Uncompensated-spins Induced Weak Ferromagnetism and Magneto-conductive Effects in Ca$_2$Mn$_2$O$_7$

Pooja Sahlot and A.M. Awasthi*

UGC-DAE Consortium for Scientific Research, University Campus, Khandwa Road, Indore- 452 001, India

*awasthi@csr.res.in

Abstract— Temperature dependent magnetization $M(T)$ study on single phase orthorhombic Ruddlesden-Popper manganite Ca$_2$Mn$_2$O$_7$ evidences long range antiferromagnetic (AFM) ordering below 123K. It also features weak ferromagnetic (WFM) character at lower temperatures. Field dependent magnetization $M(H)$ depicts shifted hysteresis loops below ~110K—confirming existence of both WFM and exchange bias, which were studied in detail. WFM is attributed to the formation of uncompensated-spin clusters within the AFM-matrix, stabilized by the high anisotropy in the manganite and featuring Dzyaloshinskii-Moriya (D-M) interaction. Temperature dependence of an averaged effective canting angle from the $M(H)$ loops is obtained, providing a quantitative measure for the evolution of induced WFM. Dielectric measurements carried out on the system exhibit magneto-conductive effects concurrent to the WFM-onset. The parameters describing temperature- & frequency-dependence of ac-conductivity evolve consistently with the magnetic configuration.

Keywords: Ruddlesden-Popper Compounds; Layered Structures; Weak Ferromagnetism; Exchange Bias Effect; Spin Reorientation; AC-conductivity

1. Introduction

Lately, octahedral reorientations in perovskites have been a topic of continuous interest, because of strong coupling with magnetic properties, owing to the structure dependence of exchange interactions between magnetic ions [1]. Exchange bias is one of the interesting magnetic properties with various practical applications [2]. Antiferromagnets (AFMs) possess large anisotropy and ferromagnets (FMs) are known to possess large exchange parameter. Interfacial coupling between these structures gives unidirectional feature to the FM part, by pinning of the FM spins, resulting in shift of the $M(H)$ hysteresis loop referred to as exchange bias (EB) [3]. This pinning is invoked by the uncompensated AFM moments at the interface. After first report discussing field cooled (FC)-EB in bulk manganites possessing dispersed FM regions in AFM base, many bulk systems have been reported showing EB [4, 5]. Apart from FC-EB Sahai et. al. [6] discussed shift in hysteresis loop for systems cooled under no application of magnetic field, referred to as zero field cooled (ZFC)-EB. Further, magneto-electric coupling driven exchange bias has been established in the bulk compensated-AFM BaMnF$_4$ by Zhou et. al. [7], Dong et. al. [8] reported a model for fully compensated AFMs, explaining the EB effect for oxide hetero-structures, stating oxygen octahedron tilting at FM/AFM interface. For compensated AFM interface, pinning effect is suggested to be caused by the D-M interactions and ferroelectric polarization present in the system.

On heading to perovskite-related structure namely Ruddlesden-Popper (R-P) compounds, stronger correlations can be expected, as there is reduction in dimensionality of the network of corner-sharing octahedra. R-P compounds with the general formula $A^{2+}_n B^{4+}O^{2-}_{3n+1}$ are structured as blocks of ‘n’ (integer) number of ABO$_2$ perovskite-like octahedron layers, with intermediary AO layers, where perovskites are pictured for $n=\infty$ [9, 10]. In some $n=2$ R-P compounds, combination of octahedral reorientations has been predicted to introduce mixed magnetic states [11]. Also FM clustering in AFM insulators has been demonstrated in slightly La-doped Sr$_2$Mn$_2$O$_7$ $n=2$ R-P system [12]. Ca$_2$Mn$_2$O$_7$ undergoes phase transition from high-temperature tetragonal crystal structure into low-temperature orthorhombic structure, with introduction of two coupled lattice modes; oxygen octahedron tilting and oxygen octahedron rotation [11, 13]. Nicole et. al. [13] determined from first principles calculations for Ca$_2$Mn$_2$O$_7$ system, to possess G-type AFM ground state, with specified direction of spins, associated with the high crystalline anisotropy [11, 13] in the system. Below the AFM ordering, additional spin-orbit interactions because of the octahedron tilt, were said to give rise to a net spin moment perpendicular to the staggered magnetic vector, estimated at 0.18µB per unit cell [11]. Later, a report on the neutron study of Ca$_2$Mn$_2$O$_7$ established these predictions [14]. Antiferromagnetic transition with Néel temperature ~115K was reported in the compound. Low temperature Neutron diffraction data evidenced weak ferromagnetism (WFM) in the G-type AFM ordering. Transition to the AFM state with $T_N=134K$ in Ca$_2$Mn$_2$O$_7$, along with the emergence of WFM below 100 K, has been shown in its magnetization [15]. Application of Dzyaloshinskii-Moriya criteria [13, 16, 17] shows that the net moment (WFM) results from the oxygen octahedron-tilt distortions. Ca$_2$Mn$_2$O$_7$ shows exchange bias, which signifies D-M interaction induced uncompensated-spin clusters in the AFM-base matrix, on lowering temperature [18]. In the present script, temperature and field dependent magnetization has been investigated for Ca$_2$Mn$_2$O$_7$. Detailed study of EB and WFM characters with temperature has been done. Frequency & temperature dependences of measured ac-conductivity have been analyzed—parametric characterization corroborate the evolution of magnetic configuration.

