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Mixed spinel structure in nanocrystalline $NiFe_2O_4$

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Nanocrystalline $NiFe_2O_4$ spinel has been synthesized with various grain sizes by high-energy ball milling. From the high-field magnetization studies and extended x-ray-absorption fine-structure, and Mössbauer measurements in an external magnetic field of 5 T applied parallel to the direction of gamma rays, we could observe that Ni^{2+} ions occupy tetrahedral sites on grain-size reduction due to milling. The Fe^{3+} spins have a canted structure and the canting angle increases with grain-size reduction. It is possible that the core Fe^{3+} spins are also canted because of the magnetocrystalline anisotropy introduced by the occupancy of the Ni^{2+} ions in the tetrahedral sites.

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I. INTRODUCTION

Spinel ferrites have the general molecular formula $(A^{2+})[B_2^{3+}]O_4^{2-}$ where A^{2+} and B^{3+} are the divalent and trivalent cations occupying tetrahedral (A) and octahedral (B) interstitial positions of the fcc lattice formed by O^{2-} ions. The magnetic properties of these oxides depend on the type of cations and their distribution among the two interstitial positions. The cation distribution and the resulting magnetic properties are found to be different and quite interesting in some nanocrystalline spinel ferrites when compared to those of their bulk counterparts. The striking example is $ZnFe_2O_4$, which, in the bulk form, is a normal spinel with the Zn^{2+} ions at the A sites and the Fe^{3+} ions at the B sites, and it exhibits antiferromagnetic ordering below 10 K. But nanocrystalline $ZnFe_2O_4$ with a grain size of about 5–20 nm is reported[1–4] to be magnetically ordered with a large magnetic moment even at high temperatures. The observed high-temperature magnetic ordering is attributed to the change in the cation distribution from the normal to the mixed spinel type where Fe^{3+} and Zn^{2+} ions occupy both the sites.[5] Our in-field Mössbauer studies[4] of nanocrystalline $ZnFe_2O_4$ could establish without any ambiguity that the ordering is of ferrimagnetic type and that the spins exhibit canting with respect to the magnetization direction. Nanocrystalline mixed spinel $MnFe_2O_4$ is also reported to undergo a change in cation distribution.[6,7] However, it is easier to observe the change in the cation distribution in normal spinels such as $ZnFe_2O_4$ and inverse spinels like $NiFe_2O_4$ rather than in mixed spinels.

$NiFe_2O_4$ is a well-known inverse spinel with Ni^{2+} ions on B sites and Fe^{3+} ions distributed equally among A and B sites. Berkowitz *et al.* have reported that ultrafine particles of $NiFe_2O_4$ coated with organic molecules exhibit strong pinning of the surface spins whereas uncoated particles do not show such behavior.[8] Morrish and Haneda have shown that $NiFe_2O_4$, in the ultrafine form, is an inverse spinel exhibiting noncollinear spin structure and that the magnetic moment at low temperatures is appreciably lower than the value for the bulk material.[9] They have proposed a model wherein the particle consists of a core with the collinear spin arrangement and a surface layer with the magnetic moment inclined to the direction of magnetization. Kodama *et al.* have done extensive work on this system and observed anomalous magnetic properties for their organic coated $NiFe_2O_4$ nanoparticles.[10,11] They have proposed a model of ferrimagnetically aligned core spins and a spin-glass-like surface layer for their particles. However, there is not a single report in the literature, to the best of our knowledge, on the change in the cation distribution when the particle size is reduced to nanometer level for $NiFe_2O_4$. Even though the observed spin canting has been explained by proposing a surface structure with broken exchange bonds[10,11] it is not mentioned whether there is any possibility that the canting is due to magnetocrystalline anisotropy also. To address these two questions we have systematically carried out high-field magnetization measurements and extended x-ray-absorption fine-structure (EXAFS) and in-field Mössbauer studies on nanocrystalline $NiFe_2O_4$ ferrites with various grain sizes.

