CHAPTER 5

A STUDY OF MAGNETISM AND MAGNETOTRANSPORT OF HALF AND OVER-DOPED Nd$_{1-x}$Sr$_x$MnO$_3$ (0.50 ≤ $x$ ≤ 0.62) POLYCRYSTALLINE THIN FILMS

5.1 INTRODUCTION

During last few years the impact of nanostructuring on the magnetic and magnetotransport properties of manganites has attracted a fair deal of attention. Recently several experimental and theoretical studies have been focused on the exploration of the effect of grain downsizing on the functional properties of doped perovskite manganites [259,263,281-288]. These studies clearly highlight the significance of broken exchange bonds between the surface Mn cations and their likely impact on the magnetic properties. It has been shown that in nano-manganites (when the size is reduced roughly to ~50 nm or below), the charge and orbitally ordered (CO-OO) ground state with antiferromagnetic (AFM) spin order becomes unstable and this gives rise to a ferromagnetic (FM) ground state [141,282]. Size induced transition from the AFM/CO to the weak ferromagnetic (WFM) state was observed in both nanowires [282] and nanoparticles [283]. It has been shown by Lu et al. [141] that destabilization of the CO-AFM state and formation of a WFM order can result in an enhancement of magnetization by two orders of magnitude. The WFM ground state in nanomanganites resulting from the destabilization AFM ground state has been regarded as a direct consequence of size reduction because when the size is small enough (e.g. ~20 nm), the effect of surface spin disordering would become more evident. However, WFM induced by the destabilization of the AFM order has been also reported in single crystals [289,290] as well as epitaxial thin films [222]. This suggests that evolution of WFM out of the CO-AFM state cannot be alone attributed to downsizing to nanometric scale and that some additional effects such as orbital disordering may also be equally important [10,222,290-292].

Singh et al. [293] have demonstrated that in Bi$_{0.25}$Ca$_{0.75}$MnO$_3$ the charge ordering (CO) is observed in bulk samples with large particle size completely disappears in the nanoparticles
and there is also an emergence of ferromagnetism. They conclude that the disappearance of CO in nanoparticles is seen to be a general phenomenon depending upon the robustness of the CO. Markovich et al. [294-296] have studied the structure property correlation in La_{1-x}Ca_xMnO_3 (0.67 ≤ x ≤ 1) and Sm_{0.10}Sr_{0.90}MnO_3 [297]. They have shown that for La_{0.33}Ca_{0.67}MnO_3 nanoparticles, the FM moment at low temperatures increases with decreasing particle size. These particles also display exchange bias (EB) effect upon field cooling and the temperature variation in EB field, remanent magnetization, and spontaneous magnetic moment for the particles with different size are dependent on magnetic coupling between the AFM core and the FM-like shell. They have also compared this with their previous work on La_{0.20}Ca_{0.80}MnO_3 system [295], in which they have shown that both systems exhibit a monotonous enhancement of weak ferromagnetism linked to the reduction in the particle size at T = 200 K. They suggested that the C-type AFM structure observed in bulk La_{0.20}Ca_{0.80}MnO_3 manganite is much more stable than the 2/3-type one in La_{0.33}Ca_{0.67}MnO_3, resulting in surviving of OO even in 15 nm La_{0.20}Ca_{0.80}MnO_3 particles and leading to an disappearance of any CO state in La_{0.33}Ca_{0.67}MnO_3 at particle size ≤ 42 nm. These results shed light on the evolution of spin configuration in electron-doped manganite nanoparticles.

