Giant magnetoelastic spin-flop with magnetocrystalline instability in La$_{1.4}$Sr$_{1.6}$Mn$_2$O$_7$

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We studied a low-field giant magnetostrictive spin-flop transition in a colossal magnetostrictive manganite La$_{1.4}$Sr$_{1.6}$Mn$_2$O$_7$ using resonant soft x-ray diffraction and soft x-ray absorption spectroscopy at the Mn $L_{2,3}$ edge. The spin-flop transition is induced by an instability of magnetocrystalline anisotropy near a critical $\epsilon_c$ orbital configuration with a balanced occupation in $d_{z^2}$ and $d_{x^2-y^2}$ states, which contribute in-plane and out-of-plane orbital angular momenta, respectively. The magnetic field drives a certain change in the orbital occupation with lattice distortion to switch the magnetic anisotropy, resulting in the spin-flop transition. These results provide a comprehensive mechanism of interplay between spin, orbital, and lattice degrees of freedom to realize a low-field giant magnetoelasticity.

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I. INTRODUCTION

Magnetoelectric coupling between magnetization and lattice strain, stems from a coupling between magnetic spin axis in an internal coordinate and lattice structure in a real coordinate through the relativistic spin-orbit coupling [1]. Recently, the magnetostriiction is utilized for actuator, motor, and magnetostriective sensor in future micromechanic devices [2]. In a ferromagnet, an external magnetic field induces only small magnetostriiction ($\Delta L/L$) by rotating magnetic domains while the spin-orbit coupling often drives relatively large magnetostriiction, and $\Delta L/L$ is enhanced even by two order of magnitude in rare-earth (4$f$) based magnetostriective materials with the large spin-orbit coupling constant [1,3]. Terfenol-D ($\text{ Tb}_2\text{Dy}_2\text{Fe}_2$) is one of the magnetostriective materials with the largest $\Delta L(H)/L$, in which the magnetic easy axis reorientates from the (111) to (100) direction resulting in strong magnetostriective behaviors [4]. It is because the $4f$ wave function under the crystal field is tightly coupled with the magnetic axis.

On the other hand, 3$d$ manganites suggest an alternative route to design giant magnetostriuctive materials with a relatively small spin-orbit coupling constant. The system exhibits complex electrical and magnetic phase diagrams as a function of doping, temperature, and even external fields, and crossing over the phase boundaries evokes the emerging phenomena involving the interplay of the charge-spin-orbital-lattice degrees of freedom [5–7]. In this context, bilayer manganites La$_{2-2x}$Sr$_{1.2}$Mn$_2$O$_7$ have attracted much attention due to not only the colossal magnetostrictance (CMR) phenomena [6–8] but also various intriguing features such as a polaronic metallic state [9], a photoinduced spin dynamics [10], and unusual charge/spin/orbital ordering behaviors [11–13]. La$_{1.4}$Sr$_{1.6}$Mn$_2$O$_7$, one of the CMR bilayered manganites, exhibits a noticeable magnetostrictive behavior. As presented in Fig. 1(a), its crystal structure consists of magnetic MnO$_2$ bilayers separated by a (La,Sr)O layer, and the magnetic structure exhibits consecutive ordering behaviors of antiferromagnetic (AFM) and ferromagnetic (FM) spin orders upon cooling through $T_N \approx 100$ K and $T_C \approx 75$ K, respectively. Upon heating across $T_C$, the interbilayer coupling switches from FM to AFM while the FM coupling within the bilayer remains and the system gets into an $A$-type AFM phase. The spin axis is mainly along the $c$ axis in both phases [6,8,14]. The magnetic switching is observable in the susceptibility ($M/H$) with varying temperature as shown in Fig. 1(b). $M/H$ exhibits two anomalies around $T_C$ and $T_N$, which are more distinguishable in the derivative shown in the inset. This AFM to FM switching leads an insulator-metal transition with two orders of magnitude resistivity reduction. This transition can be also driven by an external magnetic field just above $T_C$ to yield CMR [8,15]. In addition, as shown in Fig. 1(c), the system exhibits huge magnetostriiction of $\Delta L_c/L_c \approx 1.2 \times 10^{-3}$ at 2 T in the $A$-AFM phase [16], and its magnitude is even comparable to the large value of the magnetostriuctive materials such as RCO$_5$ and RFe$_2$ (R = rare earth) obtained at low temperature (4 K) with a higher magnetic field ($H \geq 6$ T) [1,3].

