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Study of coercive force for $y\text{ZnFe}_2\text{O}_4-(1-y)\text{CoFe}_2\text{O}_4$ magnetic nanoparticles system

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The coercive forces are taken out from the loops of magnetisation cycle for $y\text{ZnFe}_2\text{O}_4-(1-y)\text{CoFe}_2\text{O}_4$ mixed magnetic nanoparticles system (y is the volume fraction of ZnFe_2O_4 particles in $y\text{ZnFe}_2\text{O}_4-(1-y)\text{CoFe}_2\text{O}_4$ magnetic nanoparticles mixed system). The results show that the coercive force of the system is increasing with the y decreasing and is interpreted by using particles chain model. The number of chains of particles under magnetic field is obtained by comparing the coercive force of the experiment and the theory of chain model. In $y\text{ZnFe}_2\text{O}_4-(1-y)\text{CoFe}_2\text{O}_4$ magnetic nanoparticles mixed system, the coercive force comes from ferrimagnetic CoFe_2O_4 nanoparticles, and paramagnetic ZnFe_2O_4 nanoparticles make the chain length of the mixed magnetic system shorter than single CoFe_2O_4 nanoparticles system.

Keywords: magnetic nanoparticles; coercive force; interaction; chain

1. Introduction

The magnetic behaviour of magnetic orderly particles depends strongly on the particles' size. Small size effect of particles has influence not only on the macro-magnetic behaviour (such as saturation magnetisation), but also on the micro-interaction (reflected in the differences in magnetisation process). Ferrite nanoparticles MFe_2O_4 ($M = \text{Co}, \text{Mn}$ and Zn etc. two divalent metal ion) are relatively stable; they are the most important part of preparing ferrofluids, which can be regarded as extensions or branches of the ultrafine particles of the research field. The in-depth study on magnetic nanoparticles will promote the development of ferrofluids. The ferrite particles whose size is around 10 nm are single domain particles, which can be regarded as a single magnetic moment. Under an external magnetic field, the magnetic moment of magnetic nanoparticles will tend to the external magnetic field direction, and with the strengthening of the external magnetic field, magnetisation gradually tends to saturation. This magnetisation process is closely related to the dipoles' interaction of inter-particles. In disperse systems (such as ferrofluids), the interaction of magnetic nanoparticles that affects magnetisation has been studied in both theory and experiment by many researchers and many models have been put forward, but

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a unified understanding of their mechanism has not yet been achieved [1–6]. There is distribution of particles size in the real ferrofluids, and it is a polydispersed system [7]. The properties of ferrofluids (magnetic property, microstructure, viscosity and so on) are different from those of a monodispersed system, and there are many difficulties in discussing the mechanism on the properties. In recent years, there have been a few theoretical researches into bidispersed systems consisting of large and small size particles without size distribution [7–10], but such a system is hard to achieve in experiment. The magnetic moment \mathbf{m} of single domain particles is proportional to volume V and the magnetic moment \mathbf{m} of spherical particles can be expressed as:

$$m = \frac{\pi d^3 M}{6} \quad (1)$$

where M is the particles' magnetisation and d is the particles' size.

Therefore, the bi-system consisting of both large and small particles can also be regarded as a system consisting of stronger and weaker magnetic particles with different m from different d . Through the way that synthesising the system consisted of two different magnetic particles to study the bidispersed system, in other words, using the magnetic bidispersed system instead of the size bidispersed system, it is easier to discuss the property of nanoparticles system accurately by combining both experiments and theories.

Bulk CoFe_2O_4 is ferromagnetic, while bulk ZnFe_2O_4 is anti-ferromagnetic. Fine particles of anti-ferromagnetic bulk materials may be paramagnetic [11]. A mixture of two different magnetic nanoparticles is a kind of solid dispersed system, which is helpful to study the effect that interaction of particles has upon magnetic. In this article, the coercive force of $y\text{ZnFe}_2\text{O}_4-(1-y)\text{CoFe}_2\text{O}_4$ magnetic nanoparticles system ($y=0, 1, 0.33, 0.5, 0.67, 0.8$) is measured and the role of weak magnetic particles in a system of magnetical bidispersion is studied.

2. Experimental methods

2.1. The preparation of the nanoparticles

With $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, ZnCl_2 , $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, NaOH , HCl as raw materials, nanoparticles were prepared by chemical co-precipitation.

The following procedure was used:

- (a) A proper proportion of NaOH solution was added to mixed solutions of ZnCl_2 and FeCl_3 by molar ratio 1:2 and the solutions were then heated until boiling. The solutions were boiled for 10 min and maintained at room temperature for 2 h. Then by washing, acetone dehydration and drying process, ZnFe_2O_4 powders were produced.
- (b) A proper proportion of NaOH solution was added to mixed solutions of $\text{Co}(\text{NO}_3)_2$ and FeCl_3 by molar ratio 1:2 and the solutions were then heated to boiling. The solutions were boiled for 3 min and maintained at room temperature for 2 h. Then by washing, acetone dehydration and drying process, CoFe_2O_4 powders were produced.
- (c) $0.5\text{ZnFe}_2\text{O}_4-0.5\text{CoFe}_2\text{O}_4$ ($y=0.5$) nanoparticles system was produced by fully mixing ZnFe_2O_4 powders and CoFe_2O_4 powders at volume ratio 1:1.

