Origin of the time dependent effects observed in phase separated systems

Devendra Kumar\textsuperscript{a}, K P Rajeev\textsuperscript{a}, J A Alonso\textsuperscript{b} and M J Mart\textsuperscript{e}nez-Lope\textsuperscript{b}

\textsuperscript{a} Department of Physics, Indian Institute of Technology Kanpur 208016, India
\textsuperscript{b} Instituto de Ciencia de Materiales de Madrid, CSIC, Cantoblanco, E-28049 Madrid, Spain
E-mail: deven@iitk.ac.in

Abstract. The phase separated state that is associated with a broad first order electronic phase transition exhibit various dynamic phenomena such as relaxation of resistivity and magnetization, cooling rate dependence, rejuvenation after ageing etc. In the case of magnetic systems, where the coexisting phases are ferro and anti-ferromagnetic, the presence of slow glass-like relaxation has led many authors to treat the phase separated state as a cluster-glass or spin-glass and it has been suggested that the observed time dependent effects are the result of inter-cluster interaction. In this work we report the time dependence resistivity data on the non-magnetic phase separated system, NdNiO\textsubscript{3}. Our experimental results rule out the possibility of the formation of glassy state. We propose that the dynamical behavior in the phase separated systems has its origin in the presence of high temperature phases in their supercooled state persisting below the first order transition temperature. These supercooled phases are metastable and they switch to the ground state stochastically. We claim that this switching gives rise to time dependent effects in the phase separated regime. We further propose that all the systems which undergo a broad first order transition will exhibit time dependence in their physical properties in the phase separated regime owing at least partially to supercooled to normal switching of the different single phase regions of the material.

1. Introduction

The study of phase separated states that develop during electronic phase transitions has attracted a lot of attention of late, particularly in the case of transition metal oxides. It is believed that many of the exotic phenomena exhibited by these compounds, such as colossal magnetoresistance and high temperature superconductivity, are strongly influenced by electronic phase separation\cite{1, 2}. In the last few decades, a large number of reports have appeared in the literature which show that the phase separated state exhibits unusual phenomena such as relaxation of resistivity and magnetization, cooling rate dependence, rejuvenation after ageing etc\cite{3, 4, 5}. While these studies clearly indicate that the phase separated state in the above systems is not in thermodynamic equilibrium, the physical origin of the dynamical behavior is not completely understood and the explanation for these observations has remained largely phenomenological. On the basis of the relaxation measurements done on manganites and cobaltates, Rivadulla and coworkers have proposed that the phase separated state can be considered as a spin-glass or a cluster-glass, and they further argued that inter-cluster magnetic interactions are responsible for the observed slow glass-like relaxation in these systems\cite{6}. But
the occurrence of time dependent effects in non-magnetic systems such as PrNiO$_3$ and VO$_2$ \cite{3, 7} rules out the possibility of invoking a spin-glass like model to explain the dynamics of phase separation in general. Another popular model to explain these time dependent effects has been proposed by Levy et al\cite{4}. In this model the time dependence is attributed to the hindered kinetics of the low temperature phase, where the boundaries of the phases relax through a hierarchy of energy barriers to attain equilibrium. While this model is quite successful in explaining some of the experimental observations, it does not provide a physical reason for the hindered kinetics of phase boundaries. This model also fails to explain the large asymmetry of time dependence seen during heating and cooling. Thus it would be very interesting to find out what actually causes the slow dynamics in phase separated materials.

We have chosen the perovskite oxide NdNiO$_3$ to study the dynamics of the phase separated state. NdNiO$_3$ is a clean system as it does not require any doping to get the phase separated state and it is also unaffected by the application of a magnetic field. These properties in combination with the existence of metallic and insulating phases over a large temperature range make it an ideal candidate for such studies. The ground state of NdNiO$_3$ is insulating, charge ordered and antiferromagnetic\cite{8, 9}. On increasing the temperature this system undergoes a temperature driven antiferromagnetic to paramagnetic transition, and an insulator to metal transition at 200 K. This metal-insulator (M-I) transition is accompanied by a large hysteresis and in the hysteresis region, the physical state of NdNiO$_3$ is phase separated and it consists of paramagnetic metallic and antiferromagnetic insulating phases\cite{3, 8}.

In this paper we report careful time and temperature dependent resistivity measurements on NdNiO$_3$. On the basis of our results we have developed a general framework that explains the origin of the glass like dynamics in phase separated states.

2. Experimental details
Polycrystalline NdNiO$_3$ samples in the form of 6 mm diameter and 1 mm thick pellets were prepared and characterized as described elsewhere\cite{10}. The preparation method uses a high temperature of 1000$^\circ$C and a high oxygen pressure of 200 bar. All the temperature and time dependent measurements were done in a home made cryostat. To avoid thermal gradients in the sample, it was mounted inside a thick-walled copper enclosure so that during the measurement the sample temperature would be uniform. All the time dependent measurements were carried by cooling the sample from 220 K to the temperature of interest to avoid any memory effects.

