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Magnetic properties and Mössbauer spectra of gamma ferric oxide and doped gamma ferric oxide

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Magnetic hysteresis, Mössbauer spectra and temperature variation of initial magnetic susceptibility of thirteen samples of doped γ-Fe_2O_3 containing cobalt or gadolinium are determined. The samples containing more than 1.0% cobalt are found to have a multi-domain configuration, and undoped γ-Fe_2O_3, gadolinium-doped γ-Fe_2O_3 and doped γ-Fe_2O_3 containing less than 1.0% (except 0.3%) cobalt have a single domain configuration. Mössbauer spectra of gadolinium-doped samples suggest that gadolinium occupies A and B sites. In cobalt-doped samples, the effective magnetic fields at A and B sites are different at room temperature and liquid nitrogen temperature. The samples which have a multi-domain configuration display an additional central doublet in Mössbauer spectra indicating that these samples contain multi-domain clusters. The saturation magnetization of gadolinium-doped γ-Fe_2O_3 is much lower, and the coercive force of cobalt-doped samples is much higher than of gadolinium-doped and undoped samples.

1. Introduction

Gamma ferric oxide (γ-Fe_2O_3) is a ferrimagnetic compound with the spinel structure, in which iron(III) cations occupy both the tetrahedral (A) and octahedral (B) sites, and is usually assumed to have a collinear magnetic structure consisting of two sublattices. The measurements of direct current electrical conductivity of γ-Fe_2O_3, cobalt-, nickel-, gadolinium- and terbium-doped γ-Fe_2O_3 prepared in static air [1, 2] carried out at different temperatures suggest the presence of adsorbed oxygen and water in γ-Fe_2O_3. These measurements determined in the different atmospheres, supplemented with the data of infrared spectra and X-ray diffraction patterns, indicate the presence of lattice water and of hydrogen ferrite phase. An addition of a small amount of cobalt to γ-Fe_2O_3 results in a marked change of the magnetic properties of γ-Fe_2O_3 [3–6]. It was, therefore, of interest to study the effect of divalent as well as trivalent dopants on the magnetic properties of γ-Fe_2O_3. In the present work, doped γ-Fe_2O_3 samples with different dopants have been synthesized under controlled experimental conditions.

2. Experimental procedure

The detailed synthesis of γ-Fe_2O_3, cobalt- and gadolinium-doped γ-Fe_2O_3 by dehydration of γ-FeOOH are reported earlier [2]. The procedures used for the measurement of X-ray diffraction patterns and magnetic properties are also given earlier [1, 7]. The constant acceleration Mössbauer spectrometer assembled in the Department of Physics, University of Poona, was used in the present work. The Mössbauer spectra were taken at room temperature and liquid nitrogen temperature. The hyperfine interaction parameters were computed using an interactive least squares "MOSFIT" Program adopted to ICL 1904S computer. The measurements of temperature variation of initial magnetic susceptibility were determined by a double-coil method [8, 9] assembled at the Indian Institute of Technology, Bombay, using a field of 1.0 Oe, and a frequency of 263 Hz. The temperature was varied between 20 and 550° C, and was measured accurately within ±1° C.

3. Results and discussion

At room temperature, the experimental value of saturation magnetization of γ-Fe_2O_3 obtained from ferrous oxalate dihydrate (sample A) is $7.10\,T\,kg^{-1}$, and that obtained from gamma ferric oxide hydroxide (sample B) is $6.15\,T\,kg^{-1}$. We may therefore assume that sample B is mainly hydrogen ferrite. When sample B is heated in a nitrogen atmosphere at 280° C for 12 h and is cooled in the same atmosphere (sample C), its saturation magnetization is enhanced to $7.15\,T\,kg^{-1}$. There is no change in the saturation magnetization when a similar heat treatment is given in static air. This observation suggests that hydrogen ferrite is transformed to γ-Fe_2O_3 after heating for 12 h in nitrogen. Thus sample B can be assumed to be the hydrogen-doped γ-Fe_2O_3. Because the saturation magnetization of sample A is somewhat lower than that expected for the vacancy-ordered γ-Fe_2O_3, it may be considered to be a mixture of vacancy-ordered γ-Fe_2O_3 and hydrogen ferrite.

