Tuning structural and magnetic properties of Fe oxide nanoparticles by specific hydrogenation treatments

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Structural and magnetic properties of Fe oxide nanoparticles prepared by laser pyrolysis and annealed in high pressure hydrogen atmosphere were investigated. The annealing treatments were performed at 200 °C (sample A200C) and 300 °C (sample A300C). The as prepared sample, A, consists of nanoparticles with ~ 4 nm mean particle size and contains C (~ 11 at.%), Fe and O. The Fe/O ratio is between γ-Fe₂O₃ and Fe₃O₄ stoichiometric ratios. A change in the oxidation state, crystallinity and particle size is evidenced for the nanoparticles in sample A200C. The Fe oxide nanoparticles are completely reduced in sample A300C to α-Fe single phase. The blocking temperature increases from 106 K in A to 110 K in A200C and above room temperature in A300C, where strong inter-particle interactions are evidenced. Magnetic parameters, of interest for applications, have been considerably varied by the specific hydrogenation treatments, in direct connection to the induced specific changes of particle size, crystallinity and phase composition. For the A and A200C samples, a field cooling dependent unidirectional anisotropy was observed especially at low temperatures, supporting the presence of nanoparticles with core–shell-like structures. Surprisingly high Mₛ values, almost 50% higher than for bulk metallic Fe, were evidenced in sample A300C.

Fe-based nanoparticles (NPs) show remarkable interest in the scientific community for various applications such as biomedicine (hyperthermia¹, targeted drug delivery², computed tomography and magnetic resonance imaging contrast agents³–⁴), catalysis⁵–⁶, magnetic fluids⁷, gas sensors⁸, high-density magnetic storages⁹, water treatment and environment protection¹⁰.¹¹. For many technological applications, the Fe-based NPs are required to fulfill challenging demands such as narrow size distribution, crystallinity and stability in air. Along with the synthesis procedure, the annealing treatments offer a valuable tool to optimize Fe and Fe oxide based NPs with respect to specific applications. Simultaneous or post annealing treatments can influence morpho-structural¹²–¹⁵ and related magnetic parameters¹⁶,¹⁷.

Annealing treatments in hydrogen atmosphere performed at moderate temperatures were reported to influence considerably the phase composition and magnetic properties in Fe and Fe oxide based nanostructures. We previously used annealing treatments in hydrogen atmosphere to remove oxidation in various Fe based nanostructures¹⁸–²¹. Snovski²² used reduction of iron oxide and iron carbide NPs in H₂ at 450 °C for 2.5 h to obtain a main α-Fe phase (91%). Kin²⁷ improved the crystallinity and increased the saturation magnetization of Fe nanoparticles by treatment in H₂ at 200 °C for 4 h. FeOOH nanorods were reduced in H₂/Ar mixture and in H₂, at temperatures between 300 and 500 °C. The surprising effects of the annealing treatments in hydrogen atmosphere on the structural and magnetic properties of Fe-based NPs prepared by laser pyrolysis are studied in this report.

Experimental details
Fe oxide nanoparticles were prepared by the laser induced pyrolysis technique, as detailed in²³. Snovski²² used reduction of iron oxide and iron carbide NPs in H₂ at 450 °C for 2.5 h to obtain a main α-Fe phase (91%). Kin²⁷ improved the crystallinity and increased the saturation magnetization of Fe nanoparticles by treatment in H₂ at 200 °C for 4 h. FeOOH nanorods were reduced in H₂/Ar mixture and in H₂, at temperatures between 300 and 500 °C. The surprising effects of the annealing treatments in hydrogen atmosphere on the structural and magnetic properties of Fe-based NPs prepared by laser pyrolysis are studied in this report.

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reaction chamber was 300 mbar. The focal spot size was kept constant at 2 mm. The iron oxide nanoparticles labeled here by sample A were prepared at a laser power of 45 W, while the temperature was 515 °C. The ethane flow (100 scm) has a double role: of carrier gas for Fe(CO)₅ vapors and of sensitizer at CO₂ laser wave-length. The synthetic air flow was also 100 scm. An Ar flow of 2000 scm was introduced in the external nozzle tube, while two equal Ar flows of 150 scm each were introduced on sides in order to flush the ZnSe windows.

