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Characterizing iron oxide nanoparticles with Mossbauer spectroscopy in a nontraditional matrix: An application of Mossbauer spectroscopy to bioinorganic nanoscience.

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Abstract

Iron-oxide nanoparticles are an intriguing material with many biological and environmental applications. Characterization of nanoparticles is both a challenging and developing science. Mossbauer spectroscopy can be used to provide information about the valence state and molecular environment of atoms in solid matrices. The components of iron in iron-oxides as nanoparticles present an array of characteristics dependent on both particle size and crystallographic environments containing the iron atoms. Solid nanoparticles in colloidal suspensions present several special challenges to obtain information useful for characterizations. Physical properties of individual components of iron in these nanoparticles that are measurable include oxidation state, quadrupole splitting and magnetic order states. A complex environment for iron within nanoparticles protected in a polymer coating and suspended as a colloid within organic solvents are characterized, to assist chemical engineers in assessing the quality of products and processes being developed. Mossbauer spectroscopy is able to discern product components with iron atoms in both tetrahedral and octahedral environments, magnetically ordered and paramagnetic states and their relative contributions, within assembled nanoparticles. These elucidated components suggest the identities and contributions to the total of iron-oxide phases in the nanoparticles.

1. Introduction

Rapid developments in the chemical synthesis of magnetic iron oxide nanoparticles offer the possibility to exploit novel magnetic and electrical properties that emerge when reducing the size of the particles.[1,2] Nanoparticles can be synthesized with controlled size, shape and even surface coatings.[3,4] In particular iron oxide nanoparticles are currently being intensely considered for medical applications due to their biocompatibility and their potential for magnetically induced hyperthermal abilities.[3] A polymer coating of oleic acids (omega-6 $C_{18}O_2$) is created on magnetic iron oxide (19 nm) nanoparticles to provide a biocompatible magnetic nanoparticle. Such applications also benefit from the precise identification of the iron phases, which is often neglected,[4] in order to tune the magnetic strength of such nanoparticle cores.

Of two predominant synthesis strategies, chemical precipitation (or a co-precipitation) and thermal decomposition are employed, the later has so far provided more consistent particle size distributions in the nanoparticle size range.[3] A further development of single stream continuous flow synthesis is employed to more optimally control temperature of reaction and resultant size distribution of particles as well as the iron-oxide phase content. This strategy appears to often yield mixtures of magnetite and maghemite in addition to simpler oxide arrangements, either a multi-phase Fe_xO/

Fe_2O_3 or multi-phase $Fe_xO/Fe_2O_3/Fe_3O_4$ product.[5] The resultant yields of these synthetic approaches then determine magnetic susceptibility of the particles which is key to their usefulness in their magnetic hyper-thermal quality.

These coated nanoparticles are provided in a colloidal solution in hexanes, which provides an additional set of challenges to the use of Mossbauer spectroscopy. Mossbauer spectroscopy is traditionally utilized to characterize the quality and relative proportions of target atoms in a solid-state matrix, which provides optimal sensitivity and resolution, for the detection of energy emissions to be counted by the method. Ionic atoms in solution are not resolvable in liquid or gaseous solution.[6] Nanoparticles also provide characterization challenges when identifying target atom states due to their increased surface proportions that provide for more diverse molecular environments than those of bulk material which are well studied.[7,14]

The magnetic qualities can be understood in terms of a predominantly antiferromagnetic coupling between next-nearest neighbor ions in the solid lattice of each particle. These couplings are nicely represented in crystallographic models such as those in Figure 1 below. The arrangement of metal atoms coordinated with oxygen in three-dimensional space and their proximities determine the magnetic characteristics of each mineral component of a system. The most common minerals of iron oxide crystals with magnetic arrangements that make up the phases of these anthropogenically produced iron-oxide particles are Magnetite, Maghemite, and Hematite.

Magnetite (Fe_3O_4) is one of the strongest ferromagnetic (FM) iron oxide compounds. It crystallizes in a cubic 'inverse spinel' structure with tetrahedral coordinated sites occupied by Fe^{3+}, and the octahedral coordinated sites equally occupied by iron atoms with both formal +3 and +2 charges.[8] The Fe^{2+} and Fe^{3+} ions in the octahedral sites are aligned ferromagnetically by a double exchange interaction. The Fe^{3+} ions on the tetrahedral sites are coupled to the Fe^{3+} in the octahedral sites by an antiferromagnetic super-exchange interaction, essentially exchanging electron density between Fe^{2+} and Fe^{3+} atoms at temperatures above a specific temperature, known as the Verwey temperature. When cooling below the characteristic Verwey transition ($T_V \sim 120$ K) its conductivity drops by two orders of magnitude, also accompanied by a slight crystallographic distortion.[9] Oxidation measurements by Mossbauer at relatively low time frame rates appear as a 2.5+ formal charge component at temperatures above the $T_{v,}$ Below the Verwey transition point Mossbauer measurements are resolved into the more accurate 2+ and 3+ components.

