2 = 0.0039.$
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off as noise. I have fitted the spectrum using the same components as the 80 K spectrum. The fit parameters are presented in table 9.44, and the fitted spectrum is displayed in figure 9.44.

Name	Lineshape	B_{HF}	E_Q	δ	b	Area	Area
		Т	$\mathrm{mm/s}$	$\rm mm/s$		%mm/s	%
Doublet 1	Lorentz		1.62	0.62	-	0.29	46.9
Doublet 2	Lorentz		0.55	0.17	-	0.33	53.1

Table 9.44: The parameters in fitting JH053A at 20 K. $\chi^2 = 0.0035$.

9.12.2 JH053D

The sample JH053D is as JH053A a liquid sample, and has much of the same properties. The recorded spectra are displayed in figure 9.45.

The features of the 80 K spectrum consist of the characteristic asymmetric doublet of magnetite and a weak sextet with a hyperfine field of approximately 50 T. I have fitted the spectrum with two doublets to account for the asymmetric doublet, and a sextet. The fit is unable to compensate for an absorption at 2.5-3 mm/s, marked in figure 9.46. The fit parameters are presented in table 9.45 and the fitted spectrum is displayed in figure 9.46.

I have fitted the 20 K spectrum in the same manner as the 80 K spectrum, since it is very similar. The fit parameters are presented in table 9.46 and displayed in figure 9.46.



Figure 9.45: Mössbauer spectra as a function of temperature of the sample JH053D.



Figure 9.46: The fitted Mössbauer spectra of JH053D liquid. Left: 80 K. Right: 20 K.

9.12.3 TEM image analysis

The sample has been investigated using TEM. From these images information about size and shape of the sample has been obtained. The majority of the particles have parallelepiped, cubic or octahedral shape. Which of these shapes the particles actually have is quite hard to tell, since the images only show a 2-dimensional projection of the particles.

The images confirm that the particles are nano-sized, and somewhat mono-disperse. However the particles are not as regular as the particles of JH046 (see section 9.10.3), which is surprising. The particles in these images are smaller, which might be the cause for poorer contrast.

I have extracted a size distribution for the particles of JH053D, from the images. The size distribution is presented in graphic form in figure 9.49, and the extracted data in table 9.47. The extracted size distribution clearly deviates from a normal distribution which is displayed for comparison in figure 9.49 for comparison.

I have measured the lattice distance of particles in JH053D from TEM images. The distance has been measured by drawing a line of arbitrary length perpendicular to the lattice plane. The line should start and end on a plane. Then the intersected planes are counted. The results are presented in table 9.48. a is the length of the line, N is the number of intersected planes and d is the measured lattice distance. The column "corr. d" was defined after I noticed that some values of d were exactly double that of the others. I have corrected these values of d to half the measured

Name	Lineshape	B_{HF}	E_Q	δ	b	Area	Area
		Т	$\mathrm{mm/s}$	$\mathrm{mm/s}$		%mm/s	%
Doublet 1	Lorentz		0.82	0.33	-	0.27	32.0
Doublet 2	Lorentz		0.47	0.12	-	0.21	25.8
Sextet 1	Lorentz(3:2:1)	50.0	0.22	0.41	-	0.35	42.2

Table 9.45: The in fitting JH053D at 80 K. $\chi^2 = 0.00141$.

Name	Lineshape	B_{HF}	E_Q	δ	b	Area	Area
		Т	$\mathrm{mm/s}$	$\mathrm{mm/s}$		%mm/s	%
Doublet 1	Lorentz		0.65	0.19	-	0.22	51.7
Doublet 2	Lorentz		0.37	0.11	-	0.09	21.2
Sextet 1	Lorentz(3:2:1)	50.2	0.58	0.18	-	0.11	27.0

Table 9.46: The parameters in fitting JH053D at 20 K. $\chi^2 = 0.00163$.



Figure 9.47: An example of a TEM image of JH053D. The magnification is 600K, and the scale is indicated by the bar, which has a length of 5 nm.

value, assuming that there were circumstances when the TEM image was recorded, that made two planes appear as one. The theoretically calculated reflection planes are listed in table G.3. Comparing the found lattice distance with the values listed in table G.2, we find a good match with both magnetite (2.53 Å) and maghemite(2.52 Å). We can therefore not use these values to distinguish between those two, but rather use them as an assurance that we are dealing with either of these two spinels, or perhaps the intermediate: non-stoichiometric magnetite.



Figure 9.48: An example of a TEM image of JH053D. The magnification is 250K, and the scale is indicated by the bar, which has a length of 10 nm.

Magnification	Ν	$ar{d}$ nm	$q \ \mathrm{nm}$	σ nm
250k, 400k, 600k	61	15.6	13.9	5.5

Table 9.47: Particle size distribution data of JH053D. Measured from TEM images of the sample. \bar{d} is the mean value, q is the median value and σ is the standard deviation. The data is obtained at the magnifications 250k, 400k and 600k



Figure 9.49: Particle size distribution in JH053D. The distribution of the mean particle edge length, measured from TEM images. A normal distribution with the same mean and standard deviation is displayed for comparison.

Particle	Magn.	х	У	a	a	Ν	d	corr. d
		pixel	pixel	pixel	nm		nm	nm
#1	600k	639	75	643	10.54	43	0.245	0.245
#1	600k	304	50	308	5.04	21	0.240	0.240
#1	600k	803	228	835	13.67	29	0.471	0.236
#1	250k	49	167	174	6.84	28	0.244	0.244
#2	250k	83	260	273	10.73	23	0.466	0.233
#3	250k	152	5	152	5.98	25	0.239	0.239
							$ar{d} =$	0.240
							$\sigma_d =$	0.005
							$q_d =$	0.240

Table 9.48: Measurement of the lattice distance of particles of JH053D. \bar{d} is the mean value, σ_d is the standard deviation and q_d is the median.

9.12.4 JH053E

JH053E is as mentioned a powder sample, and the Mössbauer spectrum series is the most extensive spectrum series in this project. The reason for the extensiveness is that the sample is very interesting considering the goals of this project. Furthermore the sample is the result of the extensive optimization of the manufacturing method. The Mössbauer spectrum series is presented in figure 9.50.



Figure 9.50: Mössbauer spectra as a function of temperature of the sample JH053E.

The temperature series shows a sextet component and a doublet at room temperature, which



both remain down to a temperature of 20 K, where the doublet disappears.

Figure 9.51: The fitted Mössbauer spectra of JH053E. Left: 295 K. Right: 240 K.

The sextet in the 295 K spectrum is asymmetric and resembles the spectrum of magnetite [41] at room temperature. I have thus fitted the spectrum with a doublet and two sextets, which initially had the parameters of magnetite. After some fitting I allowed the parameters to vary freely, to reveal misfit with the magnetite model. At this stage I have made no guess towards the origin of the doublet. The fit parameters are shown in table 9.49 and the fitted spectrum is shown in figure 9.51.

Name	Lineshape	B_{HF}	E_Q	δ	b	Area	Area
		Т	$\mathrm{mm/s}$	$\mathrm{mm/s}$		%mm/s	%
Magnetite A	S-L(3:2:1)	49.0	-0.02^{*}	0.29	0.44	0.68	14.6
Magnetite B	S-L(3:2:1)	46.0	-0.03^{*}	0.66	0.24	1.60	34.1
Doublet 1	Lorentz	-	0.86	0.40	-	2.41	51.3

Table 9.49: The found fit parameters for the spectrum of JH053E at 295 K. * indicates that this parameter has been restricted during a part of the fitting procedure. $\chi^2 = 0.00945$.

Comparison of the magnetite fit parameters with the table values (see table G.1), reveals only very small deviations, leading me to the conclusion that it is highly likely that the sextet consists of magnetite.

Based on the good 295 K fit, I have fitted the spectra of 240 K, 180 K using the same model. The results of these fits are presented in table 9.50 and table 9.51, and in figure 9.51 and figure 9.52 respectively. Based on the magnetite model, I did not allow the quadrupole shift to vary during these fits, since magnetite has a cubic structure. Note that the hyperfine fields and the isomer shifts of the sextets slowly increase as temperature is lowered, in accordance with theory (2nd order Doppler shift).

Due to the complex nature of the magnetite, and the interaction of the components causing the sextets, I have allowed the relative areas of the A and B components to vary, only keeping the ratio of their total area constant compared to the doublet component area. The relative areas of the sextet components as function of temperature is not essential for the identification of the magnetic phase, and this is therefore deemed acceptable.

The 143 K and the 120 K spectra are quite similar to the previous spectra. The hyperfine fields increase slowly with lower temperature, and it is still clear that the magnetite structure is



Figure 9.52: The fitted Mössbauer spectra of JH053E. Left: 180 K. Right: 143 K.

Name	Lineshape	B_{HF}	E_Q	δ	b	Area	Area
		Т	$\mathrm{mm/s}$	$\mathrm{mm/s}$		%mm/s	%
Magnetite A	S-L(3:2:1)	49.3	-0.01*	0.28	0.44	1.04	17.5
Magnetite B	S-L(3:2:1)	46.9	0.00^{*}	0.68	0.01	1.72	29.1
Doublet 1	Lorentz	-	0.86	0.44	-	3.15	53.3

Table 9.50: The found fit parameters for the spectrum of JH053E at 240 K. * indicates that this parameter has been locked during fitting. $\chi^2 = 0.01111$.

Name	Lineshape	B_{HF}	E_Q	δ	b	Area	Area
		Т	$\mathrm{mm/s}$	$\mathrm{mm/s}$		%mm/s	%
Magnetite A	Lorentz(3:2:1)	49.7	-0.01*	0.41	-	2.38	31.1
Magnetite B	Lorentz(3:2:1)	47.1	0.00^{*}	0.78	-	1.51	19.8
Doublet 1	Lorentz	-	0.85	0.47	-	3.75	49.1

Table 9.51: The found fit parameters for the spectrum of JH053E at 180K. * indicates that this parameter has been locked during fitting. $\chi^2 = 0.00970$.



Figure 9.53: The fitted Mössbauer spectra of JH053E. Left: 120 K. Right: 100 K.

intact, since there are two sextets with mainly unchanged parameters. I have therefore fitted the spectrum using the same components as in the previous spectra. The fit parameters for the fits are found in table 9.52 and table 9.53 and in figure 9.52 and figure 9.53 respectively.

Name	Lineshape	B_{HF}	E_Q	δ	b	Area	Area
		Т	$\mathrm{mm/s}$	$\mathrm{mm/s}$		%mm/s	%
Magnetite A	Lorentz(3:2:1)	50.3	-0.01*	0.41	-	0.75	8.9
Magnetite B	Lorentz(3:2:1)	48.4	0.00^{*}	0.71	-	3.81	45.1
Doublet 1	Lorentz	-	0.76	0.48	-	3.88	46.0

Table 9.52: The found fit parameters for the spectrum of JH053E at 143 K. $\chi^2 = 0.04740$.

Name	Lineshape	B_{HF}	E_Q	δ	b	Area	Area
		Т	$\mathrm{mm/s}$	$\rm mm/s$		%mm/s	%
Magnetite A	S-L(3:2:1)	50.9	-0.06	0.46	0.02	1.83	22.4
Magnetite B	S-L(3:2:1)	48.5	-0.01	0.74	0.00	2.05	25.1
Doublet 1	Lorentz	-	0.86	0.49	-	4.29	52.5

Table 9.53: The fitted spectrum of JH053E at 120 K. $\chi^2 = 0.01093$.

According to literature [60] the Verwey transition occurs in stoichiometric magnetite at approximately 118 K. But when considering nano-particles and non-stoichiometric magnetite, the transition may in some cases be suppressed, and in other cases the temperature at which it occurs may decrease significantly [3, 4, 22].

Name	Lineshape	B_{HF}	E_Q	δ	b	Area	Area
		Т	$\mathrm{mm/s}$	$\mathrm{mm/s}$		%mm/s	%
Magnetite A	Lorentz(3:2:1)	51.0	0.00^{*}	0.41	-	2.14	26.2
Magnetite B	Lorentz(3:2:1)	50.3	0.00^{*}	0.83	-	1.68	20.5
Doublet 1	Lorentz	-	0.85	0.51	-	4.35	53.2

Table 9.54: The found fit parameters for the spectrum of JH053E at 100 K. * indicates that this parameter has been locked during fitting. $\chi^2 = 0.00833$.

In the 100 K spectrum we start to see the first indications of the onset of the Verwey transition. I have fitted the spectrum as the previous spectra with two sextets and one doublet. In order to observe the Verwey transition clearly I have not allowed the quadrupole shift to vary. The onset of the Verwey transition is marked by a disappearance of the distinct two magnetite sextets seen in the previous spectra. Thus the overall spectrum sextet (which consists of 5 to 6 components) becomes more symmetric. The resulting fit presented in table 9.54 and figure 9.53 shows two sextets with a similar hyperfine field.

Name	Lineshape	B_{HF}	E_Q	δ	b	Area	Area
		Т	$\mathrm{mm/s}$	$\mathrm{mm/s}$		%mm/s	%
Magnetite A	Lorentz(3:2:1)	50.6	-0.01*	0.44	-	2.50	29.5
Magnetite B	Lorentz(3:2:1)	49.8	0.00^{*}	0.91	-	1.61	19.0
Doublet 1	Lorentz	-	0.77	0.50	-	4.37	51.5

Table 9.55: The found fit parameters for the spectrum of JH053E at 80 K. * indicates that this parameter has been locked during fitting. $\chi^2 = 0.04194$.

The 80 K and the 50 K spectra show a further development of the spectrum, and the change in the found values of the isomer shifts and hyperfine fields reflect this. I have fitted the 80 K and



Figure 9.54: The fitted Mössbauer spectra of JH053E. Left: 80 K. Right: 50 K.



Figure 9.55: The fitted Mössbauer spectrum of JH053E at 20 K.

the 50 K spectra with the same components as the previous spectra. The fit results are presented in table 9.55 and table 9.56 respectively, and figure 9.54.

