

Article

Intriguing Prospects of a Novel Magnetic Nanohybrid Material: Ferromagnetic FeRh Nanoparticles Grown on Nanodiamonds

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Abstract: A novel endeavor based on the synthesis, characterization and study of a hybrid crystalline magnetic nanostructured material composed of bimetallic iron–rhodium nanoalloys, grown on nanodiamond nanotemplates, is reported in this study. The development of this hybrid magnetic nanomaterial is grounded in the combination of wet chemistry and thermal annealing under vacuum. In order to assess, evaluate and interpret the role and special properties of the nanodiamond supporting nanotemplates on the growth and properties of the bimetallic ferromagnetic Fe–Rh nanoparticles on their surfaces, unsupported free FeRh nanoparticles of the same nominal stoichiometry as for the hybrid sample were also synthesized. The characterization and study of the prepared samples with a range of specialized experimental techniques, including X-ray diffraction, transmission and scanning transmission electron microscopy with energy dispersive X-ray analysis, magnetization and magnetic susceptibility measurements and ⁵⁷Fe Mössbauer spectroscopy, reveal that thermal annealing of the hybrid sample under specific conditions (vacuum, 700 °C, 30 min) leads to the formation of a rhodium-rich FeRh alloy nanostructured phase, with an average particle size of 4 nm and good dispersion on the surfaces of the nanodiamond nanotemplates and hard ferromagnetic characteristics at room temperature (coercivity of ~500 Oe). In contrast, thermal annealing of the unsupported free nanoparticle sample under the same conditions fails to deliver ferromagnetic characteristics to the FeRh nanostructured alloy phase, which shows only paramagnetic characteristics at room temperature and spin glass ordering at low temperatures. The ferromagnetic nanohybrids are proposed to be exploited in a variety of important technological applications, such as magnetic recording, magnetic resonance imaging contrast and magnetic hyperthermia agents.

Keywords: hybrid; magnetic; nanostructures; nanoparticles; nanodiamonds; iron–rhodium; TEM; Mössbauer spectroscopy



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1. Introduction

In the last 30 years, nanomaterials have been the subject of extensive scientific research, both on theoretical and experimental levels, featuring remarkable properties of great scientific and technological importance. Their exploitation in a wide range of technologically important existing, as well as rising, fields, such as information storage, catalysis, green energy, electronics, food and construction, biomedicine and biopharmaceuticals, to mention some, reveal their ability to provide extraordinary properties in relevance to the conventional bulk counterpart materials. An important part of a nanomaterial's properties pertains to its magnetic characteristics.

Magnetic bimetallic alloys based on iron constitute a category of materials with significant magnetic properties, utilized in many fields of technological applications [1]. In

particular, for the FeRh system, the intermetallic compound around the equiatomic composition was first discovered by Fallot and Hocart in 1938 to possess a unique ability to raise its magnetization values with increasing temperature, above a critical transition temperature, which alters with compositional variations [2]. Since then, many works combining several experimental characterization and computational techniques have appeared, attempting to comprehend to a considerable extent this interesting magnetic behavior [3–7]. It is generally understood that this behavior emerges from the peculiar nature of the FeRh system that undergoes a metamagnetic transition, during which an interaction between its structural and magnetic properties is developed as temperature (T) deviates. In particular, in the near equiatomic stoichiometries, the bulk FeRh system presents a chemically ordered CsCl-type α' -B2-bcc structure, but it can also be found in a disordered γ -fcc structure. The fcc phase presents paramagnetic (PM) characteristics at room temperature (RT). In contrast, the B2-bcc phase incurs a very interesting and unusual first-order isostructural metamagnetic transition from the antiferromagnetic (AFM) to the ferromagnetic (FM) order between a critical temperature range of about 77 and 97 °C [5,8–10]. This first-order transition is also accompanied by a concurrent increase in the cell volume of about 1%. However, over the last decades several studies have designated the difficulty of achieving a stable critical temperature point in nanostructured FeRh, as the preparation of such FeRh samples is influenced by factors, such as particle morphology, phase composition, heat treatment, presence of external magnetic fields and pressure [11–14].

Thus, by applying different strategies for realization of the desirable magnetically ordered B2-bcc phase, following different physical and chemical routes, and involving bulk, nanoparticle (NP) or thin film forms, in most cases, the presence of non-magnetic γ -fcc residues was additionally observed. The fcc variant formed in such FeRh systems is well known to possess PM characteristics at RT and as the temperature drops below the magnetic critical-freezing transition temperature (T_f) of about 80 K, this phase acquires magnetically spin-glass (SG) behavior [15–17]. For fcc FeRh NPs, the disordered atomic nature of the fcc structure coincides with a random orientation of uncompensated moments of the nanostructured grains. At low temperatures, below the T_f range, the exchange interaction width is greater than the domain size of the fcc FeRh NPs and that leads to the freeze of the corresponding magnetic moments in cluster-glass arrangements. Thus, in that temperature range the sample magnetizes collectively and the susceptibility value is low. However, as the temperature increases, the exchange interaction depletes, indicative of the weaker exchange coupling of the atoms at the grain boundaries or interfaces of the NPs. For the temperature in which the grains of the NPs become uncoupled, a maximum in the susceptibility value is signaled. Therefore, it is the deformation of the atoms that entails the decoupling between the grains at the interface and results in the conversion between the static magnetic arrangement and the PM or superparamagnetic (SPM) state [16,18].

Furthermore, of great scientific interest is the stabilization of the FeRh FM phase at RT and below [19]. Since nanosized crystals present significant deviations in interatomic distances and unit-cell distortions with respect to the bulk [20], such a realization could combine the significant magnetic characteristics of the bulk structures with the unique structural and magnetic properties of the equivalent nanophases, in order to promote these nanostructures to be exploited in a vast field of new and emergent technological applications. Up to date FeRh systems have been proposed to be utilized in thermally assisted magnetic recording (TAMR) [21,22], storage media applications [23], thin films for antiferromagnetic spintronics [24,25], novel applications in medicine, such as magnetic hyperthermia [26,27], and as magnetocaloric materials for switchable high contrast ratio magnetic resonance imaging (MRI) labels [28], as well as RT AFM memory resistors [29] and high magnetostrictive materials [30,31].

Following the trend of our group's endeavor on the development of hybrid magnetic nanostructured materials [32,33], we report here the synthesis, characterization and study of the structural, morphological and magnetic properties of a new line of hybrid nanostructured system composed of FeRh NPs grown on nanodiamonds (NDs) nanotem-

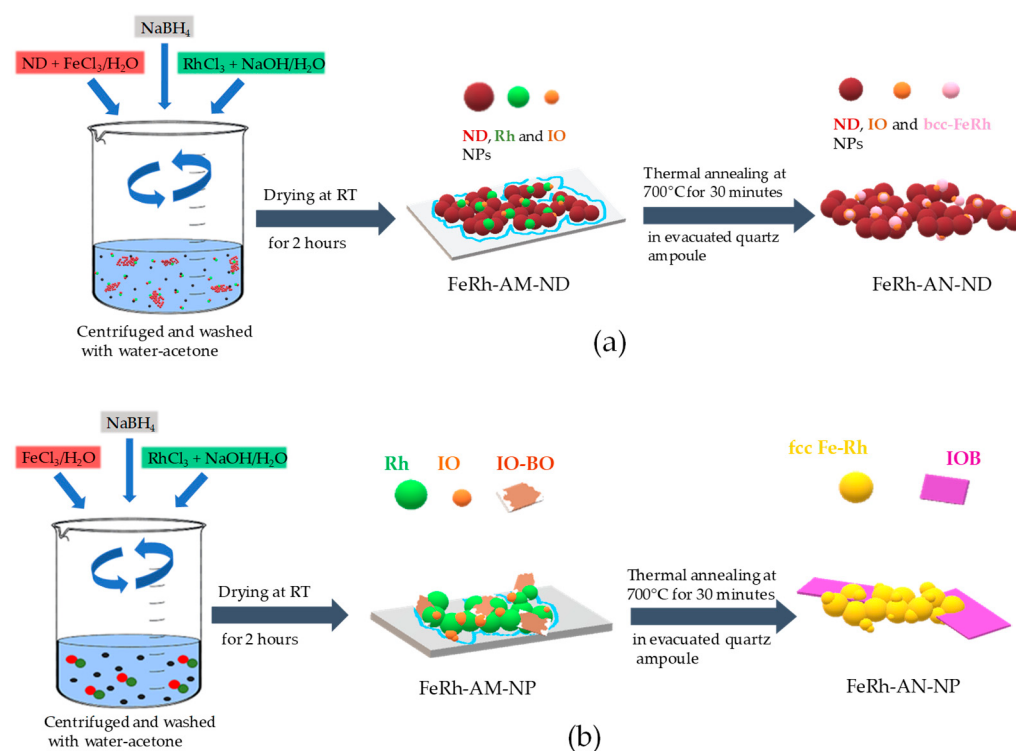
plates. It is well known that diamonds possess remarkable structural, morphological, mechanical, electrical and thermal properties [34–36]. In particular, great interest has been attracted on diamonds in nanoscale, due to their bio-compatibility, chemical stability and their ability to form aggregated clusters with thickness of the order of the size of a few nanoparticles (~10 nm) and lengths of several tens to hundreds of nm, with great specific area volumes [34,36]. These characteristics render NDs perfect candidates as matrices for the development of other nanostructures on their surfaces. Thus, these potent ND nanomatrices constitute ideal platforms for a variety of new technological applications [37].

