

"Understanding the effect of correlations on
Thermopower and Hall effect in sodium cobaltates:
A numerical study of Kubo formulas on finite
clusters"

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May 19th 2006

Mike Peterson and Jan Haerter:
Preprint in preparation



Work supported by

DMR 0408247

- Numerical work on evaluating Kubo formulas for conductivities on triangular lattice clusters.
- Exact evaluation by brute force summation over all energy states of small clusters, upto 12 or 14 sites in 2-d.
- Use of all symmetries in order to achieve diagonalization.
- Clever clusters help a lot: want to preserve translation invariance, local triangular geometry, and also achieve small enough flux so one is in the linear B regime:
- Artificial “Molecules” such as the Platonic solid, the Icosahedron- a 12 site perfect triangular lattice with 5 fold coordination, or more convoluted objects.
- Gives first quantitative results for interesting but notoriously hard objects such as thermopower and Hall constant.

Motivation:

Experiments:

$\text{Na}_x \text{CoO}_2$: Happy symbiosis of basic theory and technology.

- Large Thermo power
- Huge B dependence of Thermopower
- Strange Hall constant

Skutterudites:

- Cages and Rattlers; or how to manipulate lattice thermal conductivity

Heavy Fermi Systems

Theory:

- Updating Boltzmann theory: long lived almost free quasi particles are not a good starting point for most of these materials.
- Effect of strong correlations on transport.
- Understanding Mott Hubbard physics: what are holes?

Hall Effect in Strongly Correlated Matter

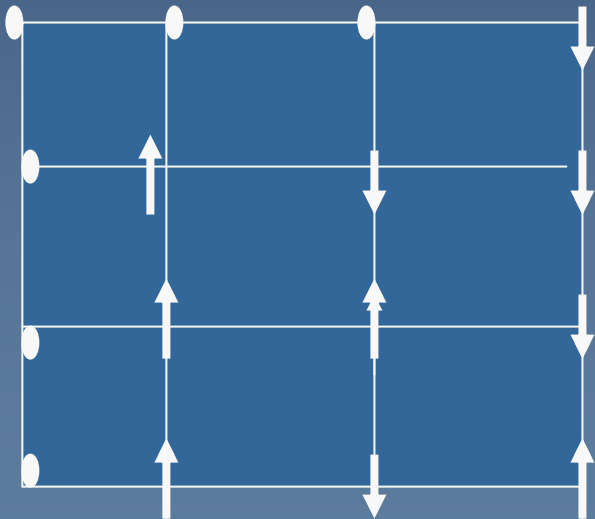
Standard expression says that Hall constant is a measure of carrier concentration:

$$R_H = 1/nec$$

Question: What is “n” for a Mott Hubbard system? Electron number of hole number (measured from half filling)?

Real space versus k space!!

$$-1/|e|n$$



Effect of correlations is profound.

It leads to a carrier freeze-out near half filling, and hence Hall constant diverges near half filling.

Need suitable transport theory for correlated matter, since Boltzmann approach fails.

Useful idea: Observe absence of relaxation time in Drude theory of several transport quantities, e.g Hall constant, thermopower, and Lorentz number. Hence w independent as well!! Can we exploit this insight?

Introduce object

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

- 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**

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

Why not compute at high frequencies from Kubo's formulas directly:

$$\sigma_{xx}(\omega) = \frac{i}{Nv\omega} \left[\langle \tau_{xx} \rangle - \frac{1}{Z} \sum \frac{e^{-\beta\varepsilon_n} - e^{-\beta\varepsilon_m}}{\varepsilon_m - \varepsilon_n - \omega} |\langle n | J^x | m \rangle|^2 \right]$$

$$= \frac{i\langle \tau_{xx} \rangle}{Nv\omega} + o(1/\omega^3)$$

Here τ is the stress tensor (k.e.) and v the cell volume

$$\sigma_{xy}(\omega) = \frac{-i}{Nv\omega Z} \sum \frac{e^{-\beta\varepsilon_n} - e^{-\beta\varepsilon_m}}{\varepsilon_m - \varepsilon_n - \omega} \langle n | J^x | m \rangle \langle m | J^y | n \rangle$$

$$= \frac{i}{Nv\omega^2} \langle [J^x, J^y] \rangle + o(1/\omega^3)$$

$$R_H^* = \frac{-i2\pi}{hB} N_V \langle [J^x, J^y] \rangle / \langle \tau_{xx} \rangle^2$$

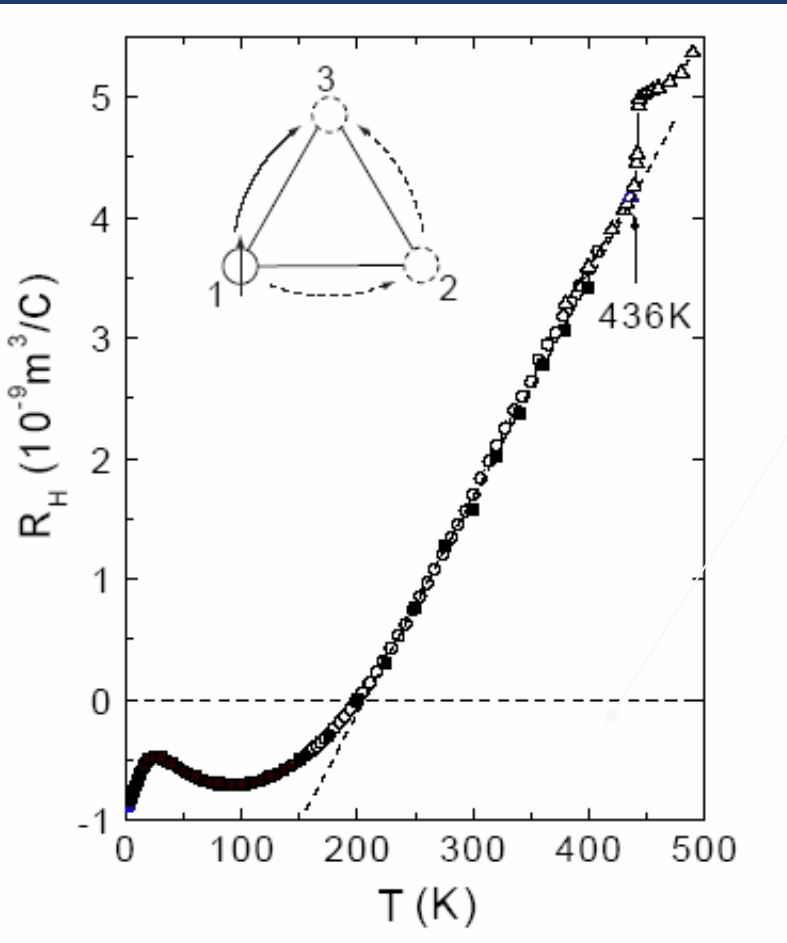
$$\omega \gg J$$

- 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 Wang¹, Nyrrisa S. Rogado², R. J. Cava^{2,3}, and N. P. Ong^{1,3}



Hall constant as a function of T for $x=0.68$ (CW metal). T linear over large range 200° to 436° .

