The Seebeck coefficient in oxides : the example of misfits and related compounds

Sylvie Hébert
Laboratoire CRISMAT
Caen, France

ENSICAEN
ÉCOLE NATIONALE SUPÉRIEURE D'INGÉNIEURS DE CAEN
& CENTRE DE RECHERCHE

NGSCES Santiago de Compostela, July 2011

cnrs
advancing the frontiers

Laboratoire CRISMAT

Cristallographie et Sciences des Matériaux

Caen

Outline

- Introduction to thermoelectric effects

How to get large ZT : nanostructuration / reduction of κ / strong electronic correlations

The Na_xCoO_2 family

- The misfit cobalt oxides

- New materials with edge shared octahedra

Introduction :
Thermoelectric effects

Thermoelectric effects

$$\Delta V \Leftrightarrow \Delta T$$

Seebeck effect ($\Delta T \Rightarrow \Delta V$) : thermogenerators

Peltier effect ($\Delta V \Rightarrow \Delta T$) : cooling systems

$S = \Delta V / \Delta T$

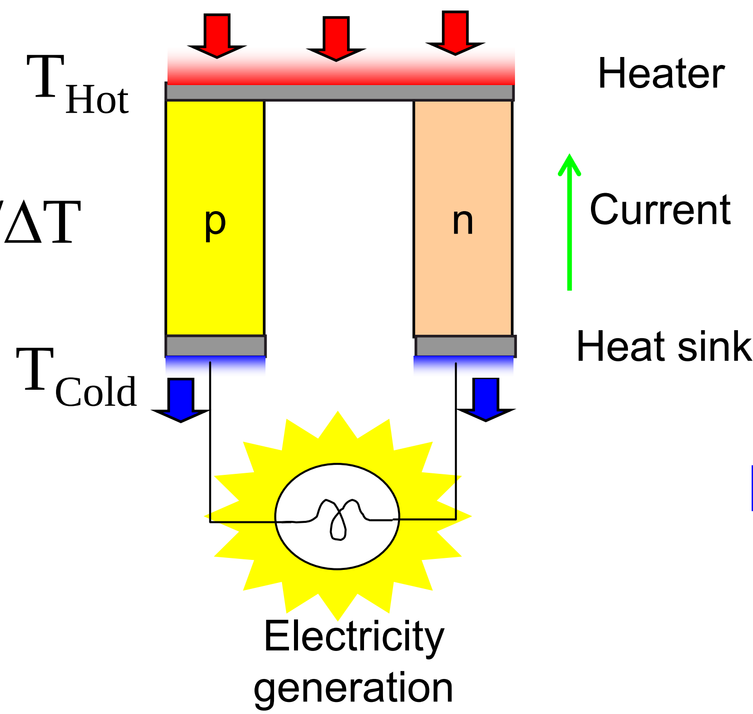


Figure of merit $$Z = \frac{S^2}{\rho\kappa}$$

Power factor $$PF = \frac{S^2}{\rho}$$

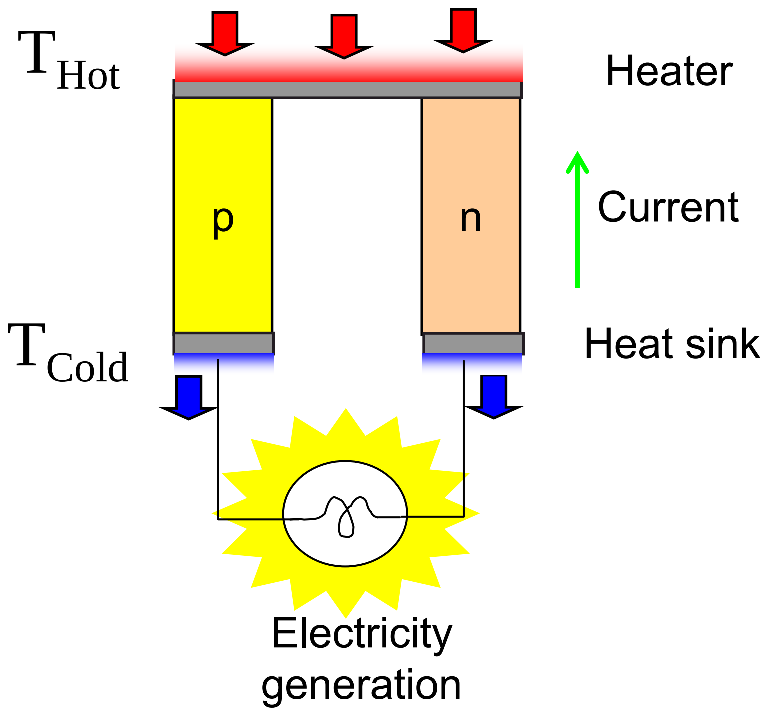
Efficiency of a thermogenerator

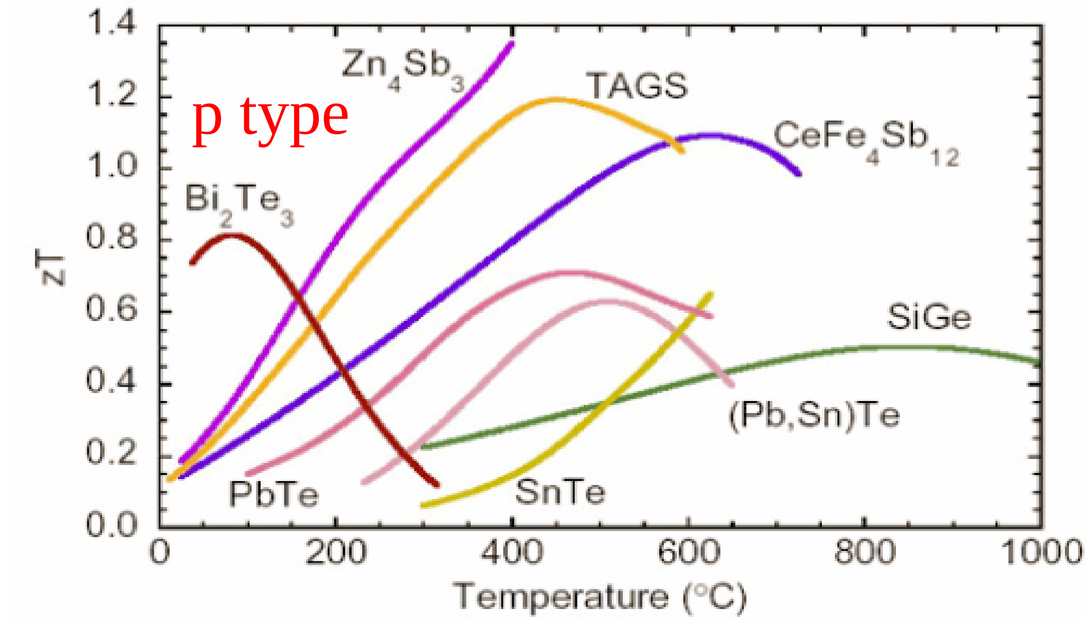
$$\eta_{max} = \frac{T_h - T_c}{T_h} \frac{\sqrt{1+ZT_m} - 1}{\sqrt{1+ZT_m} + \frac{T_h}{T_c}} = \eta_{Carnot} \frac{\sqrt{1+ZT_m} - 1}{\sqrt{1+ZT_m} + \frac{T_h}{T_c}}$$

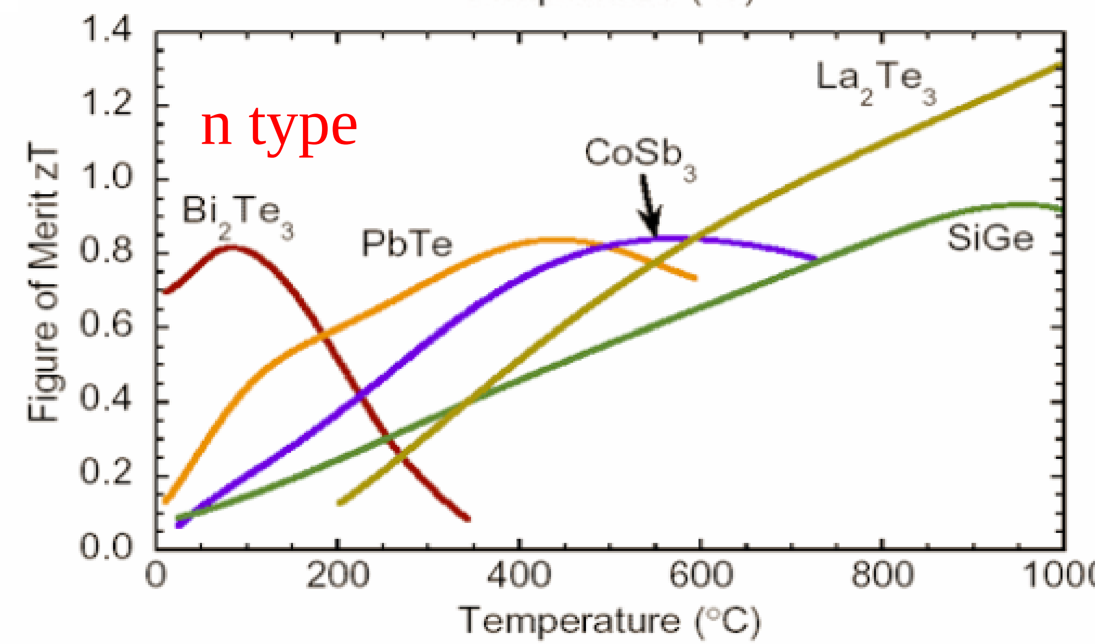
For applications : n and p type materials with

ZT > 1

Classical thermoelectrics







J. Snyder et al., Nature Materials 7, 105 (2008)

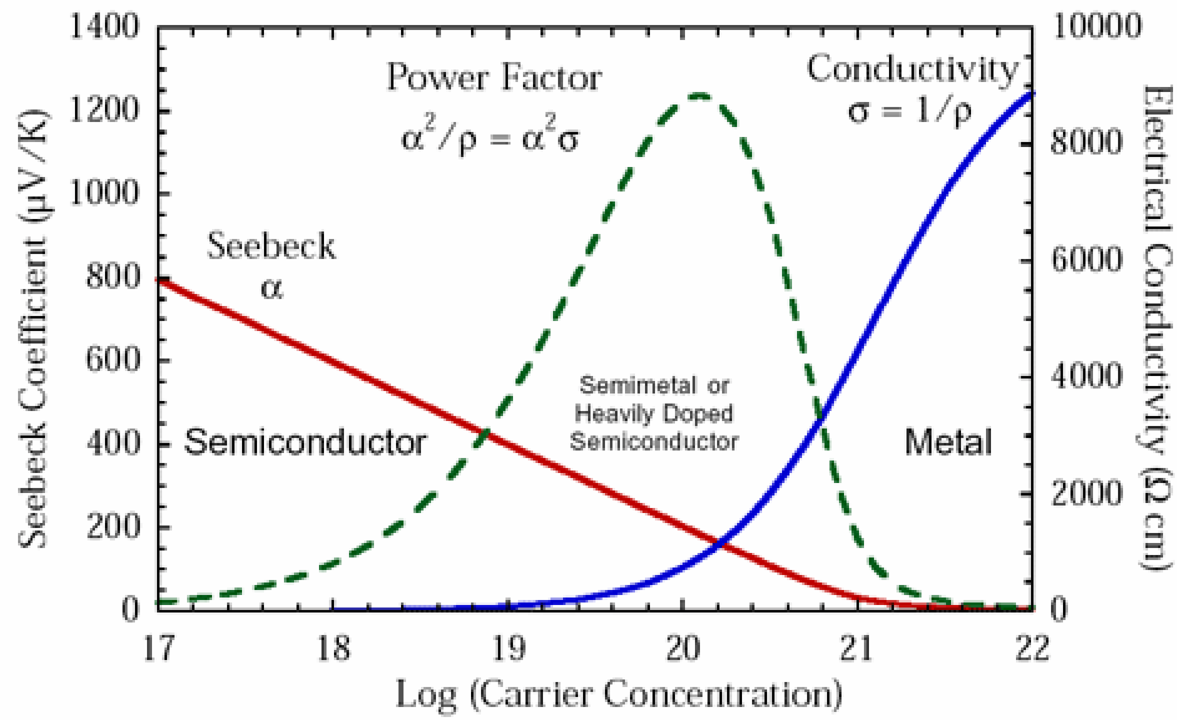
Thermoelectric materials

How to get a large $ZT = \frac{S^2 T}{\rho \kappa}$????

Problem : S, κ, ρ are linked through the Density of States (n)

$PF = S^2/\rho$

Heavily doped semi-conductors and semi-metals are the best candidates



$$ZT = \frac{S^2T}{\rho\kappa} = \frac{S^2T}{\rho(\kappa_e + \kappa_l)}$$

‘PGEC’

Phonon glass – Electron crystal

G. Slack, Handbook of Thermoelectricity (1995)

Power factor
Modification of DOS

- Nanostructuration
- Electronic correlations

Lattice part of thermal conductivity

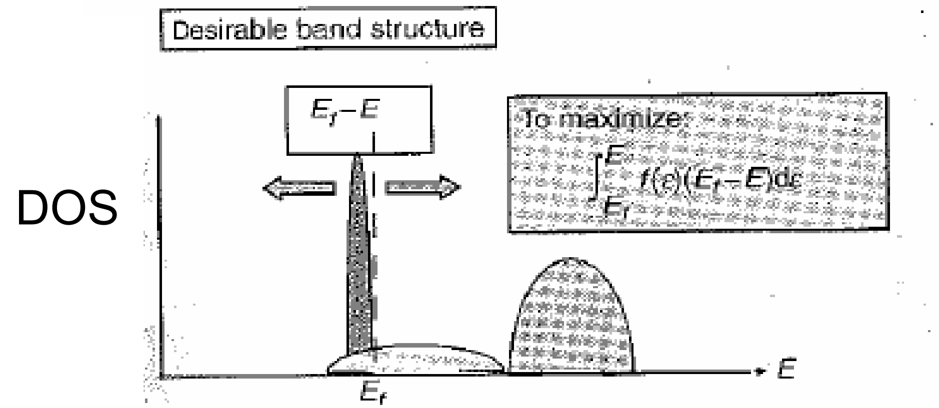
- Nanostructuration
- ‘Rattling’

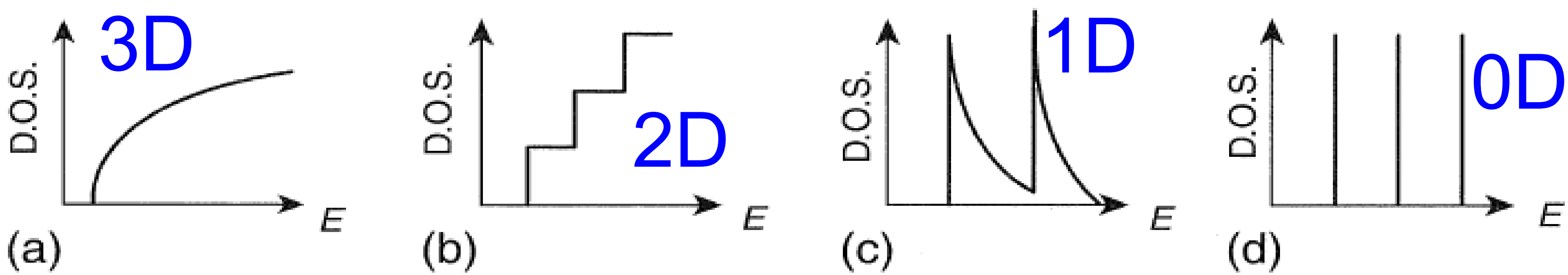
Introduction :
Nanostructuration

Mott's formula

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

Tse et al., Handbook of Thermoelectricity (2006)





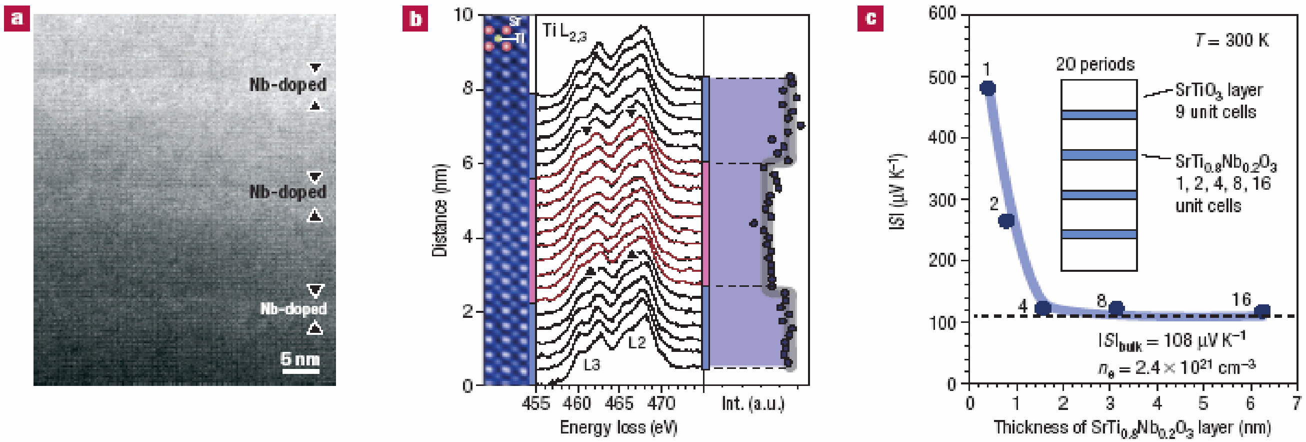
increase of S

Hicks et Dresselhaus, PRB47, 12727 (1993)
Hicks et Dresselhaus, PRB47, 16631 (1993)

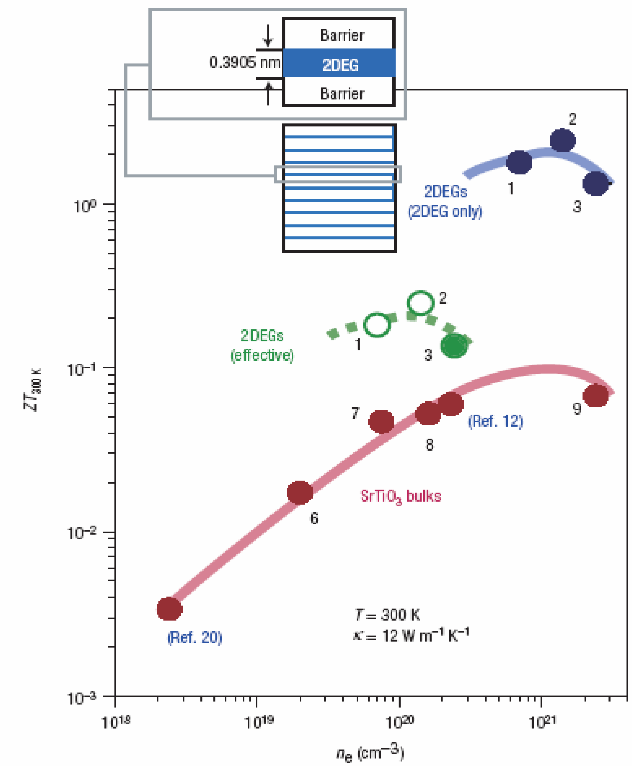
Giant thermoelectric Seebeck coefficient of a two-dimensional electron gas in $SrTiO_3$

HIROMICHI OHTA[1,2,3*], SUNGWNG KIM[4], YORIKO MUNE[1], TERUYASU MIZOGUCHI[5], KENJI NOMURA[3], SHINGO OHTA[1], TAKASHI NOMURA[1], YUKI NAKANISHI[1], YUICHI IKUHARA[5], MASAHIRO HIRANO[3], HIDEO HOSONO[3,4] AND KUNIHITO KOUMOTO[1,2]

[1]Nagoya University, Graduate School of Engineering, Furo-cho, Chikusa, Nagoya 464-8603, Japan
[2]CREST, JST, 4-1-8 Honcho, Kawaguchi 332-0012, Japan
[3]ERATO-SORST, JST, in Frontier Collaborative Research Center, Tokyo Institute of Technology, 4259 Nagatsuta, Midori, Yokohama 226-8503, Japan
[4]Frontier Collaborative Research Center, Tokyo Institute of Technology, 4259 Nagatsuta, Midori, Yokohama 226-8503, Japan
[5]Institute of Engineering Innovation, The University of Tokyo, 2-11-16 Yayoi, Bunkyo, Tokyo 113-8656, Japan
*e-mail: h-ohta@apchem.nagoya-u.ac.jp



