Magnetic Interactions and the Mössbauer Effect in Coated Ferrihydrite Nanoparticles

by

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Under the supervision of Professor James Welsh

ABSTRACT

Ferrihydrite, $Fe_5HO_8 \cdot 4H_2O$, has low crystallinity and is fairly ubiquitous in nature. It is best studied using magnetism and Mössbauer spectroscopy. Further, because ferrihydrite readily adsorbs a variety of materials, it usually occurs as coated particles. The purpose of this study was to determine the effects of the coatings on the magnetic properties of ferrihydrite and to understand the magnetic properties of these coated nanoparticles. A single batch of synthesized ferrihydrite was divided into five samples. One of these samples was left uncoated, the remaining four samples were coated with sugar, lactose, ascorbate, and alginate respectively. Samples coated with lactose or ascorbate did not provide useful information because these coatings interacted with the ferrihydrite, producing a new material that affected the magnetic properties of the ferrihydrite. The data from the remaining three samples was consistent enough to be useful in drawing conclusions. ZFC/FC curves, AC susceptibility curves, and hysteresis loops were obtained for these samples to investigate the effects of coatings on the magnetic interactions between the ferrihydrite nanoparticles. Mössbauer spectroscopy was also applied as a non-magnetic means of determining how the coatings affected these magnetic interparticle interactions. Ultimately, the data overwhelmingly showed a decrease in interactions between coated nanoparticles. These results will facilitate future studies of natural ferrihydrite.

ACKNOWLEDGEMENTS

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INTRODUCTION

Ferrihydrite, $Fe_5HO_8 \cdot 4H_2O$, is an amorphous iron oxyhydroxide. It is geologically young and is commonly found in soils containing soluble silicate or organic material that is undergoing rapid early weathering. The presence of silicate and organic material in soils inhibits the formation of more crystalline iron oxides (Childs, 1992). Under warmer and dryer conditions, ferrihydrite ages to become goethite or hematite (Berquó et al., 2007). Some believe that it may also become magnetite or maghemite, given appropriate conditions (Jambor and Dutrizac, 1998). In addition to soils, ferrihydrite occurs in association with hydrothermal vents, is an important constituent of mine wastes, and has been identified in Mars surface samples. It also occurs as the core of ferritin, the main iron storage protein (Jambor and Dutrizac, 1998).

In soils, ferrihydrite is a cementing agent and provides pigmentation. It controls iron content in water by precipitating out when there is an oversaturation of iron (Jambor and Dutrizac, 1998), and is important in the adsorption of trace elements (Rancourt et al., 2001). Because of it is inexpensive, has a large surface area, and has high adsorptive capacities, ferrihydrite is useful in the removal of pollutants from water (Jambor and Dutrizac, 1998). It is especially important as an arsenic adsorbent, and is used to remove excess arsenic from mine wastewaters.

Ferrihydrite is antiferromagnetic, a situation in which the electrons spins align in an alternating pattern, thereby cancelling each other out. Therefore, the magnetization observable in ferrihydrite results from extra uncompensated spins that typically exist on the surface of the particle. The strength and direction of this magnetization is called a magnetic moment.

Ferrihydrite's net magnetization is strongly dependent on temperature. The addition of thermal energy increases randomization of the orientation of the magnetic moments. When thermal energy is removed, an applied magnetic field can be used to align the magnetic moments. Above a certain temperature, called the blocking temperature, thermal energy causes significant randomization of the magnetic moments, and the net magnetization is lower. A higher blocking temperature indicates that the particles have stronger magnetizations and are interacting more strongly. Below the blocking temperature, the magnetic moments are essentially frozen. Because blocking temperature is related to particle size, the blocking temperature can then be plugged into an equation to calculate particle sizes.

Below its blocking temperature, ferrihydrite exhibits superparamagnetic behavior, where application of a magnetic field causes the individual particles to align with the magnetic field. In non-superparamagnetic behavior, the magnetic moments within the particles move independently when a field is applied.

For this study, the magnetic properties of coated and uncoated ferrihydrite were compared. Because ferrihydrite adsorbs many trace elements, naturally occurring ferrihydrite particles are often coated with a layer of adsorbed ions. This affects the magnetic properties, especially for samples with thicker coatings. It is the purpose of this study to examine the effects of coatings on the magnetic properties of ferrihydrite. Ideally, the magnetic interactions between particles will be reduced or blocked completely by the increase in interparticle distances created by the coatings, and by the presence of the coatings themselves. The magnetic properties of non-interacting ferrihydrite nanoparticles can then be understood more fully and applied to other studies.

PREVIOUS WORK

Guyodo et al. (2005) studied the basic magnetic properties of uncoated ferrihydrite nanoparticles using Mössbauer spectroscopy, transmission electron microscopy, and x-ray absorption spectroscopy. Using both field-cooled (FC) and zero-field-cooled (FC) methods, they demonstrated a general increase in blocking temperatures with increasing particle size. They also used these methods to show that ferrihydrite exhibited superparamagnetic behavior below its blocking temperature. An additional ferromagnetic-like magnetic moment that resulted from uncompensated spins was also detected.

Berquó (2007) also studied the effects of particle size on the magnetic properties, and explored the possibility of using ferrihydrite to help interpret the record of the earth's magnetic field. Smaller ferrihydrite samples exhibited blocking temperatures below 300K, as is common in ferrihydrite. Blocking temperatures increased with increasing particle size to a maximum of 422K for the largest sample. It was determined that particles larger than 10 nm could carry remanent magnetization. However, particles of this size are uncommon, so ferrihydrite is not likely to be useful for investigating the magnetic record.

