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

(11 February - 1 March 1991)

" Characterization of HTS Materials by Neutron Scattering "

presented by:

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

Characterization of HTS materials by Neutron Scattering.

First lecture: General remarks on Neutron Scatt.,
structures
magnetic ordering
densities of states : phonons
: magnetic excitation
role of impurities
"Do magnetic moments exist in High T_c Superconductors?"

Second lecture: Details about magnetic dynamics
Phonon anomalies

Experimental results from different sources:

ILL-Grenoble: Schärpf et.al., Rossat-Mignod et al.

BNL-Brookhaven: Shirane et al .....

Paris-Karlsruhe: Pintschovius, Reichardt, ...

Neutron scattering, general remarks.

The neutron interacts with

a) nuclei: $H_{Nn} \sim b + \tilde{b}\, \vec{S} \cdot \vec{\mu}_N$

(b: scalar; $\vec{S}$: nuclear spin; $\vec{\mu}_N$: neutron spin)

b) magnetization densities:

$$H_{Nm} \sim \vec{m}^{\perp} \cdot \vec{\mu}_N$$

Interaction is weak ⇒ Born approx. applicable.

⇒ Cross section for
momentum transfer $\vec{\kappa}$
energy transfer $\hbar\omega$

is directly proportional to

a) density-density correlation function (for nuclei)

$$\sum_{ij} \int \langle e^{i\vec{\kappa}\cdot\vec{R}_i(0)} e^{-i\vec{\kappa}\cdot\vec{R}_j(t)} \rangle e^{i\omega t} dt$$

⇒ information about <u>structures</u>
+ <u>lattice dynamics</u>

structures: $\sim \sum \langle e \ldots \rangle$

dynamics: $\sim \sum \int e^{i\vec{k}\cdot(\vec{R}_i^0-\vec{R}_j^0)} \langle \vec{u}_i \cdot \vec{u}_j(t) \rangle e^{i\omega t}\, dt$

displacements

$\sim$ displacement-displacement correlation fct.

$\sim$ "phonons".

b) magnetization - magnetization (spin-spin) corr. fct

$$\sim \sum \int e^{i\vec{k}\cdot(\vec{R}_i-\vec{R}_j)} \langle \vec{S}_i \cdot \vec{S}_j(t) \rangle e^{i\omega t}\, dt$$

$\Rightarrow$ information about <u>magnetic ordering</u>

\+ <u>magnetic excitations</u>

Separation of different correlation functions possible

i) through indirect information + experience

ii) polarization analysis (technically difficult,

Accessible wavelengths: atomic distances up to ∞

Accessible energy transfers: $\hbar\omega \gtrsim 100$ meV

$\sim 1000\ k_B K$

– Large samples necessary!

In principle we can learn everything about lattice properties (structure + dynamics) + magnetic properties (order + fluctuations).

nothing about: electronic charge distributions
" polarizabilities.

In practice: Almost everything about the lattice
a lot (or not so much) about magnetism
a little bit (indirectly) about electronic charges.

Up to now:

Intensive studies of magnetic properties
(BNL, ILL)

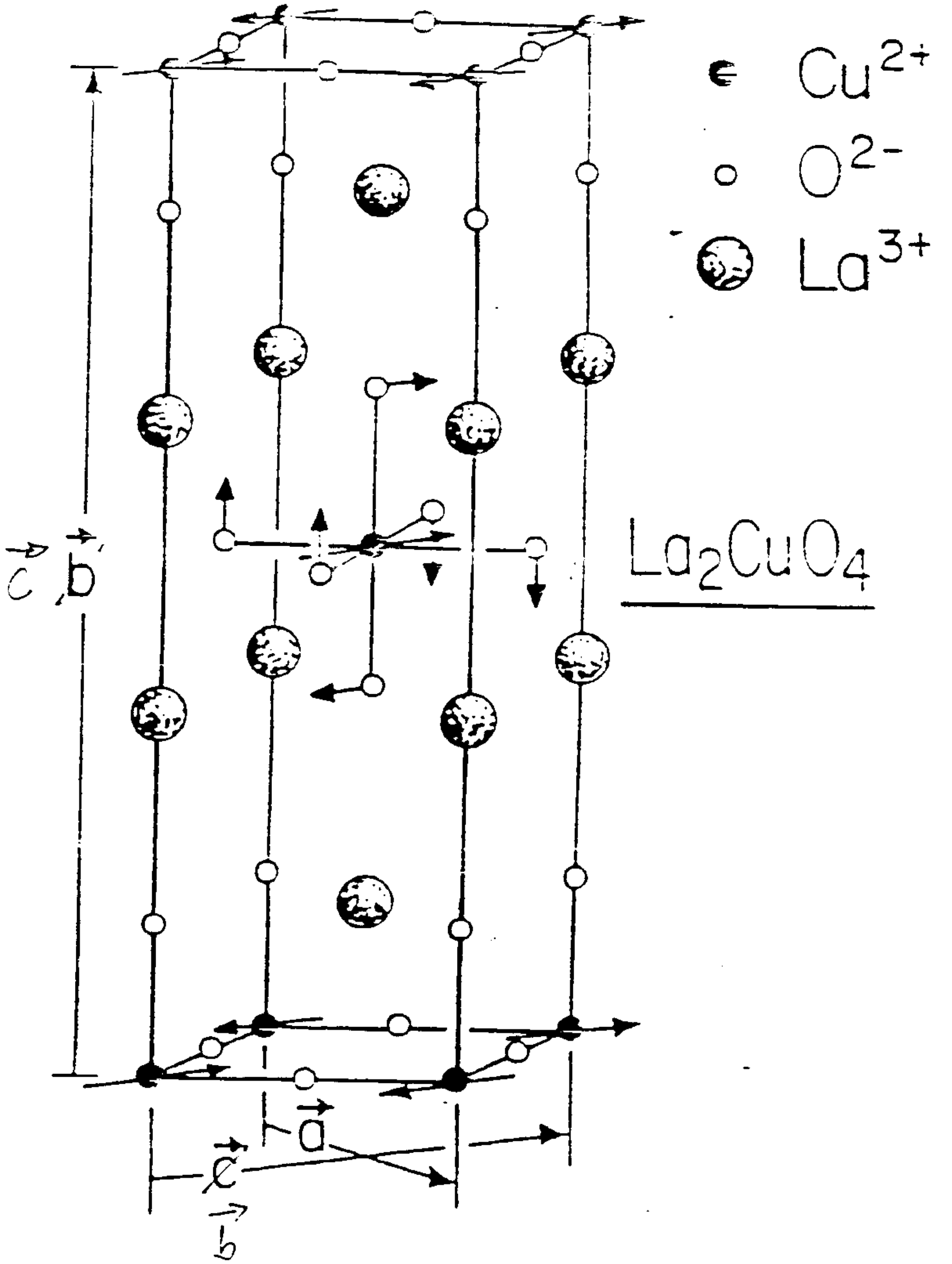
$(La....)_2 Cu O_4$

$Y Ba_2 Cu_3 O_{6+\delta}$

"Superconductivity because of or despite of magnetism?"

Less attention to lattice dynamics

But: Interesting phonon anomalies
(Paris-Karlsruhe)


