UNITED NATIONS EDUCATIONAL, SCIENTIFIC AND CULTURAL ORGANIZATION
INTERNATIONAL ATOMIC ENERGY AGENCY
INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS

SMR/917 - 16

SECOND WORKSHOP ON SCIENCE AND TECHNOLOGY OF THIN FILMS

(11 - 29 March 1996)

" Giant magnetoresistance oxides."

presented by:

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List of important publications in the area of GMR:

(a) Thin flm and granular films (metallic)

1. M.N. Baibich et.al , Phys. Rev. Letts. 61, 2472 (1988)

2.P.M.Levy , Solid State Physics 47, 367 (1994)

3. A.E. Bekowitz et.al , J. Appl. Physics 73, 5320 (1994)

(b) Oxides

1. K.Chanara et.al , Appl. Physics Letts. 63, 1990 (1993)

2. R. von Helmholt et.al, Phys Rev. Letts 71, 2331 (1994)

3. M. McCormack et.al , Appl. Phys. Letts. 64, 3045 (1994)

4. H.L. Ju et.al , Appl. Phys. Letts. 65, 2108 (1994)

5. R. Mahendiran et.al , Appl. Phys. Letts. 66, 233 (1995)

6. A. Urishibara et.al , Phy. Rev B 51, 14 103 (1995)

7. Y. Moritomo et.al , Phys. Rev B 51, 16 491 (1995)

8. H.Y. Hwang et.al, Phys. Rev. Letts. 75, 914 (1995)

9. R. Mahendiran et.al , Phys. Rev B 53, 3348 (1996)

10. R. Mahendiran et.al , Phys. Rev B 53, May (1996)

11. R. Mahesh et.al , Appl. Phys. Letts. , April (1996)

Giant magnetoresistance in perovskite oxides.

1. Magnetoresistance - why study it ?

2. Materials showing giant magnetoresistance (GMR)

Multilayer and granular films, nanostructured materials.

3. The GMR in perovskite oxides

Basic observations

Structure, chemistry and the physics

4. The thin film aspect of the GMR materials

Growth, nanostructure and special properties if any distinct from the bulk.

Magnetoresistance : (Change in resistance in a magnetic field)

$\Delta\rho(H)=\rho(H)-\rho(0)$; **MR ratio (%)** $=\Delta\rho/\rho(0)$

Caution : often MR defined as $\Delta\rho/\rho(H)$

When the MR is negative and $\Delta\rho/\rho(0) \approx -100\%$

$\Delta\rho/\rho(H) \rightarrow -\infty$!

Magnetoresistive sensors (generally used as films) need

1. **Large** $\Delta\rho(H)$ **in low H**
2. **Reproducible MR and long life time**
3. **Fast response for high bandwidth data reading**
4. **Low electrical noise (conductivity noise)**

Magnetoresistance can be positive or negative:

Positive MR

1. Orbital effects : Generally small in pure metals. In hopping conductivity region can be substantial. Large in some semiconductors.

2. Pair breaking in superconductors : Large effects.

Negative MR

1. Suppression of Quantum interference : negative MR in the weak localization limits (generally not too large)

2. Magnetic origin (scattering from spins): can be very large in materials with ferromagnetic interactions.

Giant magnetoresistance (GMR)

Materials showing large magnetoresistance

* Interesting Physics !

* Applications → MR Heads for magnetic storage media

(t > 1985 use in mainframes)

↓

Large resistance change in low field (10^{-2}T)

Noise - low

Rapid-response

Future ? Data density in magnetic tape & disk > $\boxed{1 \text{ Gb/sq.inch}}$

↓

MR read Head size ≃ 10μm

↓

High sensitivity in low fields (< 10^{-2}T) } materials technology

low noise (1/f noise) ↔

Thin film & Lithography Compatible (Small size ≳ 1μm)

Search for new materials for sensitive MR sensors:

1. Ferromagnetic alloys like permalloy (Ni-Fe)

already in use in computer read head and the current work horse

*2.**Metallic Multilayer films (e.g, Fe/Cr) of alternate FM thin layers coupled antiferromagnetically (t > 1988)**

*3. **Granular films or ribbons consisting of ferromagnetic globules (e.g, Co) in an AFM or noble metal matrix (Cu). (t>1992)**

*4. **Bulk (polycrystalline or single crystal) and epitaxial films of oxides of general formula (t > 1994):**

[illegible]

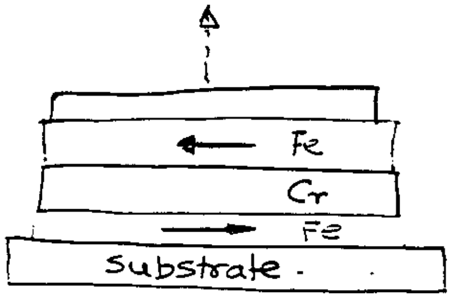
Multilayers :

(Baibich et.al Phys. Rev. Letts. 61, 2472 (1988)

Typical structure:

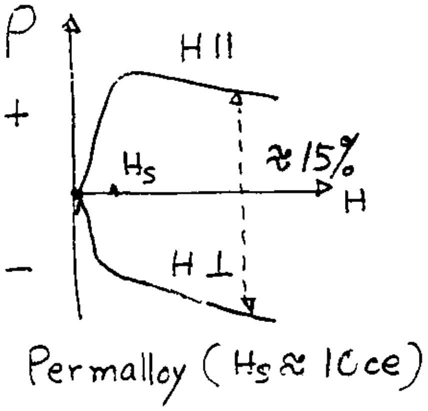
$t_{Fe} \simeq 15 \mathring{A}$

$t_{Cr} \simeq 12 \mathring{A} - 16 \mathring{A}$

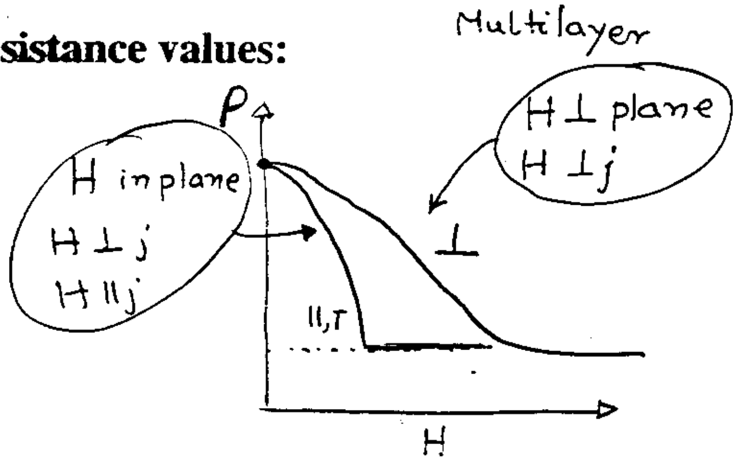


Grown by Molecular Beam Epitaxy

Typical magnetoresistance values:



Permalloy ($H_s \approx$ 10oe)



Thin film aspect :

- ✻ Growth of defect free layers with almost atomic level control.
- ✻ No short between two FM layers.

Granular solids

can be made as thin films, ribbon and even bulk

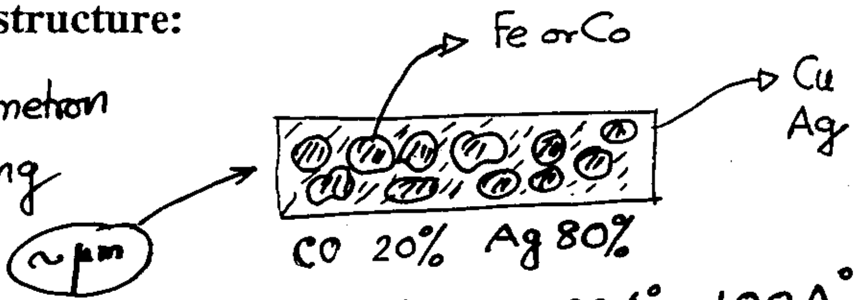
(Berkowitz et.al Phys. Rev. Letts. 68, 3745 (1992) and

Xiao et.al Phys. Rev. Letts. 68, 3749 (1992)

Uses immiscibility gap of constituent elements

Typical structure:

d.c magnetron
Sputtering



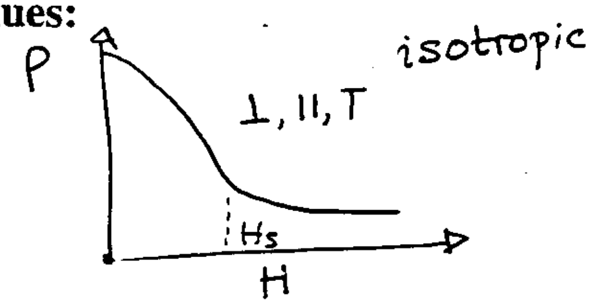
Magnetic clusters 20Å – 100Å
(Matrix it self may have Comparable grain size)

Typical magnetoresistance values:

5K ~ 60% - 80%

RT ≳ 10%

H_s ~ 0.5 - 1T



Thin film Aspect:

* Monodispersed particle!

* Multilayers with granular structure

The oxide Materials

ABO_3 $\left\{ \begin{array}{l} \text{1. K. Chanara et. al. Appl. Phys. Lett. } \underline{63}\text{, 1990 (1993)} \\ \text{2. R. von Helmholt Phys. Rev. lett. } \underline{71}\text{, 2331 (1994)} \end{array} \right.$

Perovskite →

1. High T_c
2. Piezoelectric
3. Dielectric
4. Metallic oxide

A = La, Nd, Pr

B = Mn

(Co)?