METHODS

Ferrihydrite was synthesized in the lab and split into five samples. One sample each was coated with lactose, ascorbate, alginate, or sucrose; one sample was left uncoated as a control sample. X-ray diffraction (XRD) patterns for each sample were obtained to verify the composition of each sample. It was discovered that the lactose and ascorbate coatings interacted with the ferrihydrite nanoparticles, affecting the magnetic properties of the ferrihydrite samples. Because this study was aimed at studying the magnetic properties of ferrihydrite and not the magnetic properties of new materials formed by chemical interactions between the coatings and the ferrihydrite, the data for these samples was disregarded.

Ferrihydrite can be difficult to characterize because of its low crystallinity and because it only occurs as nanoparticles between about 1 and 50 nm. Consequently, the most reliable means of identifying and studying ferrihydrite are by low-temperature magnetism and Mössbauer spectroscopy.

Investigations into the magnetic interactions in each sample were carried out using a SQUID (superconducting quantum interference device) Magnetometer. Different trials carried out using the magnetometer could be plotted, yielding zero-field-cooled and field-cooled (ZFC and FC) curves, AC susceptibility curves, and hysteresis loops.

ZFC (also known as isothermal remanent magnetization or IRM) data are obtained by cooling a sample in the absence of a magnetic field, thus "freezing" the magnetic moments of the sample in their original state. The sample is then warmed in an applied magnetic field. The magnetization of the sample is measured throughout the warming process. As shown in the white curve in Figure 1, the magnetization slowly increases as the magnetic moments are

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unfrozen until reaching a noticeable peak (as indicated by the arrow). The temperature at which this peak occurs is the blocking temperature (T_B) for the sample (Hansen and Mørup, 1999). The blocking temperature can be used to determine how magnetic interactions between particles change for
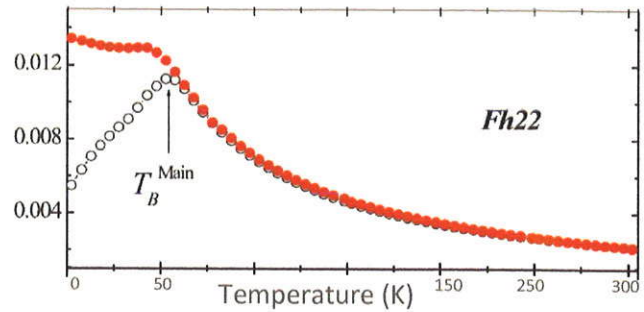

Figure 1: Sample ZFC/FC curve from Berquó (2007) for ferrihydrite showing a definite peak in magnetization at the blocking temperature. The blocking temperature peak occurs around 50K.

each of the samples. Above the blocking temperature, thermal energy randomizes the magnetic moments, decreasing the net magnetization. FC (or thermoremanent magnetization, TRM) curves measure the magnetization of the sample when a field is applied during the cooling process. This is represented by the red curve in Figure 1.

AC susceptibility curves measure the magnetic moment induced in a samples by an alternating, time dependent (AC) field. AC measurements are very sensitive to small changes in the magnetization of the sample because they track changes in the slope of the magnetization graph instead of the value itself. At the frequencies used in this experiment, two values were obtained because of a lag between the peak magnetization of the sample and the peak strength of the applied AC magnetic field. These two values were the in phase the larger of the curves shown in Figure 2, and out of phase (with the driving field) values shown in
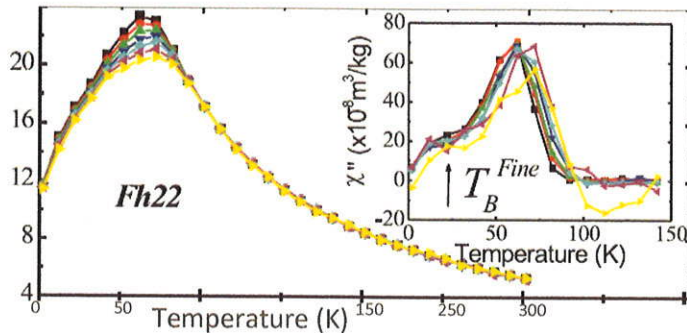

Figure 2: Sample AC susceptibility curves from Berquó (2007) for ferrihydrite, again showing a definite peak at the blocking temperature. As with the ZFC/FC curves, the blocking temperature peak occurs around 50K. The larger curve is the in-phase component of the AC magnetization, and the inset is the out of phase values.

the inset of Figure 2 (Martien, 2000). In this experiment, a variety of frequencies ranging from 1 Hz to 1000 Hz were tested.
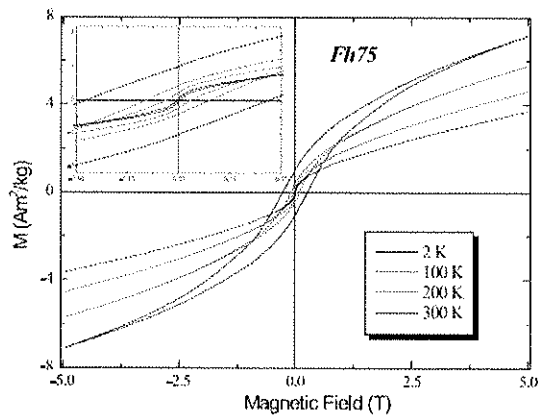

Figure 3: Sample hysteresis loops for ferrihydrite from Berquó (2007). The inset is a close-up of the middle portion of the graph. Wasp-waistedness would be characterized by a pinching of the loops near the center.

