Theory of thermoelectric effects in strongly correlated systems

Sriram Shastry

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Collaborators:

Mike Peterson, Jan Haerter,

UCSC, Santa Cruz, CA

Subroto Mukerjee

UC Berkeley

1. [arXiv:0706.1058]
   Title: Dynamical thermal response functions for strongly correlated one-dimensional systems
   Authors: Michael R. Peterson, Subroto Mukerjee, B. Sriram Shastry, Jan O. Haerter

2. arXiv:0705.3867
   Title: Thermoelectric effects in a strongly correlated model for Na$_x$CoO$_2$
   Authors: Michael R. Peterson, B. Sriram Shastry, Jan O. Haerter

3. arXiv:cond-mat/0608005
Title: Finite temperature properties of the triangular lattice t-J model, applications to Na$_x$CoO$_2$
Authors: Jan O. Haerter, Michael R. Peterson, B. Sriram Shastry
Phys. Rev. B 74, 245118 (2006)

4. arXiv:cond-mat/0607293
   Title: Strong Correlations Produce the Curie-Weiss Phase of Na$_{x}$CoO$_2$
   Authors: Jan O. Haerter, Michael R. Peterson, B. Sriram Shastry
   Phys. Rev. Lett. 97, 226402 (2006)

5. arXiv:cond-mat/0508711
   Title: A Sum Rule for Thermal Conductivity and Dynamical Thermal Transport Coefficients in Condensed Matter -I
   Authors: B Sriram Shastry
   Phy. Rev. B 73, 085117 (2006)

Plan of the talk

- Brief motivation: Heavy fermi systems and Mott Hubbard systems
    - The curious case of the Curie Weiss Metal
- New theoretical formalism based on ``high frequency approach''
    - Insight from Hall constant (SSS 1994)
    - Sum rule for thermal conductivity and thermopower. 2006
    - Kelvin's formulas versus Onsager Kubo and high frequency
- Hall constant in high Tc and on triangular lattice.
- Thermopower in 2-d models for describing sodium cobaltate.
- New insights and predictions for frustrated lattices with correlations.

Heavy Fermi systems $CeCoIn_5$

Mott Hubbard system NaxCoO2 (sodium cobaltate)

Terasaki:

Highest value of thermopower for a good metal for x~.68 and also Figure of Merit promising

Ong-Cava: Curie Weiss metal phase of NCO at x~.68

Where local moment type magnetic susceptibility coexists with good metallicity, B sensitive Thermopower….very anamolous.

Superconductivity on hydration is a bonus, but value of doping is a vexed issue.

Important NMR work of H Alloul shows that a mixed valence exists for large x, hence one should be cautious about sweeping claims.

We aim at concrete calculations of thermopower, Hall constant and figure of merit for correlated single band metal. (Mott Hubbard). This is a very difficult problem and has never been tackled for all ranges of parameters. Qualitative insights are also unavailable..

First serious effort to understand Hall constant in correlated matter:

S S, Boris Shraiman and Rajeev Singh, Phys Rev Letts (1993)

Introduced object

$$R_H^* = \lim_{B\to 0} \lim_{\omega\to\infty} \rho_{xy}(\omega)/ B$$

- **Easier to calculate than transport Hall constant**
- **Captures Mott Hubbard physics to large extent**

Motivation: **Drude theory** has

$$\sigma_{xy}(\omega) = \sigma_{xy}(0)/(1+i\omega\tau)^2$$

$$\sigma_{xx}(\omega) = \sigma_{xx}(0)/(1+i\omega\tau)$$

Hence **relaxation time cancels out in the Hall resistivity**

$$\rho_{xy}(\omega) = \frac{\sigma_{xy}}{(\sigma_{xx})^2}$$

$$\tau^{xx} = \frac{q_e^2}{\hbar} \sum \eta_x^2 \; t(\vec{\eta}) \; c^\dagger_{\vec{r}+\vec{\eta},\sigma} c_{\vec{r},\sigma}$$

$$\sigma^{\alpha,\beta}(\omega_c) = \frac{i}{\hbar N_s v \omega_c} \left[\langle \tau^{\alpha,\beta} \rangle - \hbar \sum_{n,m} \frac{p_n - p_m}{\epsilon_n - \epsilon_m + \hbar\omega_c} \langle n|\hat{J}_\alpha|m\rangle \langle m|\hat{J}_\beta|n\rangle \right]$$

$$[\rho^{x,y}(\omega)]_{Lim_{\omega\to\infty}} \to constant$$

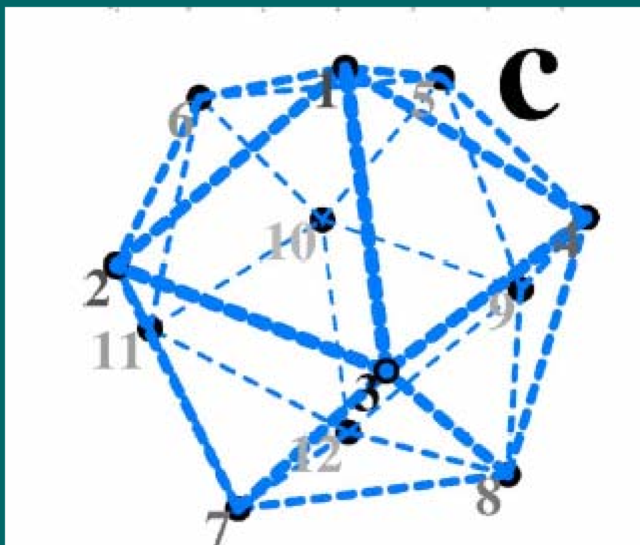
$$\mathrm{R}_H^* = \frac{-iN_s v}{B\hbar}\frac{\langle[J^x, J^y]\rangle}{\langle\tau^{xx}\rangle^2}$$

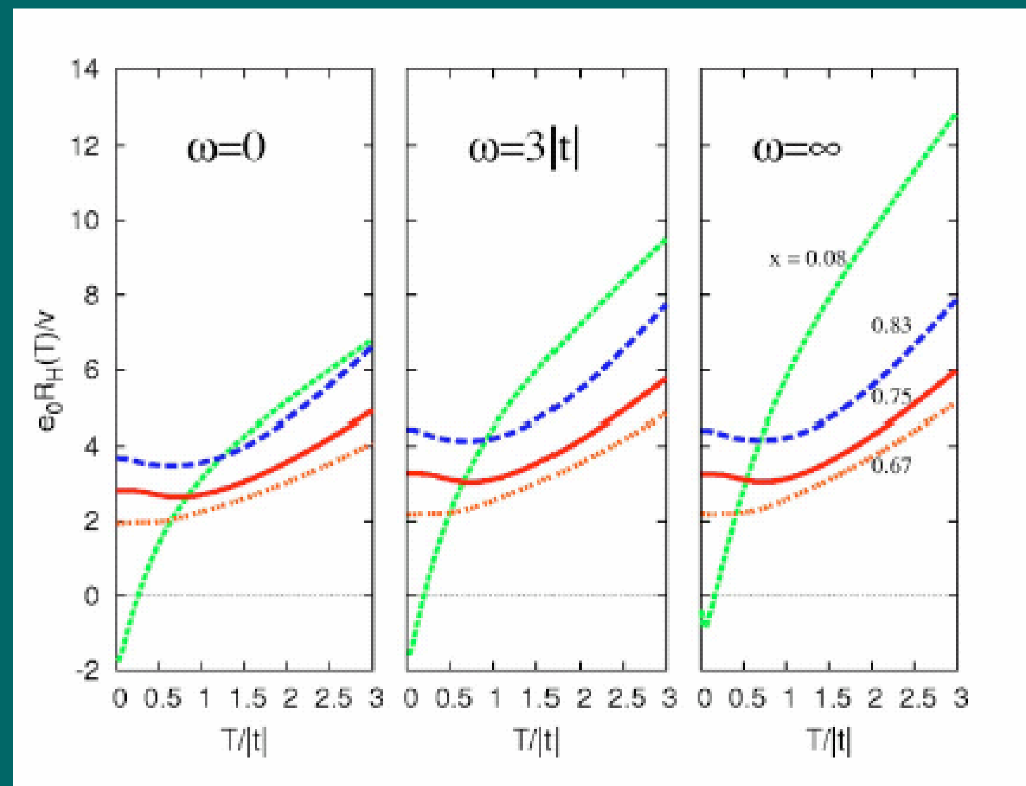
- •Very useful formula since
  - •Captures Lower Hubbard Band physics. This is achieved by using the Gutzwiller projected fermi operators in defining J's
  - •Exact in the limit of simple dynamics (e.g few frequencies involved), as in the Boltzmann eqn approach.
  - •Can compute in various ways for all 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, not too useful for Hubbard model.
  - •This asymptotic formula usually requires ω to be larger than J
  - •BENCHMARKING needed….

PHYSICAL REVIEW B **74**, 245118 (2006)

Finite-temperature properties of the triangular lattice *t-J* model and applications to Na_xCoO_2

Jan O. Haerter, Michael R. Peterson, and B. Sriram Shastry





Exact numerical computation for clusters shows frequency dep is small, of O 15% in all cases except well understood exceptions

Use same guiding principle for thermoelectric phenomena:

Seek combinations of peltier coefficient, electrical and thermal conductivity such that relaxation time t cancels out. For these cases, the Kubo formulas can be pushed to high frequencies to give meaningful information..

Turns out that there are three different objects that are analogous to the Hall constant.

