Electric field controlled magnetization and charge-ordering in Pr$_{0.6}$Ca$_{0.4}$MnO$_3$

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HIGHLIGHTS

- Modulation of magnetization by electric field in Pr$_{0.6}$Ca$_{0.4}$MnO$_3$ (PCMO) is presented.
- The melting of charge-ordering state in PCMO is possible by applying a small voltage of ≤2.5 V.
- Electric field control of metamagnetic transition is observed in PCMO.
- Low-power spintronics device (e.g., spintronics field effect transistor) can be fabricated by using these materials.

GRAPHICAL ABSTRACT
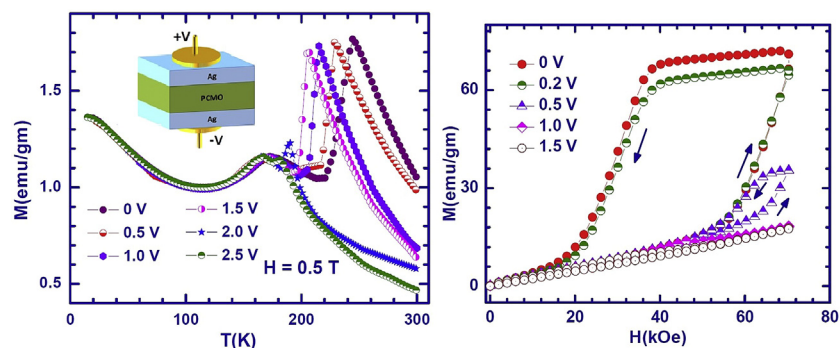
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ABSTRACT

In this paper, we present the observation of the electric field control on the charge-ordering and metamagnetic transitions during the magnetization measurements in a single crystal of Pr$_{0.6}$Ca$_{0.4}$MnO$_3$ (PCMO). We have demonstrated that the complete melting of charge ordering can be realized in a single crystal of PCMO by applying a voltage as small as 2.5 V, which otherwise needs magnetic fields in excess of 11 T. The maximum change in magnetization with applied voltage occurs across the charge-ordering transition temperature (T$_{CO}$ = ~ 235 K). Even though the electric field does not seem to affect the magnetic ordering, we see a clear evidence at low temperatures for the occurrence of the metamagnetic transitions at higher fields with the application of electric field.

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1. Introduction

Mixed valent doped perovskite manganites of the type $R_{1-x}D_x$MnO$_3$ (with R as a trivalent rare earth metal and D as a divalent alkali earth metal) are one of the most studied strongly correlated systems due to the fact that several physical parameters like spin, charge, orbital and lattice interact simultaneously and

result in a variety of physical phenomena including colossal magnetoresistance (CMR), charge/orbital ordering, complex magnetic ordering, etc [1,2]. In addition, the application potential of these manganites is enormous due to which research efforts have been directed towards using these materials in practical devices.

In mixed valent manganites, $Pr_{1-x}Ca_xMnO_3$ (for $0.3 \leq x \leq 0.7$) a charge-ordered insulator (COI) phase exists [2,3], which can be melted into a metallic phase by extrinsic strain i.e., the application of external magnetic [3] fields or electric [4] fields, electromagnetic radiation [5], pressure [6] etc. Tremendous efforts have been devoted to lower the melting magnetic field for charge ordering in $Pr_{1-x}Ca_xMnO_3$ (PCMO) [2–8]. Charge ordering (CO) in manganite is interesting as it competes with double exchange responsible for magnetic ordering and induce numerous interesting properties [7–9]. It is found that the charge ordering of PCMO in some conditions can be destroyed by applying a large magnetic field as up to 40 T [6]. However, it is found that the melting fields can be lowered in PCMO thin films [8]. Extreme research has been going on in manganite to demonstrate electric field effect on colossal magnetoresistance (CMR), electroresistance (ER), magnetic anisotropy and charge-ordered states [4,10–17]. However, in previous researches, mainly transport properties have been studied, but the systematics in term of magnetization were not studied nor a mechanism determined.

