Thermoelectric Transport Coefficients Sodium Cobaltates

Sriram Shastry,
UCSC, Santa Cruz, CA

Berkeley

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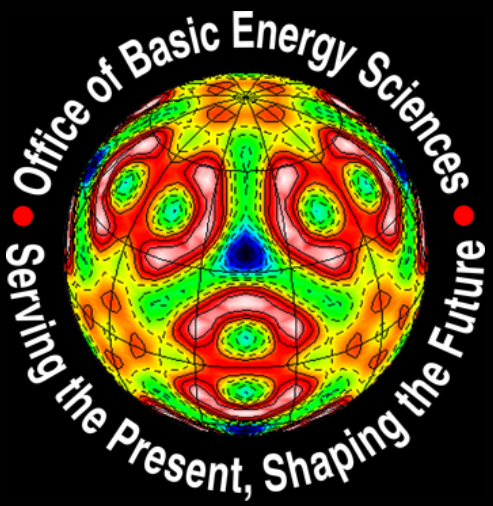


Collaborators:

Mike Peterson (Maryland)

Jan Haerter (Hamburg)

Subroto Mukherjee (Berkeley)

- New Materials with large S and Z
- Results for $Na_{.68}$ CoO_2 and predictions for a hole doped counterpart.
- Some theory

Introduction and Motivation

Requirements for applications:

Large Seebeck coefficient S

Large figure of merit Z T at 300K

$$Z\,T = \frac{S^2 T \sigma}{\kappa}$$

•Seeking simultaneously :

•High S (thermopower or Seebeck)

•High electrical conductivity σ

•Low Thermal conductivity κ

Semiconductor World

•Bi_2Te_3

•Superlattices

1999-2003 ⟶

Correlated Materials

•Heavy fermions: good metals and large d.o.s.

•Mott Hubbard systems:

•$Na_{.68}$ Co O_2: Terasaki, Ong Cava ….

Large enhancement of the thermopower in Na_xCoO_2 at high Na doping

Minhyea Lee[1], Liliana Viciu[2], Lu Li[1], Yayu Wang[1,†], M. L. Foo[2], S. Watauchi[2], R. A. Pascal Jr.[2], R. J. Cava[2] and N. P. Ong[1]

that is destroyed by field [5]. Initial measurements [1] showed that, in the as-grown composition, Na_xCoO_2 displays moderately large thermopower S and conductivity σ. However, the prospects for thermoelectric cooling applications faded when the figure of merit Z was found to be small at this composition ($0.6< x <0.7$). Here we report that, in the poorly-explored high-doping region $x >0.75$, S undergoes an even steeper enhancement. At the critical doping $x_p \sim 0.85$, Z (at 80 K) reaches values $\sim$40 times larger than in the as-grown crystals. We discuss prospects for low-temperature thermoelectric applications.

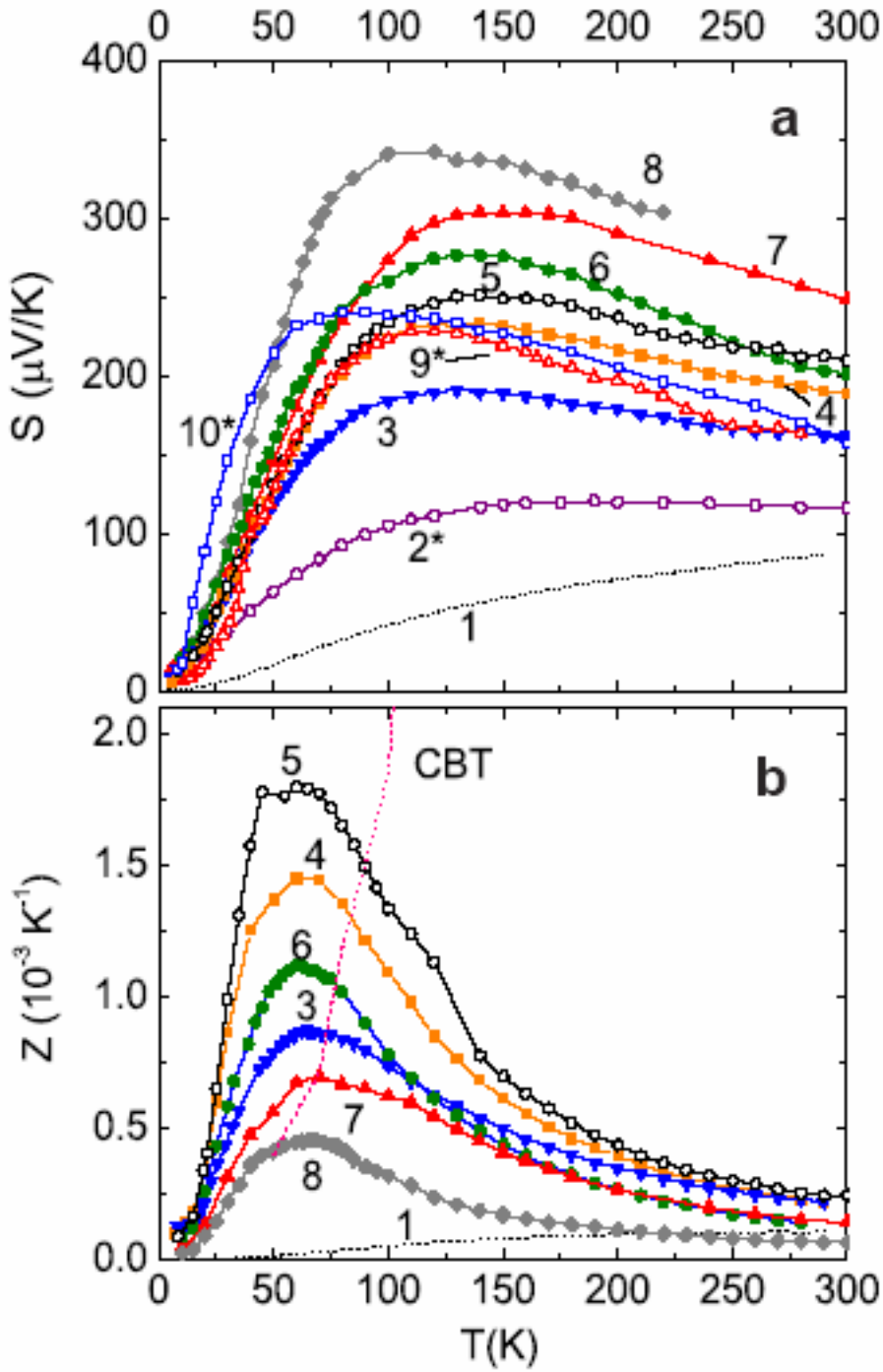


FIG. 2: The in-plane thermopower S (Panel a) and the figure of merit Z (Panel b) in Na_xCoO_2. In Sample 1 (Panel a), S is very similar to that of Terasaki *et al.* [1]. As x increases into phase H_2 (2*–4), the profile of S develops an increasing bulge near 130 K that grows rapidly to peak values of 200-250 μV/K. In the mixed-phase region, S further increases to 300-350 μV/K (Samples 5–8), before settling down to 228 μV/K in the limit $x \rightarrow 1$ (Samples 9*). A striking pattern is that the S-T profiles (all hole-type) are nominally similar in shape in the mixed-phase region. The exception is Sample 10* in which $f \sim 1/200$ (see Supplementary Information). Panel b shows curves of $Z = S^2/\rho\kappa$, with κ measured separately (not shown). As x increases from 0.71 (Sample 1), the peak value of Z increases steeply to 1.8×10^{-3} K^{-1} in Sample 5. At higher x, the peak value of Z falls rapidly because of the sharp increase in ρ. At 80 K, Z in Sample 5 is $\sim$40 times larger than that in Sample 1. The dashed line labeled CBT is Z reported [17] for $CsBi_4Te_6$.

Enhanced thermopower in an intergrowth cobalt oxide $Li_{0.48}Na_{0.35}CoO_2$

Zhi Ren,[1] Jingqin Shen,[1] Shuai Jiang,[1] Xiaoyang Chen,[1] Chunmu Feng,[2] Zhu'an Xu,[1] Guanghan Cao[1*]
[1] *Department of Physics, Zhejiang University, Hangzhou 310027, People's Republic of China and*
[2] *Test and Analysis Center, Zhejiang University, Hangzhou 310027, People's Republic of China*
(Dated: February 2, 2008)

We report the measurements of thermopower, electrical resistivity and thermal conductivity in a complex cobalt oxide $Li_{0.48}Na_{0.35}CoO_2$, whose crystal structure can be viewed as an intergrowth of the O3 phase of Li_xCoO_2 and the P2 phase of Na_yCoO_2 along the c axis. The compound shows large room-temperature thermopower of $\sim$180 μV/K, which is substantially higher than those of Li_xCoO_2 and Na_yCoO_2. The figure of merit for the polycrystalline sample increases rapidly with increasing temperature, and it achieves nearly 10^{-4} K^{-1} at 300 K, suggesting that $Li_xNa_yCoO_2$ system is a promising candidate for thermoelectric applications.