0.8ZnFe₂O₄-0.2CoFe₂O₄ ($y=0.8$) nanoparticles system was produced by fully mixing ZnFe₂O₄ powders and CoFe₂O₄ powders at volume ratio 4:1. Similarly, we can obtain 0.33ZnFe₂O₄-0.67CoFe₂O₄ ($y=0.33$) nanoparticles system and 0.67ZnFe₂O₄-0.33CoFe₂O₄ ($y=0.67$) nanoparticles system.

- (d) X-ray diffraction (XRD, D/Max-RC) was used to analyse structures of the above samples, energy dispersive spectrometer of X-ray (EDX, Norton 8000) was used to analyse the atom ratio between M (Co, Zn) and Fe, and transmission electron microscopy (TEM,H-600) was used to observe the particle morphology and analyse/examine the particle size.

2.2. The measurement of the magnetic properties

HH-15 vibrating sample magnetometer (VSM) was used to measure the specific magnetisation σ curves of the six samples at room temperature and the largest magnetic field was 0.95 T. The specific saturation magnetisation of the CoFe₂O₄ nanoparticles is estimated from the relation of $\sigma_s \sim 1/H$ in high field [12]. The magnetisation M is achieved by

$$M = \sigma \cdot \rho \quad (2)$$

where ρ is the density of the nanoparticles. To the y ZnFe₂O₄-(1- y)CoFe₂O₄ particles system, the density is

$$\rho = y \times \rho_1 + (1 - y) \times \rho_2 \quad (3)$$

where ρ_1 is the density of ZnFe₂O₄, ρ_2 is the density of CoFe₂O₄, $\rho_1 = 5.32 \text{ g cm}^{-3}$ and $\rho_2 = 5.23 \text{ g cm}^{-3}$, respectively.

3. Experimental results and analysis

3.1. The XRD and EDX measurement of the particles

The XRD spectra of ZnFe₂O₄ and CoFe₂O₄ particle samples are given in Figure 1. From Figure 1(a) and (b), it can be seen that the diffraction peak is broad while the particle size is very fine. By analysing XRD spectra of the two samples, it can be determined that the above two samples are ZnFe₂O₄ and CoFe₂O₄ particles, respectively.

The crystallite size, D_{311} , was obtained, determined by the Scherr formula using the half-maximum width of the (311) X-ray diffraction line (Figure 1(a) and (b)): $D_{\text{XRDZnFe}_2\text{O}_4} = 4.05 \text{ nm}$, $D_{\text{XRDCoFe}_2\text{O}_4} = 10.06 \text{ nm}$.

The atom ratio of about 1:2 between $M(\text{Co, Zn})$ and Fe by EDX for both CoFe₂O₄ and ZnFe₂O₄ particles can be obtained. The quantitative results for the samples are listed in Table 1.

3.2. The morphology and size of the particles from TEM

TEM observation indicated that the morphologies of both the CoFe₂O₄ and ZnFe₂O₄ particles are basically spherical as shown in Figure 2.

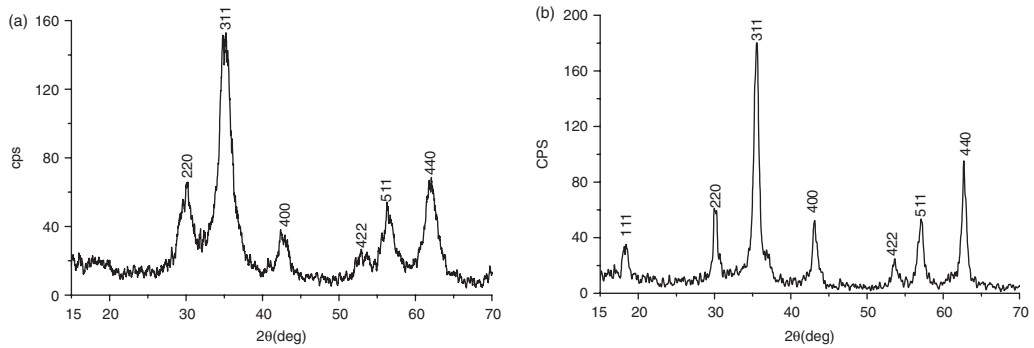


Figure 1. (a) XRD spectra of ZnFe_2O_4 particles and (b) XRD spectra of CoFe_2O_4 particles.

Table 1. The quantitative results of EDX.

Element	Atom%	Atom% error	Element	Atom%	Atom% error
Fe	67.20	+/- 1.19	Fe	63.10	+/- 1.14
Co	32.80	+/- 1.30	Zn	36.90	+/- 2.03
Total	100		Total	100	

Using statistical analysis from TEM photographs, the size distribution of CoFe_2O_4 can be illustrated as particles shown in Figure 3(a). The median value of the particles' diameter is 12.76 nm and the distribution function is as follows:

$$f(x)_{\text{CoFe}_2\text{O}_4} = \frac{1.1366}{x} \exp[-4.06(\ln x - 2.55)^2]. \quad (4)$$

The size distribution of ZnFe_2O_4 particles can be also illustrated as shown in Figure 3(b). The median value of the particles' diameter is 4.22 nm and the distribution function is as follows:

$$f(x)_{\text{ZnFe}_2\text{O}_4} = \frac{1.5341}{x} \exp[-7.39(\ln x - 1.44)^2]. \quad (5)$$

The sizes from the TEM photographs measurements are larger than the X-ray measurements.

