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Nanocrystalline alloys: Synthesis and characterization of non-stoichiometric Co_2FeAl nanocrystals

Lana T. Huynh, Stephanie N. Bonvicini, Arthur C. Pinon, and Simon Trudel

Abstract: Non-stoichiometric Co_2FeAl nanoparticles are formed by the in-solution thermal decomposition of the corresponding metal acetylacetonate complexes in the presence of capping ligands, followed by reduction of the obtained material under an H_2 -containing atmosphere. Transmission electron microscopy indicates sub-100 nm nanoparticles are obtained, with reasonable size control. Magnetic measurements indicate that the saturation magnetization, Bloch behaviour, magnetization reversal, spin-wave stiffness, and exchange stiffness are all comparable to those observed for bulk and thin-film Co_2FeAl , indicating these nanomaterials are promising for use in nanoparticle-based spintronic devices.

Key words: magnetic nanoparticles, nanoparticle synthesis, multimetallic nanoparticles, magnetic properties.

Résumé: Des particules fines déviant de la stoechiométrie Co_2FeAl ont été synthétisées par la décomposition de complexes métalliques acétylacétone en présence de molécules surfactantes, suivi de la réduction de cet intermédiaire sous atmosphère d'hydrogène. Des particules de moins de 100 nm sont observées par microscopie électronique à transmission, avec un certain contrôle du diamètre. Les propriétés magnétiques telles que mesurées indiquent que la saturation magnétique, le comportement Bloch, le renversement magnétique et les interactions spin-spin sont comparables à celles du matériau Co_2FeAl , suggérant que ces particules fines peuvent trouver une utilité dans des dispositifs spintroniques.

Mots clés: nanoparticules magnétiques, synthèse de nanoparticules, nanoparticules intermétalliques, propriétés magnétiques.

1. Introduction

Metal alloys, such as cobalt-based ternary alloys with general composition Co_2MZ (where M is a transition metal and Z is a main-group element), are attractive materials due to their high magnetization, potential use in spin-dependent devices, and in some cases, predicted half-metallic properties.¹ The latter property, in particular, has drawn considerable attention to cobalt-based Heusler compounds.^{2,3} The use of half-metallic materials, which is to say that their Fermi level is only occupied by one spin,^{2,3} allows for the maximization of tunneling magnetoresistance ratios in tunneling junction devices, and thus their pursuit is of technological interest.⁴ Amongst the Heusler compounds, Co_2FeAl is of great interest as it has a high Curie temperature of $\sim 1000\text{ K}$,² a low Gilbert damping constant,⁵ and was proven to have high spin polarization in high-performance magnetic tunneling junction devices.^{6,7}

While ternary alloys have been extensively studied in the bulk and thin-film forms,¹⁻³ to date cobalt-based nanocrystalline ternary alloys have only received limited attention.⁸⁻¹²

Nanocrystalline alloys can be used as the active layer in, for example, granular magnetoresistance devices;¹³⁻¹⁶ while such devices are not as performing as fully epitaxial multilayered thin-film stacks,¹⁷ they greatly benefit from ease of processing and greatly lowered cost.

Previous research on the synthesis and characterization of nanoscaled Co_2FeZ ($Z = \text{Ga}, \text{Al}$) alloys have relied on the thermal decomposition of simple metal salts. The first reports on nanoscaled Co_2FeGa ^{8,9} relied on the thermal decomposition of precursor salts impregnated onto fumed silica; a modification of the precursor ratios leads to the formation of Fe_2CoGa nanoparticles.¹⁸ The resulting Co_2FeGa nanoparticles (embedded in silica) attained the L_{21} structure.^{8,19} Similarly, Kumar *et al.* synthesized $\text{Co}_{2.12}\text{Fe}_{1.06}\text{Al}_{0.81}$ nanoparticles by reducing chloride and nitrate salts under hydrogen.¹⁰ Du and co-workers synthesized $\text{Co}_{2.05}\text{Fe}_{1.03}\text{Al}_{0.92}$ nanoparticles via co-precipitation of metal-salt precursors, followed by thermal de-oxidization under reducing atmosphere.¹¹ Both Du and Kumar reported that the nanoparticles were a mixture of B2 and A2 phases.²⁰ It is worth noting that in all these reports⁸⁻¹¹ (as is the case here) the compound is non-stoichiometric and departs to varying degrees from the nominal Co_2FeAl composition. Finally, Philip and coworkers reported on the preparation of Co_2FeAl nanowires *via* an electrospinning route.¹²

In this paper, we take a hybrid approach to form non-stoichiometric Co_2FeAl nanoparticles; metal-oxide 'precursor' nanoparticles are first obtained by adapting the synthesis by Chaubey *et al.*,²¹ followed by reduction through annealing under hydrogen.¹¹ The structure and magnetic properties are then investigated. It is found that despite atomic disordering and non-stoichiometry, the nanoparticles maintain excellent magnetic properties on par with those of bulk Co_2FeAl .