Hysteresis loops result from a sample's "memory" of a previously applied field. These loops illustrate the magnetization of a sample as the applied magnetic field changes, as shown in Figure 3. Characteristics of the hysteresis loops (like wasp-waistedness and asymmetry) can provide insights to magnetic characteristics of the sample. For example, the presence of multiple types of magnetic materials may cause the loops to be wasp-waisted (pinched in the middle). Each hysteresis loop was run at a variety of temperatures to determine how the loops changed.

The ferrihydrite was further analyzed using Mössbauer spectroscopy and X-ray diffraction (XRD). Mössbauer spectroscopy is used to investigate the Mössbauer effect (Mössbauer, 1958 and Vandegrift and Fultz, 1997) in a given sample. The Mössbauer effect is a recoilless emission or absorption by an atom of a photon from a radioactive source; it provides information about the oxidation states of the iron in the ferrihydrite and about particle interactions. XRD spectra were used to investigate the structure of the ferrihydrite samples to determine whether the ferrihydrite had interacted with its coating.

RESULTS

XRD patterns for each of the five samples are shown in Figure 4. The peaks characteristic ferrihydrite occur at 2θ angles of 41° and 73° and are most visible in the uncoated sample. These peaks are again visible, though less pronounced, in the sugar-coated and alginate-coated samples. The ascorbate- and lactose-coated samples show significant peaks below 2θ angles of 30°. These are interpreted to be a result of the formation new substances. Any measurement of interactions between the ferrihydrite nanoparticles was clouded by the magnetic properties of this new substance, so these two samples were not used to investigate how magnetic interactions between nanoparticles changed for coated samples.
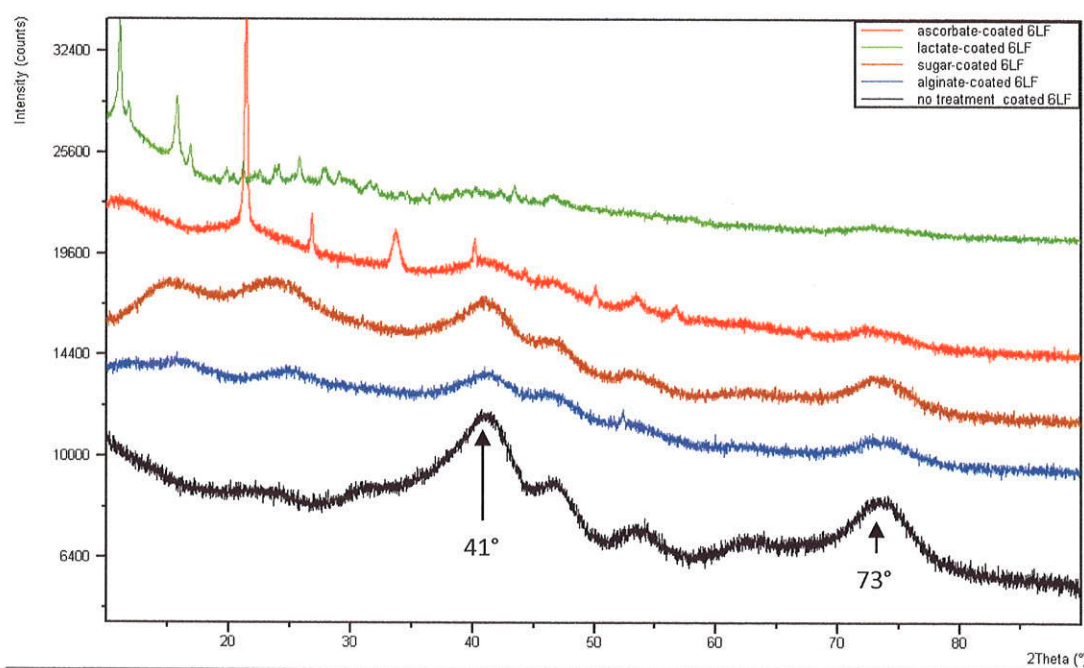

Figure 4: X-ray diffraction patterns for each of the five samples of ferrihydrite. The peaks at 41 and 73 are characteristic of ferrihydrite. Their presence in the sugar-coated, alginate-coated, and uncoated samples verifies the presence of ferrihydrite in the samples. The extra peaks below 30 in the ascorbate- and lactose-coated samples support the belief that a new substance formed as a result of interactions between these samples and their respective coatings.

