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## ARTICLE

## Iron Oxide Nanoparticles by High Energy Electron Beam Assisted - Synthesis

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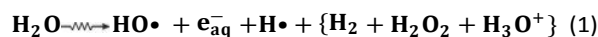
New approaches in the synthesis of magnetite (Fe<sub>3</sub>O<sub>4</sub>) nanoparticles (NPs) are of considerable interest due to their potential applications in various fields, such as biomedicine, industry, environmental remediation, and catalysis. This study presents a novel approach for synthesizing Fe<sub>3</sub>O<sub>4</sub> NPs using high energy Electron Beam (EB) irradiation starting from organic (acetylacetonates) iron precursors. EB irradiation is a challenging nanoparticle synthesis method being at the same time efficient and rapid. The synthesis develops at room temperature and is based on the water radiolysis process. It eliminates the need for chemical-reducing agents and may provide precise control over particle formation. Using high energy EB irradiation of an organic Fe precursor, we demonstrate the successful synthesis of well-dispersed Fe<sub>3</sub>O<sub>4</sub> NPs with controlled size, morphology and magnetic properties, as proven by morpho-structural, Mössbauer Spectroscopy and magnetic investigations. In particular, using organic iron precursors, such as iron acetylacetonates, NPs with distinct surface characteristics and improved thermal stability compared to those synthesized from inorganic precursors were obtained. These findings suggest that integrating organic precursors in EB-assisted synthesis can enhance the functional properties of Fe<sub>3</sub>O<sub>4</sub> NPs, making them more suitable for specific applications. The versatility of this method opens up new avenues for the targeted design of nanomaterials with specific functionalities, paving the way for advanced applications in various technological fields. The current study is also motivated by the lack of literature data on the synthesis of metallic iron or iron oxide NPs mediated by EB radiolysis.

## 1. Introduction

Fe<sub>3</sub>O<sub>4</sub> nanoparticles (NPs) have attracted sustained interest owing to their favorable magnetic characteristics—high magnetic moment and saturation magnetization coupled with relatively low coercivity—and their good biocompatibility. These properties underpin a broad spectrum of biomedical applications, including targeted drug delivery,<sup>1,2</sup> magnetic resonance imaging (MRI) contrast enhancement<sup>3,4</sup>, magnetic fluid hyperthermia,<sup>5–7</sup> and biosensing.<sup>8,9</sup> Additional uses span industrial processes,<sup>10,11</sup> biocatalysts,<sup>12,13</sup> and environmental remediation.<sup>14</sup>

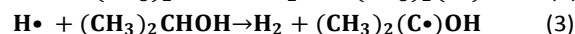
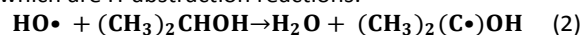
Synthesis strategies have focused on precise control of particle size, morphology, crystallinity, and surface chemistry. A variety of chemical routes have been established, each with distinct advantages and limitations,<sup>15</sup> including (a) pyrolysis, (b) sol–gel, (c) co-precipitation, (d) thermal decomposition, and (e)

hydrothermal methods, among others. Beyond these conventional chemistries, non-ionizing radiation–assisted syntheses (e.g., microwaves,<sup>16,17</sup> ultrasound<sup>18</sup>) and ionizing-radiation approaches (γ-rays or electron beams, EB<sup>19–21</sup>) have been explored. The latter rely on water radiolysis—a cascade of ionization, excitation, dissociation, and recombination events triggered by energy deposition in aqueous media—thereby generating a chemically active environment rich in short-lived reactive species according to the global scheme (reaction (1))<sup>22–27</sup>:



During radiolysis, numerous elementary reactions occur.<sup>28–30</sup> Of particular synthetic value are solvated electrons (e<sub>aq</sub><sup>-</sup>) and hydrogen atoms (H•), which possess highly negative reduction potentials (E<sub>0</sub>(H<sub>2</sub>O/e<sub>aq</sub><sup>-</sup>) = -2.87 V; E<sub>0</sub>(H<sup>+</sup>/H•) = -2.3 V), enabling the replacement of conventional, often non-eco-friendly reductants. Concurrently, oxidizing transients such as hydroxyl radicals (•OH) are formed but can be efficiently scavenged by alcohols (e.g., 2-propanol (IPA)).

Given the reactivity and the oxidation reactions of HO• radical, it may favor certain reaction pathways. The usage of IPA may further scavenge the HO• and H• according to equations (2) and (3) which are H-abstraction reactions:



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Formation of the  $\alpha$ -alcohol radical  $(CH_3)_2(C\cdot)OH$  rather than the  $\beta$ -alcohol radical  $(\cdot CH_2)(CH_3)(CH)OH$  is supported by several studies, where H-abstraction reactions from the  $\alpha$ -carbon occurs with yields ranging 85.5-96%.<sup>23</sup> The remainder up to 100% are HO abstraction (1.2%) and  $\beta$ -carbon hydrogen abstraction reactions (13.3%)<sup>23</sup>. The resulting  $(CH_3)_2(C\cdot)OH$  radical remains however the major product, and exhibits a strong reducing character. P. Wardman describes reaction of hydroxyl radical HO $\cdot$  with tertiary alcohols like tert-butanol  $(CH_3)_3COH$ , secondary alcohols like IPA  $(CH_3)_2CHOH$ , or the reaction with formate  $(HCO_2^-)$ <sup>24</sup>.

