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FERROMAGNETIC RESONANCE IN MnZn FERRITE – PVC POLYMER COMPOSITE MATERIALS: THEORY AND EXPERIMENTS

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The present study is devoted to the microwave measurements performed on the manganese–zinc (MnZn) sintered ferrite with the chemical composition ≈ $Mn_{0.37}Zn_{0.57}Fe_{2.06}O_4$ and composite materials based on this ferrite in powder form and non–magnetic polyvinyl chloride (PVC) polymer matrix. The prepared composite samples had the same particle size distribution 0–250 μm but different ferrite particle concentrations: 10, 20, 30, 40, 56, 60 and 80 vol%. Ferromagnetic resonance (FMR) experiments were performed on the composite samples using an experimental set–up utilizing the principle based on the detection of microwave signal reflected from a sample under test and proportional to the absolute value of scattering parameter S_{11} (reflection coefficient).

Keywords: ferromagnetic resonance, wave–guide, reflection coefficient, sintered ferrite, ferrite polymer composite

1 INTRODUCTION

It is known that the behaviour of all microwave ferrite–based devices and elements can be explained in terms of one or more of the following effects: Faraday rotation, ferromagnetic resonance, field displacement, nonlinear effects (amplification and frequency doubling), spin waves (magnetostatic waves). The strong absorption occurring when an elliptically polarized high–frequency magnetic field is perpendicular to the direction of magnetization, called ferromagnetic resonance (FMR), is a useful tool that can be used to determine the values of saturation magnetization M_s, or magnetic polarization $J_s = \mu_o M_s$, with $\mu_o = 4\pi\cdot 10^{-7}$ H/m the permeability of free space [1–3], the size distribution of magnetic particles [4], etc.

Ferrites or ferrite elements are widely used in microwave devices, isolators, circulators, phase shifters, etc. Due to very high electrical resistivity, remarkable flexibility in tailoring the magnetic properties, ease of preparation, and, last but not least, price and performance considerations make ferrites the first choice materials for microwave applications. However, the frequency range of operation, the power handling capacity and the temperature sensitivity of ferrite–based devices should be improved. One of the possible solutions is to use ferrite–polymer composite (FPC) materials consisting of magnetic filler (ferrite powder with defined granulometry and/or morphology) in a non–magnetic matrix (e.g. polymer insulating material). FPC materials have been a subject of recent extensive research [5–8]. Electromagnetic properties of these materials depend on the electrical and magnetic properties of individual constituents (magnetic particles, dielectric polymer matrix, functional chemical fillers) as well as on the method of preparation [9, 10]. We have studied the frequency dispersion of complex permeability of composite materials based on MnZn [8, 10, 11] or NiZn [9, 12] sintered ferrite and PVC polymer matrix and showed that the dispersion of permeability is due to domain wall and/or magnetization rotation contributions and that the critical frequencies (resonance/relaxation) are much higher than that of used sintered ferrite due to arising of demagnetising fields of magnetic particles in composites. We have also studied the FMR on some of these materials [1–3], namely NiZn ferrite – PVC polymer composites, and determined the saturation magnetic polarization of $Ni_{0.3}Zn_{0.7}Fe_2O_4$ sintered ferrite. As it was shown in [1, 2], the results of the measurements at two distinguished positions of disc – with magnetization (a) perpendicular and/or (b) parallel to the sample surface – has led to different values and the measurement using a vibrating sample magnetometer (VSM) gave the third results. Therefore we have also tried another experiment [3]: the disc under FMR measurement was magnetized in many different directions with respect to its axis of rotation and for evaluation of the experiments, the well-known Kittel's relation (valid for a general ellipsoid) described in [13] has been used. At each magnetization direction, using the rotational transformations, the components of actual demagnetizing tensor were computed. The most probable value of J_s for NiZn sintered ferrite was determined by means of least mean square (error) method giving the results in the best agreement with those obtained using VSM.

