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Origins of the significant improvement in nanocrystalline Samarium–Cobalt's magnetic properties when doping with Niobium

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ABSTRACT

$SmCo_7$-based compounds are prototypical rare-earth based hard magnetic materials that are the backbone of numerous devices and applications. We have found that by doping the $SmCo_7$ phase with Niobium (e.g. $SmCo_{6.7}Nb_{0.3}$), the enhanced coercivity being measured. Using a combination of microstructural and compositional characterization techniques with ab initio calculations, we find that the Nb-doping stabilizes the nanocrystalline nature of the material by residing at the 2e site of the $SmCo_7$ structure, decreases the average grain size, and substantially increases the magnetocrystalline anisotropy constant (K) (e.g. from 1.25×10^7 erg/cm^3 for $SmCo_7$ to 1.40×10^7 erg/cm^3 for $SmCo_{6.7}Nb_{0.3}$). A significant enhancement in coercivity with Nb doping is attributed to the increased K and the reduced grain size.

1. Introduction

Sm–Co systems are often used for high-temperature permanent magnets, where the two compounds $SmCo_5$ (space group P6/mmm) and Sm_2Co_{17} ($P6_3/mmc$) are central to most applications [1,2]. $SmCo_5$ has a very high magnetocrystalline anisotropy constant, K, with a large anisotropy field, $H_a \sim 200$ kOe [1] but relatively low saturation magnetization ($M_s = 790$ emu/cm^3), while Sm_2Co_{17} has a significantly lower magnetocrystalline anisotropy ($H_a \sim 65$ kOe) but a much larger magnetization ($M_s = 955$ emu/cm^3) [3,4] at room temperature. For applications, the largest possible magnetic response (magnetization) over the largest field range (set by the magnetocrystalline anisotropy measured by H_a), is optimal. For this reason, $Sm(Co,M)_7$ compounds (where M is a doping element) [5,6] have been the focus of intensive investigations as these compounds can exhibit both high saturation magnetizations and large magnetic anisotropies [7–10]. In terms of rare-earth magnet system, there is a driving economic force to find a replacement for Neodymium and Dysprosium rare-earth-based magnets, and Sm–Co based system are strong contenders [11].

The $SmCo_7$ compound is metastable with a $TbCu_7$-type structure but a doping element can be employed to stabilize the phase, and enhance the magnetic properties such as the coercivity (H_c), [7,10] that is the germane attribute for useful magnets at high temperature (>500 °C) [12]. Stabilizing elements M = Ti, Zr, Hf, Si, Ga, Cu and V have been examined previously [9,13–17]. A further increase in H_c is possible by increasing the magnetocrystalline anisotropy (since $H_c \propto 2K/M_s$) and decreasing the grain size of bulk samples [18,19].

In this work, a large increase of the coercivity (H_c) was found experimentally in the stable phase of $SmCo_{6.7}Nb_{0.3}$, whose origin was identified to be a significant reduction in grain size and increase in H_a. While grain size can be observed clearly by experiments such as transmission electron microscopy (TEM) and X-ray diffraction (XRD), the experimental determination of H_a requires corroboration from theoretical calculations. This is because H_a is measured by observing the easy and hard axis magnetization of a powder sample encased in epoxy that has had its overall magnetization "pre-aligned" in an applied field as the epoxy cures. However, the procedure necessary to powder the sample induces the decomposition of the $SmCo_7$ phase ($SmCo_7 \rightarrow SmCo_5 + Sm_2Co_{17}$), making it problematic to attribute change of H_a to the phase of interest.