- Seebeck coefficient (Peltier/conductivity)
- Lorentz number (thermal cond/electrical cond)
- Figure of merit (S^2/Lorentz)

Therefore we need exact Kubo type formulas giving frequency dependent Peltier constant, electrical and thermal conductivity.

Surprisingly: Only electrical conductivity is known in literature, not other two!!!

One finds that:

$$\kappa(\omega_c) = \frac{i}{\hbar\omega_c T}\frac{1}{\mathcal{L}}\left[\langle\Theta^{xx}\rangle - i\int_0^\infty e^{i\omega_c t'}\,dt' < [\hat{J}_x^Q(t'),\hat{J}_x^Q(0)] >\right].$$

Here we commute the Heat current with the energy density to get the thermal operator

$$\Theta^{xx} = -\lim_{k_x\to 0}\frac{d}{dk_x}[\hat{J}_x^Q(k_x),\hat{K}(-k_x)]$$

The sum rule for the real part of the thermal conductivity (an even function of ω) follows

$$\int_0^\infty Re\;\kappa(\omega)d\omega = \frac{\pi}{2\hbar T\mathcal{L}}\langle\Theta^{xx}\rangle. \tag{1}$$

Comment: New sum rule.

Not known before in literature.

Electrical conductivity is well known:

$$\sigma(\omega_c) = \frac{i}{\hbar\omega_c}\frac{1}{\mathcal{L}}\left[\langle\tau^{xx}\rangle - i\int_0^\infty e^{i\omega_c t'}\ dt'\langle[\hat{J}_x(t'), \hat{J}_x(0)]\rangle\right].$$

Hence at high frequency we see that:

$$\begin{aligned}
\kappa &\sim ic\langle\Theta^{xx}\rangle/\omega \\
\sigma &\sim ic\langle\tau^{xx}\rangle/\omega \\
Ratio &\sim \frac{\langle\Theta^{xx}\rangle}{\langle\tau^{xx}\rangle}
\end{aligned}$$

Thermo-power follows similar logic:

$$< \hat{J}_x >= \sigma(\omega) E_x + \gamma(\omega)(-\nabla T)$$

then the thermopower is

$$S(\omega) = \frac{\gamma(\omega)}{\sigma(\omega)}.$$

$$\Phi^{xx} = -\lim_{k \to 0} \frac{d}{dk_x} [\hat{J}_x(k_x), K(-k_x)].$$

This is the thermo electric operator

$$\gamma(\omega) = \frac{i}{\hbar \omega_c T \mathcal{L}} \left[< \Phi^{xx} > -\hbar \sum_{n,m} \frac{p_n - p_m}{\epsilon_n - \epsilon_m + \hbar \omega_c} \langle n | \hat{J}_x | m \rangle \langle n | \hat{J}_x^Q | m \rangle \right].$$

High frequency limits that are feasible and sensible similar to R*

$$\mathbf{L}^* = \frac{\langle \Theta^{xx} \rangle}{T^2 \langle \tau^{xx} \rangle} \tag{1}$$

$$\mathbf{Z}^* T = \frac{\langle \Phi^{xx} \rangle^2}{\langle \Theta^{xx} \rangle \langle \tau^{xx} \rangle}. \tag{2}$$

$$S^* = \frac{\langle \Phi^{xx} \rangle}{T \langle \tau^{xx} \rangle}. \tag{3}$$

Hence for any model system, armed with these three operators, we can compute the Lorentz ratio, the thermopower and the thermoelectric figure of merit!

So we naturally ask

- what do these operators look like
- how can we compute them
- how good an approximation is this?

In the paper: several models worked out in detail

- Lattice dynamics with non linear disordered lattice
- Hubbard model
- Inhomogenous electron gas
- Disordered electron systems
- Infinite U Hubbard bands

- Lots of detailed formulas: we will see a small sample for Hubbard model and see some tests...

Thermo power operator for Hubbard model

$$\Phi^{xx} = -\frac{q_e}{2}\sum_{\vec{\eta},\vec{\eta'},\vec{r}}(\eta_x+\eta'_x)^2 t(\vec{\eta})t(\vec{\eta'})c^\dagger_{\vec{r}+\vec{\eta}+\vec{\eta'},\sigma}c_{\vec{r},\sigma} - q_e\mu\sum_{\vec{\eta}}\eta_x^2 t(\vec{\eta})c^\dagger_{\vec{r}+\vec{\eta},\sigma}c_{\vec{r},\sigma} + \frac{q_eU}{4}\sum_{\vec{r},\vec{\eta}}t(\vec{\eta})(\eta_x)^2(n_{\vec{r},\bar{\sigma}}+n_{\vec{r}+\vec{\eta},\bar{\sigma}})(c^\dagger_{\vec{r}+\vec{\eta},\sigma}c_{\vec{r},\sigma}+c^\dagger_{\vec{r},\sigma}c_{\vec{r}+\vec{\eta},\sigma}). \tag{1}$$

This object can be expressed completely in Fourier space as

$$\Phi^{xx} = q_e\sum_{\vec{p}}\frac{\partial}{\partial p_x}\left\{v_p^x(\varepsilon_{\vec{p}}-\mu)\right\}c^\dagger_{\vec{p},\sigma}c_{\vec{p},\sigma} \tag{2}$$

$$+\frac{q_eU}{2\mathcal{L}}\sum_{\vec{l},\vec{p},\vec{q},\sigma,\sigma'}\frac{\partial^2}{\partial l_x^2}\left\{\varepsilon_{\vec{l}}+\varepsilon_{\vec{l}+\vec{q}}\right\}c^\dagger_{\vec{l}+\vec{q},\sigma}c_{\vec{l},\sigma}c^\dagger_{\vec{p}-\vec{q},\bar{\sigma}'}c_{\vec{p},\bar{\sigma}'}. \tag{3}$$

$$\tau^{xx} = \frac{q_e^2}{\hbar}\sum\eta_x^2\,t(\vec{\eta})\,c^\dagger_{\vec{r}+\vec{\eta},\sigma}c_{\vec{r},\sigma}\quad\text{or} \tag{1}$$

$$= \frac{q_e^2}{\hbar}\sum_{\vec{k}}\frac{d^2\varepsilon_{\vec{k}}}{dk_x^2}c^\dagger_{\vec{k},\sigma}c_{\vec{k},\sigma} \tag{2}$$

Free Electron Limit and Comparison with the Boltzmann Theory

It is easy to evaluate the various operators in the limit of $U \to 0$, and this exercise enables us to get a feel for the meaning of these various somewhat formal objects. We note that

$$\begin{aligned} \langle \tau^{xx} \rangle &= \frac{2q_e^2}{\mathcal{L}} \sum_p n_{\vec{p}} \, \frac{d}{dp_x} \left[v_{\vec{p}}^x \right] \\ \langle \Theta^{xx} \rangle &= \frac{2}{\mathcal{L}} \sum_p n_{\vec{p}} \, \frac{d}{dp_x} \left[v_{\vec{p}}^x (\varepsilon_{\vec{p}} - \mu)^2 \right] \\ \langle \Phi^{xx} \rangle &= \frac{2q_e}{\mathcal{L}} \sum_p n_{\vec{p}} \, \frac{d}{dp_x} \left[v_{\vec{p}}^x (\varepsilon_{\vec{p}} - \mu) \right] . \end{aligned} \tag{1}$$

At low temperatures, we use the Sommerfield formula after integrating by parts, and thus obtain the leading low T behaviour:

$$\langle \tau^{xx} \rangle = 2q_e^2 \rho_0(\mu) \langle (v_{\vec{p}}^x)^2 \rangle_\mu$$

$$\langle \Theta^{xx} \rangle = T^2 \frac{2\pi^2 k_B^2}{3} \rho_0(\mu) \langle (v_{\vec{p}}^x)^2 \rangle_\mu \tag{1}$$

$$\langle \Phi^{xx} \rangle = T^2 \frac{2q_e \pi^2 k_B^2}{3} \left[\rho_0'(\mu) \langle (v_{\vec{p}}^x)^2 \rangle_\mu + \rho_0(\mu) \frac{d}{d\mu} \langle (v_{\vec{p}}^x)^2 \rangle_\mu \right] , \tag{2}$$

We may form the high frequency ratios

$$
\begin{aligned}
S^* &= T\frac{\pi^2 k_B^2}{3q_e}\frac{d}{d\mu}\log\left[\rho_0(\mu)\langle (v_{\vec{p}}^x)^2\rangle_\mu\right] \\
L^* &= \frac{\pi^2 k_B^2}{3q_e^2}.
\end{aligned}
\tag{1}
$$

It is therefore clear that the high frequency result gives *the same* Lorentz number as well as the thermopower that the Boltzmann theory gives in its simplest form.

New Formalism:*

- •Settles the Kelvin- Onsager debate.
  - •Kelvin derived reciprocity between Peltier and Seebeck Coefficient using only thermodynamics,
  - •Onsager insisted that Dynamics is needed to establish reciprocity.
  - •According to Wannier's book on Statistical Physics "Opinions are divided on whether Kelvin's derivation is fundamentally correct or not".

*[1] Shastry, Phys. Rev. B 73, 085117 (2006)

*[2] Shastry, 43rd Karpacz (Poland) Winter School proceedings (2007)

For a weakly interacting diffusive metal, we can compute all three S's. Here is the result:

Velocity averaged over FS

Density Of States

Energy dependent relaxation time.