2. Experimental Details

Practicing conventional solid state synthesis technique, single phase polycrystalline Ca$_2$Mn$_2$O$_7$ was synthesized at 1300 °C using CaCO$_3$ and MnCO$_3$ precursors and structurally characterized by powder XRD using Bruker D8 advance diffractometer with Cu-K$_\alpha$, X-ray radiation ($\lambda=1.5405$ Å), as reported elsewhere [18]. Using a Quantum Design SQUID-VSM, zero-field cooled (ZFC) and field cooled (FC) $M(T)$ and low temperatures $M(H)$ were measured. AC-conductivity measurements were performed using Novocontrol Alpha-A Broadband Impedance Analyzer and Oxford Nanosystems Integra 9T magnet-cryostat.

3. Results and Discussion

3.1. Magnetic properties

Figure.1 (left y-axis) shows zero field cooled (ZFC) dc- magnetic susceptibility ($\chi=M/H$) vs. temperature ($T$) measurement under 100 Oe field for Ca$_2$Mn$_2$O$_7$. Mn-spins’ short-range ordering induced broad hump is observed around 155K, consistent with the published reports [19]. Well-built correlations below 123K induce the long-range AFM ordering. At temperatures well above the AFM ordering, the expected (linear) Curie-Weiss behavior; $\chi=C/(T-\theta)$ is seen in the inverse susceptibility $1/\chi$ vs. temperature plot (fig.1: right/bottom inset). The fitting yields -ve $T$-axis intercept $\theta=C/\chi$, which further confirms the mentioned AFM-ordering, and the Curie constant is found to be $C=0.0217$ K-emu/(gm-Oe). The effective magnetic moment $\mu$ of Mn$^{4+}$ ions is involved in the Curie constant as $C=\mu^2g^2/(3A_mB_h)$, where $N_A$ is the Avogadro number, $B_h$ is the Boltzmann constant, and $A_M$ is the atomic mass of the magnetic ion. Hence obtained value of $\mu=3.09\mu_B$ is fairly close to the theoretically anticipated [20] moment 3.84$\mu_B$ for the Mn$^{4+}$ ions. Temperature dependence of dc magnetic susceptibility $\chi$ shows a change (maximum) in slope at ~110K, below the AFM ordering.
To probe the magnetic character (below AFM transition) of the system in detail, the field dependent magnetization isotherms taken at low temperatures are shown in fig.2(a), (b). Observed maxima in slope of $M(H)$ isotherms ($dM/dH$, descending curve, fig.2(c), (d)) at higher fields ($H_{SR}$) suggest spin reorientations near ~50 kOe. $H_{SR}$ increases beyond $T_N$, reaching a maximum near 75K (fig.2(e)). Barrier-enhancement of field-driven spin reorientation with departure from $T_N$ has been observed in other systems [21]. Decrease in $H_{SR}$ with further cooling below 75K is explained by the established WFM nature, observed in ZFC-$\chi$(T) (fig.1). On lowering temperature below 110K, the system shows clear hysteresis, along with the exchange-bias (EB) effect, as evident from the shift of $M$-$H$ isotherms towards the negative field-direction from the $H$ = 0 center, as reported previously [18]. For a comprehensive analysis presented here, $M(H)$ isotherms were further recorded at yet lower temperatures; albeit, because of their primary AFM nature, hysteretic $M(H)$ loops escape magnetization saturation at high fields. Nonetheless, overlap in descending and ascending curves of the isotherms at high-fields indicates the ‘effective saturation’ of the WFM subsystem [22]. This eliminates the possibility of minor-loop effects under low maximum fields, as unable to reverse the FM moments. Also, here the maximum applied field of 70 kOe is much higher than the observed coercivity ($\leq$ O(800 Oe), fig.2(a)) of the WFM phase. Concurrent appearance of the exchange-bias with the onset temperature of WFM below ~105K suggests their inter-dependence. In the bulk CaMn$_2$O$_4$, nucleation of clusters of uncompensated-spins in the AFM-matrix phase, giving WFM below 110K is claimed [18]. With further cooling, octahedral correlations enhance the growth of short-ranged WFM clusters. Disappearance of large divergence (at 100 Oe) of FC-ZFC $M$-$T$ curves, upon the application of 7T field, hysteresis behaviour in $M(H)$ isotherms, and the small remnant magnetization observed below the ordering temperature, are all consistent with the formation of magnetic clusters of uncompensated moments. EB in CaMn$_3$O$_7$ is a bulk effect; attributed to the pinning of coupled WFM, caused by the D-M interaction. A theoretical work on D-M interaction induced pinning effect has been reported by Dong et. al. [8], supporting the EB effect observed here. Hence, the manifestation of exchange bias in CaMn$_3$O$_7$ is a signature of the D-MI-induced uncompensated-spins clusters, and we further analyze the same as follows.

