

LaCoO₃: A Mixed Spin-State Unusual Paramagnet

Using temperature-dependent bulk-sensitive hard X-ray photoelectron and soft X-ray absorption spectroscopies from 80 to 650 K, it is shown that LaCoO₃ transforms from a low-spin insulator to a mixed-spin-state bad metal.

LaCoO₃ has long been considered a prototype of the spin-state transition seen in several transition-metal compounds. It is known to exhibit a paramagnetic insulating state at low temperatures, undergoing an insulator-to-metal transition at around 450–550 K. However, its temperature-dependent electronic structure has remained an open question for more than 50 years. Now, in an international collaboration of researchers from Germany, Japan, and Taiwan, this long-standing question has been carefully answered using the techniques of bulk-sensitive hard X-ray photoelectron spectroscopy (HAXPES) and soft X-ray absorption spectroscopy (XAS) carried out as a function of temperature (T) across the insulator-to-metal transition.¹ In combination with full atomic-multiplet configuration-interaction cluster model charge-transfer calculations, the authors could clearly show that the low temperature insulating nearly pure (90%) low-spin (LS) t_{2g}^6 state transforms into a mixed spin-state bad metal with gradually increasing high-spin (HS) $t_{2g}^4e_g^2$ state admixture (Fig. 1), thus clarifying the electronic structure of this unusual perovskite oxide.

The authors first carried out bulk-sensitive T-dependent HAXPES at the Max-Planck-NSRRC HAXPES endstation at the Taiwan undulator beamline SP 12U1 at SPring-8, Japan. Figure 2 shows the low-T (80 K) and high-T (650 K) Co 2p core level HAXPES spectra compared with full-multiplet configuration-interaction cluster calculations of the LS and HS Co 2p photoemission spectra of LaCoO₃. The low-T (80 K) experimental spectrum was successfully reproduced as a sum of the calculated spectra consisting of 90% LS and 10% HS states. Furthermore, the high-T (650 K) experimental spectrum was successfully reproduced as a sum of the calculated spectra consisting of 50% LS and 50% HS states.

Next, the authors obtained T-dependent valence band spectra using HAXPES, as shown in Fig. 3 (see next page), top left panel. From this, it is seen that the Co 3d states at a 0.8 eV binding energy is systematically suppressed with increasing temperature. Interestingly, the intensity at the Fermi level remains small at all temperatures, including at 650 K, where LaCoO₃ is deep in the metallic phase. This indicates that LaCoO₃ should be classified as a bad metal at high temperatures. As shown in the bottom left panel, the configuration-interaction calculations of the Co 3d photoemission can be suitably reproduced using the same electronic parameters.

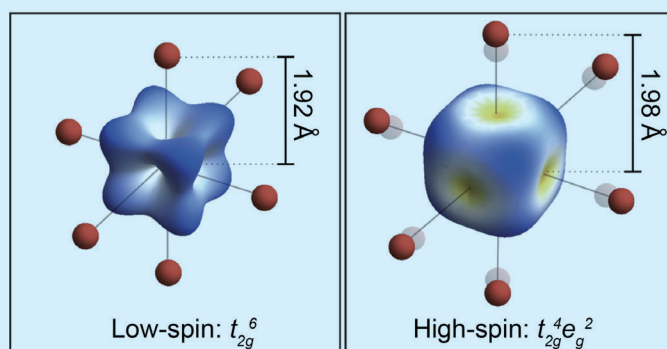


Fig. 1: Local ionic Co³⁺ 3d charge density in the CoO₆ octahedron: LS with the t_{2g}^6 configuration (left) and HS with the $t_{2g}^4e_g^2$ (right) configuration. The electron density for t_{2g} is shown in blue, and that for e_g is shown in yellow. The red dots indicate the positions of the oxygens (faint red dots on the right denote the LS positions). [Reproduced from Ref. 1]