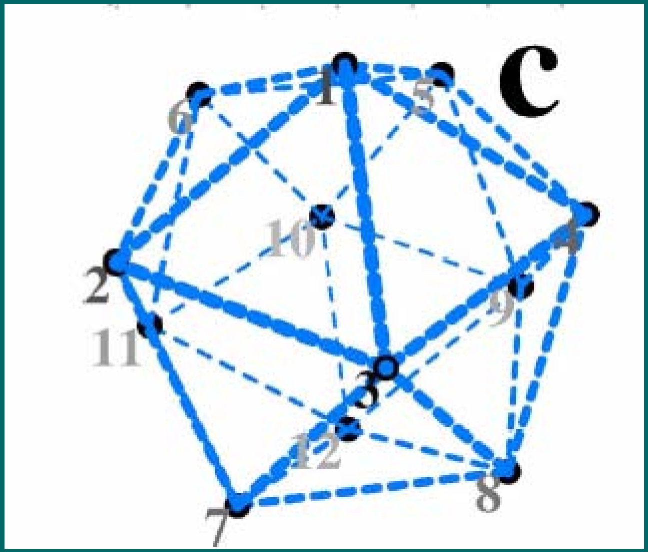
$$S = T\frac{\pi^2 k_B^2}{3q_e}\frac{d}{d\ \varepsilon}\ln[\rho(\varepsilon)\langle(v^x)^2\rangle_\varepsilon \tau(\varepsilon)]_{\varepsilon\to\mu} \text{ Onsager- Kubo-Mott formula}$$

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

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

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

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



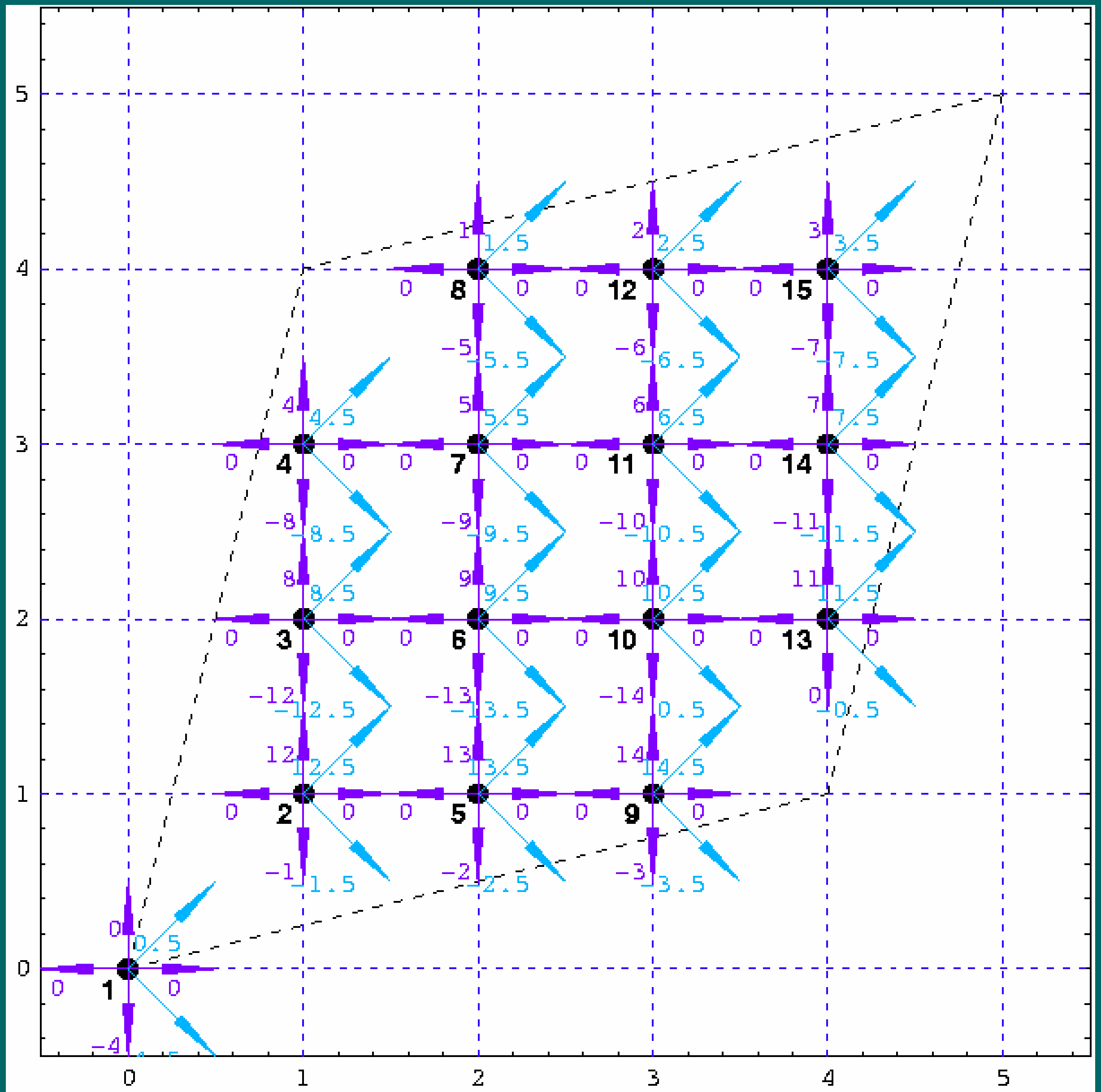
Data from preprint with Mike Peterson and Jan Haerter (in preparation)

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

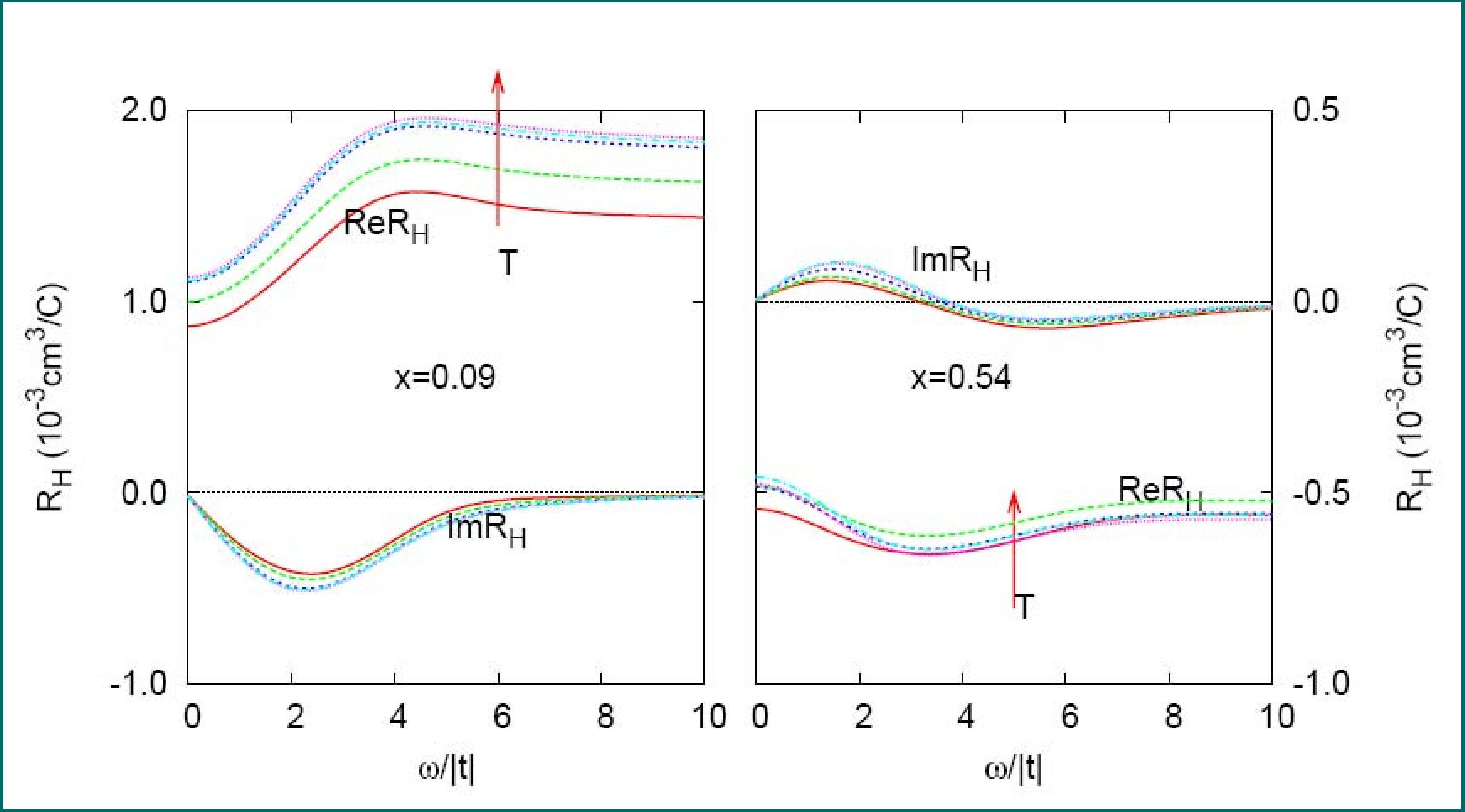
Modeled by t-J model with only two parameters “t=100K” and “J=36K”. Interested in Curie Weiss phase. Photoemission gives scale of “t” as does Hall constant slope of R_h and a host of other objects.