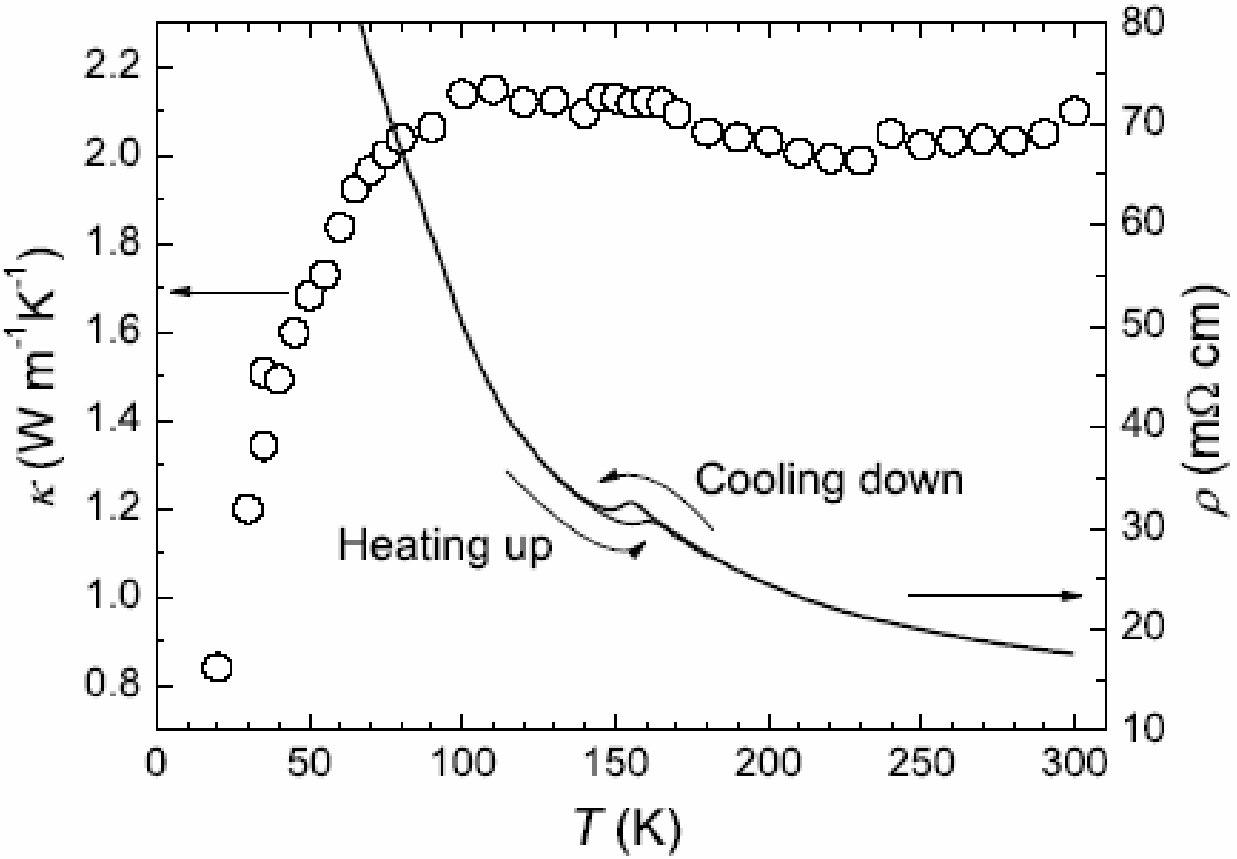


FIG. 3: Temperature dependence of electrical resistivity and thermal conductivity for the as-annealed LNCO polycrystalline sample.

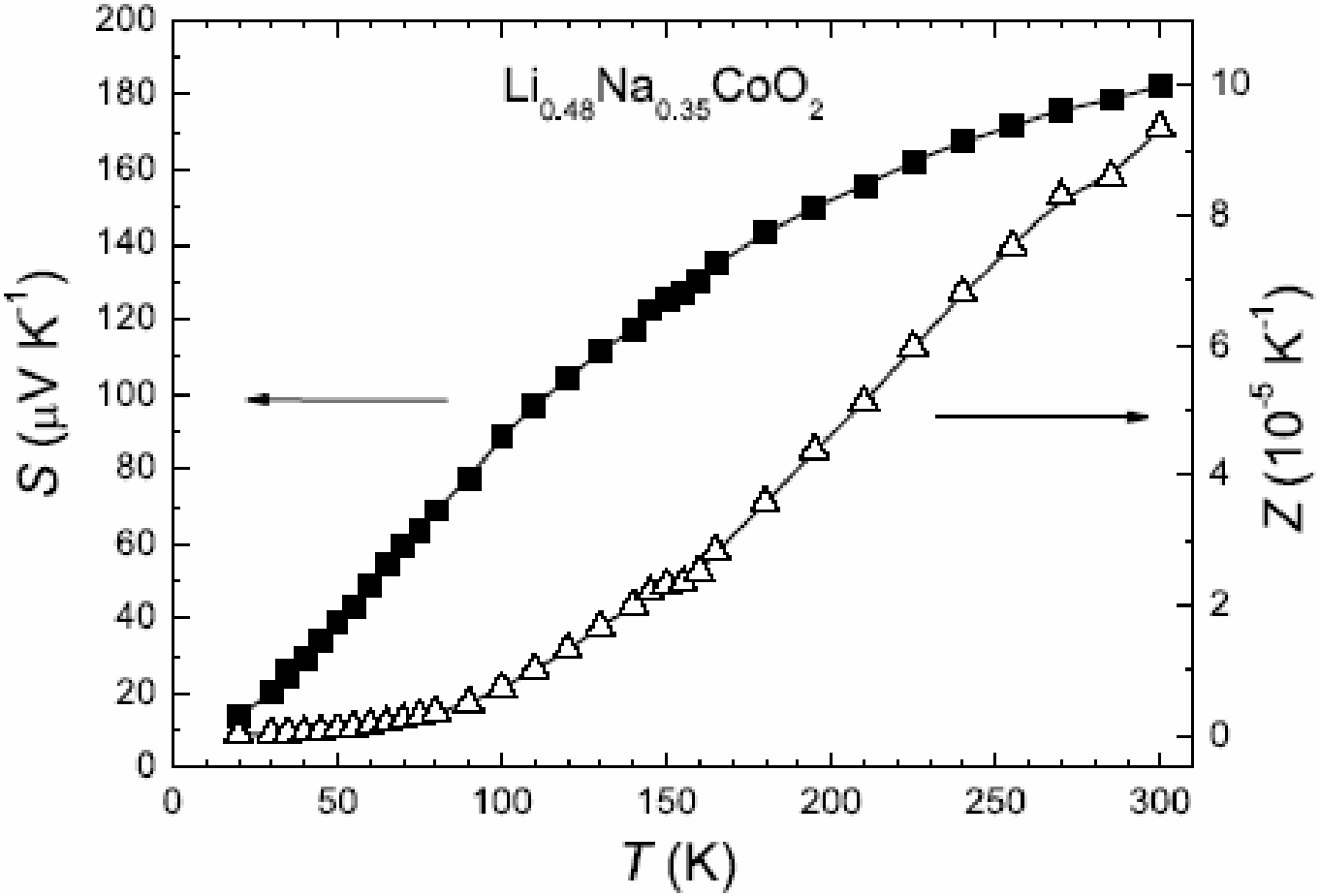


FIG. 4: Temperature dependence of thermopower (S) and figure of merit (Z) for the as-annealed LNCO polycrystalline sample.

Correlated systems and Thermoelectric effects in them are hugely challenging

In general Mott Hubbard systems have interesting transport near the insulating state:

But:….

Perturbative calculations are hard to do, since there is no small parameter

Bloch Boltzmann Drude theory is suspect since quasiparticles are poorly defined and short lived.

Kubo formulas are exact, but hardly helpful !

E.g. they require a knowledge of the d.c. conductivity σ to compute the thermopower. This is next to impossible today since σ contains the essence of T linear resistivity: the core of High Tc.

This is akin to the directions from your expensive GPS:

"The road to Lhasa from Kathmandu"

Make at left at the Everest and go down the Zanang valley !!.

BADLY NEEDED

A NEW ROAD!!

HINT for a new route comes from the Hall constant.

