

Crystalline Order Effects on the Magnetic Properties of Superlattices made of Cobalt Nanocrystals

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Abstract. We present the magnetic property evolution in long-range ordered fcc supracrystals of Co nanocrystals (NCs) induced mainly by nanocrystallinity. By increasing the nanocrystalline order of individual NCs, ac susceptibility measurements indicate a significant increase in the ‘interaction-to-anisotropy’ energy ratio, a trend favourable for the formation of SFM state in these 3D supracrystals.

1. Introduction

Materials based on magnetic nanocrystals (NCs) have been exploited in various applications such as ultra-high density magnetic information storage, magnetic sensors, and biomedical field [1] for the last few decades. Interestingly, there remain many questions related to the fundamental ‘magnetism’ of nanoparticles, and we continue to discover their new properties.

Interacting, single-domain magnetic NCs are known to undergo a superparamagnetic (SPM)-to-superspin glass (SSG) transition at sufficiently high concentrations [2]. By further increasing the inter-particle interaction, creating of a long-range ordered state; *i.e.*, superferromagnetic (SFM) state is said to be possible. Together, these magnetic states created by magnetic nanoparticles now form a new branch of magnetism called "Supermagnetism" [3]. Previously, we reported SSG-like magnetic properties of 3D supracrystals characterized by long-range face-centered cubic (fcc) ordering, made of low anisotropy 8 nm-Co NCs [4]. In this paper, we investigate the effect of nanocrystalline order of Co NCs (from almost amorphous to single-domain hcp) on the onset of SSG state in long-range ordered fcc supracrystals.

2. Experimental Section

2.1. Synthesis of cobalt nanocrystals and elaboration of supracrystals

All materials were used without further purification: cobalt acetate, dodecanoic acid, sodium borohydride are from Aldrich, iso-octane and hexane from Fluka, and sodium di(ethylhexyl) sulfosuccinate (NaAOT) from Sigma. The synthesis of cobalt(II) bis(2-ethylhexyl)sulfosuccinate, (Co(AOT)₂) was described previously [5]. Cobalt nanoparticles are synthesized by soft chemical reduction in reverse micelles under a N₂ atmosphere. The resulting spherical Co NCs, (7.4 nm in



diameter) are coated with dodecanoic acid and has a 9.4 % size distribution (*i.e.* 68% of NCs have diameters equal to $7.4 \text{ nm} \pm 0.7 \text{ nm}$). As synthesized, Co NCs possess highly disordered polycrystalline structure, with individual crystalline domains (typical size $\leq 1 \text{ nm}$) showing a likely fcc organization. The electronic diffraction pattern of as-synthesized Co NCs reveals (not shown here) two diffuse rings indicating a very low crystallinity. To form 3D supracrystals, a Highly Oriented Pyrolytic Graphite substrate ($10 \times 5 \text{ mm}^2$) is immersed horizontally in a colloidal solution of Co NCs dispersed in hexane. The solvent is then slowly evaporated at room temperature under N_2 . The end product is 3D superlattices composed of a few hundred layers of Co NCs [6]. GISAXS study indicates that these supracrystals, mainly found at the border of the substrate, are characterized by long-range fcc mesoscopic order. The corresponding structural parameters: the stacking periodicity, the centre-to-centre interparticle distance (D_{c-c}) and the edge-to-edge interparticle distance (D_{i-p}) are found in Table 1 in the following section. After deposition, the 3D supracrystals are placed in a closed quartz capsule with a N_2 atmosphere and annealed at various temperatures (220, 250 and 350 °C) for 15 min. These samples are named; Native, S220, S250 and S350, respectively.

3. Results and Discussions

3.1. Nanocrystallinity and supracrystallinity evolution due to annealing

The annealing performed up to 220 °C does not impact the various mesoscopic organizations and thus structural parameters remain unchanged. The electronic diffraction pattern does not reveal any detectable nano-crystallographic transition compared to the native state. Conversely, annealing at 250 °C and higher induces significant improvement of the nanocrystallinity of NCs. In S250 sample, the diffraction pattern shows the coexistence of the (111) diffuse ring of likely fcc-Co and 5 diffuse rings (weaker in intensity) corresponding to 5 planes belonging to the Co hcp phase, indicating a clear structural transition from poorly crystallized fcc- to hcp-Co polycrystals having various coherence lengths. At the highest temperature (350 °C), the electronic diffraction and the HRTEM studies revealed predominantly hcp-single-crystalline NCs [7]. The GISAXS patterns shows that the fcc mesoscopic order of 3D supracrystals keep their integrity without coalescence at all annealing temperatures, although they become slightly *dense* with increasing temperature. This behavior, which is attributed to a decrease in D_{i-p} due to heating, is related to the supracrystal coherence length increase. The key supracrystalline structural parameter evolutions are listed in Table 1.

