High Magnetic Field Magnetization and Phase Transitions Studies in $A_2Mo_3O_8$ (A = Fe, Mn) Polar Magnetic Systems

Brief Introduction:

Multiferroic systems are very promising for low power memory devices in recent days. Among these multiferroics, Type –III multiferroics have collinear magnetic structure rather than complex structure where polarization are in built, driven by chemical ordering, show large change in polarization at transition temperature and hence strong ME coupling. The polar magnets family $A_2Mo_3O_8$ (A: divalent transition metal ion) having hexagonal crystal structure, crystallizes in space group *P6₃mc* is recently considered as type-III multiferroics being studied in recent times due to the promising magneto-electric (ME) enhancement and tuning magnetic properties by playing with the substitution of magnetic ions with different transition metal ions at A-site. The isostructural compound $A_2Mo_3O_8$ are very interesting due to having different magnetic ground states. $Fe_2Mo_3O_8$ and $Mn_2Mo_3O_8$ exhibit antiferromagnetic (AFM) and ferrimagnetic (FIM) ordering at 60K and 40K, respectively, with strong anisotropy along polar c-axis whereas $Co_2Mo_3O_8$ show AFM order and $Ni_2Mo_3O_8$ has unique zigzag/stripy type AFM order. Recently large ME effect was observed in $Fe_2Mo_3O_8$ and it was also demonstrated that the ME effect can be tuned to large extent by doping with non-magnetic Zn or Mg ion at Fe site and with magnetic Fe ion at Mn-site to realize linear ME effect on these compounds which leads to the enhanced ME coefficient. Recently, the metamagnetic transition or spin reorientation transition from AFM to FIM and FIM to spin-flop (SF) state were observed in parent/Zn-doped $Fe_2Mo_3O_8$ and Fe-doepd $Mn_2Mo_3O_8$, respectively at moderate magnetic field in magnetization (M-T) and polarization (P-H) measurements [1-2]. In addition, the high magnetic field (HMF) studies upto 66T, were done to realize the fully spin polarized state and multistage ME states with the multistep behavior correspond metamagnetic transition through M-T and P-H measurements in $Fe_2Mo_3O_8$ [3] which will possibly pave the path to design low power consumption multistage ME devices. The polar magnets $Mn_2Mo_3O_8$ though exhibits the transition from FIM to SF state at moderate applied field at 2K, the fully spin polarized state were not realized from best of our knowledge present in the literature and may be observed in HMF measurements in this compound. It is imminent to think that the HMF properties such as distinct multistage ME states and rich magnetic phases can be explored via HMF measurements in $Mn_{2-x}Ni_xMo_3O_8$ and $Fe_{2-x}Co_xMo_3O_8$ compound to elucidate the intermediate metamagnetic transition and electric polarization.

Measurements carried out at IMR

Magnetization measurements on Pulsed field setup in $Mn_{2-x}Ni_xMo_3O_8$ compounds

We have carried out high field dependent magnetization measurements under pulsed field on $Mn_{2-x}Ni_xMo_3O_8$ (x = 0., 0.5, 0.75) and in $Fe_{2-x}Ni_xMo_3O_8$ (x =0, 0.1, 0.2) up to field limit of 30 T. All measured data is depicted in Fig 1. Figure 1(a) show a clear cusp around 4-6 T for x = 0

