

Element-Specific Study of Magnetic Anisotropy and Hardening in $\text{SmCo}_{5-x}\text{Cu}_x$ Thin Films

Georgia Gkouzia,* Damian Günzing, Ruiwen Xie,* Teresa Weßels, András Kovács, Alpha T. N'Diaye, Márton Major, J. P. Palakkal, Rafal E. Dunin-Borkowski, Heiko Wende, Hongbin Zhang, Katharina Ollefs, and Lambert Alff



Cite This: *Inorg. Chem.* 2023, 62, 16354–16361



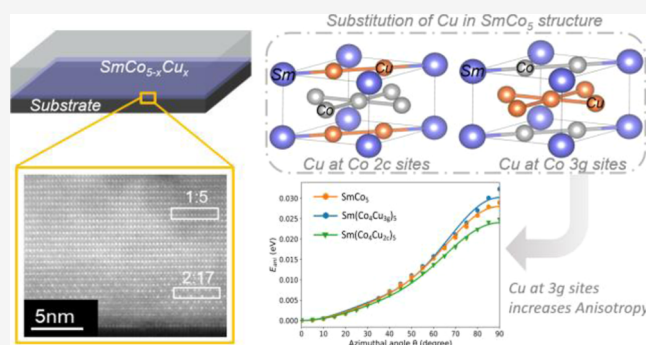
Read Online

ACCESS |

Metrics & More

Article Recommendations

ABSTRACT: This work investigates the effect of copper substitution on the magnetic properties of SmCo_5 thin films synthesized by molecular beam epitaxy. A series of thin films with varying concentrations of Cu were grown under otherwise identical conditions to disentangle structural and compositional effects on the magnetic behavior. The combined experimental and theoretical studies show that Cu substitution at the Co_{3g} sites not only stabilizes the formation of the SmCo_5 structure but also enhances magnetic anisotropy and coercivity. Density functional theory calculations indicate that $\text{Sm}(\text{Co}_4\text{Cu}_{3g})_5$ possesses a higher single-ion anisotropy as compared to pure SmCo_5 . In addition, X-ray magnetic circular dichroism reveals that Cu substitution causes an increasing decoupling of the Sm 4f and Co 3d moments. Scanning transmission electron microscopy confirms predominantly SmCo_5 phase formation and reveals nanoscale inhomogeneities in the Cu and Co distribution. Our study based on thin film model systems and advanced characterization as well as modeling reveals novel aspects of the complex interplay of intrinsic and extrinsic contributions to magnetic hysteresis in rare-earth-based magnets, i.e., the combination of increased intrinsic anisotropy due to Cu substitution and the extrinsic effect of inhomogeneous elemental distribution of Cu and Co.



1. INTRODUCTION

SmCo_5 -based permanent magnets were developed in the 1960s and were known to possess an extremely strong uniaxial magnetic anisotropy of about $K_1 = 17.2 \text{ MJ/m}^3$.^{1–3} The large magnetocrystalline anisotropy energy (MAE) arises due to the spin–orbit coupling of the localized and partially filled 4f shell of Sm and the spin–orbit coupling of the itinerant 3d electrons of cobalt in a strong crystal electric field.^{4,5} Besides, SmCo_5 exhibits a relatively large energy product $(\text{BH})_{\text{max}}$ up to 200 kJ/m^3 and a Curie temperature of 1020 K. The SmCo_5 phase has a hexagonal crystal structure with a space group of $P6/mmm$.

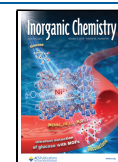
In practical applications, SmCo_5 -based permanent magnets are widely used in motors, generators, actuators, etc.⁶ These magnets are made from complex alloys, such as Sm–Co–Cu–Fe–Zr derived from the $\text{Sm}_2\text{Co}_{17}$ -type, and require sophisticated heat treatments during fabrication, which lead to the emergence of a unique microstructure.^{7,8} The increased demand for high $(\text{BH})_{\text{max}}$ magnets, in particular for high-temperature applications in renewable energy technologies, has spurred recent interest in the various phenomena leading to high coercivity.^{6,9} It is well-known that phase decomposition of

the starting alloy results in a cellular microstructure of $\text{Sm}_2\text{Co}_{17}$ (2:17) with a SmCo_5 (1:5) intergranular phase and a Zr-rich platelet.^{10,11} The SmCo_5 phase is Cu-rich, and the $\text{Sm}_2\text{Co}_{17}$ phase is Fe-rich. The magnetic properties of $\text{SmCo}_{5-x}\text{Cu}_x$ polycrystalline bulk at low temperatures were studied by Oesterreicher et al. in 1979. In this paper, the largest increase in coercivity was observed for Cu substitution levels of $x = 4$ in $\text{SmCo}_{5-x}\text{Cu}_x$.¹² Over the years, various studies have investigated the role of the individual elements Cu, Fe, and Zr in intrinsic and extrinsic magnetic properties.¹³ Nevertheless, a complete understanding that could help overcome the so-called Brown's paradox and help in the development of novel green magnets is still lacking.^{14–17}

Sm–Co thin films offer precise control over nanostructure, making them an ideal candidate for providing model structures

Received: June 1, 2023

Published: September 22, 2023



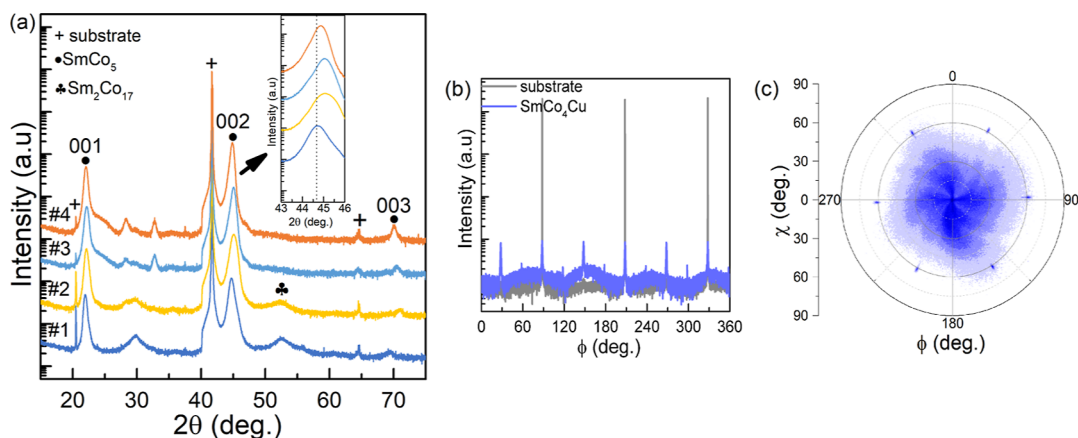


Figure 1. (a) θ - 2θ XRD patterns of (#1) $\text{SmCo}_{4.5}\text{Cu}_{0.5}$, (#2) SmCo_4Cu , (#3) $\text{SmCo}_{3.5}\text{Cu}_{1.5}$, and (#4) SmCo_3Cu_2 thin films grown onto a single crystalline Al_2O_3 substrate at 550°C . At 41.67° , the 006 reflection of the Al_2O_3 substrate is marked with the plus sign. (b) ϕ Scan of the SmCo_4Cu film (blue) grown on a single crystalline Al_2O_3 substrate (gray) at 550°C . (c) Pole figure of the SmCo_5 reflection of the SmCo_4Cu film.

