Neutron Study of Magnetic Phase Transition in SrCoO$_3$ Thin Films

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Introduction

The broad range of transition metal oxide functionalities, including superconductivity, magnetism, and ferroelectricity, can be tuned by a careful choice of parameters such as strain, oxygen content, or applied electric and magnetic fields [1–9]. This tunability makes transition metal oxide materials ideal candidates for use in developing novel information and energy technologies

SrCoO$_3$ is a fascinating transition metal oxide material system. SrCoO$_{3-\delta}$ has long been studied due to its propensity to form oxygen-vacancy-ordered structures as the oxygen content is decreased. The system undergoes well-defined structural phase transitions between distinct topotactic phases, from a cubic perovskite phase at SrCoO$_3$ to brownmillerite SrCoO$_{2.5}$. The ties between the structural and functional properties of the material are obvious as a magnetic phase transition from ferromagnetic (FM) SrCoO$_{3.0}$ with T$_C$=280–305 K to antiferromagnetic (AFM) SrCoO$_{2.5}$ with TN=570 K accompanies the structural transition.

SrCoO$_{2.5}$
Brownmillerite | Antiferromagnetic | T$_N$ = 570 K

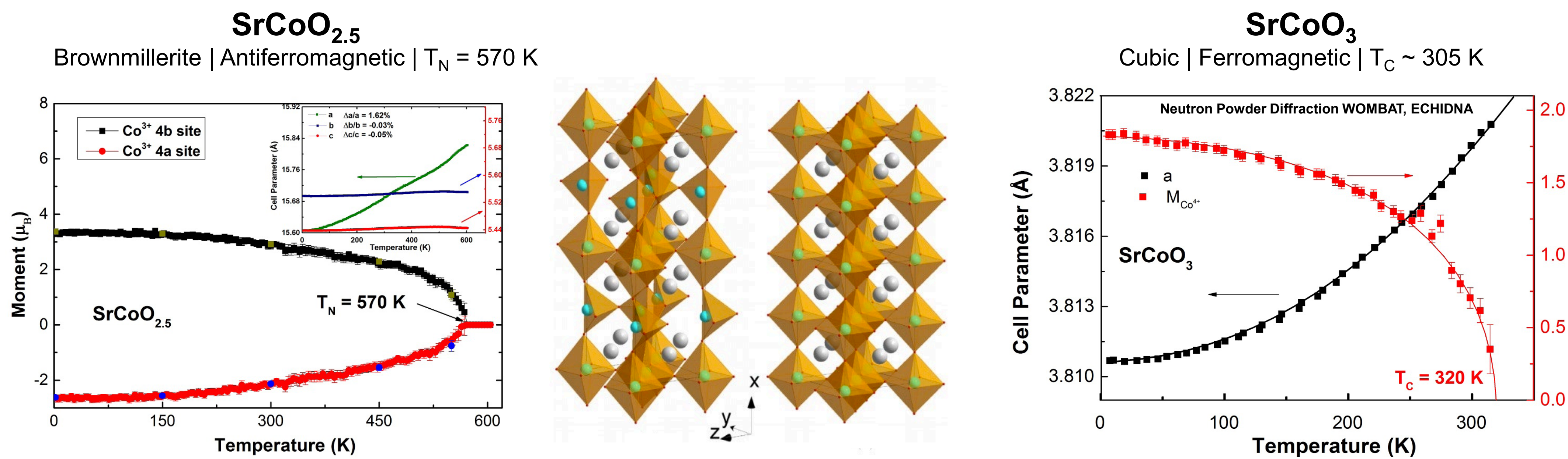### SrCoO$_3$
Cubic | Ferromagnetic | T$_C$ ~ 305 K

Figure 1: Magnetisation as a function of temperature of brownmillerite SrCoO$_{2.5}$ with the insert depicted both the cell parameter and magnetic moment of the Co^{2+} ion (left), Schematic depiction of the brownmillerite and cubic perovskite structure of Strontium Cobaltite (centre). Cell parameter and magnetic moment of the Co^{2+} ion of cubic SrCoO$_3$ as a function of temperature (right)