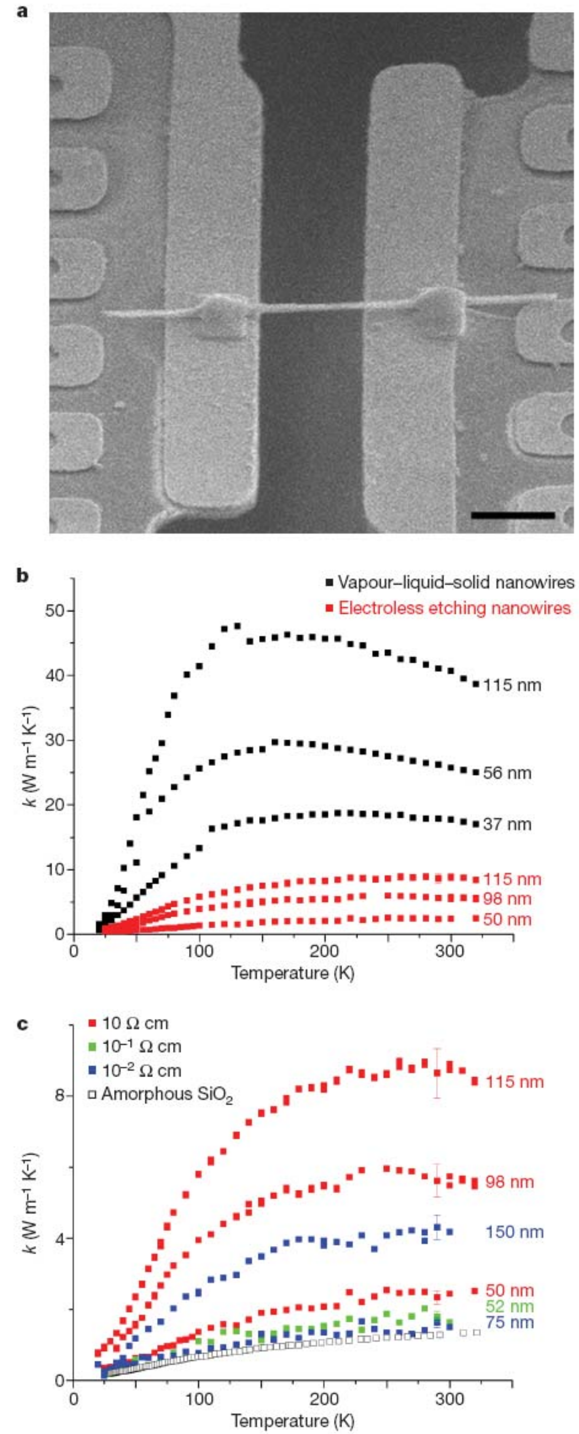
Nature Materials, 6, 129 (2007)



Extrapolation to ZT_{2DEG} = 2.4 at 300K

Silicium nanowires

A. I. Hochbaum et al., Nature 451, 163 (2008)
A. I. Boukai et al., Nature 451, 168 (2008)



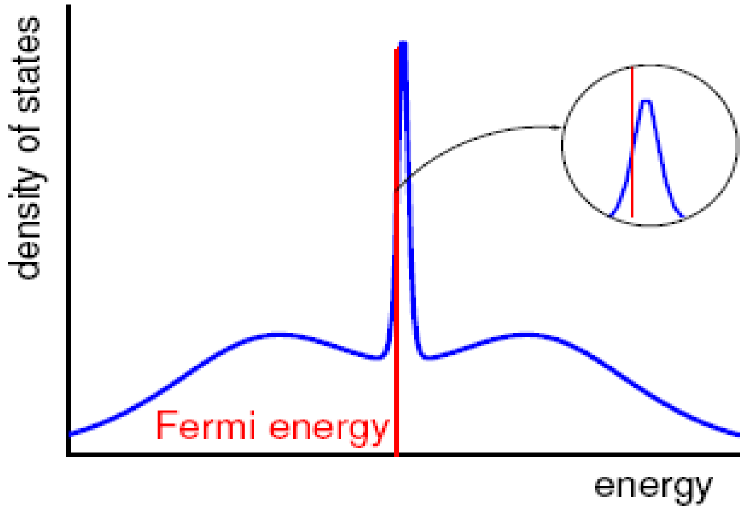
Bulk Si : ZT ~ 0.01 at 300K

↳ZT = 0.6 at 300K
for nanowires

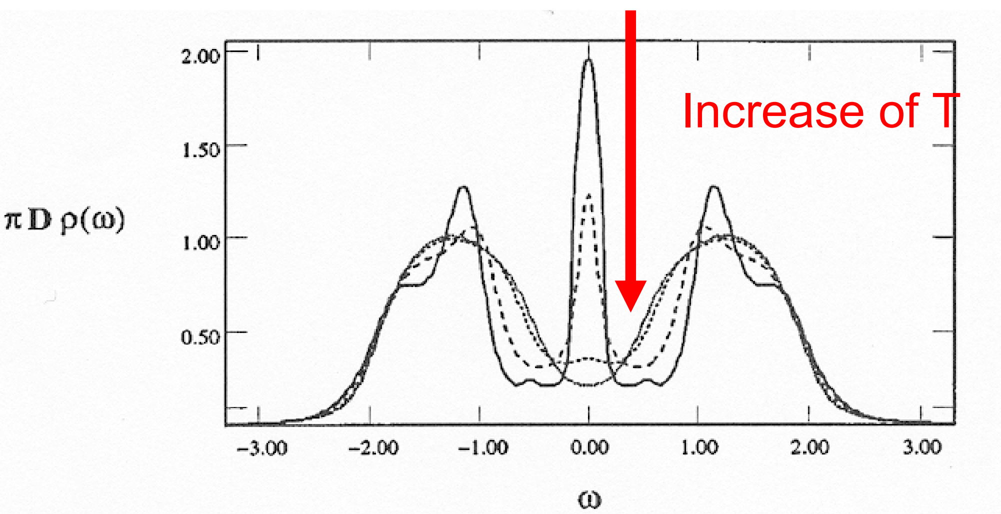
ZT enhancement mainly due to phonons :
Reduction of κ + phonon drag for S

Introduction :
Electronic correlations

Electronic correlations



Modification of DOS



Kondo insulators, Heavy fermion compounds, oxides…

A. Georges et al, Review of Modern Physics 68, 13 (1996)

Low T limit

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

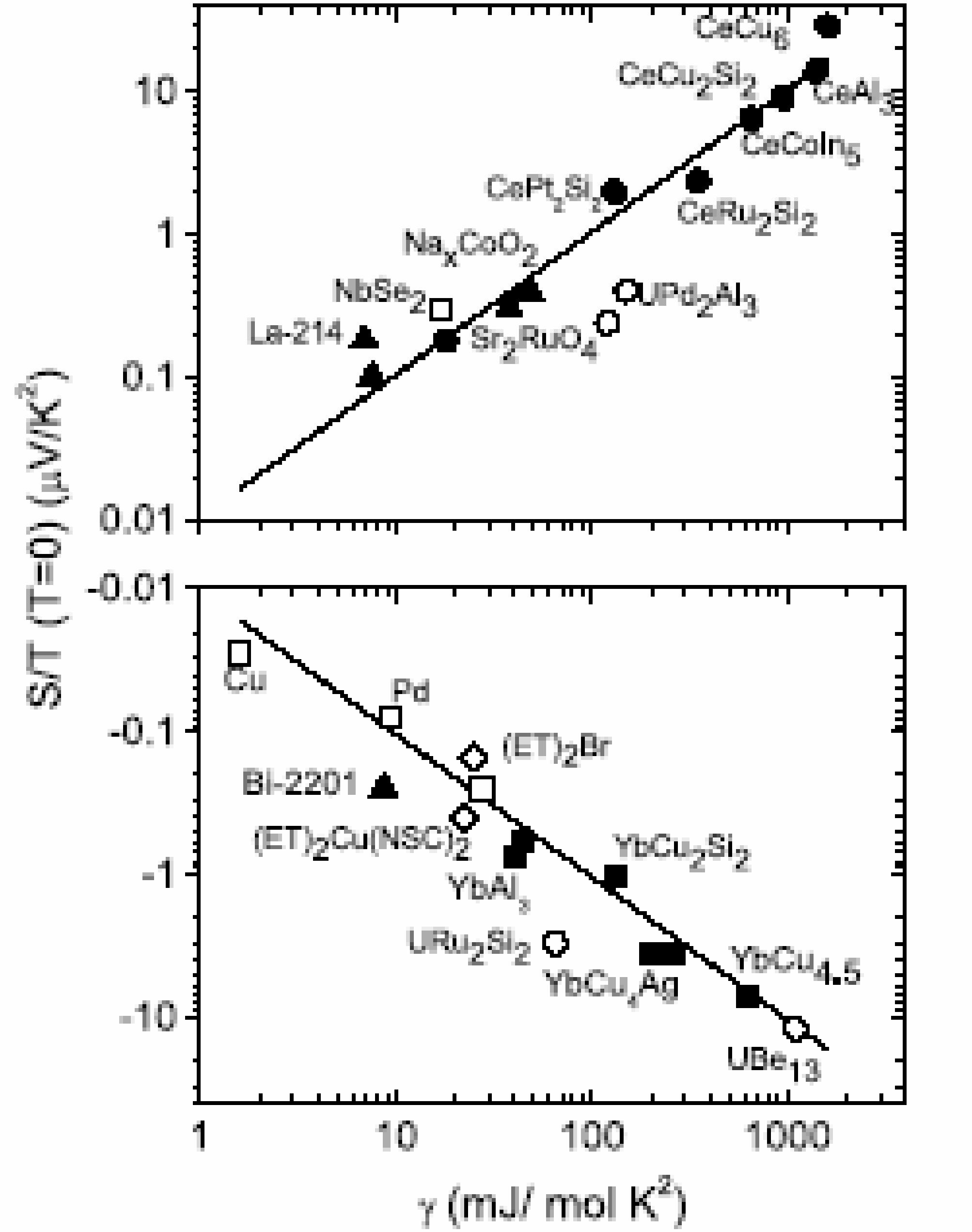
$$C_{el} / T = \gamma = \frac{\pi^2}{3} k_B^2 N(E_F)$$

Universal value for the ratio of S / γ

Limit T→ 0

$$q = \frac{S}{T} \frac{N_{Av} e}{\gamma} = cste$$

$$0.5 < |q| < 2$$



K. Behnia et al. JPCM 16, 5187 (2004)

High T limit : Hubbard model

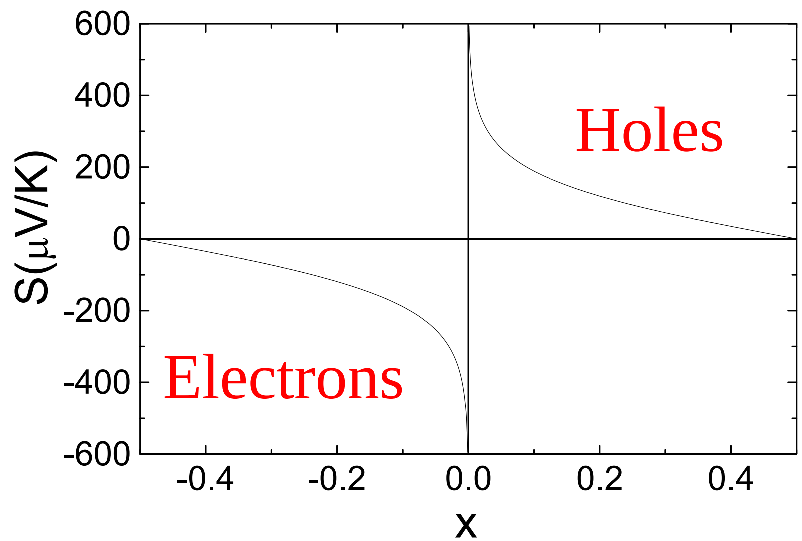
$$S = \frac{-S^{(2)}/S^{(1)} + \mu/|e|}{T} \rightarrow \frac{\mu/|e|}{T} \qquad \text{for } T \rightarrow \infty$$

$S^{(1)}$, $S^{(2)}$: depends on v and Q, velocity and energy operators
Valid for narrow band systems with strong interactions

Limit $T \rightarrow \infty$: S ~ entropy / carrier

$$S = \frac{-k_B}{|e|} \ln\left(\frac{1-x}{x}\right)$$

x = carrier concentration



P. Chaikin et al. Phys. Rev. B 13, 647 (1976)

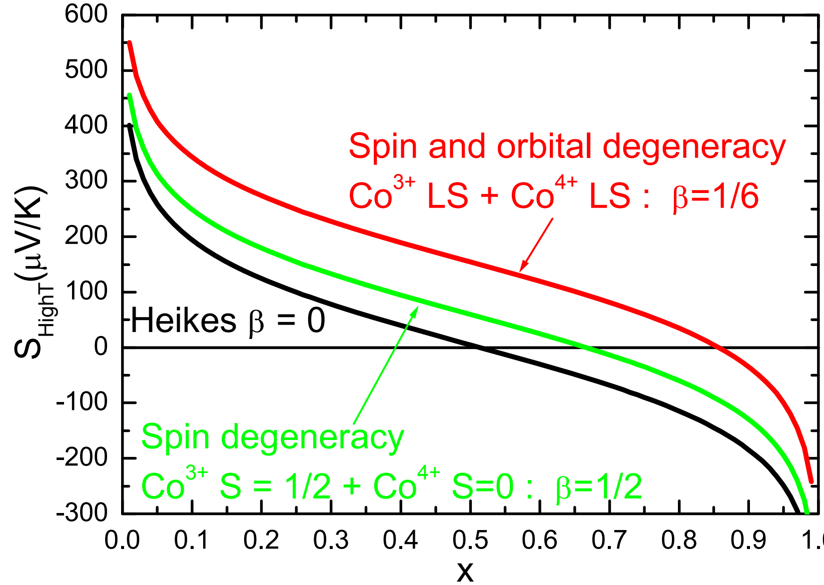
Spin and orbital degeneracy

Narrow band systems with strong interactions : the Hubbard model

$$S = \frac{-S^{(2)}/S^{(1)} + \mu/|e|}{T} \rightarrow \frac{\mu/|e|}{T} \quad \text{for } T \rightarrow \infty$$

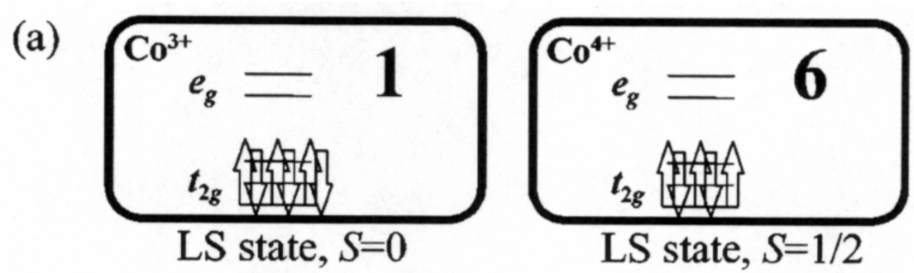
Limit T →∝ : S ~ entropy / carrier

$$S = \frac{-k_B}{|e|}\ln\left(\frac{1-x}{x}\right)$$



+ Spin and/or orbital degeneracy β

$$S = -\frac{k_B}{|e|}\ln\left(\beta\frac{1-x}{x}\right)$$



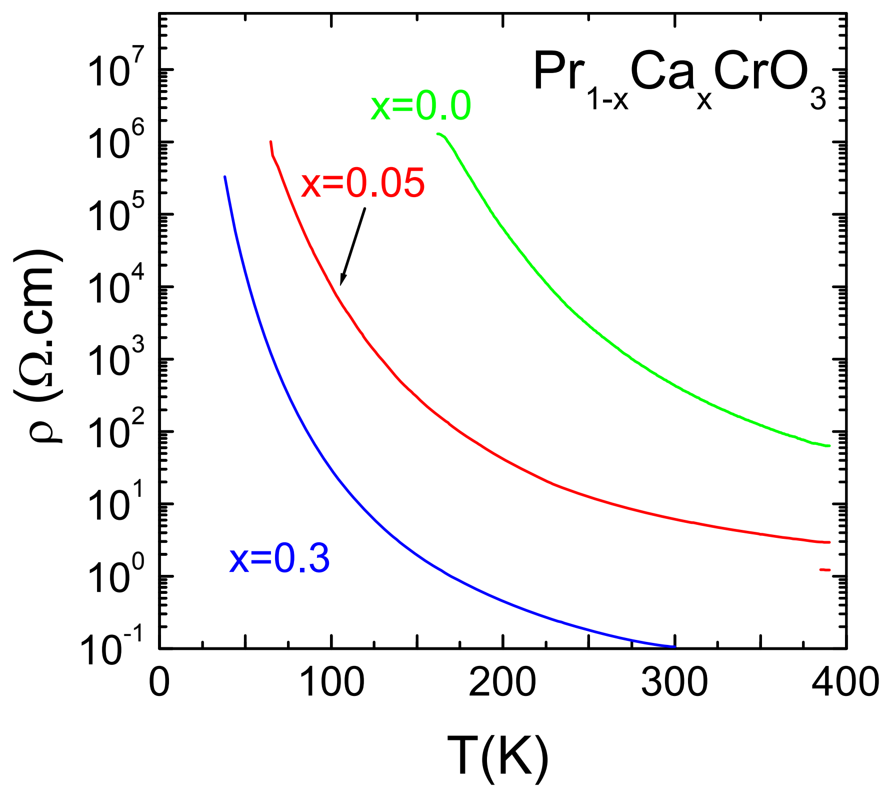
$g_4/g_3 = 6$

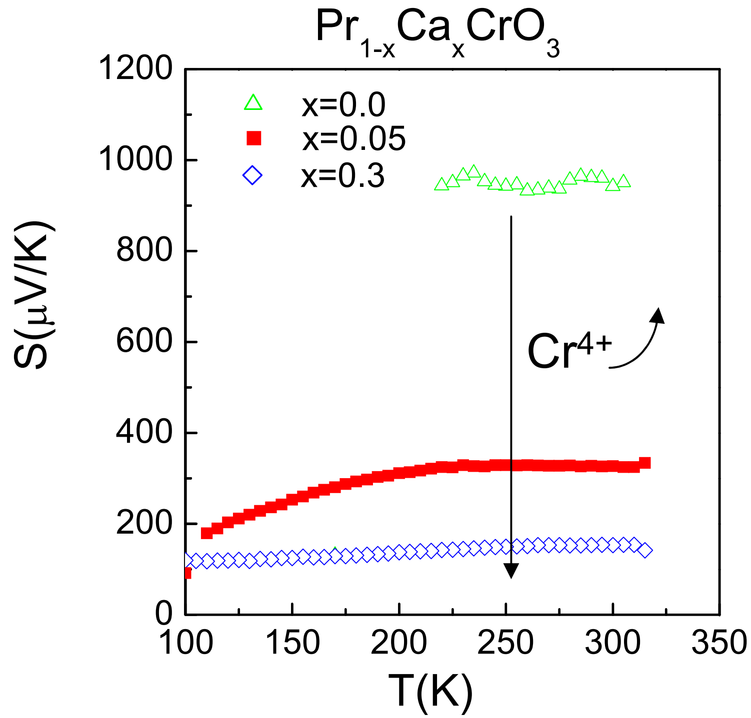
Chaikin et al. Phys. Rev. B 13, 647 (1976)
J. P. Doumerc JSSC 110, 419 (1994)
Koshibae et al., Phys. Rev. B 62, 6869 (2000)