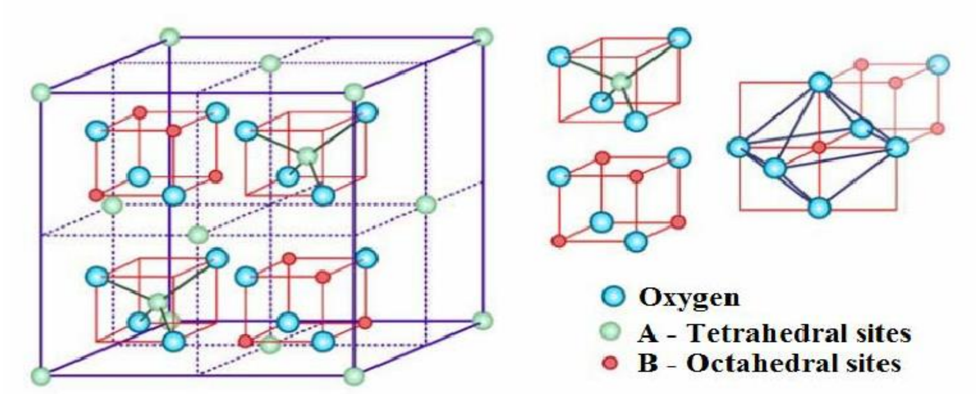
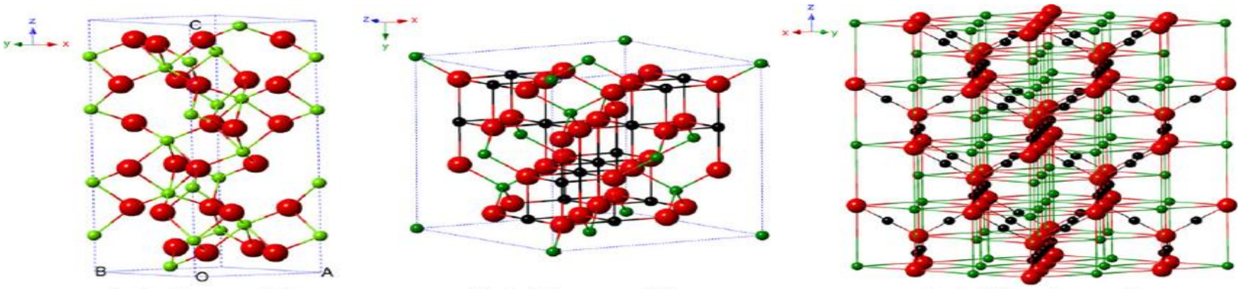


Figure 1. Crystallographic model of Magnetite structure (inverse spinel).

Maghemite (γ-Fe_2O_3) is a ferromagnetic material below 948 K.[8] It crystallizes in the inverse spinel structure similar to magnetite. In contrast to magnetite, eight Fe^{3+} ions are located in tetrahedral sites (A-sites) and sixteen Fe^{3+} occupy the octahedral sites (B-sites). The FM property in maghemite is the result of Fe^{3+} in the B sites of the spinel structure.[9] The saturation magnetization of maghemite is 380 kA/m which is smaller compared to 480 kA/m of magnetite, making it less susceptible to magnetic manipulations.[5]

Apart from the above mentioned oxide phases there are also the phases α-Fe_2O_3, β-Fe_2O_3 and ε-Fe_2O_3. Among those, Hematite, (α-Fe_2O_3) is the most abundant in nature.[8] The other two phases are metastable and are formed by reduction of α-Fe_2O_3 at high temperatures.[10,14] Hematite is antiferromagnetic below 948 K.[9] It also shows a transition from weak ferromagnetism into antiferromagnetic state at 260 K, known as the Morin transition.[9] It crystallizes in a rhombohedral structure at room temperature. With X-ray diffraction measurements one can easily distinguish it from Magnetite, Maghemite and Wüstite.[10] A fourth, far less common iron oxide that could be present in these phase mixtures is Wüstite. In our studies Hematite was suspect as being present in the second batch of untreated samples. Wustite was reported in literature as a possible contribution to a similar iron-oxide nanoparticle synthesis approach, where Mossbauer was not utilized to characterize products.[4]



(a) Hematite
Rhombohedral, $R\bar{3}c$

(b) Magnetite
cubic, Fd3m

(c) Maghemite
Cubic, $P4_332$/Tetragonal, $P4_12_12$

Figure 2. Crystallographic comparisons of primary constituents found in samples analyzed. The most common occurring iron oxides. Figure is free license courtesy of chemistrystackexchange.com

Wüstite (Fe_xO) is a non-stoichiometric phase with a known stability range from x = 0.83 to 0.96. at room temperature.[1,9] Wüstite is paramagnetic and crystallizes in a rock salt structure, which is a close-packed solid lattice with fe^{2+} ions occupying the b interstitial sites. Below the Néel temperature T_n = 198 k, Wüstite orders antiferromagnetically.[9] The paramagnetic to antiferromagnetic transition is accompanied by a slight elongation along a direction where the crystal becomes rhombohedral. The magnetic ordering can be understood in terms of a predominantly antiferromagnetic coupling between some next-nearest neighbor ions.[8] Wüstite is the least magnetically manipulatible component discussed in this work and has clear distinction from the other iron-oxide minerals in Mossbauer spectra.[14]