Rao and Bhat [298] have studied nanowires and nanoparticles of robustly charge ordered manganite Pr_{0.50}Ca_{0.50}MnO_3. Their findings also confirm the destruction of charge order and induction of weak FM component in the nanowires and nanoparticles. According to them the FM phase is the dominant equilibrium phase and is irreversible and is attributable to size induced surface disorder thus bringing out the similarities between the size- and doping-induced disorders. Zhang et al. [299] group have shown that for bulk La_{0.25}Ca_{0.75}MnO_3 compound, the robust charge ordering is weakened, accompanied with an appearance of a FM cluster glass state on decreasing particle size. They concluded that, these results can be attributed to the surface spins which gradually change the magnetic configuration of the particle via exchange coupling and magnetic interactions with decreasing particle size. Lu et al. [141,300] have shown for La_{0.40}Ca_{0.60}MnO_3 nanoparticles, that the decreasing of the size may affect significantly the magnetic properties of La_{0.40}Ca_{0.60}MnO_3 because of the broken exchange bonds between the surface Mn cations. However, while the size is small enough e.g. ~ 20 nm, the effect of surface spin disordering would become more evident, and thus results in the spin-glass-like state at low T, although this spin-glass-like behavior is not very significant. The effect of material downsizing can have more dramatic effect in the vicinity of boundaries separating different phases, like ferromagnetic metal (FMM), antiferromagnetic
metal (AFM-M), antiferromagnetic insulator (AFM-I), and charge ordered insulator (COI), that is, in the regions of the phase diagram where there is strong phase coexistence. Among the manganites, Nd$_{1-x}$Sr$_x$MnO$_3$ (NSMO) possesses very strong phase coexistence in the composition range $0.48 \leq x \leq 0.63$ and has several bicritical regions [284]. In case of NSMO, the AFM phase spans the whole overdoped region $(0.50 \leq x \leq 1)$ wherein the A-type AFM (antiferromagnetically coupled two dimensional ferromagnetic order) metallic phase occurs up to $x \sim 0.63$ and above that C-type AFM insulator (antiferromagnetically coupled one dimensional ferromagnetic order) state takes over. The phase boundary at $x \sim 0.63$ that separates A- and C-type AFM phases has been shown to possess fairly large FM contribution [222,289,290]. In single crystals and epitaxial thin films [222,289,290] this FM and the associated transition has been attributed to the strong orbital fluctuation/disorder in the proximity of the A-C phase boundary. Nanostructure materials by virtue of their larger surface to volume ratio are expected to undergo unexpected modifications in structure and magnetotransport properties. Nanocrystalline thin films can have even more pronounced modifications in their physical properties because in addition to its large surface to volume ratio the local epitaxy and strain could also make their contribution to the electronic phase evolution. Thus in nanostructured thin films the local epitaxy and the local strain states can be regarded as an additional degree of freedom to tune and to complement the WFM at the A-C AFM phase boundary in NSMO. However, nanocrystalline thin films of this material have not been investigated so far. In the present work, we show that the A-AFM metallic phase in nanocrystalline thin films (having crystallite size $< 20$ nm) of over-doped NSMO ($x \sim 0.60$-$0.62$) can be destabilized resulting in the occurrence of a FM metallic phase. In addition to small magnetic moment, remanence, large coercivity, the presence of FM phase is also suggested by the EB effect.

In the present chapter we present our study on the impact of nanostructuring on structure and magnetotransport properties of Nd$_{1-x}$Sr$_x$MnO$_3$ thin films in the composition range $0.50 \leq x \leq 0.62$. Nanostructured thin films (~300 nm thick) were deposited on LaAlO$_3$ (001) substrates by the nebulized chemical spray pyrolysis technique.

5.2 FILM DEPOSITION AND CHARACTERIZATION TECHNIQUES

5.2.1 SYNTHESIS OF POLYCRYSTALLINE Nd$_{1-x}$Sr$_x$MnO$_3$ ($x \sim 0.50$, 0.55, 0.60 and 0.62) THIN FILMS
The nanocrystalline thin films (~300 nm thickness) have been prepared on single crystal LaAlO₃ (001) substrates by the well known nebulized chemical spray pyrolysis technique [115]. Films were deposited at 300°C by spraying a homogeneous 0.2 molar aqueous solution of Nd(NO₃)₃.6H₂O (~99.9 %), Sr(NO₃)₂ (~99.99 %) and Mn(NO₃)₂.4H₂O (~98.5 %) nitrates dissolved in deionized water. The cationic ratio was Nd/Sr/Mn = 1-x/x/1, (where, x = 0.50, 0.55, 0.60, and 0.62). All films were annealed in air at 920°C for two hours and then cooled to room temperature slowly.

5.2.2 CHARACTERIZATIONS OF FILMS

Several characterization techniques have been used to study different properties of this film. Structural and microstructural characterization were done by powder X-ray diffraction (XRD, X’Pert PRO PANalytical, CuKα radiation), scanning electron microscopy (SEM) equipped with energy dispersive X-ray spectroscopy (EDS) facilities (SEM, Model: LEO 0440 SEM equipped with ISIS 300 Oxford Microanalysis system) and high resolution transmission electron microscopy (HRTEM, FEI Tecnai G² F30 STWIN, 300 kV FEG). We measured the DC magnetization in the temperature range 4 – 300 K using a SQUID magnetometer (MPMS-XL/quantum design). The cationic composition of films was probed by energy-dispersive X-ray spectroscopy (EDS or EDX) analysis. Temperature dependent DC magnetization was measured by a commercial SQUID magnetometer (MPMS-XL) and the temperature and low magnetic field dependent electrical transport was measured by a homemade four probe setup.