Annealing treatments in hydrogen atmosphere were performed at 200 °C (sample A200C) and 300 °C (sample A300C), in order to reduce oxidation. The heat treatment under hydrogen was performed using an apparatus based on stainless steel tubing. Prior to annealing, the tubes were degassed for 2 h at 300 °C under 10⁻³ mbar. The samples were annealed afterwards for 4 h at the above temperatures in flowing hydrogen gas (99.9999% purity, 100 ml/min flow rate).

The phase composition was further investigated by X-ray diffraction (XRD) using a Bruker D8 Advance diffractometer with Cu Kα radiation (wavelength 1.5406 Å) and a LiF crystal monochromator. Rietveld refinements of the XRD data were performed with the MAUD software.

The morphology and structure of the as-synthesized NPs was observed by transmission electron microscopy (TEM) and selected area electron diffraction (SAED) analysis, using a Philips CM 120ST (120 kV) Electron Microscope. Additional High Resolution Transmission Electron Microscopy (HRTEM) images have been also obtained using a JEOL 2100 Electron Microscope. The elemental analysis was performed by energy-dispersive X-ray spectroscopy (EDX) attached to a scanning electron microscope (Philips XL30 CP) with an acceleration voltage of 15 kV.

The magnetic measurements were performed using a Superconducting Quantum Interference Device (SQUID) magnetometer (MPMS 7T from Quantum Design). Mössbauer spectroscopy (MS) measurements were recorded on a constant acceleration spectrometer, in transmission geometry and using a ⁵⁷Co(Rb) source. The temperature dependent spectra were collected via a close cycle cryostat (Janis) and a couple of field dependant spectra were collected via a cryomagnet (ICE Oxford Ltd.). The NORMOS computer program was used for the least-squares fitting of the Mössbauer spectra. The isomer shifts were reported relative to α-Fe at room temperature.

Results and discussion

The as-synthesized nanoparticles were analysed by EDX in order to evaluate the elemental composition. The sample is homogeneous and contains 11(3) at.% C, 53(1) at.% O and 36(1) at.% Fe. The resulted Fe/O ratio is 0.68 close to the specific value (0.667) for maghemite (γ-Fe₂O₃).

TEM analysis and SAED images of sample A are presented in Fig. 1. The powder contains spherical shaped nanoparticles branched in a chain-like agglomeration (Fig. 1a). The particle size distribution is a mono-modal one and its fitting with Log-Normal Function provided a mean particle size of 3.15 nm (Fig. 1c). The HRTEM image (Fig. 1b) and the insertion with an image refining by Fourier Transformation revealed the internal crystal-line structure of some NPs matching the (220) and (311) interplanar distances of γ-Fe₂O₃ crystalline phase. The SAED patterns (Fig. 1d) for as-synthesized powder exhibit diffuse rings that could be ascribed to Fe₃O₄ and/or γ-Fe₂O₃ phases (identified by the 2.52, 2.95, 1.61 and 1.48 Å reflections). There is no evidence in the SAED image for α-Fe or other Fe carbides around 2.01–2.05 Å distances.

Rietveld refinements of the XRD data for samples A, A200C and A300C are given in Fig. 2. Table 1 shows the main crystallographic parameters resulted from Rietveld refinements as well as the reliability fit parameters. The broad and slightly asymmetric peaks of sample A indicate NPs with specific structure in-between of very distorted main crystallographic parameters resulted from Rietveld refinements as well as the reliability fit parameters. The temperature usually found in a wide range of 10⁻⁹–10⁻¹² s,

\[ \tau_M = \frac{K_V}{k_B T} \]  

(1)

where \( \tau \) is the Néel relaxation time, \( \tau_0 \) is the attempt time (characteristic of material and slightly dependent on temperature) usually found in a wide range of 10⁻⁹–10⁻¹² s, \( k_B \) is the Boltzmann constant, \( K \) is the magnetic anisotropy constant, \( V \) is the particle volume, \( T \) is the temperature.

