

X-ray magnetic circular dichroism of the spinel-type oxide CoV_2O_4 Yosuke Nonaka^{1,*}, Goro Shibata¹, Rui Koborinai², Keisuke Ishigami¹, Shoya Sakamoto,¹
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1 Introduction

The spinel-type oxides are suitable compounds for the precise discussion of the relationship between the orbital states and the crystal structures because of the absence of GdFeO_3 -type distortion usually present in the perovskite-type oxides. Among them, spinel-type vanadates AV_2O_4 are studied as model systems to study novel phases emerging from the orbital degrees of freedom and the geometrical spin frustration of the $V^{3+} [t_{2g}^2]$ ions.

MnV_2O_4 shows a large negative magnetostriction (contraction along the magnetic field direction) induced by anti-ferro orbital order of the V^{3+} ions accompanied by a structural phase transition at a ferrimagnetic transition temperature $T_N = 57\text{K}$ [1]. On the other hand, FeV_2O_4 shows a positive magnetostriction (elongation along the magnetic field direction). This material does not show the orbital order of the V^{3+} ions, and the positive magnetostriction is caused by the elongation of FeO_4 tetrahedra with the orbital active $\text{Fe}^{2+} [e_g^3 t_{2g}^3]$ ion [2]. CoV_2O_4 has no structural phase transition down to 4K. However, magnetostriction and its temperature-dependent sign reversal have been reported [3]. Thus, detailed studies of the spin and orbital states are required to identify the spin and orbital states of the V and Co ions in CoV_2O_4 .

In this study, we have performed x-ray absorption spectroscopy (XAS) and x-ray circular magnetic dichroism (XMCD) spectroscopy measurements on CoV_2O_4 bulk single crystals.

2 Experiment

Bulk single crystals of CoV_2O_4 were grown by the floating zone method. In order to avoid the formation of the V_2O_3 impurity phase, the compositions of the feed rod was not stoichiometric (Co : V = 1 : 2) but containing 50% excess Co relative to the stoichiometric one (Co : V = 1.5 : 2). The Co:V ratio of the synthesized single crystals was estimated to be 1.21:1.79 by induction-coupled plasma analysis.

The XAS and XMCD measurements at the Co and V $L_{2,3}$ edges were performed at the BL-16A of KEK-PF. The spectra were taken in the total electron yield mode at 29 K under a magnetic field (H) of 1.0 T. The x-ray incident angle was fixed to keep the optical axis parallel to the cubic $[111]$ direction, and the magnetic field was applied along the $[001]$, $[110]$, and $[111]$ directions (in the cubic notation)

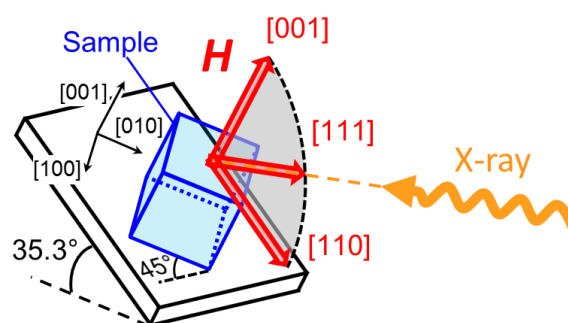


Fig. 1: Geometric arrangement in our XAS and XMCD experiment. The optical axis is parallel to the cubic $[111]$ direction.

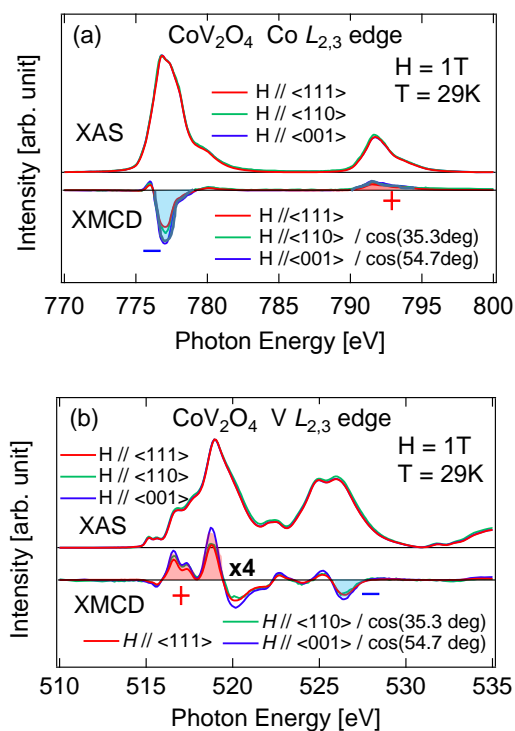


Fig. 2: XAS and XMCD spectra at the (a) Co $L_{2,3}$ and (b) V $L_{2,3}$ edges under the magnetic field of 1.0 T along the $[001]$, $[110]$, and $[111]$ directions.