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We turned to first-principles density functional theory-based calculations incorporating spin polarization using the Vienna ab initio simulation package (VASP) with a precise potential for each element [37,38]. The simulations were used to obtain the site occupation, magnetization, and H_a. Our approach was to calculate the magnetism using superstructures of $SmCo_{7-x}Nb_x$ ($x = 0$ and 0.3) based on a 25 atom unit cell where Nb was placed at different positions (described below) were built to perform the calculations (with limitations set due to the restriction of computation capability as a result of nonlinear characteristics of relativistic effect in simulations [39]). The simulations indicated the origin of the significant increase in coercivity, H_c (compared to pure $SmCo_7$) by incorporating the effects of Nb-doping, calculating the resultant H_a, and bringing together the effects of grain size and H_a. This work has been different from previous work [20] that the composition has been modified for comparing different Sm–Co systems. Detailed analyses based on first-principles density functional theory will be addressed. Besides, different analytical instruments used here, XRD and TEM, will be discussed.

2. Experimental and simulation methods

2.1. Materials and synthesis

The materials were obtained from Gredmann Company and the purity of Sm was 99.9%, and for Co and Nb, 99.99%. Alloy ingots with a nominal composition $SmCo_{7-x}Nb_x$ ($0 \leqslant \times \leqslant 0.5$) were prepared by arc melting [20,27,28]. The ingots were melted four times to ensure homogeneity, and then melt spun in an Ar atmosphere with a copper wheel at a speed of 40 m/s using a single-roller melt spinner.

2.2. Structural and compositional measurements

The overall crystal structure and composition of the samples was determined by X-ray powder diffraction (XRD) using a Shimadzu XRD 6000 with Cu Kα radiation collected using a step scanning mode with a step width of 0.02° (2θ) and a sampling time of 6 s in the range of $20° \leqq 2\theta \leqq 120°$, where θ is the diffraction angle. XRD patterns were Rietveld-refined using GSAS (general structure analysis system) [43]. And these patterns clearly indicated the $SmCo_7$ phase (Fig. 1) [20].

Samples for transmission electron microscopy (TEM) measurements were prepared from pieces of melt spun ribbon whose thicknesses were reduced to less than 100 nm using a dual beam focused ion beam mill (DB-FIB, FEI Nova NanoLab 200) with a 5 kV operating voltage and ~10 pA to 5 nA cutting current. A JEM 2100 F TEM was used to collect the high resolution images and electron diffraction patterns. Both images and electron diffraction patterns were matched to simulated versions made using the multislice software package [40–42]. Multislice uses first-principles calculations based on crystal structure information, permitting a quantitative analysis of TEM measurements thought its image and pattern renditions, and established the spatial arrangement of the atoms in a structure. This information was used as the initial input for the ab initio calculations.

2.3. Ab initio calculations

The ab initio (first principles) calculations were based on density functional theory (DFT) [45] with a generalized gradient approximation (GGA) [46], using the Vienna ab initio simulation package VASP [37,38]. The starting point of the calculations were the arrangements of Sm and Co atoms for the $SmCo_5$ (Fig. 1(a)) and $SmCo_7$ (Fig. 1(b)) structures. To incorporate relativist effects into both structures for calculating the magnetism responsible for K and H_a, a larger $2 \times 2 \times 1$ supercell was constructed of $SmCo_5$ unit cells (k-points: $4 \times 8 \times 6$) to create a $SmCo_{7.3}$ structure (essentially the same as the $SmCo_7$ structure), where Sm atoms were then substituted by Co–Co dumbbells with a ratio of 2/8, as shown in Fig. 2(a)–(c). Based on the different ratios of lattice constants for $SmCo_5$, k-points $12 \times 12 \times 16$ were sued. Also, $SmCo_7Nb_{0.3}$ was simulated by replacing one Co atom with Nb in the unit cell.

K values were obtained from the simulations in the following way: $SmCo_7$ has a hexagonal structure, so its magnetic anisotropy energy (E_{MAE}) can be described by $E_{MAE} = K_0 + K_1 \sin^2\theta + K_2 \sin^4\theta$, where θ is the angle between the direction of the magnetization and the easy axis, and K_0, K_1, and K_2 are zeroth, first and second order magnetocrystalline anisotropy constants specific to the system [12] that represent the field-to-anisotropy directional dependencies. The magnetic moment configuration (that makes up the magnetization) in simulations were set to be parallel to the c-axis (easy axis) for Sm, and parallel to the basal plane (hard axis) for Co [13,47]. The difference of the total energies between that required to align the magnetization with the hard and easy axis was $\Delta E_{MAE} = K_1 + K_2 = K$, ($k$-points = $6 \times 12 \times 8$). For comparison with the simulations, experimental values of K were determined from the field-dependent magnetization using the relationship $H_aM_s/2 = K_1 + 2K_2 \approx K$ [12] where H_a and M_s are obtained from hysteresis loop measurements. For example, the ab initio calculated $K = 7.56 \times 10^7$ erg/cm^3 for $SmCo_5$ agreed very well with the measured value [1] of 7.7×10^7 erg/cm^3 (2% difference between experiment and simulation values).

