Cation Distribution in $ZnFe_2O_4$ Precipitated from the Aqueous Solution

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On the particles of $ZnFe_2O_4$ chemically precipitated from the aqueous solution, the relation between the preparation method and the cation distribution is investigated. The results are as follows :

(1) The fine particles of $ZnFe_2O_4$ rapidly co-precipitated from Fe^{3+}-Zn^{2+} mixed aqueous solution exhibited a superparamagnetic behavior. The superparamagnetism disappeared gradually by annealing above 300°C. From the result it is suggested that A-sites may be partially occupied by ferric ions in process of the formation of the crystal, so that the magnetic clusters with such cation distribution as $Zn_{1-x}^{2+}Fe_x^{3+}[Zn_x^{2+}Fe_{2-x}^{3+}]$ ([ ] ; B-site), which lead to the superparamagnetism, may be formed in the particle.

(2) The particles of $ZnFe_2O_4$ gradually precipitated from Fe^{2+}-Zn^{2+} mixed aqueous solution exhibited a paramagnetic behavior at room temperature, so that the cation distribution of the particles of $ZnFe_2O_4$ is equal to that of normal spinel ferrite.

It was, therefore, found that the cation distribution in $ZnFe_2O_4$, which was chemically precipitated from the aqueous solution, was greatly influenced by the rate of the crystal formation.

I. INTRODUCTION

In normal $ZnFe_2O_4$, the non-magnetic zinc ions preferentially occupy the tetrahedral A-sites and all the ferric ions are in octahedral B-sites. Therefore, normal $ZnFe_2O_4$ is paramagnetic at room temperature in the absence of the strong A-B interaction and becomes antiferromagnetic below 9°K due to the weak B-B interaction. However, if a part of ferric ions occupy the A-sites, there would occur the stronger interactions between the ferric ions in A and B-sites. In fact it was reported that, $ZnFe_2O_4$ prepared by the ordinary ceramic method exhibited a superparamagnetic behavior when quenched from the temperature higher than 1000°C and the thermal anomaly in the vicinity of 9°K was not observed in the quenched $ZnFe_2O_4$. For these phenomena the authors assumed the persistence of short range ordering above the Néel temperature. Lotgering[3] pointed out that $ZnFe_2O_4$ had the cation distribution of $Zn_{1-x}^{2+}Fe_x^{3+}[Zn_x^{2+}Fe_{2-x}^{3+}]O_4$ ([ ] ; B-site, $x <$ 0.05) from susceptibility measurements of a rapidly cooled and annealed sample of $ZnFe_2O_4$. It was also found that the high pressure squeezed $ZnFe_2O_4$ exhibited the superparamagnetic behavior due to the formation of magnetic clusters, that is, the stacking fault in which some ferric ions are slipped into tetrahedral sites through the crystal slip[4]. Besides, the analogous behaviors have been observed
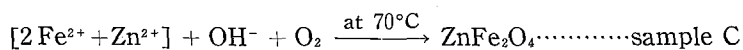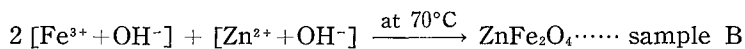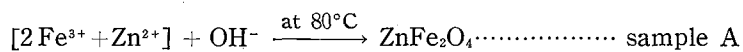
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in solid solutions of zinc ferrite with various inverse spinel ferrites[1,5~7].

In the present work we investigated the relation between the preparation method and the magnetic property of $ZnFe_2O_4$ chemically precipitated from the aqueous solution. Consequently it was found that $ZnFe_2O_4$ rapidly precipitated for a few minutes exhibited a superparamagnetic behavior at room temperature, and while the magnetic property of $ZnFe_2O_4$ gradually precipitated for about seven hours was similar to that of normal $ZnFe_2O_4$. From these phenomena it is concluded that the cation distribution is closely connected with the rate of the crystal formation from the aqueous solution.

