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Mössbauer spectral investigations of ultrafine rare-earth iron garnets

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Ultrafine rare-earth iron garnets (RIG) in the crystallite size range 1.0–35 nm, prepared by the citrate precursor method have been investigated by Mössbauer spectroscopy at room temperature. The crystallites of 10–35 nm size show two six-line spectra corresponding to tetrahedral and octahedral Fe^{3+} with isomer shifts, δ, and magnetic hyperfine fields, H_{hf}, comparable to the bulk polycrystalline garnets. However, 1.0–1.5 nm crystallites (X-ray amorphous) show a quadrupole split doublet due to superparamagnetic nature with isomer shifts ($0.3\ mm\,s^{-1}$) intermediate between tetrahedral and octahedral values of bulk garnets. The relative increase in the tetrahedral δ and the decrease in the octahedral δ indicate, respectively, an increase of tetrahedral Fe–O bond distance and a decrease of octahedral Fe–O bond distance in the ultrafine state, in complete agreement with the observations made earlier in the spectrochemical investigations. The lines are broad (linewidth $= 0.65\ mm\,s^{-1}$) and the quadrupole splittings are relatively larger ($\Delta E_Q = 1.0\ mm\,s^{-1}$) indicating large deviation from cubic symmetry at the Fe^{3+} sites.

1. Introduction

During the last few years ultrafine particles of magnetic materials have attracted considerable attention because of their unique structural and magnetic properties and the possible applications in electronic and chemical industries [1–3]. Their magnetic properties differ substantially from the bulk materials and depend on the particle size. The ultrafine particles of the smallest size range may be effectively all surface and they offer as attractive an avenue for the study of surfaces as do thin films [3, 4]. Rare-earth iron garnets, $R_3Fe_5O_{12}$, which possess a three sublattice ferrimagnetic structure could be excellent materials to study the effect of finite size on magnetic properties. The crystalline garnet structure consists of alternating distorted oxygen polyhedra, FeO_4 tetrahedra (d-site) and FeO_6 octahedra (a-site), which share the corners to form a continuous three-dimensional framework. The oxygen atoms in this framework also define distorted triangular dodecahedra consisting of eight oxygens, RO_8, which coordinate the rare-earth, R^{3+}, ions.

Mössbauer spectroscopy is an ideal technique for the study of the magnetic properties and the molecular level structures of ultrafine particles [5]. The ultrafine particles of magnetic materials are typically superparamagnetic below a certain size range [6]. Superparamagnetism is due to the thermal fluctuations of the magnetic moment of the particle which leads to zero average moment for the sample. The relaxation time of the magnetic moment of a single domain particle is given by

$$\tau = \tau_0 \exp(KV/kT)$$

where V is the volume of the particle, K is the anisotropic constant, $\tau_0 = 10^{-9}$ s, k is the Boltzmann constant and T is the absolute temperature. Depending on the size of the particle, τ varies between 1 and 10^{-9} s. Thus superparamagnetic properties depend upon the measuring time. In γ-resonance spectroscopy on ^{57}Fe, the observation time is 10^{-8} s. Therefore, superparamagnetic particles of various magnetic oxides have been studied by Mössbauer spectroscopy at low temperatures [3–7]. It has been found that thermal fluctuations of the magnetic moment lead to the disappearance of the hyperfine structure of the spectra and also lead to a broadening of the lines above a certain temperature, the so-called blocking temperature. However, a careful analysis of the Mössbauer spectral parameters such as isomer shift, δ, quadrupole splitting, ΔE_Q, and linewidth at room temperature, give useful information on the oxidation states of iron, oxygen coordinations and the symmetry of iron sites. These aspects of ultrafine rare-earth iron garnets in the size range 1.0–35 nm have not been studied in the literature by Mössbauer spectroscopy. Therefore, in the present study, ultrafine rare-earth iron garnets, $R_3Fe_5O_{12}$, where R = Sm, Tb, Dy, Ho, Er, Yb and the mixed garnets where R = (YNd) and (YGd) have been investigated to probe into the local molecular structure and the interesting magnetic properties exhibited due to the ultrafine particle nature.

2. Experimental procedure

The ultrafine rare-earth iron garnets (RIG) were prepared by thermal decomposition of citrate precursors.