e.g → $LaMnO_3$

Mn^{3+} ions

AFM insulator

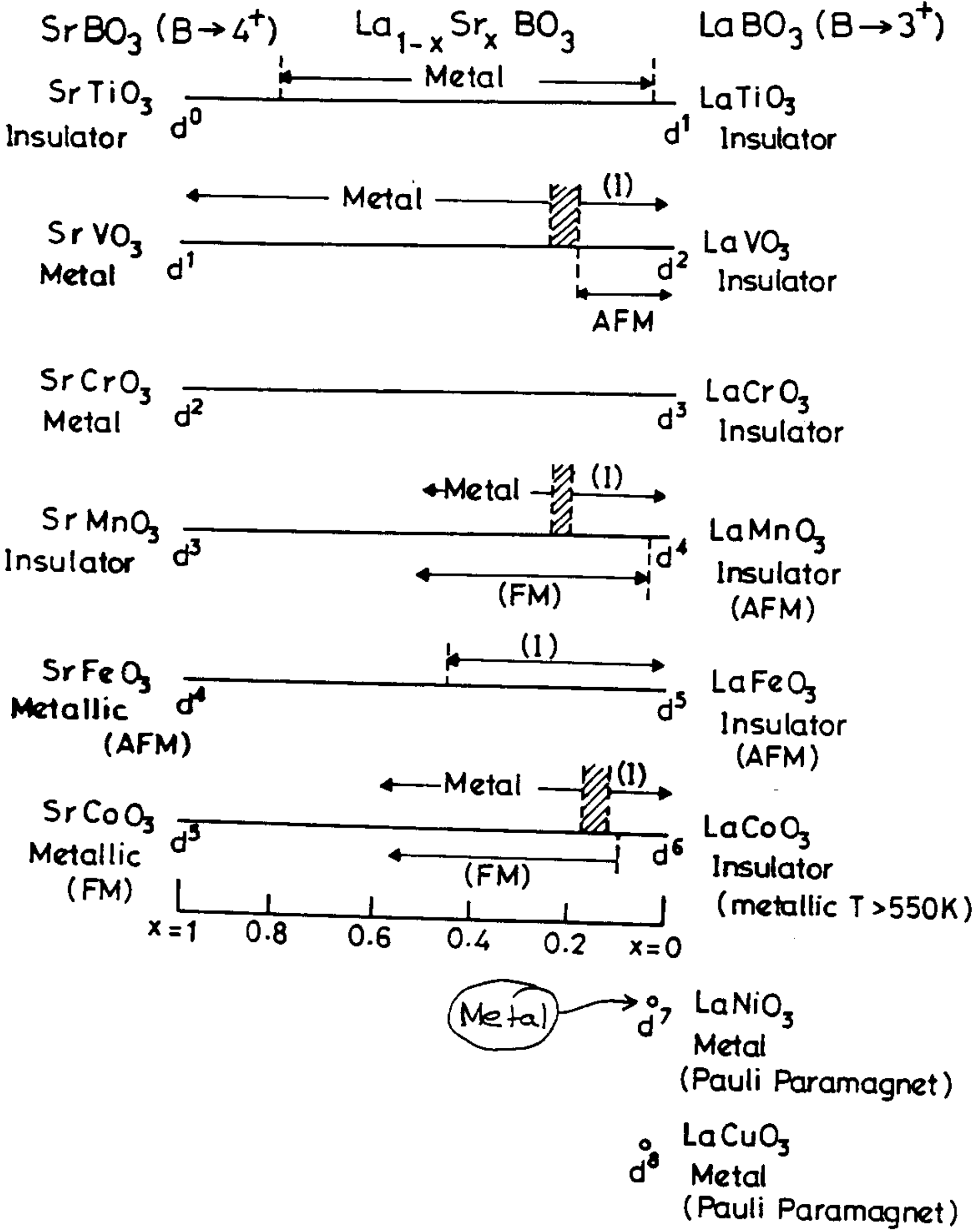
Can be seen in film & bulk (polycryst & Crystalline forms)

Substitution of divalent metal in A-site

e.g → $La_{1-x}A_xMnO_3$

Mn^{3+}/Mn^{4+} → Ferromagnetic metal

"King Fisher" of Oxides



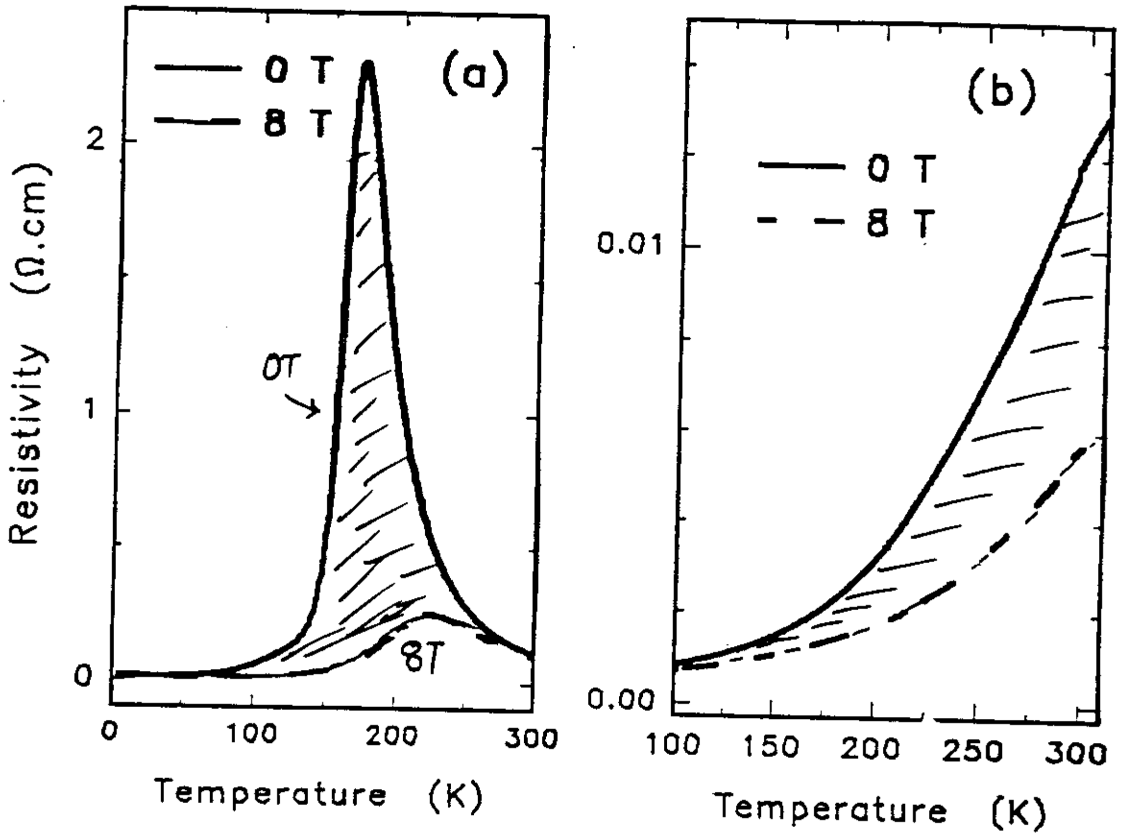
↓ $LaCuO_3$ + LaO

Raychaudhuri (Adv. Phys. 1995)

ABO_3 class ⟶ La_2CuO_4

Giant Magnetoresistance in epitaxial oxide film.

Substrate : $LaAlO_3$ or $SrTiO_3$



$Nd_{0.7}Sr_{0.3}MnO_3$

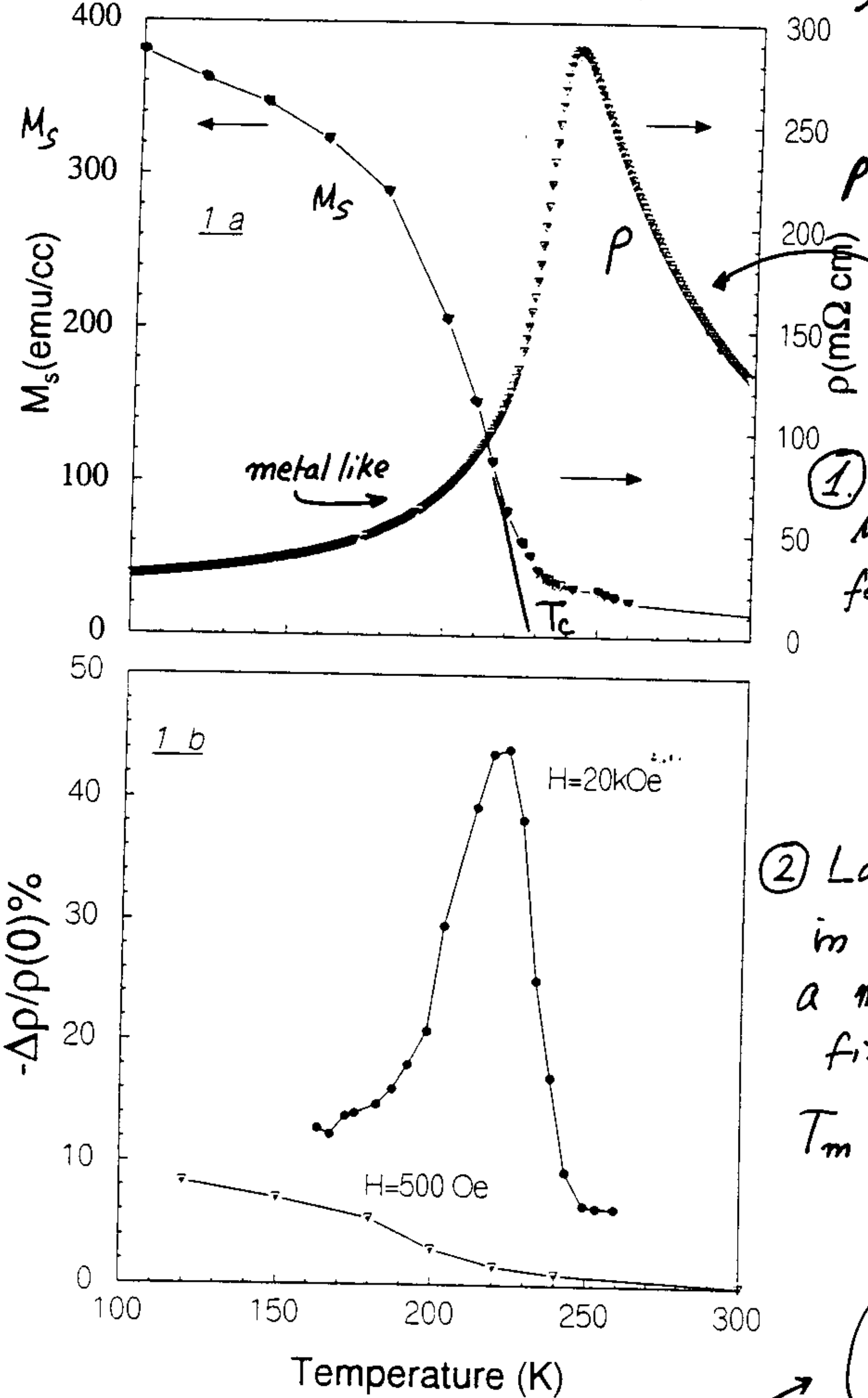
$La_{0.7}Ba_{0.3}MnO_3$

$\frac{\Delta\rho}{\rho} \rightarrow > 90\%.$

Basic Observations

$Ca^{2+} \to La^{3+}$ $Mn^{3+} \to Mn^{4+}$

cubic e.g. $La_{0.8}Ca_{0.2}MnO_3$ ($Mn^{4+} \approx 25\%$)