II. EXPERIMENT

Nickel ferrite was synthesized in polycrystalline form by the conventional ceramic method from a mixture of high-purity α-Fe_2O_3 and NiO taken in the atomic ratio 1:1, respectively. The formation of a single phase spinel was confirmed from the x-ray powder-diffraction measurements using a Huber x-ray diffractometer and Fe-$K\alpha$($\lambda = 1.9373$ Å) radiation. The milling of the as-prepared

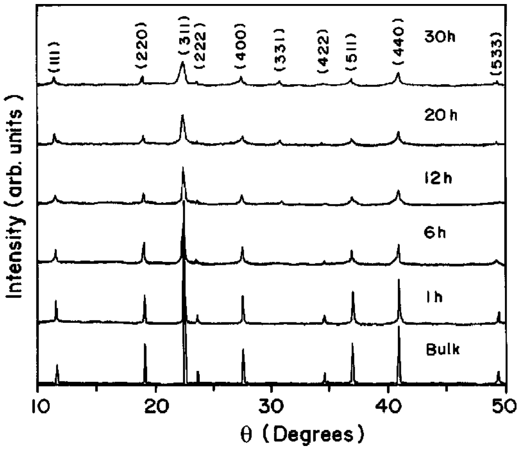

FIG. 1. XRD patterns for the nanocrystalline $NiFe_2O_4$ milled for various times.

$NiFe_2O_4$ was carried out in air in a planetary ball mill (Fritsch Pulverisette, P7) with tungsten carbide balls and vials to reduce the grain size. After selected milling times a small amount of powder was removed each time from the vials for analysis. The ^{57}Fe Mössbauer spectra at room temperature were recorded at the University of Madras, India using a Wissel constant acceleration Mössbauer spectrometer and a ^{57}Co(Rh) source, and those at 4.2 K in zero field and 5-T magnetic field were recorded at the National Research Institute for Metals, Tsukuba, Japan. The EXAFS measurements were done at Tohoku University, Sendai, Japan using a rotating-anode-type x-ray generator (Rigaku R-EXAFS 2100S) with an Mo target as the x-ray source and a Johansson-type single-crystal Ge(220) monochromator. The zero-field-cooled (ZFC) and field-cooled (FC) magnetization curves were obtained from 5–300 K in a magnetic field of 9 T by using a vibrating sample magnetometer (PPMS, Model 6000, Quantum Design) at Sendai.

III. RESULTS AND DISCUSSION

A. X-ray studies

The x-ray powder diffractograms (XRD) of the bulk $NiFe_2O_4$ and the samples milled for various times are shown in Fig. 1.

The reflections are characteristic of the spinel phase. The diffraction peaks of the milled samples are broadened, which can be the result of the reduced grain size and the atomic level strain introduced during milling. The average grain size has been evaluated from the full width at half maximum of the reflection (311) in the XRD pattern using a Scherrer formula. The grain size is found to decrease with milling time and reaches 10 nm for 30 h milling.

B. Mössbauer studies

The room-temperature Mössbauer spectra of the samples milled for various times, shown in Fig. 2, were fitted with Lorentzian-shaped lines by the method of least squares. The spectra are broadened and the large linewidths are due to the presence of multiple hyperfine fields at Fe^{3+} nuclei at *A* and *B* sites. An acceptable fit of the spectra was obtained only when the data were fitted with three sextets. The Mössbauer parameters resulting from the least-squares fitting are given in Table I. The center shifts are correct to ±0.01 mm/s, quadrupole splittings to ±0.02 mm/s, and the hyperfine magnetic fields are correct to ±1 kOe. The weighted average hyperfine field decreases from 498 kOe for the 1-h milled sample to 480 kOe for the 30-h milled sample. The decrease in the values of hyperfine fields from that of the bulk $NiFe_2O_4$ (Ref. 12) (506 kOe for the *A* site and 548 kOe for the *B* site) at room temperature is due to the collective excitations in small particles as has been explained by Mxrup *et al.*[13]

