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SMR 1232 - 16

XII WORKSHOP ON
STRONGLY CORRELATED ELECTRON SYSTEMS

17 - 28 July 2000

IMPURITIES IN HIGH Tc MATERIALS

AS STUDIED BY NMR

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

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IMPURITIES AS PROBES OF THE MAGNETIC PROPERTIES OF THE CUPRATES

- H.A , P. MENDELS , J. BOBROFF NMR
  A. MAC FARLANE , Y. YOSHINARI , A. MAHAJAN μSR

  PHYSIQUE DES SOLIDES (ORSAY)

- F. RULLIER-ALBENQUE TRANSPORT - IRRADIATIONS

  ECOLE POLYTECHNIQUE AND SPEC C.EA SACLAY

- G. COLLIN , N. BLANCHARD PHY.S SOL (ORSAY)
  (LLB SACLAY)
  JF. MARUCCO , V. VIALLET , D. COLSON
  LCNS ORSAY (SPEC)

  SAMPLES
  THERMOGRAVIMETRY
  X-RAYS

- M. HERITIER , M. GABAY , P. LEDERER , H. SCHULZ†, J. FRI[illegible]
  (ORSAY) A. GEORGES. THEORY

OUTLINE

(I) IMPURITIES AND DEFECTS

- CHOICE OF DEFECTS
- T_c DEPRESSION AND RESISTIVITY
- ORIGIN OF THE SCATTERING RATE ?

(II) THE NMR PROBE

- DILUTE TRANSITION METAL IMPURITIES IN NOBLE METAL HOSTS
- SATELLITES AND MAINLINE
  LOCAL AND LONG DISTANCE PROPERTIES

(III) LONG DISTANCE EFFECTS IN CUPRATES

- PSEUDOGAP AND PHASE DIAGRAM
- $\chi'(r)$: STAGGERED RESPONSE IN A CORRELATED HOST SYSTEM
  MAGNETIC CORRELATION LENGTH $\xi(T)$

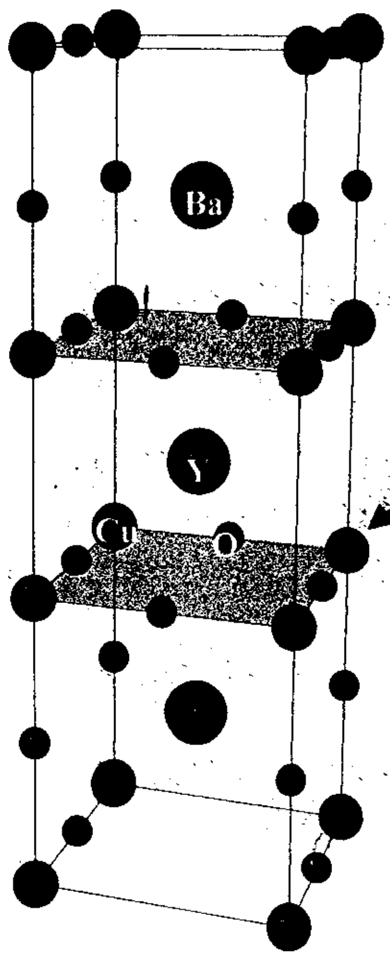
(IV) LOCAL MOMENTS : MAGNETIC (Ni) AND SPINLESS IMPURITIES (Zn, Li, ..)

- MACROSCOPIC SUSCEPTIBILITIES
- ^{89}Y NMR : SPATIAL STRUCTURE OF THE INDUCED MOMENT
  UNIVERSALITY OF SPINLESS DEFECTS → SPIN / CHARGE
- ^{7}Li NMR : EVIDENCE FOR KONDO EFFECT
- EVOLUTION OF THE LOCAL MOMENT BELOW T_c

(V) CONCLUSIONS

Which impurity ?

CuO_2

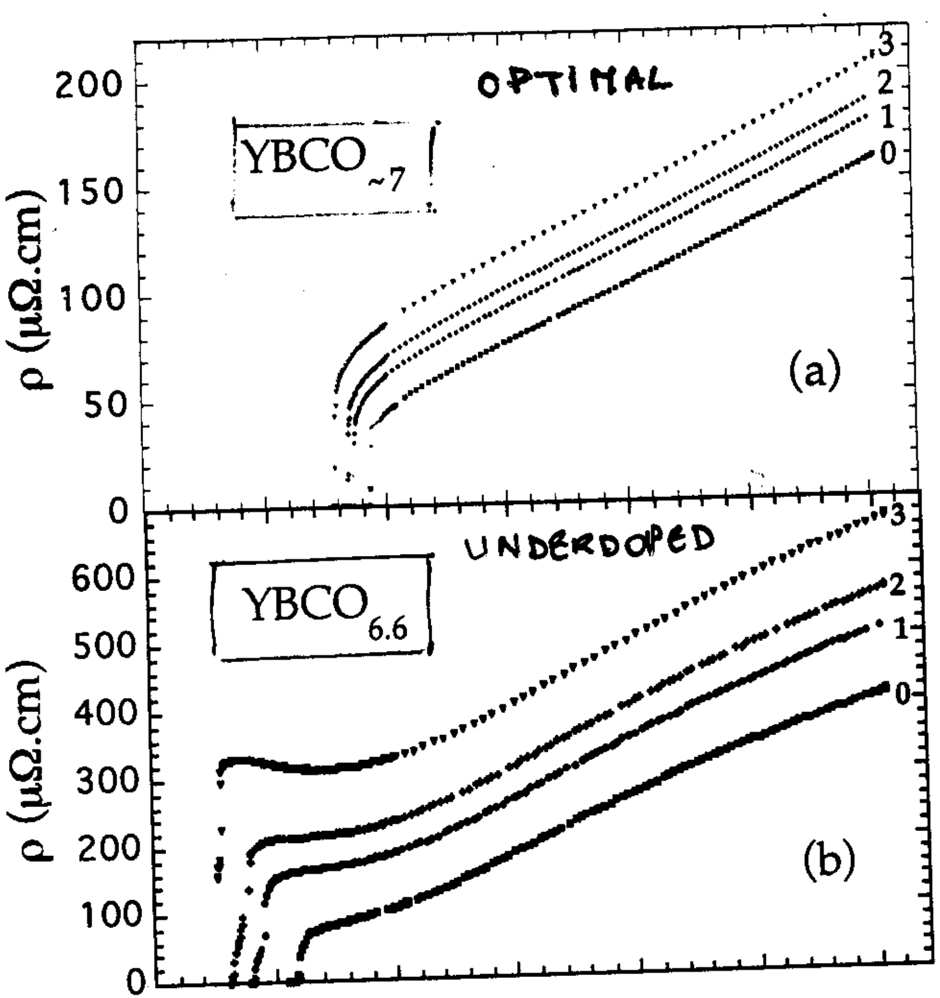


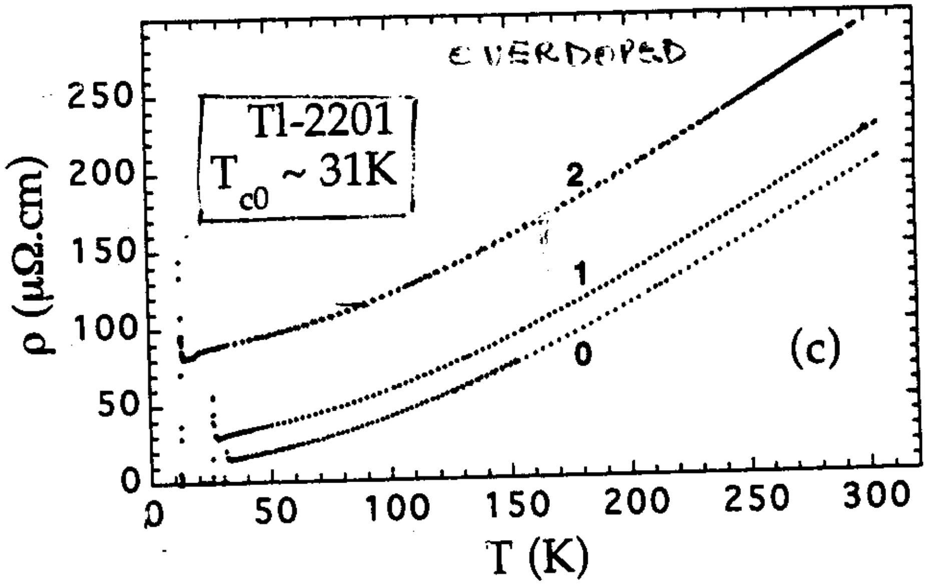
Dilute in-plane defects :

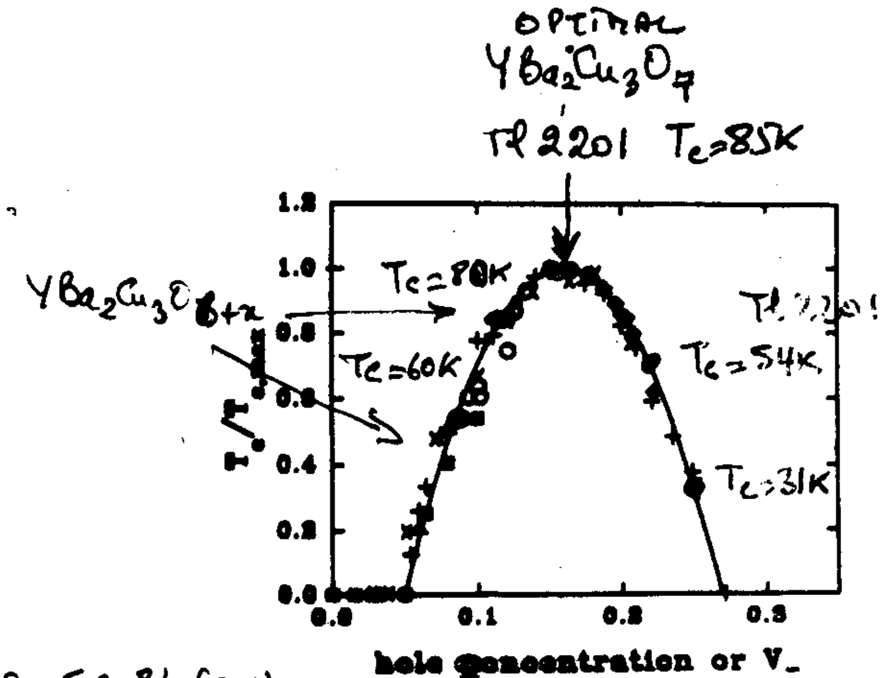
- Ni^{2+} spin 1
- Zn^{2+} no spin
- Li^{+} no spin
- e^{-} irradiation : vacancy

F. RULLIER-ALBENQUE
SPEC - SACLAY

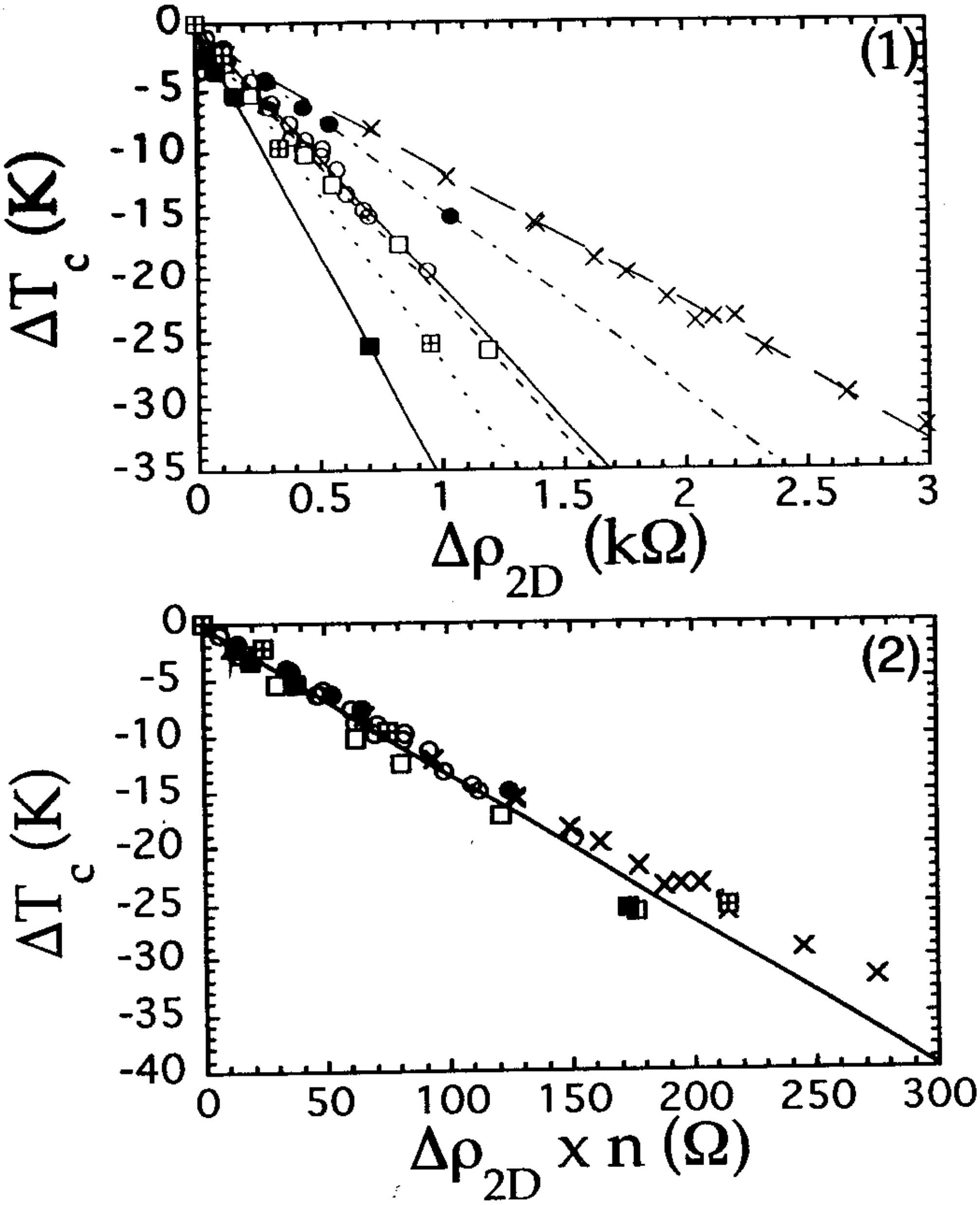
Probes the role of a spin/charge local perturbation







