

Electronic and Magnetic Properties of YCrO_3 Single-crystal using X-Ray Magnetic Circular Dichroism

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1. **INTRODUCTION:** Diluted magnetic semiconductors (DMSs) have grabbed deeply the researchers' intention in their activities, in the past few years. Promising applications in spintronic, optoelectronic, and piezoelectric materials have motivated researches [1], as well as semiconductor oxide-based DMSs represent a significant interest because they become ferromagnetic when the substitution is achieved by transition metal elements. Yttrium chromite (YCrO_3) material exhibits interesting physical properties, principally the coexistence of magnetic and ferroelectric properties that allow its applications in spintronic, optoelectronic, thermistors among others being one of the most investigated bi-ferroic materials at room temperature [1,2]. electronic analysis through spectroscopic based soft x-ray absorption spectroscopy (XAS) and x-ray magnetic circular dichroism (XMCD) experiments. Looby and Katz [3] reported that the YCrO_3 crystalline structure as monoclinic, but subsequently Katz [4] suggested the possibility of an orthorhombic structure. Latter on this was confirmed by the work of Geller and Wood [5], which discovered that YCrO_3 crystallizes in a centro-symmetric perovskite orthorhombic structure with space group Pnma. Bulk YCrO_3 , where lattice parameters (Ångstrom) ($a = 5.5237$, $b = 7.5343$, $c = 5.2427$) were used, and lattice relaxation was not taken into account. Three atoms are considered; one is yttrium atom occupying site in the positions (0, 0, 0) and one chromium atom is placed in the position (1/2, 1/2, 1/2), while oxygen ions have been localized at the positions: (0, 1/2, 1/2), (1/2, 1/2, 0), and (1/2, 1/2, 0). The yttrium and chrome (3s, 4d) and the oxygen (2s, 2p) electrons were treated as part of the valence states [6].

According to Judin et al. [7] magnetism studies single crystals of YCrO_3 is antiferromagnetic, presenting a weak ferromagnetism below $T_N = 141$

K. The ferromagnetism was attributed to canted anti-ferromagnetism combined with the ferroelectricity associated to the local non-centrosymmetric around chromium ions, although to be weak effects, turning yttrium chromite an interesting bi-ferroic material from the scientific point of view. Thus, it motivated us to study the magnetic properties of YCrO_3 nanoparticles by means of synchrotron-based X-ray Absorption Spectroscopy (XAS) and X-ray Magnetic Circular Dichroism (XMCD). It is well known that XAS and XMCD are one of the most sensitive techniques for detecting the influence of local structure on ferromagnetic ions, and temperature magnetic phase transitions.

2. **EXPERIMENT:** Polycrystalline YCrO_3 powder was synthesized by a modified polymeric precursor method, which was successful applied to the synthesis of YAlO_3 and whose details are described in Ref. [8]. Stoichiometric quantities of yttrium nitrate, $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Acros Organics Co., 99.9%) and chromium nitrate $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Acros Organics Co., 99.9%) were completely dissolved in water with citric acid in 3:1 M ratio of acid to metal. Separately D-sorbitol was also water dissolved in the molar ratio of 3:2 (citric acid/D-sorbitol). Both solutions were merged in a single vessel and stirred at 80 °C, during about 12 h, to remove the water excess and to complete the chemical reactions. The product was a homogeneous and stable gel with violet coloration. The gel was dried at 250 °C for 1 h using a heating rate of 0.5 °C/min, producing a dark brown porous material. After crushed, the dried powder was submitted to an additional pyrolytic thermal treatment at 700 °C for 12 h, under N_2 flux, to remove the excess of

additives, avoiding uncontrolled firing. This procedure yielded black amorphous particles having irregular shapes, which were grinded to obtain a very fine powder using a ball mill with yttria

