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Metamagnetic behaviour and effect of field cooling on sharp magnetization jumps in multiferroic Y_2CoMnO_6

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Abstract – We present sharp magnetization jumps and field-induced irreversibility in magnetization in multiferroic Y_2CoMnO_6 . The appearance of magnetic relaxation and field sweep rate dependence of magnetization jumps resembles the martensite-like scenario and suggests the coexistence of E^* -type antiferromagnetic and ferromagnetic phases at low temperatures. In Y_2CoMnO_6 , the critical field required for the sharp jump can be increased or decreased depending on the magnitude and direction of the cooling field; this is remarkably different from manganites or other metamagnetic materials where the critical field increases irrespective of the direction of the applied field cooling. The cooling field dependence on the sharp magnetization jumps has been described by considering exchange pinning mechanism at the interface, like in the exchange bias model.

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Introduction. – Metamagnetic materials exhibit a first-order irreversible phase transition between two energetically competing magnetic phases. Recently, the metamagnetic phase transition has received a renewed research attention because of its presence in diversified complex magnetic systems. This phenomenon is manifested by sharp jumps in the magnetization with external perturbations like magnetic field [1], temperature [2–4] and pressure [5]. Technological significance is high when the sharp jumps in magnetization are also associated by abrupt changes in other functional properties like magnetocaloric, magnetostriction and magnetoresistance [6,7]. Experiments have established that these metamagnetic phase transitions are independent of the microstructure and indeed related to the intrinsic nature of the materials [8].

Over the last decade, the magnetic-field-induced metamagnetic phase transition has been studied extensively in various systems like phase-separated manganites [1] and intermetallic alloys such as Nd_5Ge_3 , Gd_5Ge_4 and

CeFe_2 etc. [9–11]. Recently, metamagnetic behaviour has also been reported in some of the well-known multiferroic systems such as BiFeO_3 and phase-separated multiferroic $\text{Eu}_{1-x}\text{Y}_x\text{MnO}_3$ ($x = 0.2, 0.25$) systems; interestingly, a coupling between metamagnetic behaviour and ferroelectric polarization with the external magnetic field has been noticed [12–14]. Though the exact origin of this effect is unclear, several mechanisms have been proposed in different systems, such as the field-dependent orbital ordering in $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Mn}_{0.95}\text{Co}_{0.05}\text{O}_3$ [15], martensitic-like transformation associated with interface strains in phase-separated systems [9–11,16], spin quantum transition in $\text{Pr}_{5/8}\text{Ca}_{3/8}\text{MnO}_3$ [17], geometric frustration in garnets [18], spin reorientation in FeRh thin films [2] and magnetic-field-induced spin flop transition in $\text{Ca}_3\text{CoMnO}_6$ [19]. In charge ordered manganite systems, the field-induced magnetization irreversibility with first-order nature was assigned to the intrinsic magnetic phase separation, *i.e.*, the coexistence of competing magnetic phases in micro/nano length scales [20], where avalanche-like growth of FM clusters in the vicinity of critical magnetic field (H_C) lead to sharp changes in magnetization. On the other hand, in the Heusler alloys the metastability

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has been ascribed to the interplay of martensitic stains among the crystallographic phases; *i.e.* a first-order structural transition from the low-temperature tetragonal martensite to a higher-temperature cubic austenite phase [21]. Such systems exhibit characteristics like, i) isothermal-field-induced sharp magnetization jumps, ii) effect of field cooling on these jumps, and iii) step-like growth in magnetic relaxation with respect to time under critical magnetic field and at constant temperature.

A detailed investigation on the effect of field cooling on sharp magnetization jumps can be found in phase-separated manganites, and some of the rare-earth alloys [10,15,16]. Incidentally, in all the investigations, the magnitude of cooling field increases the critical field required for a sharp jump irrespective of the direction of cooling field, and this issue has not been addressed elaborately in the literature.

