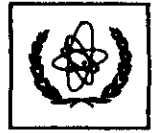




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**SMR.959 - 3**

**MINIWORKSHOP ON STRONG ELECTRON CORRELATIONS**  
**"Disorder and Interaction in Quantum Systems**  
**and Their Classical Analogs"**

**(1 - 19 July 1996)**

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**"Switching of the Gapped Singlet Spin Liquid State**  
**to an Antiferromagnetically Ordered State**  
**in Sr [Cu<sub>1-x</sub>Zn<sub>x</sub>]<sub>2</sub>O<sub>3</sub>"**

**Masaki Azuma**  
**Kyoto University**  
**Institute for Chemical Research**  
**Laboratory of Solid State Chemistry**  
**Kyoto 611**  
**Japan**

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***These are preliminary lecture notes, intended only for distribution to participants.***

**Switching of the  
Gapped Singlet Spin Liquid State  
to an  
Antiferromagnetically Ordered  
State in  $\text{Sr}(\text{Cu}_{1-x}\text{Zn}_x)_2\text{O}_3$**

**Masaki Azuma**      **Inst. Chem. Res., Kyoto Univ**  
**Mikio Takano**      **Synthesis, Susceptibility**  
**Zenji Hiroi**

**Kenji Ishida**      **Osaka Univ.**  
**Yoshio Kitaoka**      **NMR**

**Kenji Kojima**      **Columbia Univ.**  
**Y. J. Uemura**       **$\mu$ SR**

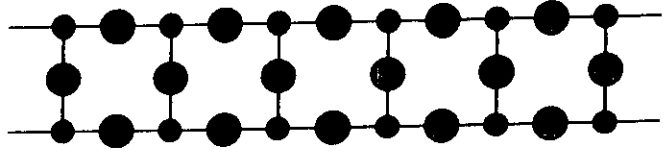
**Minoru Nohara**      **ISSP Univ. Tokyo**  
**Hidenori Takagi**      **Specific Heat**

**Roger Eccleston**      **ISIS RAL**  
**Neutron scattering**

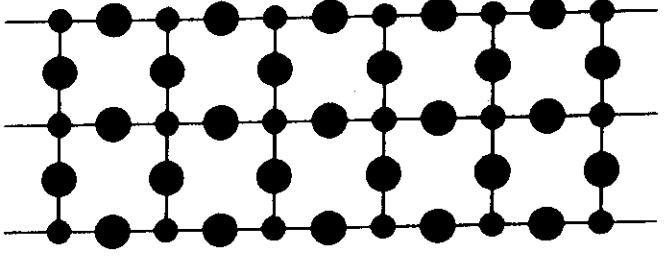
1D chain



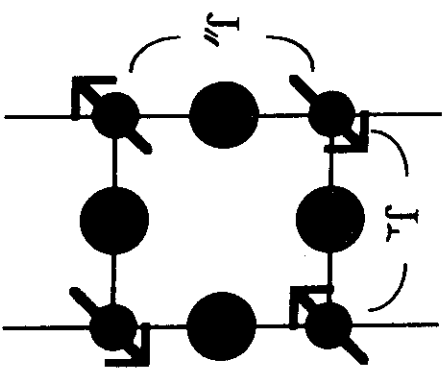
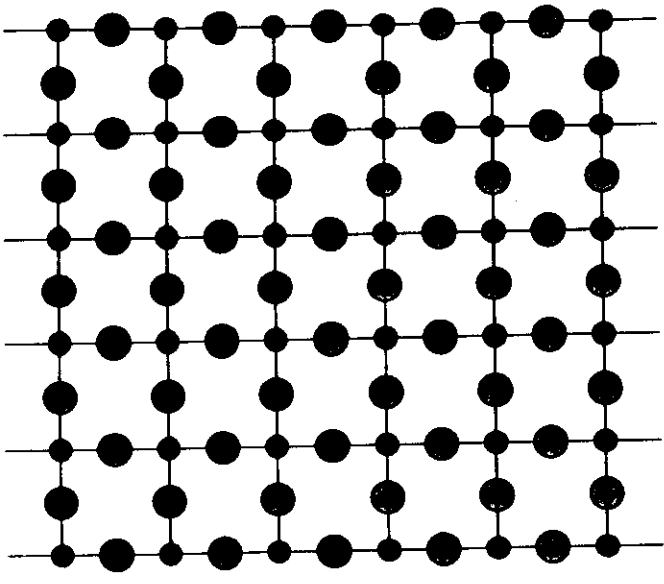
spin ladder



2D square lattice



...



**Heisenberg type**

**$S=1/2$ ,  $J_{//}$ ,  $J_{\perp}$ : antiferromagnetic**

# Surprises on the Way from One- to Two-Dimensional Quantum Magnets: The Ladder Materials

Elbio Dagotto and T. M. Rice

To make the transition from the quasi-long-range order in a chain of antiferromagnetically coupled  $S = 1/2$  spins to the true long-range order that occurs in a plane, one can assemble chains to make ladders of increasing width. Surprisingly, this crossover between one and two dimensions is not at all smooth. Ladders with an even number of legs have purely short-range magnetic order and a finite energy gap to all magnetic excitations. Predictions of this ground state have now been verified experimentally. Holes doped into these ladders are predicted to pair and possibly superconduct.

"d-wave" state, which places them in a different universality class of 1D systems than the Luttinger liquids found in single chains and odd-leg ladders.

## Theoretical Aspects of the $S = 1/2$ Heisenberg Model on Ladders

The properties of  $S = 1/2$  Heisenberg AF models defined on 1D chains or on 2D square lattices are well-known. The model is defined by the Hamiltonian

$$H = J \sum_{\langle i, j \rangle} S_i \cdot S_j$$

The unexpected discovery of high-temperature superconductivity (1) in lightly doped antiferromagnets has sparked renewed interest in low-dimensional quantum magnets. The parent cuprate insulators are now considered the best examples of planar spin- $1/2$  antiferromagnets with isotropic and predominantly nearest-neighbor coupling. They show simple long-range antiferromagnetic (AF) order at low temperatures in agreement with theory, which predicts an ordered ground state for the  $S = 1/2$  AF Heisenberg model on a two-dimensional (2D) square lattice (2). The 1D AF Heisenberg chain is also well understood. A famous exact solution found by Bethe many years ago (3) showed that quantum fluctuations prevent true long-range AF order, giving instead a slow decay of the spin correlations at a rate that varies essentially inversely with the separation between the spins. Therefore, it came as a great surprise when numerical calculations found that the crossover from chains to square lattices, obtained by assembling chains one next to the other to form "ladders" of increasing width, was far from smooth. Although there is no apparent source of frustration, quantum effects lead to a dramatic dependence on the width of the ladder (given by the number of coupled chains).

Ladders made from an even number of legs have spin-liquid ground states, so called because of their purely short-range spin correlation. An exponential decay of the spin-spin correlation is produced by a finite spin gap, namely, a finite energy gap to the lowest  $S = 1$  excitation in the infinite ladder. These even-leg ladders may therefore be regarded as realizations of the unique, coherent singlet ground state proposed some years ago by Anderson in the

context of 2D  $S = 1/2$  AF Heisenberg systems (the so-called resonance valence bond state) (4).

A ladder with an odd number of legs behaves quite differently and displays properties similar to those of single chains at low energies, namely gapless spin excitations and a power-law falloff of the spin-spin correlations, apart from logarithmic corrections. This dramatic difference between even-leg and odd-leg ladders predicted by theory has now been confirmed experimentally in a variety of systems.

Two-leg  $S = 1/2$  ladders are found in vanadyl pyrophosphate ( $\text{VO})_2\text{P}_2\text{O}_7$  and in some cuprates like  $\text{SrCu}_2\text{O}_3$  (Fig. 1) ( $m$ -leg ladder denotes  $m$  coupled spin- $1/2$  chains). Measurements of the spin susceptibility show that it vanishes exponentially at low temperature, a clear sign of a spin gap. Neutron scattering and muon spin resonance measurements are consistent with short-range spin order in the 2-leg ladders, although as we stressed before, they are unfrustrated spin systems that classically should order without a spin gap. Further nuclear magnetic resonance (NMR) measurements have confirmed the large spin gap in the excitation spectrum.

Three-leg ladders ( $\text{Sr}_2\text{Cu}_3\text{O}_7$ ) by contrast show longer range spin correlations and even true long-range order at low temperature because of weak interladder forces. There is excellent agreement between theory and experiment, confirming that there is a dramatic difference between even- and odd-leg  $S = 1/2$  Heisenberg AF ladders.

Doped chains have long fascinated theorists because they form unusual quantum liquids, so-called Luttinger liquids, with many unique properties (5). Although doping experiments in ladder compounds are just starting, extensive theoretical studies have been made of doped ladders. Again, a clear difference between even- and odd-leg ladders is predicted. Even-leg ladders are especially interesting because a variety of techniques reveal hole pairing in a relative

where  $i$  is a vector labeling lattice sites where spin- $1/2$  operators  $S_i$  are located,  $\langle i, j \rangle$  denotes nearest-neighbor sites, and  $J (> 0)$  is the AF exchange coupling that provides the energy scale in the problem. This scale is material dependent and ranges from a few millielectron volts to, in the case of high-temperature superconductors, about 0.1 eV. On 2D square lattices, the Heisenberg model has a ground state with long-range AF order, whereas in 1D chains, the spin-spin correlation decays slowly to zero as a power law. Neither system has a spin gap, that is, there is no cost in energy to create an excitation with  $S = 1$ .

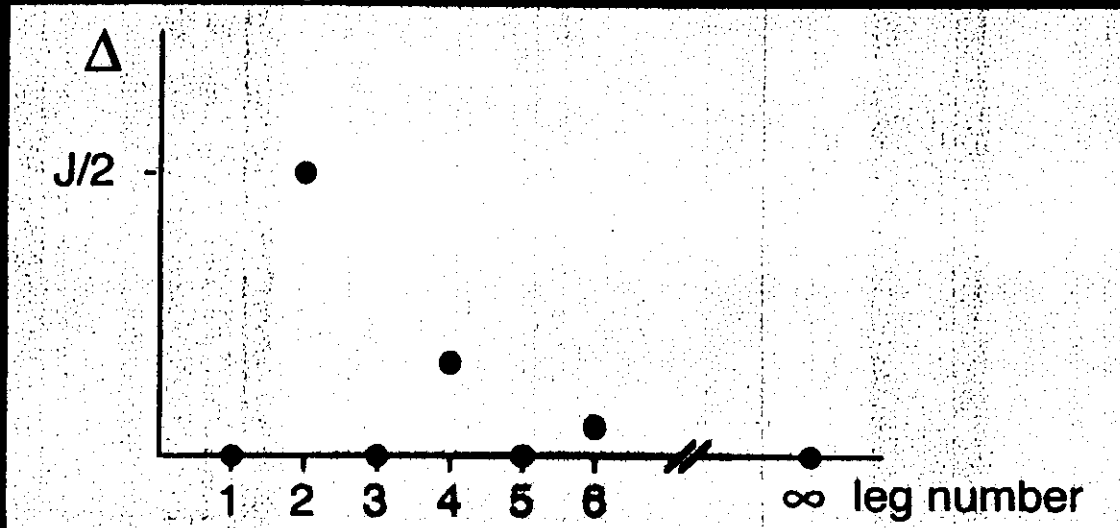
The field of ladder systems started when Dagotto et al. (6) [see also (7, 8)] found evidence that 2-leg ladders have a finite spin gap, because a finite energy is needed to create a  $S = 1$  excitation. They started with the simple limit obtained by generalizing Eq. 1 so that the exchange coupling along the rungs of a 2-leg ladder (denoted by  $J'$ ) is much larger than the coupling  $J$  along the chains. This idealization has the advantage that rungs interact only weakly with each other, and the dominant configuration in the ground state is the product state with the spins on each rung forming a spin singlet. The energy in this limit is approximately  $E_{\text{gs}} = -3/4J'N$ , where  $N$  is the number of rungs and  $-3/4J'$  is the energy of each rung singlet state  $|\Psi\rangle_S = (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)/\sqrt{2}$  ( $\uparrow$  and  $\downarrow$  are the spin-up and spin-down eigenvectors of the spin operator in the  $z$  direction). The ground state has a total spin  $S = 0$  because each rung is in a spin singlet. To produce a  $S = 1$  excitation, a rung singlet must be promoted to a  $S = 1$  triplet  $|\Psi\rangle_T = (|\uparrow\uparrow\rangle, |\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle)/\sqrt{2}, |\downarrow\downarrow\rangle$ . An isolated rung-triplet has an energy  $J'$  above the rung singlet. The coupling along the chains cre-

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## What are interesting of spin ladders?

