``Enseigner la recherche en train de se faire''

COLLÈGE DE FRANCE
1530

Chaire de
Physique de la Matière Condensée

THERMOELECTRICITE: CONCEPTS, MATERIAUX ET ENJEUX ENERGETIQUES

Antoine Georges

Cycle 2012-2013

Cours 3 – 10 avril 2013

- Seebeck coefficient in the localized limit :
- The Heikes and Shastry-Kelvin formulas
- Applicability to transition-metal oxides ?

These slides are just illustrations of the lecture notes also available on the website

I am most grateful to Jernej Mravlje for his help in preparing this lecture (and to S.Hebert/A.Maignan for discussions)

Séminaire – 10 avril 2013

- Séminaire : 11h15 -

Sylvie HÉBERT, CRISMAT, Caen

Oxydes pour la thermoélectricité

Excerpt from abstract:

Le but de ce séminaire est de présenter les différentes familles d'oxydes intéressantes pour la thermoélectricité, en particulier Na_xCoO_2 pour les oxydes de type p, et des oxydes de type 'conducteurs transparents' pour les types n, et d'introduire les différents mécanismes proposés pour expliquer ces propriétés. Les spécificités des oxydes, par rapport aux matériaux thermoélectriques plus 'classiques', seront soulignées.

The Heikes and Shastry-Kelvin approximations to the thermoelectric power

$$\alpha_H = \frac{\mu}{eT} = -\frac{1}{e}\frac{\partial S}{\partial n}|_E$$

$$\alpha_{SK} = \frac{1}{e}\frac{\partial \mu}{\partial T}|_n = -\frac{1}{e}\frac{\partial S}{\partial n}|_T$$

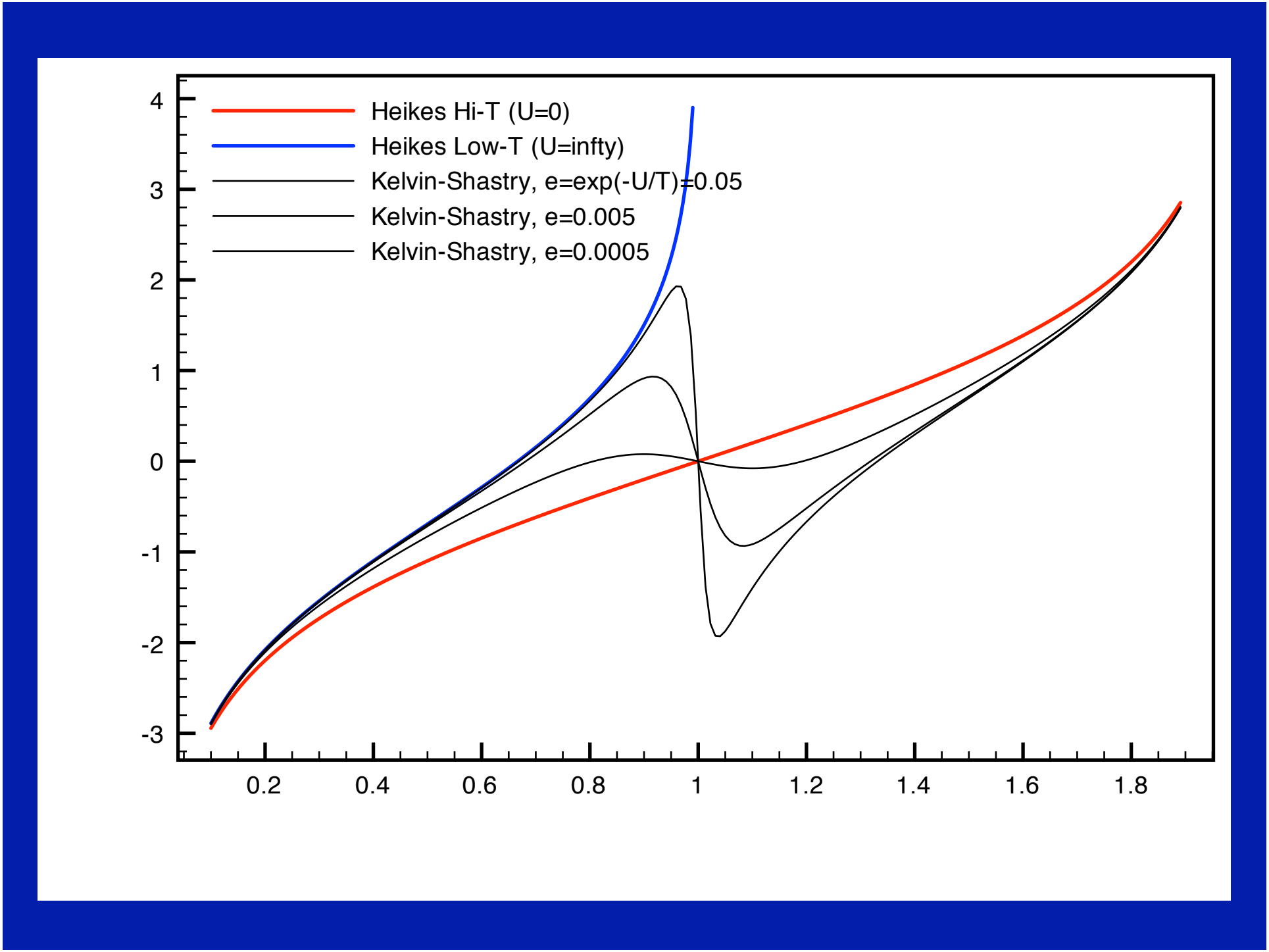
Single-orbital atomic limit

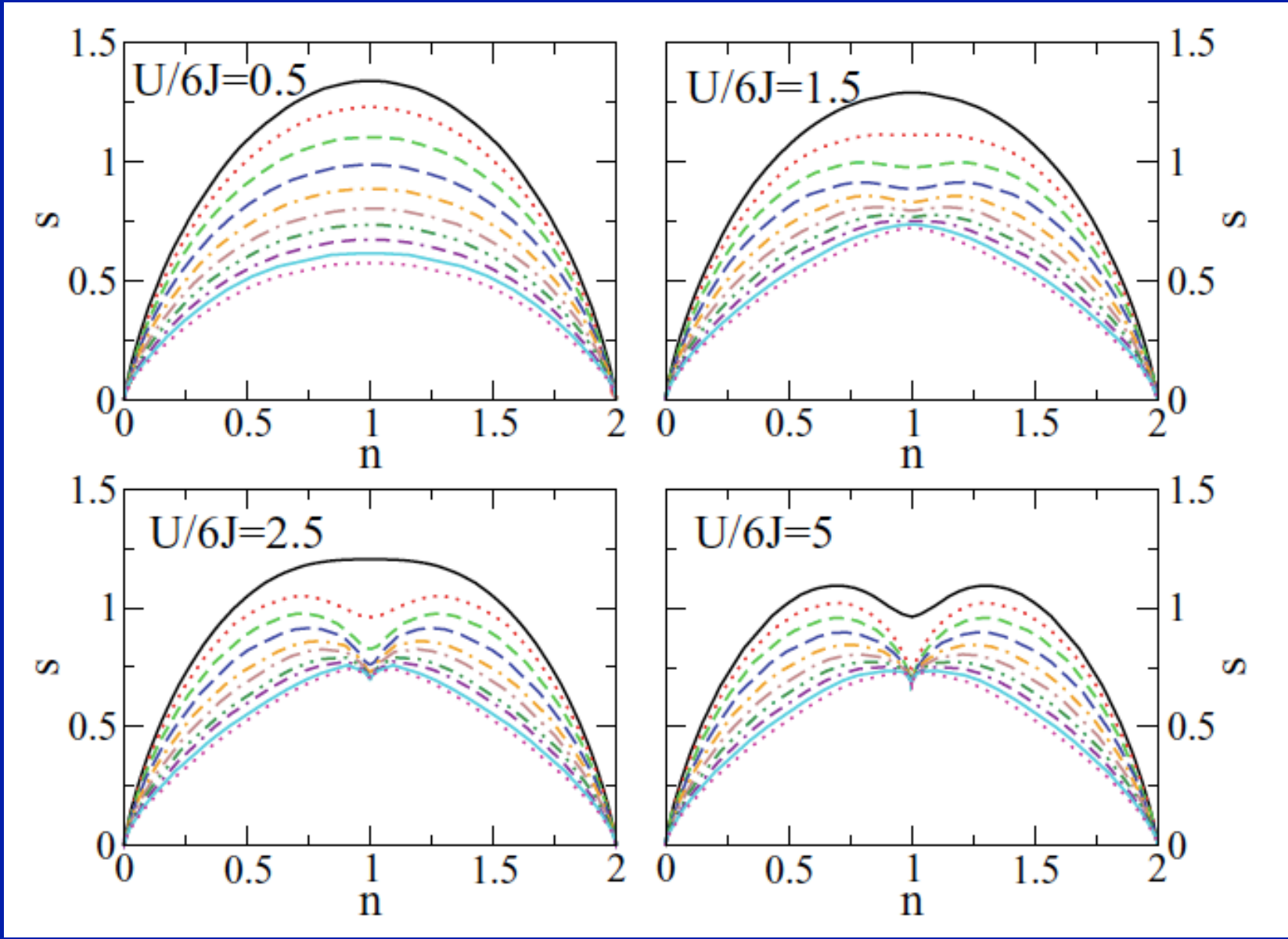
T >> U:

$$S/k_B = -2\left[\frac{n}{2}\ln\frac{n}{2} + (1-\frac{n}{2})\ln(1-\frac{n}{2}\right] \quad , \quad \alpha = -\frac{1}{e}\frac{\partial S}{\partial n} = \frac{k_B}{e}\ln\frac{n}{2-n}$$

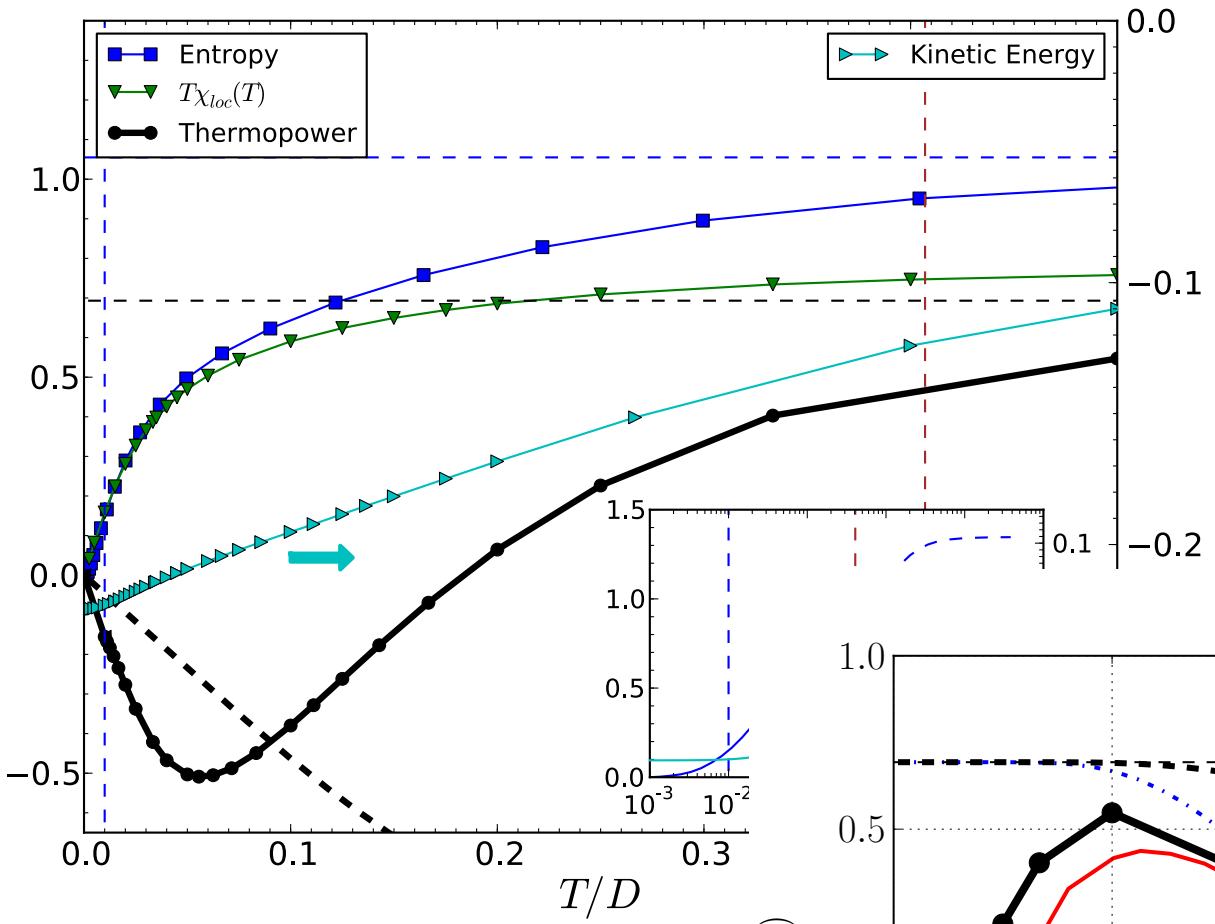
T* < T << U:

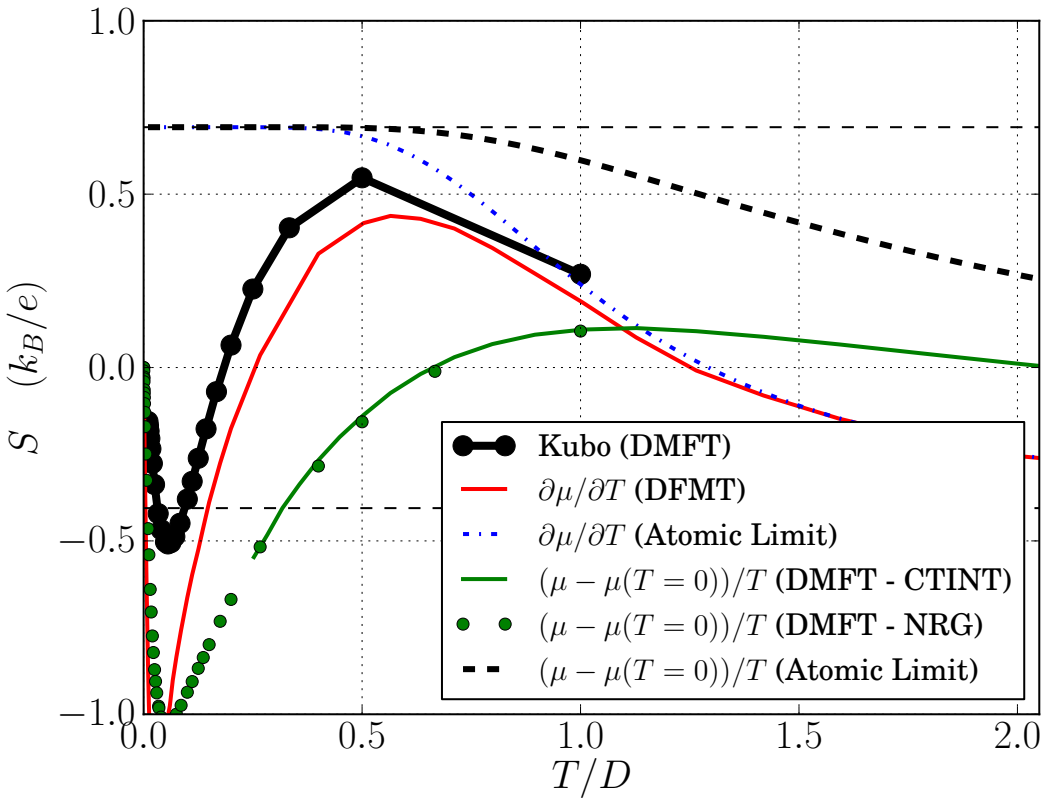
$$S/k_B = -\left[(1-n)\ln(1-n) + 2\frac{n}{2}\ln\frac{n}{2}\right] \quad , \quad \alpha = -\frac{1}{e}\frac{\partial S}{\partial n} = -\frac{k_B}{e}\ln\frac{2(1-n)}{n}$$

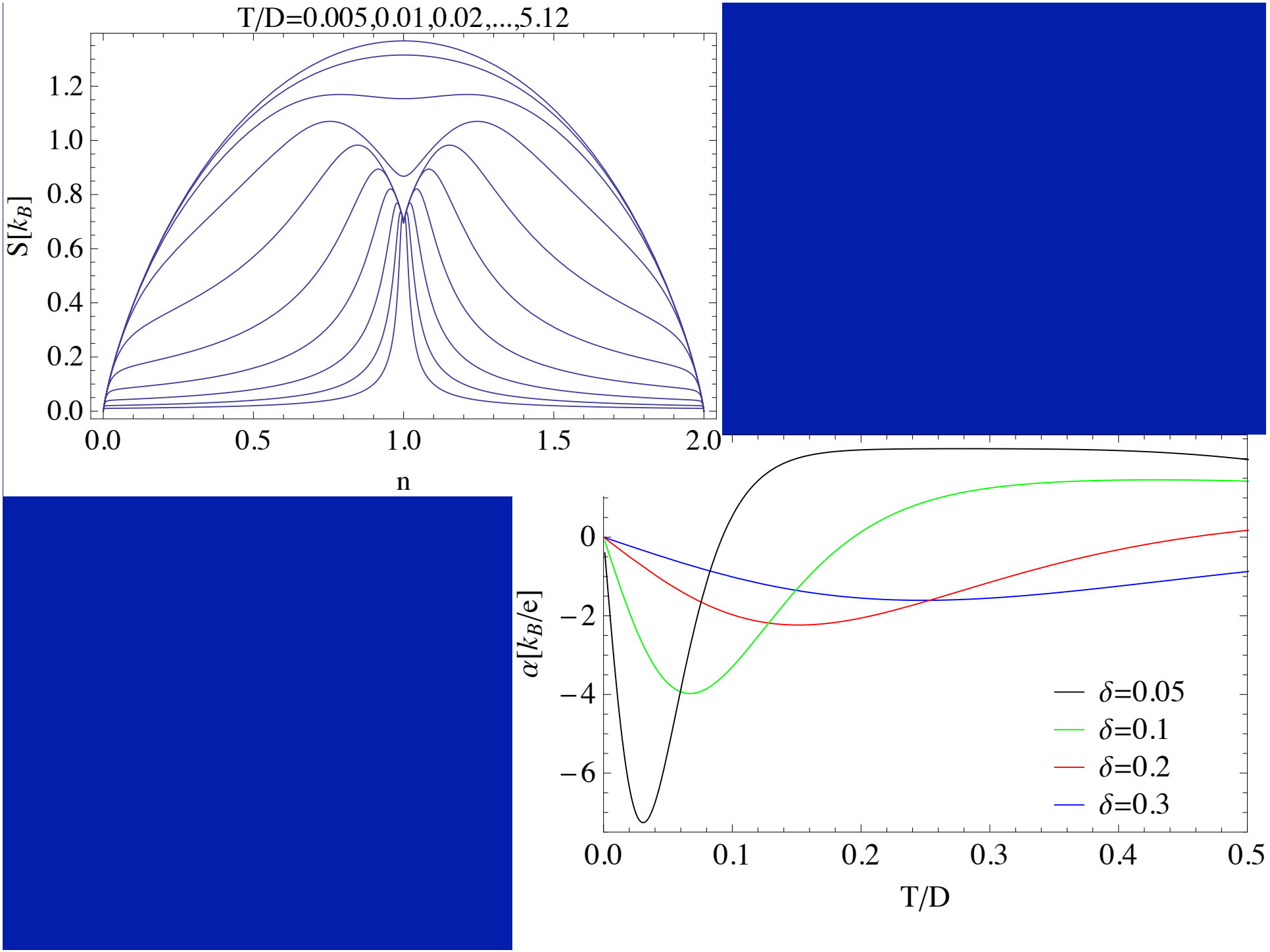

Heikes Hi-T (U=0)
Heikes Low-T (U=infty)
Kelvin-Shastry, e=exp(-U/T)=0.05
Kelvin-Shastry, e=0.005
Kelvin-Shastry, e=0.0005
4
3
2
1
0
-1
-2
-3
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8

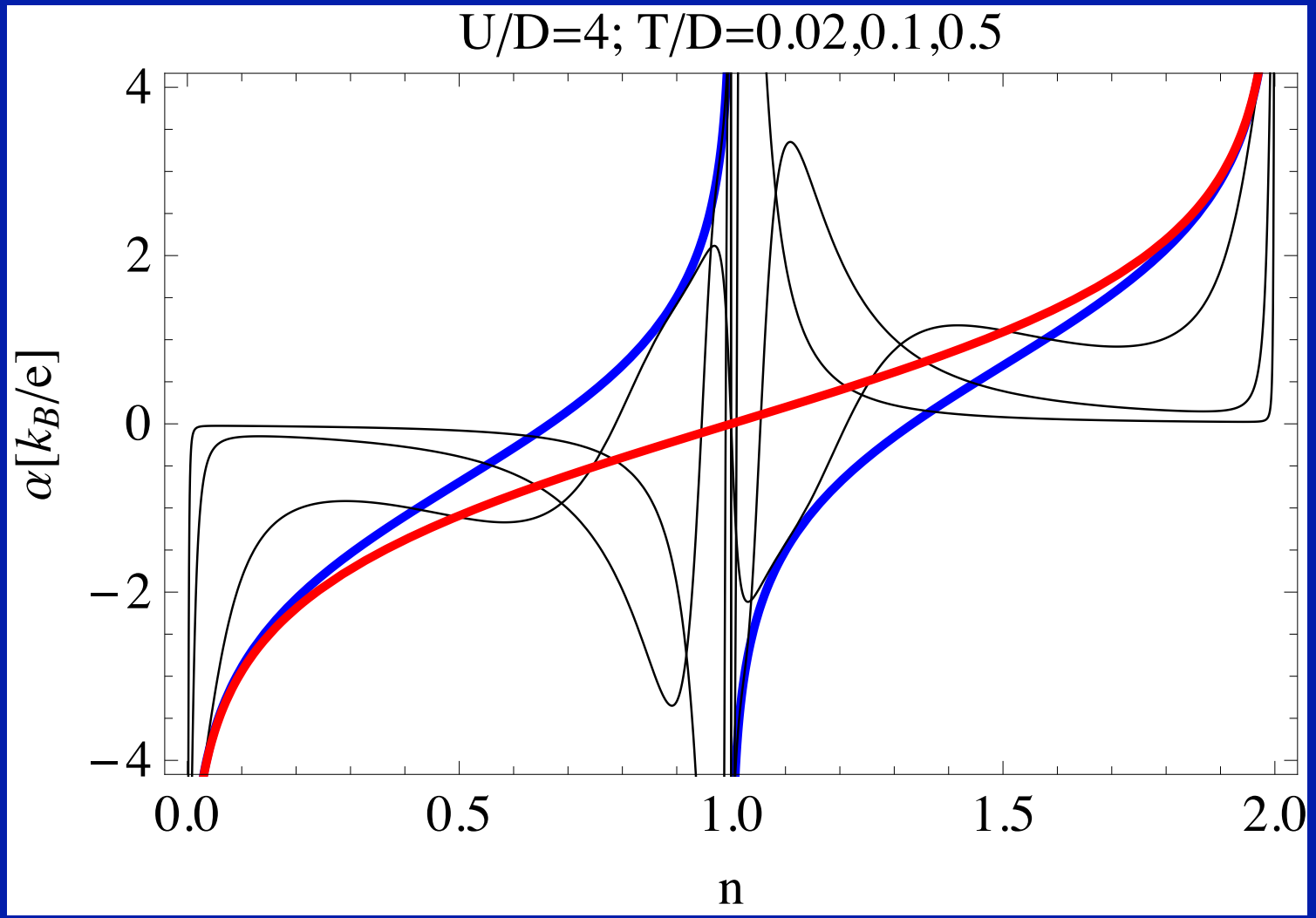


Entropy vs. Density, 1-band Hubbard model, DMFT T/D=1,…,1/10


Entropy
$T\chi_{loc}(T)$
Thermopower
Kinetic Energy
1.0
0.5
0.0
−0.5
0.0
−0.1
−0.2
0.0
0.1
0.2
0.3
T/D
1.5
1.0
0.5
0.0
0.1
10^{-3}
10^{-2}


