The temperature dependent anisotropy constants of epitaxially grown PrCo$_{5+x}$

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The temperature dependent anisotropy of a highly textured epitaxial Pr–Co film with a single orientation of the crystallographic c-axis along MgO[001] is investigated by measuring angle dependent hysteresis loops at various temperatures. The measured magnetization curves are compared with calculated magnetization curves, which allows for a full analysis of the temperature dependent anisotropy constants of first and second order, $K_1$ and $K_2$ and the determination of the saturation polarization. The analysis reveals that the Pr$_{15.4}$Co$_{84.6}$ film undergoes a spin reorientation transition from an easy axis anisotropy to an easy cone anisotropy at 108 K. The room temperature values of $K_1$ and $K_2$ measured for this Pr$_{15.4}$Co$_{84.6}$ film are 5.0 MJ m$^{-3}$ and 0.5 MJ m$^{-3}$, respectively. The difference to the bulk PrCo$_5$ single crystal values is ascribed to the high Co content of the Pr$_{15.4}$Co$_{84.6}$ film. © 2010 American Institute of Physics.

I. INTRODUCTION

RECo$_5$ (RE=rare earth) compounds are of both fundamental and technological interest, due to their excellent intrinsic magnetic properties such as a high Curie temperature $T_C$, a high saturation polarization $J_s$, and a complex and often temperature dependent magnetocrystalline anisotropy (MCA). RECo$_5$ compounds crystallize in a hexagonal CaCu$_5$ structure ($P6/mmm$) (Co occupies 2$c$ and 3$g$ sites and RE takes 1$a$ site).$^{1,2}$ The simple crystal structure of the RECo$_5$ phase and the existence of isostructural compounds with different RE or transition metal species make the RECo$_5$ compounds a suitable model system to investigate the atomistic origin of MCA and its effects on the magnetic properties.

So far as PrCo$_5$ is concerned, it meets the requirements to qualify for a permanent magnet material and possesses the highest theoretical energy product within the RECo$_5$ series. Furthermore, PrCo$_5$ exhibits a spin reorientation (SR) transition from an easy axis anisotropy along the crystallographic c-axis (which persists above the transition temperature) to an easy cone anisotropy around 107 K.$^3$

In our earlier report,$^4$ we revealed that epitaxial Pr–Co films ($\approx80$ nm) can be prepared on Cr buffered MgO(110) substrates in a wide composition range with a single orientation of the c-axis which lies in the film plane along the MgO[001] substrate edge. In that series, Pr–Co films crystallize in different phases like the PrCo$_7$ structure$^{5,6}$ and the PrCo$_5$ and Pr$_2$Co$_7$ phases, which exist in a certain composition range. These highly textured epitaxial Pr–Co films exhibit excellent intrinsic and extrinsic magnetic properties. Pr–Co films in the composition range of 15.4$\leq$Pr at. % $\leq$ 20.4 crystallize in a mixed phase of the hard magnetic hexagonal PrCo$_5$ and Pr$_2$Co$_7$ phases and possess an energy density value of up to $(BH)_{\text{max}}=310$ kJ m$^{-3}$ at room temperature. However, this energy density value measured for a Pr$_{15.4}$Co$_{84.6}$ film, with a room temperature saturation polarization $J_S=1.4$ T, is below the theoretical energy density value of $(BH)^{\text{th}}_{\text{max}}=J_S^2/4\mu_0=390$ kJ/m$^3$, which holds for $J_R=J_S$ and $\mu_0H_C>1/2J_S$ (Ref. 7). In this Pr–Co film with its coercivity of $\mu_0H_C=0.66$ T, the condition of $\mu_0H_C>1/2J_S$ is not satisfied and therefore raises the question concerning the limits in coercivity and possible improvements. For both, the upper theoretical limit of coercivity and the detailed coercivity mechanism a precise knowledge of the MCA as the main origin of coercivity has to be known. Furthermore, to test coercivity models such as coherent rotation, nucleation, and domain wall pinning, a good set of temperature dependent data for the saturation polarization and the anisotropy constants $K_1$ and $K_2$ is needed.$^8$

In this paper, we carefully examine the MCA, including the SR, in an epitaxial Pr$_{15.4}$Co$_{84.6}$ film with an energy density of 310 kJ/m$^3$ and determine the temperature dependency of the anisotropy constants and saturation polarization. To this end, magnetization measurements are carried out at various temperatures with the field applied at different angles with respect to the texture axis of the sample and are compared with the calculated magnetization curves. The full set of $K_1(T)$, $K_2(T)$, and $J_S(T)$ data for this thin film sample is discussed with respect to values found in single crystals and with respect to the measured coercivity.