The details of the preparation method and the various properties of the samples are given in section **II.** Magnetic properties and annealing effects are described in section **III.** Furthermore in section **IV** the relation between the preparation method and the magnetic property is discussed.

II. EXPERIMENTAL

The samples were prepared as follows :

$$[2\,Fe^{3+}+Zn^{2+}] + OH^- \xrightarrow{\text{at }80°C} ZnFe_2O_4 \cdots\cdots\cdots\cdots\cdots\text{ sample A}$$

$$2\,[Fe^{3+}+OH^-] + [Zn^{2+}+OH^-] \xrightarrow{\text{at }70°C} ZnFe_2O_4 \cdots\cdots\text{ sample B}$$

$$[2\,Fe^{2+}+Zn^{2+}] + OH^- + O_2 \xrightarrow{\text{at }70°C} ZnFe_2O_4 \cdots\cdots\cdots\cdots\text{sample C}$$

Sample A was precipitated by adding $Fe(NO_3)_3$–$Zn(NO_3)_2$ mixed aqueous solution to an excess NaOH aqueous solution at 80°C. Sample B was prepared by heating at 70°C after mixing two kinds of solution containing each precipitate which was obtained by adding an excess NaOH solution respectively to $Fe(NO_3)_3$ solution and to $Zn(NO_3)_2$ solution at room temperature. Sample C was obtained by adding solid NaOH to $FeSO_4$–$ZnSO_4$ mixed aqueous solution at 70°C and simultaneously by passing air bubbles through the solution. Each solution has a little excess of Zn over stoichiometric atomic ratio (Zn/Fe=1/2). The precipitates thus obtained were washed with distilled water and dried at 70°C in air. Normal $ZnFe_2O_4$, namely sample D, was prepared by the ordinary ceramic method. Powders of ZnO and Fe_2O_3 were mixed in the required ratio and then fired at 1000°C for 30 hours. After pulverizing and remixing of the products, they were sintered at 1000°C for 30 hours in air and followed by slow cooling. Sample E was obtained by quenching normal $ZnFe_2O_4$ from 1100°C in air.