1.0
0.5
0.0
−0.5
−1.0
0.0
0.5
1.0
1.5
2.0
T/D
$S\ \ (k_B/e)$
Kubo (DMFT)
$\partial\mu/\partial T$ (DFMT)
$\partial\mu/\partial T$ (Atomic Limit)
$(\mu - \mu(T=0))/T$ (DMFT - CTINT)
$(\mu - \mu(T=0))/T$ (DMFT - NRG)
$(\mu - \mu(T=0))/T$ (Atomic Limit)


T/D=0.005,0.01,0.02,...,5.12
S[k_B]
n
0.0
0.2
0.4
0.6
0.8
1.0
1.2
0.0
0.5
1.0
1.5
2.0
$\alpha[k_B/e]$
T/D
0
−2
−4
−6
0.0
0.1
0.2
0.3
0.4
0.5
δ=0.05
δ=0.1
δ=0.2
δ=0.3

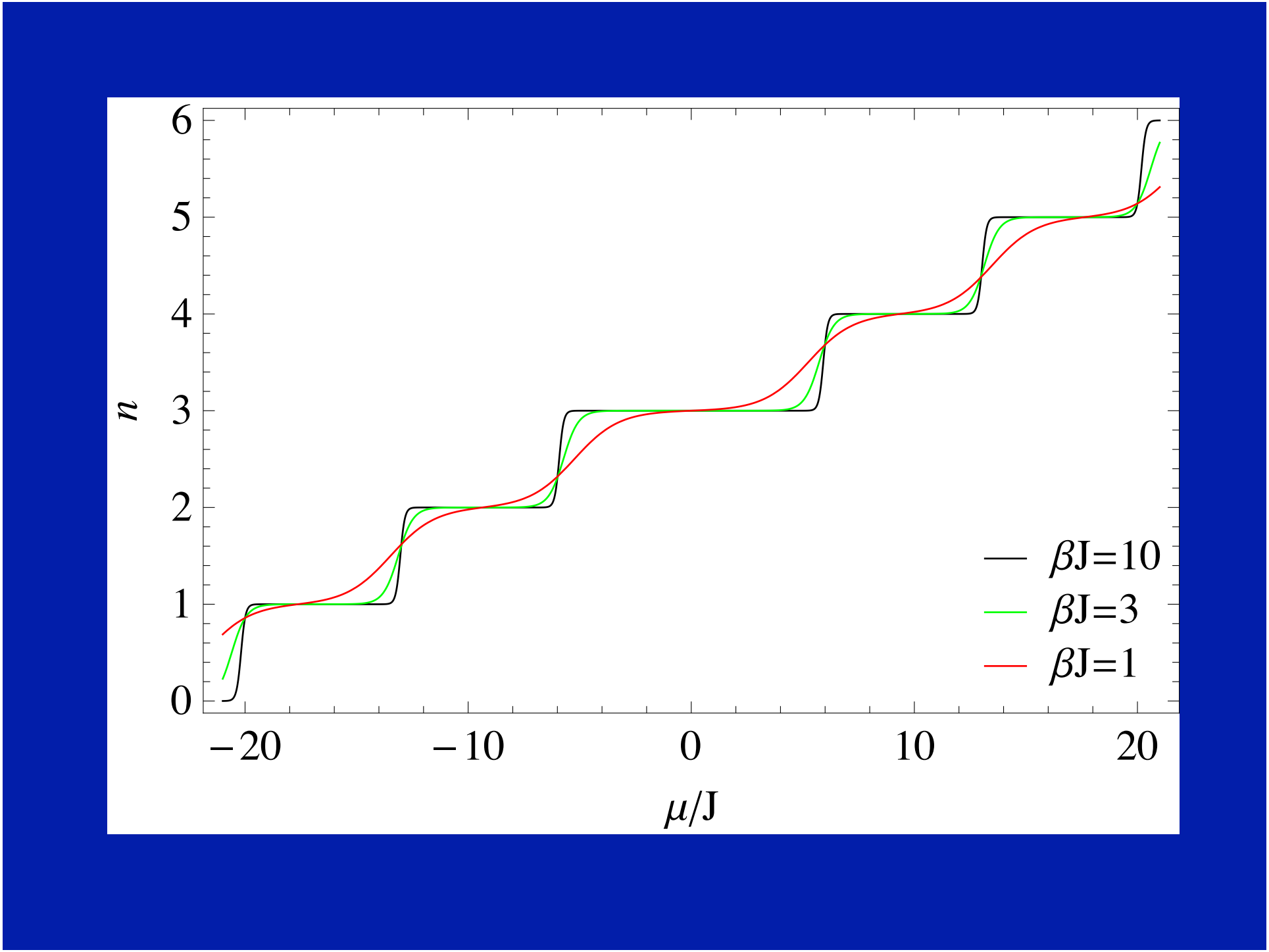

U/D=4; T/D=0.02,0.1,0.5
4
2
0
−2
−4
α[k_B/e]
0.0
0.5
1.0
1.5
2.0
n

Multiorbital atom (ex: t_{2g} shell)

$$H = (U - 3J)\frac{\hat{n}(\hat{n}-1)}{2} - 2J\boldsymbol{S}^2 - \frac{J}{2}\boldsymbol{L}^2$$

N	S	L	Degeneracy	Energy
0,[6]	0	0	**1**	$0,[15\mathcal{U}]$
1,[5]	1/2	1	**6**	$-5J/2,[10\mathcal{U}-5J/2]$
2,[4]	1	1	**9**	$\mathcal{U}-5J,[6\mathcal{U}-5J]$
2,[4]	0	2	5	$\mathcal{U}-3J,[6\mathcal{U}-3J]$
2,[4]	0	0	1	$\mathcal{U},[6\mathcal{U}]$
3	3/2	0	**4**	$3\mathcal{U}-15J/2$
3	1/2	2	10	$3\mathcal{U}-9J/2$
3	1/2	1	6	$3\mathcal{U}-5J/2$

$$\mathcal{U} \equiv U - 3J$$


6
5
4
3
2
1
0
n
−20
−10
0
10
20
μ/J
βJ=10
βJ=3
βJ=1

Heikes, multi-orbital:

Hi-T (T>U):