Cu2+
O2-
La3+
La2CuO4
c b
a
c
b

La_2CuO_4

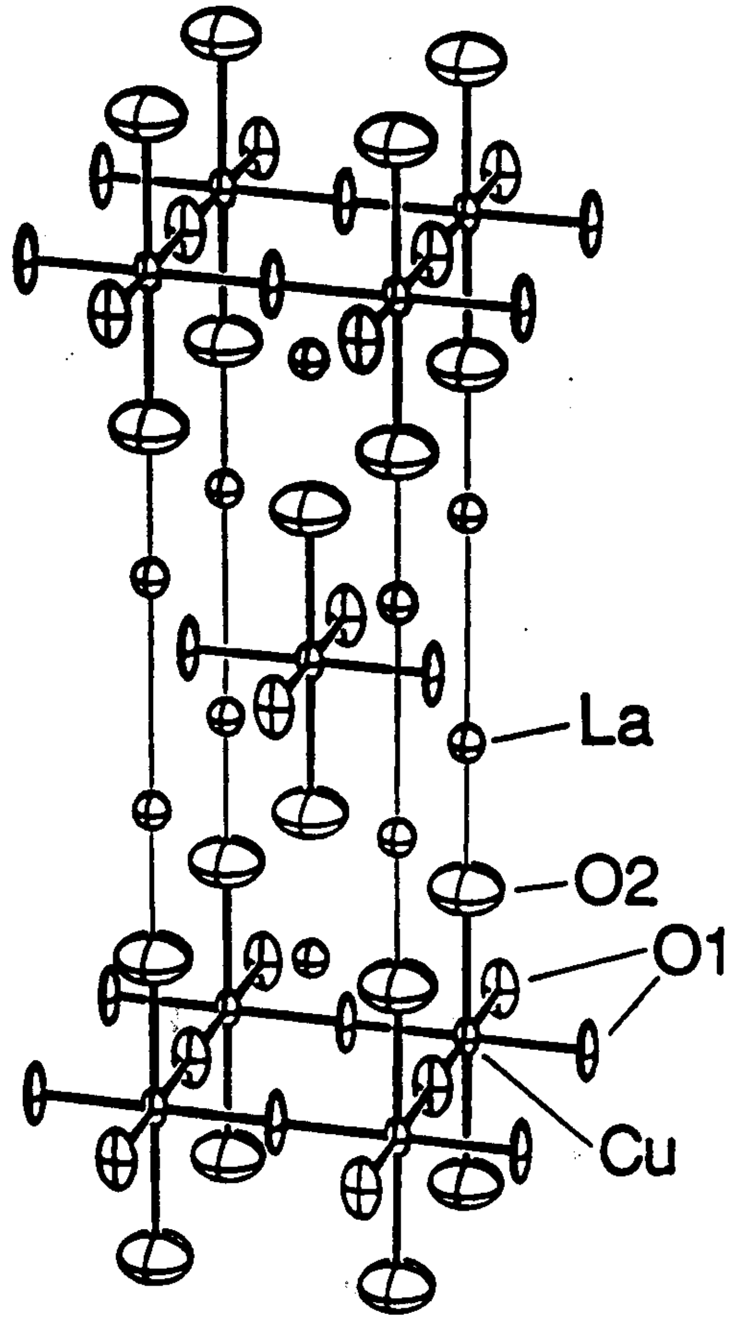
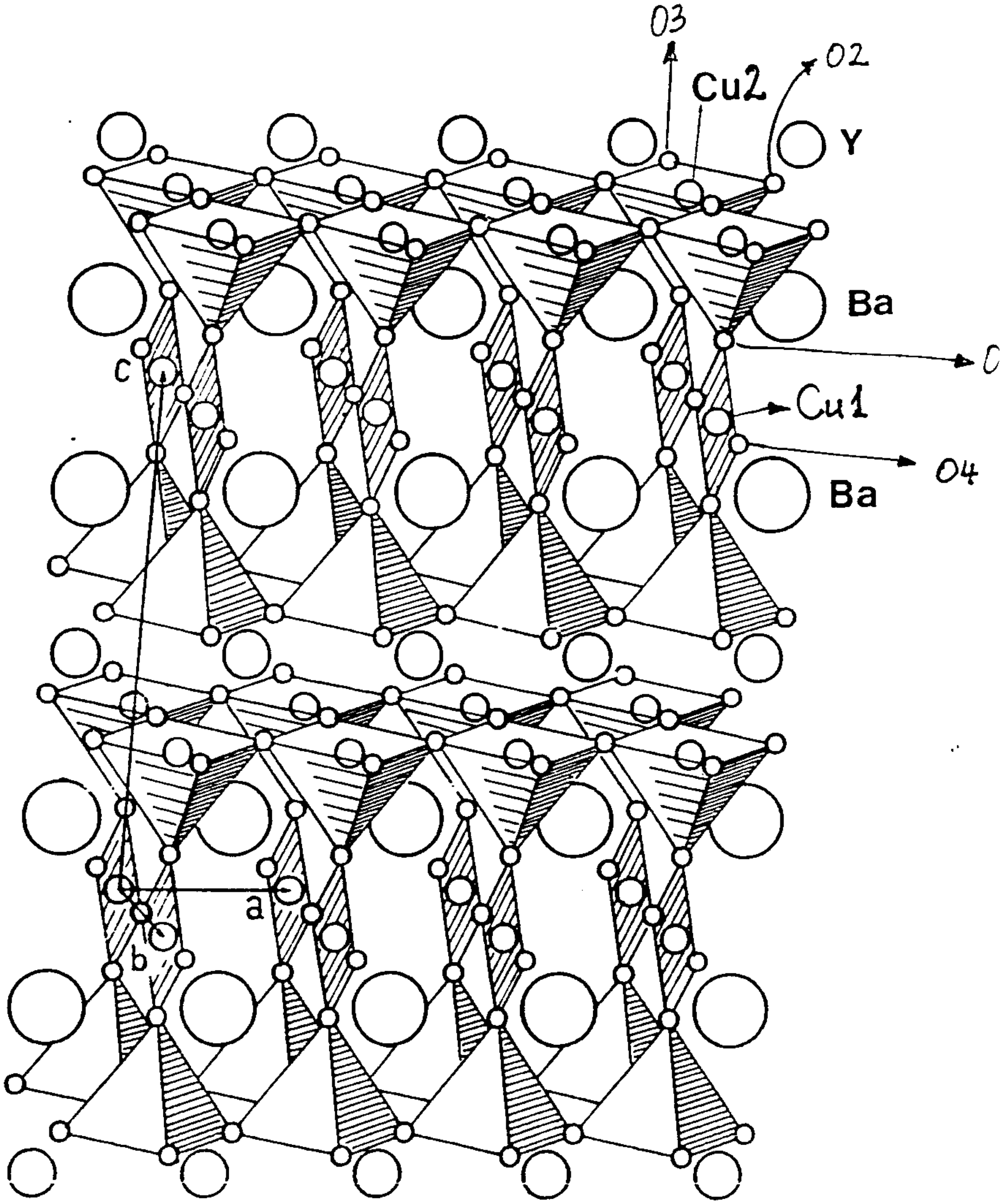


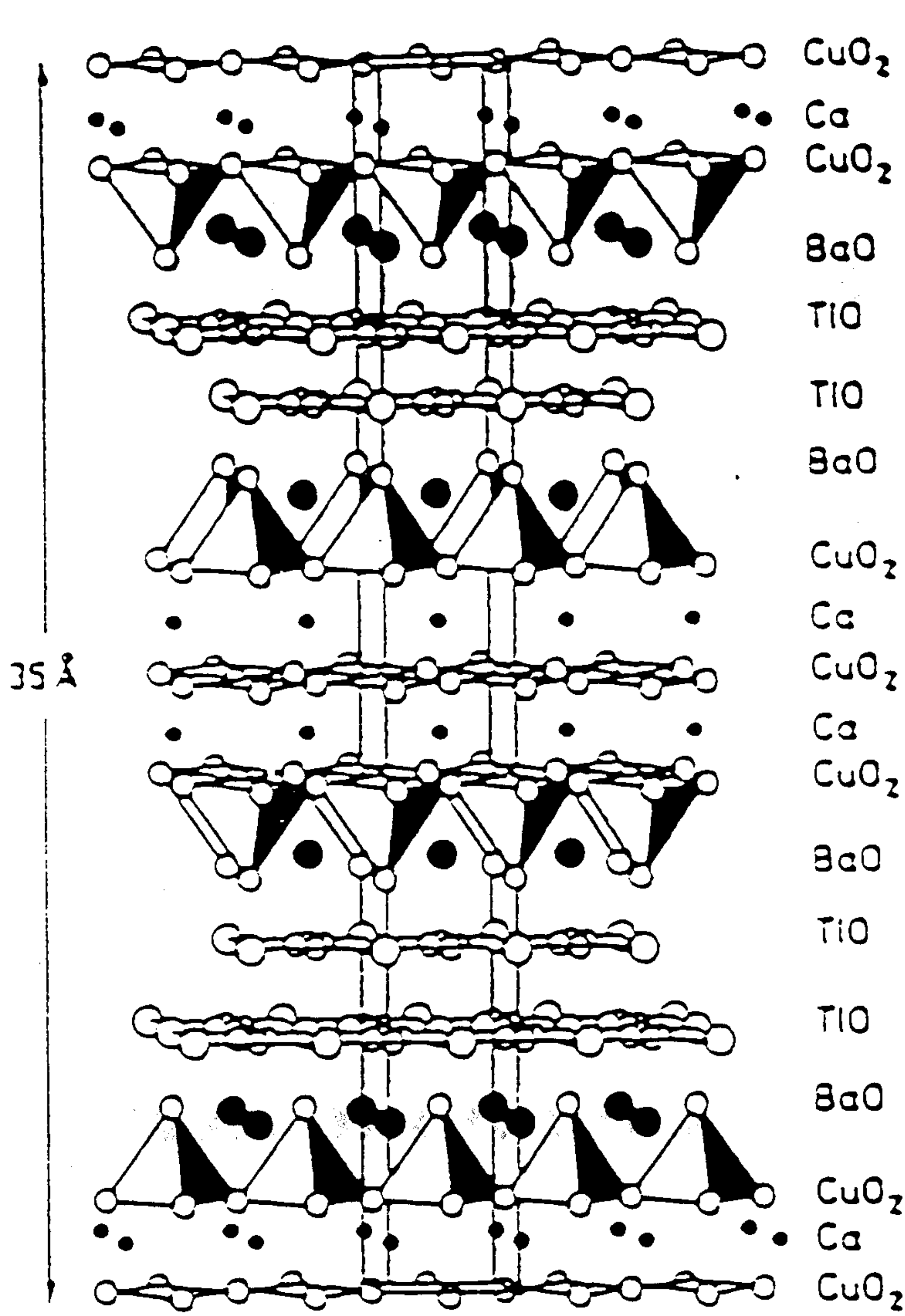
FIG. 2. The crystal structure of La_2CuO_4, with (O1, O2) denoting the sites denoted (O_{xy}, O_z) in the text. The ellipsoids reflect the probability density resulting from neutron scattering refinements of the structure. The probability density can reflect both dynamic and quasistatic, uncorrelated displacements from the ideal sites.

that is not

$YBa_2Cu_3O_7$



Tl 2223 ; $T_c \cong 125$ K



Common elements: CuO_2 planes

+ other planes.

"Other planes" have secondary role of

a) stabilizing crystallographic structure

b) controlling electron densities (carrier concentration) in CuO_2 planes

Example: Y-plane may be replaced by 3-valent rare earth (large magn. moment) without consequences on superconductivity.

