

3.1.Introduction:-

Geometrically frustrated magnetic systems have attracted much attention due to their interesting magnetic properties [1–3]. In these systems, spin ordering is suppressed by competing exchange interactions well below the Curie temperature. ABO_2 -type triangular-lattice antiferromagnets in which not all the interactions are minimized simultaneously, are the popular examples of geometrically frustrated systems [4-7].

Crednerite $CuMnO_2$ is an ABO_2 -type triangular-lattice antiferromagnet. The crystal structure of $CuMnO_2$ consists of isosceles-triangular lattices. It has a monoclinic structure with $C2/m$ space group; it is distorted from the hexagonal delafossite structure because of Jahn–Teller effect of Mn^{3+} ions that have crystal-field splitting in e_g orbitals due to d^4 electronic configuration. Moreover, different directions in the triangular ab plane become inequivalent: there exist for each Mn two short and four long Mn–Mn distances in the plane.

It is observed that the exchange interaction at short bonds is stronger, which, with the uniaxial magnetic anisotropy of Mn^{3+} (spins are oriented predominantly along the long Mn–O bonds), leaves the system frustrated. This degeneracy is lifted below magnetic transition: at $T < T_N = 65K$ and the structure changes from monoclinic to triclinic (space group $C1$) due to magnetostriction [8].

Furthermore, in nonstoichiometric crednerite with a small excess of copper ($Cu_{1.04}Mn_{0.96}O_2$), the in plane magnetic ordering remains practically the same as for pure $CuMnO_2$, the interlayer exchange coupling changes from antiferromagnetic in $CuMnO_2$ to ferromagnetic in $Cu_{1.04}Mn_{0.96}O_2$ and vice versa [9]. It is well known that such interlayer coupling is required to make a real three-dimensional long-range magnetic ordering.

In the present investigation we have tried to address the question of such interlayer coupling by doping Fe on the Mn site in $CuMnO_2$. Recent neutron diffraction studies have revealed the magnetic structure of $CuMnO_2$ and the crystal structure deformation associated with the magnetic ordering [8,10].

The magnetic structure below $T_N = 65 K$ is the collinear one with the magnetic propagation vector $\mathbf{k}_1 = (\frac{1}{2} \frac{1}{2} \frac{1}{2})$. In addition to $\mathbf{k}_1$, they observed the other group of

the magnetic Bragg reflections which are assigned by $k_2 = (\frac{1}{2} \frac{1}{2} 0)$. While the intensity for k_1 is dominant, that for k_2 is speculated to be caused by a small amount of impurity of $\text{Cu}_{1+x}\text{Mn}_{1-x}\text{O}_2$ [8].

Trari *et al.* [11] reported the magnetic susceptibility of $\text{Cu}_{1+x}\text{Mn}_{1-x}\text{O}_2$ (with $x=0 - 0.2$), suggesting that the magnetic susceptibility is highly sensitive to the atomic disorders. However, the minor fraction for k_2 has not been investigated thus far. The structural phase transition also occurs below T_N from the monoclinic $C2/m$ to the triclinic $C\bar{1}$ in CuMnO_2 [8,10]. The degeneracy in the exchange interaction paths between base sites and apex sites in isosceles triangular lattice, J_2 , is lifted by the distortion. In the present investigation we have doped Fe on the Mn site and observed the significant fraction of k_2 . In nonstoichiometric crednerite with a small excess of copper ($\text{Cu}_{1.04}\text{Mn}_{0.96}\text{O}_2$), the in-plane magnetic ordering remains practically the same as for pure CuMnO_2 , but the interlayer exchange coupling changes from antiferromagnetic in CuMnO_2 to ferromagnetic in $\text{Cu}_{1.04}\text{Mn}_{0.96}\text{O}_2$ and vice versa. It is well known that such interlayer coupling is required to make a real three-dimensional long-range magnetic ordering. In the present investigation we have tried to address the question of such interlayer coupling by doping Fe on the Mn site in CuMnO_2 .

3.2.Experimental :

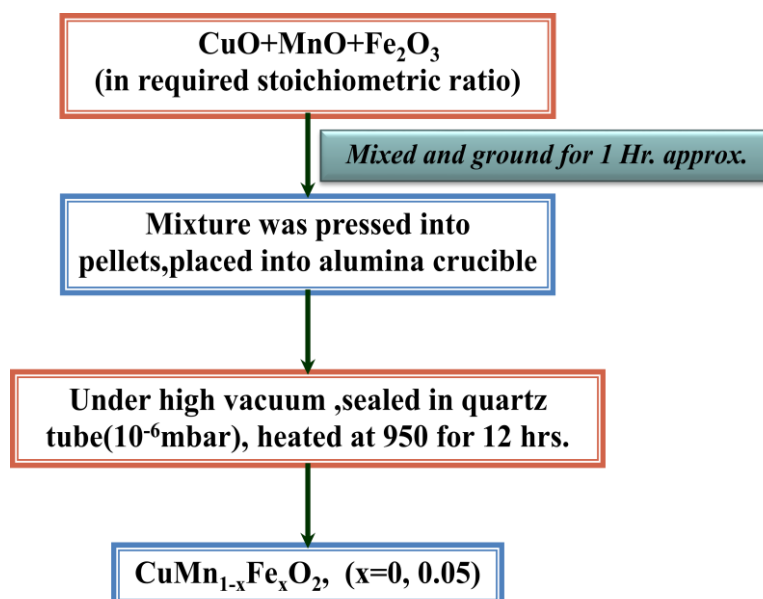


Fig.3.1 Block diagram of solid state reaction technique to synthesize Fe doped CuMnO_2 .

The $\text{CuMn}_{1-x}\text{Fe}_x\text{O}_2$ (with $x=0.0$ and 0.05) samples were prepared by solid state reaction in an evacuated quartz tube. Powders CuO , MnO and Fe_2O_3 were mixed in appropriate ratio and pressed into pellets. The pellets were then placed in an alumina crucible, sealed in quartz tube under high vacuum ($\sim 10^{-6}$ m.bar) and heated at 950°C for 12hrs.

3.3.Results and Discussions :

3.3.1. Synchrotron X-ray diffraction:

Powder XRD data were recorded using ADXRD beam line (on bending magnet port BL-12) of the Indus-2(2.5GeV,100mA) Synchrotron radiation (SR) source at Raja Ramanna Centre for Advanced Technology(RRCAT), Indore, India. The diffraction data were collected on a image plate (mar 345) detector. The diffraction images were integrated using FIT2D program. Wave length and sample to detector distance were accurately calibrated using XRD pattern of LaB_6 NIST standard. The observed XRD patterns were analyzed by Rietveld method using the Fullprof-2K software Package.

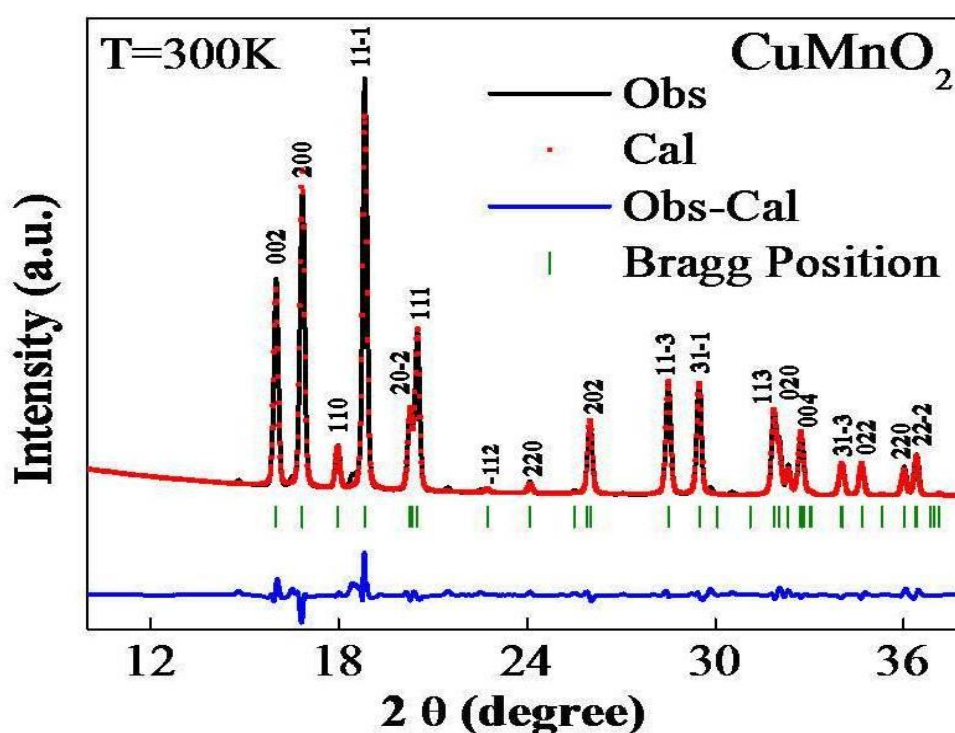


Fig.3.2. Rietveld refinement of synchrotron X-ray powder diffraction data of CuMnO_2 at room temperature.