to understand the specific role of individual defects on the magnetic properties. Nevertheless, due to the thermodynamic instability of the SmCo_5 phase, in thin films, complex decomposition phenomena do occur. We have recently discovered a novel phase decomposition regime in molecular-beam epitaxy (MBE)-grown thin films, resulting in the coexistence of SmCo_5 and $\text{Sm}_2\text{Co}_{17}$ blocks at the nanoscale with a width of only a few nanometers.¹⁸ These films have low coercivity due to their high crystallinity, phase purity, and fully coherent interfaces between SmCo_5 and $\text{Sm}_2\text{Co}_{17}$. In contrast, sputtered thin films grown at much higher particle energies have a more complex precipitation nanostructure made up of various Sm-rich phases such as SmCo_3 and Sm_2Co_7 , which can lead to ultra-high coercivity primarily due to pinning at low-symmetry grain boundaries.¹⁹

Typically, different buffers and underlayers made from Ru, Cr, or Cu have been used to ease the growth of Sm-Co thin films. Textured Cr and Ru buffer layers promote the c -axis orientation and improve the magnetic properties. Above all, Cu has been widely studied because it not only facilitates the out-of-plane orientation but also has been found to have the unique advantage of stabilizing the CaCu_5 structure.^{20–22} Nevertheless, the magnetic properties of the Sm-Co layer will be affected by diffusion processes from these buffer layers.

In this work, we have established a direct growth process of Cu-substituted $\text{SmCo}_{5-x}\text{Cu}_x$ samples on sapphire without using any additional underlayer, which eliminates the potential impact of diffusing elements. We use computational and experimental methods to characterize the element-specific magnetic properties and illuminate the role of Cu incorporation in SmCo_5 and its effect on coercivity.

2. METHODOLOGY

2.1. Experimental Part. The base pressure of the used MBE chamber was 10^{-10} mbar. The $\text{SmCo}_{5-x}\text{Cu}_x$ thin films were deposited by e-beam co-evaporation from elemental Sm, Co, and Cu sources. The films were deposited onto c -axis-oriented Al_2O_3 substrates, known to promote the c -axis orientation of the SmCo_5 phase. First, a temperature scan was carried out showing that the most favorable temperature for growing a crystalline SmCo_5 layer in this setup was 550°C . The substrates were heated from the backside using a diode laser, a technique that avoids contamination from vacuum

heaters. Before evaporation, the substrates were annealed at 540°C for 1 h in the MBE chamber to obtain a clean crystalline substrate surface. For all samples, the deposition rate of the samarium was kept constant at 0.1 \AA/s . The individual deposition rates of cobalt and copper were changed, but the sum of the deposition rate (Co plus Cu) was kept constant at 0.1 \AA/s . A series of $\text{SmCo}_{5-x}\text{Cu}_x$ films were produced with $x = 0.5, 1, 1.5,$ and 2 . The evaporation rates during the growth of the thin films were controlled by using quartz crystal microbalances. The quality of the films was monitored using in situ reflection high-energy electron diffraction.

X-ray diffraction (XRD) with Cu $K\alpha$ radiation on a Rigaku SmartLab system was carried out for the crystallographic and structural characterization of the films. The thicknesses of the films were determined to be $30 \text{ nm} \pm 2 \text{ nm}$. The magnetic properties of the films were measured by a superconducting quantum interference device (SQUID) in two directions, out-of-plane (OOP) and in-plane (IP) of the substrate surface, using the MPMS-XL magnetometer by Quantum design. The measurements have been performed at 300 K with external fields up to 6 tesla. The diamagnetic contribution from the Al_2O_3 substrate has been subtracted by correcting the slope between 4 and 6 tesla. The coupling of Sm and Co moments has been studied using X-ray magnetic circular dichroism (XMCD) by recording element-specific hysteresis loops. For structural and spectroscopic characterizations, scanning transmission electron microscopy (STEM) and energy-dispersive X-ray spectroscopy (EDX)²³ were used in combination on cross-sectional specimens that were prepared along the c -axis using a focused Ga ion beam (FIB) sputtering. The STEM images and EDX maps were processed using Velox software (Thermo Fisher Scientific).

2.2. Computational Part. In order to evaluate the single-ion anisotropy (SIA) of Sm^{3+} , the crystal field parameters (CFPs) were calculated in the framework of density functional theory (DFT) using the WIEN2k program.²⁴ The generalized gradient approximation was employed for the exchange–correlation functional. The experimental lattice parameters of SmCo_5 were adopted in the calculations. Regarding the Cu-doped cases, including $\text{Sm}(\text{Co}_4\text{Cu}_{3g})_5$ and $\text{Sm}(\text{Co}_4\text{Cu}_{2c})_5$, the lattice parameters were fixed to those of SmCo_5 considering the relatively small volume change. Therefore, the solely chemical effect of Cu can be explicitly probed. The RMT \times

K_{\max} was set to 7, and a k -mesh of $9 \times 9 \times 9$ was sampled in the Brillouin zone. For the calculation of CFPs, we followed the method proposed by Novák et al.,²⁵ in which the local Hamiltonian in the basis of Wannier functions is expanded by a series of spherical tensor operators. In specific, the self-consistent field (SCF) calculation was first performed without spin polarization and with 4f electrons in the core. Subsequently, a non-SCF calculation was carried out treating 4f as valence states so that the 4f states were allowed to hybridize with the transition metal 3d states. In addition, we shifted the energy of 3d states 0.4 Ry lower to assure appropriate hybridization strength. The Bloch states from the 4f energy window were then transformed to Wannier functions using the Wien2wannier interface²⁶ followed by the standard Wannierization process by Wannier90.²⁷

The obtained CFPs were then used to construct the atomic Hamiltonian of Sm by including the Coulomb interactions (\hat{H}_U), the spin-orbit coupling, and the Sm-transition metal exchange coupling (\hat{H}_{ex})

$$\hat{H}_{at} = \hat{H}_U + \lambda \sum_i \hat{s}_i^z + \hat{H}_{CF} + \hat{H}_{ex} \quad (1)$$

The eigenvalue of the Hamiltonian was solved using the Lanczos algorithm as implemented in the Quany code.²⁸ By varying the magnetization direction corresponding to the exchange coupling term, the eigenvalue was then obtained as a function of azimuthal angle, which give rise to the SIA.

3. RESULTS AND DISCUSSION

3.1. Crystal Structure. Figure 1a shows the XRD patterns of the $\text{SmCo}_{5-x}\text{Cu}_x$ films grown onto 001-oriented Al_2O_3 substrates. The main 006 reflection of the substrate appears at 41.67° . The 001-oriented Al_2O_3 promotes the growth of c -axis-textured $\text{Sm}(\text{Co,Cu})_5$ films, as indicated by the presence of 00*l*-type reflections.

