EVALUATION OF MAGNETIC POLYMER COMPOSITE PARAMETERS FROM FMR MEASUREMNT

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Summary The article proposes an evaluation procedure for determining the magnetic parameters, particularly the saturation magnetic polarization of $Ni_{0.3}Zn_{0.7}Fe_2O_4$ powder embedded in non–magnetic polymer from FMR measurements. Dependence of the reflected microwave signal magnitude and phase on the ferrite powder of 0.23 to 0.80 volume fraction, in polyvinyl chloride (PVC) matrix has been investigated in microwave X-band, using moulded capsules above 1 mm thick and approximately 10 mm in diameter as experimental samples.

1. INTRODUCTION

While Ni-Zn ferrites possessing high permeability and low losses to be advantageous for use in RF band [1], ferrite polymer composites fabricated by embedding the ferrite particles into a non–magnetic polymer matrix have some interesting and promising properties [2]. The magnetic properties of composites are substantively determined by the ferrite filler, their mechanical properties are influenced mainly by the polymer matrix. Although ferrite polymer composites have a lower permeability in comparison with Ni-Zn ceramic ferrites they show for instance a greater stability in a harsh environment.

In studies of the complex permeability spectra of ferrite polymer composite materials based on an Mn-Zn ferrite and PVC matrix [3-4] it was shown that in the frequency range above 100 MHz the permeability of composites and their resonance frequencies are higher than those of sintered ferrites and this could possibly be attributed to the demagnetising effects of ferrite particles and their aggregates in composites.

The effect of the filler fraction volume concentration in composite on the required bias field at which the ferromagnetic resonance at a given frequency occurs has been studied with aim to determine the effective field and magnetic polarization of the composite.

2. SAMPLES

The $Ni_{0.3}Zn_{0.7}Fe_2O_4$ ferrite powder, used as the filler, was prepared by conventional ceramic method with particle size up to 250 μm. As sintered, it had the initial permeability $\mu_i \approx 2500$ and suitable responses for applications below 1 MHz. By mixing and moulding several flat cylindrical samples were prepared with ferrite volume fractions $\xi = 0.23, 0.48, 0.55, 0.63, 0.73$ and 0.80. All having height and diameter of around 1.3 mm and 9.5 mm, respectively. A ball (nearly the sphere with diameter of about 1.4 mm) of the sintered ferrite for a comparison measurement was also fabricated. It should be noted that to prepare samples with a higher filling factor was not easy and at present we were not able to get over the 0.8 volume fraction limit. Moreover samples with higher powder content did not posses smooth enough surface if compared to those with a lower volume fraction of the filler. Details of the space distribution of powder particles in composite samples used for the measurements were not known.

3. MEASUREMENT SET-UP

The block diagram is in Fig. 1. During the measurement, the sample placed in a wave-guide is in a constant (*dc*) magnetic field H_0, produced by a Weiss electromagnet. In the same direction to this, by means of Helmholtz coils, a weak (several mT) subsidiary low frequency (72 Hz) magnetic field H_a is added, enabling to extract the useful signal (typically below mV) deeply buried in noise. The *dc* magnetic field H_0, changed in small steps (approximately each 5 seconds) is measured by a Hall probe and recorded to SR 850 DSP lock-in amplifier memory.

