Magnetic, Transport and electron magnetic resonance studies of nanomanganite $Nd_{0.67}Sr_{0.33}MnO_3$

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Introduction to Rare Earth Manganites

General Formula : $A^{3+}_{1-x}\, B^{2+}_{x}\, Mn^{3+}_{1-x}\, Mn^{4+}_{x}\, O^{2-}_{3}$

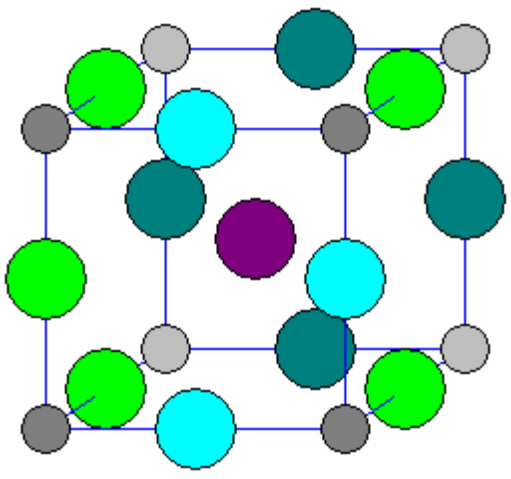
A : Rare earth Ion La^{3+} ,Pr^{3+} ,Nd^{3+}

B : Divalent Ion Ca^{2+} ,Pb^{2+} ,Sr^{2+}

Phenomena Exhibited by the Manganites

- **Colossal Magnetoresistance (CMR)**
- **MI transition concurrent with FM-PM transition**
- **Charge Ordering , Orbital Ordering**
- **Phase Separation**

Perovskite Structure

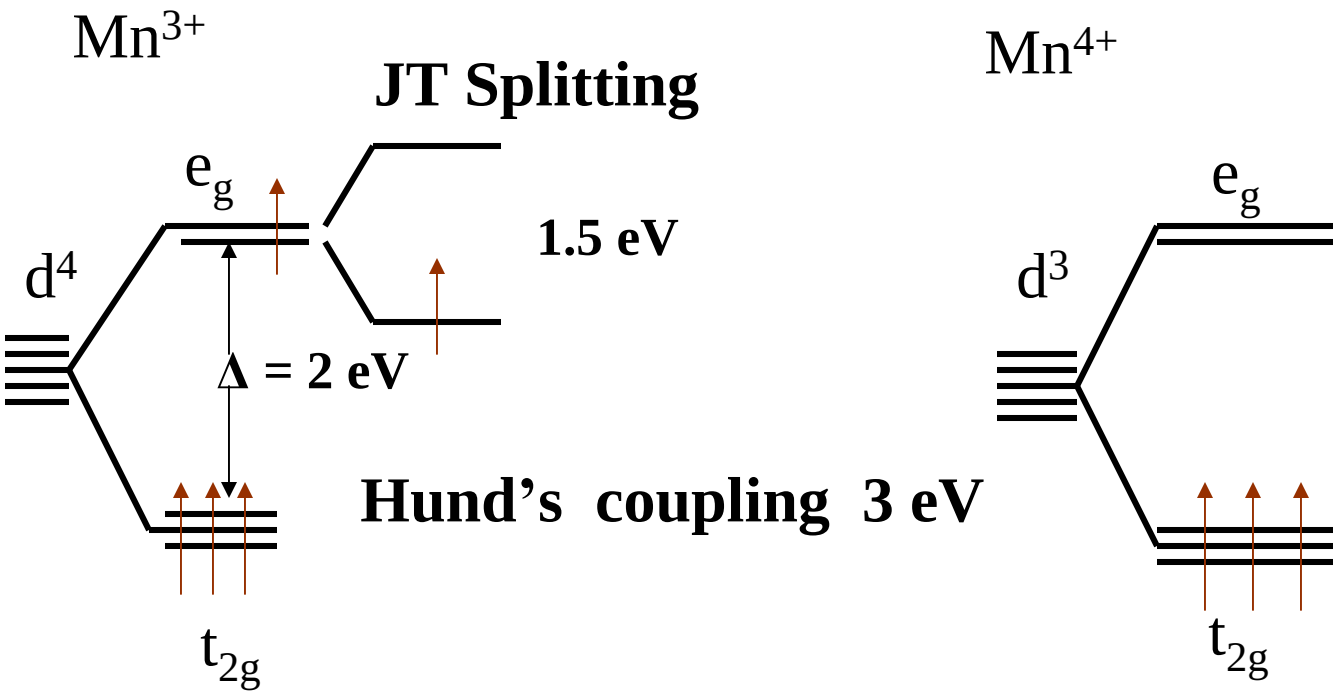


A or B : Body Centre (purple)

Mn : Corners (gray)

O : Midpoints of the edges (green & blue)

Electronic Configuration



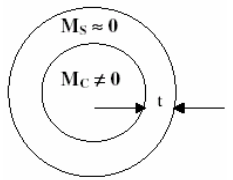
Hole Doping : Doping of Divalent ion in $AMnO_3$ introduces Mn^{4+}

Electron Doping : Doping of trivalent ion in $BMnO_3$ introduces Mn^{3+}

Nanomanganites - Properties-Importance

• Magnetic recording, magnetic data storage and magnetic field sensors etc…

•Tuning of intrinsic colossal magneto resistance (CMR) with the particle size leads to intergranular magneto resistance (IMR) which is due to the spin polarized tunneling between the neighbouring grains. IMR can be increased by decreasing the grain size.



• Reduction of saturation magnetization with the particle size due to the enhancement of outer layer (shell) thickness as the particle size decreases.

• In nano range, each grain consists of core and shell. Core exhibits the properties similar to the bulk and the outer shell consists of oxygen faults, vacancies and dangling bonds.

- **Magnetic Calorific Effect (MCE) reduces with the surface to volume ratio. Core shows the first order magnetic phase transition and the shell shows the second order. The nano crystal exhibits the second order phase transition by hiding the intrinsic behaviour.**

- **Exhibiting the superparamagnetic behaviour, surface spin glass behaviour, large coerceivities and improved low field magneto resistance (LFMR) as compared to their corresponding bulk values.**

- **Tuning of magnetic phase transitions with the particle size.**

- **Increase in resistivity with the decrease of particle size.**

Motivation

• **The above mentioned properties are addressed only for the limited number of nanomanganite systems (LCMO, LSMO) and are not studied in other systems. The transport and magnetic properties of this system (NSMO) are studied for the first time in our report.**

• **There are very few EMR reports on nanomanganite systems which gives the information about the interaction mechanisms, spin-orbit couplings, nanoscopic phase separations and magnetic phase transitions.**

