Spin glass and exchange bias behavior in magnetically frustrated Ni₁₋ $_xMg_xCr_2O_4$ (x = 0.0 - 0.50)

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1	Spin glass and exchange bias behavior in magnetically frustrated
2	$Ni_{1-x}Mg_xCr_2O_4 (x = 0.0 - 0.50)$
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4 5 6	Department of Physics, Indian Institute of Technology Guwahati, Guwahati-781039, India.
7	Abstract: Single-phase polycrystalline samples of $Ni_{1-x}Mg_xCr_2O_4$ (x = 0.0 - 0.50) were prepared
8	by sol gel route and their structural and magnetic properties were studied. Structural
9	transformation from tetragonal $(I4_1/amd)$ to cubic $(Fd\overline{3}m)$ phase is observed at room
10	temperature due to Mg substitution. Mg substitution gives rise to reduction in ferrimagnetic and
11	antiferromagnetic transition temperatures along with a signature of spin glass like phase in
12	samples of intermediate compositions, i.e., for $x = 0.10$, 0.20 and 0.30. <i>The observed stretched</i>
13	exponential type relaxation of thermoremanent magnetization and the highly frustrated
14	magnetic behavior confirm the glassy magnetic phase. Significant increase in exchange bias
15	field under field cooled condition for the Mg substituted samples is observed. The origin of
16	exchange bias in theses samples is explained by considering exchange anisotropy between the
17	ferrimagnetic and antiferromagnetic components of canted spin. The training effect of exchange
18	bias field is also observed.
19	Keywords: Spinel chromite; frustrated magnetism; spin glass; exchange bias.
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1 Introduction:

Frustration in a magnetic system can leads to unique state of magnetic phases [1, 2]. It is 2 interesting to study such magnetic system as it is difficult to predict their behavior. Magneto-3 4 elastic coupling and spin disorder are the two most important phenomena that can take place in a frustrated magnet [3]. If the frustration is strongly connected to atomic lattice, magneto-elastic 5 coupling occurs in order to remove the ground state degeneracy [4]. Chromium based spinels are 6 7 an important class of magnetic materials that show glassy spin structure and several low 8 temperature transitions due to the presence of frustration [5 - 7]. In addition, the investigation of exchange bias (EB) behavior in spinel chromite has drawn considerable research interest due its 9 10 relevance in applications such as magnetic read head and spintronic devices [8 - 10]. In normal spinels with general chemical formula AB_2O_4 the $A^{2+}(Co^{2+}, Ni^{2+}, Fe^{2+} etc.)$ cations occupy the 11 tetrahedral sites, while the $B^{3+}(Cr^{3+}, Fe^{3+}, Al^{3+}$ etc.) cations occupy the octahedral sites [11 - 13]. 12 Spinel chromite ACr₂O₄ with magnetic or non-magnetic A site ion is one of the interesting class 13 of magnetic materials due to several applications in light or heat sensitive micromechanical 14 devices, catalytic material or gas sensors and also due to their interesting magneto-dielectric, 15 16 magneto-elastic, magneto-resistive and multiferroic properties [14 - 17]. In general, these chromites crystallize in cubic crystal structure with space group $Fd\overline{3}m$. However, Jahn – Teller 17 (JT) active ions such as $A = Ni^{2+}$, Cu^{2+} , and Fe^{2+} at tetrahedral sites induce a structural transition 18 from cubic to tetragonal structure [17, 18]. 19

Normal spinel nickel chromite (NiCr₂O₄), which crystallizes in tetragonal crystal 20 21 structure attracts much attention for its rich physical and chemical properties. It is ferrimagnetic 22 (FIM) in nature with Curie temperature $T_c = 70$ K [19]. An additional transition occurring at T_N = 31 K is due the antiferromagnetic (AFM) ordering of the transverse components of magnetic 23 moment [20]. This compound crystallizes in cubic phase at high temperature with space group 24 25 $Fd\overline{3}m$. When lowering the temperature, the symmetry of the nickel chromite decreases to tetragonal at 320 K driven by the cooperative JT effect associated with the Ni²⁺ cations in the 26 tetrahedral position [21, 22]. As a result, despite the presence of pyrochlore lattice formed by 27 Cr³⁺ ions the possibility of frustration is canceled out by the JT distortion. However, with non-JT 28 magnetic A^{2+} (Mn²⁺, Co²⁺) ions the system can survive frustration and can lead to spin glass like 29 spiral ordering [13]. ACr₂O₄ (A = Zn²⁺, Mg²⁺), with a non-magnetic A²⁺ cations can give rise to 30

frustrated AFM [23]. Recently in Ni₉₅Zn_{0.05}Cr₂O₄ short-range glassy behavior, multiferroic 1 properties and magnetostructural coupling have been reported [3]. So, the choice of A site cation 2 3 and the substitution at A site can result in interesting magnetic properties due to the modulation of different exchange interactions between the sublattices. The magnetic structure of NiCr₂O₄ 4 contains two magnetic sublattices at tetrahedral (A) and octahedral (B) sites respectively. Two A 5 sites are grouped into a single sublattice while four B sites are grouped into two sublattices with 6 7 each sublattice having both longitudinal and transverse components of magnetic moment [20]. The AFM exchange interaction among B sites results in magnetic frustration in the system [24]. 8

