

The High-Frequency Susceptibility of Certain Superparamagnetic Ferrites

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ABSTRACT

The susceptibility of small crystallites of nickel and nickel-iron ferrite, precipitated in the manner of Schuele and Deetscreek, has been studied as a function of hydrothermal growth and frequency. The degree of superparamagnetism shown by nickel ferrite crystallites grown for various periods is correlated with the broadening of the microwave resonance, and the paramagnetic relaxation frequency is found to be approximately 6 GHz. An equation has been developed which describes the size and temperature dependence of the low-frequency susceptibility of single-domain ferrite particles. The effects of ferrous ion content and solution pH on the growth rate and the susceptibility after long growth periods are related. Efforts to reduce the internal fields in the particles and increase the susceptibilities to quasi ferrimagnetic levels are discussed.

PROBLEM STATUS

This is a final report on this phase of the problem; work on other phases is continuing.

AUTHORIZATION

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THE HIGH-FREQUENCY SUSCEPTIBILITY OF CERTAIN SUPERPARAMAGNETIC FERRITES

INTRODUCTION

In certain high-frequency applications it is desirable to employ a powdered material of high magnetic susceptibility* and low physical density. Such a material has been sought for some time, but the realization of one of the above properties has always been obtained at the expense of the other. The materials now in use may exhibit susceptibilities near ten in the high-density sintered form but degrade rapidly to susceptibilities much less than one when broken into low-density powders. One solution may be the use of strongly magnetic ferrite particles, so small that the assembly of the individual moments behaves paramagnetically. Such a material is said to be superparamagnetic, and by reducing the internal fields in the particles, a susceptibility of one could be obtained at densities below 1 g/cm^3 .

Reducing the internal fields also increases the susceptibilities of nonsuperparamagnetic powders, but at the same time it lowers the frequency to which they exhibit that susceptibility. This frequency, above which the susceptibility is very nearly zero, is the resonant frequency of the individual magnetic moments in the internal fields of the particles. It is on the order of 1 GHz in many ferrites. In a paramagnetic assembly, however, the resonance would be destroyed by the thermal agitation of the moments, and the susceptibility would gradually relax to zero at some higher frequency.

Such a relaxation depends on the relaxation frequency being greater than that of the resonance. Compromising between the high susceptibilities of ferrimagnetism and the thermal fluctuations but low susceptibility of paramagnetism, the relaxation frequency for a particle in which the thermal and magnetic energies are equal is thought to be on the order of 4 GHz. Schuele, Shtrikman, and Treves (1) have investigated superparamagnetic nickel and cobalt ferrite powders prepared in a similar manner to that used here and give 0.4 GHz as a lower bound. Since the relaxation frequency in superparamagnetic ferrites could well be higher than the 4-GHz figure, reducing the internal fields in such particles could yield a material of high susceptibility and low density that would retain its susceptibility well into the GHz region.

In the next section the paramagnetic Langevin function will be modified to describe the size and temperature dependence of the susceptibility of an assembly of single-domain ferrite particles, and the susceptibility and density of a powder which may have the desired high-frequency response will be estimated. The two following sections will describe the methods of susceptibility measurement and precipitation and growth of the crystallites. The effects of ferrous ion concentration and pH of the solution will be related. Paramagnetic behavior will be shown to exist in the small-particle, nickel ferrite samples, and efforts to reduce the internal fields will be discussed. The section on high-frequency results will show the correlation between the degree of superparamagnetism exhibited at low frequencies and destruction of the microwave resonance. The theoretical fit of the low-frequency nickel ferrite data to the modified Langevin function will be used to calculate the paramagnetic relaxation frequency.

*The mks system of units is used throughout this report, and the word susceptibility and symbol χ' denote the real part of the complex initial susceptibility.

THEORY

Ferrite particles smaller than approximately 150 \AA in radius consist of a single domain in which all the spins of the individual atoms act cooperatively to form a single large magnetic moment. Since superparamagnetism is apparent only for particles of even smaller size, the discussion below will be limited to single-domain particles where the susceptibility arises only from the simultaneous rotation of the spins.

The magnetic moment resides in many "internal fields" within each particle. The crystalline anisotropy itself, which is a function of the chemical composition of the ferrite, gives rise to four preferred directions in each crystallite of nickel ferrite and magnetite (ferrous ferrite). These four bi-directional preferred directions, along each of the body diagonals of the cubic crystal, may be thought of as eight unidirectional internal magnetic fields paired oppositely along each diagonal. Shape and other anisotropies also give rise to "internal fields," and the net real field from neighboring particles may add still another.

Consider a large, single-domain particle in which the moment is tightly bound to one of the internal fields. In such a case the moment m behaves as if it were in a single magnetic field H . It will align itself with H such that its most probable component in that direction is (Ref. 2)

$$m_H = mL(a), \quad a = m\mu_o H/kT, \quad (1)$$

where $L(a)$ is the Langevin function

$$L(a) = \coth a - \frac{1}{a} \quad (2)$$

shown in Fig. 1, and is equal to the cosine of the most probable angle between m and H , $\mu_o = 4\pi \times 10^{-7}$ wb/amp-meter, k is Boltzman's constant, T is the Kelvin temperature, and a is therefore the ratio of the maximum magnetic energy of interaction between m and H to the thermal energy of the magnetic moment. Of course for a large particle, $L(a)$ is very nearly unity and the moment fluctuates with only small amplitude about the internal field. If a small measuring field h is applied at an angle θ with respect to H , the change in m_H in the direction of h is

$$\Delta m_H = m_H \frac{h}{H} \sin^2 \theta. \quad (3)$$

Assuming an "average" m and H in a polycrystalline assembly but a random distribution of directions of H ,

$$\overline{\Delta m_H} = \frac{2}{3} m_H \frac{h}{H} \quad (4)$$

is the average moment in the direction of h (Ref. 3a). The net magnetization that follows h at low frequencies and the resulting susceptibility are then

$$M_h = \frac{2}{3} N m \frac{h}{H} L(a) \quad (5)$$

and

$$\chi' = \frac{M_h}{h} = \frac{2}{3} \Lambda p \frac{M_s}{H} L(a), \quad (6)$$

where N is the number of particles per unit volume, Λ is the volume fraction of ferrite in the powdered sample, and for a single-domain particle m is equal to the average spontaneous magnetization per unit volume times the volume of the particle. The average spontaneous magnetization per unit volume may be written pM_s , where M_s is the saturation magnetization of the bulk ferrite and p is a predominantly volume-dependent factor between zero

