First-principles study of soft ferromagnetism in ultrathin freestanding $LaMnO_3$ films

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Abstract: Owing to small coercive fields and weak magnetic anisotropy, soft ferromagnetic films are extremely useful for nanoscale devices that need to easily switch spin directions. Recently large-area, high-quality, ultrathin freestanding $LaMnO_3$ films on Si are synthesized in experiment and soft ferromagnetism both along the in-plane and out-of-plane directions is found when the film thickness is reduced to 4 nm. Spectroscopy measurements reveal a large Mn valence variation in $LaMnO_3$ thin films from 3+ in the bulk-like interior to approximately 2+ in both surface regions where considerable hydrogen infiltration occurs due to the water dissolving process. We argue that the vanishing magnetic anisotropy between the two directions is a consequence of two coexisting magnetic easy-axis in different atomic layers of the $LaMnO_3$ film. Our first-principles calculations show that protonation of $LaMnO_3$ decreases the Mn valence and switches the magnetic easy-axis from in-plane to out-of-plane as Mn valence approaches 2+ from its 3+ bulk value and we think that when the surface region has comparable size to the bulk-like interior in ultrathin freestanding $LaMnO_3$ films, the magnetic anisotropy of the entire film vanishes, and thus the coercive field is reduced, leading to the experimentally observed multidirectional soft ferromagnetism. Our work demonstrates that ultrathin freestanding films can exhibit new functional properties that are absent in homogeneous materials, concomitant with their convenient compatibility with Si-based devices.

Background

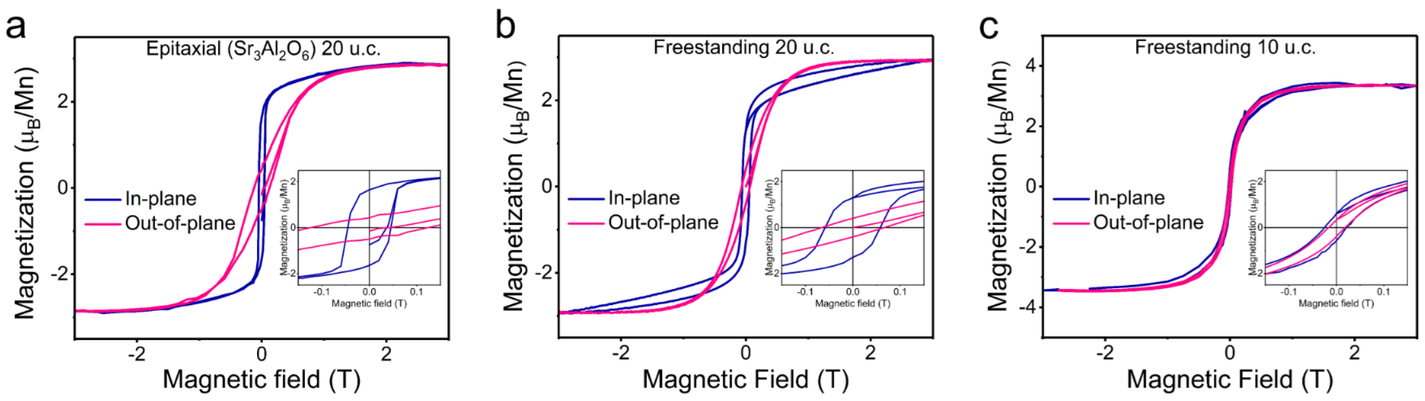

Figure 1 Hysteresis loops measured at T = 5 K along IP and OOP directions of $LaMnO_3$ films.. **(a)** the epitaxial 20 u.c. (on intact $Sr_3Al_2O_6$ layer). **(b)** 20 u.c. freestanding. **(c)** 10 u.c. freestanding samples.

It was found experimentally that the strong magnetic anisotropy (MA) of the epitaxial film is systematically suppressed in the ultrathin freestanding $LaMnO_3$ films.

Result

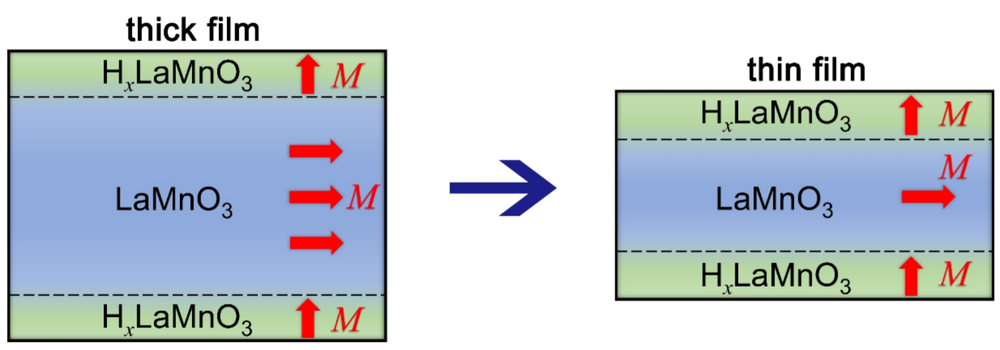

Figure 2 Schematic illustration of a $LaMnO_3$ freestanding thick film (left panel) and thin film (right panel).

