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New States of Stable and Unstable Quantum Matter
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Electronic and Magnetic Properties of Low-Dimensional Spin Systems

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Electronic and Magnetic Properties of Low-Dimensional Spin Systems

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Enhancement of Quantum Effects:

- Low dimensional structural configurations
- Competing Interactions
- Low Spin Values (S = 1/2)

Suppression of Phase Transitions at $T \neq 0$ K

Examples:

Spins and electrons on a planar, triangular lattice

→ $\mathbf{Na_xCoO_2}$

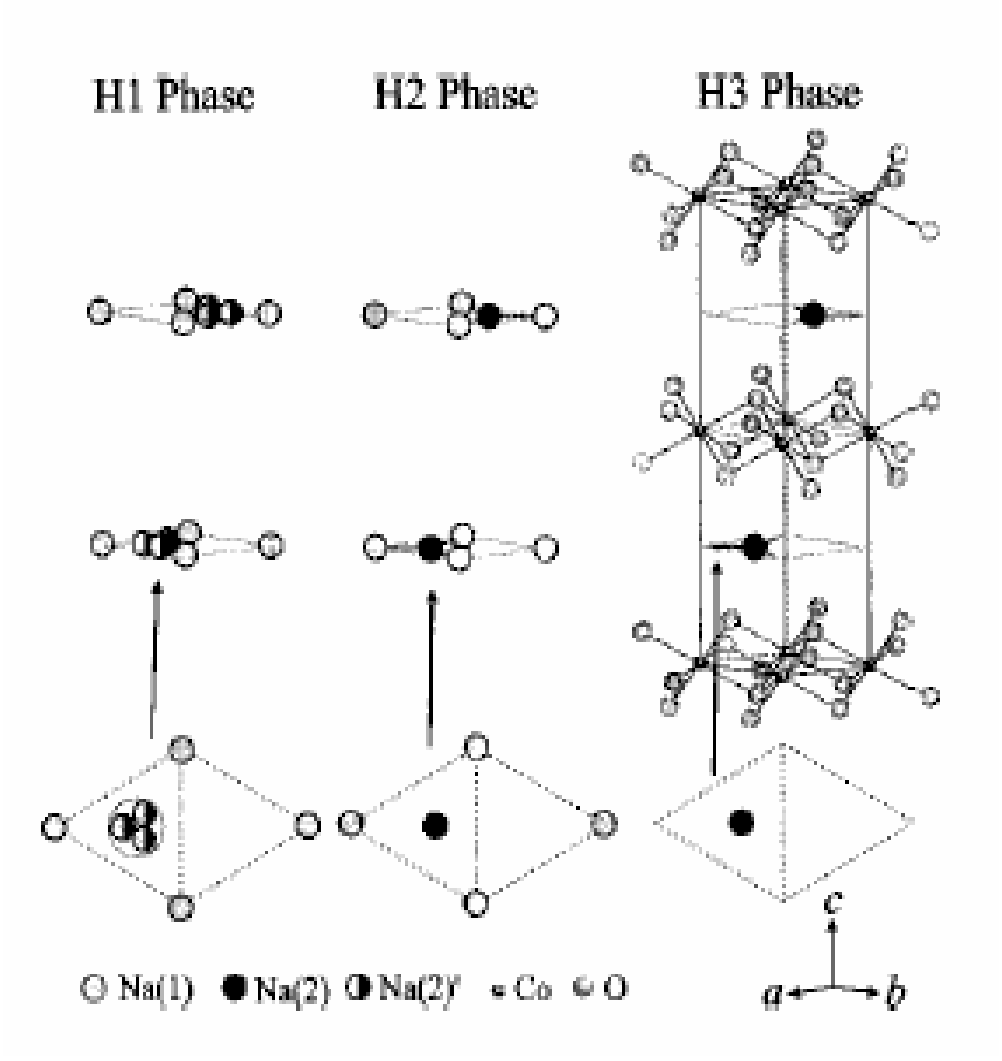
See also:
PRB **69**, 100404 (2004); PRB **72**, 214407 (2005): PRB **74**, (2006)

Spins on spiraled chains, resulting in a ladder with periodic boundaries along the rungs

→ $\mathbf{Na_2V_3O_7}$

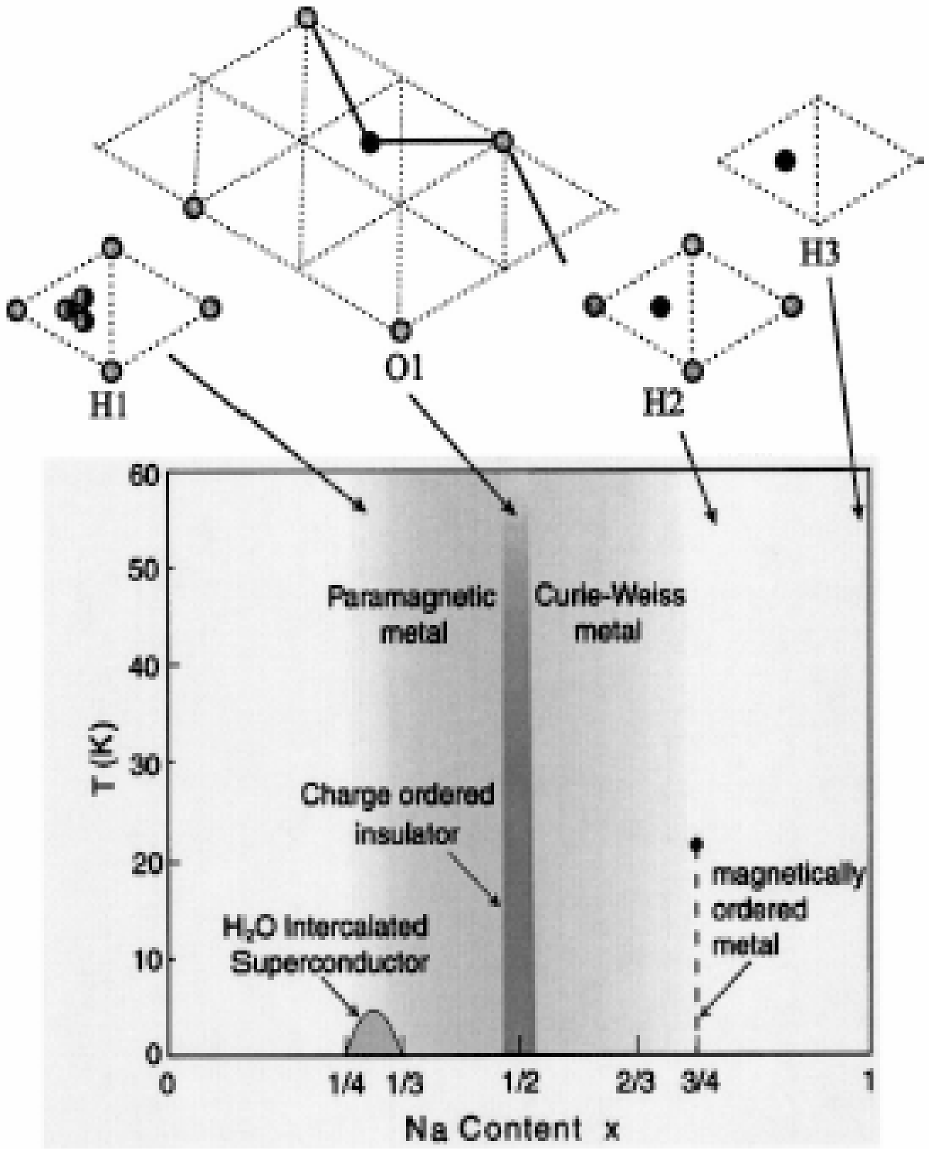
See also:
PRL **90**, 167202 (2003); PRB **72**, 064431 (2005)

Na_xCoO_2 : structural aspects



(Q. Huang, et al., PR B **70**, 184110 (2004))

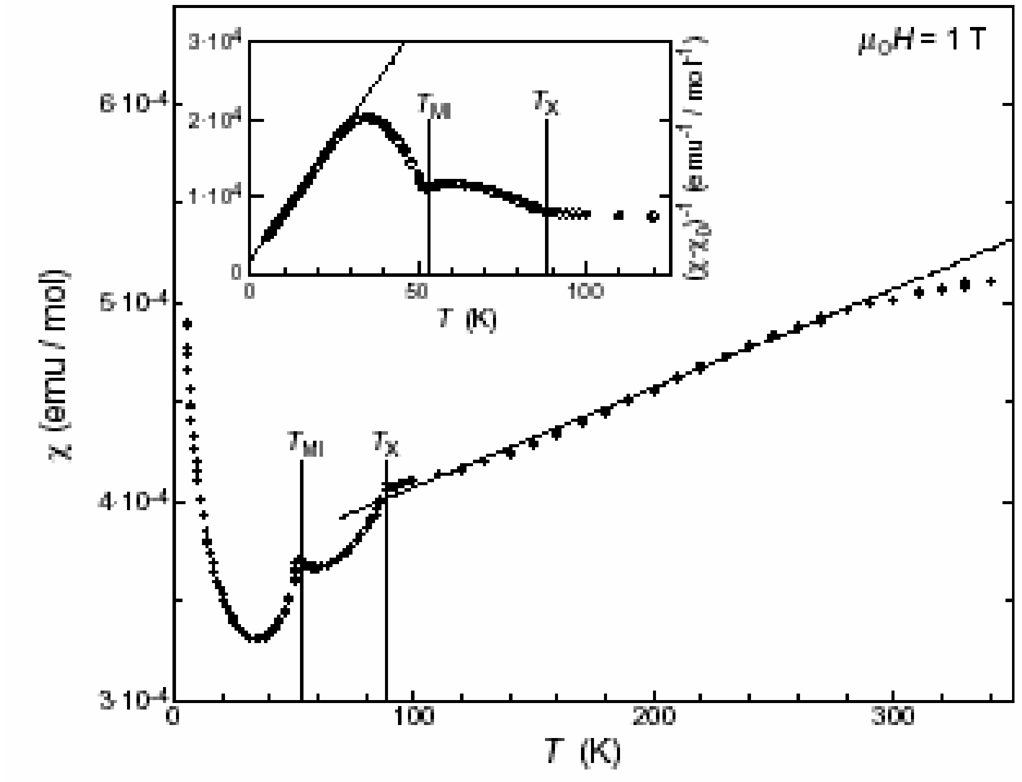
Structure vs Phases



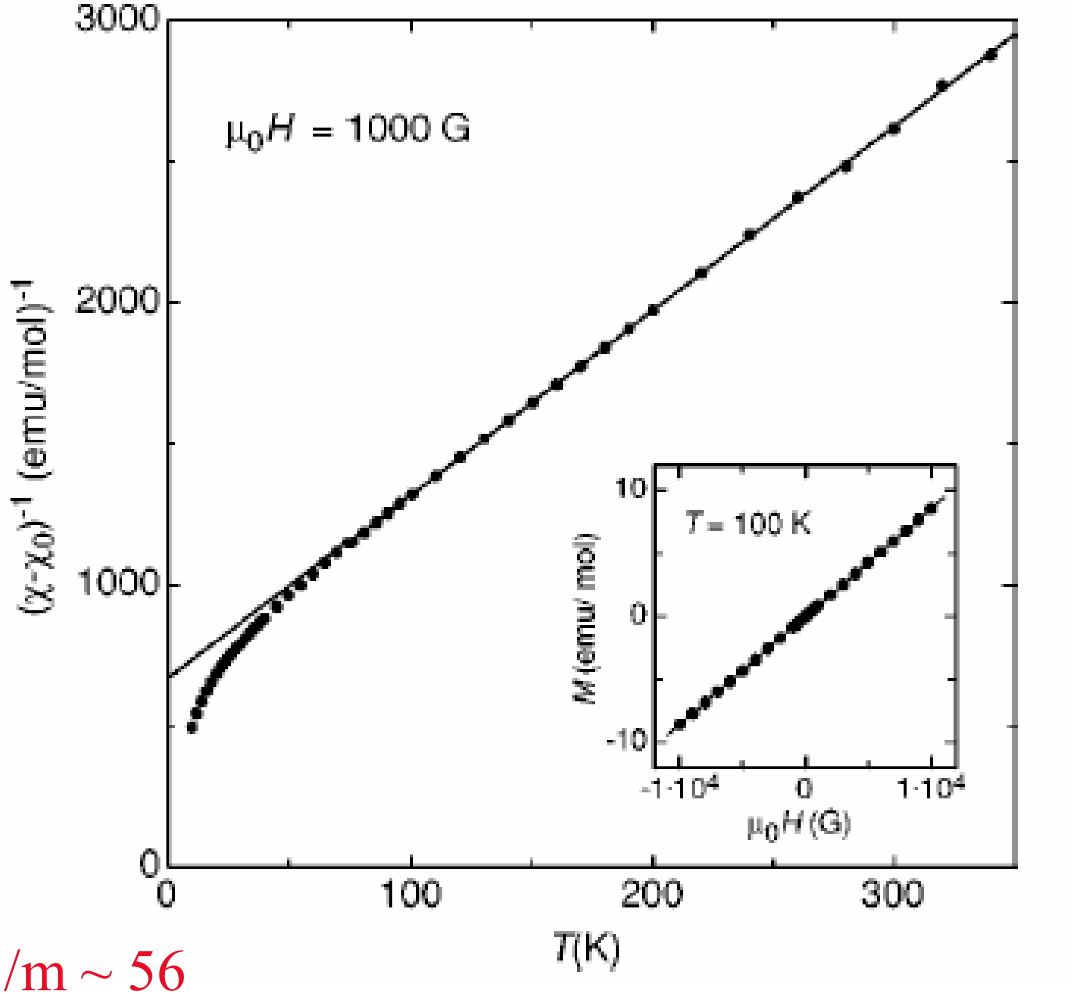
Foo et al., PRL **92**, 247001 (2004)