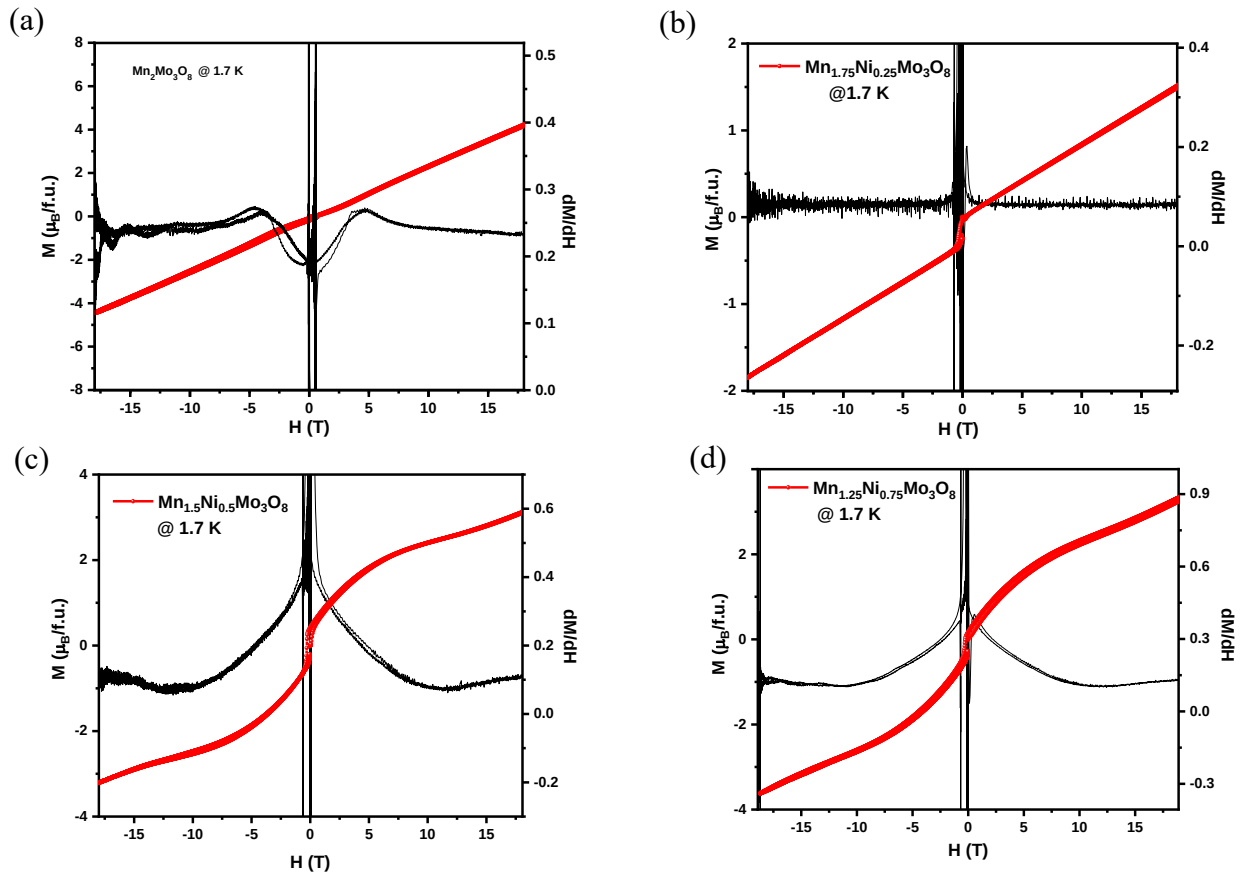


Figure 1. Field dependent magnetization measurements under pulsed magnet of field limit of 30 T on polycrystalline compounds $Mn_{2-x}Ni_xMo_3O_8$ (a) x =0, (b) x =0.25, (c) x = 0.5, and (d) x = 0.75.

shows a clear spin reorientation transition (SRT) which is well known for $Mn_2Mo_3O_8$ compound. In addition, no further spin reorientation is observed for this compound up to 30 T. For x = 0.25, compound show and small ferrimagnetic behavior at 1.7 K also rules out the possibility of SRT. Furthermore, small ferromagnetic/ ferrimagnetic establishment remained for x = 0.5 and x = 0.75 and also shows deviation from in the M vs H plot.

Polarization measurements on Pulsed field setup in $Mn_2Mo_3O_8$ single crystal

In this section we have carried out the pulsed field dependent polarization measurements on single crystal of $Mn_2Mo_3O_8$ in H// c configuration. Measurements were done at represented temperatures: 4.2 K, 12 K, 33 K and 40 K as shown in Fig. 2. The spin flop phase were appeared at 4-6 T field window at specific temperatures viz. 4.2 K, and 13 K. Above these temperature, spin flop phase vanishes off. In general, the electric polarization as a function of field is expressed by $\Delta P = P_0+\alpha H+\beta H^2$, where P_0 represents the difference of P(H) and P(H = 0) in the same magnetic phase and usually is zero. When a magnetic field-induced metamagnetic transition occurs, P0 is the difference of P(H = 0) between the two different magnetic phases The obtained data of polarization as a function of field are fitted via above equation. The linear magnetoelelctric effect (ME) dominates in low field and low temperature region. High field

and region is dominated by second order ME effect. Spin flop phase are characterized by the linear and quadratic ME effect. The ferrimagnetic state dominates foe linear ME effect in $Mn_2Mo_3O_8$ system which is governed by the exchange striction mechanism. Also, when system achieved spin flop state, spin remains collinear, rules out the Dzyaloshinskii-Moriya Interaction (DMI) in spin flop state and exchange striction again governed at this phase.