$Nd_{1-x}Sr_xMnO_3$ phase diagram

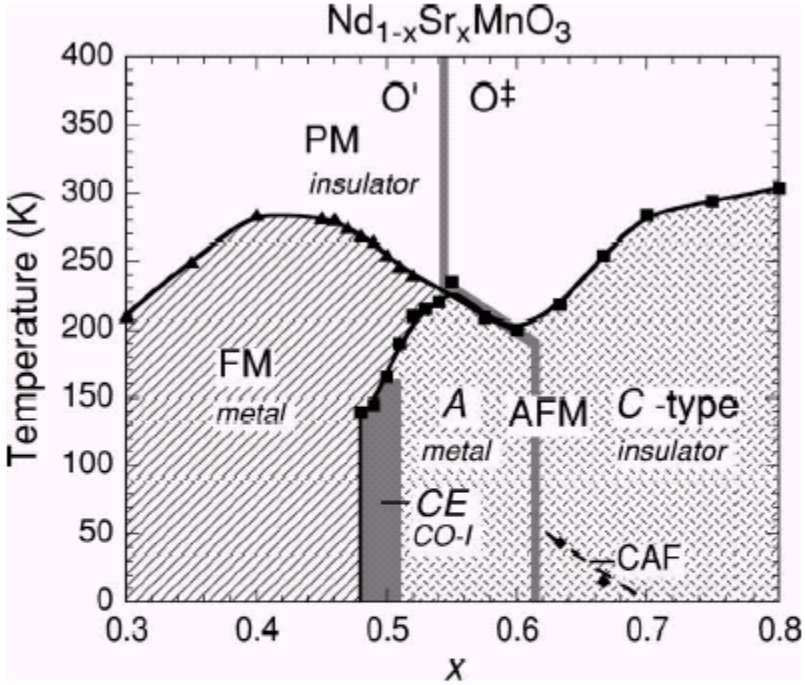


FIG. 1. Phase diagram of $Nd_{1-x}Sr_xMnO_3$ (Ref. 12). Each phase is denoted by capitalized labels; PM: paramagnetic insulating, FM: ferromagnetic, AFM: antiferromagnetic, CO-I: charge-ordered insulator, CE: *CE*-type charge/spin order, A: *A*-type antiferromagnetic order, C: *C*-type antiferromagnetic order, CAF: possible canted antiferromagnetic order.

Experimental details:

- **Sample preparation - Sol-gel method**

•X-ray diffraction (XRD) to know the phase purity and Transmission electron microscopy (TEM) was used to measure the grain size and it's distribution.

•Resistivity measurements were done both in the presence (7T) and in the absence of magnetic field down to liquid nitrogen temperature from room temperature to study the transport properties.

- **AC susceptibility measurements were performed from room temperature down to 77K to study the magnetic phase transitions.**

- **Electron Magnetic Resonance measurements were performed from 10K to 300K to study the spin dynamics.**

Results:

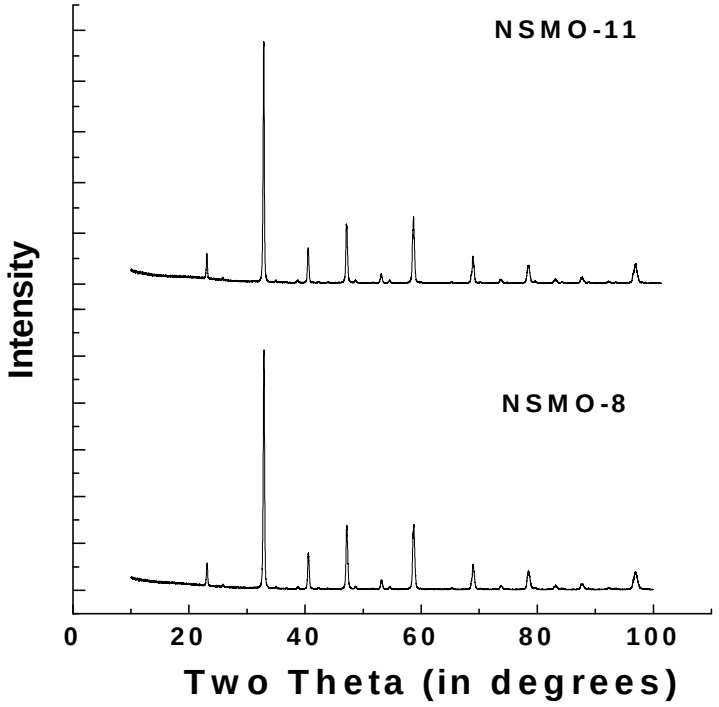
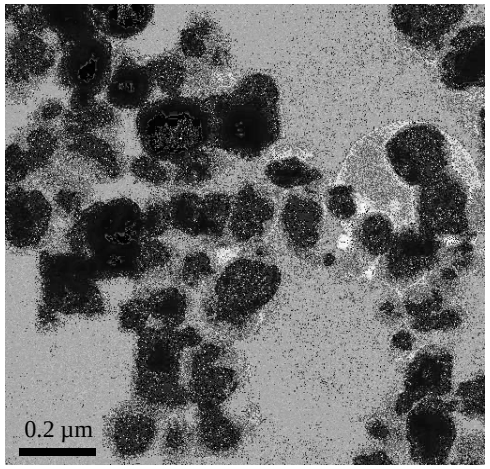


Fig 1

XRD micrograph

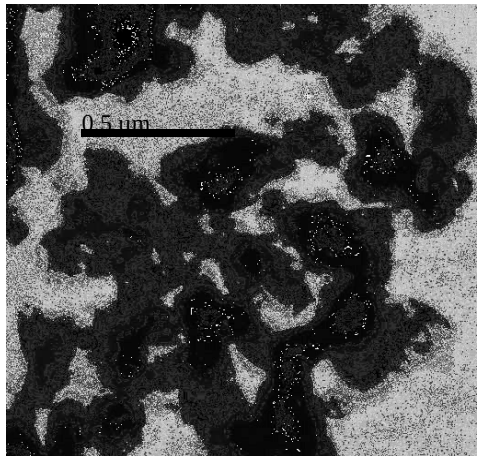
NSMO-8

Mean grain size 20nm



NSMO-11

Mean grain size 35nm



TEM micrographs

Unit cell: orthorhombic, a = 5.45 A^o , b = 5.43 A^o, c = 7.71 A^o, , space group is P_BNM.

Bulk values: a = 5.46 A^o , b = 5.45 A^o , c = 7.73 A^o

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Effect of grain size:

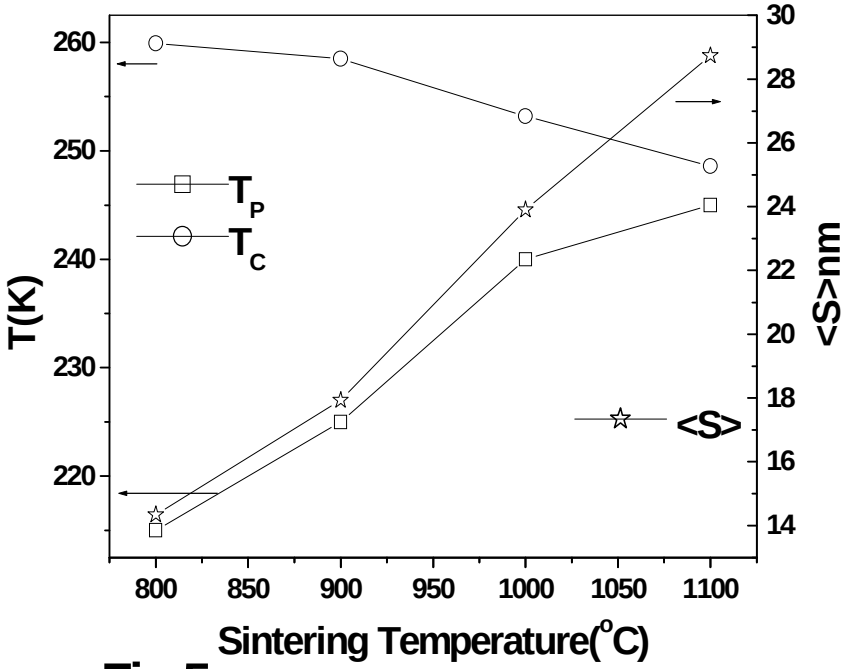


Fig 5

- With the sintering temperature, grain size increases.
- With the decrease in grain size, T_c (ferromagnetic-paramagnetic transition temperature) increases.
- As the grain size decreases, T_p (metal-insulator transition temperature) decreases.

