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LETTER

Magnetic properties of nanocrystalline Co–Ni ferrite

Z. P. Niu · Y. Wang · F. S. Li

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A spinel structure which is formed by a nearly close-packed fcc array of anions with holes partly filled by the cations can be represented by the formula AB_2O_4 [1], A represents metallic ions located in A interstitial (tetrahedral) sites and B metallic ions located in B (octahedral) sites. Due to the large electronegativity of oxygen, the ionic type of bonds prevails in almost all oxide spinels [2]. Magnetic properties of nanoparticles have been of great interest in recent years partly because of the development of high-density magnetic storage media with nanosized constituent particles or crystallites [3, 4]. Much attention have been attracted by the investigation of nanophase spinel ferrite particles owing to their technological importance in the application areas, such as microwave devices, high speed digital tape and disk recording, ferrofluids, catalysis, and magnetic refrigeration systems [5]. Magneto-optical properties of $CoFe_2O_4$ and $NiFe_2O_4$ have been investigated in references [6–9]. The investigation of ferromagnetic resonance properties in $Co_xNi_{1-x}Fe_2O_4$ with low cobalt concentration ($X \leq 0.1$) were performed many years ago [10–13]. Cobalt ferrite, $CoFe_2O_4$, is a well-known hard magnetic material [14]. Recently, Ni^{2+} ions were added to Co ferrite films to improve the magnetic recording properties of cobalt ferrite films, which are promising as high-density perpendicular recording media [15, 16]. To our knowledge, the systematic investigation of the magnetic properties of nanocrystalline Co–Ni ferrite $Co_xNi_{1-x}Fe_2O_4$ with x variated from 0 to 1 has not been reported. In this article, the crystal structure and the magnetic properties of nanosized Co–Ni ferrite prepared by the polyvinyl alcohol (PVA) sol-gel method are reported.

$Co_xNi_{1-x}Fe_2O_4$ ($0.0 \leq x \leq 1.0$) ferrite powders were produced by the PVA sol-gel method [17]. Cobalt nitrate, nickel nitrate and ferric nitrate were mixed at a Co:Ni:Fe ion ratio of x:1–x:2 and dissolved in deionized water, this mixture was then added to the aqueous PVA solution with continuous stirring for 30 min. After that, the mixed solution was dehydrated at 80 °C until the dry gel-type precursor was obtained. Portion of this precursor was calcined at 800 °C for 2 h, yielding the materials examined in this work.

The crystallographic properties of the samples were examined by powder X-ray-diffraction (XRD) measurements with CuK_α radiation (Philips x' pert, Holland). The macromagnetism measurements were performed using a vibrating sample magnetometer (VSM) (Lakeshore 7304, USA).

Figure 1 shows X-ray diffraction patterns of $Co_xNi_{1-x}Fe_2O_4$. All samples were found to be single phase spinel. The average particle sizes as determined from the X-ray diffraction line breadths are about 34 ± 2 nm. The lattice constant a_0 of each sample listed in Table 1 is obtained by plotting the lattice constant versus the Nelson–Riley function and extrapolating the result to $\theta = 90°$. A comparison between the lattice constant of the nanosized $Co_xNi_{1-x}Fe_2O_4$ and that of the bulk material [1] is shown in Fig. 2. The lattice constant a_0 increases almost linearly with the increasing cobalt concentration (x). This can be explained by the fact that the ionic radius of Co^{2+} (0.78 Å) is larger than that of Ni^{2+} (0.69 Å). The larger value of the lattice constant for the nanosized $Co_xNi_{1-x}Fe_2O_4$ than for the bulk material with x ranging from 0 to 1.0 may be due to the lattice expansion induced by the reduced particle size

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Z. P. Niu (✉) · Y. Wang · F. S. Li
Key Lab for Magnetism and Magnetic Materials of Ministry of Education, Lanzhou University, Lanzhou 730000,
People's Republic of China
e-mail: niuzp@lzu.edu.cn

