Strain Induced Spontaneous Magnetization in Perovskite Cobalt Oxide

Electronic phases with the nanometer-scale self-organization of electrons are ubiquitously observed in correlated electron systems. In *d*-electron transition metal oxides, versatile quantum states have been realized by tuning the effective one-electron band-filling or band-width. Here we show that control of the spin-state degree of freedom (low/intermediate/high spin states) gives rise to a new complex spin-orbital superstructure with spontaneous magnetization in a thin film of perovskite $LaCoO_3$. A tiny crystal-lattice strain can promote the spin-state transition of Co ions and the ordering of Co-3*d* orbitals modulates the spin exchange interactions to produce the unique ferrimagnetic structure.

Entanglement among the charge, spin and orbital degrees of freedom in *d*-electron transition-metal compounds is a key ingredient to control emergent quantum states such as unconventional superconductivity and magnetically induced ferroelectrics (multiferroelectricity). The control of magnetic/electronic states has been ubiquitously achieved by tuning material parameters such as the effective *d*-electron band-width or band-filling. In addition to these well-known approaches, in a certain class of the transition-metal compounds, there is a unique material tuning parameter, the spin-state variability (such as low, intermediate, and high spin states) of constituent magnetic ions, which is strongly tied with the orbital degree of freedom for correlated electrons.

The perovskite $LaCoO_3$ is known as a prototype of the spin-state crossover material and has attracted much attention in recent decades. In this system, the nominally trivalent Co-ion (Co^{3+}) may take three different spin states as shown in Fig. 1: the low-spin (LS) state with filled 3*d* t_{2g} manifold (*S*=0), intermediate-spin (IS) state with active e_g and t_{2g} orbital degrees of freedom (*S*=1), and high-spin (HS) state with active t_{2g} orbital degree of freedom (*S*=2). Although the ground state is a nonmagnetic phase with LS-state in the bulk form as shown in Fig. 2(a), it has been reported that spontaneous magnetization is observed in the epitaxial thin film of $LaCoO_3$ while keeping its insulating nature [1, 2]. Several models have been proposed to explain the strain induced magnetization: the chemically inhomogeneous state including ferromagnetic metallic patches originating from unintentionally doped carriers or the ferromagnetism mediated by the orbital ordering. However, to the best of our knowledge, there is no experimental report exploring the microscopic spin-orbital structure for this enigmatic magnetic phase. Here we investigated the spin-orbital state for the epitaxial thin film of $LaCoO_3$ by magnetization measurements and resonant X-ray diffraction [3].

A single crystalline film (60 nm thick) of $LaCoO_3$ was fabricated on $(LaAlO_3)_{0.3}(SrAl_{0.5}Ta_{0.5}O_3)_{0.7}$ (LSAT) substrate with (110) orientation by pulsed laser deposition. Synchrotron-radiation X-ray diffraction was performed to detect the fundamental and superlattice reflections at BL-3A and BL-4C, Photon Factory of KEK, Japan.

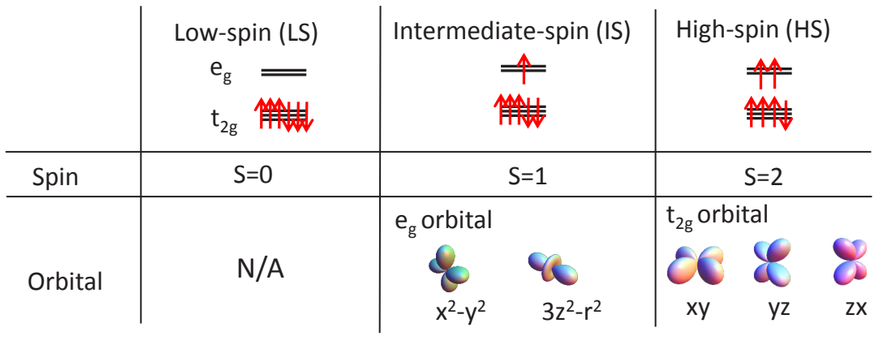

Figure 1: The spin state variability of Co^{3+}-ion. The schematic of t_{2g} orbitals for the IS-state is omitted for clarity.