In this study, we have investigated the evolution of structural and magnetic properties of
 NiCr₂O₄ upon Mg substitution. The observed glassy magnetic phase in the Mg substituted
 NiCr₂O₄ single phase polycrystalline compound can be explained by the presence of magnetic
 frustration and relaxation mechanism, while the field cooled exchange bias (FC EB) behavior
 can be explained by considering competing AFM and FIM components of magnetic moments.

14 **Experimental Details:**

Polycrystalline samples of $Ni_{1-x}Mg_xCr_2O_4$ (x = 0.0 – 0.50) were synthesized by using sol-15 gel method. Stoichiometric ratio of Ni(NO₃)₂ \cdot 6H₂O, Mg(NO₃)₂ \cdot 6H₂O and Cr(NO₃)₃ \cdot 9H₂O of 16 17 99% purity were weighed, dissolved in distilled water and mixed in a beaker. Citric acid and ethylene glycol were added to the solution and the solution was heated slowly to evaporate the 18 solvent, leaving a precipitate. The precipitate was grinded and pre-sintered at 600 °C followed by 19 20 an intermediate sintering at 800 °C. Final sintering was performed at 1100 °C for 24h. For phase identification powder X-ray diffraction pattern was recorded at room temperature using a Rigaku 21 X-ray diffractometer (XRD) (TTRAX III) using Cu-K α ($\lambda = 1.5406$ Å) radiation. The particle 22 size and microstructure of samples were analyzed by recording microstructural images using 23 ZEISS make FESEM (Σ IGMA). The magnetization data were recorded by using Vibrating 24 Sample Magnetometer (VSM) probe installed in Quantum Design Physical Property 25 Measurement System (PPMS) fitted with a superconducting magnet of 9T capacity. 26

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1 Results and Discussion:

Room temperature XRD patterns along with Rietveld refinements are shown in Fig. 1(a-2 3 d). All the samples are in single-phase form with tetragonal structure $(I4_1/amd)$ for x = 0 and cubic structure ($Fd\overline{3}m$) in Mg doped samples. For x = 0 the lattice parameters are found to be a 4 = b = 5.8299 Å and c = 8.4363 Å and they are comparable to earlier reports [22, 25]. All Mg 5 substituted samples exhibit cubic structure with lattice constant varying from a = 8.3186 Å for 6 x = 0.05 to a = 8.3252 Å for x = 0.50 as given in Table 1. The increase in lattice parameters in 7 the Mg substituted cubic systems can be understood in terms of replacement of smaller Ni²⁺(0.55 8 9 Å) ions by $Mg^{2+}(0.57 \text{ Å})$ ions [26]. The structural transformation confirms that some of the JT active Ni²⁺ ions are replaced by JT inactive Mg²⁺ ions such that it drives the system into higher-10 symmetric cubic structure at room temperature. 11





Fig. 1. (a) Room temperature XRD patterns of $Ni_{1-x}Mg_xCr_2O_4(x = 0.0 - 0.50)$ along with Rietveld refinement for (b) x = 0.0, (c) x = 0.50 and (d) magnified view of (113) and (311) peaks.

The FESEM micrographs of the samples are shown in Fig. 2(a - g) and the variation of average particle size with Mg substitution is shown in Fig. 2(h). FESEM micrographs reveal that they exhibit broad particle size distribution over a scale of 50 nm to 850 nm. We have observed a decrease in average particle size with increase in Mg concentration in the present series. The elemental mapping for x = 0.0 and 0.05 (Fig. 3.) confirms the uniform distribution of various elements in the samples. All samples show similar kind of morphology with most of the particles having bi-pyramidal shape.

