

## Characteristic of Hyperfine Magnesium Ferrite Particles Possessing Shape Anisotropy

Going Yim\* · Chai Suck Yim

\*Pai Chai University · LG Chem. Co.

### Abstract

The ferrimagnetic resonance technique, with the inclusion of shape anisotropy effects, was used to obtain information about the early stages in the precipitation of magnesium ferrite from iron-doped magnesia. The very small magnesian ferrite particles were produced by precipitation method from solid solution of iron ion in single crystal magnesia. The temperature dependence of the resonance anisotropy field for a coherent assembly of hyperfine magnesium ferrite precipitates was investigated in the range 100~400K. The results are interpreted in terms of the shape anisotropy of the precipitates.

*Keywords : Magnesian ferrite, Crystal and shape anisotropy, Ferrimagnetic resonance, Anisotropy field, Ferrimagnetism*

### 1. Introduction

Magnesian ferrite has a nominal composition  $MgFe_2O_4$ . The unit cell is composed of  $32O^{2-}$  ions on a slightly distorted fcc lattice. If the structure were ideal inverse spinel, eight  $Fe^{3+}$  ions would be in tetrahedral interstices and eight  $Fe^{3+}$  ions along with eight  $Mg^{2+}$  ions would be in octahedral sites. If this ideal inverse spinel structure were the actual structure, the crystal would be antiferromagnetic, however, with no net

ferrimagnetic moment. The observed net moment is attributed to a nonideal inverse distribution of cations between octahedral and tetrahedral sites.

The Neel theory of ferrimagnetism<sup>1)</sup> is universally used with excellent success in determining the cation distribution in bulk magnesian ferrite<sup>2-5)</sup>. The ferrite precipitated from magnesia will not be stoichiometric but will be saturated in magnesia. Blackman<sup>4)</sup> reported that the solubility limit of MgO in  $MgFe_2O_4$  is indicated by the formula  $[(MgO)_{0.09}$

MgFe<sub>2</sub>O<sub>4</sub>] at 1350°C in air. Assuming the cation lattice to be complete with the defects assigned to the O<sup>2-</sup> lattice and assuming no Fe<sup>2+</sup>, this corresponds<sup>4)</sup> to Mg<sub>1.05</sub>Fe<sub>1.95</sub>O<sub>3.97</sub>.

The magnetic behavior of systems consisting of isolated single-domain particles depends on the relative magnitude of the thermal energy with respect to the anisotropy part of the magnetic energy of the particles. When these two energies are comparable, the direction of magnetization of the particles undergoes thermal fluctuation<sup>6-8)</sup>.

Precipitation hardening of MgO doped with iron has been studied by Groves<sup>9)</sup> and Wirtz<sup>10)</sup>. The precipitate was shown to be magnesioferrite, nominally MgFe<sub>2</sub>O<sub>4</sub>, in the shape of octahedra bounded by {111} planes that project as squares on the {100} planes. Particle size may be characterized by the edge length,  $\epsilon$ , lying parallel to the {110} directions and related to particle volume through the equation  $\epsilon=(6v)^{1/3}$ .

The precipitation kinetics of Fe<sup>3+</sup> ion: MgO was investigated using superparamagnetic analysis of ferrimagnetic resonance data reported by Biasi<sup>11)</sup>. However, since the shape anisotropy of the precipitates was neglected, it was not possible to extend the analysis to very small particle size. In this study, the ferrimagnetic resonance technique, with the inclusion of shape anisotropy effects, was used to obtain information about the early stages in the precipitation of magnesium ferrite from magnesia doped with iron.

## 2. Background

The theory of magnetic resonance of bulk magnetic materials was developed long ago<sup>12-14)</sup>. Some of its results may be summarized as follows:

1) The resonance field of an unstressed sample magnetized to saturation by a strong external field is a function of the  $g$  factor, of the magnetocrystalline anisotropy field,  $H_a$ , and the demagnetization field,  $H_s$ .

2) The anisotropy field may be expressed by

$$H_a = k/M \quad (1)$$

where  $k$  is the anisotropy constant and  $M$  is the sample magnetization.

3) The demagnetization field depends on the shape of the sample. If the sample has the shape of an ellipsoid of rotation around the direction of the applied field, the demagnetization field may be expressed as<sup>14)</sup>

$$H_s = -nM \quad (2)$$

where  $n$  is called the anisotropy form factor and is a function of the sample dimensions.  $n$  is positive for an oblate ellipsoid and negative for a prolate ellipsoid of rotation.

