Memory and pressure studies in Na$_x$CoO$_2$ cobaltites

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Abstract. We present a detailed study on the memory effect results in Na$_{0.5-x}$CoO$_2$ single crystals. We analyze the temperature dependence of the nonvolatile current-pulse-induced resistance memory state. These results allow us to have more insight in the mobility of Na$^+$ ions induced by current and their effect on the memory effect. We also developed X-ray diffraction studies under pressure at ambient temperature in the Na$_{0.5}$CoO$_2$ powder compound. An orthorhombic to hexagonal phase transition was observed at 9GPa. This transition can be explained taking into account the Na ions displacement between two allowed positions. These structural results allow us to confirm that the non-volatile resistive commutation can be interpreted by the displacement of the Na ions induced by the current pulses.

1. Introduction

The cobaltite system has attracted the interest of the condensed matter community due to their unexpected properties, like superconductivity under hydration, a charge ordered state at $x = 0.5$, huge thermoelectric effect. In a recent work [1], resistive memory effects in single crystals of Na$_{0.5-x}$CoO$_2$ have been shown. This result gives to this type of lamellar system a new and very promising application in the field of storage data devices.

In particular, the Na$_{0.5-x}$CoO$_2$ compound has two main transition temperatures. The first, at 87K, could be associated with an antiferromagnetic order and gap (32±7)% of the Fermi surface (FS)[2]. At 53K occurs the charge order transition, which localizes (90±6)% of the remaining FS, so only (3±1.5)% of the high-temperature FS survives both transitions. This small fraction of the FS that is available at low temperatures implies that the transport properties will be very sensitive to slight changes in stoichiometry or disorder.

The crystal structure at ambient pressure of the Na$_{0.5}$CoO$_2$ compound corresponds to an orthorhombic phase and Pnmm space group [3]. In this structure the Na atoms can occupy two
different positions: $Na(1)$ in between two $Co$ ions of consecutive layers or $Na(2)$ in the center of the triangular sub lattice of $Co$.

2. Experimental results

In order to have more insight on the $Na_{0.5-\delta}CoO_2$ non-volatile resistive commutation memory effects, we performed a detailed analysis of the temperature dependence on the resistive switching phenomena. The synthesis and former memory studies are published elsewhere [2]. These studies were complemented by high-pressure X-ray diffraction measurements.

2.1. Memory studies

The temperature evolution of the non-volatile resistive commutation on single crystals of $Na_{0.5-\delta}CoO_2$ is presented in the figure 1 (a). In this figure, the variation of the resistance induced by the application of a series of current pulses is plotted as a function of the temperature, during a cooling and a warming process. The high resistance state was induced by the application of 15 cycles of 250ms square current pulses with alternate polarities. Taking into account the current effect on the resistance state presented in reference [1], the first square pulse induces a high resistance state and the rest of the pulses will not affect this state. We choose the number of cycles in order to avoid any transient behavior in the switching states. It is important to mention that the polarity sequence was strictly conserved during all the experiment. The low resistance state was recovered by 15 cycles of sinusoidal current pulses with 1s period. The sinusoidal pulses protocol induces a reduction of the resistance state because in the last sine profile the current is increased from -$I_{MAX}$ to 0A. In order to have a direct correlation with transport properties of the sample we plot in the same figure the resistive virgin curve with the critical temperatures marked with black arrows (87K and 53K).

From this figure, we can obtain substantial information about the mobility of the interstitials $Na^+$ ions in these materials. The applied pulses do not affect the resistance state between ambient temperature and 150K. Below this temperature, we obtained a controlled and reversible change in the resistance state by the application of square and sinusoidal pulses. This is a clear evidence that above 150K the order of the interstitials are not affected by the current pulses, in other words after the applied square pulses the $Na^+$ ions recover the same arrangement than before the pulses. That means that, at ambient pressure, for $T<150K$ the $Na^+$ are blocked and their arrangement can be controlled by external parameters.

Another evidence of this temperature mobility limit can be obtained from the temperature cycle done on the crystal sample B, see figure 1 (b). The dotted black line represents the virgin resistive curve. The blue open squared curve, named cycle A, corresponds to the temperature cycling of the high resistive state induced by a square current pulse of 0.8A and 250ms at 60K (solid green arrow). One can clearly see that, at 150K, the virgin and the cycle A curves collapse. A new temperature cycle, the red circles curve named cycle B, bears no difference with the virgin curve. This behaviour was observed in all the samples studied, and it shows that, systematically, above 150K the low resistive state was recovered implying that the $Na^+$ ions can move freely rendering their rearrangement possible.

As the temperature is lowered, the effect of the pulses increases down to the vicinity of the 87K transition where it starts to decrease down to the charge order transition at 53K. This diminution could be related with the spin density wave transition at 87K. For temperatures lower than the charge order transition, the number of un-gapped charge carriers is $\sim$3% of the high-temperature carriers, meaning that even a subtle change in the $Na^+$ sub lattice will generate a huge effect in the transport properties of the sample.
2.2. Structural pressure studies

The angle dispersive X-ray diffraction studies on \( Na_{0.5}CoO_2 \) powder samples were performed at the ID27 high-pressure beamline of the European Synchrotron Radiation Facility using monochromatic radiation (\( \lambda = 0.3738\text{Å} \)) and diamond anvil cells with 450μm culet diamonds. The transmitting pressure media was neon and the pressure was determined using the shift of the fluorescence line of the ruby. The diffraction patterns were collected with a CCD camera, and the intensity vs. 2Theta patterns were obtained using the fit2d software [4]. A completely Rietveld refinement was done with the GSAS- EXPGUI package [5]. The characterization and the transport properties measurements of this powder samples are published in reference [6].

The evolution of the diffraction patterns with the external pressure is shown on figure 2. At ambient pressure and temperature, the compound has a space group of the orthorhombic type (\( Pnmmz \)), and this structure is stable up to 9GPa. At this pressure, a structural phase transition to a hexagonal space group (\( P6_3/mmc \)) was observed. It is important to mention that this hexagonal phase is the same found in the rest of the Na concentration phase diagram. A detailed analysis of the diffraction data with pressure will be published elsewhere. This phase transition can be associated with the displacement of the \( Na \) atoms that occupy the \( Na(1) \) position in the orthorhombic phase to the \( Na(2) \) in the hexagonal one. This evidence of a displacement of the Na atoms by external pressure can also be produced by other parameters, like current pulses.
3. Discussion

The structural results under pressure obtained in the Na$_{0.5}$CoO$_2$ powder samples give us very interesting evidences of the possible microscopic mechanism responsible of the current pulses non-volatile memory effects. The external applied pressure induces a contraction of the lattice parameter, therefore the reduction of the distance of Co from successive layers forces the displacement of the Na atoms that occupy the Na(1) position to the Na(2) one. An identical phase transition was observed in the Na$_{0.5-\delta}$CoO$_2$ single crystals. The effect on the electrical resistivity of pressure and, hence, of this displacement, has been described in reference [2]. It results in a very strong change on the low temperature conductance of the sample, due to the fact that the small amount of carriers (3% of the FS), not gapped below 50K, is trapped by the new positioning of the Na ions. Extending this reasoning to our pulsed measurements, we can attribute the non-volatile resistance memory effects at low temperature by the current pulses to a similar repositioning of the Na in the Na$^+$ sub lattice induced by the electric field of the applied pulses.

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