CuO_2 - plane essential for superconductivity, magnetism

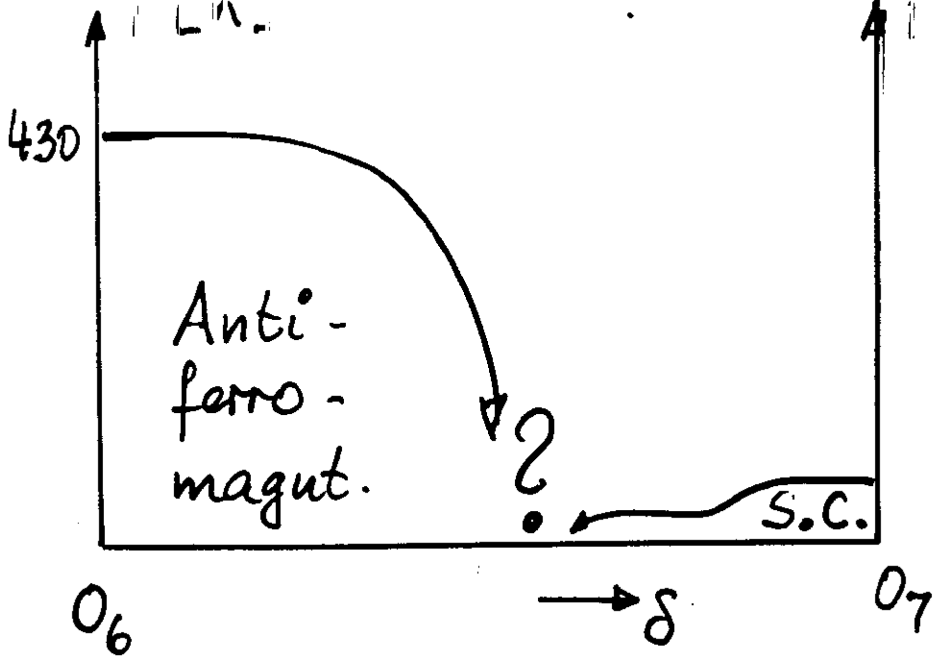
In La_2CuO_4, $YBa_2Cu_3O_6$: Cu^{2+}

⇒ One hole missing from full 3d-shell.

~ Spin ½ ; → antiferromagnetism.

"Doping" CuO_4 plane $La_{2-x}Sr_xCuO_4$, $YBa_2Cu_3O_{6+\delta}$

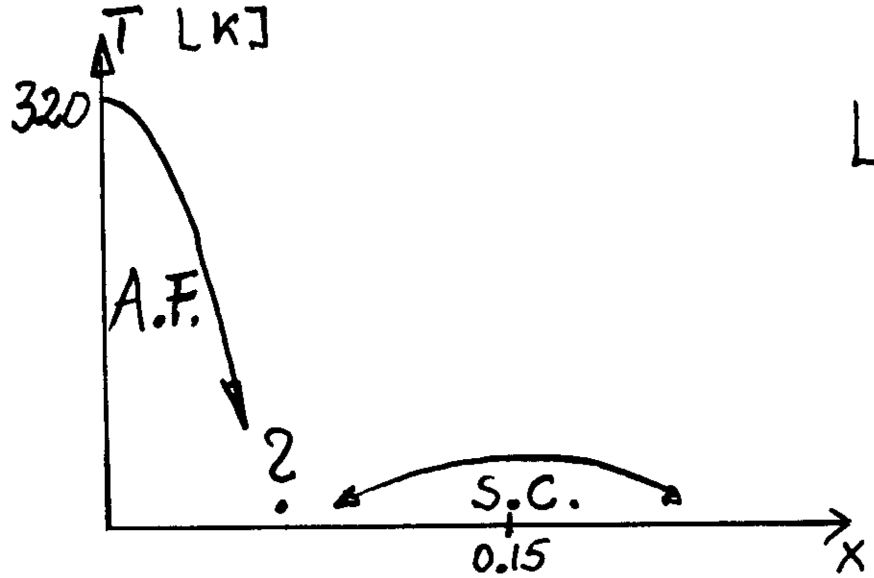
→ No magnetic order but Superconductivity



$YBa_2Cu_3O_{6+\delta}$

$\delta \sim 0 \Rightarrow CuO_2$ plane magnetic

$\delta \sim 1 \Rightarrow CuO_2$ planes superconducting



$La_{2-x}Sr_xCuO_4$
Ba_x

like above

Question: Magnetism disappears by

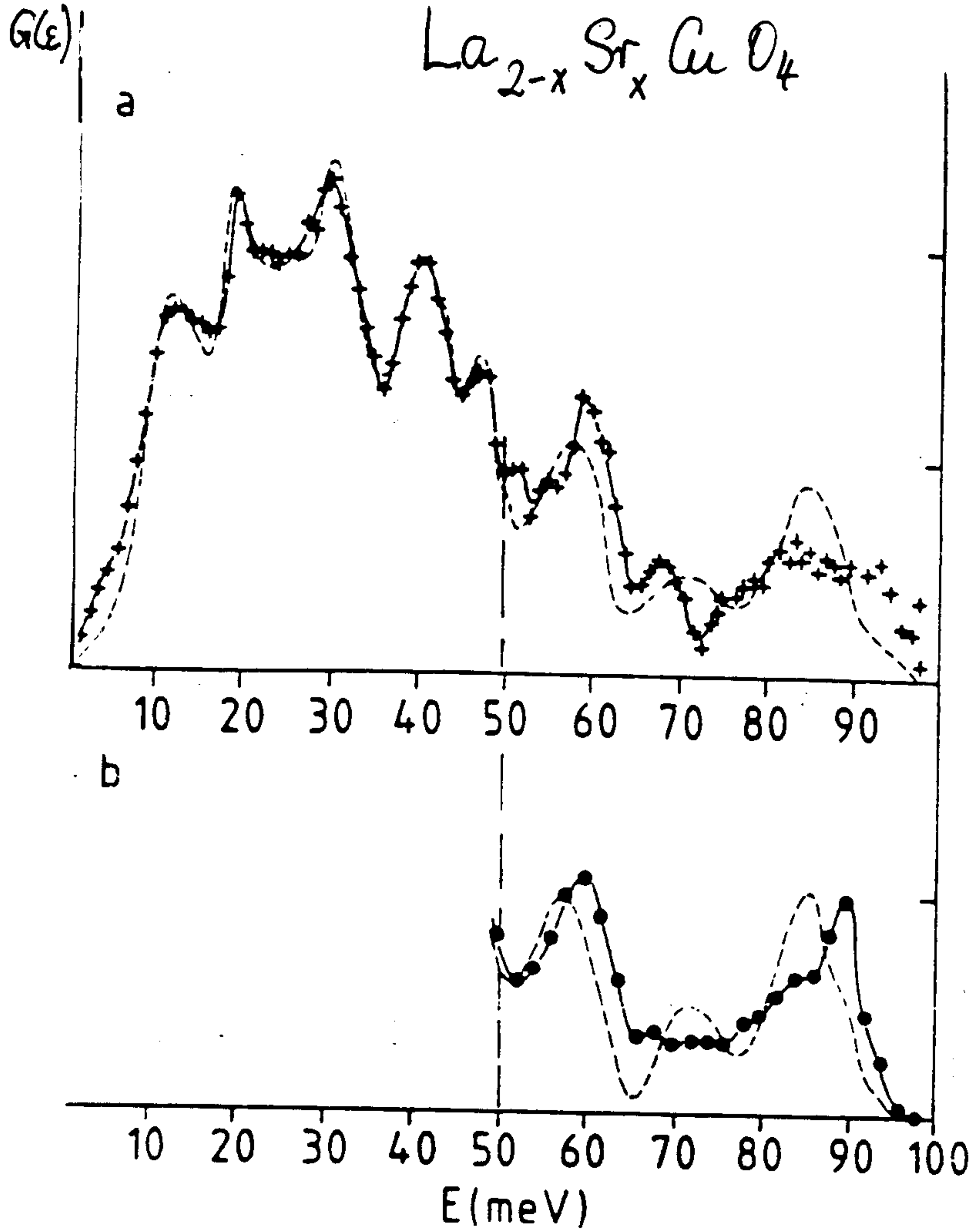
loss of long range order only (retaining moments + short range order)

