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Growth-induced non-planar magnetic anisotropy in FeCoZr-CaF₂ nanogranular films: Structural and magnetic characterization

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The relation between nanoscale structure, local atomic order and magnetic properties of (FeCoZr)_x(CaF₂)_{100-x} (29 ≤ *x* ≤ 73 at. %) granular films is studied as a function of metal/insulator fraction ratio. The films of a thickness of 1–6 μm were deposited on Al-foils and glass-ceramic substrates, by ion sputtering of targets of different metal/insulator contents. Structural characterization with X-ray and electron diffraction as well as transmission electron microscopy revealed that the films are composed of isolated nanocrystalline *bcc* α-FeCo(Zr) alloy and insulating *fcc* CaF₂ matrix. They grow in a columnar structure, where elongated metallic nanograins are arranged on top of each other within the columns almost normal to the substrate surface. Mössbauer spectroscopy and magnetometry results indicate that their easy magnetization axes are oriented at an angle of 65°–74° to the surface in films with *x* between 46 and 74, above the electrical percolation threshold, which is attributed to the growth-induced shape anisotropy. Interatomic distances characteristic for metallic state of α-FeCo(Zr) nanograins were revealed by X-ray Absorption Spectroscopy. The results show a lack of surface oxidation of the alloy nanograins, so the growth-induced orientation of nanograins in the films cannot be attributed to this effect. The study is among the first to report a growth-induced non-planar magnetic anisotropy in metal/insulator granular films above the percolation threshold and to reveal the origin of it. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4891016>]

I. INTRODUCTION

Patterned nanostructured films with non-planar, i.e., perpendicular, magnetic anisotropy of oriented nanogranules or nanoarrays, are considered as promising materials for high density recording media,^{1,2} magnetic fields distribution sensors, and magnetic tunnel junctions.³ Among the recently reported methods of preparation of magnetically oriented planar structures are the template-assisted synthesis of magnetic nanoarrays with shape anisotropy^{4–6} and formation of Pt, Pd-3d metal compounds with *L*₁₀ structure exhibiting a high magnetocrystalline anisotropy.⁷

Recent studies report on perpendicular magnetic anisotropy in granular composite films containing metallic nanograins embedded into non-magnetic (insulating) matrices.^{8–10} It is worth noting that intrinsic growth-induced magnetic anisotropy is quite unusual phenomenon for granular films and was reported only for a few systems like granular Co_xAg_{1-x},⁸ Co-Zr-O,⁹ and Co-Al₂O₃ films,^{10–12} Co-rich Co-Ag and Co-Cu granular materials,^{13,14} or for (Fe-Ni-Co)-fluoropolymer films.¹⁵ At low content of metallic nanograins, when their volume fraction, *f_v*, is lower than 0.5, the magnetizing process of granular films is usually considered as a coherent rotation of magnetic moments of single-domain

superparamagnetic (SP) nanograins. At a high metallic phase content (*f_v* > 0.5), such systems are characterized with superferromagnetic (SF) long-range order resulting from combination of exchange and dipole-dipole interaction of SP nanograins.

Some earlier studies^{10–12,16} were focused on the relationship between the grain magnetic anisotropy and intergrain interaction in SF ensembles of nanograins with respect to the coercive field and the process of magnetization reversal. For example, a characteristic dependence of coercive field *H_C* vs. angle between easy magnetization axis and magnetic field direction is established for (CoFeB)_{0.6}(SiO₂)_{0.4} films below percolation limit, with strong in-plane anisotropy.¹⁶ Moreover, magnetization reversal in granular Co_x(Al₂O₃)_{1-x} films of perpendicular magnetic anisotropy containing magnetically interacting nanograins, is theoretically analyzed in Refs. 10–12.

It is generally accepted that the origin of perpendicular magnetic anisotropy in granular films is related to a preferential arrangement of metallic nanograins in the direction perpendicular to the film surface, resulting in the growth of columnar-like nanograins or nanograin agglomerations.^{10,12,14,17} Sun *et al.*⁹ attributed the appearance of columnar metallic nanograins to the oxygen-containing atmosphere during deposition and to oxygen presence in Co-Zr-O films that lead to surface oxidation of nanograins. However, the recent reports on Co-Al₂O₃, FeCoZr-Al₂O₃, and FeCoB-SiO₂ films sintered by similar ion-sputtering technology did not reveal a general

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relation of perpendicular magnetic anisotropy to the composition of nanograins and matrix as well as to the oxygen pressure in the deposition chamber.^{10,12,17–19} Thereafter, the driving force and the physical nature of such specifically shaped columnar metallic structures growing inside non-magnetic (insulating) matrices are still disputable.

The present paper reports on results of a systematic study of the structure, phase composition at nanoscale, and magnetic properties of FeCoZr-CaF₂ granular films revealing perpendicular magnetic anisotropy. Synthesis of the films with nanograins embedded into oxygen-free CaF₂ matrix in Ar atmosphere excludes uncontrolled and undesirable oxidation of nanograins and clarifies possibility of matrix and nanograins surface oxidation with respect to the formation of perpendicular magnetic anisotropy.

II. EXPERIMENT

The FeCoZr-CaF₂ nanocomposite films of the thickness 1–6 μm were deposited onto Al and glass-ceramic uncooled substrates ($T_{\text{sub}} \sim 373$ K) by dc ion sputtering, with a 2 keV argon ion gun, at 0.28 nm/s deposition rate. The Ar pressure in the chamber was kept at 67 mPa. Sputtering targets were composed of Fe₄₅Co₄₅Zr₁₀ alloy plates, with strips of CaF₂ of varied coverage on their top. In this way, the metal/insulator volume ratio in the deposited films could be controlled by choosing the appropriate coverage ratio of the constituents.²⁰ The composition of (FeCoZr)_x(CaF₂)_{100–x} ($29 \leq x \leq 73$ at. %) films was verified with energy dispersive X-ray spectroscopy (EDX) in a scanning electron microscope and by Rutherford backscattering spectrometry (RBS).²¹

X-ray diffraction (XRD) structural analysis was carried out with an Empyrean PANalytical diffractometer using a diffracted beam graphite monochromator and an X'Celerator linear detector (Cu K_α radiation). The data were collected with a divergent-beam optics (using 1/32" divergence and 1/16" anti-scatter slits) at a grazing incidence of 5° with respect to the sample surface, and the detector scanning the 2θ space over the 10°–120° range. Lanthanum hexaboride (LaB₆—NIST, Standard Reference Material 660a) was used for determination of instrumental broadening of diffraction peaks. The experimental data were analyzed with the profile fitting program *FullProf*²² based on the Rietveld method. The background intensity was refined with a polynomial fitting and the peak shape was approximated with a pseudo-Voigt function.