1. Intermediates between 1D and 2D  
new, yet to be known.
2. Even-legged ladders vs odd-legged ladders

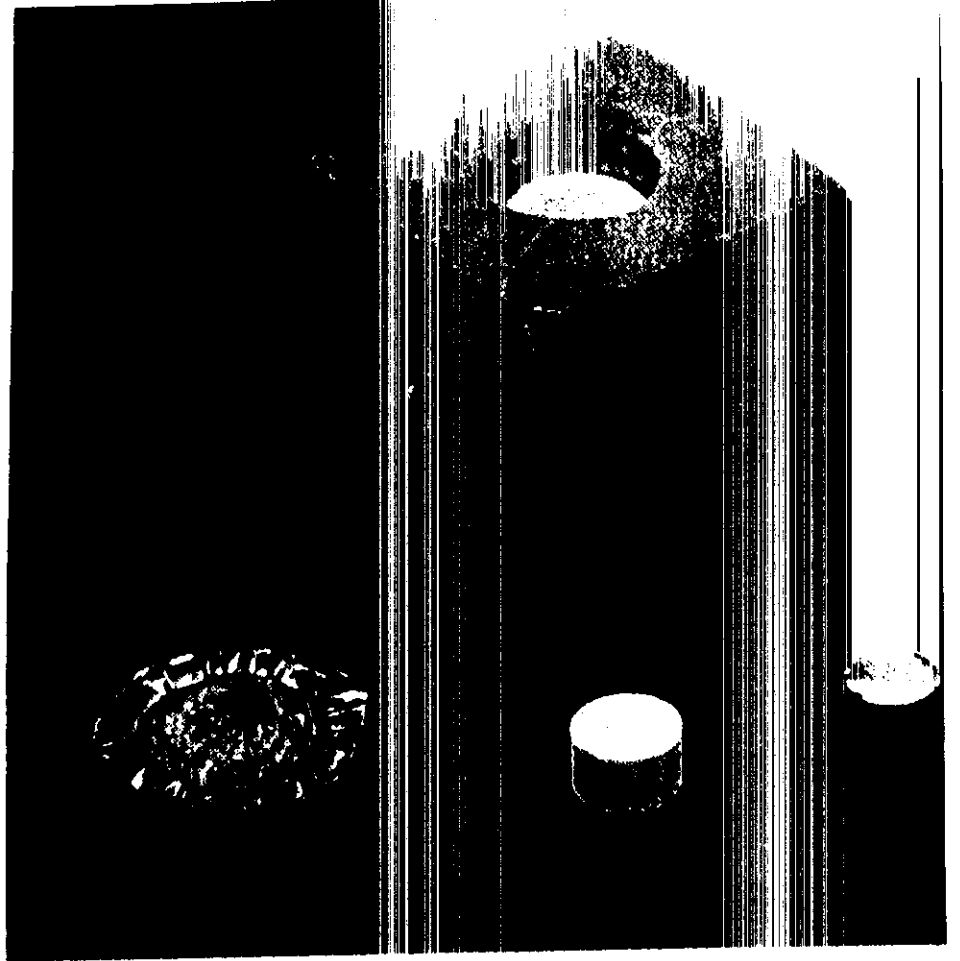
### (i) undoped ladders

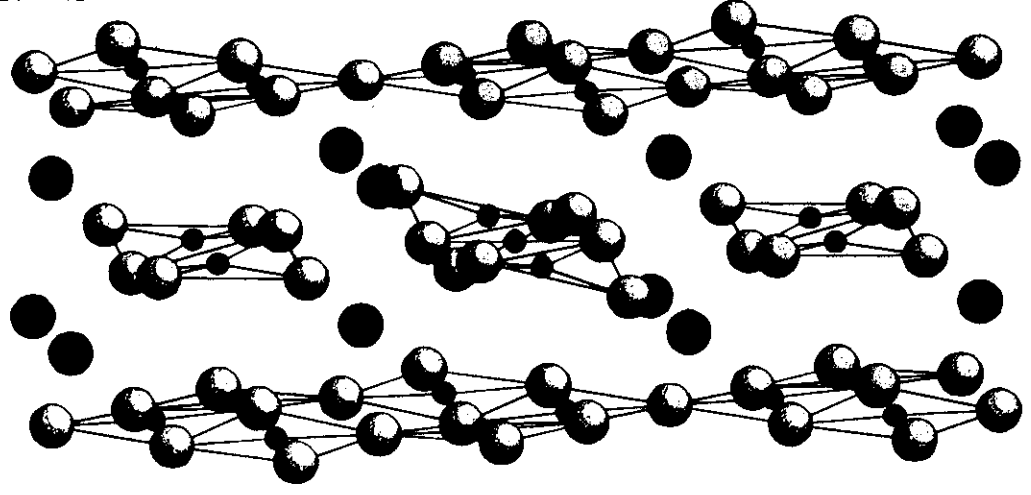
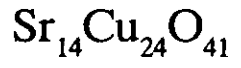
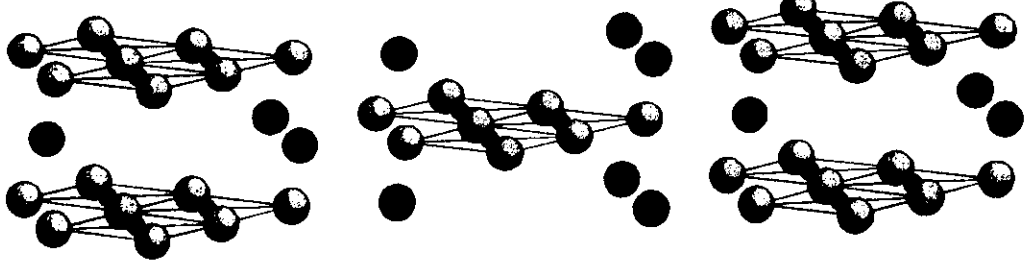
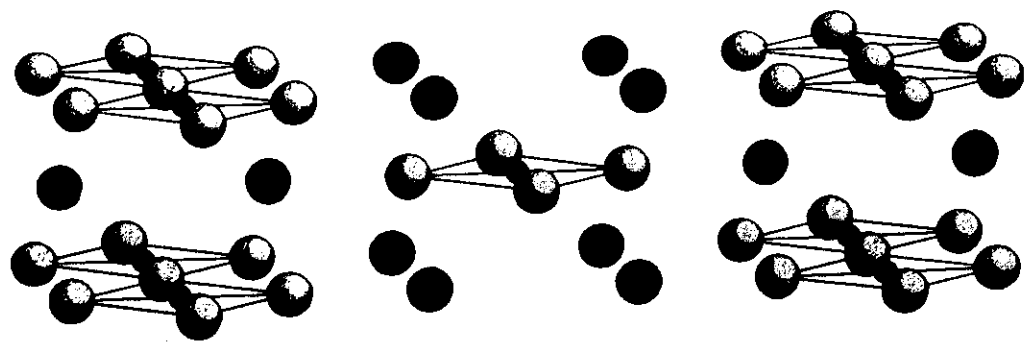
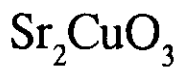