ZFC/FC Data

The data from the ZFC/FC curves (Figure 5) were the most helpful for determining particle interactions. Most notable in these data is a depression of the peak, which represents blocking temperature, for the coated samples, shown in Figure 5B and C. The peak for the uncoated sample, Figure 5A, is consistent with typical blocking temperature values for ferrihydrite.
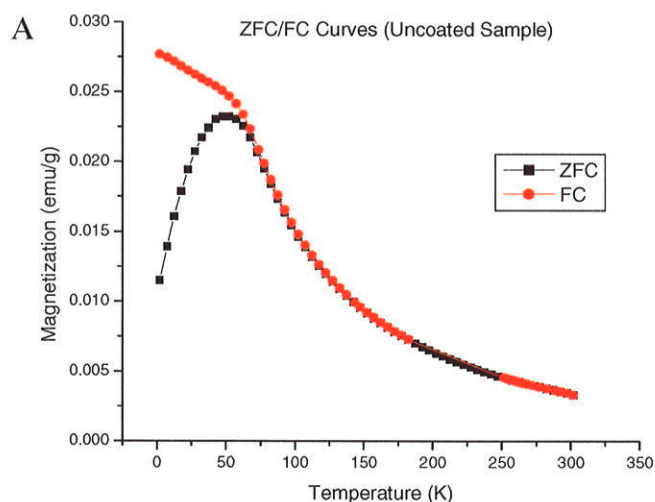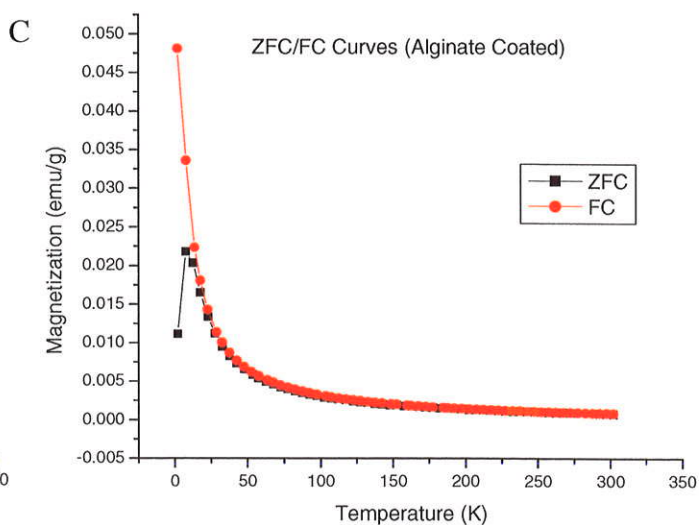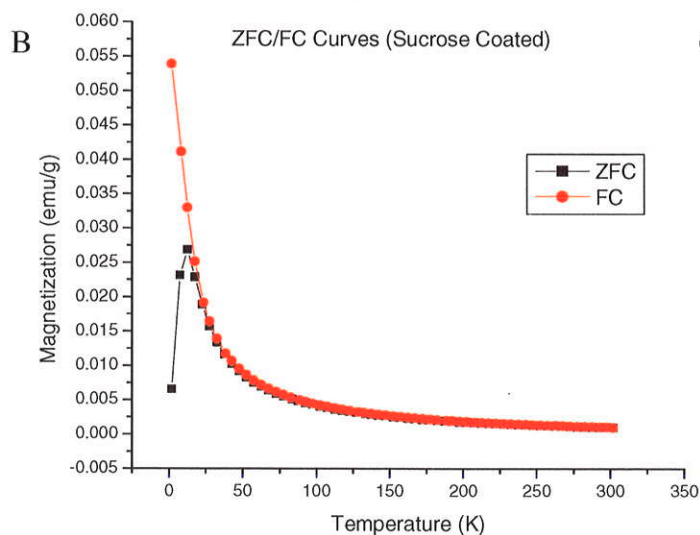
A

Figure 5: ZFC/FC curves for the uncoated sample (A) and the samples coated in sugar (B) and alginate (C). The blocking temperatures are the temperatures at which the ZFC magnetization peaks. The depression of the blocking temperatures in the coated samples indicates decreased particle interactions.

B

C

Hysteresis Data

The data from the hysteresis loops support the decrease in interparticle interactions for coated particles illustrated in the ZFC curves because the loops become a line at lower temperatures for the sugar-coated (Figure 6B) and alginate-coated (Figure 6C) samples than for the uncoated sample (Figure 6A). The temperature at which these loops become a line is indicative of the blocking temperature. All three hysteresis loops also show an exchange bias (a shift – in this case to the left), and the coated samples displayed a small degree of wasp-waistedness (a narrowing of the hysteresis loop at the point where the applied field is zero).
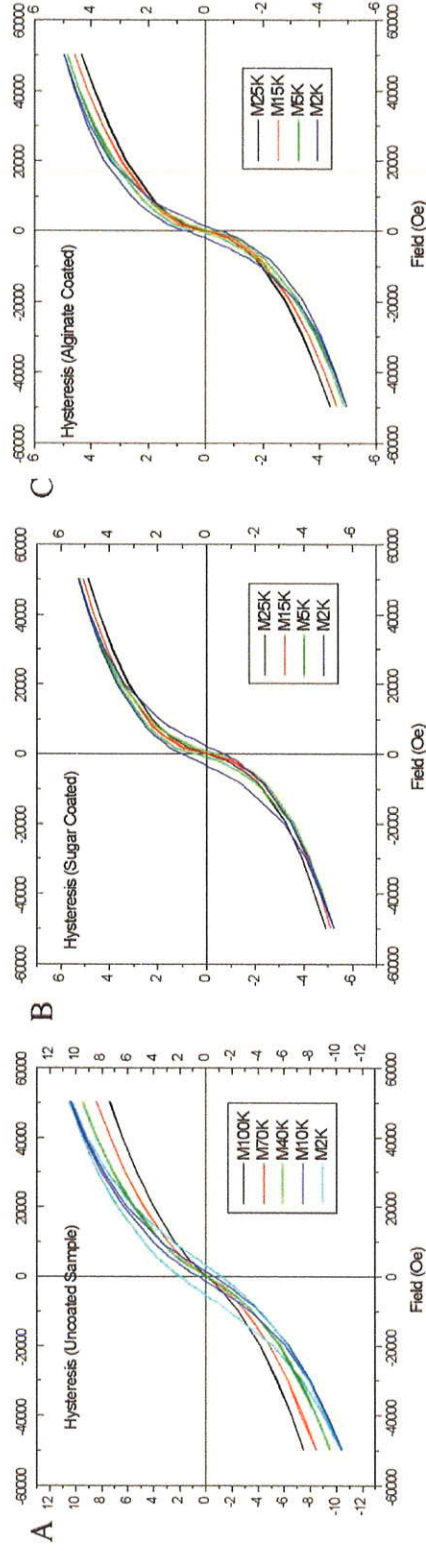
Figure 6: Hysteresis loops for the uncoated sample (A) and the sugar-coated (B) and alginate-coated (C) samples used in this experiment. The hysteresis loops are characterized by some exchange bias and wasp-waistedness. The decrease in particle interactions exhibited by the ZFC curves is supported by decrease in temperature at which the hysteresis loops become a line (blocking temperature).

