Optimisation du facteur de mérite : l'exemple des oxydes de cobalt

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GDR Thermoélectricité, Nancy, juillet 2009

Plan de l'exposé

• **Introduction : comment augmenter ZT?**

↳ **Nanostructuration**

Augmentation du facteur de puissance

+ réduction de la conductivité thermique

↳ **Réduction de la conductivité thermique**

↳ **Corrélations électroniques**

Augmentation du facteur de puissance

• **Les oxydes de cobalt à structure lamellaire désaccordée**

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

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

$\sigma(E) = en(E)\,\mu(E)$

S dépend de n(E), et de la position de E_F

- **Résistivité** : $\rho^{-1} = \mathrm{en(E)}\mu(\mathrm{E})$

Forte mobilité

- **Conductivité thermique**

Terme électronique lié à ρ^{-1} (Wiedemann Franz)

Terme de réseau à minimiser

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

‘PGEC’

Phonon glass – Electron crystal

Découplage électrons – phonons?

G. Slack, Handbook of Thermoelectricity (1995)

Facteur de puissance

Modification de DOS

- Nanostructuration
- Corrélations électroniques

Conductivité thermique phononique

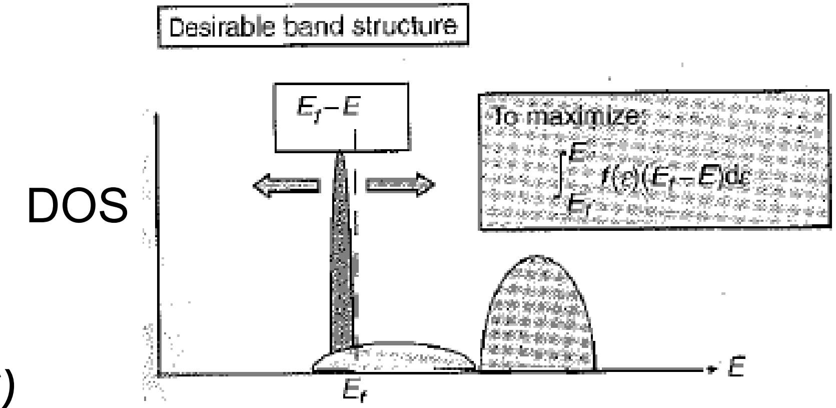
- ‘Rattling’
- Nanostructuration

Nanostructuration

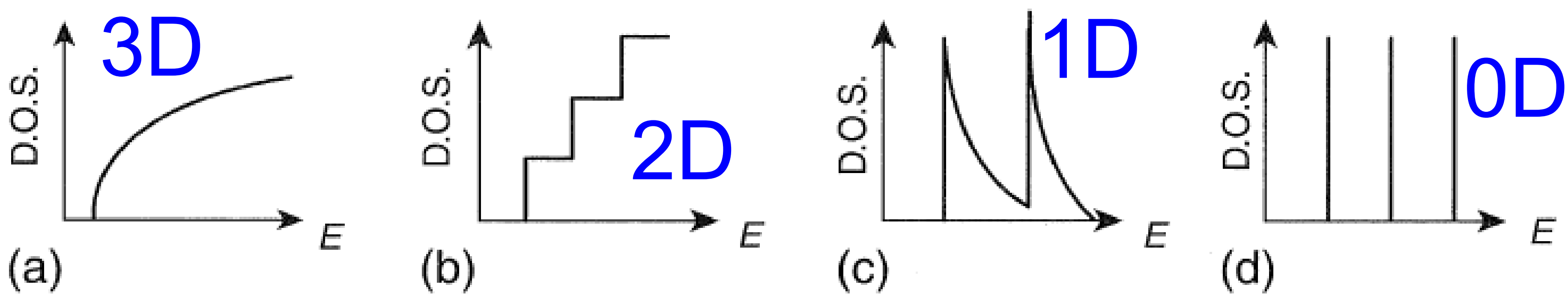
Formule de Mott

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

Tse et al., Handbook of Thermoelectricity (2006)



Nanostructuration



modification de la DOS

↳ **augmentation de S**

Hicks et Dresselhaus, PRB47, 12727 (1993)

Hicks et Dresselhaus, PRB47, 16631 (1993)

Superréseaux Bi_2Te_3/Sb_2Te_3

ZT = 2.5!

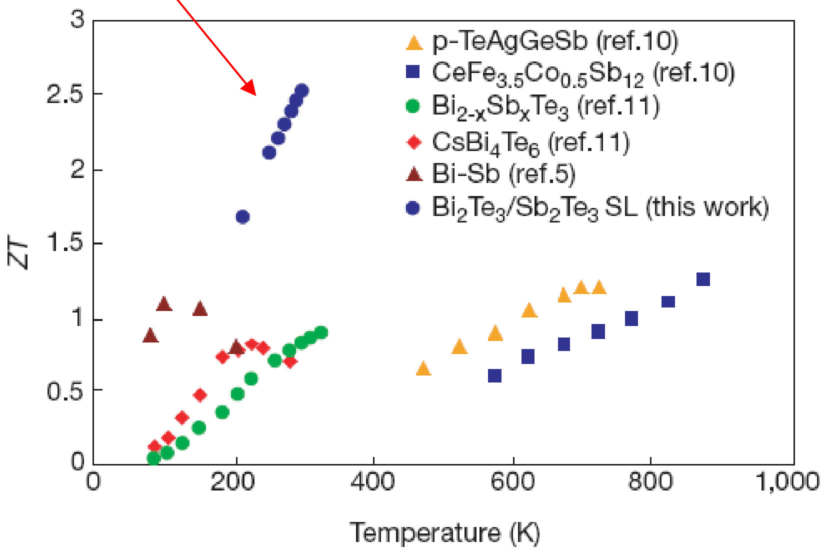


Figure 3 Temperature dependence of *ZT* of 10Å/50Å p-type Bi_2Te_3/Sb_2Te_3 superlattice compared to those of several recently reported materials.

Venkatasubramanian et al., Nature 413, 597 (2001)

Amélioration de la mobilité

\+

Réduction de κ_L

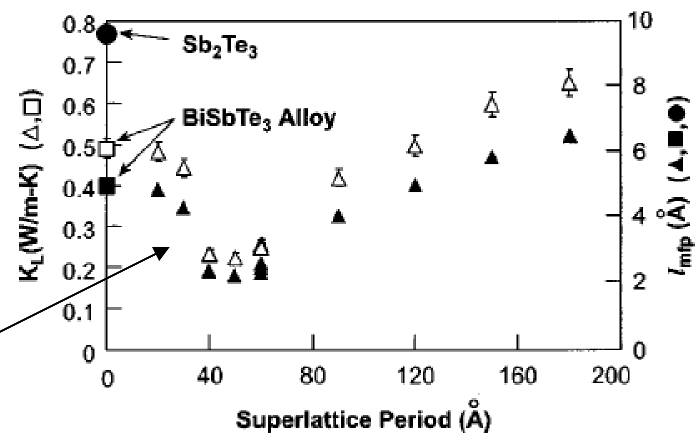


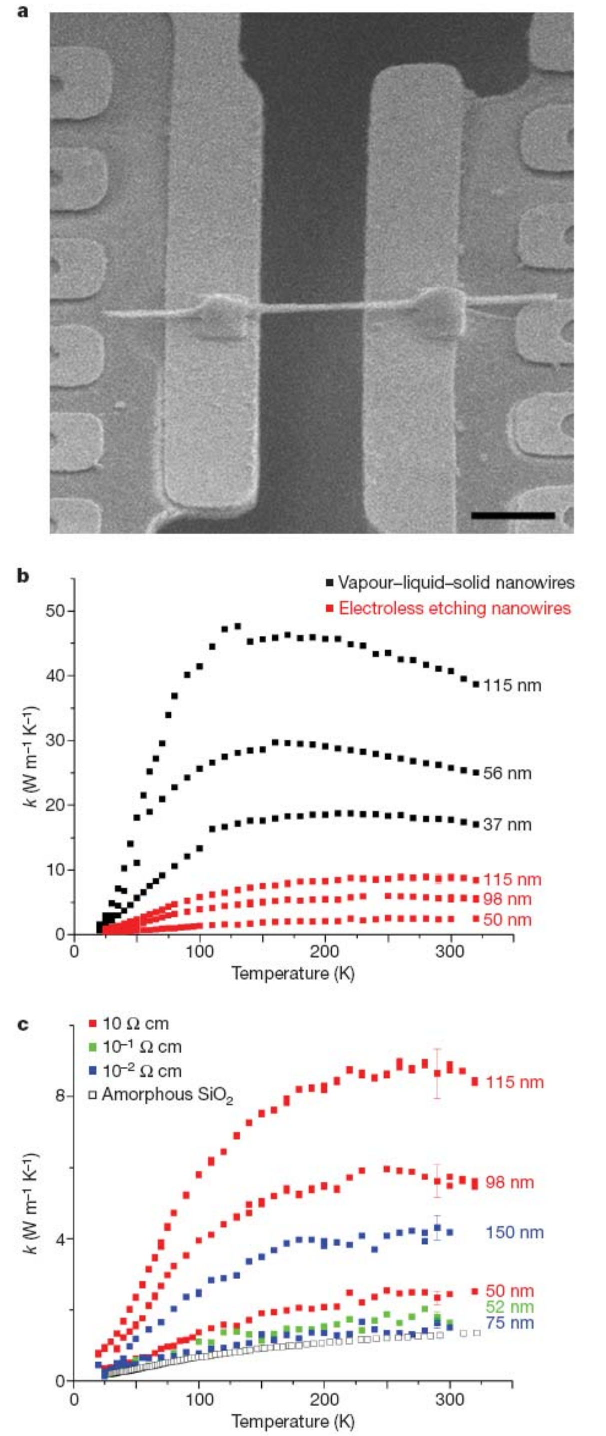
FIG. 3. Experimental lattice thermal conductivity (K_L) and calculated average phonon mean free path (l_{mfp}) as a function of the period in Bi_2Te_3/Sb_2Te_3 superlattices and other reference materials. Note: There are three data points, almost on top of each other, at the 60 Å period, corresponding to 30 Å/30 Å, 10 Å/50 Å, 20 Å/40 Å structures.

Diffusion des phonons aux interfaces

Venkatasubramanian, PRB61, 3091 (2000)

Nanofils de silicium

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



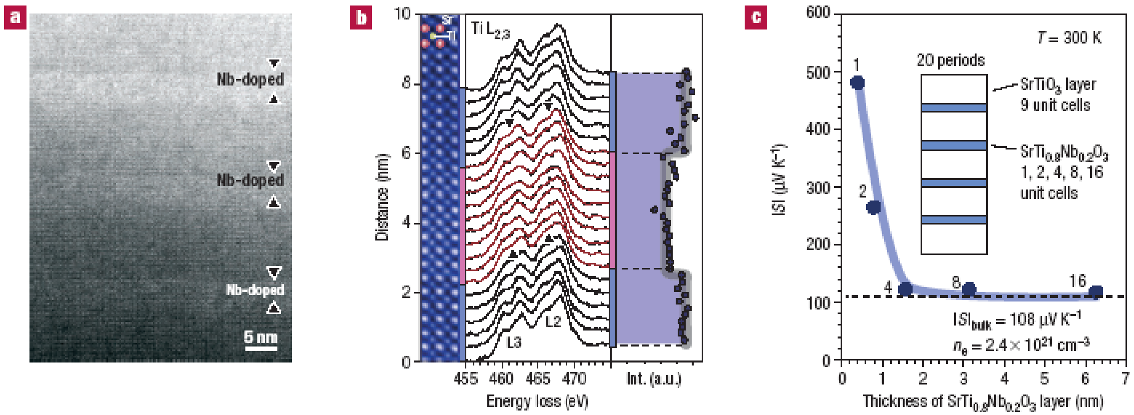
Si : ZT ~ 0.01 à 300K

↳ZT = 0.6 à 300K
pour les nanofils

Effet principalement lié aux
Phonons :
réduction de κ + phonon drag pour S

2D electron gas in $SrTiO_3$

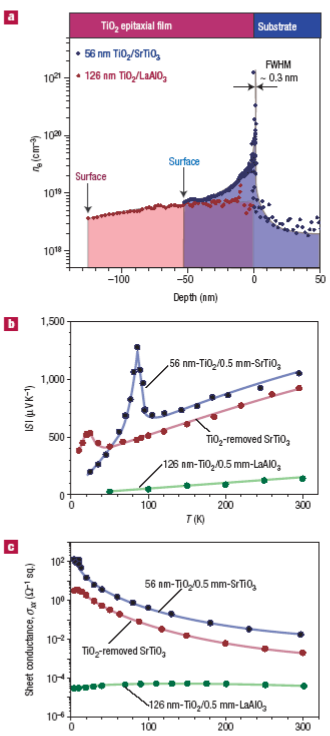
H. Ohta et al., Nat. Mater. 6, 129 (2007)



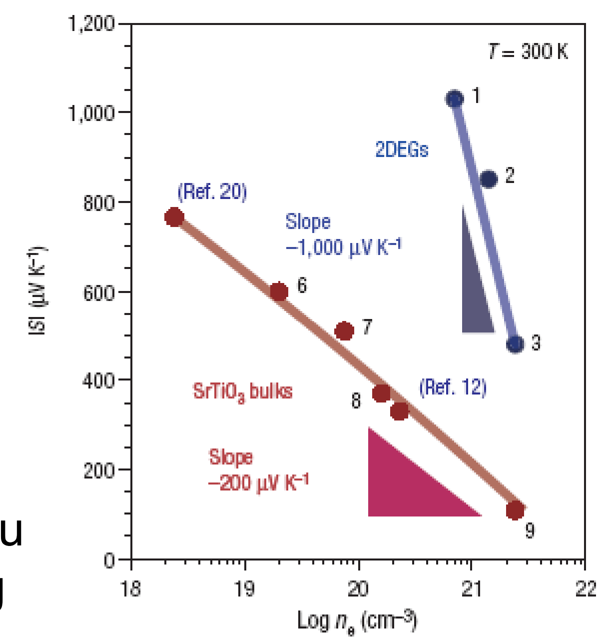
Nanostructuration :
Augmentation de S

$$\sigma_{\text{eff.}} = \sigma_{\text{2DEG}} / (1 + N_{\text{barrier}})$$

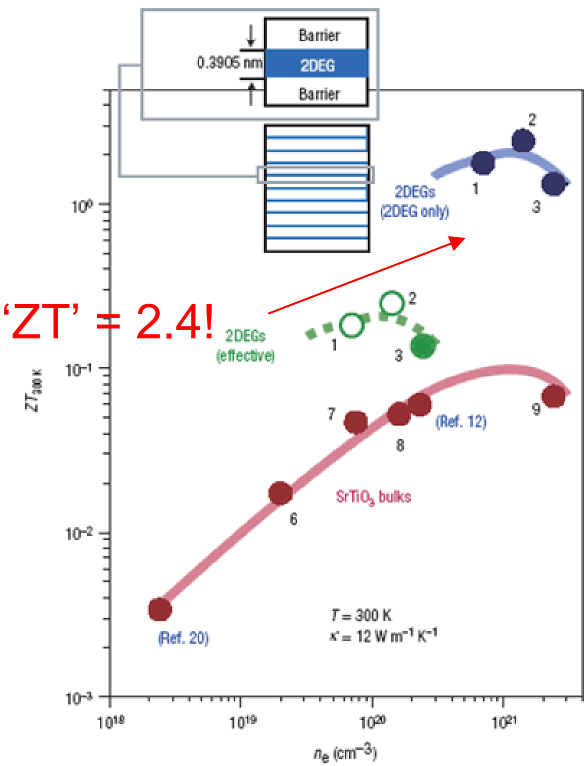
$$ZT_{\text{eff.}} = ZT_{\text{2DEG}} / (1 + N_{\text{barrier}})$$



Pic de S lié au phonon drag



$$|S| = -k_B/e \cdot \ln 10 \cdot A \cdot (\log n_e + B)$$

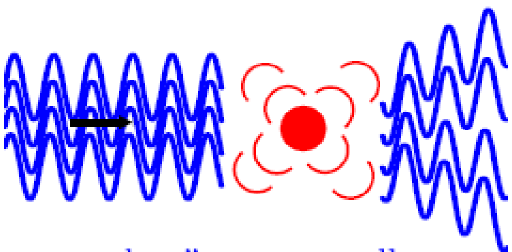


'ZT' = 2.4!

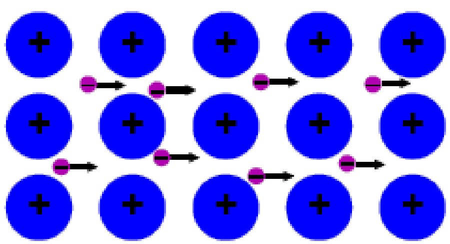
κ mesuré sur monocristal de $SrTiO_3$

Réduction de la conductivité thermique
‘Phonon glass’

Phonon glass / Electron crystal



"Phonon glass" $\rightarrow \kappa$ small



"Electron crystal" $\rightarrow \sigma$ large

• Atomes lourds
dans des cages ('rattling')

• Structures cristallines complexes

• Solutions solides

• Matériaux composites
Diffusion sur les défauts ponctuels
Diffusion par les joints de grains

• Nanostructures

Nanograins $Si_{95}Ge_5$ dopés P

Increased Phonon Scattering by Nanograins and Point Defects in Nanostructured Silicon with a Low Concentration of Germanium

G. H. Zhu,[1] H. Lee,[2] Y. C. Lan,[1] X. W. Wang,[1] G. Joshi,[1] D. Z. Wang,[1] J. Yang,[1] D. Vashaee,[3] H. Guilbert,[1] A. Pillitteri,[1] M. S. Dresselhaus,[4] G. Chen,[2,*] and Z. F. Ren[1,*]