### (ii) doped ladders

even-legged : d wave superconductivity  
odd-legged : Tomonaga-Luttinger liquid

3. Competition between quantum spin liquid state and magnetic state





$\text{SrCuO}_2 + \text{CuO}$   
4.5 GPa 1100°C

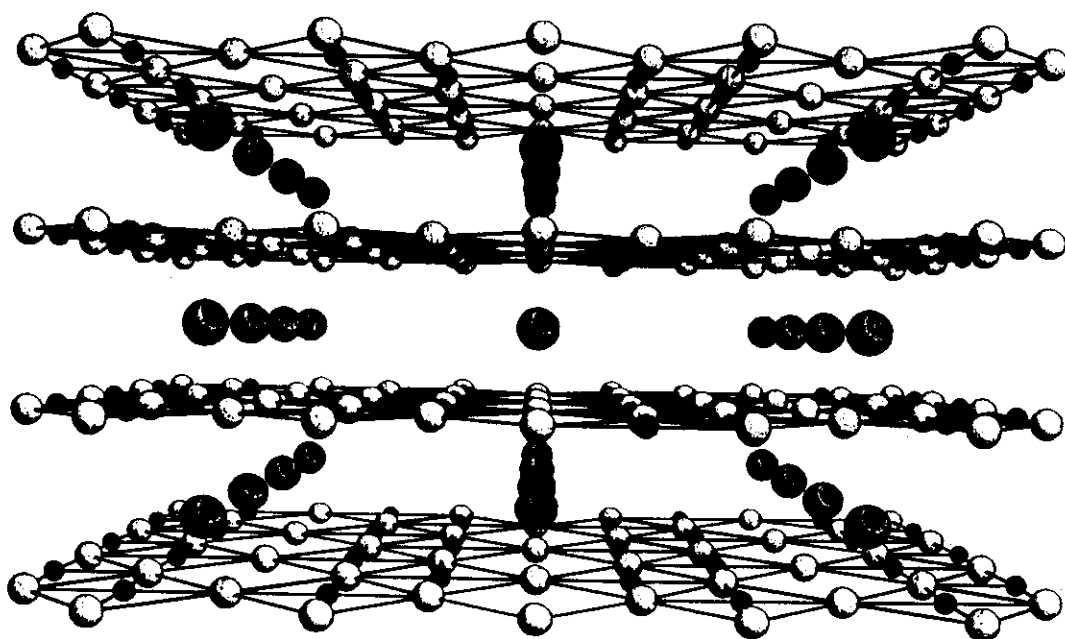


$\text{SrCu}_2\text{O}_3$   
2-leg ladder

$2\text{SrCuO}_2 + \text{CuO}$   
3 GPa 1000°C

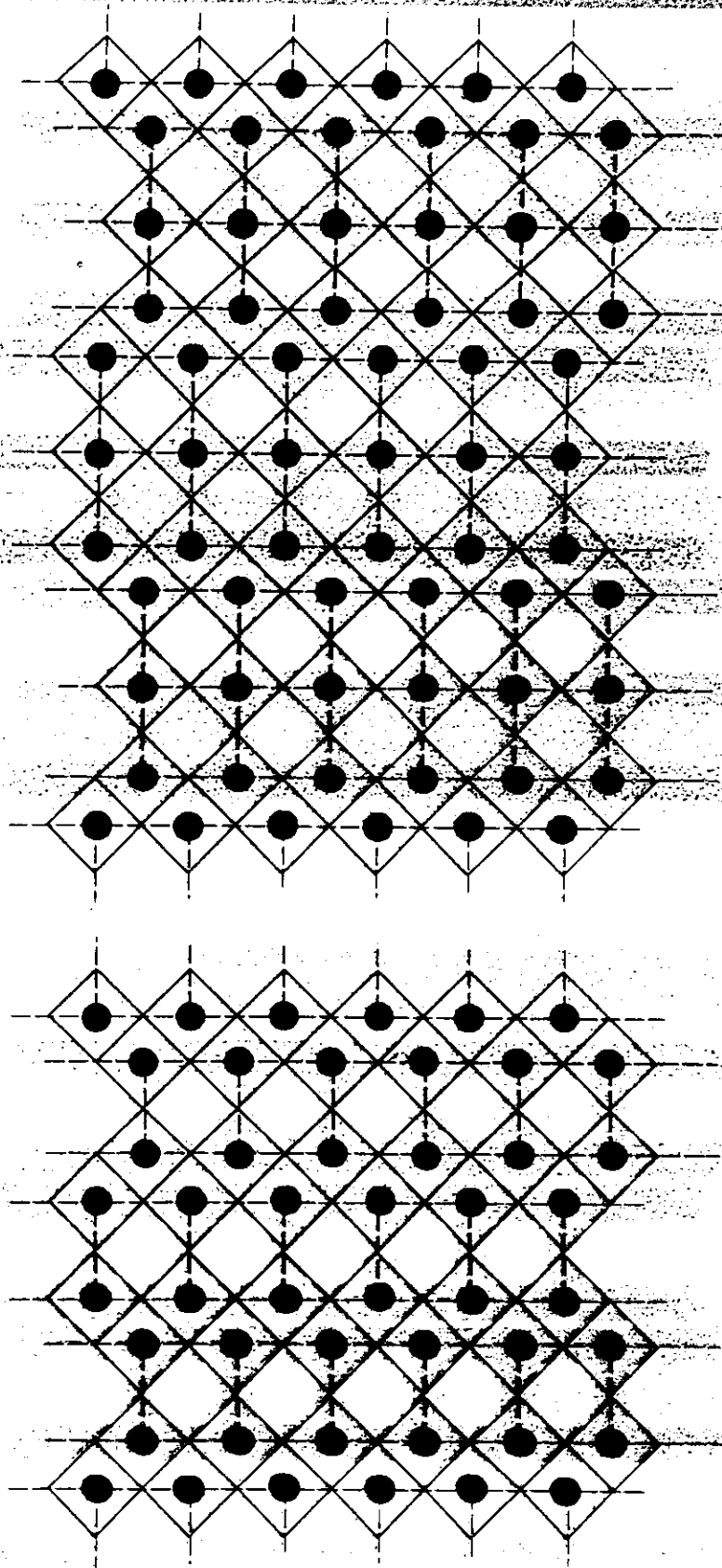


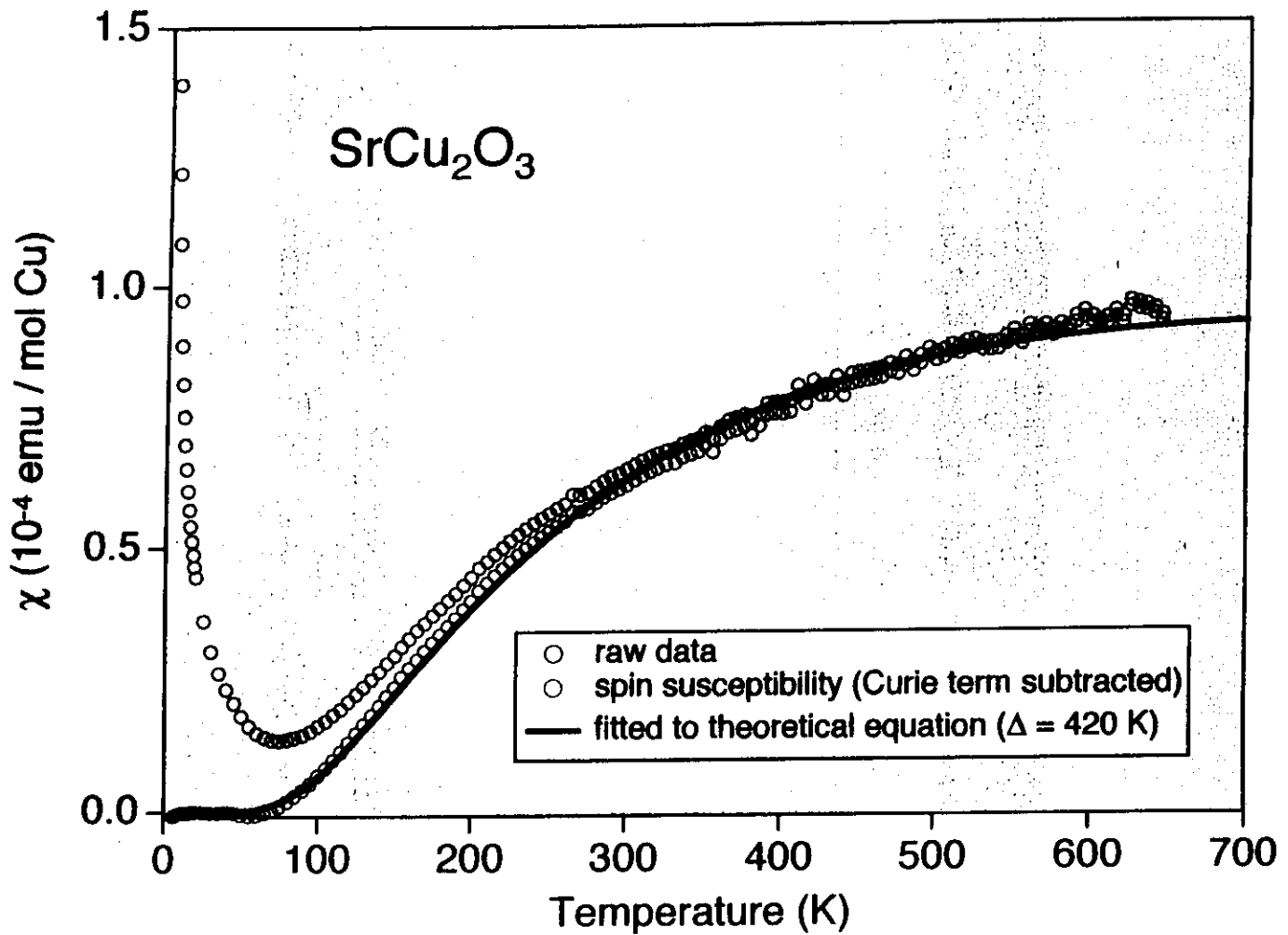
$\text{Sr}_2\text{Cu}_3\text{O}_5$   
3-leg ladder



$\text{SrCu}_2\text{O}_3$

Spin Ladders of  $\text{SrCu}_2\text{O}_3$  (2-leg) and  $\text{Sr}_3\text{Cu}_3\text{O}_5$  (3-leg)





below 20 K

$$\chi = 9.86 \cdot 10^{-4} / (T + 2.03) \text{ emu / Cu mole}$$

0.26% of Cu spin is free

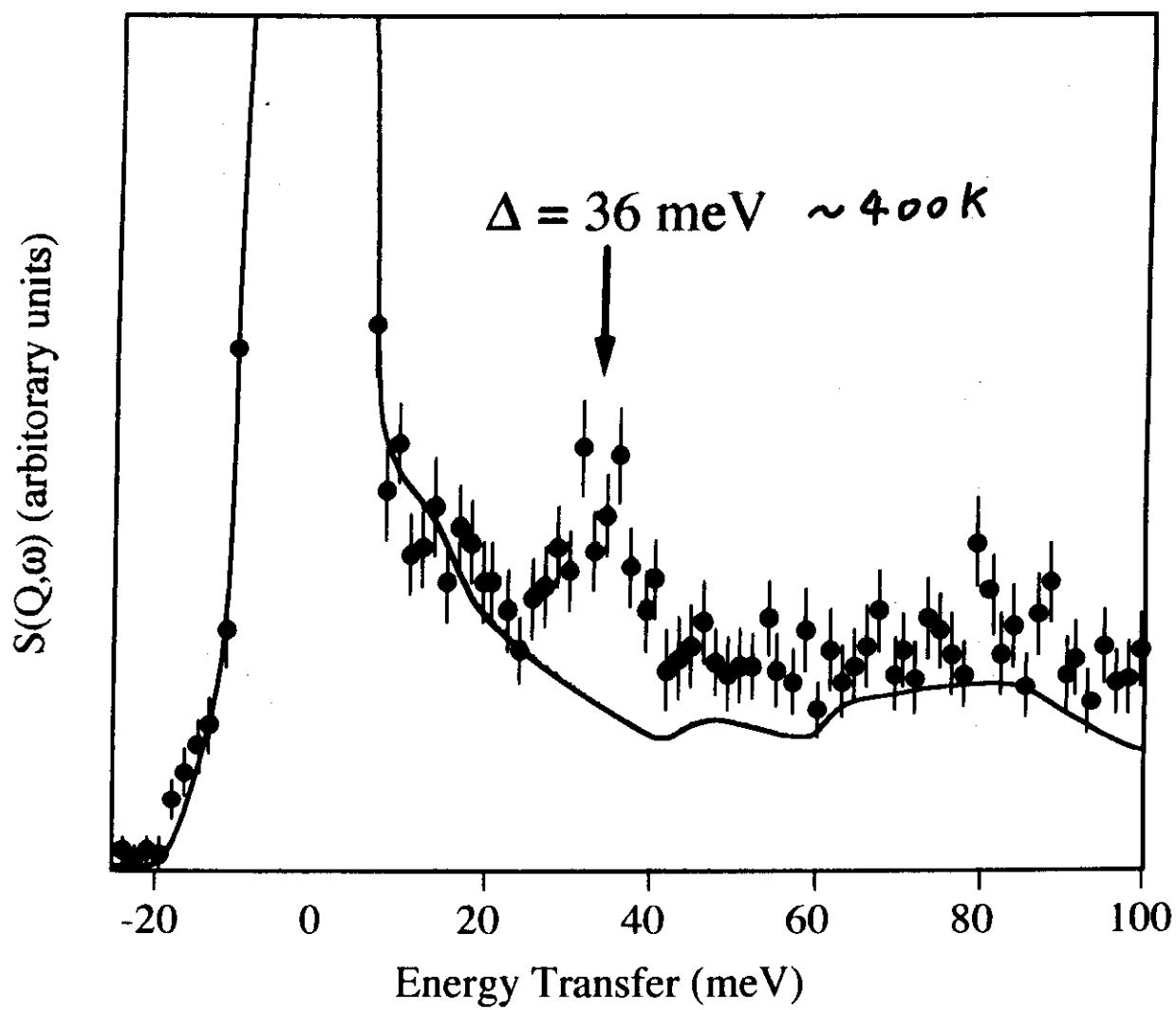
after subtraction of the Curie component

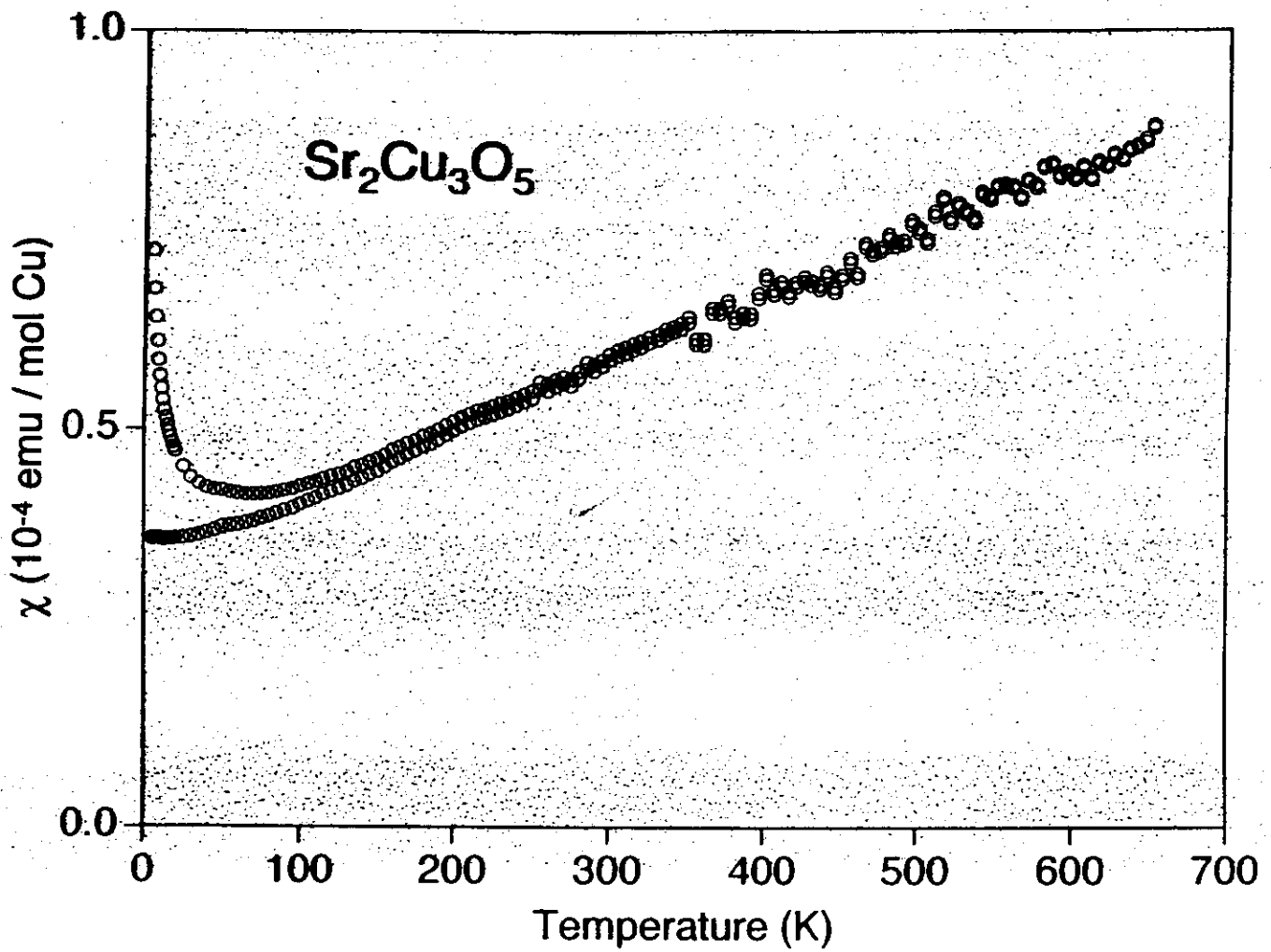
$$\chi = 4 \cdot 10^{-3} T^{-1/2} \exp(-420 / T)$$

