

Supporting Information of: Review: Determining Effective Magnetic Anisotropy in Magnetic Nanoparticles Systems using DC-Magnetometry Methods

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1 Synthesis Methods

1.1 Materials

All chemical reagents used in the syntheses, including iron(III) acetylacetonate, cobalt(II) acetylacetonate, iron(III) chloride hexahydrate, iron(II) chloride tetrahydrate, cobalt(II) chloride hexahydrate, sodium oleate, oleic acid, oleylamine, 1,2-octanediol, benzyl ether, and organic solvents (ethanol, toluene, cyclohexane), were purchased from Sigma-Aldrich. The reagents were of analytical grade and used without further purification.

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1.2 Synthesis via Thermal Decomposition

A set of magnetic nanoparticles (MNPs) was synthesized utilizing high-temperature thermal decomposition methods, with varying precursors and reaction parameters to control size and composition [1, 2].

IONP6.4 and IONP17: Pure magnetite nanoparticles with diameters ranging from 6 nm to 17 nm were synthesized via a high-temperature thermal decomposition method. The precursor mixture was prepared using iron(III) acetylacetonate (3 mmol), sodium oleate (2 mmol), and benzyl ether (20 mL) as the solvent. The final nanoparticle diameter was systematically controlled by adjusting the volume of oleic acid, which acts as a surfactant in the system. The procedure began with an initial heating of the mixture at 120 °C for 1 hour. Subsequently, under an inert nitrogen N₂ atmosphere, the temperature was raised to 300 °C and maintained under reflux for 1 hour. By employing oleic acid volumes of 4.5 mL and 4.0 mL, magnetite samples with diameters of 6 nm (IONP6.4) and 17 nm (IONP17) were produced. A detailed structural and magnetic characterization of these specific samples, alongside their specific power absorption performance for magnetic hyperthermia applications, has been previously reported by da Silva *et al.* [3].

IONP8: A mixture comprising iron(III) acetylacetonate (30 mmol, 1.06 g), sodium oleate (2 mmol, 0.6085 g), oleic acid (12.5 mmol, 4 mL), and benzyl ether (20 mL) was heated in an open system at 100 °C for 1 hour to ensure the complete evaporation of residual water. Following this step, the system was sealed, connected to a reflux condenser, and purged with an inert N₂ atmosphere. The solution was then heated to 298 °C and kept under reflux for 1 hour. After cooling to room temperature, the synthesized MNPs were purified by washing with ethanol and subjected to magnetic separation twice. The clean nanoparticles were subsequently redispersed in toluene.

IONP7.9, CIONP8.1, and CIONP9.1: Oleic acid-coated MNPs (pure magnetite and cobalt-doped variants) were obtained by dispersing Fe(III) and Co(II) acetylacetonates (6 mmol total) in benzyl ether (120 mmol), 1,2-octanediol (6 mmol), oleic acid (9 mmol), and oleylamine (9 mmol). The stoichiometry of each sample was accurately controlled by adjusting the Fe/Co acetylacetonate ratio in the precursor solution. The reaction mixture was heated to approximately 100–120 °C for 20 minutes under a continuous N₂ flow and vigorous mechanical stirring. Afterward, the N₂ flow was removed, and the solution was heated to the reflux temperature (298 °C) at a controlled heating rate of 3 °C/min, where it was maintained for 60 minutes. The extensive structural characterization of these specific samples, particularly regarding the control of their effective anisotropy and its subsequent impact on the magnetic hyperthermia performance upon cobalt doping, has been detailed by De Almeida *et al.* [4].

1.3 Synthesis via Aqueous Co-precipitation

A second set of samples was synthesized via the chemical co-precipitation method in an aqueous medium [5–7].

IONP9.1 and IONP8C: Pure magnetite nanoparticles were synthesized at room temperature by dissolving iron(III) chloride hexahydrate (0.0172 mol) and iron(II) chloride tetrahydrate (0.0086 mol) in distilled water. Co-precipitation was induced by the addition of a strong base. The resulting batch was divided into two portions. The first portion, labeled **IONP9.1**, was kept bare without any organic capping. The second portion, labeled **IONP8C**, was functionalized using a mixture of oleic acid, ammonia, and distilled water to coat the nanoparticle surfaces. This organic capping allowed the IONP8C sample to be stably dispersed and stored in cyclohexane.

CIONP11 and CIONP10C: Cobalt-doped magnetite nanoparticles (target stoichiometry Co_{0.2}Fe_{2.8}O₄) were synthesized following a similar co-precipitation route, but the reaction

was conducted under constant heating at 90 °C. To achieve the desired cobalt doping, 20% of the Fe(II) precursor was replaced with cobalt(II) chloride hexahydrate. Similar to the pure magnetite batch, the resulting sample was divided into two portions: a bare sample (**CIONP11**) and an oleic acid-functionalized sample (**CIONP10C**), with the latter being stably dispersed in cyclohexane.

Structural and Magnetic Characterization

Structural characterization was performed via powder X-ray diffraction (XRD) using a Bruker D2 Phaser diffractometer with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$), operating at 30 kV and 10 mA at room temperature. The corresponding X-ray diffraction patterns can be consulted in Section S2 of the Supporting Information. Transmission electron microscopy (TEM) images were acquired using a JEOL JEM 2100F (200 kV) for the thermal decomposition samples (excluding IONP8), and a FEI Talos F200C for the remaining sets. For TEM measurements, dilute suspensions of the nanoparticles in cyclohexane or toluene were drop-cast onto ultrathin carbon-coated copper grids. The stoichiometry and chemical composition of the Co-doped samples were determined by Total Reflection X-Ray Fluorescence (TXRF) using a Bruker S4 T-STAR equipped with a Mo source. Furthermore, the organic mass fraction was quantified using a TA Instruments 2950 TGA HR V5.3C thermogravimetric analyzer. Samples were heated to 1000 °C at 5 °C/min under an Ar flow (60 mL/min). The analysis indicated an organic content of approximately 10–15% by mass, which was subsequently subtracted to normalize the magnetic measurements to the magnetic oxide mass. Relevant structural parameters are summarized in Table 1 of the main article.

Magnetic measurements were carried out using a SQUID magnetometer (Quantum Design MPMS3). Isothermal magnetization curves $M \times H$ were recorded at various temperatures between 2 K and 300 K under DC fields ranging from -7 T to +7 T. Key magnetic parameters

for the determination of K_{eff} , such as saturation magnetization M_s , remanent magnetization M_r and coercive field H_C were extracted from these hysteresis loops at each temperature. Additionally, the temperature dependence of magnetization was analyzed using Zero Field Cooling (ZFC) and Field Cooling (FC) protocols with a probe field of 50 Oe and a sweep rate of 4 K/min. These curves provide the blocking temperature distribution $f(T_B)$, the mean blocking temperature $\langle T_B \rangle$ and qualitative insights on how interactive and polydisperse the system is. All relevant magnetic data and corresponding curves can be consulted in Section S3 of the Supporting Information.

2 XRD Data and Analysis

The X-ray diffraction data were analyzed to investigate the structural properties of the synthesized samples and to estimate their average crystallite size. The average crystallite diameter $\langle D_{\text{XRD}} \rangle$ was calculated based on the Scherrer equation:

$$\langle D_{\text{XRD}} \rangle = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

where K is a dimensionless shape factor (0.89 for spherical particles and 0.94 for cubic particles), λ is the X-ray wavelength of the source ($\lambda = 1.5418 \text{ \AA}$ Cu $K\alpha$), θ is the Bragg diffraction angle, and β is the line broadening at half the maximum intensity (FWHM), after subtracting the background. The experimental diffraction profiles were mathematically fitted employing Gaussian and Pseudo-Voigt distributions on the (311) peak. All identified diffraction peaks were indexed, consistent with the standard patterns for magnetite (COD number 1010369).

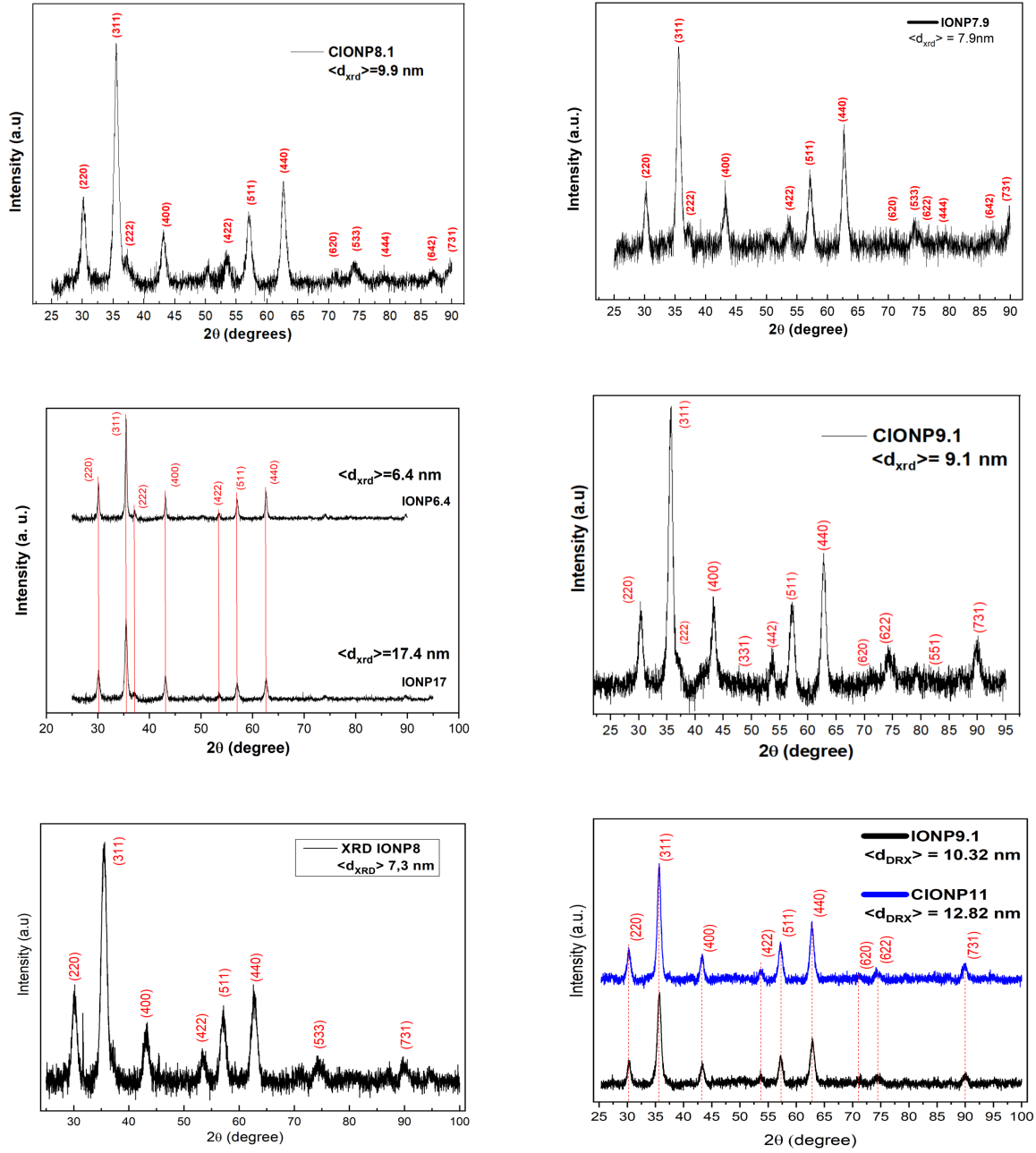


Figure 1: XRD patterns for the magnetite and cobalt-doped ferrite samples. XRD measurements for IONP8C and CIONP10C were not performed, as their magnetic cores are identical to those of IONP9.1 and CIONP11, respectively.

3 Fits Methods and Results

3.1 ZFC-FC

The mean blocking temperature was determined according to Eq. (9) and subsequently used to estimate K_{eff} within the τ_N model framework. The average particle volume was calculated as $\langle V \rangle = \pi \langle D_{\text{TEM}} \rangle^3 / 6$ for spherical particles and $\langle V \rangle = \langle D_{\text{TEM}} \rangle^3$ for cubic samples. To obtain $\langle D_{\text{TEM}} \rangle$, a log-normal distribution was fitted to the diameter histograms derived from TEM images:

$$f(D) = \frac{1}{\sqrt{2\pi}\sigma D} \exp \left[-\frac{\ln^2(D/D_0)}{2\sigma^2} \right] \quad (2)$$

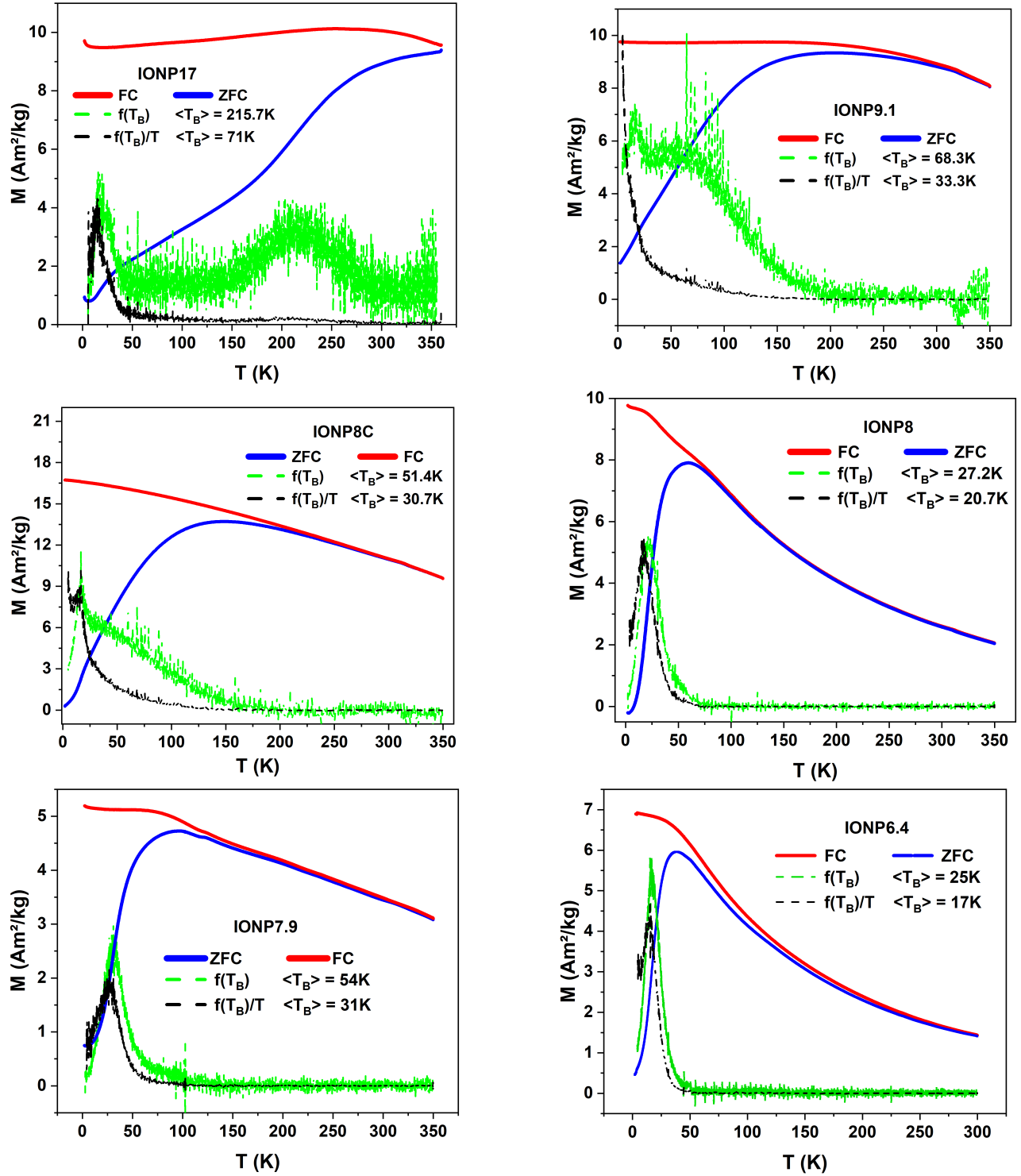


Figure 2: Zero-Field-Cooled (ZFC) and Field-Cooled (FC) magnetization curves for the pure magnetite samples.

