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Charge Doping Effects on Magnetic Properties of Single Crystal $\text{La}_{1-x}\text{Sr}_x(\text{Cr}_{0.2}\text{Mn}_{0.2}\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2})\text{O}_3$ ($0 \leq x \leq 0.5$) High Entropy Perovskite Oxides

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Abstract

The influence of hole doping on magnetic properties is mapped for the compositionally complex high-entropy oxide ABO_3 perovskite $\text{La}_{1-x}\text{Sr}_x(\text{Cr}_{0.2}\text{Mn}_{0.2}\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2})\text{O}_3$ ($0 \leq x \leq 0.5$). It is found that aliovalent *A*-site substitution is a viable means to manipulate the magnetically active *B*-site sublattice. A series of single-crystal films are synthesized and show a general trend toward stronger ferromagnetic response and a shift in magnetic anisotropy as the Sr concentration increases. Magnetometry demonstrates complex and non-uniform responses similar to rigid and uncoupled composites at intermediate dopings. This behavior points to the presence of locally inhomogeneous magnetic phase competition, where ferromagnetic (FM) and antiferromagnetic (AFM) magnetic contributions create a frustrated matrix containing uncompensated spins at the boundaries between these regions. The observations are discussed in the context of known responses to hole doping in the less complex ternary $\text{La}T_M\text{O}_3$ ($T_M = \text{Cr, Mn, Fe, Co, Ni}$) oxides and are found to be different than a simple sum of the doped parents. The results are summarized in a preliminary magnetic phase diagram.

Introduction

Local elemental diversity and the accompanying combination of site-to-site interactions dictate the global phase and functionality of materials. However, the role of these microstates is often

beholden to very small amounts of doping as to avoid disrupting crystallinity. Recent developments in entropy-assisted synthesis are allowing an extraordinary increase in the number of microstates present on uniform crystal lattices [1–3], where five or more elements can be hosted and well-mixed on a single sublattice despite the massive amount of site-to-site disorder. This method of creating high entropy oxides (HEOs) is still in its infancy, but it appears to be a generally viable approach that can be applied to many different crystal structures, including spinel [4,5], perovskite [6,7], Ruddlesden-Popper [8], and rock salt [9–11]. Mechanistically, the complex set of local microstates present in these systems is suggested as the driving influence that leads to unexpected and often exceptional properties related to magnetism [4,5,7,11–13], ion conductivity [14–16], catalytic tunability [17], thermal transport [6,18], and electronic character [19]. These observations promise the ability to access never before possible combinations of diverse local interactions on uniform crystal lattices that are likely to lead to new physical behaviors. However, due to the innate complexity present, gaining a general fundamental understanding of these chaotically populated systems is challenging. For this reason, it is important to work toward identifying how slight and iterative manipulation of the local interaction landscape works to drive the emergence of macroscopic functional responses.

The ABO_3 perovskites host two cation sublattices and are well studied in ternary compounds. In strongly correlated transition metal oxide (TMO) perovskites, such as LaT_MO_3 ($T_M = Cr, Mn, Fe, Co, Ni$), the B -site sublattice generally acts as the magnetically and electronically dominant sublattice, where slight changes to the B -site charge state, coordination, or bond symmetry can dictate the functional properties. A conventional approach to interrogate and control these phases is to use the A -site sublattice to impart changes on the functionally active B -sites. As an example, substitutional doping on the A -site can be used to shift the local charge, spin, and exchange interactions of the neighboring B -sites. In the case of the TMOs, iterative doping studies are often conducted to gain general insights into how changes to microstate might drive macroscopic responses. This often results in the revelation of rich phase diagrams such as that seen in $La_{1-x}Sr_xMnO_3$ (LSMO), where various types of magnetic, orbital, electronic, and structural order can be observed [20]. Here, iteratively replacing the La^{3+} with Sr^{2+} drives charge compensation on the B -site Mn which can lead to the opening of $Mn^{3+}-O^{2-}-Mn^{4+}$ double exchange pathways and ferromagnetism (FM) from the parent antiferromagnetic (AFM) state [21]. Similarly in $La_{1-x}Sr_xCoO_3$ (LSCO), Co^{3+} is pushed from the low-spin state to the high-spin Co^{4+} state which initiates