or

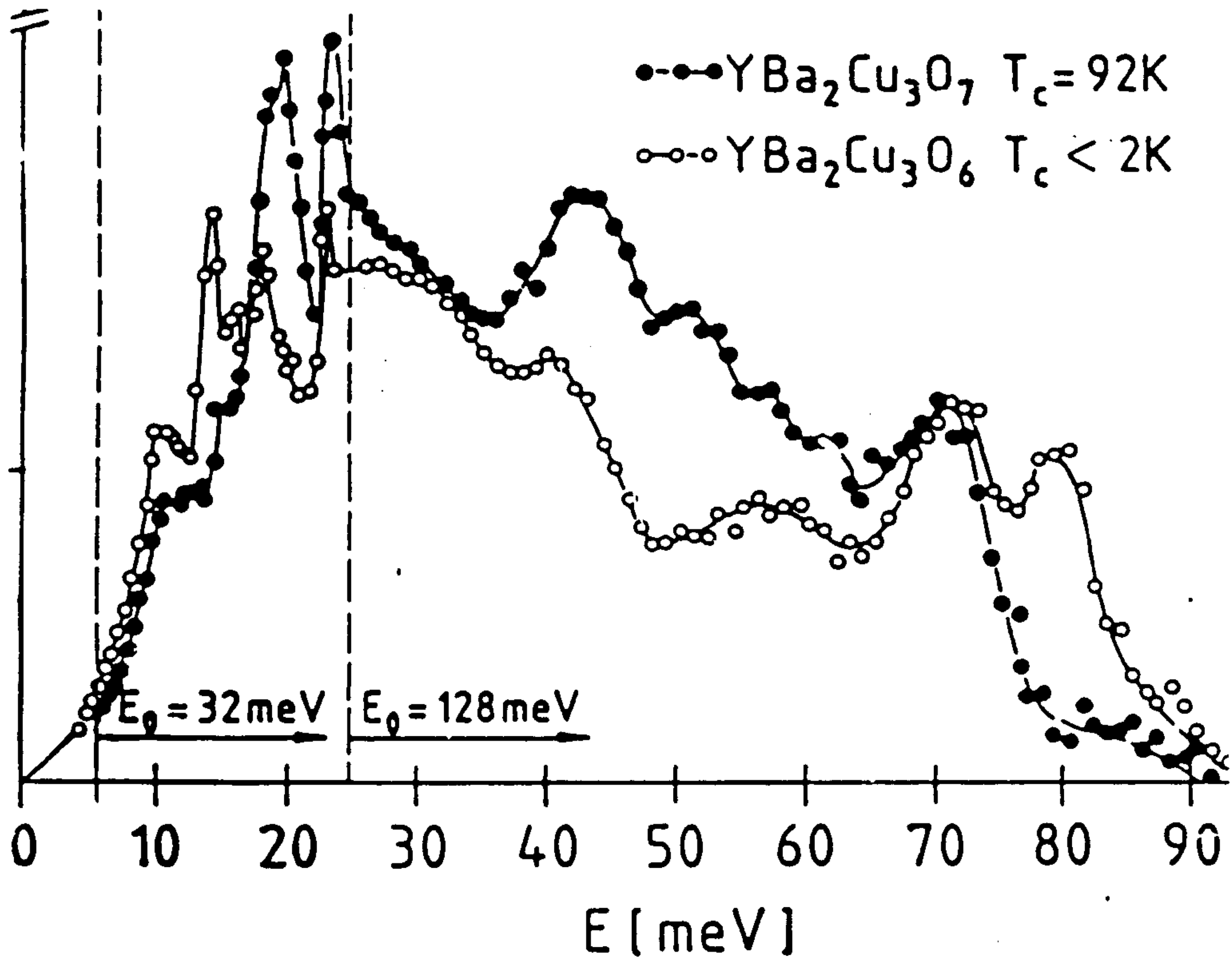
disappearance of local magnetic moments

?

(To be discussed later).



and b. Generalized phonon density of states $G(\hbar\omega)$ for O_4. **a** Measurement at 300 K (crosses) in energy gain of the ns. The dashed curve is the result for $La_{1.85}Sr_{0.15}CuO_4$ from **b** Measurement at 6 K with $E_0 = 128$ meV for La_2CuO_4)

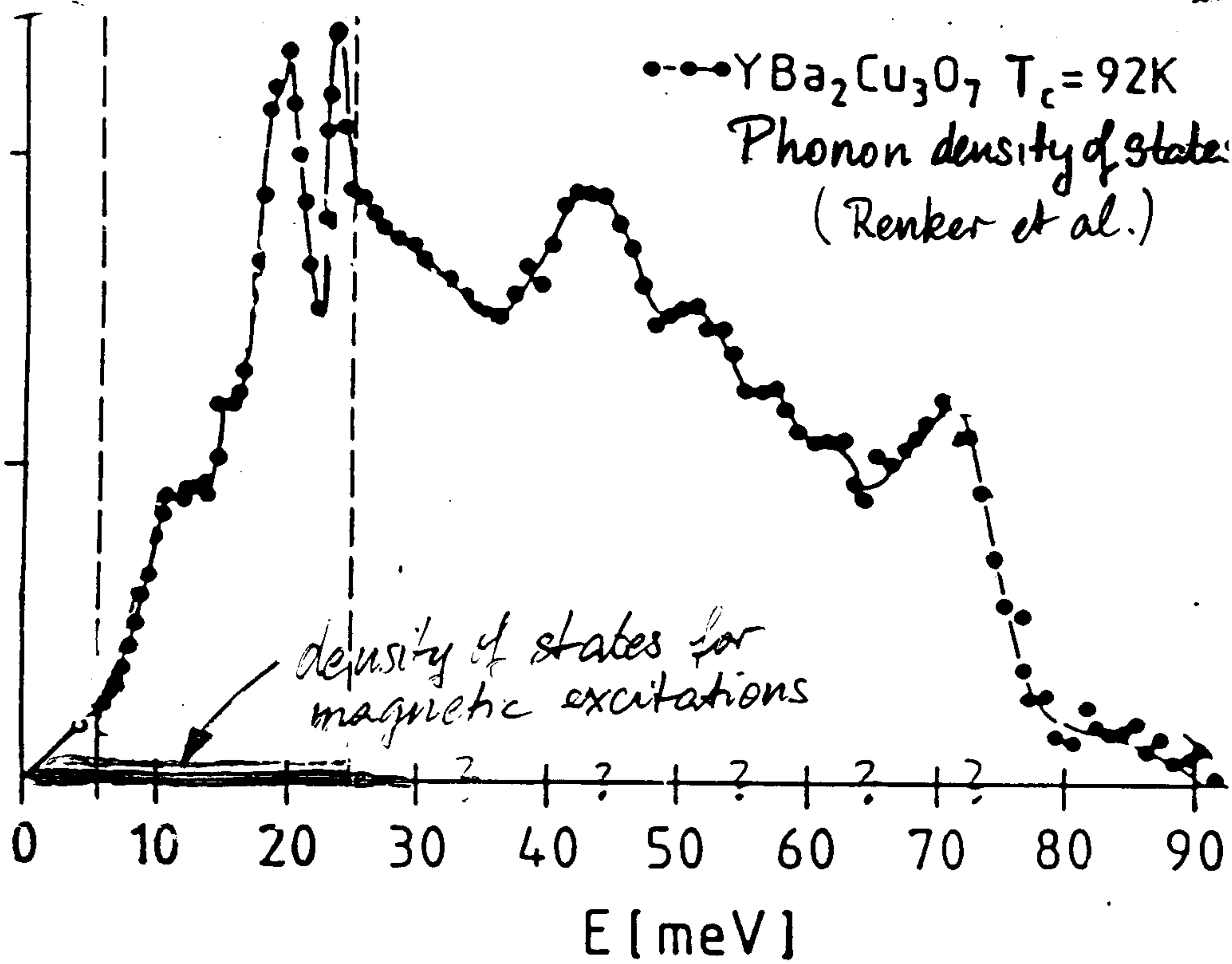


Generalized phonon density of states $G(\hbar\omega)$
(Renker et al.)

Energy scale for phonons ~ 90 meV ~ $1000\, k_B$

(Typical for all High T_c materials)

High energy oxygen vibrations.



Number of magnetic degrees of freedom orders of magnitude smaller than lattice degrees of freedom in energy range $< \sim 25-30$ meV.

Purely magnetic signal for general q has to be extracted by polarization analysis: Measure spin flip intensities for polarization in z, x, y direction (x-y plane = scattering plane)

$$\Rightarrow I_{magn} \sim 2\, I_{SF}^{(\vec{P} \parallel \vec{z})} - I_{SF}^{(\vec{P} \parallel \vec{x})} - I_{SF}^{(\vec{P} \parallel \vec{y})}$$

Total amplitude of magnetic fluctuations
or

Do magnetic moments survive in HT_c Supercond.?

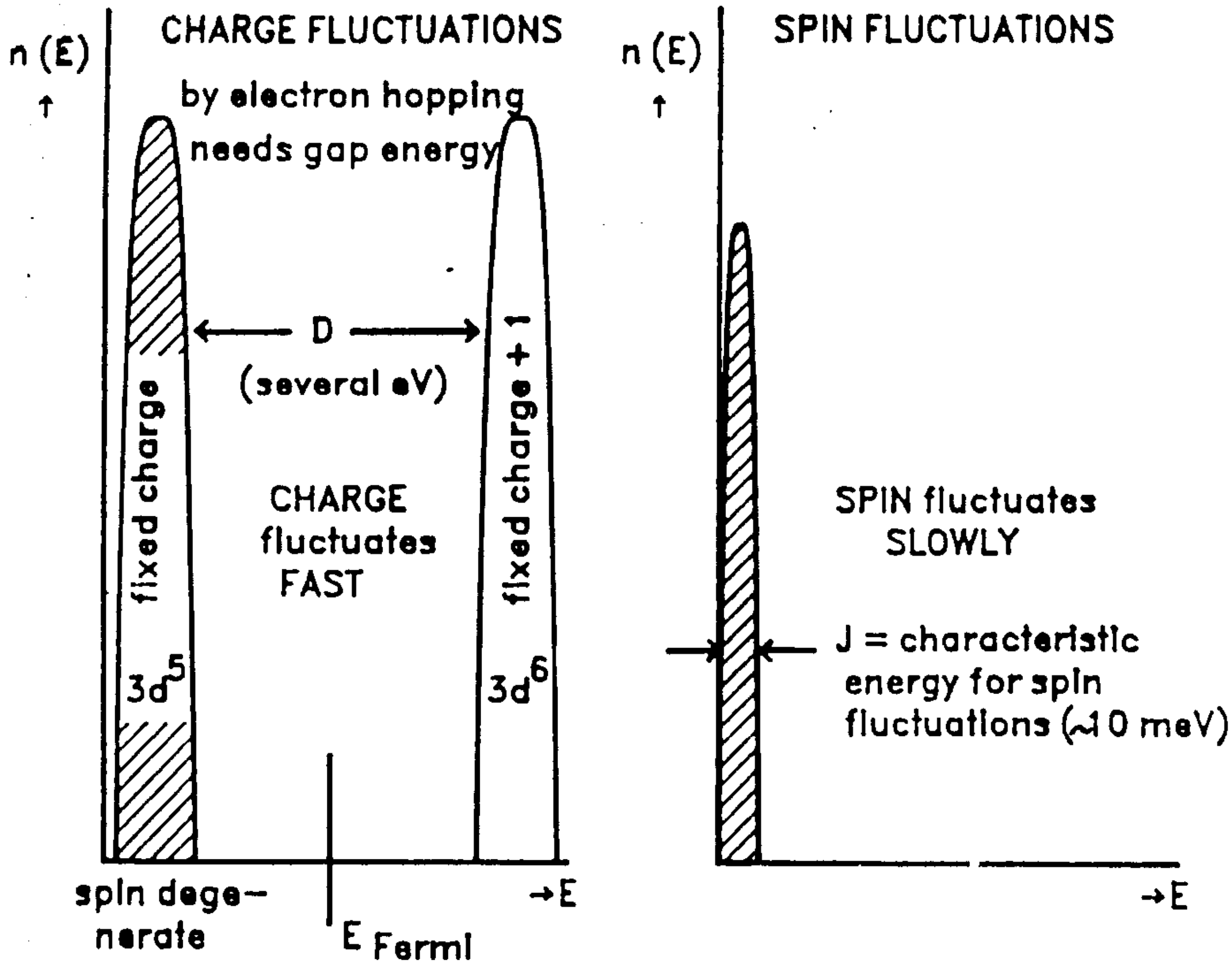
Existence of magnetic moments requires
- separation of charge- and spin-excitation spectrum
- charge excitations: high energy, ~ eV
- spin excitations : low energy ~ 10-100 meV