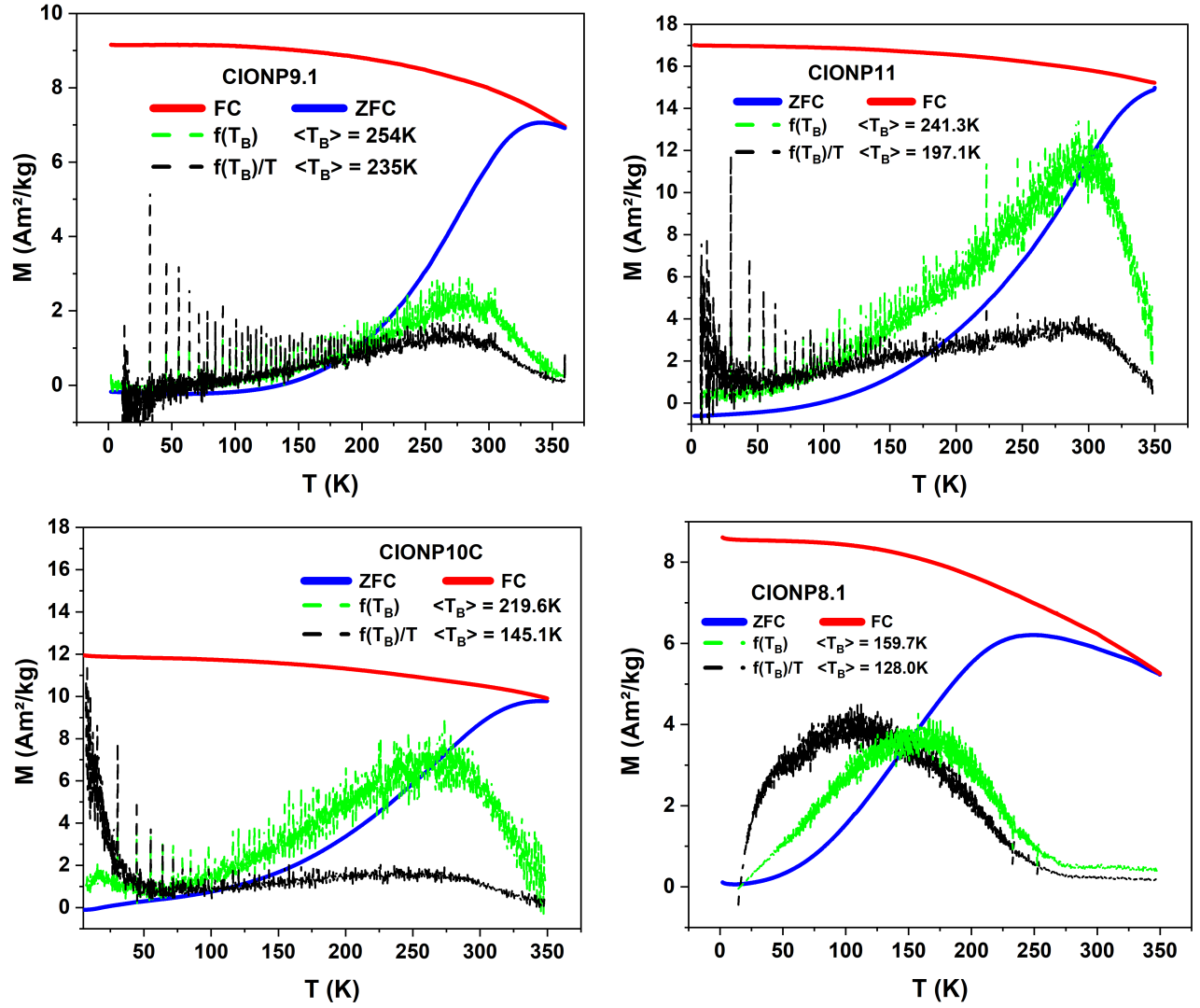


Figure 3: Zero-Field-Cooled (ZFC) and Field-Cooled (FC) magnetization curves for the Cobalt-doped ferrite samples.

3.2 MxH

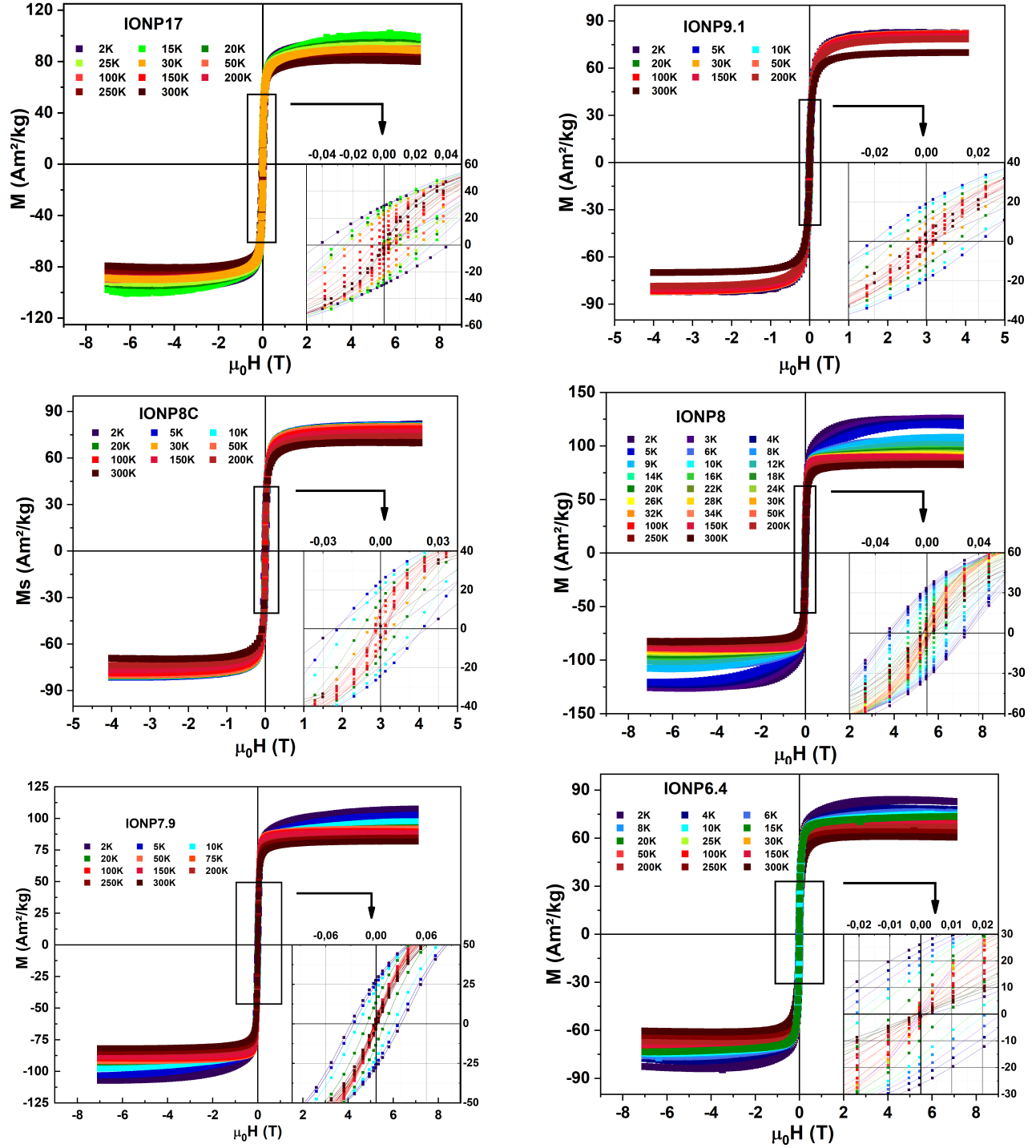


Figure 4: Field-dependent magnetization curves ($M \times H$) for the pure magnetite samples.

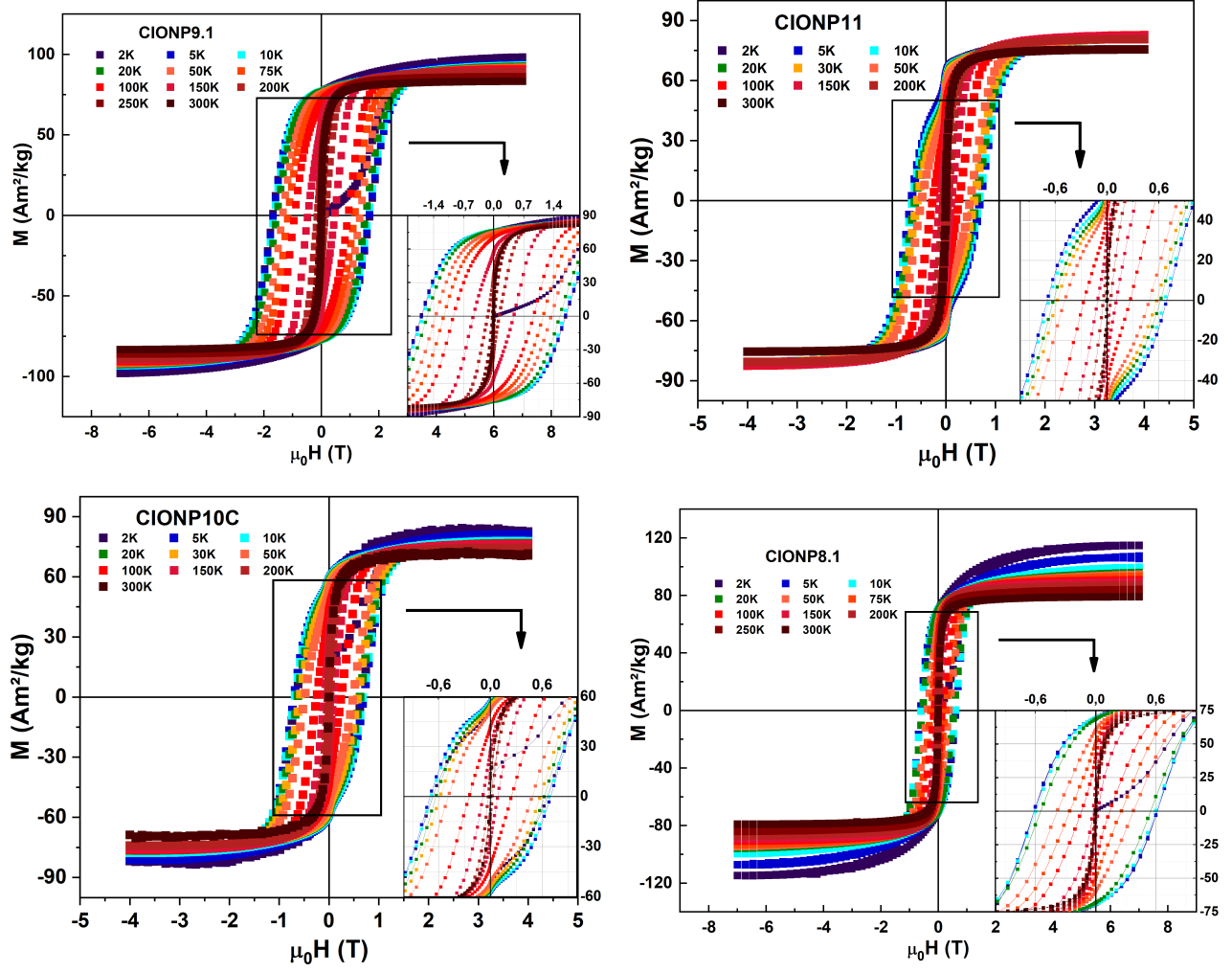


Figure 5: Field-dependent magnetization curves ($M \times H$) for the Cobalt-doped ferrite samples.

3.2.1 Data extracted from MxH curves

Table 1: Experimental magnetization data (M_s , M_r), squareness ratio (M_r/M_s), and coercive field ($\mu_0 H_C$) for the IONP6.4, IONP17 and IONP7 samples studied. No uncertainties are associated, as the values are direct estimates from the experimental curves.

