INTERNATIONAL ATOMIC ENERGY AGENCY
UNITED NATIONS EDUCATIONAL, SCIENTIFIC AND CULTURAL ORGANIZATION

INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS
34100 TRIESTE (ITALY) - P.O.B. 586 - MIRAMARE - STRADA COSTIERA 11 - TELEPHONE: 2240-1
CABLE: CENTRATOM - TELEX 460392 - 1

SMR/455 - 24

EXPERIMENTAL WORKSHOP ON HIGH TEMPERATURE SUPERCONDUCTORS & RELATED MATERIALS (BASIC ACTIVITIES)

12 - 30 MARCH 1990

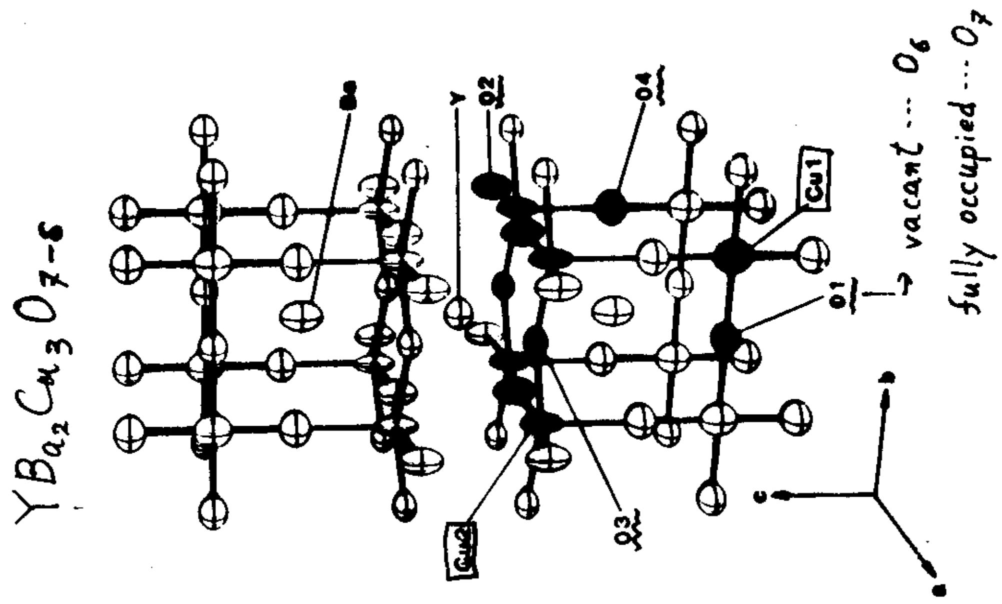
MAGNETIC NUCLEAR RESONANCE

Part II

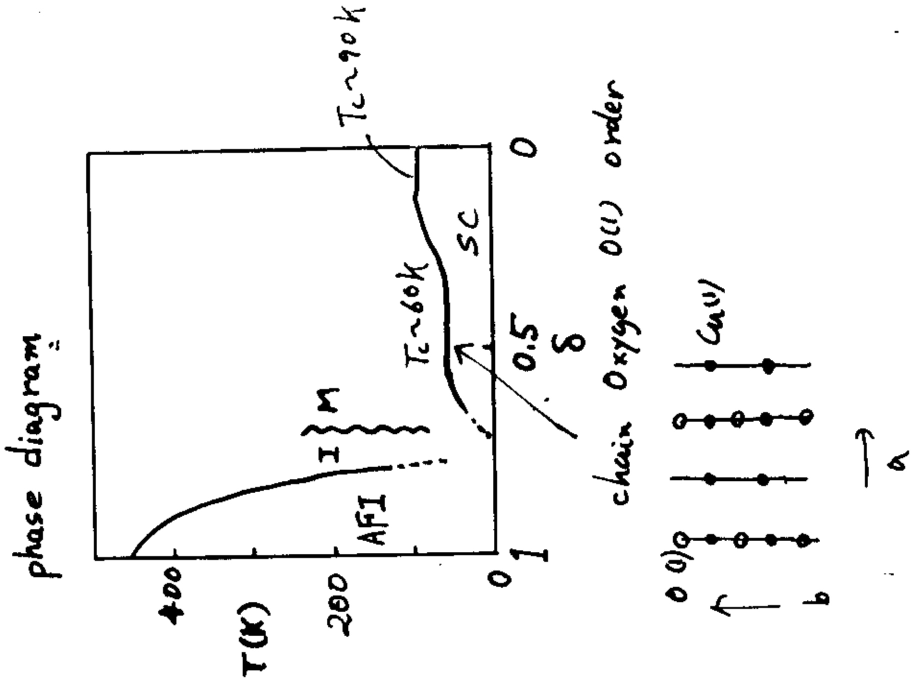
MASASHI TAKIGAWA

Los Alamos National Laboratory
Group P-10, MS-K764
New Mexico
Los Alamos 87545
U.S.A.

$YBa_2Cu_3O_{7-\delta}$

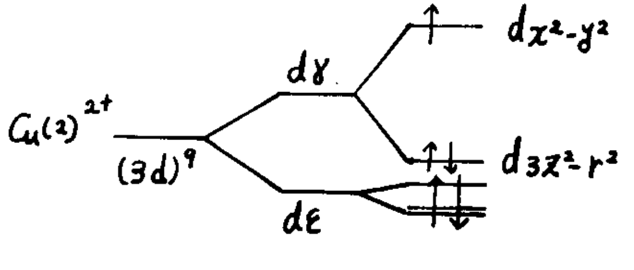


phase diagram:



Electronic Structure

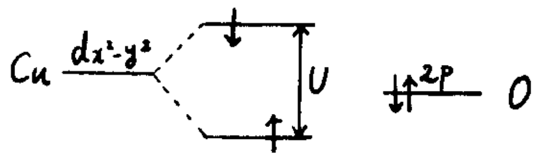
• $YBa_2Cu_3O_6 \Rightarrow Y^{3+}\ Ba^{2+}\ \underset{\text{plane } 3d^9}{\underline{Cu(2)^{2+}}}\ \underset{\text{chain } 3d^{10}}{\underline{Cu(1)^{1+}}}$



large Coulomb energy U $\Rightarrow$ Antiferromagnetic
localized d-hole Insulator $T_N \sim 400$

• upon doping $0 \xrightarrow{\delta} 1$ ($Cu(1) \rightarrow 2+$)

- Holes are doped also in the plane. ---- $Cu(2)O_2^{(2-}$
  [destroy antiferro. order
  metallic conduction $\Rightarrow$ superconductivity
- Doped hole states are mainly of O-2p charac



[X-ray absorption
electron energy loss spectroscopy (EEL

[1] single or two component(s) spin in the CuO_2 planes

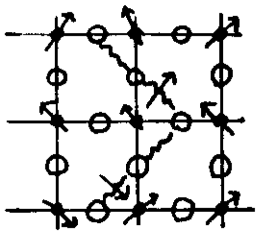
$$\chi_{spin} = \chi_{Cu} + \chi_{hole}$$

(Johnston: 2D localized ↑ Pauli-like ↑)

$$\chi_{spin} = \chi_{Cu-O}$$

(ref 17)

a) two band picture (Aharony et al, Emery et.al)



- O hole spins destroy Cu-Cu AF order. (flustration)

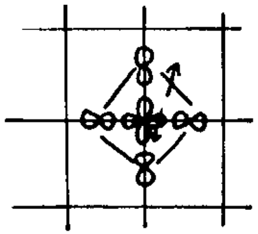
$-\updownarrow-\phi-\updownarrow-$ $J_{Cu-O} \gtrless 0$ ... p_π / ... p_σ

(↑)

- Mobil holes (quasi particles) carry spin, moving in the Cu d-spin background

- two distinct spin degrees of freedome

b) single band picture (Zhang and Rice, Sawatzky) local singlet formation (ref. 18)



- oxygen holes make local singlet with Cu spin.
- Mobile holes do not carry spin

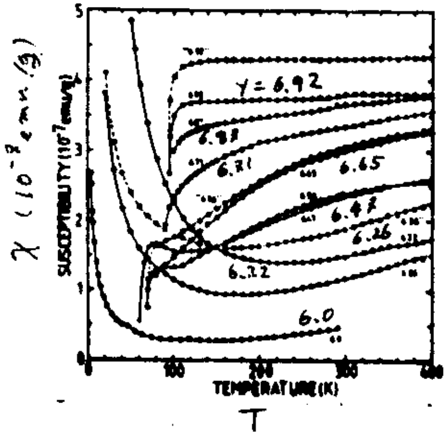
⇒ equivalent to single band model. (t-J model)

magnetic susceptibility

s

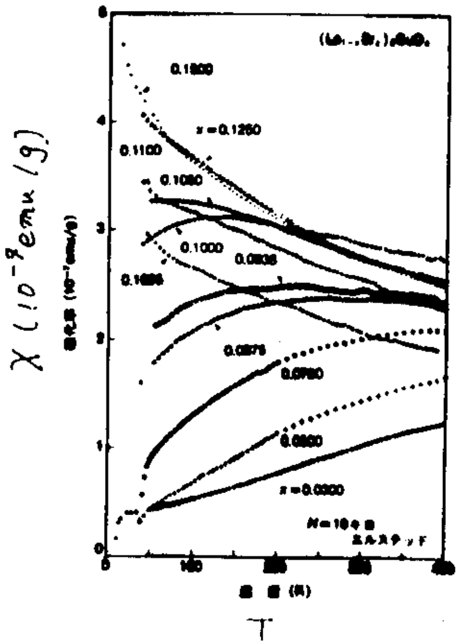
$YBa_2Cu_3O_y$

(Nakazawa and Ishikaw) (ref. 19)