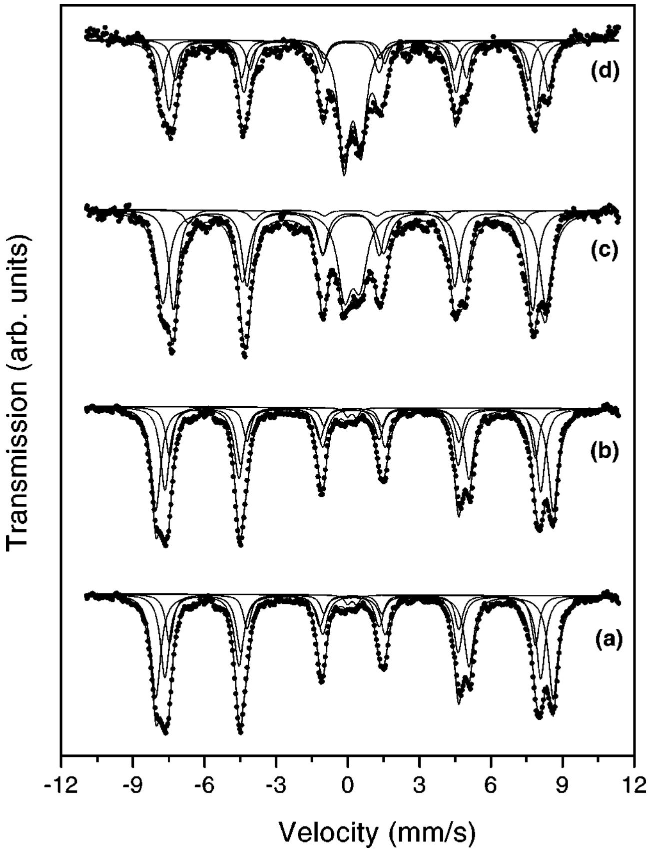

FIG. 2. Room-temperature Mössbauer spectra for the nanocrystalline $NiFe_2O_4$ milled for various times of (a) 1, (b) 6, (c) 20, and (d) 30 h.

The sextet with the largest hyperfine field value and the largest center shift is assigned to the Fe^{3+} ions at the *B* sites and the sextet with the smallest center shift is assumed to arise from the Fe^{3+} ions occupying the *A* sites. The third sextet with the smallest hyperfine field may be attributed to Fe^{3+} ions in the grain boundaries or on the surface. It should be pointed out here that the grain boundaries should exist in these samples as the particles are welded against each other on mechanical milling. The center shift of this third sextet lies in between those of the *A* and *B* sites.

Apart from the well-defined sextets, the Mössbauer spectra also consist of a superparamagnetic doublet whose intensity increases as the particle size decreases with milling time. The quadrupole splitting of this doublet also increases with

TABLE I. Mössbauer parameters such as center shift (CS) relative to that of α-Fe at 300 K, quadrupole splitting (QS), the hyperfine magnetic field $\langle B \rangle$, linewidth (Γ), and relative intensities I_{rel} at 300 K for the nanocrystalline $NiFe_2O_4$ ball milled for various times.

Milling time (h) [Grain size (nm)]	Site	CS (mm/s)	QS (mm/s)	B (kOe)	Γ (mm/s)	I_{rel} (%)
1	*A*	0.26	0.14	488	0.44	34.4
(60)	*B*1	0.39	0.02	515	0.48	46.6
	*B*2	0.32	0.02	475	0.38	17.8
		0.29	0.38		0.30	1.2
6	*A*	0.29	0.14	481	0.44	34.9
(40)	*B*1	0.41	0.02	509	0.45	42.4
	*B*2	0.31	0.08	469	0.40	18.3
		0.28	0.51		0.50	4.4
20	*A*	0.29	0.10	466	0.47	35.0
(15)	*B*1	0.37	0.04	497	0.62	43.0
	*B*2	0.33	0.19	432	0.51	5.0
		0.30	0.64		0.70	17.0
30	*A*	0.26	0.10	476	0.47	34.3
(10)	*B*1	0.38	0.01	503	0.40	21.2
	*B*2	0.29	0.01	458	0.40	16.8
		0.31	0.70		0.55	27.7

