

# TEMPERATURE DEPENDENCE OF THE FMR SPECTRUM OF MAGNETIC NANOPARTICLE AGGLOMERATES IN A NONMAGNETIC MATRIX

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**Abstract.** Sample composed of 60 wt.%  $\alpha$ -Fe and 40 wt.%  $\text{Fe}_3\text{C}$  nanoparticle agglomerates (with a typical size of  $\alpha$ -Fe nanocrystallites of 17 nm and  $\text{Fe}_3\text{C}$  of 46 nm) dispersed at a concentration of 0.1 wt.% in a nonmagnetic matrix (wax) has been prepared. The agglomerates have been characterized by XRD method. Ferromagnetic resonance (FMR) measurements of the sample have been carried out at different temperatures. An intense and broad magnetic resonance absorption line has been recorded. With decreasing temperatures the resonance line has shifted in the direction of higher magnetic fields and its intensity and linewidth displayed an unusual behaviour. The resonance line could be fitted by a superposition of two Lorentzian lines: one centred at lower magnetic field and the other placed at higher resonance magnetic field, showing a strongly decreased integral intensity with decreasing temperatures. At higher temperatures (over 100K) a magnetic resonance absorption from  $\alpha$ -Fe nanoparticle agglomerates dominates the spectrum and the integral intensity strongly decreases with decreasing temperature. Below 100K the magnetic resonance absorption arising from  $\text{Fe}_3\text{C}$  nanoparticle agglomerates is recorded. The matrix freezing phenomena has a prominent influence on the FMR spectra of  $\alpha$ -Fe nanoparticle agglomerates.

## 1. INTRODUCTION

The notion of Magnesia - gr. Magic Islets, may be introduced in teaching magnetism, especially if analysing the interaction between magnetic nanoparticles. Providing appropriate hosting matrices they could be utilized as technologically functional materials with 'magic', exotic properties. In a recent decade the physical properties of systems of magnetic nanometer-scale particles (nanomagnetism) and especially embedded in non-magnetic matrixes are the object of an intensive research due to their unique magnetic properties making them very appealing from both the theoretic

cal and technological point of view (the active component of ferrofluids, recording tape, flexible disk recording media, biomedical materials and catalysts) [1-9]. The macroscopic physical properties of nanostructured magnetic systems depend on the structure, size, and morphology of the constituent phases and on the type and strength of the magnetic coupling between them. For an assembly of non-interacting agglomerate nanoparticles in non-magnetic matrixes, the magnetic properties depend mainly on interaction inside them (between nanoparticles). The kind of nonmagnetic matrix is very important in the magnetic resonance phenomena and it could have an essential influence on their

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relaxation processes. For interacting particles, the dipole-dipole and the exchange interactions compete with the anisotropy energy in the orientation of their magnetic moments. Strong enough interparticle interaction could convert the individual relaxation into a collective dynamical behaviour. The intercrystallite interactions are dominating in the magnetic properties of bulk nanocrystalline materials. The compound  $\text{Fe}_3\text{C}$  (iron carbide, cementite) is one of the most important phases in metallurgy (steels or cast irons) [10-12]. The physical properties of pure cementite are investigated very intensively because their application could be extended to different areas [13,14]. The iron atoms in  $\text{Fe}_3\text{C}$  compound are located in two different crystalline positions and theoretically calculated magnetic moments are:  $\text{Fe}(1)=1.98 \mu_B$ ,  $\text{Fe}(2)=1.74 \mu_B$  [15]. Below Curie temperature  $T_c = 488\text{K}$  cementite is in a ferromagnetic state. One of the important applications of magnetic nanoparticles is the preparation of magnetic materials with high coercivity and the cementite could be used there very successfully [16].

The aim of this work is the preparation, characterization, and the studies of temperature dependence of the FMR spectrum of the 60 wt.%  $\alpha$ -Fe+40 wt.%  $\text{Fe}_3\text{C}$  magnetic nanoparticle aggregates embedded at low filling factors in a wax matrix (non-magnetic), at about 0.1 wt % concentration.