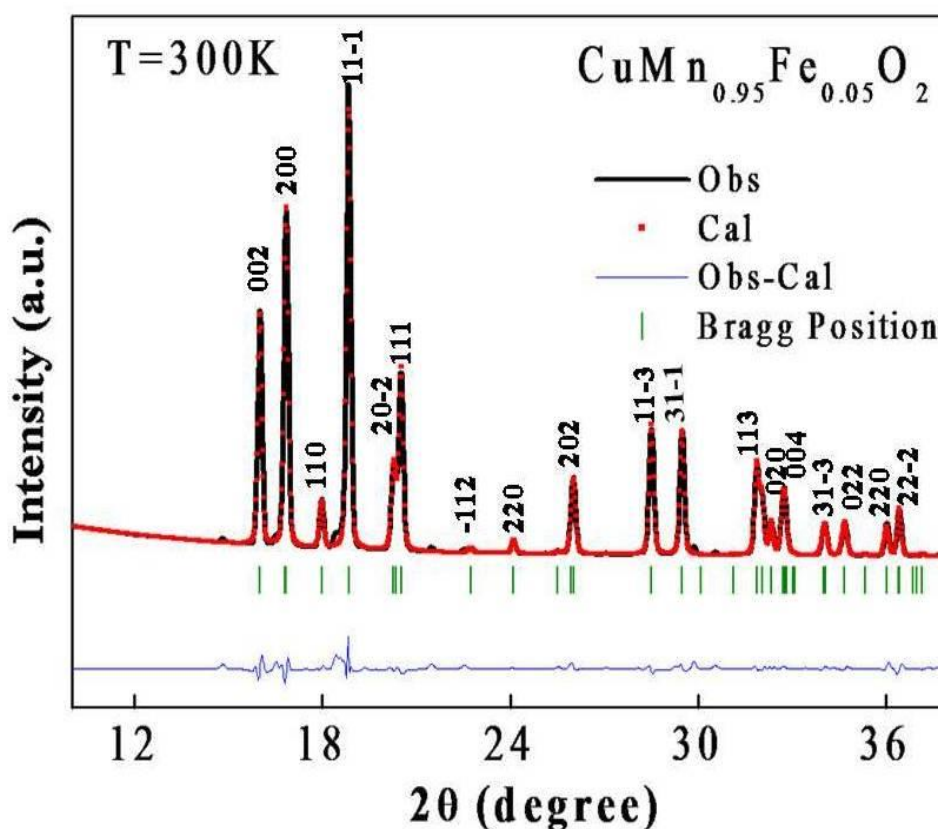


Fig.3.3. Rietveld refinement of synchrotron X-ray powder diffraction data of $\text{CuMn}_{0.95}\text{Fe}_{0.05}\text{O}_2$ at room temperature.

The results of the refinements of room temperature (RT) synchrotron x-ray diffraction (Fig.3.2) and (Fig.3.3), we have shown the representative NPD pattern at 300 K of $\text{CuMn}_{0.95}\text{Fe}_{0.05}\text{O}_2$ data are in agreement with those previously reported for polycrystals of CuMnO_2 [Ref.12] and show the typical crednerite structure [13] with space group $C2/m$. The Mn^{3+} ions occupy the $2a$ Wyckoff site (0,0,0), which is octahedrally coordinated by oxygen ions in the $4i$ site ($x, 0, z$). Mn ions are arranged in planes of isosceles triangles with a short Mn-Mn bond length directed along the b axis (2.8876(8) Å) and longer Mn-Mn bonds (3.1531(5) Å) in the other two triangular directions 110 and $1\bar{1}0$. The MnO_2 layers are linked by nonmagnetic Cu^+ ions (Wyckoff site $2d$:0, 0.5, 0.5) and are linearly coordinated by two oxygen ions forming O-Cu-O dumbbells perpendicular to the ab plane.

The cell volume of $\text{CuMn}_{0.95}\text{Fe}_{0.05}\text{O}_2$ (92.1062 Å³) is slightly larger than that of CuMnO_2 (91.9023 Å³); it corresponds mainly to a decrease of a , an increase of the β

angle, and a small increase of b and c . The changes in the β angle, a and b parameters will have effects on the exchange interactions between ab planes and in the basal plane, respectively. In the same way, the dilution on the Mn site, because of the small substitution of Fe for Mn, induces a smaller (Mn-O) average distance 2.0446(3) Å compared to 2.0451(5) Å for CuMnO₂ and a smaller Jahn-Teller distortion of the MnO₆ octahedra (by comparing the $\delta = d(\text{Mn-O})_{\text{apical}}/d(\text{Mn-O})_{\text{equatorial}}$). The irregularity in the triangular Mn lattice in the basal plane also increases very slightly with the shortest Mn-Mn distance (2.8877(3)Å) which is slightly longer than in CuMnO₂ (2.8876(8)Å) and also the two longest distances (3.1532(1)Å) are larger than in CuMnO₂ (3.1531(5)Å). At room temperature, the Cu-O distances also slightly vary by the substitution, close to 1.8392(5) Å in CuMnO₂ and to 1.8470(1) Å in CuMn_{0.95}Fe_{0.05}O₂.

Table 3.1 Rietveld refinement of room temperature Synchrotron XRD of CuMnO₂ and CuMn_{0.95}Fe_{0.05}O₂.

Sample/Parameters	CuMnO ₂ 300K	CuMn _{0.95} Fe _{0.05} O ₂ 300K
Space group	C 2/m	C 2/m
Cell parameters		
a (Å)	5.6063(3)	5.6064(3)
b (Å)	2.8876(8)	2.8877(3)
c (Å)	5.8990(3)	5.8990(3)
Cell volume (Å) ³	92.6774	92.6823
α (deg)	90	90
β (deg)	103.965(3)	103.961(3)
γ (deg)	90	90
Atomic positions		
O (4i)x	0.4073	0.39978
y	0	0
z	0.17890	0.17789
Mn-Mn (Å)	2.8876(8) ×2 3.1531(5) ×4	2.8877(3) ×2 3.1532(1) ×4
Cu-O (Å)	1.8392(5) ×2	1.8470(1) ×2
Bragg R factor	4.139	2.886
R _F	2.601	2.101
R _P	9.70	8.07
R _{wp}	10.09	9.72
X ²	2.44	1.98