In the XRD patterns, we observe reflections assigned to the SmCo_5 and $\text{Sm}_2\text{Co}_{17}$ phases. In Table 1, the lattice parameters

Table 1. Lattice Parameters c and 2θ Values for the Series of the $\text{SmCo}_{5-x}\text{Cu}_x$ Thin Films^a

| sample name | c lattice parameter (Å) | 2θ (deg) |
|---|---------------------------|-----------------|
| $\text{SmCo}_{4.5}\text{Cu}_{0.5}$ | 4.0505 | 44.711 |
| SmCo_4Cu | 4.015 | 45.116 |
| $\text{SmCo}_{3.5}\text{Cu}_{1.5}$ (bulk) | 4.01 | 45.186 |
| $\text{SmCo}_{3.5}\text{Cu}_{1.5}$ | 4.022 | 45.043 |
| SmCo_3Cu_2 | 4.037 | 44.861 |
| SmCo_5 (bulk) | 4.006 | 45.233 |
| $\text{Sm}_2\text{Co}_{17}$ (bulk) | 12.233 | 44.393 |

^aThe bulk values are taken from ref 30 for reference.

c of our thin films are listed, and the bulk SmCo_5 and $\text{Sm}_2\text{Co}_{17}$ values are given as references 29, 30. Our c -axis values for $\text{SmCo}_{5-x}\text{Cu}_x$ with $x = 1.5$ and $x = 2$ are close to literature values, while our values for $x = 0.5$ and $x = 1$ are larger. This observed non-linear peak shift of the 002 reflection shown in the inset of Figure 1a can be consistently explained when considering that at this position the 002 reflection from the 1:5 and the 004 reflection from the 2:17 phase overlap, with the 004 reflection of 2:17 at a lower diffraction angle as observed previously.¹⁸ Therefore, when the 2:17 phase is eliminated at increased Cu content ($x \approx 1.5$), the peak maximum shifts close

to the expected value of $\text{SmCo}_{3.5}\text{Cu}_{1.5}$. For $x \geq 1.5$, the values coincide again with the expected bulk values. Note that the phase purity of the 1:5 phase is significantly higher than that of typical sputtered thin films; however, reflections from a small amount of residual Sm-rich phases can still be detected around 29 and 30° . Nevertheless, the overall crystal structure remains consistent predominantly 1:5 throughout the series.

Azimuth scans have been used to confirm crystal lattice symmetry and epitaxial relations. Here, we show a ϕ -scan of the diffraction peak of the SmCo_4Cu sample with respect to the substrate. Figure 1b shows the 104 reflection (gray $2\theta = 35.03^\circ$ and $\chi = 38.02^\circ$) of the substrate which is rhombohedral and the SmCo_4Cu sample (blue) which is hexagonal. The ϕ -scan shows three peaks which indicate the 3-fold symmetry of the Al_2O_3 substrate. Six peaks are obtained for the SmCo_4Cu film which shows the 6-fold symmetry and proves its hexagonal phase. The observed peaks correspond to the 201 reflection of the SmCo_5 phase. The pole figure of the 201 reflections, Figure 1c, shows the high-intensity Bragg peaks in blue. The distribution of the reflections indicates a crystalline, highly textured film.

3.2. Magnetization Measurements. Cu is usually used as a dopant in SmCo_5 thin films grown onto Cr or Ru buffer layers.^{31,32} As mentioned above, in this work, no additional underlayers have been used, and the $\text{SmCo}_{5-x}\text{Cu}_x$ films were deposited directly on top of Al_2O_3 substrates. The hysteresis loops of the out-of-plane direction are shown in Figure 2. The

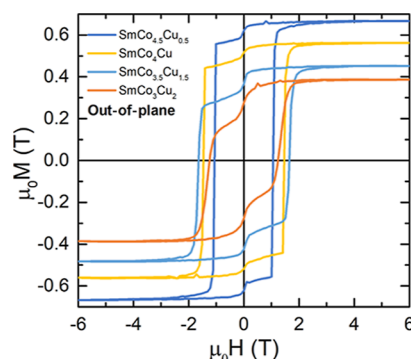


Figure 2. Magnetization curves of the $\text{SmCo}_{5-x}\text{Cu}_x$ thin films measured in the OOP direction as a function of the applied field at 300 K.

easy axis of magnetization is out-of-plane for all samples, while the hard axis is in-plane, as shown in Figure 3. Starting from the film with the lowest Cu concentration, a remanent magnetization of 0.6 T can be observed and the coercivity reaches 1.08 T. Upon increasing the Cu ratio, the coercivity drastically increases up to 1.64 T, whereas the remanent and saturation magnetizations, as expected due to Cu dilution of Co moments, decrease (see Figure 4). A further increase of Cu results in a rapid decrease of coercivity to 1.23 T.

There are two sites where Cu can substitute Co, namely, Co_{2c} and Co_{3g} , as shown in Figure 5.³³ As the thin film microstructure is similar in all cases predominantly 1:5, we assume that extrinsic contributions to the coercivity are comparable—but with the exception of the distribution of the substitutional element copper. The Cu distribution will be addressed in Section 3.4. Therefore, we suggest that the increased coercivity is at least partly correlated with an increased intrinsic anisotropy resulting from Cu substitution at

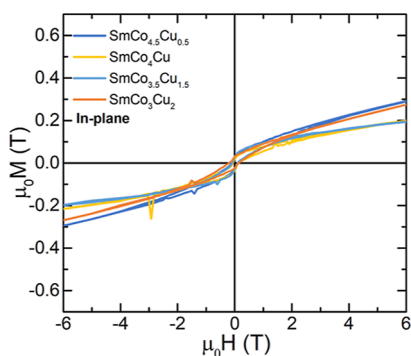


Figure 3. Magnetization curves of the $\text{SmCo}_{5-x}\text{Cu}_x$ thin films measured in the IP direction as a function of the applied field at 300 K.

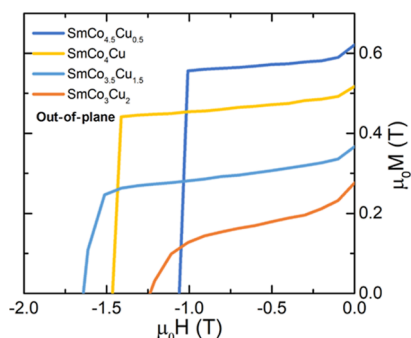


Figure 4. Demagnetization curves of the $\text{SmCo}_{5-x}\text{Cu}_x$ thin films as a function of the applied field at 300 K.