In this paper, we present the effect of voltage or electric field on the charge ordering (CO) transition during magnetization measurement in a $Pr_{0.6}Ca_{0.4}MnO_3$ (PCMO) single crystal. For a comparison, the effect of magnetic field on the CO transition in the same PCMO single crystal is also investigated.

2. Experimental

Single crystals of $Pr_{0.6}Ca_{0.4}MnO_3$ (PCMO) provided by the Warwick group [2], were grown using an infrared image furnace by the floating zone method. A rectangular piece (lateral size 1 mm × 2 mm and thickness of 0.5 mm) of the PCMO single crystal was cut from the as grown rod for the present measurements. Top and bottom faces of the sample (across the thickness) were covered with silver pads for electrical connection (see inset of Fig. 1).

Magnetization measurements were carried out using a SQUID Magnetometer (MPMS-XL, Quantum Design Inc). The sample rod was suitably modified to apply the required voltages across the sample from a Keithley Source Meter (Keithley-2602A).

3. Results and discussion

The magnetization measurements were recorded as a function of temperature, magnetic field and applied voltage (electric field) across the sample. In order to make sure that the attachment of the voltage leads does not affect the magnetization measurements, we measured the zero field-cooled (ZFC) and field-cooled (FC) magnetization of $Pr_{0.6}Ca_{0.4}MnO_3$ (PCMO) single crystal as a function of temperature in an applied magnetic field of 100 Oe (0.01 T) with zero applied voltage across the sample. Magnetization of PCMO, as shown in Fig. 1, is almost identical to the reported magnetization [2,7] with a Charge-Ordering (CO) transition (e.g., $T_{CO} = \sim 235$ K) followed by antiferromagnetic ordering transition (i.e., $T_{N1} \sim 175$ K) and canted antiferromagnetic ordering transition (i.e., $T_{N2} \sim 25$ K).

To study the effect of electric field on magnetic/charge ordering transitions, we measured the field-cooled magnetization as a function of temperature in an applied magnetic field of 0.5 T after applying different voltages across the sample, the results of which are shown in Fig. 2. Two interesting features are clearly visible in the magnetization data; (i) the charge ordering temperature (T_{CO})
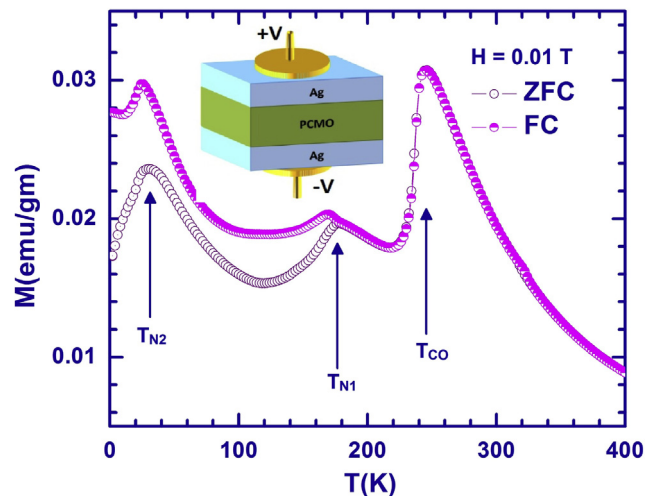

Fig. 1. Zero Field-Cooled (ZFC) and Field-Cooled (FC) magnetization as a function of temperature (T) in an applied magnetic field of 0.01 T for the $Pr_{0.6}Ca_{0.4}MnO_3$ (PCMO) single crystal. Arrows highlight the three transitions, T_{N1}, T_{N2} and T_{CO}. Inset shows the schematic of sample configuration used for magnetization measurements.

shifts drastically (~ 10 K) even for a very small voltage of 0.5 V applied across the sample and (ii) the magnetization decreases with applied voltage in the temperature range, 300 K down to the charge ordering transition temperature. This shifting of the charge-ordering temperature as a function of applied voltage suddenly ceases and the charge ordering disappears altogether for an applied voltage of 2.5 V. Thus, it is clear that the melting of charge ordering occurs for applied voltages ≥2.5 V. It is observed that the T_{CO} decreases linearly at a rate of 20 K/V with increase in voltage as shown in the inset of Fig. 2.