In addition to oxygen stoichiometry, strain can also be used to tune the system. Using first-principle calculations, Lee and Rabe have simulated the effect of strain and due to a large polar instability have predicted that the magnetic state of SrCoO$_3$ can be tuned through compressive or tensile strain [1]. As seen in Fig. 2, an AFM-FM transition is predicted at both a tensile strain of ~2.0% and a compressive strain of approximately −0.8%. This is caused through a simultaneous structural phase transitions between phases with different distortions and rotational patterns of the CoO$_6$ octahedra, as described by the Goodenough-Kanamori rules. Furthermore, it was predicted that the magnetic phase transitions would be accompanied by ferroelectric (FE) and metal-insulator transitions due to the strong coupling between the lattice, electric polarization, and electronic band gap.
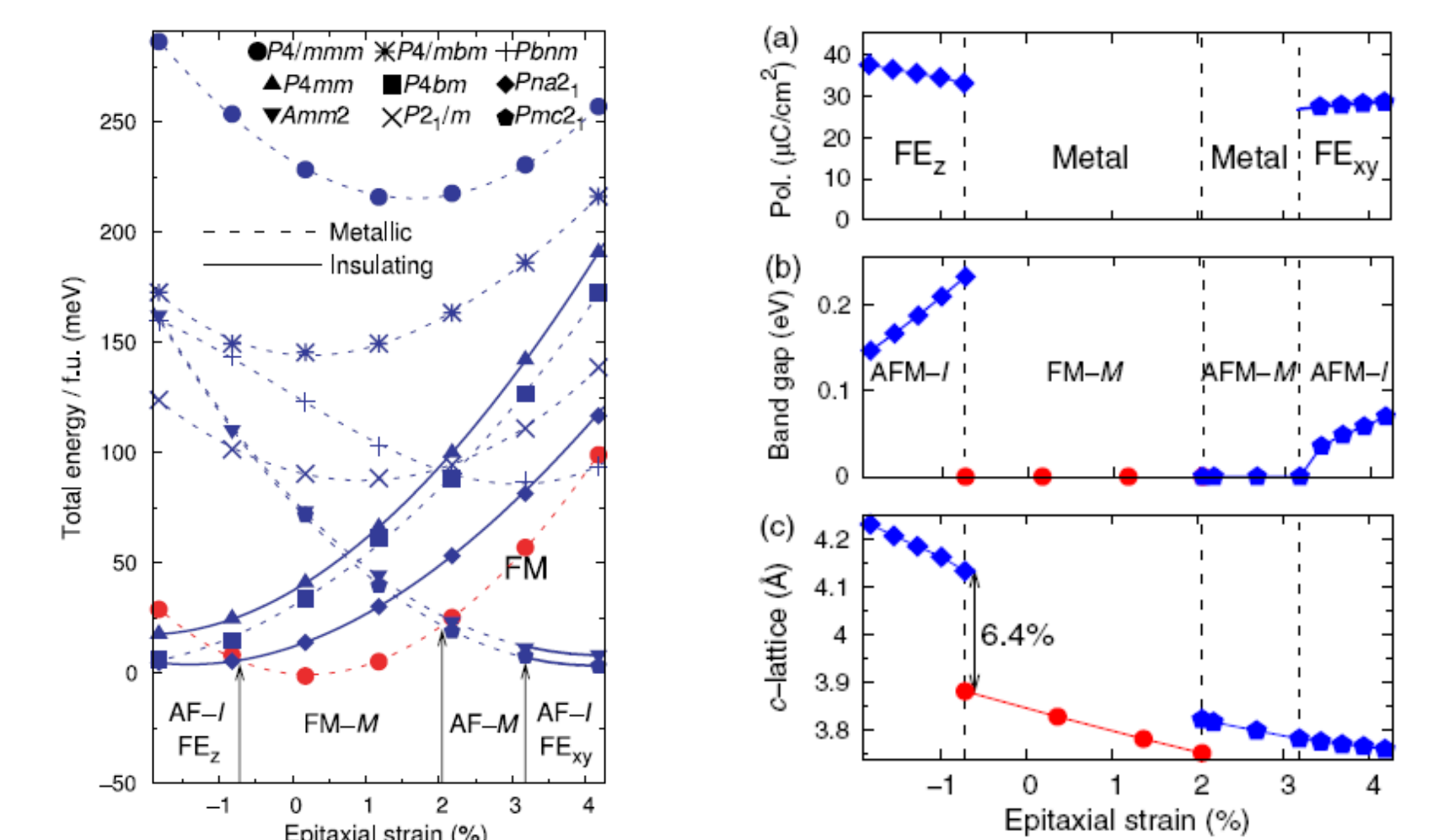