The present paper follows the goals investigated in [1–3] with MnZn ferrite as a filler and PVC as a matrix in prepared composites, and the effect of ferrite filler concentration on the bias field at which the FMR at a given frequency occurs has been studied from the viewpoint of the determining the saturation magnetic polarization of composites and sintered ferrite. Each sample under test was magnetized at different angles (0–90°) with respect to its axis of rotation.

2 EXPERIMENTAL

The samples used in FMR experiments were polymer ferrite composite materials. As a filler, a commercially available

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MnZn sintered ferrite (type H21 – a product of S+M Components, Czech Republic) with initial permeability $\mu_i = 1900 \pm 20$ %, Curie temperature $T_c \approx 476$ K, and mass density $\rho = 4.8$ g/cc was used. The structural analysis showed that the MnZn ferrite consists of 37 wt% MnO, 12 wt% ZnO and 51 wt% Fe_2O_3 (composition $\approx Mn_{0.37}Zn_{0.57}Fe_{2.06}O_4$). Magnetic particles were prepared by mechanical granulation of this sintered ferrite, the obtained ferrite powder was sieved, and the particle size 0–250 μm was reached. Some 10, 20, 30, 40, 56, 60 and 80 vol% of thus treated ferrite powder were added to the composites. Finally, the cylindrical composite samples (with a height of $h = 1.3$ mm and a diameter of $D = 9.5$ mm) were prepared by means of a simple mixing and moulding process. It should be noted that composite samples with a higher concentration of filler than 80 vol% were not easy to prepare. Moreover, the samples with higher ferrite content did not posses smooth enough surface in comparison with those with a lower ferrite content. Also details of the space distribution of ferrite particles in composite samples were not known. Finally, it should be pointed out that FMR measurements depend on the shape of composite samples i.e. on their demagnetizing factors, which are precisely defined only in case of an ellipsoid of rotation and derived bodies like cylinders (or thin discs) and spheres providing the samples can be magnetized homogeneously. Therefore, during the evaluation of measurements, we should take special care: the magnetization distribution in planar composite samples due to their non–ellipsoidal shape is no more uniform and this gives rise to non–uniform internal fields, affecting the operation of device based on such composite materials. For this reason, the demagnetizing effects cannot be neglected.

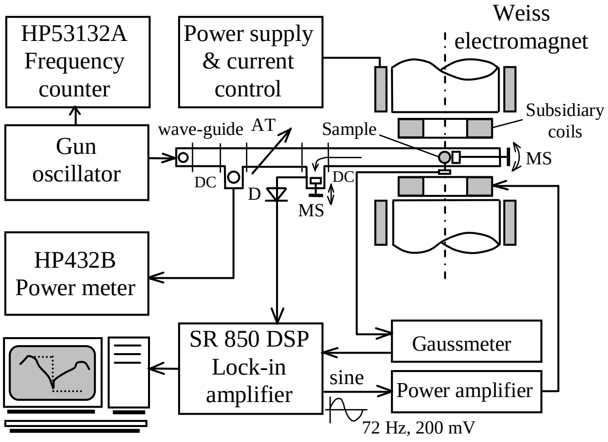

Fig. 1. Block diagram and operation principle of set–up.

The block diagram and view of the used experimental set–up are shown in Figs. 1 and 2, respectively. When an elliptically polarized high–frequency field is perpendicular to the direction of magnetic polarization, an intensive absorption of microwave radiation by the sample is mirrored as a drop of the detected voltage, being proportional to reflected power. At the measurement, a stationary (bias) magnetic field (generated by Weiss electromagnet) having also a small sine component (modulating current in subsidiary air coils) was applied. The modulation of magnetic field was provided to be able extract the useful signal from noise by means of synchronous lock–in detector (amplifier) tuned to the modulating current frequency $f_{mod} = 72$ Hz.

