Relaxation effects in the charge-ordered state of La$_{0.5}$Ca$_{0.5}$MnO$_3$

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We report an experimental study of the time dependence of the resistivity and magnetization of charge-ordered La$_{0.5}$Ca$_{0.5}$MnO$_3$ under different thermal and magnetic field conditions. A relaxation with a stretched exponential time dependence has been observed at temperatures below the charge ordering temperature. A model using a hierarchical distribution of relaxation times can explain the data.

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Recently, mixed-valent perovskite manganese oxides (A$_{1-x}$B$_x$MnO$_3$: A = La, Pr, Nd; B = Ca, Sr, Ba) have stimulated a great deal of research interest due to their remarkable electronic and magnetic properties. An interplay among the charge carriers, magnetic coupling, orbital ordering and structural distortion leads to a variety of physical properties ranging from ferromagnetic (FM) metal to antiferromagnetic (AFM) charge-ordered (CO) insulator depending on the concentration of doping (x), temperature, and magnetic field. According to the phase diagram, at low temperatures La$_{1-x}$Ca$_x$MnO$_3$ is a FM metal for 0.17 < x < 0.5 and an AFM charge-ordered insulator for 0.5 < x < 0.88. The region of Ca doping in the vicinity of x = 0.5 is of special interest because a commensurate (1:1) charge ordering of Mn$^{3+}$ and Mn$^{4+}$ ions occurs at low temperatures. This charge ordering can be destroyed (“melted”) by the application of a modest magnetic field, resulting in a FM metallic state.

Surprisingly, the strength of this “melting” field is an order of magnitude smaller than the charge ordering temperature (T$_{CO}$) on the energy scale. Also the CO manganites (at x = 0.5) exhibit a memory effect. For example, once driven into a metallic state by application of a magnetic field, La$_{0.5}$Ca$_{0.5}$MnO$_3$ tends to retain the metallic state even if the magnetic field is removed. Moreover, a fine balance between the kinetic energy and the Coulomb repulsion of the charge carriers in the presence of magnetic field results in an electronic phase separation (the coexistence of the FM metallic and AFM CO phases) for certain values of magnetic field and temperatures. A detailed understanding of the “melting” of the CO state and the electronic phase separation is lacking at present. In an effort to better understand the dynamics of the competing interactions in charge-ordered La$_{0.5}$Ca$_{0.5}$MnO$_3$, we present here a study of the relaxation of the magnetization and resistivity under various field and temperature conditions.

Polycrystalline samples of La$_{0.5}$Ca$_{0.5}$MnO$_3$ and La$_{0.47}$Ca$_{0.53}$MnO$_3$ were prepared from stoichiometric amounts of La$_2$O$_3$, CaCO$_3$ and MnCO$_3$ by a standard solid-state reaction technique. X-ray powder diffraction and neutron diffraction show a single-phase structure with no detectable impurity phases. Magnetization was measured with a commercial SQUID magnetometer, and resistivity was measured by a standard 4-probe technique.

At the charge ordering temperature (T$_{CO}$ = 150 K) the resistivity of La$_{0.5}$Ca$_{0.5}$MnO$_3$ increases sharply to a large, insulating value at low temperature (Fig. 1a, H = 0 curve). From magnetization and neutron scattering we find that the onset of the charge ordering is accompanied by a transition to the antiferromagnetic state. As shown in Fig. 1a, application of a 5 T magnetic field to zero field cooled (ZFC) La$_{0.5}$Ca$_{0.5}$MnO$_3$ has little effect on the resistivity. On the contrary, if the sample is cooled in a magnetic field of 5 T, the resistivity of the sample is lower than the zero field value by several orders of magnitude. This suggests that the charge ordering is partially destroyed by cooling down in a magnetic field. All these results are in agreement with prior work.

The time dependencies of the resistivity and magnetization were studied after the following types of magnetic and thermal treatments: Path 1 - the sample was cooled in a magnetic field, then the field was decreased to zero; Path 2 - the sample was cooled in zero magnetic field, then the magnetic field was increased to the required value; Path 3 - the sample was cooled in zero magnetic field, the magnetic field was applied, then the magnetic field was decreased to zero. In Fig. 1b we show the time dependence of the resistivity (ρ(t)) of La$_{0.5}$Ca$_{0.5}$MnO$_3$ taken after the sample was cooled to 12 K in a field of 5 T and the field was then switched off (Path 1). The data were taken during approximately 27 hours. The change in resistivity during this process from the starting point (1) to the ending point (2) is shown in Fig. 1a as 1 → 2. The field cooled (FC) state appears to be a metastable state, because the resistivity does not return to the zero field value when the magnetic field is switched off, but rather relaxes slowly with time nonexponentially. A logarithmic time dependence can fit some portions of the relaxation curve, but cannot fit the entire ρ(t) curve. We found that the time dependence of the resistivity can be fit with a stretched exponential dependence (Fig. 1b):