1.1 An Overview of Mossbauer Spectroscopy:

Rudolf Ludwig Mössbauer was a German physicist best known for his 1957 discovery of recoilless nuclear resonance fluorescence for which he was awarded the 1961 Nobel Prize in Physics.[1,2,3] Mössbauer spectroscopy is considered by many to be one of the most sensitive analytical tools known to science. It is a very sensitive analytical tool capable of measuring the minute differences of energies in the excited and ground states of an atomic nucleus. Most other types of spectroscopy measure details used to examine the properties of molecular and electronic properties. It is Mössbauer that is sensitive to atomic nuclei and the affectations upon it of the surrounding electron field gradient. The atomic nuclei bely information about the distribution of electron density surrounding the nucleus and is further affected by the distributions of nearby electronic charge and magnetic fields. It is also a more direct method for determining some materials' properties that are otherwise more difficult to obtain information about, such as oxidation state and states of magnetic ordering for target atoms.[3,6,14]

Of the many specific atoms that can be studied by the Mossbauer effects, the most common is Iron (^{57}Fe).[3,9,14] There are near to forty elements that can be examined in a solid state by Mossbauer Spectroscopy, each with a specific target atom setup required. A few Mossbauer isotopes are more common because of the facility to which they can be studied as well as the prevalence of the isotope in nature, as well as materials of interest. Other commonly studied elements are Tin (Sn), Gold (Au), Europium (Eu).[3,9,14] Most other Mossbauer nuclides require more highly specialized facilities, shielded for energy intrusions, high activity energy sources or cyclotron proximity to harness specific gamma energy emissions.[11]

Mossbauer's nuclear resonance spectroscopy measures an effect when an occurrence of specific quanta of energy from a source are absorbed in a sample and resultant emissions are detected. The absorption of specific quantized energy induces an excited energy state of an atom's nucleus and when it relaxes to a ground state a photon is emitted. Each element has a characteristic energy attributable to the difference between ground and excited states of the nucleus. So also the energetic state of a target atom can be examined by its characteristic emissions when excited and then decaying to ground state, when a modulation of source energy is provided. Mossbauer spectroscopy utilizes the Doppler effect of subtly altering the incidence gamma beam by moving the source closer and farther away from the sample in line with the detector. The measurement of energy is subsequently reported as a relative velocity usually in units of millimeters per second (mm/s). A spectrum is obtained by graphing counts of detection compared to energy (as velocity). The spectrum obtained conveys characteristic signals that can be matched to physical properties of the atom's nucleus. A Mossbauer spectroscopist fits the spectrum with signals to elucidate information about the nucleus, the atom as a whole and even the electronic and magnetic environments that the atoms inhabit.

As with any sensitive technology there is an art to determining the meanings of subtler effects on the signals produced. Signals appear in a spectrum is both shape and position. Position is related in terms of energy shift from a determined reference point. In the case of ^{57}Fe analysis alpha-iron (α-Fe), which is zero valent, is commonly used as the reference.[3,9,14] The degree of shift from the specific energy for a signal is characteristic of the electron environment that surrounds a target nucleus. Hence oxidation state (valence state) of an absorber is determined by its characteristic shift. This shift is often referred to as chemical shift or isomer shift (δ). Shift is also more subtly influenced by temperature.[9,14] Isomer shift is also utilized in conjunction with quadrupole splitting and Magnetic field splitting (H_{eff}) to indicate further environmental conditions of the absorber atom. The coordinated environment which determines the crystalline structure of a mineral and even the bond distance between the target nucleus and its nearest neighbor affect the signal characteristics.[3,9,14]

Three categories of signal shapes appear as a result of energy splitting in iron analysis. A singlet is produced as the simplest signal where there is no magnetic splitting and the nucleus of the target atom has complete symmetry. A doublet in Mössbauer spectroscopy is a signal that represents only quadrupole splitting of a signal indicating a paramagnetic component. Quadrupole splitting is the effect spectroscopically realized when a quadrupole moment within the atomic nucleus of the atom exists, distorting the nuclear envelope from perfect symmetry. This distortion is recognized as a probability function of the nuclear radius which is affected by the electronic gradient of its surrounding electron density. It is also described more simply as a linear mathematical representation of an asymmetrical shape of the electron density surrounding the target in three dimensions.[14] A third prominent signal shape in Mossbauer iron spectrum is the sextet. The sextet is a representation of magnetic order. Each peak of the sextet represents an energy shift within the nucleus from ground state of spin to one of an excited state. The parameters of the signal include amplitude of each peak of the signal, which indicates the populations of detection at these discrete energies as well as the strength of the internal magnetic field within the nucleus which is represented by the width of the spread between peaks within the signal. A signal may exhibit only one or any of these traits simultaneously. Structural configurations also affect the appearance of signal components comprising the Mössbauer spectra. The orientation of a solid lattice to the trajectory of the source beam as well as the degree of organization of the solid lattice affect the signal shapes. Particle size may also affect the manifestation of magnetic order, small nanoparticles (< 2 nm) resist intrinsic magnetic order signals, an effect identified as superparamagnetic. Component signals may subtly shift or widen with the influences of neighboring electron densities to target atoms. Thus the elucidation of structure and magnetic properties in Mössbauer spectra is achieved through careful fitting of proposed signals into the spectrum results presented experimentally. Ordinarily proposed signals are graphically overlaid on the experimental results to create a fit. In many cases overlapping signals convolute the experimental spectrum, which presents as a sum of signals. These overlapping signal components must be individually identified and justified. Experimentally, every shoulder or extra width of a peak is the result of overlapping signals.