4) When the above conditions 1) and 3) are satisfied, the following relation holds:

$$h\nu/\psi g = H + \lambda H_a + H_s \quad (3)$$

where  $h\nu/\psi g$  is a constant,  $H$  is the magnitude of the applied magnetic field, and  $\lambda$  is a factor which depends only on the angles between the applied field and the crystallographic axes.

In a magnetic resonance experiment, the resonance field is measured for several orientations of the applied field and for several sample geometries. The results are then used to calculate the three unknowns in equation (3), i.e.,  $g$ ,  $k$ , and  $M$ .

When the sample consists of small particles embedded in a diamagnetic matrix, the quantities  $H_a$  and  $H_s$  in equation (3) must be replaced by suitable averages, so that the thermal fluctuations of the magnetic moments of the particles are taken into account.

### 3. Theory

The anisotropy field of a coherent assembly of small magnetic particles is given by Biasi<sup>15,16</sup>:

$$H_a = H_c + H_s \quad (4)$$

where  $H_c$  and  $H_s$  are the contributions of crystal and shape anisotropy, respectively, and the averages are taken over a distribution in thermal equilibrium.

If both crystal and shape anisotropy are cubic, it can be shown<sup>11,15,16</sup> that:

$$H_c = k / (n_0 I_s) \cdot (1 - 10x^{-1} \coth x + 45x^{-2} - 105x^{-3} \coth x + 105x^{-4}) / (\coth x - x^{-1}) \quad (5)$$

$$H_s = n \eta_0 I_s (\coth x - x^{-1}) \quad (6)$$

where  $I_s$  is the intrinsic magnetization of the particles and  $x = I_s v H / kT$ , and  $v$  is the average particle volume.

Whenever  $x \gg 1$ , or  $v \gg kT / I_s H$ , equation (5) becomes

$$H_a = H_{a\infty} (1 - 9x^{-1}) \quad (7)$$

where  $H_{a\infty} = k / I_s$  is the anisotropy field for particles of infinite size. Equation (7) may also be written as

$$v_{(a)} = \frac{k T}{I_s H} \frac{9}{1-a} \quad (8)$$

where  $a = H_a / H_{a\infty}$ .

For small  $x$ , the crystal anisotropy,  $H_c$  varies as the third power of  $x$ , while the shape anisotropy,  $H_s$  varies linearly with  $x$ . Therefore, for  $x$  sufficiently small, crystal anisotropy becomes negligible as compared with shape anisotropy and the value of the anisotropy form factor can be obtained from magnetic resonance measurements.

Magnetic resonance measurements yield the value of  $a$  as a function of aging time and aging temperature. Equation (8) may then be used to determine the corresponding values for  $v$ . Finally, by plotting  $v$  as a function of the aging time, it is possible to determine the growth rate at aging temperature.

### 4. Experimental

Small magnesium ferrite ( $\text{MgFe}_2\text{O}_4$ ) particles were produced by precipitation from a solid solution of  $\text{Fe}^{3+}$  ion in single crystal  $\text{MgO}$ , using the technique described by Kruse<sup>17</sup>. The iron content of the solution-treated crystals was 1.87

cation %, as determined by chemical analysis. The samples were aged at 700°C in air. The anisotropy field was measured at room temperature and 9.05GHz for several aging times using standard ferromagnetic resonance techniques<sup>18,19</sup>.

### 5. Results and Discussions

For large aging times, and hence large particle sizes, the anisotropy field,  $H_a$  was found to be negative, and a good fit to equation (5) was obtained, as reported Biasi<sup>11,20</sup>. A different behavior was observed for small aging times.

The anisotropy field was positive and increased with aging time. When the anisotropy field was plotted against inverse absolute temperature, the data could be fitted fairly accurately to equation (6), This is shown in Figure 1 for an aging time of one hour at 700°C.

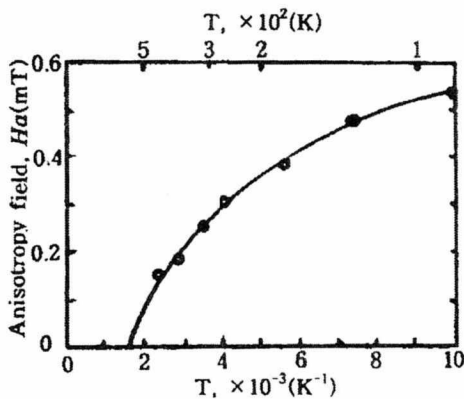


Figure 1. Temperature dependence of anisotropy

field of magnesioferrite precipitates in magnesia.

The shape of the curve in Figure 1 is a fit to equation (6) with  $n=0.031$ ,  $v=3.4 \times 10^{-25} \text{m}^3$ .