Mössbauer spectra of samples A, B and C consist of six well-resolved narrow bands (half-band width $0.285\,mm\,sec^{-1}$) (Fig. 1) in the intensity ratio 3 : 2 : 1 :

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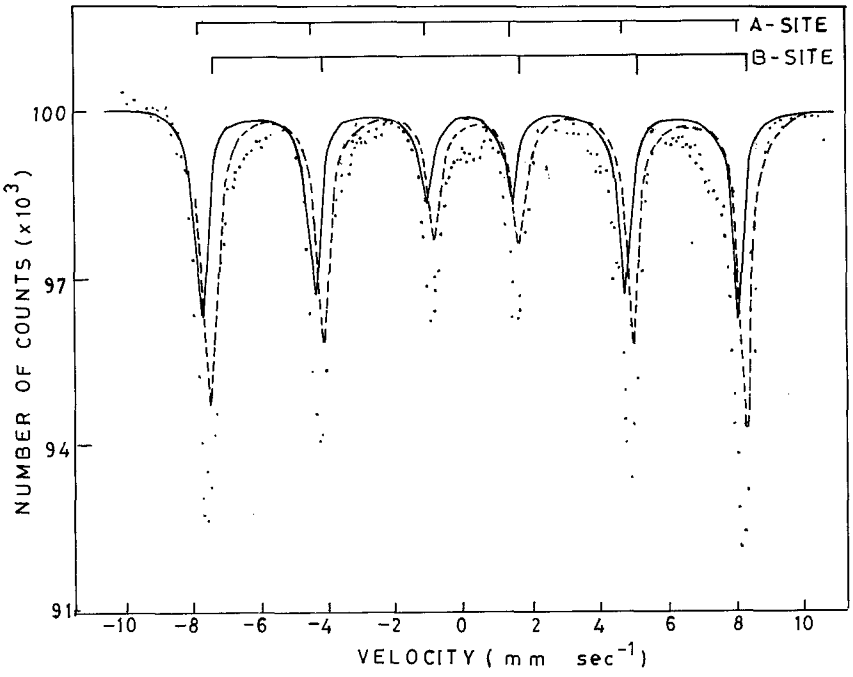

Figure 1 Computer-fitted room-temperature Mössbauer spectra of γ-Fe_2O_3.

1:2:3. The best fit of the experimental curve is obtained as superposition of two six bands (see Fig. 1). The line width corresponding to the B-site (0.27 ± 0.03 mm sec^{-1}) is found to be slightly larger than that for the A-site (0.22 ± 0.03 mm sec^{-1}). The isomer shift and hyperfine field of these samples are very comparable (Table I). No quadrupole splitting is observed for both the sites. The area ratio of the B-site to the A-site sextet was found to be 1.62. Therefore, the area ratio of these samples should, theoretically, lie between 1.50 and 1.67 depending upon the percentage of γ-Fe_2O_3 with hydrogen and vacancy, respectively [10]. Because sample B can be considered to be hydrogen-doped γ-Fe_2O_3, it will be profitable to synthesize the doped samples of γ-Fe_2O_3 using the γ-FeOOH method.

The X-ray diffraction patterns of cobalt- and gadolinium-doped samples are similar to that of the undoped sample of γ-Fe_2O_3, and corresponding to a tetragonal configuration [11]. From X-ray diffraction it is observed that the intensity of the (3 2 1) line is greater in the cobalt-doped samples and is less in the case of gadolinium-doped samples. The presence of the (3 2 1) line indicates an increase in the density of atoms in the (3 2 1) plane. This is possible through replacement of hydrogen and/or occupation of vacant

TABLE I Magnetic properties and Mössbauer spectra* of γ-Fe_2O_3 and doped γ-Fe_2O_3 at room temperature

