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Yasumasa Goto

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Yasumasa Goto

*Department of Chemistry, Faculty of Science,
Kyoto University, Sakyo-ku, Kyoto*

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It was found that ZnFe_2O_4 exhibited a superparamagnetic behavior due to the formation of magnetic clusters inside the specimen when squeezed by an anvil under the pressure of $(1\sim 3)\times 10^4$ kg/cm² at room temperature. From the analyses of the magnetization curves, the mean magnetic moment of a cluster was calculated to be of the order of 10^{-17} emu and its temperature dependence was also determined from the initial susceptibility. The number of the clusters involved in 1 gr of the squeezed ZnFe_2O_4 was about 10^{17} which varies almost proportionally with applied pressure. It is suggested that the magnetic cluster may be the stacking fault formed by squeezing in which some ferric ions are slipped into tetrahedral sites during the crystal slip. The superparamagnetism disappears gradually by annealing above 400°C and the activation energy for the recovery was about 1.7 eV.

§ 1. Introduction

In an elementary cell of the spinel structure, eight tetrahedral sites (A-sites) and sixteen octahedral sites (B-sites) are occupied by cations. Each A-site cation is surrounded by twelve B-site cations with the most favorable magnetic interaction angle. A B-site cation has six B-site cations and six A-site cations as nearest neighbors. The metal-oxygen-metal angle between B-sites is unfavorable for the superexchange interaction. In ZnFe_2O_4 , which is known to have the normal spinel structure, the non-magnetic zinc ions occupy the A-sites and all the ferric ions are in B-sites. Therefore, the strong A-B interaction does not exist in the compound. Because of the weak B-B interaction, ZnFe_2O_4 is reported to become antiferromagnetic below 9°K. However, if a part of ferric ions enter into A-sites for some reason, there would occur the stronger interactions between the ferric ions in B and A-sites. The cause of the superparamagnetism in the solid solution of 90 ZnFe_2O_4 -10 NiFe_2O_4 reported by Ishikawa¹⁾ and the analogous behavior in quenched ZnFe_2O_4 reported by Sekizawa²⁾ are both ascribable to such interaction.

The magnetic properties of ZnFe_2O_4 is so closely connected with the geometrical arrangement of ions that we may expect the appearance of magnetically anomalous behaviors when the crystal is deformed by

any means. The present paper deals with the effects of plastic deformation induced by the high pressure squeezing. As a result, we found that the superparamagnetism appears in the squeezed ZnFe_2O_4 and it disappears by high temperature annealing. The effects may give informations about a relationship between the imperfections and magnetic properties in complex ionic compounds. And the observed phenomena may be also closely connected with the disaccommodation of ferrimagnetic materials.

§ 2. Experimental Procedures

The specimens of ZnFe_2O_4 were prepared by the ordinary ceramic method. Powders of ZnO and Fe_2O_3 were mixed in the required ratio and then were 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. About 0.5 gr of the powder specimen was squeezed uniaxially under the pressure of $1\times 10^4\sim 3\times 10^4$ Kg/cm² using a modified apparatus³⁾ of Bridgman's anvil. The section area of the piston is about 0.7 cm². Before and after the treatment, magnetization, susceptibility and remanent magnetization were measured with a high sensitive magnetic torsion balance and an astatic magnetometer. Recovery of the induced magnetic property was also studied by annealing the squeezed specimens in the

temperature range from 400° to 500°C. At the same time precise X-ray examinations were carried out.

§ 3. Experimental Results and Discussions

1) Superparamagnetism induced by pressure squeezing

The ordinary $ZnFe_2O_4$ is, as well known, paramagnetic above 9°K. The temperature dependence of the magnetization (measured in the magnetic field of 6,000 Oe.) of the virgin specimen is shown in Fig. 1 (a), which indicates the normality of the starting material. After squeezing, however, the magnetization increased remarkably with

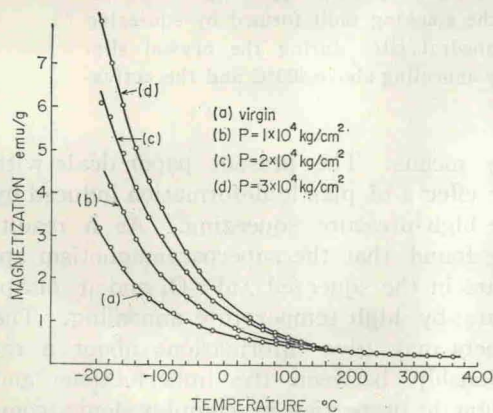


Fig. 1. Magnetization vs temperature curves of a virgin specimen and some squeezed specimens, measured in the magnetic field of 6000 Oe.