A further advantage of radiochemical synthesis is its operation near ambient temperature and pressure. Uniform nucleation is essential for obtaining monodisperse, colloiddally stable NPs. Ionizing radiation can deliver spatially homogeneous energy deposition throughout the reaction volume when the irradiation geometry is appropriately configured. Consequently, accurate dosimetry and optimal irradiation-cell design are critical for controlling nucleation and growth kinetics.<sup>31</sup> Cobalt-60  $\gamma$ -sources are the most frequently employed ionizing sources for radiolytic nanoparticle synthesis.<sup>32-34</sup>  $\gamma$ -irradiation enables access to diverse nanoarchitectures, from single-phase materials<sup>35,36</sup> to multiphase systems—including alloy-like structures<sup>37,38</sup> and bi-/multi-metallic core-shell NPs.<sup>39</sup> In addition to standard synthetic variables (solvent, surfactant, pH), the absorbed dose is a key handle for tailoring composition and structure. For iron-containing systems, the dose can modulate the  $Fe^{2+}/Fe^{3+}$  ratio<sup>40</sup> and thereby direct phase selection (e.g.,  $Fe_3O_4$  vs. other iron oxides such as  $\alpha$ - $FeOOH$ ), consistent with proposed  $\gamma$ -induced nucleation-growth mechanisms for iron-oxide formation.<sup>41</sup>

High-energy electron beams represent an alternative ionizing source for radiolysis-based synthesis of metallic NPs.<sup>42-44</sup> EB irradiation offers high dose rates, short processing times, room-temperature operation, and fine, real-time tunability of the dose rate via pulse current, repetition frequency, irradiation geometry, and exposure time. For magnetic systems, EB-driven syntheses have demonstrated dose-dependent improvements in magnetic properties, as reported for Ni-based NPs up to ~300 kGy.<sup>45</sup> Although EB facilities are less ubiquitous than  $\gamma$ -sources, EB irradiation is increasingly utilized in radiolytic syntheses<sup>28,46</sup>, modern accelerators also enabling highly homogeneous volumetric irradiation and precise pulse-frequency control for dose-rate adjustment.<sup>47</sup>

Under pulsed ionizing irradiation, chemistry proceeds in two coupled regimes: (i) radiolysis during the pulse (typically microseconds for industrial EB sources), and (ii) interpulse evolution (milliseconds), wherein the system can be chemically "quiescent" (NPs largely unchanged) or reactive (solvent, alcohols, and surfactants interact with nascent clusters). These regimes can overlap kinetically, rendering EB-assisted radiolysis a versatile, highly tunable platform. In situ transmission electron microscopy (TEM) has provided valuable real-time insight into EB-induced radiolysis at hundreds of keV.<sup>49,50</sup>

Despite these advantages, EB-driven radiolytic synthesis of iron-oxide magnetic nanoparticles (MNPs) has only been reported

very recently by Dietrich et al.<sup>22</sup>, who synthesized  $Fe_3O_4$ /maghemite from  $FeCl_3 \cdot 6H_2O$  inorganic precursor in a microemulsion process involving the use of surfactant (Triton X-100), toxic organic solvents (cyclohexane) and tetramethylammonium hydroxide (TMAH) as precipitation reagent. However, we demonstrate herein the EB-radiolysis synthesis of  $Fe_3O_4$  NPs from organic iron precursors (acetylacetonates) without the use of organic solvents and typical precipitation agents (NaOH), and provide a comprehensive morpho-structural and magnetic characterization of the resulting materials.

## 2. Experimental.

Iron-oxide nanoparticles (NPs) were synthesized radiolytically using 5.5 MeV EB pulses of 4  $\mu s$  with 50Hz repetition rate<sup>47, 48</sup> delivered by the linear electron accelerator ALID-7 at the National Institute for Laser, Plasma and Radiation Physics (Romania) (see Fig. S1 in the supplementary information (SI)). Two independent attempts were performed employing  $Fe(acac)_3$  as the Fe (III) precursor in IPA with NaOH 1M in deionized and degassed water, while varying the EB dose rate. Iron (III) acetylacetonate precursors can facilitate control over particle morphology and surface chemistry owing to their coordination environment and thermal decomposition characteristics.<sup>51</sup> The chemical substances were purchased from Sigma Aldrich and used as received.

The first attempt involved 0.15 g of  $Fe(acac)_3$  precursor dissolved in 5 mL distilled water under vigorous stirring for 30 minutes, under the addition of 0.85 mL NaOH 1M and 0.2 mL of IPA, to neutralize the oxidative species. The precursor solution was placed in a small glass under the accelerator irradiation window for irradiation along with other samples which are not of interest for the present discussion. All samples were arranged on a circular area corresponding to the EB radiation footprint recorded on a piece of glass. The radiation dose rate during the experiment was 5 kGy/min, measured with a graphite calorimeter<sup>47,48</sup>.

Continuous irradiation of 5 kGy / min for 60 min delivered a total dose of 300 kGy. The resulting solid was magnetically separated and washed repeatedly with distilled water (IONP-300kGy sample).

In the second attempt, the precursor loadings were adjusted to increase nanoparticle yield. Specifically, 0.75 g  $Fe(acac)_3$  was dissolved in 25 mL of distilled water under vigorous stirring, followed by the addition of 4.25 mL NaOH 1M and 1.0 mL IPA. The reaction mixture was transferred to a polyethylene vessel forming a 25 mm-thick liquid layer to enhance dose uniformity during irradiation; this thickness matches the depth-dose profile of a 5.5 MeV electron beam in water. The irradiation was performed at a dose rate of 8 kGy / min for 50 min to a total absorbed dose of 400 kGy. After irradiation, the resulting black suspension was collected by magnetic separation, washed several times with distilled water, and finally redispersed in absolute ethanol (IONP-400kGy sample).