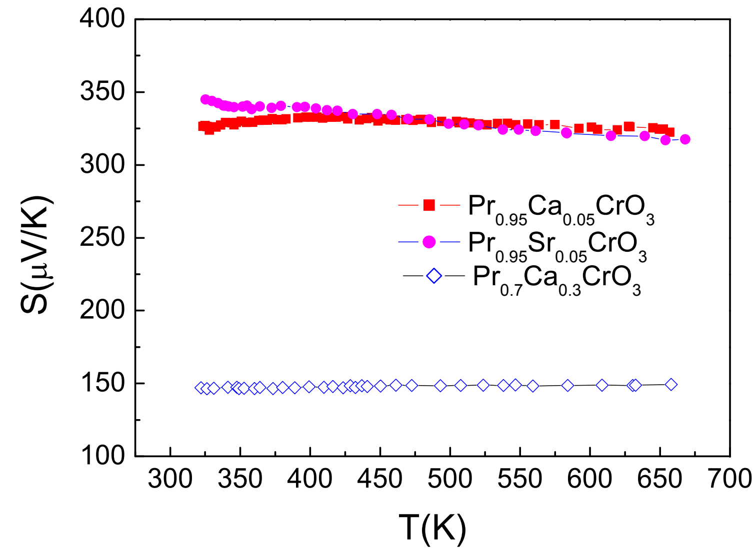
Orthochromites

Semiconducting behavior

$Pr^{3+}_{1-x}Ca^{2+}_{x}Cr^{3+/4+}O_3$: $3d^3/3d^2$



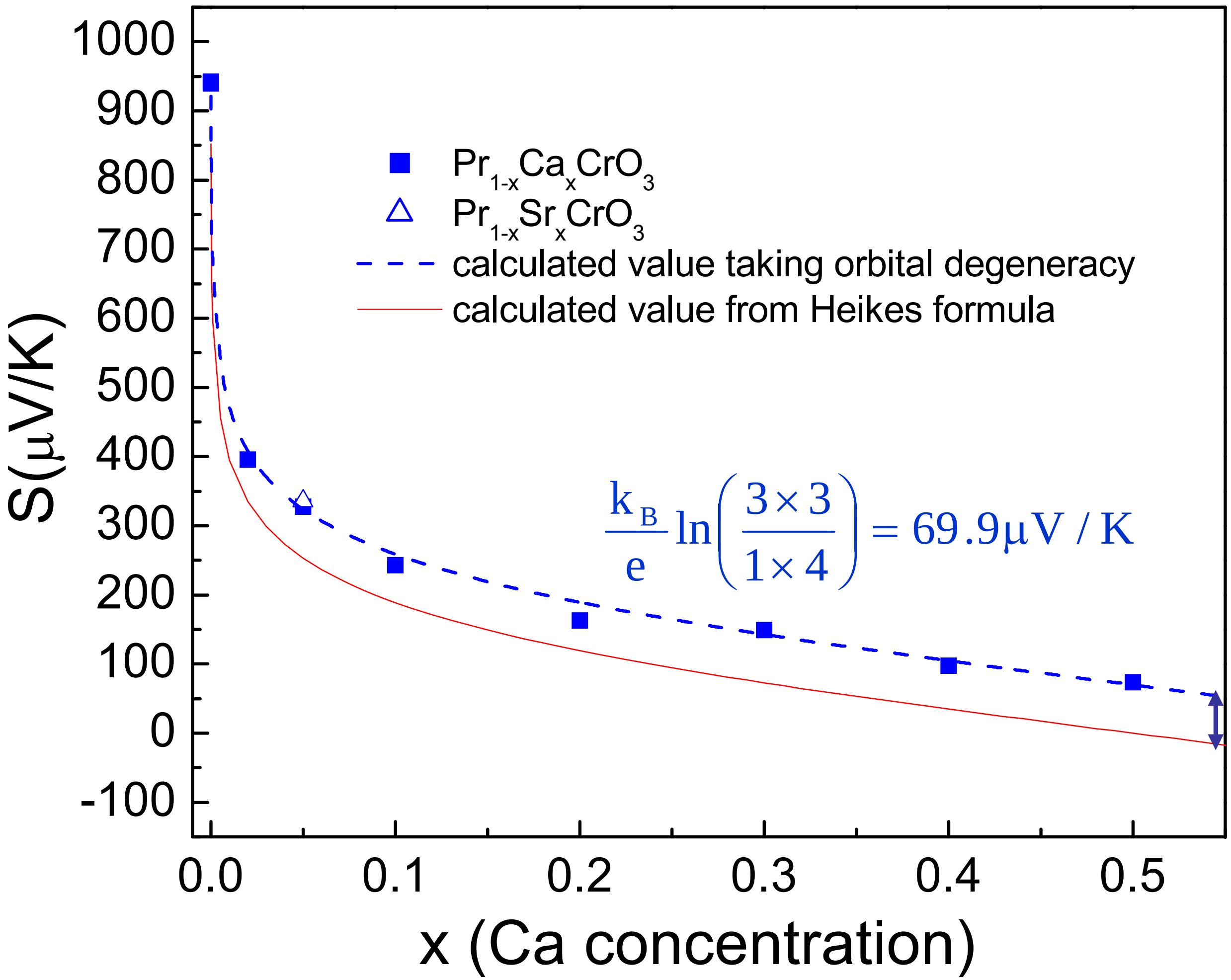




S. Pal et al., Eur. Phys. J. B 53, 5 (2006)

Heikes formula with spin and orbital degeneracy

$$S = \frac{-k_B}{|e|}\ln\left(\frac{1-x}{x}\right) + \frac{k_B}{|e|}\ln(\Gamma_{orb}\Gamma_{spin})$$



$3d^3$	$3d^2$
$\Gamma_{orb}=1$	$\Gamma_{orb}=3$
$\Gamma_{spin}=4$	$\Gamma_{spin}=3$

Marsh and Parris, Phys. Rev. B 54, 7720 (1996)

Introduction :

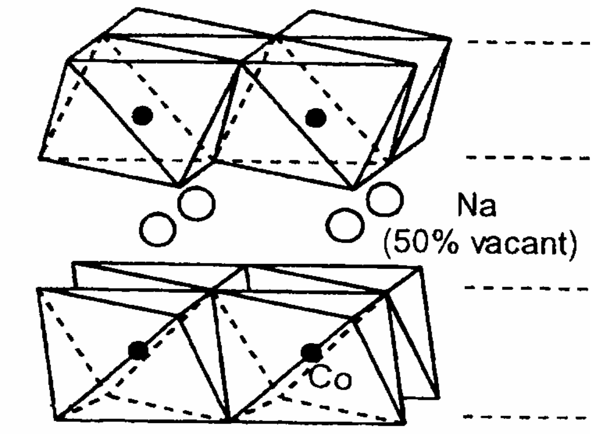
Na_xCoO_2

$Na_{0.7}CoO_2$

‘ Phonon Glass / Electron crystal ’

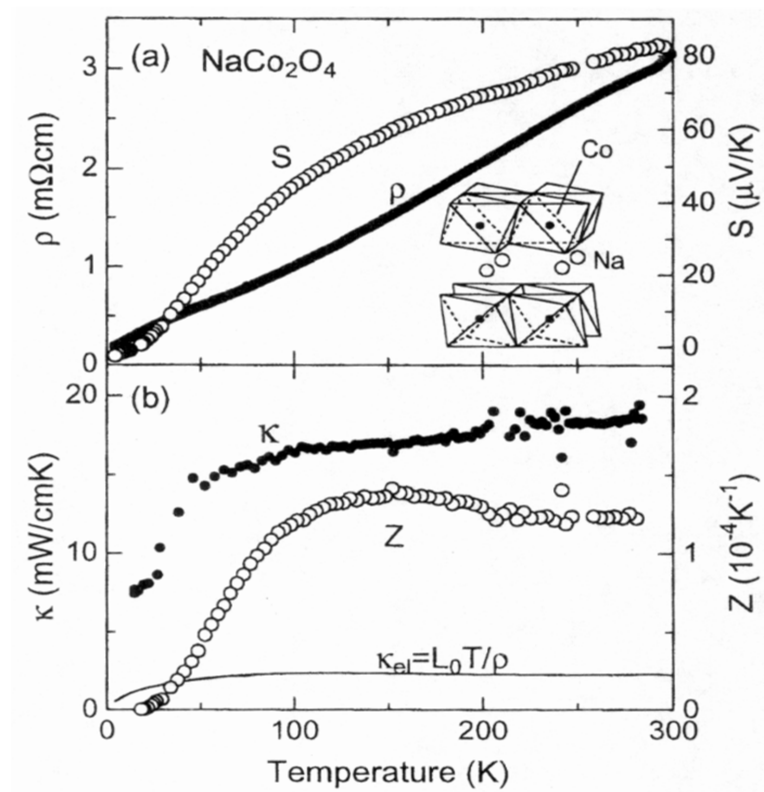
I. Terasaki et al., Phys. Rev. B 56, R12685 (1997)

Na_xCoO_2 : $Na^+_x Co^{3+}_x Co^{4+}_{1-x} O_2$



Triangular lattice
Co^{3+} ($3d^6$) / Co^{4+} ($3d^5$)
S = 0 and S = 1/2

Measurements on polycrystals



At 300K

Small κ (polycrystals) **$\kappa \sim 2 Wm^{-1}K^{-1}$**

(crystals) **$\kappa \sim 5 Wm^{-1}K^{-1}$**

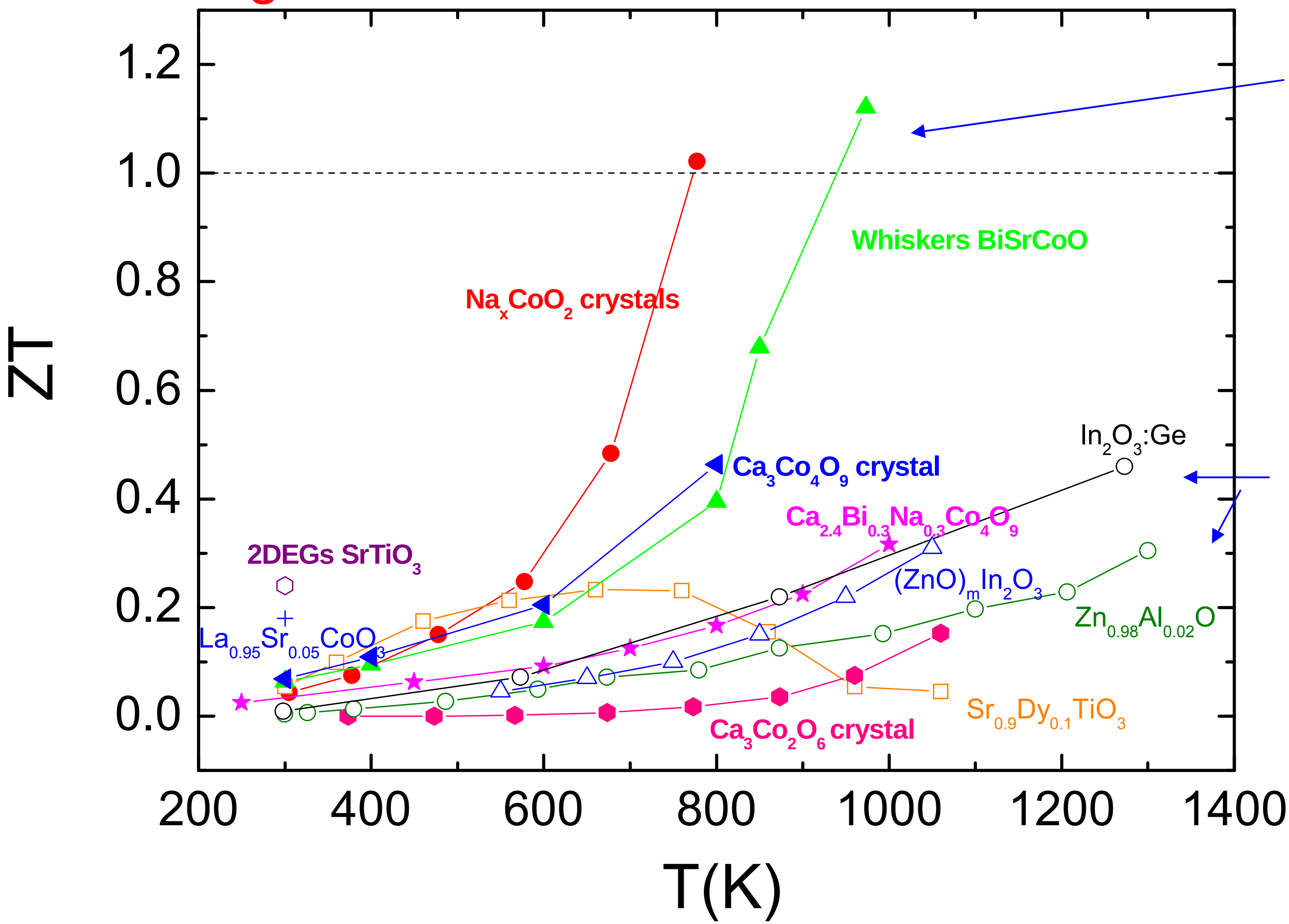
Power factor $P=S^2/\rho$ at 300K

$Na_{0.7}CoO_2$
$P= 50\ 10^{-4}\ WK^{-2}m^{-1}$

Bi_2Te_3
$P= 40\ 10^{-4}\ WK^{-2}m^{-1}$

ZT of oxides

Oxides :
Potentially stable in air,
at high T



p type :
Na_xCoO_2,
Misfit oxides

n type : TCOs

NaxCoO2 _ Fujita : JJAP 40, 4644 (2001); SrTiO3 _ Muta : J. Alloys and compounds 350, 292 (2003); Ca2.4Bi0.3Na0.3Co4O9 _ Xu : APL80, 3760 (2002); Whiskers BiSrCoO _ Funahashi : APL81, 1459 (2002); Ca3Co2O6 _ Mikami : JAP94, 10 (2003); 2DEGs(SrTiO3) _ Ohta : Nature Materials 6, 129 (2007); Ca3Co4O9 crystal _ Shikano : APL 82, 1851 (2003); LaSrCoO _ Androulakis : APL84, 1099 (2004); ZnAlO _ Ohtaki : JAP79, 1816 (1996)

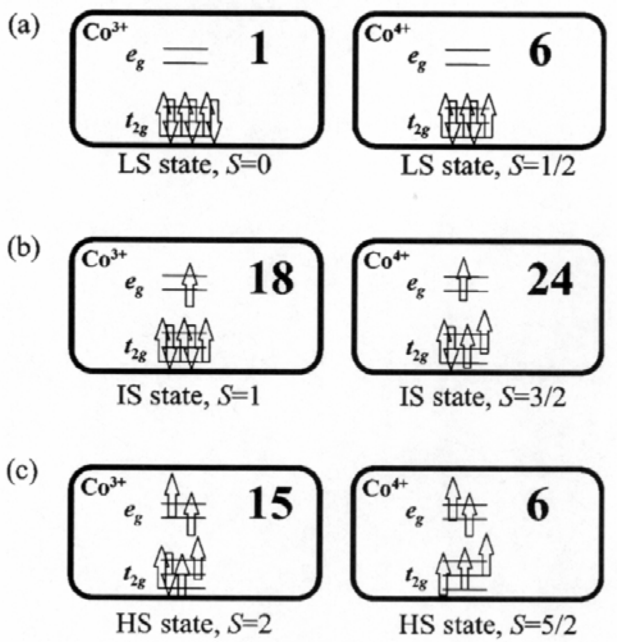
Origin of large S?

Localized picture : the generalized Heikes formula

At high T :

$$S = -\frac{k_B}{|e|}\ln\left(\frac{g_4}{g_3}\frac{1-x}{x}\right)$$

Spin and Orbital Degeneracy
Co^{3+} ($3d^6$)/Co^{4+} ($3d^5$)

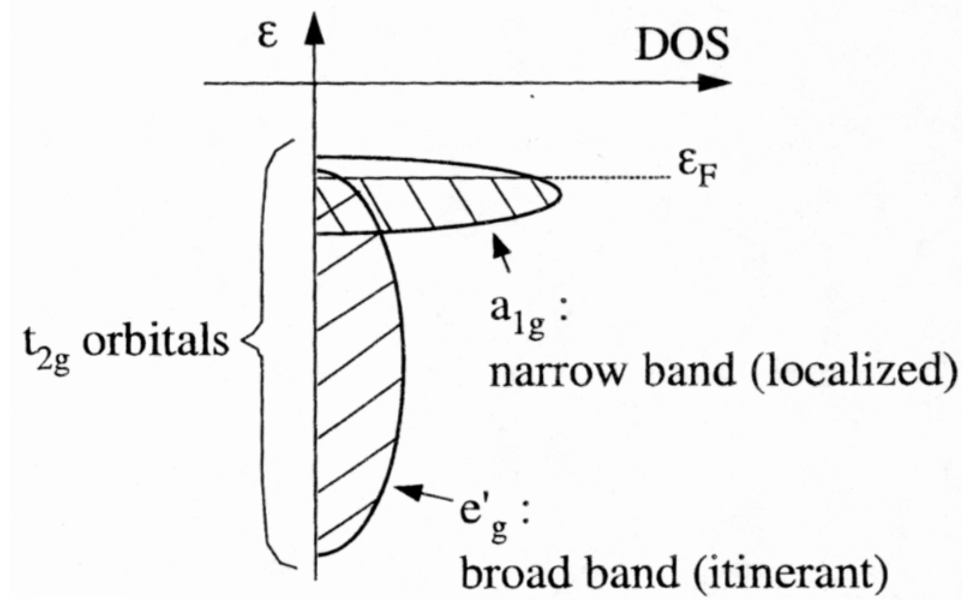


LS states due to CdI_2 layers
$g_4/g_3 = 6$

W. Koshibae et al., Phys. Rev. B 62, 6869 (2000)

Band structure calculations :

Lifting of the t_{2g} levels degeneracy due to rhombohedral crystalline field of CdI_2 layers



$$\frac{S}{T} = \frac{\pi^2 k^2}{3e}\left(\frac{d\ln(\sigma)}{dE}\right)_{E=E_F}$$

Peak in DOS : large S
\+ Metallicity

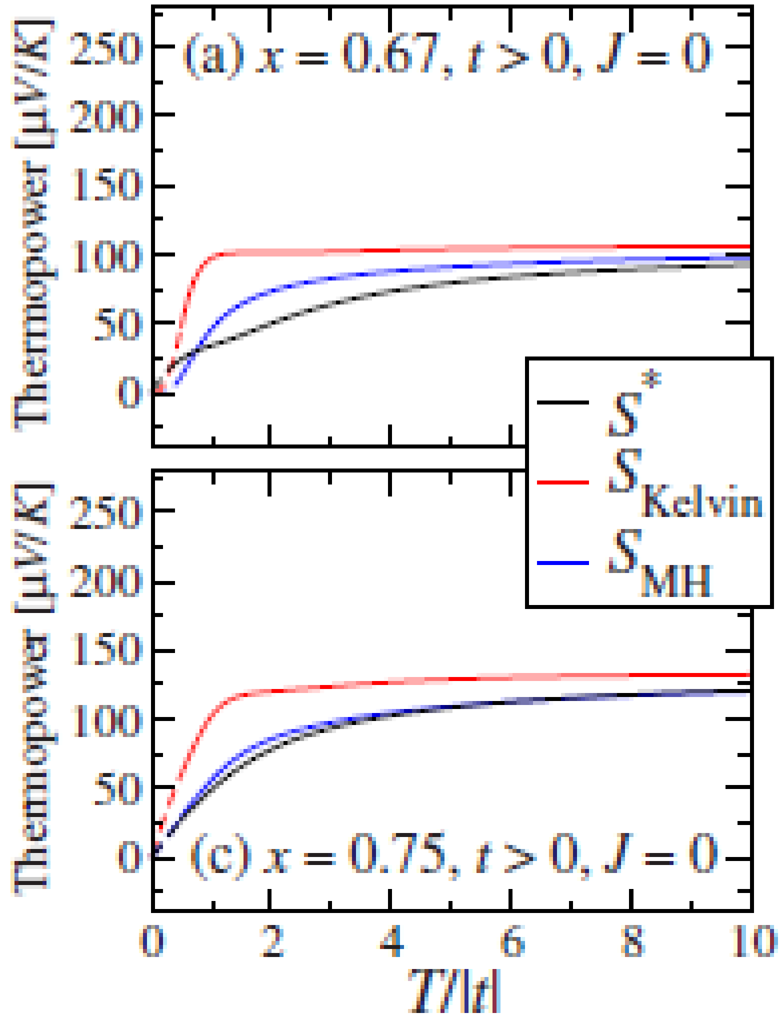
D. J. Singh, Phys. Rev. B 61, 13397 (2000)
T. Yamamoto et al., Phys. Rev. B 65, 184434 (2002)