Susceptibility ($\chi = M/H$) as a function of temperature measured under zero field cooled 1 (ZFC) and field cooled (FC) conditions for an applied field of H = 200 Oe are shown in Fig. 4 & 2 3 5. Samples with x = 0.0, 0.05 and 0.10 show typical FIM behavior while the rest of the samples i.e., for $0.20 \le x \le 0.50$ behave antiferromagnetically. For T < T_c, significant irreversibility 4 between ZFC and FC curves appears indicating the presence of non-collinear ferrimagnetism and 5 canted magnetic moment in x = 0.0 - 0.10 samples. At 10 K for H = 200 Oe, the value of 6 irreversibility in magnetization is found to be $\Delta M/M_{ZFC} = (M_{FC} - M_{ZFC})/M_{ZFC} = 9.72$, for x = 7 0.0 sample. These values for x = 0.05 and 0.10 samples are found to be 11.41 and 22.08 8 respectively. The FIM transition temperature (T_c) values for the samples x = 0.0, 0.05 and 0.10 9 are found to be 70 K, 57 K and 42 K respectively. The T_C value for the parent compound is 10 comparable to that reported in literature [27, 28]. We observed a clear inflection in the χ – T 11 plots of x = 0.0, 0.05, 0.10 samples at 29 K, 27 K and 22 K respectively due to the ordering of 12 AFM component (T_N) of spin structure. In addition to the observed FIM and AFM transitions in 13 x = 0.10 sample, we have observed a step like transition around T_f = 34 K as shown in Fig.4 (d) 14 in an expanded scale. This may be due to the short-range glassy magnetic phase as a result of 15 enhancement of frustration triggered by the substitution of nonmagnetic Mg. 16

From the ZFC and FC susceptibility (χ) curves of x = 0.20 and 0.30 samples, a fall in magnetization value starting from 34 K followed by an enhancement in its value for T < 22 K have been observed as shown in Fig. 5. Recently, similar type of complex magnetic transition has been reported in FIM Ni_{0.95}Zn_{0.05}Cr₂O₄ compound and is explained in terms of short-range glass like magnetic structure due to the canting nature of magnetic moments [3]. However, in our system magnetic behaviors in both x = 0.20 and x = 0.30 samples are dominated by the strong AFM interaction.



Fig. 2: FESEM images of $Ni_{1-x}Mg_xCr_2O_4$ (x = 0.0 – 0.50).

2



Fig 3: Elemental mapping for x = 0.0 and 0.05 samples.

3 Table 1: Structural and Magnetic parameters of $Ni_{1-x}Mg_xCr_2O_4$.

Samples ⇒	x = 0	x = 0.05	x = 0.10	x = 0.20	x = 0.30	x = 0.40	x = 0.50
Parameters							
Lattice	a = b = 5.8299	a = 8.3186	a =8.3206	a = 8.3214	a = 8.3222	a = 8.3248	a = 8.3252
Parameters (Å)	c = 8.4363						
M_0 (emu/mol)	-	-	349.93	1.46	1.27	-	-
M (amy/mal)			9.40	0.45	0.26		
M_{sg} (emu/mol)	-	-	8.40	0.45	0.20	-	-
τ (Sec)	-		750 ± 4	1460 ± 10	685 ± 18	-	-
n	-		0.41	0.37	0.42	-	-
T _C (K)	70	57	42	-	-	-	-
$T_{N}(K)$	29	27	22	19	20	18	17
T _f (K)		-	34	30	29	-	-



Fig. 4: Temperature dependent susceptibility (χ) under zero field cooled (ZFC) and field cooled (FC) conditions for (a) x = 0.0, (b) x = 0.05 and x = 0.10 samples. (d) χ – T plots in the expanded scale in the low temperature region.

5 In order to justify and investigate the nature of glassy magnetic phase in x =0.10, 0.20 and 0.30 samples we have studied the relaxation of thermoremanent magnetization 6 at T = 25 K, i.e., below the spin glass transition temperature (Fig. 6). For this study, the 7 samples were first ZFC to T = 25 K and then a magnetic field of 6 T was applied. After reducing 8 9 the applied field to zero, the remanent magnetization M(t) was measured as a function of time up to t = 10000 s. Glassy magnetic system shows long-lasting magnetization relaxation. Fig. 6 10 (a) & (b) show the normalized magnetization decay $(M(t)/M(t_0))$ for the FIM and AFM 11 samples respectively. Where $M(t_0)$ stands for initial magnetic moment at t = 0 s. It can be 12 13 noted, $M(t)/M(t_0)$ rapidly drops to a nearly constant value for non-spin glass sample, while it



Fig. 5: Temperature dependent susceptibility (χ) under zero field cooled (ZFC) and field cooled
(FC) conditions for x = 0.20, 0.30, 0.40, and 0.50.

4 keeps continuously decreasing for spin glass system [29]. From Fig. 6 it is clear that among 5 all the samples, only x = 0.10, 0.20 and 0.30 samples are showing such kind of glass like 6 relaxation.

7 The time dependent thermoremanent magnetization curve can be well explained by a stretched exponential function $M(t) = M_0 + M_{sg} \exp(-(t/\tau)^{1-n})$ [30]. Here M_0 is related to 8 the intrinsic FIM component and M_{sg} is attributed to the contribution from glassy magnetic 9 phase. The rate of relaxation is defined by the parameters τ and *n*, where *n* lies in the range of 10 0 to 1. The values of all the fitted parameters are presented in Table 1. The fitted values of *n* are 11 considerably smaller than one which indicates that relaxation is due to the activation against 12 13 multiple anisotropy barriers as observed in spin glass system [31]. The relaxation in thermoremanent magnetization suggests that the competition between FIM and AFM coupling 14 15 leads to the spin glass state due to the significant frustration in magnetic system.