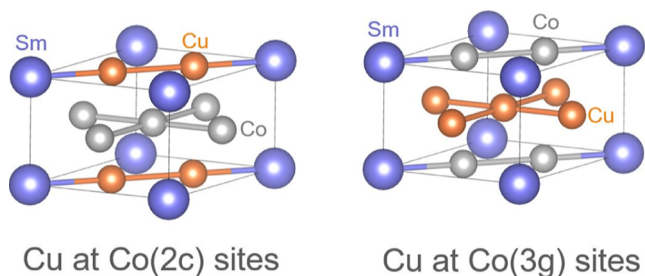


Figure 5. Schematic representation of the occupation of Cu at Co 2c sites and at Co 3g sites in the SmCo_5 crystal structure.

the Co_{3g} sites. A similar suggestion has been made for $\text{Y}(\text{Co,Cu})_5$,³⁴ a system which also behaves in thin films similar to the here investigated $\text{Sm}(\text{Co,Cu})_5$.^{18,35} To corroborate this hypothesis, we discuss the described DFT-based modeling in Section 3.5. The IP magnetization measurements shown in Figure 3 further support an increased anisotropy for SmCo_4Cu and $\text{SmCo}_{3.5}\text{Cu}_{1.5}$. Another factor leading to increased intrinsic anisotropy is the improved crystallization of the 1:5 phase due to Cu substitution.³⁶ Interestingly, in the OOP loops shown in Figure 4, a small kink appears at the zero field. This kink might be associated with the presence of a residual soft magnetic nanocrystalline or amorphous phase that is not strongly coupled to the hard-magnetic phase.³⁷

3.3. Element-Specific Measurements. XMCD spectra and element-specific hysteresis curves have been recorded at the bending magnet beamline 6.3.1 of the Advanced Light Source (ALS) at the Lawrence Berkeley National Laboratory. The measurements were carried out using an applied magnetic field of up to 1.9 T with a fixed polarization at ambient

temperatures. The samples have been measured in the OOP direction, parallel to the magnetic easy c -axis. As a detection method, X-ray-excited optical luminescence (XEOL) was used, which probes the full thickness of the film, due to the luminescence of oxygen in the Al_2O_3 substrate.³⁸ In this way, element-specific hysteresis loops have been recorded at fixed energies at the XMCD maxima and minima for Co $L_{2,3}$ -edges (779.2 and 794.5 eV) and Sm $M_{4,5}$ -edges (1082.5 and 1109.3 eV).

The strength of element-specific hysteresis measurements is the quantitative separation of the individual contributions from the Co and Sm magnetic moments.³⁹ The normalized element-specific hysteresis curves are shown in Figure 6. The Co and

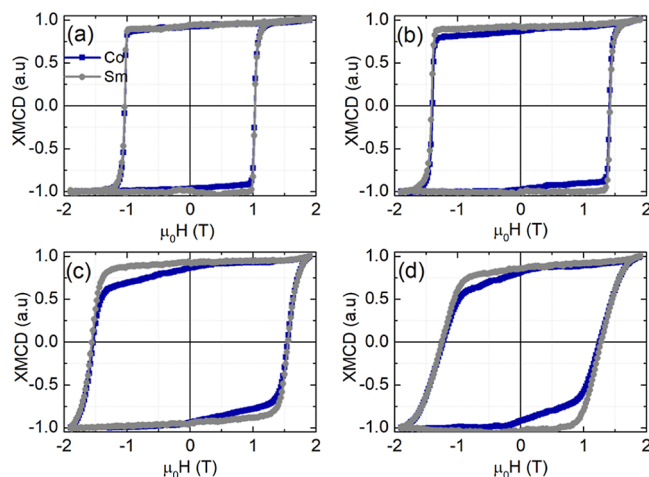


Figure 6. Element-specific hysteresis loops for the Sm $M_{4,5}$ (gray) and Co $L_{2,3}$ -edges (blue) recorded at room temperature applying positive and negative 1.9 T external fields in the OOP direction for the following samples (a) $\text{SmCo}_{4.5}\text{Cu}_{0.5}$, (b) SmCo_4Cu , (c) $\text{SmCo}_{3.5}\text{Cu}_{1.5}$, and (d) SmCo_3Cu_2 .

Sm curves do not deviate significantly for the $\text{SmCo}_{4.5}\text{Cu}_{0.5}$ film shown in Figure 6a. This confirms the stronger exchange coupling between the rare-earth Sm and the transition metal Co. Upon the increase of Cu substitution, a gap between Co and Sm appears in the second quadrant's demagnetizing curves. The measured data indicates that the substitution of Cu in the Co sub-lattice causes a continuous decoupling of the Sm and Co moments and softens the Co moment. The dilution with Cu is also the reason for the reduced total magnetization of the films. In contrast, samarium moments are only softened at higher Cu concentrations, which is also supported by the reduced critical temperature of the Cu-rich compounds.

3.4. Structure and Chemical Composition of SmCo_4Cu . The structure and elemental distribution of the SmCo_4Cu sample were studied in cross-sectional geometry. Figure 7a shows the structure of the sample in a high-resolution high-angle annular dark-field (HAADF) STEM image. Note the presence of a characteristic “dumbbell” pattern in the Sm-Co-Cu that indicates the formation of the 2:17 phase at the interface to the Al_2O_3 substrate. The rest of the layer shows a uniform 1:5 phase formation. The thickness of the 2:17 phase is approximately 7 nm. The transition from 2:17 to 1:5 phase is continuous, i.e., no sharp boundaries were observed.

Figure 7b shows the chemical composition distribution of individual elements extracted from EDX/STEM spectrum

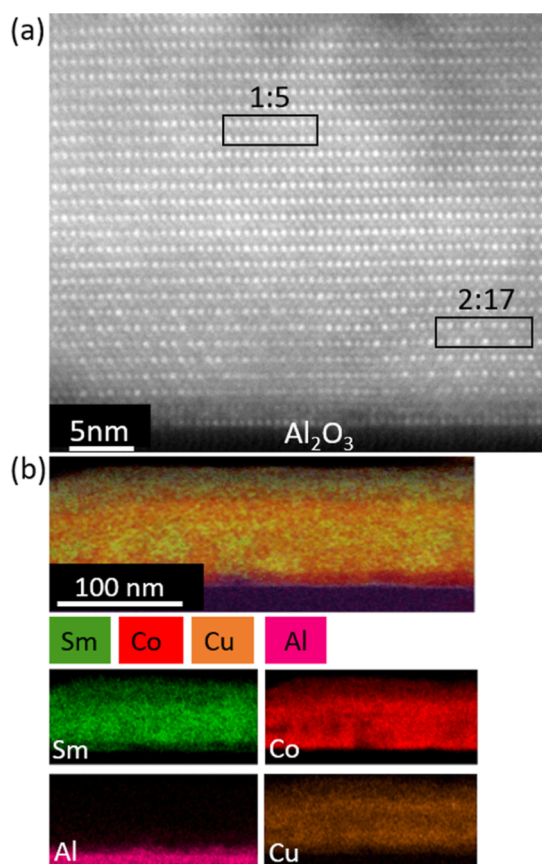


Figure 7. (a) High-resolution HAADF STEM image showing the interface of the SmCo_4Cu thin film to the Al_2O_3 substrate. The dumbbell pattern of atomic columns reveals the presence of the $\text{Sm}_2\text{Co}_{17}$ phase. (b) Chemical composition mapping of Sm, Co, and Cu extracted from STEM/EDX spectrum imaging. Note that the distribution of Co and Cu is not uniform.

imaging. The Co and Cu maps reveal an inhomogeneous distribution of the elements, suggesting Cu- and Co-rich regions. These inhomogeneities might be responsible for the zero-field kink in the SQUID measurement, which is absent in the XMCD measurement (see Figures 4 and 6).