3.3. Measurement of magnetisation curves

Measurement results of the curves of magnetisation cycle for the six samples are shown in Figure 4. The coercive force H_c is obtained from the magnetisation loops of the particles at room temperature, as shown in Table 2. Obviously, H_c decreases as y increases.

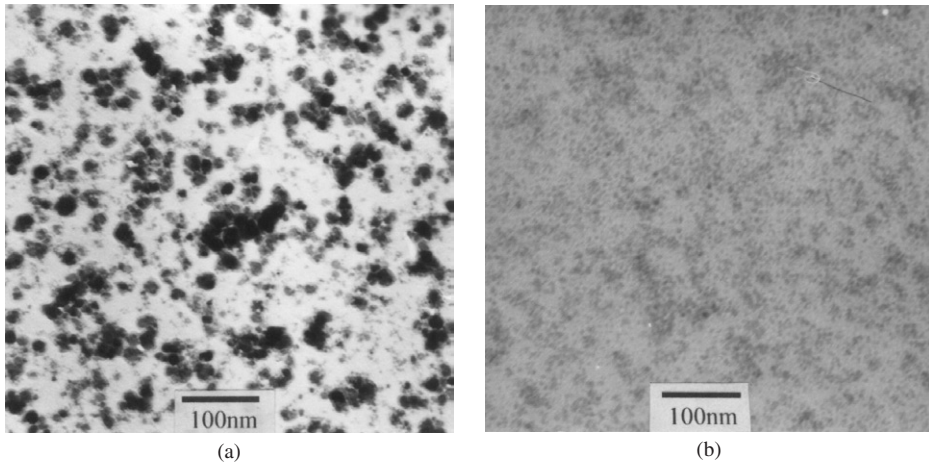


Figure 2. TEM photographs of (a) CoFe₂O₄ particle and (b) ZnFe₂O₄ particle.

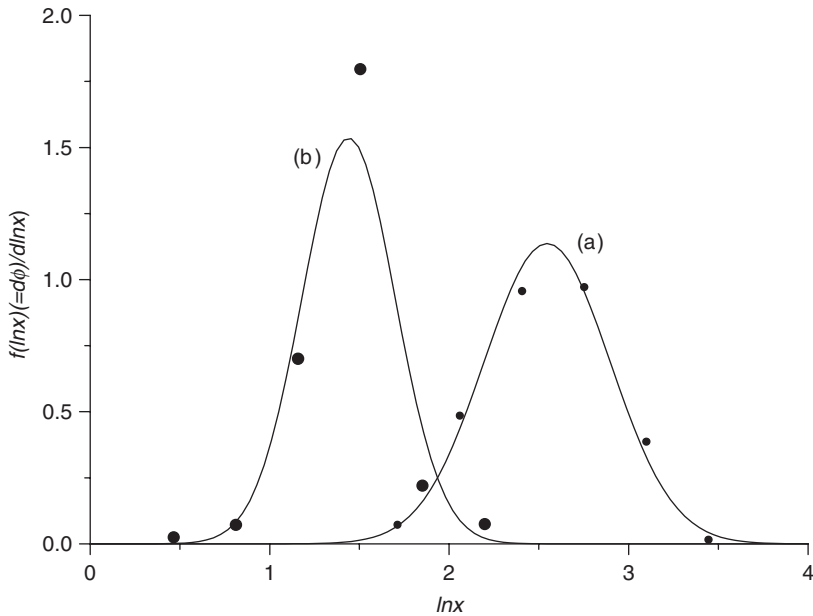


Figure 3. The size distribution for the (a) CoFe₂O₄ particles and (b) ZnFe₂O₄ particles. ● experiment values of ZnFe₂O₄ particles; ● experiment values of CoFe₂O₄ particles; (—) curves of distribution.

The saturation magnetisation M_s of CoFe₂O₄ particles obtained by $M \sim 1/H$ relations at the high fields is $10^3 \text{ A} \cdot \text{M}^2$. ZnFe₂O₄ particles are paramagnetic and M value is $10^3 \text{ A} \cdot \text{M}^2$ at 0.95 T.

The critical diameter of the single-domain magnetic for cubic crystal system [13]:

$$D_c = \frac{9\sqrt{AK}}{\pi M_s^2}. \tag{6}$$

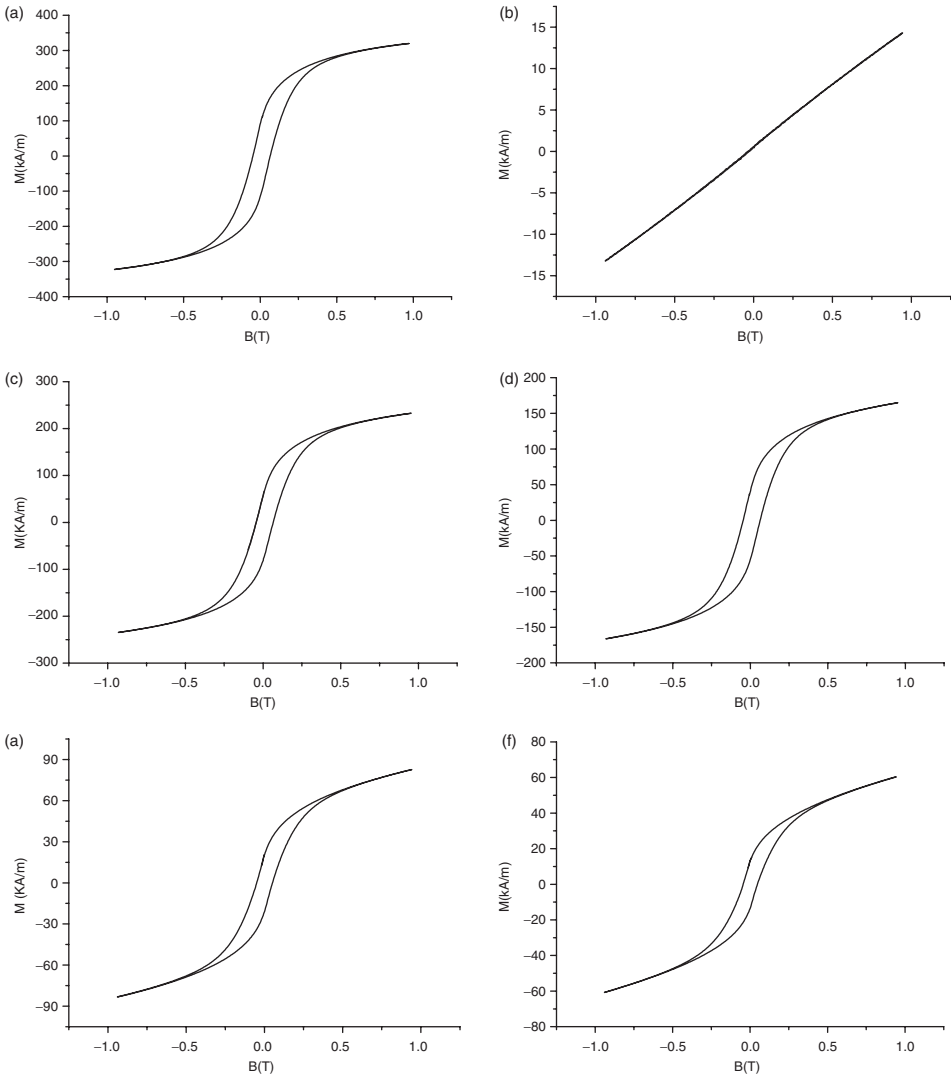


Figure 4. The magnetisation loops of $y\text{ZnFe}_2\text{O}_4-(1-y)\text{CoFe}_2\text{O}_4$ mixed magnetic nanoparticles system, (a) CoFe_2O_4 particles, (b) ZnFe_2O_4 particles, (c) $0.33\text{ZnFe}_2\text{O}_4-0.67\text{CoFe}_2\text{O}_4$ particles, (d) $0.5\text{ZnFe}_2\text{O}_4-0.5\text{CoFe}_2\text{O}_4$ particles, (e) $0.67\text{ZnFe}_2\text{O}_4-0.33\text{CoFe}_2\text{O}_4$ particles and (f) $0.8\text{ZnFe}_2\text{O}_4-0.2\text{CoFe}_2\text{O}_4$ particles.

Table 2. The coercive force H_c measured by VSM for $y\text{ZnFe}_2\text{O}_4-(1-y)\text{CoFe}_2\text{O}_4$ nanoparticles system mixed.

y	0	0.33	0.50	0.67	0.80	1
H_c (kA m ⁻¹)	44.47	43.70	43.65	39.37	36.37	0

where K is the anisotropy constant, M_s is the saturation magnetisation, A is the exchange constant and can be estimated from $A \approx k_B T_c / a$, where k_B is the Boltzmann constant, T_c is the Curie temperature, a is the crystal lattice constant.

When the values of bulk CoFe_2O_4 are substituted into Equation (6) ($K = 1.8 \times 10^6 \text{ erg cm}^{-3}$, $M_s = 400 \text{ Gs}$, $T_c = 793 \text{ K}$, $a = 0.838 \text{ nm}$), we can obtain $D_c = 274.513 \text{ nm}$.

At room temperature, the superparamagnetic critical size of CoFe_2O_4 particles is about 14 nm [14]. The range of the size is $4.6\text{--}36.8 \text{ nm}$ for CoFe_2O_4 particles diameter measured. Therefore, the CoFe_2O_4 particles consist of ferromagnetic and superparamagnetic particles. The ratio of superparamagnetic particles in CoFe_2O_4 particles number can be obtained as

$$\int_0^{14} f(x)_{\text{CoFe}_2\text{O}_4} dx = \int_0^{14} \frac{1.1366}{x} \exp[-4.06(\ln x - 2.55)^2] dx = 0.6.$$

This shows that the CoFe_2O_4 particles prepared are single domain ones. The superparamagnetic particles number is 60% and the ferromagnetic particles number is 40% at room temperature.

