Direct evidence of Co-3*d* orbital change associated with spin crossover in $LaCoO_3$ obtained by X-ray Compton scattering

Trivalent Co oxides exhibit exotic physical and chemical properties, which are attributed to the multiple degrees of freedom on the spin, orbital and lattice arising from the $3d^6$ electronic configuration of Co^{3+}. One of the examples, $LaCoO_3$, has been attracting widespread interest from researchers because of its unusual spin crossover phenomena. The substance shows broad magnetic anomalies at around 100 and 500 K [1]. The magnetic anomaly at around 500 K is accompanied by an insulator-to-metal transition (IMT). This phenomenon is considered to be the temperature-induced spin crossover from the nonmagnetic low-spin (LS) ground state to magnetic excited states on the basis of the ligand-field theory premising the local Co-3*d* under a six-coordinated crystalline electric field. Despite the decades of research history and the extensive efforts of researchers, there is still controversy as to what the magnetic excited state induced around 100 K is: intermediate spin (IS) with $S = 1$ or high spin (HS) with $S = 2$. The IS state, which has one degree of freedom on e_g orbitals, is strongly supported by experiments exhibiting Jahn-Teller distortion and/or fluctuation, although an IS first excited state is contradictory to ligand-field theory. Several pieces of spectroscopic evidence support the HS state, which is inconsistent with the magnitude of the measured magnetization and the ferromagnetic correlation among Co-spins revealed by neutron scattering experiments. Thus, neither spin-state model can comprehensively explain all the important experimental findings, leaving us with unsolved riddles and controversy. Very recently, experimental results suggesting the collective character of spin crossover and the necessity of the models to take into account a nonlocal electronic structure have been suggested. Therefore, detailed experimental research on the electron-orbital states of Co-3*d* responsible for the spin crossover is desirable for understanding the spin crossover phenomena of $LaCoO_3$.

To investigate the characteristics of Co-3*d* electron-orbital states in $LaCoO_3$, such as the symmetry and distribution, we have conducted X-ray Compton scattering experiments using SPring-8 **BL08W** [2,3]. The X-ray Compton scattering experiments enable the imaging of the electron density distribution in the momentum space. The technique is bulk-sensitive and measurements can be obtained at high temperatures and under high magnetic fields, which are advantages over angle-resolved photoemission spectroscopy (ARPES). The Compton profiles $J(p_z)$ obtained by Compton scattering experiments reflect the projection of the three-dimensional electron momentum density $\rho(p_x, p_y, p_z)$ onto the z axis [4], which lies along the scattering vector

$$J(p_z) = \iint \rho(p_x, p_y, p_z)\, dp_x dp_y \quad (1)$$

The electron momentum density (EMD) can be reconstructed from $J(p_z)$ measured along several crystallographic directions [4]. Comparison of EMDs below and above the temperature of the spin crossover of $LaCoO_3$ reveal the Co-3*d* electron-orbital states responsible for its spin crossover phenomena.

Figure 1(a) shows the reconstructed difference 2D-EMD between 10 and 270 K across the 100 K spin crossover. The experiments across the 500 K spin crossover also yielded a similar result. These findings

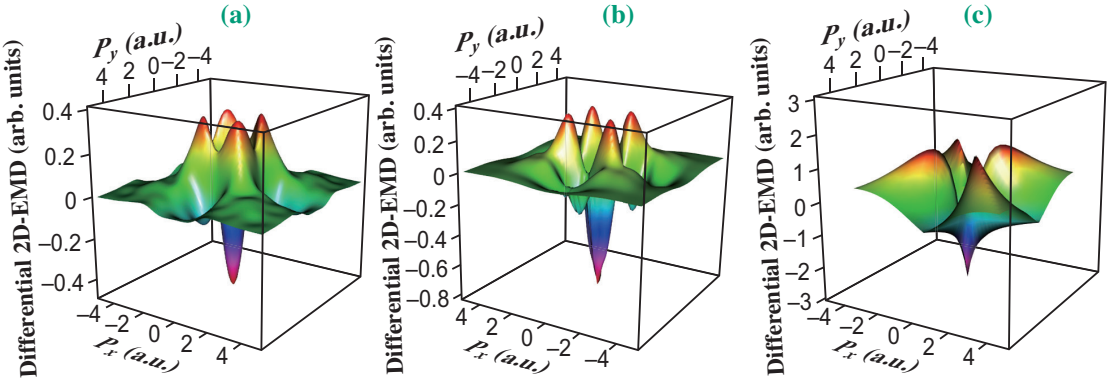

Fig. 1. Aerial views of the difference two-dimensional electron momentum density (2*d*-EMD) of Co-3*d* in $LaCoO_3$ between 10 and 270 K for **(a)** measured and **(b)** calculated molecular orbitals (MO) and **(c)** calculated atomic orbitals (Atom).

unambiguously demonstrate that the symmetry change due to electron transfer between t_{2g} and e_g orbitals is responsible for both the spin crossovers at around 100 and 500 K [2,3].