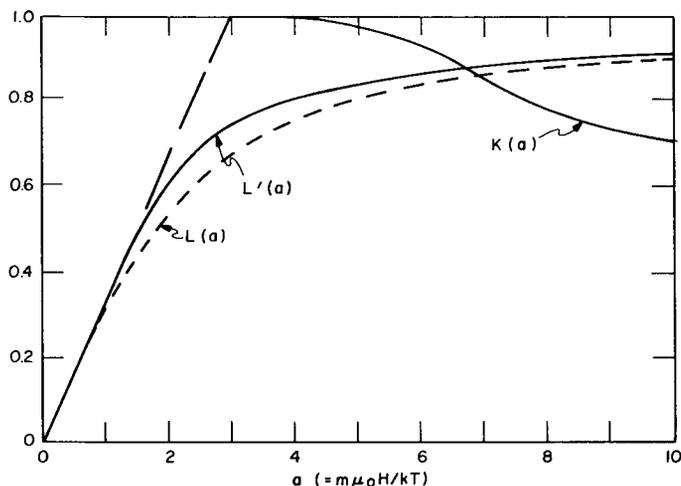


Fig. 1 - The Langevin function $L(a)$, modified Langevin function $L'(a)$, and $K(a)$, given by Eqs. (9) and (10), as a function of the ratio of magnetic energy to thermal energy.

and one. This as yet unspecified factor arises from the nonalignment of the spins at and near the surface of the particle with respect to the uniformly aligned interior spins. Two main reasons for such nonalignment are the lack of complete exchange interactions with neighboring spins and the influence of surface anisotropies (4). For large particles, ρ is near unity, but as the particle size decreases and the surface-to-volume ratio increases, the nonalignment of the surface spins may cause an appreciable reduction in ρ . Possibly the lowest value of ρ encountered during this work was 0.2, derived from susceptibility and saturation magnetization measurements on polycrystalline assemblies of particles approximately four unit cells in diameter. However, other evidence, to be discussed later, indicates that the reduction was not due entirely to this effect and 0.2 may be a gross underestimate.

As one looks at particles of smaller and smaller volume, a decreases and the excursions of m about H grow larger. The susceptibility contributed by the alignment of the moment with this original internal field thus decreases with $L(a)$. However, the wandering magnetic moment spends an increasing amount of time in regions dominated by other internal fields and intermediate regions. The alignment of the moment with the "other internal fields," being equally as random in direction as the original field, adds to the susceptibility. Thus, one would expect a slightly higher susceptibility than that determined by $L(a)$.

For extremely small particle sizes or very high temperatures, assuming $\rho \equiv 1$ or an infinite Curie temperature, the ratio of magnetic energy to thermal energy is very small and the moment is essentially free of the internal fields. In such an extreme case the aggregate behavior of the ferrimagnetic moments may be considered to be truly paramagnetic. The susceptibility (2) is then given by

$$\chi' = \frac{Nm}{h} L\left(\frac{m\mu_0 h}{kT}\right) = \mu_0 \rho^2 \frac{\Delta V M_s^2}{3kT}, \quad (7)$$

where $L(a)$ is very nearly equal to $a/3$ for very small values of a and V is the volume of the particle. Applying the same approximation to Eq. (6), it is seen that the results are identical except for an averaging factor of two-thirds.

It therefore appears that the susceptibility of an assembly of single-domain ferrite particles may be given empirically by

$$\chi' = K(a) \Lambda p \frac{M_s}{H} L'(a), \quad (8)$$

where $L'(a)$ is a modified Langevin function that is equal to $L(a)$ for very small and very large values of a and slightly greater than $L(a)$ for intermediate values and $K(a)$ is a factor equal to unity for small values of a and equal to two-thirds for large values of a . Two arbitrarily chosen functions for $L'(a)$ and $K(a)$ are shown in Fig. 1. They are given by

$$L'(a) = \begin{cases} a/3 & \text{for } a \leq 1.3 \\ \frac{a^3 + 10.7a^2 + 8.47a + 1.2}{a^3 + 11.7a^2 + 18.47a + 14.7} & \text{for } a \geq 3. \end{cases} \quad (9)$$

where the two are joined by a smooth curve for $1.3 < a < 3$, and

$$K(a) = \frac{(2/3)a^7 + 10^6}{a^7 + 10^6}. \quad (10)$$

Substituting the above functions into Eq. (8), using the temperature variation of the saturation magnetization for bulk nickel ferrite (3b) with $p \equiv 1$, assuming the magnitude and temperature variation of the internal field to be that due to the first-order crystalline anisotropy constant (5), and normalizing the susceptibility to 10 at 298°K, the temperature dependence of the susceptibility is shown by the discrete values in Fig. 2. The four values of a at 298°K were chosen to give an approximate fit to the experimental data shown by the solid curves for samples of nickel ferrite of varying particle size. Although Eq. (8) with the two functions given in Eqs. (9) and (10) do not describe the behavior of the susceptibility in detail, the relative magnitudes of the calculated and experimental susceptibilities agree within 10%. Furthermore, due to the temperature variation, the results presented in Fig. 2 cover values of a from 0.6 to 12.5. The experimental data for samples of smaller particle sizes than those shown here also agree with the calculated temperature dependence of the susceptibility; hence, the general shape of $K(a)$ times $L'(a)$ is approximately correct. For large values of a , Eq. (8) approaches the well-known approximation of

$$\chi' = \frac{2}{3} \Lambda \frac{M_s}{H} \quad (11)$$

for large, single-domain particles. Thus, the magnitude of the susceptibility given by Eq. (8) and of the two functions $K(a)$ and $L'(a)$ is approximately correct.