a FM phase transition [22]. Conversely, $\text{La}_{1-x}\text{Sr}_x\text{CrO}_3$ and $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ remain AFM with hole doping and only show a drop in ordering temperature with increasing Sr concentration [23–25]. In these previous works, hole doping experiments helped to clarify the fundamental mechanisms driving functionality and led to the discovery of unexpected and novel behaviors. Extending this systematic process to configurationally complex materials may then provide important insights that can help guide our understanding of the mechanisms driving this unexplored class of materials.

$\text{La}(\text{Cr}_{0.2}\text{Mn}_{0.2}\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2})\text{O}_3$ (L5BO) is a compositionally complex perovskite oxide that demonstrates interesting magnetic and structural responses in which large amounts of spin and magnetic exchange disorder lead to extraordinary diversity of microstates [12,26,27]. In this work, modification of these local states through hole doping is found to provide a means of controlling magnetic phase and anisotropy. The doping experiments rely on substitutional doping on the A-site sublattice and are found to have no adverse effect on crystal quality. X-ray diffraction and reflectivity measurements show that all films are single phase, coherently strained, epitaxial to the substrate, and possess low surface roughness. Crystalline quality is vital to investigations into fundamental magnetic processes, as this reduces possible extrinsic effects such as grain boundaries and structural inhomogeneities that are present in ceramic and powder samples. Through magnetometry measurements, hole doping is found to provide a means of controlling the FM bonds in $\text{La}_{1-x}\text{Sr}_x(\text{Cr}_{0.2}\text{Mn}_{0.2}\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2})\text{O}_3$ ($0 \leq x \leq 0.5$) (LS5BO) films. The increasing phase fraction of FM is found to coincide with a change in the blocking temperature of the FM, which indicates smaller average domain sizes with increasing Sr. At low doping, the presence of locally inhomogeneous magnetic phase competition, where uncoupled soft (uncompensated moments) and hard magnetic contributions preclude direct coupling of AFM and FM magnetic regions. The coupling of these phases is found to be tunable with Sr doping.

Methods

Stoichiometric ceramic targets for each of the LS5BO compositions are prepared via conventional solid-state reaction at 1000 °C. Films are grown via pulsed laser deposition on SrTiO_3 (0,0,1) substrates using a KrF excimer laser at a fluence of 0.85 J/cm² and a repetition rate of 5 Hz with oxygen partial pressure held at 90 mTorr for all samples. Substrate temperature during growth is composition dependent and held at 625 °C, 635 °C, 635 °C, and 700 °C for Sr 0%, 10%, 30%,

and 50%, respectively. All films are cooled from growth conditions under 200 Torr oxygen pressure.

XRD and XRR measurements are performed using a four-circle high-resolution x-ray diffractometer utilizing $\text{CuK}\alpha_1$ radiation (Panalytical X'Pert Pro). Magnetization measurements conducted on a Quantum Design MPMS3 magnetometer are corrected for substrate background by subtracting the diamagnetic background signal from collected data.

Results and Discussion

A series of single crystal LS5BO films are grown with $x = 0, 0.1, 0.3,$ and 0.5 with typical thickness of $\sim 50\text{nm}$. These samples are designated by their Sr concentration on the A-site sublattice as Sr 0%, 10%, 30%, and 50% for x values 0, 0.1, 0.3, and 0.5 respectively. **Fig. 1a** shows the $(0\ 0\ 2)$ diffraction scans revealing single crystals with no secondary phases and high crystalline uniformity inferred from well-defined Laue fringes. The film thickness determined from the Laue fringes (crystalline thickness) in each case matches the thickness determined from XRR (total thickness), giving strong evidence that phase segregation does not occur in the films. Each film's roughness is $< 3\text{ nm}$ over the $5\text{ mm} \times 5\text{ mm}$ area, which is comparable to the expected roughness from the miscut angle of the substrate (**Fig. 1b**). The in-plane lattice parameter of the films relative to the STO substrate is revealed from reciprocal space maps about the $(1\ 1\ 3)$ peaks. From **Fig. 1c**,