Figure 2: Total energies of various structures formed in response to epitaxial strain (left). Simulated ferroelectric polarisation (a), Band gap (b), and c-lattice parameter in response to strain (right)
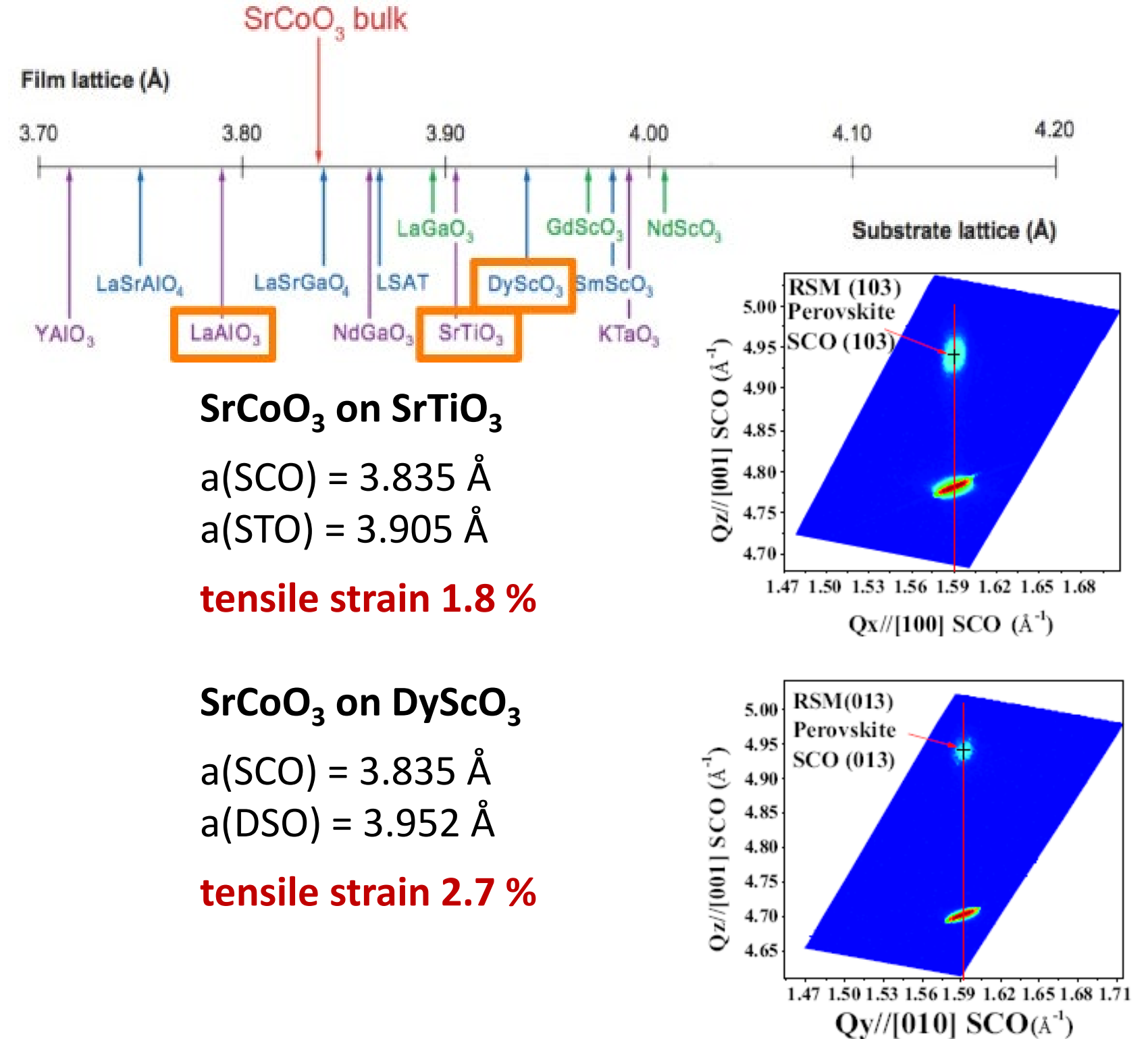
Experimental