Assume the parameters of a powdered sample to be

$$M_s = \alpha(2.7 \times 10^5 \text{ amp/meter})$$

$$r = \beta(47.5 \text{ \AA})$$

$$\Lambda = \gamma(8\%)$$

$$\mu_o H = \delta(0.034 \text{ wb/meter}^2).$$

If $\alpha = \beta = \gamma = \delta = 1$, the values are those for nickel ferrite particles 47.5 Å in radius, packed to a density (Λ times the density of the ferrite) of 0.43 g/cm³, and acted on by the internal fields due only to the crystalline anisotropy of the ferrite. Such a limitation would arise only for nonstressed spherical particles separated sufficiently as to be

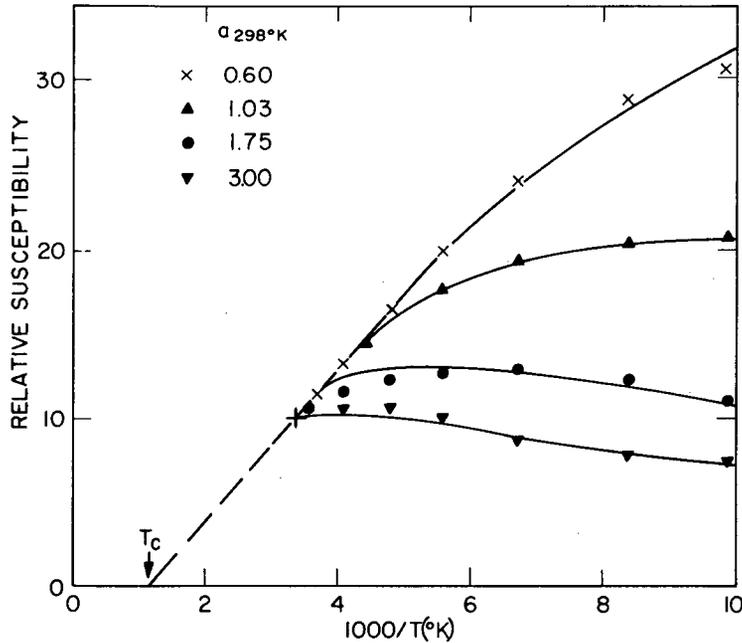


Fig. 2 - The temperature dependence of the susceptibility as given by Eq. (8), when normalized to 10 at 298°K. The solid curves are those for the nickel ferrite powders shown in Fig. 6 corrected for the error in temperature.

noninteracting and is taken here only as an example. Given the above parameters and $p = 1$, Eq. (8) becomes

$$\chi' = 0.80 \alpha \gamma \delta^{-1} K(a\beta^3 \delta) L'(a\beta^3 \delta) \tag{12}$$

at room temperature. Under the condition that

$$m\mu_o H \leq kT, \tag{13}$$

i.e.,

$$\alpha\beta^3 \delta \leq 1, \tag{14}$$

$L'(a)$ is equal to $a/3$, $K(a)$ is essentially unity, and the susceptibility is

$$\chi' = 0.27 a^2 \beta^3 \gamma. \tag{15}$$

Equation (15), as another form of Eq. (7), and the experimental confirmation of the paramagnetic relaxation frequency being greater than 0.4 GHz for nickel and cobalt ferrites obeying the equality in Eq. (13) form the bases for the present work. If the internal fields in the above example could be reduced by a factor of four, Eq. (14) would allow a like increase in the volume of each particle, resulting in a susceptibility slightly greater than one at 0.43 g/cm³. This is somewhat optimistic in that ferrites generally show internal fields two to three times larger than those resulting from the crystalline internal fields alone. Thus, one would expect to have to reduce the internal fields by a factor of six to obtain a susceptibility of one at 1 g/cm³. If such a reduction is possible, the resulting material would prove useful in a number of applications.

The realization of the desired material therefore depends on two factors. First, the internal fields in the superparamagnetic particles must be lowered by a factor of six to increase the susceptibility. Second, the relaxation frequency must be high enough to allow the material to retain its susceptibility well into the GHz region if it is to be of practical value.

SUSCEPTIBILITY MEASUREMENTS

The powders produced during this investigation were measured at 1 kHz and from 1 to 12 GHz at a density of 1.4 g/cm^3 . The 1-kHz measurements provided a general evaluation of the sample and the determination of its low-frequency susceptibility. These values were obtained by noting the change in mutual inductance of a 1.3-millihenry inductor upon insertion of a cylindrical sample into one of its two oppositely wound secondaries. The method was calibrated by comparing such readings for samples of differing susceptibilities with those obtained for the same samples in spherical holders. Computed fields and mutual inductances then yielded the actual susceptibility as a function of change in mutual inductance.

Measurements of susceptibility as a function of temperature were obtained using a cylindrical holder with the bulb of a hydrocarbon thermometer inserted through one end. The exterior of the inductor was bathed in liquid nitrogen until the sample reached 77°K . The device was then removed from the bath, and the changes in mutual inductance (sample-in, sample-out) were noted as the powder warmed to room temperature. The bulb of the thermometer, being located at the end of the holder through which most of the heat entered the sample, led to slightly erroneous temperature readings. The effect of this on the data will be discussed later.

