JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN VOL. 17, SUPPLEMENT B-I, 1962
PROCEEDINGS OF INTERNATIONAL CONFERENCE ON MAGNETISM AND CRYSTALLOGRAPHY, 1961, VOL. I

Ferromagnetic Resonance in Very Fine Particle Ferrites*

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Ferromagnetic resonance has been performed at 9,200 Mc/s on a series of very fine particle nickel ferrites. The particles ranged in size from 18Å to 200Å and the samples used are completely random. Results show that with decreasing particle size (1) the line width decreases and shows an anomalous increase at very small particle sizes (2) average g-value increases (3) power absorption normalized to 1 mg of sample decreases (4) the symmetry of the absorption line becomes more regular. These results are discussed on the basis that the magnetization and applied field are not aligned and that there is an uneven distribution of particle moments near the easy direction as opposed to the hard.

1. Introduction

The very fine particle nickel ferrites are prepared by a hydrothermal process at a constant temperature near 100°C.[1] Except for the smallest particles the particles of each sample are roughly spherical in shape, fairly uniform in size and are believed to be strain free. After vacuum extraction of water from the forming solution, the particles stick together into a brittle mass which can be crushed into a fine powder. Each grain of the powder consists of a great number of single domain particles whose crystalline orientations are completely random with respect to one another. Twenty samples were used and the average particle diameter of the samples covered a size range of 18Å to 200Å. Any doubt as to whether the smaller particles were nickel ferrites was dispelled by chemical analysis, x-ray and electron diffraction and their d. c. susceptibility behavior.[2] The ferrite powder of a sample was contained in a small glass capsule to confine it roughly in a small spherical volume, and the capsule placed in a quartz tube which contained a small quantity of DPPH.** The resonance measurements were performed with a spectrometer which operates at 9,200 Mc/s and utilizes 100 Kc/s modulation. The quantity of ferrite per sample is approximately one milligram,* ensuring that, at resonance, the detector bias was maintained in the proper range and that the cavity Q value did not vary appreciably.

2. Experimental results

The absorption lines obtained, in general, consists of a single broad peak varying in width from 700 to 1300 oersted. As shown in curve (a) of figure (1) the general tendency is for smaller particles to have smaller line widths. However, the anomalous rise of line width vs. particle size curve for the smallest particles is apparently due to a broadening mechanism different from that of randomly oriented internal fields due to magnetocrystalline anisotropy of individual particles in a sample. The line widths of

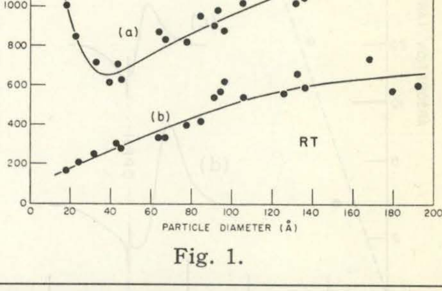

Fig. 1.

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* This work has been supported by the Wright Air Development Division under Contract No. AF (616)-7499.

** Diphenyl picryl hydrazyl, $g=2.0036$ used as reference marker.

* The small moisture content of the particles was accounted for in normalizing the power absorption.

all the samples increased with decreasing temperature over a temperature range of 103°K to 467°K. In fact this variation as a function of temperature for the medium size particles follows closely the temperature variation of the first order anisotropy constant K_1, (curve (a) of figure (2)).

The line shapes are quite regular and symmetrical for the smaller particles, becoming more and more distorted for the larger size particles. For the larger particles, the rise of the absorption curve is steeper on the low field side, the fall on the high field side being gentler. Curves (c) and (d) respectively of figure (3) show the general shapes of the differentiated absorption curves, for relatively small and relatively large particle samples. The location of the center of gravity $H_{c.g.}$ of the absorption lines shows a shift of several hundred oersted to the low field side of the DPPH marker. The magnitude of this shift is an increasing function of particle size as shown in curve (b) of figure (1). This range of shift is equivalent to an average g value ($\bar{g}$) of 2.1 to 2.5 where $\bar{g}$ is defined by $\bar{g}H_{c.g.}=2.0036\,H_{DPPH}$.

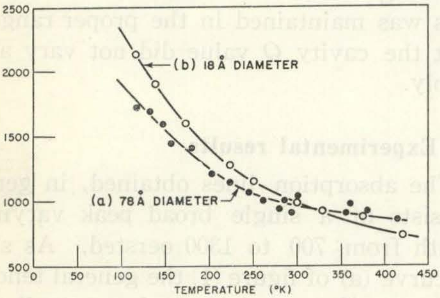

Fig. 2.