In the 50 K fit the two sextets have similar isomer shifts and hyperfine fields, which is interesting.

Name	Lineshape	B_{HF}	E_Q	δ	b	Area	Area
		Т	$\mathrm{mm/s}$	$\rm mm/s$		%mm/s	%
Magnetite A	Lorentz(3:2:1)	51.4	-0.01^{*}	0.50	-	1.99	21.4
Magnetite B	Lorentz(3:2:1)	50.3	0.00^{*}	0.60	-	2.17	23.4
Doublet 1	Lorentz	-	0.85	0.54	-	5.13	55.2

Table 9.56: The found fit parameters for the spectrum of JH053E at 50 K. * indicates that this parameter has been locked during fitting. $\chi^2 = 0.02007$.

At 20 K the doublet disappears and becomes a sextet, or possibly several. Since the transition temperature is this low, and the doublet has remained unchanged during the cooling process, and since the absorption lines are broad and undeveloped, it is reasonable to assume that this phase

Name	Lineshape	B_{HF}	E_Q	δ	b	Area	Area
		Т	$\mathrm{mm/s}$	$\rm mm/s$		%mm/s	%
Sextet 4	Lorentz(3:2:1)	51.7	0.00^{*}	0.57	-	2.37	22.7
Sextet 3	Lorentz(3:2:1)	50.7	0.00^{*}	0.44	-	3.48	33.4
Singlet 2	Lorentz	-	-	0.00^{*}	-	0.47	4.5
Sextet 6	S-L(3:2:1)	37.1	0.00^{*}	0.21	2.70	4.11	39.4

Table 9.57: The found fit parameters for the spectrum of JH053E at 20 K. * indicates that this parameter has been locked during fitting. $\chi^2 = 0.02525$.

is paramagnetic.

I have fitted the magnetite sextets have been fitted with two unnamed sextets, since the splitting of the doublet makes it hard to distinguish between the sextets. I have chosen to fit the newly split component with a sextet with broad lines and a large asymmetry parameter. Furthermore the spectrum contains a singlet at 0 mm/s, which I have chosen to fit with a singlet. I have locked the isomer shift of the singlet during fitting to improve the accuracy of the fit. I have found this necessary due to the complexity of the spectrum. The result of the fitting procedure is presented in table 9.57 and figure 9.55.

I have not been able to determine which iron oxide is represented by the doublet component which is split at 20 K. However, the low magnetic ordering temperature implies that it may be poorly crystalline, which would make ferrihydrite a candidate.

To illustrate the Verwey transition figure 9.56 showing the variation in hyperfine field and isomer shift as function of temperature has been produced. From room temperature to around 100 K there is a steady tendency in the hyperfine fields of the sextets. At this point the hyperfine field of the B component changes considerably, and the hyperfine fields of the two components become comparable, a tendency which continues towards lower temperatures.

Similarly when considering the isomer shifts of the sextets, there is a tendency of growing isomer shift with lower temperatures down to around 100 K. At 80 K there are strange fluctuations in the B component, after which the value drops towards that of the A component. These fluctuations might not have a physical origin, but are rather caused by the fitting process, which attempts to fit a 2 component model to a physical system which requires 5 or 6 fitting components. At lower temperature the isomer shifts of the components behave similarly.

These observations are clear signs and evidence of the Verwey transition in the sample. The transition is estimated to occur between 118 K which is the theoretical value, and around 100 K. This is reasonable since there are reports of the Verwey transition of slightly non-stoichiometric magnetite at temperatures as low as 81.5 K [3].

The Verwey transition is in [3, 4] shown to be very sensitive to the degree of stoichiometry, which can explain that the Verwey transition seems to occur over a temperature range, since the degree of stoichiometry of the particle material most likely is related to the particle size. Furthermore particle size alone might have an influence on the Verwey temperature.

To investigate the unknown doublet component in the spectra, a new Mössbauer spectrum series was made with an applied external field of 0.1 T^8 parallel to the gamma ray direction. The spectra from this series are shown in figure 9.57.

With a point of origin in the fitted spectrum of JH053E at 295 K, I fitted the 295 K 0.1 T spectrum using two sextets and one doublet. The reason for reusing the previous fit is to be able to identify changes. I had to fix the isomer shift of the A component during fitting, since it had a tendency to assume non-physically meaningful values. The resulting spectrum is displayed in

⁸In the Mössbauer measurements log these measurements are registered as 0.2 T. However after measurements I discovered that the magnets had been applied incorrectly, yielding an effective magnetic field of 0.1 T.



Figure 9.56: Hyperfine field and isomer shift of the A and B magnetite components as function of temperature in sample JH053E. Notice the shift in hyperfine field and the isomer shift tendencies in the area of 100-118 K. The hyperfine field error bars are 1 T and the isomer shift error bars are 0.1 mm/s. These error values are estimated.



Figure 9.57: Mössbauer spectra as a function of temperature of the sample JH053E with an external field of 0.1 T applied somewhat parallel to the gamma ray direction.

figure 9.58 and the fit parameters in table 9.58.


Figure 9.58: The fitted Mössbauer spectra of JH053E with an applied magnetic field of 0.1 T \parallel . Left: 295 K. Right: 143 K.

Name	Lineshape	B_{HF}	E_Q	δ	b	Area	Area
		Т	$\mathrm{mm/s}$	$\mathrm{mm/s}$		$\rm \%mm/s$	%
Magnetite A	S-L(3:x:1)	49.1	-0.02	0.28^{*}	0.47	0.99	19.2
Magnetite B	S-L(3:x:1)	45.9	0.02	0.71	0.10	1.74	33.7
Doublet 1	Lorentz	-	0.86	0.40	-	2.43	47.2

Table 9.58: The found fit parameters for the spectrum of JH053E at 295 K and 0.1 T \parallel . * indicates that the parameter has been restricted during the fitting procedure. $\chi^2 = 0.01654$.

Name	Lineshape	B_{HF}	E_Q	δ	b	Area	Area
		Т	$\mathrm{mm/s}$	$\mathrm{mm/s}$		$\rm \%mm/s$	%
Magnetite A	Lorentz(3:x:1)	50.1	-0.07	0.42	-	1.72	24.5
Magnetite B	Lorentz(3:x:1)	48.7	-0.04	0.87	-	1.61	22.9
Doublet 1	Lorentz	-	0.88	0.48	-	3.69	52.5

Table 9.59: The found fit parameters for the spectrum of JH053E at 143K and 0.1T \parallel . $\chi^2 = 0.01234$.

Name	Lineshape	B_{HF}	E_Q	δ	b	Area	Area
		Т	$\mathrm{mm/s}$	$\rm mm/s$		$\rm \%mm/s$	%
Magnetite A	Lorentz(3:x:1)	50.8	-0.03	0.45	-	1.89	24.9
Magnetite B	Lorentz(3:x:1)	49.7	-0.03	0.89	-	1.27	16.7
Doublet 1	Lorentz	-	0.89	0.51	-	4.44	58.4

Table 9.60: The found fit parameters for the spectrum of JH053E at 80 K and 0.1 T \parallel . $\chi^2 = 0.02354$.

Name	Lineshape	B_{HF}	E_Q	δ	b	Area	Area
		Т	$\mathrm{mm/s}$	$\mathrm{mm/s}$		$\rm \%mm/s$	%
Sextet 1	Lorentz(3:x:1)	50.3	0.31	0.65	-	3.09	35.4
Sextet 2	Lorentz(3:x:1)	50.7	-0.58	0.56	-	2.21	25.4
Sextet 3	S-L(3:x:1)	37.6	-0.05	0.54	1.23	3.43	39.3

Table 9.61: The found fit parameters for the spectrum of JH053E at 20 K and 0.1 T \parallel . $\chi^2 = 0.02052$.



Figure 9.59: The fitted Mössbauer spectra of JH053E with an applied magnetic field of 0.1 T \parallel . Left: 80 K. Right: 20 K.

The 143 K and 80 K spectra of the sample with applied field do not reveal anything new compared to the previous 143 K and 80 K spectra, and I have therefore fitted the 143 K and 80 K spectra in a similar fashion. The resulting fit is presented in table 9.59 and table 9.60 respectively, and in figure 9.58 and figure 9.59 respectively.

At 20 K the doublet does as in previous 20 K spectrum split. However the central singlet and doublet seen in the 20 K 0 T spectrum. I have therefore only fitted the spectrum with three sextets, two for the magnetite component, and one for the newly split component. The resulting fit is presented in table 9.61 and figure 9.59.

In the fitting of the 295 K spectrum the isomer shift of the A component is kept fixed, but in the remaining fits the isomer shift has been allowed to vary. This results in an isomer shift of the A component, which is higher than when the external field was absent. This is a phenomenon that I am unable to explain.

Comparison between the spectra with and without an applied field, reveal that there is no significant difference between the spectra. This implies that the doublet component is not ferrior ferromagnetic, since it does not respond to an external field. Thus this phase is either antiferromagnetic, or not magnetic at all. The magnetite component does not react to the applied field, which is unusual, and may be due to a high degree of anisotropy in the sample.

However the 20 K spectrum with applied field does not contain the central doublet and singlet present in the 20 K spectrum without an applied field, which indicates that this component is in fact affected by the magnetic field, and most likely consists of magnetite.

A possible explanation for the missing reaction of the split magnetite component to the applied magnetic field is the quality of the magnet used. After the measurements it was brought to my attention, that the magnetic field might be poorly homogeneous.

9.12.5 Conclusion

Taking into account the Mössbauer analysis on the three subsamples and the TEM images, it is my conclusion that the sample JH053 consists of a large portion of non-stoichiometric magnetite, along with an equally large portion of an unidentified material.

The large portion of unidentified material in the sample, might explain why the TEM images do not show such regularly shaped particles as the sample JH046.

The ratio A to B in stoichiometric magnetite is 1:2. From the 295 K spectrum with no applied

field, I have found this ratio to be

$$\frac{[A]}{[B]} = \frac{14,6}{34,1} \simeq \frac{1}{2.3} \simeq 1:2, \qquad (9.20)$$

which implies that the magnetite is close to stoichiometric. From comparison with [41], and in particular [52], I estimate the x parameter in $\text{Fe}_{3-x}O_4$, 0 < x < 1/3, to 0.05 ± 0.05 .

Although I have measured the particle size, I have for consistency estimated the particle size from ω and the Mössbauer spectra to be ${\sim}10{\text{-}}20\,\mathrm{nm}.$

9.13 Analysis conclusion

Previously in this section the samples have been analyzed individually. In this section the samples will undergo a collective analysis.

9.13.1 Synthesis of iron oxides

Sample name	Found composition
JH030	Goethite, stoichiometric
JH032	Magnetite, non-stoichiometric, $x \simeq 0.2 \pm 0.05$
JH032a	Maghemite, stoichiometric
JH036	Maghemite, stoichiometric
JH037	Maghemite, stoichiometric
JH041	Maghemite, stoichiometric
JH046	Magnetite, non-stoichiometric
JH047	Maghemite, stoichiometric
JH048	Maghemite
JH050	Maghemite, possibly amorphous
JH053	Magnetite, non-stoichiometric, $x \simeq 0.05 \pm 0.05$

Table 9.62: Sample composition summary, based on analysis.

The analysis reveals that the manufactured iron oxides manufactured through synthesis are goethite, maghemite and magnetite.

It is of course interesting to know how pure/stoichiometric the manufactured samples are. From the Mössbauer analysis, it would seem that the goethite sample is stoichiometric and quite well crystallized. Also the maghemite samples are stoichiometric although there in some cases are signs of amorphous material, and in some cases non-stoichiometric maghemite. Non-stoichiometric maghemite may be magnetite which has been oxidized further, but not fully to form maghemite.

Magnetite has proved difficult to manufacture in stoichiometric form. Several attempts have resulted in non-stoichiometric magnetite, and only one attempt has resulted in magnetite close to stoichiometry.

9.13.2 Particle size

The samples JH046 and JH053 are practically identical, except the parameter ω (see equation (7.1)), which according to theory determines particle size. The ratio, a, between the ω 's of the samples is calculated as

$$a = \frac{\omega_{JH046}}{\omega_{JH053}} = \frac{11.22}{5.95} = 1.9 \pm 0.2, \qquad (9.21)$$

the ratio, b, between the mean particle sizes of the samples is calculated as

$$b = \frac{d_{JH046}}{\bar{d}_{JH053}} = \frac{28.4 \, nm}{15.6 \, nm} = 1.8 \pm 0.2 \,, \tag{9.22}$$

and the ratio, c, between the medians of the particle size of the samples is calculated as

$$c = \frac{q_{JH046}}{q_{JH053}} = \frac{25.9}{13.9} = 1.9 \pm 0.2, \qquad (9.23)$$

where I have estimated the uncertainty values. Comparison of a to b and c reveals a good correspondence between the ratios, and in my opinion this result shows that particle size control is possible. However since the calculations are based only one pair of samples, this is not hard evidence.

9 SAMPLE ANALYSIS

The analysis of the particles in the TEM images reveals that the manufactured particles are not mono-disperse. Furthermore the size distribution is not a normal distribution, which was expected. The reason for this is unknown, and it has been a cause of much speculation.

The core of the speculation has been if the particle distribution extracted from the TEM images does reflect the size distribution of the manufactured particles, or whether the distribution has been distorted by one or more of the links along the way from synthesis to distribution.

If the distribution does reflect the actual size distribution, and assuming that the particles manufactured inside the reverse micelles reflects the size of the micelle, the distribution of micelles can not be normal. Since the micelles dynamically merge and split, there must exist some mechanism which favors large reverse micelles compared to smaller micelles. Such a mechanism could be difference in the surface tension of small and large micelles.

If the real size distribution is not reflected by the extracted distribution, there must be factors distorting the distribution. The first of these possible sources is the particle filtering, in which it is much easier to extract large particles due to their large volume to surface ratio, which is important in both magnetic and centrifugal filtering.

