

Electronic structure of Co ions in Sr-substituted LaCoO_3

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Introduction

In the solid solution system of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$, the electronic structures of Co 3d electrons become complicated, having two or more different spin states such as low-spin (LS), intermediate spin (IS, ${}^3T_1; t_{2g}^5 e_g^1$) and high-spin (HS) states. When La^{3+} in LaCoO_3 is replaced by Sr^{2+} , the constituent Co^{3+} ion changes to Co^{4+} with doping of a hole. The existence of long-range ferromagnetic order has been reported for the samples of $0.2 \leq x \leq 1$ in magnetization measurements and X-ray and neutron diffraction studies [1-3]. As increasing Sr contents, the superexchange interaction of $\text{Co}^{3+}\text{-O-Co}^{4+}$ becomes more dominant and stronger than the interactions of $\text{Co}^{4+}\text{-O-Co}^{4+}$ and $\text{Co}^{3+}\text{-O-Co}^{3+}$, where Co^{3+} and Co^{4+} ions are stable in the HS and LS states, respectively [4].

A site-selective and valence-selective XMCD study is required for the Co K absorption edge to elucidate the relationship between magnetic property and crystal structure in terms of the hybridization between the 3d and 4p states through the ligand 2p state. In this study, we also calculate the electronic structures of both ground and 1s core-hole states for the systems of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$, by using the discrete-variation Hartree-Fock-Slater method.

Experimental

XANES and XMCD experiments were carried out on the BL-3A. The horizontally polarized white X-rays were monochromatized by the Si(111) double-crystal monochromator. The beam size limited by a slit was $3^{(H)} \times 2^{(V)}$ mm² at the sample position. The intensity after transmitting through the sample was measured with 300 mm ionization chamber which was filled with 75% N_2 + 25% Ar gas. The difference in the absorption coefficients for right- and left-circularly polarized X-rays was measured with spins parallel and antiparallel to the direction of light travel. The incident beam was guided into a synthetic single crystal of (001) diamond with a thickness of 0.492 mm in order to produce circularly polarized X-rays. A standard transmission setup was used with the Faraday arrangement, where X-rays irradiates the sample through a pair of pinholes in rare-earth magnets in a magnetic field of 0.4 T. The diffraction studies were carried out on the BL-10A.

Results and discussion

A negative XMCD peak B was clearly observed for pure LaCoO_3 at $E = 7.719$ keV within the threshold region of the main edge. A positive XMCD peak C appeared at $E = 7.723$ keV by Sr substitution of La in

LaCoO_3 ($x \geq 0.2$). A negative XMCD peak A was also observed at the pre-edge, which can be explained as the hybridization with the neighboring Co^{4+} in the dipole transition. The dispersion-type XMCD signals at the main edge may be rationalized with the hypothetical double-exchange interaction between Co^{3+} and Co^{4+} . The first-principles calculations reproduced well the experimental spectra of X-ray magnetic circular dichroism (XMCD) at the Co K-absorption edge, where a hybridization of Co 3d and O 2p stabilizes a magnetic state of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$.

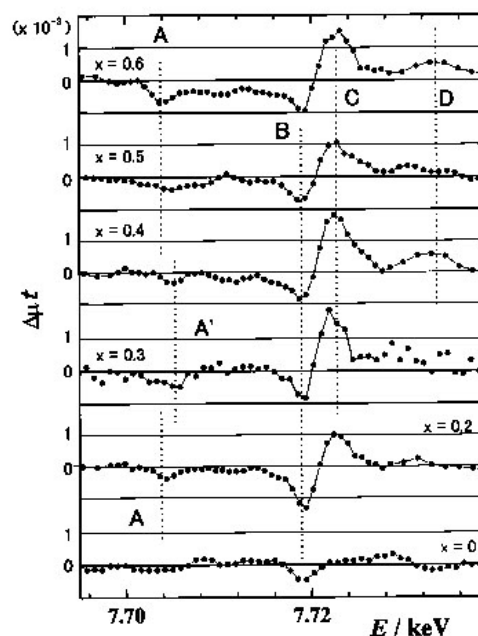


Fig. 1: XMCD spectra of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ ($0 \leq x \leq 0.6$) at the Co K edge.

References

- [1] G.H. Jonker, J.H. Van Santen, Physica 19, 120 (1953).
- [2] P. Ganguly et al., J. Phys. Cond. Mat. 6, 533 (1994).
- [3] V.G. Sathe et al., J. Phys.:Cond. Mat. 8, 3889 (1996).
- [4] H. Taguchi et al., Materials Res. Bull. 13, 1225 (1978).

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