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Electric field induced collapse of the charge-ordered phase in manganites

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Abstract

The colossal electroresistance in manganites accompanies the insulator-to-metal phase transition induced by the electric field. A phenomenological phase transition model is proposed to study this electric field induced collapse of the charge-ordered phase. The hysteresis of the phase transition is well explained using the effective medium approximation. The volume fraction of the metallic region at the metal-to-insulator transition point is estimated as 30%.

Manganites, a typical class of strongly correlated electron system, have been intensively studied in the last decade due to their unusual behaviours such as colossal magnetoresistance (CMR) [1]. The existence of abundant phases in manganites, which have different macroscopic properties but are all close to each other in free energy, is not only a challenge for basic physical research but also opens up opportunities for potential applications. The phase transition induced by a magnetic field, e.g. from a charge-ordered (CO) antiferromagnetic (AFM) phase to a ferromagnetic (FM) phase, can cause an insulator-to-metal transition (IMT) [2, 3]. However, attempts to utilize the CMR effect have been rather fruitless and an important drawback is that the required magnetic field is too large to realize magnetic storage. In addition, the IMT can be induced by many perturbations other than a magnetic field, e.g. hydrostatic pressure [4] or substrate strain [5], electric field or current [6–11], photon illumination by an infrared laser [12], visible light laser [13] or x-rays [14]. These phenomena open up new approaches for applications of manganites.

Compared to others, the transition switched by an electric voltage or electric current may be more convenient for potential applications. Many experimental studies on the electric effect have argued that there are three main actions on the conduction:

(1) The Joule self-heating effect can raise the local temperature (T) and change the resistivity (ρ) correspondingly since ρ is T-dependent [15–18];

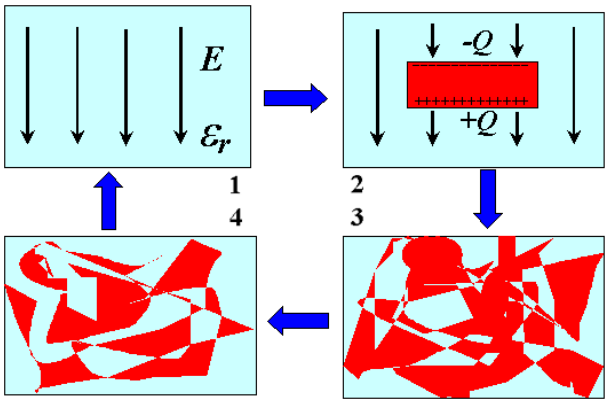

Figure 1. A full cycle of the collapse and rebuilding of the CO state in an electric field. The red (dark) part indicates the conductive FM region while the cyan (light) background stands for the insulated CO AFM matrix. The first/third step is the high/low resistivity state, while the second/fourth step is the upper/lower critical point, respectively.

(This figure is in colour only in the electronic version)

(2) the interface between the metal electrode and perovskite oxide may cause polarity-dependent resistive switching under a pulsed electric field when two-wire measurements are performed [19, 20];
(3) the melting of the CO state can give rise to a colossal negative electroresistance (CER), because the original CO state is insulated while the final FM phase is conductive [7, 8, 11].

The magnitude of the resistivity change in the CER effect is similar to that of CMR. In some cases these actions may coexist and compete with each other.

The CER effect, which was first observed in $Pr_{0.7}Ca_{0.3}MnO_3$ [6], shows a first-order transition feature: an obvious hysteretic region characterized by two distinct critical electric voltages. The upper threshold for turning the high resistivity (HR) state to the low resistivity (LR) state is larger than the lower threshold which prevents the transition from the LR state to the HR state. The upper threshold voltage, which makes the CO phase collapse, decreases with applied magnetic field and is minimized to zero when the magnetic field is strong enough to melt the CO state alone. These phenomena can also be found in other manganites with a CO phase [9–11]. Some theoretical explanations have been proposed, e.g. the depinning of the randomly pinned charge solid [8]. However, our current understanding of the CER effect remains insufficient. In particular it is not clear in theory whether the CO collapse is induced by the electric field or the electric current. And when the CO state collapses and rebuilds remains unpredictable. In this paper, the CER effect will be studied using a phenomenological phase transition model based on the idea of phase separation (PS) and dielectric breakdown [6, 7].