Magnetic susceptibility χ(T)

$Na_{0.5}CoO_2$



$Na_{0.7}CoO_2$



T > 100 K: Pauli-type χ(T) → $D(E_F)$ → $m^*/m \sim 56$

T < 25 K: Curie-Weiss χ(T) → $p_{eff} = 0.11\ \mu_B/Co$

$\theta_p = 2.5$ K

⇒ 2 phase transitions at $T_X = 88$ K and $T_{MI} = 53$ K

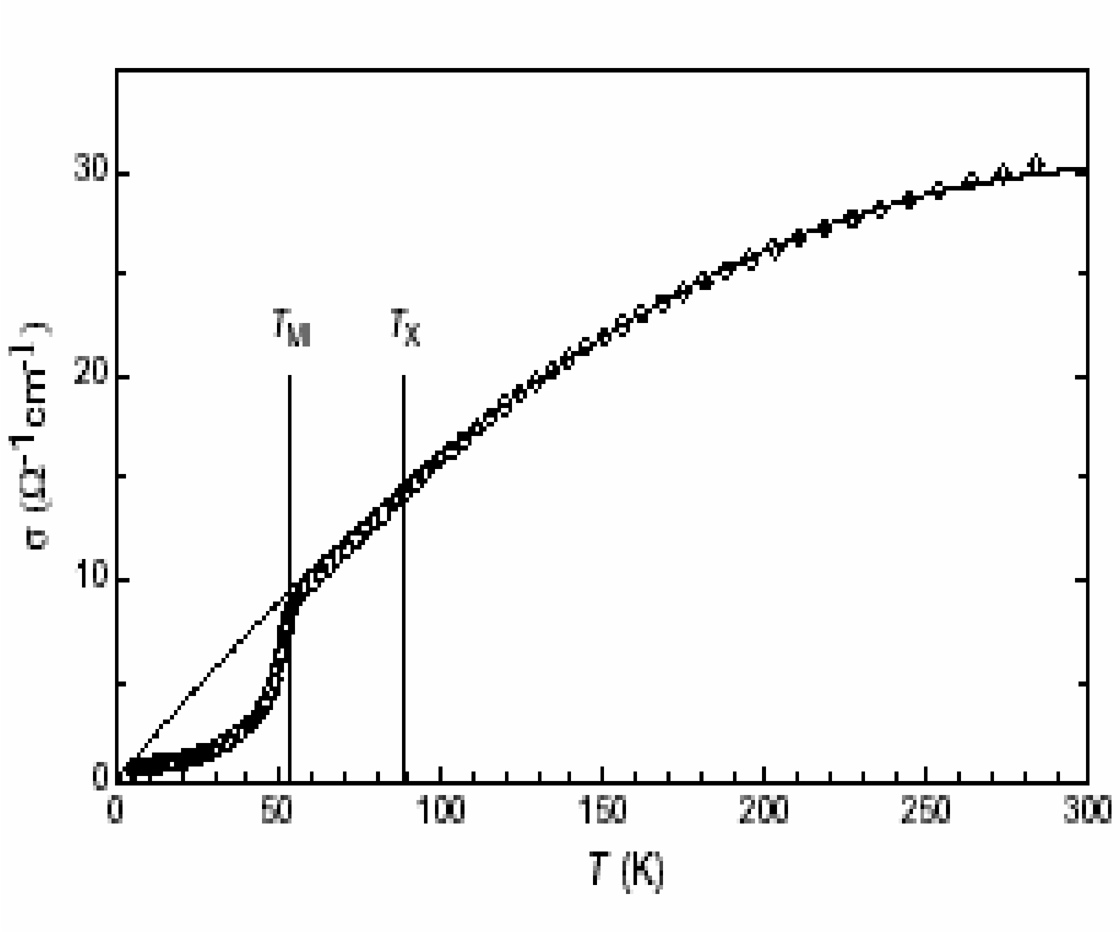
T > 100 K: Curie-Weiss χ(T)

→$p_{eff} = 1.1\ \mu_B/Co$; $\theta_p = -103$ K

→ ~ (1-x) Co^{4+} (S = 1/2) !

Electronic conduction

electrical conductivity $\sigma(T)$ of $Na_{0.5}CoO_2$:



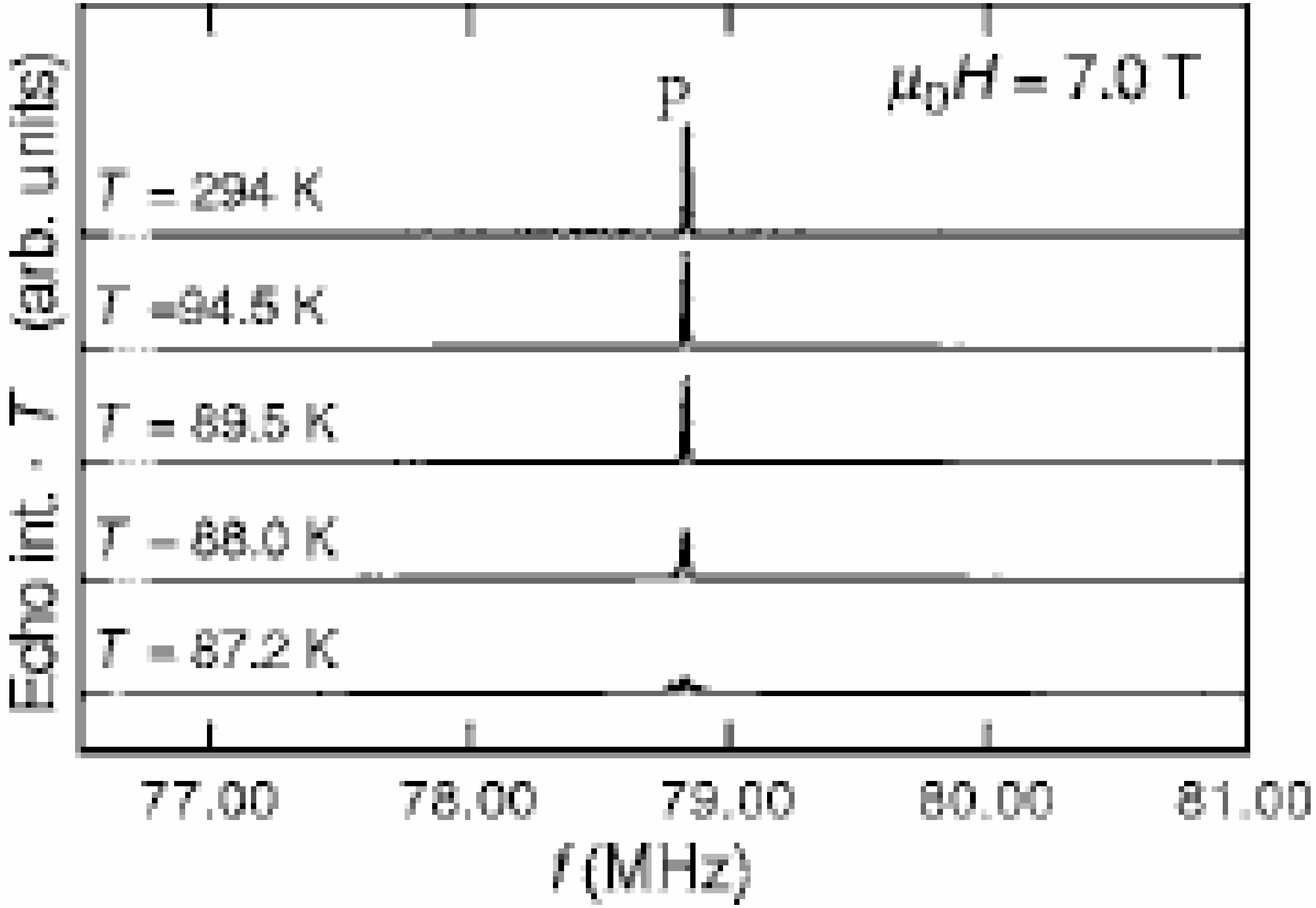
$Na_{0.7}CoO_2$:

metallic conductivity

residual resistance $\rho_0 \sim 50\ \mu\Omega cm$

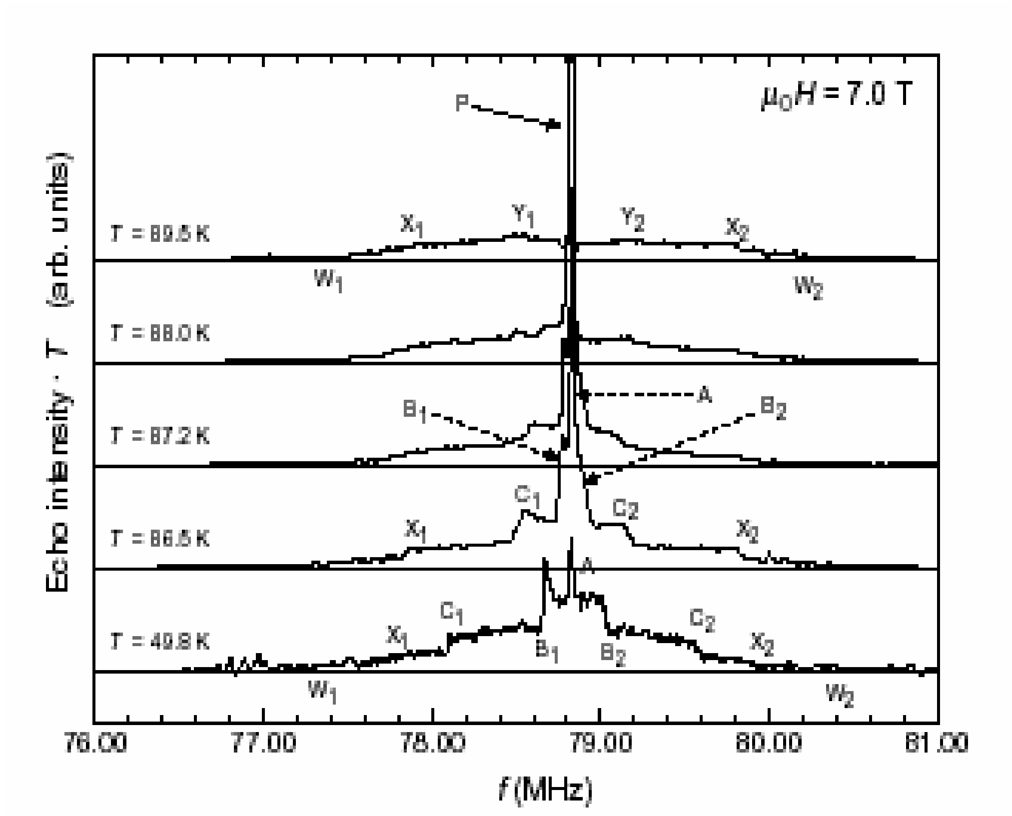
$\rho(T) = \rho_0 + r \cdot T$ for $T < 100$ K

^{23}Na NMR above $T_X = 88$ K



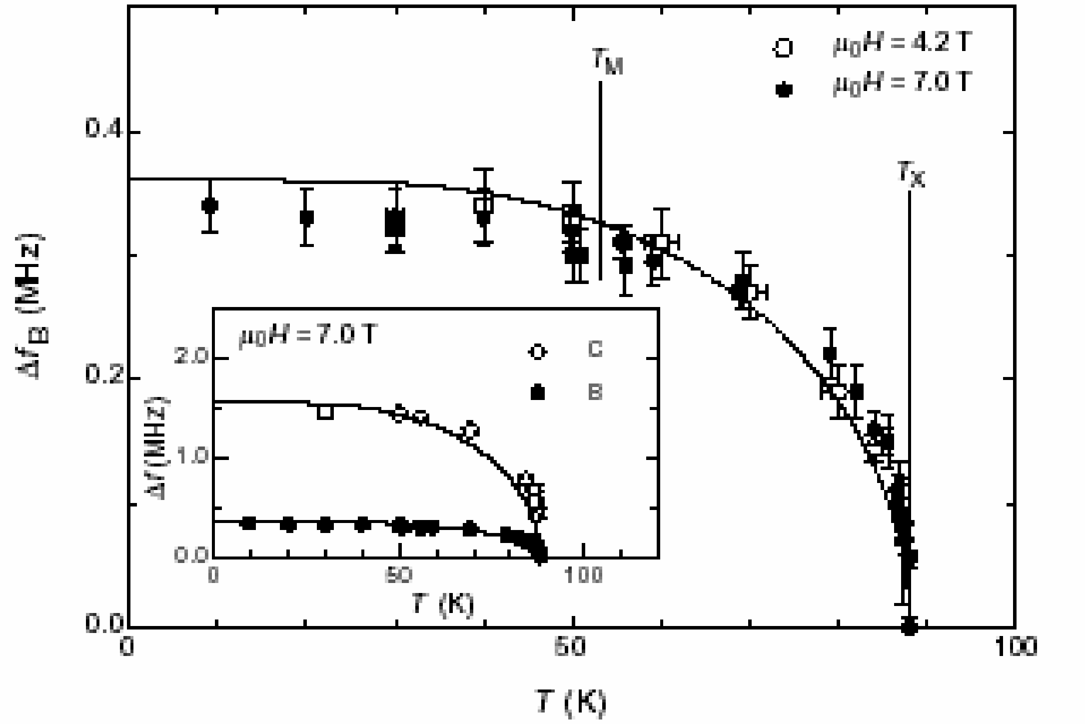
Evidence for the onset of magnetic order in $Na_{0.5}CoO_2$ at T_X

