ELECTRON MAGNETIC RESONANCE OF MANGANESE COMPOUNDS

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INTRODUCTION

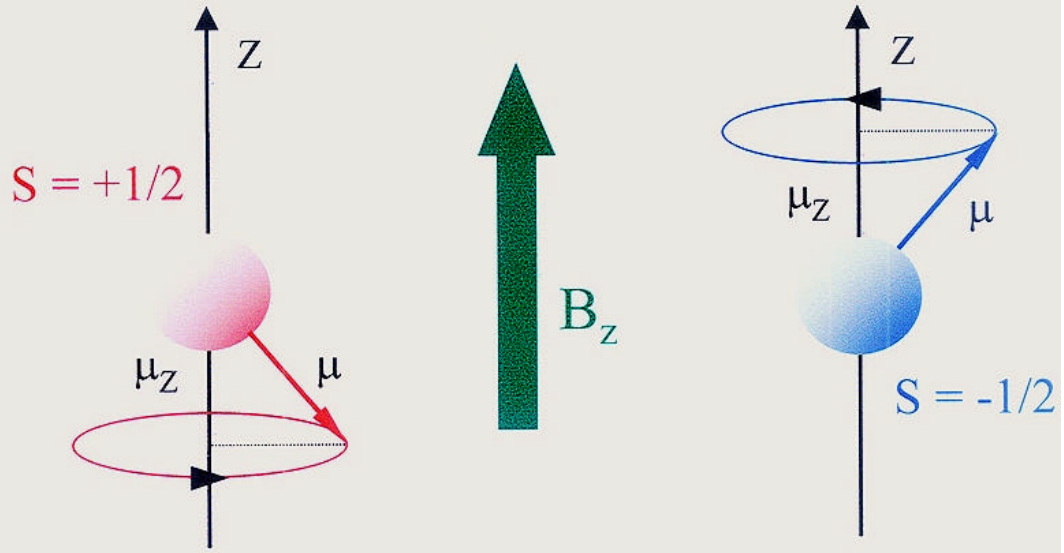
This talk will introduce the various forms of electron magnetic resonance:

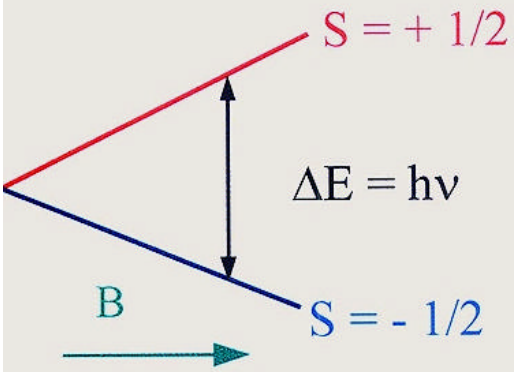
Electron Paramagnetic Resonance	**EPR (or ESR)**
Antiferromagnetic Resonance	**AFMR**
Ferromagnetic Resonance	**FMR**

and discuss the information derived from some typical experiments on manganese compounds.

The aim is to provide the background required to understand a resonance paper and also to allow an informed judgement as to when resonance could provide valuable information on a new material.

Spin 1/2 Resonance





$N_{+1/2} / N_{-1/2}$

$\downarrow$

$\exp(- \Delta E / kT)$

ESR: $\nu = \Delta E / h = (g_e \mu_B / h) B$

$= 28$ GHz / T for $g = 2$

NMR : $\nu = \Delta E / h = (g_N \mu_N / h) B$

Proton $\nu = 43$ MHz / T

Cobalt $\nu = 10$ MHz / T

General Scheme for Magnetic Resonance

(1) Energy levels split by **magnetic field and / or**
electric field gradient (S > 1/2)

(2) Radio frequency field to induce transitions between levels.

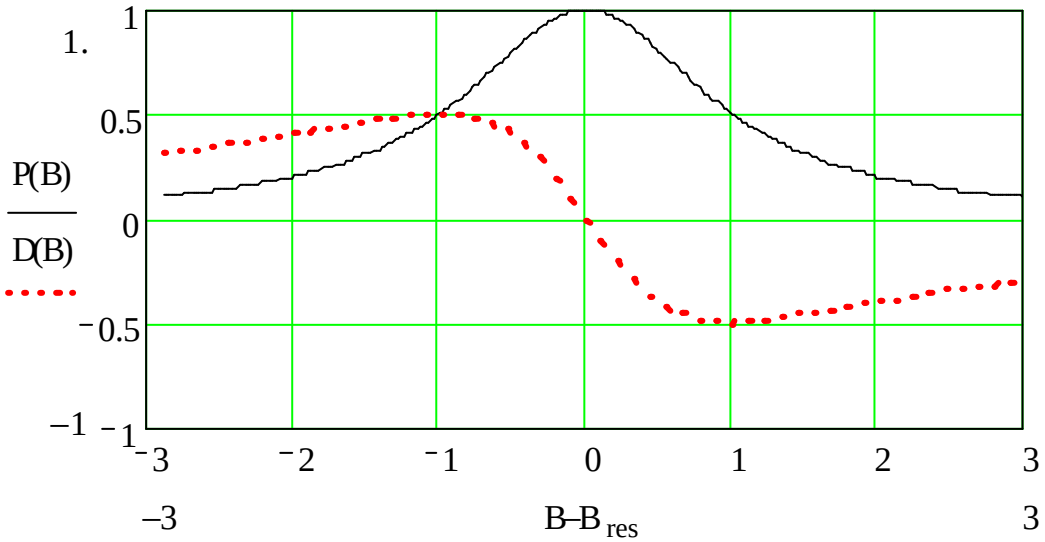
Note: Linearly polarized radiation is used that can be resolved in to two counter-rotating circularly polarized components. Only one sense of rotation is usually important.

(3) Effect on circuit written as complex susceptibility

$$Z = j\omega L\,(1 + \chi' - j\chi'')$$

χ' **(red)** **changes tuning of circuit (dispersion).**

χ'' **(black)** **changes power absorbed.**



(4) At resonance $\chi'' \sim \frac{\text{(static spin susceptibility x frequency)}}{\text{linewidth}}$

Real part of electron susceptibility for each resonance may be found by integrating power absorbed over all range of (frequency or field) sweep.

Relaxation

Identify two relaxation times for spin system:

Within spin system (transverse relaxation time) T_2

From spin system to "lattice" (longitudinal relaxation) T_1

Linewidth

Two ways line can be broadened

(a) homogeneous line broadening (lifetime of upper level)

For Lorentzian line $\Delta\nu_{FWHM} = 2 / \gamma T_2$

[γ **is the gyromagnetic ratio (** ω / B_0 **at resonance) and**

$\Delta\nu_{FWHM}$ **is the full linewidth at half power absorption.]**

(b) inhomogeneous line broadening ("line" is now envelope of distribution of level splittings)

For strongly exchanged coupled systems such as manganites expect

$$T_1 = T_2.$$

Pulsed techniques give best values of relaxation times but relaxation in manganites is only nanoseconds so not possible.

Detection of electron resonance

Two possibilities:

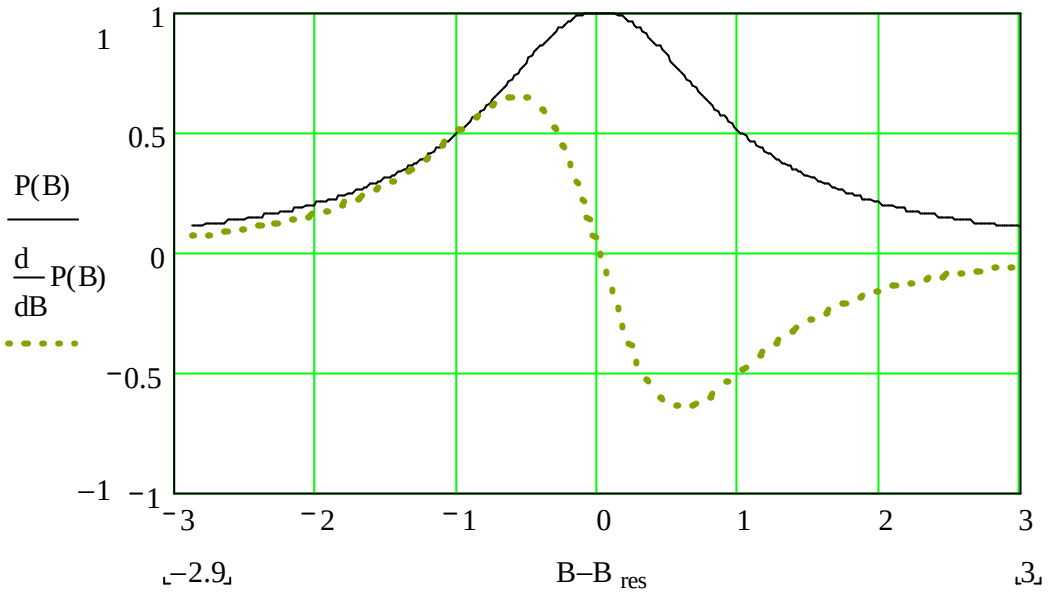
(i) Direct detection of power absorbed

Leads to at least approximate lineshape. Used for very broad lines (kG) and very high frequency / field measurements where stability poor.

(ii) Detection of differential of line by modulating magnetic field a fraction of linewidth.

Ideally, integration then gives true lineshape.

Double integration then gives real part of the susceptibility for that resonance.



(Note that $\Delta_{FWHM} = \sqrt{3}\,\Delta_{peak\ to\ peak}$ for a Lorentzian line.)

Technique (frequency / fields for g = 2)

Standard 9 GHz / 0.3 T (3 cm wavelength)

Waveguide plus tuned cavity for sample.