In this paper we studied a giant magnetostriective spin-flop transition in La$_{1.4}$Sr$_{1.6}$Mn$_2$O$_7$ at a low in-plane magnetic field ($\sim 0.1$ T). The spin and orbital states were investigated by using resonant soft x-ray scattering (RSXS) and x-ray absorption
spectroscopy (XAS) at Mn $L_{2,3}$ edges. The RSXS results manifest the magnetic-field-driven spin-flop transition. A magnetic anisotropy switch plays a crucial role to trigger this transition, accompanying a certain change in the orbital occupation together with the magnetostrictive lattice distortion. Using theoretical configuration interaction (CI) model calculations, we demonstrated that this low-field giant magnetostrictive spin-flop is driven by a magneto-crystalline instability near a balanced occupation in $d_{3z^2-r^2}$ and $d_{3z^2-r^2}$.

II. EXPERIMENT

High-quality La$_{1.4}$Sr$_{1.6}$Mn$_2$O$_7$ single crystals were grown by a floating zone method. The magnetization was obtained by using a commercial magnetic property measurement system. The crystal exhibits consecutive magnetic transitions [see Fig. 1(b)] as in the previous reports [8,14]. The RSXS and XAS measurements were performed at the 2A beamline in Pohang Light Source. A clean and shiny (001) surface was prepared by cleaving in situ by a floating zone method. The magnetization were obtained by using a commercial magnetic property measurement system. The remnant AFM order parameter at 20 K was estimated to $\sim 15\%$, indicating that some portion of AFM order is affected by the field. Figure 2(a) displays the RSXS scans along the (001) fixed $q$ energy scan presented in Fig. 2(c) displays identical line shape for the $\sigma$ and $\pi$ polarizations. The AFM order parameter, which is obtained from the integrated area, was monitored as a function of temperature shown in Fig. 2(d). Upon heating above 80 K, the order parameter decreases and disappears at $T_N \approx 100$ K. It shows a sharp $\theta = 0.014408-2$ [see the inset in Fig. 2(d)], the intensities are given by $E \parallel c$ and $E \perp c$ spectra without changing the experimental geometry. The degree of linear polarization was better than 98% for both polarizations. Many-body cluster model CI calculations code (XTLS 9.0) [18] were performed for a Mn$_6$O$_6$ octahedron including the O $2p$ to Mn $3d$ charge transfer effects, the Mn $3d$ $L\cdot S$ coupling, full atomic multiplets, and the tetragonal distortion for different spin axes $c$ (out-of-plane direction at $T = 78$ K. It shows a sharp $\theta = 0.014408-2$ [see the inset in Fig. 2(d)], the intensities are given by $E \parallel c$ and $E \perp c$, with the phase competition. Despite large changes in both intensities $I_\sigma$ and $I_\pi$ with temperature, the ratio $I_\sigma/I_\pi$ remains constant value $I_\sigma/I_\pi \approx 0.86$ [see the inset in Fig. 2(d)], which corresponds to the spin axis 20° tilted from the $c$ axis, consistently with the previous results [8,14].

We performed the RSXS measurements under $H \parallel a$ to explore how the AFM order is affected by the field. Figure 3(a) shows the field dependent (001) AFM peak intensities $I_\sigma$ and $I_\pi$. In the $ac$ scattering plane for the $\theta$-2$\theta$ reflection [see Fig. 2(a)], the intensities are given by $I_\sigma = m^2_\sigma \cos^2 \theta + m^2_\pi \sin^2 \theta$ and $I_\pi = m^2_\sigma \cos^2 \theta + m^2_\pi \sin^2 \theta + 4m^2_\pi \sin^2 \theta \cos^2 \theta$, where $m_\sigma$, $m_\pi$, and $m_c$ denote the $a$-, $b$-, and $c$-axis components of the local spin moments, respectively [20]. Here the scattering angle $2\theta \approx 57^\circ$ at $h\nu = 643$ eV, and $I_\pi$ and $I_\sigma$ are only attributed to the AFM components. At $H = 0$ (A), $I_\pi$ and $I_\sigma$ are maximized with $I_\pi/I_\sigma \approx 0.86$ and $I_\pi - I_\sigma$ is finite with nonvanishing $m_\pi$ due to the spin axis tilting. There is no
crystallographic distinction between the a and b axis, and thus $m_a$ is equal to $m_b$ at $H = 0$ (average over the magnetic domains). As $H$ along the a axis increases, $I_0$ abruptly drops at $H_C \approx 540$ Oe while $I_x$ gradually decreases with small kink features at $\pm H_C$ and $I_x - I_0$ increases. At $H \approx 1000$ Oe (B), $I_x$ vanishes, meaning that $m_a = 0$ and $m_c = 0$ in the AFM component and $I_x - I_0$ becomes maximized (maximum $m_b$). It indicates that the spin axis of the AFM component flops from the nearly c to b axis.