3.5. Discussion. The magnetization curves of the $\text{SmCo}_{5-x}\text{Cu}_x$ films measured at room temperature are shown in Figure 2. It is clear that Cu substitution affects the coercivity which reaches a maximum value of 1.64 T. The presence of Cu at low concentrations enhances coercivity up to the $\text{SmCo}_{3.5}\text{Cu}_{1.5}$. Following the XRD patterns, the 1:5 phase is by far the predominant phase in all samples. A small fraction of

the 2:17 phase which seems to be induced from the substrate (rather than to a nanoscale phase decomposition as described previously)¹⁸ is fully suppressed for higher Cu substitution. XMCD element-specific hysteresis loops proved that Cu substitution results in an increasing decoupling of the Sm and Co moments. Last but not least, electron microscopy measurements showed that the films are dominated mainly by the 1:5 phase.

We first discuss the effect of Cu substitution on the intrinsic magnetic anisotropy of SmCo_5 , especially the SIA of Sm^{3+} . While intuitively one would expect an immediate decrease of intrinsic magnetic anisotropy, the computational methods described in Section 2.2 show a different and more complex behavior. The calculated CFPs B_{lm} for SmCo_5 , $\text{Sm}(\text{Co}_4\text{Cu}_{3g})_5$, and $\text{Sm}(\text{Co}_4\text{Cu}_{2c})_5$ are listed in Table 2. SmCo_5 belongs to the point group D_{6h} ; therefore, only B_{20} , B_{40} , B_{60} , and $B_{6\pm 6}$ retain. In particular, the magnitude of B_{20} is dominant and determines largely the magnetic anisotropy of Sm^{3+} , i.e., a negative B_{20} indicates uniaxial magnetic anisotropy. Note that the energy shift for transition metal 3d states was selected to be -0.4 Ry. By varying the energy shift to -0.2 and -0.6 Ry, the corresponding B_{20} are -1328 and -977 K, respectively. In addition, depending on the specific experimental measurement and fitting methods, the values of CFPs, especially for B_{40} , B_{60} , and $B_{6\pm 6}$, could differ largely. The value of B_{20} with an energy shift of -0.4 Ry in the current work is comparable with those of refs 40 and 41. Here, we would like to stress that we control the value of the energy shift to be the same for SmCo_5 and Cu-doped SmCo_5 , so that the CFP difference can be ascribed to the potential difference Sm senses in the different crystalline environments. With Cu occupying the 3g sites (Figure 5), B_{20} is more negative, indicating that the SIA of Sm^{3+} is indeed enhanced. In contrast, the Cu doping on the 2c site tends to lower the SIA of Sm^{3+} . Note that the number of nonzero B_{lm} parameters in $\text{Sm}(\text{Co}_4\text{Cu}_{3g})_5$ is larger due to the lower symmetry.

Another important aspect to be considered is the exchange coupling between the Sm and its neighboring Co atoms, which can be weakened upon introducing non-magnetic Cu atoms into the system. The exchange field in SmCo_5 is set to be 250 T according to previous experimental⁴² and theoretical⁴¹ work, while for $\text{Sm}(\text{Co}_4\text{Cu}_{3g})_5$ and $\text{Sm}(\text{Co}_4\text{Cu}_{2c})_5$, the exchange fields are rescaled based on the calculated J_{SmCo} values contributed from the first-nearest neighbors of Sm with respect to the J_{SmCo} of SmCo_5 . Such exchange coupling parameters are evaluated using the OpenMX⁴⁶ code in the LDA + U regime, with $U = 6.7$ eV and $J = 0.7$ eV for the Sm 4f states. Accordingly, we set the exchange fields of Sm-

Table 2. CFPs (in Units of Kelvin) for $\text{Sm}^{3+}\text{Co}_5$, $\text{Sm}^{3+}(\text{Co}_4\text{Cu}_{3g})_5$, and $\text{Sm}^{3+}(\text{Co}_4\text{Cu}_{2c})_5$ ^a

| B_{lm} (K) | SmCo_5 | Sankar ref 40 | Tils ref 42 | Tie-Song ref 43 | Givord ref 44 | Buschow ref 45 | Patrick ref 41 | $\text{Sm}(\text{Co}_4\text{Cu}_{3g})_5$ | $\text{Sm}(\text{Co}_4\text{Cu}_{2c})_5$ |
|--------------|-----------------|---------------|-------------|-----------------|---------------|----------------|----------------|--|--|
| B_{20} | -1068 | -840 | -652 | -660 | -400 | -360 | -800 | -1380 | -867 |
| $B_{2\pm 2}$ | | | | | | | | 168 | |
| B_{40} | 5 | 200 | | -360 | 0 | 0 | -177 | 77 | -91 |
| $B_{4\pm 2}$ | | | | | | | | 102 | |
| $B_{4\pm 4}$ | | | | | | | | -44 | |
| B_{60} | -473 | 0 | | 0 | 800 | 0 | 71 | -472 | -430 |
| $B_{6\pm 2}$ | | | | | | | | -14 | |
| $B_{6\pm 4}$ | | | | | | | | -34 | |
| $B_{6\pm 6}$ | 494 | 6 | | 0 | 0 | 0 | -121 | 501 | 456 |

^aFor comparison, the experimental values and one theoretical result (ref 41) are also listed.

($\text{Co}_4\text{Cu}_{3g}$)₅ and $\text{Sm}(\text{Co}_4\text{Cu}_{2c})_5$ to 201 and 230 T, respectively. The Coulomb interaction parameters and the spin–orbit coupling strength are taken from ref 47. By varying the exchange field direction which is represented by the azimuthal angle θ , Figure 8 shows the eigenvalue E_{ani} of \hat{H}_{at} as a function

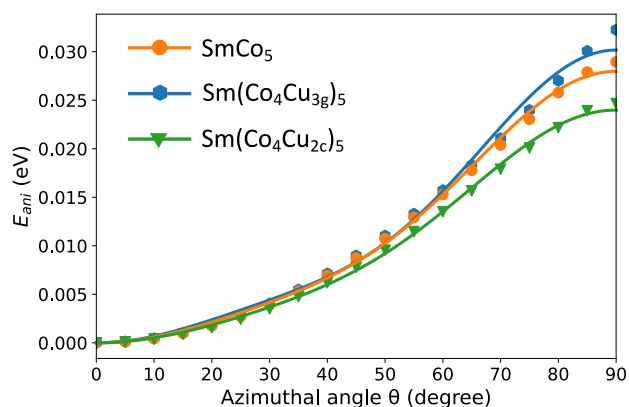


Figure 8. Ground-state energy of the Sm 4f shell in SmCo_5 (orange circle), $\text{Sm}(\text{Co}_4\text{Cu}_{3g})_5$ (blue hexagons), and $\text{Sm}(\text{Co}_4\text{Cu}_{2c})_5$ (green triangle) as a function of magnetization direction represented by the azimuthal angle θ .