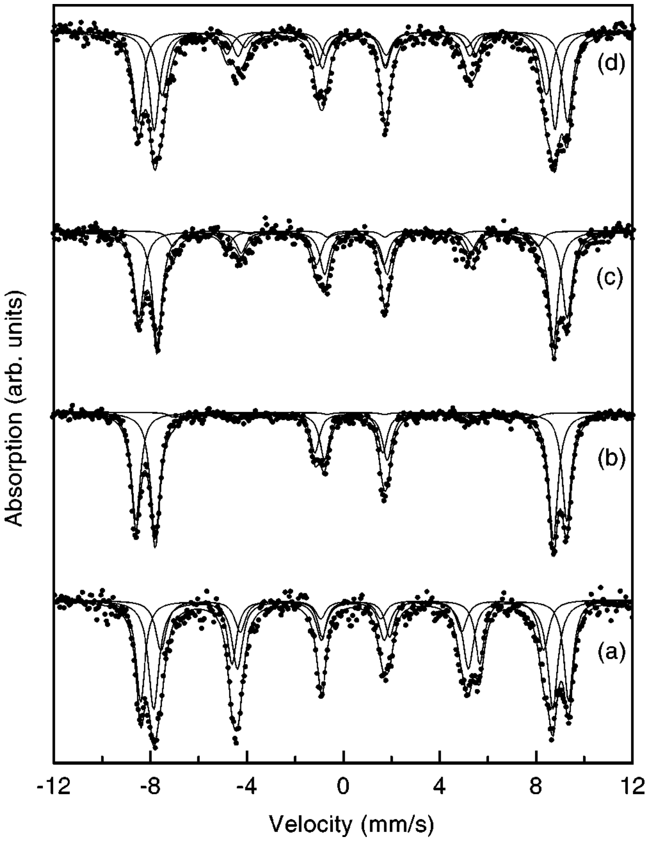

FIG. 3. Mössbauer spectra recorded at 4.2 K for the $NiFe_2O_4$ spinel (a) 20-h milled in zero field, (b) 1-h milled in an external field of 5 T, (c) 20-h milled in an external field of 5 T, and (d) 30-h milled in an external magnetic field of 5 T.

milling time obviously due to the increase of disorder on milling. The superparamagnetic doublet disappears when the samples are cooled to 4.2 K as seen from the representative 4.2-K Mössbauer spectrum of the 20-h milled sample shown in Fig. 3.

Figure 3 also shows the Mössbauer spectra of the 1-, 20-, and 30-h milled samples at 4.2 K in an external magnetic field of 5 T applied parallel to the direction of gamma rays. Table II gives the Mössbauer parameters of nanocrystalline $NiFe_2O_4$ as obtained from the least-squares fitting of the in-field Mössbauer spectra.

The Mössbauer spectra in Fig. 3 show well-resolved outer lines as the applied field adds to the magnetic hyperfine field at the *A* site and subtracts from the hyperfine field at the *B* site. This facilitates the ability to obtain more reliable and relative intensities for the sextets. The outermost sextet arises from Fe^{3+} ions on the *A* sites, the middle one from the *B* site Fe^{3+} ions, and the third one from the Fe^{3+} ions at the grain boundaries or surfaces. The relative intensity of the third sextet increases with milling time as the grain-boundary volume should increase with grain-size reduction on continued milling. There are two interesting results that one can derive from these spectra. The first one is the decrease in the relative intensity of the *A*-site sextet with milling time. This is possible only if some Ni^{2+} ions are forced into the tetrahedral (*A*) sites on milling. The number of such Ni^{2+} ions entering into the *A* sites is found to increase with milling time. Bulk $NiFe_2O_4$ is known to be a well-known inverse spinel with all the Ni^{2+} ions on the *B* sites and the Fe^{3+} ions distributed equally between the tetrahedral and octahedral sites. It is interesting to observe that milling in a high-energy ball mill could change the cation distribution from the in-

TABLE II. Mössbauer parameters of nanocrystalline $NiFe_2O_4$ milled for 1, 20, and 30 h at 4.2 K in an external magnetic field of 5 T applied parallel to the direction of gamma rays: center shift (CS) values relative to that of α-Fe measured at 300 K, quadrupole splitting (QS), effective field $\langle B_{\mathrm{eff}} \rangle$, hyperfine field $\langle B \rangle$, linewidth (Γ), average canting angle (θ), and relative intensities I_{rel}.

