Mössbauer spectroscopic studies of self-assembled monodispersed FePt nanoparticles

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Received April 29, 2006; Accepted June 5, 2006

Abstract

The FePt nanoparticle assemblies are chemically and mechanically robust and can support high-density magnetization reversal transitions. The 4 nm FePt particles with organic ligand encapsulation are synthesized by wet chemical technique and studied for their magnetic properties using Mössbauer spectroscopy. The face-centered cubic (fcc) to face-centered tetragonal (fct) phase transformation does not occur above 833 K. The Mössbauer spectra show the presence of superparamagnetic and ferromagnetic fractions for the as-prepared and annealed FePt nanoparticles. The magnetocrystalline anisotropy is reduced and Fe-Pt-C surface layer is formed after the samples are annealed at 623 K, which results in the decrease of superparamagnetic blocking temperature from 55 K to 10 K. Two sextets are observed at 10 K with a large magnetic hyperfine field for one of the components due to the modulations of the electronic charge density.

(Key words: FePt / nanoparticles / Mössbauer spectroscopy / anisotropy)

Introduction

Since the nanocrystalline particles have large surface to volume ratio and the arrangement of atoms at the surface happens in such a way that it leads to minimum energy configuration. The ferromagnetic nanoparticles are in the single domain range and are utilized in various applications such as magnetic fluid, particulate magnetic recording media, permanent magnets, catalysts and biomedical applications. The FePt nanoparticles have high magnetocrystalline anisotropy energy, which are best suited for perpendicular recording and for increased storage density[1,2]. In FePt nanoparticles, a structural transition occurs at 833 K and the face-centered cubic (fcc) structure gets transformed into an ordered face-centered tetragonal (fct) intermetallic state phase[3]. The fct phase has a high uniaxial magnetocrystalline anisotropy and good chemical stability[4]. Thus, in the recent times a large number of research work have been devoted towards FePt alloys both as nanoparticles and thin films[2,5,6]. Besides the pure FePt alloys, other materials are combined with FePt to form the pseudo-binary alloys, composites and bilayers[7-9]. Also, several synthesis routes are being employed to prepare and design the FePt nanoparticles to meet the desired technologies[4,10-12]. However, since the nanoparticles are highly reactive, oxide coatings are formed at the surface, which complicates the interpretation of the physical measurements in order to distinguish the signals from the surface and the core. The basic need is to prepare self-organized two- and three-dimensional arrays of the monodispersed hard magnetic FePt nanoparticles having well-controlled particle size, composition, crystal structure and interparticle spacings. Such perfectly designed FePt nanoparticles can be synthesized with the use of organic ligands, which separate one particle from another, prevent

agglomeration and particle size distribution. The organic ligand shell encapsulates the FePt nanoparticles and influences the magnetic and electronic configuration of the FePt core. In this study, the magnetic properties of organic ligand encapsulated 4 nm FePt particles are explored with Mössbauer spectroscopy. The wet-chemical procedure has been employed to prepare the nanoparticles with monodispersed arrays. X-ray diffraction (XRD), Rutherford backscattering spectroscopy (RBS), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) has been employed for the characterization and structure-property investigation of the monodispersed nanoparticles.

Materials and Method

The FePt nanoparticles were synthesized by the wet chemical technique[4]. Two reactions were initiated together at 573 K in inert atmosphere and in the presence of oleic acid and oleyl amine. Platinum acetylacetonate [$Pt(acac)_2$] was reduced by 1, 2-hexaddecanediol and iron carbonyl [$Fe(CO)_5$] was decomposed in high temperature solutions and the evaporating fraction was condensed and recycled to the reaction zone. The thermal decomposition of $Fe(CO)_5$ resulted in Fe particles and the presence of Pt atoms and clusters catalyzed the reaction to occur at lower temperatures. Thus the disordered FePt nanoparticles were stabilized with oleic acid and oleyl amine. The particles were washed, centrifuged and dispersed in hexane. The FePt nanoparticles thus formed are stable against oxidation in air.

Results and Discussion

The XRD pattern reveals the fcc structure and the lattice parameter is 3.836 Å. The stoichiometry is determined by Rutherford backscattering spectroscopy (RBS) and the fraction of Fe is 50.2 %. Upon annealing at 833 K, the fcc structure does not get transformed to the expected fct structure, only slight variation in the lattice parameter is observed. Fig. 1 shows the TEM image of the monodispersed self-assembled FePt two-dimensional arrays. The mean diameter (D) is 4 nm and the particle size distribution σ (D) = ±0.3 nm. As revealed by the high resolution transmission electron microscopy (HRTEM) image, in each particle, twenty atomic layers are resolved and the lattice fringes correspond to [111] plane in the fcc structure. A core-shell structure results because of the encapsulation of the FePt core with the organic ligand shell without any oxide shell formation.

