Transition metal perovskites

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Outline:

Prospective in thermoelectrics- stability at high temperatures, possibility to enhance the thermoelectric power by means of the spin degree of freedom , depression of thermal conductivity - “disorder or fluctuations (spin,orbital)”

Introduction

- Electrical conductivity, Charge transfer vs Mot Hubbard insulator
-Thermoelectric power, electron transport, thermoelectricity

Thermoelectric phenomenology

Electrical and thermal transport , magnetism from 4 K up to 300 K(λ),800 K(χ,**M**),1200 K (***S***,ρ)

MATERIALS

Mn^{3+}/Mn^{4+} perovskites: ferromagnetic double-exchange ⇔ degenerate carriers vs. antiferromagnetic super-exchange ⇔ orbitaly polarized, insulating charge ordered electronic states.

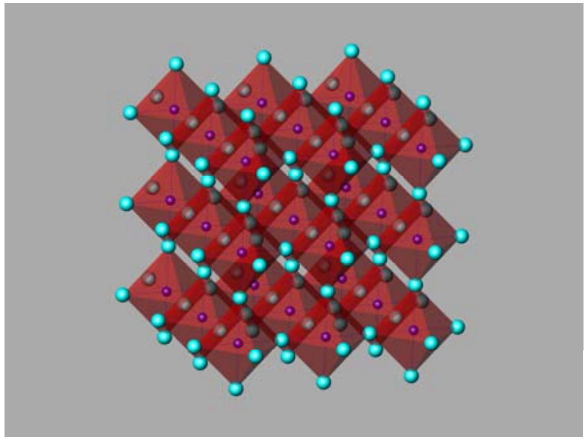
Co^{3+}/Co^{4+} perovskites : the minute energy difference between the low-spin ground-state (filled t_{2g}) vs magnetic one (active e_g states) ⇔the origin of “exotic” charge carriers and thermal properties

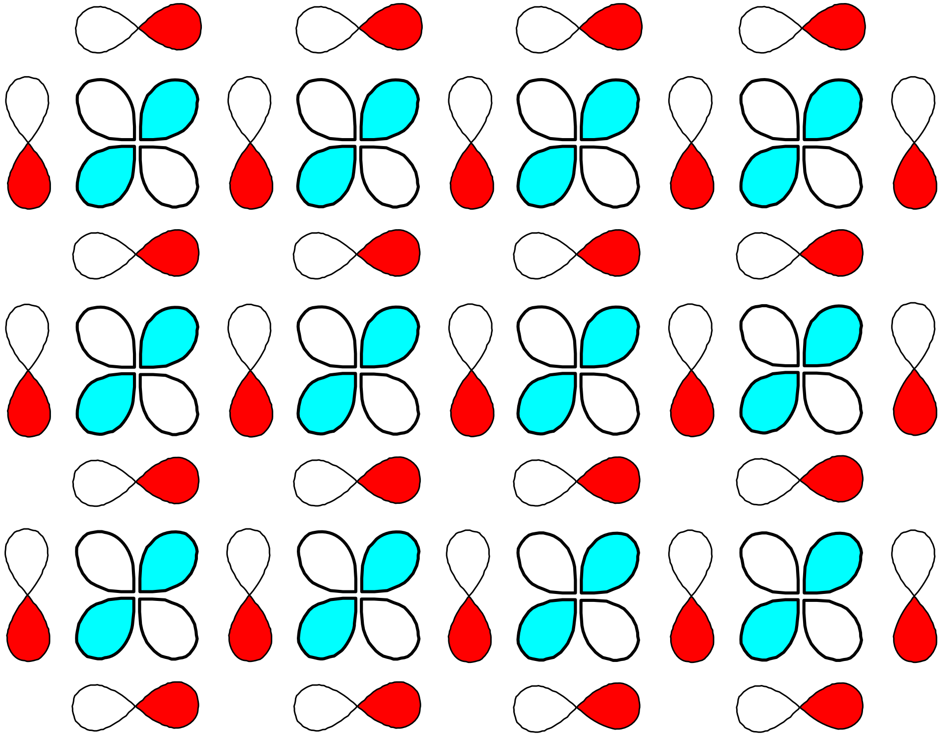
Cr^{3+}/Cr^{4+} (t_{2g}) and Fe^{3+}/Fe^{4+} (e_g) perovskites with identical concentration of both species documented;
chromite represents likely a unique example of material with a pronounced role of orbital entropy in the thermopower.

Ferromagnetic $SrRuO_3$ has a high positive thermoelectric power and low thermal conductivity ⇔a close link between the thermal and electron transport and magnetism; published results of the thermoelectric power of isoelectronic $SrFeO_3$ and $SrRuO_3$ are confronted. The role of charge compensation effect due to Na^{1+} for Sr^{2+} substitution is probed on solid solutions $Sr_{1-x}Na_xRuO_3$ ($x = 0.0 – 0.25$) is documented.

As a novelty one of the most conducting perovskite $SrMoO_3$ in connection with nitridation ($SrMoO_2N$) is also mentioned.

Orbital Overlap in the t_{2g} Band

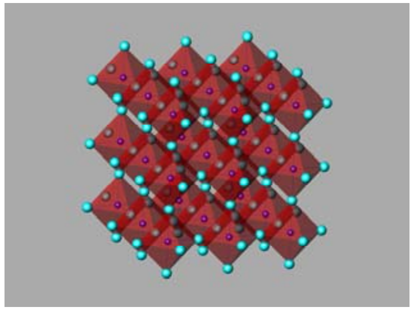


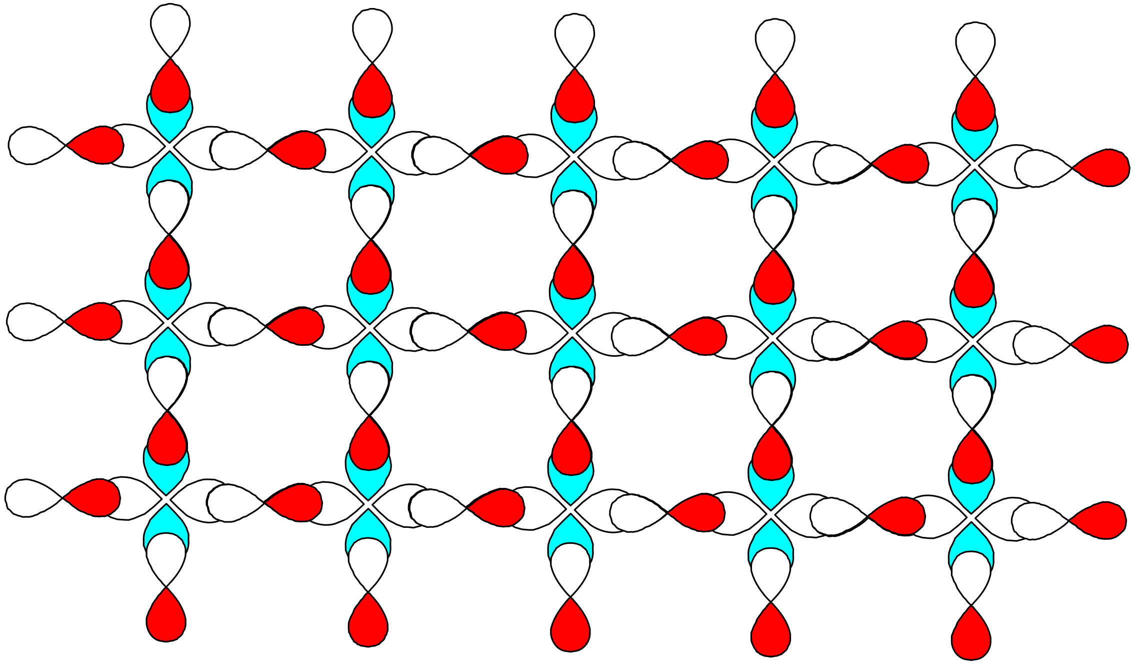


Γ point ($k_x=k_y=k_z=0$)

π bonding in MO_6 framework

Orbital Overlap in the e_g Band

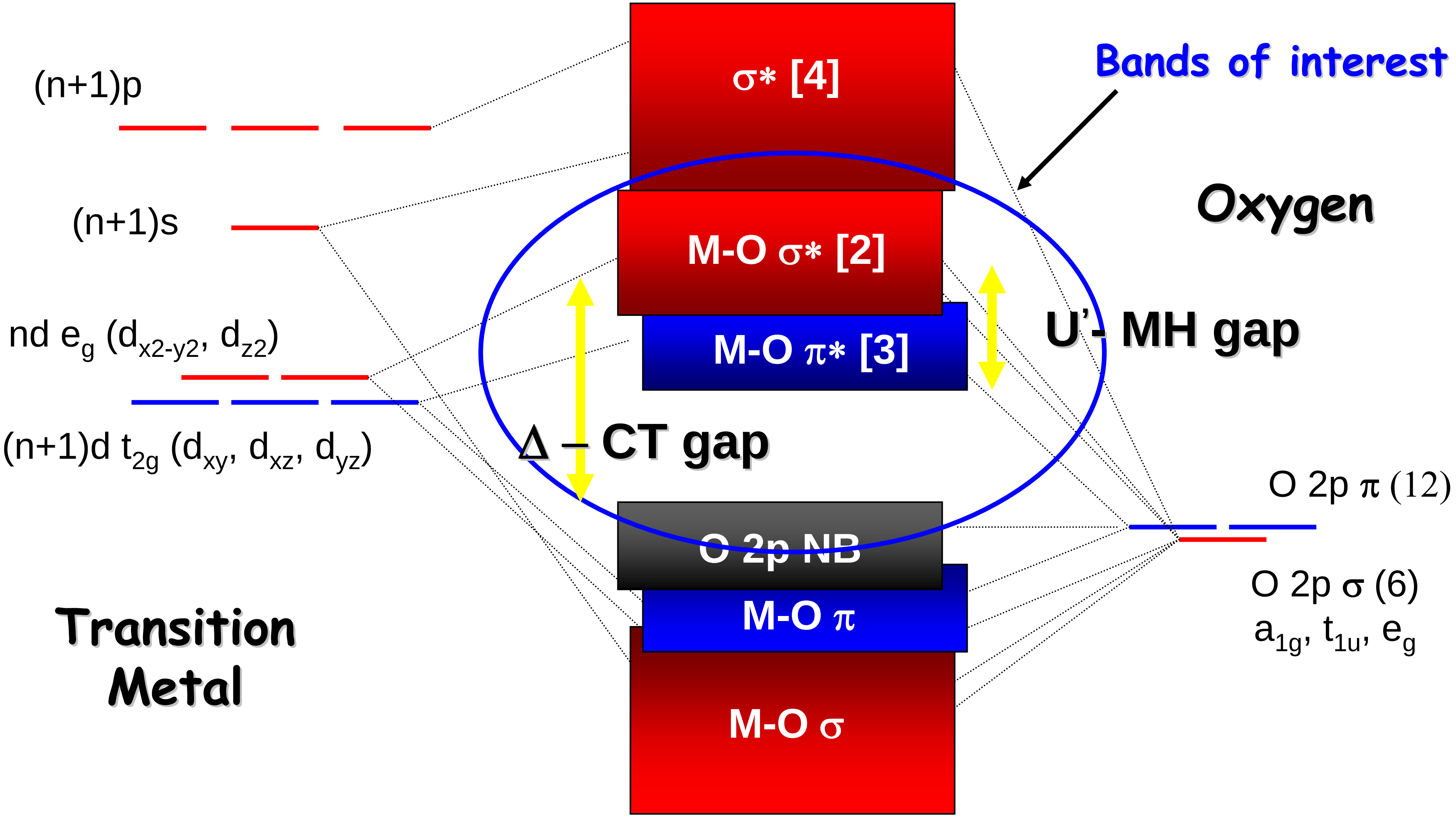




Γ point ($k_x=k_y=k_z=0$)

σ bonding in MO_6 framework

Key features of band structure of perovskites



Simple Band Structure

Key features of band structure of perovskites

- Considerations⇔energy is gained (lowered, system is stabilized) via hybridization between occupied and empty orbitals with same symmetry⇔AFM or FM interaction inferred

- **e_g - e_g hybridization is stronger than t_{2g} - t_{2g} hybridization because of greater overlap.**

- Simple projection in Superexchange and Double-exchange

Spin polarized Energy Diagram

Figure of merit – Thermoelectric parameters

$$\boxed{ZT = \frac{\alpha^2 \sigma}{\kappa} T}$$

$$\kappa = \kappa_e + \kappa_{ph}$$

Minimize κ_{ph}: usual strategies apply olso to oxides

Wiedemann-Franz law valid :

$$\kappa_e = \underbrace{\frac{\pi^2 k^2}{3e^2}}_{L_0} \times \sigma T$$

J. Hejtmanek et. al, Phys. Rev B, 66, (2002) 014426

Large α-values required

semiconductor doped oxides (high T)

or

highly correlated metallic oxides

Thermal Conductivity of Solids

- **Solids transmit thermal energy by three modes**

– Elastic vibrations of the lattice moving through the crystal in the form of waves

– Free electrons moving through the lattice carry energy similar to the case in gasses

– Magnetic excitations can also carry heat by a similar way as phonons

$$\lambda_{\text{total}} = \lambda_{\mathbf{phon}} + \lambda_{\text{e}} + \lambda_{\text{mag}}$$

Respective thermal conductivity:

$$\lambda = \frac{1}{3}\underset{\substack{\uparrow \\ \text{Specific heat}}}{C}\underset{\substack{\uparrow \\ \text{Velocity}}}{v}\underset{\substack{\nwarrow \\ \text{Mean free path}}}{\ell}$$

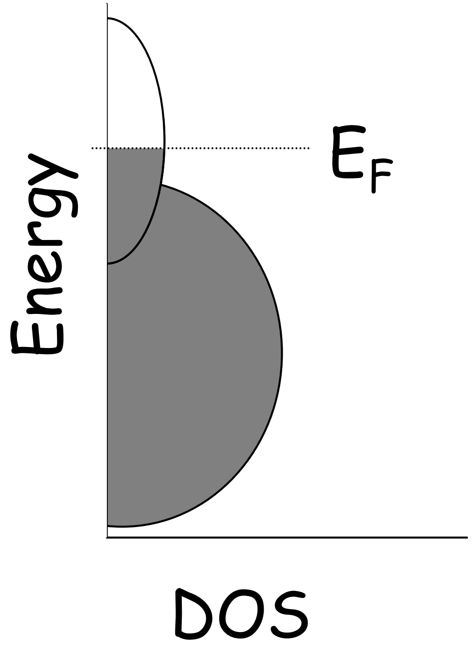
Thermopower in metals

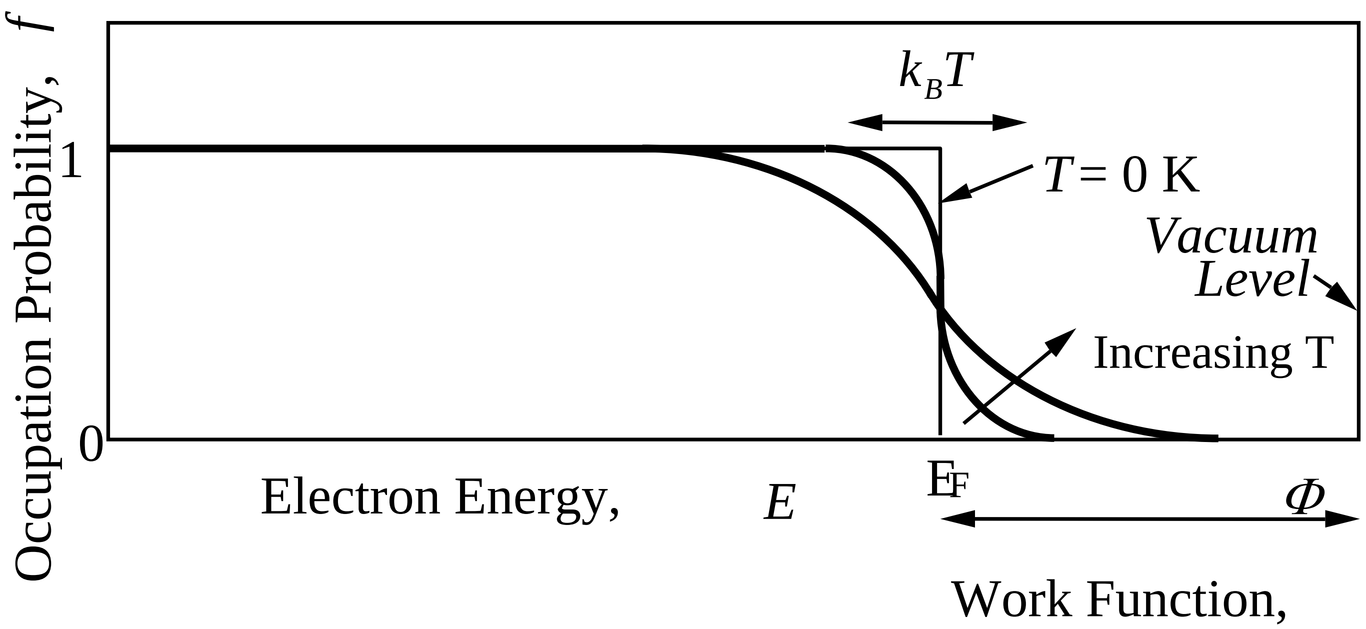
(Band Structure View Point)