In our current study the realization of hybrid crystalline magnetic nanostructures combining FeRh NPs grown on NDs (FeRh/NDs) has relied on the use of wet chemical methods involving reduction of metallic salts using the borohydride (NaBH_4) agent and annealing treatments under controlled conditions. In order to compare and evaluate the influence of the NDs matrix to the growth and properties of the nanoalloy FeRh phases, unsupported free FeRh NPs were also synthesized following the same preparation route. The resulting samples were characterized and studied with the use of X-ray diffraction (XRD), transmission electron microscopy (TEM) and high-resolution TEM (HRTEM), scanning TEM (STEM) with high-angle angular dark field (HAADF) and energy-dispersive X-ray spectroscopy (EDS) analyses, magnetization measurements and ^{57}Fe Mössbauer spectroscopy. The results reveal that, in the case of the hybrid annealed sample the formation of the desirable nanostructured FM FeRh phase is realized. On the contrary, for the unsupported annealed sample, the formation of the PM fcc FeRh phase is favored, proclaiming the important role of the NDs nanotemplates basis. Furthermore, the annealed hybrid FeRh/NDs system, whose synthesis and characterization is reported for the first time in the literature, exhibits interesting magnetic properties, which render this material a promising candidate for many contemporary, as well as novel, technological applications.

2. Materials and Methods

2.1. Materials Synthesis

The synthesis procedure of the hybrid crystalline magnetic FeRh/NDs nanostructures, with nominal Fe:Rh atomic ratio of 1:1, comprises of an initial wet chemical stage followed by a thermal annealing treatment under controlled conditions stage. For the first stage, alongside the as-made hybrid sample (FeRh-AM-ND), a free as-made unsupported FeRh NPs sample (FeRh-AM-NP), with the same nominal Fe:Rh = 1:1 atomic stoichiometry, was also prepared. In this work, the wet chemical route is based on the use of the (NaBH_4) agent [38]. In particular, in the first stage, 270 mg of NDs ($\geq 97\%$ Aldrich 636428) were suspended in a beaker containing 30 mL deionized H_2O to afford a fine aqueous slurry. In another beaker, 200 mg of NaOH were dissolved in 20 mL of deionized H_2O , followed by the addition of 40 mg of RhCl_3 (98% Aldrich 307866). The mixture was stirred for 2 h until full dissolution of the rhodium salt (RhCl_3 is insoluble in water but soluble in alkaline solutions). At this point the pH of the solution was brought to 6–7 by concentrated HCl (37%) prior to the addition of 30 mg anhydrous FeCl_3 (97% Aldrich 157740) dissolved in 1 mL of deionized H_2O . The pH-adjustment was necessary in order to avoid alkaline precipitation of iron (III). The resulting solution was further diluted with water until reaching a total volume of 40 mL. The nominal mass concentration of the FeRh alloy in this sample was calculated at 10 wt%. After combining the salt solution with the NDs slurry, 300 mg of NaBH_4 (99% Aldrich 213462) were rapidly added and the mixture was stirred for 20 min at ambient conditions. The material was centrifuged and washed with deionized water and acetone prior to air drying to produce the as-made hybrid sample FeRh-AM-ND. In the second stage, the FeRh-AM-ND sample was sealed under vacuum (10^{-3} Torr) in a quartz ampoule, which was afterwards thermally annealed at 700 °C for 30 min, affording the FeRh-AN-ND sample (Scheme 1a).



Scheme 1. Graphic representation of the as-made and annealed samples' synthesis procedure for the hybrid FeRh/NDs (a) and unsupported FeRh free-NPs (b) cases.

For the free NPs unsupported samples, 40 mg of RhCl₃ (98% Aldrich 307866) and 30 mg of anhydrous FeCl₃ (97% Aldrich 157740) were dissolved in deionized water, as also described above for the hybrid sample, to produce 40 mL of salt solution. The latter was poured into 30 mL deionized H₂O, followed by the rapid addition of 300 mg NaBH₄ (99% Aldrich 213462) under vigorous stirring. The mixture was stirred for 20 min under ambient conditions. The as-formed precipitate was allowed to settle and rinsed with deionized water and acetone prior to air drying, acquiring the as-made unsupported sample FeRh-AM-NP. In the same manner as for its hybrid counterpart, a subsequent thermal annealing process of the FeRh-AM-NP sample sealed in a quartz ampoule under vacuum (10^{-3} Torr) at 700 °C for 30 min took place, affording the FeRh-AN-NP sample (Scheme 1b). The comparison between the properties of the hybrid and unsupported samples is designed to evaluate the effect of the presence of NDs, leading thus to a deeper understanding and a better interpretation of the NDs' matrix role in the growth of the nanoalloy phases during the synthesis procedure.

The nature of the nanostructured phases, their crystal structure, morphology, particle size, auto-arrangement and dispersion onto the ND matrices are expected to critically affect the magnetic properties of the prepared hybrid materials, features that can be controlled through the preparation conditions (synthesis procedure, annealing temperature and duration, NPs concentration deposited onto the NDs substrate).

2.2. Materials Characterization

The initial characterization of the structural and morphological properties of the prepared samples was carried out by powder XRD, using Cu K_α radiation on a Bruker Advance D8 diffractometer (Bruker, Billerica, MA, USA). Additional measurements of the morphology, stoichiometry and average particle size were conducted by TEM and HRTEM using a JEOL JEM 2011 microscope (JEOL Ltd., Tokyo, Japan) with resolution capability of 0.194 nm, and STEM measurements focused on Z-contrast HAADF observations, as well as EDS analyses, which were performed on a 200 kV JEOL JEM-F200 microscope (JEOL Ltd., Tokyo, Japan) comprising a cold field-emission source and equipped with an Oxford

X-Max 65T EDS analyzer (Oxford Instruments, Abingdon, UK). Before performing the TEM measurements, the samples were dispersed in ethanol and suspended in ultrasound for 10 min. A drop of very dilute suspension was placed on a carbon-coated Cu grid and allowed to dry by evaporation at ambient temperature. The investigation of the magnetic properties of the samples was carried out with a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS XL-7, Quantum Design Inc., San Diego, CA, USA) through magnetization (M) and mass magnetic susceptibility (χ_g) measurements. The M versus ($vs.$) the external magnetic field (H) hysteresis loops were collected at constant temperatures of 2, 300 and 400 K in fields up to 70 kOe. The zero-field-cooled (ZFC) and field-cooled (FC) χ_g vs. T curves were recorded upon warming the samples in the temperature range from 2 to 420 K under different external magnetic fields of 99 and 999 Oe, after cooling them in zero magnetic field, and on cooling, immediately after the warming procedure under the above-mentioned magnetic fields, respectively. ^{57}Fe Mössbauer spectroscopy measurements were carried out in order to gain a deeper insight into the samples' iron-bearing phases' magnetic, morphological and structural characteristics and properties. The Mössbauer spectra (MS) were collected in transmission geometry at sample temperatures of 300, 77 and 11 K using constant-acceleration spectrometers, equipped with $^{57}\text{Co}(\text{Rh})$ sources kept at RT, in combination with a liquid N_2 bath (Oxford Instruments Variox 760, Oxford Instruments, Abingdon, UK) and an He gas closed-loop (ARS DMX-20) Mössbauer cryostats. Metallic $\alpha\text{-Fe}$ at RT was used for the velocity calibration of the spectrometers and all isomer shift (IS) values are given relative to this standard. The experimentally recorded MS were fitted and analyzed using the IMSG code [39].

3. Results

3.1. XRD

The XRD diagrams of the pristine NDs, FeRh-AM-NP, FeRh-AM-ND, FeRh-AN-NP and FeRh-AN-ND samples are presented in Figure 1. In Figure 1a, two dominant broad diffraction peaks corresponding to the fcc NDs structure at 43.9 (111) and 75.4 (220) degrees 2θ are depicted. From this diagram it is noted that the pristine NDs sample follows the nominal nanocrystal structure and purity as provided by Aldrich. In Figure 1b the pattern of the FeRh-AM-NP sample presents a very broad diffraction peak centered at ~ 42 degrees 2θ . This broad peak spans a range of 2θ values of at least 5 degrees (given as full width at half maximum), that may contain the contributions of the main diffraction peaks of the fcc FeRh alloy phase, with its main (111) peak at 41.8 degrees and lattice constant $a = 3.740 \text{ \AA}$ (ICDD PDF 01-074-5849), the fcc metallic elemental Rh phase with its main (111) peak at 41.1 degrees and lattice constant $a = 3.803 \text{ \AA}$ (ICDD PDF 00-005-0685) and the B2-bcc FeRh alloy phase with its main (110) peak at 42.8 degrees and lattice constant $a = 2.987 \text{ \AA}$ (ICDD PDF 01-073-2618). Apart from this peak, a secondary broad diffraction peak can also be noticed at ~ 36 degrees 2θ . This peak corresponds to the main (311) diffraction peak of a spinel-type $\gamma\text{-Fe}_2\text{O}_3$ (maghemite) iron oxide (IO) phase (ICDD PDF 00-039-1346). The XRD diagram of the FeRh-AM-ND sample reveals the dominant contributions from the (111) and (220) atomic planes of the ND structure, as well as the less intense and broad diffraction peaks of the spinel-type IO and FeRh or elemental Rh fcc phases at ~ 36 and ~ 42 degrees 2θ , respectively (Figure 1c).