The TEM apparatus has a limited resolution, and the thicker the sample, the larger the contrast, which make larger particles appear more clear. Therefore smaller particles may be poorly visible or invisible.

I have done the measurements of the size of the particles by eye on a computer. I may have been unable to distinguish very small particles with are clustered, thereby have overlooked these.

Models of the AOT/iso-octane/water system [5] predict that the micellar size distribution is normal. Therefore it is likely that either the assumption that the micellar size dictates the particle size is wrong, or the washing procedure favors extraction of large particles.

I find it most likely that it is the washing procedure which distorts the particle size distribution by filtering out the small particles, since there are no indications that the micellar size does not dictate particle size. In fact, the control of the particle size presented earlier points to the contrary.

The fact that the waste fluid in many cases had a color similar to the manufactured particles supports this assumption. The shape of the distributions indicates, however, that a certain fraction of the manufactured particles are significantly larger than average.

9.13.3 Oxidation

From observations of the color development of the samples, it would seem that the particles, at least at the surface, have a high tendency to be further oxidized. Several samples have been black or dark brown when sealed in container after drying, and have become red within days. Other samples have appeared black, and within minutes have changed color to reddish/brown, even when submersed in washing liquid.

There are signs that this oxidation affects the entire sample, and not just the surface layer. This result is based on the observation that the samples JH046, JH047, JH048, JH050 and JH053 have been manufactured under similar conditions, and the yield has had similar color properties. However, the time interval from production to Mössbauer measurement has varied from several weeks for JH046, JH047 and JH048, to a few hours for JH053E, and the results of the Mössbauer investigations have also been widely different. The samples JH046, JH047, JH048 were all black or gray brown after drying. At measurement time this color had changed to reddish-brown. As shown in table 9.62, these samples show maghemite or highly non-stoichiometric magnetite, whereas JH053E, which still was gray/black when sealed in the Mössbauer experimental setup, shows magnetite, of a much higher degree of stoichiometry.

9.13.4 Particle washing

The consistency of the manufactured samples and the TEM images reveal that even after through washing, the samples still contain a significant amount of surfactant material. In TEM images many of the samples where located within what appeared to be surfactant material. The surfactant has proved very difficult to wash out entirely, which also is reported by [12].

In Mössbauer spectra some of the samples showed signs of particle-particle interaction of varying strength. A part of these variations may be due to variations in inter-particle distance, causing great variations in particles separation.

9.13.5 Analysis methods

I have with significant success identified the manufactured iron oxides using Mössbauer spectroscopy. The analysis has been somewhat hampered by significant particle interaction, and transition effects, but Mössbauer spectroscopy has proved its force in identifying the different iron phases.

Transmission electron microscopy has also proved to be a powerful technique for measuring particle size, lattice distance, and for investigating the shape of nano-particles.

10 Future perspectives

10.1 Proposal for improvement of size control

Assuming that it is difficult to improve the dispersity of the manufactured particles through synthesis tuning, it may be possible to improve the magnetic filtering technique. During the washing process it should be possible to subject the solution to a magnetic field which would extract the magnetic particles in the solution more efficiently. However, this requires a special device.

I am presenting my suggestion for such a filtering device in schematic form in figure 10.1.



Figure 10.1: A schematic of the proposed magnetic filtering device. The controllable electromagnets are marked B_1 - B_5 , and the orientation of the field indicated by arrows.

The device consists of a thin pipe with an array of electromagnets (B_1-B_5) in side pipes. The magnetic field of the electro magnets should be individually adjustable. This provides usage of the magnetic array as both a capture device for magnetic magnetic material, as well as a filtering device.

The force on a magnetic moment, μ , in a magnetic field \vec{B} is given by

$$\vec{F}_m = \mu \nabla |\vec{B}|,\tag{10.1}$$

in high magnetic fields (>0.1 T) [10]. However, the mass, m, of a magnetic particle is approximately (disregarding canting of surface spins) proportional to the magnetic moment of the particle

$$\mu = m\sigma_s,\tag{10.2}$$

where σ_s is the saturation magnetization of the material. With no friction the acceleration of the particles would therefore be identical. Assuming a homogenous material density of the particles, the magnetic force, F_m , is related to the radius, r, of the particles as:

$$F_m \propto r^3. \tag{10.3}$$

The friction forces, F_f , acting on a particle are proportional to the surface area of the particle, which is proportional to the square of the particle radius

$$F_f \propto r^2. \tag{10.4}$$

Combining the expressions above we arrive at an expression for the acceleration of the particles

$$a = \frac{F_m - F_f}{m} = c_1 r^3 - c_2 r^2, \tag{10.5}$$

where c_1 and c_2 are proportionality constants. Inserting values for small and large particles it is clear that the acceleration towards the magnetic field of large particles will be larger than that of the smaller particles. Therefore the large particles are likely to be captured by a magnetic field sooner than small particles.

Considering nano-particles, the surface spins are canted and do therefore not contribute as much to the total magnetic moment as non-surface spins. Small particles have a larger fraction of the total spins sited at the surface, which further diminishes the total magnetic moment, adding to the difference in behavior of small and large particles in a magnetic field.

If the electromagnets all are set to exhibit an equally powerful magnetic field, it will act as a capture device for magnetic material.

The device can act as a filtering device, if the magnets have an increasingly powerful magnetic field. The array will be more likely to attract particles with large magnetic moments. The array will act as a filtering device by capturing the largest particles in the first capture side pipes (with the smallest magnetic field), and the smallest magnetic particles in the last pipe (with the largest magnetic field).

By adjusting the liquid flow through the pipe, the efficiency of the filtering device can be optimized.

The large amount of values in the device provides the possibility to seal the device in various ways to avoid oxygen contamination. Furthermore the pressure exchange pipe (dotted lines) makes it possible to keep the entire system sealed and Argon filled during filtering, without pressure differences between the upper and lower container.

In figure 10.1 the magnets are aligned perpendicular to the main pipe. However, if these are turned to form a different angle with the main pipe the gradient of the magnetic field will be larger, and the magnetic field will capture particles more efficiently, since the force on magnetic particles in a strong magnetic field (>0.1 T) is given by (10.1). The force will be parallel to the magnetic field gradient:

$$\vec{F} \mid \mid \nabla \mid \vec{B} \mid. \tag{10.6}$$

To provide an estimate of the magnitude of magnetic field of the magnets, I have to put forth some considerations. I have during synthesis successfully extracted magnetic material from a separation funnel using a 0.4 T magnet. However, it was clear from the color of the waste liquid that this was insufficient to extract all the material.

The diameter of the separation funnel was large $(\sim 10 \text{ cm})$. The magnet did very efficiently capture nearby $(\sim 3 \text{ cm})$ material. Material which due to liquid motion came within this zone was quickly, within seconds, attracted. Material observed to be attracted in this manner is of course not nano-sized, and is agglomerated material, with a large total magnetic moment.

The Mössbauer analysis of the material collected with the magnet revealed that it in all cases consisted of maghemite or magnetite, which have a large saturation magnetization ($\sim 60 \text{ Am}^2 \text{kg}^{-1}$ and $\sim 90 \text{Am}^2 \text{kg}^{-1}$). Some samples could not at all be collected by the applied magnetic field, and some were only weakly attracted.

If the thin pipe is set to have a diameter of 5 mm, the liquid flow velocity is moderate ($\sim 5 \text{ mm/s}$) and the magnets are located 3 cm from the pipe, a field of approximately 0.1 T should be sufficient to collect the agglomerations of magnetic material. A field of 0.2-0.3 T should be sufficient to collect the smaller magnetic particles. However, a much larger magnetic field (1-2 T) would at this distance be necessary to collect the smallest particles (5-10 nm). Such large fields are unrealistic, but there are some improvements that can be made. The flow velocity could be decreased to improve the capture efficiency of the magnets, and the magnets could be moved closer to the thin pipe. To improve collection of small particles, the large particles could be collected first, and the waste could then be passed through the filtering device again. However, the device would probably still be unable to collect weakly magnetic material as hematite which has a saturation magnetization of $\sim 0.4 \text{ Am}^2 \text{kg}^{-1}$.

The estimates presented in this section, are intended as guidance, and to establish the efficiency of the filtering device, it would have to be tested.

11 Conclusion

In the following I will try to make some conclusions regarding the topics treated in this project. I will make conclusions for each topic separately.

11.1 Reverse micellar technique

The main result of the work with the reverse micellar technique, is that I have implemented the technique to manufacture materials of a predetermined composition and size.

I have successfully manufactured magnetite, magnemite and goethite using the reverse micellar technique. This has been done by varying the parameters of the manufacturing process. The manufactured material has been characterized by Mössbauer spectroscopy.

There are strong indications, but not evidence, that the manufactured iron oxide species depends on the surfactant/solvent system.

Synthesis using the AOT/iso-octane system has in all cases resulted in either maghemite or magnetite.

Most of the effort during synthesis has been put in tuning and developing the AOT-system for magnetite and magnemite synthesis. However, I have made two manufacturing attempts with using CTAB as surfactant. A manufacturing attempt using the CTAB/chloroform system also resulted in magnemite.

Using a different CTAB system, consisting of CTAB/n-butanol/octane, I was able to manufacture goethite. This has been reproduced by a group at DTU. I have, on the other hand, never manufactured goethite during a large number of experiments with AOT. This supports that there is a strong connection between the surfactant/solvent system and the species of the manufactured material.

I have determined that the outcome of the reverse micellar technique is very sensitive to pH level and electrochemical potential of the synthesis solutions, confirming predictions from Pourbaix diagrams. The oxidation state of iron is highly affected by the pH value, which therefore must be controlled throughout the experiment. The electrochemical potential is dictated by present oxygen, and other oxidizing agents in the solutions, and must also be controlled throughout the experiment.

I chose to tune the AOT/iso-octane system, due to its simplicity, and due to its ability to produce the material of interest.

Initially I attempted to produce magnetite, since it was supposed to be the easiest iron oxide to produce [12]. From magnetite, magnetite could be produced by further oxidation, by for instance hydrogen peroxide. However, it is my conclusion that the opposite is in fact the case.

It has proved easy to manufacture maghemite fully oxidized. If no measures were taken to decrease the amount of present oxygen, the manufactured material consisted of maghemite. Furthermore maghemite was often the result of an unsuccessful attempt to manufacture magnetite.

As mentioned, magnetite has proved a difficult material to manufacture since it is easily oxidized further to maghemite. I have, however, manufactured several samples consisting of magnetite with a degree of stoichiometry ranging from very close to stoichiometric to non-stoichiometric close to maghemite.

The relatively high control of the stoichiometry of magnetite has been achieved by controlling the oxygen level in the environment. A further tuning of the manufacturing procedure, should make it possible to manufacture stoichiometric magnetite using the reverse micellar technique.

Examination of the material manufactured using the CTAB/chloroform synthesis reveals that the manufactured maghemite is well crystallized.

I have discovered that it is possible to successfully produce goethite of a high crystalline quality using the CTAB/n-butanol/octane system. The chemical synthesis setup used for manufacturing

of goethite has only been tried once, which is why sheer luck can not be ruled out. However, a group at DTU has reproduced the synthesis of goethite using my recipe, and confirmed my findings. I therefore consider it very likely the result is reproducible.

11.2 Particle properties

From the particle distributions extracted from TEM images, I have shown that particle size control is possible, and that it is dependent on the water to surfactant ratio, ω . I have investigated two samples, which have been manufactured by an identical procedure. The samples differ only in the value of ω . The ratio between the ω 's of the samples is 1.9 and the ratio between the mean particle sizes is 1.8 (and the size median ratio is 1.9).

The mean particle size of the samples is 28.4 nm and 15.6 nm, and ω is $\simeq 11$ and $\simeq 6$ for JH046 and JH053 respectively.

I have not found the manufactured particles to be mono-disperse. The particles sizes are distributed over a broad range, which can be illustrated by particle sizes ranging from 9 nm to 57 nm in JH046 and from 7 nm to 30 nm in JH053. The standard deviations of these samples are 10.3 nm and 5.5 nm respectively.

I have not found the size distribution of the particles to be normal, but more similar to a γ distribution (with appropriate parameters). A large portion of the particles have sizes around or just below the mean value, whereas there is a significant portion which have sizes stretching up to twice the mean size. The distribution shape is similar for both samples, and is reflected by the median values of 25.9 nm and 13.9 respectively.

I have from the samples found that the particles differ in shape. Although TEM images only reveal the two-dimensional projection of the true shape, it is my conclusion that the sample JH046 consists of octahedral particles, whereas the particles in JH053 contains a wide variety of shapes. The particle shape can most likely be attributed to the pH value of the synthesis solution. Both of the investigated samples consist of magnetite, and according to [17] the particle shape of magnetite depends on the pH in which it is synthesized.

I have investigated the magnetic properties of the manufactured particles using Mössbauer spectroscopy, and identified the composition of the manufactured samples to be goethite, maghemite and magnetite.

From the Mössbauer spectra of the manufactured goethite sample I have determined that the magnetic environment of the iron ions is quite homogenous, which implies that the particles are well crystallized. This makes the reverse micellar technique interesting for goethite research, since it is difficult to synthesize well crystallized goethite.

I have found that the goethite particles are nano-sized since they respond to a magnetic field, which is only seen in nano-sized goethite, and is due to canting.

My analysis of the Mössbauer spectra of the maghemite samples reveals that the particles often are superparamagnetic at room temperature, which indicates small particles. However, I have found the superparamagnetic ordering to take place over a wide range of temperatures, which indicates large spread in particle sizes. All samples exhibit a high degree of particle-particle interaction, implying clustering of the particles. A part of the broad range in ordering temperature can also be accounted to the particle-particle interaction.

I can not dismiss that the wide temperature range in which the ordering occurs in some samples, is due to poorly crystallized material. In fact, several samples contain a central nonordered component which does not order until at very low temperatures.