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2. Results and Discussion

2.1. Structural characterization

The as-prepared material isolated after solution synthesis was investigated by means of PXRD, and found to be a metal-oxide product, ostensibly an iron-cobalt-aluminum-containing spinel ferrite (Fig. 1a). The sample could be solvated in hexanes, suggesting the nanocrystals are coated with a capping ligand, *i.e.* oleic acid and oleylamine in this case. In our hands, metallic nanoparticles were never directly obtained as when CoFe nanoparticles were formed;²¹ we attribute this discrepancy to the presence of aluminum in the reaction. The highly oxophilic Al^{3+} ion is not easily reduced under these conditions despite our efforts to work under strictly air-free conditions, leading to an oxide product. The stoichiometric composition is thus determined by charge-balancing; a spinel ferrite with 2:1:1 Co:Fe:Al composition is unlikely, leading to non-stoichiometric Co_2FeAl nanoparticles (*vide infra*).

Fig. 1. (a) X-ray diffractograms for as-synthesized nanoparticles, and nanoparticles following annealing under 10:90 $\text{H}_2:\text{N}_2$ at 500 °C. (b) X-ray diffractograms nanoparticles following annealing under 10:90 $\text{H}_2:\text{N}_2$ at 500, 700, 900, and 1100 °C. Asterisk (*) denotes impurity. In both (a) and (b), the expected pattern for L_{21} -ordered Co_2FeAl is presented.²²

Upon annealing under a reducing atmosphere at 500 °C, all Bragg reflections arising from the spinel phase decreased to the baseline, with the appearance of two new peaks at 2θ ca. 45.0 ° and 65.5 ° (Fig. 1a), assigned to the (220) and (400) Bragg reflections for the Co_2FeAl compound.²³ At this point, the samples could no longer be solvated in hexanes, indicating the capping ligands were likely calcined during the annealing step. For the sample annealed at 500 °C, a cubic unit cell parameter a of 0.5693(2) nm is determined (Table 1 and Fig. 2a), in relatively good agreement with the 0.5730 nm reported for bulk Co_2FeAl .²² We ascribe this discrepancy to

the non-stoichiometric nature of our product, as the composition of this material was determined to be $\text{Co}_{1.2}\text{Fe}_{1.3}\text{Al}_{1.5}$ by means of EDXS (Table 1). Considering confidence in EDXS measurements, it can be stated with certainty all samples are non-stoichiometric (compared to Co_2FeAl), and appear clustered around two distinct compositions (samples prepared at 500 and 900 °C, and 700 and 1100 °C, respectively). A stoichiometric product may be accessible by tuning the ratio of precursors – a strategy often used when forming bimetallic nanoparticles such as CoFe ,^{21,24} Fe_3Si ,²⁵ or MPt ($M = \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$).²⁶ This will be the focus of our future efforts.

The absence of (111) and (200) reflections indicates the material is A_2 -ordered, as these two reflections are characteristic of L_{21} - and B_2 -ordered materials, respectively. It has been reported that annealing Heusler compounds can lead to an improvement in atomic ordering,^{27–30} as such we annealed metal-oxide samples at temperatures of 700 °C, 900 °C, and 1100 °C. As can be seen in Fig. 1b, the (111) and (200) reflections are still not observed after these thermal treatments, indicating the A_2 structure is thermodynamically robust in these nanoscaled non-stoichiometric Co_2FeAl samples. At 1100 °C, the presence of an impurity is observed. In all cases, a is lower than expected for Co_2FeAl , as all samples are seen to be non-stoichiometric (*c.f.* Table 1 and Fig. 2a).