Fig. 6: Normalized relaxation of thermoremanent magnetization of (a) x = 0.0 - 0.10 (b) x = 0.20
- 0.50 along with fitted data for (c) x = 0.10, (d) x = 0.20 and x = 0.30.

8

Studying the temperature dependence of inverse susceptibility by using molecular field theory is an excellent approach to understand the magnetic properties. According to molecular field theory of ferrimagnetism for $T > T_C$ the hyperbolic nature of inverse susceptibility can be characterized by the following expression [32, 33],

$$\chi^{-1} = \left(\frac{(T-\Theta)}{C}\right) - \left(\frac{\xi}{(T-\Theta')}\right)$$
(1)

9 Here, the first term is the hyperbolic asymptote in the high temperature region and has a Curie-10 Weiss form and the second term stands for hyperbolic behavior near the FIM transition 11 temperature. We fitted our experimental data to Eq. (1) as shown in Fig. 7 and the fitted 12 parameters are presented in Table 2. A clear kink at T = 232 K observed in the inverse 13 susceptibility curve of x = 0.05 (Fig. 7 b), can be attributed to the decreased JT transition

temperature from 320 K for x = 0 sample due to the substitution of JT inactive Mg²⁺ ions. 1 However, we did not observe any such kink for x = 0.10 sample in the paramagnetic (PM) 2 3 region. Thus, the Mg substituted samples are more stable in the cubic crystal structure at room temperature due to the shifting of JT distortion below the room temperature. In order to fit the 4 inverse susceptibility of x = 0.05 sample we consider the PM region below the onset of JT 5 distortion i.e. for T < 232 K. Here the parameter Θ , is known as the asymptotic Curie 6 temperature and it represents the strength of AFM exchange interaction between Ni²⁺ and Cr³⁺. 7 The characteristic temperature Θ' should be close to T_C [34], which can be seen in our case. The 8 closeness of Θ' and T_C confirms the long-range FIM ordering in these samples. The difference 9 between Θ' and T_C generally gives an idea of broadening of magnetization about FIM 10 transition temperature. With increase in broadening, the magnetic disorder increases and the 11 12 FIM state changes from long-range to short-range order [35]. Although there is an overall FIM ordering in the sample but considerable short-range order can produce spin glass like 13 dynamics below T_C. From earlier reports it is confirmed that magnetic interaction in bulk 14 NiCr₂ O_4 is long range FIM in nature [36], so closeness of Θ' and T_C is expected. However, for 15 x = 0.10, the difference between these two temperatures is distinguishable. The difference can be 16 attributed to the increase in magnetic disorder in the sample. The parameter ξ , in the hyperbolic 17 term represents the curvature in the inverse susceptibility plot. If $\xi \rightarrow 0$, Eq. 1 takes the form of a 18 straight line i.e. the typical Curie-Weiss law. The ξ value is found to decrease with Mg 19 substitution as given in Table 2 and it confirms domination of Curie-Weiss law term. The spin 20 only effective magnetic moment per formula unit of NiCr₂O₄ is 6.16 µ_B which is small as 21 compared to the value obtained from the molecular field theory fitting (6.6 $\mu_B/f.u.$). Though, the 22 angular momentum of the system is largely quenched by the JT distortion at T = 320 K, but some 23 24 contribution from partially quenched orbital magnetic moment cannot be neglected [28, 37]. We have observed a larger effective magnetic moment for x = 0.10 compared to the expected value 25 of $\mu_{eff} = 6.10 \ \mu_B$ per formula unit, which further confirms the unquenched orbital magnetic 26 moment of Ni²⁺ in the tetrahedral sites of cubic structure due to considerable suppression of JT 27 distortion by Mg²⁺ substitution. The electronic configuration of Ni²⁺ in the tetrahedral 28 environment is $e_{a}^{4}t_{2a}^{4}$. Due to the triply degenerate energy levels of t_{2g} caused by the similar 29 shape of orbitals d_{xy} , d_{yz} and d_{zx} one orbital can be transformed into another orbital by simple 90⁰ 30 rotation about proper axis. This orbital motion of electron gives rise the orbital magnetic moment 31