3.3.2. Study with Neutron diffraction:

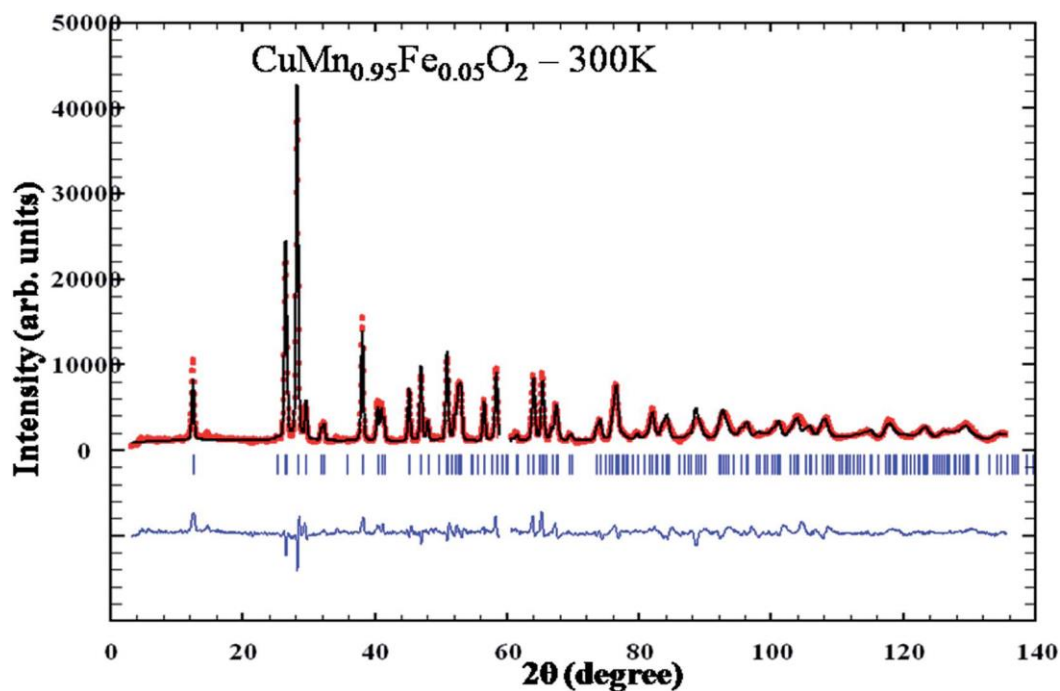


Fig. 3.4: Rietveld refinement of neutron powder diffraction data of $\text{CuMn}_{0.95}\text{Fe}_{0.05}\text{O}_2$ at room temperature.

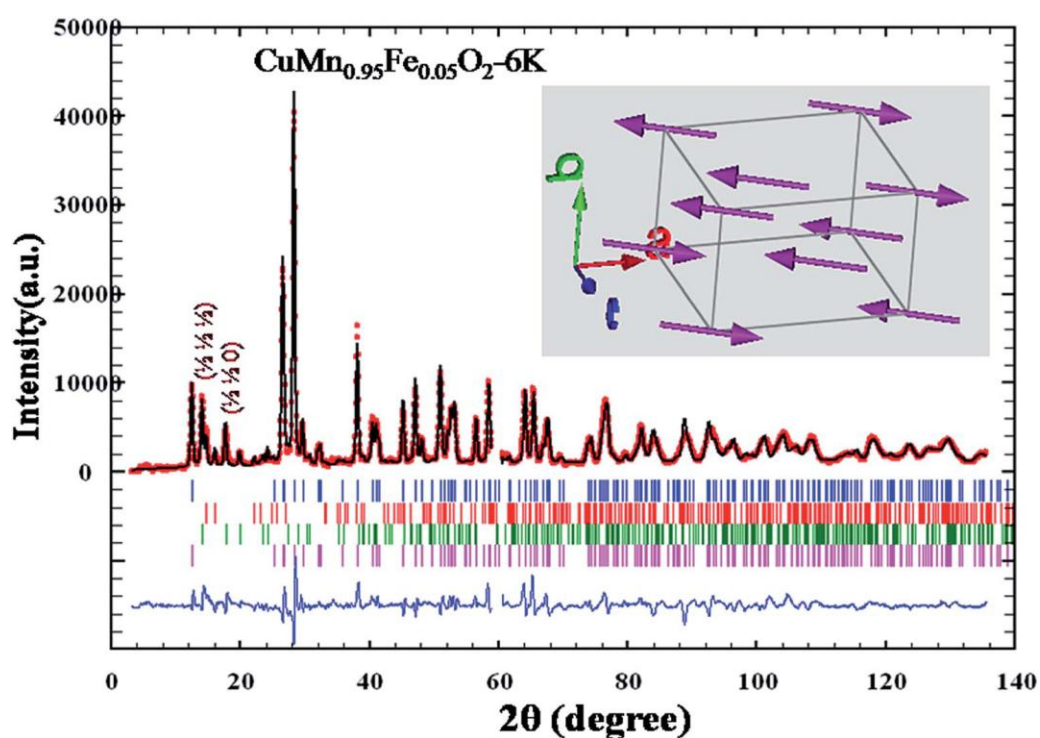


Fig. 3.5 Rietveld refinement of neutron powder diffraction data of $\text{CuMn}_{0.95}\text{Fe}_{0.05}\text{O}_2$ at 6K.

We have also measured the Neutron diffraction at 6K for both CuMnO_2 and $\text{CuMn}_{0.95}\text{Fe}_{0.05}\text{O}_2$. In fig.3.4-3.5 we have shown the neutron diffraction pattern of $\text{CuMn}_{0.95}\text{Fe}_{0.05}\text{O}_2$. On lowering the sample temperature superlattice reflections in both these compounds are observed indicating the antiferromagnetic nature of these compounds. On lowering of temperature we do not observe the splitting of the (220) reflection (the splitting of which indicates the transition from monoclinic to triclinic structure) [28].

A marginal improvement in the fit is obtained in the triclinic phase but we have analysed the diffraction in the monoclinic structure in $C2/m$ space group at 6K. The cell parameters of Fe doped CuMnO_2 ($a=5.5582(4)$ Å, $b=2.8850(2)$ Å, $c=5.8986(4)$ Å, $\beta=104.230(7)^\circ$), significantly differ from those of CuMnO_2 ($a=5.5675(5)$ Å, $b=2.8759(2)$ Å, $c=5.8811(5)$ Å, $\beta=104.058(1)^\circ$). Compared to RT, the difference in the cell volume is more at low temperature (LT) in Fe doped CuMnO_2 . In this low temperature structure, the oxygen atoms occupy a general symmetry lattice site (x , y , z) and the Oxygen position at low temperature also varies with Fe doping.

Dealing with the triangular Mn-array in the (a , b) plane, the Mn-Mn shortest edge of the triangle is slightly elongated (from 2.8759 Å along [010] to 2.8850 Å along [110]). In the MnO_6 octahedron at low temperature, the two long apical Mn-O distances are 2.2574 Å, while the four equatorial distances are (1.9278 Å). While, for CuMnO_2 in the MnO_6 octahedron at low temperature, the apical Mn-O distances are 2.2618 Å, and the equatorial distances are 1.9277 Å indicating that Fe doping decreases the distortion in MnO_6 octahedra.

For nonstoichiometric $\text{Cu}_{1.04}\text{Mn}_{0.96}\text{O}_2$ sample also the distortion in MnO_6 octahedra is decreased [9]. Therefore, no change in the chemical structure is observed on Fe doping, although the magnetic structure is found to be different on Fe doping. The structural parameters obtained from the analysis are summarized in Table 3.1. In the case of CuMnO_2 the superlattice reflections were indexed using the two propagation vectors $\mathbf{k}_1 = (\frac{1}{2} \frac{1}{2} \frac{1}{2})$ and $\mathbf{k}_2 = (\frac{1}{2} \frac{1}{2} 0)$. The intensities corresponding to $\mathbf{k}_2$ were very weak in agreement with Damay et al.¹², but not absent as reported previously in this compound [29]. The magnetic structure described by $\mathbf{k}_1$ consists of antiferromagnetic chains in the (a , b) plane coupled antiferromagnetically along the c -axis.

The components of the moment are $3.2\mu_B$ and $1.9\mu_B$ along a and c -axes corresponding to $3.3\mu_B$. For k_2 vector the magnetic moment is $0.9(3)\mu_B$ and oriented along c -axis. There may be a large inaccuracy in the reported moment value as the intensity is very weak. The total moment is lower than the expected moment of $4\mu_B$ for Mn^{3+} in HS state. Fe is found to substitute at the Mn site. It results in a large increase in the intensity of $(\frac{1}{2} \frac{1}{2} 0)$ reflection corresponding to k_2 . The moment oriented along a and c are $2.4\mu_B$ and $2.0\mu_B$, respectively leading to a total moment of $2.7\mu_B$. The moment corresponding to k_1 vector is $1.8 \mu_B$. A net increase in the moment ($4.5 \mu_B$) is observed as expected for a mixture of Mn^{3+} ($4 \mu_B$) and Fe^{3+} ($5 \mu_B$), which is nearly equal to the saturation value of the $Cu(Mn,Fe)O_2$ sample. The appearance of k_2 propagation vector indicates the ferromagnetic coupling between ab planes.