Sample no.	Concentration of dopants	Coercive force, H_c (±0.25 A m^{-1})	Saturation magnetization, M_s (±0.04 T kg^{-1})	Ratio of remanence coercive force to coercive force (H_r/H_c)	Ratio of M_R/M_s	Hyperfine field, H_n (±5.0 KOe)	
						A-site	B-site
A	γ-Fe_2O_3 from $Fe_2C_2O_4 \cdot 2H_2O$	3.52	7.10	2.00	0.64	493.8	496.1
B	γ-Fe_2O_3 from γ-FeOOH	3.52	6.15	2.00	0.65	493.8	496.0
C	Sample B heated at 280° C in N_2 atmosphere	3.52	7.15	2.00	0.66	494.1	496.3
I	Co doped: 0.3%	3.52	6.07	2.03	0.63	488.6	494.9
II	0.5%	3.58	5.88	2.00	0.61	483.0	490.0
III	0.75%	3.69	5.86	2.03	0.63	482.0	488.0
IV	1.0%	3.87	5.68	2.11	0.56	478.8	485.0
V	3.0%	5.28	5.60	2.14	0.58	476.3	483.0
VI	5.0%	5.28	5.56	2.28	0.57	473.4	481.8
VII	10.0%	6.03	5.56	2.25	0.59	470.9	480.0
VIII	15.0%	6.54	5.20	2.31	0.58	470.0	479.1
IX	Gd doped: 0.3%	3.49	5.02	1.84	0.58	455.0	458.5
X	0.50%	3.52	5.06	1.84	0.57	456.1	458.5
XI	0.75%	3.46	5.00	1.82	0.60	455.8	458.5
XII	1.0%	3.46	4.60	1.83	0.58	456.0	458.5
XIII	1.5%	3.52	3.80	1.82	0.59	455.6	458.4

*The computer-fitted Mössbauer spectra show negligible quadrupole splitting, and the isomer shift (for A site 0.24 mm sec^{-1} and for B site 0.32 mm sec^{-1} with respect to iron foil) remains constant within experimental accuracy.

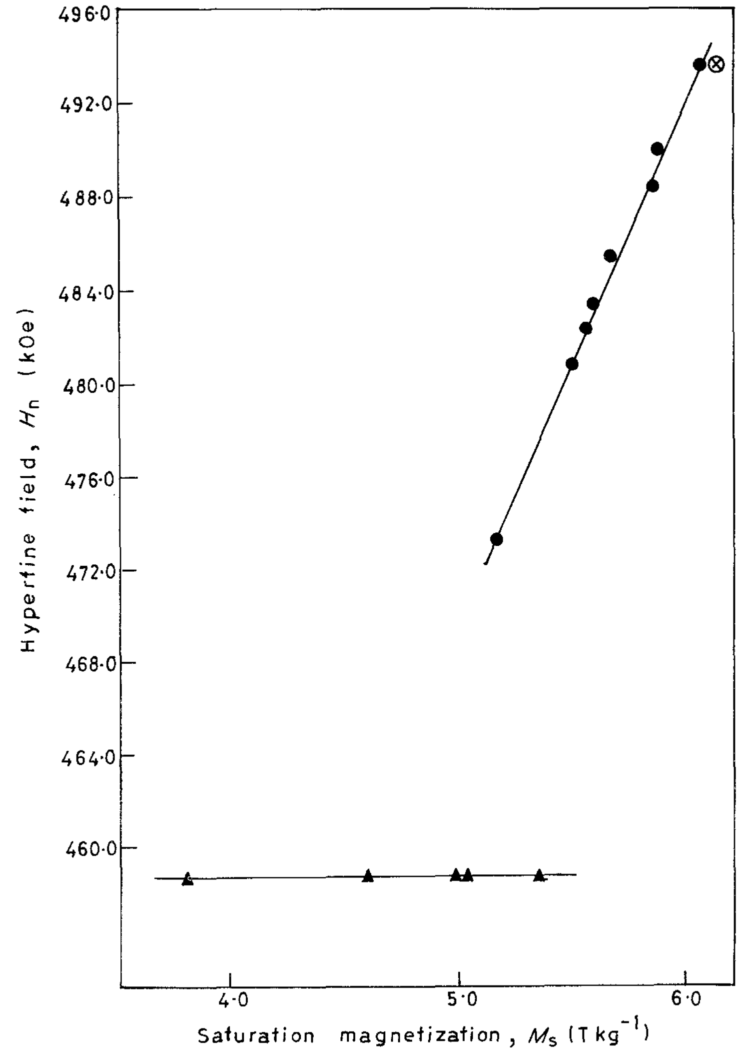

Figure 2 Plot of hyperfine field (H_n) against saturation magnetization (M_s). (⊗) undoped γ-Fe_2O_3; (●) cobalt-doped γ-Fe_2O_3; (▲) gadolinium-doped γ-Fe_2O_3.

site by cobalt and gadolinium, specifically on the B-site. This is a significant new observation which directly gives evidence of preferential diffusion of cobalt or gadolinium in the γ-Fe_2O_3 lattice during the precipitation process.

