Evidence of kinetically arrested supercooled phases in the perovskite oxide NdNiO$_3$

Evidence of kinetically arrested supercooled phases in the perovskite oxide NdNiO₃

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Abstract
We report the time and temperature dependent response of thermopower in the non-magnetic
perovskite oxide NdNiO₃. We find that on cooling below the metal–insulator transition
temperature the system evolves into a phase separated state which consists of supercooled
metallic and insulating phases. This phase separated state exhibits out of equilibrium features,
such as cooling rate dependence and time dependence. The existence of these dynamical
features is attributed to the transformation of supercooled metallic phases to the insulating state.
On cooling, a small fraction of the supercooled phases get kinetically arrested in a glassy state
and these supercooled phases remain in that state down to low temperature. In the heating cycle
the arrested states de-arrest above 150 K and this results in the reappearance of time dependent
features.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The first-order phase transition (FOPT) has been a topic of fundamental importance in the field of condensed matter physics. The materials undergoing such a transition often exhibit a phase separated state in the vicinity of the transition. The phase separated state in many FOPT compounds displays a variety of interesting phenomena such as colossal magnetoresistance, CMR [1–3], time dependent resistivity and magnetization [4–6], dependence of physical properties on rate of temperature change and enhanced $1/f$ noise [7–9]. From the last decade onwards, the main focus of research in FOPT studies is centered around understanding the origin of the phase separated state and its response to various perturbations such as magnetic and electric fields, pressure, x-ray and laser illumination, strain, temperature variation etc [10–16]. These studies reveal that coexisting phases have nearly equal free energies and the application of an external perturbation decreases the free energy of one phase relative to the other phase, giving rise to a large change in the observed physical properties. Later it was found that even in the absence of any apparent perturbations, such as mentioned above, the relative volumes of the coexisting phases can shift such that the total free energy decreases, which results in a time dependence of physical properties at a fixed temperature [5, 17].

The existence of a mixed phase region with nearly equal free energies has its origin in the phenomenon of metastability, in particular supercooling or superheating. In a temperature driven first-order transition, when heterogeneous nucleation is missing, a region of high temperature phase can survive below the thermodynamic transition temperature T_C as a supercooled (SC) metastable phase [18]. The homogeneous nucleation will start when the thermal energy is of the order of the free energy barrier that separates the SC state from the ground state [19]. Each SC phase has a characteristic temperature T^* known as the limit of metastability. Below this temperature the energy barrier separating the metastable state from the ground state vanishes and the SC phase is free to flip to the ground state. The SC phase will flip to the ground state only when their kinetics are not frozen i.e. their glass formation temperature T_g is less than the limit of metastability T^* [20]. Now if the glass forming temperature is higher than the limit of metastability, the SC phase will remain trapped down to low temperatures even when the free energy barrier vanishes. On subsequent

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heating the kinetics of these trapped phases will be restored to the metastable state above the temperature $T > T_g$. In a phase separated system where the SC phases are not trapped in a glass-like state, the thermally activated stochastic switching of SC phases to the ground state will give rise to non-Debye relaxation in the physical properties [17]. So for $T_g < T^*$ time dependent effects will be observed only in the cooling cycle, while for $T_g > T^*$ time dependent effects will be observable both in the heating and cooling cycles.

Here we have used the compound NdNiO$_3$ to understand supercooling and glass formation in a polycrystalline material where a distribution of SC regions coexist, with each one of the different SC regions having a unique T^* [17]. NdNiO$_3$ belongs to the family of rare earth nickelates and undergoes a temperature driven metal to insulator transition and a para to antiferromagnetic transition at 200 K [21, 22]. Now, for the study of the dynamics of a phase separated system such as NdNiO$_3$, the ideal probe to determine the fractional volume of the constituting phases could perhaps be a muon spin relaxation experiment [23]. But with the lack of access to such facilities we depend on transport properties such as resistivity and thermopower to probe the system. These measurements suffer from the effects of percolation and inter-crystallite contact resistance and do not allow us to do an accurate estimate of the constituent volume fractions at temperatures far below the percolation threshold [24]. While thermopower and resistivity measurements on NdNiO$_3$ as functions of temperature have been reported earlier by others, in this work we focus our attention on the dynamical aspects of the M–I phase transition through time dependent thermopower measurements. We find that at temperatures far below the percolation threshold, thermopower measurements are more sensitive to the presence of minority phases than that of resistivity. Further investigations suggest that on cooling the sample below the metal–insulator transition temperature, T_{MI}, while a majority of SC regions transform to the insulating state, a small fraction of SC regions get kinetically arrested in a glassy state. These SC regions present in the glassy metallic state exist down to low temperatures.