Microstructural studies have been performed with a transmission electron microscopy (TEM) at a standard and at a high resolution (HRTEM), using Philips EM400T and Philips CM200 microscopes, operating at 120 kV and 200 kV, respectively. The films deposited on Al substrates, thinned with an ion-beam for the planar or cross-sectional view were analyzed. The Selected Area Electron Diffraction (SAED) and Fast Fourier Transform (FFT) patterns obtained were calibrated with bulk crystalline Al and Si references. The data were analyzed with Gatan Digital Micrograph and ELD software.

X-ray Absorption Spectroscopy (XAS) experiments were performed at the beamline C of HasyLab/DESY

synchrotron laboratory (Hamburg).²³ Bending magnet X-ray radiation was monochromatized with a pair of flat Si single crystals cut along (1 1 1) and (3 1 1) surface. The measurements were carried out at Fe, Co K-edges and Zr K-edge, respectively. The absorption spectra were detected in the total fluorescence yield by means of passivated implanted planar Si (PIPS) diode. The sample surface was aligned at 45° to the incident beam and the detection angle was chosen to be close to 90° in order to minimize Thompson scattering background. The analysis of the spectra was performed with the IFEFFIT package.²⁴

The dc mass susceptibility (χ) and magnetization (M) were measured at the temperature range from 2 K up to 350 K in magnetic fields H up to 90 kOe using the Vibrating Sample Magnetometer (VSM) option of a Quantum Design Physical Property Measurement System (PPMS). During measurements, magnetic field was applied respectively in the directions parallel and perpendicular to the thin film surface. χ and M values were corrected by subtracting the diamagnetic response of the substrate from the experimental data. In the cases where both the composition and the thickness of the thin film could be determined, the magnetic moment in Bohr magnetons per compound atom Fe_{0.5}Co_{0.5} (denoted by FeCo) was calculated.

The ⁵⁷Fe transmission and conversion electron Mössbauer spectroscopy measurements were performed using a conventional constant acceleration type spectrometer with a 20 mCi ⁵⁷Co in Rh source moving at room temperature (RT). The absorber was fixed in a top loading type cryostat and the spectra were recorded at RT and at 78 K. The spectra were analyzed with MOSMOD and HDISTR software accounting for distributions of effective hyperfine magnetic field (B_{hf}) and quadrupole splitting ($\Delta = (eQV_{zz}/2)(1 + \eta^2/3)^{1/2}$, where eQ is the electric quadrupole moment of ⁵⁷Fe nucleus in the excited state, V_{zz} is the maximum component of the electric field gradient, η is the asymmetry parameter) based on the method published by Rancourt.^{25,26} Values of center shift δ are related to α -Fe at RT.

III. RESULTS

A. Structure and phase composition

Structure and phase composition of the samples obtained were studied with X-ray diffraction. The XRD patterns from (FeCoZr)_x(CaF₂)_{100–x} ($29 \leq x \leq 73$) films deposited onto Al foils along with Rietveld refined curves are shown in Figure 1. Detailed results of Rietveld analysis of some selected XRD patterns are shown in Figure 2. An inspection of Table I and the fitted unit cell parameters (a) collected there shows that the nanogranular films consist of nanocrystalline *bcc* α -FeCo(Zr) alloy¹⁸ and *fcc* CaF₂ compound.²⁷

A considerable increase of the line widths and a gradual disappearance of α -FeCo(Zr) peaks at higher 2θ angles with decreasing x can be noted. The tendencies are opposite for the CaF₂ phase. A complex (asymmetric and broadened) shape of the α -FeCo(Zr) phase (110) diffraction peaks for $44 \leq x \leq 65$ corresponds to two *bcc* cubic phases with similar unit cell parameters a but with much different line widths. The phase denoted as α -FeCo(Zr) (1) with much broader

FIG. 1. X-ray diffraction patterns (dots) and results of the Rietveld refinement denoted by solid black line (best fit) of $(\text{FeCoZr})_x(\text{CaF}_2)_{100-x}$ ($29 \leq x \leq 73$) nanogranular films deposited on Al substrate. The base lines of the patterns are arbitrarily off-set for clarity. Two sets of vertical arrows above the pattern with $x = 29$ indicate the positions of Bragg peaks of the refined *fcc* CaF_2 (space group $Fm\bar{3}m$) and *bcc* $\alpha\text{-FeCo(Zr)}$ (space group $Im\bar{3}m$) phases, respectively. The third set of vertical arrows below the $x = 73$ pattern denotes the allowed positions of Bragg peaks of the Al substrate.

lines (existing solely for $x < 44$) shows noticeably larger unit cell parameter a as compared to the $\alpha\text{-Fe}_{50}\text{Co}_{50}$ nanoalloy phase ($a = 2.86 \text{ \AA}$)²⁸ or to the disordered $\alpha\text{-Fe}_{50}\text{Co}_{50}$ bulk alloy ($a = 2.8550 \text{ \AA}$)²⁹ possibly due to dissolution of some F atoms inside the $\alpha\text{-FeCo}$ -based phase. The second phase, $\alpha\text{-FeCo(Zr)}$ (2), with narrower lines, which is practically the sole one in the film with $x = 73$, shows the unit cell parameter a values very close to that of the $\alpha\text{-Fe}_{50}\text{Co}_{50}$ phase.

To estimate the grain size of the crystalline phases, the Scherrer method (in the form implemented in *FullProf* program²²) was used to model the peak broadening above the instrumental width. For the purely Lorentzian shape of the peak, it reduces to $\Delta(2\theta)_L = (360\lambda)/(\pi^2 D \cos\theta)$, where $\Delta(2\theta)_L$ denotes its full width at half maximum (FWHM),

FIG. 2. Selected X-ray diffraction patterns of $(\text{FeCoZr})_x(\text{CaF}_2)_{100-x}$ ($29 \leq x \leq 65$) nanogranular films deposited on Al substrate (dots) together with the results of their Rietveld refinements denoted by solid black line (best fit) and partial contributions of CaF_2 phase (dashed blue line) and two $\alpha\text{-FeCo(Zr)}$ phases: type (1), dotted red line and type (2), dashed-dotted green line. The phases are additionally marked by arrows with appropriate labels. The upper set of vertical bars below each pattern represents the Bragg peak positions corresponding to the CaF_2 phase, while the lower two sets refer to the positions of the *bcc* $\alpha\text{-FeCo(Zr)}$ type (1) and type (2) phases.