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The details of preparation and thermal decomposition studies of the citrate precursor have been presented elsewhere [8]. The precursors were decomposed at 450 °C to obtain RIG materials and then heat-treated for 4 h each in air atmospheres at various temperatures in the range 450–1000 °C to obtain the ultrafine RIG materials in the size range 1.0–35 nm. The Mössbauer spectra were recorded at room temperature (295 K) using a ^{57}Co source deposited on a rhodium matrix. The spectra were analysed using a Nuclear Data Inc. Model ND62 multichannel analyser. The experimental spectra were curve fitted with a least-squares curve fitting computer program using a Digital Equipment Corporation DEC-1090 computer assuming Lorentzian line shapes. The isomer shifts were calculated with respect to α-Fe.

3. Characteristics of ultrafine rare-earth iron garnets

Ultrafine rare-earth iron garnets were characterized in detail by XRD, TEM and BET surface area measurements as described elsewhere [9]. In the heat-treatment temperature range 450–600 °C, the ultrafine garnets exhibit only a broad hump in the XRD pattern corresponding to $d_{420} = 0.2$–0.35 nm, indicating the existence of a highly strained disordered state having a crystallite size of 1.0–1.5 nm. Above 600 °C, the crystallites grow to 10–35 nm monoliths with $d_{420} = 0.275$–0.285 nm, with negligible lattice strain. The larger d_{420} spacing for crystallites of 1.0–1.5 nm size compared to 10–35 nm, corresponds to the relative increase of specific volume of the RIG lattice. The larger size-induced strain is suggested to be responsible for the distortion and instability of the garnet lattice. Such a lattice expansion with decreasing particle size has been reported for various metallic and non-metallic fine particle systems [10–12].

The specific volume change in ultrafine RIG materials of 1.0–1.5 nm crystallite size is attributed to the modifications of various oxygen polyhedra in the ultrafine state, deduced from the spectrochemical studies as follows [13]. Ultrafine RIG exhibit IR absorptions corresponding to an expanded garnet lattice and the dodecahedra, which support the observed increase in specific volume in the XRD studies. The shift of optical absorptions to higher energy compared to bulk crystalline garnets support the above observation. Moreover, the parameters calculated from the optical spectra, namely the Racah parameter, B, and the ligand field parameter, Δ, directly give an indication of the cation–anion distances in the oxygen tetrahedra and octahedra in the structure. The ultrafine RIG comprising 1.0–1.5 nm crystallites show larger B (tet) compared to the bulk crystalline garnets indicating an increase of Fe$_d$–O bond distances. The ligand field parameters Δ (tet) are smaller than the bulk garnets, which again indicate an increase of Fe$_d$–O bond distance. In contrast, in the case of FeO$_6$ octahedra, smaller B (oct) and larger Δ (oct) are observed which indicate a decrease in Fe$_a$–O bond distances. Therefore, the overall increase of specific volume observed in 1.0–1.5 nm crystallites is associated with an increase of Fe$_d$–O and R$_c$–O bond distances leading to a relative expansion of tetrahedra and dodecahedra and a relative decrease of Fe$_a$–O bond distances leading to a contraction of octahedra.

The crystallites of 10–35 nm size exist as monolithic ferrimagnetic particles [9]. In the temperature - dependent magnetization studies they exhibit the same the Curie temperatures and magnetizations as the bulk crystalline garnets. However, the 1.0–1.5 nm crystallites exist in the disordered state as aggregates with strong interparticle dipolar interactions and exhibit superparamagnetism. The observed magnetization of these crystallites is attributed to the weakening of the anisotropic R_c^{3+}–O^{2-}–Fe_d^{3+} coupling in the disordered state which allows the antiparallel Fe^{3+} sublattice magnetization to dominate [14].

