

# Thermoelectrics II: $\mu$ SR in Layered Manganese Oxides Chemical Pressure Effects

*Jun Sugiyama*

(Toyota Labs.)

*Jess H. Brewer*

(TRIUMF & UBC)

Eduardo J. Ansaldo

(Univ. of Saskatchewan)

Hiroshi Itahara

(Toyota Labs.)

Toshihiko Tani

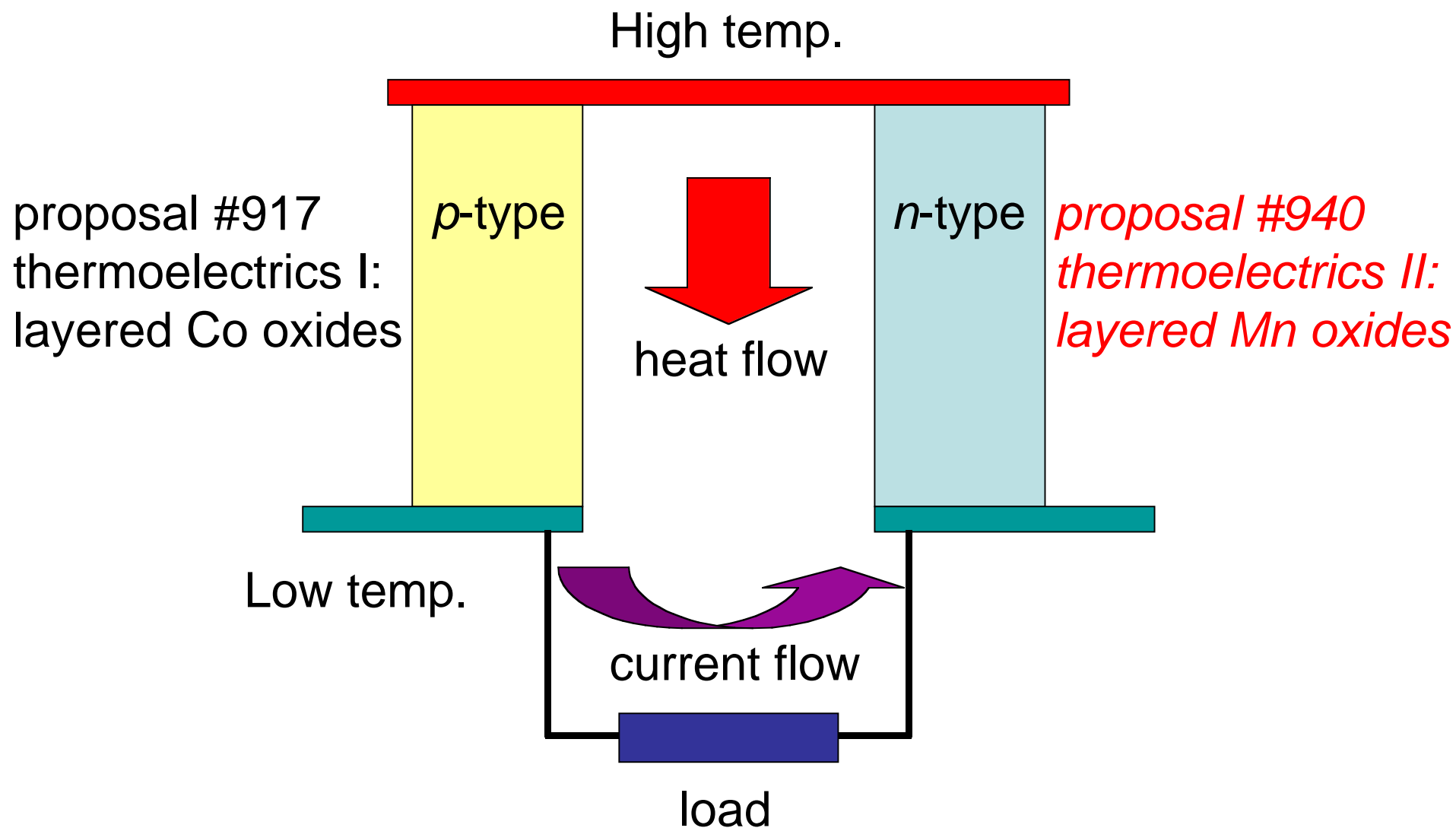
(Toyota Labs.)

Ryoji Asahi

(Toyota Labs.)

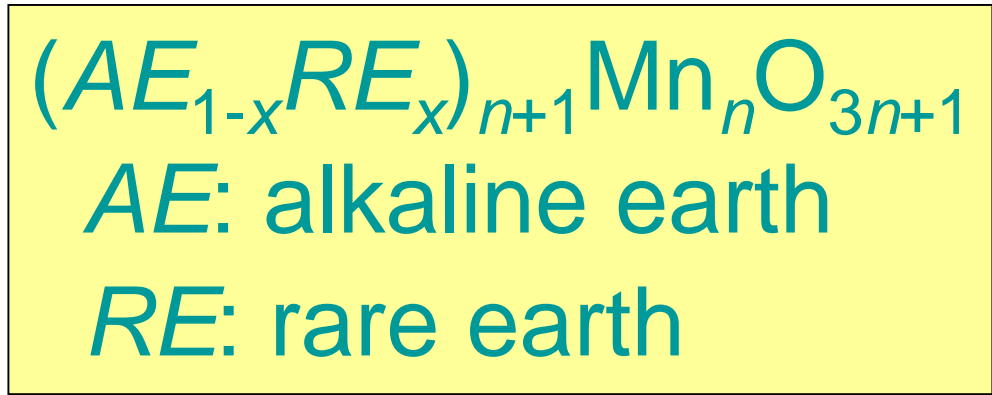
*initial request : 48 shifts on M20 or M15*