F. Rullier-Albenque et al - Europhysics letters 50, 81 (00)


(1)
0
-5
-10
-15
-20
-25
-30
-35
ΔT_c (K)
0
0.5
1
1.5
2
2.5
3
Δρ_2D (kΩ)
(2)
0
-5
-10
-15
-20
-25
-30
-35
-40
ΔT_c (K)
0
50
100
150
200
250
300
Δρ_2D x n (Ω)

d-WAVE SUPERCONDUCTOR

$$\boxed{\Delta T_c = -\frac{\pi}{4k_B}\frac{\hbar}{\tau}}$$

$$\Delta\rho_{2D} = \frac{m^*}{ne^2}\frac{1}{\tau}$$

$$\boxed{\Delta T_c = -\frac{\pi e^2\hbar}{4m^* k_B}\Delta\rho_{2D}\cdot n}$$

$n \Rightarrow$ number of carriers per CuO_2 plane

Here $n = n_h$ (not $1-n_h$)

UNIVERSAL BEHAVIOUR
UNDERDOPED TO OVERDOPED

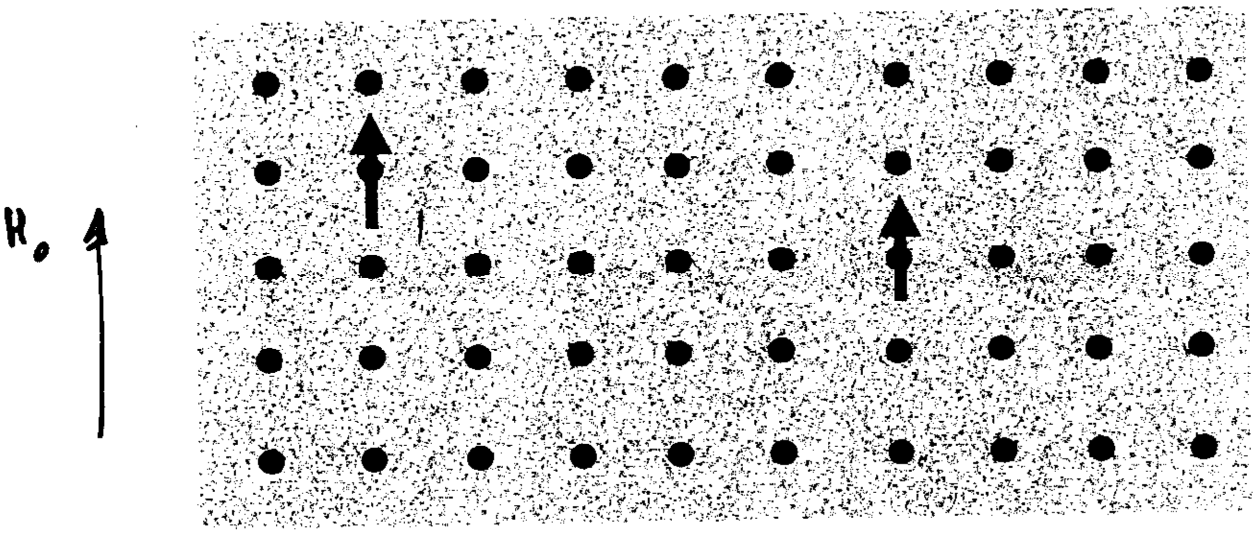
→ CUPRATES = DOPED INSULATOR

→ ORIGIN OF $1/\tau$?

UNITARITY ?

NMR in dilute alloys

Case of a metal with dilute magnetic impurities

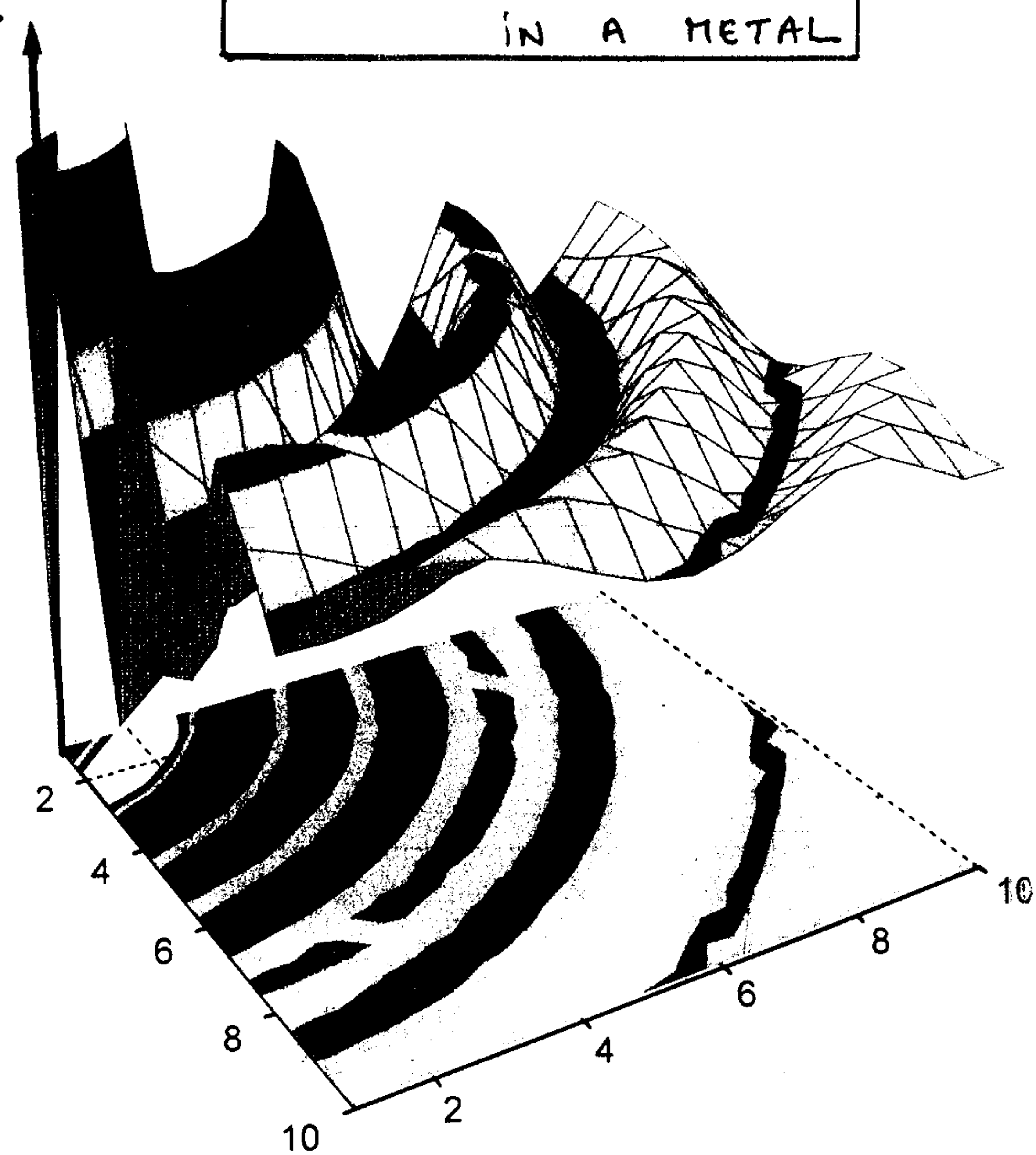


NMR of the impurity : $K = A_{hf}\,\chi_0(\text{impurity})$?

usually impossible !

MAGNETIC IMPURITY IN A METAL

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

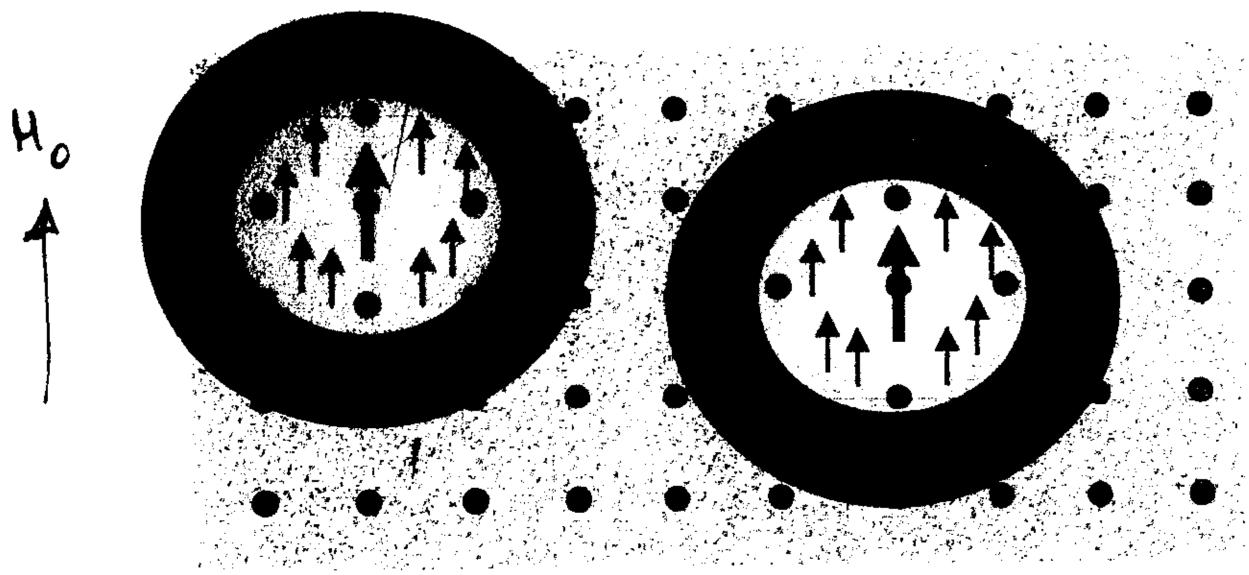


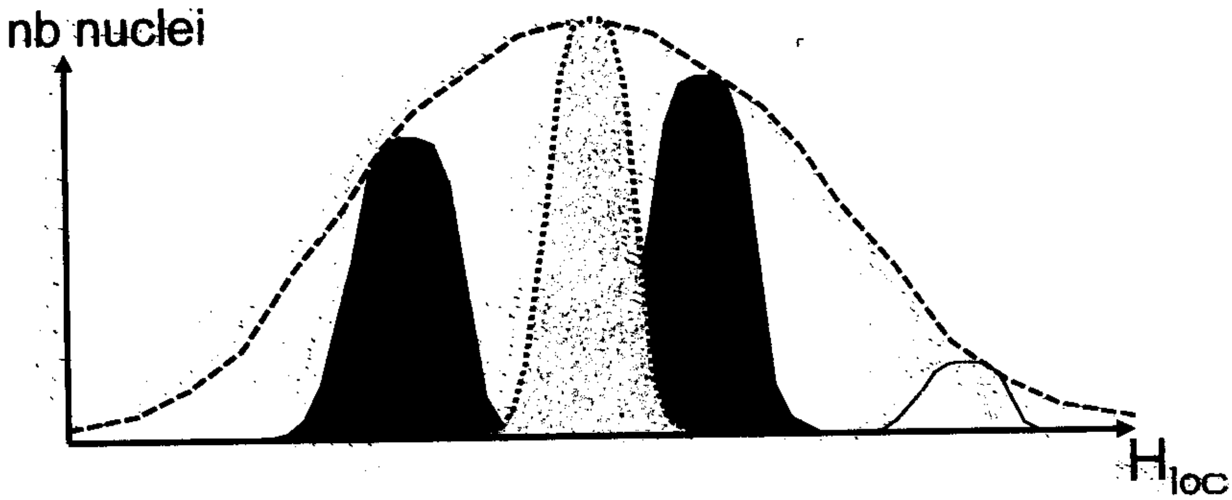
RKKY

$$\chi'(r) \propto J \frac{\cos 2k_F r}{r^2} \frac{\langle S_z \rangle}{H} n(E_F)$$

FOR NON INTERACTING ELECTRONS

$\Longrightarrow$ NMR lineshape and linewidth.





