Experimental report

06/09/2022

Proposal: **5-54-337** **Council:** 4/2020

Title: Magnetic structure of Fe-substituted $CoCr_2O_4$ multiferroic thin films

Research area: Physics

This proposal is a resubmission of 5-54-314

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Samples: $Co(Cr_{1-x}Fe_x)_2O_4/Al_2O_3$
$Co(Cr_{1-x}Fe_x)_2O_4/MgAl_2O_4$

Instrument	Requested days	Allocated days	From	To
D17	6	4	09/03/2021	11/03/2021
			14/05/2021	19/05/2021

Abstract:

Multiferroic materials in which multiple order phenomena coexist have been the subject of intense research over the past decade. Although single component multiferroic materials are rare, the research efforts in these systems are driven by the possibility to directly control magnetic order by electric fields through a robust magnetoelectric coupling. For a range of device applications, the integration of the material in a thin film is necessary, in which the reduced dimensionality and proximity effects can drastically alter the magnetic structure through interface phenomena and strain. In this proposal, we aim to investigate the magnetic structure of Fe-doped $CoCr_2O_4$ single component multiferroic thin films. The results will establish the magnetic ordering of the parent compound with different interface and strain scenarios and elucidate the mechanism leading to intrinsic exchange bias and magnetic compensation upon substitution. The results will be pivotal for understanding the magnetic behaviour upon cation substitution in a thin film multiferroic and provide the ground for further tuning and stabilization of the desired functional properties.

Magnetic structure of Fe-substituted $CoCr_2O_4$ multiferroic thin films

Proposal 5-54-337 dealt with the structural and magnetic investigation of pure and Fe-substituted $CoCr_2O_4$ (CCO) thin films grown on two different substrates, namely $MgAl_2O_4$ (MAO) and Al_2O_3 (ALO), leading to a different strain and anisotropy axis orientation in the film. The first stage of the experiment concentrated on confirming the magnetic uniformity and signal obtained from pure CCO by investigating two films each with different thickness, 30 nm and 50 nm. PNR data was recorded at room temperature and after field cooling in 2 T at 30 K and 2 K. These temperatures were chosen to be above the multiferroic transition at 26 K, but below the ferrimagnetic transition at 96 K, while 2 K represents the base temperature below the multiferroic transition. Since CCO has a strong anisotropy along the [001] direction and is oriented out-of-plane for growth on MAO, two magnetic fields of 4 T and 1 T were applied to saturate the film and subsequently observe the reduction of the moment in lower fields due to rotation or domain formation. Due to the expected low spin-asymmetry (SA), no spin-flip analysis was attempted.