Recently, improper magnetic multiferroicity was predicted in Y_2NiMnO_6 and found experimentally in $\text{Lu}_2\text{CoMnO}_6$ and Y_2CoMnO_6 (YCMO) double perovskite systems, where the E^* -type AFM ordering with collinear $\uparrow\uparrow\downarrow\downarrow$ spin structure breaks the spatial inversion symmetry and leads to the spontaneous polarization [22–24]. Such simultaneous existence of both AFM and ferroelectric ordering is of significant interest in data storage and spintronic applications [25,26]. In this report, we present the field-induced sharp magnetization jumps similar to the martensite-like scenario at low temperatures in the YCMO polycrystalline sample. In contrast to other metamagnetic systems, in YCMO, the magnitude of the critical field required for a sharp jump can be changed depending on the magnitude and direction of the cooling field; this has been described based on the exchange bias and interface pinning mechanism.

Experimental results and discussion. – A polycrystalline YCMO sample was prepared by a conventional solid state method, crystal structure, and lattice parameters obtained from the Rietveld refinement match well with the previous report (monoclinic crystal structure with space group $P 2_1/n$ and crystallographic parameters: $a = 5.233 \text{ \AA}$, $b = 5.590 \text{ \AA}$, $c = 7.470 \text{ \AA}$ and $\beta = 89.948^\circ$) [24]. Temperature and magnetic-field dependence of dc susceptibility measurements were done by Quantum Design SQUID-VSM magnetometer. Room temperature and low temperature ($\sim 10 \text{ K}$) X-ray absorption spectra (XAS) of Co- $L_{2,3}$ and Mn- $L_{2,3}$ data collected at the Dragon beam line of the National Synchrotron Radiation Research Centre in Taiwan with energy resolution of 0.25 eV at the Co- L_3 edge ($\sim 780 \text{ eV}$).

Figure 1(a) shows the temperature variation of dc magnetization under zero-field-cooled (M_{ZFC}) and field-cooled warming (M_{FCW}) modes with 0.01 T dc field. A paramagnetic (PM) to FM transition is obtained at 75 K followed by a weak anomaly $\sim 55 \text{ K}$ related to slow spin dynamics [23]. The large irreversibility between FC and ZFC of $M(T)$ data at the onset of magnetic ordering can

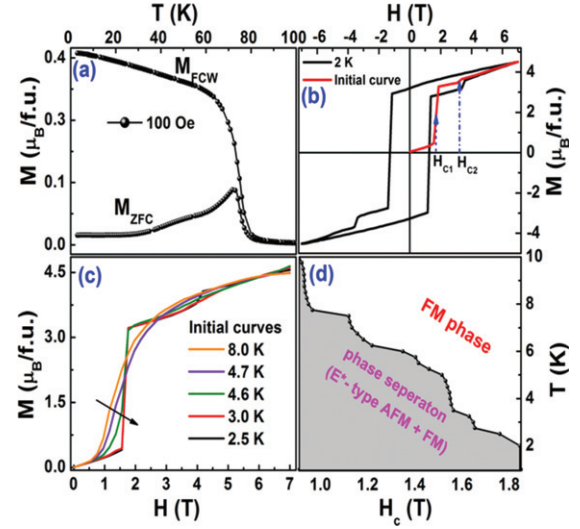


Fig. 1: (Colour on-line) (a) M vs. T data in ZFC, FCW mode for 0.01 T field; (b) isothermal $M(H)$ at 2 K ; (c) virgin branch of $M(H)$ curves at different temperatures; and (d) temperature-dependent magnetic phase diagram obtained from the virgin branch of $M(H)$ curves.

be related to magnetic anisotropy or glassy behaviour. In this regard, we have measured $M(T)$ at different fields (like 1 T , 3 T and 5 T) (not shown here) and magnetic irreversibility near to $\sim 55 \text{ K}$ disappears with the field; this indicates that the observed broad magnetic anomaly is not related to the SG feature [27], rather it is related to the slow dynamics of the domain-wall motion [23]. The M vs. H curve at 2 K is shown in fig. 1(b). It can be seen that the virgin branch of the curve increases with two sharp jumps, one at $H_{C1} \sim 1.86 \text{ T}$ and other at $H_{C2} \sim 2.4 \text{ T}$, respectively. A magnetization of $\sim 4.5 \mu_B/\text{f.u.}$ at a 7 T field has been observed, which is smaller than the theoretically calculated spin only contribution of $\sim 6 \mu_B/\text{f.u.}$ However, in $\text{Lu}_2\text{CoMnO}_6$ single crystalline sample [28], the saturation magnetization has been achieved at moderate fields ($\sim 3 \text{ T}$) in contrast to its polycrystalline sample, where saturation was found at 60 T . This hints at the important role of magnetic pinning forces on the macroscopic magnetism in polycrystalline samples.