increasing applied pressure. The results are shown by the curves (b), (c) and (d) in Fig. 1. The applied pressure was 1×10^4 , 2×10^4 and 3×10^4 Kg/cm², respectively, and they were measured in the same magnetic field as that in the case of virgin specimen. The increase in magnetization of the squeezed specimens becomes pronounced at lower temperature. The magnetization vs. magnetic field curves were also studied at -196° C and 17° C, the results of which are shown in Fig. 2. The curves marked with (a) is that of virgin specimen and (b), (c) and (d) are those of the specimens which were respectively subjected to the treatments under the pressure of 1×10^4 , 2×10^4 and 3×10^4 Kg/cm². In these specimens no remanent magnetization could be detected with an astatic magnetometer at room temperature even after the magnetization in the field of 20,000 Oe.

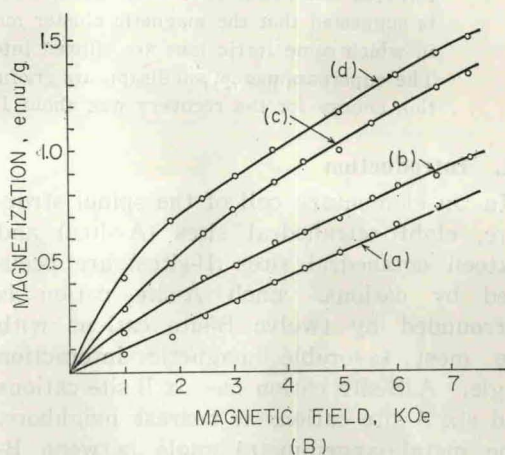
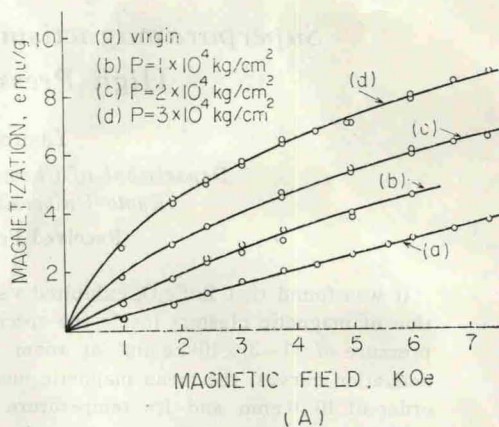


Fig. 2. Magnetization vs magnetic field curves of a virgin and some squeezed specimens measured at -196° C (A) and 17° C (B).

These anomalous behaviors enable us to suppose the many magnetic clusters have been formed during the treatment and they exhibit a kind of superparamagnetic behavior. To see the validity of the supposition, the increments of magnetization I , which were calculated by subtracting the magnetization values of virgin specimen from those of squeezed ones, were tested by the Langevin equation,

$$\frac{I}{I_0} = L\left(\frac{\mu H}{kT}\right)$$

$$I_0 = N\mu$$

where I_0 is an induced saturation magnetization and μ is the mean magnetic moment of a cluster and N is the number of clusters. The magnetization curves at liquid nitrogen temperature (Fig. 2A) can be represented by a single Langevin equation as can be seen

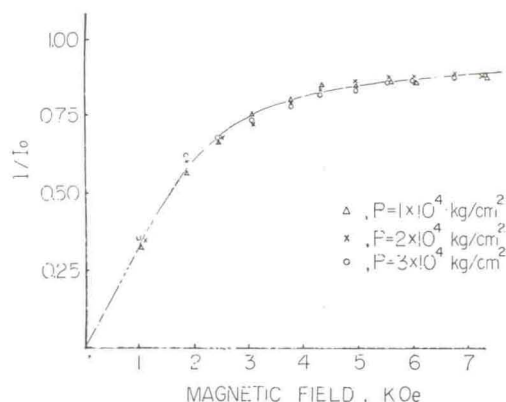


Fig. 3. Field dependence of normalized magnetization that was induced by squeezing, measured at -196°C . Solid curve represents the most favorable Langevin function. I_0 s are taken as 5.62, 3.32 and 1.80 emu/g for applied pressures of 1×10^4 , 2×10^4 and 3×10^4 Kg/cm², respectively.

