α-Fe nanopowder synthesised in low-pressure microwave plasma and studied by Mössbauer spectroscopy

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Abstract. An iron-based nanocomposite has been prepared by the microwave plasma method: Fe(CO)₅ vapour was introduced into an argon discharge at ~1 kPa. The synthesised nanopowder was passivated in situ with a mixture of Ar and air. The as-prepared nanopowder was characterised by XRD, TEM, Raman and Mössbauer spectroscopies. In the XRD pattern of the nanopowder the α-Fe (dₓRD = 14 nm, 76 wt.%) and Fe₃O₄ (dₓRD = 3 nm, 24 wt.%) phases were identified only. α-Fe cores covered with oxide shells were observed under TEM. A huge increase of Mössbauer absorption was observed after the sample was cooled down to 5 K. The results of magnetic and thermal properties studies at low and high temperature are presented. The heat capacity of the sample exhibited an unexpectedly high value of 599 J/kg/K.

1. Introduction
Magnetic nanoparticles (MNPs) attract the attention of the materials science community because of their unique magnetic and electronic properties [1,2]. Among MNPs iron-based nanoparticles gained high attention [3], especially for their prospective medical applications. α-Fe, γ-Fe and Fe₃C nanoparticles were studied predominantly as the catalysts for growing carbon nanotubes (CNTs). Recently, zero-valent iron nanoparticles are considered for environmental applications [4].

Microwave-induced plasma operated at low pressure [5] offers high power density, moderate temperature, easy scalability and various applications in materials processing. Experimental devices employ freely expanding microwave-induced plasma (MIP), in which case, in the most of used configurations, a quartz tube intersects a rectangular wave guide with a surfaguide wave launcher. MIPs were used to synthesise Fe nanopowders [6-8], Co and Fe-Co nanoparticles [9].

In the present article, we describe the synthesis of α-Fe nanoparticles in a microwave induced plasma. Iron pentacarbonyl Fe(CO)₅ has been used as a precursor.

2. Experimental
Our experimental set up was straightforward and similar to those previously used (Fig. 1a in Ref. [10]; Fig. 1 in Ref. [11]). The Ar discharge was generated at low pressure in a cylindrical 45 mm outer diameter fused silica reactor passing through a special launcher, surfaguide (SURFG 439 by Sairem,
France) [11], powered by a microwave (2.45 GHz) generator with regulated power up to 2 kW maximum. Fe(CO)₅ vapour was transported from a reservoir to the discharge by argon. Particulate products were trapped at a filter before a rotary pump.

The operating conditions for the LP16 sample were as follows: gas pressure 1.36 kPa, microwave power 500 W, Ar flow 280 sccm and Fe(CO)₅ flow 1.75 g/min. The Fe(CO)₅ injection point was situated 33 cm downstream from the launcher. Deposition time was 4 minutes. After the deposition, the powder was passivated under 280 sccm of Ar for 2 hours and then the reactor was filled with Ar to 10⁻² Pa and left so for 72 hrs before collecting the powder. The as-synthesised amount was 0.5 g.

The composition of the nanopowder was examined by X-ray diffraction (XRD) on a PANalytical X’Pert Pro MPD device. The XRD pattern fitting was done with a commercial software and database and it yielded weight fraction \( F \) and mean crystallite size \( d_{XRD} \) for a given phase [12,13]. Transmission electron microscopy (TEM) observations were carried out on a Philips CM12 microscope with a wolfram cathode. Raman micro-spectroscopy measurements were performed on a Jobin Yvon microscope Labram HR-800. The spectra were excited with Kr⁺ laser radiation (the wavelength of 532.2 nm). In order to avoid thermally induced phase transformation during the collecting of the Raman spectrum, the power of 0.3 mW was used. Mössbauer spectra were obtained in standard transmission geometry with \(^{57}\)Co in Rh matrix. A CCS-800 Mössbauer closed cycle refrigerator system from Janis was used for low-temperature measurements. The spectra were fitted with the CONFIT program using a transmission integral and we obtained the values of relative spectrum area \( A \) for a given phase and spectral component parameters: hyperfine magnetic induction \( B_{HF} \), quadrupole shift \( \varepsilon_Q \), quadrupole splitting \( \Delta E_Q \) and isomer shift \( \delta \) (against \( \alpha\)-Fe) [14]. A physical properties measurement system PPMS 9 from Quantum Design was used for low temperature magnetic (ACMS option) and heat capacity measurements (HC option). A vibrating sample magnetometer EG&G PARC was employed for high-temperature magnetic measurements.

