Complex magnetism, Griffiths-like phase, Large Spontaneous and Conventional Exchange Bias Effect in Eu_2CoMnO_6

Abhijit Nayak[1], Nasiruddin Mondal[2], Devajyoti Mukherjee[2], Krishnamurthy Jyothinagaram[1]

[1]Department of Physics, National Institute of Technology, Andhra Pradesh, Tadepalligudem, abhijit.sclr@nitandhra.ac.in
[2]School of Physical Sciences, Indian Association for Cultivation of Science, Kolkata, West Bengal, psnm2251@iacs.res.in

Rapid quenching of the double perovskite Eu_2CoMnO_6 from high temperatures unveils a frozen B-site disordered state, giving rise to the coexistence of a low-temperature antiferromagnetic (AFM) phase (T_N =13K) and a high-temperature ferromagnetic (FM) phase (T_c = 114K). This magnetic phase separation drives the emergence of a large negative spontaneous exchange bias (SEB) of 1 T and a positive conventional exchange bias (CEB) of 1.5 T under a cooling field (H_{FC} = 7 T) at 2.5 K. Above T_C, persistent ferromagnetic correlations reveal a Griffiths-like phase (GP) with a Griffiths disorder parameter $\lambda = 0.81$. These findings demonstrate how quenched disorder and phase competition can be utilised to engineer robust exchange bias effects in complex oxide systems.

***Index Terms*— Complex magnetism, Griffiths-like phase, Large Exchange Bias Effect, Multiple valences of Co and Mn.**

I. INTRODUCTION

Exchange bias (EB) is pivotal in spintronic devices such as spin valves and magnetic tunnel junctions, where it provides magnetic layer stabilization and controlled spin polarization [1]. EB typically arises from the interfacial coupling between distinct magnetic phases, often requiring the coexistence of ferromagnetic (FM) and antiferromagnetic (AFM) order [2]. Double perovskites like Eu_2CoMnO_6 (ECMO) offer a natural platform for such phase coexistence. In the ordered structure, strong Co^{2+}–O–Mn^{4+} superexchange drives FM behavior, while B-site disorder introduces competing AFM interactions [3], [4]. In this study, rapid quenching of Eu_2CoMnO_6 enhanced B-site disorder, stabilizing a low-temperature AFM phase alongside the intrinsic FM phase. This phase coexistence resulted in the observation of a large negative spontaneous exchange bias (SEB) of 1 T and a positive conventional exchange bias (CEB) of 1.5 T under a cooling field of 7 T at 2.5 K. The simultaneous presence of SEB and CEB within a single material offers significant advantages for spintronic applications, enabling intrinsic magnetic pinning and tunable exchange coupling without the need for complex multilayer structures. High field measurements are being performed to further confirm the intrinsic exchange bias effect.

II. SYNTHESIS DETAILS

Polycrystalline Eu_2CoMnO_6 (ECMO) was synthesized via a conventional solid-state reaction. Stoichiometric amounts of Eu_2O_3 (preheated at 900 °C for 12 hours to remove moisture), Co_3O_4, and MnO_2 were thoroughly mixed, ground, and pressed into 15 mm diameter pellets under 10 MPa pressure. The pellets were sintered in a tubular furnace at temperatures between 900–1300 °C (in 100 °C increments) for 24 hours with intermediate grindings. Final sintering was performed at 1350 °C, followed by rapid quenching to room temperature.

III. PXRD ANALYSIS

Room-temperature PXRD data were analyzed using Rietveld refinement, confirming that all reflections index to the monoclinic space group $P2_1/n$ (SG No. 15) without any impurity phases, as shown in Fig. 1.

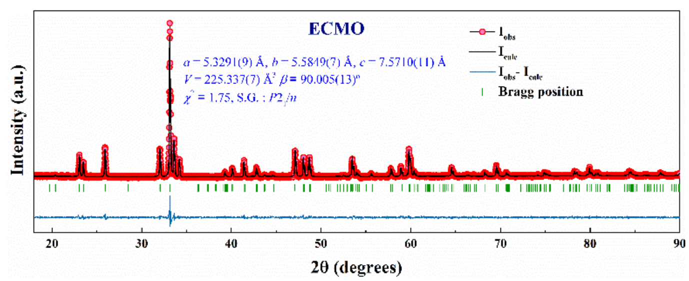

Fig. 1. PXRD pattern of ECMO along with the Rietveld refinement.

