Study of Electronic and Magnetic Characteristics of CoMn$_2$O$_4$ Nanoparticles using X-Ray Magnetic Circular Dichroism

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Introduction: Spinel structure metal oxides have been the subject of current investigation due to their unique optical, electronic, mechanical and thermal characteristics. According to Bragg and Nishikawa, the AB$_2$O$_4$ spinel, is made up of a cubic, densely packed arrangement of cations that have more than one oxidation state and are occupied by oxygen atoms in the tetrahedral (A) and octahedral (B) sites. Spinel's cationic distribution is expressed by the formula (A$_{1-x}$B$_x$)[A$_x$B$_{2-x}$]O$_4$, where x represents the degree of inversion **[1-2]**. Normal spinels are created when x=0, while inverted spinels are created when x=1. A mixed spinel is produced when x selects a number halfway between 0 and 1. Spinel oxides characteristics can be significantly changed by the cation distribution. Cation site choice is influenced by ion size, ion electronic configuration, and the strength and symmetry of the crystals present at the site **[3]**. The type of magnetic ordering formed in the material is determined by the dominant exchange contact between and within the octahedral (B) and tetrahedral (A) sub-lattices. A-B interactions are more powerful than A-A or B-B interactions, according to Neel's two sub-lattice paradigm. Ferrimagnetic ordering is caused by the disparity between the amount of ions present in the tetrahedral and octahedral sites and by the robust exchange interaction between the sub-lattices **[4]**. When compared to Fe-rich spinel oxides (such as Fe$_3$O$_4$, MnFe$_2$O$_4$, and NiFe$_2$O$_4$), magnetic properties of Mn-rich spinel oxides (ZnMn$_2$O$_4$, CoMn$_2$O$_4$, and FeMn$_2$O$_4$) are investigated relatively less. This might be because Mn-rich spinels have complicated magnetic behaviour and low-temperature magnetic measurement systems are necessary. Instead of adhering to Neel's antiparallel spin, Mn$_3$O$_4$ is a ferrimagnetic spinel that exhibits a triangle spin arrangement as proposed by Yafet and Kittel **[5]**. Magnetic dilution effect can be seen, leading to weak exchange contacts, when non-magnetic ions like Mg or Zn are substituted at tetrahedral sites. However, when magnetic ions like Co, Ni, or Fe are used in place of Mn ions, complex magnetic behaviour is seen. This could be because the lattice sites are varying for exchange with one another. Understanding this complicated behaviour seen in the magnetic ion substituted Mn-rich spinels is therefore urgently needed. Therefore a study carried out using advanced synchrotron-based X-ray Absorption Spectroscopy (XAS) and X-ray Magnetic Circular Dichroism (XMCD) technique for the CMO samples to unveil their magnetization behaviour.

Experiment: The polycrystalline CMO nanopowders were synthesized using co-precipitation method. The ultra-pure precursors $CoCl_2 \cdot 6H_2O$ and $MnCl_2 \cdot 6H_2O$ were used to prepare the high-purity polycrystalline samples of CMO. A clear solution was produced after combining the initial ingredients in a stoichiometric ratio with DI water. The required amount of concentrated ammonia solution was introduced to keep the pH of the solution at 7. A greenish-blue colloidal gel was created by heating it to 80° C, then dried at temperatures above 100° C until it was completely transformed into CMO powder. The CMO product was permitted to cool to room temperature before the powder was obtained and was calcined for 3h at 300° C. The finished result was a greyish-pink colour. After that, the material was annealed for 3h at 700° C. The furnace-cooled samples were pulverised into a fine powder. The single phase of the substance was confirmed by characterizing the produced samples using a Rigaku Smart Lab powder X-ray diffractometer. The variable polarisation soft x-ray beam-line BL-16A of the Photon Factory was used to perform X-ray spectroscopy, scattering, and imaging studies (KEK, Japan). The experimental geometry for the investigations of x-ray magnetic circular dichroism (XMCD) and soft x-ray absorption (XAS) is shown in Figures 1 and 2. A 5 T superconducting magnet was used to place the sample in the 10^{-9} Torr vacuum chamber. Right and left circularly polarised (RCP and LCP) x-rays were used to measure the XAS and XMCD signals at varying magnetic fields of 0T, 1T and 2T using the surface-sensitive total electron yield (TEY) technique near the Co $L_{2,3}$ and Mn $L_{2,3}$ absorption edges (only the XAS data of 1T has been shown here).
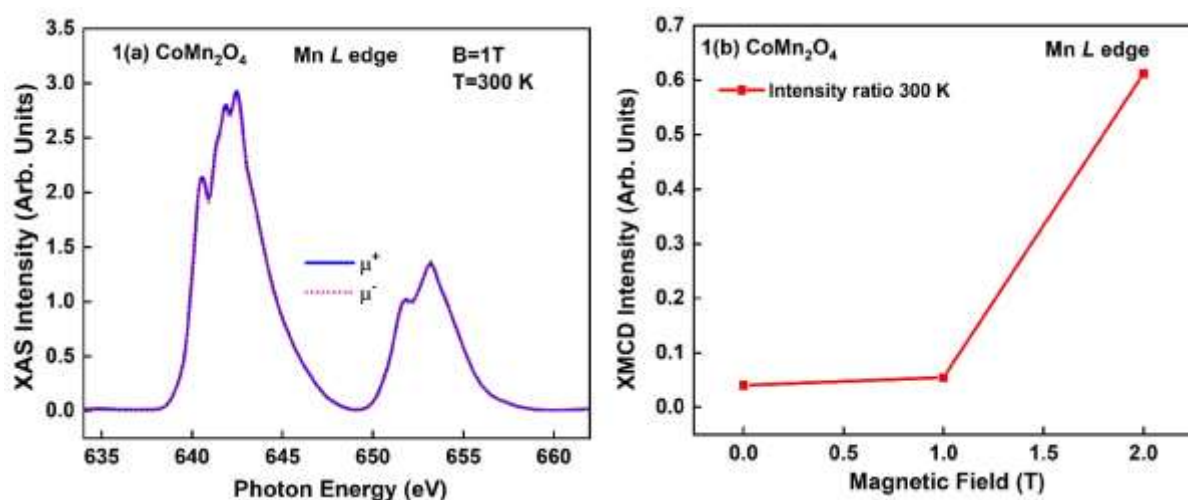