Magnetic NPs are in a magnetic dynamic (superparamagnetic) regime above a temperature called blocking temperature (\( T_B \)) whereas at temperatures lower than \( T_B \), they are in a magnetic frozen regime specific of a bulky-like material. \( T_B \) can be defined as the temperature for which the superparamagnetic relaxation time equates the measuring time window of the experimental method (\( \tau_{ex} \)). It results:

\[ T_B = K_V (\ln \frac{\tau_{ex}}{\tau_0})^{-1} / k_B \]  

(2)

\( \tau_{ex} \) is specific to the employed experimental technique and therefore \( T_B \) is not uniquely defined. In magnetometry, \( T_B \) is investigated under the zero-field cooled—field cooled (ZFC–FC) protocol. In the ZFC sequence, the magnetization curve is obtained when the sample is cooled in the absence of a magnetic field and then the magnetization is measured at increasing temperature under a very small applied field, removing the degeneracy...
**Figure 1.** TEM analyses for sample A—as-synthesized nanoparticles: (a) TEM image at low resolution, (b) HRTEM image with an insertion containing the Fourier Transformed Image in order to evaluate inter-planar distances, (c) the particle size distribution fitted with Log normal function, and (d) a SAED image with identified inter-planar distances. Core–shell-like structures of NPs might be tentatively assumed according to the additional HRTEM data presented in the supplementary material.

**Figure 2.** Rietveld refinements of the XRD data for samples: A (A), A200C (B), and A300C (C).
of the two minima of the magnetic anisotropy energy. In the FC sequence, the magnetization curve is obtained when the sample is initially cooled down in the same small applied magnetic field, which also remains applied during the measuring process at increasing temperature. The typical measuring time, $\tau_M$, for DC magnetometry is about 10 s and conventionally $T_B$ is provided by the maximum of the ZFC curve.

The ZFC–FC curves of samples, A, A200C and A300C, measured in a field of 50 Oe, are presented in Fig. 3. Specific to NPs in sample A is $T_B = 106(1)$ K corresponding to a magnetization of 1.46 emu/g. The ZFC curve for the sample A200C provides only an almost insignificant slightly increased $T_B$ of 110(1) K, corresponding to a magnetization of 1.49 emu/g. However, the very close blocking temperatures associated to NPs in the two samples in conditions of a significant variation of the average particle size (about 5 and 10 nm, respectively) clearly indicate via relation (2) a significant difference of the corresponding anisotropy constants in the two samples (e.g. a few times lower $K$ in sample A200C as in A) which was assumed to be related to a different oxidation state of Fe in the oxide NPs. To note the slight decrease of the ZFC curves at $T > T_B$ for both samples A and A200C, providing evidence for either a very large size distribution of NPs and/or the presence of a fraction of interacting NPs. In case of sample A300C, the nanoparticle size increases about 5 times relative to sample A200C. According to relation (2), $T_B$ should increase by 125 times in conditions of a same anisotropy constant of NPs in sample A200C and A300C. The experimental increase of $T_B$ at only some 350 K in sample A300C is therefore in direct agreement with a decrease of the anisotropy constant of NPs in this sample by more than one order of magnitude relative to sample A200C. This can be simply explained by the phase composition of the involved NPs in sample A300C, dealing with single-phase metallic Fe, as revealed by XRD and also subsequently presented by MS results. However, the increasing trend of ZFC profile of sample A300C and the clear branching point at about 350 K indicate a low amount of superparamagnetic NPs above 350 K, the main signal corresponding rather to a long range magnetic structure specific to strongly interacting magnetic single-domain NPs.

The magnetic hysteresis curves of samples A, A200C and A300C, are shown in Fig. 4. The insets of Fig. 4 show the hysteresis curves of the mentioned samples collected after cooling the sample in an external magnetic field of 50 Oe. To note the specific negative shifts of the hysteresis loops in the case of samples A and A200C, better evidenced after cooling the samples in an applied field. This well-known behavior is due to the presence of unidirectional anisotropy in a nanometer size ferromagnetic-like phase interfaced to an antiferromagnetic-like phase. Among the macroscopic effects of such interfacial interactions are: (1) the increased coercivity of the multi-phase system and (2) the above mentioned shift of the hysteresis loop, denoted as an exchange bias field. Figure 5 shows the evolution of both the coercive field ($H_C$) and exchange bias field ($H_E$) with temperature. The $H_C$ values change considerably in the case of samples A and A200C, from > 700 Oe at low temperatures down

