Thermal relaxation in charge ordered $\text{Pr}_{0.63}\text{Ca}_{0.37}\text{MnO}_3$ in presence of a magnetic field

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We report observation of substantial thermal relaxation in single crystal of charge ordered system $\text{Pr}_{0.63}\text{Ca}_{0.37}\text{MnO}_3$ in an applied magnetic field of $H = 8\text{T}$. The relaxation is observed when the temperature is scanned in presence of a magnetic field in the temperature interval $T_{MH} < T < T_{CO}$ where $T_{CO}$ is the charge ordering temperature and $T_{MH}$ is charge melting temperature in a field. In this temperature range the system has coexisting charged ordered insulator (COI) and ferromagnetic metallic (FMM) phases. No such relaxation is observed in the COI state in $H = 0\text{T}$ or in the FMM phase at $T < T_{MH}$ in presence of a magnetic field. We conclude that the thermal relaxation is due to two coexisting phases with nearly same free energies but separated by a potential barrier. This barrier makes the transformation from one phase to the other time-dependent in the scale of the specific heat experiment and gives rise to the thermal relaxation.

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Rare earth manganites with general chemical formula $\text{Re}_{1-x}\text{Ae}_x\text{MnO}_3$, has attracted widespread interest because of a variety of fascinating properties like colossal magneto-resistance (CMR) and charge ordering (CO) [1,2]. For certain values of $x$ close to 0.5, these compounds undergo a first order transition at a temperature $T_{CO}$, where the Mn$^{3+}$ and Mn$^{4+}$ species arrange themselves in a commensurate order in the lattice. The charge-ordered state is an insulating state. An interesting aspect of this charge ordered insulating (COI) state (which is also accompanied by orbital ordering) is that it is unstable under a number of external perturbations like electric and magnetic fields, x-rays, optical radiation etc. In presence of an applied magnetic field, the sample undergoes an insulator-metal transition (generally termed as “melting”) from a COI state to a ferromagnetic metal (FMM) state. In presence of magnetic field, the temperature where this melting occurs is termed as $T_{MH}$.

In this paper our particular interest is the region $T_{MH} < T < T_{CO}$ in presence of an applied magnetic field. Evidence is now gathering that in this region (which we call mixed charge ordered region, (MCO)) the two phases, namely the charge ordered insulating (COI) phase and the spin ordered ferromagnetic metallic (FMM) phase coexist. This coexistence is due to electronic phase separation between two phases of nearly the same free energy. Recent transport (including non-linear transport), noise, magnetization experiments etc. have shown that in this class of manganites electronic phase separation is a very commonly occurring phenomenon [3,4]. In this communication we report an interesting observation that in the region of coexisting phases (which has been created by applying a magnetic field below $T_{CO}$) large thermal relaxation effects arise during the measurement of specific heat. From our experiments we concluded that though the two coexisting phases have nearly the same free energy (and nearly the same specific heat) they are separated by an energy barrier which makes the time of conversion of one phase to the other measurable in the time scale of specific heat experiments. This leads to the observation of thermal relaxation. We also correlate these measurements to observed hysteresis in the I-V curve and low energy conductance noise.

Present investigation was carried out on a single crystal of $\text{Pr}_{0.63}\text{Ca}_{0.37}\text{MnO}_3$ which has been grown by float zone technique and has been used in a number of previous experiments by our group particularly in investigation of non-linear transport studies in the MCO region and electric field induced instabilities. $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ is a prototypical charge-ordered system, which because of its small average cation radius $< r_A >$ remains insulating for all values of $x$. This system is unique and perhaps the most studied among all the charge-ordered systems. The resistivity ($\rho$) vs. $T$ curve in zero field and in a field of $H = 8\text{T}$ are shown in the inset (b) of figure 1. Inset (a) of the same figure shows the H-T phase diagram of our sample. We have performed our experiments along the constant $H = 8\text{T}$ line shown by an arrow in the inset. The COI state can be melted to a FMM state by application of a magnetic field of $8\text{T}$ at $T_{MH} \approx 90\text{K}$. This particular composition shows both charge and orbital ordering below $T_{CO} = 236\text{K}$ and the antiferromagnetic (AFM) ordering occurs at $T_N = 170\text{K}$.