① Becomes Metallic in ferromagnetic state

② Large change in R in a magnetic field

$T_m \sim T_c$

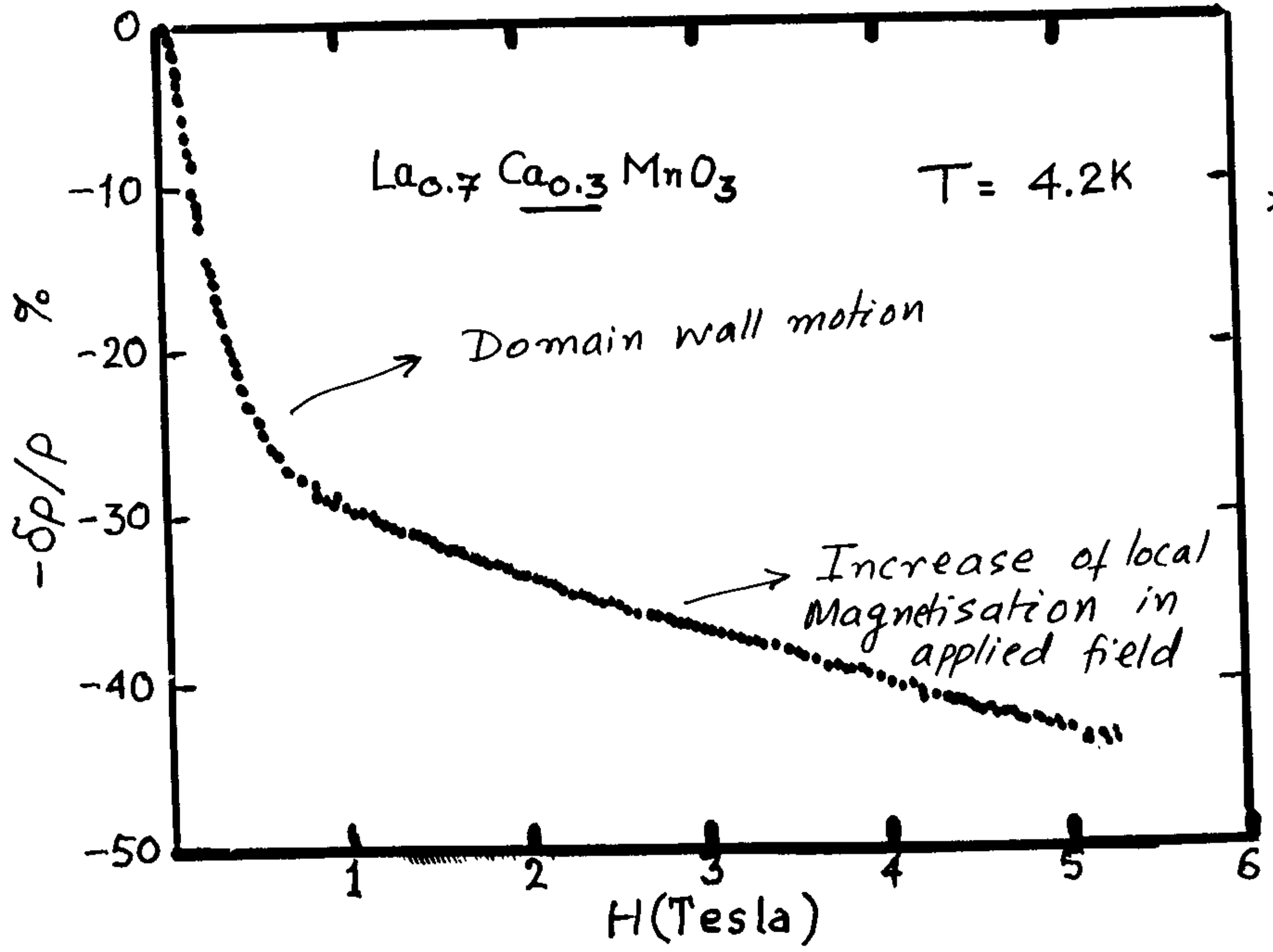
Fe? Ni?

Negative magnetoresistance ⟶ Associated with ferromagnetic order.

Why unusual (occurs at high Temp.)

$g\mu_B H \ll k_B T$

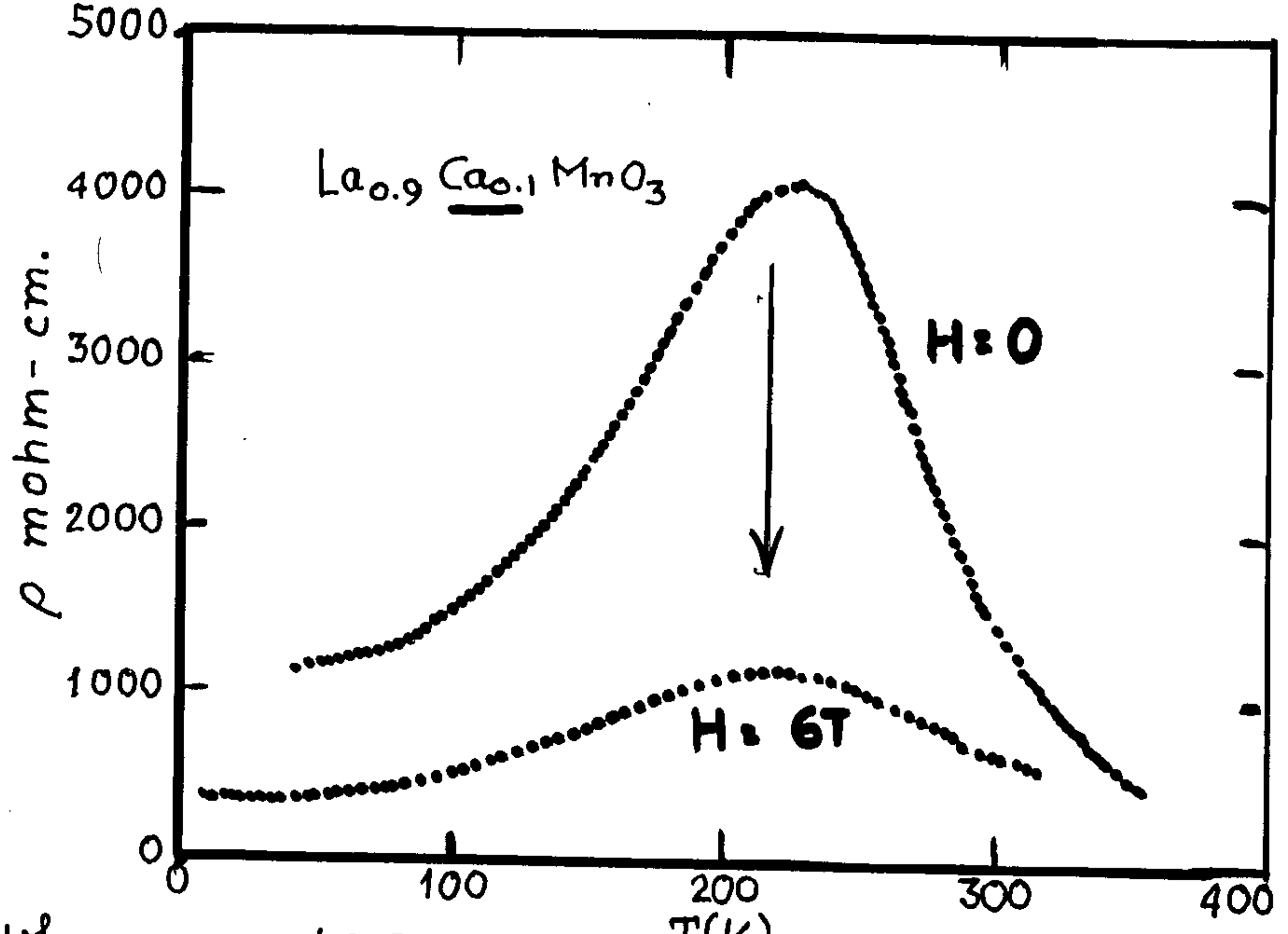
⟨Dependence of MR on H⟩



* Absence of anisotropy:
$\vec{j} \parallel \vec{H}$ & $\vec{j} \perp \vec{H}$
Same MR

* near T_c where MR shows a peak contribution from domain wall motion not seen.