Examples: Transition metal oxides (T14)

Itinerant magnetism (Fe, Ni, Cr) (T15)

Rare earth magnetism (T16)

≙ HTS ??

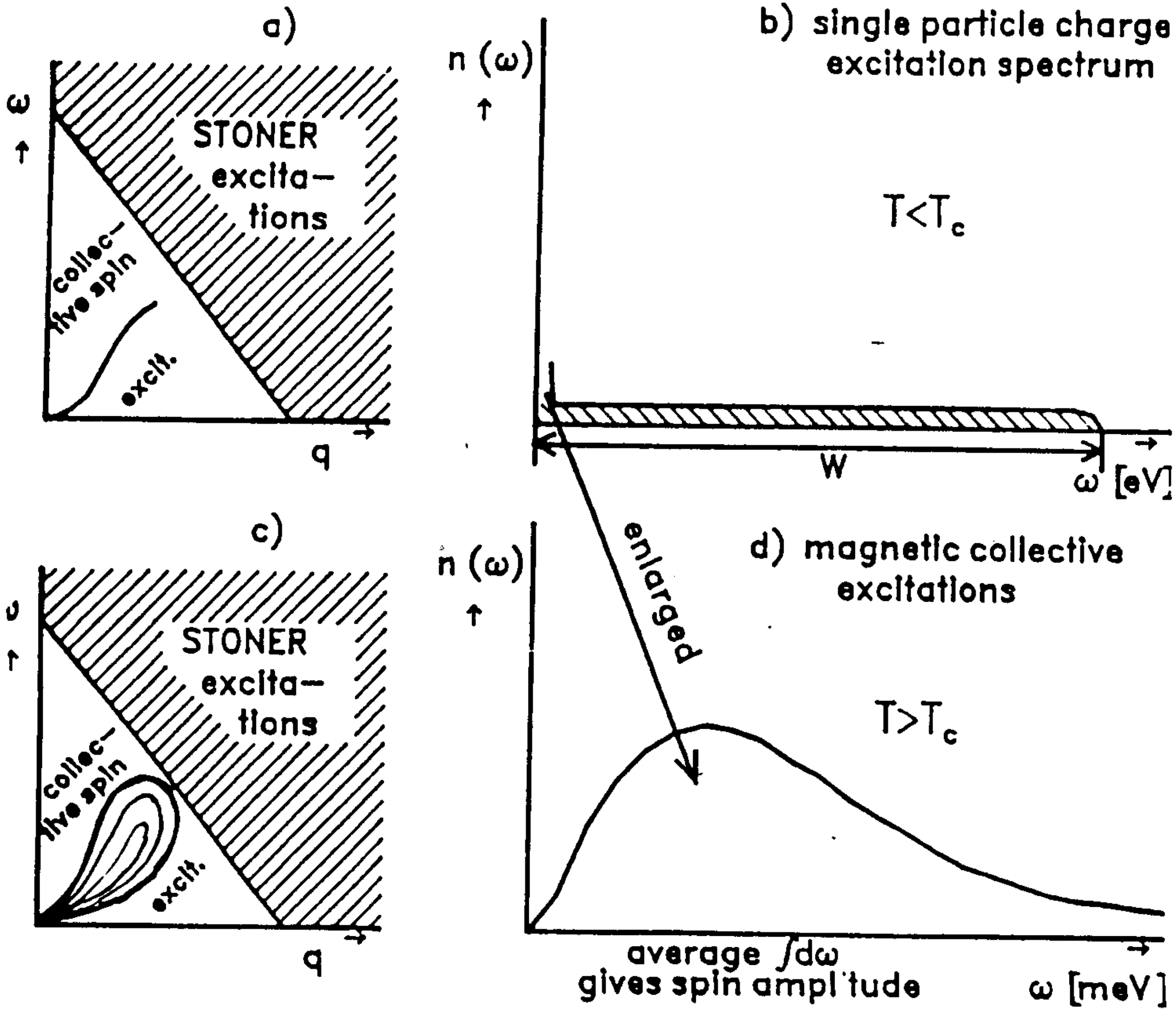


resulting spin dynamics after averaging process
well described with constant spin amplitude ~~and~~ only angular freedom

Examples:
Transition metal
oxides

MnO, NiO, ... CuO

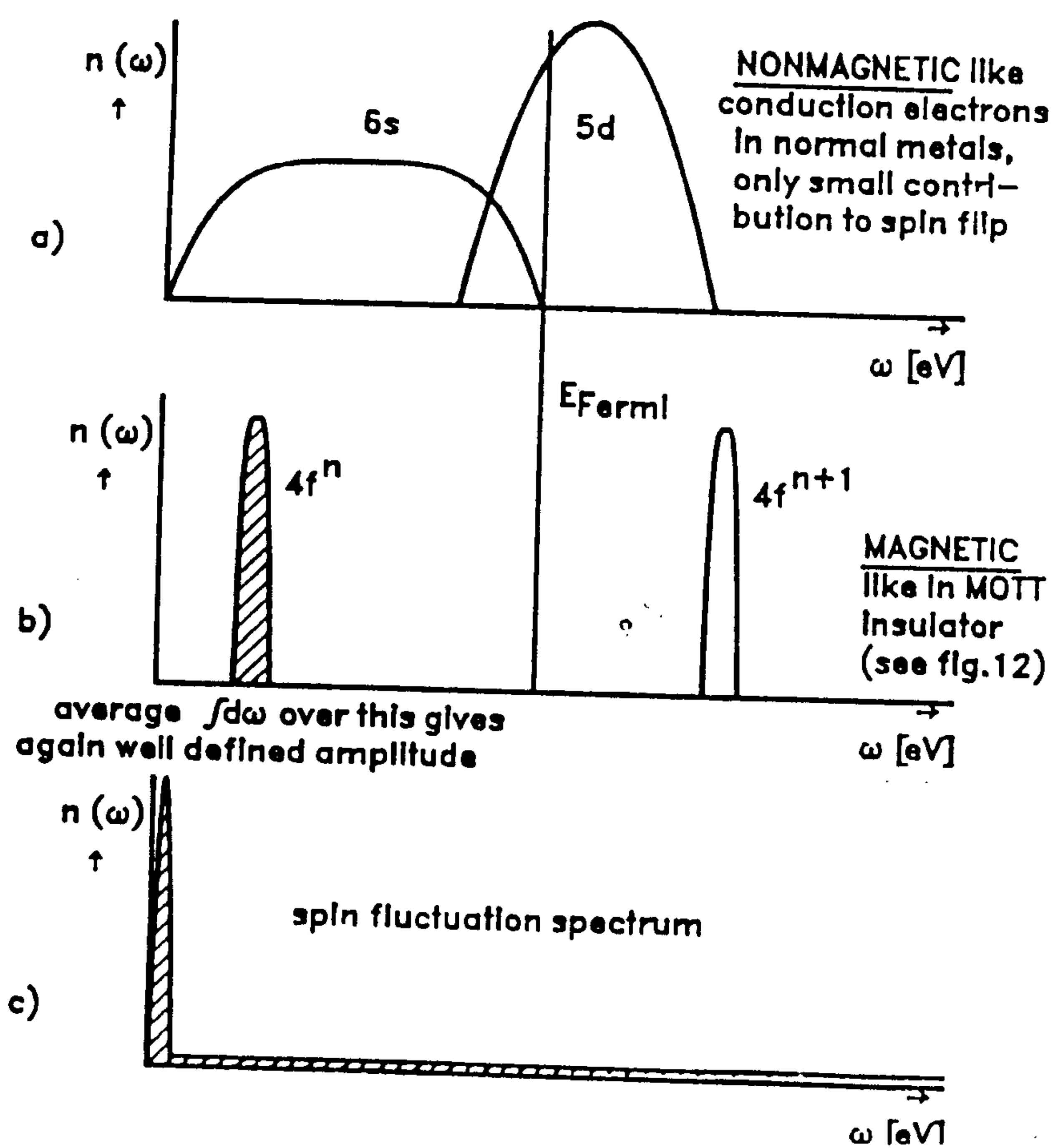
plitude in magnetic insulators of the Mott type, hopping curs virtually over times D^{-1} or J^{-1} respectively (as a



Examples:
Transition meta[...]
Fe, Ni (ferro[...]
Cr (antiferrom[...]

Amplitude fluctua[...]
possible!