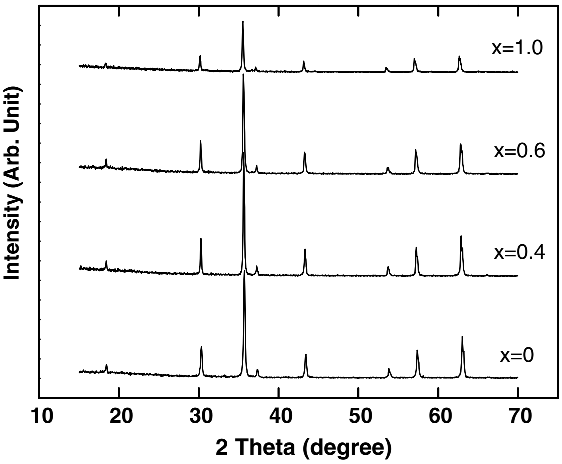

Fig. 1 X-ray diffraction patterns of $Co_xNi_{1-x}Fe_2O_4$ (x = 0.0, 0.4, 0.6, 1.0)

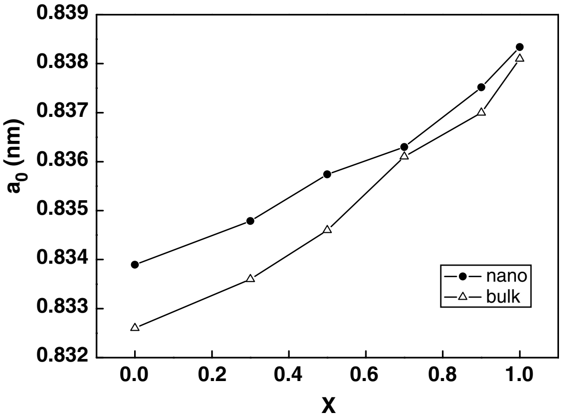

Fig. 2 Dependence of the lattice parameter on cobalt concentration for $Co_xNi_{1-x}Fe_2O_4$

and increased surface–body ratio in $Co_xNi_{1-x}Fe_2O_4$ ferrite nanoparticles.

Some typical room temperature hysteresis loops of $Co_xNi_{1-x}Fe_2O_4$ are shown in Fig. 3 with field up to 12 kOe. The maximum magnetization (M_s) in field of 12 kOe, residual magnetization ratio (M_r/M_s) and coercivities (H_c) for all samples are summarized in Table 1. Figure 4 shows the dependence of M_s on cobalt concentration (x). The increase of cobalt concentration yields the monotonic increase of M_s, which may be caused by the substitution of Ni^{2+} ions by Co^{2+} ions on octahedral sites. The magnetic moment μ per ion for Co^{2+} ions (3 μ_B) is larger than that for Ni^{2+} ions (2 μ_B). Therefore, the increasing Co^{2+} concentration (x) on octahedral sites may result in an increasing magnetic moment per formula of $Co_xNi_{1-x}Fe_2O_4$, and equivalently, an enhancement of magnetization. As shown in Fig. 5, with the increasing cobalt concentration, the residual magnetization ratio (M_r/M_s) and coercivities (H_c) increase in the range of low concentration and then decrease in the range of high concentration. At high cobalt concentrations, a decreasing coercivity and simultaneously, an increasing saturation magnetization have been observed, which can be easily controlled by increasing the content of cobalt in $Co_xNi_{1-x}Fe_2O_4$. Similar results have been reported in modified Ba-ferrite and Sr-ferrite [18, 19]. Our observations may have some significance. Magnetic recording medium, for instance, requires a high saturation magnetization and a moderately high coercivity [20]. Sometimes, a too high coercivity is not suitable for recording medium application and has to be modified, and it is important to keep a high saturation magnetization when the coercivity is reduced [18]. The coercivity of an array of single domain particles interacted with each other is given by [21]

$$H_c(p) = H_c(0)(1 - p).$$

Here p is the volume fraction, which can be described as v_p/v_s, v_s is the total volume of the sample, and v_p the total volume of single domain particles in the sample. $H_c(0)$ is the coercivity of an array of non-interacting particles with uniaxial anisotropy, given by [22]

$$H_c(0) = 0.48H_A$$

$H_A = 2K/\mu_0 M_s$, so we obtain

$$H_c(p) = 0.96K(1 - p)/\mu_0 M_s.$$

It may be roughly assumed that the value of p is same for all the samples considering the fact that all the samples were prepared and examined almost under the same conditions. If this model (array of single domain particles interacted with each other) is qualitatively applicable to our samples. There will be a dependence of anisotropy constant K on the cobalt concentration x, which can be evaluated from the given values of M_s and H_c for our samples (Fig. 6). As the anisotropic effect of Co^{2+}, especially Co^{2+} in B sites, is strong it usually outweighs other possible contributions to the induced anisotropy [23]. In the range of low concentrations Co^{2+} ions may be considered as isolated. This may explain the approximate linear dependence of K on x in the low x range (Fig. 6). In the range of high concentrations Co^{2+} ions cannot be considered as isolated and contributions of more complicated local configurations including pairs become important. For example, isolated Co^{2+}–Co^{2+} pairs might induce a quadratic dependence of K on x [24]. This might cause the complicated variation of K in the range of high cobalt concentration as shown in Fig. 6. Similar phenomenon have been demonstrated in $Co_xNi_{1-x}Fe_2O_4$ systems [25, 26] but not been reported in $Co_xNi_{1-x}Fe_2O_4$ systems yet.