2. Methods

Spherical monodisperse iron oxide nanoparticles with oleic acid coating were synthesized by thermal decomposition in presence of oleic acid.[8] The resultant solution was then cooled to room temperature. The thus prepared nanoparticles were separated by centrifugation and washed with acetone. Nanoparticles were concentrated by centrifugation and decantation then suspended in hexanes for long-term storage. The iron-oxide nanoparticle cores remain coated with the oleic acid shell. A portion of these materials was further treated with heat in a humid ambient atmosphere for up to 1 hour to "oxidize" the coated nanoparticles. Initial characterizations of the two sets of nanoparticles, treated and non-treated was carried out by transmission electron microscopy and magnetic susceptibility measurement at Clemson University's Rich Laboratories by the Mefford Research Group. Transmission electron microscopy (TEM) images were obtained with a H-7600 microscope (Hitachi). Magnetometry measurements of the samples were performed using a Quantum Design MPMS5 superconducting quantum interference device (SQUID) magnetometer in applied magnetic fields up to 50 kOe.

Mossbauer spectroscopic measurements were first conducted of two samples labelled oxidized and non-oxidized at UNCA's Materials Research Group Laboratory. Each sample received of colloidal suspension containing oleic acid coated iron-oxide nanoparticles was condensed by volatilization of hexanes in vacuum, via a glove box. The condensed material was loaded into 3cm^2 Acrylite™ containers to a 3 mm depth. Prepared sample containers were placed in a linear alignment with an oscillating ^{57}Cobalt gamma source (Ritverc GmbH, St. Petersburg, Russia) and a gas phase detector. An array of Ortec high-voltage power source, signal amplifier and counting components produced the reference signal as a detector/counter assembly in a transmission mode arrangement. Linear source motion was created with a Mossbauer Drive transducer. Low temperature measurements were taken by placing the sample in a helium 4K Cryostat (Advanced Research Systems, Inc.), placed in line with the source-detector linear arrangement and controlled by a Lakeshore model 331 Temperature controller. Temperature probes were placed in the heat column and at the perimeter of the plastic sample container. Signals were quantified in 512 channels and graphically assembled into spectra with Wissoft 2003 software. Obtained spectra was fit utilizing Lorentzian style line shaping in a custom analysis program labelled "Recoil." Fitment was recorded in terms of isomer shift (δ), quadrupole splitting, magnetic hyperfine field (H_{eff}), line width, component area and a statistical criterion(χ^2). Instrumental error for the velocity scale or spectral point +/-0.5 channel. Reference signal was folded against a standard α-Fe foil absorber at 295K to determine zero shift and optimal peak width.