$$\Delta = 420 \text{ K}$$

M. Troyer et al., Phys. Rev. B 50, 13515 (1994)

$\text{SrCu}_2\text{O}_3$   $T=25\text{K}$   $E_i = 250\text{ meV}$

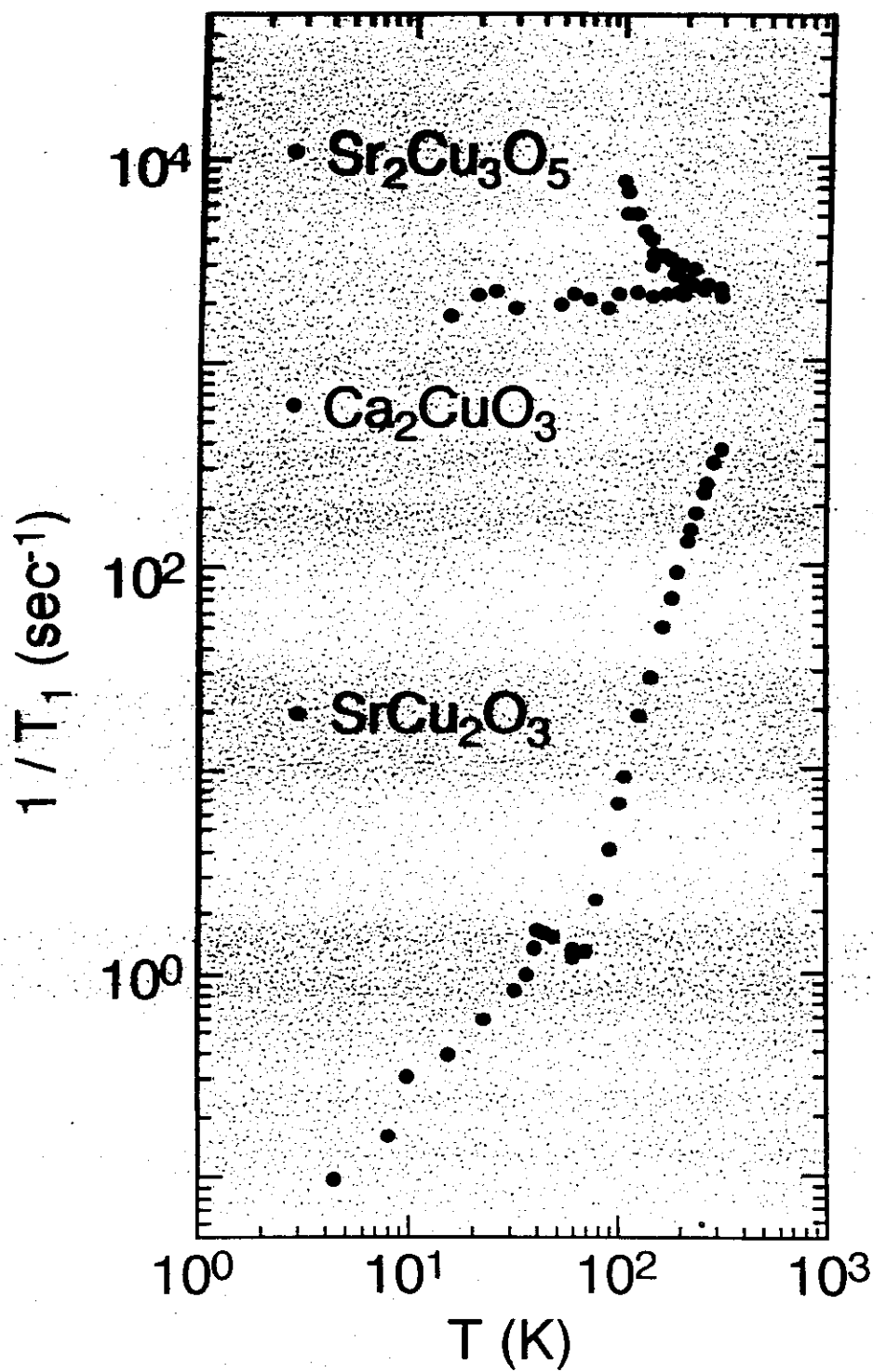




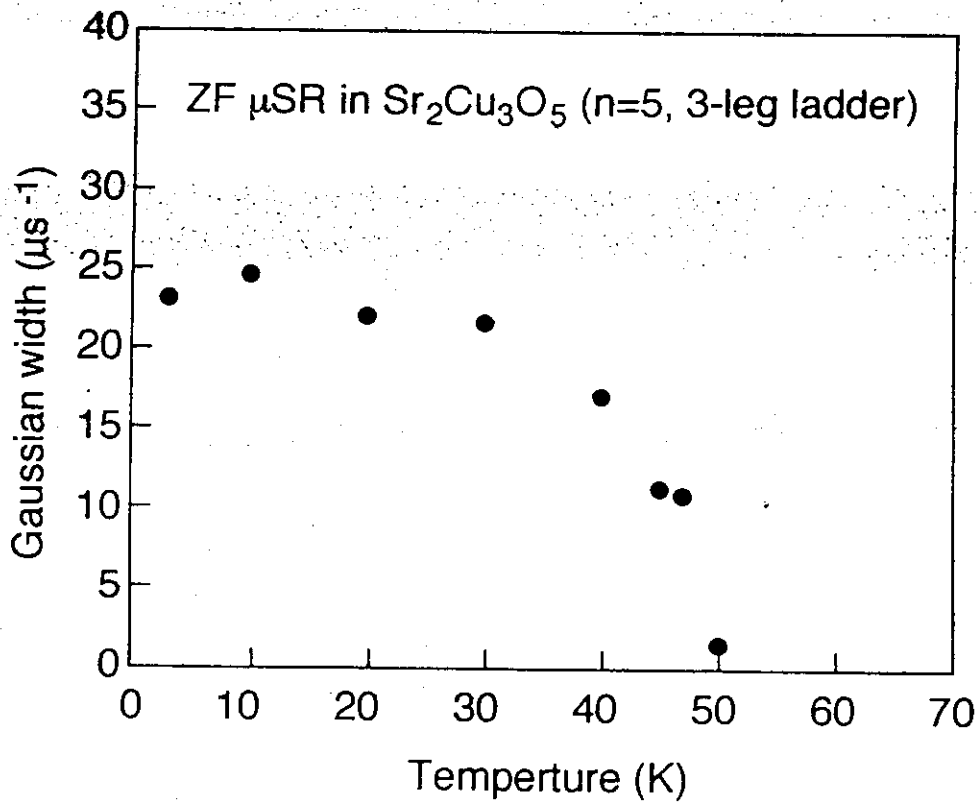
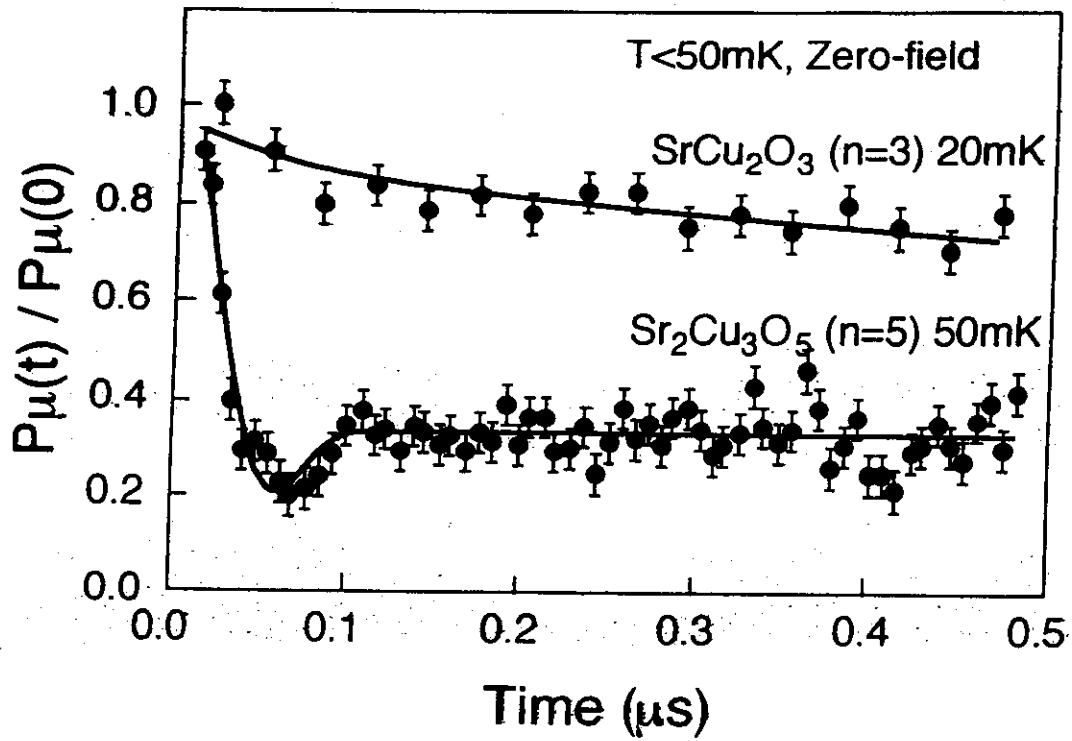
Finite susceptibility at the lowest temperature  
→ gapless

different from Bonner-Fisher type

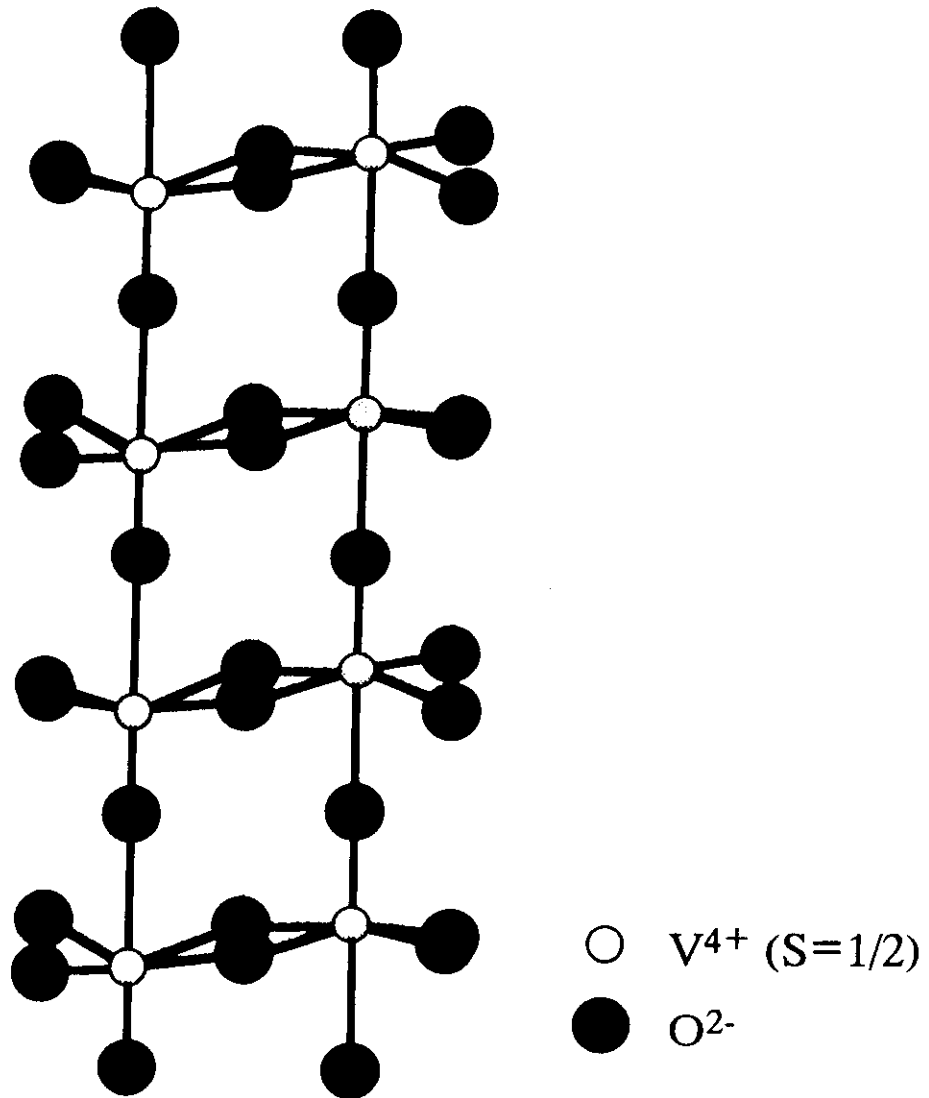
$^{63}\text{Cu}$  NMR  $1/T_1$



# $\mu$ SR



# V-O Ladder of $(VO)_2P_2O_7$



Alternating chain : 11.3meV (131K) , 7.9meV (92K)

D. C. Johnston, J. W. Johnson, D. P. Goshorn and A. J. Jacobson:  
Phys. Rev. B 35 (1987) 219.

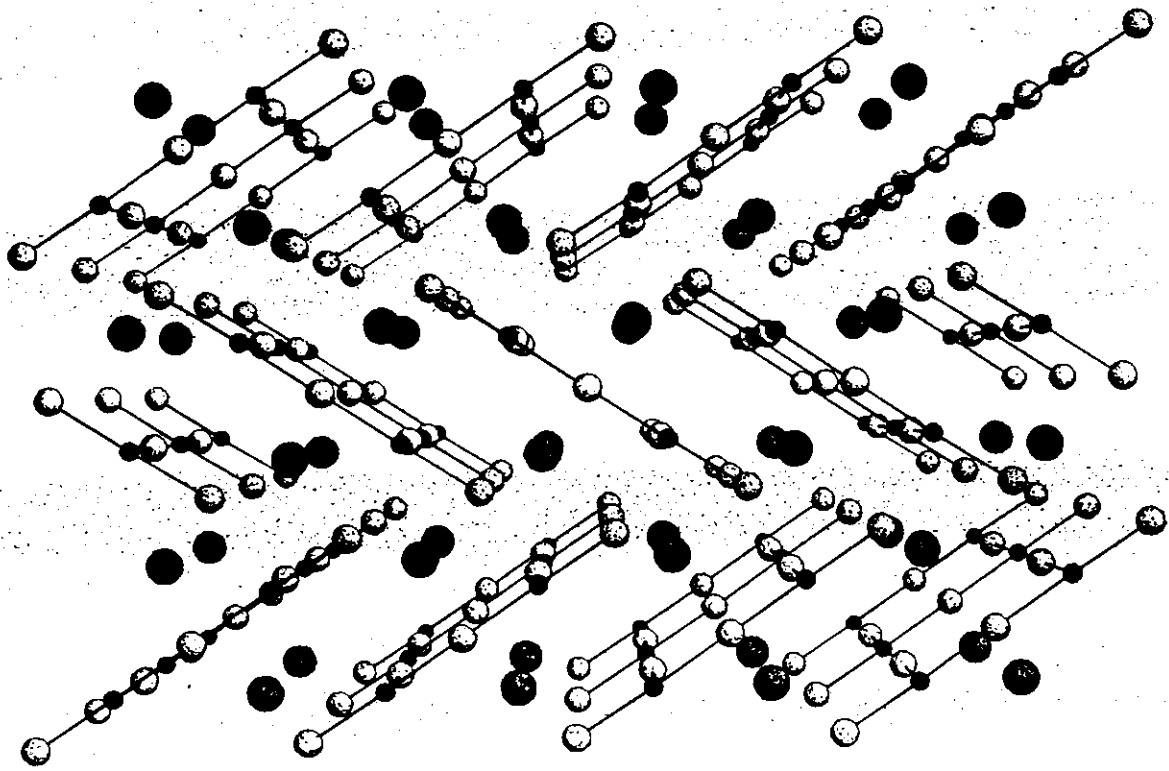
Spin ladder :  $J = 7.76\text{meV}$  (90.0.K) ,  $J' = 7.82\text{meV}$  (90.7K)

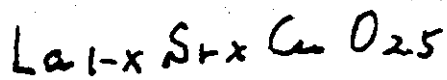
T. Barnes and J. Riera:  
Phys. Rev. B 50 (1994) 6817.