Even though the applied voltage affects the charge ordering, it has no obvious effect in magnetization values at low temperatures (i.e., below 150 K). This is in dire contrast with the effect of the application of magnetic field on the ordering temperatures, as shown in Fig. 3, where we have shown the field-cooled magnetization of the same PCMO single crystal as a function of temperature at different applied magnetic fields starting from 1 T to 9 T.
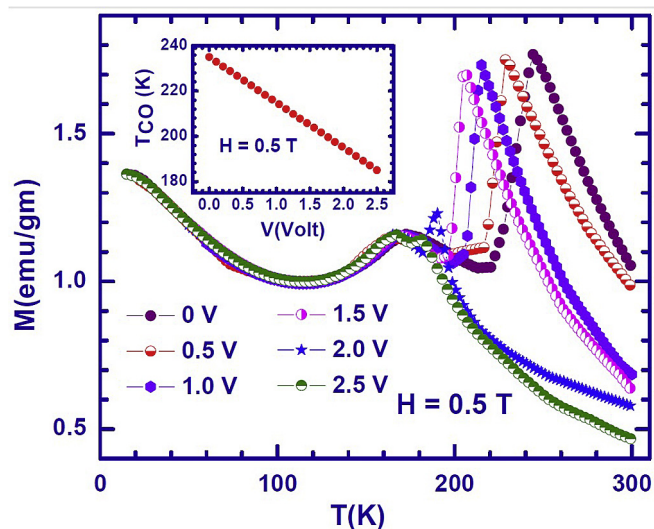

Fig. 2. Field-Cooled (FC) magnetization as a function of temperature (T) in an applied magnetic field of 0.5 T with applied voltage of 0 V, 0.5 V, 1 V, 1.5 V, 2 V and 2.5 V.

It is observed that the two antiferromagnetic transitions at $T_{N1} \sim$ 175 K and $T_{N2} \sim$ 25 K can be altered (melted) by applying large magnetic fields while the charge-ordering transition ($T_{CO} = \sim$ 235 K) cannot be destroyed even after applying a magnetic field as high as 9 T even though the T_{CO} deceases (non linearly) with increasing applied magnetic fields (decreases only by 10% for 9 T, see inset of Fig. 3). The observed shift in charge-ordering transition temperature with magnetic field is in agreement with the observation by N. Biskup et al. [7], where they could observe the vanishing of the charge ordered state only after the application of a magnetic field of ~ 11 T.

The change in magnetization as a function of applied voltage across the CO region is further confirmed through the magnetization measurements as a function of applied field at three different temperatures, 200 K, 225 K and 250 K. Fig. 4, shows the magnetization as a function of magnetic field with different applied voltages of 0 V, 1 V and 2 V, respectively. At 250 K, close to charge-ordering transition (T_{CO}), the change in magnetization as a function of applied voltage is very prominent; magnetization decreases as the applied voltage increases, as expected from the magnetization behaviour shown in Fig. 2. At 200 K, magnetization with applied voltages of 0 V and 1 V are almost same but a decrease in magnetization is observed at 2 V. However, at 225 K magnetization increases with applied voltage of 1 V in comparison with zero applied voltage but a further increase in voltage results in a decrease in the magnetic moment. The changes observed in magnetization as a function of magnetic field (in Fig. 4) at different temperatures with varied applied voltage are consistent with the results observed in the magnetization as a function of temperature (in Fig. 2).

