Theory of thermoelectric properties of Cobaltates

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We present the main results from a recently developed formalism, for computing certain dynamical transport coefficients for standard models of correlated matter, such as the Hubbard and the t-J model. The aim is to understand the physics of the Curie Weiss metallic phase of Na_xCoO_2 with its large thermopower.

The case of the Hall constant in correlated matter is used to motivate the new method. The extension is made to evaluate and estimate the Seebeck coefficient, the Lorentz number L, and the figure of merit Z, in terms of novel equal time correlation functions. Along the way, we note a hitherto unknown sum rule for the dynamical thermal conductivity for many standard models, precisely analogous to the famous f-sum rule for the electrical conductivity.

The new formalism is tested against simple settings, such as the free (non interacting) electron system within the Boltzmann approach. Further, computational results are provided for testing the frequency dependence of these variables in certain standard models. Finally some new predictions made regarding triangular lattice systems, motivated by the sodium cobaltate $Na_{.68} Co O_2$, are displayed.

Motivation and Plan

- Sodium cobaltate Na_xCoO_2 Curie Weiss Phase: High Seebeck coeff S for a metal
- Current theories for S cannot handle strong correlations, beyond simplest Mott Heikes approximation.
- New formalism, and **two new** formulas for S that capture correlations
- Applications to NCO, comparison with experiments and new predictions.

The t J Model for the Cobaltates

Simple model to capture correlations in sodium cobaltates

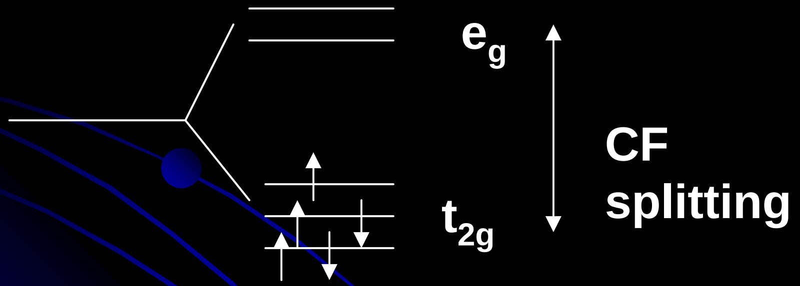
Important NMR paper from Kolkata-Japan collaboration

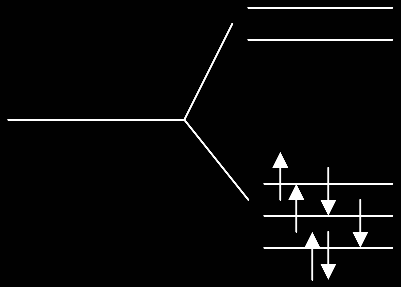
$Na_{.7}CoO_2$

Due to CF splitting low spin state of Co $^{(4+)}$ spin ½, Co$^{(3+)}$ spin 0

Co $^{(4+)}$ 5-d electrons Spin1/2

Co $^{(3+)}$ 6-d electrons Spin 0





Missing state is with 4 electrons in t2g, i.e. the Co$^{(5+)}$ state. This is due to correlations. By a particle hole transformation we get the tJ model

$$\mathrm{H}_{Hubbard} = T + U \sum_j n_{j,\uparrow} n_{j,\downarrow}$$

$$\mathrm{H}_{tJ} = P_g T P_g + J \sum_{<ij>} \vec{S}_i . \vec{S}_j$$

Obtained as $U \to \infty$ limit of Hubbard model. P_g is the Gutzwiller projector which carries the information about the reduced Hilbert space, i.e. the elimination of the $Co^{(5+)}$ state

While the Hubbard type models are easier, esp for weak coupling, thanks to Perturbative treatments, the tJ model is A VERY HARD problem.

Formalisms and methods for computing S.

- Current approaches: Boltzmann eqn+ Fermi liquid theory give low T behavior : Good for weakly correlated systems

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

• Heikes Mott formula for semiconductors and very narrow band systems: Purely thermodynamic: Used by Beni Chaikin for Hubbard

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

•Kubo formula: Rigorous but intractable!

$$S = -\frac{\mu(T)}{q_e T} + \frac{\int dt d\tau \langle J_E(t-i\tau)J\rangle}{\int dt d\tau \langle J(t-i\tau)J\rangle}$$

New Formalism:*

- **Novel way for computing thermopower of isolated system (absolute Thermopower)**
- **Leads to correct Onsager formula (a la Kubo)**
- **Leads to other insights and other useful formulae**
- **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)**

ANALOGY between Hall Constant and Seebeck Coefficients

New Formalism SS (2006) is based on a finite frequency calculation of thermoelectric coefficients. Motivation comes from Hall constant computation (Shastry Shraiman Singh 1993- Kumar Shastry 2003)

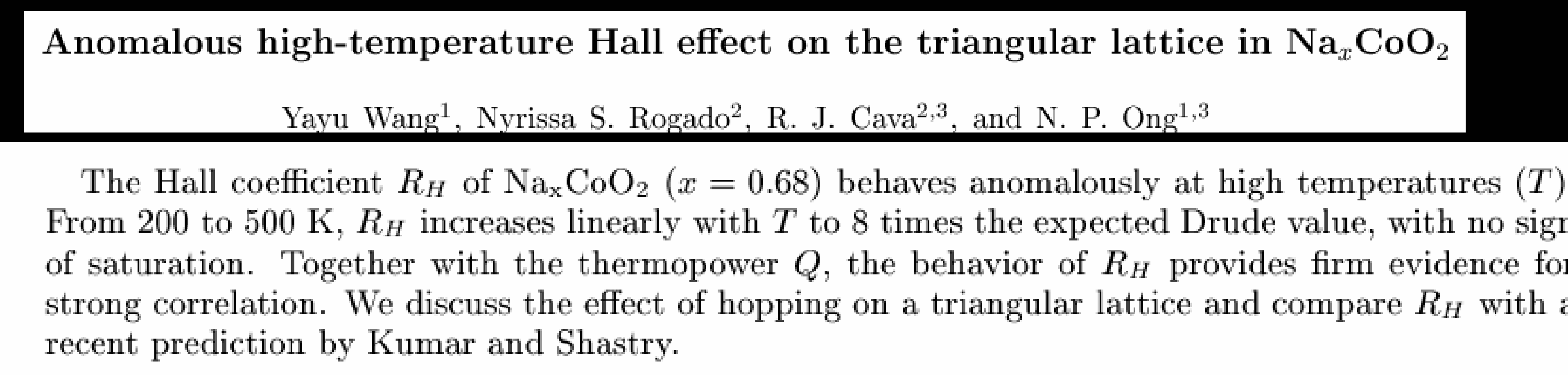
$$\rho_{xy}(\omega) = \frac{\sigma_{xy}(\omega)}{\sigma_{xx}(\omega)^2} \to BR_H^* \text{ for } \omega \to \infty$$