SrCoO$_3$ thin films were grown on SrTiO$_3$ (100) (STO) and DyScO$_3$ (110) (DSO) substrates by a Pascal pulsed laser deposition (PLD) system with a 248-nm KrF excimer laser [2]. These substrates possess different lattices sizes which allow different degrees of tensile strain to be applied to the as-grown SrCoO$_3$ films. Briefly, the substrates were ultrasonically cleaned and annealed at 900 °C for 30 min in 100 mTorr of oxygen to form clear atomic terraces. The films were grown at a substrate temperature of 900 °C, oxygen pressure of 100 mTorr, laser energy of 4.5 J cm^{-2}, and frequency of 1 Hz. An in-situ annealing between 600 –750 °C in 600 Torr of oxygen was then carried out to form SrCoO$_3$ without any oxygen deficiency.

In order to ascertain the quality of the as SrCoO$_3$ thin film grown on the various substrates, the films were characterized by X-ray diffraction (XRD), x-ray reflectivity, atomic force microscopy (AFM), magnetometry through physical properties measurement system (PPMS), and elastic neutron scattering through the triple-axis spectrometer TAIPAN

SrCoO$_3$ on SrTiO$_3$
a(SCO) = 3.835 Å
a(STO) = 3.905 Å

tensile strain 1.8 %

SrCoO$_3$ on DyScO$_3$
a(SCO) = 3.835 Å
a(DSO) = 3.952 Å

tensile strain 2.7 %

Figure 3: Lattice spacing of SrCoO$_3$ and different substrates (top), RSMs around the (103) and (013) peaks from SrCoO$_3$ grown on DSO [2]
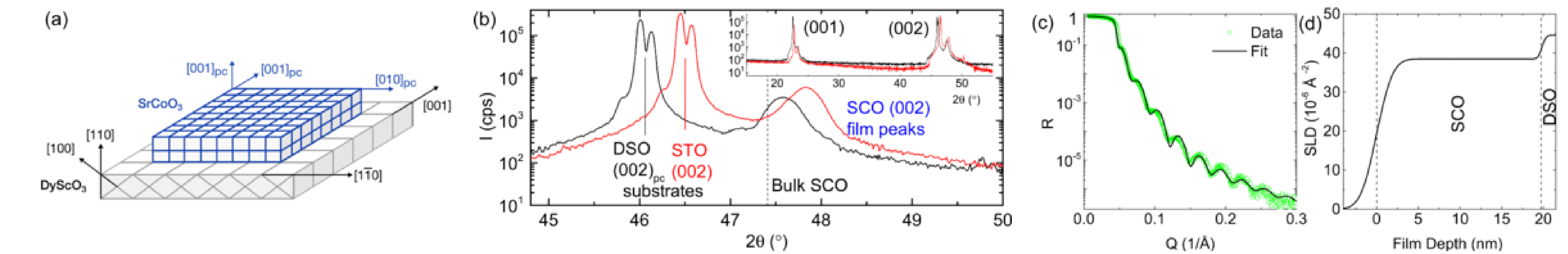
Results