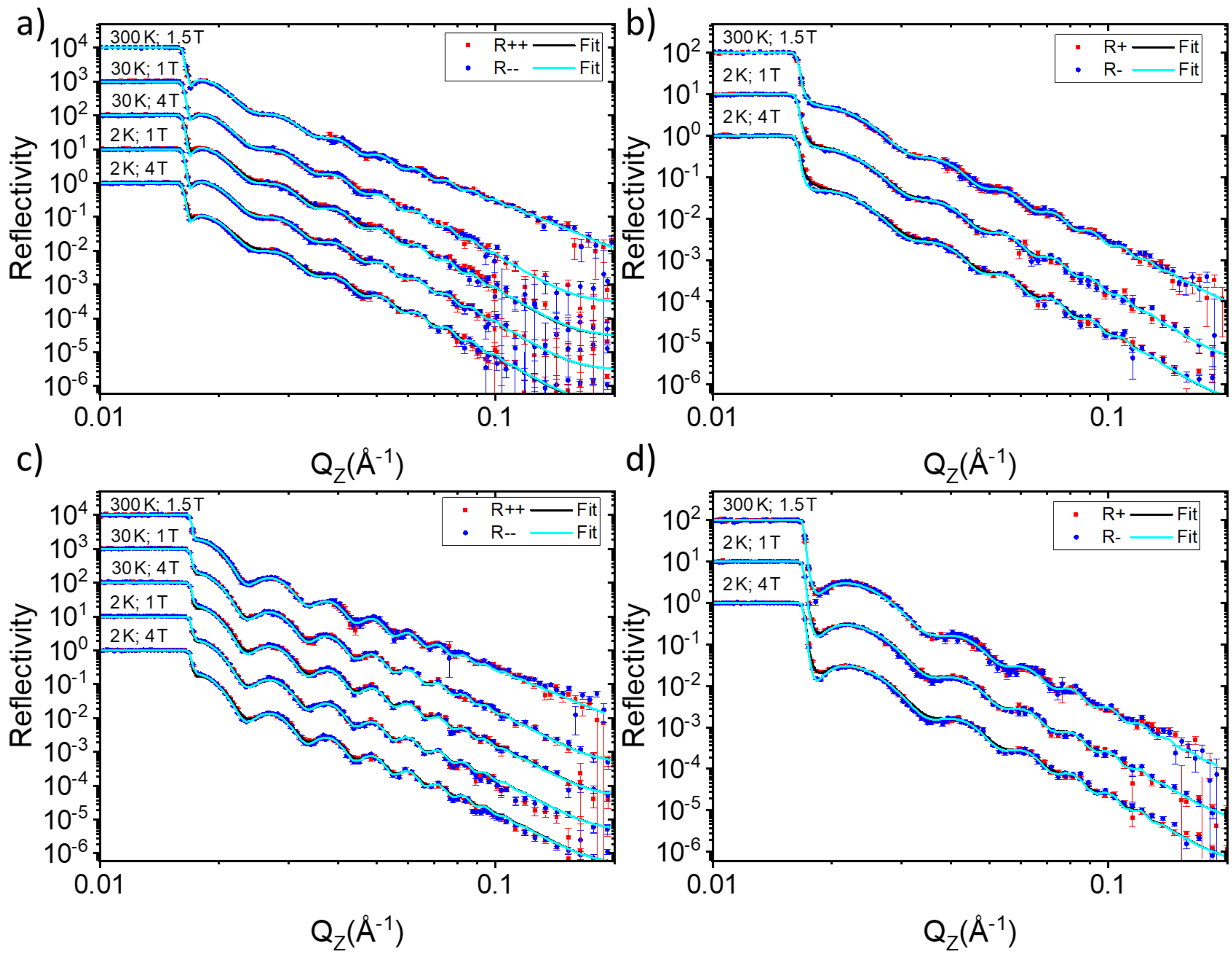

Figure 1: PNR data and fits of pure CCO. a) CCO(50nm)/MAO, b) CCO(30nm)/MAO, d) CCO(50nm)/ALO, e) CCO(30nm)/ALO. The data is offset vertically for clarity.

The PNR data shown in Figure 1 was fitted with a slab model allowing for a variation of the scattering length density and magnetization near the interface and the surface. The data was co-refined with x-ray reflectometry with the exact same structural model, only allowing for a potential scattering length variation due to off-stoichiometry. The obtained values, presented for XRR and PNR in Figure 2 a,b are within 1% of the expected literature value for both probes. The fits reveal a homogeneous CCO layer, but with a more gradual interface profile observed in the samples on ALO. Here the different symmetry of the substrate or chemical out-diffusion could lead to a modification of the CCO phase.

The magnetic sensitivity to the magnetic depth profile was increased by also co-refining the SA to effectively have the magnetic signal included twice in the fitting process (once by the 2-channel PNR data and once by the SA). Similar to the chemical structure, a homogeneous magnetic profile is observed. The profiles of the two samples on ALO indicate a small increase of the magnetization towards the substrate, which could stem from the different phase observed in the chemical profile. However, this small variation is within the uncertainty of the fit due to the overall very small moment of COO thin films. The magnetic parameters obtained for the different films are 0.18±0.03 μ_B/f.u. for CCO(50 nm)/MAO, CCO(30 nm)/MAO and CCO(50 nm)/ALO. The thinner sample on ALO, CCO(30 nm)/ALO, shows a slightly reduced moment of 0.15±0.03 μ_B/f.u., which is just within the error of the fits, but nevertheless apparent in the fitting.

