

FMR study of magnetic nanoparticles embedded in non-magnetic matrix

N. Guskos ^{a,b,*}

co-operating with

E.A. Anagnostakis ^a, **A. Guskos** ^b

^a Solid State Section, Department of Physics, University of Athens, Panepistimiopolis, 15 784 Zografos, Athens, Greece

^b Institute of Physics, Szczecin University of Technology, Al. Piastow 17, 70-310 Szczecin, Poland

* Corresponding author: E-mail address: nguskos@phys.uoa.gr

Received 02.04.2007; published in revised form 01.09.2007

Materials

ABSTRACT

Purpose: The aim of this review is recapitulating the FMR study of low concentration of magnetic nanoparticles in non-magnetic matrices.

Design/methodology/approach: Magnetic nanoparticles exhibit a variety of anomalous magnetic properties and they could be used for forming low concentration in different matrices. This way, they are being found to be allowing for effectively novel applications of FMR (ferromagnetic resonance) for easier trustworthy characterisation of a variety of materials. α -Fe, Co, Fe₃C, γ -Fe₂O₃, Fe₃O₄ magnetic nanoparticles have been used as low concentration fillers in paraffin, concrete, resin and polymers/copolymers.

Findings: For all these matrices, the intensities of the FMR spectra are recorded decreasing with temperature lowering in the high temperature region, whilst the resonance locus is shifted to the direction of lower magnetic field, essentially changing the resonance condition. These parameters of the FMR spectra are seen depending upon kind of nanoparticle host in such a way that this method could be useful for studying dynamical processes of the matrices. Interestingly enough, a very low concentration of magnetic nanoparticles embedded in the non-magnetic matrix could modify its glass-state emanation or melting transition.

Research limitations/implications: Composite systems containing magnetic nanoparticles promise the potential for high-density data storage, biomedical applications, catalysis, and nanotechnology sensor materialisation, among other envisaged utilisations.

Originality/value: Continue attempting to decipher the mystery and fruitfulness of magnetic nanoparticle distributions.

Keywords: Metallic alloys; Nanoparticles; Magnetic materials

1. Introduction

The allegory of “magnetising” as “persuasively attractive” appears righteous to our perception, concerning our nanotechnology research evolving through the recent 10 years into the behaviour of novel composite systems of ensembles of various types of magnetic nanoparticles dispersed into inert hosts

[1-14]. The attraction has been inspiring us into attempting to consider, prepare, characterise, and study -mainly by using ferromagnetic resonance spectroscopy (FMR)- typically homogeneous distributions of several different species of magnetic nanoinclusions, or even combinations of them, functioning at selectable filler at low concentration within alternative non-magnetic matrices. The persuasiveness, on the

other hand, seems to be pouring out of the reproducible soundness of the findings, the allusion to cost-effective applicability, and even exotic circumstances of magnetoelastic coupling of the nanofiller ensemble to a polymeric host.

The following nanocomposite systems have been to-date investigated carefully by our research team [10, 15-21]:

- a) Dispersion of cementite (iron carbide, Fe_3C) nanoparticle agglomerates in a graphite matrix. Powder samples with differing cementite content, synthesised by carburization of nanocrystalline iron with either methane or ethylene – hydrogen mixture and characterized by XRD and TEM to possess iron carbide nanocrystallites of mean size of 41 – 67 nm, have been submitted to FMR measurements either at room temperature (RT) or with the ambient temperature as a parameter lowered from RT to liquid helium point. The samples have, in general, exhibited a broad and intense FMR absorption derivative spectrum decomposable into two Lorentzian lineshapes centred at a lower and a higher applied magnetic field, respectively, with the main high-field component shifting towards lower magnetic field for decreasing temperature. The temperature evolution of the FMR signal curve has been linked to both a phase transition at 75 K tantamount to the freezing of the diamagnetic carbon matrix and the emanation of the spin-glass state below 30 K. Notably, the FMR signal prime descriptors (resonance field, linewidth, and integral signal intensity) are found to clearly depend on the concentration of the nanofiller and to be conditioned by the exact process of preparation.
- b) Samples of nanocrystalline Co_3O_4 prepared at various calcinations temperatures and with various amounts of structural additives. RT Magnetic resonance spectra of theirs have been attributed to divalent cobalt ions and found to be undersigned by calcination temperature and the presence of the CaO and Al_2O_3 additives, with samples calcinated at higher temperatures showing an almost symmetrical, intensive spectrum lineshape.
- c) Distribution of multiphase mixture of (c. 1) magnetite (Fe_3O_4) and cementite nanoparticles among graphite nanocrystallite surroundings, and (c. 2) $\alpha\text{-Fe/C}$, $\text{Fe}_3\text{C/C}$ and $\alpha\text{-Fe/Fe}_3\text{C/C}$ nanoinclusions, ultimately immersed into polymeric matrix (wax, epoxy resin or ether-ester copolymer) at different, low nanofiller concentrations [10, 12, 15, 17, 18, 20, 22-26]. Monitoring of the sample FMR spectrum temperature evolution has registered the interplay between thermal fluctuations and inter-particle interactions at the high temperature regime, as well as rather abrupt modifications (especially for the resonance field temperature-gradient) pertaining to matrix freezing effects at critical points when lowering the temperature. Furthermore, for certain multiphase nanoparticle distribution nanofillers, a Verwey transition concurrent with a significant skin depth variation and the subsequent enforcement of nanoparticle agglomerate contribution has been interestingly singled out.
- d) Inclusion of maghemite ($\gamma\text{-Fe}_2\text{O}_3$) nanoparticles in the form of either solid powder or suspension at very low concentration into non-magnetic multiblock copolymeric matrices [14, 27-32]. Independently of the dispersion state of the nanofiller, the effect of temperature lowering upon the FMR spectrum (in particular, with respect to the resonance field shift) alludes to a magnetoelastic coupling of the maghemite nanoparticle ensemble to the copolymeric host dynamically relaxing through matrix- freezing critical points. A pertinent effective magnetic

moment model considering potential consequences of the thermal contraction of the host medium has been discussed.

These investigations have been allowing us to correlate the macroscopic behaviour of magnetic nanoparticle systems with the structure, size, and morphology of the constituent phases as well as with the type and strength of the inter-particle and inter-agglomerate magnetic coupling: The dipole – dipole and exchange inter-particle interactions compete with an anisotropy energy barrier in the orientation of their magnetic moments, whereas strong inter-particle interaction could convert the individual superparamagnetic relaxation into a collective dynamical process. The temperature evolution of the FMR effect for the nanocomposite system may discriminate the nanoparticle conglomerate contribution from the individual nanoparticle one. Another source of temperature lowering – induced significant alterations in the FMR spectrum descriptors (resonance field, linewidth, integral intensity, mainly) has been deduced to be the occurrence of critical phenomena in the polymeric matrix, especially the freezing processes connected with the arrested movements of certain matrix fragments.

Composite systems containing magnetic nanoparticles promise the potential for high-density data storage, biomedical applications, catalysis, and sensor materialisation, among other envisaged utilisations. We are, therefore, eager to continue attempting to decipher the mystery and fruitfulness of magnetic nanoparticle distributions.