3. Results:

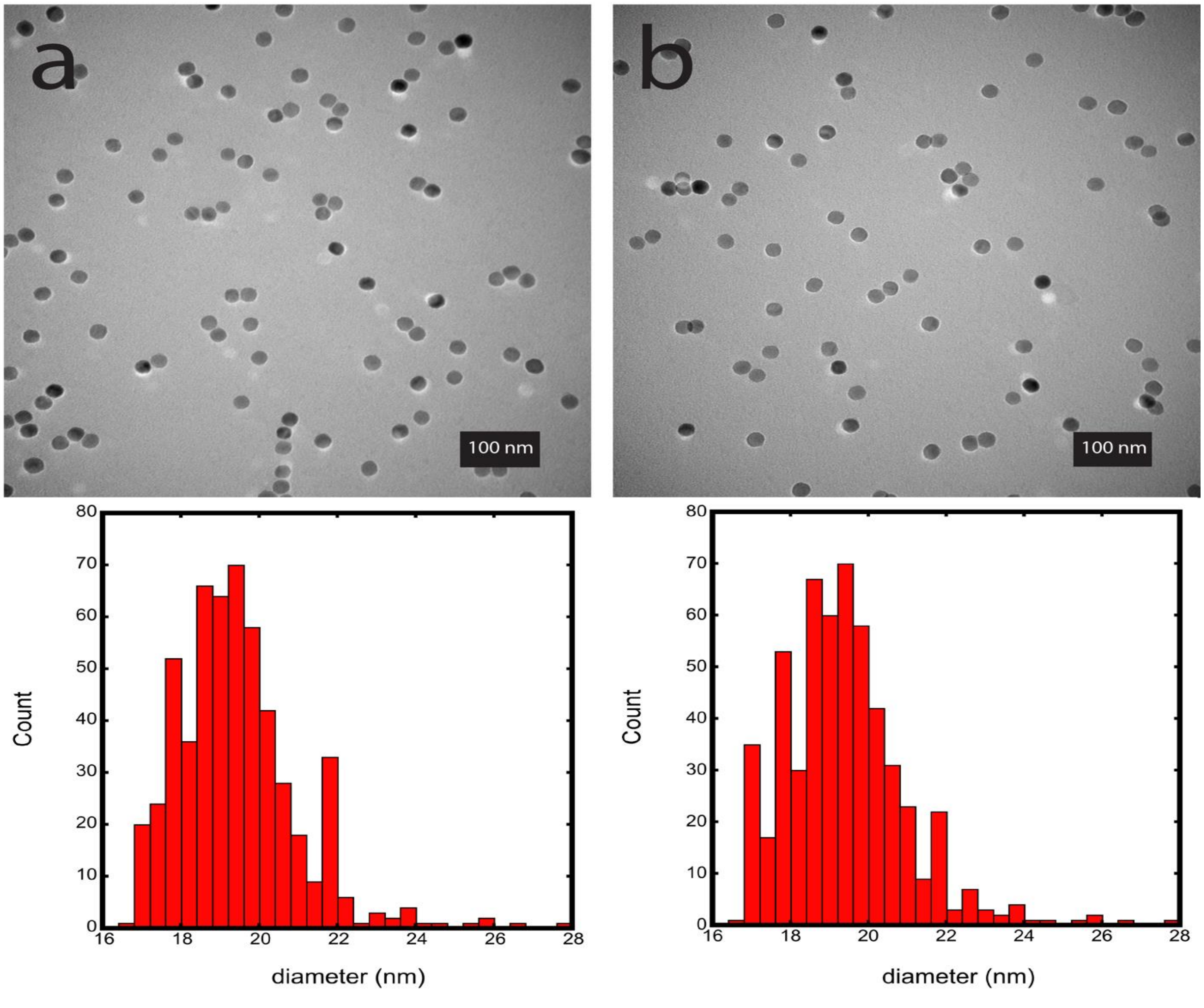


Figure 3. (a, b) TEM images of as-prepared iron oxide NPs with diameter near 20 nm of diameter. Both size distribution charts demonstrate less than 2 nm deviation from 19 nm target. Images provided by Mefford Research Group, Rich Labs at Clemson University.