Mössbauer analysis reveals that I have manufactured magnetite particles. However, most manufactured magnetite samples have a high degree of non-stoichiometry, which I have put down to post synthesis oxidation. I have carefully manufactured one sample which is close to stoichiometry, in which I have observed clear signs of the Verwey transition. However, even this sample exhibits signs of oxidation, illustrating the difficulty in producing magnetite. I have in several cases found the magnetic hyperfine field of the iron oxides in the samples to be lower than the magnetic hyperfine field of bulk material. This is most likely due to canting of the surface spins in the particle surfaces, since a large portion of the iron ions sites in the sample are sited near the surface.

11.3 Unsolved issues

There are several unsolved issues regarding the reverse micellar technique. One of the most critical issues is the reproducibility of the synthesis. During the work in the laboratory, the success rate of the experiments has been somewhat varying.

In some cases I have been able to, within reasonable boundaries, explain the unsuccessful outcome of the synthesis, but in other cases there has been no apparent logical reason. This seems to indicate that the synthesis is very sensible to certain/some external influences.

I have shown the particle size control to be possible, but more experiments are needed to investigate the connection between ω and particle size further. For instance I have not had time to investigate if the connection is the same for all iron oxides, although theory predicts this.

If the reverse micellar technique is to have practical application or a more important role in scientific research, better control of the size particle size has to be developed.

Rather than modifying the synthesis, it is my opinion that this is most efficiently achieved by optimizing the washing and filtering process. A tuning of the filtering process will make it possible to control the size distribution better, and make it possible to manufacture iron oxides and other oxides with a narrow size distribution.

Magnetic filtering could be made using a powerful electromagnet, but the mechanical filtering should also be possible. I have provided a suggestion for optimization of the magnet filtering process in section 10.

The largest unknown factor in the synthesis has been the unknown level of oxygen in the synthesis solutions.

Ideally the oxygen-free solutions should be used for synthesis for improved oxygen control. During synthesis a controlled amount of oxygen could then be injected into the system, to facilitate oxide formation. A device could be designed for filtering and washing, which would be able to wash the manufactured material several times in a protecting atmosphere, without exposing the material to oxygen.

As mentioned in the analysis the samples contain a significant amount of surfactant remains after washing. Surfactant remains interfere with measurements on the material, and therefore as much of it should be removed as possible. By thorough washing I have been able to lower the amount of surfactant in the samples, but I have been unable to remove the surfactants entirely.

I have not been able to produce hematite, and I have argued that the approach used for hematite production probably was wrong. I believe, however, that with the right choice of synthesis followed by heating it could be possible manufacture hematite.

During the analysis of the Mössbauer spectra I have encountered some components, which I have been unable to identify completely. However, this has not hampered the analysis of the spectra, and the conclusions derived from it.

11.4 Relation to the Mars exploration

I have not been able to manufacture hematite, which makes a comparison of the magnetic properties of hematite and magnemite impossible.

However, I have in the analysis of the samples demonstrated several times, that the magnetic properties of nano-particles differ significantly from that of bulk material. Especially the reduced magnetic hyperfine field of the nano-particles has been evident.

It is believed that the Martian dust particles are composed of many smaller grains of different material. The grains of the magnetic material are likely single domain particles. The saturation magnetization of the grains is therefore proportional to the magnetic moment. Along with superparamagnetism, this may provide a piece in the puzzle of explaining the small magnetic moment of the Martian dust, compared to that of the magnetic iron oxides maghemite and magnetite. However, little is known about the size of the grains of the Martian dust particles, so this has yet to be investigated.

A Analysis of additional samples

This section contains the analysis of the samples that are not considered very important and interesting. However, the samples contain valuable information, which has been used in the analysis conclusion, and for the conclusion of the project.

A.1 JH036

The sample JH036 was manufactured using iso-octane as solvent, AOT as surfactant and FeSO₄ as iron salt. It has an ω of 12.59.

It was intended as a copy of JH032, but during formation it became brown rapidly. After manufacturing the sample was characterized as: Fluid form, dark brown, very magnetic. A detailed log of the manufacturing process is found in section C.6.

It has been investigated using Mössbauer spectroscopy and the obtained spectra are shown in figure A.1.



Figure A.1: Mössbauer spectra as a function of temperature of the sample JH036.

The 295 K spectrum shows a singlet, and no signs of any other component. There with a strange narrowing of the singlet near the peak (marked in figure A.2), which may indicate that the singlet is composed of more than one component. I have fitted the spectrum with a singlet and a doublet, to account for the narrowing. The resulting fit is presented in table A.1 and figure A.2.

In the 80 K spectrum a sextet component has appeared, and I have therefore added a sextet component to the fit. Furthermore the central singlet has become wider, and now bears more resemblance with a doublet. However, I have kept both the singlet and the doublet, to observe



Figure A.2: The fitted Mössbauer spectra of JH036. Left: 295 K. Right: 80 K.

Name	Lineshape	B_{HF}	E_Q	δ	b	Area	Area
		Т	$\mathrm{mm/s}$	$\mathrm{mm/s}$		$\rm \%mm/s$	%
Singlet 1	Lorentz	-	-	0.39	-	22.6	72.1
Doublet 1	Lorentz	-	1.12	0.40	-	8.7	27.9

Table A	A.1:	The	Mössi	bauer f	it	parameters	for	JH036	at	295K.	χ^2	=0.0	943	332.
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the development. The found fit is presented in table A.2 and figure A.2.

Name	Lineshape	B_{HF}	E_Q	δ	b	Area	Area
		Т	$\mathrm{mm/s}$	$\rm mm/s$		$\rm \%mm/s$	%
Singlet 1	Lorentz	-	-	0.50	-	31.0	63.8
Doublet 1	Lorentz	-	1.07	0.51	-	11.7	24.0
Sextet 1	Lorentz	47.5	-0.18	0.55	-	5.9	12.2

Table A.2: The Mössbauer fit parameters for JH036 at 80K. $\chi^2 = 0.06477$.

At 24 K the spectrum has become magnetically ordered, but it still shows signs of nano-particle effects. The lines are symmetric across the center, but very wide. An interesting feature is that the lines 2 and 5 are narrower than lines 1 and 6. Due to the symmetry I have only fitted the spectrum with one sextet. The quadrupole shift has been allowed to vary, but shows no significant deviation from zero. Although I have restricted the sextet to an area ratio of 3:2:1, the fit matches quite well. The fit is presented in table A.3 and figure A.3.

Name	Lineshape	B_{HF}	E_Q	δ	b	Area	Area
		Т	$\mathrm{mm/s}$	$\mathrm{mm/s}$		$\rm \%mm/s$	%
Sextet 1	S-L(3:2:1)	48.3	-0.02	0.50	1.57	61.4	100.0

Table A.3: The Mössbauer fit parameters for JH036 at 24K. $\chi^2 = 0.13947$.

The 15 K spectrum is similar to the 24 K spectrum, but the lines have become narrower, and the depth of the lines 2 and 5 are is smaller than that of lines 1 and 6. Due to the similarities I have fitted the 15 K spectrum in the same manner as the 24 K spectrum. However, I have not allowed the quadrupole shift to vary during fitting. The fit is presented i table A.4 and figure A.3.



Figure A.3: The fitted Mössbauer spectra of JH047. Left: 24 K. Right: 15 K.

Name	Lineshape	B_{HF}	E_Q	δ	b	Area	Area
		Т	$\mathrm{mm/s}$	$\mathrm{mm/s}$		$\rm \%mm/s$	%
Sextet 1	S-L(3:2:1)	48.6	0.00^{*}	0.51	0.70	61.1	100.0

Table A.4: The Mössbauer fit parameters for JH036 at 15K. * indicates that this parameter has been locked during fitting. $\chi^2 = 0.23319$.



Figure A.4: Mössbauer spectra as a function of applied magnetic field of the sample JH036 at 80 K. Note that these spectra were obtained using different experimental apparatus. 0 T was obtained at Ørsted laboratory, and 0.5 T at DTU.

To investigate the sample further a spectrum was produced while the sample was subjected to an external magnetic field perpendicular to the gamma ray direction. The spectrum with and without an applied field is shown figure A.4.

The spectrum with applied field shows a significant magnetic ordering, induced by the applied field. From this we learn that the sample is ferri- or ferromagnetic. I have fitted the spectrum with



Figure A.5: The fitted Mössbauer spectrum of JH036 at 80 K and $0.5 T \perp$.

Name	Lineshape	B_{HF}	E_Q	δ	b	Area	Area
		Т	$\mathrm{mm/s}$	$\mathrm{mm/s}$		$\rm \% mm/s$	%
Sextet 1	S-L(3:4:1)	48.5	0.03	0.52	4.70	27.0	45.6
Doublet 1	Lorentz	-	1.53	0.51	-	32.2	54.4

Table A.5: The Mössbauer fit parameters for JH036 at 80 K with a perpendicularly applied field of 0.5 T. $\chi^2 = 0.10436$.

a doublet to account for the central depression, and a sextet with area constraint 3:4:1 to account for the ordered component. The result of the fitting process is presented in table A.5 and figure A.5.

The quadrupole shift has been found to be close to zero except in the 80 K 0 T spectrum, where it probably originates in the fitting algorithm, rather than in physical effects. A quadrupole shift of zero implies a cubic structure. The simple order of the spectrum sextet at low temperatures implies a single iron oxide phase sample. These facts leave only magnetite and maghemite as candidates. However, magnetite can be eliminated as an option, due to its complex spectrum at low temperature, and complex path of order during cooling.

It is therefore my conclusion that the sample with high probability consists of maghemite, which also matches the values found in fitting. Comparison with [44, 59] support this conclusion.

From ω and the Mössbauer powder spectra I roughly estimate the particle size to be ${\sim}10{-}15\,\mathrm{nm}.$

A.2 JH047

The sample JH047 was manufactured using iso-octane as solvent, AOT as surfactant and FeSO₄ as iron salt. It has an ω of 4.76.

It was manufactured as a copy of JH046, with a ω 2 times smaller. It was intended to test the linear particle size dependence of ω .

Just after manufacturing the sample was characterized as consisting of black, very magnetic particles. In the first thin dust layers inside the storing tube, the color had a tendency towards red-brown. A detailed log of the manufacturing process can be found in section C.10.



Figure A.6: Mössbauer spectra as a function of temperature of the sample JH047.

The 295K spectrum of JH047 shows clear signs of superparamagnetism, by the dominating doublet around zero velocity. But not all the material in the sample is superparamagnetic, since the spectrum shows signs of a broadened sextet, seen as a shallow, wide absorption. The doublet has a shape not compatible with only one Lorentzian doublet, and I have therefore fitted it with two doublets. The fit is shown in table A.6 and figure A.7.

Name	Lineshape	B_{HF}	E_Q	δ	b	Area	Area
		Т	$\mathrm{mm/s}$	$\mathrm{mm/s}$		$\rm \% mm/s$	%
Sextet 1	S-L(3:2:1)	41.8	-0.24	0.37	3.67	8.7	34.4
Doublet 1	Lorentz	-	0.61	0.41	-	4.5	17.6
Doublet 2	Lorentz	-	0.74	0.39	-	12.2	48.0

Table A.6: The Mössbauer fit parameters for JH047 at 295K. $\chi^2 = 0.02444$.

The 80 K spectrum is very symmetric, showing both a well ordered magnetic phase and an unordered phase in the form of a doublet. The doublet is probably a superparamagnetic component. However the doublet can not be fitted satisfactory using only one doublet, and I have therefore fitted it with two doublets. I have fitted the ordered phase with a sextet. The resulting fit is found



Figure A.7: The fitted Mössbauer spectra of JH047. Left: 295 K. Right: 80 K.

in figure A.7 and table A.7.

Name	Lineshape	B_{HF}	E_Q	δ	b	Area	Area
		Т	$\mathrm{mm/s}$	$\mathrm{mm/s}$		$\rm \%mm/s$	%
Sextet 1	S-L(3:2:1)	48.3	-0.07	0.51	0.92	38.0	69.4
Doublet 1	Lorentz	-	0.73	0.51	-	15.1	27.6
Doublet 2	Lorentz	-	0.57	0.53	-	1.6	3.0

Table A.7: The Mössbauer fit parameters for JH047 at 80 K. $\chi^2 = 0.17467$.

The 20 K spectrum shows characteristics of a spectrum of two overlapping sextets, line 1 is narrower than line 6, a feature of magnetite and in some cases maghemite. The asymmetry is small, and the spectrum matches maghemite spectra shown in [44] well. It can however not be rejected that the maghemite might be slightly non-stoichiometric i.e. not fully oxidized. Furthermore maghemite actually consists of two overlapping sextets, for the A and B sites, with slightly different isomer shifts. Since both maghemite and magnetite consist of more than one sextet I have fitted the spectrum with two sextets. The result of the fitting is shown in table A.8 and figure A.8.

Name	Lineshape	B_{HF}	E_Q	δ	b	Area	Area
		Т	$\mathrm{mm/s}$	$\rm mm/s$		$\rm \% mm/s$	%
Sextet 1	S-L(3:2:1)	51.6	0.01	0.52	0.46	20.1	36.0
Sextet 2	S-L(3:2:1)	49.4	-0.10	0.50	1.11	35.8	64.0

Table A.8: The Mössbauer fit parameters for JH047 at 20 K. $\chi^2 = 0.16867$.

Considering the result the fitting of the temperature series, I conclude that the sample consists of maghemite. The spectra are symmetric, and there is no sign of the complex spectra of magnetite below the Verwey transition. The quadrupole shift close to zero, which implies a cubic crystal structure, supports this conclusion. The slight difference between the lines 1 and 6 seen in the 20 K spectrum is also seen in maghemite particles in literature [44].

From ω and the Mössbauer powder spectra I roughly estimate the particle size to be ~15-20 nm.



Figure A.8: The fitted Mössbauer spectrum of JH047 at 20 K.

A.3 JH050

The sample JH050 was manufactured using iso-octane as solvent, AOT as surfactant and FeSO₄ as iron salt. It has an ω of 17.46.

It was manufactured as a copy of JH048, with a ω 1.5 times larger. It was, as JH047, intended to test the linear particle size dependence of ω .