Sample	T (K)	M_s (A·m ² /kg)	M_r (A·m ² /kg)	M_r/M_s	$\mu_0 H_C$ (mT)
IONP6.4	2	83.5	26.3	0.315	35.5
	4	78.7	23.7	0.301	31.5
	6	76.3	21.2	0.278	26.1
	8	74.8	18.6	0.249	21.1
	10	73.6	16.0	0.217	16.9
	15	73.3	9.7	0.132	8.3
	20	72.9	4.5	0.062	2.6
	25	72.9	0.4	0.005	0.1
	30	72.4	0.0	0.000	0.0
	50	72.1	0.0	0.000	0.0
	100	70.8	0.0	0.000	0.0
	150	69.1	0.0	0.000	0.0
	200	67.0	0.0	0.000	0.0
	250	63.9	0.0	0.000	0.0
	300	61.0	0.0	0.000	0.0
IONP8	2	125.1	33.8	0.270	29.3
	3	123.4	33.3	0.270	31.2
	4	123.2	32.1	0.261	29.4
	5	121.4	31.0	0.255	27.4
	6	117.8	29.8	0.253	25.4
	8	111.1	27.3	0.246	21.9
	9	108.2	26.1	0.241	19.9
	10	105.4	24.2	0.230	18.5
	12	101.5	21.7	0.214	15.3
	14	99.2	18.9	0.191	12.5
	16	97.0	15.1	0.156	9.8
	18	95.6	12.0	0.126	7.4
	20	94.5	9.9	0.105	5.4
	22	93.2	7.1	0.076	3.9
	24	92.7	5.1	0.055	2.6
	26	91.5	3.1	0.034	1.5
	28	90.9	1.3	0.014	0.6
	30	90.2	0.2	0.002	0.1
	32	89.9	0.0	0.000	0.0
	34	89.3	0.0	0.000	0.0
	50	89.2	0.0	0.000	0.0
	100	88.4	0.0	0.000	0.0
	150	89.0	0.0	0.000	0.0
	200	84.8	0.0	0.000	0.0
	250	83.0	0.0	0.000	0.0
	300	82.8	0.0	0.000	0.0
IONP17	2	97.4	29.2	0.300	41.7
	8	129.0	31.0	0.240	35.0
	10	122.0	30.5	0.250	34.1
	15	100.4	28.6	0.285	30.7
	20	95.0	25.8	0.272	26.7
	25	93.0	24.3	0.261	24.5
	30	90.1	22.8	0.253	22.0
	50	88.6	19.2	0.217	18.4
	100	87.4	14.4	0.165	11.0
	150	86.2	10.2	0.118	7.2
	200	85.6	6.2	0.072	3.7
	250	84.3	1.9	0.023	1.0
	300	81.8	1.4	0.017	0.7

Table 2: Consolidated magnetic properties (M_s , M_r , $\mu_0 H_C$) and squareness ratio (M_r/M_s) for CIONP8.1, IONP7.9, and CIONP9.1 samples. No uncertainties are associated, as the values are direct estimates from the experimental curves.

Sample	T (K)	M_s ($\text{A}\cdot\text{m}^2/\text{kg}$)	M_r ($\text{A}\cdot\text{m}^2/\text{kg}$)	M_r/M_s	$\mu_0 H_C$ (mT)
CIONP8.1	2	114.7	69.3	0.604	613.8
	5	105.7	69.3	0.656	613.4
	10	99.6	69.3	0.696	599.1
	20	96.0	68.3	0.711	548.3
	50	94.7	59.9	0.633	376.3
	75	93.4	50.4	0.540	257.1
	100	91.0	39.7	0.436	141.7
	150	89.5	17.4	0.194	24.5
	200	87.2	0.1	0.001	3.6
	250	84.2	0.0	0.000	0.0
	300	79.1	0.0	0.000	0.0
IONP7.9	2	106.2	32.5	0.306	30.0
	5	102.1	26.0	0.255	26.7
	10	97.8	22.3	0.228	20.5
	20	93.0	13.8	0.148	10.7
	30	91.4	8.8	0.096	6.1
	50	89.7	0.5	0.006	0.2
	75	89.0	0.0	0.000	0.0
	100	88.9	0.0	0.000	0.0
	150	87.2	0.0	0.000	0.0
	200	84.6	0.0	0.000	0.0
	250	81.6	0.0	0.000	0.0
	300	79.9	0.0	0.000	0.0
CIONP9.1	2	98.2	76.5	0.779	1688.5
	5	94.0	76.6	0.815	1674.1
	10	93.4	76.7	0.821	1640.6
	20	92.8	76.3	0.822	1543.9
	50	92.0	75.1	0.816	1346.7
	75	91.3	73.2	0.802	1157.2
	100	90.8	69.9	0.770	931.3
	150	90.0	56.2	0.624	470.5
	200	89.3	34.5	0.386	134.7
	250	86.0	14.3	0.166	22.0
	300	83.3	1.2	0.014	1.0

Table 3: Experimental magnetization data (M_s , M_r), squareness ratio (M_r/M_s), and coercive field ($\mu_0 H_C$) for the samples IONP9.1, IONP8C, CIONP11 and CIONP10C. No uncertainties are associated, as the values are direct estimates from the experimental curves.

Sample	T (K)	M_s (A·m ² /kg)	M_r (A·m ² /kg)	M_r/M_s	$\mu_0 H_C$ (mT)
IONP9.1	2	82.2	21.0	0.255	23.7
	5	81.4	19.0	0.233	20.5
	10	81.3	17.0	0.209	17.2
	20	81.2	12.5	0.154	11.6
	30	81.1	9.1	0.112	8.0
	50	81.0	4.8	0.059	3.8
	100	80.7	0.9	0.011	0.0
	150	79.5	0.0	0.000	0.0
	200	77.5	0.0	0.000	0.0
	300	69.9	0.0	0.000	0.0
IONP8C	2	81.9	25.7	0.314	23.7
	5	81.4	24.4	0.300	21.8
	10	80.9	21.3	0.263	17.0
	20	80.5	14.6	0.181	9.8
	30	80.3	9.7	0.121	5.8
	50	80.0	3.0	0.038	1.4
	100	78.8	0.0	0.000	0.0
	150	76.7	0.0	0.000	0.0
	200	73.8	0.0	0.000	0.0
	300	69.9	0.0	0.000	0.0
CIONP11	2	81.5	61.3	0.752	700.4
	5	80.8	60.7	0.751	689.4
	10	80.8	57.7	0.714	666.3
	20	80.8	56.1	0.694	616.8
	30	80.8	54.8	0.678	573.9
	50	81.0	52.4	0.647	489.0
	100	82.5	43.7	0.530	266.0
	150	82.0	31.1	0.379	107.5
	200	80.6	17.7	0.220	41.0
	300	75.5	0.0	0.000	0.0
CIONP10C	2	83.3	58.5	0.702	708.7
	5	81.2	57.8	0.712	697.0
	10	77.7	57.3	0.737	679.4
	20	76.7	55.8	0.728	624.3
	30	76.2	54.5	0.715	578.5
	50	76.1	51.5	0.677	484.6
	100	76.2	41.2	0.541	244.5
	150	75.9	26.4	0.348	85.3
	200	74.3	12.2	0.164	22.2
	300	71.3	0.0	0.000	0.0

3.3 Kneller's law Fits Results

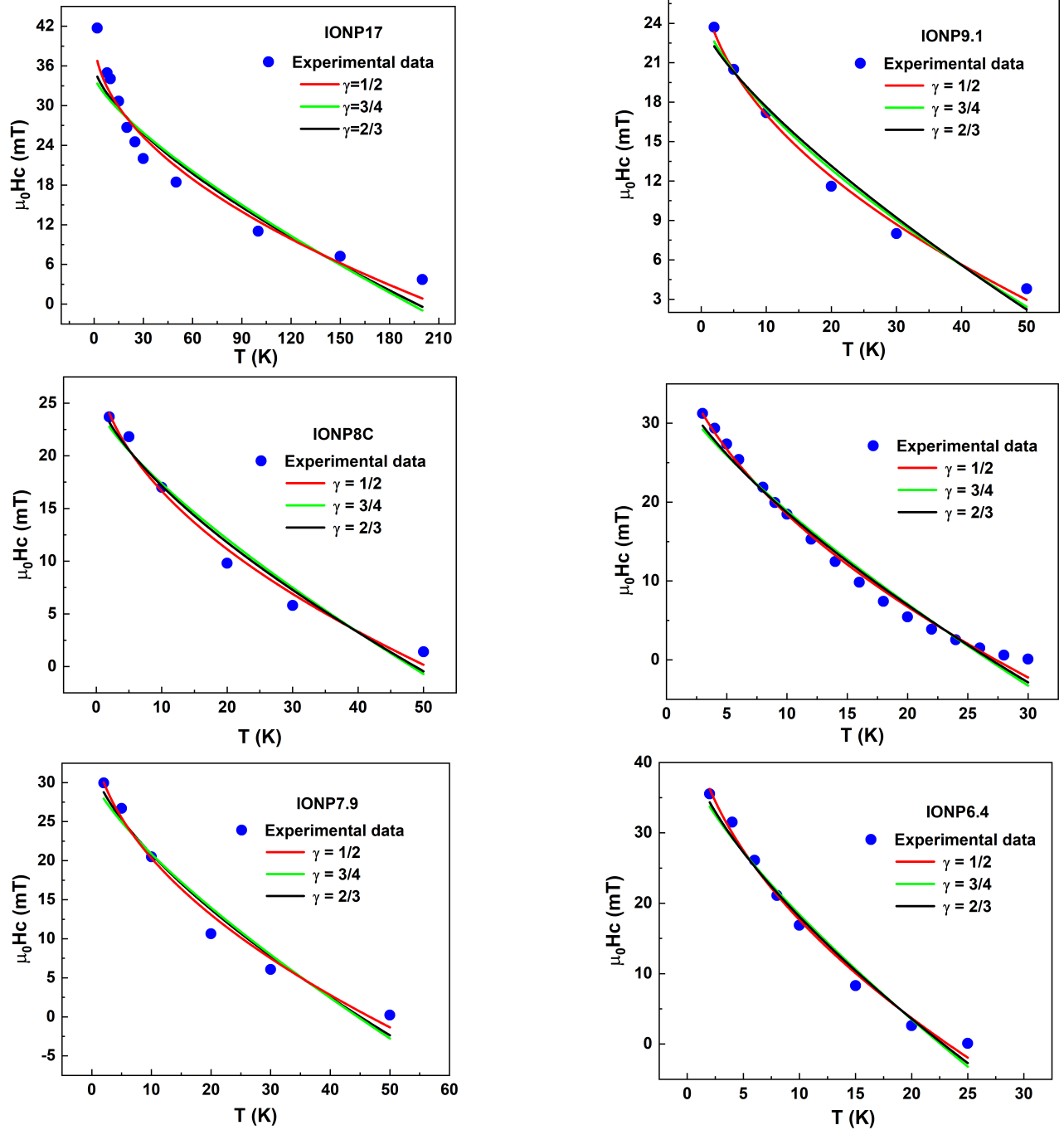


Figure 6: Temperature dependence of the coercive field (H_C) fitted with Kneller's law for the pure magnetite samples.

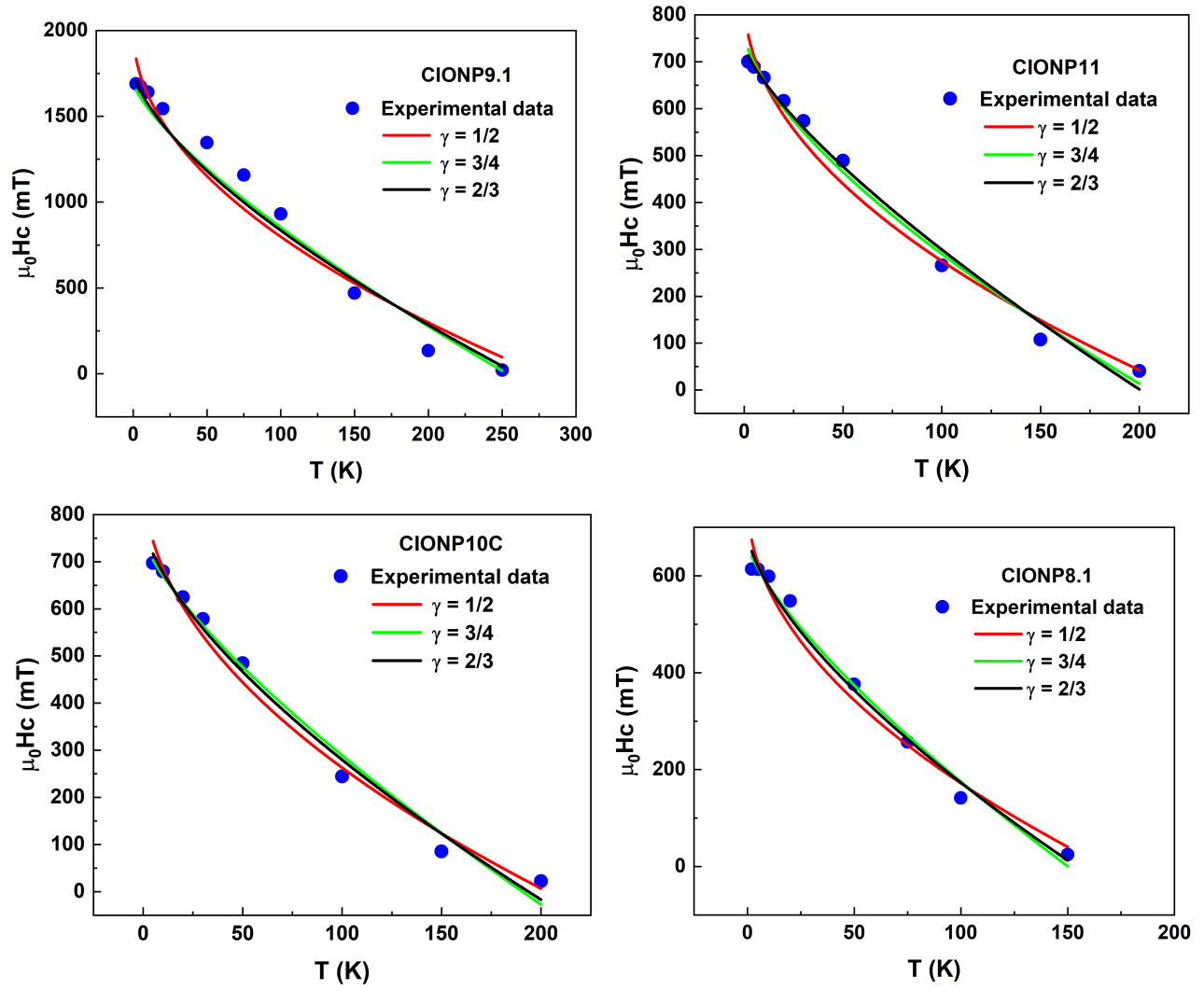


Figure 7: Temperature dependence of the coercive field (H_C) fitted with Kneller's law for the Cobalt-doped ferrite samples.

Table 4: Fit results of $H_C(T)$ using Kneller's model, given in Eq. 13 for all samples. Fits were performed for $h_c = 0.479$ (uniaxial), $h_c = 0.32$ (cubic, $K_1 > 0$) and $h_c = 0.19$ (cubic, $K_1 < 0$).