Inelastic neutron scattering  $\rightarrow$  Spin gap,  $\Delta = 3.7\text{meV}$

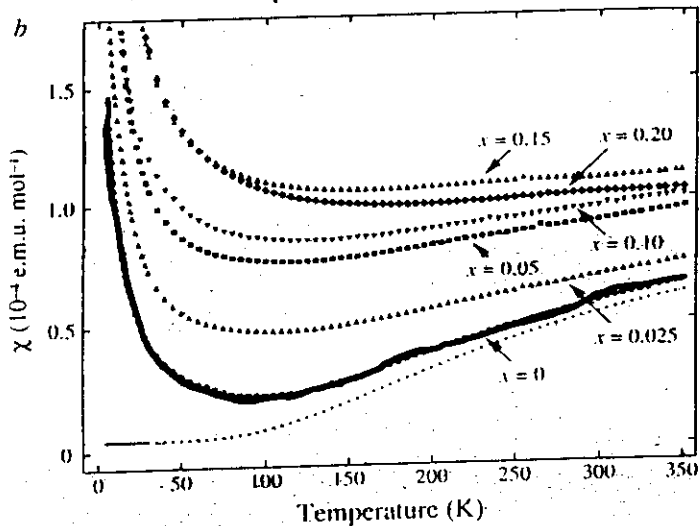
R. S. Eccleston, T. Barnes, J. Body and J. W. Johnson:  
Phys. Rev. Lett. 73 (1994) 2626.

LaCuO<sub>2.5</sub> 6GPa 900°C



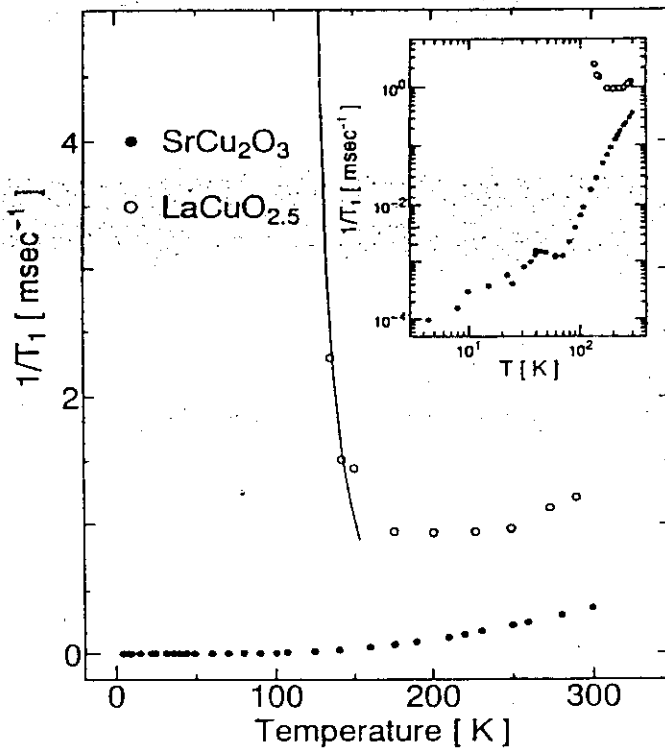
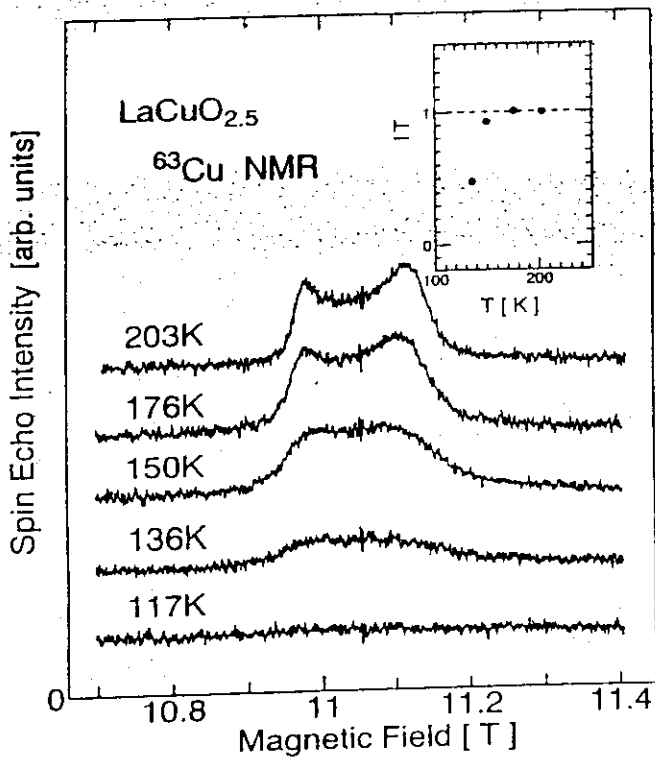
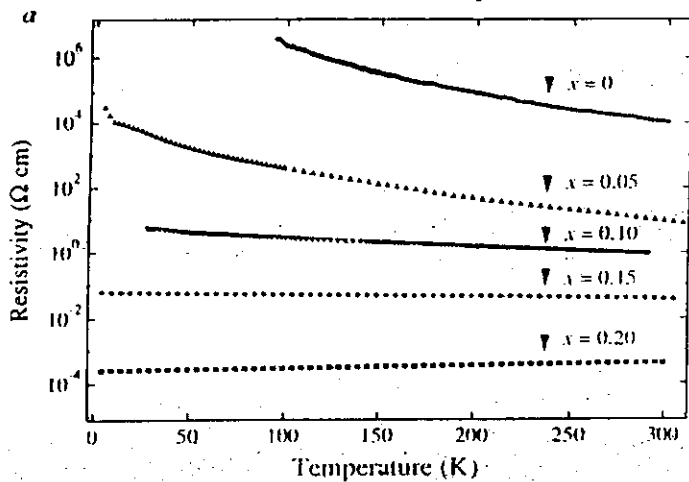


Susceptibility

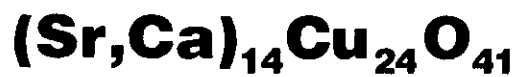


$\Delta \sim 480 \text{ K}?$

Resistivity



Magnetic Order! below 120 K



Cu<sub>2</sub>O<sub>3</sub> sheet (2-leg ladder) + CuO<sub>2</sub> chain (CuGeO<sub>3</sub>-like)

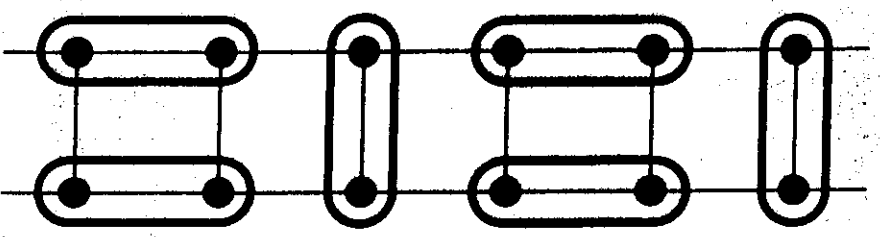
Already doped with hole, Cu<sup>2.24+</sup>

Ca content increases → conductive

Sr<sub>0.4</sub>Ca<sub>13.6</sub>Cu<sub>24</sub>O<sub>41.84</sub> (synthesized at high oxygen pressure)

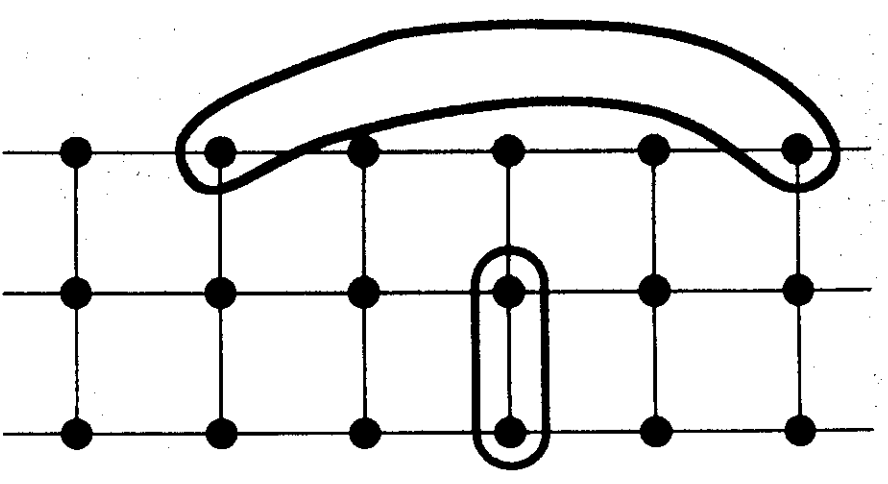
Superconducting at 3GPa (Akimitsu et al, 9K, 5%)

Short-range RVB (2-leg)



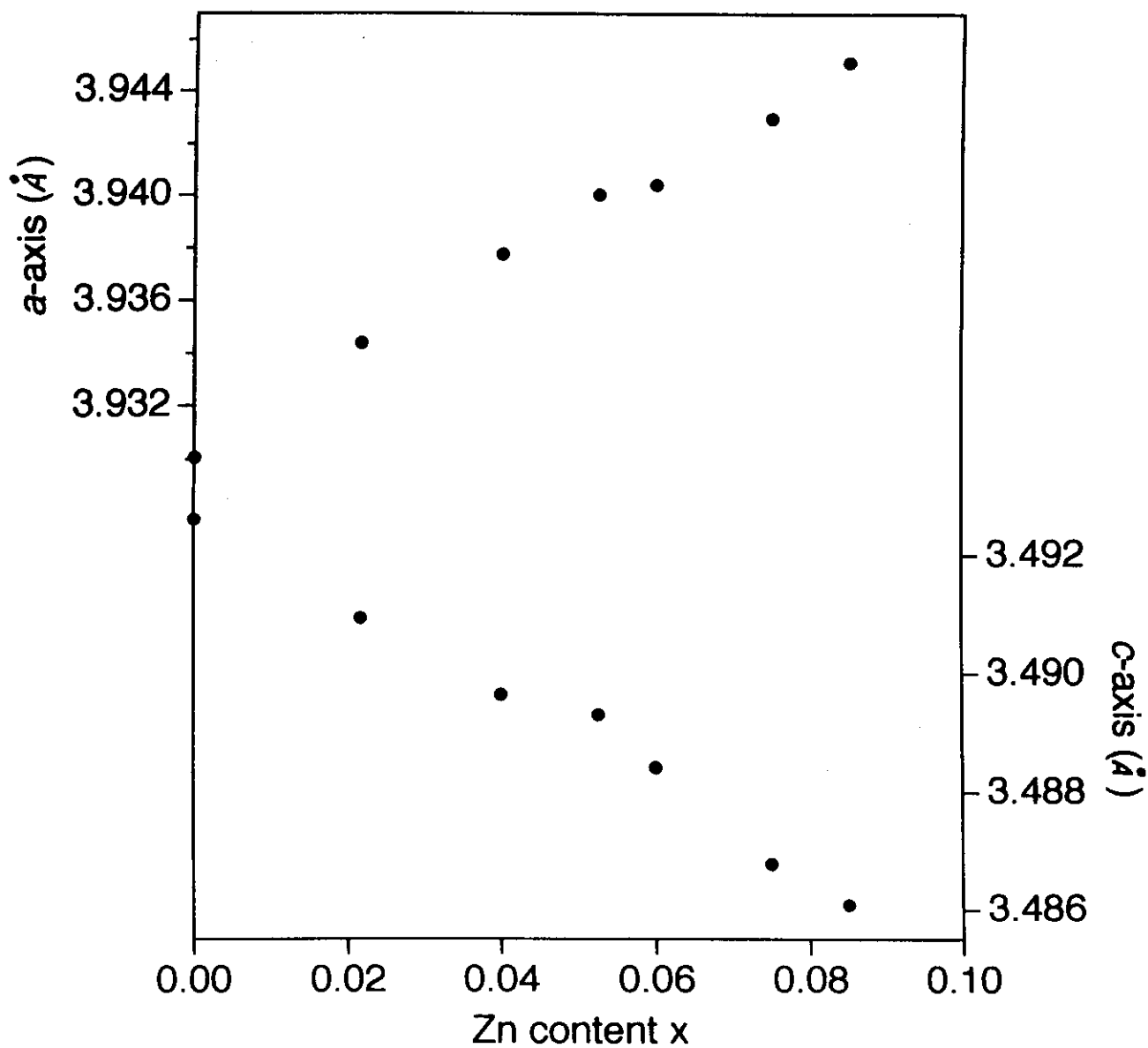
nonmagnetic impurity  
→ localized moment?