4. Discussion

4.1. Interaction energy the particles

According to the diameter distribution function of CoFe_2O_4 nanoparticles (4), the average magnetic moment is [15]

$$\begin{aligned} \langle m \rangle &= \frac{\pi}{6} M_s \int_0^\infty x^3 f(x) dx \\ &= 6.89 \times 10^{-19} (\text{A m}^2). \end{aligned}$$

ZnFe_2O_4 particles are paramagnetic and the greatest average magnetic moment in the magnetic field is

$$\langle m \rangle = \frac{\pi}{6} M_{0.95\text{T}} \int_0^\infty x^3 f(x) dx$$

where $M_{0.95\text{T}}$ is the magnetisation at 0.95 T . Substituting $M_{0.95\text{T}}$ and ZnFe_2O_4 diameter distribution function (5), thus

$$\langle m \rangle = 7.61 \times 10^{-22} (\text{A m}^2),$$

obviously, the average magnetic moment between CoFe_2O_4 particles is far bigger than the biggest magnetic moment of ZnFe_2O_4 particles.

The interaction of single-domain magnetic particles can be regarded as the interaction of magnetic dipole. Interaction energy between i and j magnetic dipole is expressed [16] by:

$$w = \left(\mu_0 m_i m_j / 4\pi r_{ij}^3 \right) [\cos(\theta_i - \theta_j) - 3 \cos \theta_i \cos \theta_j] \tag{7}$$

where μ_0 is the vacuum permeability, r_{ij} is the particles' distance, θ_i, θ_j are the angle between magnetic moment and central connections line. When $\theta_i = \theta_j = 0$, the interaction

energy of two CoFe_2O_4 dipole particles (diameter 12.76 nm) linked by head-to-tail ($r_{ij} = a$), can be calculated as about 2.63×10^{-20} J. When the magnetic moment of ZnFe_2O_4 is the largest of all, the interaction energy of two ZnFe_2O_4 dipole particles (diameter 4.22 nm) is about 1.14×10^{-24} J. While one CoFe_2O_4 particle with $m = 6.89 \times 10^{-19}$ (A m^2) and one ZnFe_2O_4 particle with $m = 7.61 \times 10^{-22}$ (A m^2) are linked by head-and-tail ($r_{ij} = (\text{diameter of } \text{CoFe}_2\text{O}_4 \text{ particles} + \text{diameter of } \text{ZnFe}_2\text{O}_4 \text{ particles})/2$), the interaction energy is about 1.04×10^{-22} J. At room temperature, the thermal energy is about $k_B T = 4.14 \times 10^{-21}$ J. Therefore, it can be known that only the dipole interaction of CoFe_2O_4 particles would be larger than the thermal energy, so that the chain of CoFe_2O_4 particles will form in the magnetisation process [17]. So, a system mixed with both CoFe_2O_4 and ZnFe_2O_4 particles can be called a system of magnetical bidispersion.

4.2. The coercive force

If there is no interaction between particles, the magnetisation M of the mixture containing N types of particles can be expressed [18] by

$$M(B) = \frac{\sum_{n=1}^N M_n(B) \Phi_{Vn}}{\sum_{n=1}^N \Phi_{Vn}} \quad (8)$$

where M_n is the magnetisation, and Φ_{Vn} is the volume fraction of the n particle. Here, Φ_{Vn} has the same meaning as y and $(1-y)$ for $y\text{ZnFe}_2\text{O}_4-(1-y)\text{CoFe}_2\text{O}_4$ nanoparticles system.

Thus, the remanence of $y\text{ZnFe}_2\text{O}_4-(1-y)\text{CoFe}_2\text{O}_4$ nanoparticles system mixed is

$$M'_r(y) = (1-y)M_{r,\text{Co}} \quad (9)$$

where $M_{r,\text{Co}}$ is the remanence of the CoFe_2O_4 nanoparticles (i.e. $y=0$ in $y\text{ZnFe}_2\text{O}_4-(1-y)\text{CoFe}_2\text{O}_4$ system). So, the remanence for M'_r of $y\text{ZnFe}_2\text{O}_4-(1-y)\text{CoFe}_2\text{O}_4$ nanoparticles system mixed can be calculated by Equation (9), as shown in Table 3. For comparison, the experiment values are also shown in Table 3.

Obviously, with y increasing, and the CoFe_2O_4 particle volume fraction decreasing, the experiment value M_r is much less than the calculation value M'_r of the remanence. But, it should be noticed that the coercive force decreases as y increases (Table 2). So, it can be judged that there is interaction in $y\text{ZnFe}_2\text{O}_4-(1-y)\text{CoFe}_2\text{O}_4$ nanoparticles mixed system. The coercive force can be related to the aggregate of the CoFe_2O_4 nanoparticles, and ZnFe_2O_4 nanoparticles can prevent CoFe_2O_4 nanoparticles from aggregating in the nanoparticles mixed system [19]. Therefore, the coercive force can be discussed from the chain aggregate model.

Table 3. The calculation and experiment value of the remanence for $y\text{ZnFe}_2\text{O}_4-(1-y)\text{CoFe}_2\text{O}_4$ nanoparticles system.

