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Nonreciprocal electromagnetic properties of nanocomposites at microwave frequencies

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We report on the effects of composition and external magnetic field on the microwave permeability tensor of Ni/γ-Fe_2O_3 nanocomposites. When compared to the zero-field case, the field measurements of the permeability tensor $\overline{\mu}$ exhibit nonzero off-diagonal components giving evidence of the nonreciprocity of wave propagation in these nanostructures. We observe that the diagonal and off-diagonal elements of $\overleftrightarrow{\mu}$ of these nanocomposites depend sensitively on their Ni content and of the applied static magnetic field. These experimental results are analyzed within a recently developed multiscale modeling [S. Mallegol *et al.*, Phys. Rev. B **68**, 174422 (2003)] and can be understood as arising from magnetostatic intergranular interactions via a mean-field approximation. The application of these heterogeneous nanomaterials open possibilities for the design of field-controlled nonreciprocal components used in microwave integrated circuit technology.

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Magnetic fine particles in the size range of a few to a few tens of nanometers show rich magnetic properties depending on surface anisotropy and chemical composition, such as superparamagnetism[1] and unusual large coercivities,[2] and with strong potential applications to microwave and millimiter-wave components. Advances in the compositional development and processing science of granular nanophases composed of magnetic nanoparticles into otherwise nonmagnetic solids suggest them to be promising candidates for cost effective, magnetically tunable microwave or nonreciprocal devices such as circulators and isolators.[3] The availability of tunable microwave devices based on magnetic nanophases would reduce the size and cost while providing strong potential benefits, i.e., low insertion loss, narrow frequency band.[4–6] Moreover, for producing novel device multifunctionality it is of paramount importance to understand how the electromagnetic properties may be changed by various external stimuli, e.g., magnetic field, mechanical stress.

On the other hand, symmetry constraints in theories of wave-matter interactions in transmission and reflection have long been an object of intense research in the condensed matter community.[7,8] The wave propagation is reciprocal if the wave attenuation and the phase retardation do not change with reversal of the direction of propagation of the wave through the medium. Propagation of a wave in an isotropic magnetized medium is an example of a nonreciprocal phenomenon. The Faraday effect can be considered as a textbook example for such nonreciprocity. The study of nonreciprocal components which are made possible by selecting the appropriate gyrotropic materials has been the subject of extensive experimental and theoretical work in recent years.[9] Despite this, there remains no conclusive understanding of the microscopic origin of the field-induced anisotropy and whether or not the mean-field (effective medium) theories constitute the most prevalent approach to describe the electromagnetic properties of granular nanophases.[10]

Polder[11] was the first to theoretically approach the problem of the tensorial analysis of the permeability in a uniformly magnetized single-domain anisotropic magnetic particle. His study revealed that the permeability is described by a second-rank Hermitian tensor

$$\overleftrightarrow{\mu}=\begin{bmatrix}\mu & j\kappa & 0\\ -j\kappa & \mu & 0\\ 0 & 0 & 1\end{bmatrix}$$

in the coordinate system such that the external field is applied in the positive z direction, with $\mu=\mu'-j\mu''$ (resp. $\kappa=\kappa'-j\kappa''$) being the diagonal term (resp. off-diagonal term), and where single prime (resp. double prime) denote real (resp. imaginary) part. Subsequently, different formalisms were developed which enable the quantification of the off-diagonal term in magnetic materials.[9,12] We should mention that for a macroscopically isotropic two-phase composite medium, off-diagonal elements of the magnetic permeability $\overleftrightarrow{\mu}$ are equal to zero. However, there should be nonzero off-diagonal elements in $\overleftrightarrow{\mu}$ for magnetically anisotropic materials, and the reciprocity is broken.[7] The preceding discussion provides the motivation for improving our understanding of the electromagnetic properties of magnetically gyrotropic media consisting of a three-dimensional uniform distribution of magnetic grains, with size in the nanometer range, within a nonmagnetic host matrix from measurements of the permeability tensor.