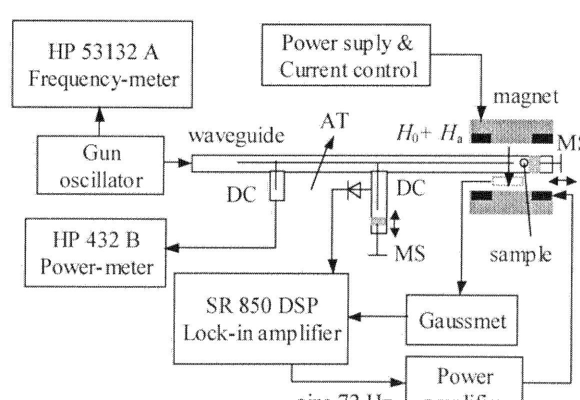

Fig. 1 Block diagram of experimental set-up

The high–frequency field (9.24 GHz), again with amplitude small compared with field H_0, is provided by microwaves excited in a X-band wave-guide by a Gun oscillator. The microwave detectors, through directional couplers (DC) before and after an attenuator (AT), pick up the signal proportional to the incident and from the sample reflected microwave power. The latter depends on actual "working point" on the resonance curve, being controlled by the external magnetic field intensity. The sample itself is glued at a movable short (MS) to optimally adjust the local microwave field. Lock-in amplifier records the first and/or (optional) the second harmonic component contained in the reflected signal due to a modulation low-frequency sine-field H_a produced by SR 850 DSP internal generator. The amplitude and phase of this signal are both recorded and the resonance is detected by the change of phase by 180 degrees and simultaneous drop of the voltage practically to zerto due to the detector selectivity of about 60 dB or even more. In case the working point on the resonance curve is by the sine modulation swept symmetrically around its top, it is possible to record the second harmonic component (magnitude and phase) in the reflected signal.

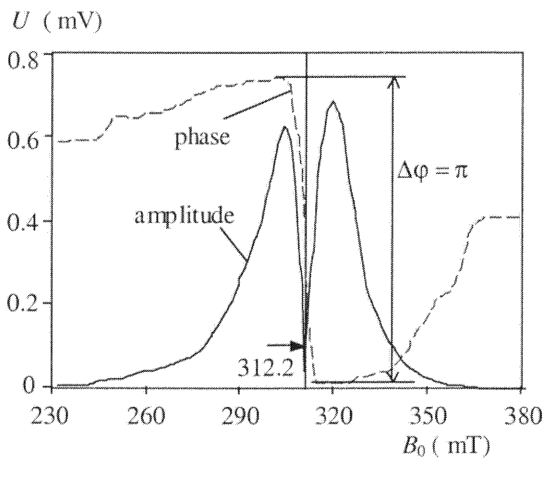

Fig. 2 Typical signals as reflected from a ball sintered from a pure powder (unity volume fraction) in a bias B_0 - the first harmonic sensed, in above described experimental set-up.

4. THEORY

The basic equations for the ferromagnetic resonance $\frac{d\vec{J}}{dt} = -\gamma \vec{J} \times \vec{H}$, and $\vec{B} = \mu_0 \vec{H} + \vec{J}$ will be used here to describe the measurements and the material properties. In complex representation we shall use the following reduced variables, (*cf* Fig. 1): $h = \frac{H_z}{H_0}$, $\mathsf{h} = \frac{\mathsf{H}}{H_0}$, $\mathsf{j}_\perp = \frac{\mathsf{J}_\perp}{J_z}$, $\xi = \frac{\omega}{\omega_0}$, with the resonant angular frequency $\omega_0 = \gamma H_0$, with $\gamma = 2.19 \times 10^4$ Vs / kgm for spin resonance (splitting factor $g = 2$). The shape of specimens will be taken into account by means of demagnetizing factors to correct

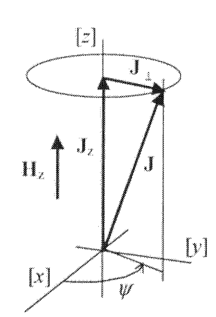

Fig. 3 To FMR measurement

the internal field intensity for respective perpendicular components $\mathsf{h}_{\perp x,y} \leftarrow \mathsf{h}_{\perp x,y} - n_{x,y}\,\mathsf{j}_{\perp x,y}$ and that for bias field $h_z \leftarrow h_z - n_z$, where in $n_{x,y,z} = J_S N_{x,y,z} / B_0$ magnetic saturation polarization J_S was substituted for J_z and $B_0 = \mu_0 H_0$. Demagnetizing factors of ellipsoid of rotation $N_{x,y,z}$ are considered below. From the basic equation, now to read

$$\begin{bmatrix} f_{\perp x} \\ f_{\perp y} \end{bmatrix} = \frac{\begin{bmatrix} h - n_z + n_y & i\xi \\ -i\xi & h - n_z - n_x \end{bmatrix} \cdot \begin{bmatrix} \mathsf{h}_{\perp x} \\ \mathsf{h}_{\perp y} \end{bmatrix}}{(h - n_z + n_y)(h - n_z - n_x) - \xi^2}$$

an intrinsic oscillation is found from the well known condition $\xi^2 = (h - n_z + n_x)(h - n_z + n_y)$. For more details see [5,6].