Basic observation - II



Why unusual? $\boxed{g\mu_B H \ll k_B T}$

AFM Insulator

$\boxed{LaMnO_3}$

Mn^{3+}

doping by divalent metal

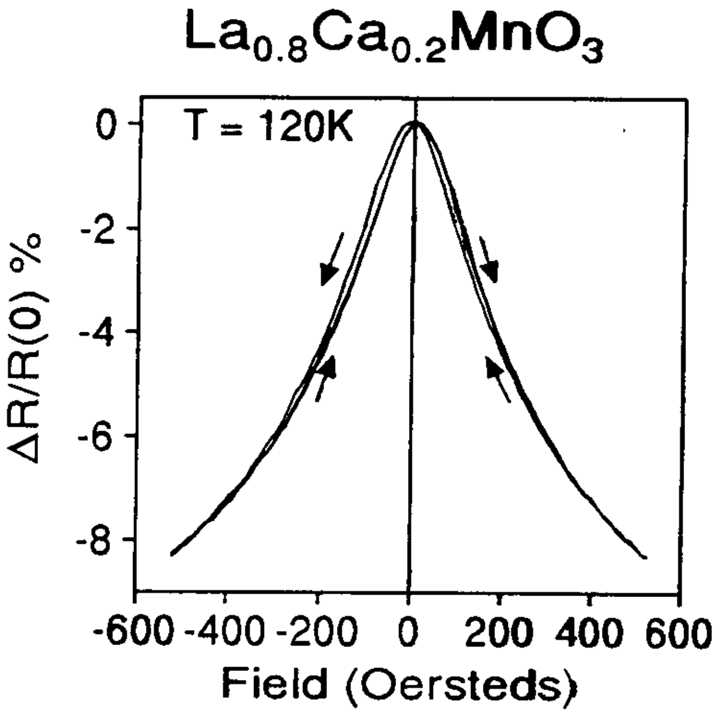
$A_x La_{1-x} Mn O_3$

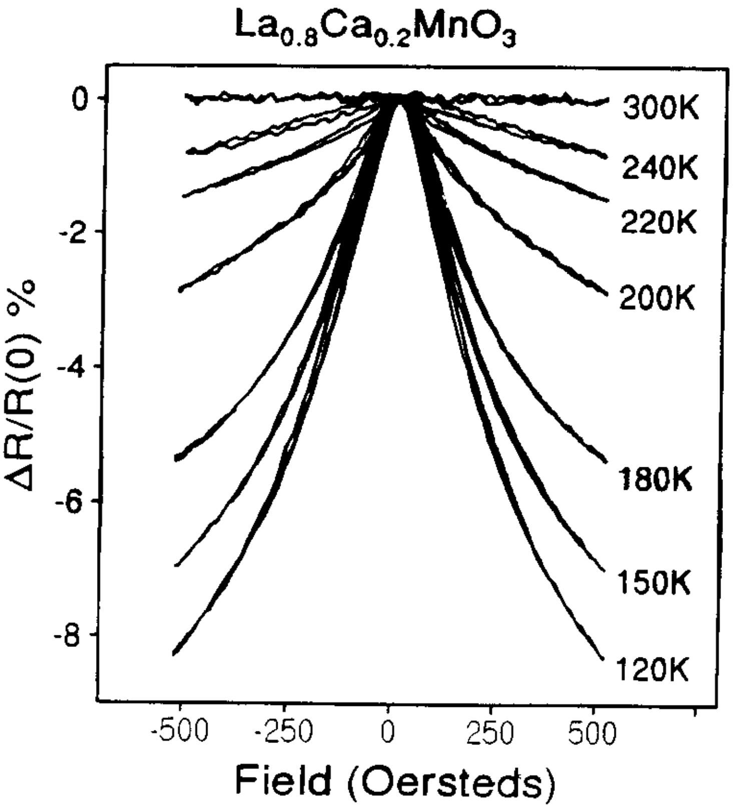
Sr, Ca, Ba : A

$x Mn^{4+} + (1-x) Mn^{3+}$

Hole doping

$\boxed{\text{Presence of } Mn^{3+} - O - Mn^{4+}}$

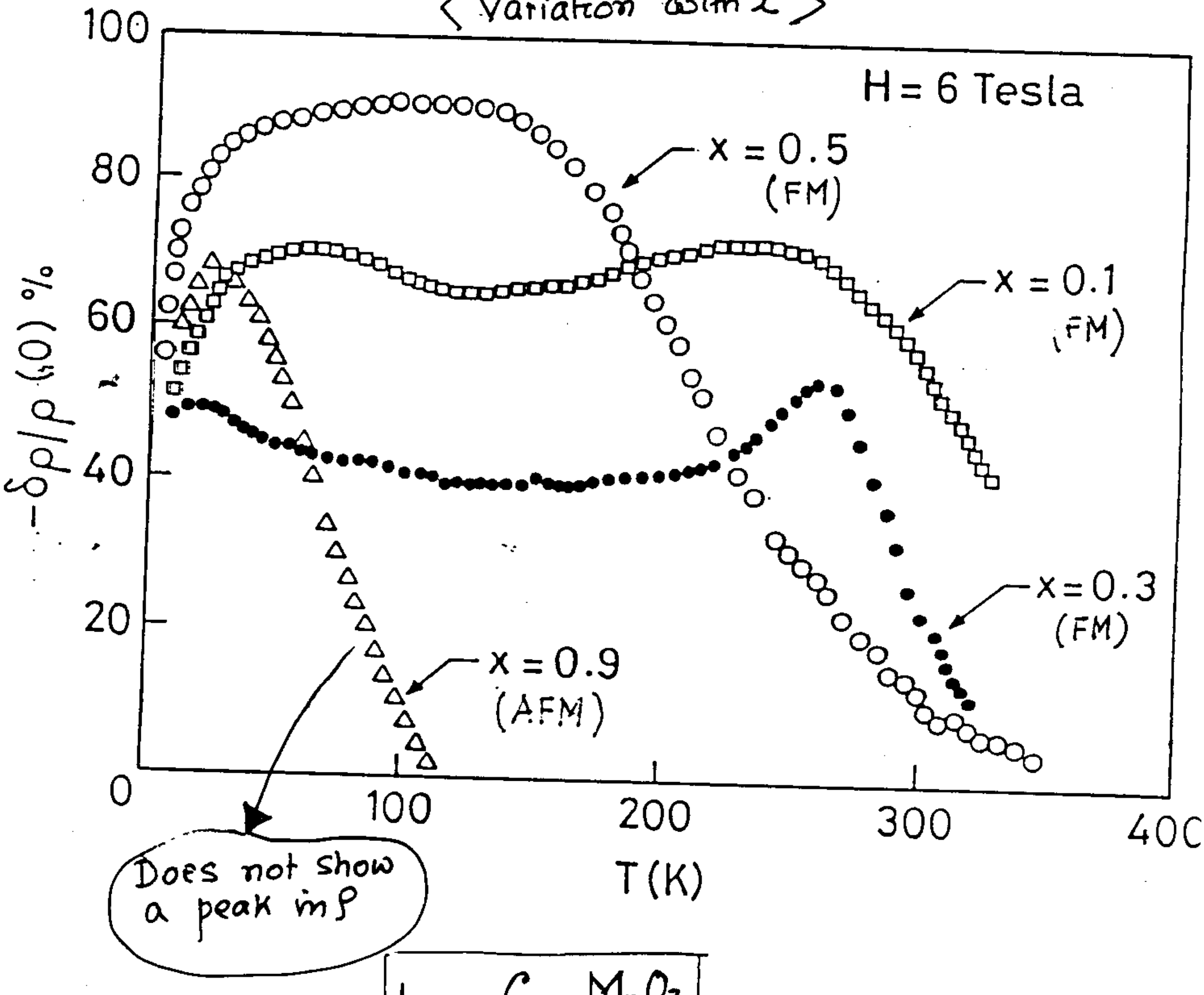




Gayathri et.al (1996)

Giant Magnetoresistance in hole-doped $LaMnO_3$: an Example

⟨Variation with x⟩



Does not show a peak in ρ

$\boxed{La_{1-x}Ca_xMnO_3}$

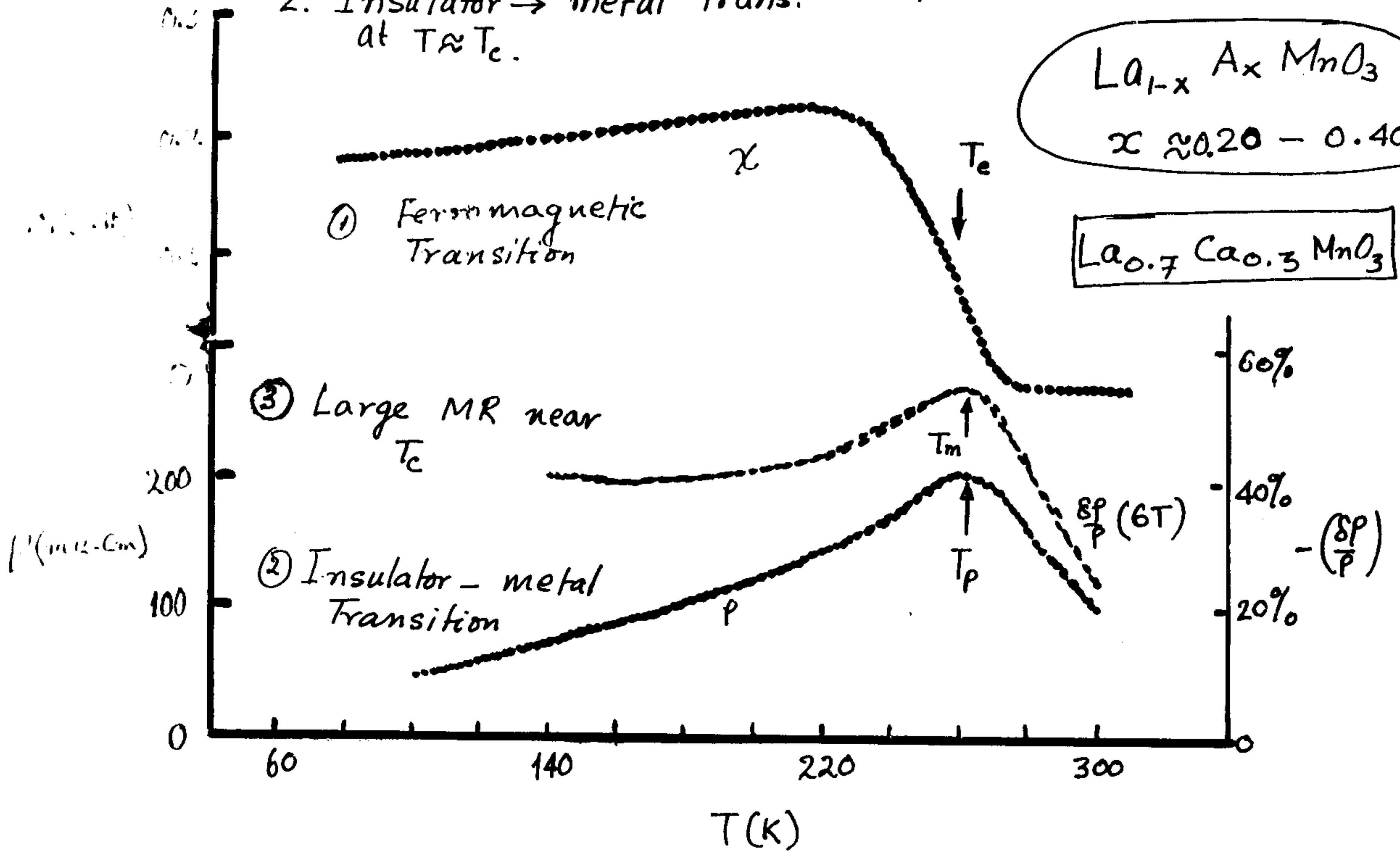
- * Large MR change near T_c over certain range of x
- * Even as $T \to 0$, MR $\simeq -50\%$ at 6 T

Basic observation · (Sum up)