It is well known that PCMO exhibits magnetic field-induced metamagnetic [7,18,19] transition to a ferromagnetic state (FIFM) which persist up to a temperature $T \leq T_{CO}$. The manifestation of metamagnetic transition is a clear signature of the coexistence of the CO-antiferromagnetic (CO-AFM) phases and the ferromagnetic (FM) phases [7,18,19]. It will be now quite interesting to investigate whether the application of an electric field has any effect on these metamagnetic transitions. In order to confirm the occurrence of metamagnetic transitions in our crystal, we first measured the magnetization as a function of magnetic field at one particular temperature (15 K) with zero applied voltage, as shown in Fig. 5. The arrows denote the direction of the magnetic field sweep (0 T $\rightarrow +7$ T $\rightarrow 0$ T $\rightarrow -7$ T $\rightarrow +7$ T). The metamagnetic transition is
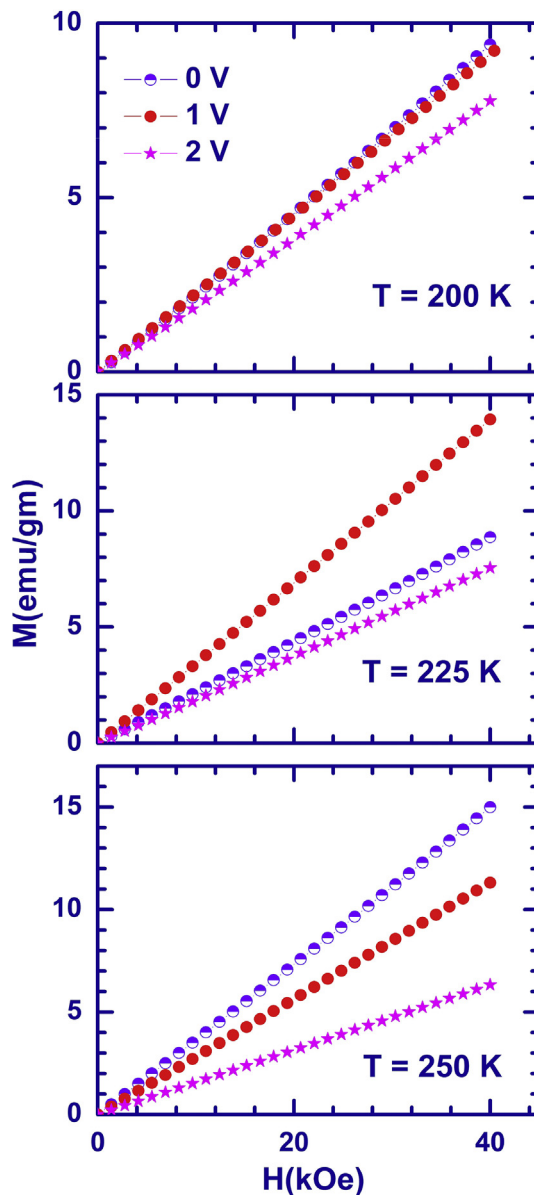

Fig. 4. Magnetization (M) curves of PCMO at 200 K, 225 K and 250 K measured with applied voltages of 0 V, 1 V and 2 V.
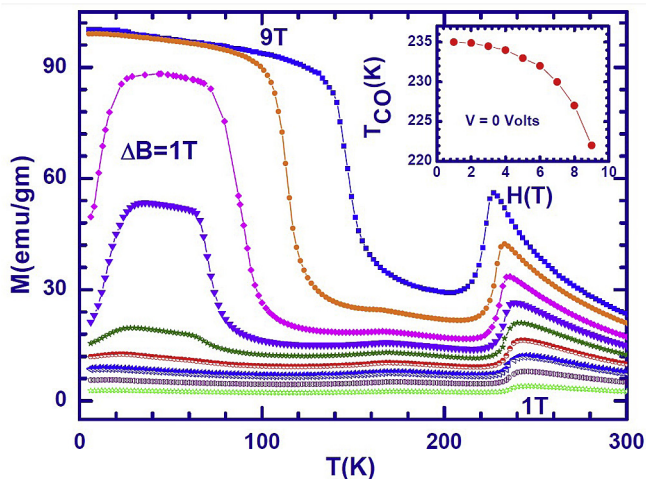