Key role of Fermi-Dirac equilibrium distribution
for the probability of electron occupation of energy level *E* at temperature *T*

$$f(E) = \frac{1}{1 + \exp\left(\dfrac{E - E_F}{k_B T}\right)}$$

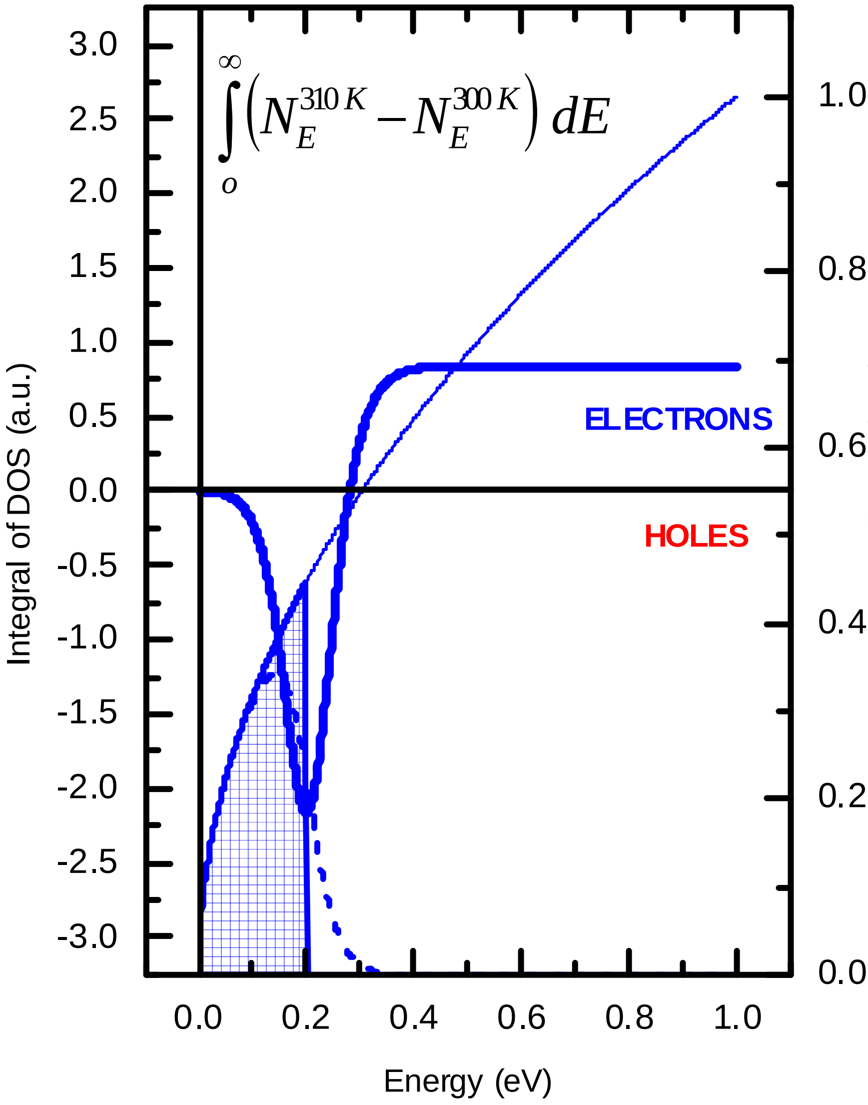
Effect of Temperature

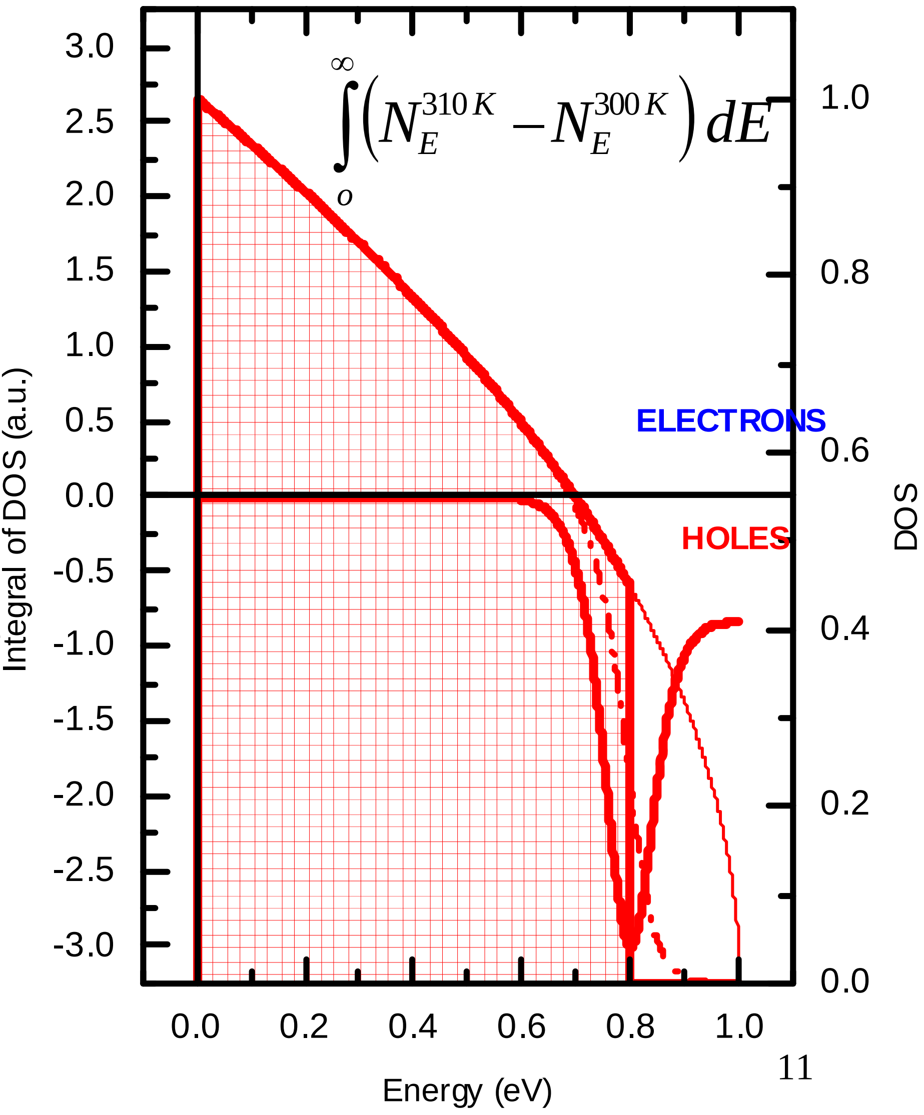




Thermopower in metals

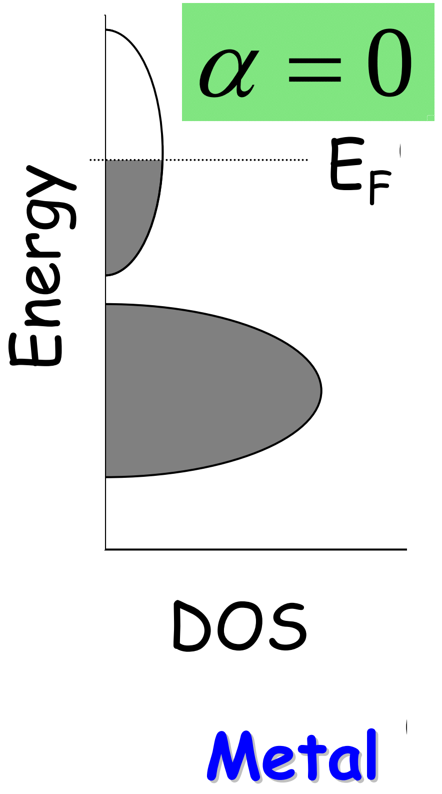
(Band Structure View Point)

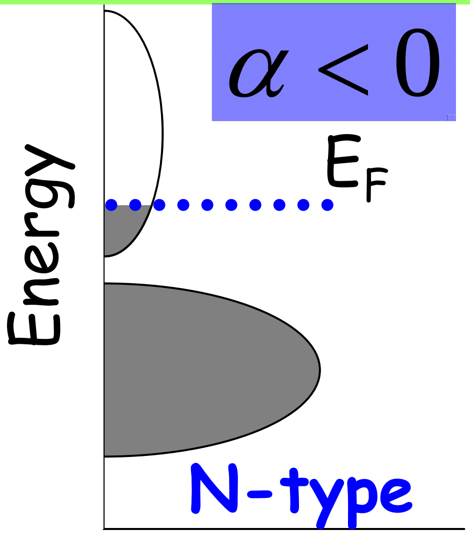


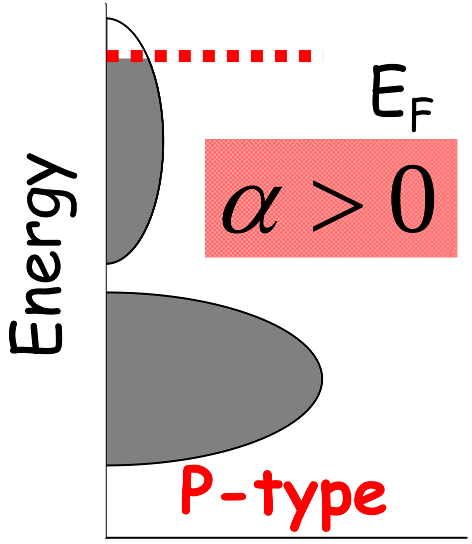


Thermopower in metals (Band Structure View Point)

$$D_e(E) = \frac{m}{\hbar^2\pi^2}\sqrt{\frac{2mE}{\hbar^2}}$$ in 3D







Thermopower:

- From energy dependent conductivity.
- Mott formula:

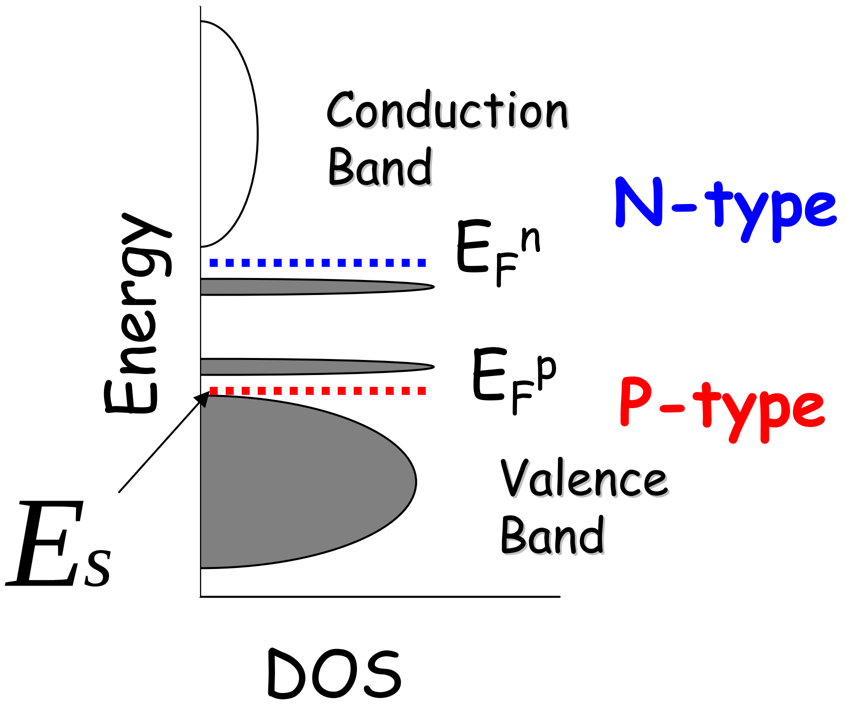
$$s = \left(\frac{\pi^2 k_B^2 T}{3e\sigma}\right)\frac{\partial\sigma}{\partial E}\Big|_{E=E_F}$$

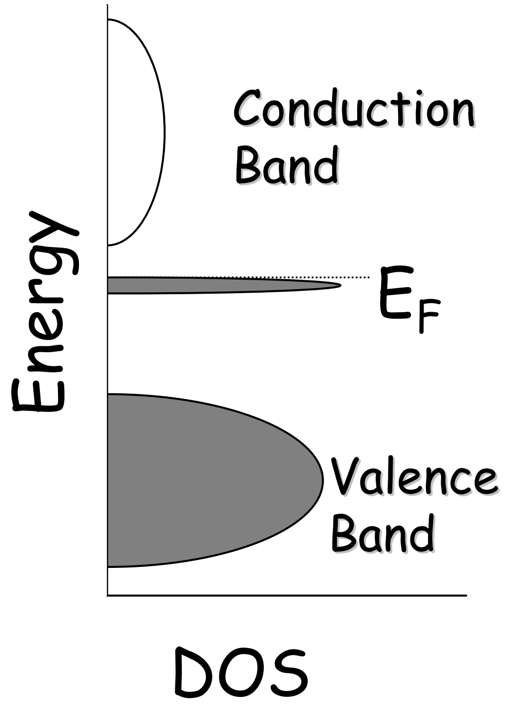
- Note log derivative (not an extensive quantity – multiplicative factors in density of states (specific heat, entropy) or in σ do not change *S*.

Density of States

-- Number of electron states available between energy *E* and *E+dE*

Thermopower in non-metals





Band gap Semiconductor

Hopping semiconductor
HEIKS (~1960)

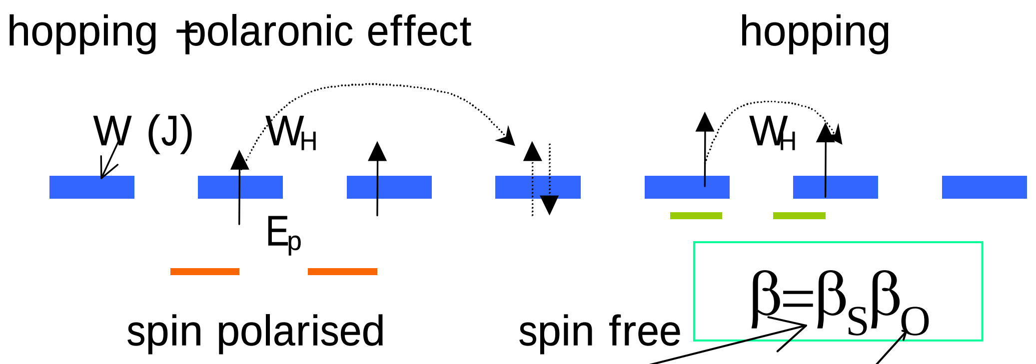
$$S_d = \frac{k_B}{e}\left(\frac{E_s}{k_B}T + B\right)$$

$$S_d = \frac{k_B}{e}\ln\left(\beta_s\beta_o\left\{\frac{1-\frac{n}{N}}{\frac{n}{N}}\right\}\right)$$