In order to extract the spin components changing across the spin reorientation transition (SRT), three distinguishable AFM domains with spin components are counted in the simulation as follows:

\[(ac)\text{-AFM} : (m_{ac}^A, m_{ac}^C),\]
\[(bc)\text{-AFM} : (m_{bc}^A, m_{bc}^C),\]
\[(b)\text{-AFM} : (m_b^A).\]

As the $H$ field is applied along the a axis, the spins tend to tilt toward the field direction, and thus an additional FM component ($m_{FM}^A$) is taken into account. The $m_{FM}^A$ is determined from the in-plane $M$-$H$ curve obtained from the SQUID measurement (see the Supplemental Material Fig. S1 [21]). The total spin moment is set to be the nominal saturated magnetization $7.4 \mu_B$/f.u. At $H = 0$ the spins are in the AFM order with the spin axis $20^\circ$ tilted from the c axis in either the ac or bc plane. There only exist (ac)- and (bc)-AFM domains with populations $p^{(ac)} = p^{(bc)} = 0.5$ and $m_a$ and $m_b$ are the same. It means that $m_{ac}^A$ and $m_{bc}^A$ in the (ac)-AFM domain and $m_{bc}^B$ and $m_{c}^B$ in the (bc)-AFM domain equally contribute to the scattering intensities with $m_{ac}^B = m_{bc}^B$. When the applied field $H$ along the a axis increases, it is expected that the (ac)- and (bc)-domain populations change unevenly and the additional $m_{FM}^A$ along the field direction is turned on. At $H > 1500$ Oe, $I_0$ becomes zero. It means that $m_{FM}^A = m_{FM}^B = 0$ and thus both the (ac)- and (bc)-AFM domain populations vanish, i.e., $p^{(ac)} = p^{(bc)} = 0$ [see Fig. 3(c)]. Now we have only canted (b)-AFM domains with $m_{FM}^A (= m_b^B)$ and $m_{FM}^A$ components.

Under the constraints described above, we simulated the measured intensity and determined ordered magnetic components as displayed in Figs. 3(b) and 3(c). Before the spin-flop transition, the $H$ field partially switches the (ac)-AFM domain into the (bc)-AFM domain with sustaining the AFM easy axis on c axis. Near the critical field, the net ordered $m_{AFM}^A$ and $m_{AFM}^B$ rapidly drop and finally become zero while $m_{FM}^A$ increases to keep the value of $I_x$, resulting from the spin-flop transition from the (ac, bc)-AFM to the (b)-AFM order. After the spin-flop transition, $m_{AFM}^A$ and $m_{AFM}^B$ gradually decreases with an increase of $m_{FM}^A$ due to the magnetic field and becomes saturated at $H \sim 4000$ Oe (see the Supplemental Material Fig. S1 [21]), consistent with the $I_x$ behavior. One can notice certain reduction in the ordered total net moment near the spin-flop transition, indicating that the competition between (ac, bc)-AFM and (b)-AFM orderings causes a certain degree of disorder in the AFM components at the domain boundaries.

