



## Particle size dependent resistivity in $\text{Pr}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$

Moumita Patra\*

Department of Physics, Raghunathpur College, Raghunathpur, Purulia-723133

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### Abstract

Transport mechanism of polycrystalline  $\text{Pr}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$  with two different grain sizes has been studied. A size induced metal insulator transition in temperature dependence resistivity ( $\rho$ ) has been observed. For the sample with larger grain size (bulk), we have noted an upturn in the lower temperature region (below 60 K) and two metallic regions. But the lower grain size compound (nano) shows insulating behavior for the whole measured temperature regime. The possible mechanism of this fascinating behavior has been analyzed with fitting of  $\rho$  vs.  $T$  data. The upturn in resistivity with smaller grain size originates from the elastic e-e interaction. The enhancement of insulating behavior with grain size reduction can be attributed to enhanced disorder around the surface.

**Keywords:** Perovskite, size-dependence, transport properties, resistivity upturn.

### 1. Introduction

Magnetic oxides with perovskite structures have proven a fertile research area due to the fascinating nature of superconducting, magnetic, and electronic properties making them promising material for multifunctional devices like magnetic memory devices, spintronic application, multiferroicity, solid oxide fuel cells etc. [1-3]. Among them the hole doped cobaltites ( $\text{R}_1\text{-xSr}_x\text{CoO}_3$ ) have received some duly attention due to the coexistence of spin state transitions and the co-existence of different magnetic phases [4-6]. The exchange bias (EB) effect, typically observed in magnetic heterogeneous structure, is a common phenomenon in these cobaltites due to their spontaneous phase co-existences [7-10]. Another important feature which makes cobaltites a suitable material for spintronics application is butterfly like tunneling magnetoresistance (TMR) [11]. A detail study on grain size dependence of EB effect shows that as a result of the decrease in grain size the overall area of the ferromagnetic/spin-glass interface as well as the fraction of frozen ferromagnetic spins have been reduced considerably, resulting in the weakening of the exchange bias effect [12].

But the electronic transport properties of cobaltites have remained less understood till date. In particular size dependence of electronic transport properties are less explored. Recently Kundu et al. observed a low temperature upturn in temperature dependent resistivity with reduction of grain size in  $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$  [13]. Frequency dependent ac susceptibility results suggest a spontaneous phase separated system with a cluster glass like state in  $\text{Pr}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$  as described in our earlier report [14]. In this paper, we carried out the temperature dependent resistivity measurements in the nanoparticles as well as bulk materials of  $\text{Pr}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$  (PSCO). Different temperature regime has been analyzed with fitting of  $\rho$  vs.  $T$  data. The upturn in resistivity with smaller grain size originates from the elastic e-e interaction which has been enhanced with reduction of grain size because of enhancement in disorder due to surface effect.

### Experimental details

The precursor of  $\text{Pr}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$  was prepared by conventional sol-gel technique as described in the literature [15]. The obtained precursor powder was pressed into pellet and finally annealed in air at  $800^\circ\text{C}$  and  $1000^\circ\text{C}$  respectively for 6 hours to get the sample of two different sizes. Single phase of the crystal structure of the sample is confirmed by the powder x-ray diffractometer (Seifert XRD 3000P) using a  $\text{CuK}_\alpha$  radiation. The temperature dependent resistivity was measured on a rectangular pellet with dimension  $6\text{mm}\times 4\text{mm}\times 2\text{mm}$  using four probe technique in a commercial cryogen-free physical property measurement system (PPMS).

The electrical contacts were made by connecting four fine copper wires to the sample using silver paste.

### Results and Discussions

Fig.1 shows the X-ray powder diffraction pattern for both the bulk as well as nano crystalline samples. Both the pattern can be well indexed with single phase orthorhombic ( $Pnma$ ) nature [JCPDS-ICDD File Nos. 01-071-1231] without any noticeable impurity as described in our earlier report [14]. But the broadened Peaks in XRD pattern for the sample heated with lower temperature ( $800^\circ\text{C}$ ) indicates that the crystallite size must be decreased from bulk to nanoscale dimensions.