2. Experimental details

Polycrystalline NdNiO$_3$ samples in the form of 6 mm diameter and 2 mm thick pellets were used in the thermopower measurements. The details of sample preparation and characterization are described elsewhere [25]. A temperature of 1000 °C and oxygen pressure of 200 bar is required to get good quality samples.

The thermopower measurements were performed in a home made cryostat. To measure the thermopower at a temperature T, the sample was sandwiched between two polished copper plates that were electrically isolated from the rest of the cryostat system. Each of these copper plates have an embedded platinum temperature sensor and a strain-gauge heater, and their temperature was controlled by Lakeshore Cryotronics temperature controllers. Temperature stability of each copper plate was better than 10 mK. For a thermopower measurement at a temperature T, one copper plate was kept at a temperature $T - \Delta T/2$ and the other one was kept at

$T + \Delta T/2$ with $\Delta T \ll T$. The voltage difference between these plates was recorded to calculate the thermopower of the material with respect to copper. The absolute thermopower was calculated by subtracting the thermopower of copper from the measured data. Solder free copper leads were used to read the voltage difference between the plates and these leads were attached to the copper plates by pressure contact, which helps in minimizing the stray thermoelectric voltages.

Below T_{MI} (200 K) NdNiO$_3$ is not in thermodynamic equilibrium and it relaxes with time, and thus any experimental result would depend on the procedure used for the measurement. We used the following procedure. While cooling we start at 300 K with the two sides of the NdNiO$_3$ pellet kept at a temperature difference of 2 K, and then record the voltage (V_{meas}) in steps of 1 K after allowing the temperature to stabilize at each point for about 30 s. In between two temperature points the sample was cooled at a fixed cooling rate of 2 K min^{-1}. During this process care was also taken to ensure that the temperature difference between the two ends of the sample remained at 2 K.[3] This procedure ensures that the temperature at the two ends of the sample vary smoothly and monotonically. This condition is important since in our earlier measurements we have observed that thermal oscillations change the physical state of the system [17]. To remove the effect of any stray thermo emf in the system, we recorded the voltage across the sample with the ends at zero temperature difference (V_{tare}) in a different run under identical experimental conditions. This stray voltage V_{tare} was subtracted from V_{meas} at each temperature before calculating the absolute thermopower. After the cooling run was over, the heating data were collected at every 1 K interval. The heating rate between two points was the same as the cooling rate used earlier. This cycle of measurement was also repeated with a different cooling and heating rate of 0.2 K min^{-1}.

It was observed that the thermopower above 200 K does not show any time dependence, and is independent of the history of the measurement. So to avoid the effect of any previous measurements all the time dependent measurements used the following protocol: for cooling cycle, first take the sample to 220 K, wait for half an hour, and then cool at 1.0 K min^{-1} to the temperature of interest and once the temperature is stabilized record the thermopower as a function of time. In the heating cycle the time dependent thermopower was done in a similar way: first take the sample to 220 K, wait for half an hour, then cool at 1.0 K min^{-1} to 85 K and then heat at 1.0 K min^{-1} to the temperature of interest, and once the temperature stabilizes record the thermopower as a function of time. It was ensured that the temperature difference between the two ends of the sample was kept fixed at 2 K during all these measurements.

3. Results

Figure 1(a) shows the thermopower of NdNiO$_3$ as a function of temperature. The thermopower is multiple valued, the cooling and heating data differing significantly from each other and
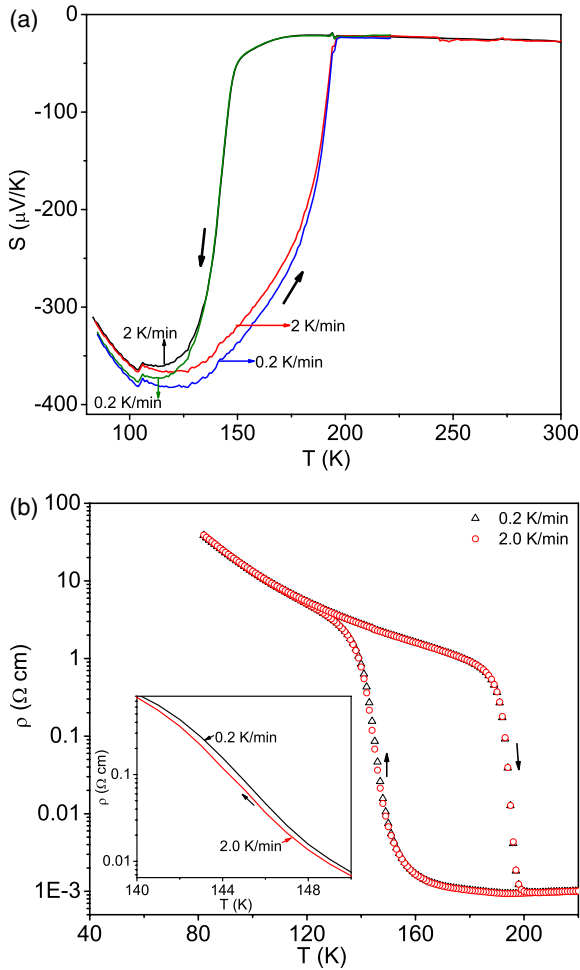
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[3] This gives the effective cooling rate of 1 K min^{-1}.

