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Atomic scale study of thermal reduction of nano goethite coexisting with magnetite

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Evolution of the local structure and magnetic properties of nano particles of goethite having magnetite as a composite due to controlled annealing treatments in vacuum has been studied using Mossbauer spectroscopy. Importance of size, defect associated with structural OH- for the observed structural and magnetic properties of goethite has been emphasized in this study. Present Mossbauer results show that thermal annealing at low temperatures (420-550 K) lead to a partial conversion / reduction of orthorhombic goethite to cubic spinel oxides such as maghemite and off-stochiometric magnetite. This study further establishes that annealing treatments beyond 650 K predominantly results in topotactic conversion of goethite to haematite. Underlying physics of the transitions of goethite to iron oxides and the important role of desorbed hydrogen for the orthorhombic to cubic structural transitions has been elucidated in this study. Copyright 2013 Author(s). This article is distributed under a Creative Commons Attribution 3.0 Unported License. [http://dx.doi.org/10.1063/1.4790614]

I. INTRODUCTION

Among iron oxy hydroxides goethite (α-FeOOH) is the most stable one naturally occurring in earth1,2 as small rod shaped particles having a large specific surface area.3 Besides being a catalyst Goethite is mainly used for adsorption of heavy elements such as uranium and gallium in water.2,3 Goethite is also used as sorbent for arsenic and plutonium.4,5 Anisotropic nano particles of maghemite (γ-Fe2O3) and magnetite (Fe3O4) have wide spread applications in magnetic recording and high density data storage devices.6 Nano particles of haematite with aspect ratio widely different from one could be produced by oxidation of rod shaped or acicular α-FeOOH.7 Subsequently these particles are thermally reduced in inert or hydrogen atmosphere to form anisotropic magnetite nano rods.7,8

α-FeOOH has an orthorhombic crystalline structure having space group Pnma with each Fe3+ ion surrounded by six oxygen ions forming an octahedron.7 Two octahedra are linked through weak hydrogen bonding that causes distortion of octahedral linking which breaks long range coherency between crystal planes. Hydroxyl bonds form zig-zag chains between oxygen planes. These flexible hydrogen bonds stabilize the structure by accommodating internal stress though there is a loss of coherency of the crystalline lattice planes. Super exchange interactions between Fe3+.-O2-.Fe3+ result in a strong anti ferromagnetic ordering with a Neel temperature of 400 K. Four sub lattices of goethite with spins inclined at an angle ±13° with respect to [010] direction contribute for the bulk magnetic structure.9 A number of interesting aspects of magnetism in bulk, spherical and rod shaped nano particles of α-FeOOH distinctly different from that of ferri10 and antiferro magnetic iron oxides11 have been addressed in literature.12,13 It has been reported that α-FeOOH when heated dehydrates to α-Fe2O3 due to removal of hydroxyl sheets and some of the oxygen in strips parallel to c-axis to form water.14 Various aspects related to the topotactical transformation of α-FeOOH

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to $\alpha$-Fe$_2$O$_3$ have been addressed in a detailed manner in the literature. In addition to $\alpha$-Fe$_2$O$_3$, indication for the formation of Fe$_3$O$_4$ in a small concentration has also been reported due to dehydration of $\alpha$-FeOOH based on low temperature induced magnetization studies. $\alpha$-FeOOH has been reported to be reduced to magnetite directly by mechano chemical means by ball milling treatment which was understood mainly due to hydrogen gas generated during the milling process. Detailed mechanism of even the well known transformation of goethite to hematite is yet to be understood completely.

The magnetic properties of goethite are strongly influenced by the degree of crystallinity which is in turn dependendent upon the size and the presence of H$_2$O. In spite of a large number of results being reported on dehydration and reduction of $\alpha$-FeOOH issues such as partial formation of magnetite, the evolution of structure and magnetic properties at distinct Fe sites in goethite due to dehydration/thermal reduction are yet to be understood completely. It is important to use techniques capable of deducing both the local structure and magnetic properties at Fe sites for a thorough understanding of the influence of OH$^-$ and oxygen related defects on structure and magnetic properties of $\alpha$-FeOOH and its evolution to iron oxides.

The local structure and magnetic properties of the bulk and nano particles of a number of important functional oxides have been studied using hyperfine techniques based on the interaction between nuclear moments of the probe atoms with electro magnetic fields at the sites of occupancies in these systems. Mossbauer spectroscopy has been extensively used to study structural and magnetic properties of oxy hydroxides and oxides of Fe based on the experimentally derived hyperfine parameters such as isomer shift, quadrupole splitting and magnetic hyperfine field as experienced by relative fractions of $^{57}$Fe resonant absorber atoms occupying distinct sites. Aspects related to structural and magnetic properties of oxy hydroxides and oxides of Fe have been addressed extensively using this technique. Time scale of $^{57}$Fe absorber based Mossbauer spectroscopy is comparable to spin relaxation time of nano particles with size up to 10 nm at room temperature thus making it a powerful tool for addressing aspects related to magnetism of nano particles. In addition the effect of particle size and crystal structure, magnetic relaxation, doping effects on the structural and magnetic properties of goethite and the transformation to hematite due to dehydration have been addressed in a detailed manner by many researchers using Mossbauer spectroscopy.