The Kelvin formula

M. R. Peterson et al., PRB82, 195105 (2010)

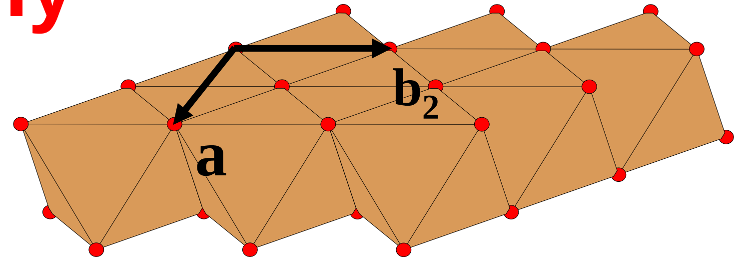
t- J model for
Na_xCoO_2 with x ~ 0.7

Heikes formula valid for T > 6 – 8 t



The misfit family

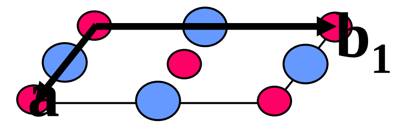
The misfit family

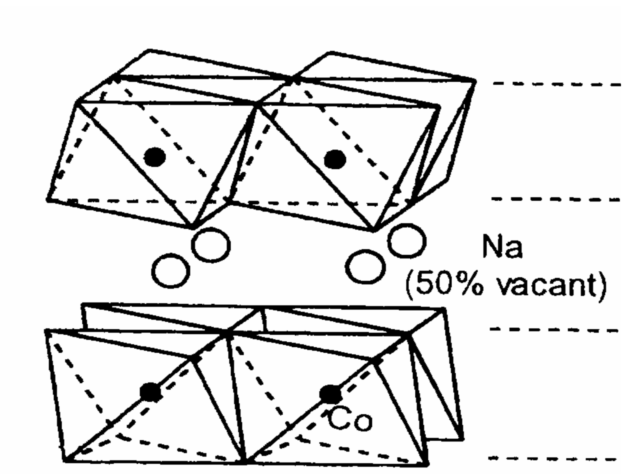


- n = 4 $[Bi_2A'_2O_4]^{RS}[CoO_2]_{b1/b2}$
A' = Ca^{2+}, Sr^{2+} or Ba^{2+}
- n = 3 $[A'_2CoO_3]^{RS}[CoO2]_{b1/b2}$
A' = Ca^{2+} or Sr^{2+}
- n = 2 $[Sr_2O_2]^{RS}[CoO2]_{b1/b2}$
$[Ca_2(OH)_2]^{RS}[CoO_2]_{b1/b2}$

$a_1 = a_2$
$c_1 = c_2$
$\beta_1 = \beta_2$

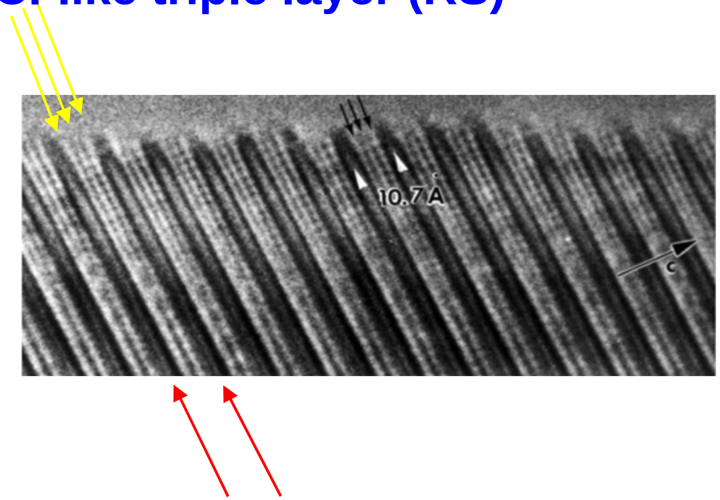
$b_1 \neq b_2$



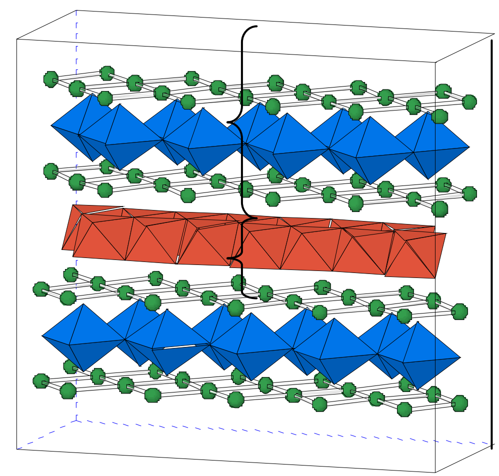


Na_xCoO_2
K_xCoO_2, …

NaCl-like triple layer (RS)

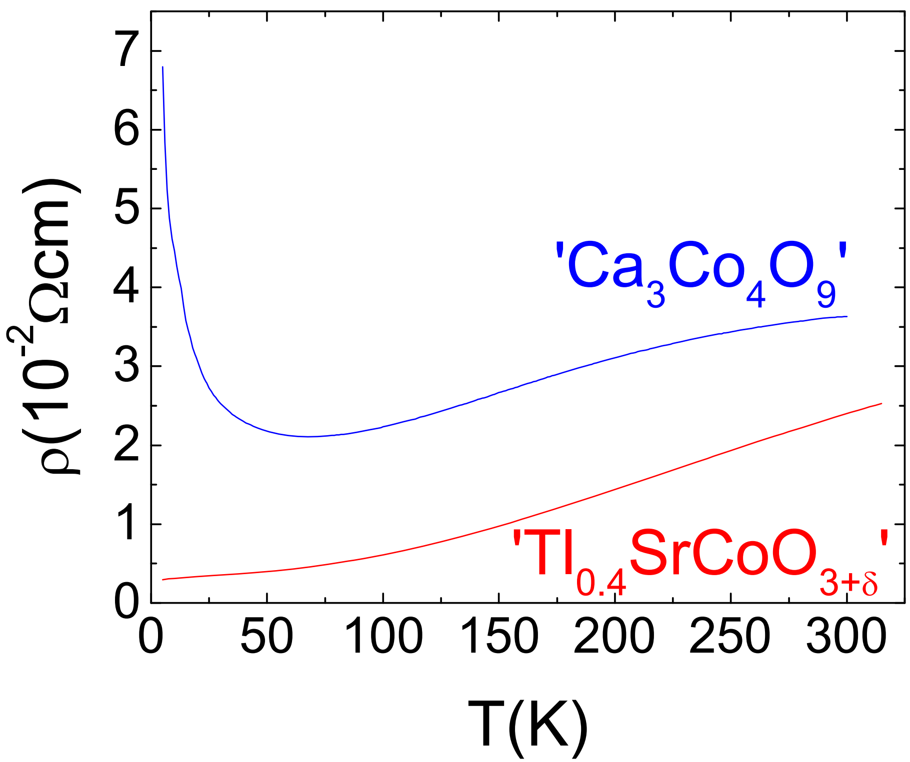


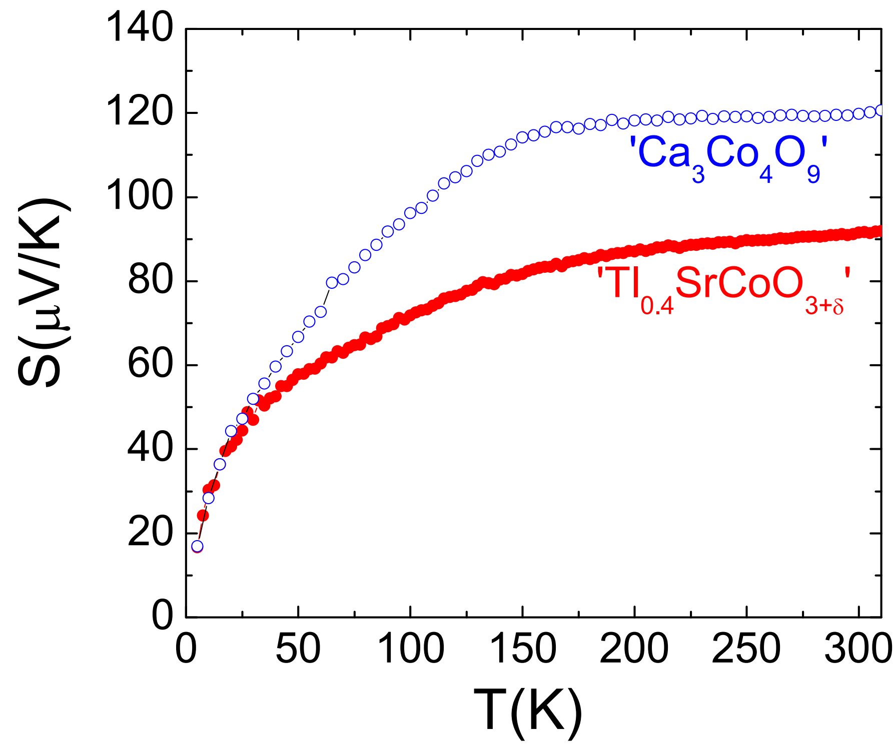
CoO_2 (type CdI_2)



Leligny et col., C. R. Acad. Sci. Paris, t. 2, Série II c, 409 (1999)
Boullay et col., Chem. Mater. 8, 1482 (1996)
Masset et col., Phys. Rev. B 62, 166 (2000)
Yamauchi et col., Chem. Mater. 18, 155 (2005)

Two different behaviours at low T





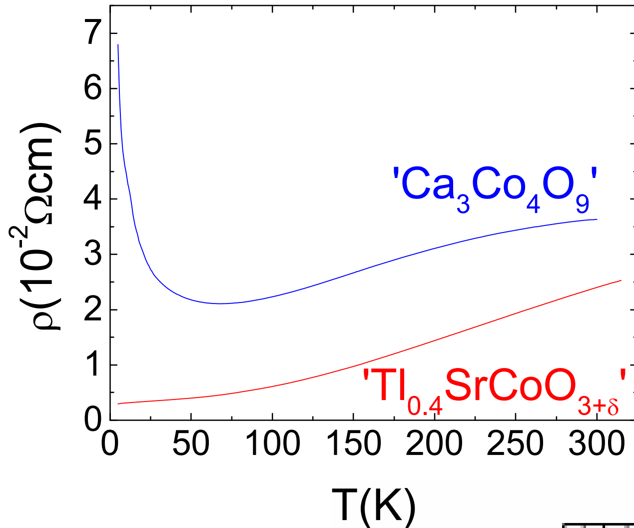
Different resistivities but same S(T)

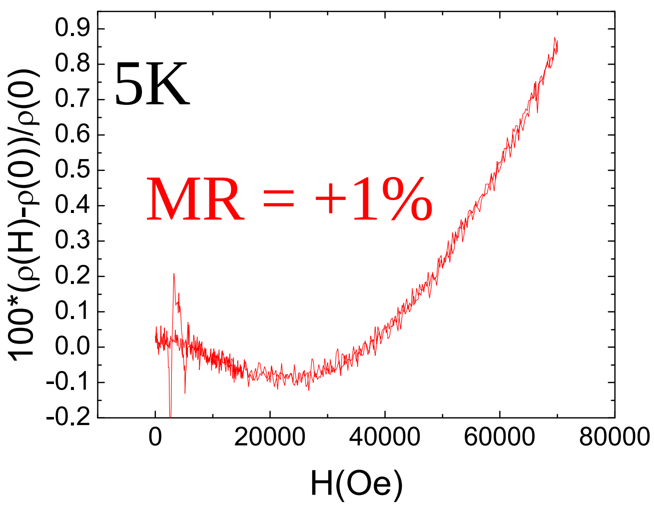
Only a shift of S

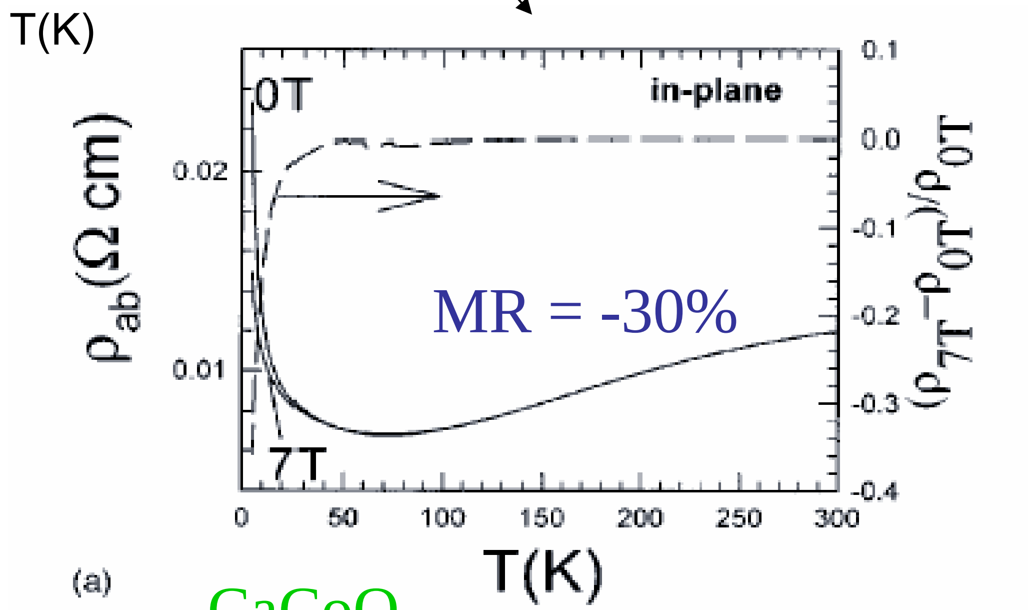
A. C. Masset et al., PRB62, 166 (2000)
S. Hébert et al., PRB64, 172101 (2001)

Low thermal conductivity

Two different behaviours at low T



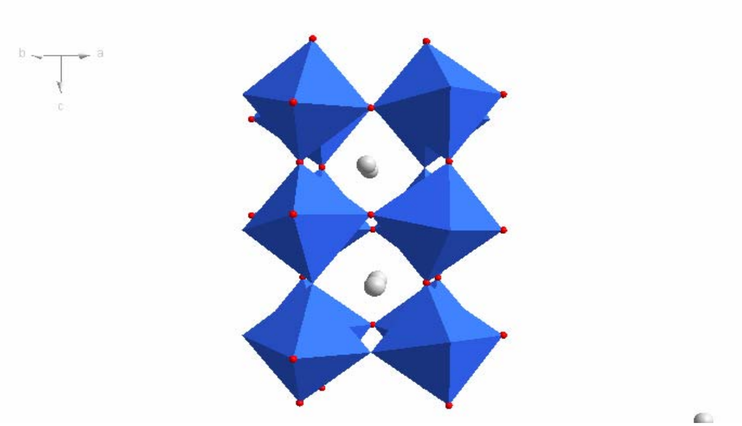




TlSrCoO
Metallic
Positive magneto-resistance
Small S (90μV/K)

CaCoO
dρ/dT<0 at low T
Negative magneto-resistance
Large S (130μV/K)

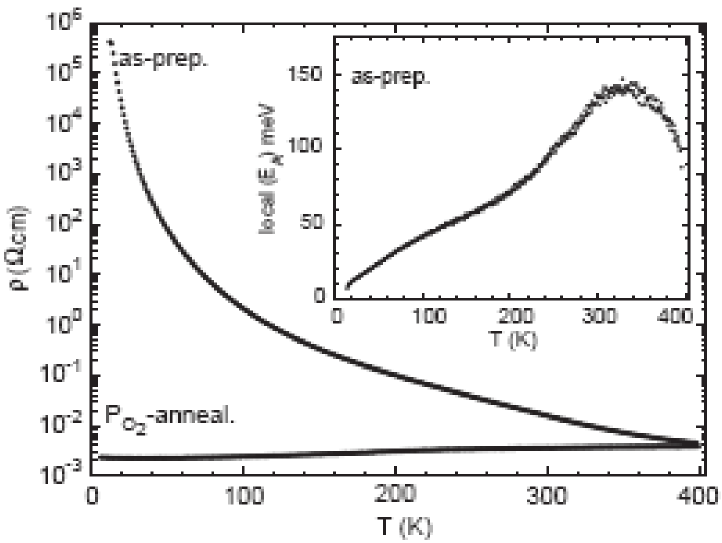
Unique behavior of CdI_2 type layers: Comparison with other oxides



Perovskite $Sr_{2/3}Y_{1/3}CoO_{8/3+\delta}$

Corner shared octahedra

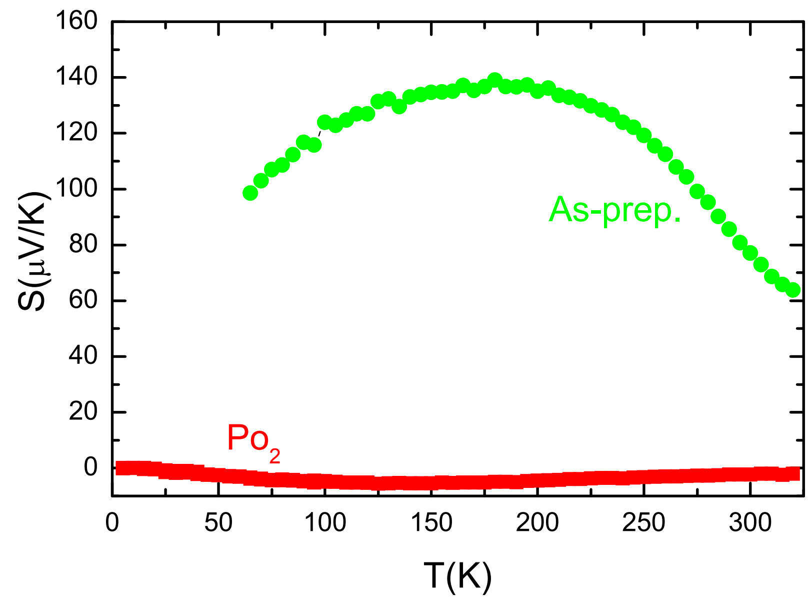
$\neq$ edge shared octahedra



Metallicity

→

Seebeck ≈ 0



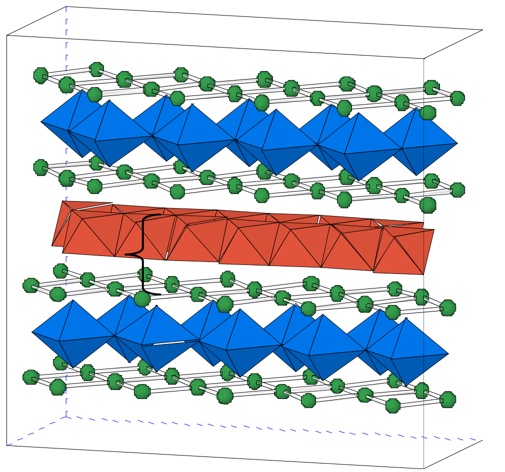
A. Maignan et al., JSSC178, 868 (2005)

Doping effect in the misfit family

$Ca_3Co_4O_9$

Ca_2CoO_3 NaCl-like

CoO_2 CdI_2-like



Electronic neutrality :

$[Ca_2CoO_{3\pm\delta}]^{RS}[CoO_2]_{b1/b2}$

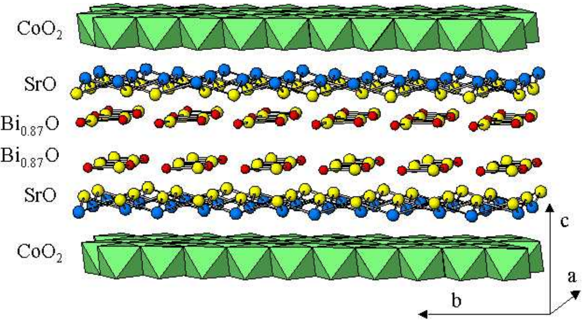
2+ 3+ 2- ν_{Co} 2-

$\alpha > 0$

$$v_{Co} = 4 - \frac{\alpha}{b_1 / b_2}$$

Modification of v_{Co} via α and b_1/b_2

Link between v_{Co} and S?