in Fig. 3, when μ/kT is taken as 1.32×10^{-3} gauss⁻¹ and I_0 s as 1.8, 3.3 and 5.6 e.m.u/(gr. of $ZnFe_2O_4$) for the applied pressure of 1×10^4 , 2×10^4 and 3×10^4 Kg/cm², respectively. The result confirms the validity of the supposition and allows the evaluation of the mean magnetic moment as well as the number of the clusters. The latter formed in 1 gr of $ZnFe_2O_4$ is calculated to be 1.3×10^{17} ($P = 1 \times 10^4$ Kg/cm²), 2.4×10^{17} ($P = 2 \times 10^4$ Kg/cm²) and 4.0×10^{17} ($P = 3 \times 10^4$ Kg/cm²), nearly proportional to the applied pressure. The mean magnetic moment of a single cluster is determined to be 1.4×10^{-17} emu at liquid nitrogen temperature and it corresponds to 500 Fe^{3+} ions. The mean size of the cluster is at present unknown, because the knowledges of the structure and molar magnetic moment of a cluster are lacking.

The temperature dependence of the mean magnetic moment inside the cluster was evaluated from the initial magnetic susceptibility vs. temperature curves (measured at 1000 Oe.) shown in Fig. 4(A). The calculation was carried out, as the former case, with the assumption that the increment of the susceptibility $\Delta\chi = \chi_{\text{squ.}} - \chi_{\text{virgin}}$ is attributed to the magnetization inside the cluster and expressed as $\Delta\chi = N\mu^2/3kT$. The result is shown in Fig. 4(B), which indicates that the temperature dependence of the magnetization inside a cluster is quite similar to the $\sigma-T$ curve of $Ni_{0.5}Zn_{0.5}[Fe_2]O_4$ or

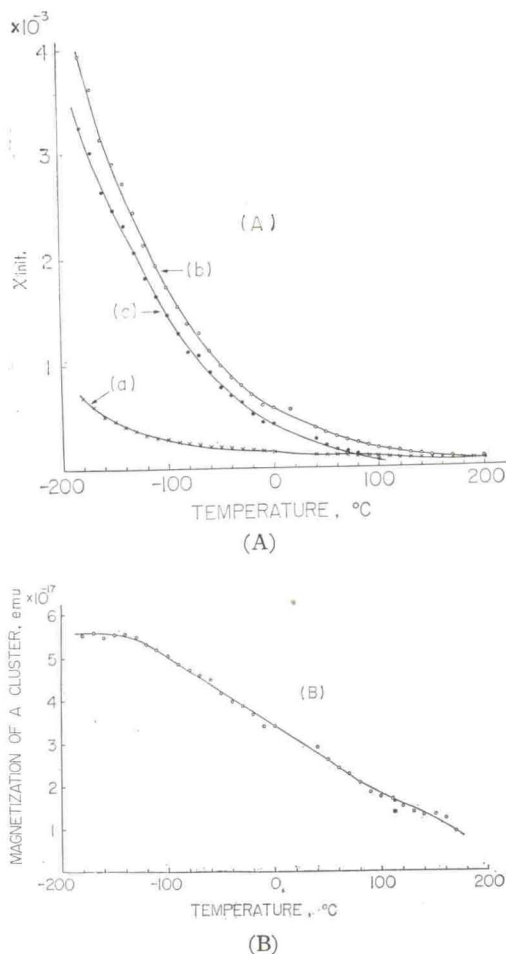


Fig. 4. (A) Initial susceptibility vs temperature curves of a virgin specimen (a), of the squeezed one ($P = 3 \times 10^4$ Kg/cm²) (b) and the difference of them (c), measured at 1000 Oe. (B) Temperature dependence of magnetization inside a cluster.

$Mn_{0.5}Zn_{0.5}[Fe_2]O_4$.