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**Table 1.** Crystallographic parameters resulted after Rietveld refinement of XRD data for samples: A, A200C, and A300C.

| Sample | Lattice parameter (nm) | Crystallite size (nm) | R.M.S microstrain (%) | Fit reliability parameters |
|--------|------------------------|-----------------------|-----------------------|---------------------------|
| A      | 0.8391 (8)             | 5.6 (6)               | 0.006 (2)             | GOF = 1.040 Rwp = 1.20% RB = 0.96% |
| A200C  | 0.8406 (2)             | 10.3 (6)              | 0.003 (1)             | GOF = 1.006 Rwp = 1.11% RB = 0.91% |
| A300C  | 0.2865 (1)             | 57.8 (4)              | 0.0005 (3)            | GOF = 1.045 Rwp = 5.84% RB = 4.63% |

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**Figure 3.** The ZFC–FC curves of the as prepared and annealed samples, A, A200C and A300C, in an applied field of 50 Oe.
to tens of Oe at room temperature (RT) recalling the typical dependence specific to superparamagnetic and non-interacting NPs:

\[ H_C = H_0 \left[ 1 - \left( \frac{T}{T_B} \right)^{1/2} \right] \]  

Figure 4. Hysteresis curves of the as prepared and annealed samples: A (a), A200C (b) and A300C (c). The inset of each figure shows the hysteresis curves collected after cooling the sample in a field of 50 Oe.

where \( H_0 \) is the coercive field in the magnetically blocked regime, e.g. at 0 K. Low finite \( H_C \) values with an almost constant trend above \( T_B \) (\(< 150 \) K) give support for a small fraction of magnetically blocked (large size) NPs in these samples. For the sample A300C, \( H_C \) decreases slowly with temperature, remaining at a still very high value at temperatures close to 350 K, considered as the blocking temperature for the small amount of non-interacting Fe nanoparticles. The observed deviation from the specific dependence (3) gives support for strongly interacting NPs in this sample.

As above mentioned in the case of Fe oxide NPs, the evidenced negative \( H_E \) values at low temperature suggest the presence of interactions between antiferromagnetic or spin disordered oxides and ferrimagnetic oxide phases, most probably in a core–shell-like configuration (which is also probed by MS results and the micromagnetic...
computations presented in the supplementary material). As expected, the exchange bias interaction is stronger after cooling the sample in the presence of a magnetic field (Fig. 5d). As a result of the field cooling procedure, $H_E$ increases more than double for sample A200C and one order of magnitude for sample A (these results will be also corroborated with the phase composition obtained from MS results in Figs. 8 and 9). The presence of the unidirectional anisotropy at low temperatures imposes also the strong increase of the coercivity in samples A and A200C, this additional effect being the reason for which the Eq. (3) is not valid for these samples too. It is to be noted here that the exchange bias field is cancelled out at a temperature of 50 K, also known as the blocking temperature of exchange bias, being marked in the following as $T_{EB}$. Hence, samples A and A200 are representative cases of nanoparticulate systems with $T_{EB} < T_B$.

The evolution of remanence ($M_R$) and saturation ($M_S$) magnetization with temperature is shown in Fig. 6. $M_R$ values of samples A and A200C are roughly similar, with a slightly increased contribution after the field cooling procedure and a much slower decrease with temperature above $T_{EB}$. Such specific behaviors of remanence provide evidence for its direct relation to the unidirectional anisotropy induced at the interface of the two distinct magnetic phases in the core–shell structure of oxide NPs. On the other hand, the much higher remanence of metallic Fe NPs in sample A300C has to be related only to the long range magnetic order inside the unidimensional chain-like organization of NPs, initially oriented along the saturation field.