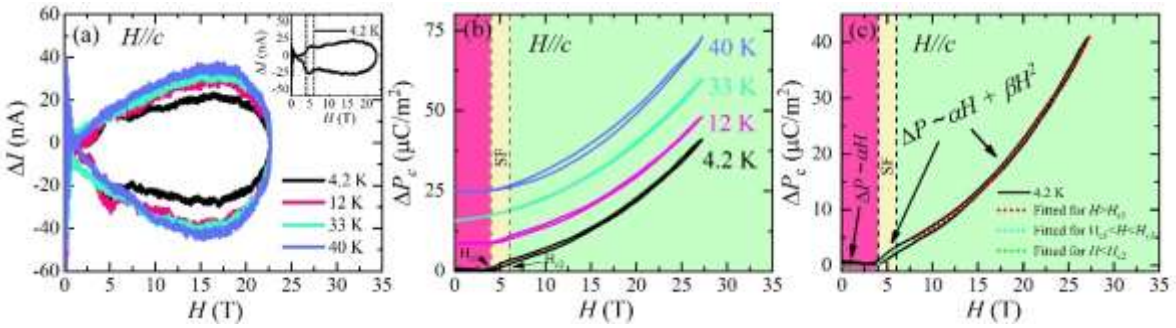
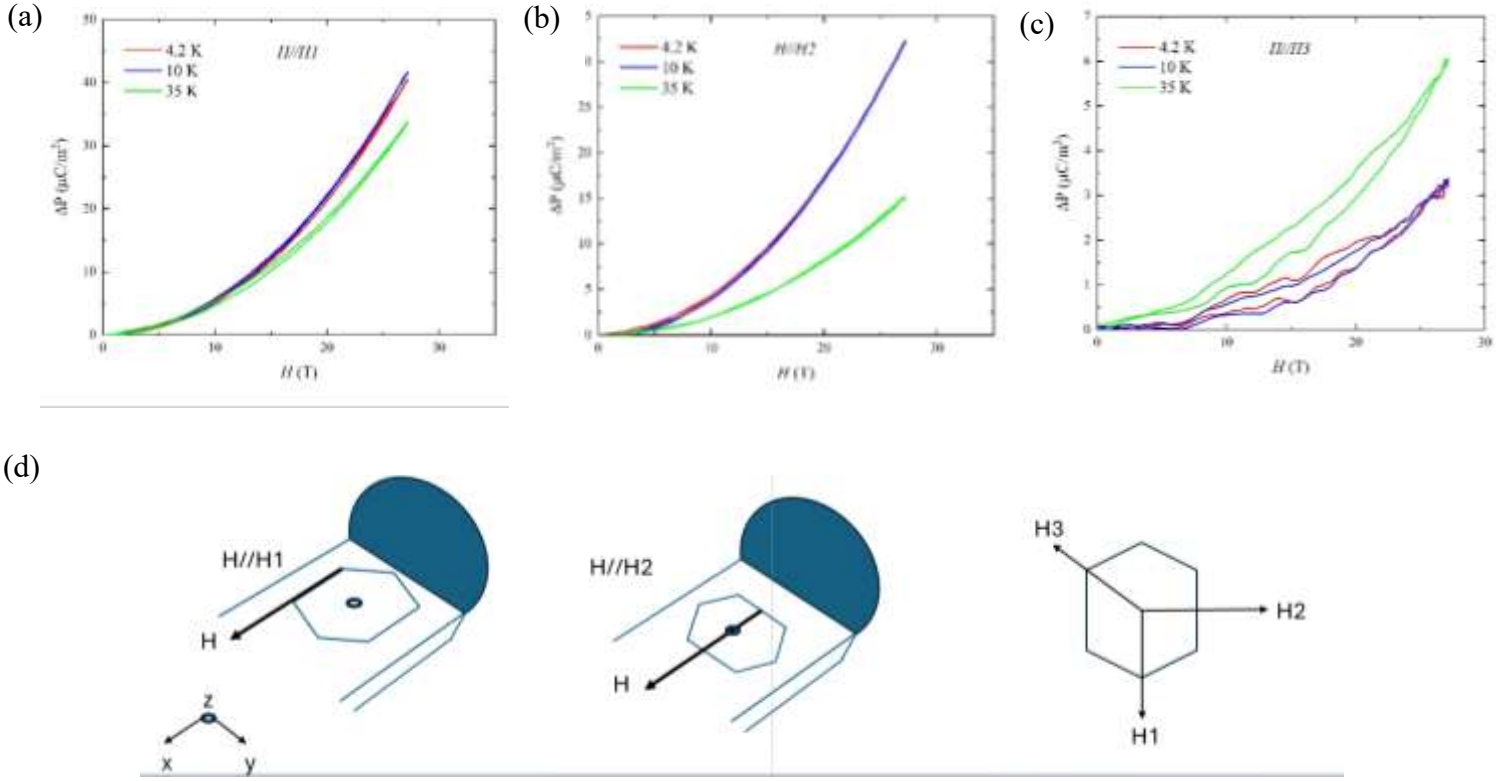