Broad-band microwave spectroscopy as adopted in this study is a well-established tool for probing the permeability spectrum of nanocomposites. The lack of experimental data in this area hinders the development of more general theoretical models about the magnetic field dependence of the gyromagnetic resonance. This is mainly due to the experimental difficulty to determine independently the diagonal and off-diagonal terms of the permeability tensor.[12] In this report, we report not only the observation of the nonreciprocity of wave propagation in Ni and γ-Fe_2O_3 nanocomposites, but also that the off-diagonal component of the permeability tensor is extremely sensitive to a static magnetic bias field applied to the whole composite sample. Furthermore, the current data indicate that the frequency-dependent response

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in the microwave frequency range can be accounted for by a mean-field approximation.

Commercially available pure Ni and γ-Fe_2O_3 powders were used as basic components of the composite materials. These nanopowders were supplied from Nanophase Technologies Corp., Burr Ridge, IL, and were used without further treatment. Control over the average particle size and shape was achieved by SEM microscopy: we obtained 35 nm and 23 nm for Ni and γ-Fe_2O_3 particles, respectively. High-resolution x-ray diffraction studies indicated that these materials were phase pure to $<1\%$. Epoxy resin (Scotchcast 265) purchased from 3M was used as organic binder. The fractional volume of voids (porosity) was deduced knowing the volume fractions of Ni, Fe_2O_3, and epoxy ($\cong 14\%$) and was controlled by density measurements. In the samples studied here, porosity was in the range 26%–29%. A series of composite samples with varying composition for the electromagnetic measurements has been prepared and consisted of parallelepipedic plates (typically, 5 mm long, 5 mm wide, and 1.8 mm thick) fabricated using the procedure already described.[4,5] In what follows we focus on three specific samples corresponding to neat Ni, and γ-Fe_2O_3, and 8 vol % Ni and 53 vol % γ-Fe_2O_3 (labeled A, B, and C, respectively, in Figs. 1 and 2).

The study of nonreciprocity requires a comparison between waves propagating in opposite directions. For that purpose, we employed a homebuilt nonreciprocal strip transmission line measurement cell. Diagonal and off-diagonal components of the permeability tensor can separately be identified, with previously unavailable precision, by monitoring the S parameters using an automatic HP 8720 A vector network analyzer. The reader is referred to Ref. 12 for the full details of the experimental setup and the procedure for measuring μ and κ.

We begin our presentation of the data by first looking at the frequency evolution of the real and imaginary parts of the permeability tensor components for different volume fractions of the magnetic phases (Ni and/or γ-Fe_2O_3) in the samples. Results of the measurements are in Figs. 1(a) and 1(d) for zero field and Figs. 2(a) and 2(d) for a magnetic field $H=2.75$ kOe. The gyromagnetic resonance in the μ'' spectrum for the sample A containing neat Ni at 1 GHz [see Fig. 1(b)] is accompanied by a second peak at 5 GHz. Such a peak is not instrumental and was ascribed to the polydispersity of the nanophases since it follows the same composition dependence as the main line. Almost identical behavior is evident in Fig. 1(b) for samples B and C. It is noteworthy that our measurements indicate that $\kappa' \cong 0$ and $\kappa'' \cong 0$ in the absence of applied magnetic field, for each studied sample. Thus, these samples are macroscopically isotropic.

Now we turn our attention to magnetic-field effects in nanocomposites. From the panel of Fig. 2, several other interesting features are revealed. The nonzero off-diagonal terms of the permeability tensor, as shown in Figs. 2(c) and 2(d), are clear signatures of the nonreciprocal behavior. Figures 2(b) and 2(d) show a single peak in the μ'' and κ'' spectra for the three samples which is attributed to the gyromagnetic resonance characterizing the dynamics of magnetization. A closer look at Figs. 2(b) and 2(d) reveals that the maximum of μ'' is coincident with the corresponding maximum of κ''. We found that the position of the gyromagnetic peak is composition and field dependent. Increasing the volume fraction of Ni to 8% had a dramatic effect on the gyromagnetic resonance peak, i.e., the amplitude of the gyromagnetic resonance peak for sample C in Fig. 2(b) is approximately twice that of the pure Ni component (sample A). In addition, the curves (b) and (d) in Fig. 2 indicate a narrower gyromagnetic resonance linewidth. It is worth noting that the amplitude enhancement of the resonance peak shows a nonmonotonic behavior upon Ni content exhibiting a local maximum at a volume fraction of about 8%.