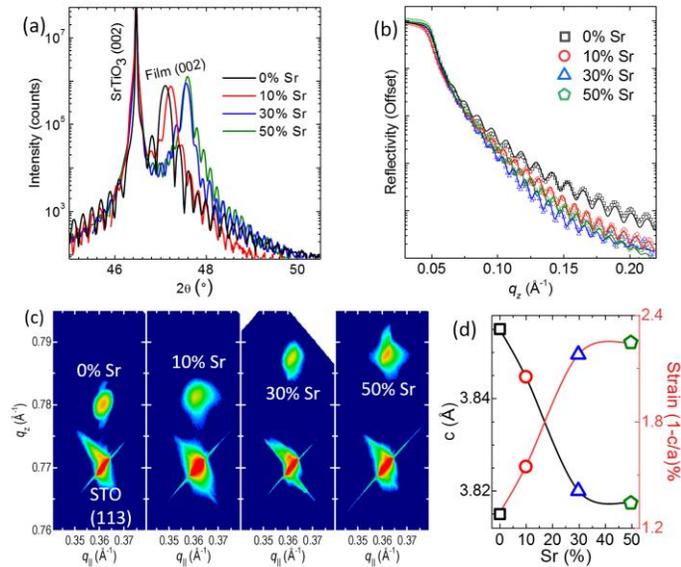


Fig. 1. X-ray diffraction and reflectivity studies for all films. (a) XRD showing the $(0\ 0\ 2)$ peak demonstrating high crystalline quality of films. (b) XRR data for each of the films demonstrating low surface roughness. (c) RSM data showing films are fully strained to the substrate. (d) Evolution of the c-axis lattice parameter and corresponding lattice strain.

it is evident that in each case the films are coherently strained. As a function of Sr doping, the lattice size contracts as expected from the smaller atomic size of Sr relative to La. Given the results of this characterization, the evolution of the c-axis size is shown in **Fig. 1d**, where the gradual contraction of the c-axis with increasing Sr is quantified. It should be noted that the strain of each film was slightly different due to the contraction in the unit cell size, this strain (c/a ratio) is also given in **Fig. 1d**.

The temperature-dependent magnetization for all films is presented in **Fig. 2**. Here, the zero-field-cooled (ZFC) and field-cooled (FC) responses are shown with the magnetic field applied in both the in-plane (IP) and out-of-plane (OOP) directions. In all cases, the magnetic transitions appear uniform with clear onset temperatures. This single transition response signals a global phase change. Had chemical segregation or structural clustering been present, these magnetization curves would present multiple transitions as a sum of local regions similarly to that observed in HEO powders and ceramics [27]. This is an important advantage of conducting these studies on the single crystal form; it is possible to investigate the inherent magnetic responses without the complications of extrinsic contributions present in materials with grain boundaries, large relative surface contributions, and size effects seen in polycrystalline and powder samples.

A general trend toward increasing FM character with increasing Sr is evident when looking at the uniformity of moment onsets as a function of temperature. Sr 0% and Sr 10% crystals both have a similar ferromagnetic blocking temperature (T_B), which is signaled by the opening of a gap between the FC and ZFC curves, at ~ 175 K. The FM T_B coincides with the thermal energy barrier blocking the alignment of