Morphology and structure of both samples were examined by transmission electron microscopy (TEM) and selected-area



electron diffraction (SAED) on a JEM-ARM200F (JEOL) instrument. X-ray diffraction (XRD) patterns were collected in  $\theta$ - $2\theta$  geometry on a Bruker D8 Advance diffractometer, and Rietveld refinements were carried out with MAUD.<sup>52</sup> Magnetic properties were measured using a SQUID magnetometer (MPMS, Quantum Design, USA) operating under the Reciprocating Sample Option (RSO) for enhanced sensitivity.<sup>57</sup>  $^{57}\text{Fe}$  Mössbauer spectra were acquired with a constant-acceleration spectrometer (SEECO, USA) using a symmetric waveform. Low-temperature measurements employed a helium closed-cycle Mössbauer cryostat (Janis, USA) mounted on a vibration-isolated table to minimize mechanical noise at the sample holder. Spectra were fitted with NORMOS<sup>53</sup> and isomer shifts are reported relative to  $\alpha$ -Fe at room temperature.

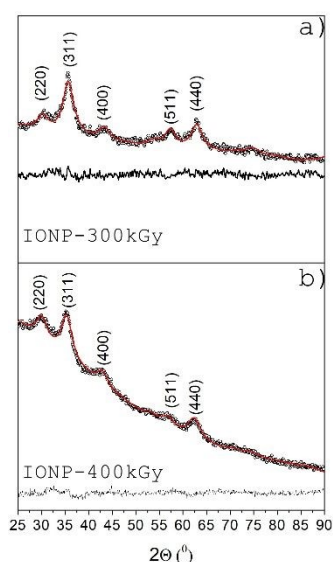
### 3. Results and discussion

#### 3.1 XRD

According to X-Ray diffraction pattern, both samples contain  $\text{Fe}_3\text{O}_4$  with cubic structure (Fig. 1). Hematite could not be detected in the spectrum.

The Rietveld refinements for sample IONP-300kGy revealed a  $\text{Fe}_3\text{O}_4$  lattice constant of 0,835(2) nm and crystal size of 4,3(2) nm. The fit reliability parameters were goodness of fit ( $\chi^2$ ) of 1,14 and weighted profile factor,  $R_{\text{wp}}$  after background extraction of 3,98%.

Similar, for sample IONP-400kGy, the  $\text{Fe}_3\text{O}_4$  lattice constant was 0,842(2) nm and the crystal size was 4,8(3) nm. The goodness of fit ( $\chi^2$ ) was 1,56 and weighted profile factor,  $R_{\text{wp}}$  after background extraction was 3,93%.



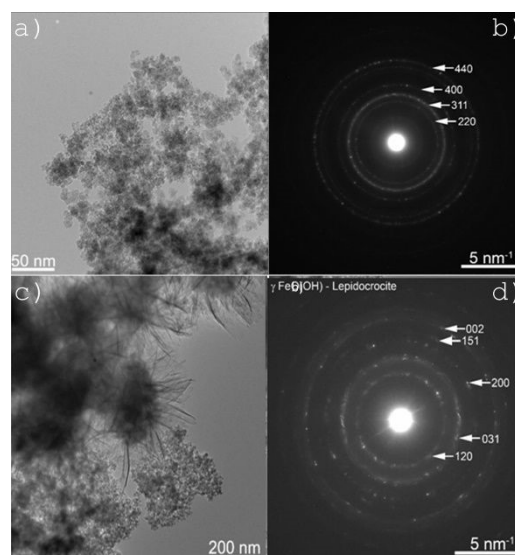
**Fig. 1** XRD spectra recorded on samples IONP-300kGy (a) and respectively IONP-400kGy (b) synthesized by radiolytic route from  $\text{Fe}(\text{acac})_3$  precursor solution irradiated with 5.5MeV EB for 60 min at 5kGy/min and respectively for 50 min at 8kGy/min.

Additionally, in SI (Fig. S2) are shown the XRD peak positions of different iron oxides and oxyhydroxides that theoretically could be generated in radiolysis synthesis, but do not appear in the

measured XRD spectra of IONP-300kGy and IONP-400kGy samples. Accordingly, the presence of hematite and wustite can be excluded due to their highest intensity peaks at  $2\theta$  of  $33.15^\circ$  and  $41.7^\circ$ , respectively, which do not appear in the experimental pattern. The XRD patterns of iron oxyhydroxides or hydroxides reported in ICDD database show high intensity peaks located in the  $2\theta$  range of  $20$ – $27^\circ$  while the experimental spectra do not indicate any peaks in this region. Only magnetite and cubic maghemite which have a very similar XRD pattern fit well the experimental data.

#### 3.2 TEM and SAED

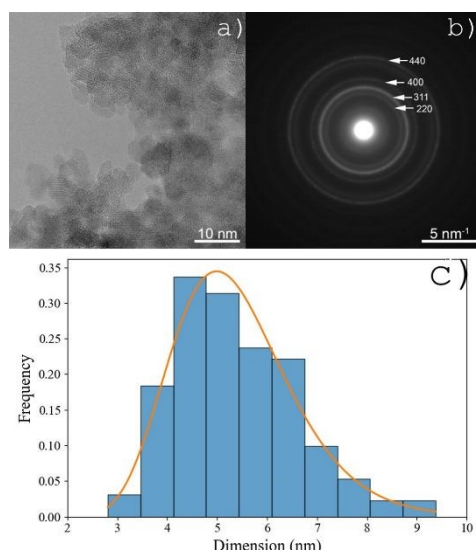
TEM analysis revealed the presence of  $\text{Fe}_3\text{O}_4/\gamma\text{-Fe}_2\text{O}_3$  nanoparticles (NPs) with an average diameter below 10 nm for both samples (Fig. 2 a, b and Fig. 3a, b). Selected-area electron diffraction (SAED) displayed continuous diffraction rings without distinct high-intensity spots, indicating the presence of small, uniformly sized nanoparticles. In the case of IONP-300kGy, a secondary morphology consisting of thin sheets and wire-like structures—likely formed by the rolling of these sheets—was observed and identified through electron diffraction as corresponding to the lepidocrocite phase ( $\gamma\text{-FeO}(\text{OH})$ ) (Fig. 2c, d).