3. Results and discussion

3.1. X-ray diffraction

The XRD pattern of the LP16 sample (Fig. 1a) was fitted with cubic \( \alpha\)-Fe (ICSD #53451, space group \text{Im}-3\text{m}, \( a = 0.2867 \) nm) and cubic magnetite \( \text{Fe}_3\text{O}_4 \) (ICSD #75627, space group \text{Fd}-3\text{mZ}, \( a = 0.8397 \) nm). The Rietveld refinement yielded for \( \alpha\)-Fe values \( d_{XRD} = 14 \) nm, \( a = 0.2867 \) nm, \( F = 76 \) wt.% and for \( \text{Fe}_3\text{O}_4 \) values \( d_{XRD} = 3 \) nm, \( a = 0.8418 \) nm, \( F = 24 \) wt.%. \( \text{Fe}_3\text{O}_4 \) has its structure (and the XRD pattern) similar to \( \gamma\)-\( \text{Fe}_2\text{O}_3 \) (maghemite), but both tetragonal maghemite Q (ICSD #87121, space group \text{P4}_{1}2_12, \( a = 0.8346 \) nm) and cubic maghemite C (ICSD #87119, space group \text{P4}_{1}32, \( a = 0.8346 \) nm) have lower values of the lattice parameter \( a \). Nevertheless, it is necessary to employ other suitable analytical methods for distinguishing \( \text{Fe}_3\text{O}_4 \) from \( \gamma\)-\( \text{Fe}_2\text{O}_3 \).

![Figure 1](image-url)  

**Figure 1.** (a) XRD pattern and (b) Raman spectrum for the as-synthesised LP16 nanopowder.
3.2. Raman spectroscopy

In the Raman spectrum of the LP16 sample (Fig. 1b) only Fe$_3$O$_4$ characteristic bands at 308, 537 and 664 cm$^{-1}$ were found. It is known that iron oxide magnetite Fe$_3$O$_4$ has a spinel structure with space group $O_h$ (above 119 K), giving rise to five Raman bands: three $T_{2g}$, one $E_g$ and one $A_{1g}$. Nevertheless it follows from the experiments that the strongest Raman band of magnetite is positioned at 670 cm$^{-1}$ and other significant but much weaker bands are at 300 and 534 cm$^{-1}$ [15]. The characteristic $\gamma$-Fe$_2$O$_3$ bands (broad structures at 350, 500 and 700 cm$^{-1}$, a peak at 210 cm$^{-1}$ and very broad bands at 1370 and 1590 cm$^{-1}$ [15]) were not found in the Raman spectrum. Hematite, $\alpha$-Fe$_2$O$_3$, if it were present, would have characteristic bands at 225, 293, 412 and 613 cm$^{-1}$ [15].

3.3. Transmission electron microscopy

The obtained electron diffractograms for the as-synthesised nanopowder confirmed the phase composition found: only the characteristic $\alpha$-Fe and Fe$_3$O$_4$ diffraction circles were observed. Morphology and agglomeration of nanoparticles (Fig. 2a) were similar to nanopowders produced by combustion methods. The large amount of very small Fe$_3$O$_4$ crystallites observed in TEM pictures corresponded to the broad Fe$_3$O$_4$ diffraction peaks found in the XRD pattern. Smaller $\alpha$-Fe crystallites were imbedded in iron oxide Fe$_3$O$_4$ and the larger ones exhibited iron oxide shells (Fig. 2b). These shells are supposed to have defective coordination configuration [16]. Particle size, morphology and connections among particles affected the measured Mössbauer spectra of this nanopowder.