The thermal relaxation of the sample was measured...
using an semi-adiabatic calorimeter operating in the 20K < T < 300K range in 0T and after field cooling in 8T. The temperature of the sample was monitored as a function of time after applying a known heat pulse. If the specific data are calculated after the sample has relaxed thermally (see discussion below) we can measure the equilibrium heat capacity. The heat capacity shown in figure 1 both for H = 0 and 8T are equilibrium specific heats. In the same graph the dotted line shows the estimated vibrational background. It can be seen that the two specific heats are nearly the same except near T_{CO}. The large peak near T_{CO} is a consequence of latent heat in the first order phase transition at T_{CO}. A complete description of the equilibrium specific heats and the estimation of the vibrational background is given elsewhere. It is important to note that in the temperature range of interest (except the region T ≈ T_{CO}), the vibrational background makes up for the bulk of the observed specific heat. The closeness of the C_{p} for H = 0 and 8T implies that the coexisting phases in the mixed charge ordered region at H = 8T have energy similar to the COI phase existing at H = 0T. (Note: There is a small latent heat release (≈ 10J/mole) when the FMM phase is heated to the COI phase at T_{MH}. The focus of this paper is the thermal relaxation experiment as described below.

In a typical measurement of heat capacity using adiabatic or semi adiabatic heat-pulse technique, a measured amount of thermal energy Q is applied to the sample producing a change in temperature ∆T. The sample temperature (T_{s}) raised above the bath temperature (T_{o}) relaxes to its original value as described by the following equation :

\[ ∆T(t) = (T_{s} - T_{o}) e^{(-t/τ_B)} \]  

where the time constant τ_{B} = C_{p} / K_{w}, K_{w} being the thermal conductance of the weak link that connects the sample to the bath. By isolating the sample from the bath (to satisfy the adiabatic condition), the relaxation time τ_{B} is made as long as experimentally convenient. Equation 1 assumes that τ_{B} \gg τ_{I}, where τ_{I} is the internal thermal equilibrium time of the sample defined as τ_{I} = L^2 / D_{th}, D_{th} is the thermal diffusivity of the sample of dimension L. As long as τ_{B} \gg τ_{I}, the thermal relaxation of the sample after the application of the heat pulse can be described by a single relaxation time as in eqn. 1. If the sample has very low D_{th} or has internal equilibrium taking place over a long time then the ratio τ_{I}/τ_{B} becomes finite and the relaxation curve (∆T - t) cannot be described by a single exponential decay.

In absence of magnetic field, we observe (both for T > T_{CO} and T < T_{CO}) that the sample thermally relaxes to the bath temperature with a long time constant, τ_{B}, which is typically \(500\) seconds. In this case the internal relaxation time, τ_{I} < 1seconds and a single relaxation time τ_{B} describes the thermal relaxation of the sample for all T.

In an applied field of 8T, for T > T_{CO} and T < T_{MH} we observe that the thermal relaxation is still governed by a single relaxation time as in the H = 0T case (see fig. 2(a) and 2(c)). However, this breaks down for the MCO state (T_{CO} > T > T_{MH}) as shown in the (∆T - t) curves in figure 2(b). The curve shows two relaxation time behavior, which occurs when τ_{I} is finite compared to τ_{B}. We have analyzed the observed thermal relaxation curve at a given T using the relation :

\[ ∆T = A exp\left(-t/τ_I\right) + B exp\left(-t/τ_B\right) \]

where A and B are constants at a given T. From the analysis of the observed relaxation curves of the MCO state at different T we evaluated τ_{I} as a function of temperature and this is shown in figure 3(a). The value of τ_{B} is ≈ 500 seconds to 1500 seconds in the whole temperature range. In the MCO state, τ_{I} (H = 8T) is much larger than τ_{I} (H=0T) which is typically ≤ 1sec. Interestingly, τ_{I} is finite and measurable only in the temperature interval T_{MH} < T < T_{CO} in a magnetic field.

Large value of τ_{I} is a manifestation that the sample reaches internal thermal equilibrium over an extended period and this makes a part of the specific heat relaxing or time dependent over the experimental time scale. We can obtain a quantity C_{inst} immediately after the heat pulse is applied without waiting for complete thermal relaxation. This is the specific heat capacity in the scale \(t \to 0\) which contain contributions of only those constituents which relax faster than the experimental time scale τ_{I}. This is less than the equilibrium specific heat C_{p}, which we measure after the sample has internally equilibrated (t \gg τ_{I}). The difference of these two ∆C = C_{p} - C_{inst} gives a measure of the time dependent or relaxing heat capacity. We plot ∆C(8T)/C_{p} as a function of T in figure 3(b). For H = 0T, ∆C = 0 whereas ∆C(8T)/C_{p} ≈ 25% in the range T_{CO} > T > T_{MH}. (There is a small contribution of ∆C persisting down to 50K, a temperature close to the spin canting temperature in zero magnetic field.)