2) Structural considerations

It has been shown in previous sections that the induced superparamagnetism in $ZnFe_2O_4$ is due to the magnetic clusters formed by squeezing. But precise X-ray analyses for pressed specimens showed no anomaly except the broadenings of diffracted lines. Sekizawa²⁾ found that the similar superparamagnetism appears when quenched from temperature higher than 1000°C . He ascribed the anomalous properties to the formation of the magnetic clusters. Ishikawa¹⁾ also observed the analogous superparamagnetism in the solid solution of 90 $ZnFe_2O_4$ -10 $NiFe_2O_4$. These phenomena

seem quite analogous in their mechanism. In normal ZnFe_2O_4 , as described in section 1, the tetrahedral A-site are occupied only by the non-magnetic zinc ions so that a strong A-B interaction does not exist. However, if an A-site is replaced by a ferric ion by any means, such as quenching* or compressing, there would occur a spin alignment among twelve B-site ferric ions surrounding the replaced A-site ferric ions, which leads to the formation of a superparamagnetic cluster. If several neighboring A-site are synchronously replaced by ferric ions, a cluster with larger size would develop, in which a magnetic order is well established by strong A-B interactions.

Such a replacement is quite conceivable to occur when the normal ZnFe_2O_4 is subjected to a plastic deformation. Stacking faults formed by the deformation will have a similar structure to that of above mentioned magnetic cluster. Grün⁵⁾ studied the plastic deformation of magnetite and concluded that the (111) close-packed plane are predominant slip plane. On the basis of this fact, Hornstra⁶⁾ and Kachi *et al.*⁷⁾ theoretically studied the ionic arrangement of the stacking fault and dislocation in the spinel and suggested several possible models. According to these theories, the structure of the stacking fault which is considered to behave as a magnetic cluster may be of the kind shown in Fig. 5. This figure is a projection of slipped region on (110) plane. The stacking order of (111) oxygen layers of normal ZnFe_2O_4 is changed from ABCABC to ABAB sequence in the slipped region. Half of the A-sites on the slipped plane are occupied by ferric ions. The Fe^{3+} (B-site)-oxygen- Fe^{3+} (A-site on the slipped plane) angle is favorable for strong exchange interaction. It is seen that the structure near the slipped region resembles to that of $\text{Zn}_{0.5}\text{Ni}_{0.5}[\text{Fe}_2]\text{O}_4$. This model is, of course, the hypothetical one; direct evidence is lacking at present experiments. But the temperature dependence of magnetization inside a cluster

* At high temperature, ZnFe_2O_4 has such a ionic arrangement expressed by usual notation as $\text{Zn}_{1-\delta}\text{Fe}_\delta [\text{Zn}_\delta\text{Fe}_{2-\delta}] \text{O}_4$ and cations distribute in A and B-sites satisfying the following distribution relation⁴⁾; $\delta^2/(1-\delta)(2-\delta) = \exp[-E/RT]$. By quenching, this arrangement will, to some extent, be retained at room temperature.

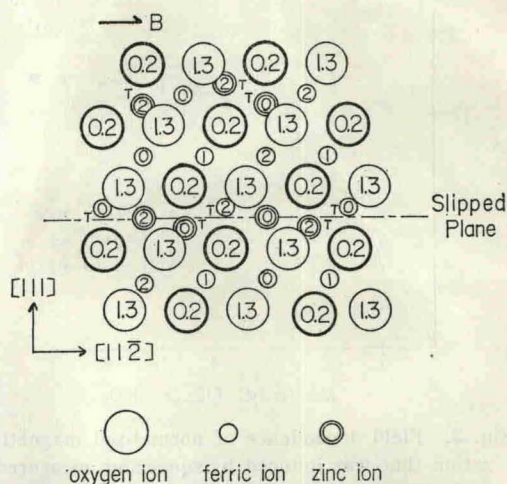


Fig. 5. The projection of the slipped region in ZnFe_2O_4 on the (110) plane. Numbers in the circles represent the heights of the ions in multiples of $a_0\sqrt{2}/8$, where a_0 is lattice constant. Cations in slipped plane are sheared, as well as the upper part, towards the [112] direction by the length $a_0\sqrt{6}/12$ that is represented by the vector **B**. The cations marked with *T* are those entered into A-sites during slipping.

shown in Fig. 4(B) may indirectly support this structure.