Fig. 3. Field-Cooled (FC) magnetization of PCMO as a function of temperature (T) in applied magnetic fields starting from 1 T to 9 T with $\Delta B = 1$ T.
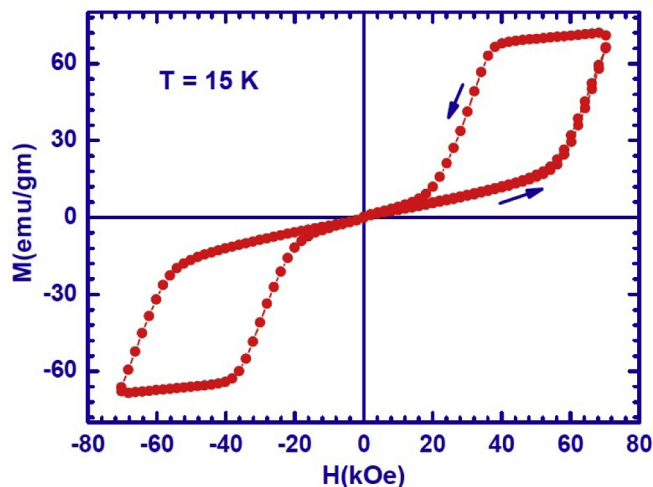

Fig. 5. Magnetization as a function of magnetic field at 15 K with zero applied voltage.
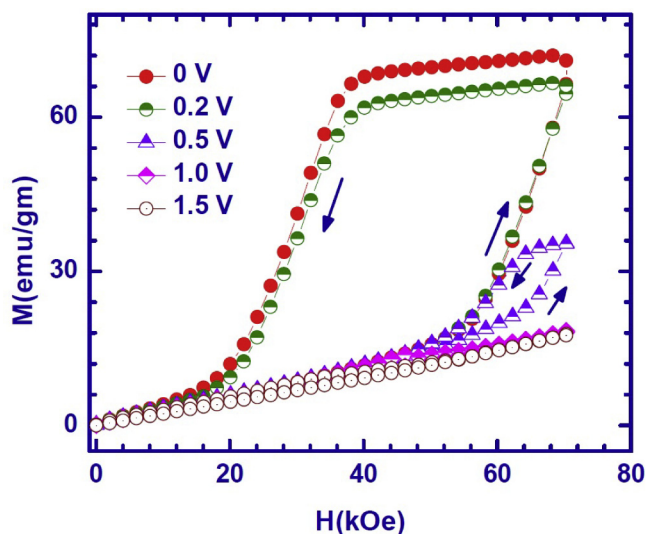
Fig. 6. Magnetization as a function of magnetic field at 15 K with applied voltages of 0.2 V, 0.5 V, 1.0 V and 1.5 V along with that of 0 V for comparison.

clearly visible (H = ~ 6 T). Also, upon reversing the magnetic field, magnetization traces a completely different path. Hence the irreversibility in AFM to FM phase change shows a spin memory effect.

Now, in order to investigate the electric field effect on the metamagnetic transition as mentioned above, we have measured magnetization as a function of magnetic field (for one quadrant) at 15 K with different applied voltages. Fig. 6 shows the variation of magnetization for applied voltages of 0.2 V, 0.5 V, 1.0 V and 1.5 V along with that of 0 V for comparison. It is very interesting to note that even a small voltage as low as 0.2 V is enough to affect the metamagnetic transition. As we increase the voltage, the metamagnetic transition shifts towards higher magnetic fields. For

voltages ≥ 1.0 V, we could observe only the reversible, paramagnetic part, and not any traces of the metamagnetic transition since these transitions might be occurring at fields higher than our measurable field limit (7.0 T.