Milling time (h)	Site	CS mm/s	QS mm/s	B_{eff} kOe	B kOe	Γ mm/s	θ (°)	I_{rel} (%)
1	*A*	0.40	0.09	553	505	0.45	14.4	46.9
(60 nm)	*B*1	0.60	0.07	511	560	0.47	14.0	51.2
	*B*2	0.61	0.06	467	515	0.47	14.1	1.9
20	*A*	0.46	0.12	550	508	0.50	30.0	41.5
(15 nm)	*B*1	0.62	0.02	509	553	0.48	30.0	51.7
	*B*2	0.63	0.02	469	513	0.45	30.0	6.8
30	*A*	0.48	0.06	552	511	0.50	34.0	34.9
(10 nm)	*B*1	0.57	0.03	515	557	0.50	34.0	37.8
	*B*2	0.60	0.07	494	536	0.56	34.0	27.3

verse spinel structure to the mixed spinel type. The relative intensities of the spectral components in Table I, however, indicate that there is no change in the *A*-site Fe occupancy. But it should be remembered that in the absence of an external magnetic field, the relative intensities obtained from the fitting are not reliable due to the high degree of overlapping of the spectral components. This report shows that $NiFe_2O_4$ could be a mixed spinel when the grain size is reduced to a few nanometers. However, Chukalkin and Shtirts[14] have reported that Ni^{2+} ions occupy *A* sites in the case of $Zn_xNi_{1-x}Fe_2O_4$ ferrites disordered by irradiating with fast neutrons of energy greater than 1 MeV. Sepelák *et al.*[15] have shown from the decrease in the ratio of the intensity of the (220) peak to that of the (222) peak $[I(220)/I(222)]$ in the x-ray diffractograms that the cations are transported from *A* sites to *B* sites in the mechanically milled $NiFe_2O_4$. However, as could be seen from Fig. 1 this ratio does not change on milling, which suggests that there is no obvious change in the relative population of the two sites for the sample in the present study. They conclude that Fe^{3+} ions occupy only the octahedral sites from the occurrence of a quadrupole-split doublet in the Mössbauer spectrum at room temperature of the 60-min milled $NiFe_2O_4$. But this needs a low-temperature measurement to eliminate the possibility of the occurrence of the doublet due to superparamagnetic effect.

The second interesting result is that the second and fifth lines of the sextets have nonzero intensity that increases with milling time. The presence of the second and fifth lines of the Mössbauer sextet in an external magnetic field applied parallel to the direction of gamma rays is because of the canting of the Fe^{3+} spins with respect to the applied field direction. Similar results have been obtained by Morrish and Haneda[9] for their ultrafine $NiFe_2O_4$ particles prepared by chemical route. They conclude that the observed phenomenon may not be a size effect but instead it may be due to surface effects with the spins on the surface layer alone having canted structure. Kodama *et al.* have reported that the $NiFe_2O_4$ fine particles coated with organic surfactant have ferrimagnetically aligned core spins and a spin-glass-like surface layer.[10]

The ground state of the Ni^{2+} ion, when it moves to the tetrahedral site, changes to an orbital triplet state as a result of the change in the sign of the crystal-field constant.[14] This leads to a partial unquenching of its orbital moment and hence to a substantial contribution to the magnetocrystalline anisotropy. Therefore, apart from the canting of surface spins because of the broken exchange bonds there is a possibility that the core spins are also canted due to the magnetocrystalline anisotropy introduced by the presence of Ni^{2+} ions in the tetrahedral sites. The average canting angle θ defined as the angle between the direction of the effective hyperfine field and the direction of applied magnetic field (γ-ray direction) was calculated using a method already reported in the literature[9,16] and the values of θ are given in Table II. Obviously, the canting angle increases with decreasing grain size.