Definition of amplitude in itinerant systems. Here already charge excitations are possible in the conduction band even



Examples:

Rare earth metals

Speculations: HTS

Oxygen electrons ≙ non[...] conduction [...]

Cu - electrons ≙ magnet[...] moments

$$S(q,\omega) \sim \sum_{ij} \int dt\, e^{i\omega t} e^{i\vec{q}(\vec{R}_i - \vec{R}_j)} \langle \vec{S}_i \cdot \vec{S}_j(t) \rangle$$

Sum rule:

$$\int_{-\infty}^{+\infty} d\omega \sum_q S(q,\omega) \sim N \langle \vec{S}^2 \rangle = N\, S(S+1)$$

"Magnetic moments exist" (= are useful concept)

if $\int_{-\Omega}^{+\Omega} d\omega \sum_q S(q,\omega)$ is sizable fraction of total intensity $N\,S(S+1)$

for $\Omega \ll$ charge excitation energy $\sim$ eV

Experimentally accessible ω integration

$\omega \lesssim 30$ meV

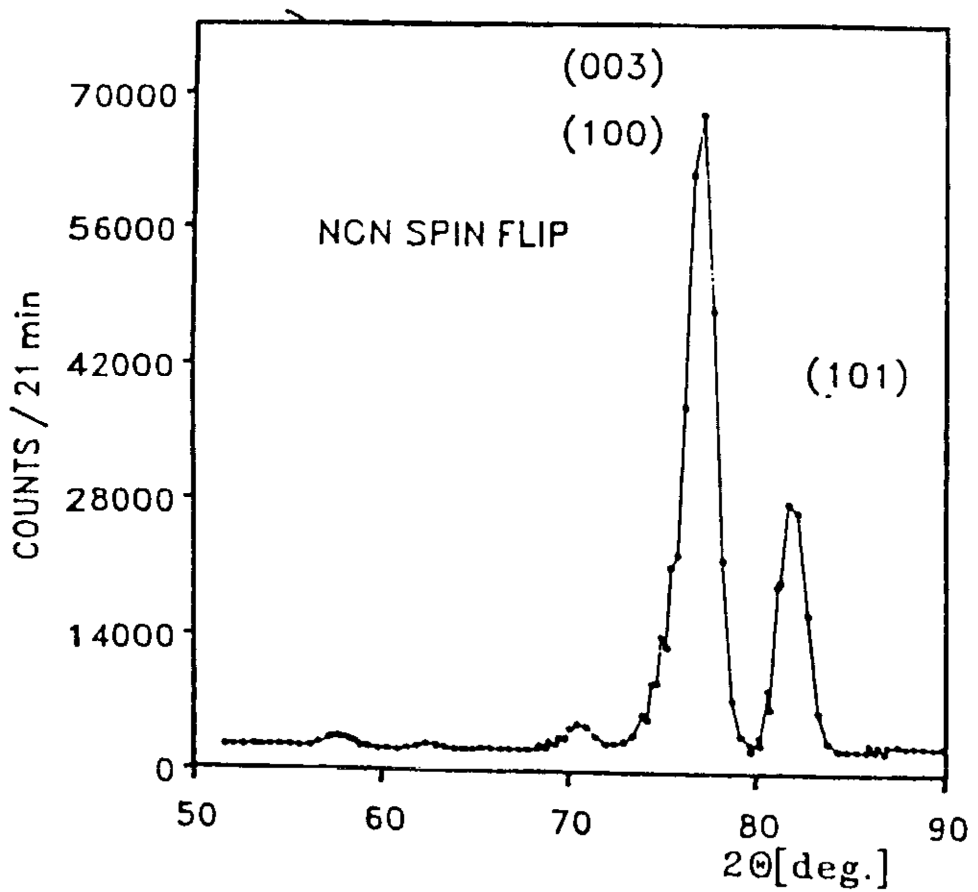
Magnetic intensity is weak compared to phonon intensity.

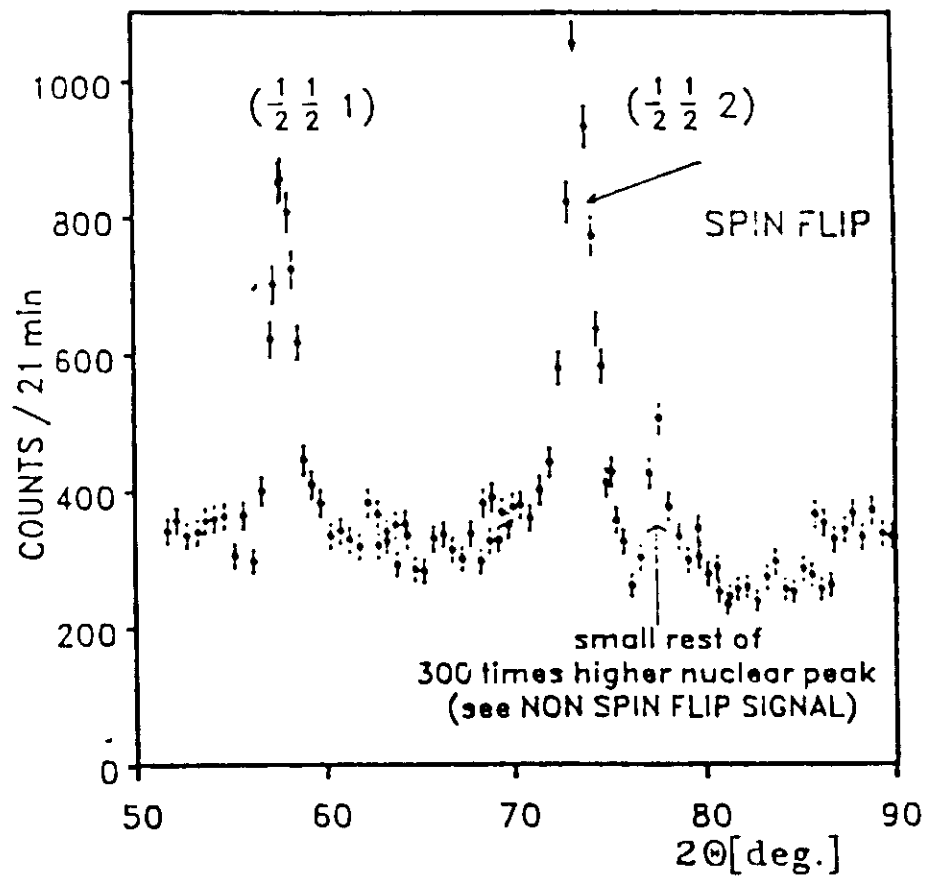
→ Polarized neutrons + polarization analysis necessary for quantitative measurements.

$YBa_2Cu_3O_{\sim 6.1}$, (sample from Philips Research Lab. Aachen.)