**Fig. 2** TEM images and SAED patterns for sample IONP-300kGy synthesized by radiolytic route from  $\text{Fe}(\text{acac})_3$  precursor solution irradiated with 5.5MeV EB for 60 minutes at 5kGy/min revealed the  $\text{Fe}_3\text{O}_4/\gamma\text{-Fe}_2\text{O}_3$  phase (a, b) Lepidocrocite phase is evidenced by SAED in a secondary morphology showing thin sheets and wires (c, d).

In the sample IONP-400kGy, the nanoparticles are organized in loosely associated clusters, exhibiting limited agglomeration and no additional iron-based crystalline phases were detected. In consequence, for this sample a size distribution of nanoparticles was computed being shown in Fig. 3c.





**Fig. 3** TEM images (a), SAED patterns (b) and size distribution (c) for sample IONP-400kGy synthesized by radiolytic route from  $\text{Fe}(\text{acac})_3$  precursor solution irradiated with 5.5 MeV EB for 50 minutes at 8 kGy/min evidenced the  $\text{Fe}_3\text{O}_4/\gamma\text{-Fe}_2\text{O}_3$  phase.

### 3.3 Magnetic and Mössbauer measurements

In order to thoroughly understand the magnetic behavior of the sediments in correlation with their real phase composition, local structure and nanoparticle characteristics, standard magnetic measurements completed with temperature dependent Mossbauer spectroscopy measurements have been performed. In addition to examining the magnetic properties of the samples, the study also yielded important data regarding the average size and size distribution of the nanoparticles. This information was derived from magnetic relaxation effects, interpreted within the framework of the Langevin theory<sup>54,55</sup>, as will be discussed subsequently.

Zero-Field-Cooled/Field-Cooled (ZFC-FC) under 100 Oe between 10 K and 300 K and hysteresis loop analyses—were performed in order to prove both the specific dynamics and magnetic monodomain behavior of the nanoparticles. ZFC-FC curves recorded for sample IONP-300kGy (Fig. 4a) exhibit features characteristic of magnetic monodomain nanoparticles with a broad size distribution and a wide range of blocking temperatures, as indicated by the broad and nearly flat maximum of the ZFC curve. Specifically, the ZFC magnetization initially increases with temperature at low values, followed by a quasi-saturation above approximately 120 K. Beyond 250 K, only a slight decrease in magnetization is observed, implying the persistence of relatively large nanoparticles whose blocking temperatures remain above room temperature (RT).

The measured magnetic response cannot be ascribed to the large acicular nanoparticles associated with the lepidocrocite secondary phase, since this phase is antiferromagnetic at low temperatures and becomes paramagnetic above RT, exhibiting negligible magnetic susceptibility. Therefore, the observed magnetic behavior is attributed exclusively to the iron oxide nanoparticles. Furthermore, the FC curve, obtained upon

cooling in an applied field of 100 Oe, diverges rapidly from the ZFC curve at decreasing temperature, maintaining consistently higher magnetization values, which confirms the magnetic monodomain nature of the iron oxide NPs.

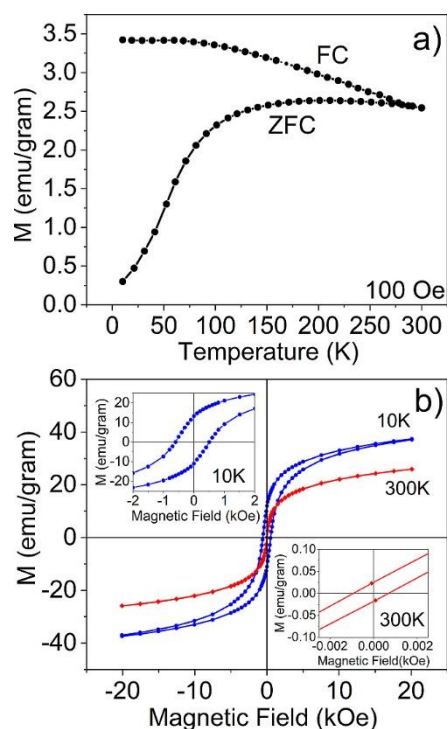
Hysteresis loops recorded at 10 K and 300 K for the IONP-300kGy are presented in Fig. 4b. The incomplete magnetic saturation at high fields even at low temperatures is characteristic of systems exhibiting partially disordered surface spins and antiferromagnetic (AFM) coupling within the sample. Therefore, a reliable estimation of the saturation magnetization can only be achieved through the *law of approach to saturation*<sup>56-57</sup>. At 10 K, the law of approach was applied in the approximation of the  $1/H$  linear dependence of magnetization over the values obtained only in high fields. Therefore, the value of saturation magnetization was estimated at  $41.8 \text{ emu g}^{-1}$  with Adj. R-square of 0.995. The value corresponds to about 46 % of the bulk  $\text{Fe}_3\text{O}_4$  value and roughly 25 % lower than that typically observed for  $\text{Fe}_3\text{O}_4/\gamma\text{-Fe}_2\text{O}_3$  nanoparticles (NPs) with an average size of  $\sim 10 \text{ nm}$  synthesized by conventional chemical routes<sup>58-60</sup>.