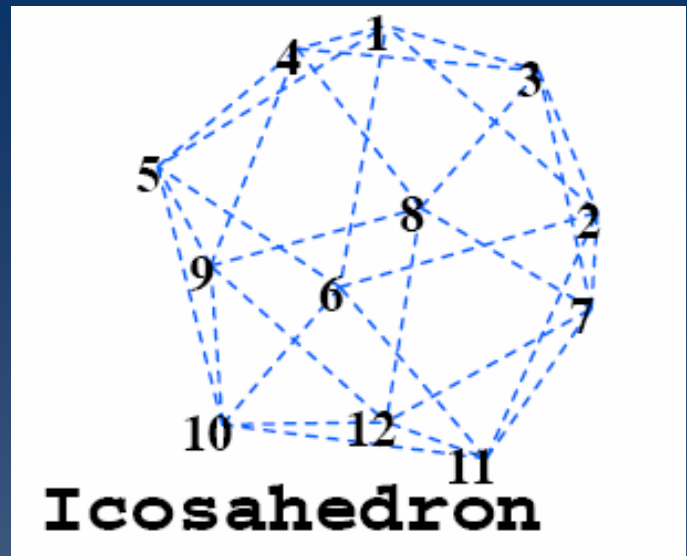
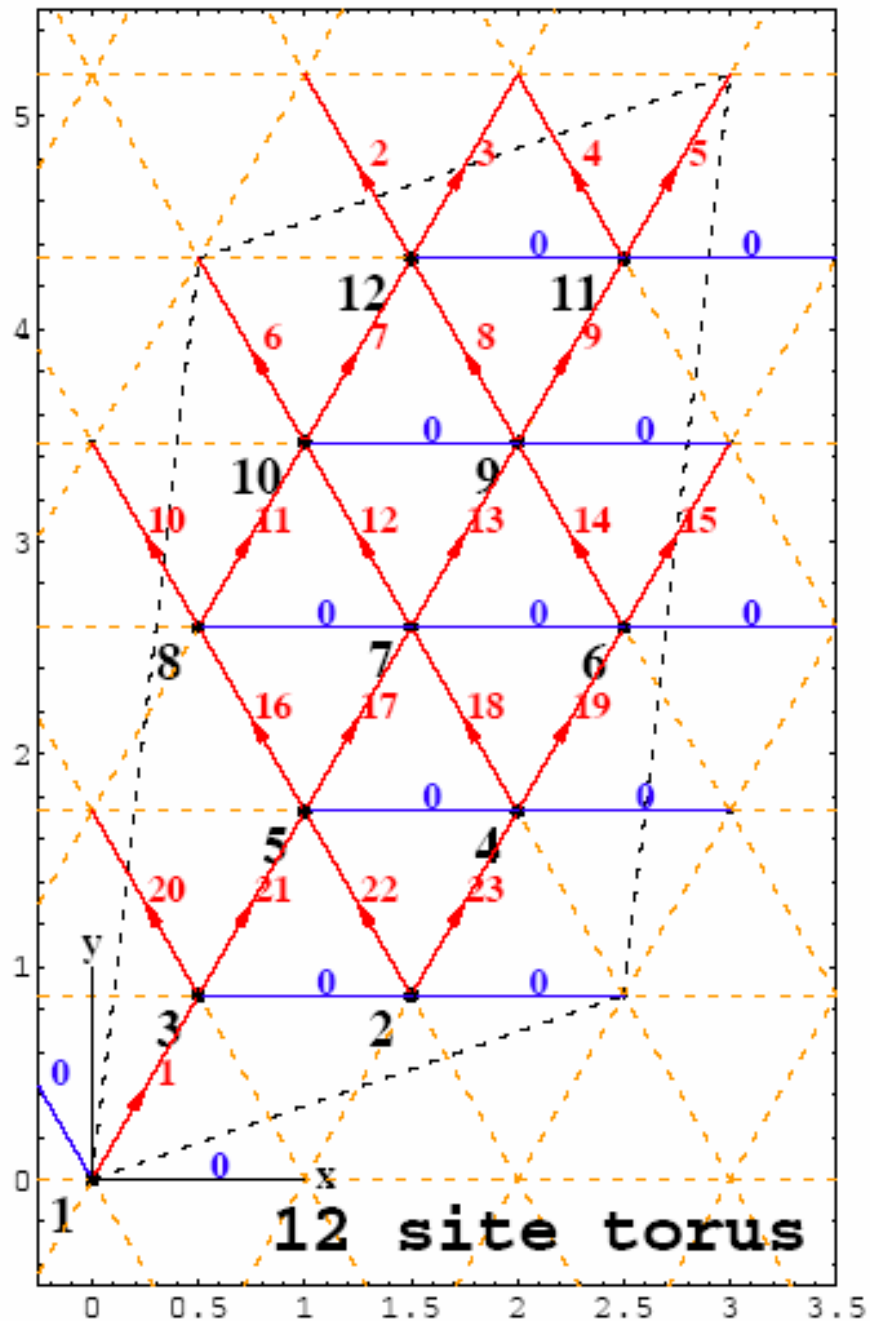
Predicted by theory of triangular lattice transport KS based upon calculation of R^* .

**STRONG
CORRELATIONS
& Narrow Bands**

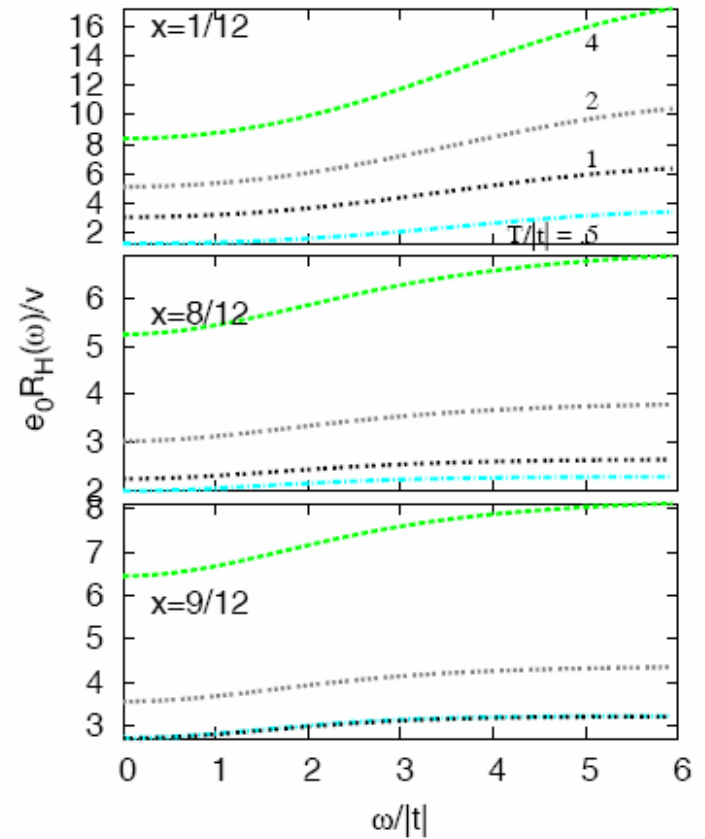
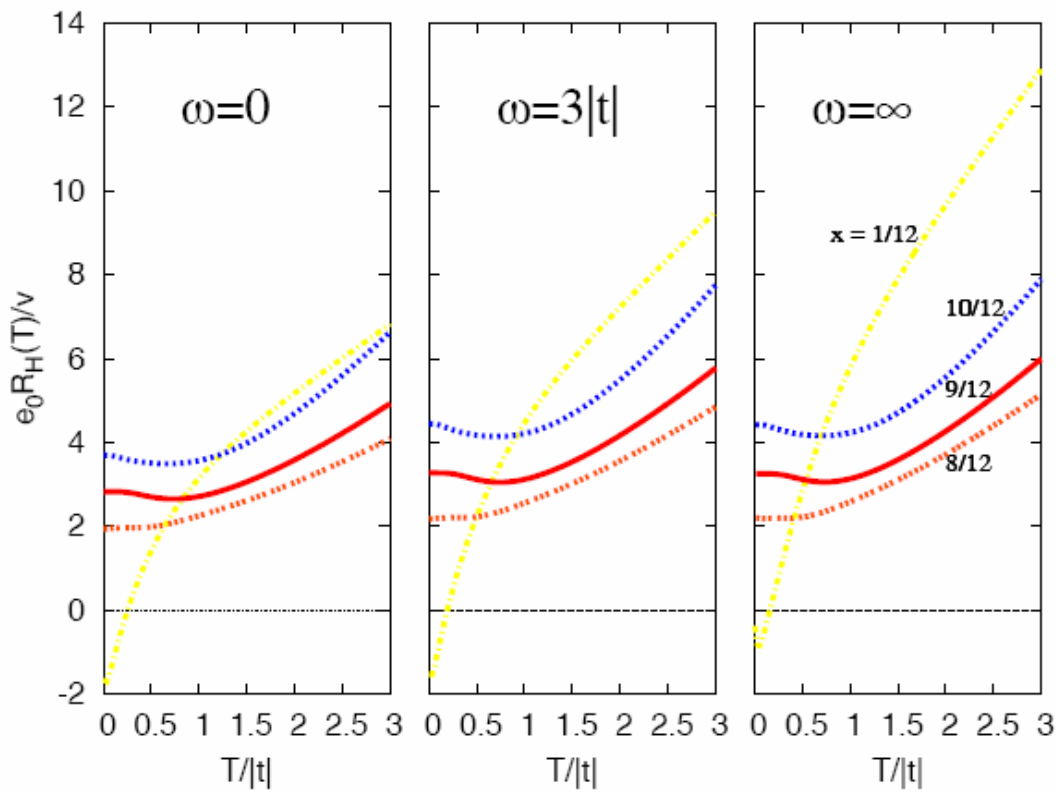
HOW GOOD IS THE LARGE w LIMIT?

WHAT ABOUT LOW w OBJECT?

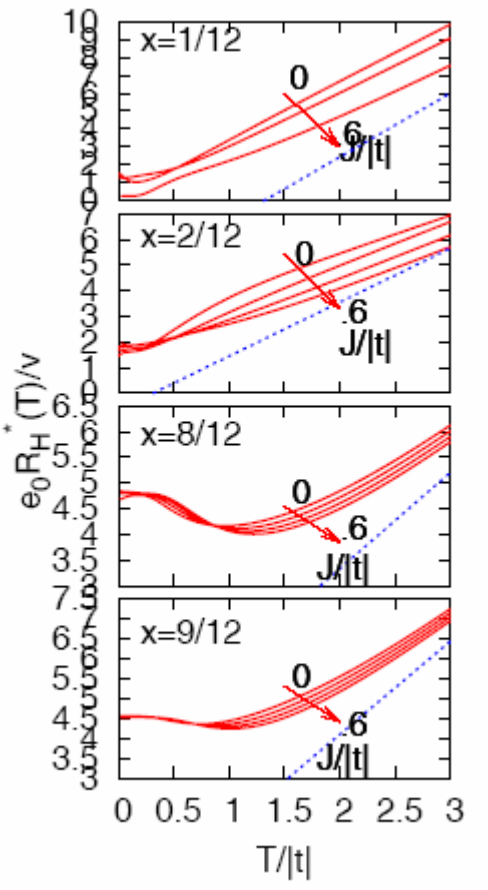
Answer: Clusters: Exact eval of Kubo formulas



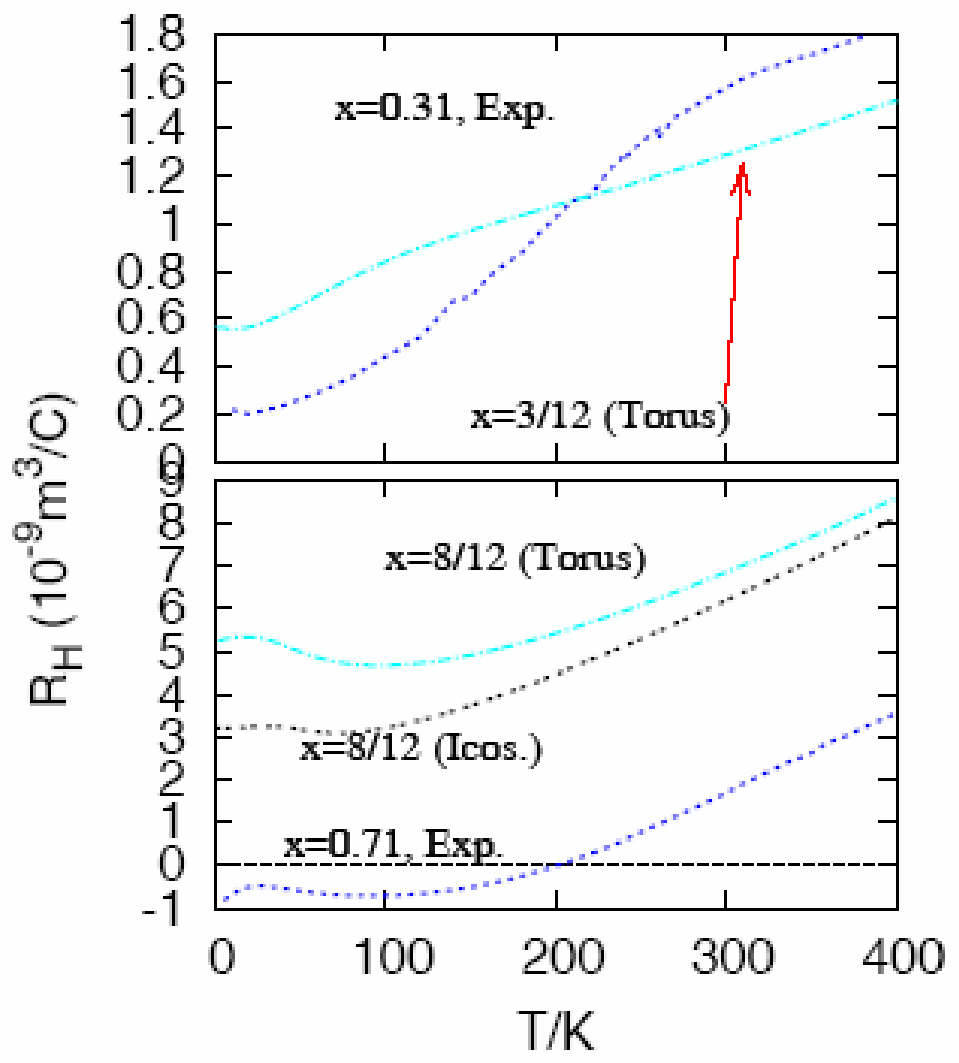
Our favourite clusters with 12 sites



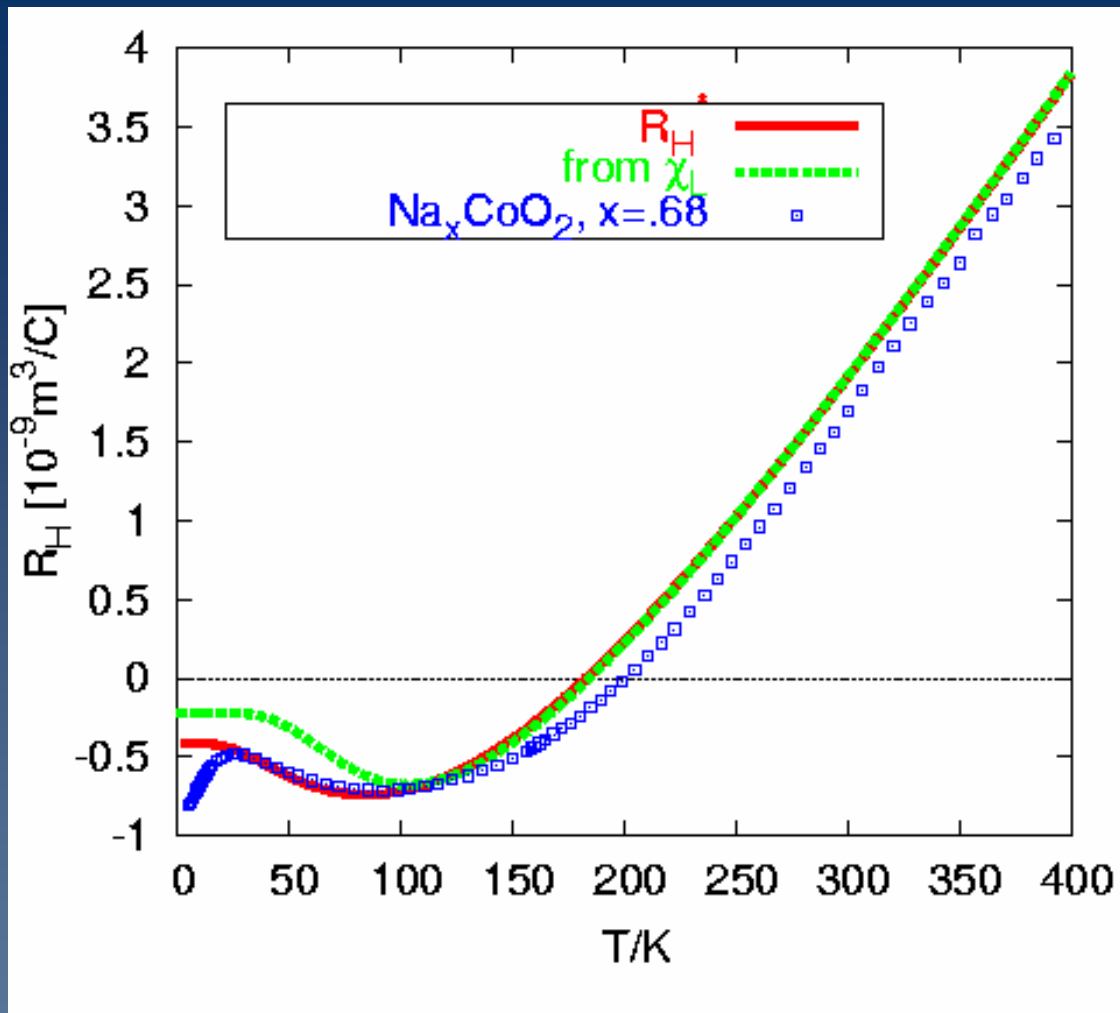
Frequency and temperature dependence of Hall constant for various fillings in the torus geometry. (similar results for ladder and also for icosahedron). T linear Hall constant common at all frequencies, and sets in at apxly same T and with similar slope (max differnece $\sim 15\%$)



Mild J dependence of slopes



How do we compare with experiments?
Ong Cava Wang..



We shift the R_H by a constant!

Surprisingly we find that the Landau diamagnetic susceptibility has an interesting correlation to R_H

$$T d^2 / dT^2 \chi_L(T) = c \quad d^2 / dT^2 R_H(T)$$

Thermopower S: in correlated matter

- Boltzmann theory + Band theory: inadequate to explain experiments in NCO. (T dependence, x dependence etc..)
- **Correlated systems: Heikes Mott Formula or Chaikin Beni approach:**
- **Need a theory that goes smoothly from low T FL type to Heikes Mott behavior**

Transport part

Entropic part

$$S = \frac{\langle\langle J_e; J_p \rangle\rangle}{T \langle\langle J_p; J_p \rangle\rangle} - \frac{\mu}{q_e T} \quad (1)$$
$$\sim \frac{\mu(0) - \mu(T)}{q_e T}$$

Scale of entropic part ~80-90 microvolt/degree. Transport part is essentially unexplored, except in fermi liquids. At low T there is cancellation between these terms.

$$S \sim T \rho'(\mu)$$

A Sum Rule for Thermal Conductivity and Dynamical Thermal Transport Coefficients in Condensed Matter - I

Cond-mat/0508711
Phys Rev 2005

SS Summer 05, August 29,
05

New formalism with new results: ->

- Thermal conductivity sum rule, analogous to plasma sum rule
- Thermo-power formula that is better than the Heikes- Mott - Zener formula. Transport contribution is evaluated and is correct at ALL temperatures for the free electron case, and presumably close to DC answer at all frequencies
- Thermoelectric figure of merit
- Lorentz ratio

Explicit results for NCO- a useful prediction regarding design of higher Thermopower materials.

WORK in progress-

Need frequency dependence of various objects

$$\kappa(\omega) \quad \rho(\omega) \quad S(\omega) \quad L(\omega) \quad Z(\omega)$$

Need to make sense of $T(\check{r}, t)$ or $T(\vec{q}, \omega)$

This is a tricky problem in non equilibrium stat mech- much thought and even more more confusion in 60's and 70's. Dormant field- but watch out since pulsed lasers are here. Ballistic regimes are much more accessible.

Luttinger makes the clever distinction between a mechanical response function and a thermodynamic response.

Luttinger's idea of transport can be generalized to finite frequencies.

$$K = K_0 + K_1 e^{-i\omega_c t}, \quad \omega_c = \omega + i0^+$$

with adiabatic switching from the infinitely remote past $t = -\infty$ as usual, and $K_0 = \sum_r K(r) = \sum_r (H(r) - \mu n(r))$. Here $H(r)$ is the energy density, and since we are mainly dealing with lattice models, we sum over r . The operator

$$K_1 = \sum_r \psi(r) K(r),$$

where $\psi(r)$ is a small (pseudo) gravitational field with some spatial variation such that its average is zero.

For long wavelengths and slow excitation Luttinger shows that

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

However, for arbitrary time and space variations, we can still compute these response functions, they correspond to either equilibrium or non equilibrium response to an APPLIED (rather than a self-consistent thermodynamical) temperature gradient.

$$\text{Re } \kappa(\omega) = \frac{\pi}{\hbar T} \delta(\omega) \bar{D}_Q + \text{Re } \kappa_{reg}(\omega) \text{ with}$$

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

Where

$$D_Q = \frac{1}{\mathcal{L}} \left[\langle \Theta^{xx} \rangle - \hbar \sum_{n,m} \frac{p_n - p_m}{\epsilon_m - \epsilon_n} |\langle n | \hat{J}_x^Q | m \rangle|^2 \right].$$

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

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

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

Meet the thermal operator Θ^{xx} : A new extensive operator that can be computed for any model.

Comment: **New sum rule.**

Exact parallel to the f-sum rule for optical conductivity.

D term related to second sound and missed by Kubo as well as Luttinger!!

So, what does Θ look like and what is its value? Answer is model dependent, and in brief, Θ is the specific heat times a velocity

$$\frac{\Theta^{xx}}{\hbar T} = \frac{1}{d} C_{\mu} v_{eff}^2$$

Thermo-power follows similar logic:

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

then the thermopower is

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

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

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

This is the thermo electric operator, a new extensive operator that can be worked out for any model using above formula. It is important since in the limit of $\omega \gg J$, the thermopower $S(\omega)$ is determined by the expectation of Φ^{xx} .

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

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

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

$$\mathcal{S}^* = \frac{\langle \Phi^{xx} \rangle}{T \langle \tau^{xx} \rangle}. \quad (3)$$

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

Here τ^{xx} is the Kinetic energy along x axis, i.e. $t c^\dagger(r + \eta_x)c(r)$

So we naturally ask

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

In the preprint: 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...

Free Electron Limit and Comparison with the Boltzmann Theory

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

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

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

$$\begin{aligned}\langle \mathcal{T}^{xx} \rangle &= 2q_e^2 \rho_0(\mu) \langle (v_{\vec{p}}^x)^2 \rangle_{\mu} \\ \langle \Theta^{xx} \rangle &= T^2 \frac{2\pi^2 k_B^2}{3} \rho_0(\mu) \langle (v_{\vec{p}}^x)^2 \rangle_{\mu}\end{aligned}\quad (1)$$

$$\langle \Phi^{xx} \rangle = T^2 \frac{2q_e \pi^2 k_B^2}{3} \left[\rho'_0(\mu) \langle (v_{\vec{p}}^x)^2 \rangle_{\mu} + \rho_0(\mu) \frac{d}{d\mu} \langle (v_{\vec{p}}^x)^2 \rangle_{\mu} \right], \quad (2)$$

We may form the high frequency ratios

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

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.

Some new results for strong correlations and triangular lattice:
Thermopower formula to replace the Heikes-Mott-Zener formula

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 $\Delta = \Delta_t + \Delta_J$ and

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

$$\begin{aligned} \Delta_J = & -\frac{1}{2} \sum_{r, \vec{\eta}, \vec{\eta}'} t(\vec{\eta}) J(\vec{\eta}') \eta_x \left[\frac{\eta_x}{2} \left\{ \vec{\mu}(\vec{r} + \vec{\eta}, \vec{r}) \cdot (\vec{S}(\vec{r} + \vec{\eta}') + \vec{S}(\vec{r} + \vec{\eta} + \vec{\eta}')) + \right. \right. \\ & \left. \left. (\vec{S}(\vec{r} + \vec{\eta}') + \vec{S}(\vec{r} + \vec{\eta} + \vec{\eta}')) \cdot \vec{\mu}(\vec{r} + \vec{\eta}, \vec{r}) + \eta'_x (\vec{S}(\vec{r} + \vec{\eta}' + \vec{\eta}') - \vec{S}(\vec{r} + \vec{\eta}')) \cdot \vec{\mu}(\vec{r} + \vec{\eta}, \vec{r}) \right] \end{aligned}$$

(2)

$$\mu^z(\vec{r}_1, \vec{r}_2) = \frac{1}{2} \left[c_{\vec{r}_1, \uparrow}^\dagger c_{\vec{r}_2, \uparrow} - c_{\vec{r}_1, \downarrow}^\dagger c_{\vec{r}_2, \downarrow} \right] \quad (3)$$

This is a useful alternative to Mott Heikes formula, and works at low T as well as high T.

Leading high temp expansion:

Note that (Chaikin- Beni)

$$\mu/k_B T = \log(n/2(1-n)) + O(\beta^2 t^2)$$

Thus for $0 \leq n \leq 1$

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

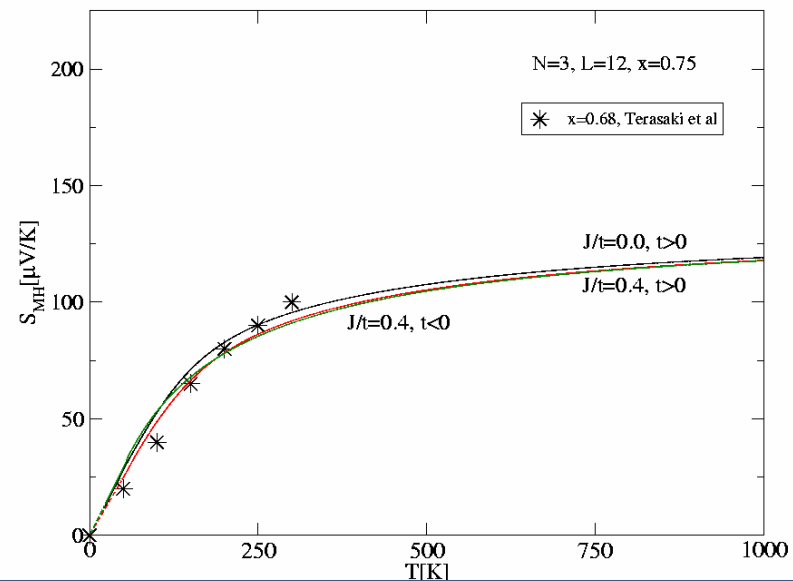
$$S^* = \frac{k_B}{q_e} \left\{ \log[2(n-1)/(2-n)] + \beta t \frac{n}{4} + O(\beta^2 t^2) \right\}$$

for $1 \leq n \leq 2$ using particle hole symmetry.

From the temperature dependence of the data of Terasaki et al and Yuyu Wang, Ong and Cava assuming $S \sim S^*$ one finds that $t = -110^0 K$, and with this, $S^* \sim 120 \mu V/K$, fairly close to the observed value.

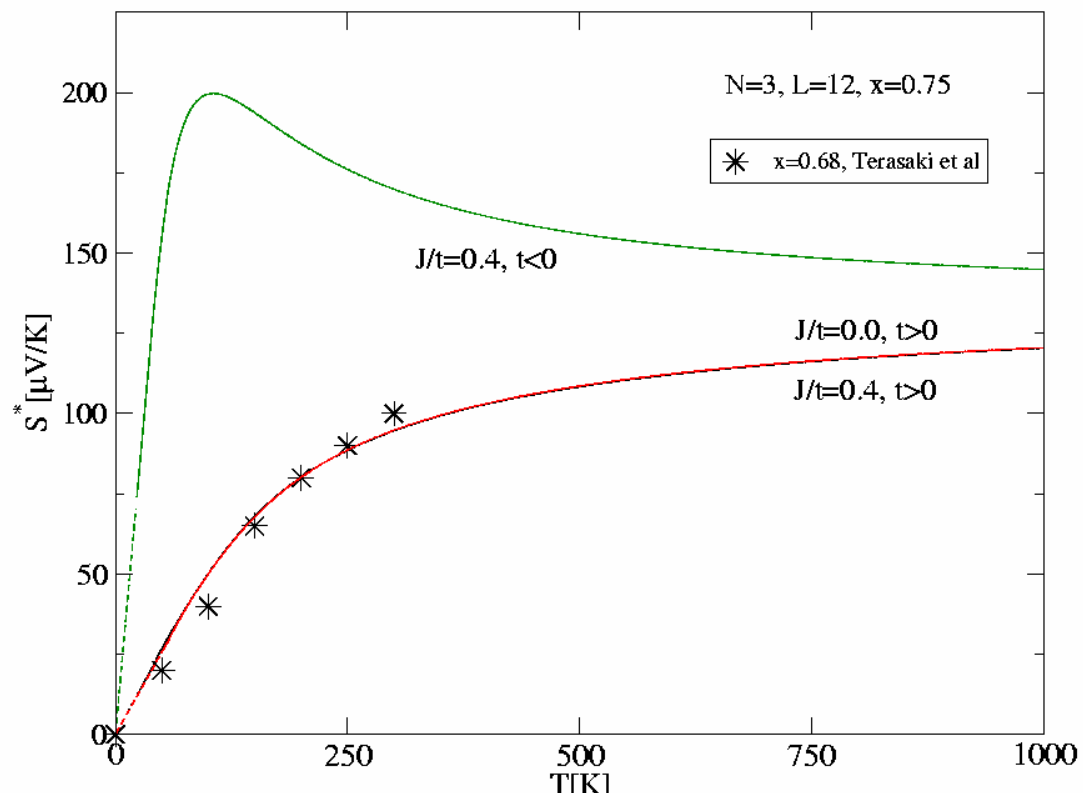
Note that in these high Temp expansions:

1. Correction is $O(\beta)$ for triangular lattice but $O(\beta^2)$ for square lattice. Hence larger transport correction for triangular lattice.
2. Prediction. If sign of t is +ve then (unfrustrated case) S will reach its asymptotic Heikes-Mott-Zener value FROM ABOVE, hence a peak in S must exist. Such a case must be the largest S for any metallic system.

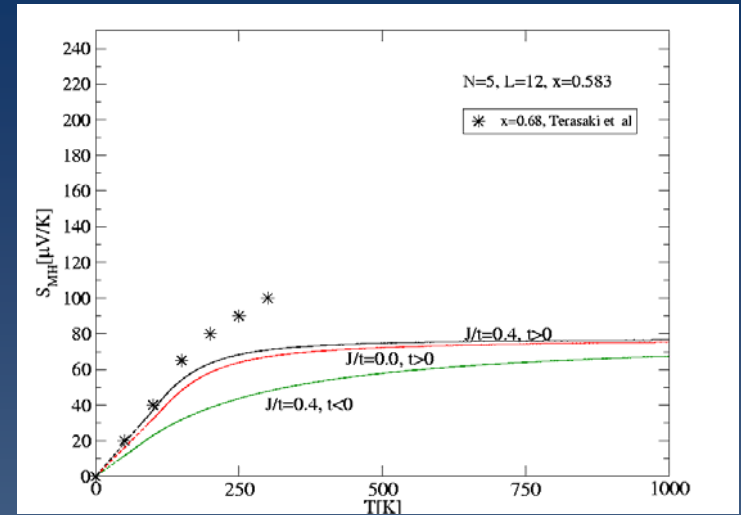
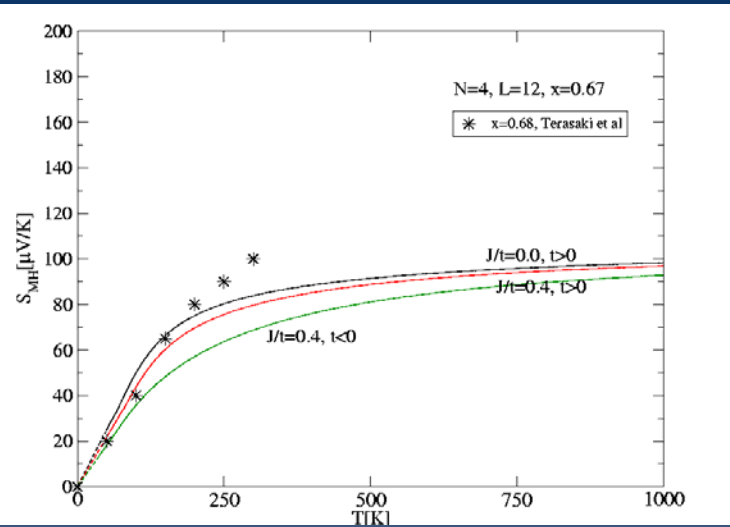


← Mott Heikes formula,
 i.e. $(\mu(0) - \mu(T)) / T$

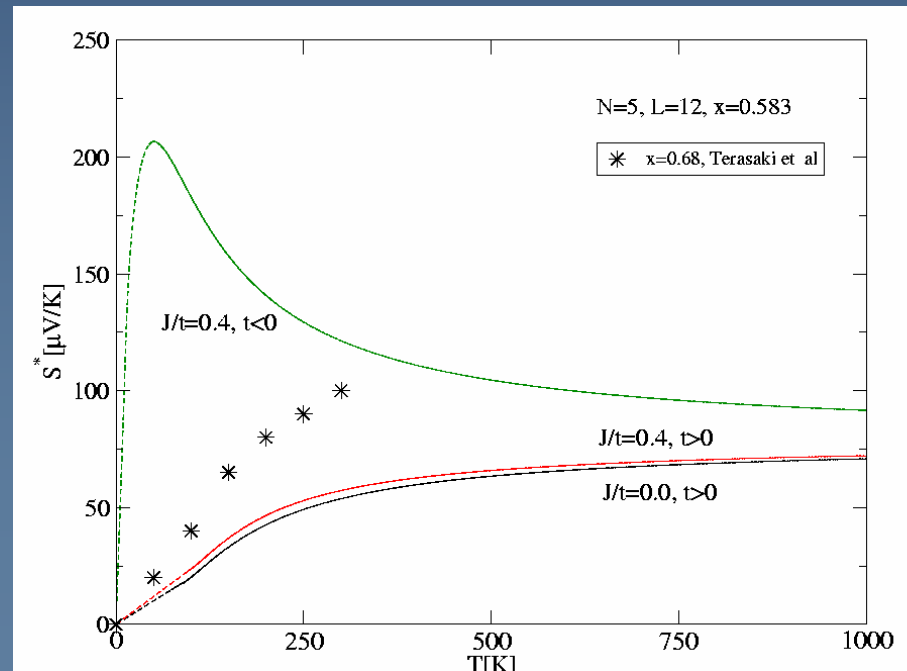
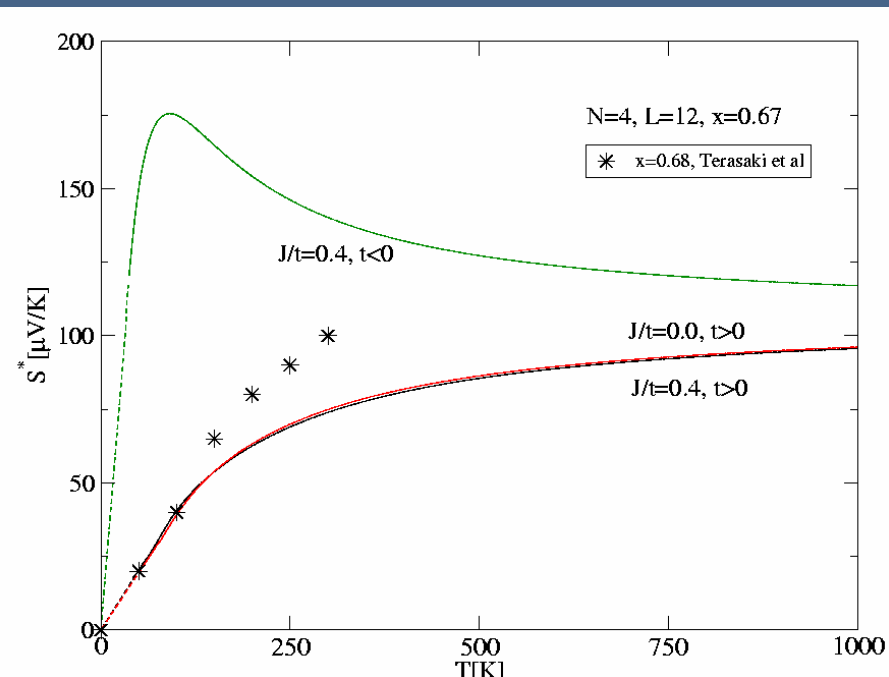
S^* for both signs of
 hopping. $X=.75$