Figure 2. Field dependent polarization measurements under pulsed magnet of field limit of 30 T on single crystal of $Mn_2Mo_3O_8$ at various temperatures. (a) represents the magneto-current (b) and time integration of magneto-current gives rise the polarization and (c) fitted polarization curve at 4.2 K

Polarization measurements on different configuration viz. H//H1, H//H2 and H//H3

Further, polarization is deduced in different measurement configuration as shown in Fig. 3



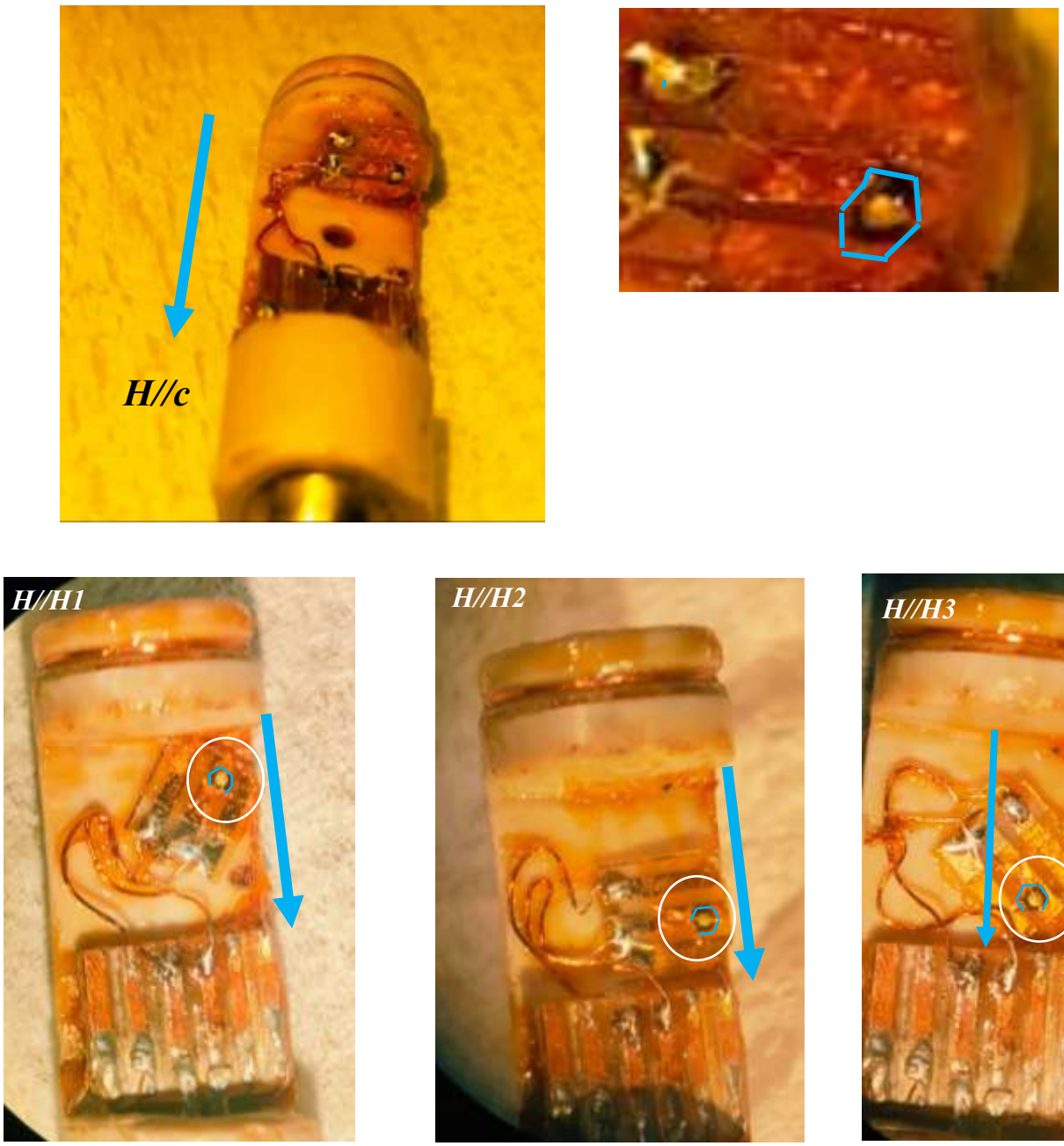


Figure 3. Field dependent polarization measurements under pulsed magnet of field limit of 30 T on single crystal of $Mn_2Mo_3O_8$ at various temperatures in different configuration. (a) H//H1 (b) H//H2 and (c) H//H3 , where H⊥c in all cases. (d) All measured configuration are shown.

Electron spin resonance spectroscopic studies on polycrystalline $Mn_{2-x}Ni_xMo_3O_8$ (x = 0, 0.75)

The temperature dependent electron spin resonance (ESR) under pulsed field at various frequencies were measured on polycrystalline Mn2Mo3O8. These measurements yield the gapped magnon below ferrimagnetic ordering i.e. T_C = 40 K. The splitting in the antiferromagnetic resonance (AFMR) mode below T_C = 40 K were observed due to presence of small anisotropy in the

polycrystalline sample. This was further analyzed by the uniaxial AFMR theory and extracted gapped magnon frequencies for both spin excitation modes w01 = 135.67 GHz and w02 = 78.97 GHz. Furthermore, the anisotropy field from the both spin excitation modes reveal the dominance of the two coupled distinct Mn site which validates the M1 mode dominated by octahedral site while tetrahedral site is dominated by M2 mode.