$$v_{Co} = 4 - \frac{\alpha}{b_1 / b_2}$$

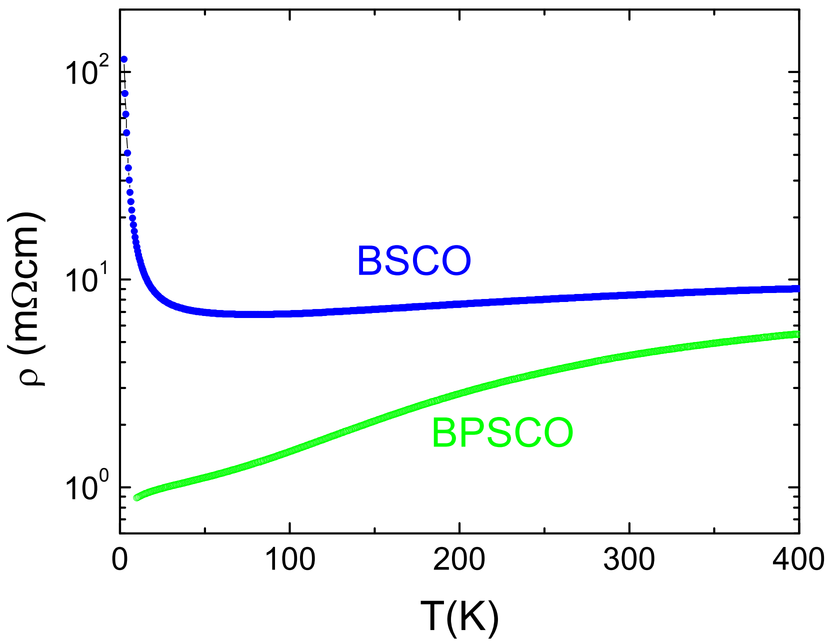
BiSrPbCoO single crystals : modification of α

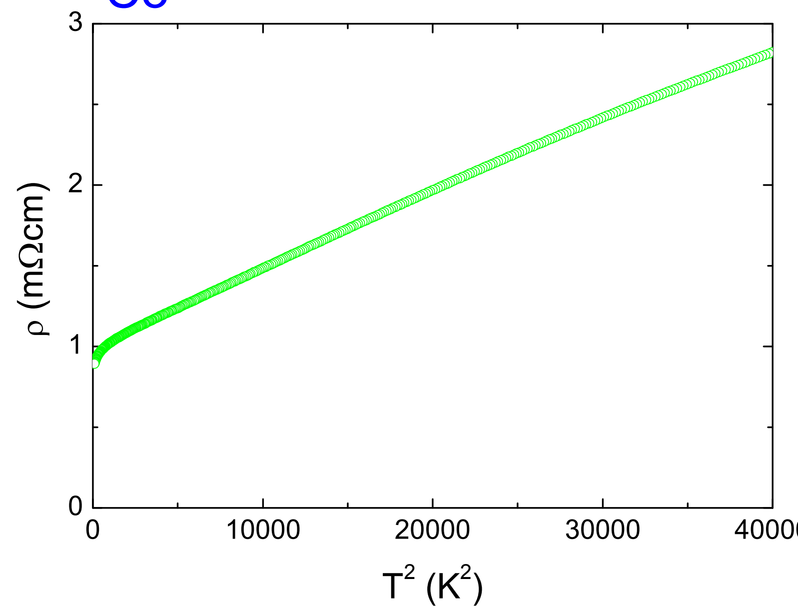
$[Bi_{1.74}Sr_2O_4][CoO_2]_{1.82}$

$[Bi_{1.5}Pb_{0.5}Sr_2O_{4-\delta}][CoO_2]_{1.86}$

Substitution of Bi^{3+} by Pb^{2+} : decrease of α

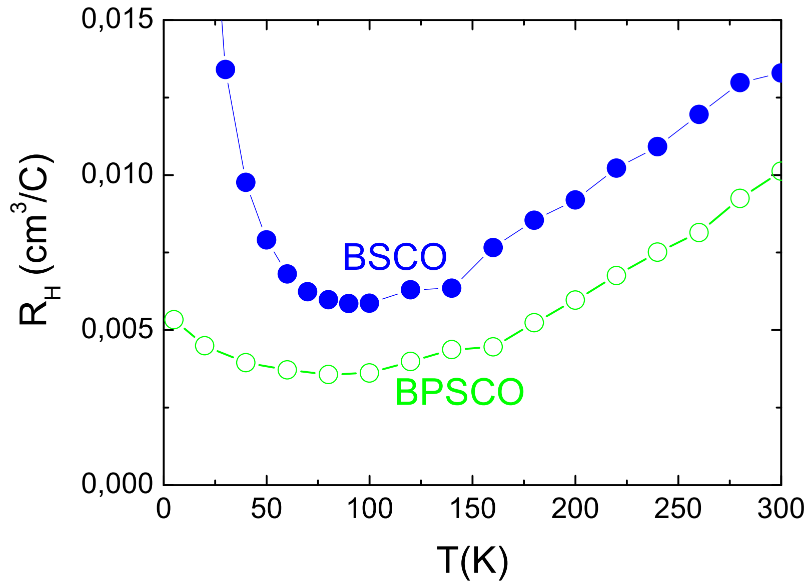
Increase of v_{Co}

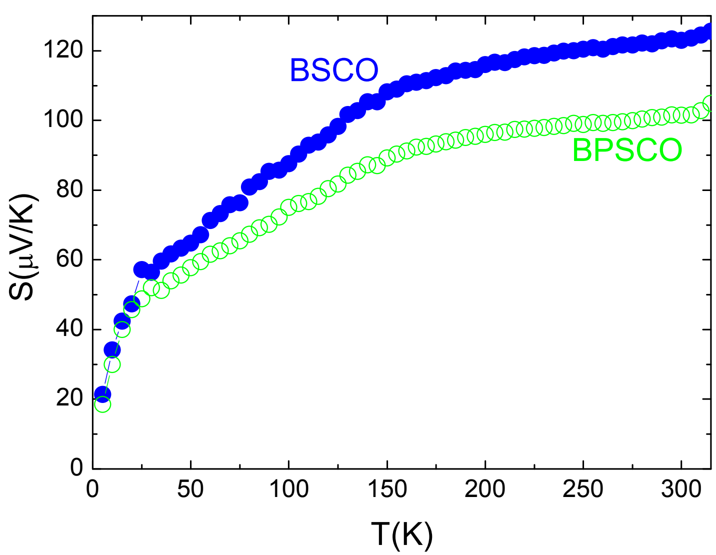




Metallic behavior down to 5K with $\rho = AT^2$

BiSrPbCoO single crystals : modification of α





t- J model : Linear T dependence of R_H

t ~10 – 40K

Justifies the Heikes formula (T/t > 6 – 8)

B. Kumar et al., PRB68, 104508 (2003)
Y. Wang et al., cond-mat/0305455
G. Leon et al. , PRB78, 085105 (2008)

At 100K

1.06×10^{21} cm^{-3} for BSCO

1.73×10^{21} cm^{-3} for BPSCO

Increase of v_{Co}

3.11

3.18

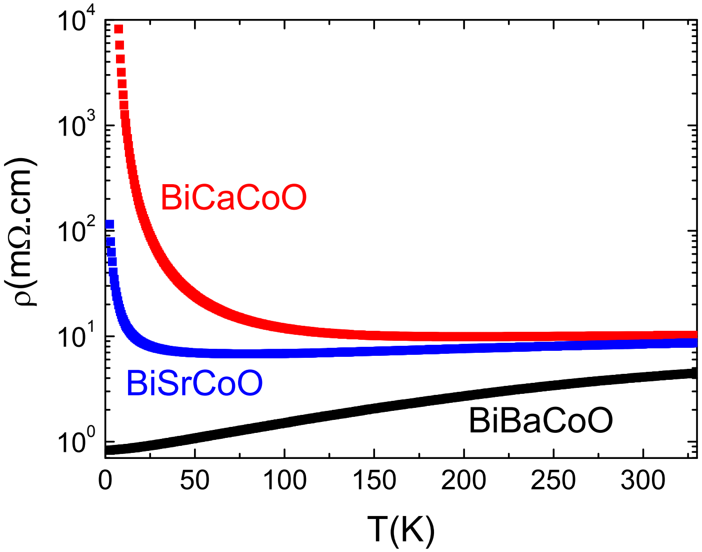
Increase of 'Co^{4+}' associated to a decrease of S

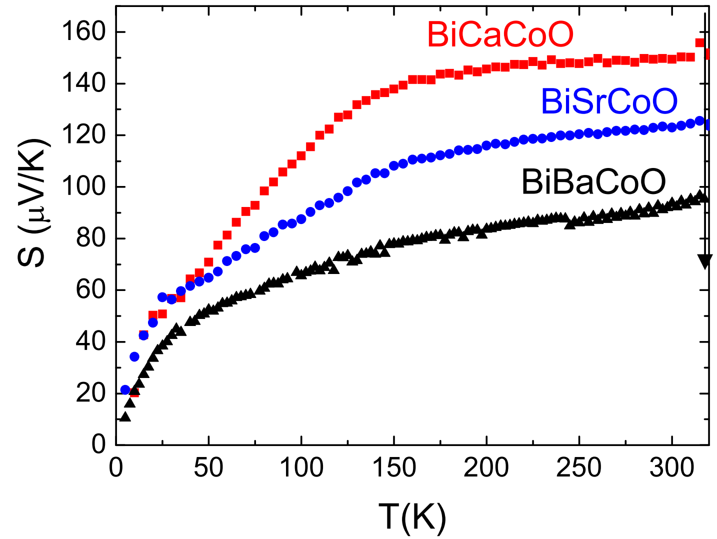
Generalized Heikes formula : increase of v_{Co}

3.59 for BSCO and 3.65 for BPSCO

W. Kobayashi et al., JPCM21, 235404 (2009)

BiCaCoO/ BiSrCoO/ BiBaCoO single crystals





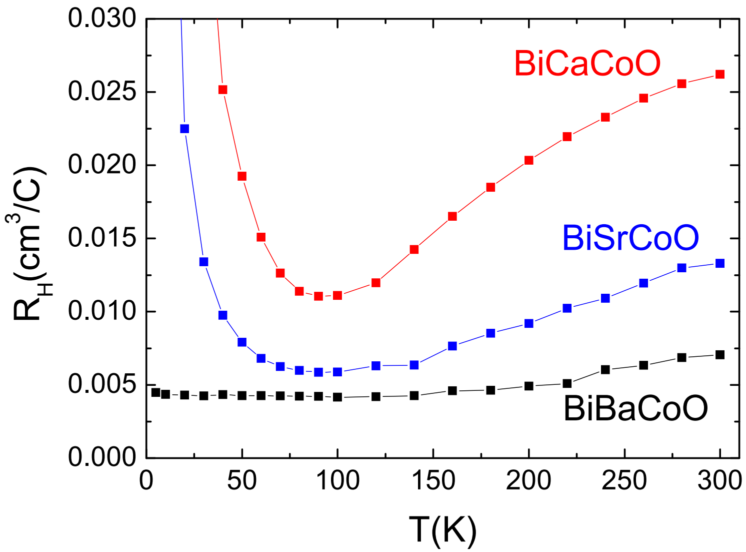
b_1/b_2

1.69

1.82

1.98

S not affected by the strong modification of ρ



If b_1/b_2 ↗ , carrier concentration ↗

$$v_{Co} = 4 - \frac{\alpha}{b_1 / b_2}$$

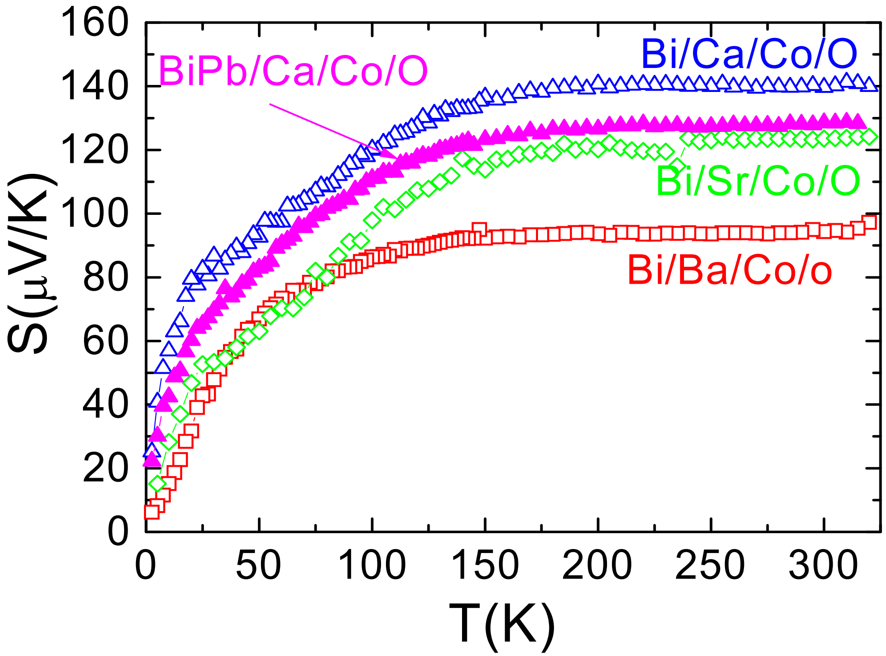
⇨S at 300K depends on doping

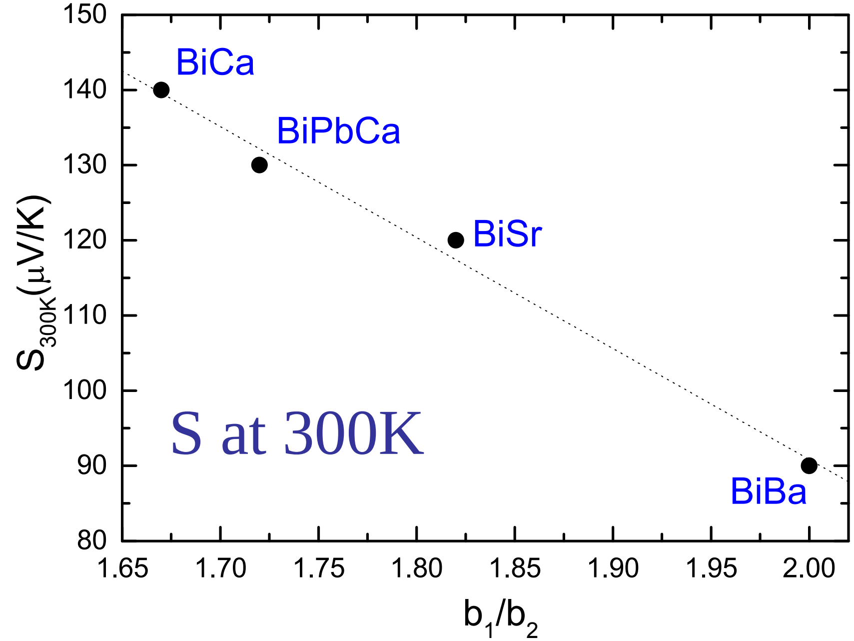
$V_{Co} = 3.05 – 3.15?$

W. Kobayashi et al.

Bi-based compounds

4 separating layers

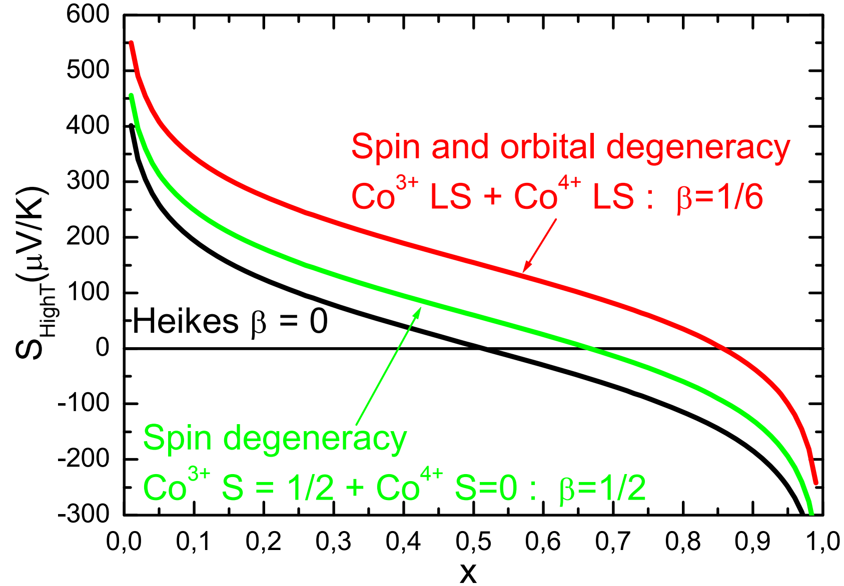




Heikes formula

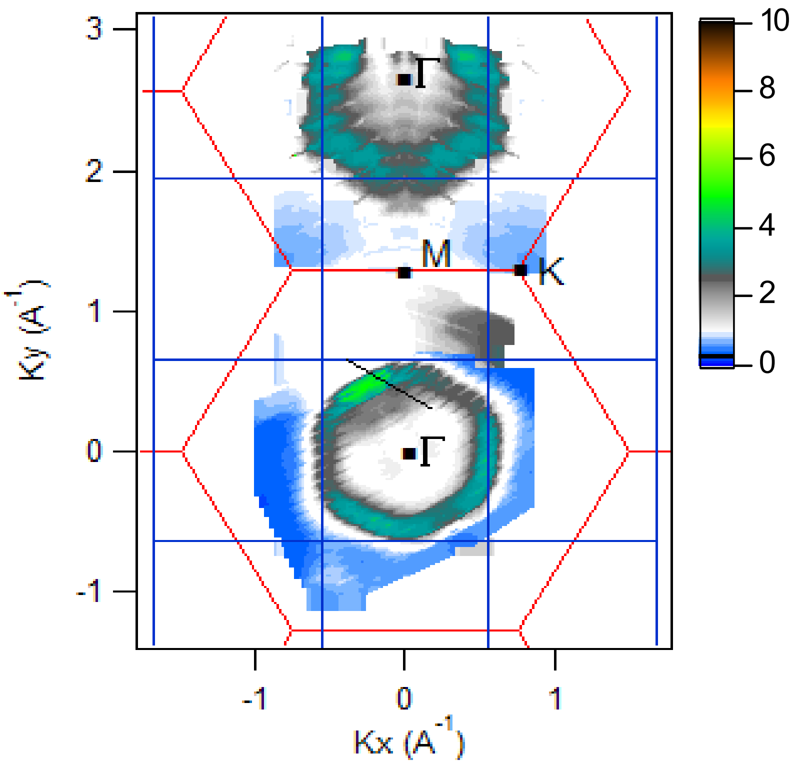
$$S = -\frac{k_B}{|e|}\ln\left(\frac{g_4}{g_3}\frac{1-x}{x}\right)$$

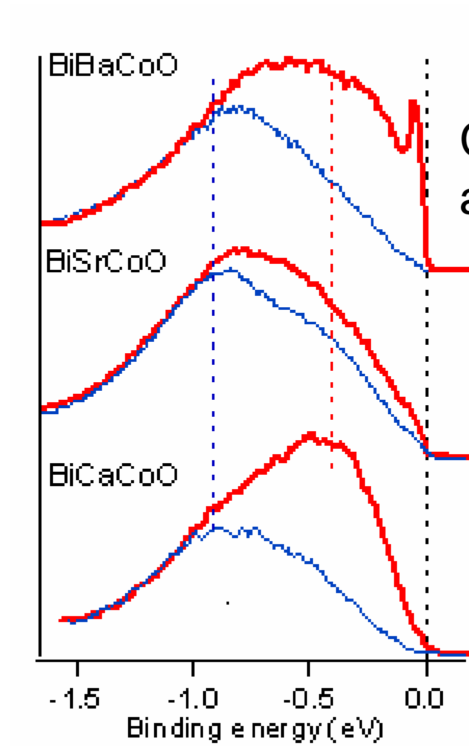
Co valency in BiCaCoO/ BiSrCoO / BiBaCoO?