This reduced magnetization arises not only from a highly disordered spin structure at the nanoparticle surface—despite the reasonably good crystallinity confirmed by SAED—but also, and more significantly, from the presence of an antiferromagnetic secondary phase, whose contribution is roughly estimated by Mössbauer Spectroscopy measurements at more than 10 wt %. At 10 K, the coercive field ( $H_c$ ) reaches about 1100 Oe, which is 7–8 times higher than that commonly reported for  $\gamma\text{-Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$  NPs obtained via standard chemical synthesis. Moreover, the hysteresis loop measured at 10 K after field cooling (FC) in 100 Oe displays a negative shift of approximately 100 Oe, indicative of exchange bias effects via unidirectional anisotropy<sup>59</sup>. Both enhanced coercivity and the loop shift provide clear evidence for the presence of unidirectional anisotropy, most likely induced by interfacial exchange interactions between the ferrimagnetic  $\text{Fe}_3\text{O}_4/\gamma\text{-Fe}_2\text{O}_3$  nanoparticles and the larger  $\gamma\text{-FeO}(\text{OH})$  particles exhibiting antiferromagnetic ordering.

At 300 K, the coercivity drastically decreases to about 1.5 Oe, reflecting a dominant superparamagnetic contribution from the  $\text{Fe}_3\text{O}_4/\gamma\text{-Fe}_2\text{O}_3$  NPs at room temperature and the decoupling of their interfacial pinning from the antiferromagnetic phase.

In the case of IONP-400kGy, the ZFC-FC magnetization curves (Fig. 5a) show a much clearly evidenced ZFC maximum around 100 K, which corresponds to the blocking temperature within the DC magnetometry time window (on the order of seconds). As expected, this value is lower than the blocking temperature obtained from Mössbauer spectroscopy (as will be seen further), owing to the much shorter characteristic time scale of the latter (order of  $10^{-8} \text{ s}$ )<sup>57</sup>. The better evidenced maximum of the ZFC curve indicates a narrow distribution of blocking temperatures of the NPs formed in this sample. The branching temperature, where the ZFC and FC curves start to diverge, being only slightly higher than  $T_B$ , supports the existence of magnetic monodomain nanoparticles with weak interparticle interactions<sup>59</sup>.





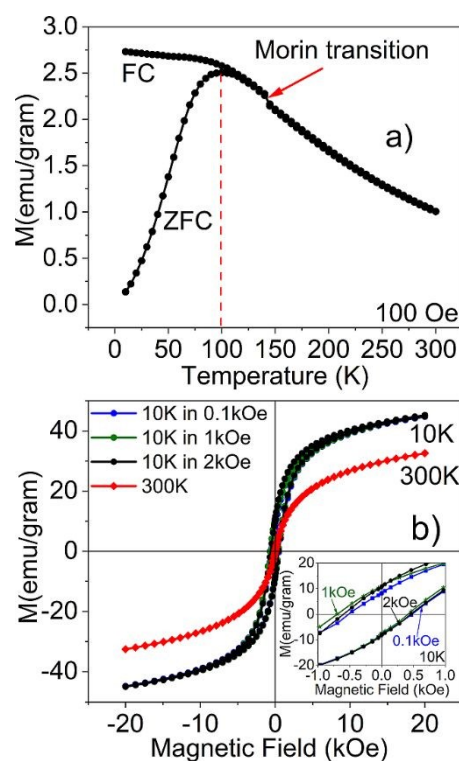
**Fig. 4** The ZFC-FC curves taken in 100Oe (a) and hysteresis loops at 10K and 300K (with a better field resolution in the inset) (b) recorded for the sample IONP-300kGy obtained from  $\text{Fe}(\text{acac})_3$  as result of the radiolytic synthesis under 5.5MeV EB and 5kGy/min for 60 minutes irradiation time.

A distinctive feature appears around 140 K, marked by a steep decrease in magnetization when the temperature exceeds 135 K. Since this temperature is more than 10 K above the Verwey transition in bulk  $\text{Fe}_3\text{O}_4$ <sup>59</sup>, and given that particle size reduction, external pressure, stress, or oxidation generally lower the Verwey temperature, this anomaly is most plausibly attributed to a small, abrupt increase in magnetocrystalline anisotropy above this point. Indeed, approximately 135 K corresponds to the isotropic point in  $\text{Fe}_3\text{O}_4$ <sup>61</sup>, where the first-order anisotropy constant  $K_1$  changes sign. Consequently, a sudden rise in anisotropy induces a slight decrease in magnetic susceptibility, contrary to the expected sharp magnetization increase typically observed above the Verwey transition<sup>62</sup>. This particular behavior, which is absent in conventionally synthesized  $\text{Fe}_3\text{O}_4$  nanoparticles, is likely associated with the unconventional electron-beam-assisted processing route employed in this work.

Concerning the hysteresis loops recorded at 10K and 300K for the IONP-400kGy (Fig. 5b) they show a close behavior to IONP-300kGy. Correspondingly, in the frame of law of approach, the saturation magnetization at 10 K in 1/H approximation, was estimated to 50  $\text{emu g}^{-1}$  value with Adj. R-square of 0.9997, suggesting the presence of a tiny fraction of antiferromagnetic phase, most probable also of oxyhydroxide.

At a careful examination of the TEM image in Fig. 3a, some small acicular formations are observed, with average length smaller than 30 nm (i.e. much smaller than in case of the IONP-300kGy)

giving a structural morphological proof for the presence of the  $\alpha\text{-FeOOH}$  phase. However, this additional phase cannot be observed by diffraction methods due to the small structural coherence lengths. The coercive field is about 500 Oe at 10K and decreases to around 20 Oe at room temperature, both values being much closer to the ones specific to size distributed  $\text{Fe}_3\text{O}_4$  NPs as compared to the case of IONP-300kGy.