AC Susceptibility

The AC susceptibility graphs shown in Figure 7 were each very similar in shape to their corresponding ZFC curves. Again, the peaks of these curves occurred at lower temperatures for the coated samples.

Figure 7: In phase (A C E) and out of phase (B, D, F) AC susceptibility data. The more narrow, lower temperature peaks of both in and out of phase AC susceptibility implies a reduction in particle interactions for coated (C, D, E, F) nanoparticles.
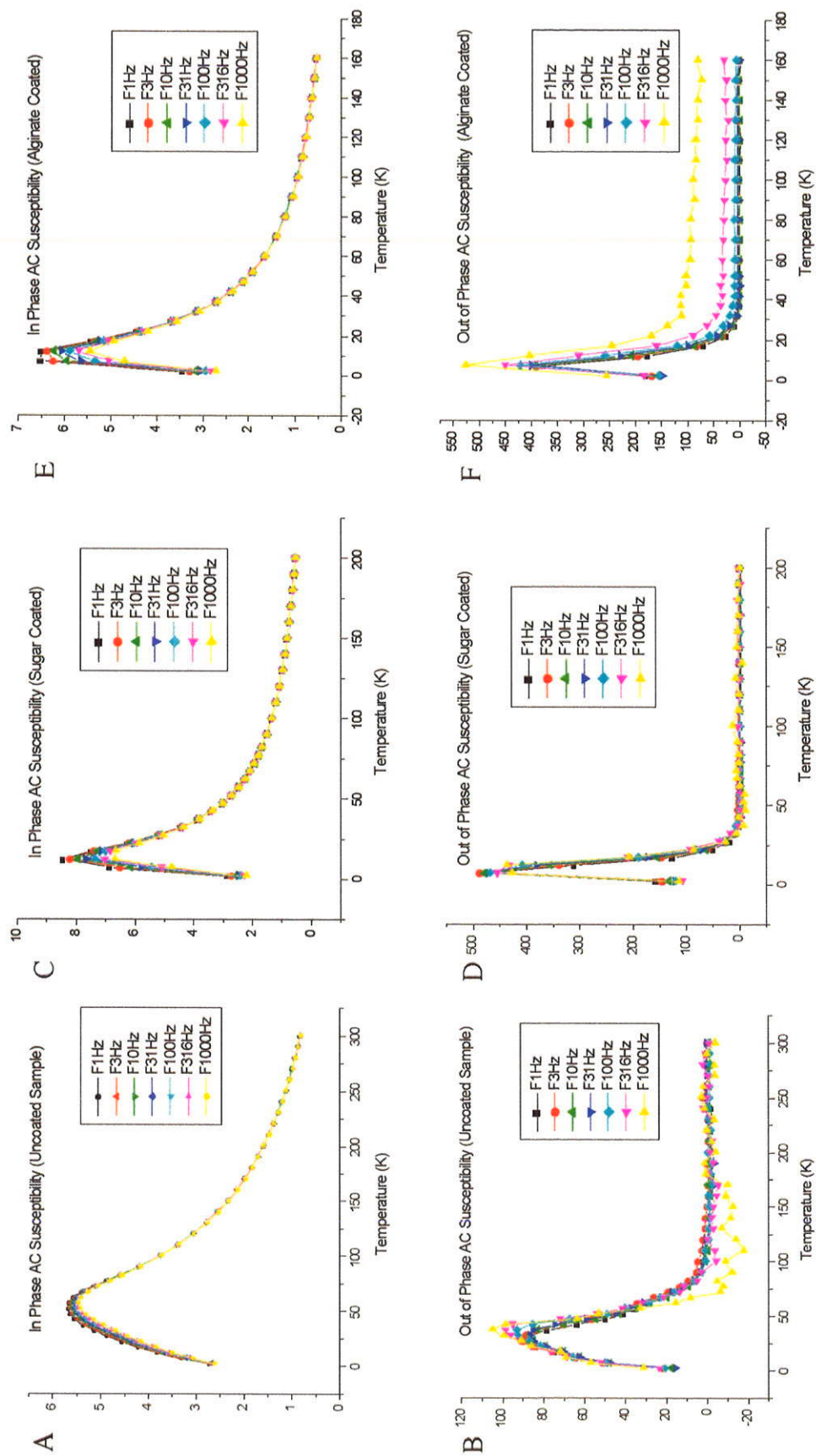
Blocking Temperatures