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

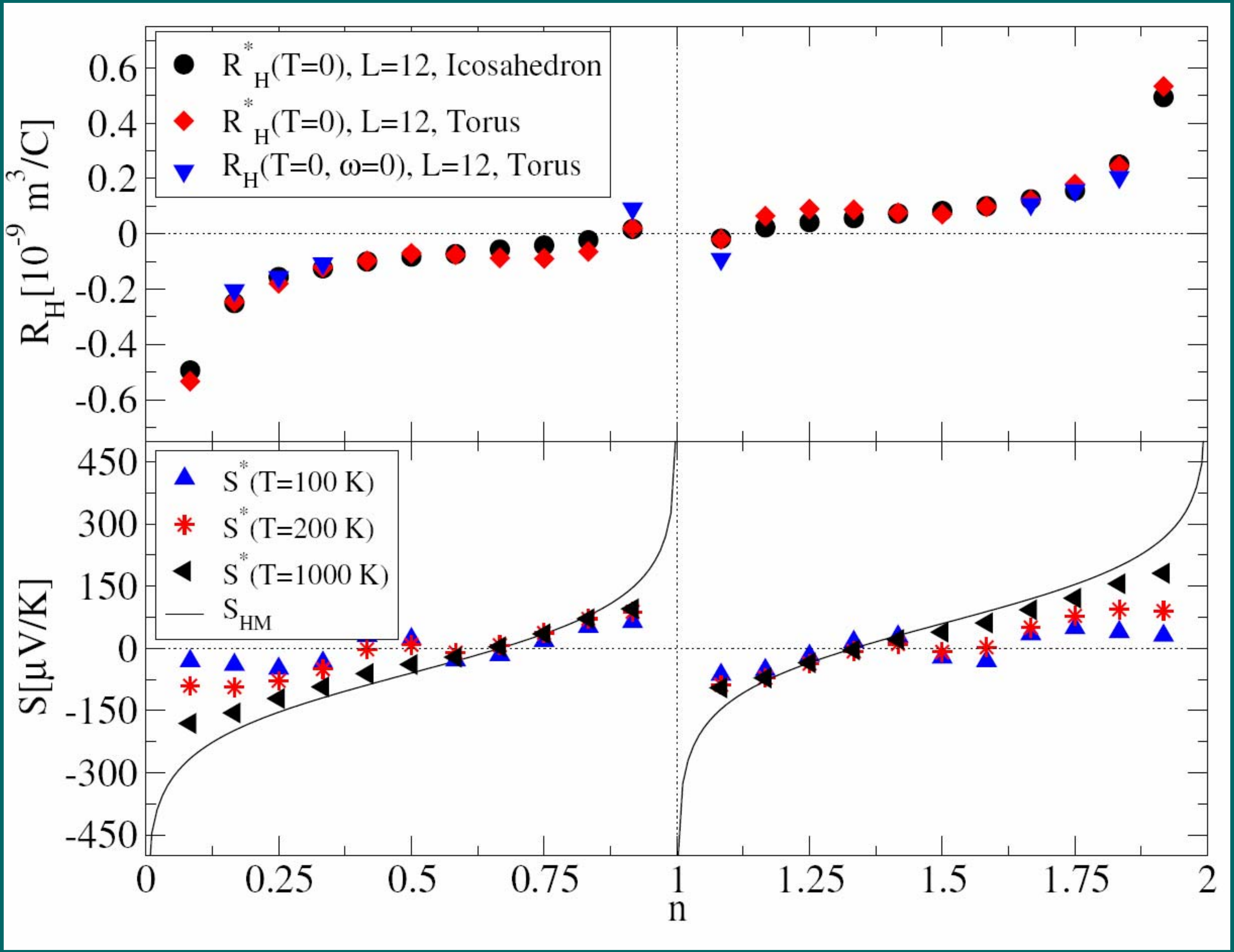
Square lattice 15 sites + pbcs with t-t'-J model



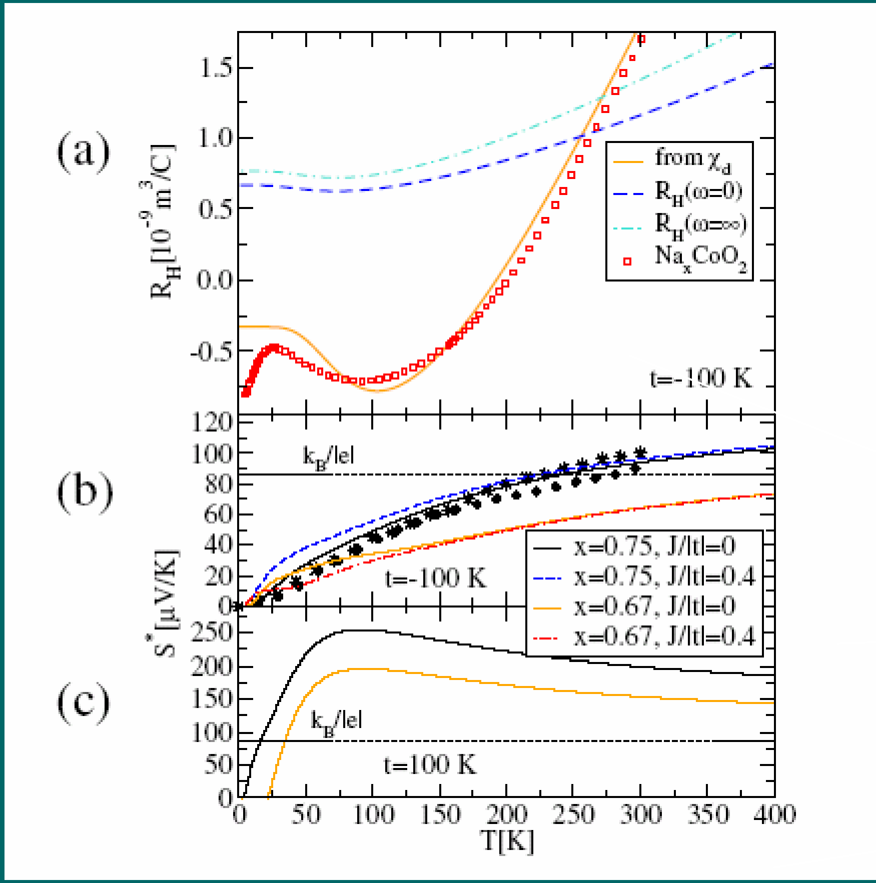
T-t'-J model, typical frequency dependence is very small . This is very encouraging for the program of x_eff

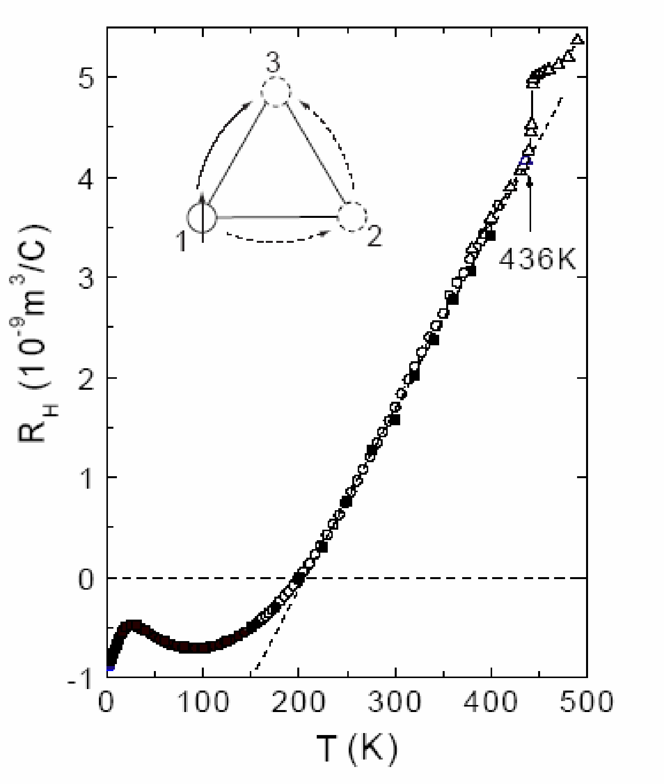


Notice that these variables change sign thrice as a band fills from 0->2. Sign of Mott Hubbard correlations.