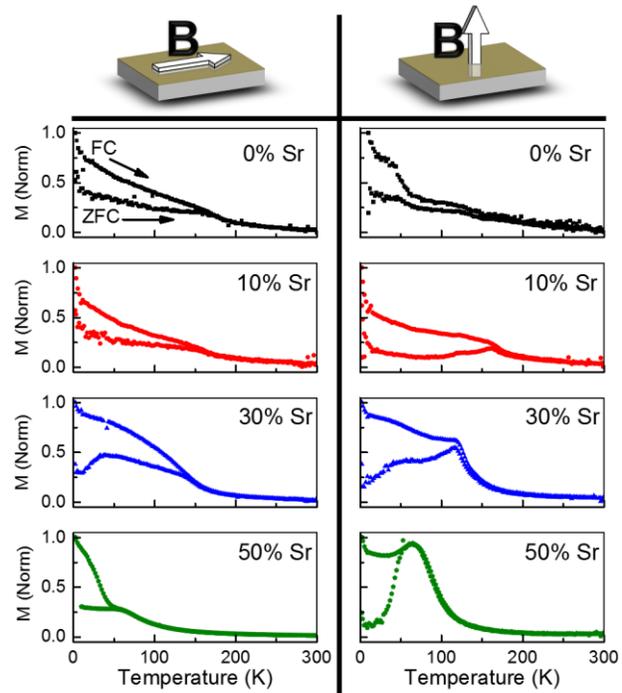


Fig. 2. Field cooled and zero field cooled magnetization as a function of temperature on warming under 1000 Oe field for all compositions. In all cases, magnetic transitions are consistent with a macroscopically coherent ordering and not the result of small pockets that correlate to parent phase transitions.

moments at low temperature. It can be affected by several features, including the magnitude of the applied field, anisotropy (K_u), and domain size. Considering the applied field is constant for each sample, the size of the FM domains should correlate with T_B , which allows for qualitative comparison of the expected FM cluster sizes as a function of doping level. However, it is worth noting that the K_u increases with substitutional doping due to lattice strain, which can increase the effective T_B . In the Sr 30%, a similar transition to that seen in the Sr 0% and 10% appears, but a kink at ~ 50 K arises in the IP configuration. This feature persists in the Sr 50% where only this sharp transition is observed. This is consistent with a transition from soft FM (or paramagnet) to a hard FM phase. The lowering of T_B , despite the increased K_u due to increasing crystalline strain which is expected to increase T_B , with increasing Sr suggests the size of the FM clusters are decreasing. This is different than doping trends observed in ternary parents to the L5BO, such as $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$, which show an increase in cluster size across this doping range.

The FM nature of the films is further investigated by measuring magnetization as a function of applied magnetic field at various temperatures for each Sr concentration. **Fig. 3** presents representative field loops taken at 10 K, 25 K, 100 K, and 250 K for each doping. By comparison