The $M_S$ values are atypical for all samples. According to the EDX characterization, the relative content of C of 11% at. should lead to an increase of less than 5% in the saturation magnetization (in emu/g) if counting only the magnetic constituent. An unexpected $M_S$ variation of Fe NPs, which decreases from 310 emu/g at 300 K to 290 emu/g at 10 K as well as the unexpected high $M_S$ value at 300 K, i.e. some 50% higher than for bulk Fe, should be mentioned for sample A300C. We tentatively relate this behavior to local changes of the electronic configurations due to the random penetration of C atoms in the bcc structure of Fe, which might represent also the reason for the decreased anisotropy constant of NPs in sample A300C and for their magnetic single-domain structure. However new experimental and theoretical studies on such hydrogenated samples are required for a deeper understanding of their magnetic behavior.

On the other hand, the $M_S$ values of the samples A and A200C are much reduced in comparison to specific values of the spontaneous magnetization of maghemite (about 75 emu/g) and magnetite (about 90 emu/g). For example, $M_S$ for the magnetic component (maghemite-like) in sample A is about 32 emu/g at 10 K, i.e. only 43% from the spontaneous magnetization of a well formed maghemite, whereas $M_S$ for the magnetic component (magnetite-like) in sample A200C is about 39 emu/g at 10 K, i.e. again only about 43% from the spontaneous magnetization of a well formed magnetite structure. Such huge discrepancies cannot be explained by a simple poor degree of crystallinity in the two samples, but rather via a core–shell structure of nanoparticles with a better formed ferrimagnetic core and a magnetic disordered shell (magnetic dead layer) with similar oxidation states as in the core. Assuming the typical maghemite magnetic structure in the NPs core and taking into account that

![Figure 5. Temperature dependence of coercive field before (a) and after (b) in-field cooling procedure. Temperature dependence of exchange bias field before (c) and after (d) in-field cooling procedure.](image-url)
only 43% of Fe ions are in the core of the 5 nm sized NPs in sample A, an average core size close to 3.5 nm and a surrounding magnetic dead layer close of 1.5 nm can be deduced. Similarly, in the case of sample A200C, NPs of average size of 10 nm will consist of a core with magnetite-like magnetic structure and average size close to 6.5 nm and a surrounding magnetic dead layer of about 3.5 nm.

The Fe phase composition, local structure and magnetic relaxation phenomena were investigated by temperature dependent $^{57}$Fe MS. The Mössbauer spectra of samples A, A200C and A300C, collected at different temperatures, are shown in Figs. 7, 8 and 9. The spectra of sample A, collected at low temperatures present a relatively broad sextet pattern and are fitted using the hyperfine magnetic field probability distribution method (Fig. 7). On the other hand, the low temperature spectra of the annealed samples show rather narrow magnetic patterns and are fitted with either superposed hyperfine magnetic field distributions and discrete sextets (sample A200C) or only a discrete sextet component (sample A300C).

The Mössbauer spectra of the as prepared sample A with the hyperfine field distributions presented on the right side of Fig. 7 show at 5 K a most probable hyperfine magnetic field of more than 52 T, specific to mainly Fe$^{3+}$ ions and suggesting the presence of distorted maghemite. The almost linear decrease of the most probable and average hyperfine magnetic fields with temperature is due to magnetic relaxation phenomena as will be subsequently discussed.

According to the saturation magnetization data, a magnetic dead layer (with random orientation of the Fe$^{3+}$ spins) has to be considered at the surface of NPs in sample A, with a corresponding contribution included within the same overall hyperfine field distribution. A more direct proof for such a core–shell magnetic structure of NPs in sample A is provided by in field MS. Field dependent Mössbauer spectra collected at a temperature of 3 K are shown in Fig. 8 together with corresponding hyperfine magnetic field distributions (on the right side of each spectrum).

