High-frequency permeability of Ni and Co particle assemblies

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A coaxial transmission line was constructed, characterized, and calibrated for the frequency dependent measurement of complex relative permeability (μ_r) and complex permittivity (ϵ_r). The permeability of Ni powder with a grain size of $< 1 \mu\text{m}$ was measured as a function of packing density to verify the system performance. 8–10 nm diameter Co nanoparticles were synthesized, dried to a powder, and measured. The real part of the permeability for the Co nanoparticles decreased over time as a result of oxidation, and decreased the overall magnetic volume due to the formation of an antiferromagnetic CoO shell. Similarly, the imaginary part of the permeability decreased as a function of oxidation. This was attributed to the insulating CoO shell reducing eddy current losses in the nanoparticle composite. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4866234>]

I. INTRODUCTION

The high-frequency properties of magnetic nanoparticles are important for possible use as high frequency inductors, electromagnetic wave absorbers,¹ for local hyperthermia,² for biosensor fabrication,³ for drug targeting,⁴ and as contrast agents for magnetic resonance imaging.⁵ In many of these applications, there will be significant magnetostatic interactions between nanoparticles, which can lead to complex behavior in the time- and frequency-dependent magnetization.⁶

This article describes the construction, calibration, and use of a coaxial transmission line⁷ to measure scattering parameters and calculate the related frequency-dependent relative magnetic permeability (μ_r) and dielectric permittivity (ϵ_r) for dense assemblies of cobalt particles in the 10 MHz–10 GHz frequency range. Unlike transmission line techniques utilizing other geometries, the coaxial geometry is unique in allowing the quantitative measurement of permeability and permittivity. This is a great advantage of our system over stripline geometries and offers a wider range of accessible frequencies than waveguide techniques.

The effect of oxidation on the high frequency electric and magnetic properties is important to understand for any potential application, especially for the oxidation-prone transition metal nanoparticles. We investigate changes in μ_r and ϵ_r in an assembly of cobalt particles as it oxidizes over several days. Two-port scattering parameter measurements were made using a vector network analyzer (VNA), and the permeability and permittivity were calculated according to the Nicolson-Ross-Weir method.^{8,9}

II. EXPERIMENTAL

A. Samples preparation

ϵ -Co nanoparticles coated with oleic acid (OA) were synthesized by the thermal decomposition of di-cobalt

octacarbonyl ($\text{Co}_2(\text{CO})_8$) in 1,2-dichlorobenzene.¹⁰ The particles were measured to be 8–10 nm in diameter using a JEOL 2000 $\times$ transmission electron microscope (TEM). After synthesis, the Co nanoparticles were precipitated by the addition of ethanol, collected with a permanent magnet, then dried under vacuum, resulting in a black powder. This rapid precipitation leads to the formation of a disordered nanoparticle assembly. The packing density was calculated as the ratio of the sample mass and toroidal sample volume.

Two commercially available Ni powders (Aldrich, 99.8%) with an average grain size of less than $1 \mu\text{m}$ and with an average grain size of less than 100 nm were used to study the effect of packing density on the permeability.

B. Measurements of $\mu_r(f)$ and $\epsilon_r(f)$

A custom coaxial transmission line was developed for measurements up to 10 GHz and was interfaced with an Agilent Technologies E5071C VNA. In the sample holder, a toroid of the magnetic material being measured replaces the dielectric around the center electrode as shown in Figure 1. Our transmission line was designed to have a characteristic impedance of 50Ω and to mate with commercially available N-type connectors. Care was taken to assure our sample length of 4 mm was less than one-quarter the wavelength at our maximum measuring frequency of 10 GHz.

The full two-port calibration using a combination of thru, short, open, and 50Ω load terminations was performed together with the port extension feature to take into account all losses, phase shifts, and reflections till the reference planes (marked in Figure 1 with dashed lines), the gaps L_1 , L_2 between the sample and these planes were found by measuring the S_{21} -parameter for the empty sample holder ($\tilde{S}_{21}^{\text{empty}}$) and assuming $L_1 \approx L_2$, following Baker-Jarvis:¹¹

$$L_1 \approx L_2 \approx \frac{c}{i4\pi f} \ln \left(\frac{1}{\tilde{S}_{21}^{\text{empty}}} \right) - \frac{L}{2}, \quad (1)$$