The microwave measurements were taken at 1, 2, 3, 4, 5.5, 8.2, 10, and 12 GHz. Data at the first five of these frequencies were taken in a 1/2-in.-O.D., 7/32-in.-I.D. coaxial slotted line. The powders were packed into shorted holders 2.5 mm deep and hot wax was spread over the surface. The measurements were continued at 8.2, 10, and 12 GHz in a waveguide slotted line on samples 1 mm thick and prepared in the same manner. Although 93% of the microwave measurements show a liberally estimated error of ± 0.02 or less, the rise in susceptibility from 8.2 to 12 GHz is 0.070 ± 0.025 for all samples measured and is considered to be a systematic error. The susceptibilities being measured are very small, and such a rise may be due to the excitation of higher-order waveguide propagation modes within the sample.

PRECIPITATION AND GROWTH OF PARTICLES

Schuele and Deetscreek (6), using the basic method due to Lefort (7), have prepared extremely small crystallites of nickel ferrite and studied their hydrothermal growth at 100°C . They found initial crystallite sizes of about 40 \AA , which grew to 180 \AA in the first 50 hours and then saturated at 190 \AA to at least 400 hours of growth. Lin (8) looked for superparamagnetism in nickel ferrite prepared by the Schuele and Deetscreek method and found such behavior in the smaller particles. This method therefore provided a means by which superparamagnetic particles could be prepared and studied as a function of size.

The method of preparation used in this investigation was essentially the same as that used by Schuele and Deetscreek. One mole of nickelous chloride and 2 moles of ferric chloride were dissolved in 2 liters of distilled water and poured quickly, with stirring, into 8 moles of sodium hydroxide dissolved in 1 liter of distilled water. The nickel ferrite precipitate thus formed was poured into smaller beakers which were set in boiling water. After the desired period of hydrothermal growth, the precipitate was filtered and air

dried for 10 to 15 days. This method differed from that of Schuele and Deetscreek in that after dissolving the chlorides and hydroxide in warmed water, precipitation was initiated with the solutions at room temperature instead of 100°C. The lower temperature was used to impede the initial growth of the crystallites in the exothermic reaction of formation. Magnetite and nickel-iron ferrites were prepared by substituting the appropriate chlorides in place of nickelous chloride.

Curves 1 and 2 in Fig. 3 show the typical increase in susceptibility with hydrothermal growth for nickel ferrite. These curves are somewhat similar to those obtained by Schuele and Deetscreek for the growth in particle size, but they do not saturate. A schematic representation of the growth is shown in Fig. 4. Assuming a saturation in particle size after 50 hours of growth, a chemical change must be assumed at the elevated temperature which leads to an increasing susceptibility. This indicates that products other than nickel ferrite are formed during precipitation. Susceptibility and magnetization measurements performed on nickel ferrite and other ferrites prepared in the same manner yield values 20% to 80% of what would be expected from theoretical calculations, assuming $p = 1$ in Eq. (6). Although the low experimental values may be attributable in part to the factor p , the increasing susceptibility long after particle-size saturation should have been attained indicates that the bulk of the reduction is due to the presence of a phase other than the ferrite. The presence of a nonmagnetic phase does not preclude a determination of the behavior of the susceptibility for such particles, but it does prevent comparisons of the magnitudes of experimentally and theoretically determined susceptibilities and the accurate calculation of size, size distributions, and other properties.

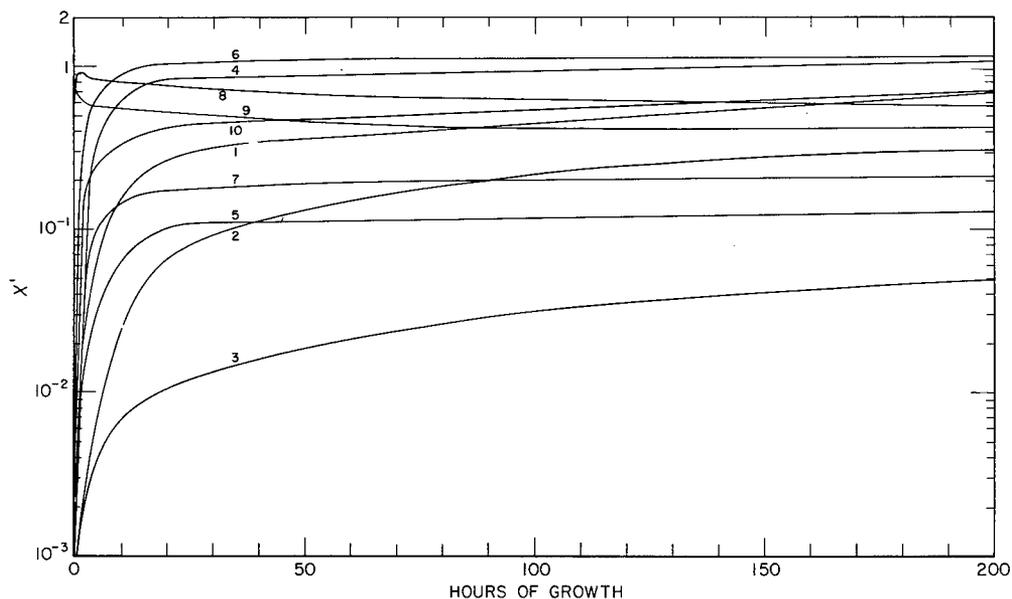


Fig. 3 - The growth curves for various samples of nickel, nickel-iron, and ferrous ferrites. The curves are identified in Table 1.

