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Magnetic Evidence of $NiCo_2O_4$ using Soft X-Ray Magnetic Circular Dichroism

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1. INTRODUCTION: The *d*-band metal oxides are renowned among materials due to the complexity of their phase diagram that exhibits a formidable array of close and almost overlapping transitions between metallic, insulating, magnetic, and even for superconducting phases [1]. Spintronics is one of the most important emerging areas of research in recent years. Its potential lies in providing high speed memory devices with less power consumption and high storage density. To date, only the ferromagnetic materials have been studied widely for their applications in spintronics devices. But ferrimagnetic spinel oxides, in some cases, can give much better performance than its ferromagnetic counterpart. The ferrimagnetic inverse spinel Nickel Cobaltite ($NiCo_2O_4$) has attracted extensive research interest for its versatile electrochemical properties, robust magnetic order, high conductivity, as well as its highly tunable nature due to the closely coupled charge, spin, orbital, lattice, and defect effects. The cation distribution in mixed-valent inverse spinel NCO can be expressed in terms of a general formula as $Co_x^{2+}\ Co_{1-x}^{3+}[Co^{3+}\ Ni_{1-x}^{2+}\ Ni_x^{3+}]\ O_4^{2-}$ where tetrahedral site is occupied by high spin Co^{2+} and Co^{3+} while Ni^{2+}, low spin Ni^{3+} and Co^{3+} occupy the octahedral sites. Out of all cations, Ni^{3+} ions exhibit a strong Jahn-Teller Distortion. Besides, further investigation will be performed to characterize the electronic and magnetic structure through spectroscopic measurements. The fundamental understanding of these phenomena will facilitate the functional design of $NiCo_2O_4$ nanoparticles for nanoscale spintronic applications. The intrinsic coupling of ferrimagnetic order and the metallic nature in $NiCo_2O_4$ makes it a unique candidate for spintronic applications. X-ray Absorption Spectroscopy (XAS) results not only provide a direct and solid evidence to the scenario of mixed-valent cation distribution of NCO but also establishes a distinction between the metallic and insulating phases in terms of their relative concentrations. Thus, enabling us to understand the mechanism responsible for such contrasting behaviors. Pairs of XAS spectra ($\mu+/\mu-$) are measured with circularly polarized x-rays with ±0.1T magnetic fields applying to the samples. The main objective of the present work is to evolve a mechanism that leads to metallic behavior in $NiCo_2O_4$ ferrimagnet and hence is related to the charge localization at Ni ions, due to possible charge/orbital ordering. Y Bitla *et al* [2] reported that $NiCo_2O_4$, in form of thin films grown at low temperatures (T<400°C) conserves metallic behaviour while that grown at higher temperatures (T>400°C) are insulators with low ferrimagnetic-paramagnetic phase transition. Such inherent coupling coexistence of ferrimagnetic order and the metallic nature makes NCO a promising candidate for spintronic devices.

2. EXPERIMENT: We propose a facile co-precipitation method and subsequently post-annealing approach where Cetrimonium Bromide (CTAB) acts as a chelating ligand and Iso-propanol (IPA) as solvent for synthesizing $NiCo_2O_4$ samples. The sample was placed a pre-heated oven of 300ºC for calcine for 2 hrs and after that the sample is annealed at 700ºC in air-atmosphere for a highly polycrystalline pure inverse spinel phase formation that has been verified through X-ray Powder Diffraction. The effects of reaction parameters such as initial molar concentration of reactants, reaction time and species of solvent on product size and shape were investigated along with the outcomes of imaging experiments were performed at the variable-polarization soft x-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 5T superconducting magnet. XAS and XMCD signals were measured at ±0T, ±1T and ±2T varying magnetic-fields (only the data of ±1T 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 Surface-sensitive total electron yield (TEY) method near Ni $L_{2,3}$

and Co $L_{2,3}$ absorption edges with right and left circularly polarized (RCP and LCP) x-rays.

3. RESULTS AND DISCUSSIONS: The XAS spectra obtained with applied magnetic fields of +1.0 and -1.0 T are denoted by μ^+ and μ^- which represent left and right circularly polarized light, respectively as shown in Fig 1(a) and 2(a). The XMCD spectrum was recorded by taking a difference between the XAS spectra with negative and positive helicity of the circular polarized light. Ni and Co, both shows a tendency of multiplet structure at their L_3 and L_2 absorption edges, respectively. Well-resolved peaks at the absorption maxima at E = 853.77 eV and 871.55 eV at the L_3 and L_2 edges, respectively are clearly observable at Ni *L* edge. This verifies that the fine structures of Ni $2p \rightarrow 3d$ transition should result from the localization of Ni *3d* electrons rather than the oxidation of the material. Co, on the other hand, have multiplet absorption peaks at L_3 edges. The L_3 peak with absorption energy, E = 780.84 eV arrives with a satellite peak at 779.42 eV; whereas, L_2 shows a singlet peak at 795.16 eV. Such results implies that unlike Ni-site, Co $2p \rightarrow 3d$ transition is non-localised and infuses