3.4. Mössbauer spectroscopy

The Mössbauer spectrum (MS) of the LP16 sample measured at 293 K (Fig. 3a) exhibits a sunken shape (valley), which is the consequence of the superparamagnetic effect: heating a sample, a sextet belonging to a magnetically ordered phase gradually collapses into a doublet when approaching the blocking temperature $T_B = (KV)/(25k_B)$ ($V$ particle volume, $K$ magnetocrystalline anisotropy constant, $k_B$ Boltzmann constant) [17]. Superparamagnetic state is described by relaxation time $\tau_{SP} = \tau_0 \exp[(KV)/(k_BT)]$ of flipping of particle magnetic moment orientation ($\tau_0 \approx 10^{-11}-10^{-9}$ s) and blocking temperature $T_B$ under which the probability of flipping is very low. Hence, a distribution of particle sizes induces a distribution of blocking temperatures, i.e. a distribution of hardly assignable sextets. The only clearly identifiable components in the MS measured at 293 K were: $\alpha$-Fe sextet ($B_{HF} = 33.1$ T, $\epsilon_Q = 0.01$ mm/s, $\delta = 0.02$ mm/s, $A = 0.43$; light red filler) [18], doublet ($\delta = 0.16$ mm/s, $\Delta E_Q = 0.38$ mm/s, $A = 0.04$; dashed line) and singlet ($\delta = 0.36$ mm/s, $A = 0.02$; full line). The doublet and the singlet belong to Fe impurities in the Al foil in which the nanopowder was wrapped [19].
The superparamagnetic effect was much weaker at 5 K (Fig. 1a). The MS measured at 5 K (with broader lines due to the vibrations caused by the closed cycle cryostat) could be better fitted with: $\alpha$-Fe sextet ($B_{HF} = 34.1$ T, $\epsilon_Q = 0.00$ mm/s, $\delta = 0.14$ mm/s, $A = 0.55$; light red filler), the superposition of five sextets (#1: $52.2$ T, $0.28$ mm/s, $0.04$ mm/s; #2: $50.4$ T, $0.03$ mm/s, $0.01$ mm/s; #3: $50.1$ T, $0.11$ mm/s, $0.24$ mm/s, $0.09$; #4: $48.2$ T, $0.17$ mm/s, $1.03$ mm/s, $0.05$; #5: $36.8$ T, $0.45$ m/s, $1.04$ mm/s, $0.04$; values given in the format $B_{HF}$, $\epsilon_Q$, $\delta$, $A$) belonging to the low-temperature Fe$_3$O$_4$ phase [20], sextet S1 ($B_{HF} = 38.5$ T, $\epsilon_Q = 0.01$ mm/s, $\delta = 0.10$ mm/s, $A = 0.04$; black line), sextet S2 ($B_{HF} = 25.9$ T, $\epsilon_Q = 0.07$ mm/s, $\delta = 0.28$ mm/s, $A = 0.06$; violet line), sextet S3 ($B_{HF} = 11.6$ T, $\epsilon_Q = 0.00$ mm/s, $\delta = 0.13$ mm/s, $A = 0.02$; yellow line), and singlet L1 ($\delta = 0.24$ mm/s, $A = 0.01$; black line). The components S1, S2, S3 and L1 belong to Fe$^{3+}$ atoms probably at surfaces or interfaces.

Figure 3. (a) Mössbauer spectra (MS) for the as-synthesised LP16 nanopowder. Sextets with light red filler correspond to $\alpha$-Fe. (b) Heat capacity $C_P$ for the compacted as-synthesised nanopowder. The low-temperature region is enlarged in the inset.

It can be seen that the absorption in the MS measured at 5 K is seven times stronger than in the MS measured at 293 K, which is a large effect rarely observed. The anomalous decrease of the absorption at 293 K can be caused by diffusive tilting motions of nanoparticles as it was already suggested [21]. Similar decrease was observed for a nanopowder synthesised by laser induced pyrolysis [22].