^{23}Na NMR



- Single central line with quadrupolar wings for T > 88 K = T_X
- New structures A, B and C below T_X
- Quadrupolar wings unaffected to T = 50 K

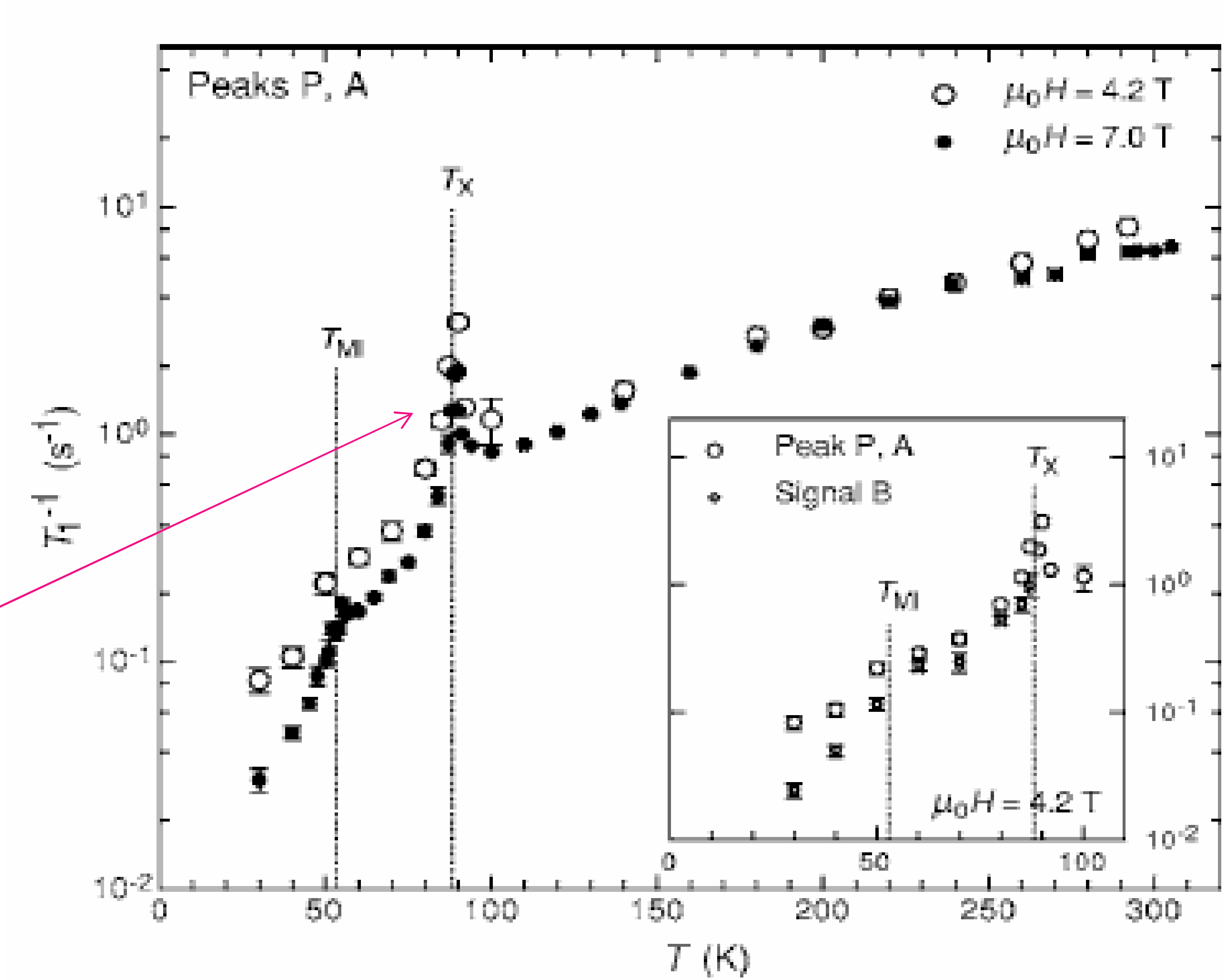
Temperature evolution of the width Δf of structures B and C



$$\Delta f_B = \Delta f_B(0) \cdot \Phi(T/T_X)$$

$$\Phi(z) = \tanh(\Phi(z)/z)$$

^{23}Na NMR spin-lattice relaxation rate



confirms onset of magnetic order

$Na_{0.5}CoO_2$

$T > T_X$:

- Paramagnetic metal: $K_P \sim \chi$
- No evidence for localized Co moments

- Single NMR line: equal hyperfine field at Na1 and Na2, i.e., uniform distribution of magnetic moment density in the conducting CoO_2 planes

- $\chi(T)$ and $T_1^{-1}(T)$ decrease with decreasing T
  → loss of electronic density of states $D(E_F)$?

- From $\chi(300\text{ K})$: $D(E_F) = \chi/\mu_B^2 V_{mol}$
- For 2D metal: $D(E_F) = m^*/\pi(h/2\pi)^2 c \rightarrow m^* \approx 56\, m_e$

- From $\sigma(300\text{ K}) = e^2 n_e l/(h/2\pi)k_F$
- For 2D metal: $k_F = (2\pi n_e c)^{1/2} \rightarrow l \approx 2.3 \cdot 10^{-8}$ cm
  → similar situation for $0.3 < x < 0.7$

$Na_{0.5}CoO_2$

$T_{MI} \leq T \leq T_X$:

- The onset of antiferromagnetic order at $T_X > T_{MI}$ (!) induces 2 magnetically inequivalent Na sites B and C with $H_{int,C}/H_{int,B} = 4.2$ and $I_C/I_B \sim 1$

- NMR spectra provide no experimental evidence for any significant charge disproportionation, neither at T_X nor at T_{MI}

- Magnetic component in the transition at T_{MI} but no significant change of staggered field at Na sites

- Origin of ordered moments unclear !

- If SDW, based on Fermi surface nesting,why not reflected in $\rho(T)$?

$Na_{0.7}CoO_2$

χ(T) indicates

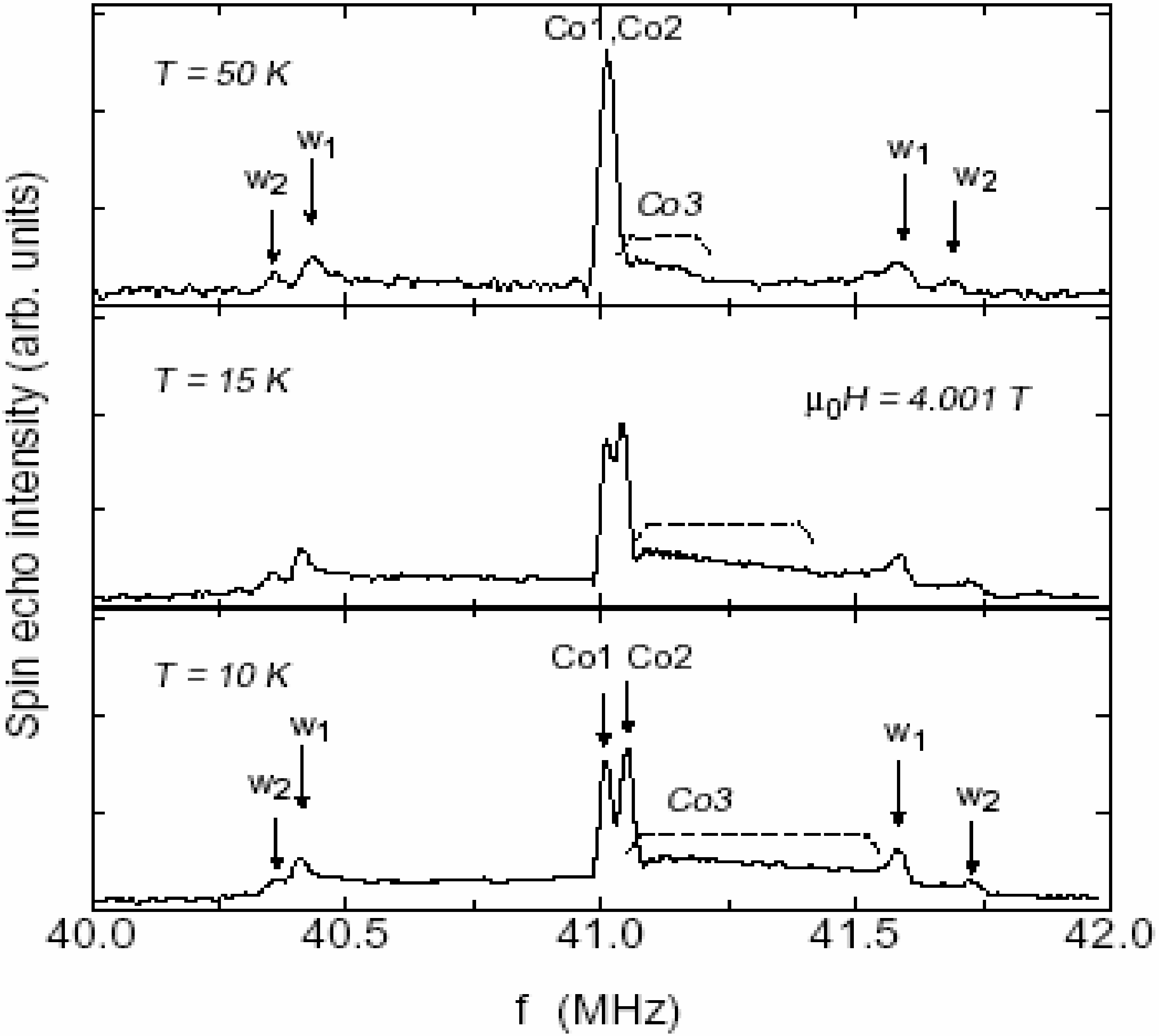
- local moments in a metallic matrix with significant afm interactions at T > 100 K

- strong reduction of both the magnitude of the moments and the afm interactions at T < 20 K

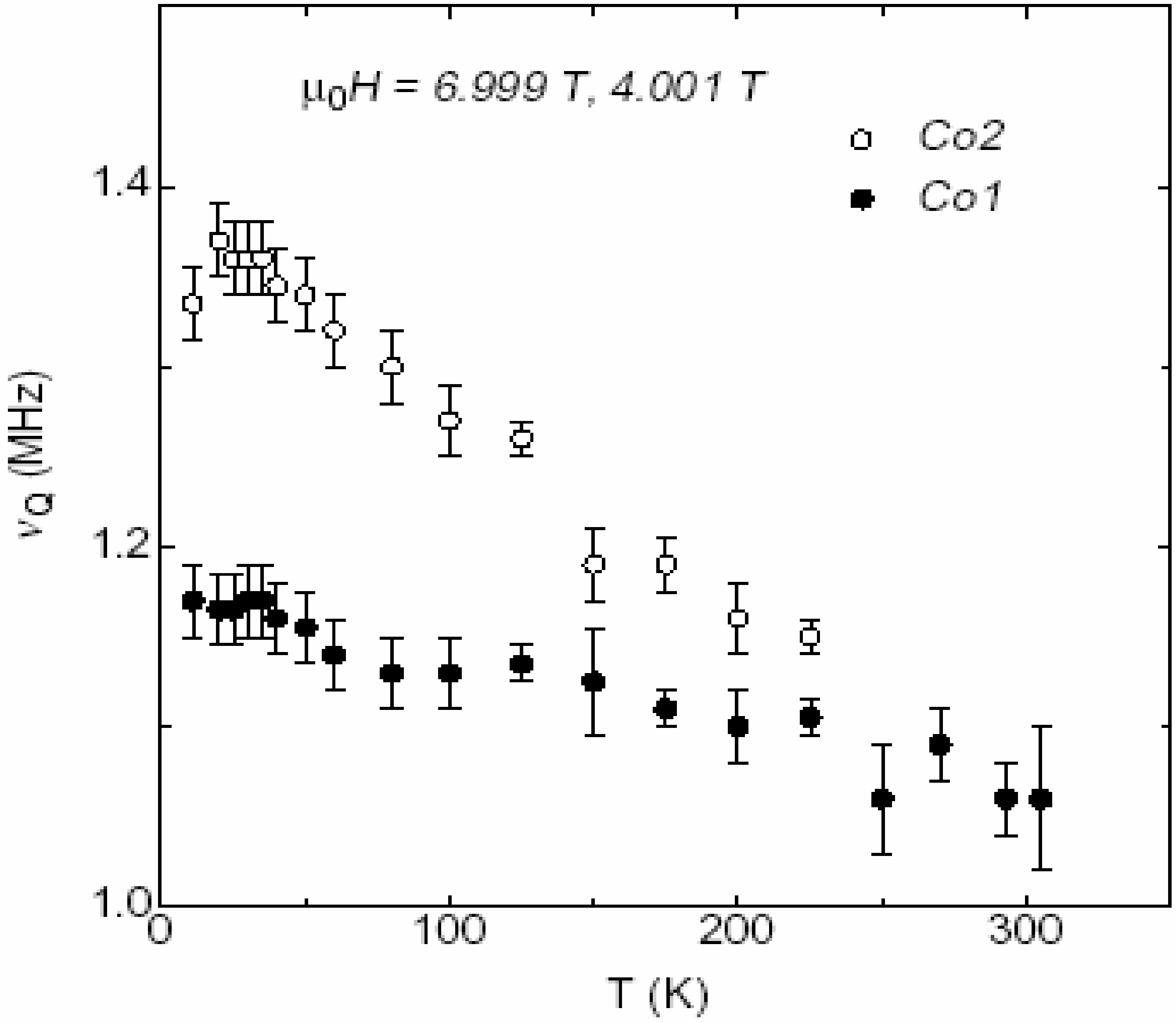
ρ(T) data reveal

- linear-in-T variation of resistivity below 100 K

$Na_{0.7}CoO_2$: ^{59}Co NMR (resonance signal)