Figure 1. (a) Temperature versus thermopower for NdNiO$_3$ for the cooling/heating rate of 2.0 and 0.2 K min^{-1}. (b) Temperature versus resistivity for NdNiO$_3$ for the cooling/heating rate of 2.0 and 0.2 K min^{-1}. Inset shows the expanded view of the resistivity plot, obtained while cooling, close to the temperature where the metallic percolation ceases (144 K).

forming a large hysteresis loop. The sign of thermopower remains negative both in the metallic and insulating state, which indicates that the charge carriers are electrons in both states. On cooling the sample below 300 K, the magnitude of thermopower decreases until 200 K. Below this temperature the thermopower shows a strong temperature dependence with its magnitude attaining a maximum at about 115 K. The thermopower data indicates that NdNiO$_3$ undergoes a metal to insulator transition at 200 K, which is consistent with the resistivity (see figure 1(b)) and earlier thermopower measurements [22]. Below 115 K, the thermopower data does not follow the band gap model ($|S| \propto 1/T$), unlike resistivity. A small jump in the thermopower has been observed at around 105 K, which is the region where the volume fraction of the metallic phases is small. Such behavior has been predicted from Bergman and Levy's theory of effective thermopower of mixed phase systems and has been experimentally observed in Al–Ge thin films [24, 26].

Below the M–I transition, thermopower shows a significant dependence on the rate of temperature change. See

Table 1. Fit parameters for a subset of time dependence data shown in figure 2. The degrees of freedom of the fits DOF $\approx$ 1000. The χ^2/DOF for 155 K is too large, indicating that we have underestimated the error in thermopower in this case. Anyway, we note that, the R^2 values are consistently good and indicate reasonably good fits.

#	T (K)	S_1/S_0	τ (10^3 s)	γ	χ^2/DOF	R^2
1	140.0	0.0426(1)	3.12(2)	0.729(1)	0.34	0.997 05
2	145.0	0.0812(1)	3.09(2)	0.782(1)	1.3	0.998 37
3	147.5	0.0905(2)	2.53(1)	0.896(1)	2.3	0.998 53
4	150.0	0.118(1)	2.34(1)	0.826(1)	3.2	0.998 61
5	152.5	0.231(1)	3.62(2)	0.776(1)	5.3	0.999 05
6	155.0	0.0673(2)	2.58(1)	0.834(2)	7.2×10^3	0.996 87

figure 1(a). A slower cooling rate of 0.2 K min^{-1} yields a higher absolute thermopower than that of the faster cooling rate 2.0 K min^{-1}. This rate dependence of thermopower is more readily seen below 125 K during a cooling run, while in resistivity, the cooling rate dependence is more significant near 145 K where the percolation of the metallic regions ceases. In the heating cycle thermopower exhibits a large rate dependence at low temperatures and this rate dependence persists up to about 180 K before disappearing as we increase the temperature towards T_{MI}. In contrast to this we did not find any significant heating rate dependence in the resistivity data (see figure 1(b)). The presence of cooling and heating rate dependence in the thermopower data indicates that the system is not in its thermodynamic equilibrium both in the cooling and as well as the heating cycle. These observations are corroborated by the data shown in figures 2 and 3.