of θ . It can be explicitly observed that Sm^{3+} in $\text{Sm}(\text{Co}_4\text{Cu}_{3g})_5$ possesses the highest SIA, while in $\text{Sm}(\text{Co}_4\text{Cu}_{2c})_5$, the SIA is the lowest. By fitting the energy curve to

$$E_{\text{ani}}(\theta) = K_1 \sin^2 \theta + K_2 \sin^4 \theta + K_3 \sin^6 \theta \quad (2)$$

we obtain K_1 of 21, 24, and 17 meV for SmCo_5 , $\text{Sm}(\text{Co}_4\text{Cu}_{3g})_5$, and $\text{Sm}(\text{Co}_4\text{Cu}_{2c})_5$, respectively. Note here that we omit the K_3' term associated with $K_3' \sin^6 \theta \cos 6\phi$ since we find K_3' rather small. Besides, the Cu doping effect on the Co sites can be approximated using YCo_5 as a prototype. It has been reported that the 3g-site doping of Cu increases the magnetic anisotropy of YCo_5 ,³⁴ while the 2c-site doping is expected to reduce the magnetic anisotropy due to a larger K_1 of Co_{2c} than that of Co_{3g} . In addition, according to our DFT calculations, the 2c-site doping is slightly energetically favorable by about 7 meV/atom as compared to the 3g-site doping. This strongly implies a statistically random distribution on both sites in reality as 7 meV amounts to a temperature of 81 K. Therefore, considering the contrasting roles played by Cu with different Wyckoff position occupations, a non-monotonous change of magnetic anisotropy with Cu doping content can be expected, as also observed in the Ce–Co-based systems.^{48,49} It is intriguing to characterize the intrinsic properties of the Cu-substituted SmCo_5 system to bridge the gap between the microscopic equilibrium properties and the macroscopic coercivity.⁵⁰

From a macroscopic point of view, Sm-rich precipitates as well as the formation of many different Sm–Co phases and structural disorder phenomena are strongly connected to high coercivity values in sputtered Sm–Co films.¹⁹ Sayama et al.⁵¹ suggested that the origin of high perpendicular anisotropy in SmCo_5 thin films on Cu buffer layers is related to the diffusion of Cu atoms into the SmCo_5 structure. Note that this diffusion effect is excluded in the presented study. The layer of $\text{Sm}_2\text{Co}_{17}$ at the substrate interface will not contribute to a systematic change of the hysteresis itself. As the defect structure is similar throughout the consistent series of thin films, we correlate the

increased coercivity to the increased intrinsic magnetocrystalline anisotropy upon Cu substitution and to the inhomogeneous distribution of Cu and Co. Since other phases, grain boundaries, and phase boundaries can be excluded for our thin film model systems, we suggest the nanoscale disproportionation of Cu and Co as an additional novel source of coercivity leading to enhanced pinning with increased Cu substitution.

4. CONCLUSIONS

In summary, our investigation of highly crystalline $\text{SmCo}_{5-x}\text{Cu}_x$ thin films grown by MBE on Al_2O_3 substrates in combination with advanced computational and characterization methods has revealed that copper substitution enhances the intrinsic magnetic anisotropy, correlated with an increase in coercivity. As a second source of increased coercivity, we have identified with EDX measurements a disproportionation of Cu- and Co-rich areas within an otherwise homogeneous 1:5 phase structure. The practical applicability of Cu to replace Co is limited of course by the induced overall reduction of the total magnetic moment, acting negatively on the $(\text{BH})_{\text{max}}$ product. XMCD provided clear evidence of a decoupling of Sm and Co moments in the presence of Cu. Electron microscopy confirmed the presence of the small amount of interfacial $\text{Sm}_2\text{Co}_{17}$ phase in the highly crystalline SmCo_5 layer. Based on thin film model systems, our study provides novel insight into the complex materials science and hardening mechanisms in rare-earth-based permanent magnetic materials by disentangling different sources of intrinsic and extrinsic contributions to the hysteresis behavior.

AUTHOR INFORMATION

Corresponding Authors

Georgia Gkouzia – Institute of Materials Science, Technical University of Darmstadt, 64287 Darmstadt, Germany;

orcid.org/0009-0002-7527-6637;

Email: georgia.gkouzia@tu-darmstadt.de

Ruiwen Xie – Institute of Materials Science, Technical University of Darmstadt, 64287 Darmstadt, Germany;

Email: ruiwen.xie@tmm.tu-darmstadt.de

Authors

Damian Günzing – Faculty of Physics and Center for Nanointegration (CENIDE), University of Duisburg-Essen, 47057 Duisburg, Germany; Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States

Teresa Weßels – Ernst Ruska-Centre for Microscopy and Spectroscopy with Electrons and Peter Grünberg Institute, Forschungszentrum Jülich, 52428 Jülich, Germany; Faculty of Physics and Center for Nanointegration (CENIDE), University of Duisburg-Essen, 47057 Duisburg, Germany

András Kovács – Ernst Ruska-Centre for Microscopy and Spectroscopy with Electrons and Peter Grünberg Institute, Forschungszentrum Jülich, 52428 Jülich, Germany;

orcid.org/0000-0001-8485-991X

Alpha T. N'Diaye – Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States

Márton Major – Institute of Materials Science, Technical University of Darmstadt, 64287 Darmstadt, Germany

J. P. Palakkal – Institute of Materials Physics, Georg-August-University of Göttingen, 37077 Göttingen, Germany; Institute of Materials Science, Technical University of Darmstadt, 64287 Darmstadt, Germany; orcid.org/0000-0002-7183-2627

Rafal E. Dunin-Borkowski – Ernst Ruska-Centre for Microscopy and Spectroscopy with Electrons and Peter Grünberg Institute, Forschungszentrum Jülich, 52428 Jülich, Germany; orcid.org/0000-0001-8082-0647

Heiko Wende – Faculty of Physics and Center for Nanointegration (CENIDE), University of Duisburg-Essen, 47057 Duisburg, Germany; orcid.org/0000-0001-8395-3541

Hongbin Zhang – Institute of Materials Science, Technical University of Darmstadt, 64287 Darmstadt, Germany

Katharina Ollefs – Faculty of Physics and Center for Nanointegration (CENIDE), University of Duisburg-Essen, 47057 Duisburg, Germany

Lambert Alff – Institute of Materials Science, Technical University of Darmstadt, 64287 Darmstadt, Germany; orcid.org/0000-0001-8185-4275

Complete contact information is available at:

<https://pubs.acs.org/10.1021/acs.inorgchem.3c01768>

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We acknowledge the financial support from the Deutsche Forschungsgemeinschaft (DFG) in the framework of the CRC/TRR 270 (Project ID. 405553726), projects A02, A03, A05, B05, and Z01/02. J.P.P. acknowledges the German Research Foundation (Deutsche Forschungsgemeinschaft - DFG) for the funding under project 429646908. The authors acknowledge Janghyun Jo for experimental help and Lea Risters for FIB sample preparation. This research used the resources of the Advanced Light Source, which is a DOE Office of Science User Facility under contract no. DE-AC02-05CH11231.

