Implications of linear correlation between hyperfine parameters in iron oxide nanoparticles

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HIGHLIGHTS

- Mossbauer studies on magnetic properties of iron oxide nanoparticles.
- Linear correlation between quadrupole splitting and magnetic hyperfine field.
- Explained by proportionality of superexchange interaction on structural distortion.
- Important role of oxygen vacancies for the interesting correlation elucidated.

ARTICLE INFO

ABSTRACT

Controlled annealing induced evolution of local structure and magnetic properties on oleic acid coated and bare nanoparticles composed of iron oxy hydroxide and cubic iron oxides were studied using Mössbauer spectroscopy. Mutually opposite variation of quadrupole splitting and magnetic hyperfine field with respect to that of isomer shift has been observed in both the cases of bare and oleic acid coated nanoparticles subjected to annealing treatments. This manifests in an interesting linear correlation between quadrupole splitting and magnetic hyperfine field. Physics of the observed linear correlation between hyperfine parameters has been elucidated based on the direct proportionality of superexchange interaction on the hyperfine contact interaction and a strong dependence of the strength of super-exchange interaction on the structural distortion and point defects mainly due to anionic vacancies. Thus the result of this study plausibly points to a strong coupling between local structure in terms of structural distortions and point defects with magnetic properties while the nanoparticles of iron oxides are subjected to coarsening and reduction.

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1. Introduction

Intensive continuing research on magnetic spinel ferrite nanoparticles has led to several technological applications in high density data storage, hyperthermia, magnetic resonance contrast reagent and in vivo drug delivery [1—6]. Bulk magnetite crystals are moderately conducting at room temperature and undergo metallic to insulating transition below Verwey temperature (T_v) 120 K, concurrent with the first order structural phase transition from high temperature ($T > T_v$) cubic to low temperature ($T < T_v$) monoclinic unit cell [7]. It has recently been shown that the nanocrystals and single crystal thin films of magnetite exhibit an electrically driven insulating to metallic phase transition below the Verwey temperature [8]. Based on the electrically driven metallic to insulating phase transition in magnetite nanostructures, a strong correlation of electrons has been deduced. A complex interplay of charge and structural degrees of freedom in magnetite is elucidated theoretically based on the amplification of electron-phonon coupling by the 3d electrons of Fe atoms [7,8] towards providing an understanding of Verwey transition [9—14]. Nanoparticles are characterized by larger value of the ratio of surface to volume compared to that of micron sized particles differing significantly in optical, structural and magnetic properties [15]. Any technique whose time scale of measurement coincides with the spin relaxation time in this temperature regime would be able to provide a detailed understanding of the magnetic properties. Time scale of [57]Fe absorber based Mössbauer spectroscopy, a hyperfine interaction based technique, is comparable to spin relaxation time of

nanoparticles with size up to 10 nm at room temperature making it as a powerful technique for addressing several aspects related to magnetic and local structural properties of iron oxide nanoparticles [16]. Hyperfine techniques [17–24], based on the interaction between nuclear moments and electro magnetic fields, provide powerful tools for the studies of local structure and magnetic properties [25–29] of nanoparticles. A large number of ^{57}Fe based Mössbauer studies have been reported on several aspects related to Ferrite nanoparticles in the literature [19–24]. Isomer shift as measured by Mössbauer spectroscopy is dictated by electric monopole interaction which basically involves the electronic charge density i.e., s electron density $\rho_s(0)$ at the nucleus. Electric quadrupole interaction is basically due to interaction between quadrupole moment of ^{57}Fe at the isomeric state of spin $I = 3/2$ with the electric field gradient at the site of occupation of ^{57}Fe absorbers in the matrix. Magnetic dipole interaction is between the magnetic dipole moment of the resonant nucleus at the isomeric state with the magnetic field at the site of ^{57}Fe. Magnetic hyperfine interaction is mainly contributed by Fermi contact field arising due to a net spin-up and spin-down s electron density at the nucleus due to spin polarization of s electrons by unpaired valence electrons. Quadrupole splitting is due to lattice caused by non-cubic distribution of external charges and significantly due to valence electrons if the charge distribution of valence electrons deviates from spherical symmetry.

Bulk ferrite AB_2O_4 has a cubic structure with oxygen atoms forming a face centered cubic close packing while cations occupy tetrahedral (A) and octahedral (B) interstitial sites. Particularly in Fe_3O_4, Fe^{3+} cations occupy eight tetrahedral sites amongst the available 64 sites, while 16 out of 32 octahedral sites are occupied equally by Fe^{3+} and Fe^{2+} cations. Hopping of electron between Fe^{2+} and Fe^{3+} via an oxygen atom at octahedral sites is understood to be responsible for the observed conductivity. Observed ferrimagnetic ordering is understood to be mainly due to high magnitude of exchange energy J_{AB} compared to exchange energies J_{AA} and J_{BB}. Each of the exchange energy is dictated by superexchange interaction between Fe^{3+}-O-Fe^{2+}. As the system remains cubic the observed electric field gradient is zero. The observed hyperfine field at Fe^{3+} with spin $5\mu_B$ occupying A site (49 Tesla) is larger than the hyperfine field of 46 Tesla at B sites occupied equally by both Fe^{3+} and Fe^{2+} with moments $5\mu_B$ and $4\mu_B$ respectively.