5.3 RESULTS AND DISCUSSION

5.3.1 STRUCTURAL AND MICROSTRUCTURAL CHARACTERIZATION

Representative 0-20 XRD patterns for all the films (x = 0.50, 0.55, 0.60, and 0.62) are shown in Figure 5.1. The XRD patterns are characterized by the diffraction maxima corresponding dominantly to (hk0) and (hk2). The two highest intensity peaks correspond to (110) and (220) planes in all the films. Apart from this the (112) and (123) reflections is also well developed in all the samples. It clearly therefore shows the films are polycrystalline in nature but have partial orientation along the (hk0). The highest intensity peaks belong to the substrate LaAlO₃. The analysis of the XRD data reveals that irrespective of the composition, all films have the orthorhombic symmetry (space group/Ibmm). Within the limit of the
resolution of the diffractometer no impurities (e.g., unreacted oxides of the cations used) and secondary phases are observed in the XRD data. Cationic composition investigated by EDS carried out at several places on all the films reveals that there is small Mn deficiency in all the films. For example for $x = 0.62$, the average cationic composition is found to be Nd/Sr/Mn $\approx 0.38/0.62/0.95$. Small variation of the compositions in the range $x \sim 0.50$-0.62 has no observable effect on the structure of these films.

All the lattice parameters and hence the unit cell volume of all the films are observed to increase with increasing $x$, i.e. $\text{Sr}^{2+}$ content. The variation of the lattice parameters is plotted in Figure 5.2. The observed increase is obviously due the larger cationic radius of the $\text{Sr}^{2+}$.

![Figure 5.1: Representative XRD pattern of all Nd$_{1-x}$Sr$_x$MnO$_3$ ($x = 0.50, 0.55, 0.60, \text{and} 0.62$) films.](image)

The surface microstructure of the films, as revealed by SEM, was found to consist of nanometric grains. Representative surface morphologies of all the films are shown in Figure 5.3. In all the films the surface is seen to consist of nanostructured grains with average size of 80 – 100 nm.
Figure 5.2: Variation of the lattice parameters with Sr content $\langle x \rangle$.

Figure 5.3: The SEM picture shows the surface morphology of all Nd$_{1-x}$Sr$_x$MnO$_3$ ($x = 0.50$, $0.55$, $0.60$, and $0.62$) films.
In addition, a fair degree of porosity is seen in all the films. This could be due to lower annealing temperature and time used to achieve small grain size.

A detailed HRTEM experiment was conducted to explore the nano and sub-nano scale microstructures. In general, all the films have the nano crystallites of about 10 to 20 nm in size were randomly distributed throughout the film microstructure. Typical TEM micrographs of $x = 0.62$ film is shown in Figure 5.4.

The nano-cristallites were mostly surrounded by the grain boundaries of relatively thin in size, viz. 1 to 2 nm in thickness. These films were also constituted of amorphous regions where the nano crystallites were embedded in it. Amorphous regions and the grain boundaries (again amorphous) were normally coexisting. The amorphous regions can be regarded as the highly disordered regions of the grain boundary in these nano-crystalline films. Lattice imaging of these nano-cristallites revealed that most of these crystals are constituted of (110) planes of orthorhombic structure. Interplanar separation between the two planes was $d_{110} = 0.38$ nm. A corresponding selected area electron diffraction pattern (SAED) is displayed as an inset in Figure 5.4b. Normally we do not observe the growth of any other set of planes in these nano crystallites, confirming the preferred growth. However, in few regions the nano crystallites grown in other directions are also revealed as illustrative examples, the lattice planes ($hkl$: 112) are marked in the microstructure (see the inset in Figure 5.4b). The lattice spacing was found to be $d_{112} = 0.27$ nm. The above HRTEM results are in excellent agreement with observed XRD patterns, which also showed the dominant growth along the (110) direction.

