Non-magnetic Impurities and the Susceptibility of Antiferromagnetic Chain Compounds

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Outline

- Introduction
- Numerical and field theory results
- $Sr_2Cu_{1-x}Pd_xO_{3+\delta}$
- Conclusions

Introduction

$$H = \sum_j \left[J \vec{S}_j \cdot \vec{S}_{j+1} - h S_j^z \right]$$

(J>0, S=1/2, $g\mu_B = \hbar = k_B = 1$)

While classical ground state has Néel order ↑↓↑↓↑↓↑↓, quantum system is disordered, even at T=0, due to strong thermal and quantum fluctuations in 1 dimension

For S=1/2 case (no Haldane gap!) system is “almost ordered”:

$$¿\,0|S_i^a S_j^b|0> ¿ \frac{\delta^{ab}(-1)^{i-j}}{|i-j|}$$

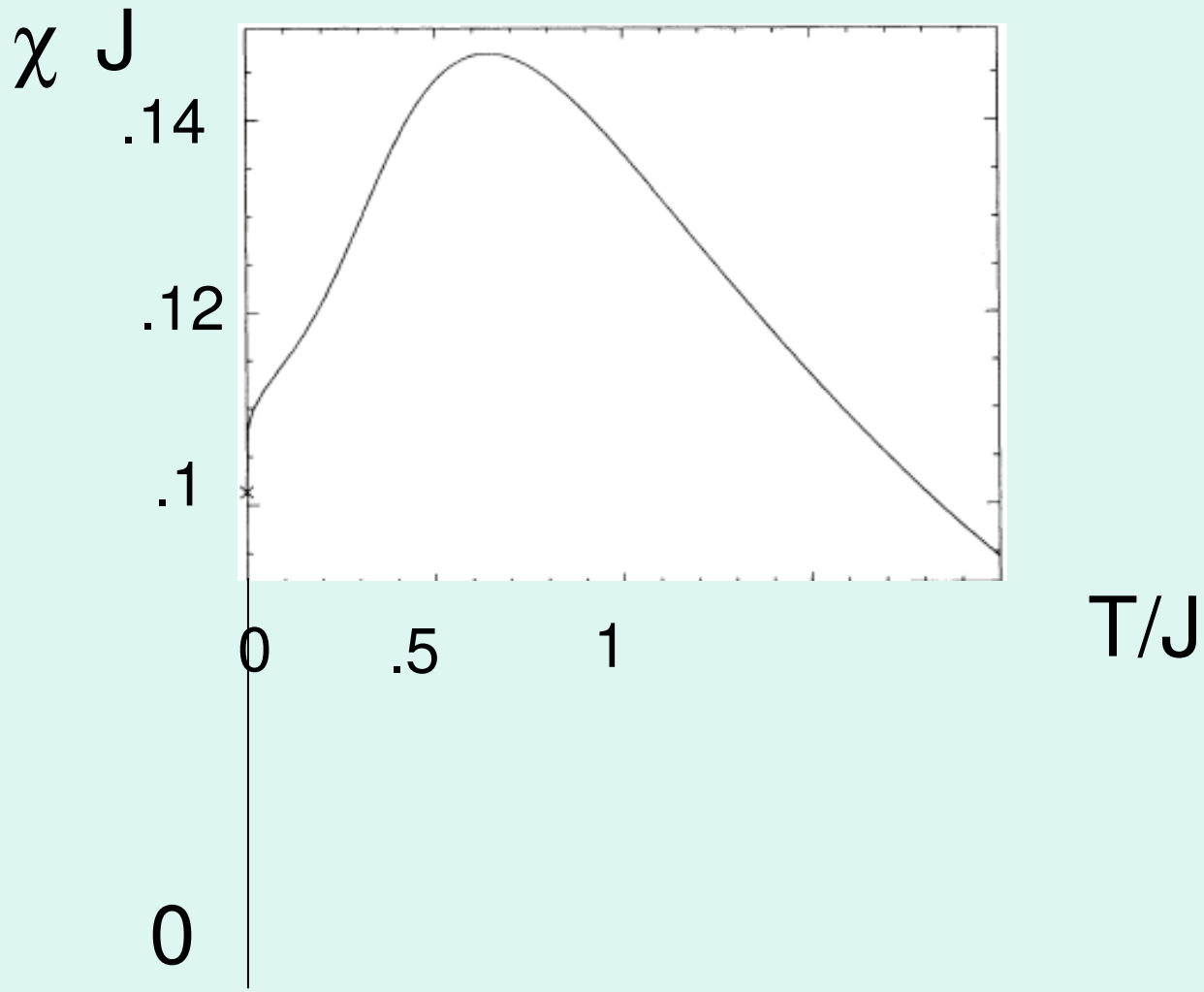
- There are gapless excitations, with
$\varepsilon(k) \to v|k|$ $(k \to 0)$, $v|k-\pi|$ $(k \to \pi)$, $v = J\pi/2$
- Not exactly spin-waves however – only 1 branch, not 2