Email: mpatra.phys@raghunathpurcollege.ac.in

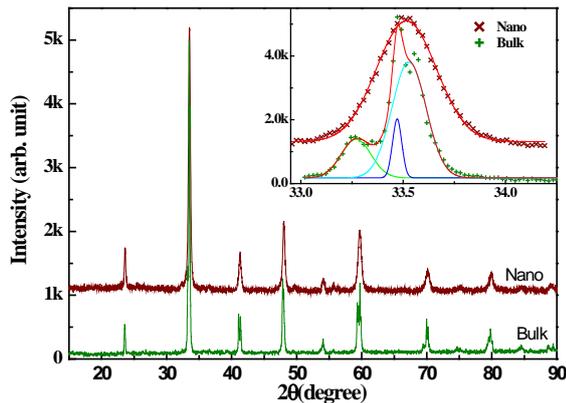


Fig. 1. XRD pattern of Nano and Bulk samples at room temperature. Inset shows the enlarged view of the peak with maximum intensity for both the samples.

Inset of Fig. 1 shows that three different peaks which are clear for the sample heated with higher temperature overlaps to a single peak due to peak broadening. The crystallite size or grain size for both the samples have been estimated using the Scherrer equation  $D = \frac{k\lambda}{w \cos \theta} \dots (1)$  where  $k = 0.9$ ,  $\lambda = 1.54084 \text{ \AA}$ ,  $w =$  full width half maxima of the concerned peak and  $\theta = \frac{1}{2}$  (peak position in radian). The crystallite size has been estimated about 7-8 nm and 50-60nm for the sample heated at 800°C and 1000°C respectively. We have designated the particle with smaller crystallite size as nano whereas the sample with larger crystallite sizes as bulk as the actual particle size is always larger than the estimated crystallite size from the XRD data.

Fig. 2 shows the temperature dependent resistivity for both the sample. As shown in the figure the temperature dependent resistivity for the bulk counterpart shows three distinct temperature regions as I. Linear metallic region (from room temperature to 250 K) II. Non-linear metallic region (>75 K) and III. An insulating region with a resistivity minimum (<75 K). The transition of linear metallic region to nonlinear metallic region can be associated paramagnetic to ferromagnetic transition temperature ( $T_c$ ) as described in earlier reports [13,14]. S. Kundu et. al. and B. Roy et. al. has reported a resistivity upturn with a resistivity minima and size induced metal insulator transition for  $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$  and  $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$  respectively [13,16]. Here also we get a resistivity upturn at lower temperature at the bulk counterpart and for the nanocrystalline sample metallic region is completely suppressed and the material shows almost insulating behavior through all the temperature region. Though a broad peak like feature is observed around  $T_c$  for this sample also.

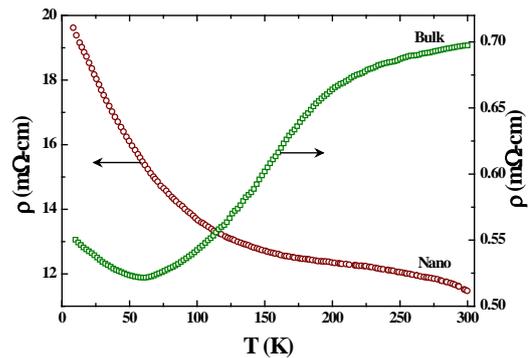


Fig. 2. Temperature dependence of resistivity for Nano and Bulk.

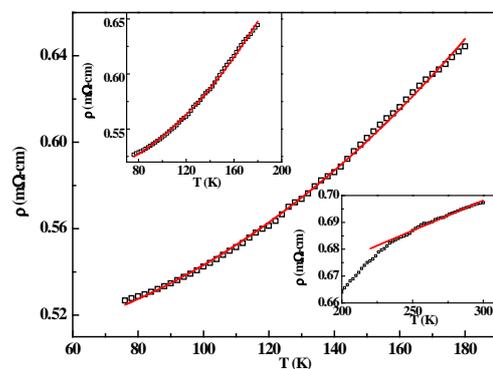


Fig. 3. Temperature dependence of resistivity for Bulk. Red line shows the fitted line using eqn. 2 as described in the text. Left inset shows the same data fitted with equation 3 and right inset shows the linear region.