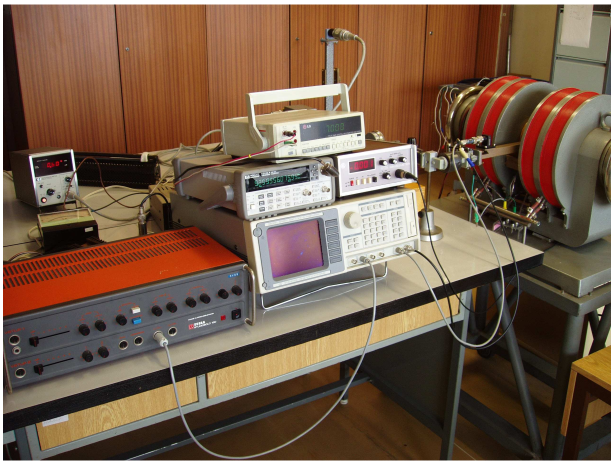

Fig. 2. View of experimental set–up.

The voltage, sensed by a microwave detector, was recorded in dependence on the applied external magnetic field. Since the modulation curve (resonant characteristic of the filled wave–guide) is highly non–linear, the lock–in detector was set sensitive to the first harmonic component i.e. to frequency of modulating field (alternatively the second harmonic component could be tuned).

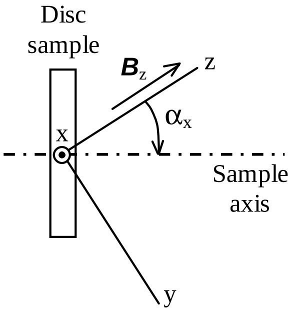

Fig. 3. The angle between the sample axis and the bias field direction.

The modulating signal was generated by internal circuitry of the lock–in detector. The resonant field was detected as a rapid change by 180 degrees in phase and, due to the detector sensitivity of about 60 dB, a drop of voltage practically to zero value occurred at the same time. During measurements, the sample under test can be rotated with respect to the external field direction by means of movable shaft (MS). The way of sample fixation on the MS (the sample was stuck on MS) enables us to change the angle α_x between its axis (sample axis) and the bias field B_z direction from outside the wave–guide, Fig. 3. The MS is placed in the wave–guide giving the possibility of FMR magnetic field measurement for different positions of the sample under test. The microwave field (of frequency

$f_o \approx 9240$ MHz) is excited in a 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.

3 RESULTS AND DISCUSSION

Figures 4 and 5 show the typical results of the FMR measurements in two well distinguished positions for low (Fig. 4) and high (Fig. 5) ferrite volume concentrations: 10 vol% and 80 vol%, respectively.

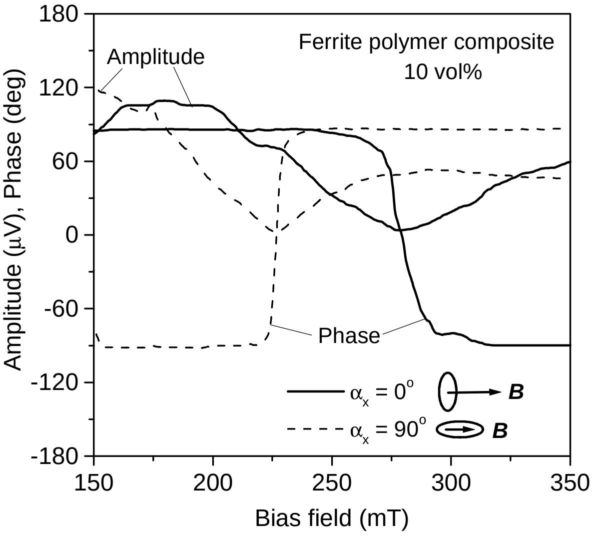

Fig. 4. The dependences of amplitude and phase of reflected signal vs. bias field of 10 vol% composite sample for two different directions of bias field.

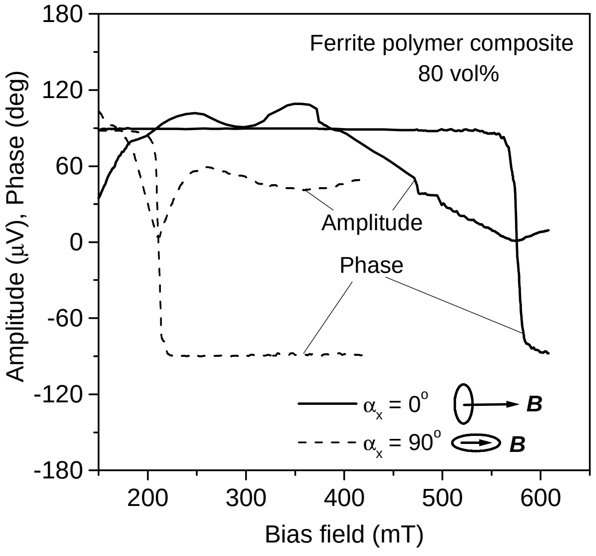

Fig. 5. The dependences of amplitude and phase of reflected signal vs. bias field of 80 vol% composite sample for two different directions of bias field.

