Co K-edge XANES and spin-state transition of $RCoO_3$ (R = La, Eu)

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Abstract

Co K-edge X-ray absorption near-edge spectra (XANES) and magnetic studies for the rhombohedral $LaCoO_3$ with low-spin (LS) state to intermediate-spin (IS) state transition $T_s \simeq 105$ K and orthorhombic $EuCoO_3$ ($T_s \simeq 300$ K) are reported. The small pre-edge feature observed is from $1s$-$3d$ dipole transition, which is weakly allowed through the hybridization of Co $4p$ states with $3d$ states of neighboring Co atoms. For $LaCoO_3$ at 300 K, pre-edge can be fitted using three peaks with energy separation P_2 - P_1 = 2.0 eV and P_3 - P_2 = 1.5 eV. Since the thermally excited IS state is a mixed $t_{2g}^5 e_g^1$ and $d^7\underline{L}$ ($t_{2g}^6 e_g^1$ or $t_{2g}^5 e_g^2$), with almost filled $t_{2g\uparrow}$ states, so the three peaks P_1, P_2, P_3 are probably corresponding to unfilled $t_{2g\downarrow}$, $e_{g\uparrow}$ and $e_{g\downarrow}$ states, respectively.

Key words: spin state transition; XANES

Rhombohedral $LaCoO_3$ ($R\bar{3}c$) with trivalent Co^{3+} ($3d^6$) is a nonmagnetic Mott insulator at low temperature which undergoes a thermally induced spin-state transition to a paramagnetic state with $T_s \simeq$ 90-100 K and a metal-insulator transition above 500 K [1-8]. It remains controversial that whether the spin-state transition is from a low-spin (LS: t_{2g}^6, S =0) state to an intermediate-spin (IS: $t_{2g}^5 e_g^1$, S = 1) state or to a high-spin (HS: $t_{2g}^4 e_g^2$, S = 2) state. The LDA+U calculation shows that IS state is energetically comparable to LS state, but much more stabilized than HS state due to the larger Co-O d-p hybridization [1]. The X-ray photoemission and absorption studies indicate that the ground state is a Co^{III} LS state with heavily mixed d^6 and $d^7\underline{L}$ ($t_{2g}^6 e_g^1$ with ligand hole) character due to strong d-p hybridization and the spin-state transition is a gradual LS-IS transition [2]. The infrared studies indicate a local lattice distortion during the LS-IS transition due to dynamical Jahn-Teller effect [3].

For orthorhombic rare earth $RCoO_3$ (Pbnm) compounds, possible $T_s \simeq 220$ K for $PrCoO_3$ and $\simeq 275$ K for $NdCoO_3$ are reported [6]. Since various reported data are confused by magnetic rare earth R^{3+} signal [5,6], in order to identify the true spin-state transition in orthorhombic phase, $EuCoO_3$ is chosen as the best candidate with nonmagnetic Eu^{3+} ground stare (J = 0) [8].

The samples $RCoO_{3+\delta}$ (R = La, Eu) were synthesized by standard solid-state reaction. Sintered pellets were annealed in O_2, air or Ar to check the variation of oxygen content. Final oxygen content parameter $\delta \simeq 0$ was crosschecked by comparing the X-ray diffraction, magnetic susceptibility and XANES data [8]. The structural studies indicate that there is no interstitial oxygen site. With fully occupied oxygen sublattice and R and Co vacancies, the correct composition is $R_zCo_zO_3$ with $z = 3/(3+\delta)$, and maximum formula unit volume is achieved at the stoichiometric $RCoO_3$. The maximum formula unit volume of 55.91 $\AA^3$ for rhombohedral $LaCoO_{3+\delta}$ and 52.83 $\AA^3$ for orthorhombic $EuCoO_{3+\delta}$ derived from X-ray diffraction studies indicate that samples prepared are very close to the stoichiometric 113 ratio ($\delta \simeq 0$) with Co^{3+} [8].

Molar magnetic susceptibility χ_m(T) in 3-T zero-field-cooled (ZFC) for $LaCoO_3$ and $EuCoO_3$ are shown in Fig. 1. The susceptibility shows similar behavior as previously reported data and decreases abruptly from $T_s \simeq 105$ K for $LaCoO_3$, although accompanying with

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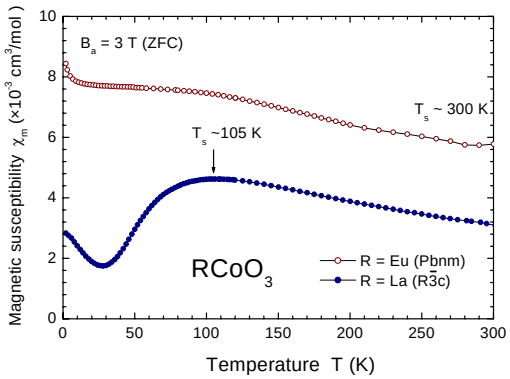