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FIG. 1. (a) Schematic cross-section of the coaxial sample holder with the sample location shown in yellow (color online). The magnetic sample is seated between Teflon bushings shown in blue (color online) that can contain both powdered and liquid samples. (b) A simplified representation of the transmission line. The reference planes shown here are those of the N-type connectors. Between the sample with fixed thickness L and reference (or calibration) planes, there are small distances L_1 and L_2 that were determined by measuring the empty sample holder.

which was used to correct the measured S -parameters $\tilde{S}_{11}$ and $\tilde{S}_{21}$

$$S_{11} = \exp\left(2i\frac{2\pi}{c}fL_1\right)\tilde{S}_{11}, \quad (2)$$

$$S_{21} = \exp\left(i\frac{2\pi}{c}f[L_1 + L_2]\right)\tilde{S}_{21}. \quad (3)$$

The transmission-reflection method developed by Nicolson, Ross,⁸ and Weir⁹ was used to determine the electrical permittivity $\epsilon(f) = \epsilon' - i\epsilon''$ and magnetic permeability $\mu(f) = \mu' - i\mu''$ from the transmission and reflection scattering parameters S_{21} and S_{11} , respectively.

FIG. 2. (a) Obtained permeability curves (real part) for nickel particles having the diameter less than 100 nm in comparison with the literature values for similar nickel particles. (b) Frequency dependence of the real part of the magnetic permeability for nickel powder with a grain size less than $1\mu\text{m}$ at different packing densities.

FIG. 3. The frequency dependent real and imaginary permeabilities of cobalt nanoparticles as a function of the length of time, they have been exposed to air.

III. RESULTS AND DISCUSSION

We verified the performance of our coaxial cell by measuring Ni powder with an average grain size of less than 100 nm and comparing our results with similar measurements of nickel powder published by Lu¹² and Zhang¹³ as shown in Figure 2(a). Our measurements agree well with those literature values. The differences are likely due to particle size. According to the Baker-Jarvis method,¹¹ we calculated the uncertainty in our data by taking into consideration errors in both the magnitude and phase of scattering parameters and propagating their contributions in quadrature. Uncertainty dominates at frequencies below 300 MHz, and is likely due to $1/f$ noise. Since all of our permeabilities were similar in magnitude, error bars have only been included in Figure 2(a) and for the packing density of $0.25\rho_{\text{bulk}}$ in Figure 2(b).

The initial permeability at 10 MHz is linearly proportional to the packing density for $0.19\rho_{\text{bulk}}$, $0.22\rho_{\text{bulk}}$, and $0.25\rho_{\text{bulk}}$, as expected for low volume fraction limit. The

densest packing studied here, $0.31\rho_{bulk}$, has a higher initial permeability that would be expected from the first three, since magnetostatic interactions between particles are becoming significant.

Although Co nanoparticles are desirable for their high moment, they are prone to oxidation. Our particles are slightly protected by their OA coating, and are carefully handled under oxygen free conditions until placement in the sample holder. To observe the influence of nanoparticle oxidation on the permeability, the powder was left in the sample holder for 5 days and measured repeatedly. Oxidation led to a decrease of the real part of relative magnetic permeability value below 3 GHz, as shown in Figure 3, since the formation of an antiferromagnetic CoO shell reduced the ferromagnetic volume in the composite.

The imaginary part of the permeability corresponds to the dissipation of energy as the magnetization is rotated. This is usually dominated by eddy current losses during the rotation of the particle magnetization. In low frequency power transformers, these losses are minimized by fabricating the transformer yoke from laminated layers of steel to minimize conductive pathways in one dimension. In higher frequency inductors, eddy current losses are minimized by using electrically insulating ferrite materials. Similarly, we attribute the reduction in the imaginary permeability, as shown in Figure 3, to the reduction of conductive pathways between nanoparticles by the formation of an insulating CoO shell.

Different methods for the passivation of Co nanoparticles have been investigated by Dobbrow and Schmidt.¹⁴ Their results show the use of alcohol and polymer coatings instead of OA can greatly reduce the oxidation sensitivity. The use of different coatings, together with larger initial nanoparticle size and higher packing density, may help preparing composites with higher magnetic permeability.

IV. CONCLUSION

The Nicolson-Ross-Weir method was used in combination with a VNA and a custom coaxial transmission line to obtain frequency dependencies of the complex permeability (μ_r) and permittivity (ϵ_r) for a dense cobalt nanoparticle composite in the frequency range of 10 MHz–10 GHz. The evolution of the permeability and permittivity was observed as the particles oxidized and is consistent with the formation of an antiferromagnetic, insulating, CoO shell.

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