$$\rho(t) = \rho_2 + (\rho_1 - \rho_2)exp[-(t/\tau)^\beta]$$

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where $\rho_1 = 446 \pm 2 \text{ ohm-cm}$, $\rho_2 = 2.135 \pm 0.005 \text{ ohm-cm}$, $\tau = 34700 \pm 400 \text{ sec}$, and $\beta = 0.330 \pm 0.001$.

When La$_{0.5}$Ca$_{0.5}$MnO$_3$ is cooled in zero applied magnetic field and then 8.5 T is applied, the resistivity decreases by many orders of magnitude, but does not reach the value obtained when cooling in 8.5 T (see Fig. 2a).

Following this procedure (Path 2), the resistivity of the sample continues to decrease as shown in Fig. 2b. This time dependence can also be fit with a stretched exponential dependence (Eq. (1)) with the following values of the parameters: $\rho_1 = 10.6 \pm 0.2 \text{ ohm-cm}$, $\rho_2 = 109 \pm 2 \text{ ohm-cm}$, $\tau = 206 \pm 20 \text{ sec}$, and $\beta = 0.192 \pm 0.004$. The time dependence of the magnetization corresponding to this process (relaxation

![FIG. 1](image1.png)  
**FIG. 1.** (a) The temperature dependence of the resistivity of La$_{0.5}$Ca$_{0.5}$MnO$_3$ in magnetic field $H = 0$ and 5 T. The thermal and magnetic history of the sample is denoted as ZFC for zero field cooling and FC for field cooling. The direction of the temperature change is shown by the arrows. (b) The time dependence of the resistivity of La$_{0.5}$Ca$_{0.5}$MnO$_3$ at $T = 12$ K taken after the sample was cooled in a magnetic field of 5 T then decreased to zero. The white dashed line is the fit described in the text.

![FIG. 2](image2.png)  
**FIG. 2.** (a) The temperature dependence of the resistivity of La$_{0.5}$Ca$_{0.5}$MnO$_3$ in magnetic fields $H = 0$ and 8.5 T. (b) The time dependence of the resistivity of La$_{0.5}$Ca$_{0.5}$MnO$_3$ at $T = 12$ K taken after ZFC and application of a 8.5 T field. The inset shows the time dependence of the magnetization taken after ZFC to 12 K and application of 5.4 T field. The white dashed lines are the fits described in the text.

after Path 2) is shown in the inset of Fig. 2b. These relaxation data were taken after the magnetic field applied to the ZFC sample had reached 5.4 T. The time dependence of the magnetization also follows a stretched exponential dependence:

$$M(t) = M_2 + (M_1 - M_2)\exp[-(t/\tau)]^\beta$$  \hspace{1cm} (2)

where $M_1 = 16.176 \pm 0.007 \text{ emu/g}$, $M_2 = 15.921 \pm 0.002 \text{ emu/g}$, $\tau = 12500 \pm 1000 \text{ sec}$, and $\beta = 0.45 \pm 0.01$.

The relaxation curves shown in Figs. 1b and 2b are representative curves - similar behavior occurs for different magnetic fields and temperatures below the CO temperature. The values of $\tau$ range from 200 sec to 7250 sec for the 8.5 T measurements and from 4350 sec to 34700 sec for the 5.4 T measurements at different temperatures. The values of $\beta$ are found to be between 0.192 and 0.45 for relaxations under different conditions. The fact that the magnetic field cannot be removed (or switched on) instantly (we used the rate 1.3 T/min) may influence the
parameters $\tau$ and $\beta$ differently at different temperatures and magnetic fields. These variations in parameter values are not understood at present and a more detailed investigation will be required.

The time dependence of the resistivity taken after the Path 3 procedure also follows a stretched exponential form. Moreover, another CO compound, $La_{0.47}Ca_{0.53}MnO_3$, exhibits similar behavior. We have not observed sudden jumps in the resistance after any of our thermal and magnetic treatments (Path 1, Path 2, and Path 3) in contrast to the jumps in the resistance observed in another CO system, $Pr_{0.67}Ca_{0.33}MnO_3$ [8].