These observations are clear evidences that the whole film is constituted of a quantum well type structure, where the low energy nano-cristallites are surrounded by high energy grain boundaries (disordered structure). In manganites these disordered regions consist mainly of the broken Mn-O-Mn bonds and hence can be regarded as magnetically disorder. Due the disordered nature of the grainboundary regions is expected to have profound impact on the magnetic as well as electrical transport properties of these compounds. The magnetization of the disordered grain boundary regions is expected to be significantly different from that of the intra-granular ordered regions. It has been shown that if the ordered intra-granular regions are FM and metallic, then the magnetization and resistivity of the disordered granular regions are lower and higher, respectively [109]. However, if the ordered intra-granular regions are AFM and insulating, the magnetization of the disordered grain boundary regions could be higher.
and the resistivity could be lower than the ordered regions. The appearance of FM order in nano-crystalline CO/OO manganites has been cited as the evidence for this [259, 301].

Figure 5.4: HRTEM micrograph showing typical microstructure of the Nd$_{1-x}$Sr$_x$MnO$_3$ film ($x \sim 0.62$). Disordered regions sandwiched between the crystalline ones can be easily discerned in both the micrographs (a & b). The major lattice spacing ($d = 0.38$ nm) has been marked in the Figure 5.4b. The less frequently observed interplanar separation has been inserted as an inset in Figure 5.4b. The SAED pattern corresponding to the microstructure is shown in the inset of Figure 5.4b.
5.3.2 MAGNETIC CHARACTERIZATION

The temperature dependence of the remnant (REM) and field cooled (FC) magnetization of all the films was measured in the temperature range 10 – 300 K. The applied DC magnetic field was $H = 500$ Oe. The magnetic field dependent magnetization of all the films was measured at $T = 5$ K. The FM transition temperature (Curie temperature, $T_C$) was determined from the $\frac{dM}{dT}$ vs. $T$ plots. The $M$-$T$, $M$-$H$ and $\frac{dM}{dT}$ - $T$ data are plotted in Figure 5.5a-d.

![Figure 5.5a: The temperature dependence of remnant (REM) and field cooled (FC) magnetization ($H = 500$ Oe) $Nd_{0.50}Sr_{0.50}MnO_3$ thin film. $\frac{dM}{dT}$ - $T$ plot used to determine the $T_C$ is shown in upper inset. $M$-$H$ plot taken at $T = 5$ K is shown in lower inset.](image)

Interestingly, in all the films the magnetization starts to increase at $T \sim 275$ K and we take this as the onset of PM-FM transition temperature. The PM-FM transition temperature $T_C$ of $x = 0.50$ film is found to be $\sim 226$ K (Figure 5.5a). The REM and FC curves show small bifurcation in the lower temperature region. The $M$-$H$ loop is well developed. The saturation and remnant magnetization is found to be $5.23 \mu_B$/Mn and $3.55 \mu_B$/Mn, respectively. It is interesting to note that in the present case the PM-FM transition temperature is lower than that of the single crystals of similar composition ($Nd_{0.50}Sr_{0.50}MnO_3$) where it occurs at $T_C \sim 250$ K. Further the observed value of the magnetization of the single crystals of similar composition is generally smaller than that observed in the present case [222,290]. In single crystals the
ground state for \( x = 0.55 \) is A-type AFM-metallic. In contrast, in the present case a clear transition to the FM state is seen at \( T_C \sim 235 \) K (Figure 5.5b).

Figure 5.5b: The temperature dependence of remnant (REM) and field cooled (FC) magnetization (H = 500 Oe) in \( \text{Nd}_{0.45}\text{Sr}_{0.55}\text{MnO}_3 \) thin film. \( \frac{dM}{dT} \) plot used to determine the \( T_C \) is shown in upper inset. M-H plot taken at \( T = 5 \) K is shown in lower inset.