## 2. EXPERIMENTAL

The sample was prepared by the carburisation of nanocrystalline iron with methane/hydrogen mixture ( $\text{CH}_4/\text{H}_2$  (2:1)) under atmospheric pressure at 580 °C. The carburisation process has been controlled by a thermobalance [17]. The nanocrystalline iron was doped with small amounts of CaO and  $\text{Al}_2\text{O}_3$  to protect the fine nanostructure of iron against sintering at elevated temperatures. The sample was sieved and the grains between 1.2 and 1.5 mm were separated for experiments. The grains were reduced with a nitrogen-hydrogen (1:3) mixture (flow of 25000  $\text{h}^{-1}$ ), under atmospheric pressure, in the temperature range from 200 to 500 °C. To avoid oxidation, the pyrophoric samples after reduction were passivated under nitrogen with traces of oxygen (0.5 vol. %) at room temperature. The sample after passivation contained iron as well as 2.9 %  $\text{Al}_2\text{O}_3$ , 3.0 % CaO and 0.3 %  $\text{SiO}_2$ .

The specific surface area of sample after reduction, determined using thermal desorption of physisorbed nitrogen, was 18  $\text{m}^2/\text{g}$ . The mean crystallite size of  $\alpha$ -Fe, determined using the XRD

method (PHILIPS X Pert XRD,  $\text{CoK}\alpha_1$ ) taking into account the width of the (200) peak of iron, amounted to 17 nm.

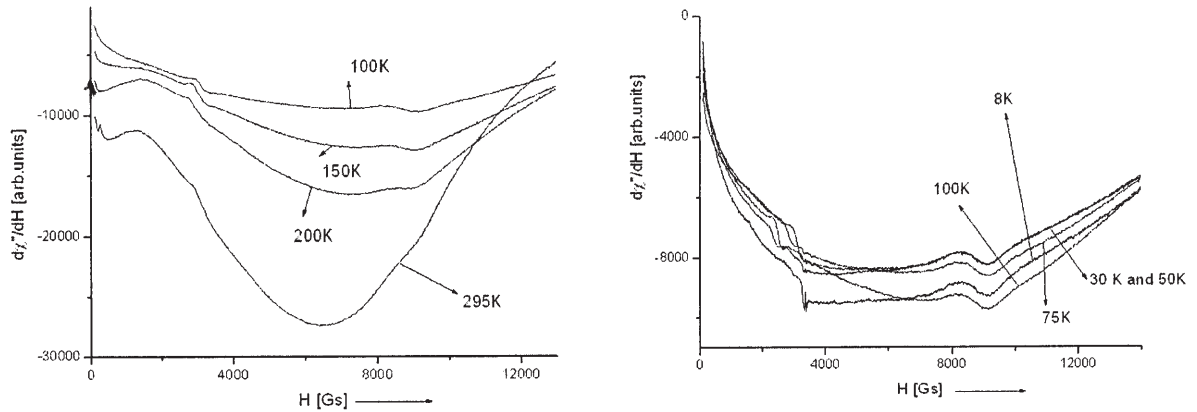
The reduced and passivated sample (1 g) was placed in a basket of thermobalance and the reduction under hydrogen was carried out at a temperature rising from 20 to 580 °C. After the reduction the carburisation process was started using a  $\text{CH}_4/\text{H}_2$  mixture (2:1) and a volume velocity of 1.2  $\text{dm}^3\cdot\text{g}^{-1}\cdot\text{min}^{-1}$ . The change of the sample mass was measured during the carburisation process. When a desired degree of carburisation was obtained (40 wt.% of  $\text{Fe}_3\text{C}$  in the sample), the chemical reaction was interrupted by rapid cooling of the sample in nitrogen atmosphere. The phase composition of the samples after carburisation was determined using the XRD method.

EPR measurements were carried out with a conventional X-band ( $\nu=9.43$  GHz) Bruker E 500 spectrometer with 100 kHz magnetic field modulation. The measurements were performed at different temperatures in the 4–300K range using an Oxford cryogenic system.

## 3. RESULTS AND DISCUSSION

The XRD spectrum of the sample is much the same as for sample III described in Ref. 13. The peaks corresponding to  $\alpha$ -Fe and  $\text{Fe}_3\text{C}$  phases are observed. The average size of the crystallites of iron carbide in the sample, calculated using the Scherrer equation, is about 46 nm.