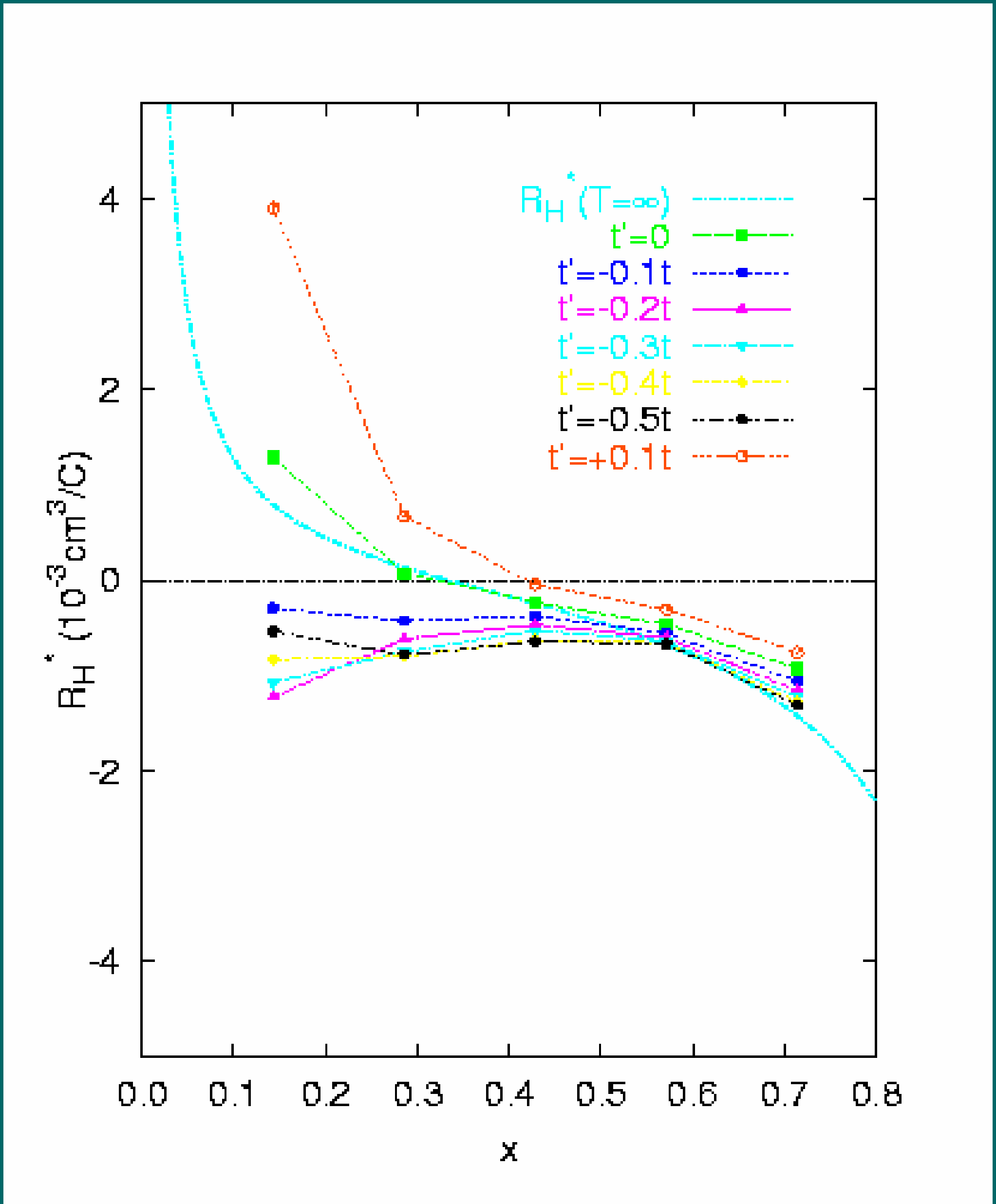
Results from this formalism:





Comparision with data on absolute scale!

Prediction for t>0 material



Preliminary computations:

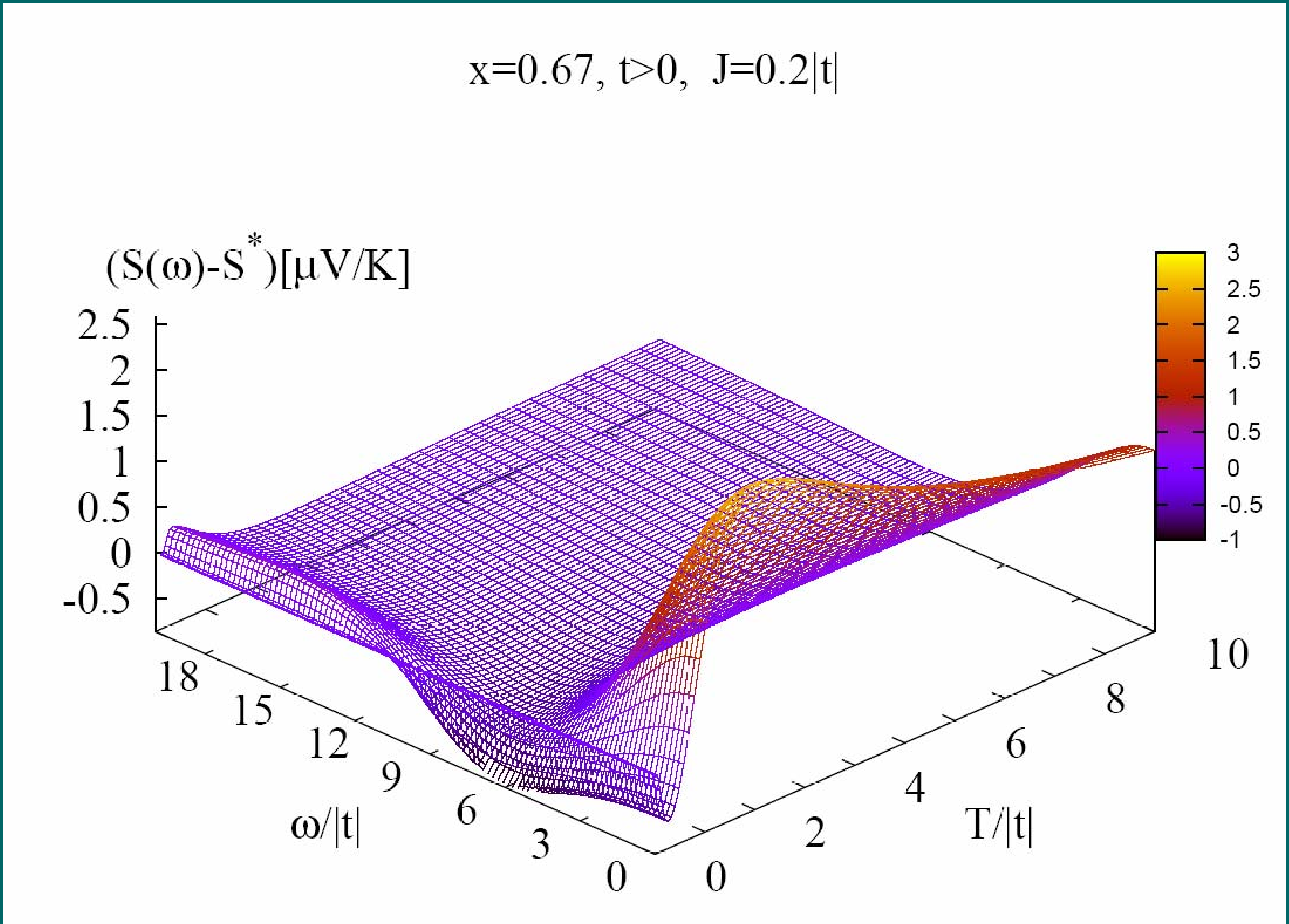
Square lattice Hall constant- sensitively dependent on t'/t sign and magnitude!!

Aim is to compare with Balakirev-Boebinger and earlier Takagi type hall number extraction.

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

A numerical benchmark: Max deviation 3% anywhere !!

As good as exact!



Leading High temperature term for the Triangular lattice and application to Sodium Cobalt Oxide

$$S^* = -\frac{\mu}{q_e T} + \frac{q_e \Delta}{T \langle \tau^{xx} \rangle}$$

where

$$\Delta = -\frac{1}{2} \sum_{\vec{\eta}, \vec{\eta'}, \vec{r}} (\eta_x + \eta'_x)^2 \; t(\vec{\eta}) \; t(\vec{\eta'}) \; Y_{\sigma', \sigma}(\vec{r} + \vec{\eta}) \; \langle c^{\dagger}_{\vec{r}+\vec{\eta}+\vec{\eta'}, \sigma'} c_{\vec{r}, \sigma} \rangle$$

This is a very useful alternate formula to the Heikes-Mott-Zener formula where the second term in Eq above is thrown out. It interpolates very usefully between the standard formulas for low temperature as well as at high temperature. The second term represents the "transport" contribution to the thermopower, whereas the first term is the thermodynamic or entropic part, which dominates at high temperaturefor S^* we can actually make a systematic expansion in powers of βt, unlike the dc counterpart.

Leading high temp expansion:

$$\langle \tau^{xx} \rangle = 6\mathcal{L}q_e^2 t \langle \tilde{c}_1^\dagger \tilde{c}_0 \rangle = 3\mathcal{L}q_e^2 \beta t^2 n(1-n). \tag{1}$$

$$\begin{aligned} \left\{ \tilde{c}_{\vec{r},\sigma}, \tilde{c}^\dagger_{\vec{r'},\sigma'} \right\} &= \delta_{\vec{r},\vec{r'}} \left\{ \delta_{\sigma,\sigma'}(1-n_{\vec{r},\bar{\sigma}}) + (1-\delta_{\bar{\sigma},\sigma'})\tilde{c}^\dagger_{\vec{r},\sigma}\tilde{c}_{\vec{r},\bar{\sigma}} \right\} \\ &\equiv Y_{\sigma,\sigma'}\,\delta_{\vec{r},\vec{r'}} \end{aligned} \tag{1}$$

