5.1 Introduction:

Geometrically frustrated magnetic systems have attracted much attention due to their interesting magnetic properties [1–3]. In these magnetic systems, spin ordering is suppressed by competing exchange interactions. ABO₂-type triangular-lattice antiferromagnets (TLA) are popular examples of geometrically frustrated systems [4-7]. A typical example of TLAs is $CuCrO_2$; it has a delafossite structure, which can be viewed as the alternate stacking of edge-shared CrO₆ octahedral layers and Cu layers along the [001] axis. Cr ions form an antiferromagnetic (AFM) triangular sublattice, and the compound enters a long-range AFM ordered state below the Neel temperature $T_N \sim 26K$ [8]. Previous powder neutron diffraction study proposed that the ground state has an out-of-plane incommensurate spiral-spin structure with an in-plane wave vector q = (0.329, 0.329, 0) below T_N [9]. In this spiral-spin ordered phase, the compound exhibits ferroelectricity driven by the magnetic order [10], whose polarization P can be tuned by usingboth magnetic and electric fields [11]. Furthermore, CuCrO₂ is a magneto-electric multiferroic material. Infact, the magnetoelectric (ME) multiferroics, in which magnetic and electric long range order coexist with a strong coupling between their order parameters, have attracted enormous attention recently owing to their potential application in spintronics and multi-state memory devices [12,13]. Furthermore, the ME coupling gives rise to novel physical effects such as large magneto-dielectric (MD) effect due to strong spin-phonon coupling [14,15].

The multiferroic property and the dc magnetization of these materials have been studied in detail. But to the best of our knowledge, ac magnetization of this material has not yet been studied. Here we report a study of the spin freezing in the frustrated multiferroic CuCrO₂ by ac-magnetization measurement. We have also introduced controlled disorder by substituting magnetic Mn-ions for the Cr-ions on the frustrated CuCrO₂ lattice. We find that such a dilution decreases the relative number of spins participating in the ice-like freezing while leaving the freezing temperature, $T_f \sim 32$ K, and its frequency dependence unchanged. Correspondingly the distribution of relaxation times associated with the freezing is broadened only slightly with increasing doping, suggesting that the freezing processes are essentially unchanged by

such dilution. The combination of these observations strongly suggests that the spin freezing transition at $T \sim 32$ K is cooperative in nature and involves the development of short-range spin-spin correlations. This kind of spin-freezing in the geometrically frustrated magnetic materials, in which the topology of the spin lattice leads to a frustration of the spin-spin interactions comprise a class of magnets displaying unique cooperative spin states [16,17]. Although geometrical magnetic frustration has been most extensively studied in materials with antiferromagnetic nearest-neighbor interactions, the effects of strong frustration have also been found in the so-called "spin ice" materials such as $Dy_2Ti_2O_7$, $Ho_2Ti_2O_7$, and $Ho_2Sn_2O_7$ [18,19], in which ferromagnetic and dipolar interactions can be frustrated [20,21]. The spins in these compounds are governed by the same statistical mechanics as the hydrogen atoms in the ground state of ordinary hexagonal ice [22,23]. The spin freezing observed in these materials is different than those observed in spin-glass materials.

5.2 Experimental:

Polycrystalline CuCrO₂ material was synthesized from high purity (99.99%) powders of Cu₂O and Cr₂O₃ by the conventional solid state reaction. The mixtures were carefully ground and pressed into pellets and sintered at 1200 °C for 12h in Platinum crucible in air. Powder X-ray diffractometer (XRD) data were recorded using ADXRD beam line (on bending magnet port BL-12) of the Indus-2 (2.5 GeV,100 mA) 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 LaB₆ NIST standard. The pelletized samples were shaped as a thin plates about 10 mm diameter and ~2.5 mm thickness with a surface area. Silver paste was used to make good electrical contacts on the flat faces for the dielectric and pyroelectric current measurements with different field. Dielectric measurements were performed within temperature region 4.2K to room temperature spanning 1Hz to 1MHz with 1V ac- excitation were performed using (Alpha-A) High Performance Frequency Analyzer (NOVO-CONTROL). We used parallel-plate copper electrodes, with silver-paste-coated sample-surfaces. In-field (5T) dielectric characterization was done using an OXFORD Nano Science Integra System along with the NOVO-Control Analyzer.