In order to explain these memory and relaxation effects, we consider the free energy of our system to be of double-well form as a function of the magnetization (Fig. 3a), as had been proposed in Ref. 3 for the interpretation of the temperature dependence of the critical field and the hysteresis in $Nd_{0.5}Sr_{0.5}MnO_3$. The ZFC $La_{0.5}Ca_{0.5}MnO_3$ is in the AFM insulating (AFM-I) state because the lowest minimum of the free energy in zero magnetic field corresponds to the AFM-I state. However, in a magnetic field the FM metallic (FM-M) state becomes the most energetically favorable state and the AFM insulating state no longer corresponds to the lowest minimum in the free energy (Fig. 3a) (in magnetic fields high enough to destroy the CO completely, the FM-M state becomes perhaps the only free energy minimum). According to this picture the FC $La_{0.5}Ca_{0.5}MnO_3$, which is in the low resistivity state, corresponds to the lowest minimum (Fig. 3a, $H > 0$, FM-M state). After the magnetic field is reduced to zero, the FM-M state is no longer the lowest minimum. Nevertheless, since the AFM-I and FM-M states are separated by an energy barrier, the system remains in this local minimum (the FM-M metastable state) and slowly relaxes with time to reach the lowest AFM-I minimum. This model qualitatively explains why the $La_{0.5}Ca_{0.5}MnO_3$ remains in the lower resistivity state even if the magnetic field has been removed. A similar explanation applies to the ZFC sample put in a magnetic field, but one not high enough for complete melting of the charge ordering.

If the free energy of the system has only one potential barrier $U$ which separates two minima, the relaxation should have only one relaxation time $\tau$ and exhibit an exponential time dependence (Debye relaxation with a time constant $\tau \propto \exp(-U/k_BT)$). In contrast, if there is a distribution of the barriers and consequently a distribution of the relaxation times, the relaxation can have a stretched exponential form (Kohlrausch law [1]):

$$q(t) = q_0 \exp[-(t/\tau)^\beta],$$

where $q(t)$ is a relaxing quantity and $0 < \beta < 1$. This type of relaxation has been observed for many complex and strongly interacting materials [10].

For glassy relaxation a model of hierarchically constrained dynamics has been suggested [11]. According to this model, the relaxation of the Kohlrausch type arises from many sequential correlated activation steps with a hierarchy of relaxation times, from fast to slow. In our case it could correspond to the appearance of small regions of the AFM phase in the FM matrix (or small regions of the FM phase in the AFM matrix depending on the thermal history) and the gradual growth of these regions to reach the most energetically favorable state. A one dimensional illustration of this process is shown schematically in Fig. 3b. If the sample is cooled down in magnetic field, we start from the FM-M state (row 1 in Fig. 3b). When the magnetic field is switched off and the system is no longer in the lowest energy minimum (corresponding to AFM-I), it starts to change its state in the following way. First, single spins change direction forming an AFM ordered groups of three spins (Fig. 3b, row 2), which corresponds to the smallest relaxation time (overcoming the smallest energy barrier).
Next, larger groups of spins change direction (Fig. 3b, row 3) resulting in larger clusters of the AFM ordering, which corresponds to a longer relaxation time. Finally, when even larger clusters move, the complete AFM ordering is achieved (Fig. 3b, row 4). A similar process can occur in a three dimensional system which has a large number of relaxation times corresponding to the distribution of the energy barriers. Since the AFM phase is insulating and FM phase is metallic, the resistivity reflects the changes in the magnetic system. The change in the resistivity is more appreciable than the change in the magnetization, perhaps, because the percolative paths for the current could be opened (or closed) during the process described above resulting in larger changes in the resistivity than in the magnetization and different $\tau$ and $\beta$ for the relaxation of magnetization and resistivity.

To summarize, we have measured the time dependence of the resistivity and magnetization of La$_{0.5}$Ca$_{0.5}$MnO$_3$ and La$_{0.47}$Ca$_{0.53}$MnO$_3$ ceramic samples after different thermal and magnetic treatments at various temperatures and magnetic fields. A stretched exponential relaxation of the resistivity and magnetization has been observed in the metastable state. The relaxation process is due to the gradual change from the AFM-I phase to the FM-M (or FM-M to AFM-I). We explain this relaxation behavior by a model with a hierarchical distribution of relaxation times from fast to slow.

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