4. Results

The Mössbauer spectra of 1.0–1.5 nm crystallites of various rare-earth iron garnets (heat-treatment temperature < 600° C) show a broad superparamagnetic doublet having quadrupole splitting $\Delta E_Q = 1.06 \pm .08$ mm s^{-1}, isomer shift $\delta = 0.33 \pm 0.03$ mm s^{-1}, as given in Table I and as shown in representative Figs 1 and 2 for Yb$_3$Fe$_5$O$_{12}$ and Y$_2$NdFe$_5$O$_{12}$. The spectra change to two sextets corresponding to the tetrahedra and octahedra for the 10–35 nm crystallites (heat-treatment temperature > 700° C) which have broader lines compared to bulk polycrystalline garnets. The tetrahedral ^{57}Fe subspectrum show $H_{hf} = 391 \pm 12$ kOe with linewidth $= 0.54 \pm 0.11$ mm s^{-1} and appears more broadened than the octahedral subspectrum which has $H_{hf} = 496 \pm 6$ kOe and linewidth $= 0.36 \pm 0.05$ mm s^{-1}. For the intermediate

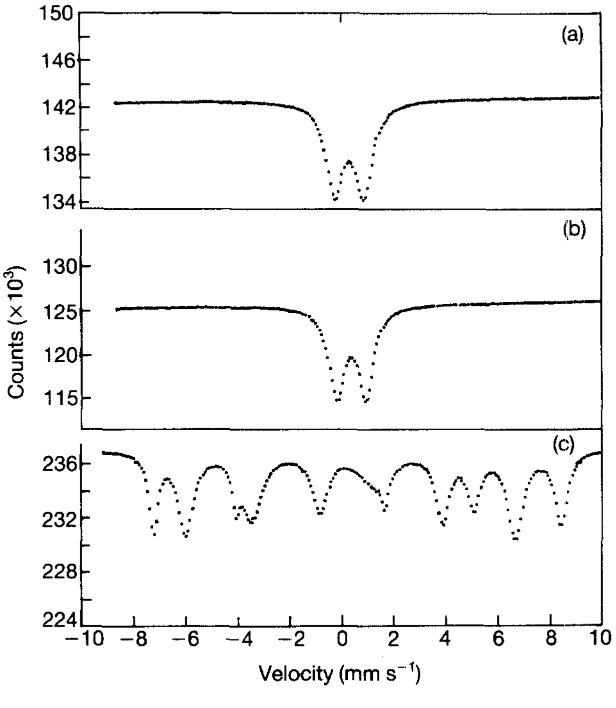

Figure 1 The room-temperature Mössbauer spectra of ultrafine Yb$_3$Fe$_5$O$_{12}$ heat treated at (a) 450 °C, (b) 600 °C and (c) 900 °C.

TABLE I Mössbauer spectral parameters for ultrafine RIG materials heat treated at various temperatures. Isomer shifts are with respect to natural iron

Samples	Amorphous RIG materials heat treated at						Crystallized RIG samples heat treated at 900°C					
	450°C			600°C			Octahedral Fe^{3+}			Tetrahedral Fe^{3+}		
	Isomer shift, δ ($mm\,s^{-1}$)	Quadrupole splitting ΔE_Q ($mm\,s^{-1}$)	Linewidth ($mm\,s^{-1}$)	Isomer shift, δ($mm\,s^{-1}$)	Quadrupole splitting ΔE_Q ($mm\,s^{-1}$)	Linewidth ($mm\,s^{-1}$)	Isomer shift, δ($mm\,s^{-1}$)	H_{int} (kOe)	Linewidth ($mm\,s^{-1}$)	Isomer shift, δ($mm\,s^{-1}$)	H_{int} (kOe)	Linewidth ($mm\,s^{-1}$)
$Dy_3Fe_5O_{12}$	0.33	1.07	0.60	0.32	1.03	0.54	0.44	488	0.42	0.19	394	0.65
$Ho_3Fe_5O_{12}$	0.33	1.07	0.71	0.33	1.07	0.68	0.39	489	0.40	0.20	395	0.68
$Er_3Fe_5O_{12}$	0.40	0.95	–	0.33	1.04	0.63	0.35	489	0.34	0.19	392	0.45
$Yb_3Fe_5O_{12}$	0.29	1.10	0.80	0.28	1.12	0.79	0.46	495	–	0.21	395	–
$Y_2NdFe_5O_{12}$	0.33	1.01	0.70	0.34	1.05	0.75	0.44	496	0.31	0.20	402	0.60
$Y_2GdFe_5O_{12}$	0.32	1.04	0.71	0.30	1.14	0.64	0.35	488	0.33	0.15	394	0.62
$Sm_3Fe_5O_{12}$	0.30	0.95	–	0.33	1.12	–	–	–	–	–	–	–
$Tb_3Fe_5O_{12}$	–	–	–	–	–	–	0.38	494	0.32	0.16	397	0.40