$\lambda = 1.54056 \text{ \AA}$, and D corresponds to D^{coh} —size of regions of coherent scattering. Assuming that such a broadening is due to the size and microstrain effects, the mean D^{coh} of the metallic grains were derived and collected together with refined cubic lattice parameters a for all the three identified phases in Table I. It should be noted that D^{coh} is obtained only for well-crystallized $\alpha\text{-FeCo(Zr)}$ (2) phase, when the Rietveld refinement of corresponding XRD patterns allows a suitable modelling and separation of size and microstrain

TABLE I. Structural data obtained from the analysis of X-ray diffraction patterns of $(\text{FeCoZr})_x(\text{CaF}_2)_{100-x}$ ($28 \leq x \leq 73$) films on Al foil and glass-ceramic substrates: a —lattice parameter, D^{coh} —the size of regions of coherent scattering.

Al foil substrate					Glass-ceramic substrate		
x (at. %)	CaF_2 a (Å)	$\alpha\text{-FeCo(Zr)}$ (1) a (Å)	$\alpha\text{-FeCo(Zr)}$ (2)		x (at. %)	CaF_2 a (Å)	$\alpha\text{-FeCo(Zr)}$ a (Å)
			a (Å)	D^{coh} (nm)			
29	5.518(2)	2.922(9)	...	...	28	5.548(4)	2.954(4)
39	5.499(2)	2.918(9)	...	...	38	5.530(5)	2.915(3)
44	5.488(3)	2.945(8)	2.865(1)	6	46	5.517(3)	2.8617(10)
58	5.479(9)	2.97(1)	2.865(2)	8	58	...	2.8563(13)
65	5.497(3)	2.95(3)	2.862(1)	5	68	...	2.8556(5)
73	5.44(2)	...	2.862(1)	7

FIG. 3. X-ray diffraction patterns (dots) with the results of the Rietveld refinement denoted by solid black line (best fit) taken from $(\text{FeCoZr})_x(\text{CaF}_2)_{100-x}$ ($28 \leq x \leq 68$) granular films deposited on glass-ceramic substrate. The base lines of the patterns are arbitrarily off-set for clarity. Two sets of vertical arrows above the pattern with $x = 28$ indicate the positions of the Bragg peaks of the refined *fcc* CaF_2 and *bcc* $\alpha\text{-FeCo(Zr)}$ cubic phases, respectively.

contributions from angular dependencies of linewidths. A crude one peak estimation of D^{coh} (neglecting microstrain effects) for $\alpha\text{-FeCo(Zr)}$ (1) phase which is highly disordered and possibly located at grain surfaces, leads to some 1–2 nm. One should also note that lattice parameters a for CaF_2 phase are larger than expected for the stoichiometric compound ($a = 5.4632(3) \text{ \AA}$)²⁷ and decrease with increasing x . This dependence indicates on a dissolution of some F atoms into the surface regions of $\alpha\text{-FeCo(Zr)}$ nanograins. As the broadening of the diffraction peaks of this phase is predominantly of microstrain character, no size parameters D^{coh} could be obtained.

The XRD patterns of the $(\text{FeCoZr})_x(\text{CaF}_2)_{100-x}$ ($28 \leq x \leq 68$) films deposited on glass-ceramic substrate are

presented along with Rietveld refined curves in Figure 3. Lower signal to noise ratios are due to smaller size of samples and lower thicknesses of the films than of those deposited on Al foil (Figure 1).

Despite of this, some similarities and differences of the phase composition and its evolution with increasing x can be noted. The main difference concerns the CaF_2 phase and its texture revealed in relative intensities of the peaks in the corresponding patterns for $x = 28\text{--}46$, and a disappearance of diffraction peaks arising from this phase for $x \geq 58$. This suggests that in the films deposited on glass-ceramic substrates, the CaF_2 phase grows possibly in an amorphous form for $x > 46$, while in the films deposited on Al foil, a crystalline CaF_2 phase is observed up to $x = 73$. However, it should be noted that structural properties of $\alpha\text{-FeCo(Zr)}$ nanograins which are of interest in this work are very similar for the samples with of the same x on both types of substrate. Very similar structural properties and almost identical values of lattice parameter a for $\alpha\text{-FeCo(Zr)}$ nanograins in films with the same x on Al foil and glass-ceramic substrates justify using both types of samples exchangeably for the study of their other physical properties.

The results of TEM microstructural and phase composition analysis of $x = 39$ film deposited on Al substrate are presented in Figure 4. The analysis reveals a mixture of very fine nanocrystalline metallic and the insulating phases. In the bright-field mode (a), the metallic nanograins appear as a dark and the insulating matrix as a bright-grey contrast. The SAED pattern (c) exhibits sharp rings which identify a *bcc* structure of $\alpha\text{-FeCo(Zr)}$ and an *fcc* structure of CaF_2 nanograins. Dark-field image (b), taken with the objective aperture centered on the 3rd diffraction ring, shows bright features which can represent either the metallic or the insulating nanograins. The graph (d) shows the extracted intensities of the diffraction rings, which correspond to the interplanar spacings of the $\alpha\text{-FeCo(Zr)}$ and the CaF_2

FIG. 4. Results of plan-view TEM analysis of $(\text{FeCoZr})_{39}(\text{CaF}_2)_{61}$ film on Al substrate: (a) bright-field image; (b) dark-field image with objective aperture centered on the 3rd diffraction ring; (c) SAED pattern taken from a large surface area; (d) intensity of the diffraction rings extracted from the shown SAED pattern, as a function of $1/d$ spacing; and (e) evaluated size distribution of the metallic nanograins.

nanocrystalline phases in the reciprocal ($1/d$) space. The lattice parameters a derived coincide with those obtained from XRD. A series of bright-field TEM images was used to determine the size distribution of α -FeCo(Zr) nanograins (e), which is characterized by the mean diameter $\langle D \rangle = 3.3 \pm 0.2$ nm (HWHM = 1.0 nm). The value of $\langle D \rangle$ for nanograins determined from TEM images is close to the size of D^{coh} obtained from XRD patterns with similar x ($D^{coh} = 2$ nm). This suggests that the metallic nanograins grow mainly as single crystals, but of a poor structural quality.