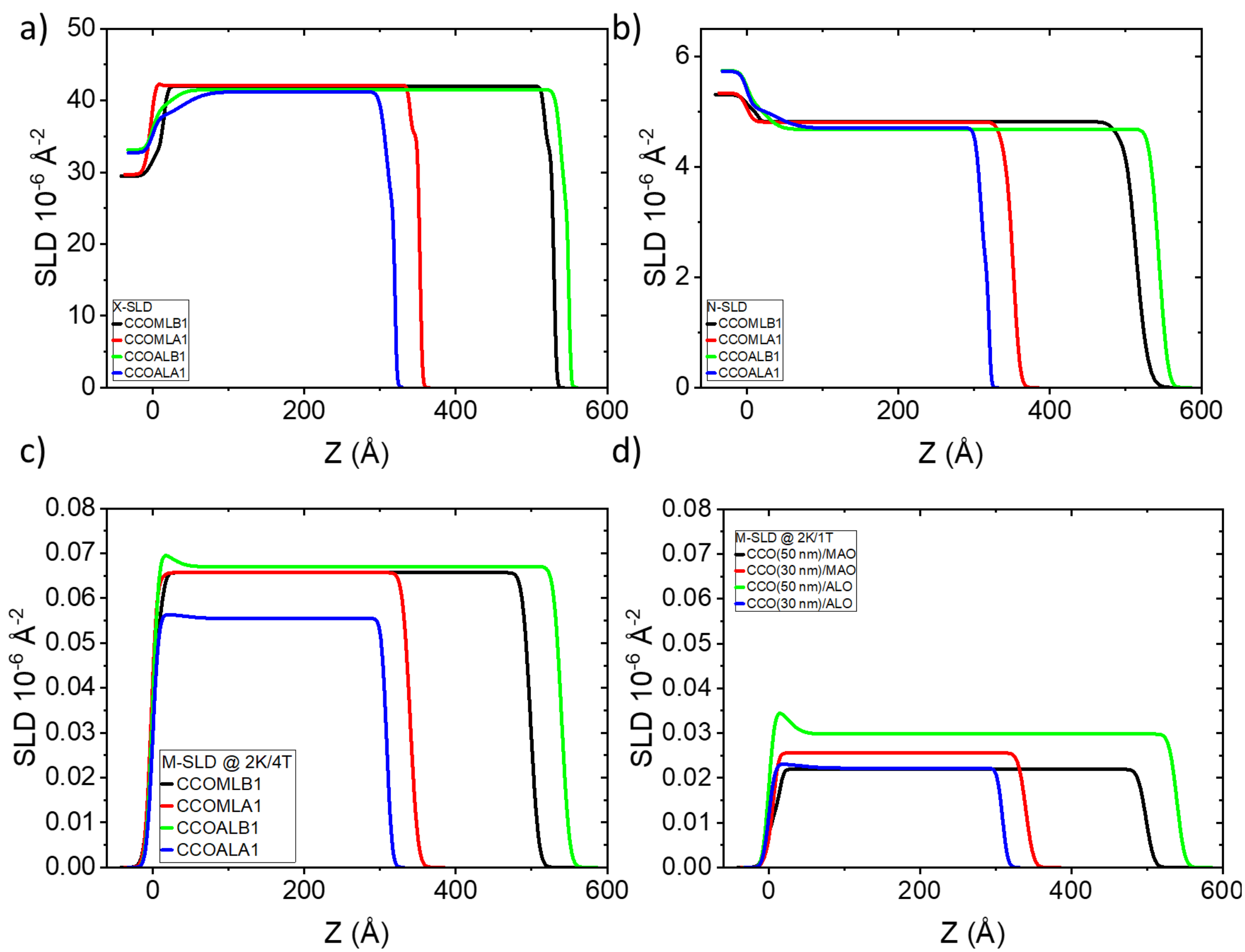

Figure 2: a) X-ray SLD profiles and b) neutron nuclear SLD profiles of the samples. c) Magnetic profile at 2K in 4T. Magnetic profiles at 2K in 1T.

All samples show a similar decrease in magnetization when the external field is lowered from 4T to 1T, which is slightly unexpected if the anisotropy axis is oriented more in-plane for ALO substrate. Further detailed magnetometry measurements will need to verify this. Measurements at 30 K have shown a very similar behavior with only slightly reduced moments compared to 2K. This is in line with reported flat magnetization profiles in the literature, where the multiferroic transition is only observed as a small step.

Finally, we managed to measure one Fe-substituted sample on ALO substrate under similar conditions. The analysis of this sample is still ongoing since the obtained profiles are not consistent and warrant further investigation. Despite showing very comparable reflectivities to the previous samples, a significant variation in the reflectivity between 2 K and 30 K is observed (Figure 3). This difference so far could only be modeled with two different structural profiles in which the SLD of the top 2/3 or the film drops and forms a sharp interface. Similarly, the magnetic profile shows a strong modulation as a function of depth. However, we do not yet consider these results entirely physical and further detailed investigation of the results is required. In addition, a comparison to the similar film on MAO substrate is needed. Within the allocated time for the experiment we did not succeed to measure further samples, and are therefore missing comparable data on Fe-substituted CCO on MAO substrates or different Fe concentrations.