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

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

$$R_H^* = \frac{-i2\pi}{hB} N\mathrm{v} < [J^x, J^y] > / < \tau_{xx} >^2$$

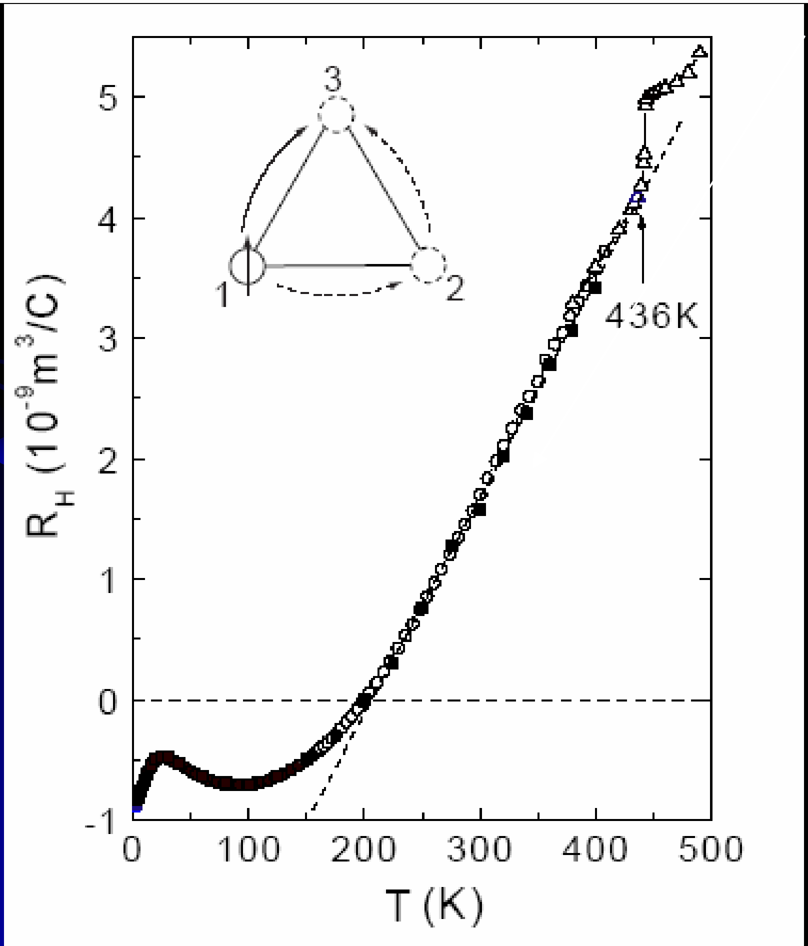
- Very useful formula since
  - Captures Lower Hubbard Band physics. This is achieved by using the Gutzwiller projected fermi operators in defining J's
  - Exact in the limit of simple dynamics (e.g few frequencies involved), as in the Boltzmann eqn approach.
  - Can compute in various ways for all temperatures (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.
  - This asymptotic formula usually requires ω to be larger than J



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]

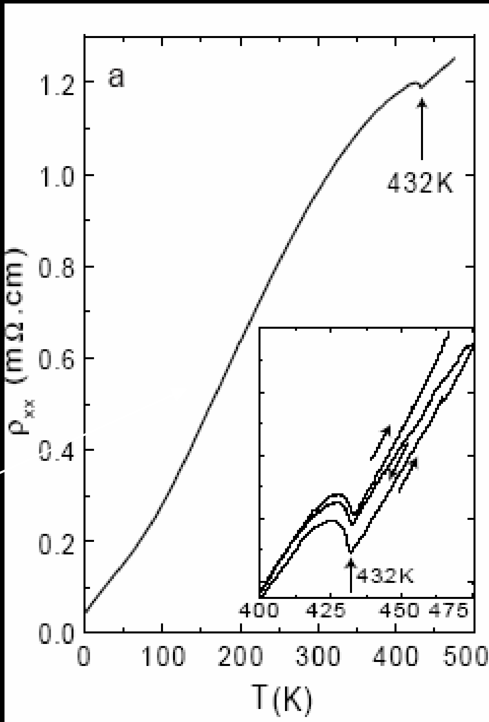
The Hall coefficient R_H of Na_xCoO_2 ($x = 0.68$) behaves anomalously at high temperatures (T) From 200 to 500 K, R_H increases linearly with T to 8 times the expected Drude value, with no sig of saturation. Together with the thermopower Q, the behavior of R_H provides firm evidence fo strong correlation.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



GOAL: Finite frequency Seebeck coeff

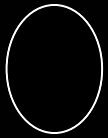
Turn on spatially inhomogeneous time dependent potential adiabatically from remote past.

Use Luttinger’s echnique

$$H_1 = \sum_j H(r_j)\psi(r_j)\exp{(\eta - i\omega)t}$$

$$H_1 \sim \sum_j \frac{H(r_j)}{c^2} V_{gravity}(r_j)$$

Dark sphere!



System of Length L, open at the two surfaces 1 and 2

T_1 Sample along x axis T_2

Choose linear gravitational potential $\psi(r_j) = \frac{x}{L}\psi_0$.

Fundamental theorem of Luttinger: Gravitational pot ~ temperature. More precisely: in a suitable limit

$$\nabla\psi(r) \rightarrow \frac{\nabla T(r)}{T}$$

1. **Compute the induced change in particle density profile:**
2. **Particles run away from hot end to cold end, hence pileup a charge imbalance i.e. a dipole moment :**
3. **Linear response theory gives the dipole moment amplitude:**

$$\begin{aligned} P_{Thermal} &= \sum_r \langle x n(r) \rangle \exp i\omega t \\ &= q_e^2 \frac{T_2 - T_1}{T} \chi_{[\sum x n(r), \sum x (H(r) - \mu n(r)]}(\omega) \end{aligned}$$

Susceptibility of two measurables A, B is written as

$$\chi_{[A,B]}(\omega)$$

Identical calculation with electrostatic potential gives:

$$P_{Elec} = q_e(\phi_2 - \phi_1)\chi_{[\sum x n(r), \sum x n(r)]}(\omega)$$

Hence: the thermo-power is obtained by asking for the ratio of forces that produce the same dipole moment! (balance condition)

$$\begin{aligned} S &= \frac{\phi_1 - \phi_2}{T_1 - T_2} \\ &= \frac{q_e}{T} \frac{\chi_{[\sum x n(r), \sum x (H(r) - \mu n(r)]}(\omega)}{\chi_{[\sum x n(r), \sum x n(r)]}(\omega)} \end{aligned}$$

We now use the usual trick to convert from open Boundary conditions to periodic (more convenient). The length L of sample along x axis is traded for a wave vector q_x of relevant physical quantities (actually L is half wavelength but the difference can be argued away).

Hence we find the formula:

$$S = \lim_{\omega \to 0, q_x \to 0} \frac{1}{q_e T} \frac{\chi_{[n_q, H_{-q} - \mu n_{-q}]}(\omega)}{\chi_{[n_q, H_{-q} - \mu n_{-q}]}(\omega)} \quad \text{Onsager-Kubo}$$

Large box then static limit

$$S_{Kelvin} = \lim_{q_x \to 0, \omega \to 0} \frac{1}{q_e T} \frac{\chi_{[n_q, H_{-q} - \mu n_{-q}]}(\omega)}{\chi_{[n_q, H_{-q} - \mu n_{-q}]}(\omega)} \quad \text{Kelvin Thermodynamics}$$

Static limit then large box

$$S^* = \lim_{\omega \gg \omega_c, q_x \to 0} \frac{1}{q_e T} \frac{\chi_{[n_q, H_{-q} - \mu n_{-q}]}(\omega)}{\chi_{[n_q, H_{-q} - \mu n_{-q}]}(\omega)} \quad \text{High Frequency}$$

Large box then frequency larger than characteristic w's

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

Density Of States

Velocity averaged over FS

Energy dependent relaxation time.

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

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

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

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

Summarizing:

•For correlated systems we can use S* provided we are interested in correlations and do not expect severe energy dependence of relaxation. ω ~J is enough to make this a good approximation. See later

•S* and also Kelvin inspired formula are useful objects since they can be computed much more easily, no transport issues. S* seems better though. Computations proceed through one of many equilibrium methods. We use exact diagonalization and Canonical ensemble methods (brute force all states all matrix elements upto 14 site t-J model)

•These expressions can also be derived from more formal starting points. Derivation given here is most intuitive.

•Similar ideas work for Hall constant, Lorentz number, thermal conductivity and Z* T. Important new sum rule for thermal conductivity: (Shastry 2006)

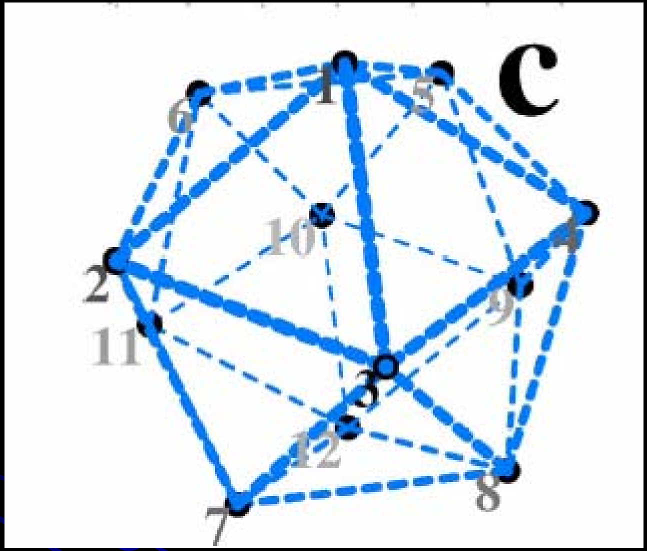
$$\begin{aligned}
\int_0^\infty Re\ \kappa_{zc}(\omega)d\omega &= \frac{\pi}{2\hbar T\mathcal{L}}\left\{\langle\Theta^{xx}\rangle - \frac{\langle\Phi^{xx}\rangle^2}{\langle\tau^{xx}\rangle}\right\}, \qquad \text{sum rule}\\
S^* &= \frac{\langle\Phi^{xx}\rangle}{T\langle\tau^{xx}\rangle}\\
\mathbf{L}^* &= \frac{\langle\Theta^{xx}\rangle}{T^2\langle\tau^{xx}\rangle} - (S^*)^2\\
\mathbf{Z}^*T &= \frac{\langle\Phi^{xx}\rangle^2}{\langle\Theta^{xx}\rangle\langle\tau^{xx}\rangle - \langle\Phi^{xx}\rangle^2}
\end{aligned}$$

The two newly introduced operators Thermal operator Θ^{xx} , and thermoelectric operator Φ^{xx} together with the stress tensor or Kinetic energy operator τ^{xx} can be computed for any given model, and their expectation as above gives all the interesting objects. One small example

Thermo power operator for Hubbard model

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

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



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

$\mathrm{Na}_{\{.68\}}\ \mathrm{Co}\ \mathrm{O}_2$

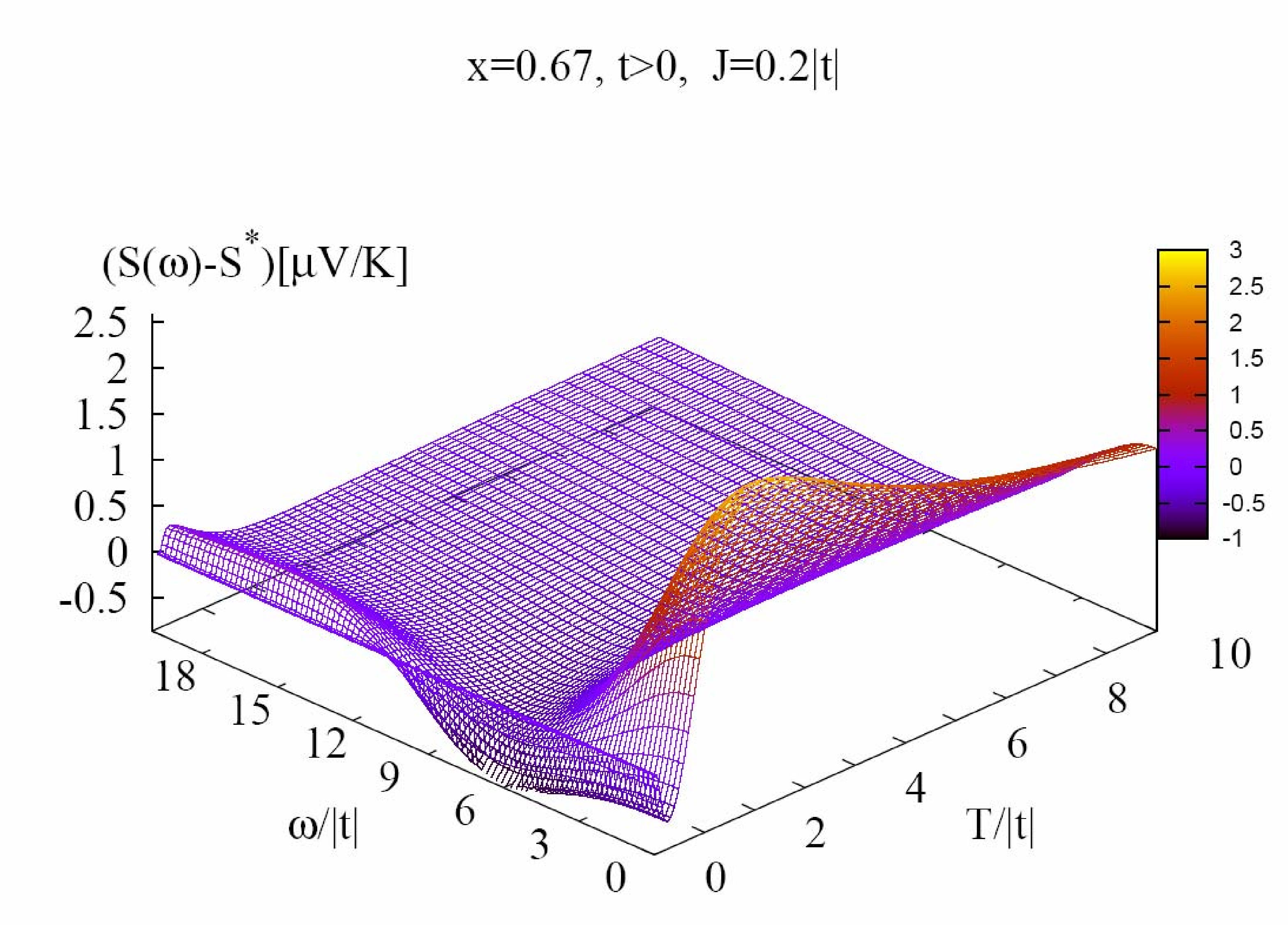
Modeled by t-J model with only two parameters “t=100K” and “J=36K”. Interested in Curie Weiss phase. Photoemission gives scale of “t” as does Hall constant slope of R_h and a host of other objects.

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

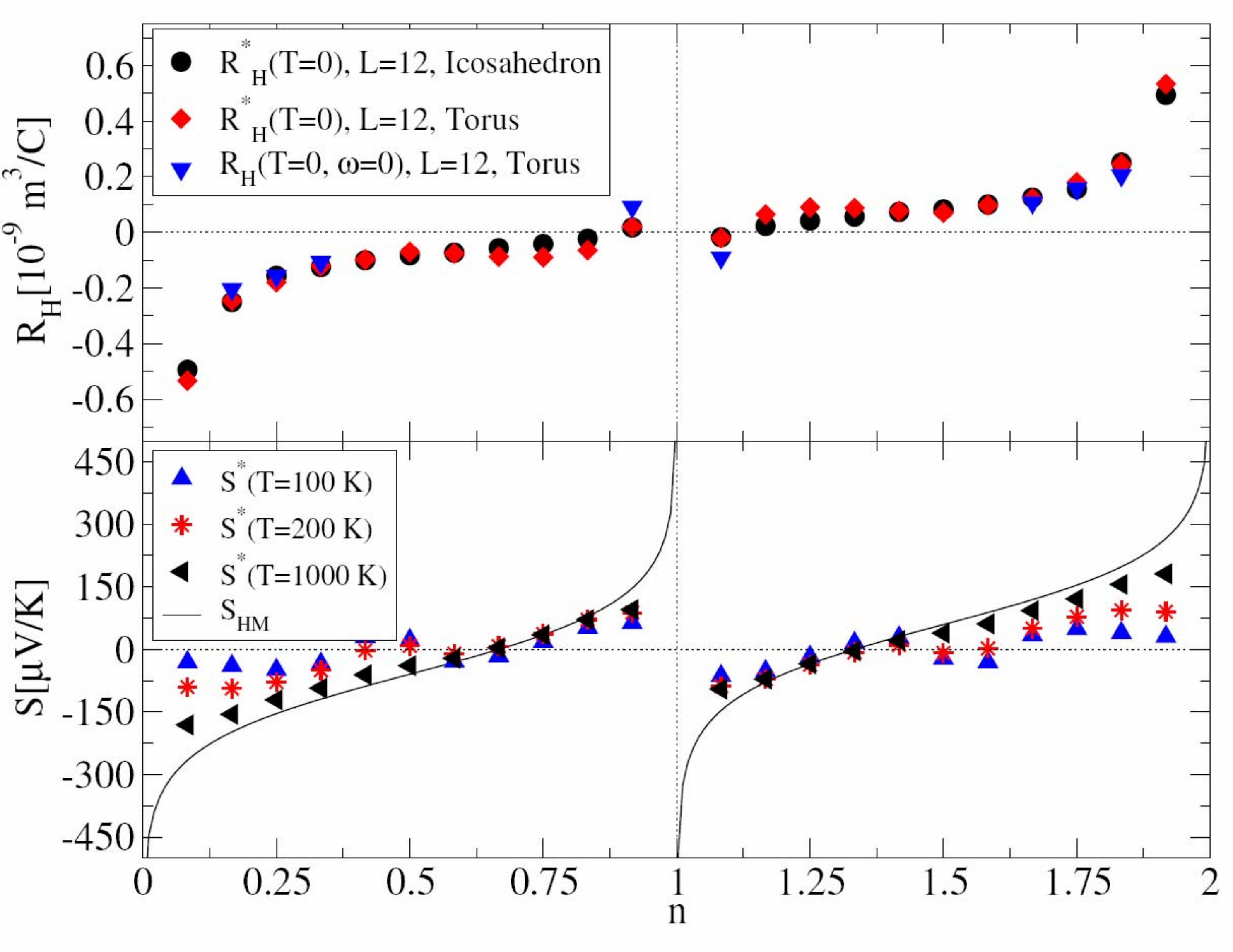
How good is the S* formula compared to exact Kubo formula?

A numerical benchmark: Max deviation 3% anywhere !!

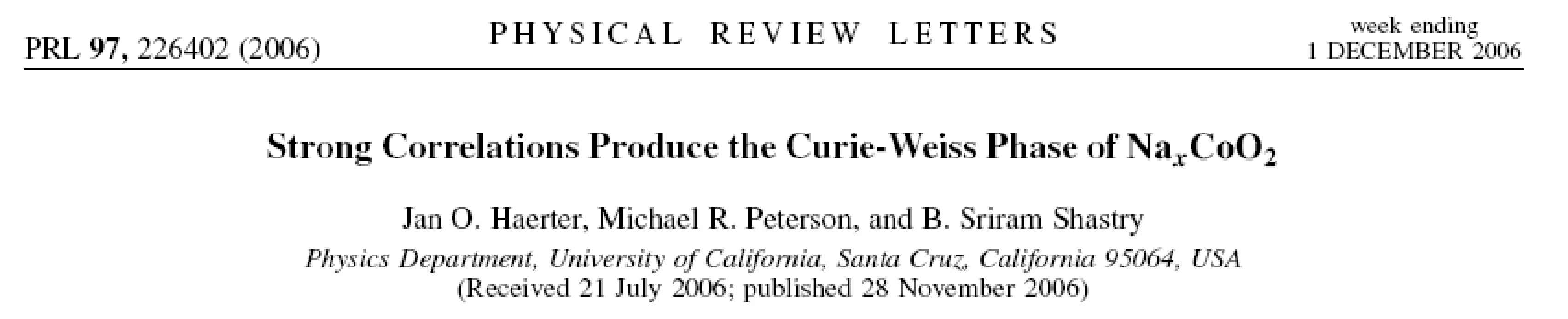
As good as exact!



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

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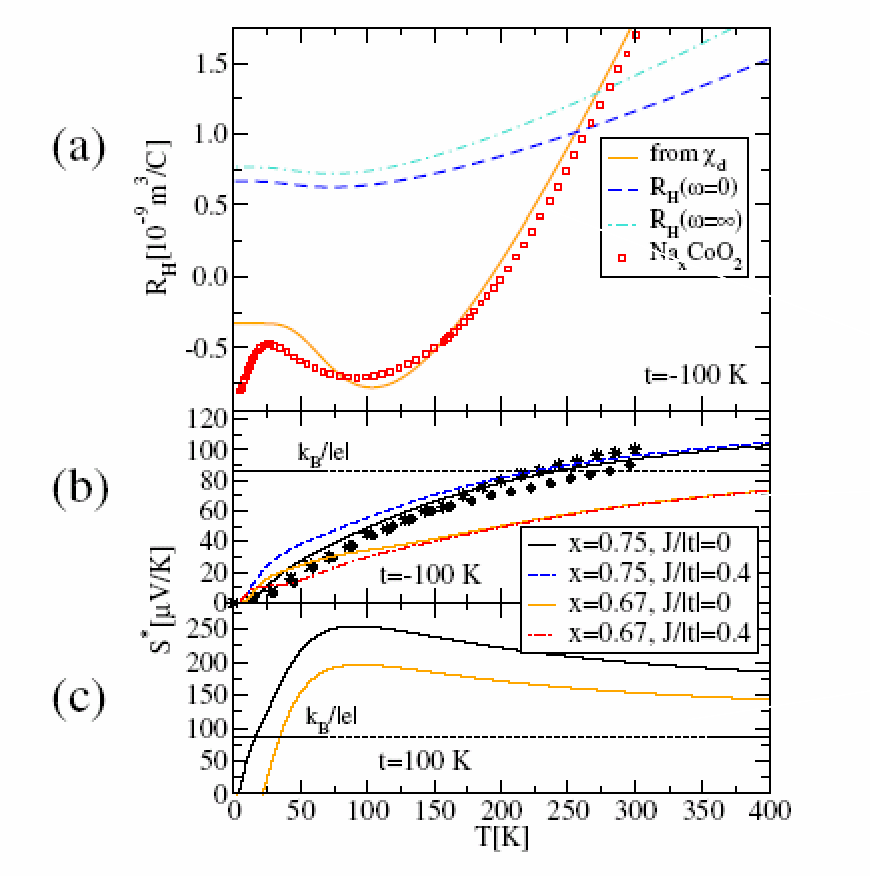
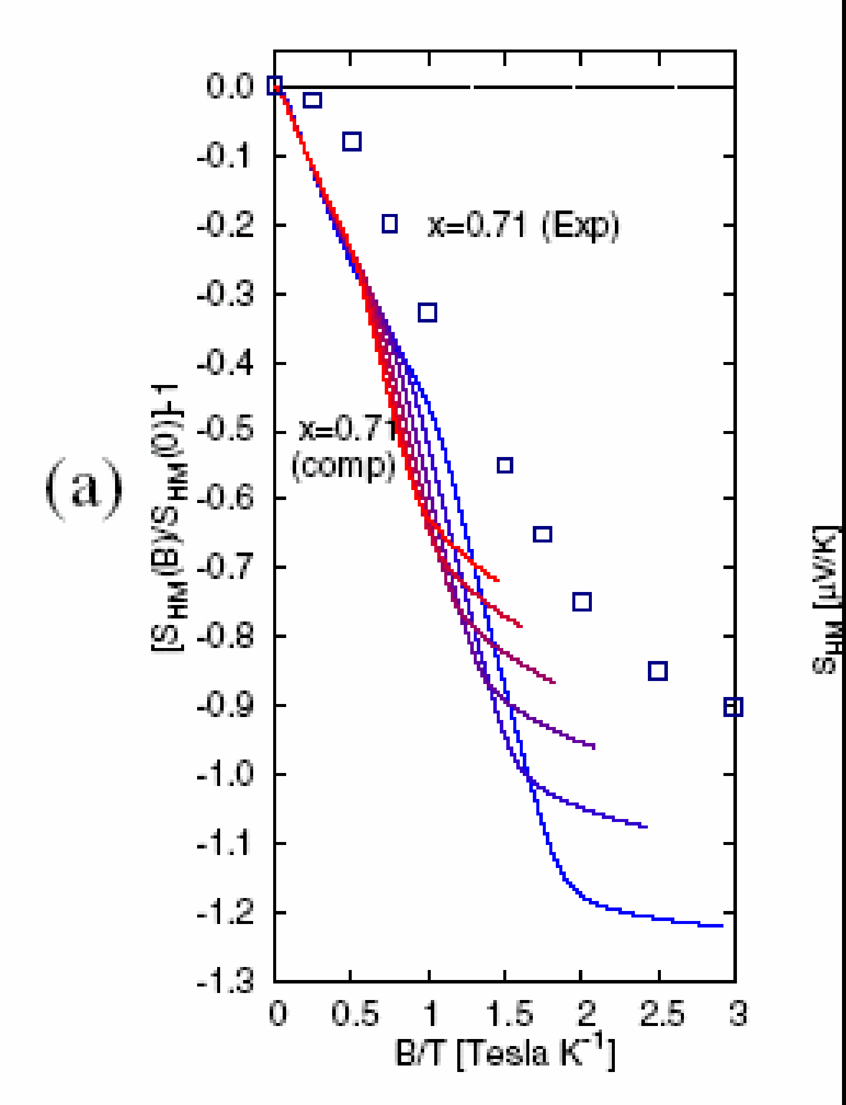


T linear Hall constant for triangular lattice predicted in 1993 by Shastry Shraiman Singh! Quantitative agreement hard to get with scale of "t"

Comparision with data on absolute scale!

Prediction for t>0 material

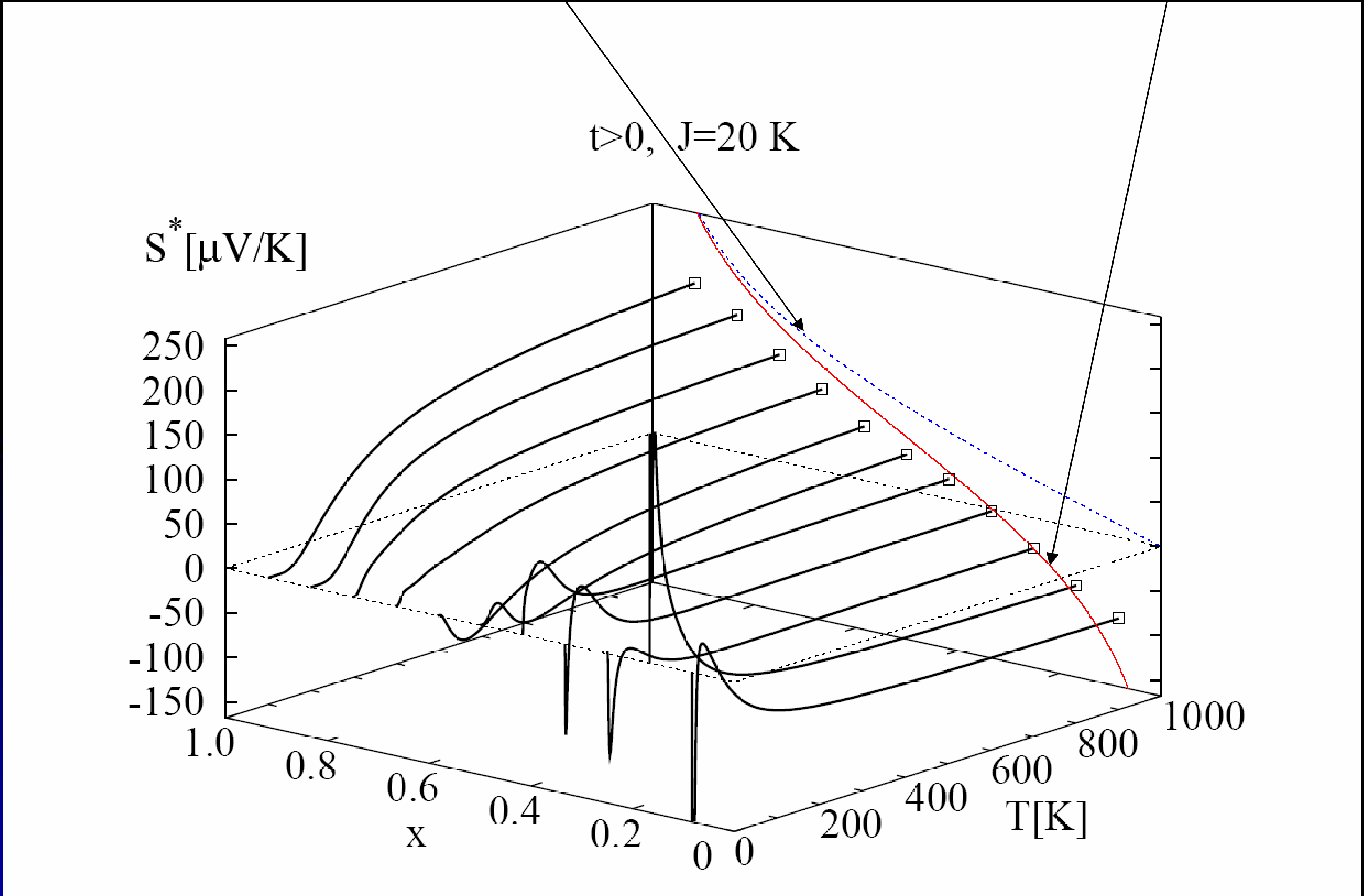


Ong et al coined the name Curie Weiss phase due to the large S and also B sensitive thermo-power. Can we understand that aspect?

Yes! Even quantitativley

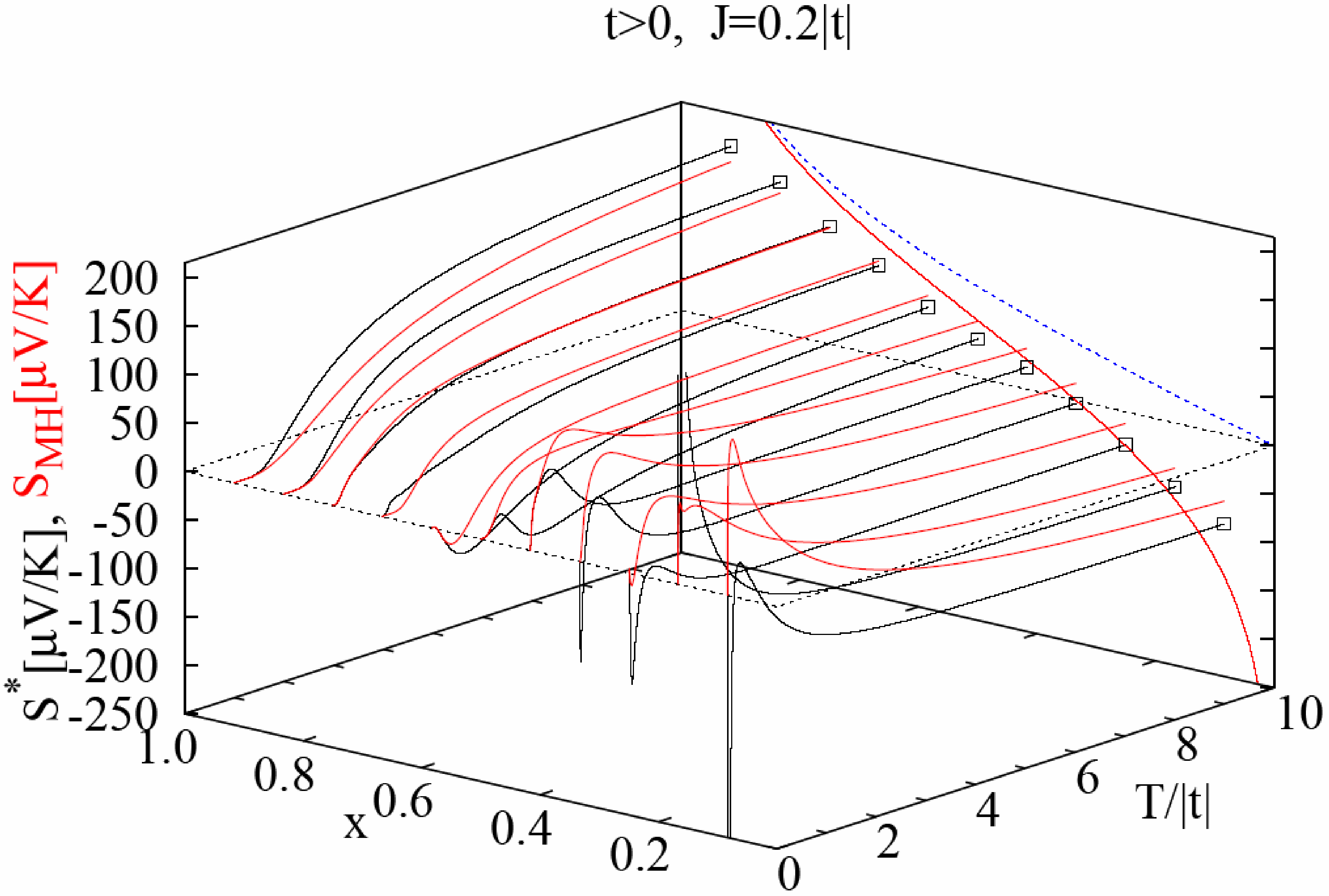
Magnetic field dep of S(B) vs data

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.

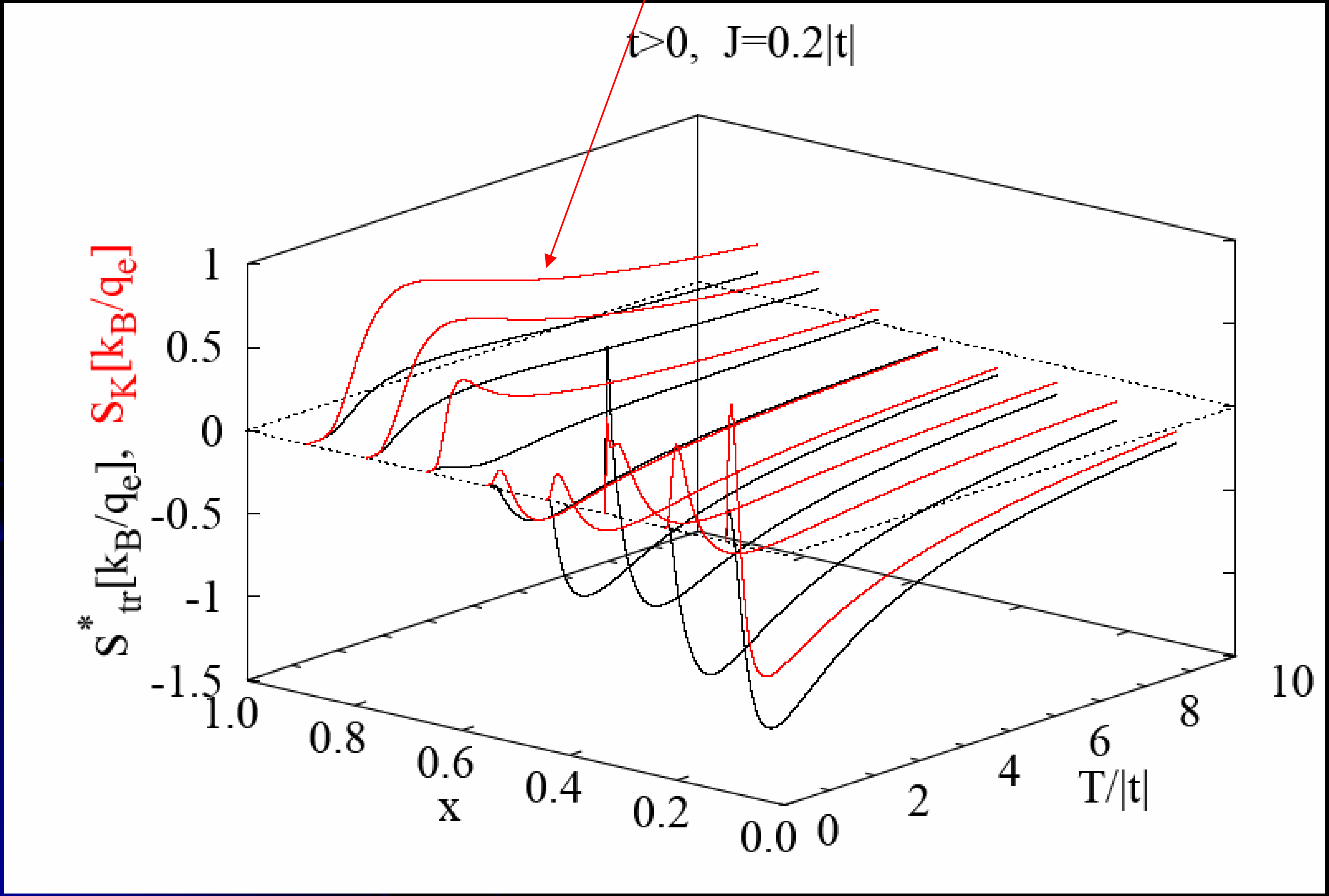


S* and the Heikes Mott formula (red) for Na_xCo O2.

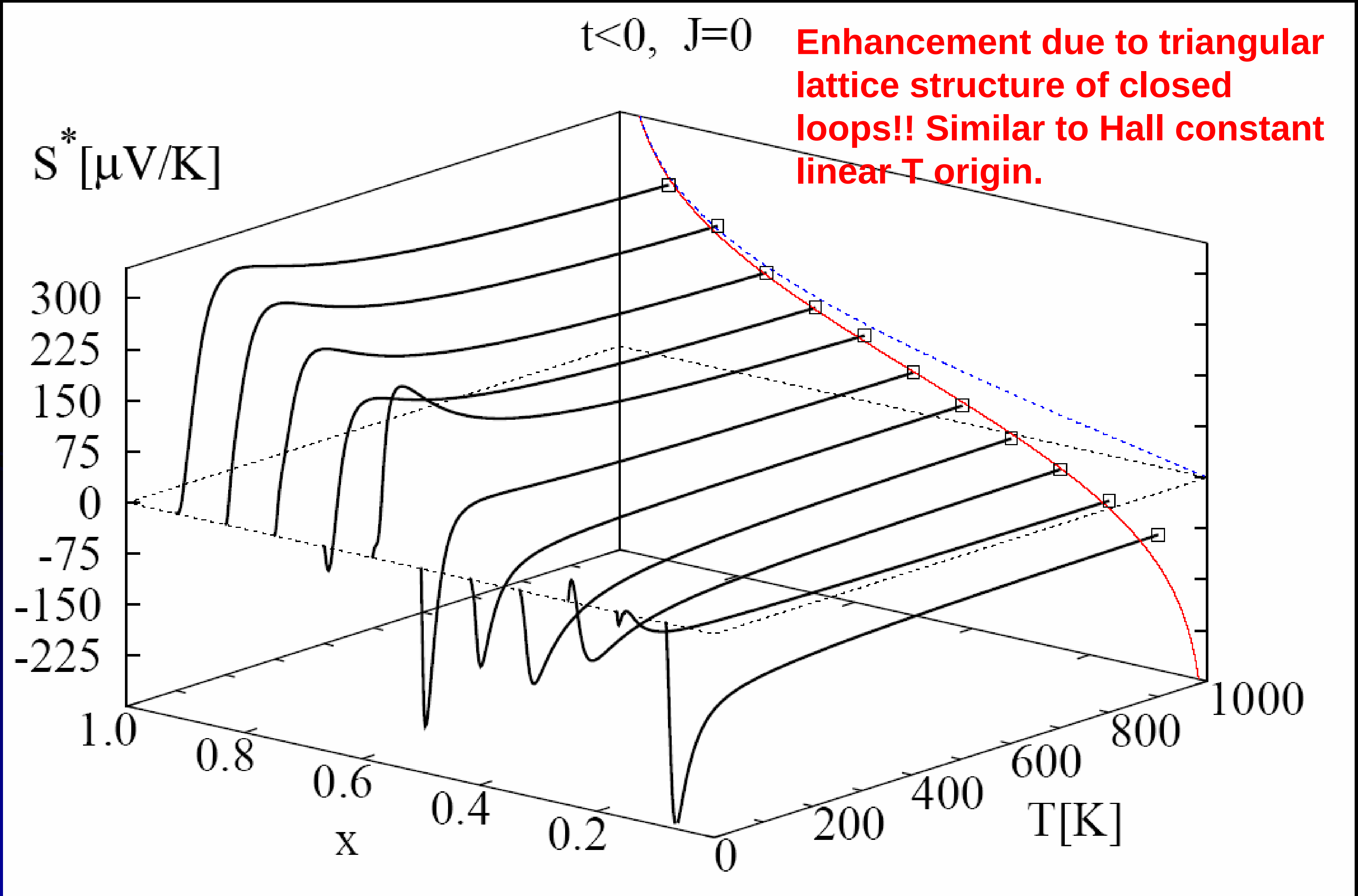
Close to each other for t>o i.e. electron doped cases



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.



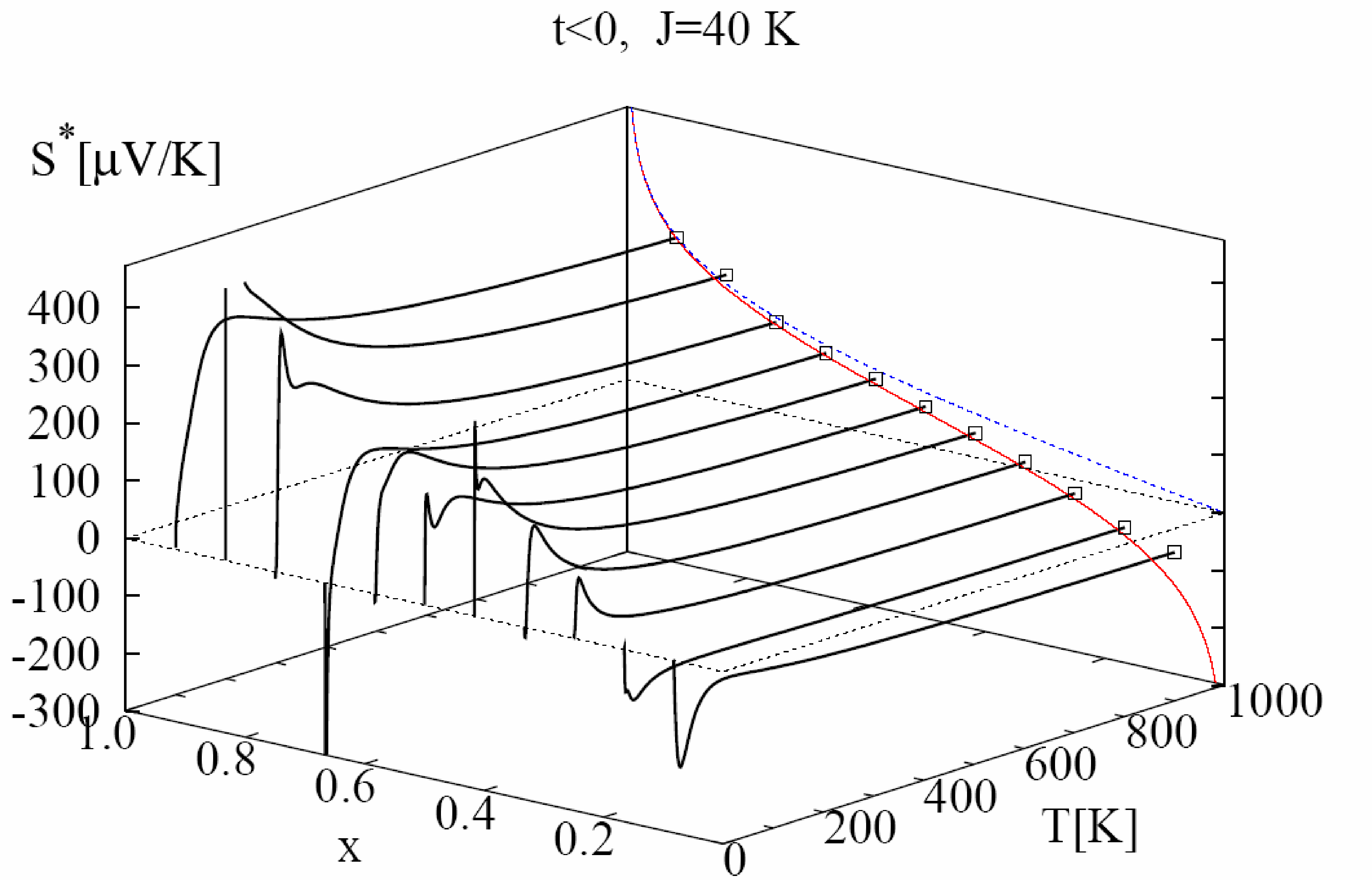
Predicted result for t<0 i.e. fiducary hole doped CoO_2 planes. Notice much larger scale of S* arising from transport part (not Mott Heikes part!!).