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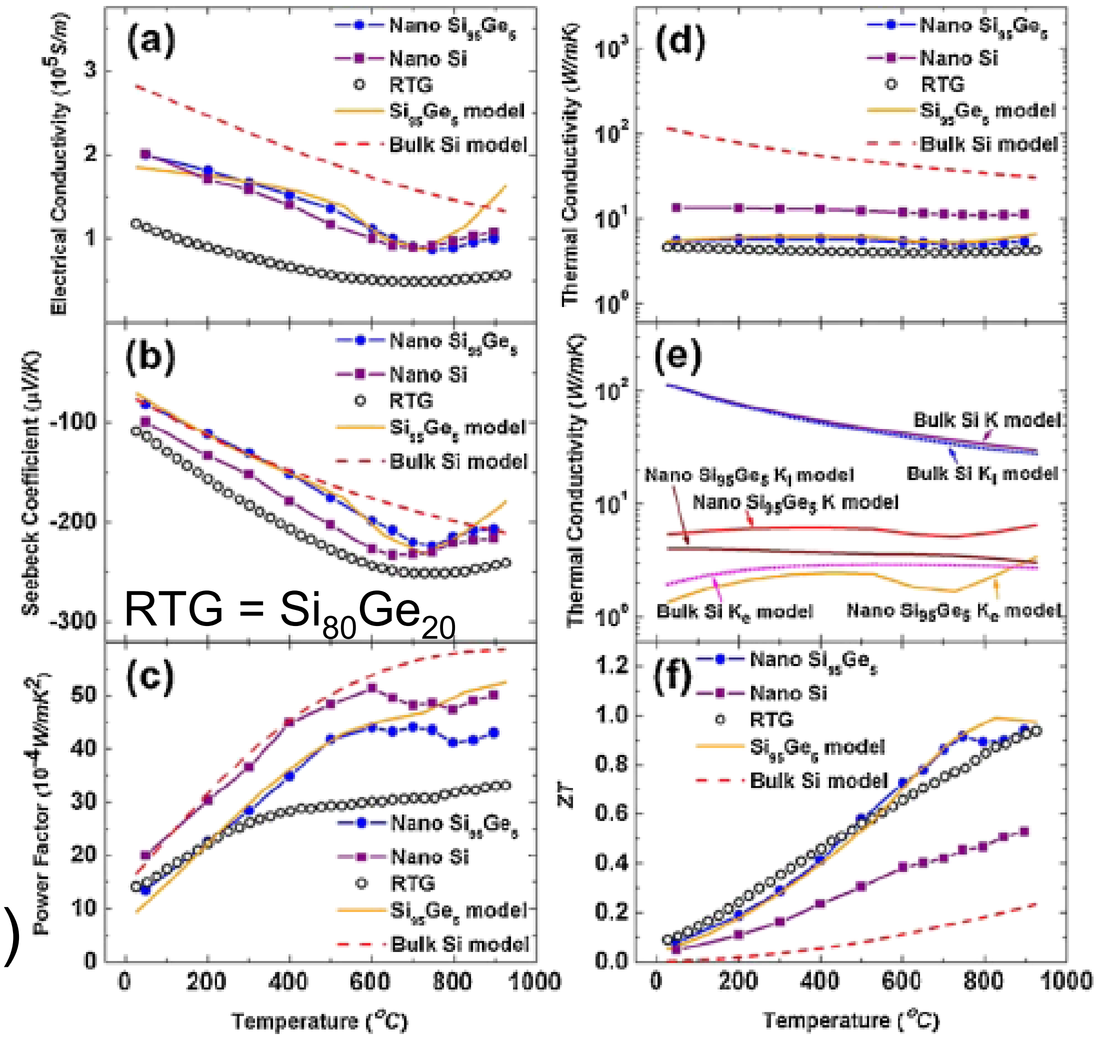
Faible composition en Ge : bonnes propriétés électriques (moins de diffusion pour les électrons et bonne solubilité du P)

Nanograins (5 -20nm) : diffusion liée aux interfaces

Ge : responsable de diffusion sur des défauts ponctuels (phonons λ <1nm)



Nanostructuration : WSe_2 et superréseaux

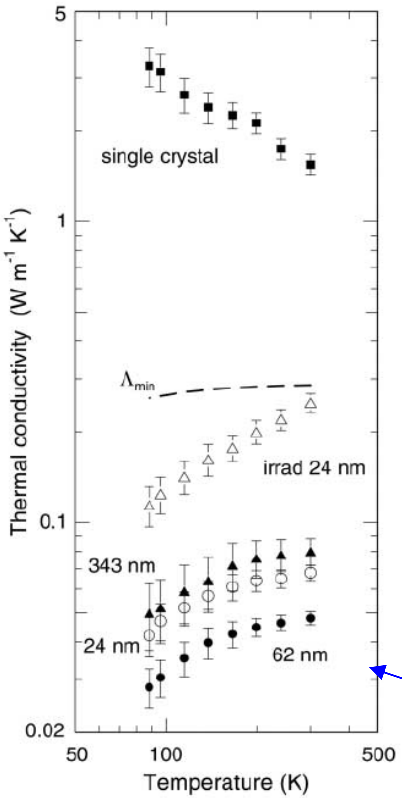
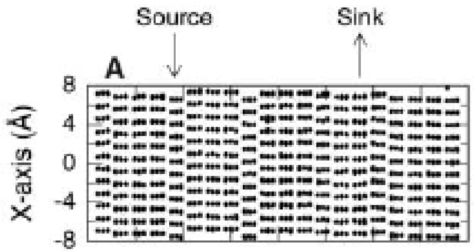


Fig. 2. Summary of measured thermal conductivities of WSe_2 films as a function of the measurement temperature. Each curve is labeled by the film thickness. Data for a bulk single crystal are included for comparison. Error bars are the uncertainties propagated from the various experimental parameters used to analyze the data (*6*). The ion-irradiated sample (irrad) was subjected to a 1-MeV Kr^+ ion dose of 3×10^{15} cm^{-2}. The dashed line marked Λ_{min} is the calculated minimum thermal conductivity for WSe_2 films in the cross-plane direction.

Couches W/Se_2



Défauts d'empilement

↳ réduction de κ

$0.05 Wm^{-1}K^{-1}$
à 300K!

Modification artificielle des empilements

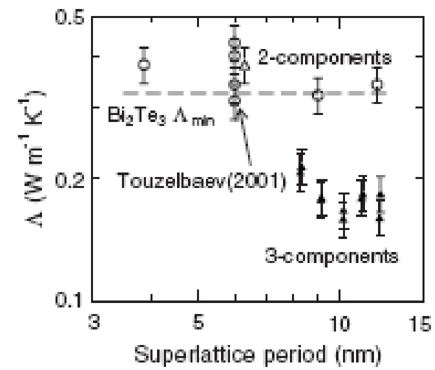


FIG. 2. Cross-plane thermal conductivity of three-component $Bi_2Te_3/TiTe_2/Sb_2Te_3$ films (filled triangle) and two-component Bi_2Te_3/Sb_2Te_3 films (open triangle) annealed at 250 °C. Open circles are thermal conductivities for Bi_2Te_3/Sb_2Te_3 superlattices in Ref. 25. Minimum thermal conductivity for Bi_2Te_3 (dashed line) was calculated using the model in Ref. 26 and is included for comparison.

Facteur de puissance en cours d'étude

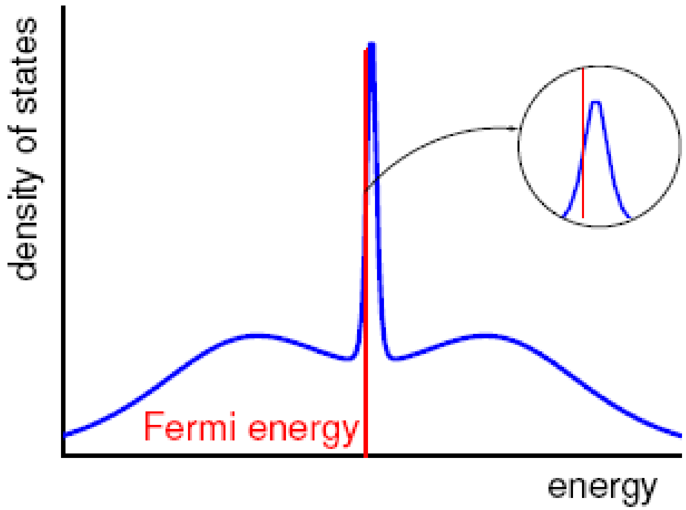
Chitirescu et al., Science315, 351 (2007); JAP104, 033533 (2008)

Corrélations électroniques

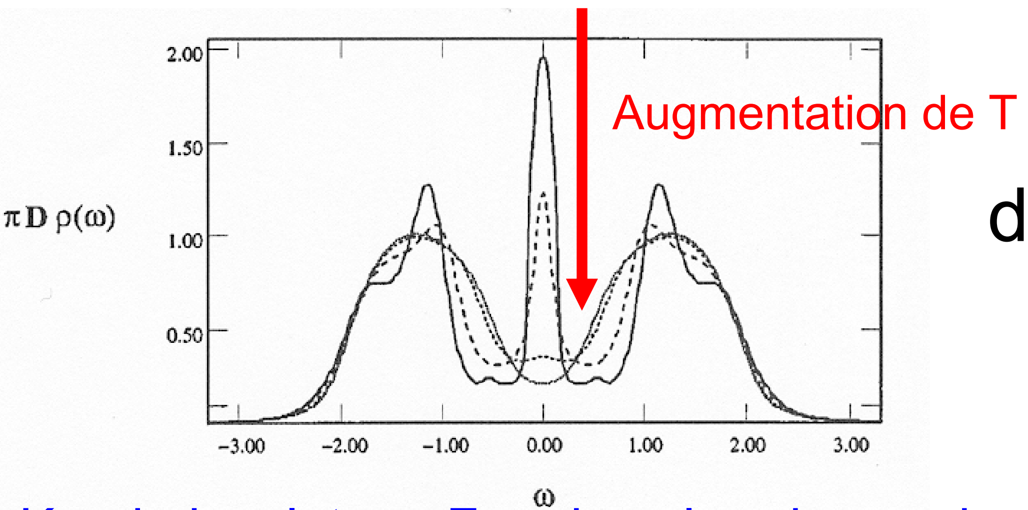
Terme diffusif

Terme haute T (formule de Heikes)

Corrélations électroniques



Modification de DOS liée aux corrélations



Dépend
de U (énergie de répulsion coulombienne),
de T

Kondo insulators, Fermions lourds, oxydes…

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

Augmentation de S liée aux corrélations électroniques

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

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

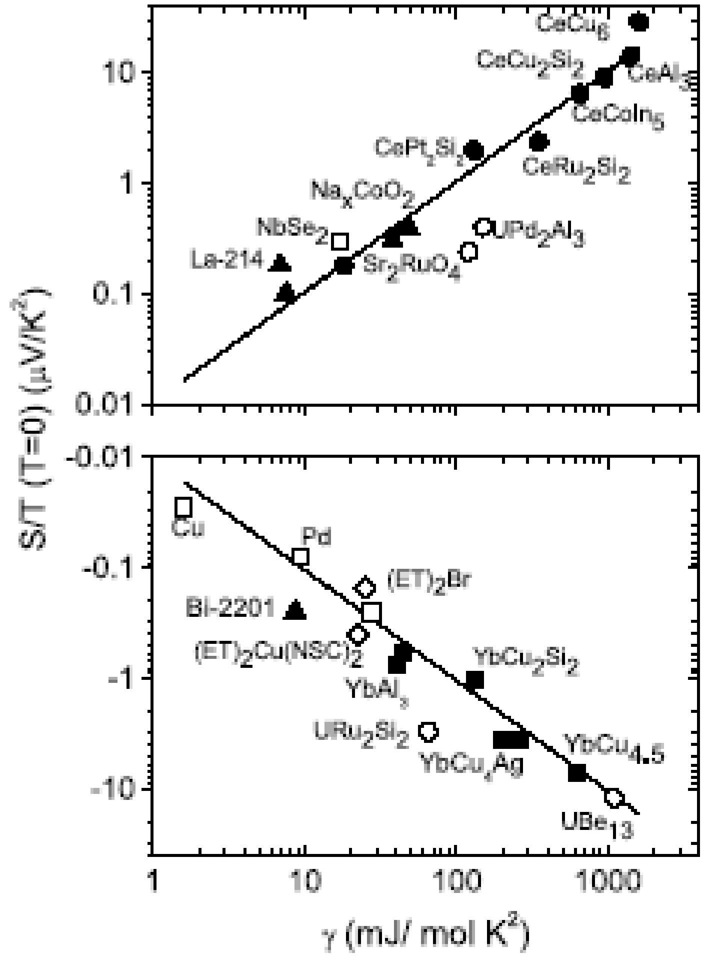
Rapport : S / chaleur spécifique C_{el}

Limite T$\longrightarrow$ 0

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

γ: partie électronique de la chaleur spécifique

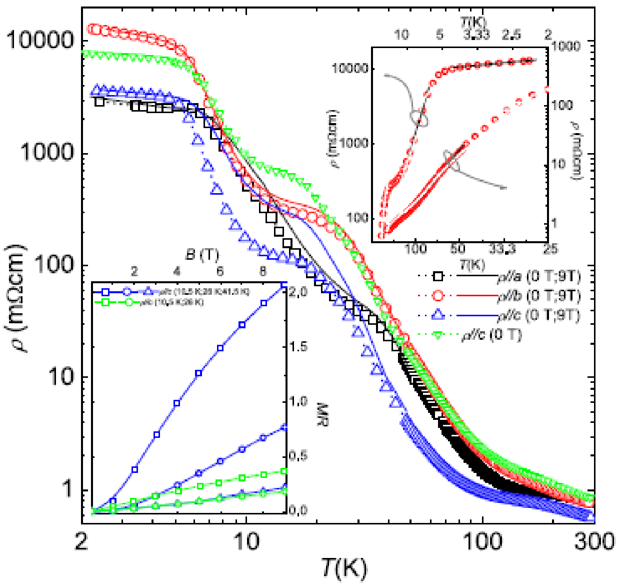
$$0.5 < |q| < 2$$

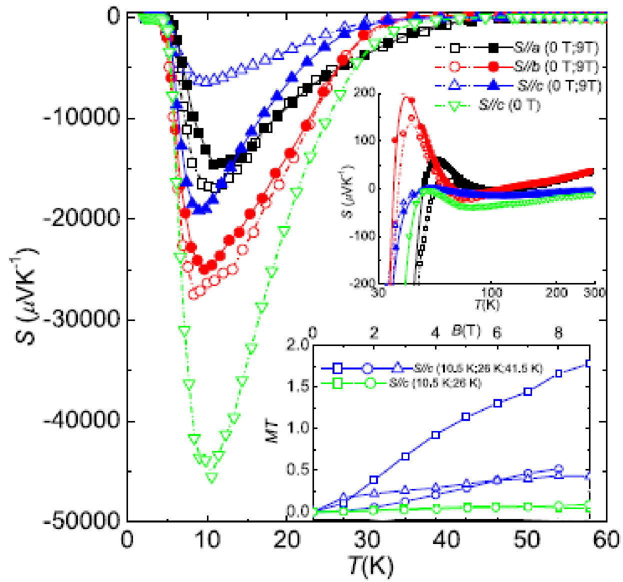


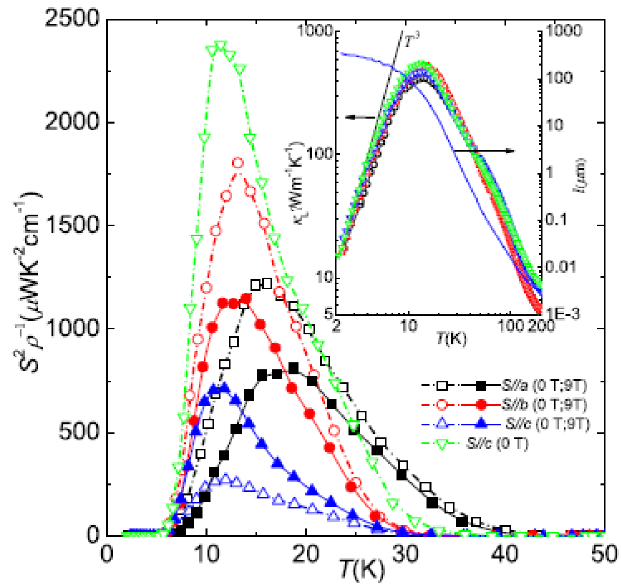
K. Behnia et al. JPCM 16, 5187 (2004)

‘Strongly correlated semiconductor $FeSb_2$’

A. Bentien et al., EPL80, 17008 (2007)





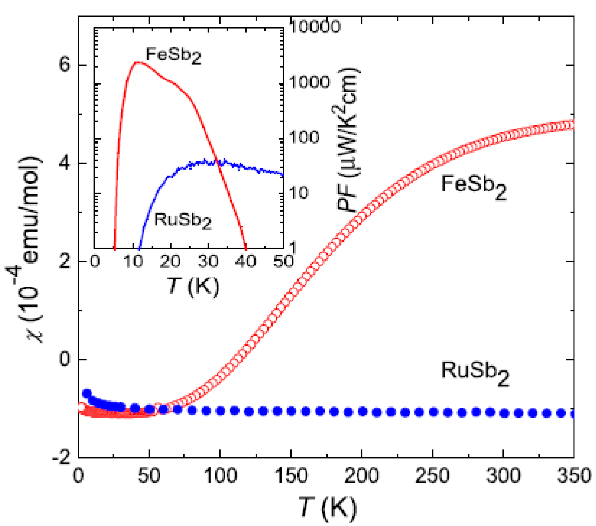


Comparaison avec $RuSb_2$, isostructural :

Pas d’effet de phonon drag (pas observé dans $RuSb_2$)

Terme diffusif *10 lié aux corrélations électroniques

P. Sun et al., PRB79, 153308 (2009)



Effet similaire observé dans FeSi

N. E. Sluchanko et al., EPL51, 557 (2000)

Modèle de Hubbard

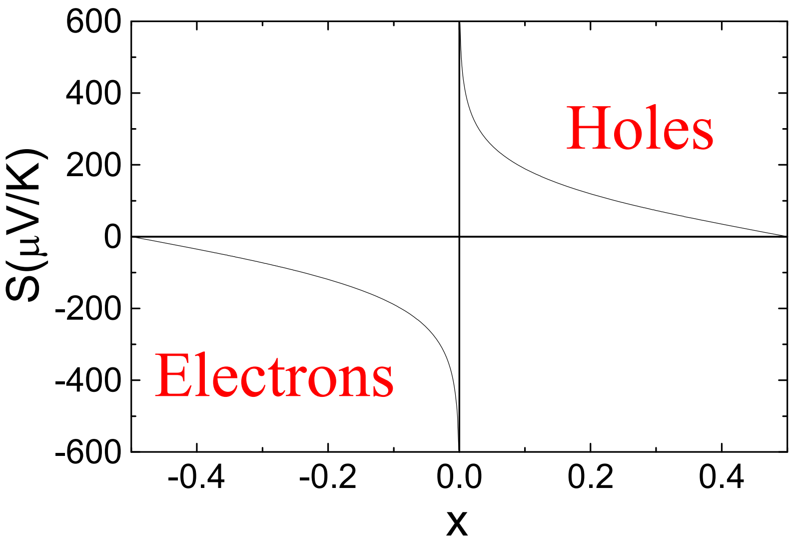
$$S = \frac{-S^{(2)}/S^{(1)} + \mu/|e|}{T} \rightarrow \frac{\mu/|e|}{T} \qquad \text{for } T \rightarrow \infty$$

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

Limit T →∝ : S ~ entropy / carrier

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

x = carrier concentration



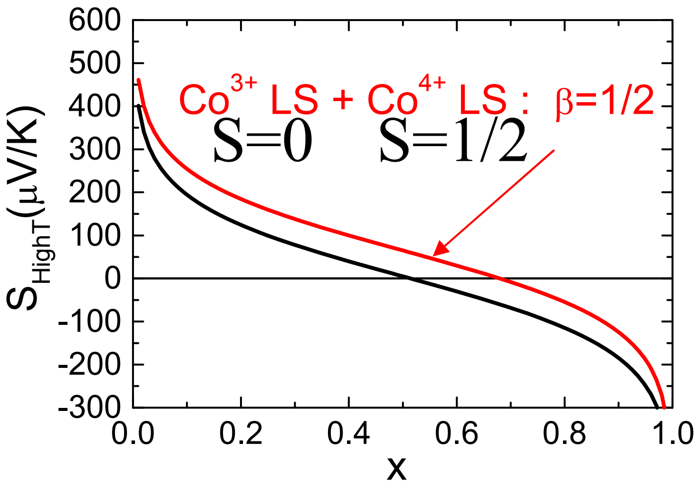
Chaikin et al. Phys. Rev. B 13, 647 (1976)