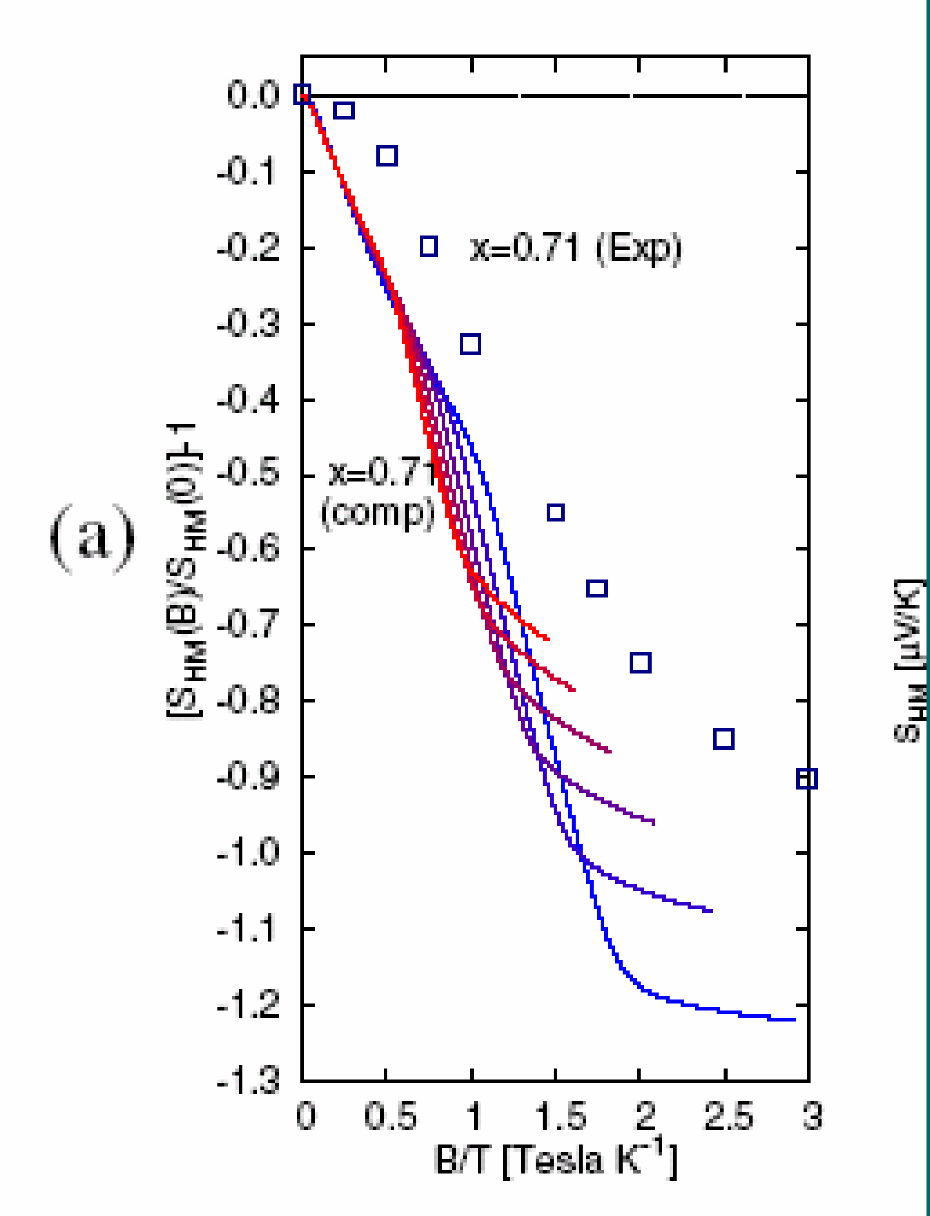
$$\Delta \sim -\frac{3}{2}\mathcal{L}t^2 \sum_{\sigma,\sigma'} \langle Y_{\sigma',\sigma}(\vec{\eta})\tilde{c}^\dagger_{\vec{\eta}+\vec{\eta'},\sigma'}\tilde{c}_{\vec{0},\sigma} \rangle. \tag{2}$$

The spins must be the same to the leading order in βt where we generate a hopping term $\tilde{c}^\dagger_{\vec{0},\sigma}\tilde{c}_{\vec{\eta}+\vec{\eta'},\sigma}$ from an expansion of $\exp(-\beta K)$, and hence a simple estimation yields

$$\Delta = -\frac{3}{4}\mathcal{L}t^3\beta n(1-n)(2-n) + O(\beta^3). \tag{3}$$

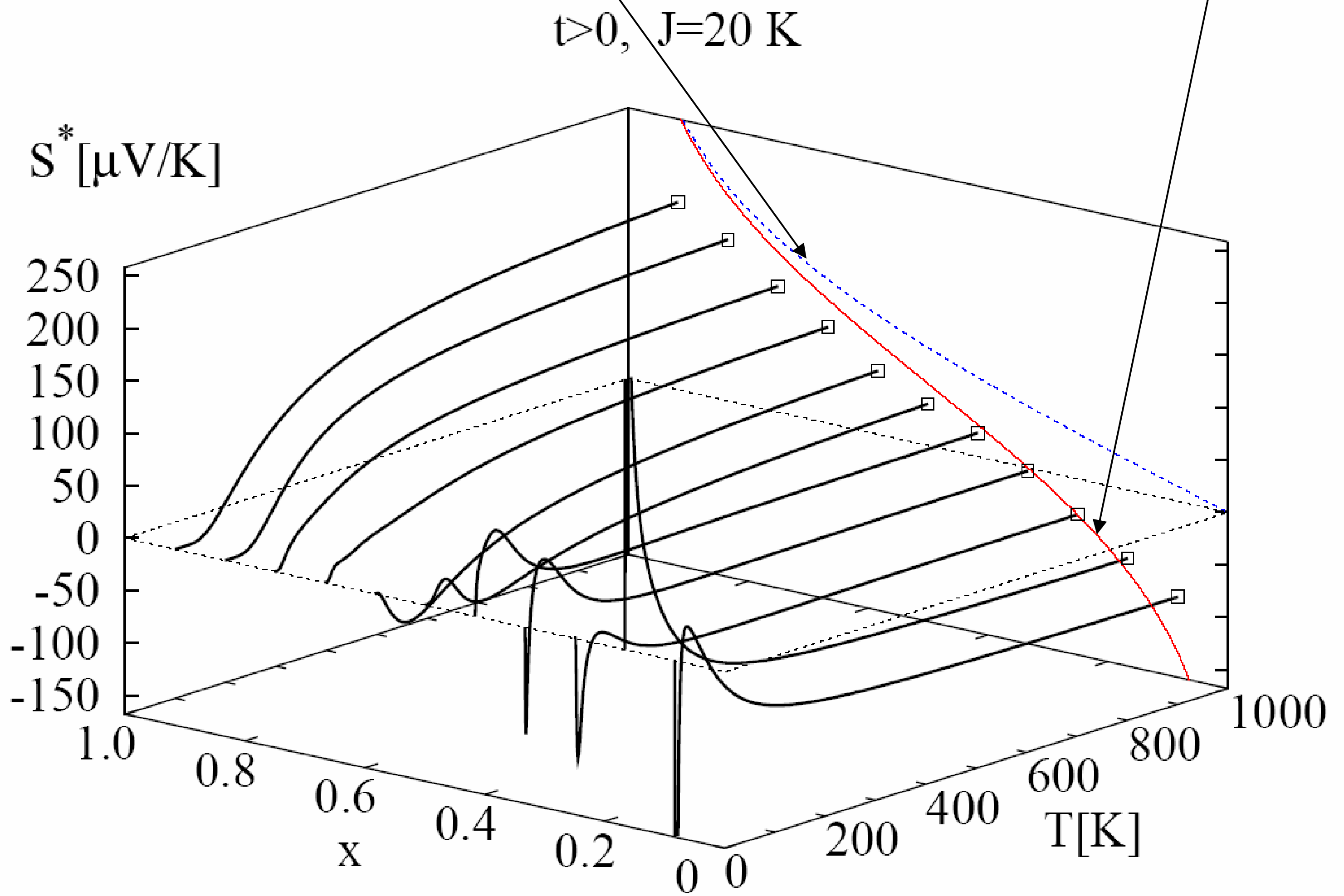
This together with $\mu/k_B T = \log(n/2(1-n)) + O(\beta^2 t^2)$ gives us the result for $0 \le n \le 1$

$$S^* = \frac{k_B}{q_e}\left\{ \log[2(1-n)/n] - \beta t \frac{2-n}{4} + O(\beta^2 t^2) \right\}, \tag{4}$$