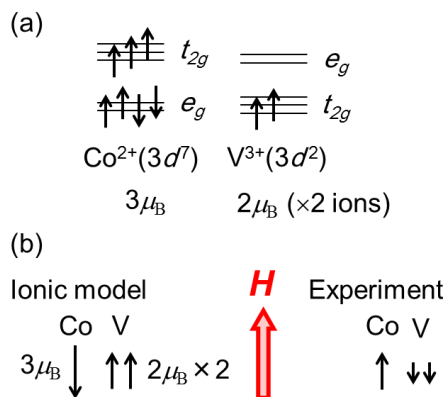


Fig. 3: Schematic pictures of electronic configurations and spin orientations. (a) Electronic configurations of the Co²⁺ ion at the tetrahedral site and the V³⁺ ion at the octahedral site. (b) Spin orientations expected from the ionic model (left) and those revealed by experiment (right).

Table 1: Parameters used in the cluster model calculations (in units of eV).

	charge transfer energy Δ	crystal field splitting $10Dq$	Slater-Koster parameter $pd\sigma$
Co ²⁺	5.6	-0.7	0.8
V ³⁺	5.0	0.9	2.5

using ‘vector magnet’ XMCD apparatus [4]. In order to obtain clean surfaces, the samples were fractured in an ultra-high vacuum.

3 Results and Discussion

Figures 2 (a) and (b) show the XAS and XMCD spectra at the Co and V $L_{2,3}$ edges. Since the x rays and the applied magnetic field were not parallel except for the case of $H//[111]$, the XMCD spectra in Fig. 2 have been divided by $\cos\theta$, where θ is the angle between the x rays and the applied field. The signs of these XMCD signals show that the magnetic moments of Co are aligned parallel to the magnetic field direction and that those of V are anti-parallel to it. This orientation of the spins are opposite to that expected from the spin moments of the ionic electronic configurations shown in Fig. 3 (a).

We have simulated the obtained XAS and XMCD spectra using the cluster model calculation. Figures 4 (a) and (b) show experimental spectra with magnetic field along the [001] direction and best-fit calculated spectra. Parameters used in the calculation are shown in Table 1. In these figures, there are differences in the relative intensities of the XMCD signals to XAS between the results of experiment and calculation. The small difference for Co- $L_{2,3}$ XMCD shown in Fig. 4 (a) is interpreted as a result of the substitution of the excess Co to the octahedral site (in the form of Co³⁺, low spin state). On the other hand, the large difference for V $L_{2,3}$ XMCD shown in Fig. 4 (b) implies spin fluctuations and/or canting of the V spins.

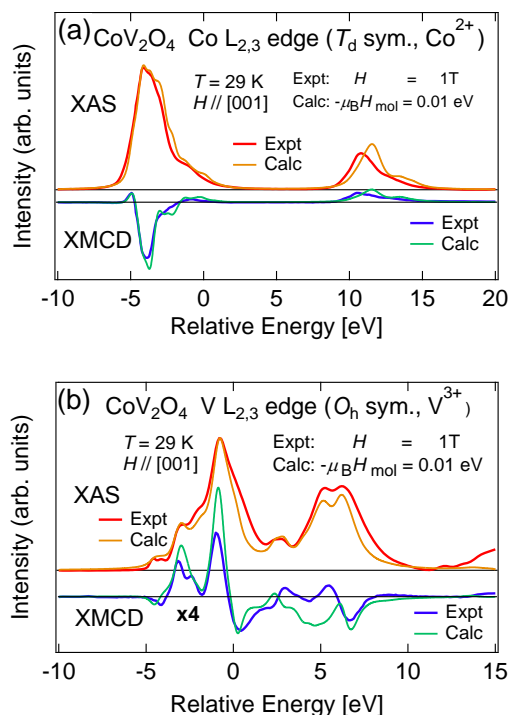


Fig. 4: Experimental and calculated XAS and XMCD spectra of CoV₂O₄ at the Co (a) and V $L_{2,3}$ (b) edges.

References

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