Fig. 1a and 1b present the FMR spectra of the investigated sample in different temperatures. Fig. 2 shows, as an example, the experimental and the fitting results of magnetic resonance absorption spectra obtained at 50K. The sample has been magnetized by a steady magnetic field up to 1.7 T prior to the microwave absorption study. It is not obvious that training in a field of 1.7 T is sufficient to align all the particles along their easy axis but the main part of magnetic domains should be oriented in the same direction. All measurements have been done in the magnetic 'easy' direction (magnetization direction). The microwave spectrum for the sample over the whole scan range is dominated by a very intense broad signal. At room temperature it could be thought as a superposition of different magnetic resonance absorption lines. An accurate fitting of the extended microwave signal has been performed using Lorentzian-type curves, taking into account the absorptions at both  $+H_{res}$  and  $-H_{res}$  fields, induced by the two oppositely rotating components of the linearly polarised rf incoming field.

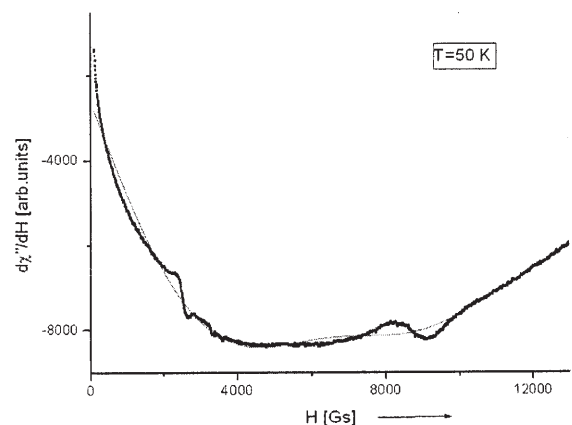


**Fig. 1.** FMR spectra of magnetic nanoparticle agglomerates embedded in a nonmagnetic matrix (wax): (a) for temperatures ranging from 295K to 100K and (b) for temperatures from 100K to 8K.

The observed microwave spectrum for the sample at various temperatures were fitted using two Lorentzian curves, one at the lower resonance magnetic field (a more intense and broader component) and the other at higher magnetic field (see Table 1). The best results were achieved by using two Lorentzian curves for lower temperatures (below 100K), which are dominated by the magnetic absorption resonance line arising mainly from  $\text{Fe}_3\text{C}$  component. In both cases the magnetic anisotropy is playing an important role. It is clear that the question of sample homogeneity cannot be answered solely by fitting to a specific functional form. Even when a single Lorentzian line seems to provide an adequate fit, such broad resonance often contains a distribution of narrower resonance lines. As the first approximation it seems that the spectrum is dominated by one kind of magnetization and using the Lorentzian-type lines could be satisfactory in explanations of the experimental results.

The detected microwave absorption line pattern is believed to originate mainly from ferromagnetic iron ions with their individual spins coupled by the exchange interaction within each nanoscale metallic grain. The most intense absorption line is obtained at room temperature (Fig. 1a), through one of the iron ion magnetic moment component, originating at the purely ferrous nanoparticle population. The integral intensity change between the room temperature and 100K may be considered as an experimental signature of the “phase transition” of pure ferrous nanoparticle magnetization ensemble arising from  $\alpha\text{-Fe}$  by an adequate percentage of the magnetization of  $\text{Fe}_3\text{C}$ . It means that the resonance absorption signal at higher temperatures is domi-

nated by  $\alpha\text{-Fe}$  agglomerates and at lower temperatures (below 100K) it is originating mainly from  $\text{Fe}_3\text{C}$ . It is suggested that the matrix freezing phenomena of the spin-lattice relaxation time are completely different for these two agglomerate phases. At room and 150K temperatures the integral intensity has not changed significantly but an essential increase of the resonance field and linewidth is observed (Table 1). Below 75K the linewidth and position of the magnetic resonance lines are comparable with those at 200K, but the integrated intensities of FMR spectra are completely different. At 50K and 30K the lines of magnetic resonance absorption have basically the same parameters (Fig. 1b) and at these lower temperatures their intensities slightly increased.