In the case of the FeRh-AN-NP sample, the XRD diagram shown in Figure 1d presents four sharp diffraction peaks at 41.5, 48.3, 70.6 and 85.3 degrees 2θ , which are representative of the (111), (200), (220) and (311) atomic diffraction planes, respectively, of the Fe_3Rh_7 phase with an fcc structure and a lattice constant of $a = 3.772 \text{ \AA}$ (ICDD PDF 03-065-6840). In addition to the Fe_3Rh_7 alloy, another crystalline phase corresponding to the iron oxyborate (IOB) Fe_3BO_5 (vonsenite) with main diffraction peaks at 35.1 (240), 37.8 and 38.1 (150) and (400), 43.7 (321), 46.9 (350), 57.6 (441), 60.2 (002), 61.6 and 61.9 (112) and (550), 66.7 (601) and 71.5 (281) degrees 2θ , and orthorhombic crystal structure with lattice constants of $a = 9.452 \text{ \AA}$, $b = 12.287 \text{ \AA}$ and $c = 3.072 \text{ \AA}$ (ICDD PDF 00-025-0395), also appears in this

diagram. The formation of this phase can be attributed to residual boron from the NaBH_4 reducing agent, most probably in the form of amorphous boron oxide (B_2O_3) (BO) in the corresponding as-made sample in combination with the presence of IOs and the influence of the annealing conditions (vide infra).

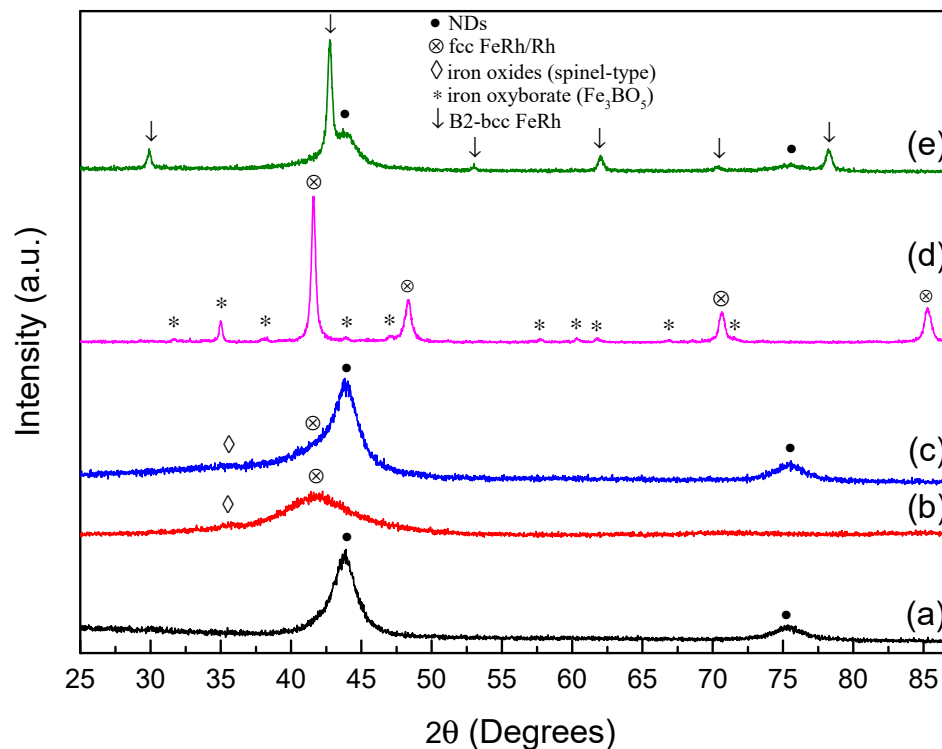


Figure 1. XRD patterns of the pristine NDs (a), FeRh-AM-NP (b), FeRh-AM-ND (c), FeRh-AN-NP (d) and FeRh-AN-ND (e) samples. The presence of different crystalline phases is depicted by the relative symbols on their main diffraction peaks.

The XRD diagram of the FeRh-AN-ND sample (Figure 1e) designates the presence of two crystal structures, one of the fcc NDs structure with relative broad diffraction peaks, and a second with relative sharp diffraction peaks appearing at 29.9 (100), 42.8 (110), 53.1 (111), 62.1 (200), 70.4 (210) and 78.4 (211) degrees 2θ , corresponding to the FeRh B2-bcc phase with a lattice constant of $a = 2.987 \text{ \AA}$ (ICDD PDF 04-002-1337). For this sample, the diffraction peaks of the IOB Fe_3BO_5 are completely absent.

The annealed samples present noticeable differences in their XRD diagrams compared to the as-made samples, which concern mainly the sharper and more intense diffraction peaks of the FeRh alloy phases, indicating their high crystallinity. Using the width of the diffraction peaks and the Scherrer formula [40], an estimation of the average coherent scattering NP domain size $\langle d \rangle$ for each crystalline phase can be performed, and the results are listed in Table 1.

The average size of the NDs NPs is consistent with the expected characteristics, preserving its nanoscale features both in the as-made and annealed hybrid samples. Thus, heating at 700 °C seems to not affect this property of the NDs matrix, which is important and indicates the structural and chemical stability of the ND's substrate. Moreover, it was not possible to derive average NPs' domain size for the spinel-type IOs due to the very large widths and reduced intensities of their diffraction peaks. Thus, very low $\langle d \rangle$ value and crystallinity or even amorphicity can be expected for this phase in the samples. In summary, the XRD studies suggest that, despite the presence of secondary impurity phases, the specific annealing conditions trigger the formation of well crystalized nanostructured FeRh alloy phases in the corresponding samples.

Table 1. Average NP coherent scattering domain size $\langle d \rangle$ values, in nm, of the crystalline phases, as estimated from the XRD diagrams using the Scherrer formula. The figures in parentheses present the estimated standard deviation referred to the last digit in each case.

Sample	NDs	γ -FeRh/Rh (fcc)	α' -FeRh (B2-bcc)	Spinel-Type Iron Oxide	Iron Oxyborate (Fe ₃ BO ₅)
Pristine NDs	3 (1)	-	-	-	-
FeRh-AM-ND	3 (1)	non-resolved	-	non-resolved	-
FeRh-AM-NP	-	2 (1)	-	non-resolved	-
FeRh-AN-ND	3 (1)	-	15 (1)	non-resolved	-
FeRh-AN-NP	-	9 (1)	-	non-resolved	30 (1)

3.2. TEM, STEM and EDS Analysis

The morphology, atomic arrangement and interconnection of the nanophases present in the samples are revealed by TEM/STEM imaging as depicted in Figures 2–5. In addition, HRTEM images and STEM/EDS maps were also collected in order to designate the structural and chemical details of these nanophases (see Supplementary Materials).

TEM images of the FeRh-AM-ND sample appearing in Figure 2 show a hybrid system consisting of relatively circular shaped metallic NPs, appearing in darker contrast than the rest of the material in the bright field images, with sizes ranging from 1 to about 6 nm, and averaging (as evident from several images, see Supplementary Materials) at (3 ± 1) nm. These metallic NPs are deposited on close packed ND NPs of individual sizes in the range of 4 nm, which form roughly round as well as irregular-shaped nanotemplate clusters, with sizes ranging from 30 to about 400 nm (Figures Figure 2a and S1). Z-contrast imaging by HAADF/STEM in Figure 2b,d reveals that the metallic NPs are well distributed on the NDs nanotemplates. EDS spectra from this sample (see Figures S2a and S3a and Table S1) denote a Fe:Rh atomic ratio between 1:9 and 2:8. EDS spot analysis was performed on the larger NPs and indicative results are given in Figure S3a and Table S1, while elemental maps of Fe and Rh (Figure S4a) show the coexistence of the two elements in the regions of the clusters where the metallic NPs are detected. Figure S5a displays an HRTEM image showing {111} lattice fringes from the ND and the metallic fcc NPs, which correspond either to elemental Rh or to Rh-rich γ -Fe_xRh_{1-x} alloy NPs.

Figure 3 reveals the morphology of the FeRh-AM-NP sample. The developed metallic NPs present roughly rounded shapes with a size distribution mainly occurring between 2 and 8 nm, averaging at 5 nm, while larger NPs are also detected. These NPs are accumulated into close packed clusters in the range of 100–300 nm. From Figure 3b it is shown that the NPs located closer to the center of the clusters are depicted as sharper and denser, suggesting relatively higher crystallinities and sizes of the corresponding nanostructured phases in comparison to the outer faded/fainted NPs of the clusters, which seem to possess more of a ‘core-shell’ structure. Due to their quite small sizes and lower crystallinity, these shells may correspond to a partial oxidized or fully oxidized IO (maghemite, γ -Fe₂O₃) composition. In some cases, as shown in Figure 3a, low-contrast platelets with a thickness of ≤ 20 nm and widths of the order of 100–200 nm are observed in this sample. From EDS analysis (Figures S2b and S3b and Table S1), the average Fe:Rh atomic ratio was found to be similar to that observed for the FeRh-AM-ND sample. However, the signals from the platelets and point EDS analyses and chemical mapping on them (Figure S3b point 3, and area indicated by arrow in Figure S4b), indicated a depletion of Rh in these formations, compared to a uniform distribution of Fe and Rh in the metallic NPs region. This shows that these platelets probably contain IOs in this sample, possibly of the maghemite type, as evidenced by XRD (and Mössbauer spectroscopy—vide infra). Moreover, the presence of the crystalline IOB Fe₃BO₅ phase in the FeRh-AN-NP sample (which originates from the annealing of this FeRh-AM-NP sample), as evidenced by XRD and Mössbauer spectroscopy (vide infra), suggests that these platelets could also contain an amorphous-glassy BO (B₂O₃) phase as residual of the NaBH₄ reducing agent, which does not contribute in XRD. This

glassy phase could serve as the source of B for the development of the IOB phase in the FeRh-AN-NP sample during annealing. Structural characterization by HRTEM of the accumulated metallic NPs in the FeRh-AM-NP sample (Figure S5b) reveals *d*-spacings of lattice fringes equal to ~ 0.22 nm on average, indicating the presence of corresponding {111} planes of either an fcc Rh-rich $\gamma\text{-Fe}_x\text{Rh}_{1-x}$ alloy or elemental Rh structure [41].