Further insight into the structure of $x = 39$ film is provided by HRTEM analysis, Figure 5. The image (a) illustrates a crystalline nature of metallic alloy nanograins and their distribution in the insulating matrix. FFT pattern (b) exhibits isolated diffraction spots that lay on the drawn rings. They could be identified and labelled, as shown in the figure. A clear separation of (0 1 1) α -FeCo(Zr) and (0 2 2) CaF_2 reflections is worth noting in this case. Image (c) was obtained by inverse mask processing. It illustrates a crystalline α -FeCo(Zr) grain embedded into the crystalline CaF_2 matrix.

The results of cross-sectional TEM analysis of $x = 57$ and $x = 73$ films are shown in Figures 6(a) and 6(b) and 6(c) and 6(d), respectively. They illustrate convincingly a columnar nature of the films. Columns of metallic nanoparticles

are seen as dark and dark grey areas, whereas the insulating phase is represented as bright regions.

The *bcc* α -FeCo(Zr) and *fcc* CaF_2 phases were identified by SAED (inset in Figure 6(a)) and FFT (inset in Figure 6(d)). The columns start growing nearly perpendicular to the substrate surface (Figure 6(c)), but as can be seen in both (a) and (c), they tend to incline with increasing distance from the substrate. Close to the top of the film, their departure from the surface normal is of 20° . Nevertheless, the columnar structure extends throughout the whole film thickness, from the interface with the substrate up to its top surface. Inset in Figure 6(c) shows that the metallic columns consist of agglomerated nanograins, approximately 3–5 nm in size, one sitting on top of another. High-resolution images in (b) and (d) show that these nanograins are elongated along the columns direction. The metallic columns are densely packed in the sample with a higher concentration of the metallic phase.

The information on the nearest neighbor environments of Fe, Co and Zr atoms has been obtained from the fluorescence detected XAS spectra in the EXAFS (Extended X-ray Absorption Fine Structure) range. Fourier transforms (FT) of the EXAFS oscillations extracted from the Fe and Co K-edge spectra of $(\text{FeCoZr})_x(\text{CaF}_2)_{100-x}$ ($29 \leq x \leq 73$) on Al substrate films as well as of α -Fe, α -Co foil standards and of $\text{Fe}_{45}\text{Co}_{45}\text{Zr}_{10}$ foil are shown in Figure 7. It should be noted that the $\text{Fe}_{45}\text{Co}_{45}\text{Zr}_{10}$ foil was produced by sputtering of the $\text{Fe}_{45}\text{Co}_{45}\text{Zr}_{10}$ target on Al foil with the same ion-beam sputtering technology as $(\text{FeCoZr})_x(\text{CaF}_2)_{100-x}$ granular films were.

The Fe EXAFS spectrum of the $x = 73$ film was simulated assuming *bcc* α -Fe structure with lattice parameter $a = 2.85$ Å (see Figure 8(a)) that is very close to $a = 2.862(2)$ Å derived from XRD pattern analysis. Positions of the main peak corresponding to the nearest neighbor shell distance of Fe and Co in films with $x < 58$, Figure 7, are similar to those of nearly amorphous $\text{Fe}_{45}\text{Co}_{45}\text{Zr}_{10}$ foil. In the case of $x = 58$, the broadened main peak of Fe and Co FT is at intermediate distance between those of the nearest neighbor shells in $\text{Fe}_{45}\text{Co}_{45}\text{Zr}_{10}$ and α -Fe (or α -Co) type long range ordered α -FeCo structure. Thus, it can be considered as superposition of two peaks corresponding to these two local Fe surroundings. This observation correlates well with the results of the analysis of the corresponding XRD pattern, where the α -FeCo(Zr) phase was found to consist of two *bcc* contributions with similar unit cell parameters a , but with much different line widths. For the film with $x = 73$, the Co environment at the distance 3 to 5 Å resembles well that of Fe in the α -Fe foil and not that in the *hcp* structure of α -Co. A smearing out of peaks corresponding to more distant neighbors with decreasing x reflects a deterioration of long range order.

Fourier transforms of the EXAFS oscillations extracted from Zr K-edge spectra of $(\text{FeCoZr})_x(\text{CaF}_2)_{100-x}$ films with $x = 28, 46$, and 67 on glass-ceramic substrate together with α -Zr, $\text{Fe}_{45}\text{Co}_{45}\text{Zr}_{10}$ foil, and ZrO_2 reference materials are shown in Figure 8(b). It is worth noting that the Zr first neighbor shell distance in films is similar to that of ZrO_2 reference and not to that of $\text{Fe}_{45}\text{Co}_{45}\text{Zr}_{10}$ foil. Thus, a formation

FIG. 5. Plan-view high resolution TEM analysis of the $(\text{FeCoZr})_{39}\text{CaF}_2)_{61}$ sample: (a) distribution of metallic nanograins (dark and dark grey areas); (b) FFT diffraction pattern showing isolated reflection spots arising from α -FeCo(Zr) and CaF_2 grains; and (c) processed image illustrating a crystalline metallic grain (dark area) embedded in the crystalline insulating matrix.

FIG. 6. Cross-sectional TEM analysis of $(\text{FeCoZr})_{57}(\text{CaF}_2)_{43}$ (a) and (b) and $(\text{FeCoZr})_{73}(\text{CaF}_2)_{27}$ films (c) and (d). Insets in (a) and (d) show SAED and FFT patterns taken from the corresponding films.

FIG. 7. Fourier transforms of the EXAFS oscillations extracted from the Fe (a) and Co (b) K-edge spectra of $(\text{FeCoZr})_x(\text{CaF}_2)_{100-x}$ ($x = 29, 58$, and 73) films on Al substrate, $\text{Fe}_{45}\text{Co}_{45}\text{Zr}_{10}$ foil, $\alpha\text{-Fe}$ foil and $\alpha\text{-Co}$ foil. Position of the first maximum corresponding to the nearest neighbor shell in the metallic phase are marked with dashed lines. Individual plots are vertically offset for clarity.