Just after drying the sample was characterized as light reddish-brownish with lumps. A transcript of the manufacturing log is found in section C.12.

The sample has been investigated using Mössbauer spectroscopy, and the temperature spectrum series is shown in figure A.9.



Figure A.9: Mössbauer spectra as a function of temperature of the sample JH050.

The 120 K spectrum has two main features, a slightly asymmetric doublet, and a very broad sextet. I have fitted these with two Lorentzian doublets to account for the asymmetry, and two sextets to account for the width of the sextet lines. The resulting fit is presented in table A.9 and figure A.10.

Name	Lineshape	B_{HF}	E_Q	δ	b	Area	Area
		Т	$\mathrm{mm/s}$	$\rm mm/s$		$\rm \% mm/s$	%
Doublet 1	Lorentz	-	0.56	0.50	-	10.4	31.5
Doublet 2	Lorentz	-	1.02	0.51	-	15.3	46.5
Sextet 1	Lorentz(3:2:1)	50.1	0.04	0.51	-	4.0	12.1
Sextet 2	Lorentz(3:2:1)	44.7	-0.06	0.47	-	3.3	9.9

Table A.9: The Mössbauer fit parameters for JH050 at 120 K. $\chi^2 = 0.04855$.



Figure A.10: The fitted Mössbauer spectra of JH050. Left: 120 K. Right: 80 K.

The 80 K has the same features as the 120 K spectrum, and the only difference is that the sextets are better developed. My considerations for fitting are the same as for the 120 K spectrum, and I have therefore fitted the spectrum using the same components. The result of the fitting process is presented in figure A.10 and table A.10.

Name	Lineshape	B_{HF}	E_Q	δ	b	Area	Area
		Т	$\mathrm{mm/s}$	$\rm mm/s$		$\rm \% mm/s$	%
Doublet 1	Lorentz	-	0.60	0.52	-	12.2	36.1
Doublet 2	Lorentz	-	0.96	0.54	-	14.5	43.0
Sextet 1	Lorentz(3:2:1)	51.2	0.12	0.52	-	4.2	12.4
Sextet 2	Lorentz(3:2:1)	47.7	-0.02	0.57	-	2.9	8.5

Table A.10: The Mössbauer fit parameters for JH050 at 80 K. $\chi^2 = 0.10241$.

In the 50 K spectrum the evolution of the sextet during cooling continued as I expected. The sextets are sharper, but the doublets have not changed much. I have therefore used the same recipe for fitting the 50 K spectrum as used in the two previous fits. The result of the fitting is presented in table A.11 and figure A.11.

Name	Lineshape	B_{HF}	E_Q	δ	b	Area	Area
		Т	$\mathrm{mm/s}$	$\mathrm{mm/s}$		$\rm \% mm/s$	%
Doublet 1	Lorentz	-	0.80	0.43	-	12.0	32.1
Doublet 2	Lorentz	-	0.83	0.60	-	16.1	42.9
Sextet 1	Lorentz(3:2:1)	51.2	0.08	0.52	-	5.4	14.5
Sextet 2	Lorentz(3:2:1)	47.6	-0.14	0.53	-	4.0	10.6

Table A.11: The Mössbauer fit parameters for JH050 at 50 K. $\chi^2 = 0.07255$.

In the 20 K spectrum the doublet has disappeared and has become a very broad sextet, clearly highly influenced by nano-particle interaction effects. I started by using the result of the 50 K spectrum fit as point of origin, but during fitting it became clear that the component "Sextet 2" in the 50 K fit was not necessary in this fit. I have therefore replaced the two sextets in the 50 K fit by one sextet. The new sextet has been fitted using a broad Split-Lorentz sextet, with



a high parameter value. The result of the fitting process is presented in table A.12 and figure A.11.

Figure A.11: The fitted Mössbauer spectra of JH050. Left: 50 K. Right: 20 K.

Name	Lineshape	B_{HF}	E_Q	δ	b	Area	Area
		Т	$\mathrm{mm/s}$	$\rm mm/s$		$\rm \% mm/s$	%
Sextet 1	Lorentz(3:2:1)	50.8	0.05	0.55	-	10.6	24.0
Sextet 3	S-L(3:2:1)	36.5	-0.08	0.55	1.40	33.7	76.0

Table A.12: The Mössbauer fit parameters for JH050 at 20 K. $\chi^2 = 0.08287$.

The high hyperfine field of the wider sextet, the early development of it and the symmetry of it, all implies that the well ordered sextet is maghemite, most likely relative large particles.

The sextet which formed in the 20 K spectrum is more difficult to identify. It has a quadrupole shift close to zero, and shows signs of interaction, implying a macroscopic magnetic moment of the particles, or that they are very close packed. The new sextet has an isomer shift identical to that of the first-formed sextet, which indicates that they may be composed of the same phase.

This leads me to believe that this component consists of very small, possibly slightly defective or poorly crystalline maghemite particles. It is however somewhat discomforting that it has a hyperfine field significantly lower than that of the high temperature sextet. The possibility that it consists of some other iron oxide can therefore not be entirely eliminated.

From ω and the Mössbauer powder spectra I roughly estimate the particle size to be \sim 30-45 nm.

B TEM images

B.1 JH046



Figure B.1: TEM image of JH046 at 27.5k magnification. The bar is 100 nm.



Figure B.2: TEM image of JH046 at 390k magnification. The bar is 20 nm.

B.2 JH053D



Figure B.3: An example of a TEM image of JH053D. The magnification is 600K, and the scale is indicated by the bar, which has a length of 5 nm.



Figure B.4: An example of a TEM image of JH053D. The magnification is 250K, and the scale is indicated by the bar, which has a length of 10 nm.

C Log of sample manufacturing

The following contains the manufacturing log books entries that are relevant, and in some way discussed in this thesis.

C.1 Stock solutions

The manufactured stock solutions of surfactant dissolved in solvent, which have been used in the synthesis of the samples, are listed below:

20/01/03	329.3 g AOT + 500 ml isooctane. Degas with Ar to remove $O_2.$ Concentration of solution is 1.48 M.
23/04/03	$97.4{\rm g}$ AOT $+$ 400 ml isooctane (NB. possibly contaminated with "parafilm" $<\!0.01{\rm g}$). Concentration of solution is $0.55{\rm M}.$
24/04/03	AOT subjected to vacuum for 24 hours. 94.3 g AOT mixed with 400 ml isooctane. Concentration of solution is 0.53 M.
26/08/03	AOT dried in "bell" drier with static vacuum for one week. 94.65 g AOT mixed with 400 ml isooctane. Concentration of solution is 0.53 M.

C.2 JH029

This section contains a transcript of the manufacturing log of JH029.

Step no.	Description
1	Add $1.32 \text{ g Fe}(\text{II})\text{SO}_4$ in 2 ml water. Dissolve.
2	12 g CTAB mixed with n-butanol to $22 g$, and octane to $62 g$
	and with 2 ml water. Stir.
3	Add 2 ml in Fe(II)SO ₄ solution.
4	Add this in CTAB solution.
5	12 g CTAB mixed with n-butanol to $22 g$,
	and octane to 62 g.
6	Added 6 ml ammonia.
	Seems reaction time is important. 5-10 min then the test tube solutions react on
	magnet.
7	45 ml of CTAB/ammonia solution. Centrifuged at 300rpm.
8	45 ml of CTAB/Fe solution. Centrifuged at 300rpm.
9	Mix on stir plate, Ar flow on top.
10	Color : green to brown to reddish.
	Does not match test tube results! Maybe too much surface in air in beaker.
11	Tossed!

Table C.1: Log entry for manufacturing of JH029

C.3 JH030

This section contains a transcript of the manufacturing log of JH030.

Step no.	Description
1	CTAB 6 g is dissolved in n-butanol to 11 g and octane to 31 g.
2	0.638 g FeSO_4 is dissolved in $2 \text{ ml H}_2\text{O}$.
3	1+2, shaked.
4	Ultrasound 5 min
5	Add ammonia NH_3 1 ml on stir plate with stirring magnet in 50 ml measuring glass.
6	Dark bluish green.
7	After 40 min: brown.
8	Lots of magnetic particles. This reproduces earlier test tube results.
9	Clean with acetone.
10	Centrifuge.

Table C.2: Log entry for manufacturing of JH030

C.4 JH032

This section contains a transcript of the manufacturing log of JH032.

Step no.	Description
22/01/03	JH032 is a repetition of JH022 with more base.
1	$519\mathrm{mg}\;\mathrm{FeSO}_4+2.5\mathrm{ml}\;\mathrm{water}+1\;\mathrm{drop}\;\mathrm{H}_2\mathrm{SO}_4$
2	$22.5 \mathrm{ml}$ AOT/isooctane 3 times diluted
3	$17.5 \mathrm{ml} \mathrm{NH}_3$
4	mix on stir plate i measuring glass overnight
22/01/03	
5	Color: blueish/greenish dark
6	All black powder on stir magnet! Strong attraction to magnet
7	Rinse
8	These particles are probably larger (agglomerated) (JH032L). Smaller particles ex-
	tracted from waste (JH032S).

Table C.3: Log entry for manufacturing of JH032.

C.5 JH032a

This section contains a transcript of the manufacturing log of JH032a, which was an attempt to manufacture hematite.

Step no.	Description						
23/01/03	JH032a as $516 \text{ mg Fe}(\text{II})\text{SO}_4 25 \text{ ml NH}_3$ sodium nitrate.						
	For α -Fe ₂ O ₃ : Heat in decalin (decahydronaphthalene, C ₁₀ H ₁₈)						
	$100 \mathrm{ml}$ decalin in ball glass. Boiling point $185^{\circ}\mathrm{C}$						
	AOT comes off at $\sim 90^{\circ}$ C, useful.						
	heat $\sim 150^{\circ}$ C						
	$\sim 85^{\circ}$ C isooctane/AOT drips off						
	$\sim 80^{\circ}$ C isooctane/water drips off						
	Centrifuge, red color.						
	Wash in chloroform.						
	Wash with water \rightarrow milling stuff						
	Centrifuge						
	Try acetone.						
25/11/03	Attempt to filter out particles. Material was stored in sealed (probably not airtight)						
	plastic tubes. Material was mixed with hardened, yet not crystalline substance. Prob-						
	ably the chloroform has boiled away.						
	Mixed with approx. 50 ml acetone						
	Centrifuged at 2000 rpm for 3 min, and decanted.						
	Mixed with approx. 40 ml acetone						
	Centrifuged at 2000 rpm for 5 min , and decanted.						
	Mixed with approx. 40 ml acetone						
	Centrifuged at 2000 rpm for 2 min, and decanted.						
	Mixed with approx. 40 ml methanol						
	Centrifuged at 2000 rpm for 5 min, then at 2500 rpm for 10 min, nut does not precip-						
	itate.						
	The methanol is boiled away in vacuum chamber overnight.						

Table C.4: Log entry for manufacturing of JH032a.

C.6 JH036

This section contains a transcript of the manufacturing log of JH036.

Step no.	Description
23/01/03	
3	$0.514\mathrm{g}\mathrm{FeSO}_4 + 2.5\mathrm{ml}\mathrm{water}1\mathrm{drop}\mathrm{H}_2\mathrm{SO}_4$
1	AOT/isooctane dilute isooctane $7.5 \mathrm{ml} \rightarrow 22.5 \mathrm{ml}$
2	$AOT/isooctane 7.5 \mathrm{ml} \rightarrow 22.5 \mathrm{ml}$
4	${\rm Add} \ {\bf 3} \ {\bf in} \ {\bf 2}, \ {\bf sonicate} \ {\bf 5} \ {\bf min} \ {\bf \rightarrow 4}$
5	Add 17.5 ml NH_3 in 1 , sonicate 5 min 5
6	Centrifuge 300 rpm 4,5
7	Add 4 and 5 in graduated cylinder
	Stir
8	Color changes too fast to brown
	2 hours
9	Rinse in Acetone

Table C.5: Log entry for manufacturing of JH036.

C.7 JH037

This section contains a transcript of the manufacturing log of JH037.

Step no.	Description				
23/01/03					
	Try new AOT. 24.2 g AOT + 100 ml isooctane ($\sim 0.5 \mathrm{M}$)				
1	$22.5\mathrm{ml}\;\mathrm{AOT/isooctane}+2.5\mathrm{ml}\;\mathrm{NH}_3$				
2	$22.5\mathrm{ml}$ AOT/isooctane				
3	$0.513\mathrm{g}\mathrm{FeSO}_4 + 2.5\mathrm{ml}\mathrm{water} + 1\mathrm{drop}\mathrm{H}_2\mathrm{SO}_4$				
4	mix 2 + 3 , no orange!				
5	Sonicate 5 min				
6	Centrifuge 300 rpm				
7	$17.5 \mathrm{ml} \mathrm{of} 1 \mathrm{in} \mathbf{2+3}, \mathrm{stir},$				
8	greenish, dark, stir 1 hour				
9	Small dark stuff on magnet, magnetic (holds paper).				
10	Rinse, magnetically separate				
11	Methanol, acetone				
12	Small "tadpoles" in sample				
13	Works fine				
14	Separate/Centrifuge. "Top" part of JH037 does not separate during centrifuging,				
	named JH037T. "Bottom" part of JH037 does separate during centrifuging.				
15	Washed JH037T with water and acetone (2-3 times).				

Table C.6: Log entry for manufacturing of JH037.

C.8 JH041

This section contains a transcript of the manufacturing \log of JH041.

Step no.	Description
24/01/03	
1	6.1 g CTAB mixed with 50 ml CHCl_3 in flask, stir. Becomes yellow.
2	6.5 g CTAB mixed with 50 ml CHCl_3 , add 1 ml NH_3 , shake
3	0.253 g Iron(II) chloride FeCl ₂ mixed with 1 ml water, and mixed with 1
4	Pour 2 into 1 in sealed ball glass with ammonia saturated Ar atmosphere. Color:
	Green.
5	Stir overnight
6	It is possible to play with the amount of base (maybe more is needed)
25/01/03	Wash/Centrifuged with acetone, methanol, chloroform (removes water then CTAB).