# Thermoelectric Conversion Elements

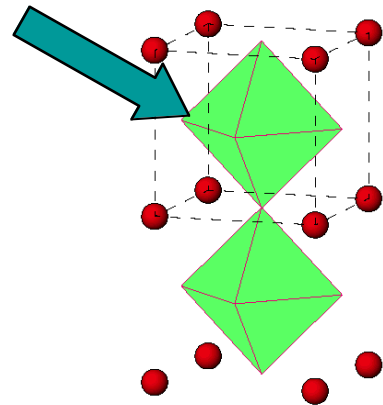


# *n*-type thermoelectrics; Ruddlesden-Popper phases of manganites

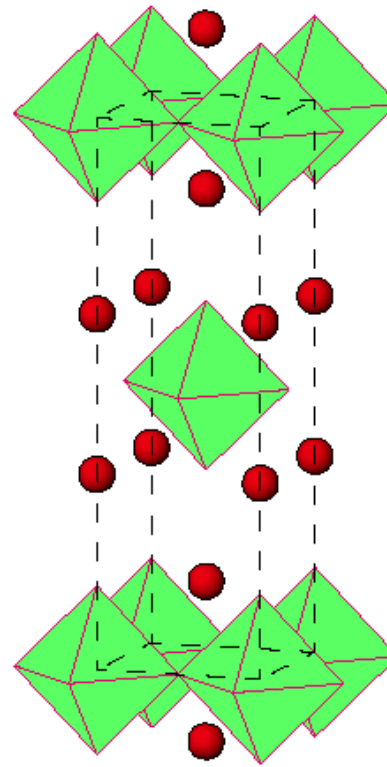
3/12



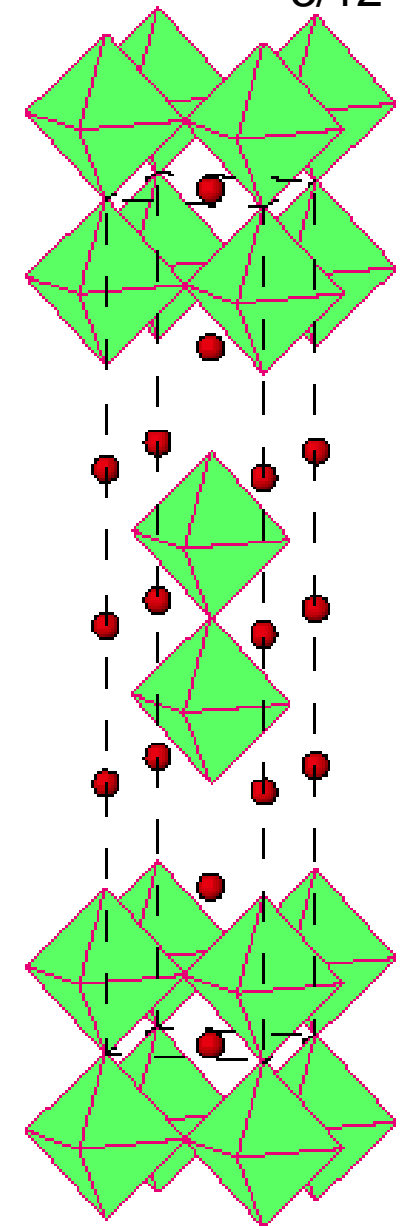
MnO<sub>6</sub> octahedra



$n=$  ;113

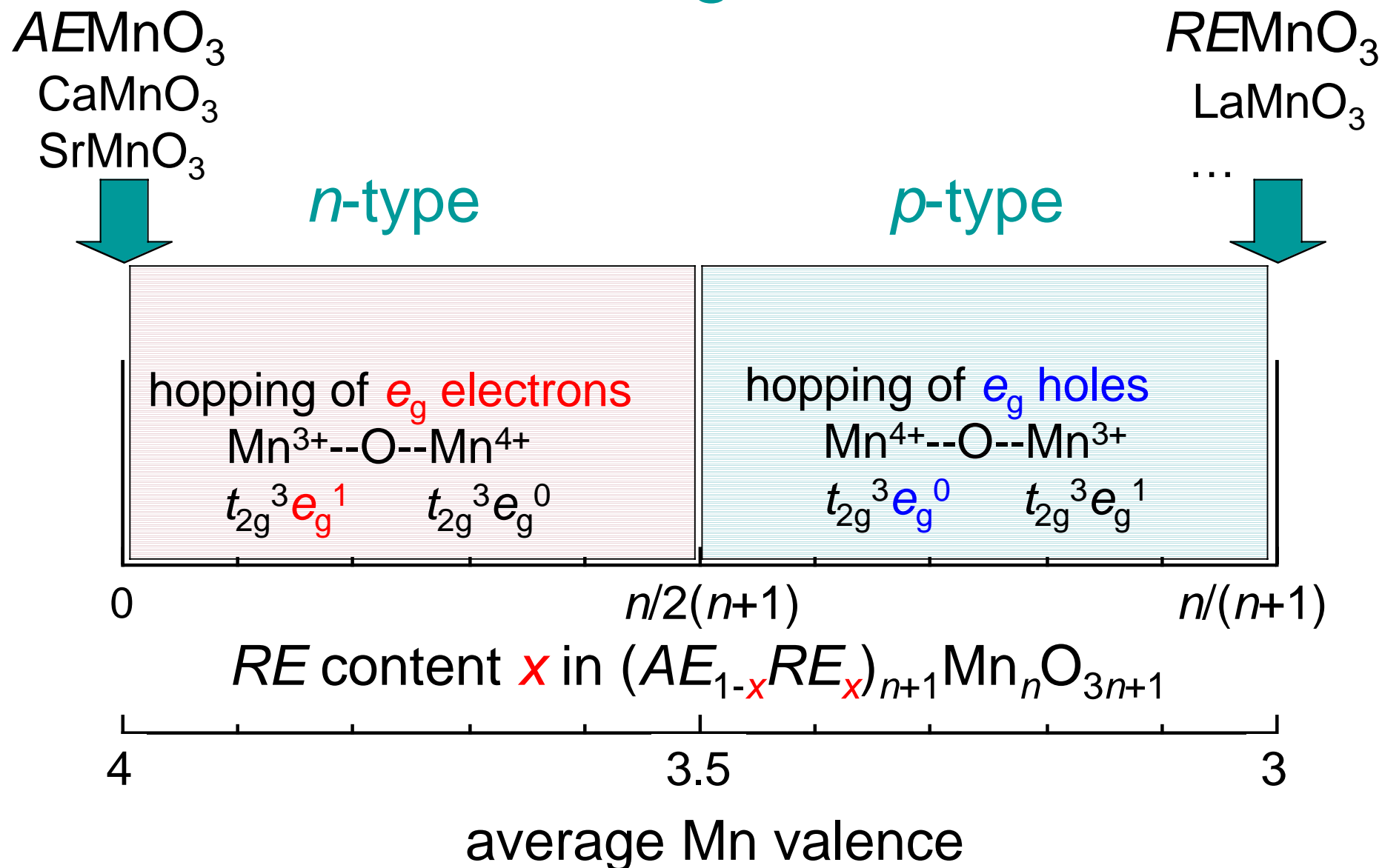


$n=1$ ;214



$n=2$ ;327

# $n$ -type & $p$ -type conductivities in manganites



# How to Apply *Chemical Pressure* to *n*-type manganites



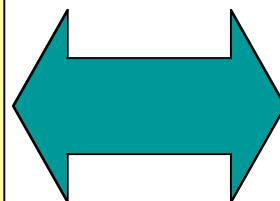
*present work*

*AE: (Sr<sub>1-y</sub>Ca<sub>y</sub>)*

*r<sub>AE</sub> (Å)*

Sr 1.31

Ca 1.18 (90%)