The observed saturation magnetization values of cobalt- and gadolinium-doped γ-Fe_2O_3 samples are lower than those reported in literature [12, 13]. A direct proportionality between the hyperfine field (H_n) and saturation magnetization (M_s) for the magnetically similar compounds has been suggested by Marshell [14, 15]. It is interesting to note that the separate Marshell straight lines (Fig. 2) are obtained for cobalt- and gadolinium-doped γ-Fe_2O_3. Thus the magnetic configuration of these doped samples is not identical, although the respective group of doped samples has similar magnetic configuration.

For such doped samples containing a low concentration of gadolinium, we do not expect the formation of a garnet, and the X-ray diffraction patterns of these samples resemble the pattern of undoped γ-Fe_2O_3. The gadolinium(III) ion with $4f^7$ electronic configuration is spherically symmetrical, and the crystal field effects are comparatively negligible. An abnormally low value of observed saturation magnetization (Table I), even for a sample containing a low concentration of gadolinium, suggests that part of the gadolinium also occupies A-sites. Because the exchange interactions between gadolinium(III) and the neighbouring iron(III) ions are usually about an order of magnitude smaller than those found between two neighbouring iron(III) ions [16], fluctuations of the magnetization direction about the energy minimum are envisaged. Such fluctuations will lead to a decrease in the hyperfine field. The Mössbauer spectra of gadolinium(III)-doped γ-Fe_2O_3 are according to this prediction (Fig. 3). These spectra are similar to that of undoped γ-Fe_2O_3 and consist of six symmetrical narrow bands except that the hyperfine field is abnormally low (Table I). The isomer shifts of these samples are slightly different from undoped γ-Fe_2O_3.

Room-temperature Mössbauer spectra of all the cobalt-doped γ-Fe_2O_3 samples displayed a broadened six-finger pattern along with the central adsorption (Figs 4 and 5). The broadening of the Mössbauer line is probably associated with the contribution of the following configuration.

$$Fe_8^{3+}[(Fe_x^{2+}M_y^{2+}H_{4-2x-2y}^{+}\square_{x-y})Fe_{12}^{3+}]O_{32}$$

In addition to the broadening of the Mössbauer lines, doped γ-Fe_2O_3 containing 0.3% and more than 1.0% cobalt show a well-resolved doublet in the centre of the Mössbauer spectra. The Mössbauer parameters for the sextets are given in Table I.

The isomer shift of cobalt-doped γ-Fe_2O_3 for the A-site almost remains the same as that of undoped γ-Fe_2O_3. For the B-site of cobalt-doped γ-Fe_2O_3 an increase in isomer shift (0.59 ± 0.03 mm sec^{-1}) value

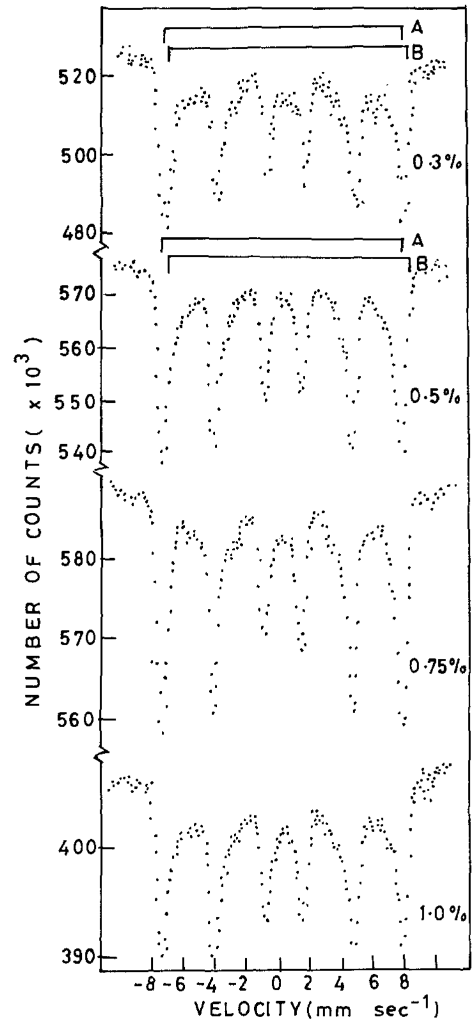

Figure 3 Room-temperature Mössbauer spectra of gadolinium-doped γ-Fe_2O_3.