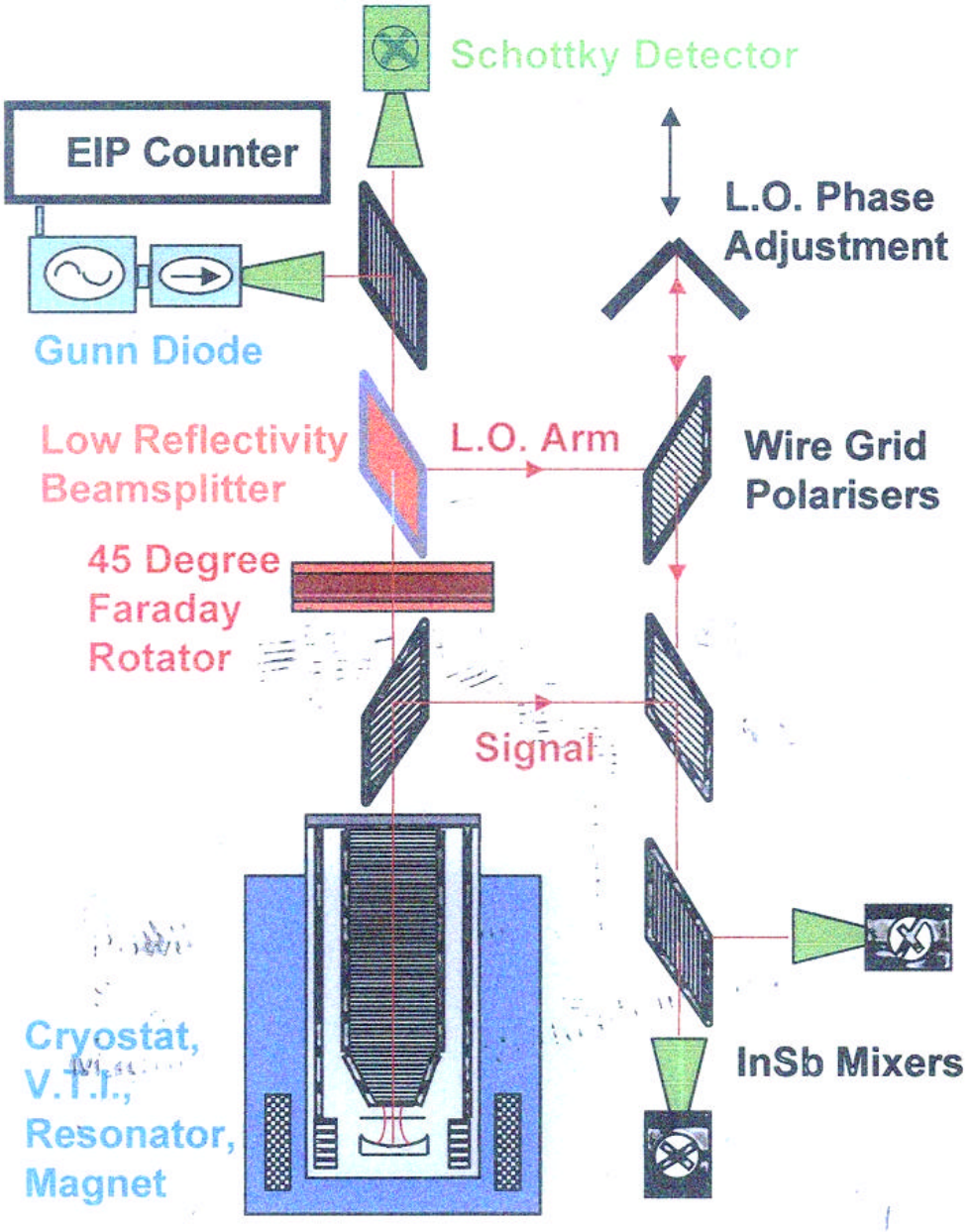
HFEPR 90 – 270 GHz / 3 –9 T

Quasi-optical technique. Stable superconducting magnets.

VHFEPR Up to 1,000 GHz using Bitter or pulsed magnets.

Direct detection usual in transmission.

Quasi-Optical Spectrometer



St. Andrews 90-270 GHz Spectrometer

(G.M. Smith et al. Rev. Sci. Instrum.

Electron resonance of dilute magnetic systems

Detect unpaired electrons in :

Transition metal ions	**Dangling bonds**
Rare earth ions	**Defects**
Free radicals	**Conduction electrons**

EPR spectra are highly sensitive to the local crystal environment

e.g. uniaxial symmetry, D due to crystal fields:

$$H = g_{//}\, \mu_B B_0 \cos\theta\, S_z + g_{\wedge}\, \mu_B B_0 \cos\theta\, S_x +$$

$$D\,[\,(S_z)^2 - S.(S+1)/3\,]$$

Different ions or environments in dilute systems produce separate spectra. Strongly exchange coupled ions such as Mn in the manganites give a single resonance with g around 2.

Antiferromagnetic resonance (AFMR)

There is one zero field resonance for antiparallel sublattices:

$\omega_0 \propto \gamma\,(B_e B_K)^{1/2}$ **(B_e exchange field, B_K anisotropy field)**

In an external field there are two resonance lines

$\omega = \omega_0 + \gamma B_0$ **and** $\omega_0 - \gamma B_0$

Ferromagnetic Resonance (FMR)

Now need to take in to account shape of sample and allow for demagnetizing fields. Neglecting magnetocrystalline anisotropy for the moment, the Kittel equation for a saturated ellipsoid is

$$\omega_0 = \gamma \{[B_0 + \mu_0 (D_y - D_z) M] [B_0 + \mu_0 (D_x - D_z) M]\}^{1/2}$$

(where D_x etc; are demagnetising factors)

Sphere $\omega_0 = \gamma B_0$

Thin film M in plane $\omega_0 = \gamma (B_0 - \mu_0 M)$

Thin film M normal to plane $\omega_0 = \gamma [B_0 (B_0 + \mu_0 M)]^{1/2}$

Allowing for a cubic anisotropy field (B_A) and axial anisotropy field (B_{2A}) the equation becomes, for a film with the external field at an angle α to the film normal and M at an angle θ:

$$\omega_0 = \gamma \{ B_0 \cos (\theta - \alpha) - B_{eff} \cos^2 \theta + 2 B_{A2} \} x$$

$$\{ B_0 \cos (\theta - \alpha) - B_{eff} \cos (2\theta) + B_{A2} [1 + \cos^2(2\theta)]\}^{1/2}$$

where $B_{eff} = \mu_0 M + B_A$

Problems for Electron Resonance studies of manganites

(1) Only the skin depth region of metallic samples observed, therefore either work in surface of bulk or use thin films.

Skin depth at frequency ν **given by** $\delta = (\pi \nu \sigma \mu)^{-1/2}$

e.g. Cu at room temperature ν **= 9 GHz,** δ **@ 600 nm.**

Note that permeability μ **(** ν**,) and conductivity** σ **(** ν**,** B_0 **)**

Leads to an asymmetric (Dysonian) line if sample thickness greater than skin depth.

(2) Thin films may have strong field dependent interaction with the substrate if it has a large dielectric constant.

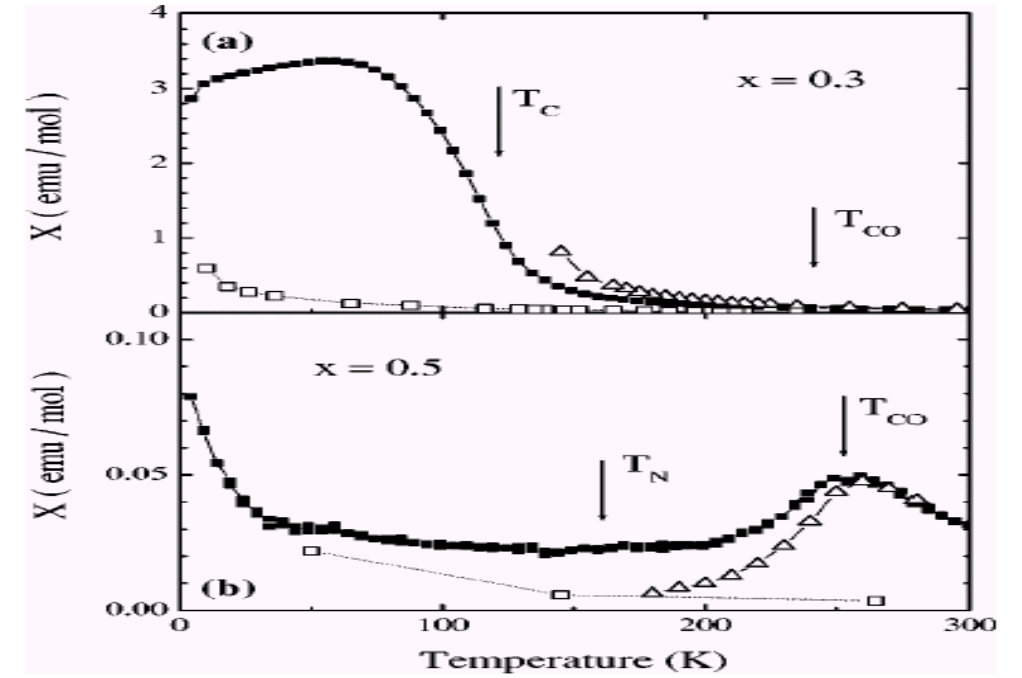
(3) Importance of second phases and sample variation may be different in resonance than in bulk measurements, i.e sample that looks "good" to one technique may still be defective.

Partial solution to these problems is to make:

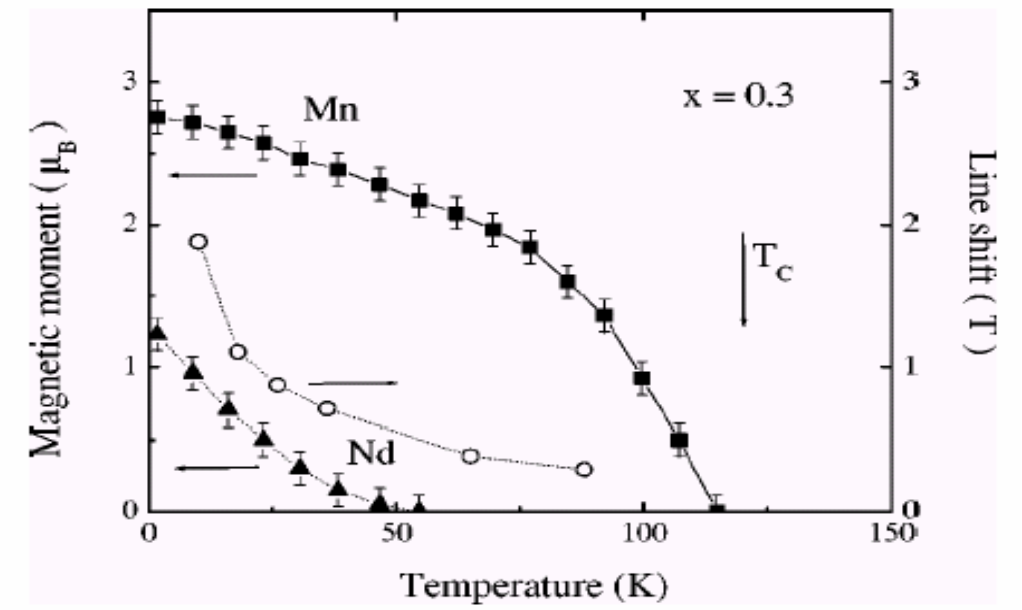
Macroscopic measurements

Neutrons, muons, NMR

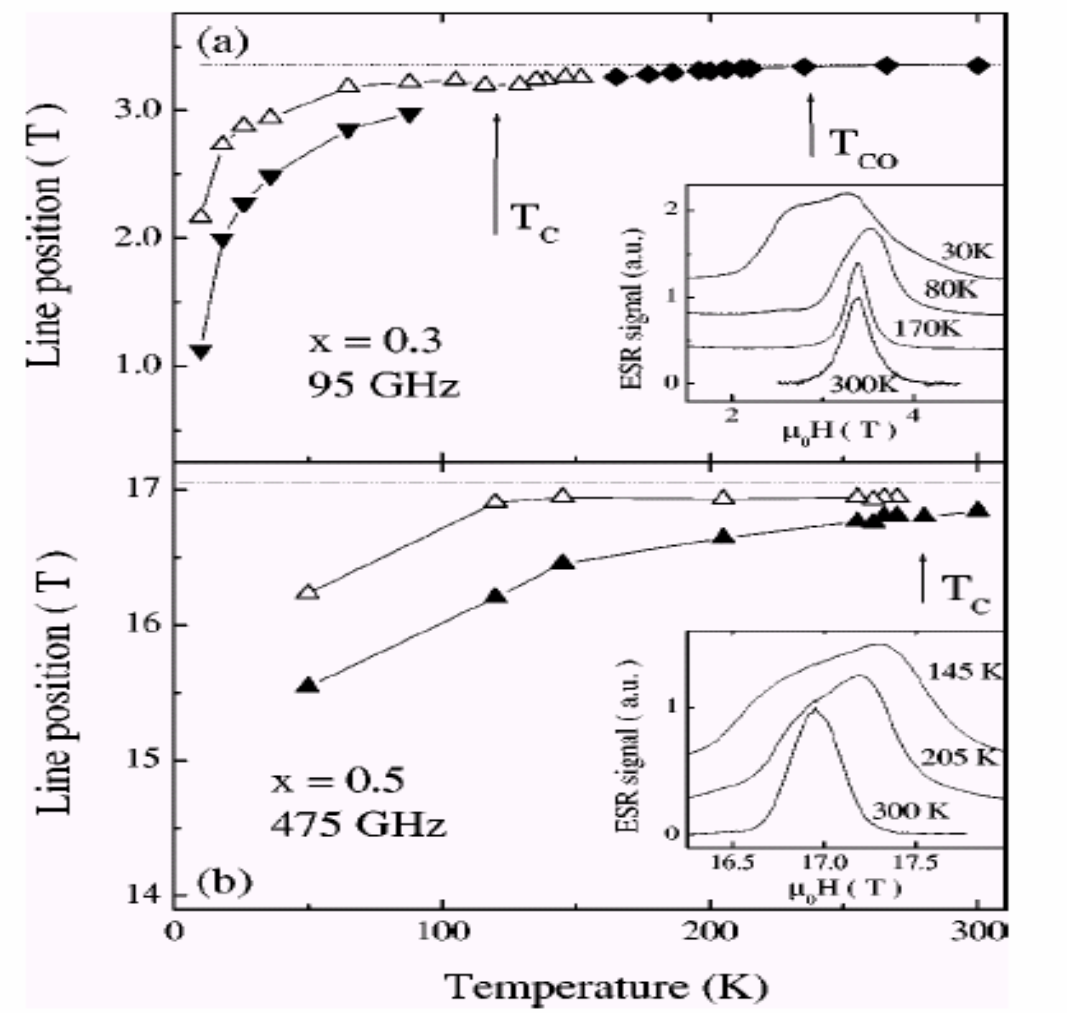
Plus wide frequency range of resonance frequencies and fields.



Susceptibility of $Nd_{1-x}Ca_xMnO_3$: dc (filled •), EPR Mn (D) and Nd susceptibility (•) deduced from Mn lineshift.



Neutron measurements of Mn and Nd moments and Nd moment deduced from Mn EPR lineshift.



EPR in the ferromagnetic phase (line corrected for sample demagnetisation field). Dashed line shows g = 1.99.

The EPR spectrum in the FM phase shows:

T above T_c : single symmetric line

lower T : double peak and shifts to lower fields

(not observed in $La_{0.67}Ca_{0.33}MnO_3$, only for Nd compounds)

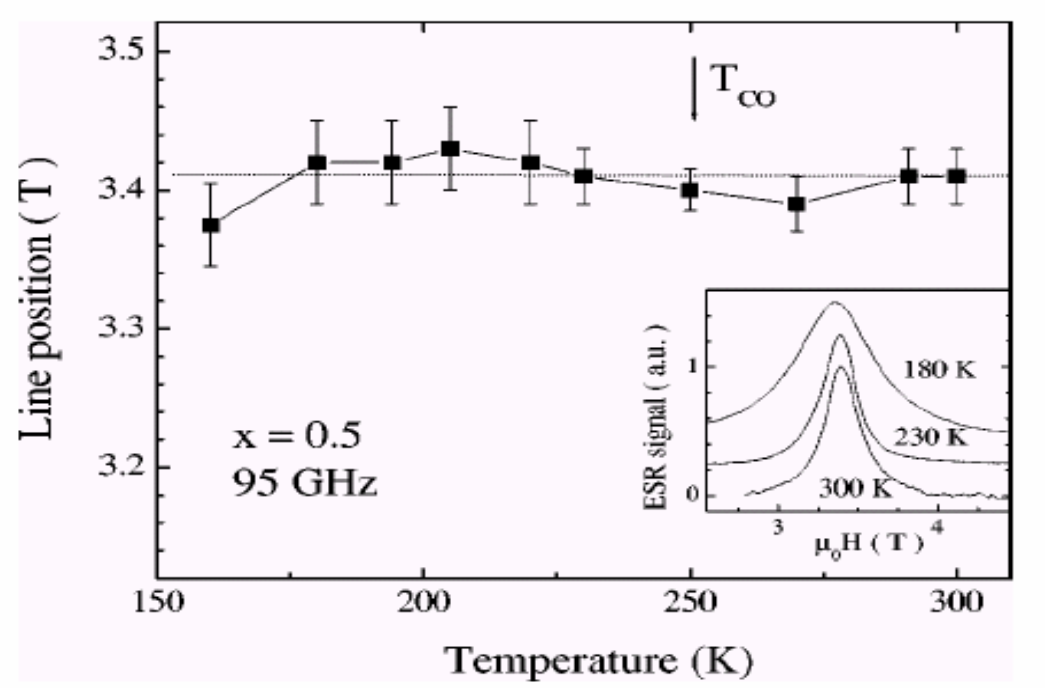
Explanation of Mn EPR spectrum in FM phase

Mn moments strongly exchange coupled leading to single FMR line.

Mn only weakly coupled to Nd. Nd EPR too broad to observe due to rapid relaxation but shifts Mn resonance:

$$d\mathbf{H}_{Mn} = l\,\mathbf{M}^{Nd} \qquad (l = 2.4\ \mathbf{T} / m_B^{Nd})$$

Nd couples FM to Mn but orders at much lower temperature.



At 95 GHz sample is in low field CO phase. EPR line corrected for sample demagnetisation field. Dotted line shows g = 1.99.

N.b. no trace of FM domains embedded in the CO matrix.

$Nd_{1-x}Ca_xMnO_3$ for x = 0.3 and 0.5

Dupont et al. Phys. Rev. B64(2001)220403

Summary of properties

	0.3	0.5
Ground state	**FM**	**AF**
Charge order (T_{CO}) K	**240**	**250**
Zero field	**T_c = 120**	**T_N = 160**
15 T field		**FM 275 K**