As shown in fig. 1(b), an irreversibility with respect to first and second branches of $M(H)$ loops (*i.e.*, field-induced sharp magnetization jumps are not observed during the second cycle, *i.e.*, $H \rightarrow 0 \text{ T}$ case) has been noticed. In fact, irreversibility is one of the common characteristics of metamagnetic systems, yet there is a subtle difference in these behaviours. Based on the nature of the irreversibility behaviour, metamagnetic systems can be classified into two categories. In type 1, the irreversible loop shows zero remanent magnetization with the strong AFM ground state; *i.e.*, CeFe_2 and $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Mn}_{1-x}\text{Co}_x\text{O}_3$ ($x = 0.05$) [11,15]. While in type-2 materials, irreversibility ends up with high remanent magnetization (or permanent transformation to FM state) like Nd_5Ge_3 [9] and YCMO. Moreover, in YCMO the virgin curve prominently

lies outside the $M(H)$ envelope (fig. 1(b)), and the metamagnetic phase transition from E^* -type AFM to FM state is of the first order in nature. The first-order metamagnetic phase transition in YCMO indicates the phase coexistence of E^* -AFM and FM phases and this complements Sharma *et al.*'s work, where magnetic inhomogeneity was probed by neutron diffraction [24]. Though metamagnetic behaviour is present up to 10 K, the abrupt nature of the field-induced transition is apparent only below 4.6 K, as shown in fig. 1(c). Here, the metamagnetic behaviour is a consequence of magnetic phase separation and the phase diagram derived from isothermal magnetization curves is shown in fig. 1(d), where the transition from phase-separated state to FM state can be realized.

Field-induced sharp jumps in multiferroic $\text{Ca}_3\text{CoMnO}_6$ was attributed to the spin flop transition from E^* -type magnetic structure ($\uparrow\uparrow\downarrow\downarrow$) to the $\uparrow\uparrow\downarrow$ Mn^{4+} (high spin $S = 3/2$) at $H_{C1} \sim 11$ T and to $\uparrow\uparrow\uparrow$ with Co^{2+} (low spin $S = 1/2$) spin flop at $H_{C2} \sim 25$ T fields [19]. Similarly, one can speculate the field-induced spin reorientation of Co and Mn ions as the possible origin of the observed metamagnetic behaviour in YCMO. Correspondingly, as shown in fig. 1(b), we have observed a change of $\sim 2.72 \mu_B$ in magnetization at the first jump and, which is close to Mn^{4+} ($S = 3/2$) spin flop transition. However, a small change of $\sim 0.64 \mu_B$ noticed at the second jump is not consistent with the spin flop of Co^{2+} (high spin $S = 3/2$) to the $\uparrow\uparrow\uparrow$ magnetic structure. Therefore, field-induced spin flop may not be a possible origin for metamagnetic behaviour.