Experimental data of NSMO material

Sample code	Compositional Formula	Sintering Temp. (^oC)	T_P	T_C	$\Delta T(T_C \sim T_P)$ (Degree Kelvin)	S (nm)	MR%
NSMO-8	$Nd_{0.67}Sr_{0.33}MnO_3$	800	215	260	45	15	45
NSMO-9	$Nd_{0.67}Sr_{0.33}MnO_3$	900	225	258	33	20	47
NSMO-10	$Nd_{0.67}Sr_{0.33}MnO_3$	1000	240	253	13	25	44
NSMO-11	$Nd_{0.67}Sr_{0.33}MnO_3$	1100	245	249	4	30	45

.

Sample code	Compositional formula	Sintering temperature (in ^{o}C)	T_P (in Kelvin)	T_C (in Kelvin)	ΔT (T_C - T_P) in Kelvin	Crystallite size S (nm)	MR%
NSMO8	$Nd_{0.67}Sr_{0.33}MnO_3$	800	215	268	45	15	45
NSMO9	$Nd_{0.67}Sr_{0.33}MnO_3$	900	225	258	33	20	47
NSMO 10	$Nd_{0.67}Sr_{0.33}MnO_3$	1000	240	253	13	25	44
NSMO-11	$Nd_{0.67}Sr_{0.33}MnO_3$	1100	245	249	4	30	45

Electrical transport and MagnetoResistance (MR)

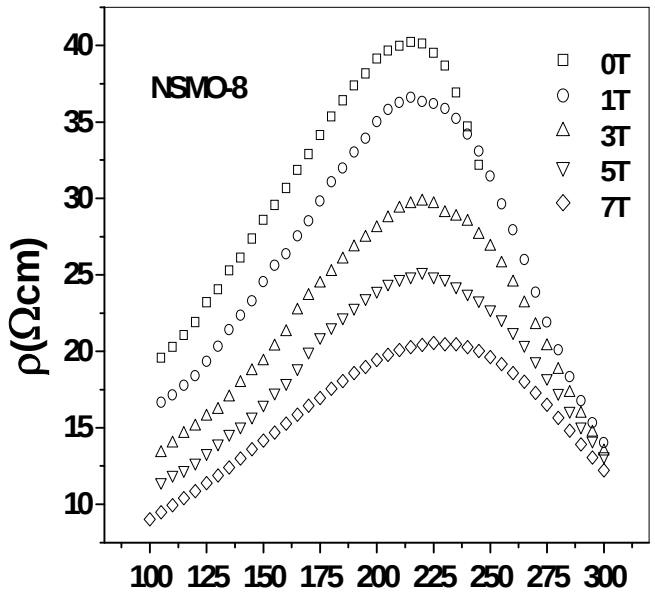
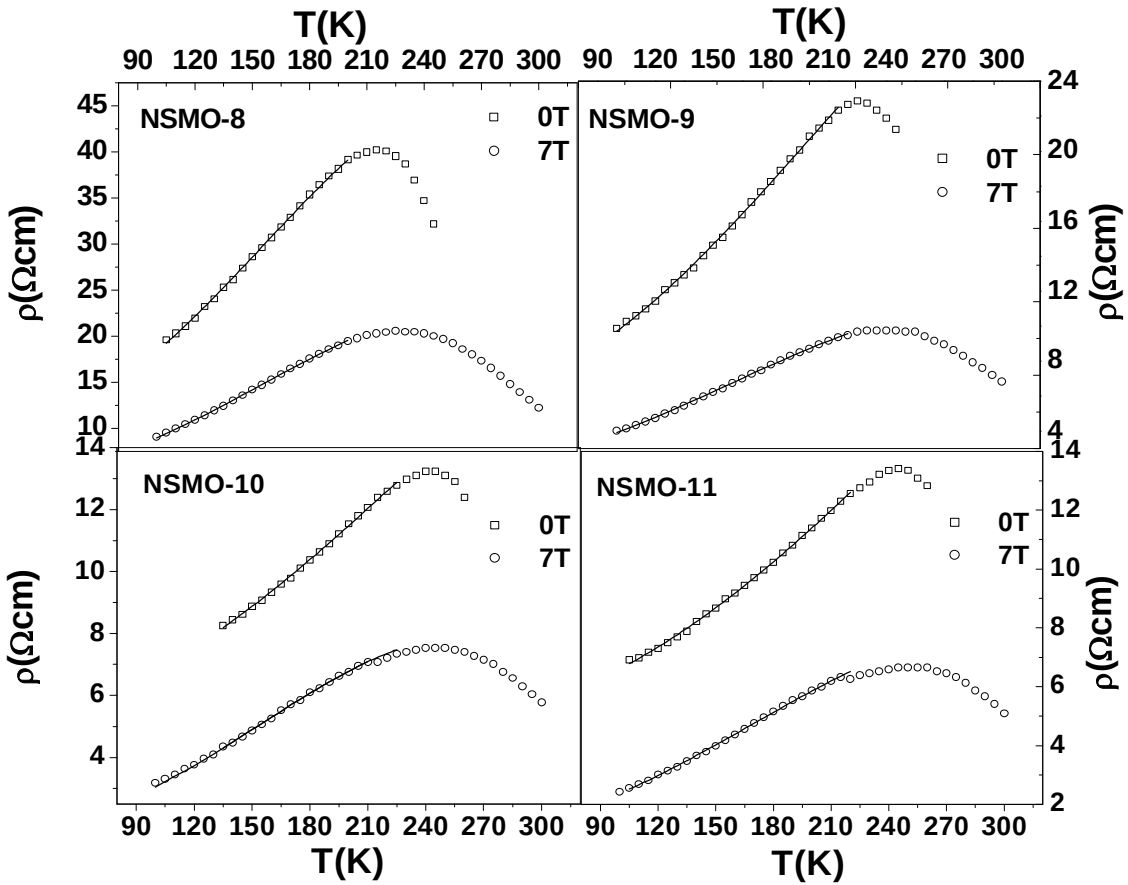


Fig 3

- In high magnetic fields resistivity decreases drastically at ferromagnetic to paramagnetic transition temperature (T_C).
- MR = ρ(H) - ρ (O)/ ρ (O)

Ferromagnetic Metallic region



- $\rho = \rho_0 + \rho_{2*}T^2$
- $\rho = \rho_0 + \rho_{2.5}*T^{2.5}$
- $\rho = \rho_0 + \rho_{2*}T^2 + \rho_{4.5}*T^{4.5}$

Fig 6

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Square of Linear Correlation Coefficient (R^2)

Sample code	$\rho = \rho_0+\rho_2T^2$	$\rho = \rho_0+\rho_{2.5}T^{2.5}$	$\rho = \rho_0+\rho_2T^2 +\rho_{4.5}T^{4.5}$
NSMO-8	0.9910	0.9894	0.9993
NSMO-9	0.9977	0.9945	0.9992
NSMO-10	0.9961	0.9946	0.9993
NSMO-11	0.9931	0.9946	0.9993

ρ_0 = grain boundary resistivity

$\rho_{2.5}$ = resistivity due to electron-electron scattering

$\rho_{4.5}$ = resistivity due to electron-magnon scattering

Sample Code	ρ_0 (Ωcm)		ρ_2 (Ωcm K^{-2})		$\rho_{4.5}$(Ωcm $K^{-4.5}$)	
	0T	7T	0T	7T	0T	7T
NSMO-8	8.75	4.09	10.00×10^{-4}	5.00×10^{-4}	4.18×10^{-10}	2.13×10^{-10}
NSMO-9	5.44	1.81	4.40×10^{-4}	2.20×10^{-4}	9.97×10^{-11}	8.39×10^{-11}
NSMO-10	5.09	1.33	1.81×10^{-4}	1.80×10^{-4}	2.94×10^{-11}	7.64×10^{-12}
NSMO-11	4.88	0.89	1.7×10^{-4}	1.50×10^{-4}	2.08×10^{-11}	5.15×10^{-12}

From the above Transport studies in ferromagnetic metallic region, it is known that…….