Table 1
Identification of Growth Curves in Fig. 3

| Curve | Ferrite | pH |
|-------|--|----------|
| 1 | NiFe_2O_4 | - |
| 2 | NiFe_2O_4 | Neutral |
| 3 | NiFe_2O_4 | Basic |
| 4 | $\text{Ni}_{0.9}\text{Fe}_{2.1}\text{O}_4$ | Neutral |
| 5 | $\text{Ni}_{0.9}\text{Fe}_{2.1}\text{O}_4$ | Basic |
| 6 | $\text{Ni}_{0.8}\text{Fe}_{2.2}\text{O}_4$ | Neutral |
| 7 | $\text{Ni}_{0.8}\text{Fe}_{2.2}\text{O}_4$ | Basic |
| 8 | Fe_3O_4 | - |
| 9 | Fe_3O_4 | - |
| 10 | $\text{Ni}_{0.85}\text{Fe}_{2.15}\text{O}_4$ | (Basic?) |

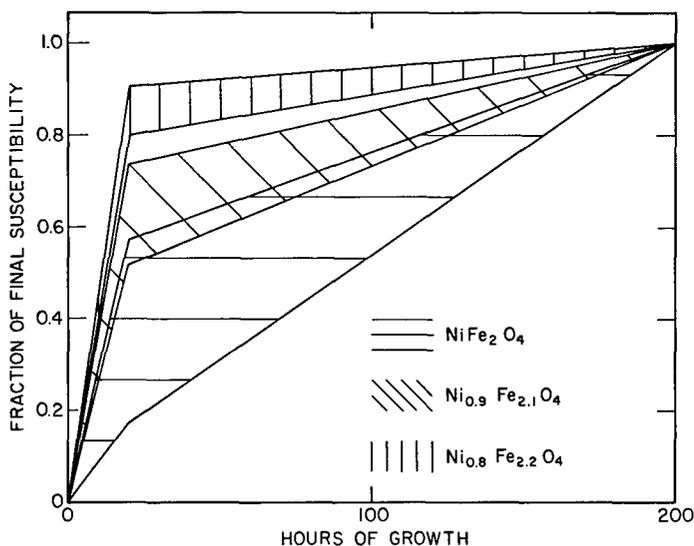


Fig. 4 - A schematic representation of the growth of nickel and nickel-iron ferrites

Figure 3 also shows the growth curves for nickel ferrite, magnetite, and certain mixed nickel-iron ferrites in neutral and basic solutions. While the pH of the solution has no noticeable effect on the relative rate of growth of the ferrite, growth in basic solutions of approximately pH 13 leads to susceptibilities lower by factors of five to nine after comparable periods of hydrothermal growth. The introduction of negative hydroxyl ions reduces the positive ion screening between the small particles and allows a greater degree of aggregation. Such aggregation may impede the dissolution of the smaller particles and growth of the larger particles, leading to lower susceptibilities.

Under the condition given in Eq. (13), the susceptibility of an assembly of superparamagnetic particles as a function of temperature is

$$\chi' = \frac{\Lambda \mu_o V_p^2}{3k} \left\{ \frac{[M_s(T)]^2}{T} \right\}, \quad (16)$$

where the variation in saturation magnetization modifies the strictly $1/T$ dependence of molecular paramagnetism. A representative plot of susceptibility vs $1/T$ is shown in Fig. 5. The straight line through the origin was found by correcting the room temperature susceptibility for the decrease in saturation magnetization from 0°K . This would be the curve followed if M_s were independent of temperature. The variation in saturation magnetization for bulk nickel ferrite (3b) was then used to correct the straight line for the expected behavior from room temperature, 298°K , to the Curie temperature $T_C = 858^\circ\text{K}$. On extending the dashed curve it is seen that both it and the experimental curve are straight lines to 250°K and differ only in slope. The steeper slope of the experimental data has a zero-susceptibility intercept of 685°K , but it is unlikely that this represents an actual 173° lowering of T_C in the small particles. As described previously, the position of the thermometer relative to the bulk of the sample leads to a reading slightly higher than the "effective temperature" of the powder. This temperature difference would be zero at 77°K , rise to a maximum at some intermediate temperature, and fall again to zero at room temperature. The steeper slope of the experimental curve represents a temperature error of 4 degrees at 250°K . This reasonable difference verifies the essential validity of the measurement and indicates that the data, allowing for the discrepancy in temperature, do follow the theoretical curve to 250°K . The behavior then departs from the curve given by Eq. (16) due to the decrease in thermal energy at the lower temperatures.

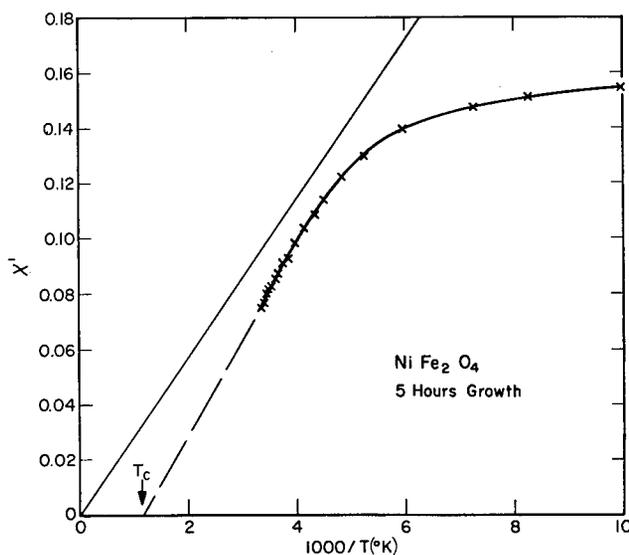


Fig. 5 - The temperature dependence of the susceptibility of nickel ferrite after 5 hours of hydrothermal growth

The theoretical curve is very close to being a straight line at the temperatures considered here; hence, the extent to which the experimental data follow a straight line of proper slope is an indication of the degree of superparamagnetic behavior. Several raw data temperature curves normalized to a relative susceptibility of ten at room

