Curie Weiss Metallic Phase of Sodium Cobaltates: Does the t-J Model stand a chance?

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•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 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:

Na $_{x}$ Co O₂ : 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?

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



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

Real space versus k space!!

$$R_H = \frac{a}{-x|e|c}$$

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. Jumping ahead: here is a Mott Hubbard system on a triangular lattice: Both Hall constant and Thermopower have three crossings as n varies from 0 to 2.

In a word: these variables are sensitive to the Mott Hubbard insulating state



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

 $R_{H^*} = \lim_{B \to 0} \lim_{\omega \to \infty} \frac{\rho_{xy}(\omega)}{B}$

•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 $\rho_{xy}(\omega) = \frac{\sigma_{xy}}{(\sigma_{xx})^2}$ resistivity Why not compute at high frequencies from Kubo's formulas directly:

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

$$= \frac{i < \tau_{xx} >}{N v \omega} + o(1 / \omega^3)$$

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

$$\sigma_{xy}(\omega) = \frac{-i}{N \vee \omega Z} \sum \frac{e^{-\beta \varepsilon_{n}} - e^{-\beta \varepsilon_{m}}}{\varepsilon_{m} - \varepsilon_{n} - \omega} < n | J^{x} | m > < m | J^{y} | n >$$
$$= \frac{i}{N \vee \omega^{2}} < [J^{x}, J^{y}] > + o(1/\omega^{3})$$

 $R_{H}^{*} = \frac{-i2\pi}{hB} Nv < [J^{x}, J^{y}] > / < \tau_{yy} >^{2}$ $\omega >> J$

•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 •PREDICTIVE POWER, or Triangular lattice (Kumar Shastry
- •PREDICTIVE POWER: e.g. Triangular lattice (Kumar Shastry 2003)

Anomalous high-temperature Hall effect on the triangular lattice in $Na_x CoO_2$

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



Hall constant as a function of T for x=.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. See later.





Our favourite clusters with 12 sites. Platonic solid with triangular faces.

Kubo formulas by introducing level broadening equal to mean level spacing as usual.



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 ~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

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

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

S

$$S = \frac{\langle \langle J_e; J_p \rangle \rangle}{T \langle \langle J_p; J_p \rangle \rangle} - \frac{\mu}{q_e T}$$

$$S = S_{Tr} + S_{Heikes}$$

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

(1)

(2)

 $S \sim T \rho^{\circ}(\mu)$

Scale of Heikes Mott entropic part ~80-90 microvolt/degree. Transport part is essentially unexplored, except in Fermi liquids. At low T there is cancellation between these terms. A Sum Rule for Thermal Conductivity and Dynamical Thermal Transport Coefficients in Condensed Matter -I

Cond-mat/0508711

S S, Phys Rev B73, 085117 (2006)

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.

Need frequency dependence of various objects

 $\overline{\kappa(\omega)} \ \rho(\omega) \ S(\omega) \ L(\omega) \ Z(\omega)$

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. This regime was first studied at Bell Labs earlier by Venki Narayanmurthy Chandra Varma (1970) who found solitonic transport of energy.

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. His T(r,t) is best thought of as an applied temp and not the thermodynamical temp.

$$K = K_0 + K_1 e^{-i\omega_c t}, \qquad \omega_c = \omega + \mathrm{i} \ \mathrm{O}^+$$

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

$$abla \psi(r) = rac{
abla T(r)}{T}$$

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.

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

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

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

Meet the thermal operator Θ^{xx} : A new extensive operator that can be computed for any model. This new operator is different from energy momentum tensor. 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

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

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

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

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 $\omega >> J$, the thermopower $S(\omega)$ is determined by the expectation of Φ^{xx} . High frequency limits that are feasible and sensible similar to R*



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

$$\langle \tau^{xx} \rangle = \frac{2q_e^2}{\mathcal{L}} \sum_p n_{\vec{p}} \frac{d}{dp_x} \left[v_{\vec{p}}^x \right]$$

$$\langle \Theta^{xx} \rangle = \frac{2}{\mathcal{L}} \sum_p n_{\vec{p}} \frac{d}{dp_x} \left[v_{\vec{p}}^x (\varepsilon_{\vec{p}} - \mu)^2 \right]$$

$$\langle \Phi^{xx} \rangle = \frac{2q_e}{\mathcal{L}} \sum_p n_{\vec{p}} \frac{d}{dp_x} \left[v_{\vec{p}}^x (\varepsilon_{\vec{p}} - \mu) \right].$$

$$(1)$$

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

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

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

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

$$(1)$$

We may form the high frequency ratios

$$S^{*} = T \frac{\pi^{2} k_{B}^{2}}{3q_{e}} \frac{d}{d\mu} \log \left[\rho_{0}(\mu) \langle (v_{\vec{p}}^{x})^{2} \rangle_{\mu} \right]$$

$$L^{*} = \frac{\pi^{2} k_{B}^{2}}{3q_{e}^{2}}.$$
(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

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

Where $\Delta = \Delta_t + \Delta_J$ and

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

$$\Delta_J = -\frac{1}{2} \sum_{r,\vec{\eta},\vec{\eta'}} t(\vec{\eta}) J(\vec{\eta'}) \eta_x [\frac{\eta_x}{2} \left\{ \vec{\mu}(\vec{r}+\vec{\eta},\vec{r}).(\vec{S}(\vec{r}+\vec{\eta'})+\vec{S}(\vec{r}+\vec{\eta}+\vec{\eta'})) + (\vec{S}(\vec{r}+\vec{\eta'})+\vec{S}(\vec{r}+\vec{\eta}+\vec{\eta'})) + \vec{S}(\vec{r}+\vec{\eta}+\vec{\eta'}) + \vec{S}(\vec{r}+\vec{\eta}+\vec{\eta'}) + \vec{S}(\vec{r}+\vec{\eta}+\vec{\eta'}) + \vec{S}(\vec{r}+\vec{\eta}+\vec{\eta'}) + \vec{S}(\vec{r}+\vec{\eta'}+\vec{\eta'}) +$$

(2)

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

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

Thus for $0 \le n \le 1$

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

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

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

From the temperature dependence of the data of Terasaki et aland Yayu 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.
- 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.

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

Prediction for hypothetical material with t<0





X=0.67

S* for both signs of hopping.



X = 0.58

Predicted hugely enhanced S for t<0 at different fillings. Note that x ->1 gets better!!





S at different fillings for usual case t>0

Minhyea Lee et al. Nature Materials, *in press*



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

t<0 prediction!



B dependence of thermopower is very strong and hence strange for a good metal: Wang, Rogado, Ong and Cava (2003) Nature:





Experiment

Theory: absolute scale computation





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....

Preliminary results on w dependence of S(w). X=.8 different values of T in different plots and also broadening. Green line is S*