*previous works*

*RE: (La<sub>1-y</sub>Nd<sub>y</sub>)*

*r<sub>RE</sub> (Å)*

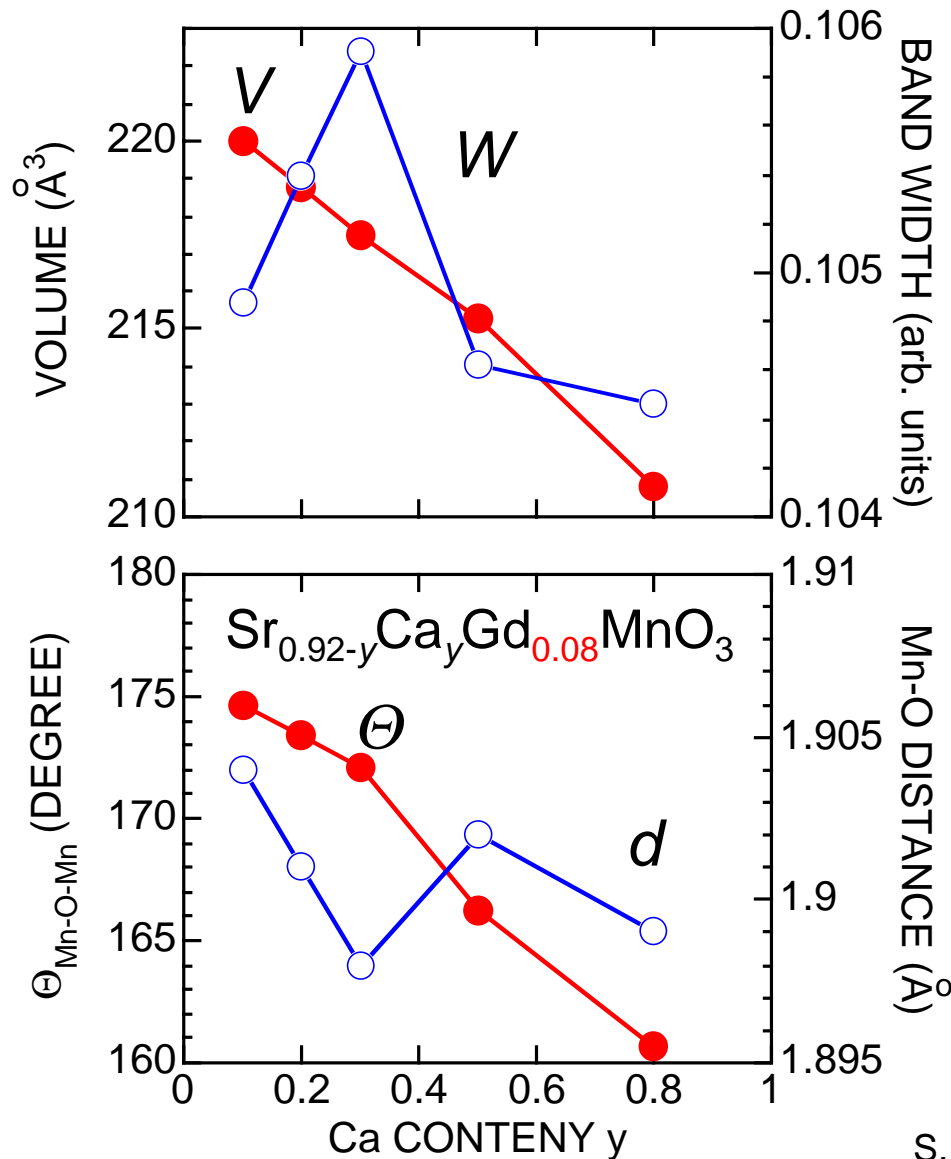
La 1.22

Lu 1.03 (84%)

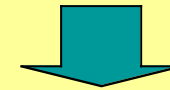
- 1) large amount of *AE* (small amount of *RE*)
- 2) no *f* electrons
- 3) stable solid solutions of Sr<sub>1-y</sub>Ca<sub>y</sub>MnO<sub>3</sub> with 0 ≤ *y* ≤ 1