Entropie de spin

Terme supplémentaire de dégénérescence de spin
dans la formule de Heikes

Pour un cation à valence mixte M^{n+} / $M^{(n+1)+}$: $$\beta = \frac{2S_n + 1}{2S_{n+1} + 1}$$

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



J. P. Doumerc JSSC 110, 419 (1994)

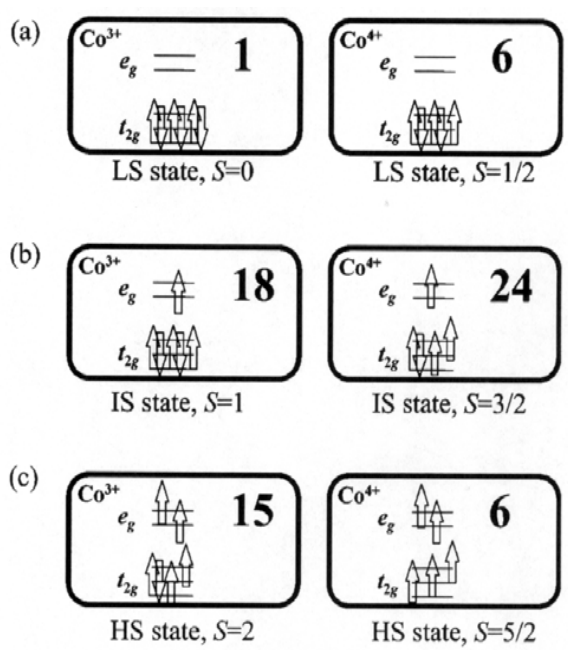
Dégénérescence de spin et d'orbitale

Co^{3+} ($3d^6$)/Co^{4+} ($3d^5$)

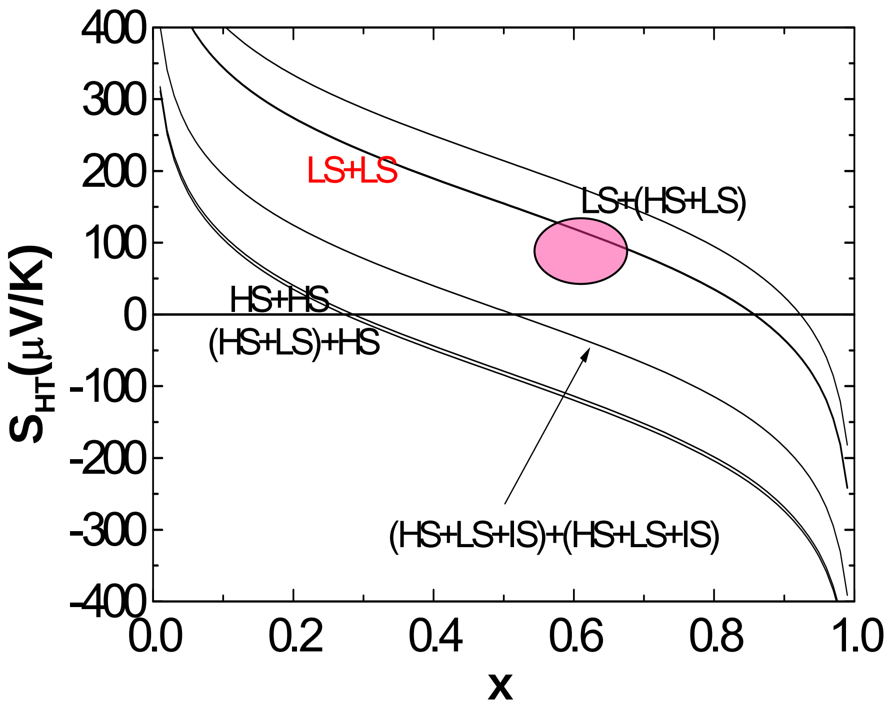
J. P. Doumerc JSSC 109, 419 (1994)

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

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



$$g_3/g_4 = 1/6$$



x : Co^{4+} concentration

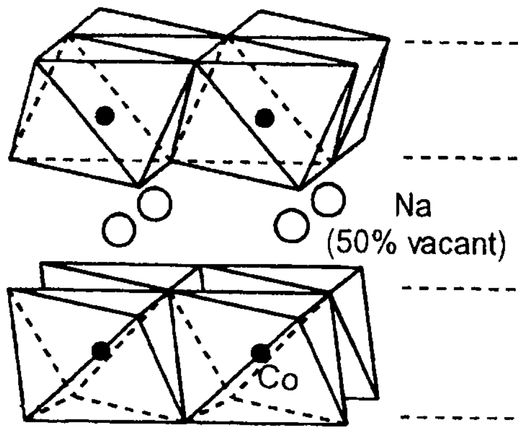
Les oxydes de cobalt
à structure lamellaire désaccordée

$NaCo_2O_4$

' Phonon Glass / Electron crystal '

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

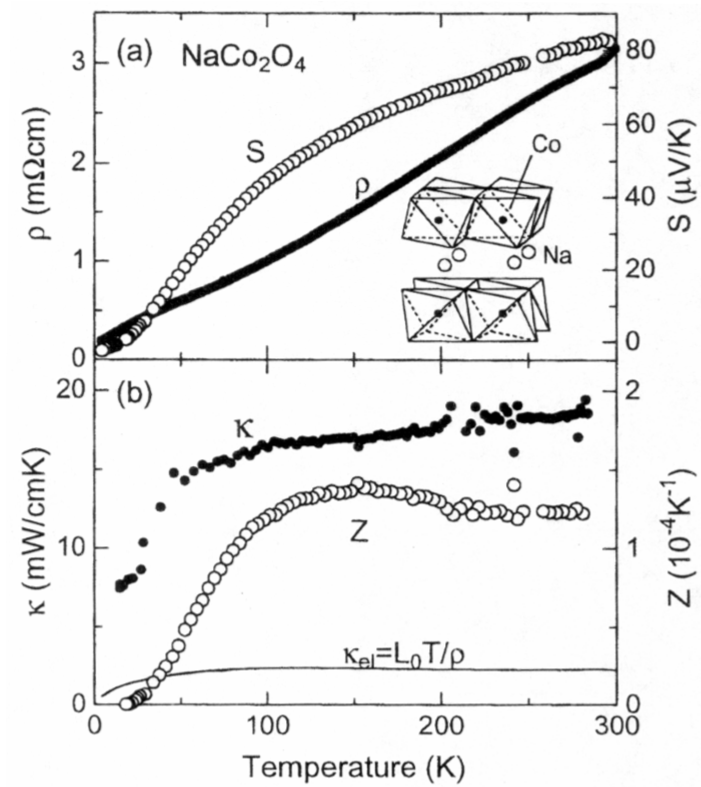
Na_xCoO_2 : $Na^+{}_x Co^{3+}{}_x Co^{4+}{}_{1-x} O_2$



Co^{3+} (3d^6) / Co^{4+} (3d^5)

Plans type CdI_2

Mesures sur polycristaux



A 300K

Métallicité (cristaux) $\rho \sim 0.2$ **mΩ cm**

Grand S **$S \sim +80$ μV/K**

Faible κ (polycristaux) $\kappa \sim 2 W m^{-1} K^{-1}$

(cristaux) $\kappa \sim 5 W m^{-1} K^{-1}$

Facteur de puissance $P=S^2/\rho$ at 300K

$NaCo_2O_4$

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

Bi_2Te_3

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

Famille des bronzes de cobalt Na_xCoO_2

C. Fouassier et al., JSSC6, 532 (1973)

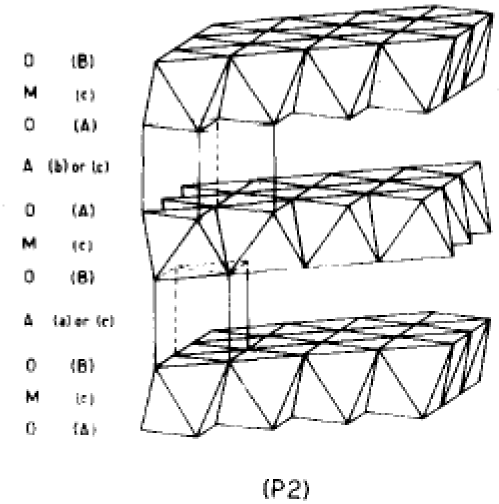


Fig. 1. Layer structure of $Na_{0.70}CoO_{2-y}$.

$Na_{0.7}CoO_{2-\gamma}$

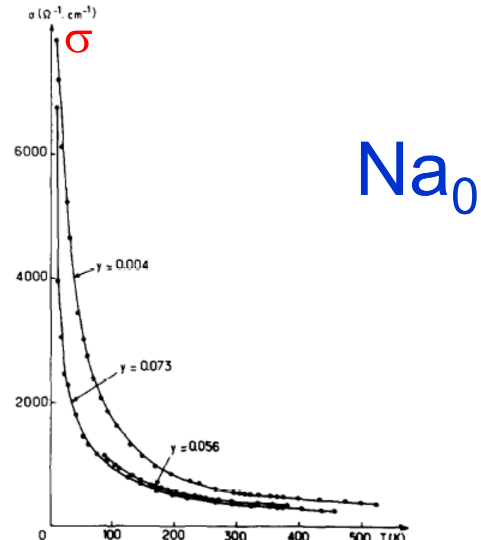


Fig. 6. Temperature dependence of the electrical conductivity of quenched pellets.

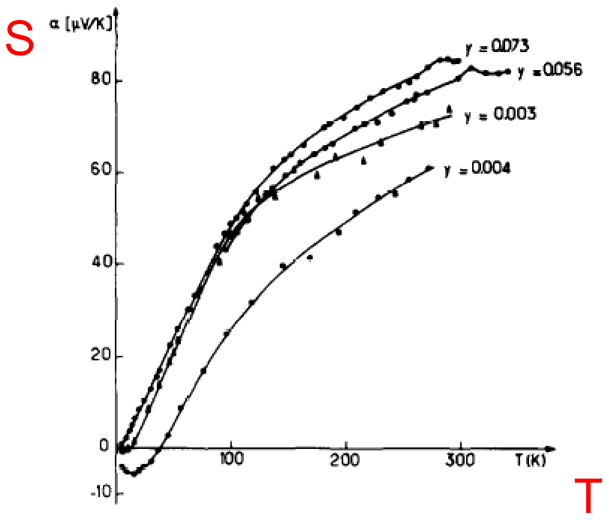
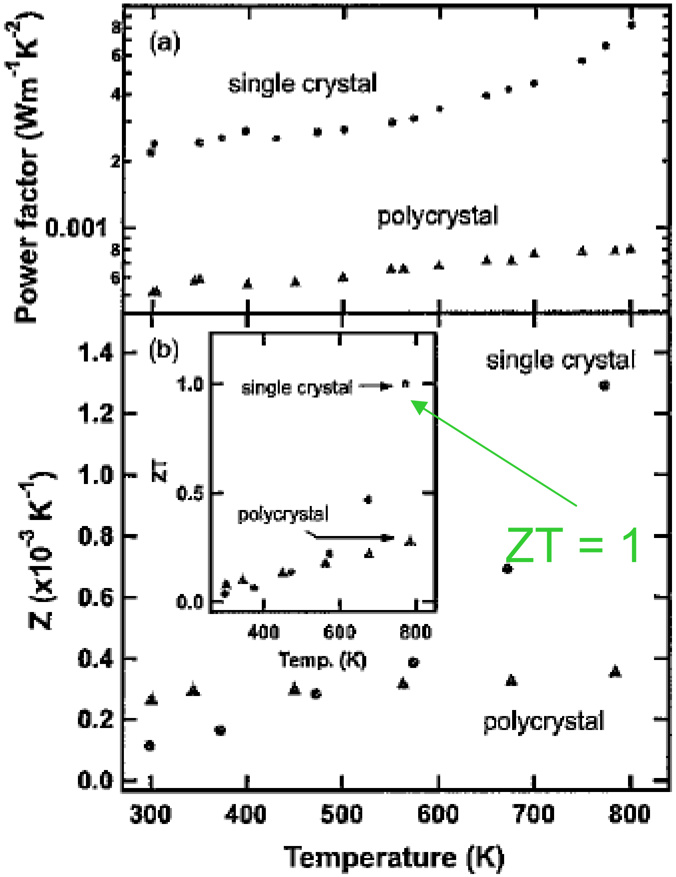


Fig. 7. Temperature dependence of the thermoelectric power of quenched pellets.

J. Molenda, C. Delmas, P. Dordor, A. Stoklosa,
Solid Stat. Ionics 12, 473 (1989)

Propriétés Haute T de Na_xCoO_2

K. Fujita et al. JJAP40, 4644 (2001)

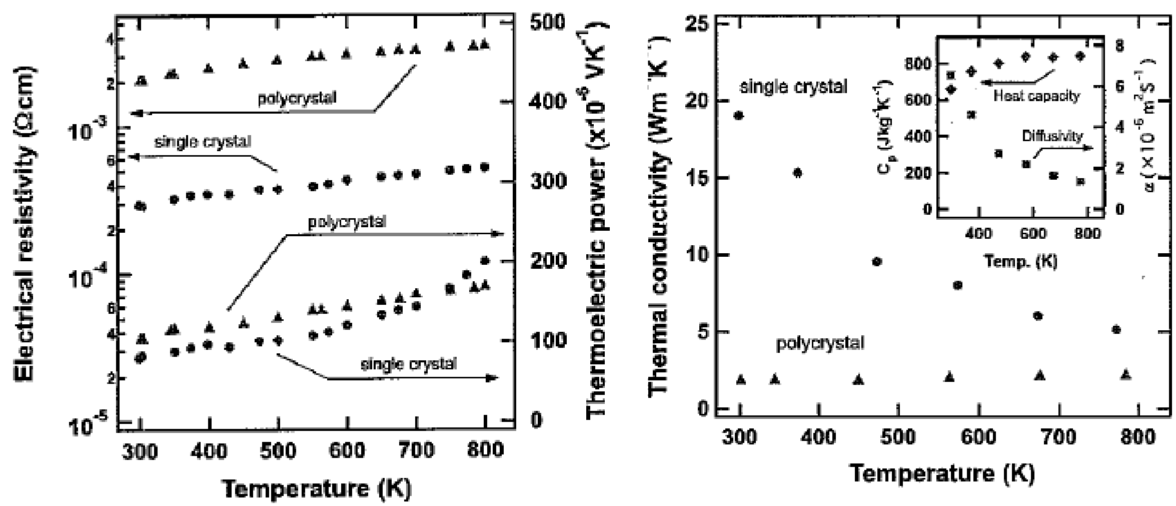


Mesures cristaux / polycristaux

Cristaux : 1.5 ×1.5 × 0.03 mm^3

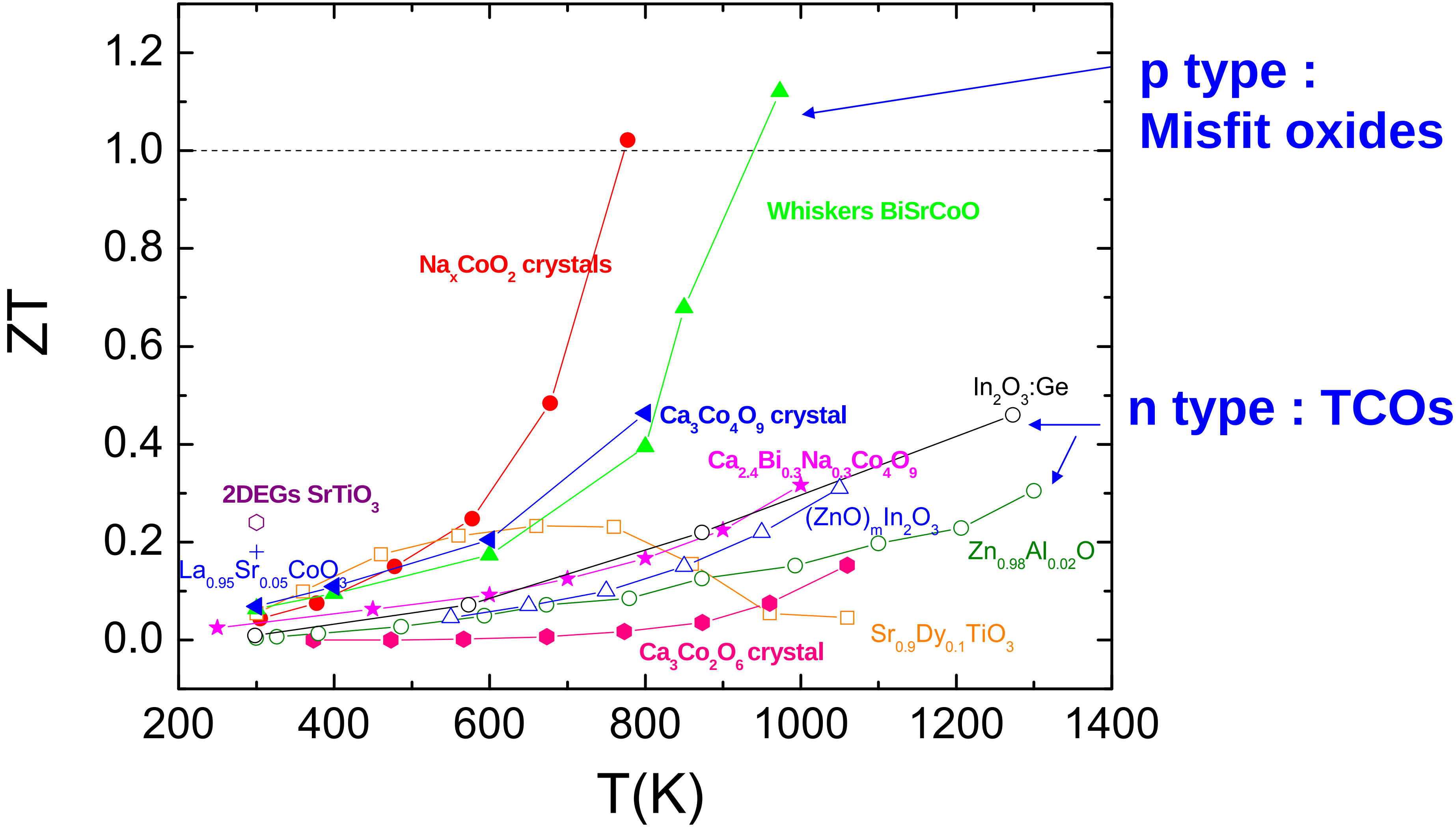
ZT ~ 1 pour les cristaux à 800K

Importance de la texturation



Oxides :
Potentially stable in air,
at high T

ZT of oxides

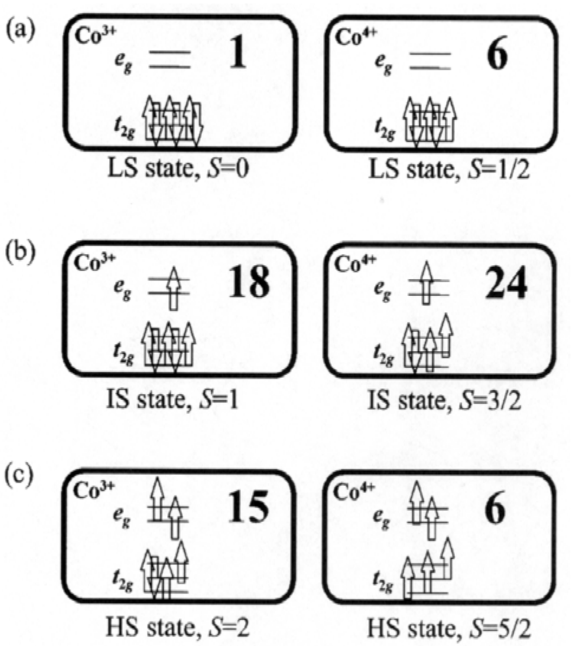


NaxCoO2 _ Fujita : JJAP 40, 4644 (2001); SrTiO3 _ Muta : J. Alloys and compounds 350, 292 (2003); Ca2.4Bi0.3Na0.3Co4O9 _ Xu : APL80, 3760 (2002); Whiskers BiSrCoO _ Funahashi : APL81, 1459 (2002); Ca3Co2O6 _ Mikami : JAP94, 10 (2003); 2DEGs(SrTiO3) _ Ohta : Nature Materials 6, 129 (2007); Ca3Co4O9 crystal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