Sample	h_c	γ	$\langle T_B \rangle$ (K)	K_{eff} (10^4 J/m ³)	M_s (A·m ² /kg)	R^2
IONP17	0.479	1/2	208.7 $\pm$ 0.6	1.52 $\pm$ 0.01	81.8	0.9895
		3/4	193.6 $\pm$ 0.4	1.51 $\pm$ 0.01		0.99894
		2/3	197.8 $\pm$ 0.3	1.59 $\pm$ 0.01		0.99523
	0.19	1/2	208.7 $\pm$ 0.6	4.53 $\pm$ 0.01		0.9895
		3/4	193.6 $\pm$ 0.4	3.81 $\pm$ 0.01		0.99894
		2/3	197.8 $\pm$ 0.3	3.99 $\pm$ 0.01		0.99523
IONP9.1	0.479	1/2	62 $\pm$ 3	1.08 $\pm$ 0.02	70	0.99353
		3/4	57 $\pm$ 4	0.92 $\pm$ 0.04		0.97012
		2/3	58 $\pm$ 4	0.96 $\pm$ 0.04		0.98003
	0.19	1/2	62 $\pm$ 3	2.72 $\pm$ 0.06		0.99353
		3/4	57 $\pm$ 4	2.3 $\pm$ 0.1		0.97012
		2/3	58 $\pm$ 4	2.41 $\pm$ 0.09		0.98003
IONP8C	0.479	1/2	51 $\pm$ 3	1.14 $\pm$ 0.04	70	0.98457
		3/4	48 $\pm$ 4	0.95 $\pm$ 0.05		0.96199
		2/3	49 $\pm$ 4	1.00 $\pm$ 0.05		0.97181
	0.19	1/2	51 $\pm$ 3	2.9 $\pm$ 0.1		0.98457
		3/4	48 $\pm$ 4	2.4 $\pm$ 0.1		0.96199
		2/3	49 $\pm$ 4	2.5 $\pm$ 0.1		0.97181
IONP8	0.479	1/2	27.3 $\pm$ 0.5	2.09 $\pm$ 0.03	82.8	0.99199
		3/4	26.73 $\pm$ 0.03	1.62 $\pm$ 0.01		0.99554
		2/3	26.95 $\pm$ 0.01	1.73 $\pm$ 0.01		0.99952
	0.19	1/2	27.3 $\pm$ 0.5	5.18 $\pm$ 0.01		0.99199
		3/4	26.73 $\pm$ 0.03	4.09 $\pm$ 0.01		0.99554
		2/3	26.95 $\pm$ 0.01	4.36 $\pm$ 0.01		0.99952
IONP7.9	0.479	1/2	46.6 $\pm$ 0.1	1.64 $\pm$ 0.01	79.9	0.99277
		3/4	44.6 $\pm$ 0.1	1.34 $\pm$ 0.01		0.99926
		2/3	45 $\pm$ 3	1.42 $\pm$ 0.08		0.96763
	0.19	1/2	46.6 $\pm$ 0.1	4.13 $\pm$ 0.01		0.99277
		3/4	44.6 $\pm$ 0.1	3.37 $\pm$ 0.01		0.99926
		2/3	45 $\pm$ 3	3.6 $\pm$ 0.2		0.96763
IONP6.4	0.479	1/2	23.2 $\pm$ 0.8	1.69 $\pm$ 0.04	61	0.98966
		3/4	22.5 $\pm$ 0.1	1.33 $\pm$ 0.01		0.9949
		2/3	22.8 $\pm$ 0.1	1.41 $\pm$ 0.01		0.99945
	0.19	1/2	23.2 $\pm$ 0.8	4.27 $\pm$ 0.02		0.98966
		3/4	22.5 $\pm$ 0.1	3.35 $\pm$ 0.01		0.9949
		2/3	22.8 $\pm$ 0.1	3.56 $\pm$ 0.05		0.99945
CIONP9.1	0.479	1/2	276.1 $\pm$ 0.5	92.3 $\pm$ 0.1	83.3	0.99492
		3/4	253.6 $\pm$ 0.6	78.1 $\pm$ 0.1		0.98915
		2/3	259.9 $\pm$ 0.2	81.5 $\pm$ 0.5		0.9989
	0.32	1/2	276.1 $\pm$ 0.5	138.2 $\pm$ 0.2		0.99492
		3/4	253.6 $\pm$ 0.6	116.8 $\pm$ 0.2		0.98915
		2/3	259.9 $\pm$ 0.2	122 $\pm$ 1		0.9989
CIONP11	0.479	1/2	220 $\pm$ 20	35 $\pm$ 1	75.5	0.97923
		3/4	201 $\pm$ 7	30.8 $\pm$ 0.5		0.99105
		2/3	205 $\pm$ 8	31.8 $\pm$ 0.6		0.99073
	0.32	1/2	220 $\pm$ 20	52 $\pm$ 2		0.97923
		3/4	201 $\pm$ 7	46.1 $\pm$ 0.8		0.99105
		2/3	205 $\pm$ 8	47.6 $\pm$ 0.9		0.99073
CIONP10C	0.479	1/2	200 $\pm$ 10	35 $\pm$ 1	71.3	0.98537
		3/4	191 $\pm$ 8	29.7 $\pm$ 0.7		0.98757
		2/3	194 $\pm$ 8	31.0 $\pm$ 0.7		0.98943
	0.32	1/2	200 $\pm$ 10	52 $\pm$ 2		0.98537
		3/4	191 $\pm$ 8	44 $\pm$ 1		0.98757
		2/3	194 $\pm$ 8	46 $\pm$ 1		0.98943
CIONP8.1	0.479	1/2	170 $\pm$ 10	33 $\pm$ 1	79.1	0.97468
		3/4	150 $\pm$ 6	29.2 $\pm$ 0.6		0.99001
		2/3	154 $\pm$ 7	30.2 $\pm$ 0.7		0.98834
	0.32	1/2	170 $\pm$ 10	50 $\pm$ 2		0.97468
		3/4	150 $\pm$ 6	43.7 $\pm$ 0.9		0.99001
		2/3	154 $\pm$ 7	45 $\pm$ 1		0.98834

3.4 Generalized Coercive Field Fits and Results

To model the coercive field using the generalized approach proposed by Nunes *et al.* [8], the blocking temperature distribution of the nanoparticles was assumed to be adequately described by a log-normal function. This approximation is physically justified by the fact that the blocking temperature of a nanoparticle is directly proportional to its magnetic volume, $T_B \propto K_{\text{eff}}V/[k_B \ln(\tau_m/\tau_0)]$. Since nanoparticle volume distributions typically follow log-normal statistics, the blocking temperature distribution naturally inherits a similar statistical profile, even when accounting for the thermal variation of K_{eff} . Phenomenologically, the temperature dependence of K_{eff} still preserves the two fundamental characteristics of $f(T_B)$: the distribution remains strictly positive and asymmetric, exhibiting an extended tail towards higher temperatures. Therefore, these characteristics are sufficient to well-approximate the overall blocking temperature distribution as a log-normal function.

By adopting the log-normal distribution, the integrals of this function possess exact analytical solutions. These solutions can be expressed in terms of the Gaussian error function (erf). By defining the auxiliary variable $Z = \frac{\ln(T/T_{b0})}{\sqrt{2}w}$, where T_{b0} is the median blocking temperature and w is the dispersion of the distribution, the mean blocking temperature of the entire nanoparticle ensemble is given by $\langle T_B \rangle = T_{b0} \exp(w^2/2)$. At a given temperature T , the fraction of magnetically blocked particles, $x_B(T)$, is analytically evaluated as:

$$x_B(T) = \frac{1}{2} [1 - \text{erf}(Z)] \quad (3)$$

The average blocking temperature of this specific blocked fraction, $\langle T_B \rangle_T$, can be expressed as:

$$\langle T_B \rangle_T = \frac{\langle T_B \rangle}{x_B(T)} \frac{1}{2} \left[1 - \operatorname{erf} \left(Z - \frac{w}{\sqrt{2}} \right) \right] \quad (4)$$

Consequently, the coercive field of the blocked fraction, $H_{CB}(T)$, is modeled taking into account the thermal softening of the anisotropy barrier:

$$H_{CB}(T) = H_{c0} \left[1 - \left(\frac{T}{\langle T_B \rangle_T} \right)^\gamma \right] \quad (5)$$

Simultaneously, the unblocked nanoparticles behave superparamagnetically. The susceptibility of this superparamagnetic fraction, $\chi_S(T)$, is computed as:

$$\chi_S(T) = \frac{25M_s^2\rho}{3K_{\text{eff}}T} \langle T_B \rangle \frac{1}{2} \left[1 + \operatorname{erf} \left(Z - \frac{w}{\sqrt{2}} \right) \right] + \frac{C}{T}. \quad (6)$$

Finally, the macroscopic coercive field of the sample, $H_C(T)$, is determined by combining the contributions of both fractions, utilizing the experimental remanent magnetization $M_r(T)$:

$$H_C(T) = \frac{M_r(T)}{\chi_S(T) + \frac{M_r(T)}{H_{CB}(T)}} \quad (7)$$

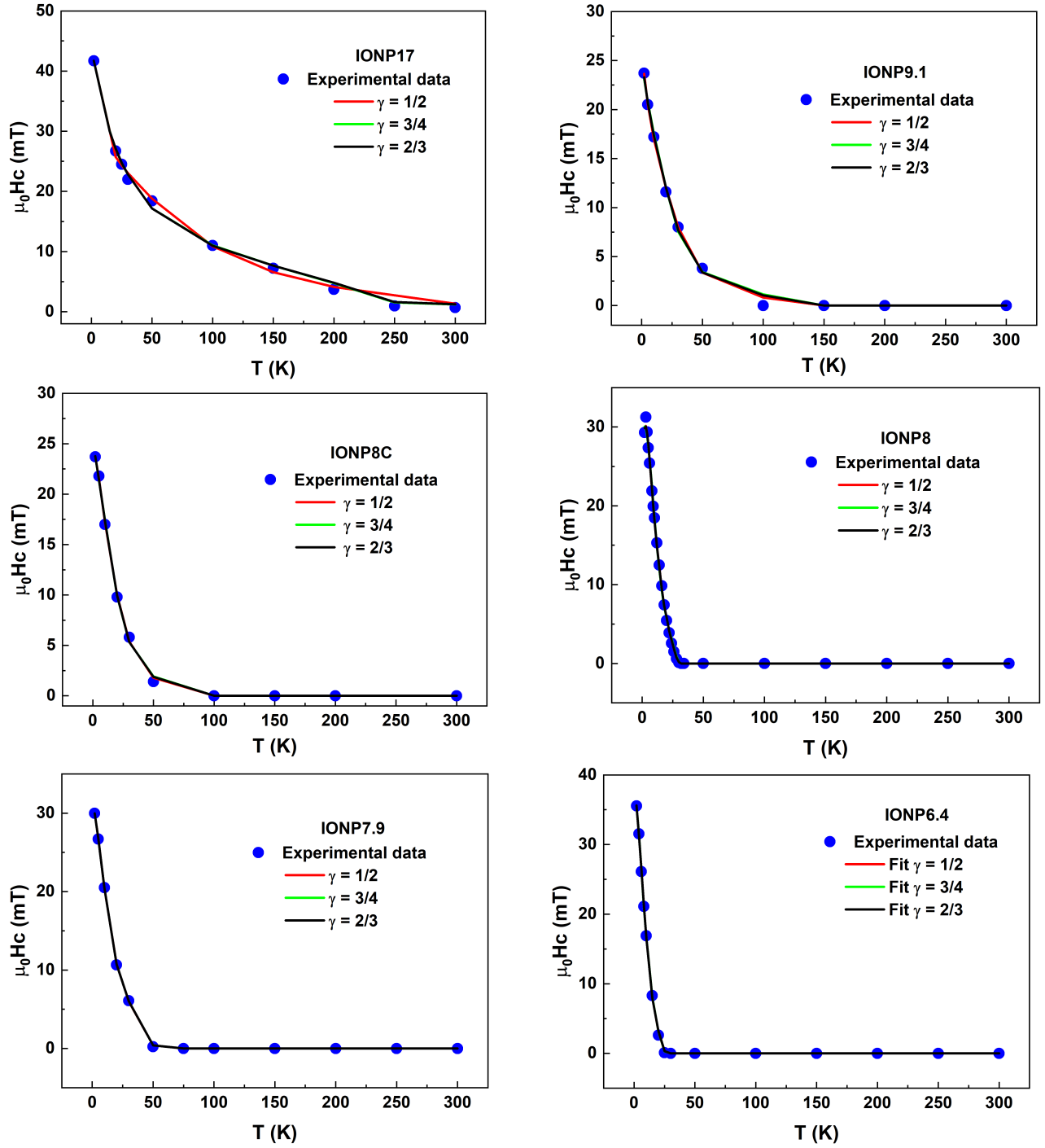


Figure 8: Temperature dependence of the coercive field (H_C) fitted with the generalized model (Nunes) for the pure magnetite samples.

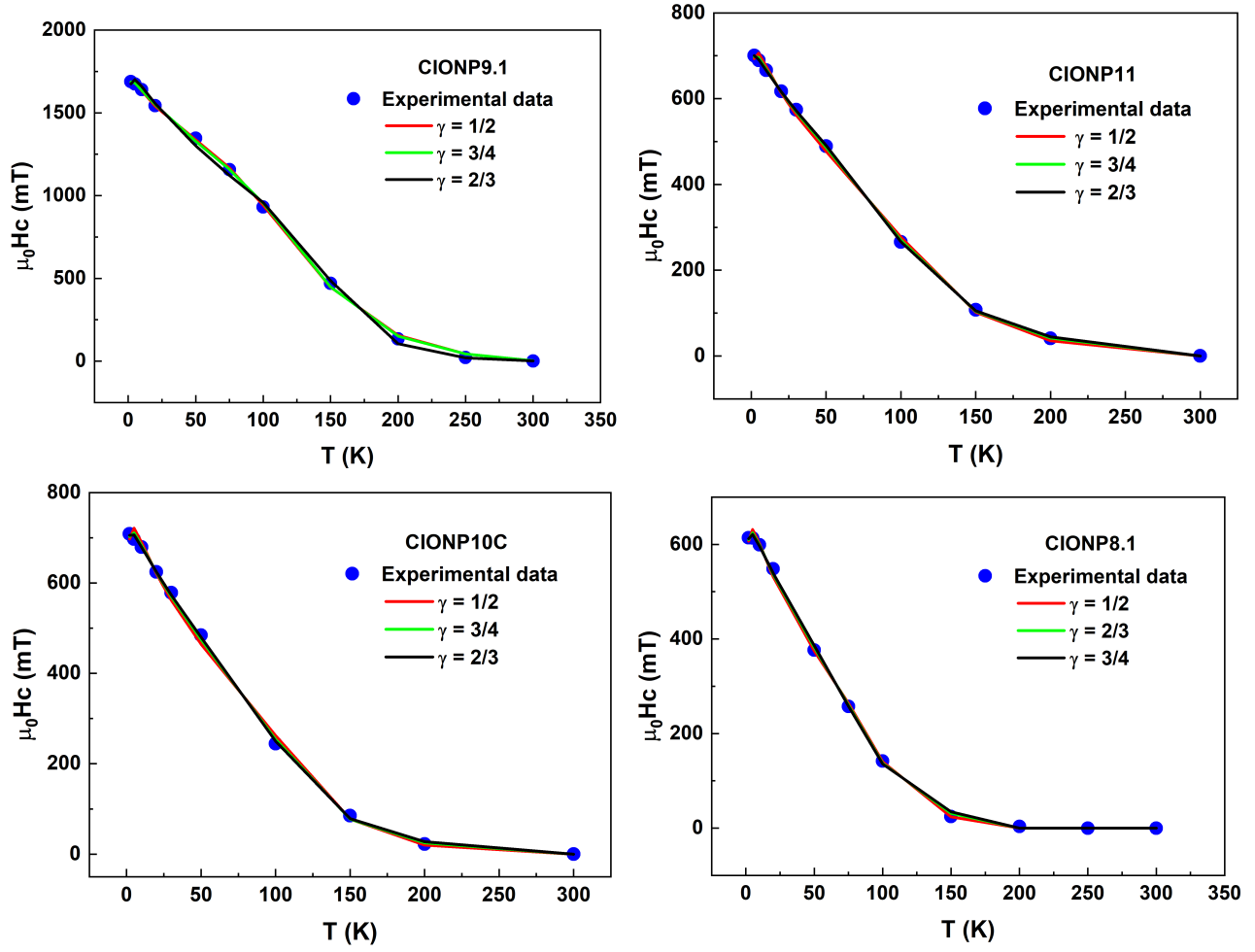


Figure 9: Temperature dependence of the coercive field (H_C) fitted with the generalized model (Nunes) for the Cobalt-doped ferrite samples.