Both the amplitude and phase were recorded for bias field perpendicular and parallel to the surface of the disc samples.

Figure 6 shows the measured dependences of resonance field B_R vs. ferrite volume concentration κ_v of composite disc samples at five different angles α_x with respect to their axis (see also Fig. 3). It can be seen that with increasing the concentration the resonance field is remarkably different for all angles. The FMR is affected by internal magnetic field and this is strongly influenced not only by the shape of the samples but also the possible internal aggregates and their mutual interactions may play a significant role. To certain extent the discrepancies or deviation from ideal linear dependences of resonance field B_R vs. concentration κ_v of composites can be explained by the surface roughness of discs, particularly of those with higher ferrite filler concentration.

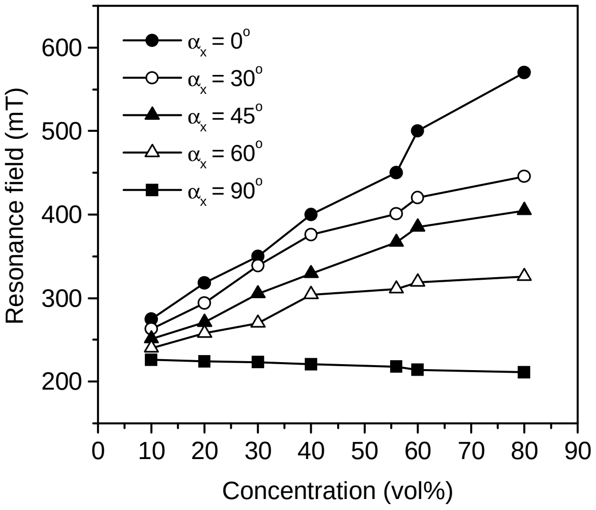

Fig. 6. The measured dependences of resonance field B_R vs. ferrite volume concentration κ_v of composite disc samples at different angles α_x with respect to their axis.

The FMR results can be evaluated by means of an approach described in [3]. The sample under test was considered to be an ellipsoid of rotation with dimensions D, h given above, and from these the basic – position demagnetizing tensor (with axis of symmetry in the external field direction) was calculated. In our case the ellipsoid semi–axis were identified as $a = b = D/2$, and $c = h/2$, thus due to $c/a < 1$ the following formula applies

$$N_c = \frac{1}{1-\lambda^2} - \frac{\lambda}{\left(1-\lambda^2\right)^{3/2}} \arcsin\left[\left(1-\lambda^2\right)^{1/2}\right] \qquad (1)$$

utilizing $N_a + N_b + N_c = 1$, we have particular results $N_a = N_b = 0.091$, $N_c = 0.817$ corresponding to the measured samples, and $\lambda = h/D$. If we use matrix representation

$$N = \begin{pmatrix} N_a & 0 & 0 \\ 0 & N_b & 0 \\ 0 & 0 & N_c \end{pmatrix} \qquad (2)$$

in arbitrary position the appropriate matrix containing nine elements is obtained by three consecutive rotational transformations around individual axis that around x axis is represented by

$$R_x = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\alpha_x & \sin\alpha_x \\ 0 & -\sin\alpha_x & \cos\alpha_x \end{pmatrix} \tag{3}$$

to give

$$N^* = R_x \cdot R_y \cdot R_z \cdot N \cdot R_z^{-1} \cdot R_y^{-1} \cdot R_x^{-1} = \begin{pmatrix} N_{11}^* & N_{12}^* & N_{13}^* \\ N_{21}^* & N_{22}^* & N_{23}^* \\ N_{31}^* & N_{32}^* & N_{33}^* \end{pmatrix} \tag{4}$$