Figure 4 presents two-dimensional maps of $I_{\sigma,\pi}$ versus temperature and applied $H$ field, obtained by accumulating the $H$-field dependencies [see Fig. 3(a)] at different temperatures. The spin-flop crossover is clearly observable in $|\partial I_{\sigma,\pi}/\partial H|$, both of which expose prominent maxima around $H_C \approx 540$ Oe in the A-AFM window ($75 \leq T \leq 100$ K), as shown in Figs. 4(c) and 4(d). The spin structures before and after the spin-flop transition are schematically depicted in Fig. 4(c). In the AFM phase, the ordered spin is aligned mostly along the c axis at $H = 0$ [14,15]. As $H$ increases, the spin axis flops around $H_C$ and the spin axis lies in the ab plane with both FM $m_a$ and AFM $m_b$. In the low temperature FM phase, the FM spins are also aligned along the near c axis at $H = 0$ and gradually turn to the $H$-field direction to become fully along the a axis at $H > 6000$ Oe with the saturated magnetization.

B. Magnetostriction and magneto-crystalline anisotropy

The RSXS study manifests the spin-flop transition induced by the $H$ field in La$_{1.4} Sr_1.6$Mn$_2$O$_7$. The spin-flop accompanies a giant magnetoelastic response with c-axis contraction and ab-plane expansion [16], implying a certain change in the orbital state. The state consists of Mn$^{3+}$ ($t_{2g}$-$e_g^5$) and Mn$^{4+}$ ($t_{2g}$-$e_g^7$) with a 7:3 ratio. The doubly degenerated $e_g$ state naturally
are presented with blue and red solid lines, respectively. (b) Cor-

incident polarization. (c) and (d) |\partial I_{\sigma}/\partial H| intensity maps are displayed. The high intensity line near 540 Oe indicates the critical field of SRT. (e) Schematic spin configuration of each point is displayed.

Thus we examined the orbital character using the Mn d

edge (2eg − 3eg) polarization dependent (001)

polarization geometries displayed in Figs. 5(c) and 5(d). The CI calculations were performed by using XTLS9.0 code [18]. In the CI calculation, we took into account the tetragonal (D4h) crystal field, a Mn 3d-O 2p hybridization, and full atomic multiplets driven by Mn 3d-3d and Mn 2p-3d Coulomb interactions. To mimic the LD spectra La14Sr14Mn8O33 (x = 0.3), we applied the 7 : 3 weighted average of Mn3+ and Mn4+ in the spectra. The occupied eg orbital in Mn3+ was selected by tuning the tetragonal distortion, i.e., elongation or compression of MnO6 octahedron for the d3z2−r2 or d5z2−r2 orbital occupation, respectively. For Mn4+, a small tetragonal distortion (elongation) reflecting the layered structure is commonly applied in both calculated LD spectra in order to capture the wider bandwidth of d3z2−r2 resulting in positive LD at the tail of each L2,3 edge. The CI calculations definitely show the sign inversion of LD at the leading edge of the L2,3 edges with certain change in the occupied eg orbital in Mn3+,

The polarization dependence can be seen more clearly in the linear dichroism (LD), the difference spectrum (E ⊥ c − E // c), as shown in Fig. 5(b). The L2,3-edge LD spectra exhibit rather complicated line shapes, but a prominent change appears near the threshold, which corresponds to the lowest energy transition Mn3+ t2g2 eg(E) → 2p t2g2 eg(A1g) with a 2p core hole. Due to the dipole selection rule, the E // c and E ⊥ c polarizations emphasize the transition to d3z2−r2 and d5z2−r2 holes, respectively. This LD signal is positive at T = 80 K (AFM phase) but becomes negative at T = 20 K (FM phase). These results tell us that the d3z2−r2 occupation dominates over the d5z2−r2 one in the AFM phase but it becomes opposite in the FM phase.