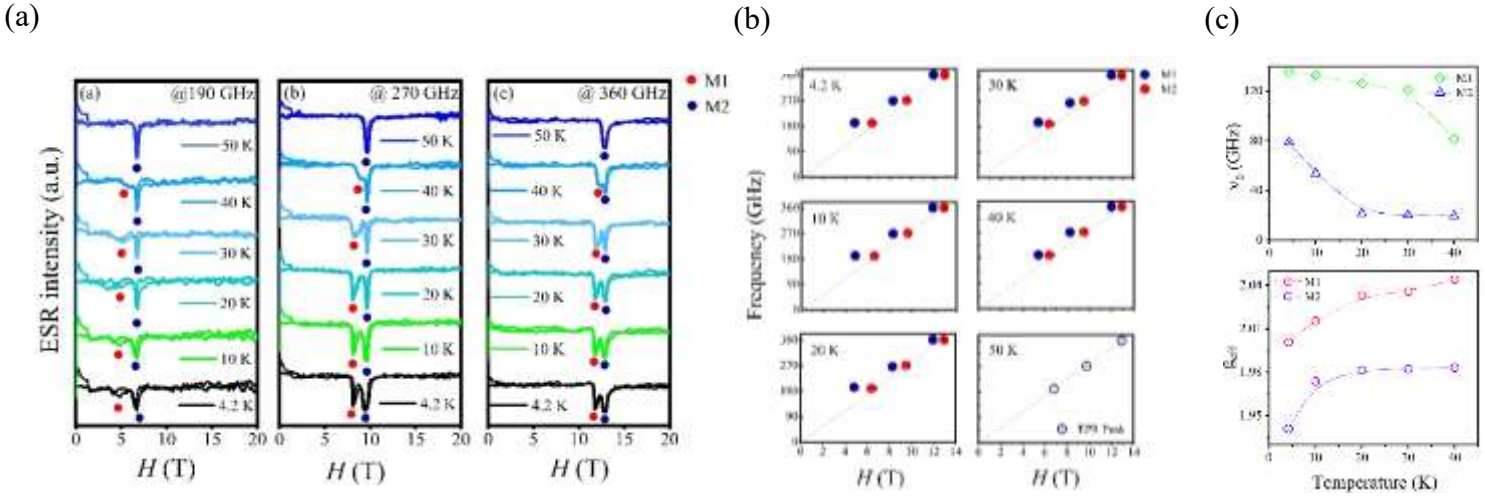


Figure 4. (a) High-field ESR spectra of $Mn_2Mo_3O_8$ system carried out at various temperature and different frequencies. (b) Frequency-field diagram to estimate gapped magnon frequency. (c) Thermal variation of gapped magnon frequency and effective *g*-values below transition temperature T_C = 40 K.

Additionally, the temperature dependent electron spin resonance (ESR) under pulsed field at various frequencies were measured on polycrystalline $Mn_{1.25}Ni_{0.75}Mo_3O_8$. These measurements yield the gapped magnon below magnetic ordering i.e. T_C ~27 K. The splitting in the antiferromagnetic resonance (AFMR) mode below T_C ~27 K were observed due to presence of small anisotropy in the polycrystalline sample. These obtained data are being analyzed for further establishments.

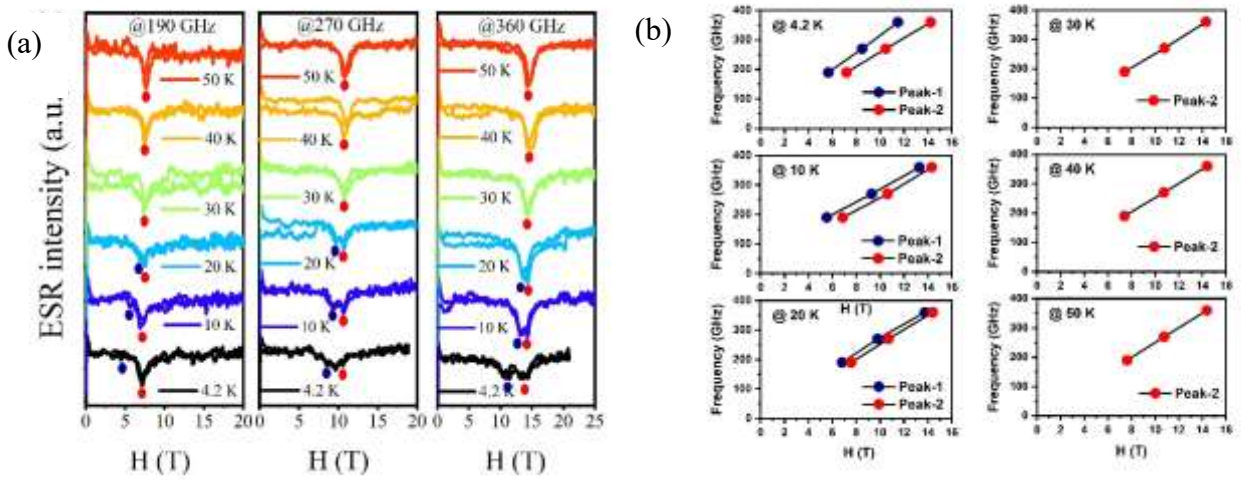


Figure 5. (a) High-field ESR spectra of $Mn_{1.25}Ni_{0.75}Mo_3O_8$ system carried out at various temperature and different frequencies. (b) Frequency-field diagram to estimate magnon gap.

Magnetization measurements on Pulsed field setup in $Fe_{2-x}Co_xMo_3O_8$ (x = 0, 0.1, 0.2) compounds

We have carried out high field dependent magnetization measurements under pulsed field polycrystalline $Fe_{2-x}Co_xMo_3O_8$ (x =0, 0.1, 0.2) compounds up to field limit of 30 T. All measured data is depicted in Fig 6. Figure 6 (a) show a monotonous linear increment on increasing field showing the antiferromagnetic ordering is robust at high field for x = 0. Some distinct features are observed for x = 0.1 and x = 0.2 compounds, where M vs H curves show some anomalous behavior, at low field region, magnetization increase linearly and around 10 T, the nonlinear behavior discernible showing the addition short range ordering or a spin reorientation for these compounds.