**Fig. 5** The ZFC-FC curves taken in 100Oe (a) and hysteresis loops at 10K and 300K (with a better field resolution in the inset) (b) recorded for the sample IONP-400kGy obtained from  $\text{Fe}(\text{acac})_3$  as result of the radiolytic synthesis under 5.5MeV EB and 8kGy/min for 50 minutes irradiation time.

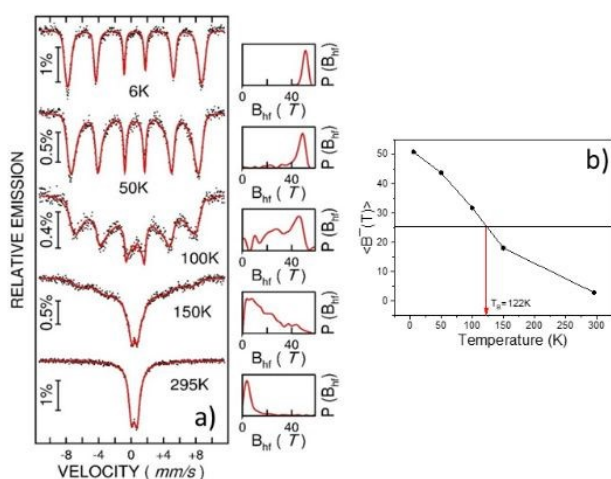
This result provides additional proof for the fact that IONP-400kGy contains a much larger amount of better formed  $\text{Fe}_3\text{O}_4$  NPs as compared to the first experiment. A last proof for the presence of a minor fraction of antiferromagnetic nanoparticles was provided by the loops obtained after cooling down the system at 10 K in fields of 100, 1000 and 2000 Oe. The loop obtained after cooling the sample in a field of 100 Oe at 10 K is characterized by an increased coercive field of 550 Oe as well as by an exchange bias field (negative shifts of the loops) of 140 Oe. These results show clearly the presence of unidirectional anisotropy also in this sample due to the interfacial interactions between the ferrimagnetic phase of  $\text{Fe}_3\text{O}_4$  nanoparticles and the secondary antiferromagnetic phase. However, the related effects are much reduced, due to the lower amount and reduced size of antiferromagnetic NPs obtained for the IONP-400kGy as compared to IONP-300kGy.

Mössbauer spectra were recorded only for the IONP-400kGy sample, which according to TEM and magnetic measurements consists predominantly of better formed  $\text{Fe}_3\text{O}_4$  nanoparticles.



Several temperatures (6, 50, 100, 150, and 295 K) were considered in order to determine the iron phase composition within the magnetic sediment and to analyze the magnetic relaxation behavior of the sample (Fig. 6a). At 6 K, the spectrum exhibits a sextet profile with broadened absorption lines, typical of magnetic nanoparticles possessing distributed Fe environments and, consequently, a range of hyperfine parameters. Accordingly, the spectra were fitted using a distribution of magnetic hyperfine fields ( $B_{hf}$ ), with the corresponding probability distributions shown to the right of each spectrum in Fig. 6b. Basically, a histogram of sextets with a linear change of isomer shifts is used. The relative areas of the sextet component are calculated using linear regression plus dumping.

The magnetic phase was identified based on the mean hyperfine parameters obtained at the lowest temperature (6 K). The magnetic relaxation processes were monitored through the temperature evolution of the  $B_{hf}$  distribution and its associated parameters<sup>11, 58, 59</sup>. As the temperature increases, the low-temperature magnetic sextet progressively collapses above 150 K into a dominant doublet component, accompanied by a shift of the main maximum in the  $B_{hf}$  distribution from approximately 51 T to below 10 T.



**Fig. 6** Mossbauer spectra recorded at 6K, 50K, 100K and 150K and 295 K for the sample IONP-400kGy obtained from Fe(acac)<sub>3</sub> precursor solution after EB irradiation with 8kGy/min dose rate for 50 minutes irradiation time (a). The probability distributions of the magnetic hyperfine field are presented on the right hand of the corresponding spectra; The temperature evolution of the mean magnetic hyperfine field providing a blocking temperature of about 122 K for most of the magnetic NPs obtained (b).

The hyperfine parameters derived from all recorded spectra—except for the spectrum at 295 K, where magnetic relaxation is completed—are summarized in Table 1. In this table,  $\langle IS \rangle$  denotes the average isomer shift,  $\langle QUA \rangle$  represents the average quadrupole splitting,  $\langle B_{hf}(T) \rangle$  corresponds to the temperature-dependent mean magnetic hyperfine field, and  $B_{hf,prob}$  indicates the most probable value of the magnetic hyperfine field.

**Table 1** Hyperfine parameters of the IONP-400kGy sample obtained and fitted via a distribution of magnetic hyperfine fields. In brackets there are errors at the last mentioned digit.