$$\alpha_H = -\frac{k_B}{e} \ln \frac{2M - n}{n}$$

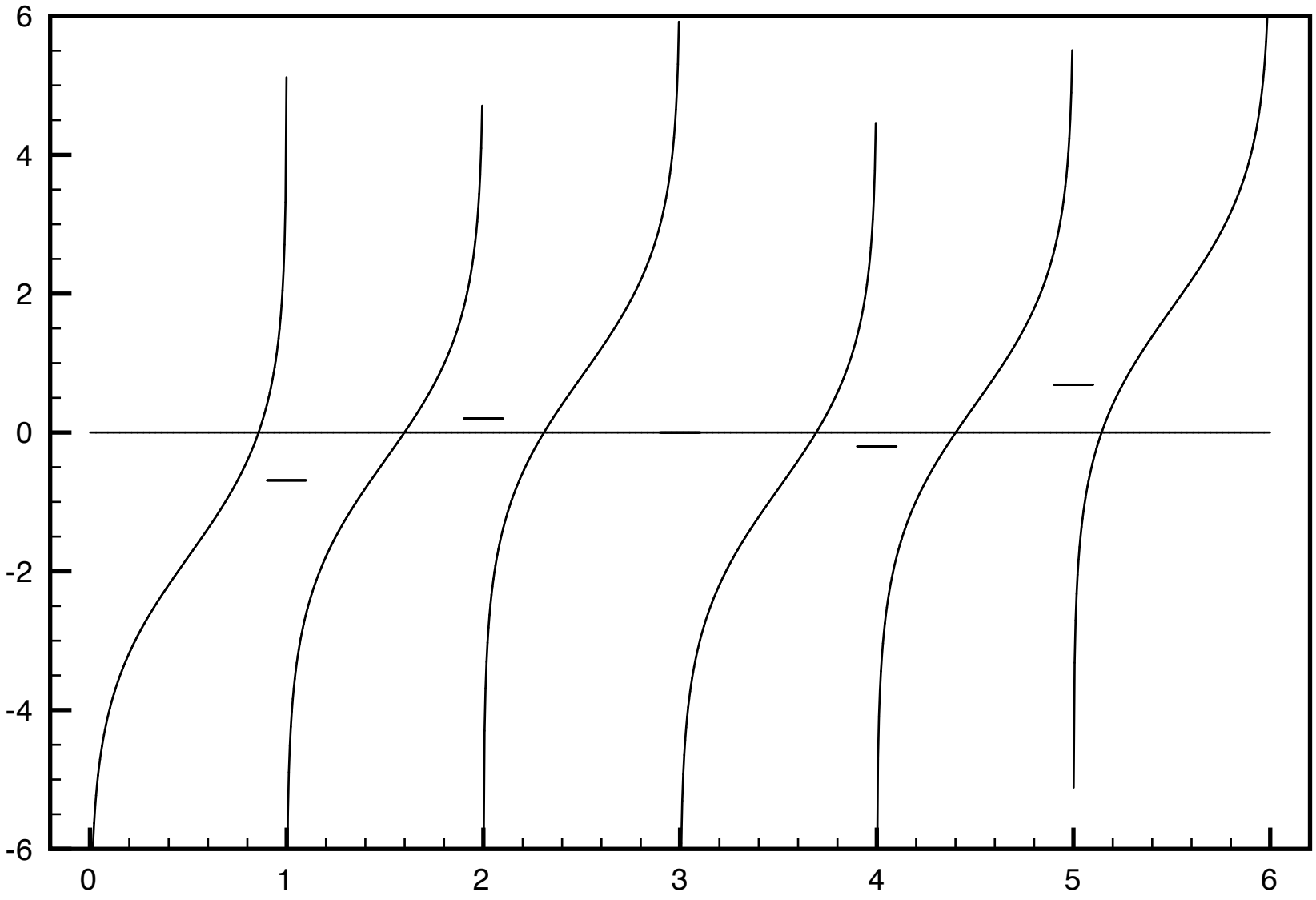
T<U, integer filling N

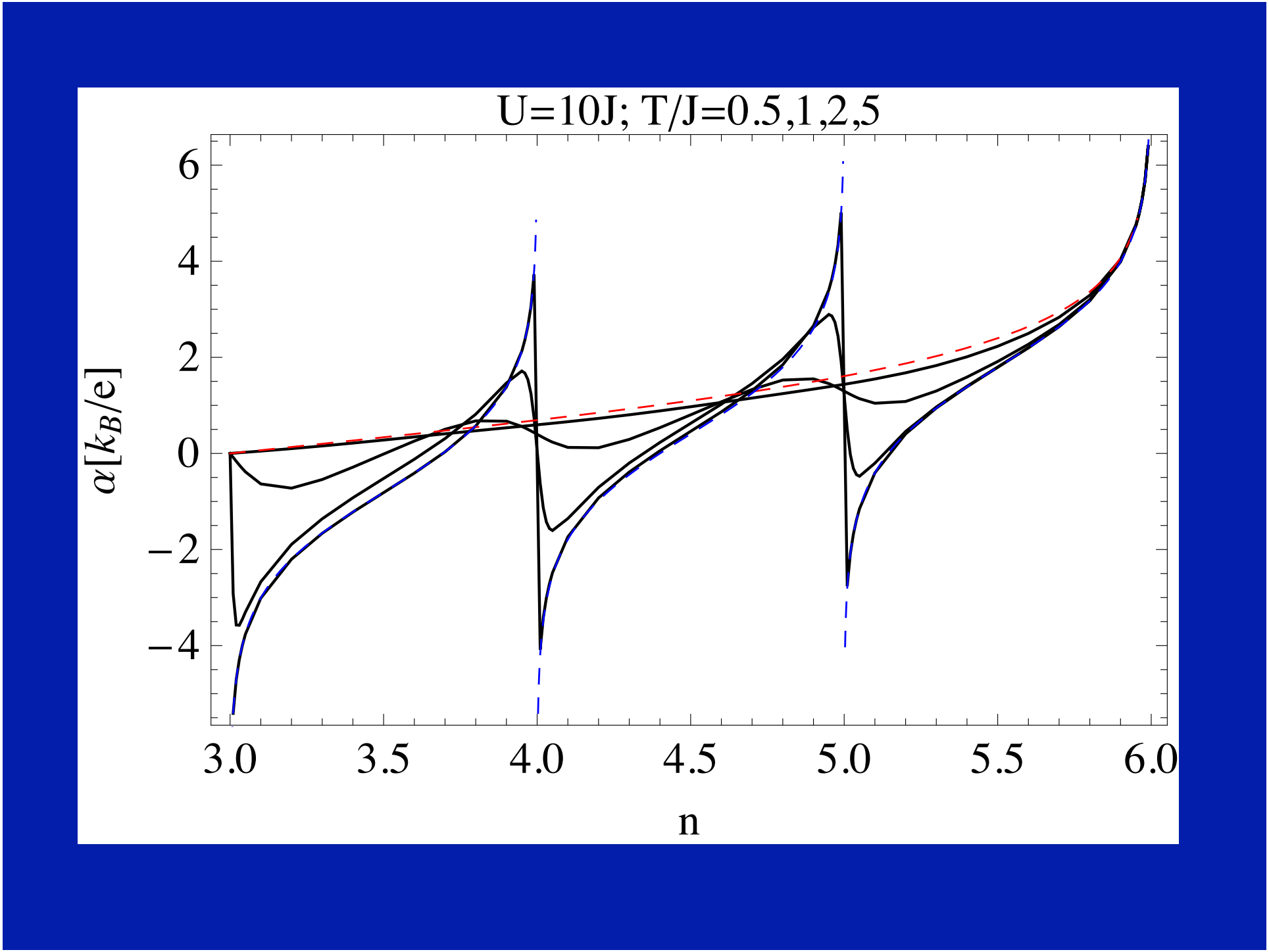
$$\alpha = \frac{k_B}{e} \ln \left[\frac{d_N}{d_{N+1}} \frac{n - N}{N + 1 - n} \right]$$

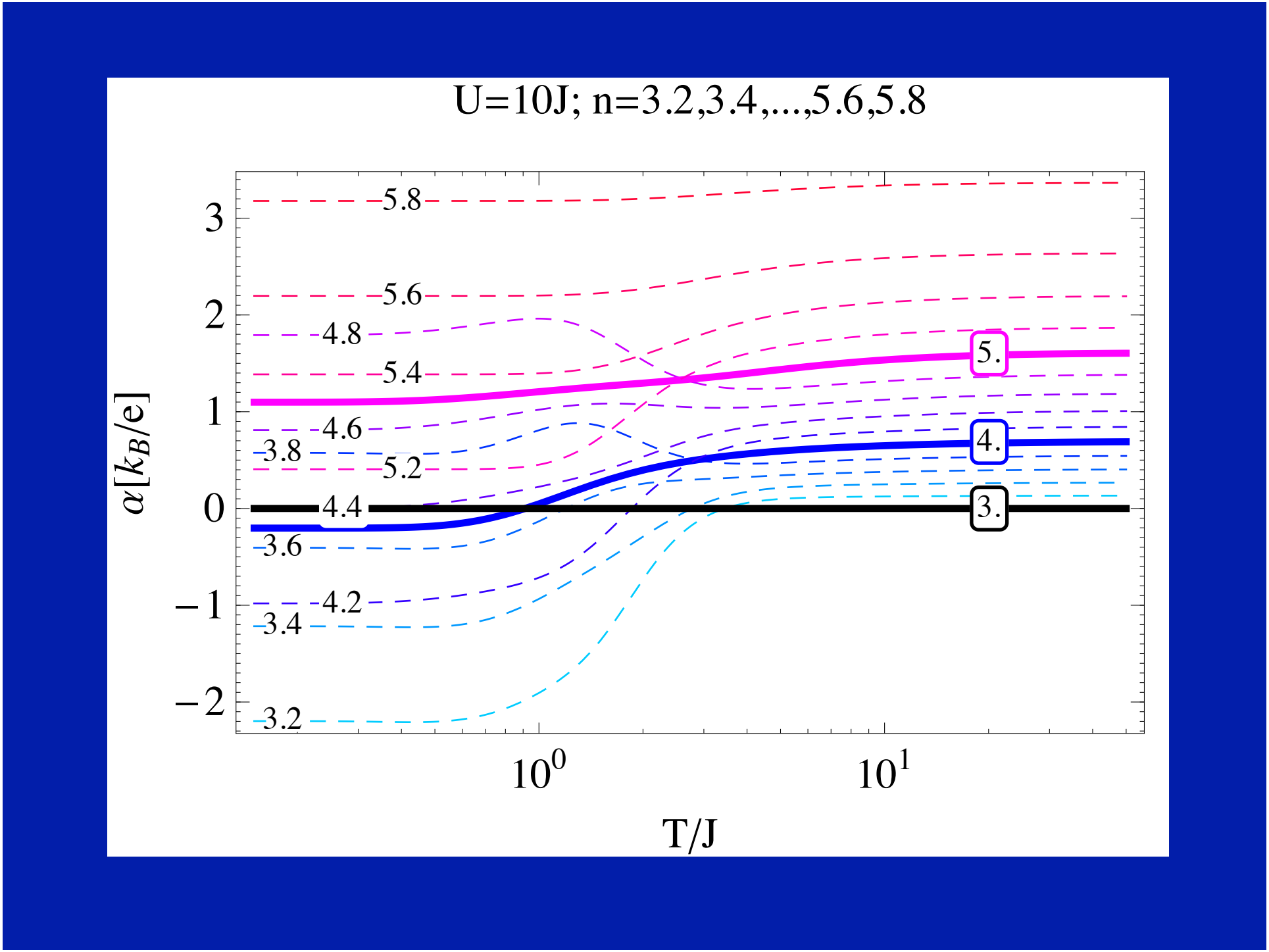
T<U, mixed valence N<n<N+1

$$\alpha = \frac{k_B}{e} \frac{1}{2} \ln \frac{d_{N-1}}{d_{N+1}}$$

case	degeneracies ; $\alpha[k_B/e]$ for $T < J < U$	$J < T < U$
$n = 1$	1,9 ; $-\log[9]/2$	1,15 ; $-\log[15]/2$
$n = 2$	6,4 ; $\log[3/2]/2$	6,20 ; $-\log[10/3]/2$
$n = 3$	9,9; 0	15,15; 0
$0 < n < 1$	1,6 ; $-\log[(1-x)/x] - \log 6$;	1,6; $-\log[(1-x)/x] - \log 6$
$1 < n < 2$	6,9 ; $-\log[(1-x)/x] - \log 3/2$	6,15; $-\log[(1-x)/x] - \log 5/2$
$2 < n < 3$	9,4 ; $-\log[(1-x)/x] - \log 4/9$	15,20 $-\log[(1-x)/x] - \log 4/3$
$U < T$	$\log[\frac{2M-n}{n}]$	


6
4
2
0
-2
-4
-6
0
1
2
3
4
5
6


U=10J; T/J=0.5,1,2,5
6
4
2
0
−2
−4
α[k_B/e]
3.0
3.5
4.0
4.5
5.0
5.5
6.0
n


U=10J; n=3.2,3.4,...,5.6,5.8
3
2
1
0
−1
−2
$\alpha[k_B/e]$
5.8
5.6
4.8
5.4
4.6
3.8
5.2
4.4
3.6
4.2
3.4
3.2
5.
4.
3.
10^0
10^1
T/J

Applicability to transition-metal oxides

I will not talk about cobaltates, leaving the topic to Sylvie Hebert's seminar

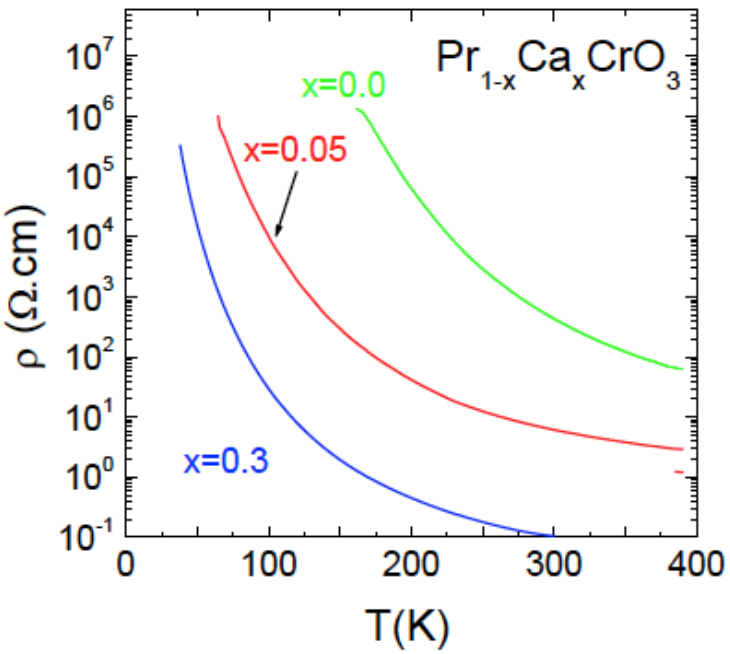
Semi-conducting oxides
for which
Heikes analysis
works

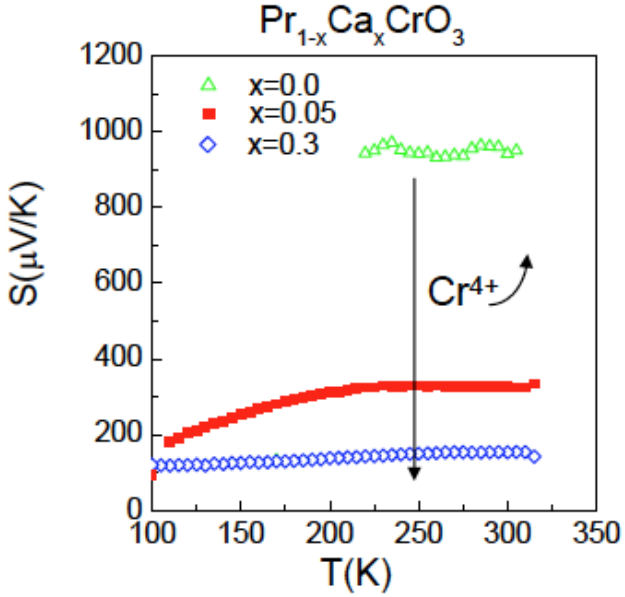
Orthochromites

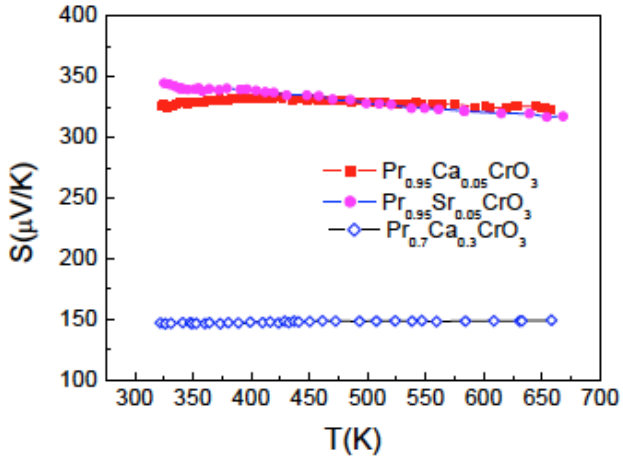
Analyse + quantitative via Heikes pour des charges localisées