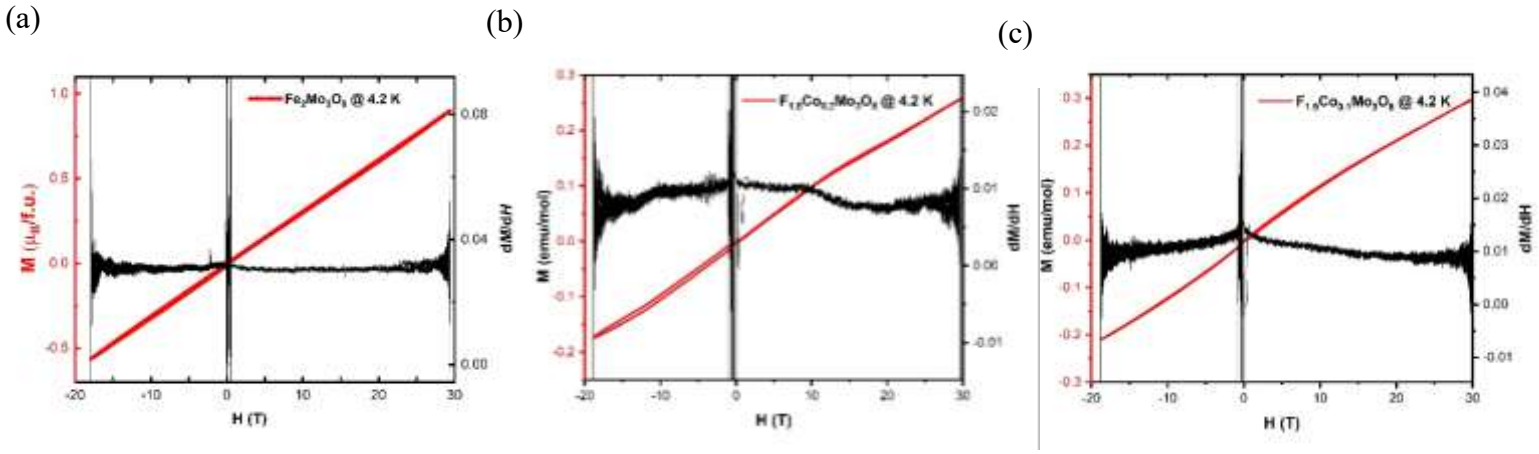
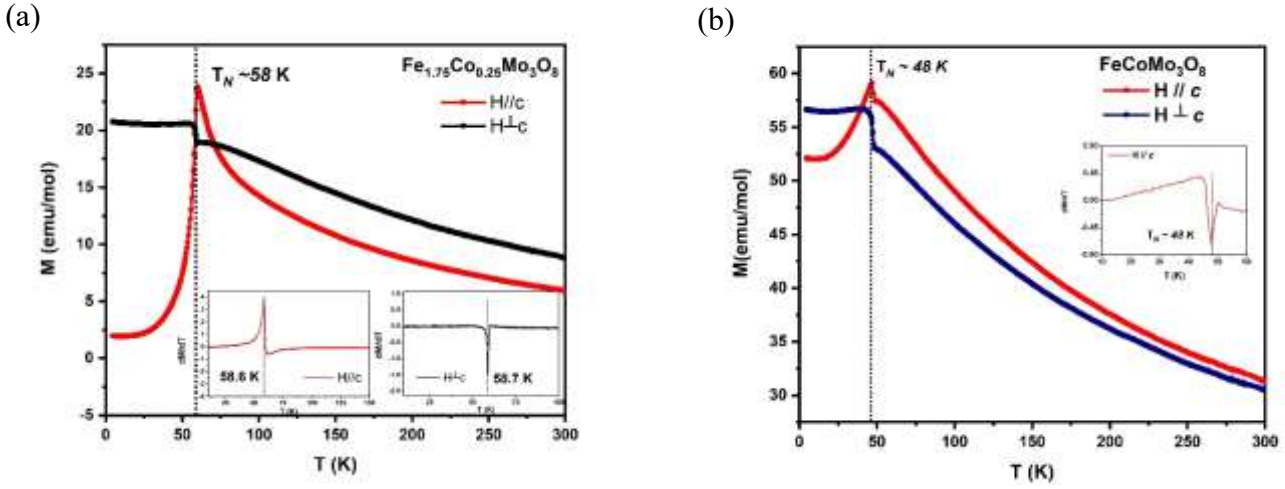


Figure 6. Field dependent magnetization measurements under pulsed magnet of field limit of 30 T on polycrystalline compounds $Fe_{2-x}Co_xMo_3O_8$ (a) x =0, (b) x =0.1 and (c) x = 0.2.