The four annealed samples were examined under a TEM to assess size and morphology (Fig. 3). As can be seen, the samples consist of sub-100 nm nanoparticles; the sample annealed at 500 °C shows a broad size distribution with the majority spanning sizes of 20–80 nm (Fig. 3a), while samples annealed at 700 and 900 °C show much tighter size distributions peaking around 36 and 38 nm (Fig. 3b and c, respectively). Individual nanoparticles could not be resolved for the sample annealed at 1100 °C (Fig. 3d), as such a size distribution could not be determined. The reasonable size monodispersity is believed to be controlled by the nucleation and growth of the metal-oxide precursor, thus opening an approach to size control by modifying precursor, reducing agent, and capping ligand concentration.

It is also worthwhile to note that while the majority of particles imaged were spherical, in some cases cubic nanoparticles were also observed (see Fig. 3e and f for samples annealed at 500 and 900 °C, respectively). This suggests that morphology may be controllable via modifications of the synthetic procedure, *e.g.* by controlling the kinetics of nanoparticle nucleation and growth,³¹ an advantage inherent to the solution-based synthesis employed here. This will be the focus of future work.

2.2. Magnetic characterization

The magnetic properties of the samples were investigated using SQUID magnetometry. For all the magnetic measurements presented here, samples were powdered, and thus the measured magnetic properties represent the average values for an ensemble of randomly oriented nanoparticles. Magnetization vs. magnetic field strength loops were recorded at 1.9 and 300 K (Fig. 4a and b, respectively). In all cases, the magnetization was saturated with a magnetic field strength of 2 T. All samples showed hysteresis up to room temperature, which is surprising for nanoscaled materials for whom superparamagnetic behavior may be expected.

Fig. 4c shows the low-field region of the $M(\mu_0 H)$ measurements at 300 K. The magnetization reversal is seen to

Table 1. Cubic lattice parameter a , EDXS-determined composition, and TEM diameter of annealed samples

T_{anneal} (°C)	a (nm)	EDXS Composition	TEM diameter (nm)
500	0.5693(2)	Co _{1.2} Fe _{1.3} Al _{1.5}	20-80
700	0.5693(2)	Co _{1.6} Fe _{1.8} Al _{0.6}	30
900	0.57019(13)	Co _{1.4} Fe _{1.3} Al _{1.4}	30
1100	0.57097(14)	Co _{1.8} Fe _{1.6} Al _{0.6}	— ^a
bulk ^b	0.5730	Co ₂ FeAl	—

^a Sintering prevents determination of individual sizes.^b Elmers et al.²²

diverge from a coherent rotation process for an ensemble of nanoparticles;³² indeed this multi-step reversal is reminiscent of such behavior observed in single-crystal epitaxial films,^{28,33–38} where a complex energy landscape through magnetization reversal – arising from combined cubic and uniaxial anisotropies – is invoked. In some cases where samples were grown on III-V semiconductor substrates, the uniaxial anisotropy was *e.g.* interpreted to stem from the anisotropy of surface dangling bonds;³⁹ this explanation is however implausible for MgO substrates^{28,35,36,40} and unsupported nanoparticles studied here. As such, we suggest this behavior is intrinsic to the Co₂FeAl compound, though the origin of this anisotropy is still debated. For non-stoichiometric Co₂MnGe epitaxial thin films on MgO, it was suggested that the non-stoichiometry could be at play⁴⁰ – a possibility for the present samples. As the samples studied here are ensembles of randomly oriented nanoparticles, several such magnetization steps are observed.

The saturation magnetization M_s is seen to increase with annealing temperature, from 110 to 148 emu g^{−1} at 1.9 K (see Table 2 and Fig. 2b). These M_s values translate to values of 4.0 to 5.3 μ_B/fu ; this is close to the expected M_s of 5 μ_B/fu expected from Slater-Pauling behavior^{41,42} and the 138 emu g^{−1} observed at 300 K for Co₂FeAl⁴³. These discrepancies can be ascribed to two factors. Firstly, it is well-known that the surfaces of magnetic materials can exhibit reduced magnetization, due to surfaces and break of symmetry at the nanoparticle's surface; similar trends have been seen for Heusler films where the M_s for Co₂FeAl is seen to be reduced from the expected value^{28,44,45}. Additionally, the materials reported here are non-stoichiometric; this can have the double effect of producing an electronic structure diverging from half-metallic behavior,⁴⁶ hence deviating from the expected 5 μ_B/fu . Nonetheless, these materials show high magnetization close to those expected of Co₂FeAl. When compared to $M_s = 192$ emu g^{−1} for CoFe nanoparticles,²⁴ the lower magnetization is expected due to the presence of non-magnetic aluminum. It is worth noting that the high magnetization obtained for these nanoparticles also opens up the possibility of using them as magnetic resonance imaging contrast agents.^{24,47}