In contrast to ferromagnetic nano particles, being anti ferro magnetically ordered the dipole interaction between nano particles of $\alpha$-FeOOH is negligible. At a temperature T, the spin relaxation time $\tau$ associated with the easy axis of magnetization of a magnetic nano particle of mean volume V with anisotropy energy $KV$ is given as $\tau = \tau_0 \exp(KV/kT)$. Anisotropy energy per unit volume for $\alpha$-FeOOH has been reported to be close to $5 \times 10^4$ J/m$^3$. The value of $\tau_0$ is of the order of $10^{-12}$ to $10^{-9}$ seconds and is almost temperature independent. If $\tau$ is much larger than the experimental observation time $\tau_m$, (i.e) $10^{-8}$ seconds (i.e the life time of the isomeric state I = 3/2 of $^{57}$Fe absorber atoms), then the resultant Mossbauer spectrum will be a sextet. The spectrum would collapse in to a doublet if $\tau \leq \tau_m$. Strong interaction between magnetic nano particles might result in a drastic decrease in the super paramagnetic relaxation. The magnetic energy of a particle interacting with neighbors is given as $E = KV \sin^2 \theta - \Sigma J_{ij} S_i S_j$, with first and second terms refer to magnetic anisotropy energy and interaction energy between spins of atoms i and j located in neighboring particles respectively. Where $J_{ij}$ is the exchange coupling constant. Several important issues related to structure and magnetic properties of $\alpha$-FeOOH have been addressed in detail in the literature.

Mossbauer measurement under the application of a moderate magnetic field might be helpful for an understanding of the nature of disordered spins. Application of an external magnetic field on a system of nano particles exhibiting magnetic ordering results in the change in the effective value of hyperfine field and/or alteration in the ratio of the intensities of lines 2 and 3, 4 and 5 respectively. The ratio of $I_{2,5}/I_{3,4}$ representing transition corresponding to $\Delta m = 0$ of a sextet is given as $4 \sin^2 \theta / (1+\cos^2 \theta)$, where $\theta$ represents the angle between the direction of $\gamma$ ray and the applied magnetic field. Thus Mossbauer spectroscopy is being used as one of the powerful techniques to study magnetic transition and also spin relaxation behavior of $\alpha$-FeOOH.
Some of the important issues related to magnetism in $\alpha$-FeOOH nano particles such as particle size effects on relaxation of spins, the role of structural OH$^-$, excess water molecules dispersed between $\alpha$-FeOOH particles modifying the magnetic interactions between them are yet to be understood completely. It has been reported that $\alpha$-FeOOH produced by Fe$^{2+}$ precursors contain excess of OH$^-$ and H$_2$O. Therefore for the present study of interest, FeSO$_4$.7H$_2$O which is a precursor of Fe$^{2+}$ is chosen as the starting material for the preparation of nano particles of $\alpha$-FeOOH. This method of preparation in general involves an addition of suitable base to the salt FeSO$_4$.7H$_2$O which is reported to result in the formation of $\alpha$-FeOOH along with Fe$_3$O$_4$. Among other factors the relative fractions of Fe$_3$O$_4$ and $\alpha$-FeOOH were reported to depend upon the value of the pH and reaction temperature. Studying the evolution of local structure and magnetic properties of the associated Fe$_3$O$_4$ particles might be useful for a further understanding of the reduction of nano particles of $\alpha$-FeOOH.

The present work aims at studying the evolution of local structure of $\alpha$-FeOOH nano particles and its effect on magnetic properties such as relaxation of spins, magnetic ordering due to controlled vacuum annealing using $^{57}$Fe Mossbauer spectroscopy. Further this study is motivated at establishing experimentally at atomic scale the transformation of $\alpha$-FeOOH to polymorphs of iron oxides if any besides $\alpha$-Fe$_2$O$_3$ due to controlled thermal reduction in vacuum and to provide an understanding of the mechanism based on the Mossbauer studies. Changes in the hyperfine parameters as experienced by Fe atoms associated with magnetite particles co existing with $\alpha$-FeOOH will be deduced to elucidate the transformation of $\alpha$-FeOOH to iron oxides.

II. EXPERIMENTAL DETAILS

In this method of preparation of nano composite of $\alpha$-FeOOH and Fe$_3$O$_4$, salt of FeSO$_4$.7H$_2$O was dissolved in an ultra high pure water and left for 10 hrs. Freshly prepared aqueous NaOH was added drop wise to FeSO$_4$.7H$_2$O solution (of concentration 0.2 mol/ lit) to a pH value of 8 to convert sulfates in to hydroxides. As soon as NaOH was added the color of the solution changed from light blue to dull green which finally turned in to a dull bluish green. The precipitate was filtered and washed with ultra high pure water several times and then by acetone. This has resulted in a brown precipitate after drying the solution for 15 days in air. Basic identification of the phases of oxy hydroxides and oxides of iron was done using XRD experiments performed with Cu K$_\alpha$ radiation of wavelength 1.54056 Å. The analytical electron microscopy was carried out using CM-200 transmission electron microscope (TEM) to find out mainly the size distribution of goethite particles with respect to the focus of the problem. TEM measurements were carried out in the as prepared composite of $\alpha$-FeOOH and Fe$_3$O$_4$ nano particles by spreading out the powder on a mesh.

Mossbauer spectrometer was operated in constant acceleration mode and in transmission geometry. $^{57}$Co dispersed in Rh matrix with a specific activity of 50 mC has been used as a source for Mossbauer measurements. Each Mossbauer spectrum has been acquired in 1024 channels. The velocity calibration were carried out using 10 μm thick iron foil at 300 K. The values of isomer shifts presented in this study are given with respect to that of $\alpha$-Fe absorber at 300 K. Spectra were fitted to Lorentzian line shapes of line width $\Gamma_i$ using a non linear least squares program to obtain hyperfine parameters such as isomer shift $\delta_i$, quadrupole splitting ($\Delta_i$) and magnetic hyperfine fields ($B_{hf,i}$) experienced by relative fractions $f_i$ of distinct $^{57}$Fe absorber atoms. The powder sample consisting of the nano particles of $\alpha$-FeOOH and Fe$_3$O$_4$ prepared as described earlier (is hence forth referred to as the starting sample) has been subjected to annealing at different temperatures at a partial pressure of the order of 10$^{-6}$ mbar for 1 hour. Mossbauer measurements have been carried out at room temperature on the sample subsequent to each annealing treatment to a good statistics with the counts in each channel close to 3-5 × 10$^6$.