The coercive field $H_c$ corresponding to the WFM character of the system is obtained from the $M$-$H$ loops shown in fig.2(a) at different temperatures. $H_c$ reduces with the increase in thermal energy, in accordance with the fluctuations induced in the anisotropy-driven spins. With the formation of WFM clusters below ~110K, $H_c(T)$ grows
exponentially on lowering temperature, as shown in fig.2(f).

The exchange bias in the system is characterized by horizontal shift ($H_{ex}$) in $M(H)$ isotherms.

$$H_{ex} = \frac{|H_+ + H_-|}{2},$$

$H_{ex}$ defined as such is obtained from $M(H)$ isotherms (fig.2(a)) for different temperatures. $H_{ex}$ is found to increase almost linearly initially, with lowering of temperature below 110K, which is explained by taking into account thermal consolidation of spins’ canting upon cooling. [23].

At low temperatures, $H_{ex}$ tends to saturate; accordingly $H_{ex}(T)$ fit in fig.2(g) exhibits the power-law dependence as $-\alpha(T-108)^\beta$; the fitted 108K is close to the WFM-emergence temperature.

The behaviour of saturation magnetization with temperature obtained for $M(H)$ isotherms (fig.2 (b)) is also explored. For bulk ferromagnets, well known $T^{1/2}$ law at low temperatures is given by Bloch [24]. Although, for other anisotropic magnetic systems like nanoparticles, modified Bloch’s law with deviation in the value of the Bloch’s exponent $\alpha$ has been suggested as [25]

$$M_s = M_{sat}(1-(T/T_{sat}))^\alpha$$

Here, in our system, best fit for temperature variation of $\alpha$-ve saturation magnetization $M_{sat}(T)$ from their $M(H)$ isotherms, is shown in fig.2 (h) left-axis, with 0K saturation magnetization $M_{sat}=0.97$ emu/gm; ordering temperature $T_{sat}=110K$; and $\alpha =1.01$. Anisotropy in the magnetic structure of the system explains the deviation in the exponent-value (from 3/2), as also reported for other bulk and nano systems [26, 27]. The finite-size effects of WFM clusters and spin-canting effect are deemed to play crucial role in this departure of saturation magnetization behaviour from the original Bloch equation. Also, the averaged spin canting ($\theta_b$) in the system is examined with decrease in temperature, obtained from the ratio of $M_{sat}$ at corresponding temperature to the maximum moment of Mn$^{2+}$ ions in the system, latter evaluated from the C-W fit. The obtained maximum canting angle is an order of magnitude larger than that earlier reported (~0.02°) for the system [19].— probably rooted in the difference in methods for calculating $M_{sat}$. Figure 2 (h) right axis shows the hence obtained values of $\theta_b(T)$, depicting increase in $\theta_b$ with decrease in temperature, replicating the $M_{sat}(T)$-behaviour. The fitted value of $T_{sat}=110K$ for $\theta_b(T)$ and $M_{sat}(T)$ agrees with the WFM-character induced in the system below ~110K, as observed in $M(T)$ data.