When comparing the M_s between samples at 1.9 and 300 K, it is apparent that the magnetization is very stable against temperature. To probe this further, we measured M_s as a function of temperature in the 1.9 - 400 K range (Fig. 4d). The M_s is seen to follow Bloch's $T^{3/2}$ law

$$M_s(T) = M_s^{0K} \left(1 - \mathcal{B}T^{3/2}\right) \quad [1]$$

in which the decrease of M_s as a function of increasing temperature is a result of the thermal population of magnons.⁴⁸ The lines in Fig. 4d are fits to Eqn. 1. The extracted parameter $\mathcal{B}$ is defined as

$$\mathcal{B} = 2.612 \frac{a^3}{16 \langle S \rangle} \left(\frac{k_B}{4\pi D} \right)^{3/2} \quad [2]$$

where $\langle S \rangle = M_s/(8\mu_B)$ is the average spin per atom (using M_s in μ_B/fu), $\frac{a^3}{16}$ is the atomic volume, k_B is Boltzmann's constant, and D is the spin wave stiffness.⁴⁹ The determined values of $\mathcal{B}$ are presented in Fig. 2c and listed in Table 2. $\mathcal{B}$ is a technologically relevant parameter in spintronic devices, where the key figure of merit is the spin polarization of the ferromagnetic electrodes.⁵⁰ There is a known proportionality between the spin polarization P and M_s ,

$$\frac{P(T)}{P^{0K}} \propto \frac{M_s(T)}{M_s^{0K}} \quad [3]$$

leading to a Bloch-like behavior of the spin polarization as a function of temperature,

$$P(T) = P^{0K} \left(1 - \mathcal{A}T^{3/2}\right). \quad [4]$$

A low value of $\mathcal{B}$ is thus preferred, leading to a weak temperature dependence of the spin polarization. The values of $\mathcal{B}$ reported here are on-par with Heusler compounds such as Co₂MnSi and Co₂FeAl, as well as relevant alloys such as CoFe.²

The spin-wave stiffness D can be estimated from the determination of $\mathcal{B}$ via Eqn. 2. The determined values (see Table 2 and Fig. 2d) are again in good agreement with those reported for ferromagnetic metals such as hcp Co, fcc Ni,² Heusler compounds, and in particular Co₂FeAl_{0.5}Si_{0.5},²⁸ Co₂MnGe,⁴⁰ and Co₂FeAl⁴⁵ (for which $D = 3.25 \sim 5.00, 3.8$, and 3.7 meV nm², respectively; these values were determined by Brillouin light scattering on epitaxial thin films).

Finally, the exchange stiffness A can be determined from

Fig. 2. Summary of measured and determined unit cell parameter (a), saturation magnetization (b), Bloch parameter B (c), spin wave stiffness (d), and exchange stiffness (e) as a function of annealing temperature. In all panels, the horizontal dotted line represents the bulk value for Co_2FeAl , and all other lines are guides to the eyes.

$$A = \frac{DM_{\text{sat}}}{2g\mu_B} \quad [5]$$

Fig. 3. Transmission electron micrographs and associated size distributions for samples annealed at (a) 500 $^{\circ}\text{C}$, (b) 700 $^{\circ}\text{C}$, (c) 900 $^{\circ}\text{C}$. (d) micrograph for sample annealed at 1100 $^{\circ}\text{C}$. (e) and (f) show cubic nanocrystals observed for samples annealed at 500 and 900 $^{\circ}\text{C}$, respectively.