II. EXPERIMENTAL

Epitaxial Pr–Co films ($\approx80$ nm) with (1100) orientation (having c-axis in the film plane only along MgO[001] substrate edge) were grown on heated Cr buffered MgO(110) substrates using pulsed laser deposition from metallic targets.$^4$
In order to investigate the temperature dependent anisotropy of an epitaxial Pr$_{15.4}$Co$_{84.6}$ film, angle dependent magnetization measurements with magnetic field applied along different angles $\alpha$ [sketch Fig. 1(b)] with respect to the texture axis (crystallographic c-axis) have been carried out at various temperatures. Measurements are performed in a split coil vibrating-sample magnetometer with a maximum field of 5 T in a temperature range between 5 and 300 K. The experimental facility allows to measure simultaneously both, the parallel and the orthogonal components of the magnetization for a given field and therefore the total (saturated) magnetization could be evaluated experimentally. From the measurement of only the parallel component of the magnetization vector it is not possible to derive the saturation magnetization of compounds, if the applied field is not large enough to saturate the sample, and it is not straightforward for compounds exhibiting SR transition. In the available experimental setup, we have access only to two (both in-plane) components of the magnetization vector. For the present case of a sample with easy axis and applied field always in the film plane, the magnetization distribution inside the sample will also be confined largely to the film plane (supported by the shape anisotropy). Thus, the additional measurement of the transversal component throughout the hysteresis allows the reconstruction of the total magnetization vector.

The measurements are carried out on a 5 mm $\times$ 5 mm epitaxial Pr$_{15.4}$Co$_{84.6}$ film with the angle $\alpha$ varying from $\alpha=0^\circ$ (parallel to c-axis: along MgO[001]) to $\alpha=90^\circ$ (parallel to in-plane hard axis: along MgO[110]) [Fig. 1(b)]. The sample is first saturated along the c-axis (easy axis at room temperature) at the highest available positive field of 5 T, then the reversed field is applied and the corresponding magnetization curves are recorded. Before starting the measurement for a new angle $\alpha$, the sample was always saturated along the c-axis at 5 T to ensure a similar initial state for every measurement. To determine the anisotropy constants a full range fitting procedure to the magnetization loops in a field range of 2–5 T is performed. The theoretical magnetization loops were calculated based on an energy minimization code including anisotropy energy developed up to second order ($K_1$ and $K_2$) and magnetostatic energy of the magnetization vector in an applied field. A realistic texture spread of $10^\circ$ was implemented by averaging over a Gauss shaped c-axis distribution around the texture axis of the sample. For a given temperature, measurements at five different angles were fitted simultaneously to derive the first and second order anisotropy constants ($K_1$ and $K_2$).