Previous experiments of non-linear transport as well as noise in this system (and related systems) have led to the conclusion that the MCO comprises of coexisting CO insulating and charge-molten FM metallic phases, as has been stated earlier. The fact that we do not see the thermal relaxation when the sample is completely in COI phase (T > T_{CO}) or completely in FMM phase (T < T_{MH}) clearly establish that the thermal relaxation arises from coexisting phases. We have analyzed the resistivity data (shown in fig. 1(b)) in the MCO region with the help of such a scenario. Using an effective medium theory we find that a fraction (f_{m}) of the FMM phase grows steadily below T_{CO}, it reaches f_{m} ≈ 0.2 at T/T_{CO} ≈ 0.8 and the percolation volume f_{m} = 1/3 at T = T_{MH} ≈ 90K. We propose that the observed relaxation is arising because of the co-existing phases,
whose relative volume fractions change as the temperature change on application of the heat pulse, have a finite time of conversion from one phase to the other. This has been elaborated below. In addition to this effect, close to $T_{MH}$ and $T_{CO}$ additional relaxation arises due to the release of the latent heat (see figure 3(b)).

It has been pointed out earlier that the observed equilibrium $C_p$ is nearly the same both for $H = 0$ and 8T and they are close to the vibrational background specific heat except the region close to $T_{CO}$. This would clearly imply that energetically the $H = 0$T CO phase and the $H = 8$T MCO phase (which a has a fair fraction of FM phase) are quite similar. If the coexisting phases in the sample would have been able to transform from one phase to the other within a time scale $<< 1$sec then our calorimetry experiment would not have distinguished between these two phases. There would not have been any thermal relaxation of the type we have observed. The situation, however, changes when there is a finite time associated with the transformation from one phase to the other coexisting phase. At any given temperature, there is an average equilibrium relative fraction ($f_m$) of the two coexisting phases. The noise experiments on these materials show that at a given temperature the equilibrium volume fraction is result of dynamic equilibrium and in the time scale of the noise experiments (typically $>1$ sec) the two phases can transform one from the other giving rise to the conductivity fluctuation. In a heat pulse experiment when we apply the pulse and the temperature changes, the equilibrium volume fraction also changes so that the volume fraction corresponds to the new temperature. The two phases though energetically similar are separated by an energy barrier which makes this change take place over a finite time. Thus the sample thermally relaxes over a longer period and the relaxation time $\tau_I$ becomes finite comparable to $T_B$.

Large resistive relaxation and delayed release of heat has been observed in similar Pr$_{1-x}$ Ca$_x$MnO$_3$ samples at lower temperature (typically for $T < 50$K) when the samples were cooled to low temperature and the applied field was cycled at a fixed temperature [1][2]. The time scales observed at those temperature were large (in the scale of $10^3$ secs or more). In our experiment the temperatures are much higher ($T_{MH} < T < T_{CO}$) and they were carried out by keeping the field constant and varying the temperature. The thermal relaxation observed by us occurs in the scale of few tens of secs presumably because we are doing the experiments at higher $T ( > 100K)$. However, the underlying physics seems to be similar in these experiments.

To conclude, we have observed that when a magnetic field is applied to a CO solid in the range $T_{MH} < T < T_{CO}$ a large thermal relaxation sets in when a heat pulse is applied. The relaxation is not seen in the pure phases at $T < T_{MH}$ or $T > T_{CO}$ or at all $T$ in $H=0$T. We explain this observation as arising from two coexisting phases (COI and FMM) of similar energy which are separated by a potential well, which imposes a finite time (measurable in the experimental time scale) of conversion of one phase to the other.

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Figure captions:

**Figure 1:** Equilibrium specific heats $C_p$ of Pr$_{0.63}$Ca$_{0.37}$MnO$_3$ single crystal in presence of 0 and 8T magnetic fields. (data from ref.) Inset (a) shows the H-T phase diagram and the arrow shows the path taken for the experiment. Inset (b) shows $\rho$ vs. $T$ for H = 0 and 8T.

**Figure 2:** Thermal relaxation curves ($\Delta T$ - t) of the sample in presence of H = 8T for three temperatures $T < T_{MH}, T_{MH} < T < T_{CO}$ and $T > T_{CO}$. Note the two relaxation time behaviour for $T_{MH} < T < T_{CO}$.

**Figure 3:** (a) Variation of sample thermal relaxation time $\tau_I$ with $T$. (b) Variation of relaxing $C_p$ with $T$ (see text). The peak near $T_{CO}$ is due to latent heat.
figure 1
Figure 3