IV. XPS ANALYSIS

XPS data were analyzed using XPSPEAK 4.1, and peak deconvolution revealed that Co exists in mixed valence states of Co^{2+} (68%) and Co^{3+} (32%), while Mn shows Mn^{3+} (45%) and Mn^{4+} (55%), as shown in Fig. 2.

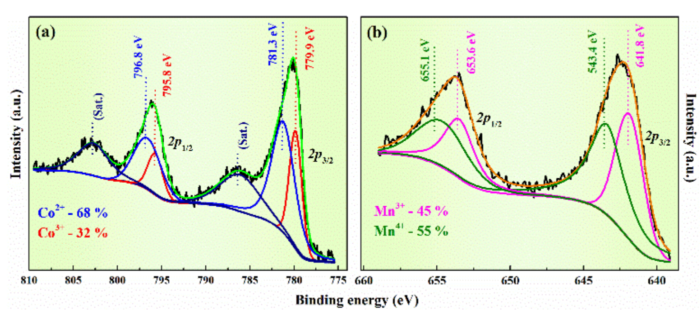

Fig. 2. XPS spectra of (a) Co and (b) Mn with the deconvoluted peaks.

V. MAGNETIC MEASUREMENTS

A. *Temperature-dependent magnetization M (T)*

Fig. 3. (a) shows the M(T) behavior of ECMO under different

magnetic fields. At 100 Oe, the system exhibits conventional ferromagnetism with a transition at 114 K. Under higher fields, an additional AFM/SG-like transition emerges, which is more clearly visible in the d*M*/dT plot as shown in the inset. The magnetic complexity becomes evident in the χ^{-1} vs. T plot, where χ^{-1} follows a linear Curie–Weiss behavior up to 178 K, before showing a downturn and the onset of long-range order at 111 K. Curie–Weiss fitting yields an effective moment μ_{eff} of 7.79 μ_B/f.u. and a positive Weiss temperature θ of 50 K as shown in Fig. 3. (b). The elevated μ_{eff} and lowered θ indicate the presence of FM clusters above T_C and mixed FM–AFM correlations at low temperatures, respectively. The observed downturn behaviour was explained in terms of Griffiths' phase, and the fitting resulted in a disorder exponent (λ) of 0.81 as shown in Fig. 3.(c), further, with the cooling with the high fields the downturn behaviour disappears resulting in a C-W behaviour as shown in Fig. 3 (d) suggesting the presence of GP like phase.

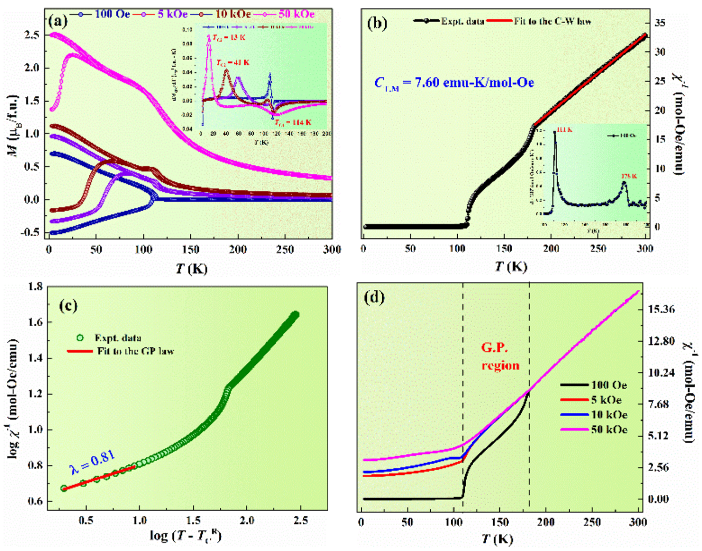

Fig. 3. (a) M (T) of ECMO with different fields, inset showing the dM_{ZFC}/dT, (b) C-W law fit in the high temperature region, (c) Griffith's phase analysis and (d) χ^{-1} with different cooling fields.