Table C.7: Log entry for manufacturing of JH041.

C.9 JH046

This section contains a transcript of the manufacturing log of JH046.

Step no.	Description			
23/04/03				
	With Argon, 100 ml narrow sealable measuring glass			
1	$0.520\mathrm{g}\;\mathrm{FeSO}_4+2.5\mathrm{ml}\;\mathrm{water}+1\;\mathrm{drop}\;\mathrm{H}_2\mathrm{SO}_4$			
2	22.5 ml AOT/isooctane stock solution(23/04/03)			
3	$22.5 \text{ ml AOT/isooctane stock solution} (23/04/03) + 2.5 \text{ NH}_3$			
4	Sonicate 1, 2, 3			
5	stir 2 add 1 (does not go clear)			
6	stir add 3 dark green			
7	looks like JH045			
8	stir 1 hour \rightarrow first frozen sample			
9	stir overnight sealed.			
24/04/03	Color: BLACK			
1	poured 10 ml into bottle with Argon			
2	Washed the rest with acetone under Argon, with powerful magnet applied. Cen-			
	trifuged, decanted \rightarrow (1. rest marked "46 1. rest"). Material on magnet highly			
	magnetic and black, saved on paper.			
3	After centrifuging mixed with chloroform under Argon and poured into separation			
	funnel under Argon.			
4	Centrifuged the fluid, does not separate.			
5	The poured-off material poured back into funnel with 100 ml methanol			
6	Used magnetic filtering in several rounds. The magnetic material poured into bottle			
	marked "46 konc.". Used methanol.			
05/04/00				
25/04/03				
8	Put 2 ml of konc. aside for TEM and Mossbauer.			
9	Drying			
28/04/03	Kesult: Brown-black very magnetic lumps. Stored under Argon.			
06/05/03	2m1 of TEM sample frozen in nitrogen for measurement at DTU.			
12/05/03	Still fish in the TEM sample.			

Table C.8: Log entry for manufacturing of JH046.

C.10 JH047

This section contains a transcript of the manufacturing log of JH047.

23/04/03					
Step no.	Description				
1	$527 \operatorname{mg} \operatorname{FeSO}_4 2.7 \operatorname{g}$ water				
2	$45 \mathrm{ml}$ AOT/isooctane stock solution $(23/04/03)$				
3	$45\mathrm{ml}\mathrm{AOT/isooctane} + 2.5\mathrm{ml}\mathrm{ammonia}$				
4	$1{+}2 ightarrow ext{yellow}$				
5	$\mathrm{Add}\ 3 \to \mathrm{blue} \to \mathrm{green}$				
6	stir overnight				
$\begin{array}{c}24/04/03\\7\\8\end{array}$	Wash with acetone - Chloroform - Methanol Magnetic separation with methanol				
$\frac{25/04/03}{9}$	Drying				
28/04/03	Result: Black, very magnetic particles. In the first thin layers, the color has a tendency towards red-brown. Stored in Argon.				

 Table C.9: Log entry for manufacturing of JH047

C.11 JH048

This section contains a transcript of the manufacturing log of JH048.

Step no.	Description				
24/04/03					
1	$522 \operatorname{mg} \operatorname{FeSO}_4 + 2.5 \operatorname{ml} \operatorname{H}_2\operatorname{O} + 1 \operatorname{drop} \operatorname{H}_2\operatorname{SO}_4$				
2	$22.5 \mathrm{ml}$ AOT/isooctane (from stock $24/04/03$)				
3	$22.5 \text{ ml AOT/isooctane} + 2.5 \text{ ml konc. NH}_3.$				
4	Mixed $1+2$ = whitish solution. Centrifuged to clear solution, lost 2ml.				
5	Added 3, color: green \rightarrow black(bottom)/red(top). Within minutes changed to black				
	overall, yet greenish at bottom.				
6	Stir overnight.				
25/04/03					
7	Green color disappeared.				
	Material stuck on drier black and very magnetic (able to lift paper).				
8	Washed with acetone then chloroform.				
9	Magnetically filtered with chloroform, then methanol.				
10	After filtering taken sample (2 ml) of konc. before drying (for TEM + Mössbauer).				
11	Drying.				
28/04/03	Result: Fine very magnetic powder. Color: grey-brown. Stored under Ar.				
06/05/03	Taken approx. 2 ml from TEM-sample and frozen it in nitrogen for DTU. Had to be				
. ,	thinned with methanol, due to lack of material. Very little left.				

 Table C.10: Log entry for manufacturing of JH048

C.12 JH050

This section contains a transcript of the manufacturing log of JH050.

Step no.	Description			
25/04/03				
1	$1.54\mathrm{g} + 7.5\mathrm{ml}\mathrm{H_2O} + (\mathrm{I}\mathrm{think}1\mathrm{drop}\mathrm{of}\mathrm{H_2SO_4}\mathrm{added},\mathrm{yet}\mathrm{not}\mathrm{sure})$			
2	45 ml AOT/isooctane (stock 25/04/03 (must be 24/04/03))			
3	$45\mathrm{ml}$ AOT/isooctane + $7.5\mathrm{ml}$ NH $_3$			
4	Centrifuged 1, sonicated 2 and 3			
5	1+2=4			
6	Centrifuged 4, lost 10 ml , meaning that 4 has a volume of 45 ml			
7	Added 48 ml 3 . From here under Argon.			
8	Put under slow stirring under Argon, over the weekend.			
28/04/03	Everything under Argon.			
9	Mixed with 250 ml acetone in separation funnel. Color: Black with green nuance.			
10	Centrifuged at speed 2. After that washed, centrifuged several times.			
11	Very hard to separate magnetically, unsure why. Maybe laking acid.			
12	With much effort, filtered out a part marked as "50 konc.". The rest dried as "50			
	Semi". This is the result of many (approx. 10) rounds of washing by methanol, and			
	prior to this acetone and chloroform.			
13	Drying			
14	Done drying. Color : light red-brown. Consistency: Had lumps. Crushed in glass,			
	and stored under Argon.			

Table C.11: Log entry for manufacturing of JH050.

C.13 JH053

This section contains a transcript of the manufacturing log of JH053.

Step no.	Description				
29/08/03					
1	$0.2836\mathrm{g}\mathrm{FeSO}_4 + 1.25\mathrm{ml}\mathrm{H_2O} + 1\mathrm{drop}\mathrm{H_2SO}_4$				
2	22 ml Stock solution (26/08/03)				
3	3=1+2				
3b	$22\mathrm{ml}$ AOT-stock + 1.25	ml NH ₃			
4	Centrifuged 3, decanted, now clear, pH=3.				
5	3b and 3 sonicated under Ar atmosphere.				
6	(12.25) 3b and 3 poured fast together. Color: green $(2 \text{ sec}) \rightarrow \text{ black } (15 \text{ sec}) \rightarrow$				
	green/black within a minute.				
7	Left stirring				
01/09/03	Color: Black, but with a vague trance of brownish/greyish.				
1	Sample JH053A taken and stored in 2 mm Mössbauer container, and frozen in liquid				
	nitrogen.				
2	Sample JH053B taken a	nd sealed under Ar.			
3	Material stuck on stirring magnet is black and highly magnetic. Possible to lift the				
	piece of paper used to clean stirring magnet, using the filtering magnet.				
4	Washing and magnetic filtering of sample:				
	$110 \mathrm{ml}$ Actone	Poured away all that did not stick to magnet,			
		except the first bottom layer.			
	$110 \mathrm{ml}$ Methanol	Poured away all that did not stick to magnet.			
	$50 \mathrm{ml}$ Methanol	Poured back the bottom layer. Poured away			
		all that did not stick to magnet.			
	40 ml Methanol	Magnetic filtering.			
	40 ml Methanol				
	$20\mathrm{ml}$ poured off	Sample taken for TEM "JH053C" under Ar.			
	Centrifuged, decanted	Sample "JH053D" stored in liquid nitrogen in			
		1 mm DTU sample holder.			
	Dried in vacuum	JH053E			

Table C.12: Log entry for manufacturing of JH053.

D Mössbauer measurement log

This section contains an overview of all Mössbauer measurements made during this thesis work. Since the measurements have been performed at both \emptyset L and DTU, the log has been divided into two sub sections containing these measurements from these two locations.

D.1 ØL Mössbauer log

Name	Vel.	Remarks	Time	В	Т
A10002	8	α -Fe foil	$12/03/02 \ 13:40 \rightarrow 14/03/02 \ 12:30$	0 T	$295\mathrm{K}$
A10010	8	JH001 0.4T	$04/04/02 \ 16:00 \rightarrow 05/04/03 \ 07:30$	$0.35\mathrm{T}\parallel$	$295\mathrm{K}$
A10012	8	JH003a	$10/04/02 \ 12:00 \rightarrow 17/04/03 \ 16:00$	$0 \mathrm{T}$	$295\mathrm{K}$
A10016	8	JH001	$23/04/02 \ 08:30 \rightarrow 25/04/02 \ 13:00$	$0 \mathrm{T}$	$14\mathrm{K}$
A10017	8	JH001	$25/04/02 \ 13:00 \rightarrow 26/04/02 \ 15:30$	$0 \mathrm{T}$	$24\mathrm{K}$
A10018	8	JH001	$26/04/02 \ 16:00 \rightarrow 28/04/02 \ 10:30$	$0 \mathrm{T}$	$30\mathrm{K}$
A10019	8	JH001	$28/04/02 \ 11:15 \rightarrow 29/04/02 \ 14:30$	$0 \mathrm{T}$	$40\mathrm{K}$
A10023	8	JH003a	$30/04/02 \ 13:00 \rightarrow 01/05/02 \ 12:00$	$0 \mathrm{T}$	$20\mathrm{K}$
A10025	8	JH003a	$01/05/02 \ 17:30 \rightarrow 02/05/02 \ 13:00$	$0 \mathrm{T}$	$40\mathrm{K}$
A10028	8	JH005	$07/05/02 \ 14:30 \rightarrow 07/05/02 \ 16:00$	$0 \mathrm{T}$	$30\mathrm{K}$
A10029	8	JH005	$07/05/02 \ 16:30 \rightarrow 08/05/02 \ 10:30$	$0 \mathrm{T}$	$35\mathrm{K}$
A10033	8	JH009	$13/05/02 \ 16:20 \rightarrow 14/05/02 \ 15:00$	$0 \mathrm{T}$	$14\mathrm{K}$
A10034	8	m JH009+F1+F3	$14/05/02 \ 16:50 \rightarrow 15/05/02 \ 11:00$	$0 \mathrm{T}$	$29\mathrm{K}$
A10059	8	α -Fe (12.5 μ)	$09/09/02 \ 08:45 \rightarrow 10/09/02 \ 09:45$	$0 \mathrm{T}$	$295\mathrm{K}$
A10067	8	JH013 (off by accident)	$27/09/02$ 14:14 $\rightarrow 27/09/02$ 17:10	$0 \mathrm{T}$	$17\mathrm{K}$
A10068	8	JH013	$27/09/02 \ 17:15 \rightarrow 30/09/02 \ 14:30$	$0 \mathrm{T}$	$17\mathrm{K}$
A10069	8	JH014 bottom a) (dark)	$30/09/02 \ 14:12 \rightarrow 02/10/02 \ 17:00$	$0 \mathrm{T}$	$17\mathrm{K}$
A10070	8	JH014 bottom a)	$02/10/02 \ 17:00 \rightarrow 04/10/02 \ 13:00$	$0 \mathrm{T}$	$30\mathrm{K}$
A10071	8	JH014 bottom a)	$04/10/02 \ 15:55 \rightarrow 07/09/02 \ 09:00$	$0 \mathrm{T}$	$40\mathrm{K}$
A10072	8	JH014 bottom a)	$07/10/02 \ 12:30 \rightarrow 08/09/02 \ 12:00$	$0 \mathrm{T}$	$50\mathrm{K}$
A10076	6	α -Fe foil	$15/10/02 \ 14:30 \rightarrow 15/10/02 \ 17:30$	$0 \mathrm{T}$	$295\mathrm{K}$
A10088	6	JH014Top	$07/11/02 \ 13:45 \rightarrow 11/11/02 \ 14:30$	$0 \mathrm{T}$	$14.8\mathrm{K}$
A10089	6	JH014Top	$11/11/02 \ 17:15 \rightarrow 12/11/02 \ 15:00$	$0 \mathrm{T}$	$40\mathrm{K}$
A10090	6	JH014Top	$12/11/02 \ 15:30 \rightarrow 20/11/02 \ 13:50$	$0 \mathrm{T}$	$60\mathrm{K}$
A10095	6	JH015b (lille prøve)	$17/12/02 \ 14:15 \rightarrow 18/12/02 \ 15:00$	$0 \mathrm{T}$	$295\mathrm{K}$
A10096	6	JH015b (lille prøve)	$18/12/02 \ 18:00 \rightarrow 19/12/02 \ 13:00$	$0 \mathrm{T}$	$78\mathrm{K}$
A10097	6	m JH015b	$19/12/02 \ 14:30 \rightarrow 23/12/02 \ 11:00$	$0 \mathrm{T}$	$13\mathrm{K}$
A10098	6	JH015b (ingen effekt)	$23/12/02 \ 13:00 \rightarrow 25/12/02 \ 19:30$	$0 \mathrm{T}$	$25\mathrm{K}$
A10099	6	m JH015b	$25/12/02 \ 20:00 \rightarrow 30/12/02 \ 10:30$	$0 \mathrm{T}$	$25\mathrm{K}$
A10100	6	m JH015b	$30/12/02 \ 11:00 \rightarrow 02/01/03 \ 15:30$	$0 \mathrm{T}$	$35\mathrm{K}$
A10101	6	JH015b	$02/01/03 \ 16:00 \rightarrow 03/01/03 \ 12:30$	$0 \mathrm{T}$	$50\mathrm{K}$
A10102	6	m JH015b	$03/01/03 \ 13:00 \rightarrow 06/01/03 \ 11:00$	$0 \mathrm{T}$	$80\mathrm{K}$
A10103	6	JH016	$06/01/03 \ 12:30 \rightarrow 07/01/03 \ 16:00$	$0 \mathrm{T}$	$80\mathrm{K}$
A10104	6	JH016	$08/01/03 \ 13:00 \rightarrow 09/01/03 \ 16:30$	$0 \mathrm{T}$	$25\mathrm{K}$
A10105	6	JH016	$09/01/03 \ 17:00 \rightarrow 14/01/03 \ 16:30$	$0 \mathrm{T}$	$15\mathrm{K}$
A10106	6	m JH01614.75K	$14/01/03 \ 10:30 \rightarrow 21/01/03 \ 18:00$	$0 \mathrm{T}$	$14\mathrm{K}$
A10107	6	JH020	$21/01/03 \ 19:30 \rightarrow 22/01/03 \ 14:30$	$0 \mathrm{T}$	$273\mathrm{K}$
A10108	6	JH022	$22/01/03 \ 18:00 \rightarrow 23/01/03 \ 09:00$	$0 \mathrm{T}$	$ ightarrow 85\mathrm{K}$
A10109	6	JH022	$23/01/03 \ 09:00 \rightarrow 29/01/03 \ 15:00$	0 T	$\rightarrow 25\mathrm{K}$