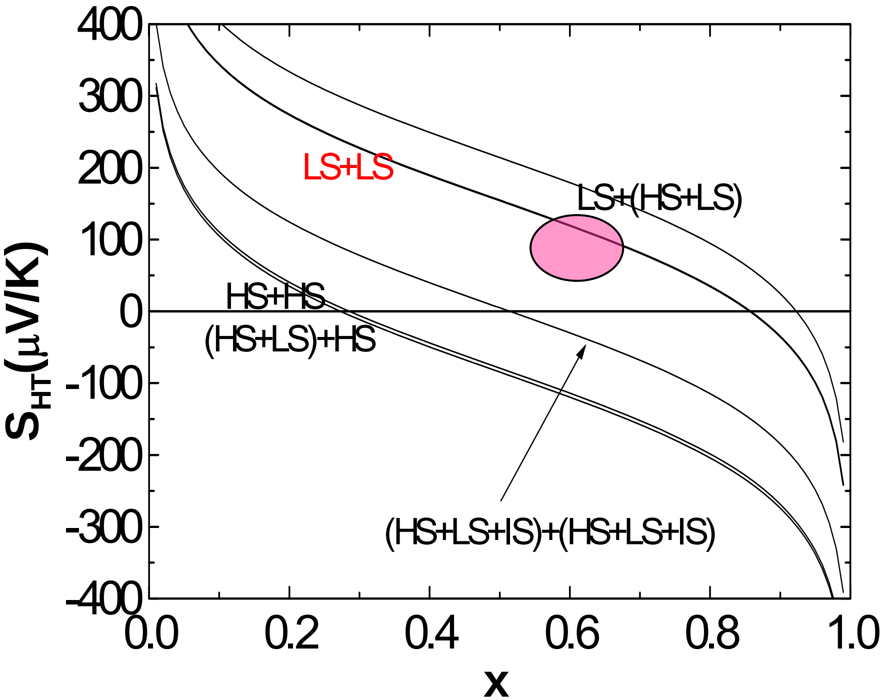
Dégénérescence de spin et d'orbitale Co^{3+} $(3d^6)$/Co^{4+} $(3d^5)$

J. P. Doumerc JSSC 109, 419 (1994)
W. Koshibae et al., Phys. Rev. B 62, 6869 (2000)

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



$g_3/g_4 = 1/6$



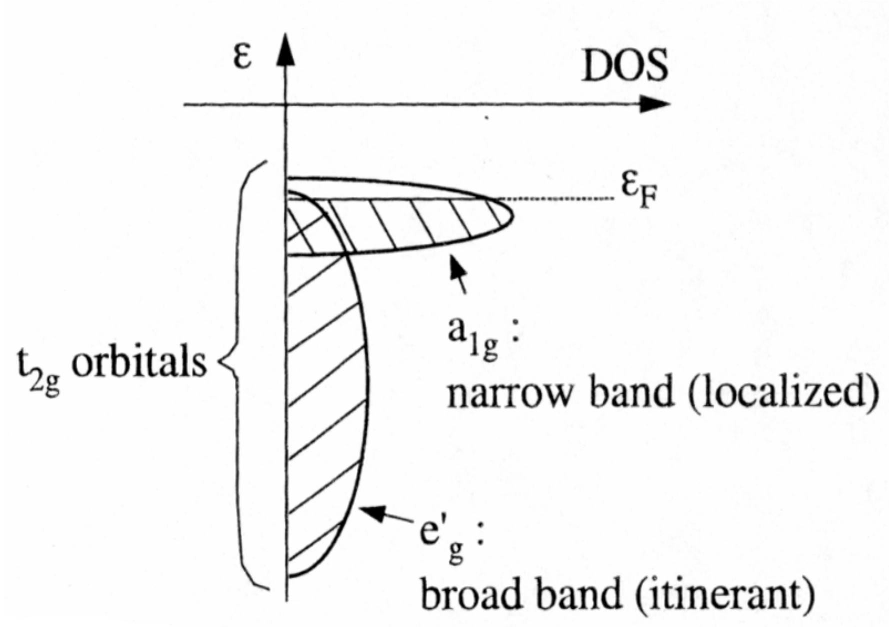
x : Co^{4+} concentration

Influence de la structure de bande?

Rhombohedral crystalline field

↳ Lifting of the t_{2g} levels degeneracy

D. J. Singh, Phys. Rev. B 61, 13397 (2000)



Peak in $N(E_F)$

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

with $\sigma = N(E) \langle v_F(E)^2 \rangle$

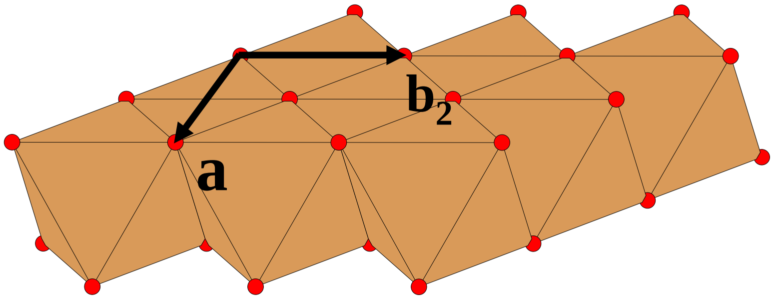
a_{1g} : localized moments / heavy holes

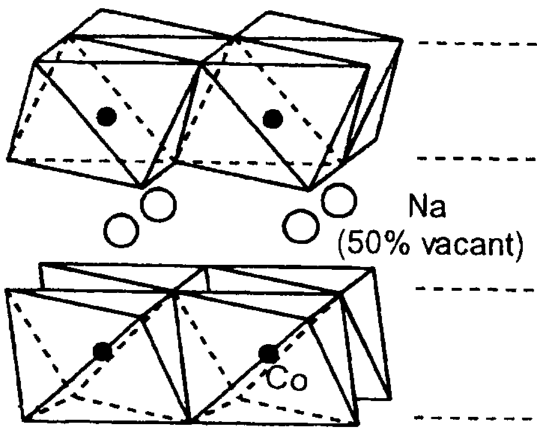
e'_g : mobile carriers / light holes

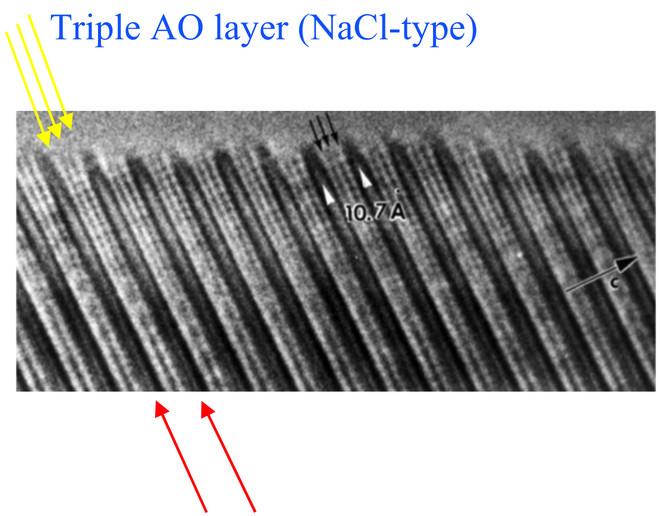
↳ **S = +110μV/K** at 300K calculated for $NaCo_2O_4$

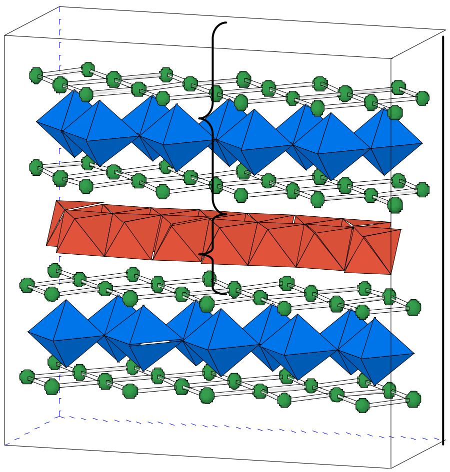
T. Yamamoto et al., Phys. Rev. B 65, 184434 (2002)

Oxydes lamellaires à base de plans CoO_2









Na_xCoO_2
K_xCoO_2, …

Famille misfit : 2, 3 ou 4 plans séparateurs

Formule de Heikes : influence du dopage?
Influence de la structure de bande : particularité des plans CoO_2 ?
Rôle des plans séparateurs?

The misfit family

- n = 4 $[Bi_2A'_2O_4]^{RS}[CoO_2]_{b1/b2}$

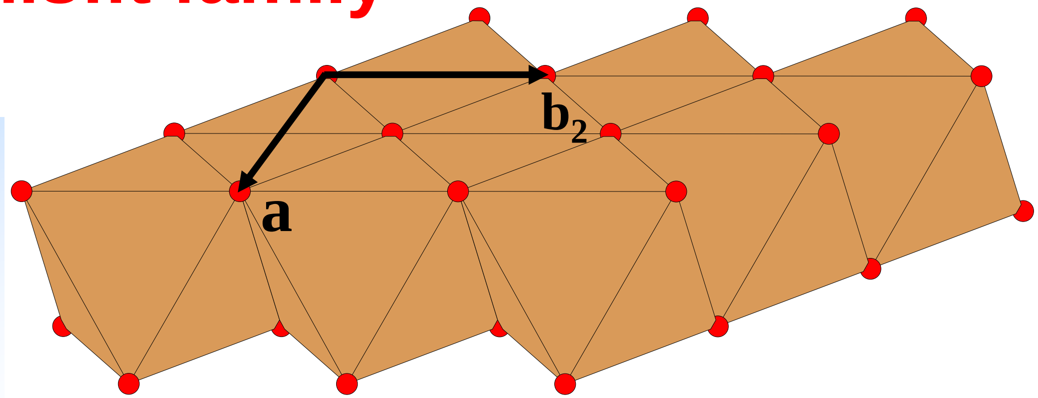
A' = Ca^{2+}, Sr^{2+} or Ba^{2+}

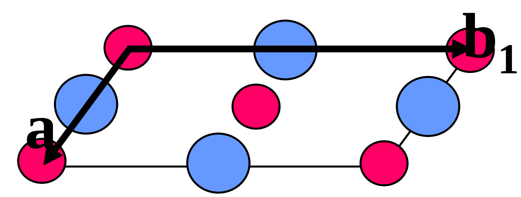
- n = 3 $[A'_2CoO_3]^{RS}[CoO2]_{b1/b2}$

A' = Ca^{2+} or Sr^{2+}

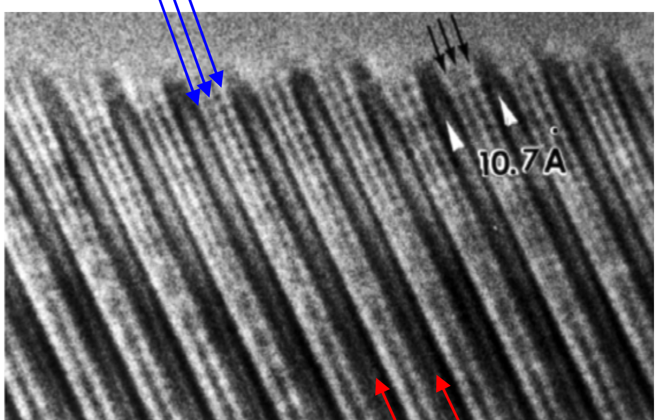
- n = 2 $[Sr_2O_2]^{RS}[CoO2]_{b1/b2}$

$[Ca_2(OH)_2]^{RS}[CoO_2]_{b1/b2}$

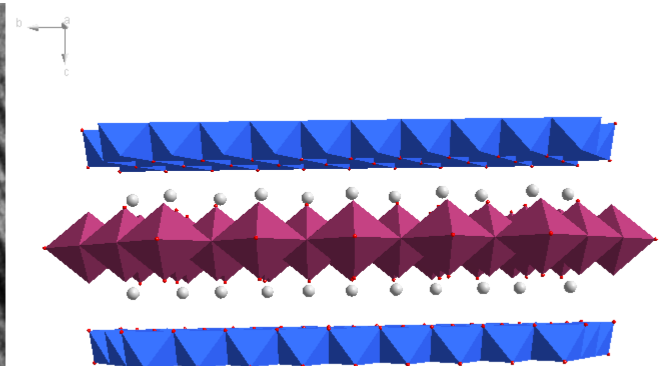




NaCl-like triple layer (RS)



CoO_2 (type CdI_2)



$a_1 = a_2$

$c_1 = c_2$

$\beta_1 = \beta_2$

$b_1 \neq b_2$

Leligny *et col.*, C. R. Acad. Sci. Paris, t. 2, Série II c, 409 (1999)

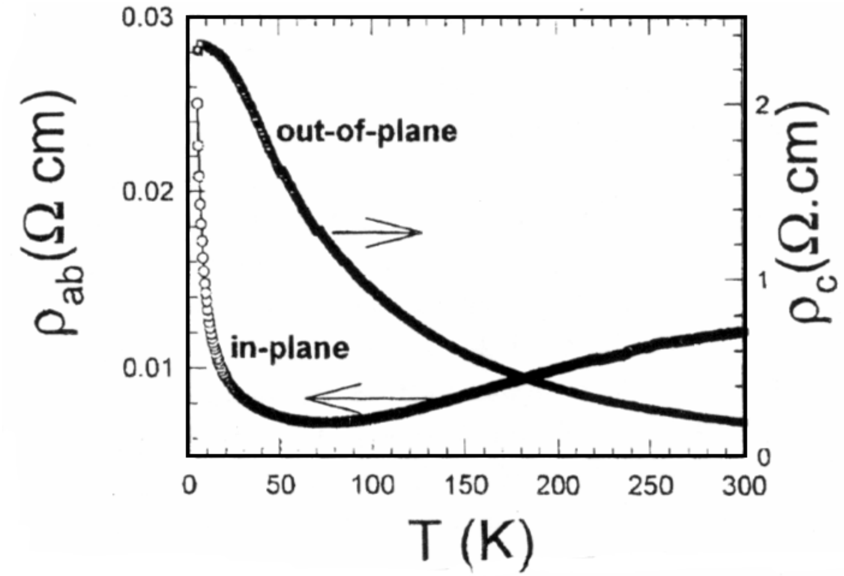
Boullay *et col.*, Chem. Mater. 8, 1482 (1996)

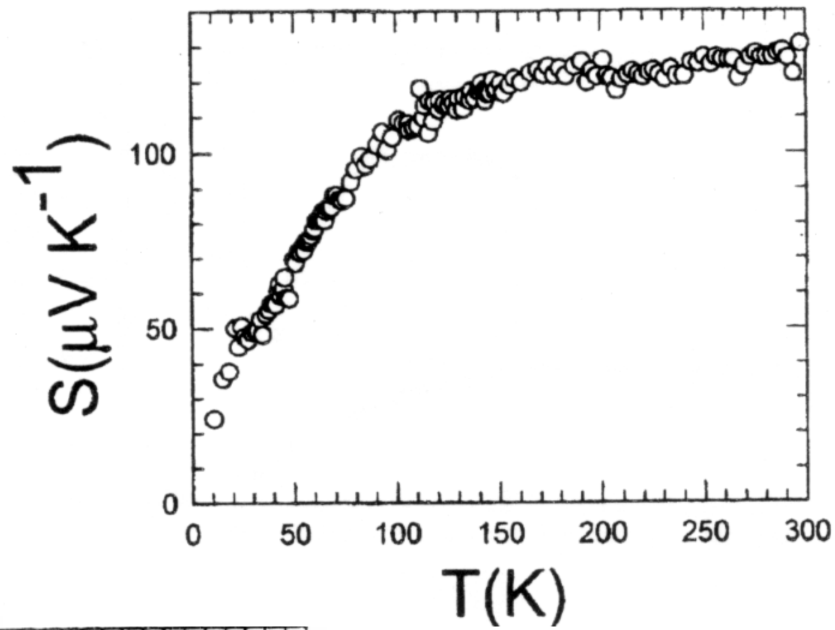
Masset *et col.*, Phys. Rev. B 62, 166 (2000)

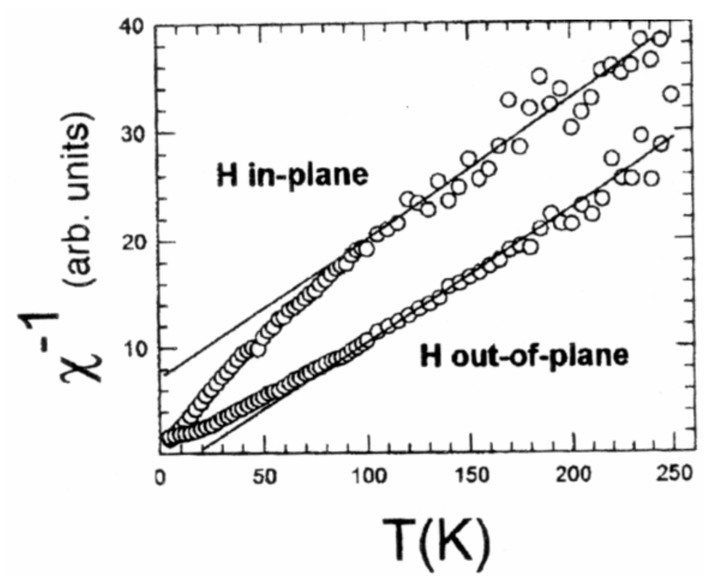
Yamauchi *et col.*, Chem. Mater. 18, 155 (2005)