FIG. 8. (a) Fourier transform of the EXAFS oscillations extracted from the Fe K-edge spectrum of $(\text{FeCoZr})_{73}(\text{CaF}_2)_{27}$ film on Al substrate together with its fit assuming bcc $\alpha\text{-Fe}$ structure with lattice parameter $a = 2.85$ Å; (b)—experimental Zr K-edge spectra of $(\text{FeCoZr})_x(\text{CaF}_2)_{100-x}$ ($x = 28, 46$, and 67) films on Al substrate, $\text{Fe}_{45}\text{Co}_{45}\text{Zr}_{10}$ foil and ZrO_2 , $\alpha\text{-Zr}$ reference samples.

of Zr-O type environments can be inferred. However, a presence of Zr-F like environments of ZrF_4 revealing local structure similar to that of ZrO_2 cannot be excluded. A lack of next neighbor peaks except the first neighbor shell is attributed to a significant disorder or amorphous-like structure. These results are consistent with the analysis of the XRD patterns, Figures 1–3, where no traces of long range ordered Zr-based phase were found.

In addition, the analysis of Zr K-edge spectra of the FeCoZr-CaF_2 nanocomposites in the XANES (X-ray Absorption Near Edge Structure) range evidences a non-metallic Zr state even in films deposited in oxygen-free (Ar) atmosphere. This supports the abovementioned assumption of the reaction between Zr and F or O that originates from a very strong affinity of Zr to these elements (the highest one of the Fe, Co, and Zr). The non-metallic Zr state observed, means in turn, that Zr atoms are likely to be located at the interface between CaF_2 matrix and α -FeCo-based metallic nanograins and only partly incorporated into their *bcc* structure.

B. Magnetic properties

In order to characterize magnetic properties and to determine blocking temperatures T_B , the low field ($H = 50$ Oe), zero field cooled (ZFC) and field cooled (FC) dc mass magnetic susceptibilities (χ) have been studied. Selected $(\text{FeCoZr})_x(\text{CaF}_2)_{100-x}$ films deposited on glass-ceramic substrate were measured as a function of temperature and the results are presented in Figure 9(a). The $\chi(T)$ dependencies for $x \leq 38$ reveal shapes typical for SP state of α -FeCo(Zr) nanograins, i.e., low-temperature splitting of FC and ZFC curves and a maximum in the ZFC curve, defined as blocking temperature (T_B). An increase of T_B (reaching 98 K for $x = 46$) with increasing x is observed followed by disappearance of a maximum and the coincidence of the FC and ZFC $\chi(T)$ curves for $x = 67$. This reflects a percolation of isolated ferromagnetic α -FeCo(Zr) nanograins and the formation of a bulk-like

ferromagnetic state. One should note that for $x = 38$, the average nanograin diameter $\langle D \rangle$, derived from the relationship $25k_B T_B = K \langle V \rangle$ (where k_B —Boltzmann constant, $T_B = 46$ K, K —magnetic anisotropy constant ($1.4 \cdot 10^6 \text{ J/m}^3$ for iron nanograins with $\langle D \rangle < 10 \text{ nm}$,³⁰), $\langle V \rangle$ —average volume of nanograin, $\langle V \rangle = \pi \langle D \rangle^3 / 6$, is of 2.8 nm, which correlates well with TEM results for $x = 39$ film (see Figure 4(e)).

The dc mass magnetization (M) vs. H isotherms for the same films were measured at selected temperatures and are shown in Figure 9(b). Magnetization values are converted into Bohr magnetons per compound $\text{Fe}_{0.5}\text{Co}_{0.5}$ atom of the FeCo alloy and characterize intrinsic magnetization of α -FeCo(Zr) nanograins. At 2 K, the $M(H)$ hysteresis loops for $x = 28$ and 38 films do not saturate even at $H = 90$ kOe, but they saturate for films with $x \geq 46$ at fields of 40 kOe (not shown in Figure 9(b)). The loops for $x = 28$ and 38 films are also characterized by significantly larger coercive fields ($H_C = 305$ Oe and 158.5 Oe for $x = 28$ and 38, respectively) and smaller values of high field magnetization than for films with $x \geq 46$. The high coercivity, unsaturated character of the field dependences of magnetization, and a reduction of its high field values at 2 K give additional support for the highly nanocrystalline character of the α -FeCo(Zr) alloy in $x = 28$ and 38 films. Unsaturated character of the $M(H)$ loops at 300 K and low values of their coercive fields indicate on predominantly SP state of α -FeCo(Zr) nanograins of the $x = 28$ and 38 films at this temperature. M vs. H dependence for the $x = 67$ film fully saturates at $T = 2$ –100 K and is close to saturation at 300 K revealing a bulk-like ferromagnetic behavior of FeCo(Zr) alloy phase in this temperature range. The $x = 46$ film shows an intermediate character (between above described extremes) of the field dependences of magnetization.

The shapes of M vs. H loops measured at 2 K, 100 K, and 300 K for the $x = 67$ film show a step-like feature at small fields, characteristic for a ferromagnetic film with some number of grains having their easy axes of magnetization in the plane of the film. The dominant part of the film

FIG. 9. The ZFC and FC temperature dependencies of magnetic susceptibility (χ) at $H = 50$ Oe (a) and parts of field dependencies of magnetization (M) at various temperatures (b) for selected $(\text{FeCoZr})_x(\text{CaF}_2)_{100-x}$ films ($28 \leq x \leq 67$) deposited on glass-ceramic substrate. Magnetic field was applied in the direction parallel to the film surface.

TABLE II. Magnetic properties of α -FeCo(Zr) nanograins in the $(\text{FeCoZr})_x(\text{CaF}_2)_{100-x}$ films, $28 \leq x \leq 74$. M —magnetization of compound $\text{Fe}_{0.5}\text{Co}_{0.5}$ atoms at $H = 90$ kOe, H_C —coercive field, H_a —anisotropy field (at $H_{||}$), and H_d —demagnetizing field (at $H_{\perp}$).