Table D.1: \emptyset rsted Laboratory Mössbauer log I. Vel. stands for velocity setting. **B** stands for applied B-field. **T** stands for temperature.
Name	Vel.	Remarks	Time	В	Т
A10110	6	JH041 magnetite?	$29/01/03 \ 15:00 \rightarrow 30/01/03 \ 13:00$	0 T	$\rightarrow 80 \mathrm{K}$
A10111	6	JH041 magnetite?	$30/01/03 \ 13:00 \rightarrow 31/01/03 \ 15:00$	$0 \mathrm{T}$	$80\mathrm{K}$
A10112	6	JH041 magnetite?	$31/01/03 \ 16:05 \rightarrow 03/02/03 \ 15:00$	$0 \mathrm{T}$	$\rightarrow 14 \mathrm{K}$
A10113	6	JH041 magnetite?	$03/02/03 \ 15:00 \rightarrow 04/02/03 \ 17:30$	$0 \mathrm{T}$	$295\mathrm{K}$
A10119	6	JH036	$15/02/03 \ 15:15 \rightarrow 17/02/03 \ 14:00$	$0 \mathrm{T}$	$295\mathrm{K}$
A10120	6	JH036	$17/02/03 \ 19:00 \rightarrow 19/02/03 \ 07:30$	$0 \mathrm{T}$	$200\mathrm{K}$
A10121	6	JH036	$19/02/03 \ 11:30 \rightarrow 20/02/03 \ 10:00$	$0 \mathrm{T}$	$80\mathrm{K}$
A10122	6	JH036	$20/02/03 \ 10:30 \rightarrow 24/02/03 \ 13:00$	$0 \mathrm{T}$	$24.6\mathrm{K}$
A10123	6	JH036	$24/02/03 \ 13:30 \rightarrow 28/02/03 \ 12:00$	$0 \mathrm{T}$	$15.2\mathrm{K}$
A10150	6	JH037T	$02/05/03 \ 15:00 \rightarrow 03/05/03 \ 19:00$	$0 \mathrm{T}$	$295\mathrm{K}$
A10151	6	JH037T	$04/05/03 \ 19{:}20 \rightarrow 05/05/03 \ 16{:}00$	$0 \mathrm{T}$	$78\mathrm{K}$
A10152	6	JH037T	$05/05/03 \ 17:00 \rightarrow 07/05/03 \ 13:00$	$0 \mathrm{T}$	$60\mathrm{K}$
A10153	6	JH037T	$07/05/03$ 14:00 $\rightarrow 08/05/03$ 16:30	$0 \mathrm{T}$	$40\mathrm{K}$
A10154	6	JH037T	$08/05/03$ 16:30 $\rightarrow 11/05/03$ 18:20	$0 \mathrm{T}$	$20\mathrm{K}$
A10155	6	JH037T	$11/05/03 \ 18:30 \rightarrow 13/05/03 \ 15:45$	$0 \mathrm{T}$	$14\mathrm{K}$
A10159	6	JH050 konc pumpe	$27/05/03 \ 16:35 \rightarrow 28/05/03 \ 16:10$	$0 \mathrm{T}$	$80\mathrm{K}$
A10160	6	JH050 konc pumpe	$28/05/03 \ 16:49 \rightarrow 31/05/03 \ 13:00$	$0 \mathrm{T}$	$50\mathrm{K}$
A10161	6	JH050 konc pumpe	$31/05/03 \ 13:40 \rightarrow 02/06/03 \ 11:35$	$0 \mathrm{T}$	$20\mathrm{K}$
A10162	6	JH050 konc pumpe	$02/06/03 \ 12:00 \rightarrow 03/06/03 \ 18:10$	$0 \mathrm{T}$	$80\mathrm{K}$
A10163	6	JH050 konc pumpe	$03/06/03$ $18:55 \rightarrow 06/06/03$ $16:20$	$0 \mathrm{T}$	$120\mathrm{K}$
A10164	6	JH050 konc pumpe	$06/06/03$ 17:24 $\rightarrow 11/06/03$ 13:20	$0 \mathrm{T}$	$295\mathrm{K}$
A10195	6	JH053E ny	$02/09/03 \ 18{:}00 ightarrow 03/09/03$	$0 \mathrm{T}$	$143\mathrm{K}$
A10196	6	JH053E ny	$04/09/03 \ 09:00 \rightarrow 05/09/03 \ 12:50$	$0 \mathrm{T}$	$80\mathrm{K}$
A10197	6	JH053E ny	$05/09/03$ 12:50 $\rightarrow 08/09/03$ 11:30	$0 \mathrm{T}$	$20\mathrm{K}$
A10198	6	JH053E ny	$08/09/03 \ 15:30 \rightarrow 09/09/03 \ 08:45$	$0 \mathrm{T}$	$295\mathrm{K}$
A10199	6	alpha-Fe folie, pumpe tændt	$09/09/03 \ 10:00 \rightarrow 09/09/03 \ 11:20$	$0 \mathrm{T}$	$295\mathrm{K}$
A10204	6	JH053E	$15/09/03$ 12:45 $\rightarrow 19/09/03$ 12:25	$0 \mathrm{T}$	$295\mathrm{K}$
A10205	6	JH053E	$23/09/03 \ 13:00 \rightarrow 21/10/03 \ 12:15$	$0 \mathrm{T}$	$100\mathrm{K}$
A10206	6	JH053E	$21/10/03 \ 13:45 \rightarrow 23/10/03 \ 12:15$	$0 \mathrm{T}$	$50\mathrm{K}$
A10207	6	JH053E	$23/10/03 \ 13:30 \rightarrow 28/10/03 \ 18:10$	$0 \mathrm{T}$	$120\mathrm{K}$
A10208	6	JH053E varmet til $180\mathrm{K}$	$28/10/03$ $18:10 \rightarrow 30/10/03$ $14:30$	$0 \mathrm{T}$	$\rightarrow 180\mathrm{K}$
A10209	6	JH053E	$30/10/03 \ 14:30 \rightarrow 03/10/03 \ 16:45$	$0 \mathrm{T}$	$180\mathrm{K}$
A10210	6	JH053E	$03/11/03 \ 17:00 \rightarrow 07/11/03 \ 14:00$	$0 \mathrm{T}$	$240\mathrm{K}$
A10211	6	JH053E	$07/11/03 \ 14{:}20 \rightarrow 10/11/03 \ 11{:}45$	$0.2\mathrm{T}\ $	$295\mathrm{K}$
A10212	6	JH053E	$10/11/03 \ 17{:}40 \rightarrow 17/11/03$	$0.2\mathrm{T}\ $	$143\mathrm{K}$
A10213	6	JH053E Fe-forurening?	$17/11/03 \ 17:40 \rightarrow 21/11/03 \ 18:48$	$0.2\mathrm{T}\ $	$20\mathrm{K}$
A10214	6	JH053E Fe-forurening?	$21/11/03 \ 19:00 \rightarrow 26/11/03 \ 15:30$	$0.2\mathrm{T}\ $	$80\mathrm{K}$
A10215	6	JH032a	$26/11/03$ 18:18 $\rightarrow 27/11/03$ 14:00	$0 \mathrm{T}$	$295\mathrm{K}$
A10216	6	JH032a med pumpe	$28/11/03 \ 17{:}00 \to 01/12/03 \ 16{:}00$	$0 \mathrm{T}$	$20\mathrm{K}$
A10217	6	JH032a med pumpe	$01/12/03 \ 18:00 \rightarrow 02/12/03 \ 12:17$	$0 \mathrm{T}$	$80\mathrm{K}$

Table D.2: \emptyset rsted Laboratory Mössbauer log II. Vel. stands for velocity setting. **B** stands for applied B-field. **T** stands for temperature.

D.2 DTU Mössbauer log

The Mössbauer log from DTU has been sorted by sample since considerations with calibration and measurements order have not been relevant for my work, since these were controlled by the staff at DTU.

Name	Sample	Time	В	Т
31010305	JH021	31/01/03	0 T	$295\mathrm{K}$
03020301	JH021	03/02/03	$0 \mathrm{T}$	$80\mathrm{K}$
05020304	JH021	05/02/03	$0 \mathrm{T}$	$50\mathrm{K}$
04020301	JH021	04/02/03	$0 \mathrm{T}$	$20\mathrm{K}$
06020303	JH021	06/02/03	$1.0\mathrm{T}$	$295\mathrm{K}$
03020303	JH030	03/02/03	$0 \mathrm{T}$	$295\mathrm{K}$
04030301	JH030	04/03/03	$0 \mathrm{T}$	$295\mathrm{K}$
27020303	JH030	27/02/03	$0 \mathrm{T}$	$80\mathrm{K}$
05030302	JH030	05/03/03	$0 \mathrm{T}$	$20\mathrm{K}$
03020305	JH032L 40 mg	03/02/03	$0 \mathrm{T}$	$295\mathrm{K}$
20030303	JH032L 160 mg	20/03/03	$1.40\mathrm{T}$	$295\mathrm{K}$
03020305	JH032L 160 mg	03/02/03	$0 \mathrm{T}$	$295\mathrm{K}$
02030301	JH032L 160 mg	02/03/03	$0 \mathrm{T}$	$250\mathrm{K}$
01030301	JH032L 160 mg	01/03/03	$0 \mathrm{T}$	$200\mathrm{K}$
03030301	JH032L 160 mg	03/03/03	$0 \mathrm{T}$	$140\mathrm{K}$
05020302	JH032L 40 mg	05/02/03	$0 \mathrm{T}$	$80\mathrm{K}$
28020301	JH032L 160 mg	28/02/03	$0 \mathrm{T}$	$80\mathrm{K}$
04030302	JH032L 160 mg	04/03/03	$0 \mathrm{T}$	$20\mathrm{K}$
03020304	JH032S 40 mg	03/02/03	$0 \mathrm{T}$	$295\mathrm{K}$
04030305	JH032S $70 \mathrm{mg}$	04/03/03	$0 \mathrm{T}$	$200\mathrm{K}$
20030305	JH032S 70 mg	20/03/03	$0.5\mathrm{T}$	$200\mathrm{K}$
04020303	JH032S 40 mg	04/02/03	$0 \mathrm{T}$	$80\mathrm{K}$
28020302	JH032S 150 mg	28/02/03	$0 \mathrm{T}$	$80\mathrm{K}$
03030303	JH032S $70 \mathrm{mg}$	03/03/03	$0 \mathrm{T}$	$20\mathrm{K}$
06040301	m JH036~115mg	06/04/03	$0\mathrm{T}$	$80\mathrm{K}$
07040303	JH036	07/04/03	$0\mathrm{T}$	$295\mathrm{K}$
16040302	JH036 $115\mathrm{mg}$	16/04/03	$0\mathrm{T}$	$23\mathrm{K}$
23040303	JH036 $115\mathrm{mg}$	16/04/03	$0.50\mathrm{T}$	$80\mathrm{K}$
22030301	JH041 $140\mathrm{mg}$	22/03/03	$0 \mathrm{T}$	$295\mathrm{K}$
24030301	JH041 $140\mathrm{mg}$	24/03/03	$1.40\mathrm{T}$	$295\mathrm{K}$
02060301	JH046L	02/06/03	$0 \mathrm{T}$	$20\mathrm{K}$
08090301	JH046P	08/09/03	$0 \mathrm{T}$	$295\mathrm{K}$
14090301	JH046P	14/09/03	$0 \mathrm{T}$	$80\mathrm{K}$
11090301	JH046P	11/09/03	$0 \mathrm{T}$	$20\mathrm{K}$
14090302	JH047	14/09/03	$0 \mathrm{T}$	$295\mathrm{K}$
19090302	JH047	19/09/03	$0 \mathrm{T}$	$80\mathrm{K}$
18090302	JH047	18/09/03	$0 \mathrm{T}$	$20\mathrm{K}$
08050304	JH048L	08/05/03	$0 \mathrm{T}$	$80\mathrm{K}$
28050301	JH048L	28/05/03	$0 \mathrm{T}$	$20\mathrm{K}$
18090303	JH048P	18/09/03	$0 \mathrm{T}$	$295\mathrm{K}$
15090304	JH048P	15/09/03	$0 \mathrm{T}$	$80\mathrm{K}$
17090303	JH048P	17/09/03	$0 \mathrm{T}$	$20\mathrm{K}$
08100301	JH053A	08/10/03	$0 \mathrm{T}$	$80\mathrm{K}$
22090304	JH053A	22/09/03	$0 \mathrm{T}$	$20\mathrm{K}$
05100301	JH053D	05/10/03	$0 \mathrm{T}$	$80\mathrm{K}$
28090302	JH053D	28/09/03	$0 \mathrm{T}$	$20\mathrm{K}$

Table D.3: DTU Mössbauer log. **B** is the applied B-field. **T** is temperature.