3.5. Thermal measurement
The as-synthesised powder was compacted and the heat capacity of the pellet ($m = 5.51$ mg) was measured at constant pressure of $1.2 \times 10^{-7}$ bar in the temperature range 3–303 K (Fig. 3b). The literature values $C_P$(bulk $\alpha$-Fe|300 K) = 449.5 J/kg/K [23] and $C_P$(bulk Fe$_3$O$_4$|300 K) = 619.5 J/kg/K [24] allow to calculate, based on the XRD result given in the subsection 3.1, the corresponding heat capacity for the bulk sample ($0.76 \times 449.5 + 0.24 \times 619.5$) J/kg/K = 490.3 J/kg/K, which is significantly lower than the experimentally obtained value of 599.0 J/kg/K for the pellet at 300 K.
The $C_P$ curve exhibited no peak at the Verwey temperature of Fe$_3$O$_4$ [24], which is the consequence of small particle size [25]. A simple mathematical fit in the range 30–305 K was $C_P = -6.02 \times 10^{-3} T + 6.63 \times 10^{-2} T^2 + 6.08 \times 10^{-4} T^3 + 6.00 \times T^{-2}$ [kJ/kg/K] (green line). In the range 3–35 K $C_P$ behaves basically as $T^3$ and either $a T^{3/2}$ term or $b T^2$ term had to be used to obtain a satisfactory fit. The best fit was $C_P = 10.48 \times 10^{-3} T^{3/2} + 6.12 \times 10^{-3} T^2 + 4.82 \times 10^{-4} T^3$ [J/kg/K] (blue line). The $b T^2$ term probably arises due to the vibrations of the atoms at surfaces [26] and the $a T^{3/2}$ term belongs to spin waves. In the framework of the Debye model [27], the low-temperature approximation $C_V = \frac{12}{5} k_B \pi^4 N \left( \frac{T}{\theta_D} \right)^3$ holds, where $k_B$ is the Boltzmann constant, $N$ is the total number of atoms, and $\theta_D$ is the Debye temperature. Using this equation, however, does not seem to provide correct $\theta_D$ for either $\alpha$-Fe particles or Fe$_3$O$_4$ particles due to their particle size distributions and morphology. We note only that it holds: $\theta_D$ (bulk $\alpha$-Fe) = 462 K (valid below 20 K) [28] and $\theta_D$ (bulk Fe$_3$O$_4$) = 550 K (valid below 100 K) [24].

3.6. Magnetic measurements

A loose nanopowder has been pressed into pellets for magnetic measurements. The measurement of the hysteresis loop (HL) at 293 K provided the values: $H_C = 31.1$ kA/m, $\sigma_R = 45.2$ Am$^2$/kg, $\sigma_S = 123.4$ Am$^2$/kg (at 1227 kA/m). The measured zero field cooled (ZFC) and field cooled (FC) curves (Fig. 4a) show the split between $\sigma_{ZFC}$ and $\sigma_{FC}$ curves over the whole measurement range. $\sigma_{ZFC}$ exhibits no maximum and $\sigma_{FC}$ remains nearly constant which indicates a broad range of blocking temperatures $T_B$ reaching above room temperature and the presence of single- and multi-domain nonsuper-paramagnetic particles in the sample. The HL measured at 4 K provided the values: $H_C = 57.1$ kA/m, $\sigma_R = 14.2$ Am$^2$/kg, $\sigma_S = 129.0$ Am$^2$/kg (at 1227 kA/m).

![Figure 4](image-url). (a) ZFC/FC curves and (b) TM curve for the as-synthesised nanopowder.

By the thermomagnetic curve measurement (TM curve) a pellet was held in the evacuated cell (~1 Pa), heated up to 1073 K (hold time 30 minutes) at the rate of 4 K/min in the external field of 3.95 kA/m and then cooled down to room temperature. The Curie temperatures $T_C$ (bulk Fe$_3$O$_4$) = 858 K and $T_C$ (bulk $\alpha$-Fe) = 1043 K [27] can be recognised on the curve measured with increasing temperature. After starting to heat the sample, $\sigma$ decreased (minimum at 622 K) and then grew (maximum at 740 K). The increase of $\sigma$ was caused by the recrystallisation/growth of Fe$_3$O$_4$ and $\alpha$-Fe.

After the whole TM measurement cycle, a HL was measured at 293 K and it exhibited the values: $H_C = 3.2$ kA/m, $\sigma_R = 5.6$ Am$^2$/kg, $\sigma_S = 142.9$ Am$^2$/kg (at 1227 kA/m). Subsequently, the phase composition was determined with XRD: $\alpha$-Fe ($d_{XRD} = 128$ nm, $a = 0.2866$ nm, $F = 62$ wt.%), Fe$_3$O$_4$ ($d_{XRD} = 41$ nm, $a = 0.8401$ nm, $F = 27$ wt.%), and FeO ($d_{XRD} = 42$ nm, $a = 0.4330$ nm, $F = 11$ wt.%). Wustite FeO (ICSD #82223, space group Fm-3m, $a = 0.4326$ nm) appeared as the result of the described heating procedure performed in vacuum.
4. Conclusions
We have synthesised $\alpha$-Fe nanoparticles in a low-pressure microwave discharge and described its structural, morphological and magnetic properties. The thermal properties of the as-synthesised nanopowder are significantly different from those of bulk samples and ought to be studied on more samples prepared by this method. The reason for the anomalously low absorption in the transmission Mössbauer spectrum measured at 293 K (compared to the spectrum measured at 5 K) was seen in the diffusive tilting motions of nanoparticles and should be further investigated.

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