The Mössbauer spectrum collected in the cryomagnet at 3 K and in the absence of the applied magnetic field, was fitted according to the previous discussion via a unimodal distribution of hyperfine magnetic fields (Fig. 8a). If a magnetic field is applied perpendicular to the direction of the γ rays, the hyperfine field distribution initially starts to enlarge (Fig. 8b). Under a 5 T applied field, the hyperfine magnetic field distribution transforms into a bimodal one, with an intense local maximum at about 47 T and a less intense one at about 57 T (Fig. 8c). Such values correspond to average effective fields obtained by the superposition of the internal hyperfine magnetic field and the applied one. The 5 T applied magnetic field induces the almost complete reorientation of the net magnetic moments of the ferrimagnetic structure along the field direction, effect which is also clearly evidenced by the increased intensity of the second and fifth absorption lines of the sextet under increasing applied magnetic fields$^{28,36}$. Hence, the two above mentioned effective fields have to correspond to Fe spins opposite to the external
field ($B_2 = 57 \, \text{T}$), respectively. In both cases the effective field is obtained by subtracting/adding the external field ($5 \, \text{T}$) to the hyperfine field ($52 \, \text{T}$). In the case of a defected spinel-like structure (cation deficient) as maghemite $\text{Fe}_3\text{O}_4$, the highest number of $\text{Fe}^{3+}$ ions belong to octahedral-like B positions providing also the net magnetic moment of the compound which is oriented along the field. To note that the hyperfine magnetic field of mainly Fermi-contact origin is antiparallel to the magnetic moment of Fe. As a direct consequence, the hyperfine magnetic field associated to $\text{Fe}^{3+}$ ions on such positions ($B_{hf}$) is antiparallel to the applied field, giving rise to the stronger component of the hyperfine field distribution centered on $47 \, \text{T}$ (Fig. 8d).

Concerning the distribution of the hyperfine magnetic field under a $5 \, \text{T}$ applied magnetic field, it can be also clearly observed a definite probability of effective fields centered on $52 \, \text{T}$, providing evidence for a significant amount of randomly oriented magnetic moments/spins/ hyperfine fields associated to $\text{Fe}^{3+}$ ions in the shell of the nanoparticle (a valid solution for the decomposition of the hyperfine magnetic field distribution by 3 components provides a median component of more than 50% contribution, in reasonable agreement with the magnetic measurements).

The spectra collected at temperatures up to room temperature on sample A200C (Fig. 9a–d), reveal relatively narrow magnetic patterns which evolve with temperature due to magnetic relaxation effects clearly evidenced by the broad collapsing magnetic pattern specific to the RT spectrum. The best fit of the 5 K and 80 K Mössbauer spectra was obtained by using four magnetic components: three narrow crystalline sextets of almost identical relative spectral areas (i.e. 15(2)% each) and a broader sextet fitted by a hyperfine field distribution, of 55(2)% relative area ($R_{hf}$) contribution and with an average hyperfine magnetic field ($<B_{hf}>$) of 49.7(2) T at 5 K and 48.4(2) T at 80 K. The hyperfine fields associated to the crystalline sextets are 51.0(1) T, 44.3(1) T and 47.5(1) T.
at 5 K and 50.1(1) T, 44.0(1) T and 46.7(1) T at 80 K. An increased isomer shift (IS) value (0.98(2) mm/s at 5 K and 0.92(2) mm/s at 80 K) corresponds to the component of the lowest $B_{hf}$ (44.3 T at 5 K) relative to the rest of the components having lower IS (~ 0.6 mm/s at 5 K and 0.5 mm/s at 80 K). Such hyperfine parameters give indications for the following assignment: the crystalline sextets with $B_{hf}$ of 51.0 T and 44.3 T at 5 K correspond to Fe$^{3+}$ and respectively Fe$^{2+}$ ions on octahedral B positions of magnetite, whereas the sextet with $B_{hf}$ of 47.5 T at 5 K corresponds to Fe$^{3+}$ ions on tetrahedral A positions of magnetite. According to $R_A$ values, a relatively well crystallized magnetite (with inverse spinel structure) is formed in the core of the nanoparticles which embed almost 45% from the total Fe (in close agreement with the magnetic measurements). The forth sextet with $<B_{hf}>$ of 49.7 T has to correspond to the defected magnetite with disordered magnetic structure in the shell of the nanoparticles, embedding 55% from the total Fe. The Mössbauer spectrum collected at 160 K on sample A200C gives an additional support for the above reasoning of nanoparticles with magnetite cores and magnetic disordered shells. In this case, the best fit was obtained via 3 magnetic components, i.e. two narrower crystalline sextets and a broader sextet which reveals a hyperfine magnetic field distribution with $<B_{hf}>$ of 43.0(2) T. With a corresponding $<IS>$ of 0.5 mm/s and $R_A$ of 57(2)%, this last sextet is evidently assigned to the very defected magnetite (with inverse spinel structure) is formed in the core of the nanoparticles which embed almost 45% from the total Fe (in close agreement with the magnetic measurements). The forth sextet is evidently assigned to the very defected magnetite of disordered magnetic structure in the particle shells. The other two sextets, S1 ($R_A = 27(2)\%$, $B_{hf} = 44.2(2)$ T and IS = 0.72(2) mm/s) and S2 ($R_A = 16(2)\%$, $B_{hf} = 47.8(2)$ T and IS = 0.34 mm/s) have been assigned to Fe$^{2.5+}$ intermediate valence ions on octahedral B positions and to Fe$^{3+}$ ions on tetrahedral A positions, respectively, as specific to well-formed magnetite above the Verwey transition.