Sample A and B were both dark brown fine particles and the particle size was found to be 60-80 Å in diameter by means of line broadening of X-ray diffraction peaks, BET method and electron microscopic observation. Figure 1 shows a microphotograph of sample A. They were clarified to be pure $ZnFe_2O_4$ from X-ray diffraction, infrared absorption and chemical analysis. It was also found that they did not contain an amorphous ferric oxide from the analysis of the magnetic property and of the recovery by annealing. The precipitates of sample A were formed immediately after adding the mixed solution to the alkaline solution at 80°C and sample B after heating at 70°C. The magnetic property and the particle size of $ZnFe_2O_4$ thus obtained did not change at all even by aging
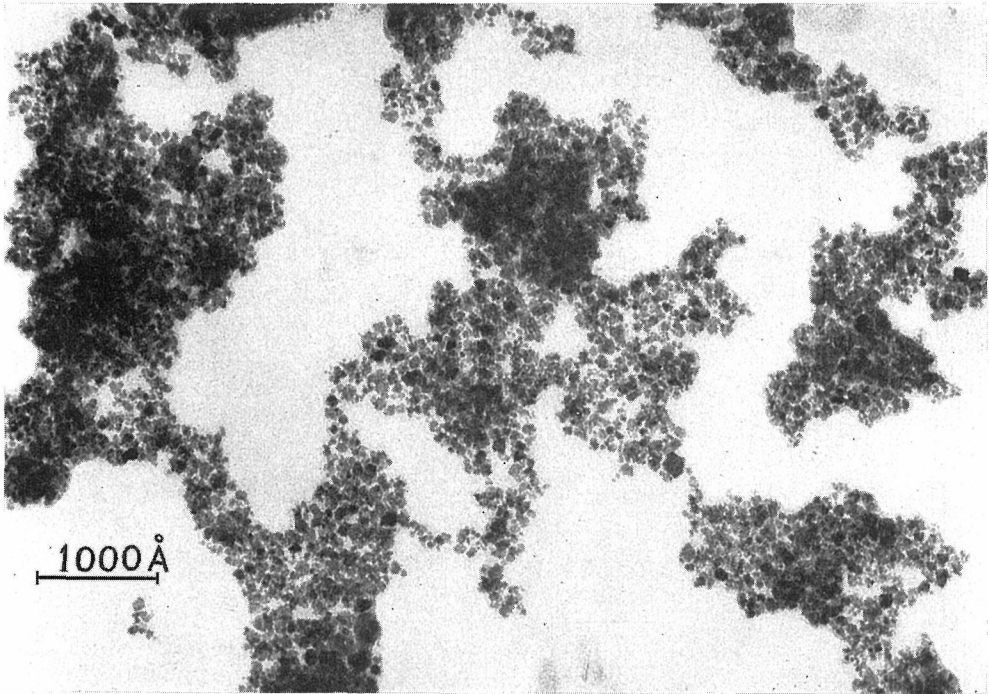
Fig. 1. Electron microphotograph of the particles of sample A obtained as the precipitates from $Fe(NO_3)_3$–$Zn(NO_3)_2$ mixed aqueons solution.
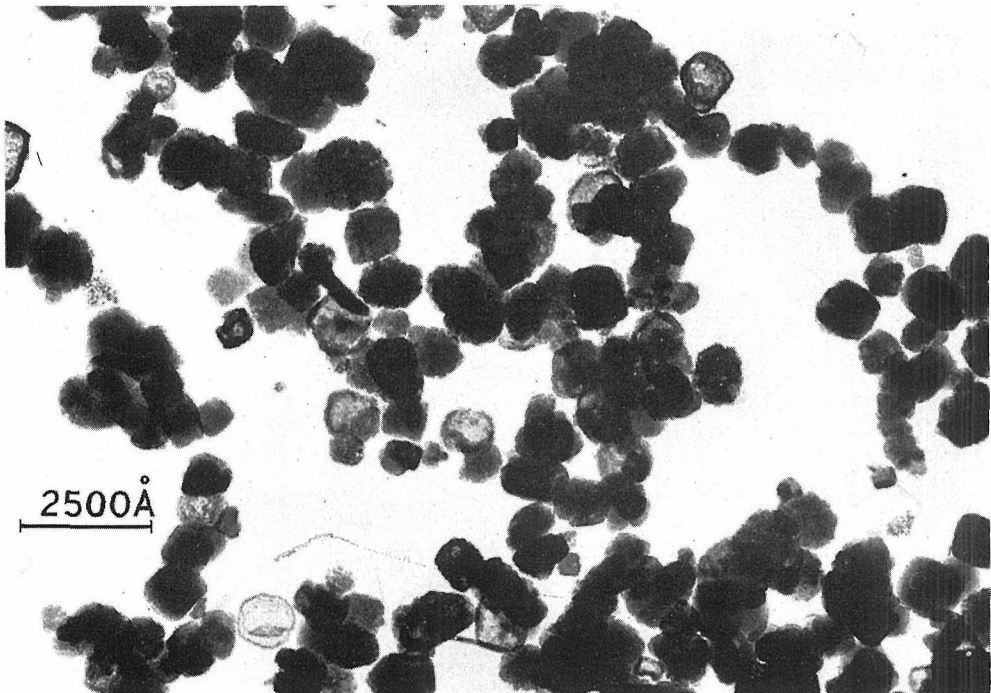

Fig. 2. Electron microphotograph of the particles of sample C obtained as the precipitates from $FeSO_4$–$ZnSO_4$ mixed aqueous solution.

for 1000 hours. Sample C, as shown in Fig. 2, was a light yellowish brown particle, the particle size being about 1000 Å, and was also found to be pure $ZnFe_2O_4$ by the analogous measurments in sample A and B. The precipitates of sample C were formed gradually in about 7 hours from the beginning of the reaction.