Shastry Shraiman Singh 1993- Kumar Shastry 2003)

$$\rho_{xy}(\omega) = \frac{\sigma_{xy}(\omega)}{\sigma_{xx}(\omega)^2} \rightarrow B R_H^* \text{ for } \omega \rightarrow \infty$$

$$R_H^* = R_H(0) \text{ in Drude theory}$$

Perhaps ω dependence of R_H is weak compared to that of Hall conductivity.

$$R_H^* = \frac{-i 2\pi}{hB} N v < [J^x, J^y] > / < \tau_{xx} >^2$$

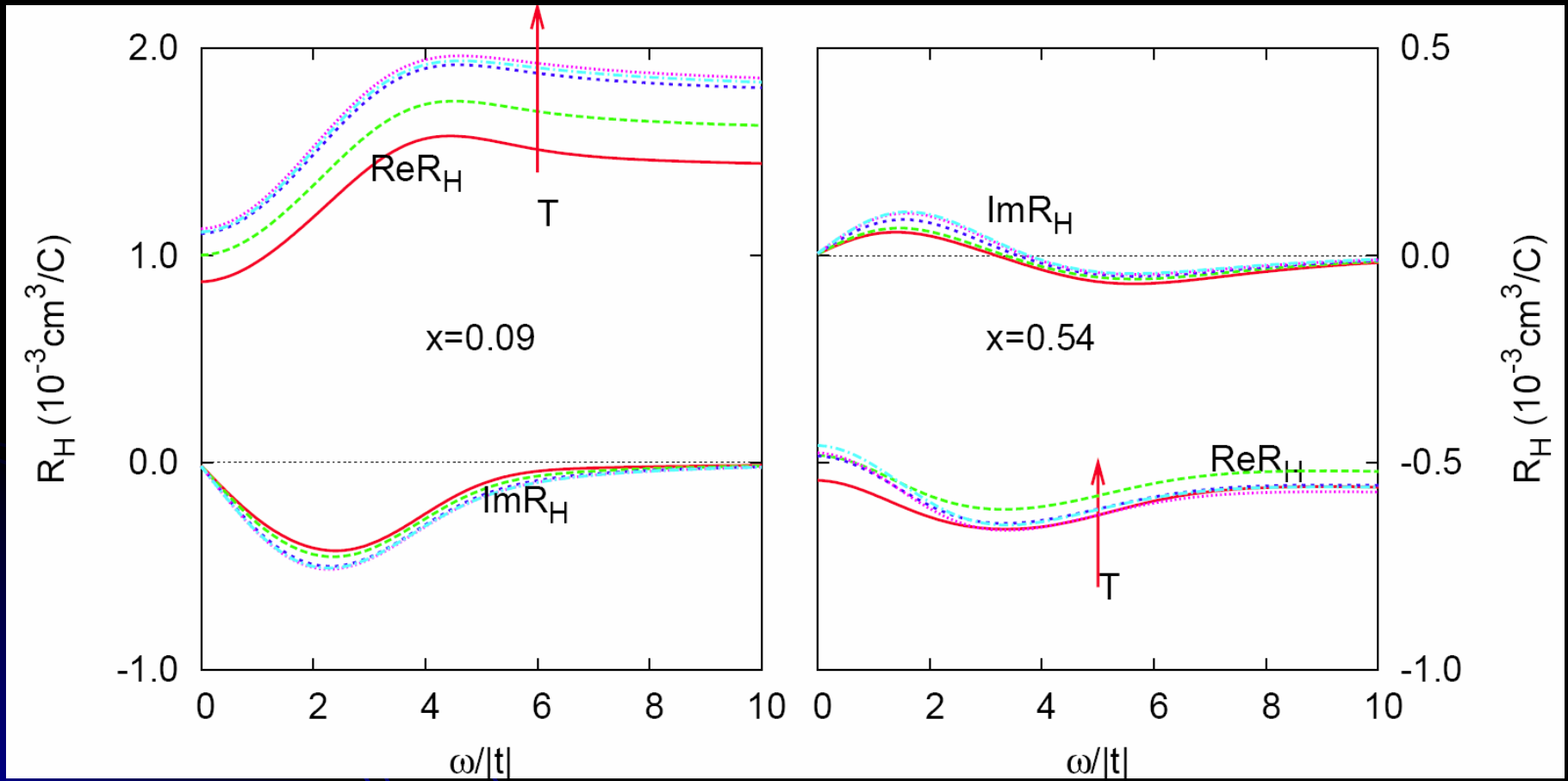
ANALOGY between Hall Constant and Seebeck Coefficients

- **Very useful formula since**
  - **Captures Lower Hubbard Band physics. This is achieved by using the Gutzwiller projected fermi operators in defining J's**
  - **Exact in the limit of simple dynamics (e.g few frequencies involved), as in the Boltzmann eqn approach.**
  - **Can compute in various ways for all temperatures (exact diagonalization, high T expansion etc…..)**
  - **We have successfully removed the dissipational aspect of Hall constant from this object, and retained the correlations aspect.**
  - **Very good description of t-J model.**
  - **This asymptotic formula usually requires ω to be larger than J**

Computation of frequency dependence of Hall constant: NCO (Haerter Shastry)

Worst case dependence

Usual dependence

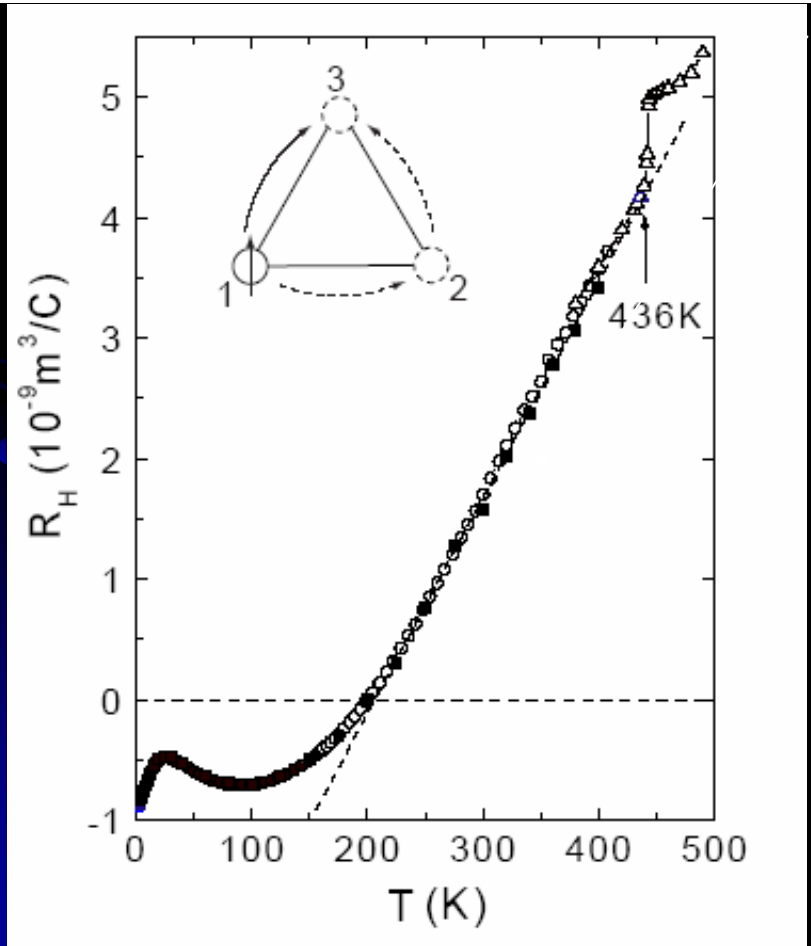


How about experiments? See next:

Anomalous high-temperature Hall effect on the triangular lattice in Na_xCoO_2

Yayu Wang[1], Nyrissa S. Rogado[2], R. J. Cava[2,3], and N. P. Ong[1,3]

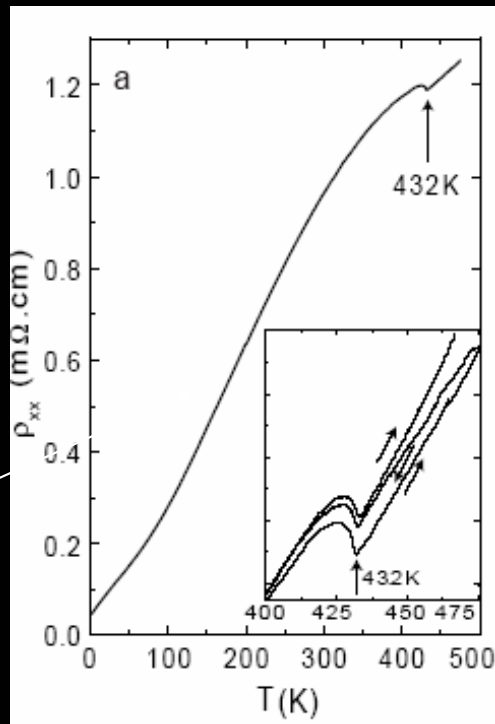
The Hall coefficient R_H of Na_xCoO_2 ($x = 0.68$) behaves anomalously at high temperatures (T) From 200 to 500 K, R_H increases linearly with T to 8 times the expected Drude value, with no sign of saturation. Together with the thermopower Q, the behavior of R_H provides firm evidence for strong correlation. We discuss the effect of hopping on a triangular lattice and compare R_H with a recent prediction by Kumar and Shastry.