Semiconducting behavior

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







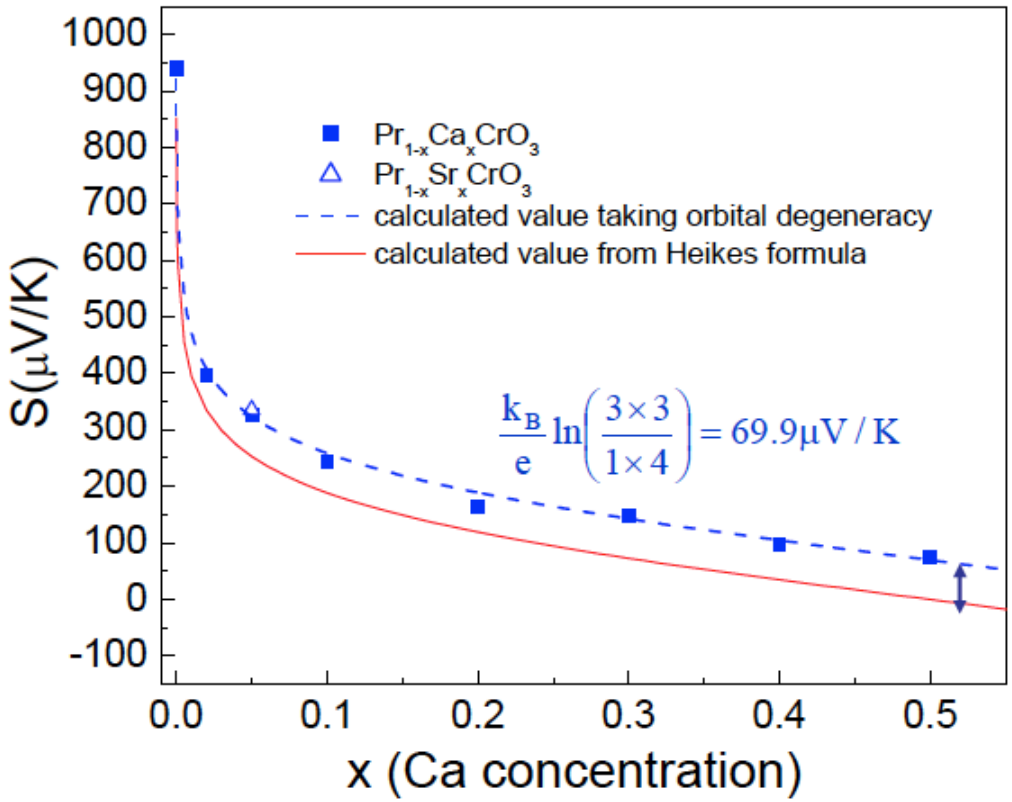
S. Pal et al., Eur. Phys. J. B 53, 5 (2006)

$Pr/CaCrO_3$: d^3/d^2

Courtesy: S.Hebert

Heikes formula with spin and orbital degeneracy

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



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

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

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

Seebeck is
~ T – independent

(important cross-check for applicability of Heikes at fixed doping level)

Q: Has Hall number been Measured ?

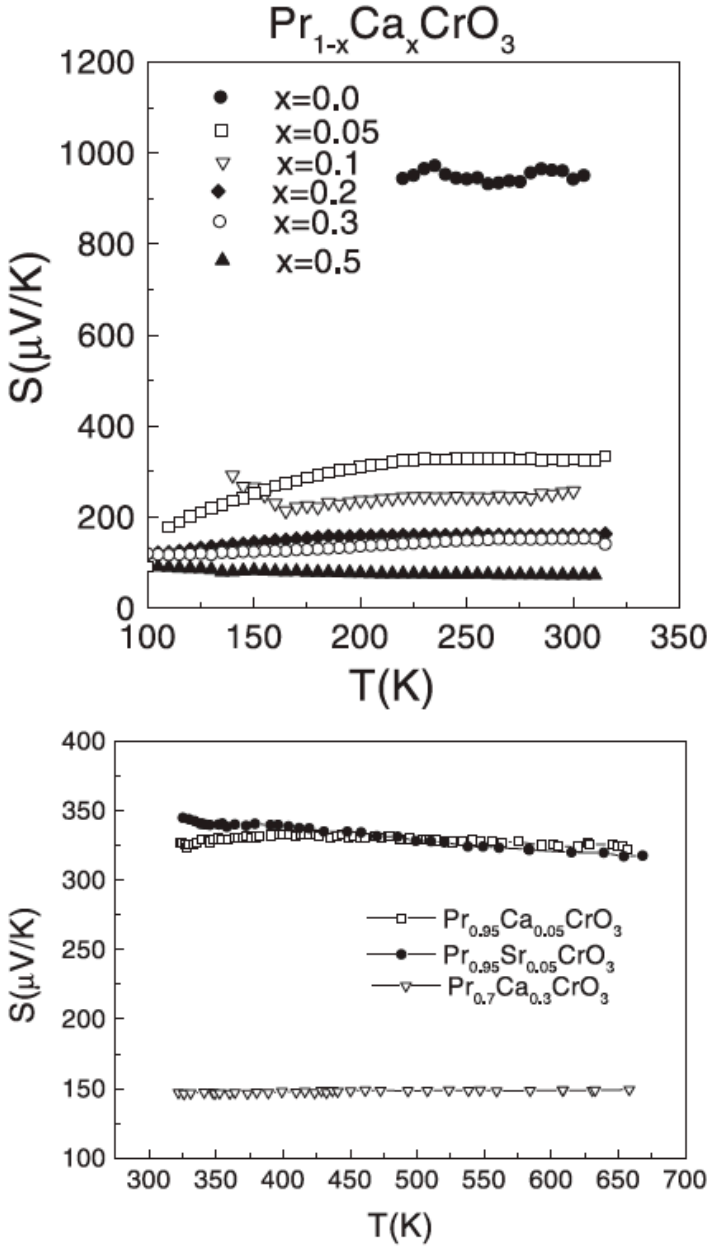


Fig. 3. (a) S vs. T plot of $Pr_{1-x}Ca_xCrO_3$ ($x = 0.0, 0.05, 0.1, 0.2, 0.3, 0.5$). (b) High temperature (up to 650 K) data of some selected samples.

$La/SrCrO_3$

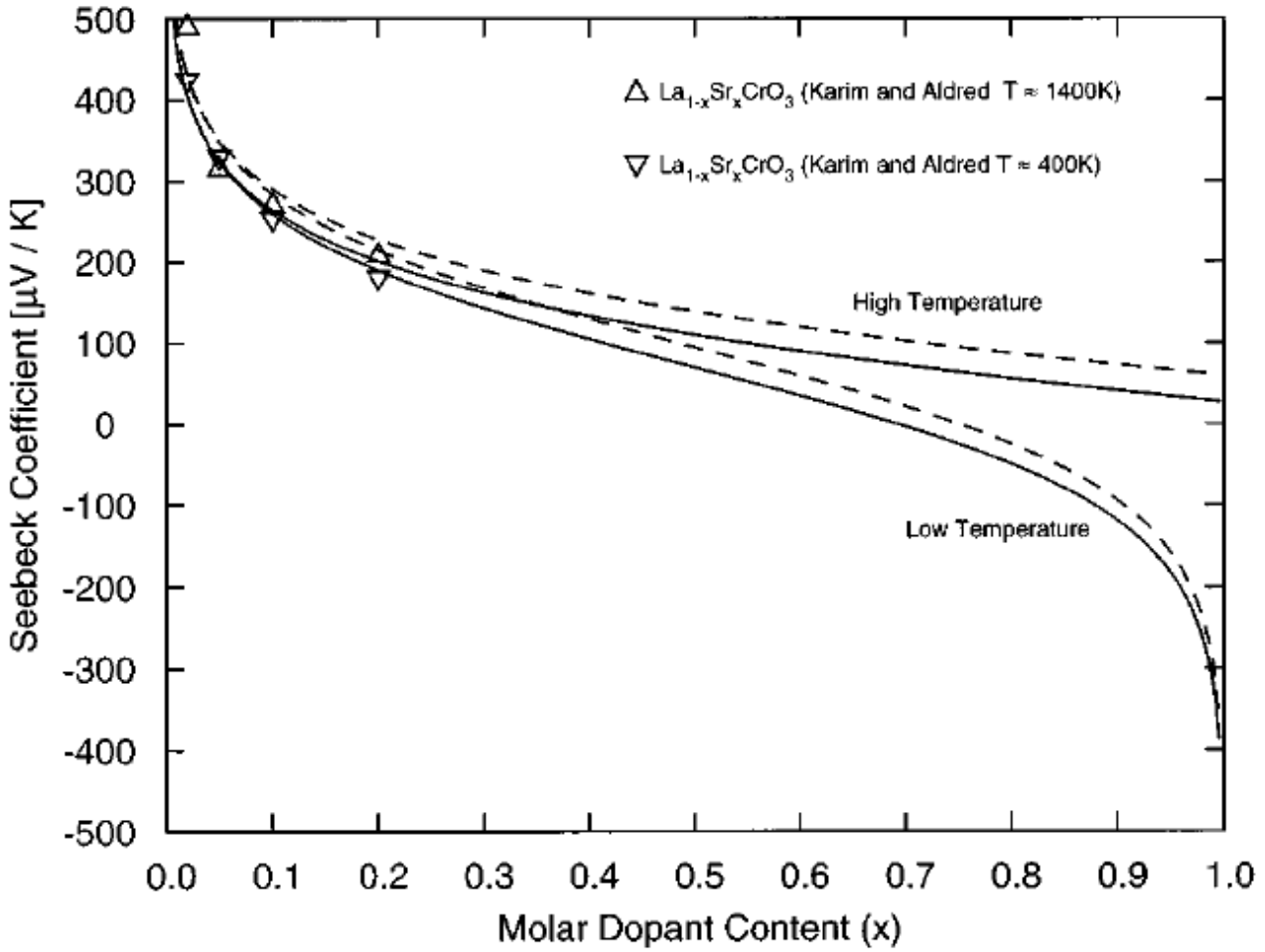


FIG. 3. Predicted high- and low-temperature limits of the Seebeck coefficient as a function of acceptor doping calculated for the $La_{1-x}Sr_xCrO_3$ series. Experimental data are from the study of Karim and Aldred (Ref. 8) for $La_{1-x}Sr_xCrO_3$ at high and low temperatures as indicated. Solid lines indicate predictions for weak magnetic coupling, dashed lines for strong magnetic coupling.