$Na_{0.7}CoO_2$: ^{59}Co NMR (quadrupolar frequencies)

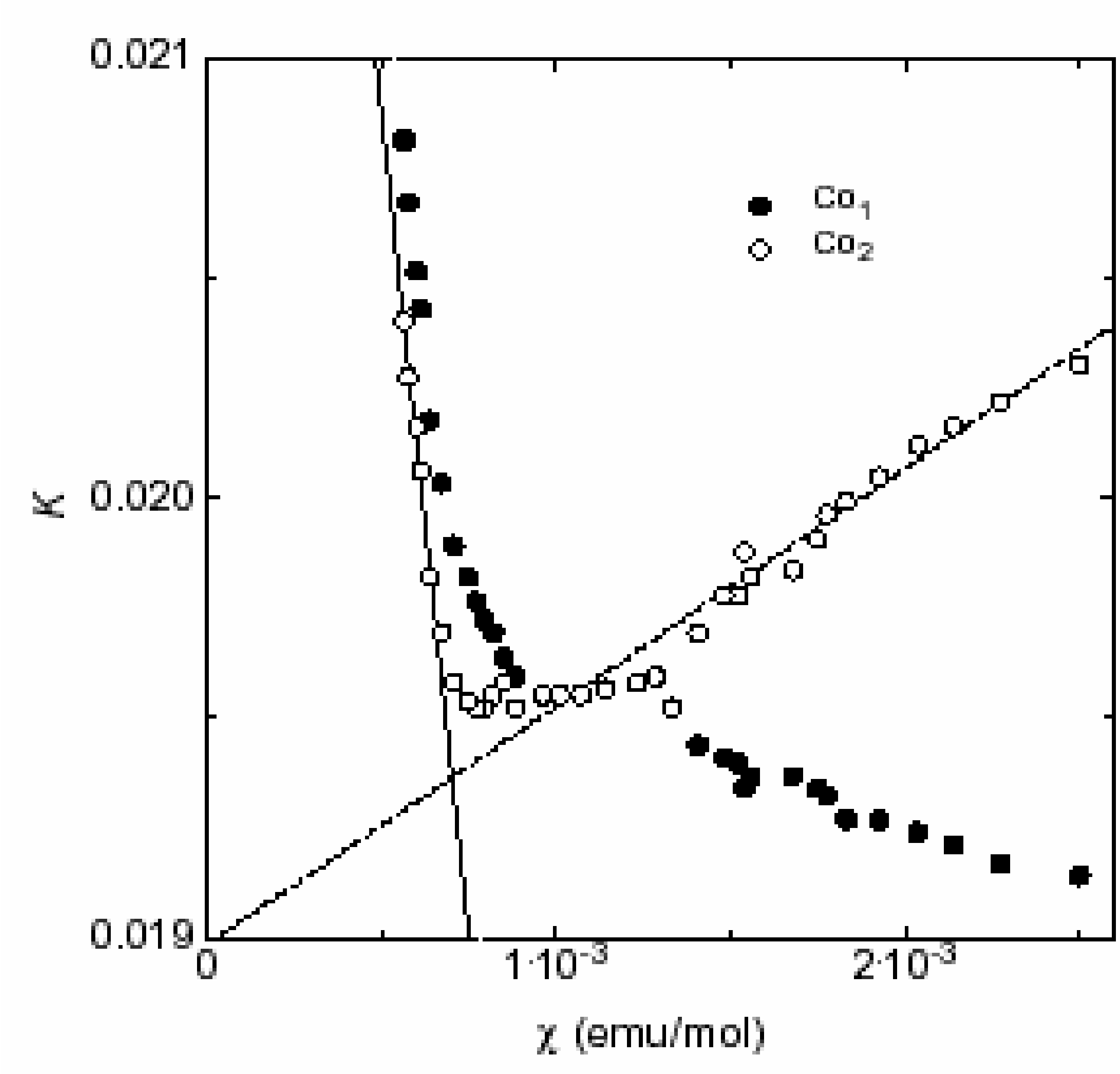


$Na_{0.7}CoO_2$: ^{59}Co NMR (Knight shift)

$K = K_0 + A\cdot\chi$

$\chi = \chi^{spin} + \chi^{orb} + \chi^{dia}$

$A \sim H_{hf}$

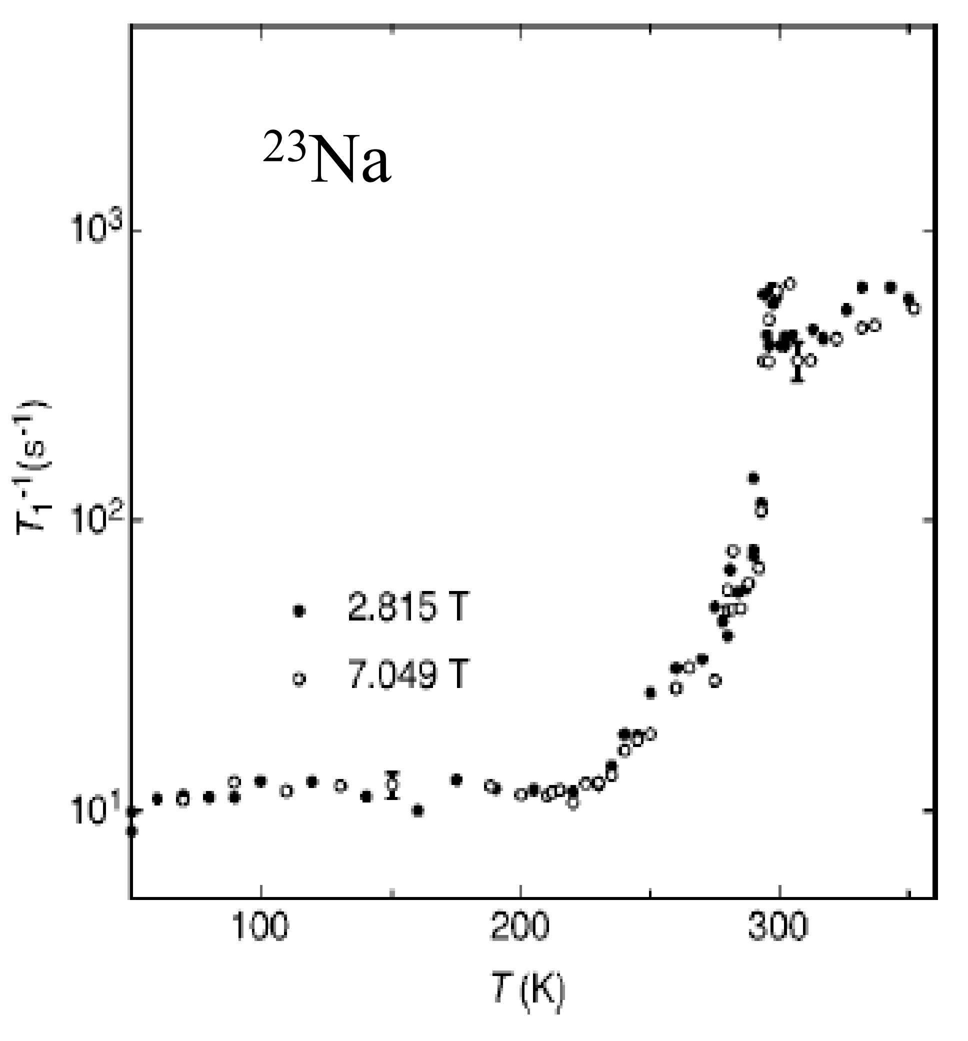


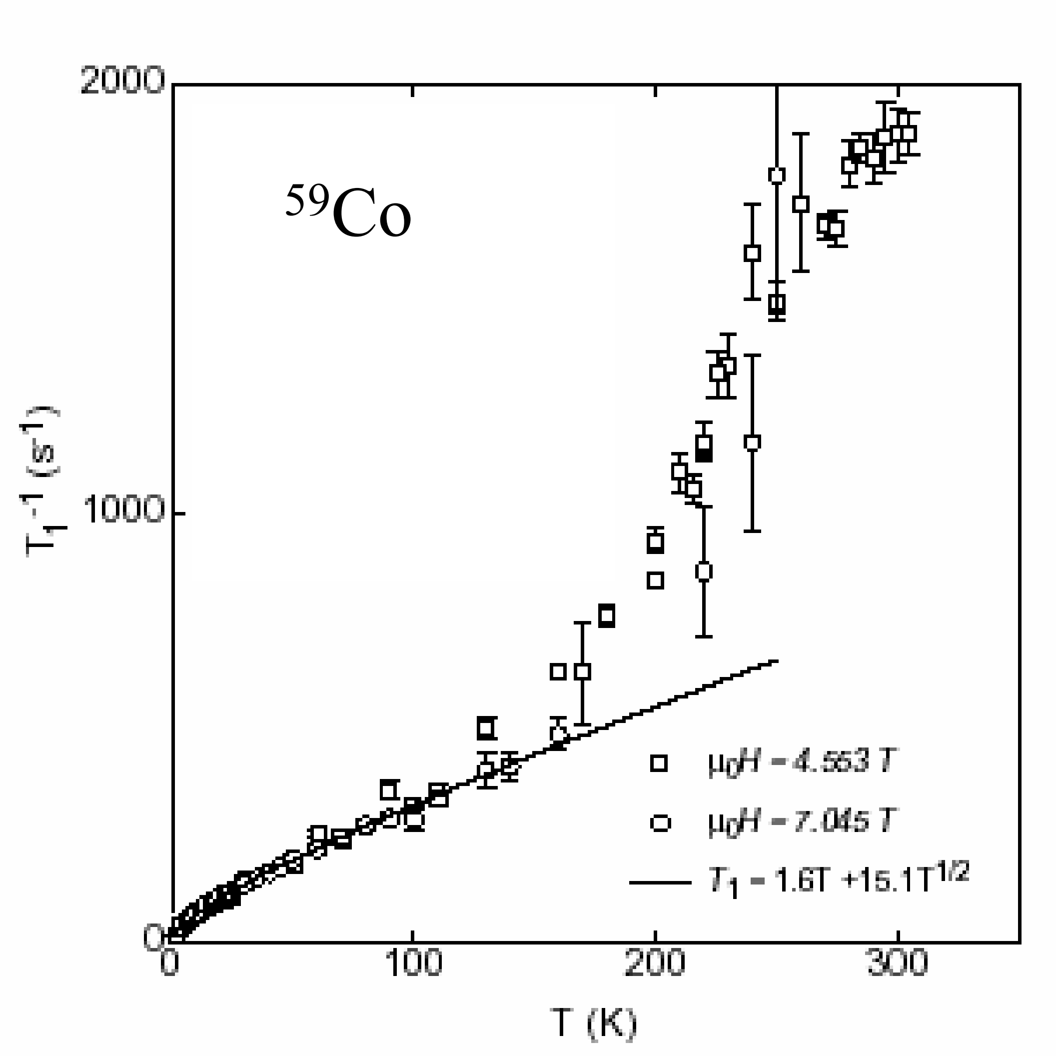
Co1: $K_0^{HT} = 0.0249$
$A^{HT} = -7.3$
$K_0^{LT} = 0.0198$
$A^{LT} = -0.28$