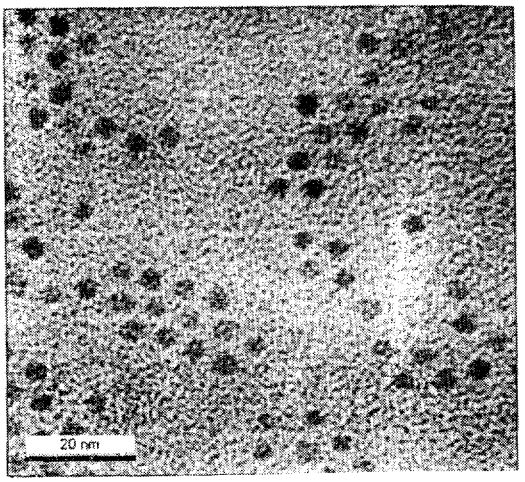

Fig. 1– TEM micrograph showing the self-assembly of the FePt nanoparticles.

However, upon annealing at 833 K, Fe-Pt-C compound formation occurs at elevated temperatures, leaving the metallic core of the nanoparticles intact without any agglomeration and growth of the particles. The XPS studies indicate that Fe_2O_3 or Fe_3O_4 components (with lesser intensity) are present along with pure Fe and Pt core levels and thus the organic ligand shell cannot completely prevent the FePt nanoparticles from oxidation.

The Mössbauer spectroscopy experiments were carried out in a standard He cryostat in

transmission geometry under He atmosphere. From the Mössbauer spectra of the FePt nanoparticles at different temperatures (Fig. 2), it is observed that the resonant signal is not detected above 250 K. This confirms the absence of any agglomeration of the particles.

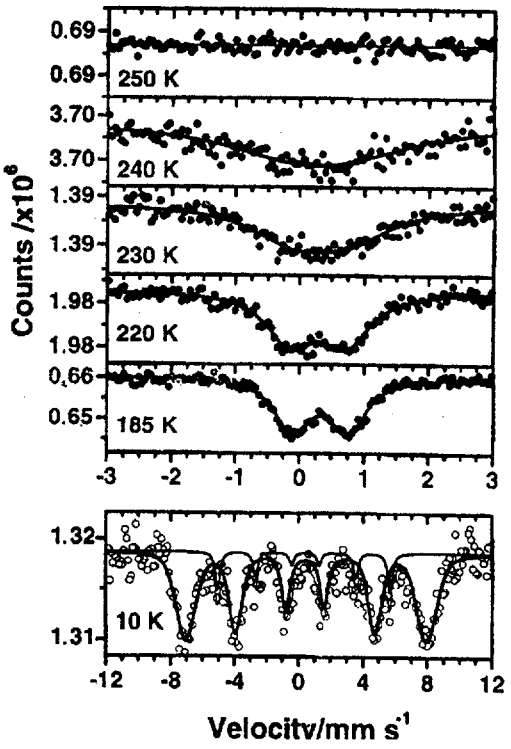

Fig. 2- Mössbauer spectra showing the line broadening due to Brownian motion and magnetic ordering at 10 K.

At 250 K, the spectrum resembles a paramagnetic sample with characteristic line broadening. The concept of Brownian motion fails when the particle size becomes comparable with the molecule size (oleic acid) of the medium. The oleic acid molecules between neighboring particles penetrate and interact with each other and the FePt nanoparticles represent a viscomechanical particle-ligand system. Hence a superlattice of the FePt particles can be considered with elastic coupling *via* the organic ligands that are bound to the particle surface. Hence the Debye-Waller factor can be treated by the vibrational properties of the superlattice. The experimental linewidth can be expressed as:

$$\Gamma(T) = A\,(T/T_0)\exp(T/T_0) + \Gamma_0 \qquad (1)$$

where Γ_0 is the temperature independent linewidth due to the hyperfine interaction, T_0 is a characteristic temperature for the elastic and viscous properties of the organic coating of the particles and A is a materials constant[5]. The values of A, T_0 and Γ_0 are determined by fitting the experimental data between 185 K and 240 K and the results are plotted in Fig. 3.

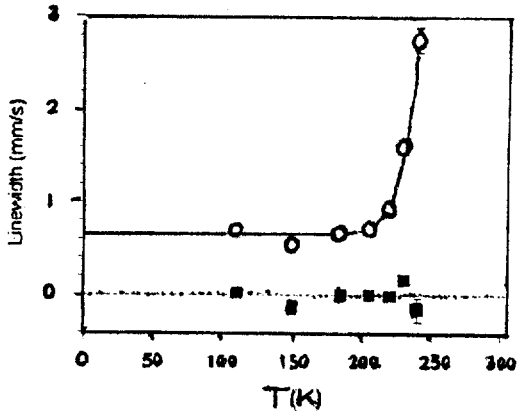

Fig. 3– Linewidth as a function of temperature. (open circles) experiment and (filled squares) experiment minus analytical approach.