As shown in Fig. 2, a difference $J(p_z)$ increases with increasing temperature, showing that a larger number of electrons are excited to e_g orbitals at higher temperatures. The magnitude of t_{2g}-e_g electron transfer can be estimated from the area intensity of difference $J(p_z)$. Figure 3 shows the temperature dependence of the area intensity of the difference $J(p_z)$. Below 300 K, a thermal-activation-like increment with increasing temperature was observed. On the other hand, a steep increment is shown at around 500 K, suggesting the cooperative character of the 500 K spin crossover [3].

The shape of $J(p_z)$ and the 2D-EMD also provide important information. The difference $J(p_z)$ shown in Fig. 2 exhibits an oscillation at approximately p_z = 2–4 atomic units (a.u.). The oscillation is characteristic of the molecular orbitals (MO) constructed by the hybridization of Co-e_g and O-2p [2,3]. The calculated 2D-EMD and the difference $J(p_z)$ are reproduced much better for the MO than for localized atomic orbitals (Atom), as shown in Figs. 1 and 2. The oscillatory behavior in the difference $J(p_z)$, which occurs above 100 K (not shown), develops with increasing temperature and becomes very prominent above 500 K (see Fig. 2). This finding indicates further development of the MO formation resulting from the progress of hybridization between Co-e_g and O-2p through the 500 K spin crossover, which might be related to the itineracy of the electrons above the IMT.

The present Compton scattering experiments demonstrate that the MO resulting from covalent bonding between Co-3d and O-2p plays an important role in the spin crossover of $LaCoO_3$. This finding strongly indicates a collective character of the spin crossover phenomena in $LaCoO_3$; i.e., the nonlocal electron-orbital states are essential for the spin crossover phenomena. Detailed theoretical analyses, such as the first-principles calculations of MO, are indispensable for further progress in the research of the spin crossover phenomena in this substance.

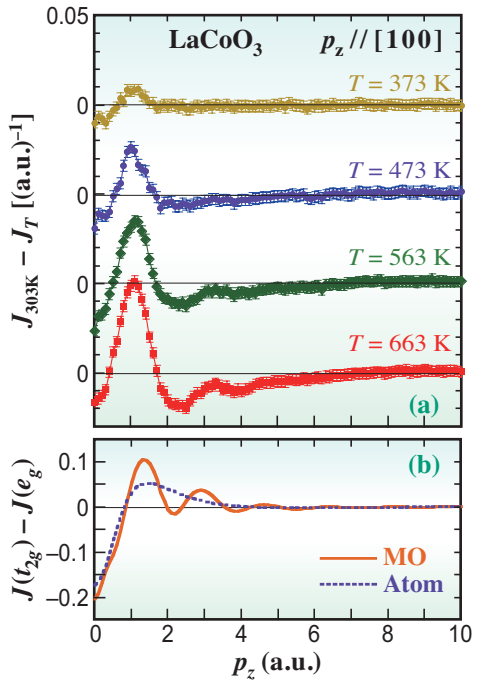

Fig. 2. **(a)** Temperature dependence of the difference Compton profiles ($J_{303\,K}$ - J_T ; T = 373 – 663 K) for $[100]_c$ direction of the pseudocubic unit cell, along with **(b)** the calculated difference Compton profiles for molecular orbitals (MO) and localized atomic orbitals (Atom).

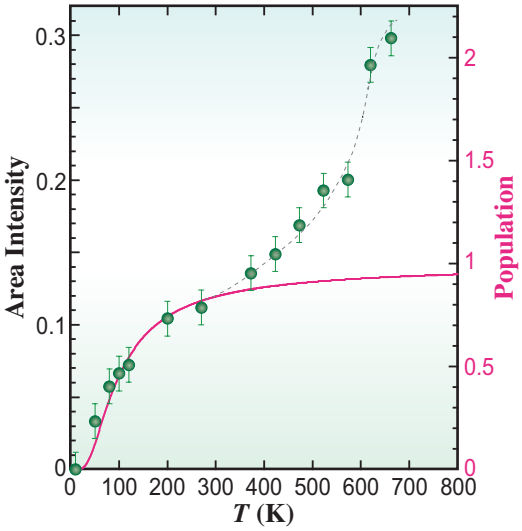

Fig. 3. Temperature dependence of the area intensity of the difference Compton profiles.

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