REFERENCES

- (1) Coey, J. M. *Magnetism and Magnetic Materials*; Cambridge University Press: Cambridge, U.K., 2010.
- (2) Strnat, K.; Hoffer, G.; Olson, J.; Ostertag, W.; Becker, J. A family of new cobalt-base permanent magnet materials. *J. Appl. Phys.* **1967**, *38*, 1001–1002.
- (3) Strnat, K. Rare earth-cobalt permanent magnets. *Handb. Ferromagn. Mater.* **1988**, *4*, 131–209.
- (4) Larson, P.; Mazin, I. Magnetic properties of SmCo_5 and YCo_5 . *J. Appl. Phys.* **2003**, *93*, 6888–6890.
- (5) Ucar, H.; Choudhary, R.; Paudyal, D. An overview of the first principles studies of doped RE-TM₅ systems for the development of hard magnetic properties. *J. Magn. Magn. Mater.* **2020**, *496*, 165902.
- (6) Gutfleisch, O.; Willard, M. A.; Brück, E.; Chen, C. H.; Sankar, S.; Liu, J. P. Magnetic materials and devices for the 21st century: stronger, lighter, and more energy efficient. *Adv. Mater.* **2011**, *23*, 821–842.
- (7) Mishra, R. K.; Thomas, G.; Yoneyama, T.; Fukuno, A.; Ojima, T. Microstructure and properties of step aged rare earth alloy magnets. *J. Appl. Phys.* **1981**, *52*, 2517–2519.
- (8) Sepelheri-Amin, H.; Thielsch, J.; Fischbacher, J.; Ohkubo, T.; Schrefl, T.; Gutfleisch, O.; Hono, K. Correlation of microchemistry of cell boundary phase and interface structure to the coercivity of $\text{Sm}(\text{Co}_{0.784}\text{Fe}_{0.100}\text{Cu}_{0.088}\text{Zr}_{0.028})_{7.19}$ sintered magnets. *Acta Mater.* **2017**, *126*, 1–10.
- (9) Gutfleisch, O. High-temperature samarium cobalt permanent magnets. *Nanoscale Magnetic Materials and Applications*; Springer New York, 2009; pp 337–372. DOI: [10.1007/978-0-387-85600-1_12](https://doi.org/10.1007/978-0-387-85600-1_12).
- (10) Maury, C.; Rabenberg, L.; Allibert, C. Genesis of the cell microstructure in the Sm (Co, Fe, Cu, Zr) permanent magnets with 2:17 type. *Phys. Status Solidi* **1993**, *140*, 57–72.
- (11) Duerschnabel, M.; Yi, M.; Uestuener, K.; Liesegang, M.; Katter, M.; Kleebe, H.-J.; Xu, B.; Gutfleisch, O.; Molina-Luna, L. Atomic structure and domain wall pinning in samarium-cobalt-based permanent magnets. *Nat. Commun.* **2017**, *8*, 54.
- (12) Oesterreicher, H.; Parker, F.; Misroch, M. Giant intrinsic magnetic hardness in $\text{SmCo}_{5-x}\text{Cu}_x$. *J. Appl. Phys.* **1979**, *50*, 4273–4278.
- (13) Staab, F.; Bruder, E.; Schäfer, L.; Skokov, K.; Koch, D.; Zingsem, B.; Adabifiroozjahi, E.; Molina-Luna, L.; Gutfleisch, O.; Durst, K. Hard magnetic SmCo_5 -Cu nanocomposites produced by severe plastic deformation. *Acta Mater.* **2023**, *246*, 118709.
- (14) Hadjipanayis, G.; Tang, W.; Zhang, Y.; Chui, S.; Liu, J.; Chen, C.; Kronmüller, H. High temperature 2: 17 magnets: relationship of magnetic properties to microstructure and processing. *IEEE Trans. Magn.* **2000**, *36*, 3382–3387.
- (15) Xiong, X. Y.; Ohkubo, T.; Koyama, T.; Ohashi, K.; Tawara, Y.; Hono, K. The microstructure of sintered $\text{Sm}(\text{Co}_{0.72}\text{Fe}_{0.20}\text{Cu}_{0.055}\text{Zr}_{0.025})_{7.5}$ permanent magnet studied by atom probe. *Acta Mater.* **2004**, *52*, 737–748.
- (16) Wu, S.; Zhang, D.-T.; Yue, M.; Wang, Y.-Q.; Shang, Z.-F.; Wu, D.; Liang, J.-M. In-situ observation of magnetization reversal process of $\text{Sm}(\text{Co}, \text{Cu}, \text{Fe}, \text{Zr})_z$ magnets with different Fe contents. *Rare Met.* **2020**, *39*, 250–255.
- (17) Shang, Z.; Yue, M.; Li, Y.; Zhang, D.; Xie, Z.; Wang, Y. The effect of multi-scale Cu distribution regulation on magnetic properties of $\text{Sm}(\text{CoFeCuZr})_z$ magnets. *J. Magn. Magn. Mater.* **2020**, *502*, 166484.
- (18) Sharma, S.; Zintler, A.; Günzing, D.; Lill, J.; Meira, D. M.; Eilhardt, R.; Singh, H. K.; Xie, R.; Gkouzia, G.; Major, M.; Radulov, I.; Komissinskiy, P.; Zhang, H.; Skokov, K.; Wende, H.; Takahashi, Y. K.; Ollefs, K.; Molina-Luna, L.; Alff, L. Epitaxy Induced Highly Ordered $\text{Sm}_2\text{Co}_{17}$ - SmCo_5 Nanoscale Thin-Film Magnets. *ACS Appl. Mater. Interfaces* **2021**, *13*, 32415–32423.
- (19) Akdogan, O.; Sepelheri-Amin, H.; Dempsey, N.; Ohkubo, T.; Hono, K.; Gutfleisch, O.; Schrefl, T.; Givord, D. Preparation, characterization, and modeling of ultrahigh coercivity Sm-Co thin films. *Adv. Electron. Mater.* **2015**, *1*, 1500009.
- (20) Seifert, M.; Neu, V.; Schultz, L. Epitaxial SmCo_5 thin films with perpendicular anisotropy. *Appl. Phys. Lett.* **2009**, *94*, 022501.
- (21) Hofer, F. Physical metallurgy and magnetic measurements of SmCo_5 - SmCu_5 alloys. *IEEE Trans. Magn.* **1970**, *6*, 221–224.
- (22) Zhang, W.-y.; Zhang, X.-d.; Yang, Y.-c.; Shen, B.-g. Effect of Cu substitution on structure and magnetic properties of anisotropic SmCo ribbons. *J. Alloys Compd.* **2003**, *353*, 274–277.
- (23) Ernst Ruska-Centre for Microscopy and Spectroscopy with Electrons. FEI Titan G2 80-200 CREWLEY. *J. Large Scale Res. Facil.* **2016**, *2*, A43.
- (24) Blaha, P.; Schwarz, K.; Tran, F.; Laskowski, R.; Madsen, G. K.; Marks, L. D. WIEN2k An APW+ lo program for calculating the properties of solids. *J. Chem. Phys.* **2020**, *152*, 074101.
- (25) Novák, P.; Knížek, K.; Kuneš, J. Crystal field parameters with Wannier functions: Application to rare-earth aluminates. *Phys. Rev. B* **2013**, *87*, 205139.
- (26) Kuneš, J.; Arita, R.; Wissgott, P.; Toschi, A.; Ikeda, H.; Held, K. Wien2wannier: From linearized augmented plane waves to maximally localized Wannier functions. *Comput. Phys. Commun.* **2010**, *181*, 1888–1895.
- (27) Mostofi, A. A.; Yates, J. R.; Lee, Y.-S.; Souza, I.; Vanderbilt, D.; Marzari, N. wannier90: A tool for obtaining maximally-localised Wannier functions. *Comput. Phys. Commun.* **2008**, *178*, 685–699.
- (28) Lu, Y.; Höppner, M.; Gunnarsson, O.; Haverkort, M. Efficient real-frequency solver for dynamical mean-field theory. *Phys. Rev. B* **2014**, *90*, 085102.
- (29) Song, X.; Lu, N.; Xu, W.; Zhang, Z.; Zhang, J. Phase transformation in nanocrystalline $\text{Sm}_2\text{Co}_{17}$ permanent magnet material. *J. Appl. Crystallogr.* **2009**, *42*, 691–696.