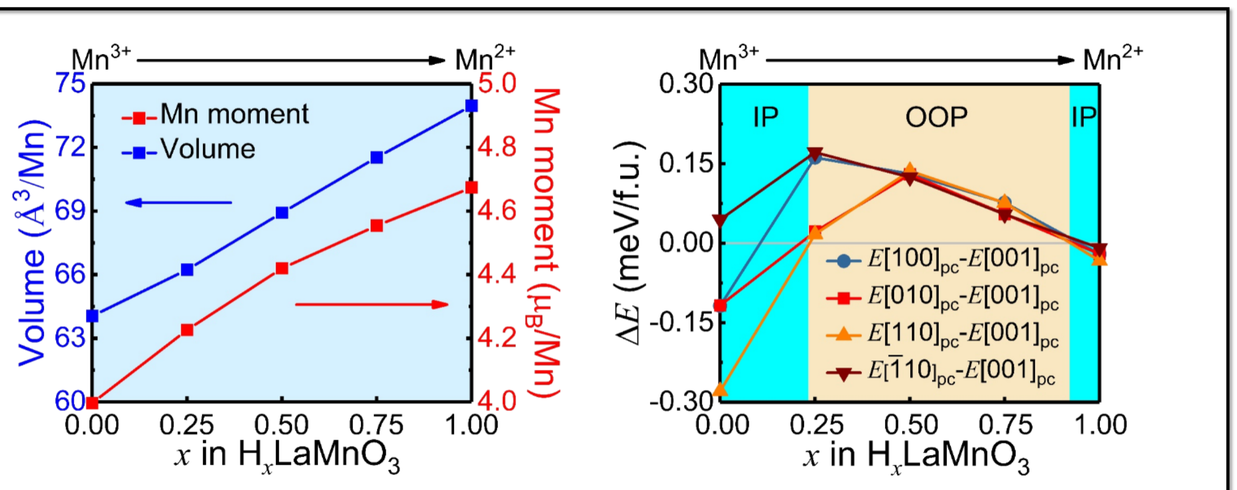

Figure 4 Protonated H_xLaMnO_3: Primitive cell volume and Mn magnetic moment as functions of hydrogen concentration x of H_xLaMnO_3 (left panel). And MA of Mn magnetic moment as a function of hydrogen concentration x in H_xLaMnO_3 (right panel).

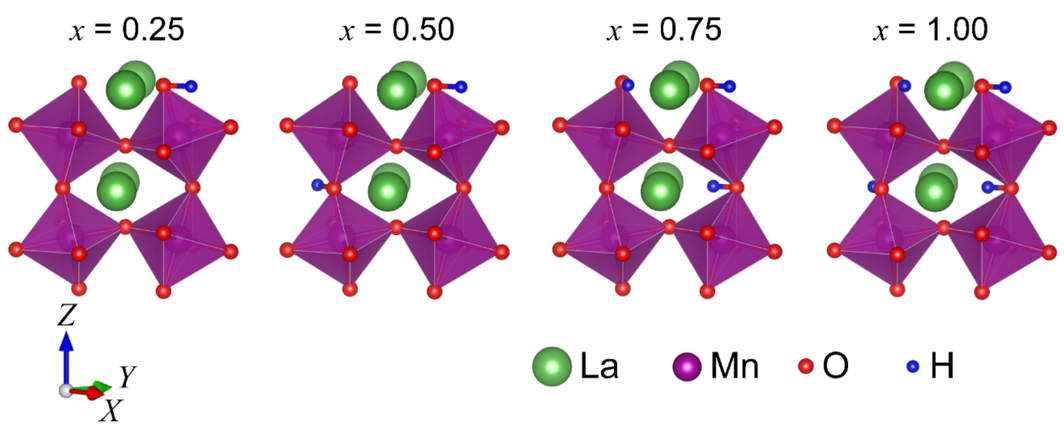

Figure 3 Crystal structure of protonated H_xLaMnO_3 for different hydrogen concentrations x.

The $LaMnO_3$ film with three regions: the top and bottom surfaces (assumed to be identical) and the bulk-like interior. In DFT calculations, hydrogen atoms energetically prefer to bond with apical oxygen atoms of protonated H_xLaMnO_3 with all different hydrogen concentrations. The calculation result shows that the injected hydrogen atoms increase the volume of H_xLaMnO_3 and donate electrons to Mn. The Mn moment correspondingly increases with hydrogen concentration x, while Mn valence decreases. And as x increases, there will be a situation where the easy axis turns from IP to OOP. It is indicate that the MA of the film is contributed by two regions, when the surface region has comparable size to the bulk-like interior in ultrathin freestanding H_xLaMnO_3 film, the MA of the entire film vanishes, and thus the coercive field is reduced, leading to the experimentally observed multidirectional soft ferromagnetism.

Reference: Qinwen Lu[#], Zhiwei Liu[#], Qun Yang[#], Hui Cao, Purnima Balakrishnan, Qing Wang, Long Cheng, Yalin Lu, Jian-Min Zuo, Hua Zhou, Patrick Quarterman, Shin Muramoto, Alexander J. Grutter, Hanghui Chen, and Xiaofang Zhai, ACS Nano 2022 16 (5), 7580-7588.

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