Figure 5.5c: The temperature dependence of remnant (REM) and field cooled (FC) magnetization (H = 500 Oe) in \( \text{Nd}_{0.60}\text{Sr}_{0.60}\text{MnO}_3 \) thin film. \( \frac{dM}{dT} \) plot used to determine the \( T_C \) is shown in upper inset. M-H plot taken at \( T = 5 \) K is shown in lower inset.
As revealed by the well-defined M-H loop, with $M_r \sim 2.64 \mu_B/\text{Mn}$ and $M_s \sim 4.74 \mu_B/\text{Mn}$, the ground state in the present case is a FM. On further increasing the Sr content to $x = 0.60$ and $x = 0.62$ the $T_C$ remains constant at $\sim 235$ K but the magnetic moment is seen to decrease drastically. The remnant and saturation magnetizations are found to be $M_r \sim 0.81 \mu_B/\text{Mn}$ and $M_s \sim 1.53 \mu_B/\text{Mn}$ for $x = 0.60$ (Nd$_{0.40}$Sr$_{0.60}$MnO$_3$) and $M_r \sim 0.63 \mu_B/\text{Mn}$ and $M_s \sim 1.17 \mu_B/\text{Mn}$ for $x = 0.62$ (Nd$_{0.38}$Sr$_{0.62}$MnO$_3$). The magnetic field corresponding to the saturation magnetization is found to be $H_S \sim 7$ kOe for $x = 0.50$ and it increases to $\sim 10$ kOe for $x = 0.55$. For higher Sr concentrations the value of $H_S$ is as high as 20 kOe. In all the films the coercivity is found to be asymmetric suggesting the presence of EB effect. For example in $x = 0.50$ film, the coercivity $H_C$ is found to be +1162 Oe and $-1210$ Oe. The observed asymmetry in coercivity is small the exchange bias is very weak. Since EB is caused by formation of FM-AFM interfaces, this also confirms the presence of both FM and AFM phases. The value of various parameters determined from the M-T and M-H data is also presented in Table 5.1.

Although the film shows well developed M-H loop, the FM ground state appears different in many respects from that of the optimally doped Nd$_{1-x}$Sr$_x$MnO$_3$ ($x \sim 0.35-0.45$)
Further, at higher Sr$^{2+}$ concentrations ($x = 0.55$ and 0.62) saturation occurs at much higher magnetic fields (~20 kOe) [10]. One possible reason for the large $H_C$ and $H_S$ in the present case could be due to the pinning of magnetic domains by the grain boundaries/amorphous regions. In the present overdoped Nd$_{1-x}$Sr$_x$MnO$_3$ ($x \sim 0.62$) films the coercivity $H_C \sim -1484$ and +1476 Oe. This is nearly an order of magnitude higher than that of the manganites ($H_C \sim 100$-200 Oe) in conventional hole doped manganites having optimum hole doping (20 - 40%) [10].

Table 5.1: The values of $T_C$, $M_r$, $M_S$ and $H_C$ for Nd$_{1-x}$Sr$_x$MnO$_3$ ($0.50 \leq x \leq 0.62$) thin films on LAO (001) single crystal substrate.

<table>
<thead>
<tr>
<th>$x$</th>
<th>$T_C$ (K)</th>
<th>$M_r$ ($\mu_B$/Mn)</th>
<th>$M_S$ ($\mu_B$/Mn)</th>
<th>(-)H$_C$ (Oe)</th>
<th>(+)H$_C$ (Oe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50</td>
<td>226</td>
<td>3.55</td>
<td>5.23</td>
<td>1210</td>
<td>1162</td>
</tr>
<tr>
<td>0.55</td>
<td>235</td>
<td>2.64</td>
<td>4.74</td>
<td>1097</td>
<td>1067</td>
</tr>
<tr>
<td>0.60</td>
<td>235</td>
<td>0.81</td>
<td>1.53</td>
<td>1359</td>
<td>1326</td>
</tr>
<tr>
<td>0.62</td>
<td>235</td>
<td>0.63</td>
<td>1.17</td>
<td>1484</td>
<td>1476</td>
</tr>
</tbody>
</table>

This observation is in agreement with the magnetization data of single crystals of similar composition reported by Akahoshi et al. [290]. Interestingly the exchange bias effect observed at $x \sim 0.62$ gets diluted when the Sr content is reduced to $x \sim 0.60$ suggesting reduced FM phase fraction. In these films the coercivity is found to be $H_C \sim -1359$ and +1326 Oe giving negligible $H_{EB} \sim$10 Oe.

In manganites the appearance of FM behaviour in AFM regime is not surprising. In nano-manganites with an AFM ground state (such as the present nano-crystalline thin films) the superexchange interaction that drives AFM is diluted by the surface disorder [285,291,292,299,301]. This induces a reorganization of the disordered surface spins and has recently been explained in terms of core-shell model [299,301]. In the core-shell model the magnetization has been expressed by,

$$M = \alpha M_{shell} \sum_{i,j} \cos \theta_{ij} + (1 - \alpha)M_{core}$$

(5.1)