To further investigate the interparticle interactions in the uncoated sample, the sugar-coated sample, and the alginate-coated sample, ZFC curves were obtained at a variety of different applied fields. The blocking temperatures for each trial were then graphed against the corresponding applied field, Figure 8. The relatively consistent values for the blocking temperatures demonstrated by the coated samples reflect a lack of particle interactions.
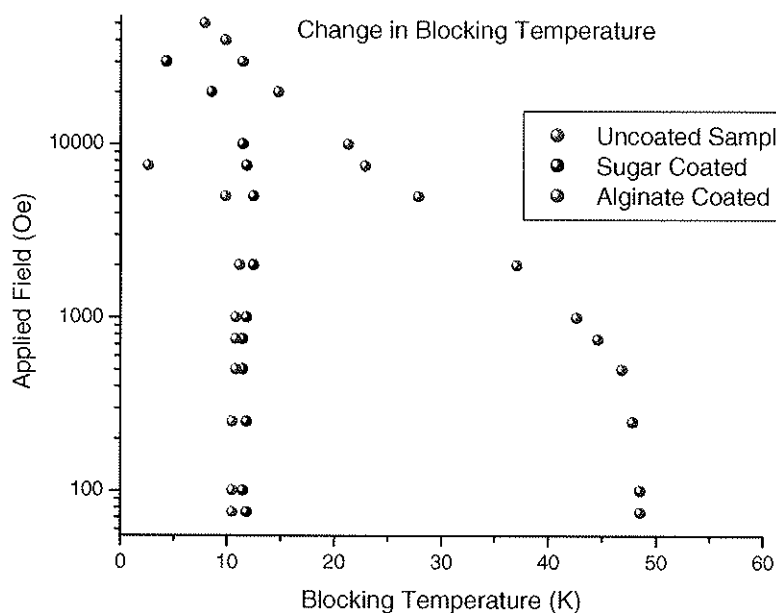
Figure 8: Change in blocking temperature at different applied fields. The relatively consistent values for blocking temperatures of the coated samples are a strong indication that the ferrihydrite in these samples is not interacting.

Mössbauer Spectroscopy

Mössbauer spectra were used as another method of investigating interparticle interactions. Mössbauer spectroscopy is useful because it examines particle interactions using means other than magnetism. The spectra shown in Figure 9A are typical for ferrihydrite. The more complex fit shown in Figure 9B indicates non-interacting particles. In Figure 9C, the extra peaks in the ascorbate-coated sample reflect the presence of a new iron phase from the interaction of the coating with the ferrihydrite.

Figure 9: The Mössbauer spectra for the uncoated sample (A) and the coated samples – the sugar-coated sample is shown above (B) – were characteristic of spectra for interacting and non-interacting 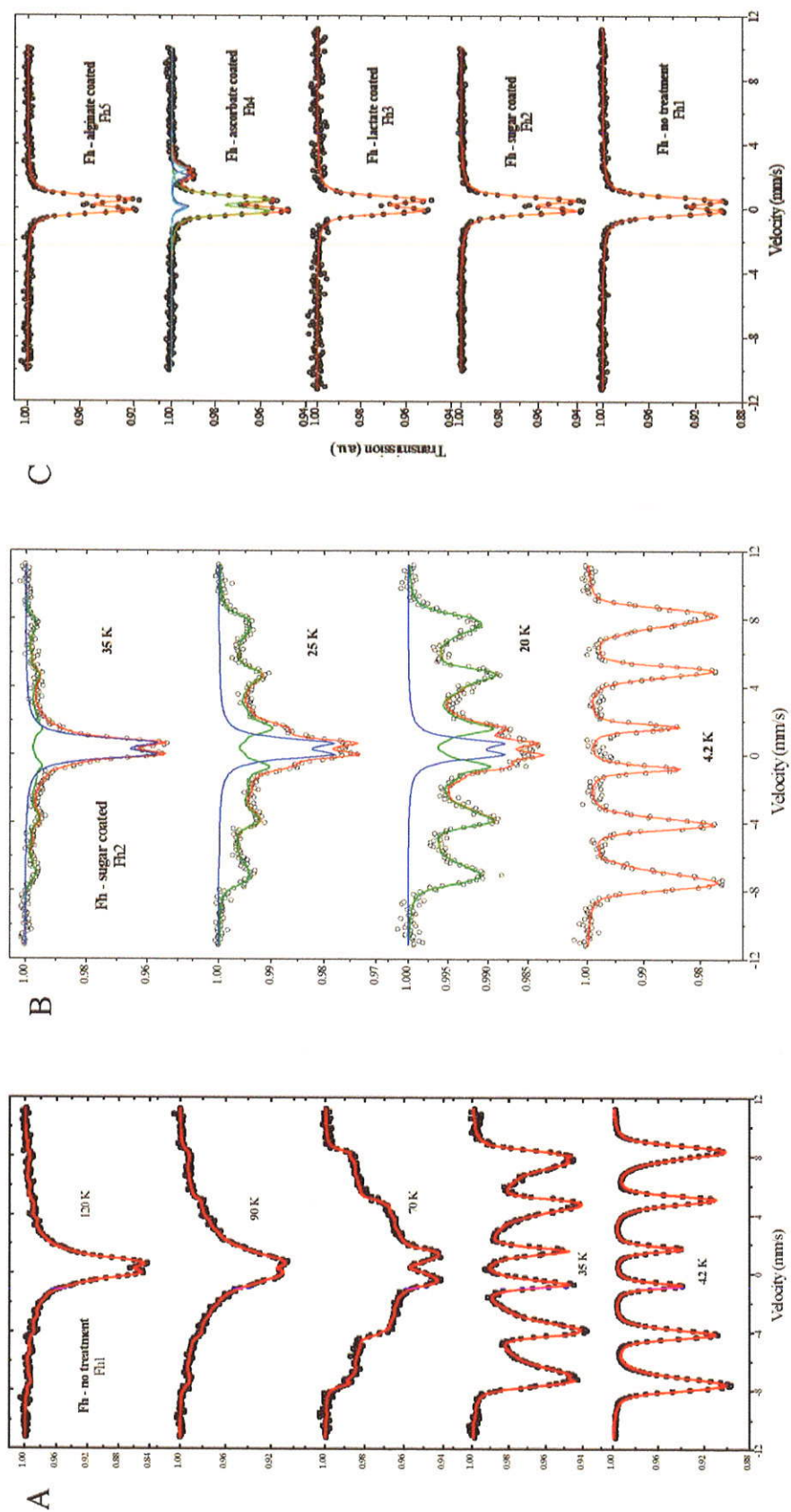samples. The Mössbauer spectrum for the ascorbate-coated sample (in C) showed the presence of iron II, a phase not present in ferrihydrite. Its presence supports the hypothesis that the coating interacted with the ferrihydrite sample.