Low T, antiferromagnetic order

ordered moment ~ .6 – .7 μ_B





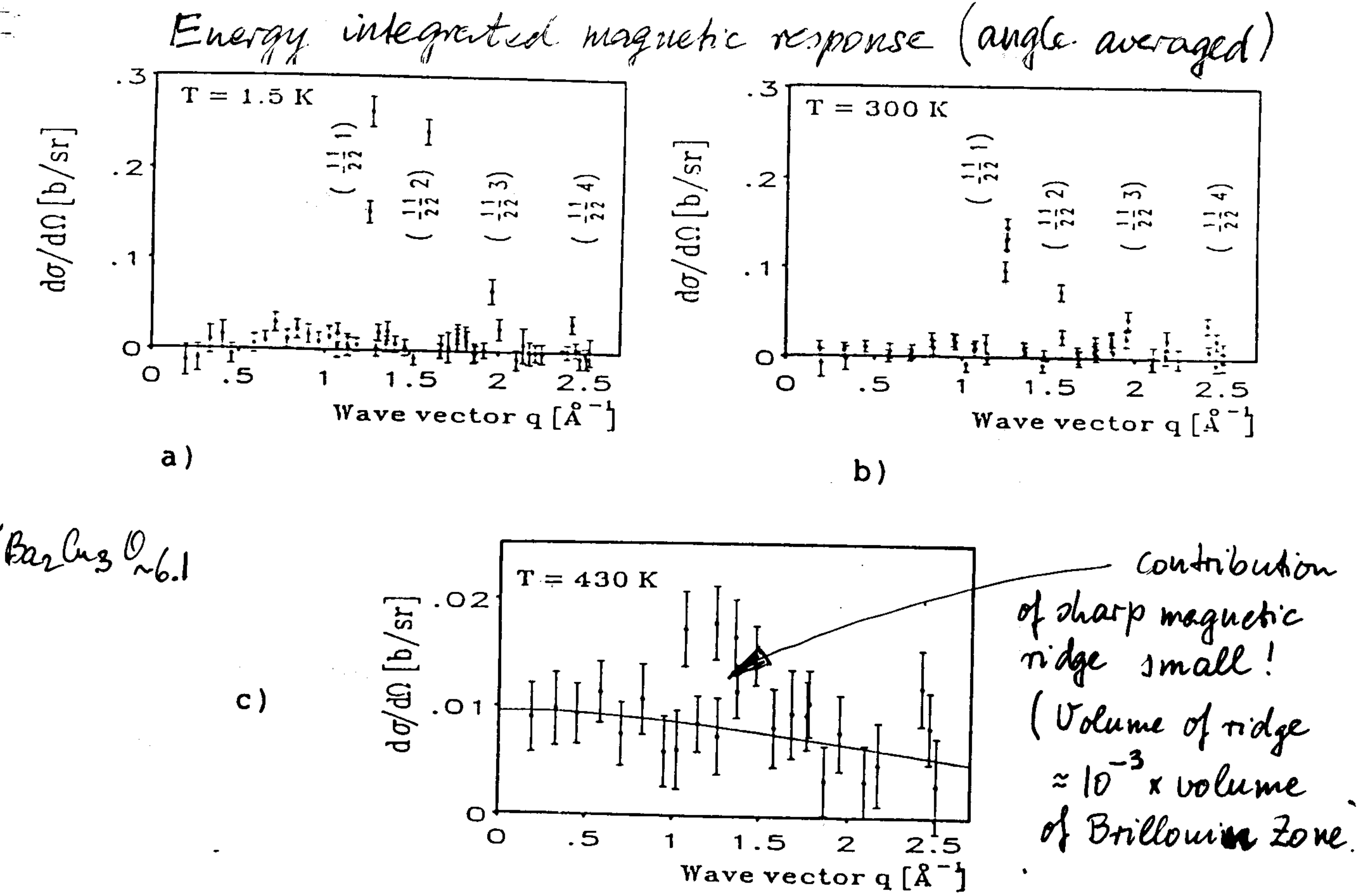
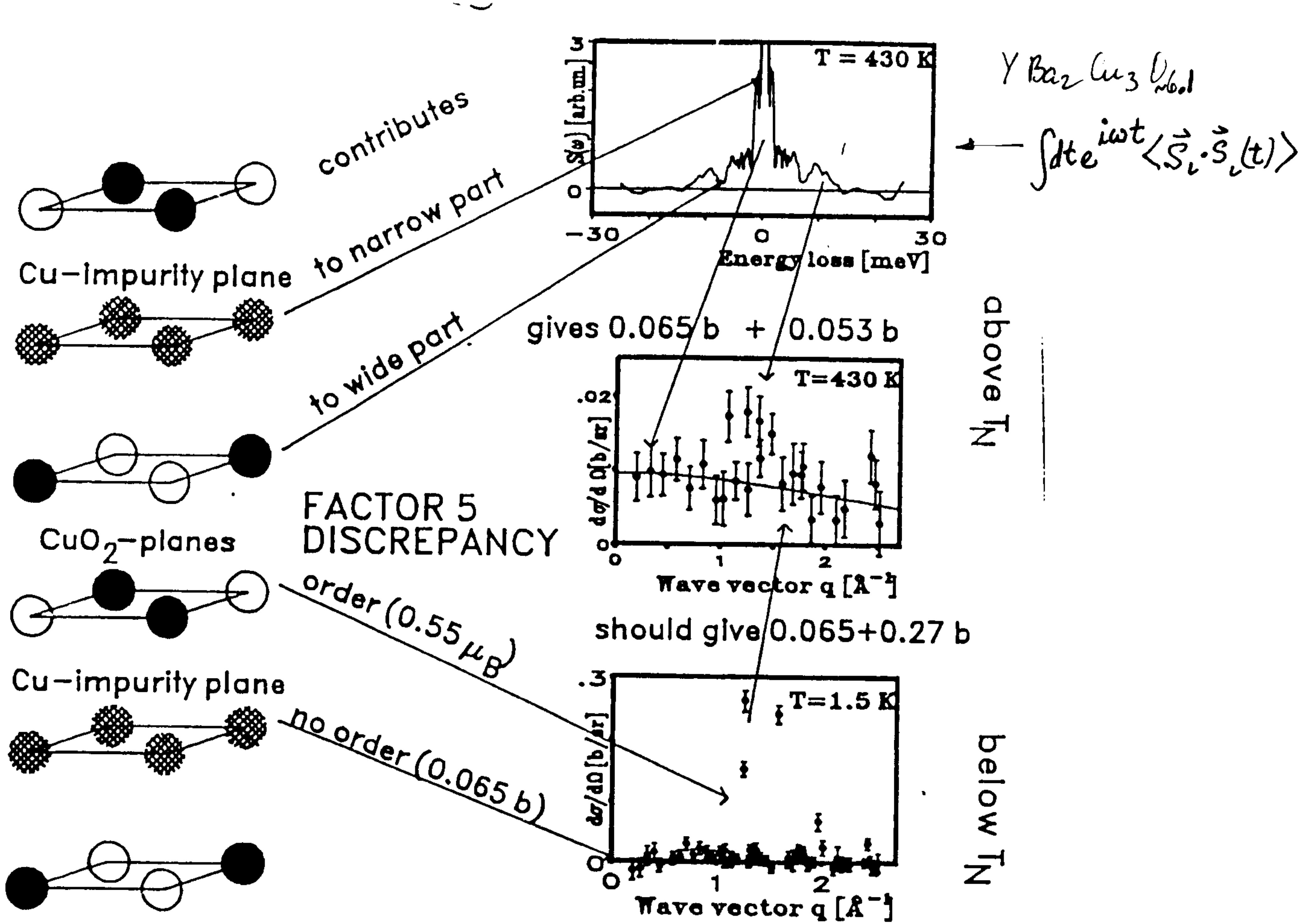


Fig.5 Paramagnetic cross section in b/sr measured between the

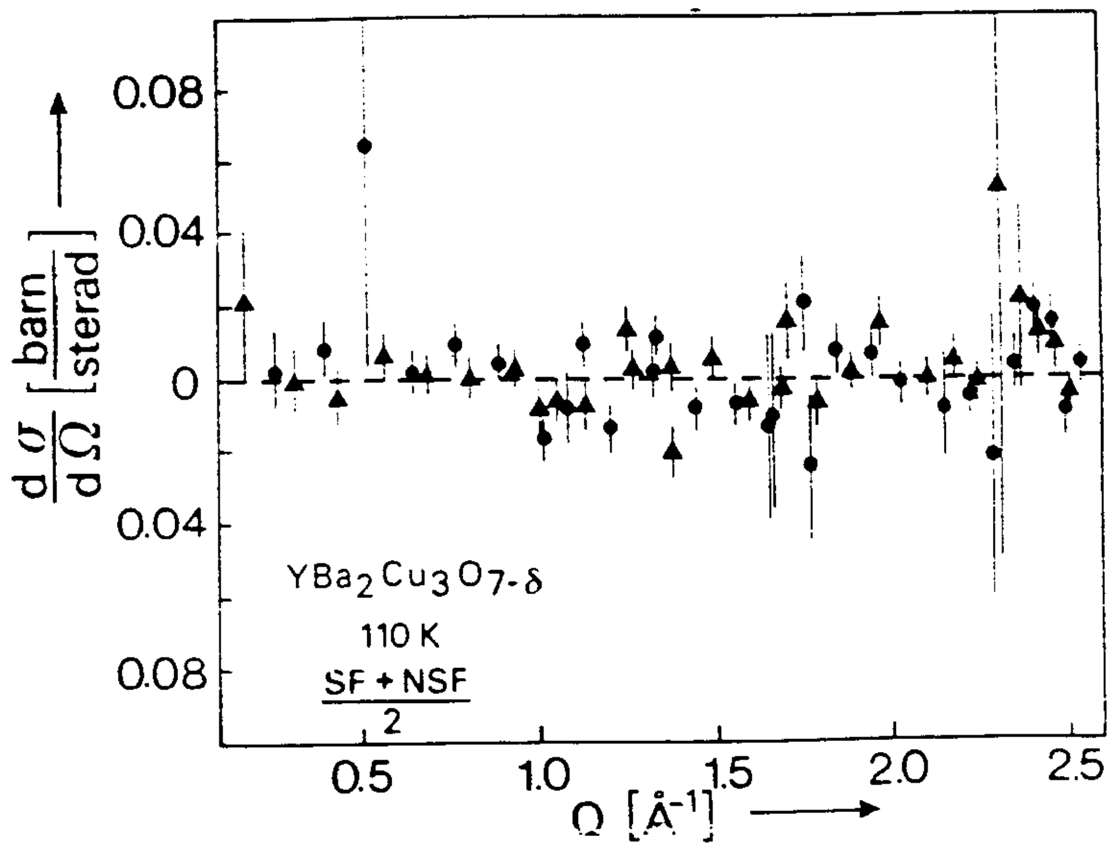


Y Ba$_2$ Cu$_3$ O$_{\sim 6.1}$
$\int dt e^{i\omega t} \langle \vec{S}_i \cdot \vec{S}_i(t) \rangle$
T = 430 K
S(ω) [arb.un.]
Energy loss [meV]
contributes
to narrow part
Cu-impurity plane
to wide part
gives 0.065 b + 0.053 b
T=430 K
dσ/dΩ [b/sr]
Wave vector q [Å^{-1}]
above T_N
CuO$_2$-planes
FACTOR 5
DISCREPANCY
order (0.55 μ_B)
should give 0.065+0.27 b
Cu-impurity plane
no order (0.065 b)
T=1.5 K
dσ/dΩ [b/sr]
Wave vector q [Å^{-1}]
below T_N

Results: $YBa_2Cu_3O_{6.9}$

$I_{exp} = 0$: No magnetism!

Error bar?



Compare intensity of Cu-spins ½ in energy window Ω. (What percentage of Cu-atoms can carry a spin within the energy window Ω?)

T = 110 K: $N_{Cu}(s=1/2;\ \Omega=12\,meV) < 1\%$

T = 300 K: $N_{Cu}(s=1/2;\ \Omega=25\,meV) < 2.5\%$

Total intensity of magnetic fluctuations
in energy range $\hbar\omega < 30$ meV
is extremely small in $YBa_2Cu_3O_{6.92}$!
$I(< 30\,\text{meV}) < 2.5\%$ of $N S(S+1)$ for $S = 1/2$.

Higher energy excitations? Yes, because of
sum rule.

