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Magnetocaloric effect in epitaxial La_{0.56}Sr_{0.44}MnO₃ alloy and digital heterostructures

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This work investigates the magnetocaloric effect of two epitaxial manganite heterostructures, one being a single layer $La_{0.56}Sr_{0.44}MnO_3$ alloy with randomly distributed La and Sr cations, the other a digitally synthesized superlattice of LaMnO₃ and SrMnO₃ fabricated to be compositionally identical to the alloy. The magnetic entropy change and relative cooling power were larger for the alloy than the superlattice, though both are suppressed relative to bulk materials. These results indicate that disorder of the A-site cation species in the perovskite structure may play a crucial role in defining the magnetocaloric effect in complex oxide materials. © 2012 American Institute of Physics. [doi:10.1063/1.3677670]

I. INTRODUCTION

The magnetocaloric effect (MCE) is a thermodynamic phenomenon that enables the entropy (and ultimately temperature) of a material to be altered by applied magnetic fields. The physical origin of the MCE is the coupling of a material's magnetic moments to an applied field, which affects the ordering of spins. The textbook example of the MCE is adiabatic demagnetization, which has been used predominantly in ultra-low temperature work. Research efforts in this area increased with the discovery of the giant MCE in materials such as $Gd_5(Si_xGe_{1-x})_4$, which highlighted the potential for realizing magnetic refrigeration near room temperature.^{1,2} Indeed, improvements in materials have led to the demonstration of highly efficient magnetic refrigeration technologies near 300 K, e.g., with Carnot efficiencies on the order of 60%, far superior to conventional vapor cycle refrigeration and thermoelectric cooling.^{3,4}

While the MCE is most frequently studied in bulk materials, there has been some effort recently to explore the MCE in nanoscale materials.^{5–12} In Refs. 5 and 6 it was shown that finite size effects can detrimentally impact the magnetic entropy change in Gd/W multilayers. In addition, studies of thin films suggest that nanoscale disorder in the material is important for magnetocaloric properties.^{7,10} Our work here underscores these findings through a comparative study of 31 nm thick epitaxial $La_{0.56}Sr_{0.44}MnO_3$ films grown in two distinct forms: a random alloy and a digitally synthesized superlattice.

II. EXPERIMENTAL

The epitaxial manganite thin film samples were grown by ozone-assisted oxide molecular beam epitaxy on TiO_2 terminated SrTiO₃ (001) substrates. The samples are depicted schematically in Fig. 1. Details of the preparation, and structural, magnetic, and electrical properties have been previously reported.¹³ The alloy sample was a single 31 nm layer with a composition of La_{0.56}Sr_{0.44}MnO₃. Growth was performed by codeposition in order to create an alloy in which La and Sr cations were randomly distributed on the A-sites of the ABO₃ perovskite structure. The 31 nm thick superlattice was grown by digital synthesis, wherein the La and Sr are deposited separately. This results in a superlattice of LaMnO₃ (LMO) and SrMnO₃ (SMO), with each layer containing distinctly either La or Sr. The superlattice structure we investigate is [(SMO/LMO)₄/LMO]₉, which has a total composition equivalent to that of the random alloy film. There is a ferromagnetic phase transition that occurs in both films at 305 K.¹³ Additionally, an antiferromagnetic transition around 250-275 K causes both materials to be canted antiferromagnets, with a sizable net moment in an applied field.¹⁴

We used a Quantum Design MPMS XL SQUID magnetometer at the Center for Nanoscale Materials at the Argonne National Lab to measure the magnetization of our samples for fields up to 6.01 T for temperatures in the range 200-350 K, with the field applied in the sample plane. The samples were zero field cooled, then saturated in 6 T. The field and temperature dependences of the magnetization were measured by raster scanning the parameter space: M was measured with H ascending at T_n , then measured with H descending at T_{n+1} . The lowest field applied was +0.01 T, which helps avoid minor loops from making the ascending and descending fields dissimilar, since the magnetization has yet to reverse (MH loops have been presented previously as supplemental material to Ref. 14). This also limits the influence of hysteretic losses in the context of cooling power. This protocol mimics the field cycling that would be used in a unipolar field environment with a simple biasing field. The M(H,T) data shown in Fig. 2 have had the diamagnetic background of the substrate subtracted, and have been normalized by the mass of the manganite material (4.14 μ g and 4.03 μ g for the alloy and superlattice, respectively). Each mass was calculated from the

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FIG. 1. (Color online) Schematic of the two epitaxial samples under investigation. The La_{0.56}Sr_{0.44}MnO₃ alloy sample was grown with the La and Sr simultaneously deposited (left). The [(SMO/LMO)₄/LMO]₉ digital superlattice (right) has discrete layers containing La and Sr. This layer sequence is repeated 9 times. The total thickness of each sample is 31 nm (81 perovskite unit cells).

film volume using a density of 6.16 g/cm³. The figure of merit most readily measured for the magnetocaloric effect is the isothermal magnetic entropy change (ΔS_m). While not directly measurable without specific heat measurements (which is a major feat for thin films), isothermal magnetometry enables one to calculate ΔS_m through the usual Maxwell Relation. Because the magnetization data is acquired isothermally at discrete steps in the H-T parameter space, we approximate the integral numerically as $\Delta S = \sum_i \frac{M_{i+1}(T_{i+1},H) - M_i(T_i,H)}{T_{i+1} - T_i} \Delta H$, where we again note that the minimum field is 0.01 T rather than the usual value of zero.