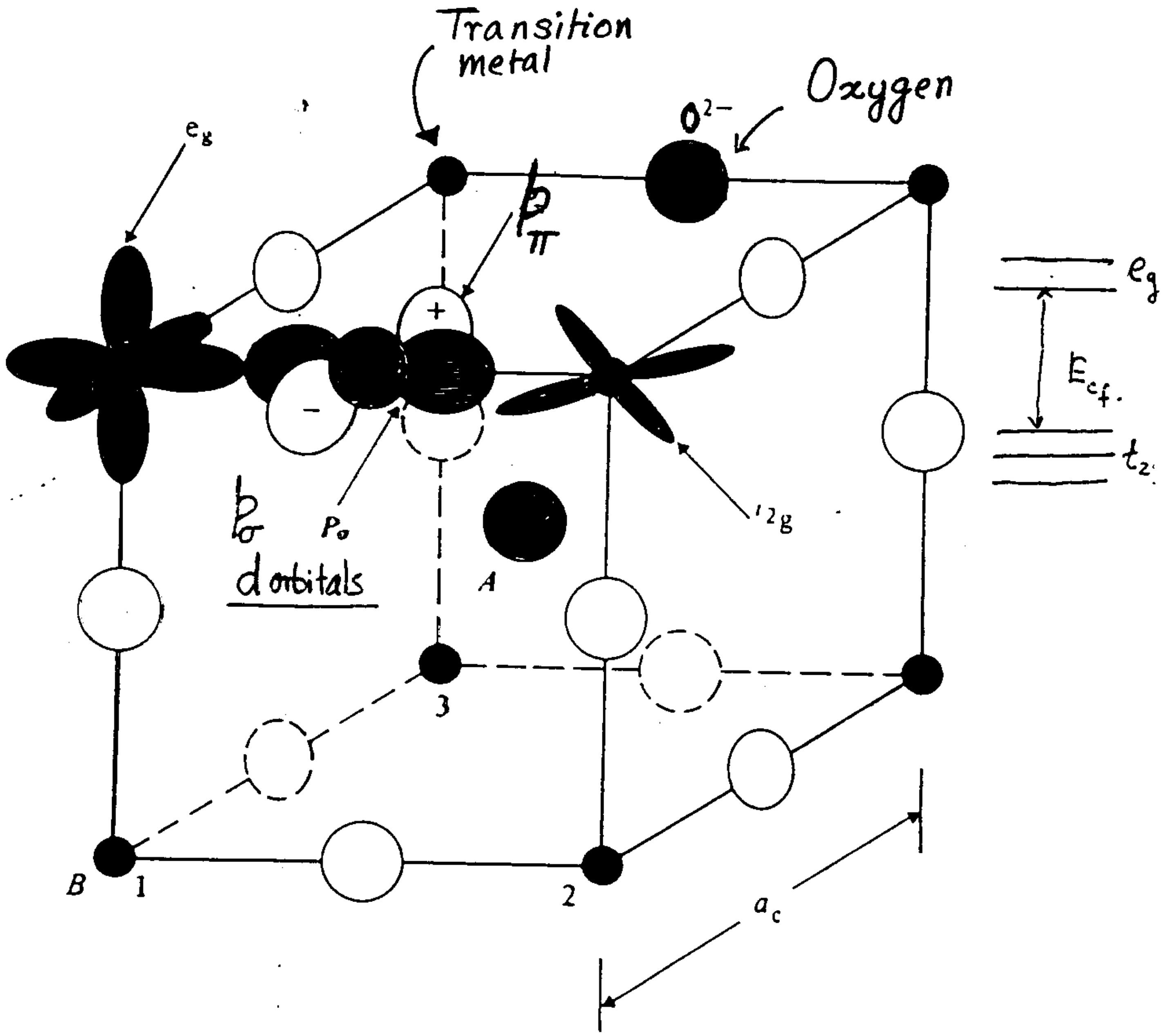
1. FM transition
   (nature of spin arrangement)
2. Insulator → metal trans.
   at $T \approx T_c$.
3. Large negative MR
   $T_m \simeq$ 150K – 350K $\sim T_c$.

$La_{1-x}A_xMnO_3$

$x \approx 0.20 - 0.40$



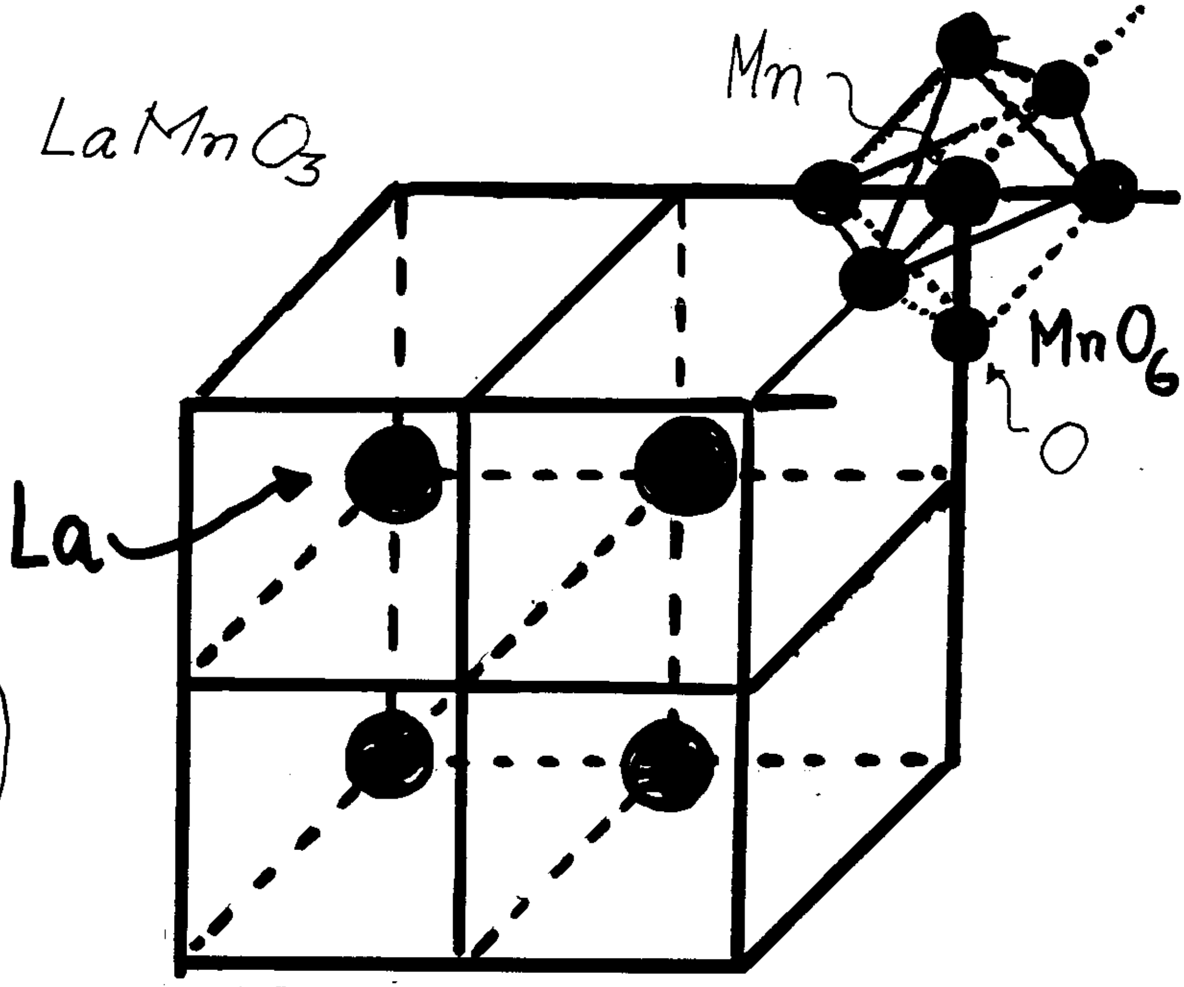
ABO_3



For electronic transport :

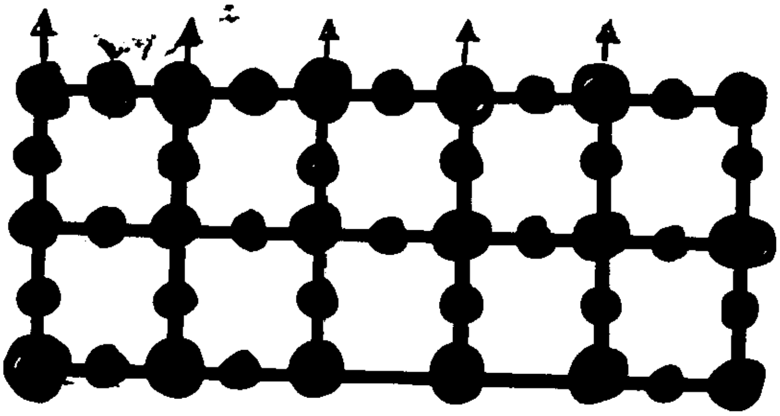
- B-O bond length }
- B-O-B bond angle } t → transfer matrix
- filling of e_g and t_{2g} orbitals
- Role of Oxygen atom (charge transfer)

Cubic $LaMnO_3$



$LiNbO_3$
$SrTiO_3$
Cuprates

Electrically (& Magnetically) Network (3-dim)



* ↑ spin at Mn site depends on valency (Mn^{3+} or Mn^{4+})

* Electron transfer from site to site depends on Mn-O-Mn angle & Mn-O distance

Since electron transfer from ion to oxygen (t) determines

ρ → Resistivity

T_c → Ferromagnetic T_c

$\Delta\rho(H)$ → MR

Any factor that changes t will change ρ, T_c & $\Delta\rho(H)$

↓

Factors determining electronic transpi

√1. Mn^{4+} Conc. (25% – 40%)

√2. Mn-O distance (Critical distance) $\boxed{\approx 1.97 Å}$

√3. Mn-O-Mn angle (≈ 180°)

√4. Physical state (clusters, Grain Size)

Making the oxide films

Pulsed Laser Ablation of a polycrystalline target of the given chemical composition.

[Also RF magnetron sputtering] [MOCVD attempts]

Conversion of optical energy to KE of the target atomic particles with energy typically 50-800eV and a beam like characteristics

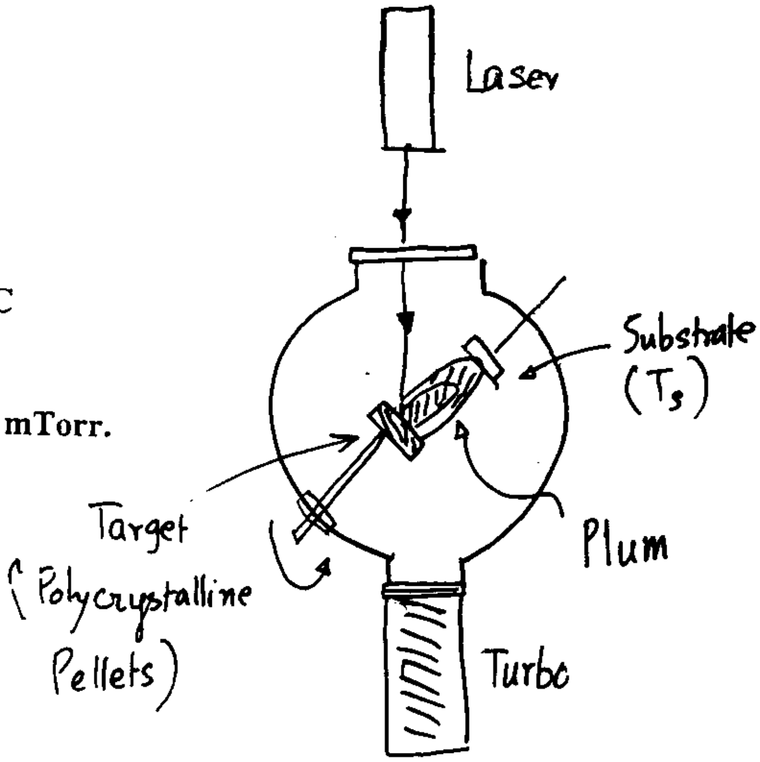
Typical :

Laser used KrF Excimer laser (248 nm, 250mJ/pulse, pulse duration 20nsec.)