For carrying out Mossbauer measurements under the application of an external magnetic field parallel to the direction of $\gamma$-ray, the sample has been sandwiched between two rare earth based ring magnets each of magnetic field strength close to 0.3 Tesla. Sample-magnet assembly is placed such that the magnets are concentric with the direction of the $\gamma$-ray.
FIG. 1. XRD spectra corresponding to (A) as prepared sample and subsequent to annealing treatment at (B) 370 K, (C) 870 K at partial pressure of $3 \times 10^{-6}$ mbar. Peaks corresponding to phases corresponding to $\alpha$-FeOOH, Fe$_3$O$_4$ and $\alpha$-Fe$_2$O$_3$ have been marked with symbols $+$, $\circ$ and $\ast$ respectively along with (hkl) indices.

III. RESULTS AND DISCUSSION

A. XRD, TEM and Mossbauer characterization of the as prepared nano composite

XRD spectra obtained in the starting sample show (Cf. Fig. 1) that the peaks could be indexed with orthorhombic (Pnma) $\alpha$-FeOOH and cubic Fe$_3$O$_4$ consistent with the reported results. The XRD spectra are characterized by sharp peaks of Fe$_3$O$_4$ while indicating the poor crystalline nature of $\alpha$-FeOOH. TEM image (Cf. Figure 2(a)) shows the presence of rod shaped particles which were deduced to be $\alpha$-FeOOH based on the analysis of micro diffraction pattern (Cf. Fig. 2(b)) obtained on these particles. Size distribution of $\alpha$-FeOOH particles as obtained based on the analysis of several such TEM images acquired is shown in Fig 2(e). This shows that about 30% of $\alpha$-FeOOH particles are in the size range 5-10 nm, while 40% are in the range of 15-20 nm and the remaining particles are larger with the size ranging between 25-40 nm. Similarly analysis of TEM images of Fe$_3$O$_4$ particles acquired (Cf. Fig. 2(c) and 2(d)) it is deduced that the Fe$_3$O$_4$ particles are much larger than that of $\alpha$-FeOOH particles with size ranging between 20 nm and 70 nm (Cf. Fig. 2(f)).

Mossbauer spectrum (Cf. Fig. 3) shown as an inset at the top right corner as obtained in FeSO$_4$.7H$_2$O exhibits a single doublet with a quadrupole splitting of 3.2 mm/sec and an isomer shift of 1.22 mm/sec, implying that all Fe ions are in the valence state of +2 and the absence of any impurity phase. Spectrum obtained in the as prepared sample composed of nano particles of $\alpha$-FeOOH along with Fe$_3$O$_4$ is shown in Fig. 3(a). The spectrum could be deconvoluted in to two doublets and four sextets thus revealing the presence of six distinct sites of Fe (Cf. Table 1). Fractions $f_5$ and $f_6$ experiencing hyperfine fields 49 and 45 Tesla could be associated with tetrahedral and octahedral sites of Fe$_3$O$_4$ in accordance with the literature.

Mossbauer spectra could be resolved in to two doublets with a relative area of 25% in addition to four sextets. The occurrence of doublets is comprehended due to the association of fractions $f_1$ and $f_2$ of Fe atoms with $\alpha$-FeOOH particles of mean size less than or close to 10 nm. It is important to note from TEM results that about 30% of $\alpha$-FeOOH particles are of mean size in the range between
FIG. 2. (a) Bright field TEM micrograph showing fine rod like α-FeOOH particles. (b) Micro diffraction pattern from a goethite particle in fig. 2(a) along zone axis [2 -1 2]. (c) Bright field TEM micrograph of Fe$_3$O$_4$. (d) Selective area diffraction pattern from magnetite particle as marked in Fig. 2(c) taken along [-114] zone axis, while (e) and (f) refer to size distribution of α-FeOOH and Fe$_3$O$_4$ particles.

5-10 nm, thus bringing out a good correlation between Mossbauer and TEM results. Further most of these particles are understood to be spatially well separated by inter dispersed water molecules. Fluctuation of easy axis of magnetization of such isolated nano particles with relaxation time less than the lifetime of the isomeric state of $^{57}$Fe with spin $I = 3/2$ is understood to result in the occurrence of two super paramagnetic doublets as seen in the Mossbauer spectrum. Doublet with a quadrupole splitting of 0.6 mm/sec and an isomer shift of 0.38 mm/sec is ascribed to fraction $f_1$ associated with
TABLE I. Hyperfine parameters as experienced by relative fractions of Fe atoms associated with nano goethite (f1, f2, f3 and f4), magnetite (f5, f6) particles in the starting sample and the polymorphs of iron oxides derived due to thermal reduction of nano goethite such as maghemite (f7) and hematite (f8). Fraction f9 refers to nano haematite while f10 and f11 refer to that of Fe atoms associated with FeO reduced from Fe3O4. Detailed description of each fractions is referred to the text. The values of intensity ratios I2,5/I3,4 are given with in parenthesis for the case of the application of an external magnetic field of 0.28 Tesla along the direction of γ ray.