Y	0.00	0.33	0.50	0.67	0.80	1.00
M'_r (kA m^{-1})	256	68.74	51.30	33.06	20.52	0
M_r (kA/m)	256	69.20	47.41	20.73	13.34	0
$ M_r - M'_r \times 100/M'_r$ (%)	0	0.67	7.58	37.30	35.01	0

If there is no external magnetic field, the intrinsic magnetic moment of ferromagnetism or ferrimagnetism nanoparticles will be random in orientation. Under the magnetic field, the magnetic moment of the nanoparticles will have a tendency to link along the direction of the magnetic field. Because the interaction energy of CoFe_2O_4 particles linked by head-and-tail is larger than the thermal energy, CoFe_2O_4 particles form a chain-like aggregate structure. When the magnetic field increases towards the negative direction, the magnetic moment along the positive direction will reverse first until the magnetic moments are opposite to the negative direction; then the corresponding magnetic field is the coercive force of the system. The magnetic reversal of the chain of spheres may have two mechanisms. One is the magnetic moment parallel rotation mechanism; the other is the symmetric fanning mechanism [20], as shown in Figure 5. In the two models of Figure 5, the spheres are all isolated; no consideration of their magnetic anisotropy is taken and, if it is assumed the particles are idealistic contacts, there only exists the magnetic dipole interaction of particles.

In order to calculate the coercive force of spheres' chain under the magnetic field, first of all the total energy of the chain should be taken into account. Disregarding magnetic anisotropy energy, the total energy of the chain is only composed of interaction energy of both the interdipoles and between the dipoles and magnetic field. The total energy is the function of angle between magnetic moment and external magnetic field. Coercive force can be obtained from the energy relationship [20]. In order to simplify the discussion, assume the magnetic moment as the average magnetic moment. Let the number of particles in a chain be n . The total energy can be expressed in parallel rotating mechanism as:

$$w_n = (\mu_0 m^2 / 4\pi a^3) n K_n (1 - 3 \cos^2 \theta) + n \mu_0 m H \cos \theta \tag{10}$$

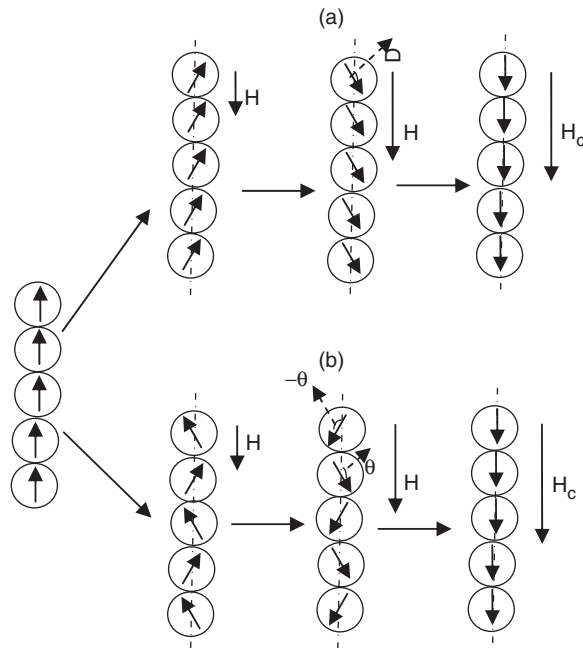


Figure 5. Rotating magnetic moment parallel mechanism inversion (a) and symmetric magnetic moment of the fan inversion mechanism (b).

where

$$K_n = \frac{\sum_{j=1}^n (n-j)}{nj^3}.$$

In the magnetisation process, the magnetic moment will rotate as the magnetic field increases. The conditions of the balance are

$$\frac{\partial w_n}{\partial \theta} = 0.$$

From Equation (10) we can obtain

$$\frac{\partial w_n}{\partial \theta} = (\mu_0 m^2 / 4\pi a^3) n K_n (6 \cos \theta \sin \theta) - n \mu_0 m H \sin \theta = 0.$$

Thus,

$$H = (m/4\pi a^3) 6 K_n \cos \theta. \quad (11)$$

When the magnetic moment of the chain of spheres is in complete reversal, $\theta = \pi$, the coercive force can be expressed

$$H_{c,n} = (m/4\pi a^3) 6 K_n. \quad (12)$$

In the symmetric fanning mechanism, the total energy can be expressed as:

$$w_n = (\mu_0 m^2 / 4\pi a^3) n L_n (\cos 2\theta - 3 \cos^2 \theta) + (\mu_0 m^2 / 4\pi a^3) n M_n (1 - 3 \cos^2 \theta) + n \mu_0 m H \cos \theta \quad (13)$$

where

$$L_n = \sum_{j=1}^{\frac{1}{2}(n-1)j \leq \frac{1}{2}(n+1)} [n - (2j - 1)] / n(2j - 1)^3$$

$$M_n = \sum_{j=1}^{\frac{1}{2}(n-2)j \leq \frac{1}{2}n} (n - 2j) / n(2j)^3 \quad L_n + M_n = K_n.$$

Using the same method with the parallel rotating mechanism, we can obtain the coercive force of symmetric fanning reversal mechanism as

$$H_{c,n} = (m/4\pi a^3) (6K_n - 4L_n). \quad (14)$$

For single CoFe_2O_4 particles, according to Equations (12) and (14), the relationship between particles number in a chain n and coercivity H_c can be calculated for two mechanisms respectively. The partial results calculated are listed in Table 4.