Energy on target :2-10 J/cm^2

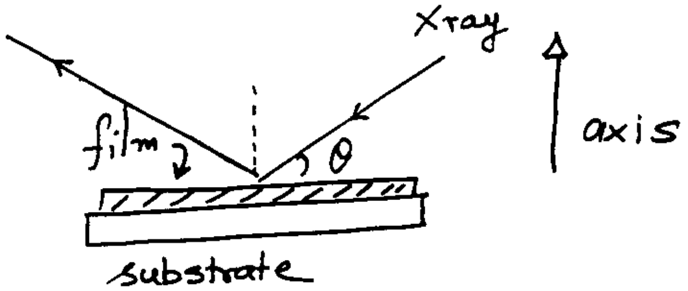
Substrate
~~target~~ temperature : 600 C-800C

Partial pressure of oxygen: Few mTorr.



Characterization of the GMRoxide films :

1. X- ray



θ-ϕ Scan

θ-2θ Scan

⟶ Fix θ & move film by angle (ϕ) around growth axis

2. Ion channeling and RBS

Hit the Surface with 3 MeV He^+

RBS ⟶ chemical Constituents.

Channeling ⟶ "Purity" of Crystallinity & Orientation

3. STM and AFM and other microscopy

Nanostructure & growth.

4. Magnetic characterization

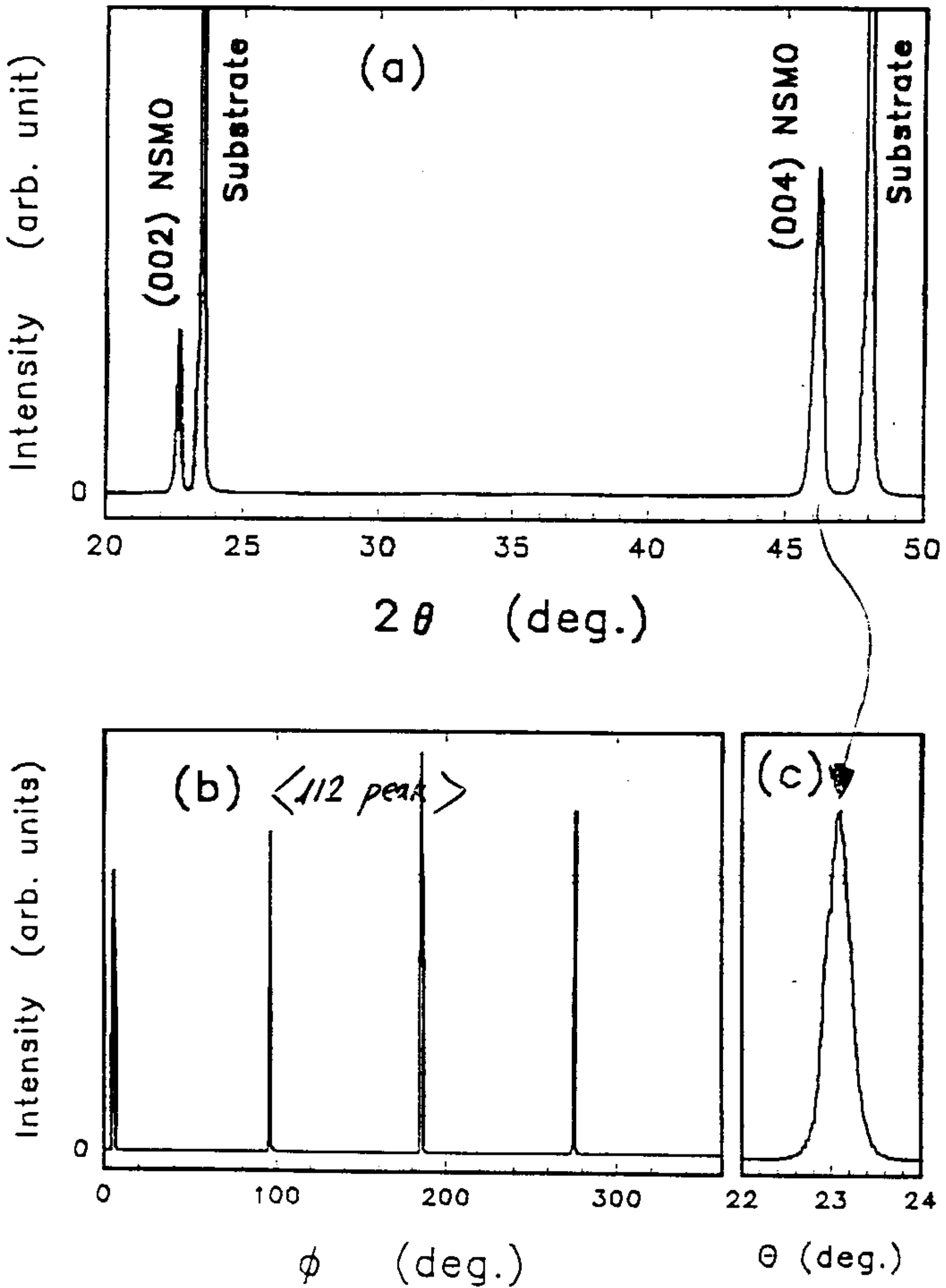
$M_s(T\to 0)$ & $M_s(T)$ Needs a "squid" or other highsensitivity magnetometer.

A good measure of goodness of film.