- **Grain boundary resistivity (ρ_0) and the resistivity due to electron-electron scattering (ρ_2) increase with the decrease of particle size and these values are larger than their bulk counterparts - size effect.**

- **Resistivity due to electron-magnon scattering or spinwave scattering ($\rho_{4.5}$) also decrease with the increase of particle size which may be due to the partial alignment of spins.**

- **All the three parameters (ρ_0, ρ_2, $\rho_{4.5}$) found to decrease with the increase of magnetic field attributed to the suppression of scattering mechanisms.**

Paramagnetic Insulating region

Variable Range Hopping (VRH) model: $T<T_p<\Theta_d/2$

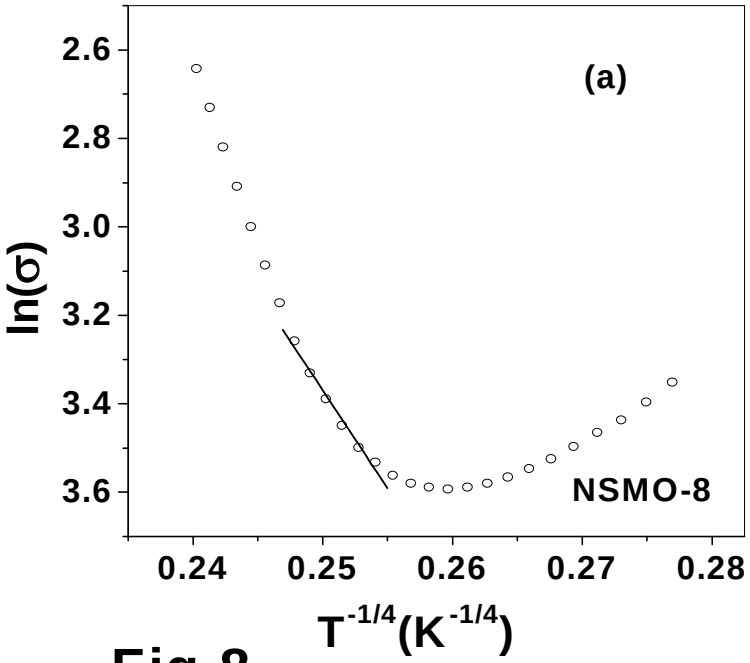

Fig 8

Mott's Equation for VRH model is

$\sigma = \sigma_0 \exp(-T_0/T)^{-1/4}$

σ_0 = pre factor

$T_o = 16\alpha^3/K_B N(E_F)$

$N(E_F)$ = density of states at the fermi level

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Polaron hopping model: Tp>T>Θd/2

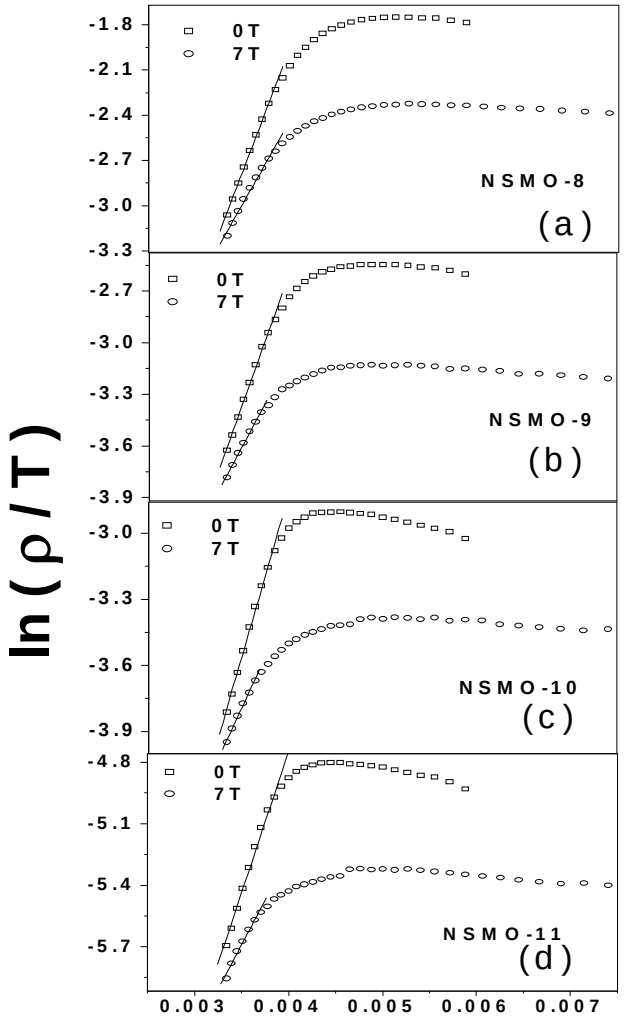

Fig 7

Adiabatic process:

$\rho = \rho_\alpha T \exp (Ep/K_B T)$

Non-Adiabatic process:

$\rho = \rho_\alpha T^{3/2} \exp (Ep/K_B T)$

It is found that the adiabatic hopping mechanism is applicable for the present system.

Fitted parameters:

Sample code	θ_D (K)	E_P (meV)		T_o (10^6 K)		$N(E_F)$ (eV^{-1} cm^{-3})	
		B=0T	B=7T	B=0T	B=7T	B=0T	B=7T
NSMO-8	530.4	140.99	95.99	3.87	0.49	5.24×10^{20}	4.14×10^{21}
NSMO-9	540.8	130.92	87.82	2.56	0.31	7.93×10^{20}	6.51×10^{21}
NSMO-10	550.5	125.95	79.28	1.05	0.20	19.25×10^{20}	9.80×10^{21}
NSMO-11	561.1	118.83	78.84	0.63	0.13	31.96×10^{20}	14.60×10^{21}

$\theta_{D/2}$ = The temperature at which the deviation from the linearity occurs.

θ_D = Debye temperature.

E_P = Activation energy.

From the above transport studies in the paramagnetic insulating phase, it is known that……

- **T_o values are found to decrease enormously and continuously with the increase of particle size and magnetic field.**
- **Consequently the density of states increase with the increase of particle size in both the presence and absence of magnetic field.**
- **Debye temperature decreases with the particle size.**
- **Activation energy values are found to increase continuously with the decrease of particle size both in the presence and in absence of magnetic field – may be due to the interconnectivity effect between two grains.**

AC susceptibility measurements:

to find out the magnetic phase transitions

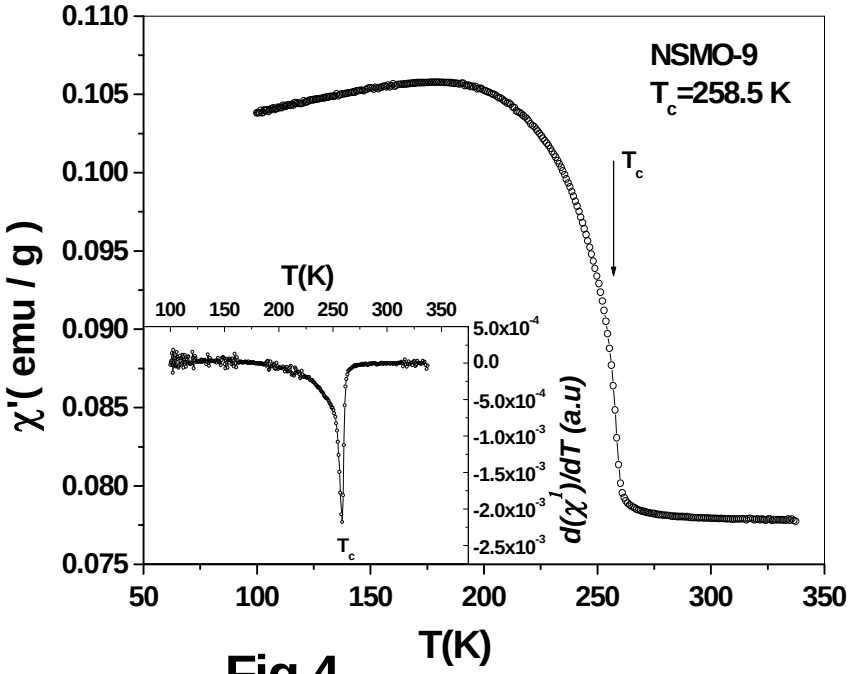

Fig 4

T_C = obtained by the inflexion point of the susceptibility graph as shown in the inset figure.

