

## Probing Electronic and Magnetic Properties of $\text{Co}_{1.5}\text{Fe}_{1.5}\text{O}_4$ Nanoparticles using X-ray Magnetic Circular Dichroism

A. KUMARI<sup>1</sup>, S. JENA<sup>1</sup>, R. PAL<sup>2</sup>, V K. VERMA<sup>3</sup>, K. AMEMIYA<sup>4</sup> and V. R. SINGH<sup>1\*</sup>

<sup>1</sup>Department of Physics, Central University of South Bihar, Gaya 824236

<sup>2</sup>Department of Chemistry, Madanapalle Institute of Technology & Science, Angallu, Madanapalle 517325, India

<sup>3</sup>Department of Physics, VIT-AP University, Amaravati 522237 A.P. India

<sup>4</sup>Photon Factory, IMSS, High Energy Accelerator Research Organization, Tsukuba, Ibaraki 305-0801, Japan

**Introduction:** The multifunctional behaviour of spinel-structured magnetic oxides, with the formula unit  $\text{AB}_2\text{O}_4$ , has attracted a lot of interest in recent years. It has broad applications in the fields of magnetically driven sensors, switches, microelectronic devices, etc. The well-known member of ferromagnetic ferrites *i.e.*,  $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$  is a very promising material for the designing of peculiar behaviour by altering the preparation method, Co concentration, and grain size-dependent magnetic parameters such as magnetization, coercivity, blocking of ferromagnetic domains [1]. At one end of the  $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$  series, the ferrimagnet magnetite is distributed with a magnetic moment of  $4 \mu_{\text{B}}$ /f.u. and a Curie temperature ( $T_{\text{C}}$ )  $\sim 850$  K. On the other hand, an antiferromagnetic  $\text{Co}_3\text{O}_4$  is distributed at another end which has a Neel temperature  $\sim 30$  K. Henceforth, the  $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$  series with cation distribution  $(\text{Co}^{2+}_{1-x}\text{Fe}^{3+x}) [\text{Co}^{2+}_x\text{Fe}^{3+}_{2-x}] \text{O}_4$  is regarded the best candidate for changing the mechanism of cation site exchange, a broad range of magnetic moment and  $T_{\text{C}}$  [2-4]. Magneto-crystalline anisotropy is a key factor in influencing the  $T_{\text{C}}$ ,  $H_{\text{c}}$ , and spontaneous magnetization of Co ferrites *i.e.*,  $\text{CoFe}_2\text{O}_4$  as well as the blocking behaviour of ferromagnetic domains. Although it is possible to obtain a variety of magnetic properties appropriate for room temperature uses, the magnetic properties in the Co-rich side of the  $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$  series have received

less attention. Therefore, more research on the Co-rich side of ferrites is required for both fundamental understanding and the development of ferrites for technological uses [1].

For this work, we have selected a typical chemical route synthesized ferrite  $\text{Co}_{1.5}\text{Fe}_{1.5}\text{O}_4$  (CFO) nanoparticles with Co and Fe in the ratio of 50:50, for analyzing its magnetization behaviour. The advanced synchrotron-based X-ray Absorption Spectroscopy (XAS) and X-ray Magnetic Circular Dichroism (XMCD) measurements for the CFO samples were carried out to unveil the magnetization behaviour of the material.

**Experiment:** The polycrystalline CFO nanopowder was synthesized via a chemical route. The precursor solution was prepared by dissolving stoichiometric amounts of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  salts into DI  $\text{H}_2\text{O}$ , which was stirred for 10 min until a transparent aqueous solution get formed. The NaOH solution was then added drop-wise in stirring condition of the resultant solution until a pH  $\sim 12$  is reached. The solution was heated at  $100\text{--}110^\circ \text{C}$  with magnetic stirring for 2 h, followed by heating at  $140\text{--}150^\circ \text{C}$  for 1 h. The black-coloured gel formed was washed several times with DI water and was dried at  $110^\circ \text{C}$ . The fluffy black ash was ground to get fine powder of CFO, which was made into pellets. The CFO pellet sample

was annealed at 200° C for 2 h. The sample's purity was validated by the X-ray powder Diffraction results, which showed no sign of contamination. X-ray spectroscopy, scattering, and imaging studies were conducted at the Photon Factory's variable polarisation soft x-ray beam-line BL-16A (KEK, Japan). Figure. 1 and 2 shows the experimental geometry for the soft x-ray absorption (XAS) and x-ray magnetic circular dichroism (XMCD) studies. The

sample was positioned in the 10<sup>-9</sup> Torr vacuum room with a 5 T superconducting magnet. XAS and XMCD signals were measured using the surface-sensitive total electron yield (TEY) mode near Co  $L_{2,3}$  and Fe  $L_{2,3}$  absorption edges with right and left circularly polarised (RCP and LCP) x-rays, with an energy resolution of ~ 0.1 eV, at 0T, 1T, and 2T varying magnetic fields (only the data of 1T has been produced here).