- ***B is configurational entropy ter***

Thermopower for hopping charge carriers

(localised picture)
hopping of charge carriers



Formulae

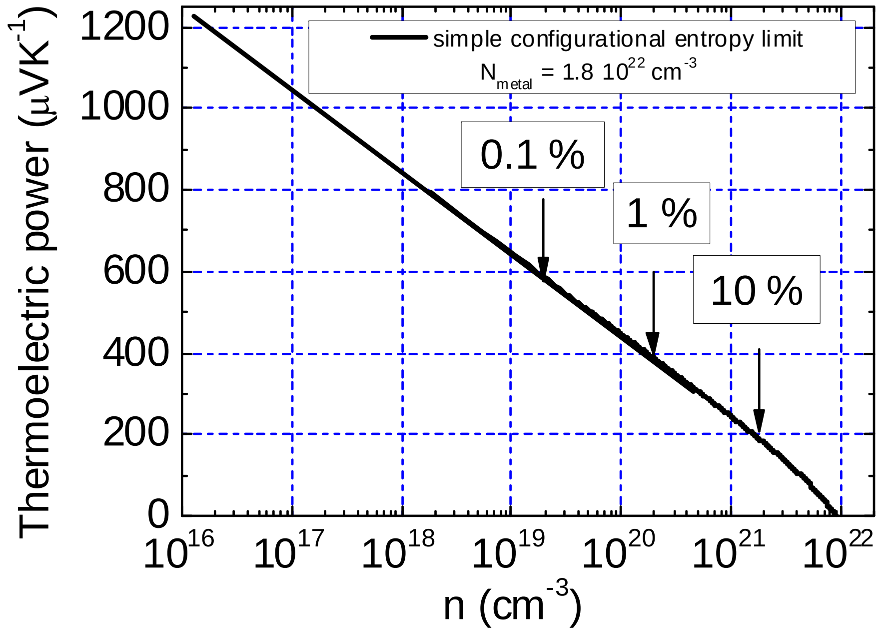
entropy

$$S = -\frac{1}{|e|}\frac{\partial \Sigma}{\partial n}$$

$$\beta = \beta_S \beta_O$$

Spin degeneracy

Orbital degeneracy e_g



$La_{1-x}A_xCoO_3$

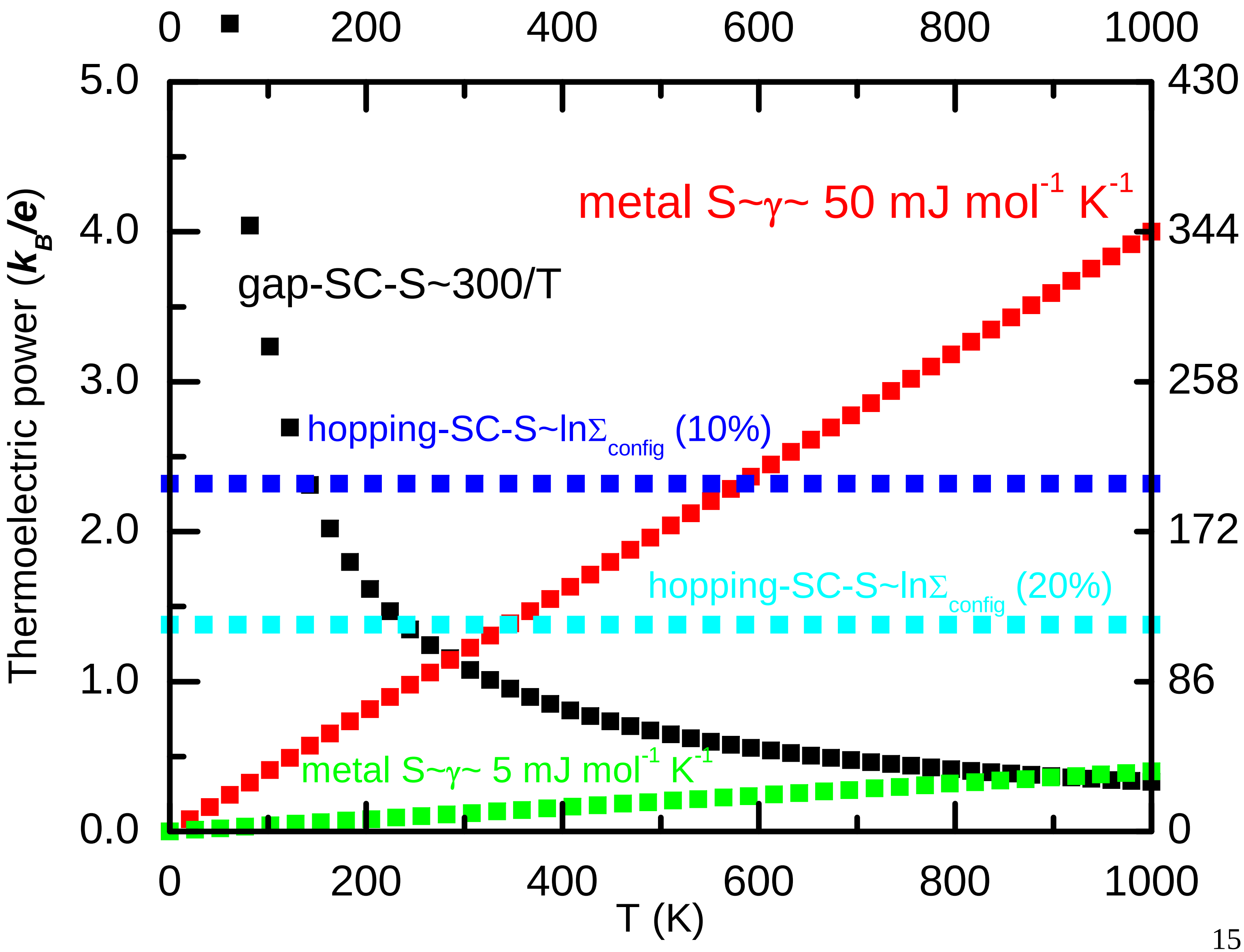
x = concentration of Co^{4+}

g_3= degeneracy of Co^{3+}

g_4= degeneracy of Co^{4+}

$$S = -\frac{k_B}{e}\ln\left[\frac{g_3}{g_4}\frac{x}{1-x}\right]$$

Thermopower-temperature dependence

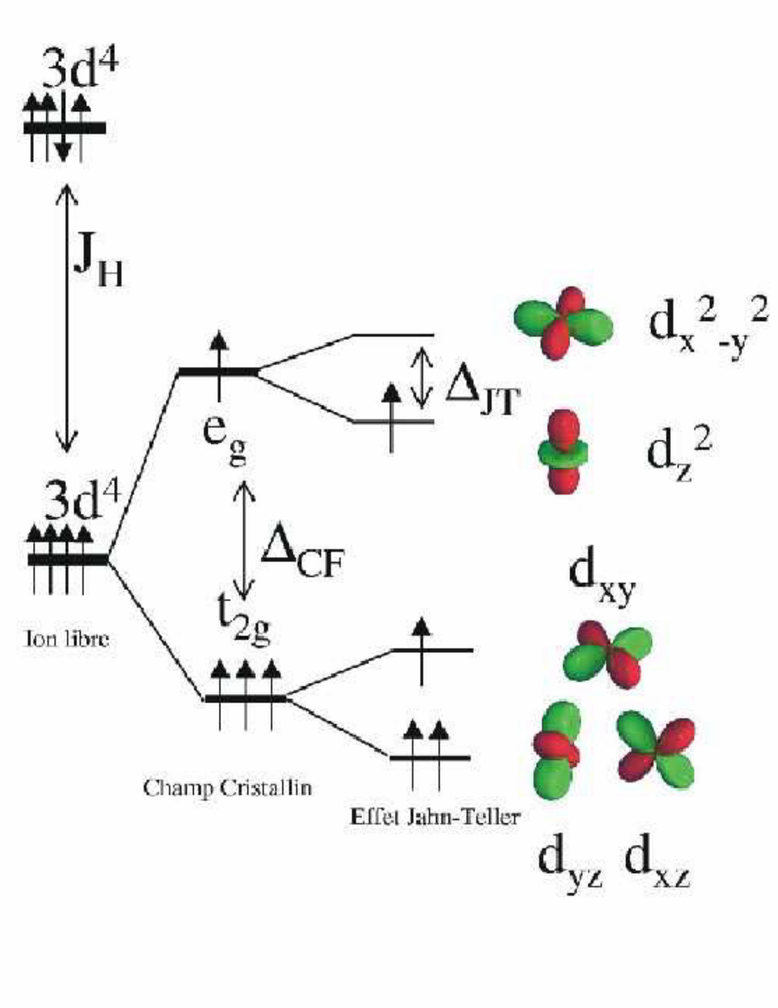


Manganites

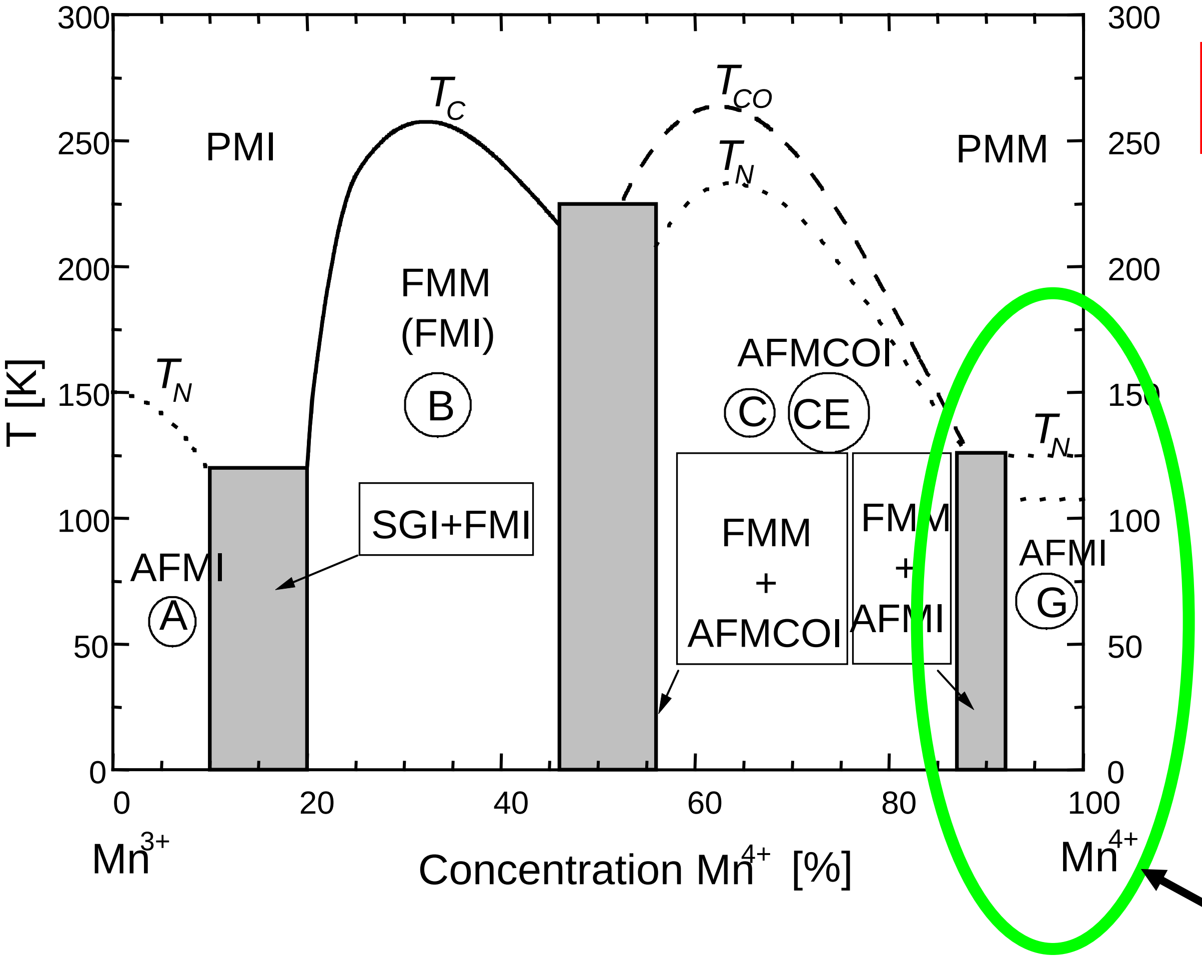
$Mn^{3+}(t_{2g}^3 e_g^1, S=2)$, JT active

$Mn^{4+}(t_{2g}^3 e_g^0, S=1.5)$

$Mn^{2+}(t_{2g}^3 e_g^2, S=2.5)$



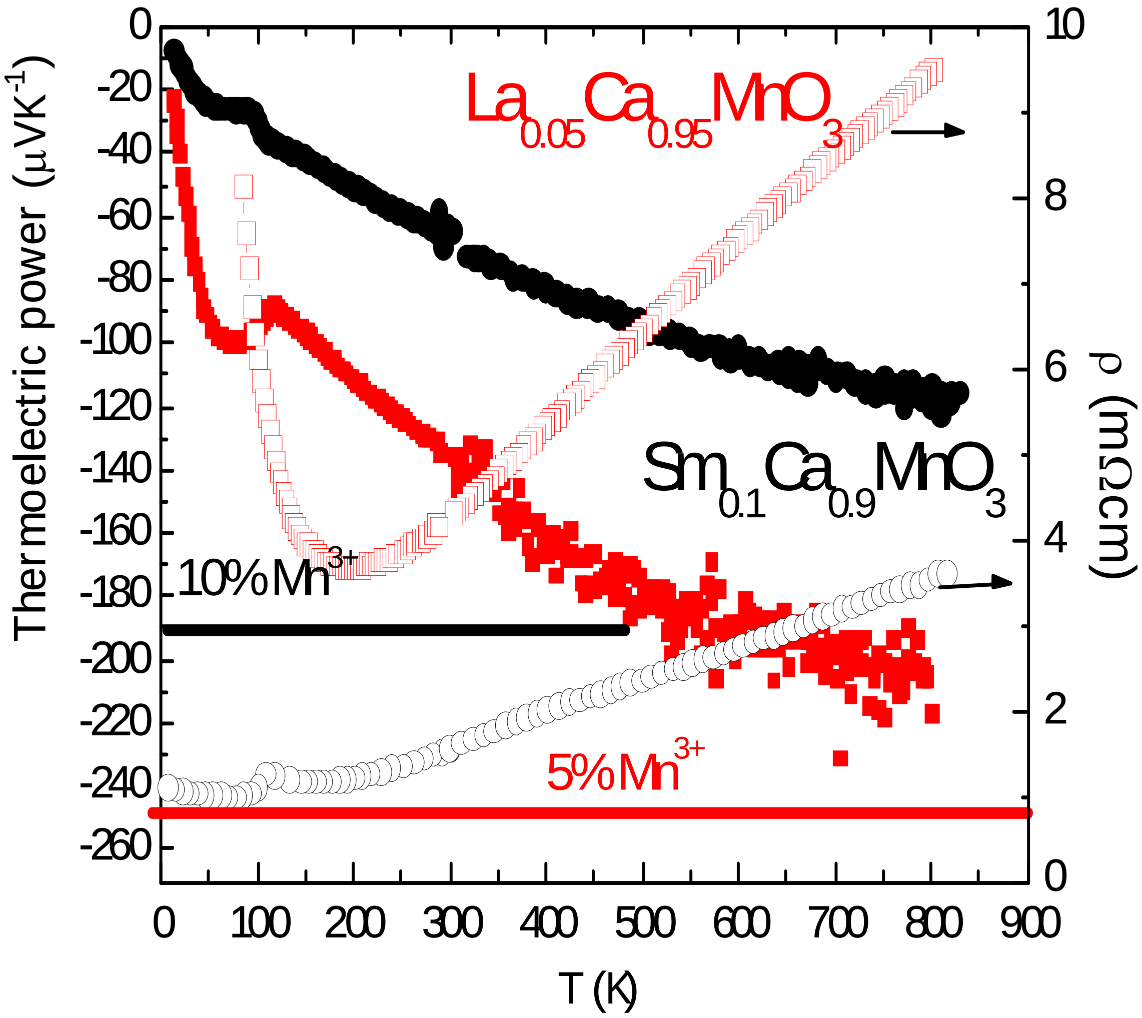
Phase diagram of Mn^{3+}/Mn^{4+} perovskites



Mn^{3+} in HS

region of interest

The thermoelectric properties of $Ca_{1-x}Re_xMnO_3$ ceramics – low doping



The best thermoelectrics in $Ca_{1-x}Re_xMnO_3$ system

-the Heiks limit for 90% Mn^{4+}

$S_{90\%} = -190\ \mu VK^{-1}$

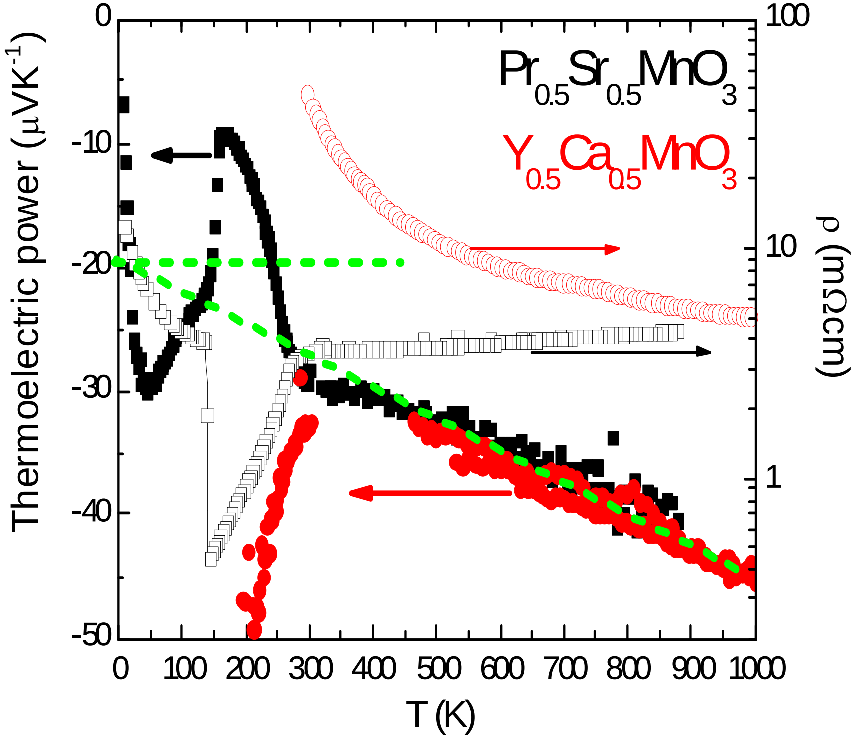
– the Heiks limit for 95% Mn^{4+}

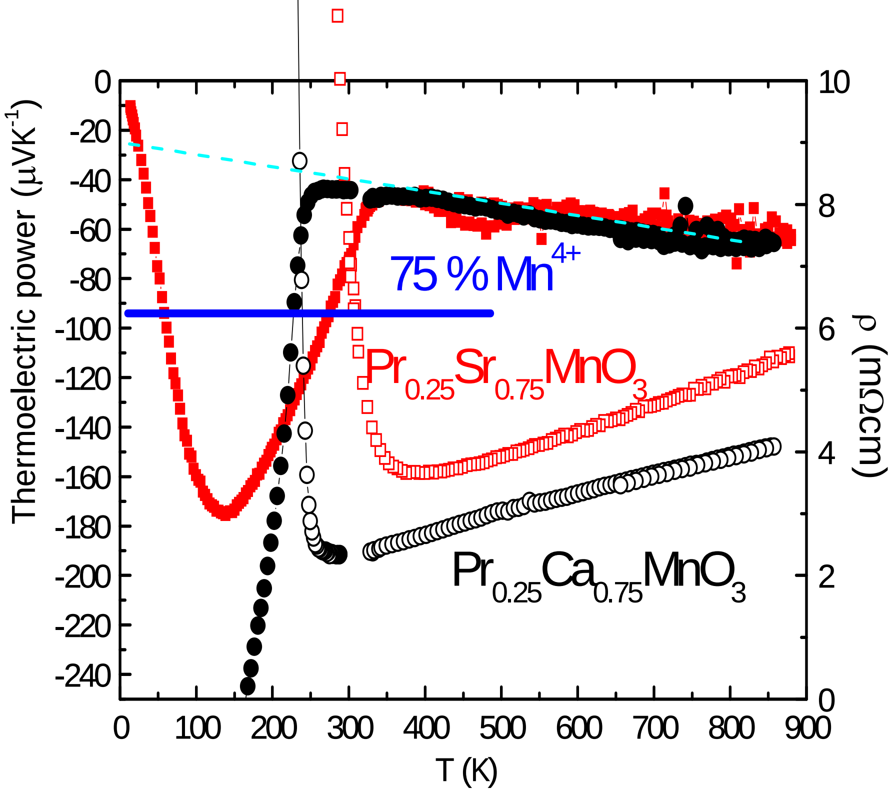
$S_{95\%} = -250\ \mu VK^{-1}$

The thermoelectric properties of Sr(Ca)$_{1-x}$Pr$_x$MnO$_{3,}$ ceramics – high doping

$$S_{mag} = \frac{k_B}{e}\ln\left[\frac{2S^{n+1}+1}{2S^{n}+1}\right]$$

For Mn^{3+}/Mn^{4+} HS = -19 μVK^{-1}





The role of tolerance factor fo 50 % Mn^{3+}

the Heiks limit for 50 % Mn^{3+}

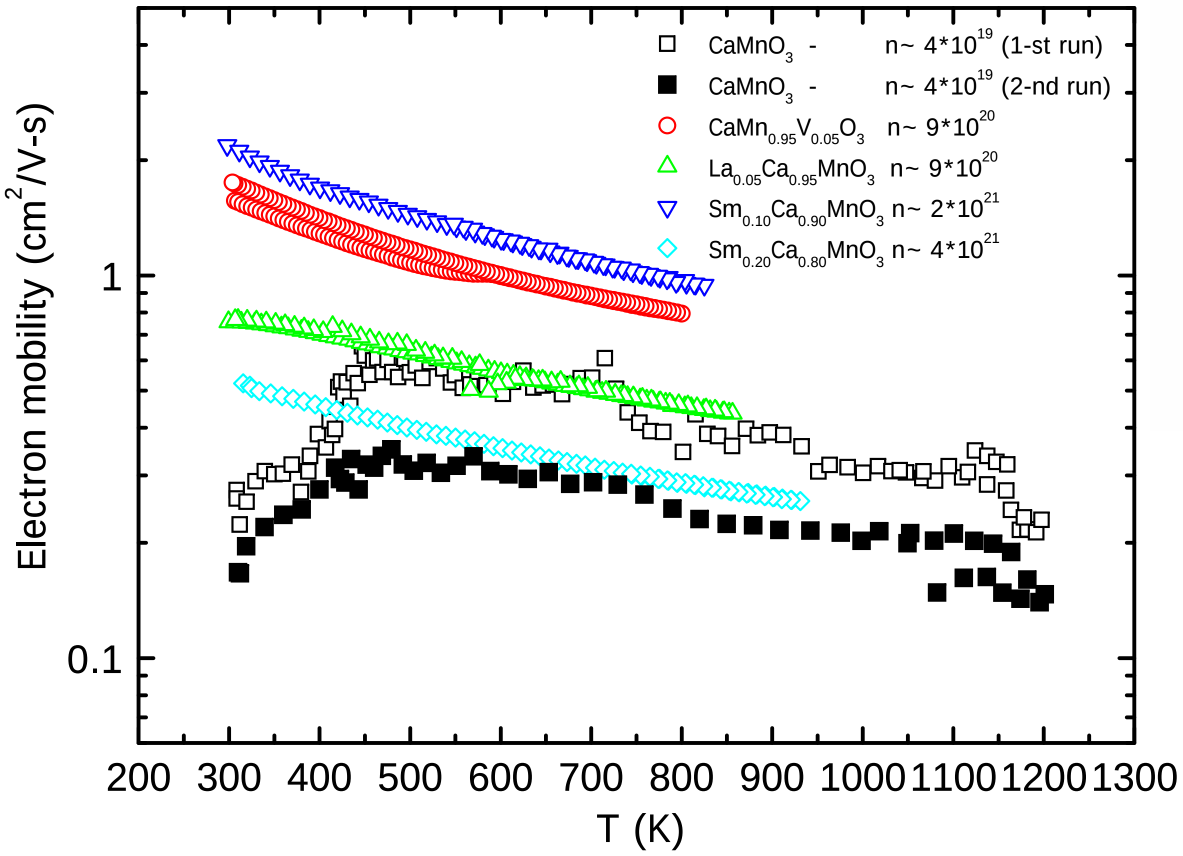
$S_{50\%}$= 0 μVK^{-1}

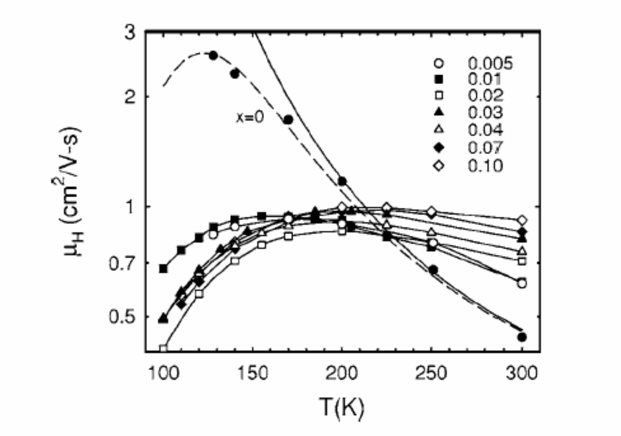
!additional degree of freedom AND diffusive component!