The obtained parameters are $A = 4.3 \times 10^{-12}$ mm/s, $T_0 = 10(1)$ K and $\Gamma_0 = 0.66(2)$ mm/s. Thus, the line broadening is associated with the local motion of the particles. The Debye-Waller factor decreases rapidly with temperature, due to the vibrations of the superlattice.

The Mössbauer data yield a blocking temperature of 55 K. The magnetocrystalline anisotropy (K) is calculated to be 0.11(3) MJ/m^3 using the Neel's expression of the exponential dependence of the superparamagnetic relaxation time on KV/kT where V is particle volume (particle

diameter = 4 nm), k is Boltzmann constant, T is temperature. At 10 K, well below the blocking temperature, the Mössbauer spectrum shows the presence of two sextets (Fig. 4).

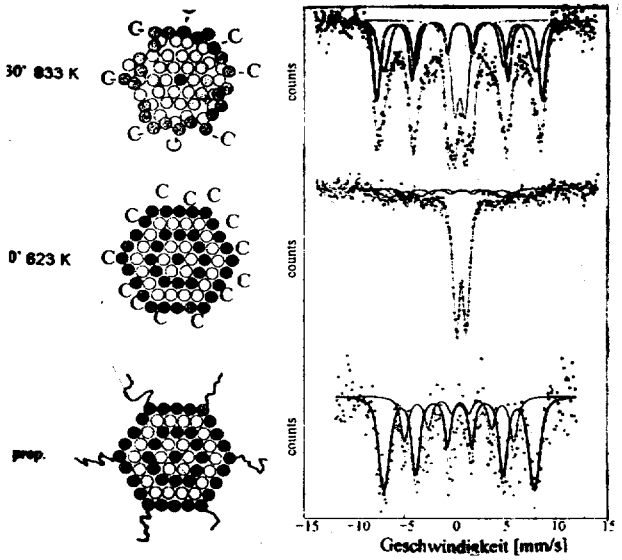

Fig. 4– Mössbauer spectra at 10 K: as-prepared state, annealed at 623 K and annealed at 833 K. The pictures represent the change in surface chemistry with annealing.

The sextet with a fraction of 13.2(1) % is assigned to the ferromagnetic FePt alloy with hyperfine field of 33.3(2) T and isomer shift of 0.41(4) mm/s (Table 1). The second sextet has large hyperfine field of 46.4(2) T and isomer shift of 0.47(4) mm/s, with a Gaussian-shaped hyperfine field distribution. The large hyperfine field is observed till the blocking temperature, which can be attributed to three effects[13,14].

Firstly, Ruderman-Kittel oscillations near interfaces and surfaces may lead to enhanced/ lowered hyperfine fields. However, this cannot account for the observed large splittings. Secondly, the periodic potential of the crystal lattice and the diameter of 18 atomic spacing of the FePt nanoparticles lead to quantum-well structures of the electron wave functions. Thirdly, the surfactant chemically binds at the particle surface through oxygen and leads to dipolar charge layer. Moreover, the large hyperfine field cannot be attributed to the presence of Fe-oxides, since the

Table 1– Mössbauer spectral parameters at 10 K for the FePt nanoparticles: (a) as-prepared, (b) annealed at 623 K and (c) annealed at 833 K.

Sample	Component	Hyperfine field B_{hf} (T)	Isomer shift IS (mm/s)	Quadrupole splitting QS (mm/s)	Line-width Γ (mm/s)
(a)	I (13 %)	33.4(2)	0.45(3)	-0.06(3)	0.4(1)
	II (87 %)	46.5(2)	0.52(2)	0.027(14)	0.60(1)
(b)	I (9 %)	32.3(2)	0.43(9)	-0.12(8)	0.9(4)
	II (20 %)	43.5(2)	0.41(1)	-0.1(1)	0.7(4)
	III (71 %)		0.49(1)	0.97(2)	0.75(3)
(c)	I (26 %)	50.8(2)	0.49(1)	-0.03(1)	0.62(6)
	II (23 %)	46.5(6)	0.46(2)	-0.01(2)	0.50(8)
	III (17 %)		0.46(2)	1.00(4)	0.93(6)
	IV (34 %)	34.1(6)	0.47(5)	-0.10(5)	0.50(5)

Fe-oxides have high volume anisotropy dominating the surface anisotropy can be ruled out, and the magnetic anisotropy measured for this system is quite low (0.1 MJ/m^3) and this value is attributed to the surface anisotropy. Hence, the origin of the high magnetic hyperfine field of the second component at 10 K can be explained based on the long-range modulations of the electronic charge density and spin density beneath the particle surface. With increase in temperature, the two sextets vanish simultaneously indicating a strong correlation between them.