NMR of a host atom

$K_{av} = A_{hf}\, \chi_0$(far from impurity)

broadening $\Delta\nu \sim \langle S_Z \rangle$. distribution of $\chi'(r)$

FOR LARGE IMPURITY CONCENTRATION

Cu - Mn

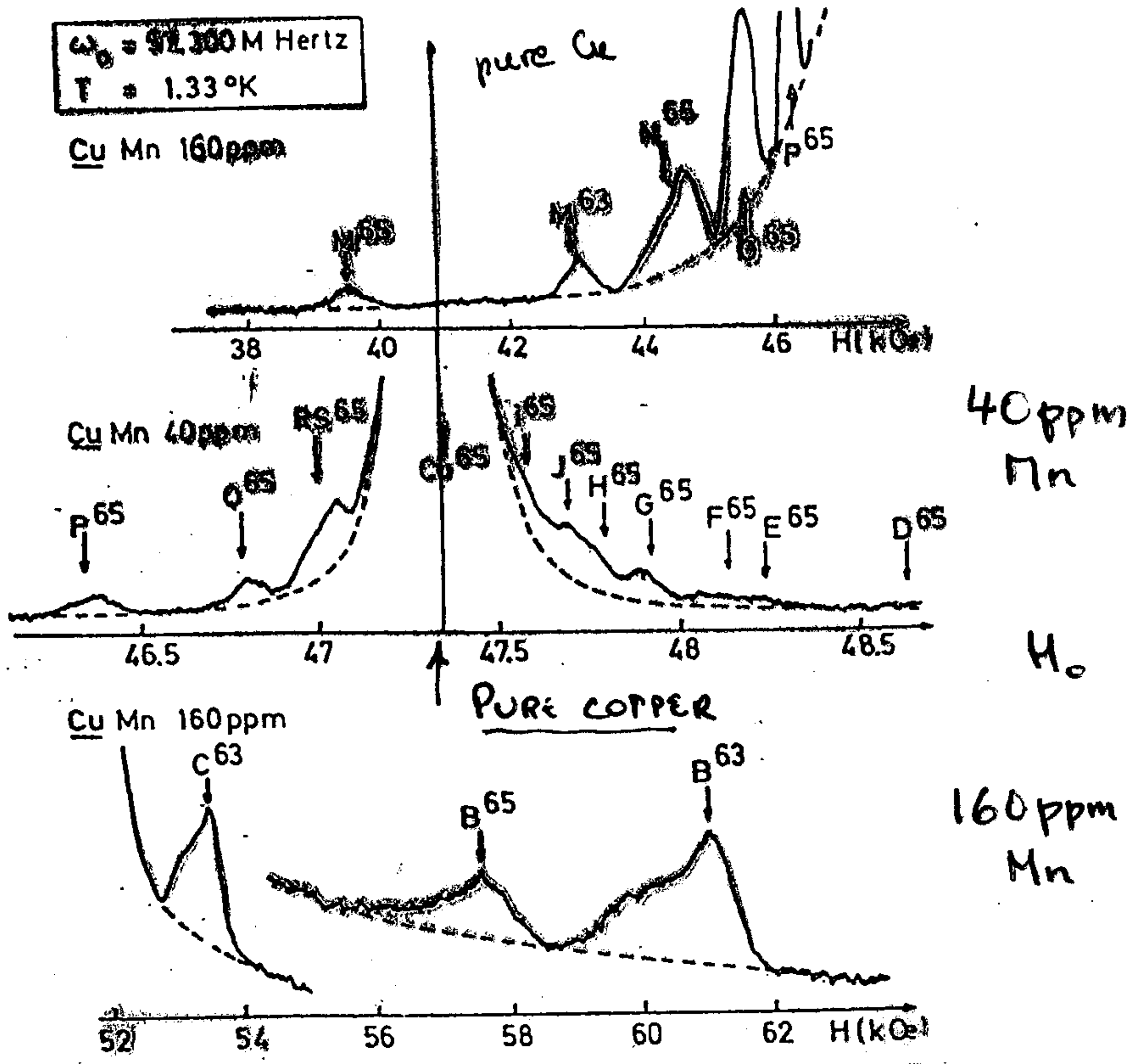
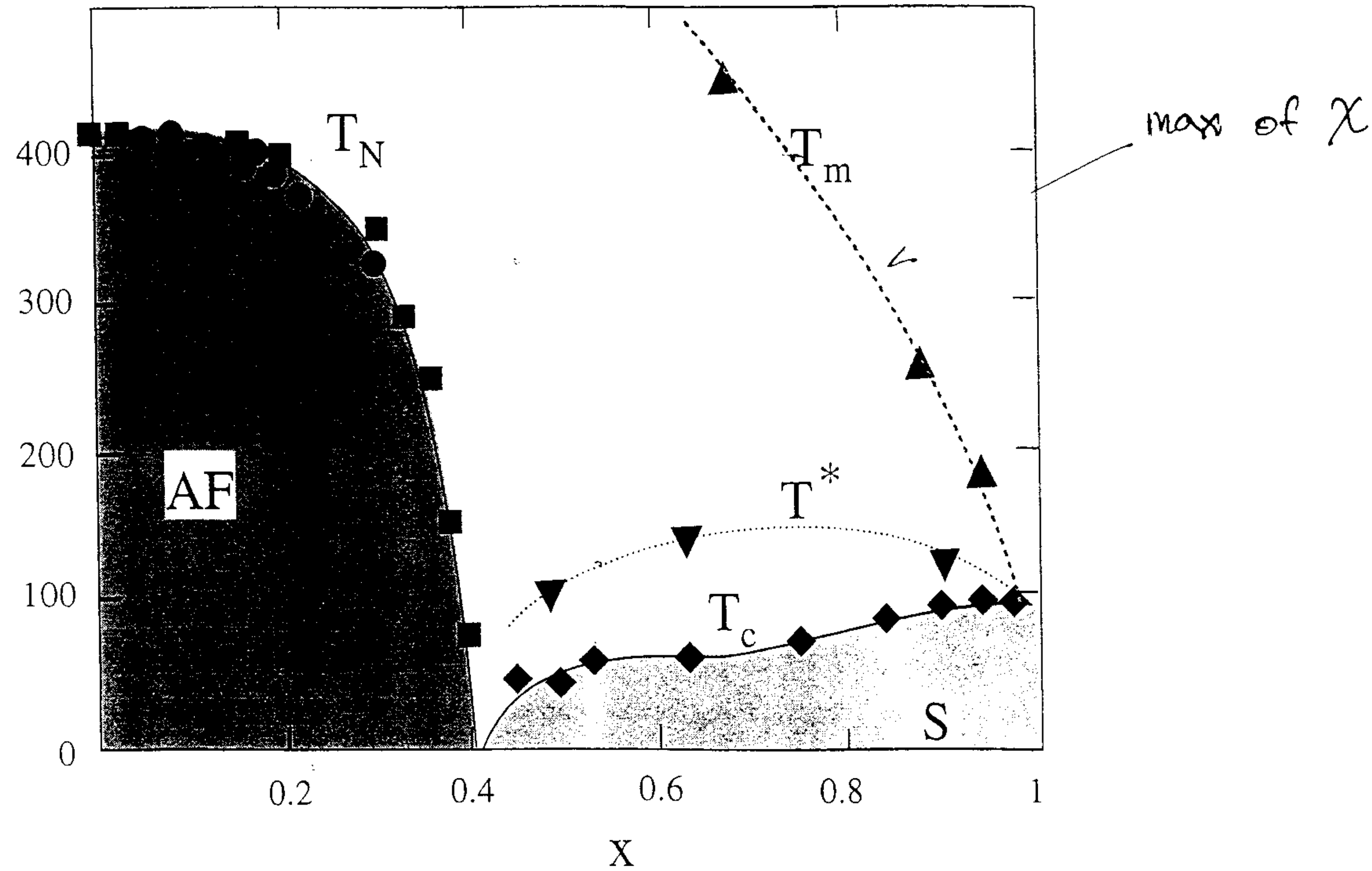


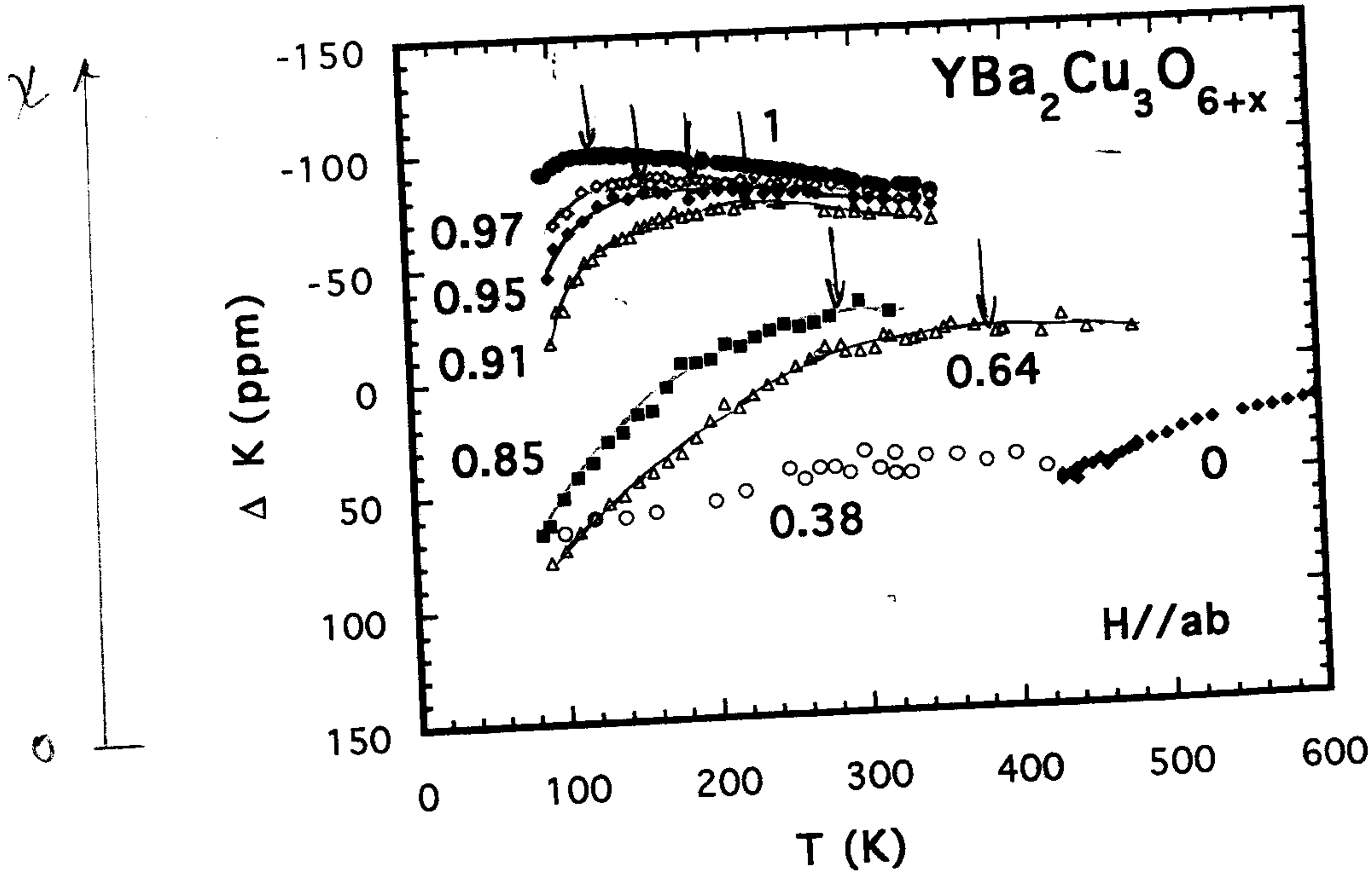
Figure 11 : Ensemble des résonances satellites observées dans Cu-Mn en fort champ et à basse température.

$YBa_2Cu_3O_{6+x}$



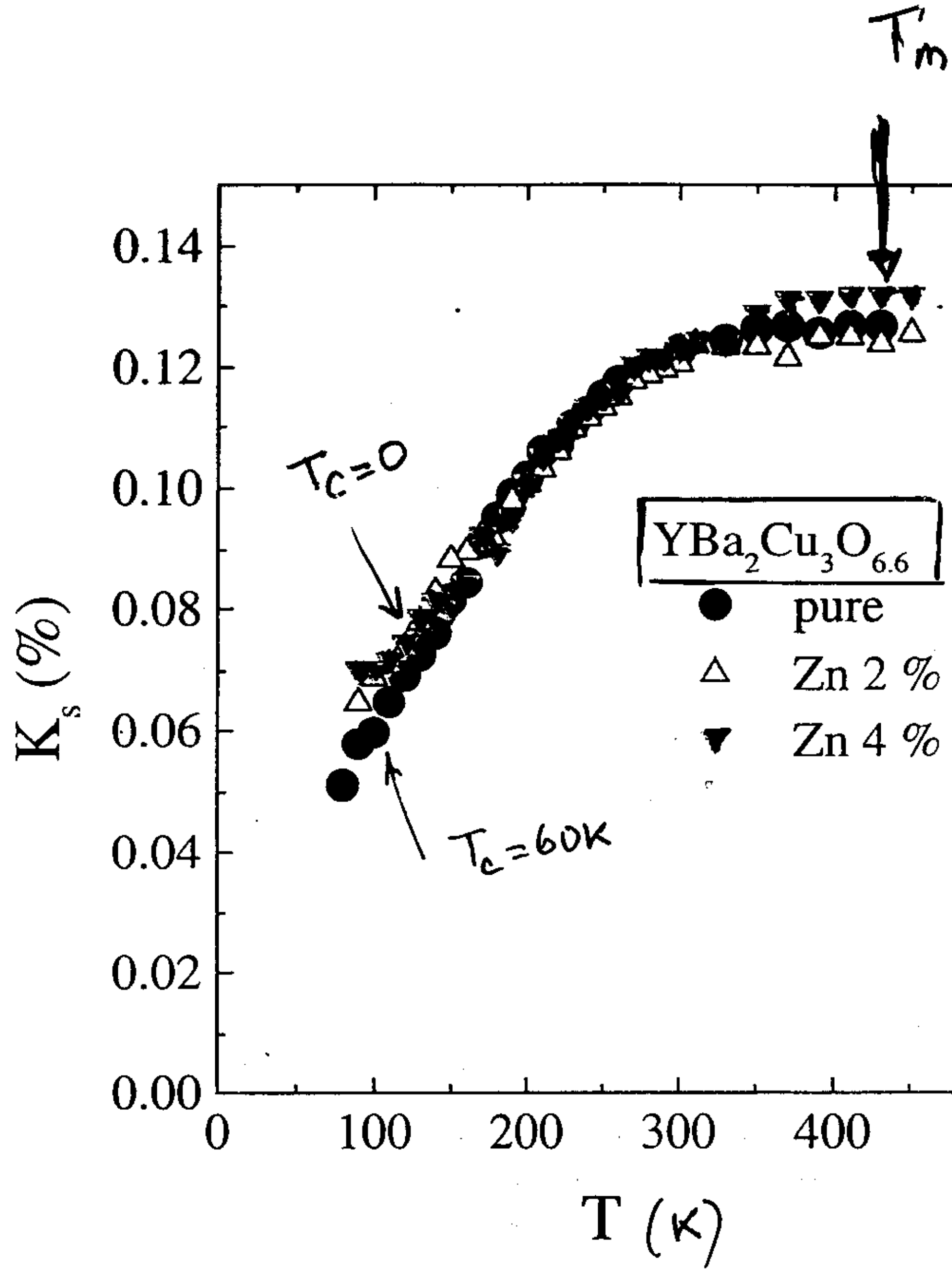
(11)