# Change in Crystal Structure: Evidence of *Chemical Pressure*

6/12



As  $y$  increases;  
 a) lattice volume.  
 b)  $\Theta_{\text{Mn-O-Mn}}$   
 c) Mn-O distance decrease.

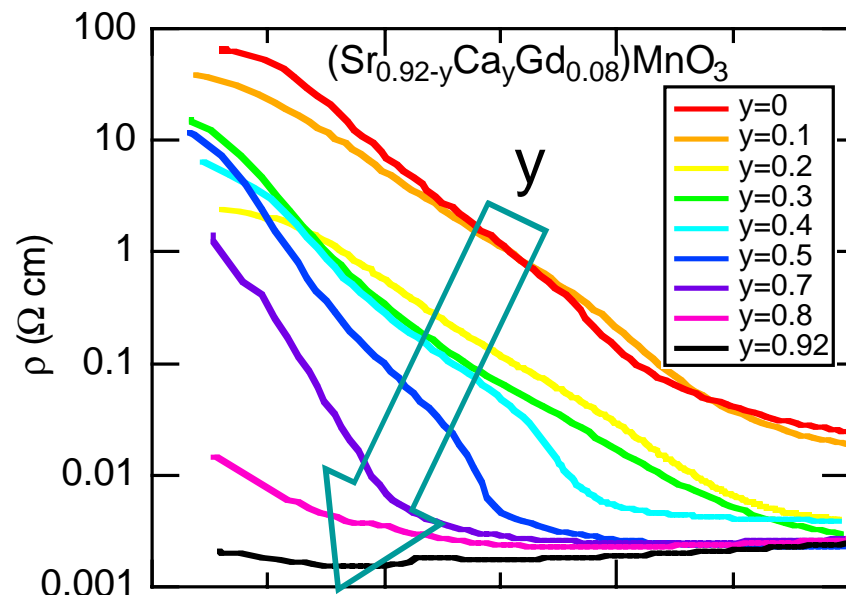


band width  $W$

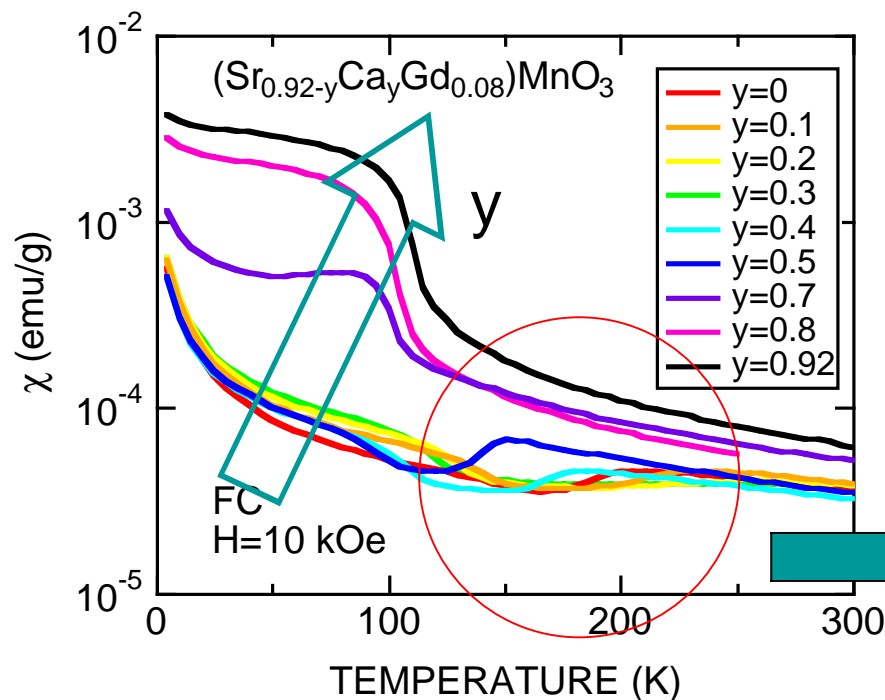
$$W \sim \cos\{(\pi - \Theta)/2\} d^{-3.5}$$