3) Annealing effect on the superparamagnetism

It was found that the superparamagnetism caused by high pressure squeezing disappears gradually by annealing in the temperature range from 400° to 500°C. By measuring the change of magnetization in the magnetic field of 6000 Oe, the degree of the recovery was followed as a function of annealing time. The results for the specimen squeezed

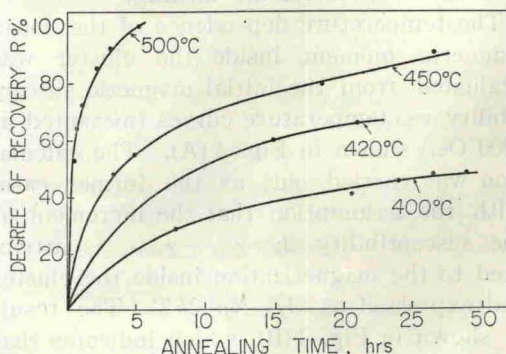


Fig. 6. Degrees of the recovery of the superparamagnetism by annealing at several temperatures.

at $3 \times 10^4 \text{ Kg/cm}^2$ are shown in Fig. 6. Measured values satisfy the following familiar equation concerning the magnetic after effect of diffusion type,

$$(1-R) = A \exp\left[-\frac{t}{\tau}\right]$$

where R represents the degree of recovery, A is a constant and τ is the relaxation time for the recovery. The $\log k$ values are plotted against the reciprocal of annealing temperature as is seen in Fig. 7, which shows practically linear relationship between them. Assuming the relation of the form;

$$\frac{1}{\tau} = B \exp\left[\frac{-Q}{kT}\right]$$

the activation energy Q for the recovery is

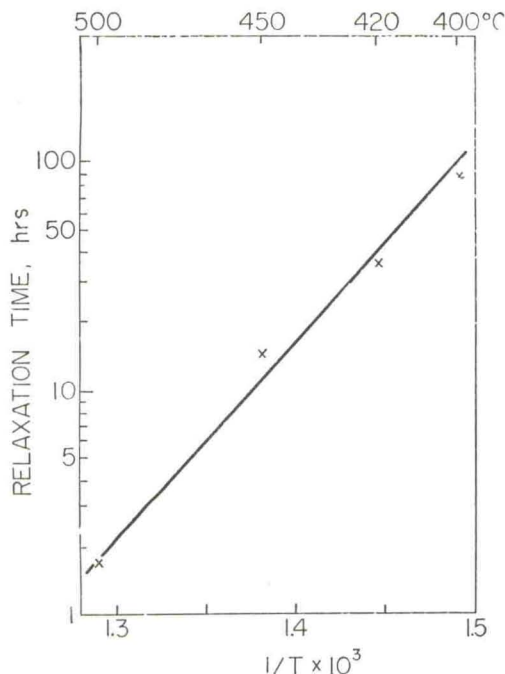


Fig. 7. Plots of relaxation time against the reciprocal of the annealing temperature.

calculated to be 1.7 eV. Sekizawa also studied the recovery of the superparamagnetism in quenched $ZnFe_2O_4$ and determined the activation energy to be 1.47 eV⁸⁾. Both of these values are far smaller than the activation energy for diffusion of ferric ion in $ZnFe_2O_4$, *i.e.* 82 Kcal/mol which was estimated by Rinder⁹⁾. As zinc ion has a strong preference to the tetrahedral site and all the ions will cooperatively migrate during annealing in present case, it is not surprising that the observed value of activation energy is far less than that of simple diffusion of ferric ion in $ZnFe_2O_4$. In any case it is sure that the recovery proceeds through some diffusion process.

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References

- 1) Y. Ishikawa: J. Phys. Soc. Japan **17** (1962) 1877.
- 2) H. Sekizawa: Preprint of Ann. Meeting of Phys. Soc. of Japan (April, 1963) p. 404.
- 3) D. T. Griggs and G. C. Kennedy: Am. J. Sci. **254** (1956) 722.
- 4) L. Néel: Compt. Rend. **230** (1950) 190.
- 5) A. Grün: Neues Jahrb. für Mineralog. **1** (1918) 99.
- 6) J. Hornstra: J. Phys. Chem. Sol. **15** (1960) 311.
- 7) S. Kachi, K. Momiyama and S. Shimizu: J. Phys. Soc. Japan **18** (1963) 106.
- 8) Private communication.
- 9) R. Rinder: Arkiv Kemi **4** (1952) 381; Ceram. Abst. (1953) 91.