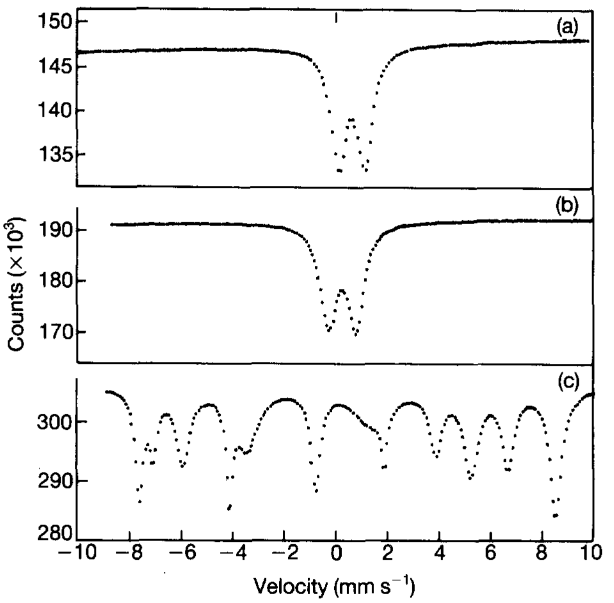

Figure 2 The room-temperature Mössbauer spectra of ultrafine $Y_2NdFe_5O_{12}$ heat treated at (a) 450 °C, (b) 600 °C and (c) 900 °C.

sized particles, i.e. 1.5 nm < crystallite size < 10 nm (heat-treatment temperature range 600–700 °C), a mixed spectra consisting of a quadrupole split doublet and broadened hyperfine split sextets are observed as shown in the representative Fig. 3 for ultrafine HoIG. However, on annealing of these intermediate sized particles at 700 °C for more than 24 h, the doublet disappears and the sextets only remain.

5. Discussion

5.1. Isomer shifts

Isomer shifts shown by the 10–35 nm crystallites are given in Table I for both tetrahedral and octahedral Fe^{3+} and the values are comparable to the bulk polycrystalline garnets [15]. However, ultrafine RIG materials comprising 1.0–1.5 nm crystallites show only a broad quadruple split doublet at room temperature with isomer shift value of $0.33 \pm .03$ mm s^{-1}. Because these materials show saturation magnetization values of 7–20 e.m.u. g^{-1} (obtained by extrapolation of the magnetization curves), which are comparable to bulk crystalline garnets, paramagnetic nature is ruled out. Therefore, the doublet indicates the superparamagnetic nature of these ultrafine particles. In the magnetization studies, the absence of saturation even in applied fields up to 10 kG and the resemblance of the magnetization plots to Langevin function curves confirm the superparamagnetic nature [9, 14]. The isomer shift $\delta = 0.33 \pm 0.03$ mm s^{-1} (Table I), exhibited by all the ultrafine garnets of 1.0–1.5 nm crystallite size confirm iron in the high-spin Fe^{3+} state [16]. Interestingly, these values of isomer shifts are greater than the tetrahedral Fe^{3+} value ($\delta = 0.24$ mm s^{-1}) and less than the octahedral Fe^{3+} value ($\delta = 0.45$ mm s^{-1}) in bulk crystalline garnets. The intermediate isomer shifts, together with the larger width of the lines, apparently indicate that the doublet has a contribution from both octahedral and tetrahedral Fe^{3+}. It has been observed in the literature that the