Long-range RVB (3-leg)

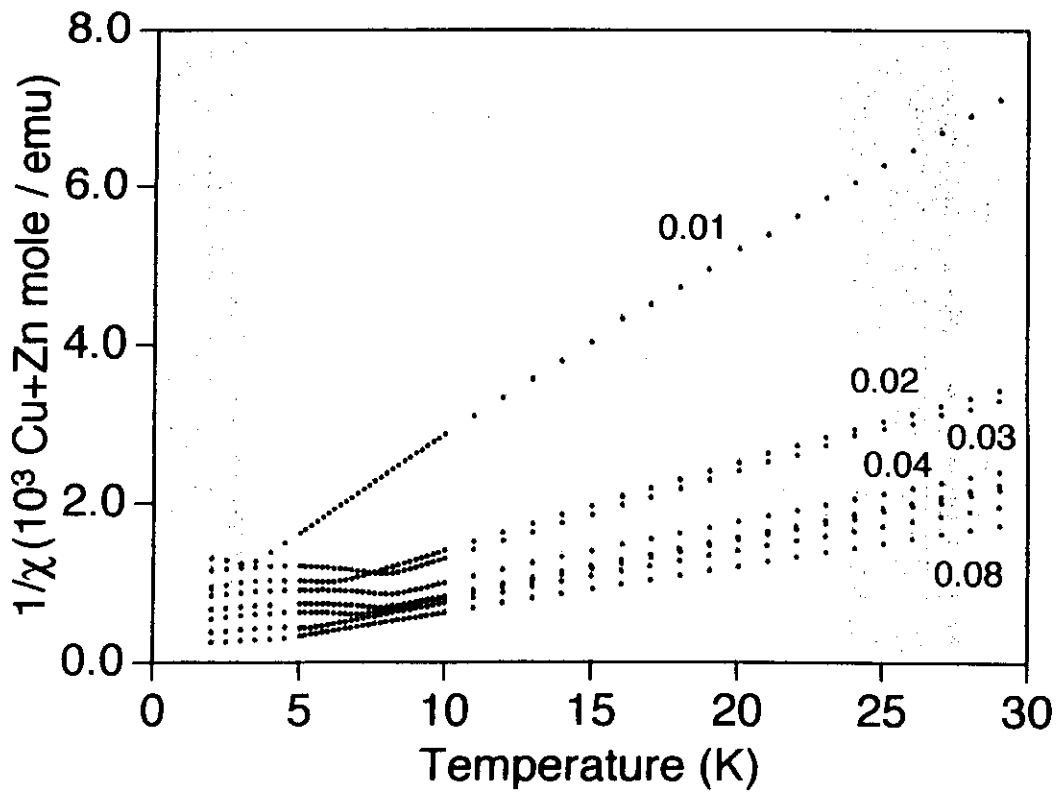
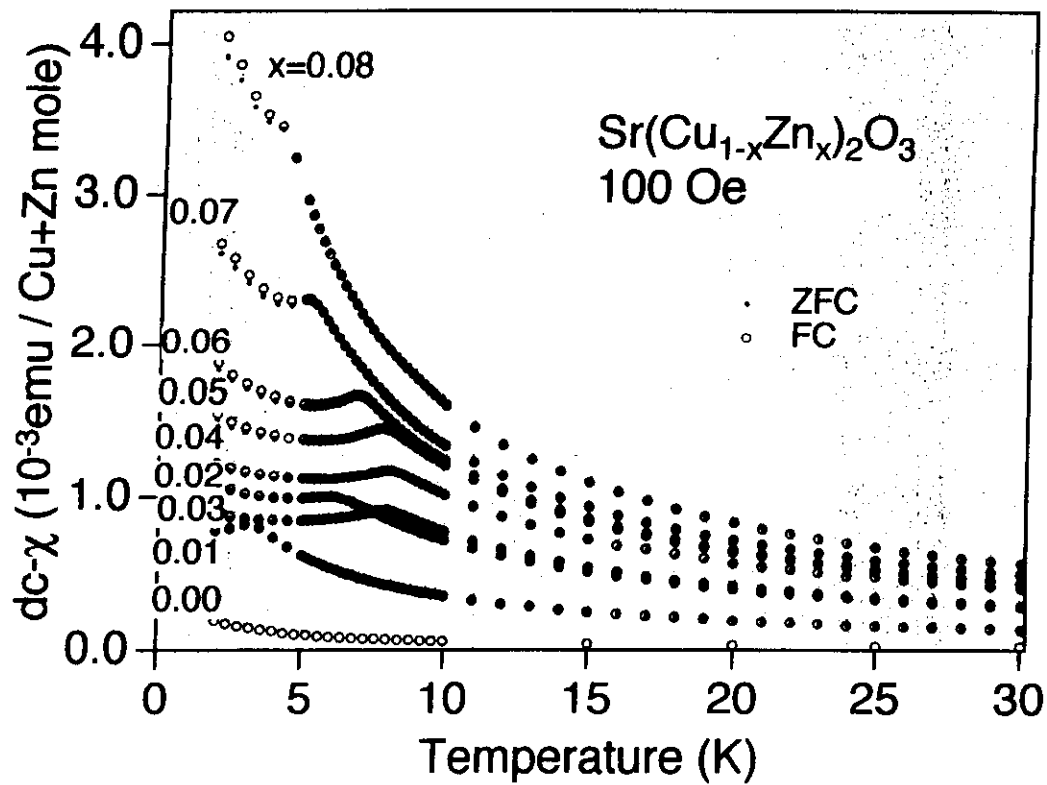


no localized moment?

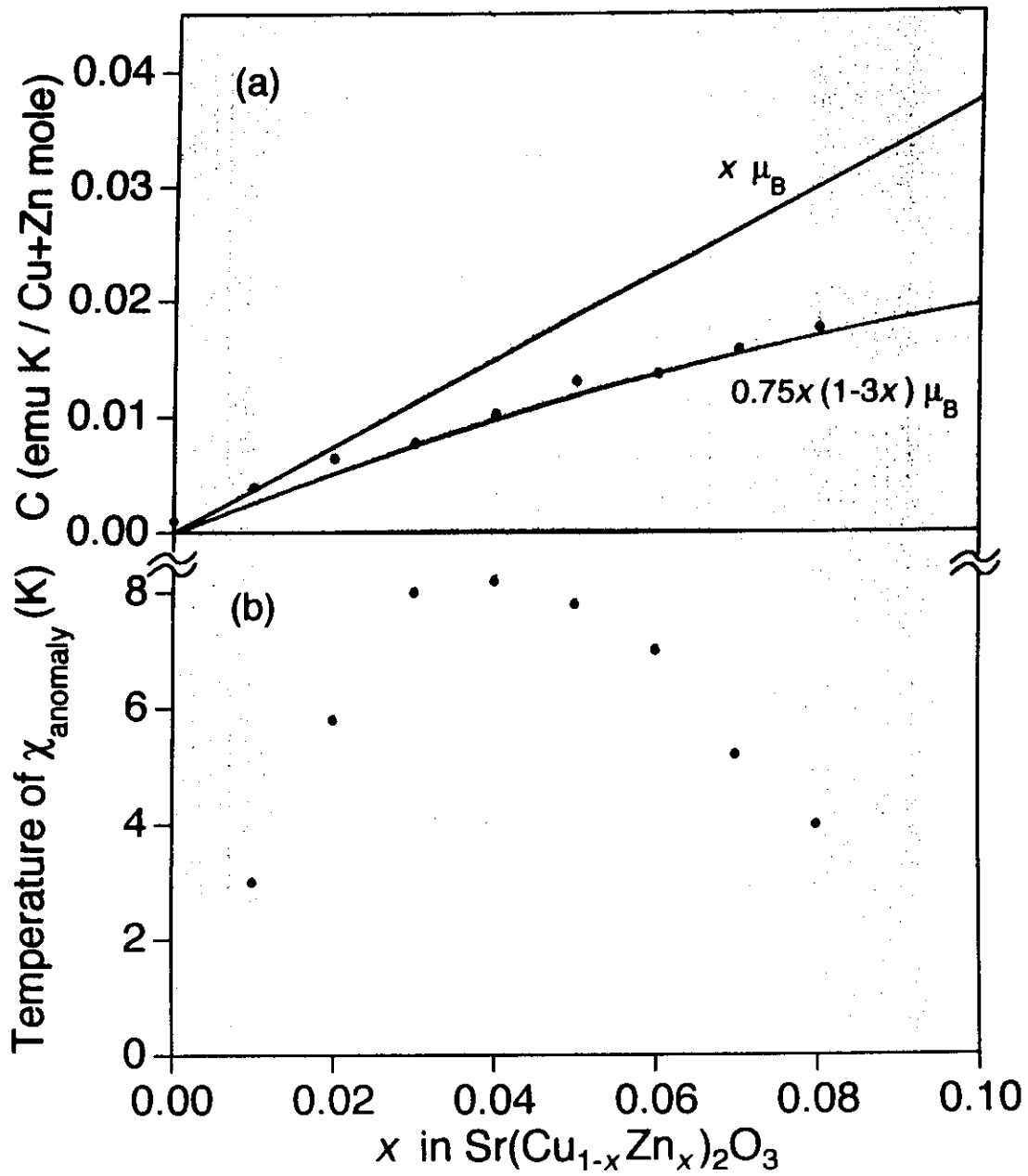
# Sr(Cu<sub>1-x</sub>Zn<sub>x</sub>)<sub>2</sub>O<sub>3</sub> (2-leg)



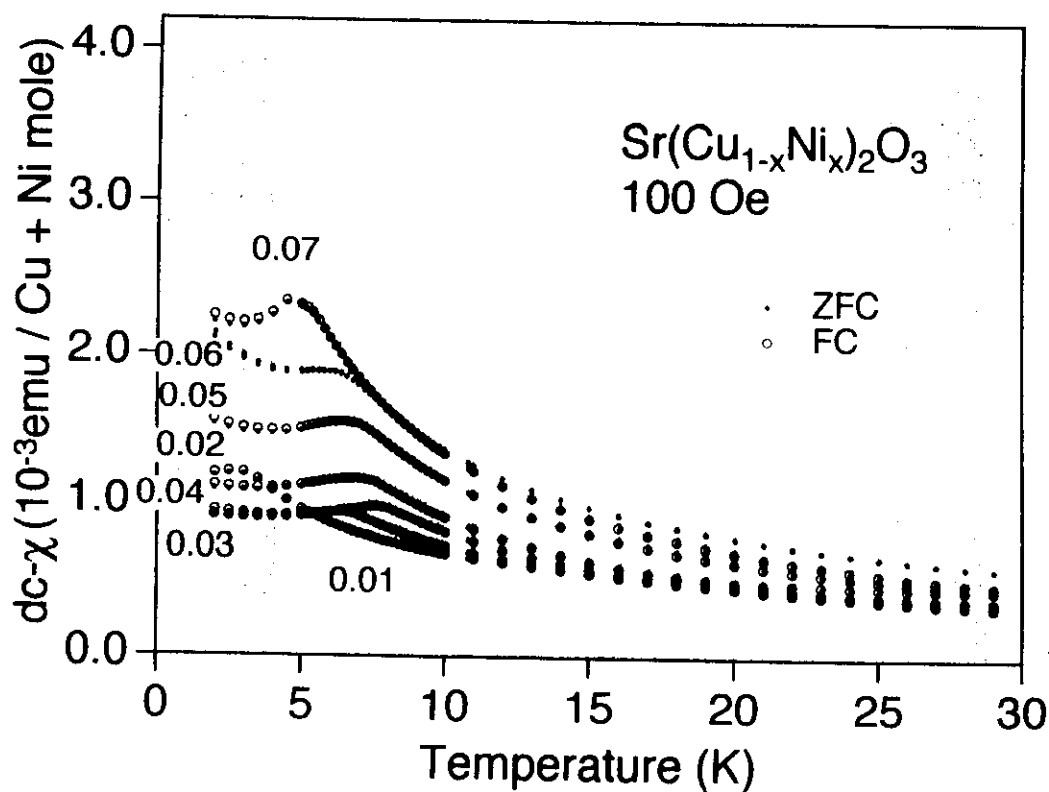
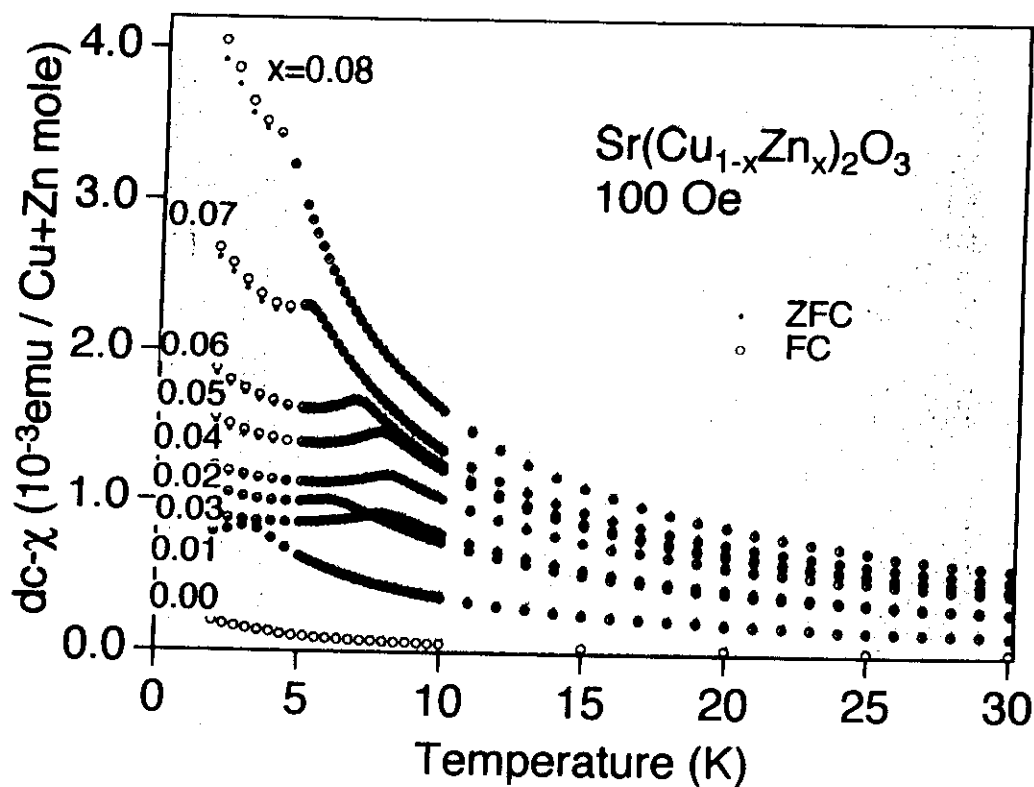
# Temperature dependence of the susceptibilities of $\text{Sr}(\text{Cu}_{1-x}\text{Zn}_x)_2\text{O}_3$