Table 5: Consolidated parameters obtained from the generalized coercive field model (Eq. 14) for the temperature dependence of H_C across all samples. The density ρ was kept fixed at 5.3 g/cm³ for Co-ferrites and 5.18 g/cm³ for pure magnetite to ensure mass-to-volume consistency. Fixed parameters during the non-linear fitting are indicated by an asterisk (*).

Sample	$\mu_0 H_C(0)$ (mT)	$\langle T_B \rangle$ (K)	σ	γ	K_{eff} (10 ⁵ J/m ³)	C (10 ⁻⁶ m ³ K/kg)	R^2
IONP17	36 ± 2	190 ± 20	0.55	1/2 ^a	1.6 ± 0.7	-500 ± 100	0.9975
	30 ± 2	190 ± 40	0.55	3/4 ^a	0.8 ± 0.2	-800 ± 100	0.99235
	32 ± 2	170 ± 20	0.6	2/3 ^a	1.7 ± 0.7	-600 ± 100	0.99236
IONP9.1	29.0 ± 0.5	54 ± 2	0.4	1/2	1.9 ± 0.7	1.3*	0.99864
	25.5 ± 0.5	43 ± 3	0.4	3/4	3 ± 1	1.3*	0.99696
	26.4 ± 0.5	46 ± 3	0.4	2/3	2 ± 1	1.3*	0.99769
IONP8C	35 ± 1	37 ± 2	0.4	1/2	1.5 ± 0.4	340 ± 70	0.99944
	28 ± 1	34 ± 2	0.4	3/4	1.6 ± 0.5	100 ± 100	0.99905
	30 ± 1	35 ± 2	0.4	2/3	1.6 ± 0.4	200 ± 90	0.99919
IONP8	48 ± 2	32 ± 2	0.7	1/2	0.61 ± 0.08	590 ± 90	0.99912
	41 ± 1	23 ± 1	0.51	3/4	1.0 ± 0.2	400 ± 100	0.99853
	42 ± 2	29 ± 2	0.67	2/3	0.69 ± 0.08	500 ± 100	0.99898
IONP7.9	40 ± 2	40 ± 6	0.7	1/2	1.0 ± 0.3	217 ± 6	0.99997
	33 ± 1	38 ± 5	0.8	3/4	0.9 ± 0.2	11 ± 4	0.99997
	34.9 ± 0.4	37.8 ± 0.9	0.7	2/3	0.99 ± 0.04	80 ± 20	0.99997
IONP6.4	49 ± 2	27 ± 2	0.66	1/2	0.44 ± 0.04	80 ± 50	0.99972
	43 ± 1	20.2 ± 0.9	0.5	3/4	0.8 ± 0.1	20 ± 50	0.99971
	45 ± 2	22 ± 1	0.5	2/3	0.68 ± 0.08	40 ± 50	0.99957
CIONP9.1	1900 ± 30	490 ± 50	0.59	1/2	1.1 ± 0.2	6 ± 3	0.99958
	1780 ± 20	290 ± 20	0.41	3/4	3.1 ± 0.6	4 ± 1	0.99952
	1880 ± 30	280 ± 10	0.3	2/3	1.4 ± 0.7	9 ± 3	0.99861
CIONP11	860 ± 20	230 ± 10	0.4	1/2	2.0 ± 0.7	26 ± 6	0.9988
	745 ± 2	196 ± 2	0.4	3/4	3.8 ± 0.2	7 ± 1	0.99995
	774 ± 5	206 ± 4	0.4	2/3	3.2 ± 0.4	13 ± 2	0.99985
CIONP10C	910 ± 20	200 ± 10	0.3	1/2	2 ± 1	32 ± 8	0.99751
	776 ± 6	173 ± 4	0.3	3/4	3.7 ± 0.7	12 ± 3	0.99967
	810 ± 10	181 ± 6	0.3	2/3	3 ± 1	18 ± 4	0.99925
CIONP8.1	820 ± 20	163 ± 7	0.3	1/2	2.0 ± 0.9	49 ± 7	0.99897
	701 ± 9	140 ± 4	0.3	3/4	5 ± 1	26 ± 5	0.99945
	730 ± 9	146 ± 4	0.3	2/3	4 ± 1	33 ± 5	0.99945

^a The Curie constant yielded a negative value, but provided the best statistical fit for this sample.

3.5 $M_s(T)$ Data and Fits

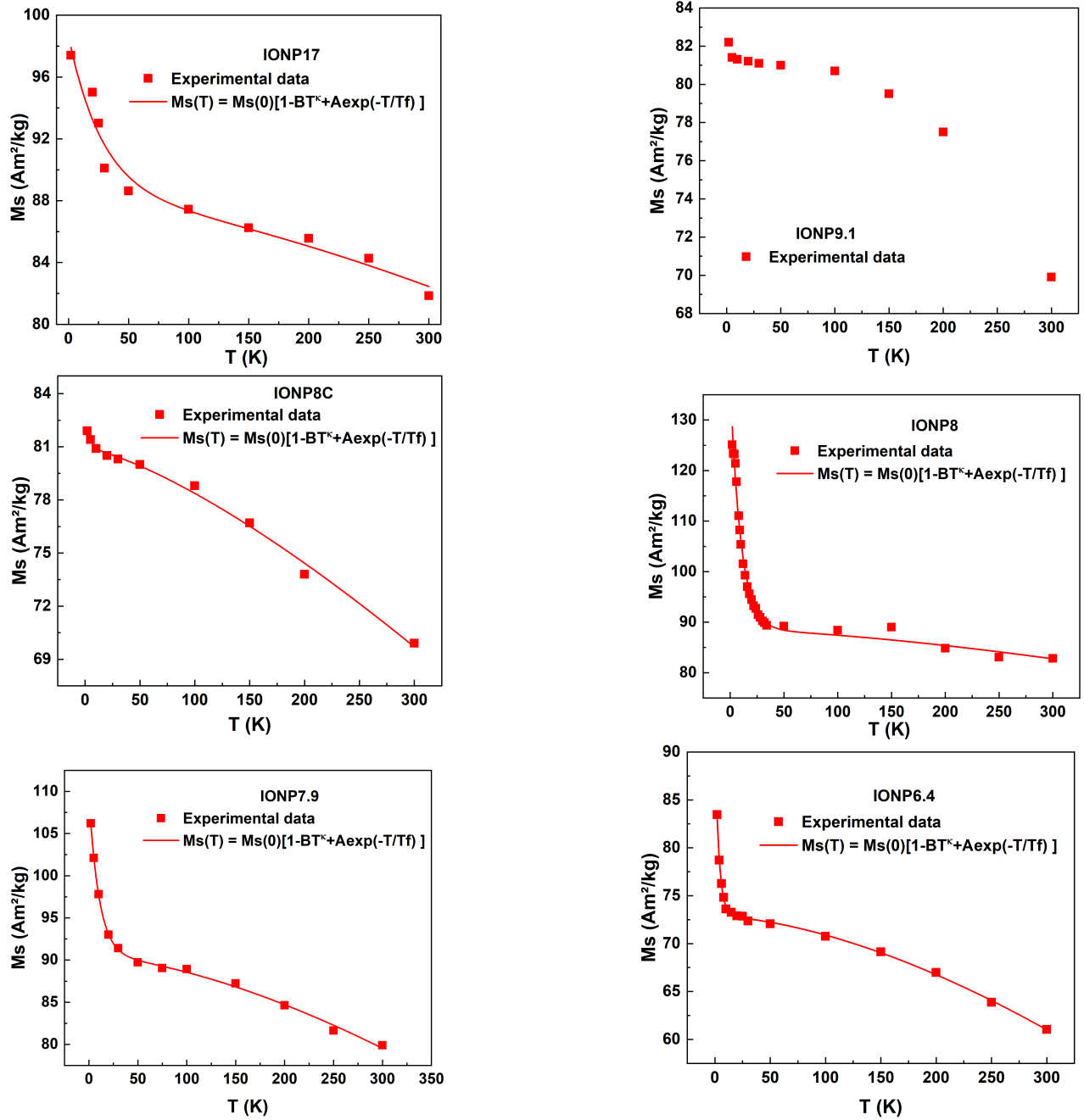


Figure 10: Temperature dependence of the saturation magnetization (M_s) for the pure magnetite samples.

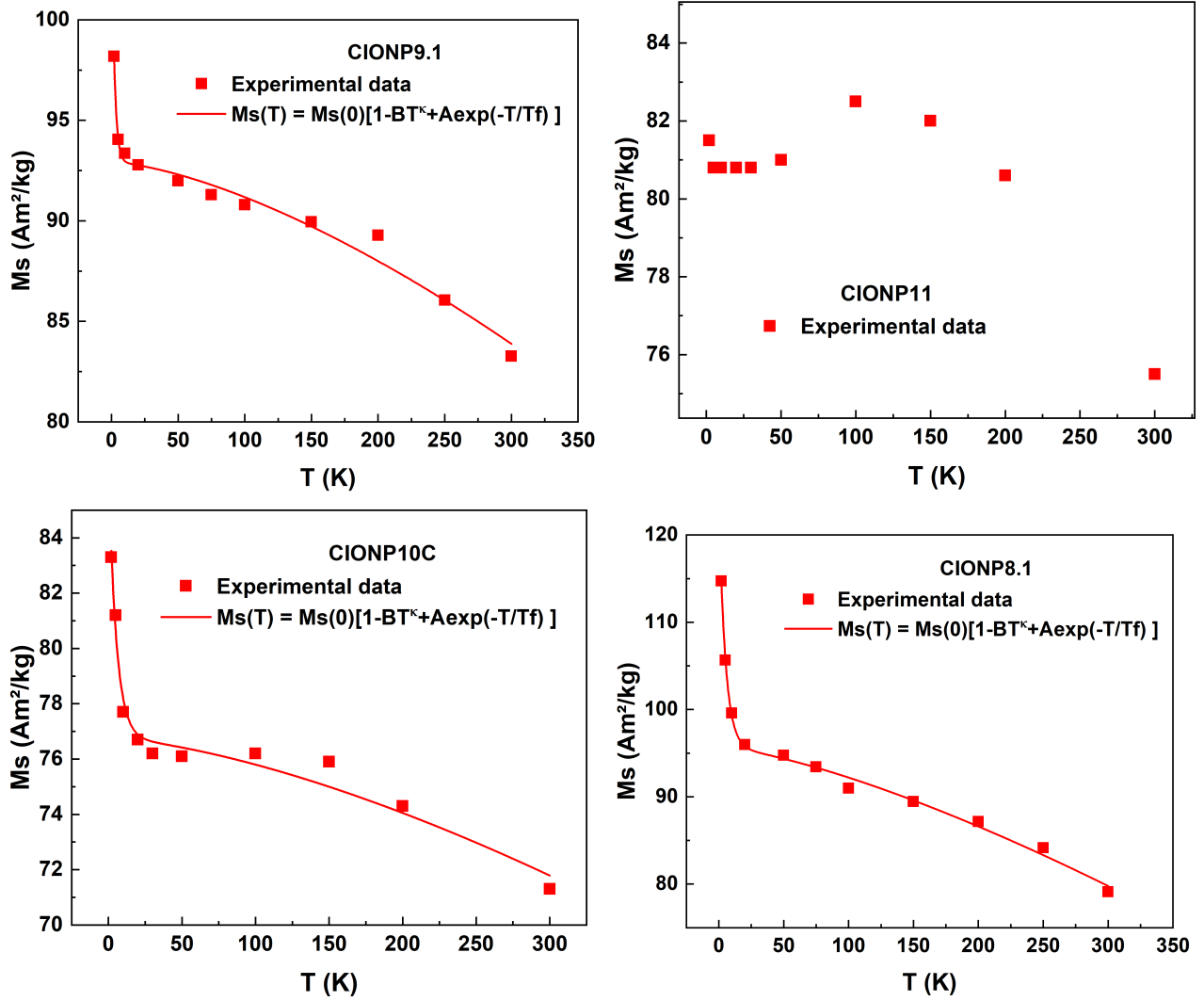


Figure 11: Temperature dependence of the saturation magnetization (M_s) for the Cobalt-doped ferrite samples.