the shell thickness ‘$\alpha$’, that can be regarded as a measure of the surface disorder, increases with decreasing crystallite size. The angle between two spins $i$ and $j$ ($\theta_{ij}$) is $180^\circ$ for the cores.
but for the shells it can attain any value $\theta_{ij} < 180^\circ$. Further we suggest that as the boundary between the core and the shell may not be sharp, $\theta_{ij}$ will show a negative gradient away from the inner part of the shells (that is, $\theta_{ij}$ will be closer to $180^\circ$ on the inner part of the shells but on the outer part it will have lowest value.) Since in the present study the average crystallite size is about 15 nm, the shell contribution is expected to be significant. In other words, as the grain size scales down, the effective FM and AFM exchange interactions $J_{FM}$ and $J_{AFM}$ are expected to be renormalized. Within the core the $J_{AFM}$ prevails and the spin ordering is AFM. The outer shell should, strictly speaking, be spin disordered and less stable than both AFM as well as the FM. One natural way for this spin disordered shell around the AFM core, to minimize or reduce the energy to achieve a stable configuration would be through reorganization of the spin order. The emergent spin order is in the form of a FM shell around the AFM core. However, the spins on the outermost regions are expected to be more parallel than those located on the inner part of the shell. The occurrence of the FM shell results in formation of natural AFM/FM interfaces that also causes EB effect. In nanosized samples coexistence of three magnetic components, viz., AFM component cores of nanoparticles, weak FM component due to reorganized surface magnetism, and additional magnetic field induced weak FM component of the cores, are possible. Thus in one possible scenario, this is phase separation at nanoscale in which weak FM component could be regarded as the nanoscale inhomogeneity present in the AFM matrix comprising of the grain cores. However, as seen in the M-T and M-H results, relatively large magnetic moment and the reasonably well developed FM transition is different from the WFM observed in other overdoped/electron doped manganites [141,222,290,299]. In fact Markovich et al. [294] conclusively shown that even for CaMnO$_{3-\delta}$ nanoparticles (~ 50 nm) a predominant AFM phase exists in the core with a weak FM component at the particle surfaces and that the magnetic behaviour is mainly determined by surface effects, which manifest themselves in high coercive fields, high irreversibility field, and asymmetric magnetic hysteresis loops attributed to the exchange bias effect.

At this point we would like to emphasize that the orbital order (OO) [291,292] which is also affected by the reduced crystallite size may play a very important role in the stabilization of the FM component. In manganites, it is generally accepted that orbital disordering, i.e., the mixed state of $3d(z^2-r^2)$ and $3d(\chi^2-\gamma^2)$ orbitals stabilizes FM phases [10,222,291,292]. At the A- to C-AFM phase boundary at $x \sim 0.62-0.63$, the presence of competing $3d(\chi^2-\gamma^2)$ and $3d(z^2-r^2)$ orbital orders should cause strong orbital fluctuations that
may be controlled by crystallite size effects and the degree of polycrystalline disorder. The important role of orbital fluctuations is also indicated by the sharp decrease in the value of magnetic moment when the Sr concentration is lowered from the value corresponding to the A-AFM, C-AFM phase boundary ($x \sim 0.62-0.63$). Hence in nanosized overdoped Nd$_{1-x}$Sr$_x$MnO$_3$, the FM phase may be due to the combined effect of reduced crystallite size and the orbital disordering/fluctuations on the spin reorganization at the crystallite shells.