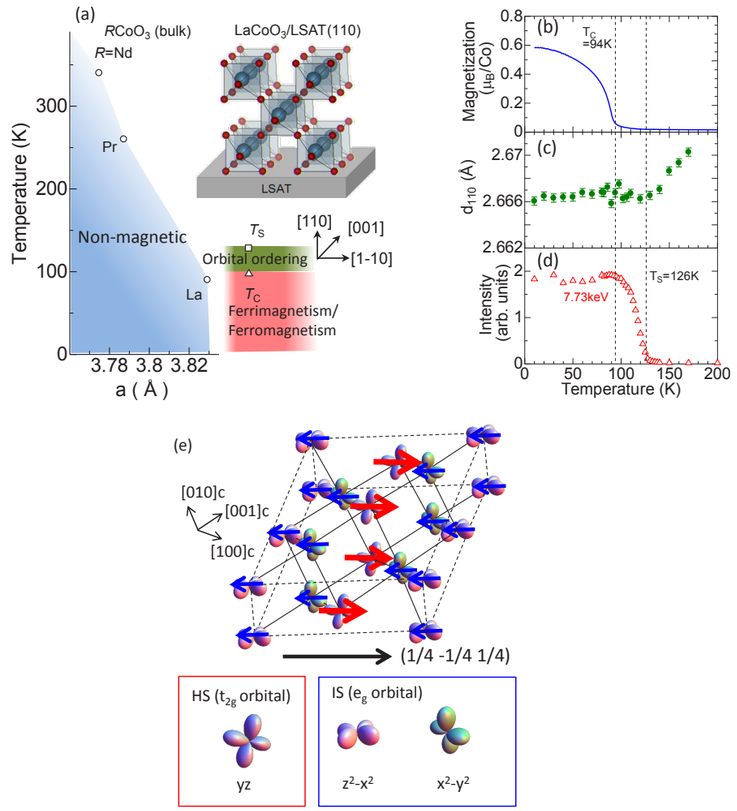

Figure 2: (a) Electronic phase diagram of $LaCoO_3$. Temperature dependence of (b) magnetization, (c) out-of-plane lattice constant and (d) intensity of superlattice reflection at (1/4 -1/4 1/4). (e) Schematic view of possible spin/orbital ordered structure. Red (blue) arrows denote the spins of HS-state (IS-state).

Figure 2(b) shows the temperature dependence of magnetization. Magnetization increases at T_C=94 K and the spontaneous magnetization is about 0.6μ_B/Co at 10 K. Figure 2(c) shows the temperature dependence of the out-of-plane lattice constant (d_{110}). As the temperature is lowered, d_{110} steeply decreases down to 126 K and shows minimal temperature dependence below 126 K. Moreover, we identified a superlattice reflection characterized by the propagation vector q = (1/4, -1/4, 1/4) below 126 K. The intensity gradually increases below 126 K and nearly saturates below T_C [Fig. 2(d)].

These results point to the existence of a structural phase transition at 126 K (T_S), which quadruples the unit cell of pseudo-cubic setting along the [100], [010] and [001] axes. On the basis of the resonant X-ray scattering at Co *K*-edge, we attributed this structural phase transition to the ordering of Co-3*d* orbital in the IS- or HS-state. Figure 2(e) shows one plausible model of spin-orbital ordering; the spin and orbital alignment is viewed as the stacking of two-dimensional sheets of IS- and HS-state sites in order of IS-IS-HS-IS with dz^2-x^2 - dx^2-y^2 - dyz - dx^2-y^2 … orbital configuration along the [1 -1 1] direction. This model is also consistent with the observed net magnetization and result of resonant soft X-ray diffraction [4].

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BEAMLINES

BL-3A and BL-4C

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