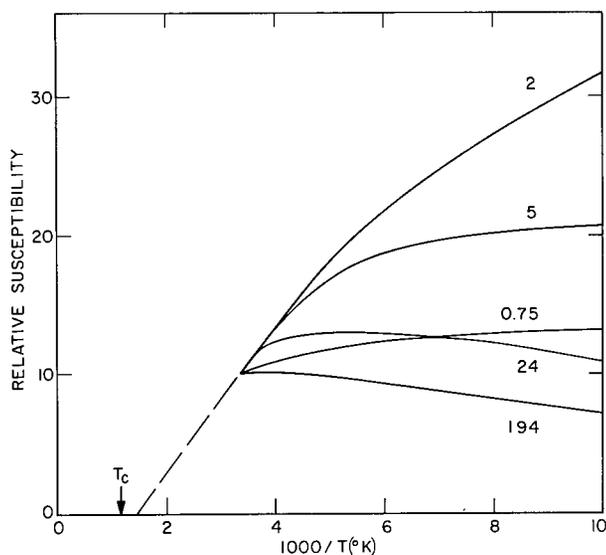


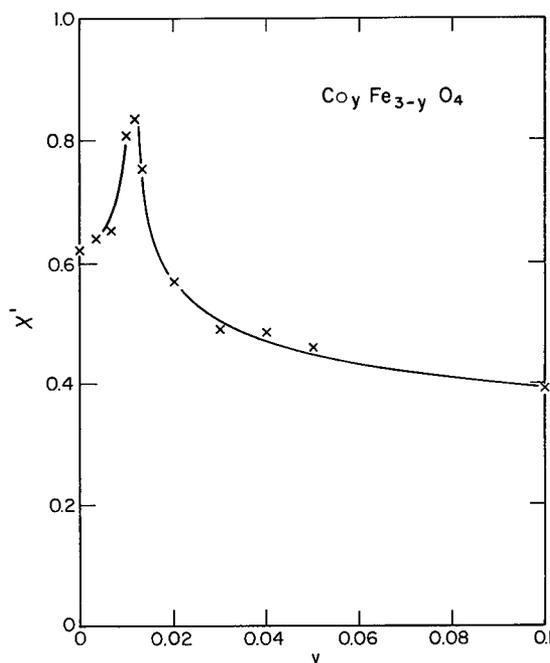
Fig. 6 - The uncorrected temperature dependence of the susceptibility of 2-, 5-, 24-, and 194-hour samples of NiFe_2O_4 and a 0.75-hour sample of $\text{Ni}_{0.85}\text{Fe}_{2.15}\text{O}_4$ normalized to 10 at 298°K

temperature are shown in Fig. 6. The decrease in paramagnetic behavior with growth time is evident for the 2-, 5-, and 24-hour samples of nickel ferrite, and the 194-hour sample fails to show any superparamagnetism.

The 24-hour sample of nickel ferrite, which appears near the threshold of paramagnetic behavior, has a low-frequency susceptibility of 0.28. This measured value is in keeping with that expected for such a powder, and a lowering of the internal fields could produce a material with the desired properties. The internal fields of a particle arise mainly from shape and crystalline anisotropies. The unit cell of a ferrite is cubic, 8 to 9 Å on an edge. Thus, a crystallite 47.5 Å in radius is only eleven unit cells in diameter and of unknown shape. Although the shape is unknown and uncontrollable at such sizes, its anisotropy may benefit slightly from chemical changes designed to reduce the crystalline anisotropy.

The data of Bickford, Brownlow, and Penoyer (9) show a zero in the first-order crystalline anisotropy constant of magnetite when cobalt is substituted into approximately 1% of the lattice sites normally occupied by ferrous ions. From Eq. (11), the internal field of a large particle is proportional to the saturation magnetization divided by the susceptibility. The data obtained for several 200-hour samples of cobalt-iron ferrite are shown in Fig. 7. Assuming the saturation magnetization to be nearly constant for small substitutions of cobalt, only a 26% decrease in the internal field was found for 1.15% cobalt. The sharpness of the variation near 1.15% indicates that a possible further reduction was not seen due to the difficulties in obtaining the precise mix desired. Although there is much published literature to draw on if magnetite is used as the basic ferrite, curves 8 and 9 of Fig. 3 show that the Schuele and Deetscreek method of preparation does not yield small particles. The two curves shown are extreme patterns with other curves showing a level or gradually decreasing susceptibility. It appears that magnetite is very soluble and rapidly attains its equilibrium size in the exothermic reaction of formation. Slight differences in the conditions of precipitation may therefore account for the $\pm 20\%$

Fig. 7 - The 200-hour susceptibility of cobalt-substituted magnetite as a function of cobalt concentration



variation in susceptibility observed for different samples of magnetite before hydrothermal growth. The substitution of cobalt into nickel ferrite and the mixed nickel-iron ferrites to be discussed next yielded much smaller changes in the internal field.

The first- and second-order crystalline anisotropy constants of two nickel-iron ferrites measured by Yager, Galt, and Merritt (10) indicated that a mixed ferrite would have a lower internal field. Several series of mixed ferrites were prepared and the combined data are shown in Figs. 8 and 9. The two curves for the zero-hour samples in Fig. 8, the lower of which is repeated in Fig. 9, show the two types of behavior found for powders prepared in seemingly the same manner. It appears that the upper curve represents a physical mix of nickel and ferrous ferrites while the lower curve represents a chemically mixed nickel-iron ferrite. After 200 hours of hydrothermal growth, however, both types of material yield the 200-hour curve of Fig. 8. Such behavior also indicates the high solubility of magnetite. While the dissolution and condensation rates are in equilibrium for the magnetite particles, the growing nickel and nickel-iron ferrites incorporate the dissolved magnetite into their lattices to yield an increasing nickel-iron ferrite concentration. The growth curves of several nickel-iron ferrites are shown in Figs. 3 and 4, where an acceleration of growth rate is seen with increasing iron content.

The 200-hour susceptibility of $\text{Ni}_{0.85} \text{Fe}_{2.15} \text{O}_4$ indicates a halving of the total internal field. The full reduction in the crystalline anisotropy is probably masked by shape and other anisotropies, but the total internal field must be reduced to increase the susceptibility. The susceptibility variation with temperature for a 0.75-hour chemically mixed $\text{Ni}_{0.85} \text{Fe}_{2.15} \text{O}_4$ powder is shown in Fig. 6. The nickel-iron ferrites do not show a straight-line portion of proper slope and hence fail to show superparamagnetic behavior on the basis of this test. The short-growth-period samples, however, do show high-frequency susceptibility variations very similar to those of superparamagnetic nickel ferrite powders.