3. Results
Figure 1(a) displays the resistivity vs temperature plot for the NdNiO$_3$. The resistivity data shows that in the cooling cycle, the system undergoes a M-I transition centered around 140 K with a spread of about 40 K. In the heating cycle, the M-I transition is rather sharp and it is centered around 190 K with a width of 10 K. Below 115 K the resistivity curves of cooling and heating cycles coincide and the log$\rho$ vs $T$ plot is linear, indicating that the sample is a bandgap insulator. The resistivity also depends on the cooling rate and it was found that a slow cooling rate yields a higher resistivity in the hysteresis region (Inset of Figure 1(a)). No heating rate dependence was found in the heating cycle. Figure 1(b) shows the time dependent resistivity data obtained in the cooling cycle. We can see that at fixed temperature, the resistivity of the sample increases with time, and the maximum increment occurs around 145 K. The time dependent resistivity data were best fitted with stretched exponential function

$$\rho(t) = \rho_0 + \rho_1 (1 - \exp(-t/\tau^{\gamma}))$$

where $\rho_0$, $\rho_1$, $\tau$ and $\gamma$ are fit parameters. No time dependence was found below 115 K and the time dependence in the heating cycle was negligible compared to that of cooling cycle.
Figure 1. (a) $\rho$ vs. $1/T$ plot for NdNiO$_3$. The blue circles represent cooling data and the red squares stand for heating data (cooling/heating rate 2.0 K/min). The solid line is a least square fit to the band gap insulator model below 115 K. The inset shows $\rho$ vs $1/T$ for three different cooling rates: lower curve (blue stars): 2 K/min, middle curve (red circles): 0.2 K/min, upper curve (black pluses): infinitely slowly ($\rho_0 + \rho_1$). The connecting lines are to guide the eyes. (b) Time dependence of resistivity while cooling, at various temperatures in the range 140 to 155 K, for a period of one hour. Maximum time dependence is seen at 145 K which is about 300%. The curve at the bottom, which looks like a straight line, shows the increase in resistivity in a heating run taken at 145 K and the change in this case is less than 0.2%.

4. Discussion

In a first order metal to insulator transition, the hysteretic region of the transport properties is phase separated and it consists of metallic and insulating phases. Our time dependent resistivity measurements on NdNiO$_3$ suggest that, in the cooling cycle, the phase separated region of the system is not in thermodynamic equilibrium. In the heating cycle, the system does not exhibit any time dependence, and behaves as a band gap insulator up to the temperature of insulator to metal transition. Similarly, in other systems where time dependent studies have been carried out without an initial disturbance by a magnetic field, the time dependent phenomena have been reported only for the cooling cycle[4, 7]. The absence of the dynamical phenomena in the heating cycle rules out the possibility of glass formation at low temperatures. In the following paragraph we have formulated a framework that we use to understand our experimental observations.

It is well known that in a first order phase transition, a high temperature phase can survive below the transition temperature ($T_C$) as a supercooled (SC) phase. A SC phase is a metastable phase and collapses to the ground state when a particular temperature known as temperature of metastability ($T^*$) is reached. For $T^* < T < T_C$, an energy barrier separates the SC phase from the stable ground state and the height of the energy barrier ($U$) is a continuous function of $(T - T^*)$. For $T < T^*$, $U$ vanishes[11]. A SC phase will flip to the ground state when (a) it attain its temperature of metastability (b) it gains enough energy through thermal fluctuations to sail over the barrier height $U$. At $T > T^*$ the SC metastable phase can cross over to the stable ground state with a probability ($p$) governed by the Arrhenius equation $p \propto \exp(-U/k_BT)$, which tells us that the barrier will be crossed with an ensemble average time constant $\tau \propto 1/p$. If we imagine an ensemble of such SC phases with the same barrier $U$, then the volume of the metastable phase will exponentially decay with a time constant $\tau$.

Our system is polycrystalline, i.e., it is made of a large number of tiny crystallites, and each
crystallite may behave as a single or multiple phase region. Thus we will be having a large collection of single phase regions (SPR’s). Each supercooled SPR will flip to the ground state abruptly. The energy required for switching of SPR, U, is an extensive parameter, so it will also depend on the volume of the SPR. This will result in a τ distribution that will depend on size distribution of SPR’s. This τ distribution will be further broadened by T* distribution of SPR’s. The switching of SPR’s with different time constants will give rise to the volume of the metallic state decaying in a stretched exponential manner with time[12].

To check the validity of our model through numerical calculations, we need the initial volume of metallic and insulating phases at any given temperature. We have calculated the metallic and insulating volume fractions from the experimental data using McLachlan general effective medium theory[13]. Taking $U = aV(T-T^*)^\alpha$, where $a \approx 2.6 \times 10^{-8}$ and $\alpha = 4.5$, we have carried out MonteCarlo simulations to calculate the time dependent insulating volume fraction[14]. Figure 2 compares the increase in insulating volume fraction in one hour obtained from the simulation ($\Delta V_{cal}$), and from the time dependent resistivity data ($\Delta V_{exp}$). We can see that ($\Delta V_{cal}$) fits well with ($\Delta V_{exp}$), which signals that our model is quite good.

5. Conclusion

In summary, our experimental results rule out the possibility of glass formation in the non-magnetic systems. Further, our numerical calculations provide serious evidence that the time dependent effects observed in the hysteresis region of a first order electronic phase separation are a combined effect of the flipping of SC phases to the ground state.

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