^{89}Y NMR



(2) Alloul Ohno Mendels PRL (1989)

^{17}O NMR

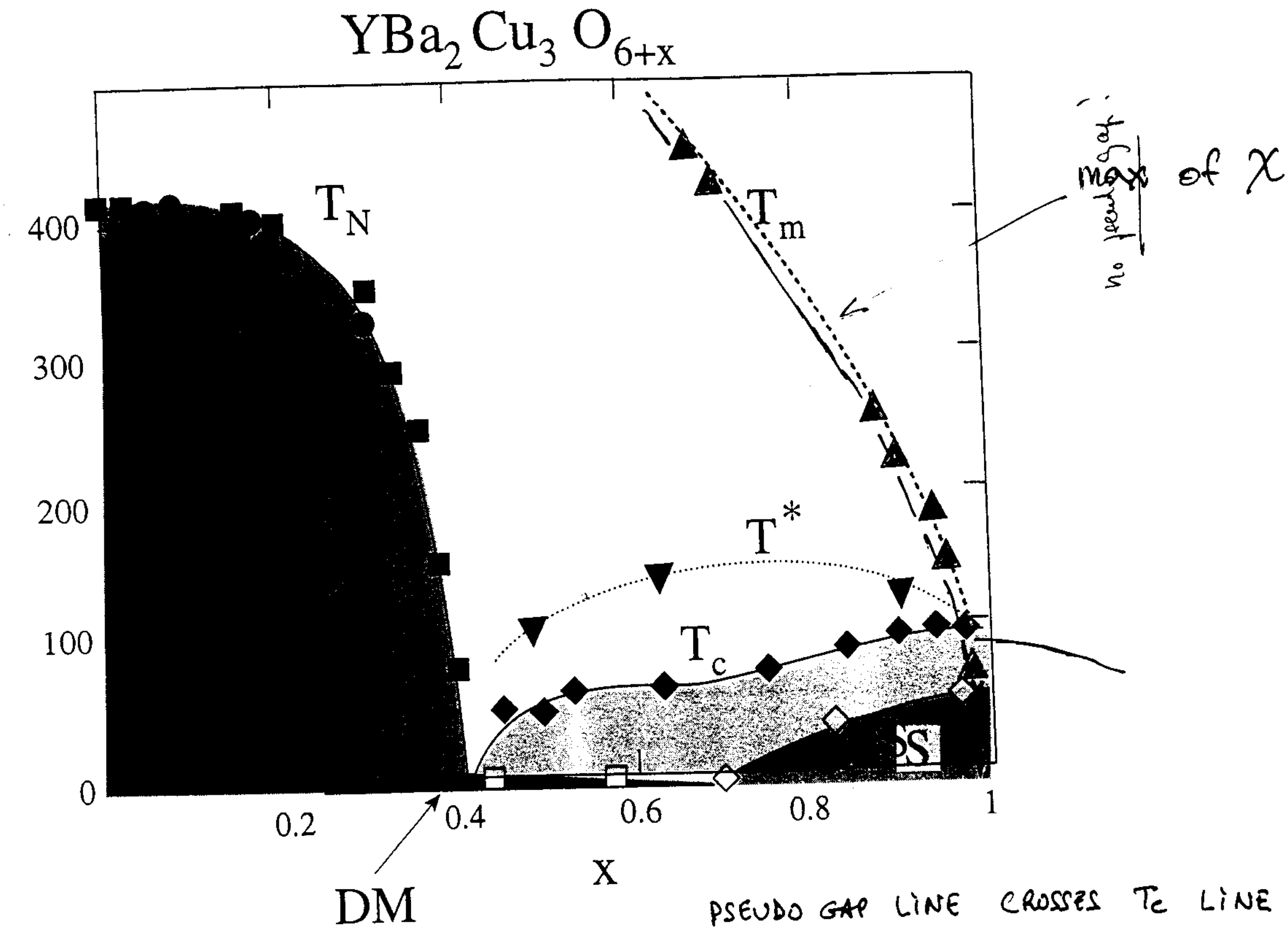


$K_s \longrightarrow \langle \chi(T) \rangle$

far from the impurities

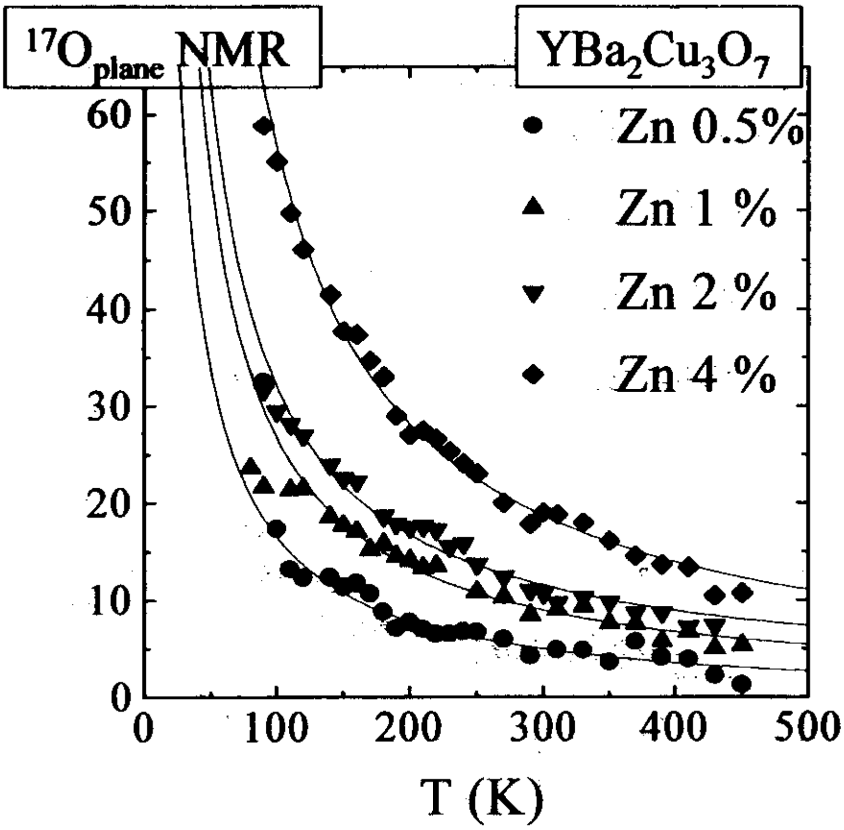
(13)

ALREADY ALLOUL et al. PRL 67, 3140 (1991) ^{89}Y NMR



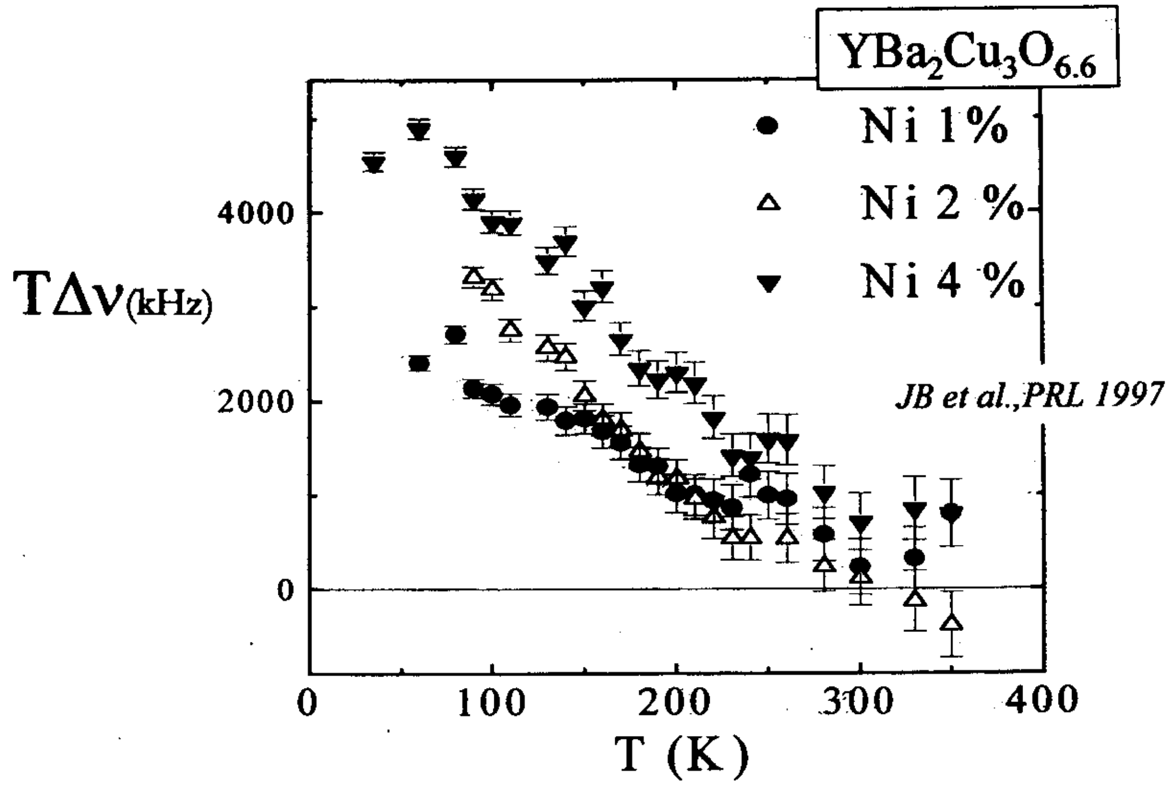
YBa2Cu3 O6+x
TN
Tm
T*
Tc
400
300
200
100
0
0.2
0.4
0.6
0.8
1
X
DM
max of χ
no pseudogap ;
PSEUDO GAP LINE CROSSES Tc LINE

RKKY-like polarization



broadening $\Delta\nu \sim \langle S_Z \rangle$. distribution of $\chi'(r)$

Long range effects above T_c

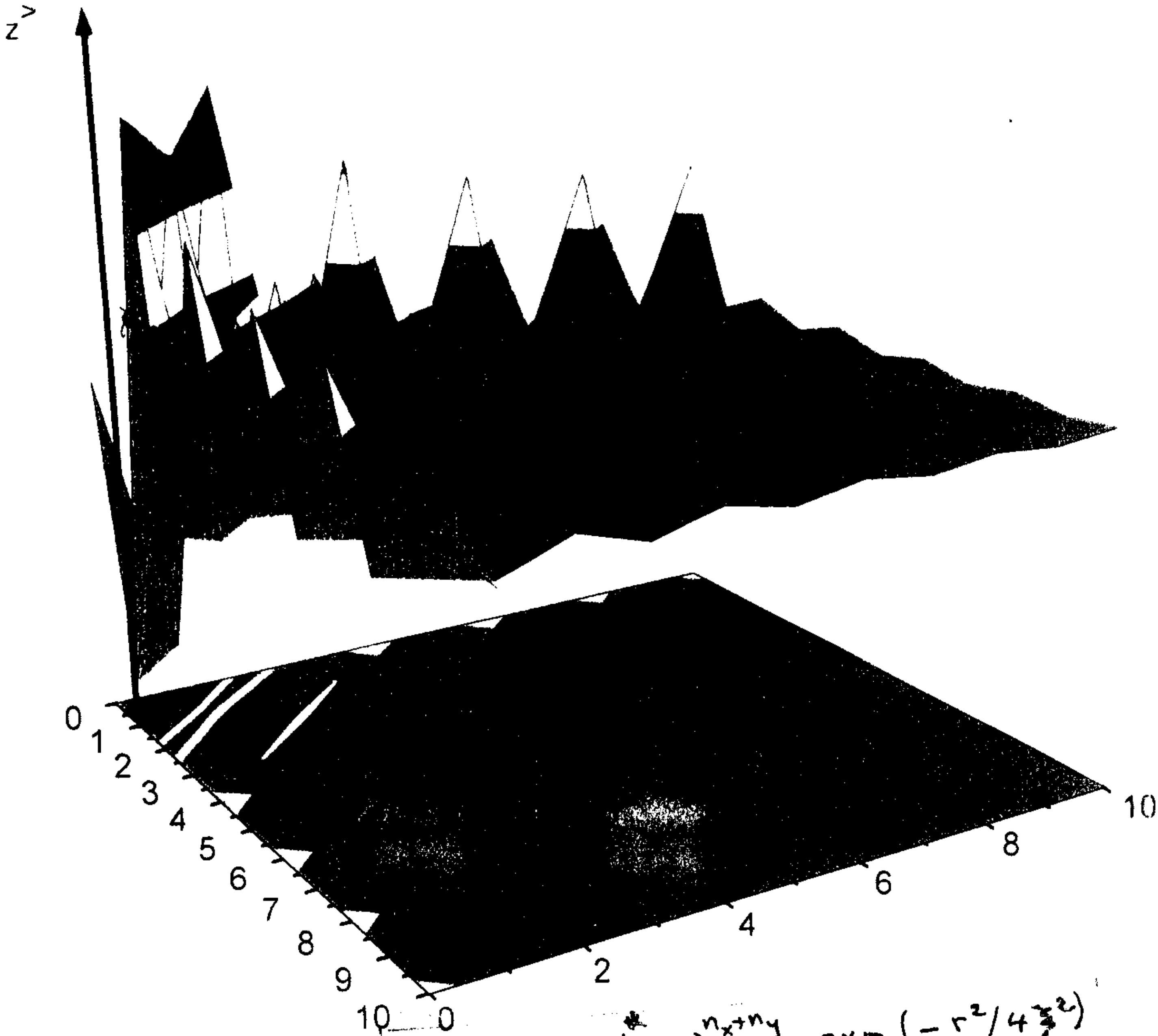


$\Delta\nu \sim \langle S_Z \rangle \cdot$ distribution of $\chi'(r)$

$\downarrow$ $1/T^2$ $\downarrow$ $1/T$ $\downarrow$ $1/T$ dependence

⟹ **Information on the T dependence of the AF correlations**

T_1 and T_2 (Slichter's group)