III. RESULTS AND DISCUSSION

Shown in Fig. 1 are the background corrected hysteresis loops of the parallel and orthogonal component of the magnetic polarization vector $\vec{J}$ measured at 220 K with the field applied along different angles ($\alpha=0^\circ$, $30^\circ$, $45^\circ$, $60^\circ$, and $90^\circ$ for parallel component and $\alpha=0^\circ$, $45^\circ$, and $90^\circ$ for orthogonal component). The field orientation with respect to the grain orientation is shown in the sketch [Fig. 1(b)]. When the field is applied along the c-axis ($\alpha=0^\circ$) a nearly rectangular hysteresis loop is observed for the parallel component $m^\parallel = \cos(\alpha-\theta)$ of magnetization [see Fig. 1(a)], as expected for an easy axis measurement (in which case only switching processes occur) of a uniaxial magnet. Here, $\vec{m}=\vec{J}/J_c$ is the normalized magnetization vector and $\theta$ is the angle between the texture axis and the vector $\vec{m}$. As shown in Fig. 1(a), the remanent polarization measured along the c-axis reaches 95% of the saturation polarization (magnetization measured at 5 T in this case) indicating a high degree of alignment of the grains along the c-axis. When the field is applied at an angle to the c-axis (which is the easy axis at this temperature of $T=220$ K) both switching and rotational processes occur. For higher angles $\alpha$ rotational processes dominate and for $\alpha=90^\circ$ (hard axis case) the magnetization process is purely rotational. Therefore, the magnetization curve measured along the hard axis of a uniaxial magnet is largely nonhysteretic with a linear increase in magnetization with the applied field [Fig. 1(a) $\alpha=90^\circ$ curve]. Furthermore, for the field applied at an angle to the c-axis ($0^\circ < \alpha \leq 90^\circ$), a progressive decrease in the magnetization with increasing angle $\alpha$ is observed. In the remanent state, the magnetic polarization vector ($\vec{J}$) is parallel to the easy axis. As we are measuring the...
component of $\mathbf{J}$ parallel to the former field axis, this projection decreases with larger $\alpha$ and the remanent polarization as a function of field follows a $\cos \alpha$ dependency. On the other hand, if a positive field is applied, irrespective of $\alpha$ the magnetization will approach the saturation polarization (at least at the anisotropy field) and thus magnetization curves measured at a large angle $\alpha$ will have a large slope as they start from a lower remanent polarization. Both trends (decrease in the remanent polarization and the increase in the slope of the magnetization curves with increase of the angle $\alpha$) are clearly visible in the measured hysteresis loops [Fig. 1(a)].

In highly textured samples (which is valid in this case), the hysteresis loop measured for the orthogonal component of the magnetization vector $[m^x = \sin(\alpha - \theta)]$ with field applied along the easy axis ($\alpha=0^\circ$; c-axis of the sample for PrCo$_3$) of a uniaxial magnet should exhibit a flat curve parallel to the field axis with negligible value of magnetization. Indeed the measured curve [Fig. 1(c) $\alpha=0^\circ$] exhibits the expected behavior. When the field is applied along the hard axis ($\alpha=90^\circ$), the orthogonal component of the magnetization vector $[m^x = \cos(\theta)]$ should follow the $\cos \theta$ (where $\theta$ is the angle between the easy axis and the vector $\mathbf{m}$) dependency as a function of applied field, and should have a closed loop (because the magnetization process is purely rotational), which is clearly observed in the measurement [see Fig. 1(c)]. Moreover, for the field applied at angles between the easy axis and hard axis ($0^\circ < \alpha < 90^\circ$) the magnetization loops measured for the orthogonal component exhibit hysteric behavior in which both the switching and rotational processes come into play. An example of a magnetization loop measured for the orthogonal component of the magnetic polarization vector with field applied at an angle of $45^\circ$ to the c-axis is shown in Fig. 1(c).

A behavior similar to that described in Fig. 1(a) but with slightly higher overall values of the magnetization is observed for magnetization loops measured at 150 K (not shown here). The increased magnetization arises from the temperature dependency of the saturation polarization of the Pr$_{15.4}$Co$_{84.6}$ film. This trend continues until the SR occurs at a certain temperature. At the SR transition temperature ($T_{SR}$), the system undergoes a transition from an easy axis anisotropy, which persists above the transition temperature, to an easy cone anisotropy and the easy magnetization directions make some angle with the c-axis (former easy magnetization direction) by the opening of a cone around the c-axis. Below $T_{SR}$, the remanence polarization measured for $\alpha=0^\circ$ has a smaller value than the saturation polarization $J_s$, which is understood from the projection of the magnetic polarization vector to the field/measurement axis. In this case, the remanence $J_R$ is determined by $\theta = \theta_{SR}$ and thus: $J_R = J_s \cos \theta_{SR}$, (where $\theta_{SR}$ is the SR angle). Now, if the field is turned on, in order to reduce the Zeeman energy the angle becomes smaller and the magnetization component parallel to the field axis becomes larger. Therefore, the magnetization curve which should be flat above $T_{SR}$ will now be slightly bent upward. It is, however, difficult to observe this small effect in the measured data at 100 K [Fig. 2(a)]. In the case of magnetization curves measured for $\alpha=90^\circ$ below $T_{SR}$, the energy (anisotropy and Zeeman energy) minimum is not observed for $\theta=0^\circ$ but for $\theta = \theta_{SR}$ [sketch Fig. 2(b)]. However, all the moments lying on the cone will average out and lead to a zero remanent polarization. When the field is applied, a small field value which is sufficient to break the symmetry of the cone will pull all moments toward the field axis and, as a result of this, a sudden increase in the magnetization is expected [sketch Fig. 2(c)]. A further increase in the magnetic field causes the rotation of the moments toward the field axis and a progressive increase in the magnetization for higher fields is expected. Therefore, a reduced slope is expected when approaching saturation polarization and consequently an extrapolation back to zero leads to a nonzero remanence value. As a result of this, the magnetization curves measured at a temperature below $T_{SR}$ for $\alpha=90^\circ$ are expected to exhibit a S-shape, which is indeed observed for the magnetization curves measured at 100 K. Also the progressive decrease in the magnetization with increasing angle $\alpha$ is still observed below $T_{SR}$. Similar hysteresis loops are measured for lower temperatures.