Here "original demagnetizing matrix N" is left–multiplied by the rotational matrices and right–multiplied by their inverses. In present case: $N_{12}^* = 0$. For each angle of rotation, using the above numeric procedure, one can evaluate the resonant field intensity at a given microwave frequency and magnetic saturation polarization from the Kittel's relation

$$B_o = \left[\left(B_R + \Delta N_1^* J_s \right)\left(B_R + \Delta N_2^* J_s \right) - \left(N_{12}^* J_s \right)^2 \right]^{1/2} \tag{5}$$

where $B_o = f_o/|\gamma|$ and is the external bias field for a hypothetical spherical sample at frequency f_o and $|\gamma|$ is the gyromagnetic ratio, and where $\Delta N_1^* = N_{11}^* - N_{33}^*$, $\Delta N_2^* = N_{22}^* - N_{33}^*$, and $\Delta N_{...}^*$, with subscript pairs, are the terms of transformed demagnetization tensor (matrix) from the first to the third row and column, respectively. It should be pointed out that using (5) requires knowing the direction of $\vec{J}_s$ for given $\vec{B}_z$ as in general these directions do not coincide.

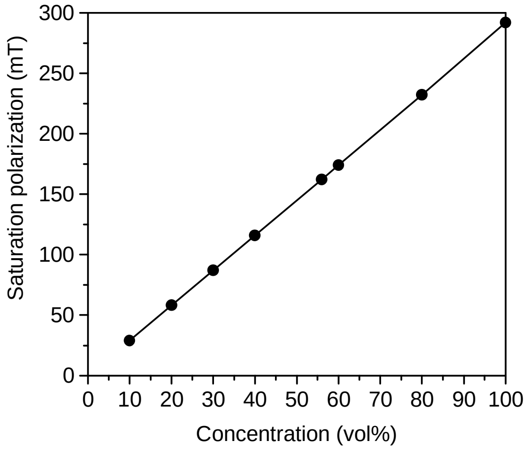

Fig. 7. The dependences of calculated saturation magnetic polarization J_s vs. ferrite volume concentration κ_v of composite disc samples.

Despite of this fact, if the "disc" sample is well saturated in a strong enough bias field, the resonance condition (5) can be simplified to

$$\xi^2 - \xi\eta q(\alpha_x) + \eta^2 g(\alpha_x) = 1 \tag{6}$$

where $q(\alpha_x) = 3\cos^2\alpha_x - 1$, $g(\alpha_x) = \cos^2\alpha_x \left(2\cos^2\alpha_x - 1\right)$, with reduced variables $\xi = B_R / B_o$, $\eta = k \cdot J_s / B_o$, and for used samples $k = (3N_c - 1)/2 = 0.743$, $B_o = 0.33$ T at chosen frequency $f_o = 9240$ MHz. Quadratic equation (6) can be solved with respect to ξ and η and from each measurement the value of J_s may be estimated. To find its value corresponding to a minimum quadratic error between measurement and its prediction we used least mean square method. As a result of the fitting procedure, by means of MATHCAD software, we got the values of J_s for composite samples (see Fig. 7). The result $J_s = 292$ mT concerning concentration 100 vol% stands for sintered ferrite. The VSM measurements, performed on sintered ferrite (100 vol%), gave similar result $J_s = 289$ mT. The values of J_s seem to be correct due to practically linear dependence of J_s vs. ferrite filler volume concentration (see also [1, 2, 5, 11, 12]).

4 CONCLUSIONS

The present work has described the experimental variations of the FMR measured on composite materials, as a function of their volume concentration in magnetic matter. The approach is based on the description of the demagnetizing effects for composite samples of finite size. The FMR results depend particularly on the internal magnetic field and are highly affected by the shape and size of a sample under test. The technique of rotating sample (as was used here) can be considered as a type of averaging, partly eliminating such errors as due to the surface roughness, misalignment of the sample in wave–guide, etc.

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