In above-mentioned samples the magnetization was measured with the magnetic torsion balance over the temperature range from liquid nitrogen temperature to 300°C. The character of "recovery", decrease of abnormality in the magnetic property of the samples was also studied by annealing in the temperature range from 300°C to 800°C.

III. RESULTS

1. Magnetic Properties

The magnetization vs. magnetic field curves of sample A, B and C are shown in Fig. 3. The magnetization values of sample C were found to be similar to that of normal $ZnFe_2O_4$, while sample A and B exhibited anomalous increase of magnetization. The temperature dependence of the magnetization of sample A and D was observed as shown in Fig. 4. The increase in magnetization of sample A becomes pronounced at lower temperatures. This anomalous behavior enable us to suppose the resemblance to the superparamagnetism due to the formation of the magnetic clusters in quenched or compressed $ZnFe_2O_4$ as has been reported by several authors[2,4]. To see the validity of the supposition, the increments of magnetization I, which were calculated by subtracting the magnetization values of normal $ZnFe_2O_4$ from those of sample A, were tested by the Langevin equation. In general the aggregate of particles which exhibits the superparamagnetism behaves magnetically in a manner analogous to the Langevin paramagnetism of moment-bearing atoms, that is,

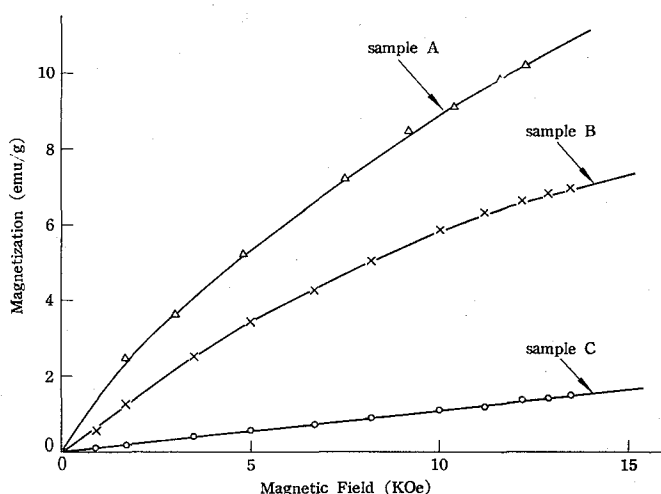$$I/I_0 = \coth \alpha - 1/\alpha = L(\alpha) \qquad (\alpha = \mu H/kT)$$

Fig. 3. The magnetization vs. magnetic field curves of the particles of $ZnFe_2O_4$ chemically precipitated from the aqueous solution, measured at room temperature.
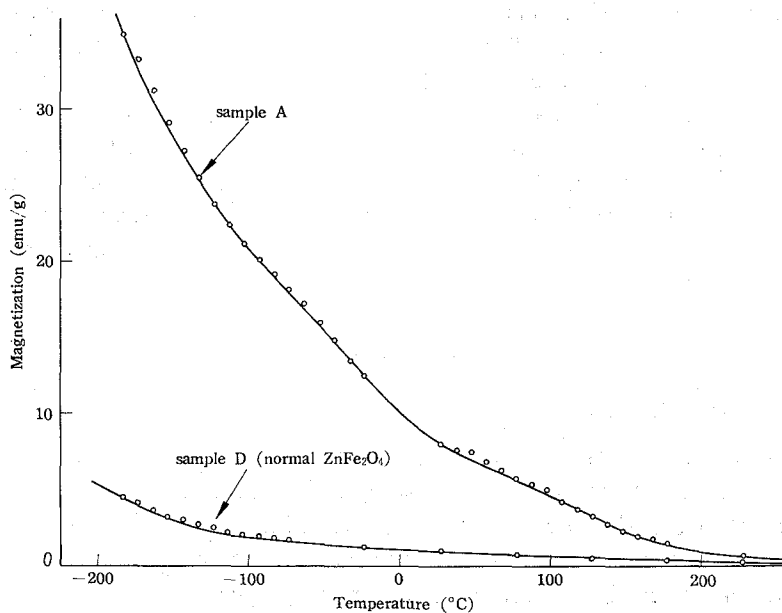
Fig. 4. Magnetization vs. temperature curves of normal $ZnFe_2O_4$ and
sample A, measured in the magnetic field of 9600 Oe.