Further, for a comparative study charge-ordering transition temperature (T_{CO}) as a function of applied magnetic field and as a function of applied voltage is plotted as shown in Fig. 7.

The shift of T_{CO} with applied magnetic field is shown in Fig. 7 (a) and inset shows the derivatives of magnetization (observed in Fig. 3) with different applied magnetic field to highlight the shift in T_{CO}. However, Fig. 7 (b) shows the equivalent shift of T_{CO} with applied voltage and inset shows the derivatives of magnetization (observed in Fig. 2) with different applied voltage to highlight the shift in T_{CO}. The results observed from Fig. 7, allow us to plot applied magnetic field as a function of voltage to find out correspond magnetic field which provide the equivalent shift in T_{CO} as by voltage. Although, magnetic field of 9 T, which is able to shift the T_{CO} to 222 K providing a maximum limit.

The results in this chapter in conjunction with N. Biskup et al. [7], bring in motivating aspects regarding the melting of charge-ordered state and metamagnetic transitions in PCMO. Even with a very small applied voltage of 2.5 V, the charge ordered state can be completely suppressed which otherwise needs a large magnetic field, as large as 11 T. Thus the applied voltage can be considered equivalent to applied fields and a correlation can be brought in as shown in Fig. 8. The reduction in T_{CO} with applied voltage is almost linear, whereas the shift of T_{CO} is nonlinear when the magnetic field is used.

Another interesting observation is that the melting of CO can be achieved without affecting the other magnetic transitions by the application of the voltage (see Fig. 2). Whereas with the application of the magnetic field, the magnetic states below the charge ordering are completely transformed into new magnetic states (see Fig. 3). Even though the applied voltage acts equivalent to the magnetic field in suppressing the charge ordering, the same applied voltage has a contradictory role on the magnetization in the
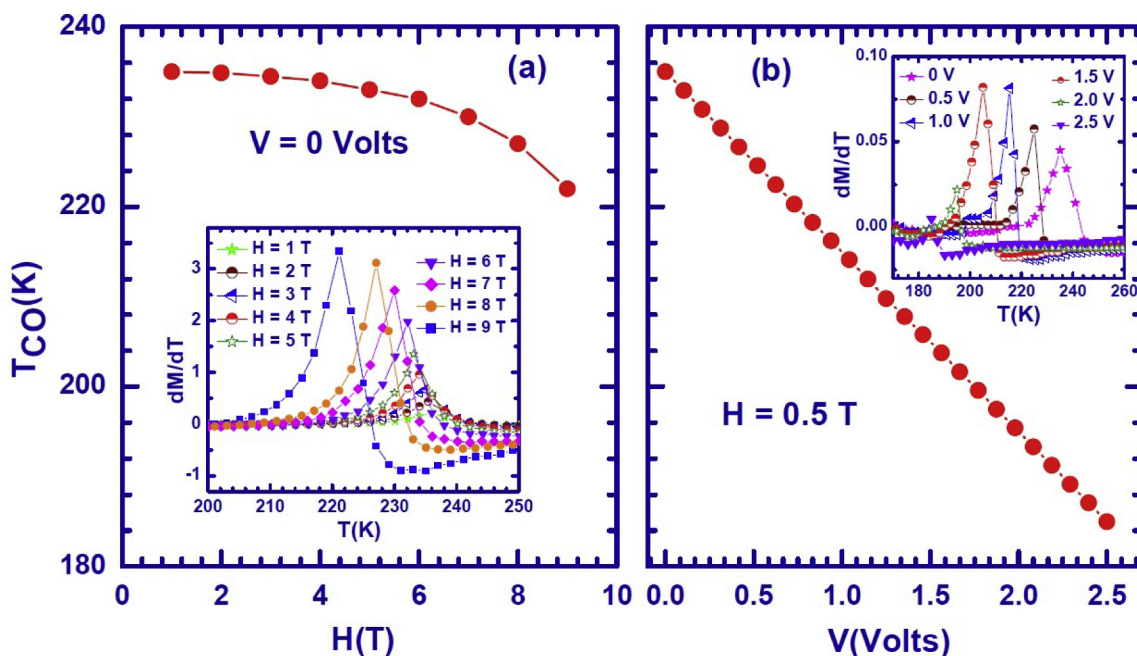