III. RESULTS

Figures 3(a) and 3(b) show the magnetic entropy change results for the alloy film and the superlattice, respectively. It is somewhat surprising that the entropy peaks occur at widely different temperatures (270 K and 295 K for the alloy and superlattice, respectively; $\Delta H = 1$ T) despite the ferromagnetic ordering temperature of 305 K each being confirmed through magnetometry.¹³ The alloy film's peak magnetic entropy change is consistently greater than the superlattice, ranging from ~66% for $\Delta H = 1$ T to ~15% for $\Delta H = 6$ T. The larger entropy ΔS_m^{max} is not unexpected for the alloy, as it has a greater moment than the superlattice (2.2 versus 1.7 μ_B per Mn). Figure 3(c) shows that the two entropy change responses collapse onto a single curve when analyzed via the universal curve method.¹⁵ This collapse



FIG. 2. (Color online) Samples of isothermal magnetization data of (a) the alloy film and (b) the superlattice between the noted temperatures. The temperature step between each isotherm is 10 K. For clarity, only a fraction of the measured isotherms are shown.

required two reference temperatures, which implies some potential influence from minority magnetic phases. However, neutron diffraction data suggest the samples are homogeneous¹⁴: the A-type spin structure was confirmed; the coherence length is close to the film thickness, which would not be possible if there were patches of ferromagnetic and anti-ferromagnetic phase separated regions, and the neutron diffraction peaks are field independent.

The relative improvement with ΔH implies different scaling behavior for the alloy and the superlattice. The entropy change peak (ΔS_m^{max}) of many relevant materials scales with field according to $\Delta S_m^{max} \alpha H^n$. For a mean field model, n is 2/3 at the ordering temperature, though some magnetic materials have larger values of n.¹⁵ Figure 4(a) shows that ΔS_m^{max} for both samples scales with field in this manner. The exponent of the alloy film is n = 0.90, while n = 1.09 for the superlattice. These are significantly different from each other and from the mean field exponent. While one expects discrepancies with mean field theory near the phase transition, the exponent at the ordering temperature is usually less than 1, as seen in the alloy film.

As with the magnetic entropy change, the relative cooling power (RCP) of the alloy sample is superior to the superlattice. RCP is essentially the area under the ΔS_m versus T curves in some range of temperature, usually estimated by the full width at half max of the entropy peak. The RCP indicates the relative potential a material may have as a magnetic refrigerant. Here, a field change of $\Delta H = 1$ T leads to RCP



FIG. 3. (Color online) Magnetic entropy change results for (a) the alloy film and (b) the superlattice for field changes ranging from 1 T to 6 T in 1 T steps. (c) A comparison of the alloy (open triangles) and superlattice (filled squares) showing that the entropy change responses collapse onto a single curve when analyzed via the universal curve method.



FIG. 4. (Color online) Magnetocaloric parameters for the alloy film (triangles) and superlattice (squares). (a) The scaling analysis $\Delta S_m^{max} \alpha H^n$ discussed in the text leads to the noted exponents, n. (b) The relative cooling power for the alloy well behaved, while that of the superlattice is nonlinear.

values of ~37 J/kg and ~22 J/kg for the alloy and superlattice, respectively. The field dependence of the relative cooling power for each sample is shown in Fig. 4(b). The RCP of the superlattice is notably nonlinear, enabling it to approach the alloy sample's RCP. Following a similar scaling analysis as above (e.g., RCP α Hⁿ), the exponent for the superlattice is 1.21, whereas it is 1.01 for the alloy. The enhancement of these scaling exponents in the superlattice implies that the moments order more readily along the applied field direction.

IV. DISCUSSION

The major difference between the alloy and the superlattice is that the spatial distribution of La and Sr cations on the A-site is random in the former, but highly ordered in the latter. It is well known that manganite properties are easily perturbed by disorder because exchange interactions in these materials are highly sensitive to the local bond environment.^{13,16,17} Cation disorder in the alloy produces an increased variation in Mn-O-Mn bond angles and lattice distortions relative to the cation-ordered superlattice. This reduces the electronic interaction (i.e., transfer integral) between neighboring Mn ions that is fundamental for the inplane, ferromagnetic double-exchange interaction,¹⁸ which weakens the spin coupling at the magnetic transition relative to the superlattice. This may explain in part why ΔS_m^{max} is found at a lower temperature in the alloy despite the equivalent ordering temperatures. Furthermore, the cation order in the superlattice may cause the spins to order more readily relative to the alloy. This may explain the superlattice's unexpectedly large exponents for the two scaling relations. Just above T_c, (e.g., up to 315 K) the susceptibility of the superlattice exceeds that of the alloy by a factor of two, lending further credibility to this interpretation.

V. CONCLUSIONS

We have compared the magnetocaloric effect in two 31 nm thick epitaxial $La_{0.56}Sr_{0.44}MnO_3$ samples grown in distinct forms, one as a single layer alloy and one as a digital superlattice composed of LaMnO₃ and SrMnO₃ layers. While neither has properties superior to the bulk¹⁹ or are themselves candidate refrigerants, both the magnetic entropy change and relative cooling power of the alloy film exceed those of the superlattice. The unique comparison in this study of the epitaxial alloy in which La and Sr randomly occupy the A-sites to the superlattice with ordered A-site occupation allows us to conclude that the entropy cation disorder plays a crucial role in the magnetocaloric effect in manganite materials. This may thus be an important structure-property relationship for future materials development.

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