For example $\quad \chi'(r) = \chi^{*} (-1)^{n_x+n_y} \exp\left(-r^2/4\xi^2\right)$

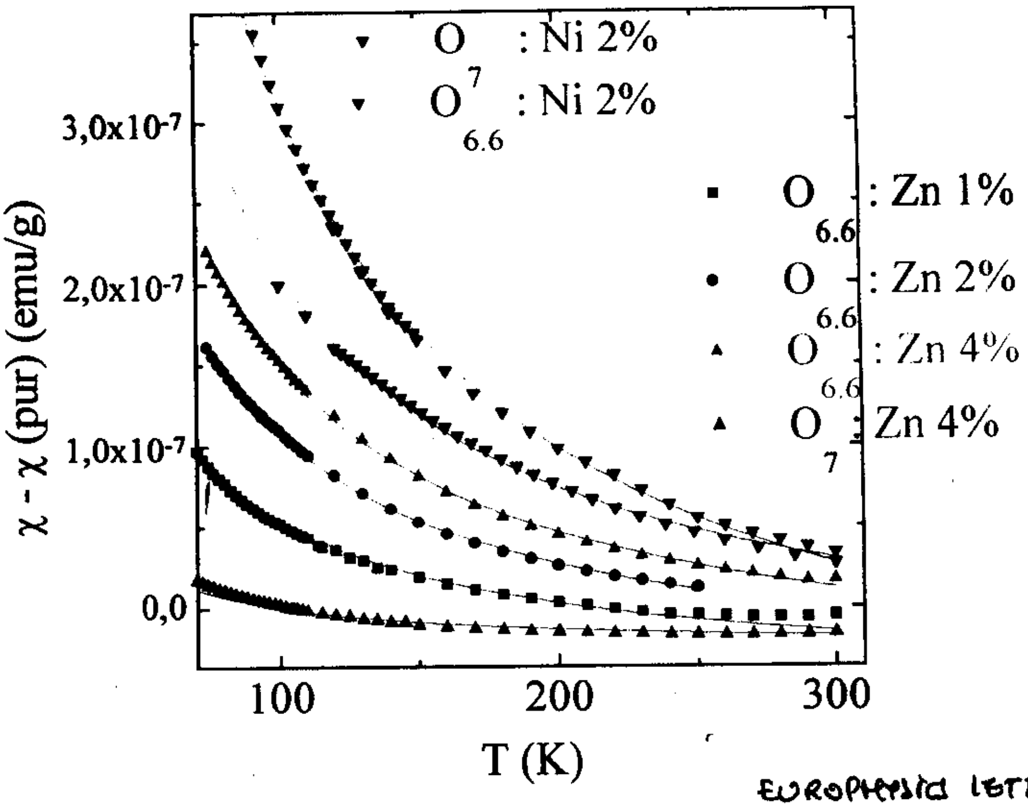
GAUSSIAN $\quad \chi'(q) = 4\pi\, \chi^{*} \left(\frac{\xi}{a}\right)^2 \exp\left[-\frac{(q-q_{AF})^2}{4\xi^2}\right]$

$T\Delta\nu \longrightarrow$ T dependence of $\chi'(r)$

$\to \quad \chi^{*}(T) \quad , \quad \xi(T)$

J. Bobroff et al PRL 79, 2117 (1997)

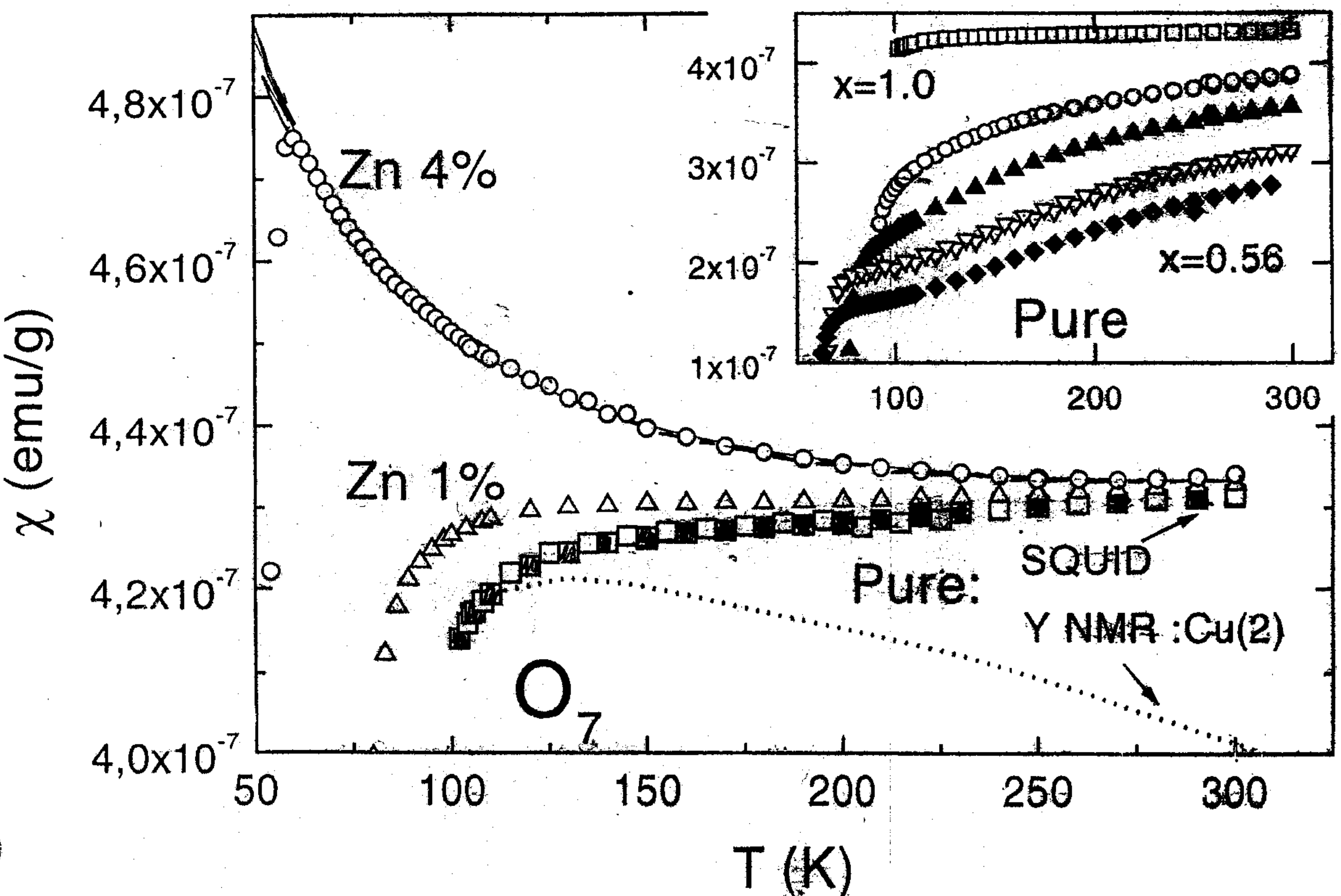
macroscopic susceptibility measurements



46, 678 (99
EUROPHYSICS LETTERS

P.Mendels *et al.*, Cond Mat 9904295

(18)



χ (emu/g)
4,8x10^-7
4,6x10^-7
4,4x10^-7
4,2x10^-7
4,0x10^-7
50
100
150
200
250
300
T (K)
Zn 4%
Zn 1%
O7
Pure:
SQUID
Y NMR :Cu(2)
4x10^-7
3x10^-7
2x10^-7
1x10^-7
x=1.0
x=0.56
Pure

MACROSCOPIC χ DATA

$$\chi_{imp} = \frac{p_{eff}^2}{3 k_B T} \qquad p_{eff}^2 = g^2 \mu_B^2 S(S+1)$$

values of p_{eff} (μ_B)

	$O_{6.6}$	O_7
Ni $3d^8$	1.6(1)	1.2(1)
Zn $3d^{10}$	1.0(1)	0.40(5)

$S = 1$
$p_{eff} = 2.82$

$S = 1/2$
$p_{eff} = 1.73$

Ni $\approx$ $S = 1/2$

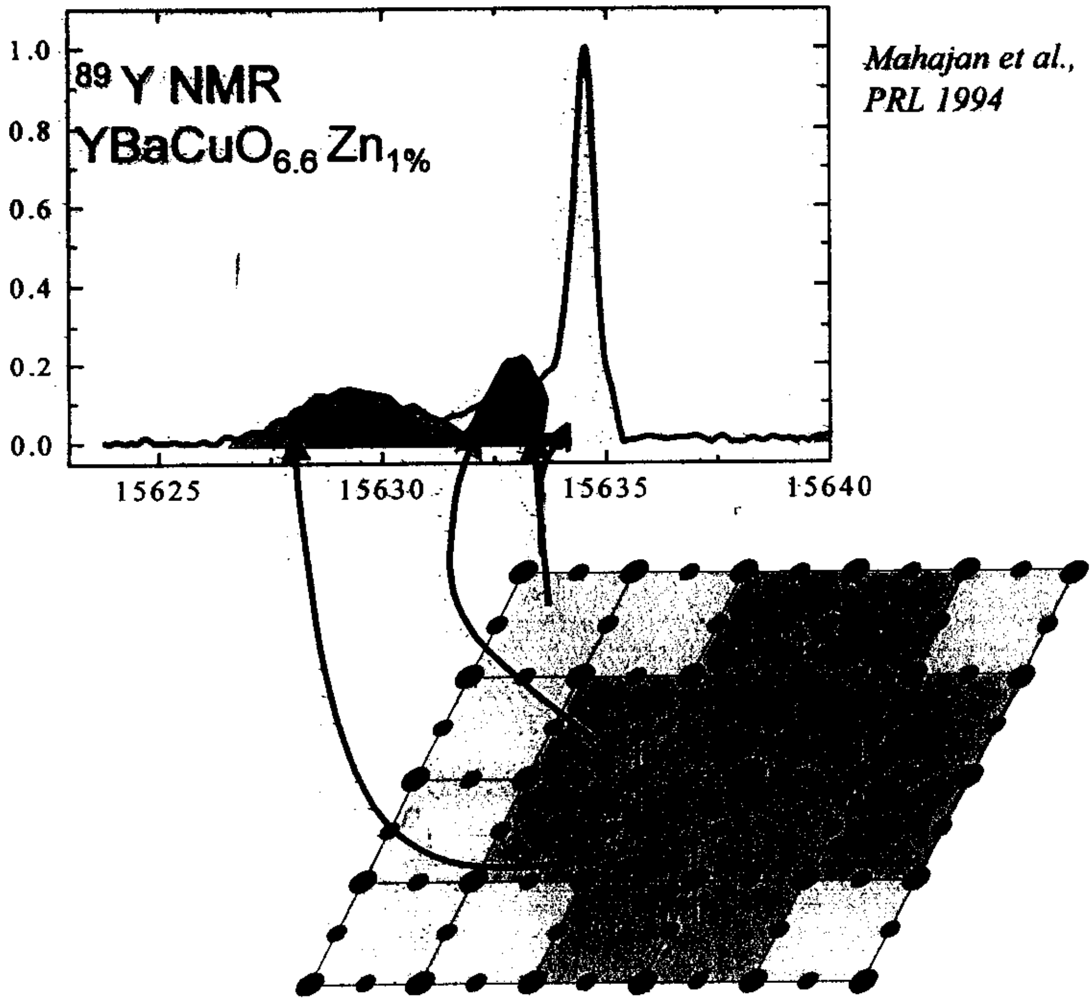
Zn $\simeq$ $S = 1/2$ (underdoped)

weak χ ($YBCO_7$)