The aim of this review is recapitulating the FMR study of low concentration of magnetic nanoparticles in non-magnetic matrices. Interpreting the FMR spectra of magnetic nanoparticle systems could be a very useful method for characterisation of matrices, especially polymers/copolymers, and their critical behaviour at different temperatures.

2. Experimental procedure

The general precursor for sample preparation has been the obtaining of nanocrystalline iron by fusion of magnetite with small amounts of calcium and aluminium structural oxides (CaO , Al_2O_3), meant to stabilise the nanocrystalline iron structure during later treatment, in an electric furnace. After fusion, the lava is cooled to RT, crushed, and sieved to yield grains of magnitude 1.2 – 1.5 mm, which are reduced with a N – H 1:3 mixture under atmospheric pressure in the 200 – 500 C temperature range. For oxidation avoidance, the pyrophoric samples are, after reduction and cooling-down, passivated under N with traces of O (0.5 vol.%) at RT. The chemical composition of such precursor samples is determined by inductively coupled plasma atomic emission spectroscopy (AES-ICP) to be, apart from Fe, 3.0 wt.% CaO and 2.9 wt.% Al_2O_3 . The average $\alpha\text{-Fe}$ crystallite size is determined by X-ray diffraction (XRD, with a Philips X'Pert equipment and $\text{CoK}_{\alpha 1}$ radiation) and calculated through Scherrer's equation to be 14 – 17 nm. The sample specific surface area is determined by thermal desorption of physisorbed N (ASAP 2010, Micromeritics) to be around 20 m^2/g .

The precursor samples destined to possess any ultimate pattern of iron – carbon coexistence (cementite, iron/cementite, iron/carbon, cementite/carbon, iron/cementite/carbon) are submitted, then, to a carburisation process monitored by thermogravimetry: Reduced and passivated grains of 1 g are placed as a single layer in a platinum basket hung in the

thermobalance and rereduced polythermally for removal of the passivating flake, with the temperature rising from 20 to 520 C at a 15 C/min rate under a hydrogen flow of $0.2 \text{ dm}^3 \text{ g}^{-1} \text{ min}^{-1}$. After reaching constant sample mass, the actual carburisation is initiated by replacing hydrogen with methane / hydrogen 2:1 mixture flow of $1.2 \text{ dm}^3 \text{ g}^{-1} \text{ min}^{-1}$ at the previous terminal temperature of 520 C. Under such conditions the process is occurring in the kinetic region of the reaction, with negligible effects of both external and internal diffusion on the reaction rate. During carburisation, the sample mass increase is being registered; whenever the desired degree of carburisation is attained, the process is stopped by rapid cooling in nitrogen atmosphere. After each desired carburisation, the respective outcome sample is characterised by XRD, transmission electron microscopy (TEM), and scanning electron microscopy (SEM) methods for phase composition analysis and distribution homogeneity and nanoconstituent regularity tracing.

As regards maghemite nanocomposites in particular, nanophase $\gamma\text{-Fe}_2\text{O}_3$ with an average particle size of 10 nm is prepared by refluxing freshly precipitated, air-dried iron hydroxide (0.4 g) in tetraline (40 ml) for 1 h under nitrogen [18]. Two alternative forms of ferrimagnetic $\gamma\text{-Fe}_2\text{O}_3$ nanoparticle configuration are, then, employed for introduction into the inert copolymeric matrix during matrix synthesis (i.e., via in situ polycondensation): Solid powder and suspension in trichloromethane, with an almost homogeneous distribution of nanoparticle agglomerates with similar shape and size of over 10 μm revealed by SEM for the former embedded in the poly(ether-ester) matrix and fine agglomerates in the range 10 – 20 nm homogeneously dispersed within the copolymeric host shown by atomic force microscopy (AFM) for the latter [32].

In each case, the ferromagnetic resonance (FMR) absorption signal derivative measurements are carried out by a conventional X-band ($\nu = 9.43 \text{ GHz}$) Bruker E 500 spectrometre with 100 kHz magnetic field modulation, with the sample placed at the centre of the TE_{102} resonance cavity – at the local microwave magnetic component maximum and in the electric component nodal plane. Sample magnetisation by a steady magnetic field of 1.6 T prior to FMR measurements is secured for saturation of any existing domain structure. Ambient temperature lowering is, before reregistering the FMR spectrum, regulated within an Oxford Instrument liquid helium flow cryostat for any region of the whole available range from RT down to 4.2 K.

3. Findings review and interpretation

3.1. Dispersion of cementite nanoparticle agglomerates in a graphite matrix

The nanocrystalline iron carbide (Fe_3C , cementite) can serve as an iron-based composite for the preparation of materials, mechanically superior to traditional ones, to be used for construction of machines and equipment. It is, also, worth studying because of its particular magnetic characteristics, rendering it applicable to the production of magnetic supports of information. Interfaces and surfaces separating different particles, layers, and crystalline or non-crystalline domains are considered crucial in controlling the properties and stability of nanostructures, under the

interplay between domain interface atomic structure – effected nanodevice disorder increase on the one hand and finite – size effects concerning individual domains on the other.

In particular, FMR absorption by magnetic nanoparticle agglomerates embedded in non-magnetic matrix does betoken the significant nanoelement magnetic behaviour and interactions, with the major FMR signal descriptors (resonance field, linewidth, and integral intensity) noticeably affected by concentration and size of nanoelements and agglomerates, among other factors. Our initial investigation of cementite nanoparticle distributions into inert graphite matrices has compared the RT FMR spectra of three samples with differing iron carbide nanocrystallite agglomerate filling (72.2, 88.2, and 83.3 wt.%, for sample I, II, and III, respectively) of the carbon host, established by a differing degree of carburisation as outlined in Section 2. Additionally, our further study has monitored the temperature evolution of the FMR spectrum of a fourth, representative, cementite nanoelement conglomerate sample during cooling from RT down to liquid helium point [10, 15, 18, 21].

The XRD analysis of the three initial samples, performed after carburisation, has led through Scherrer's equation to a mean iron carbide nanocrystallite size of 58, 41, and 67 nm for specimen I, II, and III, respectively. In the XRD angular profile of some samples, apart from the iron carbide peaks -dominant for all samples- (one of which superimposes the Fe(110) spectral line), the graphite peak weakly appears: Sample graphitisation percentage is calculated on the basis of the Maire and Mering formula to be rather low (38 %) plausibly corresponding to hollow carbon filaments, interestingly verified through high-resolution TEM imaging exhibiting local carbon nanotubes distinctively capped by single iron carbide nanoparticles at their end. These carbon nanotubes are seen to be of internal diameter around 30 nm and external around 40 nm compatible with the determined magnitude of cementite nanocrystallites within the investigated samples [10, 15, 18].