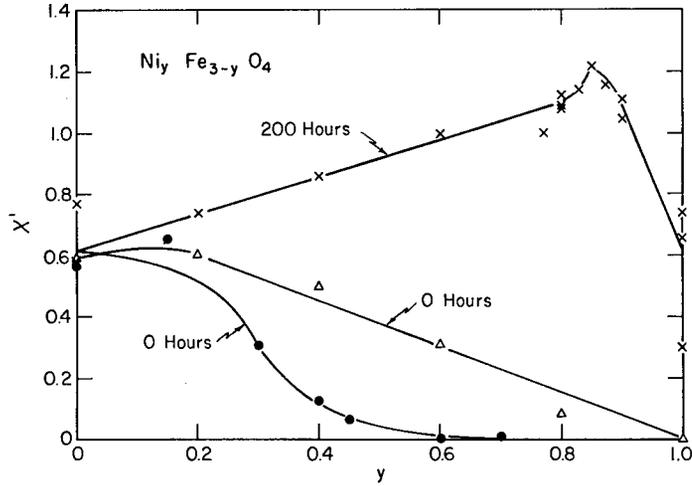


Fig. 8 - The zero and 200-hour susceptibility of nickel-iron ferrites and suspected nickel ferrite-iron ferrite mixtures as a function of nickel concentration

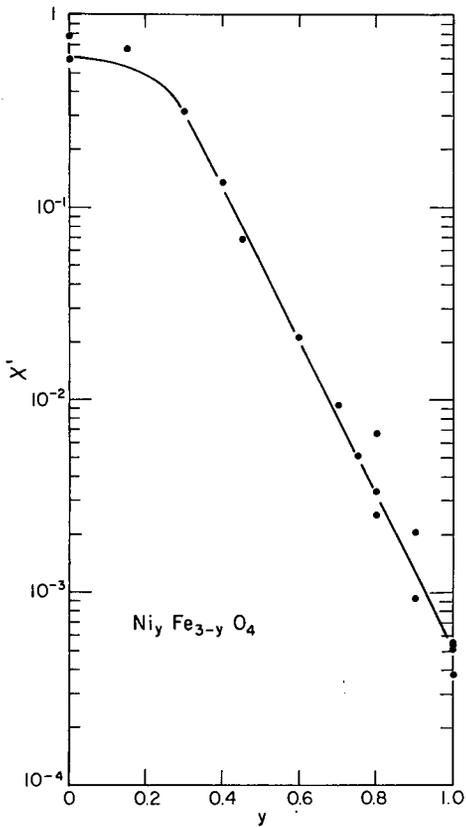


Fig. 9 - The zero-hour susceptibility of nickel-iron ferrites as a function of nickel concentration

HIGH-FREQUENCY RESULTS

In general the susceptibility of an assembly of large, single-domain particles is nearly constant from dc to microwave frequencies, where it drops precipitously due to the collective spin resonance. Magnetite and the long-growth-period samples of nickel and nickel-iron ferrite exhibit this behavior in Figs. 10, 11, and 12. The resonance, however, broadens monotonically with decreasing growth period in the nickel and nickel-iron ferrites and degenerates into an apparent relaxation for short growth periods. This is the behavior one would expect as the magnetic energy decreases and thermal fluctuations begin to destroy the resonance of the individual moments.

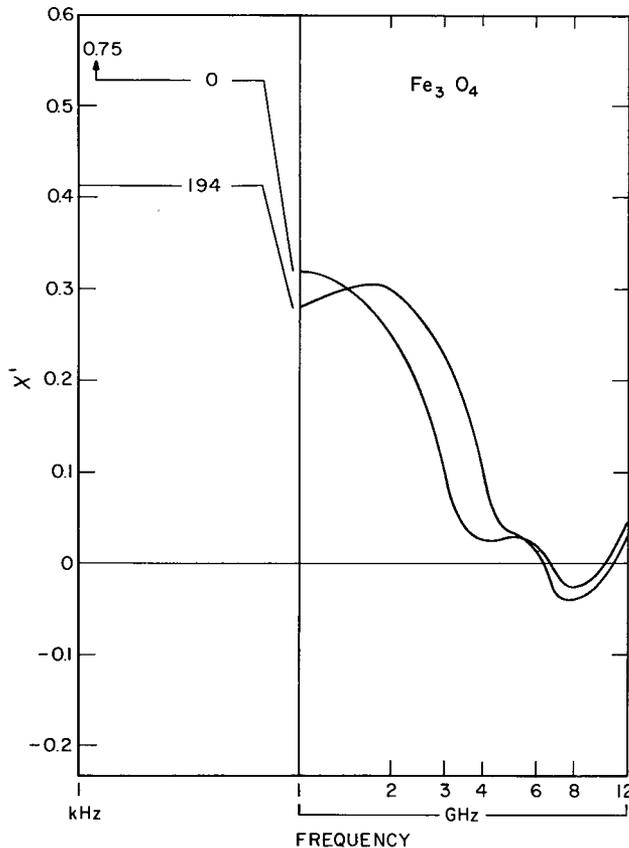


Fig. 10 - The frequency dispersion of the magnetite sample represented by curve number 9 in Fig. 3