Co2: $K_0^{HT} = 0.0246$
$A^{HT} = -7.3$
$K_0^{LT} = 0.0190$
$A^{LT} = +0.54$

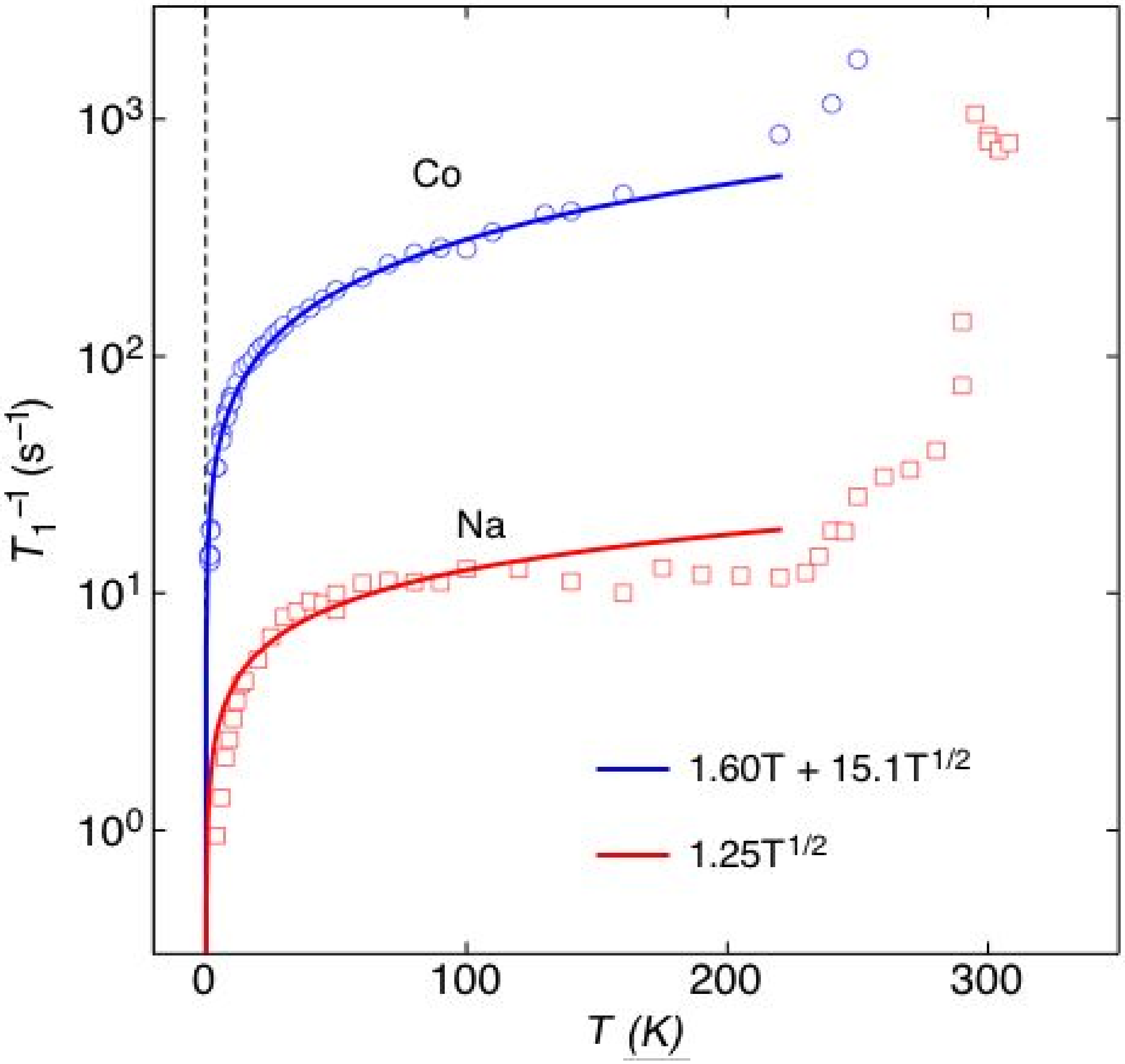
Note change of sign of the hyperfine coupling !

$Na_{0.7}CoO_2$: ^{23}Na and ^{59}Co NMR (spin-lattice relaxation)





$Na_{0.7}CoO_2$: ^{23}Na and ^{59}Co NMR (spin-lattice relaxation)



^{59}Co NMR :

$$T_1^{-1} = 1.6\ T + 15.1\ \sqrt{T}$$

^{23}Na NMR :

$$T_1^{-1} = 1.25\ \sqrt{T}$$

Analysis of $T_1^{-1}(T)$ at low temperatures

Approximation : $\mathbf{(T_1^{-1})^{tot} = (T_1^{-1})^{orb} + (T_1^{-1})^{spin}}$

nearly afm system :

$$\mathbf{(T_1^{-1})^{spin} \sim (T_1^{-1})_0^{spin} \sqrt{\chi_Q}(T) \sim T/\sqrt{(T - T_N)}}$$

with $(T_1^{-1})_0^{spin} \sim T$, as the bare spin contribution

$$\mathbf{(T_1^{-1})^{orb} = 2C(\gamma_N H_{hf}^{orb})^2 N_{t2g} (N_{t2g} + 4 N_{eg}) T}$$

$C = 2k_Bh$
N_i = local densities of states

(T. Moriya, JMMM **14**, 1 (1979))

^{59}Co NMR :

$$T_1^{-1} = 1.6\,T + 15.1\sqrt{T}$$

$T_N \approx 0$ K

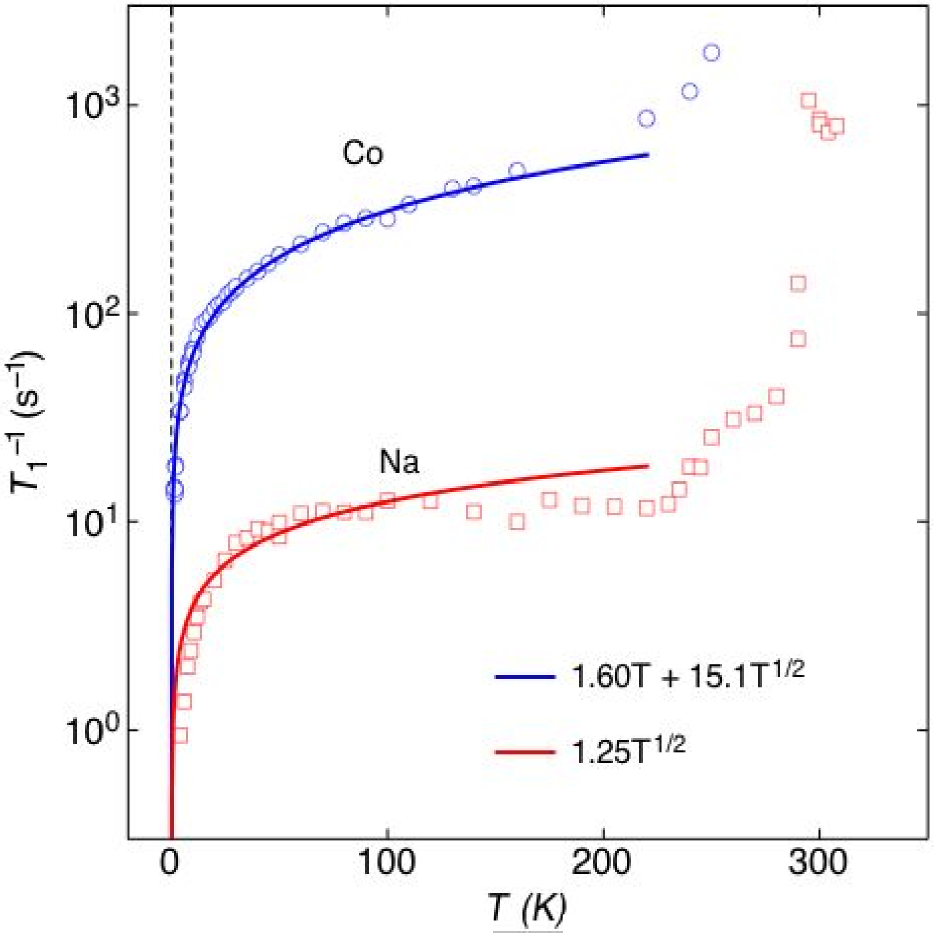
^{23}Na NMR :

$$T_1^{-1} = 1.25\sqrt{T}$$

with $N_{eg} = 0$ for Na_xCoO_2 (theory)

$N_{t2g} = 0$ for Na sites

$N_{t2g} = 1.2 \cdot 10^{11}$ states/erg per Co ion



$Na_{0.7}CoO_2$

From ^{23}Na and ^{59}Co NMR :

- formation of inequivalent Co sites with decreasing temperatures below 300 K

- strong reduction of spin-lattice relaxation rates $T_1^{-1}(T)$ below 300 K

- unusual variation of hyperfine fields at Co nuclei upon cooling

- unusual reductions of spin-lattice relaxation rates T_1^{-1} below 300 K

- itinerant charge carriers confined to Co planes, i.e., Na planes are insulating

- no magnetic order above 0.1 K, but close to afm instability

Puzzles in relation with the Na_xCoO_2 series

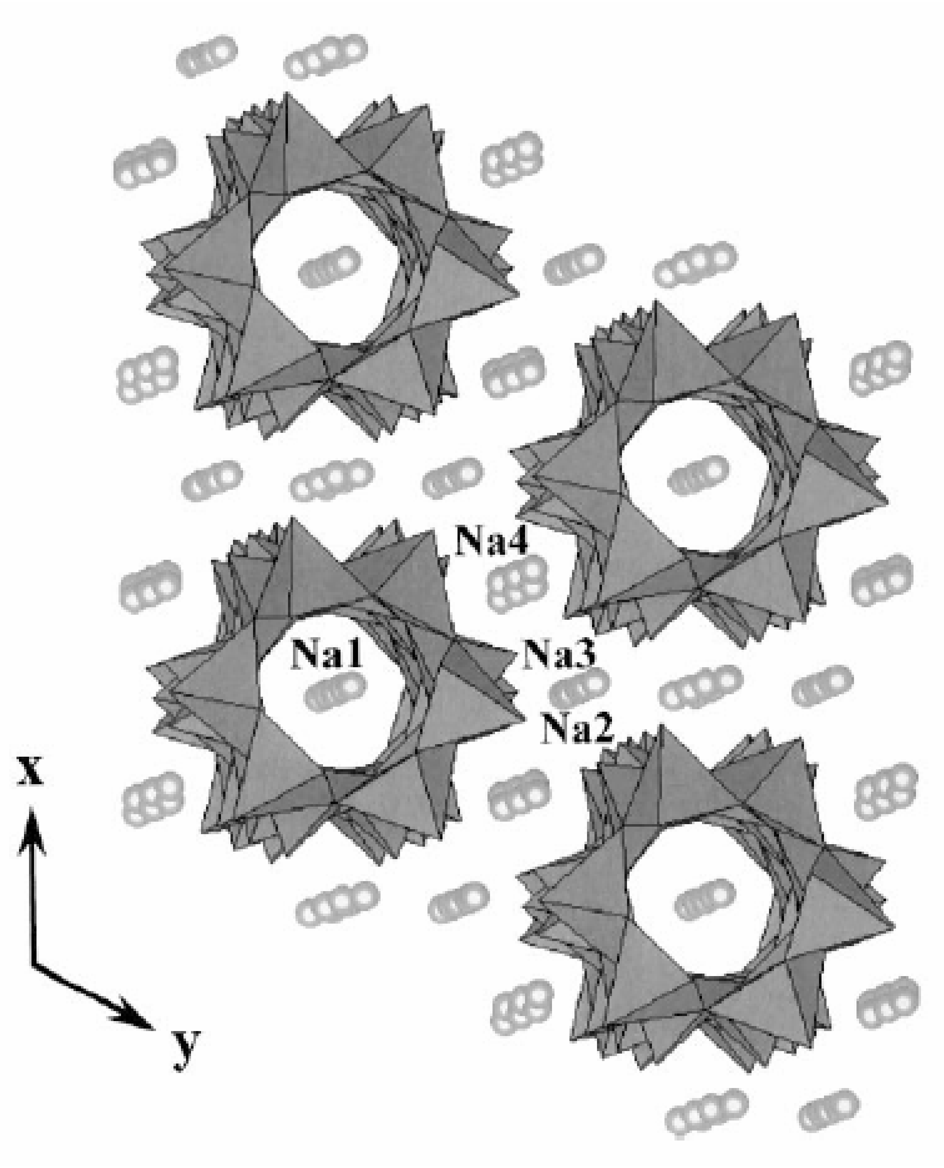
Unclear electronic structure
Strong correlations?