Case 1

Let the sample, almost a flat disk with the principal to lateral half-axes ratio $\lambda = \frac{a}{b} < 1$, be biased by H_0 perpendicular to its plane, than

$N_z = \frac{1}{1-\lambda^2} - \frac{\lambda}{(1-\lambda^2)^{3/2}} \arcsin(\sqrt{1-\lambda^2})$, and $N_x = N_y$.

To reach the resonant frequency ($\xi = 1$) the intensity must be $h_1 = 1 + n$, using a shortened notation $n = n_z - n_x$ and $N_z \equiv N$ due to $N_x + N_y + N_y = 1$, denoting $k = (3N-1)/2$ we can write: $\frac{J_S}{B_0} = \frac{h_1 - 1}{k}$, or since $\frac{H_1}{H_0} = h_1 = \frac{\mu_0 H_1}{\mu_0 H_0} = \frac{B_1}{B_0}$, also $B_1 = B_0 + J_S k$, where B_0 and B_1 refer to the magnetic flux densities outside a spherical sample and the disk having the magnetic polarizations J_0 and J_S respectively – since for $k = 0$ (or $N = 1/3$) the ellipsoid turns to be a sphere.

Case 2

Consider a sphere and an ellipsoid of rotation as before but let the ellipsoid (almost a flat disk) now to be biased by H_0 in parallel to its plane (magnetized along the one of its lateral, say x axes). The principal to lateral half-axes ratio is the same as before. Let the magnetic polarization of the sphere and the ellipsoid be J_0 and J_S, and the bias intensity for intrinsic resonance to occur in the disk be H_2. In this case using notation as before, $\frac{1}{h_2} - h_2 = n$, since $N_x = \frac{1 - N_z}{2}$, with $n = \frac{J_S}{B_0} k$

we can write: $\frac{J_S}{B_0} = \frac{1}{k}(\frac{1}{h_2} - h_2)$ or $J_S = \frac{1}{k}(\frac{B_0^2}{B_2} - B_2)$

since $h_2 = \frac{H_2}{H_0} = \frac{B_2}{B_0}$, where B_0 and B_2 refer to the magnetic flux densities outside the sphere and disk with magnetic polarizations J_0 and J_S respectively. Now

$h_2 = -\frac{n}{2} + \sqrt{1 + (\frac{n}{2})^2}$, or $B_2 = -J_S \frac{k}{2} + \sqrt{B_0^2 + (J_S \frac{k}{2})^2}$.

5. RESULTS AND THEIR EVALUATION

Typical curves at the two different positions of the capsules relative to *dc* bias $B_0 = \mu_0 H_0$ are in Fig. 4. A graph of reduced values, as measured for the different compositions is in Fig. 5, (see also Tab. 1 and Tab. 2).

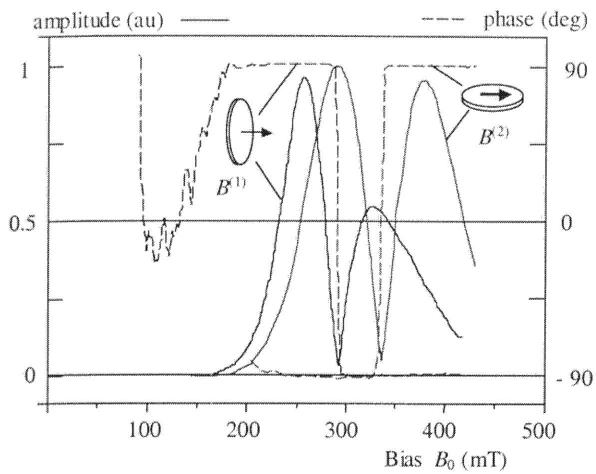

Fig. 4 Amplitude and phase of the reflected signal as a fun-ction of bias field for ξ = 0.23 volume fraction of composite sample. The first harmonic component was recorded for the two different positions.