5.3 Results & Discussions:

5.3.1Synchrotron X-ray diffraction:

The temperature dependence of Synchrotron X-ray diffraction (XRD) pattern of CuCrO₂ shows (Fig.5.1) a single phase with space group R-3M. The lattice parameters are a=2.9757(1) Å and c=17.1080(9) Å at room temperature in the hexagonal setting, which can be described as a stacking of layers made of edge sharing CrO₆ octahedra linked through Cu⁺ ions coordinated linearly to two oxygen ions forming O-Cu-O "dumbbells" which is perpendicular to *ab* plane. The volume of the unit cell in hexagonal system is given as $V = 0.866 \times a^2 \times c$ and the ratio of lattice parameter, $c/a = (8/3)^{1/3}$. Within the instrumental resolution the temperature dependence of synchrotron XRD between room temperature down to 28 K shows no structural transition in selected temperature range. Rietveld refinements were performed on the high resolution pattern from 300 K down to 28 K, temperature range. All the diffraction peaks could be indexed to the corresponding structure (R-3M, No. 166, H setting), and there is no secondary phase of the sample. Due to the deviation of O-Cr-O bond angle from 90° in octrahedra, even though six Cr-O bond lengths are equal, inducing a deformation in CrO₆ octahedra. The refined parameters, selected atomic distances and bond angles are listed in Table1 which shows that Cr-O bond length and bond angle Cr-O-Cr decreases in temperature range between 300K to 28 K. The value of bond length Cr-O decreases from 2.0315(6) Å to 2.0045(7) Å and corresponding bond angle Cr-O-Cr is 96.16(6) to 95.87(7). Also the ratio of degrees of deformation, $\frac{O-O_{in}}{O-O_{out}}$ (where, $O-O_{in}$ is the length between two oxygen atoms corresponding to the edge parallel to the hexagonal plane in CrO₆ octahedra which is equal to a and O-O_{out} is the length of two oxygen atoms corresponding to two consecutive oxygen planes on each side of Cr^{3+} layer) from 1.11365 to 1.1080, as a result the state of being relaxed of the compression along c of the CrO₆ octahedra. The Mn-doped sample (Fig.5.2) also shows a single phase. The refined parameters are given in Table 2.



Fig.5.1: Rietveld refinement profiles of Synchrotron X-ray diffraction data of the CuCrO₂ sample. The red circles represent the observed data while solid line through circles is the calculated profile, vertical tics below curves represent allowed Bragg-reflections for the wurtzite phase. The difference pattern is given below the vertical tics.

 Table5.1: Rietveld refinement of the synchrotron X-ray diffraction pattern of CuCrO₂ at different temperature.

Temperature	300K	100K	40K	30K	28K
	2 07560(16)	2 08260(20)	2 07457(8)	2 07/23(20)	2 07630(17)
d(A)	2.97309(10)	2.98200(20)	2.97437(8)	2.97423(20)	2.97030(17)
c(A)	17.1080(9)	17.1505(13)	17.1063(4)	17.1033(11)	17.1143(9)
CellVolume(V) A ³	131.1914	132.1288	131.0796	131.0266	131.2935
Oz	0.10687(17)	0.10570(20)	0.10470(20)	0.10650(20)	0.10636(19)
Cu-O	1.828(3)	1.813(3)	1.791(3)	1.822(3)	1.820(3)
Cr-O	1.9995(15)	2.0146(18)	2.0182(18)	2.0019(18)	2.0045(17)
Cr-Crin	2.97569(11)(16)	2.98260(20)	2.97457(6)	2.97423(14)	2.97630(12)
O-Oin	2.97569(11)	2.9826(20)	2.98457(6)	2.97523(14)	2.97630(17)
O-O0ut	2.672(3)	2.709(4)	2.728(4)	2.680(4)	2.686(4)
O-Oin/O-Oout	1.11365(8)	1.1109	1.11038	1.10978	1.1080
Cu-O-Cr	120.77(10)	121.27(12)	121.68(12)	120.93(12)	120.99(11)
Cr-O-Cr	96.16(6)	95.50(7)	94.94(7)	95.95(7)	95.87(7)
O-Cr-Oin	96.16(6)	95.50(7)	94.94(7)	95.95(7)	95.87(7)
O-Cr-Oout	83.84(13)	84.50(7)	85.06(16)	84.05(16)	84.13(15)



Fig.5.2: Rietveld refinement profiles of Synchrotron X-ray diffraction data of the $CuCr_{0.95}Mn_{0.05}O_2samples.$