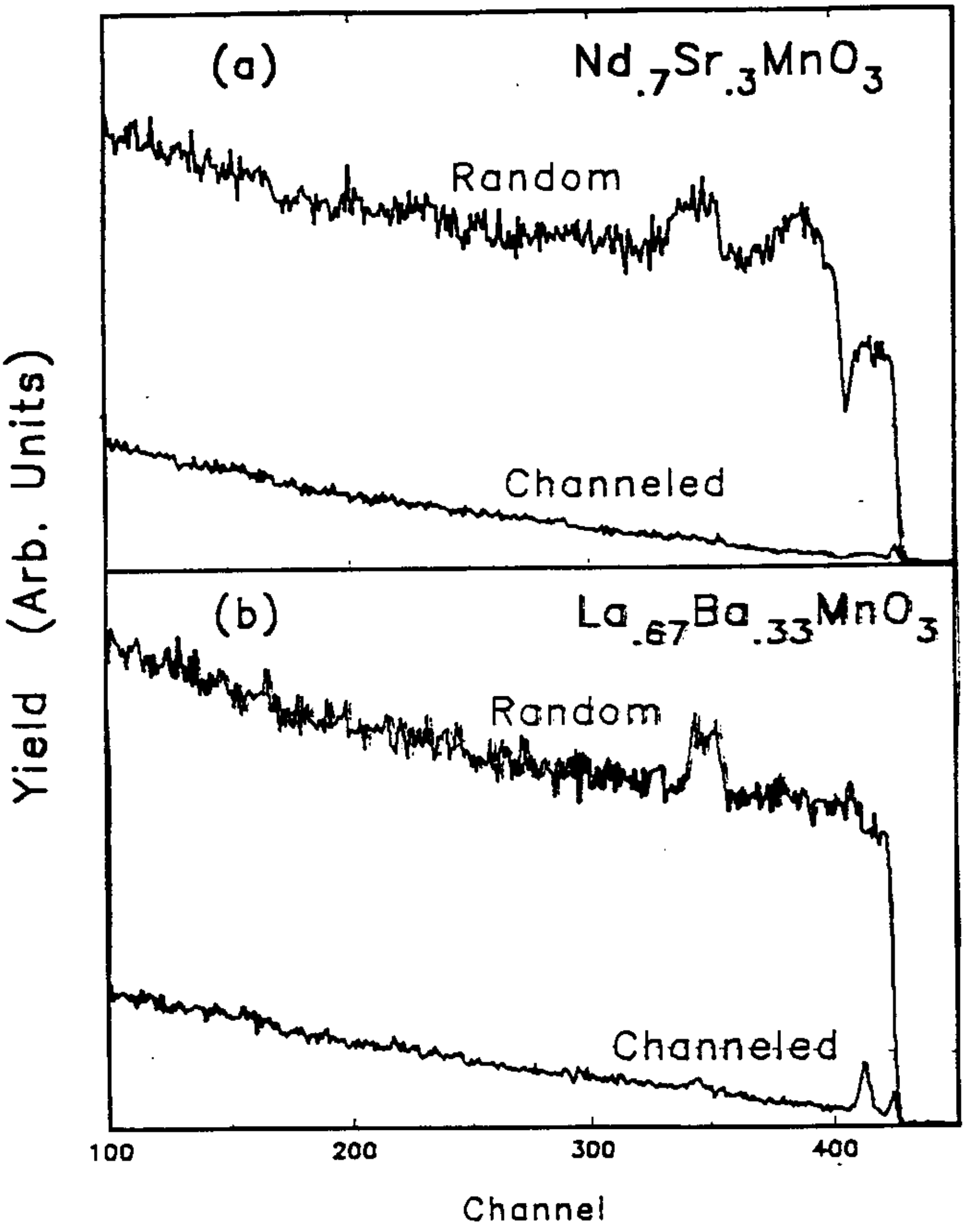
$Nd_{0.7}Sr_{0.3}MnO_3$ on $LaAlO_3$

Checking Epitaxy

(001) Growth direction

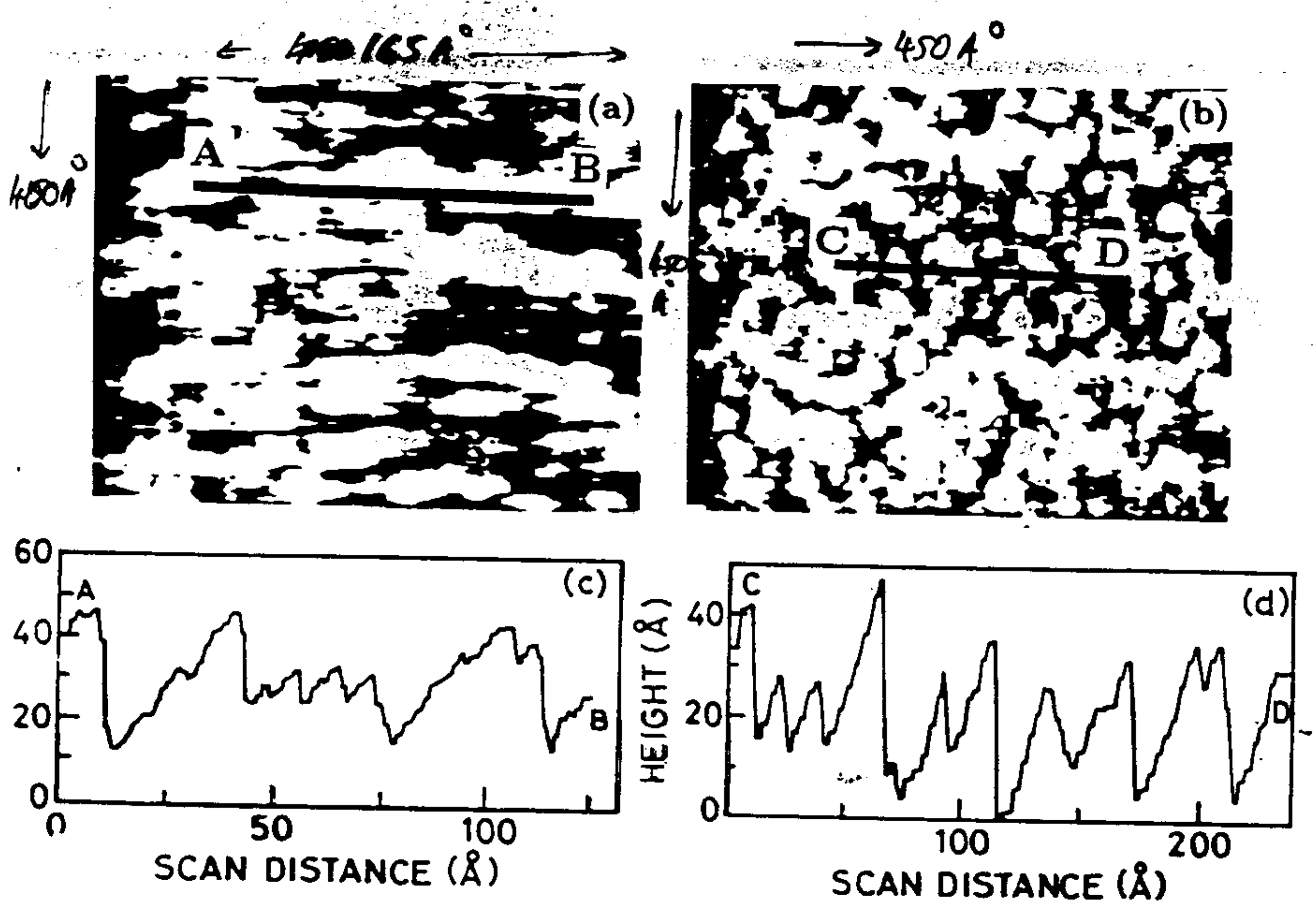


FWHM ≈ 0.3° – 0.5°



Minimum in channeling ≈ 3%-5% of random RBS

Courtesy:- Centre for Superconductivity Research
Univ. of Maryland
College Park
(Xiong et.al. APL 1995)



I ≈ 2 nA,   V ≈ 0.5V
Scan time 5s (128 × 128)
Corrected for Tilt.

Ramaswamy et. al   J. Appl. Physics (1996)

[Slide]

→ { Step Heights ≈ (n ±[illegible]) a
a ≈ Cubic lattice Constant ≈ 3.9A° }
rms roughness typical ≈ 2a

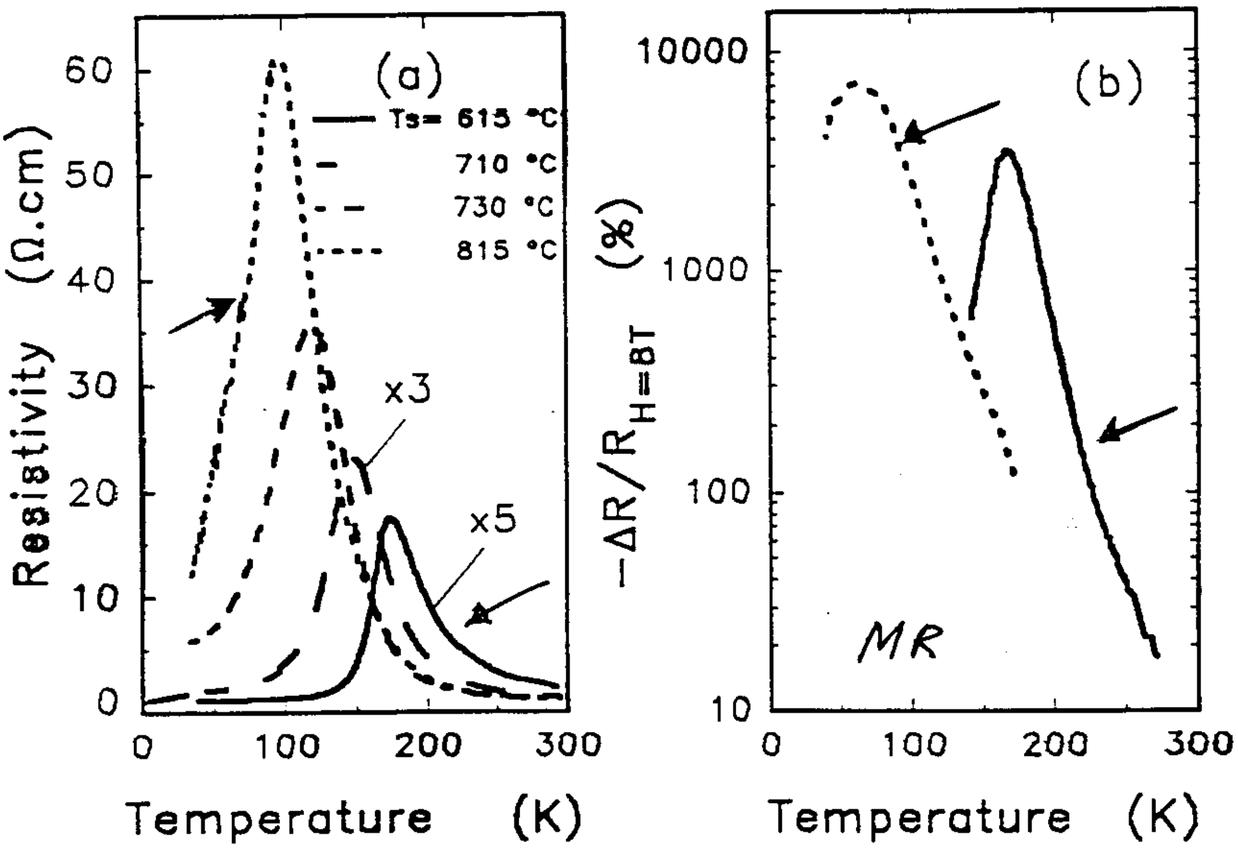
Thin film

1. Growth parameter optimization

(Oxygen partial pressure

→ Substrate Temperature

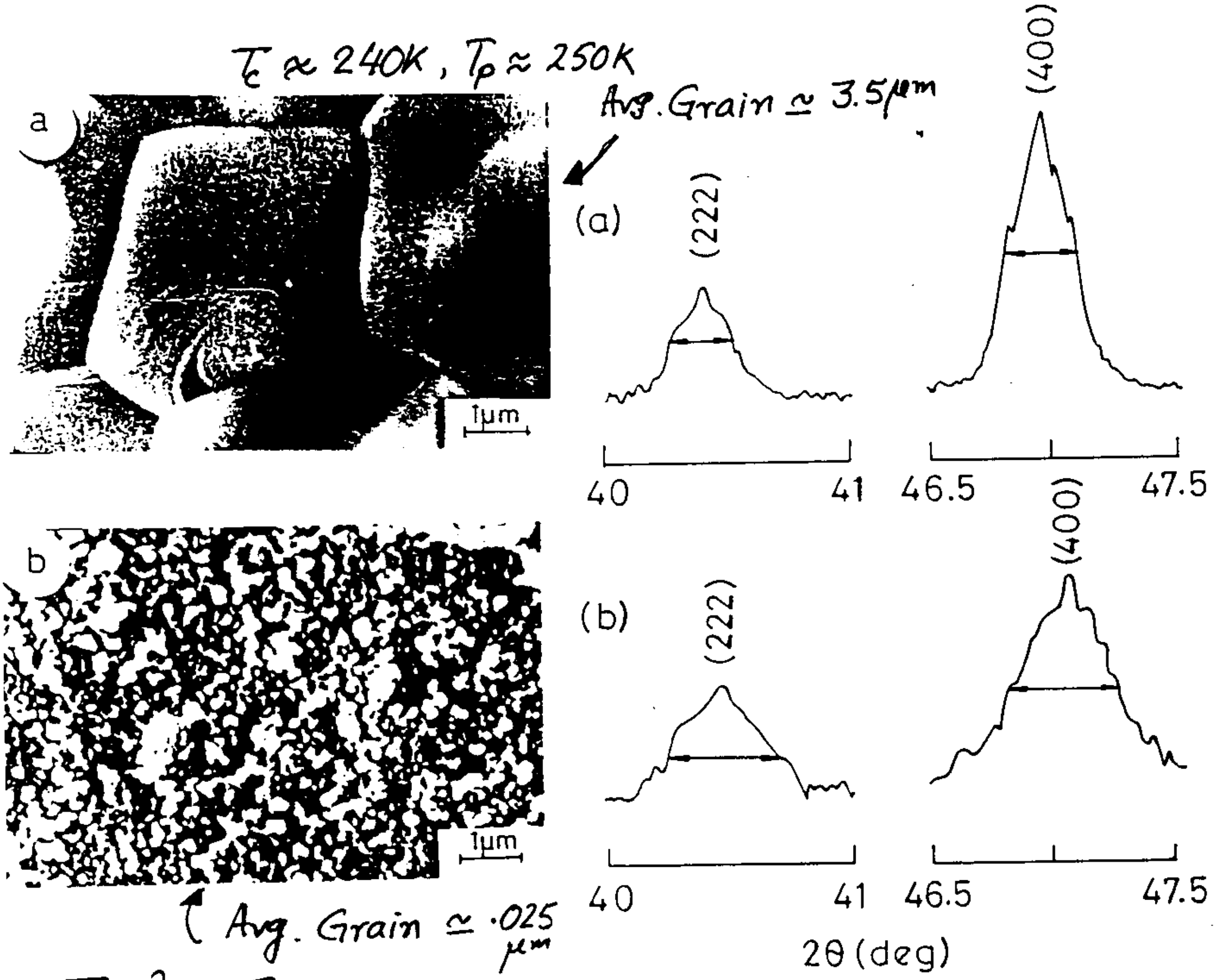
→ Post deposition Anneal)



$La_{0.7}Ca_{0.3}MnO_3$

Effect of
Grain Size :-

- Heat treatment Condition.
- Control of Mn^{4+} content.