Recently Modi et. al. shows that for semiconducting  $\text{Pr}_{1-x}\text{Sr}_x\text{CoO}_3$  compounds (low doping), the high-temperature resistivity data is fitted with the small polaron hopping (SPH) model and the variable range hopping (VRH) model. Whereas in metallic compounds (high doping range) the domination of e-e scattering has been observed [17]. So, in order to explain the temperature dependent resistivity behavior in our sample in the non-linear metallic region the data is fitted with general power law equation as  $\rho = \rho_0 + \rho_n T^n \dots (2)$  as shown in figure 3. Interestingly the obtained value of  $n$  is 2.15 which is quite close to the  $T^2$  dependence in metallic region and it is well established that it originates from the inelastic e-e interaction [18,19]. As  $n$  slightly differs from 2 the data in this region has been fitted with another equation as  $\rho = \rho_0 + \rho_e T^2 + \rho_m T^{4.5} \dots (3)$  as shown in the left inset of figure 3. We get a good fit with this equation which indicates the presence of electron-magnon interaction along with electron-electron interaction. But the value of  $\rho_m$  ( $7.92 \times 10^{-15}$ ) is much smaller than the value of  $\rho_e = (4.32 \times 10^{-9})$ .

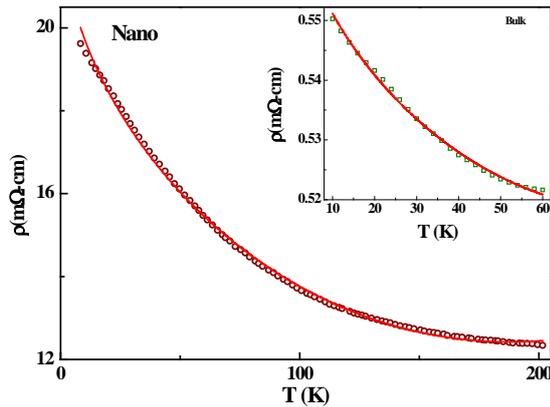


Fig. 4. Upturn in resistivity fit by equation for nano. Inset shows the upturn region fitted by same equation for bulk.

Another fascinating observation of this work is enhancement of low temperature upturn with decreasing grain sizes. Previously it has been reported that elastic e–e interaction is the dominant mechanism which gives rise to the low temperature upturn and resistivity minimum in  $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$  compound with lower grain sizes [13]. As shown in fig. 4, the low temperature upturn in resistivity can be well fitted with the equation  $\rho = \rho_0 - \rho_{ee}T^{\frac{1}{2}} + \rho_p T^p \dots$  (4) where the second term comes from electron-electron interaction and the third term is due to inelastic scattering. The parameters obtained from the fitting is given in the table 1.

Table I. Parameters obtained from fit with the equation 4

| Parameters                            | Nano                    | Bulk                   |
|---------------------------------------|-------------------------|------------------------|
| $\rho_0$ (Ω-cm)                       | 0.02286                 | $5.77 \times 10^{-4}$  |
| $\rho_{ee}$ (Ω-cm-K <sup>-1/2</sup> ) | $9.8928 \times 10^{-4}$ | $8.23 \times 10^{-6}$  |
| $\rho_p$ (Ω-cm-K <sup>-p</sup> )      | $3.7175 \times 10^{-8}$ | $5.66 \times 10^{-10}$ |
| $p$                                   | 2.16                    | 2.31                   |

From the fitting parameters as given in table 1 we can see that both the  $\rho_0$  and  $\rho_{ee}$  increase with decreasing grain size. This increment can be attributed to enhanced e–e interaction with decrease of grain size to the enhanced disorder in the sample around the surface region of the grains as the value of  $\rho_0$  is actually a measure of disorder in the sample.

### Conclusion

In conclusion, we have investigated the transport mechanism in  $\text{Pr}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$  with two different grain sizes. Temperature dependent resistivity

shows a resistivity upturn at lower temperature region which is enhanced with the smaller grain sizes. Fitting parameter in the nonlinear metallic region indicates that the transport mechanism can be attributed from e–e interaction and electron–magnon interaction. Whereas the resistivity upturn can be originated from the elastic e–e interaction. The enhancement of this interaction with reduction of grain size is attributed to enhanced disorder in the sample (surface effect).

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