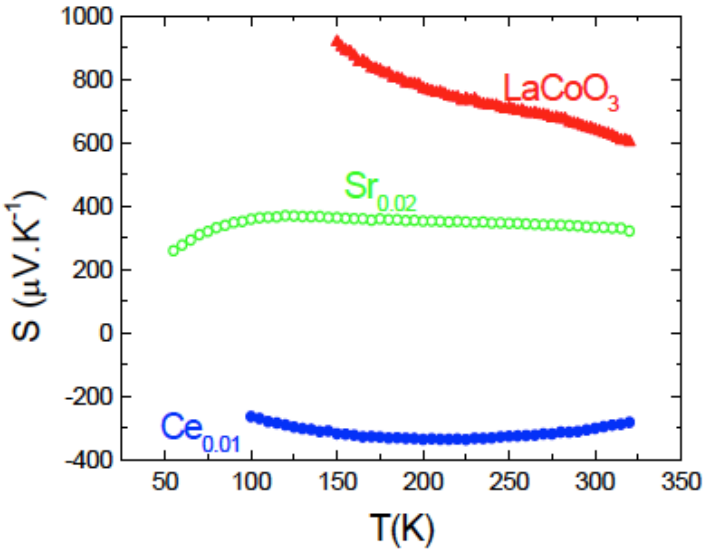
Marsh and Parris
PRB, 1996

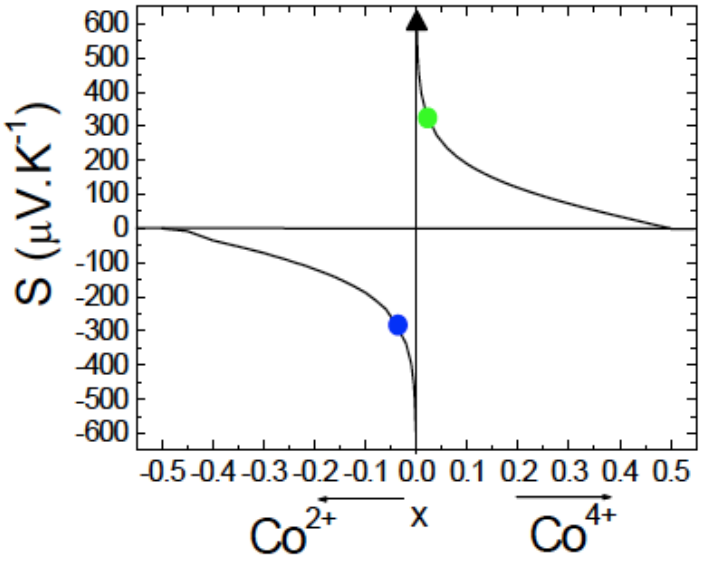
$LaCoO_3$: A site substitution

$LaCoO_3$ x~0 : $La^{3+}Co^{3+}O_3$

Sr^{2+} x>0 : $La_{1-x}Sr_xCo^{3+}Co^{4+}O_3$

Ce^{4+} x<0 : $La_{1-x}Ce_xCo^{3+}Co^{2+}O_3$





A. Maignan et al., EPJB 39, 145 (2004)

$LaCoO_3$: Co3+ filled t_{2g} shell, band insulator

A case where Heikes works qualitatively, but not quantitatively: $La/SrVO_3$ [d^2/d^1]

PHYSICAL REVIEW B **83**, 165127 (2011)

Thermoelectric response in the incoherent transport region near Mott transition: The case study of $La_{1-x}Sr_xVO_3$

M. Uchida,[1] K. Oishi,[1] M. Matsuo,[2,3] W. Koshibae,[4] Y. Onose,[1,5] M. Mori,[2,3] J. Fujioka,[5] S. Miyasaka,[6] S. Maekawa,[2,3] and Y. Tokura[1,4,5]

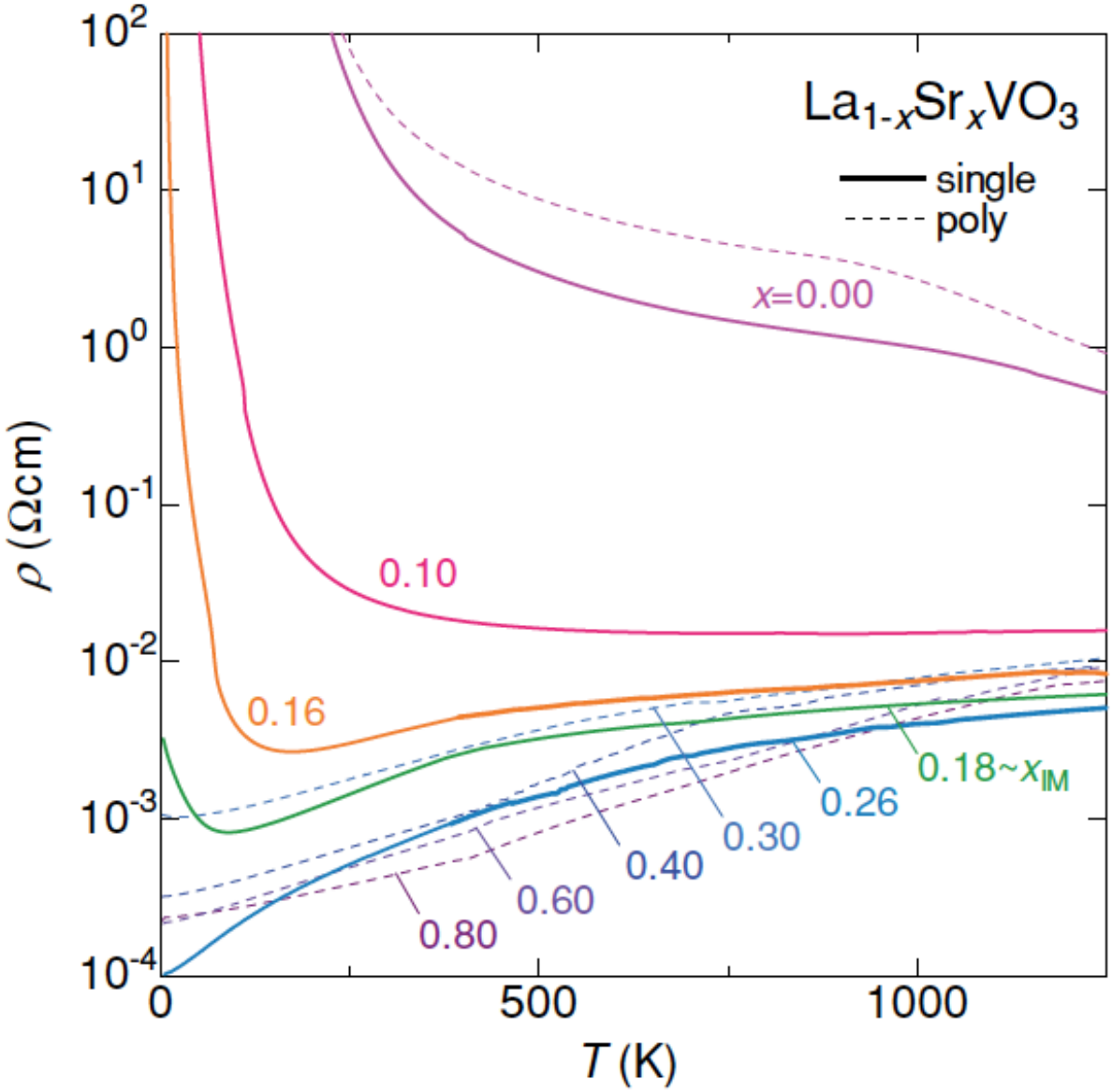
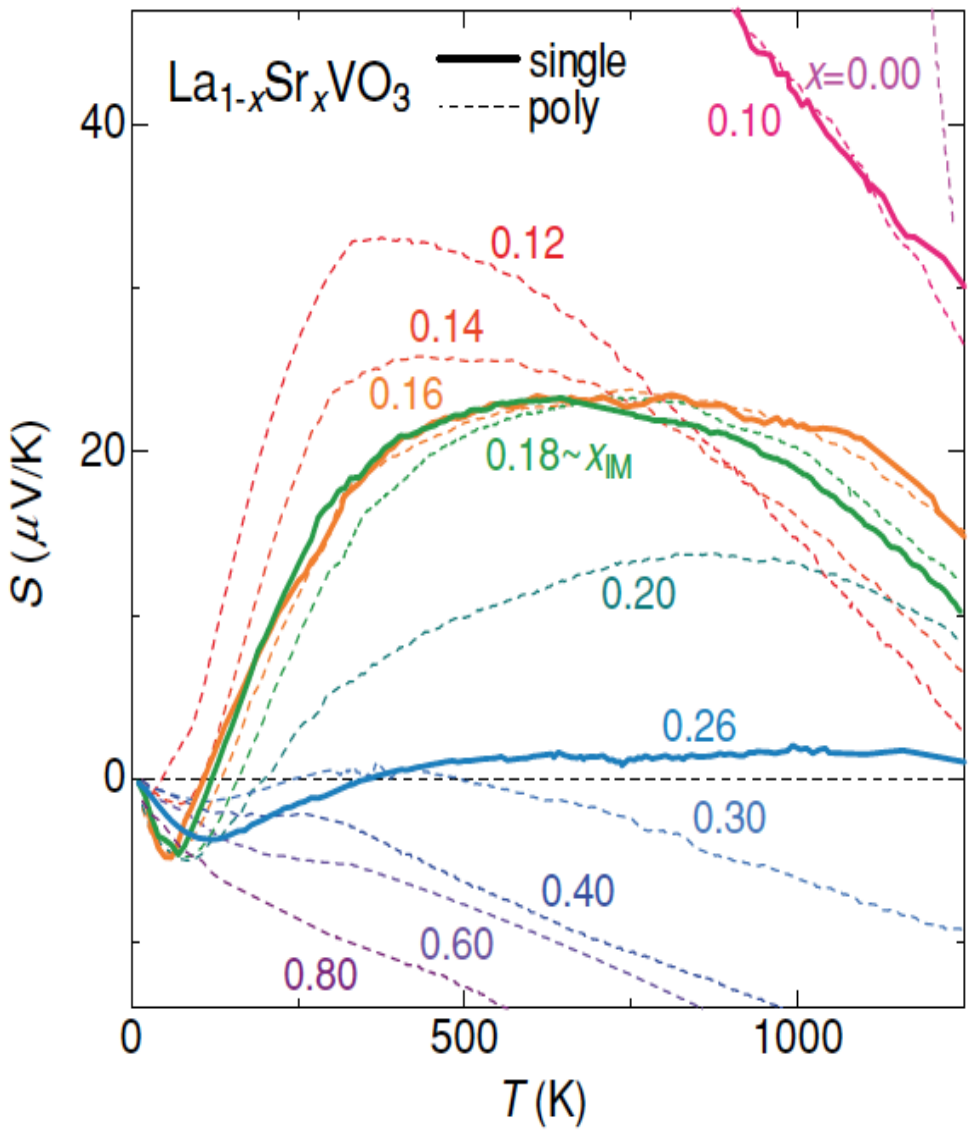


FIG. 1. (Color online). Temperature dependence of the resistivity ρ in $La_{1-x}Sr_xVO_3$. The solid and dashed lines represent the data for the single crystals and polycrystals, respectively.