Further, we investigate the Co and Mn valence states through the XAS, performed at the Mn and Co- L edges in sample current mode using synchrotron radiation from the 6 m high-energy spherical monochromator (HSGM) beamline at the National Synchrotron Radiation Research Center in Taiwan. In fig. 2, XAS spectra at 300 K and 10 K are shown to establish the spin states of Co and Mn, respectively. As shown in the figure, the Co- $L_{2,3}$ edge peaks (fig. 2(a)) match well with the CoO and Mn- $L_{2,3}$ edges (fig. 2(b)) lie in the same energy position as MnO_2 , confirming the divalent state of Co and tetravalent state of Mn, respectively. The room temperature spectra of YCMO are similar to that of the $\text{LaCo}_{0.5}\text{Mn}_{0.5}\text{O}_3$, and $\text{EuCo}_{0.5}\text{Mn}_{0.5}\text{O}_3$ systems [29,30]. Further, from fig. 2 it can be noticed that the spectral line shape and absorption energies are similar for 300 K and 10 K XAS data, which means that temperature has no effect on the valance state of Co^{2+} and Mn^{4+} . Moreover, based on neutron diffraction results at 4 K on isostructural $\text{Lu}_2\text{CoMnO}_6$ reported by Vilar *et al.*, it is clearly demonstrated that both Co^{2+} and Mn^{4+} ions are in the high-spin state of $S = 3/2$ [23]. This observation precludes the spin state crossover as the possible source for the observed field-induced sharp jumps.

On the other hand, the field-induced metamagnetic transition with sharp jumps in $M(H)$ data could be depicted by the martensite-like scenario. In YCMO, after cooling the sample in ZFC mode, at low temperature,

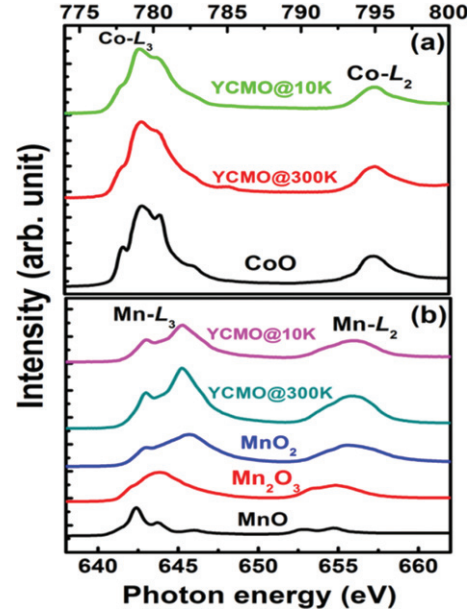


Fig. 2: (Colour on-line) XAS of YCMO at the (a) Co- $L_{2,3}$ and (b) Mn- $L_{2,3}$ edges at 10 K and 300 K with references of Co^{2+}O , Mn^{2+}O , $\text{Mn}_2^{3+}\text{O}_3$ and Mn^{4+}O_2 spectra.

the E^* -type AFM ordering would be dominant along with small FM clusters. In fact in most of the metamagnetic manganites such phase separation has been observed with predominant AFM state [31].

The minor phase of FM nucleation sites grow with the increase of the magnetic field during the isothermal magnetization process, consequently there will be a continuous change in the interface area between FM and AFM matrix. At a critical field, the Zeeman energy of an external field overcomes the magnetostriction energy related to the strain at the FM/AFM domain interface. Such martensitic-strains-related structural distortion can induce a burst-like growth of the FM phase with large magnetization at the expense of AFM domains. And in the martensitic-like scenario, one can expect magnetic spin relaxation phenomena and ramp rate dependence of sharp jumps as discussed below.

The dynamics of magnetic spin relaxation phenomena in the phase-separated YCMO has been done in the vicinity of the critical field. In this protocol, initially the system is brought from PM state to a low temperature (~ 3 K) under ZFC mode, and then by applying a constant magnetic field, magnetization is allowed to evolve with time. Magnetization as a function of time for different magnetic fields (H) is shown in fig. 3(a). Here, for $H < 1.845$ T, $M(t)$ shows a gradual increase with time (inset to fig. 3(a)), while for $H = 1.85$ T, after a certain incubation time, a sudden jump in the relaxation curve with a high value of magnetization can be noticed. In other words, this is the time required for the applied field energy to overcome the magnetoelastic barrier which appears across the co-existing interfaces [1,15]. For $H > 1.85$ T, the magnetization is time independent, which suggests the complete