ANALYSIS

The data from the ZFC curves was especially effective at conveying a change in magnetic interactions. Blocking temperatures were determined from the peak of the ZFC curves (Hansen and Mørup, 1999), and are displayed below in Table 1. The data and trends from the ZFC curves were reflected in the AC susceptibility curves, giving credence to the conclusions drawn from the ZFC curves. However, because blocking temperatures are easier to discern from ZFC curves, the AC data was not directly used in analysis.

Sample	Uncoated	Sugar Coated	Alginate Coated
Blocking Temperature	49.46 K	12.47 K	10.63K

Table 1: Blocking temperatures for the uncoated, sugar-coated, and alginate-coated samples. The values for the blocking temperatures were taken to be the temperature at which the ZFC curve peaked.

The depression of the blocking temperature for the sugar- and alginate-coated samples is suggestive of a decrease in interparticle magnetic interactions. When magnetic particles interact, they appear larger because the interactions cause multiple adjacent particles to act like a single large particle or make it difficult to distinguish particle boundaries. Blocking temperatures are higher for larger particles, as described in the Néel-Arrhenius law (Néel, Aléonard, Brissonneau, 1963).

$$\tau = \tau_0 e^{E_a/k_B T}$$

In this equation τ and τ_0 are time constants, k_B is the Boltzman constant, T is the temperature (in this case blocking temperature), and E_a is the energy barrier that must be overcome, where

$$E_a = K_{eff} V.$$

K_{eff} is the effective anisotropy constant and V is the volume of the nanoparticle, which is assumed to be spherical. The diameter of the particle can then be found using

$$d = \sqrt[3]{\frac{6 k_B T}{K_{eff} \pi} \ln \left(\tau / \tau_0 \right)}.$$

The natural log of τ/τ_0 is assumed to be 25 because τ is roughly 72 billion times τ_0. The magnetocrystalline anisotropy constant, 170 kJ/m^3 is used for K_{eff}. The resulting diameters are shown in Table 2 (below).

Sample	Uncoated	Sugar Coated	Alginate Coated
Diameter	5.77 nm	3.64 nm	3.45 nm

Table 2: Particle size estimates calculated using the Néel-Arrhenius Law. The size estimates for the coated samples are much closer to the measured particle size of 3.7 nm.

Actual particle sizes could be approximated using images from a tunneling electron microscope (TEM) (Figure 10).
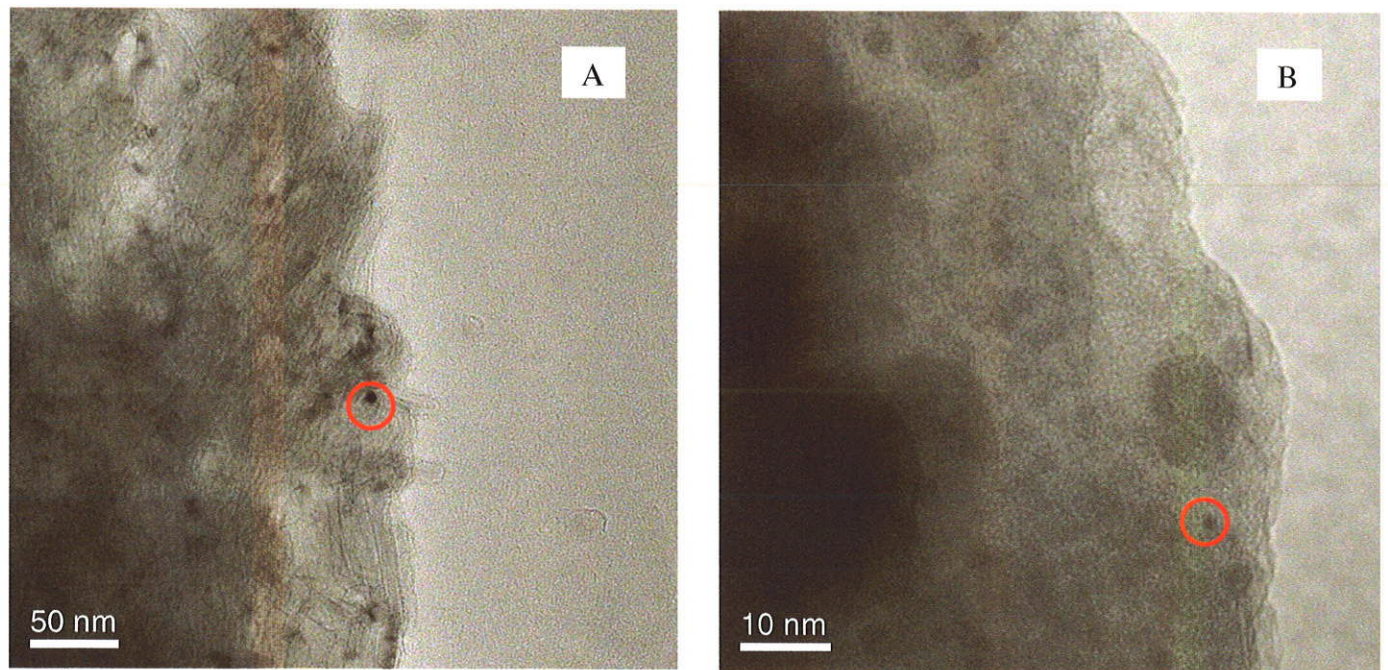