3.6 $M_r(T)$ Data and Fits

Following the same argument used for the coercive field, the thermal dependence of the remanent magnetization, $M_r(T)$, was modeled by assuming a log-normal distribution for the blocking temperatures. The macroscopic remanence is governed by the intrinsic magnetization decay of the blocked nanoparticles multiplied by the probability of a particle remaining

magnetically blocked at a given temperature T . Since the integral of the distribution over all temperatures is normalized to unity, the exact analytical expression used to fit the experimental data is given by:

$$M_r(T) = \frac{M_r(0)}{M_s(0)} M_s(T) \frac{1}{2} \left[1 - \operatorname{erf} \left(\frac{\ln(T/T_B)}{\sqrt{2}w} \right) \right] \quad (8)$$

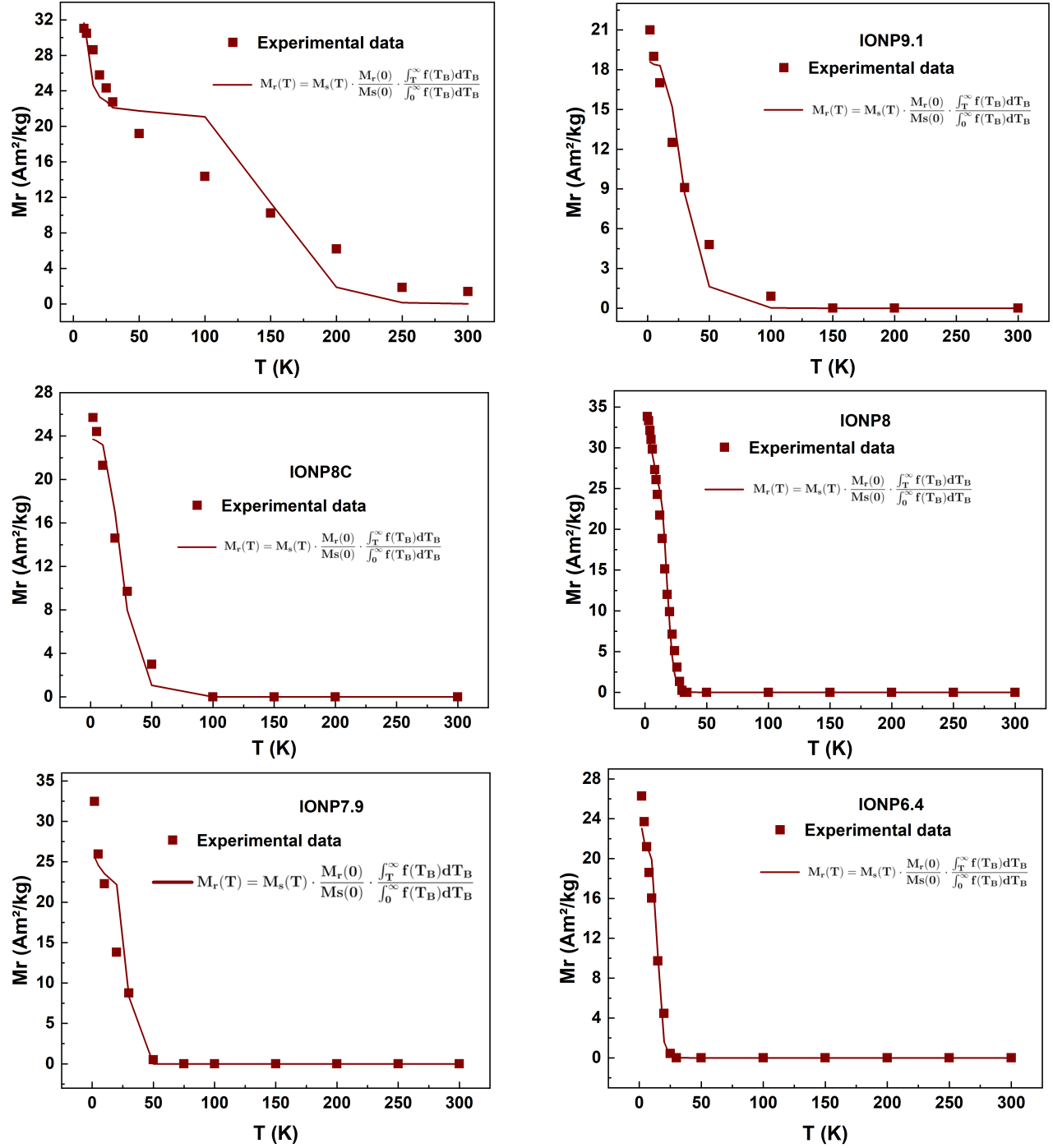


Figure 12: Temperature dependence of the remanent magnetization (M_r) for the pure magnetite samples.

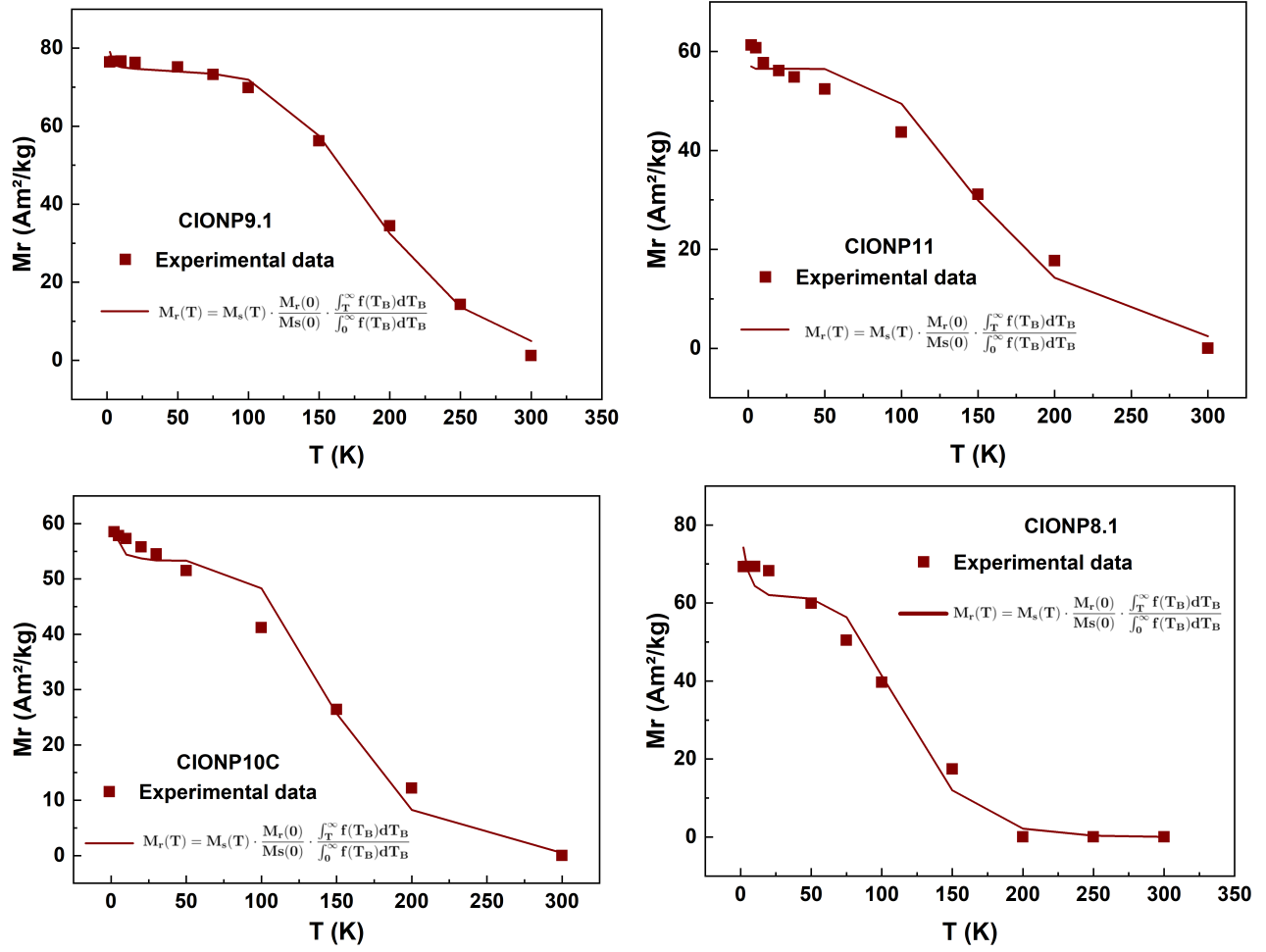


Figure 13: Temperature dependence of the remanent magnetization (M_r) for the Cobalt-doped ferrite samples.

3.7 Actis-Zélis Fits and Results

The approach to saturation model originally proposed by Actis *et al.* was modified to account for hysteretic effects by shifting the expansion point from $H = 0$ to $H = H_C$. Replacing the external field $\mu_0 H$ with the effective field $\mu_0(H - H_C)$ shifts the expansion to the physically relevant saturation regime. This adjustment eliminates systematic errors associated with residual hysteresis in intermediate field regimes, a critical correction for highly anisotropic samples like cobalt ferrites where the applied field is not sufficiently larger than the coercive

field. Furthermore, a linear susceptibility term (χH) was added to account paramagnetic / diamagnetic contributions:

$$M_{FSR}^P(H) = M_s \left[1 - \frac{k_B T}{\langle \mu \rangle \mu_0 (H - H_C)} - \frac{4}{15} \left(\frac{K_{\text{eff}}}{M_s} \right)^2 \frac{1}{(\mu_0 (H - H_C))^2} \right. \\ \left. + \left(\frac{4}{3} \frac{k_B T}{\langle \mu \rangle} - \frac{16}{105} \frac{K_{\text{eff}}}{M_s} \right) \left(\frac{K_{\text{eff}}}{M_s} \right)^2 \frac{1}{(\mu_0 (H - H_C))^3} \right] + \chi H. \quad (9)$$

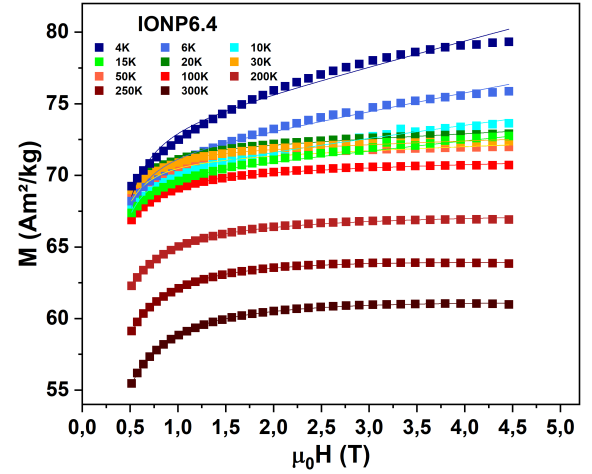
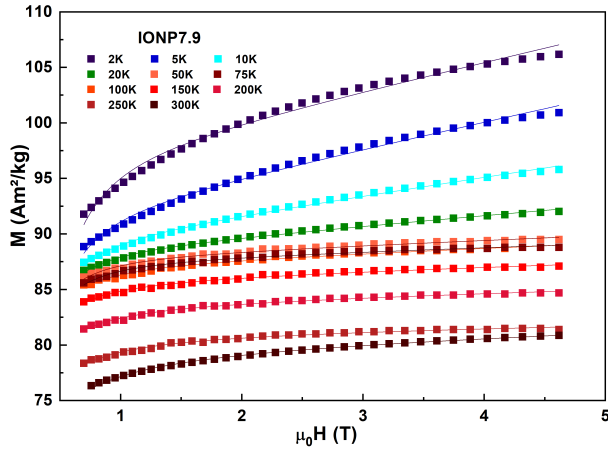
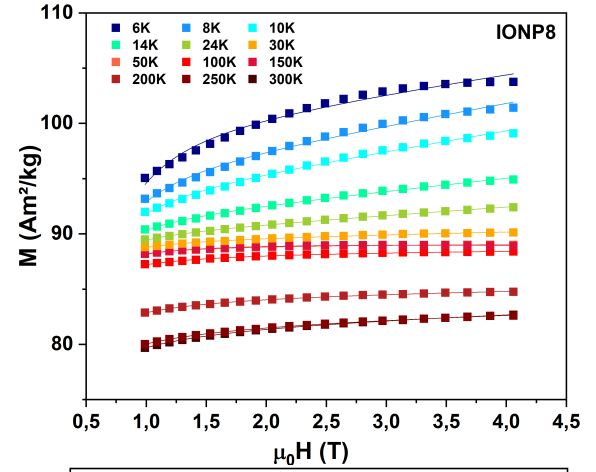
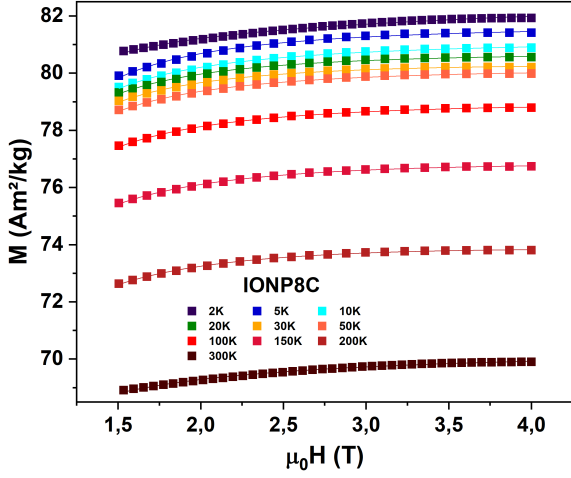
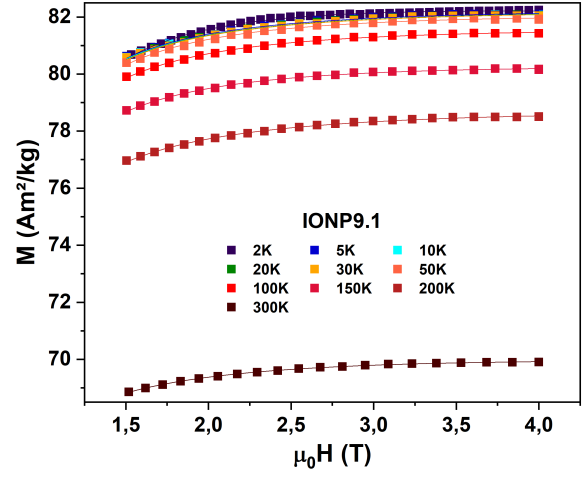
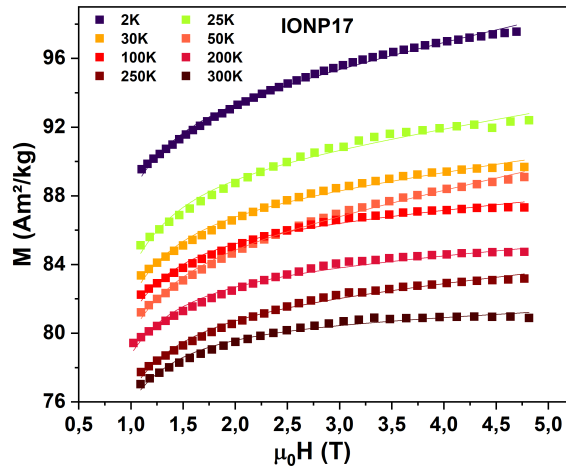


Figure 14: High-field magnetization fits for the pure magnetite samples.