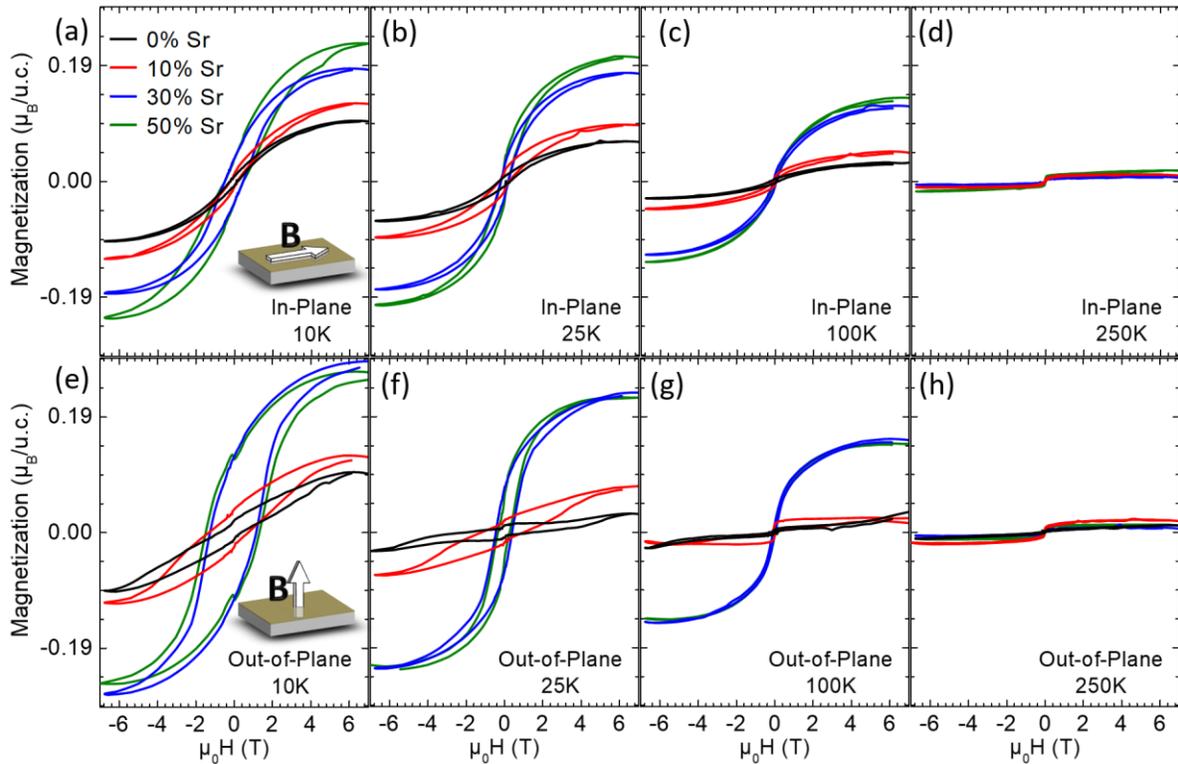


Fig. 3. Examples of field dependent magnetic responses for different Sr compositions at 10 K, 25 K, 100 K, and 250 K for field applied in-plane (a-d) and out-of-plane (e-h).

of the IP loops (**Fig. 3a-d**), the saturation magnetization (M_s) increases with Sr concentration at low temperature. This is especially evident as Sr concentration moves from 0% toward 30%, where both Sr 30% and Sr 50% saturate around $0.2\mu_B$ /unit cell (u.c.). In addition, increasing hole doping toward the highest levels induces a much larger coercivity, though the loops at 10 K do not fully saturate. Turning to the OOP direction (**Fig. 3e-h**), each of the concentrations exhibit a higher coercivity and M_s (approaching $0.3\mu_B$ /u.c. for Sr 30% and Sr 50%) than their IP loops. This points to the FM component having an easy axis in the OOP direction for each of the films. The magnetic hysteresis loops and the temperature dependence led to the conclusion that increasing Sr concentration increasing M_s and K_u , while simultaneously decreasing T_B . These results taken together again indicate that, as Sr concentration increases, the size of the FM clusters are decreasing while simultaneously increasing in number or absolute moment. The presence of FM clusters existing in a background AFM matrix should produce uncompensated or frustrated spins along the cluster walls. If present, changes to domain boundary compositions would leave

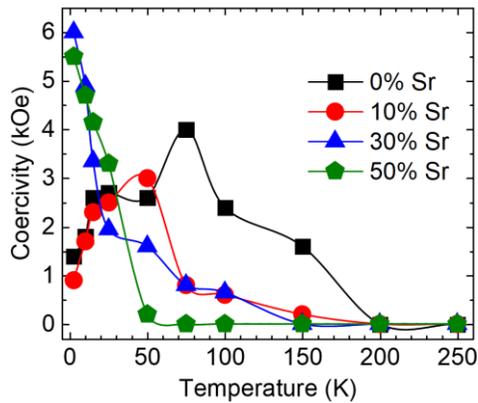


Fig. 4. A comparison of in-plane magnetic coercivity with temperature shows a drop in coercivity with temperature for low Sr concentrations and an increase in coercivity for higher Sr concentrations.

signatures in the macroscopic temperature-dependence coercivities and hysteretic responses [28–30].