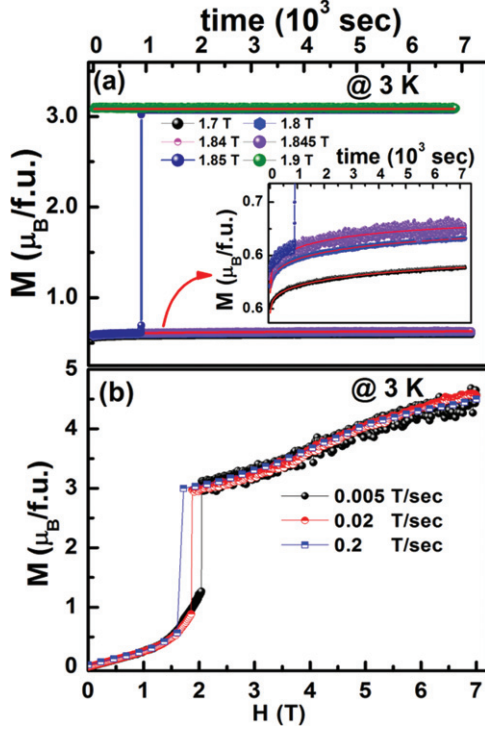


Fig. 3: (Colour on-line) (a) M vs. time at 3 K under different fields in the vicinity of the metamagnetic phase transition (the red line represents the stretched exponential function fit to $M(t)$ data); the inset is the magnified view of the M vs. time; and (b) isothermal initial $M(H)$ curves at 3 K for different field sweep rates.

transformation to the FM state. Further, we have fitted this $M(t)$ data (represented with a solid line) to the stretched exponential function of the form, $M(H, t) = M(H, 0) + [M(H, \infty) - M(H, 0)]\{1 - \exp(-t/\tau)^\beta\}$, where β is the dispersion parameter lying between 0 and 1 and τ is the relaxation time for the magnetic spins, which is related to the energy barrier between metastable states. With increasing applied field, the τ value decreases. A τ value of ~ 5192 s at 1.7 T matches with the phase separated manganite systems [32] and it decreases to ~ 1900 s in the vicinity of $H_C \sim 1.845$ T which indicates the decrease of the energy barrier between the metastable states near the phase transition.

We have also studied the magnetization jumps in YCMO by varying the sweep rate of the magnetic field. In fig. 3(b), under ZFC mode, the first cycle of the $M(H)$ curve recorded for different applied field sweep rates (0.005, 0.02 and 0.07 T/s) is shown. For the lowest sweep rate, the jump is observed at a critical field (H_C) ~ 1.95 T. With the increase of the sweep rate, H_C gets shifted to the lower field side and for 0.2 T/s, $H_C \sim 1.56$ T. For lower sweep rates, the lattice has an adequate time to adapt the induced strains, while for higher sweep rates, like an impulse, strain propagates rapidly and converts to the FM phase [32]. The magnitude of the sweeping field increases the volume fraction of the FM phase at the expense of AFM background.