Powder Samples **loosely packed for 9 and 35 GHz**

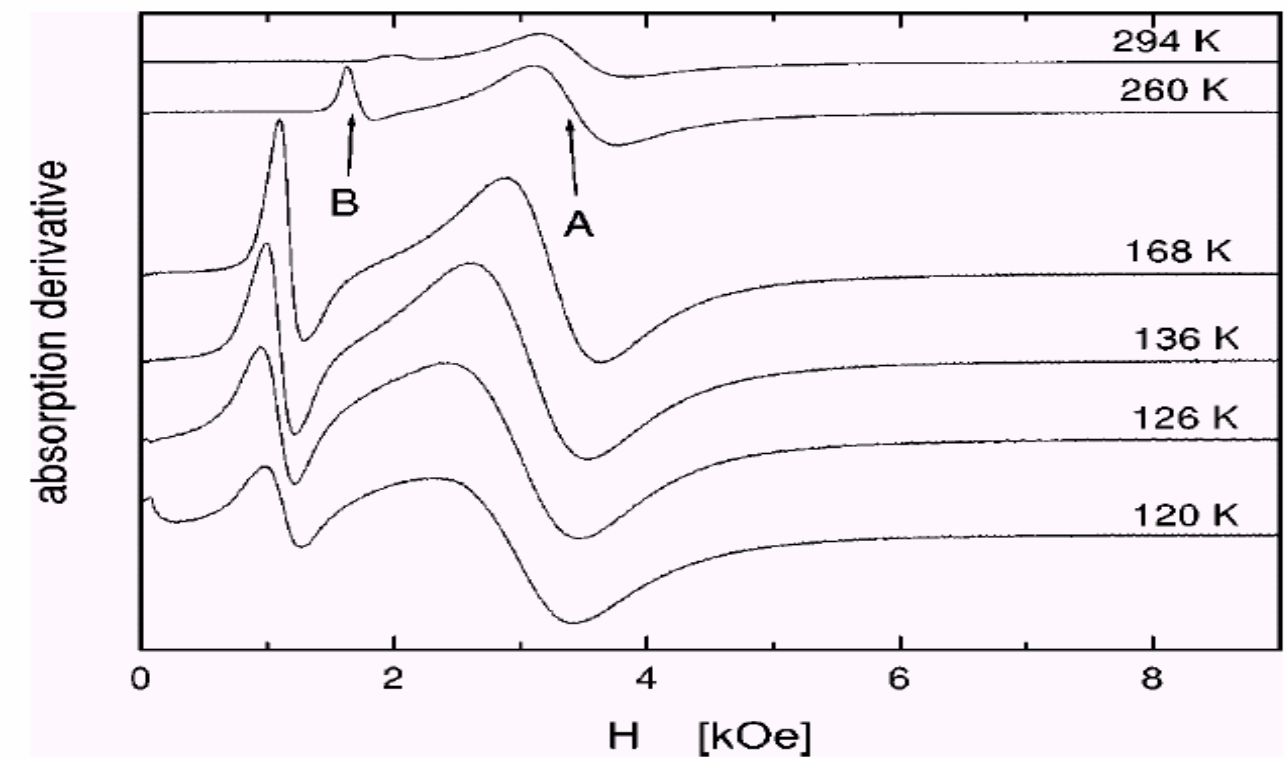
pellet 9 x 0.9 mm for 95 –475 GHz

Field **Normal to axis of pellet**

$dH_{demag} @ m_0 M$

Other measurements

Magnetization to 23 T **Neutrons**



1. EPR of $La_{1.2}Sr_{1.8}Mn_2O_7$ at 9.5 GHz with H in the (a,b) plane.

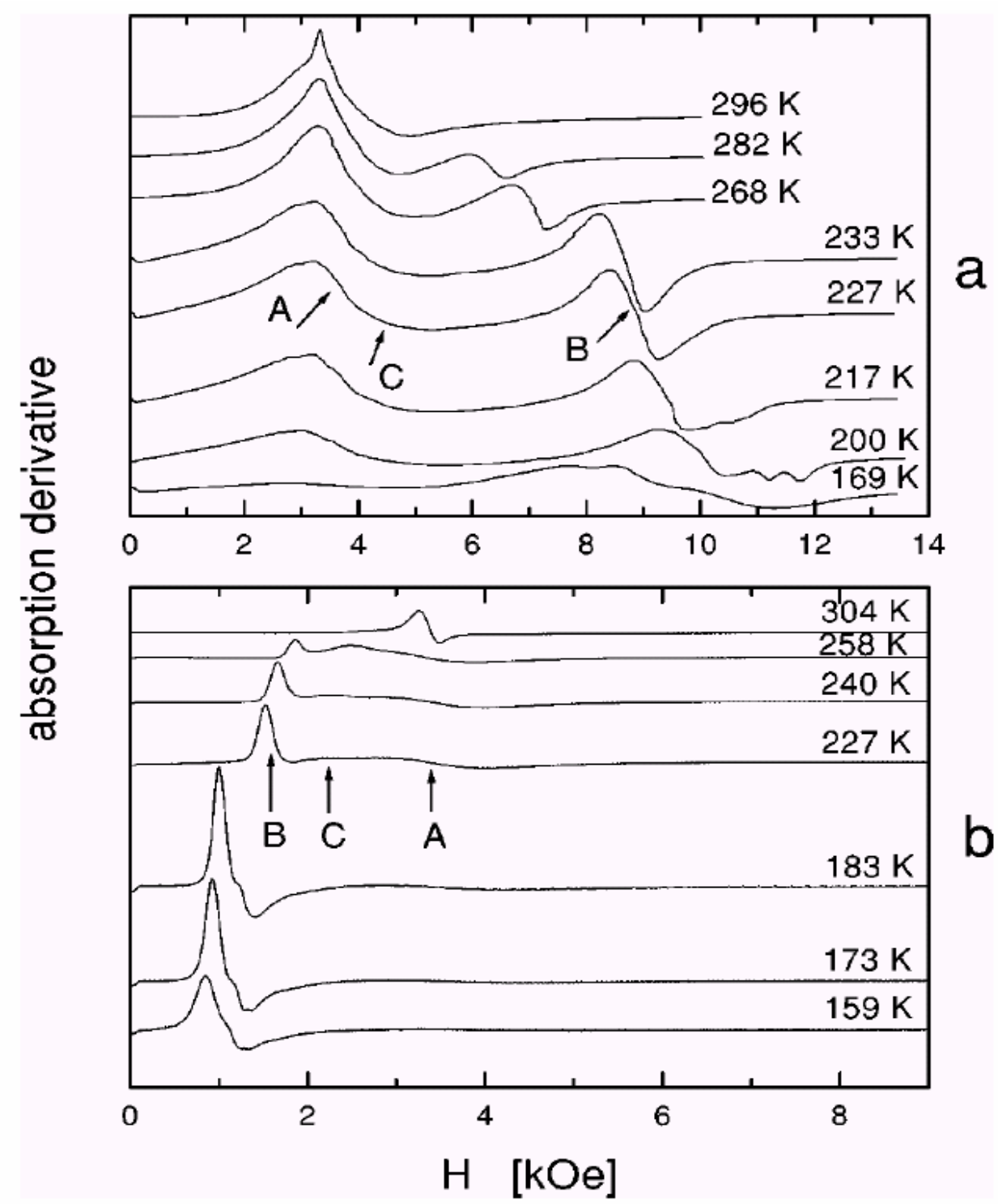
Line A

Due to exchange coupled Mn^{3+} - Mn^{4+} ions.

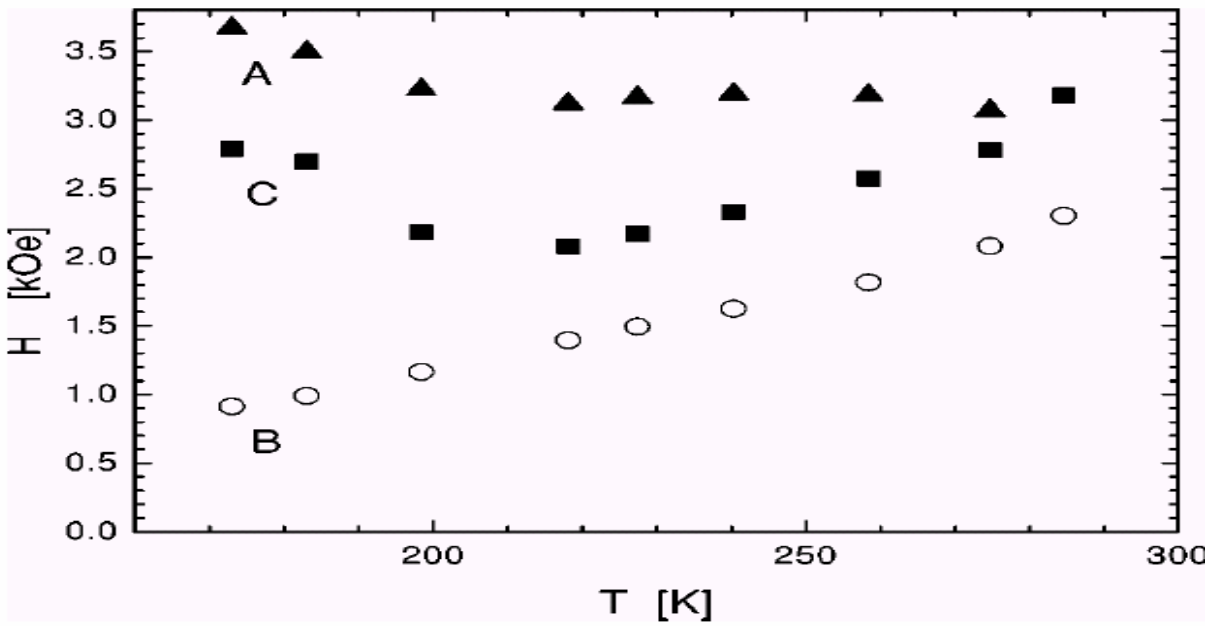
g –factor close to 2. Shifts of line with temperature due to magnetization of paramagnetic sample and Dzialoshinsky – Moriya (DM) interaction.

Line B

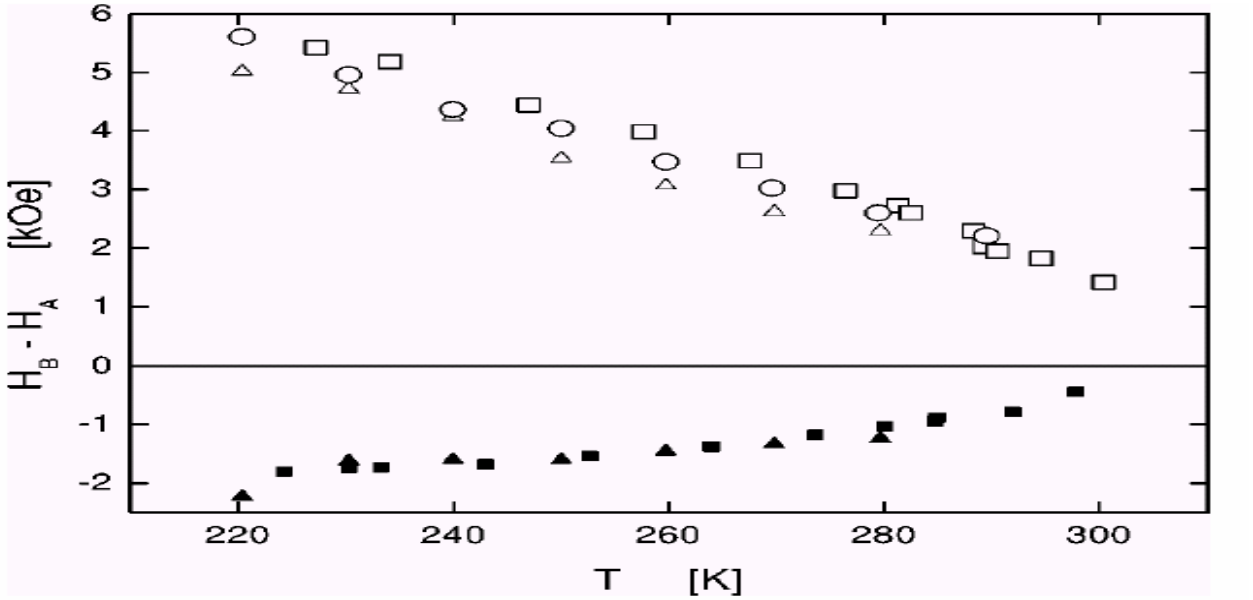
Has been attributed to intralayer FM clusters but could be due to second phase FM below 270 K.



2. EPR of $La_1Sr_2Mn_2O_7$ at 9.5 GHz with (a) H parallel to c and (b) H in the (a, b) plane.



3. Resonance fields for $La_1Sr_2Mn_2O_7$ at 9.5 GHz as function of temperature with H in the (a, b) plane.



4. Shift of B line of $La_1Sr_2Mn_2O_7$ relative to A line at 9.5 GHz (squares), 75 GHz (triangles), and 150 GHz (circles).
H parallel to c (open symbols), H in the (a, b) plane filled symbols.