B. *Field-dependent magnetization M (H)*

Fig. 4(a) shows the ZFC *M (H)* loop of ECMO measured at 2.5 K, exhibiting a complete shift towards the positive field axis, characteristic of negative SEB. The loop shift, quantified as $H_{EB} = |H_{c1} + H_{c2}|/2$ (where H_{c1} and H_{c2} are left and right coercive fields, respectively), yielded a large H_{SEB} of 1 T at 2.5 K, persisting up to 20 K. To explore CEB, field-cooled *M (H)* measurements were performed after cooling the sample to 5 K under various H_{CF} as shown in Fig. 4(b). The highest negative H_{CEB} of 1.36 T was observed for H_{CF} = 1 T, followed by a decrease at higher fields, attributed to the enlargement of FM clusters and the inverse relation between magnetization and exchange bias, described by

$$H_{EX} = \frac{-J_{EX} \cdot S_{FM} \cdot S_{AFM}}{T_{FM} \cdot M_{FM}} \qquad (1)$$

where J_{EX} is the interfacial exchange coupling, S_{FM} and S_{AFM} are the spins, T_{FM} is the FM layer thickness, and M_{FM} is the magnetization. Temperature-dependent CEB measurements as shown in Fig. 4(c) under H_{CF} = 7 T, reveal that EB emerges near 20 K, as shown in Fig. 4(d), coinciding with AFM/SG ordering, and increases with decreasing temperature, reaching a maximum of 1.5 T at 2.5 K. The onset of EB near the AFM transition suggests pinning of FM spins at the FM/AFM interfaces, requiring additional field for realignment, thus leading to loop shifts.

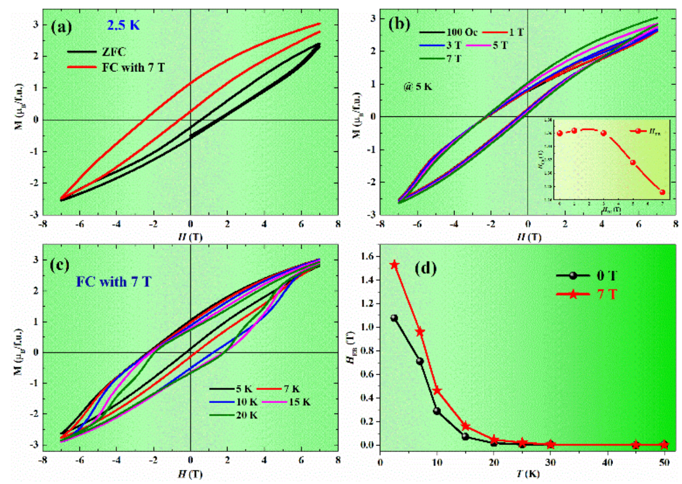

Fig. 4. *M* (H) of ECMO at (a) 2.5 K with ZFC and FC (with 7 T), (b) 5 K with different cooling fields, inset showing the variation of H_{EB} with H_{FC}, (C) with H_{FC} of 7 T at different temperatures and (d) variation of H_{SEB} and H_{CEB} with temperature.

References

[1] R L Stamps, "Mechanisms for exchange bias," J. Phys. D: Appl. Phys. 33 R247, doi: 10.1088/0022-3727/33/23/201

[2] J Nogues and I. K. Schuller, "Exchange bias," J. Magn. Mag. Matr. 192 (1999) 203-232, doi:10.1016/S0304-8853(98)00266-2

[3] R. I. Dass and J. B. Goodenough, "Multiple magnetic phases of $La_2CoMnO_{6-\delta}$ (0<~δ<~0.05)," *Phys. Rev. B*, vol. 67, no. 1, p. 014401, Jan. 2003, doi: 10.1103/PhysRevB.67.014401.

[4] A. Nayak *et al.*, "Effect of Co–Mn Ordering on Defect-Induced Modulation of Complex Magnetic, Metamagnetic, Griffiths Phase, and Exchange Bias-like Behavior of Eu_2CoMnO_6," *J. Phys. Chem. C*, vol. 129, no. 14, pp. 6976–6990, Apr. 2025, doi: 10.1021/acs.jpcc.4c07914.