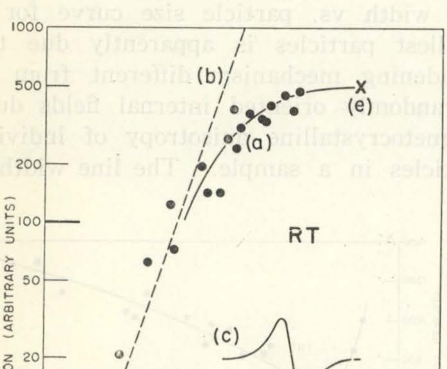

Fig. 3.

The area under the absorption curve represents the imaginary part χ'' of a. c. susceptibility or the power absorption. The absorption, normalized to 1 m. g. of sample, is not a constant for all particle sizes. Curve (a) of figure (3) shows the drastic decrease of absorption as the particle size nears the lower limit of the studied range. Data from much larger sintered particles outside the range considered, (point e of curve (a)) show a levelling off of power absorption with larger particle size. The curvature on a full logarithmic plot shows that the power absorption is not a simple power law of particle diameter. For the sake of comparison, curve (b) of figure (3) shows the d. c. susceptibility χ_0 plotted in arbitrary units. It is a straight line representing a cube law.

3. Discussion

Consider first the local magnetic field H_{loc} at a particular particle produced by its near neighbors. This random H_{loc} can easily be shown to be of the order of 100 oersted. It can be shown that H_{loc} adds symmetrically to the applied field $H_{d.c.}$. This accounts for only approximately 10% of the line broadening. It does not account for the shift and the distortion.

The correct order of magnitude of the major broadening can be found by the application of the Kittel-Bickford equation.[3] However, even the more general VanVleck and MacDonald equations indicate a symmetrical and unshifted line.[4,5] This arises from the assumption of approximate alignment of $H_{d.c.}$ and the magnetic moment in their derivations. In the X-band experiments we do not always have this simplified situation. A more general consideration shows that the uneven distribution of particle moments around the easy and hard directions can explain the distortion and the shift at least qualitatively.[6] We indicate this briefly as follows.

The general form of the resonance equation may be written as

$$\frac{\omega^2}{\gamma^2}=\frac{1}{M^2}\left[\frac{\partial^2 E}{\partial\phi_\xi^2}\cdot\frac{\partial^2 E}{\partial\phi_\eta^2}-\left(\frac{\partial^2 E}{\partial\phi_\xi\partial\phi_\eta}\right)^2\right], \quad (1)$$

where the total free energy E is a function of the direction cosines α_1, α_2, α_3 of the particle magnetization $\boldsymbol{M}$ with respect to the principal crystalline axes of the particle; alternately E may be written as a function of the small angles ϕ_ξ, ϕ_η. The meaning of ϕ_ξ, ϕ_η is obvious from figure (4), ξ, η, ζ forming a mutually perpendicular set of axes with ζ the direction of the static equilibrium magnetization.

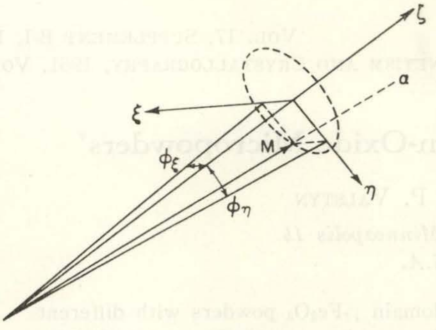

Fig. 4.

Referred to the ξ, η, ζ axes the direction cosines of $\boldsymbol{M}$ become

$$\alpha_1'=\sin\phi_\xi,\ \alpha_2'=\sin\phi_\eta,\ \alpha_3'=[1-\sin^2\phi_\xi-\sin^2\phi_\eta]^{1/2}$$

An orthogonal transformation which brings the third crystalline axis into ζ transforms equation (1) to

$$\frac{\omega^2}{\gamma^2}=\frac{1}{M^2}\cdot$$
$$\times\left[\left(\frac{\partial^2 E}{\partial\alpha_1'^2}-\frac{\partial E}{\partial\alpha_3'}\right)\left(\frac{\partial^2 E}{\partial\alpha_2'^2}-\frac{\partial E}{\partial\alpha_3'}\right)-\left(\frac{\partial^2 E}{\partial\alpha_1'\partial\alpha_2'}\right)^2\right] \quad (3)$$