P. MENDELS et al EUROPHYSICS LETTERS
46, 678 (1999)

impurity magnetism above T_c

Zn^{2+} or Li^{+} (no spin) $ Cu^{2+} spin 1/2

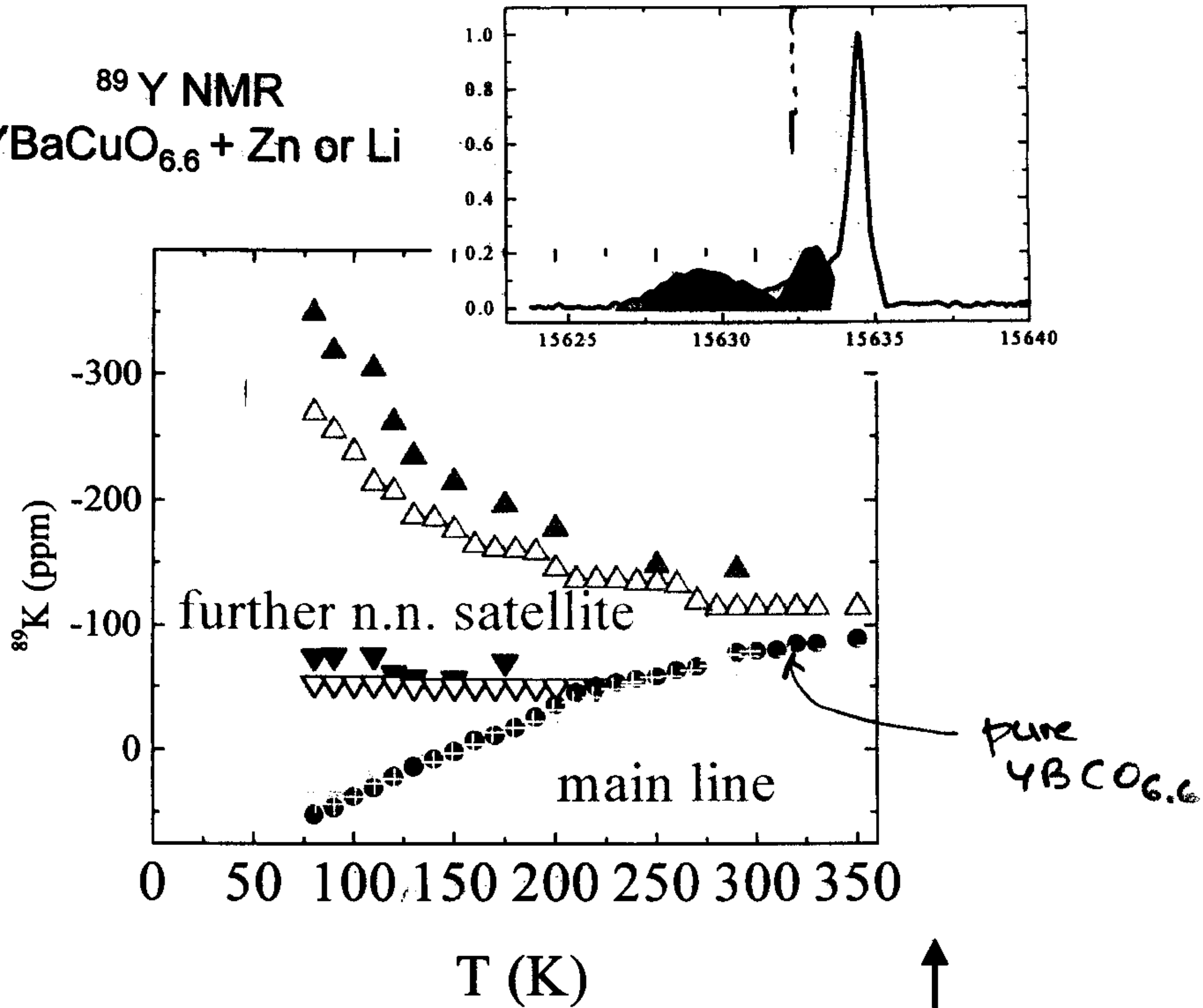


Mahajan et al., PRL 1994

⟹ induced local moments on nn Cu

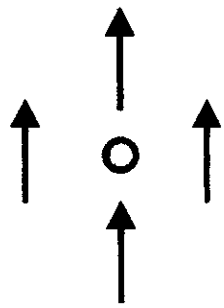
Susceptibility of the induced moments

^{89}Y NMR
$YBaCuO_{6.6}$ + Zn or Li



⟹ Curie law on nn Cu

⟹ χ(far from impurity) not affected



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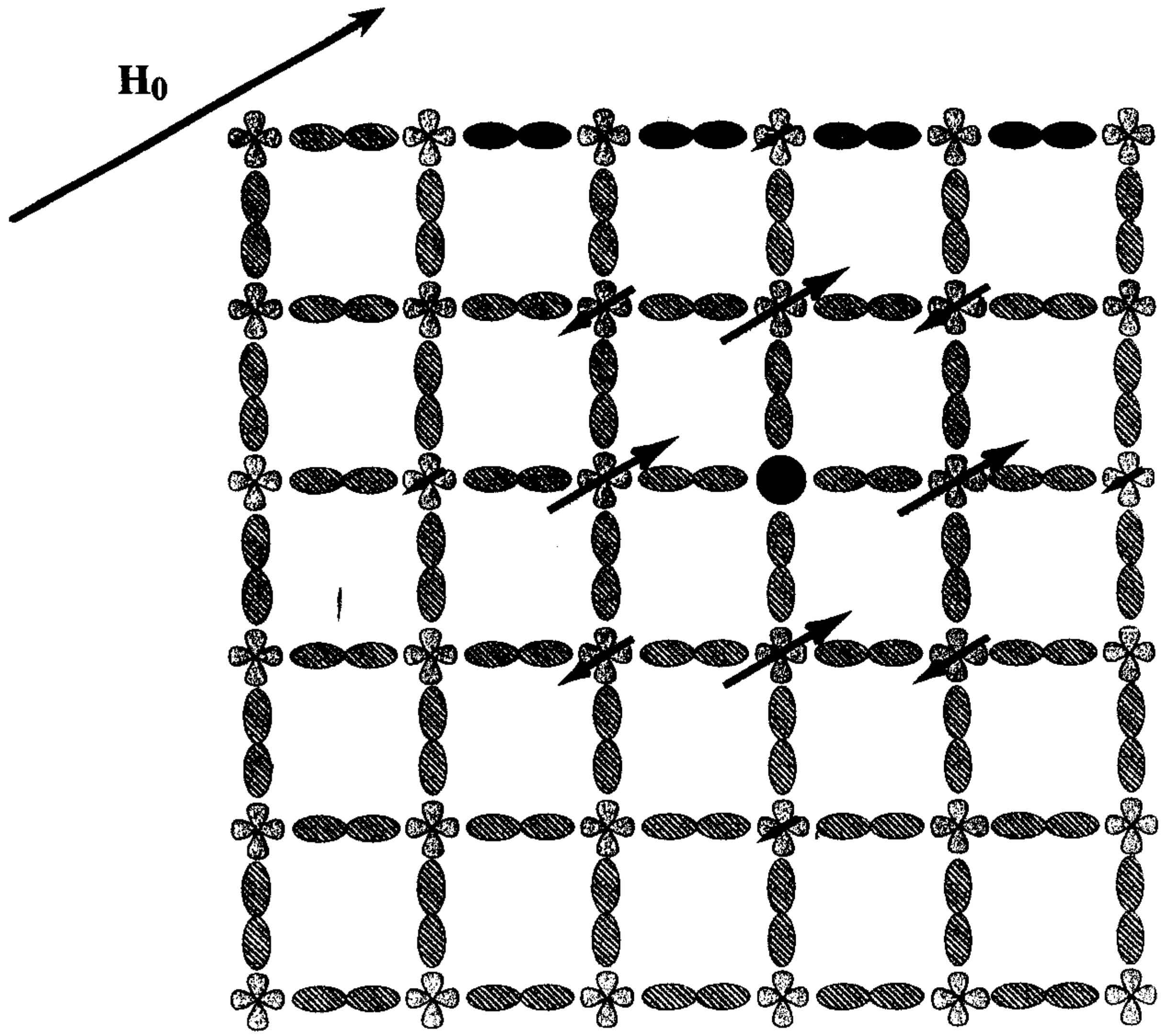

H_0

Universality of these induced moments

- ***Spinless** universal characteristic in high-T_c cuprates :*

  Zn, Li, vacancy in YBCO

  • Alloul et al PRL 91 (Walstedt *et al.*, PRB 1993; Mahajan et al., PRL 1994; Bobroff et al., PRL 1999; Julien et al., PRL 2000)

  Al in LaSrCuO (Ishida et al., PRL 1996)

- *other correlated systems :*

  - nickelates

    YBaNiO S=1 AF chain + Mg (spin=0)

    ! staggered mag. (F. Tedoldi *et al.*, PRL 1999)

  - Spin Peierls

    $CuGeO_3$ S=1/2 + Mg,Zn,Ni,Si

    ! AF state stabilized (Oseroff *et al.*, PRL 1995) Mg Kiryukhin PRL 79

  - spin ladders

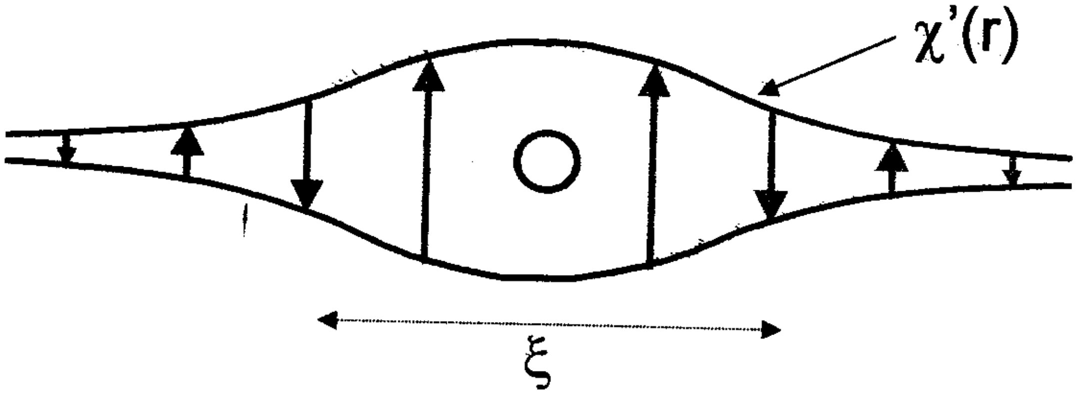
    2 leg SrCuO + Zn

    ! AF state stabilized (Azuma *et al.*, PRB 1997)

Impurity magnetism above T_c

the main idea :

a staggered AF magnetization stabilized by a vacancy in a correlated AF background



Millis, Monien & Pines

- A vacancy in a 2D Heisenberg AF

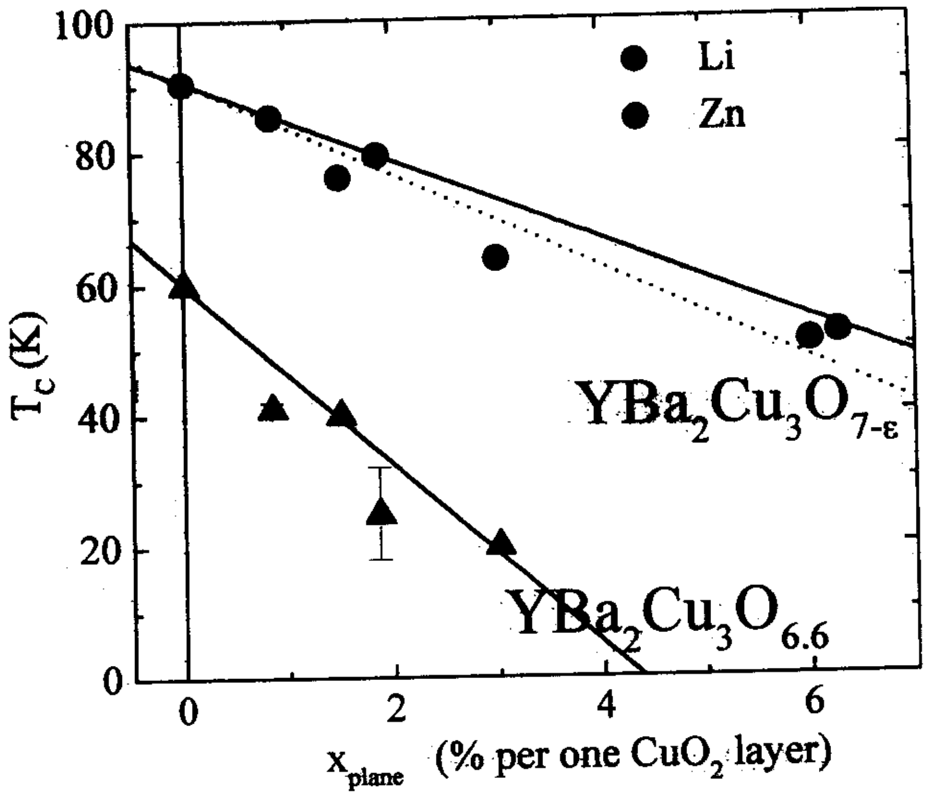
  ! $\langle S_Z \rangle$ increases Bulut et al., PRL 1989
- A vacancy in a t-J model : idem Poilblanc et al., PRL 1994
- A vacancy in a RVB AF state

  ! enhancement of AF correlations Martins et al., PRL 1996
- spinon/holon approach : Gabay et al., Physica C 1994; Nagaosa et al., PRB 1995

Question : the effect of doping ?