Figure 2 displays a subset of the time dependent thermopower data recorded at fixed temperatures in the cooling run. The data are presented as $S(t)/S_0$, where $S_0 \equiv S(t = 0)$, so that the values are normalized for easy comparison. We found that below 170 K, the absolute value of thermopower increases with time. A maximum relative increase in thermopower of about 14% was observed for a period of 1 h at 152.5 K. The time dependence of thermopower is lower both above and below this temperature. Below 120 K, we did not find any detectable time dependence in the system. All the time dependence data were fitted to a stretched exponential form

$$S(t) = S_0 + S_1(1 - e^{-(\frac{t}{\tau})^\gamma}), \qquad (1)$$

where S_0, S_1, τ and γ are fit parameters with $S(t)$, S_0 and S_1 having negative value. The fits are quite good with R^2 value greater than 0.995 in most cases. See table 1.

Figure 3 shows a part of the time dependent thermopower data recorded at fixed temperatures in the heating runs. We did not find any significant time dependence up to 150 K. Above 150 K, the magnitude of thermopower increases with time. The maximum relative increase in thermopower in 1 h is around 1%, which is much smaller than that seen in the cooling runs. Above T_{MI}, the thermopower data is stable and no time dependence or cooling/heating rate dependence was observed.
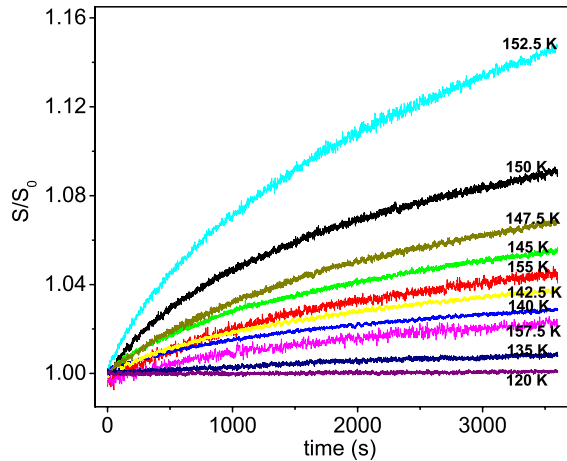
Figure 2. Time dependence of thermopower while cooling, at various temperatures in the range of 157.5–120 K, for a period of 1 h.
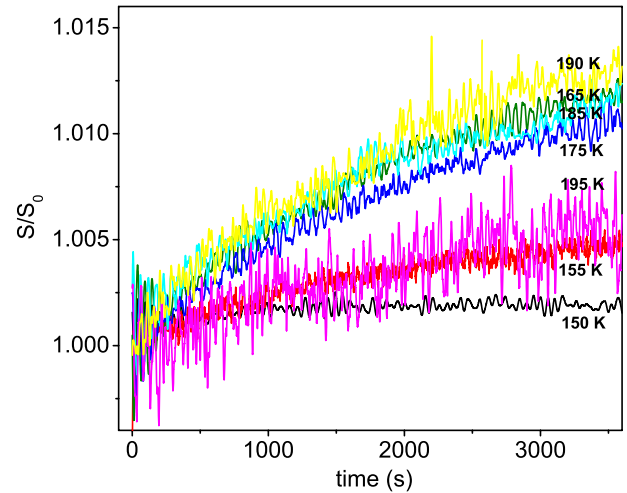

Figure 3. Time dependence of thermopower while heating from 85 K, at various temperatures in the range of 150–200 K, for a period of 1 h.

4. Discussion

The presence of out of equilibrium features in thermopower is similar to that observed in our resistivity measurements reported earlier [17]. Based on those observations we had proposed a model to understand the behavior of the phase separated regime. The model is as follows: the high temperature metallic phase survives below the metal to insulator transition in its supercooled metastable state. The supercooled metallic phase is not a single entity, but instead is made up of various regions which can make a transition or switch from the metallic to the insulating state independent of the neighboring regions. These regions are referred to as switchable regions (SR). Each SR in its metallic state has to cross an energy barrier U to go to its insulating state and the barrier strength was determined to be $U = cV(T - T^*)^{1/4}$, where V is the volume of the SR, T^* is its temperature of metastability, and c is a constant. An SR will switch to the insulating state if (a) it attains its temperature of metastability or (b) it gains enough energy from thermal fluctuations so that it can cross the energy barrier U. For $T^* < T < T_{MI}$ and $T_g < T$, supercooled phases will switch over to the insulating state stochastically, which will cause time dependence in the physical properties. No time dependence in resistivity was observed in the heating cycle [17]. On the basis of this it was claimed that all the SRs switch to the insulating state on cooling implying that $T^* > T_g$ for all of them.