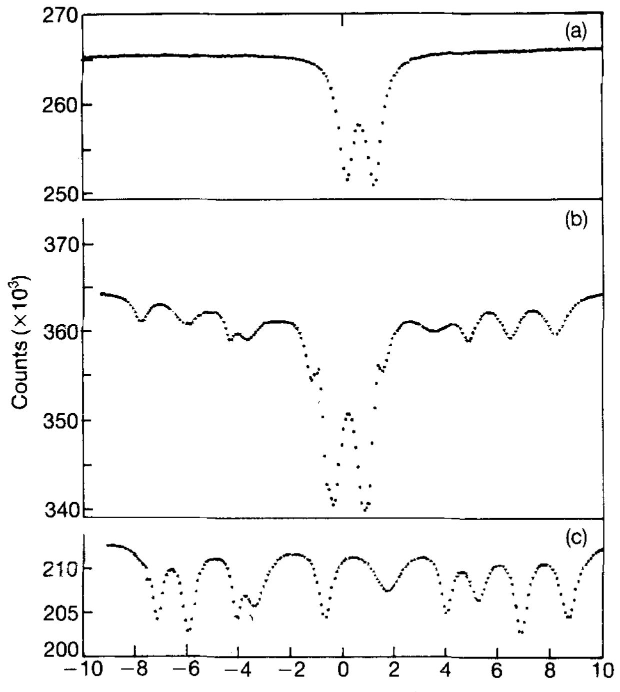

Figure 3 The room-temperature Mössbauer spectra of ultrafine $Ho_3Fe_5O_{12}$ heat treated at (a) 450 °C, (b) 700 °C and (c) 900 °C.

YIG prepared by a similar citrate method showed two weakly resolved sextets corresponding to tetrahedral and octahedral Fe^{3+} at liquid helium temperature, which further confirm the presence of both tetrahedral and octahedral Fe^{3+} [17]. It is interesting to note that in ultrafine crystallites the isomer shift of the doublet is greater than that of the tetrahedral Fe^{3+} and smaller than the octahedral Fe^{3+} in bulk crystalline garnets. These observations have special significance because the isomer shifts have direct correspondence with the covalent bond distances. The isomer shift, δ, depends mainly on the s-electron density at the nucleus. In the MO bonding model, the s-electrons, especially 4s, form σ-bonds with one of the ligand p-orbitals, which are strongly influenced by the cation–anion distances. The closer the ligand oxygen is to iron in the oxygen polyhedra, greater the s-electron density at the iron nucleus and the lower the isomer shift. Therefore, the smaller isomer shift of octahedral Fe^{3+} in ultrafine garnets compared to bulk crystalline garnets indicates a decrease of octahedral Fe–O bond distance. By a similar argument, the increase of tetrahedral δ value in ultrafine garnets indicates an increase of tetrahedral Fe–O bond distance compared to bulk crystalline garnets. These observations, interestingly, are in complete agreement with the conclusions of a contraction of octahedra and an expansion of the tetrahedra made earlier from optical reflectance studies [13] and discussed in Section 3.

In addition, an improved symmetry at the Fe^{3+} sites is usually accompanied by an increase in isomer shifts [18]. Therefore, a decrease in isomer shift of the octahedral Fe^{3+}, apparently indicate a greater distortion or greater asymmetry at this site in ultrafine crystallites compared to bulk crystalline garnets. From the observations it can be concluded that the disorder, increase of specific volume and the lattice strain are a direct consequence of the modification of the oxygen polyhedra in 1.0–1.5 nm crystallites of rare-earth iron garnets.