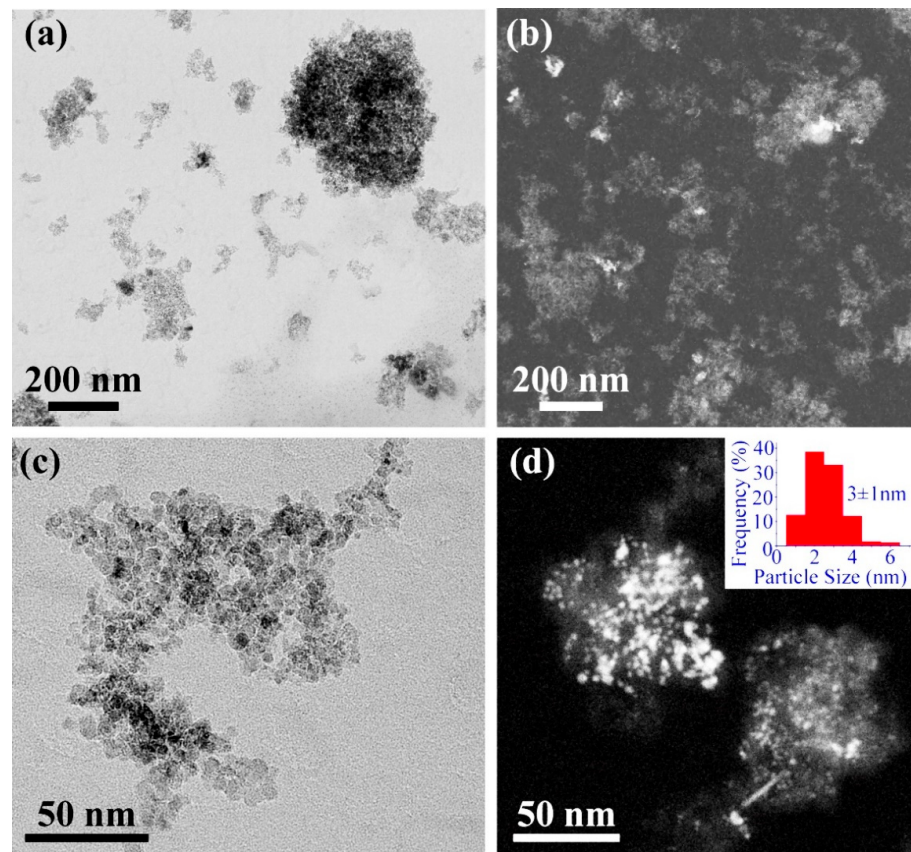


Figure 2. Low (a,b) and high (c,d) magnification TEM and STEM images of the FeRh-AM-ND sample. Images (a,c) are bright-field TEM images. Images (b,d) are Z-contrast HAADF/STEM images clearly showing the metallic NPs (brighter due to their higher atomic number) within the larger ND clusters. The inset in (d) is a histogram of the metallic NPs size distribution.

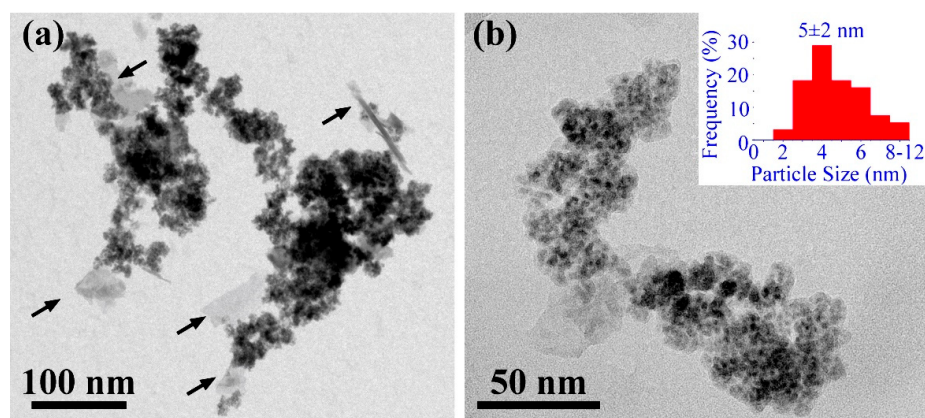


Figure 3. Bright field TEM images of characteristic aggregated metallic NPs clusters found in the FeRh-AM-NP sample. Arrows in (a) point to sheet-like, low-contrast platelets, distinguished from the rather spherical aggregated NPs. The inset in (b) is the histogram of the particle-size distribution of the individual metallic NPs.

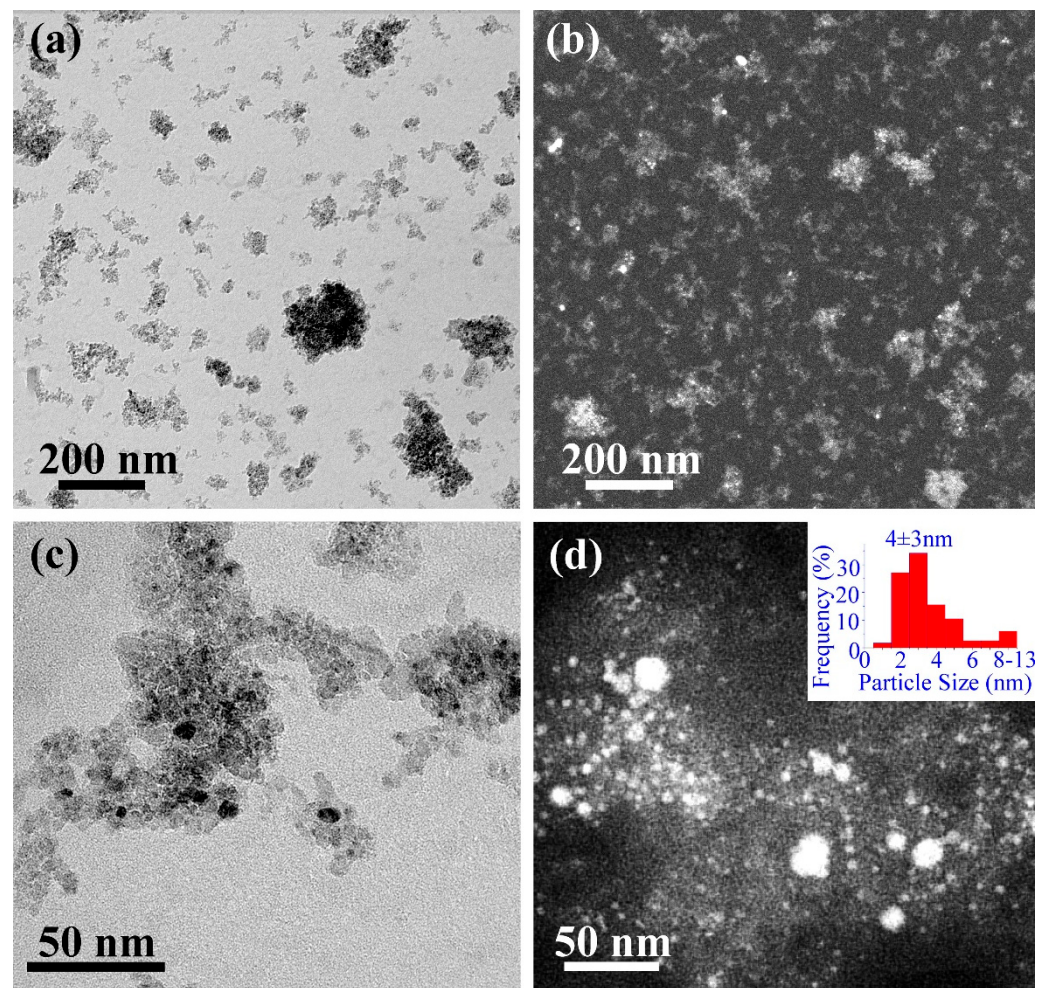


Figure 4. Low (a,b) and high (c,d) magnification TEM and STEM images of the FeRh-AN-ND sample. Images (a,c) are bright-field TEM images. Images (b,d) are Z-contrast HAADF/STEM images clearly showing the FeRh/NDs hybrid clusters in (b), as well as individual FeRh NPs (brighter due to their higher atomic number) in the hybrids in (d) after the annealing. The FeRh NP size distribution histogram is presented as an inset in (d).

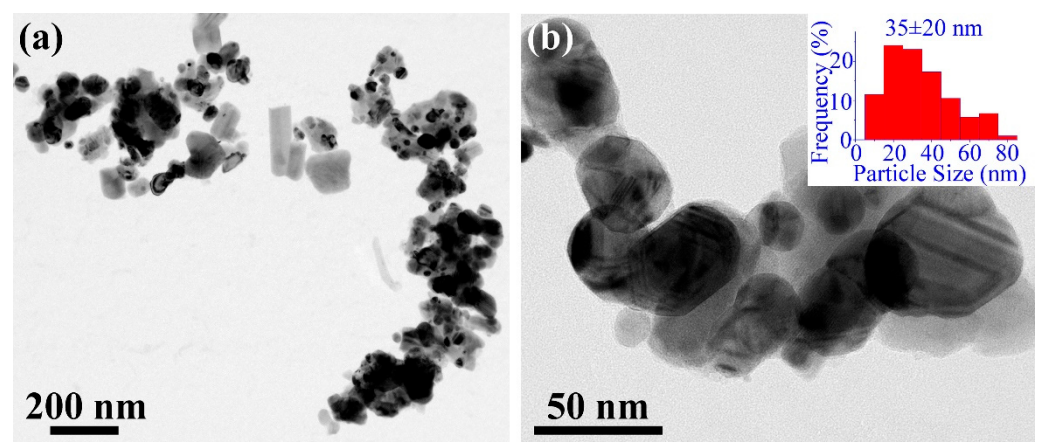


Figure 5. Bright field TEM images from the FeRh-AN-NP sample. (a) Lower magnification image showing a mix of aggregated almost spherical NPs and larger elongated platelets. (b) Higher magnification image showing extended defects (twins) inside the spherical-type NPs. The size distribution of the spherical-type NPs is presented as inset in (b).