$Ca_3Co_4O_9$ single crystals

A. C. Masset et al., Phys. Rev. B 62, 166 (2000)



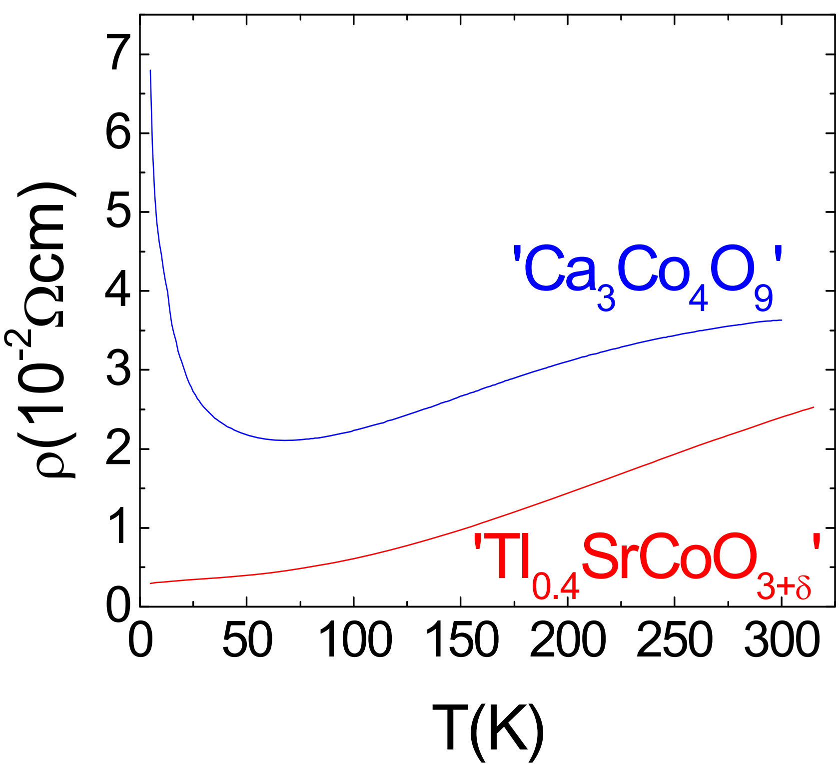


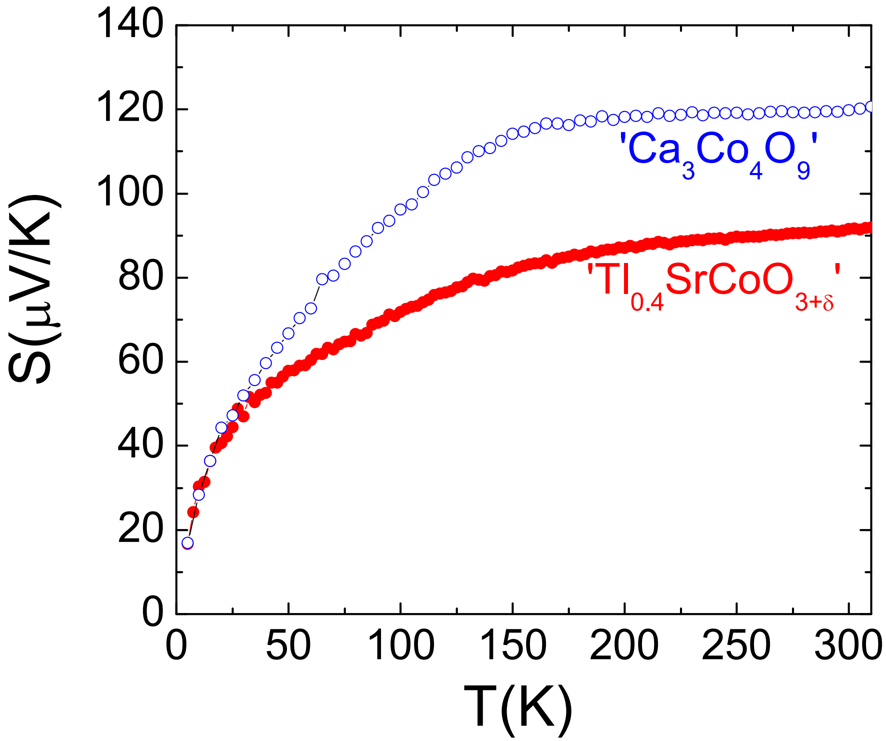


Magnetic measurements : Co^{3+} LS / Co^{4+} LS

Metallicity + Large S

Two different behaviours at low T

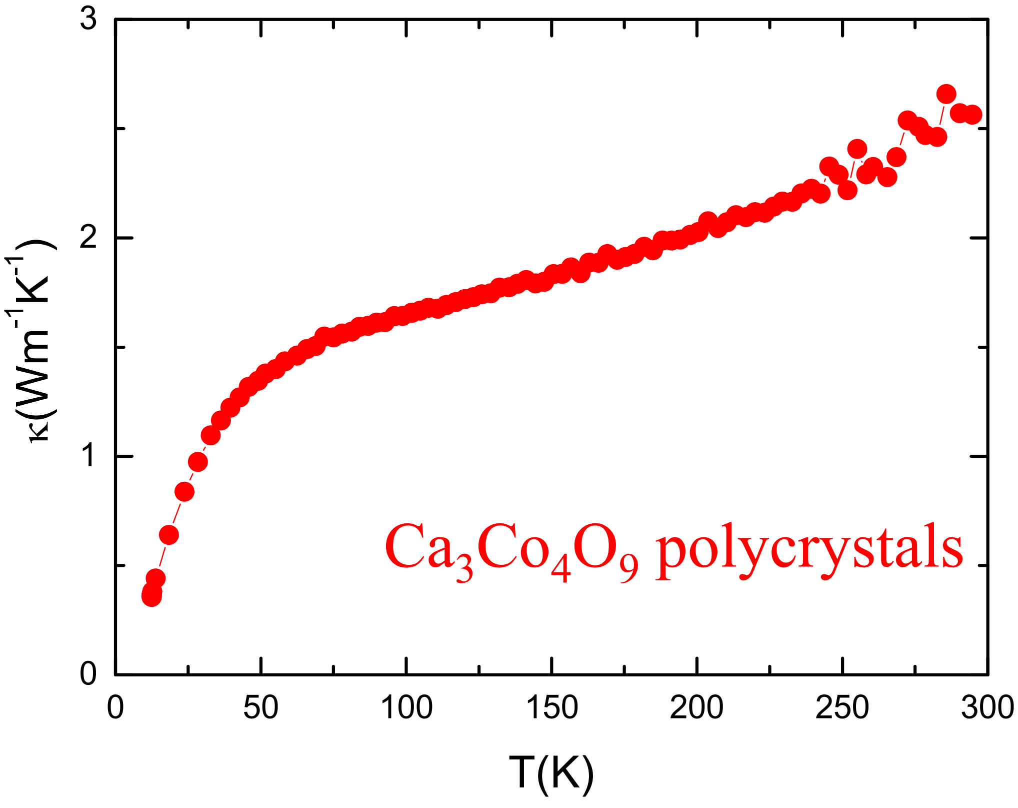




Different resistivities but same S(T)

Only a shift of S

Thermal conductivity



Wiedemann-Franz law :

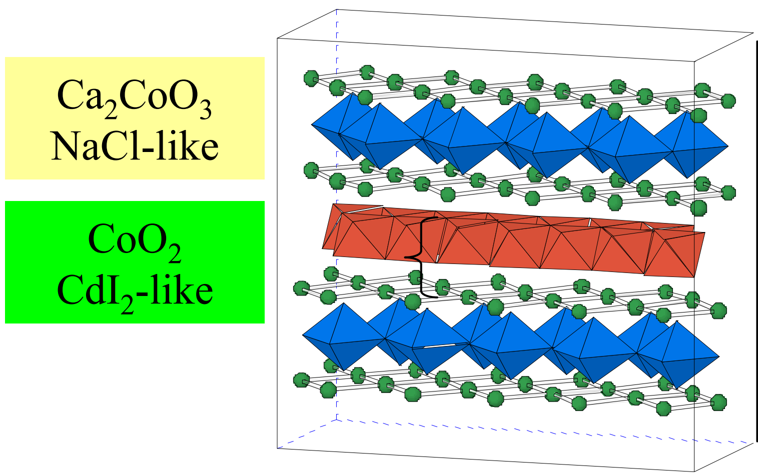
$$\frac{\kappa_{el}}{\sigma T} = \frac{3}{2}\left(\frac{k_B}{e}\right)^2$$

$\kappa_{el} \sim 0.03 Wm^{-1}K^{-1}$ at 300K

κ mainly from phonons

Influence du dopage dans les misfits

$Ca_3Co_4O_9$



Electronic neutrality :

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

2+ 3+ 2- ν_{Co} 2-

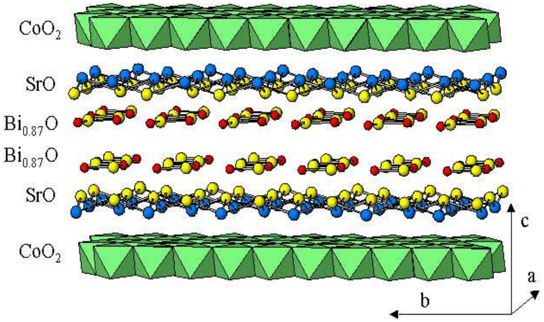
$\alpha > 0$

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

Modification de v_{Co} via α et b_1/b_2

Lien entre v_{Co} et S?

BiSrPbCoO single crystals : modification of α

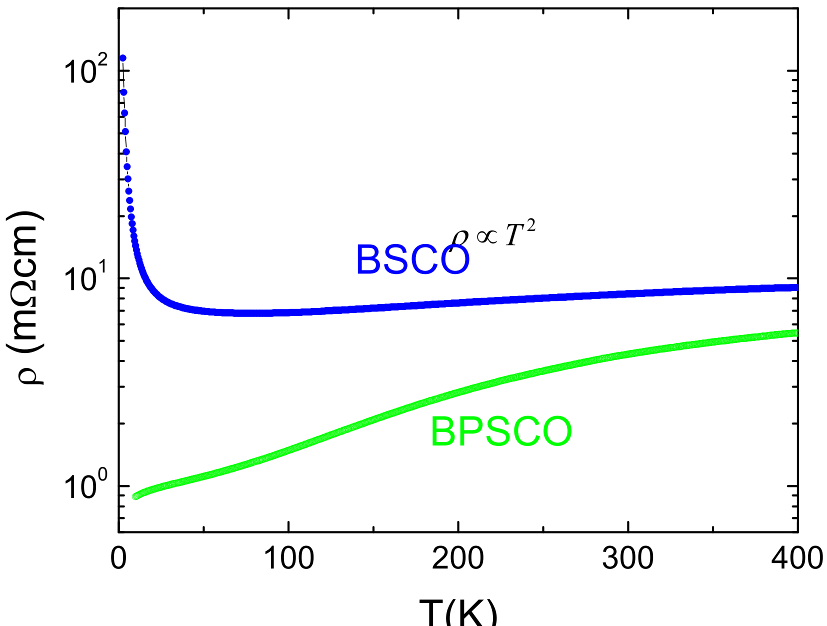


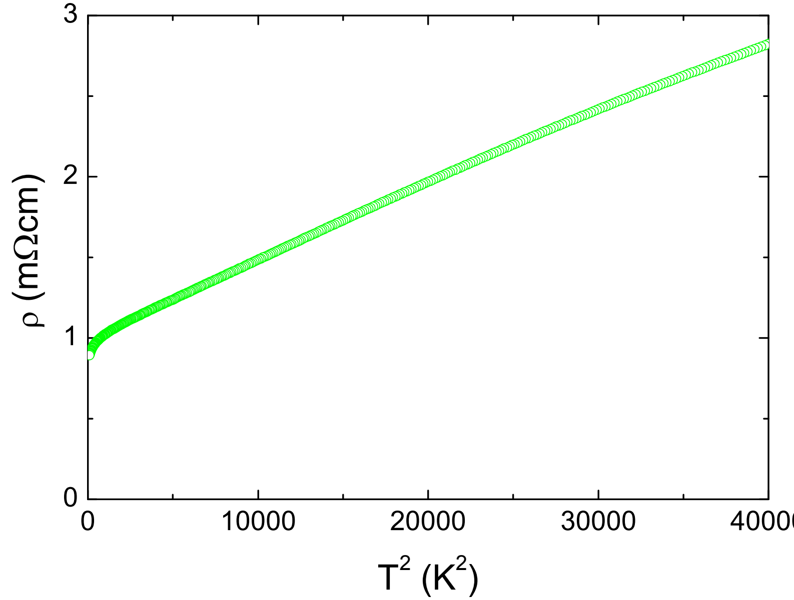
$$v_{Co} = 4 - \frac{\alpha}{b_1 / b_2}$$

$[Bi_{1.74}Sr_2O_4][CoO_2]_{1.82}$ $[Bi_{1.5}Pb_{0.5}Sr_2O_{4-\delta}][CoO_2]_{1.86}$

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

Increase of v_{Co}

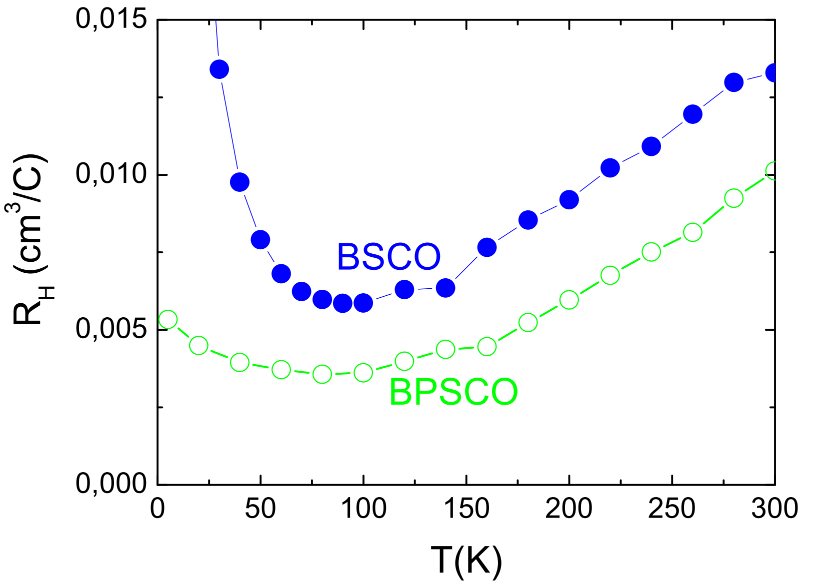




Metallic behavior down to 5K with $\rho = AT^2$

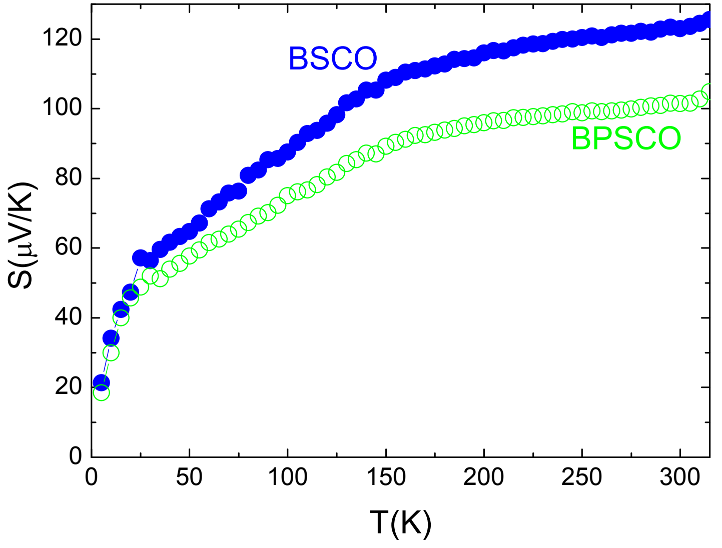
Characteristic of electronic correlations

BiSrPbCoO single crystals : modification of α



At 100K
1.73×10^{21} cm^{-3} for BPSCO
1.06×10^{21} cm^{-3} for BSCO

Increase of v_{Co}
3.109 for BSCO
3.178 for BPSCO



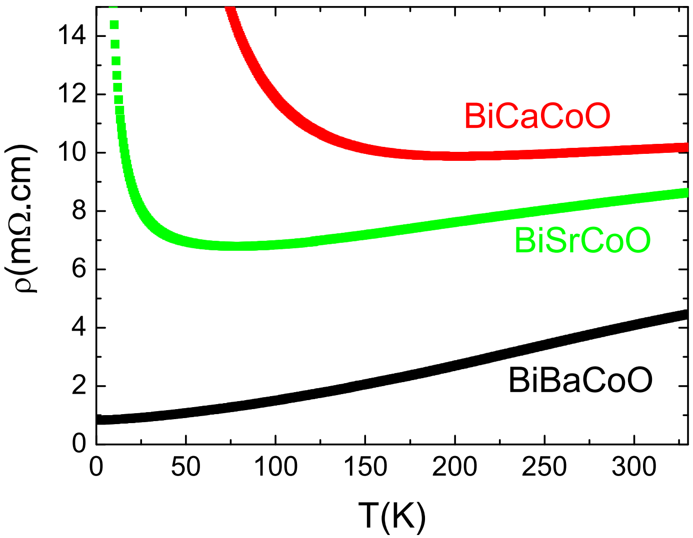
Increase of 'Co^{4+}' associated to a decrease of S

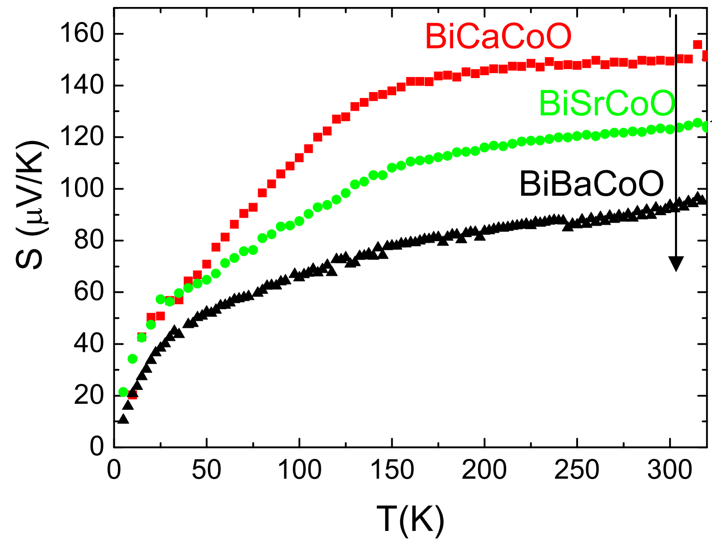
From the generalized Heikes formula, increase of v_{Co}