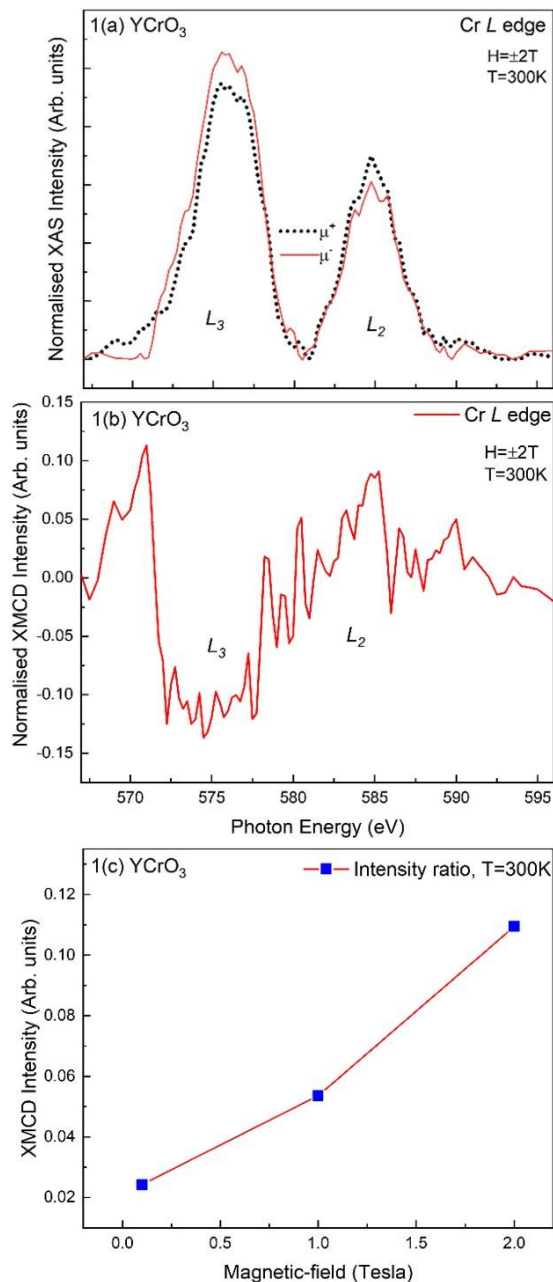


Fig 1(a) Normalised XAS spectra and Fig 1(b) Normalised XMCD spectra of Ru $L_{2,3}$ site. Fig 1(c) XMCD/XAS Intensity ratio w.r.t. applied magnetic-field $\pm 0.1T$, $\pm 1.0T$ and $\pm 2.0T$.

stabilized zirconia spheres. The last stage was the calcination of this black powder by fast heating at 1300°C for 3 h, producing single-phase YCrO_3 powders having good crystallinity. X-ray spectroscopy, scattering, and imaging experiments were performed at the variable-polarization soft x-

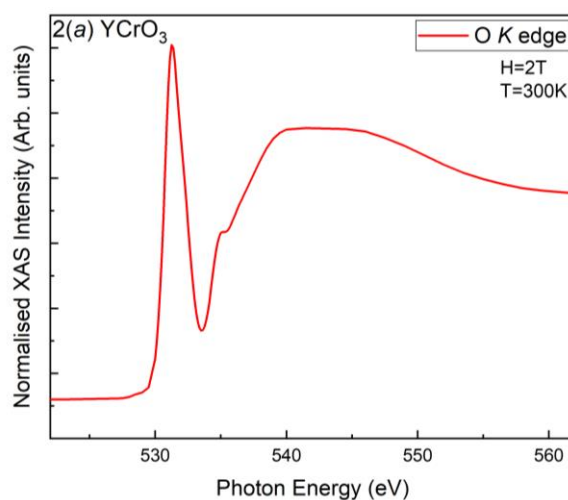


Fig 2(a) Normalised XAS spectra of O K-edge w.r.t. applied magnetic-field $\pm 2.0T$.

ray beam-line BL-16A of the Photon Factory (KEK, Japan). Experimental geometry of soft x-ray absorption (XAS) and x-ray magnetic circular dichroism (XMCD) experiments are shown in Fig. 1 and 2. The sample was placed in the vacuum chamber with a pressure of 10^{-9} Torr equipped with a 5 T superconducting magnet. XAS and XMCD signals were measured at $\pm 0.1T$, $\pm 1T$ and $\pm 2T$ varying magnetic-fields (only the data of $\pm 2T$ has been produced here) with right and left circularly polarized (RCP and LCP) x-rays having an energy resolution of 0.1 eV using the bulk-sensitive total fluorescence yield (TFY) method near Ru $M_{4,5}$ and V $L_{2,3}$ absorption edges with right and left circularly polarized (RCP and LCP) x-rays.

