Concerning bachelor project (010501) by Karl Olaf Christensen and Jari í Hjøllum:

Stable wüstite, FeO, nano particles, manufacturing and magnetic properties

The report submitted by Karl Olaf Christensen and Jari í Hjøllum is very well organized starting with an introduction (Chapter 3) that states the problem investigated and puts it into a context in accordance with the general fields of activity of the Mars/Mössbauer group. The introduction also contains an evaluation of the general course of the project undertaken. As also judged by the advisors, the project has been very big – too big in fact – for a bachelor project.

The following chapters (4 and 5) introduce the set-up used for fabrication of the particles that has been the subject of studies – and the main technique of analysis: Mössbauer spectroscopy. The description of the apparatus includes a description of the conditions under which the particles were produced. The authors appear very modest: It is not quite clear from the description how large an amount of work it has required to make the experiments successfully. A thorough description of Mössbauer spectroscopy is given as of the kinds of effects that can be investigated using this technique. No mention is made of recoil – and of recoilless scattering (and the nuclear Zeeman effect is also a hyperfine interaction). However, the description of the theoretical background is concise and excellent. A few minor flaws in the description of the way a few elements of the experimental set-up works is more than compensated by the fact that Karl Olaf Christensen and Jari í Hjøllum set up the instrumentation to work by themselves (proportional counter as detector and the single channel analyser (SCA) is integrated into the MCA). Due to a move of the Mössbauer laboratory, the instrumentation was not in working condition when Karl Olaf Christensen and Jari í Hjøllum started on their project. Not only did they assemble a Mössbauer spectrometer, they also made a small computer program to convert files from the format of the PC-based multichannel analysers to the format of the program used for analysis: MacFit. This is also a major part of the work that the modesty of the authors prevents them from mentioning.

Chapter 6 describes the constraints and conditions under which the particles were produced and the characteristics of production parameters are given in a table.

In chapter 7 Karl Olaf Christensen and Jari í Hjøllum describe the theory of magnetic properties of small particles and various contributions to magnetic anisotropy. They explain the concept of domains and the different kinds of magnetically ordered structures that are commonly encountered in iron-oxides. A section on superparamagnetic relaxation and on the properties of a few selected bulk iron oxides completes this chapter. This chapter contains a few points not so clearly explained, but considering the complexity of the subject "magnetic properties of nanoparticles" this can certainly be excused. For example, on page 14 when $k_B T \geq KV$: If $\tau << 10^{-10}$ns no magnetic splitting will be observed in the Mössbauer spectrum. The phenomenon is called fast superparamagnetic relaxation.

Chapters 8 and 9, "Discussion of experimental results and Conclusions" are the culmination of the work. Here Karl Olaf Christensen and Jari í Hjøllum describe how the Mössbauer spectra have been analysed, for selected samples in considerable detail. Based on the results of their analysis, Karl Olaf Christensen and Jari í Hjøllum introduce a model of growth of the oxide particles and based on this model and their experimental results, they propose a detailed model of the structure of the particles they have produced. The model accounts for both the actual parameters used in production of the particles, for the relative areas found for the different constituents in the Mössbauer spectra and finally their model gives a very good estimate for the anticipated linear dimensions of the particles. This estimate was confirmed at a very late state of the project – and therefore this confirmation was not at the disposal of the authors when they developed their model.
Karl Olaf Christensen and Jari í Hjøllum conclude that they have managed to drive the sputtering source in a way that ensured a stable production of small particles, they found a way to, within certain limits, to control the particle size and they found a possible reason that one cannot produce hematite or maghemite directly in this apparatus. The plasma temperature may be too high for either of these phases or their precursors to be stable during production.

Using their model for the structure of the particles they have produced, Karl Olaf Christensen and Jari í Hjøllum explain how it is possible that the metastable phase wüstite may be stabilized and observed in the Mössbauer spectra.

Finally, they conclude that the results of the work do not have anything directly to say concerning the oxidized Martian surface minerals.

The analysis and discussion presented in these chapters is competent, full of good ideas – in short: just excellent. The report will constitute an excellent starting point for further studies in the field.

Karl Olaf Christensen and Jari í Hjøllum have made an impressive experimental work – both producing their samples in the hollow cathode cluster source and setting up and using the Mössbauer spectrometer. They have worked very professionally with great enthusiasm and during their work, they have both demonstrated that they are highly skilled experimental workers, and they have interpreted their results in a way that demonstrates a high level of ambition and – for their level of experience – an unusual scientific maturity.

In spite of numerous minor leaps and errors of beauty here and there, we have agreed with censor, Per Morgen, on the grade 13 for the work.

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Page 4: Two important points are missing in this section on the sputter source: a discussion of the base pressure in the source (gas impurities), and a discussion of the implications of the nanoparticles's kinetic energy during impact on the sample holder (low, so neither the particles nor the holder are damaged).

On page 15, bottom: particles need not necessarily be superparamagnetic because they are single domain. Fast superparamagnetic relaxation is, however, explained in much more detail on page 16.

In section 7.4. the temperatures at which hematite is antiferromagnetic and weakly ferromagnetic are switched. There seem to be a "cut and paste" error in the section on maghemite. Maghemite is unstable above about 600 K. The Curie temperature of maghemite is difficult to measure because it is above the temperature at which maghemite decomposes/transforms into hematite. Moreover, since hematite is essentially an antiferromagnet, the ordering temperature should be named a Neél temperature.

The characteristic observation time in Mössbauer spectroscopy is not given by the mean life time of the excited state, but rather by the Larmor precession time of the spin of the nucleus, which is about one ns.

In the tables with Mössbauer results, one could wish that also the line widths were given.

Some points of criticism regarding presentation of the Mössbauer spectra:

1. A description of the calibration of the spectra is missing.
2. Missing definition of the term "misfit".
3. It is preferable to show all data points as error bars instead of a continuous line, and to show the corresponding fit as a continuous line on top of the spectrum.
4. An idea: Plot the difference spectrum, i.e. the difference between the measured spectrum and the model. Then it is easier to see how convincing the fit is.

To distinguish between quadrupole splitting and quadrupole shift, one often use different symbols for the two: E_Q or ΔE_Q for a quadrupole splitting and ε for a quadrupole shift.

In table 6, one misses the magnetic hyperfine fields found in magnetite.

A little more details as an introduction to the Cabrerra-Mott model is to be desired.

The proposal on page 24 that the interaction from an iron-core on the magnetic moments of a covering magnetite layer will cause the magnetic structure to collapse, is very hard to believe – usually interactions do not work that way.

The g-factor of the ground state is negative.