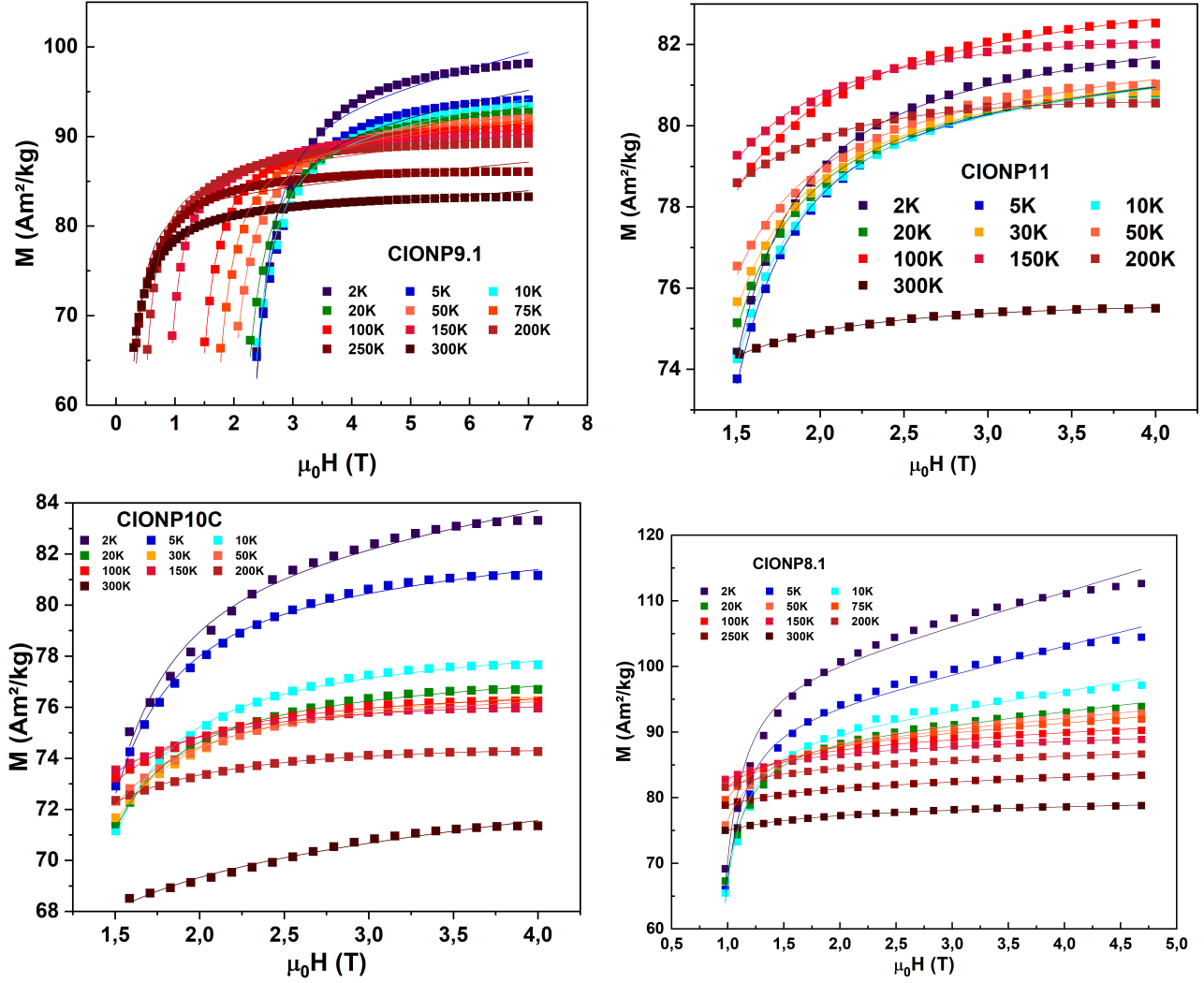


Figure 15: High-field magnetization fits for the Cobalt-doped ferrite samples.

Table 6: Consolidated results of the high-field fit for IONP9.1, IONP8C, CIONP11 and CIONP10C analyzed samples. Uncertainties were rounded according to the standard errors provided by the fits.

Sample	T (K)	K_{eff} (10^4 J/m ³)	$\mu_0 H_C$ (mT)	M_s (A·m ² /kg)
IONP9.1	2	19.6 ± 0.2	23.7	83.29 ± 0.06
	5	17.2 ± 0.3	20.5	82.49 ± 0.09
	10	17.0 ± 0.3	17.2	82.41 ± 0.07
	20	17.3 ± 0.3	11.6	82.50 ± 0.08
	30	17.3 ± 0.3	8.0	82.53 ± 0.09
	50	17.6 ± 0.3	3.8	82.54 ± 0.08
	100	16.9 ± 0.2	0.0	82.13 ± 0.06
	150	16.0 ± 0.2	0.0	81.05 ± 0.05
	200	15.1 ± 0.2	0.0	79.26 ± 0.06
	300	10.0 ± 0.2	0.0	70.97 ± 0.03
IONP8C	2	17.9 ± 0.3	23.7	81.44 ± 0.06
	5	17.0 ± 0.3	21.8	81.71 ± 0.08
	10	15.9 ± 0.3	17.0	81.10 ± 0.06
	20	15.4 ± 0.2	9.8	80.94 ± 0.06
	30	15.4 ± 0.2	5.8	80.75 ± 0.05
	50	15.1 ± 0.2	1.4	80.48 ± 0.05
	100	14.5 ± 0.2	0.0	79.48 ± 0.05
	150	13.3 ± 0.2	0.0	77.70 ± 0.04
	200	11.8 ± 0.2	0.0	75.10 ± 0.03
	300	$7.0 \pm 0.5^*$	0.0	70.85 ± 0.05
CIONP11	2	17.2 ± 0.2	700.4	80.7 ± 0.1
	5	17.4 ± 0.1	689.4	80.1 ± 0.1
	10	17.2 ± 0.2	666.3	80.0 ± 0.1
	20	17.0 ± 0.2	616.8	80.1 ± 0.1
	30	17.0 ± 0.2	573.9	80.1 ± 0.2
	50	17.3 ± 0.3	489.0	80.2 ± 0.2
	100	20.2 ± 0.4	266.0	82.0 ± 0.2
	150	21.4 ± 0.3	107.5	82.9 ± 0.1
	200	19.6 ± 0.2	41.0	81.69 ± 0.07
	300	13.0 ± 0.2	0.0	76.19 ± 0.04
CIONP10C	2	18.8 ± 0.6	708.7	79.8 ± 0.5
	5	18.2 ± 0.3	697.0	79.8 ± 0.2
	10	16.6 ± 0.2	679.4	76.9 ± 0.2
	20	16.0 ± 0.2	624.3	76.1 ± 0.1
	30	15.8 ± 0.2	578.5	75.8 ± 0.2
	50	16.1 ± 0.3	484.6	75.9 ± 0.2
	100	18.8 ± 0.3	244.5	76.7 ± 0.1
	150	19.5 ± 0.3	85.3	76.8 ± 0.1
	200	17.8 ± 0.3	22.2	75.16 ± 0.07
	300	15 ± 1	0.0	69.8 ± 0.4

Table 7: Consolidated results of the high-field fit for IONP6.4, IONP17 and IONP8 analyzed samples. Uncertainties were rounded according to the standard errors provided by the fits.

Sample	T (K)	K_{eff} (10^4 J/m ³)	$\mu_0 H_C$ (mT)	M_s (A·m ² /kg)
IONP6.4	4	7.9 ± 0.4	31.5	72.2 ± 0.3
	6	6.9 ± 0.2	26.1	70.7 ± 0.1
	10	6.5 ± 0.2	16.9	70.0 ± 0.1
	15	6.44 ± 0.01	8.3	69.7 ± 0.1
	20	6.41 ± 0.01	2.6	71.7 ± 0.1
	30	6.32 ± 0.01	0.0	71.6 ± 0.1
	50	6.1 ± 0.1	0.0	71.3 ± 0.1
	100	5.90 ± 0.01	0.0	70.5 ± 0.1
	200	5.23 ± 0.01	0.0	67.4 ± 0.1
	250	5.02 ± 0.01	0.0	65.2 ± 0.2
	300	4.85 ± 0.01	0.0	62.3 ± 0.1
IONP17	2	18.9 ± 0.5	41.7	91.7 ± 0.2
	25	19.4 ± 0.7	24.5	88.1 ± 0.3
	30	18.5 ± 0.5	22.0	86.2 ± 0.2
	50	17.6 ± 0.5	18.4	83.2 ± 0.2
	100	18.1 ± 0.5	11.0	85.2 ± 0.2
	200	16.8 ± 0.5	3.7	82.5 ± 0.2
	250	17.3 ± 0.5	1.0	80.4 ± 0.2
	300	17.2 ± 0.5	0.7	80.2 ± 0.2
IONP8	6	19 ± 1	25.4	98.1 ± 0.5
	8	15.6 ± 0.9	21.9	94.2 ± 0.4
	10	12.9 ± 0.7	18.5	92.3 ± 0.2
	14	10.2 ± 0.5	12.5	90.6 ± 0.1
	24	7.49 ± 0.01	2.6	89.6 ± 0.1
	30	6.89 ± 0.01	0.1	89.4 ± 0.1
	50	6.04 ± 0.01	0.0	89.1 ± 0.1
	100	5.18 ± 0.01	0.0	88.4 ± 0.1
	150	3.04 ± 0.01	0.0	89.9 ± 0.1
	200	2.49 ± 0.02	0.0	84.8 ± 0.1
	250	$2.3 \pm 0.5^*$	0.0	82.3 ± 0.1
	300	$1.0 \pm 0.5^*$	0.0	82.1 ± 0.1

Table 8: Consolidated results of the high-field fit for CIONP8.1, IONP7.9 and CIONP9.1 analyzed samples. Uncertainties were rounded according to the standard errors provided by the fits. In some cases, K_{eff} was kept fixed (*) based on the experimental data to ensure a proper fit.

Sample	T (K)	K_{eff} (10^4 J/m ³)	$\mu_0 H_C$ (mT)	M_s (A·m ² /kg)
CIONP8.1	2	15.8 ± 0.5	613.8	91 ± 1
	5	14.6 ± 0.4	613.4	86.6 ± 0.8
	10	14.5 ± 0.3	599.1	85.3 ± 0.6
	20	15.6 ± 0.2	548.3	85.8 ± 0.3
	50	17.1 ± 0.2	376.3	86.5 ± 0.2
	75	17.1 ± 0.3	257.1	86.8 ± 0.2
	100	17.3 ± 0.3	141.7	87.1 ± 0.2
	150	15.8 ± 0.3	24.5	86.9 ± 0.1
	200	12.5 ± 0.3	3.6	84.89 ± 0.08
	250	10.1 ± 0.3	0.0	81.90 ± 0.07
	300	8.3 ± 0.4	0.0	78.38 ± 0.07
IONP7.9	2	14.5 ± 0.5	30.0	95.2 ± 0.3
	5	11.4 ± 0.4	26.7	90.5 ± 0.2
	10	9.2 ± 0.3	20.5	88.5 ± 0.1
	20	8.4 ± 0.2	10.7	88.1 ± 0.1
	50	7.8 ± 0.3	0.2	87.9 ± 0.1
	75	7.6 ± 0.3	0.0	87.7 ± 0.1
	100	6.6 ± 0.3	0.0	87.4 ± 0.1
	150	4.4 ± 0.4	0.0	86.3 ± 0.1
	200	2.5 ± 0.7	0.0	84.3 ± 0.1
	250	$1.5 \pm 0.5^*$	0.0	81.8 ± 0.1
	300	$1.0 \pm 0.5^*$	0.0	79.9 ± 0.1
CIONP9.1	2	29.7 ± 0.7	1680.0	88.1 ± 0.9
	5	28.9 ± 0.6	1670.0	86.6 ± 0.9
	10	28.7 ± 0.5	1640.0	86.3 ± 0.7
	20	27.9 ± 0.4	1540.0	86.2 ± 0.6
	50	26.6 ± 0.3	1340.0	86.8 ± 0.4
	75	23.7 ± 0.3	1150.0	86.8 ± 0.3
	100	21.2 ± 0.2	930.0	86.6 ± 0.2
	150	17.3 ± 0.2	470.0	86.7 ± 0.2
	200	14.0 ± 0.2	134.0	85.5 ± 0.2
	250	10.5 ± 0.2	22.0	83.3 ± 0.2
	300	8.9 ± 0.1	1.0	81.2 ± 0.2

3.8 $K_{\text{eff}}(T)$ Plots and Fits

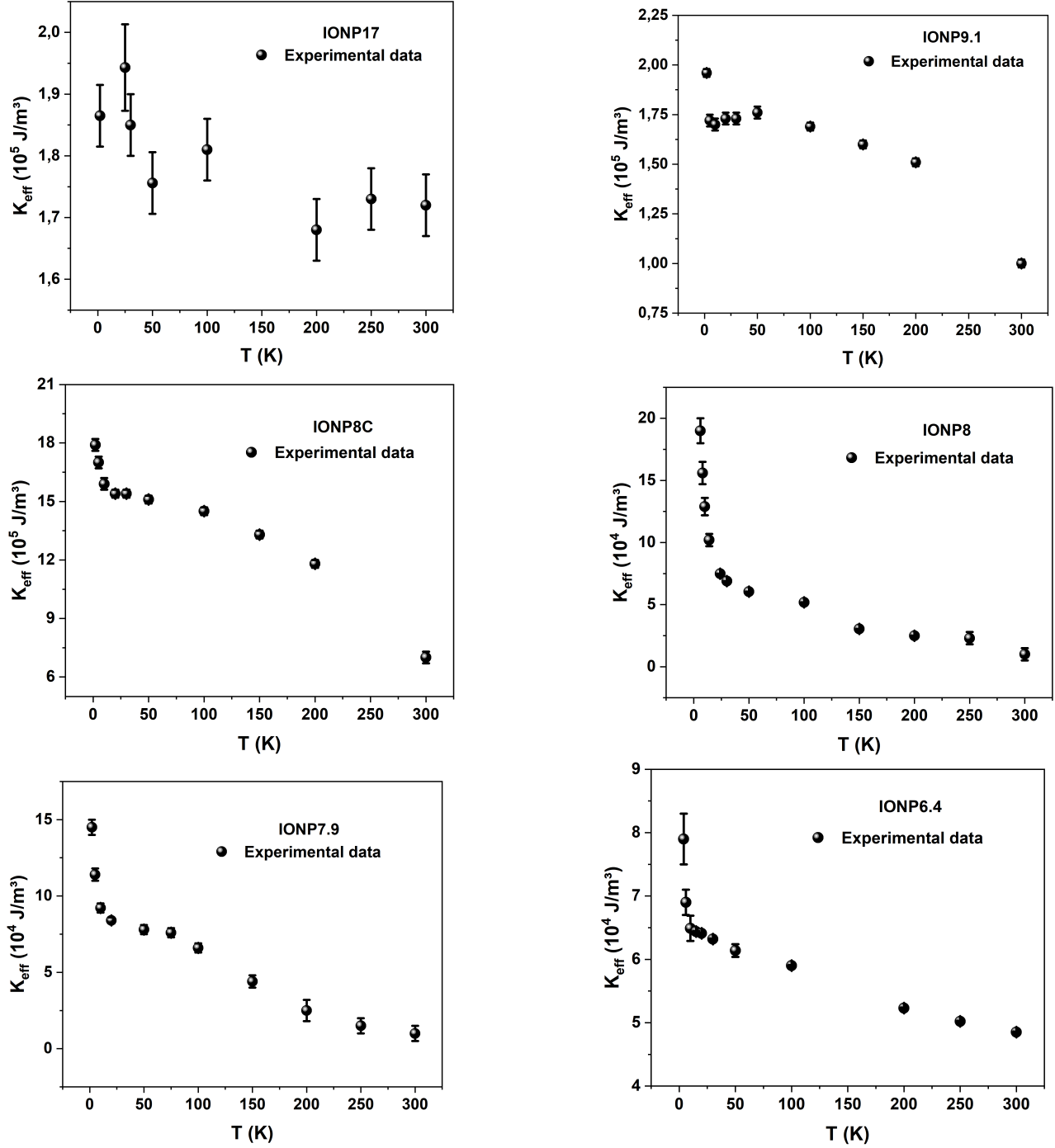


Figure 16: Temperature dependence of the effective anisotropy constant (K_{eff}) for the pure magnetite samples.