TEM/STEM images shown in Figure 4 depict the morphological appearance of the FeRh-AN-ND sample. This system exhibits a better spatial dispersion of the formed hybrid nanostructures in comparison to the previous samples. Both ND and metallic FeRh NPs here possess roughly spherical shapes. We observed a reduction in the NDs' nanotemplate cluster size after the thermal annealing process relative to that of the FeRh-AM-ND sample, which now ranges between 20 and 80 nm. Z-contrast imaging by HAADF/STEM in Figure 4b,d revealed that the metallic NPs are evenly distributed on the NDs nanotemplates. For the majority of metallic NPs, the average diameter increased only slightly from that of the FeRh-AM-ND sample as a consequence of the thermal annealing treatment and was measured at (4 ± 3) nm, becoming simultaneously slightly broader. Moreover, most of the metallic NPs in this sample are more round-shaped and well-formed compared to those of the FeRh-AM-ND sample. However, there are also some larger spherical metallic NPs with diameters exceeding 8 nm. EDS spectra of ND/NPs hybrid clusters in this sample reveal average Fe:Rh atomic ratios from about 3:7 up to 4:6, with the latter being determined in clusters comprising only small metallic NPs with average diameter of <5 nm (Figure S2c). On the other hand, larger NPs showed ratios between 2:8 and 3:7 (Figure S3c and Table S1). Chemical mapping of hybrid NDs/NPs clusters (Figure S4c) reveal the presence of both Fe and Rh at the same spatial positions where the metallic NPs are detected. The HRTEM image of Figure S5c shows a metallic NP embedded in a ND/NPs cluster of the FeRh-AN-ND sample with lattice fringe d -spacing of ~ 0.30 nm, corresponding to the {100} planes of the CsCl-type B2 α' -FeRh phase (we note that a similar d -spacing does not exist in either ND or fcc FeRh and hence it serves to distinguish this phase by HRTEM—see Supplementary Materials). Further confirmation of the bcc FeRh phase was provided from selected area electron diffraction as illustrated in Figure S6. These features provide yet another proof of the NDs nanotemplates' ability to grow and host very small metallic NPs of high crystallinity uniformly distributed on their surfaces after thermal annealing [32,33].

On the other hand, annealing under vacuum at 700 °C of the FeRh-AM-NP sample changes considerably its morphology. This is revealed by the TEM images of the FeRh-AN-NP sample presented in Figure 5. A mix of aggregated almost spherical NPs on the one hand and larger elongated platelets on the other hand was observed. Diffraction contrast from the spherical NPs indicates the presence of twin boundaries, which are characteristic structural defects of fcc metallic crystals. On the other hand, the platelets did not exhibit such defects. The metallic NPs in this sample are considerably larger than those of the FeRh-AM-NP sample. This is attributed to the NPs' growth which is a consequence of thermal annealing at high temperatures in combination with the high NP proximity and aggregation found already in the parent FeRh-AM-NP sample before annealing. The size of the spherical NPs presented a broad distribution as displayed in the inset of Figure 5b. The average metallic NP diameter was found at (35 ± 20) nm, i.e., there is a 7-fold increase compared to those of the FeRh-AM-NP sample. An overall EDS spectrum from the FeRh-AN-NP sample presented in Figure S2d suggests an average Fe:Rh atomic ratio of 3:7. EDS spot analyses (Figure S3d and Table S1), as well as elemental mapping (Figure S4d) also revealed that the platelets contain only Fe as a metallic element, indicating that they are composed of IOs, and in particular IOBs, as suggested by XRD, while the high contrast spherical NPs are Rh-rich with an Fe:Rh atomic ratio of 1:9. This was further confirmed by the HRTEM observations, as shown in Figure S5d, whereby a {111} lattice spacing of ~ 0.22 nm was again measured in the spherical NP, corresponding to the aforementioned fcc metallic structure, while lattice fringes of ~ 0.38 nm d -spacing in the platelets are attributed to the {220} planes of the IOB Fe_3BO_5 structure [42,43].

3.3. Magnetization and Magnetic Susceptibility Measurements

The magnetic properties of the hybrid NDs and unsupported FeRh nanostructured samples before and after annealing are unfolded through their M vs. H under constant T and χ_g vs. T under constant applied H (H_{ap}) measurements. These measurements appear in Figures 6 and 7, respectively, and reflect the compositions, stoichiometries, structures

and morphologies, as well as the dispersions, interconnections and interactions of the NPs present in the samples.

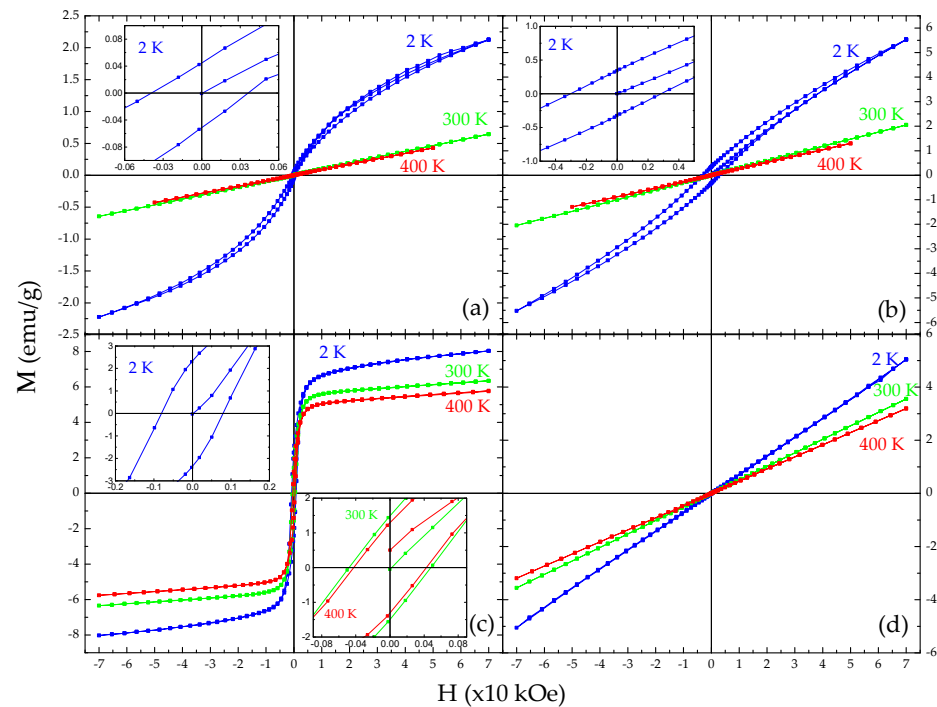


Figure 6. Magnetization versus applied magnetic field measurements of the FeRh-AM-ND (a), FeRh-AM-NP (b), FeRh-AN-ND (c) and FeRh-AN-NP (d) samples measured at 400 (red), 300 (green) and 2 K (blue). The insets show the features of the loops around zero applied field for each temperature in more detail.

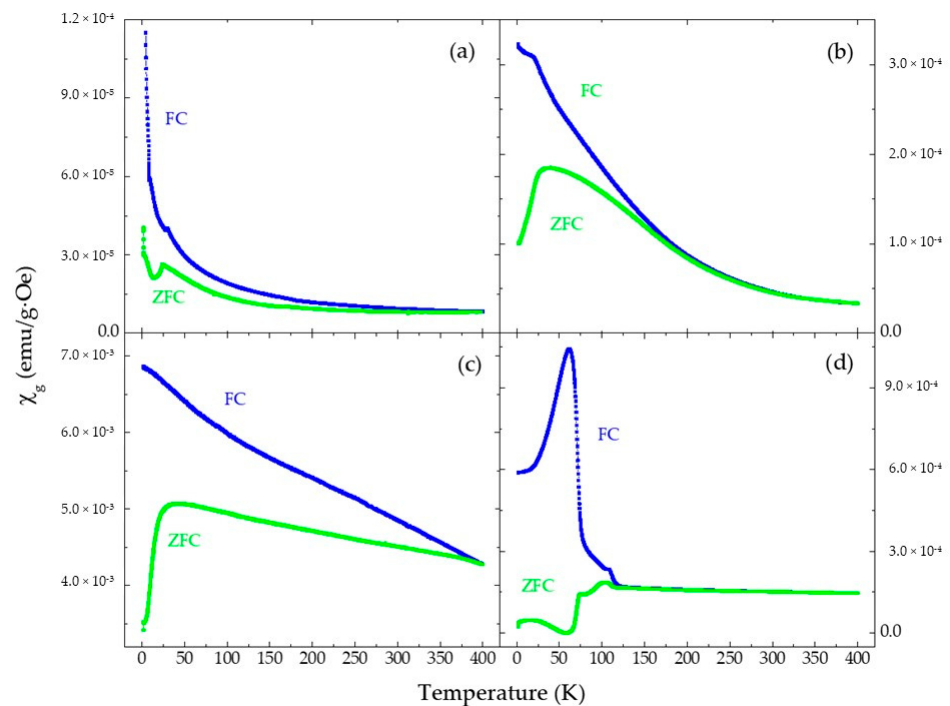


Figure 7. Mass magnetic— χ_g susceptibility versus temperature measurements of the FeRh-AM-ND (a), FeRh-AM-NP (b), FeRh-AN-ND (c) and FeRh-AN-NP (d) samples measured under an applied external field of 99 Oe following ZFC (green) and FC (blue) modes.