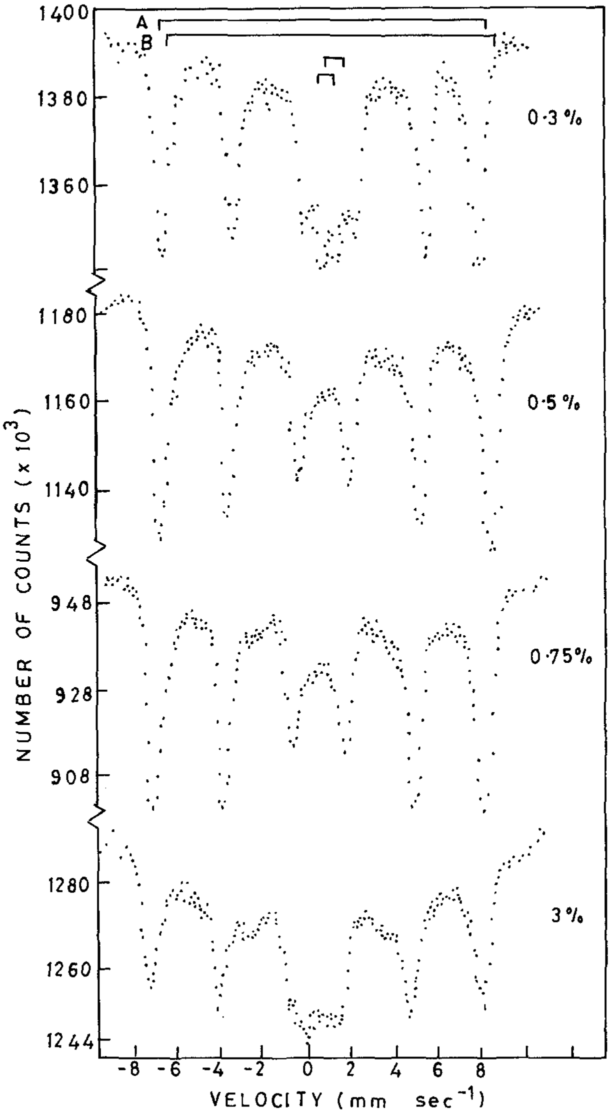

Figure 4 Room-temperature Mössbauer spectra of 0.3 to 3.0% cobalt-doped γ-Fe_2O_3.

compared to the undoped γ-Fe_2O_3 is seen. This probably shows that although there is not much change in the bonding of iron atoms at the A-site, some change in the bonding does take place at the octahedral B-site due to cobalt concentration. The hyperfine field for all the cobalt-doped γ-Fe_2O_3 samples are found to be less than that of pure γ-Fe_2O_3 (see Table I). The hyperfine field for both A and B sites is found to be different. This clearly indicates that the addition of cobalt has created nonequivalent sites of iron ions on the B-site. The area ratio of the B-site sextet to the A-site sextet was found to be the same. Therefore, cobalt enters vacant sites or replaces iron atoms or hydrogen.

The two doublets representing the central absorption show an interesting behaviour. The isomer shift of one doublet remained almost the same within about 0.11 mm sec^{-1} for all the samples. For the other doublet, the isomer shift remained almost the same at 0.51 mm sec^{-1} for all the samples. These isomer shift (IS) values clearly indicate that the valence state of iron ions responsible for producing the doublets is Fe^{3+}. The quadrupole splitting of the first doublet (with low IS) ranges between 0.62 and 0.93 mm sec^{-1} ($\pm$ 0.03 mm sec^{-1}) and that for the other doublet (with high IS) ranges between 0.77 and 1.02 mm sec^{-1} ($\pm$0.03 mm sec^{-1}). The low value of the quadrupole splitting also indicates that the doublets must be due to Fe^{3+} ions. Scanning electron microscopy and particle size distribution of doped γ-Fe_2O_3 containing 0.3% and more than 1.00% cobalt show a wide particle size distribution ranging from 80 nm to about 140 nm, while the other doped sample and undoped γ-Fe_2O_3 have a particle size of 105 to 110 nm.