Fig. 7. (a) Charge-ordering transition temperature (T_{CO}) as a function of applied magnetic field and inset shows the derivatives of magnetization with different applied magnetic field to highlight the shift in T_{CO}. (b) T_{CO} as function of applied voltage with applied magnetic field of 0.5 T and inset shows the derivatives of magnetization with different applied voltage to highlight the shift in T_{CO}.
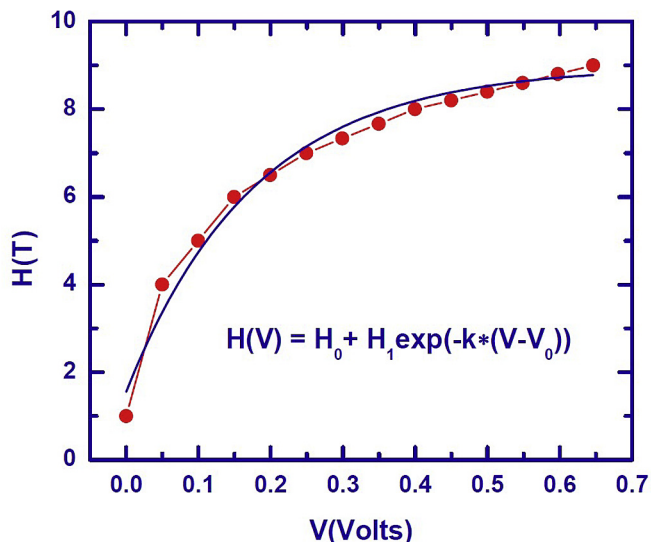
$$H(V) = H_0 + H_1 \exp(-k*(V-V_0))$$

Fig. 8. Voltage as a function of applied magnetic field and blue line shows the fitting of the curve. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

temperature range from 300 K down to the charge ordering temperature, where we observe a decrease in magnetization with the increase in applied voltage.

The exact reason why the magnetization in this region should decrease with the application of voltage is not clear, but may be explained on the basis of reports, where the fluctuation in the charge-ordered states is seen to persist even at temperatures above the room temperature [2,20,21]. Even though there is no clear understanding as to the reason for the melting of charge ordered state, one of the possibilities is the formation of Zener-polarons in PCMO reported by Daoud-Aladine et al. [20]. They observed that the Mn ions remain in an intermediate valence state due to the formation of Mn-Mn dimers, known as Zener-polarons (ZP), which has also been reported by J.-S Zhou et al. [21], for $La_{1-x}Sr_xMnO_3$ system previously. An applied electric field is expected to de-pin the randomly pinned charge carriers within the Mn pairs due to double exchange (DE) and a polaronic-like distortion[13]. The reason for the suppression of metamagnetic states by applied voltages needs further investigations. Low-power spintronics devices (e.g., spintronics field effect transistor) can be fabricated by using these materials as channel material of a prototypical field effect device [22]. Also, it will be interesting to see whether such change in magnetization can also be observed directly by measuring the magnetization of PCMO thin film in the presence of applied gate voltage using insulating or ferroelectric gate [22].

4. Conclusion

In conclusion, we have shown that the magnetization, charge-ordered state and metamagnetic transitions can be tuned by applied electric fields in a PCMO single crystal. We have observed that the charge-ordered state can be completely melted by applying a few volts, which may be attributed to the de-pinning of randomly pinned charge carriers within the Mn pairs due to vibronic electronic states. Low-power spintronics devices (e.g., spintronics field effect transistor) can be fabricated by using these materials as channel material of prototypical field effect devices.

Acknowledgments

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