Table 3.2. Rietveld refinement of the Neutron powder diffraction data for $CuMnO_2$ and $CuMn_{0.95}Fe_{0.05}O_2$ at 6K.

Sample/parameters	$CuMnO_2$	$CuMn_{0.95}Fe_{0.05}O_2$
	6K	6K
Space group	C2/m	C2/m
Cell parameter		
a (Å)	5.5675(5)	5.5582(4)
b (Å)	2.8759(2)	2.8850(2)
c (Å)	5.8811(5)	5.8986(4)
Cell volume (Å) ³	91.3454	91.6842
α (deg)	90	90
β (deg)	104.058	104.230(7)
γ (deg)	90	90
Atomic positions		
O (4i)x	0.4081(5)	0.4087(5)
y	0	0
z	0.1802(4)	0.1790(4)
Mn-O' (Å)	2.2618(×2)	2.2574(×2)
Mn-O'' (Å)	1.9277(×4)	1.9278(×4)
Mn-Mn (Å)	3.1332(×4) 2.8759(×2)	3.1312(×4) 2.8850(×2)
Bragg R factor	4.139	2.886
R_{wp}	10.09	9.72
χ^2	2.44	1.98

3.3.3. X-ray Photoemission Spectroscopy Study:

We have also studied the electronic structure of CuMnO_2 and $\text{CuMn}_{0.95}\text{Fe}_{0.05}\text{O}_2$ using X-ray photoemission spectroscopy (XPS). The purpose of this study was to investigate any role of the electronic structure on the magnetic properties of CuMnO_2 .

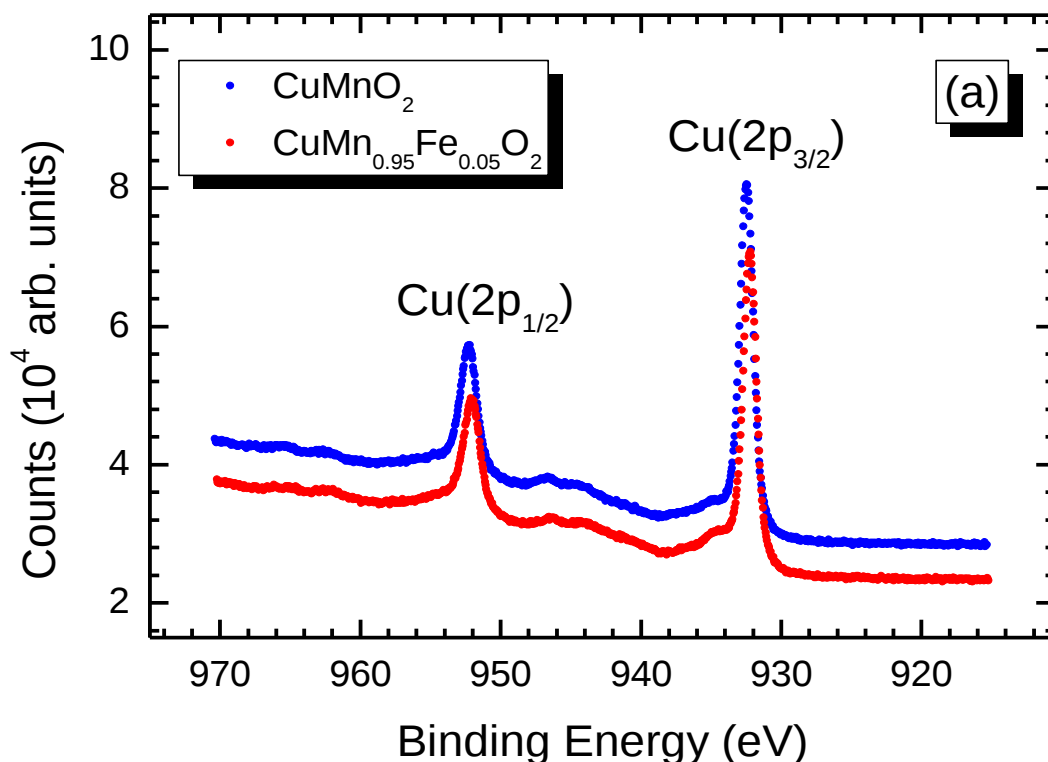


Fig.3.6. XPS core level spectra of Cu2p, blue dots for CuMnO_2 and red dots for $\text{CuMn}_{0.95}\text{Fe}_{0.05}\text{O}_2$.

The XPS core level spectra of Cu2p, Mn2p and Fe2p and O1s are shown in Fig.(3.6-3.9). Fig. 3.6 shows high resolution spectra of Cu2p core level. Two clear distinct states of $\text{Cu}(2p_{3/2})$ and $\text{Cu}(2p_{1/2})$ are separated at 19.75 eV and 19.9 eV for CuMnO_2 and $\text{CuMn}_{0.95}\text{Fe}_{0.05}\text{O}_2$, respectively. Fig 3.7 shows core level spectra of Mn2p. Two separate states of $\text{Mn}(2p_{3/2})$ and $\text{Mn}(2p_{1/2})$ observed at 641.6 eV and 652.95 eV for CuMnO_2 and 641.3 eV and 652.9 eV for $\text{CuMn}_{0.95}\text{Fe}_{0.05}\text{O}_2$, respectively

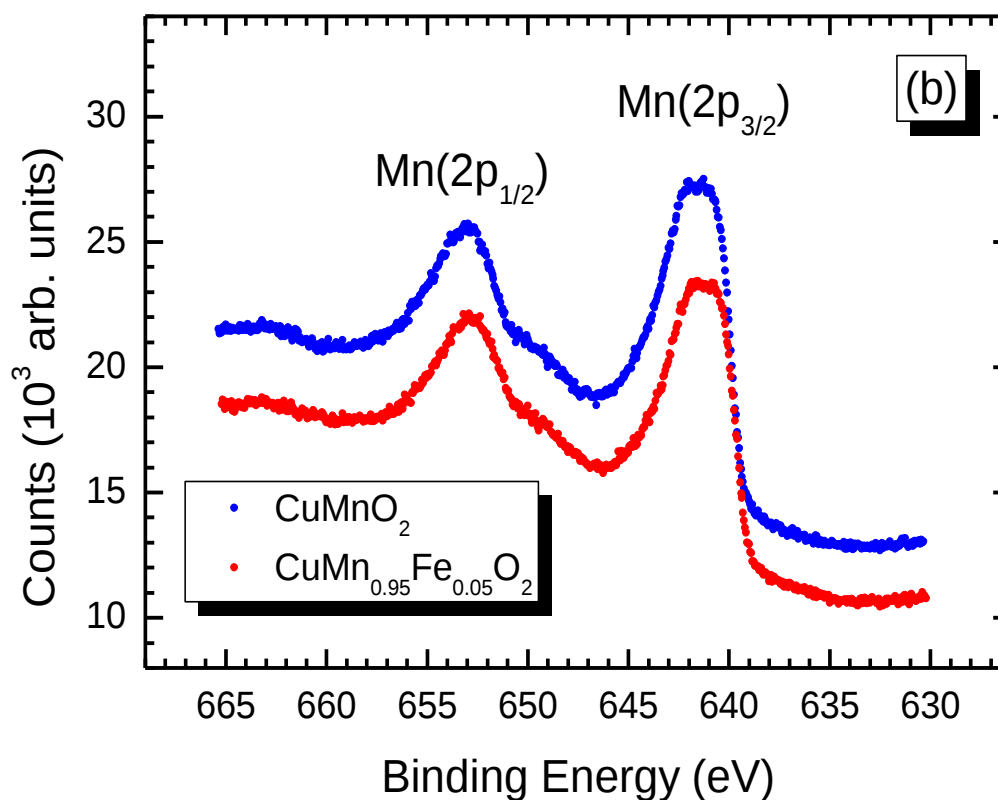


Fig.3.7. XPS core level spectra of Mn2p, blue dots for CuMnO₂ and red dots for CuMn_{0.95}Fe_{0.05}O₂.