Figure 10: TEM images of sugar-coated (A) and alginate-coated (B) ferrihydrite. A ferrihydrite nanoparticle is circled in each image, to give an idea of particle sizes.

Using images like these, the particles were estimated to be about 3.7 nm in diameter. This value is much closer to the values determined for the particles with coatings. The actual particle size is not especially relevant, but the more accurate size estimate for coated particles indicates a decrease in particle interactions for these particles because the calculations are not corrupted by magnetic interactions. Further, the correspondence between the particle sizes from calculations and from image measurements indicate that the particles are not aggregated. Were they aggregates, the data would be useless because it would measure the particle interactions for the aggregates instead of the individual particles.

The change in blocking temperature for different field strengths can also be suggestive of changes in particle interactions (Luo et al, 1991). Unless the applied field is of a high enough magnitude, particle interactions and the interaction energy dominate the behavior of the system. Therefore, the steady nature of the blocking temperature indicates a lack of field dependence and a lack of particle interactions because nothing imparts a change on the value of the blocking temperature. The lack of particle interactions is due to the increased interparticle distance resulting from the coatings.

The AC susceptibility data showed, both for in-phase and out-of-phase susceptibility, a depression in the peak susceptibility for the coated particles. The temperatures at which the peaks occurred for each sample was very similar to the blocking temperatures found in the ZFC curves. Additionally, the relatively constant nature of the peak for the coated samples indicates, once again, a lack of particle interactions. This is not seen in the uncoated sample, where the peak migrates to higher temperatures at higher frequencies because the particle interactions are more difficult to overcome at lower frequencies (Martien, 2000).

This decrease in particle interactions was further supported by the data from Mössbauer spectroscopy. As the temperature is raised from 4.2 K, the Mössbauer spectrum from the uncoated sample slowly collapses from a sextet to a collapsed hyperfine field and then becomes a doublet above 100 K. This is the expected behavior for interacting particles. Non-interacting ferrihydrite particles should go from a sextet to a combined sextet and doublet before becoming a doublet at a temperature significantly lower than for interacting particles (Bødker et al., 2000; Mørup et al., 1995). This was the behavior observed in the coated samples. In the Mössbauer

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spectra from one of the samples with interacting coatings, an additional doublet indicated the presence of iron II, an iron phase which is usually not present in ferrihydrite. This doublet is outlined in blue on the spectrum from the ascorbate-coated sample.

The hysteresis loops support the conclusion that particle interactions were largely blocked by the coatings. Above the blocking temperatures of each sample, the hysteresis loops were essentially lines. Above its blocking temperature, ferrihydrite is superparamagnetic, and this is characteristic of superparamagnetic materials (Berquó et. al., 2007). The hysteresis loops for the coated samples narrowed to the point of being a line at much lower temperature than did the hysteresis loops for the uncoated sample, indicating a lower blocking temperature.

The hysteresis loops were also characterized by wasp-waistedness and an exchange bias which provided further insight as to the nature of the ferrihydrite. The exchange bias likely results from disordered spins at the surface of the ferrihydrite nanoparticles. The lack of order would make it more difficult to align the magnetic moments, as a result of competing magnetic interactions. The wasp-waistedness of the hysteresis loops is most probably associated with a small distribution of grain sizes in each sample (Roberts, et al., 1995). Having a variety of grain sizes in one sample may be reflected in a distribution of the magnetic coercivities of that sample. The would-be hysteresis loops for each coercivity are added to make the hysteresis loop for a given sample. The small degree of wasp-waistedness visible in these hysteresis loops can be readily explained by a grain size distribution that includes single-domain grains and superparamagnetic grains (Roberts et al., 1995).

CONCLUSION

By using Mössbauer spectroscopy, AC susceptibility, and hysteresis loops to support the interpretations of the ZFC curves, the significant reduction in magnetic interactions between coated ferrihydrite nanoparticles is evident. The depression of the blocking temperature seen in the curves of the coated particles is typical for particles as interactions decrease. Further, the higher degree of alignment between actual particle size and calculated particle size for the coated samples is highly indicative of reduced particle interactions. The hysteresis loops showed some variety in individual grain sizes in their wasp-waistedness. However, because the wasp-waistedness of the hysteresis loops was small, it is unlikely that this was significant enough to affect the size comparisons made using the ZFC data.

A better understanding of how particle interactions change for coated particles is beneficial because most naturally-occurring ferrihydrite is coated. Up to this point, the majority of the research concerning ferrihydrite has used uncoated particles. Research including coated particles did not provide data for uncoated particles in comparison. By using a single original sample and adding a coating, it is possible to understand how the magnetic properties of coated ferrihydrite differ from the magnetic properties of uncoated ferrihydrite, without the addition of unnecessary variables. This will facilitate future studies of natural ferrihydrite and the environmental iron cycle and mining processes in which it is important (Jambor and Dutrizac, 1998).

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