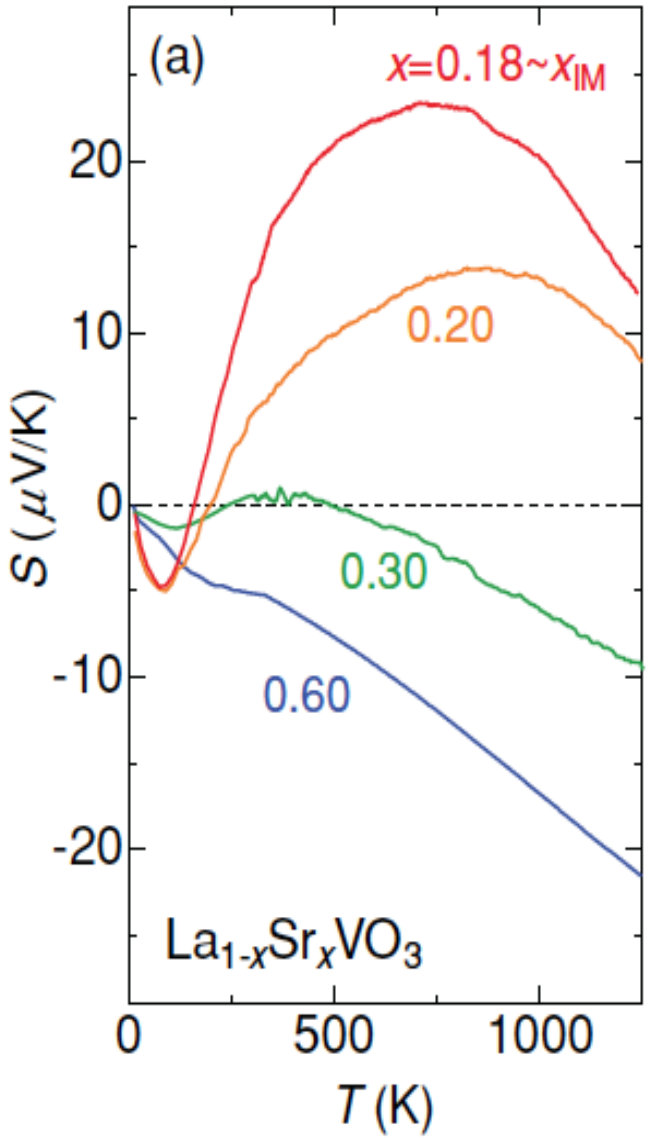


FIG. 3. (Color online). Temperature dependence of the thermopower S in $La_{1-x}Sr_xVO_3$. The solid and dashed lines represent the data for the single crystals and polycrystals, respectively.

Qualitatively quite similar to Hubbard model calculations above

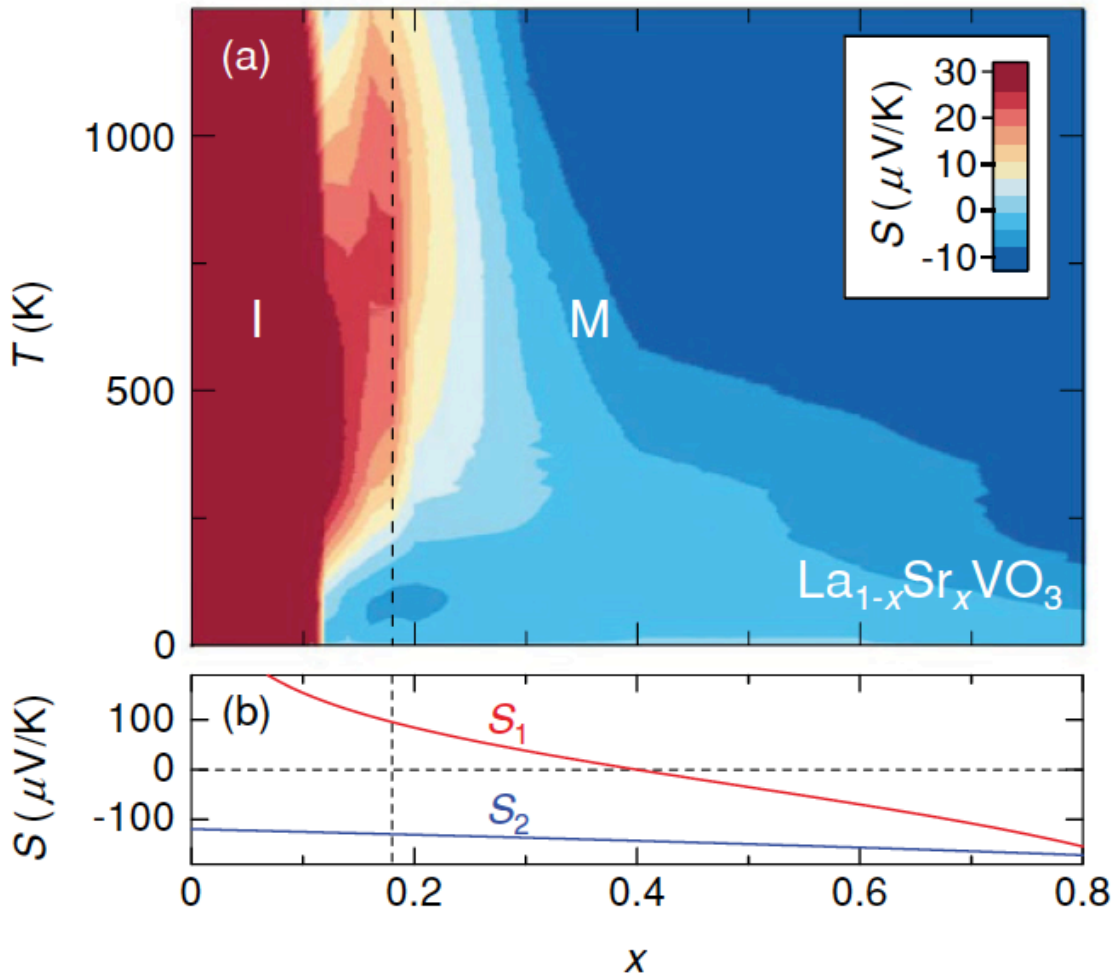
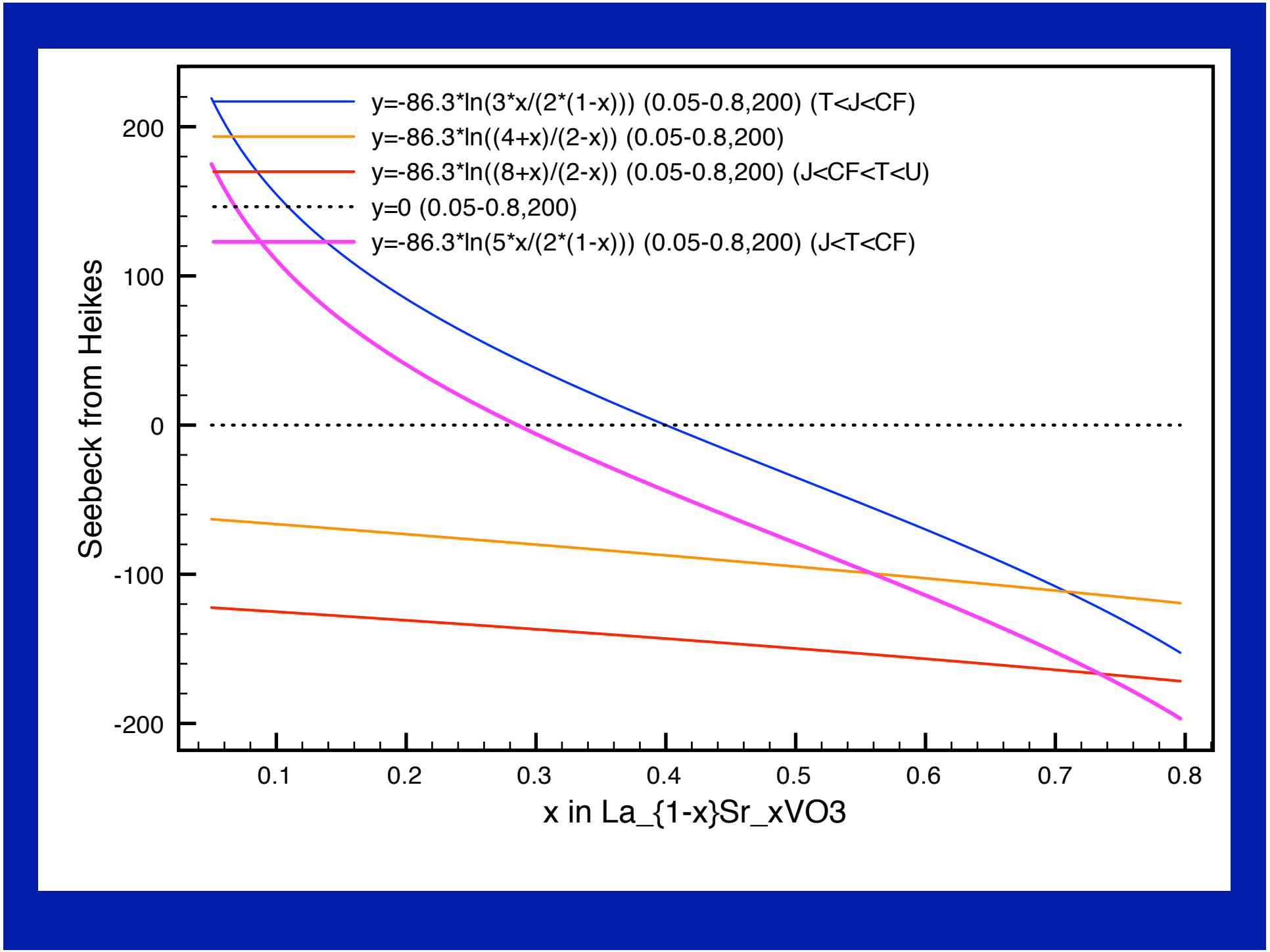


FIG. 4. (Color online). (a) Evolution of the thermopower S in the T-x phase diagram. The vertical dashed lines indicate the critical doping level x_{IM} for the insulator (I)-metal (M) transition at the ground state. The region with large S-gradient around x_{IM} corresponds to the incoherent metallic state as expected for the Heikes formula to be valid. (b) Doping variation of S in two high-temperature limits S_1 ($k_{\mathrm{B}}T \ll U$) and S_2 ($U \ll k_{\mathrm{B}}T$) in the Heikes formula with consideration of nearly degenerate t_{2g} or (t_{2g} plus e_g) orbitals (see text).


y=-86.3*ln(3*x/(2*(1-x))) (0.05-0.8,200) (T<J<CF)
y=-86.3*ln((4+x)/(2-x)) (0.05-0.8,200)
y=-86.3*ln((8+x)/(2-x)) (0.05-0.8,200) (J<CF<T<U)
y=0 (0.05-0.8,200)
y=-86.3*ln(5*x/(2*(1-x))) (0.05-0.8,200) (J<T<CF)
Seebeck from Heikes
200
100
0
-100
-200
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
x in La_{1-x}Sr_xVO3

Metallic oxides: The example of Ruthenates

$Sr/CaRuO_3$, Sr_2RuO_4: d^4 materials
Metals with intermediate to large electronic correlations
Fermi liquid to `less good' metal crossover as T increases
Hund's coupling physics important
cf. 2011-2012 lectures

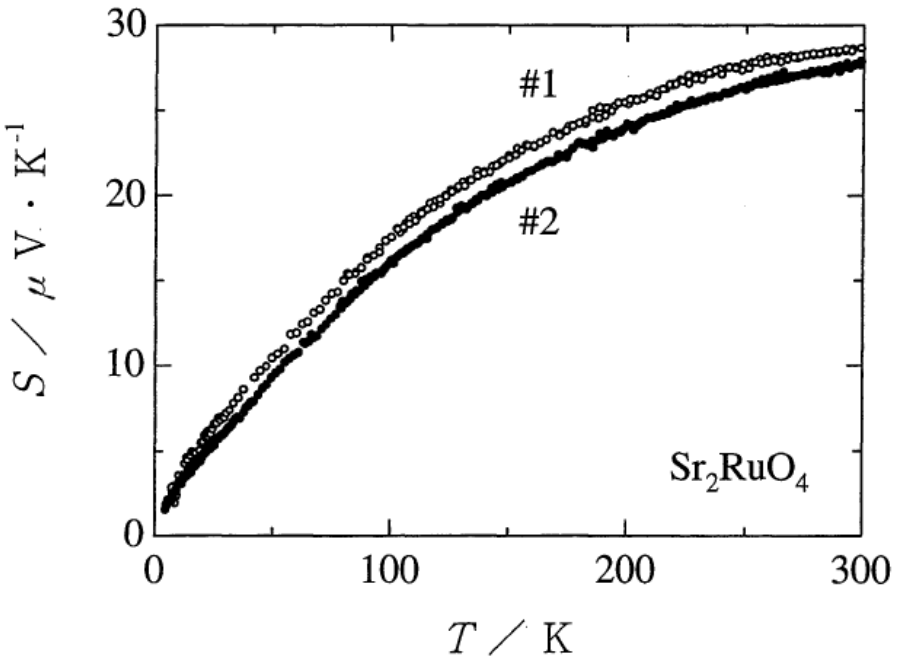


Fig. 1. Thermopower of Sr_2RuO_4 measured along the two-dimensional *ab* plane. Open and closed circles are for samples 1 and 2, respectively.