E TEM log

E.1 TEM log 19-05-02

Log from TEM session 19-05-2003. Present are Erik Johnson, Jari Hjøllum, Luise Theil Kuhn

Image no.	Magnification	Remarks
8084	x4.4k	
8085	x44k	
8086	x44k	
8087	x3.4k	
8088	x27.5	20kV. Magnetite (Fe ₃ O ₄) nanoparticles.
		Carbon grid "A6" (made from JH046).
8089	x27.5	
8090		Diffraction on 8088
8091	x27.5	
8092	x27.5	
8093		Diffraction on 8092 . D= 620 nm.
8094	x27.5k	
8095	x27.5k	
8096	x27.5k	
8097	x27.5k	
8098		Diffraction
8099	x27.5k	
8100	x390k	Planes visible
8101	x390k	Planes visible
		Sample change to "A7" (made from JH048)
8102	x50k	
8103		Diffraction
8104	x50k	
8105	x38	
8106	x50k	
		Sample change, more material needed. Made from JH048
8107	x50k	
8108		Diffraction
8109	x50k	
8110	x50k	
8111	x50k	
8112	x50k	
8113	x50k	
8114	x50k	
		Film taken out.

Table E.1: Transcript of TEM logbook.

F Carbon nano-onion particles

TEM images were made from the sample JH048 liquid. The particles were found to have spherical shape, which was surprising. However, the number of particles found was also surprisingly low, since only 6 particles were found.

Two of the particles are shown in figure F.1 and figure F.2.



Figure F.1: TEM images of one of the largest spherical particles of JH048: Particle #1 at 600k magnification. The bar has a length of 5 nm.

The spherical particles appear to be composed of concentric spheres, which is very unusual.

To identify the composition of the particles, I have measured the lattice distance of the particles. The lattice distance data is presented in table F.2.

The mean lattice distance is found to be 3.29 Å. Materials found to have x-ray diffraction lines close to this are carbon, lepidocrocite, maghemite, and the data of these are listed in table F.1.

Initially carbon in some form can not be ruled out, since the particles are deposited on a carbon grid, which sometimes [36] can contain carbon nano-tubes. Graphite and C60 have reflection planes close to the measured lattice distance, and are therefore included in table F.1.

It is very unlikely that the onion shell particles consist of multi-walled carbon nano-tubes seen from the end. However, there are examples of carbon nano onions creation under intense radiation and above 673 K. These carbon nano onions can go through three stages. In the first stage nanotubes and fullerenes (such as C60), which can be created from graphite, transform into onion-like fullerenes (onions). The onions consist of closed concentrically nested graphitic shells with an inter-shell distance of 0.335 nm. Under continued intense radiation and the electron shells



Figure F.2: TEM images of one of the largest spherical particles of JH048: Particle #6 at 600k magnification. The bar has a length of 5 nm.

Mineral	Lattice distance
	Å
Maghemite	2.95
Carbon, graphite	3.35
Carbon, C60	2.56
Lepidocrocite	3.29

Table F.1: A listing of minerals with x-ray reflection lines close to the found lattice distance of JH048L. The data is found at [62].

shrink by rearrangement and closure of vacancies, down to shell distances of 0.22 nm at the center. Further radiation may produce diamond particles at the core [27, 38, 53].

Comparing the lattice distance of the found particles with those found in literature, and the images with those in literature [6], I find it very likely that the onion-like particles in our sample are indeed carbon nano onions. We may even have created these ourselves during the TEM session, since the TEM used has a quite intense electron beam.

To investigate the particles further, I have made a measurement of the inter-shell distance variation. The shell distance was measured in segments of 5 shells, starting at first clear shell from the surface. The measured data is presented in figure F.3. These data reveal that the particles are still at stage 1, where the shell distance is constant.



Figure F.3: The variation in shell distance of the spherical particles. Three particles have been analyzed, and the shell spacing measured over segments of 5 shells, where segment 1 is at the surface. The dotted lines are placed at the distances 0.335 nm, 0.29 nm and 0.22 nm.

I have measured the size of the particles in the sample. The diameter of the particles was measured across the center of the particles. The size distribution of the particles without the shell of soap material is presented in table F.3 and figure F.4.

The particle diameter is found to match that reported in literature, where it is reported that the diameter of carbon onions particles ranges from 2 shells to several hundred [6].



Figure F.4: The size distribution of the round particles of JH048.

,							
Particle	Magn.	х	У	a	a	Ν	\mathbf{d}
		pixel	pixel	pixel	nm		nm
#1	600k	536	346	638	10.45	32	0.326
#1	600k	364	160	398	6.51	20	0.326
#2	600k	167	59	177	2.90	10	0.290
#2	600k	154	44	160	2.62	9	0.291
#3	600k	285	158	326	5.34	16	0.334
#4	600k	299	35	301	4.93	15	0.329
#4	600k	225	243	331	5.42	16	0.339
#5	600k	156	297	335	5.49	16	0.343
#5	600k	155	129	202	3.30	9	0.367
#6	600k	944	192	963	15.77	47	0.336
#6	600k	357	323	481	7.88	23	0.343
						$ar{d} =$	0.329
						$\sigma_d =$	0.022

Table F.2: A measurement of the lattice distance of particles of JH048 liquid.

Particle	Res.	Δx_1	Δy_1	Z 1	Δx_2	Δu_2	Z9	\overline{z}	d
	nm/pixel	pixel	pixel	pixel	pixel	pixel	pixel	pixel	nm
#1	0.01637	2310	15	2310	15	2235	2235	2273	37.2
#2	0.01637	712	108	720	20	708	708	714	11.7
#3	0.01637	2148	608	2232	732	2100	2224	2228	36.5
#4	0.01637	822	93	827	117	990	997	912	14.9
#5	0.01637	1065	12	1065	39	1101	1102	1083	17.7
#6	0.01637	2040	1536	2554	1818	2310	2940	2747	45.0
								$ar{d} =$	27.2
								$\sigma_d =$	14.0

Table F.3: A measurement of the size distribution of particles of JH048 liquid.

G ⁵⁷Fe Mössbauer minerals

This section contains data on Mössbauer minerals that have been used throughout the thesis.

G.1 ⁵⁷Fe Mössbauer data

Below the Mössbauer spectroscopy parameters for selected iron compounds are listed.

Name	Temp.	B_{hf}	δE	E_Q
	Κ	Т	$\mathrm{mm/s}$	$\mathrm{mm/s}$
Hematite	295	51.7	0.37	-0.10
Hematite	80	54.2	0.48	0.20
Hematite	4.2	54.2	0.49	0.20
Goethite	295	38.1	0.37	-0.13
Goethite	80	50.1	0.48	-0.13
Goethite	4.2	50.1	0.48	-0.13
Magnetite A	295	49.0	-0.01	0.26
Magnetite B	295	46.0	0.00	0.67
Maghemite	295	49.9	0.32	0.01
Maghemite	80	52.6	0.44	0.01
Maghemite	4.2	52.6	0.44	0.01

Table G.1: Mössbauer parameters for selected Mössbauer minerals. Values from [42].

G.2 Crystallographic data

Below the crystallographic parameters for selected iron compounds are listed.

Name	Crystal	a	b	с	D_1	D_2	D_3
	system	Å	Å	Å	Å	Å	Å
Magnetite	cubic, inv. spinel	8.391			2.53(1)	1.483(0.85)	1.614(0.85)
Maghemite	cubic, spinel	8.339			1.61(1)	2.52(1)	2.95(1)
Lepidocrocite	orthorhombic	3.868	12.525	3.066	6.26(1)	3.29(0.9)	2.47(0.8)
Goethite	orthorhombic	4.596	9.957	3.021	4.18(1)	2.69(0.3)	2.452(0.25)
Hematite	hexagonal	5.0317		13.737	2.69(1)	1.69(0.6)	2.51(0.5)
Akaganéite	cubic, bcc				1.635(1)	3.311(1)	7.4(1)

Table G.2: Crystal data for selected minerals. a,b,c are lengths of unit cell edges. D_1 , D_2 , D_3 are main X-ray diffraction lines. The number in parenthesis is the relative intensity. Values from [20, 62].

G.3 X-ray reflections

This section contains calculated reflections of selected iron oxides. The calculations have been performed using Oxford Cryosystems Crystallographica [1].

h	k	1	Ν	d 2θ	\mathbf{F}^2]	h	k	1	Ν	d 2θ	\mathbf{F}^2
				Å							Å	
1	1	1	8	4.84455 18.2976	3063.76]	1	1	1	8	4.81452 18.4127	9921.01
3	1	1	16	2.52998 35.4514	66679.3		2	2	0	4	$2.94828 \ \ 30.2902$	11110
1	1	3	8	2.52998 35.4514	66679.3		1	1	3	8	2.5143 35.6799	48270.5
2	2	2	8	2.42227 37.0839	12648.5		3	1	1	16	2.5143 35.6799	48270.5
3	1	3	16	$1.92503 \ 47.1738$	846.79		2	2	2	8	2.40726 37.3237	12721.9
3	3	1	8	$1.92503 \ 47.1738$	846.787		3	1	3	16	1.9131 47.486	3909.12
4	2	2	16	$1.71281 \ 53.4512$	16944.9		3	3	1	8	1.9131 47.486	3909.11
2	2	4	8	$1.71281 \ 53.4512$	16944.9		4	2	2	16	1.70219 53.8113	7316.75
1	1	5	8	1.61485 56.9791	50839.3		2	2	4	8	1.70219 53.8113	7316.75
5	1	1	16	1.61485 56.9791	50839.3		5	1	1	16	$1.60484 \ 57.3672$	37853.7
3	3	3	8	1.61485 56.9791	39908.3		1	1	5	8	$1.60484 \ 57.3672$	37853.7
5	1	3	16	1.41834 65.788	1412.38		3	3	3	8	$1.60484 \ 57.3672$	28576.4
3	1	5	16	1.41834 65.788	1412.38		4	4	0	4	$1.47414 \ \ 63.004$	185015
5	3	1	16	$1.41834 \ 65.788$	1412.38		5	1	3	16	$1.40955 \ 66.2508$	4192.88
4	2	4	16	$1.3985 \ \ 66.8425$	1.23863		3	1	5	16	$1.40955 \ 66.2508$	4192.88
4	4	2	8	$1.3985 \ \ 66.8425$	1.2386		5	3	1	16	$1.40955 \ 66.2508$	4192.88
5	3	3	16	$1.27962 \ 74.0211$	32974.7		4	2	4	16	$1.38983 \ 67.3147$	1.2202
3	3	5	8	$1.27962 \ 74.0211$	32974.7		4	4	2	8	$1.38983 \ 67.3147$	1.22017
4	4	4	8	$1.21114 \ 78.988$	37109.8		5	3	3	16	$1.27169 \ 74.5607$	24201
5	1	5	16	$1.17498 \ 81.926$	1711.02		3	3	5	8	$1.27169 \ 74.5607$	24201
5	5	1	8	$1.17498 \ 81.926$	1711.02		4	4	4	8	$1.20363 \ 79.5782$	50719.8
5	5	3	8	$1.09242 \ 89.6779$	27994.7		5	1	5	16	$1.16769 \ 82.5478$	4156.05
5	3	5	16	$1.09242 \ 89.6779$	27994.7		5	5	1	8	$1.16769 \ 82.5478$	4156.05
5	5	5	8	0.968909105.31	24655.5		5	5	3	8	$1.08565 \ 90.3907$	20880.2
<u>.</u>						-	5	3	5	16	$1.08565 \ 90.3907$	20880.2
							5	5	5	8	0.962905106.252	18635.2

Table G.3: Left: Calculated reflections of magnetite with h,k,l=1-5. Right: Calculated reflections of maghemite with h,k,l=1-5.

H Physical constants

H.1 Common constants

Quantity			Value
Bohr magneton	$\mu_{ m B}$	=	$9.27 \cdot 10^{-24} \mathrm{J/T}$
Boltzmann constant	$k_{\rm B}$	=	$1.38062 \cdot 10^{-23} \mathrm{JK}^{-1}$
Electronic gyromagnetic ratio	g	=	2.0023
Electron charge	e	=	$1.60219 \cdot 10^{-19} \mathrm{C}$
Planck constant	h	=	$6.62620 \cdot 10^{-34} \mathrm{Js}$
	\hbar	=	$1.05459 \cdot 10^{-34} \mathrm{Js}$
Vacuum permeabilitet	μ_0	=	$4\pi \cdot 10^{-7} \mathrm{NA}^{-2}$
		=	$12.566370614 \cdot 10^{-7} \mathrm{NA}^{-2}$
Speed of light in vacuum	c	=	$299.792458 \cdot 10^6{\rm m/s}$

Table H.1: Common physical constants in SI units. Values reproduced from [20, 29].

H.2 ⁵⁷Fe Mössbauer constants

Quantity			Value
Mean lifetime	$ au_l$	=	$141.1 \cdot 10^{-9} \mathrm{s}$
g-factor, excited state	g_e	=	-0.10355
g-factor, ground state	g_g	=	0.181208
Nuclear magneton	$\dot{\beta_n}$	=	$5.0505 \cdot 10^{-27} \mathrm{JT}^{-1}$
Quadrupole moment, ground state	Q_{q}	=	$0\mathrm{m}^2$
Quadrupole moment, excited state	$Q_e^{"}$	=	$0.21 \cdot 10^{-28} \mathrm{m}^2$
Cross section for resonant absorption	σ_0	=	$2.57 \cdot 10^{-22} \mathrm{m}^2$
Transition energy	E_0	=	$14.41 \cdot 10^3 \mathrm{eV}$

Table H.2: Constants relevant for ⁵⁷Fe Mössbauer spectroscopy in SI units. Values reproduced from [42].

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