The thermoelectrics in A$_{1-x}$Pr$_x$MnO$_3$ system – the Heiks limit for 25% Mn^{3+}

HEIKS $S_{75\%}$=-95 μVK^{-1}

The temperature dependence of the charge carrier mobility for Mn^{4+} rich manganites





J. L. Cohn, C. Chiorescu, and J. J. Neumeier, Phys. Rev B, 72, (2005) 024422

-μ similar to that observed in $Sr_{1-x}La_xTiO_3$

Cobaltites

Co^{3+}_{LS} ($t_{2g}^6e_g^0$, S=0)

Co^{3+}_{IS} ($t_{2g}^5e_g^1$, S=1) , JT active, spin-orbit interaction

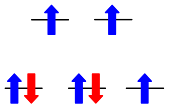
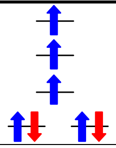
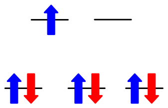
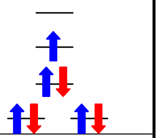
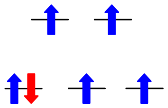
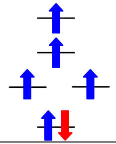
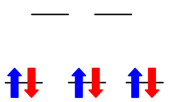
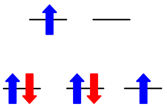
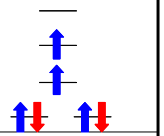
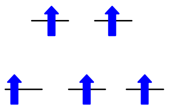
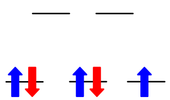
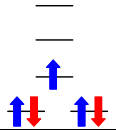
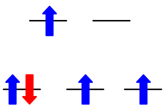
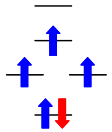
Co^{3+}_{HS} ($t_{2g}^4e_g^2$, S=2) , JT active

Co^{4+}_{LS} ($t_{2g}^5e_g^0$, S=0.5) , spin-orbit interaction

Co^{4+}_{IS} ($t_{2g}^4e_g^1$, S=1), JT active, spin-orbit interaction

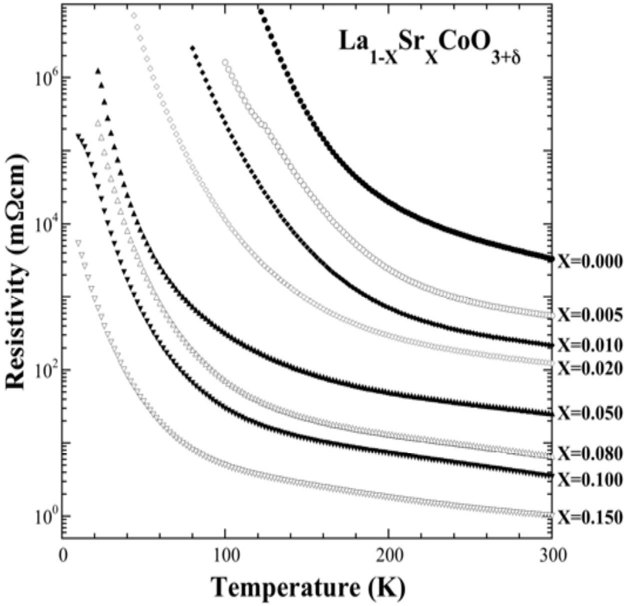
Co^{2+}_{HS} ($t_{2g}^5e_g^2$, S=1.5) , spin-orbit

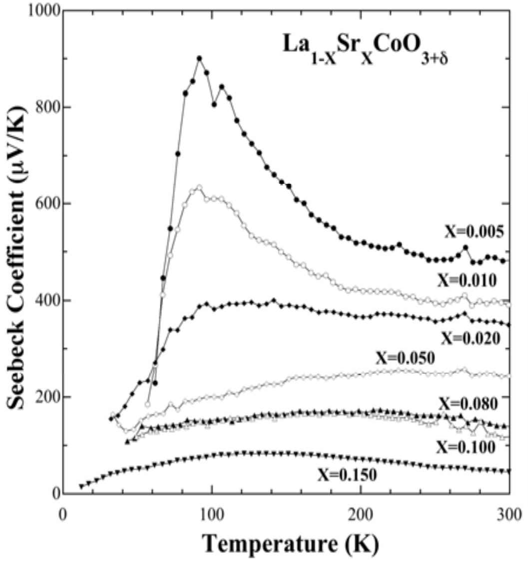
Possible spin states and total degeneracy of ground-states of Co^{2+}, Co^{3+} a Co^{4+} species (S=Spin only number neglecting orbital moment)

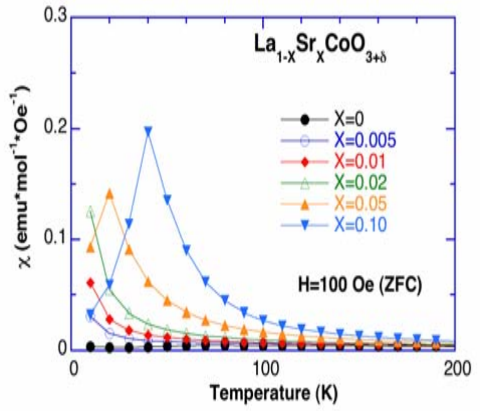
Ionic state	**HS** ($J_H > \Delta_{CF}$)		**LS** ($J_H < \Delta_{CF}$)		**IS** ($J_H \sim \Delta_{CF}$)	
	No distortion	Distortion ($\Delta_{JT} \gg 0$)	No distortion	Distortion ($\Delta_{JT} \gg 0$)	No distortion	Distortion ($\Delta_{JT} \gg 0$)
Co^{2+}	 $G_{spin} = 4$ $G_{orb} = 3$ **Gtot = 12**	 $G_{spin} = 4$ $G_{orb} = 1$ **Gtot = 4**	 $G_{spin} = 2$ $G_{orb} = 2$ **Gtot = 4**	 $G_{spin} = 2$ $G_{orb} = 1$ **Gtot = 2**	×	×
Co^{3+}	 $G_{spin} = 5$ $G_{orb} = 3$ **Gtot = 15**	 $G_{spin} = 5$ $G_{orb} = 1$ **Gtot = 5**	 $G_{spin} = 1$ $G_{orb} = 1$ **Gtot = 1**	×	 $G_{spin} = 3$ $G_{orb} = 6$ **Gtot = 18**	 $G_{spin} = 3$ $G_{orb} = 1$ **Gtot = 3**
Co^{4+}	 $G_{spin} = 6$ $G_{orb} = 1$ **Gtot = 6**	×	 $G_{spin} = 2$ $G_{orb} = 3$ **Gtot = 6**	 $G_{spin} = 2$ $G_{orb} = 1$ **Gtot = 2**	 $G_{spin} = 4$ $G_{orb} = 6$ **Gtot = 24**	 $G_{spin} = 4$ $G_{orb} = 1$ **Gtot = 4**

3D oxide perovskites –transport and magnetism

Sr,Ba-doped $LaCoO_3$ LS—LS/HS —IS σ^*



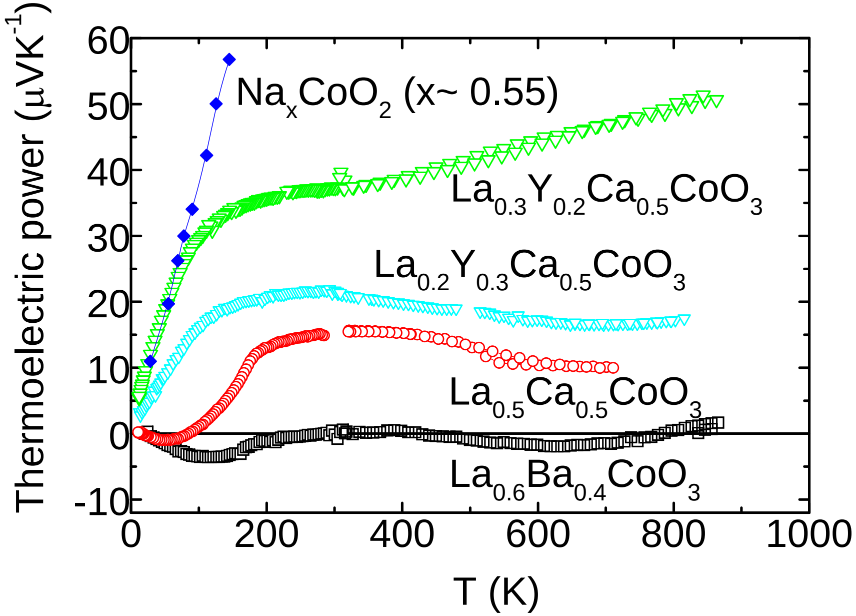


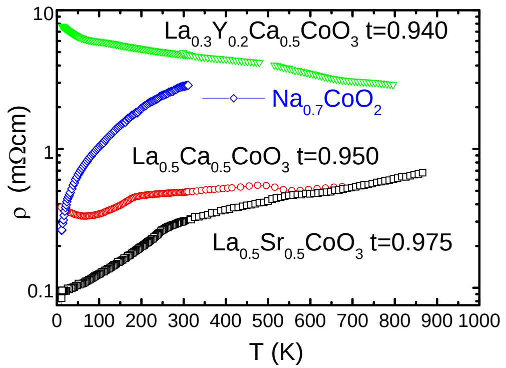


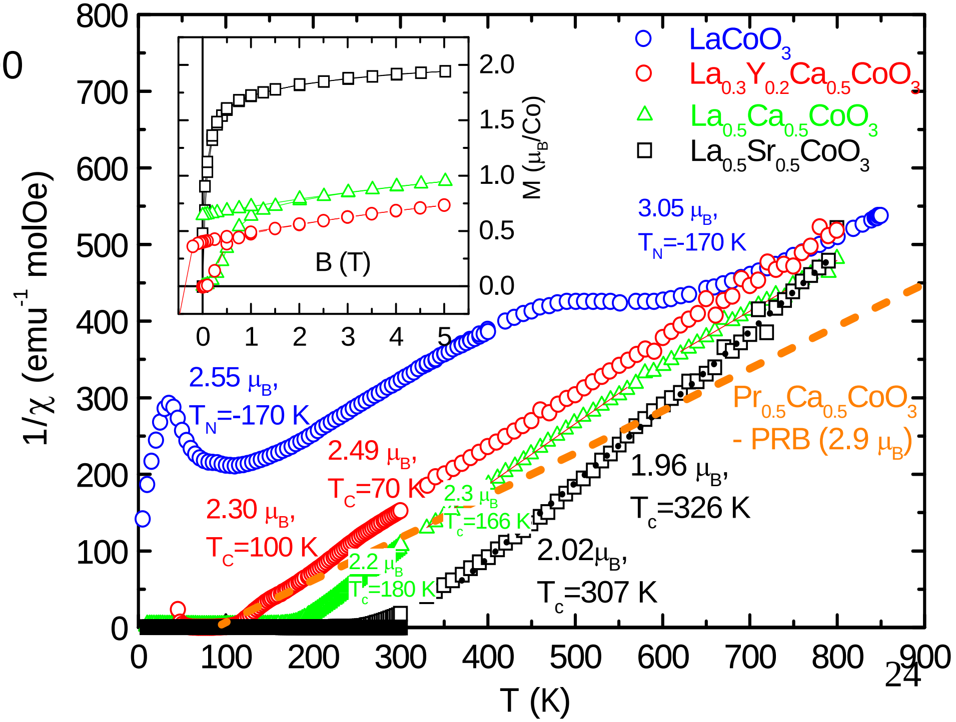
- ➢M-I transition is linked with magnetic one, metallic samples are FM with enhanced metallicity below Tc ($t_{2g}^5\sigma^*$)

- ➢For low x the thermoelectric power is temperature weakly dependent, the absolute value at room temperature corresponds to that deduced from a simple configurational entropy approximation (x=0.005 S_{Heiks}= 455 μVK^{-1}⇔S_{exp}~500 μVK, x=0.05 S_{exp}~250 μVK^{-1} ⇔ S_{Heiks}~ 257 μVK^{-1})

Co^{3+}:Co^{4+} =1:1; role of tolerance factor *t*

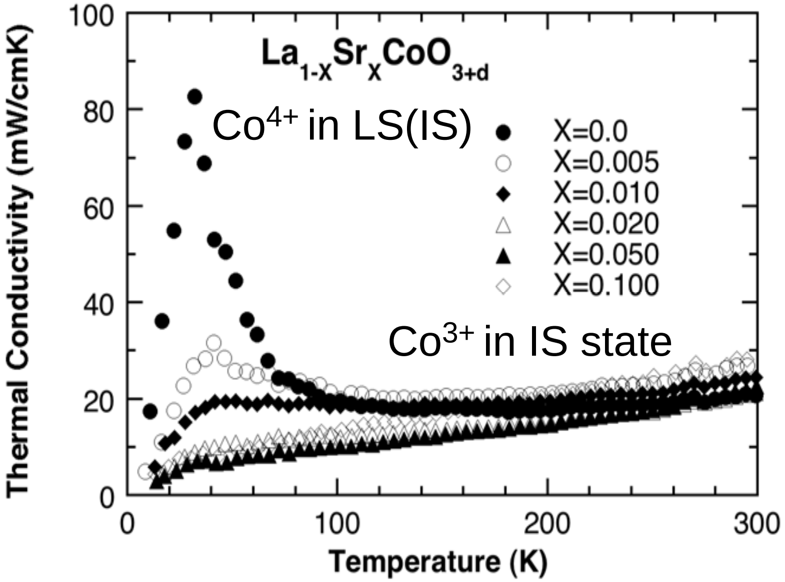


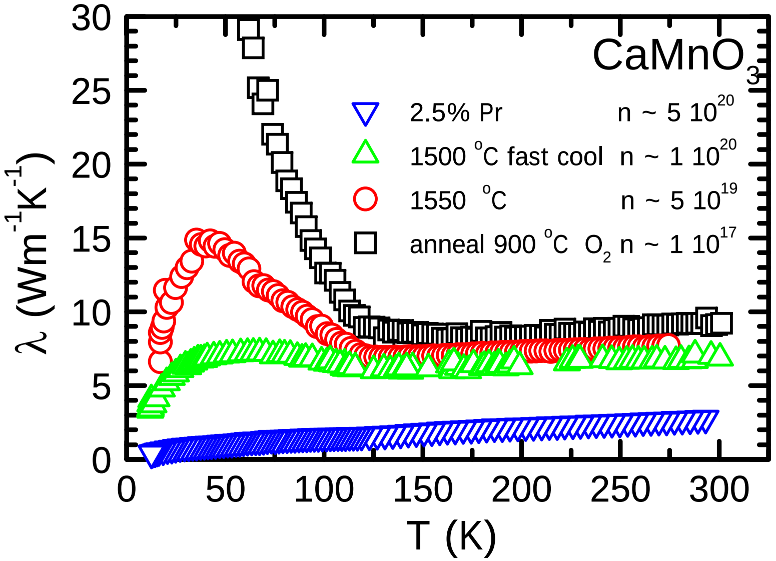




- ➢The ferromagnetic moment and T_c decreases with decreasing ***t***
- ➢ the low temperature metallic resistivity changes to temperature activated behaviour
- ➢the generalised Heikes formula explains the hopping conductivity (La-Y-Ca) supposing the IS spin state of both Co^{3+} and Co^{4+}
- ➢Ferromagnetic metallic state (La-Sr) is characterized by negative thermoelectric power corresponding to the $t_{2g}^{5}\sigma^{*0.5}$ electronic configuration (IS Co^{3+} and LS Co^{4+})

Sr-doped $LaCoO_3$ LS-HS, $CaMnO_3$, spin fluctuations





➢Thermal conductivity is high for LS Co^{3+}, Co^{4+}

➢ the depressed thermal conductivity in $Ln_{1-x}A_xCoO_3$ is due to fast electron fluctuations between LS / HS Co^{3+} species (LS⇔HS+LS)

➢the gradual stabilization of IS Co^{3+} species of $t_{2g}^5\ \sigma^{*0.5}$ character

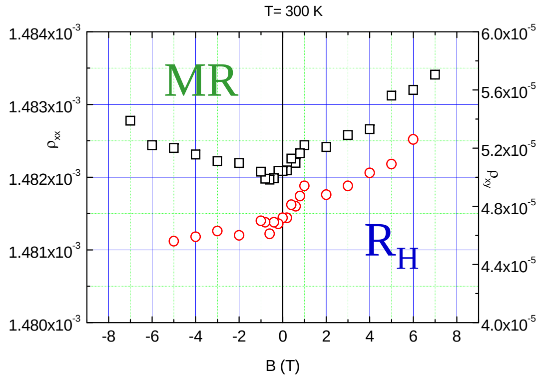
➢spin density fluctuations are supposed to decrease the thermal conductivity in pure $CaMnO_3$ above T_N

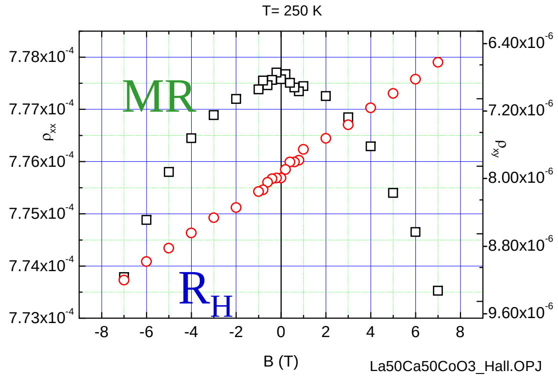
Cobaltites –magnetotransport & carrier concentration (n/Co)
Anomalous Hall Effect