2.4. Magnetic measurements

The field-dependent magnetization of the samples at 300 K was measured using a Quantum Design PPMS (Physical Property Measurement System) with a maximum applied field of 90 kOe.

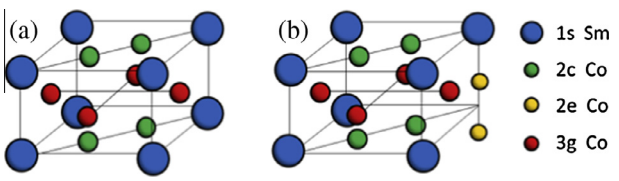

Fig. 1. Structures of (a) $SmCo_5$ and (b) $SmCo_7$. The lattice parameters of structure (a,b) are $a = 4.891$ Å, and $c = 4.056$ Å. The angles of the structure (a,b) are $\alpha = \beta = 90°$, and $\gamma = 60°$.

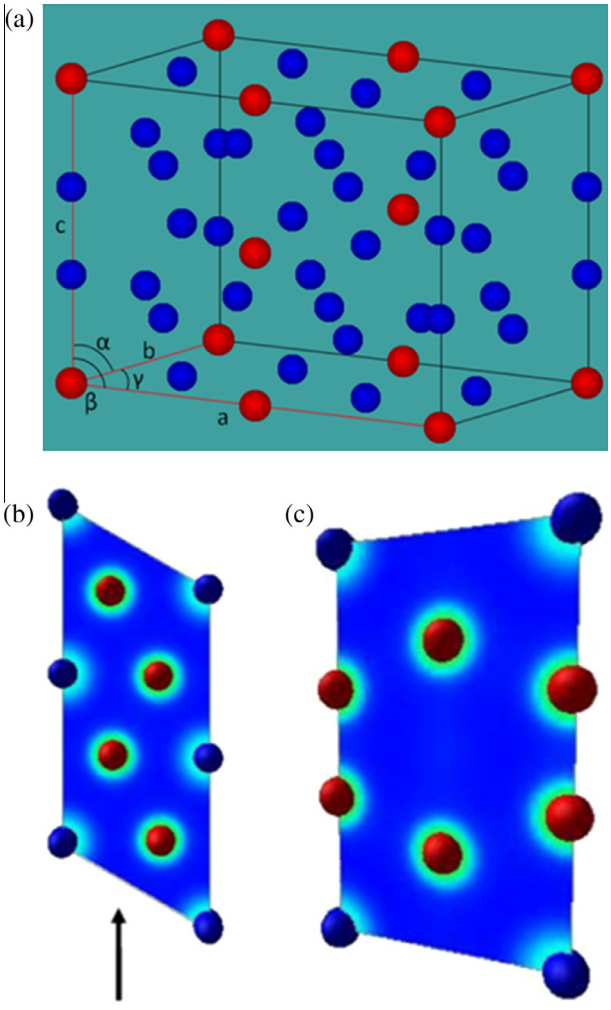

Fig. 2. Structure of 25-atom $SmCo_{7.3}$ (a–c) used for ab initio calculation. (a) unit cell view, (b) top view, (c) view from the arrow. The lattice parameters of the unit cell (a) are $a = 9.782$ Å, $b = 4.891$ Å, and $c = 8.112$ Å. The angles of the unit cell (a) are $\alpha = \beta = 90°$, and $\gamma = 60°$.