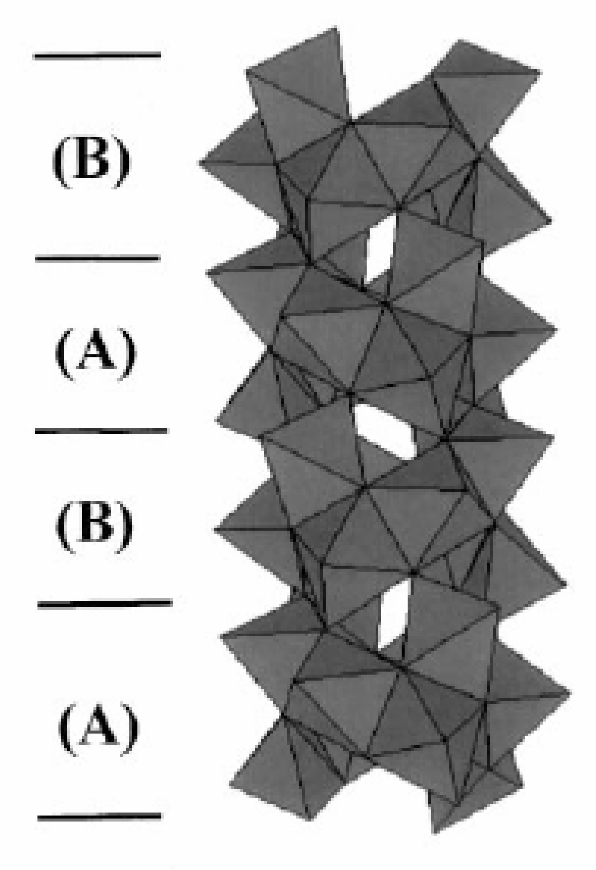
Co 3d electrons:
- local moments versus itinerant charge carriers
- very short mean free path, high effective mass ($Na_{0.5}CoO_2$)
- T-induced modification of 3d electron system ($Na_{0.7}CoO_2$)

Difficulties in relating magnetic and electronic properties

Quantum criticality:
- low dimensions and frustration ?
- ionic configuration instability ?

Transition metal oxide nanotube system : $Na_2V_3O_7$





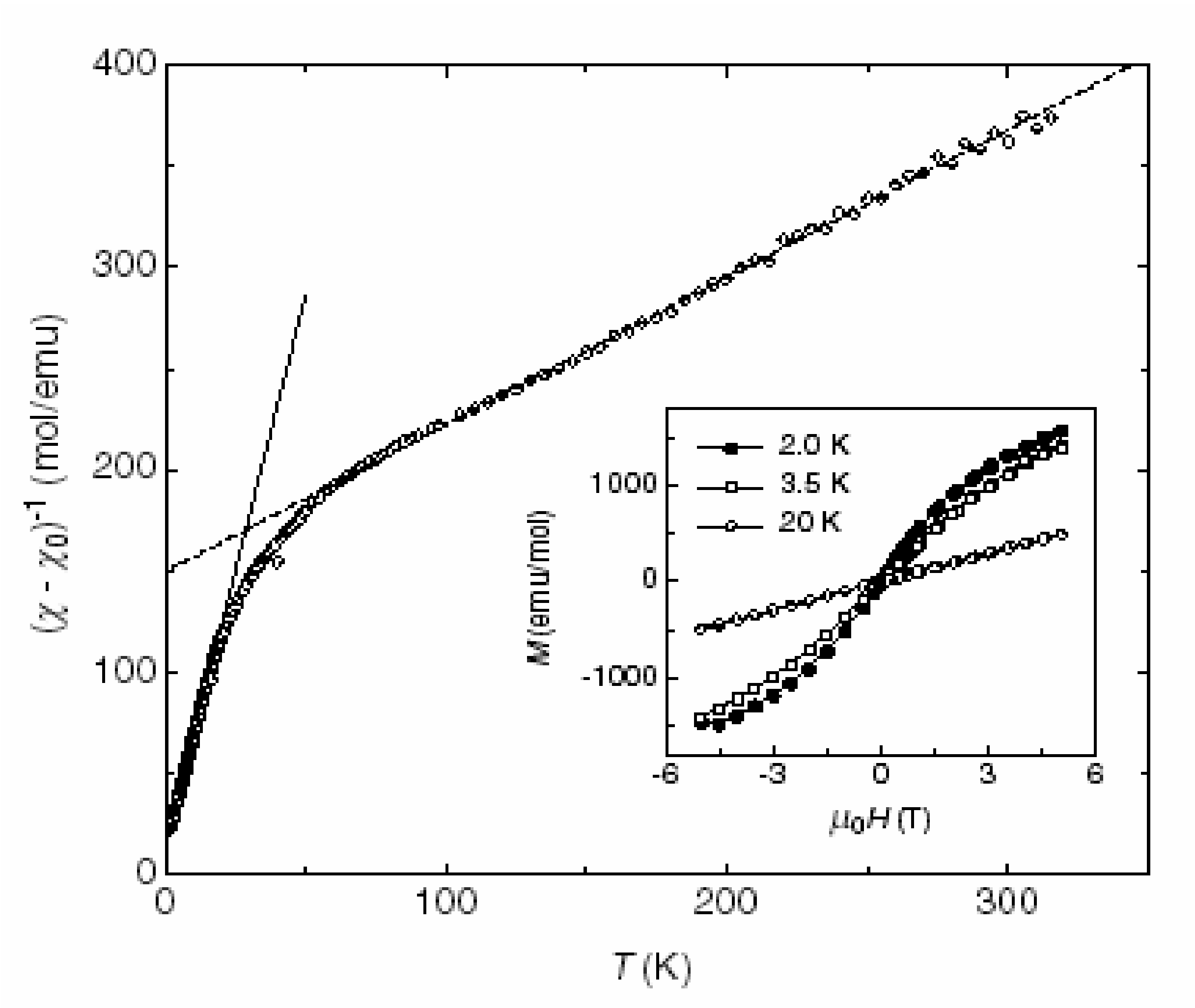
(Millet et al., J Solid State Chem. **147**, 676 (1999))

Spin S = 1/2 ladders with periodic boundary conditions along the rung direction

⇒ 9 V sites per ring around tube

Magnetic susceptibility

$$\chi(T) = \chi_{\mathrm{dia}} + \frac{C}{(T-\Theta)}$$



T > 100 K :

C = 1.4 emuK/mol → 1.9 μ_B/V^{4+}
Θ= - 200 ± 30 K

1.9 < T < 20 K :

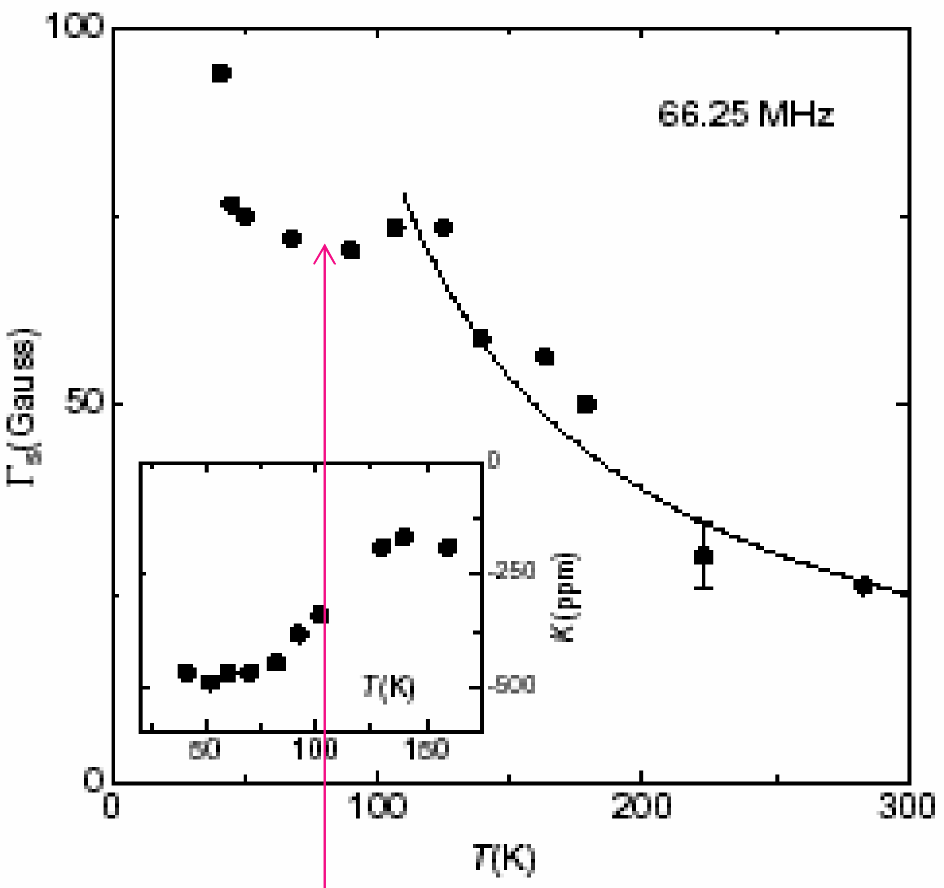
C = 0.178 emuK/mol
Θ = - 2.2 K

- **gradual compensation of moments : 8 of 9 moments per ring form singlets below 20 K**
- **n_{mag} : number of uncompensated moments/number of all V sites**

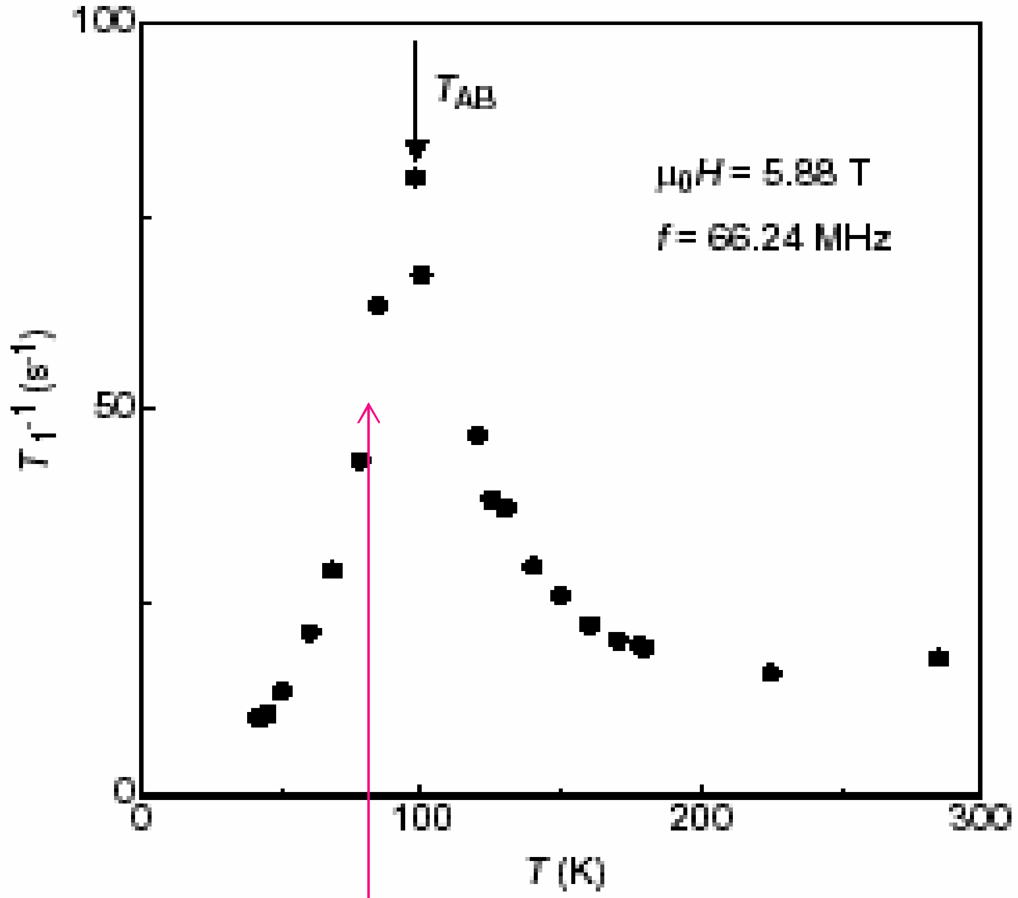
⇒ T > 100 K : n_{mag} = 1; T < 20 K : n_{mag} = 1/9