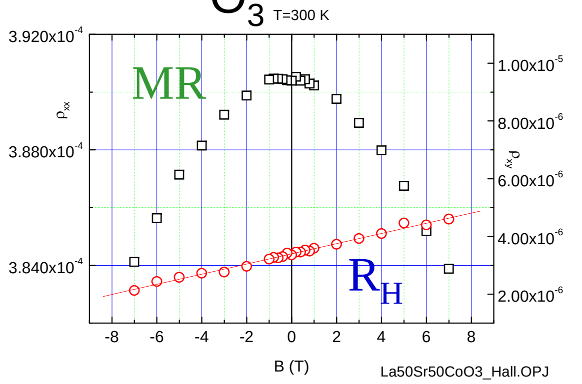
$Na_{0.7}CoO_2$

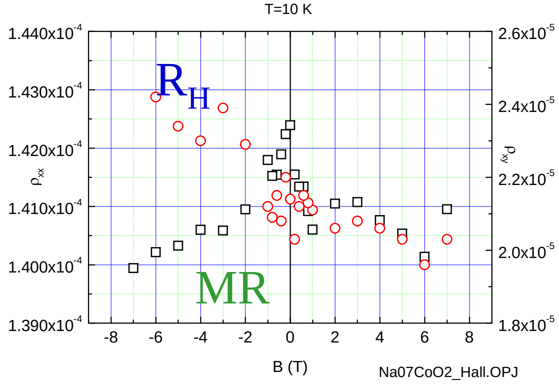
$La_{0.5}Ca_{0.5}CoO_3$

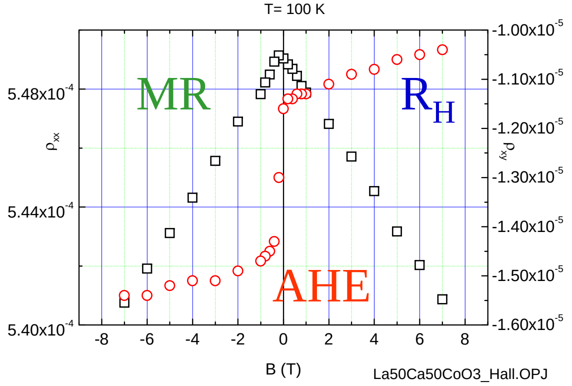
$La_{0.5}Sr_{0.5}CoO_3$

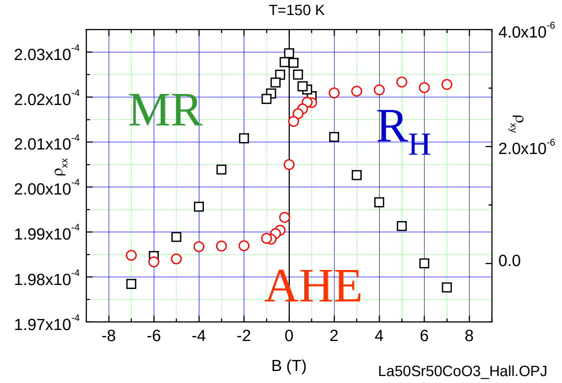






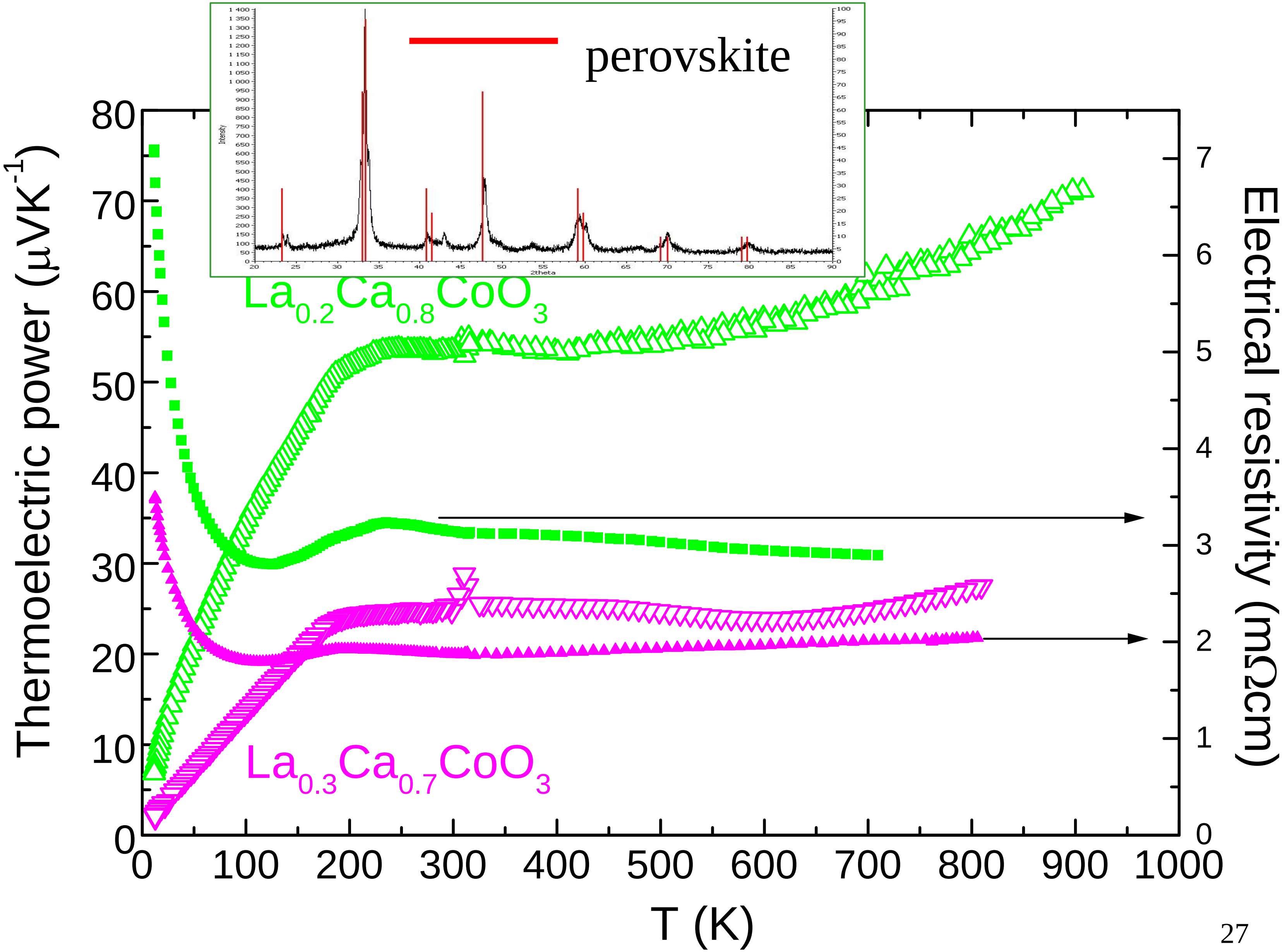




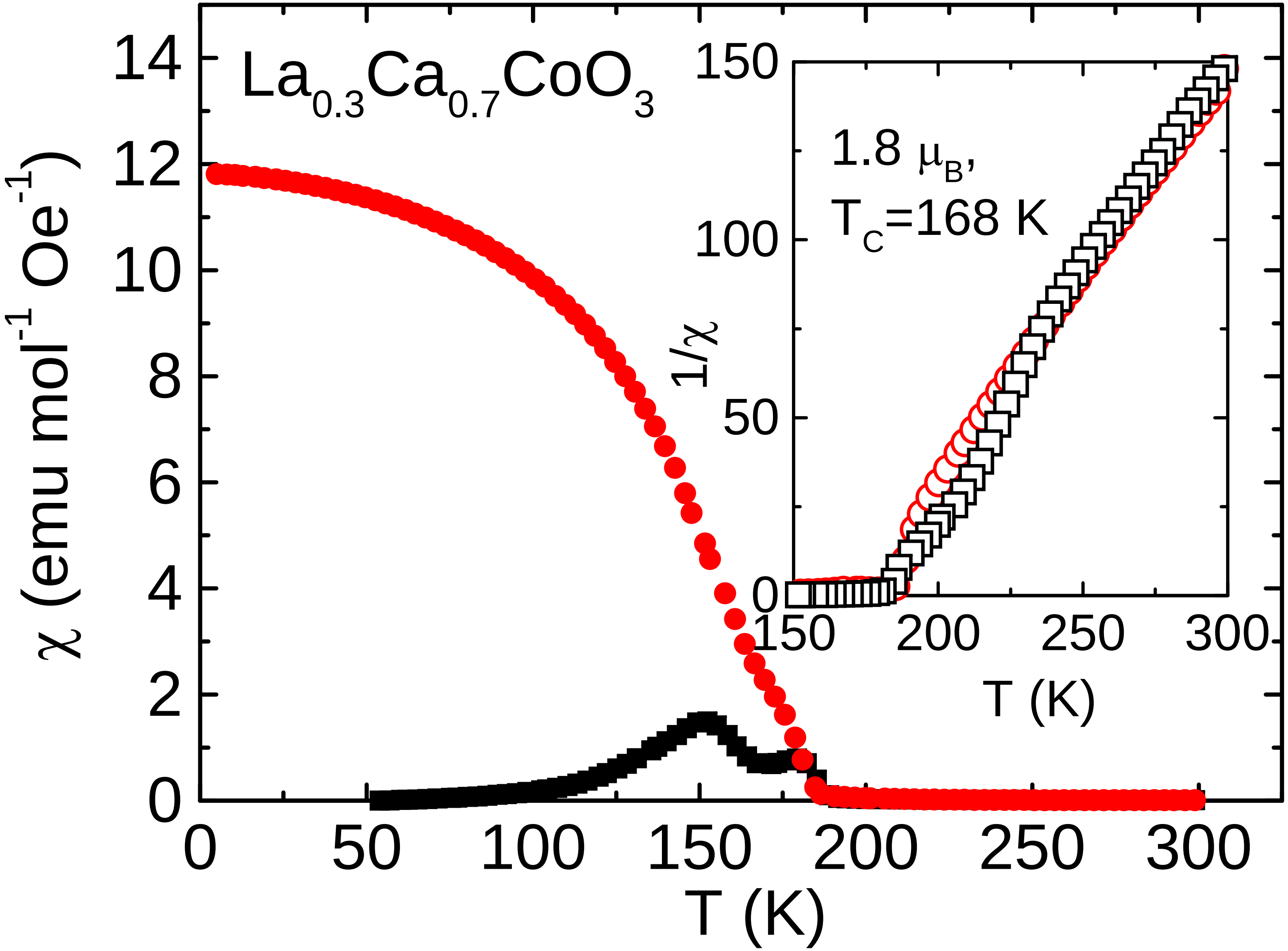


T	$Na_{0.7}CoO_2$	$La_{0.5}Ca_{0.5}CoO_3$	$La_{0.5}Sr_{0.5}CoO_3$
5	-0.04	0.3	0.7
20	-0.06	0.3	0.7
100	0.02	0.3	0.8
150	~0	0.17	0.3
200	0.02	0.1	0.6
225		0.13	0.6
250		0.25	
300	0.03	0.4	0.25
350	0.03	0.3	0.2

THERMOELECTRIC PERFORMANCE 3D oxide perovskites $La_{1-x}Ca_xCoO_3$



Magnetic properties of $La_{0.3}Ca_{0.7}CoO_3$ – magnetic susceptibility



Chromites

Cr^{4+} (t_{2g}^{2}, S=1.0, O=3)

$G_{spin}=3$, $G_{orb}=3$, $G_{tot}= 9$

Cr^{3+} (t_{2g}^{3}, S=1.5, O=1)

$G_{spin}=4$, $G_{orb}=1$, $G_{tot}= 4$

$$\frac{\mathrm{Cr}^{3+}}{\mathrm{Cr}^{4+}} = 1$$

$$S_{mag} = -\frac{k_B}{e}\ln\left(\frac{G_{spin}^{Cr^{3+}}}{G_{spin}^{Cr^{4+}}}\right) = -29\mu VK^{-1}$$

$$S_{mag+orb} = -\frac{k_B}{e}\ln\left(\frac{G_{tot}^{Cr^{3+}}}{G_{tot}^{Cr^{3+}}}\right) = +69\mu VK^{-1}$$

PRL **96,** 046408 (2006)

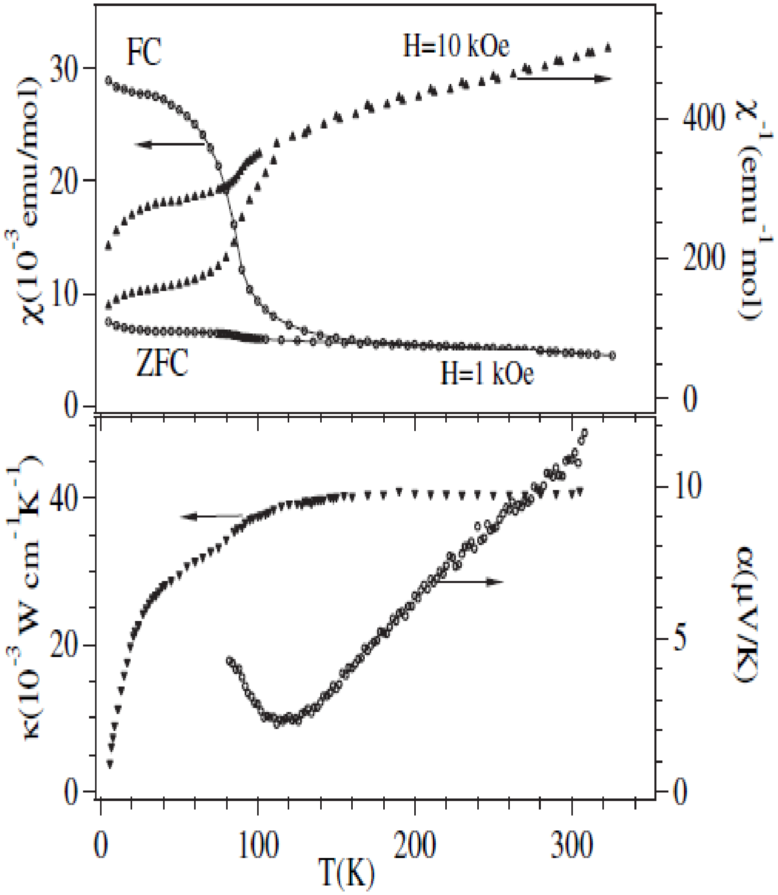
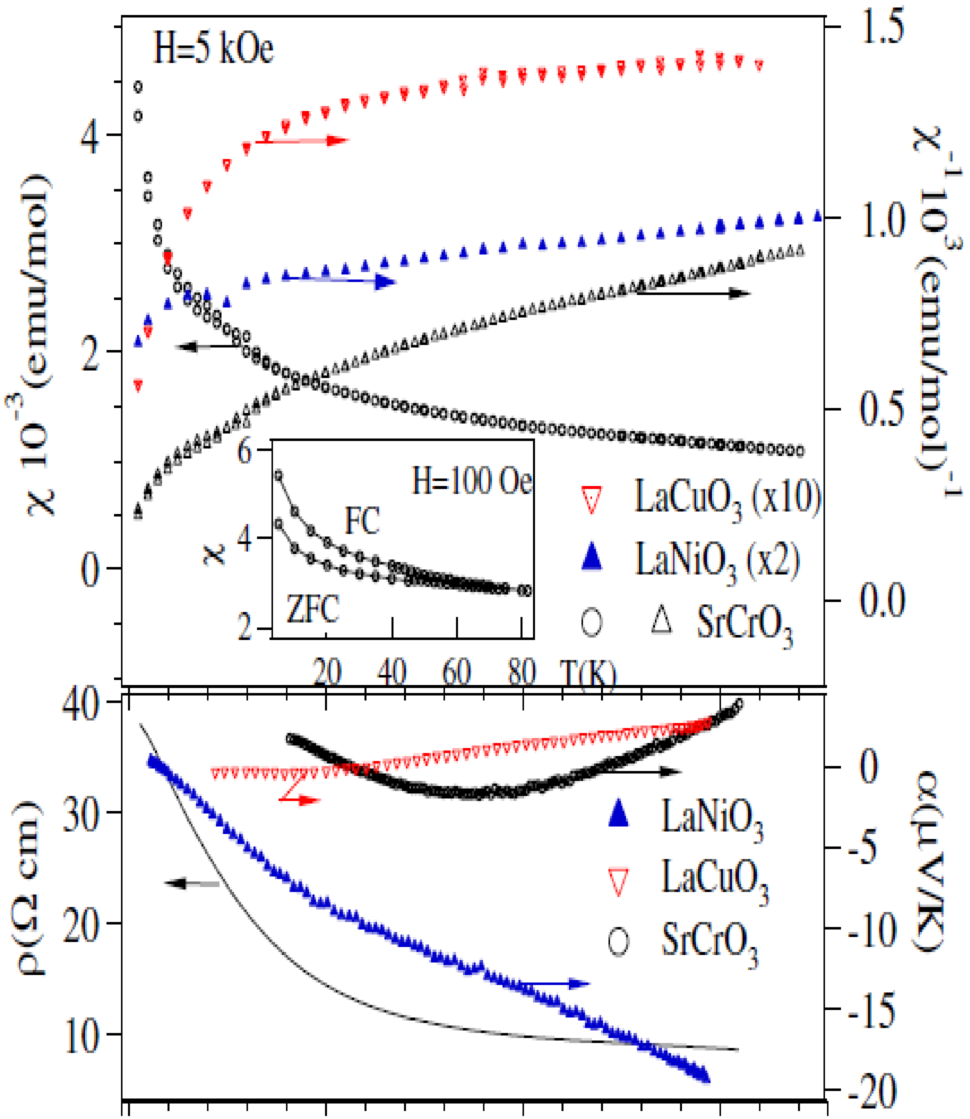
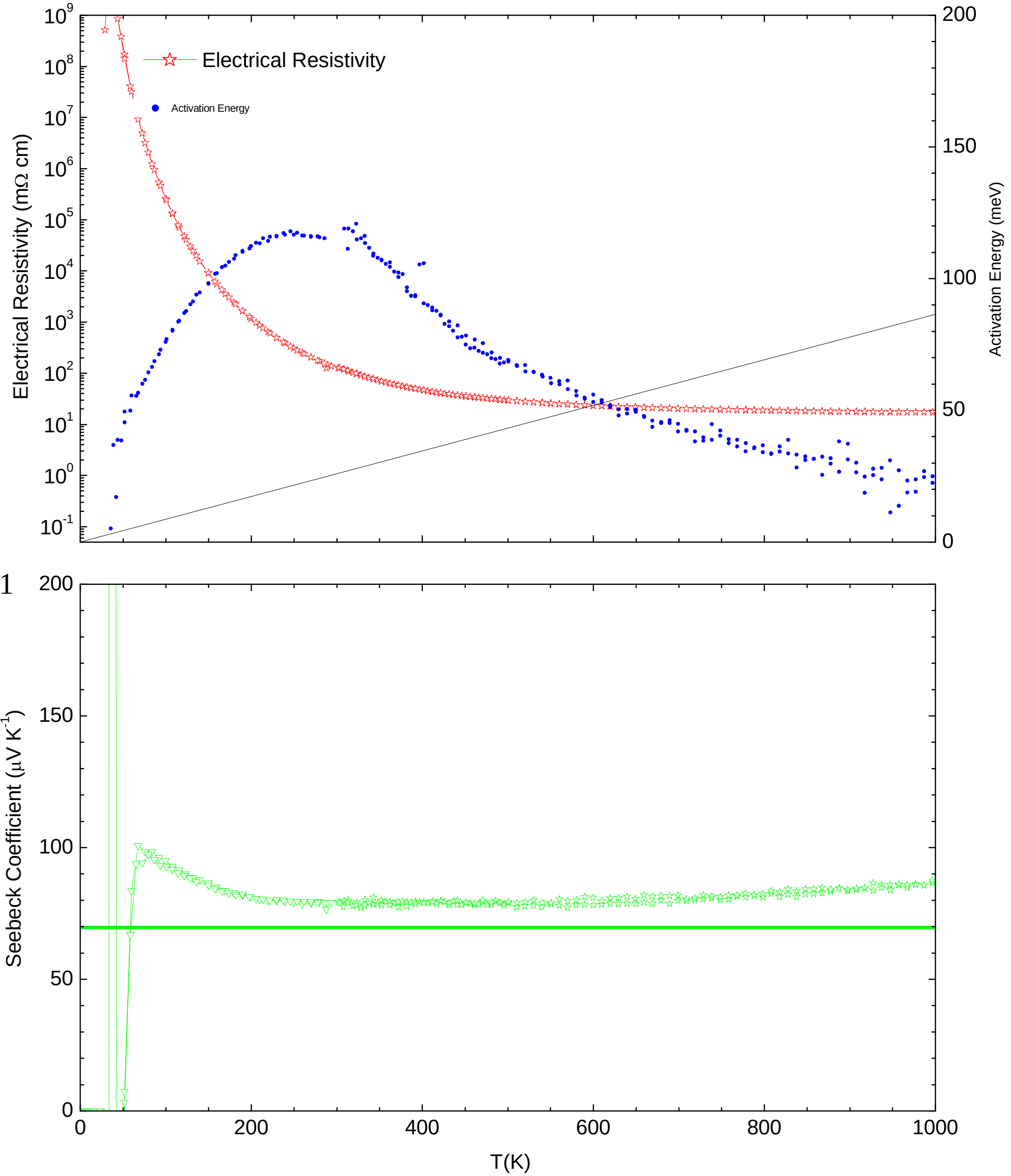


FIG. 3. The same as Fig. 2 (without resistivity) for $CaCrO_3$. Inset: magnetization to 5.5 T at 5 K.