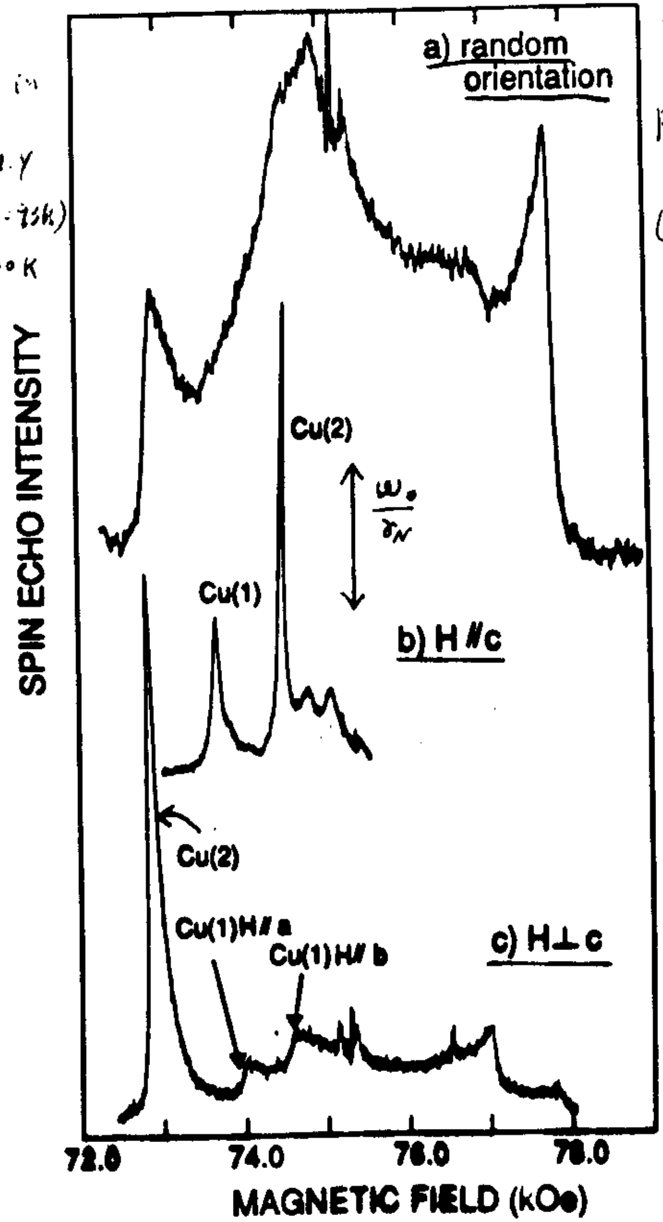


$(La_{1-x}Sr_x)_2CuO_4$

(Uchida et al.)



^{63}Cu NMR spectra in $YBa_2Cu_3O_{7-y}$ ($y \sim 0.03$, $T_c \sim 93K$) 85MHz, 100K



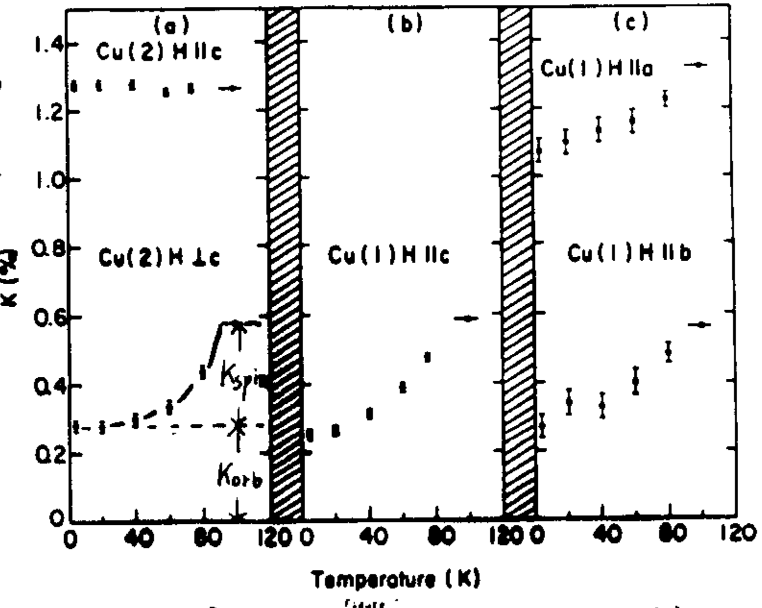
Takigawa, Hammel, Hettner, Fisk
Phys. Rev. B 39, 300 ('89)
(ref. 23)

Fig 1

Cu Knight shift in $YBCO_7$ (Barrett et al, 90) (ref. 2?)

$K = K_{spin} + K_{orb}$

K_{orb}: T-indep.
$K_{spin}(T \to 0) = 0$



	$K(T > T_c)$ (%)	$K(4.2k)_{orb}$ (%)	K_{spin} (%)
Cu(1) c	0.59	0.25 ± 0.01	0.33 ± 0.01
Cu(1) a	1.32	1.08 ± 0.04	0.25 ± 0.04
Cu(1) b	0.56	0.27 ± 0.04	0.29 ± 0.04
Cu(2) c	1.27	1.28 ± 0.01	−0.01 ± 0.01
Cu(2) ab	0.58	0.28 ± 0.02	0.30 ± 0.02

Anisotropy of $1/T_1$

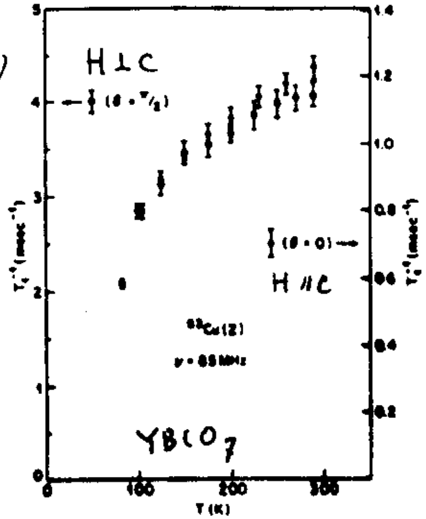
(Walstedt et al.) (ref.37)

$$1/T_1)_{H\parallel z} \propto \left[|A_x|^2+|A_y|^2\right] \sum_q \frac{\mathrm{Im}\,\chi(q,\omega)}{\omega_0}$$

simple expectation

$$\frac{(1/T_1)_{ab}}{(1/T_1)_c} = \frac{\{K_s(c)\}^2+\{K_s(a,b)\}^2}{2\{K_s(a,b)\}^2}$$

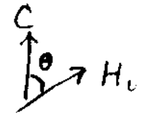
$$= \frac{1}{2}$$



experiment: $\frac{(1/T)_{ab}}{(1/T_1)_c} = 3.6$ (at 100 K)

Cu Knight shift

$$K_{spin}(\theta) = K_{iso} + K_{ax}(3\cos^2\theta - 1)$$



$$\begin{cases} K_{iso} = 0.23 \pm 0.02 \ \% \\ K_{ax} = -0.13 \pm 0.01 \ \% \end{cases}$$

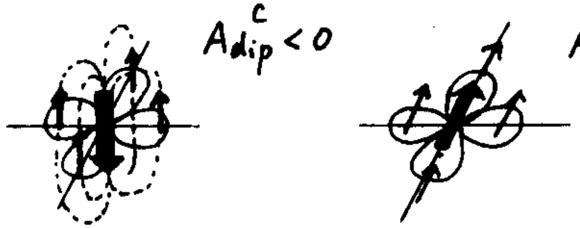
- negative K_{ax} : consistent with the hyperfine field from a spin in $d_{x^2-y^2}$ orbital

$$\overleftrightarrow{A}_d = A_{cp} + \overleftrightarrow{A}_{dip}$$

($A_{cp}<0$) ⇑ modified by spin-orbit coupling

dipolar field

$A^c_{dip} < 0$ $\qquad$ $A^{ab}_{dip} > 0$



$\Rightarrow K_{ax} < 0$

- positive K_{iso} : incompatible with $\langle \overleftrightarrow{A}_d \rangle = A_{cp} < 0$

$\Rightarrow$ transferred hyperfine field from neighboring Cu sites. (Mila, Rice)

- $K_{ax} = \frac{1}{3}(A^c_d - A^{ab}_d)\chi_d / N_A\mu_B$

$A^c_d - A^{ab}_d \simeq 230$ kOe/μ_B : (±20% characteristic of Cu^{2+} $d_{x^2-y^2}$ state) (ref.3)

$\chi_d = 9.2 \times 10^{-5}$ emu/mole.Cu

spin susceptibility due to planar Cu d-holes.