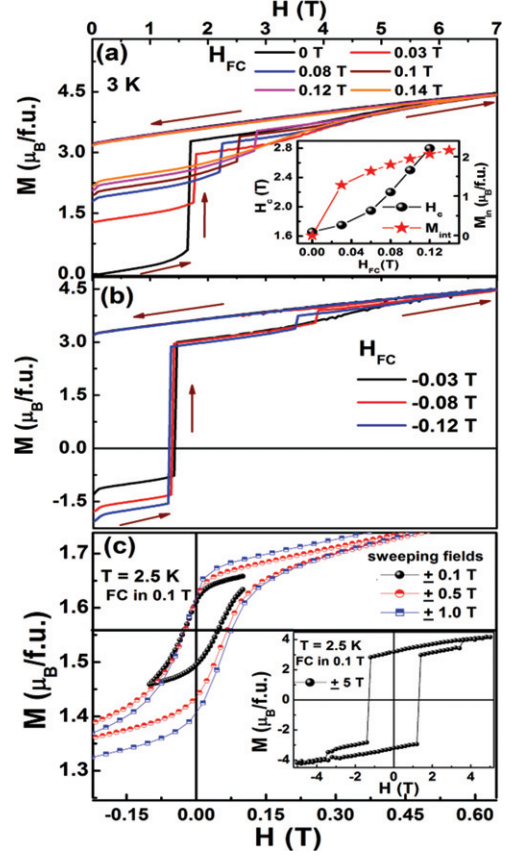


Fig. 4: (Colour on-line) Initial and second branches of the $M(H)$ loop at 3 K under different (a) $+H_{FC}$ and (b) $-H_{FC}$. The arrows indicate the field sweep direction. The inset of (a) shows the variation of the critical field (H_C), and the initial value of magnetization (M_{in}) at 3 K for various $+H_{FC}$ and (c) FC- $M(H)$ loops at 2.5 K with different sweeping fields and its inset shows for ± 5 T sweeping fields.

In metamagnetic systems, the critical field required for a sharp jump often increases with field cooling (irrespective of direction of the applied field). In YCMO, we have measured the first and second branches of the $M(H)$ loop (with constant sweep rate ~ 0.05 T/s), after cooling the system from PM state to 3 K under different field-cooled (H_{FC}) conditions. In fig. 4(a) the results are shown and compared with the ZFC case (*i.e.*, $H_{FC} = 0$ T). On cooling the system under different H_{FC} , a certain volume fraction of the sample is converted to the FM phase, correspondingly the initial magnetization (M_{in}) value at $H = 0$ T increases with H_{FC} as shown in the inset of fig. 4(a). Further, with the increase of H_{FC} , H_C shifts towards higher fields and the variation of both H_C and M_{in} with H_{FC} is nonlinear (inset of fig. 4(a)). This behaviour is in contrast to manganites where, H_C varies linearly with H_{FC} . For $H_{FC} \geq 0.14$ T the magnetization data does not show a sharp jump; instead a gradual variation with the sweeping field is observed. Additionally, we have investigated the dependence of H_C by cooling the sample in the negative fields.

Figure 4(b) shows the first and second branches of the $M(H)$ loop for $H_{FC} = -0.03, -0.08, -0.1$ T. Here, the H_C value is smaller than the ZFC value of 1.845 T and decreases further for higher negative cooling fields. This behaviour is in clear contrast with other metamagnetic systems like $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Mn}_{0.95}\text{Co}_{0.05}\text{O}_3$, where H_C was found to increase with the magnitude of H_{FC} and does not depend on the direction of the cooling field [15]. It can be understood that for type-1 materials, there is no directional dependence of the cooling field, and either direction of the applied field would always increase H_C . While in type-2 systems, due to the remanent magnetization, there exists a clear FM and AFM interface which is responsible for the directional dependence of H_C with H_{FC} . It has been realized that the spin pinning mechanism is likely to be related to the martensitic accommodation of strain across the magnetic interfaces and at H_C the interface overcomes the pinning force by releasing a large strain [33]. Here the cooling field (H_{FC}) modulates the interface spin structure, such that it increases or decreases H_C . The effect is interface driven and resembles exchange bias (EB) phenomena. But the conventional EB effect is absent for the obvious reason that for higher fields during $M(H)$ measurement the entire AFM phase changes to FM and consequently no interface anisotropy exists. However, one can verify the interface exchange coupling after H_{FC} by performing the minor loop magnetization measurements (with sweeping field $< H_C$ in ZFC condition). As shown in fig. 4(c), with the increase of the hysteresis measurement field, the FC hysteresis loop shift towards positive field and magnetization values implies the existence of interface exchange coupling. Further, for sweeping fields larger than ± 1.0 T (*i.e.*, for ± 5 T as shown in the inset to fig. 4(c)), the FC $M(H)$ loop does not show any shift and suggests that the interface coupling (or simply the FM/FM interface) has disappeared.