The temperature dependence of the IP coercivity is shown in **Fig. 4** for each Sr concentration. Coercivity increases as temperature is reduced for the Sr 30% and Sr 50% films. This behavior when taken with the other observations, points to the coexistence of FM and AFM regions in these films. Here, percolated FM regions can be coupled to the AFM phase domains through magnetic exchange, where uncompensated spins at boundaries appear to decrease with increasing

Sr [31,32]. Coercivity also increases for the Sr 0% and Sr 10% films as temperature drops below the blocking temperature; however, the coercivity falls at low temperatures. This reduction of coercivity can be the result of an increase in FM cluster size. This is enabled by domain propagation between clusters, which will produce a lower coercivity in comparison to isolated FM clusters. Conversely, this may be due to local pinning of uncompensated moments at the frustrated magnetic boundary between AFM and FM regions. This leaves the question as to how the phase

coexistence and inter-domain couplings evolve to influence the complex loop shapes and decreased coercivity observed in the lower dosed Sr 0% and Sr 10% crystals.

Fig. 5 provides a more in-depth look at how magnetic responses change as low concentrations of Sr are introduced by comparing undoped (Sr 0%) and low doped (Sr 10%) materials. At temperatures above 15 K, we observe the emergence of complicated magnetic responses that are consistent with coexisting but uncoupled magnetic phases. In the 0% sample, a soft magnetic component is superimposed on a linear field-dependent moment

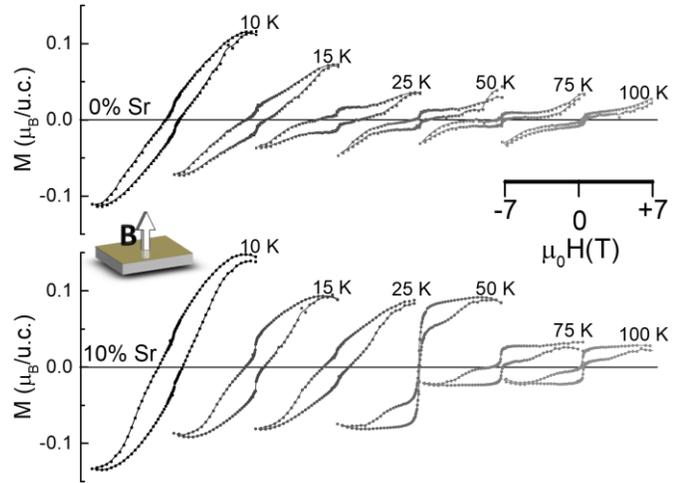


Fig. 5. Evolution of out-of-plane magnetization for Sr 0% (top) and Sr 10% (bottom) films show that low concentrations of Sr can induce an uncoupled magnetic response.

suggesting a soft FM phase coexisting with a paramagnetic or weak and unsaturated AFM. Magnetic phases appear to harden below 15 K and become dominated by a more conventional FM response. In the Sr 10% case, the soft component saturates as one might expect from a soft FM or superparamagnet, but again this soft component does not appear to couple to the hard component. This is particularly clear at 50 K, where the soft loop switches near the zero-field crossing without impacting the hard component. Previous work on $\text{La}(\text{Cr}_{0.2}\text{Mn}_{0.2}\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2})\text{O}_3$ has shown coexistence of AFM and FM orders that can lead to unusual exchange biasing responses manifesting as a vertical shift in magnetization loop under field cooling which also coincides with a decrease in coercivity [33]. The evolution of the hysteresis loops observed in this work suggests that there exists a soft magnetic component at the boundary region between FM and AFM phases at higher temperatures which transitions a sharper coupled boundary as energy is reduced at low temperatures. The soft component becomes rigid, likely influenced by coupling to the hard component which gives rise to a uniform coercivity. This understanding provides an explanation for the drop in coercivity coinciding with the change in loop shape—an effect which would be expected with a growth in the size of the FM region through coupling to the soft magnetic component at the interface between AFM and FM portions of the film.