In thermopower measurements, during cooling, we got the maximum time dependence at around 152.5 K, while in the case of resistivity the maximum time dependence occurs around 145 K. The maximum magnitude of change in thermopower in 1 h (ΔS) is $\approx$14%, which is much smaller than that of resistivity ($\Delta \rho \approx 200\%$) [17]. We notice that the change in thermopower in 1 h ΔS is much closer to the change in insulating volume fraction ($\Delta V \approx 8\%$) [17]. The time dependence of thermopower in the cooling cycle can be understood on the basis of our model. As we have discussed in the previous paragraph, below T_{MI}, the SRs

present in the SC state stochastically switch to the insulating state, which enhances the volume fraction of insulating phase with time. This increase in insulating volume fraction results in a higher magnitude of thermopower. Thermopower being a transport property, the change in thermopower is also affected by percolation effects and thus the behavior of the time dependence of thermopower and the time dependence of insulating volume fraction will not have a one-to-one monotonic correspondence.

Below 120 K no detectable time dependence was observed in the thermopower, but cooling rates of 2 and 0.2 K min^{-1} lead to slightly different low temperature states with differing thermopower. This suggests that a tiny fraction of SRs must remain in the supercooled state even below 120 K. Since we did not find any time dependence below 120 K, we argue that the kinetics of these SRs are arrested and they end up in a glass-like state. Now, the question arises why there is no rate dependence in resistivity below 120 K, neither in cooling runs nor in the subsequent heating runs. To answer this question we suggest that the small fraction of SRs trapped in the glassy state are not detectable in a resistivity measurement. This idea is in consonance with the fact that thermopower measurements show a small time dependence of about 1% over a period of an hour in heating runs (figure 3), while no detectable time dependence was observed in the heating runs of resistivity measurements [17].

The advantage of thermopower over resistivity in detecting tiny amounts of SC metallic regions (SRs) dispersed in an insulating matrix can perhaps be understood as follows. When the fraction of SC metallic regions is small they will be completely surrounded by insulating regions. Now the net contribution of a tiny metallic region embedded in an insulating matrix on the total resistivity of the material will be determined by the resistance of the metallic region plus its inter-crystallite resistances in the current path. Now we conjecture, based on our experience on the contact resistance of polycrystalline NdNiO$_3$, that the inter-crystallite resistance

between a metallic and an insulating crystallite will be very high compared to the resistance of the metallic crystallite. This implies that the tiny metallic region will be essentially shut out of the current path and will not be able to affect the resistivity of the material significantly. The boundary effects are much less significant in the case of thermopower compared to resistivity because the thermal conductivities of the metallic and insulating regions are comparable and this makes the thermopower sensitive to the embedded metallic regions [27, 28].

In a heating run, the SRs present in a glassy state will remain arrested in that state until their respective T_g's are attained. In cooling runs we found a time dependence down to 120 K while in heating runs we did not find any time dependence until 150 K, which suggests that the SRs which are arrested in the glassy state have their T_g's above 150 K. On heating the system above 150 K, the kinetics of the SRs gets de-arrested and they can cross the free energy barrier U and flip to the insulating state with a probability of flipping $\propto \exp(-U/k_B T)$. In the time dependence data presented in figure 3 the flipping of the SRs to the insulating state raises the insulating volume fraction with time and this enhances the magnitude of thermopower with time. The fact that we get a noticeable time dependence all the way up to T_{MI} suggests that the T_g's are distributed quite broadly up to T_{MI}. We might now say that each SR has a unique temperature of metastability T^* and a unique temperature of kinetic arrest T_g. In a cooling run, the majority of the SRs present in the supercooled state switch to the insulating state by the time their T^* is attained and only a small fraction of SRs get arrested in the glassy state; this suggests that the majority of the SRs have their T^* greater than T_g.

5. Conclusion

Our experimental results and analyses suggest the following picture for the NdNiO$_3$ system. Below T_{MI} the system consists of SC metallic and insulating regions. Each of the SC metallic region has a unique temperature of metastability T^* and a unique temperature of kinetic arrest T_g. For the majority of the SC regions T^* is greater than T_g. Thus when the sample is cooled below T_{MI}, while the majority of the SC regions switch to the insulating state when their temperature of metastability is reached, a small fraction of the SC regions which have $T_g > T^*$ get arrested in a glassy state and remain in that state down to low temperature. Such SC regions have their T_g greater than about 150 K. In a heating run, these SC metallic regions remain trapped in their glassy metallic state until their temperature of kinetic de-arrest (T_g) is reached. Above this temperature, these regions switch over to the insulating state stochastically.

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