In our model, a bulk CO phase manganite is submitted to a homogeneous electric field E, as shown in figure 1, step 1. The relative dc dielectric constant of this CO phase is ε_r. The energy of the CO phase is lower than the FM phase in zero field. The energy gap between them can be simply estimated as $\mu_0 H_c M_s$, because the material can gain Zeeman energy from the magnetic field for the FM spin arrangement, but none for the AFM spin arrangement. Here μ_0 is the magnetic permeability of vacuum, $\mu_0 H_c$ is the critical value of magnetic field (in tesla) to break the CO state and M_s is the saturated magnetization of the FM state. Considering the FM state of manganites is half-metallic with almost 100% polarization of 3d electrons, M_s (per mol) equals $N_A g_L \mu_B S$, where N_A is the Avogadro number, g_L is the Landé factor of

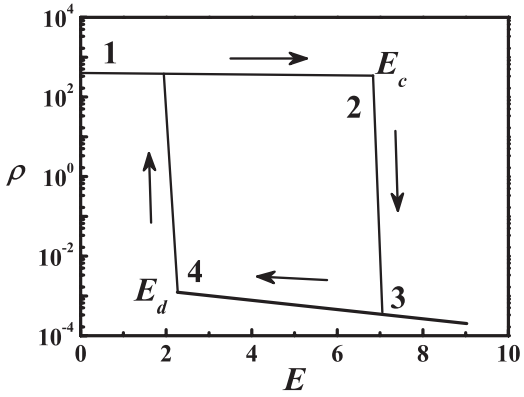

Figure 2. Sketch of resistivity change in a full cycle as a function of electric field, corresponding to the four steps in figure 1. The scale of the axis is just a guide to the eyes.

spin, μ_B is the Bohr magneton and S is the spin momentum of Mn 3d electrons in unit of the Planck constant $\hbar$. Besides magnetic field, electric field can also modulate the system energy. For the AFM CO insulator, charges are mainly localized and dielectric polarization (**P**) can be estimated as $\varepsilon_0\varepsilon_r\mathbf{E}$, where ε_0 is the permittivity of free space. This polarization lowers the energy per volume by $\mathbf{P}\cdot\mathbf{E}$. In contrast, in the FM metal region the carriers are itinerant and can assemble on the surface driven by electric field. These surface charges build an inner field opposing to the external field E, as shown in figure 1, step 2. The existence of the FM region reduces the thickness of the CO region and raises the electric field in the CO phase. This effect leads to a decrease in the polarization energy by $\varepsilon_0\varepsilon_r E^2 V$, as further proved in the appendix, where V is the FM volume. Thus, if a FM region embedded in the CO matrix can be generated, the critical electric field E_c should be enough to fill the energy gap between the CO/FM phase:

$$\varepsilon_0\varepsilon_r E_c^2 V = N_A\mu_0 H_c g_L \mu_B S, \tag{1}$$

where the quantity of the FM phase has been normalized.

From the above equation we obtain $E_c \sim \sqrt{H_c}$, a relationship between the critical electric field and critical magnetic fields to melt the CO phase, which is different from the $E_c \sim H_c$ estimated by Sacanell *et al* [17]. All parameters in equation (1) can be measured under the same conditions. When the electric field E is below E_c, the CO phase is stable against the FM transition. The material remains a poor conductor and is less susceptible to the increasing electric field. However, once E is beyond E_c, some regions in the material will become FM metal. The electric field on the remaining insulated region will be enhanced because the effective thickness of the CO dielectric is decreased. This is a positive feedback process that induces a collapse of the CO phase. Consequently, the percolative conductive paths run through the bulk material, as shown in figure 1, step 3. The system turns to the LR state and the remnant CO regions are short-circuited. The whole process is sketched in figure 1, step 1–2–3, and the corresponding relationship between ρ and E is sketched as the curve 1–2–3 in figure 2. These consequences of our model are consistent with the experimental observations. In experiments, the resistivity shows an abrupt colossal drop when the applied voltage is over a threshold, while below the threshold the conductivity is almost independent of the voltage [6].