High-temperature ^{23}Na NMR

Linewidth

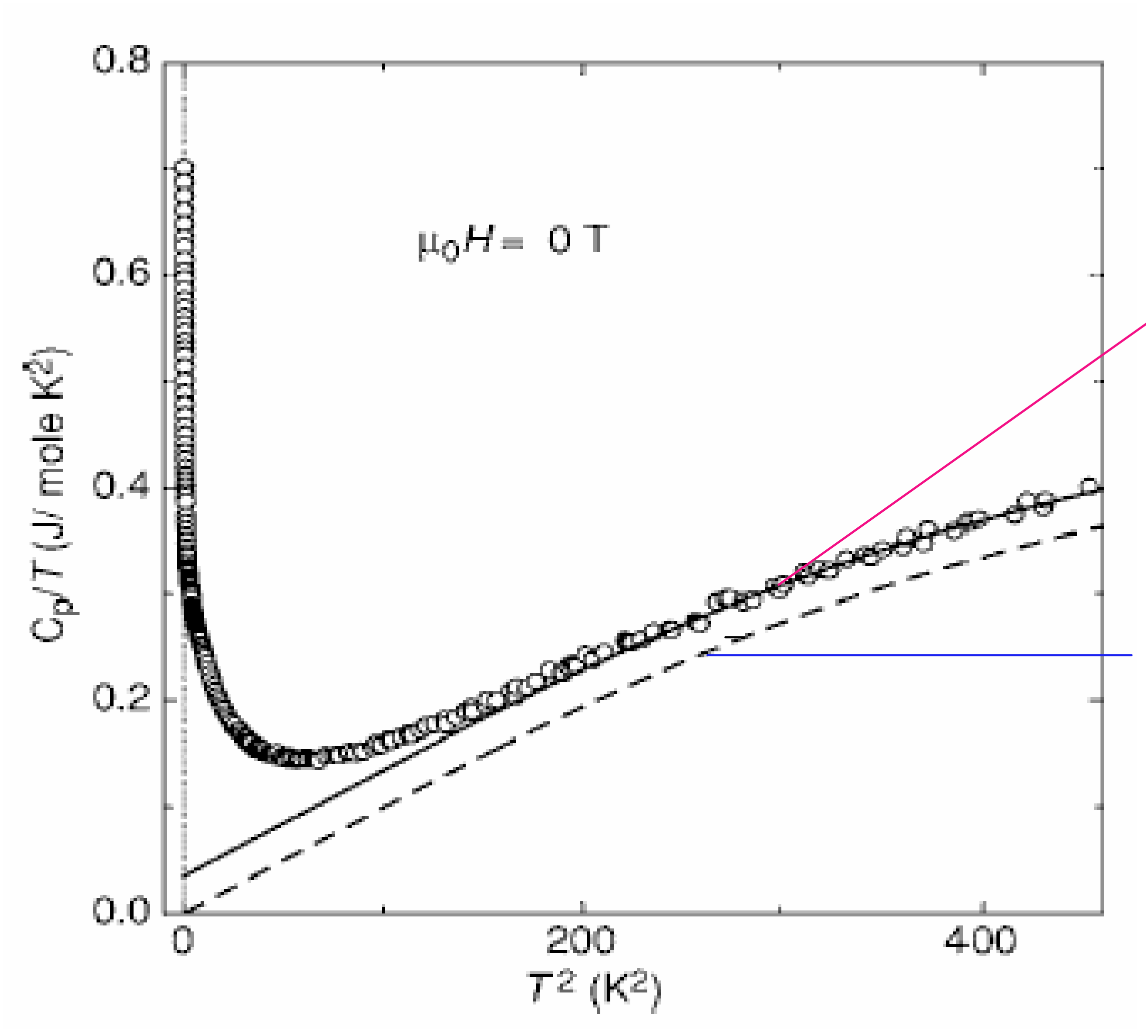


Spin-lattice relaxation



Consistent with decrease of n_{mag}

Specific heat at low temperatures (T < 22 K)



T > 15 K :

$$C_p = \gamma \cdot T + C_{DE}$$

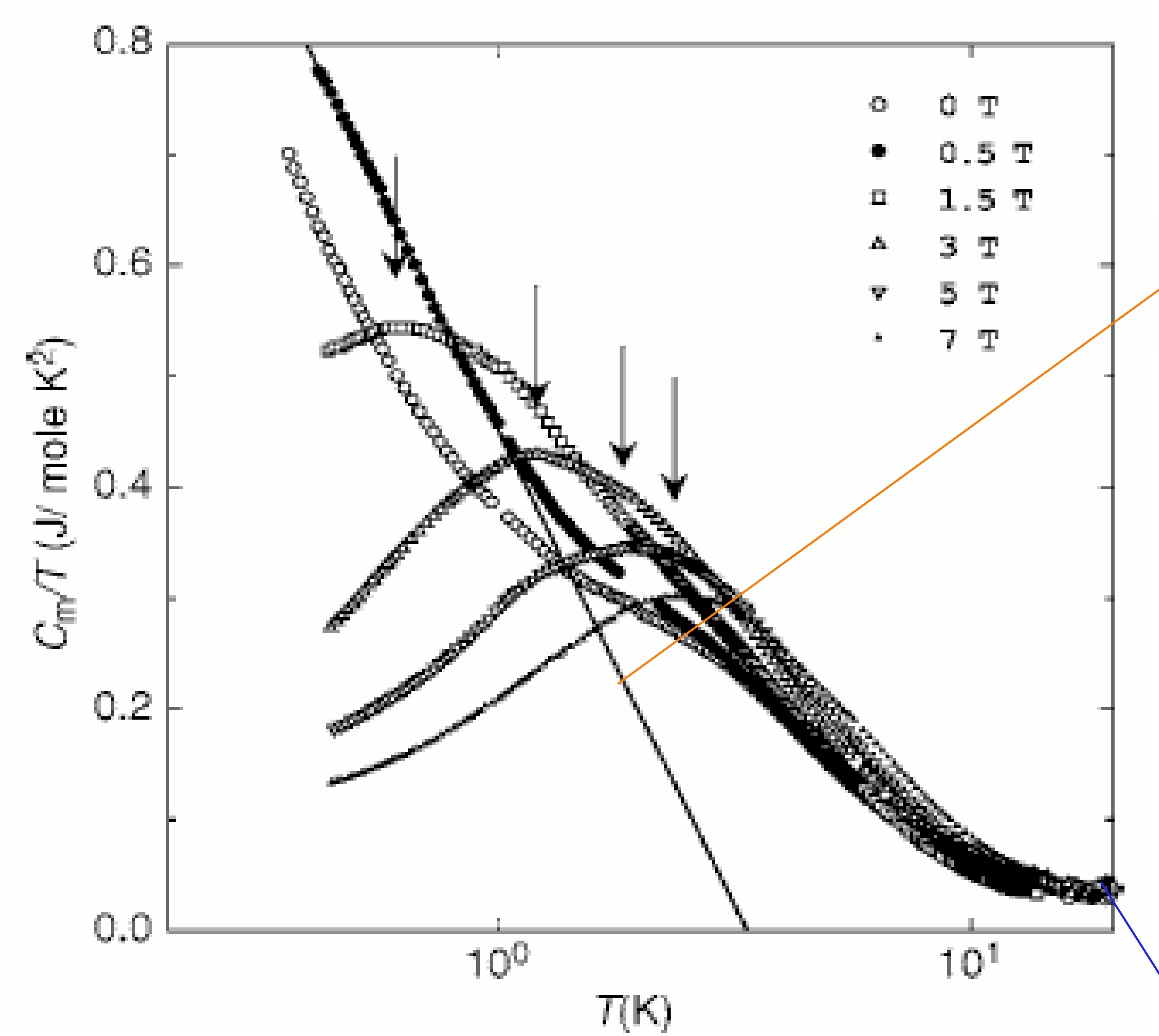
γ = **35 mJ/molK^2**

C_{DE}:

- **Debye-type contribution with Θ_D= 125 K,**
- **Einstein mode at ω_E = 88 cm^{-1}**

$\Rightarrow$ **Problem : Significance of the γ-term in an insulator**

Magnetic field dependence of the specific heat below 15 K



$$C_m = C_p - C_{DE}$$

$$C_m(T)/T = -0.38\ln(T/T_K)$$

$$T_K = 3.2\text{ K}$$

γ term field independent !

⇒ excess specific heat below 15 K : $C_m = \gamma \cdot T + C_{st}$

Low-temperature specific heat of $Na_2V_3O_7$

T < 15 K :

- dominated by magnetic excitations of the dimers (singlet-triplet)