RESULTS AND DISCUSSIONS: The XAS spectra obtained with applied magnetic fields of +2.0 and -2.0 T are denoted by μ^+ and μ^- which represent left and right circularly polarized light, respectively as shown in Fig 1. The XMCD spectrum was recorded by taking a difference between the XAS spectra with negative and positive helicity of the circular polarized light. It is known from literature that, YCO is a anti-ferromagnetic metal at room-temperature [3]. In the YCO single-crystal, the Cr absorption spectra shows a multiplet structure at the L_3 and L_2 edges. Well-resolved peaks at the absorption maxima at $E = 575.31$ eV and 576.89 eV exhibits a doublet structure at the L_3 edge, whereas, maxima at $E = 584.95$ eV at L_2 edge is clearly observable. This verifies that the fine structures of Cr $2p \rightarrow 3d$ transition should result from the localization of Cr $3d$ electrons rather than the oxidation of the surface. since Cr $3p$ can be further oxidized to higher valence states, oxygen-rich secondary phases can emerge. Cr $3d^5$ was assumed as an initial state and Cr $3d^3$ was the final configuration. The observed fine structure of the XAS spectrum of Cr also corresponds to the one

calculated from the multiplet effects [Fig. 1(a)]. XMCD signal measured in a magnetic field of $B = 2.0$ T as shown in Fig.1(b) for Cr-edges. Despite that the magnitude of the XMCD measured at the $L_{2,3}$ edges of Cr is clear that the signs of the dichroic signals are the same. The XMCD signal at the Cr L_2 edge is notably suppressed, indicating magnetic ordering due to fully occupied t_{2g} level. The XMCD/XAS intensity ratio w.r.t. the variable magnetic field with ± 0.1 T, ± 1.0 T and ± 2.0 T are shown in Fig 1(c) for Cr-edges. This result is quite relatable with the XMCD graphs. Fig 1(c) exhibits that the intensity ratio of XMCD/XAS is increasing with increasing magnetic-field. The presence of Oxygen K-edge is shown in Fig 2(a). The sharp pre-edge peak at $E = 531.35$ eV indicates the presence of oxidised Cr^{3+} , which also influences the intensity of O at K-edge.

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References:

- [1] A. G. El hachimi, M. L. OuldNE, H. Zaari, A. Benyoussef and A. El Kenz, *J Supercond Nov Magn.* **30**, pages483–488 (2017).
- [2] B. Pal, X. Liu, F. Wen, M. Kareev, A. T. N'Diaye, P. Shafer, E. Arenholz, and Jak Chakhalian, *APPLIED PHYSICS LETTERS* **112**, 252901 (2018).
- [3] J.T. Looby, L. Katz, *J. Am. Chem. Soc.* **76**, 6029–6030 (1954).
- [4] L. Katz, *Acta Crystallogr.* **8**, 121–122 (1955).
- [5] S. Geller and E.A. Wood, *Acta Crystallogr.* **9**, 563–568 (1956).
- [6] A.N.L. Jara, J. F. Carvalho, A. F. Júnior, L.J.Q. Mai and R. C. Santana, *Physica B: Condensed Matter* **546**, 67–72 (2018).
- [7] V.M. Jüdin and A.B. Sherman, *Solid State Commun.* **4**, 661–663 (1966).
- [8] J.F. Carvalho, F.S. De Vicente, S. Pairis, P. Odier, A.C. Hernandez and A. Ibanez, *J. Eur. Ceram. Soc.* **29** 2511-2515 (2009).

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