Fig. 1. Molar magnetic susceptibility χ_m(T) in 3-T field (ZFC mode) for rhombohedral $LaCoO_3$ and orthorhombic $EuCoO_3$.

a small Curie-Weiss-like contribution from magnetic impurities below 30 K with small $\chi_m(2\ \mathrm{K}) = 2.9 \times 10^{-3}$ cm^3/mol [2,3]. For $EuCoO_3$, low susceptibility value in all temperature range indicates a T_s near or above 300 K which is masked by the magnetic signal of Eu^{3+} excited state (J = 1) [8].

The Co K-edge XANES spectra for $RCoO_3$ (R = La, Eu) are shown in Fig. 2. The energy is calibrated by a Co metal foil with threshold edge energy of E_0 = 7709 eV. The E_0 for two standards CoO (Co^{2+}) and Co_2O_3 (Co^{3+}) indicates a substantial shift of E_0 with increasing Co formal valence. Almost identical E_0 for La and Eu samples indicates that they are very close to the stoichiometric composition with Co^{3+}.

The K-edge XANES is sharp with a long, low energy tail. The main edge is attributed to 1s-4p dipole transition to Co 4p states. Since the crystal structure of the $RCoO_3$ system is identical to the $LaMnO_{3+\delta}$ system (Pbnm for $\delta \simeq 0$ and R$\bar{3}$c for $\delta > 0$). The shape

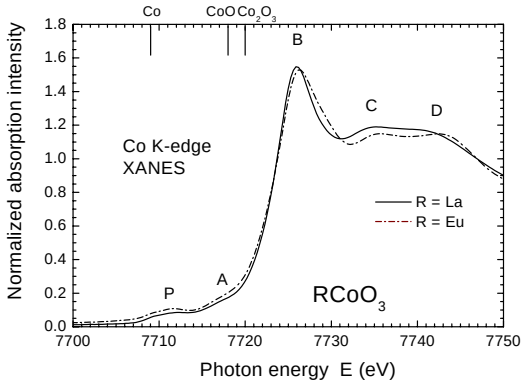

Fig. 2. Co K-edge XANES for $RCoO_3$ (R = La, Eu). The threshold edge energy of two standards (CoO, Co_2O_3) and Co metal foil are indicated.

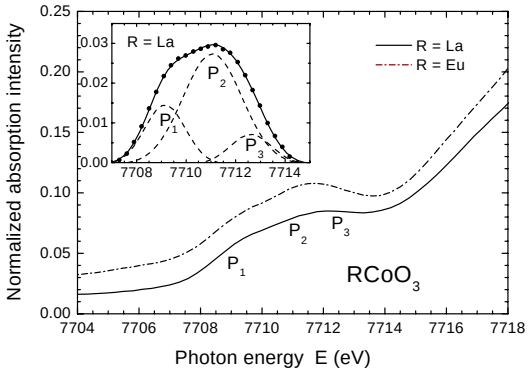

Fig. 3. Low intensity pre-edge region of Co K-edge XANES for $RCoO_3$ (R = La, Eu). The pre-edge P can be fitted with three peaks P_1, P_2 and P_3 (inset for $LaCoO_3$).

of the edge with features labeled as A, B, C, D can be explained by the 4p partial density of states, broaden by the finite lifetime of 1s core hole. The Co 4p states, like Mn 4p state, are highly delocalized and extend over several Co atoms. The observed small pre-edge feature P is corresponding to 1s-3d dipole transition, which is weakly allowed through the hybridization of 4p states with 3d states of neighboring Co atoms.

Fig. 3 shows the low intensity pre-edge P feature for $RCoO_3$ (R = La, Eu). For $LaCoO_3$ at 300 K, pre-edge P can be fitted with three peaks P_1, P_2, P_3 after subtracting the smooth background, with energy separation P_2 - P_1 = 2.0 eV and P_3 - P_2 = 1.5 eV. Since the ground state is a Co^{III} LS state with heavily mixed d^6 and $d^7\underline{L}$ ($t_{2g}^6 e_g^1$), the thermally excited IS state at 300 K may be a mixed $t_{2g}^5 e_g^1$ and $d^7\underline{L}$ ($t_{2g}^6 e_g^1$ or $t_{2g}^5 e_g^2$), with almost filled $t_{2g\uparrow}$ states. This indicates that the allowed 1s-3d dipole transition is into unfilled $t_{2g\downarrow}$ and e_g states. The three peaks P_1, P_2, P_3 are probably corresponding to unfilled $t_{2g\downarrow}$, $e_{g\uparrow}$ and $e_{g\downarrow}$ states, respectively [8].

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