| Sample            | i | Γi (mm/s) | δi (mm/s) | Δi (mm/s) | B\(\text{hf}\) (Tesla) | fi(%) |
|-------------------|---|-----------|-----------|-----------|-----------------|------|
| As Prepared       | 1 | 0.58      | 0.38      | 0.63      | -               | 16   |
|                   | 2 | 0.71      | 0.46      | 1.56      | -               | 06   |
|                   | 3 | 1.22      | 0.39      | -0.12     | 37.4            | 15   |
|                   | 4 | 2.30      | 0.40      | -0.31     | 23.9            | 21   |
|                   | 5 | 0.57      | 0.33      | 0.02      | 49.0            | 06   |
|                   | 6 | 0.95      | 0.39      | 0.11      | 44.9            | 22   |
| B\(\text{ext}\) = 0.28 T | 1 | 0.55      | 0.34      | 0.64      | -               | 15   |
|                   | 2 | 0.97      | 0.46      | 1.91      | -               | 07   |
|                   | 3 | 1.39      | 0.36      | -0.08     | 34.6 (1.95)     | 30   |
| B\(\text{ext II}\) γ-rays | 4 | 0.46      | 0.42      | -0.22     | 26.7 (3.35)     | 04   |
|                   | 5 | 0.57      | 0.30      | 0.05      | 47.1 (0.11)     | 05   |
|                   | 6 | 1.00      | 0.43      | 0.12      | 43.1 (1.3)      | 24   |
| Ta = 423K(1h) 3 × 10\(-6\) mbar | 1 | 0.61      | 0.37      | 0.75      | -               | 09   |
|                   | 2 | 0.77      | 0.42      | 1.93      | -               | 05   |
|                   | 3 | 1.04      | 0.37      | -0.18     | 36.3            | 10   |
|                   | 4 | 2.22      | 0.38      | -0.12     | 25.1            | 19   |
|                   | 5 | 0.60      | 0.33      | 0.09      | 48.1            | 21   |
|                   | 6 | 0.93      | 0.39      | 0.13      | 44.1            | 15   |
|                   | 7 | 0.47      | 0.35      | -0.04     | 50.3            | 21   |
| Ta = 623K(1h) 3 × 10\(-6\) mbar | 5 | 0.59      | 0.31      | 0.07      | 49.1            | 33   |
|                   | 6 | 1.13      | 0.42      | 0.06      | 45.1            | 31   |
|                   | 8 | 0.48      | 0.39      | -0.16     | 51.0            | 28   |
|                   | 9 | 2.68      | 0.29      | 1.02      | -               | 08   |
| Ta = 873K(1h) 3 × 10\(-6\) mbar | 5 | 0.54      | 0.30      | 0.08      | 49.5            | 34   |
|                   | 6 | 0.81      | 0.54      | 0.08      | 45.7            | 32   |
|                   | 8 | 0.37      | 0.31      | -0.17     | 51.7            | 34   |
| Ta = 873K(1h) 8 × 10\(-6\) mbar | 5 | 0.48      | 0.35      | 0.06      | 48.4            | 18   |
|                   | 6 | 1.08      | 0.48      | 0.06      | 43.7            | 19   |
|                   | 8 | 0.38      | 0.34      | -0.13     | 50.5            | 26   |
|                   | 8a| 0.33      | 0.39      | -0.21     | 51.9            | 29   |
|                   | 9 | 2.68      | 0.29      | 1.02      | -               | 08   |
| Ta = 1073K(1h) 3 × 10\(-6\) mbar | 5 | 0.43      | 0.31      | 0.01      | 49.03           | 36   |
|                   | 6 | 0.46      | 0.66      | 0.03      | 46.03           | 54   |
|                   | 10| 0.49      | 0.95      | 0.48      | -               | 05   |
|                   | 11| 0.46      | 0.91      | 0.85      | -               | 05   |

super paramagnetic particles of α-FeOOH.42 Other super paramagnetic doublet corresponding to α-FeOOH and characterized by a high quadrupole splitting of 1.5 mm/sec is understood to be due to fractions (f2) associated with OH\(^{-}\) vacancies. Presence of OH\(^{-}\) vacancies makes oxygen atoms to move closer to Fe atoms resulting in a distortion of FeO\(_6\) which is manifested as a large value of quadrupole splitting. Also OH\(^{-}\) dangling bonds present in particles of size less than or equal to 10 nm provide electro static repulsion between them and these are separated by inter dispersed water molecules.

Hyperfine parameters as experienced by relative fractions f3 and f4 associated with α-FeOOH and displaying sextets are shown in the Table I. The hyperfine field of 38 Tesla with a negative value of quadrupole splitting close to -0.12 mm/sec is seen to be close to that of the microcrystalline α-FeOOH particles.41 Hence we interpret that the fraction f3 of Fe atoms is associated with nano
FIG. 3. Mossbauer spectra obtained in (a) starting sample composed of nano goethite along with magnetite particles and (b) with the application of external magnetic field of strength 0.28 Tesla applied parallel to the direction of the γ-ray. Inset shows the Mossbauer spectrum as obtained in FeSO$_4$ 7 H$_2$O implying that all Fe exhibit a valence of +2. These spectra are deconvoluted into different components due to various relative fractions $f_i$ of absorber atoms experience distinct hyperfine interactions as explained in the text.

particles of size greater than 20 nm and experiencing strong exchange coupling. The sites associated with $f_4$ are characterized by a larger line width and lower hyperfine field as compared to that of $f_3$. Hence $f_4$ is understood to be due to Fe atoms associated with nano particles in the size range of 10-20 nm having defects such as OH$^-$ vacancies at surface. Average magnetic coordination number is reduced as finite size effects become pronounced in the case of nano particles.\textsuperscript{45} Four distinct sites of Fe is understood to be dependent upon the size of α-FeOOH and the associated magnetic interactions as discussed in correlation with TEM results. A high value of Mossbauer line width implying an appreciable distribution in the magnitude of super exchange interaction and hence the hyperfine fields in α-FeOOH particles is consistent with the results reported based on detailed temperature dependent Mossbauer studies and models.\textsuperscript{11, 16}