- Various experiments have been done on highly 1D chain compounds ($J_\perp/J \ll 1$): magnetic susceptibility, neutron scattering, electron spin resonance, NMR
- I focus here on (zero field) magnetic susceptibility (per unit length):

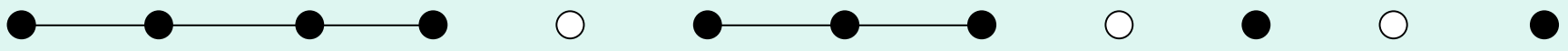
$$\chi \equiv \frac{\left\langle \left(\sum_j S_j^z \right)^2 \right\rangle_{h=0}}{LT}$$

- For a 2 or 3D AF there is a rather subtle signal at T_N, which is strongly influenced by anisotropy
- For 1D case, there is no Néel transition and χ is a perfectly smooth function

Susceptibility for pure (infinite length) chain (from Eggert, Affleck, Takahashi, 1994)



- Real materials contain impurities: crystal dislocations, dopants, …
- In some cases these have simple but dramatic effect of breaking up chains into random finite length segments

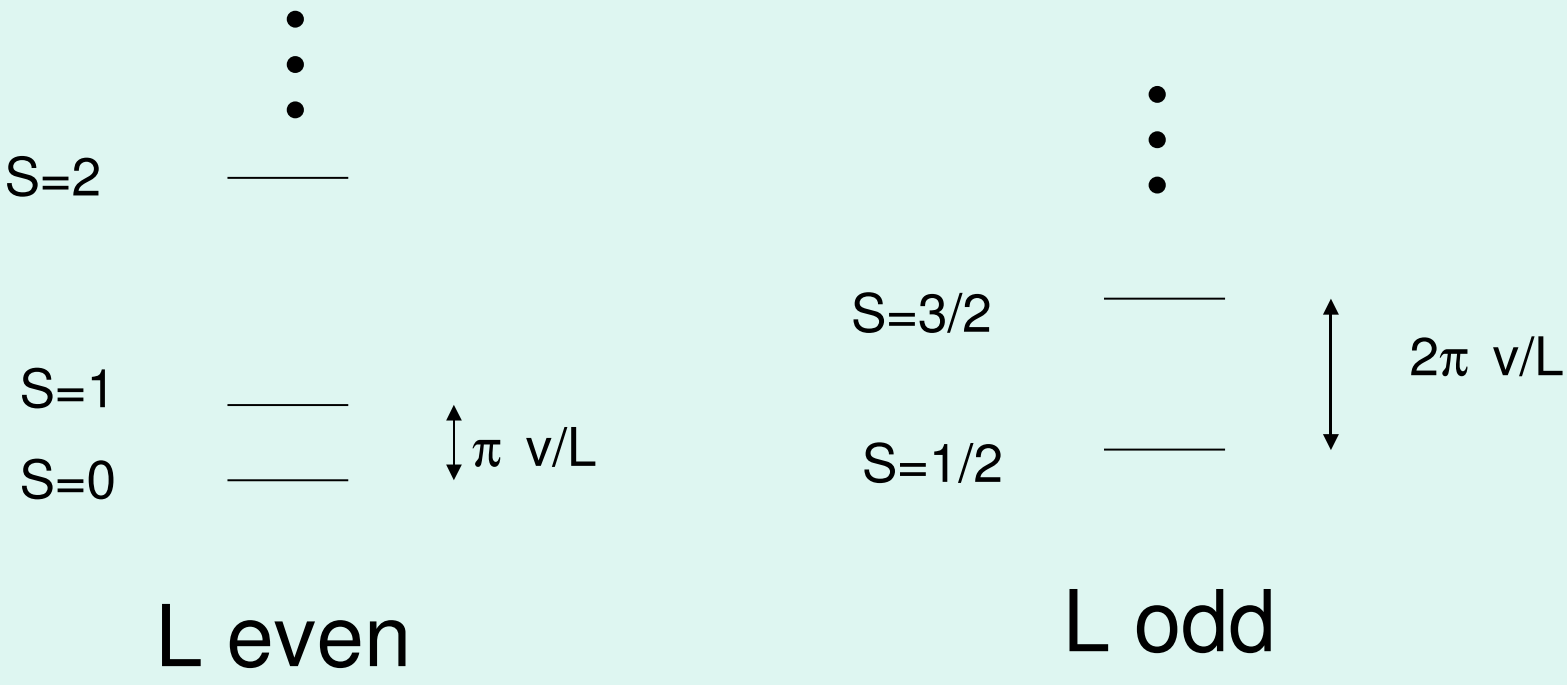


I first consider this simple model here and mention other interactions that bridge gaps between chain segments later

- N.B. an odd length segment has a total spin of ½ and an even length segment has a total spin of 0 in ground state
- So, at low enough T, every odd length segment just acts like a paramagnetic S=1/2 impurity, contributing $1/(4T)$ to χ - which diverges at $T \to 0$