3.59 for BSCO and 3.65 for BPSCO

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

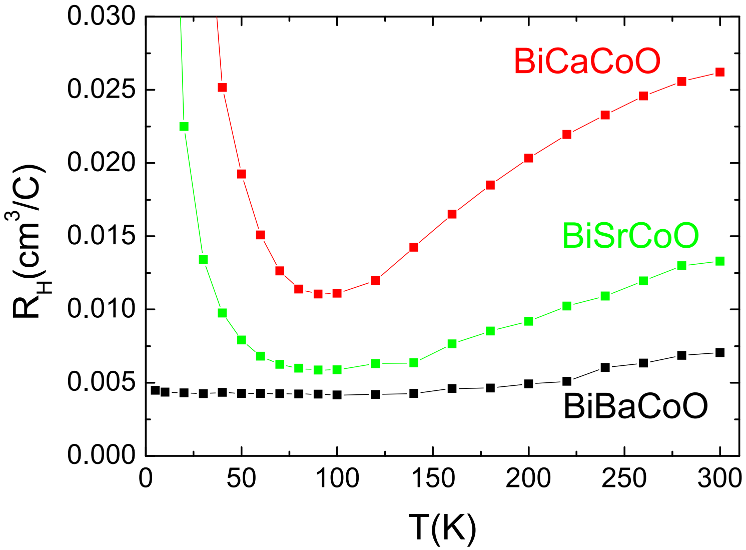
BiCaCoO/ BiSrCoO/ BiBaCoO single crystals





b_1/b_2 ↗

S not affected by the strong modification of ρ



If b_1/b_2 ↗, carrier concentration ↗

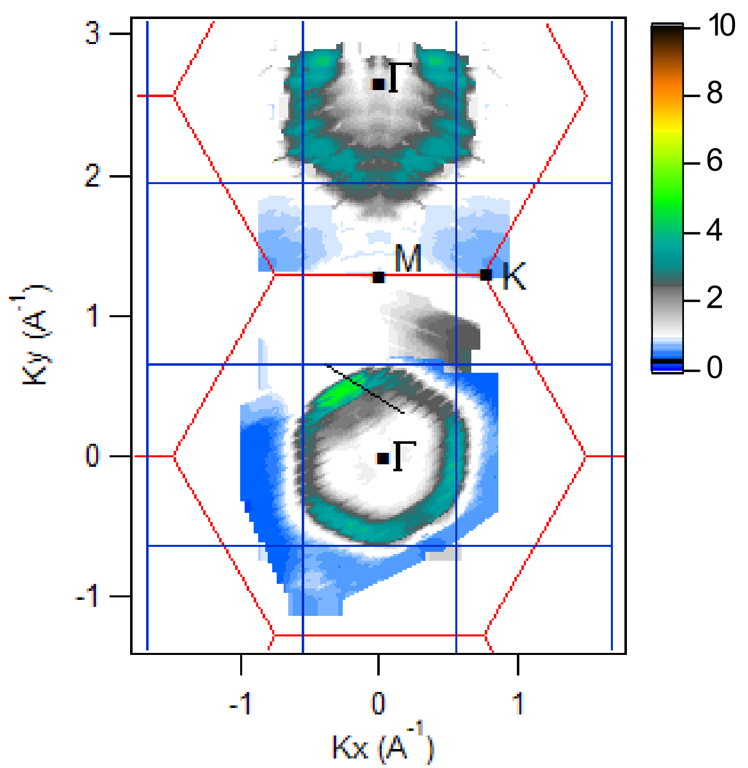
$$v_{Co} = 4 - \frac{\alpha}{b_1 / b_2}$$

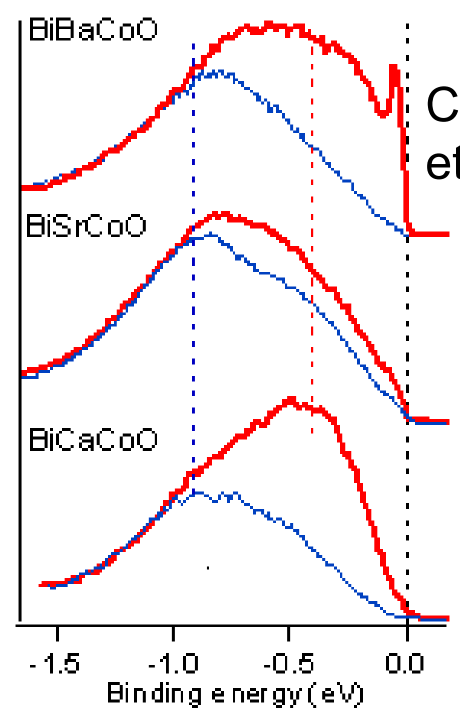
↳S at 300K depends on doping

$V_{Co} = 3.05 - 3.15$ (Hall effect)?

W. Kobayashi et al.

Carrier concentration changes with misfit ratio b_1/b_2





Collaboration with V. Brouet et al., LPS Orsay

Reliable data for v_{Co} are obtained for BiBaCoO

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

k_F=0.57±0.05 Å^{-1} for BiBaCoO

→ similar to k_F of Na_xCoO_2 (x=0.7)

→ $Co^{3.3+}$ for BiBaCoO

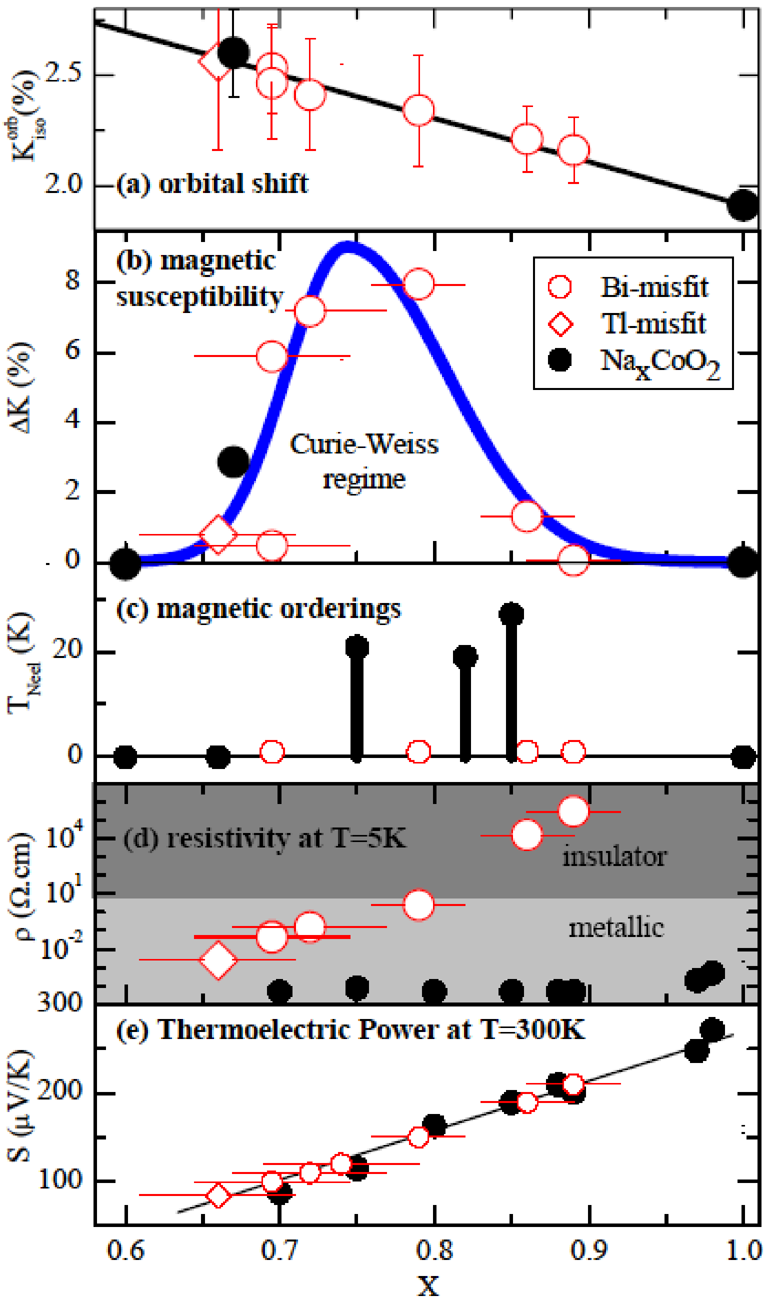
V. Brouet et al., PRB76, 100403 (2007)

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

$Co^{3.2+}$ for BiSrCoO

$Co^{3.1+}$ for BiCaCoO

Comparison with Na_xCoO_2



NMR experiments

Comparison of Seebeck coefficients of misfits and Na_xCoO_2

Confirms the Co^{4+} content determined through ARPES measurements

b_1/b_2

Bi/Ca/Co/O : 3.1

Bi/Sr/Co/O : 3.2

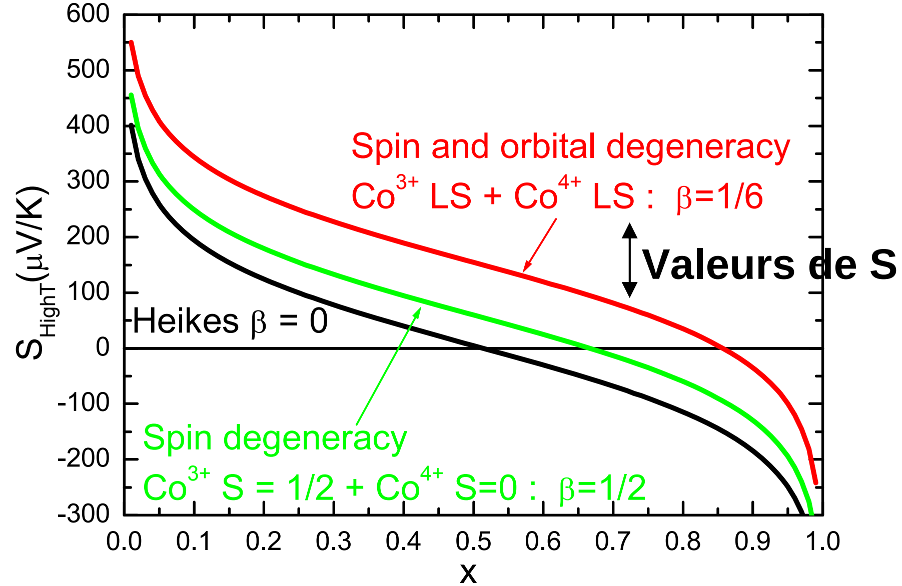
Bi/Ba/Co/O : 3.3

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

J. Bobroff et al., PRB76, 100407 (2007)

Heikes formula

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



Co valency in BiCaCoO/ BiSrCoO / BiBaCoO

Heikes $g_3/g_4 = 1/6$ S at 300K	Hall effect	ARPES BiBaCoO	NMR
3.5 -3.7	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)

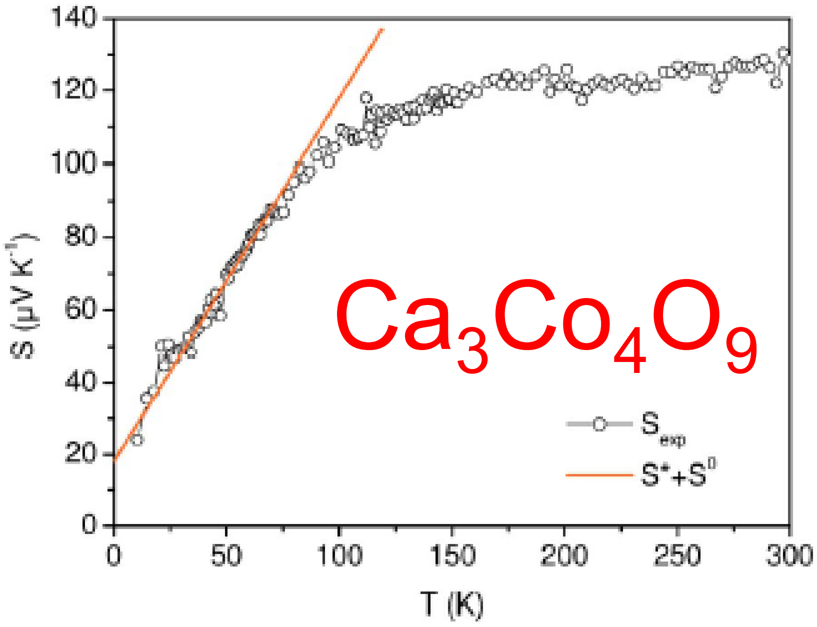
g_3 / g_4 = 1/2 instead of 1/6?

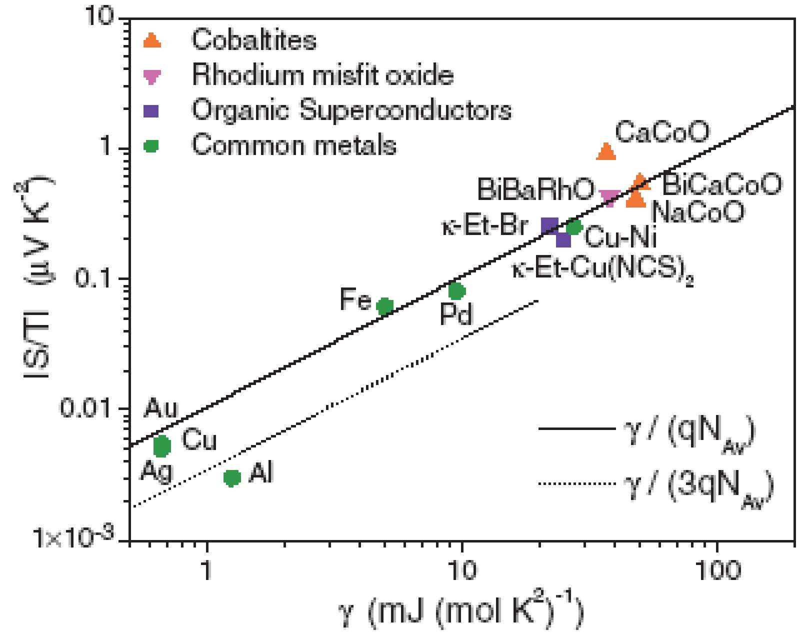
Confirms the results in BiCaCoO : v_{Co} = 3.24

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

Importance des corrélations électroniques

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



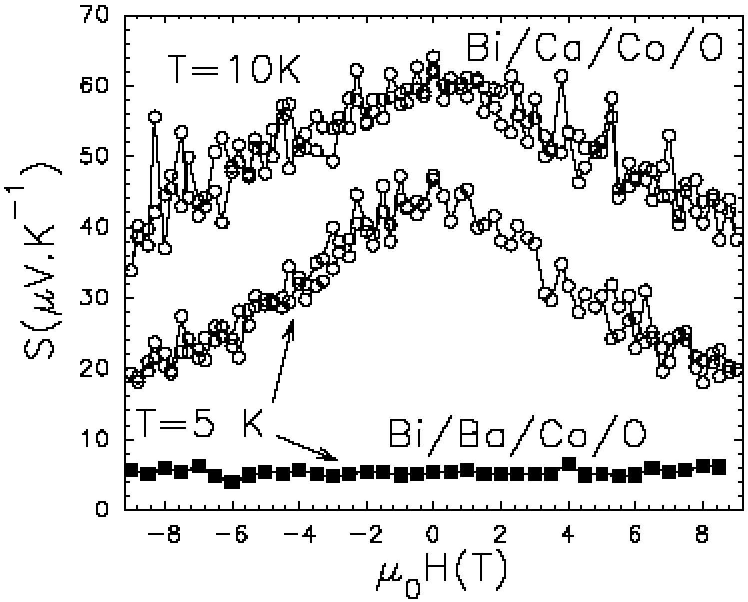


P. Limelette, PRB71, 233108 (2005)

P. Limelette, PRL97, 046601 (2006)

Spin entropy at low T

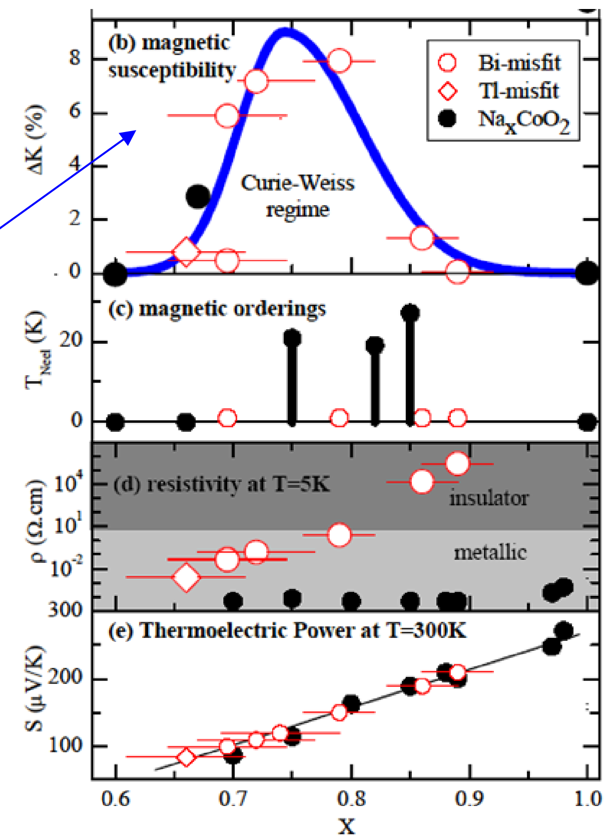
Misfit BiCaCoO

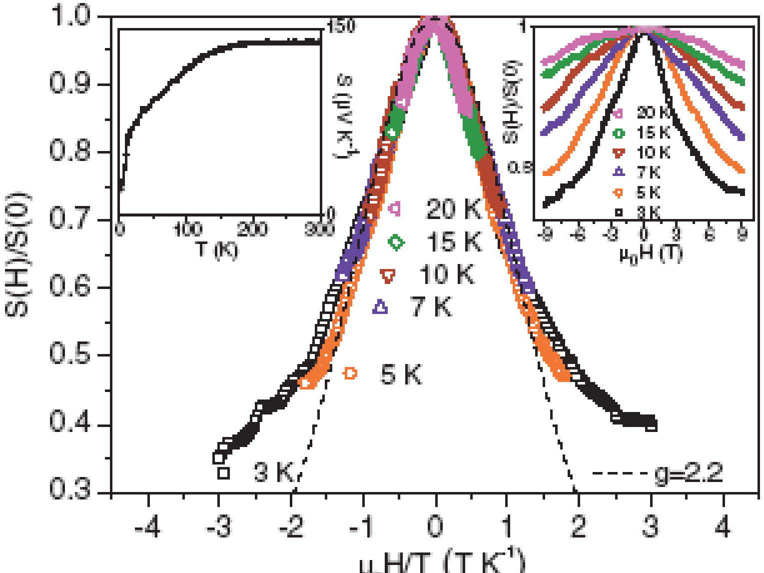


A. Maignan et al., JPCM15, 2711 (2003)

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

Peak of susceptibility





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

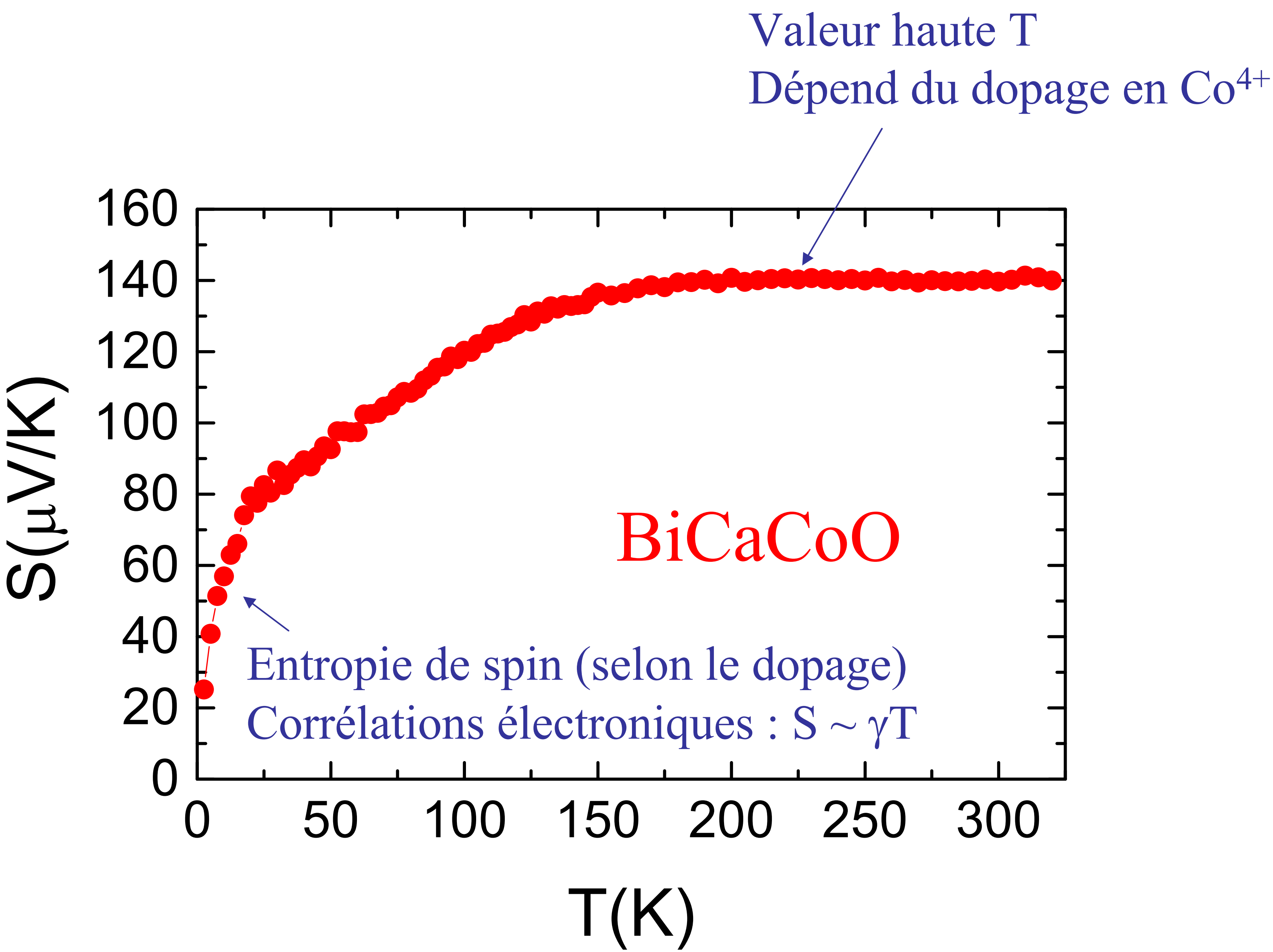
$$S(x)/S(0) = (\ln[2\cosh(x)] - x\tanh[x])/\ln(2).$$