Temperature	300K	100K	50K	29K	27K	11K
$(CuCr_{0.95}Mn_{0.05}O_2)$						
Space group	R3-M	R3-M	R3-M	R3-M	R3-M	R3-M
Cell Parameters						
a(A)	2.97510(14)	2.96746(12)	2.96620(10)	2.96527(10)	2.96567(10)	2.96502(9)
c(A)	17.0957(12)	17.0868(9)	17.0945(7)	17.0971(7)	17.100(7)	17.0994(14)
Cell Volume(V) A3	131.0451	130.3050	130.2531	130.1912	130.2484	130.1868
Oz	0.0995(5)	0.1046(3)	0.1048(3)	0.10490(20)	0.10500	0.1050(20)
Bond Lengths						
Cu-O	1.701(9)	1.787(5)	1.792(50)	1.793(3)	1.796(3)	1.795(3)
Cr-O	2.066(5)	2.015(3)	2.013(3)	2.0115(18)	2.0109(18)	2.0106(18)
Cr-Crin	2.97510(14)	2.96746(8)	2.96620(7)	2.96527(7)	2.96567(7)	2.96502(6)
Cr-Crout						
(O-Oin	2.97510(14)	2.96746(8)	2.96620(7)	2.96527(7)	2.96567(7)	2.96502(6)
O-O0ut	2.868(10)	2.727(6)	2.722(6)	2.719(5)	2.714(4)	2.716(4)
O-Oin/O-Oout	1.03734	1.08817	1.0897	1.090573	1.092730	1.09168
Bond						
Angles(degree)						
Cu-O-Cr	123.8(3)	121.76(18)	121.70(18)	121.67(12)	121.63(12)	121.63(12)
Cr-O-Cr	92.10(19)	94.85(11)	94.93(11)	94.97(7)	95.02(7)	95.01(7)
O-Cr-Oin	92.10(19)	94.85(11)	94.93(11)	94.97(7)	95.02(7)	95.01(7)
O-Cr-Oout	87.9(4)	85.2(2)	85.1(2)	85.03(16)	84.98(16)	84.99(16)

Table5.2:	Rietveld refinement of the synchrotron X-ray diffraction pattern of
	$CuCr_{0.95}Mn_{0.05}O_2$ at different temperature.

5.3.2 Ferroelectric Property: Pyroelectric measurement

In order to observe the existence of ferroelectric ordering Pyroelectric current measurement were performed in CuCrO₂, which is collected under various fields (electric field 400 kV/m and magnetic fields 3T and 5T). Due to the small electric polarization the sample does not show P-E loop and consequently we have performed pyroelectric measurement. Before the measurement, cooling was done from 40 K to 2 K with a poling field 400 kV/m and then shorted after switching off the electric field to discharge any charges accumulated on the sample surface or inside the sample. Then pyroelectric current was recorded (Fig.5.3) with warming the sample at a rate of 5 K/min. at different external fields. No peak of pyroelectric current is observed at zero fields (Fig.5.3a). However, in the presence of the positive and negative poling electric fields of 400kV/m, a symmetric peak in the pyroelectric state around T_N . The peak intensity increases with increasing magnetic fields. The pyroelectric current and polarization are directly related to the magnetic phase transition. The temperature

dependence of remnant polarization, which is obtained by integrating of pyroelectric current with respect to time, is shown in the Fig.5.3. It is obvious that no electric polarization was observed in CuCrO₂ without fields (Fig.5.3b). However, in the presence of poling electric field of 400 kV/m, the sign reversal of polarization observed by reversing the direction of poling electric field. The polarization starts developing just above T_N which increases with lowering temperature. The observed magnitude of polarization in presence of magnetic field 3T and 5T becomes ~32 μ C/m² and ~37 μ C/m² respectively (Fig.5.3b). The experimental results show that, no spontaneous electric polarization observed in CuCrO₂ in absence of fields. When 5% Mn is doped on Cr site the P(T) behavior with magnetic field remains same except the decrease in polarization and slight decrease in transition temperature (Fig.5.3 c and d).



Fig.5.3:The pyroelectric current with temperature, in presence of poling electric field 400 kV/m, magnetic fields 3T and 5T respectively for CuCrO₂ and CuCr_{0.95}Mn_{0.05}O₂ (a and c) respectively.Electric in presence of poling electric field 400 kV/m, magnetic fields 3T and 5T respectively for CuCrO₂ and CuCr_{0.95}Mn_{0.05}O₂ (b and d).

