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X-ray magnetic circular dichroism of $La_{1-x}Ca_xCoO_3$ ($x \leq 0.35$)

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Introduction

The compound $LaCoO_3$ is of particular interest because it has a spin-state transition where a nonmagnetic insulator broadly transforms into a paramagnetic phase around 50 K and a metallic phase around 500 K. Magnetic susceptibility has a maximum broad peak around 100 K and is much smaller than calculated one on the assumption of low-spin ground and high-spin excited states [1]. With the occupied O 2*p* and the unoccupied 3*d*(e_g) states, the spin-state transition has highly mixed characteristics between Mott-Hubbard and charge transfer types. The paramagnetic behavior above 100 K is attributed to the intermediate-spin state ($t_{2g}^5e_g^1$; S = 1) [2,3].

The influence of charge carrier doping to $LaCoO_3$ can be observed when trivalent La^{3+} (r_{IR} = 1.36 Å) coordinated by twelve oxygen ions is partially substituted by divalent alkali-earth metals of remarkably different ionic radii r_{IR} such as Ca^{2+} (r_{IR} = 1.34 Å), Sr^{2+} (r_{IR} = 1.44 Å) or Ba^{2+} (r_{IR} = 1.61 Å). In $La_{1-x}M_xCoO_3$ doping with larger Sr^{2+} and Ba^{2+} yields spin glass behavior ($x \leq 0.18$; $x \leq 0.20$) and ferromagnetic order ($0.18 < x \leq 0.30$; $0.20 < x \leq 0.30$) at low temperature, respectively, while doping with Ca^{2+} shows only ferromagnetic order for $x \leq 0.30$ [4]. It is found that for Sr doping the ferromagnetic-order temperature is the highest and the resistivity is the lowest [4]. Non-dependence on the ionic radii between Sr and Ca remains to be clarified. Therefore, in this report we present a site- and valence-selective study of X-ray magnetic circular dichroism (XMCD) at the Co *K* absorption edge to elucidate the relationship between magnetic property and crystal structure.

Experimental

XANES and XMCD experiments were carried out on the BL-6C. The intensity after transmitting through the sample was measured with ionization chambers, where front chamber was 50 mm in length and filled with pure N_2, while rear chamber was 300 mm and filled with 75% N_2 + 25% Ar gas. In XMCD measurements, the absorption difference between right-circularly and left-circularly polarized X-rays was measured in connection with spin parallel and antiparallel in the direction of X-ray travel. 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 circularly-polarized beam was produced by a phase retarder, where a synthetic single crystal of diamond (001) was set to have the scattering plane inclined by 45° from the vertical plane and to be close to the 111 Bragg condition in the asymmetric Laue case.

Results and discussion

Figure 1 shows XMCD spectra of $La_{1-x}Ca_xCoO_3$ ($x \leq 0.35$) measured at the Co *K* absorption edge, which is compared with those of $La_{1-x}Sr_xCoO_3$. A negative XMCD peak was clearly observed at E = 7.719 keV within the threshold region of the main edge for $La_{1-x}Ca_xCoO_3$, suggesting the existence of the intermediate-spin state of Co^{3+}. A positive XMCD peak appeared at E = 7.723 keV by Ca substitution of La in $LaCoO_3$. The dispersion-type XMCD signals at the main edge may be rationalized with the double-exchange interaction between Co^{3+} and Co^{4+}, where a hybridization of Co 3*d* and O 2*p* can stabilize a magnetic state of $La_{1-x}Ca_xCoO_3$.

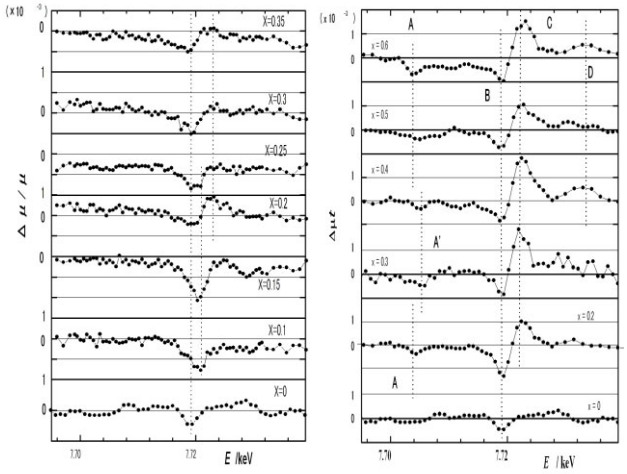

Fig. 1: XMCD spectra of $La_{1-x}Ca_xCoO_3$ (left) and $La_{1-x}Sr_xCoO_3$ (right) at the Co *K* edge.

References

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