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## 1. Introduction

The magnitude and importance of production and industrial utilization of **manufactured nanoparticles (MNPs)** has been increasing rapidly in recent years [1]. Among them, magnetite nanoparticles are found to be exceedingly useful in various application fields such as catalysis [2], biomedical diagnostic and therapeutic applications [3] as well as environmental remediation [4]. Magnetite is a favorable choice in these applications on account of their advantageous material properties, such as high Curie-temperature, high levels of magnetization, high specific surface area, superparamagnetism along with chemical stability, low toxicity and good biocompatibility under physiological conditions, among others [3]. However, magnetite has long been known to be prone to oxidation under ambient atmosphere [5], leading to partially oxidized, non-stoichiometric magnetite, to maghemite, or to a mixture of the two as intermediate product [6]. The effect of oxidation can be especially pronounced in the case of nanoparticles that display an enhanced surface to volume ratio with respect to larger-size, bulk-like particles [6]. Though maghemite and non-stoichiometric magnetite do share many of the advantageous properties of magnetite, there are also key differences that make unambiguous characterization of corresponding particles desirable from the applications point of view: while the mass magnetization of magnetite (92-100 Am<sup>2</sup>/kg) exceeds that of maghemite (60-80 Am<sup>2</sup>/kg) by a considerable margin [7], the magnitude of first order magnetic anisotropy is also known to decrease with decreasing Fe<sup>2+</sup> concentration of non-stoichiometric magnetite [8]. These physical properties are especially important in the field of biomedical applications [3].

While bulk maghemite and magnetite can be well distinguished on the basis of their room temperature <sup>57</sup>Fe Mössbauer spectra (Figure 1), when prepared in the nanoparticle form, pronounced levels of oxidation combined with relaxation effects such as collective magnetic excitation complicates the room temperature <sup>57</sup>Fe Mössbauer spectrum of (nominally) magnetite nanoparticles in a way that makes it questionable whether and to what extent the studied sample can be regarded as magnetite, non-stoichiometric magnetite, maghemite or a mixture of these phases.

Under ambient conditions stoichiometric bulk magnetite includes Fe<sup>3+</sup> at the tetrahedral sites, and Fe<sup>2+</sup> along with Fe<sup>3+</sup> at the octahedral sites of the inverse spinel structure. Above the Verwey temperature (~119K in the case of bulk magnetite) electron delocalization between Fe<sup>2+</sup> and Fe<sup>3+</sup> at the octahedral sites leads to fast electronic relaxation and correspondingly averaged hyperfine interaction parameters, that are visualized in the corresponding <sup>57</sup>Fe Mössbauer spectrum as a single sextet subspectrum commonly referred to as the fingerprint of a Fe<sup>2.5+</sup> state of iron at the octahedral sites of the spinel (Table 1). In contrast, the <sup>57</sup>Fe Mössbauer spectrum of maghemite is often well described by a single sextet only (Figure 1) [9], though Fe<sup>3+</sup> at tetrahedral and octahedral positions could be possible to discriminate on the basis of their characteristic isomer shift values [12].

**Table 1.** Comparison of typical <sup>57</sup>Fe Mössbauer parameters of bulk magnetite and maghemite at room temperature, as adapted from [12].