- Goal of this project was to go beyond this simple observation and calculate χ quantitatively as a function of T and impurity density

Field Theory and Numerical Results

Simple observation: excitation gap ~ π v/L



- So, for even L, $\chi \sim e^{-\pi v/(LT)}$ and for odd L, $\chi \sim 1/(4LT)+O(e^{-2\pi v/(LT)})$
- But, *these formulas are only true for* $LT \ll \pi v = \pi^2 J/2$, i.e. short L and/or low T
- i.e., T must be small compared to finite size gap for these results to apply
- If impurities are very dilute (average L long) we may never see this behaviour

There is actually a simple, semi-quantitative formula for χ based on Luttinger liquid (free boson) approximation:
Excitations are simply a combination of a rigid rotator and a collection of harmonic oscillators
-any state is specified by total S^z quantum number and excitation numbers of harmonic oscillators

$$H = \frac{\pi v}{L}\left[(S^z)^2 + \sum_{n=1}^{\infty} n a_n^+ a_n \right] - hS^z$$

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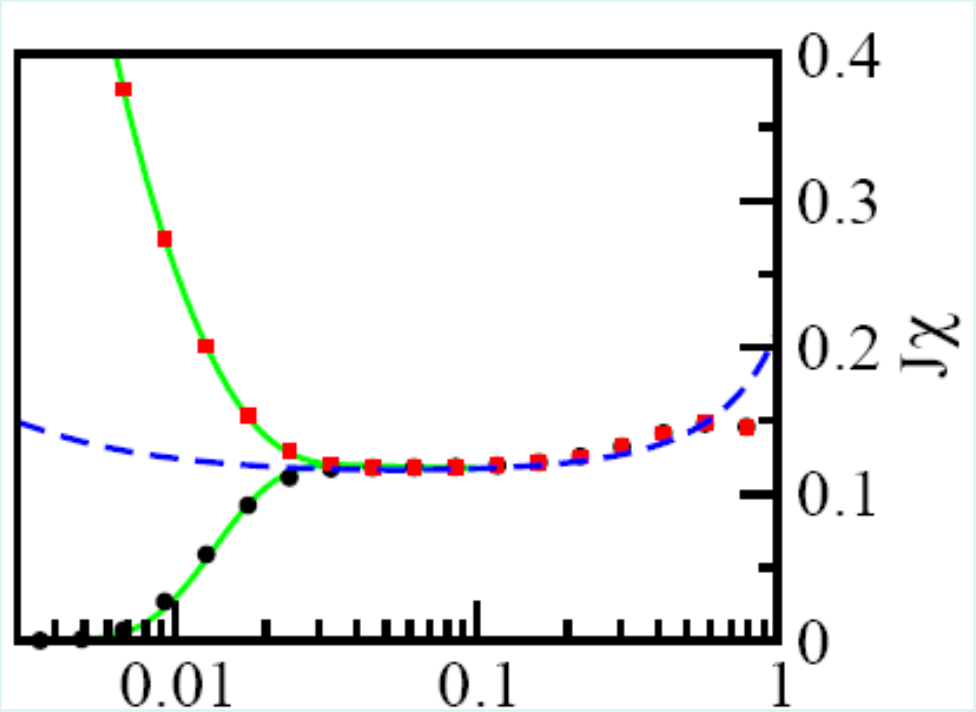
- S^z=integer (L even) or ½-integer (L odd)
- Harmonic oscillator excitations make