5.2. Quadrupole splitting

The Mössbauer spectrum makes a valuable contribution to the knowledge of the surrounding iron ions. A comparison of the Mössbauer spectral parameters with other oxygen-coordinated iron compounds is a direct method of identification of oxygen coordinations. The quadrupole splitting of the superparamagnetic doublet corresponding to the 1.0–1.5 nm crystallites of ultrafine RIG is $\Delta E_Q = 1.05 \pm 0.08$ mm s^{-1} (Table I). These values are comparable to the tetrahedral Fe^{3+} ($\Delta E_Q = 0.9$ mm s^{-1}) in bulk crystalline garnets [15]. In other oxygen surroundings, such as in α-Fe_2O_3 and the spinel type γ-Fe_2O_3 or Fe_3O_4, the Fe^{3+} ions experience smaller field gradients [19, 20]. The quadrupole splitting is a measure of the strength of the electric field gradient around the ^{57}Fe nucleus which, in turn, is a measure of the deviation from cubic symmetry [21]. It is interesting to note (Table I) that for all the ultrafine RIG materials comprising 1.0–1.5 nm crystallites, the quadrupole splitting is rather large ($\Delta E_Q = 1.05 + 0.08$ mm s^{-1}) compared to tetrahedral Fe^{3+} in bulk crystalline garnets ($\Delta E_Q = 0.9$ mm s^{-1}). This is also true in the case of intermediate sized particles, the Mössbauer spectra for which are shown in Fig. 3. The larger quadrupole splitting values indicate the considerable deviation from cubic symmetry, that is the symmetry of oxygen coordinations. The broad quadrupole split doublet probably has a contribution from both tetrahedral and octahedral Fe^{3+}. The greater asymmetry at the octahedral Fe^{3+} site indicated earlier by the smaller isomer shift, explains the large quadrupole splitting for octahedral iron. A large quadrupole splitting or the absence of a sharp quadrupole absorption for octahedral Fe^{3+} has been reported for non-crystalline rare-earth iron garnets prepared by d.c. sputtering and twin-roller quenching methods, respectively [22, 23]. The absence of a sharp absorption for octahedral Fe^{3+} can be related to the widening of the lattice with a corresponding distortion of the oxygen octahedra [24]. The greater deviation from cubic symmetry and the resulting greater quadrupole splitting could be the result of very small crystallite size. Similar results have also been reported in the case of non-crystalline YIG prepared by the citrate method [17].

An increase of symmetry at the Fe^{3+} site is usually accompanied by a decrease in quadrupole splitting and an increase of isomer shift [18]. However, the small increase in crystallite size from 1.0–1.5 nm in the heat-treatment temperature range 450–600 °C in the ultrafine RIG materials is accompanied by a very small decrease in isomer shift values and an increase of quadrupole splitting (Table I). This probably indicates that the local symmetry at the Fe^{3+} sites in ultrafine garnets is further affected due to lattice distortion. The largest increase in quadrupole splitting in the case of

$Sm_3Fe_5O_{12}$ explains its relative instability compared to other RIG materials. It is evident that the apparent increase in crystallite size from 1.0 nm to 1.5 nm size is not due to the growth of crystallites, but it indicates the increase of specific volume due to greater disorder, because of the increase of lattice strain also observed in this temperature range [9]. It is noteworthy that the magnetization also decreases in this temperature range [14]. The greater deviation from cubic symmetry could be responsible for the destabilization of the X-ray amorphous state which eventually leads to the formation of 10–35 nm crystallites.

5.3. Magnetic hyperfine fields

In ultrafine RIG crystallites of 10–35 nm size obtained on heat treatment above 700 °C, two well-resolved six-line spectra corresponding to the tetrahedral and octahedral Fe^{3+} are observed (Figs 1 and 2). The hyperfine fields for these crystallites are comparable to the reported values for bulk crystalline garnets (Table I). The simultaneous presence of a magnetically split component and a quadrupole split doublet in Fig. 3 indicates a particle-size distribution and the coexistence of larger sized ferrimagnetic particles and the smaller sized superparamagnetic particles. The magnetically split component consists of two sextets corresponding to tetrahedral and octahedral Fe^{3+} in garnets. However, the hyperfine fields for tetrahedral (375 kOe) and octahedral (480 kOe) are smaller than the respective values, 394 and 485 kOe, for bulk crystalline garnets. It must be emphasized that the saturation hyperfine fields in microcrystals is, in general, different from the observed magnetic field at the nuclei in larger crystals at the same temperature for the following reasons. The demagnetizing fields to the magnetic splitting are negligible in larger crystals consisting of several domains. But in single domain microcrystals of ferro- and ferrimagnetic materials, the demagnetizing fields give a significant contribution. The values of hyperfine fields in microcrystals and in large crystals may also be different due to different magnetic structures [25]. Another reason for the difference in hyperfine fields in microcrystals and large crystals is that the magnetic hyperfine fields of surface atoms may be different from that of the bulk value, as reported in other fine-particle materials [26]. The surface effects are, however, important for one or two surface layers and will be predominant in particles of the smallest size range and could be responsible for the small reduction in hyperfine fields observed in ultrafine garnets. The reduction in hyperfine fields in ultrafine crystallites could also be due to the so-called collective magnetic excitations. In ultrafine particles, the magnetization vector may fluctuate in directions close to an easy direction of magnetization. Because the correlation time of these fluctuations is short compared to the time scale of the Mössbauer spectroscopy, the observed magnetic splitting of the spectra is proportional to an average value of the hyperfine field, and hence smaller than it would be in the absence of fluctuations. Such lowered hyperfine fields have been reported in ultrafine crystallites of ^{57}Fe-containing compounds such as α-FeOOH [7].