Positive Kiso

- Mila and Rice (Physica C 157, 561 ('89)) (ref.30)

CuO₂ plane

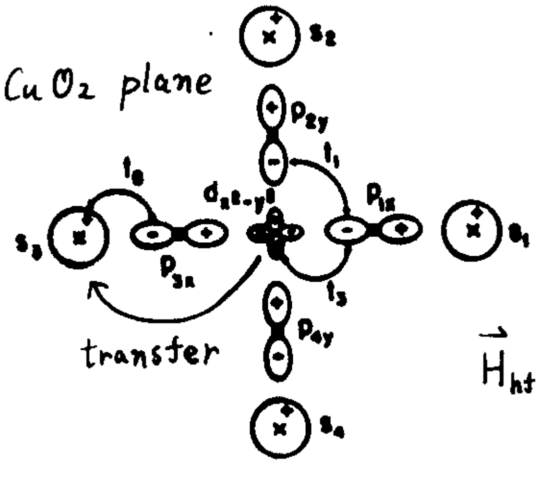


Fig.1

$$|\phi\rangle = \alpha_d\, |d_{x^2-y^2}\rangle + \alpha_p\, |P\rangle + \alpha_s\, |S\rangle$$

$$\vec{H}_{hf}(i) = \underbrace{\overleftrightarrow{A}_d \cdot \vec{S}_i}_{\text{on site}} + \underbrace{\sum_j B \cdot \vec{S}_j}_{\text{transfer}}$$

$$K_\alpha = (A_d^\alpha + 4B)\, \chi_d$$

if no pair spin correlations.

$$1/T_1)_\alpha \propto \frac{1}{2}\left(A_d^{\beta\,2} + A_d^{\gamma\,2}\right) + 4B^2 \quad \text{('add incoherently)}$$

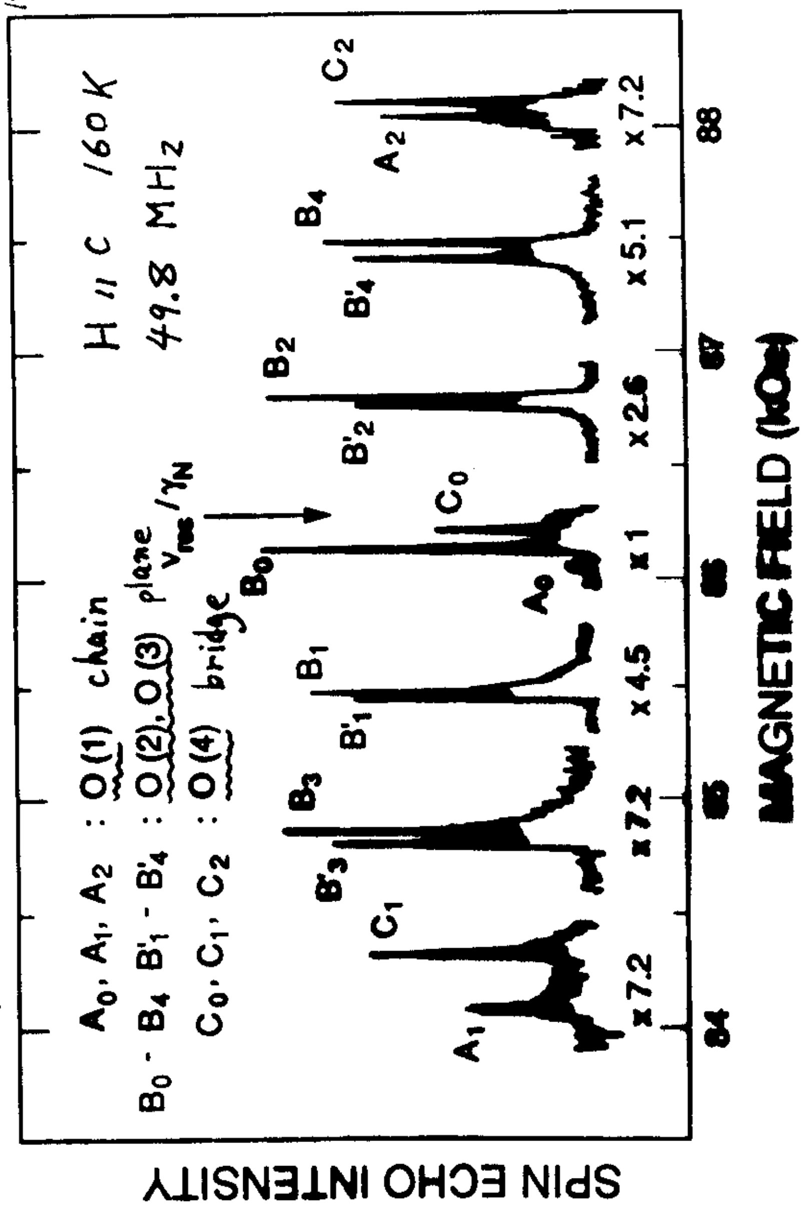
hyperfine parameters $A_d^c = -170,\ A_d^{a,b} = 35\quad B = 42$ kOe/

$\Rightarrow K_c = 0$

$\dfrac{(1/T_1)_{ab}}{(1/T_1)_c} = 2.7$ [better agreement by considering the AF correlations

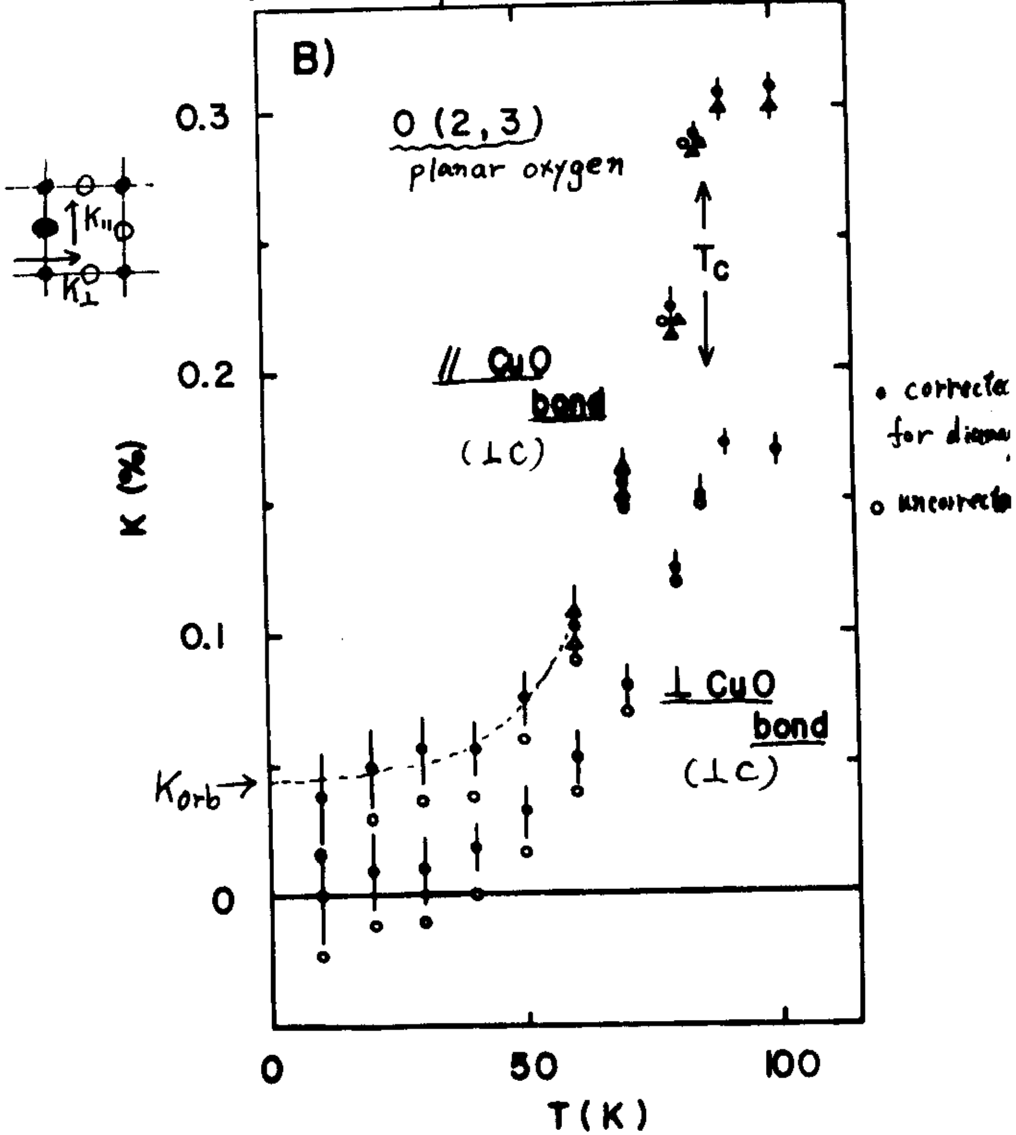
Takigawa, Hammel, Hetter (ref.15), Fisk, Thompson, Phys. Rev.