Hall constant as a function of T for x=.68 (CW metal). T linear over large range 200^0 to 436^0 (predicted by theory of triangular lattice transport KS)

STRONG CORRELATIONS & Narrow Bands

T Linear resistivity



For a weakly interacting diffusive metal, we can compute all three S's. Low T limit :

Here is the result:

Density Of States

Velocity averaged over FS

Energy dependent relaxation time.

$$S = T\frac{\pi^2 k_B^2}{3q_e}\frac{d}{d\,\varepsilon}\ln[\rho(\varepsilon)\langle(v^x)^2\rangle_\varepsilon \tau(\varepsilon)]_{\varepsilon\to\mu}$$ Onsager- Kubo-Mott formula

"Exact"

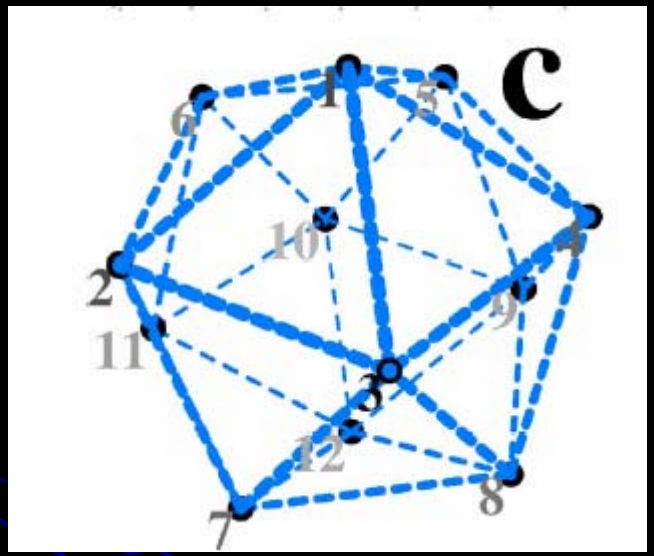
$$S = T\frac{\pi^2 k_B^2}{3q_e}\frac{d}{d\varepsilon}\ln[\rho(\varepsilon))]_{\varepsilon\to\mu}$$ Kelvin inspired formula

Easy to compute for correlated systems, since transport is simplified!

But S* is better in this limit

$$S^* = T\frac{\pi^2 k_B^2}{3q_e}\frac{d}{d\varepsilon}\ln[\rho(\varepsilon)\langle(v^x)^2\rangle_\varepsilon]_{\varepsilon\to\mu}$$ High frequency formula

Clusters of t-J Model + Exact diagonalization: all states all matrix elements.



Data from paper with Mike Peterson and Jan Haerter Phs Rev 2007

$Na_{\{.68\}}$ Co O_2

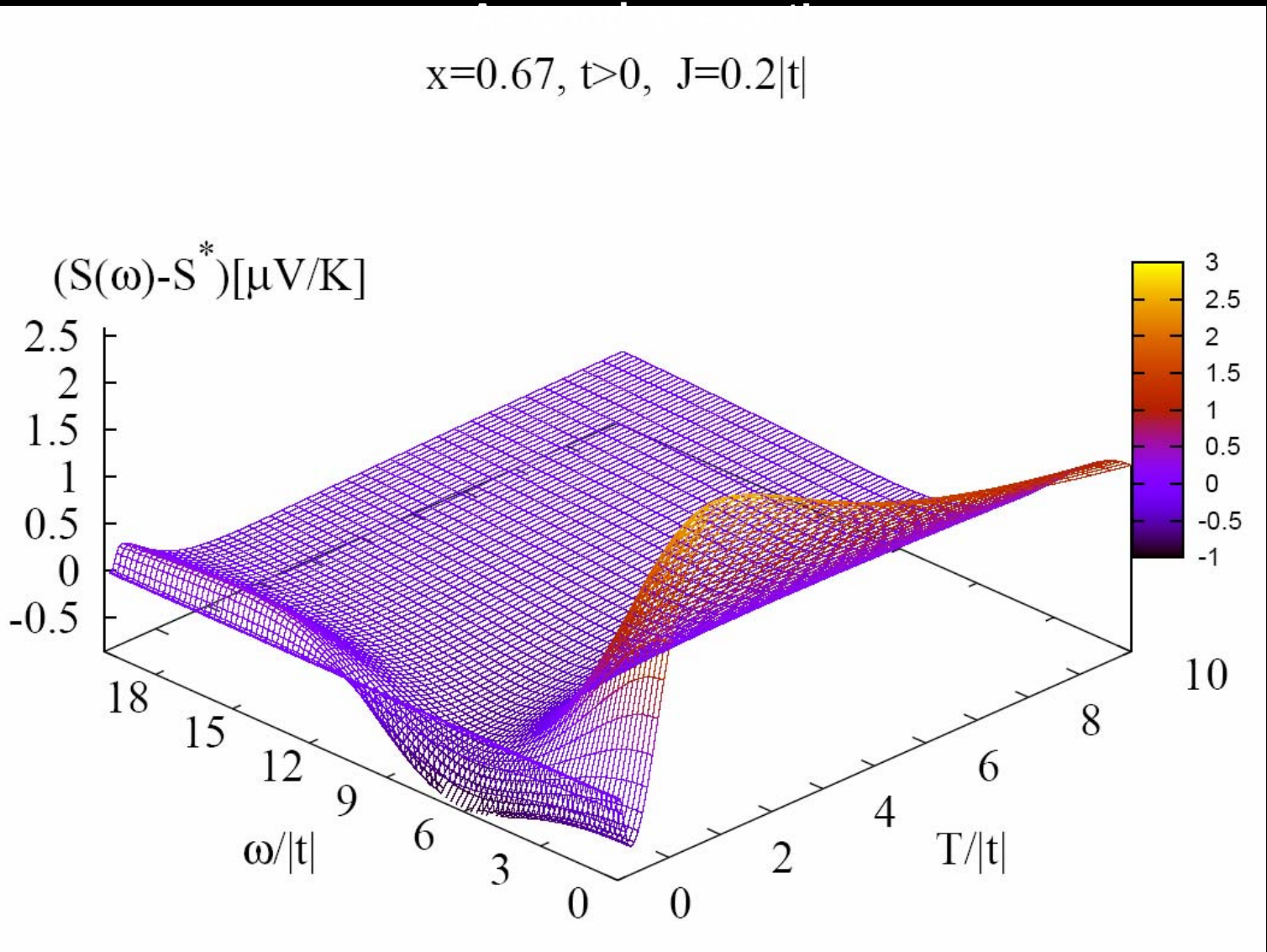
Modeled by t-J model with only two parameters "t=100K" and "J=36K". Interested in Curie Weiss phase. Photoemission gives scale of "t" as does Hall constant slope of R_H and a host of other objects.

REMARK: Low value of t is taken from Photoemission of Zahid Hasan et al (Princeton). This is crucially and surprisingly smaller than LDA by factor of 10!!

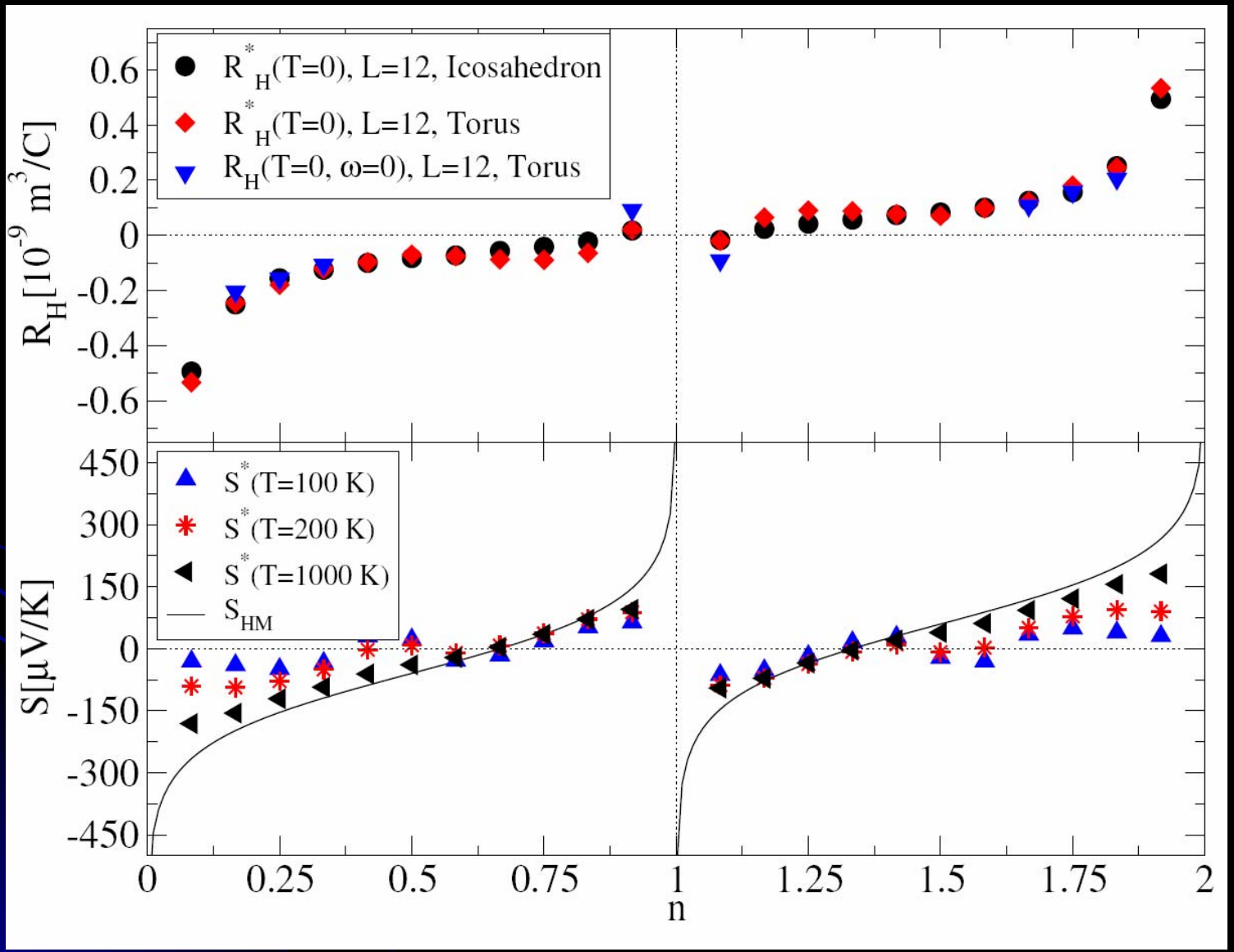
One favourite cluster is the platonic solid Icosahedron with 12 sites made up of triangles. Also pbc's with torii. Sizes upto 15 sites.