But: For $\hbar\omega_{magn} \sim \hbar\omega_{charge} \sim$ eV

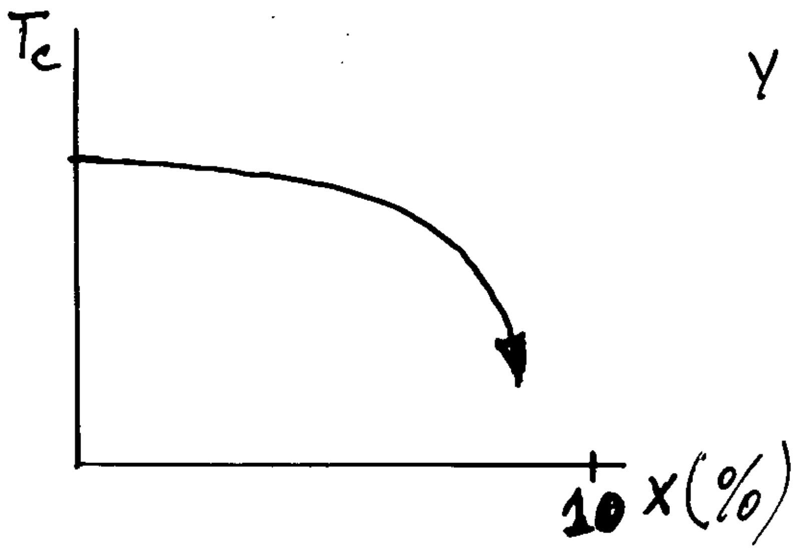
"magnetic moments" no useful concept.
"No magnetic moments" but
electrons with <u>charge and spin</u>.

CuO_2 planes are magnetic for $YBa_2Cu_3O_6$,
but have no well defined magnetic
moments for superconducting $YBa_2Cu_3O_7$

Fe has "large" magnetic moment ($S = 2$, or $5/2$).

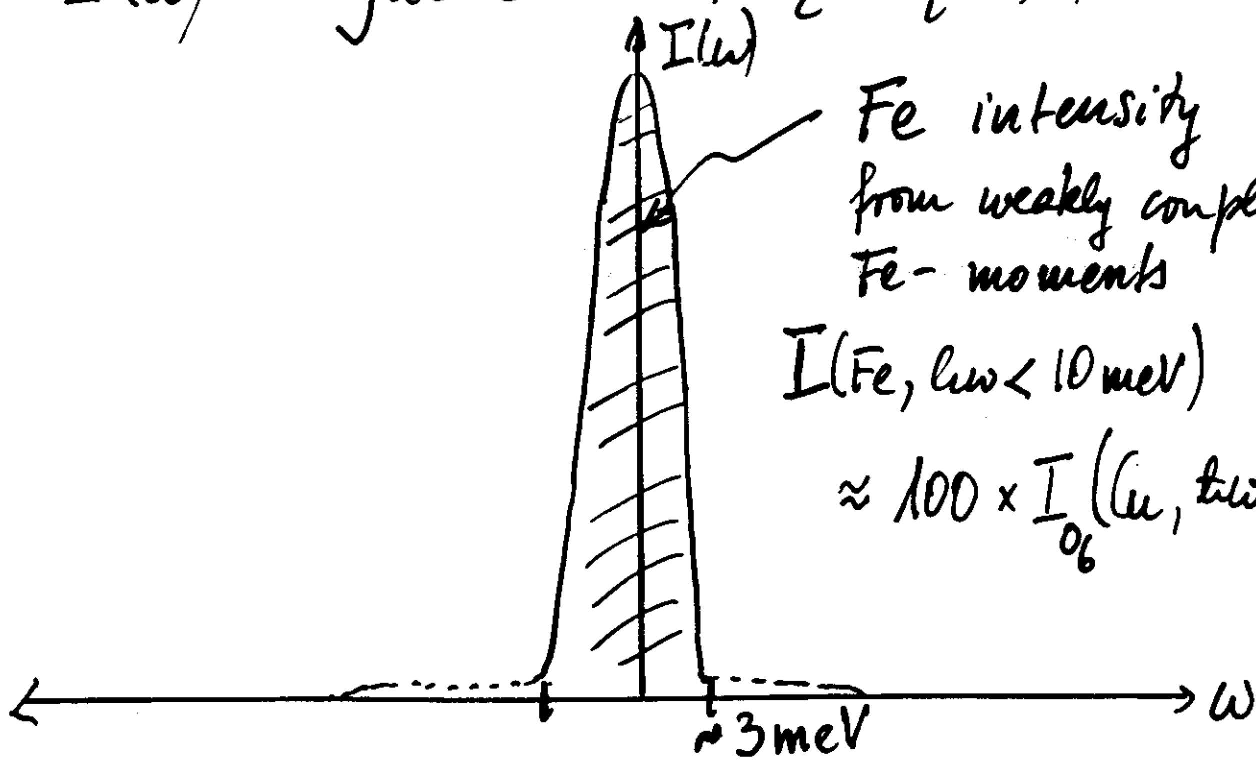
Total intensity $\sim S(S+1)$

$$I_{tot}(Fe) \gg I_{tot}(Cu)$$



$YBa_2Cu_{3-x}Fe_xO_{\sim 7}$

$$I(\omega) = \int dt\, e^{i\omega t} \langle \vec{S}_i \cdot \vec{S}_i(t) \rangle$$



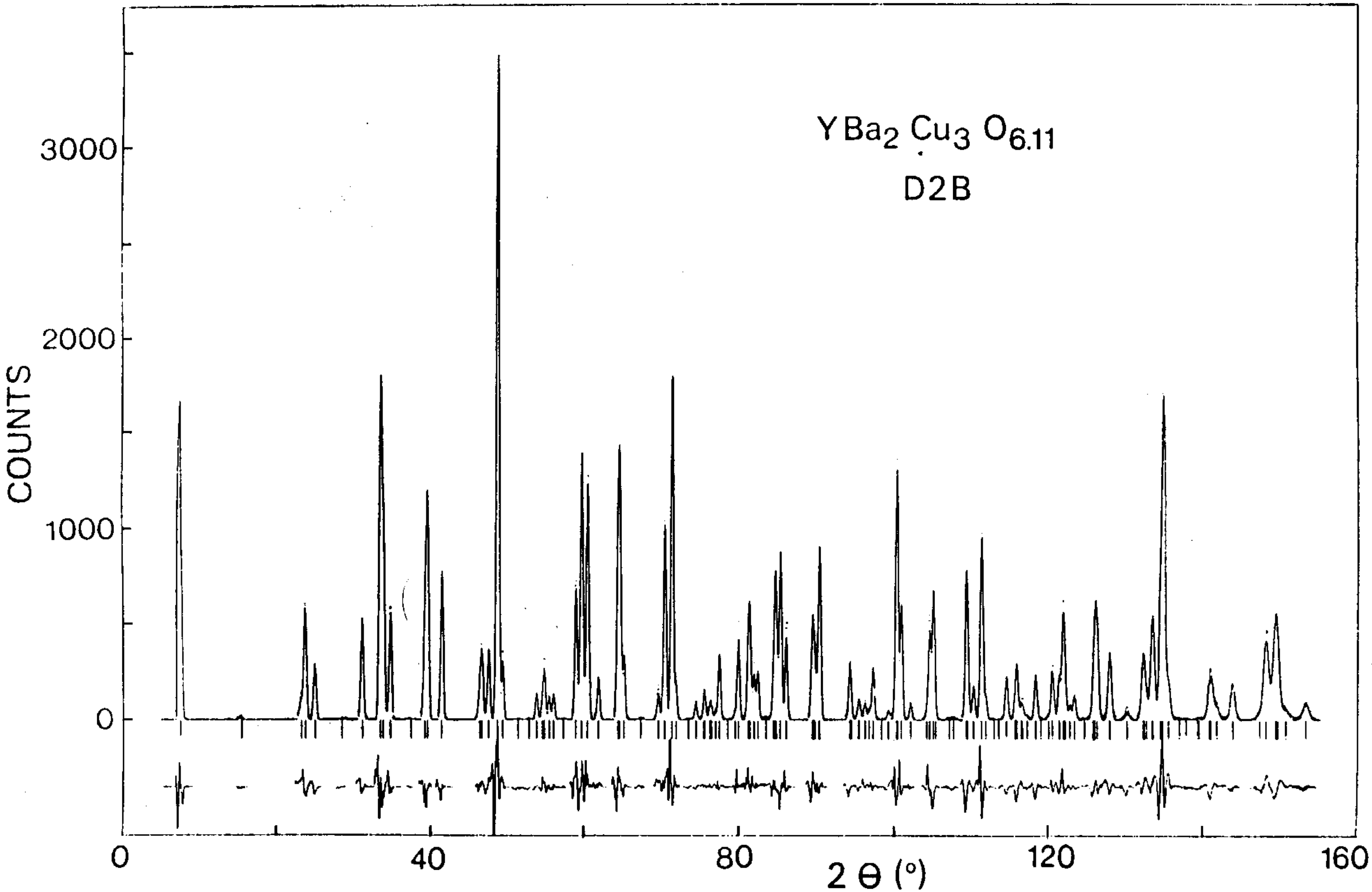
$$I(Fe, \hbar\omega < 10\,meV) \approx 100 \times I_{06}(Cu, \hbar\omega < 10\,meV)$$

Similar behaviour for Cu-spins in intermediate concentrations

$\sim YBa_2Cu_3O_{\sim 6.4}$

Cu-moments in chains are "weakly coupled impurity moments".

Total intensity of magnetic fluctuations in chains (impurity) for $\hbar\omega < 10$ meV is large compared to total intensity of CuO_2 planes!


YBa2 Cu3 O6.11
D2B
COUNTS
0
1000
2000
3000
0
40
80
120
160
2 θ (°)