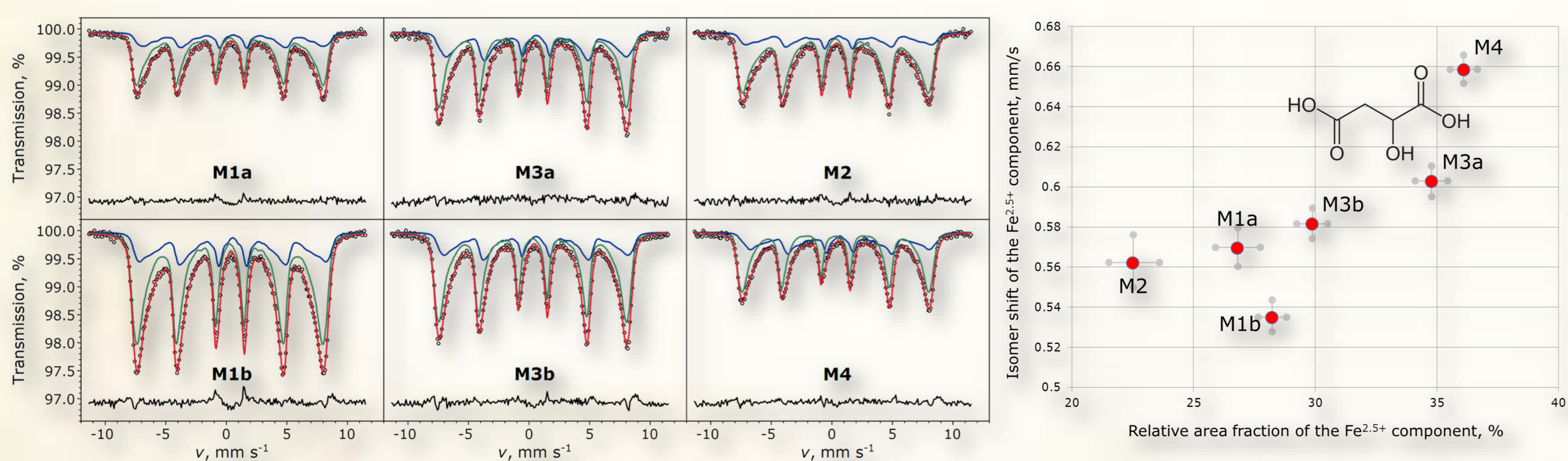
Compound	Site and oxidation state	B <sub>hf</sub> , T	δ, mm/s	Relative area
Magnetite, Fe <sub>3</sub> O <sub>4</sub>	Fe <sup>3+</sup> (tetrahedral site)	49.1	0.28	1
	Fe <sup>2.5+</sup> (octahedral site)	46.0	0.66	1.9
Maghemite, γ-Fe <sub>2</sub> O <sub>3</sub>	Fe <sup>3+</sup> (tetrahedral site)	49.8	0.24	1
	Fe <sup>3+</sup> (octahedral site)	49.8	0.36	1.66

The above outlined, relatively clear picture changes drastically when magnetite is prepared in the form of nanoparticles: in the room temperature <sup>57</sup>Fe Mössbauer spectra heavy line broadening can appear [6,13,14], either due to hyperfine parameter distribution(s) caused by (possibly various) non-stoichiometric compositions present in the sample and/or due to relaxation phenomena such as collective magnetic excitations along with the possible influence of interparticle magnetic interactions. As a result, the sextet signals of the tetrahedral and octahedral iron ions may overlap in a way that renders unambiguous decomposition of the spectra rather hopeless unless the exact nature of broadening is known and taken into account via suitable constraints. Especially in such ambiguous cases often it seems to be impossible to identify the signal of Fe<sup>2.5+</sup> or Fe<sup>2+</sup> in the spectra via the usual decomposition method, and therefore the presence of magnetite in the sample (as opposed to maghemite) remains largely questionable. Some further hints in this regard may be obtained by turning to additional experimental methods such as XRD and TEM, for example, but in general it is rather difficult to reach a level of certainty that would be required for a reliable judgment concerning the suitability of the particles for a particular application area. <sup>57</sup>Fe Mössbauer spectroscopy (**MS**) measurements performed at low temperatures and in external magnetic fields may also contribute to the clarification of the overall sample composition [13], though this in itself does not resolve the problem one encounters in connection with the decomposition of room temperature Mössbauer spectra. One should also consider that a change in sample temperature and the application of an external magnetic field may well affect the electronic state of matter in a less than obvious way, and from a clear result observed for such an altered state one cannot always reliably extrapolate to the state of matter under different experimental circumstances. It is therefore of both practical and theoretical interest to look for reliable ways to perform the decomposition of heavily broadened room temperature <sup>57</sup>Fe Mössbauer spectra of magnetite nanopowders.