The ^{57}Fe hyperfine fields at *A* and *B* sites calculated from the effective fields are given in Table II. These are comparable to the values reported in the literature for bulk $NiFe_2O_4$.[12] This agreement is an expected one since the collective excitations and superparamagnetic relaxations responsible for the reduction in hyperfine magnetic fields at room temperature in ultrafine particles should disappear at low temperatures.

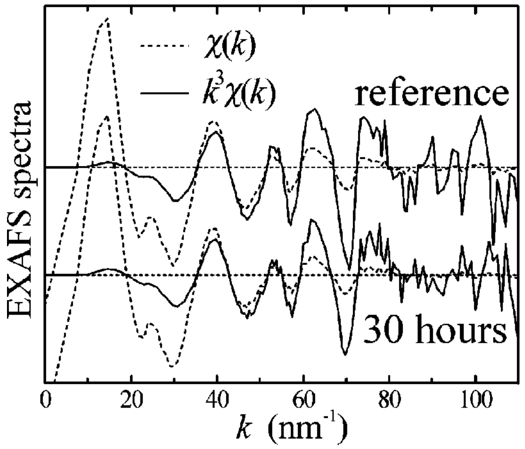

FIG. 4. The EXAFS spectra of (a) bulk nickel ferrite and (b) the 30-h milled sample.

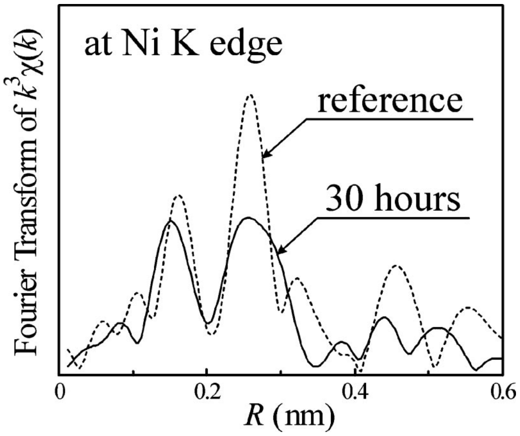

FIG. 5. Fourier-transformed profiles of (a) bulk nickel ferrite and (b) the 30-h milled sample.

C. EXAFS studies

The EXAFS at the high-energy side of the absorption edge of a certain element gives us the environmental atomic structure around the absorption atom. Fig. 4 shows the EXAFS spectra, $\chi(k)$, and k^3 weighted $\chi(k)$ of these $NiFe_2O_4$ samples at the Ni-K absorbtion edge.

The Fourier-transformed profiles, as shown in Fig. 5, describe the sharp peak between 0.2 and 0.3 nm for the bulk reference sample that corresponds to the Ni-Ni or Ni-Fe bond and the peak position suggests that the Ni^{2+} ions occupy the octahedral sites. On the other hand, in the case of the 30-h milled sample broadening of this peak, arising from these cation pairs, to the farther side and also the shift of the Ni-O peak at about 0.2 nm to a lower distance are found. The distance between Ni-Ni or Ni-Fe will be 0.292 nm when the Ni ions are occupied in the octahedral site alone and hence a sharp peak around 0.292 nm will be observed. On the other hand, when the Ni ions are occupied in the tetrahedral site alone, the bond length of Ni-Ni or Ni-Fe will be 0.357 nm and a peak will be observed having its maximum around 0.357 nm. If we have Ni ions both in tetrahedral and octahedral sites, then we could expect a broad peak containing the peaks at two different bond lengths. Thus, the corresponding peak would have its maximum at a distance between 0.292 and 0.357 nm. Considering these facts, the profile of the sample milled for 30 h suggests the partial inversion of Ni ions from octahedral to tetrahedral sites as reflected in peak broadening and a shift.

D. Magnetization studies

The zero-field-cooled and field-cooled saturation magnetization curves measured for the 1- and 30-h milled samples in an applied field of 9 T are given in Fig. 6. The separation between ZFC and FC curves, even though it is very small especially for the 1-h milled sample, gives an indication that there is a nonequilibrium magnetization state below 50 K for the ZFC case.