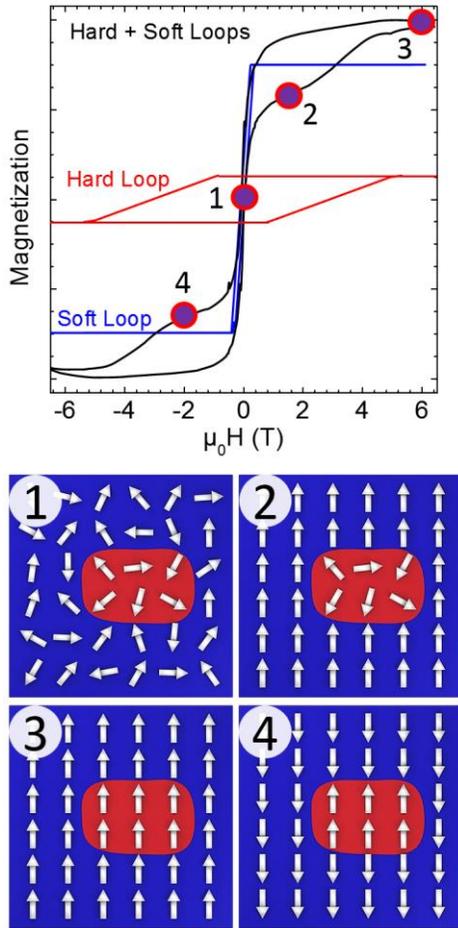


Fig. 6. The addition of hard and soft loops leading to exchange spring behavior(top) with a micromagnetic cartoon (bottom)representation of behavior of local competing magnetic responses along the experimental loop as field is swept from zero field (1) to high positive field (2-3) and then to intermediate negative field (4).

The mixed-magnetic phase response observed in the 0% and 10% samples can occur when soft (low coercivity) and hard (high coercivity) magnetic regions coexist in a material. A simplified example is illustrated in **Fig. 6**. Here, the soft portion of the film rotates with field while the hard component, subject to its coercivity, lags. This is represented in the cartoon where the local moments in each of the components are shown for various portions of the uncoupled magnetic components contributing to the loop. The wasp-waisted hysteresis loops, observed in the OOP direction for Sr 0% and 10% cases, are the first indication of noteworthy interplay between the different magnetic phases in the films. Prior to this work, FM and AFM phases were known to exist in L5BO. However, the emerging multi-component loops confirm the presence of a third contribution to magnetic phase. The third contribution is attributed to the boundary between FM and AFM phases in the film where uncompensated spins can emerge. This creates a frustrated magnetization having an apparent PM-like or soft FM-like loop response to field that can be entirely decoupled from the FM clusters in the film.

Unlike the Sr 0% and Sr 10% crystals, the magnetization loops for the Sr 30% and 50% crystals are dominated by a FM component that gives no sign of the soft/hard mixed magnetic phases. The magnetic anisotropy for these higher Sr concentrations dictates the easy axis of magnetization and increased coercivity in the out-of-plane direction. When the magnetic field is applied in-plane, the FM component is extremely soft at intermediate temperatures until being purely PM above the FM blocking temperature. While the FM component increases for these higher concentrations, the relatively low M_s (~10% of total possible moment) and the expected presence of local AFM

exchange couplings between some of the transition elements suggest that AFM order is still a dominant feature in these films.

From the observations above, a phenomenological phase diagram is constructed for $\text{La}_{1-x}\text{Sr}_x(\text{Cr}_{0.2}\text{Mn}_{0.2}\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2})\text{O}_3$ ($0 \leq x \leq 0.5$) in **Fig. 7**. The magnetic frustration is most prevalent at 10% Sr where the presence of uncompensated moments—behaving as a soft FM—in addition to an emerging hard FM portion of the film both contribute on a similar scale to the magnetization. This generates a loop shape exhibiting two uncoupled phases which become rigidly coupled at low temperature. A shift towards a dominant FM order with increasing Sr concentration likely couples to an increase in the average valence of the transition metal on the *B*-site sublattice. This is suggested by a shift towards FM, which