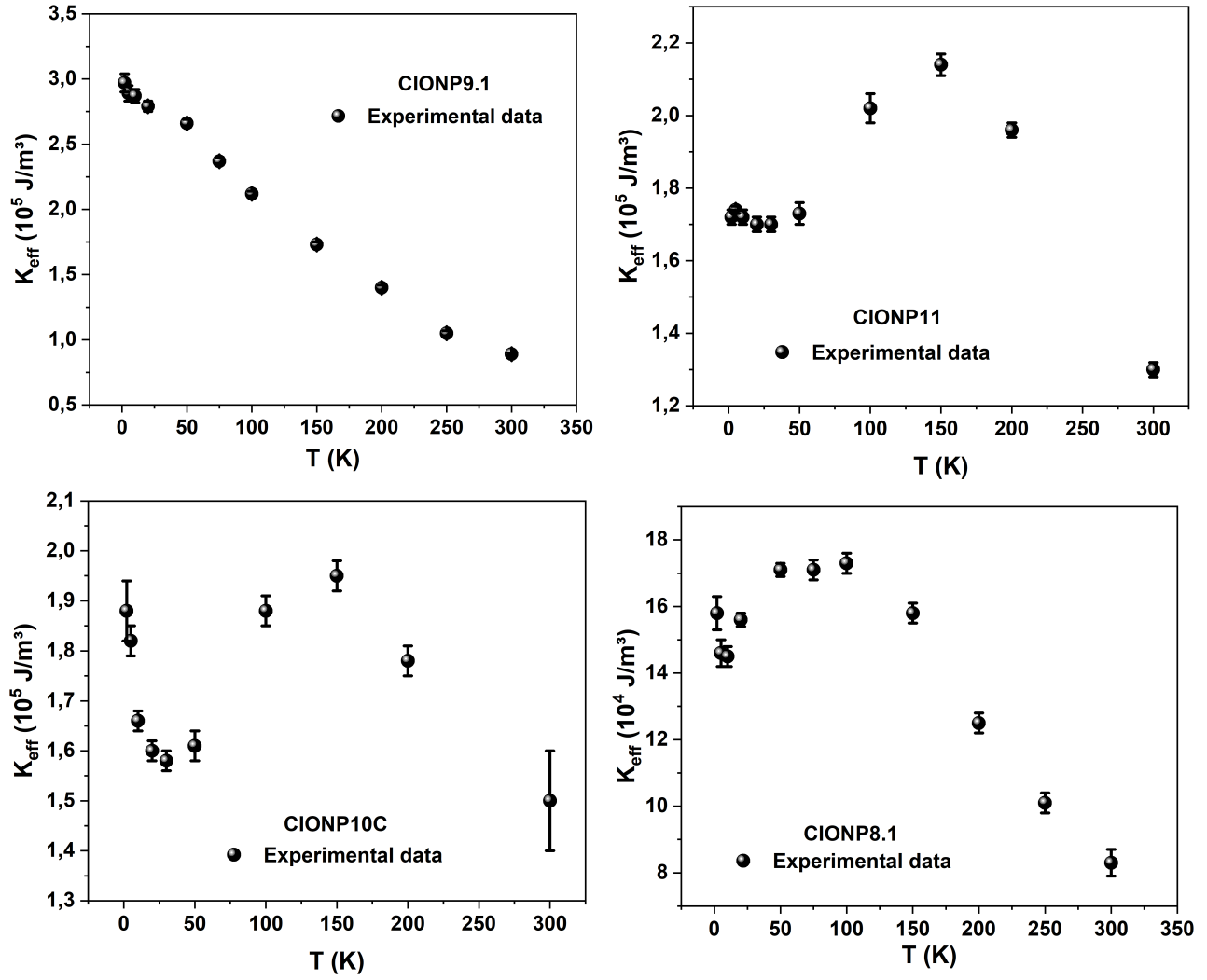


Figure 17: Temperature dependence of the effective anisotropy constant (K_{eff}) for the Cobalt-doped ferrite samples.

3.9 K_{eff} (Ms) Plots and Callen-Callen Fits

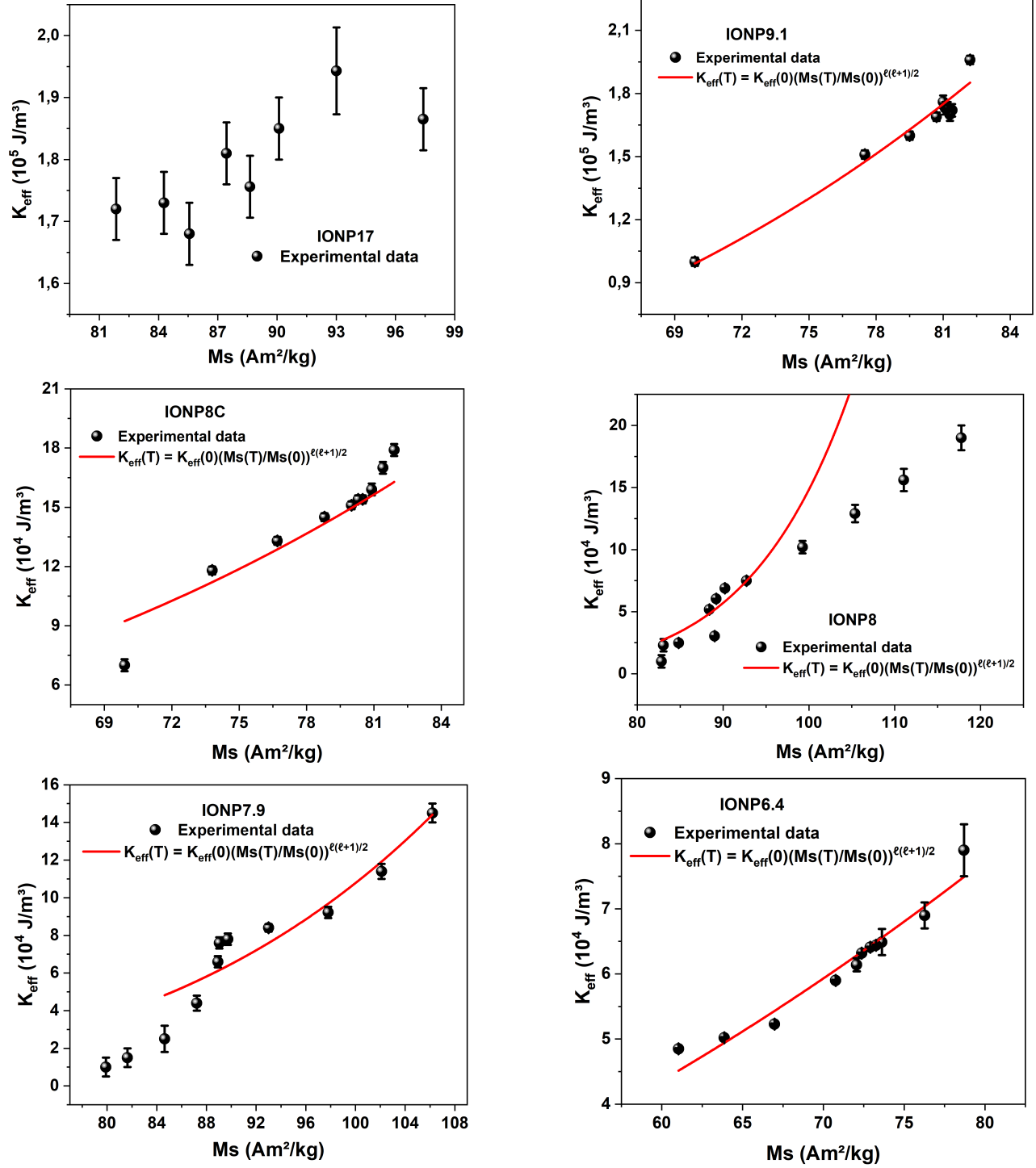


Figure 18: Effective anisotropy constant (K_{eff}) versus saturation magnetization (M_s) fitted with the Callen-Callen power law for the pure magnetite samples.

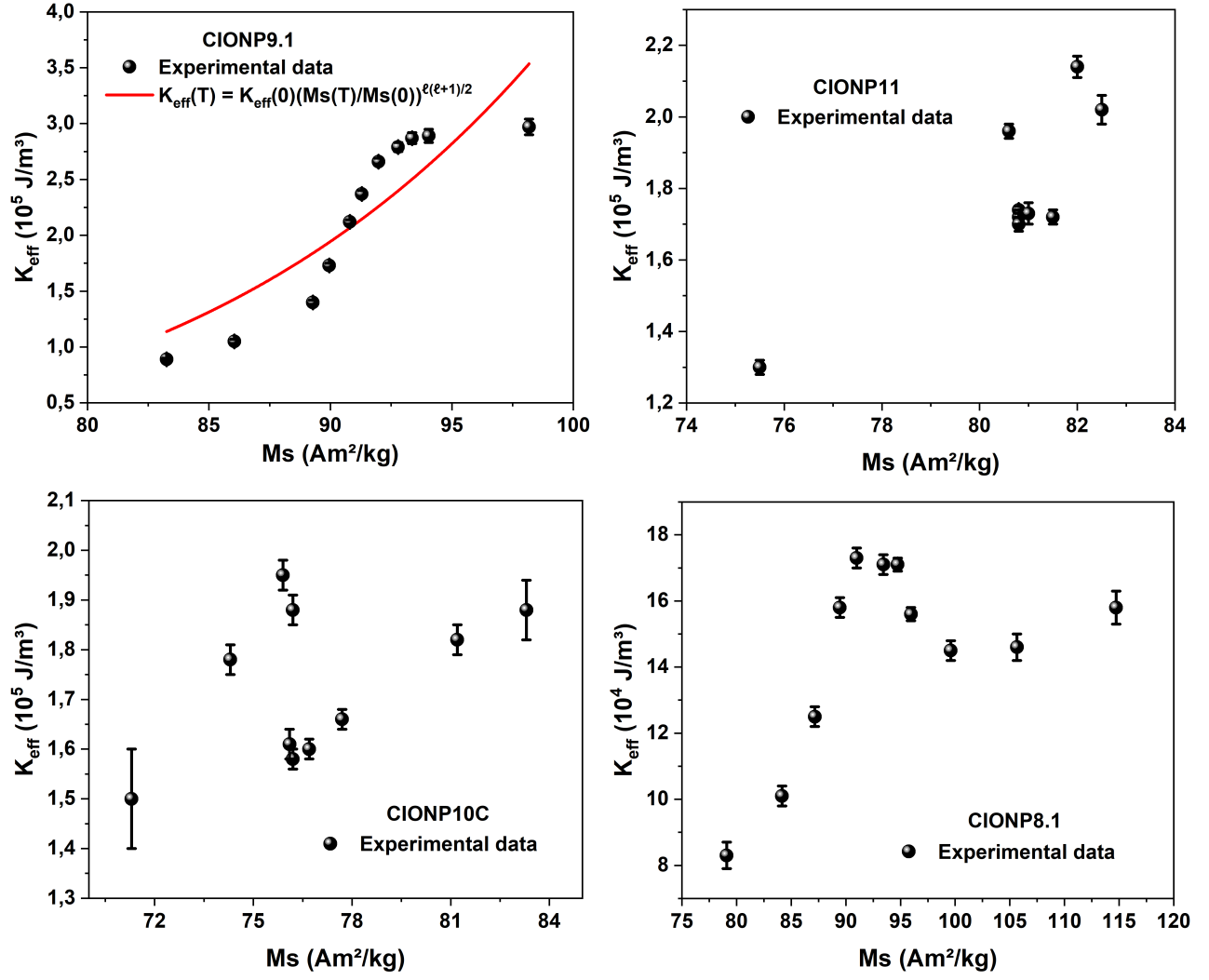


Figure 19: Effective anisotropy constant (K_{eff}) versus saturation magnetization (M_s) fitted with the Callen-Callen power law for the Cobalt-doped ferrite samples.

4 Comparative Tables

Table 9: Comparison between the mean blocking temperatures $\langle T_B \rangle$ obtained from each method for all synthesized samples.

Sample	Mean Blocking Temperature $\langle T_B \rangle$ (K)				
	Néel	Néel $\times 1/T$	Kneller	Generalized H_C	Remanence
IONP17	216	71	194	190	150
IONP9.1	68	33	62	54	29
IONP8C	51	31	51	37	26
IONP8	27	21	27	32	19
IONP7.9	54	31	45	40	25
IONP6.4	25	17	23	27	15
CIONP9.1	254	235	260	283	192
CIONP11	241	197	201	196	153
CIONP10C	220	145	194	173	148
CIONP8.1	160	128	150	140	117

Table 10: Comparison of the effective anisotropy constant (K_{eff}) obtained via different analytical methods. All values are expressed in SI units (10^4J/m^3). For Kneller's law, the reported values correspond to the uniaxial anisotropy assumption ($h_c = 0.479$). The high-field values were extracted at the lowest measured temperatures ($T \leq 6$ K).

Sample	Néel Relaxation		Kneller's Law $H_C(T)$ Fit	Generalized H_C Nunes Model	Remanence $M_r(T)$ Fit	High-Field LAS / Actis Model
	$f(T_B)$	$Tf(T_B)$				
IONP17	1.41	0.46	1.51 ± 0.01	16 ± 7	1.1 ± 0.1	18.9 ± 0.5
IONP9.1	5.98	2.92	1.08 ± 0.02	19 ± 7	2.5 ± 0.2	19.6 ± 0.2
IONP8C	7.15	4.27	1.14 ± 0.04	15 ± 4	3.5 ± 0.2	17.9 ± 0.3
IONP8	3.53	2.69	1.73 ± 0.01	6.1 ± 0.8	2.4 ± 0.1	19 ± 1
IONP7.9	7.26	4.12	1.34 ± 0.01	10 ± 3	3.96 ± 0.03	14.5 ± 0.5
IONP6.4	3.42	2.25	1.41 ± 0.01	4.4 ± 0.4	2.03 ± 0.09	7.9 ± 0.4
CIONP9.1	22.25	20.60	81.5 ± 0.5	31 ± 6	16.9 ± 0.3	29.7 ± 0.7
CIONP11	12.49	10.20	30.8 ± 0.5	38 ± 2	7.9 ± 0.4	17.2 ± 0.2
CIONP10C	15.28	10.10	31.0 ± 0.7	37 ± 7	10.3 ± 0.4	18.8 ± 0.6
CIONP8.1	19.81	15.88	29.2 ± 0.6	50 ± 10	15 ± 2	15.8 ± 0.5

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