$$I_0 = N\mu$$
$$\chi = (I/H)_{initial} = N\mu^2/3\,kT$$

where I_0 is an induced saturation magnetization, μ is the mean magnetic moment
of a cluster and N is the number of clusters. From the analysis of the magneti-
zation vs. magnetic field curves of sample A and D at liquid nitrogen and room
temperatures, as shown in Fig. 5, it is found that the increments of magnetization
of sample A can be represented by the Langevin equation as can be seen in Fig. 6,
so that the anomalous magnetic property of sample A and B is interpreted by
superparamagnetism induced by magnetic clusters. The mean magnetic moment
of a single cluster, which was evaluated from the Langevin equation, was $0.71 \times$
10^{-17} emu at liquid nitrogen temperature and 1.33×10^{-17} emu at room temperature.
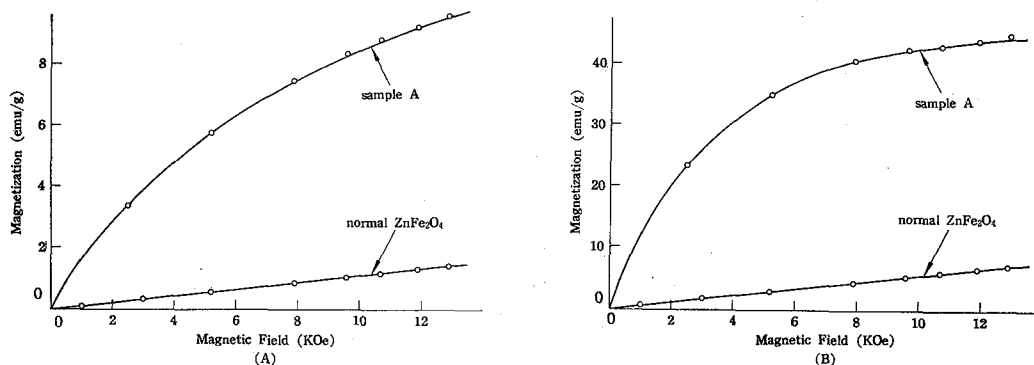This result may seem to be contrary to the fact that the spontaneous magnetization

Fig. 5. Magnetization vs. magnetic field curves of normal $ZnFe_2O_4$ and
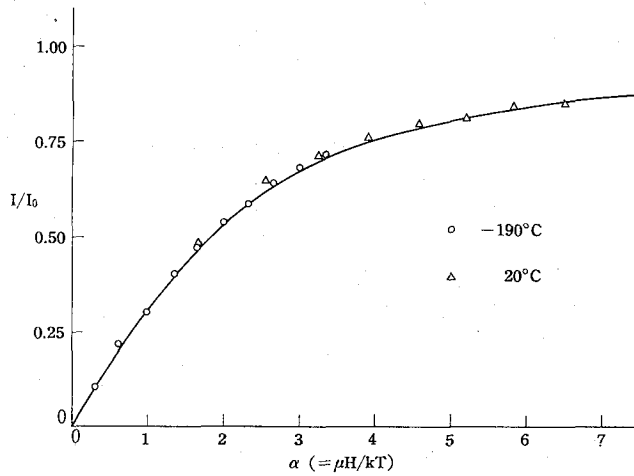sample A, measured at 20°C (A) and −190°C (B).