That the relaxation in nickel ferrite is thermally induced is evidenced by the correlation between the degree of superparamagnetic behavior exhibited by each sample in Fig. 6 and its high-frequency dispersion. The 24-hour sample, which appears to be near the threshold of paramagnetism in Fig. 6, also shows an intermediate behavior in its dispersion. Assuming that this is the result of the resonance and the relaxation frequencies being approximately equal for this size particle, the relaxation frequency for an infinitely small particle or at an infinitely high temperature is (Ref. 1)

$$f_0 = f \cdot e^a = 1 \cdot e^{1.75} = 5.8 \text{ GHz},$$

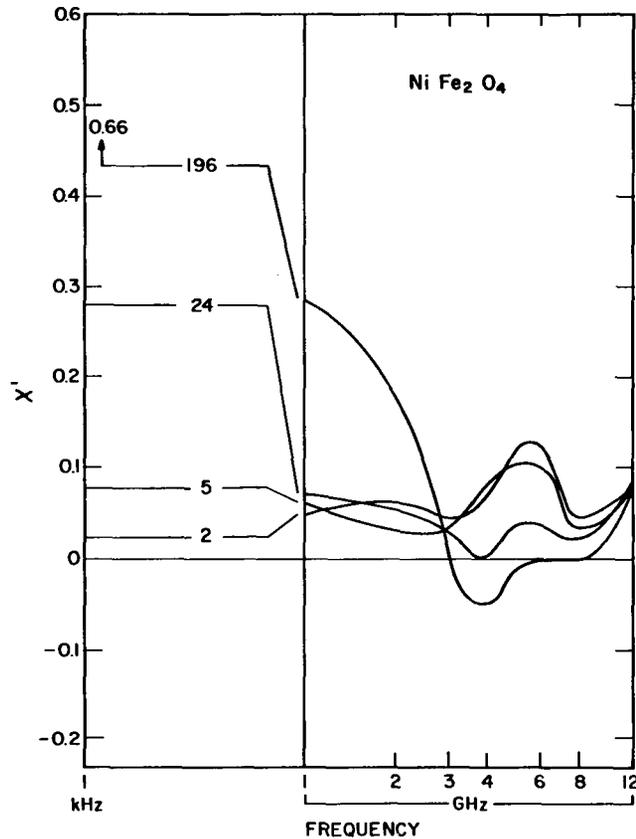


Fig. 11 - The frequency dispersion of the nickel ferrite sample represented by curve number 1 in Fig. 3

where f is the relaxation frequency for a particle described by $a (= m\mu_0 H/kT)$, and the resonance frequency for nickel ferrite has been found to be approximately 1 GHz. The essential validity of the above assumption may be seen by considering the 2-hour sample. For this sample a is approximately 0.6 and the relaxation frequency is therefore 3.2 GHz. This is above the natural resonance frequency of 1 GHz, which has been destroyed, but it is below the resonance at 5.5 GHz, which is retained. Thus, it is seen that the relaxation frequency for a given particle must exceed the resonance frequency by only a small factor to have the desired destructive effects.

The short-growth-period powders of $\text{Ni}_{0.85}\text{Fe}_{2.15}\text{O}_4$, although not indicating superparamagnetism on the basis of susceptibility variation with temperature, show a high-frequency dispersion similar to that found for superparamagnetic nickel ferrite. The additional broadening of the 5.5-GHz resonance indicates a slightly higher f_0 than that found for nickel ferrite. Thus, the relaxation frequency appears to be a function of the chemical composition of the ferrite. The change, however, is small and does not portend that changes in the relaxation frequency would be more easily achieved than those in reducing the internal fields. While halving the internal fields increased the low-frequency susceptibility of $\text{Ni}_{0.85}\text{Fe}_{2.15}\text{O}_4$, the high-frequency susceptibilities of those samples exhibiting relaxational effects do not show an increase over that of nickel ferrite.

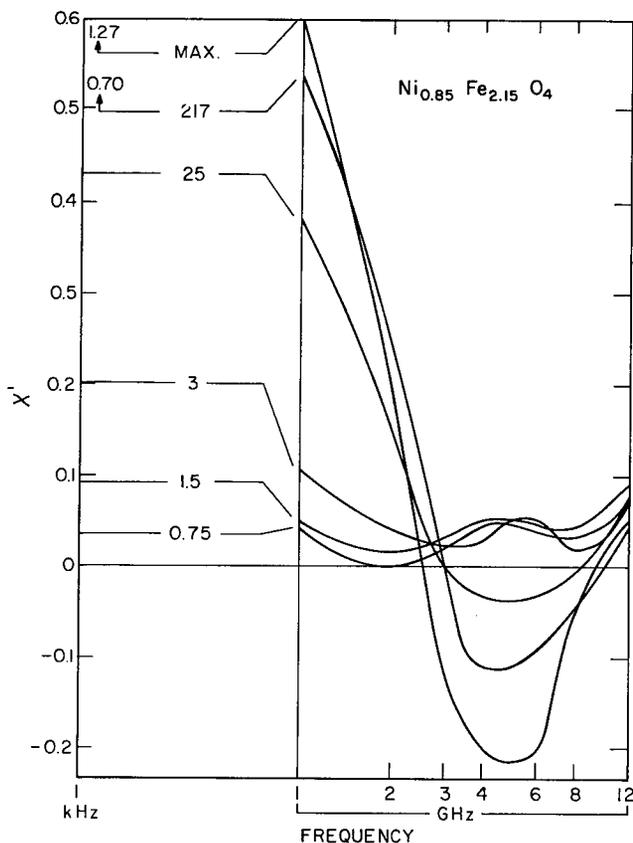


Fig. 12 - The frequency dispersion of the $\text{Ni}_{0.85}\text{Fe}_{2.15}\text{O}_4$ sample represented by curve number 10 in Fig. 3 and a maximum growth powder grown in a neutral solution

CONCLUSION

In summary, small crystallites of nickel and nickel-iron ferrite have been prepared by rapid precipitation from relatively concentrated solutions of the appropriate salts and grown hydrothermally at 100°C . In those crystallites grown for short periods the normal ferrimagnetic resonance at zero applied field is destroyed, and the resulting frequency dependence can be interpreted as a thermal relaxation. An equation has been developed which describes the low-frequency susceptibility of single-domain particles and, in conjunction with the high-frequency data, allows one to estimate the paramagnetic relaxation frequency of nickel ferrite to be approximately 6 GHz. The reductions in the internal fields necessary for high susceptibilities in superparamagnetic powders were not achieved and consequently the susceptibilities are small.

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