How good is the S* formula compared to exact Kubo formula?

A numerical benchmark: Max deviation 3% anywhere !!



Notice that these variables change sign thrice as a band fills from 0->2. Sign of Mott Hubbard correlations.



Results from this formalism:

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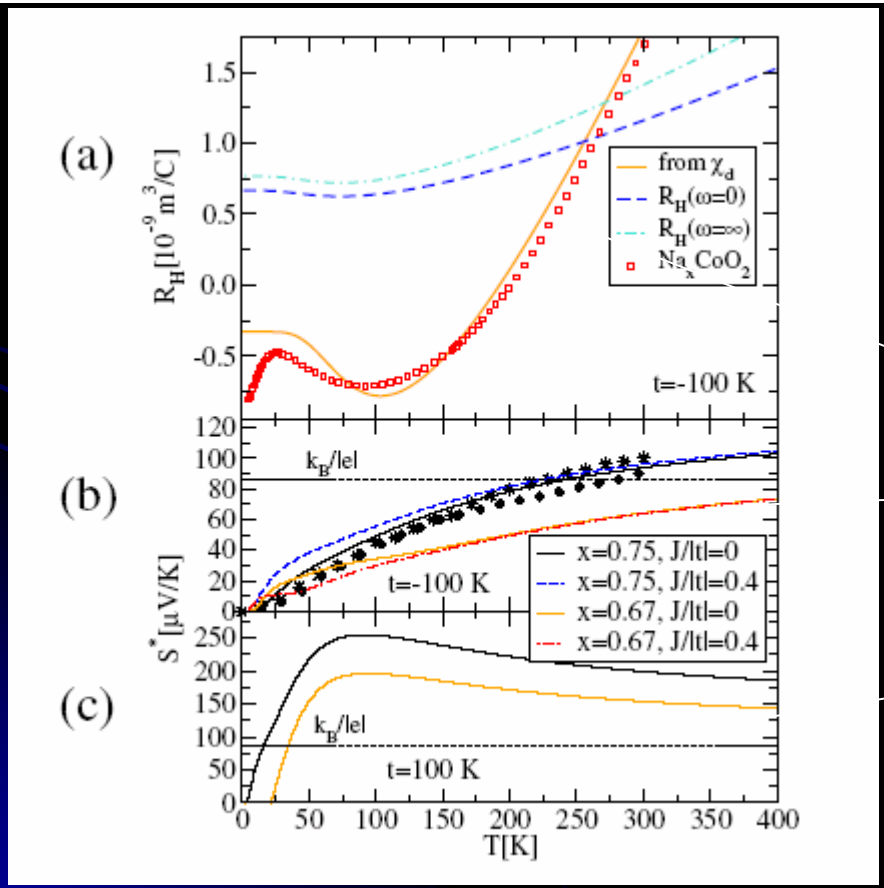
Strong Correlations Produce the Curie-Weiss Phase of Na_xCoO_2

Jan O. Haerter, Michael R. Peterson, and B. Sriram Shastry
Physics Department, University of California, Santa Cruz, California 95064, USA
(Received 21 July 2006; published 28 November 2006)



T linear Hall constant for triangular lattice predicted in 1993 by Shastry Shraiman Singh! Quantitative agreement hard to get with scale of "t"

Comparision with data on absolute scale!

Prediction for t>0 material

The various formulas

$$S_{Heikes-Mott} = \frac{\mu(0)-\mu(T)}{q_e T}$$

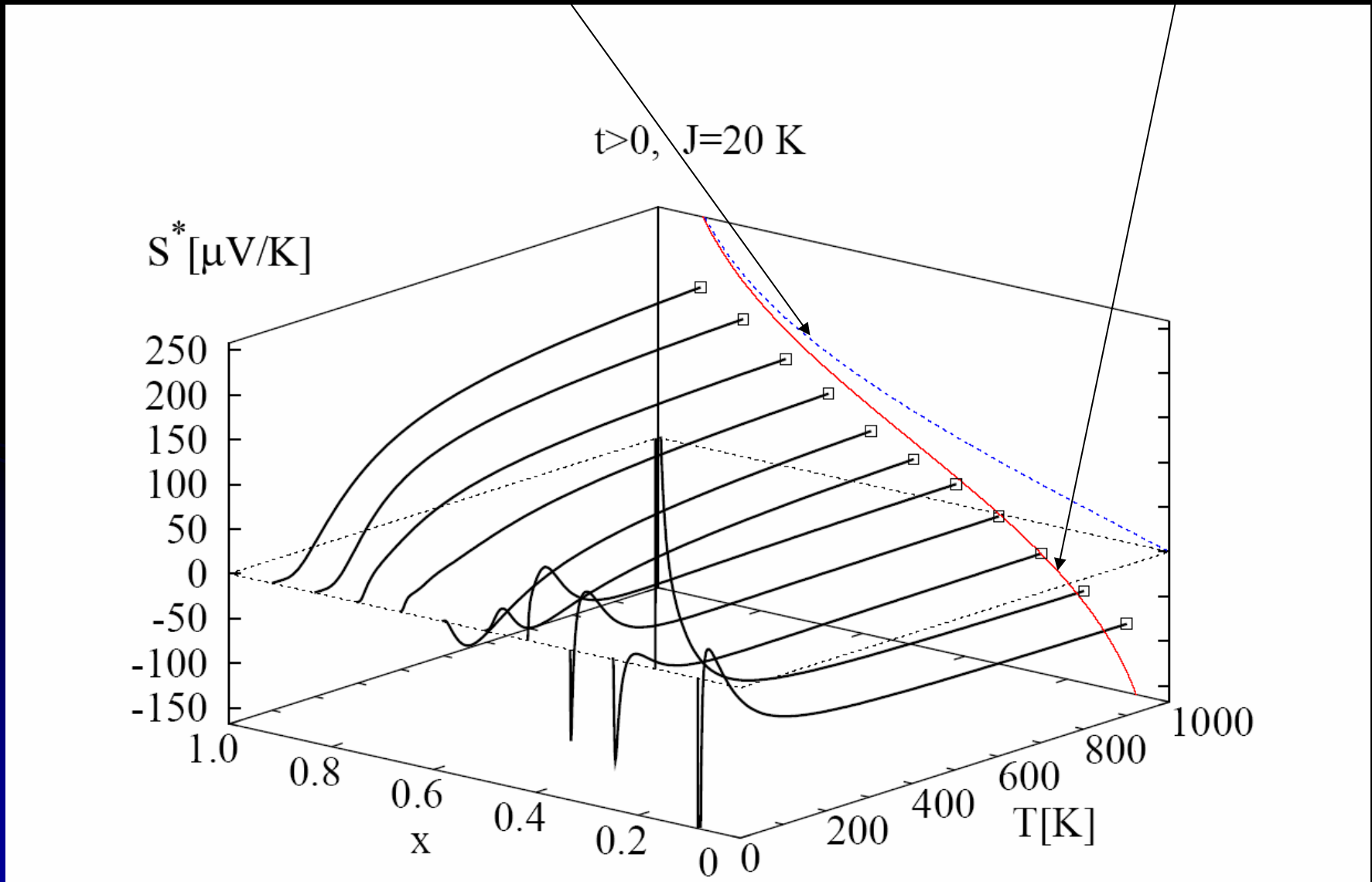
Throws out " transport part" and keeps only a thermodynamic contribution.

$$S^* = \frac{\langle \Phi^{xx} \rangle}{T \langle \tau^{xx} \rangle} - \frac{\mu(T)}{q_e T}$$

"Transport part"