When a sample contains particles of various sizes, it will be characterized by a range of spin-flip time, τ_F, which is given by [17]

$$\tau_F = \tau_0 \exp (K V_{eff} / K_B T)$$

where K is the anisotropy, V_{eff} the volume of the particles, K_B the Boltzmann constant, T the temperature, τ_F the relaxation time of spin flip and τ_0 lies between 10^{-10} and 10^{-12} sec. For static cases, $\tau_F \gg \tau_L$, where τ_L is the Larmor precession time and under such conditions a six-finger pattern is observed. For $\tau_F \ll \tau_L$ superparamagnetism is observed. The existence of a spread in volume, V_{eff}, and the extremely strong dependence of τ_F upon V_{eff} ensures that the range of τ_F encompasses both extremes. It is, therefore, natural to expect the coexistence of a central peak and hyperfine structure. It is assumed that doped γ-Fe_2O_3 containing 0.3% and more than 1.00% cobalt is not perfectly homogeneous but is comprised of a set of independent magnetic regions. We may then

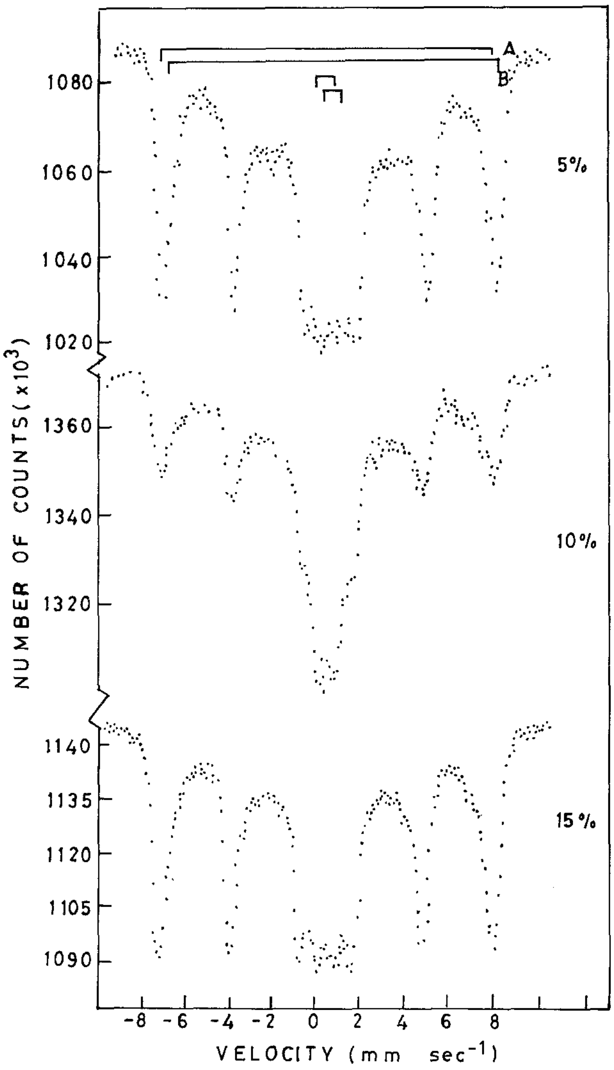

Figure 5 Room-temperature Mössbauer spectra of 5.0 to 15.0% cobalt-doped γ-Fe_2O_3.

imagine each such volume, V_{eff}, flipping back and forth with a flip time, τ_F. At low temperature, the energy barrier KV_{eff} is high and thus τ_F is long compared to τ_L. Hence no relaxation effects should be observed. As temperature approaches T_N (Neel temperature), $K \rightarrow 0$ and the spin-flip frequency increases, so that relaxation phenomena corresponding to superparamagnetism may be discerned. Because there is a spread in KV_{eff}, it gives rise to the simultaneous presence of a strong central absorption and hyperfine structure in the Mössbauer spectrum. In view of the scanning electron microscopy, the above argument seems to be more probable.