The M vs. H loops of the FeRh-AM-ND sample recorded at 400 and 300 K present a linear PM behavior throughout all H values (Figure 6a). However, at 2 K a hysteresis with ferro/ferrimagnetic features emerges, superimposed to yet a strong linear PM contribution denoted by the lack of saturation at high H values. The loops' characteristics are listed in Table 2 for all samples. The high positive dM/dH slopes at high fields and the development of coercive fields (H_C) at low T are features that indicate a magnetic NP assembly experiencing strong SPM relaxation at high T, while being partially magnetically blocked at low T [44,45]. The χ_g vs. T ZFC branch for the FeRh-AM-ND sample taken with $H_{ap} = 99$ Oe, appearing in Figure 7a, starts descending from an initial χ_g maximum at 2 K and exhibits a local maximum at ~ 27 K, denoting a blocking temperature (T_B) at this point for at least a part of the sample's NPs assembly, followed by a monotonic decrease along the remaining T range. The FC branch follows a similar trend of monotonically increasing χ_g with decreasing T, disrupted only by a narrow local maximum found again at ~ 27 K. Increasing H to 999 Oe (Figure S7) causes the ZFC and FC χ_g vs. T branches to virtually coincide in an asymptotic increase in χ_g with reducing T at low temperatures with no sign of saturation or any local maximum, revealing that the strong PM contribution is the dominant factor in this sample, overwhelming any SPM characteristics at high H_{ap} values. These characteristics provide evidence for the existence of an assembly of small SPM NPs experiencing very weak or vanishing interparticle interactions, due to their spatial isolation on the surfaces of the NDs nanotemplates, as pointed out by TEM measurements, in combination with a strong PM contributing factor [44,46–48].

Table 2. Parameters of the magnetic properties of the isothermal loops of Figure 6.

Sample	T (K)	M_{max+} (emu/g)	M_{max-} (emu/g)	M_{R+} (emu/g)	M_{R-} (emu/g)	H_{C+} (Oe)	H_{C-} (Oe)
FeRh-AM-ND	400	0.43	−0.43	0.00	0.00	0.00	0.00
	300	0.64	−0.64	0.00	0.00	0.00	0.00
	2	2.23	−2.22	0.04	−0.05	400	−390
FeRh-AM-NP	400	1.29	−1.29	0.00	0.00	0.00	0.00
	300	2.05	−2.05	0.00	0.00	0.00	0.00
	2	5.53	−5.53	0.34	−0.33	2870	−3030
FeRh-AN-ND	400	5.75	−5.76	1.29	−1.29	−425	425
	300	6.35	−6.35	1.43	−1.56	500	−505
	2	8.03	−8.03	2.29	−2.40	800	−795
FeRh-AN-NP	400	3.19	−3.19	0.00	0.00	0.00	0.00
	300	3.55	−3.55	0.00	0.00	0.00	0.00
	2	5.03	−5.06	0.00	0.00	0.00	0.00

In respect to the FeRh-AM-NP sample, the M vs. H loops at 400 K and 300 K appearing in Figure 6b present a clear linear PM behavior, whereas a ferro/ferrimagnetic sigmoidal-shaped curve, as in the FeRh-AM-ND sample, with non-saturated M values and non-zero H_C s, are developed at 2 K. However, in this sample the H_C values at 2 K listed in Table 2 are about one order of magnitude larger and the area within the loop is quite bigger than those of the FeRh-AM-ND sample, indicating 'harder' ferromagnetic characteristics for the present sample at low temperatures. Moreover, the ZFC and FC branches of the χ_g vs. T variation in Figures 7b and S7 present more typical characteristics for a magnetic NPs assembly shaped by the interplay between the magnetic anisotropy and thermal energies. The characteristic large widths around the maxima of the ZFC curves found at $T_B = 37$ K ($H_{ap} = 99$ Oe) and $T_B = 25$ K ($H_{ap} = 999$ Oe), and the bifurcation temperatures found at $T_{irr} \sim 200$ K ($H_{ap} = 99$ Oe) and $T_{irr} \sim 100$ K ($H_{ap} = 999$ Oe) reflect the dominant SPM behavior of a magnetic NPs assembly with particle size distribution, which is moreover influenced substantially by interparticle magnetic interactions within it [44,47,48]. These features come

as a consequence of the magnetic NPs' high proximity and interconnection in this particular sample, which confirms, in addition, the results of the XRD and TEM measurements.

The thermal annealing treatment causes different evolutions of magnetic properties between the as-made hybrid FeRh/NDs and unsupported FeRh NPs samples to arise. In particular, in Figure 6c, the M vs. H loops of the FeRh-AN-ND sample measured at all temperatures reveal clear ferro/ferrimagnetic characteristics with hysteresis, accompanied however with constant and non-vanishing dM/dH slopes at high H values that are indicative of the contribution of at least a second PM or SPM phase. The H_{CS} , which are quite symmetric regarding their positive and negative values, increase from ~ 425 Oe at 400 K to ~ 800 Oe at 2 K (Table 2). The χ_g vs. T curves are characteristic for an assembly of FM NPs showing SPM features with a maximum in the ZFC branch at $T_B \sim 40$ K both with $H_{ap} = 99$ (Figure 7c) and 999 Oe (Figure S7). In addition, the decrease in the χ_g values for these branches is constant and less abrupt for T above T_B , compared to the corresponding curves observed for the FeRh-AM-ND sample. The variation of χ_g in the FC branch shows a continuous increase over the whole temperature range with a very weak tendency for saturation at T below 100 K. The two χ_g vs. T branches coincide only at the highest measured temperature (400 K) for both H_{ap} values, suggesting an increased average size, as well as increased size distribution for the magnetic NPs compared to those found for the FeRh-AM-ND sample. Thus, it seems that the assembly of magnetic NPs in this sample includes contributions from both strong FM characteristics attributed to the magnetically blocked NPs with high magnetic anisotropy and moderate SPM relaxation characteristics due to their reduced particle size. These results are in perfect agreement with XRD and TEM-STEM analyses, in which the formation of a well crystallized and size-dispersed assembly of small magnetic NPs is featured. It is also worth noticing that no AFM-to-FM metamagnetic transition is observed for this sample, validating thus the contribution of a dominant FM phase with SPM relaxation characteristics along the whole measured temperature length.

On the contrary, in the case of the FeRh-AN-NP sample, it is evident from Figure 6d and the values of Table 2 that either pure PM or/and AFM behaviors are the only contributions to the loops' measured isothermals at 400, 300 and 2 K. However, the χ_g vs. T measurements reveal a system with PM properties from 400 K down to about 120–110 K, that 'wakes-up' below 114 K and erupts again below 75 K (Figure 7d). These late temperatures signal the characteristic transitions from PM to frustrated AFM state at $T_N = 114$ K and from frustrated AFM to weak-ferromagnetic (WFM) or canted AFM state at $T_{WFM} = 75$ K of the Fe_3BO_5 phase [42,49,50]. At low temperatures below 40 K this phase is known to return gradually to a very complex AFM or ferrimagnetic structure with multiple AFM sublattices. These results justify completely the M vs. H measurements and are in line with the results of the XRD and TEM measurements. On the other side, any contribution from a SPM phase existing in the sample is masked below 114 K from the dominant contributions of the bulk Fe_3BO_5 phase's magnetic characteristics.

3.4. ^{57}Fe Mössbauer Spectroscopy

The iron-contained phases developed in the samples, their crystal structures, particle size, interconnection and morphology, as well as their magnetic properties, are further investigated by means of the atomic-level-probing technique of ^{57}Fe Mössbauer spectroscopy. The ^{57}Fe MS of the as-made samples (FeRh-AM-ND and FeRh-AM-NP) recorded at RT (300 K), 77 K and 11 K are shown in Figure 8, while those of the annealed samples (FeRh-AN-ND and FeRh-AN-NP) recorded at the same temperatures are presented in Figure 9.

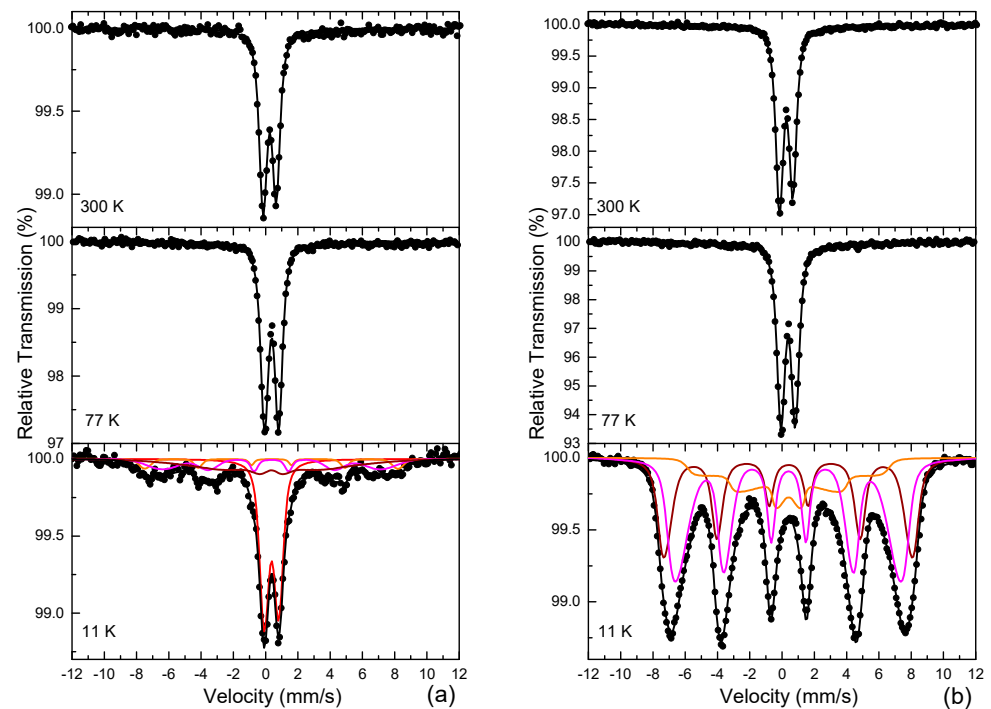


Figure 8. ^{57}Fe Mössbauer spectra of the FeRh-AM-ND (a) and FeRh-AM-NP (b) samples recorded at different temperatures. The points correspond to the experimental data and the continuous lines to the components used to fit the spectra.