has been seen with the parent oxides LaCoO_3 and LaMnO_3 and through a gradual transition to lower Neel temperatures in LaCrO_3 and LaFeO_3 [22–25,34,35]. Ni^{4+} is considered an exotic charge state for Ni, so there are no examples of high-quality hole doped LaNiO_3 . This suggests that the entropy stabilization process may enable charge compensation in the easier to oxidize Mn, Cr, and Co. How charge compensation ties to crystal

phase formation and stability in configurationally complex oxides such as these is an open question at present. Given the clear transition towards FM, it is likely that a shift towards Mn^{4+} and Co^{4+} enable double exchange pathways which drives the observed increase in the FM volume fraction as Sr concentration increases. A crude approximation of this effect, which was used to model $(\text{La,Sr})\text{MnO}_3$ [36], is the local enhancement of FM at lattice sites near Sr. If we consider this model of double exchange in the LS5BO system, we have observed the emergence of robust but local FM clusters with increasing Sr which mimics the experimental result. This explanation is also consistent with the observation that the soft magnetic behavior critical to the two-phase loop shape in Sr 0% and Sr 10% samples begins to disappear as the FM phase becomes more dominating in

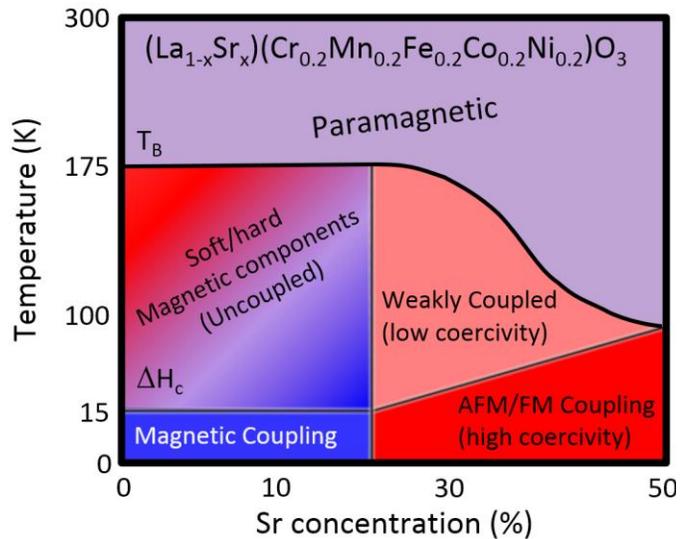


Fig. 7. Proposed magnetic phase diagram for the LS5BO system. The temperatures are chosen based on the blocking temperature (T_B) of the FM component and the change in coercivity (ΔH_c) at low temperature.

the Sr 30% and Sr 50% compositions. However, the remaining difficulty is in understanding the observed decrease in T_B , which couples to a decrease in FM domain size. For this, we see two possible scenarios: (1) the loss of the glassy region of uncompensated moments decreases the effective FM size as these moments can couple to the FM, or (2) the change in charge state, while enabling double exchange in some cases, may diminish FM in others. For example, while $\text{Fe}^{3+}\text{-O-Mn}^{3+}$ is known to give rise to FM, $\text{Fe}^{3+}\text{-O-Mn}^{4+}$ may not. Future x-ray absorption spectroscopy and circular dichroism studies may shed light on which of these scenarios drives function.

Utilizing the traditional method of substitutional doping, the fundamental properties of configurationally complex materials are described. Hole doping does not have an adverse effect on the crystallinity of the high entropy oxide films. Through hole doping, it is found that the magnetic phase can be tuned – both increasing M_s and decreasing T_B . The magnetic responses are consistent with the presence of FM clusters which grow in number (evident from M_s) but decrease in size (evident from T_B). From these results the first proposed phase diagram of an entropy stabilized oxide is provided, opening a new avenue for exploration of this rapidly expanding materials class.

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