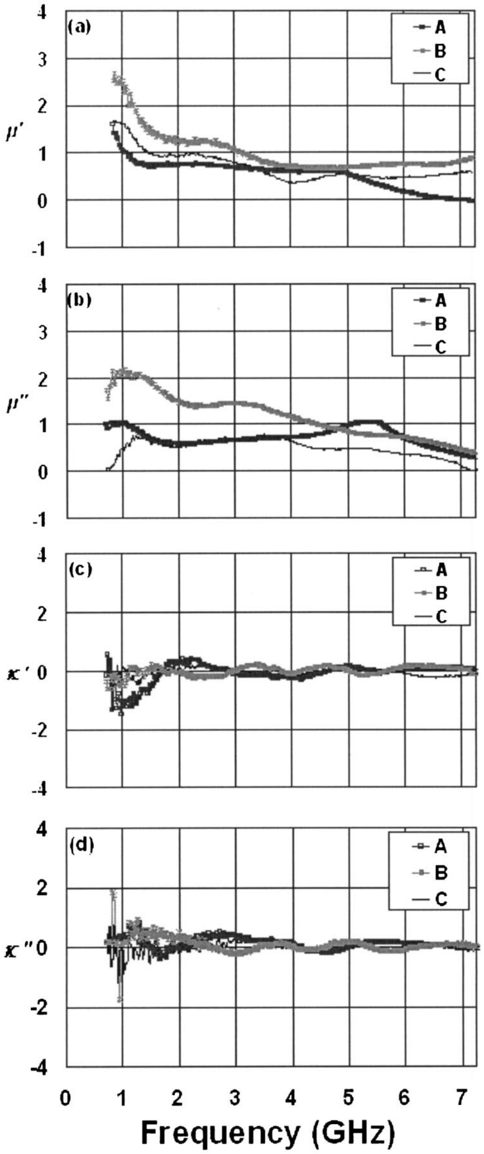

FIG. 1. (a) Zero-field frequency dependence of the components μ and κ of the effective permeability tensor: (a) real part μ', (b) imaginary part μ'', (c) real part κ', (d) imaginary part κ''. (A) Sample containing neat Ni; (B) sample containing neat γ-Fe_2O_3; (C) sample containing 8 vol % Ni and 53 vol % γ-Fe_2O_3. Room temperature.

Figure 3 shows the dependence of the resonance peak frequency as a function of the Ni content. For $H=2.75$ kOe we find a monotonic decreasing behavior as the Ni content is increased, which is consistent with the gyromagnetic behav-