We set $\dfrac{\partial^2 E}{\partial\alpha_1'\partial\alpha_2'}=0$ which is equivalent to a rotation around the ζ direction. If we consider the particle to be spherical and single domain with the first order anisotropy term in K_1 dominant, the resonance equation (3) can be shown to have the form

$$\frac{\omega^2}{\gamma^2}=\frac{1}{M^2}$$
$$[\boldsymbol{M}\cdot\boldsymbol{H}+K_1 f_1(\alpha_1\alpha_2\alpha_3)][\boldsymbol{M}\cdot\boldsymbol{H}+K_1 f_2(\alpha_1\alpha_2\alpha_3)] \quad (4)$$

which is similar to the Kittel-Bickford equation but with different forms for $f_1(\alpha_1,\ \alpha_2,\ \alpha_3)$ and $f_2(\alpha_1,\ \alpha_2,\ \alpha_3)$. These functions are evaluated for the static equilibrium direction and we can still define an effective internal field. However the effect of f_1, f_2 cannot explain the asymmetric shift of the individual particles unless the distribution of particle moments prefers the easy direction to the hard direction.

The relatively regular line shapes obtained for the smaller particles (where $KV<kT$) are probably due to the fact that the instantaneous orientations of the particles are determined by the thermal fluctuations rather than the equilibrium between the anisotropy and magnetostatic energies. The decrease in power absorption in the smaller particles is probably also related to thermal fluctuation in the population of the spin states but may also be due to a different relaxation mechanism in those smaller particles. The anomalous broadening for the extremely small particles probably arises from the irregularity in shape expected in such particles and the large surface area.

The general features of the experimental results obtained in this study are also observed in various other types of fine particle ferrites. We should like to mention that in using ferromagnetic resonance to measure the first order crystalline anisotropy constant of single domain magnetic material in fine particle form, the two extremes of highly distorted and anomalously broadened line shapes should be avoided.

References

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DISCUSSION

L. R. Bickford: Doesn't the theory of Schlömann apply to your case?

C. J. LIN: I had considered the possibility of applying Dr. Schlömann's theory, but it is very hard to believe that definite spin wave modes could be excited in such small particles.

L.R. Bickford: I mean the earlier paper which predicted the asymmetric line shape for polycrystalline materials.

C.J. Lin: In our case, each grain of the sample consists of numerous single domain, single crystal particles and hence is quite different from Schlömann's case.

T. MIYADAI: Have you examined such a sample diluted in a non-magnetic substance?

C. J. LIN: We wish very much to do such kind of experiment but it is very hard to disperse the individual particles. We can disperese some of them for electron microscopic observation but most of them stick together.

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Ferrimagnetic Resonance of Iron-Oxide Micropowders*

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Ferrimagnetic resonance phenomena of single-domain γ-Fe_2O_3 powders with different particle shape distributions were studied at two frequencies: 24,116 Mc and 9,480 Mc. One of the powders had particles with close to spherical shape, which made it possible to estimate the g-factor, the first-order anisotropy constant, and the spin-spin relaxation time of γ-Fe_2O_3. The values obtained are: $g=1.97\pm0.02$, $K_1=-3.0\times10^5$ ergs/cm³, $\tau_2=1.2\times10^{-10}$ sec. The resonance field of the acicular powders was lower than that of the spherical powder. The experimental data are in contradiction with theoretical results based on the Stoner-Wohlfarth model. The origin of this discrepancy is discussed.

Introduction

So far, few studies of the resonance phenomena of single-domain ferrimagnetic particles have been carried out. Brown, Hanton, and Morrish[1] investigated, theoretically and experimentally, the resonance absorption of suspensions of iron-oxide powders in zero applied steady magnetic field. Employing the Stoner-Wohlfarth model for a single-domain particle[2], they derived an expression for the absorption which was a simple function of the shape distribution of the particles in the powder, and their experimental results were in agreement with the theory. The present work is an investigation of the resonance phenomena of single-domain γ-Fe_2O_3 powders with different shape distributions when a steady magnetic field is applied. The results give some information on the properties of single-domain particles. Moreover, the fact that the particles of one of the powders were very close to spherical made it possible to estimate the g-factor, the first-order anisotropy constant, and the spin-spin relaxation time of γ-Fe_2O_3. An accurate determination of these quantities is at present impossible since no γ-Fe_2O_3 single crystal has as yet been grown.

Experiments

The experiments were carried out at room temperature and with two different frequencies: 24,116 Mc and 9,480 Mc. Three γ-Fe_2O_3

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* This research was supported in part by the U. S. Air Force through the Air Force Office of Scientific Research (ARDC).