Equation (1) can be extended to explain more phenomena in CER. On the one hand, the hysteretic feature is obvious in the electric field induced first-order phase transition. There are two electric field thresholds in a full cycle, which construct an approximate rectangular loop

in the E–ρ diagram, as shown in figure 2. The two critical values correspond to the first-order CO-to-FM/FM-to-CO transitions, respectively. The upper threshold E_c for the IMT transition has already been derived. In the following, the other metal-to-insulator transition (MIT), which occurs when E is turned down to the lower threshold E_d, will be investigated. Since the LR state is an inhomogeneous state with percolating character, the MIT point should be a terminal of the percolation, as shown in figure 1, step 4–1. Here, an effective medium approximation is used to approach the phase coexistence system. Equation (1) is used once more, with ε_r replaced by an effective dielectric constant ε_e. It is reasonable that the existence of metallic regions increases the electric field in the insulated regions and increases the macroscopic dielectric constant, as proved by Kundys *et al* [21]. With this substitution, the following relationship is obtained:

$$\frac{E_c}{E_d} = \sqrt{\frac{\varepsilon_e}{\varepsilon_r}}. \tag{2}$$

In Asamitsu *et al*'s experiment on $Pr_{0.7}Ca_{0.3}MnO_3$ single crystal, the upper threshold of voltage is about 750 V and the lower one is about 250 V (measured at 20 K with a 0.99 mm span between electrodes) [6]. The ratio E_c/E_d is 3. In other words, ε_e is about $9\varepsilon_r$. According to the self-consistent effective medium theory (coherent-potential approximation, CPA), the effective dielectric constant of a two-component mixture system is [22]:

$$\varepsilon_e = \tfrac{1}{4}(P + \sqrt{8\varepsilon_A\varepsilon_B + P^2}), \tag{3}$$

where P is defined as $(3c-1)\varepsilon_A - (3c-2)\varepsilon_B$, ε_A is the dielectric constant of one component with volume fraction c and ε_B is the dielectric constant of the other component with volume fraction $(1-c)$. Although a strict dc dielectric constant for the metal is hard to define, the calculation of the effective dielectric constant needs a value of ε_A. Considering the FM phase of manganites is a bad metal, it remains reasonable to substitute $\varepsilon_B/\varepsilon_A \sim 0$ [21] and $\varepsilon_e = 9\varepsilon_B$ into equation (3). The metal volume fraction c is found to be about 30% on the edge of the MIT (point 4 in figure 2). This fraction is only slightly smaller than the percolative threshold (point 3 in figure 2) of the effective medium theory in a three-dimensional systems, namely 1/3. In experiments, there is an increase in resistivity before the MIT, responding to the slight decrease of the metal volume fraction (from 1/3 to 30%), as sketched in figure 2, curve 3–4. When E is below E_d, the metal state becomes unstable and turns back to the CO state. This first-order phase transition is also a positive feedback process. In addition, if the relation between c and E can be found by other means, the lower threshold E_d can be obtained from equations (2) and (3) by reverse derivation. It should be noted that $\varepsilon_e \sim 200\varepsilon_B$ was found in the CMR process of $Pr_{0.7}Ca_{0.3}MnO_3$ at 10 K [21]. However, this does not contradict our result because the FM persists after the magnetic history [21] enhancing the ε_e while it is absent in the CER loop [6]. The reason for these difference between CMR and CER remains unclear and is beyond the present work.