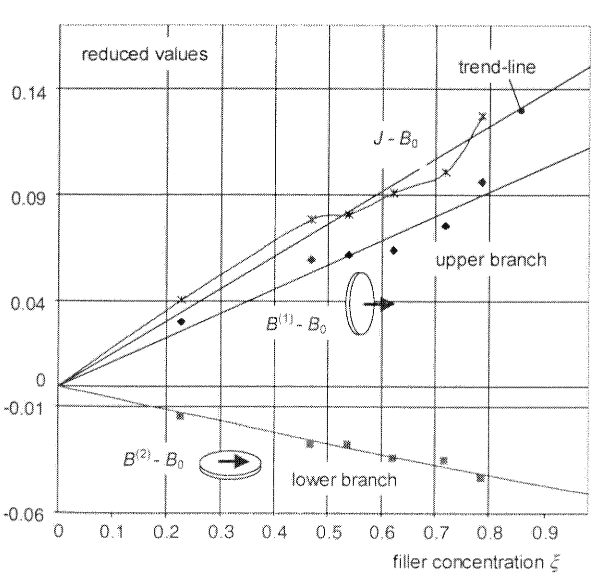

***Fig. 5** Amplitude and phase of the reflected signal as a fun-ction of bias field for ξ = 0.23 volume fraction of composite sample. The first harmonic component was recorded for the two different positions.*

Superscripts in braces denote the respective measure-ment positions. For each composition $\xi \in \langle 0.23,\ 0.8 \rangle$

$$B_{0v} = \frac{B_v^{(2)}}{2}\left(-1+\sqrt{5+\frac{4B_v^{(1)}}{B_v^{(2)}}}\right) \qquad (1)$$

is evaluated, and the mean $\langle B_0 \rangle = \frac{1}{m}\sum_v B_{0v}$ from m measurements is than taken be the correct value (for a sphere) and used throughout the article as B_0, according to theory not dependent on ξ. Table 1 gives the results of measurement in two distinguished positions above referred to as Case 1 and Case2.

Tab. 1. Bias required for resonance to occur at 9.24 GHz. Measure-ments of $B^{(1)}$ and $B^{(2)}$ - at two different positions of the sample.

ξ	$B_v^{(1)}$ (mT)	$B_v^{(2)}$ (mT)	$B_{0v} - \langle B_0 \rangle$ (mT)
0.2326	336	291	0.2
0.4762	365	278	0.5
0.5479	365	278	1.0
0.6319	370	272	-2.5
0.7317	381	270	-1.0
0.8010	402	262	0.9
1	418	255	← estimated *

$\langle B_0 \rangle$ = 305.5 mT

At each composition from the capsule dimensions parameter $k_v = \frac{3N_v - 1}{2}$ is evaluated (to get also $\langle k \rangle$, from) and again, using

$$J_{Sv}^{(1)} = \frac{B_v^{(1)} - \langle B_0 \rangle}{k_v}, \quad J_{Sv}^{(2)} = \frac{1}{k}\left(\frac{\langle B_0 \rangle^2}{B_v^{(2)}} - B_v^{(2)}\right) \qquad (2)$$

the average $J_{Sv}^{A} = \frac{J_{Sv}^{(1)} + J_{Sv}^{(2)}}{2}$ (alternatively the geomet-ric mean value $J_{Sv}^{A'} = \sqrt{J_{Sv}^{(1)} J_{Sv}^{(2)}}$) is obtained. Then, based on a simplified assumption that magnetic polarization of a sample is proportional to the volume concentration of the filler (ξ) – neglecting all possible interaction, ordering and packing issues – the linear regression fit with a fixed intercept is used to estimate $J_S = 0{,}1506$, a value pertinent to 100 % packing ($\xi = 1$) from the trend line, see Fig. 2, the upper curve. Points (asterisks) are the averaged values evaluated from (1). According to the theory the upper branch in Fig. 2 is a straight line $B_1 = B_0 + k\,J_S(\xi)$. Using $\langle B_0 \rangle$ and $\langle k \rangle$ in place of B_0 and k as the above described mean values lead to another estimation $J_S = 0{,}1505$, as very close to the above one. Contrary, the lower branch is given by a curve

$$B_2 = -J_S(\xi)\frac{k}{2} + \sqrt{B_0^2 + \left(J_S(\xi)\frac{k}{2}\right)^2} \qquad (3)$$

which also should be the best-fitted to measured values. To do this, one can denote $\eta = J_S(\xi)\frac{k}{2}$, and altering this value to minimize the approximation error of $B_2 = -\eta + \sqrt{\langle B_0 \rangle^2 + \eta^2}$ with respect to values measu-red. This correction may be accounted for the uncertainty in determining either of k and $J_S(\xi)$. This treatment gives value of $J_S = 149.8$ mT, providing the best fit for $\eta = 0.18$, and as final result $J_S = 150.2$ mT. This is close to the value of 165 mT as measured on the reference sphere by a vibration magnetometer method, see accompanying paper [J. Franek, R. Dosoudil, M. Ušáková] at this conference.