- C_m independent of external magnetic field for T > 15 K

- component of C_m varying linearly with T

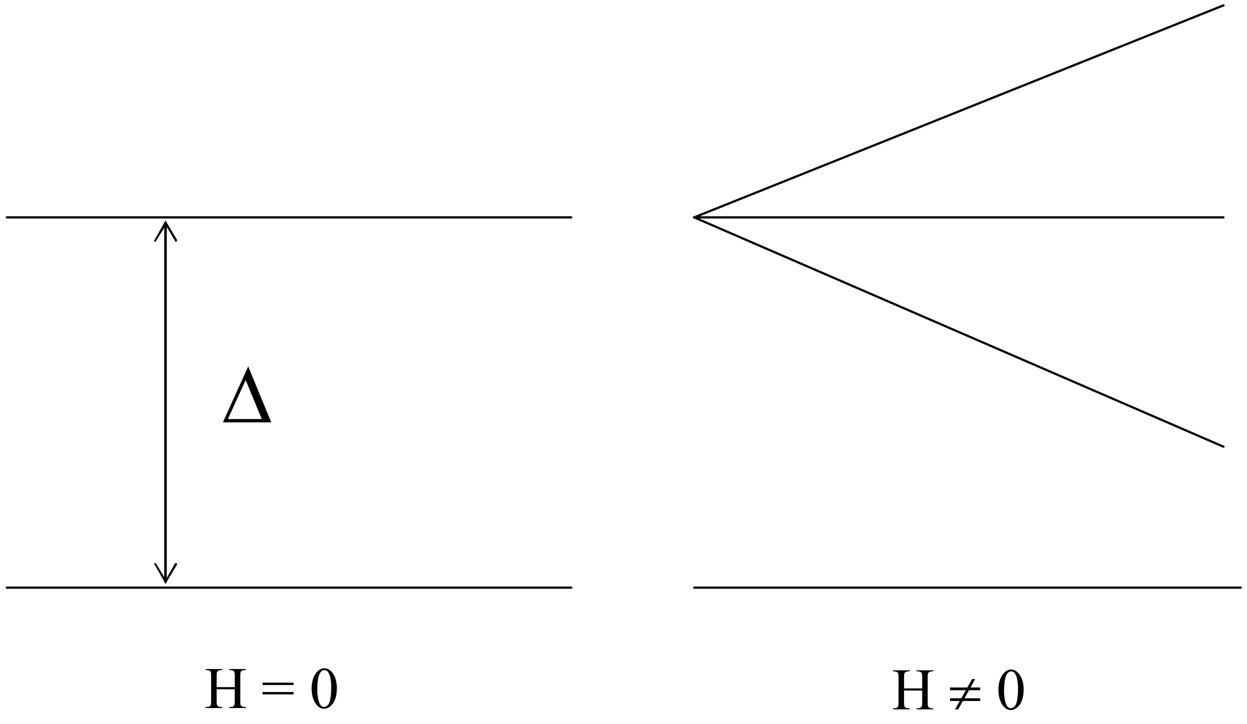
$$C_m = \gamma \cdot T + C_{st}$$

Concentrate on excess specific heat $C_{st}(T,H)$ via model calculation

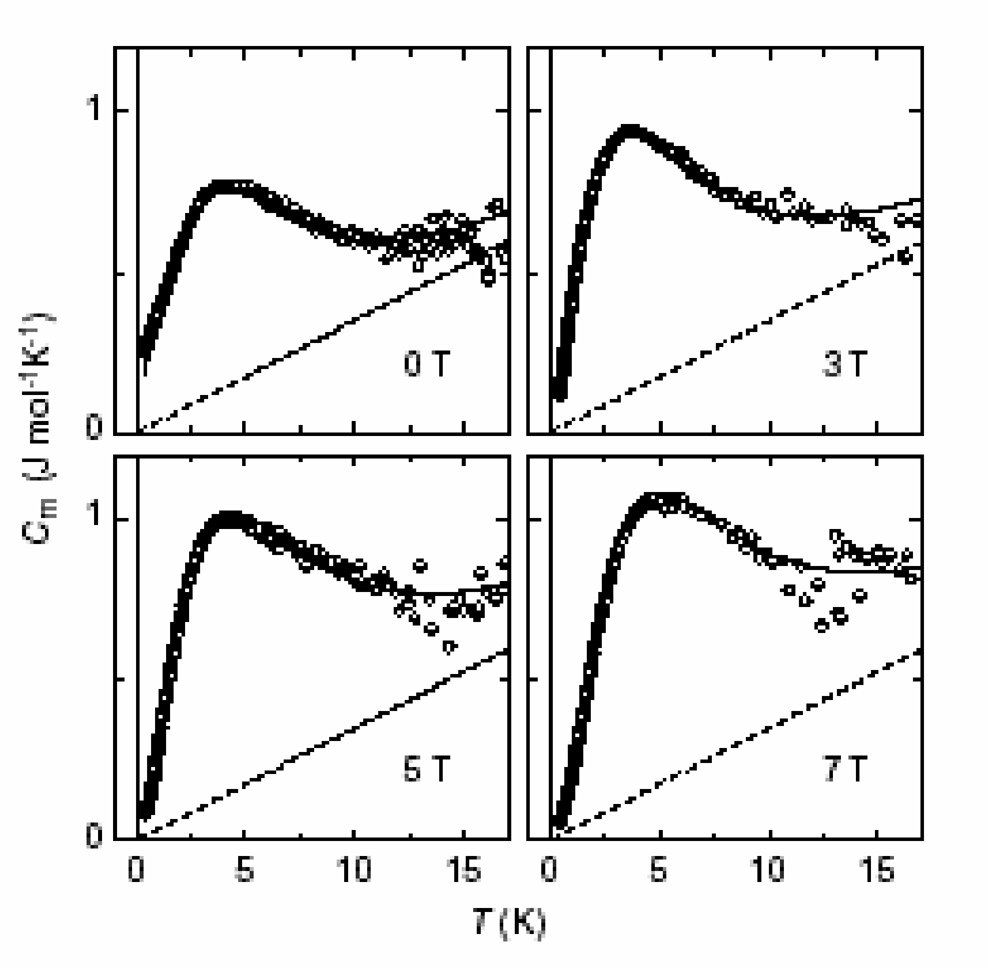
The model

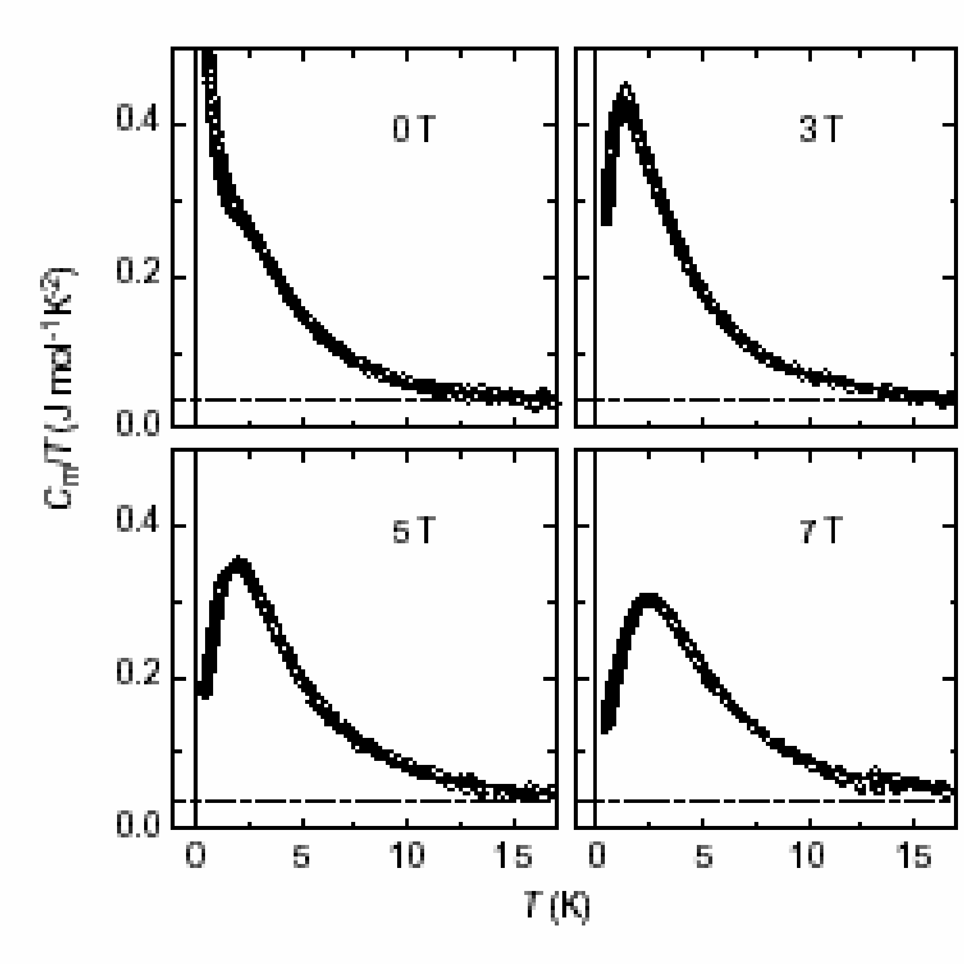
- Assume a collection of dimers with varying singlet-triplet gaps Δ

- Optimize the fit to the experimental data by varying the probability distribution of Δ



The fits



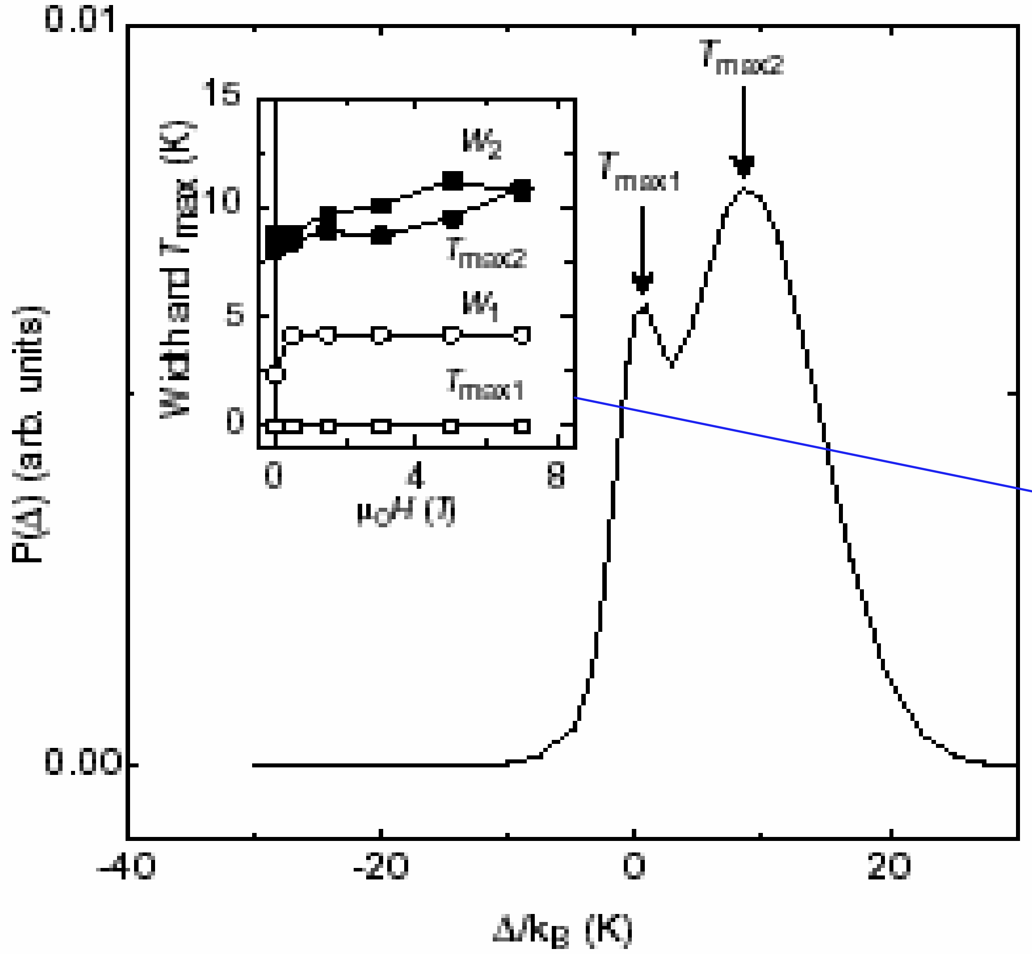


$C_m(T) = \gamma T + C_{st}$

$C_m(T)/T$

are based on

the probability distribution P(Δ)



$$P(\Delta) = \frac{0.055}{W_1\sqrt{(\pi)}}\exp\left\{-\left[\frac{\Delta - k_B T_{max1}}{W_1}\right]^2\right\} + \frac{0.11}{W_2\sqrt{(\pi)}}\exp\left\{-\left[\frac{\Delta - k_B T_{max2}}{W_2}\right]^2\right\}.$$

Fit parameters are :

W_1, T_{max2}, W_2

Note that $T_{max1} = 0$

Δ > 0 : singlet ground state
Δ < 0 : triplet ground state

only 1/9 of all V moments involved !

Magnetic features of $Na_2V_3O_7$

- At high temperatures, all V moments act as antiferromagnetically interacting local moments ($\mu_V \sim 1.9\ \mu_B$) → $n_{mag} = 1$
- With decreasing temperature, 8 out of 9 V spins per ring dimerize, leaving 1 spin per ring uncompensated
- From $\chi(T)$: Dimerization starts at T ~ 100 K and is completed at T ~ 20 K → $T \leq 20$ K → $n_{mag} = 1/9$

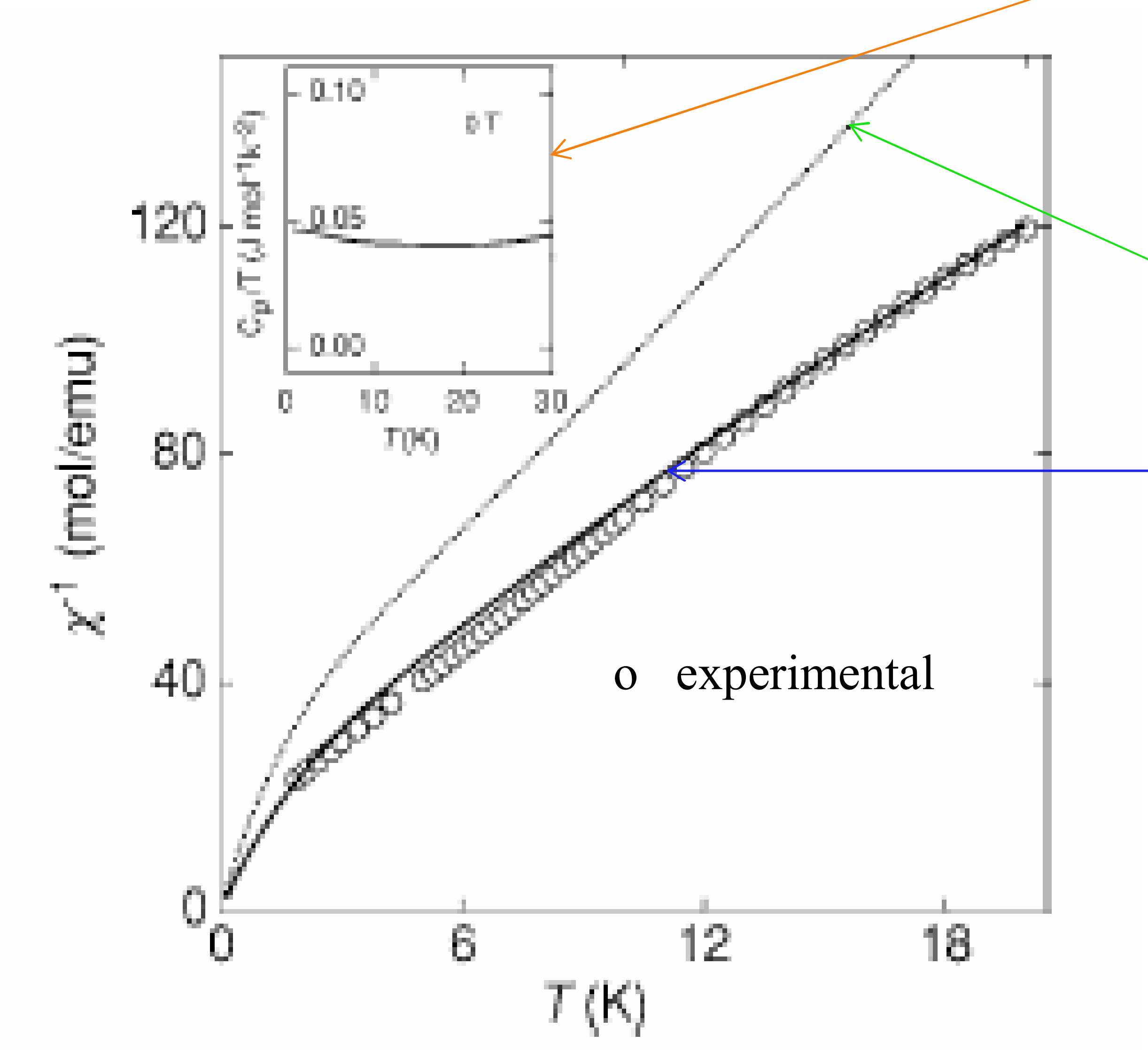
Data of the ^{23}Na NMR (linewidth, T_1^{-1}) and of the entropy S(T) confirm this interpretation (see Phys. Rev. Lett. 90, 167202 (2003) and Phys. Rev. B **72,** 064431 (2005))

⇒ The low temperature features of $Na_2V_3O_7$ are dominated by dimer excitations and — from $\chi(T)$ below 1 K — the response of arbitrarily distributed individual spin moments.

In order to capture the specific heat contribution varying linerarly with temperature (γT) and to reproduce the total magnetic susceptibility, dimers with larger singlet triplet gaps, involving 8/9 of all V moments, need to be considered:

$$P_3(\Delta) = \begin{cases} 1.26 \times 10^{-3}, & -15\ \mathrm{K} < \Delta/k_B < 250\ \mathrm{K}, \\ 1.00 \times 10^{-2}, & 250\ \mathrm{K} < \Delta/k_B < 350\ \mathrm{K}, \\ 0, & \text{otherwise.} \end{cases}$$

Inclusion of $P_3(\Delta)$ results in :



linear-in-T contribution to $C_p(T)$ from $P_3(\Delta)$

from $P(\Delta)$ alone

including $P_3(\Delta)$

$Na_2V_3O_7$

S = 1/2 spin ladders with periodic boundary conditions: spin tubes

Dimerization of spin moments upon decreasing temperature
→ leads to increasing magnetic disorder

Low-temperature features dominated by singlet-triplet excitations

Possible spin freezing below 0.1 K

Spin system close to quantum critical point