T_C values of NSMO

Bulk = 200 K

NSMO-11 = 249 K

NSMO – 10 = 253 K

NSMO – 9 = 258 K

NSMO – 8 = 260 K

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From the above susceptibility measurements, it is known that……

- **As the particle size decreases from 30 nm to 15 nm, the ferromagnetic to paramagnetic phase transition temperature (T_C) increases from 248 K to 260 K. The T_C of this compound in it's bulk form is 200 K. An upward shift of 60 K is observed when the particle size is decreased.**

WHY? May be due to the Unit cell volume contraction

(order of 1% - 2%) and the reduction in the unit cell anisotropy parameter.

- **The above changes cause the decrease and increase of bond length and bond angle respectively, enhances the bandwidth and transfer integral which pushes the electron to hop easily and thereby shows the enhancement in T_c.**

Motivation behind the EMR work in Manganites

- **Manganites are strongly correlated electron systems where the charge, spin, orbital and lattice degrees of freedom are interrelated**

- **EMR is a microscopic probe to complex Spin Dynamics**

- **Sensitive to Spin-Orbit Coupling (through the shift in the g value of the Spectra)**

- **Sensitive to Spin-Spin and spin lattice couplings(through the linewidth).**

- **EMR is sensitive to the local environment of the Spins.**

Issue related to the EMR in manganites

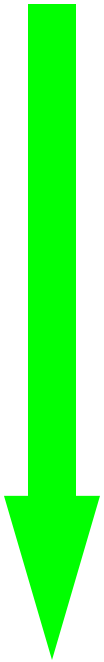
Origin of ESR signal in Manganites

Two magnetic ions are : Mn^{3+} , S = 2 Mn^{4+} ,S = 3/2

Both Ions contribute to EMR line Intensity

(Causa et. al. PRB, 58,1998)

UNPAIRED ELECTRONS IN A MAGNETIC FIELD



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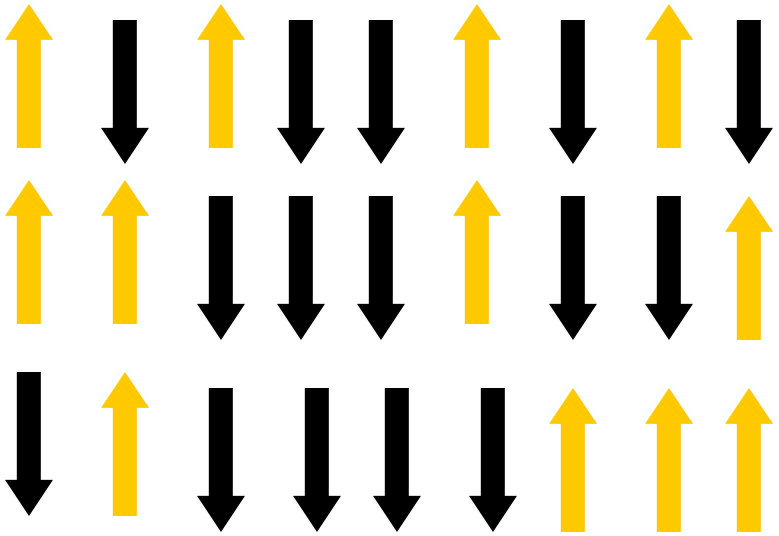
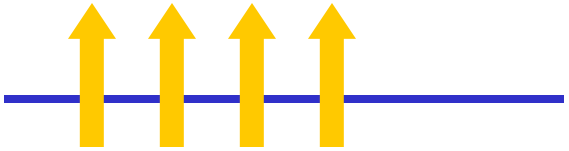
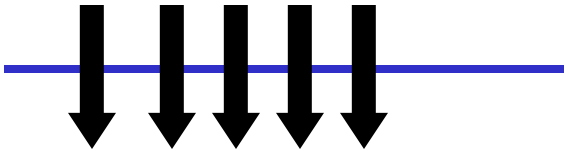


$N_\beta/N\alpha = \exp(-\Delta E/K_B T)$

Boltzmann distribution

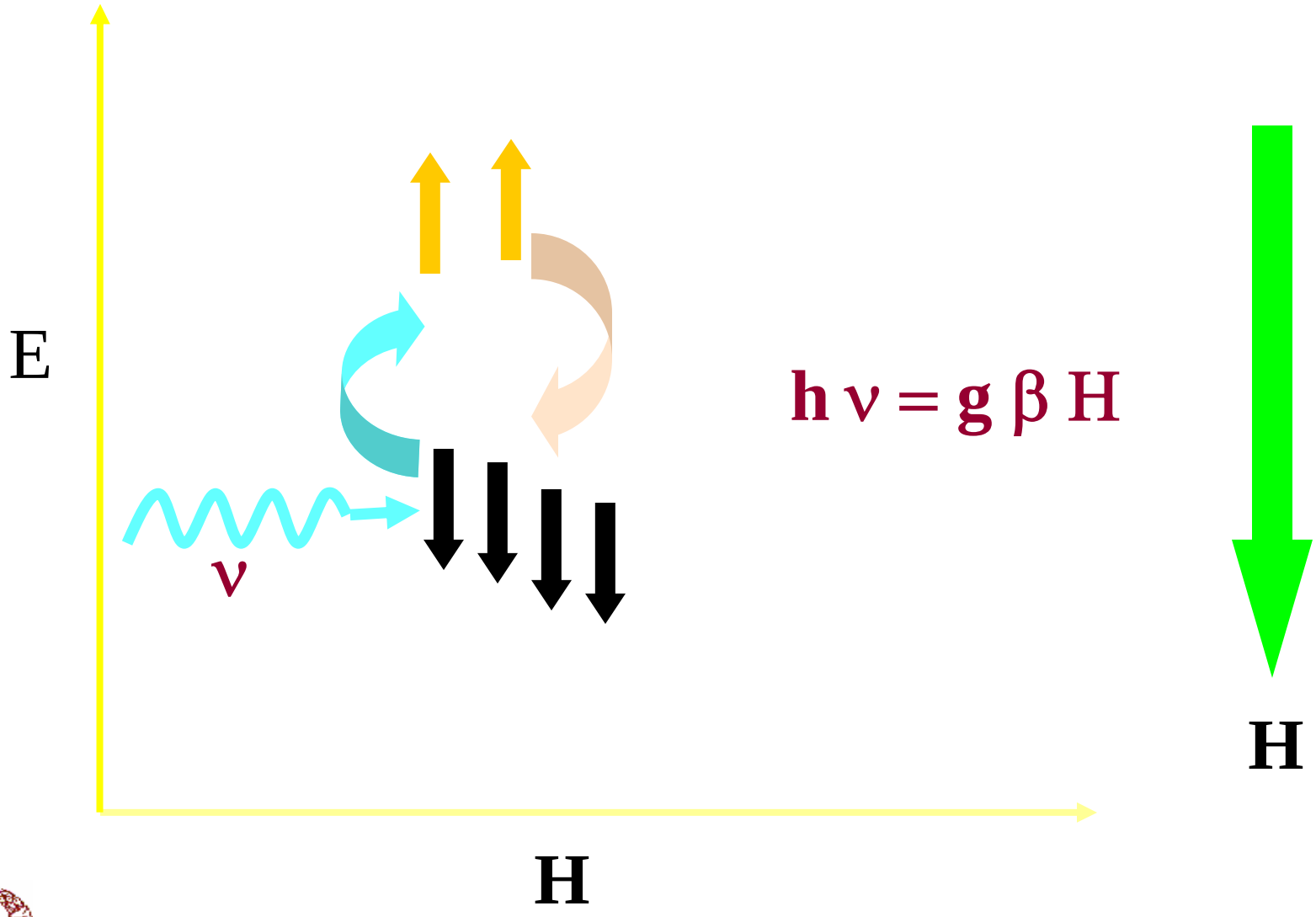


E_β



E_α

THE EPR PHENOMENON



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EMR experimental details:

- **The EMR experiments were carried out using the Bruker ER 200D ESR spectrometer having the temperature ranges from 4 K to 300 K.**
- **To isolate the nanoparticles electrically and magnetically, they were dispersed in the paraffin wax and the EMR experiments were done on the dispersed nanoparticles.**
- **DPPH was used as a field marker to measure the g – value accurately.**

Why EMR studies of nanomanganites?

- **EMR is very sensitive local probe in condensed matter physics which gives the information about the complex spin dynamics, charge states, g-value, internal magnetic fields and magnetic phase transitions (if any) in strongly correlated systems.**

- **Individual (isolated) grain response is obtained by dispersing the nano powder in the diamagnetic paraffin wax which is not possible in other magnetic experiments, which shows the sensitivity of EMR technique.**

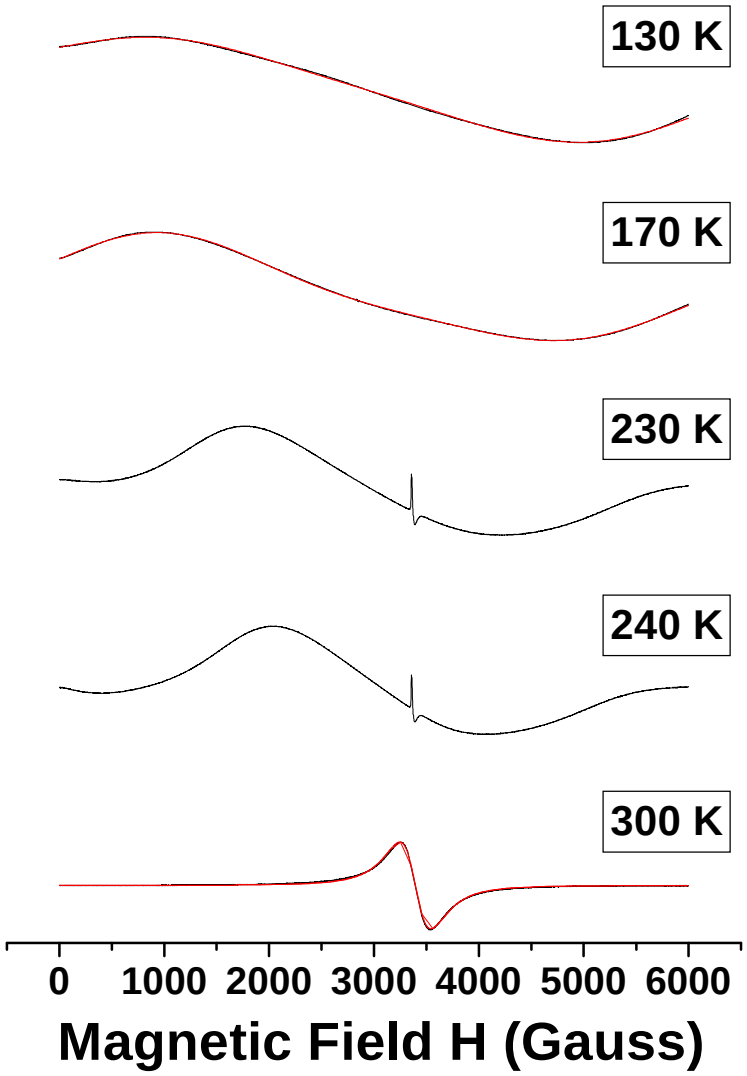
- **The information is obtained by fitting the EMR signals in to appropriate line shape, extract the parameters (line width, resonance field and intensity) by fitting and plot them with the temperature.**

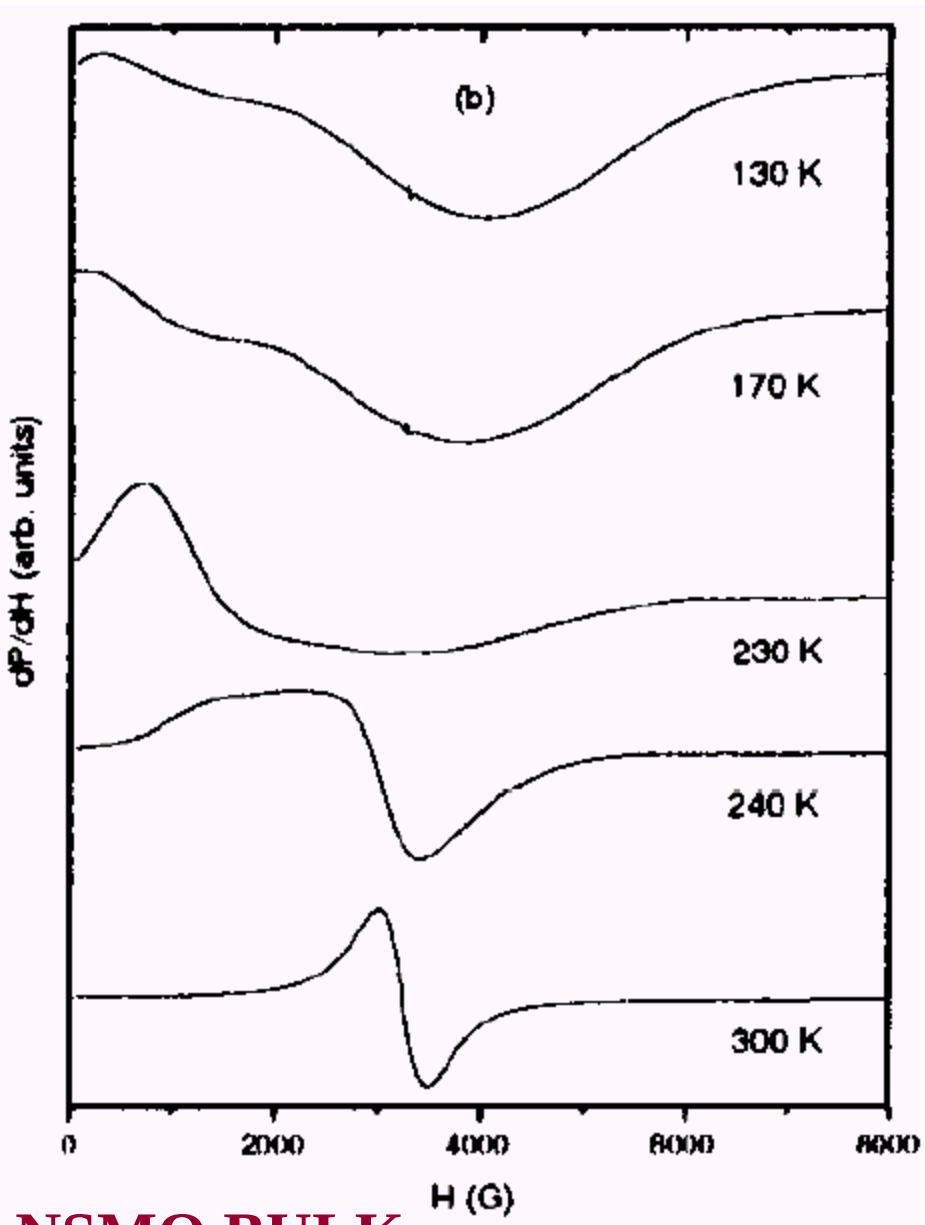
• There are very few reports (Shames etal) of EMR studies of nanomangnites. In their study (mostly in paramagnetic region), it is shown that nanomanganites (La0.7Sr0.3MnO3) are less homogeneous when compared to their bulk counterparts and didn't address the nanoparticle properties in ferromagnetic region.