Figure 4:(a) Schematic of the lattice directions of the SCO film and DSO substrate. (b) X-ray diffraction of SCO/DSO (black) and SCO/STO (red) showing the (002)pc substrate peaks and (002)pc film peaks. The dashed line denotes the location of the bulk (002)pc SCO peak. The inset presents the entire scan along the (pseudo)cubic (00l) directions of the substrates. (c) X-ray reflectivity of the 20 nm thick SCO/DSO film. (d) The scattering length density (SLD) across the SCO/DSO film [3]

The properties of the as-grown SrCoO$_3$ film can be see in Fig. 4. From the XRD pattern shown in panel (b), it is clear that we have obtained perovskite (δ> 2.75) due to the absence of the superstructure peaks. Furthermore, the tensile-strain applied by the substrate on the film has caused a shift to the diffraction peaks. From the x-ray reflectivity data, we can further see the quality of the film and estimate the SrCoO$_3$ film grown on DSO to be ~ 20 nm thick and that on STO to be ~40 nm (data not shown).

The effect of tensile-strain on magnetic of the SrCoO$_3$ film can be seen from the magnetometry and neutron diffraction studies. Fig. 5 presents the temperature evolution of the (001) peak via neutron diffraction and magnetometry measurement. Allowing for the STO phase transition at 105K and their lack of magnetic transition, the increase of the in intensity the (001) peak below 170K can be attributed to a FM transition. This is confirmed by magnetisation measurement where T$_C$ was shown to be at 170K. The reduced T$_C$ is an effect of the epitaxial strain which also reduced the Co moment from 2.5µB/f.u to 1.1µB/f.u