# Metal-to-Insulator Transition in

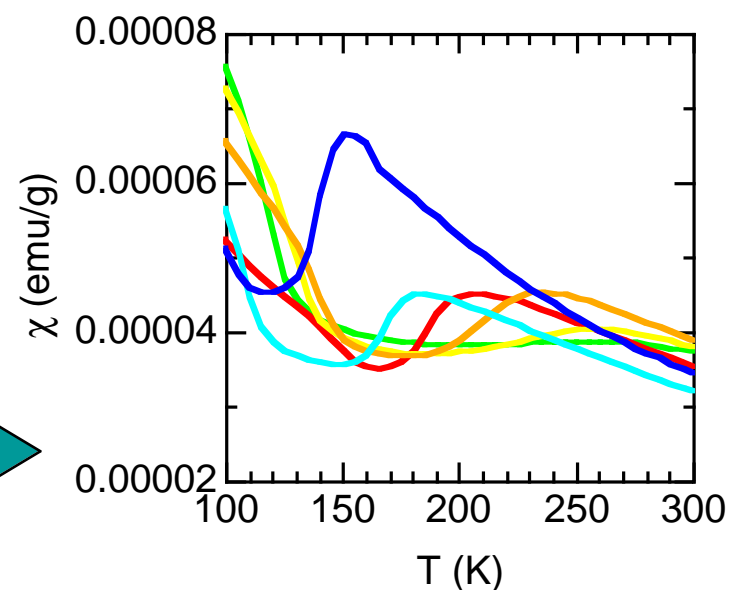
## $\text{Sr}_{0.92-y}\text{Ca}_y\text{Gd}_{0.08}\text{MnO}_3$ by *Chemical Pressure*



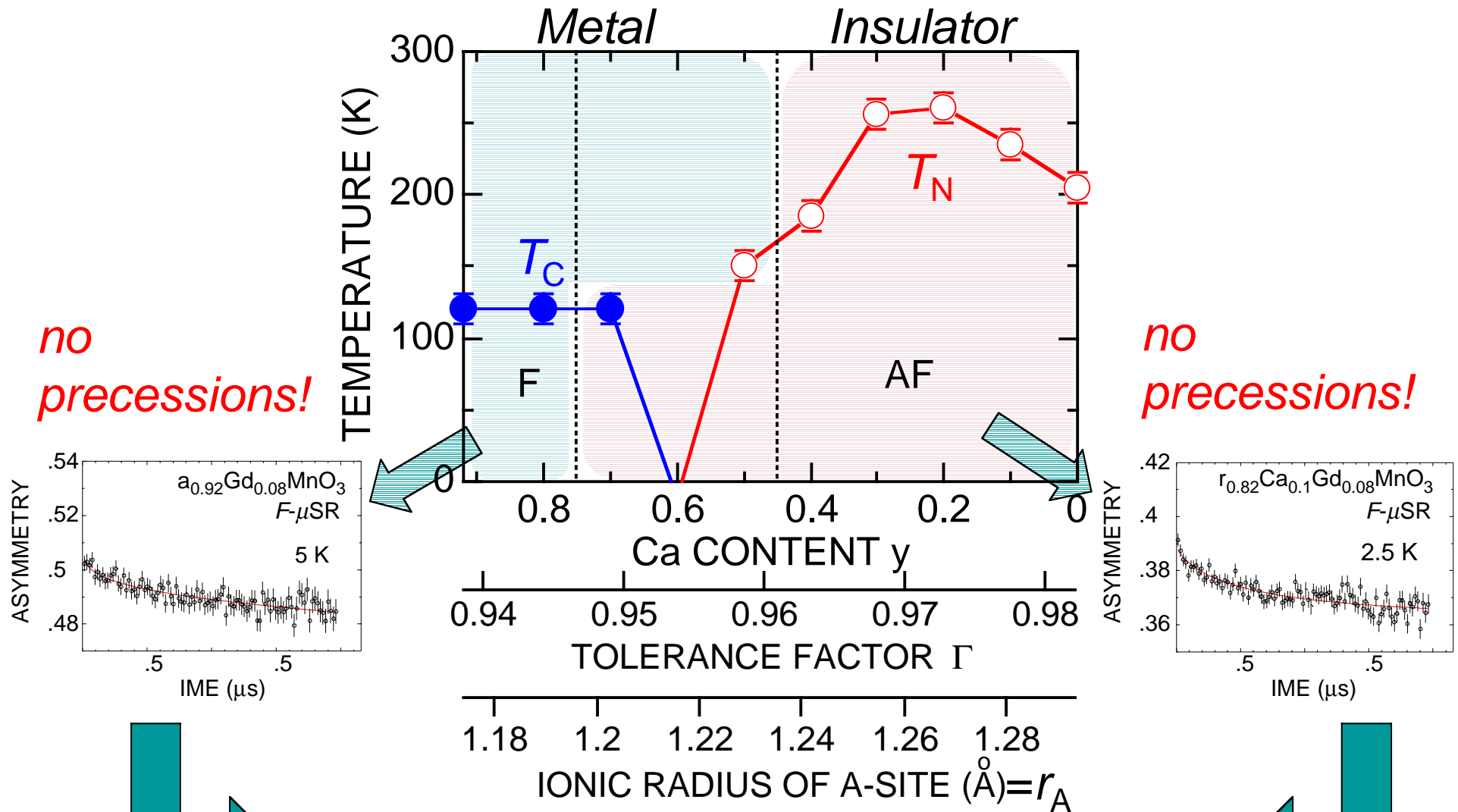
Carrier concentrations are *roughly same* for all samples.