In the FMR absorption field-derivative spectra, furthermore, of all samples intense resonance absorption shifted in the direction of low magnetic field is observed with broad linewidth. Resonance field, linewidth, and integral intensity (calculated as the product of the magnetic resonance signal amplitude by the square of the peak-to-peak linewidth) are found to soundly depend on the cementite content of each specimen. An accurate fitting of the extended resonance absorption signal has been performed through employment of two Lorentzian-type curves, taking into account absorption induced by the two oppositely rotating components $+H_r$ and $-H_r$ of the linearly polarised radio frequency (rf) incoming experimental electromagnetic field. The fitting of the resonance absorption signal lineshape by two Lorentzian curves, resting at separated magnetic fields, suggests the potential functioning of a rather strong magnetic anisotropy, seen through FMR spectra and fitting parameters to become more pronounced with decreasing iron carbide inclusion concentration in the inert carbon matrix. The spectrum resonance field is, also seen to be shifting to higher values with decreasing Fe_3C content. We have come to visualise that the detected absorption resonance spectrum pattern is tantamount to ferromagnetic iron ions with their individual spins being coupled through exchange interaction within each nanoscale metallic grain. The localized spin is, believably, subjected to a total magnetic field -owing to non-

separated ferromagnetic nanoparticles- describable by the superposition of a “demagnetization” term (arising from uncompensated magnetic poles at the surface due to arrangement configurations of the atomic magnetic dipoles within a ferromagnetic substance), a “nanoparticle dipole field” term (extending from -mainly directly- neighbouring nanoparticles), an “agglomerate dipole field” (possible in the case of important agglomerate concentration within the diamagnetic matrix and taken as codifying the then inter-agglomerate dipole-dipole interaction), and the actual externally applied magnetic field term. According to such a scheme, the “internal” magnetic field sensed by the localised spin would comprise the three first terms of the above superposition, whereupon the FMR resonance condition should read:

$$h\nu = g\mu_B \cdot (H_{\text{appl}} - H_{\text{int}}), \quad (1)$$

with h being Planck constant, ν the resonance frequency, μ_B Bohr magneton, H_{appl} the externally applied magnetic field, and H_{int} the considered effective internal magnetic field (distributed mainly in the direction of the external one). We have, indeed, managed to interpret the peculiarities of the FMR spectrum parameters, as noticed between different samples, with the additional invocation of Eq. (1) and its context.

Regarding, now, the temperature evolution of the FMR spectrum of cementite nanoparticle conglomerates dispersed in a carbon matrix, we have studied a fourth sample obtained after carburisation with ethylene – hydrogen 1:3 mixture under total flow of $1.3 \text{ dm}^3 \text{ g}^{-1} \text{ min}^{-1}$ at 673 K. The respective XRD analysis has yielded a Scherrer mean iron carbide nanocrystalline size of 46 nm, whereas the SEM surface imaging has registered the presence of $\text{Fe}_3\text{C}/\text{C}$ nanoelement agglomerates of size ranging from 0.5 to 4 μm . Fig. 1a presents the FMR spectra of $\text{Fe}_3\text{C}/\text{C}$ in polymer matrix at room temperature (RT), whereas their temperature dependence is given in Fig. 2. The FMR spectrum is parametrised by ambient temperature being lowered from RT to liquid helium point with the sample premagnetised and predemagnetised several times in magnetic fields up to 1.6 T, thus having been allowed to exhibit afterwards the same FMR spectrum for both directions of the FMR experiment magnetic sweep. (Note that, in general, a magnetically unpretreated sample shows an FMR spectrum shifting to higher magnetic field for downfield experimental magnetic sweeping.) Each of the FMR spectra consists of a very intense and strongly asymmetric absorption curve shifted in the direction of low magnetic fields and is successfully fitted by two Lorentzian-type lineshapes, one with near-zero resonance field and the other being the high-resonance- field component.

A significant change in the resonance line intensity is accompanied by a strong shift of the resonance field with decreasing temperature for the high-field component. The line intensity against temperature for this component is exhibiting a minimum at about 30 K. These features along with the clustering phenomena inside agglomerates indicate the occurrence of some kind of phase change with respect to a dual mode (iron surviving carburisation / cementite) nanoparticle distribution magnetisation: Probably, inside the sample the spin-glass phase is forming below 30 K. Additionally, the value of the resonance field temperature-gradient is one order of magnitude larger below 75 K, supposedly

arising from a freezing phenomenon at this temperature, effected through arrest of molecular movements of the non-magnetic matrix. Therefore, though in principle FMR is limited mainly by inhomogeneous broadening stemming from a random orientation of anisotropic magnetic elements dispersed in an inert host, we have managed to extract valuable information pertaining to both a spin-glass state formation and the dynamics of the freezing of the diamagnetic matrix.

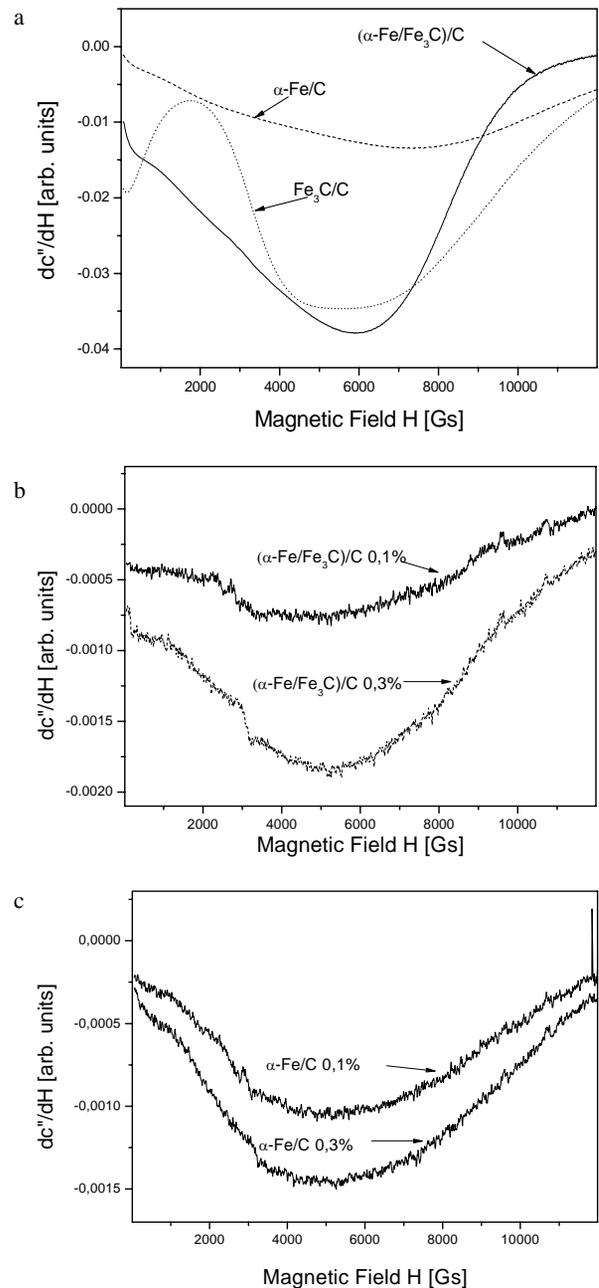


Fig. 1. The FMR spectra of $\alpha\text{-Fe}/\text{C}$, $(\alpha\text{-Fe}/\text{Fe}_3\text{C})/\text{C}$, and $\text{Fe}_3\text{C}/\text{C}$ (a), $(\alpha\text{-Fe}/\text{Fe}_3\text{C})/\text{C}$ with different concentrations (b), $\alpha\text{-Fe}/\text{C}$ with different concentrations (c) in polymer matrix at room temperature