Conversely, Fig. 6 present the magnetisation and neutron measurement of the SrCoO$_3$ film grown on DSO. From the magnetisation measurement, an absence of FM ordering is observed. Through applying a Curie-Weiss fit, the presences of an AFM spin correlation is indicated. In order to determine the type of AFM ordering, neutron scattering was used. By conducting a scan in the Q$_{hhl}$, a peak at the $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ position is seen. This indicates that the film has a G-type AFM structure with a T$_N$ at 150K.
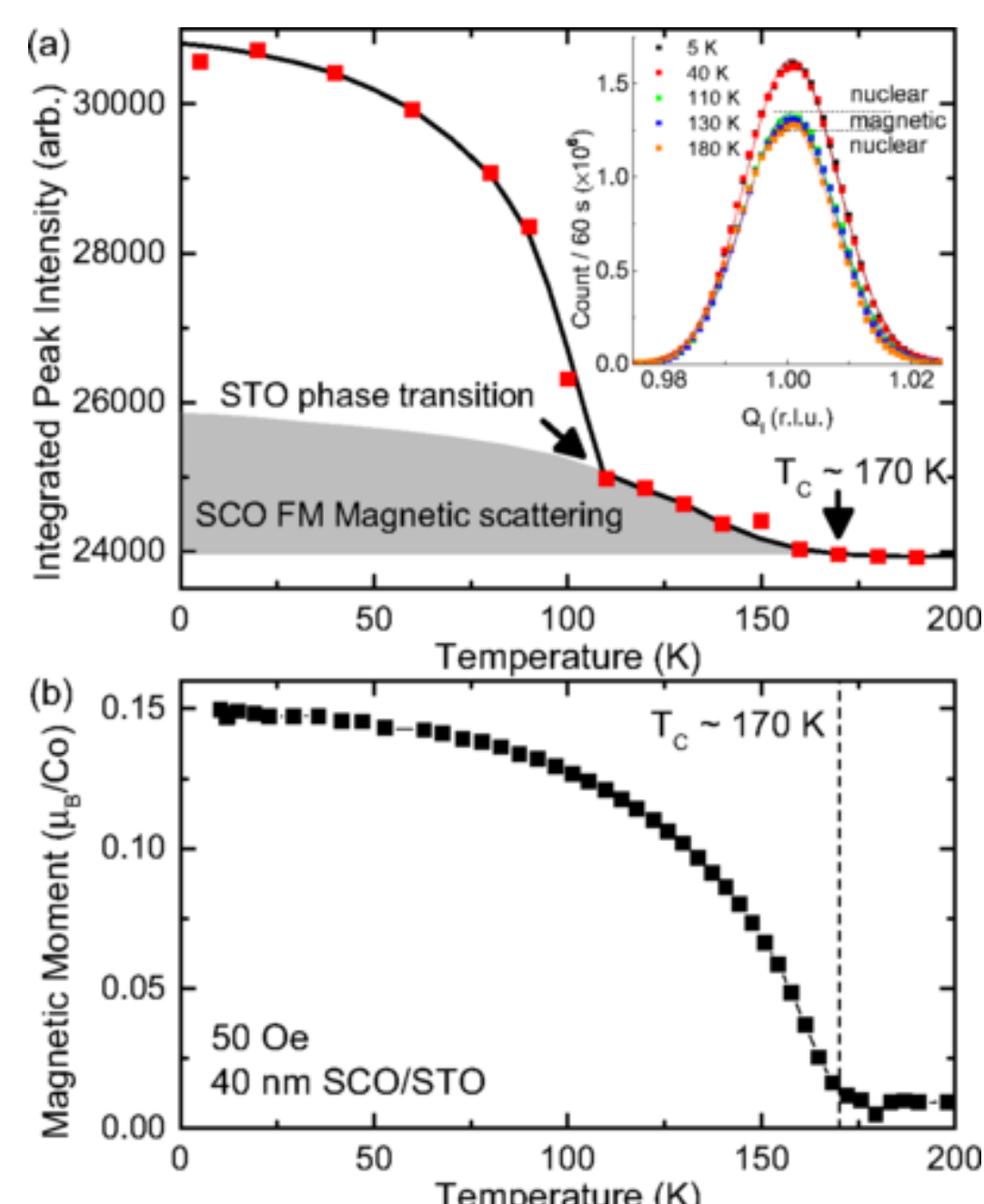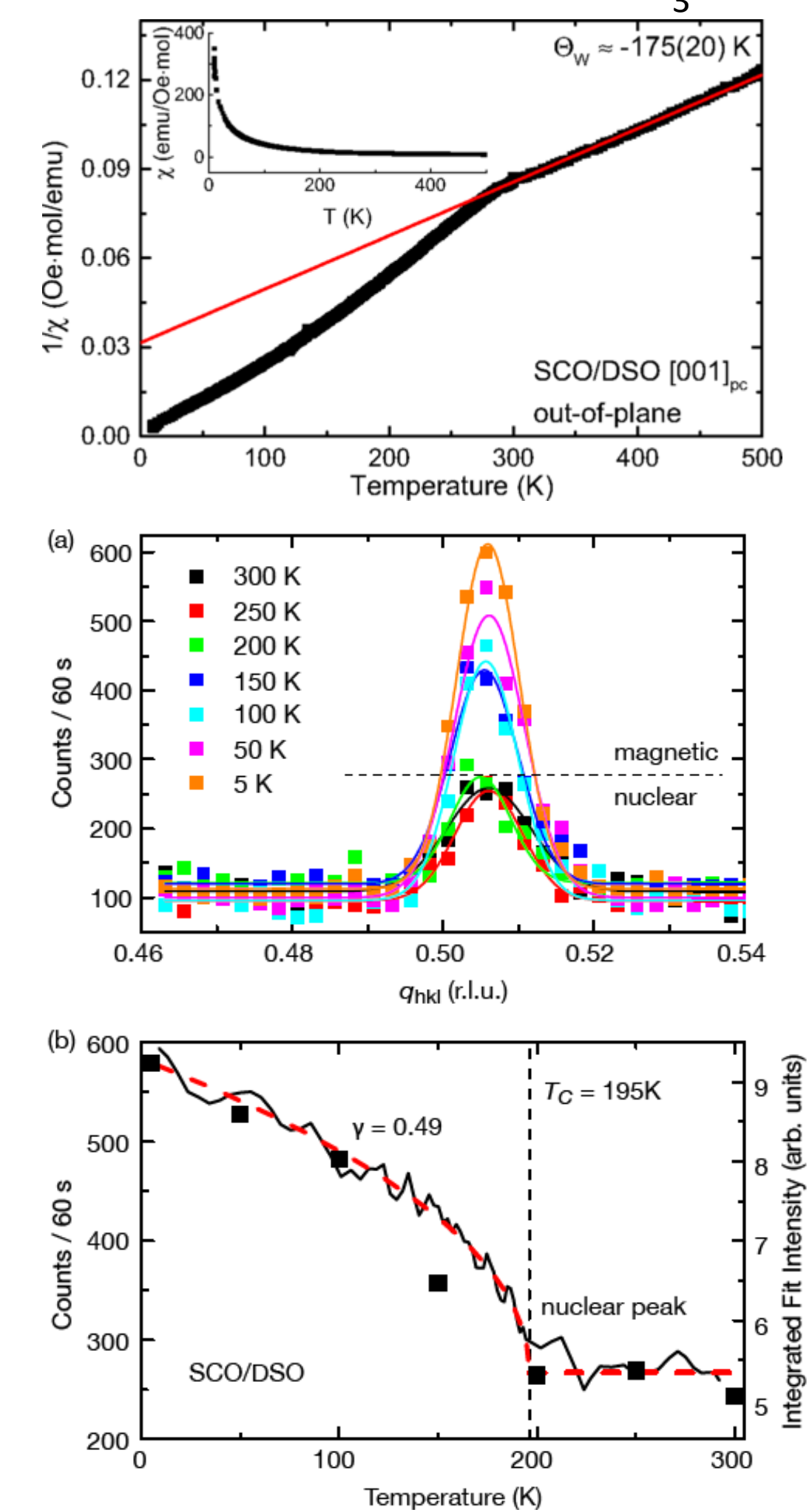
Figure 5. (a) Temperature dependence of the neutron diffraction intensity of the (001) peak. The black line serves as a guide to the eye (inset: raw data with Gaussian fits for selected temperatures). (b) Magnetisation measurement of the same film [3]