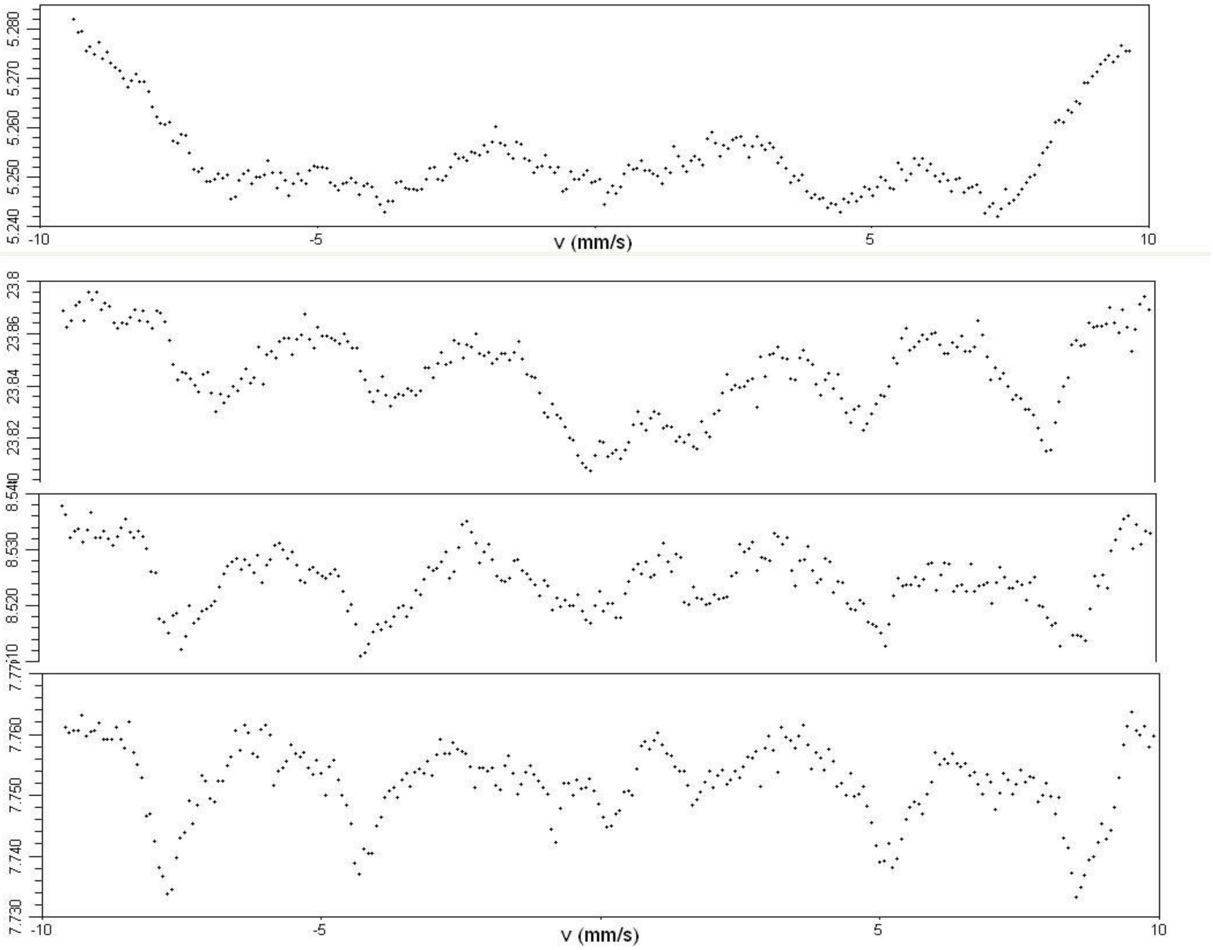


Figure 4. Initial Mossbauer spectra obtained (top to bottom) at room temperature (295K), 180K, 100K and 11K.

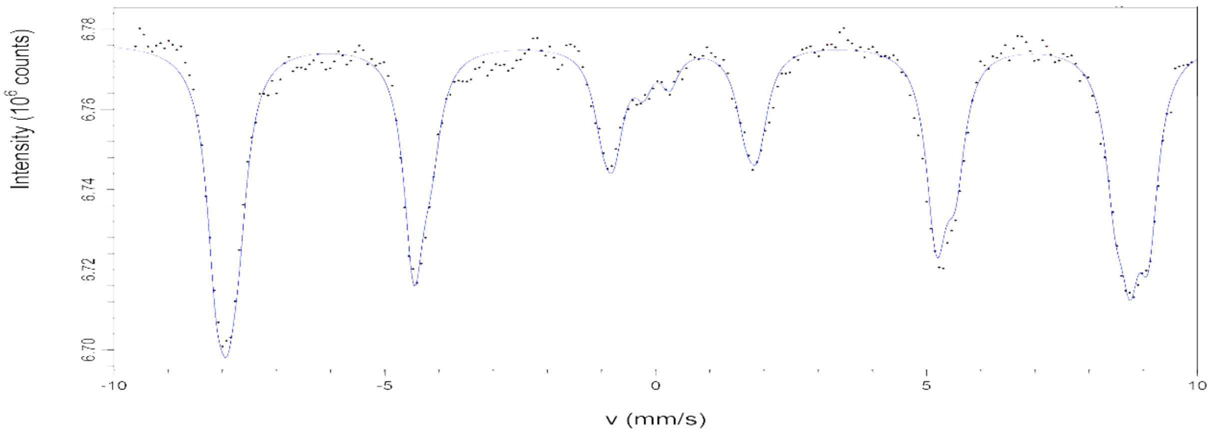


Figure 5. Spectrum of washed and condensed “oxidized” sample at 11K, reveals components that resemble fairly pure maghemite mineral with a small percentage (3%) of paramagnetic component.

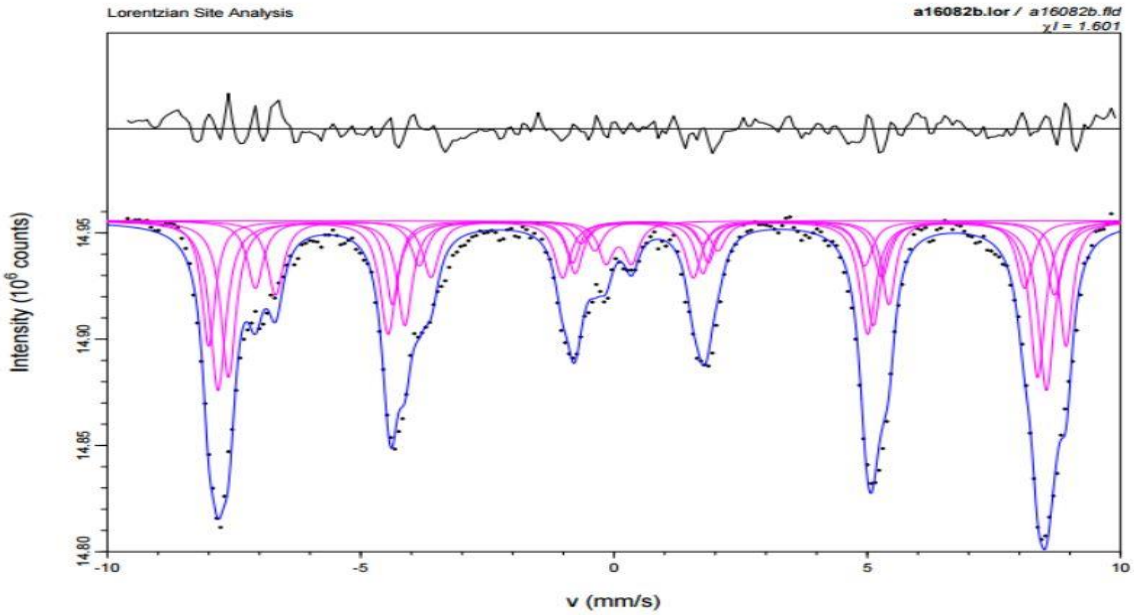


Figure 6. Spectral fitment of non-oxidized material at 150K, revealing components suggesting the sample has a composition of 18% magnetite, 63% maghemite/magnetite solution and 16% Hematite with near 3% paramagnetic material (seen as a doublet).

