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Superparamagnetism in $ZnFe_2O_4$ Induced by High Pressure Squeezing

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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 $(1\sim3)\times10^4$ kg/cm^2 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 Ishikawa$^{1)}$ and the analogous behavior in quenched $ZnFe_2O_4$ reported by Sekizawa$^{2)}$ 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 $1\times10^4\sim3\times10^4$ Kg/cm^2 using a modified apparatus$^{3)}$ of Bridgman's anvil. The section area of the piston is about 0.7 cm^2. 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 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/cm^2, 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/cm^2. 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.

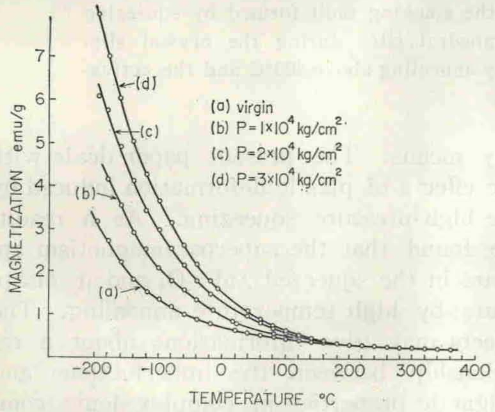

Fig. 1. Magnetization vs temperature curves of a virgin specimen and some squeezed specimens, measured in the magnetic field of 6000 Oe.

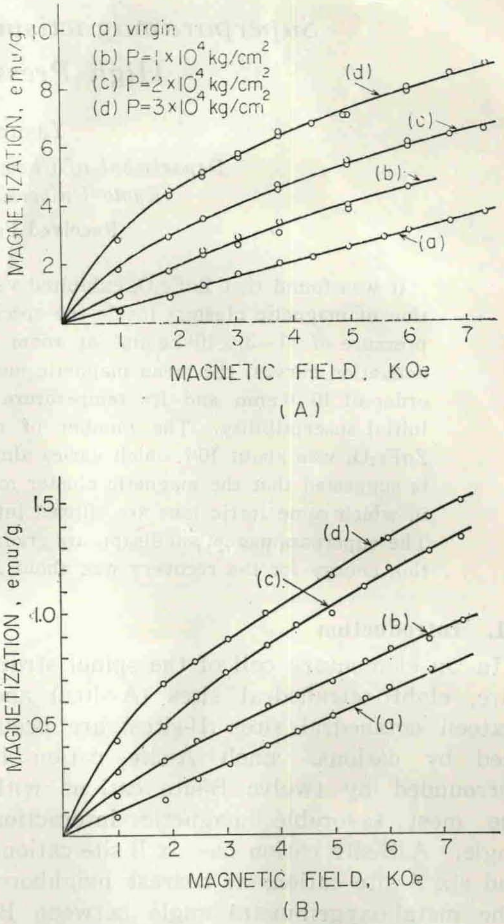

Fig. 2. Magnetization vs magnetic field curves of a virgin and some squeezed specimens measured at −196°C (A) and 17°C (B).

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