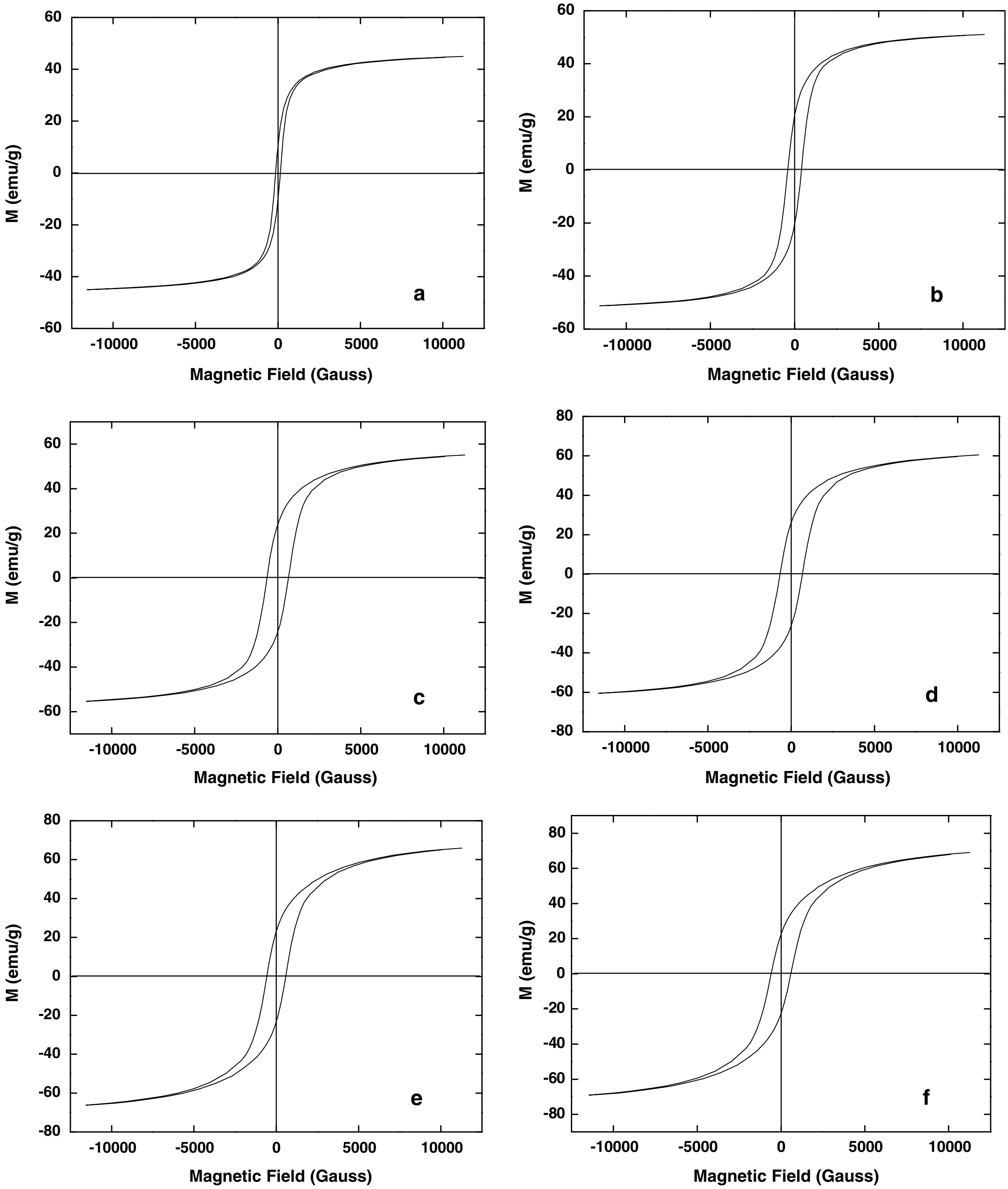

Fig. 3 Hysteresis loops of $Co_xNi_{1-x}Fe_2O_4$ with (**a**) $x = 0.0$, (**b**) $x = 0.2$, (**c**) $x = 0.4$, (**d**) $x = 0.6$, (**e**) $x = 0.8$, and (**f**) $x = 1.0$