- (30) International Center for Diffraction Data (ICDD). *PDF 04-004-4243 and PDF 01-078-8777*.
- (31) Yin, S.; Wang, H.; Zhao, H.; Jiang, Y.; Wang, J. The effects of Cu doping on crystalline structure and magnetic properties of $\text{SmCo}_{5-x}\text{Cu}_x$ thin films grown on Ru (0002). *J. Appl. Phys.* **2013**, *114*, 213908.
- (32) Cui, W.; Ma, L.; Sepehri-Amin, H.; Takahashi, Y.; Hono, K. The influence of grain morphology and easy axis orientation on the coercivity of $\text{Sm}(\text{Co}_{0.9}\text{Cu}_{0.1})_5$ thin films. *Acta Mater.* **2016**, *107*, 49–58.
- (33) Haider, S. K.; Ngo, H. M.; Kim, D.; Kang, Y. S. Enhancement of anisotropy energy of SmCo_5 by ceasing the coupling at 2c sites in the crystal lattice with Cu substitution. *Sci. Rep.* **2021**, *11*, 10063.
- (34) Okumura, H.; Fukushima, T.; Akai, H.; Ogura, M. First-principles Calculation of Magnetocrystalline Anisotropy of $\text{Y}(\text{Co}, \text{Fe}, \text{Ni}, \text{Cu})_5$ Based on Full-potential KKR Green's Function Method. **2022**, arXiv preprint arXiv:2204.07384.
- (35) Sharma, S.; Ohmer, D.; Zintler, A.; Major, M.; Radulov, I.; Kunz, U.; Komissinskiy, P.; Xu, B.; Zhang, H.; Molina-Luna, L.; Skokov, K. P.; et al. Induction of uniaxial anisotropy by controlled phase separation in Y-Co thin films. *Phys. Rev. B* **2020**, *102*, 014435.
- (36) Ohtake, M.; Nukaga, Y.; Kirino, F.; Futamoto, M. Effects of substrate temperature and Cu underlayer thickness on the formation of SmCo_5 (0001) epitaxial thin films. *J. Appl. Phys.* **2010**, *107*, 09A706.
- (37) Kneller, E. F.; Hawig, R. The exchange-spring magnet: a new material principle for permanent magnets. *IEEE Trans. Magn.* **1991**, *27*, 3588–3560.
- (38) Kallmayer, M.; Schneider, H.; Jakob, G.; Elmers, H.; Balke, B.; Cramm, S. Interface magnetization of ultrathin epitaxial $\text{Co}_2\text{FeSi}(110)/\text{Al}_2\text{O}_3$ films. *J. Phys. D: Appl. Phys.* **2007**, *40*, 1552–1557.
- (39) Stöhr, J. Exploring the microscopic origin of magnetic anisotropies with X-ray magnetic circular dichroism (XMCD) spectroscopy. *J. Magn. Magn. Mater.* **1999**, *200*, 470–497.
- (40) Sankar, S.; Rao, V.; Segal, E.; Wallace, W.; Frederick, W.; Garrett, H. Magnetocrystalline anisotropy of SmCo_5 and its interpretation on a crystal-field model. *Phys. Rev. B* **1975**, *11*, 435–439.
- (41) Patrick, C. E.; Staunton, J. B. Temperature-dependent magnetocrystalline anisotropy of rare earth/transition metal permanent magnets from first principles: the light RCO_5 (R= Y, La-Gd) intermetallics. *Phys. Rev. Mater.* **2019**, *3*, 101401.
- (42) Tils, P.; Loewenhaupt, M.; Buschow, K.; Eccleston, R. Crystal and exchange fields in SmCo_5 studied by inelastic neutron scattering. *J. Alloys Compd.* **1999**, *289*, 28–31.
- (43) Tie-Song, Z.; Han-Min, J.; Guang-Hua, G.; Xiu-Feng, H.; Hong, C. Magnetic properties of R ions in RCO_5 compounds (R= Pr, Nd, Sm, Gd, Tb, Dy, Ho, and Er). *Phys. Rev. B* **1991**, *43*, 8593–8598.
- (44) Givord, D.; Laforest, J.; Schweizer, J.; Tasset, F. Temperature dependence of the samarium magnetic form factor in SmCo_5 . *J. Appl. Phys.* **1979**, *50*, 2008–2010.
- (45) Buschow, K.; Van Diepen, A.; De Wijn, H. Crystal-field anisotropy of Sm^{3+} in SmCo_5 . *Solid State Commun.* **1974**, *15*, 903–906.
- (46) Terasawa, A.; Matsumoto, M.; Ozaki, T.; Gohda, Y. Efficient algorithm based on liechtenstein method for computing exchange coupling constants using localized basis set. *J. Phys. Soc. Jpn.* **2019**, *88*, 114706.
- (47) Tripathi, S. XMCD investigation at M4,5 edges of the rare earth elements in high-performance permanent magnet. Ph.D. Thesis; Universität Stuttgart, 2018.
- (48) Lamichhane, T. N.; Onyszczak, M. T.; Palasyuk, O.; Sharikadze, S.; Kim, T.-H.; Lin, Q.; Kramer, M. J.; McCallum, R.; Wysocki, A. L.; Nguyen, M. C.; Antropov, V. P.; Pandey, T.; Parker, D.; Bud'ko, S. L.; Canfield, P. C.; Palasyuk, A. Single-Crystal Permanent Magnets: Extraordinary Magnetic Behavior in the Ta-Cu- and Fe-Substituted CeCo_5 Systems. *Phys. Rev. Appl.* **2019**, *11*, 014052.
- (49) Xie, R.; Zhang, H. Mixed valence nature of the Ce 4f state in CeCo_5 based on spin-polarized DFT + DMFT calculations. *Phys. Rev. B* **2022**, *106*, 224411.
- (50) Matsumoto, M. Magnetism trends in doped Ce-Cu intermetallics in the vicinity of quantum criticality: Realistic Kondo lattice models based on dynamical mean-field theory. *Phys. Rev. Mater.* **2020**, *4*, 054401.
- (51) Sayama, J.; Mizutani, K.; Asahi, T.; Ariake, J.; Ouchi, K.; Osaka, T. Origin of perpendicular magnetic anisotropy of SmCo_5 thin films with Cu underlayer. *J. Magn. Magn. Mater.* **2006**, *301*, 271–278.