x (at. %)	Field direction	T (K)	M (μ_B/FeCo)	M (emu/g)	H_C (Oe)	H_a or H_d (kOe)
Glass-ceramic substrate						
28	$H_{\parallel}$	2	1.54	149	305.1	...
		100	1.50	145	8.8	...
		300	1.43	139	5.6	...
38	$H_{\parallel}$	2	1.59	154	158.5	2.6
		100	1.52	147	11.0	2.6
		300	1.45	141	8.3	2.6
46	$H_{\parallel}$	5	1.63	158	105.5	2.6
		100	1.60	156	21.7	2.6
		300	1.55	150	12.6	3.0
67	$H_{\parallel}$	2	1.62	158	38.0	1.5
		100	1.62	157	29.3	1.5
		300	1.60	156	28.5	1.8
	$H_{\perp}$	2	1.62	157	237.6	11.0
		100	1.59	155	190.6	10.7
		300	1.56	151	125.8	10.5
Al substrate						
73	$H_{\parallel}$	2	...	...	41.0	1.4
		100	...	...	36.3	1.3
		300	...	...	31.2	1.3

shows almost linear field dependence up to saturation, which corresponds to easy axes out of plane and the anisotropy field, H_a , related to a hard axis saturation of 1.5–2 kOe.^{10–12} Similar features are also observed in magnetic hysteresis loops measured at 5 K and 100 K for the $x = 46$ film and at 2 K for the $x = 38$ film, but the saturation corresponds to higher H_a fields of 2–3 kOe. A pronounced linear field dependence up to the respective anisotropy field, H_a , points on the domination of easy axes of magnetization lying out-of-plane in these films. Recalling a columnar character of the α -FeCo(Zr) nanograins which grow nearly perpendicular to the substrate surface (revealed by TEM analysis) one can try to estimate the tilting angle θ between the normal to the films surface and the resultant direction of magnetic moments (the easy axis). The following relation can be used $\theta = 90^\circ - \arccos(M_r/M_s)$,³¹ where M_r —is remanence, M_s —is saturation magnetization at H_a . For $x = 67$ film characterized at 2 K by $M_r = 42$ emu/g and $M_s = 153$ emu/g the derived θ angle

amounts to 16° . This value seems to be in a reasonable agreement with what is visible on cross-sectional TEM images shown in Figures 6(c) and 6(d) for $x = 73$ film. A difference between the values of the angle estimated by these two methods can be related, e.g., to slightly different x for these two samples. Characteristic shapes of magnetic hysteresis loops for films with x equal to 67, 46, and 38 evidence predominantly out-of-plane orientations of their easy magnetization axes, which is quite unexpected for ion-beam sputtered granular nanocomposite films, which usually show random orientations of nanograins.¹⁹ Table II summarizes values of magnetization M at $H = 90$ kOe, coercive field H_C , anisotropy field H_a , and demagnetizing field H_d extracted from $M(H)$ loops when magnetic field is applied in parallel ($H_{||}$) and perpendicular ($H_{\perp}$) directions to the film surface.

For a comparison with the magnetometry results of the films on glass-ceramic substrate, one film deposited on Al substrate with $x = 74$ was also measured and the results are shown in Figure 10. In this case, the magnetic moment (μ) values measured were not corrected for magnetic contribution of the Al substrate. One should note a significant difference in the temperature dependences of ZFC and FC μ values recorded at $H = 50$ Oe, Figure 10(a), with respect to the corresponding χ vs. T curves for the $x = 67$ film deposited on glass-ceramic substrate, Figure 9(a).

In particular, it reveals a slight decrease of μ with decreasing T , rather unexpected for ferromagnetic film, in contrast to an usual increase with decreasing T when measured at $H = 10$ kOe. Such a behavior can easily be explained in view of almost perfect perpendicular character of magnetic anisotropy in the film on Al substrate. In other words, to align magnetic moments when the field is applied in the film plane, its value has to be higher when the temperature is lower, due to an increase of the magnetocrystalline anisotropy with decreasing temperature. It is also worth noting that magnetic hysteresis loop for $x = 74$ film on Al substrate demonstrates considerably lower remanence (μ_r) and lower magnetic susceptibility close to the origin (see Figure 10(b)) than the corresponding film on glass-ceramic substrate. The observed features of $\mu(T)$ and $\mu(H)$ curves indicate more pronounced out-of-plane magnetic anisotropy in the film on Al substrate with respect to the film on glass-ceramic substrate.

Magnetization loops at 2 K for the $x = 67$ film deposited on glass-ceramic substrate measured with H applied parallel and perpendicular to the film surface are presented in

FIG. 10. The FC (at $H = 50$ Oe and 10 kOe) and ZFC temperature dependences of magnetic moment, μ , (a) and parts of its magnetic field dependencies $\mu(H)$ at selected temperatures (b) for the $(\text{FeCoZr})_{74}(\text{CaF}_2)_{26}$ film deposited on Al substrate. Magnetic field was applied in the direction parallel to the film surface.

FIG. 11. Parts of field dependencies of magnetization (M) at 2 K for the $(\text{FeCoZr})_{67}(\text{CaF}_2)_{33}$ film deposited on glass-ceramic substrate. Magnetic field is applied in the parallel (a) and perpendicular (b) direction to the film surface. The insets show the regions of the dependencies close to the origin.

Figures 11(a) and 10(b). According to classical considerations for magnetizing process of ferromagnetic films³¹ when external magnetic field is applied perpendicularly to films surface, strong demagnetizing field $H_d = 4\pi M$ appears in the direction opposite to the resultant magnetization. As a consequence, a higher external field is necessary for aligning magnetic moments of the grains. This shifts the saturation of $M(H)$ curve to higher fields corresponding to H_d . Indeed, it can be observed in Figure 11(b) that for film with high metallic phase content ($x = 67$) measured in perpendicular geometry the $M(H)$ curve saturates at the demagnetizing field $H_d > 10$ kOe. The other characteristic feature of $M(H)$ curve measured in direction perpendicular to the film plane is the enhanced H_C value (~ 126 Oe at RT and ~ 238 Oe at 2 K) as compared to with the case of parallel geometry ($H_C \sim 29$ Oe and ~ 38 Oe, respectively) (see Table II).

The ^{57}Fe Mössbauer spectra of $(\text{FeCoZr})_x(\text{CaF}_2)_{100-x}$ ($29 \leq x \leq 73$) films on Al foil recorded in the transmission mode at RT are shown in Figure 12(a).

Except for the concentration $x = 73$, where only one magnetic component could be fitted, the spectra were satisfactorily fitted with two components: a broadened magnetic sextet (with static distribution of the hyperfine field B_{hf}) and an asymmetric quadrupole doublet. The hyperfine magnetic field distributions for the magnetic component, $P(B_{\text{hf}})$,

derived from the spectra are presented in Figure 12(b), and the sets of hyperfine parameters (δ , Δ , $\langle B_{\text{hf}} \rangle$) derived are summarized in Table III.