Table 1 : Supracrystal structural parameters

	Native	220 °C	250 °C	350 °C
(111) Stacking periodicity (nm)	8.49	8.49	8.32	8.00
Center-to-Center dist. D_{c-c} (nm)	10.4	10.4	10.2	9.8
Inter-particle distance, D_{i-p} (nm)	3	3	2.8	2.4

3.2. Magnetization Studies.

The nanocrystallinity effect was clearly seen in the magnetic behavior of supracrystals. As depicted in Figure 1 (left), the transition temperature T_c , defined as the position of zero-field-cooled (ZFC) magnetization peak, increases from 110 K (Native) to 290 K (S350) [7] passing through a minimum value of 102 K (S220). The ac susceptibility as a function of temperature and frequency showed usual ‘critical slowing down’ behavior signaling the existence of collective states below T_c in all samples (not shown). Using the Vogel-Fulcher model [8] for weakly-interacting systems, the particle anisotropy energy E_a and the effective temperature T_o (related to the interaction energy between NCs) are extracted. The anisotropy energy was found to increase from about 1360 to 1700 K, again exhibiting an anomalous behavior for the S220 (Figure 1 Right).

It has previously been suggested that at low annealing temperatures, where the re-crystallization is barely initiated, nanocrystalline structure become highly heterogeneous among NCs. The anomalous

behavior as well as the broad ZFC-peak and a relatively high ZFC magnetization at the lowest temperature observed in S220 sample here are most likely due to such structural inhomogeneity among NCs [9]. Furthermore, the notion of ‘average’ values of E_a and T_o determined using the V-F law may no longer be valid in S220. As a general trend; however, we remark that the value of T_o , related to the dipolar interaction energy, grows much faster than the anisotropy energy; *i.e.*, E_a grows by mere 25% from Native to S350, whereas a nearly 400% gain was observed in T_o values between the two samples (from 53 K to 237 K). This can be partially explained by the reduced interparticle distance between NCs, the S350 sample in particular, that enhances the dipolar interactions among them (*cf.* Table 1). Thus the ‘interaction-to-anisotropy’ energy ratio becomes larger with improved nanocrystallinity, a condition favorable for the formation of a dipolar SFM state [3][10].

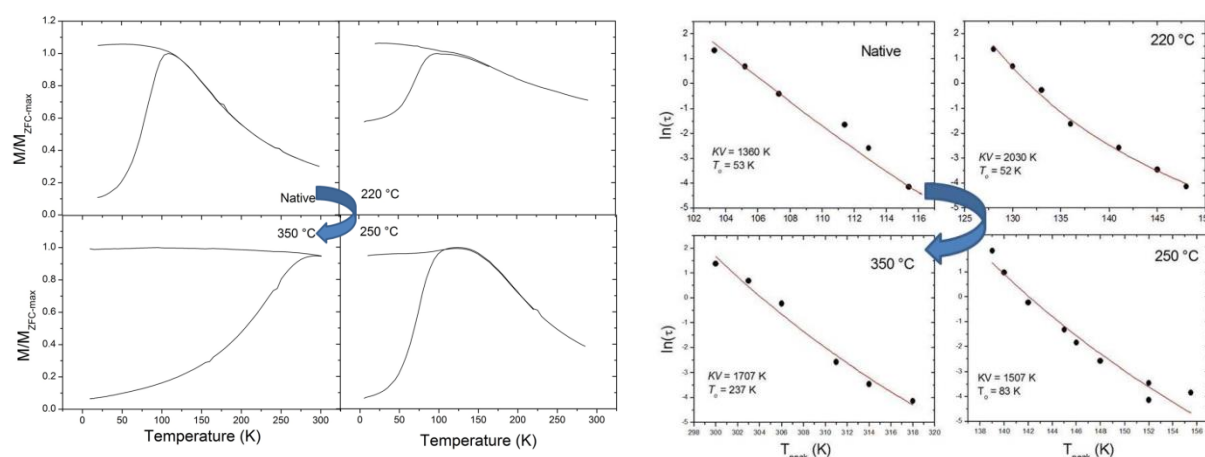


Figure 1: (left) ZFC/FC magnetization (normalized) measurements of Native, S220, S250 and S350 samples, presented clockwise from top left. All measurements were taken under an applied magnetic field of 10 Oe. (right) Evolution of frequency dependent transition (or collective blocking) temperature of all four samples. τ is the inverse of applied ac field frequency f ($\tau = 1/2\pi f$) and T_{peak} is the temperature at which in-phase ac-susceptibility attains the maximum value at a given frequency. Solid lines are fits to the V-F law.

4. Summary

Within long-range ordered 3D fcc supracrystals made of Co nanocrystals, the nanocrystalline order combined with the mesoscopic order was found to influence both the NC anisotropy energy (E_a) as well as the interaction energy ($\sim T_o$) with T_o growing much faster than E_a . Further increase in interaction energy may result in the creation of a superferromagnetic state in 3D supracrystals.

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