Summary for $La_1Sr_2Mn_2O_7$

AF so A line only weakly dependent on temperature

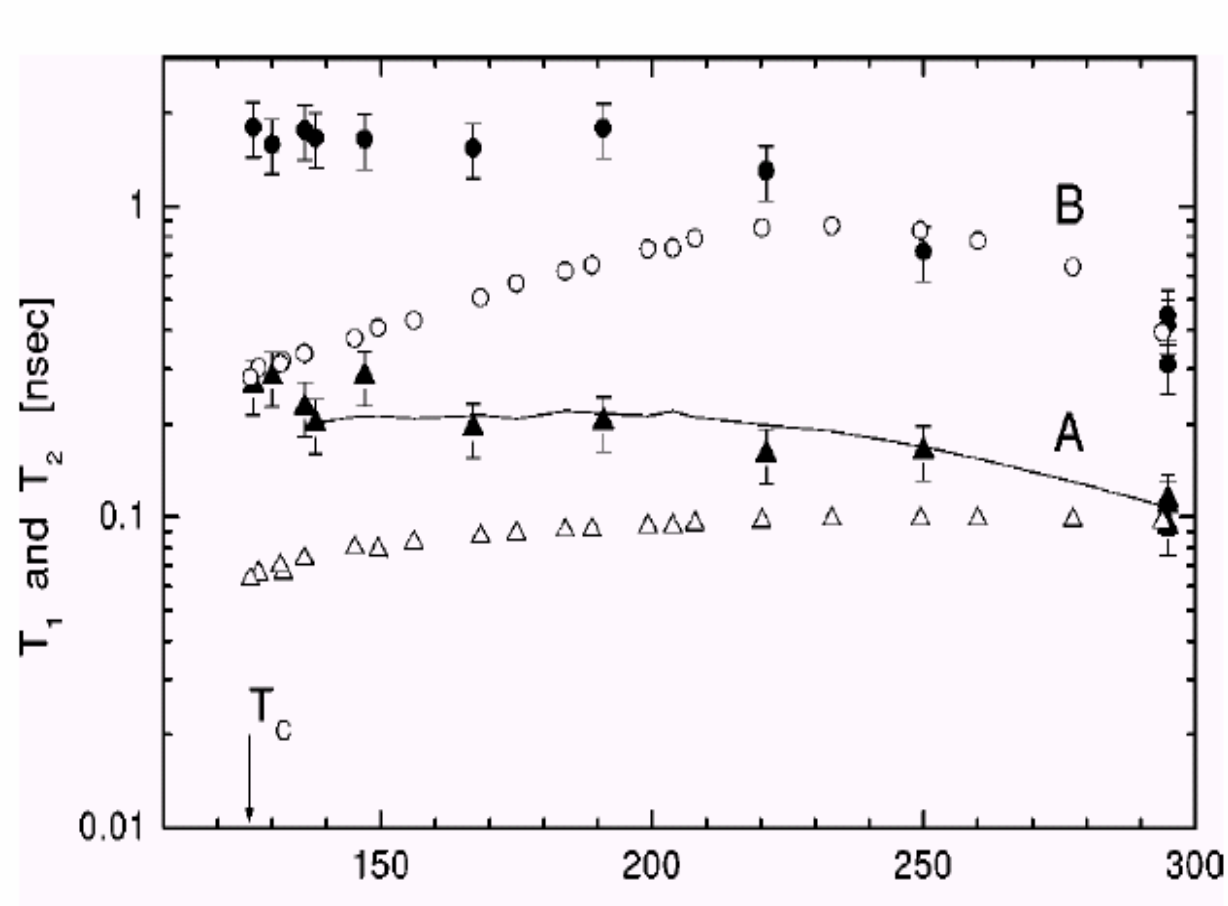
(H_B – H_A) independent of frequency so due to magnetization not g - factor anisotropy.

H_B as a function of angle from c – axis correct for easy – plane FM or thin platelet so could be second phase rather than true magnetic clusters (polarons).

EPR Susceptibility

Sum of integrated lines for both samples gives total susceptibility in agreement with torque measurements so all spins accounted for. Lines have different temperature dependence confirming B is from FM phase and showing evidence of short range order far above ordering temperatures

Origin for line C not clear, could be another spurious phase or magnetic polarons.



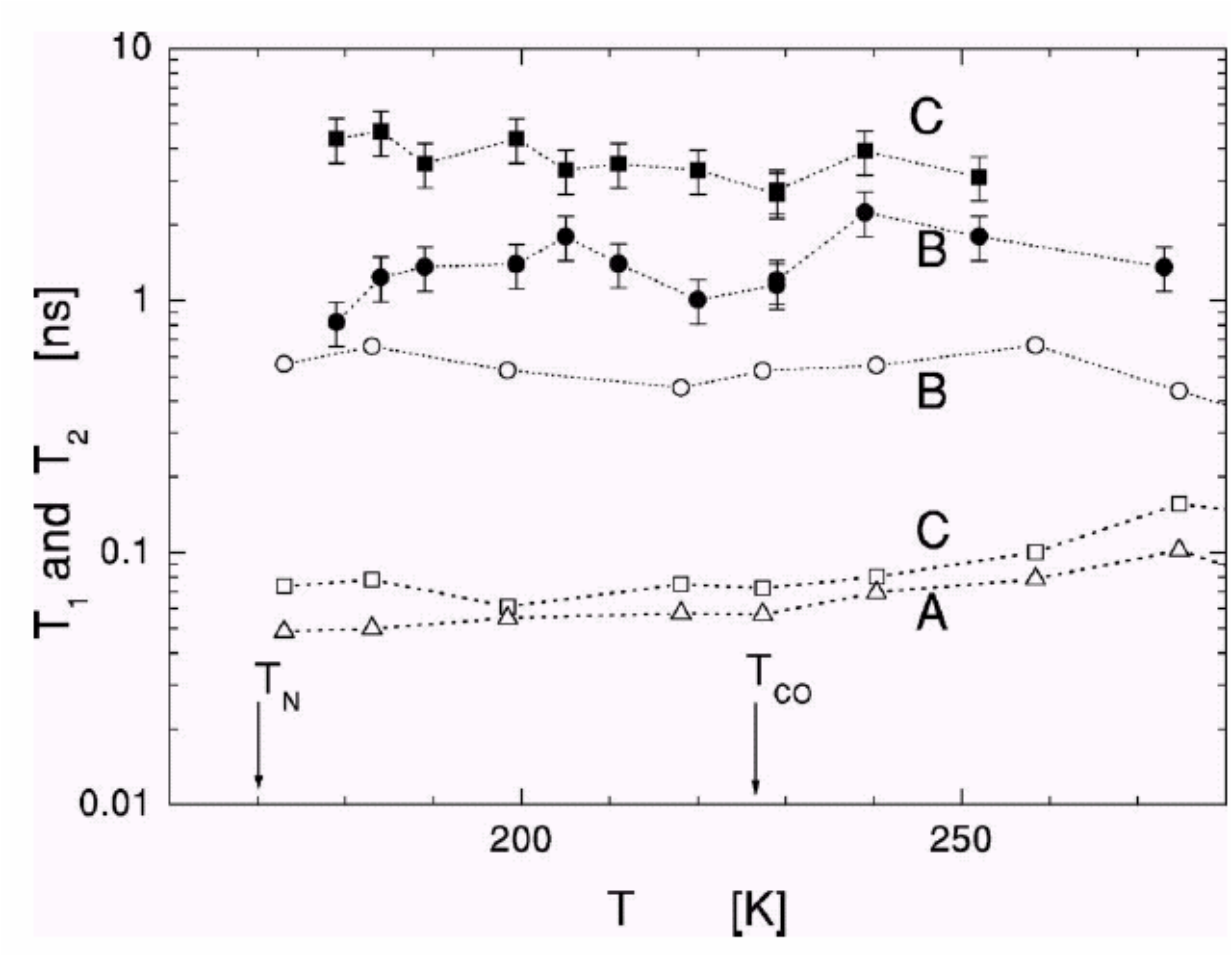
5. Longitudinal relaxation time (T_1), solid symbols, and transverse relaxation time (T_2), open symbols, for $La_{1.2}Sr_{1.8}Mn_2O_7$ with H in the (a, b) plane.

Solid line is T_1 = const. T c(T) for each line. (Huber)

(c(T) from EPR spectrum.)

T_2 defined as g times half width of Lorentzian line.

T_1 measured by cw method.



6. Longitudinal relaxation time (T_1), solid symbols, and transverse relaxation time (T_2), open symbols, for $La_1Sr_2Mn_2O_7$ with H in the (a, b) plane. (T_1 for A line is too short to measure accurately, less than 10^{-10} s.)

Note large ratio of T_1 / T_2 for C line due to inhomogeneous broadening.

(Expect $T_1 = T_2$ for strongly exchange narrowed lines)

Electron spin resonance and relaxation studies of double-layered manganites

F. Simon, V. A. Atsarkin, V. V. Demidov, R. Gaal, Y. Moritomo, M. Miljak, A. Janossy, and L. Forro´

Phys. Rev. B 67 (2003) 224433

$La_{2-22x}Sr_{1+12x}Mn_2O_7$ (x = 0.4 and 0.5)