Heikes (S at 300K)	Hall effect
3.5 -3.7 for $g_4 / g_3 = 6$	3.05 -3.15

Carrier concentration changes with misfit ratio b_1/b_2





ARPES

Collaboration with V. Brouet et al., LPS Orsay

Reliable data for v_{Co} are obtained for BiBaCoO

$$v_{Co} = 4 - \frac{\alpha}{b_1/b_2} \quad (\alpha\text{=const})$$

$Co^{3.2+}$ for BiSrCoO

$Co^{3.1+}$ for BiCaCoO

single hole-like fermi surface (a_{1g} character)

$k_F = 0.57 \pm 0.05$ Å^{-1} for BiBaCoO

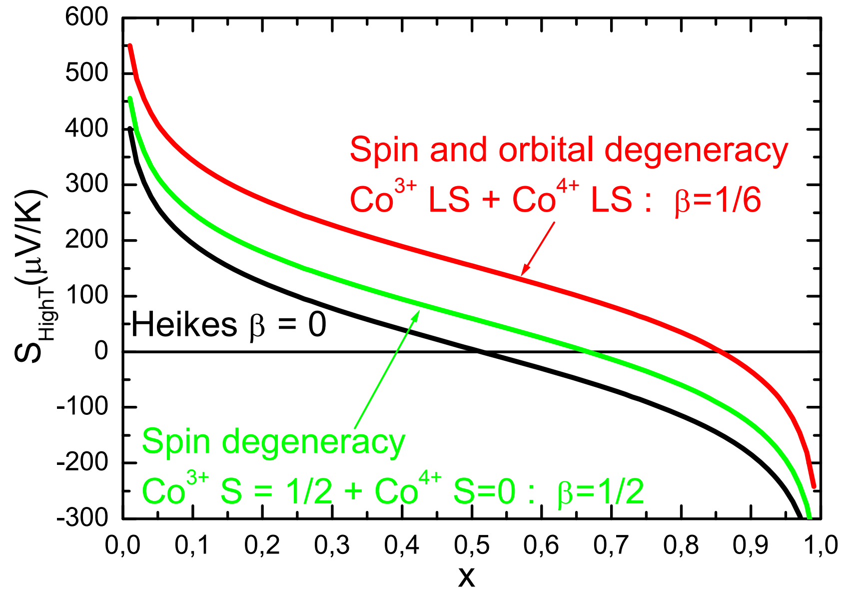
→ similar to k_F of Na_xCoO_2 (x=0.7)

→ $Co^{3.3+}$ for BiBaCoO

V. Brouet et al., PRB76, 100403 (2007)

Heikes formula

$$S = -\frac{k_B}{|e|}\ln\left(\frac{g_4}{g_3}\frac{1-x}{x}\right)$$



Co valency in BiCaCoO/ BiSrCoO / BiBaCoO

Heikes (S at 300K)	Hall effect	ARPES BiBaCoO	NMR
3.5 -3.7 for $g_4 / g_3 = 6$ **3.1 – 3.3 for $g_4 / g_3 = 2$**	3.05 -3.15 *W. Kobayashi et al.*	3.3 *V. Brouet et al., PRB76, 100403 (2007)*	3.1 -3.3 *J. Bobroff et al., PRB76, 100407 (2007)*

$g_4 / g_3 = 2$ instead of 6

Confirms the results in BiCaCoO : $v_{Co} = 3.24$

M. Pollet et al., JAP101, 083708 (2007)

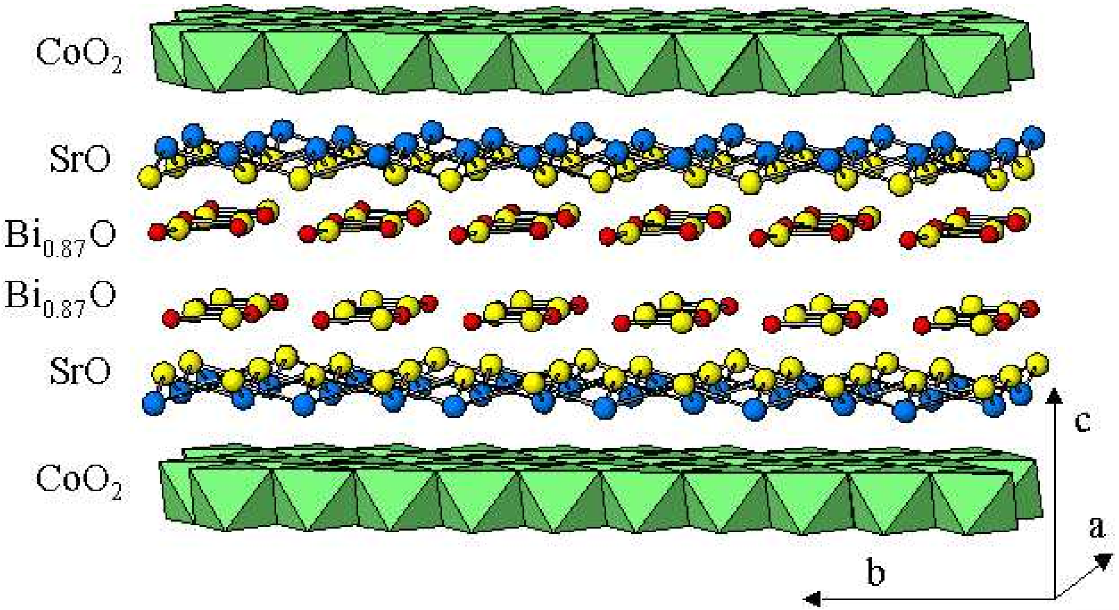
Orbital filling in Na_xCoO_2 and misfit cobaltites with edge-shared CoO_6

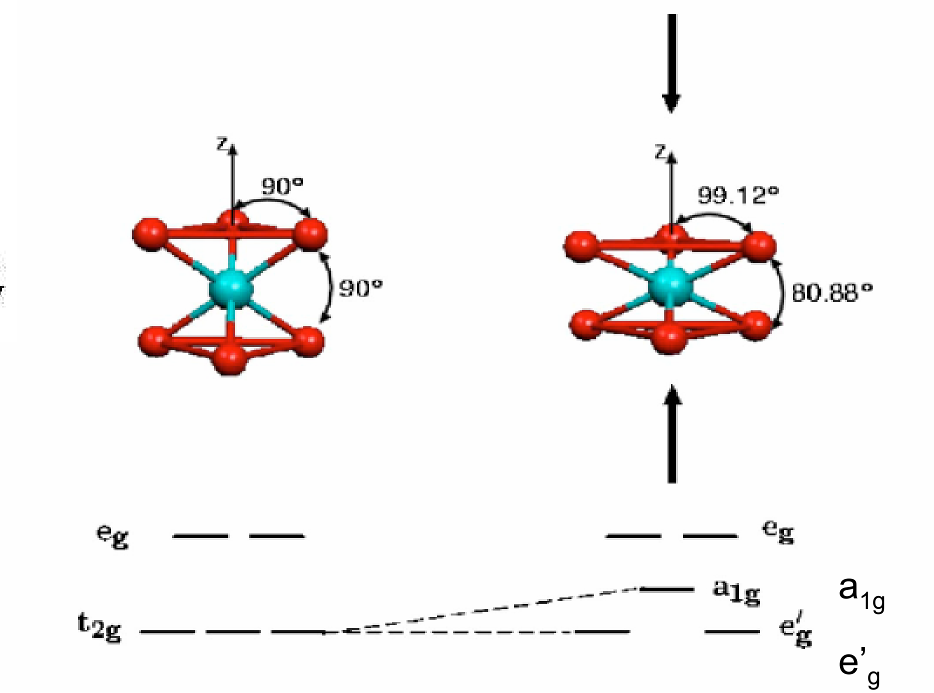
LS Co^{3+}/Co^{4+} mixed-valency

↓

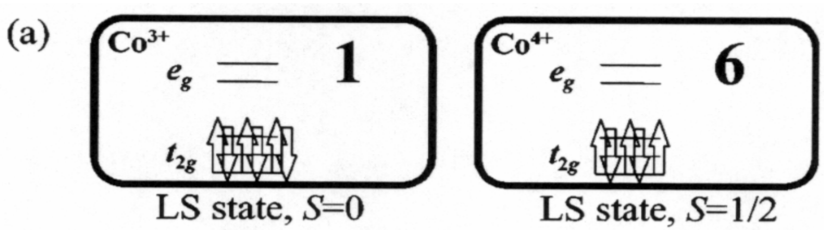
metallicity

MB Lepetit PHYSICAL REVIEW B 74, 184507 (2006)





Ligand field splitting :
trigonal distortion



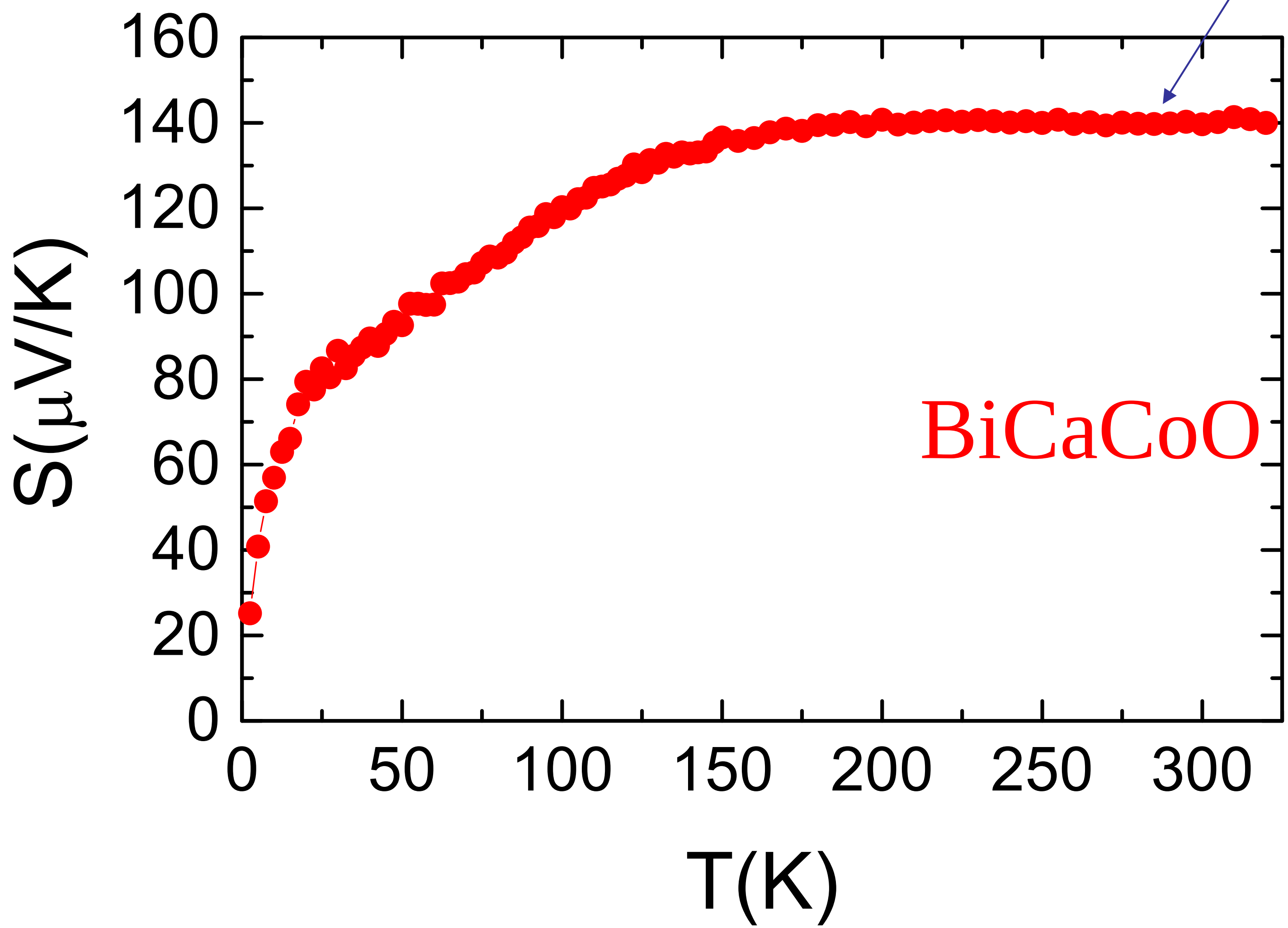
$\beta = g_4 / g_3 = 6$

1 for Co^{3+} but 2 instead of 6 for Co^{4+}

$\beta = 2$

Thermoelectric power of misfits

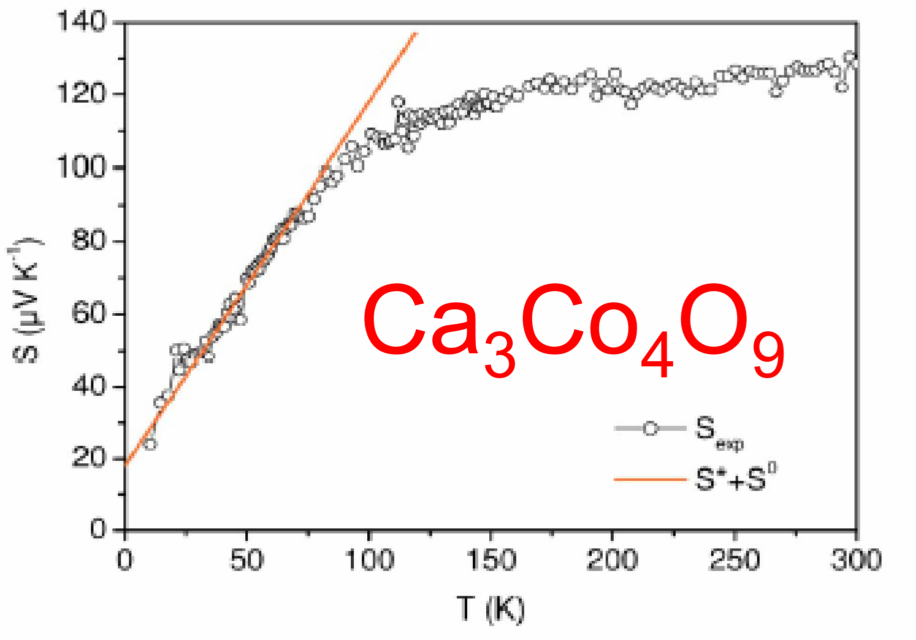
High T Seebeck, depends on Co^{4+}
(Heikes formula with $\beta = 2$)



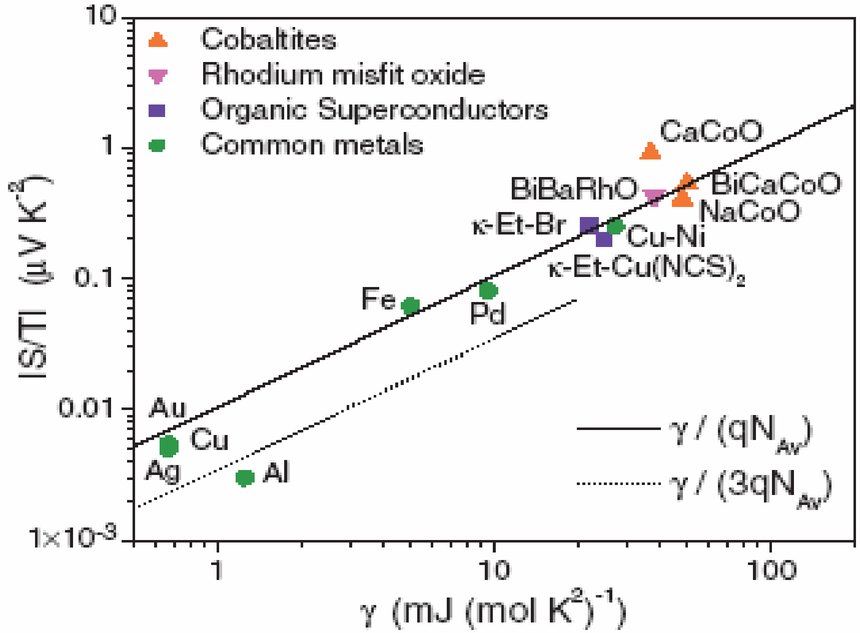
t small :
Validity of hte
Heikes formula
at 300K

Low T : Electronic correlations

For T→0 $$q = \frac{S}{T}\frac{N_{Av}e}{\gamma} = cste$$ $S \sim \gamma T$



P. Limelette, PRB71, 233108 (2005)



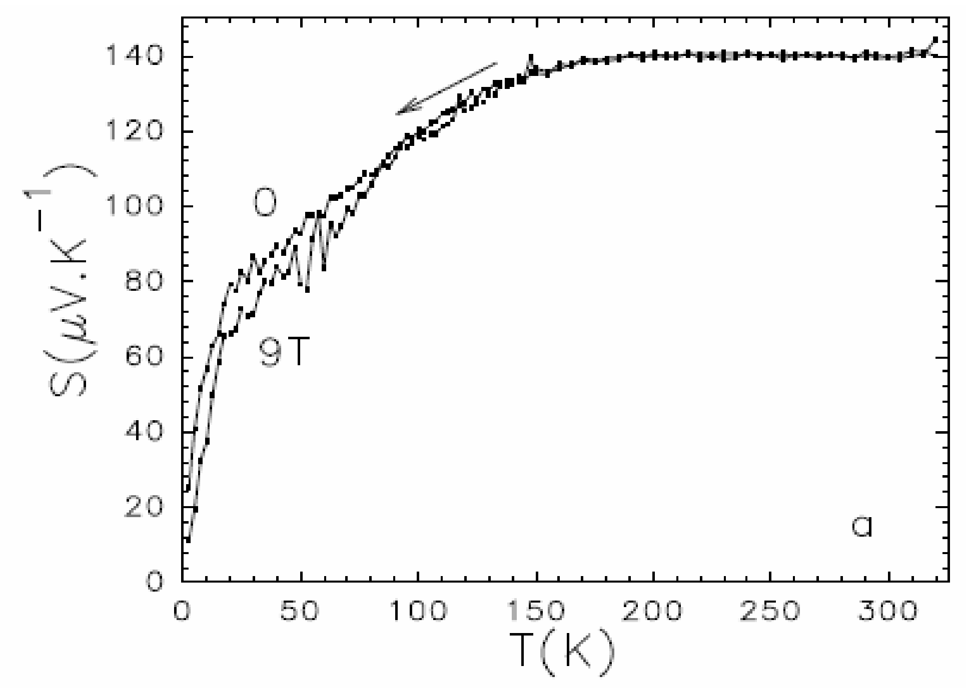
P. Limelette, PRL97, 046601 (2006)

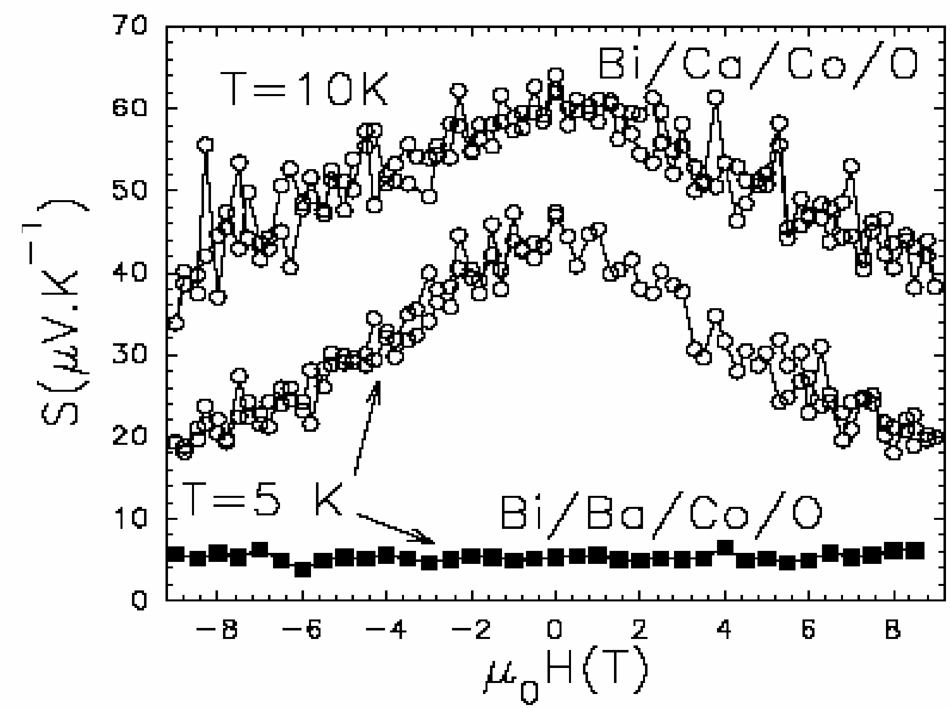
K. Behnia et al. JPCM 16, 5187 (2004)