From Table 4, it can be seen that, as the particles number in the chain increases, the coercive force becomes higher and higher. In the magnetic moment parallel reversal mechanism and the symmetry fanning reversal mechanism, the coercive force of the former is larger than the latter. The coercive force of CoFe_2O_4 can be obtained as $H_C = 44.47 \text{ kA m}^{-1}$ from the experiment. Comparing the theory result of the above two

Table 4. The relationship between the particles number in a chain n and coercive force H_c .

n	H_c (kA m ⁻¹)	
	A	B
1	0	0
2	45.51	15.17
7	88.94	35.51
8	91.40	36.70
9	93.33	37.64
10	94.89	38.40
39	105.60	43.69
64	107.08	44.42
100	107.91	44.84
1000	109.26	45.51
10,000	109.39	45.58
100,000	109.40	45.58

A – parallel reversal mechanism of magnetic moment; B – symmetry fanning reversal mechanism of magnetic moment.

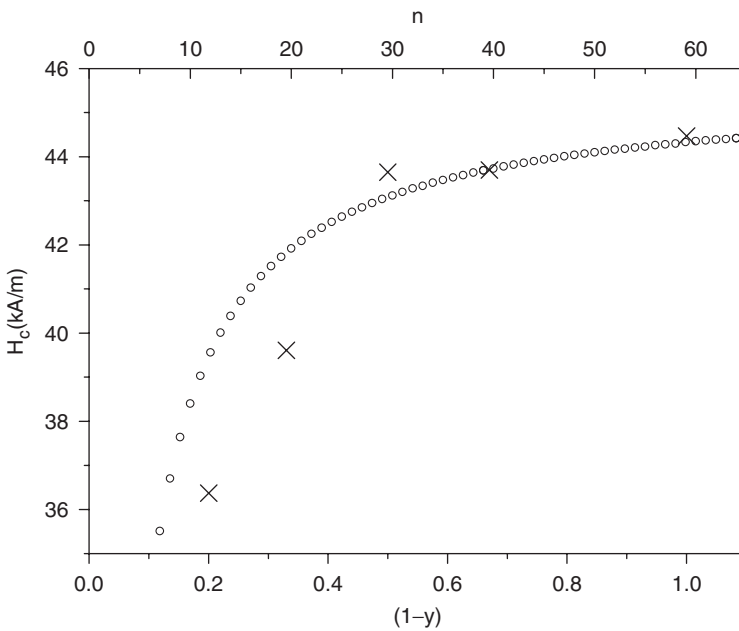


Figure 6. The relations of the coercive H_c versus the CoFe_2O_4 particle volume fraction $(1 - y)$, and versus CoFe_2O_4 particles number in a chain n for the symmetry fanning reversal model of chain. \times – H_c versus $(1 - y)$, \circ – H_c versus n .

models, it can be known that the experimental result is consistent with the symmetry fanning reversal mechanism and that the corresponding number of particles is about 64.

In $y\text{ZnFe}_2\text{O}_4-(1-y)\text{CoFe}_2\text{O}_4$ magnetic nanoparticles mixed system, ZnFe_2O_4 is weak magnetic particles and its coercive force is 0. Compared with the magnetic of

CoFe₂O₄, the magnetic of ZnFe₂O₄ can be neglected. For the bidispersed system constituted with strong and weak magnetic nanoparticles, strong magnetic CoFe₂O₄ particles may form a chain of spheres aggregating which present in a 'sea' of weak magnetic ZnFe₂O₄ particles [21]. Therefore, the coercive force of the $y\text{ZnFe}_2\text{O}_4-(1-y)\text{CoFe}_2\text{O}_4$ magnetic nanoparticles system is still produced by chains of CoFe₂O₄. According to the magnetic moment symmetry fanning reversal mechanism and the experimental results in Table 2, we can see that when the coercive force of 0.33ZnFe₂O₄-0.67CoFe₂O₄ in experiment is 43.70 kA m⁻¹, the corresponding number of particles in the chain is 39; that when the coercive force of 0.5ZnFe₂O₄-0.5CoFe₂O₄ in experiment is 43.65 kA m⁻¹, the corresponding number of particles in the chain is 29; that when the coercive force of 0.67ZnFe₂O₄-0.33CoFe₂O₄ in experiment is 39.37 kA m⁻¹, the corresponding number of particles in chain is 20, and that when the coercive force of 0.8ZnFe₂O₄-0.2CoFe₂O₄ in experiment is 36.37 kA m⁻¹, the corresponding number of particles in chain is only 8.

In Figure 6, the relations of coercive force H_c versus n and versus $(1-y)$ are shown. Clearly, both relations are similar and n has a linear relation with $(1-y)$. This shows that the length of the CoFe₂O₄ particles chains becomes shorter because of ZnFe₂O₄ particles mixing in the $y\text{ZnFe}_2\text{O}_4-(1-y)\text{CoFe}_2\text{O}_4$ particles system.

5. Conclusions

The size of CoFe₂O₄ nanoparticles prepared is about 12.76 nm, while the particles size of prepared ZnFe₂O₄ is about 4.22 nm and the particles size of ZnFe₂O₄ is only one-third of CoFe₂O₄.