and contribute to the total magnetic moment of the system. In NiCr₂O₄, t_{2g} energy levels split into 1 two energy levels due to the JT distortion taking place just above the room temperature. 2 3 Therefore, the orbital magnetic moment is partially quenched. But with Mg substitution the JT distortion decreases and contribution from the orbital magnetic moment is higher compared to 4 that of NiCr₂O₄. This is one of major possible reasons behind the high value of experimental 5 effective magnetic moment of x = 0.10. In case of x = 0.05, we have fitted the inverse 6 susceptibility data below (T < 232 K) the onset of JT distortion transition temperature and the 7 experimental effective magnetic moment is close to the theoretical spin only magnetic moment 8 (6.13 $\mu_{\rm B}$). Considering spin- orbital coupling in the system the effective magnetic moment of 9 ions can be expressed as $\mu_{eff} = g\sqrt{J(J+1)}$ in the unit of μ_B . With L = 3, S = 1 and g = 5/4 for 10 Ni²⁺ the effective magnetic moment is 5.59 μ_B , while that is for Cr³⁺ is 3.87 μ_B (spin only). 11 Hence, the resultant effective theoretical magnetic moment for x = 0.10 compound is found to be 12 7.62 μ B/f.u. and is close to our experimental value of 7.5 μ B/f.u. 13

From the fitting of inverse susceptibility, we can see the frustration index (f = 16) for x = 0.10 compound is much higher than those of other two FIM samples. So it is possible that such a frustrated magnetic behavior gives rise to glassy state below the transition temperature $T_f = 34 \text{ K}$.

ſ	Sample	Θ(K)	С	ξ	Θ' (K)	$\mu_{eff}(\mu_B/f.u.)$	
			(emu K/Oe	(Oe mol			$f = \left \frac{T_{C}}{T_{C}} \right $
			mol)	K/emu)			
	x = 0.0	-720	5.56	1058	72	6.6	10
-	x = 0.05	-403	4.63	602	61	6.1	7
	x = 0.10	-670	7.14	460	56	7.5	16

17 *Table 2*: Parameters obtained from fitting of inverse susceptibility.

18

Magnetization as a function of applied magnetic field was recorded for all the samples at T = 5 K as shown in Fig. 8(a & b). The unsaturated hysteresis loops for $x \le 0.10$ samples indicate the presence of non-collinear magnetic structure of these compounds. For NiCr₂O₄ the value of spontaneous magnetization (Table 3) is found to be 0.257 μ B/*f.u.* at T = 5 K by linearly extrapolating the high field magnetization to zero field and is comparable to earlier report [38]. The appearance of similar hysteresis loop and comparable coercivity values for x = 0.05 and 0.10

samples confirm the FIM nature of these samples. The observed large value of coercivity indicates the existence of competing AFM component along with a long- range FIM interaction. For $x \ge 0.20$ the predominant linear behavior of M-H curves confirms the strong AFM interaction in these samples. The complete magnetic phase diagram of our system is shown in Fig. 9.





Fig. 7: Fitting of inverse susceptibility with Molecular field theory.



Fig. 8: (a) ZFC M-H curves at 5 K and (b) the magnified M-H loops near coercive field for x ≥
20.



5

Fig. 9: Magnetic phase diagram of Ni_{1-x} Mg_xCr₂O₄ series.

In order to investigate EB effect in these FIM compounds, the magnetic hysteresis loops were recorded at T = 5 K after FC the samples at an applied field of 0.5 T from room temperature. We have observed a shifting of M-H loop for all the samples along the negative H axis as shown in Fig. 10. However, the shifting in the M-H loop for the parent compound is

small as compared to the Mg substituted samples. It is noted that the value of EB field also
 depends on measuring field and FC field. The values of EB field for the samples are presented in
 Table 3.

The shifting of hysteresis loop can be attributed to the presence of competing FIM and AFM moments in the system and can be explained by the model proposed by Tomiyasu and Kagomiya [20]. According to this model A sublattices are classified in to A1 - A2 pairs and B sublattices are classified into B1 - B3 and B2 - B4 pairs for FIM (longitudinal) ordering along [100] and AFM (transverse) ordering along [001].

9

10 *Table 3*: Magnetic Parameters obtained from M-H loops recorded at 5 K.

Sample	H _C (Oe)	$M_{S}(\mu_{B}/f.u.)$	H _{EB} (Oe)
x = 0.00	7384	0.26	91
x = 0.05	8486	0.24	590
x = 0.10	7855	0.23	747

11

In spinel chromite uncompensated magnetic moment can exist due to the magnetic 12 frustration occurring in the octahedral (B) pyrochlore sublattice [39]. In NiCr₂O₄, for T < T_{C_2} A 13 sublattices moment μA (= μ_{A1-A2}) is aligned along the field direction and dominates over the net 14 B sublattices moment μB (= μ_{B1-B3} - μ_{B2-B4}). So, under FC condition far above from the Curie 15 temperature, the net magnetic moment of the sublattices is oriented along the field direction. 16 Therefore, in the first quadrant of the hysteresis loop (initial curve) at a particular temperature, 17 18 the uncompensated magnetic moment contributes to the total magnetic moment in the positive direction. As the direction of magnetic field is gradually reversed (second quadrant), it is quite 19 20 difficult to align μA along the field direction due to the strong AFM interaction with μB . The substitution of nonmagnetic Mg²⁺ ions in the A sites further decreases μA and hence the value of 21 22 μB component becomes quite dominant. As the μB component exerts a torque on the μA of ions, a relatively larger negative magnetic field is required to align the magnetic moment in the 23 reverse direction. This asymmetric behavior in the ascending and descending branches of M-H 24 loop gives rise to shift in hysteresis loop towards the negative field axis. With decrease in 25 temperature the AFM interaction is strengthened and it gives rise to larger exchange bias field 26 27 (H_{EB}) .