^{17}O NMR spectra in $YBa_2Cu_3O_{7-y}$ (y~0.05) 160K, 49MHz



$K = K_{spin} + K_{orb} = \alpha \chi_{spin} + \beta \chi_{orb}$

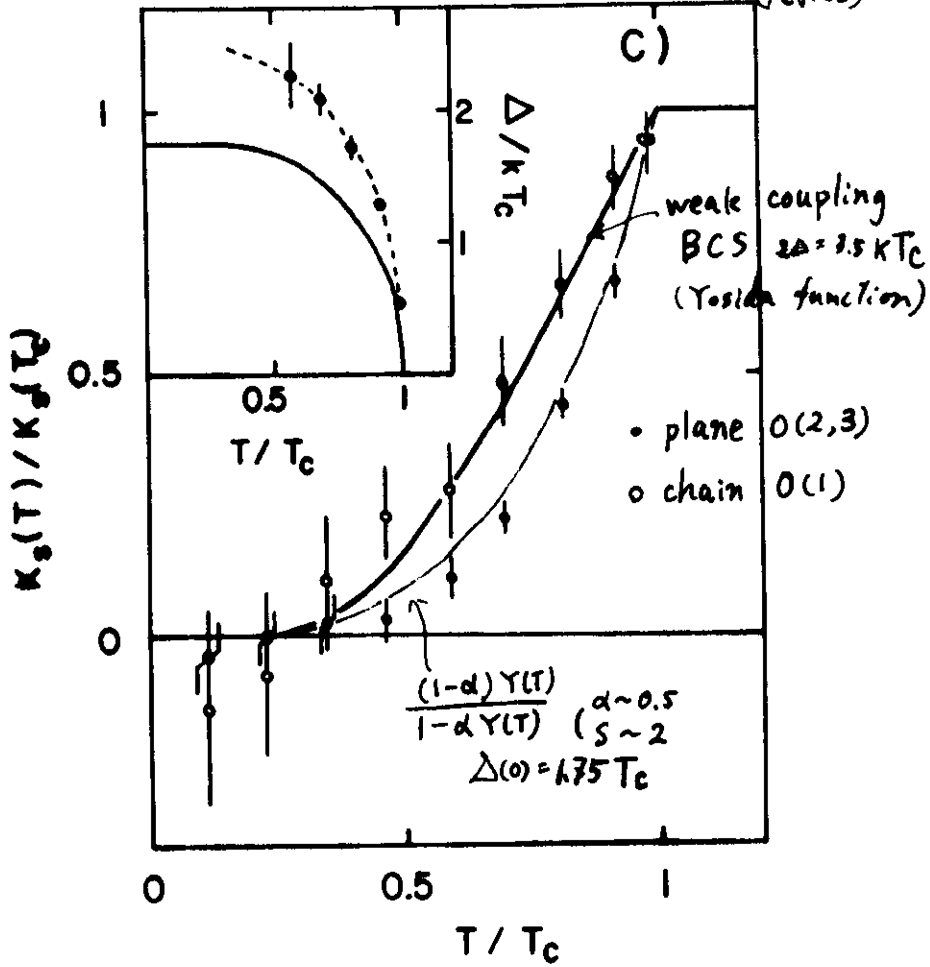
assume $K_{spin} \to 0$ as $T \to 0$. (ref. 26)



M. Takigawa
Fig 2(B)

spin susceptibility in the superconducting state
more rapid decrease of planar χ_s than chain χ_s
S-wave pairing

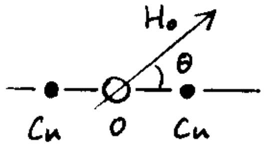
(ref. 26)



M Takigawa
Fig. 2(C)
reduction 45%

Oxygen Knight shift (O(2,3) sites)

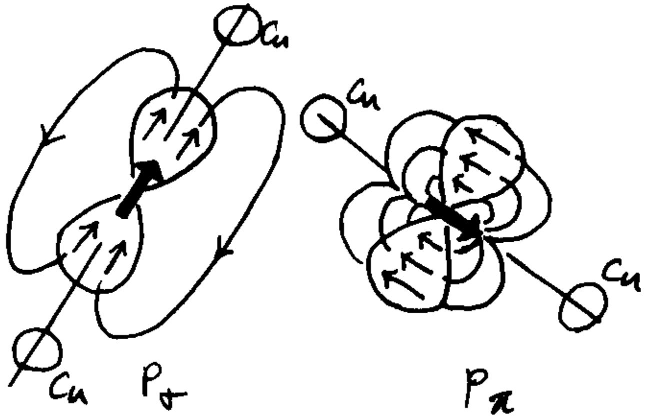
$$K_{spin}(\theta) = K_{iso} + K_{ax}(3\cos^2\theta - 1)$$



$$\begin{cases} K_{iso} = 0.19 \pm 0.02 \ \% \\ K_{ax} = 0.033 \pm 0.003 \ \% \end{cases}$$

K_{iso} : Fermi contact field from 2s state spin.

K_{ax} : dipolar field from a spin in 2p state.



P_σ $\quad$ $K^{\parallel} > K^{\perp}$

P_π $\quad$ $K^{\parallel} < K^{\perp}$

Exp. $K^{\parallel} > K^{\perp}$

spin density resides on $2p_\sigma$ orbitals.

spin susceptibility from Oxygen 2p-state.

$$\chi_p = \frac{K_{ax}}{A_p} N_A \mu_B = 2.1 \times 10^{-5} \text{ emu/mole O}$$

$$(A_p = 90 \text{ kOe}/\mu_B)$$

$$\chi_d = 9.2 \times 10^{-5} \text{ emu/mole. Cu}$$

$$\boxed{\chi_{Cu} : \chi_O = \chi_d : 2\chi_p \simeq 7 : 3}$$

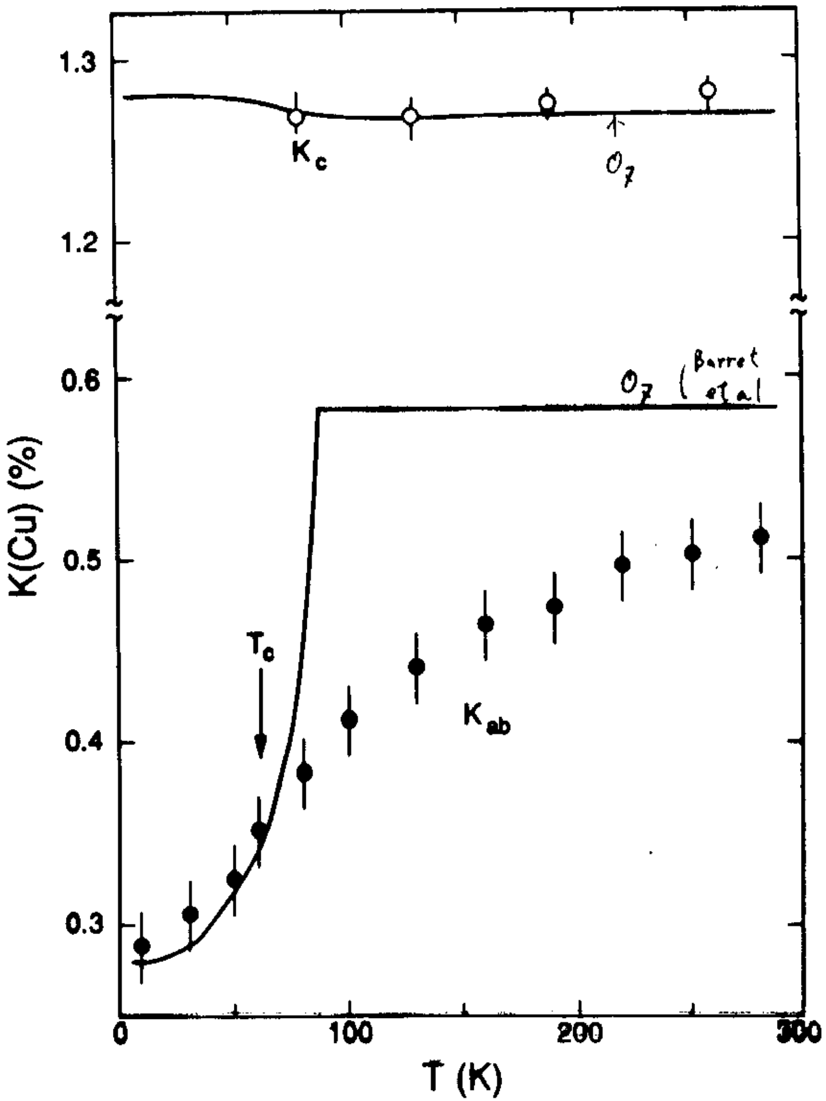
- How much of χ_p is due to mobile doped holes?

$$\chi_p = \underbrace{\chi_{hole}}_{\text{mobile holes}} + f_\sigma \chi_{Cu}$$

$\chi_{hole} = 0$ in the single band picture. (local singlet)