The $x = 29$ spectrum shows a predominant asymmetric doublet ($\delta = 0.10(2)$ mm/s, $\Delta = 0.69(2)$ mm/s) located on a smeared broad hump of magnetic origin. Basing on XRD, TEM, and magnetometry data as well as on previously reported results,¹⁹ it is assigned to α -FeCo(Zr) nanograins in an SP state. Contribution of magnetic sextet ($\langle B_{\text{hf}} \rangle = 199$ –331 kGs) increases with x , which evidences gradual agglomeration of magnetically interacting α -FeCo(Zr) nanograins, in agreement with magnetometry results (see Figure 8). The derived values of δ in the range of 0.03(1)–0.10(2) are typical for FeCoZr foil confirming a metallic, non-oxidized state of Fe. At $x = 73$ magnetically split spectrum reveals the ratio of line intensities in the sextet $h_1:h_2:h_3:h_4:h_5:h_6$ amounting to 3:~0.3:1:1:~0.3:3 instead of 3:2:1:1:2:3 expected for random orientation of magnetic moments. The coefficient defined as $K = h_2/h_3$ equals 0.3 for the $x = 73$ sample at RT. Its value is very similar also at $T = 78$ K and reflects an out of plane orientation of magnetic moments in α -FeCo(Zr) nanograins with respect to the film surface.³²

The angle θ between the normal to the film surface and the magnetic moments in nanograins, estimated from the relationship $\theta = \arccos\{[(4 - K)/(4 + K)]^{1/2}\}$ ³² is of 20° for

FIG. 12. The ^{57}Fe Mössbauer spectra recorded in the transmission mode (a) together with their fits and the derived hyperfine field distributions (b) of $(\text{FeCoZr})_x(\text{CaF}_2)_{100-x}$ ($39 \leq x \leq 73$) films on Al substrate.

TABLE III. Experimental values of the center shift δ , quadrupole splitting/shift* (Δ/Δ^*), the mean hyperfine magnetic field $\langle B_{\text{hf}} \rangle$, the ratio of line intensities $K = h_2/h_3$ in sextets and the relative area of the components of the spectrum A for $(\text{FeCoZr})_x(\text{CaF}_2)_{100-x}$ ($29 \leq x \leq 73$) films at $T = 300$ and 78 K, obtained from fits of the corresponding Mössbauer spectra. $\Delta^* = (eQV_{zz}/4)[2 - (3 - \eta \cos 2\psi) \sin^2 \theta]$, where θ and ψ are polar coordinates of hyperfine field in conventional electric field gradient tensor coordinate system.

x (at. %)	T (K)	δ (mm/s)	Δ/Δ^* (mm/s)	$\langle B_{\text{hf}} \rangle$ (kGs)	K	A (%)
29	300	0.10 (2)	0.69 (2)	...	...	85
			0.55 (4)*	0	...	15
39	300	0.04 (3)	0.56 (4)	...	...	26
			-0.10 (3)*	199 (4)	1.52	74
44	300	0.07 (1)	-0.03 (1)*	286 (5)	1.21	89
			0.48 (4)	...	...	11
58	300	0.05 (1)	-0.01 (1)*	321 (2)	0.52	96
73	300	0.03 (1)	-0.001 (1)*	331 (2)	0.30	100
73	78	0.04 (1)	-0.001 (1)*	351 (1)	0.27	100

$x = 73$, which is close to $\theta = 16^\circ$ derived from cross-sectional TEM images for $x = 67$ sample on Al substrate. One should note that conversion electron Mössbauer spectroscopy (CEMS) spectrum of $x = 67$ film deposited on glass-ceramic substrate shows very similar hyperfine parameters ($\delta = 0.03(1)$ mm/s, $\langle B_{\text{hf}} \rangle = 335$ kGs) and the ratio of line intensities (3:~0.5:1:1:~0.5:3), which corresponds to $\theta \sim 25^\circ$ (see Figure 12(a)). A comparison of Mössbauer spectra recorded for $x = 58, 73$ films on Al foil (Figure 12(a)), and $x = 67$ film on glass-ceramic substrate (Figure 13(a)) evidences that contribution of out of plane (perpendicular) anisotropy component is more pronounced in the case of films deposited on Al foil.

IV. DISCUSSION

Structural and phase characterization of the films studied evidence that they contain *bcc* α -FeCo(Zr) alloy nanograins distributed in the crystalline *fcc* or amorphized CaF_2 matrix. Phase composition and local atomic order are similar for films deposited onto glass-ceramic and Al substrates, so that magnetic properties of the corresponding films sintered on both substrates could be analyzed comparatively, except for the films with the highest alloy content, x where differences in the crystallinity of the CaF_2 matrix are observed. Cross-sectional TEM images of films with $x \geq 57$ indicate a columnar-like structure of *bcc* α -FeCo(Zr) and CaF_2 phases

with columns slightly tilted (up to $\sim 20^\circ$) with respect to the surface normal at the top of the film and almost perpendicularly oriented columns at the film-Al substrate interface. Due to relatively large film thickness (up to $6 \mu\text{m}$) compared to the column width (a few nm), originally perpendicular columns do not preserve strictly their orientation as the film grows in thickness, but exhibit some deviation from this direction.

EXAFS and Mössbauer spectroscopies reveal that the local atomic order around Fe and Co in nanograins corresponds to a *bcc* α -FeCo(Zr) phase with different degree of disorder and indicate a lack of noticeable nanograins oxidation. At the same time, the nearest neighborhood of Zr atoms is found to correspond to ZrO_2 and/or ZrF_4 phase type environments formed due to oxidation of sputtered Zr species with residual oxygen/fluorine in sputtering chamber. A possible formation of Zr oxide originates from very high zirconium affinity to oxygen with the formation enthalpy of $+0.8$ eV/molecule for Zr-O bond, as compared with Fe-O ($+2.4$ eV/molecule) and Co-O ($+3.0$ eV/molecule) bonds. High gettering ability of zirconium with respect to oxygen or fluorine possibly obstructs efficient incorporation of Zr atoms into the FeCo-based nanoalloy grains, prevents their oxidation and possibly favors the observed preservation of *bcc* crystalline structure of nanograins, similar to that in the starting material.