Fig. 3.8 exhibit Fe2p core level spectra of CuMn_{0.95}Fe_{0.05}O₂ compound shows the spin-orbit splitting of the Fe2p level, manifested as Fe2p_{3/2} and Fe2p_{1/2}. The difference between these two Fe peaks is 13.5 eV, which confirms the presence of Fe₂O₃ phase formation. These observed doubly states are due to the spin-orbit coupling. Slight shifting in the states with Fe doping occurs due to change in interaction energy between Cu and transition metal ion. These data clearly suggest that Cu is in +1 state and both Mn and Fe are in +3 state.

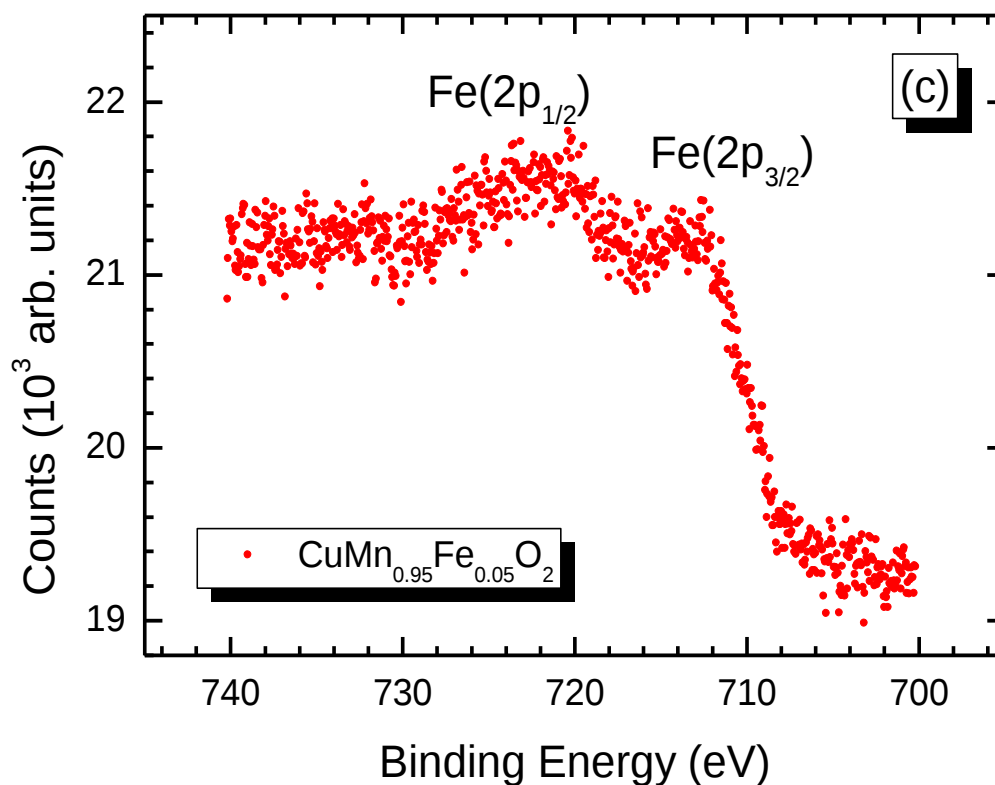


Fig.3.8. XPS core level spectra of Fe2p for $\text{CuMn}_{0.95}\text{Fe}_{0.05}\text{O}_2$.

Fig 3.9 shows the spectra of Oxygen which has two peak structures. Two peaks marked as X observed at 529.8 eV and 529.6 eV and Y at 531.55 eV and 531.1 eV for CuMnO_2 and $\text{CuMn}_{0.95}\text{Fe}_{0.05}\text{O}_2$, respectively. The first peak marked as X, is characteristic peak of “ O^{2-} ” ions of the lattice oxygen, while peak Y denotes O(1s) lateral structure. This lateral peak corresponds to the ionizations of weakly adsorbed species [14] and also the ionizations of oxygen ions with particular coordinates, more specifically integrated in the subsurface. This suggests that the existence, in the subsurface of oxygen ions that bear lower electron density than the “ O^{2-} ” ions. Normally, these oxide ions can be described as “ O^- ” species or excess oxygen. When the density of Lattice oxygen varies, the area ratio of these two peaks i.e. X and Y also changes.

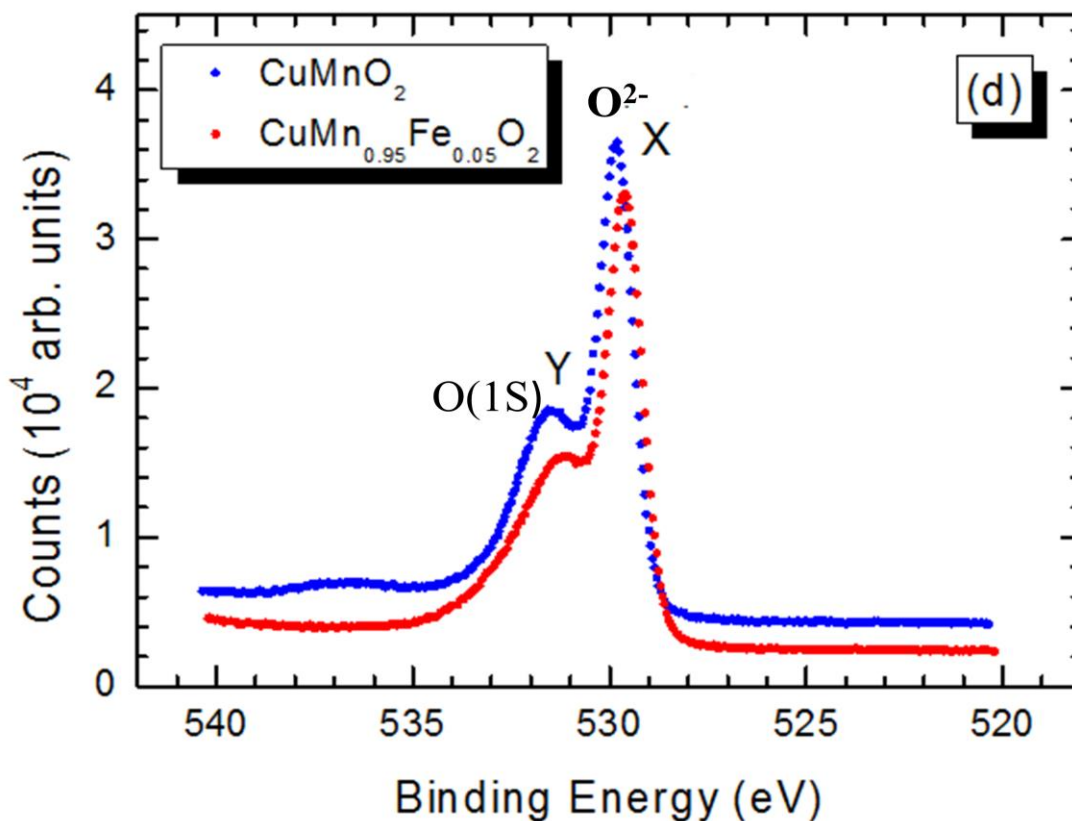


Fig.3.9. XPS core level spectra of O1s, blue dots for CuMnO_2 and red dots for $\text{CuMn}_{0.95}\text{Fe}_{0.05}\text{O}_2$.

Valence level spectra of CuMnO_2 and $\text{CuMn}_{0.95}\text{Fe}_{0.05}\text{O}_2$ samples are shown in Fig.4. Four features (A, B, C, D) can be identified in the experimental spectra of both the samples. Feature A relate to state of dominant Cu 3d atomic character while B and C relate to the hybridization with Cu 3d and Mn 3d to O2p [15]. Feature D is a tail like structure near the Fermi level, E_F . The electronic states near the Fermi level are mostly responsible for the electronic properties.