$Na_{0.7}CoO_2$

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

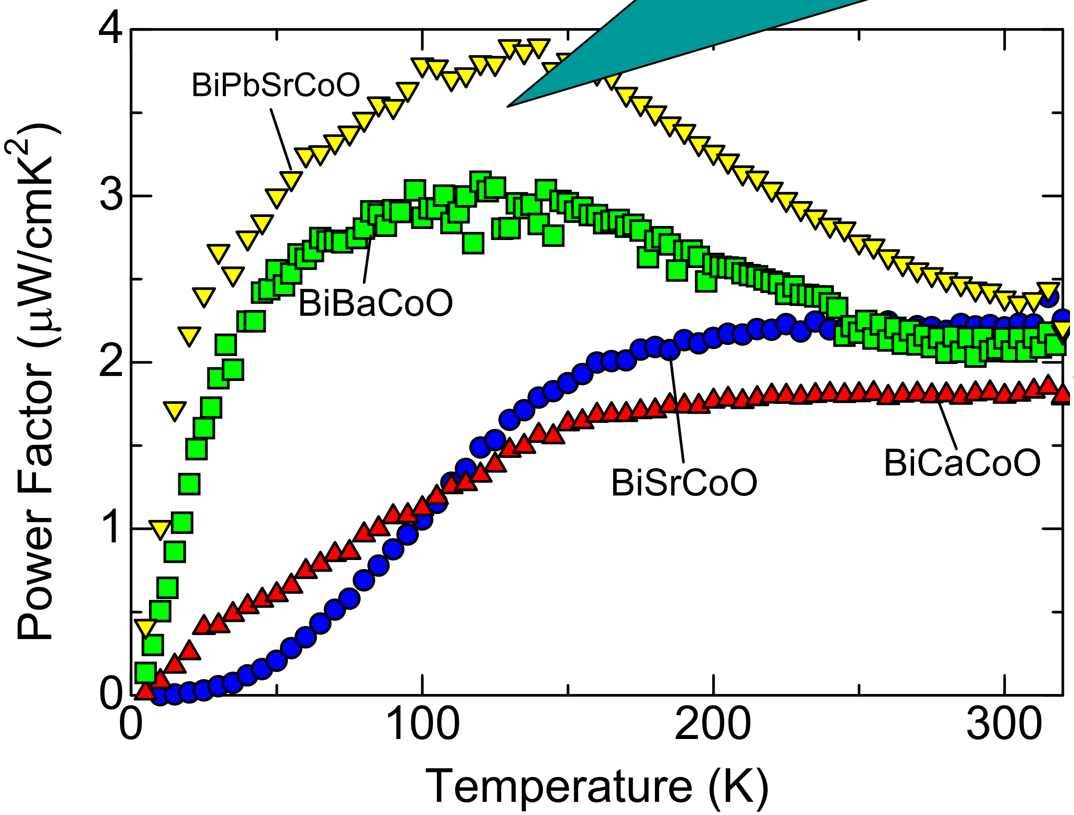
Y. Wang et al., Nature423, 425 (2003)

Pouvoir thermoélectrique des misfits



Power factor P in Bi family

enhancement for BiBaCoO and BiPbSrCoO



P is almost independent of carrier concentration

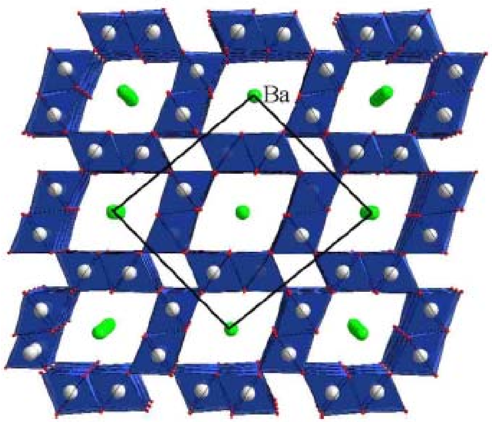
2.10^{-4} $Wm^{-1}K^{-2}$

What is the origin?

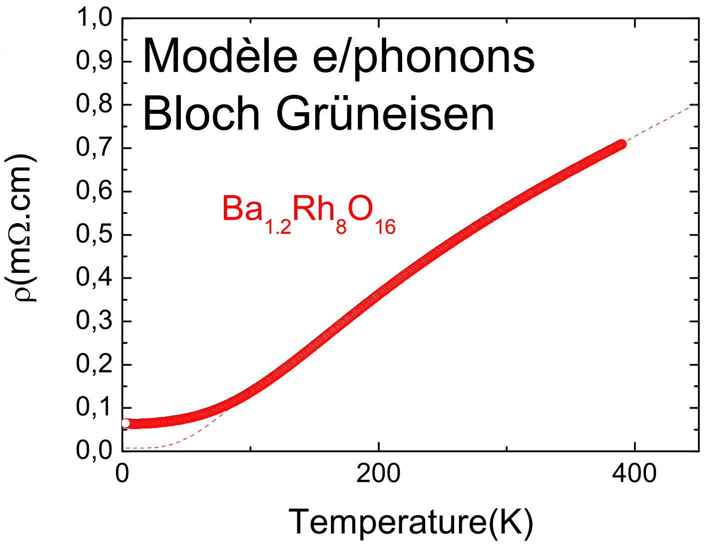
In conventional semiconducting thermoelectric material such as Bi_2Te_3, *n* is an important parameter to tune the properties.

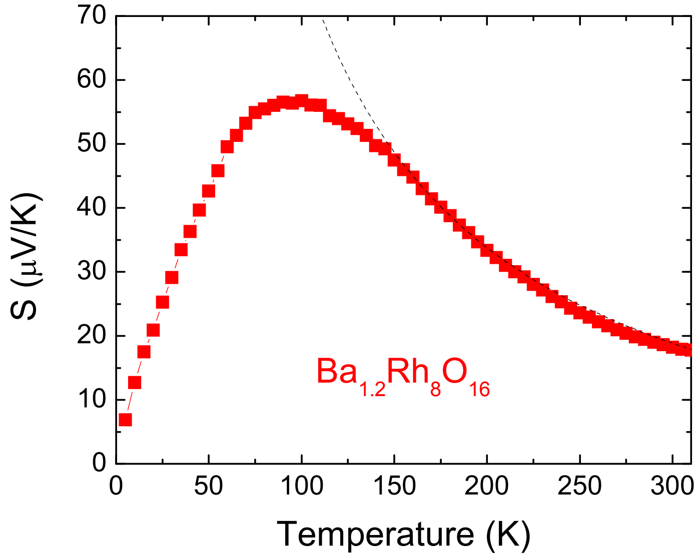
How to modify the electronic properties?
Other structures with CdI_2 type layers?

$Ba_{1.2}Rh_8O_{16}$ hollandite



Quasi 1D structure

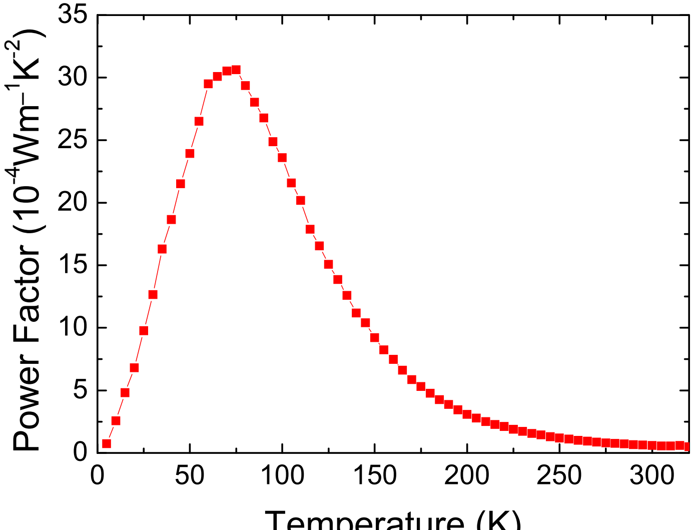




Tunnels made of edge shared octahedra

Needle like single crystals

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



For comparison : 190.10^{-4} $Wm^{-1}K^{-2}$
for $Na_{0.88}CoO_2$ at 75K

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

Na_xCoO_2
Misfits

Conductivité thermique

Mesures sur monocristaux par la méthode d'Harman

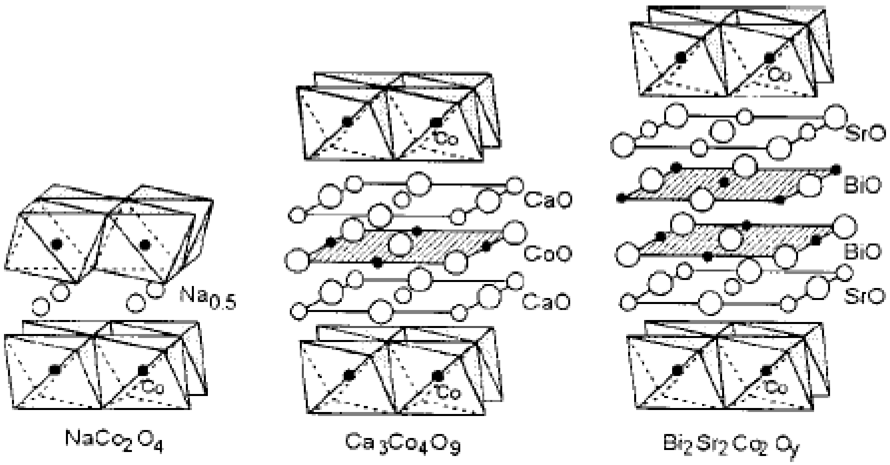
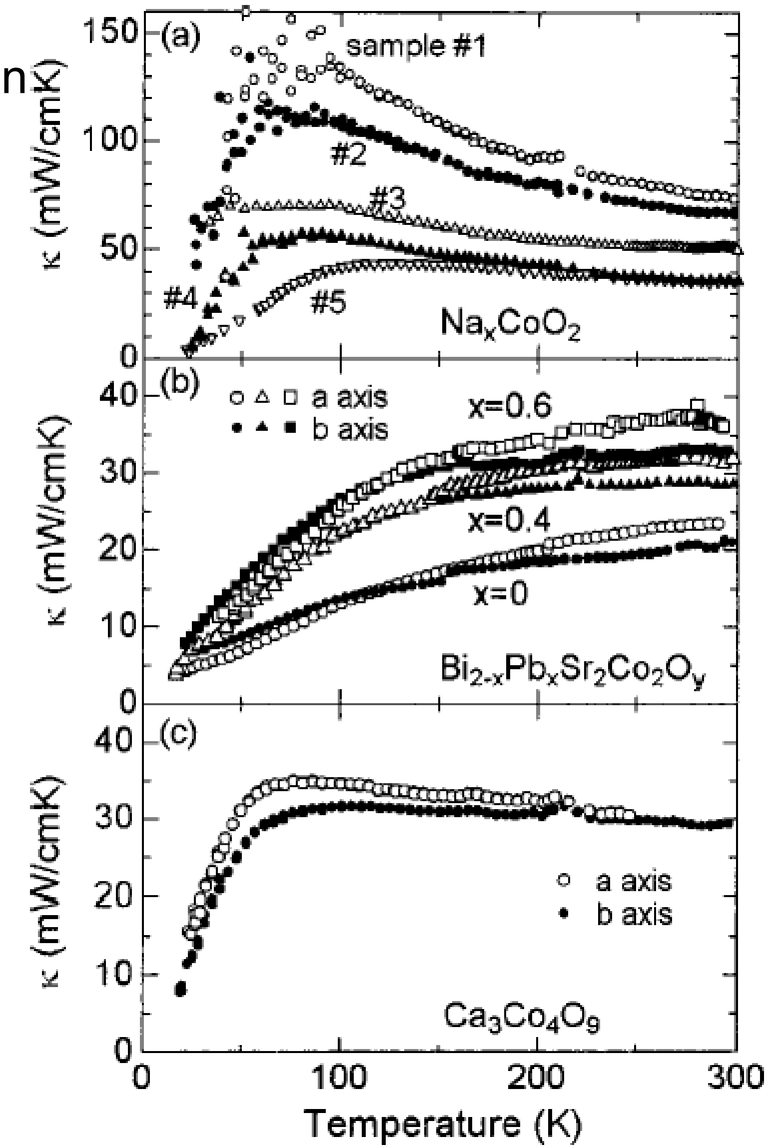


FIG. 1. Crystal structure of the layered cobalt oxides.

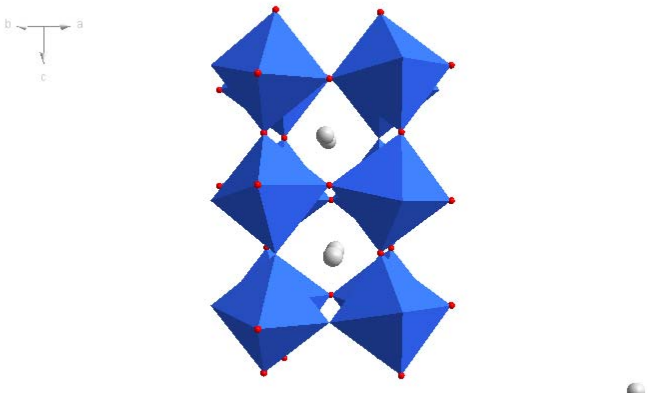


κ légèrement plus faible dans les misfits

Influence de l'incommensurabilité?

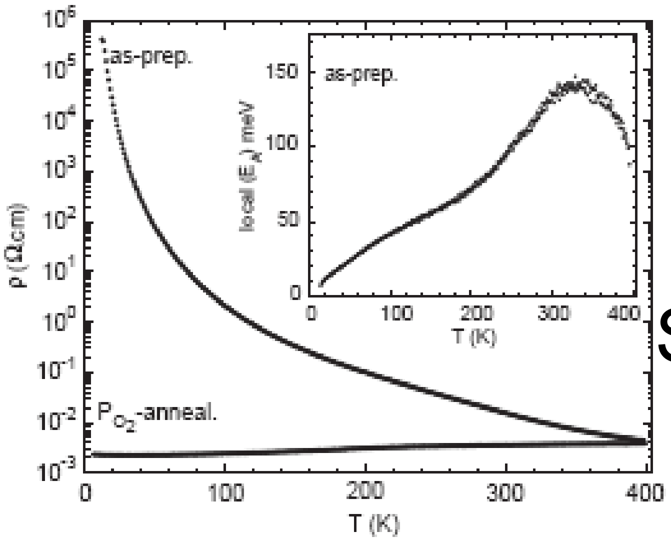
A. Satake et al., JAP96, 931 (2004)

Comportement unique des plans CdI_2 : Comparaison avec d'autres oxydes



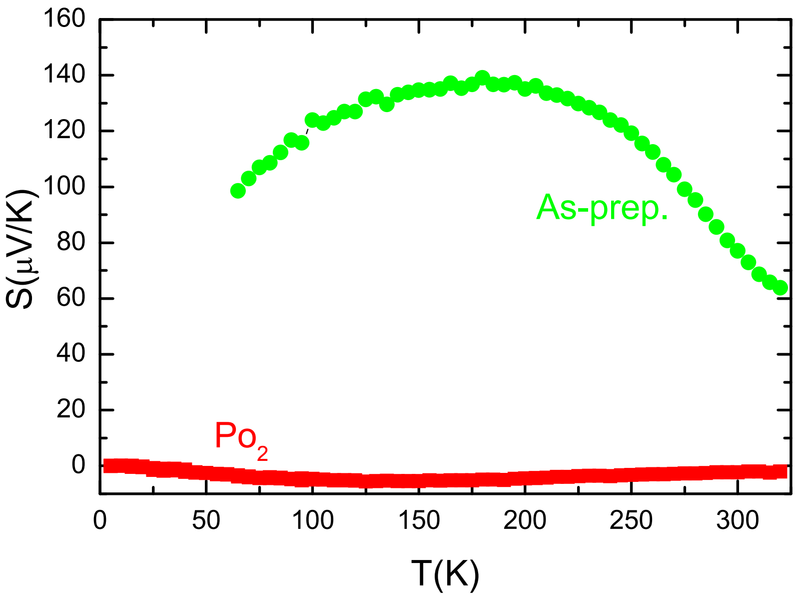
Perovskite $Sr_{2/3}Y_{1/3}CoO_{8/3+\delta}$

Octaèdres liés par les sommets
($\neq$ liés par les arêtes)