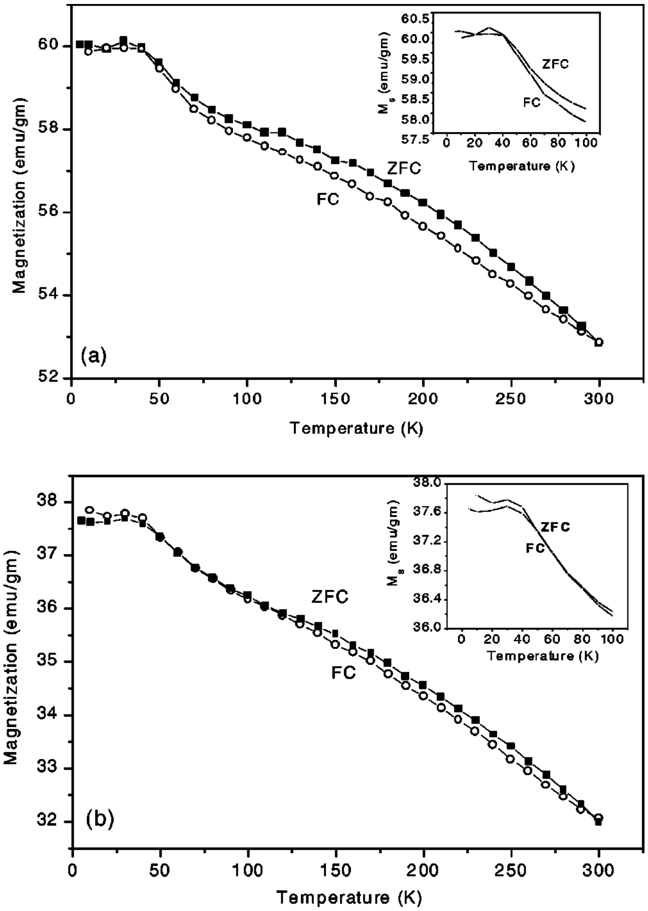

FIG. 6. Zero-field-cooled and field-cooled saturation magnetization curves for (a) 1- and (b) 30-h milled samples in an applied field of 9 T.

It is, therefore, clear that the high-energy ball-milled ultrafine particles of $NiFe_2O_4$ exhibit spin-glass-like surface disorder as has been observed by Kodama *et al.*[10] for their organic coated milled particles. Hysteresis loop shift has been observed in the field-cooled state at low temperatures in the present study also. Another interesting observation is that the saturation magnetization of the 1-h milled sample at 5 K is 60 emu/gm, which is higher than the value of 55 emu/gm reported for the bulk $NiFe_2O_4$.[17] The 8% increase in the value of M_s could be possible only if the cation distribution for nanocrystalline $NiFe_2O_4$ changes from the well-known inverse spinel type to a mixed spinel one. In the inverted spinel structure the net magnetization comes from the Ni^{2+} moments in the B sites alone as the Fe^{3+} moments from the A and B sites cancel each other. In the mixed spinel type some Ni^{2+} ions occupy the tetrahedral A sites and hence the net magnetization should be higher than that for the inverse spinel structure as the Ni^{2+} magnetic moment $(3.0\mu_B)$ in the A sites is smaller than that of the Fe^{3+} magnetic moment $(5\mu_B)$. For the 8% increase in the magnetization it is necessary that about 3.5% of Ni^{2+} ions should occupy the tetrahedral sites, and the value obtained from the in-field Mössbauer studies is about 6%.

IV. CONCLUSIONS

$NiFe_2O_4$ is found to have the mixed spinel structure when the grain size is reduced to a few nanometers as confirmed by in-field Mössbauer, magnetization, and EXAFS measurements. In addition to the canting of surface spins because of the broken exchange bonds it is suggested that the core spins could also have canted spin structure due to the large magnetocrystalline anisotropy resulting from the occupation of the tetrahedral sites by Ni^{2+} ions. The difference in the hyperfine fields of the bulk and nanocrystalline $NiFe_2O_4$ is clearly due to the presence of superparamagnetic and collective excitations at high temperatures.

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