The annealing treatment at 300 °C successfully determines the well crystallization of the nanoparticles in the bcc structure of metallic α-Fe, as evidenced by the specific hyperfine parameters at 6 K ($B_{hf}=34.1(1)$ T and IS = −0.06(1) mm/s) of the main narrow crystalline sextet (Fig. 9c). However, an additional broader magnetic sextet ($B_{hf} = 48.9(5)$ T) has improved the fit quality, being tentatively assigned to local Fe positions in the bcc structure.
structure, randomly surrounded by interstitial C atoms. Such high values of $B_{hf}$ indicate magnetic moments larger than $3\mu_B$ and cannot be assigned to an Fe oxide phase due to the corresponding IS of 0.05(3) mm/s specific to a metallic phase.

The evolution of the reduced hyperfine magnetic field $B_{hf}/B_0$ (with $B_0$ the $B_{hf}$ value at the lowest temperature of 5 K in this case) for the as-prepared and annealed samples, A and A200C, is shown in Fig. 10. In the case of the as-prepared sample, the average hyperfine magnetic fields provided by the probability distributions were considered. For the A200C sample, the hyperfine magnetic fields of magnetite provided by the weighted average of the $B_{hf}$ values corresponding to all the discrete sextet contributions were considered. It can be observed that the temperature induced decrease of the $B_{hf}/B_0$ values for sample A is much faster than for sample A200C, providing evidence of much finer maghemite NPs than of the magnetite NPs.

In the case of non-interacting magnetic NPs relaxing in the regime of collective excitations, the hyperfine magnetic field decreases linearly with the temperature according to the equation:

$$B_{hf} = B_0 \left(1 - \frac{k_B T}{2KV}\right)$$

where, $B_0$ is the $B_{hf}$ value in the magnetic frozen regime, e.g. much below $T_m$, $k_B$ is the Boltzmann’s constant, $K$ is the anisotropy constant and $V$ is the volume of the nanoparticle.

From Eq. (4), the barrier energy $KV$ of magnetic NPs in samples A and A200C can be obtained, assuming that the anisotropy constant is an effective anisotropy constant assigned to the overall volume of the core–shell NP. The $KV$ values obtained from the experimental slopes of the linear dependences in Fig. 10 are shown in Table 2.

An absolute value for the effective anisotropy constant of core–shell magnetite NPs with average size of 10 nm in sample A200C of about $2.4 \times 10^4$ J/m$^3$ is straightforwardly obtained from Table 2. This value is double relative to the typical magneto-crystalline anisotropy of bulk magnetite, indicating rather extrinsic origin due to irregular shape and/or the shell–core magnetic structure. In a similar way, a much higher effective anisotropy constant, i.e. of about $8.2 \times 10^4$ J/m$^3$, is obtained for the NPs with average size of 5 nm in sample A. This value is reasonably close to the value of $7.7 \times 10^4$ J/m$^3$ reported by Phan for NP of average size of 6 nm with maghemite core, providing so an additional support for maghemite core/shell configuration of NPs in the as-prepared sample A.

A final discussion related to the contradictory aspects of the exchange bias fields induced at the lowest measuring temperatures by in zero field and in applied field cooling procedure in samples A and A200C deserves to be mentioned in the context of the different core–shell configurations in the two samples. To note here that such atypical exchange bias structures of type ferrimagnet/spin disordered layer, which deviate from the typical ferromagnetic/antiferromagnetic structures, were previously reported in excellent reviews by Nogues and Phan.