$T_c \approx 240K$, $T_p \approx 250K$

Avg. Grain ≃ 3.5μm

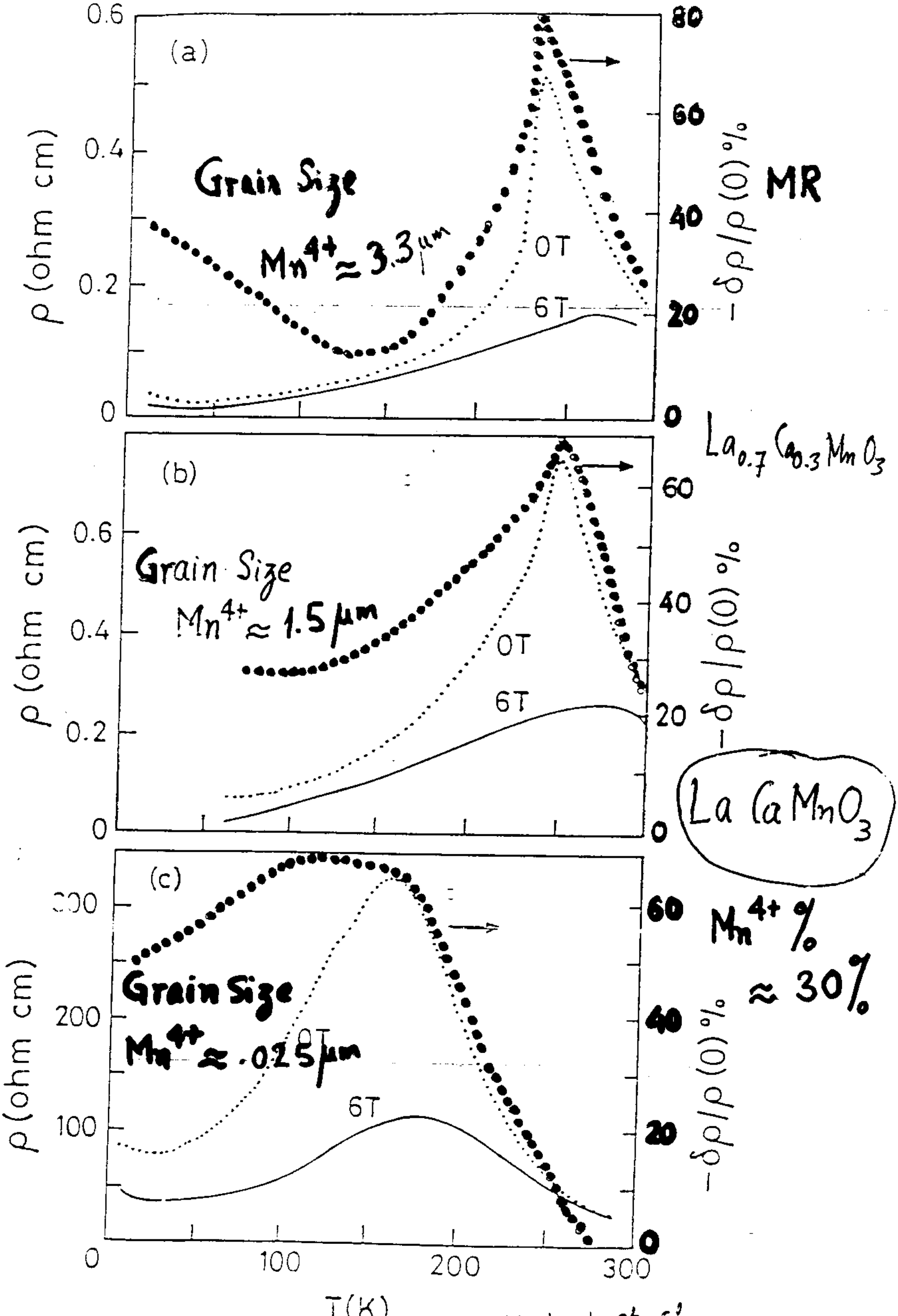
Avg. Grain ≃ ·025 μm

$T_c = ?$, $T_p \approx 160K$

Mahesh et.al.

Appl. Phys. Letts.
(April, 1996)

Fig 1 Mahesh et al



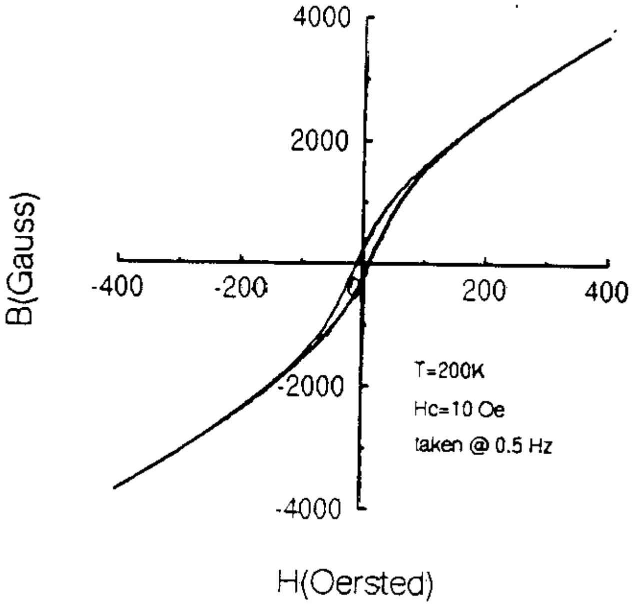
Mahesh et. al

FIG 2

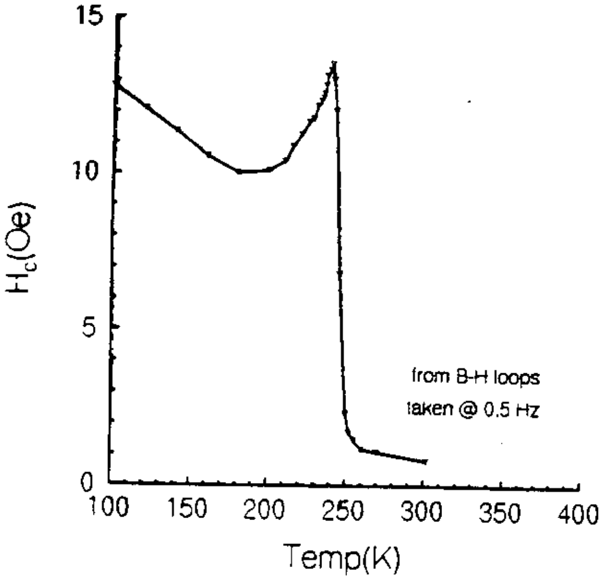
Mahesh et al

Appl. Phys. Letts. (April, 1996)

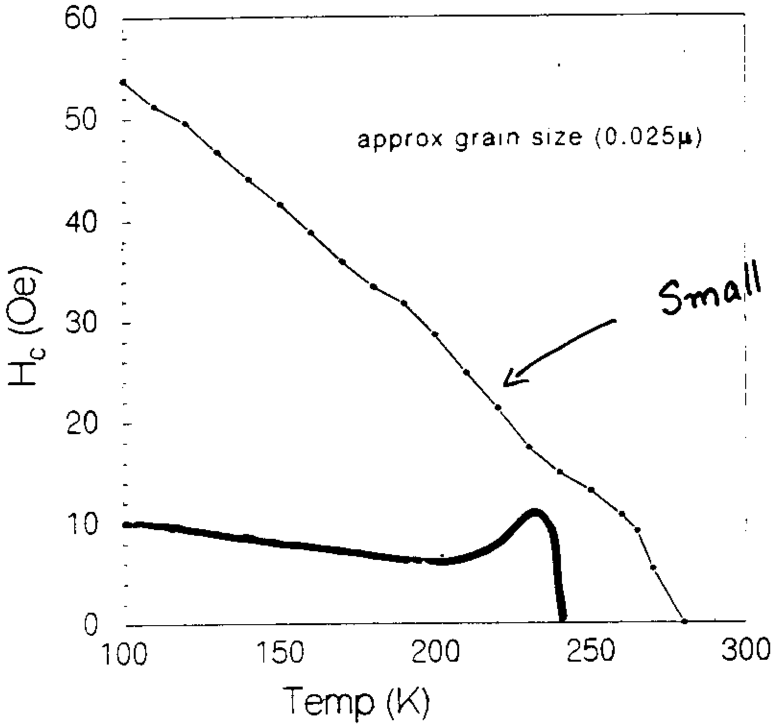
B-H loop ($La_{0.8}Ca_{0.2}MnO_3$)



Dasgupta, Ghosh & others (1996)
J. Appl. Physics

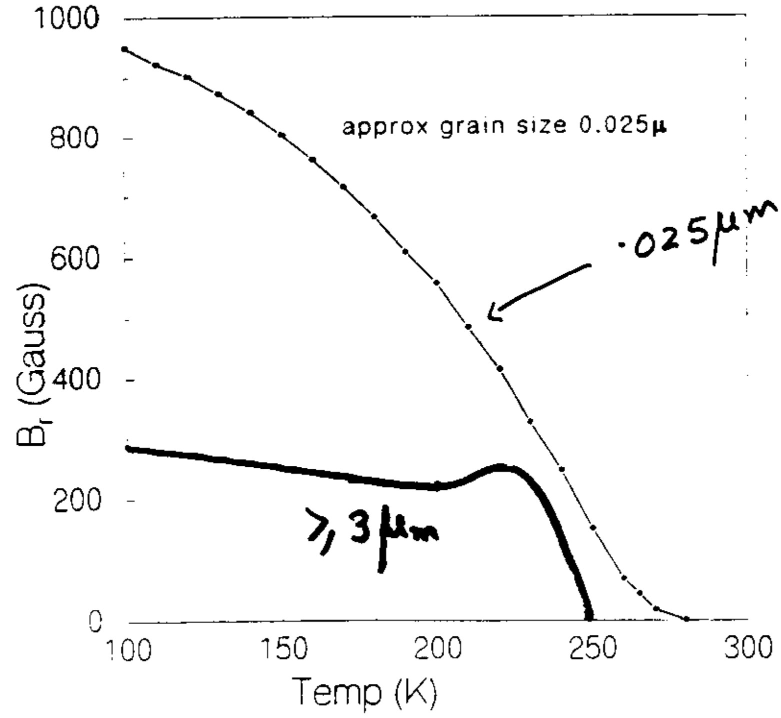


$La_{0.7}Ca_{0.3}MnO_3$ (small grained)



Small grain .025μm

— Large Grain $\gtrsim$ 3μm



.025μm

$\geq$ 3μm

Decrease of Grain Size increases both H_c & B_r