**Fig. 2.** Experimental (fat line) and simulated (thin line) magnetic resonance spectra at 50K of the investigated sample. The line above 8000 Gs is due to impurities in the sample holder.



**Table 1.** Values of the parameters of magnetic resonance absorption lines at different temperatures.

Temperature, [K]	Integral intensity, $I_1$ [arb.units]	Linewidth $\Delta H_1$ [Gs]	Resonance field $H_{res}$ [Gs]	Integral intensity, $I_2$ [arb. units]	Linewidth $\Delta H_2$ [Gs]	Resonance field $H_{res}$ [Gs]
295	175(1)	7060(10)	300(10)	59(1)	5470(10)	5160(10)
200	180(1)	9380(10)	880(10)	38(1)	6460(10)	6310(10)
150	112(1)	8740(10)	2319(10)	13(1)	5310(10)	7210(10)
100	51(1)	7930(10)	2655(10)	4(1)	4150(10)	7720(10)
75	56(1)	9060(10)	910(10)	5(1)	5400(10)	7640(10)
50	56(1)	9050(10)	920(10)	5(1)	5430(10)	7620(10)

On decreasing temperature from room temperature to 150K, a lowering of the microwave signal intensity is observed, which could be attributed to the decreasing portion of pure ferrous nanograins within the dual phase (pure iron phase and cementite phase) of metallic particle distribution. The ratio of the most intense line at these temperatures  $I_{295}/I_{150}$  is around 1.6 while with the decrease of temperature the ratio  $I_{295}/I_{100}$  is around 3.4. The integral intensity of resonance line is over two times lower between 150K and 100K. The integral intensity of the resonance line essentially decreases while responsible processes could also have an influence on the character of the first line. The intensity ratio of the most intense line at 200K and weaker line at 100K is around 3.5. The essential part of the decreasing integral intensity ratio must be due to reduction of the relaxation processes from  $\alpha$ -Fe to  $\text{Fe}_3\text{C}$  agglomerates. In the nonmagnetic matrix an increase of rigidity of the lattice with decreasing temperatures has a strong influence on the relaxation phenomena connected with the heat transfer to the lattice. This could significantly change the spin-lattice relaxation time  $T_1$ . Another phenomenon, that may influence the spin-lattice relaxation, is a strong exchange coupling of spins creating the ferromagnetic ordered state. In the agglomerates of  $\alpha$ -Fe the exchange interaction between nanoparticles and inside a nanoparticle is stronger than in the agglomerates of  $\text{Fe}_3\text{C}$ . The spin-lattice relaxation time of  $\alpha$ -Fe agglomerates is smaller than for  $\text{Fe}_3\text{C}$  agglomerates. The matrix freezing phenomenon of the magnetic resonance absorption processes for the  $\alpha$ -Fe agglomerates is dominating at higher temperatures. At lower temperatures the effects connected with the spin-lattice relaxation time are prevailing such that the resonance absorption line from  $\alpha$ - $\text{Fe}_3\text{C}$  agglomerates is appearing as more intense (see Fig. 1b).

A significant change in the resonance line intensity is accompanied by a strong shift of the resonance position ( $H_{res}$ ) versus applied external magnetic field with decreasing temperatures (Table 1). This feature along with the clustering phenomena inside agglomerates indicates on the occurrence of a kind of phase change as regards the dual phase nanoparticle distribution of magnetization. This is clearly observed when the dominance of pure ferrous nanoparticles is succeeded by the prevalence of ferrous cementite nanoparticles [13].

