

# Valence State and Spin States and Spin State Transition of Co in $\text{LaCo}_{0.5}\text{Rh}_{0.5}\text{O}_3$

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## Abstract

We have observed that the *Rh substitution* for Co in  $\text{LaCo}_{0.5}\text{Rh}_{0.5}\text{O}_3$  leads to the spectral feature at the Co- $L_{2,3}$  absorption edge taken at 300 K similar to that in  $\text{LaCoO}_3$  taken at 650 K, in which the spin state of magnetic  $\text{Co}^{3+}$  ion is controversially discussed in the past decades and can be easily clarified by studying  $\text{LaCo}_{0.5}\text{Rh}_{0.5}\text{O}_3$  without worrying oxygen loss induced at high temperature. Our combined experimental and theoretical x-ray absorption spectroscopy (XAS) at the Co- $L_{2,3}$  and the experimental Rh- $L_{3,2}$  edges indicated a nearly 1:1 mixture of high spin (HS) and low spin (LS)  $\text{Co}^{3+}(3d^6)$  and a LS  $\text{Rh}^{3+}(4d^6)$  in contrast to a  $\text{Co}^{2+}/\text{Rh}^{4+}$  state found in  $\text{Ca}_3\text{CoRhO}_6$  at room temperature. Upon cooling only a small part of HS  $\text{Co}^{3+}$  ions was converted to a LS state until 10 K in  $\text{LaCo}_{0.5}\text{Rh}_{0.5}\text{O}_3$ . The Co  $K\beta$  x-ray emission spectra revealed a gradual spin state transition from a mixed LS/HS at ambient pressure to a complete LS state of  $\text{Co}^{3+}$  ion up to 14 GPa. The theoretical and experimental intensity ratio  $I(L_3)/I(L_2)$  on the Co- $L_{2,3}$  edges and a comparison between the difference spectrum of  $K\beta$  x-ray emission of  $\text{LaCo}_{0.5}\text{Rh}_{0.5}\text{O}_3$  taken at ambient pressure (AP) and 14 GPa and that of  $\text{S}_2\text{CoRuO}_6$  (SCRO) taken at AP and 39.6 GPa exclude the intermediate spin state of  $\text{Co}^{3+}$  in  $\text{LaCo}_{0.5}\text{Rh}_{0.5}\text{O}_3$ .

**Keywords:** x-ray absorption spectroscopy, spin state transition, high pressure