5.4. Linewidths

In ultrafine crystallites of 10–35 nm size as well as in the intermediate sized particles, both tetrahedral and octahedral subspectral lines show larger linewidths compared to bulk crystalline garnets. The broadening of lines could be due to the ultrafine particle nature which leads to a larger surface contribution, because recent calculations have shown that the variations in hyperfine fields at the surface may result in a small line broadening [27]. This should, in fact, lead to uniform broadening of the tetrahedral and octahedral lines. However, tetrahedral subspectrum show relatively larger linewidth in ultrafine garnets (Table I). In the Mössbauer spectra, the width of the tetrahedral line is a sensitive probe of the direction of magnetization [28, 29]. In fact, when the magnetization is along the ⟨111⟩ crystallographic direction in RIG, the structure is rhombohedral and all the tetrahedral sites have their symmetry axes at an angle of 55° from the direction of magnetization. The tetrahedra are, therefore, all equivalent and there is only one sextet of tetrahedral lines with a strictly Lorentzian line shape. When the magnetization moves away from the ⟨111⟩ direction, the angle between the symmetry axes of the tetrahedral sites and magnetization has no longer a uniform value. Thus the lines of the tetrahedral subspectrum split and lead to the line broadening of the ultrafine RIG materials. Another possible reason for the line broadening of the ultrafine RIG materials is a contribution of the growth-induced magnetic anisotropy. If that is so, prolonged heating at higher temperatures should remove this broadening.

The linewidth of the quadrupole split lines of 1.0–1.5 nm crystallites is also quite large, as shown in Table I. In Mössbauer spectra, if the quadrupole split lines are sharp, the coordination spheres of all the Fe^{3+} ions are identical. If the peaks are broad, the electric field gradient differs from iron to iron and hence their coordination spheres may differ. In the earlier discussions, it has been found that the octahedral Fe^{3+} ion does not give a sharp absorption. However, it is possible that the octahedrally coordinated Fe^{3+}, which has a smaller quadrupole splitting, contributes to the central portion of the doublet lines but does not resolve into independent doublet lines owing to the weaker magnetic ordering of the octahedral sublattice. In fact, in the low-temperature Mössbauer spectra, the non-crystalline YIG was reported to show a broad octahedral absorption with a lower hyperfine field (compared to bulk crystalline garnets), an indication of the weaker ordering of the octahedral sublattice [17]. Moreover, they also observed a weakening of the central portion of the superparamagnetic doublet on applying a magnetic field indicating the magnetic ordering of the sublattice contributing to the doublet. In general, the broad lines observed for the 1.0–1.5 nm crystallites are an indication that the local symmetry is considerably worse compared to bulk crystalline garnets and that the ultrafine crystallites of the smallest size range differ from the bulk garnets on a local molecular scale.

6. Conclusions

Mössbauer spectral investigations of ultrafine RIG in the 10–35 nm size range at room temperature show two sextets characteristic of tetrahedral and octahedral sublattices with isomer shifts and magnetic hyperfine fields comparable to bulk crystalline garnets. In contrast, 1.0–1.5 nm crystallites exist as nonporous aggregates with magnetic interaction among the crystallites and show superparamagnetic doublet Mössbauer spectra. These quadrupole split doublets have an isomer shift larger than the tetrahedral and smaller than the octahedral Fe^{3+} in bulk crystalline garnets indicating, respectively, a relative increase of tetrahedral Fe–O bond distance (or an expansion of tetrahedra) and a decrease of octahedral bond distance (or a contraction of octahedra) in the ultrafine state. These observations are complementary to the results of the spectrochemical investigations made earlier and substantiate the increase of specific volume observed in XRD. The larger linewidth of the quadrupole split lines indicates that the local symmetry is considerably worse and that the ultrafine crystallites of the smallest size range differ from bulk at the local molecular level.

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