Temperature dependent magnetization measurements on single crystals of $Fe_{2-x}Co_xMo_3O_8$ (x = 0.25, 1)

The temperature dependent magnetization on single crystal of were carried out from 300 -5 K at external field of 0.1 T in H//c and H⊥c configuration. For x = 0.25, the antiferromagnetic ordering is observed at T_N = 58 K and for x = 1.0, spin orders at T_N = 48 K. The negative value of Curie-Weiss temperatures show the robustness of antiferromagnetic ordering.



(c) (d)

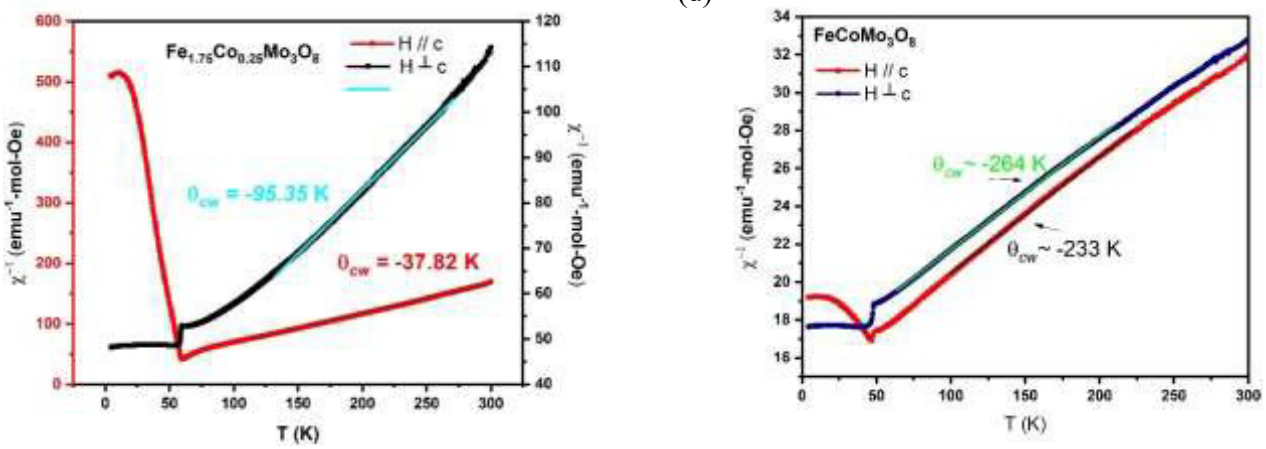


Figure 7. Temperature dependent magnetization measurements at 0.1 T on single crystal of $Fe_{2-x}Co_xMo_3O_8$ (a) x =0.25, (b) x = 1. (c) represents the inverse susceptibility curve as a function of temperature for (c) x = 0.25 and (d) x =1.

So these are the measurements which were carried out on single crystals and polycrystalline compound of $Mn_{2-x}Ni_xMo_3O_8$ and $Fe_{2-x}Co_xMo_3O_8$. at IMR. Tohoku university, Japan. For $Mn_2Mo_3O_8$ compound, the high-field magnetization, polarization and ESR data are analyzed and compiled in the form of manuscript along with the $Fe_2Mo_3O_8$ compound, where magnetization is analyzed and added to this in manuscript. Moreover, rest of the data are being analyzed for further establishments. So far, we have proposed manuscripts based on the measurements are following:

(1) On the Magneto-structural Signatures in $Mn_2Mo_3O_8$ Polar Magnets through high-field ESR and LT-SPXRD studies.

(2) Structural Evolution, High-Field magnetization, Electronic structure and Mössbauer Spectroscopic Studies in Polar Altermagnet $Fe_2Mo_3O_8$.

References:

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[3] Q. Chen, A. Miyake, T. Kurumaji, K. Matsuura, F. Kagawa, S. Miyahara, Y. Tokura, and M. Tokunaga, Phys. Rev. B **109**, 094419 (2024).

Turpu Goverdhan Reddy, Tarun Pratap Singh, Guru Ghasidas Vishwavidyalaya, Bilaspur
E-mail : tg.reddy@ggu.ac.in, tarunpratap96@gmail.com