The fitting was made by assuming a dependence of  $I_s$  on  $T$  of the form  $I_s = I_0[1-(T/T_c)^2]^{1/2}$ , with  $I_0=2.6 \times 10^5 \text{A/m}$  and Curie temperature,  $T_c=250^\circ\text{C}$ (10). The parameters  $n$  and  $v$  were then chosen to give the best fit to equation (6). This procedure yielded  $n=0.031$  and  $v=3.4 \times 10^{-19} \text{cm}^3$ . The fact that  $n$  is small and positive is consistent with the morphology of the precipitates(10).

For intermediate aging times, between 6 and 20 hours, the room-temperature anisotropy field decreased with aging time as shown in Figure 2. This is the range where  $H_c$  and  $H_s$  are of the same order and the full equation (4) must be used.

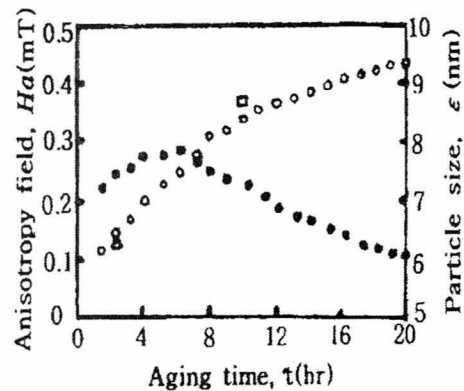


Figure 2. Anisotropy field at 27°C(•) and particle size(○, △, □) as functions of aging time. This study: •, ○ ; ref.<sup>10</sup>: △ ; ref.<sup>17</sup>: □.

Once the value of  $n$  is known, equation (4) can be used to determine the particle size as a function of aging time. The crosses in Figure 2 show the values of  $\varepsilon=(6v)^{1/3}$  computed from equation (4) with  $T=27^\circ\text{C}$ ,  $n=0.031$ ,  $H=0.29\text{T}$ ,  $I_s=2.37\times 10^5\text{A/m}^{(10)}$  and  $k/I_s=-9.8\text{mT}^{(11)}$ . The computed particle sizes for aging times of 2 and 10 hours are fairly close to the sizes measured directly by electron microscopy<sup>(10,17)</sup> and indicated by a square and a triangle in Figure 2.

## Acknowledgements

We wish to thank Dr. T. C. Park of Systems Research Laboratories, Inc. for the magnetic resonance measurements and computer results.

## References

- 1) Neel, L., *Am. Phys.*, **3**, 137 (1948).
- 2) Kriesseman, C. J. and Harrison, S. E., *Phys. Rev.*, **103**, 857 (1956).
- 3) Epstein, D. J. and Frackiewicz, B., *J. Appl. Phys.*, **29**, 376 (1958).
- 4) Blackman, L. C. F., *Trans. Faraday Soc.*, **55**, 391 (1959).
- 5) Mozzi, R. L. and Paladino, A. E., *J. Chem. Phys.*, **39**, 435 (1963).
- 6) Neel, L., *Ann. Geophys.*, **5**, 99 (1949).
- 7) Bean, C. P. and Livingston, J. D., *J. Appl. Phys.*, **30**, 120S (1959).
- 8) Neel, L., *Compt. Rend.*, **228**, 664 (1949).
- 9) Groves, G. W. and Fine, M. E., *J. Appl. Phys.*, **35**, 3587 (1964).
- 10) Wirtz, G. P. and Fine, M. E., *J. Appl. Phys.*, **38**, 3729 (1967).
- 11) de Biasi, R. S. and Devezas, T. C., *J. Am. Ceram. Soc.*, **59**, 55 (1976).
- 12) Macdonald, J. R., *Proc. Phys. Soc.*, (London), **164**, 968 (1951).
- 13) Artman, J. O., *Phys. Rev.*, **105**, 62 (1957).
- 14) Vonsovskii, S. V., *Ferromagnetic Resonance*, Pergamon, Oxford, 1966.
- 15) de Biasi, R. S. and Devezas, T. C., *J. Appl. Phys.*, **49**, 2466 (1978).
- 16) de Biasi, R. S. and Devezas, T. C., *Phys. Lett. A*, **50**, 137 (1974).
- 17) Kruse III, E. W. and Fine, M. E., *J. Am. Ceram. Soc.*, **55**, 32 (1972).
- 18) Yager, W. A., Galt, J. K., and Merritt, F. R., *Phys. Rev.*, **99**, 1203 (1955).
- 19) Tannenwald, P. E., *Phys. Rev.*, **100**, 1713 (1955).
- 20) de Biasi, R. S. and Devezas, T. C., *Physica*, **86-88B**, 1425 (1977).