no contribution to χ which is simply obtained from differentiating with respect to h the (partial) partition function:

$$Z(h) = \sum_m \exp\left[-\pi v m^2 / (LT) - hm \right]$$

(sum restricted to integer or ½-integer m For L even or odd respectively)

- This gives a χ with the expected asymptotics at $LT \ll \pi v$ and $\chi \to 1/(2\pi v)$ for $LT \gg \pi v$ (for L even *or* odd)
- This is actually correct asymptotically at $T \ll J$, $L \gg 1$, for any ratio LT/J
- However, corrections to it are quite large for any reasonable L or T
- Corrections only vanish like 1/ln (J/T), 1/ln L
- We can make further progress 2 ways:
  1. higher order field theory calculations
  2. numerical work



L=100

L=99

field theory

NB- low T asymptotics at T<.03J~π v/L

- approximately constant at higher T

- Higher order field theory results are obtained by keeping sine-Gordon interaction in addition to free boson Hamiltonian:

$$H = \int_0^L \left[\frac{v}{2} \Pi^2 + \frac{v}{2} \left(\frac{\partial \varphi}{\partial x} \right)^2 + \lambda \cos\left(\sqrt{8\pi}\varphi \right) \right]$$

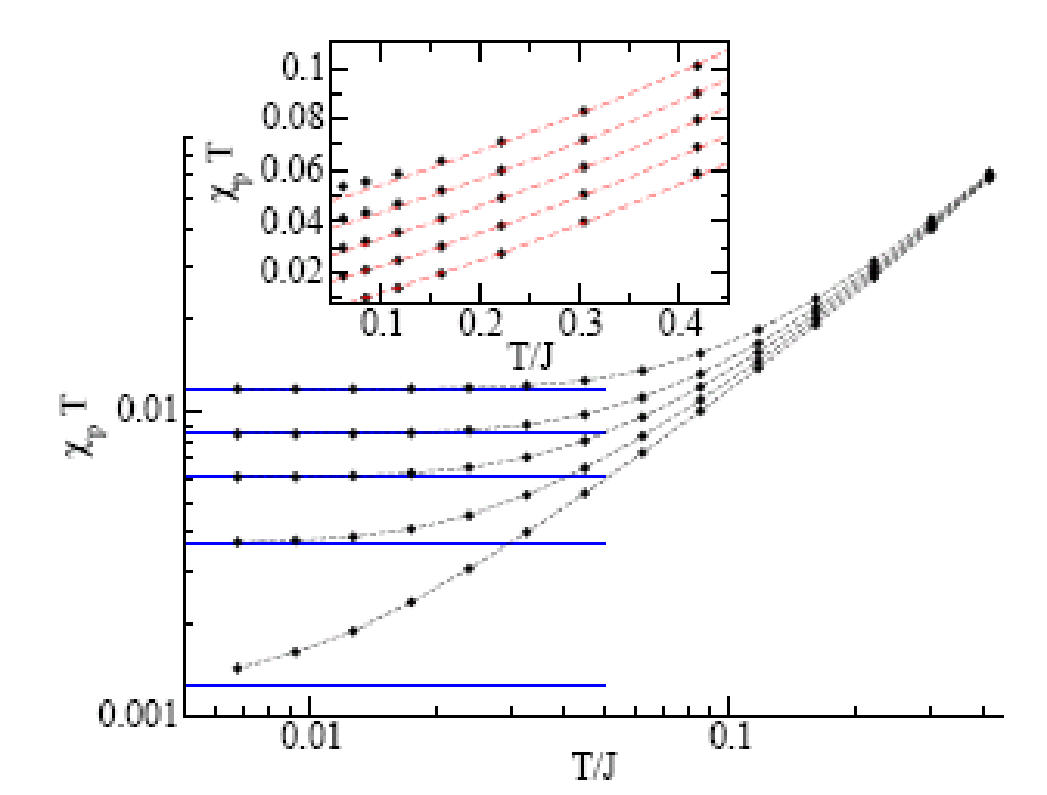
- We did 1st order perturbation theory in λ (at finite L and T!)
- Must use $\lambda \sim 1/[4 \ln(\min\{L, J/T\})]$ from renormalization group treatment