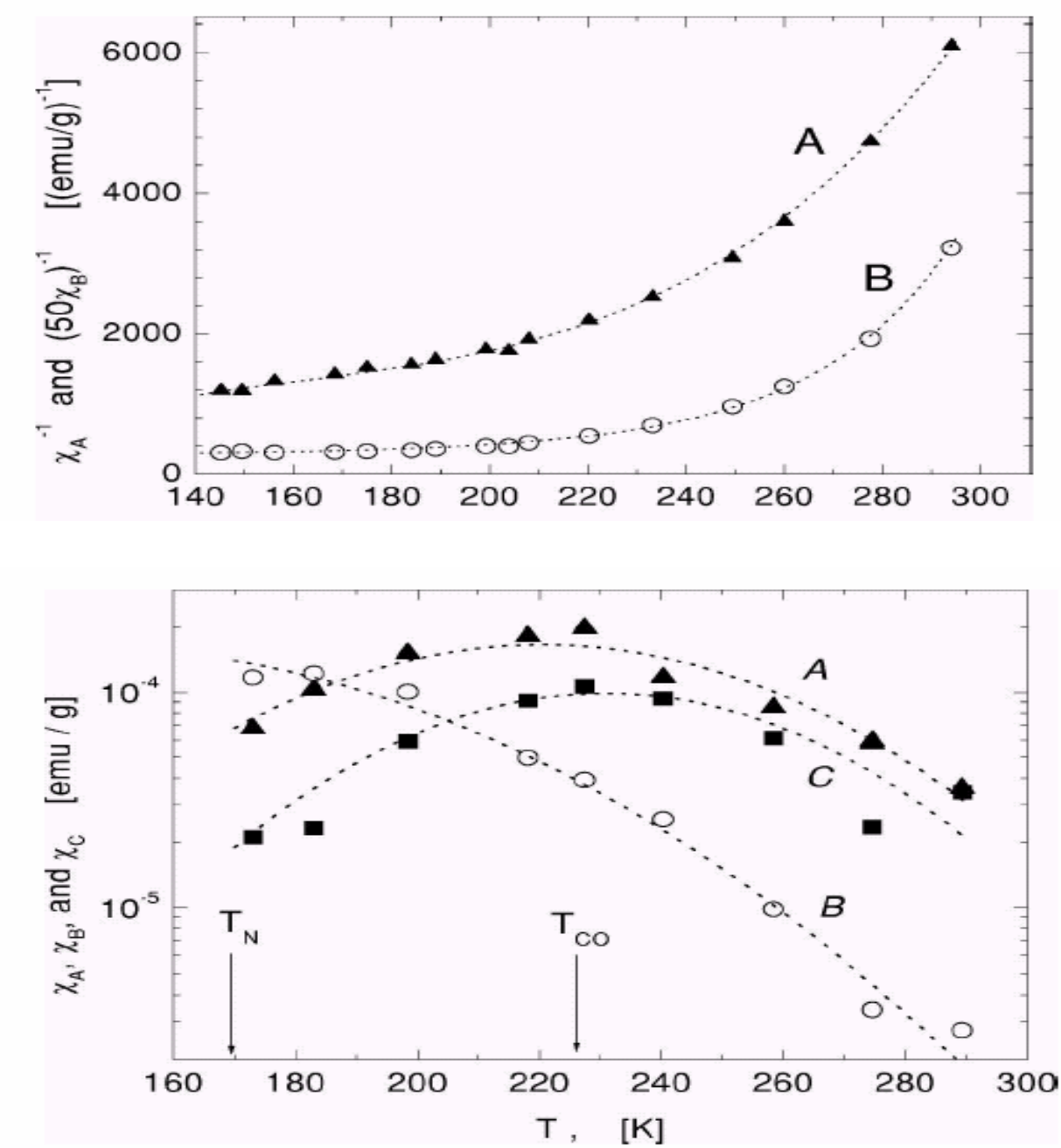
Summary of Properties

	$La_{1.2}Sr_{1.8}Mn_2O_7$	$La_1Sr_2Mn_2O_7$
Ground state	**FMM**	**AFI**
Charge order (K)	**----**	**226**
Magnetic order	**T_C = 126**	**T_N = 170 K**

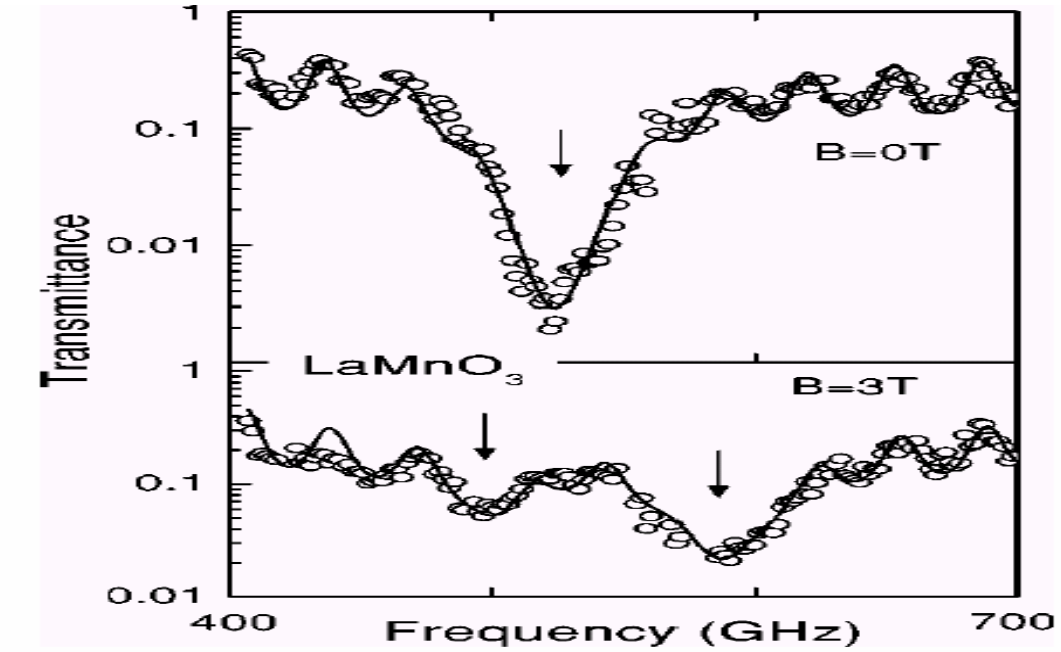
Samples:	**Single crystal platelets (floating zone)**	**0.7–0.9 mm thick**
EPR	**9.5, 75 and 150 GHz spectra and 9.5 GHz relaxation**	

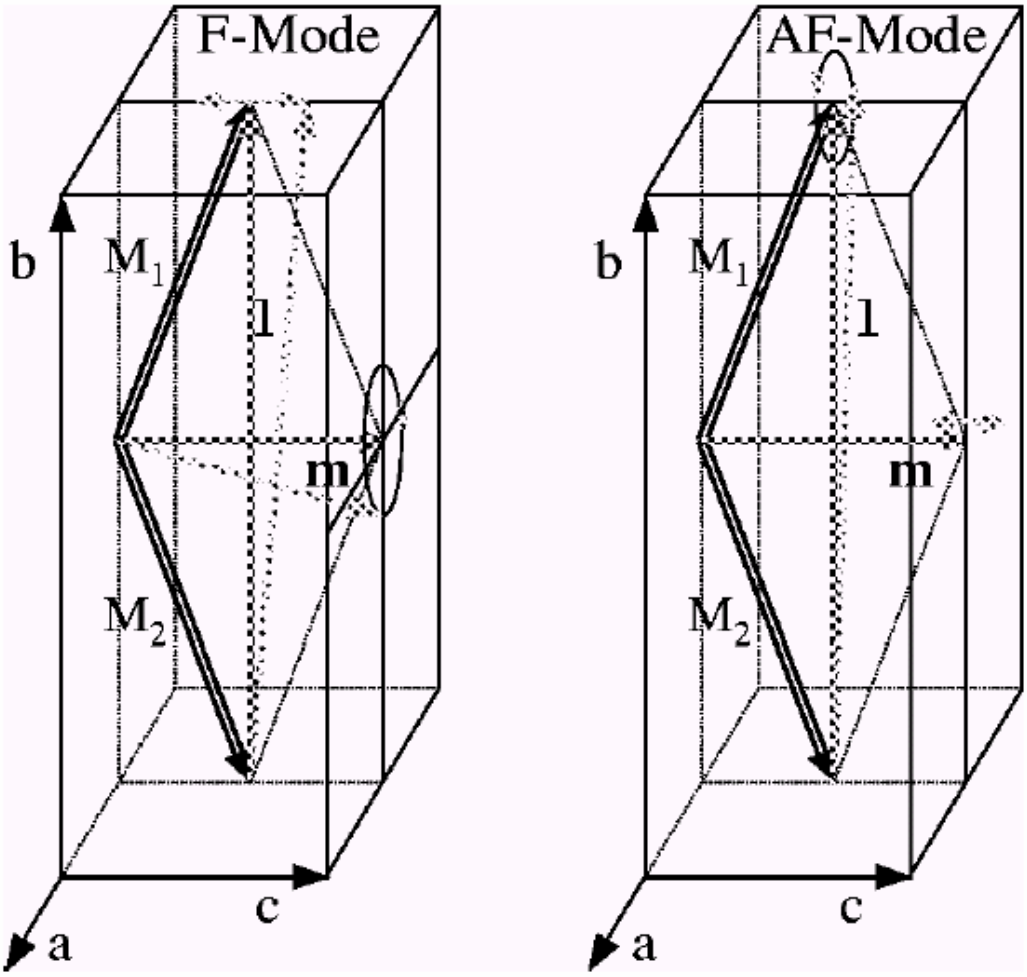
Other measurements

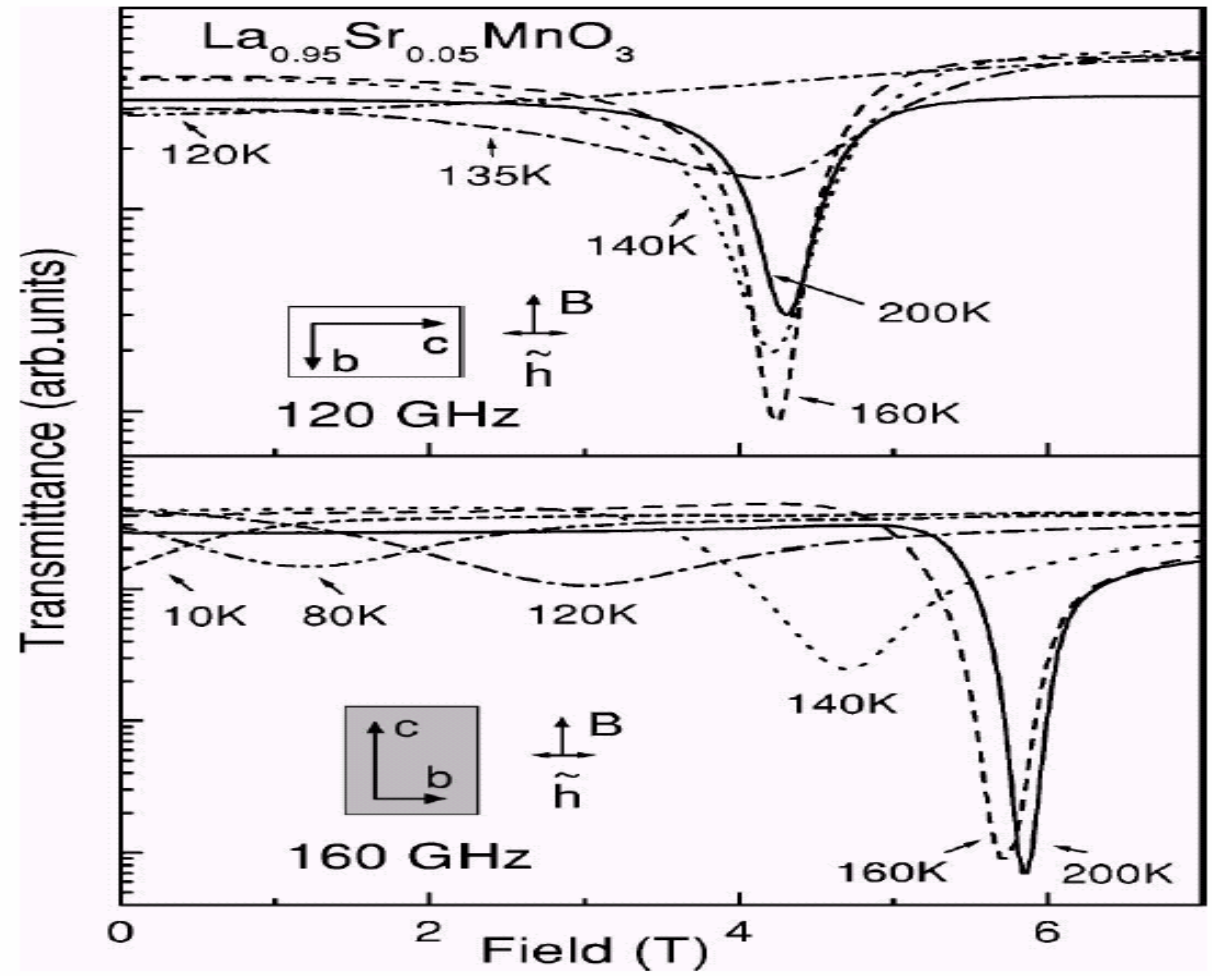
Magnetization



EPR susceptibilities for $La_{1.2}Sr_{1.8}Mn_2O_7$ (top) and $La_1Sr_2Mn_2O_7$ (bottom) as a function of temperature.


