Magnetic anisotropy in thin films of Prussian blue analogues

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tively studied systematically.10–15

Material parameters that are important include the film thickness, the spin-polarization, the saturation magnetic moment, and the exchange interactions. There is an increasing demand for novel architectures involving controlled magnetic anisotropy in ferromagnetic films and nanostructures. Accordingly, the ability to manipulate the underlying magnetic states of the spin polarizers is desirable. In addition to traditional solid-state materials, molecule-based magnetic systems are being investigated.16

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The motivation to understand the origins of this anisotropic phenomenon is amplified by the ability to control the magnetization of Prussian blue analogues by photo-irradiation or pressure.16 However, the magnetic response of the photo-controllable A-Co-Fe system is complicated by the multiple stable oxidation states of the Co and Fe ions and by orbital angular momentum contributions. Consequently, the Rb-Ni-Cr Prussian blue analogue, a ferromagnet system possessing a spectrum of long-range ordering temperatures, $T_c \sim 60 - 90 \text{ K}$, depending on stoichiometry was chosen as the centerpiece for the present work because the magnetic and physical properties of this system are robust and the ions have stable oxidation states that possess no first-order angular momentum.

Finally, it is important to stress the significance of our findings. Although the study of the magnetism of solid-state films is a mature field, the extensions to molecule-based magnetism are just beginning to emerge. For example, with the drive to develop new devices, applications with single crystals are being explored.18

However, the exploitation of molecule-based magnetic films may be more attractive for industrial fabrication, and devices based on metal-phthalocyanines and metal[TCNE:tetracyanethylene] are two examples of work in this direction. In our work, the origins of the magnetic anisotropy in films of Prussian blue analogues will be linked to demagnetization effects after we have systematically eliminated all other plausible explanations, some of which are not issues in traditional solid-state magnetic films. As a result, our results provide a foundation from which the magnetism in films of Prussian blue analogues may be understood and employed in new devices.

II. EXPERIMENTAL DETAILS

The synthesis of the powder samples followed established protocols, while the films were generated using sequential adsorption methods that are detailed elsewhere.14 Briefly stated, the film synthesis consists of using a solid support, such as Melinex 535, and immersing it in an aqueous solution of Ni$_{2+}$ ions and then in another aqueous solution of Cr(CN)$_6^{3-}$ containing Rb$^+$ ions. After each immersion step, washing with water...
is essential to remove the excess ions, and the process can be iterated multiple cycles to yield films of varying thicknesses and morphologies. For this work, two films, one of 40 cycles and the other of 400 cycles, are reported. Whereas the powder samples consisted of small polycrystals with diameters of ~60 nm, which are magnetically in the “bulk” limit,22 the 40 cycles and 400 cycles films had thicknesses of ~200 nm and ~2 μm, respectively. Finally, other Rb-M’-M Prussian blue analogue films were investigated, including Rb-Co-Cr, Rb-Cu-Cr, Rb-Zn-Cr, Rb-Ni-Fe, Rb-Co-Fe, Rb-Cu-Fe, and Rb-Zn-Fe.14,15

The chemical compositions and the physical properties of all samples were established by a suite of techniques, which yielded Rb₇Ni₄[Cr(CN)₆]₂.9·nH₂O.14,15 For the magnetization measurements, a commercial (Quantum Design) magnetometer was used in conjunction with a home-made in situ rotator.23 The powder samples were mounted in gelcaps, while the film samples were either cut and stacked in a plastic box or measured individually in a straw holder. A single 400 cycles film, a stack of ten 40 cycles films, and ~100 μg of powder embedded in 1-ecosane were employed for the cw-ESR measurements performed at either 50 GHz or 116 GHz, using a resonant cavity coupled to a cryostat and superconducting magnet at the NHMFL-Tallahassee. Transmission and reflection x-ray diffraction (XRD) studies were performed at 20 K, 110 K, and 300 K by using the instruments at the University of Guelph. Care was taken to avoid long term vacuum pumping of the sample at room temperature, since variations due to reversible dehydridation-hydration were observed as the (200) peak shifted to higher 2θ and broadened. Data were collected for nominally 24 h at each temperature, and a blank Melinex film was also measured to assist with the background subtraction arising from the solid support.

III. RESULTS

The anisotropic magnetic response in Prussian blue analogues was initially observed in magnetization measurements27 and this behavior is shown for the Rb-Ni-Cr films in Figs. 1 and 2. Differences between the ZFC and FC data are related to a spin-glass-like response,27,28 while the anisotropy of the thin and thick films is strikingly similar as the external magnetic field is applied parallel or perpendicular to the surface of the films, hereafter referred to as B ∥ and B ⊥, respectively. This behavior is also present, albeit to a somewhat weaker degree, in spin-cast samples but is not observed in films that were synthesized in a manner that corrupts their two-dimensional nature by generating discontinuities and roughness.10

To date, ESR investigations of Prussian blue analogues have been limited to the Rb-Mu-Fe system that ferromagnetically orders near 10 K.29,30 In our work, the nature of the anisotropy was explored, and the 116 GHz results for the thick film and additional details are available elsewhere.15

