Temperature dependence of FMR spectrum of Fe$_3$C magnetic agglomerates

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Abstract. The sample of iron carbide has been prepared using carburisation of iron with ethylene/hydrogen mixture. After carburisation, the sample was characterized by using XRD and scanning electron microscopy. XRD revealed the presence of cementite phase only. The mean size of cementite crystallites was determined to be 46 nm. The FMR absorption signals have been investigated in the temperature range from liquid helium up to room temperature. The asymmetric, very broad and intense FMR line was registered and decomposed in two Lorentzian-shape components (low- and high-field). The main high-field component shifts toward low magnetic fields with decreasing temperature. At 75 K a phase transition was observed due to the freezing of the non-magnetic matrix. Additionally, the spin glass state was recorded below 30 K.

1. Introduction
Nanocrystalline iron carbide Fe$_3$C (cementite) is a very important compound for potential applications in catalysis, gas sensors and in possible reduction of the cost required to produce bulk quantities of metallurgical materials [1-5]. The mechanical properties [6] of this compound are especially important in ferrous metallurgy [7]. Recently, ferromagnetic resonance (FMR) has been used to study the iron carbide nanoparticles dispersed in a nonmagnetic matrix [8,9]. A very broad and intense, asymmetric FMR line with unusual behaviour was recorded and investigated for various cementite concentrations and for variable temperatures.

The aim of this work is to study the temperature dependence of FMR spectra of the Fe$_3$C prepared by carburisation of iron with ethylene or ethylene – hydrogen mixture method.

2. Experimental
The sample of iron carbide has been prepared by carburisation of nanocrystalline iron with ethylene – hydrogen mixture. The nanocrystalline iron used in experiments was obtained using the preparation method described in reference [10].

The carburization process was monitored using the thermogravimetric method. The grains of the sample (0.5 g) were placed as a single particle layer in a platinum basket hung in the thermobalance.
Before the carburisation process, the sample was reduced (to remove the passivation layer) under a hydrogen flow until a constant mass of the sample was reached. Then, the carburisation process was started, through the addition of ethylene to hydrogen (C\textsubscript{2}H\textsubscript{4}: H\textsubscript{2} = 1: 3). The carburisation has been carried out under a total flow of 1.3 dm\textsuperscript{3}·g\textsuperscript{-1}·min.\textsuperscript{-1} at the temperature of 673 K. The increase of the mass of the sample during carburisation was registered. When a specific degree of carburisation was reached, the process was stopped by rapid cooling of the sample in nitrogen atmosphere. The samples after the carburisation have been characterised by XRD (Philips X’Pert equipment, (CoK\textsubscript{α} radiation) and SEM (Digital scanning electron microscope Zeiss LEO) methods.

The FMR measurements were carried out at room temperature, using Bruker E 500 spectrometer working in the X-band (\(\nu = 9.43\) GHz) of microwave absorption at 100 kHz magnetic field modulation. The investigated samples, containing nanoparticles of iron carbide dispersed in wax matrix, were placed into quartz tubes of 4 mm in diameter. Wax was used to enable easy handling of the sample.

3. Results and discussion
The XRD spectrum of the sample after carburisation has shown that the obtained pattern corresponds to the Fe\textsubscript{3}C phase. Other iron carbide phases were not detected. The mean crystallite size of the obtained iron carbide, calculated using Scherrer’s equation, has been found to be 46 nm. The scanning electron microscopy image of the surface of the carburised sample has revealed the presence of agglomerates of various sizes in the 0.5 - 4 \(\mu\)m range.

![Figure 1. The FMR spectra of iron carbide at different temperatures: above 130 K (upper panel), below 100 K (lower panel)](image)

A strong magnetic material like Fe\textsubscript{3}C should be subjected to a special preparation procedure to increase its magnetic rigidity. Before the FMR measurements have been done the sample had been magnetized and demagnetized several times in magnetic fields up to 1.6 T. This process has allowed recording of the same FMR spectrum independent of the direction of the magnetic sweep (downfield or upfield). This is especially important for the low magnetic field part of the FMR spectrum that is rather sensitive (for magnetically untreated sample the spectrum shifts to higher magnetic field in the case of sweeping the field from higher to lower values). Fig. 1 presents the FMR spectra for a sample of iron carbide for all investigated temperatures. A very intense and strongly asymmetric absorption line shifted in the direction of the low magnetic fields has been recorded. An accurate fitting of the extended FMR signal has been performed using Lorentzian-type curves, taking into account the
absorption at both $+H_r$ and $-H_r$ fields, induced by the two oppositely rotating components of the linearly polarised rf incoming experimental field. The FMR spectra of iron carbide were successfully fitted by using two Lorentzian-type curves, having the resonance magnetic fields near zero (low-field component) and at higher fields (high-field component).

A significant change in the resonance line intensity is accompanied by a strong shift of the resonance position ($H_r$) versus applied external magnetic field with decreasing temperatures for the high-field component (Fig. 2). The line intensity vs. temperature curve for that component has a rather interesting shape, with a minimum at about 30 K (Fig. 3). These features along with the clustering phenomena inside agglomerates indicate on the occurrence of a kind of “phase change” with respect to the dual phase nanoparticle distribution of magnetization. This was clearly observed when the dominance of pure ferrous nanoparticles was succeeded by the prevalence of ferrous cementite nanoparticles [11]. Probably, inside the sample the spin glass phase is forming below 30 K. Additionally, the value of the $dH_r/dT$ gradient is one order of magnitude larger below 75 K (Fig. 2) and it is suggested that it could arise from the so called freezing phenomenon at this temperature (a significant part of molecules of the stabilized material is frozen in their movements).

The localized spin is subjected to the total magnetic field from non-separated ferromagnetic nanoparticles. That field could be described by the sum of three terms:

$$H_{tot} = H_{dem} + H_{dip} + H_{app}$$

where the first term represents the demagnetising field ($H_{dem}$), the second term the dipole field ($H_{dip}$) from the neighbouring nanoparticles and the third term the applied field ($H_{app}$). 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 self-magnetic demagnetising field.

In our case the internal magnetic field could be distributed mainly in the direction of an applied external field. Then, the resonance condition may be written as:

$$h\nu = g\mu_B(H_{app} - H_{in})$$

where $\nu$ is the resonance frequency, $\mu_B$ is Bohr magneton, $H_{app}$ is the external magnetic field and $H_{in}$ is internal magnetic field.

![Figure 2](image1.png)  
**Figure 2.** The temperature dependence of the FMR resonance field $H_r$ for the high-field component.

![Figure 3](image2.png)  
**Figure 3.** The temperature dependence of the FMR integrated intensity $I$ for the high-field component.

The increasing magnetic nanoparticles concentration within the magnetic liquid or a nonmagnetic matrix could lead to an increase in the magnetic resonance linewidth and intensity [8,9]. The FMR is limited mainly by a strong inhomogeneous broadening arising from a random orientation of the anisotropic magnetic particles when studying dispersed magnets but it could provide a lot of useful information. The temperature dependence of the FMR spectrum informs of two very important processes, one being the formation of the spin glass state and the second of the freezing of the nonmagnetic matrix.
In conclusion, the sample of iron carbide prepared by carburisation of nanocrystalline iron with ethylene-hydrogen mixture was composed of irregular shape agglomerates. The temperature dependence of the FMR spectrum has shown a strong change of the intensity and the value of the resonance field. The value of the temperature gradient of the internal magnetic field increases at 75 K by more than one order of magnitude and it is suggested that at this temperature a freezing process takes place. Below 30 K the spin glass state has been observed.

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5. References

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