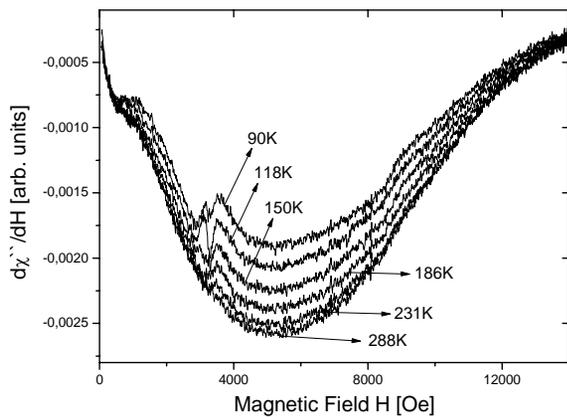


Fig. 2. The temperature evolution of FMR spectra of $\text{Fe}_3\text{C}/\text{C}$ in polymer matrix

3.2. Samples of nanocrystalline Co_3O_4

Cobalt oxides, due to their magnetic and catalytic properties, are used in a wide range of applications in various fields of industry, including pH sensors, gas tracers, and prototype magnetic functional materials and devices. Cobalt oxide nanostructures are highly sensitive to nanoparticle size as well as to concentration of defects or heterogeneous phases. In transition metal compounds, in particular those containing iron(II) and cobalt(II), spin-state transitions between the low-spin and the high-spin states occur.

The samples of nanocrystalline Co_3O_4 studied have been prepared at various calcination temperatures and with various amounts of structural additives. XRD analysis following preparation has yielded a Scherrer mean nanocrystallite size around 50 nm for a calcination temperature of 500 C as compared to another above 100 nm for calcination at 900 C. RT Magnetic resonance spectra of theirs [35] have been attributed to divalent cobalt ions and found to be undersigned by calcination temperature and the presence of the CaO and Al_2O_3 additives. Samples calcinated at higher temperatures show an almost symmetrical, intensive spectrum lineshape, whilst the linewidth depends sensitively on the sample thermal preparation process and increases with calcination temperature lowering.

Furthermore, we are currently still studying cobalt nanoparticles dispersed at low concentration in paraffin and concrete [33, 34]: Fig. 3 presents the FMR spectra of cobalt nanoparticle dispersion in paraffin at different temperature. The intensity of the FMR signal of cobalt nanoparticle essentially decreases with decreasing temperature, similarly to findings regarding nanocrystalline iron systems.

3.3. Multiphase distributions into inert host

One of the multiphase dispersions investigated has been a mixture of magnetite (Fe_3O_4) and cementite nanoparticles among graphite nanocrystallite surroundings, ultimately immersed as a nanofiller into a polymer composite of epoxy resin hardened thermally, after having been poured into the mold, by triethanolamine.

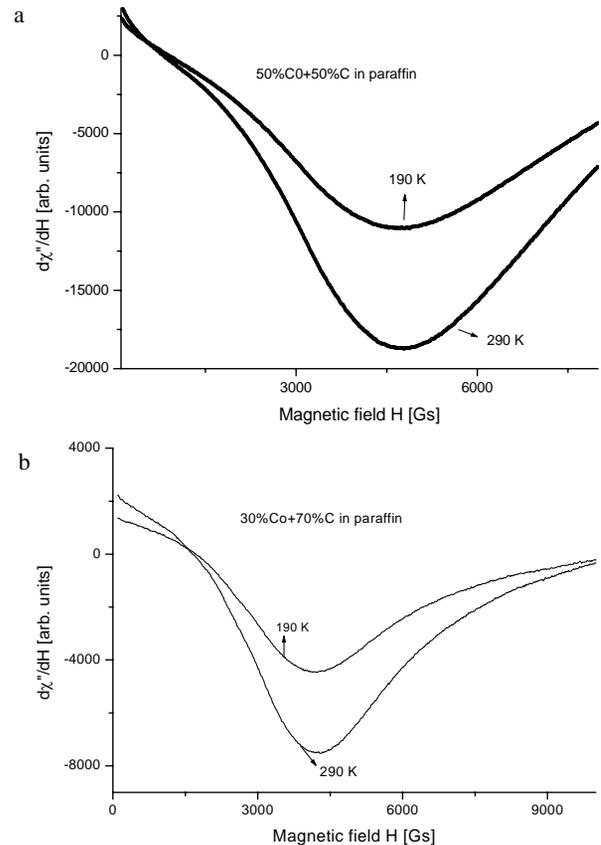


Fig. 3. The FMR spectra magnetic cobalt nanoparticles in paraffin at different temperatures for (a) lower- and (b) higher-concentration magnetic nanoparticles

The final composition contained 10 wt.% of the carburised multiphase nanoparticle structure, 40.8 g of polymeric epoxy resin, and 2.4 g of the hardener; reproducible FMR spectra obtainment from different parts of the sample indicated a plausibly homogeneous distribution of the carburised nanostructure within the inert matrix.

As evidenced by XRD analysis during preparation, the precarburisation iron nanocrystallite average size has been around 17 nm, whereas according to postcarburisation XRD and TOC determination the multiphase nanocomposition consisted of cementite nanoparticles by 29 wt.%, magnetite nanoelements by 35 wt.%, and carbon nanocrystallites by 36 wt.%, the mean size of cementite, magnetite, and graphite nanocrystallites being between 30 – 50 nm. SEM imaging, at that, has led to the recognition of fine graphite fibers with similar shape and size (diameter below 1 μm) almost regularly distributed amidst the nanoparticles of various species.

Fig. 4 presents the FMR spectrum of such a Fe_3O_4 nanoparticle system, as those participating in the final polymeric multiphase nanocomposite, measured at RT. An intense resonance absorption derivative curve is generally observed in the FMR spectra of our magnetite / cementite / graphite nanofiller immersed in the polymeric matrix, with a slightly asymmetric lineshape which can be fitted by the superposition

of two separate Lorentzian lines including the tail of the resonance absorption at negative field owing to the linearly polarised incoming rf EM field. A relatively narrow resonance signal is, thus, derived with g-factor $g = 2.25(1)$ and peak-to-peak linewidth $\Delta H_{pp} = 1.34(2)$ kG, as well as a rather broad one with $g = 1.78(2)$ and $\Delta H_{pp} = 6.1(1)$ kG, being similar to the details of the broad FMR spectra of cementite nanoparticle agglomerate distributions synthesised through the same carburisation route from nanocrystalline iron [12]. The dominant narrow line broadens shifting gradually to lower fields with temperature lowering down to 81 K, whilst the broad component further broadens till beyond detection already below 150 K. Most remarkably, an abrupt change of the resonance spectra occurs below 81 K within a very narrow temperature interval of less than 1 K, revealing a very intense and broad FMR line spanning the whole magnetic field range, on which some structure appears at lower temperatures.