25

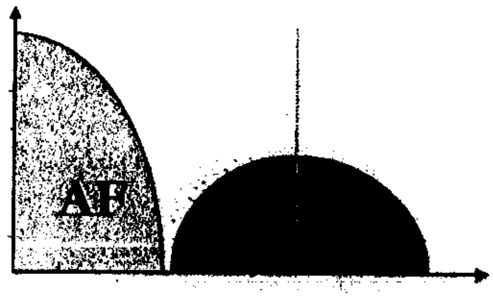
Spinless impurity effect on T_c



! Universal effect of a spinless defect

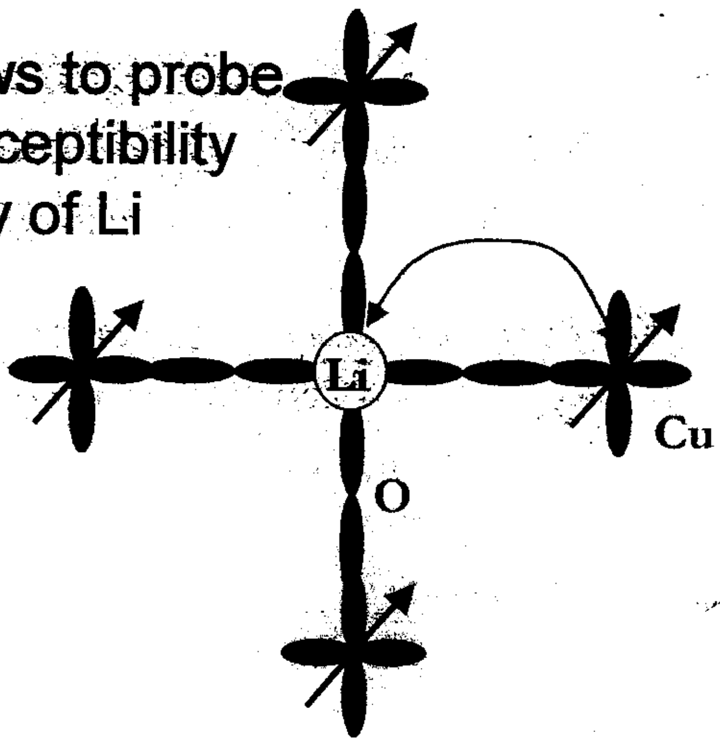
→ Impurity scattering rate is sensitive to the spinless character, not to the charge

evolution with carrier doping ?



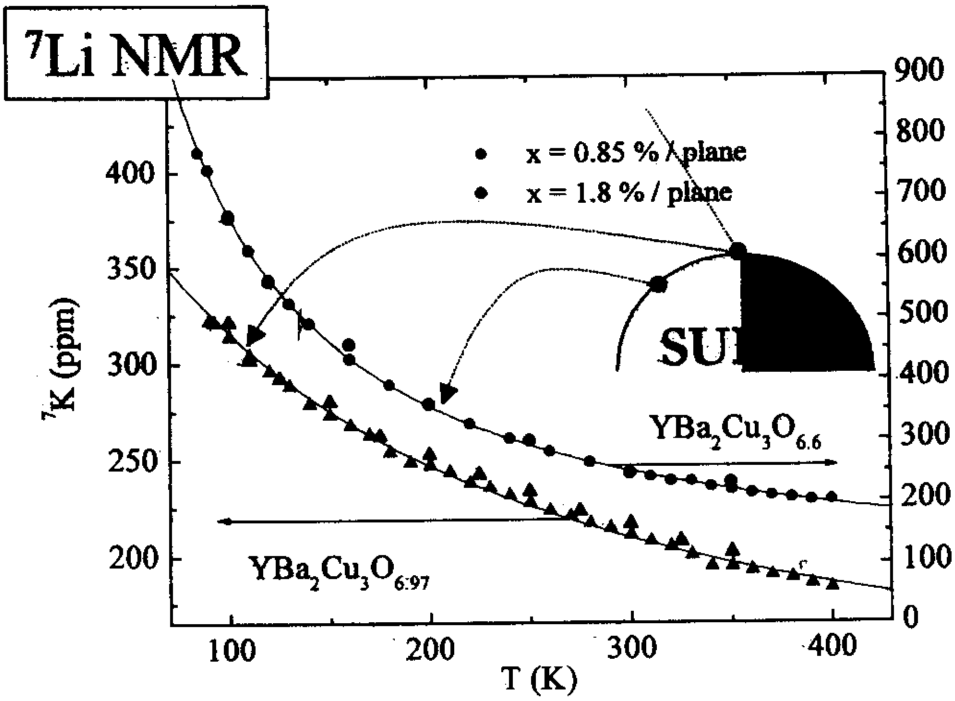
The appropriate tool : ^{7}Li NMR

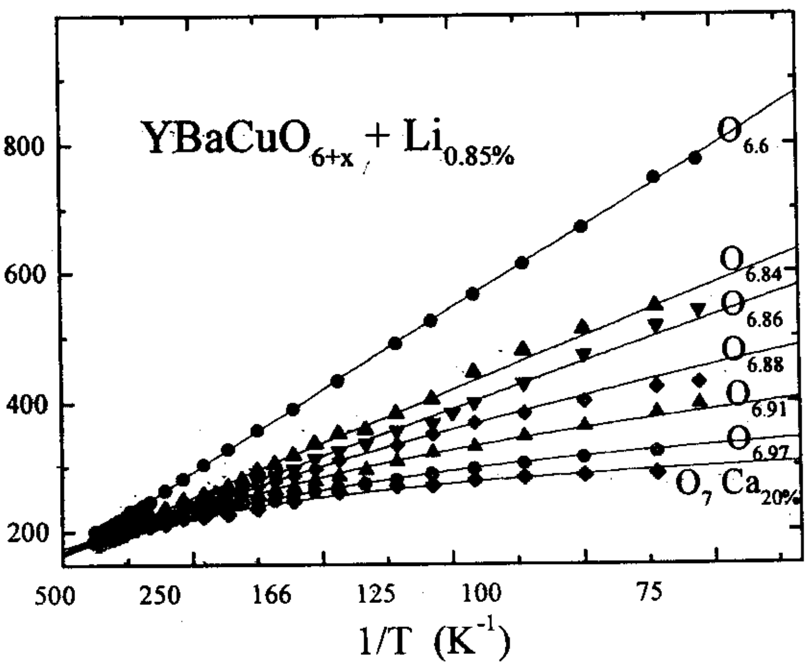
^{7}Li NMR allows to probe the local susceptibility in the vicinity of Li