Mössbauer spectra of 3.0% cobalt-doped γ-Fe_2O_3 are recorded at liquid nitrogen temperature and also at 373 K. It is observed that the central absorption disappeared completely at liquid nitrogen temperature but, on the other hand, it increased considerably at temperatures higher than room temperature, i.e. 373 K (Fig. 6). These observations indicate that the central absorption is due to the superparamagnetic component present in 0.3% and more than 1.0% cobalt-doped γ-Fe_2O_3. Therefore, the two doublets could be considered to be superparamagnetic spectra displayed by Fe^{3+} ion on tetrahedral and octahedral sites, respectively. The quadrupole interaction experienced by the superparamagnetic Fe^{3+} ions on the octahedral site and the concentration of cobalt ions could possibly distort the symmetry on the tetrahedral site giving rise to the quadrupole interaction experienced by Fe^{3+} ions on the tetrahedral site. The initial magnetic susceptibility measurement of these samples will help to analyse the presence of the superparamagnetic particles and the clusters of particles with single domains.

The study of the temperature variation of initial magnetic susceptibility (X_i) curves of samples A, B and C show a typical Hopkinson effect [18]. For these samples, X_i increases with increasing temperature giving a peak value at the transformation temperature (Fig. 7b). This is a characteristic behaviour of samples having a single domain structure. Similarly, samples II to IV and IX to XIII are found to be single domain from the X_i–T behaviour.

The X_i values of samples I and V to VIII do not show any observable change in the temperature range 25 to 405° C. A sharp decrease is observed at the Curie temperature (405° C) which corresponds to an irreversible transformation of γ-Fe_2O_3 and α-Fe_2O_3 (Fig. 7a). These samples thus display the X_i–T behaviour characteristic of a multidomain structure [18]. The X_i–T curve of superparamagnetic samples shows X_i to decrease as T increases.

On the basis of these criteria, the samples which do not show the central Mössbauer absorption are found to be of single domain configuration, and the samples which show the central Mössbauer absorption have multidomain configuration. Because the central Mössbauer absorption is supposed to be due to the paramagnetic species, the samples which show the X_i–T behaviour characteristic of multidomain grains, are probably clusters of particles having single domains. It is significant to note here that the particle size of samples used in the present work was 80 to 140 nm.

All the samples studied in the present work showed a definite hysteresis loop at room temperature and liquid nitrogen temperature. The coercive force of cobalt-doped samples was much higher than that of other samples (Table I). It is interesting to observe that the coercive force (H_c), saturation magnetization (M_s) and M_R/M_s are increased for samples I, V to VII at liquid nitrogen temperature. The plot of H_cM_s against cobalt-doped concentration (figures not shown), does not show a linear trend at room temperature, but does show a reasonable linear relationship at liquid nitrogen temperature. It is already observed from the X_i–T curve that most of the cobalt-doped γ-Fe_2O_3 sample contains single domain particles and because H_cM_s is proportional to anisotropy in the case of single domain particles, one can conclude that the anisotropy is proportional to cobalt concentration at liquid nitrogen temperature. The deviation from the linear relationship at room temperature could be due to the clusters of single domains present in samples I, V to VII. The ratio of the remanence coercive force to coercive force of cobalt-doped samples is higher than that of the undoped sample; this ratio does not show any significant change on doping with gadolinium