In order to evaluate the saturation polarization $J_s$, the vector sum of the parallel and orthogonal components of the magnetic polarization vector for a given field value at a particular angle and temperature is carried out (Fig. 3). This process is repeated for different field values as well as for several field angles and temperatures and from which averaged value of $J_s$ (averaged over all angles) as a function temperature are constructed. The temperature dependency of $J_s$ obtained from this analysis for the epitaxial Pr$_{15.4}$Co$_{84.6}$ film (open circle) together with the scaled saturation polarization of bulk PrCo$_3$ (solid line) is plotted in Fig. 3(b). With decreasing temperature $J_s$ increases and follows quite well the expected temperature dependency of the saturation polarization of bulk PrCo$_3$.\footnotemark[1]
In the following, the evaluation of the anisotropy constants from the measured magnetization curves is considered. To determine the anisotropy constants a full range fitting procedure to the magnetization curves in a field range of 2–5 T (in the first quadrant of the demagnetizing branch) is performed. The theoretical magnetization curves were calculated based on an energy minimization code including anisotropy energy developed up to second order \( (K_1 \text{ and } K_2) \) and magnetostatic energy of the magnetic polarization vector in an applied field.\(^{10}\) A realistic texture spread of \(10^\circ\) was implemented by averaging over a Gauss shaped c-axis distribution around the texture axis of the sample. For a given temperature, measurements at five different angles were fitted simultaneously to derive the first and second order anisotropy constants \( K_1 \) and \( K_2 \). The first quadrant magnetization curves (open circles) of the \( \text{Pr}_{15.4}\text{Co}_{84.6} \) film together with the calculated curves (lines) for five different angles at temperatures 300 and 100 K are shown in Fig. 4. The measured curves fit quite well to the calculated curves and the analysis leads to the determination of the first and second order anisotropy constants. Values of \( K_1 = 4.6 \text{ MJ/m}^3 \) and \( K_2 = 1.6 \text{ MJ/m}^3 \) are obtained at room temperature from this analysis. However, the measured value of \( K_1 = 4.6 \text{ MJ/m}^3 \) at room temperature is lower compared to the bulk single crystal value of \( K_1 = 7.7 \text{ MJ/m}^3 \) for \( \text{PrCo}_5 \) (Ref. 3), whereas the value of \( K_2 = 1.6 \text{ MJ/m}^3 \) is much higher compared to the value of \( K_2 = 0.05 \text{ MJ/m}^3 \) known for bulk \( \text{PrCo}_5 \). This difference might be caused by the fact that, in most cases, in order to determine the anisotropy constants of \( \text{PrCo}_5 \) single crystals, the Sucksmith and Thompson approach\(^{11}\) has been used, which only makes use of the hard axis curve to determine the anisotropy constants. Therefore, to effectively compare the anisotropy constant values obtained for the \( \text{Pr}_{15.4}\text{Co}_{84.6} \) film with the bulk \( \text{PrCo}_5 \) single crystal values, only the magnetization curves measured for \( \alpha = 90^\circ \) have been analyzed, in a similar way to the simultaneous analysis of 5 angles. It turns out that the observed values of \( K_1 = 5.0 \text{ MJ/m}^3 \) and \( K_2 = 0.6 \text{ MJ/m}^3 \) from the analysis of only the hard axis curve are more close to the values observed for bulk \( \text{PrCo}_5 \). The still existing difference is ascribed to the high Co content of the \( \text{Pr}_{15.4}\text{Co}_{84.6} \) film, which is optimized for high saturation polarization. It is known that the substitution of Co dumbbells for Co/RE atoms in the RECo\(_5\) structure will lead to a reduced anisotropy, as has been measured, e.g., for YCo\(_5\) and SmCo\(_5\) (Refs. 12 and 13). The different results obtained from the two fitting procedures on the same sample are, however, unexpected and so far its origin is not yet clear. In the subsequent discussion the anisotropy constants obtained from the analysis of the hard axis curve are used. The anisotropy constants \( K_1 \) and \( K_2 \) as a function of temperature are shown in Fig. 5(a).