![FIG. 1: (Color online) The temperature dependences of the zero-field-cooled (ZFC) and field-cooled (FC) magnetizations, \( M(T) \), normalized to the FC values at \( T = 2 \) K, \( M_0 \), are shown for (a) low, \( B = 10 \) mT, and (b) high, \( B = 4 \) T, applied magnetic fields. For clarity, the data for the thin film are not shown in (b). The anisotropic response for \( B \) applied parallel (∥) or perpendicular (⊥) to the films is strikingly similar for both thin and thick films. The field-induced shift of \( T_c \) from ~70 K to ~100 K is observable. For each panel, the solid lines are the results of analysis using demagnetization factors (see text).](image1.png)

![FIG. 2: The angular variation of \( M \) is shown for the case of the thick film when \( B = 4 \) T and \( T = 10 \) K. The discrete steps of 1.5° are detectable, and the data were taken continuously at each angle that was held for a period of 5 min. The data for the thin film and additional details are available elsewhere.](image2.png)
IV. DISCUSSION

After inspecting the comprehensive set of experimental results, several points are immediately obvious. Firstly and simply stated, the films possess magnetic anisotropy that is not manifested in polycrystalline powder samples that are normally studied. Secondly, the data indicate that the underlying anisotropy prevails for thin and thick films, so the anisotropy does not explicitly arise from influences coming from direct interaction with the solid.
support but does depend upon the two-dimensional organization of the sample generated during the film fabrication process. Furthermore, the values of $T_c$ are independent of the orientation of the magnetic field, meaning the anisotropy does not originate from variations of the superexchange parameter, $J$. Thirdly, the ESR results, namely the line shapes of the powder spectra and the frequency independence of the magnitude of the line splittings, cannot be reconciled by the presence of an anisotropic g-tensor. Finally, magnetostriction or other structural changes are not observed at any temperature, so the cubic symmetry is preserved to an extent that does not permit it to be a possible explanation of the anisotropy.

With the elimination of several common mechanisms as the possible sources of the anisotropic response, magnetostatic interactions remain as a plausible explanation. Indeed, the uniaxial nature of the anisotropy is consistent with dipolar interactions. In addition, demagnetizing effects ($H_{\text{effective}} = H_{\text{lab}} - N M$, where $N$ is the demagnetizing factor) model the data well when using the theoretical value to normalize the high field, saturation magnetization value of $1.47 \times 10^5$ A/m, namely, $\langle S_{Ni_j} \rangle_{\text{max}} = 1$ and $\langle S_{Cr_z} \rangle_{\text{max}} = 3/2$.[15,33,34] The low field magnetization in the perpendicular orientation can be reproduced quantitatively from the parallel orientation if $N_{\|} = 0.07$ and $N_{\perp} = 0.86$, Fig. 1a, where domains are expected to obey $2N_{\|} + N_{\perp} = 1$.[33,34] The high field magnetization can also be reproduced but not as directly, since the high field susceptibility has a significant experimental uncertainty because $dM/dH$ is orders of magnitude smaller than $M/H$ in this range. Nevertheless, the uniformly magnetized film limit, vide infra, namely $N_{\|} = 0$ and $N_{\perp} = 1$, reasonably reproduces the observed trends (Fig. 1b).

The ESR data can also be explained by the presence of demagnetization effects.[24–36] Specifically, taking the equations of motion for a spin in $B$ along the $z$-axis, the resonance condition is

$$\omega_0^2 = g^2 \mu_B^2 [B_x + (N_y - N_z)\mu_0 M_z] [B_z + (N_x - N_z)\mu_0 M_x].$$  

(1)

For a perfect sphere, $N_x = N_y = N_z = 1/3$, so the resonance condition should be isotropic and have no magnetization dependence. In practice, there may be small deviations from spherical symmetry for the powder, and the resonance condition may be written as

$$\omega_{0,\text{powder}} = g \mu_B [B - \mu_0 M_z],$$

(2)

where $\delta$ takes care of deviations from spherical symmetry. For the powder data, Figs. 2 and 3, a shift of $\sim 10$ mT is present in the fully magnetized state compared to the paramagnetic state. This observation is consistent with a value of $\delta \sim 0.05$, and the shift is similar to the one reported for Rb-Mn-Fe,[29] where it was attributed to demagnetizing effects. For a uniformly magnetized film oriented perpendicular to $B$, the resonance condition is

$$\omega_{0,\|} = g \mu_B [B - \mu_0 M_z],$$

(3)

whereas for the parallel orientation, the resonance condition is

$$\omega_{0,\perp} = g \mu_B [B(B + \mu_0 M_z)]^{1/2}. $$

(4)

Ergo, the temperature dependence of the main lines can be predicted with $N_{\|} = 0$ and $N_{\perp} = 1$, and the results are in excellent agreement with the data (Fig. 4a).

V. CONCLUSIONS

In summary, the observed magnetic anisotropy of the Rb-Ni-Cr Prussian blue analogue films is attributable to demagnetization effects arising from their two-dimensional geometry. Additional evidence for the magnetic domain-field interactions is garnered from the extensive data sets collected on the aforementioned Rb-M$^\prime$-M Prussian blue analogues.[14,15] Having identified magnetic domains as the origin of the anisotropy, additional studies, such as magnetic imaging of the surfaces, will provide a deeper understanding of the architecture and dynamics of the domains. Finally, a systematic approach for determining the nature of magnetic anisotropy in coordination polymers has been presented and will be important as this class of materials is investigated for physical properties applicable to spintronic applications.

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