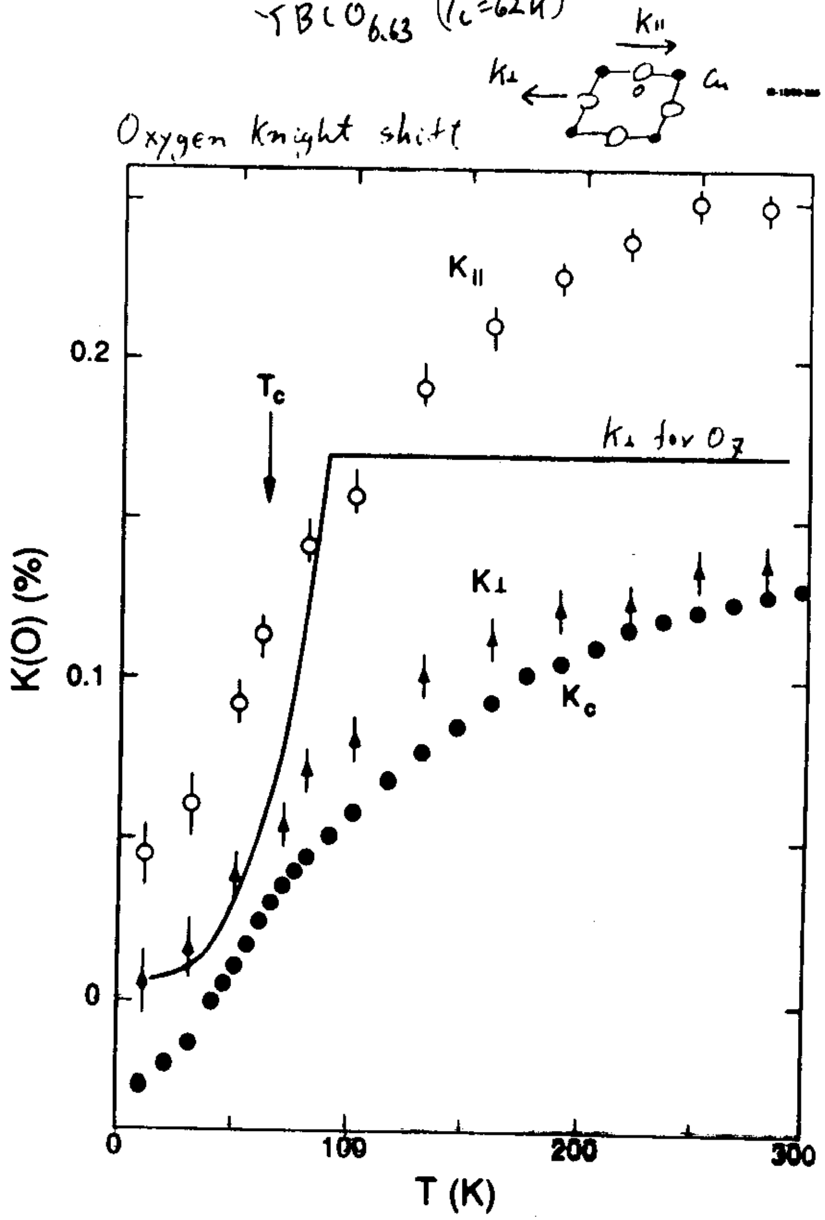
covelency effect.
A part of Cu-d spin density is transferred to neighboring O 2p state.

Cu Knight shift YBCO$_{6.63}$ (T_c=62K)



YBCO$_{6.63}$ (T_c=62K)

Oxygen Knight shift



Oxygen
- $^{17}K_c$
- $^{17}K_{ax} = (K_{\parallel} - K_{\perp})/3 \Rightarrow$ O − $2p_\sigma$ (spin density on)
- $^{17}K_{iso} = (K_{\parallel} + K_{\perp} + K_c)/3 \Rightarrow$ O − 2s

Copper $^{63}K_{ab} \Rightarrow$ Cu − 3d

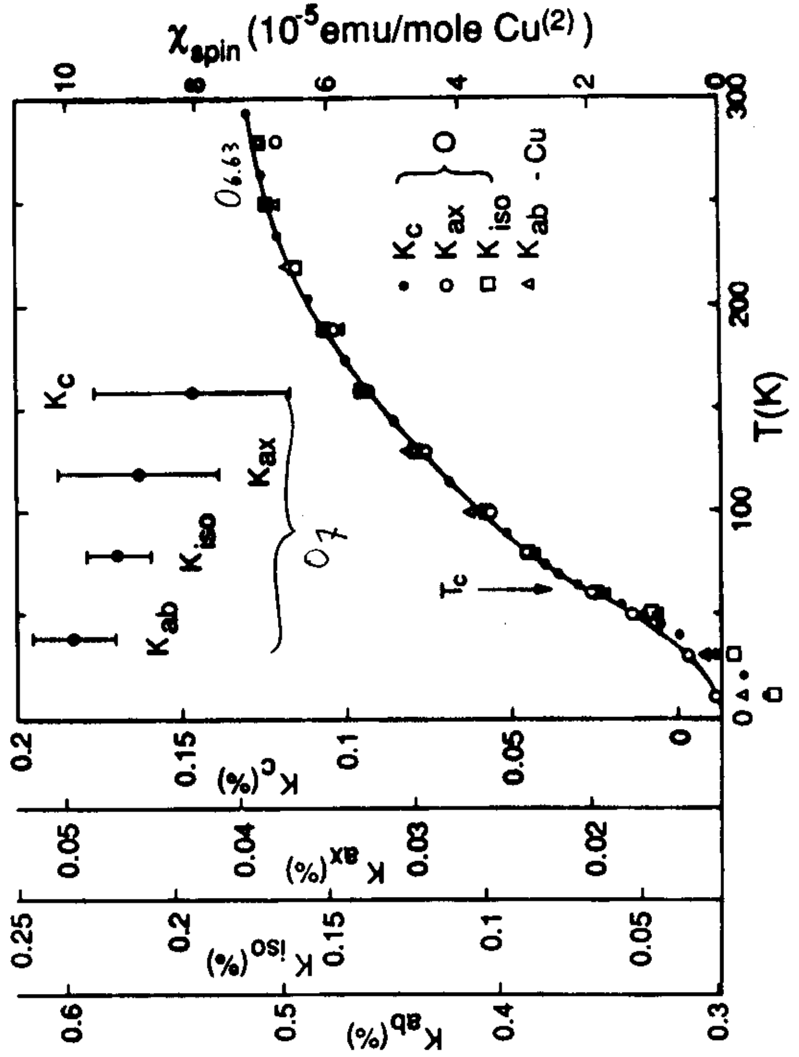
<u>All Knight shift components show the same T-dependence.</u>

$$K_i(T) = A_i \chi_{spin}(T) + \underbrace{K_i(T=0)}_{\text{orbital}}$$

A_i, $K_i(T=0)$: independent of y

- single spin component in the CuO_2 planes $\Rightarrow$ unique spin susceptibility. $\chi_{spin}(T)$
- y-independence of A_i (Allouls' Y knight shift) supports Zhang-Rice singlet ?

$\frac{\chi_p}{\chi_d}$: independent of T and y.



81

<u>Significant reduction of χ_{spin} with decreasing temperature.</u>

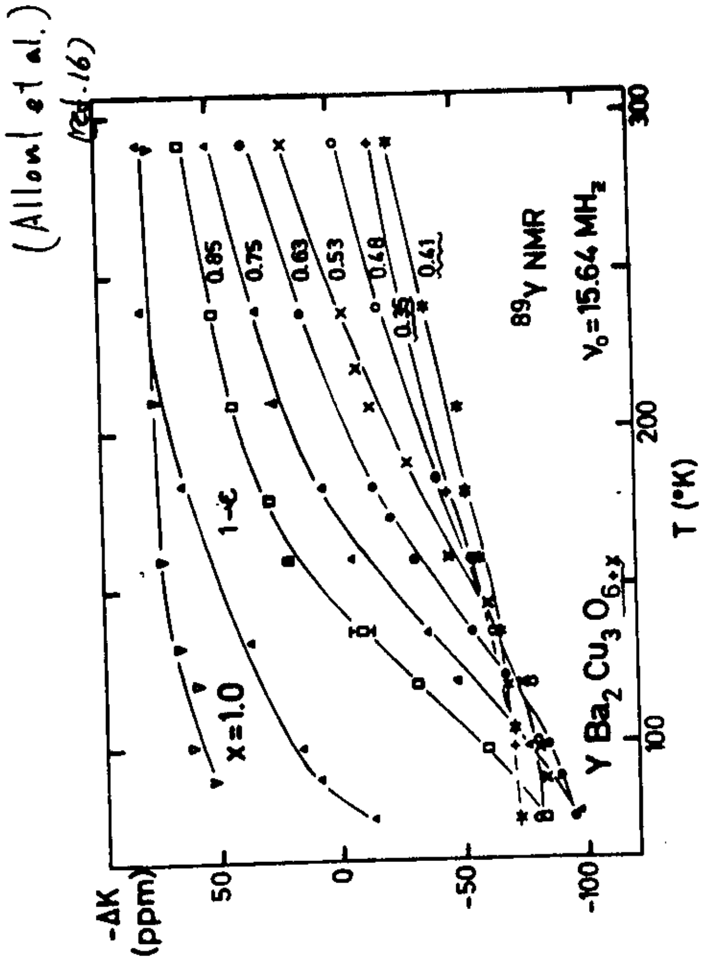
speculations.

- T-dependent density of state $N(E_F)$
  (pseudo-gap in $N(E)$ due to short range AF correlations, (Kampf, Schrieffer))
- preformed singlet pair (Warren et al.)
- spin-gap : a general property of a disordered quantum spin system.