S. Hirano and J. Sugiyama; *in preparation for publication.*



# Magnetic phase diagram & preliminary $\mu$ SR of $\text{Sr}_{0.92-y}\text{Ca}_y\text{Gd}_{0.08}\text{MnO}_3$



inhomogeneous  $H_{\text{int}}$ : phase separation ?

# Proposed Experiment

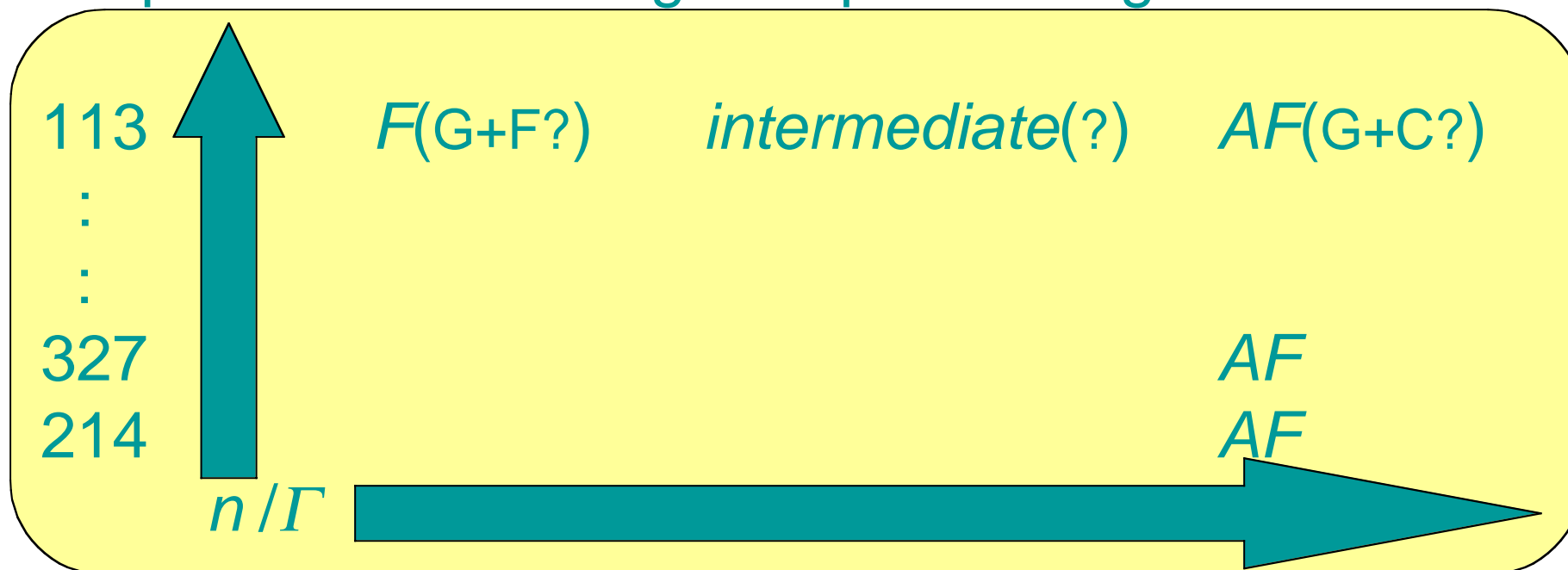
$H_{\text{int}}$  of  $((\text{Sr}_{1-y}\text{Ca}_y)_{1-x}\text{RE}_x)_{n+1}\text{Mn}_n\text{O}_{3n+1}$  as functions of;  
 temperature