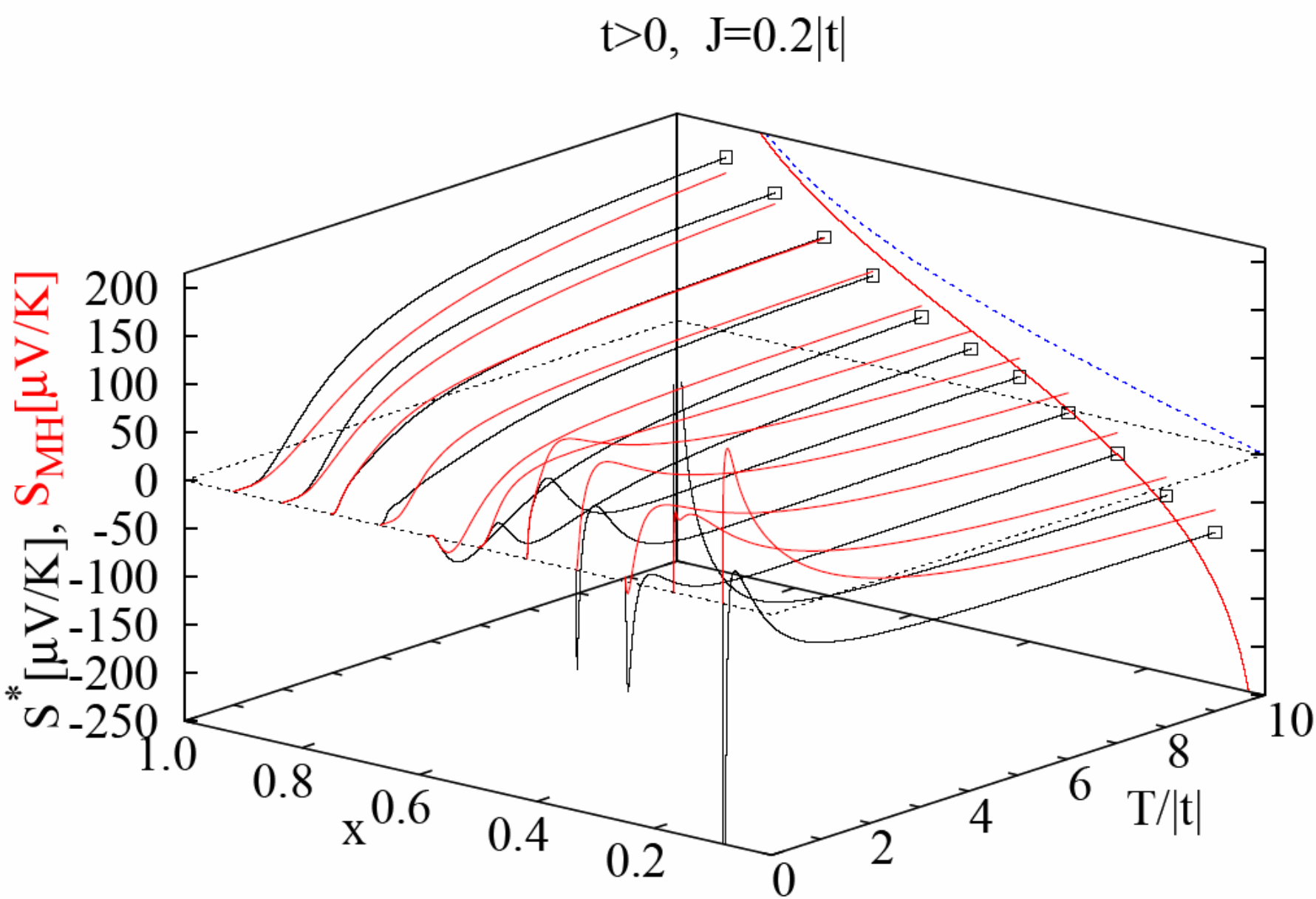
$$S_{Kubo} = \frac{\langle\langle J^E(t) J(0) \rangle\rangle}{\langle\langle J(t) J(0) \rangle\rangle} - \frac{\mu(T)}{q_e T}$$

Typical results for S* for NCO type case. Low T problems due to finite sized clusters. The blue line is for uncorrelated band, and red line is for t-J model at High T analytically known.

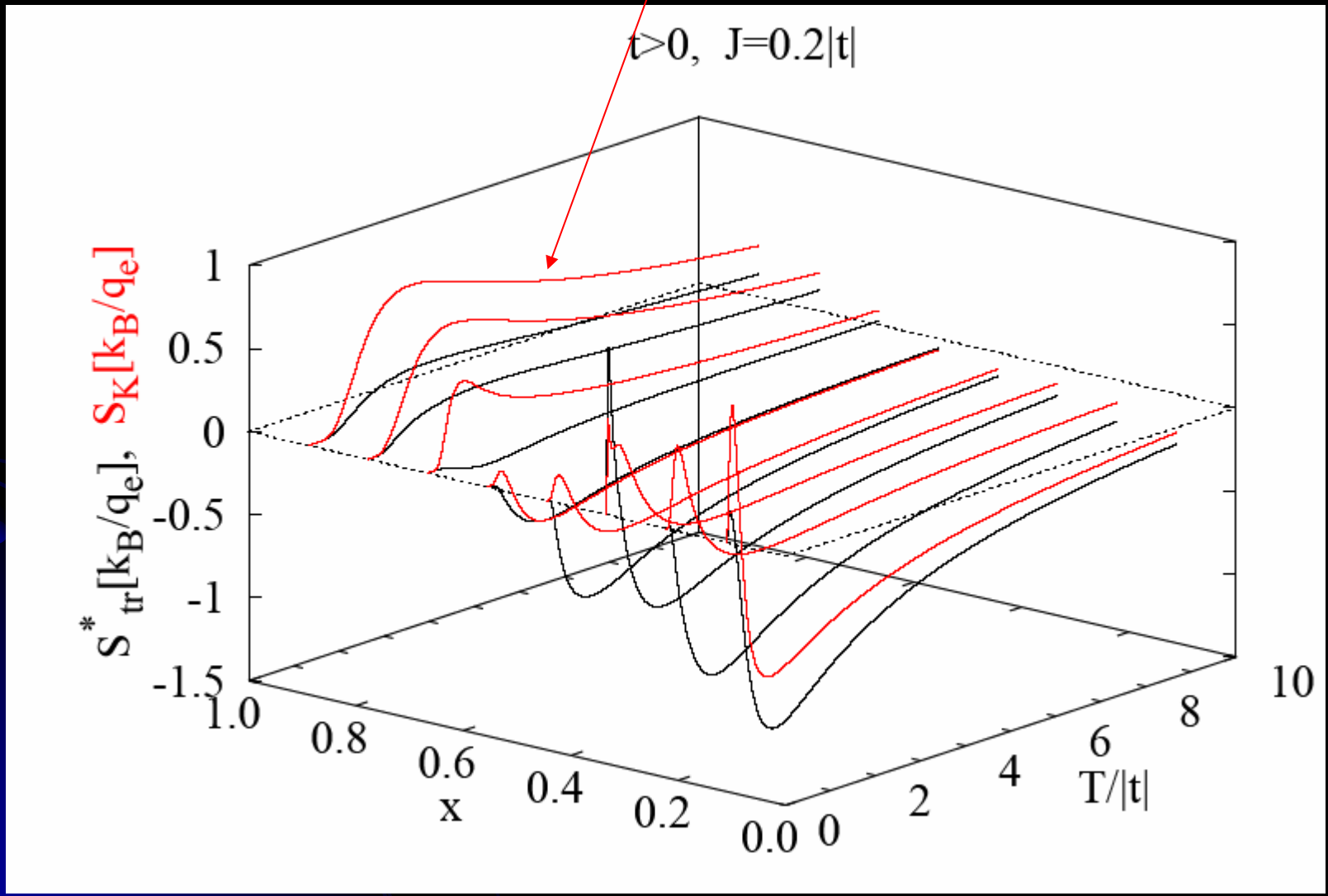


S* and the Heikes Mott formula (red) for Na_xCo O2.