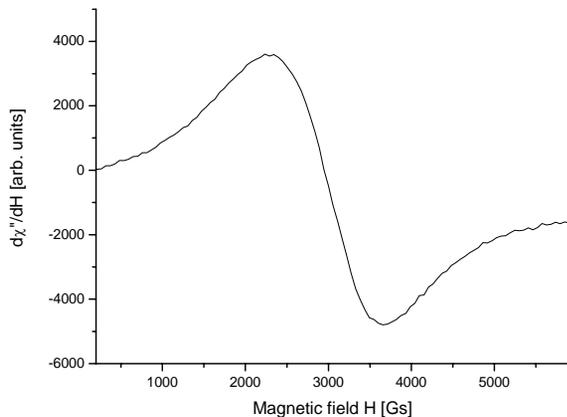


Fig. 4. The FMR spectra of Fe_3O_4 nanoparticle distribution in resin at room temperature

Fig. 5 presents the temperature dependence of the resonance field for the narrow FMR component Lorentzian line in the 4.2 – 300 K temperature range. This type of temperature variation has been frequently observed in the FMR spectra of iron oxide nanoparticle ensembles, signifying the gradual suppression of the averaging effect of thermal fluctuations or the emergence of spin-glass freezing with temperature lowering. Comparison with the RT FMR spectra of fine powdered magnetite as well as cementite specimens shows that the observed FMR curve is considerably shifted towards $g = 2.0$ and appears quite narrower, the presence of thermofluctuational effects at high temperature thus alluded to. On the other hand, the FMR spectrum for an assembly of randomly oriented, non-interacting, spherical (and, thus, with no shape anisotropy) magnetite nanoparticles would lead to a distinct asymmetric powder spectrum on account of the cubic magnetocrystalline anisotropy of magnetite, yielding an effective peak-to-peak linewidth $\Delta H_{pp} = 0.78$ kG, being smaller than the actually monitored one. Moreover, the FMR linewidth of bulk magnetite would be expected to narrow at lower temperatures, reaching a minimum value at the compensation point above the Verwey temperature. A sizable

contribution to the effective magnetic anisotropy of the high temperature FMR curve by demagnetising fields as well as inter-particle interactions can be accordingly inferred. However, in the former case the low-field shift of the FMR line would require a negative shape anisotropy such as that produced by oblate ellipsoids, whereas inter-particle interactions of either dipolar or exchange origin have been invariably predicted to shift the FMR curve to lower fields in parallel to broadening and amplitude reduction, in qualitative agreement with the observed behaviour of our hosted multiphase dispersion samples. Additionally, the abrupt change of the resonance spectra recorded below 81 K coincides with a sharp anomaly resolved in the temperature-gradient of the ac conductivity of our samples (Fig. 5). This behaviour is attributable to the Verwey transition of magnetite nanoparticles, with the pertinent rf EM-field skin-depth variation (from 33 μm above 81 K to 520 μm below the Verwey critical temperature) rendering large nanoparticle conglomerates dominant upon dictating the FMR effect character at lowering the experimental temperature below 81 K.

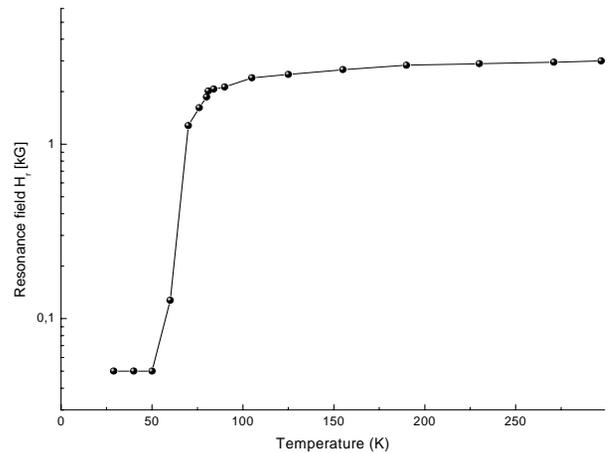


Fig. 5. Temperature dependence of the resonance field H_r of the FMR spectra of Fe_3O_4 nanoparticle system

Other multiphase nanocomposition dispersions treated by our team have been those of $\alpha\text{-Fe}/\text{C}$ nanoelements, $\text{Fe}_3\text{C}/\text{C}$, and $(\alpha\text{-Fe}/\text{Fe}_3\text{C})/\text{C}$ nano-inclusions, ultimately immersed into polymeric matrix (wax, epoxy resin or ether-ester copolymer) at different, low nanofiller concentrations [10, 12, 15, 17, 18, 20, 22-26]. FMR measurements (Fig. 1 and 2) have singled out two distinct types of spectrum constituents, one originating from iron carbide nanoparticles and the other from $\alpha\text{-Fe}$ nanocrystallites. In general, the FMR spectra are seen to intimately correlate to the exact sample preparation process as well as the concentration of each species of magnetic nanoparticles within the hosting inert matrix. Monitoring of the sample FMR spectrum temperature evolution has registered the interplay between thermal fluctuations and inter-particle interactions at the high temperature regime, as well as rather abrupt modifications (especially for the resonance field temperature-gradient) pertaining to matrix freezing effects at critical points when lowering the temperature.

3.4. Inclusion of maghemite ($\gamma\text{-Fe}_2\text{O}_3$) nanoparticles into non-magnetic multiblock copolymeric matrices

As already commented upon, magnetite oxide nanoparticles attract particular interest due to their unique magnetic properties stemming from the complex interplay between the intrinsic magnetic response of the individual particles, determined by finite size and surface effects, on the one hand, and the diversity of inter-particle interactions on the other, rendering them distinctively different from those of their bulk counterparts. Enhanced anisotropy and spin disorder at the outer nanoparticle layers competing with the bulk-like behaviour of core spins have been proposed to account for the low-temperature magnetic response of nanocrystallites of ferrimagnetic oxides such as nickel ferrite (NiFe_2O_4) and maghemite ($\gamma\text{-Fe}_2\text{O}_3$), including the reduction of the magnetic moment, non-saturated magnetisation, high-field irreversibility, and shifted hysteresis loops after field-cooling [1-7].

The existence of a ferrimagnetic core surrounded by a surface layer of canted spins has been identified for maghemite nanoparticles, undergoing a spin-glass-like transition to a frozen state at around 50 K [2, 5]. Inter-particle interactions, mainly of dipolar and, to a lesser extent, exchange/superexchange origin, may also have a pronounced effect on the static and dynamic properties of nanoparticle assemblies. A transition from the superparamagnetic to a collective state has been discerned in the limit of strong interactions for maghemite nanoparticles, resembling to some extent that of spin glasses [2]. Single domain nanoelements interacting via dipolar and short-range exchange forces have been successfully utilised in investigations of metallic nanoparticles and granular magnetic solids. On the other hand, experimental work on maghemite nanoparticles dispersed in polymeric matrices bearing different surface coatings has emphasised the contribution of surface effects and the diversity of magnetic properties, indicating that the particle microstructure as well as the host medium can significantly affect the magnetic response of such systems. Polymers, in particular, may serve as excellent matrices for magnetic nanoparticles in order to synthesise nanocomposite functional materials combining the functionality and mechanical properties of the polymer with the idiosyncrasy of the magnetic inclusions, the interactions of the (agglomerates of the) nanoelements becoming especially important.