$Pr_{0.5}Ca_{0.5}CrO_3$

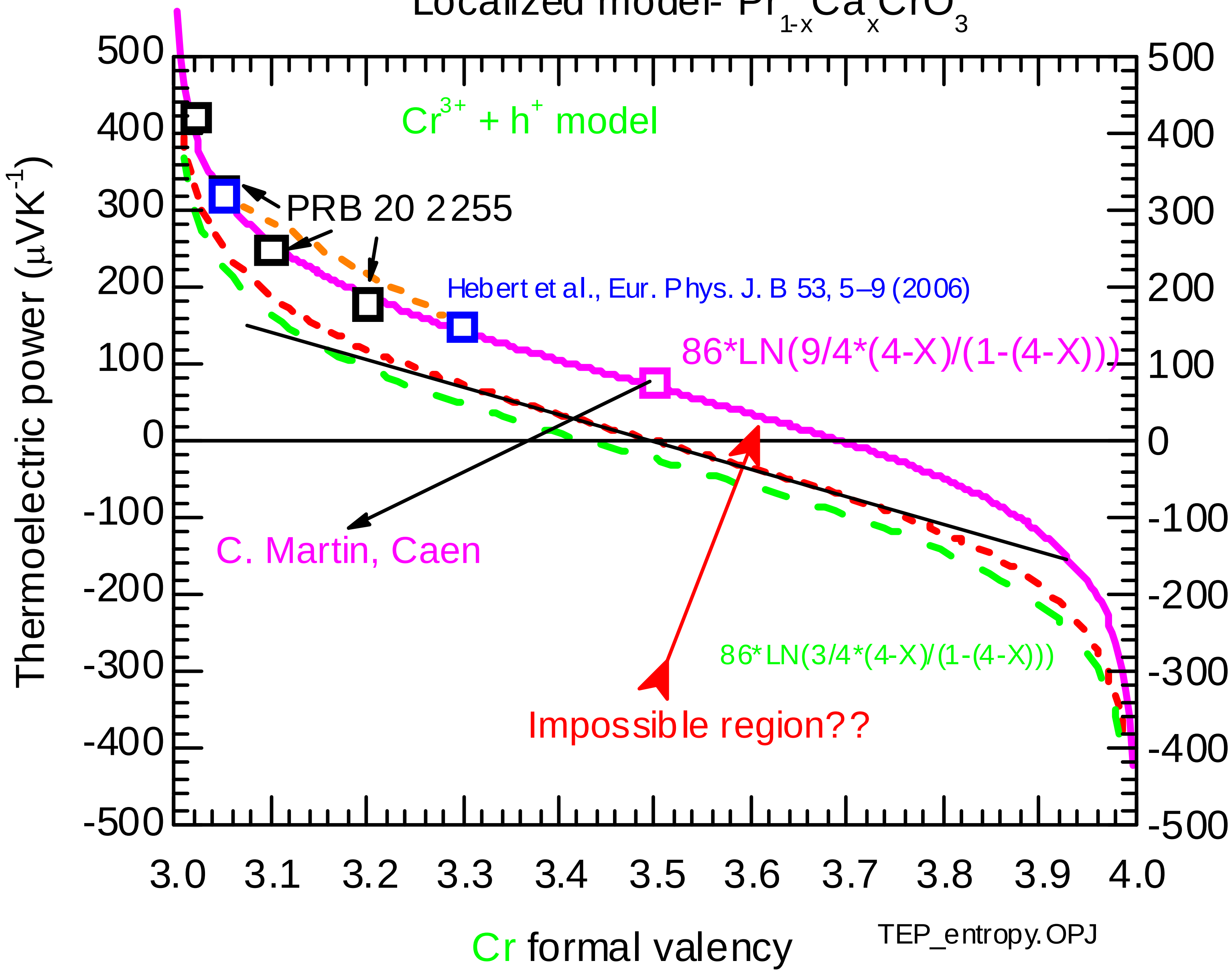


$$S_{mag+orb} = -\frac{k_B}{e}\ln\left(\frac{G_{tot}^{Cr^{3+}}}{G_{tot}^{Cr^{3+}}}\right) = +69\,\mu VK^{-1}$$

- ➢complex configurational entropy approximation applies

- ➢**(magnetic, orbital contribution) S_{Heiks}= +69μVK^{-1}**

Localized model- $Pr_{1-x}Ca_xCrO_3$



Ferrites

LS Fe^{4+} ($t_{2g}{}^4$, S=1.0, O=3)

$G_{spin}=3$, $G_{orb}=3$, $G_{tot}= 9$

HS Fe^{4+} ($t_{2g}{}^4$, S=2.0, O=2)

$G_{spin}=5$, $G_{orb}=2$, $G_{tot}= 10$

HS Fe^{3+} ($t_{2g}{}^5$, S=2.5, O=1)

$G_{spin}=6$, $G_{orb}=1$, $G_{tot}= 6$

$$\frac{\mathrm{Fe}^{3+}}{\mathrm{Fe}^{4+}}=1$$

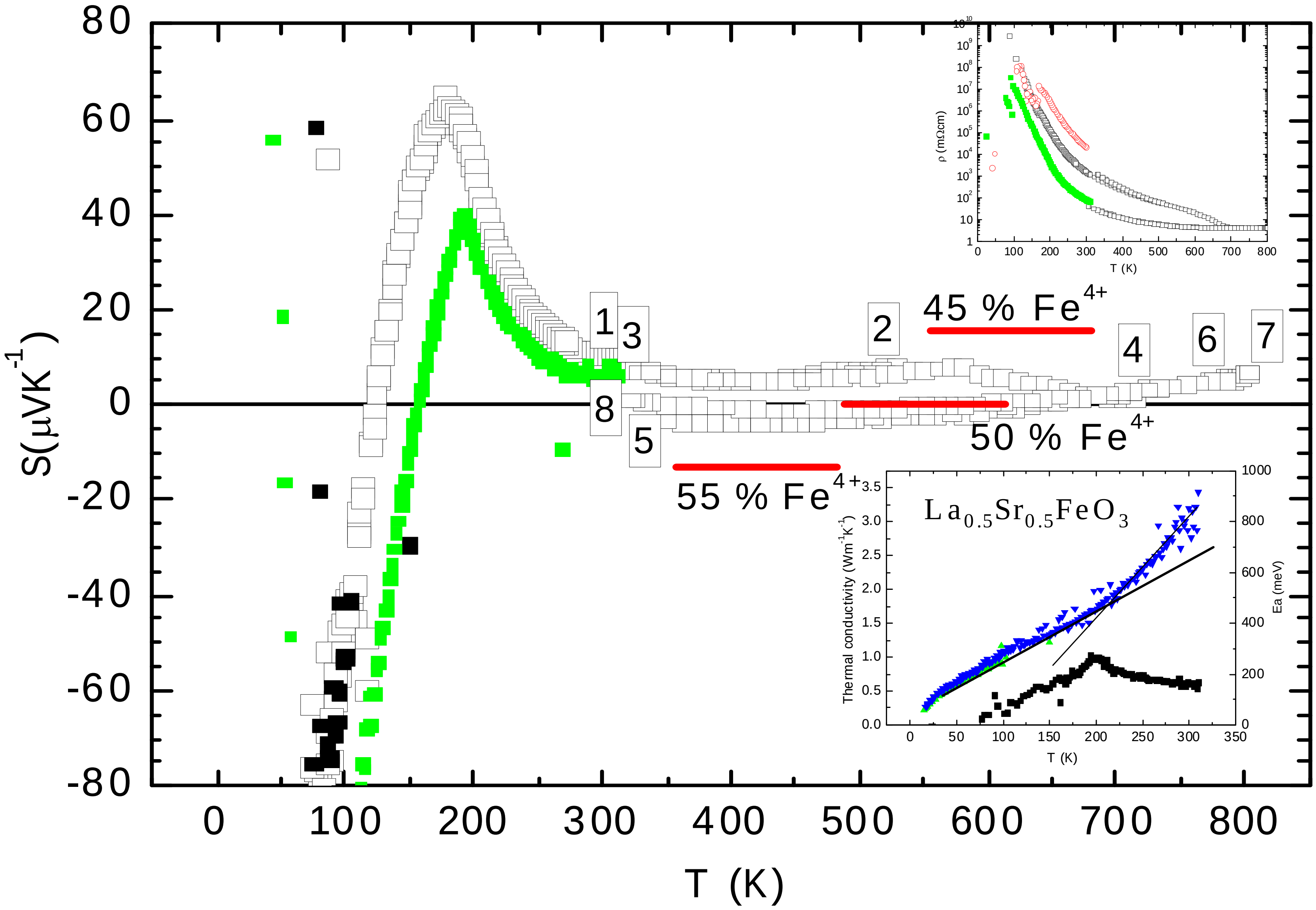
$$S^{LS}{}_{mag} = -\frac{k_B}{e}\ln\left(\frac{G_{spin}^{Fe^{3+}}}{G_{spin}^{Fe^{4+}}}\right) = -59\mu VK^{-1}$$

$$S^{HS}{}_{mag} = -\frac{k_B}{e}\ln\left(\frac{G_{spin}^{Fe^{3+}}}{G_{spin}^{Fe^{4+}}}\right) = -16\mu VK^{-1}$$

$$S^{LS}{}_{mag+orb} = -\frac{k_B}{e}\ln\left(\frac{G_{tot}^{Fe^{3+}}}{G_{tot}^{Fe^{3+}}}\right) = +35\mu VK^{-1}$$

$$S^{HS}{}_{mag+orb} = -\frac{k_B}{e}\ln\left(\frac{G_{tot}^{Fe^{3+}}}{G_{tot}^{Fe^{3+}}}\right) = +44\mu VK^{-1}$$

La$_{0.5}$Sr$_{0.5}$FeO$_3$ – oxidation during measurement



- ➢a simple configurational entropy approximation applies

(no magnetic, no orbital contribution) $S_{Heiks} = 0\ \mu VK^{-1}$

$SrFeO_{3-\delta}$

E. Hemery, thesis, Victoria University of Wellington,2007

HS Fe^{4+} 2S+1=5, O=2, SO=10
LS Fe^{4+} 2S+1=3, O=3, SO=9
HS Fe^{3+} 2S+1=6, O=1, SO=6
S~ -18μVK^{-1}

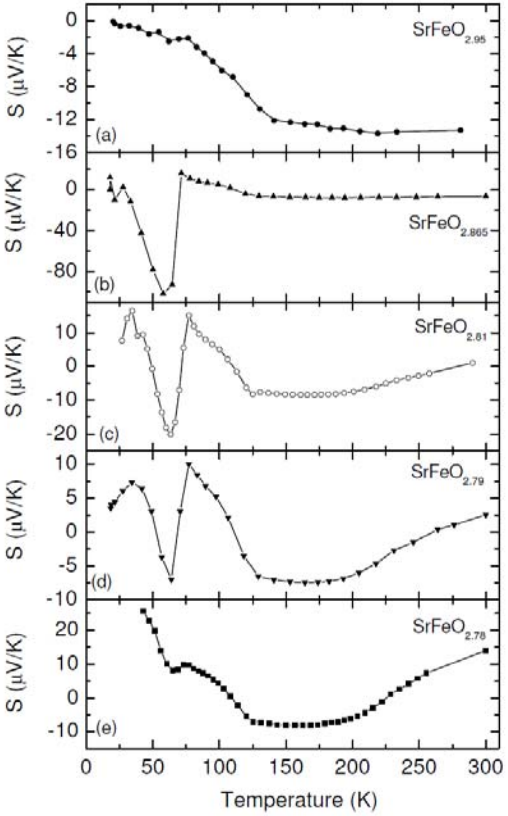


Figure 7.8: TEP versus temperature for (a) $SrFeO_{2.95}$, (b) $SrFeO_{2.865}$, (c) $SrFeO_{2.81}$, (d) $SrFeO_{2.79}$ and (e) $SrFeO_{2.78}$.

E. Hemery, thesis, Victoria University of Wellington,2007

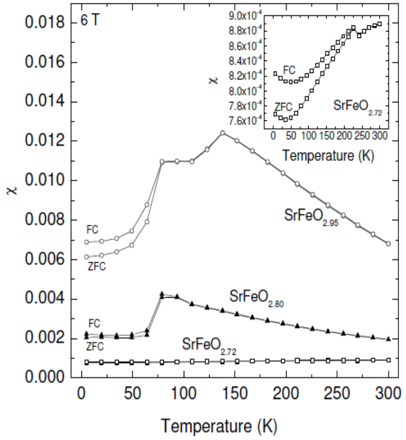


Figure 7.3: Zero Field Cooled (ZFC) and Field Cooled (FC) magnetisation at 6 T for $SrFeO_{2.95}$, $SrFeO_{2.80}$ and $SrFeO_{2.72}$. Inset: zoom in of the $SrFeO_{2.72}$ measurement.

$$S^{HS}{}_{mag} = -\frac{k_B}{e}\ln\left(\frac{G_{spin}^{Fe^{3+}}}{G_{spin}^{Fe^{4+}}}\right) = -16\mu VK^{-1}$$

- configurational entropy approximation applies above 150 K
- (magnetic, no orbital contribution) S_{Heiks}=-16 μVK^{-1}

SrFeO$_{3-\delta}$

E. Hemery, thesis, Victoria University of Wellington,2007

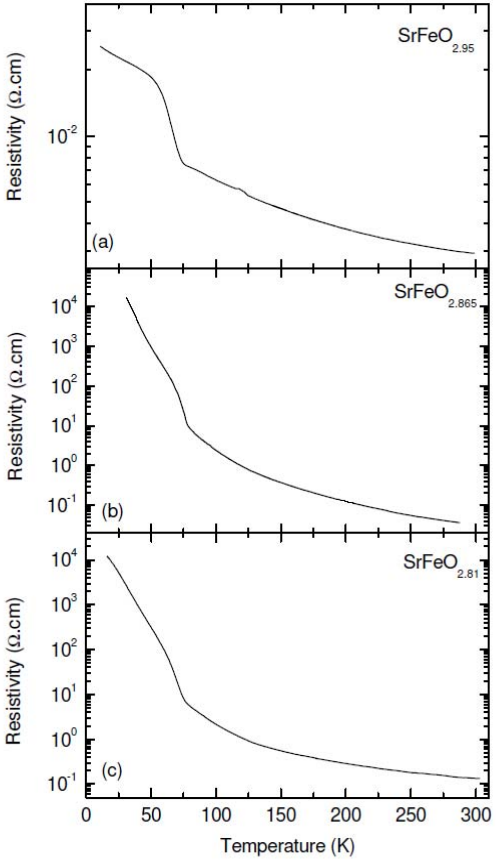


Figure 7.6: Temperature dependence of the resistivity for (a) SrFeO$_{2.95}$, (b) SrFeO$_{2.865}$ and (c) SrFeO$_{2.81}$.

Ruthenates

Ru^{5+} (t_{2g}^3, S=1.5, O=1) *N*o mixing entropy, only magnetic or orbital

G_{spin}=4, G_{orb}=1, G_{tot}= 4

$$S^{LS}{}_{mag} = -\frac{k_B}{e}\ln\left(\frac{G_{spin}^{Ru^{5+}}}{G_{spin}^{Ru^{4+}}}\right) = +25\mu VK^{-1}$$

Ru^{4+} (t_{2g}^4, S=1.0, O=3)

$$S^{LS}{}_{mag} = -\frac{k_B}{e}\ln\left(\frac{G_{spin}^{Ru^{4+}}}{G_{spin}^{Ru^{3+}}}\right) = +35\mu VK^{-1}$$

G_{spin}=3, G_{orb}=3, G_{tot}= 9

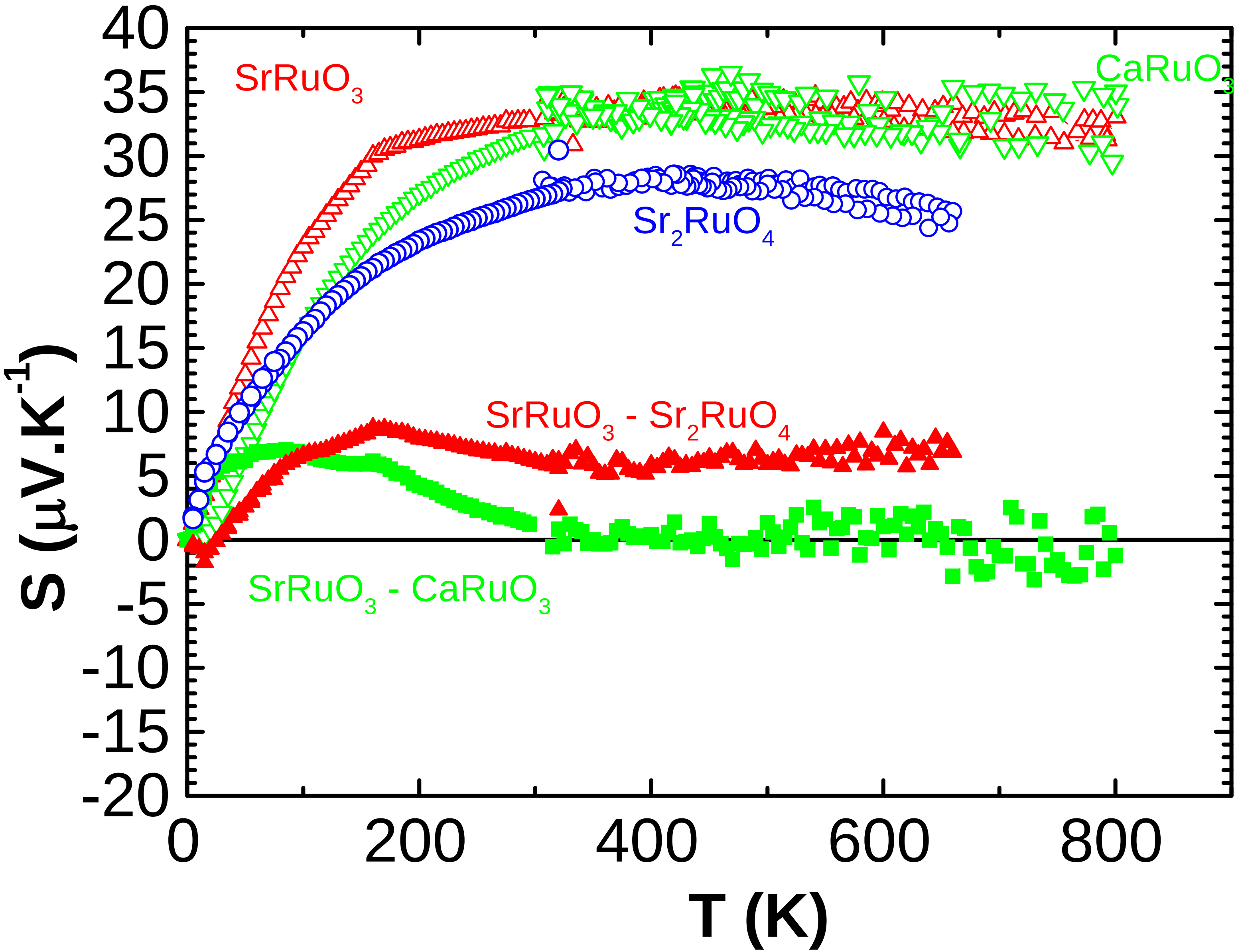
$$S^{LS}{}_{mag+orb} = -\frac{k_B}{e}\ln\left(\frac{G_{tot}^{Ru^{5+}}}{G_{tot}^{Ru^{4+}}}\right) = -69\mu VK^{-1}$$

$$S^{LS}{}_{mag+orb} = -\frac{k_B}{e}\ln\left(\frac{G_{spin}^{Ru^{4+}}}{G_{spin}^{Ru^{3+}}}\right) = +35\mu VK^{-1}$$