5.3.3 ELECTRICAL TRANSPORT CHARACTERIZATION

The temperature dependent resistivity was measured in the temperature range 5-300 K and the data are plotted in Figure 5.6. The $x = 0.50$ film shows an insulator-metal transition (IMT) at temperature $T_{\text{IM}} \sim 230$ K, which is slightly higher than its $T_C \sim 226$ K, at $T < T_{\text{IM}}$ the $\rho - T$ curve shows broad hump like feature around $T \sim 150$ K (shown by an arrow). This could be attributed to the presence of small CO clusters in the FM matrix. In single crystal form this compound shows a strong rise in the resistivity around CO temperature $T_{\text{CO}} \sim 150$ K. This is suppressed in the present. The main reason for this is the suppression or disordering of the CO/OO state due nano-structuring induced disorder that results in surface phase separation [259,301]. In the lower temperature region, the $\rho$-T curve shows an upturn (shown by an arrow). Such an upturn has generally attributed to the presence of grain boundary disorder, which in the present case is enhanced due to nano-structuring. On further increasing the Sr$^{2+}$ content, the IMT is first increases to $\sim 270$ K for $x = 0.55$ and then decreases $\sim 223$ K and $\sim 205$ K, respectively for $x = 0.60$ and 0.62. The low temperature upturn is absent in the $x = 0.55$ film but it reappears again in $x = 0.60$ and $x = 0.62$ samples. The occurrence of insulator-metal transition in the films with Sr$^{2+}$ concentration 0.55 – 0.62 is rather surprising. As per the phase diagram of Nd$_{1-x}$Sr$_x$MnO$_3$ no IMT is observed in the composition range $0.55 \leq x \leq 0.62$ [10]. The ground state in this composition range is AFM metallic. One possible reason for occurrence of IMT in this could be the following. As described in the previous section that in the electron doped or the over doped regime a weak FM ground sate arises due to the surface phase separation caused by the nanostructured nature of these films. As pointed out earlier, such an state has been reported in several other over doped manganites also [10,141,222,259,283-300]. Hence, we consider phase separation to be the cause for the IMTs even when Mn$^{4+}$ / Mn$^{3+} \geq 1$. This is also supported by the M-T and M-H data of these films that has been already discussed above. Here we would like to mention that, in relation to phase separation in manganites, the synthesis condition also play important role through
micro-structural modification. As described earlier, the increase in the structural disorder with Sr\(^{2+}\) content could also play an important role in phase separation in the present films. Further, the surface phase separation also plays very important role in manganite thin films [259].

![Figure 5.6: ρ-T curve for Nd\(_{1-x}\)Sr\(_x\)MnO\(_3\) (x = 0.50, 0.55, 0.60, and 0.62) thin films on LAO (001) substrate.](image)

Recently it was shown that oxygen vacancies, that induce quenched disorder, play very important role in phase separation in manganites could cause metamagnetic phase with appreciable metallic phase fraction in the charge ordered manganite thin films [260]. Thus the suppression of the CO in the vicinity of half doping could be caused by enhanced FMM phase fraction.
The higher IMT ~ 270 K in case of Nd$_{0.45}$Sr$_{0.55}$MnO$_3$ could be due to the metallic nature of the A-type AFM phase. The nano-structuring disorders the A-type AFM order in the interface/surface regions, and induces weak FM, while the metallic nature remains the same. Hence the fraction of the FM metallic phase increases as compared to $x = 0.50$ film. The enhanced fraction of the metallic phase could be the source of higher IMT in $x = 0.55$ film. The decrease in IMT at $x = 0.60$ and 0.62 is possibly due to the the reduced fraction of the weak FM metallic phase.

5.3.4 LOW FIELD MAGNETORESISTANCE

The temperature dependence of magnetoresistance (MR) was measured in the temperature range 77-300 K at magnetic field $H = 4$ kOe. The MR-T data is plotted in Figure 5.7.

As seen in Figure 5.7, the MR-T curve of $x = 0.50$ shows two MR peaks first at 218 K (MR = 4.72\%) and second at 113 K (MR = 5.28 \%), for $x = 0.55$, 0.60 and 0.62 MR peaks observed at 218 K (MR = 3.69 \%), 208 K (MR = 3.12 \%) and 178 K (MR = 2.91 \%) respectively. The MR-T peak is sharper for $x = 0.50$ and $x = 0.55$ films. This could be due to the larger FM phase fraction in these films. In the $x = 0.50$ film, a second peak is also seen.
around T ~ 110 K. Since this temperature corresponds to the broad hump observed in its $\rho$ - T data, the origin of the MR peak can be attributed to the presence of the CO-AFM cluster in the FM matrix.

