Thermoelectric effects and Correlated materials

Mahendra Lal Sirkar Lecture

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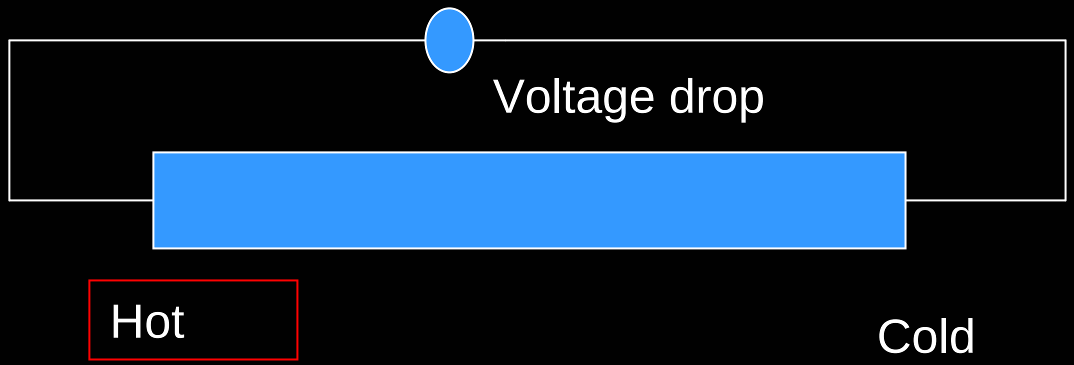
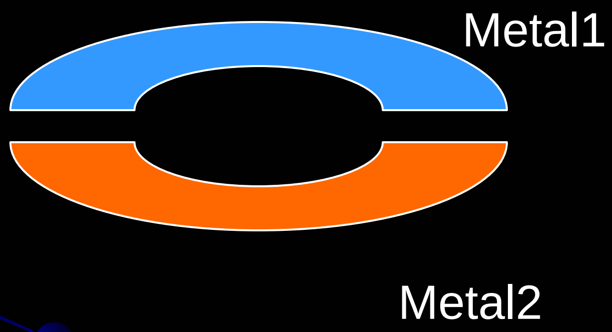
Abstract:
Thermoelectricity is a foundational topic in statistical mechanics, dealing with reversible heat generation from a current flow. Kelvin established reciprocity using thermodynamic arguments in the nineteenth century. This is mysterious since transport is not within the domain of thermodynamics, and indeed Onsager later gave the correct framework during his seminal work on reciprocity. With regard to the Kelvin, I point out the origin of the mysterious "flaw in the ointment". Strangely enough, Kelvin's argument produces a fairly useful, if inexact estimator of thermopower in certain situations.

After this historical footnote, I turn to the transition metal oxide Correlated materials, which are classical Mott Hubbard systems. Here the time honoured Bloch-Boltzmann equation approach meets a dead end, and must be discarded. (I display a cartoon based on the science fiction series Star Trek. A detailed knowledge of this series is helpful for understanding this part of the talk!).

A new formalism, using dynamical heat response, enables a quantitative understanding of the sodium cobaltate materials. It also provides some new predictions for as yet unknown materials, with extremely large thermopower.

Thermoelectricity: Some background





Current source if we maintain the two ends of the junction at a different T. (Space applications)

Refrigerator if we pass current from external source (laptops, car seat coolers or heaters)

Enormous industry in 21st century.

19th century History:

Seebeck, Peltier, Thomson(=Kelvin)..

$$\frac{1}{\Omega}\langle \hat{J}_x \rangle = L_{11}E_x + L_{12}(-\nabla_x T/T)$$
$$\frac{1}{\Omega}\langle \hat{J}^Q_x \rangle = L_{21}E_x + L_{22}(-\nabla_x T/T),$$

where $(-\nabla_x T/T)$ is regarded as the *external driving thermal force*, and $\hat{J}^Q_x$ is the heat current operator.

$$S = \frac{\Delta V}{\Delta T} = \frac{L_{12}}{TL_{11}}$$

Seebeck coefficient, defined for vanishing current (also called Thermopower).

$$L_{12} = L_{21}$$

- Famous Reciprocity "proven" by Kelvin using only thermodynamics. 1850's
- Re-proven by Lars Onsager 1930's using dynamics
- **According to Wannier's book on Statistical Physics "**Opinions are divided on whether Kelvin's derivation is fundamentally correct or not**".**

Search continues for materials with better Thermopower as well as Figure of merit Z

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

- Seeking simultaneously :
- High S (thermopower or Seebeck)
- High electrical conductivity σ
- Low Thermal conductivity κ

Holy grail

Z T ~ 1

at low T.

OLD HAT

The use of semiconductors in thermoelectric refrigeration

By H. J. GOLDSMID, B.Sc., and R. W. DOUGLAS, B.Sc., F.S.G.T., F.Inst.P., Research Laboratories, The General Electric Co. Ltd., Wembley, Middlesex

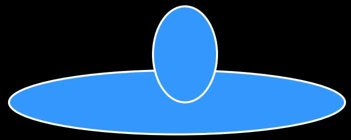
[*Paper received 6 July*, 1954]

In the past the possibility of thermoelectric refrigeration has been considered, but all attempts to produce a practical refrigerator have failed owing to lack of suitable thermocouple materials. In this paper it is proposed that semiconductors should be used and the factors governing their selection are discussed. It is concluded that the semiconductors should be chosen with high mean atomic weights and that they should be prepared with thermoelectric powers lying between 200 and 300 $\mu V.^{\circ}C^{-1}$. Preliminary experiments have led to the production of a thermocouple consisting of bismuth telluride, Bi_2Te_3, and bismuth, capable of maintaining 26° C of cooling.

Tribute to Mr H Julian Goldsmid

in 1954… | in 2004…

Honouring H Julian Goldsmid's contributions to thermoelectrics

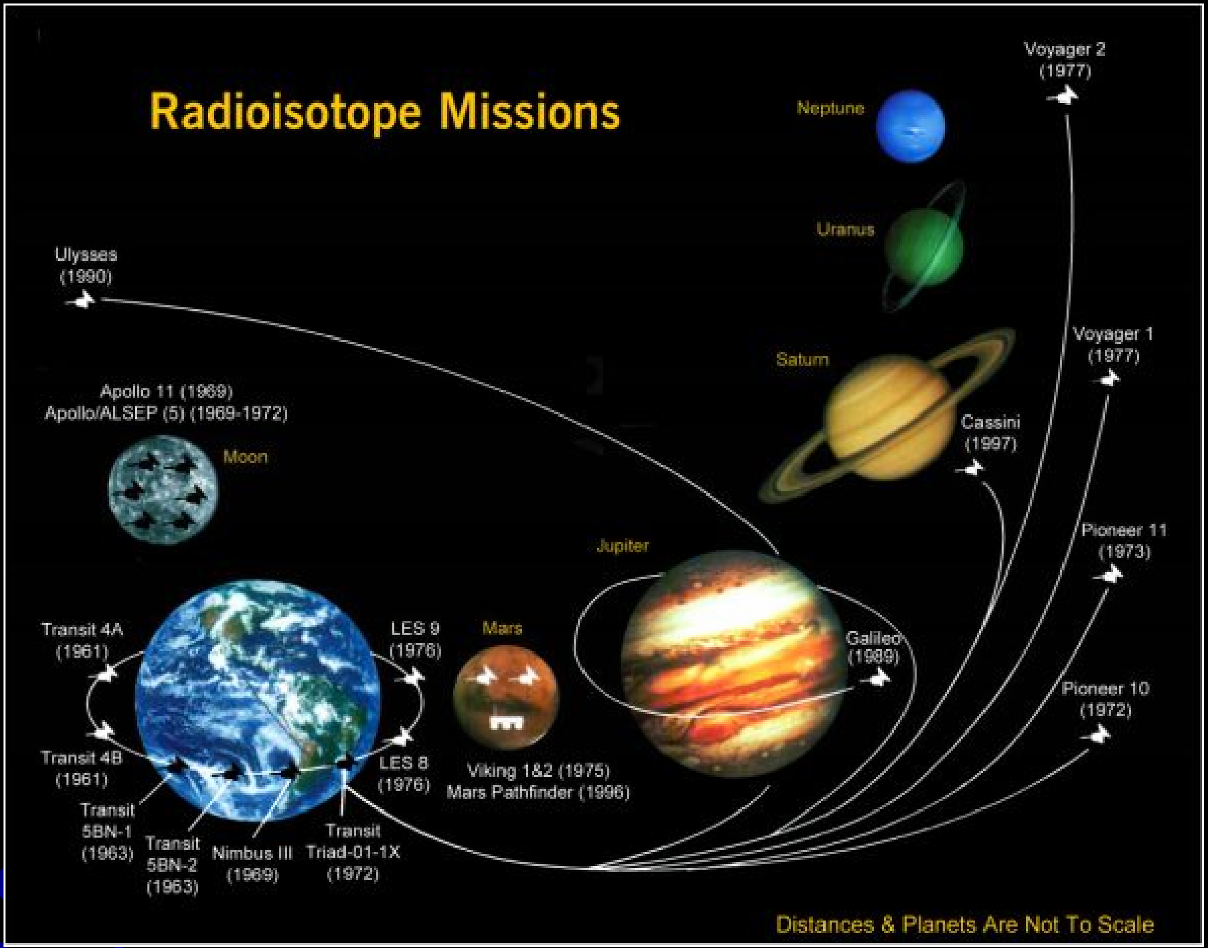
New: 

A Few Recent Headlines:

NASA:
"Thermoelectric Materials &
Technology for Future High Power Deep Space Science Missions."

The challenges and promises of oxides:
"**A Challenge to Create Novel Oxide Thermoelectrics**".

Thermoelectric Conversion System
thermoelectric technology as part of a concerted effort in Japan to
help prevent global warming.



The Cassini spacecraft, which is orbiting Saturn, is the most ambitious effort in planetary space exploration ever mounted. Cassini is a sophisticated robotic spacecraft which will orbit the ringed planet and study the Saturnian system in detail over a four-year period. This mission would not be possible if it were not for thermoelectrics which convert radioisotope heat into electricity.

What is new or interesting about all this from the Basic science point of view?

Fundamental interest in Condensed matter physics has moved in a direction away from simple non interacting systems towards strongly interacting systems.

Perturbation theory is inapplicable since there is **nothing small**.

From

Fermi liquid metals (Al, Cu,…the works!) and semiconductors (Bi_2Te_3 ….)

To

Oxide materials living on the edge.

Mott Insulating state and its doped descendents.

No “standard techniques available”: a great new frontier.

Zone of comfort:

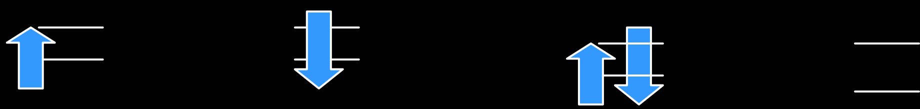
Bloch Boltzmann theory

Correlated metals and standard models of condensed matter physics:

From

Hubbard model

Single atom: Coulomb repulsion U on a s-like orbital.



Energy= e

Energy= e

Energy= 2e +U

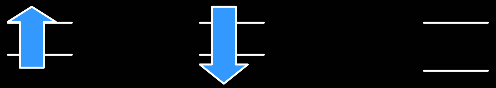
Energy= 0

$$H = -\sum_{i,j,\sigma} t_{ij} c^{\dagger}_{i\sigma} c_{j\sigma} + U \sum_j n_{j\uparrow} n_{j\downarrow}$$

To

The tJ model

Energy= e



Energy= e

Energy= 0

$$H = P_G T P_G + J \sum_{ij} \vec{S}_i . \vec{S}_j$$

Gutzwiller projector eliminates all doubly occupied states. J is small ~ t^2/U.

Eliminating states from Hilbert space changes the rules of QM. No longer canonical fermions but correlated fermions with different anticommutation relations.

Lose perturbation theory framework: Wick's theorem no longer valid, no Dyson eqn, no proper self energies….no fermi liquid, no……..no…no….

Also no Bloch Boltzmann theory:

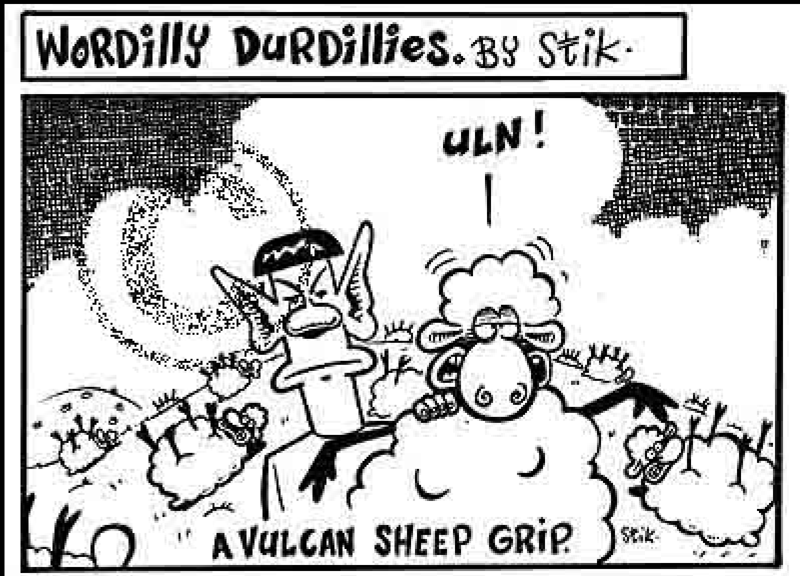
Boltzmann eqn uses the distribution function

$$f(\vec{k},\vec{r},t) = f_0(\vec{k}) + \delta f(\vec{k},\vec{r},t)$$

The first term is the equilibrium quasiparticle fermi fn, but it does not really exist in correlated systems if there is no fermi liquid!

Hugely unpopular statement. But it is true:
Most physicists find it hard to give up
Boltzmann eqn approach.

A very false approach for correlated matter, unfortunately very Strongly influential and pervasive



wikipedia

Vulcan death grip –
Derived from a Star Trek classic episode where a non- existan "Vulcan death grip" was used to fool Romulans that Spock had killed Kirk.

We have so far explained:

- What is thermopower or Seebeck coefficient and why it is interesting.
- What is a correlated metal (tJ model versus Hubbard model)
- What is the Boltzmann equation approach.

New formalism for computing transport in correlated systems. (New sum rule for thermal conductivity similar to the f-sum rule, Kelvin Onsager debate etc…)

Successes in explaining new class of materials Sodium cobaltates

New predictions for a new class of materials with even higher thermopower.

•**Kubo Onsager formulas "without tears", i.e alternate simple formulas!**

•**Finite ω response functions:**
•**Motivation and formalism**
•**New sum rule,**
•**Two new fundamental operators: Thermal operator ϑ and thermoelectric operator Φ.**

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.

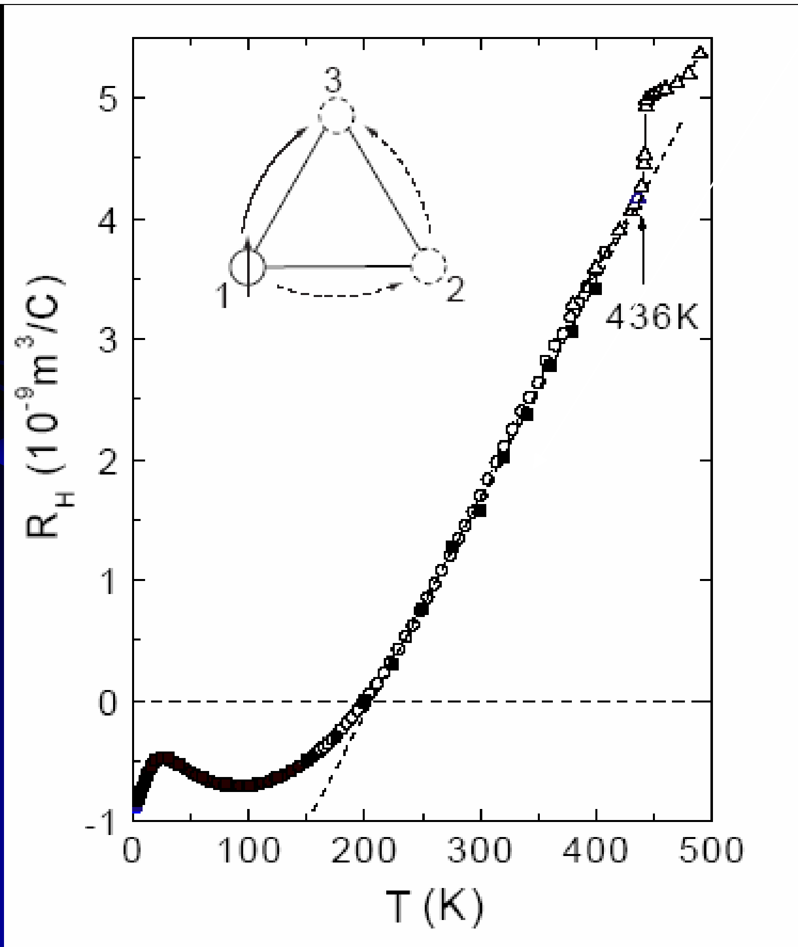
$$R_H{}^* = \frac{-i2\pi}{hB} N\text{v} < [J^x, J^y] > / < \tau_{xx} >^2$$

- 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]

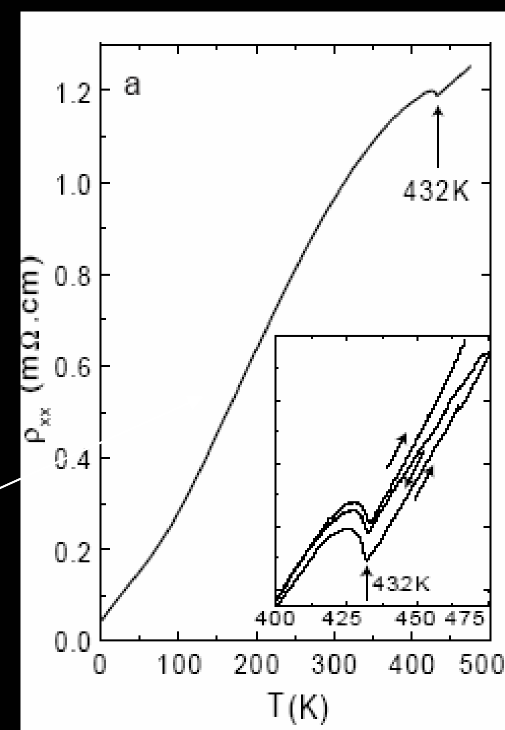
The Hall coefficient R_H of Na_xCoO_2 ($x = 0.68$) behaves anomalously at high temperatures (T)
From 200 to 500 K, R_H increases linearly with T to 8 times the expected Drude value, with no sign
of saturation. Together with the thermopower Q, the behavior of R_H provides firm evidence for
strong correlation. 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



Finite frequency thermal response functions:

Needed in many contexts, e.g. imagine a Si chip at 20 GHZ and its power dissipation. Neglected area with rather surprising new results. SS Phys Rev 2006

$$
\begin{aligned}
S^* &= \frac{L_{12}(\omega)}{L_{11}(\omega)T} \\
L^* &= \frac{L_{22}(\omega)}{T^2 L_{11}(\omega)} \\
Z^*T &= \frac{(S^*)^2}{L^*}
\end{aligned}
$$

All objects to be computed at large frequencies.

$$\begin{aligned}\frac{1}{\Omega}\langle \hat{J}_x\rangle &= L_{11}E_x + L_{12}(-\nabla_x T/T)\\ \frac{1}{\Omega}\langle \hat{J}^Q_x\rangle &= L_{21}E_x + L_{22}(-\nabla_x T/T),\end{aligned}$$

where $(-\nabla_x T/T)$ is regarded as the *external driving thermal force*, and $\hat{J}^Q_x$ is the heat current operator.

$$\kappa_{zc} = \frac{1}{TL_{11}}(L_{22}L_{11} - L_{12}L_{21}).$$

We want finite frequency versions of these…..Turn to Luttinger

$$K_{tot} = K + \sum_x K(\vec{x})\psi(\vec{x},t).$$

Here $K = \sum_x K(\vec{x})$, and $K(\vec{x}) = H(\vec{x}) - \mu n(\vec{x})$ is the *grand canonical* Hamiltonian

We can define the local temperature through

$$\delta T(\vec{x},t) = \frac{\delta \langle K(\vec{x},t)\rangle}{C(T)}.$$

Luttinger writes

$$\begin{aligned}
\frac{1}{\Omega}\langle \hat{J}_x\rangle &= L_{11}E_x + L_{12}(-\nabla_x T/T) + \hat{L}_{12}(-\nabla_x \psi(\vec{x},t)) \\
\frac{1}{\Omega}\langle \hat{J}^Q_x\rangle &= L_{21}E_x + L_{22}(-\nabla_x T/T) + \hat{L}_{22}(-\nabla_x \psi(\vec{x},t)),
\end{aligned}$$

Let $\psi(\vec{x},t) = \psi_q \exp\{-i(q_x x + \omega t + i0^+ t)\}$, (adiabatic switching implied) and the electric potential $\phi(\vec{x},t) = \phi_q \exp\{-i(q_x x + \omega t + i0^+ t)\}$ thus write

$$\delta J(q) = (iq_x)L_{11}(q_x,\omega)\phi_q + (iq_x)\left[L_{12}(q_x,\omega)\frac{\delta T_q}{T} + \hat{L}_{12}(q_x,\omega)\ \psi_q\right],$$

In equilibrium (i.e. static inhomogeneous limit) there is no net current therefore

$$0 = L_{12}(q,0)\frac{\delta T_q}{T} + \hat{L}_{12}(q,0)\psi_q.$$

However,

$$\lim_{\vec{q}\to 0}\psi(\vec{q},0) = -\lim_{\vec{q}\to 0}\frac{\delta T_q}{T}.$$

Hence We conclude that:

$$\lim_{q\to 0}\left[L_{12}(q,0) - \hat{L}_{12}(q,0)\right] = 0$$

Luttinger's identity

$$L_{ij}(q,\omega) = \hat{L}_{ij}(q,\omega)$$

Basic assumption of our work:

Generalized Luttinger's identity

Can compute RHS mechanically. Extension satisfies Causality, Onsager reciprocity and also Hydrodynamics at small q, w

$$\hat{J}_x^Q = \hat{J}_x^E - \frac{\mu}{q_e}\hat{J}_x,$$

where $\hat{J}_x^E$ is the *energy current* and $\hat{J}_x$ the charge current.

$$\hat{J}_x^Q = \lim_{q_x \to 0} \frac{1}{q_x}\left[K, K(q_x)\right].$$

$$\hat{J}_x^Q(\vec{q}) = \sum_x \hat{J}_x^Q(\vec{x}) \exp(i\vec{q}.\vec{x}), \quad \text{so that } \hat{J}_x^Q = \lim_{q \to 0} \hat{J}_x^Q(\vec{q}).$$

$$\begin{aligned} \delta\hat{J}_x &= L_{11}(q_x,\omega)(iq_x\phi_q) + L_{12}(q_x,\omega)(iq_x\psi_q) \\ \delta\hat{J}_x^Q &= L_{21}(q_x,\omega)(iq_x\phi_q) + L_{22}(q_x,\omega)(iq_x\psi_q). \end{aligned}$$

$$K_{tot} = K + [\rho(-q_x)\phi_q + K(-q_x)\psi_q]\exp\left(-i\omega t + 0^+ t\right),$$

We can reduce the calculations of all L_{ij} to essentially a single one, with the help of some notation. Keeping q_x small but non zero, we define currents, densities and forces in a matrix notation as follows:

	i=1	i=2
	Charge	Energy
$\mathcal{I}_i$	$\hat{J}_x(q_x)$	$\hat{J}^Q_x(q_x)$
$\mathcal{U}_i$	$\rho(-q_x)$	$K(-q_x)$
$\mathcal{X}_i$	$E^x_q = iq_x\phi_q$	$iq_x\psi_q.$

The perturbed Hamiltonian can then be written as

$$K_{tot} = K + \sum_j Q_j e^{-i\omega_c t}, \quad \text{where} \quad Q_j = \frac{1}{iq_x}\mathcal{U}_j\mathcal{X}_j.$$

$$\langle \mathcal{I}_i \rangle = -\sum_j \chi_{\mathcal{I}_i, Q_j}(\omega_c),$$

$$\begin{aligned}
\chi_{A,B}(\omega_c) &= -i\int_0^\infty dt\; e^{i\omega t - 0^+ t}\langle [A(t), B(0)]\rangle \\
&= \sum_{n,m} \frac{p_m - p_n}{\varepsilon_n - \varepsilon_m + \omega_c} A_{nm} B_{mn} \\
&= -\frac{1}{\omega_c}\left[\langle [A,B]\rangle + \sum_{n,m}\frac{p_m - p_n}{\varepsilon_n - \varepsilon_m + \omega_c} A_{nm}([B,K])_{mn}\right].
\end{aligned}$$

$$L_{ij}(q_x,\omega) = \frac{i}{\Omega\omega_c}\left[-\langle [\mathcal{I}_i, \mathcal{U}_j]\rangle \frac{1}{q_x} - \sum_{n,m}\frac{p_m - p_n}{\varepsilon_n - \varepsilon_m + \omega_c}(\mathcal{I}_i)_{nm}(\mathcal{I}_j^\dagger)_{mn}\right].$$

For arbitrary frequencies the Onsager functions read as

$$L_{ij}(\omega) = \frac{i}{\Omega\omega_c}\left[\langle\mathcal{T}_{ij}\rangle - \sum_{n,m}\frac{p_m - p_n}{\varepsilon_n - \varepsilon_m + \omega_c}(\mathcal{I}_i)_{nm}(\mathcal{I}_j)_{mn}\right],$$

$$\langle\mathcal{T}_{ij}\rangle = -\lim_{q_x\to 0}\langle[\mathcal{I}_i,\mathcal{U}_j]\rangle\frac{1}{q_x}.$$

The operators $\mathcal{T}_{ij}$ are not unique, since one can add to them a 'gauge operator" $\mathcal{T}_{ij}^{gauge} = [P, K]$ with arbitrary P. These fundamental operators play a crucial role in the subsequent analysis, since they

These important operators are written in a more familiar as follows:

Stress tensor	Thermal operator	Thermoelectric operator
$\mathcal{T}_{11}$	$\mathcal{T}_{22}$	$\mathcal{T}_{12} = \mathcal{T}_{21}$
τ^{xx}	Θ^{xx}	Φ^{xx}
$-\frac{d}{dq_x}\left[\hat{J}_x(q_x), \rho(-q_x)\right]_{q_x\to 0}$	$-\frac{d}{dq_x}\left[\hat{J}_x^Q(q_x), K(-q_x)\right]_{q_x\to 0}$	$-\frac{d}{dq_x}\left[\hat{J}_x(q_x), K(-q_x)\right]_{q_x\to 0}$

The thermoelectric operator can also be written as

$$\Phi^{xx} = \mathcal{T}_{21} = -\frac{d}{dq_x}\left[\hat{J}_x^Q(q_x), \rho(-q_x)\right]_{q_x\to 0},$$

$$
\begin{aligned}
L_{ij}(\omega) &= \frac{i}{\omega_c}\mathcal{D}_{ij} + \frac{1}{\Omega}\int_0^\infty dt\; e^{i\omega_c t} \int_0^\beta d\tau\; \langle \mathcal{I}_i(t-i\tau)\mathcal{I}_j(0)\rangle \\
\mathcal{D}_{ij} &= \frac{1}{\Omega}\left[\langle \mathcal{T}_{ij}\rangle - \sum_{nm}\frac{p_n - p_m}{\varepsilon_m - \varepsilon_n}(\mathcal{I}_i)_{nm}(\mathcal{I}_j)_{mn}\right]
\end{aligned}
$$

Generalized Kubo formulas for non dissipative systems. Contain a stiffness term that is interesting and non trivial.

Comment [1]: D terms is nonzero for supersystems- including integrable models. (No additional hypothesis needed as in Luttinger's paper on Superfluids.

Comment[2]: Sum rule for thermal conductivity is new.

``Sum rule for thermal conductivity and dynamical thermal transport coefficients in condensed matter '', B Sriram Shastry, Phys. Rev. B 73, 085117 (2006)

$$\int_{-\infty}^{\infty} \frac{d\nu}{2} \Re e \sigma(\nu) = \frac{\pi \langle \tau^{xx} \rangle}{2\Omega}$$

F sum rule

$$\int_{-\infty}^{\infty} \frac{d\nu}{2} \Re e \kappa(\nu) = \frac{\pi \langle \Theta^{xx} \rangle}{2T\Omega}, .$$

Thermal sum rule

$$\int_{-\infty}^{\infty} \frac{d\nu}{\pi} \Re e \kappa_{zc}(\nu) = \frac{1}{T\Omega} \left[\langle \Theta^{xx} \rangle - \frac{\langle \Phi^{xx} \rangle^2}{\langle \tau^{xx} \rangle} \right].$$

Zero current thermal conductivity where explicit value of μ is not needed.

Thermo power operator for Hubbard model

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

This object can be expressed completely in Fourier space as

$$\Phi^{xx} = q_e\sum_{\vec{p}}\frac{\partial}{\partial p_x}\left\{v_p^x(\varepsilon_{\vec{p}}-\mu)\right\}c^{\dagger}_{\vec{p},\sigma}c_{\vec{p},\sigma} + \frac{q_eU}{2\mathcal{L}}\sum_{\vec{l},\vec{p},\vec{q},\sigma,\sigma'}\frac{\partial^2}{\partial l_x^2}\left\{\varepsilon_{\vec{l}}+\varepsilon_{\vec{l}+\vec{q}}\right\}c^{\dagger}_{\vec{l}+\vec{q},\sigma}c_{\vec{l},\sigma}c^{\dagger}_{\vec{p}-\vec{q},\bar{\sigma}'}c_{\vec{p},\bar{\sigma}'}.$$

$$\tau^{xx} = \frac{q_e^2}{\hbar}\sum\eta_x^2\,t(\vec{\eta})\,c^{\dagger}_{\vec{r}+\vec{\eta},\sigma}c_{\vec{r},\sigma}\quad\text{or}$$
$$= \frac{q_e^2}{\hbar}\sum_{\vec{k}}\frac{d^2\varepsilon_{\vec{k}}}{dk_x^2}\,c^{\dagger}_{\vec{k},\sigma}c_{\vec{k},\sigma}$$

$$
\begin{aligned}
\Theta^{xx} &= \sum_{p,\sigma} \frac{\partial}{\partial p_x} \left\{ v^x_{\vec{p}} (\varepsilon_{\vec{p}} - \mu)^2 \right\} \; c^\dagger_{\vec{p},\sigma} c_{\vec{p},\sigma} + \frac{U^2}{4} \sum_{\eta,\sigma} t(\vec{\eta}) \eta_x^2 (n_{\vec{r},\bar{\sigma}} + n_{\vec{r}+\vec{\eta},\bar{\sigma}})^2 c^\dagger_{\vec{r}+\vec{\eta},\sigma} c_{\vec{r},\sigma} \\
&-\mu U \sum_{\vec{\eta},\sigma} t(\vec{\eta}) \eta_x^2 (n_{\vec{r},\bar{\sigma}} + n_{\vec{r}+\vec{\eta},\bar{\sigma}}) c^\dagger_{\vec{r}+\vec{\eta},\sigma} c_{\vec{r},\sigma} \\
&-\frac{U}{8} \sum_{\vec{\eta},\vec{\eta}',\sigma} t(\vec{\eta}) t(\vec{\eta}') (\eta_x + \eta'_x)^2 \left\{ 3 n_{\vec{r},\bar{\sigma}} + n_{\vec{r}+\vec{\eta},\bar{\sigma}} + n_{\vec{r}+\vec{\eta}',\bar{\sigma}} + 3 n_{\vec{r}+\vec{\eta}+\vec{\eta}',\bar{\sigma}} \right\} c^\dagger_{\vec{r}+\vec{\eta}+\vec{\eta}',\sigma} c_{\vec{r},\sigma} \\
&+\frac{U}{4} \sum_{\vec{\eta},\vec{\eta}',\sigma} t(\vec{\eta}) t(\vec{\eta}') (\eta_x + \eta'_x) \eta'_x c^\dagger_{\vec{r}+\vec{\eta},\sigma} c_{\vec{r},\sigma} \left\{ c^\dagger_{\vec{r}+\vec{\eta},\bar{\sigma}} c_{\vec{r}+\vec{\eta}+\vec{\eta}',\bar{\sigma}} + c^\dagger_{\vec{r}-\vec{\eta}',\bar{\sigma}} c_{\vec{r},\bar{\sigma}} - h.c. \right\} .
\end{aligned}
$$

Hydrodynamics of energy and charge transport in a band model:

This involves the fundamental operators in a crucial way:

$$\left\{\frac{\partial}{\partial t}+\frac{1}{\tau_c}\right\}\delta J(r)=\frac{1}{\Omega}\langle\tau^{xx}\rangle\left[\frac{1}{q_e^2}\frac{\partial\mu}{\partial n}(-\nabla\rho)-\nabla\phi(r)\right]+\frac{1}{\Omega}\langle\Phi^{xx}\rangle\left[\frac{1}{C(T)}(-\nabla K(r))-\nabla\Psi\right]$$

$$\left\{\frac{\partial}{\partial t}+\frac{1}{\tau_E}\right\}\delta J^Q(r)=\frac{1}{\Omega}\langle\Phi^{xx}\rangle\left[\frac{1}{q_e^2}\frac{\partial\mu}{\partial n}(-\nabla\rho)-\nabla\phi(r)\right]+\frac{1}{\Omega}\langle\Theta^{xx}\rangle\left[\frac{1}{C(T)}(-\nabla K(r))-\nabla\Psi\right]$$

Einstein diffusion term of charge

Energy diffusion term

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

$$\frac{\partial K(r)}{\partial t}+\nabla J^Q(r)=p_{ext}(r)$$

Continuity

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.

In General Kubo formulas are incorrect for non dissipative systems. The correct forms are:

$$\kappa(\omega) = \frac{i}{T(\omega + i0^+)} D_Q + \frac{1}{T\mathcal{L}} \int_0^\infty dt e^{i\omega t} \int_0^\beta d\tau \langle \hat{J}_x^Q(t - i\tau) \hat{J}_x^Q(0) \rangle.$$

$$\sigma(\omega) = \frac{i}{T(\omega + i0^+)} D_M + \frac{1}{T\mathcal{L}} \int_0^\infty dt e^{i\omega t} \int_0^\beta d\tau \langle \hat{J}_x(t - i\tau) \hat{J}_x(0) \rangle.$$

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

The two newly introduced operators Thermal operator Θ^{xx} , and thermo-electric 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

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

What about Kelvin-Onsager?

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

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.

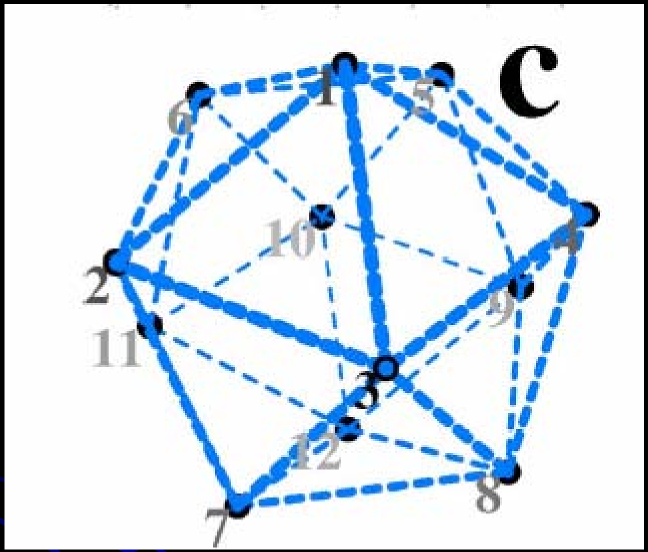
$$S = T\frac{\pi^2 k_B^2}{3q_e}\frac{d}{d\ \varepsilon}\ln[\rho(\varepsilon)\langle(v^x)^2\rangle_\varepsilon\tau(\varepsilon)]_{\varepsilon\to\mu}\ \text{Onsager- Kubo-Mott formula}$$

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

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

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

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

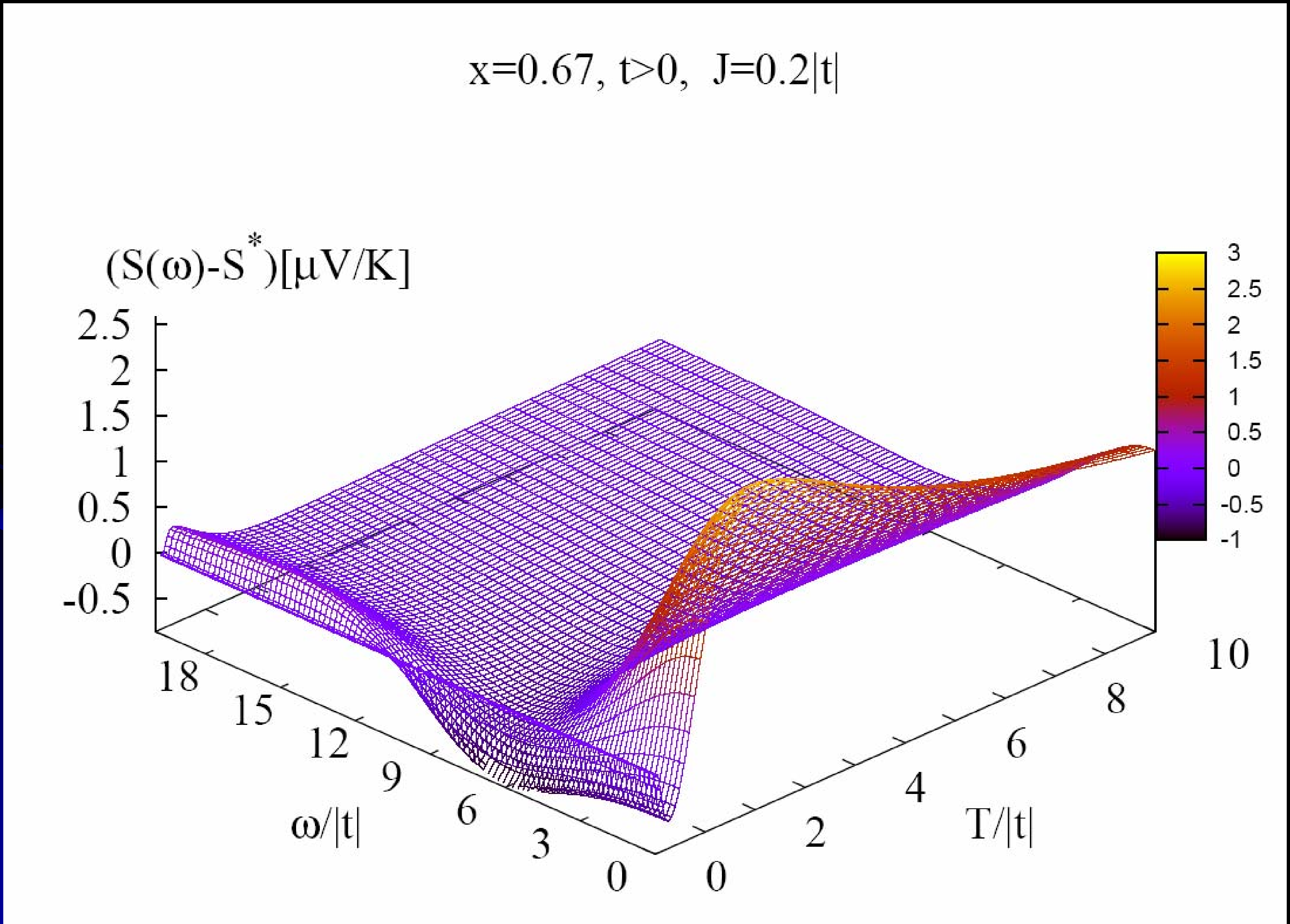
Modeled by t-J model with only two parameters “t=100K” and “J=36K”. Interested in Curie Weiss phase. Photoemission gives scale of “t” as does Hall constant slope of R_h and a host of other objects.

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

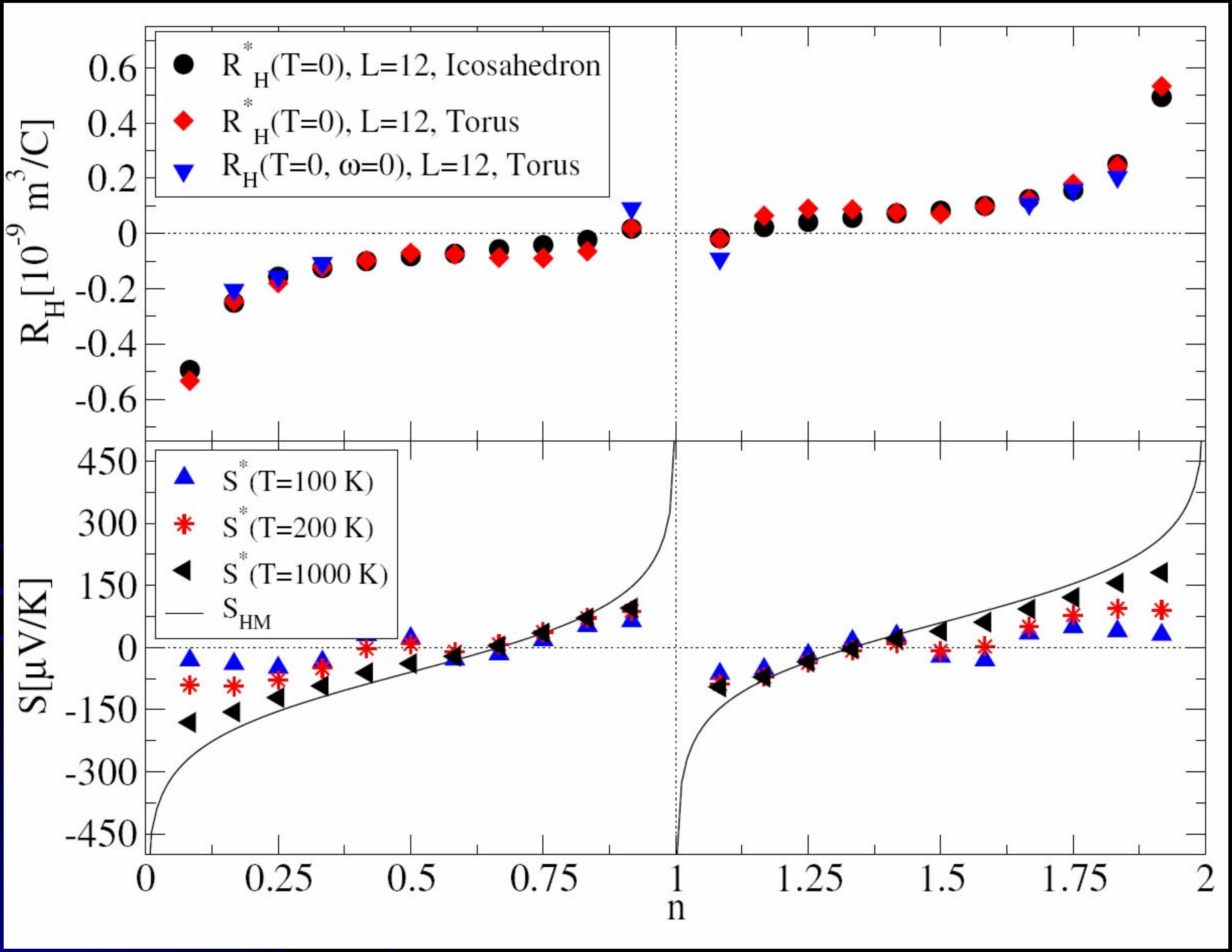
How good is the S* formula compared to exact Kubo formula?

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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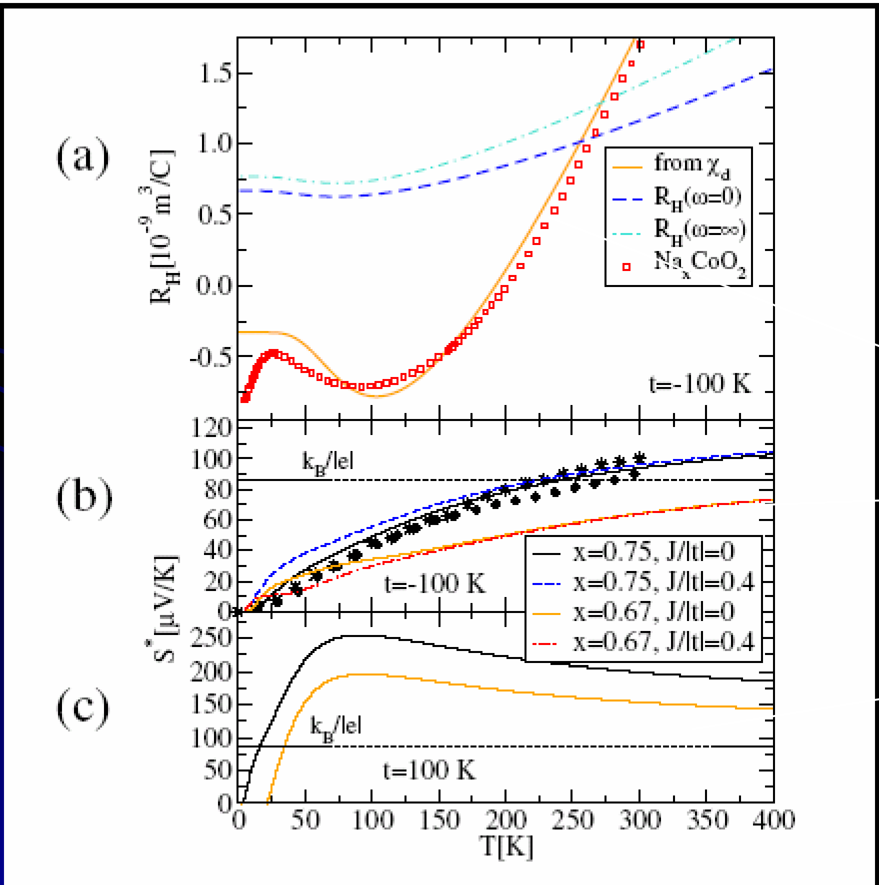
(Received 21 July 2006; published 28 November 2006)

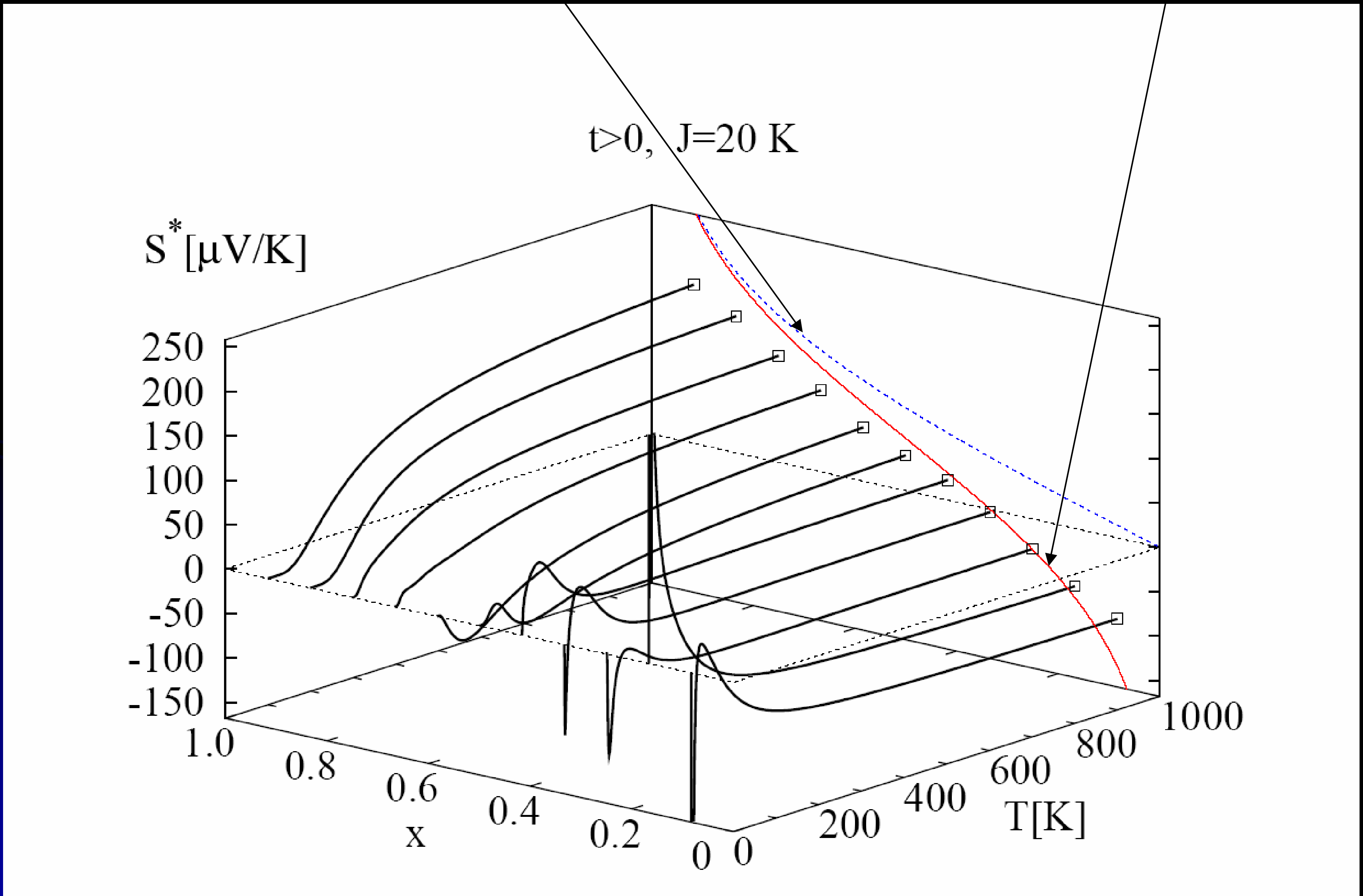


T linear Hall constant for triangular lattice predicted in 1993 by Shastry Shraiman Singh! Quantitative agreement hard to get with scale of "t"

Comparision with data on absolute scale!

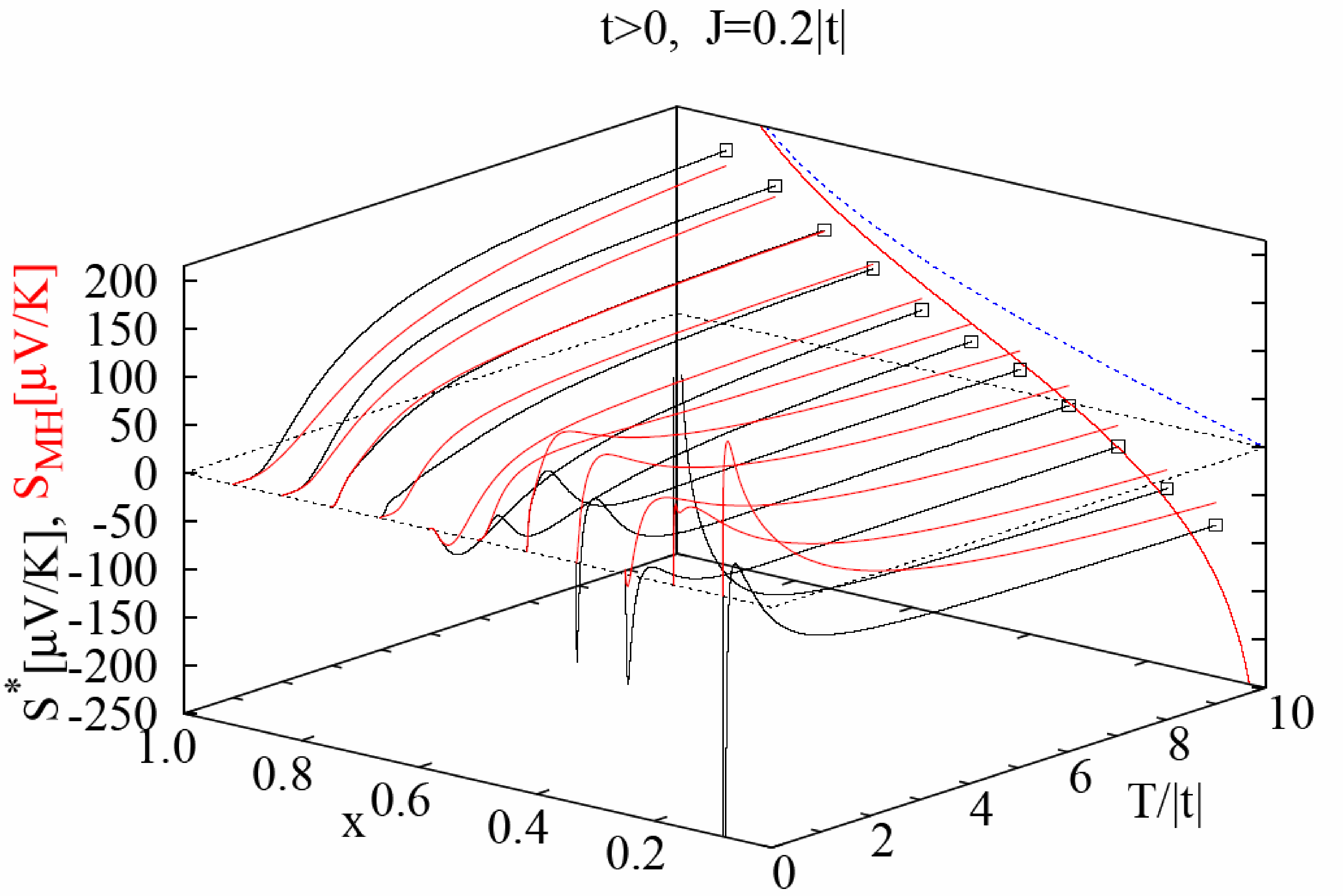
Prediction for t>0 material

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.

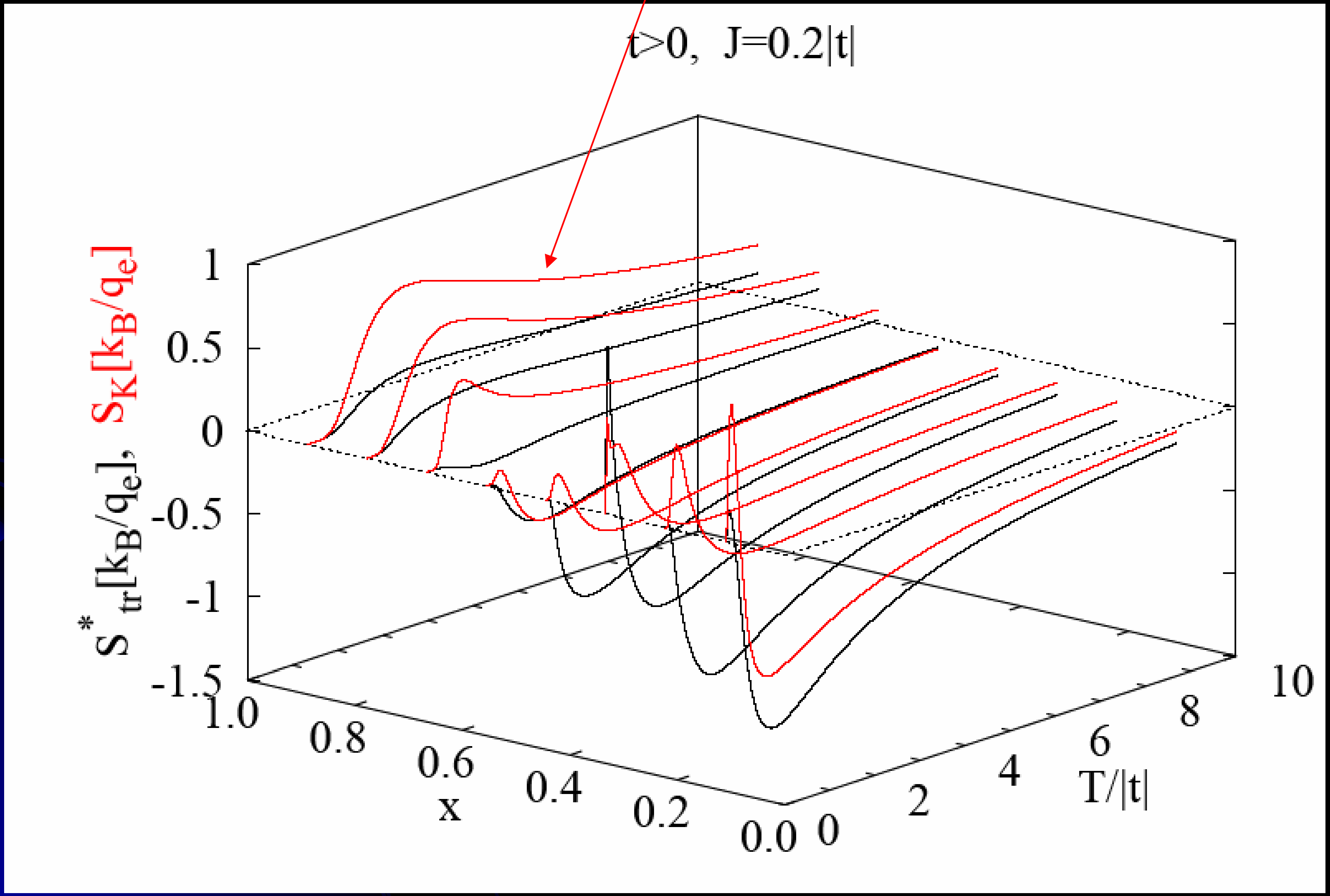


S* and the Heikes Mott formula (red) for Na_xCo O2.

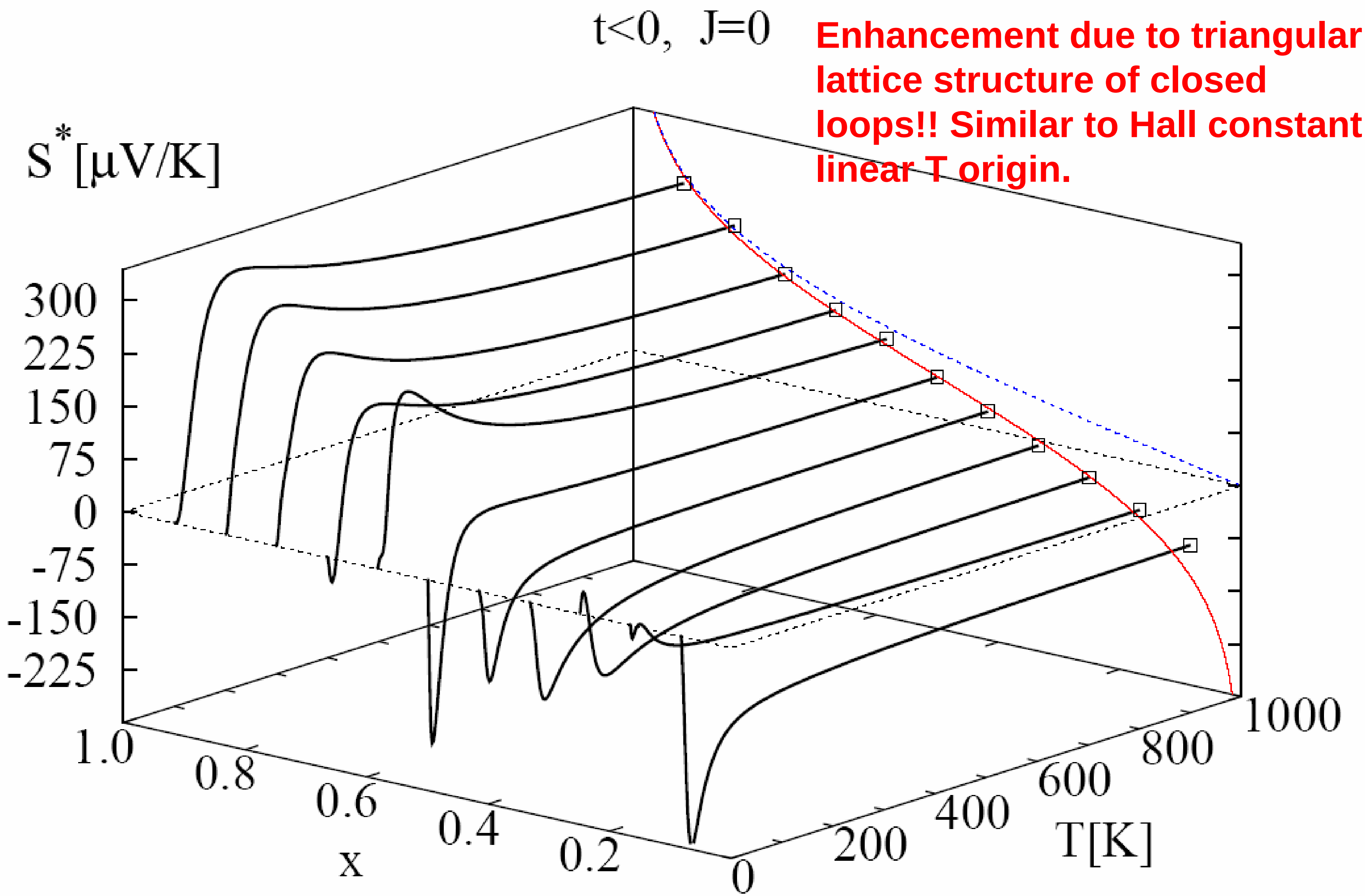
Close to each other for t>o i.e. electron doped cases



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.



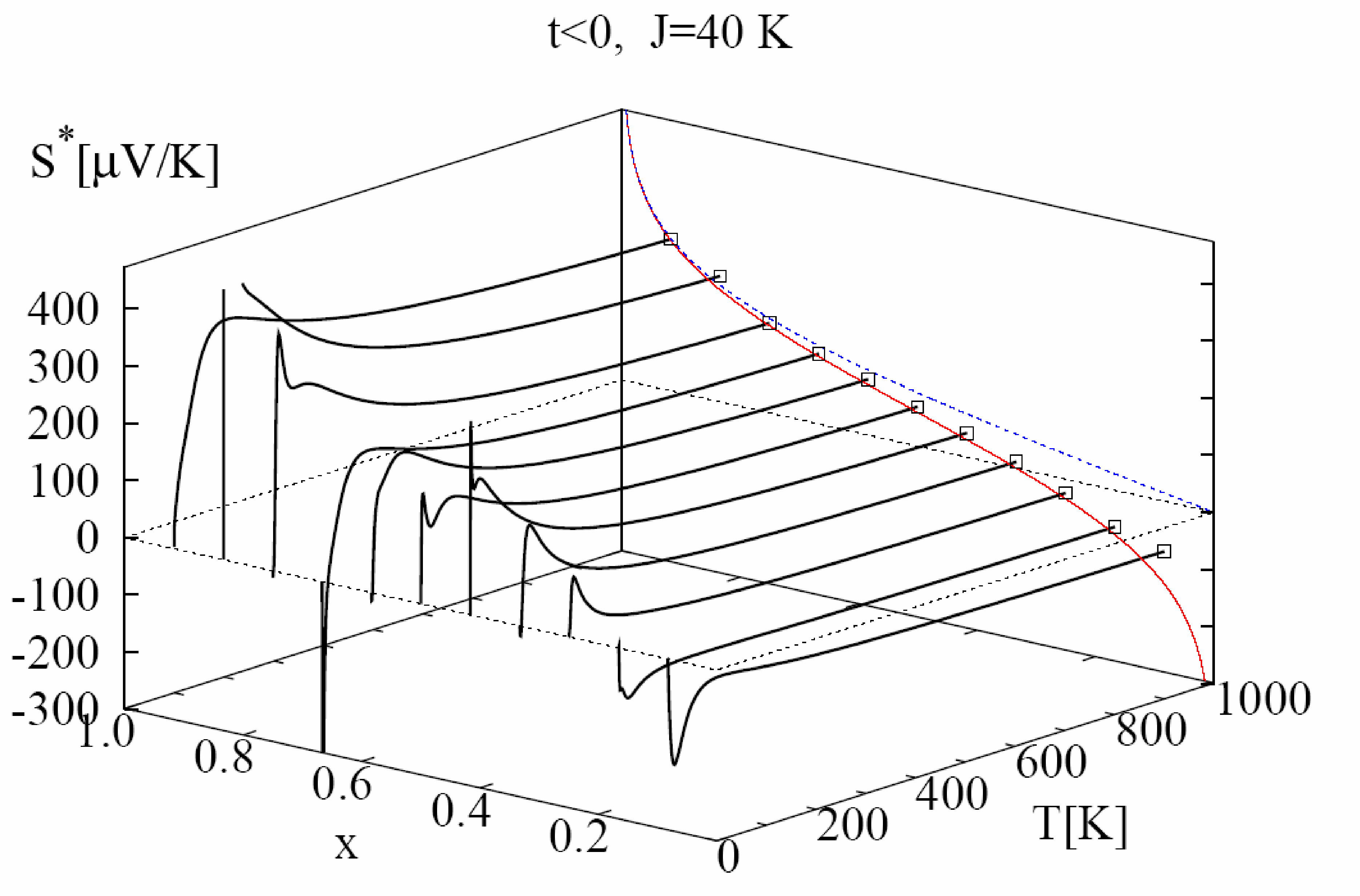
Predicted result for t<0 i.e. fiducary hole doped CoO_2 planes. Notice much larger scale of S* arising from transport part (not Mott Heikes part!!).



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

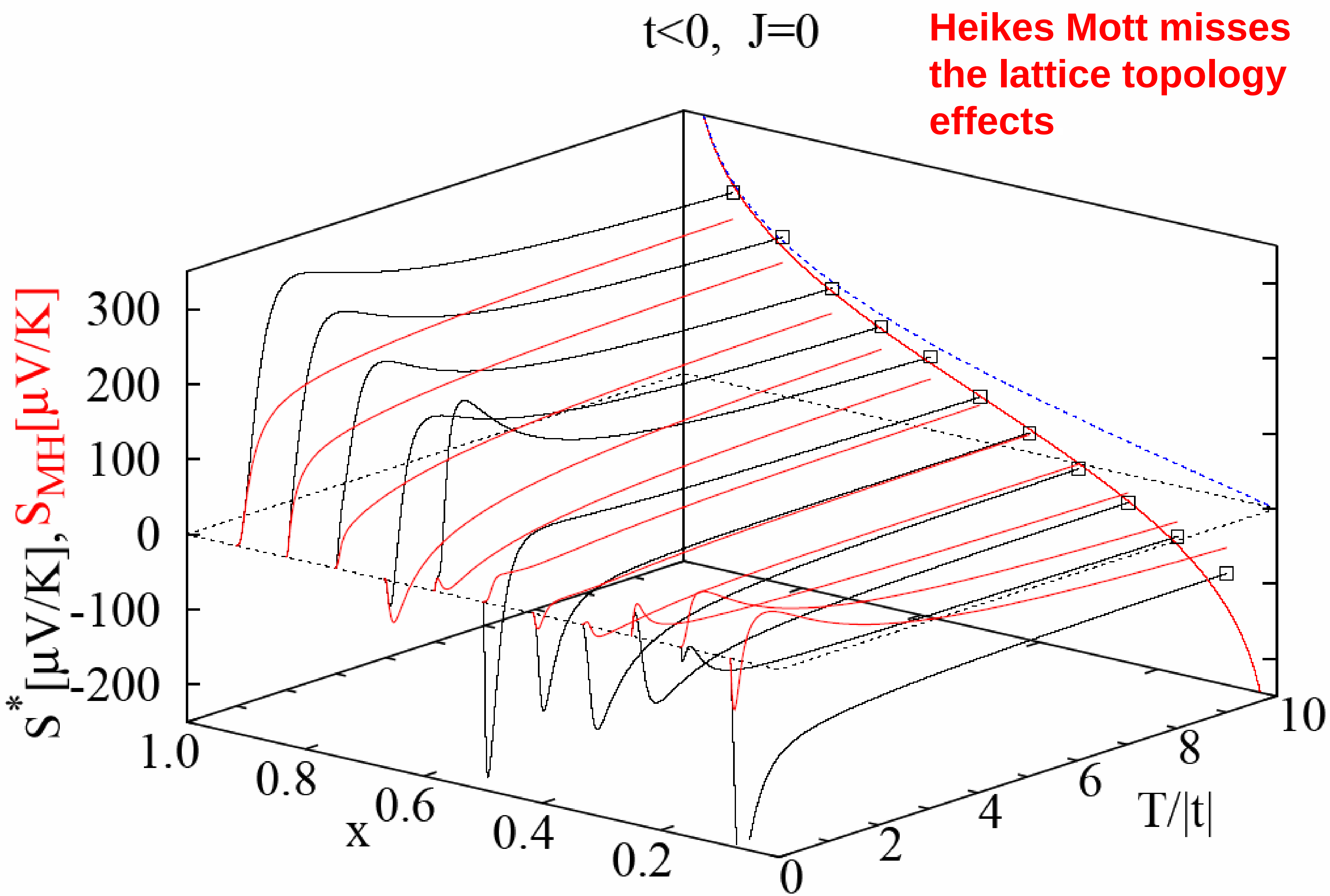
Predicted result for t<0 i.e. fiducary hole doped CoO_2 planes.

Different J higher S.



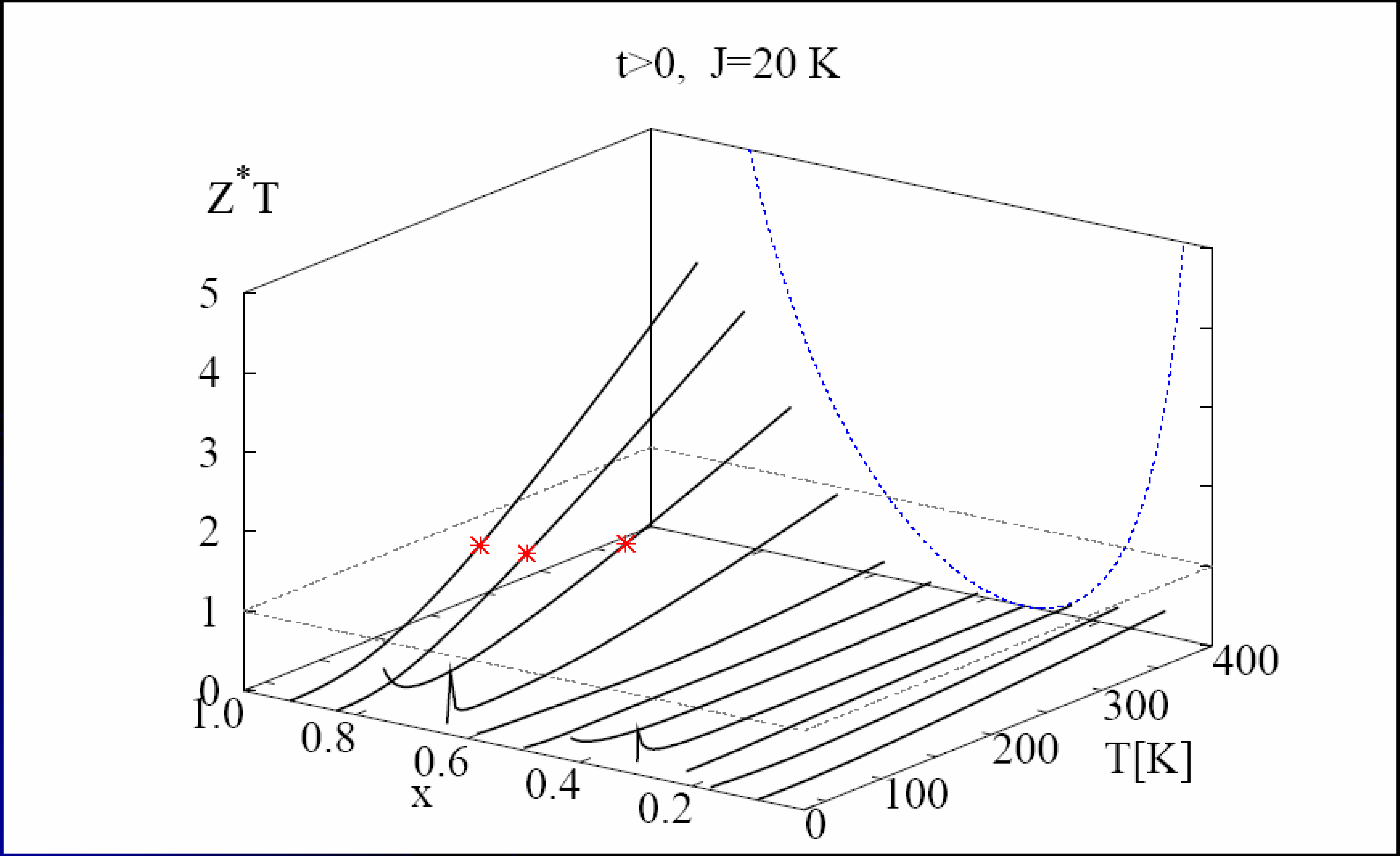
Predictions of S* and the Heikes Mott formula (red) for fiducary hole doped CoO2.

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.



Conclusions

- Basic science + applications are possible in condensed matter physics
- Theory can be useful even today, in surprising ways: e.g. prediction of material properties.
- Solid state chemistry is closer to modern correlated matter than much of traditional correlated matter physics.
- Oxides will always have a future!!