Fig. 6. Field dependence of normalized magnetization of sample A, measured at −190°C and 20°C respectively. Solid curve represents the Langevin function.
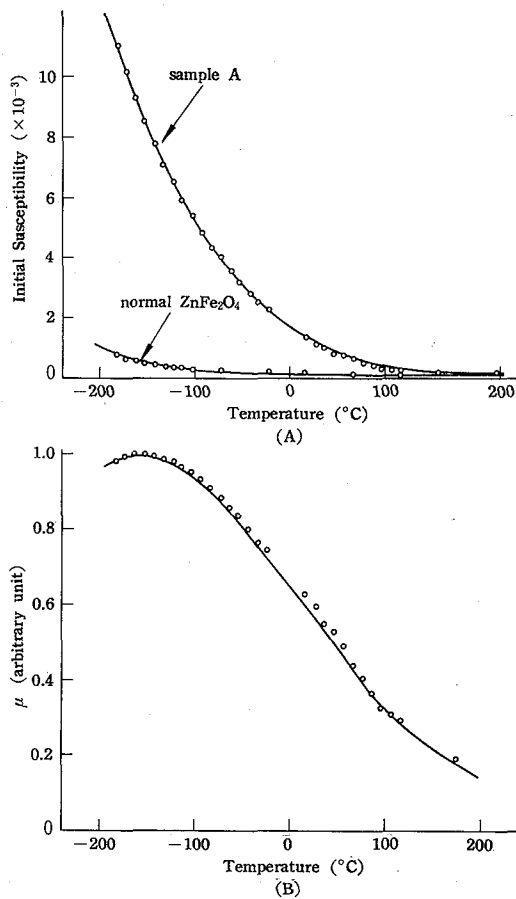

Fig. 7. (A) Initial susceptibility vs. temperature curves of normal ZnFe₂O₄ and sample A, measured at 900 Oe.
(B) Temperature dependence of normalized magnetization of a magnetic cluster.

of the ferrimagnetic particle generally decreases by thermal fluctuations as temperature rises. This contradiction can be explained by the model that the Curie temperature of each magnetic cluster is different, so that some magnetic clusters with lower Curie temperature, which probably have small values of μ, disappear as temperature rises and clusters with large values of μ are still alive.

The temperature dependence of the mean magnetic moment of each cluster was evaluated from the initial magnetic susceptibility vs. temperature curves (measured at 900 Oe) shown in Fig. 7 (A). The calculation was carried out from the Langevin equation with the assumption that the increment of the susceptibility $\Delta \chi = \chi_{sample\ A} - \chi_{sample\ D}$ is attributed to the magnetization of the cluster. For brevity the number of clusters N is assumed to be temperature independent. The result is shown in Fig. 7 (B), which indicates that Curie temperature of the cluster is in the vicinity of 200°C as has been noted by Goto[4].
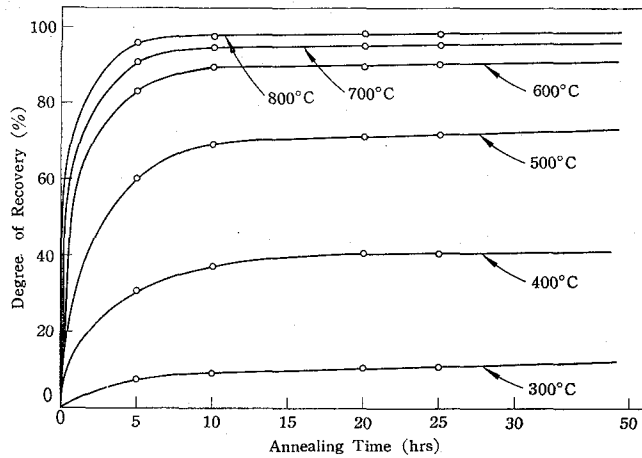
2. Annealing Effect on the Superparamagnetism