Temperature variation of H_{EB} and coercive field (H_C) is studied for x = 0.10 sample 1 with a maximum field of ± 6 T. As shown in Fig. 11 (a), the exponential rise in magnitude of 2 3 H_{EB} with decrease in temperature can be fitted to the exponential function of the form H_{EB} = $H_{EB}(0) \exp(-T/T_1)$. Where, $H_{EB}(0)$ is the value of H_{EB} at T = 0 K and T_1 is a constant. The 4 best fitted parameters are found to be $H_{EB}(0) = 2241 \pm 5$ Oe and $T_1 = 4.99 \pm 0.09$ K. The 5 exponential rise of H_{EB} with decrease in temperature can be undestood by growth of long 6 range AFM ordering and corresponding increase in exchange anisotropy between FIM and 7 8 AFM components at low temprature. The temperature dependance of coercive field (H_c) is found to follow modified Kneller's law [40], $H_C(T) = H_C(0)[1-(T/T_B)^{\alpha}]$. Where, $H_C(0)$ is the 9 coercivity at T = 0 K, T_B is the blocking temperature and α is a constant. In case of 10 nanoparticles (single domain), T_B represent the superparamagnetic blocking temperature and 11 $\alpha = 0.5$. Since, we are dealing with polycrystalline (multi domain) particles, therefore a 12 deviation from original Kneller's law can be expected. From the fitted data as shown in Fig. 13 11 (b), the value of $H_C(0)$ is found to be 10554 Oe. The estimated values of T_B and α are 14 found to be 41.2 K and 0.64 respectively. 15

EB behavior depends on both cooling field (H_{FC}) and maximum measuring field 16 (H_{max}). Fig. 12 (a) & (b) show the variation of H_{EB} for x = 0.10 sample with respect to H_{FC} and 17 H_{max} respectively. In order to study the effect of H_{FC} on H_{EB} , we recorded M-H data after 18 cooling the sample at 0.05, 0.1, 0.5, 1, 3 and 5 T respectively. As shown in the inset of Fig. 12 19 (a), the initial increase in H_{EB} for H_{FC} upto 1 T can be attributed to the consolidation of 20 magnetic domains due to applied higher cooling magnetic field. However, for cooling field 21 $H_{FC} > 1T$ the H_{ER} value decreases due to possible permanent allignment of some of the 22 components of magnetic moment along the field direction, thereby reducing the anisotropic 23 exchange interaction between FM and AFM components. Fig. 12 (b) shows hysteresis loops 24 recorded at various maximum measuring field. For each loop, the sample was cooled down to 25 5 K from room temperature at a field 0.5 T and measurements were carried out in the field 26 ranges $H_{max} = \pm 1, \pm 2, \pm 3, \pm 6$ and ± 9 T. To avoid the training effect, each hystersis loop was 27 recorded after demagnetizing the sample by warming to room tempearture, removing of the 28 stray magnetic field in oscillating mode and field cooling to 5 K again. We have observed a 29 monotonic decrease in H_{EB} with increase in measuring field. For $H_{max} \leq 3$ T, mostly minor 30

- 1 loop is observed with considerable vertical shift in magnetization. The decrease of H_{EB} with
- 2 increase in measuring field can be understood in terms of dominant Zeeman energy which
- 3 overcomes the exchange anisotropy.



5 Fig. 10: Magnetic hysteresis loop recorded at 5 K under ZFC and FC conditions for (a) x = 0.0, 6 (b) x = 0.05 and (c) x = 0.10. Insets show the loop in expanded scale close to H_C.



Fig. 11: Temperature dependence of (a) exchange bias (H_{EB}) and (b) coercivity (H_C) for x = 0.10.



5 Fig. 12: (a) Cooling field (H_{FC}) dependence of exchange bias and (b) the maximum measuring 6 field (H_{max}) dependence of exchange bias for x = 0.10.