$y\text{ZnFe}_2\text{O}_4-(1-y)\text{CoFe}_2\text{O}_4$ nanoparticles mixed system is a typical system of magnetism bidispersed. In this system, the coercive force merely comes from strong magnetic CoFe₂O₄ particles. From the characteristics of both the coercive force H_c decreasing and the remanence M_r deviating from the calculation value with the particle volume fraction of ZnFe₂O₄ particles y increasing as well as the average interaction energy of between the CoFe₂O₄ particles stronger than $k_B T$, it can be judged that the coercive force is in relation to CoFe₂O₄ nanoparticles aggregating for the $y\text{ZnFe}_2\text{O}_4-(1-y)\text{CoFe}_2\text{O}_4$ ($0 < y < 1$) nanoparticles system. Under the magnetic field, the strong magnetic particles would form a chain-like structure. The number of particles in a chain can be obtained from the coercive force. Comparing the CoFe₂O₄ nanoparticles with $y\text{ZnFe}_2\text{O}_4-(1-y)\text{CoFe}_2\text{O}_4$ nanoparticles mixed system, we can know that weak magnetic particles make the chain length of particles shorter. This accords with the light transmission change law of ferrofluids made up of similar systems, which will be reported in another paper. Therefore, we can infer that speciality of ferrofluids of magnetism bidispersion may be different from one of magnetism monodispersion. This will be further researched.

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References

- [1] A.O. Ivanov and O.B. Kuznetsova, *Magnetic properties of dense ferrofluids: an interparticle correlations*, Phys. Rev. E 64 (2001), pp. 041405-1–041405-12.
- [2] A.F. Pshenichnikov, *Equilibrium magnetisation of concentrated ferrocolloids*, J. Magn. Magn. Mater. 145 (1995), pp. 319–326.
- [3] A.F. Pshenichnikov and V.V. Mekhonoshin, *Equilibrium magnetisation and microstructure of the system of superparamagnetic interacting particles: numerical simulation*, J. Magn. Magn. Mater. 213 (2000), pp. 357–369.
- [4] G.A. Ewijk, G.J. Vroege, and A.P. Philipse, *Susceptibility measurements on a fractionated aggregate-free ferrofluid*, J. Phys.: Condens. Matter 14 (2002), p. 4915.
- [5] T. Kristof and I. Szalai, Phys. Rev. E 68 (2003), p. 041109.
- [6] L. Qiang, L. Jian, W. Yue, and B. Lang, *Experimental study on magnetisation behaviour of $0.8\text{ZnFe}_2\text{O}_4-0.2\text{MnFe}_2\text{O}_4$ magnetic nanoparticles*, J. Southwest China Normal Univ. (in Chinese) 29(9) (2007), pp. 47–51.
- [7] J.P. Huang, Z.W. Wang, and C. Holm, *Structure and magnetic properties of mono- and bi-dispersed ferrofluids as revealed by simulations*, J. Magn. Magn. Mater. 289 (2005), pp. 234–237.
- [8] G.M. Rany and S.H.L. Klapp, *Density functional study of the phase behavior of asymmetric binary dipolar mixtures*, Phys. Rev. E 69 (2004), pp. 041201-1–041201-11.
- [9] G.M. Rany and S.H.L. Klapp, *Phase behavior of bidisperse ferrocolloids*, Phys. Rev. E 70 (2004), pp. 061407-1–061407-9.
- [10] G.M. Rany and S.H.L. Klapp, *Density – functional study of model bidisperse ferrocolloids in an external magnetic field*, J. Chem. Phys. 122 (2005), pp. 224902-1–224902-6.
- [11] W.J. Schuele and V.D. Deetscreek, *Appearance of a weak ferromagnetism in fine particles of antiferromagnetic materials*, J. Appl. Phys. 33 (1962), pp. 1136–1137.
- [12] M. Holmes, K. O’Grady, R.W. Chantrell, and A. Bradbury, *The effect of particles interactions on the initial susceptibility of a ferrofluid*, IEEE Trans. Magn. 24 (1988), pp. 1659–1661.
- [13] W. Gong, H. Li, Z.G. Zhao, and J.C. Chen, *Ultrafine particles of Fe, Co and Ni ferromagnetic metals*, J. Appl. Phys. 84 (1991), pp. 5119–5121.
- [14] S. Toshihiko, I. Tetsuo, S. Masahiro, and I. Nobuo, *Magnetic properties of ultrafine ferrite particles*, J. Magn. Magn. Mater. 65 (1987), pp. 252–256.
- [15] H. Yan, L. Jian, Y. Guofeng, and B. Lang, *The treatment of the calculation of the ferrofluids’ intensity of magnetisation*, J. Southwest China Normal Univ. 30 (2005), pp. 281–283 (in Chinese).
- [16] B. Huke and M. Lücke, *Magnetic properties of colloidal suspension of interaction magnetic particles*, Rep. Prog. Phys. 67 (2004), pp. 1731–1768.
- [17] C. Holm and J.-J. Weis, *The structure of ferrofluids: a status report*, Curr. Opin. Coll. Inter. Sci. 10 (2005), pp. 133–140.
- [18] C.P. Bean, *Hysteresis loops of mixture of ferromagnetic micropowders*, J. Appl. Phys. 26 (1955), pp. 1381–1383.
- [19] R.E. Rosenswag, *Theory for stabilization of magnetic colloid in liquid metal*, J. Magn. Magn. Mater. 201 (1999), pp. 1–6.
- [20] I.S. Jacobs and C.P. Bean, *An approach to elongated fine-particle magnets*, Phys. Rev. 100 (1955), pp. 1060–1067.
- [21] Z.A. Yu and I.L. Yu, *Structural transformations in polydisperse ferrofluids*, Coll. J. 65 (2003), pp. 778–787.