5.3.4 Magnetic Study

Fig. 5.3 shows the temperature dependent FC and ZFC magnetization M(T) curves of undoped and Mn-doped CuCrO₂ at a magnetic field of 5 kOe between 5 and 300 K. It is observed in the M(T) curve that there is a bifurcation, between ZFC and FC curves below $T_{irrev} = 72$ K and a sharp cusp in ZFC curve around Tp = 48 K (defined by the maximum value of magnetization after ZFC process), which are indications of frustrated behavior.[24]



Fig.5.4: Temperature dependence of ZFC and FC magnetization M(T) for CuCrO₂ and CuCr_{0.95}Mn_{0.05}O₂ at different magnetic fields.

Fig. 5.5 shows the isothermal M(H) curve for Mn-doped and undoped CuCrO₂ at 5K. It is observed that CuCrO₂ is behaving as anti-ferromagnet and as Mn is doped there is a deviation from linearity occurs which indicates the induced ferromagnetism.



Fig.5.5. Isothermal M(H) curves for CuCrO₂ and CuCr_{0.95}Mn_{0.05}O₂at 5K.

In order to further illustrate the frustrated behavior, temperature dependent dc magnetization with different fields, frequency and field dependent ac susceptibility, and isothermal remanent magnetization are performed. We have seen that in this system the frustrated behavior differs significantly from those of a spin glass. Fig. 5.4 shows the temperature dependence of ZFC and FC M(T) for CuCrO₂ at different magnetic fields. The magnetization increases with increasing magnetic field, while the Tp shifts to lower temperatures with increasing magnetic field. One of the closely studied properties of conventional spin glasses is how the freezing temperature (commonly taken as the bifurcation point between the FC and ZFC magnetization) evolves with applied magnetic field. In conventional spin glasses, a sufficiently strong applied field quenches the glass state, and the temperature at which the glass state appears decreases monotonically and usually quite rapidly with increasing applied magnetic field (the so-called AT or GT lines). As shown in Fig.5.4, the temperature of this bifurcation in CuCrO₂ is only weakly dependent on applied field (the application of a magnetic field actually slightly increases the freezing temperature observed in the ac susceptibility data discussed in the following). On the other hand, the percentage difference between the two data sets decreases with applied field, and above 3T we observed no difference between the FC and ZFC magnetization.



Fig. 5.6 Real and imaginary part of ac susceptibility for CuCrO₂ as a function of temperature with several fixed frequencies.

In contrast to magnetization studies, ac susceptibility measurements with varying frequency allow a direct probe of the spin relaxation time. The characteristic behavior of the high temperature ac susceptibility(Fig.5.5)shows the freezing at $T \sim 32$ K. In order to examine the spin relaxation process in detail, ac susceptibility data were taken in the vicinity of this low temperature freezing over a relatively broad range of low frequencies (5-500 Hz). With the magnetization showing a bifurcation, we expect the ac susceptibility in our frequency range to freeze out above this temperature as has been observed in previous reports [26,27,28], which has been described as one kind of spin-freezing. As shown in Fig.5.5, $\chi''_{ac}(T)$ does have a maximum and then drops to a minimum value around 25K for a higher frequency (>100 Hz). The minimum value is the indication of T_N. The ac data taken in a magnetic field show that a field enhances $T_{f}(Fig.5.6.)$, which is consistent with the behavior observed in Dy₂Ti₂O₇ pyrochlore system where similar kind of transition was found at T ~16 K which has been attributed as the spin-ice state. [29] However, the frequency dependence of T_f can be fit to an Arrhenius law $(f=f_0e^{-2Ea/kBT}_f)$, suggesting that this relaxation is thermally activated.



Fig.5.7: Real part of ac susceptibility with temperature for CuCrO₂ at different dc magnetic field.

With the above-presented data, we can contrast the $T < T_{\text{spin-freezing}}$ with the wellstudied transition to a spin glass state. The basic signatures of the spin freezing, i.e., an irreversibility in the magnetization and a frequency dependent maximum in $\chi''_{ac}(T)$ in the absence of other thermodynamic signatures of a phase transition, are qualitatively consistent with spin-glass freezing seen in both highly disordered systems and in site-ordered geometrically frustrated antiferromagnets.[30-32] Upon closer inspection, however, the detailed behavior of this spin-freezing is somewhat different from the cooperative freezing in spin glasses, with the most obvious qualitative difference being that the application of a field enhances the freezing temperature. This is in sharp contrast to the behavior of both the disorder-based spin glasses and spin-glass transitions observed in site ordered geometrically frustrated antiferromagnets [33-35].