Magnetic properties of films with low alloy content ($28 \leq x \leq 39$) indicate that they predominantly contain non-interacting SP nanograins with $33 \text{ K} \leq T_B \leq 46 \text{ K}$ and average size of 3 nm as estimated from TEM and low field ZFC $\chi(T)$ curves. In this case, a lack of saturation in $M(H)$ dependencies at the highest H and H_C values decreasing with increasing temperature, as well as quadrupole doublet observed in Mössbauer spectra at RT, reflect an SP state of α -FeCo(Zr) nanograins. Mössbauer spectroscopy and magnetometry data show that the onset of ferromagnetic state at 300 K corresponds to $x > 39$, when ferromagnetic sextet and magnetic saturation at 90 kOe are observed.

At higher contents of the metallic phase, $x = 46\text{--}73$, the films reveal significant non planar magnetic anisotropy, increasing with x . Out-of-plane orientation of easy magnetization axis in the films studied is evidenced, first of all, in the ratio of line intensities 3:~0.3:1:1:~0.3:3 of RT Mössbauer spectra measured in transmission and conversion electron modes (see Figures 12(a) and 13(a)). This is also

FIG. 13. The RT ^{57}Fe CEMS spectrum together with its fit (solid line) (a) and the derived hyperfine fields distribution (b) for $x = 67$ film on glass-ceramic substrate.

supported with obstructed in-plane aligning of magnetic moments revealed in M vs. H dependences and relatively large $H_a \sim 1.5\text{--}3$ kOe (see Figures 9(b) and 11(a)).

In the case of $x = 67$ film, the average angle between the normal to the film surface and easy magnetization axis corresponds to $\theta \sim 20^\circ$ and $\sim 16^\circ$ as derived from Mössbauer spectroscopy and magnetometry, respectively. It is worth noting that in the films studied, a perpendicular magnetic anisotropy is observed far above the electrical percolation threshold x of 58, where conductivity of metallic character is observed. The formation of percolation network is confirmed by temperature dependences of the resistivity of FeCoZr-CaF₂ films reported in Ref. 33 which show positive temperature coefficient of the electrical resistivity and close to zero magnetoresistance effect already at $x = 58$. It is worth noting that previously reported results on perpendicular magnetic anisotropy^{10–12,34} consider only the cases of Co_x(Al₂O₃)_{100–x} films with $x \leq 61$, where electrical percolation is not yet achieved.

Complementary structural, magnetic, and spectroscopic study of granular films enables a critical consideration of previously discussed reasons,^{8–15} which might promote perpendicular anisotropy in the context of texture effects, surface oxidation of nanograins, composition of matrix, or the influence of substrate temperature during deposition. In particular, XRD analysis of the films with $58 \leq x \leq 73$ does not indicate any preferred crystallographic orientation for *bcc* α -FeCo(Zr) nanograins that could cause the appearance of perpendicular magnetic anisotropy in these films. At the same time, cross-sectional images obtained for films with $x \geq 57$ clearly reveal columnar form of the metallic phase consisting of agglomerated elongated nanograins. For that reason and in view of the results reported for Co-Al₂O₃ films obtained with similar technology,^{10–12} the occurrence of out-of-plane anisotropy should be attributed to the formation of columnar-like structure with pronounced shape anisotropy.

A possible surface oxidation of *bcc* α -FeCo(Zr) metallic nanograins can be excluded as a factor promoting perpendicular magnetic anisotropy in granular films as the EXAFS and Mössbauer spectroscopies reveal non-oxidized Fe and Co metallic state. Next, taking into consideration results reported in Refs. 10–12, the effect of matrix seems to be insufficient for the formation of elongated nanogranules, as a non-planar magnetic anisotropy was previously observed for both Al₂O₃ and CaF₂ matrices. It should be noted, however, that a vast microstructural research of thin films like Al₂O₃, CaF₂, and MgB₂ reveals their strong columnar growth^{35–37} at some defined synthesis conditions. This feature of CaF₂ matrix of the films studied could also promote growth-induced arrangement of α -FeCo(Zr) nanograins in columnar-like structures.

Considering the factors influencing the growth of elongated nanograin structures in FeCoZr-CaF₂ films, one should focus on the temperature of the substrate during deposition. The FeCoZr-CaF₂ films studied were deposited onto glass-ceramic and Al substrates at the temperature of 100 °C. Similarly, as reported by Timopheev *et al.*,¹² perpendicular magnetic anisotropy was observed for Co-Al₂O₃ sputtered onto glass-ceramic substrate at the temperature of 150 °C. This explains tentatively the formation of nanocolumns

modelled in kinetic Monte-Carlo simulations and reported by Rosenthal *et al.*,¹⁵ where high surface mobility of atoms at low condensation coefficient of metal on polymer, together with high metal deposition rate vs. polymer component, were considered as crucial points for the transition from growth of spherical clusters to nanocolumns.

V. CONCLUSIONS

The (FeCoZr)_x(CaF₂)_{100–x} ($28 \leq x \leq 73$) nanogranular films studied contain a mixture of *bcc* α -FeCo(Zr) and *fcc* CaF₂ nanograins. At $x < 46$, α -FeCo(Zr) grains (2–3 nm in size) are dispersed in the nanocrystalline CaF₂ phase and are predominantly superparamagnetic. At a higher alloy content, the films grow in a columnar structure, with regularly distributed isolated alloy and matrix columns, a few nm wide, stretching in length from the substrate to the top of the films. The orientation of columns is nearly perpendicular to the film plane at the substrate interface, but tilts by up to $\sim 20^\circ$ off the normal. The alloy columns consist of *bcc* α -FeCo(Zr) nanocrystalline grains (3–5 nm), slightly elongated along the column. Such a columnar structure explains the occurrence of non-planar, shape induced magnetic anisotropy in the films, appearing already below the electric percolation threshold ($x \sim 58$). The effect is more pronounced for increased alloy content (up to $x = 74$). The alignment of easy magnetization axes of nanograins corresponds to an average angle $16^\circ\text{--}20^\circ$ with respect to the normal to the film plane.

The origin of columnar growth is attributed to the deposition conditions, where the elevated substrate temperature allows for a sufficient atomic mobility and the two phases— α -FeCo(Zr) and CaF₂—can separate and form such a structure.

The results presented are among the first that evidence growth-induced non-planar magnetic anisotropy in metal/insulator granular films above the percolation threshold and reveal the origin of this phenomenon.

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