Impurity magnetism above T_C

evolution with doping





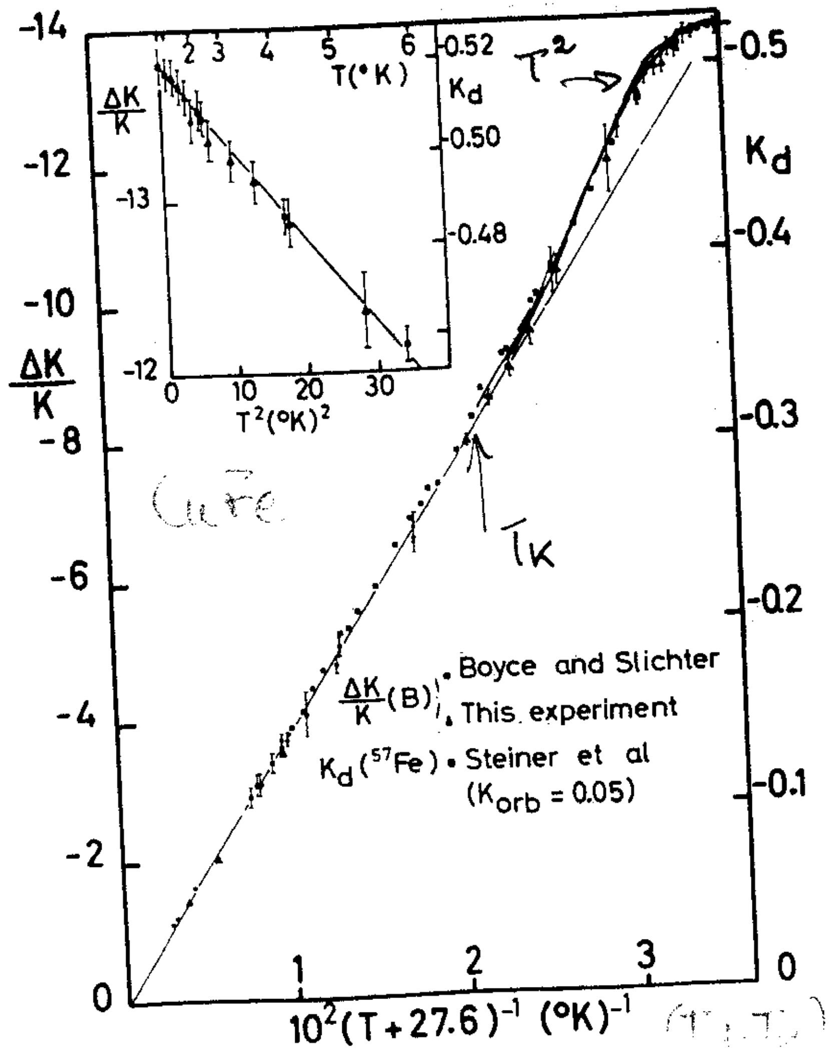
$$\chi = \frac{C}{T + \Theta}$$

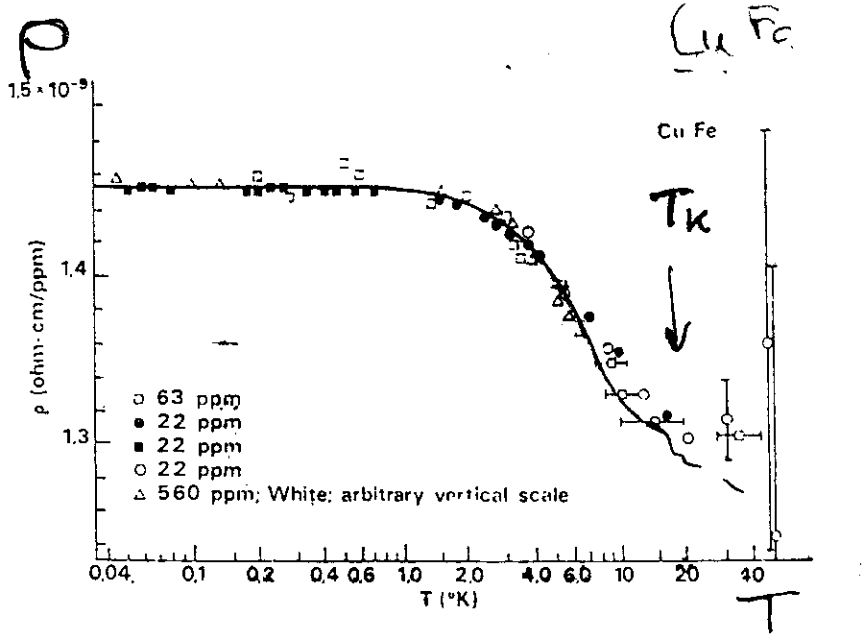
KONDO EFFECT IN DILUTE ALLOYS

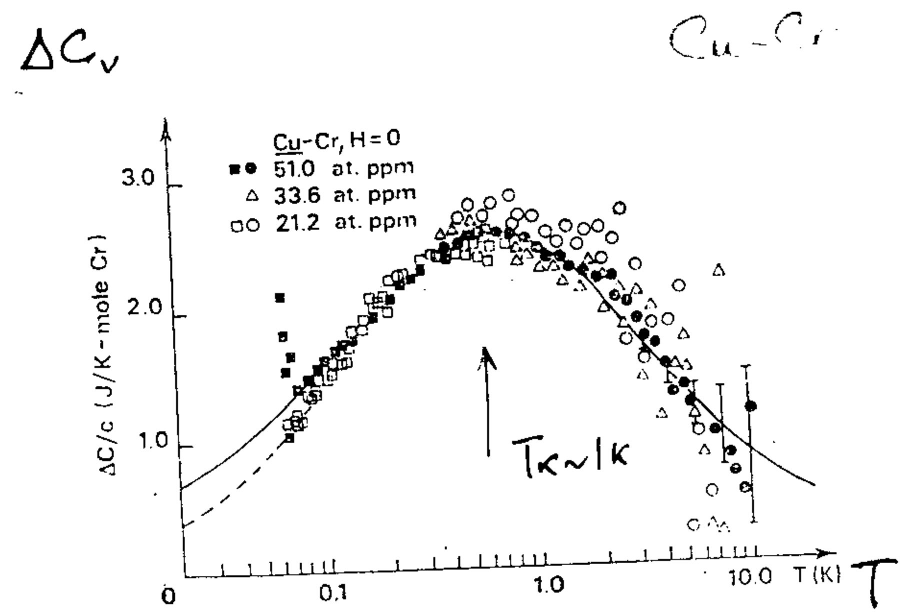
LOCAL MOMENT

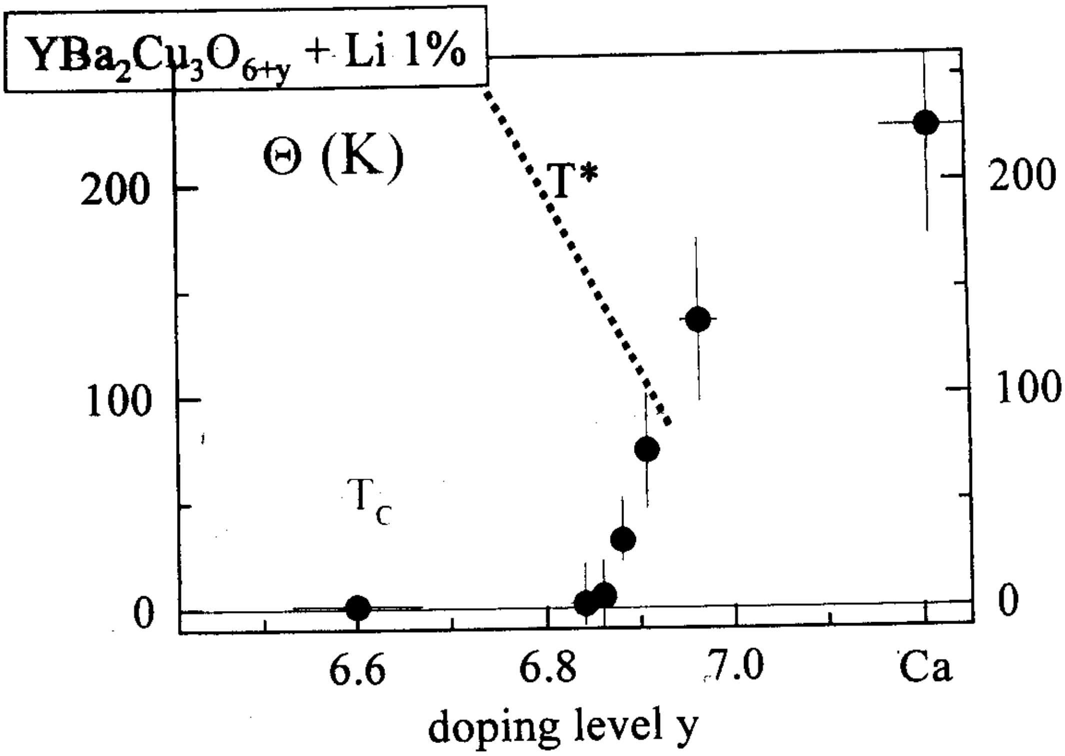
$$H = -J\vec{S}\cdot\vec{s}$$

$T \ll T_K$
- SINGLET FORMATION
- RESONANT STATE AT FERMI LEVEL









! Kondo-like behavior in $C/(T+\Theta)$ due to carrier doping

JB et al.,PRL 1999

! Analogy also from T_1 of Li NMR :

scaling $\tau_{impurity} \sim \chi_{impurity}$

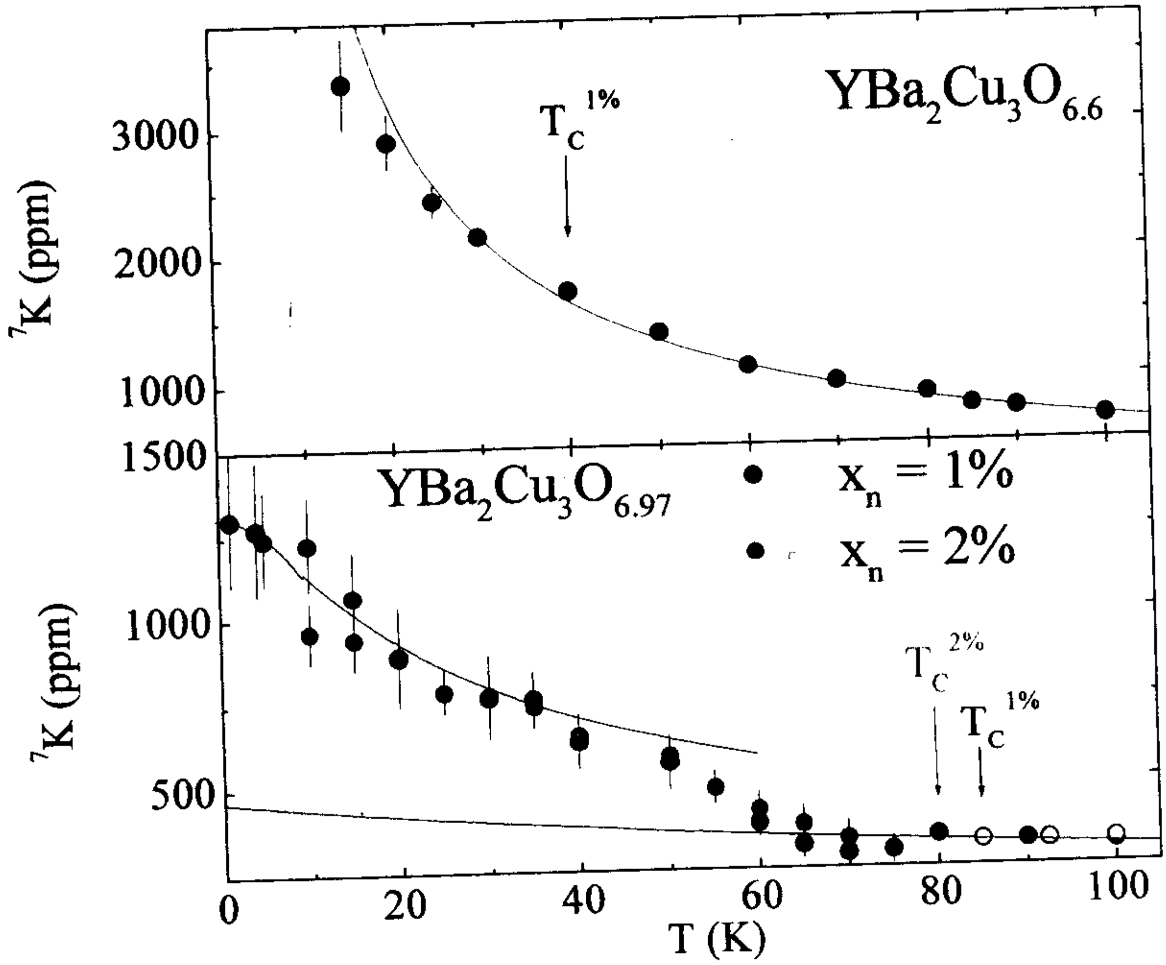
but not only for $T<\Theta$

MacFarlane et al.,PRL 2000

! Induced moments in overdoped regime

And below T_c?

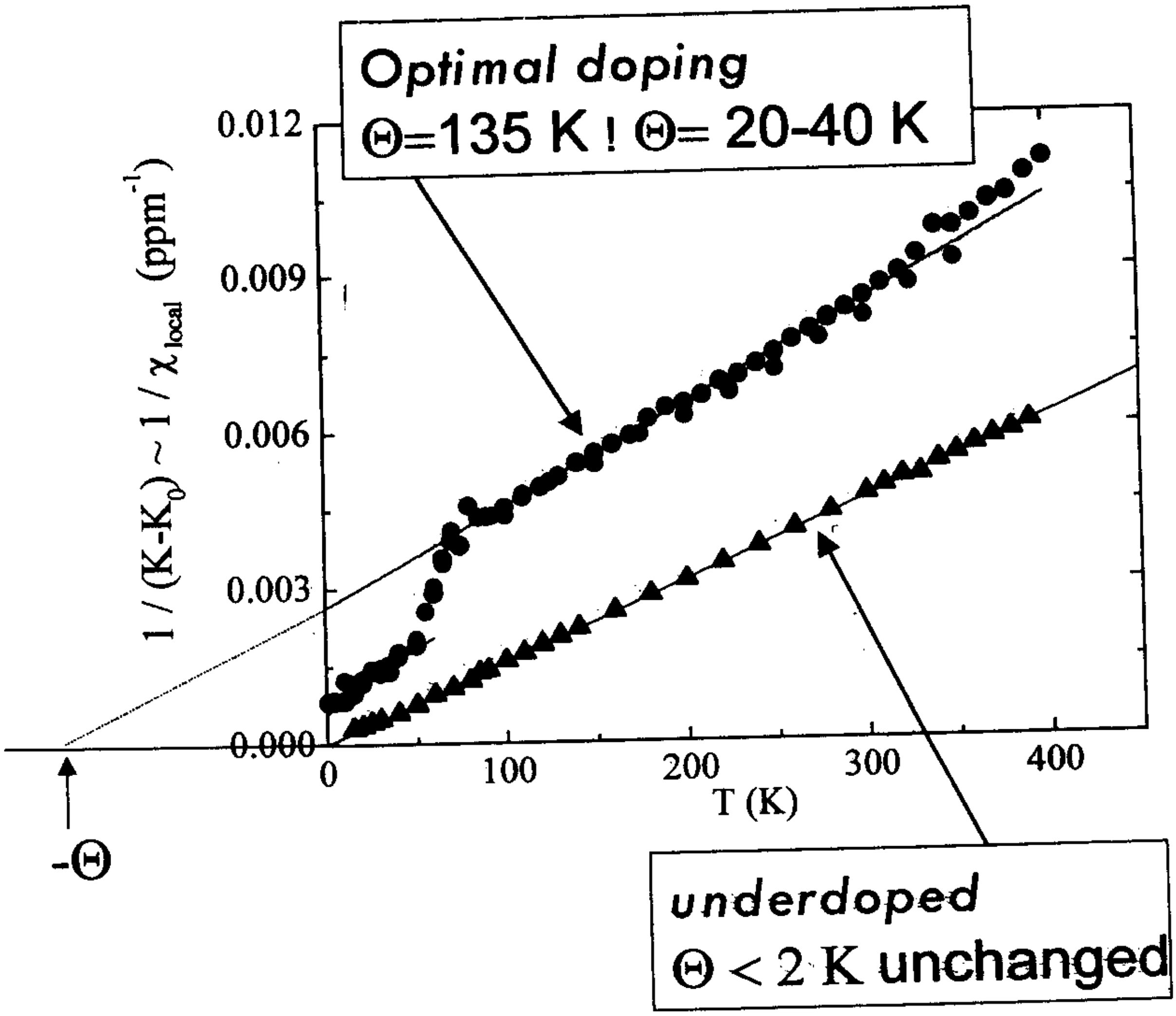
^7Li NMR below T_C



(31)

And below T_c?

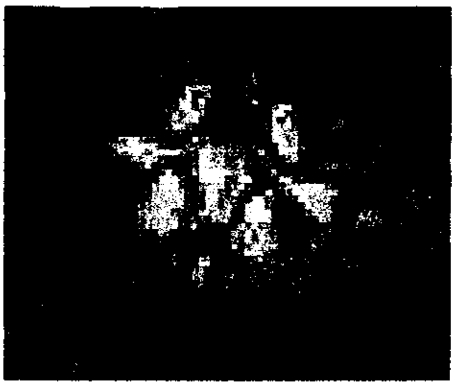
^{7}Li NMR below T_C

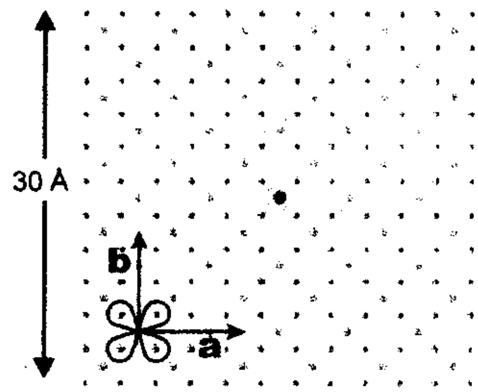


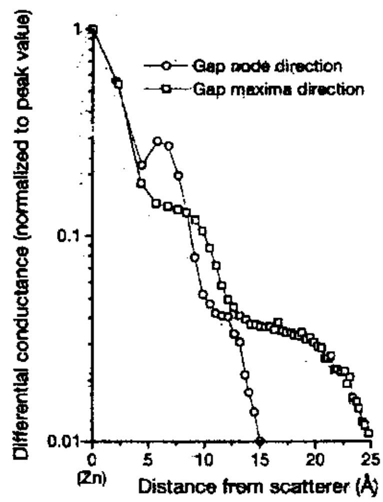
⇨ Any gap reduces *the Kondo screening* (pseudogap, supra)
(Cassanello & Fradkin, PRB 97; Nagaosa & Lee, PRL 97;;
Gonzalez & Ingersent, PRB 98; Simon & Varma, PRB 99))

And below T_c ?

- **S.T.M experiments** (Pan et al., Nature 2000) :
  Zn in Bi2212







Residual anisotropic D.O.S around the Zn defect

CONCLUSION

IMPURITIES AND DEFECTS

- ALLOW TO REVEAL THE EXISTENCE OF ELECTRON CORRELATIONS IN THE CUPRATES (EVEN OVERDOPED)

- REDUCE T_c BUT PSEUDO GAP ROBUST (FAR FROM IMPURITIES)

  INFORMATIONS ON PHASE DIAGRAM

MAGNETIC IMPURITIES (Ni)

- DOES NOT DISTURB THE MAGNETISM OF CuO_2 PLANE

  $S \sim 1/2$ WEAKLY COUPLED TO THE CARRIERS

SPINLESS IMPURITIES (Zn^{2+}, Li^{+}, Al^{3+})

- INDUCE LOCAL MOMENT

  $S \sim 1/2$ STRONGLY COUPLED TO THE CARRIERS

  ⇓

  KONDO EFFECT (χ AND T_{SF})

- KONDO TEMPERATURE DECREASES

  IN THE PSEUDO-GAP AND SUPERCONDUCTING PHASE

- UNIVERSAL BEHAVIOUR SPINLESS EFFECT

  NO EFFECT OF CHARGE

  LARGE SCATTERING $\tau^{-1}_{transport}$

  SHOULD BE ASSOCIATED WITH THIS RESONANT KONDO EFFECT