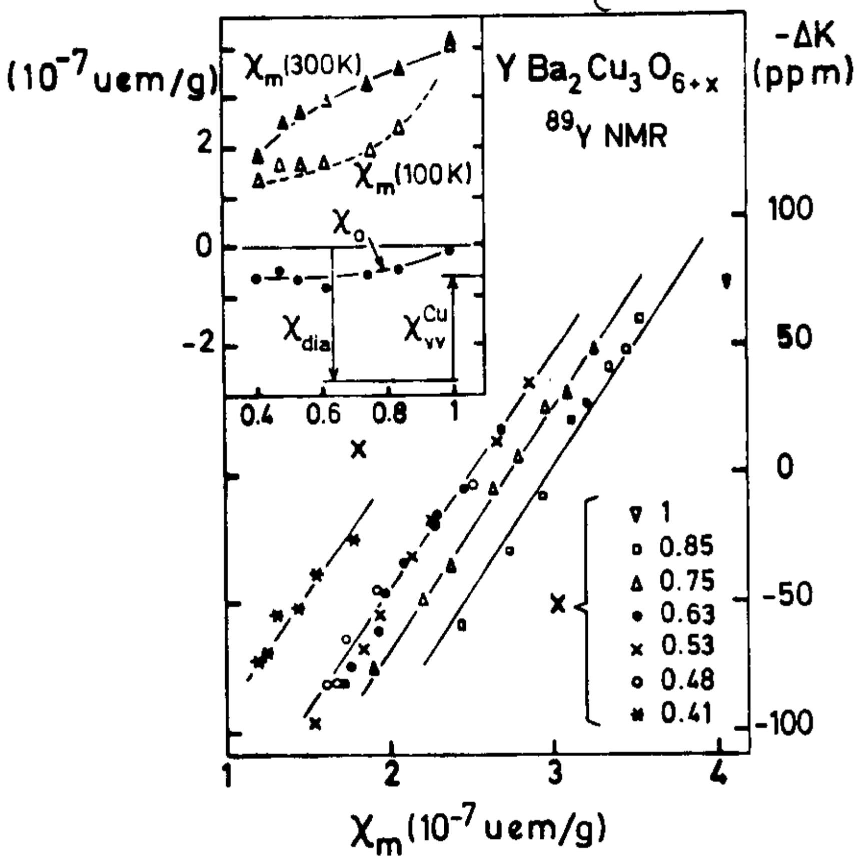
  $\chi_s \to 0$ as $T \to 0$

similar behavior

- $(La\,Sr)_2 Cu O_4$ (Kitaoka et al) ($K(0)$)
- $La_2 Cu O_{4+\delta}$ (Hammel et al) $K(Cu)$
- $(TPr) Ba_2 Cu_3 O_7$ (Reyes et al) $K(Cu)$



Alloul et al.
(ref. 16)

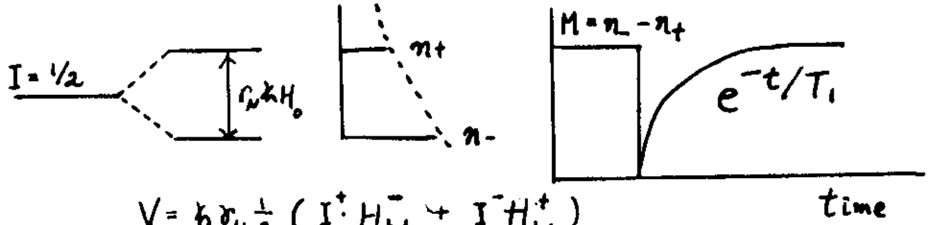


$\frac{\chi_p}{\chi_d}$: constant from $O_{6.4}$ to $O_{7.0}$

[2] spin dynamics

nuclear spin relaxation : caused by fluctuations of $\vec{H}_h$

transition between Zeeman levels



$$V = \hbar \gamma_N \frac{1}{2} (I^+ H_{hf}^- + I^- H_{hf}^+)$$

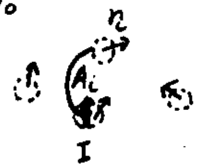
$$1/T_1 \propto | H_{hf}^+ (\omega_0) |^2 \qquad (\vec{H}_{hf} = A \vec{S}_i)$$

$$\propto A^2 \int_{-\infty}^{\infty} \langle S_i^+(t) S_i^-(0) \rangle e^{i\omega_0 t}$$

generally.

$$\frac{1}{T_1} = \frac{\gamma_N^2 k_B T}{2\mu_B^2} \sum_q |A_q|^2 \frac{\mathrm{Im}\,\chi(q,\omega_0)}{\omega_0}$$

$$\underset{\sim}{A_q} = \sum_i A_i e^{i \vec{q} \vec{r}_i}$$



q-dependent hyperfine coupling (form factor)

$$\vec{H}_{hf} = \sum_i A_i \vec{S}_i = \sum_q A_q \vec{S}_q$$

$$\langle H_{hf}^+(t) H_{hf}^-(0) \rangle = \sum_q |A_q|^2 \langle S_q^+(t) S_{-q}^-(t) \rangle$$

- Lorentzian spin fluctuation spectrum

$$\frac{\mathrm{Im}\,\chi(q,\omega)}{\omega} = \pi \frac{\chi_q \Gamma_q}{\omega^2+\Gamma_q^2} \xrightarrow[\omega\to 0]{} \pi\frac{\chi_q}{\Gamma_q}$$

- Fermi liquid without strong magnetic correlation.

$$\chi_q/\mu_B^2 \sim 1/\hbar\Gamma_q \sim \rho(\varepsilon_F)$$

$$\sum_q \mathrm{Im}\,\chi(q,\omega_0)/\omega_0 \sim \pi\hbar\mu_B^2\rho(\varepsilon_F)^2 = \pi\hbar\,\chi_s^2/\mu_B^2$$

↑ uniform (q=0) spin susceptibili

for non-interacting electron:

$$\sum_q \mathrm{Im}\,\chi(q,\omega_0)/\omega_0 = \pi\hbar\,\chi_s^2/(2\mu_B^2) \quad \text{(exact)}$$

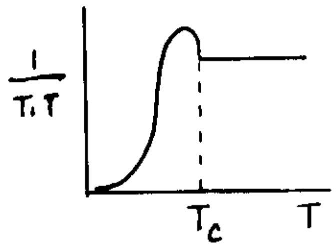
- If A_q is local (i.e. q-independent) and isotropic,

$$\frac{1}{T_1\cdot T\cdot K^2} = \frac{\pi\hbar\gamma_N^2 k_B}{\mu_B^2} \equiv S \quad \text{(Korringa relation)}$$

universal constant.

- superconducting state

BCS (Hebel-Slichter) peak



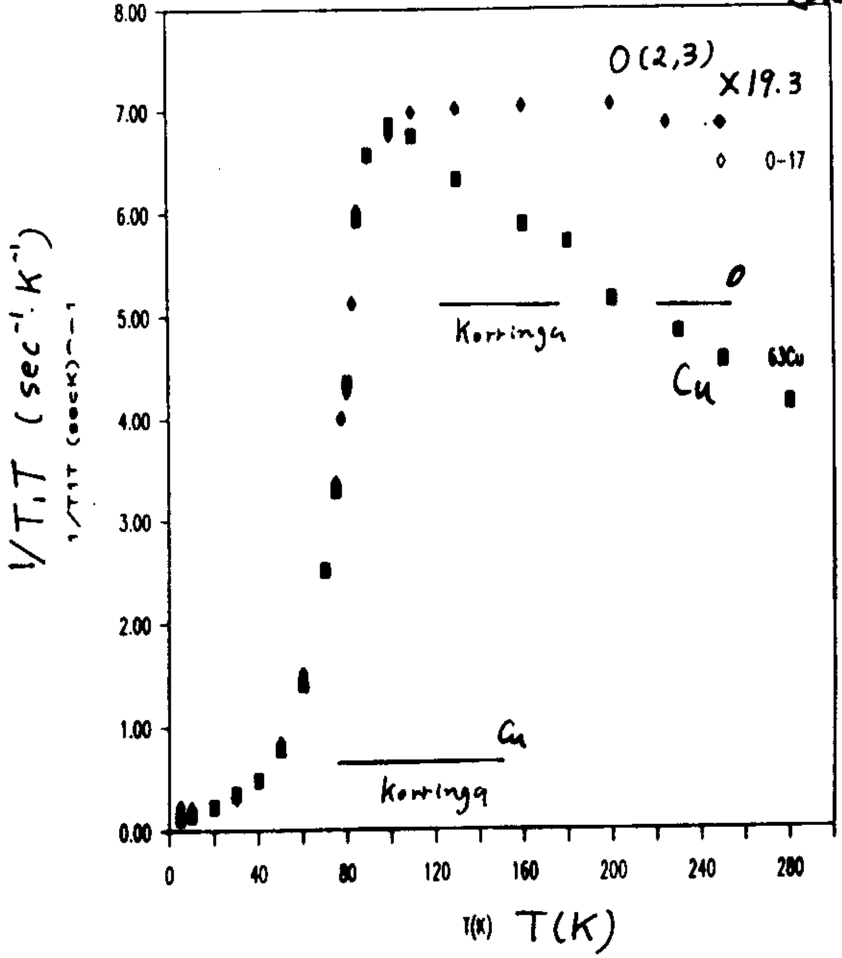
YBCO 7-y (ref.35) Cu 1/(T1T)

$y \simeq 0.05$ ($T_c = 92\,K$)

63Cu & 170 1/T1T vs Temperature

YBCO-6.94

Warren et al.
Kitaoka et al.
Imai et al
Barret et al.