Fig. 8. Degree of the recovery in sample A annealed
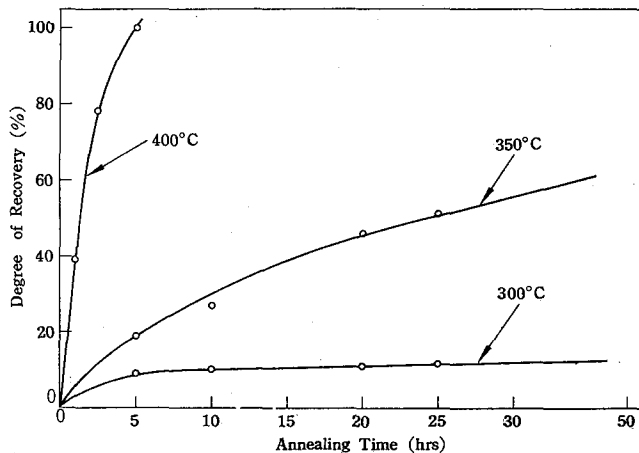at several temperatures.

Fig. 9. Degree of the recovery of sample E annealed
at several temperatures.

It was found that the superparamagnetism of sample A disappeared gradually by annealing in the temperature range from 300°C to 800°C. The degree of recovery at several annealing temperatures was evaluated from the change of magnetization measured in the magnetic field of 10000 Oe at room temperature and the results are shown in Fig. 8 as a function of annealing time. Figure 9 also shows the analogous relation on sample E obtained by quenching normal $ZnFe_2O_4$ from 1100°C in air. Consequently the superparamagnetism of sample E disappeared by annealing at 400°C for 5 hours as has been remarked by Sekizawa[2]. According to Goto[4] the superparamagnetism of squeezed $ZnFe_2O_4$ disappears by annealing at 500°C for 5 hours. However, the degree of the recovery of sample A is about 90% by annealing at 600°C for 5 hours, and then the remaining 10% recovered completely by annealing at 800°C for 100 hours. From these phenomena it is found that the rate of the recovery of sample A is much slower than that of quenched or squeezed $ZnFe_2O_4$.

IV. DISCUSSION

1. Cation Distribution of the Fine Particles of $ZnFe_2O_4$

It has been shown in the previous section that the superparamagnetism of sample A is due to the magnetic clusters formed in process of the formation of the crystal from the aqueous solution. In normal $ZnFe_2O_4$, as described in section I, the tetrahedral A-sites are occupied only by zinc ions with no magnetic moment and all the octahedral B-sites by the ferric ions, so that the strong A-B interaction does not exist. But owing to the weak B-B interaction $ZnFe_2O_4$ has, as shown in Fig. 10(A), an antiferromagnetic spin alignment below 9°K. However, if A-site zinc ions are partially replaced by B-site ferric ions by any means, such as quenching or compressing, there would occur, as in Fig. 10(B), the strong A-B interactions among B-site ferric ions surrounding the replaced A-site ferric ions, so that many magnetic clusters with such a cation distribution as $Zn_{1-x}^{2+}Fe_x^{3+}$ [Zn_x^{2+} Fe_{2-x}^{3+}] are formed in $ZnFe_2O_4$, which lead to the superparamagnetic behavior.
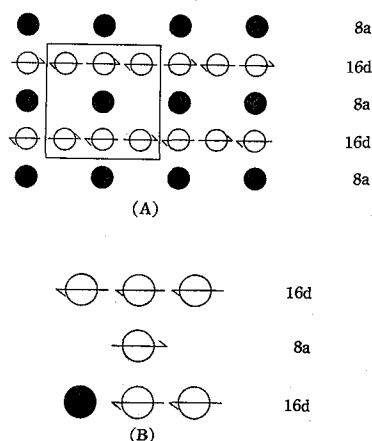