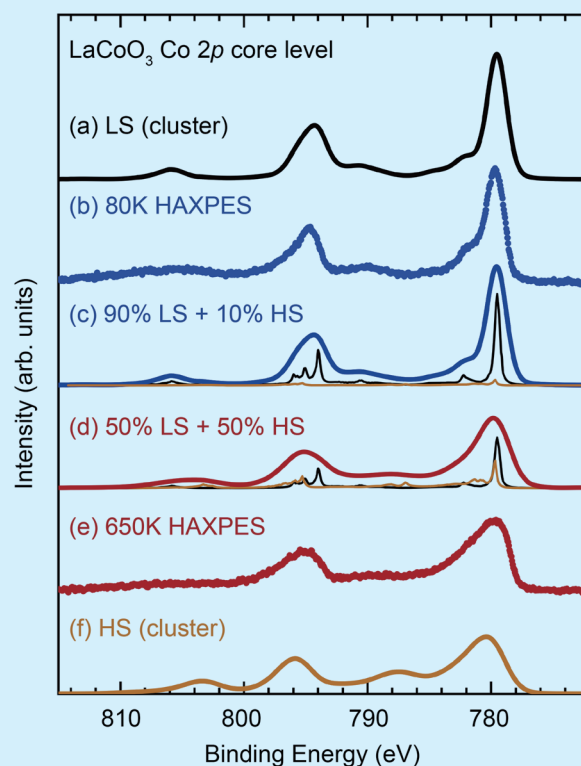


Fig. 2: Full-multiplet configuration-interaction cluster calculations of the (a) LS and (f) HS Co 2p photoemission spectra of LaCoO₃. Co 2p HAXPES experimental spectra at (b) 80 K (e) 650 K. Theoretical simulation of the Co 2p spectra at (c) 80 K and (d) 650 K using an incoherent sum of the calculated LS and HS spectra with a ratio of 90% LS and 10% HS or 50% LS and 50% HS, respectively. The spectra are normalized to the integrated total intensity. The thin lines represent calculations with reduced broadening of the LS and HS components, with overall intensity divided by a factor of 5 for clarity. [Reproduced from Ref. 1]

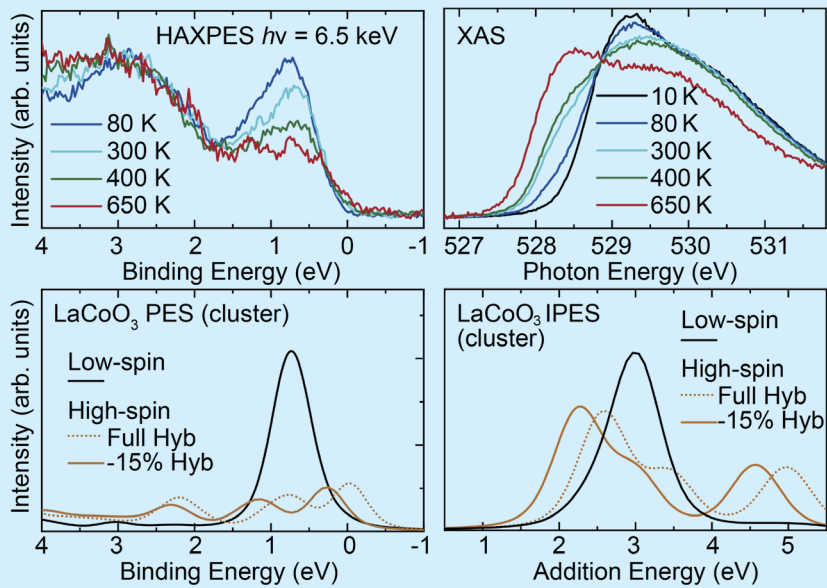


Fig. 3: The valence band HAXPES (top left) and the pre-edge region of the XAS (top right) spectra of LaCoO₃ at different temperatures. Bottom: Configuration-interaction calculations of the Co 3d photoemission (PES, bottom left) and inverse photoemission spectra (IPES, bottom right) using $10Dq = 0.75$ eV for the LS state and 0.40 eV for the HS state. The HS calculations are performed with (solid line) and without (dotted line) the hybridization reduction to model the presence or absence, respectively, of local lattice relaxations. [Reproduced from Ref. 1]

Finally, as shown in the top right panel, the authors carried out T-dependent XAS at the Dragon beamline **TLS 11A1** at the NSRRC in Taiwan. The pre-edge region spectral features of the O-K XAS from 527 to 531 eV are due to transitions from the O 1s core level to the O 2p orbitals that are mixed with the unoccupied Co 3d t_{2g} and e_g states. A clear strong transfer of spectral weight is observed from the higher-energy structure at around 529.3 eV to the lower-energy structure at around 528.4 eV on increasing temperature from 10 to 650 K. These changes are due to a spin-state transition and can be reproduced suitably by configuration-interaction calculations of the inverse photoemission spectra, as shown in the bottom right panel. The authors conclude that at low temperatures, the LS Co³⁺ ion has its t_{2g} shell completely occupied,² and only transitions to the higher-lying empty e_g states are possible. In contrast, at higher temperatures, with a portion of the Co ions in the HS state,² the t_{2g} states become partially unoccupied, thereby allowing transitions to the lower-lying t_{2g} states, and this leads to the appearance of the 528.4 eV structure.

In summary, the T-dependent photoemission and X-ray absorption spectra for bulk LaCoO₃ exhibit clear changes across the gradual spin-state and insulator-to-metal transitions. Reduction of the band gap was observed with increasing temperature, but the near-Fermi-level intensity remained small even in the metallic phase. The spectra could be explained quantitatively in terms of the sums of the LS and HS Co³⁺ spectra. (Reported by Ashish Chainani)

This report features the work of Liu-Hao Tjeng and his collaborators published in Phys. Rev. X 13, 011037 (2023).

TLS 11A1 (Dragon) MCD, XAS

SP 12U1 HAXPES

- HAXPES, XAS
- Materials Science, Condensed-matter Physics

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