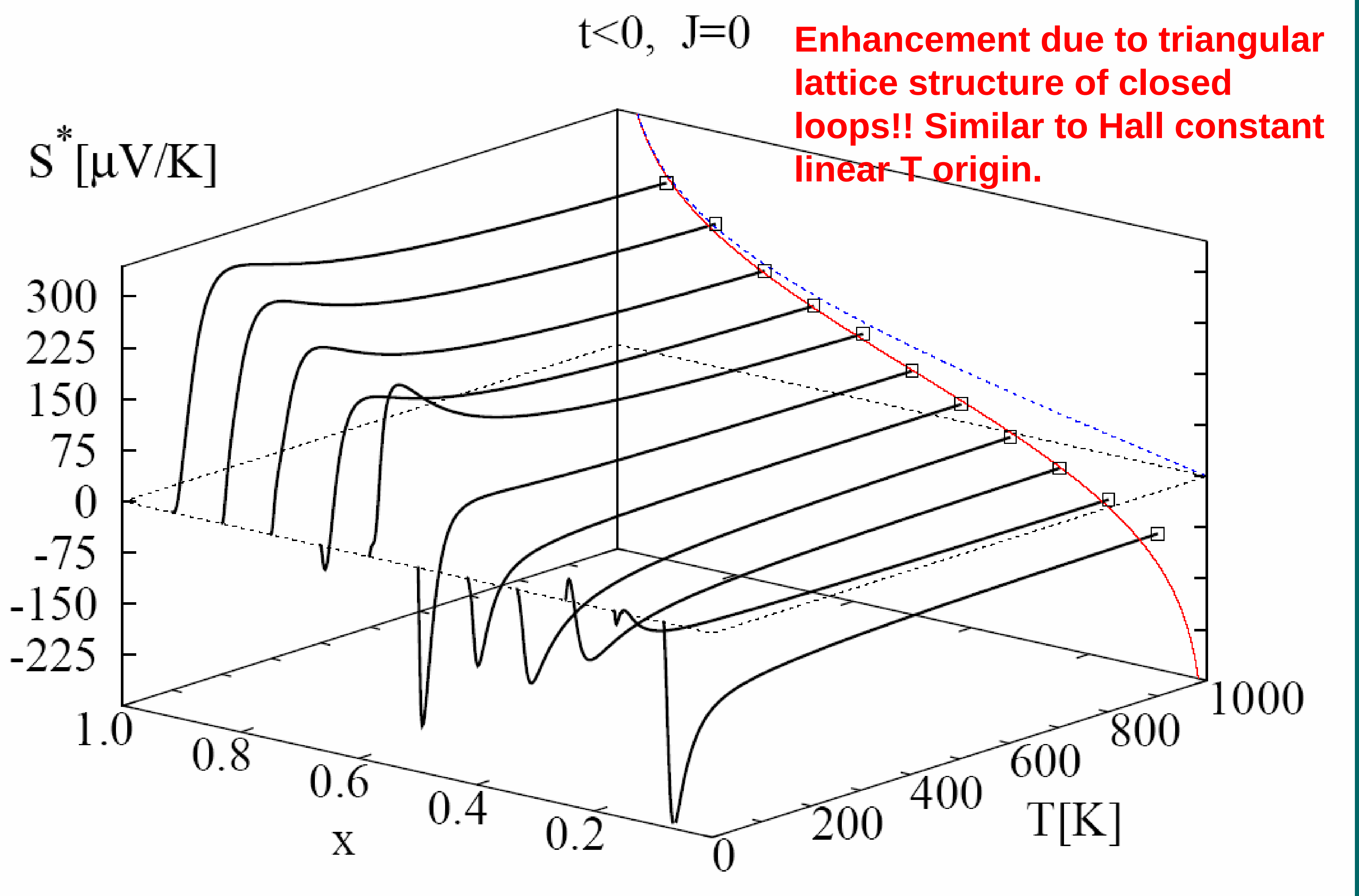


B dependence of thermopower is quantitatively explainable by our model!

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.

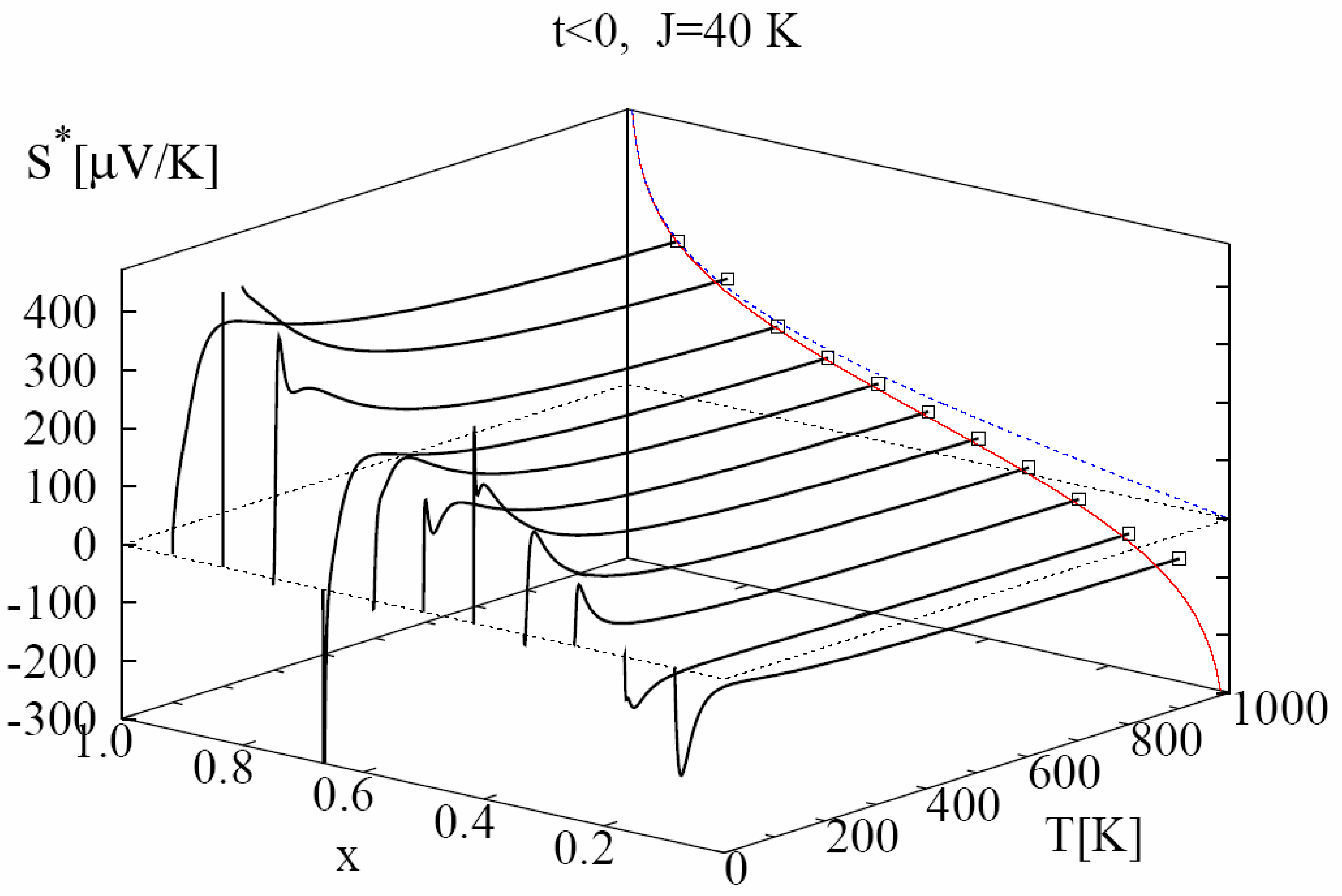


Predicted result for t<0 i.e. fiducary hole doped CoO_2 planes. Notice much larger scale of S* arising from transport part (not Mott Heikes part!!).



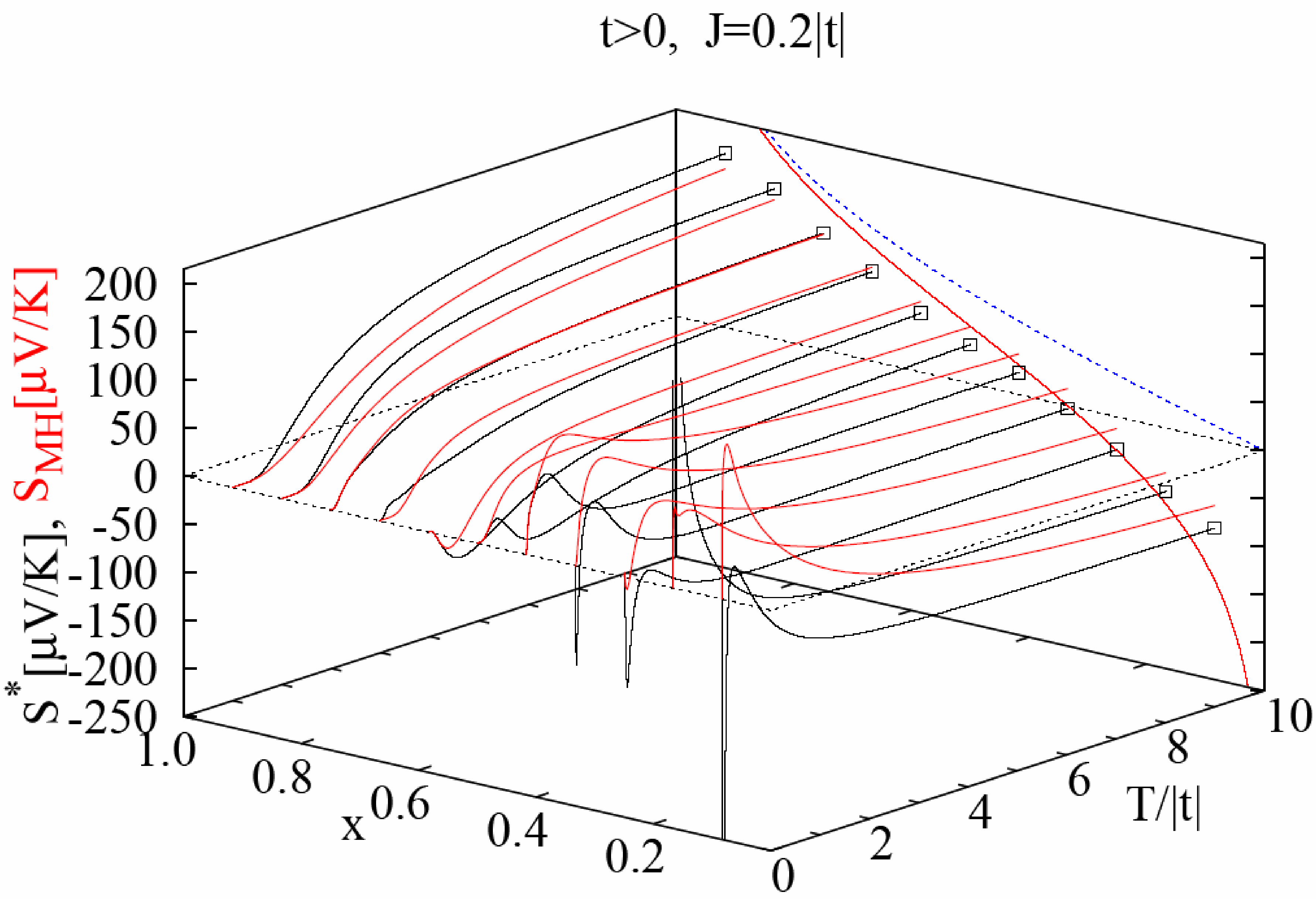
Predicted result for t<0 i.e. fiducary hole doped CoO_2 planes.