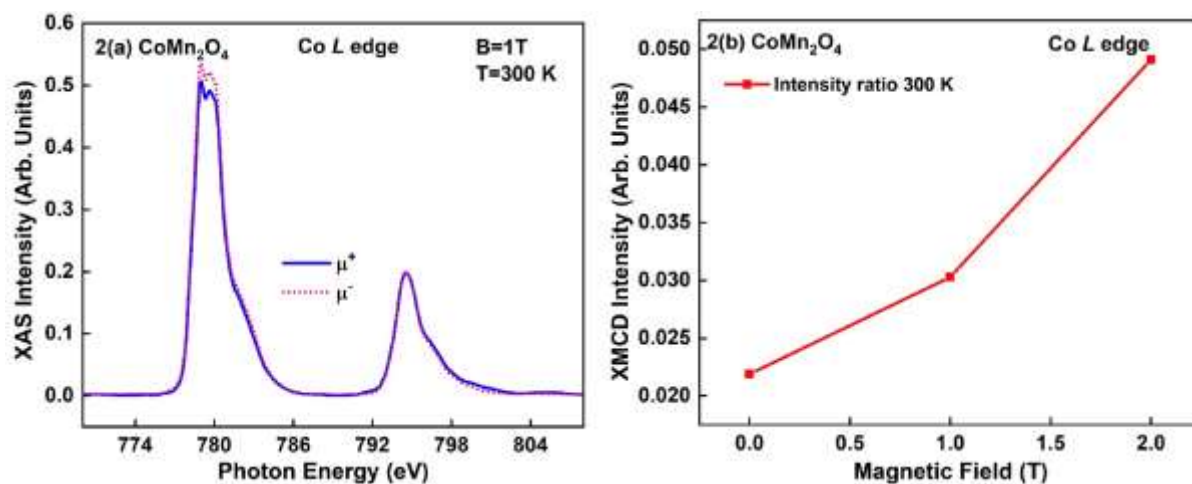*Figure 1(a) XAS spectra, 1(b) XMCD intensity ratio for Mn L-edge w.r.t applied field of 0, 1 and 2T.*

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

Results and Discussions: The XAS spectra collected at the applied magnetic field strength of +1.0 and -1.0T are represented by μ^+ and μ^-. The symbols μ^+ and μ^- denotes left and right circularly polarized light as shown in Figure 1(a) and 2(a). The XMCD spectrum was collected by taking a difference of two XAS spectra with opposite helicities *i.e.,* negative and positive of the circularly polarized light. It is known from the literature that; CMO shows a paramagnetic behaviour at room temperatures. In the CMO, the Mn 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= 779.01 eV; here the L_2 peak shows singlet feature at 794.53 eV. Well-resolved peaks at the absorption maxima of Mn L_3-edge at E = 640.55 eV and 642.5 eV exhibits a doublet structure at the L_3 edge, whereas, maxima at E = 651.85 eV at L_2 edge is clearly observable. This verifies that the fine structures of the Mn $2p \rightarrow 3d$ transition should result from the localization of Mn $3d$ electrons rather than the oxidation of the surface. Henceforth, based on obtained result it can be concluded that unlike Mn, 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 Mn $L_{2,3}$ edges are not shown here. The XMCD signal at the Mn L_2 edge and Co L_2 edge is notably suppressed, indicating magnetic ordering due to fully occupied t_{2g} level. The XMCD intensity ratio w.r.t. the variable magnetic field with 0T, 1T and 2T are shown in Figure 1(b) for Co and Mn-edges. This result is quite relatable with the XMCD graphs. Figure 1(b) and 2(b) exhibits that the intensity ratio of XMCD data increases with increasing magnetic-field strength.

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