The localised spin on the Fe ion is subjected to the total magnetic field from non-separated ferromagnetic nanoparticles and it could be described by the following three terms:

$$\vec{B}_{tot} = \vec{B}_{dem} + \vec{B}_{dip} + \vec{B}_{app}.$$

The first term represents the demagnetising field, the second term the dipole field from the neighbouring nanoparticles and the third term the applied field. In a ferromagnetic material the arrangements of the atomic magnetic dipoles may give rise to the uncompensated magnetic poles at the surface, and these create the so-called demagnetising field. If  $\vec{M}$  is the saturation magnetisation of each single domain nanoparticle, then the demagnetisation field in the interior of the particle is  $\vec{B}_{dem} = -\mu_0 D \vec{M}$  (for a particle of ellipsoidal shape magnetized in a principle direction). The value of  $D$  depends on the shape of the sample:  $D=4\pi/3$  for a spherical sample,  $D=0$  for a foil magnetized parallel to the foil plane. Calculating the dipole term is complicated since it depends on the geometrical arrangement and the orientation of the magnetization of the neighbouring nanoparticles.

The magnetic nanoparticles are supposed to be a system possessing a very high resultant spin arising from the coupling of individual spins by the ex-

change interaction (with a giant magnetic moment over  $10^3 \mu_B$ ). These ensembles of single-domain particles (each of the size of the order of several nm) could be agglomerated and after application of an external magnetic field they could be magnetized. The two observed resonance lines, one at lower and the other at higher magnetic field are positioned almost symmetrically to a resonance position of paramagnetic species at room temperatures [13]. Thus the internal magnetic field could be distributed mainly in two directions – parallel and antiparallel to the applied external field. Then, the resonance condition could be transformed to:

$$h\nu = g\mu_B(B_{app} \pm B_{in}),$$

where  $\nu$  is the resonance frequency,  $\mu_B$  is Bohr magneton,  $B_{app}$  is the external magnetic field and  $B_{in}$  is an internal magnetic field. The broader and more intense resonance line at lower magnetic field overlaps the other line. Similar behaviour has been reported for other materials [18, 19]. Usually, the lowest resonance field occurs for the external field applied in the easy direction and for a weak ferromagnetic material it is observed that the microwave resonance field position is shifted to higher magnetic fields. Concentration dependence of  $Fe_3C$  in a nonmagnetic matrix (wax) has shown that the increase of the concentration of magnetic agglomerate nanoparticles has generated an increase of the linewidth and shifted the position of resonance line to higher magnetic field [14].

An increasing magnetic nanoparticle concentration in a magnetic liquid or nonmagnetic matrix could lead to an increase in the magnetic resonance linewidth [14,20]. It has been shown that the exchange effects can give a significant shift of the resonance field [21]. For the sample under study the shift of resonance field for  $\alpha$ -iron in the direction of low magnetic fields at higher temperatures is significantly greater than for lower temperatures (see Table 1). The fact that the lineshape of magnetic resonance line is described very satisfactory by a Lorentzian-type function suggests that the exchange interactions with a small anisotropy are dominant. Otherwise the dipolar interactions among particles dispersed in a diamagnetic matrix could produce a non-symmetrically broadened line. The thermofluctuational effects on the FMR spectra of  $Fe_3O_4$  have been observed [22-24] in which the iron oxide nanoparticles evidence the gradual suppression of the averaging effect of thermal fluctuations or the emergence of spin-glass like freezing as the temperature is decreasing.

In our cases of two magnetic  $\alpha$ -Fe or  $Fe_3C$  entities the FMR spectrum has been described by two Lorentzian lines with parallel and antiparallel orientations to the magnetic field magnetization. For magnetite the FMR spectrum of an asymmetric line could be described by two Lorentzian lines similar to the case of axial symmetry in which parallel and perpendicular components dominate the spectrum [25].

#### 4. CONCLUSIONS

Intense magnetic resonance absorption spectra are recorded for the sample containing iron and iron carbide embedded in a nonmagnetic matrix. The temperature dependence of the spectra has shown their extraordinary behaviour. The spin-lattice relaxation time strongly depends on the kind of magnetic nanoparticle agglomerates and it is suggested that strong exchange interactions between the magnetic nanoparticles could have an essential influence on them. At higher temperatures the FMR spectrum is dominated by a signal arising from the magnetic  $\alpha$ -Fe compound whereas at low temperatures it is dominated by magnetic  $Fe_3C$  component. The matrix freezing phenomena is largely responsible for the observed extraordinary temperature behaviour of the FRM spectra in a binary magnetic system. In forthcoming paper more measurements using several other samples will be presented.

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