Here we contribute to this field by the <sup>57</sup>Fe MS, X-ray diffractometry (**XRD**), transmission electron microscopy (**TEM**) and ferromagnetic resonance (**FMR**) spectroscopy characterization of magnetite nanoparticles prepared under different conditions that influenced their overall level of oxidation.

## 4. Discussion

<sup>57</sup>Fe Mössbauer spectra of the samples display unresolved broad peaks with an inward shoulder reflecting collective magnetic excitations. There are various different decompositions/interpretations possible, also into several sextet subcomponents, although none of them stands out as a most reasonable one. Thus, we have chosen a simple but versatile decomposition into two hyperfine magnetic field distributions: one associated with Fe<sup>3+</sup> and the other with Fe<sup>2.5+</sup>, and fitted the 6 spectra simultaneously, by assuming that all of them display the same isomer shift for the Fe<sup>3+</sup> subcomponent. The isomer shift and the relative area fraction of the Fe<sup>2.5+</sup> component was allowed to vary in the spectra. The common isomer shift of the Fe<sup>3+</sup> component as given by the fit is 0.30(1) mm/s. The fit results thus obtained show reasonable correlation with results obtained via TEM, XRD and, especially, FMR. Samples **M3a**, **M3b** and **M4** display the highest concentration and isomer shift of the Fe<sup>2.5+</sup> component, the highest crystallite size and lattice parameter, whereas in addition **M3a** and **M3b** show the highest levels of magnetic anisotropy according to FMR. Common feature of these samples is that they were prepared via the use of a coating agent. Comparing **M3a** (dried at RT) with **M3b** (dried at 80°C) it appears that drying at a higher temperature reduces Fe<sup>2.5+</sup> concentration and isomer shift, as well as magnetic anisotropy and lattice parameter. Comparing **M2** (prepared without coating agent) with **M4** (prepared with coating agent) clearly reveals that the use of coating agent helps to preserve magnetite structure in the resulted particles. Due to strong correlations, in this approach the standard deviations of parameters are best calculated having all other parameters fixed. The gray error bars on the graph below refer to StD values calculated in this way.



**Figure 1.** Theoretical room temperature <sup>57</sup>Fe Mössbauer spectra of bulk maghemite (top) and magnetite (bottom) on the basis of [9,10], the latter as copied from the MossWinn Internet Database [11].