Mossbauer spectrum obtained in the starting sample with the external magnetic field of strength 0.3 Tesla applied parallel to γ-ray direction is shown in Fig. 3(b). The values of the intensity ratios $I_{2.5}/I_{3.4}$ for different Fe sites associated with α-FeOOH and Fe$_3$O$_4$ with the application of external magnetic field are shown in the table along with the values of effective hyperfine fields. The values of the above ratio suggest that the spins of Fe atoms occupying tetrahedral and octahedral sites of magnetite could be understood to be collinear and slightly canted respectively.\textsuperscript{55} High value of $I_{2.5}/I_{3.4}$ corresponding to sextets associated with $f_4$ is consistent with the canted nature of spins and is understood to be due to OH$^-$ vacancies. Application of the external magnetic field is seen to result in a decrease in the spin disordering of Fe atoms associated with the fraction $f_4$. This results in an increase in the fraction $f_3$ attributed to crystalline like α-FeOOH at the cost of $f_4$. It is commonly agreed that the surface of nano particles of α-FeOOH contain defects resulting in a large line width in the Mossbauer spectra characteristic of distribution in the hyperfine fields.\textsuperscript{11, 16}

This observation elucidates the important role played by surface spins for accounting for the super exchange interactions between closely spaced anti ferromagnetic goethite particles.
Having identified in detail the distinct sites of Fe atoms associated with nano particles of $\alpha$-FeOOH of different size and Fe$_3$O$_4$, the following discussion is mainly based on the evolution of the fractions of Fe atoms associated with distinct phases of iron oxides due to thermal reduction of $\alpha$-FeOOH.

### B. Thermal evolution of goethite to polymorphs of iron oxides

A few representative Mossbauer spectra obtained in the starting sample subjected to annealing treatments at different temperatures are shown in Fig. 4. The variations of fractions (viz., $f_1$, $f_2$, $f_3$, $f_4$) associated with $\alpha$-FeOOH and ($f_5$, $f_6$) corresponding to Fe$_3$O$_4$ nano particles and their evolutions with annealing treatments are shown in Fig. 5. Magnitude of these fractions are seen to be constant for annealing treatments up to 370 K. Spectrum analysis shows that annealing at 420 K results in the formation of $\gamma$-Fe$_2$O$_3$ with the value of this fraction ($f_7$) becomes 0.2. Concomitantly there is a reduction in the relative fraction of Fe$_3$O$_4$ by 5%. (Cf. Table I). Hence it can be understood that the occurrence of $\gamma$-Fe$_2$O$_3$ with the value of $f_7$ as 20% has resulted from the conversion of 15% of $\alpha$-FeOOH, and the remaining fraction of 5% due to oxidation of Fe$_3$O$_4$. Color of the sample has become more brownish in accordance with an increase in $\gamma$-Fe$_2$O$_3$. Annealing at 520 K results in the formation of a fraction ($f_8$) of about 25% of $\alpha$-Fe$_2$O$_3$ as converted from $\alpha$-FeOOH (Cf. Fig. 5). Also a reduction in the relative fraction of Fe atoms associated with $\gamma$-Fe$_2$O$_3$ by 10% is observed due to annealing treatment at 520 K concomitantly leading to an increase in the relative fraction of Fe$_3$O$_4$. The fraction $f_7$ associated with $\gamma$-Fe$_2$O$_3$ becomes zero following the annealing at 620 K leading to an associated relative increase in the fraction of Fe$_3$O$_4$ by 15%. Thus the fraction of Fe atoms associated with Fe$_3$O$_4$ becomes 60% following the annealing at 620 K. Annealing beyond 500 K
results in the formation of $\alpha$-Fe$_2$O$_3$ phase as indicated by fraction $f_8$, due to topotactic transformation of $\alpha$-FeOOH. Thus it is seen that OH$^-$ play an important role in the conversion of $\alpha$-FeOOH to $\gamma$-Fe$_2$O$_3$ in the temperature interval 400-450 K, while the partial reduction of $\alpha$-FeOOH to Fe$_3$O$_4$ is observed in the annealing interval of 500-625 K.

Comparison of this result with that of the as prepared sample containing 60% and 40% of $\alpha$-FeOOH and Fe$_3$O$_4$ respectively, it could be deduced that the annealing treatments of the sample at low temperatures (<625 K) and at low partial pressure results in the conversion of a relative fraction of 15% of $\alpha$-FeOOH to Fe$_3$O$_4$. Primary stages of reduction of $\alpha$-FeOOH occur at temperatures less than 450 K were the formation of $\gamma$-Fe$_2$O$_3$ while the reduction of $\alpha$-FeOOH to Fe$_3$O$_4$ takes place during annealing treatments between 500-625 K. Formation of $\alpha$-Fe$_2$O$_3$ is observed to occur beyond 500 K. Subsequent to annealing at 625 K the fraction of $\alpha$-Fe$_2$O$_3$ is seen to be around 40% (Cf. Fig. 5) implying that about 70% of $\alpha$-FeOOH has got topotactically converted in to $\alpha$-Fe$_2$O$_3$ in the annealing interval 500-625 K. Reduction of $\alpha$-FeOOH involves removal of excess H$_2$O, loosely bound OH- and strongly bound structural OH- at different temperatures of annealing. Having understood the over all evolution of $\alpha$-FeOOH containing the nano composites of Fe$_3$O$_4$, the evolution of the local structure and magnetic properties of $\alpha$-FeOOH nano particles is discussed in the following section.