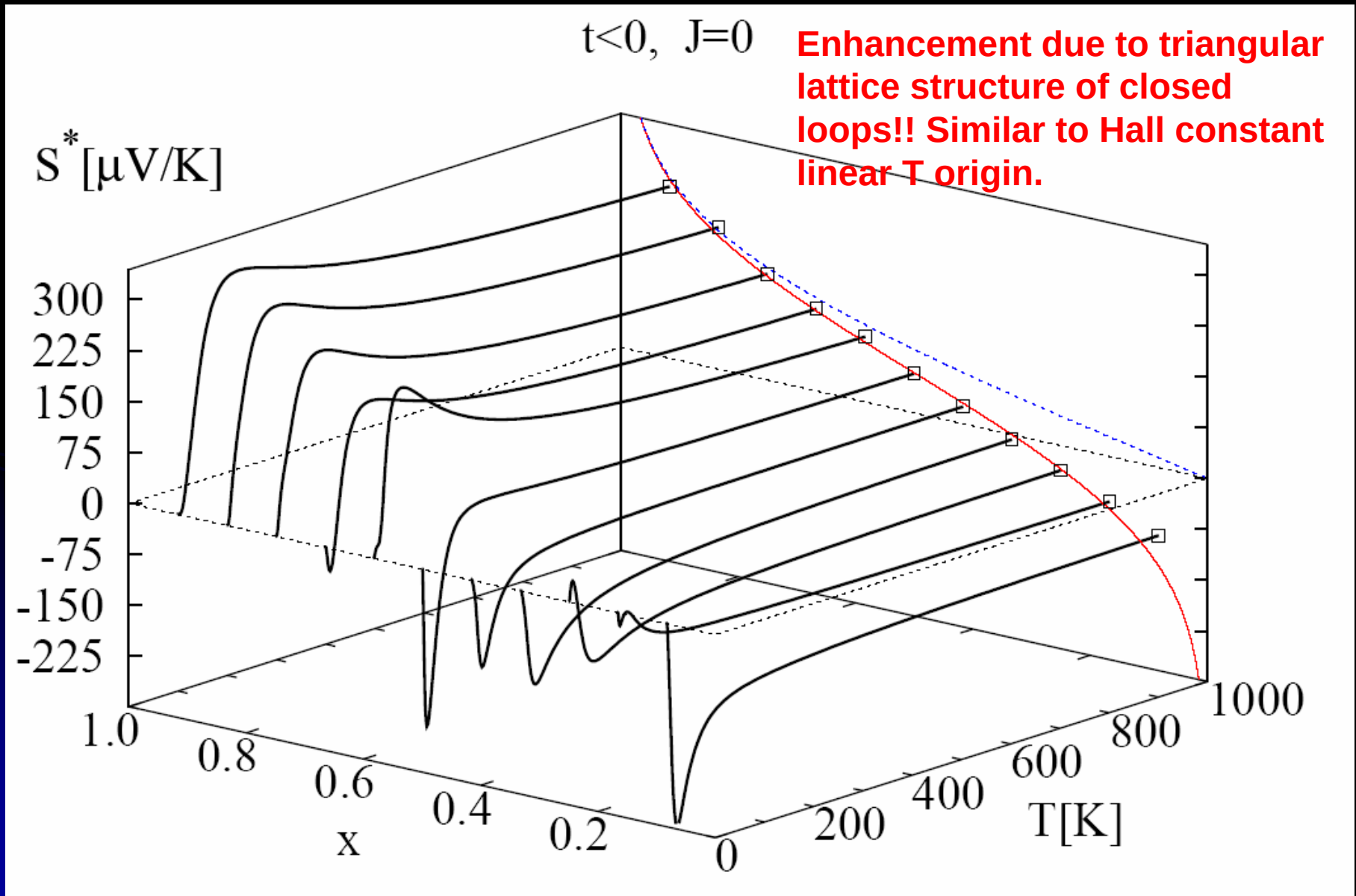
Close to each other for t>o i.e. electron doped cases



Kelvin Inspired formula is somewhat off from S* (and hence S) but right trends. In this case the Heikes Mott formula dominates so the final discrepancy is small.



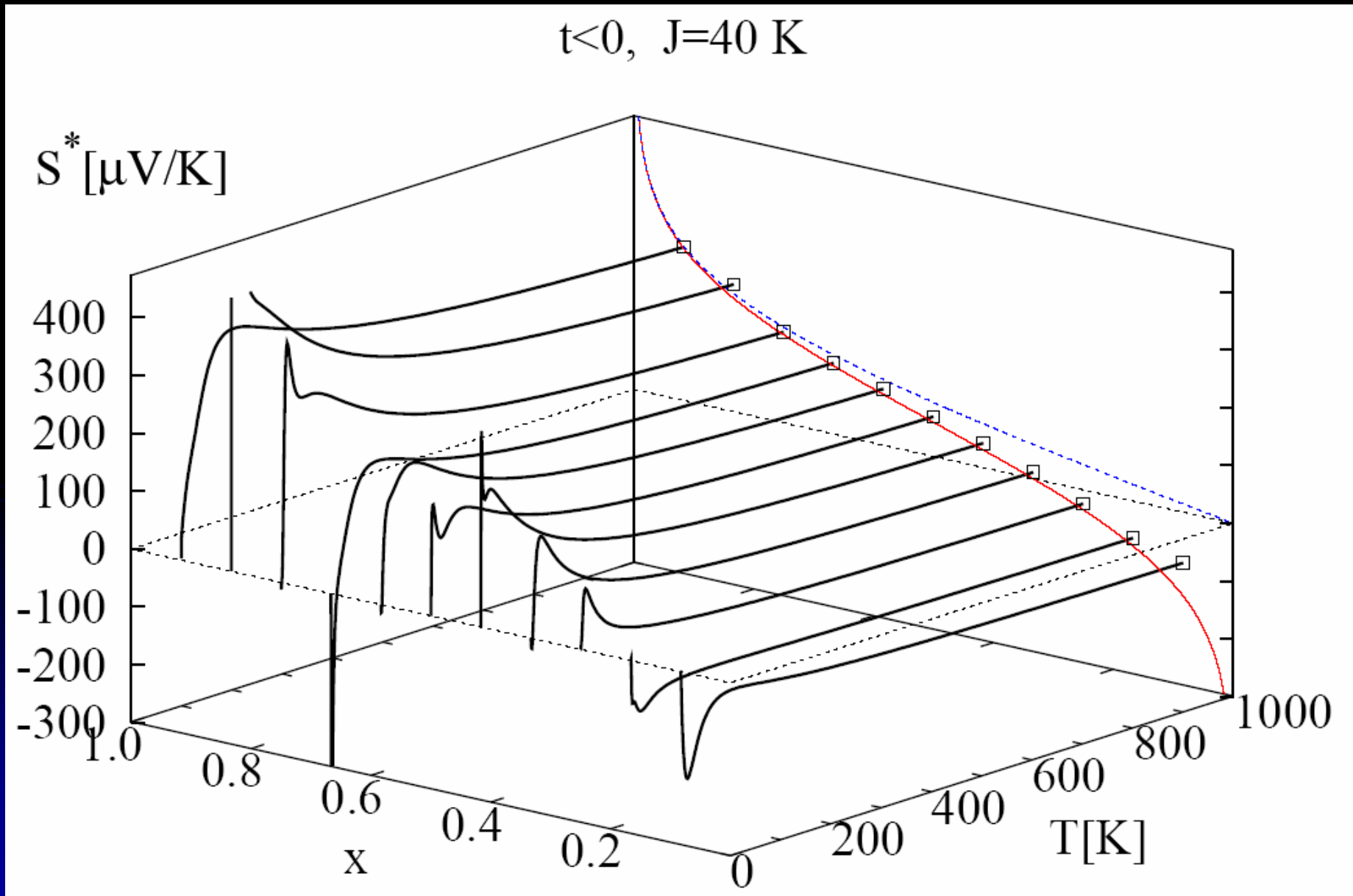
Predicted result for t<0 i.e. fiducary hole doped CoO_2 planes. Notice much larger scale of S* arising from transport part (not Mott Heikes part!!).



Enhancement due to triangular lattice structure of closed loops!! Similar to Hall constant linear T origin.

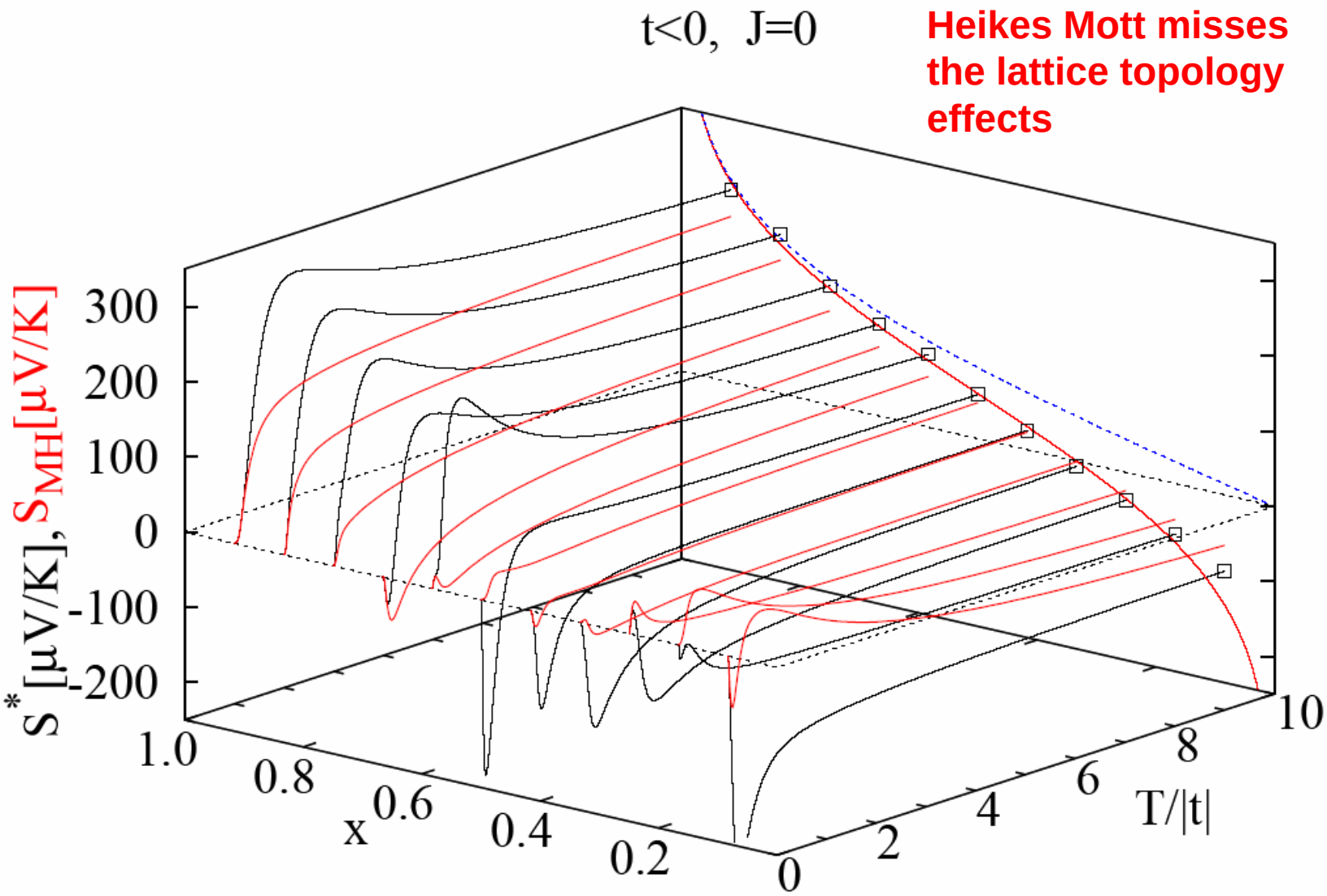
Predicted result for t<0 i.e. fiducary hole doped CoO_2 planes.