There is an argument that the CER might be induced by electric current too. This is possible when the polarized carriers in the FM region are pumped into the neighbouring CO region. Then the AFM CO insulator is polarized to the FM metal. However, this idea is incomplete, because the polarized carrier may rebound instead of penetrating at the interface of the AFM region when the driving field (E) is not strong enough. Our work just reveals the threshold E_c, only beyond which the current can flow though the CO region.

Finally, the E_c estimated from our model is compared with the experimental result for $Pr_{0.7}Ca_{0.3}MnO_3$. Using the data $H_c \sim 4$ T [6] and $\varepsilon_r \sim 80$ [23] at 20 K, the calculated E_c is $\sim 10^7$ V m^{-1}, while the experimental value is $\sim 10^6$ V m^{-1} [6]. It seems that the calculated E_c is compatible with the measured one at the same order of magnitude. In fact, considering the simplicity of the model, the quantitative difference between them is not remarkable, and

may be ascribed to the following effects: (1) In experiments, the leakage current can heat the material and raise the local T. In the work of Asamitsu *et al*, T jumped from 20 to 25 K when the CO collapse occurred. Because ε_r is strongly dependent on T [23], the increase of ε_r due to increasing T will reduce E_c. In addition, H_c is also dependent on T [2]. (2) $Pr_{0.7}Ca_{0.3}MnO_3$ is in a spin canted AFM phase rather than a ideal AFM state at low T [2, 21]. In this case, the energy difference between the CO/FM phases would be less than $\mu_0 H_c M_s$ because of the nonzero magnetic moment in the CO phase. (3) Due to the anomalous shapes of the FM clusters, the local electric field may be somewhat larger than the average value at the edge of the phase interface, where point discharge becomes inevitable. Due to its positive feedback feature, the CO will collapse in advance with smaller E_c. If it is possible to consider all those effects a much better agreement between the calculated and measured values of E_c may be obtained. For comparison, the $E_c \sim H_c$ relation given in [17] can also be used to estimate the critical electric field, which is about 10^5 V m^{-1} for $Pr_{0.7}Ca_{0.3}MnO_3$. This field is smaller than the real value in this case. This relation may be more suitable for the LaPrCaMnO series in which PS is natural even without a field. In the case of PrCaMnO, dielectric breakdown may be the main factor in the CER [6, 7]. Certainly, the effect of the electric field on the CO state in manganites is more complicated and various behaviours other than the collapse are also displayed [18]. The present model grasps the main physical features of the high electric field induced CO phase collapse which is one of the most prominent effects in manganites.

In conclusion, we have proposed a phenomenological phase transition model to study the electric field induced collapse of the charge-ordered phase in manganites. The upper and lower critical values for the hysteretic region of electric field induced phase transitions are well explained using the effective medium approximation.

Acknowledgments

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Appendix

For simplification, the AFM CO dielectric is assumed to be a unit area cuboid of thickness d, as shown in figure 1, step 1. The applied voltage between the upper and lower surfaces is U. Therefore, the uniform electric field E is U/d and the polarization energy is:

$$E_P = -\varepsilon_0 \varepsilon_r E^2 d. \tag{4}$$

When an unit area FM slab of thickness d is inserted into the CO medium, the thickness of the CO dielectric becomes $d - a$, as shown in figure 1, step 2. Here the FM phase is metallic and the electric field is zero. Consequently, the electric field in the CO phase above and below the FM slab is increased to $U/(d - a)$. The polarization energy is:

$$E'_P = -\varepsilon_0 \varepsilon_r \left(\frac{U}{d-a}\right)^2 (d-a) = E_P + E_P \frac{a}{d-a}. \tag{5}$$

Since the FM slab is very small ($a \ll d$, so $d \sim d - a$), the energy reduction is $\varepsilon_0 \varepsilon_r E^2 a$. Here the polarization energy in the FM slab is negligible because the electric field in the FM slab is in proportion to $\varepsilon_r/\varepsilon_m$, which is near zero [21].

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