Transmittance
1
0.1
0.01
B=0T
LaMnO3
1
0.1
0.01
B=3T
400
Frequency (GHz)
700


F-Mode
b
M1
1
m
M2
c
a
AF-Mode
b
M1
1
m
M2
c
a



Above T_N @ 140 K there is a single resonance line. The FMR mode of the canted AF (lower panel) goes to a frequency of 180 GHz in zero field at low temperature.

At 120 GHz the AFMR (upper panel) is not visible at low temperature but is found at 420 GHz in zero field and low temperature.

HFEPR of spin dynamics of $La_{1-x}Sr_xMnO_3$ (x £ 0.175)

Ivannikov et al. Phys. Rev. B65(2002)214422

Summary of Properties

x	0	£ 0.1	0.1–0.15	0.15 – 0.175
Ground state	**AFI**	**canted AFMI (modulated)**	**FMI**	**FMM**
Zero field		**T_N @ 140 K**	**T_C @ 150 K**	**@ 220 K**

Samples single crystals by floating zone

(twinned except for x = 0.05)

platelets 8 x 8 x 1 mm

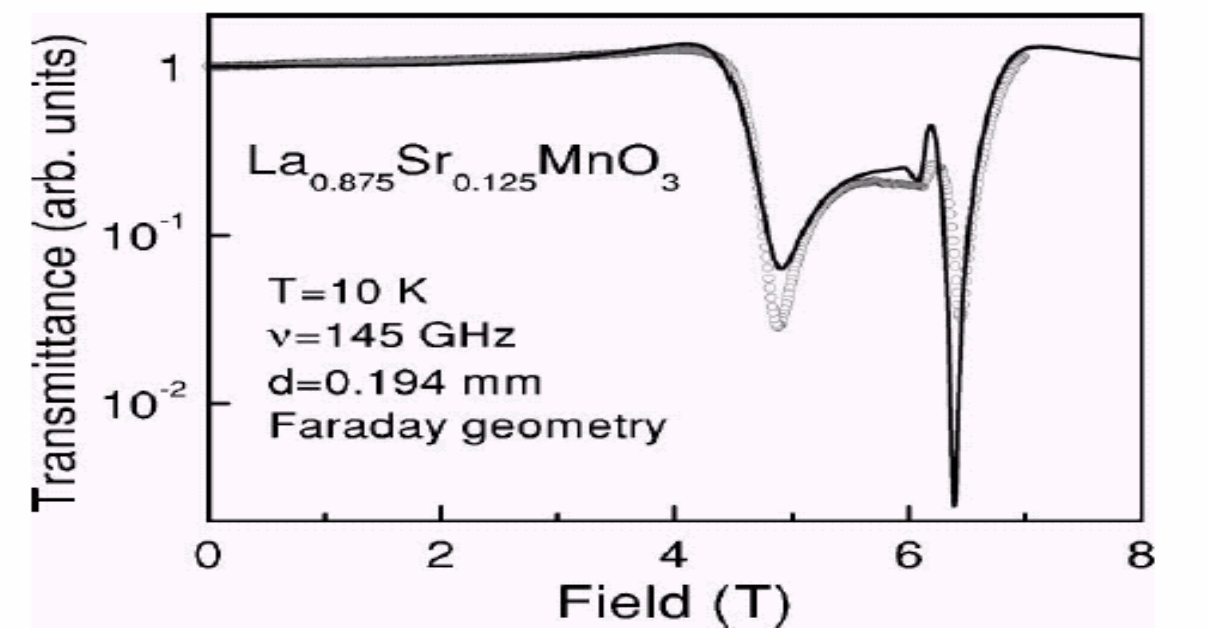
Frequency range 40 – 700 G

Transmission Frequency sweep or field sweep to 8 T

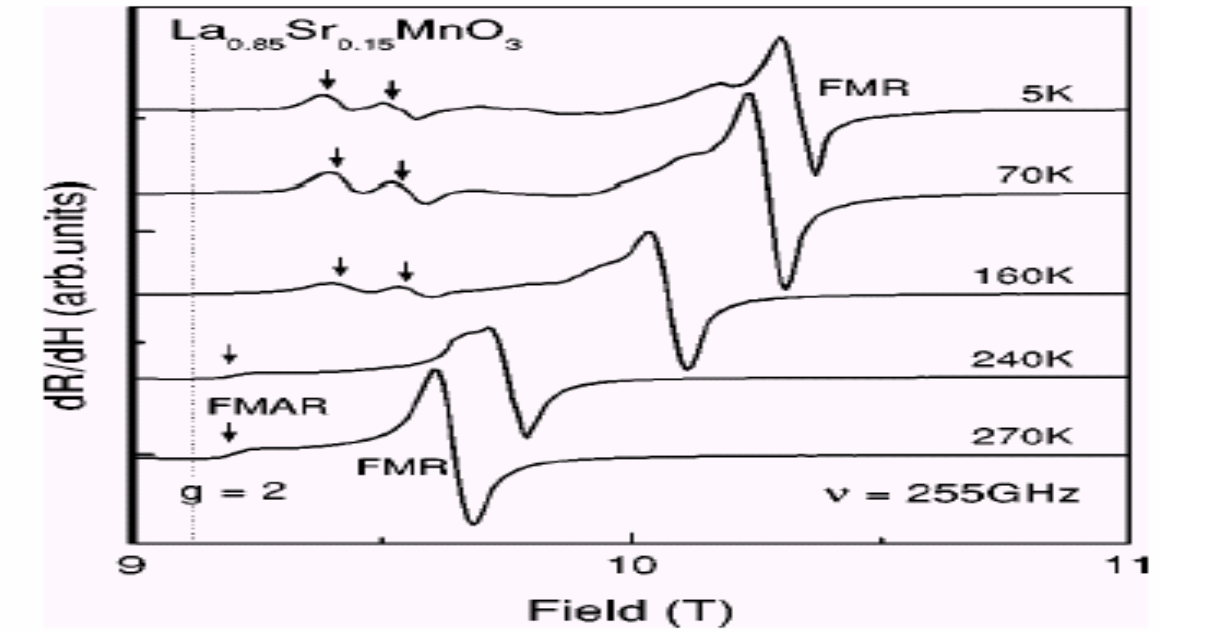
Reflection Field sweep to 16 T

Other measurements

Magnetization **Resistivity**



The FMR spectrum of a ferromagnet may be complicated by electrodynamic effects, here there is only a single resonance line. Experiment (symbols) and theory (full line).



FMR and FMAntiresonance in thick metallic sample.

Microwave absorption in a $La_{0.7}Sr_{0.3}Mn0_3$ film

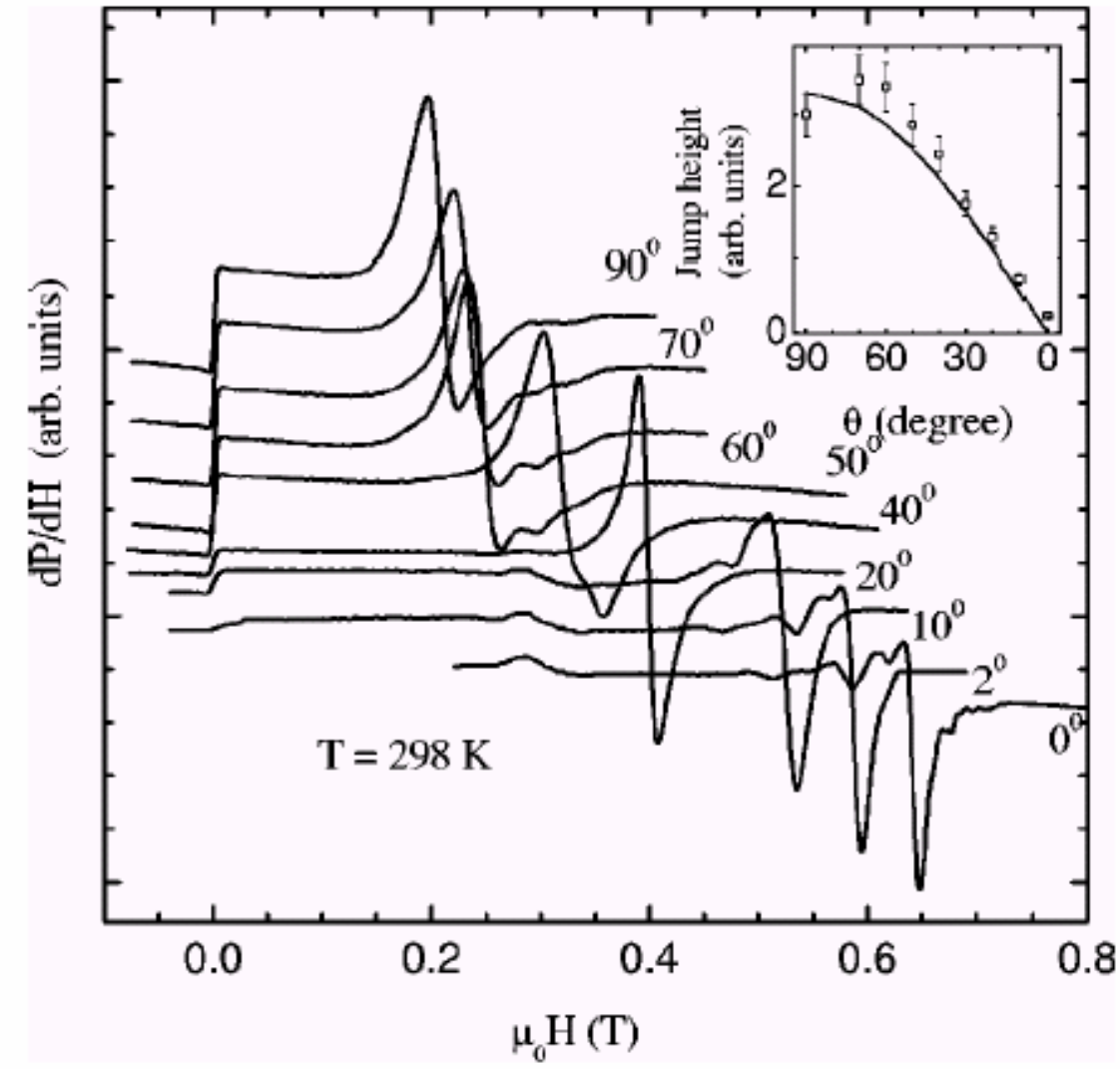
Lyfar et al. Phys. Rev. B69(2004)100409

Ground state	**FM**	**T_C @ 316 K.**
Sample	**0.3 mm thick on 0.3 mm (001) orientated $SrTiO_3$ substrate.**	
Resistance	**Maximum at 320 K**	
CMR	**20% at 310 K.**	
EPR	**9 GHz**	**(100 – 400 K)**
	Single narrow line T > T_C	
	Easy plane FM below T_C	