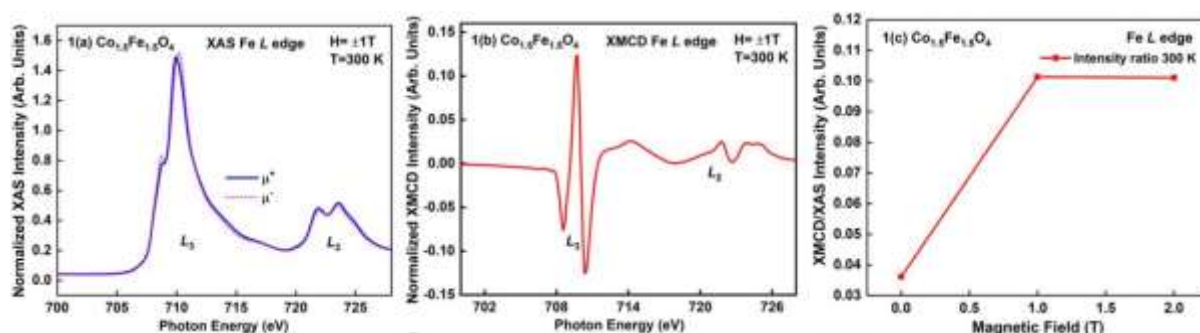


Figure 1(a) Normalised XAS spectra, 1(b) Normalised XMCD spectra of Fe L-edge at applied field of 1T. 1(c) XMCD intensity ratio for Fe L-edge w.r.t applied field of 0T, 1T and 2T.

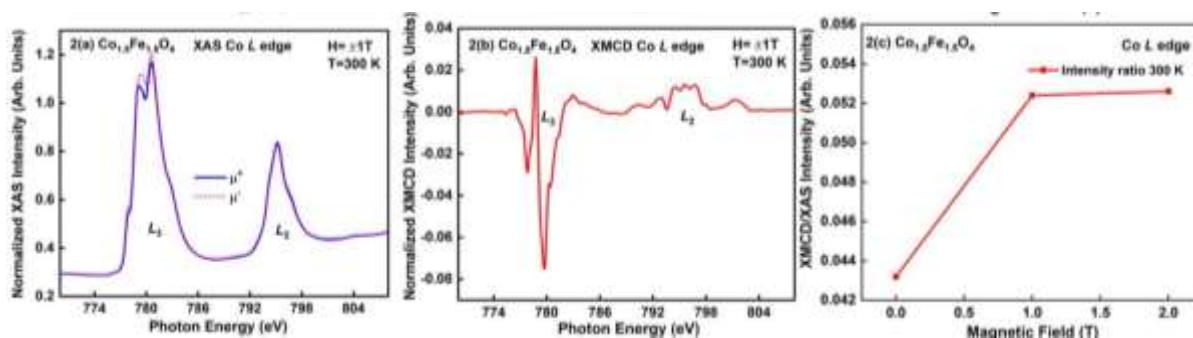


Figure 2(a) Normalised XAS spectra, 2(b) Normalised XMCD spectra of Co L-edge at applied field of 1T and 2(c) XMCD intensity ratio for Co L-edge w.r.t applied field of 0T, 1T and 2T respectively.

**Results and Discussions:** The XAS spectra obtained with applied magnetic fields of +1.0 and -1.0T are represented by  $\mu^+$  and  $\mu^-$ . The symbol  $\mu^+$  and  $\mu^-$  represents left and right circularly polarized light as depicted in Figure 1(a) and 2(a). The XMCD spectrum was collected by taking a difference of two XAS spectra with negative and positive helicity of the circularly polarized light. It is known from the literature that; CFO acts as soft-ferromagnetic at room temperatures. In

the CFO, the Fe and Co absorption spectra both shows a multiplet structure at the  $L_3$  edges. From XAS spectra Co L edge, it is clear that Co shows multiple absorption peak at  $L_3$  edge along with a satellite peak positioned at  $E = 779.07$  eV; here the  $L_2$  peak shows singlet feature at  $795.12$  eV. Well-resolved peaks at the absorption maxima of Fe  $L_3$ -edge at  $E = 710.13$  eV and  $708.75$  eV exhibits a doublet structure at the  $L_3$  edge, whereas, maxima at  $E = 721.9$  eV at  $L_2$  edge

is clearly observable. This verifies that the fine structures of the Fe  $2p \rightarrow 3d$  transition should result from the localization of Fe  $3d$  electrons rather than the oxidation of the surface. Henceforth, based on obtained result it can be concluded that unlike Fe, Co  $2p$  to Co  $3d$  transition is not-localized and infuses more oxidation of the material. XMCD signal collected for Co  $L_{2,3}$  and Fe  $L_{2,3}$  edges at the H=1T, are depicted in Figure 1(b) and 2(b). The XMCD signal at the Fe  $L_2$  edge and Co  $L_2$  edge is notably suppressed, indicating magnetic ordering due to fully occupied  $t_{2g}$  level. The XMCD intensity w.r.t. the variable magnetic field with 0T, 1T and 2T are shown in Figure 1(c) for Co and Fe-edges. This result is quite relatable with the XMCD graphs. Figure 1(c) and 2(c) exhibits that the intensity ratio of XMCD is increasing with increasing magnetic-field.

**Acknowledgements:** The experiments at the Photon Factory was approved by the Program Advisory Committee (Proposal Nos. 2021G501). Authors acknowledges support from UGC-BSR Start-up Research Grant F. 30-395/2017(BSR).

**References:**

1. R.N. Bhowmik, A.T. Satya, A. Bharathi, J. Alloys Compd **559**, 134–141 (2013).
2. G.H. Jonker, J. Phys. Chem. Solids **9**, 165 (1959).
3. A.V. Ramos, J.-B. Moussy, M.-J. Guittet, M.G. Soyer, C. Gatel, P.B. Guillemaud, B.W. Fonrose, E. Snoeck, Phys. Rev. B **75**, 224421 (2007).
4. V.G. Harris, A. Geiler, Y. Chen, S.D. Yoon, M. Wu, A. Yang, Z. Chen, P. He, P.V. Parimi, X. Zuo, C.E. Patton, M. Abe, O. Acher, C. Vittoria, J. Magn. Mater. **321**, 2035 (2009).

\*Corresponding Email: [vijayraj@cusb.ac.in](mailto:vijayraj@cusb.ac.in)