## 2. Experimental

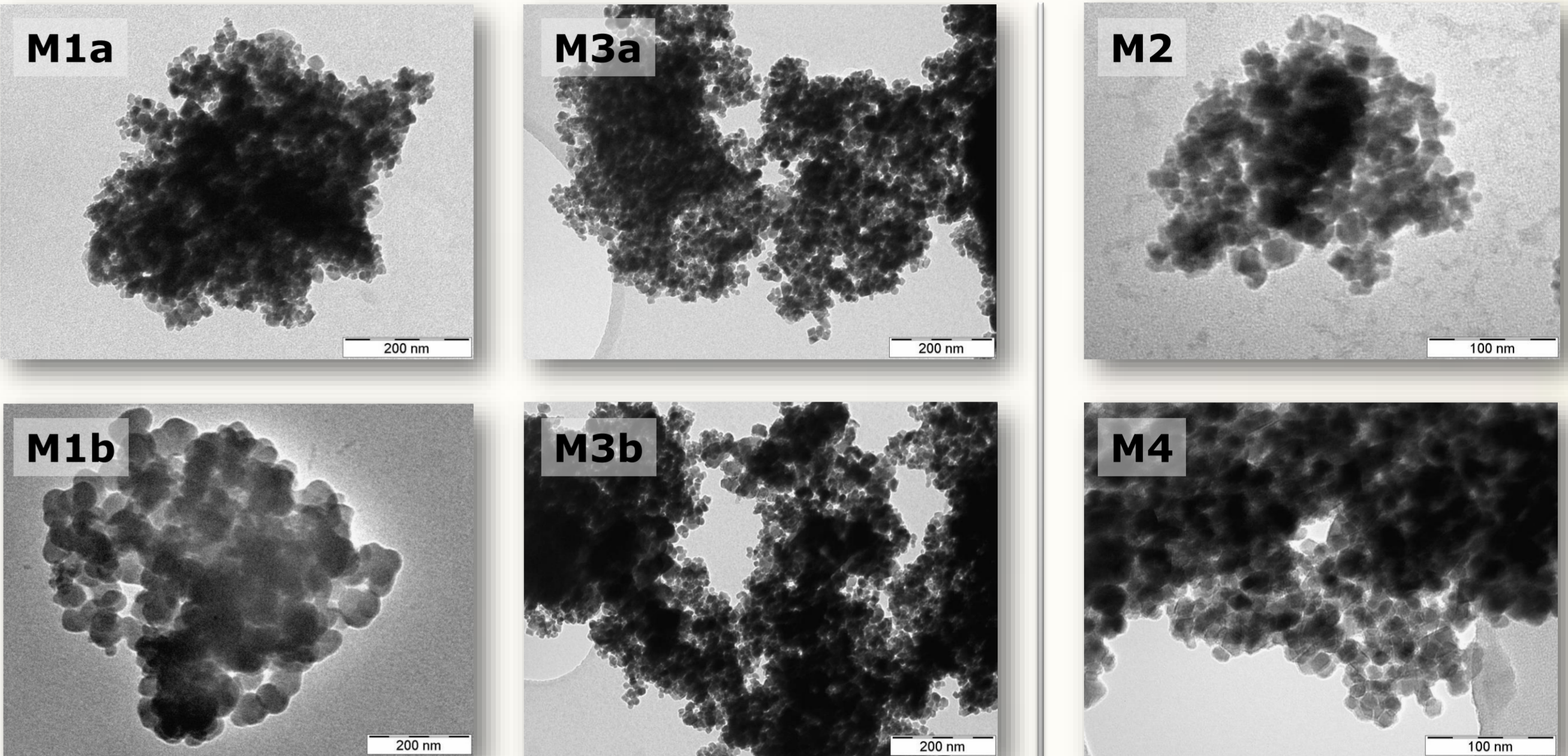
The experiments were carried out by the following equipment. Philips PW3710 based PW1050 Bragg-Brentano goniometer system used with Cu Kα radiation along with graphite monochromator (XRD), Morgagni 268D (100 kV) transmission electron microscope (TEM), Bruker ElexSys E500 X-band spectrometer (EPR/FMR), WISSEL spectrometer applied in transmission geometry along with a source of <sup>57</sup>Co in Rh matrix providing the γ-rays with ca. 20 mCi activity (<sup>57</sup>Fe MS).

Fe<sub>3</sub>O<sub>4</sub> nanopowders were prepared via chemical co-precipitation method starting from mixed solution of Fe<sup>2+</sup> and Fe<sup>3+</sup> salts in strongly alkaline aqueous medium. FeSO<sub>4</sub>·7H<sub>2</sub>O and FeCl<sub>3</sub>·6H<sub>2</sub>O were used as reagent grade metal precursors and NaOH for pH adjustment in starting solutions. In a typical synthetic procedure, 17.15 g FeSO<sub>4</sub>·7H<sub>2</sub>O and 35.5 ml FeCl<sub>3</sub> solution (3.50 M) were dissolved in 500 ml distilled water and the pH was adjusted using NaOH solution prepared by dissolving 20.7 g NaOH in 200 ml distilled water. After the alkaline solution was added, the color of the solution changed from orange to black rapidly. In the next step the reaction mixture was homogenized via vigorous stirring for 15 minutes at room temperature either **under air** (samples **M2**, **M4**) or **under nitrogen atmosphere** (samples **M1a**, **M1b**, **M3a**, **M3b**). The solution was heated to reflux at 100°C for 2 hours. After the reaction was completed, the obtained particles were filtered and purified by washing several times with distilled water, and then **dried at room temperature** (samples **M1a**, **M3a**) or **80°C** (samples **M1b**, **M2**, **M3b**, **M4**). 53.0 mg of **malic acid** dissolved in 200 ml distilled water was used as **coating agent** in case of samples **M3a**, **M3b**, **M4**.