The estimated values presented in Table 2 and Fig. 2e range from 13.2 to 19.6 pJ m^{-1} ; again, these are in good agreement with the reported value of 15.5 pJ m^{-1} for Co_2FeAl .⁴⁵

The magnetization of the nanocrystalline samples were examined under FC and ZFC conditions (Fig. 5). In a typical superparamagnetic sample, a transition from blocked to superparamagnetic behavior is observed, with the clear identification of a blocking temperature T_B , where the two FC/ZFC measurements converge and above which the magnetization is

T_{anneal} (°C)	M_s , 1.9 K (emu g ⁻¹) [(μ_B /fu)]	$\mu_0 H_c$, 1.9 K (mT)	B (10 ⁻⁶ K ^{-3/2})	D (meV nm ²)	A (pJ m ⁻¹)
500	110 [4.0(3)]	80	4.6(3)	3.8	13.2
700	127 [4.6(2)]	20	3.23(19)	4.4	17.5
900	140 [5.0(2)]	20	2.86(16)	4.5	19.6
1100	148 [5.3(3)]	10	3.52(8)	3.8	17.3
bulk	[4.96] ^a	—	3.76 ^b	3.7(1) ^c	15.5(5) ^c

^a Buschow et al.⁴³; ^b Trudel et al.²; ^c Gaier et al.⁴⁵

Table 2. Magnetic properties of annealed samples

Fig. 4. Measured magnetization versus field strength curves for all powdered samples at (a) 1.9 K and (b) 300 K. (c) Normalized magnetization M / M_s close to remanence shows complex magnetization reversal behavior. (d) Saturation magnetization as a function of temperature. Lines are fits to the Bloch $T^{-3/2}$ law (Eqn. 1).

seen to decrease as temperature is further increased.¹⁷ The behavior observed in our samples deviates from typical superparamagnetism. First, the magnetization for all the FC curves is very stable over the temperature range studied here, which is consistent with the results of Fig. 4d. This would indicate the

blocking temperature is above 400 K in these samples, with samples annealed at 500 and 1100 °C hinting the blocking temperature may be close to 400 K. The effective anisotropy constant K_{eff} can be evaluated as

$$K_{\text{eff}} \approx 25 \frac{k_B T_B}{V}$$

(V being the nanoparticle's volume);¹⁷ this estimate provides a value $K_{\text{eff}} \geq 1.2 \text{ kJ m}^{-3}$, which is consistent with values for Heusler compounds such as $\text{Co}_2\text{Cr}_{0.6}\text{Fe}_{0.4}\text{Al}$;^{2,35} for which values between 1.1 and 3.7 kJ m^{-3} are reported. Given the size distributions observed, it may have been expected a fraction of the sample ensemble show superparamagnetic behaviour, which is not what we observed. As such we emphasize this effective anisotropy constant is likely an absolute lower limit. Additionally, abrupt jumps in the magnetization are observed, which is again not consistent with superparamagnetic behavior where smooth changes are observed. As discussed above, a complex magnetization reversal behavior is observed, which is inconsistent with coherent magnetization reversal of the nanoparticles' moment. A plausible explanation for the abrupt changes in the FC/ZFC curves is the sudden depinning of the nanoparticle's moment from along certain local magnetic easy axes to allow it to align with the applied magnetic field; this depinning is made possible by thermal excitation as the sample is warmed. As the changes are significant in magnitude, it may be inferred that dipolar interactions allow many local nanoparticles to reorient their magnetization in a single event.^{51,52}

3. Conclusion

To summarize our work: sub-100 nm, A2-ordered non-stoichiometric Co_2FeAl nanoparticles were formed by the solution-based synthesis of metal-oxide precursor nanoparticles followed by reduction under H_2 -containing atmosphere. Extensive magnetic measurements show the nanoparticles do not behave superparamagnetically; rather the body of magnetic properties characterized here (saturation magnetization, Bloch behavior, magnetization reversal) are reminiscent of bulk or thin-film Co_2FeAl . This suggests these nanomaterials are promising for use in nanoparticle-based spintronic devices. Our future work, building on the synthetic approaches established in this report, will probe this question, and establish whether high spin polarization is indeed conserved in these nanoscaled Co_2FeAl materials.

Fig. 5. Measured magnetization versus temperature for powdered samples cooled in the absence (ZFC, empty symbols) or presence (FC, filled symbols) of a 10 mT field. All measurements done under an applied field strength of 10 mT. Apart from the sample annealed at 500 °C, samples exhibit complex behavior that cannot be explained by conventional superparamagnetic behavior.