Parameter	6K	50K	100K	150K
$\langle IS \rangle$ (mm/s)	0.45(2)	0.45(2)	0.46(2)	0.44(2)
$\langle QUA \rangle$ (mm/s)	-0.01(2)	-0.01(2)	-0.03(2)	-0.01(2)
$B_{prob}$ (T)	51.0(2)	49.0(2)	undefined	undefined
$\langle B_{hf}(T) \rangle$	50.9(2)	43.8(2)	31.8(2)	18.1(2)

According to Table 1, the mean isomer shift at the lowest investigated temperature (6 K) of 0.45 mm s<sup>-1</sup> and the mean magnetic hyperfine field of 50.9 T are characteristic of defective  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and/or Fe<sub>3</sub>O<sub>4</sub> phases.<sup>11, 58, 59</sup> Consequently, the analyzed sample is presumed to consist of fine magnetic nanoparticles with a defective spinel structure, ranging from predominantly Fe<sub>3</sub>O<sub>4</sub>-like to partially  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>-like configurations. A pronounced asymmetry is observed between the intensities of the first and sixth Mössbauer spectral lines, a feature typically associated with Fe<sub>3</sub>O<sub>4</sub> above the Verwey transition temperature.<sup>60</sup> That means, the Verwey temperature is lower than 6K for the present nanoparticles, supporting the different origin of the slight variation of magnetization in ZFC-FC curves at 140K. Although, the 6K Mössbauer spectrum does not support directly the presence of oxyhydroxide phases (their range of magnetic hyperfine fields can be framed under the distribution probability picked at about 51 T), a direct evidence of goethite ( $\alpha$ -FeOOH) traces is provided by the 150K Mössbauer spectrum. While the spectral contribution of iron oxide nanoparticles is almost relaxed, the still persisting local peaks in the hyperfine magnetic field distribution at 39 and 41 T give evidence of  $\alpha$ -FeOOH magnetically unrelaxed nanoparticles which is the only oxyhydroxide phase with magnetic order (i.e. antiferromagnetic) at this temperature. The relative area under the overall distribution, corresponding to the mentioned hyperfine magnetic fields is of about 10%, suggesting a similar relative amount of Fe ions which contribute to the antiferromagnetic phase. The mean quadrupole splitting exhibits a negligible value, indicative of a distributed configuration of Fe ions, as expected in this system.

The blocking temperature  $T_B$  within the Mössbauer time window can be defined from the temperature dependence of the magnetic hyperfine field distribution, as the temperature at which the mean magnetic hyperfine field decreases to half its maximum value,<sup>58, 59</sup> corresponding to the transition from the blocked to the superparamagnetic regime. From Fig. 6b, the value of  $T_B=122$  K is obtained. The progressive and gradual decrease of  $\langle B_{hf} \rangle$  with temperature suggests a distribution of blocking temperatures associated with Fe<sub>3</sub>O<sub>4</sub> nanoparticles of various sizes, centered around 122 K. Nevertheless, a fraction of nanoparticles remains magnetically frozen even above 122 K, consistent with the presence of larger particles corresponding to a better-developed Fe<sub>3</sub>O<sub>4</sub> phase.

Both Mössbauer spectroscopy and magnetic measurements can provide an estimation of the involved size of the magnetic NPs.



A first route is to use the definition of the blocking temperature through the magnetic relaxation time<sup>59</sup>. Accordingly, the blocking temperature corresponds to that temperature where the relaxation time equates the time window of the used experimental technique,  $\tau_M$ :

$$\tau_M = \tau_0 \exp(KV/kT_B) \quad (4)$$

where  $KV$  is the anisotropy energy of the NP,  $\tau_0$  is a time constant of the considered system and  $k$  is the Boltzmann constant. The most precise determination is obtained in case of temperature dependent Mössbauer spectroscopy investigation (the time window is precisely determined at  $5 \cdot 10^{-9}$  s) where  $T_B = 122$  K. Assuming for the case of quasi-spherical magnetite NPs, a typical value of  $K = 2 \cdot 10^4$  J/m<sup>3</sup> and typical values for  $\tau_0$  in the range of  $10^{-9}$  to  $10^{-10}$  s, average particle sizes in the range from 5 to 7 nm are obtained. More imprecise results on the particle size would be obtained from the ZFC-FC evaluation of the blocking temperature, from the simple reason of the more imprecise estimation of the DC magnetometry time window (usually in the range from 1 to 100 s). However, the  $M(H)$  data collected at a given temperature can be used better in this respect, avoiding so the uncertainties related to  $\tau_0$ ,  $\tau_M$  and  $K$  values. Accordingly, the magnetization of the magnetite NPs system, each nanoparticle carrying the magnetic moment  $\mu$ , can be expressed as:

$$(H, T) = M_S L(x) + \chi_p \cdot H \quad (5)$$

where  $L(x)$  is the Langevin function with  $x = (\mu H/kT)$  and  $\chi_p$  a residual susceptibility responding for combined effect of paramagnetic centers and field induced change of noncollinear spin structure in the system<sup>54, 55</sup>. The average magnetic moment of the nanoparticle can be expressed according to S.I. Both limits of the  $L(x)$  functions, i.e. for  $x \ll 1$  and  $x \gg 1$ , can be used for the estimation of the magnetic volume of the nanoparticles<sup>59</sup>. The condition  $x \gg 1$  corresponding to the approximation  $L(x) = 1$  is fulfilled for the measurements taken at the lowest temperature and in the highest fields. Accordingly,  $M_S$  and  $\chi_p$  in equation (2) was roughly estimated from the intersect and slope of the linear dependence in high fields of the  $M(H)$  curve collected at 10 K. Values in the range of 30-35 emu/g and 0.0002-0.0004 emu/g/Oe, respectively, were estimated, depending on the highest field values considered.