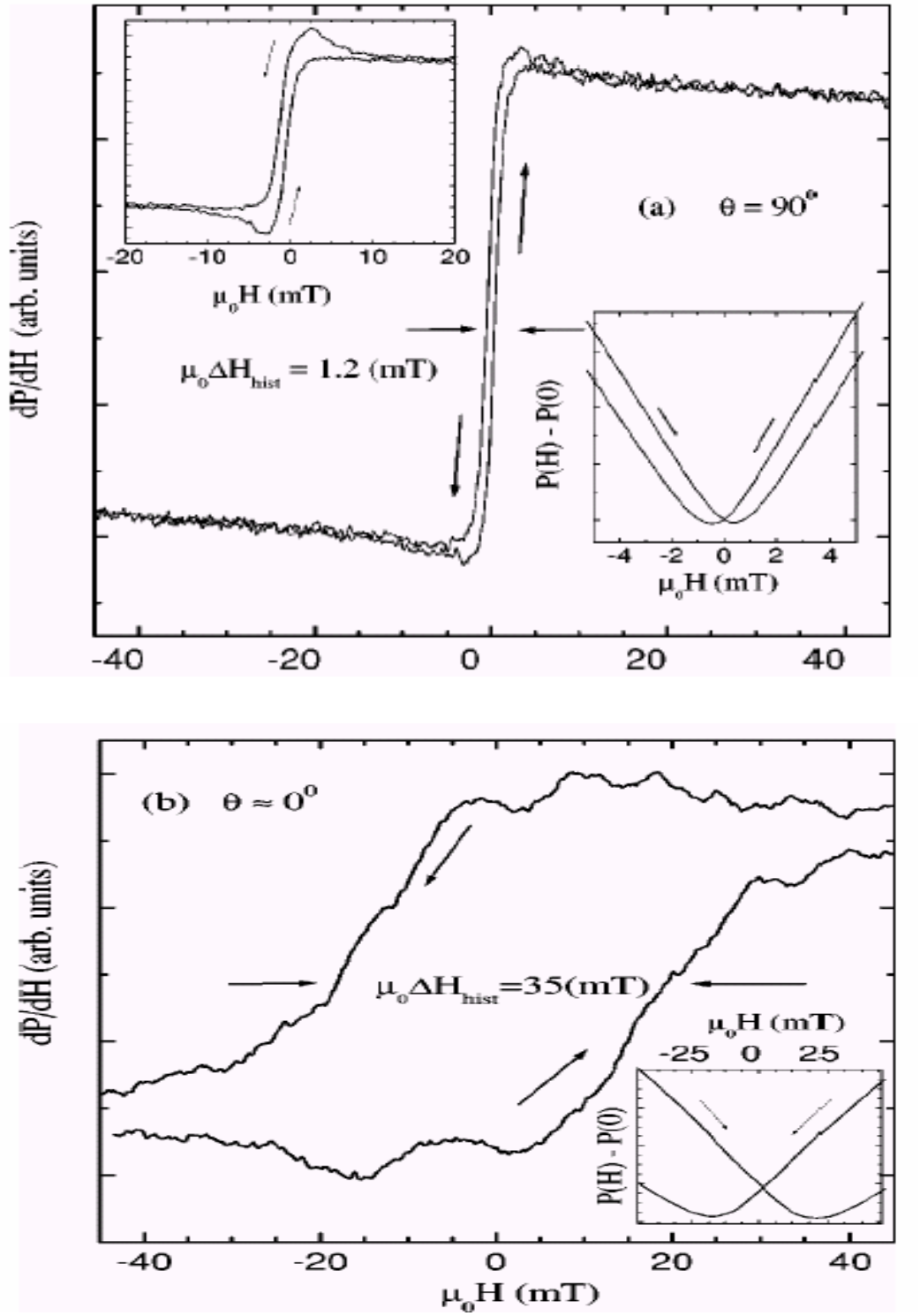
(Power also absorbed at zero field.)

Zero field signal not seen for films on $LaAlO_3$ substrates.

(The large dielectric constant of SrTiO3 leads to an induced electric field at the interface. Therefore losses related to CMR.)



FMR and jump at zero field of a $La_{0.7}Sr_{0.3}MnO_3$ on a $SrTiO_3$ substrate. N.b. q = 90 is in plane.



Jump at zero field of a $La_{0.7}Sr_{0.3}MnO_3$ film on a $SrTiO_3$ substrate. N.b. q = 90 is in plane.

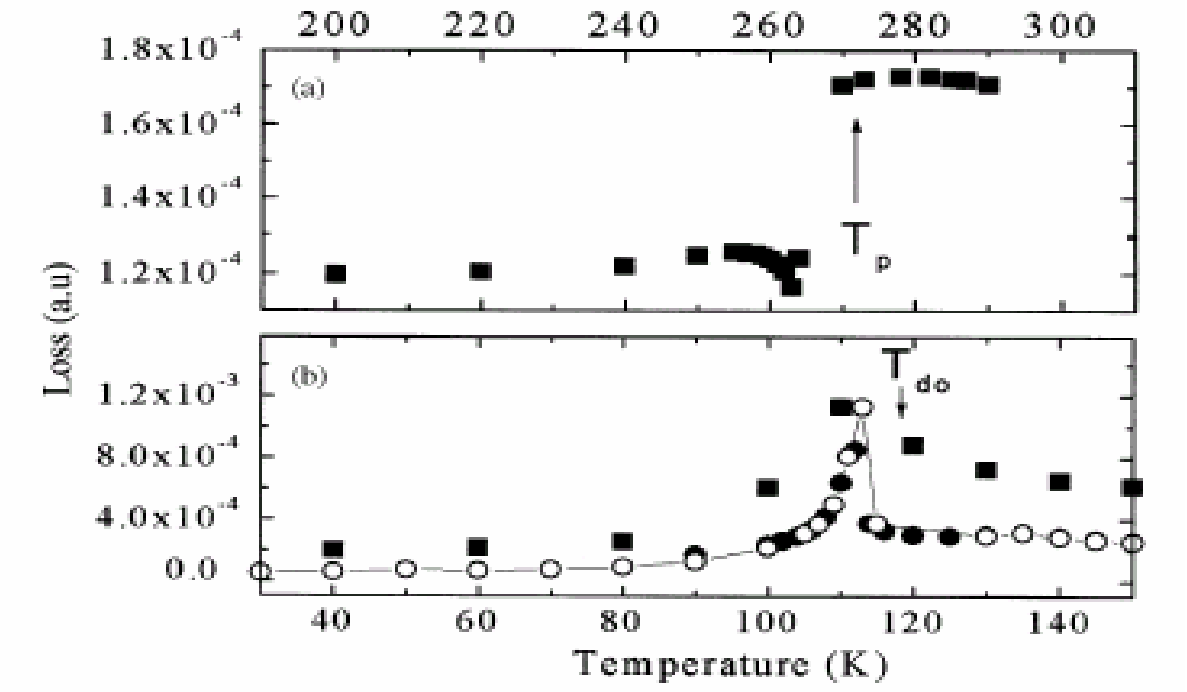
Searching for evidence of metallic cluster formation in $La_{0.9}Ca_{0.1}MnO_3$

Yates, Kapusta, Riedi, Ghilvelder, Cohen, JMMM 260(2003)105

Combination of dc resistivity, magnetization, 55Mn NMR, ac susceptibility and microwave impedance measurements of single and polycrystalline materials.

Samples are FMI at LT but NMR shows motionally narrowed peak so isolated FMM clusters

Do microwaves reveal non-percolative clusters?



Microwave loss at 9 GHz as function of T. (a)bulk sample of $La_{0.67}Ca_{0.33}MnO_3$ (bulk metal) and (b) single crystal of $La_{0.9}Ca_{0.1}MnO_3$ on warming (closed circles) and cooling (open circles) and bulk sample (squares).

Summary for $La_{0.9}Ca_{0.1}MnO_3$

(1) Dc resistivity shows material is a bulk insulator so less than 20% of material is metallic.

(2) Magnetization suggests 50+% FM.

(3) Therefore carriers not in extended states.

(3) NMR shows FM due to both super-exchange and double exchange. DE clusters of nanometre size.

(4) Microwave signal should be inverted for nm size clusters

It was proposed that the $La_{0.9}Ca_{0.1}MnO_3$ signal (only seen well below T_C) was a FMR in the anisotropy field.

$$\omega_0 = \gamma [B_K (B_K + \mu_0 M)]^{1/2}$$

Leads to reasonable B_K value of about 0.4 T at 100 K.

Much higher frequencies needed to probe nm size particles.

CONCLUSIONS

Electron resonance can provide unique information from

Field for resonance

Linewidth

Relaxation times

However need more:

resonance measurements over a wide frequency / field range

comparison of bulk and microscopic techniques on same sample

studies within skin depth of good crystals to supplement crushed samples and thin films

non-resonant microwave measurements over wide frequency range.

ACKNOWLEDGEMENTS

Dr. Graham Smith (St. Andrews):
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Professor Cz. Kapusta:
For many years of joint research and invitation to this meeting.