Different J higher S.



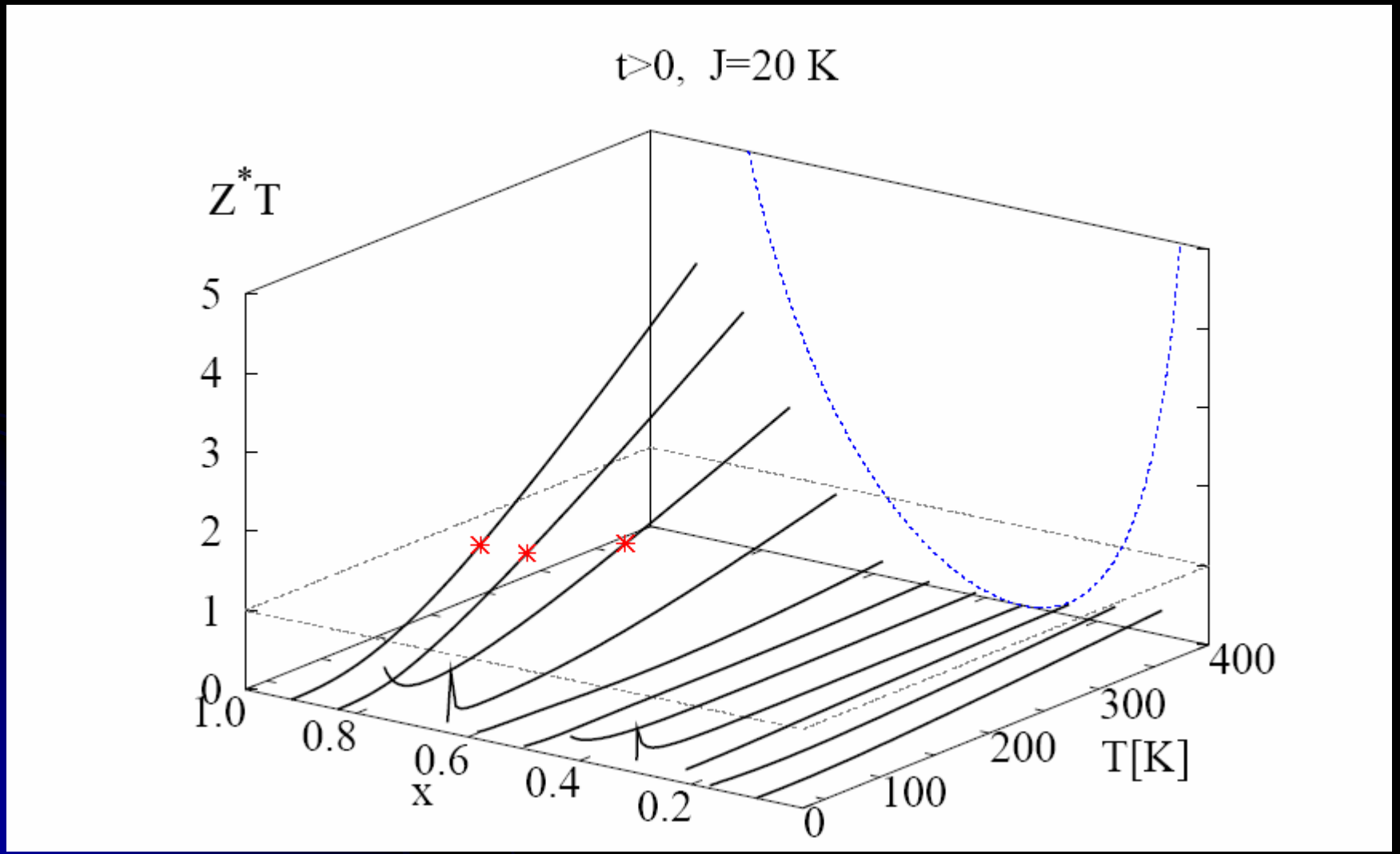
Predictions of S* and the Heikes Mott formula (red) for fiducary hole doped CoO2.

Notice that S* predicts an important enhancement unlike Heikes Mott formula



Z*T computed from S* and Lorentz number. Electronic contribution only, no phonons. Clearly large x is better!!

Quite encouraging.



Phenomenological eqns for coupled charge heat transport

- Meaning of the new operators becomes clear.
- Some interesting experiments using laser heating are suggested.

$$\left[\frac{1}{\tau}+\frac{d}{dt}\right]\langle \hat{J}_x^Q(\vec{r},t)\rangle = -\frac{D_Q}{\tau}\nabla\langle K(\vec{r}t)\rangle - \frac{c_1}{\tau}\nabla\langle \rho(\vec{r}t)\rangle - \left\{\frac{\langle \Theta^{xx}\rangle_0}{\Omega}\nabla\psi(\vec{r}t)+\frac{\langle \Phi^{xx}\rangle_0}{\Omega}\nabla\phi(\vec{r}t)\right\}$$

and

$$\left[\frac{1}{\tau}+\frac{d}{dt}\right]\langle \hat{J}_x(\vec{r},t)\rangle = -\frac{c_2}{\tau}\nabla\langle K(\vec{r}t)\rangle - \frac{D_c}{\tau}\nabla\langle \rho(\vec{r}t)\rangle - \left\{\frac{\langle \tau^{xx}\rangle_0}{\Omega}\nabla\phi(\vec{r}t)+\frac{\langle \Phi^{xx}\rangle_0}{\Omega}\nabla\psi(\vec{r}t)\right\}$$

Hydrodynamics of energy and charge transport in a band model:

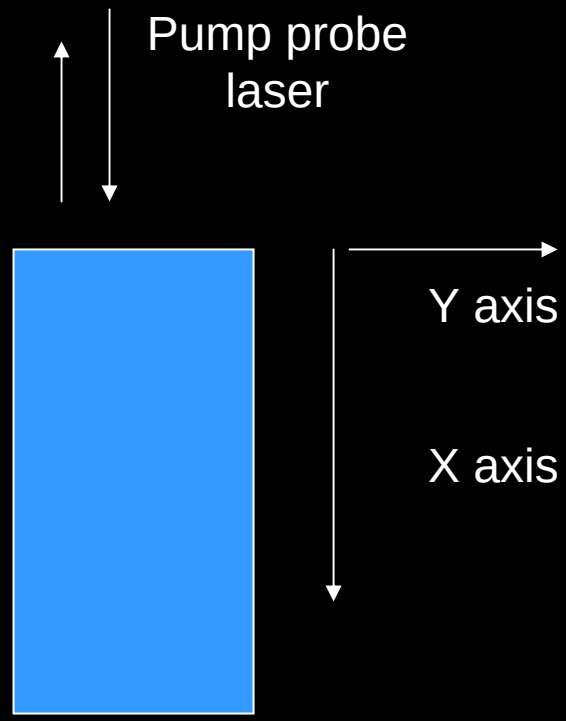
This involves the fundamental operators in a crucial way:

Continuity

$$\frac{\partial \rho}{\partial t} + \nabla J(r) = 0$$

$$\frac{\partial K(r)}{\partial t} + \nabla J^{Q}(r) = p_0 \delta(x)$$

Input power density



These eqns contain energy and charge diffusion, as well as thermoelectric effects. Potentially correct starting point for many new nano heating expts with lasers. Work in progress. Preprint soon

The inertial terms contribute for initial rise of the energy and heat current.

Exact coupling term term

$$\left\{ \frac{\partial}{\partial t} + \frac{1}{\tau_E} \right\} \delta J^Q(r) = -\frac{1}{\Omega} \langle \Theta^{xx} \rangle \left[\nabla \Psi \right] + \text{rest}$$

Hence a δ(t) heat pulse gives an initial jump in current that is a **measure of the sum rule**.

Also energy density responds inertially initially. Initial response to pulses of heat and charge are a good measure of these coefficients.

Conclusions

- Hole doping prediction of large S
- Low bandwidth in NCO is the big factor leading to enhanced S (not orbital degeneracy).
- Dynamical heating experiments can address interesting and fundamental questions “what is energy and what is temperature”.