The anisotropy constant \( K_1 \) decreases with decreasing temperature, changes its sign at \( T = 108 \text{ K} \), and reaches a value of \( K_1 = -4.8 \text{ MJ/m}^3 \) at 20 K. On the other hand, \( K_2 \) increases monotonically with decreasing temperature and reaches a value of \( K_2 = 16.1 \text{ MJ/m}^3 \) at 20 K. A sign reversal of \( K_1 \) at 108 K and \( K_1, K_2 \) values which satisfy the condition \( 2K_2 > -K_1 \) (Ref. 14) below 108 K manifest a SR transition from an easy axis to an easy cone anisotropy. The SR angle \( \theta_{SR} \) (cone angle with respect to the c-axis) which is a function of \( K_1 \) and \( K_2 \), varies with temperature according to...
As performed on an epitaxial SmCo5 film,\textsuperscript{15} is needed. This highly coercive Pr–Co films, a coercivity analysis, e.g., such judging the quantified MCA for its potential in creating information based on the coercivity reducing microstructural parameter beyond the scope of this work. We restrict to a simple estimation, going a SR transition. Therefore the coercivity analysis is however, not straightforward in the case of Pr–Co under-temperature dependent anisotropy measurement of Pr\textsubscript{15.4}Co\textsubscript{84.6} \textsuperscript{15} and large increase in \(K_2\) at low temperature this film exhibits a SR transition at \(T=108\) K. The values of \(K_1=5.0\) MJ/m\(^3\) and \(K_2=0.6\) MJ/m\(^3\) measured at room temperature for the Pr\textsubscript{15.4}Co\textsubscript{84.6} film differ from those of bulk PrCo due to the high Co content of the Pr\textsubscript{15.4}Co\textsubscript{84.6} film. These intrinsic set of data \([K_1(T), K_2(T), J_s(T)]\) are useful for the coercivity analysis, which is essential to boost the coercivity and to improve the energy density of the epitaxial Pr–Co films.

\section*{IV. CONCLUSIONS}

In summary, angle dependent hysteresis loops measured at various temperatures were carried out to determine temperature dependent saturation polarization, the anisotropy constants and the SR transition of an epitaxial Pr\textsubscript{15.4}Co\textsubscript{84.6} film with a high energy density. Due to a sign change in \(K_1\) and large increase in \(K_2\) at low temperature this film exhibits a SR transition at \(T=108\) K. We thus conclude that the MCA of the prepared high moment \((J_s=1.4\) T\) Pr\textsubscript{15.4}Co\textsubscript{84.6} film is sufficient to reach the maximum theoretical energy density, if a microstructure as in the isostructural SmCo5 film is achieved.

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\begin{thebibliography}{15}
\bibitem{} In an applied magnetic field, the total energy density for a hexagonal crystal of CaCu\textsubscript{5} type can be written as \(E_{\text{in}}=K_1 \sin^2 \theta+K_2 \sin^2 \theta-HJ_x \cos(\alpha-\theta),\) where \(K_1\) and \(K_2\) are anisotropy constants, \(\theta\) is the angle between the crystallographic c-axis and the magnetic polarization vector, \(H\) is the magnitude of the external field, \(J_x\) is the saturation polarization and \(\alpha\) is the angle between the c-axis and applied field direction.
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