$H_{\text{ext}}$

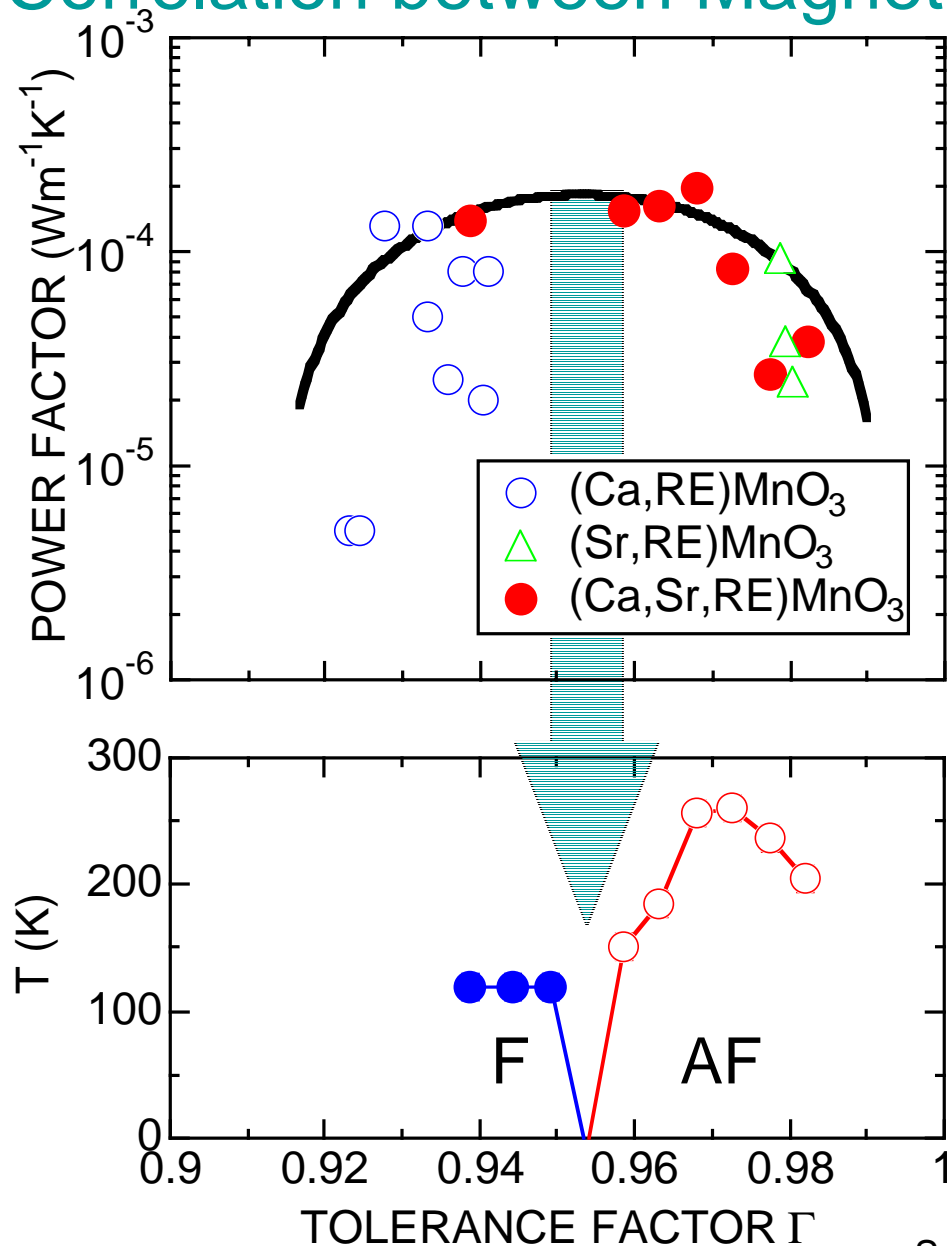
chemical pressure (tolerance factor  $\Gamma$ )

layer number  $n$

Purpose: detailed magnetic phase diagram



# Correlation between Magnetism & Transport Properties



optimal value of  $\Gamma$   
 ( $\sim 0.955$ ) for  $PF$

phase boundary  
 between AF & F

Is competition between  
 AF and F significant?

