

The Origin of Magnetic Ordering in $\text{Sr}_3\text{YCo}_4\text{O}_{10+x}$

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The oxygen-deficient perovskite $\text{Sr}_3\text{YCo}_4\text{O}_{10+x}$ (SYCO) exhibits the highest ferromagnetic ordering temperature of the perovskite cobaltates with $T_c = 335\text{K}$ ¹. However, there is no consensus on the precise atomic structure of this material. What is known is that SYCO exhibits antiferromagnetic ordering with asymmetric spin-up and spin-down magnetic moments, characteristic of *ferrimagnetism*. Here we report a combined investigation of SYCO using aberration-corrected scanning transmission electron microscopy (STEM) and density functional theory calculations. The resulting structural model of this compound, based on density functional theory (DFT) calculations constrained by our experimental atomic-resolution electron microscopy observations, describes the origin of the magnetic ordering and accounts for the available experimental data from this compound.

Figure 1 shows atomic resolution annular bright field STEM images viewed along $\langle 100 \rangle_p$ and $\langle 110 \rangle_p$ directions based on a pseudo-cubic perovskite structure. These images obtained using a Nion UltraSTEM200 at 200 kV are the result of summing ten sequentially acquired frames after alignment by cross-correlation, with no other image processing. Guided by these images a new model of the SYCO structure was constructed (Fig.1a). Our DFT calculations indicate that the lowest energy structure displays a G-type antiferromagnetic spin ordering of the Co ions in agreement with previous measurements. The DFT results indicate that within the oxygen-deficient layer the high spin (HS) cobalt magnetic moments are anti-ferromagnetically ordered. More interesting is the spin ordering in the fully oxygenated layers where the formation of columns with intermediate spin (IS) are formed. The variations in spin states are directly reflected in the crystal structure. The fully oxygenated layers have two different types of CoO_6 octahedra, in which the calculated in-plane Co-O bond length of every IS Co atom is smaller than the corresponding bonds of the HS Co atoms (Fig. 1 b,c,d).

This calculated spin structure of SYCO is different from those of previously published models²⁻⁵. Thus, guided by theoretical results on Co-O distances projected on different planes, the atomic-scale images of different orientations, especially of the fully oxygenated planes, allow the unambiguous extraction of the underlying structure and provide the origins of magnetic ordering in SYCO.

References:

- [1] W. Kobayashi *et al.* *Phys. Rev. B* 72, 104408 (2005).
- [2] D.V. Sheptyakov *et al.* *Phys. Rev. B* 80, 024409 (2009).
- [3] H. Nakao *et al.* *J. Phys. Soc. Jpn.* 80, 023711 (2011).
- [4] D.D. Khalyavin *et al.* *Phys. Rev. B* 83, 140403 (2011).
- [5] J.L. Bettis *et al.* *Chem. Mater.* 24, 3117-3119 (2012).

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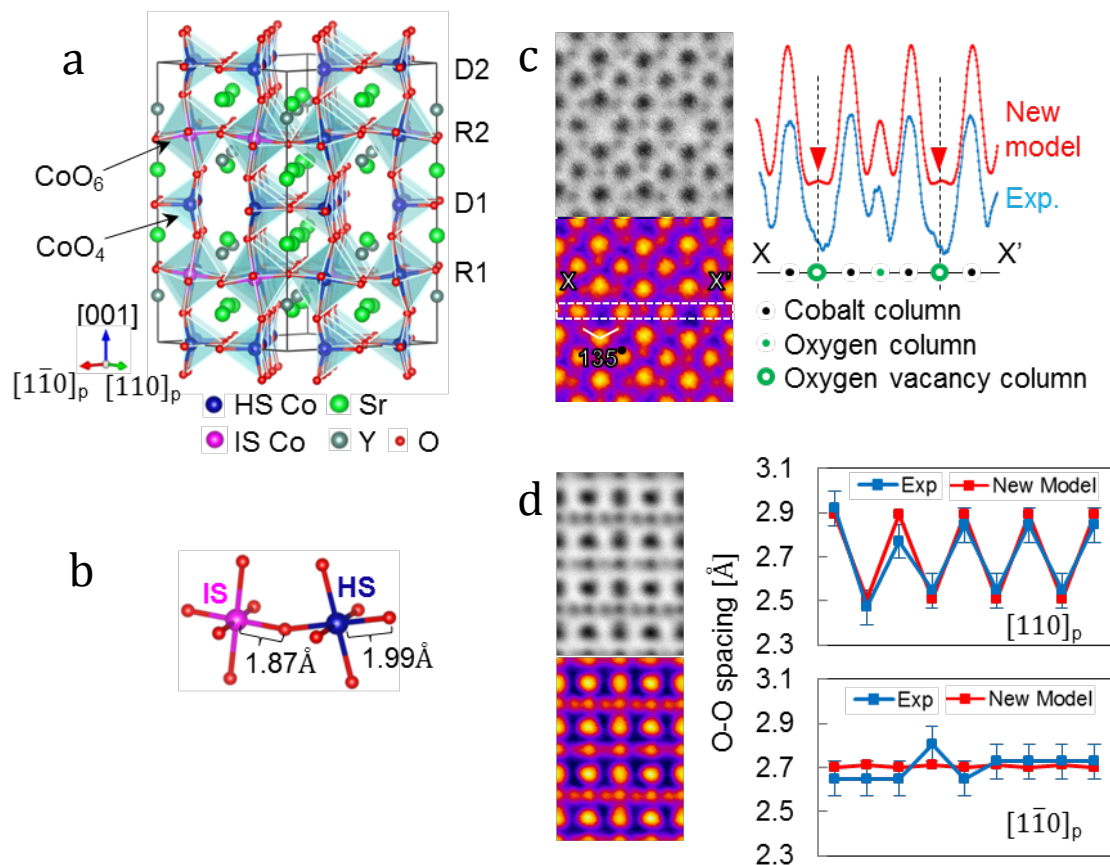


Figure 1. The magnetic structure of SYCO. (a) Illustration of the new crystal structure of SYCO with fully oxygenated (R1-R2) and oxygen deficient (D1-D2) layers. (b) Schematic of the Co-O bonds associated with the alternating high spin state (HS) and intermediate spin state (IS) cobalt. (c) annular bright-field [100]_p image with intensity profile across the dashed rectangle through the oxygen-deficient Co-O plane. (d) annular bright-field <110>_p image with O-O spacings within the fully oxygenated Co-O layer as seen in orthogonal <110>_p directions.