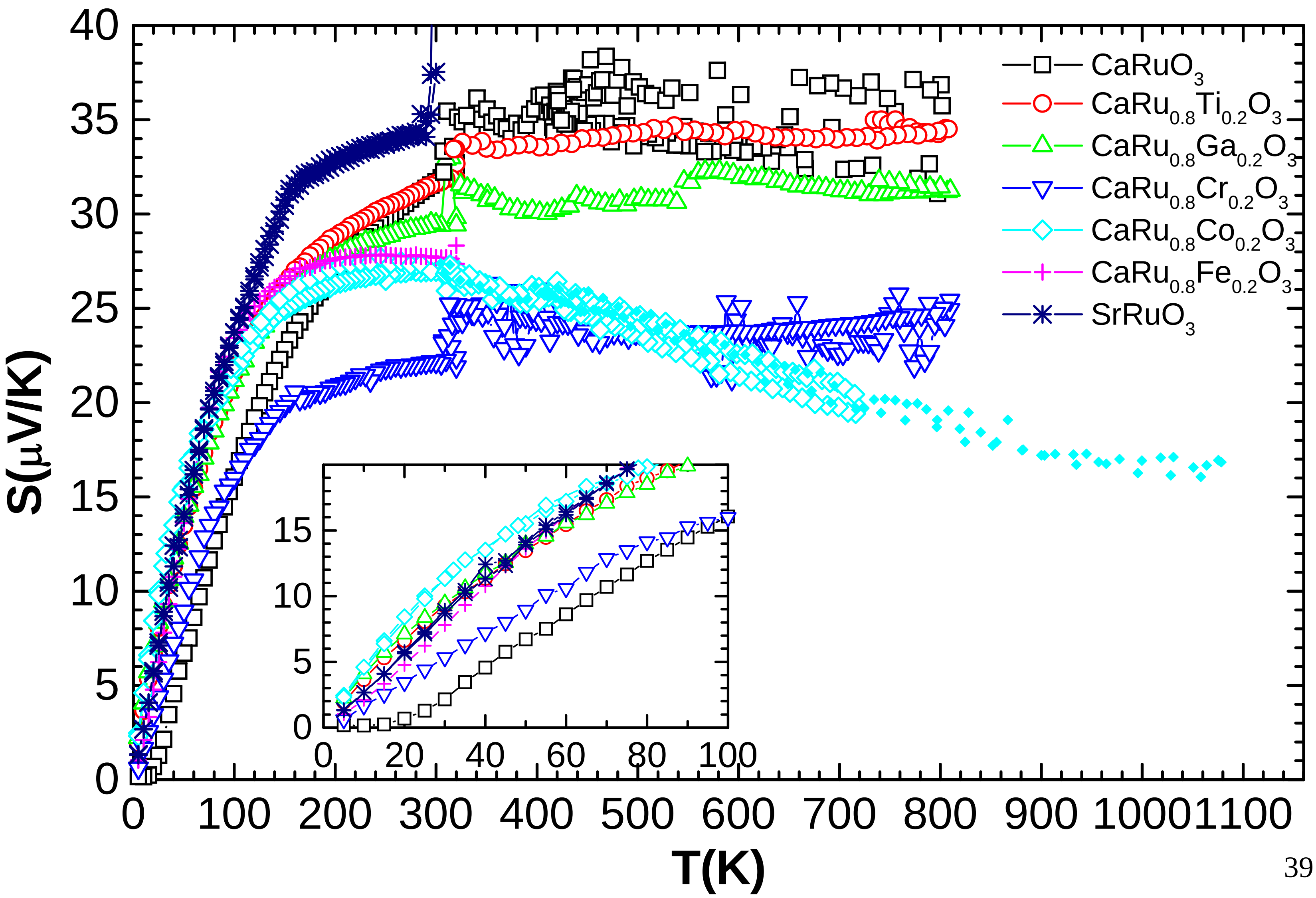
Ru^{3+} (t_{2g}^5, S=0.5, O=3)

G_{spin}=2, G_{orb}=3, G_{tot}= 6

Ru-perovskites –CW behaviour (FM, AFM, PM)

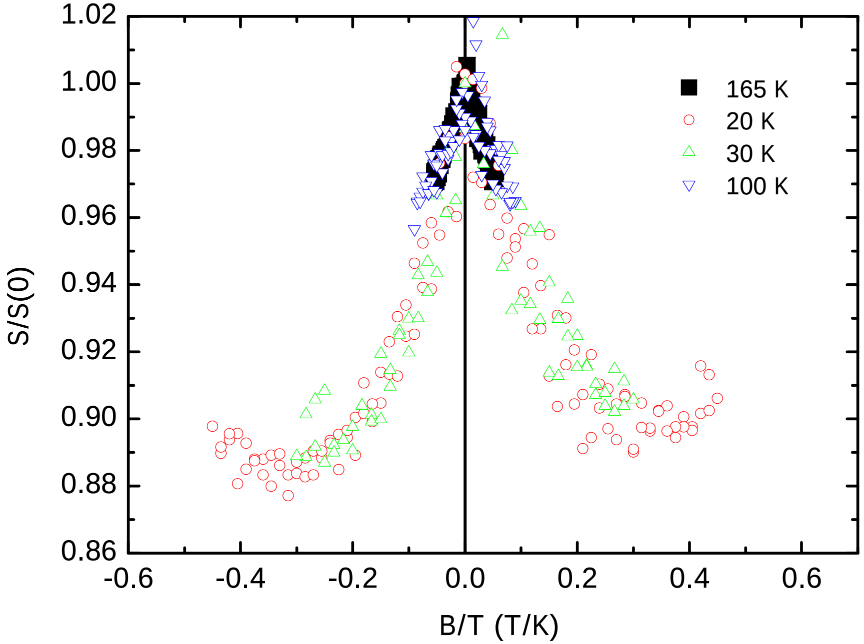


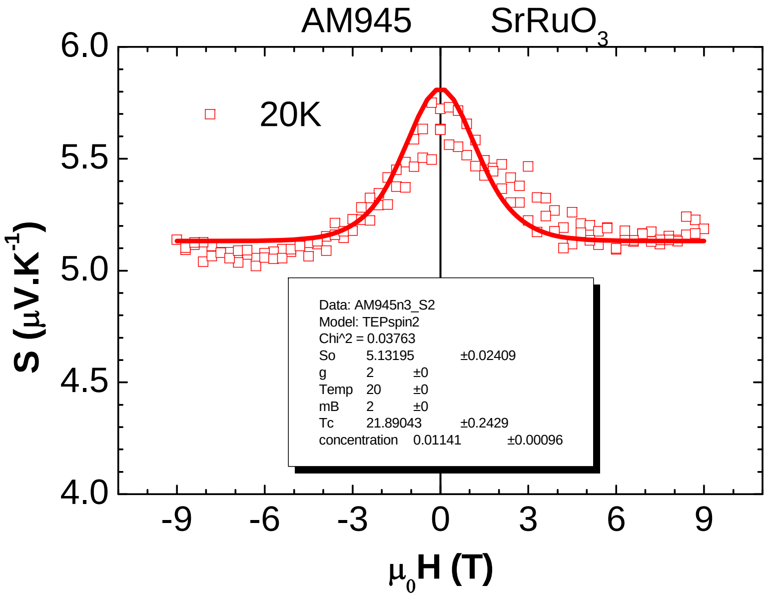
Ru-perovskites –CW behaviour (FM, AFM, PM)



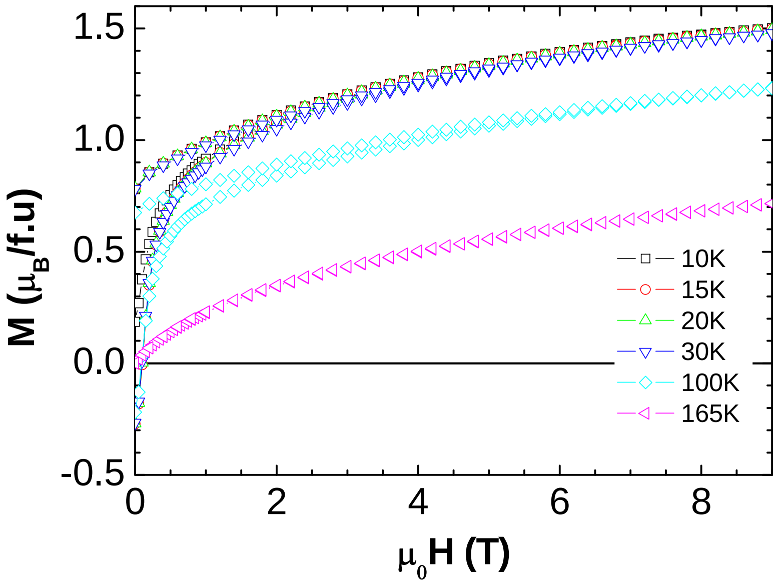
Ru-perovskites – magnetism

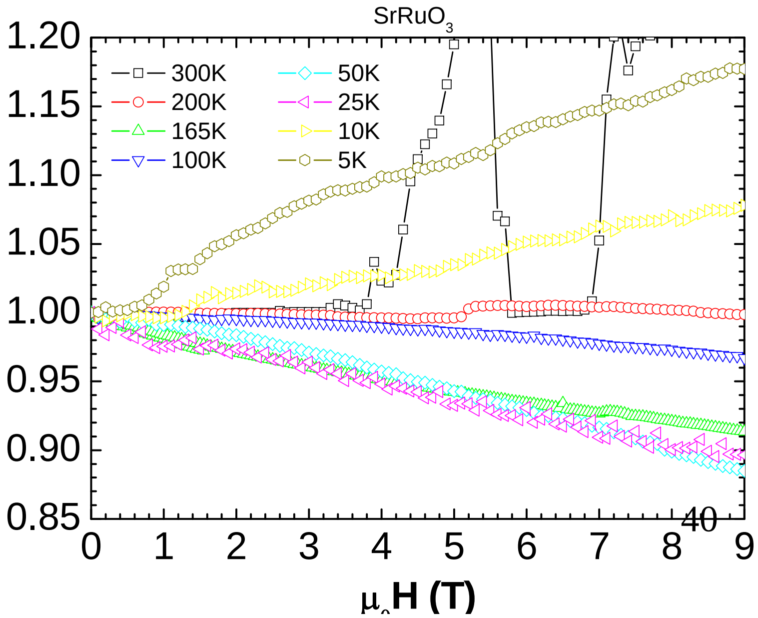
$SrRuO_3$





```
Data: AM945n3_S2
Model: TEPspin2
Chi^2 = 0.03763
So        5.13195        ±0.02409
g         2         ±0
Temp      20        ±0
mB        2         ±0
Tc        21.89043       ±0.2429
concentration   0.01141        ±0.00096
```





Properties of metallic ruthenates

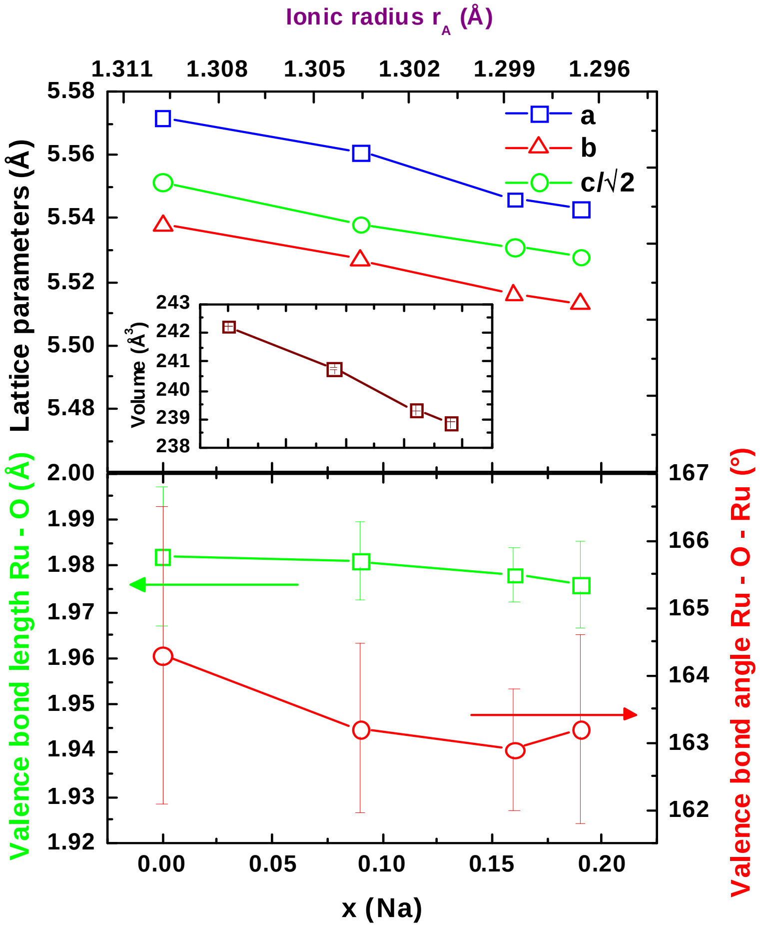
(Directly taken or calculated on a base of Reference below

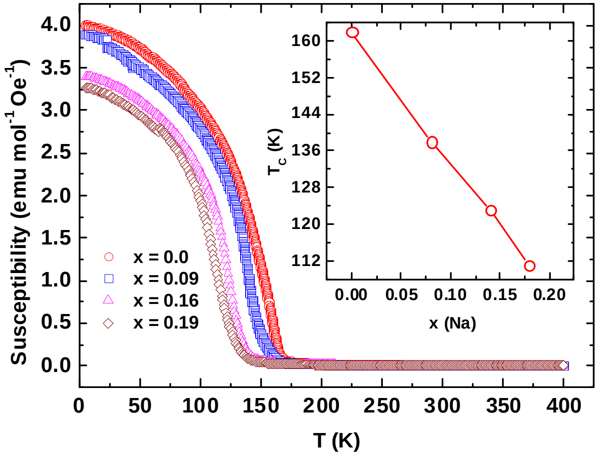
	$CaRuO_3$	$Ca_{0.83}Sr_{0.17}RuO_3$	$Ca_{0.5}Sr_{0.5}RuO_3$	$Ca_{0.25}Sr_{0.75}RuO_3$	$SrRuO_3$	$BaRuO_3$	Sr_2RuO_4	RuO_2
μ_{eff} (μ_B)	2.1 2.2	2.4	2.8	2.8	2.8,2.8	-	4.95	
Θ_C (K)	-57 -68	14	57	82	+170 170	-	-2100	
$\chi_o^{experiment}$ $*10^{-4}$ (emu $mol^{-1}Oe^{-1}$)	6.9 7	29	13	21	8.7 9	<3		1.39
γ ($Jmol^{-1}K^{-2}$)	-74 75	95	60	95	29 30	7.7		5.77
m^*/m_0 ($\sim \gamma/\gamma_{bare}$)	6 m_0				3.4 m_0			
$\chi_o^{calcul} = 3\mu_B^2\, \gamma/\pi^2 k_B^2$ (emu $mol^{-1}Oe^{-1}$)$*10^{-4}$	10	12.8	8.1	12.8	3.9			0.78
$R_W = \pi^2 k_B^2/3\mu_B * \chi_o^{exp}/\gamma$	0.7	2.26	1.6	1.6	2.3	<2.9		1.7
$n^{200\ K}(cm^{-3}) * 10^{22}$	+1.5 0.9		+0.9	+0.9	+1.2 +1.8	+0.7	->10 (comp)	5.6
$n^{5\ K}(cm^{-3}) * 10^{22}$	-3		+0.3	+0.3	-1.8			5.0 (77K)
$\rho^{300\ K}(\mu\Omega cm)$	~200 200 3000		~600		~200 200 1000	~100	~100 20000	35 330
$S^{800\ K}$ (μVK^{-1})	32				32		24 (700 K)	10
$S^{300\ K}$ (μVK^{-1})	32				34		28	0
$S^{20\ K}$ (μVK^{-1})	0.6				5.0		5.7	2.7
$S/T^{10\ K}$ (μVK^{-2})	0.0 !!				0.27		0.28	0.12

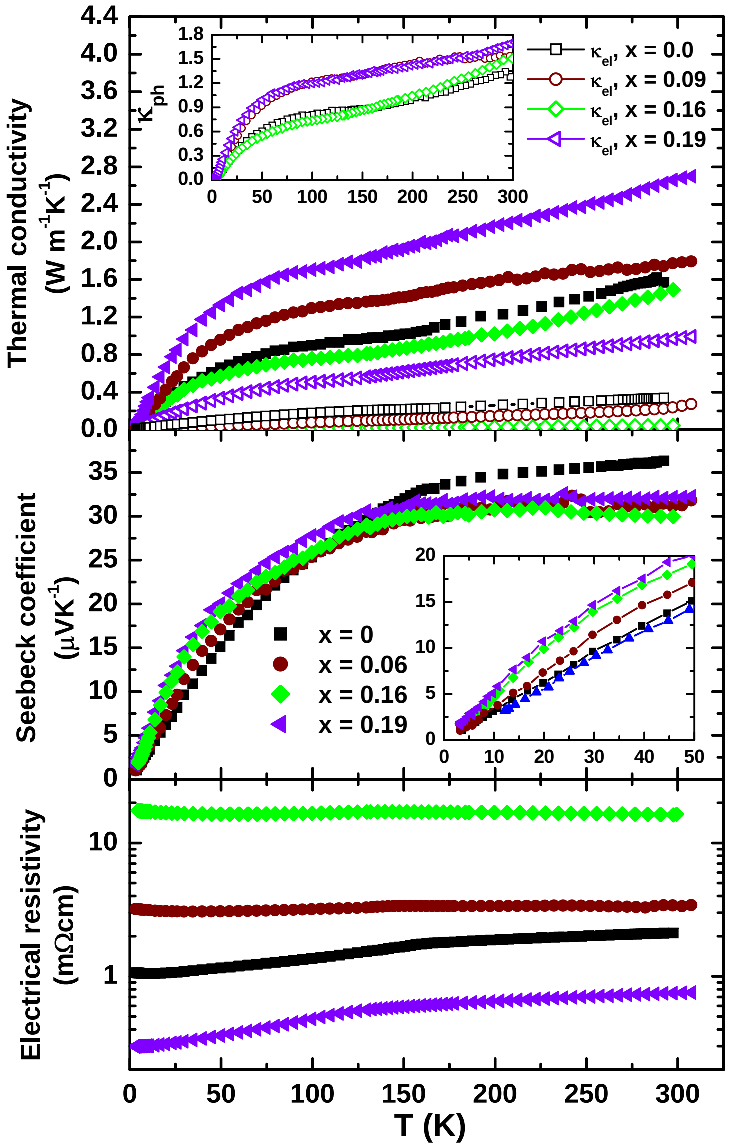
Reference: J. Appl.Phys, 81(8), 4978, PRB, 51, 16432, PRB,63,R 161102, PRB,56, 321, Phys.Rev.,37,303(1931), PhysRevB,Vol1,1494(1970), our data