A comparison of the valence band spectra for the two samples reveals that the density of states is negligibly small but finite at E_F . The density of states slightly increases with Fe doping. Therefore, insulating property decreases with Fe doping. The XRD and Neutron diffraction data also support this.

It is observed from Table 3.1 that on Fe doping Cu-O bond length increases and Mn-O bond length decreases. This will lead to the increase of bandwidth and as a consequence band gap will decrease [15]. Moreover, it has been observed (Table3.1)

that on Fe doping c axis is elongated leading to weaker Cu3d-O2p hybridization. In the valence band spectra (Fig.3.10) also it is found that in $\text{CuMn}_{0.95}\text{Fe}_{0.05}\text{O}_2$ the B and C features are reduced with respect to the A feature in accordance with the XRD and Neutron diffraction data (Table 3.2).

It is worthwhile to mention that the valence band spectrum of CuMnO_2 differs from that of CuCrO_2 [Ref.16] in respect of non-existence of the shoulder at the upper part of the valence band indicating that Mn 3d is located away from the Fermi level. The most interesting feature is the shift of Fermi level towards lower binding energy for both CuMnO_2 and $\text{CuMn}_{0.95}\text{Fe}_{0.05}\text{O}_2$ unlike CuCrO_2 [15,16]. Similar behavior is observed in K doped SrCu_2O_2 [17].

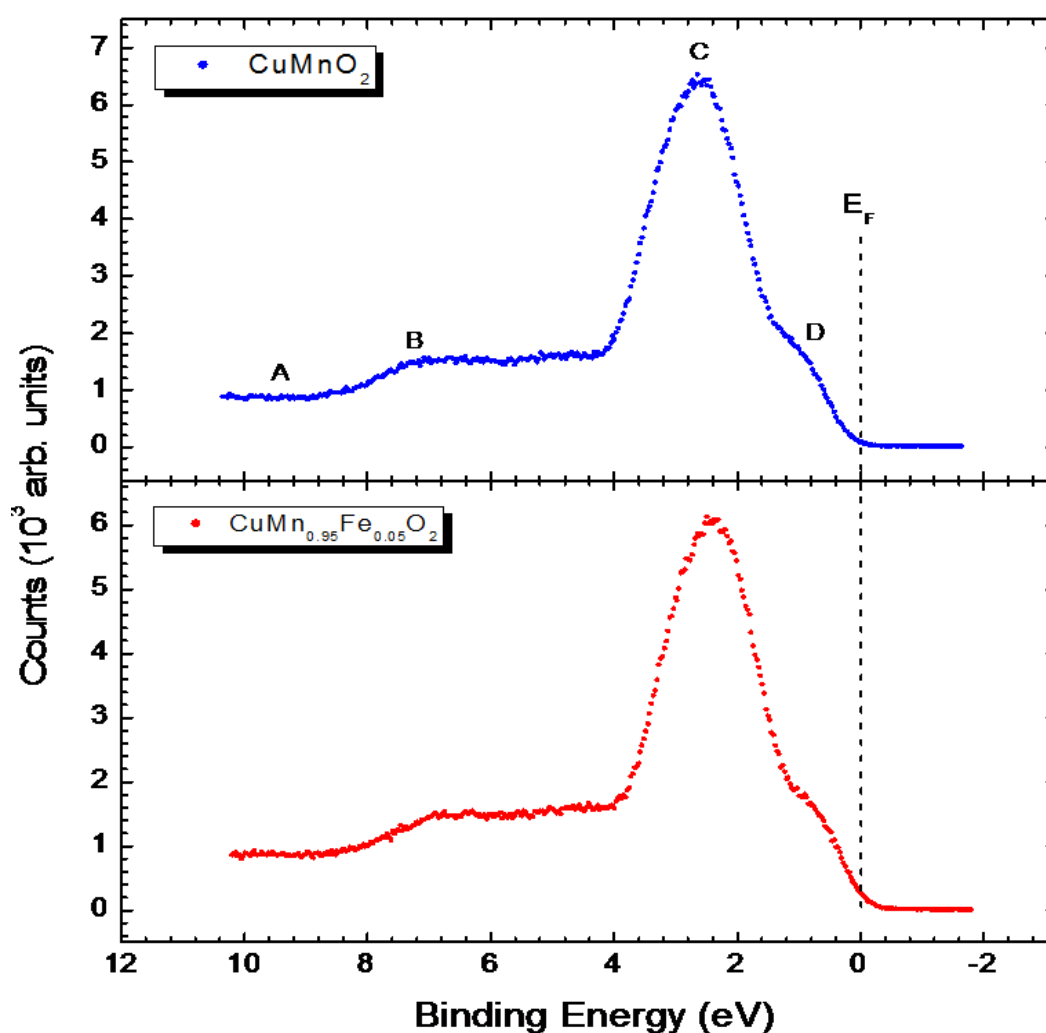


Fig 3.10. Valence-band XPS spectra of CuMnO_2 and $\text{CuMn}_{0.95}\text{Fe}_{0.05}\text{O}_2$. (bluedots for CuMnO_2 and red dots for $\text{CuMn}_{0.95}\text{Fe}_{0.05}\text{O}_2$).

This shift is related to low activation energy of CuMnO_2 . Furthermore, with Fe doping it is observed that shift in Fermi energy is slightly larger than that in undoped sample. This is close to the further change in activation energy. Therefore, the photo emission spectroscopy measurements confirm the movement of Fermi level towards the valence band edge on Fe doping. The shift in the valence band on Fe doping is accompanied by corresponding shifts in core level binding energies. Similar kind of movement is observed in CuCrO_2 with Mg doping [17]. In the present investigation the $\text{Cu}2p_{3/2}$ peak shifts with Fe doping from 932.45 eV to 932.2 eV. The decrease in band gap or increase in conductivity might be the indication of increased ferromagnetism with Fe doping.

3.3.4. Electronic transport property study (Resistivity Measurement):

In order to understand the intrinsic characteristic, we have also studied the temperature dependence of resistivity for both CuMnO_2 and $\text{CuMn}_{0.95}\text{Fe}_{0.05}\text{O}_2$ compounds. The exponential decrease in resistivity with the increase in temperature indicates the semiconducting nature of both the samples. The plot of $\ln \rho$ versus $1000/T$ (Fig.3.11) shows that thermally activated band conduction is the dominant mechanism at high-temperature region. The thermally activated resistivity at high-temperature region follows the Arrhenius law

$$\rho(T) = \rho_0 \exp[E_a/k_B T]$$

where k_B is the Boltzmann's constant and E_a is the activation energy. The deviation from the linear fit indicates that thermal activation mechanism is not valid at lower temperature region.

The variable-range-hopping (VRH) conduction of polarons has been found to dominate in this temperature region. The conduction mechanism due to the variable range hopping of polaron at low temperature can be described by the Mott's equation [27]

$$\rho(T) = \rho_0 \exp[T_0/T]^{1/4}$$

where ρ_0 and T_0 are constants and are given by $\rho_0 = \{ [8\pi\alpha k_B T / N(E_F)]^{1/2} \} / (3e^2 v_{ph})$ and $T_0 = 18\alpha^3 / [k N(E_F)]$ where v_{ph} ($\sim 10^{13} \text{ s}^{-1}$) is the phonon frequency at Debye temperature, $N(E_F)$ is the density of localized electron states at the Fermi level, and α is the inverse localization length. The activation energy (E_a) at higher temperature for the samples has been calculated using Arrhenius law, and values are 0.96 eV and 0.90 eV respectively for CuMnO_2 and $\text{CuMn}_{0.95}\text{Fe}_{0.05}\text{O}_2$. The difference in the values in activation energy is 0.06 eV which is consistent with that obtained from XPS Valence band spectra.