In Table 2 are calculated values of saturation magnetic polarization according above to presented method using (1) to (3).

Tab. 2. Evaluation of the composite saturation magnetic polarization $J^{(1)}$ and $J^{(2)}$ from resonance at 9.24 GHz: - at two different positions.

ξ	$J_{Sv}^{(1)}$ (mT)	$J_{Sv}^{(2)}$ (mT)	$J_{Sv}^{(A)}$ (mT)	$J_{Sv}^{(A')}$ (mT)
0.23	40.8	39.9	40.4	40.4
0.47	79.7	77.4	78.5	78.5
0.54	83.0	78.9	81.0	80.9
0.63	86.1	96.9	91.5	91.3
0.73	101.1	101.5	101.3	101.3
0.80	129.2	125.3	127.3	127.3
1	150.5	149.8	150.2	150.2

$J_S = 150.6$ mT ← trend-line ↑ estimated *

Note that (1) would assures $J_{Sv}^{(1)}$ and $J_{Sv}^{(2)}$ be exactly the same values if instead of $\langle B_0 \rangle$ rather B_{0v} was used in (2).

6. DISCUSSION AND CONCLUSIONS

Measurement of the reference ferrite sintered sample (a small ball with 100% filler) gave a higher value $B_0 = 312.2$ mT than should be expected, *cf* Tab.1. This sample prepared by grinding for hours in a ball mill may not be even a body of rotation, however, its aspect ratio 1.22 nearly corresponds to that of 1.12 at which the difference could be assigned to the ball demagnetising factor providing the bias field was directed along its shorter dimension. Since it is difficult to glue the ball with required orientation – a better solution is to master a "shift" allowing rotate the sample under measurement.

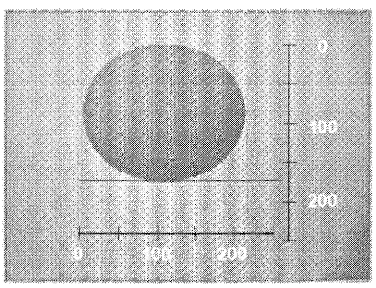

***Fig. 6** A ball, how far it was from a perfect sphere? Revealed by a profile projector - aspect ratio of 216/177 (= 1.22).*

Another issue is the filling at least from two aspects: (i) it is troublesome to have prepared capsules with a higher filling factor – this can be circumvented by the described measurement method as far as the prediction of its properties is in question, (ii) the distribution of the powder particles and interactions of their aggregates are important, as well as how are they reflected in properties of the capsule (or another shape of the sample as a sheet *etc*).

The measurement showed that something is likely be happening around from $0.5 < \xi < 0.7$, as implied by the rippling character of the upper curve in Fig. 5. The ferromagnetic resonance is influenced by internal magnetic field and this is highly affected not only by the shape of the sample but also the possible internal aggregates and their mutual interactions may play an important role. To certain extent the discrepancies or deviation from a straight line may explained by the surface roughness of capsules, particularly those with higher content of the ferrite powder.

We found interesting that the lower branch seems better to fit then the upper does, in spite of the lower absolute values. It seems plausible that there are quite different interactions to be expected in the respective positions. Much more "neighbours" may be found in position 2 (than in 1) in the direction along the waveguide and the *hf* field at the sample edges is different as depends on z co-ordinate.

The main goal of this approach was, however, not only to attempt find a way how to determine the values of J_S (since other methods *eg* magnetometric are as well cumbersome if using not homogeneously magnetized samples) but also to get some information about the microwave properties of a "capsules" as prepared. By other words – to get evidence about *hf* features of different compositions what is definitely not a simple question of the ferrite filler volume fraction in a polymer matrix due to the interactions of individual powder particles and their assemblies.

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