89073614 2 AMD

(ref.35)

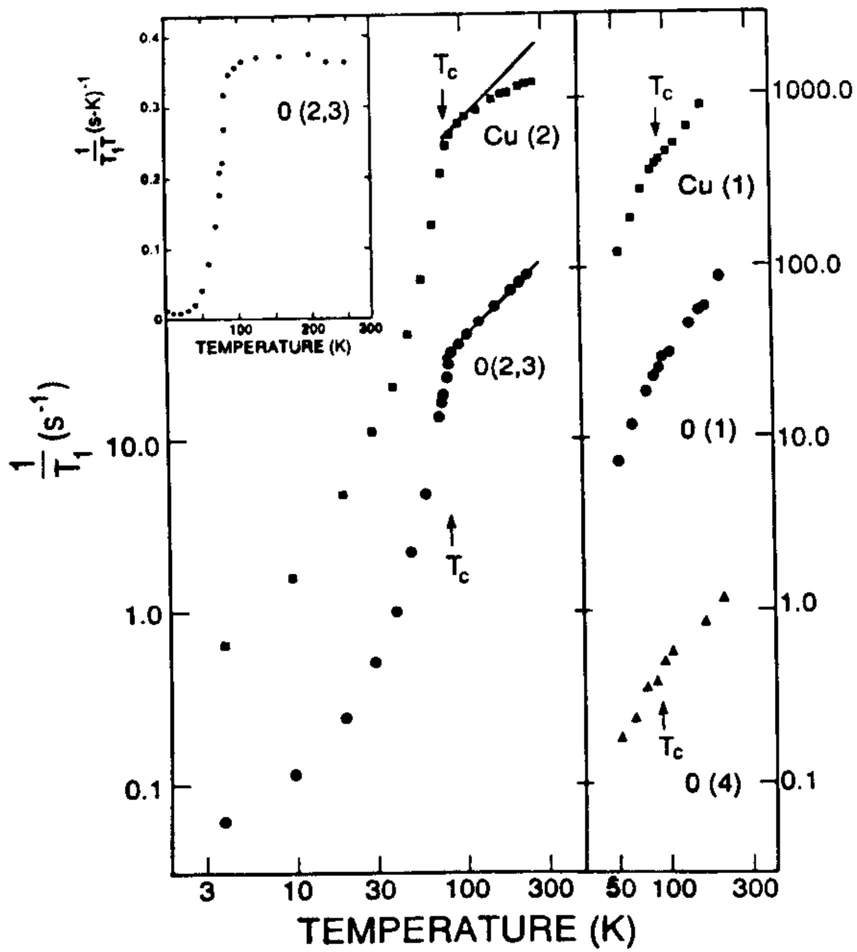


FIG. 2

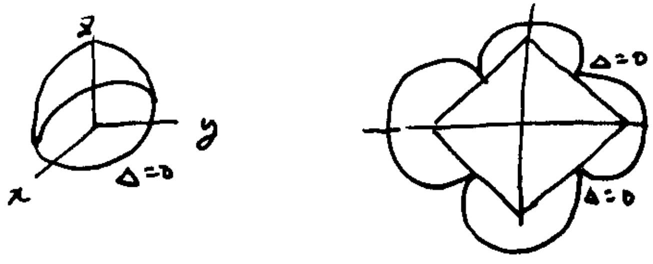
Absence of Hebel-Slichter peak (coherence)

possibilities

1) anisotropic superconducting gap

3-dim $\Delta = \Delta(\vec{k}) = \Delta_0 \cos\theta$

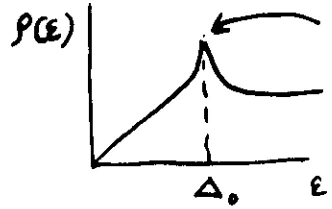
2-dim $\Delta(\vec{k}) = \Delta_0 (\cos ak_x - \cos ak_y)$



polar state.

d-wave pairing

quasi-particle density of state



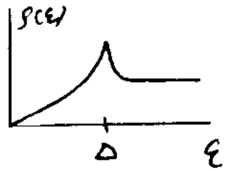
singularity is removed.

Absence of Hebel - Slichter peak

1) anisotropic (d-wave) pairing

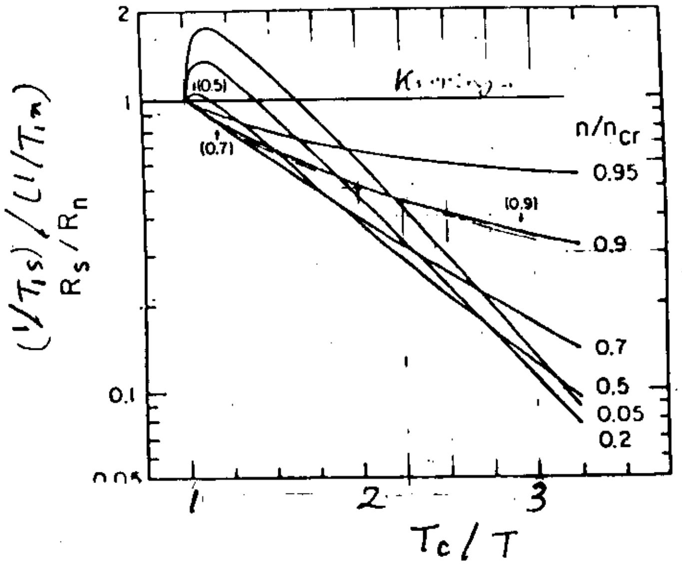
$\Updownarrow$ x

(penetration depth, photoemission etc.)



$1/T_1 \propto T^3$

2) pair breaking (magnetic impurity Griffin and Ambegaokar '64)



$\mathcal{H} = -J \vec{\sigma}\cdot\vec{s}$

$\Uparrow$

impurity spin

break time reversal symmetry

T-dependent pair breaking (by spin fluctuations)

(inelastic magnetic scattering, spin fluctuations)

significant pair breaking effect only near Tc.

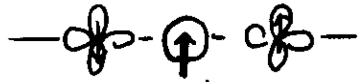
(L. Coffey, Kuroda and Varma)

Enhancement of the Korringa product.

$$\frac{1}{T_1 T k^2 S} \sim \quad \overset{Cu}{11 \quad (15)} \quad \Big\} \quad \overset{O}{1.4 \quad (2.5)}$$

(Millis, Monien, Pines)

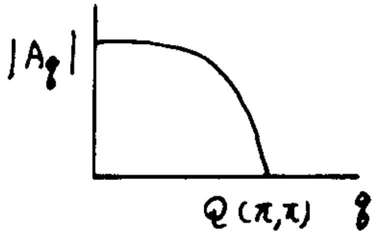
- large enhancement at Cu $\Rightarrow$ $\chi(q)$ has a peak at $q_0 \neq 0$
- oxygen relaxation



dominant source: O_{2s}–Cu_{3d} mixing

$$\vec{H}_{hf} = A\,(\vec{S}_i + \vec{S}_{i+1})$$

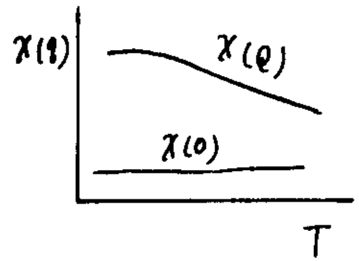
$$= \sum_q \underbrace{A\,(1+e^{iq_x a})}_{= A_q \text{ (form factor)}} \cdot \vec{S}_q$$



small enhancement at O

$\Downarrow$

<u>$\chi(q)$ must have a peak at $Q = (\pi,\pi)$</u>



- Identical T-dependence of $\frac{1}{T_1T}$ at Cu and O <u>below Tc</u>.

$\Downarrow$

$\left[\begin{array}{l} \chi_Q \text{ becomes T-independent below Tc} \\ \text{AF correlations persist below Tc} \end{array}\right.$

Random Phase Approximation (RPA)
(Dynamical Hartree-Fock method)

external field $\quad H(\vec{r},t) = H_q e^{i(\vec{q}\cdot\vec{r}-\omega t)}$

response $\chi(q,\omega)$

internal (exchange) field. $\quad J_q s_q e^{i(\vec{q}\cdot\vec{r}-\omega t)}$

response of non-interacting system. $\chi_0(q,\omega)$

magnetization
$$S(\vec{r},t) = S_q e^{i(\vec{q}\cdot\vec{r}-\omega t)}$$

$$\left[\begin{array}{l} S_q = \chi_0(q,\omega)\,(H_q + J_q S_q) \\ \chi(q,\omega) = S_q/H_q \end{array}\right. \Rightarrow \frac{1}{\chi_0(q,\omega)} = \frac{1}{\chi(q,\omega)} + J_q$$

$$\chi(q,\omega) = \frac{\chi_0(q,\omega)}{1 - J_q\chi_0(q,\omega)}$$

Hubbard model

$$\mathcal{H} = \sum_k \varepsilon_k a^\dagger_{k\sigma} a_{k\sigma} + \underbrace{\sum_i U n_{i\uparrow} n_{i\downarrow}}_{\displaystyle = \frac{1}{2}NU - \frac{1}{2}\frac{U}{N}\sum(S^+_q S^-_{-q} + S^-_{-q} S^+_q)}$$

$$S^+_q = \sum_k a^\dagger_{k\uparrow} a_{k+q\downarrow}$$

Effect of magnetic correlations. (Ref. 14)

RPA (Moriya '63) $\quad \chi(q,\omega) = \dfrac{\chi_0(q,\omega)}{1 - J\chi_0(q,\omega)}$

$$\frac{1}{T_1 T} \propto \sum_q \frac{\mathrm{Im}\,\chi(q,\omega_0)}{\omega_0} = \sum \frac{\mathrm{Im}\,\chi(q,\omega_0)/\omega_0}{(1 - J\chi_0(q))^2} = \sum_q \left(\frac{\chi(q)}{\chi_0(q)}\right)^2 \frac{\mathrm{Im}\,\chi_q(}{\omega_0}$$