The field cooling dependence of H_C is reminiscent of a positive EB effect where it is believed that the interface is AFM coupled ($J < 0$) [34]. We have assumed the exchange coupling $J < 0$ at the FM and AFM interface in YCMO to explain the magnetization jump (H_C) in the initial curve with different field cooling conditions (H_{FC}). Figure 5 shows the initial $M(H)$ loops after cooling the system in $H_{FC} = 0$ and ± 0.1 T and schematics of one FM/AFM interface with their initial interface states at $H = 0$ T and final state (at $H = 7$ T). Here, “A” depicts the spin state for $H_{FC} = 0$ with dominant E^* -AFM state with randomly oriented FM clusters. During the first branch, FM clusters start to grow in volume adjacent to the E^* -AFM neighbour with large pinning force. At H_C , the Zeeman energy overcomes the pinning force, and magnetization jumps due to burst-like growth of FM clusters at the expense of AFM domains and converts to FM ordering as depicted in the “F” state. The scenario is different for the field-cooled case, where there exists a remanent magnetization due to the partial conversion to the FM phase due to the increasing number of FM

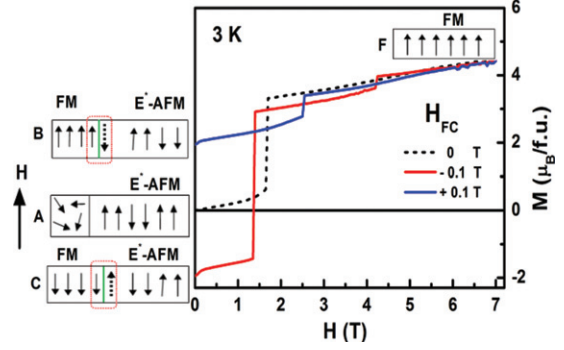


Fig. 5: (Colour on-line) Schematic representation of the resultant interface spin configuration to illustrate the initial and final magnetic states after cooling the system under 0 T and ± 0.1 T.

nucleation sites and their size with H_{FC} and hence a clear FM/ E^* -AFM interface with negative exchange coupling ($J < 0$) such that the interface spin structure is aligned antiferromagnetically with the FM neighbourhood. Now, H_C depends on the sign and strengths of the FM layer, interface spin structure and the external magnetic field. For $H_{FC} = +0.1$ T, as shown in “B” the FM layer is already in the direction of the applied magnetic field while the interface is negatively coupled, and this leads to the interfacial exchange or pinning energy to the total magnetoelastic energy that restrains the magnetization jump. To overcome such a total oppositional force one needs to apply more Zeeman energy in terms of external field which indicates the shifting of the metamagnetic sharp jump towards the high field side. With the increase of H_{FC} , the FM phase grows in volume, and the interface pinning energy also increases, and such a situation leads to a higher critical field H_C .

For $H_{FC} \geq 0.14$ T, the induced FM phase dominates as evidenced from the large $M_{in}(= 2.1 \mu_B/\text{f.u.})$ and magnetization shows a smooth variation. While for $H_{FC} = -0.1$ T, the FM spins are in the opposite direction of the sweeping magnetic field (evident from the negative value of the M_{in}), while the pinned interface spins in the AFM region is in the direction of the applied field as shown in “C” and this favours the magnetization jump. The H_C value depends mainly on the FM Zeeman energy, but this may not vary with H_{FC} . However, with increasing the magnitude of $-H_{FC}$, the critical field shifts towards lower fields due to the proportional increase in the area of the interface that favours the jump. Hence, the induced exchange pinning across the interface of FM/AFM phases is responsible for the shifting of the sharp jump across the metamagnetic phase transition. The model can also be valid for the type-I case, in particular for manganites where there is an evidence of a glassy phase [35]. And this glassy phase recovers after the removal of the magnetic field and the system is back to the situation like the “A” state either before or after the field cooling. However, the number of nucleation sites increases with the magnitude

of the field cooling and hence it increases H_C but remains independent of the direction of the cooling field.

Conclusions. – In conclusion, the field-induced sharp magnetization jumps at low temperatures and magnetization irreversibility with large remanence suggests the magnetic phase separation in YCMO. The time-dependent magnetic relaxation, field sweep rate and field-cooled dependence of sharp jumps are consistent with the martensitic scenario and suggest that such a field-induced phase transition from the E^* -type AFM and FM ordering is of first order in nature. We find that the critical field can be increased or decreased depending on the direction of field cooling. The dependence of H_C on the magnitude and direction of field cooling reveals the role of the interface exchange pinning like in the exchange bias model.

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