Métallicité

Seebeck ≈ 0



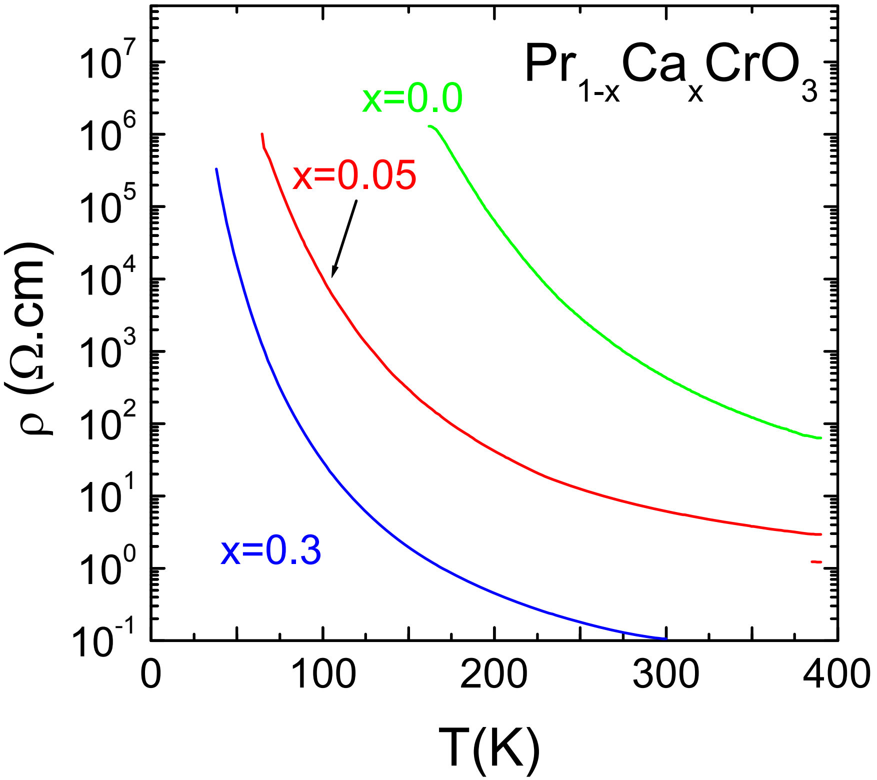
A. Maignan et al., JSSC178, 868 (2005)

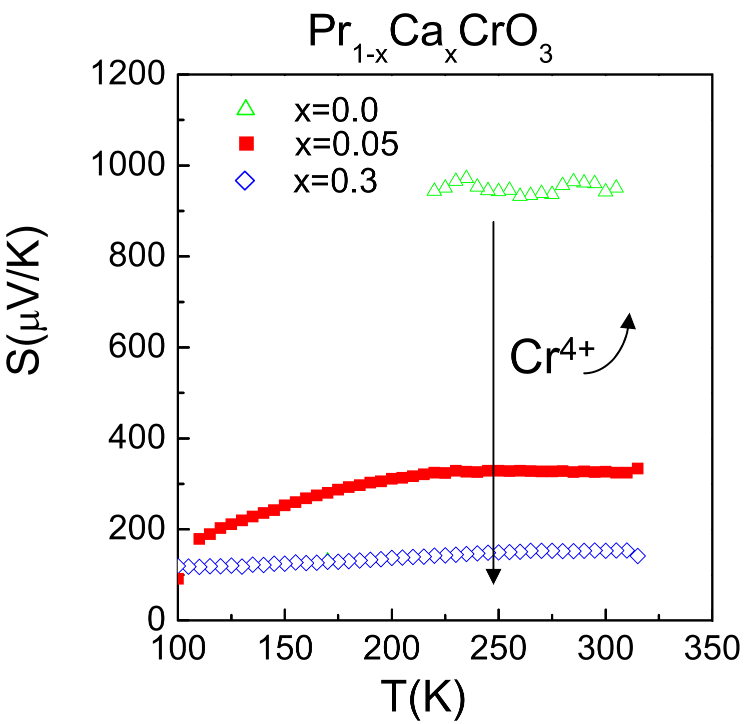
Type p : $Pr_{1-x}Ca_xCrO_3$

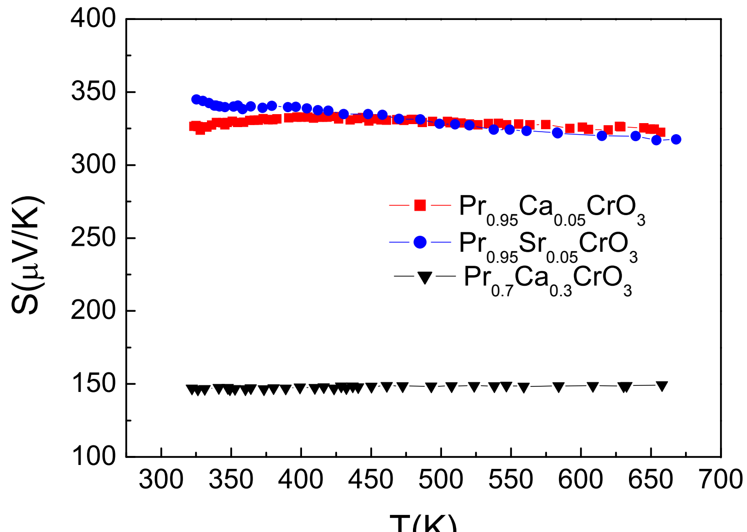
Les orthochromites

Comportement semi-conducteur

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



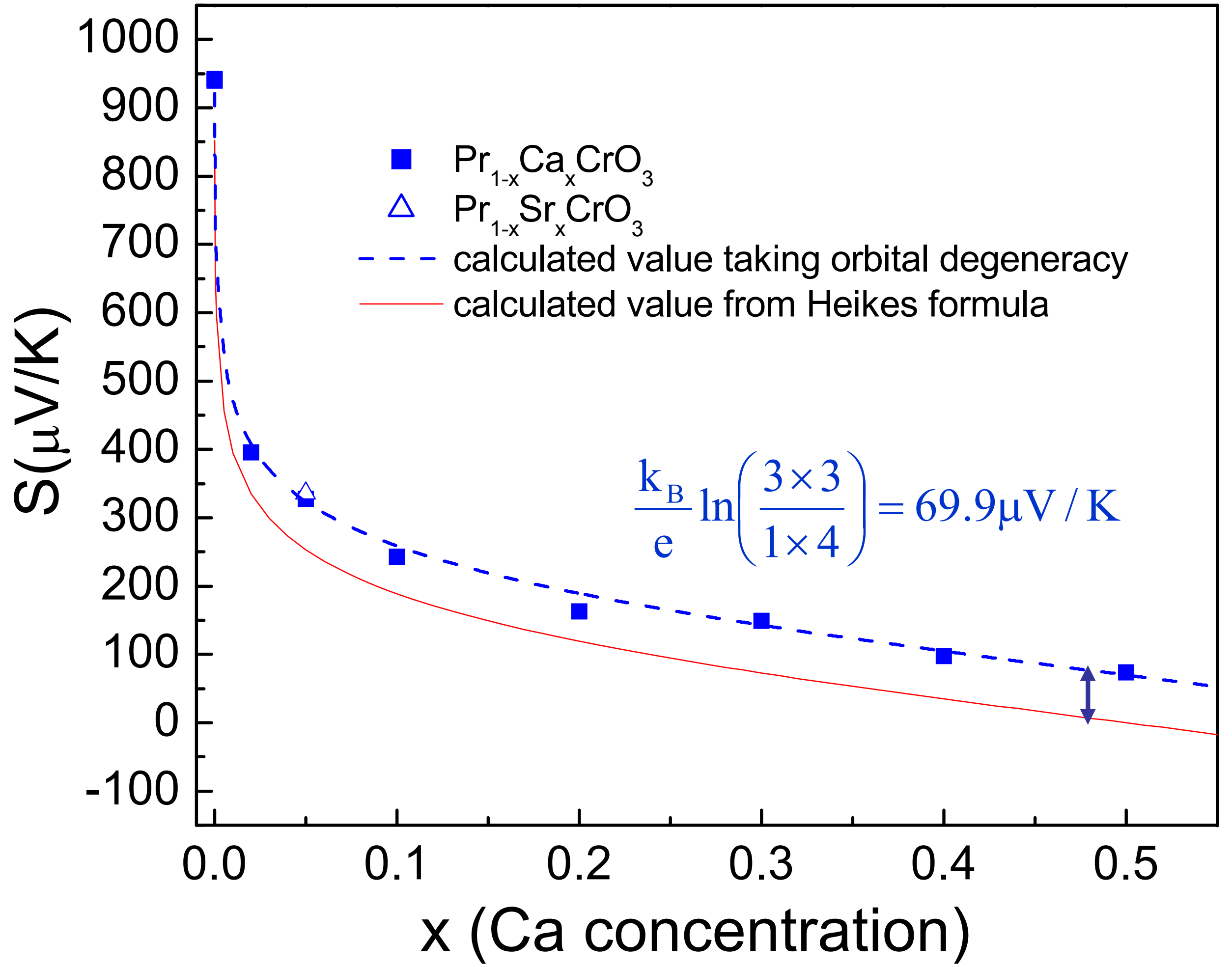


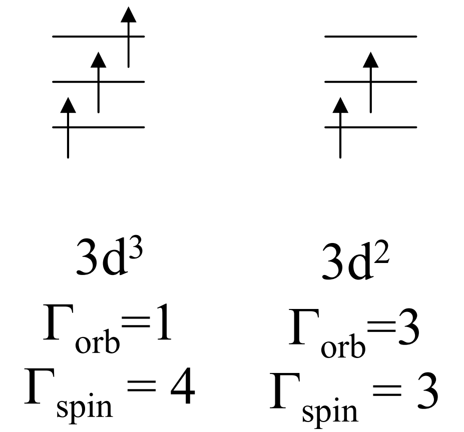


S. Pal et al., Eur. Phys. J. B 53, 5 (2006)

Type p : $Pr_{1-x}Ca_xCrO_3$

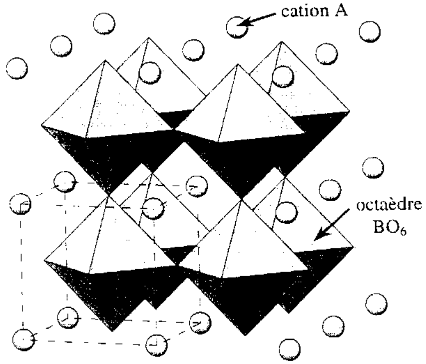
Formule de Heikes, avec dégénérescence de spin et d'orbitales





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

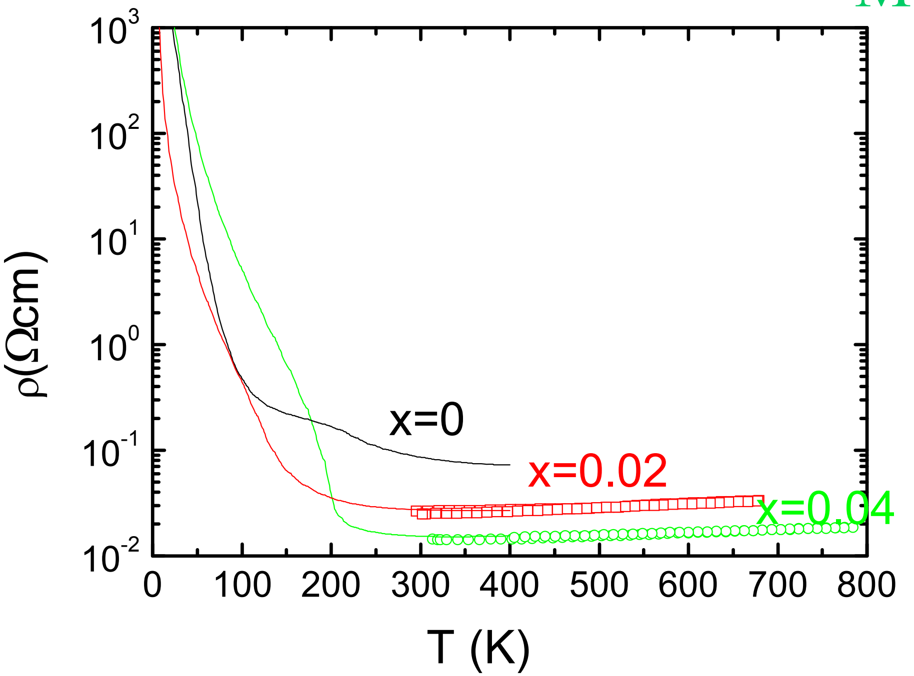
Marsh and Parris, Phys. Rev. B 54, 7720 (1996)

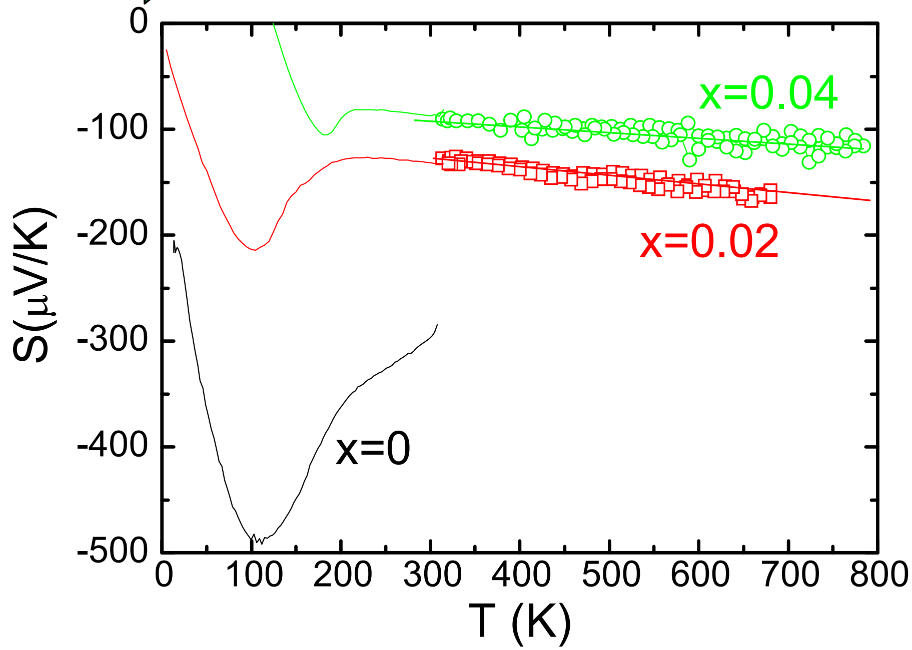


n type :
Manganese oxides $SrMn_{1-x}Mo_xO_3$

$SrMnO_3$: Mn^{4+}

Mo^{6+} → Mn^{3+}/Mn^{4+}





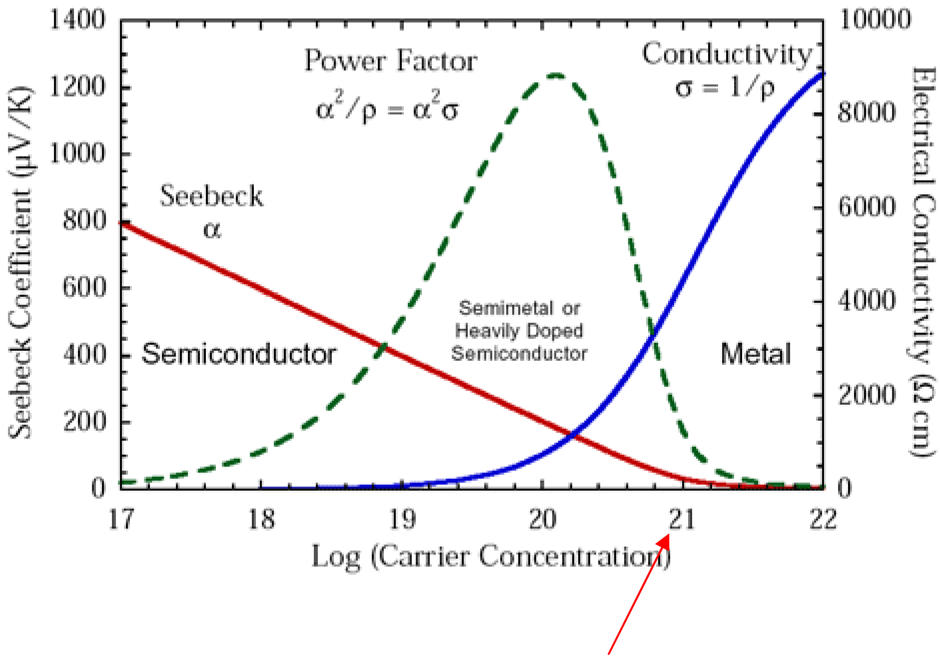
Metallic up to high T / S linear in T : $S = \pi^2 \times k_B/3e \times k_B T(\partial \ln \sigma(E)/\partial E)$

Power factor increases as T increases :

PF = $9.10^{-4} Wm^{-1}K^{-2}$ for x=0.02 at 800K

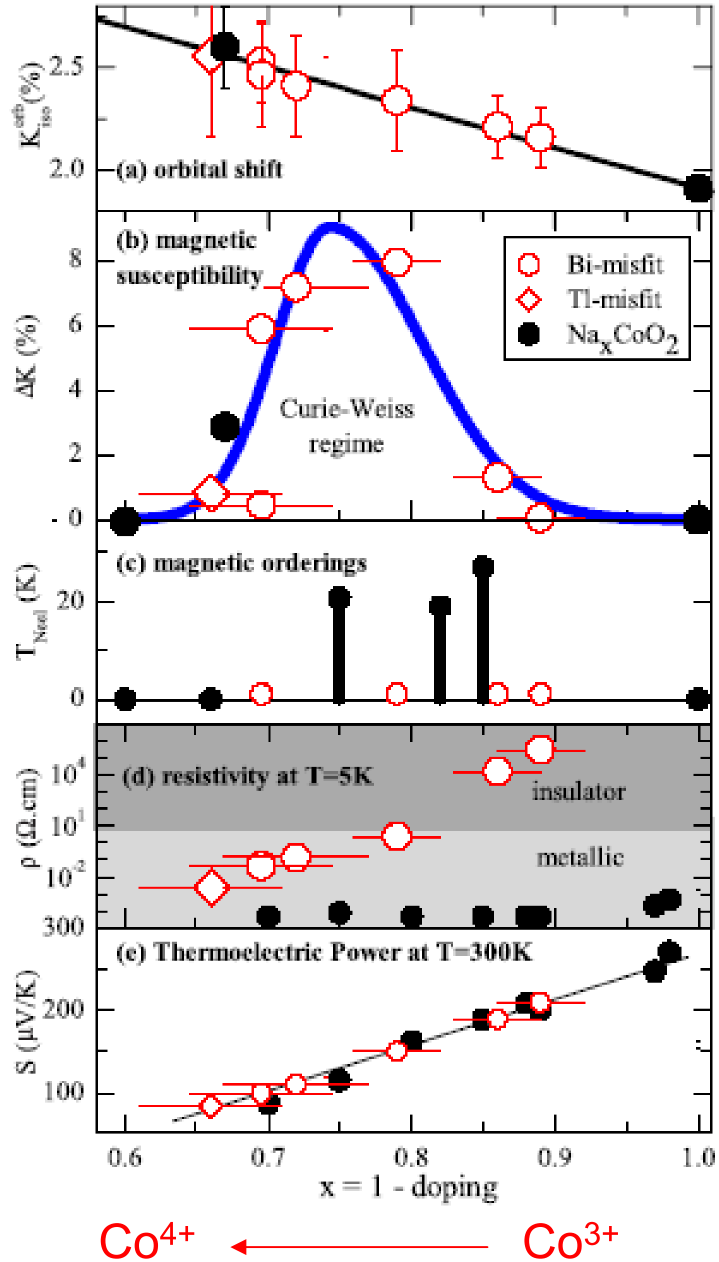
A. Maignan et al., Phys. Rev. B 58, 2578 (1998), J. Hejtmanek et al., PRB60, 14057 (1999)

Conclusion



Misfits

- Taux de porteurs élevé ~ 10^{21}cm^{-3}
- Coexistence métallicité + valeur élevée de S
- Formule généralisée de Heikes , avec $\beta = ½$



Paramètre misfit

↳Rôle crucial du dopage

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

↳Influence des plans séparateurs?

Résistivité

Conductivité thermique?

J. Bobroff et al. PRB76, 100407 (2007)

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