← Positive Seebeck,
Maximum around 30μV/K
At T ~ 300K

Yoshino et al. JPSJ 2008

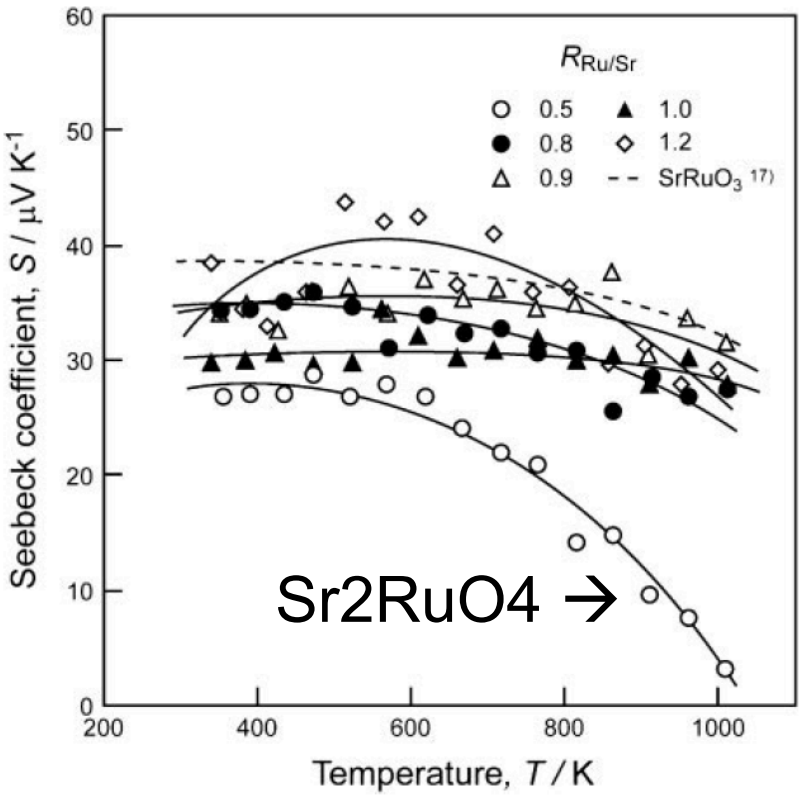
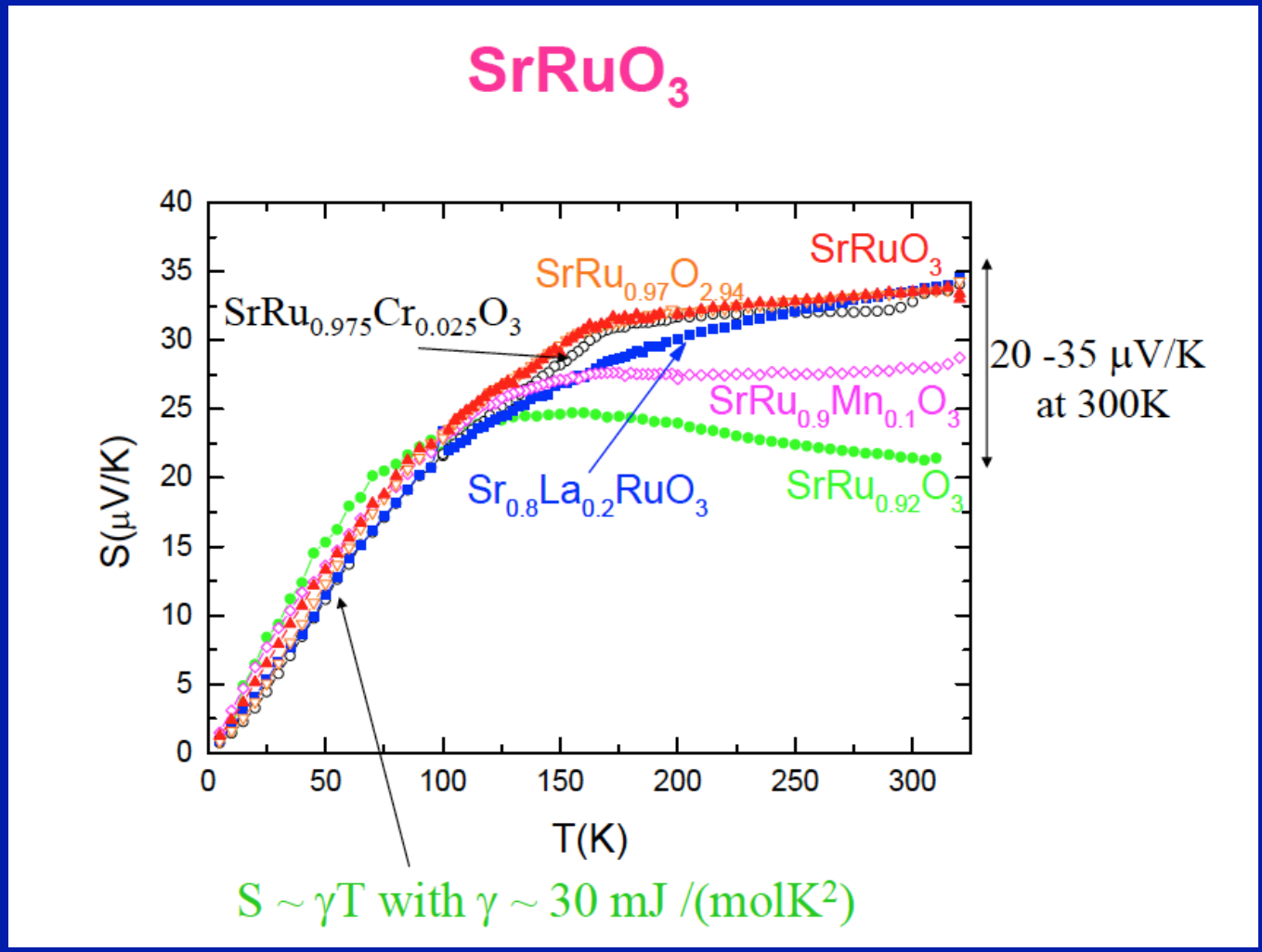


Fig. 8 Temperature dependence of Seebeck coefficient of Sr-Ru-O compounds.

Decreases above 300K,
Tendancy to become
negative at hi-T ? →

Keawprak et al. Mat. Trans (2008)

Max at 30μV/K rather universally seen in ruthenates.
Insensitive to doping. Crossover between good and poorer metal

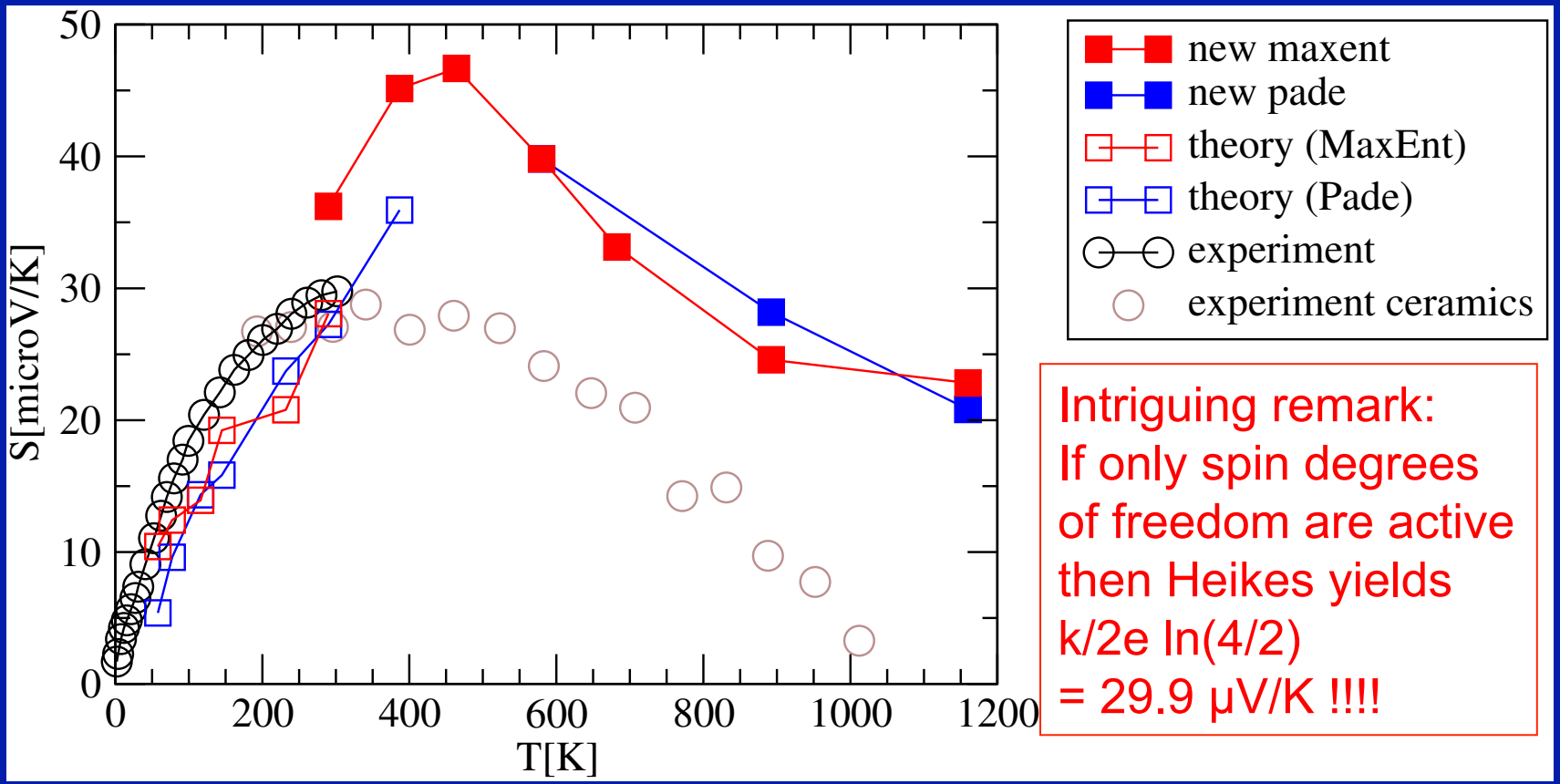


Klein et al. PRB 2006 & PhD thesis (CRISMAT)

Naive Heikes taking into account spin and orbital for t_{2g}, $T \ll J_H$ would yield a negative value $-k/2e \ln(3/2) \sim -17.5$ μV/K !

LDA+DMFT approach is able to obtain a ~ correct answer, and Shastry-Kelvin when used with DMFT works well…

(Jernej Mravlje, unpublished)



Intriguing remark:
If only spin degrees of freedom are active then Heikes yields
$k/2e \ln(4/2)$
= 29.9 μV/K !!!!

Conclusions

- Heikes estimates in atomic limit are applicable to the most insulating oxides
- Metallic materials require a different approach
- Matching between a low-T degenerate metal, intermediate-T poor metal and hi-T Heikes limit is a complex problem on which progress can now be made with techniques such as DMFT
- Relaistic applications to materials start to appear – more work needed
- Doped insulators + Frustration key to large Seebeck values