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

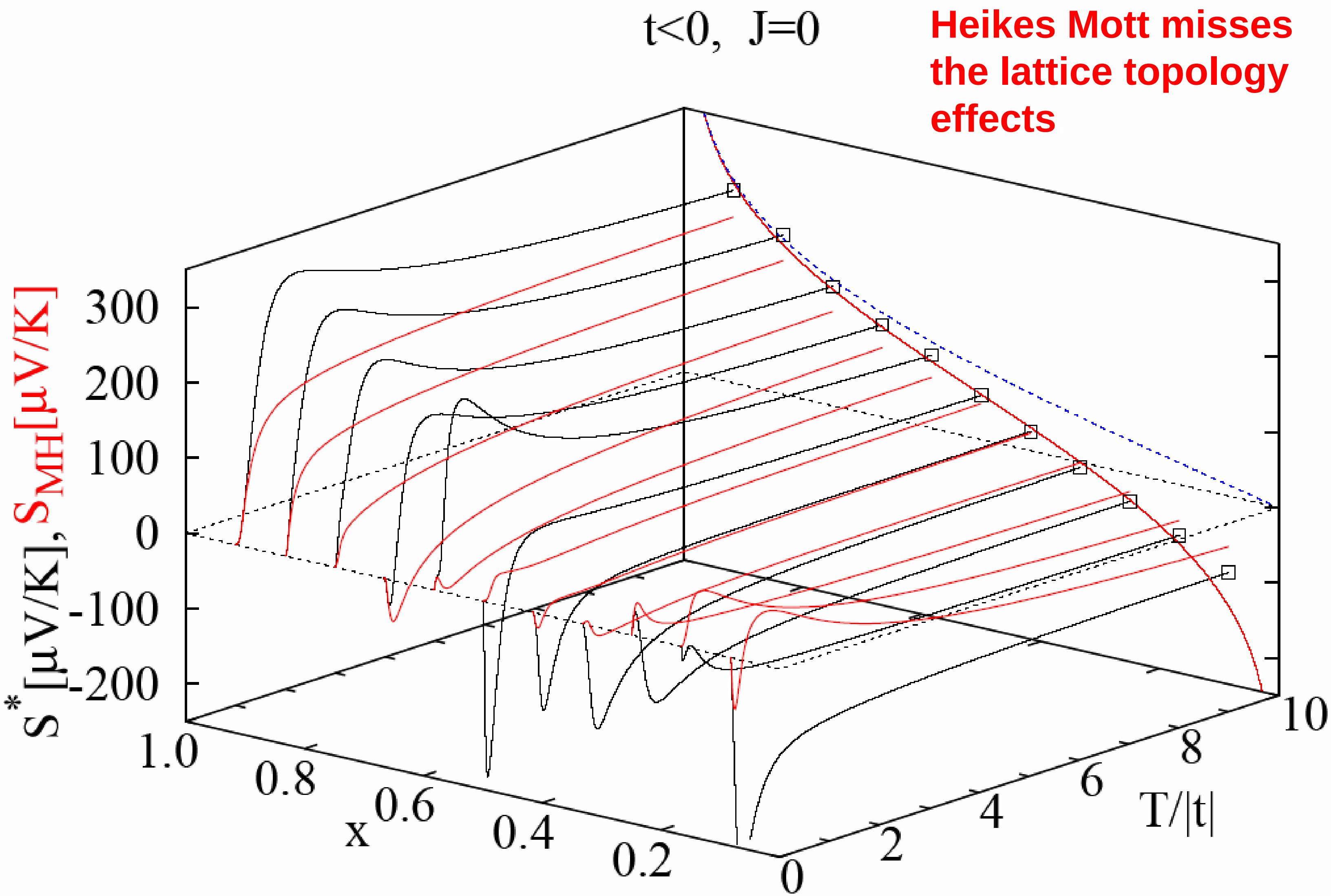
Predicted result for t<0 i.e. fiducary hole doped CoO_2 planes.

Different J higher S.



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

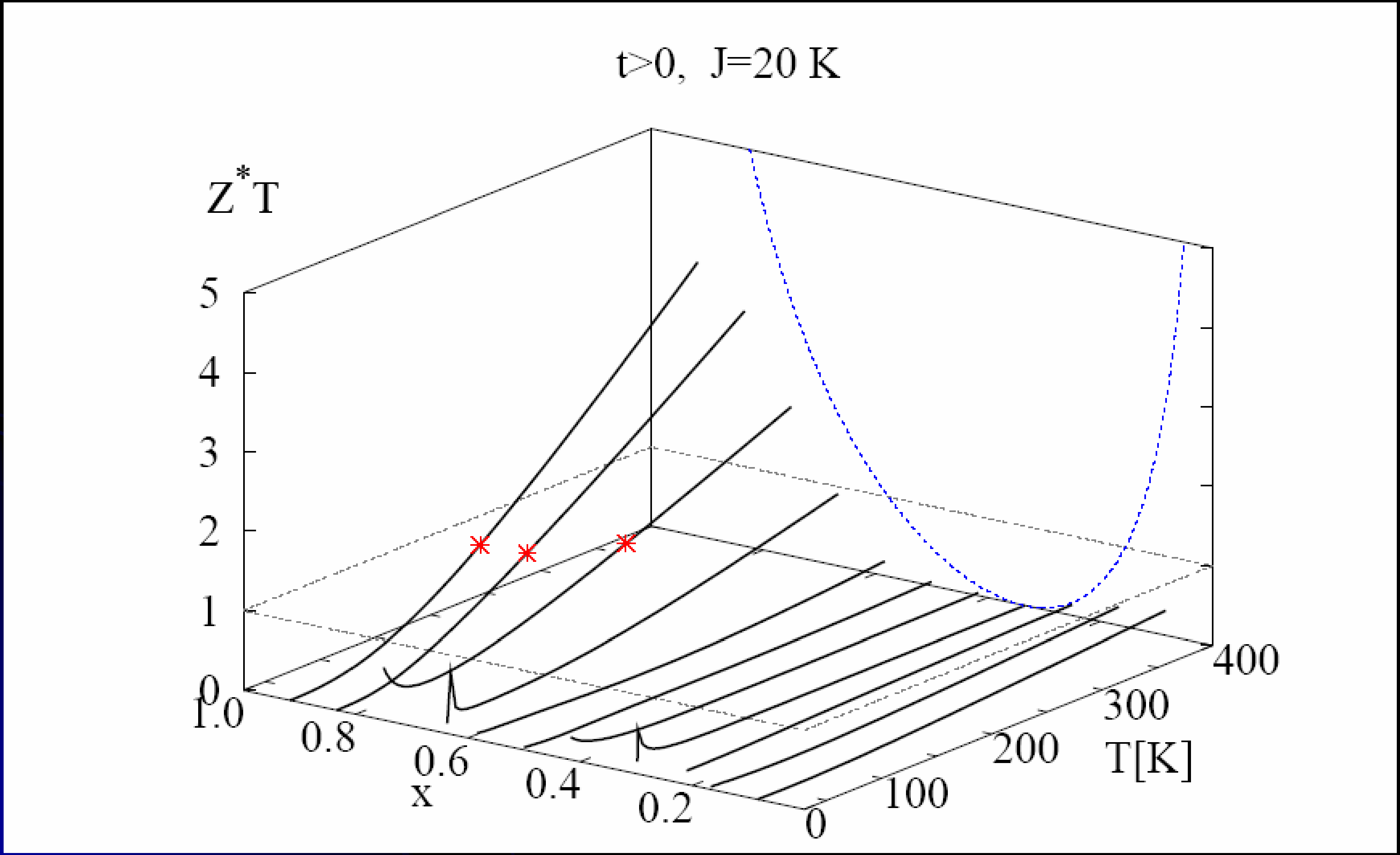
Notice that S* predicts an important enhancement unlike Heikes Mott formula



Heikes Mott misses the lattice topology effects

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

Quite encouraging.



Materials search Guidelines

- Frustrated lattices are good (Hexagonal, FCC, HCP,….)
- Favourable Sign of Hopping predicted by theory
- Low bandwidth metals good
- Hole versus electron doping same as changing sign of hopping!

Conclusions:

- New and rather useful starting point for understanding transport phenomena in correlated matter
- Kubo type formulas are non trivial at finite frequencies, and have much structure
- We have made several successful predictions for NCO already
- Can we design new materials using insights gained from this kind of work?

Useful link for this kind of work:

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