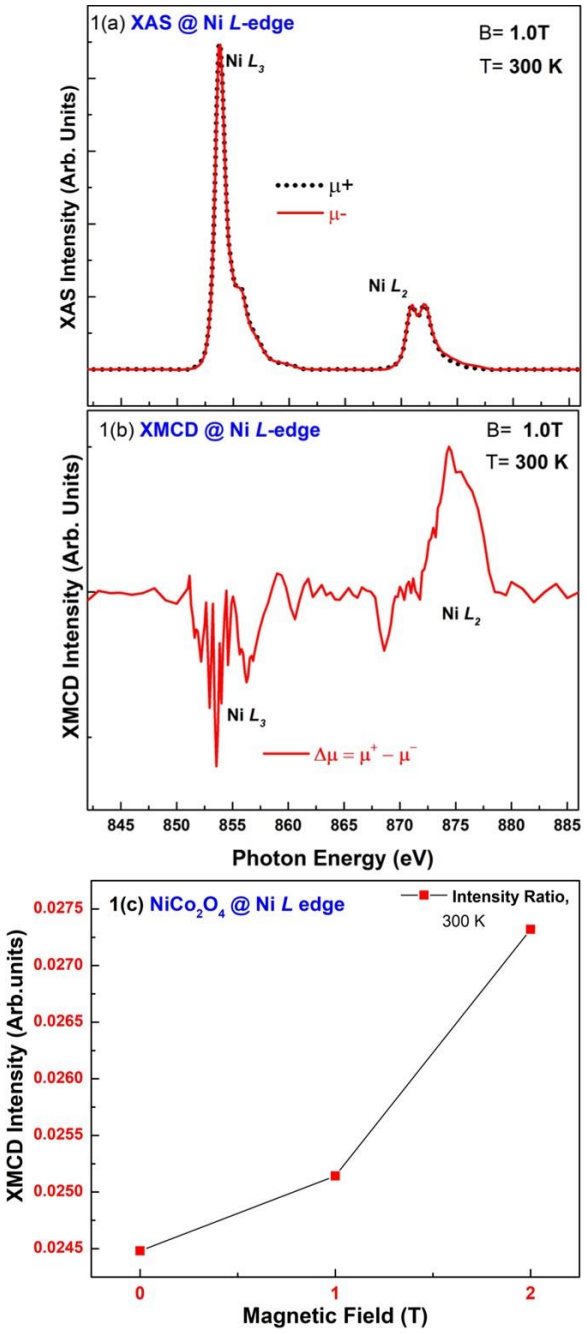

Fig 1(a) Normalised XAS spectra and Fig 1(b) Normalised XMCD spectra of Ni $L_{2,3}$ site. Fig 1(c) XMCD/XAS Intensity ratio w.r.t. applied magnetic-field 0 T, ±1.0 T and ±2.0 T .

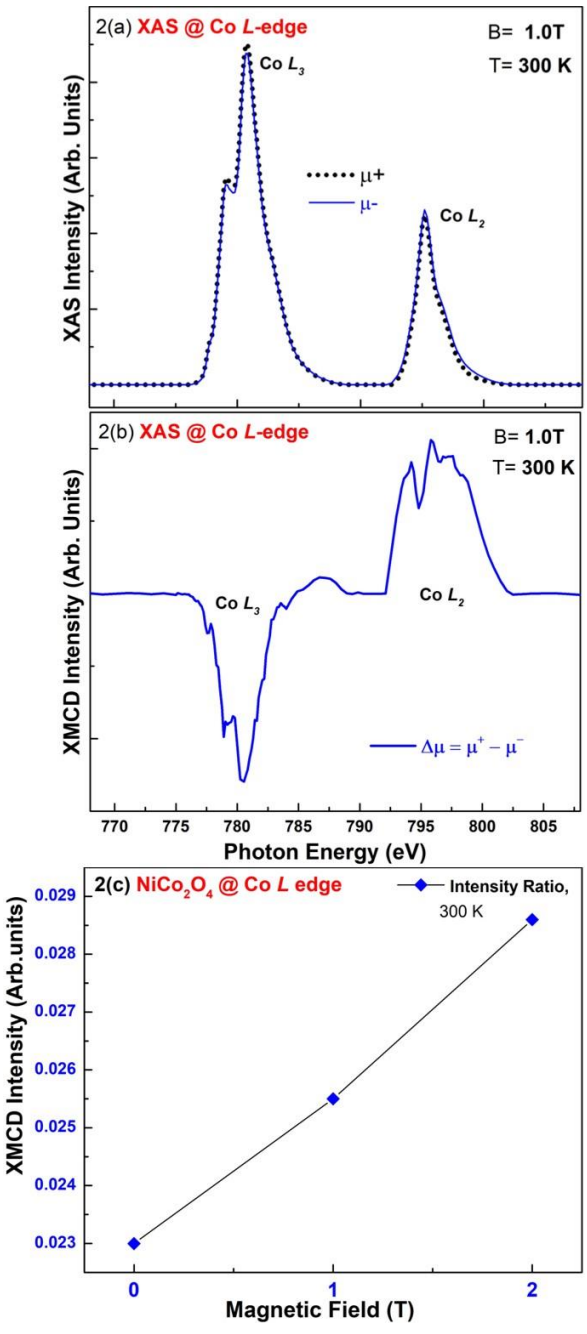

Fig 2(a) Normalised XAS spectra and Fig 2(b) Normalised XMCD spectra of Co $L_{2,3}$ site. Fig 2(c) XMCD/XAS Intensity ratio w.r.t. applied magnetic-field 0 T, ±1.0T and ±2.0T.

more oxidation of the material. XMCD signal measured in a magnetic field of B =1.0 T (as produced here) for Ni $L_{2,3}$ and Co $L_{2,3}$ is shown in Fig.1(b) and Fig.2(b), respectively. The XMCD feature of Ni and Co $L_{2,3}$ is anti-parallel to each other. The XMCD/XAS intensity ratio w.r.t. the variable magnetic field with 0 T, ±1.0T and ±2.0T are shown in Fig 1(c) for Ni-edges and in Fig 2(c) for Co-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. Fig 2(c) produces a steeper increasing ratio with increasing magnetic-field. This suggests that Co involves more in magnetic anisotropy which indicates an increase in ferromagnetism of the NPs. If anyone wants for a quantitative spin and orbital magnetic moment calculation, through sum-rule [3-7] it can be derived.

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