Different J higher S.



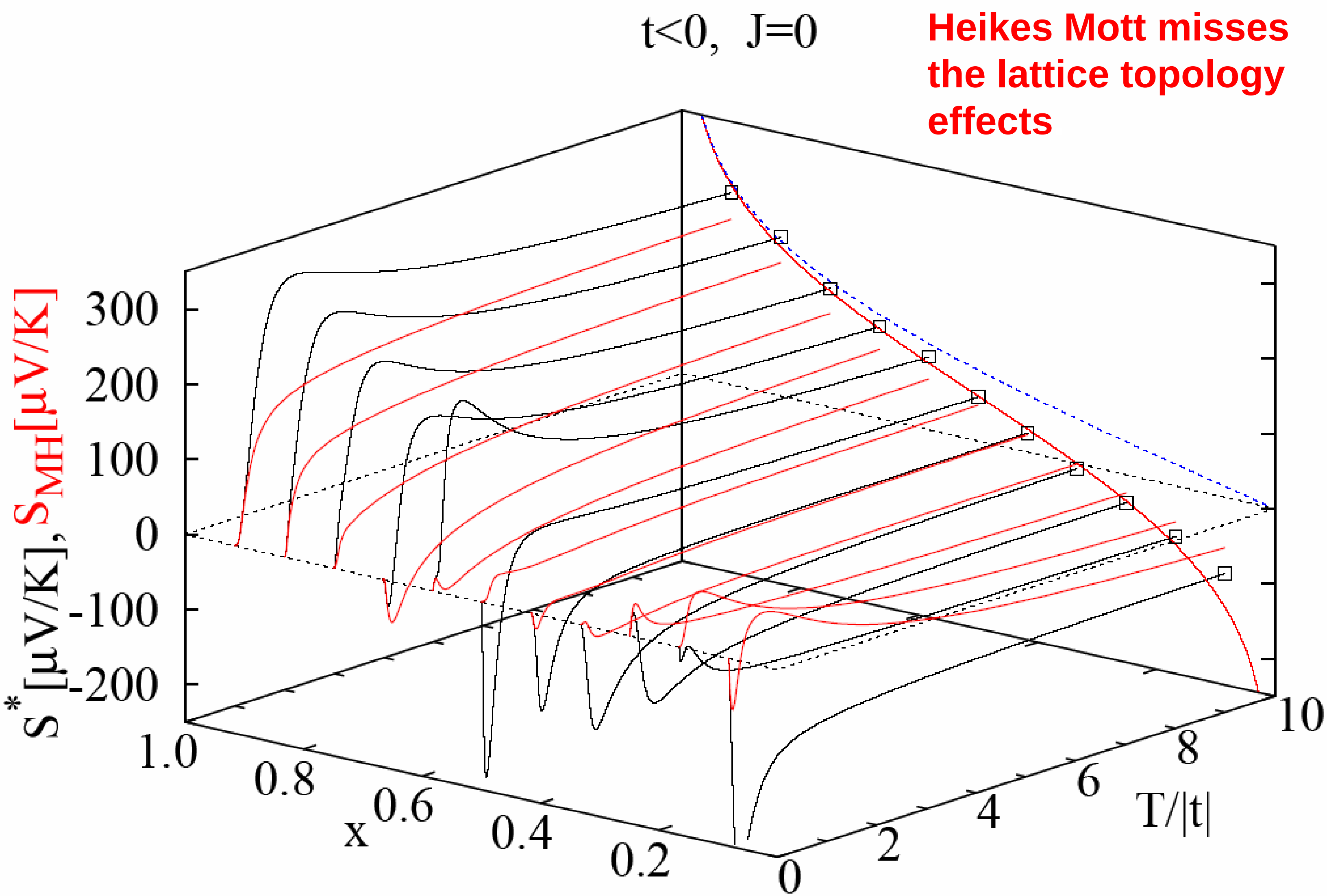
S* and the Heikes Mott formula (red) for Na_xCo O2.

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



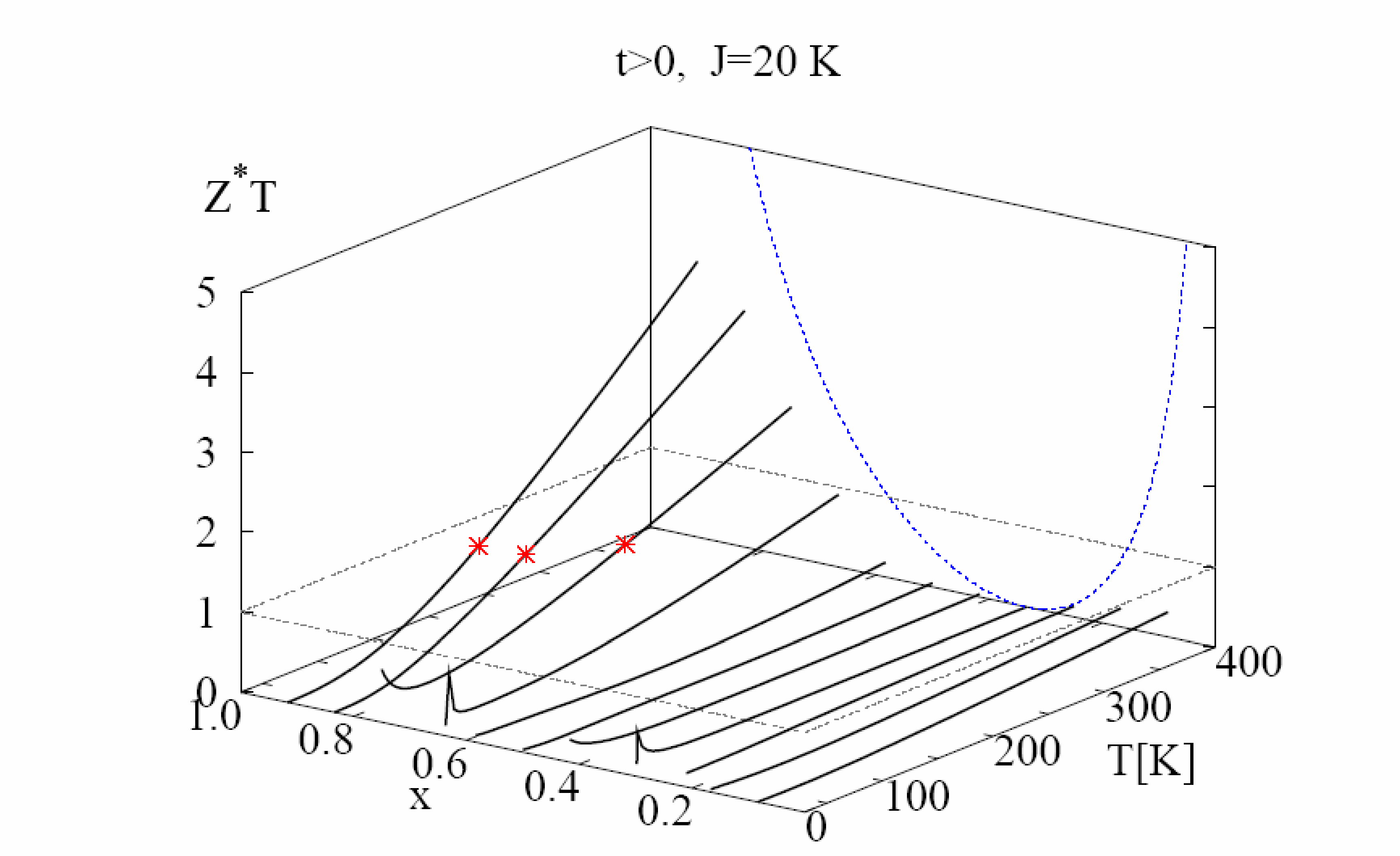
Predictions of S* and the Heikes Mott formula (red) for fiducary hole doped CoO2.

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.



Conclusions:

•New and rather useful starting point for understanding transport phenomena in correlated matter

•Can we design new materials using insights gained from this kind of work?

1. Narrow bands are good for large thermoelectric power
2. X~0, i.e. proximity to Mott insulating state is tempting since S is large, but in reality, x~1 much better for both S and FOM!!
3. New insight: Frustration of hopping (Not J) gives a boost to the S and FOM
4. Look in FCC, HCP, hexagonal narrow band metals!!

http://physics.ucsc.edu/~sriram/sriram.html

Useful link for this kind of work: