Simple Insights into Thermopower of correlated matter

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June 13, 2012

Work supported by
DOE, BES DE-FG02-06ER46319

Three aspects of the thermopower

- Thermodynamical
- Dynamical
- Relaxational

Example:

$$S_{\mathrm{Mott}} = T\,\frac{\pi^2 k_{\mathrm{B}}^2}{3q_{\mathrm{e}}}\,\frac{\mathrm{d}}{\mathrm{d}\mu}\,\ln[\rho_0(\mu)\langle (v_p^x)^2 \tau(p,\mu)\rangle_\mu],$$

Expecting an **additive decomposition** is too simplistic in interacting systems but the three piece analogy gives some intuition.

Name	Formula	Context
Kubo-Onsager	$\frac{1}{T}\frac{\int_0^\infty dt \int_0^\beta d\tau \langle \hat{J}_x^E(t-i\tau)\hat{J}_x(0)\rangle}{\int_0^\infty dt \int_0^\beta d\tau \langle \hat{J}_x(t-i\tau)\hat{J}_x(0)\rangle} - \frac{\mu(T)}{q_e T}$	Exact and mostly unusable.
Mott	$T\frac{\pi^2 k_B^2}{3q_e}\frac{d}{d\mu}\ln[\rho_0(\mu)\langle(v_p^x)^2\tau(p,\mu)\rangle_\mu]$	Free electron metals with weak scattering (elastic or otherwise)
Heikes Mott	$S_{\mathrm{HM}} = \frac{\mu(0)-\mu(T)}{q_{\mathrm{e}}}$	Semi conductors High T
S*	$S^* = \frac{\langle \Phi^{xx}\rangle}{T\langle \tau^{xx}\rangle}$	Correlated matter (after removal of U scale) Neglects relaxational part. Large ω >> ω_c
Kelvin	$\frac{1}{q_e}\left(\frac{\partial S}{\partial N}\right)_{T,V}$	Correlated matter Low ω but thermodynamic part only

Historically there have been many ideas relating thermopower to thermodynamical variables- starting with Lord Kelvin himself in 1854!

Experimentalists view it as entropy per particle!

[6] K. E. Grew, Phys. Rev. 41, 3561 (1932).
[7] A. W. Foster, Phil. Mag. 18, 470 (1934)

Thermoelectric Anomaly Near a Critical Point

G. A. Thomas, K. Levin, and R. D. Parks

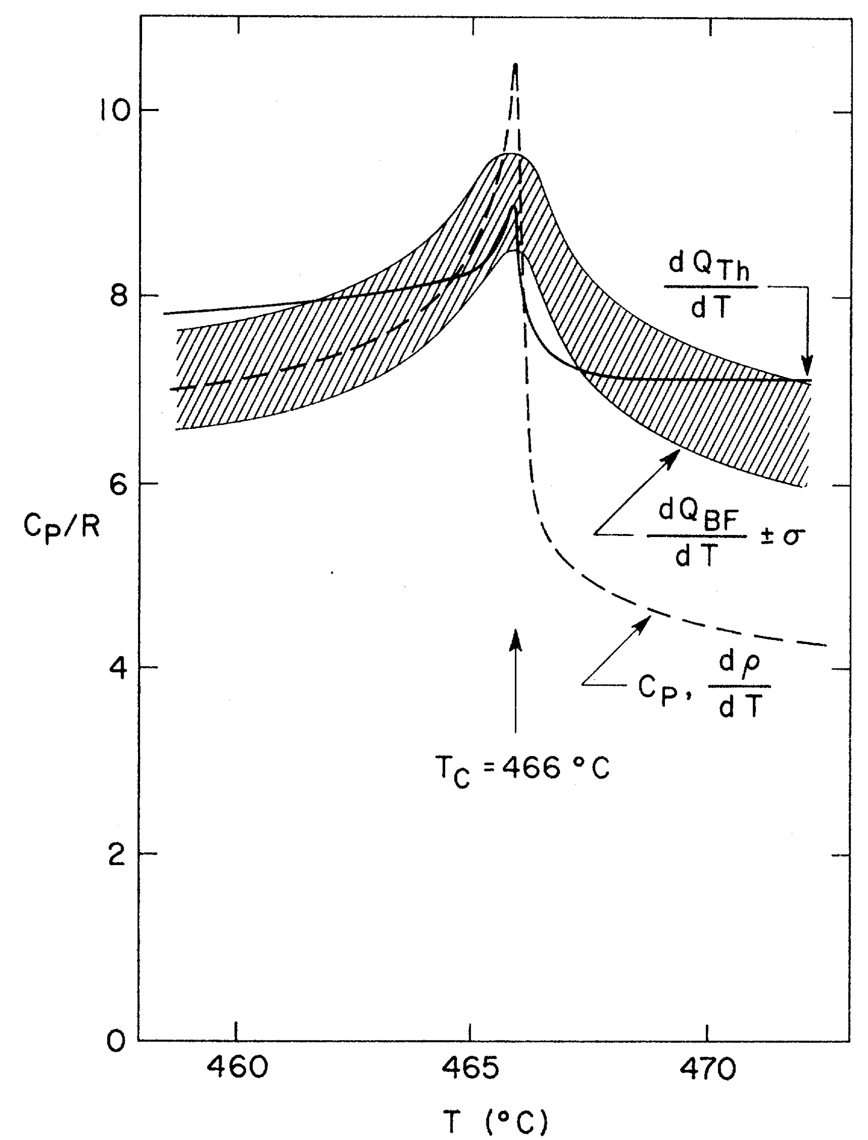
PHYSICAL REVIEW LETTERS 6 NOVEMBER 1972

$$Q = \frac{\pi^2 k_B{}^2 T}{3|e|} \frac{\partial \rho(\epsilon_F)}{\partial \epsilon_F} [\rho(\epsilon_F)]^{-1},$$

$$\rho(\epsilon_F) = m/n(\epsilon_F) e^2 \tau(\epsilon_F).$$

$$1/\tau_c = K_0 k_F{}^{-3} \int_0^{2k_F} I(k,T) k^3 \, dk$$

Nickel



Our interest started with Sodium Cobaltate (Na_xCoO_2) where we (Shastry Shraiman and Singh PRL 1993) had an old standing prediction on the T dependence of the Hall constant from 1993.

Ong et al were studying the large thermopower found, it was quite mysterious for many reasons.

Pushed by me Ong et. al. studied the T dependence of the Hall constant.

Pushed by Ong et. al., I studied the thermopower!!

- Thermoelectric response through linear response obscure at that point.
- Analogies to electrical response remained unknown
- Drude weight, and sum rules were not known.

In view of Hall constant studies:

- High frequency viewpoint from dynamical susceptibility is natural and required exploration
- Luttinger's gravitational potential analogy for thermal response is best way.

Shastry B S 2006 *Phys. Rev.* B **73** 085117

Rep. Prog. Phys. **72** (2009) 016501

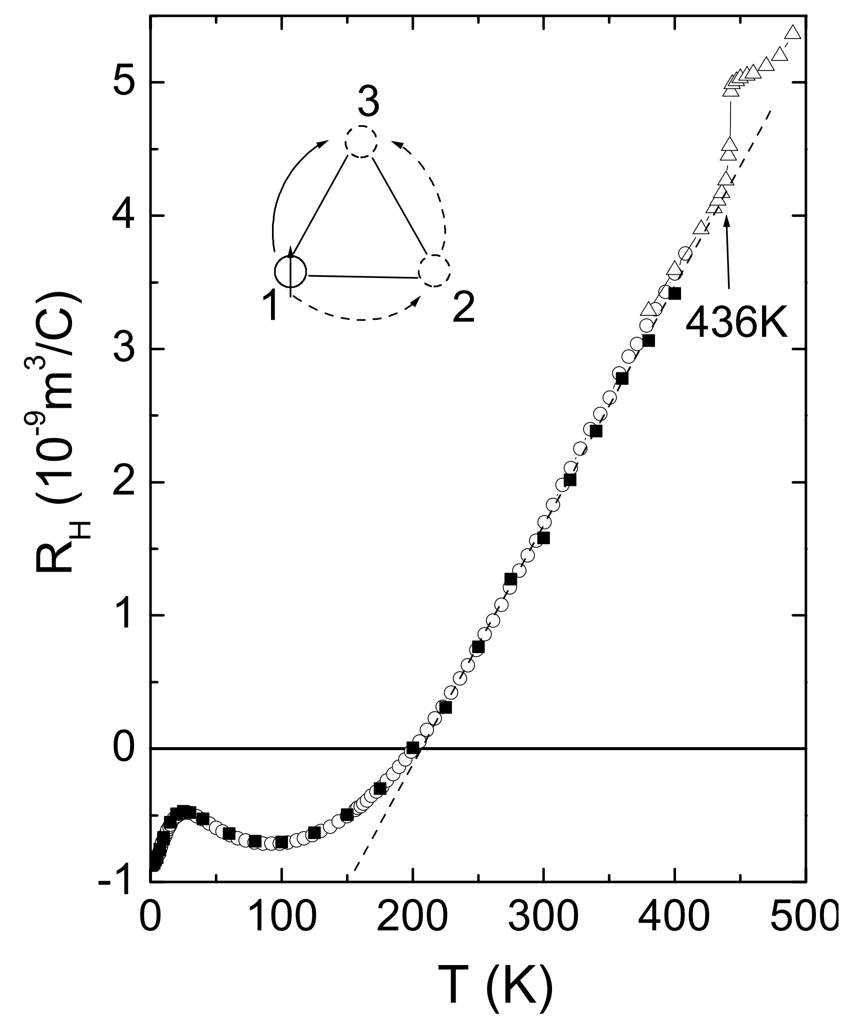


Figure 2. Experimental temperature dependence [34] of the Hall coefficient of sodium cobaltate $Na_{0.68}CoO_2$ over a broad range of temperatures. The sample is in the so-called Curie–Weiss metallic phase. The inset stresses the crucial role of the triangular closed loops in giving rise to the surprising behaviour.

Lessons from Hall constant studies

Linear Response

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

Stress tensor

$$\tau^{\alpha\beta} = q_e^2 \sum_{k,\sigma} \frac{\mathrm{d}^2\varepsilon(k)}{\mathrm{d}k_\alpha \mathrm{d}k_\beta} c_\sigma^\dagger(k) c_\sigma(k),$$

$$R_H(\omega) = \lim_{B\to 0} \frac{\sigma_{xy}(\omega)}{\sigma_{xx}^2(\omega)}$$

$$R_H^* \equiv \lim_{\omega\to\infty} R_H(\omega) = \frac{-\mathrm{i}N_s v}{B\hbar} \frac{\langle[\hat{J}_x, \hat{J}_y]\rangle}{\langle\tau^{xx}\rangle^2}.$$

$\hbar\omega \gg \{|t|, U\}_{\max}$, Hubbard

$\hbar\omega \gg \{|t|, J\}_{\max}$. t J model

$$\Re e R_H(0) = R_H^* + \frac{2}{\pi}\int_0^\infty \frac{\Im m R_H(\nu)}{\nu}\,\mathrm{d}\nu.$$

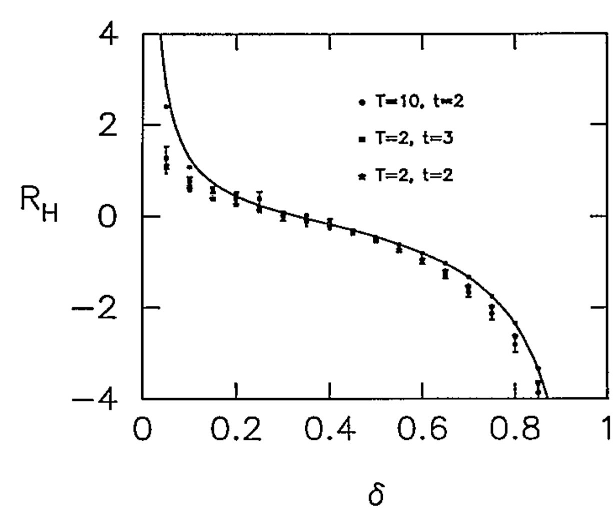
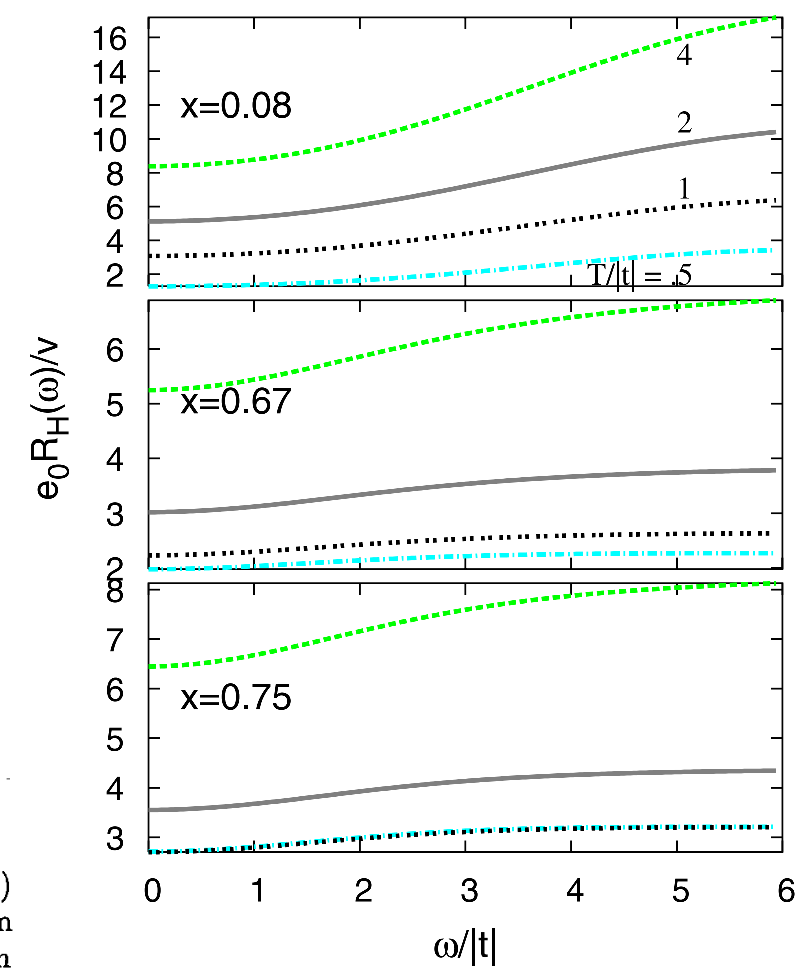


FIG. 2. Solid curve is R_H^* (in units of 0.3×10^{-3} cm^3/C) vs δ at $T=\infty$, Eq. (11), and the three sets of points are from the Padé approximants at three sets of values of T and t in units of J.



Luttinger's thermal response formalism at finite frequencies:

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

$$K = \sum_x K(\vec{x}) \text{ and } K(\vec{x}) = H(\vec{x}) - \mu n(\vec{x})$$

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

$$\boxed{\lim_{\vec{q}\to 0}\psi_q = -\lim_{\vec{q}\to 0}\frac{\delta T_q}{T}.}$$

Important notation

	$i=1$	$i=2$
	Charge	Energy
$\mathcal{I}_i$	$\hat{J}_x(q_x)$	$\hat{J}_x^Q(q_x)$
$\mathcal{U}_i$	$\rho(-q_x)$	$K(-q_x)$
$\mathcal{Y}_i$	$E_q^x = \mathrm{i}q_x\phi_q$	$\mathrm{i}q_x\psi_q.$

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

Linear response

$$K_{\rm tot} = K + \sum_j Q_j \mathrm{e}^{-\mathrm{i}\omega_c t},$$

$$\text{where } Q_j = \frac{1}{\mathrm{i}q_x}\mathcal{U}_j\mathcal{Y}_j.$$

$$L_{ij}(q_x,\omega) = \frac{1}{\Omega}\lim_{\mathcal{Y}_j\to 0}\langle\mathcal{I}_i\rangle/\mathcal{Y}_j.$$

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

$$\lim_{q_x\to 0}\langle[\mathcal{I}_i,\mathcal{U}_j]\rangle = 0$$

$$\langle[P,K]\rangle = \frac{1}{\mathcal{Z}}\mathrm{Trace}[\mathrm{e}^{-\beta K}(PK - KP)] \equiv 0.$$

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

where

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

Three fundamental operators can be defined as:

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

Zero current thermal conductivity

$$\kappa_{zc}(\omega) = \frac{1}{T}\left[L_{22}(\omega) - \frac{L_{12}(\omega)^2}{L_{11}(\omega)}\right],$$

thermopower $S(\omega) = \dfrac{L_{12}(\omega)}{TL_{11}(\omega)}$,

Lorentz number $\boldsymbol{L}(\omega) = \dfrac{\kappa_{zc}(\omega)}{T\sigma(\omega)}$,

figure of merit $\boldsymbol{Z}(\omega)T = \dfrac{S^2(\omega)}{\boldsymbol{L}(\omega)}$.

Sum rules

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

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

High frequency limit

$$\hbar\omega \gg \{|t|, U\}_{\max}, \quad \text{Hubbard}$$

$$\hbar\omega \gg \{|t|, J\}_{\max}. \quad \text{t J model}$$

High freq thermopower $S^* = \dfrac{\langle \Phi^{xx} \rangle}{T \langle \tau^{xx} \rangle}.$

High freq Lorentz number $L^* = \dfrac{\langle \Theta^{xx} \rangle}{T^2 \langle \tau^{xx} \rangle} - (S^*)^2.$

High freq figure of merit $Z^* T = \dfrac{\langle \Phi^{xx} \rangle^2}{\langle \Theta^{xx} \rangle \langle \tau^{xx} \rangle - \langle \Phi^{xx} \rangle^2}.$

$$\Re e S(\omega) = S^* + \frac{\mathcal{P}}{\pi} \int_{-\infty}^{\infty} \frac{\mathrm{d}\nu}{\nu - \omega} \Im m S(\nu),$$

$$\Re e \boldsymbol{L}(\omega) = \boldsymbol{L}^* + \frac{\mathcal{P}}{\pi} \int_{-\infty}^{\infty} \frac{\mathrm{d}\nu}{\nu - \omega} \Im m \boldsymbol{L}(\nu),$$

$$\Re e \boldsymbol{Z}(\omega) = \boldsymbol{Z}^* + \frac{\mathcal{P}}{\pi} \int_{-\infty}^{\infty} \frac{\mathrm{d}\nu}{\nu - \omega} \Im m \boldsymbol{Z}(\nu).$$

Context: Consider an effective model system obtained by focusing on one (or a few) bands after eliminating higher energy states.

Best for tJ type models, (but not ideal for large U Hubbard systems).

High frequency transport calculation is therefore reduced to computing the equal time average of these three many body operators- much easier than doing time dependence- and yet already very challenging.

Hubbard model thermopower can be found from self energy alone!! (no need for vertex)
Shastry Aspen (2008), DMFT with Arsenault, Tremblay et al (2008)

$$\langle \Phi^{xx} \rangle = \frac{q_e}{\beta} \sum_{\mathbf{k},n,\sigma} e^{i\omega_n 0^+} \quad G_\sigma(\mathbf{k}, i\omega_n) \Bigg\{ \Sigma_\sigma(\mathbf{k}, i\omega_n) \ \frac{\partial^2 \varepsilon_{\mathbf{k}}}{\partial k_x^2} + \frac{\partial}{\partial k_x} \ \left(\frac{\partial \varepsilon_{\mathbf{k}}}{\partial k_x} (\varepsilon_{\mathbf{k}} - \mu) \right) \Bigg\},$$

Hubbard model

t-J model

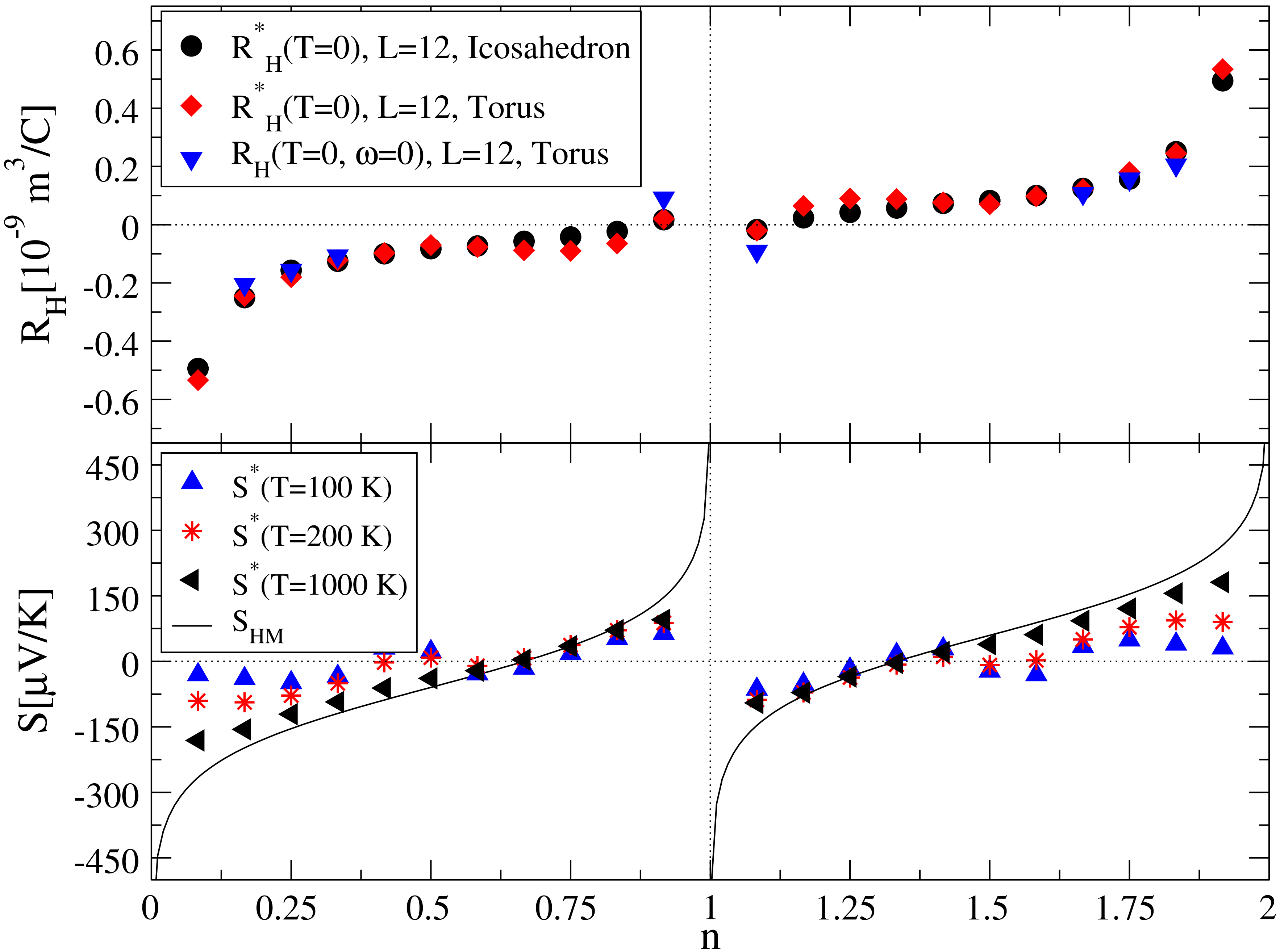
$$\Phi^{xx} = -\frac{q_e}{2} \sum_{\vec{\eta}, \eta', \vec{\sigma}, \sigma', \vec{x}} (\eta_x + \eta'_x)^2 t(\vec{\eta}) t(\vec{\eta}') Y_{\sigma',\sigma} \times (\vec{x} + \vec{\eta}) \tilde{c}^{\dagger}_{\vec{x}+\vec{\eta}+\vec{\eta}',\sigma'} \tilde{c}_{\vec{x},\sigma} - q_e \mu \sum_{\vec{\eta},\sigma,\vec{x}} \eta_x^2 t(\vec{\eta}) \tilde{c}^{\dagger}_{\vec{x}+\vec{\eta},\sigma} \tilde{c}_{\vec{x},\sigma}$$

where

$$\delta_{\vec{x},\vec{x}'} \{ \delta_{\sigma,\sigma'} (1 - n_{\vec{x},\bar{\sigma}}) + (1 - \delta_{\bar{\sigma},\sigma'}) \tilde{c}^{\dagger}_{\vec{x},\sigma} \tilde{c}_{\vec{x},\bar{\sigma}} \} \quad \equiv Y_{\sigma,\sigma'} \delta_{\vec{x},\vec{x}'}.$$

Exact diagonalization tJ model
10-27 site clusters
Peterson Haerter and Shastry

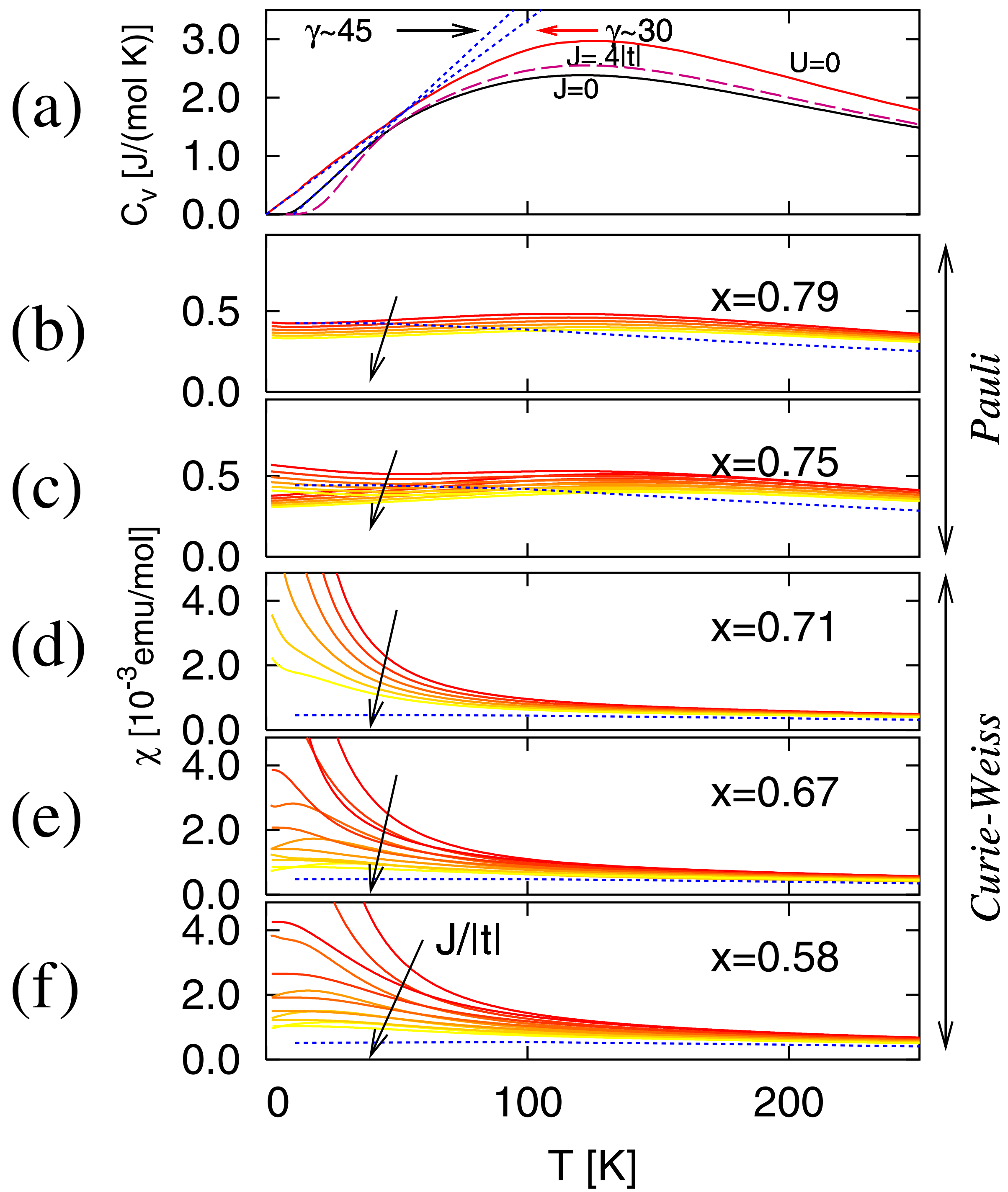
- Particle Hole symmetry
- Comparing Hall constant and Seebeck coefficients
- Mott Hubbard holes at half filling are evident



Electrothermal transport coefficients at finite frequencies

Rep. Prog. Phys. **72** (2009) 016501 (23pp)

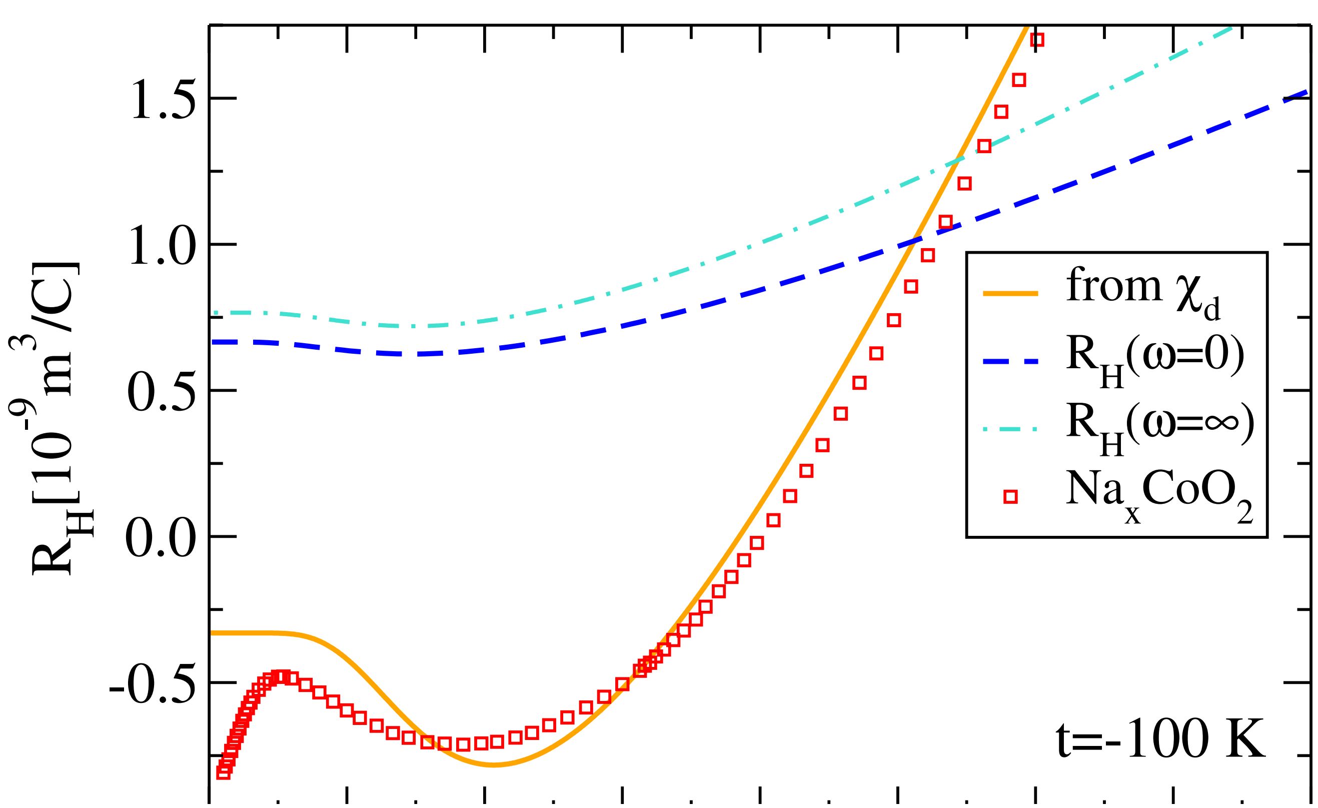
Where is the insight and can it help the material design enterprise?



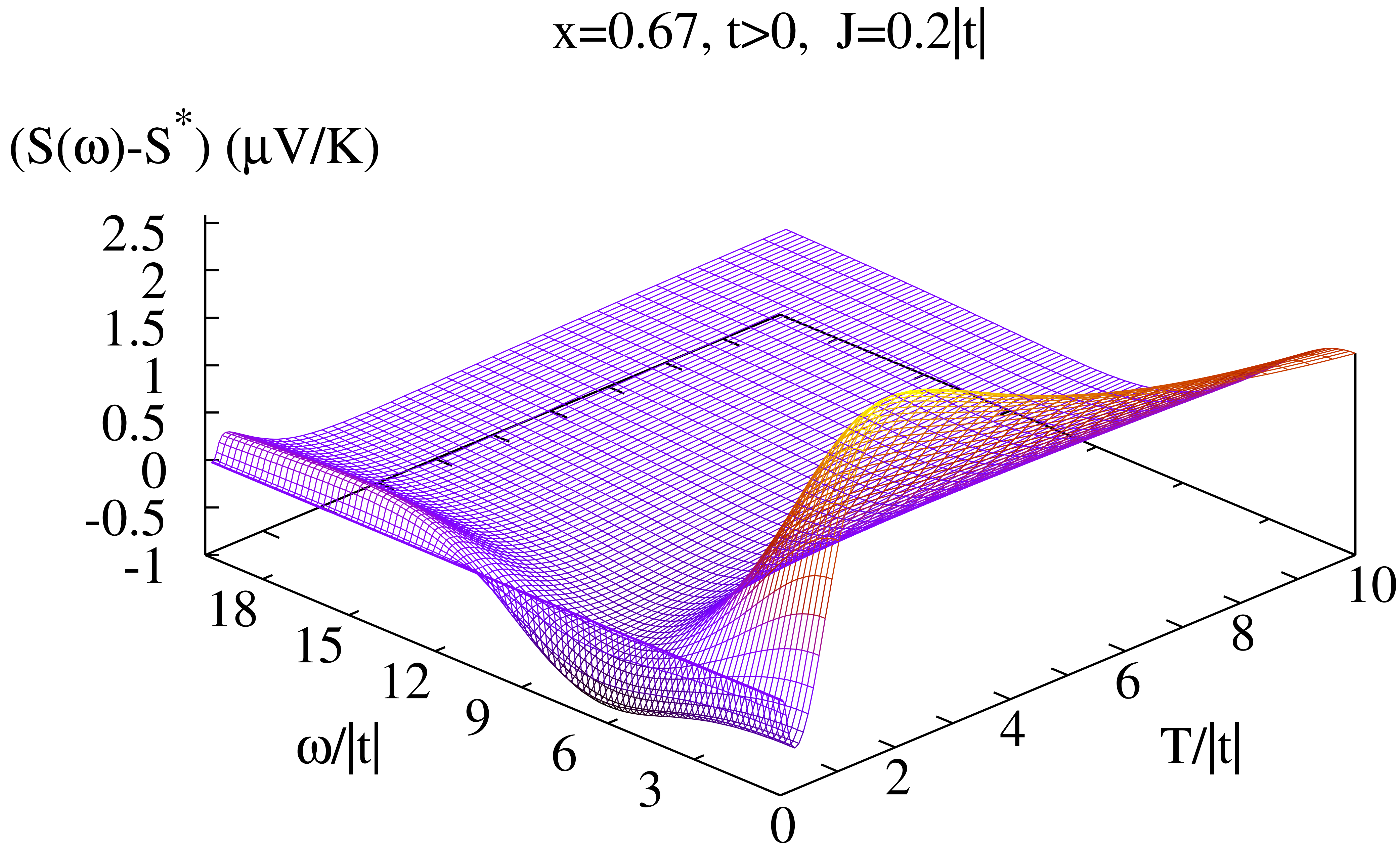
Strong Correlations Produce the Curie-Weiss Phase of Na_xCoO_2

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

PRL **97,** 226402 (2006)

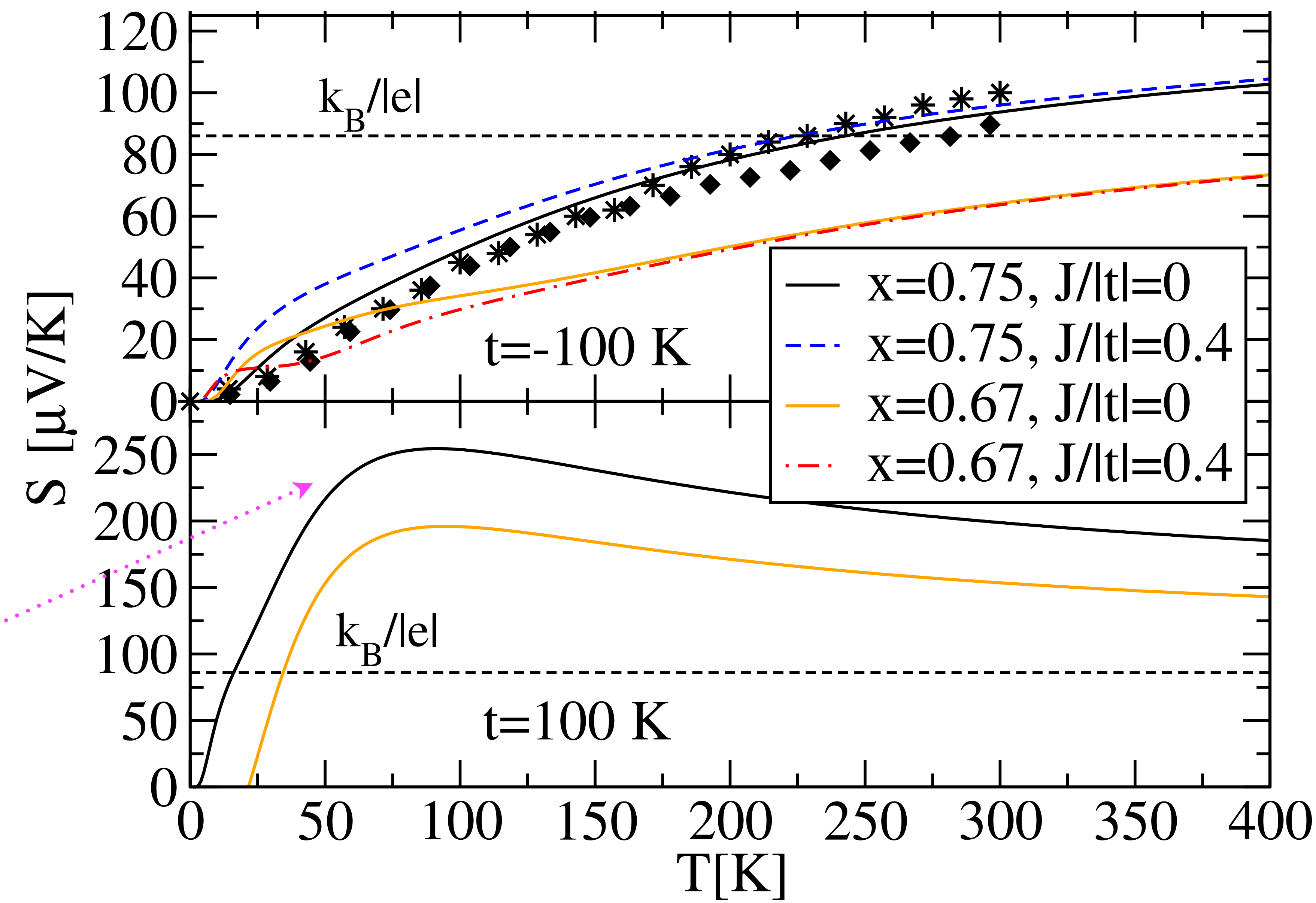


Exact calculation of Kubo formula
summing all states triangular lattice clusters



Here S* is ~ 100 microVolts, hence maximum error is about 3%!!!

Data versus calculation for NCO



Predicted material with even higher thermopower!! Due to *electronic frustration*- a phrase coined by us.

Where did this insight come from and can it be used?

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

Sign of hopping in triangular, and FCC, HCP lattices is explicitly involved.

Prediction: Hole doping should yield greater thermopower than electron doping. Also true for FCC, HCP lattices

Michael R. Peterson

B. Sriram Shastry

PHYSICAL REVIEW B **82**, 195105 (2010)

Kelvin formula for thermopower

Exact

$$S(q_x,\omega) = \frac{\chi_{\rho(q_x),\hat{K}(-q_x)}(\omega)}{T\chi_{\rho(q_x),\rho(-q_x)}(\omega)}$$

Slow limit i.e. $\omega \to 0$ first. Wrong but interesting
Captures thermodynamic contribution

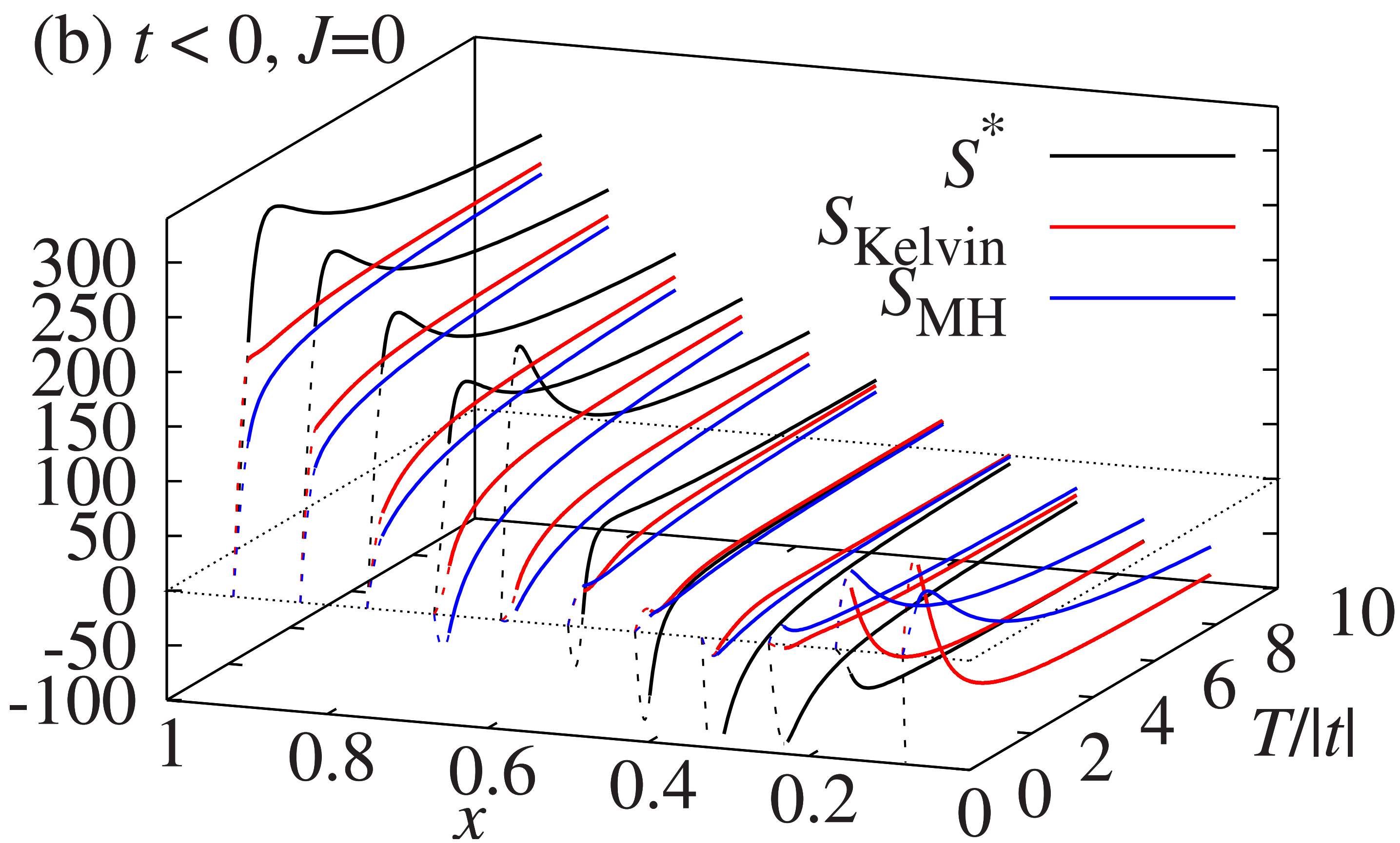
$$S_{\text{Kelvin}} = \lim_{q_x \to 0} \frac{\chi_{\rho(q_x),\hat{K}(-q_x)}(0)}{T\chi_{\rho(q_x),\rho(-q_x)}(0)}$$

$$S_{\text{Kelvin}} = \frac{1}{q_e T} \frac{\frac{d}{d\mu}\langle \hat{H} \rangle - \mu \frac{d}{d\mu}\langle \hat{N} \rangle}{\frac{d}{d\mu}\langle \hat{N} \rangle}$$

$$S_{\text{Kelvin}} = \boxed{\frac{1}{q_e}\left(\frac{\partial \mathcal{S}}{\partial N}\right)_{T,V}} \quad \boxed{:\frac{-1}{q_e}\left(\frac{\partial \mu}{\partial T}\right)_{N,V}}$$

$$S_{Heikes} = \frac{1}{q_e}\left(\frac{\partial \mathcal{S}}{\partial N}\right)_{E,V}$$

Note the thermodynamic "banana skin". Const energy not T in Heikes formula- makes huge difference.



Low particle density better for S
Frustration is captured in S* but not Kelvin

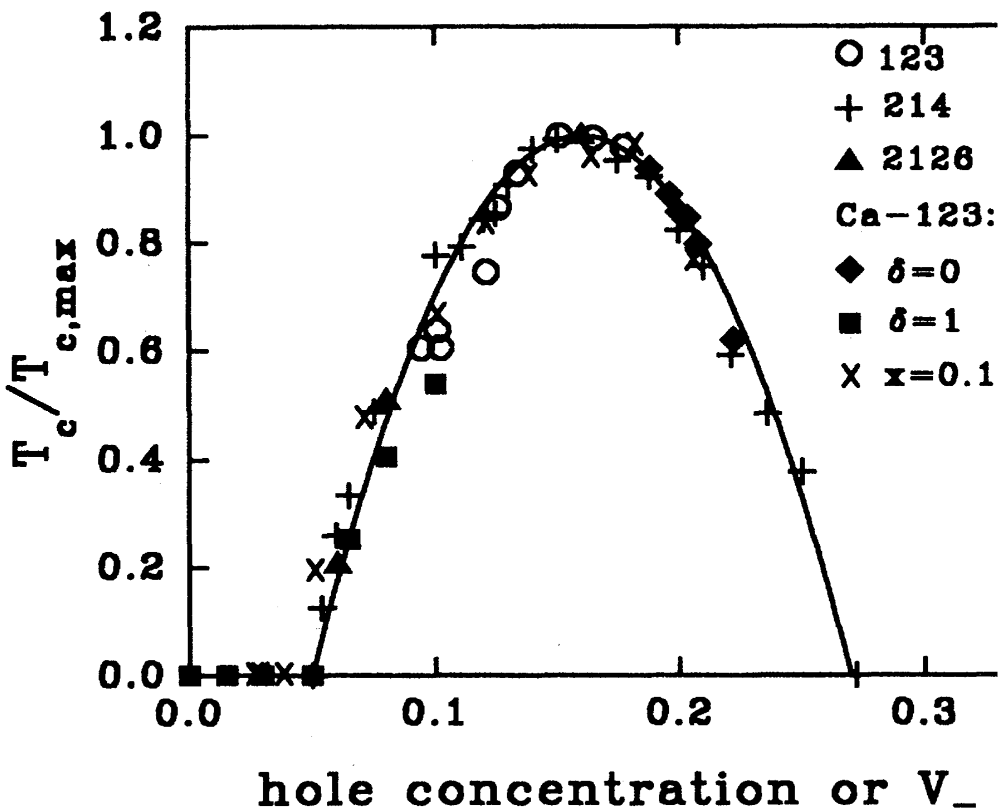
$$\lim_{T \to 0} S_{Kelvin} \to A\ T$$

With correct coefficient
unlike Heikes Mott as shown in
Professor Antoine Georges's previous lecture

A possibly useful insight:

Tallon Obertelli Homma Hor universal crossing of Thermopower may be understood as a peak in entropy as a function of doping at optimal doping- and hence hints towards a QCP!

$$S_{290} = -139p + 24.2 \qquad \text{for } p > 0.155.$$



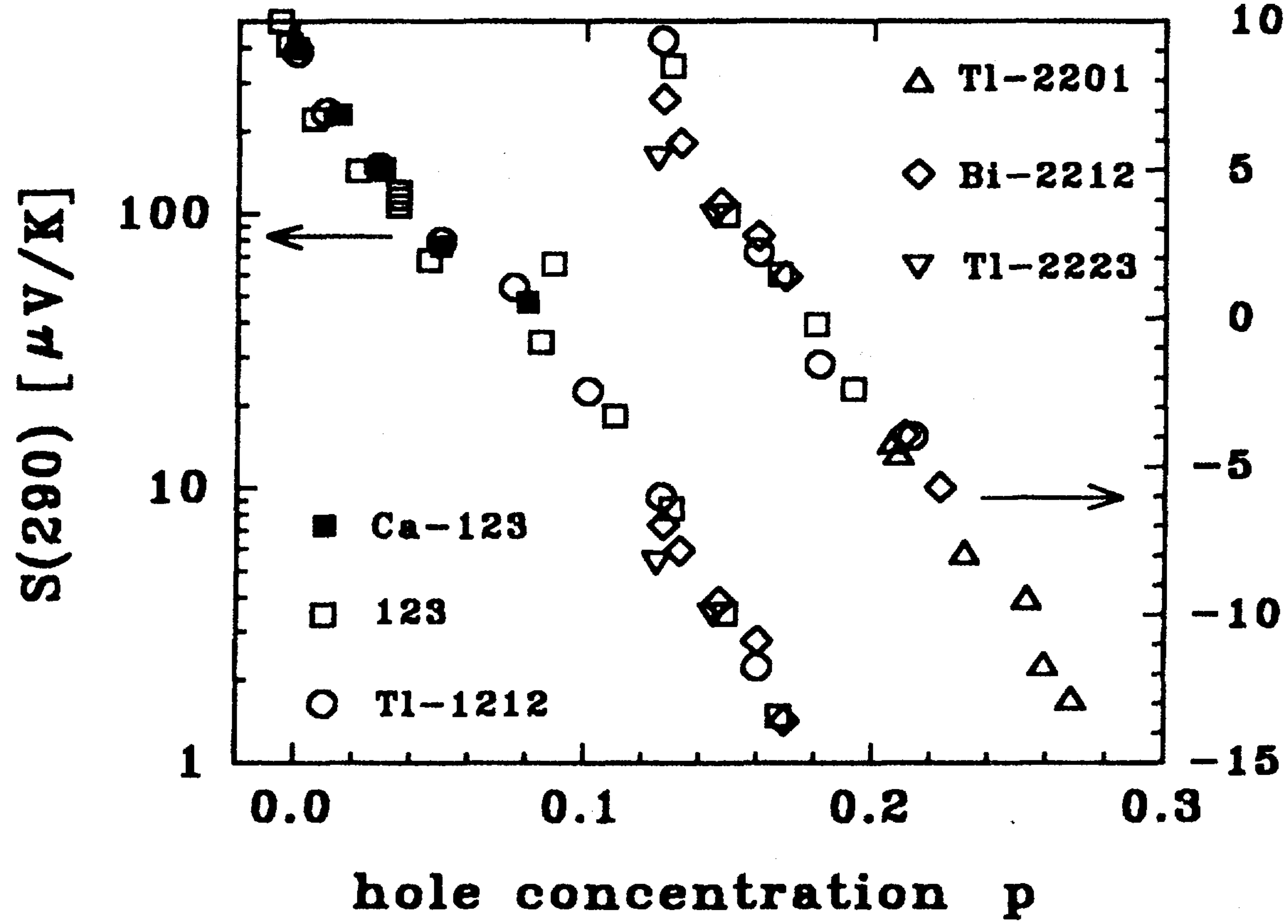


FIG. 3. Room-temperature thermoelectric power plotted as a function of hole concentration for various HTSC's as reported in Ref. 8 and for oxygen-deficient ($\delta \approx 0.98$) $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ for which $p = x/2$. The underdoped side has a logarithmic scale and the overdoped side a linear scale.

Thermopower and quantum criticality in a strongly interacting system: parallels with the cuprates

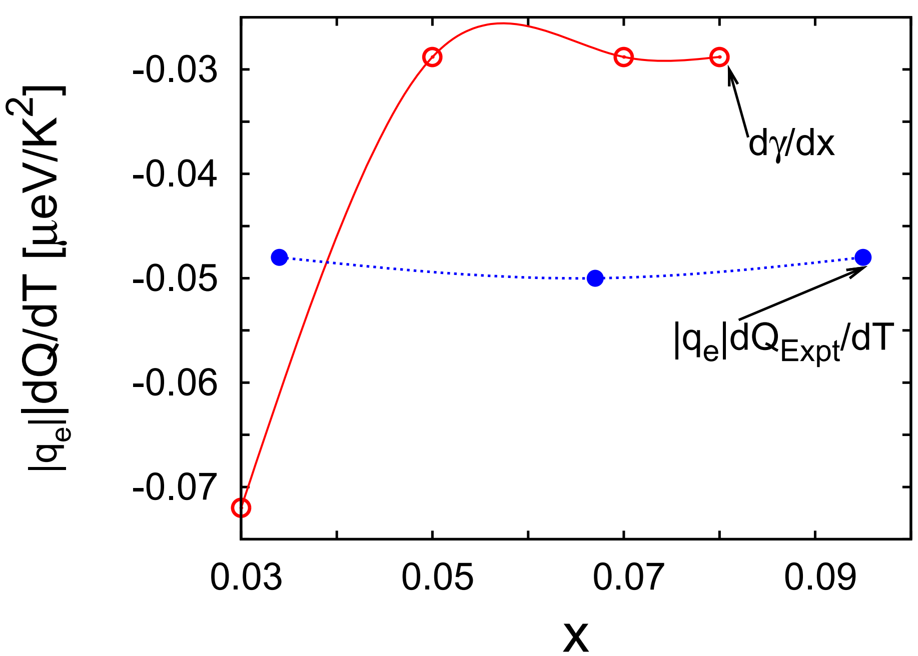
New Journal of Physics **13** (2011) 083032 (9pp)

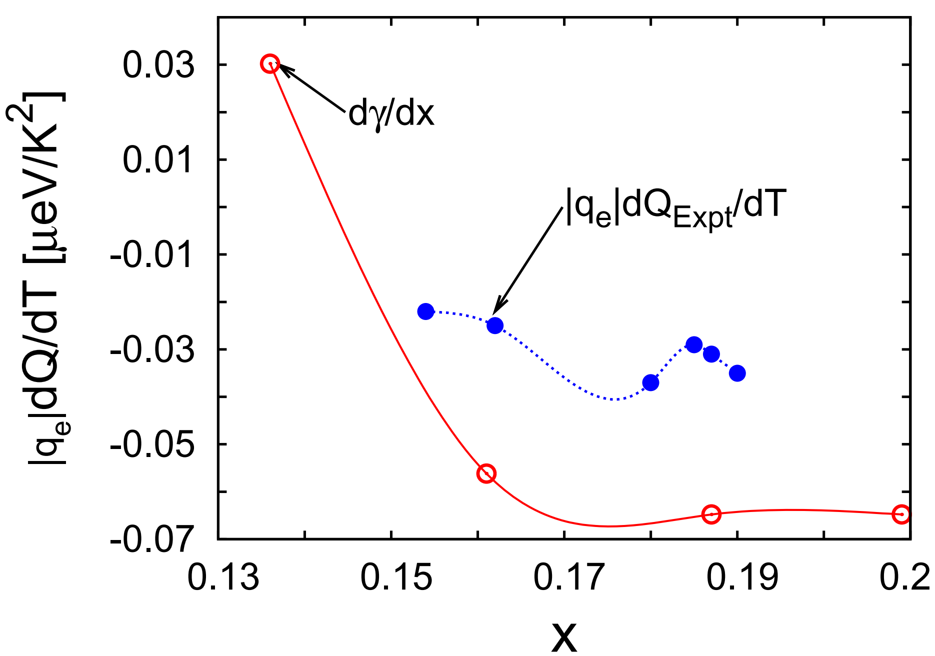
Arti Garg[1,3], B Sriram Shastry[1], Kiaran B Dave[2] and Philip Phillips[2]

We may interpret this experiment assuming Kelvin's formula:
The approximate validity of Kelvin's formula here would imply

$$\frac{dQ}{dT} = \frac{1}{q_e}\frac{d^2 S}{dT\,dN} = \frac{1}{q_e}\frac{d\gamma}{dN}$$

$$S = \gamma\ T$$





Summarizing:
Useful to have simple approximate formulas-
lead to simple and powerful insights that exact formulas cannot *ever* give us!!