We have comparatively studied the magnetic properties of maghemite nanoparticles embedded in a multiblock poly(ether-ester) copolymer in the form of solid powder (sample I) and as a dilute suspension (sample II). In the former case, maghemite grains form large agglomerates of diameter over 10 μm (as revealed by SEM), whilst the dilute suspension of the filler material in trichloromethane results in nanoscale particles forming fine agglomerates in the range 10 – 20 nm (as evidenced by AFM) homogeneously dispersed in the copolymeric matrix [14, 27, 31]. Fig. 6 presents the temperature evolution of the FMR spectrum for two type-I samples of maghemite nanocomposite with different nanofiller concentration. A single resonance curve with an asymmetric lineshape is observed. Identical FMR spectra are obtained from different parts of each type of sample as well as after freezing at liquid nitrogen point, showing that the nanoparticles and their conglomerates are indeed homogeneously dispersed in the

copolymeric matrix. According to the resonance field H_r and peak-to-peak linewidth ΔH_{pp} determined for a type-I sample, with nanofiller concentration 0.1 wt.%, ($H_r = 2.99(1)$ kG, $\Delta H_{pp} = 1.18(1)$ kG) and a type-II sample, with same nanofilling percentage, ($H_r = 3.22(1)$ kG, $\Delta H_{pp} = 1.10(1)$ kG), the FMR spectra are much broader than expected for an assembly of randomly oriented, spherical, non-interacting maghemite nanoparticles [26].

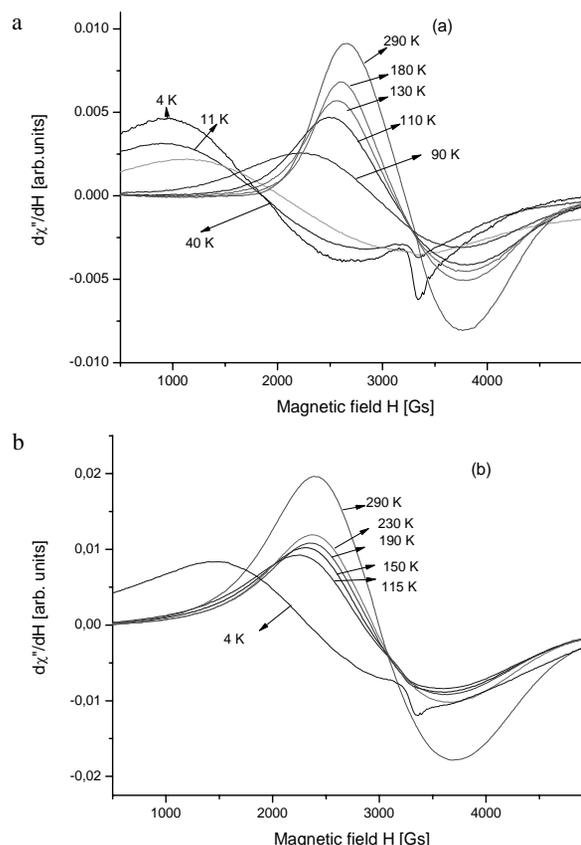


Fig. 6. Temperature dependence of FMR spectra of $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles dispersed in copolymeric matrix at concentration of wt. (a) 0.1 % and (b) 0.3 %

Dynamic narrowing of the FMR spectra due to superparamagnetism has been frequently observed at high temperatures for dilute suspensions of iron oxide nanoparticles, leading to the counter-deduction that both sample types I and II are not in the pure superparamagnetic state, in agreement with their aggregated morphology and the dc magnetisation results [14, 31]. Severe spectral broadening, except for the case of increased damping, may arise from a wide size and shape distribution and, most importantly, an increase of the effective anisotropy and the presence of interparticle interactions [2]. Furthermore, microscopic simulations of the FMR spectra of fine particle systems have indicated that pure dipole-dipole interactions affect only weakly the resonance field, whereas exchange coupling of the nanoparticle moments causes a rapid decrease of it [4]. A strong variation of the effective resonance field is also expected through an increase of the magnetic

anisotropy, which however would depend upon the sign of the anisotropy constant. Given the presence of similar magnetic anisotropy and size distribution of the individual nanoparticles constituting the two nanocomposites, a stronger interaction effect may, then, be inferred from the larger low-field shift of the resonance field.

A relatively weak shift of the resonance field toward lower values is observed for both samples with temperature lowering down to 120 K. At even lower temperatures, a marked decrement of the resonance field is monitored at nearly identical rates for both samples, as directly evidenced from the respective temperature-gradient temperature-evolution. This variation, reflecting an increase of magnetic anisotropy or even inter-particle interactions, points to a common effect for both samples, regardless of the dispersion state of the maghemite nanoelements in the poly(ether-ester) copolymer. On the other hand, significant differences are observed in the temperature evolution of the resonance field at actually low temperatures. In particular, the fast decrease of the resonance field with temperature lowering gradually ceases and nearly levels off below 20 K for sample I, whereas a minimum of the resonance field occurs at about 10 K for sample II, followed by a sharp increase at lower temperatures, reflected in corroboration in the sign reversal of the corresponding temperature-gradient evolution.

We have managed to interpret such FMR spectrum temperature-evolution peculiarities to the presence of critical phenomena in the polymeric matrix, especially the freezing processes connected with the arrested movements of certain matrix fragments [14, 31]. The copolymer has a critical point at which the local rotations of the ether group freeze, most importantly around 110 – 120 K, for which temperature interval the rotations of the benzene rings freeze (instance of γ -relaxation). A matrix effect can be accordingly suggested, pertinent mainly to the modification of the magnetic anisotropy of the individual nanoparticles as well as their mutual interactions. With the assumption of a chemically inert interaction between the polymer matrix and the ferrimagnetic nanoparticles, a magnetoelastic effect may be invoked through the stress exerted on the nanoparticles by the elastic deformation of the surrounding matrix accompanying the freezing of the copolymer. Stress anisotropy or even modification of the surface anisotropy of the maghemite nanoparticles may then arise, triggering the rapid resonance field shift for both samples. Nevertheless, elastic stresses would also strengthen interaction effects either by reducing the average inter-particle distance or even enhance the exchange coupling by bringing into close contact more nanoparticles in aggregated assemblies such as in type-I samples. Interaction effects may thus underlie the differences in the temperature-evolution of the FMR spectrum linewidth below 120 K for the two sample types, which –according to numerical calculations- vary significantly due to dipolar and exchange influences. Furthermore, the diversity of inter-particle interactions pertinent to the different dispersion state of the two nanocomposite types and their reinforcement by the mechanical distortion of the matrix can be implicated to account for the different behaviours of the FMR spectrum parameters below 30 K. Such interpretations we have found non-contradicting a simulative model of an effective magnetic moment modifiable by thermal contractions of the copolymeric matrix [28].

4. Conclusions

Magnetic nanoparticles exhibit a variety of anomalous magnetic properties and they could be used for forming low concentration in different matrices. This way, they are being found to be allowing for effectively novel applications of FMR (ferromagnetic resonance) for easier trustworthy characterisation of a variety of materials. α -Fe, Co, Fe_3C , γ - Fe_2O_3 , Fe_3O_4 magnetic nanoparticles have been used as low concentration fillers in paraffin, concrete, resin and polymers/copolymers. For all these matrices, the intensities of the FMR spectra are recorded decreasing with temperature lowering in the high temperature region, whilst the resonance locus is shifted to the direction of lower magnetic field, essentially changing the resonance condition.

For the cementite nanoparticle agglomerate system, though in principle FMR is limited mainly by inhomogeneous broadening stemming from a random orientation of anisotropic magnetic elements dispersed in an inert host, we have managed to extract valuable information pertaining to both a spin-glass state formation and the dynamics of the freezing of the diamagnetic matrix.

Samples of nanocrystalline Co_3O_4 calcinated at higher temperatures show an almost symmetrical, intensive spectrum lineshape, whilst the linewidth depends sensitively on the sample thermal preparation process and increases with calcination temperature lowering.

Multiphase dispersions investigated, as a mixture of magnetite and cementite nanoparticles among graphite nanocrystallite surroundings ultimately immersed as a nanofiller into a polymer composite of epoxy resin, have produced quite interesting deductions. Notably, the abrupt change of the resonance spectra recorded below 81 K coinciding with a sharp anomaly resolved in the temperature-gradient of the ac conductivity of our samples and attributable to the Verwey transition of magnetite nanoparticles.

As for the inclusion of maghemite (γ - Fe_2O_3) nanoparticles into non-magnetic multiblock copolymeric matrices, we have managed to interpret the obtained FMR spectrum temperature-evolution peculiarities by correlation to the presence of critical phenomena in the polymeric matrix, especially the freezing processes connected with the arrested movements of certain matrix fragments. A low concentration of magnetic nanoparticles could change essential glass transition in polymer [27].

These investigations have been allowing us to correlate the macroscopic behaviour of magnetic nanoparticle systems with the structure, size, and morphology of the constituent phases as well as with the type and strength of the interparticle and inter-agglomerate magnetic coupling: The dipole – dipole and exchange interparticle interactions compete with an anisotropy energy barrier in the orientation of their magnetic moments, whereas strong interparticle interaction could convert the individual superparamagnetic relaxation into a collective dynamical process. The temperature evolution of the FMR effect for the nanocomposite system may discriminate the nanoparticle conglomerate contribution from the individual nanoparticle one. Another source of temperature lowering – induced significant alterations in the FMR spectrum descriptors (resonance field, linewidth, integral intensity, mainly) has been deduced to be the occurrence of critical phenomena in the polymeric matrix, especially the freezing processes connected with the arrested movements of certain matrix fragments.

Composite systems containing magnetic nanoparticles promise the potential for high-density data storage, biomedical applications, catalysis, and nanotechnology sensor materialisation, among other envisaged utilisations. We are, therefore, eager to continue attempting to decipher the mystery and fruitfulness of magnetic nanoparticle distributions.