Figure 6. 1/χ measured for the SrCoO$_3$/DSO film. The redline shows the Curie-Weiss fit to the high temperature data with the inset showing the susceptibility (top), Neutron diffraction scans of the $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ peak at different temperatures (middle) and the intensity of the reflection as function of temperature (bottom)

Phase	magnetic type	T$_C$ - T$_N$
SrCoO$_3$ (bulk)	FM	305 K
SrCoO$_3$ (film) 0.8% strain	FM	250 K
SrCoO$_3$ (film) 1.7% strain	FM	200 K
SrCoO$_{2.875}$ (bulk)	FM	220 K
SrCoO$_{2.75}$ (bulk)	FM	160 K
SrCoO$_{2.5}$ (bulk)	AFM	570 K
SrCoO$_3$ (film) 2.8 % strain	AFM	195 K 325 K

New Magnetic Phase
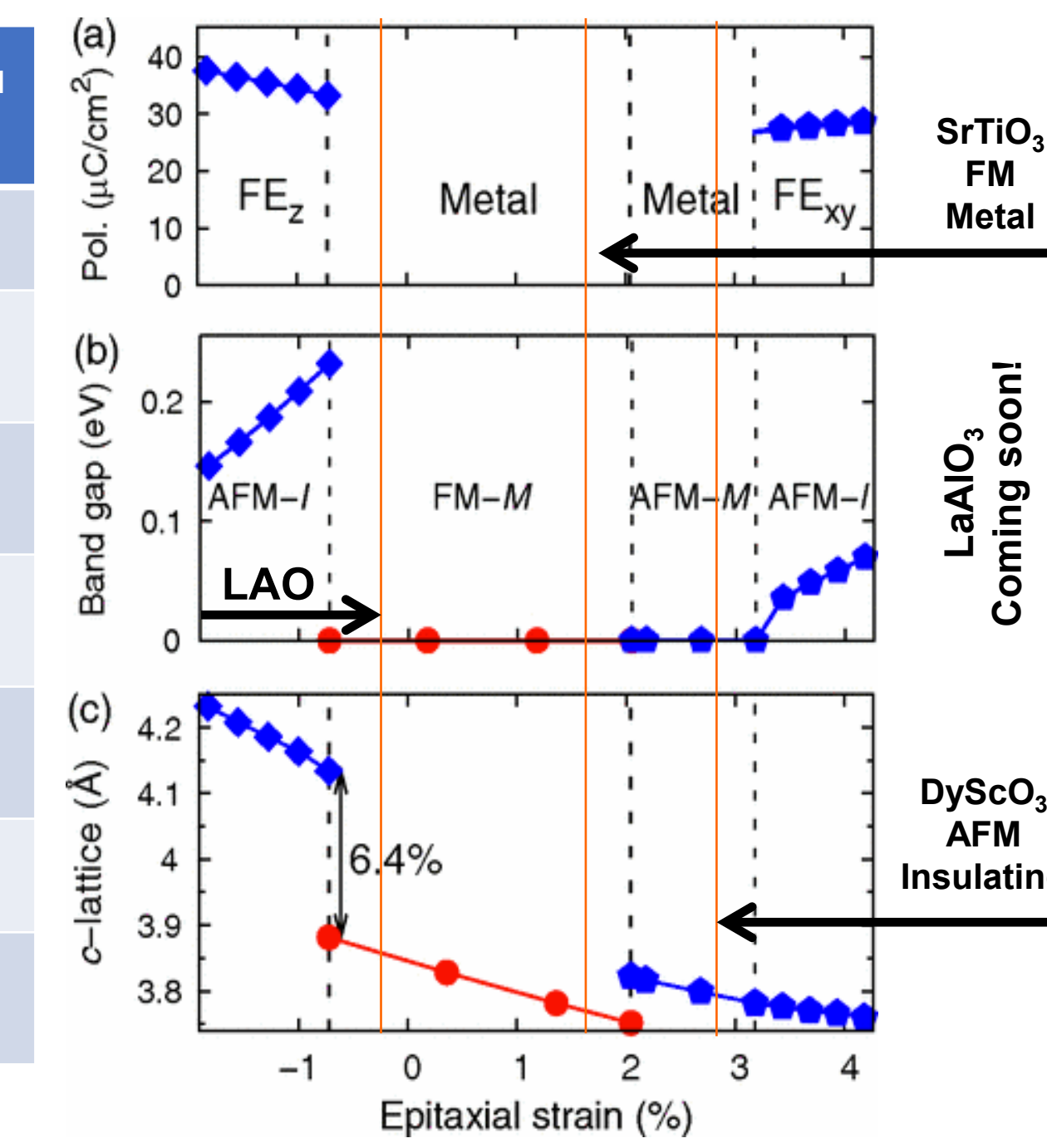
Conclusion

From the result presented, we have observed a theoretically predicted strain-induced magnetic phase transitions in SrCoO$_3$ thin films. When a moderate tensile strain is applied (STO at 1.8%), SrCoO$_3$ remains as a FM metal (4 t$_{2g}$ 1 e$_g$) with a slightly reduced T$_C$. However, with increasing tensile-strain (DSO at 2.7%), SrCoO$_3$ changes to an AFM Mott insulator (5 t$_{2g}$)

The results presented here represent a step in obtaining different functionalities in SCO. These observations confirm the predicted strong coupling between structure (via strain) and magnetism in SCO and demonstrate how this coupling can be used to tailor the magnetic properties of the material.

References
[1] Lee and Rabe, Phys. Rev. Lett. 107, 067601 (2011)
[2] S. Hu et. al, Adv. Mater. Interfaces 2, 150012 (2015)
[3] S. Callori, et al. Phys. Rev. B 91, 140405 (R) (2015)