Low T : Spin entropy

BiCaCoO : excess of S at low T

A. Maignan et al., JPCM 15, 2711 (2003)





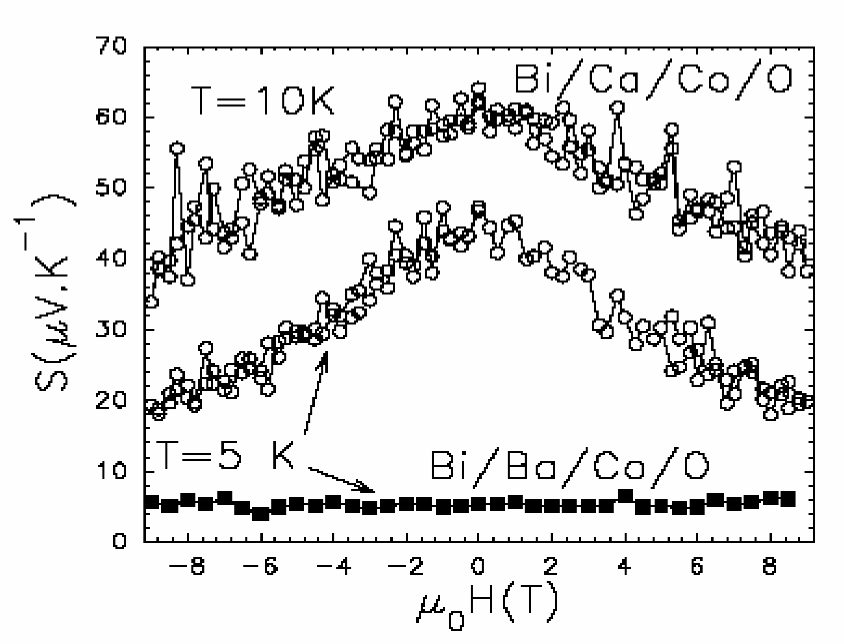
Observed also in Na_xCoO_2

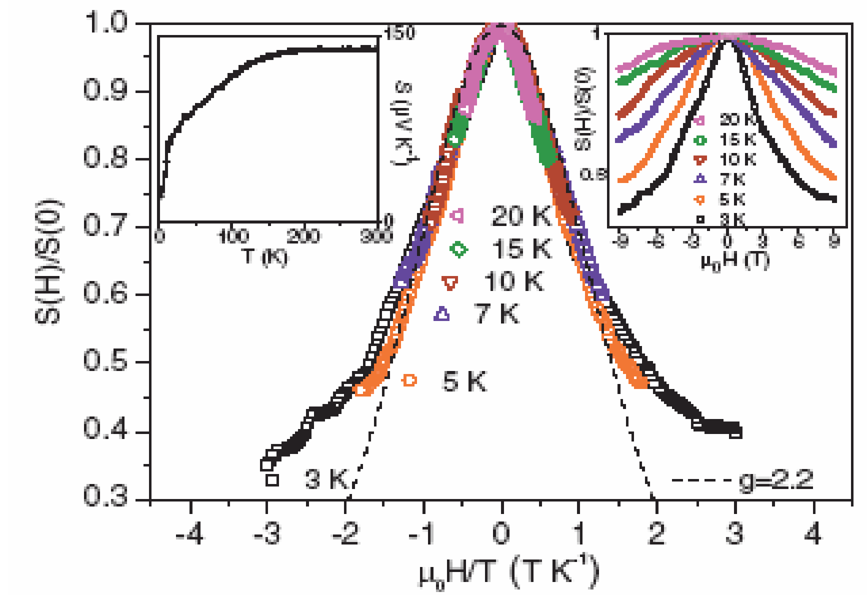
[Wang et al. Nature 423, 425 (2003)]

Spin entropy at low T

Misfit BiCaCoO

Decrease of S under field at low T
Due to the alignement of paramagnetic spins





Scaling law for S(H) : paramagnetic spins S=1/2
Brillouin function

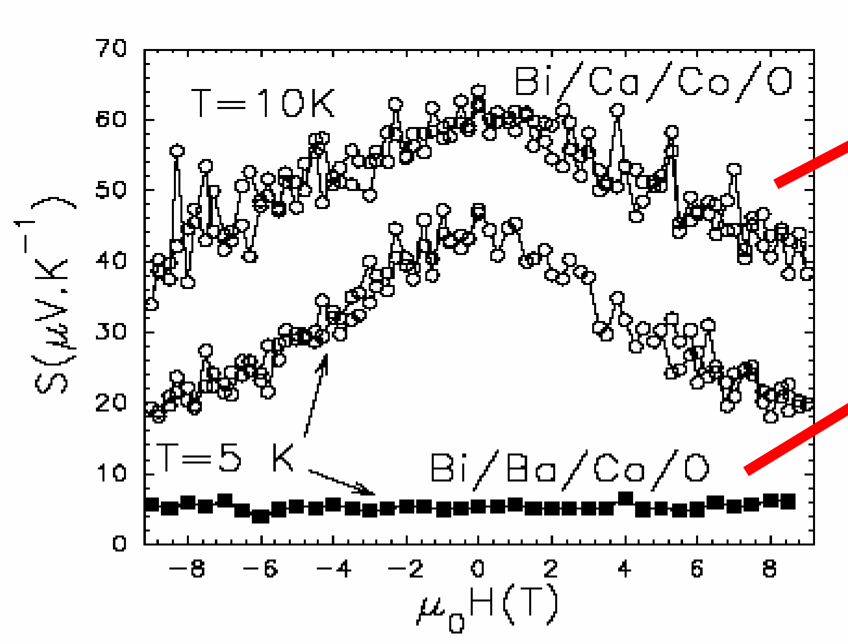
$$S(x)/S(0) = (\ln[2\cosh(x)] - x\tanh[x])/\ln(2).$$

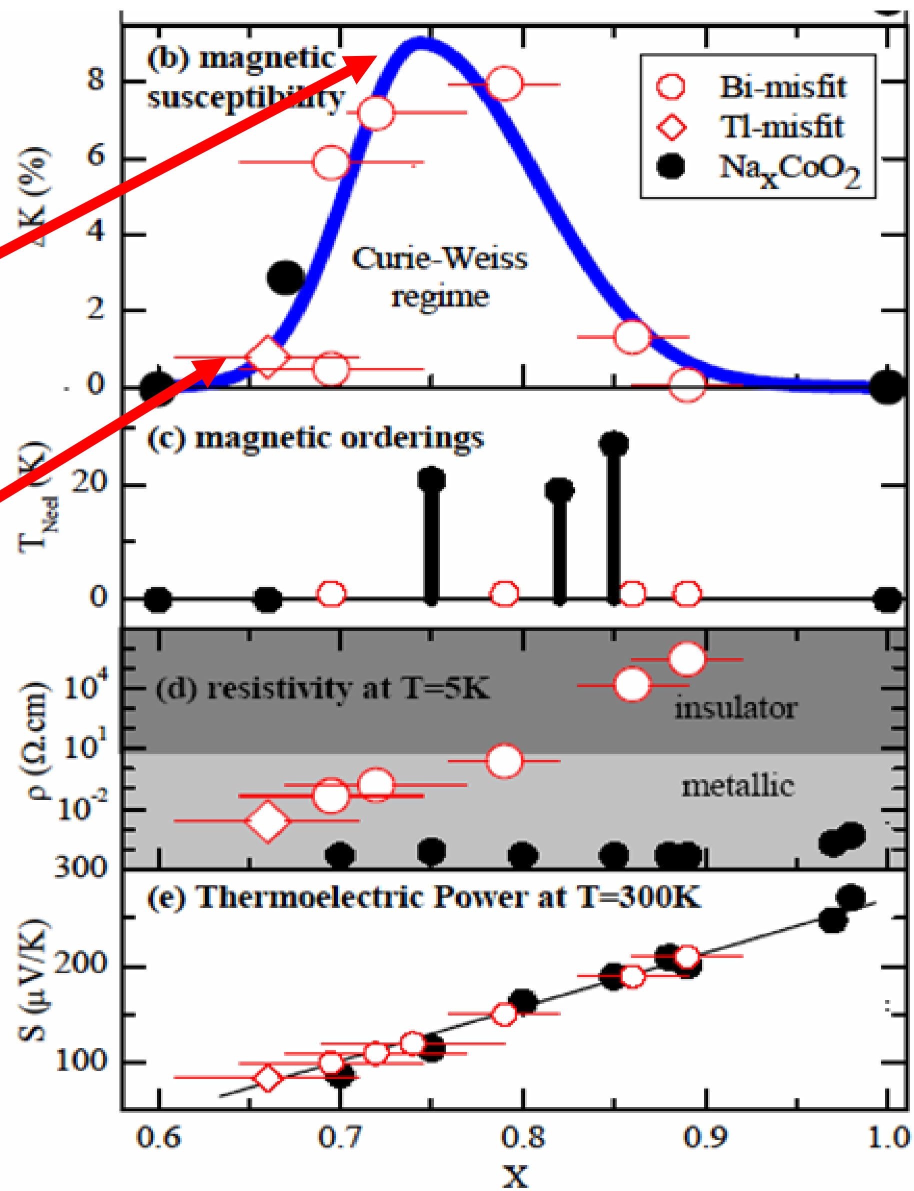
$Na_{0.7}CoO_2$

P. Limelette et al., PRL97, 046601 (2006)

Y. Wang et al., Nature423, 425 (2003)

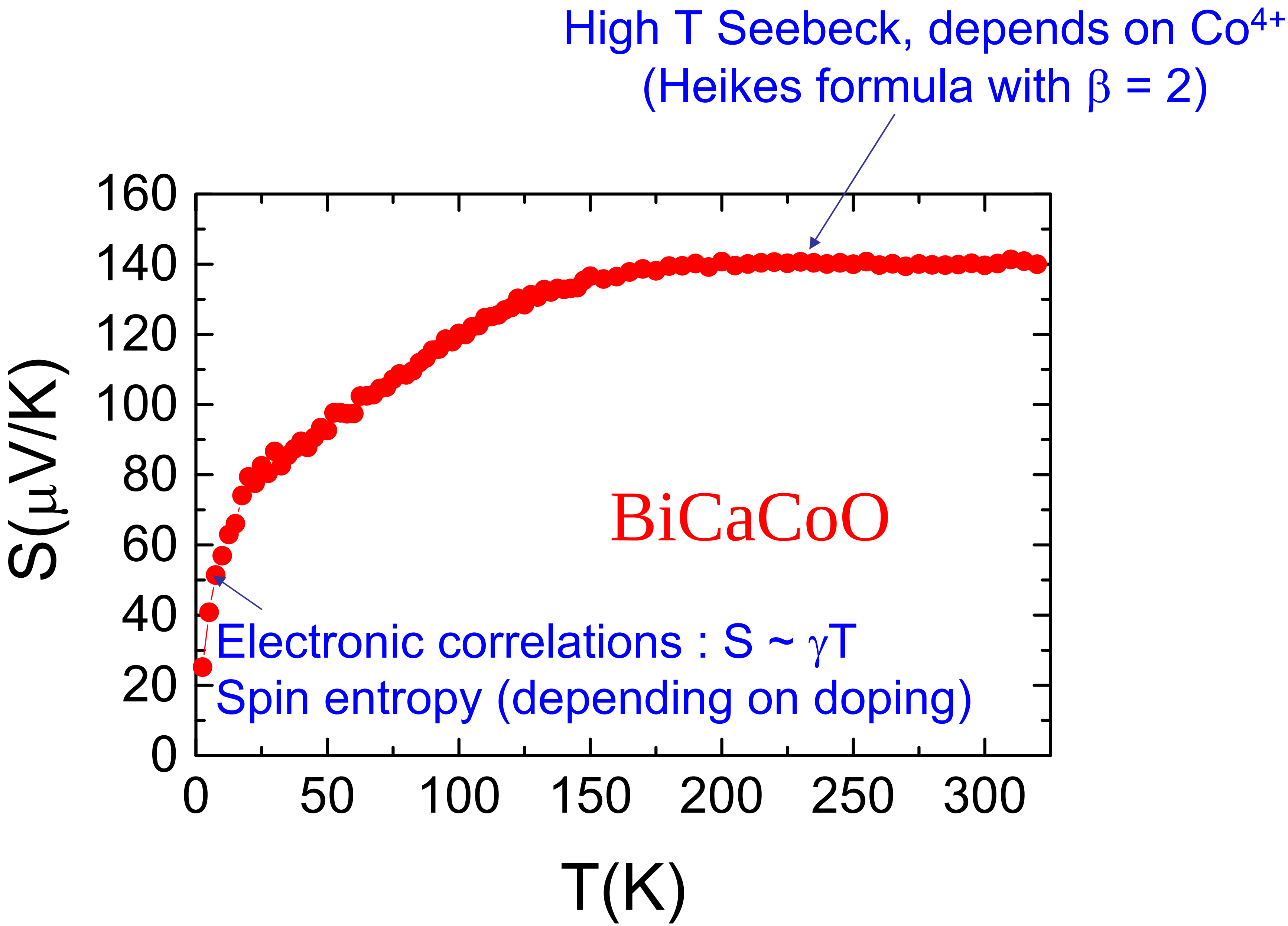
Spin entropy at low T





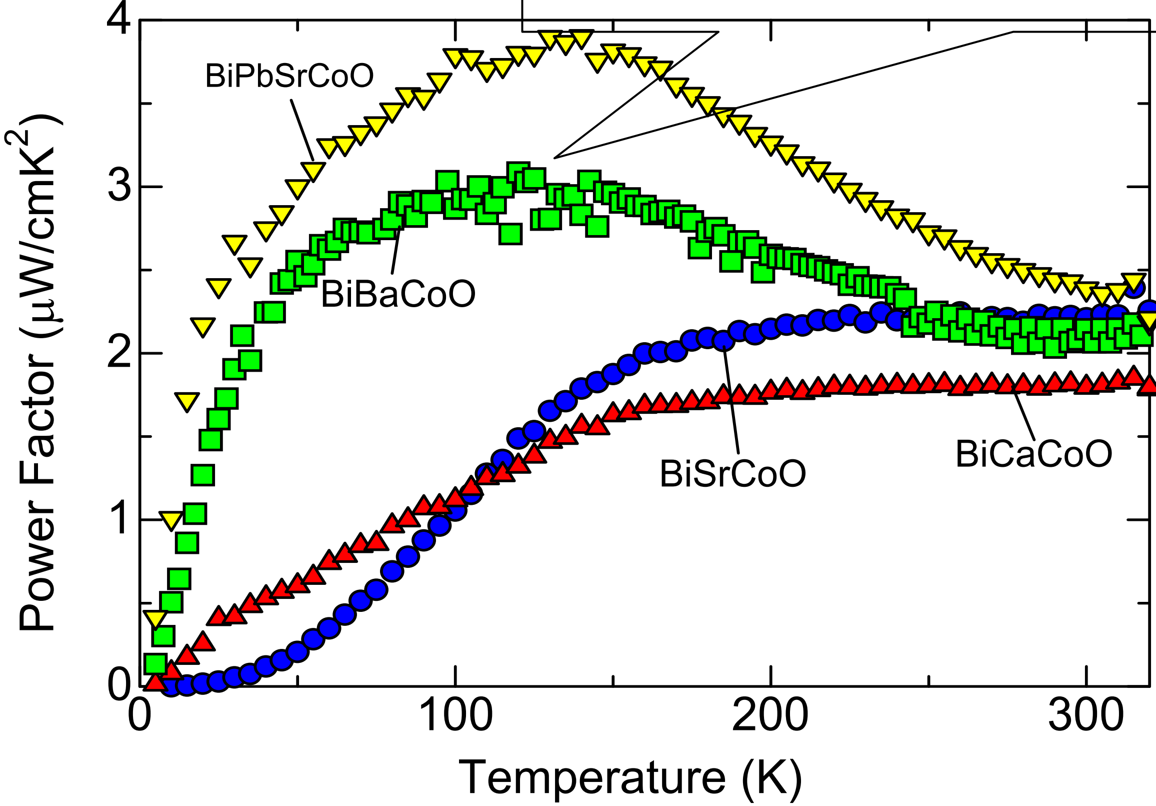
Determination of susceptibility by NMR
Collaboration with J. Bobroff (LPS)
J. Bobroff et al., PRB76, 100407 (2007)

Thermoelectric power of misfits



Power factor

enhancement for BiBaCoO and BiPbSrCoO



P is almost independent of carrier concentration

2.10^{-4} $Wm^{-1}K^{-2}$ at 300K

In conventional semiconducting thermoelectric material such as Bi_2Te_3, *n* is an important parameter to tune the properties.

How to modify the electronic properties?
Influence of the block layer?

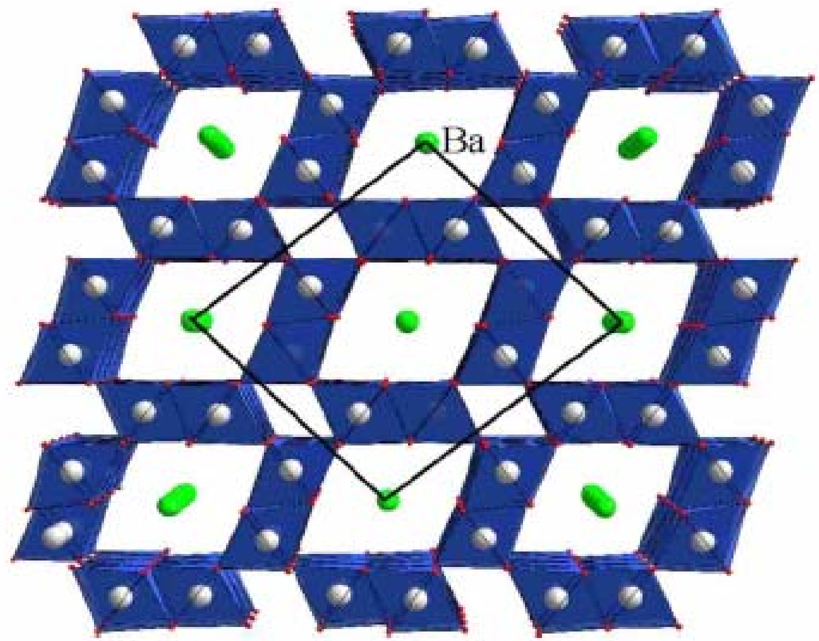
Hollandites

$Ba_{1.2}Rh_8O_{16}$ hollandite

Quasi 1D structure

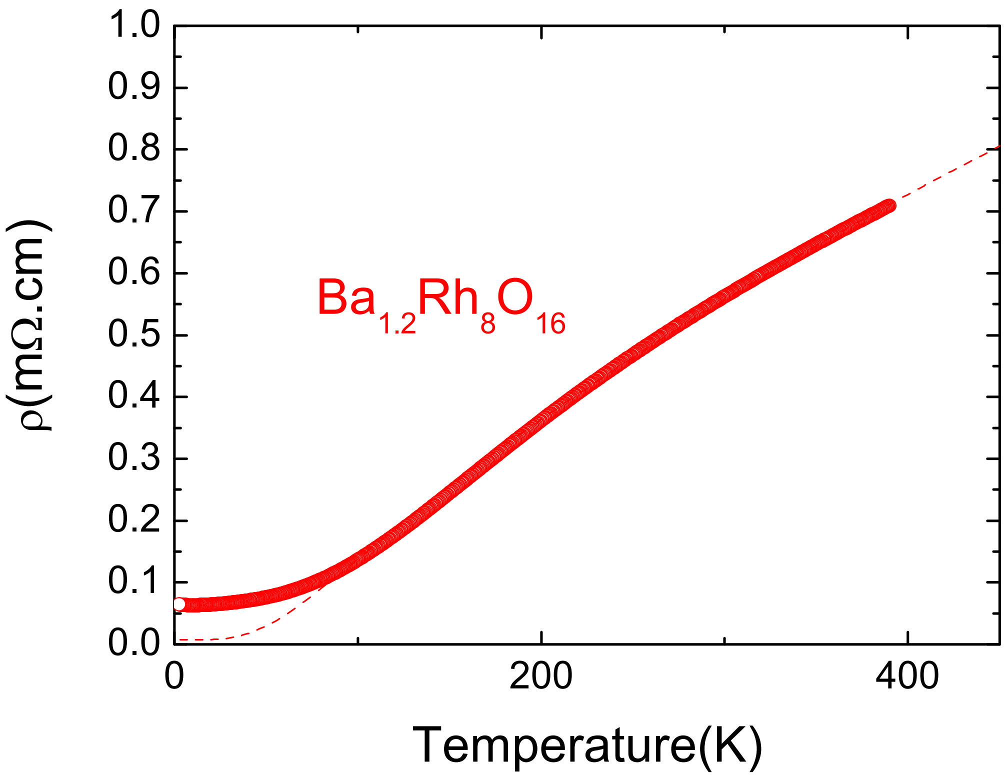
Tunnels made of edge shared octahedra

Needle like single crystals



W.Kobayashi et al., PRB79, 085207 (2009)