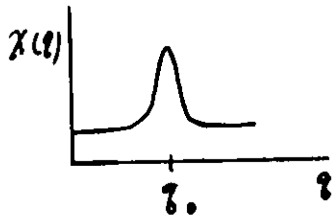
$$K \propto \chi_s = \left(\frac{\chi_s}{\chi_0(0)}\right)\chi_0(0)$$

$$\Rightarrow \frac{1}{T_1 T K^2 S} = \frac{\langle (\chi(q)/\chi_0(q))^2 \rangle}{(\chi_s/\chi_0(0))^2}$$

nearly ferromagnetic

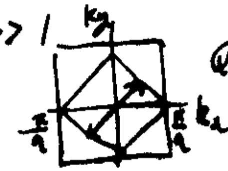
$$\frac{1}{T_1 T K^2 S} \ll 1$$

nearly antiferromagnetic



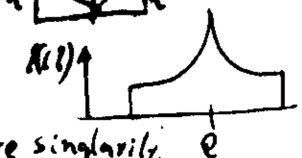
$$\frac{1}{T_1 T K^2 S} \gg 1$$

2-dim Hubbard model (square latt



$Q = (\frac{\pi}{a}, \frac{\pi}{a})$

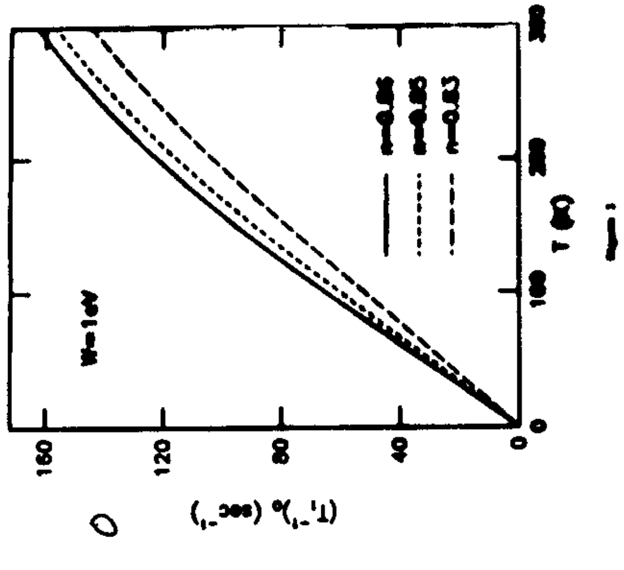
half filled

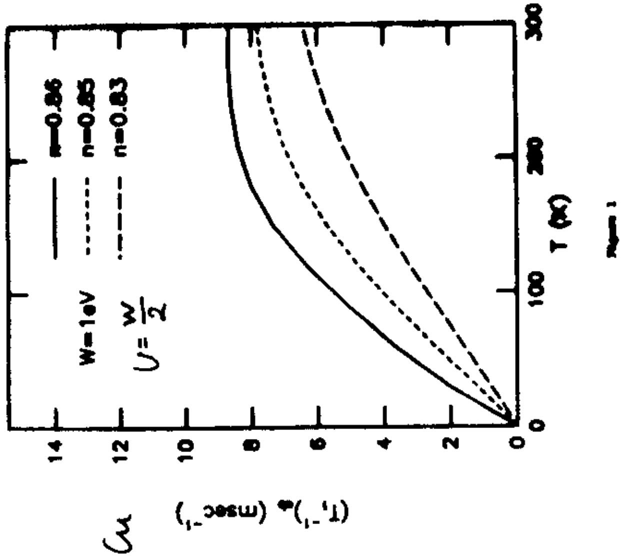


Van Hove singularity.

Bulut, Hone, Scalapino, Bickers (ref. 25)

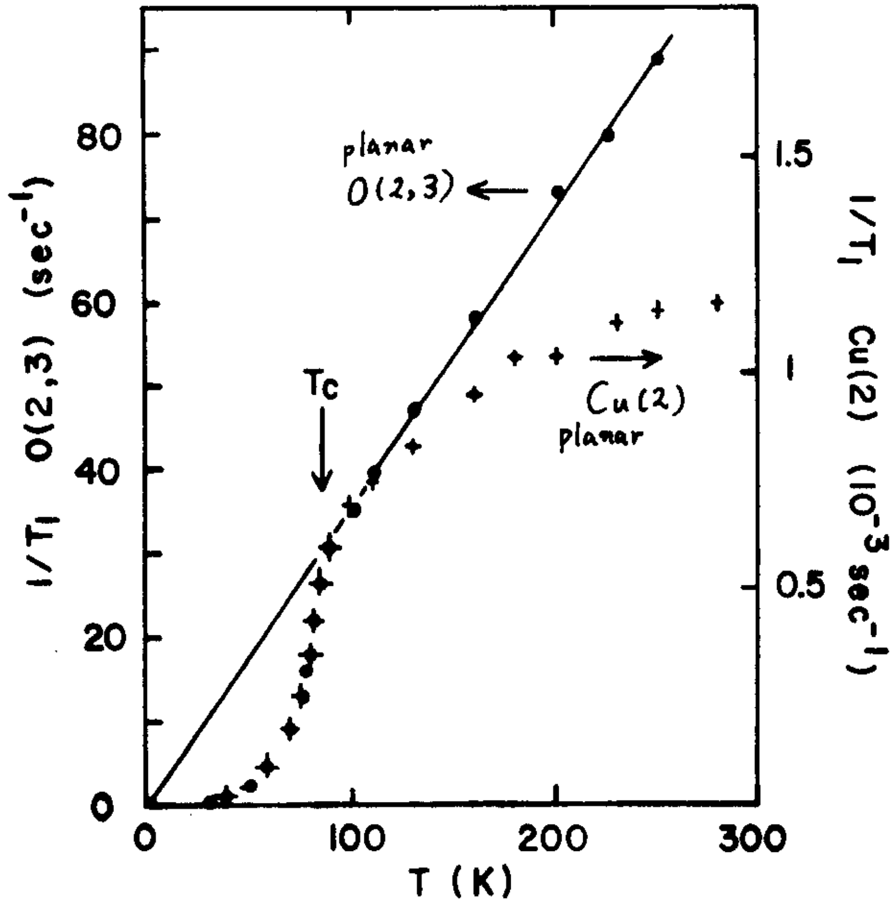
RPA single band 2D Hubbard model (tight binding)





18

Cu(2) data : same as NQR $1/T_1$ (ref. 27) by { Warren et. al, Kitaoka et. al, Imai et. al }



Y : similar to O

(Markert et al.)
(Alloul et al.)

M. Takigawa

Phenomenology (Millis, Monien and Pines)(ref. 24)

RPA expression $\chi(q,\omega) = \dfrac{\chi_0(q,\omega)}{1-J\chi_0(q,\omega)}$

$$\chi''_{AF}(q,\omega) = \frac{\chi''(q,\omega)}{\{1-J\chi_0'(q,\omega)\}^2 + \{J\chi_0''(q,\omega)\}^2} \qquad \chi_0''(q,\omega) = \pi\frac{\omega}{\Gamma}\chi_0$$

$$J\chi_0'(q,\omega=0) = F_q$$

Strong AF correlation $\Longrightarrow 1-F_Q \ll 1 \qquad Q=(\pi/a,\pi/a)$

expansion around Q

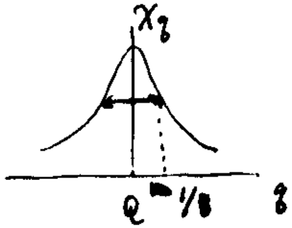
$$F_q = F_Q - q^2\xi_0^2$$

static susceptibility

$$\chi'(q,\omega=0) = \chi_q = \frac{\chi_0(q)}{1-F_q} \simeq \frac{\chi_0(Q)}{1-F_q} = \frac{\chi_0(Q)}{1-F_Q}\,\frac{1-F_Q}{1-F_q}$$

$$= \chi_Q\frac{1-F_Q}{1-F_Q+q^2\xi_0^2} = \chi_Q\frac{1}{1+q^2\xi_0^2/(1-F_Q)}$$

definition of AF correlation length



$$\chi_q = \frac{\chi_Q}{1+q^2\xi^2} \Rightarrow 1-F_Q = (\xi_0/\xi)^2$$

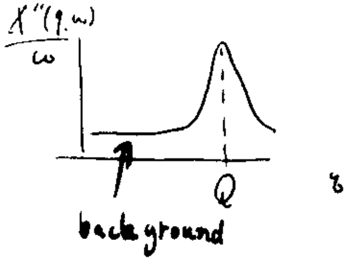
dynamical susceptibility.

$$\chi''_{AF}(q,\omega) = \frac{\pi\frac{\omega}{\Gamma}\chi_0}{(1-F_q)^2+\pi^2\omega^2J^2\chi_0^2/\Gamma} \qquad (J\chi_0)^2\sim 1$$

$$(1-F_q)^2 = 1-F_Q+F_Q-F_q$$
$$= (\xi_0/\xi)^2 + q^2\xi_0^2$$
$$= (\xi_0/\xi)^2(1+q^2\xi^2)$$

$$\chi''_{AF}(q,\omega) = \frac{\pi\omega\chi_0}{\Gamma}\,\frac{(\xi/\xi_0)^4}{(1+q^2\xi^2)^2+\frac{\pi^2\omega^2}{\Gamma^2}\left(\frac{\xi}{\xi_0}\right)^4}$$

$\omega\to 0$ $$\frac{\chi''_{AF}(q,\omega)}{\omega} = \frac{\pi\chi_0}{\Gamma}\,\frac{(\xi/\xi_0)^4}{(1+q^2\xi^2)^2}$$



$$\left.\frac{\chi''(q,\omega)}{\omega}\right|_{\omega\to0} = \frac{\chi_0\pi}{\Gamma}\left(1+\frac{(\xi/\xi_0)^4}{(1+q^2\xi^2)^2}\right)$$

difference for Cu and O ---- hyperfine coupling