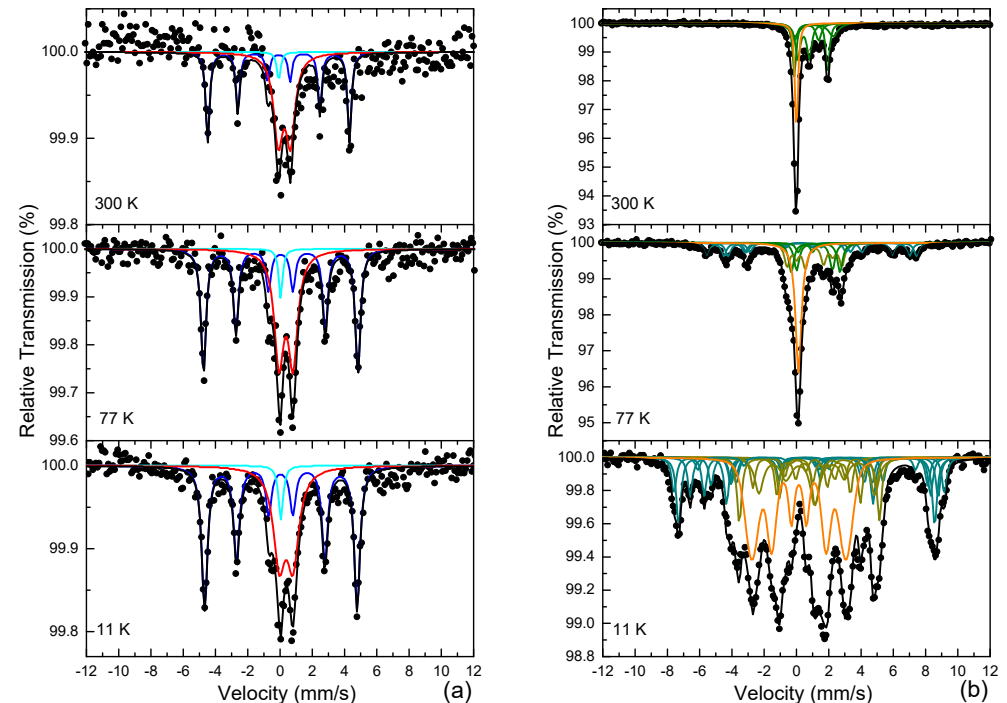


Figure 9. ^{57}Fe Mössbauer spectra of the FeRh-AN-ND (a) and FeRh-AN-NP (b) samples recorded at different temperatures. The points correspond to the experimental data and the continuous lines to the components used to fit the spectra.

The 300 and 77 K MS of both as-made samples are identical and are composed of a single quadrupole split contribution with relative broad resonant lines. We used one quadrupole split component with a spreading of QS values (ΔQS -Gaussian type) to fit these

spectra. The resulting Mössbauer parameters (MPs) values for the RT MS of all samples are listed in Table 3, while those of the 77 K and 11 K spectra are given in Supplementary Materials (Table S2). The MPs values of this component for both samples indeed coincide within the experimental error limits. From these values it is evident that this contribution corresponds to high-spin Fe^{3+} ions in oxygen first neighbor environment. However, the evolution of the MS at 11 K is quite different between the FeRh-AM-ND and FeRh-AM-NP samples. For the former a broad magnetically split contribution is developed at 11 K, in superposition to the still existing significant quadrupole split contribution, while for the latter the broad magnetically split part is the only one contributing to the 11 K spectrum and the quadrupole split part is completely absent. The magnetically split part of the MS for both samples is modeled by a set of magnetic components, for which a spreading (ΔB_{hf} -Gaussian type) of the hyperfine magnetic field (B_{hf}) values, either symmetric or asymmetric with respect to the central B_{hf}^{C} value, was allowed to describe the observed line broadening. The MPs of the magnetically split components in the spectra of both samples (Table S2) correspond again to Fe^{3+} ions in oxygen environment, and acquire similar values, as was the case for the quadrupole split components.

Table 3. Mössbauer hyperfine parameters as resulting from the best fits of the corresponding spectra of the samples recorded at 300 K. IS is the isomer shift (given relative to α -Fe at 300 K), $\Gamma/2$ is the half line-width, QS is the quadrupole splitting and ΔQS is the total spreading of QS values around the central QS^{C} value (wherever this parameter is used), 2ϵ is the quadrupole shift, B_{hf} is the hyperfine magnetic field and AA is the relative spectral absorption area of each component used to fit the spectra. Typical errors are ± 0.02 mm/s for IS, $\Gamma/2$, 2ϵ and QS, ± 3 kOe for B_{hf} and $\pm 5\%$ for AA.

Sample	IS mm/s	$\Gamma/2$ mm/s	QS^{C} or 2ϵ mm/s	B_{hf} kOe	ΔB_{hf} or ΔQS kOe or mm/s	AA %	Site-Phase	Color
FeRh-AM-ND	0.35	0.22	0.81	0	0.23	100	Fe^{3+} -IO/IHO (SPM)	Black
FeRh-AM-NP	0.36	0.22	0.83	0	0.21	100	Fe^{3+} -IO/IHO (SPM)	Black
FeRh-AN-ND	0.03	0.14	-0.02	273	0.00	45	Fe-bcc B2 α' -FeRh	Blue
	0.03	0.14	0.00	0	0.00	4	Fe-bcc B2 α' -FeRh (SPM)	Cyan
	0.38	0.35	0.76	0	0.00	51	Fe^{3+} -IO/IHO (SPM)	Red
FeRh-AN-NP	0.11	0.10	0.00	0	0.00	22	Fe-fcc γ -FeRh	Orange
	0.55	0.17	0.71	0	0.00	23	Fe^{2+} - Fe_3BO_5	Olive
	0.74	0.19	1.49	0	0.00	13	$\text{Fe}^{2.5+}$ - Fe_3BO_5	Olive
	1.01	0.12	2.06	0	0.00	25	Fe^{2+} - Fe_3BO_5	Olive
	1.19	0.36	2.39	0	0.00	17	Fe^{2+} - Fe_3BO_5	Olive

It is evident from these results that the iron-bearing phases in both as-made samples are not referring to iron atoms in the metallic or alloyed state. They suggest the presence of IOs or/and iron oxyhydroxides (IOHs), and in particular, the quadrupole splitting (QS) and quadrupole shift (2ϵ) values of the corresponding components are characteristic of either SPM γ - Fe_2O_3 , or ferrihydrite ($\text{Fe}_5\text{HO}_8 \cdot 4\text{H}_2\text{O}$) NPs [51,52]. Regardless of the exact stoichiometry of these IO or IOH NPs' phases, the complete magnetically resolved 11 K spectrum for the case of the FeRh-AM-NP sample, combined with the corresponding partially magnetically split spectrum of the FeRh-AM-ND sample, reflect the different magnetic interactions experienced by these NPs in each sample at this temperature. More specifically, the spatial isolation of the IO/IOH NPs on the surfaces of the ND nanotemplates, as evident from TEM and magnetization measurements, attributes only weak or vanishing interparticle magnetic interactions that lead to the conservation of the SPM properties for a substantial part (~50% according to the absorption area of the quadrupole split component) of these NPs in the FeRh-AM-ND sample at this reduced temperature. On the other hand, the spatial proximity, agglomeration and high interconnection of the corresponding NPs in the FeRh-AM-NP sample, ascribes to them strong interparticle magnetic interactions,

which cause the complete cessation of the SPM relaxation, as “sensed” by the Mössbauer spectroscopy technique, for all NPs at this temperature [20,32,33,44,46–48,53,54].