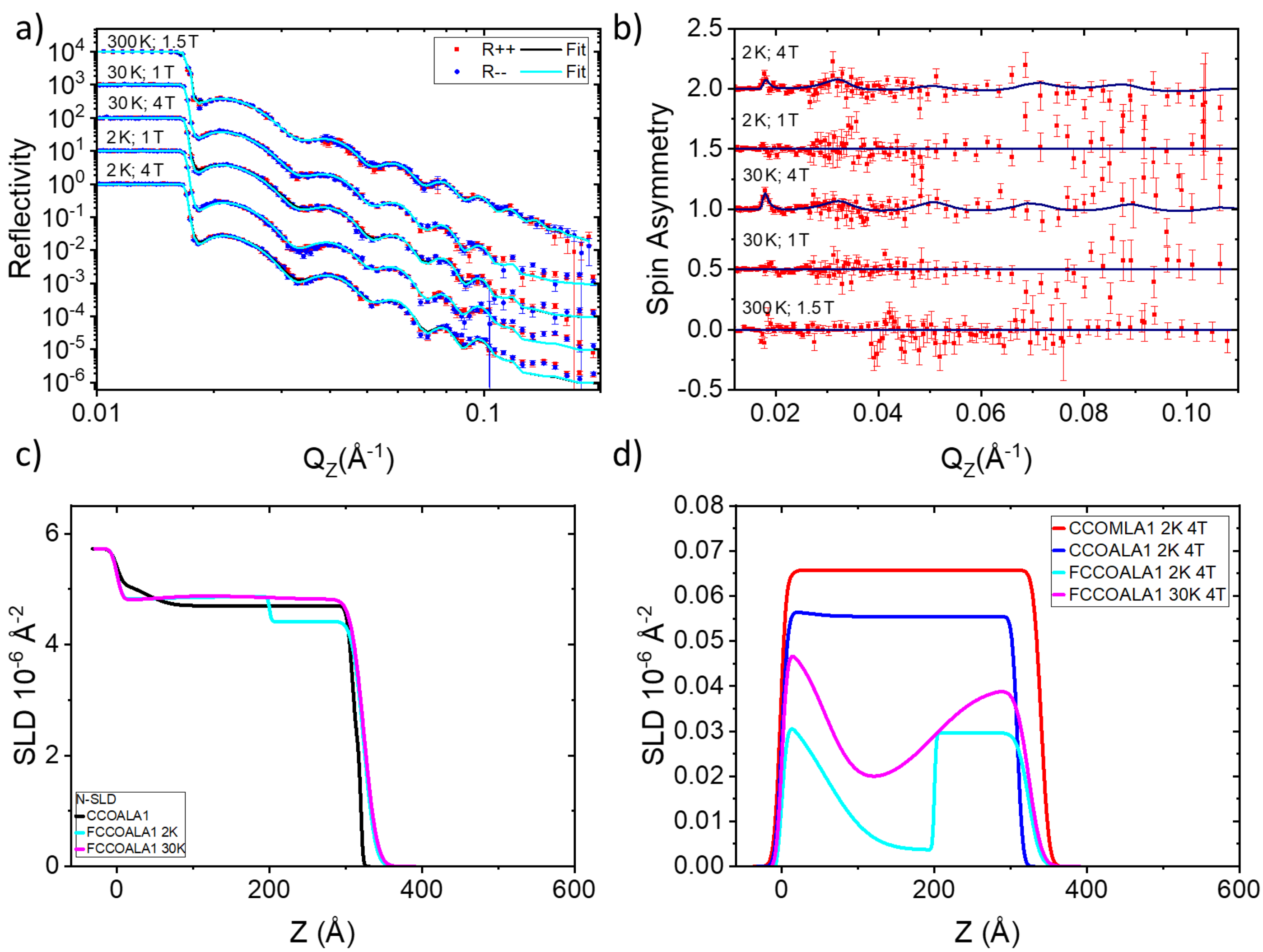

Figure 3: PNR results of Fe-substituted CCO(30 nm)/ALO. a) PNR data and fits, b) spin asymmetry, c) nuclear SLD profile d) magnetic SLD profile. The models obtained for other samples are included for comparison. The PNR data and spin asymmetry are vertically offset for clarity.