• There are some theoretical and experimental reports on nanomanganites which address the core-shell model and estimated the shell thickness.

• Two NMR signals were observed from nano La0.7Sr0.3MnO3 manganite. It is observed that one signal comes from the core (due to $Mn^{3+/4+}$) and the other signal comes from the shell (due to Mn^{+4} only).

• EMR is being the the most sensitive to the presence of unpaired electrons and their environment, in this study we have shown the presence of core and shell regions in naoparticle which are different in magnetic nature.





NSMO NANO **NSMO BULK** JAP 93, 8334 (2003)

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FMR lineshape (in ferromagnetic phase)

Two Gaussian absorption model

$$P = p_0 + \frac{A_1}{\Delta H_1 \sqrt{\pi/2}} e^{-2\frac{(H-H_{01})^2}{\Delta H_1^2}} + \frac{A_2}{\Delta H_2 \sqrt{\pi/2}} e^{-2\frac{(H-H_{02})^2}{\Delta H_2^2}}$$

EMR lineshape (in paramagnetic phase)

Single Lorentzian derivative model

$$\mathbf{dP/dH = d/dH * A\ [\Delta H/(\Delta H)^2 + (H - H_0)^2]}$$

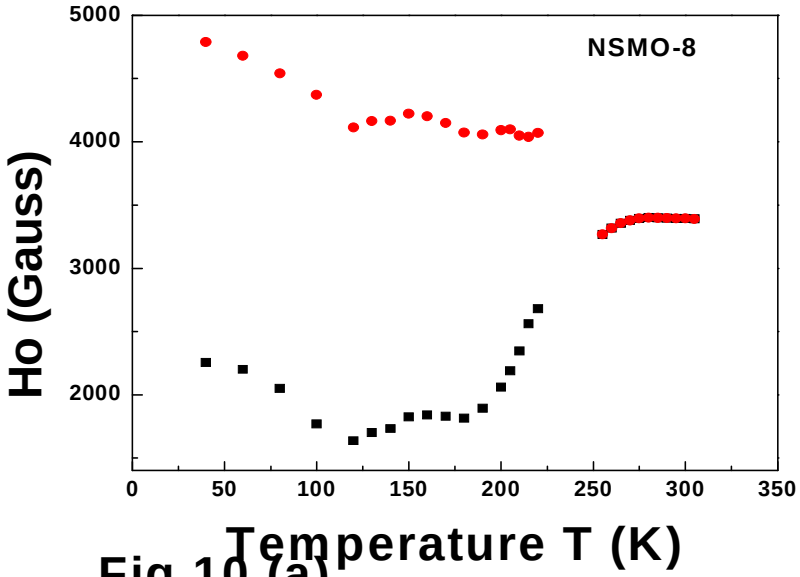

Fig 10 (a)

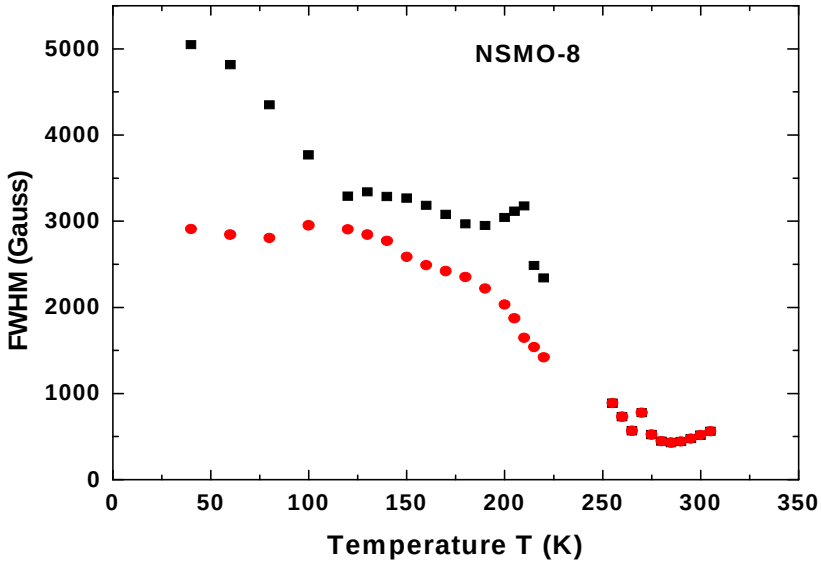

Fig 10 (b)

Core signal

Shell signal

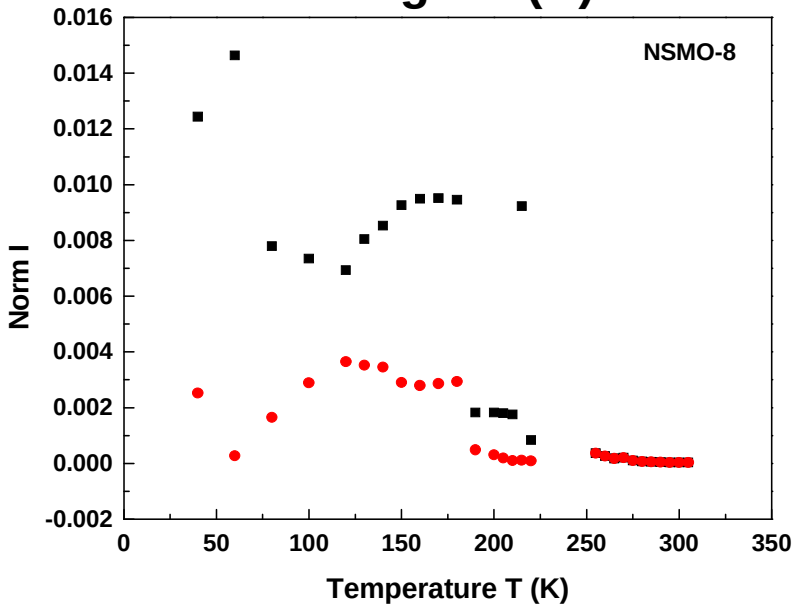

Fig 10 (c)

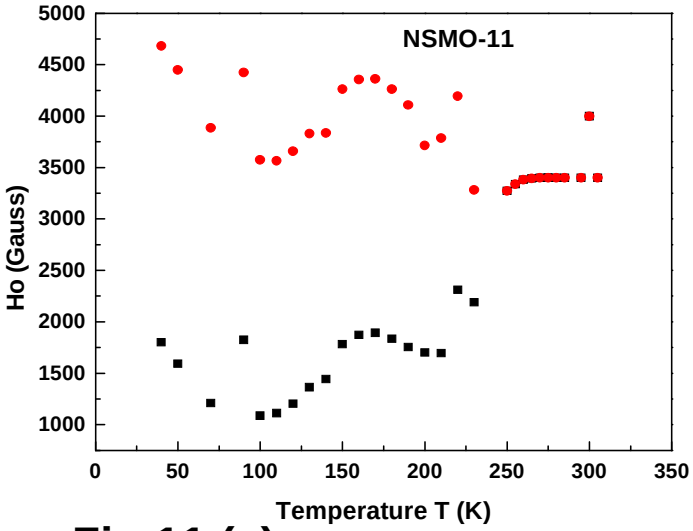

Fig 11 (a)