The MS of the annealed samples are quite different in shape, both from those of the as-made samples, as well as between each other, as evident from the comparison of Figures 8 and 9. The MS of the FeRh-AN-ND sample in Figure 9a combine the contributions of a magnetically split component with relatively sharp resonant lines, which reflects high crystallinity for the corresponding phase represented by this component, and a quadrupole split broad central doublet at all temperatures. Unsuccessful attempts to adequately fit these spectra with only two such components led to the need for the inclusion of an additional minor singlet central component to the fitting model at all temperatures. The resulting MPs values listed in Tables 3 and S2, denote that the sextet and the singlet acquire identical ISs, characteristic of a metallic FeRh alloy. In particular, the MPs of the sextet correspond to a well ordered FM CsCl-type B2-bcc α' -FeRh structure [5,13,17]. It becomes thus apparent combining the XRD, TEM, magnetization/magnetic susceptibility and current Mössbauer spectroscopy measurements that the main contribution in this sample originates from a well crystallized ordered nanostructured B2 α' -FeRh phase. Due to the existing particle size distribution and their spatial isolation on the surfaces of the NDs nanotemplates, however, the smaller B2-type FeRh NPs must experience very strong SPM relaxation that leads to the complete collapse of their B_{hf} values. This part of the FeRh NPs assembly is represented by the minor singlet in the MS. On the other side, the MPs values of the quadrupole split doublet also signify the presence of Fe^{3+} ions in IOs. These IOs could have been developed as native oxides on the surfaces of the FeRh NPs in a core-shell structure, or as stand-alone phases during the annealing procedure. In either case, these IOs experience strong SPM relaxation throughout the whole measured temperature range, as the development of any magnetically split part in the MS presenting their characteristics is suppressed even at temperatures as low as 11 K.

The spectrum of the FeRh-AN-NP sample recorded at RT (Figure 9b) combines the contributions of a set of quadrupole split doublets and a central singlet. A set of four quadrupole split components and a singlet were used to fit this spectrum adequately. The resulting MPs listed in Table 3 suggest that the quadrupole split components correspond to the $Fe^{2.7+}$, $Fe^{2.5+}$ and Fe^{2+} valence states of the mixed-valence oxyborate Fe_3BO_5 phase [42], detected in this sample by XRD and TEM measurements. The singlet acquires MPs that correspond to a PM disordered fcc γ -FeRh phase, also detected by XRD and TEM. The evolution of the MS at lower temperatures confirms the presence of these two phases in this sample. In particular, the fittings at 77 K combine the contributions of the characteristic magnetically split and Fe^{2+} magnetically frustrated components of the Fe_3BO_5 phase, while at 11 K the development of the complex full magnetically split spectrum for this phase is also evident [42]. The FeRh phase retains its PM characteristics at 77 K, but develops magnetic splitting with broad resonant lines, as expected from the magnetic spin-glass properties of this phase [5,13,15–17] at 11 K.

4. Discussion

The results of all experimental characterization techniques used in the present study reveal that in the parent FeRh-AM-ND and FeRh-AM-NP samples, any FeRh alloy NPs fail to develop directly in the first stage of the synthesis; rather the presence of metallic Rh and IO/IHO NPs separately, however with immediate spatial proximity and interconnection, is confirmed in these samples. The strong resistance, on the one hand, of metallic Rh against, and the high susceptibility, on the other hand, of Fe towards oxidation, should be the main reasons for this outcome, for which the $NaBH_4$ reducing agent seems to succeed in producing Rh NPs from the $RhCl_3$ salt, but misses to construct a FeRh alloy directly.

This lack of development of any FeRh alloyed phase in the first stage is recovered by the application of the second stage in the synthesis, which includes annealing of the parent samples in evacuated quartz ampoules at high temperatures, a procedure which delivers further reduction conditions to the system. It seems that the metallic Rh and IO/IHO

NPs, due to their spatial proximity, are combined in this second stage to deliver FeRh NPs which are grown on the surfaces of the ND nanotemplates of the FeRh-AN-ND sample and develop a single alloy FM B2-bcc α' structure, even though this phase is Rh-rich. As a consequence, the excess iron remains as IO either as a very thin layer in the FeRh NPs or as separate SPM NPs. On the other hand, the FeRh NPs formed without the support of the NDs nanotemplates in the FeRh-AN-NP sample, although also Rh-rich, fail to develop the FM B2-bcc α' -FeRh structure and remain in the PM γ -fcc structure.

It becomes thus clear that the NDs play the most significant role for the development of this FM phase. In particular, since in the parent FeRh-AM-ND and FeRh-AM-NP samples there is no preformed FeRh alloy NPs, we propose that the source of carbon atoms originating from the graphitic layers natively appearing on the surfaces of the NDs [34–36], not only provides the desired additional reducing conditions for the growth of the FeRh alloy NPs during the annealing stage [32,33,55], but inflict their development in the FM B2-bcc α' -FeRh structure. This could be a consequence of a partial diffusion of C atoms within this FeRh alloy structure, e.g., in interstitial positions, forcing its stabilization. The characteristic sign of this behavior could be found through the fact that the lack of this source of C atoms in the parent FeRh-AM-NP sample leads to the stabilization of the fcc PM γ -FeRh phase in the corresponding FeRh-AN-NP sample treated under the same annealing conditions. Moreover, the restraint of FeRh NP size growth during annealing in the case of the hybrid sample, due to their isolation and uniform distribution on the NDs nanotemplates surfaces, could also provide the appropriate conditions for sustaining the FM B2-bcc α' -FeRh structure within these reduced NPs size limits. In this frame, the lack of saturation of this sample's magnetization values in the M vs. H measurements, even at temperatures as low as 2 K, could be attributed to the NPs' SPM behavior due to their reduced sizes; the contribution of the SPM B2-bcc-type α' -FeRh singlet in the MS of this sample at all temperatures reinforces this result. This behavior in the M vs. H measurements, however, cannot be distinguished by the SPM behavior of the residual IO/IHO NPs at all temperatures, as established by Mössbauer spectroscopy. On the other hand, the size growth for the already well interconnected Rh and IO/IHO NPs of the unsupported FeRh-AN-NP sample could also provide the conditions for the development of larger sized FeRh alloyed NPs, for which the PM fcc structure is assumingly more favorable.

Another finding of this study that is worth mentioning and analyzing is the existence of only single-phase alloy FeRh NPs in both FeRh-AN-ND and FeRh-AN-NP annealed samples, however, of different crystal structures, although the stoichiometry of the FeRh alloy is found to fall in the Rh-rich side of the phase diagram, where a binary-phase system composed of both FM α' -B2-bcc and PM γ -fcc is predicted for Rh at compositions up to about 75% [15,56–58]. For the FeRh alloys in the α' region, that is at and below—regarding the Rh content—the equiatomic composition, Mössbauer spectroscopy studies reveal the presence of two different first neighbor environments for the Fe atoms: one composed of 0–4 Fe and 8–4 Rh atoms, which corresponds to the Fe atoms in the predicted correct CsCl-type positions (FeI), and a second composed of 8 Fe and 0 Rh atoms, which corresponds to the anti-site defects of the CsCl-type structure (FeII) [5,16]. It is found that the IS and B_{hf} values of the FeII atoms are shifted substantially from those of the FeI atoms [5,16], so these sites are clearly distinguishable in the Mössbauer spectra. The existence of one sharp Fe magnetically split component with the FeI characteristics of the equiatomic composition at all measured temperatures in the MS of the FeRh-AN-ND sample denotes that the first neighbor environment of all Fe atoms in the NPs of the B2-bcc α' -FeRh structure is stable and identical, and is composed always only of eight Rh atoms, with no detectable anti-site Fe atoms in the structure. In the FeRh-AN-ND sample the FeRh phase is indeed Rh-rich roughly between 60% and 70% at. Rh. This is confirmed both from the lattice constant extracted from the XRD measurements, which is compatible with the lattice constant of the alloys at this compositional range [56,59], and from the results of the STEM EDS analyses. We propose that the growth of this Rh-rich FeRh phase with such distinct Fe first neighbor environment should again be a consequence of the C atoms diffusion from

the NDs' graphitic surface layers. On the other hand, the further increased Rh content, evident by the XRD and STEM EDS measurements found for the alloy FeRh NPs of the FeRh-AN-NP sample, and the lack of available C atoms, restrain the development of the B2-bcc phase and the NPs remain at the γ -fcc structure even after the thermal annealing at 700 °C.

5. Conclusions

In this work we have succeeded in producing a new magnetic nanohybrid material by growing ferromagnetic CsCl-type B2-bcc α' -FeRh nanoparticles on nanodiamonds, following a two-stage synthesis procedure involving wet chemistry and thermal annealing under vacuum. The FeRh nanoparticles, of average 4 nm size, are evenly distributed on the surfaces of the nanodiamond nanotemplates and although Rh-rich (between 60% and 70% at.), they are ferromagnetic throughout a temperature range from 2 K to 400 K, without adopting any antiferromagnetic to ferromagnetic transition. Due to the reduced sizes of the FeRh nanoparticles and their spatial isolation on the nanodiamond nanotemplates, the material reveals signs of superparamagnetic relaxation in its magnetic measurements.

The inability of growing such ferromagnetic FeRh nanoparticles without the support of the nanodiamond nanotemplates under the same synthesis conditions, signifies the importance of this substrate to the production of the hybrid nanomaterial, and reveals a suggested diffusional role of the carbon atoms existing in the surface graphitic layers of the nanodiamond assemblies to the development of the ferromagnetic FeRh nanoparticulate phase during the annealing synthesis stage.

The use of the nanodiamond dense assemblies as the base for the growth of yet another magnetic nanocrystalline system provides clear evidence of the efficiency this supporting nanomaterial, and the synthetic method contributes to the development of novel magnetic hybrid nanostructures. Furthermore, by tuning the synthesis conditions, a range of different magnetic nanohybrids can be produced by this two-stage method, following the needs and scopes of the desired applications in a range of important contemporary technological fields.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/met12081355/s1>. Figures S1–S6: additional TEM, HRTEM, HAADF, EDX and STEM-chemical mapping images of all samples. Table S1: atomic ratios from EDS spot analysis on corresponding Figures. Figure S7: mass magnetic susceptibility versus temperature measurements of all samples with $H_{ap} = 999$ Oe. Table S2: Mössbauer hyperfine parameters from the best fits of the corresponding spectra of all samples recorded at 77 K and 11 K.

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