Indeed, it is confirmed in the theoretical many-body configuration interaction (CI) calculations for the LD spectra in which this sign inversion occurs with the change in the occupied orbital from d3z2−r2 to d5z2−r2. The calculations reproduce the overall LD line shapes for both orbital occupation cases as displayed in Figs. 5(c) and 5(d). The CI calculations were performed by using XTLS9.0 code [18]. In the CI calculation, we took into account the tetragonal (D4h) crystal field, a Mn 3d-O 2p hybridization, and full atomic multiplets driven by Mn 3d-3d and Mn 2p-3d Coulomb interactions. To mimic the LD spectra La14Sr14Mn8O33 (x = 0.3), we applied the 7 : 3 weighted average of Mn3+ and Mn4+ in the spectra. The occupied eg orbital in Mn3+ was selected by tuning the tetragonal distortion, i.e., elongation or compression of MnO6 octahedron for the d3z2−r2 or d5z2−r2 orbital occupation, respectively. For Mn4+, a small tetragonal distortion (elongation) reflecting the layered structure is commonly applied in both calculated LD spectra in order to capture the wider bandwidth of d3z2−r2 resulting in positive LD at the tail of each L2,3 edge. The CI calculations definitely show the sign inversion of LD at the leading edge of the L2,3 edges with certain change in the eg orbital occupation. Besides the sign inversion of the leading edge feature, the overall features of the observed LD spectra are also well reproduced in the calculated ones.

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dominated by the AFM phase although the FM phase partially develops below $T_C \simeq 75$ K. Upon cooling across the AFM-FM transition, the $c$ lattice constant contracts significantly while the $ab$ ones expand [16]. Compression of the MnO$_6$ cage along the $c$ axis [11] makes partial transfer of the occupied $d_{3z^2-r^2}$ electrons into the $d_{x^2-y^2}$ states. This orbital occupation change is also driven by the in-plane $H$ field. The LD line shape switches again in the magnetic field at $T = 80$ K (also at $T = 60$ K) as shown in the right panel in the figure. These results manifest that the giant magnetoelasticity in the AFM phase is induced by switching the dominant occupied orbital from $d_{3z^2-r^2}$ to $d_{x^2-y^2}$ accompanied by the spin-flop transition involving a change of the magnetocrystalline anisotropy (MCA).

In order to understand the microscopic mechanism of the magnetoelasticity, we explore how the lattice distortion affects the orbital occupation and MCA. The many-body cluster model model calculation is performed for Mn$^{3+}$ ($d^5$) in an MnO$_6$ octahedron with a variation of the tetrahedral distortion $\Delta c/c$, the elongation ratio of Mn-O (apical) distance along the $c$ axis. Figure 6(a) shows the calculation results for the $d_{3z^2-r^2}$ and $d_{x^2-y^2}$ occupations for two different spin axes. The positive (negative) $\Delta c/c$ represents an elongated (compressed) octahedron. The occupation number $n_{3z^2-r^2}$ and $n_{x^2-y^2}$ vary with $\Delta c/c$ although their sum is nearly constant. Interestingly, as the spin lies along the $z$ axis ($x$ axis), the $L \cdot S$ coupling effectively lowers the $d_{3z^2-r^2}$ ($d_{x^2-y^2}$) energy to increase $n_{3z^2-r^2}$ ($n_{x^2-y^2}$) slightly and contributes positive $\Delta L = L_z - L_y$ (negative $\Delta L$) even for $\Delta c/c = 0$, in which $n_{3z^2-r^2} = n_{x^2-y^2}$ and $L_{x,y} = 0$ without the $L \cdot S$ coupling (Supplemental Material Fig. S3 [21]). This result shows that the $L \cdot S$ coupling lowers the system energy by inducing an unquenched orbital moment even in the perfect octahedron. In the second order perturbation theory of the $L \cdot S$ coupling for the Mn$^{3+}$ ion in the crystal field, the orbital moments are estimated to be $L_z = 3n_{3z^2-r^2}\xi_{3d}/10Dq$ and $L_y = 4n_{3z^2-r^2}\xi_{3d}/10Dq$ with the Mn 3d spin-orbit coupling constant $\xi_{3d}$ (2045 eV), and the crystal field splitting $10Dq$ [22]. Suppose $10Dq = 1.5$ eV, the unquenched moment is estimated to be $L_z = 0.09$ ($L_y = 0.12$) for the unoccupied hole number $n_{3z^2-r^2} = 1$. These ionic orbital moment values are reduced by the covalency and partial orbital occupations in the MnO$_6$ with Mn 3d-O 2p hybridization as in Fig. 6(b).