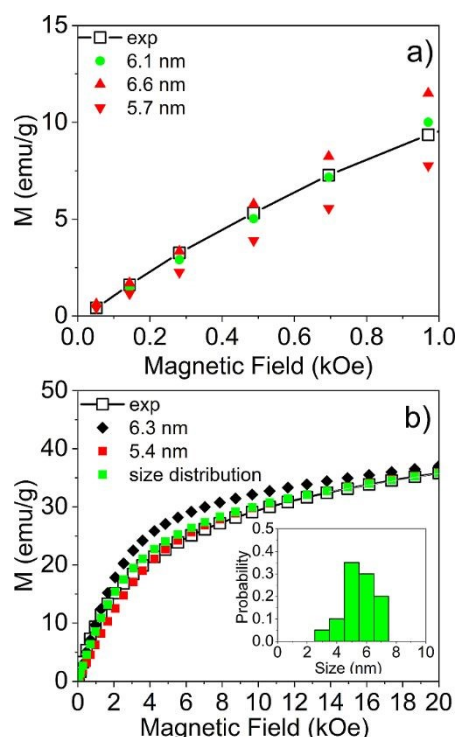
In the next step, the  $M(H)$  curve collected at 300 K and renormalized by a factor of 1.1 for disregarding the influence of the antiferromagnetic phase was considered for the evaluation of the nanoparticle size due to both the minimal influence of the residual susceptibility and negligible coercive fields.

The case of  $x \ll 1$ , leading to  $L(x) = x/3$  corresponds to the linear variation of magnetization in low applied magnetic fields, according to the equation:

$$M(H) = (288 \cdot V \cdot M_S / 3 \cdot k \cdot T) \cdot H + \chi_p \cdot H \quad (6)$$

The dependence of the experimental magnetization versus the field in the range of low fields, estimated for different of nanoparticle sizes are shown in Figure 7a (the plotted results are obtained for  $M_S = 33$  emu/g and  $\chi_p = 0.0003$  emu/g/Oe, being quite insensitive their variation in the previously mentioned range of values). The best fit of the experimental results is

achieved for an average size of 6.1 nm for the magnetite nanoparticles, in close agreement with both TEM and Mössbauer estimations. The dependence of the experimentally derived  $M(H)$  curve at 300 K over the full range of magnetic fields as well as the corresponding dependences for nanoparticle average sizes of 6.3 nm and 5.4 nm (slightly higher and slightly lower than 6.1 nm) are shown in Figure 7b. This time the magnetization in high fields is very sensitive to the value of  $M_S$ , providing clearly the best convenient value of  $M_S = 33$  emu/g. However, it can be observed that depending on the deviation from an average size, nanoparticles of lower size give a better approximation of the experimental magnetization in high fields whereas the ones of higher size give a better estimation of magnetization in low fields. Therefore, the best agreement with the experimental magnetization over the whole range of magnetic fields was obtained via the size distribution presented in the inset of Figure 7b.



**Fig. 7** Renormalized magnetization curve at 300 K in the range of low magnetic fields and simulated curves for different average sizes of magnetite nanoparticles (a) and renormalized magnetization curves over the whole range of magnetic fields and simulated curves for different average sizes as well as for distributed sizes (b) which distribution probability is shown in the inset.

#### 4. Conclusions

The obtained results demonstrate the versatility and effectiveness of electron-beam (EB) radiolytic synthesis for producing iron-based nanoparticles (NPs) from organic acetylacetonate precursors, without the need for chemical reducing agents. Comprehensive morpho-structural, magnetic, and Mössbauer analyses confirmed the formation of well-



dispersed, crystalline Fe<sub>3</sub>O<sub>4</sub>/γ-Fe<sub>2</sub>O<sub>3</sub> nanoparticles as the main phase, accompanied by either γ-FeO(OH) or α-FeOOH as a secondary component. The relative content and crystallinity of the Fe<sub>3</sub>O<sub>4</sub>/γ-Fe<sub>2</sub>O<sub>3</sub> phases can be significantly tuned by adjusting the processing parameters, with the irradiation dose exerting the most pronounced influence. Specific conditions—using Fe(acac)<sub>3</sub> as precursor and EB irradiation at 5.5 MeV to a total dose of 400 kGy (8 kGy min<sup>-1</sup>)—lead to magnetic nanoparticles with improved morpho-structural and magnetic characteristics. The average size of the nanoparticles as well as the size distribution evaluated by Mössbauer spectroscopy and magnetic measurements are in good agreement with results obtained by TEM investigations. Interestingly, these EB-synthesized nanoparticles exhibit certain magnetic behaviors atypical of particles with similar size and morphology obtained via conventional chemical methods, warranting further fundamental investigation. Moreover, iron-based nanoparticles, particularly Fe<sub>3</sub>O<sub>4</sub>, possess broad technological applicability, providing strong motivation for continued exploration of this innovative EB-assisted route. The use of accelerated electrons to induce water radiolysis represents a promising, rapid, cost-effective, and environmentally friendly approach for large-scale nanoparticle synthesis. Overall, the findings highlight the potential for tailored fabrication of nanoparticles with customized properties for targeted applications. Future studies should assess the feasibility of employing alternative iron precursors in EB-assisted synthesis, paving the way for advanced applications in biomedicine, environmental remediation, and catalysis through the controlled design of magneto-functional nanomaterials.

### Author contributions

Conceptualisation: C. Comanescu, N. Iacob, G. Craciun; data Curation: C. Radu, A. Kuncser, P. Palade, V. Kuncser; formal analysis: G. Craciun, E. Manaila; methodology: C. Comanescu, N. Iacob; project administration: N. Iacob; supervision: N. Iacob, C. Comanescu; validation: A. Kuncser, V. Kuncser, G. Craciun, E. Manaila; writing – original draft: C. Comanescu, V. Kuncser, N. Iacob; writing – review & editing: C. Comanescu, G. Craciun, E. Manaila, C. Radu, A. Kuncser, P. Palade, V. Kuncser, N. Iacob.

### Conflicts of interest

There are no conflicts to declare.

### Data availability

The data supporting the findings of this study are available from the corresponding author upon reasonable request.

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