Training effect is an interesting characteristics of EB phenomena. The training effect refers to the gradual and monotonous decrease of H_{EB} when the sample is cycled through consecutive hysteresis loops at a fixed temperature. In order to investigate training effect in x = 0.05 compound eight consecutive hysteresis loops (n = 8) have been recorded at 5 K after field cooling through T_C with $H_{FC} = 0.5$ T. Consecutive hysteresis loops are shown in Fig. 13 (a),

where the inset shows the plot in the expanded scale close to M = 0. The observed training effect may be due to relaxation of transverse component (AFM) along an equilibrium configuration by each reversal process. It is found that the variation of H_{EB} with n follows a power law for $n \ge 2$:

$$H_{EB}(n) - H_{EB}(\infty) \propto 1/\sqrt{n}$$
 (2)

5 Where $H_{EB}(\infty)$ is the EB field after infinite number of loops. The value of $H_{EB}(\infty)$ is found to be 6 448 Oe from the fitted data as shown in Fig. 13 (b).



7

4

Fig. 13: (a) Consecutive M-H loops recorded at T = 5 K for x = 0.05 with index n = 1 to n = 8.
Inset shows the loops in expanded scale (b) H_{EB} as a function of n along with fitted data using Eq. 2.

11 Conclusion:

Polycrystalline Ni_{1-x}Mg_xCr₂O₄ (x = 0.0 - 0.5) samples were synthesized by sol gel route. Rietveld 12 refinement of XRD patterns at room temperature confirms the phase purity of the samples and 13 transformation from tetragonal $(I^{4_{1}/amd})$ to cubic $(Fd\overline{3}m)$ crystal structure upon Mg 14 substitution. The magnetic structure of x = 0.10 compound is found to be complex showing 15 16 multiple magnetic transitions. In addition to the long-range FIM and AFM transitions, a spin glass like behavior is observed around $T_f = 34$ K in x = 0.10 sample. No FIM transition is 17 observed for $x \ge 0.20$, except the appearance of glassy magnetic phase for x = 0.20 and x = 0.3018 samples due to the influence of strong AFM interaction. The stretched exponential type magnetic 19 20 relaxation supports the observed glassy phase in the samples. Exchange bias field is found to be

1 enhanced significantly with Mg substitution and is explained in terms of competing FIM and

2 AFM components of magnetic moment. Temperature variations of H_{EB} and H_C were analyzed

3 based on exponential law and modified Kneller's law respectively. Training effect of H_{EB}

4 follows the typical power law behavior.

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9 *References*:

- V. Tsurkan, S. Zherlitsyn, S. Yasin, V. Felea, Y. Skourski, J. Deisenhofer, H.-A. K. von Nidda, J. Wosnitza, A. Loidl, Phys. Rev. Lett., 110 (2013), 115502.
- S. H. Lee, C. Broholm, W. Ratcliff, G. Gasparovic, Q. Huang, T. H. Kim, S. W. Cheong,
 Nature, 418 (2002), 856.
- K. Devi Chandrasekhar, J. Krishna Murthy, J.-Y. Lin, H. C. Wu, W. J. Tseng, A.
 Venimadhav, H. D. Yang, Phys. Rev. B, 94 (2016), 205143.
- 4. S. Bordács, D. Varjas, I. Kézsmárki, G. Mihály, L. Baldassarre, A. Abouelsayed, C. A.
 Kuntscher, K. Ohgushi, and Y. Tokura, Phys. Rev. Lett., 103 (2009), 077205.
- 18 5. M. Nogues and J.L. Dormann, J. Magn. Magn. Mater., 54-57 (1986), 87-88.
- 6. T. G. Aminov, G. G. Shabunina, E. V. Busheva, V. M. Novotortsev, Inorg. Mater., 53
 (2017), 11.
- 7. A. D. LaForge, S. H. Pulido, R. J. Cava, B. C. Chan, A. P. Ramirez, Phys. Rev. Lett., 110
 (2013), 017203.
- 8. S. Guo, X.H. Liu, W.B. Cui, W. Liu, X.G. Zhao, D. Li, Z.D. Zhang, J. Appl. Phys., 105
 (2009), 064702.
- C. Tsang, R.E. Fontana, T. Lin, D.E. Heim, V.S. Speriosu, B.A. Gurney, M.L. Williams,
 IEEE Trans. Magn., 30 (1994), 3801.
- 27 10. J. C. S. Kools, IEEE Trans. Magn., 32 (1996), 3165.
- 28 11. E. prince, J. Appl. Phys., 32 (1961), 685.
- 29 12. G. Ueno, S. Sato, Y. Kino, Acta Cryst. C, 55 (1999), 1963.