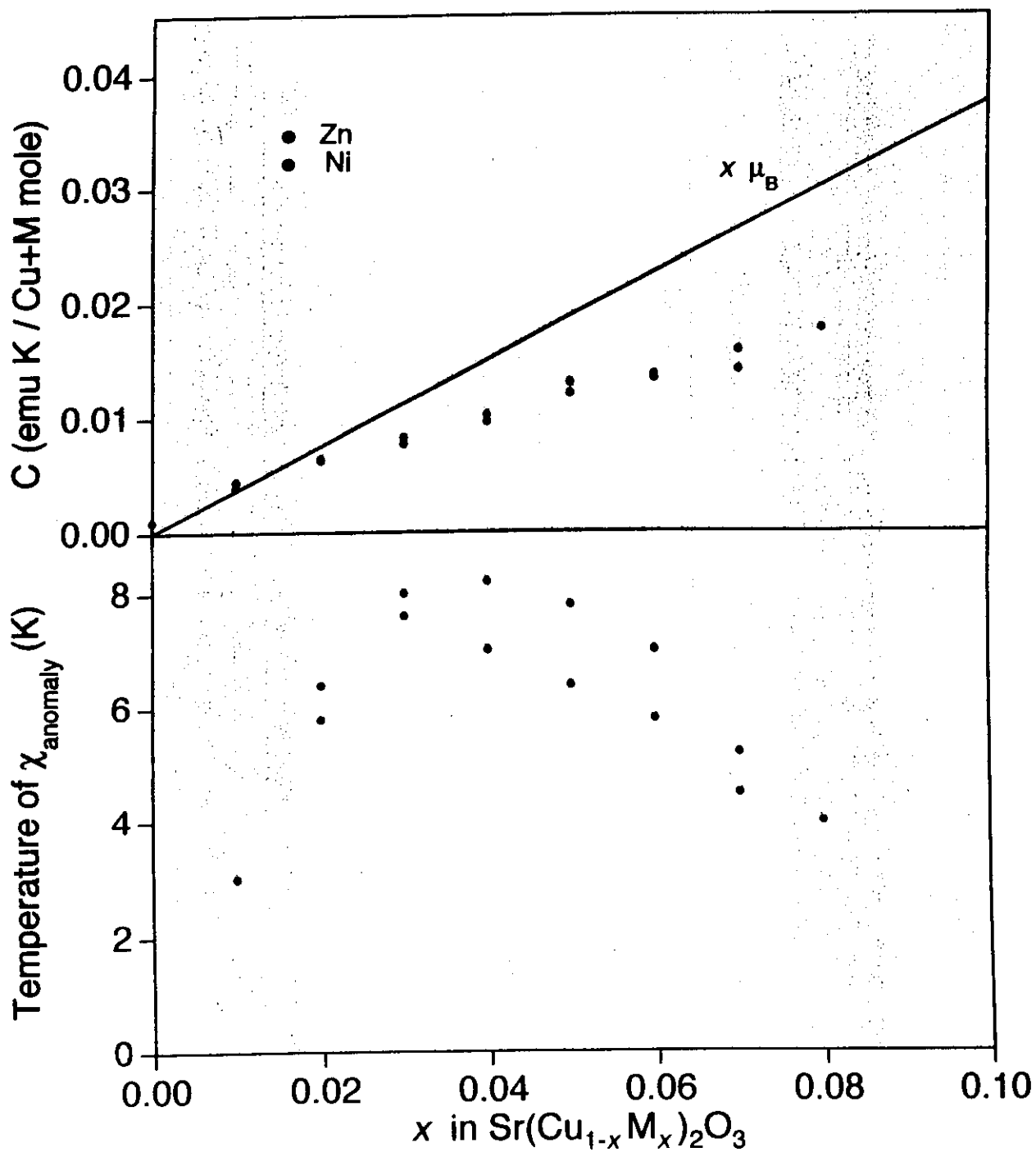
# Curie constant and Neel temperature of $\text{Sr}(\text{Cu}_{1-x}\text{Zn}_x)_2\text{O}_3$



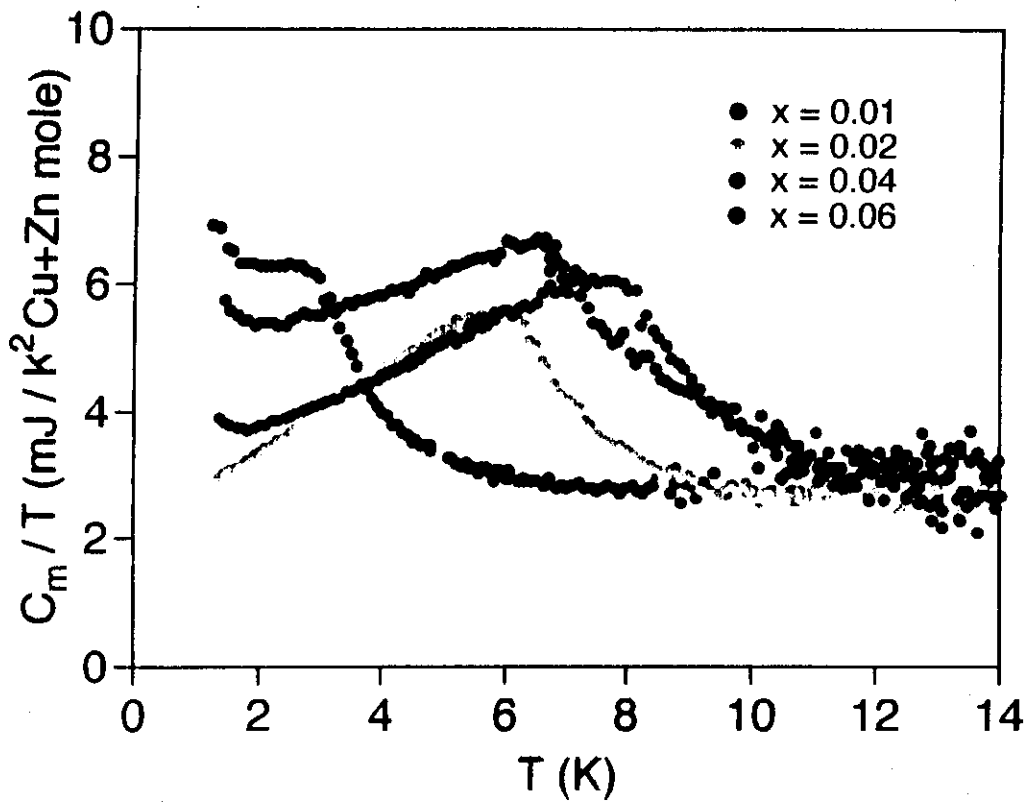
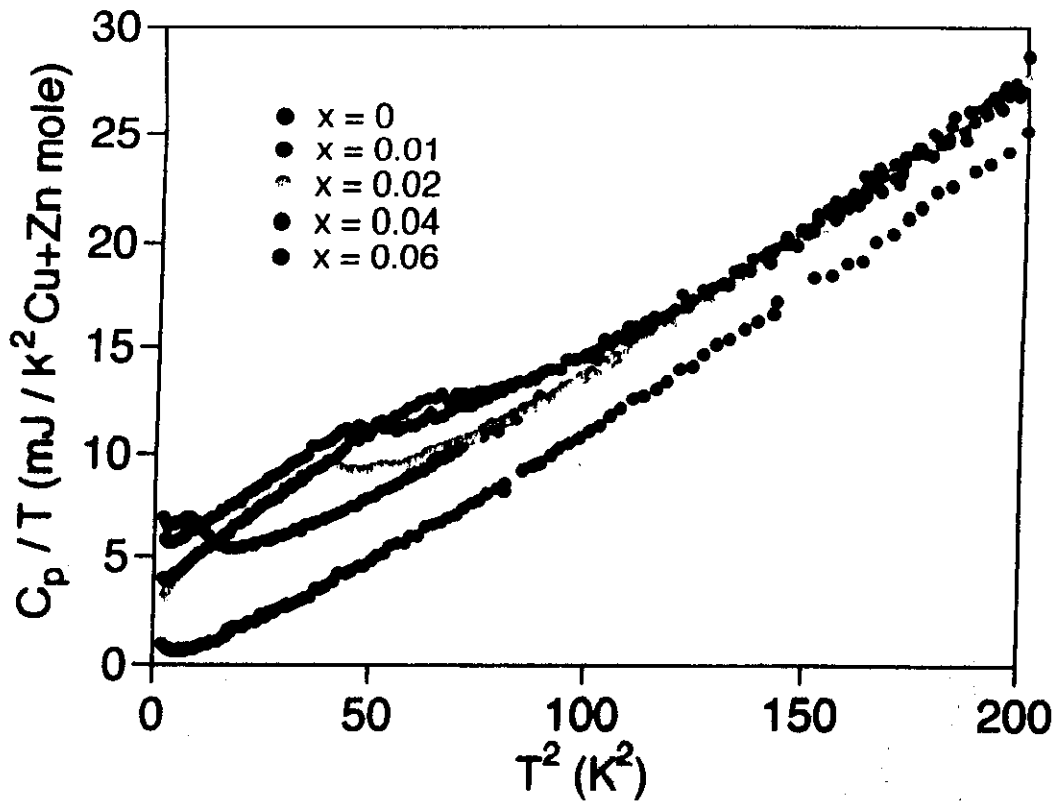
# Temperature dependence of the susceptibilities of $\text{Sr}(\text{Cu}_{1-x}\text{Zn}_x)_2\text{O}_3$ and $\text{Sr}(\text{Cu}_{1-x}\text{Ni}_x)_2\text{O}_3$



# Impurity concentration dependence of Curie constant and Neel temperature



# Specific heat of $\text{Sr}(\text{Cu}_{1-x}\text{Zn}_x)_2\text{O}_3$



# Specific heat of $\text{Sr}(\text{Cu}_{1-x}\text{Zn}_x)_2\text{O}_3$

non dope

$$T \rightarrow 0 : C_p \rightarrow 0$$

large spin gap  $\rightarrow$  no magnetic contribution

$$C_p = 9.9 \times 10^{-2} T^3 + 1.3 \times 10^{-4} T^5 = C_l$$

$$\Theta_D \sim 400\text{K}$$

doped samples

$\lambda$  - type anomaly  $\rightarrow$  AF transition

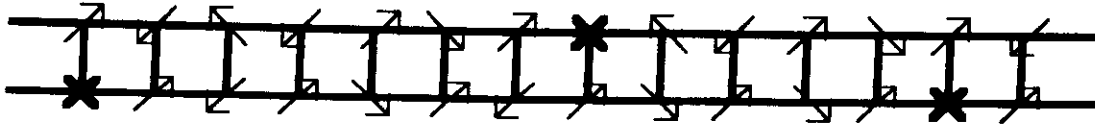
$$C_p = C_l + \gamma T \quad (T > T_N)$$

$\gamma$ : characteristic of 1D Heisenberg AF system

$$\gamma = 2Nk_B^2/3J \text{ for homegenious chain}$$

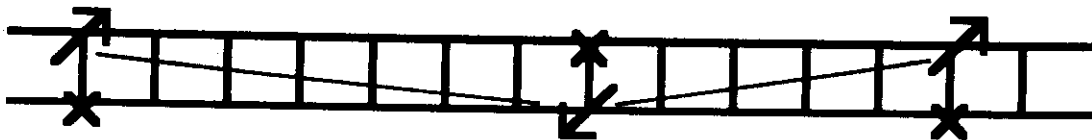
$$\gamma = 3\text{mJ} / \text{K}^2, \text{ independent to Zn content}$$