The destabilization of the AFM-CO and appearance of FM or weak FM behaviour along with the IMT in the present investigation has been explained in terms of the surface disorder caused by nanostructuring and the occurrence of orbital fluctuations in the studied composition region. Nearly similar behaviour is also shown by all the manganites. As discussed by Rao et al. [282] several possible mechanisms that cause the destabilization of the COI state and vanishing of the AFM transition with a concomitant appearance of weak FM metallic ground state in nanostructured manganites have been proposed. In 1962 [302] L. Neel proposed that fine particles of AFM materials should exhibit weak ferromagnetism and/or superparamagnetism. He saw this as a consequence of uncompensated spins on the two FM sublattices that constitute the AFM lattice. In manganites thus other factors, substrate induced strain also destabilize the COI-AFM state and give rise to FM state [303]. In case of Pr$_{0.5}$Ca$_{0.5}$MnO$_3$ free standing nanowires Rao et al. [282], have proposed that the strain arising from the surface-coordination deficiency induced bond contraction and concomitant changes in the electronic band structure due to quantum confinement effects could be the possible cause for the destabilization of AFM-COI and appearance of the FM metallic state. Rao et al. [283], have also studied the destabilization of the AFM-COI in nanoparticles of Nd$_{0.5}$Ca$_{0.5}$MnO$_3$. According to them the surface disorder is the mechanism of the suppression of the CO transition and following two mechanisms are possible. In manganites the CO in the vicinity of the half doping is a result of in-commensurate configurations associated with the movement of extended charge-ordering planar defects also known as dis-commensurations. In nanoparticles, these dis-commensurations could get pinned at the surface and hence blocking the establishment of long-range CO. Alternatively, the disorder present in the surface extending to a few layers into the interior of the nanoparticles may prevent the formation of the long-range charge ordered state. However, the ferromagnetic order can still occur due to the short-range nature of the exchange interactions since the FM fluctuations are already present at higher temperatures. A. Biswas et al., have studied the impact of nanostructuring on the AFM-CO transitions in Pr$_{0.5}$Sr$_{0.5}$MnO$_3$ [286]. Their results demonstrate that as the particle size is reduced, the formation of the CO state is highly disturbed and the fraction of the AFM-CO state in the nanoparticles may be too small to dominate over the FM interaction. This result in the vanishing of the distinct FM-AFM transition seen in single crystalline and large
particle size samples, the PM-FM transition remains nearly unaffected. S. Dong et al. have theoretical shown that in nanostructured manganites the surface phase separation plays a very important role in the destabilization of the AFM-CO and appearance of a weak FM [259]. In the vicinity of the half doping the FM caused by the destabilization of AFM-CO state is generally not a canonical FM state but has signatures of a metamagnetic state akin to clusters glass [141,285,286].

As discussed earlier in this chapter, in Nd\textsubscript{1-x}Sr\textsubscript{x}MnO\textsubscript{3} (0.50 ≤ x ≤ 0.63) the charge order in believed to be locked to x~0.50 [263,290]. In this compound there are two types of orbital orders (OO). The first is the d(x\textsuperscript{2}−y\textsuperscript{2}) or planar-type (2D) OO located in 0.52 ≤ x ≤ 0.63, accompanying the A-type AF order in which the x\textsuperscript{2}−y\textsuperscript{2} electrons are conducting within the FM plane. The other is the 3d(z\textsuperscript{2}−r\textsuperscript{2}) rod-type OO state located in 0.63 ≤ x ≤ 0.80, accompanying the C-type AF order in which charge dynamics shows one-dimensional like behavior along the FM chain. These two OO states meet in a bicritical manner around x = 0.63. It should be noted that the orbital-ordering temperature, T\textsubscript{OO} ~400–600 K is much higher than that of the AF ordering temperature T\textsubscript{N} ~200–250 K. Near the phase boundary, a weak ferromagnetic (WFM) phase emerges at low temperatures. The origin of which still remains an unsettled question. In the present case, the occurrence of the weak FM behaviour and the IMT in the region where AFM transitions are expected (T\textsubscript{N} ~200–250 K) could has been explained in terms of the surface disorder induced destabilization of the AFM or AFM-CO and orbital fluctuations.

**5.4 SUMMARY**

- Over doped Nd\textsubscript{1-x}Sr\textsubscript{x}MnO\textsubscript{3} (x ~ 0.50-0.62) polycrystalline thin films having average crystallite size ~15 nm have been studied in relation to their magnetic and magnetotransport properties.
- These films exhibit anomalous weak ferromagnetism in the electron doped or over doped regime.
- The ferromagnetic transition temperature remains almost independent of the Sr content.
- The magnetization is observed to decrease with increase in Sr content and the drop is very abrupt beyond x = 0.55.
- The occurrence of this ferromagnetism especially beyond $x = 0.55$ has been explained in terms of the surface phase separation due to spin reorganization at reduced crystallite size and enhanced orbital disordering.
- The saturation field and coercivity are much larger than observed in the conventional doping range ($x = 0.35 – 0.40$).
- Signature of weak exchange bias effect is also seen. The exchange bias is also weakened by the nano-structuring.
- All the films show a well insulator to metal transition and the IMT increases till $x = 0.55$ and decreases beyond.
- The low field magnetoresistance is very small and appreciably lower than the values generally observed for the doping range $x = 0.35 – 0.40$. 