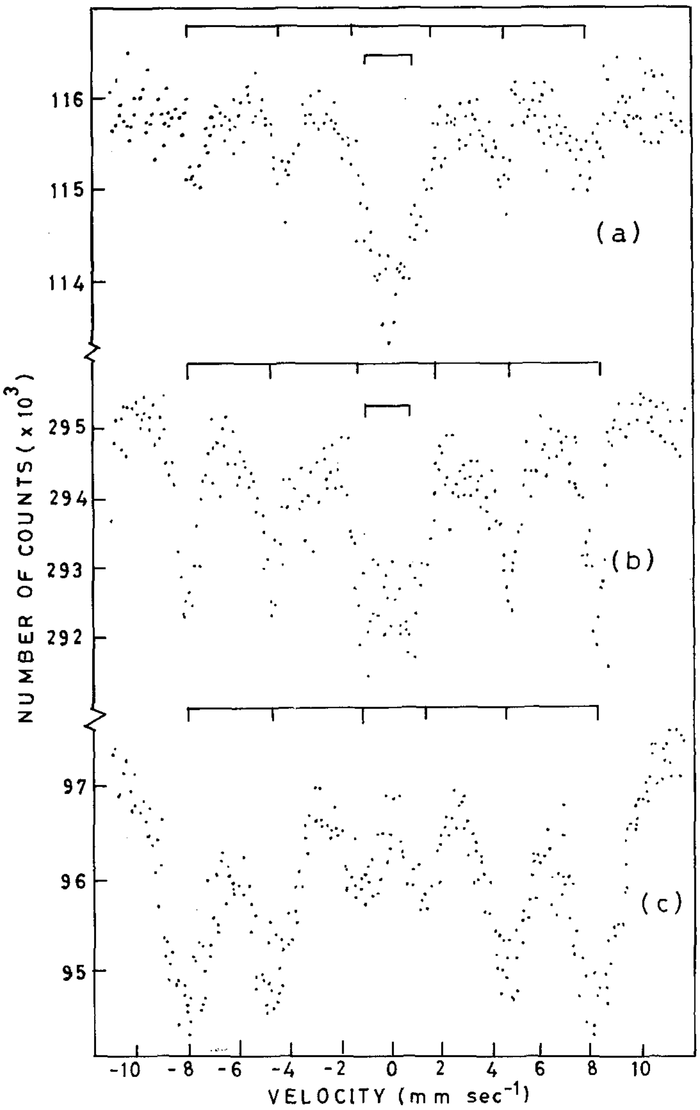

Figure 6 Mössbauer spectra of 3.0% cobalt-doped γ-Fe_2O_3 at (a) 373 K, (b) room temperature, (c) 80 K.

(Table I). Thus there is an enhancement of magnetic anisotropy on cobalt doping.

4. Conclusions

1. The low value of hyperfine field and the saturation magnetization of gadolinium-doped γ-Fe_2O_3 suggest that the gadolinium ion occupies both A and B sites and the magnetization direction of gadolinium ion fluctuates about the energy minimum.

2. Doped γ-Fe_2O_3 containing 0.3% and more than 1.0% cobalt shows a well-resolved doublet in the centre of the six-line Mössbauer spectra indicating the presence of some type of paramagnetic species in these samples. The data on the temperature variation of the

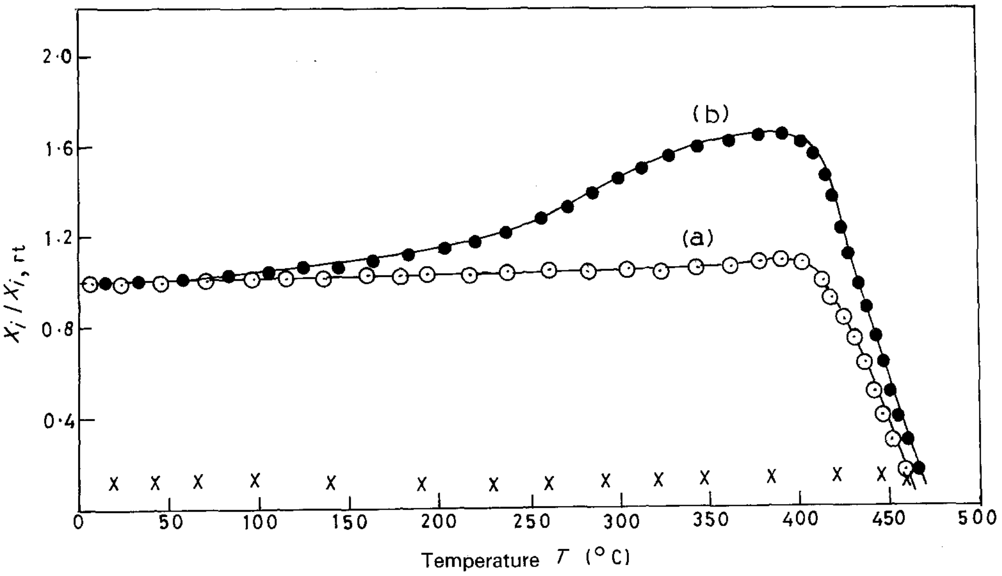

Figure 7 Plot of $X_i/X_{i,rt}$ against T for (a) multidomain structure, (b) single domain structure. (●, ⊙) Heating cycle, (×) cooling cycle.

initial magnetic susceptibility suggest that these samples have a multidomain configuration. Thus the central doublet is associated with single domain clusters. All other samples are found to be single domain.

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