References

- [1] D.E. Speliotis, Magnetic recording beyond the first 100 Years, *Journal of Magnetism and Magnetic Materials* 193 (1999) 29-35.
- [2] Yu.A. Koksharov, S.P. Gubin, I.D. Kosobudsky, G.Yu. Yurkov, D.A. Pankratov, L.A. Ponomarenko, M.G. Mikheev, M. Beltran, Y. Khodorkovsky, A.M. Tishin, Electron paramagnetic resonance spectra near the spin-glass transition in iron oxide nanoparticles, *Physical Review B* 63 (2000) 012407.
- [3] E. Troc, A. Ezzir, R. Cherkaoui, C. Chaneac, M. Nogues, H. Kachkachi, D. Fiorani, A.M. Testa, J.M. Greneche, J.P. Jolivet, Surface-related properties of γ -Fe₂O₃ nanoparticles, *Journal of Magnetism and Magnetic Materials* 221 (2000) 63-79.
- [4] R. Berger, J.C. Bissey, J. Klava, H. Daubric, C. Estournes, Temperature dependence of superparamagnetic resonance of iron oxide nanoparticles, *Journal of Magnetism and Magnetic Materials* 234 (2001) 535-544.
- [5] Yu.A. Koksharov, D.A. Pankratov, S.P. Gubin, I.D. Kosobudsky, M. Beltran, Y. Khodorkovsky, A.M. Tishin, Electron paramagnetic resonance of ferrite nanoparticles, *Journal of Applied Physics* 89 (2001) 2293-2298.
- [6] X. Chen, W. Kleemann, O. Petravic, O. Sichelschmidt, S. Cardoso, P.P. Freitas, Relaxation and aging of a superferromagnetic domain state, *Physica Review B* 68 (2003) 054433.
- [7] C.T. Hsieh, J.T. Lue, Electron spin resonance studies on quantum tunneling in spinel ferrite nanoparticles, *European Physica Journal B* 35 (2003) 357-364.
- [8] J.L. Wilson, P. Poddar, N.A. Frey, K. Mohomed, J.P. Harmon, S. Kotha, J. Wachsmuth, Synthesis and magnetic properties of polymer nanocomposites with embedded iron nanoparticles, *Journal of Applied Physics* 95 (2003) 1439-1443.
- [9] Y. Xiaotun, X. Lingge, N.S. Choon, C.S.O. Hardy, Magnetic and electrical properties of polypyrrole-coated γ -Fe₂O₃ nanocomposite particles, *Nanotechnology* 14 (2003) 624-629.
- [10] U. Narkiewicz, N. Guskos, W. Arabczyk, J. Typek, T. Bodziony, W. Konicki, G. Gasiorek, I. Kucharewicz, E.A. Anagnostakis, TEM and magnetic resonance studies of iron carbide nanoparticle agglomerates in carbon matrix, *Carbon* 42/5-6 (2004) 1127-1132.
- [11] P. Dutta, A. Manivannan, M.S. Sehra, N. Shah, G.P. Huffman, Magnetic properties of nearly defect-free maghemite nanocrystals, *Physica Review B* 70 (2004) 174428.
- [12] N. Guskos, E.A. Anagnostakis, V. Likodimos, J. Typek, U. Narkiewicz, Ferromagnetic resonance and ac conductivity of a polymer composite of Fe₃O₄ and Fe₃C nanoparticles dispersed in a graphite matrix, *Journal of Applied Physics* 97 (2005) 0204304.
- [13] N. Guskos, J. Typek, M. Maryniak, Z. Roslaniec, D. Petridis, M. Kwiatkowska, FMR Study of γ -Fe₂O₃ magnetic nanoparticles in a multiblock poly(ether-ester) copolymer matrix, *Materials Science* 23 (2005) 971.
- [14] N. Guskos, V. Likodimos, S. Glenis, J. Typek, M. Maryniak, Z. Roslaniec, M. Baran, R. Szymczak, D. Petridis, M. Kwiatkowska, Matrix effects on the magnetic properties of γ -Fe₂O₃ nanoparticles dispersed in a multiblock copolymer, *Journal of Applied Physics* 99 (2006) 084307.
- [15] N. Guskos, E.A. Anagnostakis, G. Gasiorek, J. Typek, T. Bodziony, U. Narkiewicz, W. Arabczyk, W. Konicki, *Molecul Physica Reports* 39 (2004) 58.
- [16] N. Guskos, J. Typek, U. Narkiewicz, M. Maryniak, K. Aidinis, Temperature Dependence of the FMR Spectrum of Magnetic Nanoparticle Agglomerates in Nonmagnetic Matrix, *Review of Advanced Materials Science* 8 (2004) 10-15.
- [17] T. Bodziony, N. Guskos, J. Typek, Z. Roslaniec, U. Narkiewicz, M. Maryniak, Ferromagnetic Resonance Study of Fe₃O₄ and Fe₃C Magnetic Nanoparticle Mixture filling the PTMO - block - PET Polyme, *Review of Advanced Materials Science* 8 (2004) 86-91.
- [18] T. Bodziony, N. Guskos, Z. Roslaniec, U. Narkiewicz, M. Kwiatkowska, M. Maryniak, Low Concentration Effect of Fe₃O₄ and Fe₃C Magnetic Nanoparticles in Non-Magnetic Matrix on the FMR Spectra, *Acta Physica Polonica A* 108 (2005) 297.
- [19] N. Guskos, J. Typek, M. Maryniak, U. Narkiewicz, I. Kucharewicz, R. Wrobel, FMR study of agglomerated nanoparticles in a Fe₃C/C system, *Materials Science* 23 (2005) 1001.
- [20] T. Bodziony, N. Guskos, J. Typek, Z. Roslaniec, U. Narkiewicz, M. Maryniak, Temperature dependence of the FMR spectra of Fe₃O₄ and Fe₃C nanoparticle magnetic systems in copolymers matrices, *Materials Science* 23 (2005) 1055.
- [21] N. Guskos, J. Typek, M. Maryniak, U. Narkiewicz, W. Arabczyk, I. Kucharewicz, Temperature dependence of FMR spectrum of Fe₃C magnetic agglomerates, *Journal of Physics: Conference Series* 10 (2005) 151-154.
- [22] N. Guskos, J. Typek, T. Bodziony, Z. Roslaniec, U. Narkiewicz, M. Kwiatkowska, M. Maryniak, Temperature Dependence of FMR Field of Magnetic Nanoparticles/Polymer Composite, *Review of Advanced Materials Science* 12 (2006) 133-138.
- [23] M. Maryniak, N. Guskos, J. Typek, I. Kucharewicz, U. Narkiewicz, Z. Roslaniec, M. Kwiatkowska, W. Arabczyk, K. Adinis, FMR Study of Polymer Composites with Nanocrystalline Iron-Carbon Fillers, *Review of Advanced Materials Science* 12 (2006) 200-205.
- [24] U. Narkiewicz, W. Arabczyk, I. Pelech, N. Guskos, J. Typek, M. Maryniak, M.J. Wozniak, H. Matysiak, K.J. Kurzydowski, FMR study of nanocarbon materials obtained by carburization of nanocrystalline iron, *Materials Science-Poland* 24 (2006) 1067.
- [25] N. Guskos, M. Maryniak, J. Typek, I. Pelech, U. Narkiewicz, Z. Roslaniec, M. Kwiatkowska, Temperature Dependence of the FMR Spectra of Polymer Composites with Nanocrystalline -Fe/C filler, *Solid State Phenomena* (2007).
- [26] N. Guskos, J. Typek, M. Maryniak, Z. Roslaniec, D. Petridis, M. Kwiatkowska, FMR study of γ -Fe₂O₃ magnetic nanoparticles in a multiblock poly(ether-ester) copolymer matrix, *Materials Science* 23 (2005) 972.
- [27] N. Guskos, J. Typek, M. Maryniak, Z. Roslaniec, M. Kwiatkowska, D. Petridis, FMR study of gamma-Fe₂O₃ magnetic nanoparticles in a multiblock poly(ether-ester) copolymer matrix, *Journal of Non-Crystalline Solid* 352 (2006) 971-976.
- [28] N. Guskos, J. Typek, M. Maryniak, FMR line shift for γ -Fe₂O₃ magnetic nanoparticles embedded in a nonmagnetic matrix, *Physica Status Solidi B* 244 (2007) 859-865.
- [29] N. Guskos, J. Typek, M. Maryniak, A. Guskos, Z. Roslaniec, D. Petridis, E. Sanderek, FMR Study of γ -Fe₂O₃ Magnetic

- Nanoparticles Embedded in a Poly(Ether-Ester) Multiblock Copolymers (Pen-block-PTMO) and (PTT-block-PTMO), *Review of Advanced Materials Science* 14 (2007) 157-162.
- [30] N. Guskos, G. Zolnierkiewicz, J. Typek, A. Guskos, Z. Czech, FMR Study of γ -Fe₂O₃ Agglomerated Nanoparticles Dispersed in Glues, *Review of Advanced Materials Science* 14 (2007) 57-60.
- [31] N. Guskos, V. Likodimos, S. Glenis, M. Maryniak, M. Baran, R. Szymczak, Z. Roslaniec, M. Kwiatkowska, D. Petridis, *Journal of Applied Physic* 99 (2006) 084307.
- [32] A.B. Bourlinos, A. Simopoulos, D. Petridis, Synthesis of capped ultrafine gamma -Fe₂O₃ particles from iron(III) hydroxide caprylate: a novel starting material for readily attainable organosols, *Chemica Materialia* 14 (2002) 899-903.
- [33] M. Sobon, I.E. Lipinski, A. Guskos, J. Typek, K. Aidinis, N. Guskos, U. Narkiewicz, M. Podsiadly, FMR Study of Carbon Coated Cobalt Nanoparticles Dispersed in Paraffin, *Review of Advanced Materials Science* 14 (2007) 11-16.
- [34] N. Guskos, M. Sobon, A. Guskos, J. Typek, I.E. Lipinski, K. Aidinis, J. Blyzko, W. Kiernozycycki, U. Narkiewicz, M. Podsiadly, Ageing Effect in Carbon-coated Cobalt Nanoparticles Embedded in a Cement Matrix Studied by FMR, *Review of Advanced Materials Science* 14 (2007) 130-134.
- [35] N. Guskos, J. Typek, M. Maryniak, G. Zolnierkiewicz, M. Podsiadly, W. Arabczyk, Z. Lenzion-Bieluń, U. Narkiewicz, Effect of calcination and structural additives on the ERP spectra of nanocrystalline cobalt oxides, *Materials Science* 24 (2006) 1095.