$\gamma T$  term in specific heat arises from whole the ladder

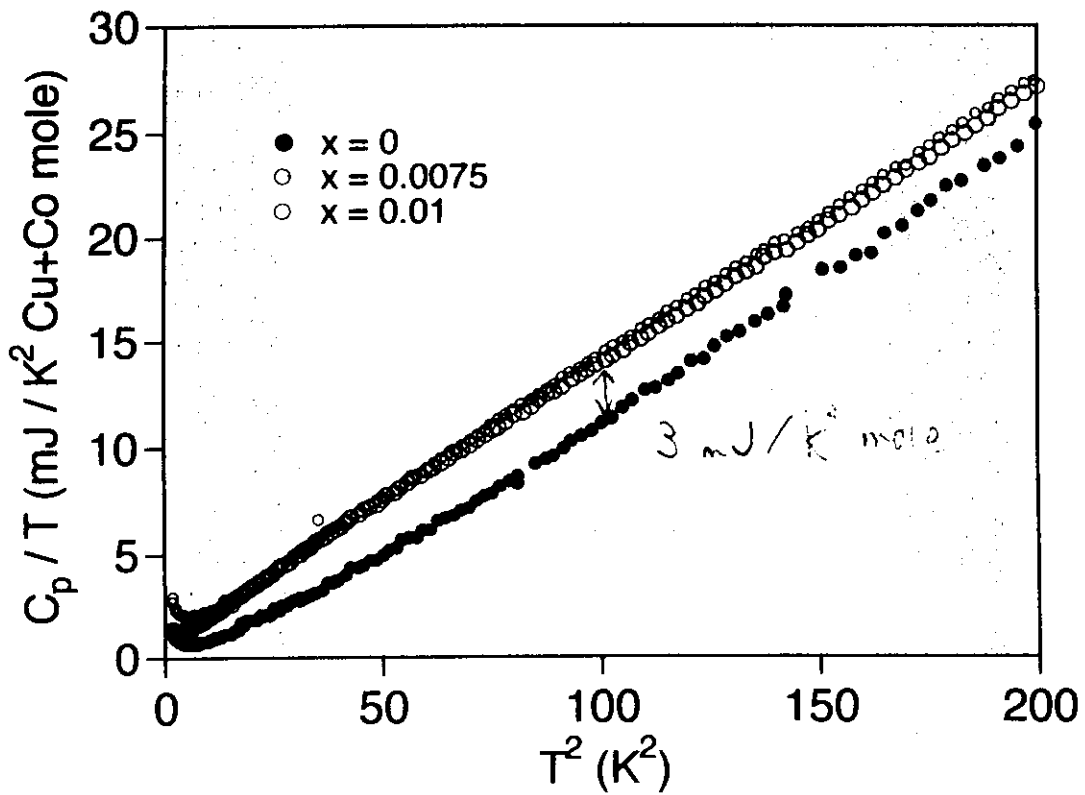
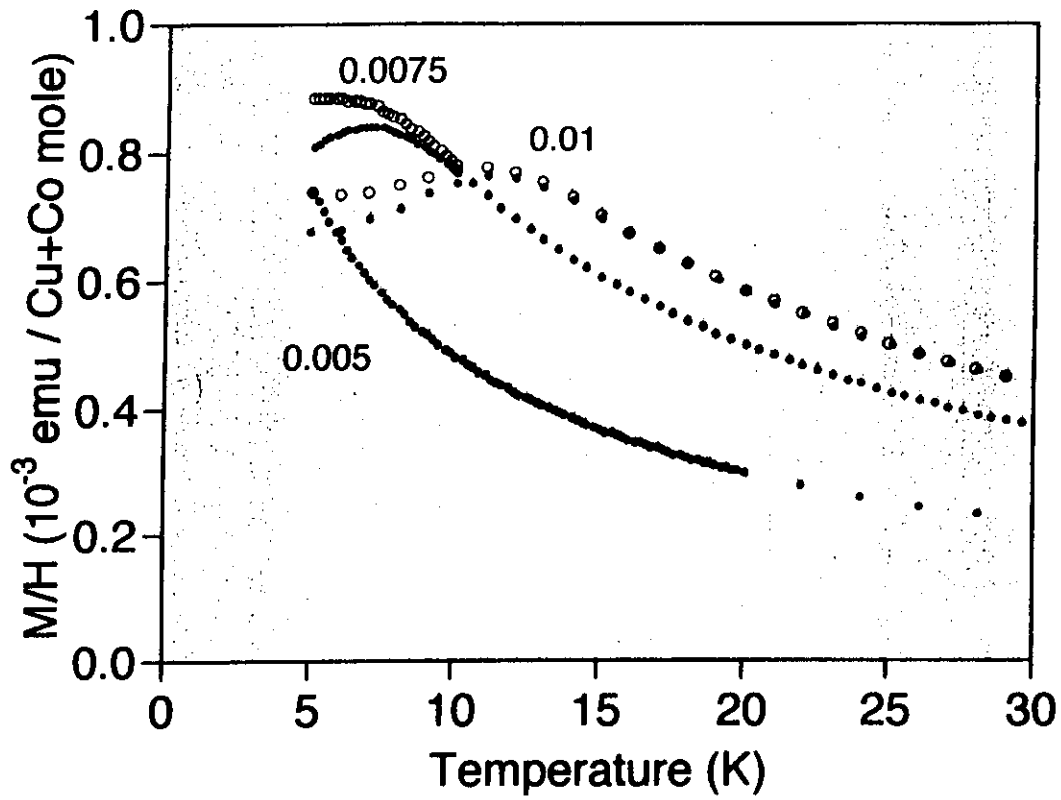
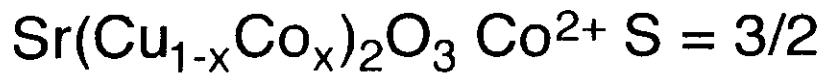


Applying  $\gamma = 2Nk_B^2 / 3J$ ,  $J / k_B = 1800$  K  
reasonable

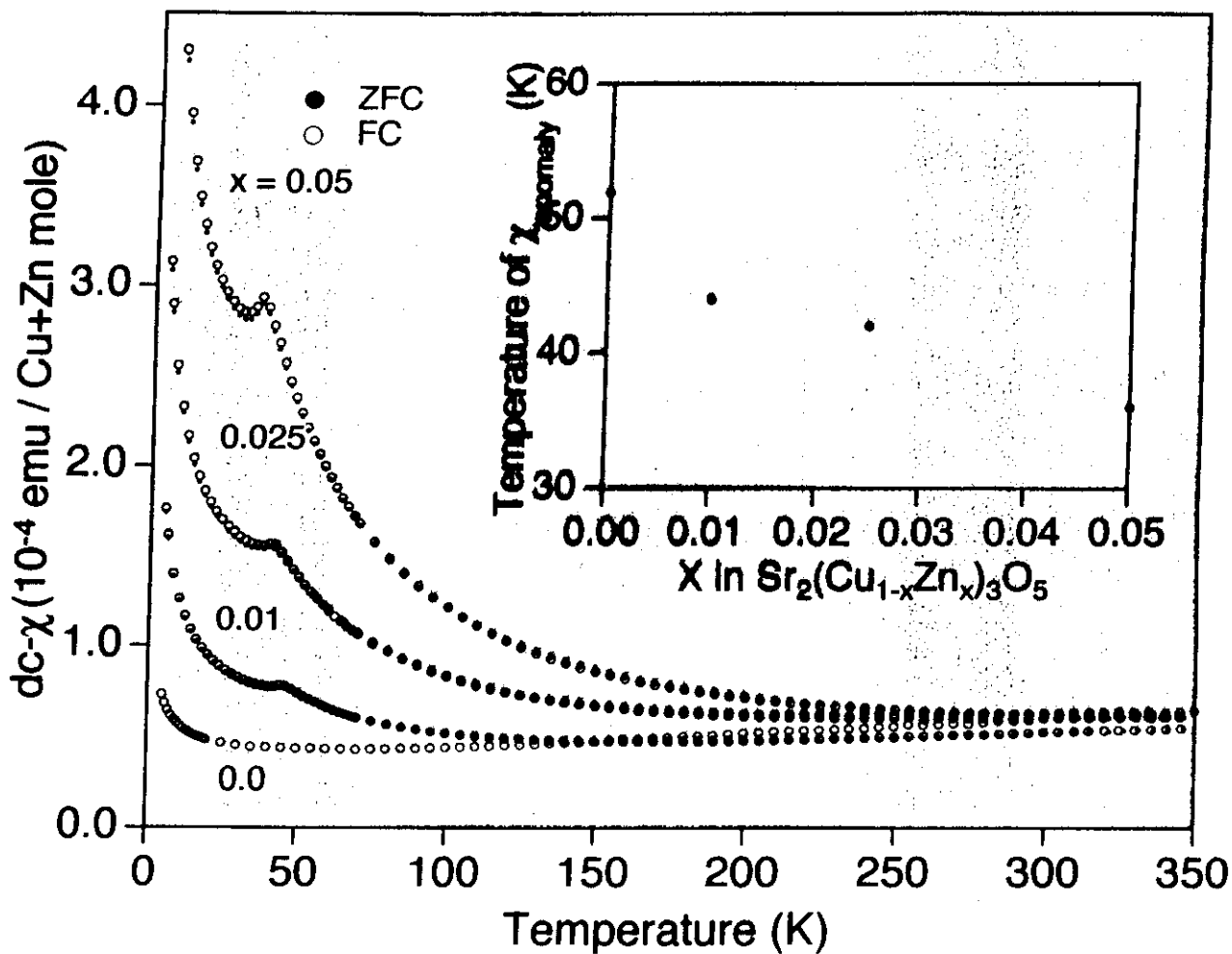
Only the localized spins near the  
impurities interact one-dimensionally



$J / k_B = 18$  K for  $x = 0.01$   
 $N / J$  : independent to  $x$



# Susceptibilities of $\text{Sr}_2(\text{Cu}_{1-x}\text{Zn}_x)_3\text{O}_5$ (3-leg ladder)



Compound	Structure	$T_N$	1D
$\text{SrCu}_2\text{O}_3$	1D chain	5 K	↓ 2D
$\text{Sr}(\text{Cu}_{0.96}\text{Zn}_{0.04})_2\text{O}_3$	2-leg ladder	8 K	
$\text{Sr}_2\text{Cu}_3\text{O}_5$	3-leg ladder	52 K	

# Impurity Effect on Spin Ladder System

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Effects of nonmagnetic impurity doping in a spin ladder system with a spin gap are investigated by the exact diagonalization as well as by the variational Monte Carlo calculations. Substantial changes in macroscopic properties such as enhancements in spin correlations and magnetic susceptibilities are observed in the low impurity concentration region, which are caused by the increase of low-energy states. These results suggest that small but finite amount of nonmagnetic impurity doping relevantly causes the reduction or the vanishment of the spin gap. This qualitatively explains the experimental result of Zn-doped  $\text{SrCu}_2\text{O}_3$  where small doping induces gapless nature. We propose a possible scenario for this drastic change as a quantum phase transition in a spin gapped ladder system due to spinon doping effects.

## Impurity Induced Antiferromagnetism in Spin-1/2 Heisenberg Two-leg Ladder Systems \*

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Based on the phase Hamiltonian representation of a spin-1/2 Heisenberg two-leg ladder system coupled antiferromagnetically, which has a spin gap if clean, it is shown that a non-magnetic impurity replacing a spin induces a staggered spin modulation. This results in the long range order of antiferromagnetism in the presence of three-dimensional coupling between the ladders. This will be in accordance with a recent experimental observation by Azuma *et al.* on  $\text{Sr}(\text{Cu}_{1-x}\text{Zn}_x)_2\text{O}_3$ .

## Rapid Suppression of the Spin Gap in Zn-doped $\text{CuGeO}_3$ and $\text{SrCu}_2\text{O}_3$

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The influence of non-magnetic impurities on the spectrum and dynamical spin structure factor of a model for  $\text{CuGeO}_3$  is studied. A simple extension to Zn-doped  $\text{SrCu}_2\text{O}_3$  is also discussed. Using Exact Diagonalization techniques and intuitive arguments we show that Zn-doping introduces states in the Spin-Peierls gap of  $\text{CuGeO}_3$ . This effect can be understood easily in the large dimerization limit where doping by Zn creates "loose"  $S=1/2$  spins, which interact with each other through very weak effective antiferromagnetic couplings. When the dimerization is small, a similar effect is observed but now with the free  $S=1/2$  spins being the resulting  $S=1/2$  ground state of severed chains with an odd number of sites. As recent numerical calculations have shown, similar arguments apply to ladders with non-magnetic impurities simply replacing the tendency to dimerization in  $\text{CuGeO}_3$  by the tendency to form spin-singlets along the rungs in  $\text{SrCu}_2\text{O}_3$ .

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## Low-Temperature Properties of the Randomly Depleted Heisenberg Ladder

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Low-temperature thermodynamic properties of the spin- $\frac{1}{2}$  Heisenberg ladder system with non-magnetic impurities are discussed using an effective Hamiltonian for the impurity-induced spins in the background of a spin liquid with a gap. It is shown that the uniform susceptibility shows Curie-like behavior in high-, intermediate-, and low-temperature regimes, with three different Curie constants. The ratio of specific heat to temperature,  $C/T$ , is divergent in the low-temperature limit, reflecting a singular distribution of the effective couplings among the impurity spins.

# SUMMARY

1. Difference between the excitation spectra of 2- and 3-leg ladder was confirmed experimentally.  
  
2-leg: spin gap, about 400K  
3-leg: gapless, get ordered below 52 K
- ② Only 1% of nonmagnetic impurity introduced into 2-leg ladder changes the host gapless and antiferromagnetically ordered.
3.  $T_N$  once increased and then decreased.  
(monotonically decreased in 3-leg ladder)
4. Enhancement of the Curie-like susceptibility was observed both in 2- and 3- leg ladders. (mysterious)