- We did Monte Carlo for L<1000 and a large range of T – data on line at PRL
- To compare with experiments, we averaged χ (L,T) over L, assuming a Poisson distribution (i.e. impurities at random positions)
- For impurity concentration p, we obtain low T asymptotics when T<<pJ:

$\chi \rightarrow p/(8T)$ (p/2 is concentration of S=1/2's)

- At pJ<<T<<J, from field theory, we get:

$\forall \chi \rightarrow \chi_0 + p/[12T\ln(3J/T)]$ where χ_0 is bulk result

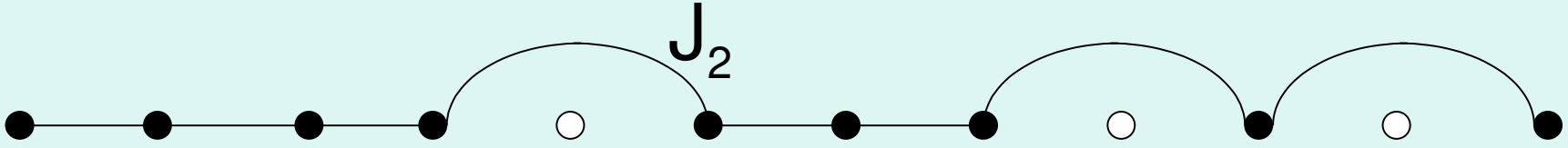


Monte Carlo data compared to T<<pJ and pJ<<T<<J field theory results for p=.01, .03, .05, .07, .10

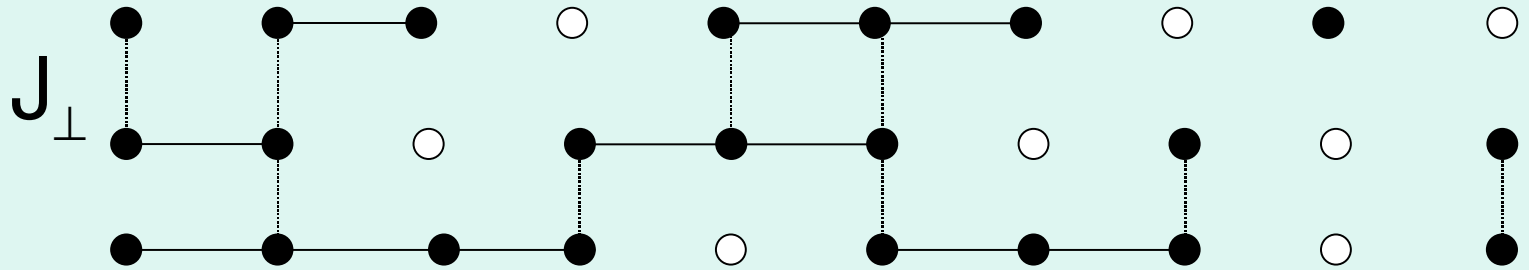
- Naïve formula would be: $\chi = \chi_0 + p/(8T)$
- We get this, approximately, even at $Jp \ll T \ll J$ but with: $p \rightarrow p/[3\ln(3J/T)] \ll p$
- N.B. *it is dangerous to fit to naïve formula!*

-this can lead to drastic underestimate of p

Corrections due to other interactions:



2nd neighbour interaction, J_2 may bridge non-magnetic impurities



- Interchain coupling, $J_\perp$ produces a connected 3D network of spins – leads to Néel order at low $T \sim J_\perp$
- Both corrections negligible at $T >> p^2 J_2, J_\perp$

$Sr_2Cu_{1-x}Pd_xO_{3+\delta}$

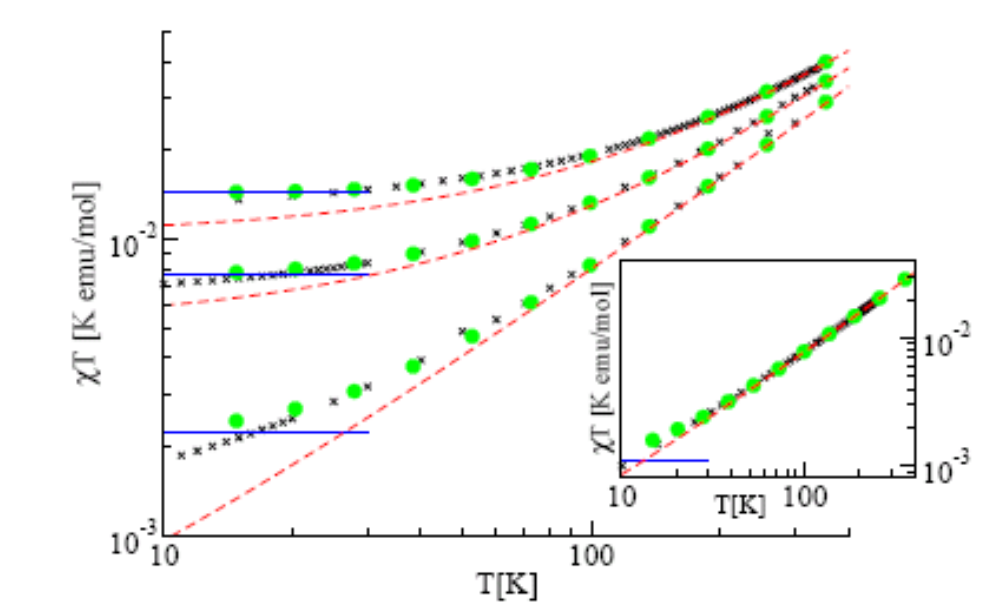
- Sr_2CuO_3 is a copper-oxide, high-T_c-like material with single Cu-O-Cu chains with J=2200 K, T_N~J'~5 K, J_2~140 K
- Experiments on nominally pure material saw a 1/T term in χ at low T (Ami et al. 1995, Motoyama et al. 1996)
- This was attributed to excess oxygen
- Disappeared with annealing

- Excess O should donate holes to Cu-O chains (2 holes per excess O)
- If holes are localized (near O's) then they could act as non-magnetic impurities
- We can fit data to our theory, finding p~.6%
- Original fitting gave p~.06% due to using naive form of χ !
- However, newer interpretation is that $Sr_2Cu(OH)_6$ forms on surface- gives nearly isolated Cu spins - Hill et al. 2002
- May explain Ami et al. powder results but not Motoyama et al. single crystals?

- Cu was partially substituted with Pd – non-magnetic dopant –Kojima et al, 2004
- Samples were not annealed (thought to be unnecessary since p=.06% !!)
- We get quite a good fit to data, taking p as a free parameter
- However, p doesn't agree so well with expected value (x)

x (Exp.)	p (Theory)	χ_0 [emu/mol]
0.0	0.006	-7.42×10^{-5}
0.005	0.012	-7.7×10^{-5}
0.01	0.014	-7.5×10^{-5}
0.03	0.024	-7.5×10^{-5}

- Due to excess O?
- Problem with x=.03 sample?



Main figure: Pd doped samples
Inset: nominally pure sample
Blue and red lines: field theory asymptotics
x – experimental data
● - Monte Carlo

Conclusions

- We have determined χ (p,T) very accurately for Heisenberg chain with random non-magnetic impurities
- Results can be used as a rather precise diagnostic for real materials
- Beware use of naïve formula – may severely underestimate impurity concentration!