Hyperfine parameters experienced by Fe atoms occupying the bulk and surface of any particles are distinctly different as the later are associated with point defects such as anionic and cationic vacancies. As the number of surface atoms increase significantly with decreasing size, the hyperfine parameters as observed in the nanoparticles become widely different from that of the bulk. In the case of Fe_3O_4 nanoparticles due to an increase in the ratio of surface to volume the surface is likely to be having cation and anion vacancies. Hence there is likely to be point defect induced quadrupole splitting. The presence of cationic, anionic vacancies and increased distortion between A-O-B could also result in a much decreased strength of superexchange interaction compared to the bulk. This suggests that there could be a strong coupling between local structure and magnetic properties in these systems. This study is aimed at looking for a possible correlation between local structure and magnetic field while the nanoparticles of iron oxides are coarsened and reduced in controlled atmosphere.

Magnetite nanoparticles as produced using different chemical methods such as sol-gel [28] and coprecipitation [29–31] with surface modification of magnetite particles leading to enhanced stability of the particles. Nano magnetite particles produced by these methods are mostly off stoichiometric with lower value of isomer shift associated with Fe atoms occupying octahedral sites while the ratio of fractions of Fe atoms occupying octahedral to

tetrahedral sites deviates from 2:1 corresponding to stoichiometric magnetite. Hence controlled post annealing treatments would mainly result in reduction of off stoichiometric to stoichiometric magnetite with the value of isomer shift corresponding to octahedral sites becoming close to 0.6 mm/s characteristic of the valence of $+2.5$ due to the presence of Fe^{2+} and Fe^{3+} at the octahedral sites while the ratio of fractional occupancy of Fe atoms at octahedral and tetrahedral sites becoming 2:1, in addition to coarsening of the particles. It has been reported that the coprecipitation method of preparation of iron oxide also results in the presence of goethite in addition to the predominant formation of off stoichiometric magnetite [29]. Hence annealing at high temperature *i.e* beyond 600 K results predominantly in the conversion of goethite to haematite. As there are both structural and magnetic transitions involved in these processes, the present study aims to look for a possible correlation if any between hyperfine parameters as experienced by Fe atoms associated with uncapped and OA capped iron oxide nanoparticles with similar size distribution as prepared using coprecipitation method.

2. Experimental details

Magnetite nanoparticles have been prepared using coprecipitation of $FeCl_3$ (1 mol/l) and $FeSO_4.7H_2O$ (0.5 mol/l) solution of molar ratio 2:1 as has been described earlier [25,26]. NaOH was mixed drop by drop to the above precursor solution which led to an increase in the pH from 3 to 10 and maintained at 10 throughout the reaction and subsequently stirred for 60 min. After dividing the solution into two halves, 8 ml of oleic acid was added and stirred at the same speed for 30 min at 348 K in one solution. In both the cases the separated precipitates were washed several times by ultra high pure water then by acetone and dried at 373 K for 6 h. This would result in nanoparticles mainly of magnetite along with goethite [29] identical in chemical nature and size in both the cases of preparation methods except for the resulting nanoparticles capped with oleic acid in one case.

Basic identification of the phases of the nanoparticles of iron oxide has been deduced based on XRD pattern and the mean size of the nanoparticles has been computed based on the values of the Bragg diffraction angle and full width at half maximum (FWHM) corresponding to most intense peaks by using Debye-Scherrer equation. As a source of Mössbauer measurements ^{57}Co dispersed in Rh matrix with a specific activity of 50 mC has been used. Mössbauer spectrometer (Wissel make) was operated in constant acceleration mode and in transmission geometry. Spectra were fitted to Lorentzian line shapes of line width Γ_i using a non linear least squares program to obtain hyperfine parameters such as isomer shift δ_i, quadrupole splitting (Δ_i) and magnetic hyperfine fields (B_{hf}^i) experienced by relative fractions f_i of distinct ^{57}Fe absorber atoms. Bare and oleic acid coated nanoparticles were subjected to annealing treatments at different temperatures at a partial pressure of about 10^{-6} mbar for 1 h. All the Mössbauer 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 $3-5x10^5$.

3. Results and discussion

Presence of α-FeOOH and cubic phase of iron oxide which could be either γ-Fe_2O_3 and/or Fe_3O_4 has been deduced using XRD patterns (Cf. Fig. 1) obtained in both the bare and oleic acid coated nanoparticles. Based on the Scherrer analysis the mean size of uncapped or bare nanoparticles of α-FeOOH and cubic phase of iron oxide were deduced to be around 12 ± 2 nm and 8 ± 3 nm respectively. The mean size of OA capped nanoparticles of α-FeOOH and