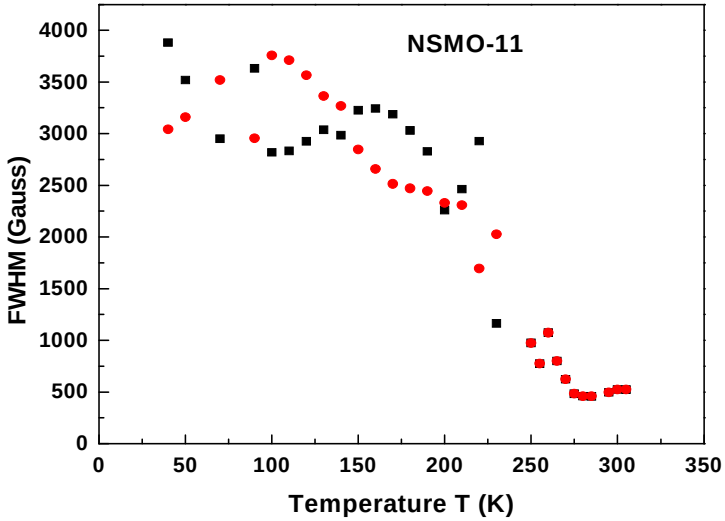

Fig 11 (b)

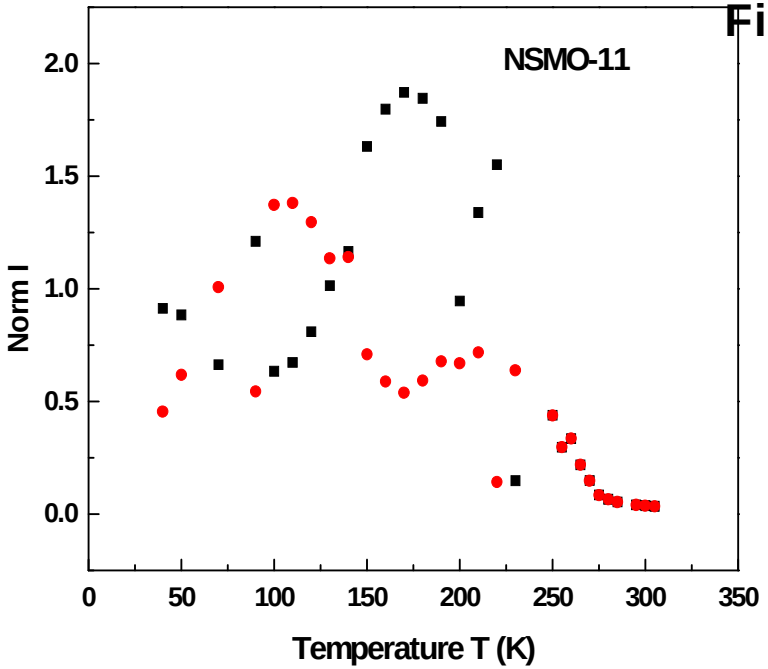

Fig 11 (c)

How to indentify the core-shell EMR signals?

• **The core region is ferromagnetically ordered and exhibits it's bulk properties. The shell spins are magnetically disordered which contains defects, vacancies and dangling bonds. So the core signal (black symbol) is more intense than the shell signal (red symbol).**

• **The core spins are subjected to the Weiss field, gets added up to the applied external field making their resonance appear at a lower field. Shell signals have larger linewidths than the core signals.**

Conclusions from the EMR results:

- **EMR signals of bulk and nano samples show different in shape in ferromagnetic phase.**
- **EMR signals fit into two Gaussians in the ferromagnetic phase of nano NSMO, indicates the presence of two signals and in the paramagnetic phase EMR signals fit into a single Lorentzian.**
- **g – value in the paramagnetic phase increases (1.9806 – 1.9852) as with the decrease of particle size. This shows that spin – orbit coupling and crystal fields are effected by the size of particle.**
- **Linewidth magnitude which gives information about the spin dynamics changes with the particle size in the paramagnetic phase.**
- **Differences are seen in the EMR properties of NSMO-8 and NSMO-11. This may be due to the presence of single domain particles in NSMO-8 and NSMO-11 contains both single and multidomain particles.**

Summery:

- **Transport properties are studied both in the presence and in the absence of magnetic field and also shown the effect of particle size .**
- **AC susceptibility measurements were done to see the effect of particle size on magnetic phase transition temperatures.**
- **EMR experiments have been done to study the effect of grain size on EMR spectral properties and probed the core – shell regions of the nanoparticle.**

Acknowledgements:

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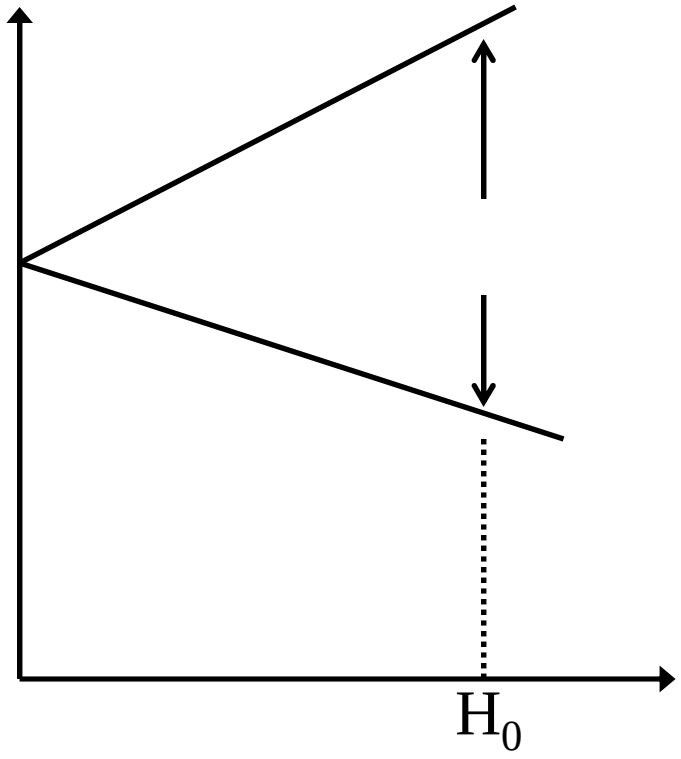
Principles of Electron Paramagnetic Resonance (EPR)

Resonant absorption of microwave radiation across the Zeeman split electronic energy levels.



υ : Frequency of microwave radiation

g: g factor

β: Bohr Magneton

H_0: Resonance Field

Parameters obtained from EPR

g : obtained from the resonant field H_0

ΔH: linewidth proportional to $1/T_2$ (T_2 is the spin spin relaxation time)

$$1/T_2 = 1/T_2' + 1/2T_1$$

Intensity: area under the curve proportional to the number of spins contributing to the EPR signal

A/B ratio: measures the asymmetry of the EPR signal from single crystals. It depends on the ratio of the sample thickness to skin depth and of the electron diffusion time T_D to T_2

Origin of linewidth

- Possible mechanisms:
- Dipolar interaction
- Crystal Field interaction
- Dzyaloshinsky Moriya (antisymmetric exchange interaction)
- Exchange narrowed dipolar linewidth:~ 3 Gauss
- Observed linewidth ~ 1800 Gauss (isotropic exchange interaction)

Huber et al., J. Appl. Phys. 83, 6949, 1998

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Origin of Linewidth

- Due to non zero orbital angular momentum of the ground state of Mn ions, in the octahedral crystal field, there is large zero field splitting providing a channel for rapid relaxation.
- Hence EPR signal is broadened out beyond observability.
- However, due to strong exchange narrowing effect, the natural linewidths are substantially reduced, rendering the EPR signals observable.

EPR Linewidths