More specifically, at 5 K, an exchange bias field of $-85$ Oe is observed in sample A200C relative to a much lower shift of only $-10$ Oe for sample A, in the case of the zero field cooling (at remanence) procedure. By contrary, after cooling the samples in only 50 Oe applied field, the exchange bias field increases at $-200$ Oe in sample A200C and at an even much higher value of $-440$ Oe in sample A. The explanation is related to the value of the net spin induced at the core–shell interface in the magnetically disordered shell side by the ferrimagnetic core.

| Sample code | Type of NP          | $KV$ ($10^{-20}$ J) |
|-------------|---------------------|---------------------|
| A           | With γ-Fe$_2$O$_3$ core | 0.34 (2)            |
| A200C       | With Fe$_3$O$_4$ core   | 1.20 (2)            |
structure, which is at remanence in the first case and ordered by the field in the second case. As also proven by MS, a higher spin disorder is expected in the 3.5 nm maghemite core of NPs in sample A relative to the 6.5 nm well-formed magnetite core of the NPs in sample A200C. Therefore, after cooling the samples without applied field (under a higher remant magnetic polarization of the core in sample A200C), the exchange bias field of this sample has to be higher relative to the one of sample A. However, by the field cooling procedure, the magnetic polarization of the NP cores should be comparable in the two samples and the magnitude of the exchange bias field is imposed only by the representative size of the ferrimagnetic phase in the core. As previously reported in the case of thin film structures\textsuperscript{29,30,40}, $H_E$ is inversely proportional to the thickness of the ferrimagnetic layer interfaced to the antiferromagnetic one. In the present case, the size of the maghemite core of NPs in sample A is almost half of the size of the magnetite core of NPs in sample A200C and therefore an almost double value of $H_E$ would be expected in sample A (experimental values are $\approx 440$ Oe relative to $\approx 200$ Oe).

Conclusions
Studies concerning the influence of annealing treatments in hydrogen atmosphere on the local structure and magnetic properties of Fe oxide nanoparticles obtained by laser pyrolysis are presented in this report. The pristine samples were formed by Fe oxide nanoparticles with an average size of about 5 nm and with a core–shell structure consisting of a better formed maghemite core (about 3.5 nm size) and a magnetically disordered shell. The annealing treatment performed at 200 °C in hydrogen atmosphere induces a partial reduction of Fe, giving rise to nanoparticles with an average size of about 10 nm and with a core–shell structure consisting of a very well formed maghemite core (about 6.5 nm size) and a magnetically disordered shell. Annealing treatments at 300 °C in hydrogen atmosphere succeeded to induce the formation of a α-Fe-like phase with the metallic nanoparticles (tens of nm in size) remaining stable with oxidation. In agreement with these changes in phase composition, as well as due to increase in particle size and crystallinity improvement, $T_B$, $H_E$, $M_S$ and $M_V$ values increase significantly after annealing at 300 °C. As for example, the saturation magnetization of the newly formed metallic phase is more than 50% higher than in bulk metallic Fe. Therefore, hydrogenation treatments seem to be even more effective in this respect as compared to more expensive and time consuming nitriding treatments leading to ordered iron nitride with martensite structure of high saturation magnetization\textsuperscript{38}. Specific aspects related to the unidirectional anisotropy of nanoparticles with core–shell magnetic structures assigned to the as prepared sample and the partially reduced sample are also discussed in detail.

Data availability
The datasets generated during and/or analysed during the current study are not publicly available from the corresponding author on reasonable request.

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Author contributions
S.G. contributed to analysis, data interpretation and wrote the draft of the manuscript; P.P., G.S., A.L., I.L. and G.P. contributed to experimental and data acquisition; F.D. contributed to design of the sample preparation; A.K. performed additional HRTEM measurements and micromagnetic calculations as well. V.K. contributed to the conception and design of the work, analysis and data interpretation and substantively revised the manuscript. All authors reviewed the manuscript.

Competing interests
The authors declare no competing interests.

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