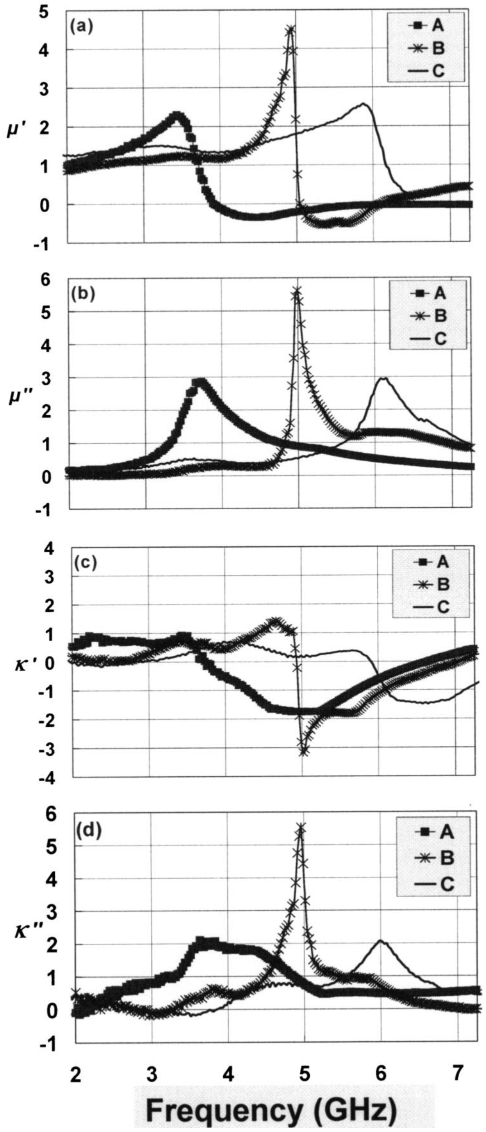

FIG. 2. (a) Frequency dependence of the real part of the components μ and κ of the effective permeability tensor: (a) real part μ', (b) imaginary part μ'', (c) real part κ', (d) imaginary part κ''. The applied magnetic field is $H=2.75$ kOe. (A) Sample containing neat Ni; (B) sample containing neat γ-Fe_2O_3; (C) sample containing 8 vol % Ni and 53 vol % γ-Fe_2O_3. Room temperature.

ior of γ-Fe_2O_3/ZnO nanocomposites that was previously characterized by our group.[6] These results can be compared with predictions for unifomly magnetized composites. Attempting to explain the origin of the nonreciprocal behavior seems to be a difficult task, primarily since, despite numerous studies accounting for the ferromagnetic exchange coupling between neighboring magnetic particles in metal/insulator nanocomposites, the details of this "exchange coupling" thereof have not been completely disentangled. While a complete multiscale modeling of inhomogeneous magnetic nanophases is beyond the scope of this report, a simplified mean-field analytic model for the magnetostatic intergranular interactions captures the observed trend in the experimental data of Fig. 3. A detailed description of this model appears elsewhere.[6,13] It is worth emphasizing that this model does not make use of any adjustable parameters, and all the parameters involved have a physical meaning. Two basic assumptions were made in Refs. 6 and 13. First, the self-consistent embedding approximation assumes that all particles of the dense array are in the same magnetic state at a given value of the applied magnetic field. Second, we also assume that the grain sizes are much smaller in comparison with the free-space wavelength, and, consequently electromagnetic waves in the nanocomposites can be treated as propagating in a homogeneous magnetic system. The saturation magnetization, M_s, the reduced magnetization, M/M_s, and, α, the Gilbert dimensionless damping coefficient which are the only physical parameters as input of our calculations (see Table I), were measured by using a vibrating sample magnetometer and by studying the ferromagnetic-resonance linewidth, respectively. Figure 3 depicts calculated values of the resonance peak frequency for various values of the volume fraction of Ni. A comparison of the calculated gyromagnetic resonance with the experimental ones demonstrates similarity in the position of the resonance peak (Fig. 3).

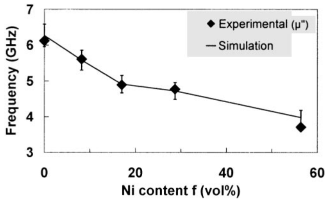

FIG. 3. Gyromagnetic peak resonance against Ni volume fraction for the samples studied. Symbols correspond to $H=2.75$ kOe. The error bars denote the data deduced from the multiscale model (Refs. 6 and 13). The line simply connects the calculated data points and reproduces measurements.

As shown in Fig. 4, the width at half-height, ΔF, of the gyromagnetic resonance peak has a nonmonotonic dependence on Ni content, and exhibits a minimum at about 8 vol%. We believe that the strong field-enhancement in permeability observed in Fig. 2, and the associated resonance peak narrowing shown in Fig. 4 are due to the exchange coupling effect which dominate the demagnetizing and magnetocrystalline anisotropy energies in the material. Neighboring grains separated by distances shorter than the magnetostatic-exchange length $\lambda_{ex}=\sqrt{A/\mu_0 M_s^2}$, where A is the exchange constant and M_s is the saturation magnetization, can be magnetically coupled by exchange interaction. This coupling averages out the magnetic anisotropy of particles, resulting in much reduced anisotropy. Consequently, the permeability of exchange-coupled nanophases can be

TABLE I. Composition and magnetic properties for the samples considered in the present work.