$$PF = S^2 \rho^{-1} = Z\kappa$$

S: Seebeck coefficient

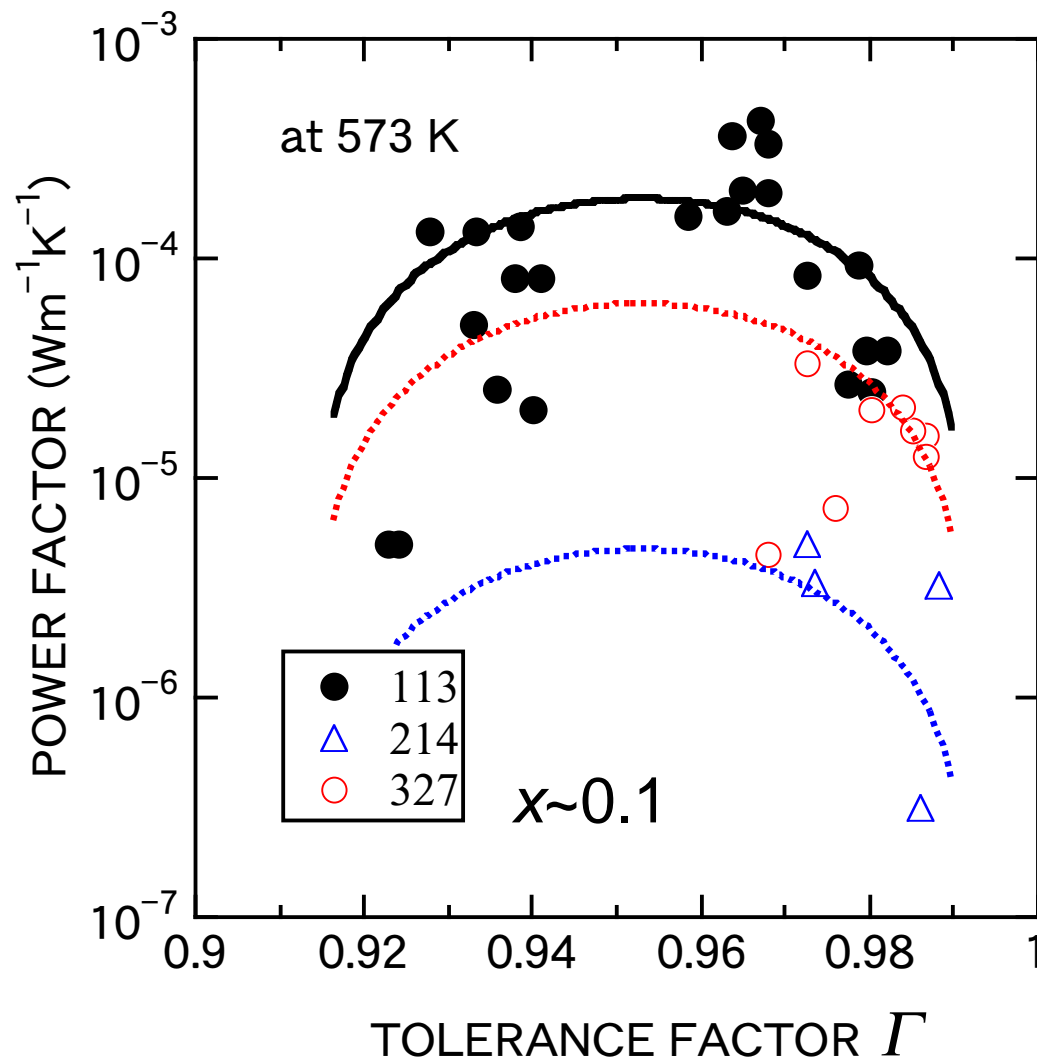
Z: thermoelectric figure of merit

$\kappa$ : thermal conductivity

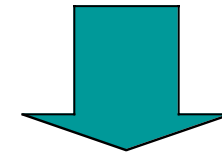
$$\Gamma = \frac{r_A + r_O}{2(r_{\text{Mn}} + r_O)}$$

# Thermoelectric Properties of $(AE_{1-x}RE_x)_{n+1}Mn_nO_{3n+1}$ with $x \sim 0.1$

11/12



Similar relationships are also observed for the  $R$ - $P$  phases of  $n=1$  & 2; 214 & 327.



*role of magnetism ?*

# Required Beam-time & Equipments <sup>12/12</sup>

**15 samples:**

5 samples of  $\text{Sr}_{1-y}\text{Ca}_y\text{Gd}_{0.08}\text{MnO}_3$  ( $0 \leq y \leq 0.92$ )

5 samples of  $(\text{Sr}_{1-y}\text{Ca}_y)_{2-x}\text{Gd}_x\text{MnO}_4$  ( $0 \leq y \leq 1, x \sim 0.1$ )

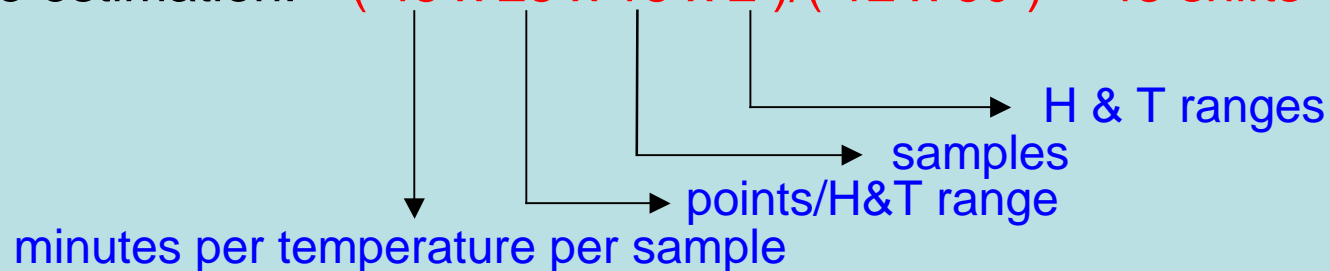
5 samples of  $(\text{Sr}_{1-y}\text{Ca}_y)_{3-2x}\text{Gd}_{2x}\text{Mn}_2\text{O}_7$  ( $0 \leq y \leq 1, x \sim 0.1$ )

temperature range:

**2.5-300 K**

beam-time estimation:

**$(45 \times 25 \times 15 \times 2) / (12 \times 60) \sim 48$  shifts**



## rough schedule

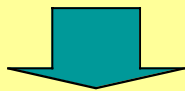
week	1st.	2nd.	3rd.	4th.
temp.	2.5-300K	2.5-300K	2.5-300K	2.5-300K
field	1mT-0.1T	1mT-0.1T	a few T	a few T
equipment	cryostat	cryostat	cryostat	cryostat
spectrometer	Omni, Omni' or LAMPF		Helios or DR	
measurement	ZF/TF/LF	ZF/TF/LF	ZF/TF/LF	ZF/TF/LF
channel	M15/M20	M15/M20	M15	M15

# High-temperature Transport Properties

How to control “*chemical pressure*” for improving thermoelectric properties?



*substitution of Sr by Ca*  
changes in crystal structure;  
distance between Mn ions  
angel of Mn-O-Mn bonds



S are similar, but  $\rho$  different



*change in mobility*