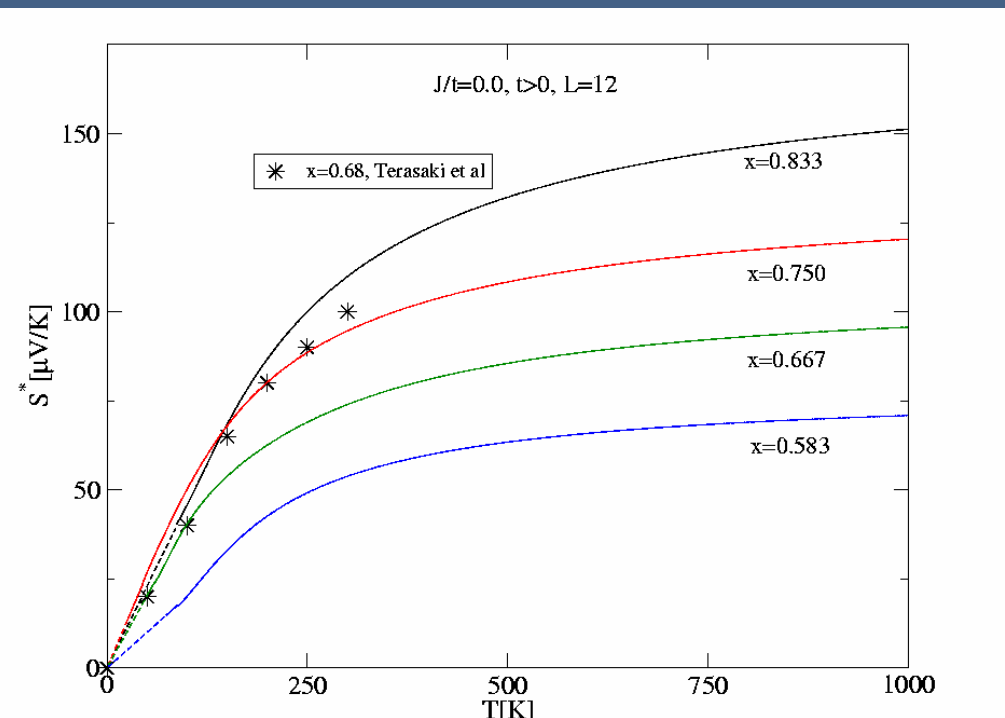
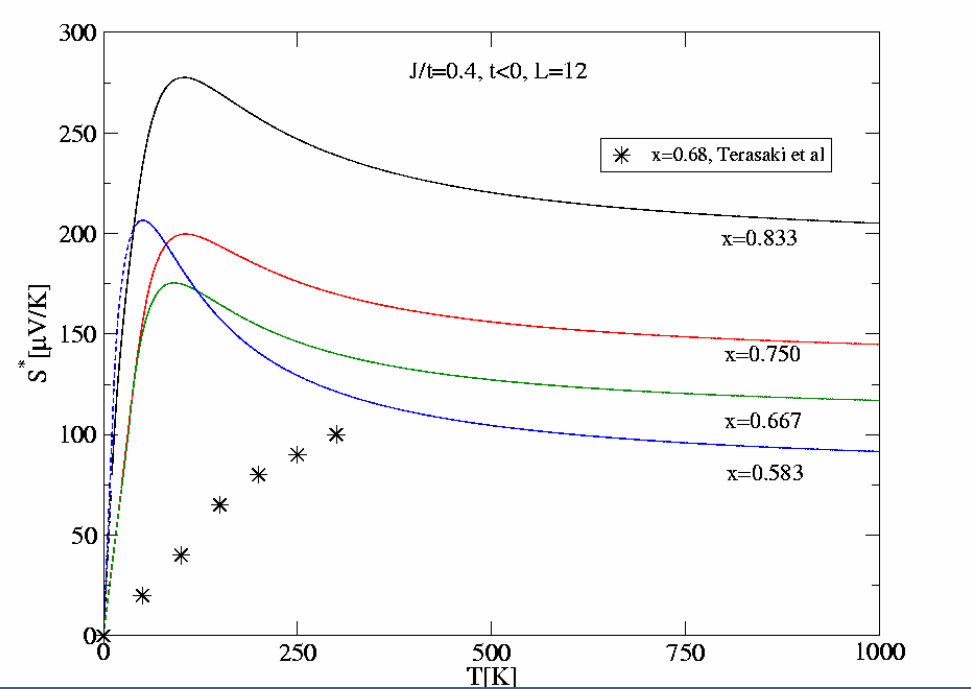


Mott Heikes formula, i.e. $(\mu(0) - \mu(T)) / T$

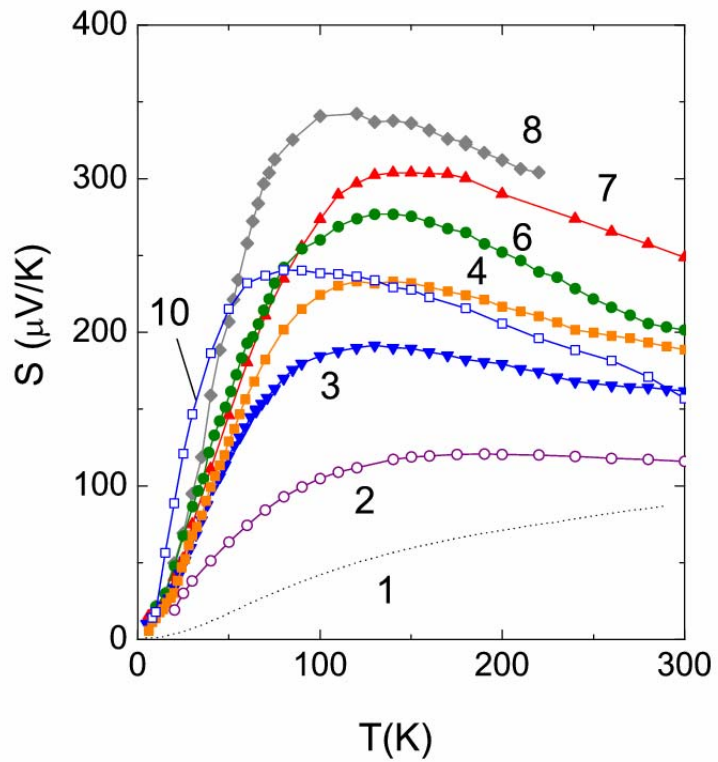


S^* for both signs of hopping.









Spectacular new data
from Phuan Ong and
Bob Cava and students.

Large density of states
derivatives....

Conclusions:

A useful way to compute transport constants in correlated matter is to combine numerics and S^* and R^* .

R^* is perhaps no more than 15% off transport values.

Role of transport corrections in the Heikes Mott Beni Chaikin formulas. We get a large correction in the proximity of almost filled bands, with opposite sign of hopping (unfrustrated case).

Sodium cobaltates are still pretty mysterious, they may not be described by single band t-J model for all fillings. Materials issues are pretty complex.

Lorentz number and possibly Nernst coefficient beckon....