4. Conclusions:

Mossbauer is traditionally a solid state analysis and our project of analyzing solid nanoparticles in a non-solid coating within a solution of solvent, poses additional challenges. The surrounding liquids interfere with the recoilless effects measured in classic Mossbauer analysis. The peak half-width becomes compromised and energy is absorbed by the energetic qualities of liquid state in the surrounding matrix of the solids. Freezing of the matrix resolves some of these issues, but complicates the speed of measurement by adding significantly to environmental preparation time as well as the cost of analysis. Nanoparticle sizes also harbor challenges to our analysis as target atom density within the sample is more likely dilute requiring more time to collect adequate interaction signals. The end result of these efforts demonstrates that three days are required at a minimum; to prepare, measure and analyze a single sample with our current facilities and source. A more active source could be utilized to vastly increase the rate of counting. It was found that even at very low temperatures (11K) 6-8 million counts was desirable to provide a spectrum that would inspire confidence in our resolution.

Washing particles to remove all traces of non-bound polymer coating would allow for denser target atoms per area to be analyzed which further increases the rate of interaction counting. Samples could also be stripped of the polymer coating bonded to the particle core, possibly through the use of acidified benzene. The solvent may denature the oleic acids and possibly not oxidize the iron mineral core, the solvent and resulting carbon chain fragments could then be separated from the NP by a magnetic field and decanting or volatilization to produce a true solid for traditional Mossbauer at room temperature.

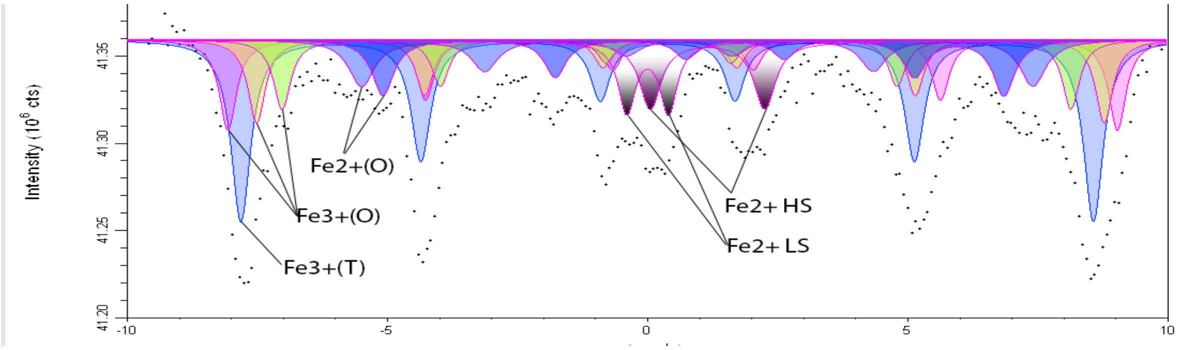


Figure 7. A model developed of components in the initial non-oxidized material measured at low temperature (11K) was developed to illustrate the tetrahedral, octahedral valence states and paramagnetic components suspected deal.

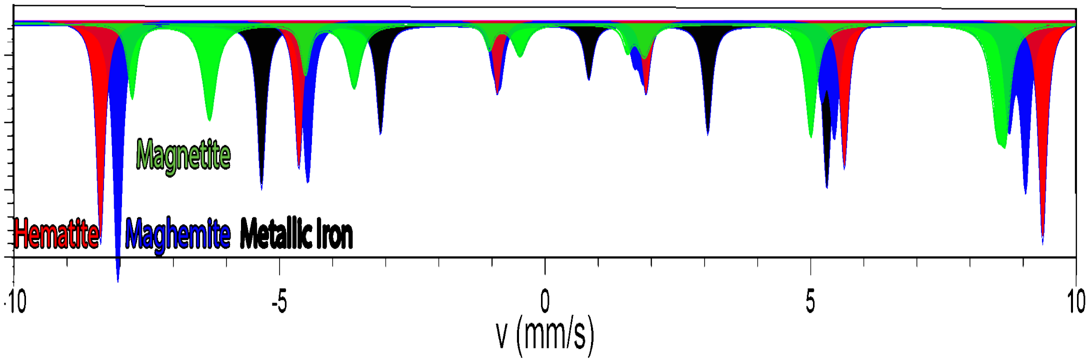


Figure 8. The final model of non-oxidized sample at 11K demonstrating ideal spectrographic signals of the components that represent the various phases included in the nanoparticle core. Note: referenced to α-Fe (metallic Iron) included in this representation.