- 1 13. K. Tomiyasu, J. Fukunaga, H. Suzuki, Phys. Rev. B, 70 (2004), 214434.
- 2 14. N. Mufti, G. R. Blake, T Palstra, J. Magn. Magn. Mater., 321 (2009), 11.
- 3 15. V. Kocsis, S. Bordacs, D. Varjas, K. Penc, A. Abouelsayed, C.A. Kuntscher, K. Ohgushi, Y.
 4 Tokura, I. Kezsmarki, Phys. Rev. B, 87 (2013), 064416.
- 5 16. A. Maignan, C. Martin, K. Singh, C. Simon, O.I. Lebedev, S. Turner, J. Solid State Chem.,
 6 195 (2012), 41.
- 7 17. K. Singh, A. Maignan, C. Simon, C. Martin, Appl. Phys. Lett., 99 (2011), 172903.
- 8 18. M. Reehuis, M. Tovar, D. M. Többens, P. Pattison, A. Hoser, B. Lake, Phys. Rev. B, 91
 9 (2015), 024407.
- 10 19. S. Klemme, J. C. van Miltenburg, Phys. Chem. Miner., 29 (2002), 663.
- 11 20. K. Tomiyasu, I. Kagomiya, J. Phys. Soc. Jpn., 73 (2004), 2539.
- 12 21. K. Siratori, J. Phys. Soc. Jpn., 23 (1967), 948.
- 13 22. O. Crottaz, F. Kubel, H. Schmid, J. Mater. Chem., 7 (1997), 143–146.
- 14 23. M. C. Kemei, S. L. Moffitt, L. E. Darago, R. Seshadri, M. R. Suchomel, D. P. Shoemaker, K.
 15 Page, J. Siewenie, Phys. Rev. B, 89 (2014), 174410.
- 16 24. B. C Melot, J. E. Drewes, R. Seshadri, E M Stoudenmire and A. P. Ramirez, J. Phys.
- 17 Condens. Matter 21 (2009), 216007.
- 18 25. J. Barman, T. Bora, S. Ravi J. Magn. Magn. Mater., 385 (2015), 93–98.
- 19 26. R. D. Shannon, Acta Cryst. A, 32 (1976), 751.
- 20 27. H. Ishibashi, T. Yasumi, J. Magn. Magn. Mater., 310 (2007), e610.
- 21 28. X. Liu, N. Yin, T. Thomas, M. Yang, J. Wang, Q. Shi, RSC Adv., 6 (2016), 112140.
- 22 29. L. T. Coutrim, E. M. Bittar, F. Garcia and L. Bufaiçal, Phys. Rev. B, 98 (2018), 064426.
- 23 30. D. Karmakar, S. K. Mandal, R. M. Kadam, P. L. Paulose, A. K. Rajarajan, T. K. Nath, A. K.
- 24 Das, I. Dasgupta, G. P. Das, Phys. Rev. B, 75 (2007), 144404.
- 25 31. K. Dey, S. Majumdar, S. Giri, Phys. Rev. B, 90 (2014), 184424.
- 26 32. L. Néel, Ann. Phys., 12 (1948), 137.
- 27 33. E. Winkler, S. B. Canosa, F. Rivadulla, M. A. López-Quintela, J. Rivas, A. Caneiro, M. T.
 28 Causa, M. Tovar, Phys. Rev. B, 80 (2009), 104418.
- 29 34. R. N. Bhowmik, R. Ranganathan, and R. Nagarajan, Phys. Rev. B, 73 (2006), 144413.
- 30 35. D. S. Williams, P. M. Shand, T. M. Pekarek, R. Skomski, V. Petkov, D. L. Leslie-Pelecky,
- 31 Phys. Rev. B, 68 (2003), 214404.

1 2 3	 36. H. Singh, T. Ono, T. Chakraborty, K. Srikanth, A. Venimadhav, R. Chandra, C. Mitra and U. Kumar, J. Nanoparticle Res., 16 (2014), 2354. 37. J. S. Smart, Phys. Rev., 94 (1954), 847.
4	38. N. Mufti, A. A. Nugroho, G. R. Blake, T. T. M. Palstra, J. Phys. Condens. Matter, 22 (2010),
5	075902.
6	39. L. G. Wang, C. M. Zhu, Z. M. Tian, H. Luo, D. L. G. C. Bao, S. L. Yuan, Appl. Phys. Lett
7	107 (2015), 152406.
8	40. N. S. E. Osman and T. Moyo, J Supercond Nov Magn, 29 (2016), 361–366.
9	
10	Highlights:
11	• Polycrystalline $Ni_{1-x}Mg_xCr_2O_4$ (x = 0.0 – 0.50) samples were synthesized by sol gel
12	route.
13	• Spin glass state was observed for the intermediate compositions $x = 0.10, 0.20$ and 0.30.
14	• Relaxation of magnetization, Exchange bias and Training effect were studied.
15	
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17	Conflict of Interest
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19	
20	There are no conflicts to declare.
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22	
23	
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26	Author statement

Ritupan Borah: Visualization, Investigation, Formal analysis, Original
 draft preparation. S. Ravi: Conceptualization, Methodology, Resources,
 Supervision, Reviewing and Editing.