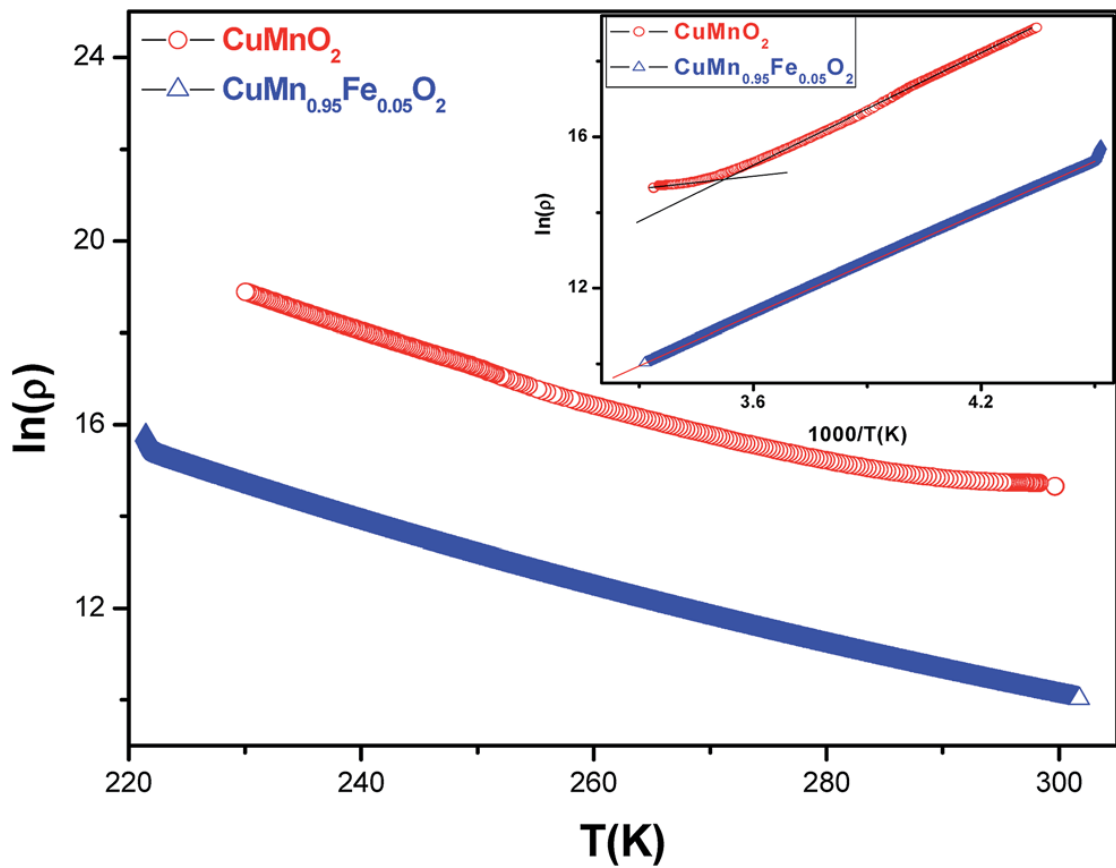


Fig.3.11. Variation of resistivity versus temperature for $\text{CuMn}_{1-x}\text{Fe}_x\text{O}_2$ (where $x = 0, 0.05$). Inset variation of $\ln \rho$ vs. $1000/T$ for ($x = 0$ and 0.05) samples.

3.3.5. Optical Property (Absorption Spectra):

The absorption curves of CuMnO_2 and Fe doped CuMnO_2 are shown in Fig.3.12. As the photon energy increases the absorption intensity increases and attains a maximum.

For the undoped sample the maximum occurs at $E=4.2$ eV whereas for the Fe doped sample it increases to 4.5 eV. The peak can be assigned to an excitonic excitation from Cu $3d+O\ 2p$ to Cu $3d+4s$ [18,19]. For the Fe doped sample the peak intensity becomes negligibly small, the reason of which is not yet clear. It deserves further study. Moreover, the optical band gaps result from the relationship between the optical absorption coefficient and the photon energy ($h\nu$) can be expressed as:

$$(\alpha h\nu)^2 = A(h\nu - E_g)$$

where A is a constant and E_g is the direct optical band gap of the material. The inset of Fig.3.12 shows the optical band gap of the Undoped and Fe doped CuMnO_2 . It is observed from the figure that both samples have two energy band gaps. The band gaps of the crednerite CuMnO_2 (4.60 eV and 4.90 eV) and $\text{CuMn}_{0.95}\text{Fe}_{0.05}\text{O}_2$ (4.60 eV and 4.79 eV) are comparable. Therefore, for both the samples an additional energy level exists near the valence band edge, as also revealed by valence band spectra (Fig. 3.10). The difference between the new band and the conduction band is 4.60 eV for both the samples. On the other hand, the new band resides 0.30 eV and 0.19 eV above the top of the valence band respectively for CuMnO_2 and $\text{CuMn}_{0.95}\text{Fe}_{0.05}\text{O}_2$. Similar, new band is observed in $\text{CuGa}_{0.8}\text{Cr}_{0.2}\text{O}_2$ film. Appearance of new band might be the reason of the shifting of Fermi level towards the valence band edge observed in Valence band spectra (Fig.3.10). Moreover, observed band gaps of these systems come in the range of wide band gap semiconductors and these values are even more than the band gap of ZnO (3.37 eV) and GaN (3.44 eV) [20-22]. Additionally, these systems show much better magnetic ordering and magnetic moment than any known diluted magnetic semiconductors, which might prove significant in the application of these materials as magnetic semiconductors.

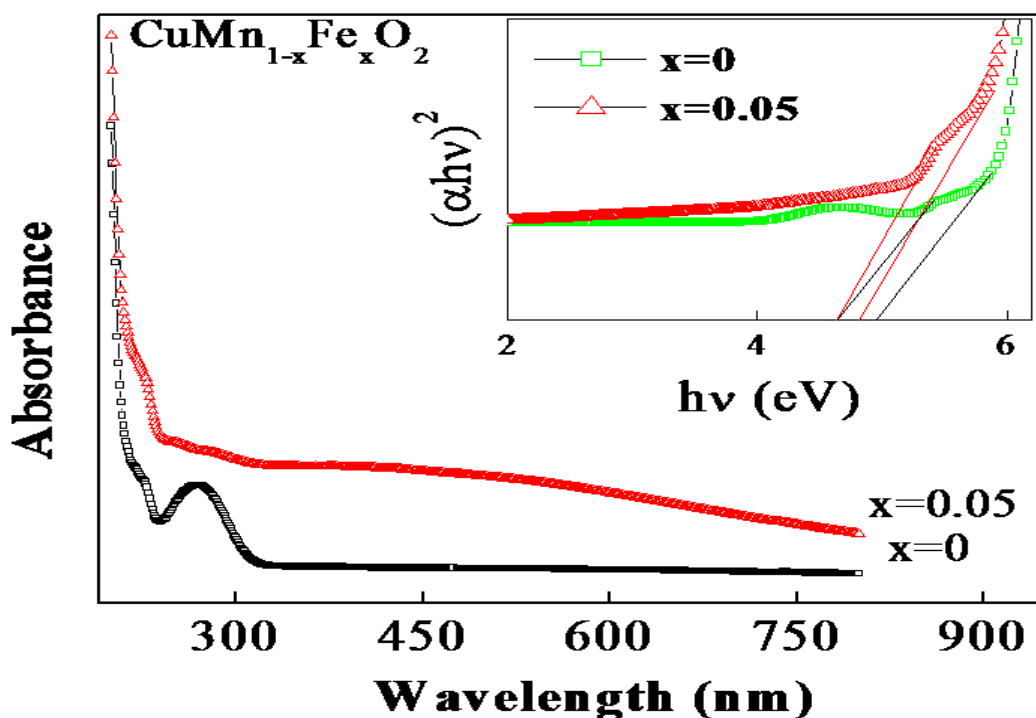


Fig.3.12. Absorption spectra of CuMnO_2 and $\text{CuMn}_{0.95}\text{Fe}_{0.05}\text{O}_2$. Inset: optical and gap from UV-Visible spectroscopic measurement of CuMnO_2 and $\text{CuMn}_{0.95}\text{Fe}_{0.05}\text{O}_2$.