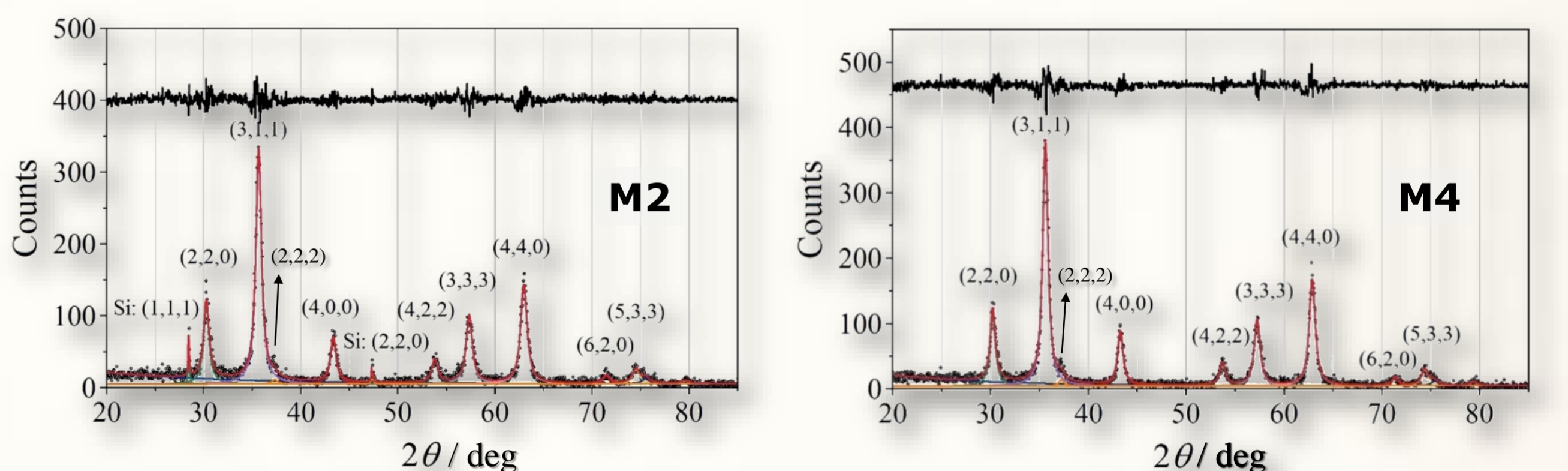
The samples for <sup>57</sup>Fe Mössbauer spectroscopy were prepared by evenly distributing 10 mg of the prepared powders over a collimated area of 0.5 cm<sup>2</sup>, and then fixing the sample geometry thus achieved by pouring melt paraffin wax over the area in question. The resulting samples had approximately 14.4 mg/cm<sup>2</sup> surface density of iron. **FMR** measurements were carried out at room temperature on 0.1 mg nanoparticle powder evenly mixed with 19.9 mg KBr in order to realize a steady random powder geometry.