C. Evolution of local structure and magnetic properties at Fe sites of $\alpha$-FeOOH nano particles due to thermal reduction

Shown in Fig. 6 are the variations of fractions of Fe atoms associated with distinct sites of $\alpha$-FeOOH with annealing temperature. Also shown in insets are the variations of hyperfine fields at these sites and the effective hyperfine field as experienced by Fe atoms occupying distinct sites in $\alpha$-FeOOH with annealing temperature. Nano particles of $\alpha$-FeOOH are stable due to their association with excess OH- and water, as predicted by theoretical model. A slight increase in the crystalline

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FIG. 5. Variation of the fractions of iron atoms associated with the phases of $\alpha$-FeOOH ($f_1$+$f_2$+$f_3$+$f_4$), Fe$_3$O$_4$ ($f_5$+$f_6$), $\gamma$-Fe$_2$O$_3$ ($f_7$) and $\alpha$-Fe$_2$O$_3$ ($f_8$) with annealing temperature.
like fraction of $\alpha$-FeOOH ($f_3$) is seen for annealing treatments above 320 K and it reached a maximum at 370 K. Dissociation of water molecules results in a decrease in the inter separation between $\alpha$-FeOOH particles in addition to some of the OH$^-$ vacancies getting filled up, leading to an enhanced super exchange interaction between $\alpha$-FeOOH particles. This leads to an increase in the value of $f_3$ at the cost of $f_4$ accompanied by a slight increase in $B_{hf}^3$. This brings out the importance of interaction between un compensated spins at the surfaces of closely spaced $\alpha$-FeOOH nano particles leading to the observed variations. Beyond 400 K, the onset temperature of the desorption of structural OH$^-$ strongly bound to $\alpha$-FeOOH, there is a decrease in the value of $f_1$ and $f_3$ (Cf Fig. 6 and Table I). Decrease in $f_1$ is understood to be due to coarsening of particles to crystalline like $\alpha$-FeOOH. Dissociation of structural OH- due to annealing treatments result in a sharp decrease in $f_3$ while only a slight change is seen in $f_4$ associated with $\alpha$-FeOOH up to 420 K. An increase in the quadrupole splitting ($\Delta_2$) associated with $f_2$ is understood to be due to the movement of O atoms closer to Fe in order to compensate for the loss of structural OH- with increase in annealing temperature. This results in large quadrupole splitting due to an increase in distortion of FeO$_6$ octahedra.

Annealing at 520 K results in a decrease in the relative fraction of $\alpha$-FeOOH to 25% from about 60% corresponding to the starting sample. The annealing treatment leads to the conversion of 0.25 of $\alpha$-FeOOH to $\alpha$-Fe$_2$O$_3$. This implies that the topotactic conversion of $\alpha$-FeOOH to $\alpha$-Fe$_2$O$_3$ becomes a competing process to the conversion of $\alpha$-FeOOH to $\gamma$-Fe$_2$O$_3$ for annealing beyond 500 K (Cf. Fig. 5). The fractions of Fe atoms associated with crystallized ($f_3$) and disordered spin ($f_4$) components of $\alpha$-FeOOH become zero, with the reduction of as high as 20% of $\alpha$-FeOOH to Fe$_3$O$_4$ takes place subsequent to annealing at 623 K. Variation of the hyperfine fields $B_{hf}^3$ and $B_{hf}^4$ associated with $f_3$ and $f_4$ respectively are shown in insets of Fig. 6. Variation of the average hyperfine field obtained as $(B_{hf}^G(T)) = (f_3 * B_{hf}^3(T) + f_4 * B_{hf}^4(T))/(f_3 + f_4)$ is also shown. Variations of $(B_{hf}^G(T))$ in the interval
FIG. 7. Mossbauer spectra corresponding to the sample annealed at 873 K. This temperature is so chosen to be much higher than 650 K marking the complete conversion of goethite to oxides. Spectra (a) and (b) refer to the sample annealed at 873 K at partial pressure of $8 \times 10^{-6}$ mbar and $2 \times 10^{-6}$ mbar respectively. Spectrum (a) clearly reveals that $\alpha$-FeOOH annealed at 870 K (well above the dissociation temperature of $\alpha$-FeOOH) and at a partial pressure close to $10^{-5}$ mbar gets predominantly converted to $\alpha$-Fe$_2$O$_3$. (b) Annealing at 873 K and at a lower partial pressure $2 \times 10^{-6}$ mbar results in an enhanced Fe$_3$O$_4$ due to $\alpha$-FeOOH $\rightarrow$ $\alpha$-Fe$_2$O$_3$ $\rightarrow$ Fe$_3$O$_4$.

300-375 K is understood due to dissociation of inter dispersed water molecules. Loss of structural OH$^-$ beyond 400 K lead to a decrease in super exchange interaction and hence in hyperfine field respectively. Thus the variation in $(B_{hf}^{\alpha}(T))$ is consistent with the stages involved in the dehydration of $\alpha$-FeOOH such as dissociation of excess water molecules and loss of structural OH$^-$ as deduced using TGA/DTA studies.\textsuperscript{14, 41}