The Mössbauer spectrum of the annealed sample (A) at 623 K (Fig. 4), indicates a major superparamagnetic doublet and a magnetic fraction. The average hyperfine field of this magnetic fraction is reduced by 6 % relative to the as-prepared sample. The presence of the superparamagnetic doublet indicates that the superparamagnetic blocking temperature has decreased from 55 K to 10 K with the first gentle annealing step. At 623 K, the crystal structure remains unchanged (confirmed from XRD) and the possible origin of the doublet arises from the large reduction in the magnetocrystalline (volume) anisotropy. The oleic acid molecules bind *via* the double bonded O to Fe surface atoms. Thermal decomposition breaks up the Fe-O bonds and the entire organic molecules to generate pure carbon as the matrix for the monodispersed FePt nanoparticles, leading to the large decrease in surface anisotropy. For the annealed state at 833 K (Fig. 4), a broad range of hyperfine fields appear in the Mössbauer spectrum. The various components are attributed to the formation of the Fe-Pt-C compounds at the surface, resulting in a core-shell structure. As a result the FePt core shrinks due to the strong chemical bonds of the Fe-Pt-C compound shell. Also, the superparamagnetic doublet at 100 K and the combination of sextets down to 10 K are observed. This fact also confirms that the envisaged fcc to fct transition has not occurred at 833 K, since the fct phase should have the large magnetocrystalline anisotropy, without any superparamagnetic doublet.

Fig. 5 shows the hyperfine field distributions at 10 K for the two batches of FePt nanoparticles and the annealed samples. For the 623 K annealed sample, hyperfine field (B_{hf}) is slightly reduced as compared to the as-prepared samples, which is due to the collective relaxation of the moment of the particles, as the particles are not completely blocked. Rather, it might point towards a change in the electronic structure.

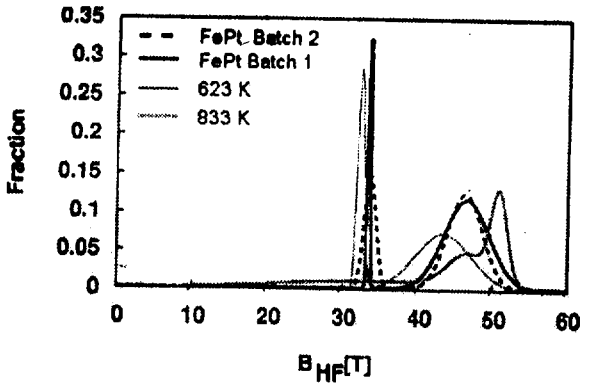

Fig. 5– Hyperfine field distributions at 10 K of the two batches of as-prepared FePt nanoparticles and the annealed samples (623 K and 833 K).

Interestingly, for the 833 K annealed sample, the magnetic component with B_{hf} = 33.5 T vanishes and instead a broad range of hyperfine fields from 10-40 K are observed, which are due to the formation of Fe-Pt-C formation at the surface. The weight of this part gets shifted towards higher hyperfine field values. Here it is interesting to point out that from the bimodal hyperfine field distribution, it is tempting to suggest the fcc to fct phase transformation: one in the disordered fcc phase and the other in the ordered fct phase. In such a case, two different blocking temperatures would be observed due to the differences in the magnetic anisotropy, which is not true in this

system. Only a single superparamagnetic blocking temperature is observed and the magnetic ordering of component I collapse in the same way as component II (Fig. 2).

Conclusions

In conclusion, 2D arrays of the densely packed, self-assembled and monodispersed 4 nm FePt particles are synthesized by wet chemical technique with organic ligands acting as the surfactant. Upon annealing to 833 K, only a change in lattice parameter is observed. When the sample is annealed, the organic molecules at the surface are decomposed and Fe-Pt-C surface layer is formed. This results in large decrease of magnetocrystalline anisotropy (having surface anisotropy contributions) and hence the superparamagnetic blocking temperature is also lowered. The Mössbauer spectra at 10 K, shows two sextet components, with one of them having large magnetic hyperfine field, which is due to the long-range modulations of the electronic charge density and spin density beneath the particle surface. The surface anisotropy has direct correlation to the surface chemistry with respect to the organic ligands and the carbon matrix.

Acknowledgements

The authors acknowledge Institute of Nanotechnology, Forschungszentrum Karlsruhe, Germany, CFN-DFG Center for Functional Nanostructures Karlsruhe, Germany. The Materials Science Department, Darmstadt University (TU) is duly acknowledged for Mössbauer data recording. We are also thankful to MHRD, New Delhi for the financial support in carrying out this research work.

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