The quantitative aggregate of WFM clusters with temperature can be determined from

$$M_{sat} = \mu_{sat} \times n \times o \times n \times VFC$$

This gives the total ‘volume fraction of Mn-clusters’ (VFC), contributing to the WFM. From $M_{sat}(T)$ fit in fig.2 (h), its 0K-value is obtained as 0.97 emu/gm. Using the above equation, approximate volume of Mn$^{2+}$ ions contributing to the WFM is evaluated as 0.89% [24]. Subsequently, the average magnetic moment per unit cell is obtained as twice of the formula-unit mass $M_{sat}$. This imparts 0.12µ/µ/unit-cell for Ca$_3$Mn$_2$O$_7$ in fair order-of-magnitude agreement with the mean-field theoretical estimate of 0.18µ/µ/unit-cell [13].

3.2. Alternating current (ac) and direct current (dc) conductivity

The electrical conductivity in the system is described as the combination of dc- and ac- components [28]. Flat/frequency-independent regime corresponds to the dc-conductivity $\sigma_d$ and frequency dependent part is ac-conductivity, which follows the Jonscher power law: $\sigma_{ac} = \sigma_d + \sigma_{ac}' \omega$ [29]; where $\omega = 2\pi f$ is alternating electric field’s angular frequency, $A$ is pre-exponential factor dependent on temperature, and $n$ is the power exponent whose behaviour w.r.t. temperature describes the mechanism of conductivity in the system. Here, conductivity in the system has been explained using the “universal law of dielectrics”, in appreciable range of temperature and frequency:

$$\sigma(\omega) = \sigma_{dc} + \sigma_{ac}' = \sigma_{dc}' \left[1 + (\omega/\omega_{c})^\gamma \right]$$

With increase in temperature the crossover frequency $\omega_{c}$ from dc- to ac-conduction ($\sigma(\omega_{c}) = \sigma_d$) shifts to higher values. Jonscher fits for $\sigma(\omega)$ plot at different temperatures shown in fig.3(a, b) give temperature dependent exponent $\gamma(T)$ and $\sigma_{dc}(T)$. There have been well established theories explaining ac-conductivity via hopping between pairs of sites. Pollak has explained dependence of the polarizability in a system on energy separation between states in which hopping occurs; along with the hopping distance [30, 31]. In Ca$_3$Mn$_2$O$_7$, evolution in the magnetic state of the system, associated with lattice distortion below 110K, affects the energy distribution of charge carriers in the crystal. And with correlations introduced in the system, multiple hopping of correlated electrons plays a significant role [32]. Here for our system, multiple hopping accounts for the higher values of Jonscher’s exponent observed [33]. Upon induced WFM below 110K, dilution of the correlations increase the temperature dependence of ac-conductivity, as also predicted by Pollak for (un)correlated electron systems [31]. Larger correlation-length for the WFM coupled electrons, therupon counts for the down-step in the Jonscher-exponent below 110K i.e., a decrease in the frequency dependency of ac-conductivity, as shown in fig.3(b)-left/bottom axes. But ferromagnetically-coupled charges show enhanced temperature dependence of $\sigma(T)$, as also observed from the $n(T)$-plot below $T_{WFM}$. At appreciable low frequencies, the Jonscher power-law fitted $\sigma_d$ (plateau region) at different temperatures seems to follow Arrhenius behaviour, as per the equation below; where the slope of $\log\sigma_d-1/T$ yields thermal activation barrier energy (W) for electrical conduction [34].

$$\sigma_d(T) = \sigma_0 e^{-W/k_BT}$$
With disorder in the system, the potential-barriers for charge-hopping get altered, with a manifest change in the activation energy. From \( \log(\sigma_T) - 1/T \) plot shown in fig.3(b)-right/top axes, this change for dc-transport amounts to a band gap reduction across 110K by some \( \approx 8.7\% \).

4. Conclusions

Weak ferromagnetism (WFM) obtained in Ruddlesden-Popper \( \text{Ca}_x\text{Mn}_2\text{O}_7 \) antiferromagnet below 110K has been studied and the temperature dependence of a discernible exchange bias was examined. WFM saturation-magnetization determined from the overlapping ascending/descending \( M(H) \)-branches is seen to follow the modified Bloch’s law, with a temperature exponent \( \alpha_B = 1.01 \). From \( M_{sat}(0K) \) imparting 0.1µunit-cell, an average volume fraction of Mn\(^{4+}\)-ions contributing to the WFM is estimated to be \( \approx 0.89\% \) at 0K.

Electrical conductivity of the system reveals the multiple hopping mechanism, and the abrupt step-change in the Jonscher power-law exponent \( (n) \) — concurrent with WFM-emergence — clearly evidences the magneto-conductive effect in the system. Signatures of the WFM have also been observed in our temperature-dependent structural investigations of the system — manifest as a steep change in the inter-octahedral Mn-O-Mn bond angle near 110K — details of which will be discussed elsewhere.

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