It is interesting to find out the effect of thermal reduction of goethite by annealing the starting sample at a temperature much higher than 650 K, well beyond the temperature of complete conversion of $\alpha$-FeOOH to iron oxides as deduced from Fig. 6. In order to understand the effect the sample has been annealed at 870 K at a vacuum of $8 \times 10^{-6}$ mbar. Analysis of the Mossbauer spectrum (Cf. Fig. 7) shows the existence of $\alpha$-Fe$_2$O$_3$ and Fe$_3$O$_4$ by relative fractions 60% and 40% respectively. This is seen to be commensurate with the starting composition of the fractions of 60% and 40% of goethite and magnetite respectively in the as prepared sample. This result shows clearly that annealing of $\alpha$-FeOOH at high temperatures (much above 650 K) and at a partial pressure as low as $10^{-5}$ mbar results only in the complete conversion of $\alpha$-FeOOH to $\alpha$-Fe$_2$O$_3$. Annealing at 870 K at a partial pressure of $3 \times 10^{-6}$ mbar results in the formation of Fe$_3$O$_4$ and $\alpha$-Fe$_2$O$_3$ with the relative fractions 0.7: 0.3. A higher volume fraction of magnetite seen in the case of sample annealed at lower partial pressure is understood to be due to partial reduction of hematite which gets formed predominantly due to conversion of $\alpha$-FeOOH to $\alpha$-Fe$_2$O$_3$, to magnetite. Mechanism of the partial conversion of $\alpha$-FeOOH directly to $\gamma$-Fe$_2$O$_3$ due to low temperature (400-500 K) annealing is discussed in the following paragraph.

D. Proposed mechanism of conversion / reduction of $\alpha$-FeOOH to $\gamma$-Fe$_2$O$_3$ / Fe$_3$O$_4$

Crystal structure of $\alpha$-FeOOH consists of an hcp array of anions (O$^{2-}$ and OH$^-$) stacked along the [010] direction with Fe$^{3+}$ ions occupying half the octahedral interstices with in a layer. Each Fe ion is surrounded by three O$^{2-}$ and three OH$^-$ to result in FeO$_3$(OH)$_3$ octahedra. Partial transformation of goethite to maghemite is observed to occur over the temperature interval 400-450
FIG. 8. Schematic of the conversion of goethite to cubic spinel meghamite and magnetite due to thermal reduction is shown. Stacking sequence of cations gets altered from that of hcp as ABAB.. in goethite to cubic close packed as ABCABC.. resulting in the conversion to meghamite in the annealing interval 375-425 K. Annealing treatments in the interval 550-650 K results in the conversion of some of the Fe$^{3+}$ ions to Fe$^{2+}$ in the ccp structure formed resulting in the reduction of α-FeOOH to off stoichiometric magnetite.

K based on the present Mossbauer results. The mechanism of the conversion of α-FeOOH to γ-Fe$_2$O$_3$ can be understood as follows. Core of goethite particles are rich in OH$^-$ while the surface of these particles are deficient in OH-. Hence OH- from water molecules get bonded with OH- dangling bonds. Annealing beyond 400 K results in a partial dissociation of H$^+$-OH$^-$ bonded with dangling bonds of α-FeOOH. This causes the desorption of hydrogen molecules which react with interface oxygen atoms giving rise to water molecule and anionic (oxygen) vacancies. Thus the creation of oxygen vacancies result in an increase in the local concentration of Fe ions. These excess Fe ions diffuse in the restacked manner to form γ-Fe$_2$O$_3$ lattice. This is shown schematically in Figure 8. A fraction of about 20% of Fe atoms are found to be associated with γ-Fe$_2$O$_3$ subsequent to annealing treatment at 420 K.

Annealing beyond 550 K results in the conversion of some of Fe$^{3+}$ to Fe$^{2+}$ in γ-Fe$_2$O$_3$ lattice which might get formed as explained above leading to the reduction of α-FeOOH to off-stoichiometric magnetite. Hence the role of desorbed hydrogen is imminent in the conversion/reduction of α-FeOOH to γ-Fe$_2$O$_3$ and Fe$_3$O$_4$ respectively. Annealing beyond 500 K (Cf. Fig. 5) is seen to result in a predominant conversion of α-FeOOH to α-Fe$_2$O$_3$ due to topotactic transformation. The role played by oxygen is thus important with respect to the formation of α-Fe$_2$O$_3$ from α-FeOOH. Though the dissociation of structural OH$^-$ would take place from α-FeOOH while subjected to annealing at high temperatures (T> 650 K) and at moderate partial pressures, the desorbed hydrogen could not result in oxygen vacancies leading to the formation of any cubic phase of iron oxide. Hence annealing beyond 650 K results only in the topotactic transformation of α-FeOOH to α-Fe$_2$O$_3$ as elucidated in the previous section (Cf. Fig. 7).

E. Study of the changes in the hyperfine parameters of the coexisting Fe$_3$O$_4$ nano particles due to thermal reduction of α-FeOOH

In the system of present study containing Fe$_3$O$_4$ and α-FeOOH in the ratio of 0.4:0.6, variations in hyperfine parameters associated with tetrahedral and octahedral sites of magnetite have been observed subsequent to annealing treatments between 350 and 600 K (Cf Fig. 9). The variations occur appreciably in the temperature interval between 350-550 K in which the desorption of excess water and structural OH$^-$ of α-FeOOH is observed to take place significantly due to thermal reduction.

The hyperfine parameters associated with Fe$_3$O$_4$ in the as prepared sample (Cf. Table 1) are found to be different from that of the bulk magnetite. Ratio of population of Fe atoms associated with octahedral and tetrahedral sites is 1:1 instead of 2:1 corresponding to that of the bulk magnetite. This implies the off-stoichiometry of the magnetite which arises due to Fe vacancies occurring at octahedral sites. Hyperfine fields $B_{hf}^5$ and $B_{hf}^6$ exhibit an increase in the temperature interval
300-370 K accompanied by a decrease in $f_5$ while the value of $f_6$ increases. Dissociation of water molecules dispersed between $\alpha$-FeOOH causes an enhanced magnetic interactions between nano particles resulting in the observed increase in the effective fields due to a decrease in the spatial separation between particles. Another important point to this effect is due to the reaction of OH$^-$ desorbed from $\alpha$-FeOOH with Fe$^{3+}$ resulting in the formation of Fe$^{2+}$. Increase in Fe$^{2+}$ in the matrix causes an increase in the value of $f_6$ at the cost of $f_5$. Further this effect results in a slight increase in the hyperfine fields at A and B sites of magnetite particles. A slight decrease in the magnetite fraction by 5% in the interval 375-420 K is plausibly understood due to the trapping of O$^{2-}$ which got desorbed from goethite resulting in the partial conversion of Fe$_3$O$_4$ to $\gamma$-Fe$_2$O$_3$. This causes an increase in the relative fraction of Fe$^{3+}$ at the cost of Fe$^{2+}$, manifested as an increase in $f_5$ at the cost of $f_6$.