## 3. Characterization of nanoparticles

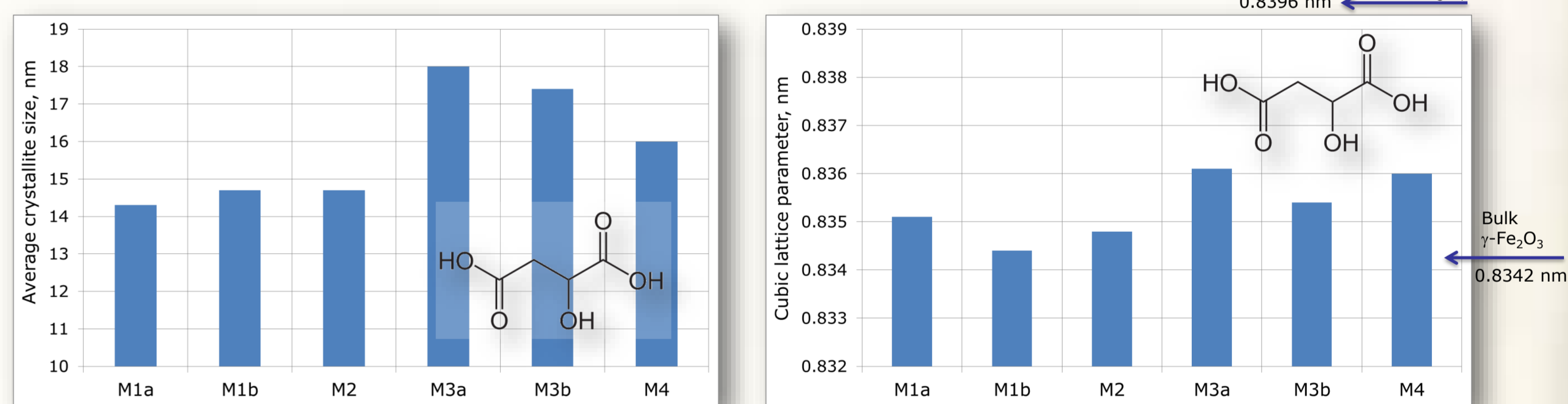
**TEM** confirmed the nanoparticle nature of the prepared powders. Sample **M1b** stands out via its relatively large particles.



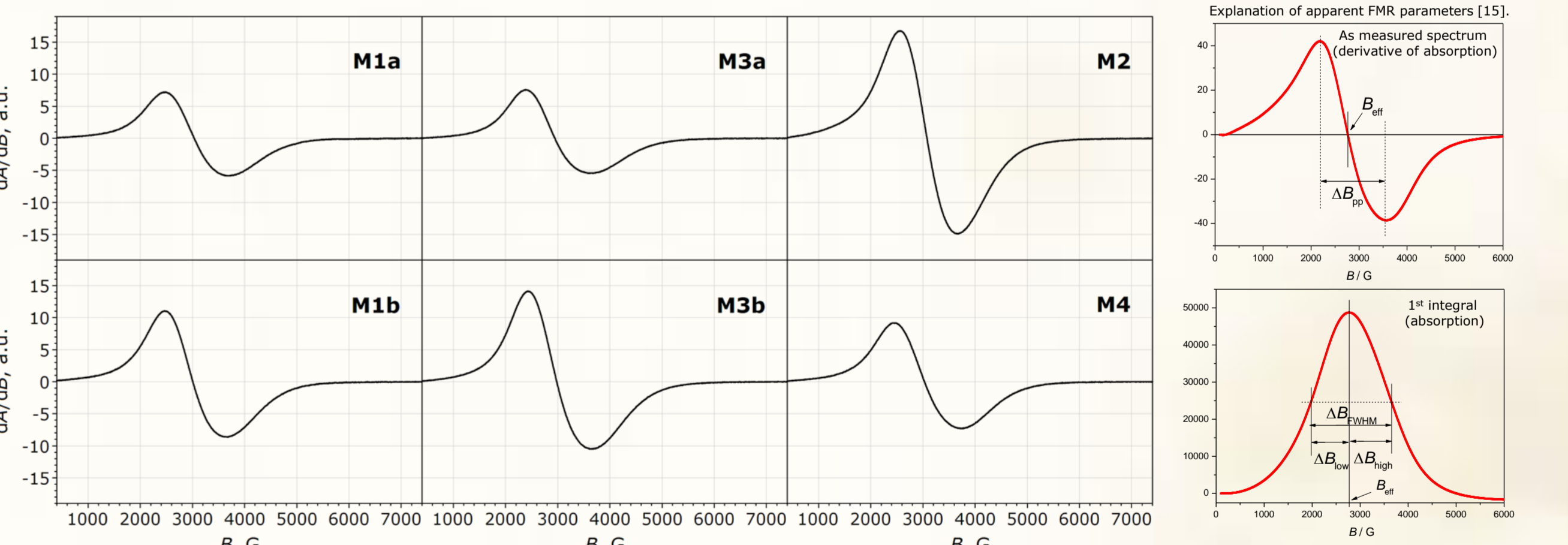
**XRD** confirmed the cubic spinel structure of all the nanoparticles without referring to secondary phases. Two examples are shown below.