Fig. 10. (A) Spin configuration of perfectly normal spinel below 9°K.
(B) Spin configuration of the magnetic cluster in disordered spinel. (○: ferric ion, ●: zinc ion)

It is, therefore, suggested that the superparamagnetism of $ZnFe_2O_4$ rapidly precipitated from the aqueous solution may be due to the magnetic clusters with the cation distribution of $Zn_{1-x}^{2+}Fe_x^{3+}[Zn_x^{2+}Fe_{2-x}^{3+}]$ by above-mentioned assumption.

The superparamagnetism induced only by the partial replacement of A-site zinc ions by B-site ferric ions disappears by short range diffusion when annealed at required temperature. In fact the squeezed and quenched $ZnFe_2O_4$ are reported by authors[2,4] to become normal $ZnFe_2O_4$ by short range diffusion when annealed in the temperature range from 400°C to 500°C. But, as shown in Fig. 8, the process of the recovery of sample A is considerably different from that of the squeezed and quenched $ZnFe_2O_4$. This anomalous behavior can be explained only by the following mechanism. A little fluctuation of the composition in each particle must be inevitable. The anomalously slow recovery from 600°C to 800°C may be due to the Fe^{3+}-rich particles of the sample. For the recovery of the disordered cation distribution of these particles the long range diffusion must occur and, therefore, the higher annealing temperature is required. Actually the solid solution of $ZnFe_2O_4$ with a little quantity of γ-Fe_2O_3 exhibited the superparamagnetic behavior, and this Fe^{3+}-rich $ZnFe_2O_4$, in which A-sites were partially occupied by ferric ions, precipitated excess ferric ions by long range diffusion when annealed in the temperature range from 600°C to 800°C and became the two phases of $ZnFe_2O_4$ and α-Fe_2O_3[7].

2. Relation between the Cation Distribution and Preparation Method of $ZnFe_2O_4$

As described in previous sections, sample A and B, which were precipitated rapidly from Fe^{3+}-Zn^{2+} aqueous solution, exhibited the superparamagnetic behavior due to the magnetic clusters formed by partial occupation of A-sites by ferric ions, but sample C, which is precipitated gradually from Fe^{2+}-Zn^{2+} aqueous solution, exhibited the paramagnetic behavior at room temperature. The difference must be attributed to the rate of the crystal formation in process of the precipitation from the aqueous solution. The particles of sample A are formed immediately after being rapidly co-precipitated from Fe^{3+}-Zn^{2+} mixed aqueous solution, so that the rate of the crystal formation is extremely fast. In sample B amorphous ferric oxides and zinc oxides are precipitated separately, and then dissolve gradually in the aqueous solution as the temperature rises and simultaneously the particles of sample B begin to be formed, so that the rate of the crystal formation of sample B is considerably slower than that of sample A. Consequently the anomalous values of magnetization of sample B are small compared to that of sample A. In sample C, $Fe_{1-x}Zn_x(OH)_2$ or mixed precipitates of $Fe(OH)_2$ and ZnO are formed from Fe^{2+}-Zn^{2+} mixed aqueous solution at 70°C, and then dissolve gradually in the solution with passing air bubbles through the solution and simultaneously the particles of sample C begin to be formed. The required time of the formation of sample A is a few minutes and that of sample B about fifteen minutes, but that of sample C about seven hours, which is much longer than that of above two samples. The particles of sample C are completely normal, while the particles of sample A and B have partially inverse cation distribution as $Zn_{1-x}^{2+}Fe_x^{3+}[Zn_x^{2+}Fe_{2-x}^{3+}]$. It is, therefore, concluded that the anomaly of the cation distribution of $ZnFe_2O_4$

chemically precipitated from the aqueous solution depends greatly on the rate of the crystal formation.

ACKNOWLEDGEMENTS

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