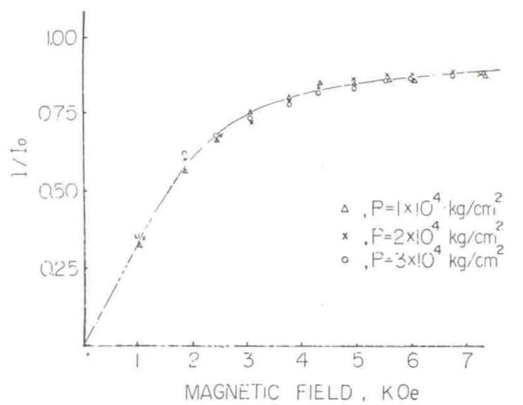
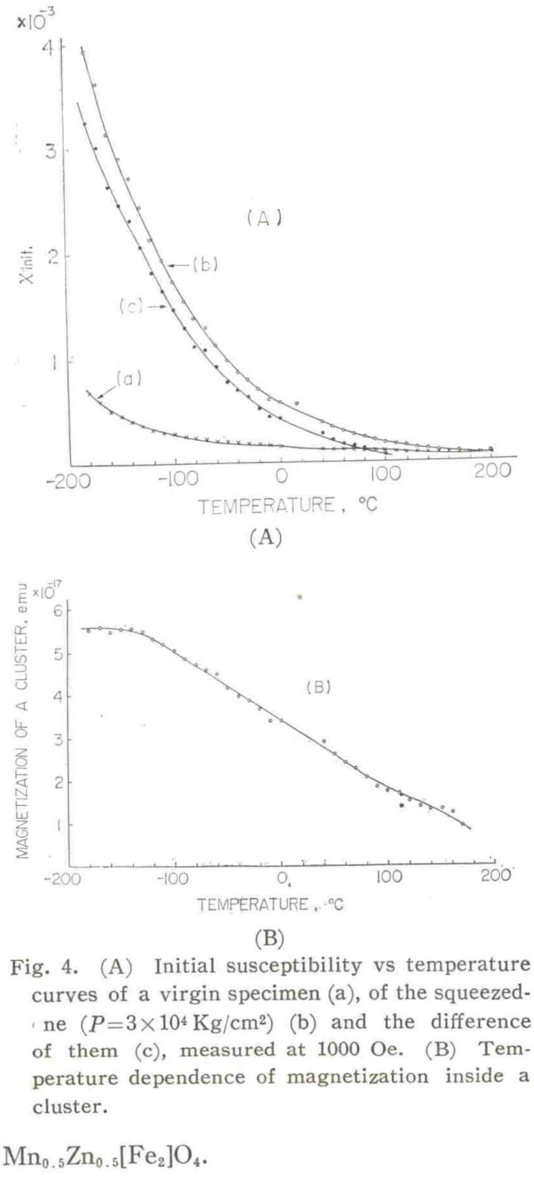


Fig. 3. Field dependence of normalized magnetization that was induced by squeezing, measured at −196°C. Solid curve represents the most favorable Langevin function. I_0s are taken as 5.62, 3.32 and 1.80 emu/g for applied pressures of 1×10^4, 2×10^4 and 3×10^4 Kg/cm², respectively.

in Fig. 3, when μ/kT is taken as 1.32×10^{-3} gauss^{-1} and I_0s 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} ($P=1\times10^4$ Kg/cm²), 2.4×10^{17} ($P=2\times10^4$ Kg/cm²) and 4.0×10^{17} ($P=3\times10^4$ 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 $\varDelta\chi=\chi_{\text{squ.}}-\chi_{\text{virgin}}$ is attributed to the magnetization inside the cluster and expressed as $\varDelta\chi=N\mu^2/3kT$. 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 $Mn_{0.5}Zn_{0.5}[Fe_2]O_4$.



(A)

(B)

Fig. 4. (A) Initial susceptibility vs temperature curves of a virgin specimen (a), of the squeezed-one ($P=3\times10^4$ Kg/cm²) (b) and the difference of them (c), measured at 1000 Oe. (B) Temperature dependence of magnetization inside a cluster.

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. Sekizawa[2] 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. Ishikawa[1] 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. Grün[5] studied the plastic deformation of magnetite and concluded that the (111) close-packed plane are predominant slip plane. On the basis of this fact, Hornstra[6] 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 $(1\bar{1}0)$ 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 $Zn_{0.5}Ni_{0.5}[Fe_2]O_4$. This model is, of course, the hypothetical one; direct evidence is lacking at present experiments. But the temperature dependence of magnetization inside a cluster shown in Fig. 4 (B) may indirectly support this structure.

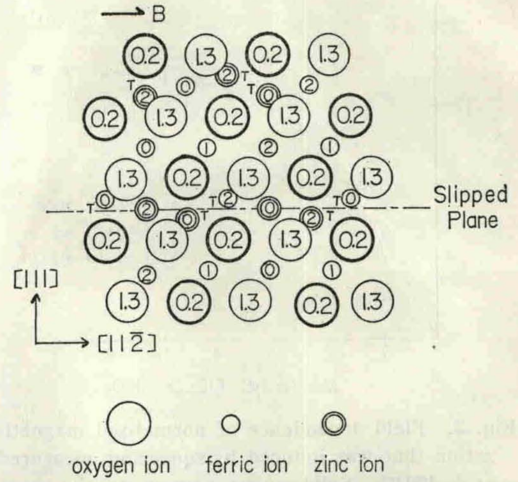


Fig. 5. The projection of the slipped region in $ZnFe_2O_4$ on the $(1\bar{1}0)$ plane. Numbers in the circles represent the heights of the ions in multiples of $a_0\sqrt{2}/8$, where a_0 is lattice constant. Cations in slipped plane are sheared, as well as the upper part, towards the $[11\bar{2}]$ direction 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.

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

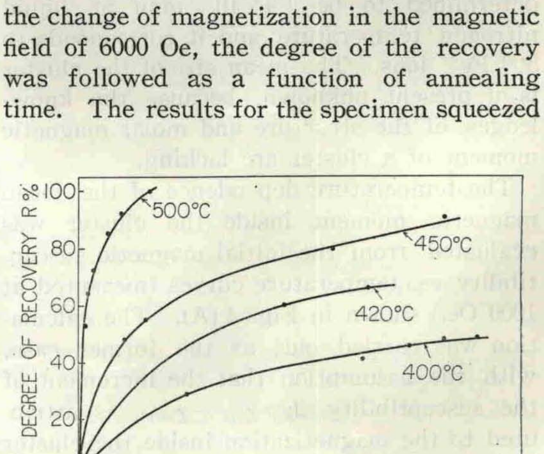


Fig. 6. Degrees of the recovery of the superparamagnetism by annealing at several temperatures.

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* At high temperature, $ZnFe_2O_4$ has such a ionic arrangement expressed by usual notation as $Zn_{1-\delta}Fe_\delta[Zn_\delta Fe_{2-\delta}]O_4$ and cations distribute in A and B-sites satisfying the following distribution relation[4]; $\delta^2/(1-\delta)(2-\delta)=\exp[-E/RT]$. By quenching, this arrangement will, to some extent, be retained at room temperature.