In the annealing interval 450-600 K, an increase in the relative fraction of iron atoms associated with magnetite particles by 20% is observed due to partial reduction of $\alpha$-FeOOH particles. An increase in the FWHM of the most intense peaks of magnetite as observed in the XRD spectrum (Cf. Fig. 1(c)) implies the decrease in the mean size of magnetite particles. This is due to the reasoning that the 20% of the magnetite are formed due to reduction of goethite particles of size as low as 5-10 nm. Annealing beyond 600 K, the temperature of complete dissociation of $\alpha$-FeOOH lead to the monotonous changes towards restoration of hyperfine parameters as that of the stochiometric Fe$_3$O$_4$. This implies that the observed variations of hyperfine parameters (Cf. Fig. 9) are due to changes in the local structure and magnetic properties at Fe sites caused by the desorbed OH$^-$ from $\alpha$-FeOOH. Therefore it can be summarized that the thermal reduction of goethite results in the formation of maghemite in the temperature regime 400 K < $T_{\text{maghemite}}$ < 450K. It is comprehended that in the annealing interval 500 K < $T_{\text{magnetite}}$ < 650 K, partial conversion of $\alpha$-FeOOH to $\gamma$-Fe$_2$O$_3$ could be taking place which gets further reduced to off stoichiometric magnetite in the interval. Annealing beyond 520 K predominantly results in the conversion of $\alpha$-FeOOH to $\alpha$-Fe$_2$O$_3$.

While plotting the variation in the mean hyperfine field which is given as $\langle B_{hf} \rangle = \frac{\sum f_i B_{hf,i}}{\sum f_i}$ with temperature three different regimes could be deduced based on the changes in the slope as shown in Fig. 10. Mean hyperfine field at 300 K is close to 30 Tesla. This is understood due to the association of 25% of Fe atoms with super paramagnetic particles of $\alpha$-FeOOH and 40% of Fe atoms
FIG. 10. Variation of the mean hyperfine field $\langle B_{hf} \rangle$ with annealing temperature of the starting sample containing $\alpha$-FeOOH and Fe$_3$O$_4$ in the ratio of 0.6:0.4 due to thermal reduction of $\alpha$-FeOOH to polymorphs of iron oxides. The above variation marks three different slopes (d$\langle B_{hf} \rangle$/dT) viz., understood to be due to (I) dissociation of inter dispersed water molecules between $\alpha$-FeOOH, (II) reduction of $\alpha$-FeOOH to $\gamma$-Fe$_2$O$_3$ and (III) due to the formation of Fe$_3$O$_4$ and $\alpha$-Fe$_2$O$_3$ respectively.

with Fe$_3$O$_4$. An increase in the mean field in the interval 300-375 K, marked as slope-I in the figure, is understood to be due to the decrease in the mean distance of separation of $\alpha$-FeOOH particles following dehydration of excess water molecules inter dispersed between them. A steep increase in the value of d$\langle B_{hf} \rangle$/dT in the interval 400 < T < 500 K (slope-II) is ascribed to the reduction of as high as 20% of $\alpha$-FeOOH to $\gamma$-Fe$_2$O$_3$. Occurrence of slope marked as III is understood to be due to the conversion of $\alpha$-FeOOH to Fe$_3$O$_4$ and $\alpha$-Fe$_2$O$_3$ in the temperature interval 500 K < T < 650 K.

IV. CONCLUSION

Summarizing, this work brings out a detailed understanding of the evolution of local structure and magnetic properties of $\alpha$-FeOOH nano particles due to controlled thermal reduction using Mossbauer spectroscopic studies. Important role played by hydrogen in the partial conversion of orthorhombic $\alpha$-FeOOH to cubic phases such as $\gamma$-Fe$_2$O$_3$ and reduction to off-stoichiometric magnetite in the temperature regimes 400-460 K and 500-625 K respectively has been elucidated in the present study for the first time using Mossbauer spectroscopy. Proton desorbed in the process of thermal dehydration of $\alpha$-FeOOH are understood to create oxygen vacancies thus increasing the concentration of Fe ions locally which diffuse in a stacked manner to result in a partial conversion of $\alpha$-FeOOH to cubic $\gamma$-Fe$_2$O$_3$. Variations in hyperfine parameters corresponding to tetrahedral and octahedral sites of the associated off stoichiometric magnetite due to thermal reduction of $\alpha$-FeOOH nano particles have been discussed in the present study thus providing a better understanding of the thermal reduction of $\alpha$-FeOOH and interaction between desorbed species such as OH$^-$, H$_2$ and O$_2^-$ with Fe atoms associated with Fe$_3$O$_4$. Topotactical formation of $\alpha$-FeOOH to $\alpha$-Fe$_2$O$_3$ is observed for annealing treatments above 500 K and this effect becomes predominant for annealing above 550 K. Results of this study might be useful for obtaining anisotropic nano particles of iron oxides from $\alpha$-FeOOH thus exploiting the large aspect ratio of the nano $\alpha$-FeOOH particles in a controlled manner.

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