To investigate the nature and origin of the transition, we have plotted " χ " as a function of frequency" for the CuCrO₂, at different temperature and below 32 K in Fig.5.8. It can be seen in Fig.5.8 that the curves " χ " vs frequency" show a systematic change in the shape and pattern with increasing temperature as it approaches towards the spin freezing transition temperature T_f. Near the freezing transition i.e at 32 K, χ'' (f) shows comparatively a sharp peak which is in general an indication of very narrow distribution of spin relaxation times near the transition temperature, since for a single characteristic relaxation time [36-38], τ , $\chi''(f)$ has a well-defined sharp peak with a maximum at $f=1/\tau$. This may indicate the transition may be caused by individual spin flipping or it may be single spin process. Again, It is clear from the Fig.5.8, that as the temperature is decreased from the spin freezing temperature 32K, the χ'' becomes slightly broader but still remains sharp enough to show very narrow distribution of relaxation times. In contrast, in spin glass like materials the distribution of relaxation times is quite broad and does not indicate a single characteristic relaxation time. Inset of (Fig.5.8a) we have plotted the normalized χ'' (to its maximum value) as a function of f/f_{peak} for two different temperatures at 32 K and 34 K. We observe from the that our experimental curves for both the temperature 32 K and 34 K are relatively narrower indicating very narrow distribution of relaxation times near and below the

freezing temperature for CuCrO₂ system as usually a broader curve indicates glassy nature of the system suggesting spreading of relaxation time. For a single ion relaxation process, it is theoretically expected that in Cole-Cole (Argand) plot of " χ " Vs χ [/]", should follow a semicircle [38]. Hence to check the theoretical prediction, in set(Fig5.8 b) we have plotted " χ " Vs χ ?" curve at different temperatures near and below the freezing temperature. From this figure, it is clear that the curves follow closely the semicircular path which again suggests the single ion nature of the spin freezing.



Fig. 5.8: Variation of imaginary part of ac susceptibility with frequency at different temperatures. Inset (a)The imaginary part of the magnetic susceptibility scaled to peak amplitude and frequency for CuCrO₂ at 32K and 34K. (b) Cole-Cole plot of the susceptibility data at different frequencies for T = 32 K.

The difference between the spin freezing in CuCrO₂ and that in spin glasses is very surprising.Probably the origin of this freezing state is purely geometrical and does not involve the structural and chemical disorder traditionally associated with glassiness in magnetic materials. These differences suggest the addition of disorder or dilution of the magnetic lattice with magnetic or nonmagnetic [8,28,33,34] ions as possible routes for investigating a crossover between observed spin freezing and spin glass behavior. The data suggest that the glassiness observed in CuCrO₂ is somehow fundamentally differentfrom that in other magnetic materials, and that different models will be needed to understand the spin freezing. The results also raise the question of whether there exist other types of frustration in site-ordered materials which will manifest glassy behavior with different characteristic behavior.

In order to observe the origin of the spin-freezing in CuCrO₂,we have doped Mn on Cr site which effectively increase one spin by completely removing one Cr ion. The dc magnetization behavior of Mn-doped sample is similar to that of undoped sample. Fig.5.9 shows the temperature variation of the real and imaginary parts of the χ_{ac} at a typical frequency of 500Hz. The plots clearly show the suppression of freezing with Mn doping, as the drop in real χ'_{ac} at T_f almost decreases abruptly with Mn doping. Also, the rise in $\chi''_{ac}(T)$ at T_f decreases over 50% from the undoped to the doped one-indicating a reduction in absorption associated with the freezing process. This might be due to the fact that Mn doping induces FM as well which in effect decreases the participating spins in freezing process. The induction of FM is also clear from M(H) curve which clearly shows the appearance of FM with Mn doping. This indicates that the peak in the $\chi''_{ac}(T)$ at T ~32K (due to the freezing) is a collective phenomenon associated with the development of spin-spin correlations, rather than a single ion effect. Furthermore it should be mentioned that the freezing temperature remains unchanged with Mn doping.



Fig5.9:Real and imaginary part of AC susceptibility for $CuCr_{0.95}Mn_{0.05}O_2$ as a function of temperature with different frequency.

Conclusion:

We have systematically studied AC magnetization of multiferroic frustrated CuCrO₂. We have observed a new spin freezing transition below 32 K and we have analyzed the nature of this transition by different ways. It is observed that this transition is thermally driven. Further, the analysis yielded the nature of the spin freezing to be a single ion process. Dilution by the replacements of Cr ions by Mn ions showed no suppression of the spin freezing transition; instead it enhanced the transition suggesting it to be fundamentally a single ion freezing process. However, further magnetic study as well as neutron experiments can help in knowing more details about the system and to completely understand the system.

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