3.3.6. Study of Magnetic property:

Figure 3.13 shows the magnetization of CuMnO_2 as a function of magnetic field. At 5K, a clear hysteresis with a coercive field of 2.46 kOe is observed. The magnetization increases almost linearly with magnetic field after the closing of the hysteresis. The magnetic properties of CuMnO_2 are controversial [30,31]. Our data match with the data in Ref.16. The data indicate the presence of the dominating AFM order with some FM ordering. The increase of high field magnetization along with the appearance of H_c indicates the emergence of an uncompensated moment.

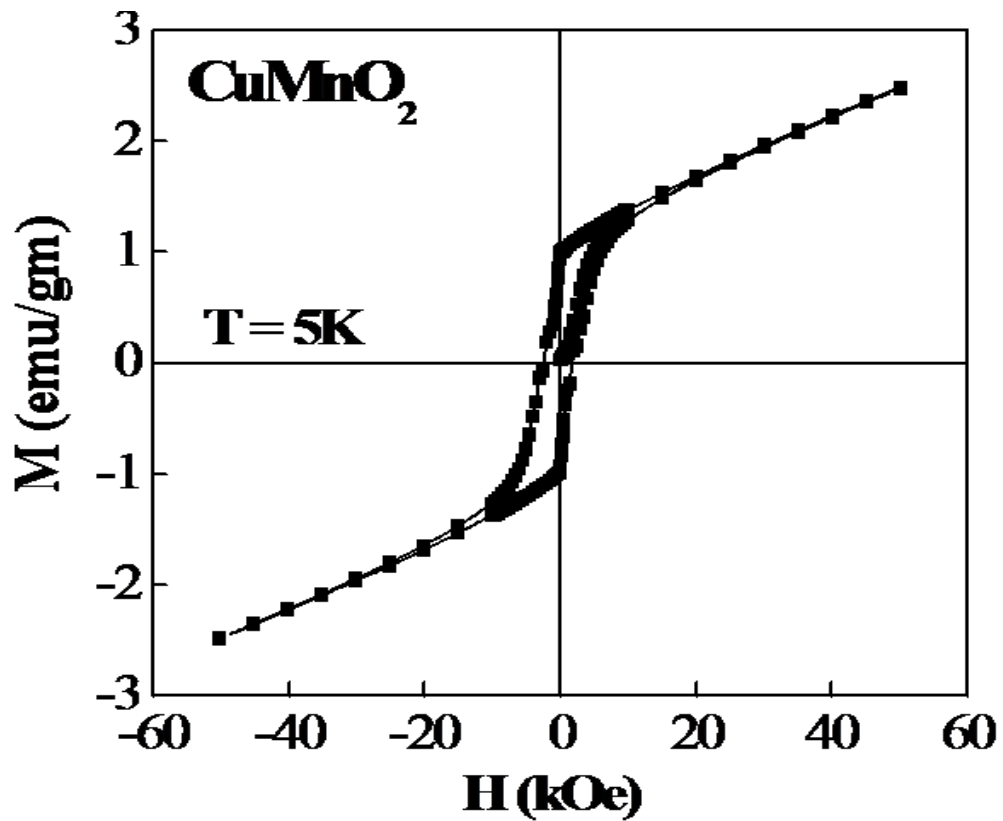


Fig.3.13. Magnetization curve $M(H)$ of CuMnO_2 at 5 K.

When Fe is doped (Fig.3.14), the magnetization is increased but the coercivity is decreased. With increase of the magnetic field the ferromagnetic correlation precipitates and the antiferromagnetic correlation is increased which is clear from the $M(H)$ curve. The change in magnetic behavior with Fe doping can be explained in term of magnetic exchanges, direct Mn-Mn interactions may be considered as dominant in-plane but indirect exchanges (via oxygen) could also play a role, all Mn-O-Mn angles being close to 90° . The super-super exchange, along Mn-O-Cu-O-Mn path ways, may also play the role for the 3D magnetic ordering. In fact super-super exchange via diamagnetic cation is quite common, as is observed in different oxides [32]. The difference in magnetic behavior with Fe doping might be due to the presence of $\mathbf{k}_2 = (\frac{1}{2} \frac{1}{2} 0)$ vector.

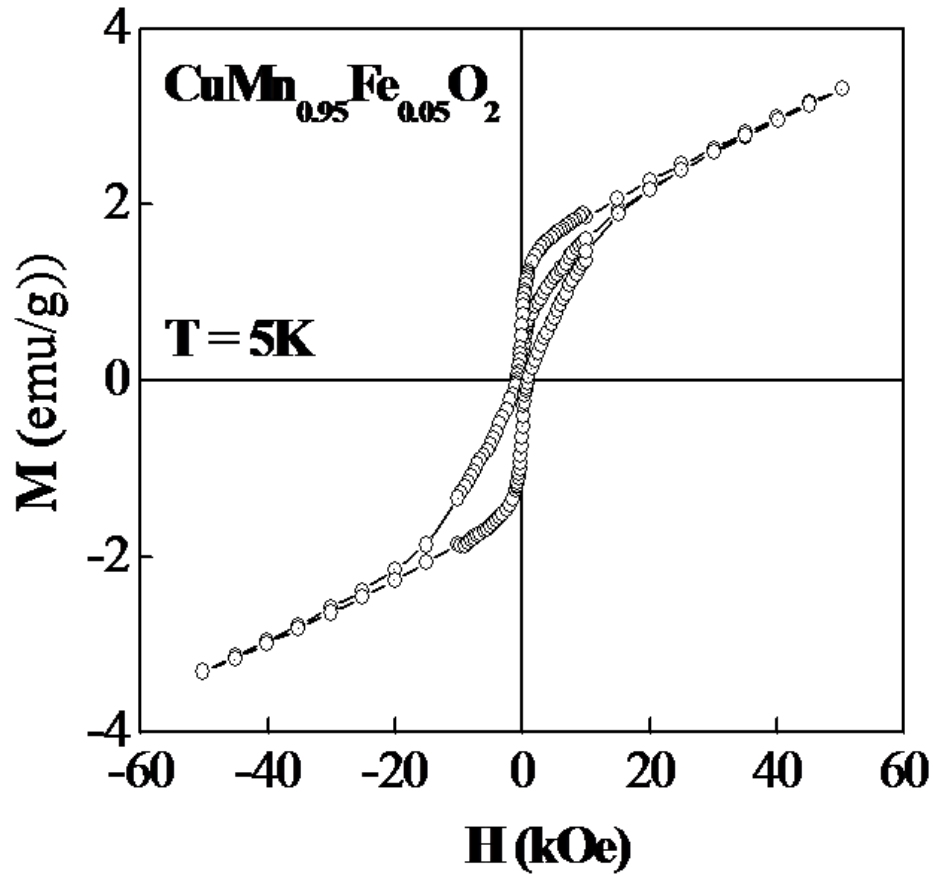


Fig.3.14. Magnetization curve $M(H)$ of $\text{CuMn}_{0.95}\text{Fe}_{0.05}\text{O}_2$ at 5 K.

3.4. Conclusion

Neutron diffraction, synchrotron x-ray diffraction, magnetic, UV-visible spectroscopic and Raman scattering measurements have been investigated on CuMnO_2 and 5% Fe doped CuMnO_2 samples, with assumption that these measurements have complementary information on structural and magnetic behaviour of the samples. On Fe doping, the apical Mn-O distances decrease while the equatorial distances slightly increase, reducing the distortion in MnO_6 octahedra.

Moreover, When Fe is doped along with $\mathbf{k}_1 = (\frac{1}{2} \frac{1}{2} \frac{1}{2})$ the magnetic peaks can also be indexed with the propagation vector $\mathbf{k}_2 = (\frac{1}{2} \frac{1}{2} 0)$ indicating the inducing the ferromagnetic coupling between ab planes. Value of magnetization is increased with Fe doping but coercivity is decreased. These might be due to direct Mn-Mn exchange and Mn-O-Cu-O-Mn super-super exchange interactions.

The UV-Vis. data showed the increase in one of the two energy gaps, on Fe doping, indicating the usefulness of these materials as wide band gap magnetic semiconductors. The Raman spectra indicate that Fe and Mn ions are in the 3+ oxidation state.

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