4. Methods

Materials. Cobalt(II) acetylacetonate ($\text{Co}(\text{acac})_2$), iron(III) acetylacetonate ($\text{Fe}(\text{acac})_3$, 99%), aluminum(III) acetylacetonate ($\text{Al}(\text{acac})_3$, 99%, sublimed), 1,2-hexadecanediol (technical grade, 90%), oleic acid (technical grade, 90%) and oleylamine (technical grade, 90%) were all purchased from Sigma-Aldrich. Oleic acid and oleylamine were degassed using standard freeze-pump-thaw methods; all chemicals were used as received.

Synthesis. The synthesis was carried out using standard air-free Schlenk-line techniques. The reaction flask was heated with a J-KEM Scientific Gemini PID temperature controller. A 2:1:1 molar ratio of precursors ($\text{Co}(\text{acac})_2$: 0.775 g, 3 mmol); $\text{Fe}(\text{acac})_3$: 0.521 g, 1.5 mmol; $\text{Al}(\text{acac})_3$: 0.476 g, 1.5 mmol) was mixed with 1,2-hexadecanediol (1.872 g, 7.2 mmol), in a mixture of previously degassed oleic acid (4.8 mL) and oleylamine (5.1 mL). The reaction flask was degassed under 93:7 Ar/H_2 for 20 min at room temperature. The reaction was then warmed to 100 °C at 3.75 °C/min, and maintained at this temperature for 10 minutes. The temperature was then raised at 4.5 °C/min to reflux and maintained there for 2 hours, after which heating was removed and the flask cooled to room temperature. The black product was exposed to air, dissolved in 10 mL of hexanes, and 40 mL of absolute ethanol were added. The mixture was centrifuged (6000 rpm, 10 min) and the mother liquor decanted and discarded. This washing process was repeated four times. Finally, the nanoparticles were suspended in hexanes, spread in a watch glass and air-dried at room temperature. The oily product was collected and stored in a glove box maintained under inert atmosphere until further use.

Annealing. The following steps were carried out under a constant flow of 90:10 N_2/H_2 in a ThermoScientific Lindberg Blue M tube furnace. The oily product was placed in an alumina crucible and mounted in a quartz tube affixed in the furnace. The sample was flushed for 20 minutes, heated to 300 °C at a rate of 10 °C/min, and then to the final annealing temperature at a rate of 5 °C/min. The final temperature was maintained for 30 min, and the sample cooled back to room temperature. A dry, black powder was collected; this solid was no longer soluble in hexanes or any other solvent.

Transmission electron microscopy (TEM). TEM imaging was performed with a Hitachi H7650 microscope operated at 60 kV. Powdered sample was dispersed in ethanol; this dispersion was drop-cast onto a carbon-coated copper grid (Ted Pella) and dried in air. Images were analyzed using ImageJ.⁵³

Powder x-ray diffraction (PXRD). A Bruker D8 Advance powder diffractometer ($\text{Cu K}\alpha = 1.5406 \text{ \AA}$, 40 kV, 40 mA) was used for phase identification. The sample was suspended in hexanes and smeared on a glass mount. Intensity was measured in the $2\theta = 10\text{--}80^\circ$ range, with a step size of 0.05° per 9 seconds.

Energy dispersive x-ray spectroscopy (EDXS). A Zeiss SigmaVP field-emission scanning electron microscope operated at 20 kV equipped with an Oxford INCA EDXS unit was used to determine the composition of the nanoparticles. Samples were prepared by dropping *ca.* 5 mg of powder onto double-sided adhesive conductive carbon tape, which was fixed on standard aluminum stubs.

Superconducting quantum interference device (SQUID) magnetometry. Magnetic properties of the samples were measured using a Quantum Design XL-7S MPMS. Samples were prepared by placing a weighed quantity of powdered sample into a gelatin capsule, which was inserted in a clear, diamagnetic straw. $M(\mu_0 H)$ measurements were conducted at temperatures of 1.9 and 300 K in a maximal field strength of 2 T. $M_s(T)$ measurements were measured in the $T = 1.9\text{--}400 \text{ K}$ range under a field strength of 2 T, after the sample had been cooled in the absence of a magnetic field. Zero-field-cooled (ZFC) magnetization of the sample was measured between temperatures of 1.9 and 400 K in a field of 10 mT, after the sample had been cooled in the absence of a magnetic field. Field-cooled (FC) measurements were done as for the ZFC measurements, with the difference that the sample was cooled from 400 K in the presence of a 10 mT field.

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