Ni content f (vol %)	M_s (emu g^{-1})	M ($H=2.75$ Oe)/M_s	α[a]
0	60.3	0.99	0.25
8	90.9	0.99	0.21
17	95.4	0.99	0.24
29	100.6	0.99	0.22
56	121.2	0.99	0.11

[a] Frequency = 10 GHz.

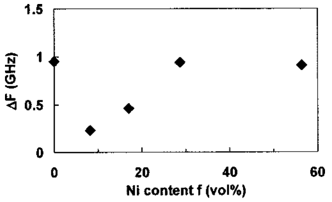

FIG. 4. The Ni volume fraction dependence of the width at half-height of the gyromagnetic resonance peak.

much higher than the permeability of samples containing larger particles. However, it remains to explain why the gyromagnetic resonance linewidth reaches a minimum at the particular value of 8 vol %.

Table I also shows the values of the Gilbert damping coefficient α for our samples. We remark that the α is nearly constant in the range of Ni volume fraction studied, and this value is consistent in magnitude with those previously reported by us[4–6] and others.[14] We observe that the embedding which provides encapsulation and prevents grain growth and agglomeration can change the local magnetic interactions of these nanophases and thus can have a significant bearing on the value of α. This makes it difficult to isolate the different contributions to the anisotropy and intrinsic (i.e., not based on inhomogeneous line broadening effects, but on all other loss mechanisms that take energy out of the spin system) damping.

Finally, a few words should be said about the relevance of the Aharoni's analysis[15] with the wide resonances reported here. The theory, concerning small ferromagnetic spheres, is valid when the magnetostatic energy is small compared to the exchange energy and predicts that the resonance frequency depends on the roots of a the derivatives of the spherical Bessel functions, and is $\sim R^{-\beta}$, where R is the radius of the sphere and $\beta \cong 0.66$ for spheres having strong surface anisotropy or $\beta = 2$ if the particle size or the surface anisotropy is considerably reduced. We note that Viau and co-workers[14] have analyzed the multiresonances observed in the effective (scalar) permeability of $\mathrm{Fe}_{0.13}[\mathrm{Ni}_{80}\mathrm{Co}_{20}]_{0.87}$ systems in terms of non uniform resonance modes resulting from the exchange energy contribution to the magnetization precession within the particles. This is clearly different from the results described in this study which concern the effective permeability tensor of magnetized and demagnetized nanophase materials composed of much smaller particles, i.e., their FeNiCo particles have a typical average size in the range between 210 and 260 nm, thus characterized by a stronger surface anisotropy.

To summarize, the microwave (tensorial) response of gyrotropic Ni/γ-$\mathrm{Fe}_2\mathrm{O}_3$ nanocomposites was used to identify their nonreciprocal properties. We have found new experimental evidence supporting a simple model, made elsewhere, for the field-induced anisotropy of nanophases that takes into account magnetostatic intergranular interactions. These results show that the amplitude of the gyromagnetic resonance (μ'' and κ'') peak for a Ni/γ-$\mathrm{Fe}_2\mathrm{O}_3$ composite sample containing 8 vol %Ni can be much larger than that of the pure Ni and γ-$\mathrm{Fe}_2\mathrm{O}_3$ components. Future work will likely explore further optimization of the electromagnetic properties of these nanostructures and will help to determine the exact mechanisms responsible for the nonreciprocity. In addition, we have ignored such chemical and structural effects, e.g., particles cluster, polycrystalline nature of the samples, surface segregation, and grain boundaries, that are present in such condensed phase systems for which a complex environment precludes a detailed microscopic understanding. Computation of results can also contribute to the acceptance or rejection of the mean-field based theories, and can also indicate directions in which new approaches should be developed. Besides being of scientific interest these multicomponent magnetic nanophases are also of significant technological interest, i.e., they can be considered as prospective granular magnetic films for tunable or nonreciprocal millimeter wave devices for monolithic microwave integrated circuit (MMIC) applications.[16]

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