$Ba_{1.2}Rh_8O_{16}$ hollandite



Metallic behavior

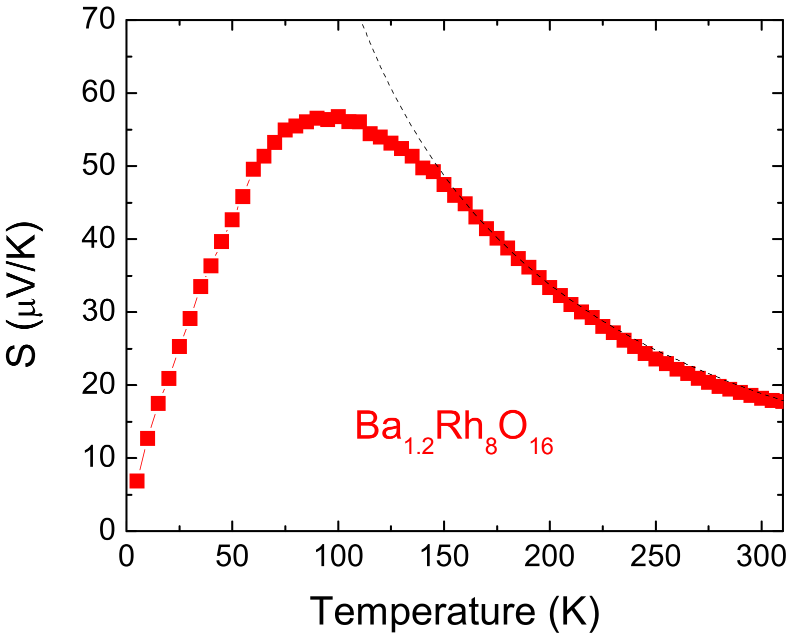
e/phonon model
to fit the resistivity

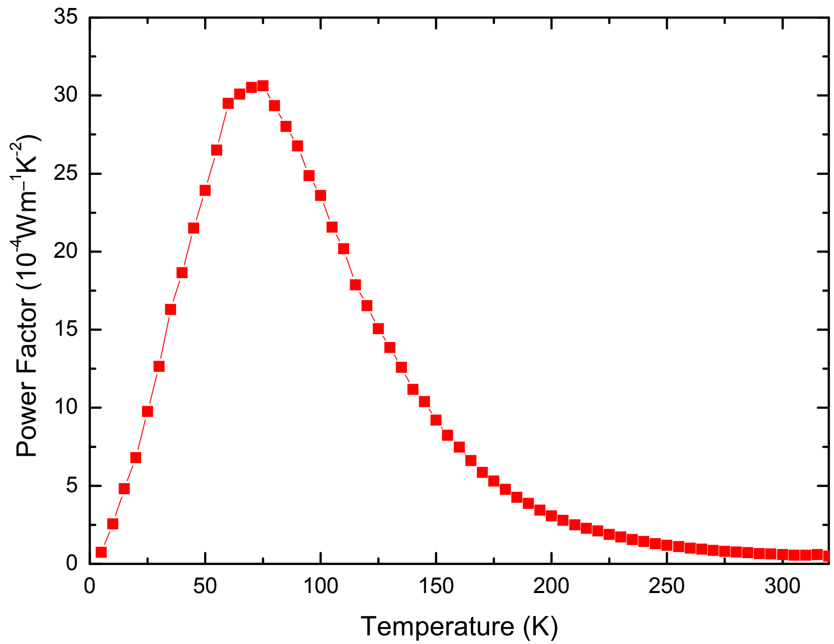
$$\rho^{-1}(T) = \rho_{sat}^{-1} + (\rho(0) + A\,(T/\theta_D)^5 J_5(T/\theta_D))^{-1}$$

with θ_D = 310K

Hall effect : 1.01×10^{22} cm^{-3} at 300K

$Ba_{1.2}Rh_8O_{16}$ hollandite



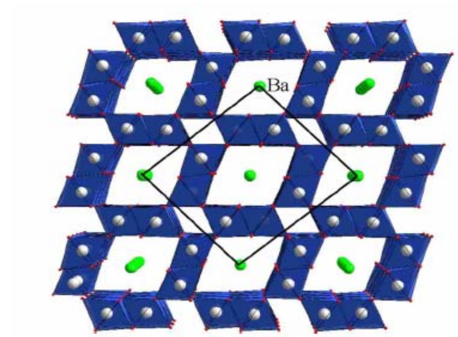


Peak of S(T) and PF at low T

PF~$Na_{0.7}CoO_2$ at 300K

For comparison : 187.10^{-4} $Wm^{-1}K^{-2}$ for $Na_{0.88}CoO_2$ at 75K

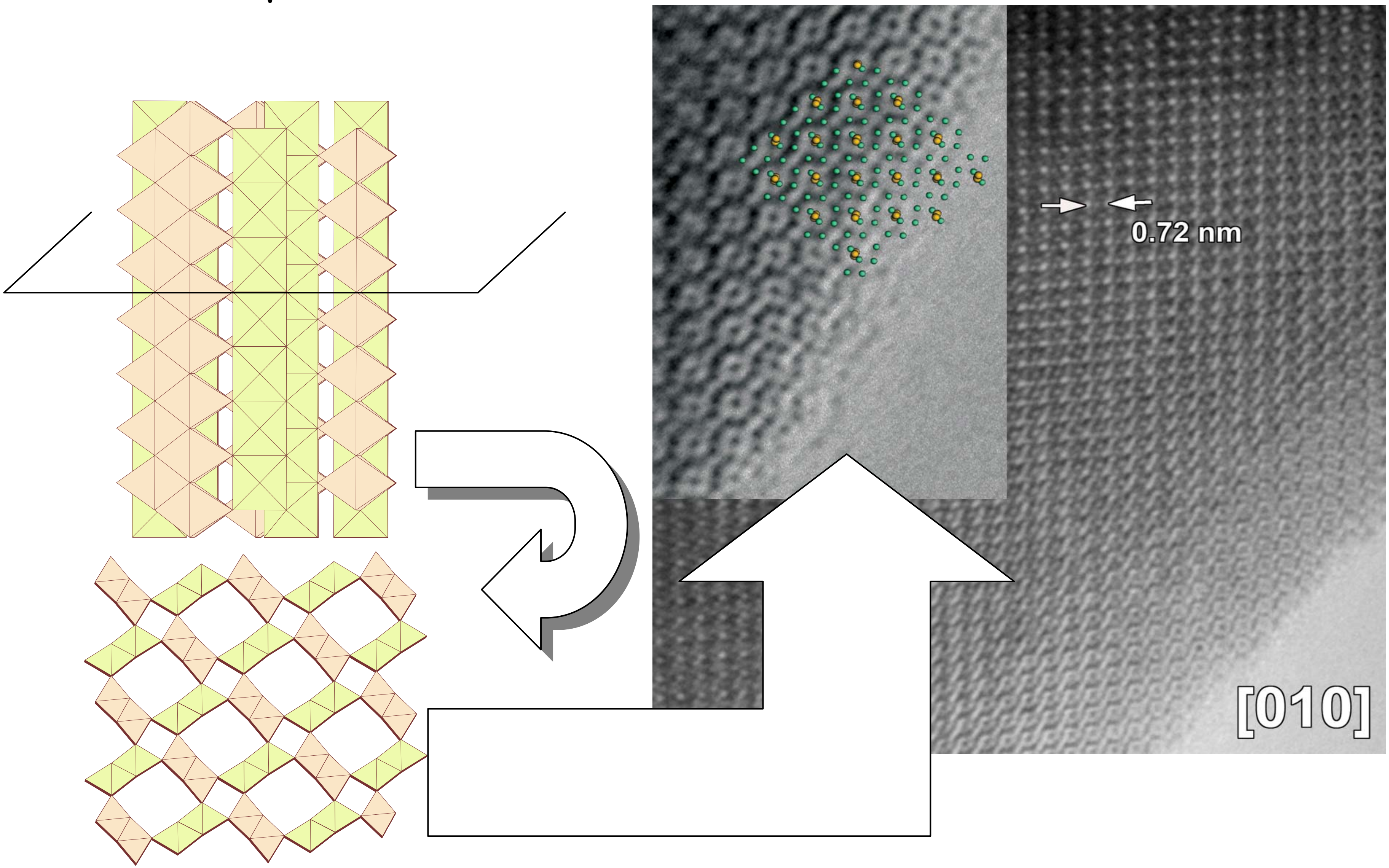
Possible shift of PF at higher T?



n type hollandite : $Pb_{1.6}V_8O_{16}$

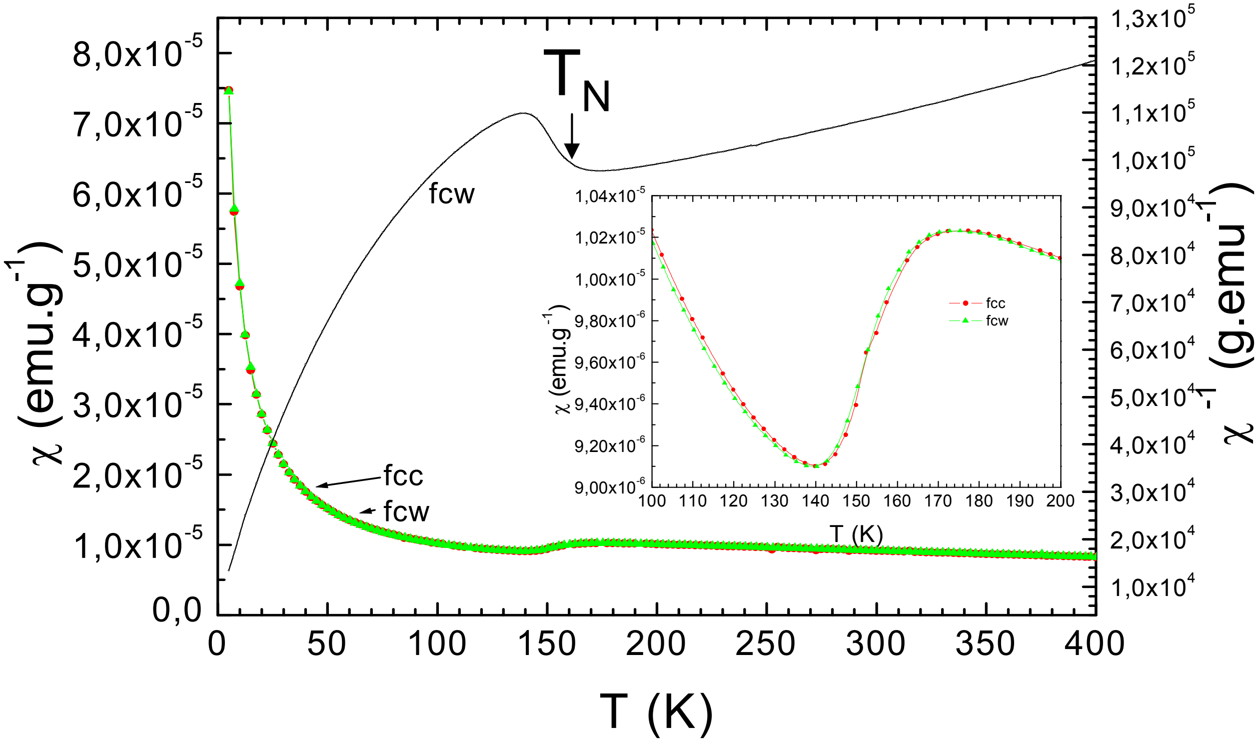
$3d^1$ / $3d^2$ with $v_v = 3.6$

Synthesis without pressure



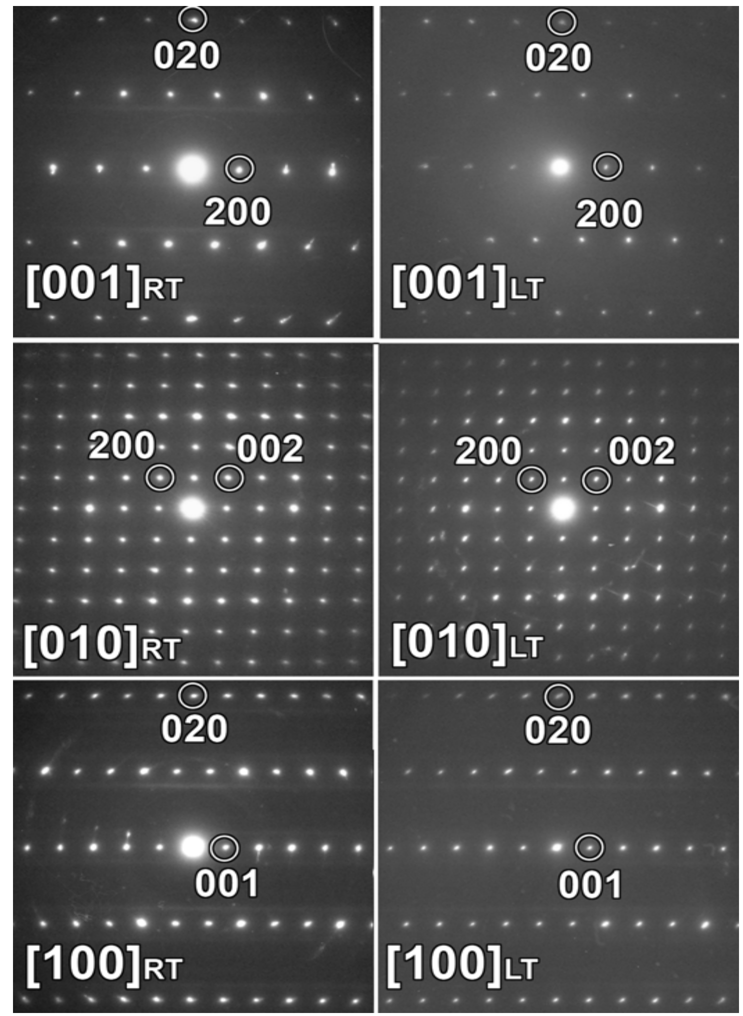
I12/m1 space group with a=10.125Å, b=2.902Å and c=9.880Å

$Pb_{1.6}V_8O_{16}$: magnetic properties



AFM ordering of the V^{3+} d^2
V^{4+} d^1

300K 100K



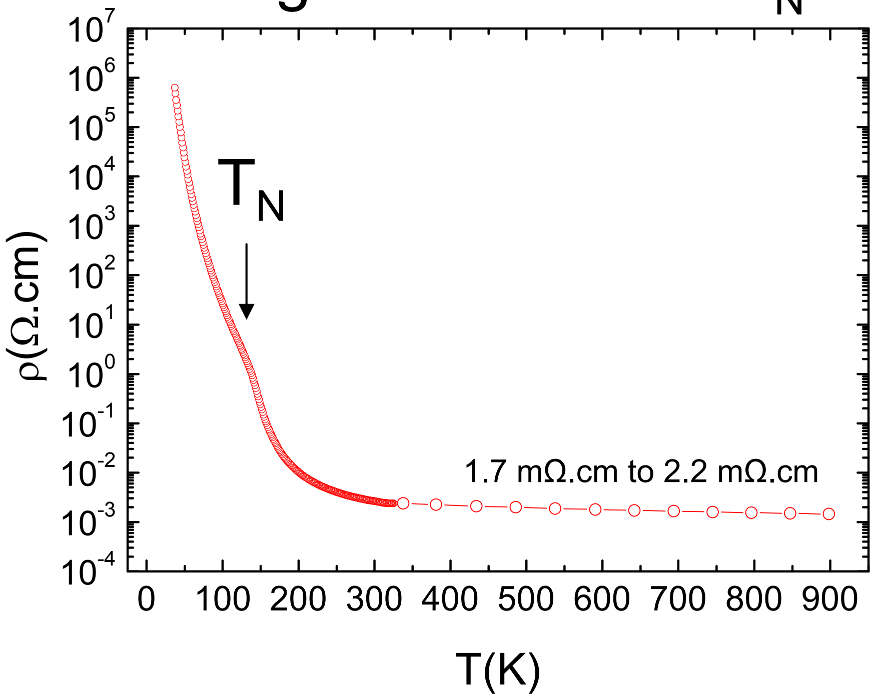
ED: no structural transition

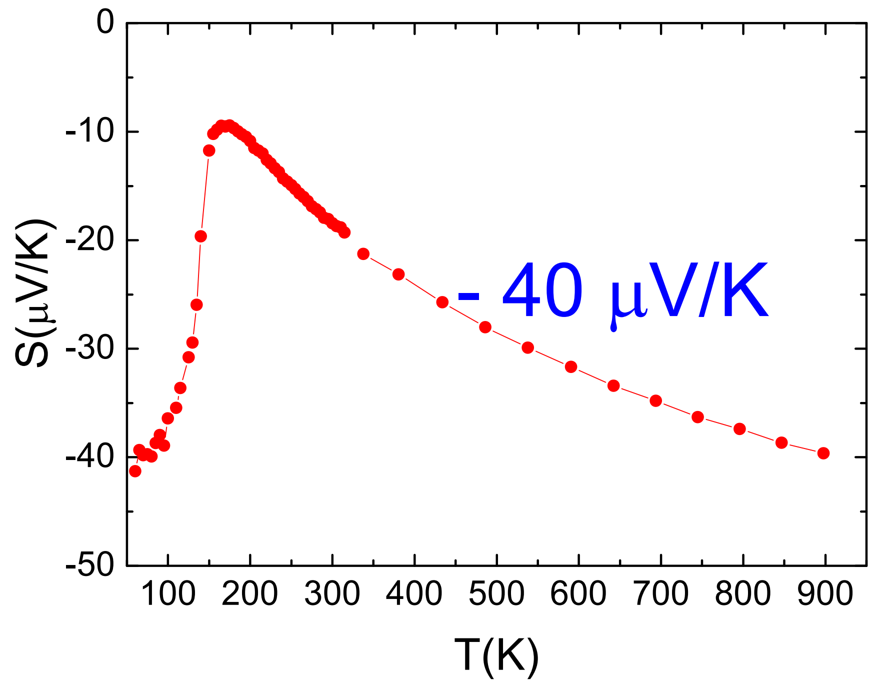
$Pb_{1.6}V_8O_{16}$: Transport properties

V_v=3.6

n type

Strong localization at T_N





$$S = -\frac{k_B}{|e|}\ln(\beta\frac{1-x}{x})$$

→ spin and orbital degeneracy terms for a V^{3+} (d^2)/V^{4+} (d^1) mixture lead to S (T→ ∞) value of ~ -35μV/K

A. Maignan et al., PRB82, 035122 (2010)

Conclusion

Several contributions to the Seebeck coefficients in misfits :

- $S \sim \gamma T$ at low T
- Spin entropy at low T depending on susceptibility
- At high T

$$S = -\frac{k_B}{|e|} \ln\left(\beta \frac{1-x}{x}\right)$$

Major role of the Heikes formula even at T ~ 300K

Collaborators

Laboratoire CRISMAT
Wataru Kobayashi (Tsukuba), Oleg Lebedev,
Antoine Maignan, Christine Martin,
Denis Pelloquin, Olivier Perez

Patrice Limelette, LEMA, Tours
Julien Bobroff, Véronique Brouet, LPS Orsay

This work is supported by FP7 European Initial Training Network
SOPRANO (GA-2008-214040)

MARIE CURIE ACTIONS

SEVENTH FRAMEWORK PROGRAMME