In conclusion, the PVA sol-gel method has been used to produce nanosized Co–Ni ferrite $Co_xNi_{1-x}Fe_2O_4$ ($0.0 \le x \le 1.0$). The lattice constants of Co–Ni ferrite nanoparticles are larger than that of bulk materials and increases with the increasing cobalt concentration (x). The increase of cobalt concentration yields the monotonic increase of M_s. The residual magnetization ratio and coercivities increase in the range of low cobalt concentration

Table 1 Lattice parameter (a_0), maximum magnetization (M_s), coercivity (H_c) and residual magnetization ratio (M_r/M_s) for $Co_xNi_{1-x}Fe_2O_4$

x	a_0 (nm)	M_s (emu/g)	H_c (Oe)	M_r/M_s
0.0	0.8339	45.0	142	0.23
0.1	0.8344	47.5	269	0.36
0.2	0.8348	51.0	404	0.40
0.3	0.8348	51.7	531	0.42
0.4	0.8355	55.1	639	0.43
0.5	0.8357	56.8	659	0.46
0.6	0.8364	60.4	671	0.43
0.7	0.8363	63.0	597	0.38
0.8	0.8370	64.9	571	0.35
0.9	0.8375	68.9	555	0.33
1.0	0.8383	70.4	586	0.32

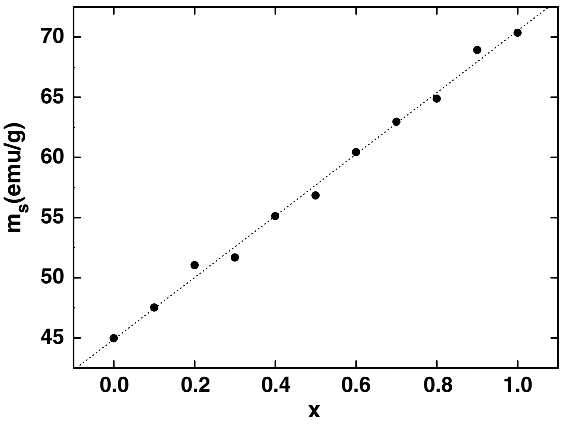

Fig. 4 Dependence of maximum magnetization on Co^{2+} concentration in $Co_xNi_{1-x}Fe_2O_4$

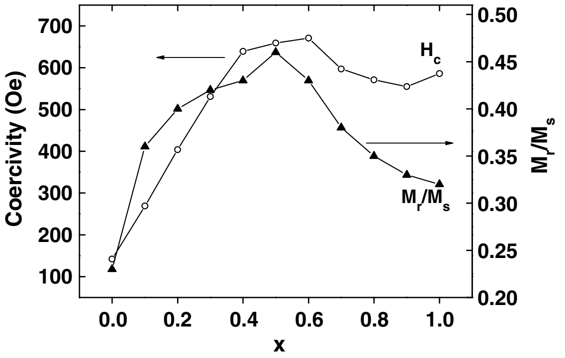

Fig. 5 Dependence of coercivity and residual magnetization ratio on Co^{2+} concentration in $Co_xNi_{1-x}Fe_2O_4$

and then decrease in the range of high concentration, which may originate from the variation of anisotropy induced by Co^{2+} ions in octahedral sites.

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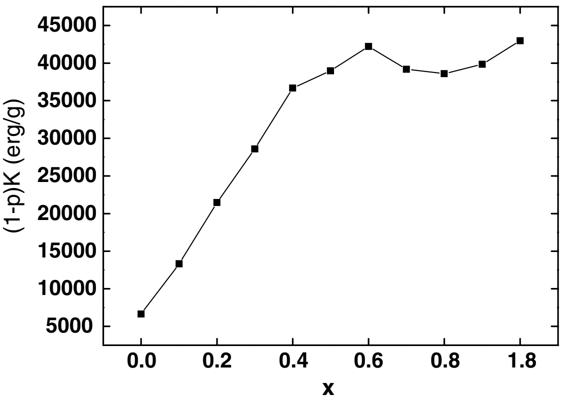

Fig. 6 Dependence of anisotropy constant K on Co^{2+} concentration in $Co_xNi_{1-x}Fe_2O_4$

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