It is concluded that, in general, core particles are composed of small crystallites (grains) of different phases of maghemite or magnetite solid solution with a possibility of less complex structured mineral (Hematite or other inverse spinel) with a possible variable volume ratio from particle to particle. Signals appearing as Fe^{2+} doublets, paramagnetic material, could be unreacted reagent, surface interacting iron, or an iron complexed with carbon chain byproduct, as it may also interact with the pi bond of an olefinic acid's carbon chain or alkane fragment during the synthesis.

While the untreated samples have a moderate amount of ideal magnetite phase included. Evidence of the Verwey transition in nano-crystalline magnetite in nonstoichiometric nanometric powders were demonstrated and are evidenced as likely in literature.[4,9,14] The presence of magnetite in our non-oxidized sample is confirmed by the Verwey transition being evident below 150K.

Oxidized samples are most entirely reminiscent of ideal Maghemite. Studies on magnetite NPs suggest that the Verwey transition shifts to lower temperatures due to the finite-size effect or vanishes below a critical size. Therefore, these samples either do not contain Fe_3O_4 or only a small fraction not showing the Verwey transition. However, no iron was identified as magnetically ordered Fe2+ at 11K which strongly suggests no ideal maghemite exists in this sample. Thus, essentially annealing in air yields a predominantly γ-Fe_2O_3 structure of NPs. The crystallographic structure of the NPs and thus the magnetic behavior depends on the thermal treatment of the NP.

Despite the liquid phase of the holding matrix, solid nanoparticles display Mossbauer signal even at room temperature. Cryostat temperatures below 30K, well below the Verwey temperature of magnetite demonstrate the best observed resolutions. Temperature points above 150K of these samples as even concentrated colloidal suspensions are difficult to resolve in reasonable time frames with only moderate activity sources.

5. Acknowledgements:

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6. References:

1. *Using the Mossbauer Effect.* Goldanski, V. I. December 1963, International Science and Technology, pp. 40-48.

2. *The Mossbauer Spectra of Chemical Compounds.* Greenwood, N. N. 2, February 1967, Chemistry in Britain, Vol. 3, pp. 56-72.

3. *Fifty Years of Mossbauer spectroscopy: from alloys and oxides to glasses and nanoparticles.* Johnson, C.I. and J.A., Johnson. 2012, Hyperfine Interact, Vol. 204, pp. 47-55.

4. *Magnetic Iron Oxide Nanoparticles: Recent trends in design and synthesis of magnetoresponsive nanosystems.* E. Tombacz, R. Turcu, V. Socoliuc, L. Vekas. August 2015, Biochemical and Biophysical Research Communications, Vol. 468, pp. 442-453.

5. *Comparative study oof iron oxide nanoparticles as- prepared and dispersed in Copaiba oil using Mossbauer spectroscopy with low and high velocity resolution.* M.I. Oshtrakh, V. Sepelak, A.F.R. Rodriguez, V.A. Semionkin, M.V. Ushakov, J.G. Santos, L.B. Silvera, E.M. Marmolejo, M. DeSouza Parise, P.C. Morais. 100, November 2011, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, pp. 94-100.

6. *Study of Iron oxide nanoparticles using Mossbauer spectroscopy with a high velocity resolution.* Oshtrakh, M. I., et al. January 2016, Spectrochimica Acta Part A: Molecular and Biomolecular spectroscopy, Vol. 152, pp. 666-679.

7. Ushakov, M.V., et al. Magnetic properties of iron oxide-based nanoparticles: Study using Mossbauer spectroscopy with high velocity resolution and magnetization measurements. September 2016. Accepted Manuscript.

8. *Continuous synthesis of iron oxide (Fe3O4) nanoparticles via thermal decomposition.* Glasgow, W., et al. 2015, Particuology, Vol. 26, pp. 47-53.

10. *Mossbauer studies of Magnetite Nanoparticles.* Shipilin, M.A., et al. 3, 2014, Journal of Surface Investigation. X-ray, synchrotron and neutron techniques, Vol. 8, pp. 557-561.

11. *Biogenic Magnetite in Humans and New Magnetic Resonance Hazard Questions.* Strbak, O. and Kopcansky, P., Frollo, I. 3, 2011, Measurement Science Review, Vol. 11, pp. 85-91.

12. *Biochemistry and the Mossbauer effect.* Fraunfelder, H. Monticello, IIIinois : s.n., 1969.

13. *Biogenic Magnetite in Humans and Magnetic Resonance Hazard Questions.* Strbak, O, Kopcansky, P and Frollo, I. 3, Bratislava, Slovakia : Measurement Science Review, 2011, Vol. 11, pp. 85-91.

14. Murad E, Cashion J. *Mossbauer Spectroscopy of Environmental Materials and their Industrial Utilization.* Boston : Kluwer Academic Publishers, 2004. ISBN 1 4020 776 2.