$SrRuO_3$ thin layers (properties at 4 K), APL 82,No.3 ,427,
Majority carriers , l = 45 Å
Minority carriers , l = 80 Å
Spin polarization ~ 50 % due to different Fermi velocity of ↑(spin up) ↓ (spin down) carriers, NOT DIFFERENT CONCENTRATION
Fermi velocity – majority ∅ $\langle \| v \| \rangle = 0.65 * 10^{5}\ ms^{-1}$
Fermi velocity – minority ∅ $\langle \| v \| \rangle = 1.1 * 10^{5}\ ms^{-1}$

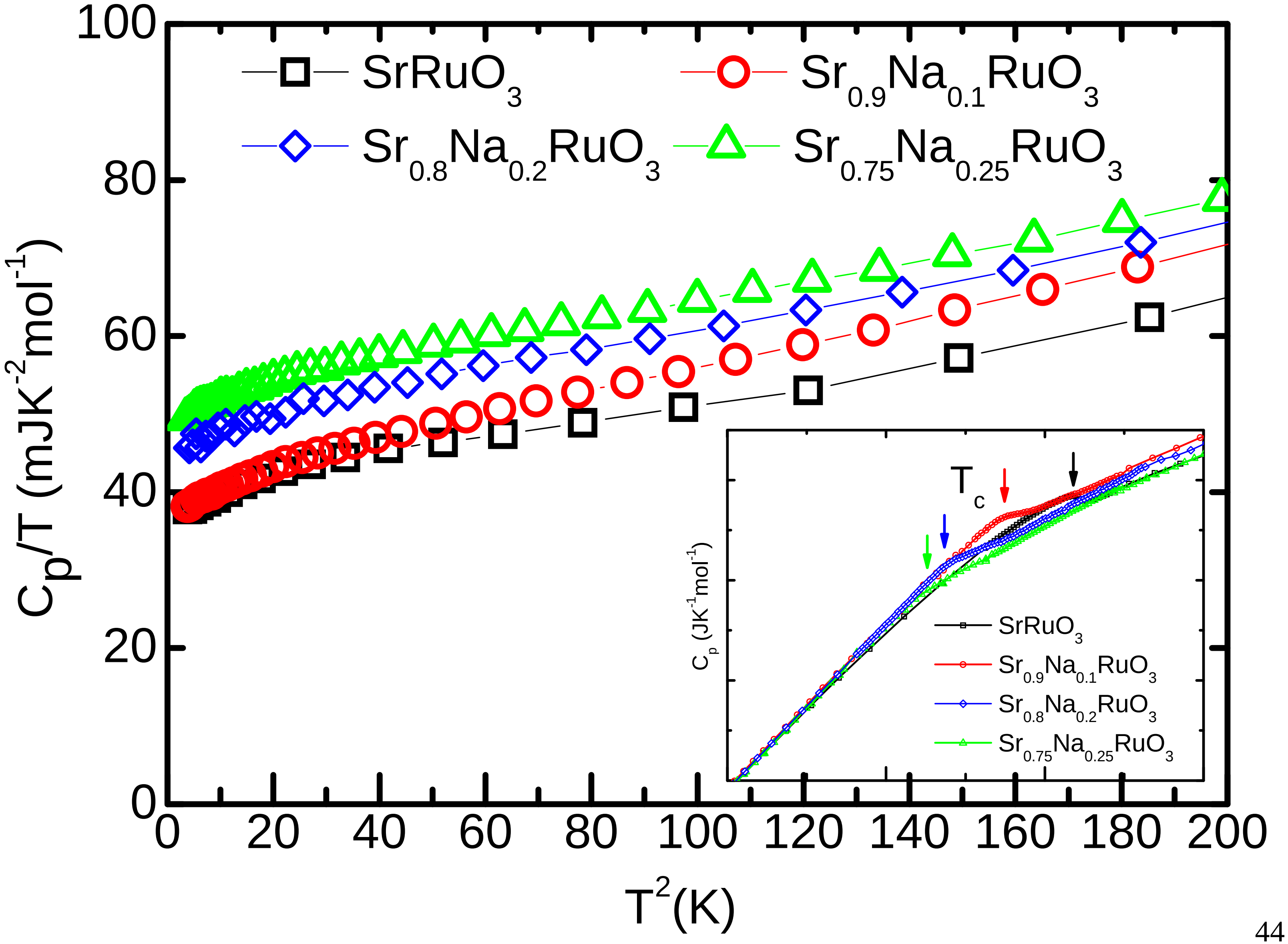
Sr$_{1-x}$Na$_x$RuO$_3$



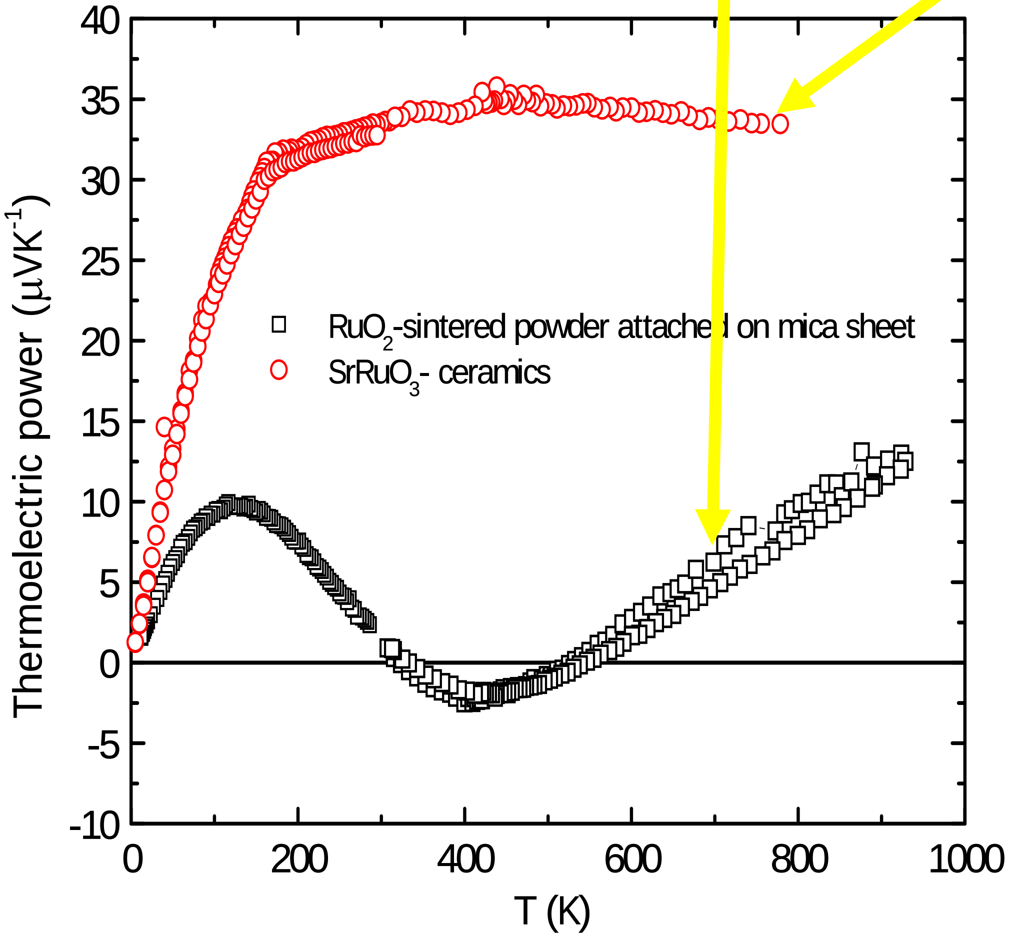




$Sr_{1-x}Na_xRuO_3$



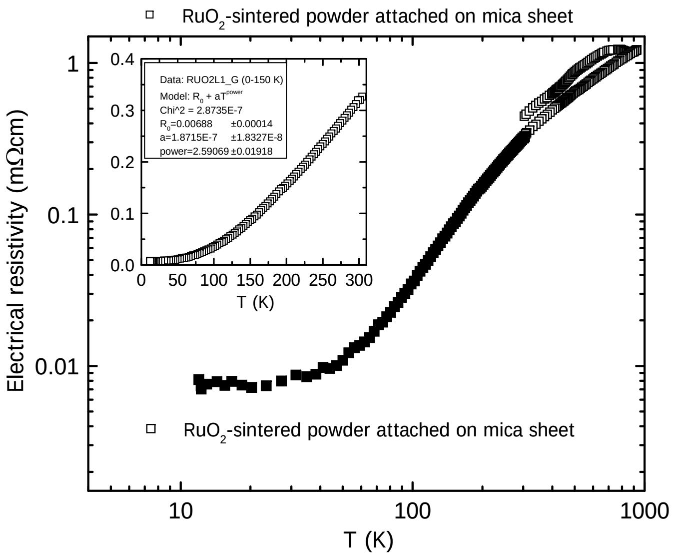
Common oxide metals
RuO_2- Pauli metal vs. $SrRuO_3$ – CW metal,



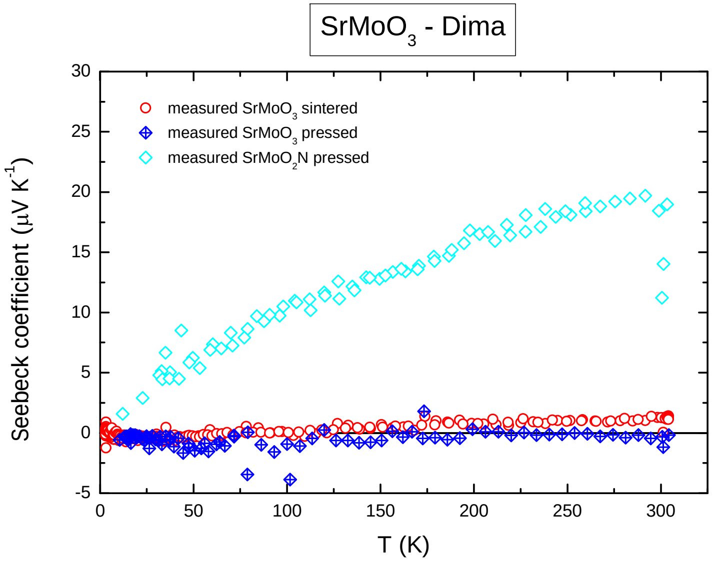
$$S_{mag} = -\frac{k_B}{e}\ln\left(\frac{2S^n+1}{2S^{n+1}+1}\right) = +35\mu VK^{-1}$$

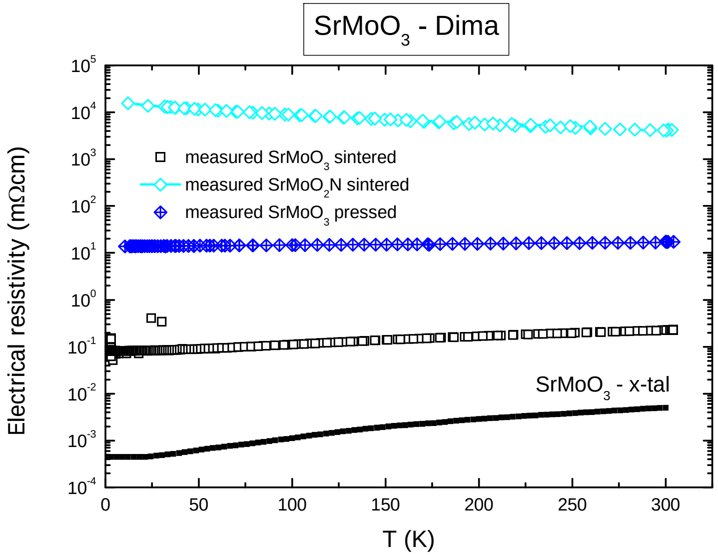
➢a configurational entropy approximation applies

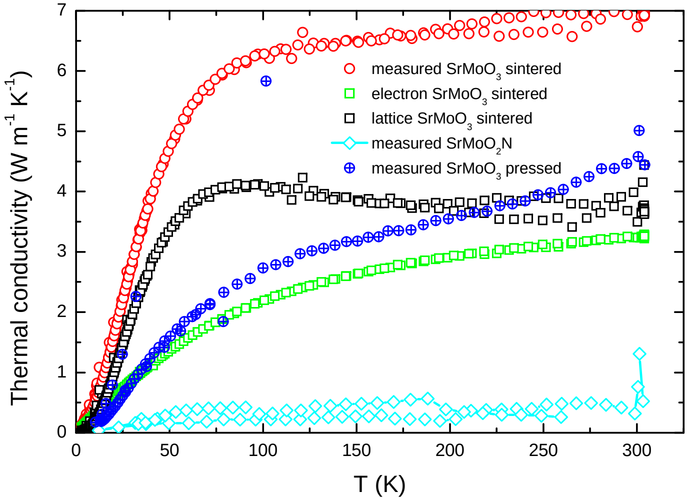
(magnetic, no orbital contribution) S_{Heiks}= +35 μVK^{-1}



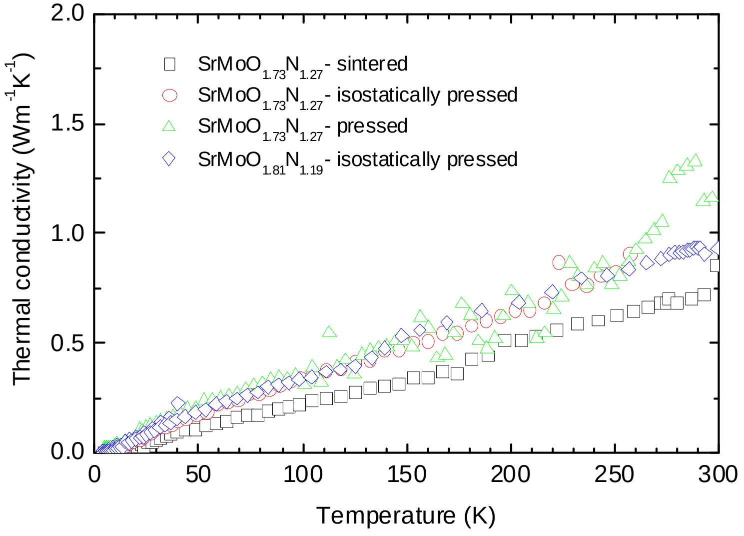
Molybdenates – sintering, synthesis, properties

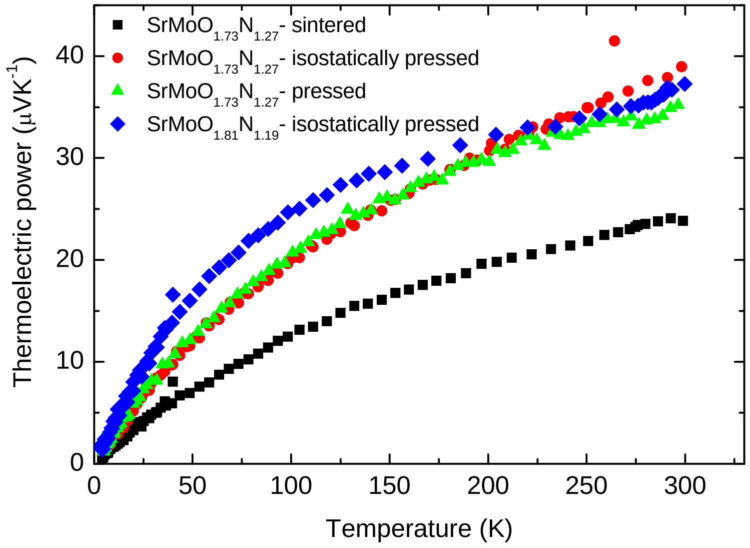


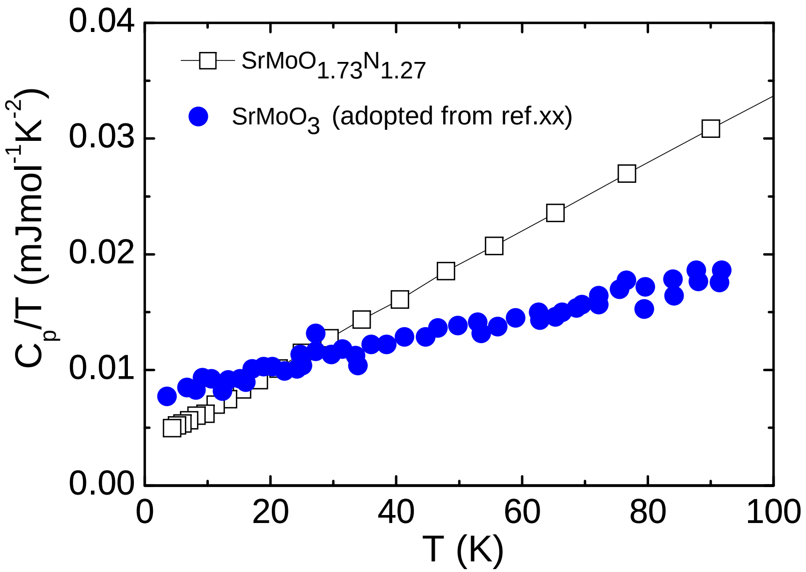


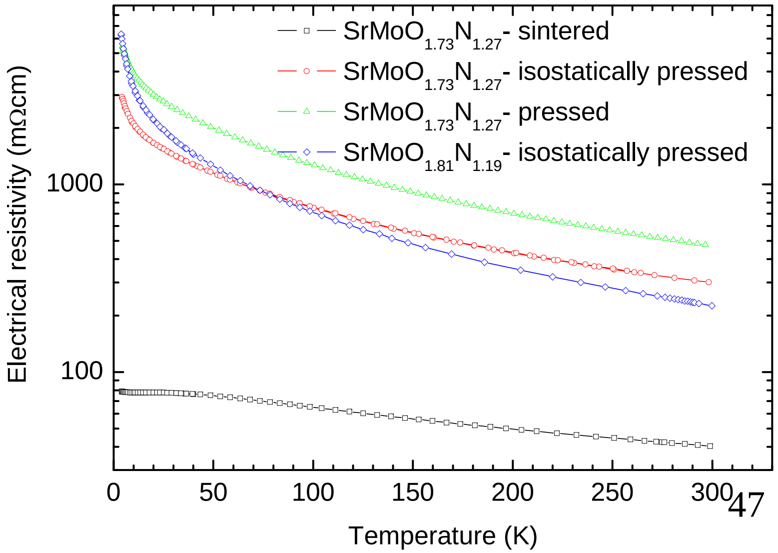


Molybdenates – oxynitride









Transition metal perovskites and thermoelectricity

- Oxide perovskites represent an interesting class of chemically stable materials with a potential to be used as high-temperature thermoelectrics
- Both diffusive “metallic” (linear od quasilinear in T) or “hopping” (temperature independent) thermopower behaviour is observed in highly electrically conducting perovskites
- Magnetic interactions of conducting electron-holes are likely at the origin of dominance of thermopower configurational entropy character over the diffusive one
- $Cr^{3+/}$ Cr^{4+} perovskites represent a unique example where the orbital degree of freedom to the configurational entropy applies
- Curie-Weiss magnetic behaviour seems to be the essential perquisite for the magnetic contribution to the thermopower
- Magnetic and/or spin-state fluctuations are efficient in lowering thermal conductivity as evidenced for Co perovskites

Acknowledgments

We acknowledge the financial support from the Grant Agency of the ASCR. and GACR, Grant No. 202/06/0051.