Fitting the **XRD** diffractograms with Lorentzians according to Bragg's law and the Scherrer equation revealed differences among the average crystallite size and the cubic lattice parameter of the samples.

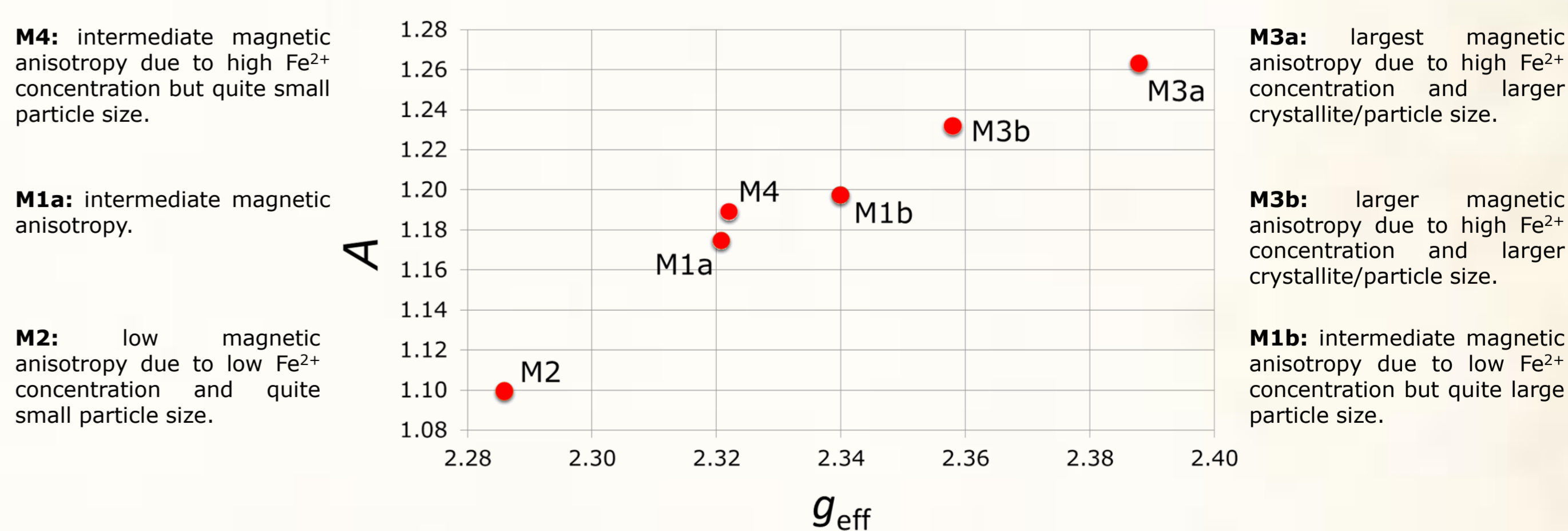


**X-band FMR spectra** reflect differences among the spectra due to differences in the magnetocrystalline anisotropy and particle size.



Subtle differences between the X-band FMR spectra can be revealed by the derived parameters *A* (anisotropy) and *g<sub>eff</sub>*, which are calculated as follows (*f* = 9.85 GHz):

$$A = \frac{\Delta B_{high}}{\Delta B_{low}} \quad g_{eff} = \frac{hf}{\mu_B B_{eff}}$$



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## 5. Conclusions

**Acknowledgement.** Financial support from the National Research, Development and Innovation Office - NKFIH/OTKA (K115913 and K115784) is gratefully acknowledged.

The sum of two hyperfine magnetic field distributions with different isomer shifts appears to be a suitable model for the decomposition of RT <sup>57</sup>Fe Mössbauer spectra of magnetite nanoparticles. Our results consistently reveal that application of the coating agent malic acid during preparation prevents oxidation of magnetite nanoparticles, while drying at the as prepared nanoparticles at higher (80°C) temperature has the opposite effect when compared to particles dried at RT.