The MCA energy is defined by the energy difference of the $L \cdot S$ coupling as the spins are aligned along the $a$ axis ($S_a$) and $c$ axis ($S_c$), and thus is determined by $L_z$, with the spin axis $c$, and $L_y$ with the spin axis $a$. Figure 6(b) shows the corresponding $L_z$ and $L_y$ calculated as a function of $\Delta c/c$. For the elongation (compression), $\Delta c/c > 0$ ($\Delta c/c < 0$), the $e_g$ occupation is dominated by $d_{3z^2-r^2}$ ($d_{x^2-y^2}$) and $\Delta L$ becomes positive (negative). This occupation imbalance gives rise to the anisotropy of unquenched orbital moments. These results strongly suggest instability in MCA very near a critical $e_g$ configuration of $n_{3z^2-r^2} \simeq n_{x^2-y^2}$ in manganites with Mn$^{3+}$, where the spin axis cooperates with the tetragonal distortion for the $e_g$ occupation change. This instability drives a giant magnetoelastic spin-flop transition in La$_{1.3}$Sr$_{1.6}$Mn$_2$O$_7$. When the $c$ spin axis is forced to be turned by an in-plane $H$ field, $d_{3z^2-r^2}$ electrons are partially transferred into the $d_{x^2-y^2}$ state in order to minimize the energy cost of the $L \cdot S$ coupling.

As the transferred electron becomes sufficiently large near $H_C$, the octahedron is compressed and $\Delta L$ switches the sign to flop the spin axis. At 80 K (AFM phase), we obtained $\Delta c(0)/c \simeq -450 \times 10^{-6}$ at $H = 3500$ Oe (Supplemental Material Fig. S4 [21]). This value is large enough to switch the dominant orbital and the sign of $\Delta L$ (MCA). In the FM metallic phase (20 K), $n_{x^2-y^2}$ becomes larger than $n_{3z^2-r^2}$ due to the compressed octahedron, but the spin axis remains along the $c$ axis. It is likely due to orbital momentum quenching of the in-plane conducting electrons. The $H$ field increases $n_{x^2-y^2}$ further to flop the spin axis to lie in the plane.

IV. DISCUSSION AND CONCLUSION

Switching of the magnetic easy axis can be induced by fine tuning of doping, pressure, strain, and external fields due to in-
timate coupling of spin, orbital, and lattice degrees of freedom. In La$_{2-x}$Sr$_{x+1}$Mn$_2$O$_7$, the magnetic axis, which is along the c axis at $x \leq 0.32$, switches into the in-plane direction at $x > 0.33$, in which the c lattice parameter is reduced [10,11] and $n_{3z^2-r^2}$ relatively decreases while the direction of magnetic anisotropy changes from the c axis to the ab plane [23]. At $x \simeq 0.32$, the spin axis switches even through photoexcitations [10]. Indeed, the similar relation between structure and magnetic anisotropy is also validated for La$_{1-x}$Sr$_{1+x}$Mn$_2$O$_4$ [24], in which the $e_g$ orbital occupation changes by transferring $d_{3z^2-r^2}$ electrons to $d_{2y^2-z^2}$ orbital [25,26]. The magnetic axis tuning was also demonstrated in La$_{0.7}$Ca$_{0.3}$Mn$_3$O$_7$ epitaxial films, in which MCA can be controlled through strain engineering [27]. In La$_{1-x}$Sr$_{x}$Mn$_2$O$_7$ ($x = 0.3$), the external magnetic field triggers to change the spin axis, and the $L \cdot S$ coupling leads a change in the $e_g$ occupation accompanied by the compressive lattice distortion, resulting in the giant magnetoelastic spin-flop at a low $H$ field (<0.1 T). These results illuminate the comprehensive mechanism for a low field giant magnetoelasticity induced by the magnetocrystalline instability and suggest a route to design new magnetostrictive materials based on the transition metal oxides.

In summary, we investigated a giant magnetoelastic spin-flop transition of a CMR manganite La$_{1-x}$Sr$_{x}$Mn$_2$O$_7$ in the presence of in-plane $H$ fields. The detailed examinations of spin and orbital states demonstrate that the transition is driven by magnetocrystalline instability near a critical orbital occupation. Due to the instability, a small field flopping of the magnetic axis leads a certain change in the orbital occupation due to the spin-orbit coupling. This change accompanies lattice distortion and magnetic anisotropy switching, resulting in the magnetostrictive spin-flop transition.

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