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EXPERIMENTAL WORKSHOP ON
HIGH TEMPERATURE SUPERCONDUCTORS
(11 - 22 April 1988)

APPLICATIONS OF NUCLEAR RESONANCE TECHNIQUES IN HIGH T_c SUPERCONDUCTORS

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Nuclear Magnetic Resonance (NMR)

A PHENOMENON observed in materials which have NUCLEI possessing magnetic moments.

RESONANCE → In tune with a natural frequency of the nuclear magnetic moments

→ In the present context →
This NATURAL FREQ. ⟹ corresponds to the freq. of gyroscopic precession of these moments in the magnetic field which they 'see' at their site.

All NUCLEI do not have magnetic moment. For instance ^{16}O nucleus has ZERO moment.

→ TABLE of NUCLEAR MOMENTS

The values of NUCLEAR MOMENTS ~ $\frac{1}{2000}$ those of electronic moments of ions.

→ Pauli first suggested that ATOMIC NUCLEI should have ANGULAR MOMENTUM and a MAGNETIC MOMENT (1924.)

NMR-Table for Isotopes of interest in HIGH-Tc WORK

Isotope (* → radio-active)	Mag. Resonance Freq. (MHz) in 10 kG. field	Natural abundance (%)	Spin in $\hbar$	Mag. moment in n.b. mag.	eQ in 10^{-24} cm^2
^1n*	29·165	····	1/2	−1·9130	····
^1H	42·577	99·9844	1/2	+2·7927	····
^7Li	16·547	92·57	3/2	3·256	$-4·2\times10^{-2}$
^{17}O	5·772	$3·7\times10^{-2}$	5/2	−1·8930	-4×10^{-3}
^{19}F	40·055	100	1/2	2·6273	····
^{25}Mg	2·606	10·05	5/2	−0·8547	····
^{27}Al	11·094	100	5/2	3·6385	0·149
← ^{39}K	1·987	93·08	3/2	0·3909	···
^{51}V	11·193	100	7/2	5·1392	0·3
^{55}Mn	10·553	100	5/2	3·4610	0·5
^{63}Cu	11·285	69·09	3/2	2·2206	−0·15
^{65}Cu	12·090	30·91	3/2	2·3790	−0·14
^{67}Zn	2·635	4·12	5/2	0·8735	···
^{69}Ga	10·218	60·2	3/2	2·0108	0·2318
^{71}Ga	12·984	39·8	3/2	2·5549	0·1461
^{87}Sr	1·845	7·02	9/2	−1·0893	···
^{89}Y	2·086	100	1/2	−0·1368	····
^{113}In	9·310	4·16	9/2	5·496	1·144
→ ^{45}Sc	10·343	100	7/2	4·7491	···

Isotope	Mag. Resonance Freq. (MHz) in 10 kG	Natural abundance (%)	Spin in $\hbar$	Mag. Moment in n.b.mag.	eQ in 10^{-24} cm^2
^{203}Tl	24·33	29·52	½	1·5960	---
^{205}Tl	24·57	70·48	½	1·6114	
^{209}Bi	6·842	100·0	9/2	4·0389	−0·4

These are particularly of interest in the NEW high-T_c materials.

Bismuth-NQR should possibly be tried.

RARE-EARTH NUCLEI

^{139}La	6·014	99·911	7/2	2·7615	0·9
^{151}Eu	10·0	47·77			

MATERIALS, which are otherwise diamagnetic, exhibit a weak paramagnetism arising due to the nuclear magnetic moments.

Nuclear Paramagnetism was first measured by (1·76K – 4·22K) Lasarew & Schubnikow, Phys. Z. Sowjet 11, 445 (1937) in SOLID HYDROGEN. They measured static magnetization by the usual $\chi(T)$ technique.

The nuclear paramagnetic contribution was DISTINGUISHED from the electronic diamagnetic contribution by its temp. variation.

Expt yielded $\mu_p \simeq$ within 10% ←

DEMONSTRATED THE EXISTENCE OF NUCLEAR MAGNETISM by a conventional magnetic method and ALSO

→ { NUCLEAR MAGNETIC MOMENTS attained THERMAL EQUILIBRIUM.

The advantage of the resonance technique is that it enables one to select out of the total magnetic susceptibility, a particular contribution of interest; one that may, for example, be relatively very weak.

The most spectacular examples of this kind, no doubt, are the observation of the feeble NUCLEAR PARAMAGNETISM of, say, Iron nuclei in iron metal against the background of enormously large electronic ferromagnetism.

Elementary Ideas of NMR(x):

$$\mathcal{H} = -\vec{\mu}\cdot\vec{H}_0$$ — Hamiltonian of a 'bare' nucleus in a d.c. mag. field $\vec{H}_0$

$$= -\gamma\hbar I_z H_0 \quad (\vec{\mu} = \gamma\hbar\vec{I})$$

$$E_m = -\gamma\hbar H_0 m$$

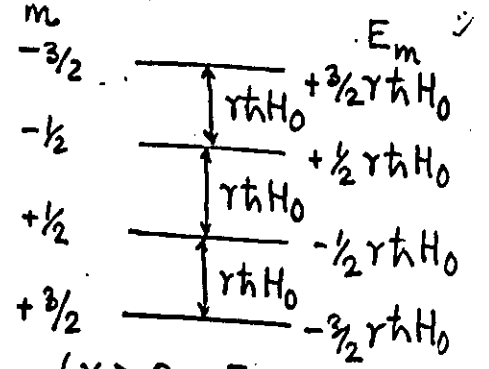
$(m = I, I-1, \ldots -I)$

$$\Delta E = \gamma\hbar H_0$$

(x) See for example, books by
① A. Abragam. &
② C.P. Slichter } on NMR.

To excite the transitions among these levels, one needs an interaction such that energy is conserved in the transition

$$\boxed{\hbar\omega = \Delta E}$$



($\gamma > 0$. For $\gamma < 0$, one can suitably modify the diag.)
Energ-level diagram for $I = 3/2$ (for Na, Cu, Cl. etc.)

and also the interaction must connect (have NON ZERO matrix element) the initial and final state

$$\mathcal{H}_{pert} = -\gamma\hbar I_x H_{1x}\cos\omega t$$

The operator I_x has matrix elements between states m and m', $(m|I_x|m')$ which are non zero for $m' = m \pm 1$.

→ Exc: Construct matrix-representations of I_x, I_y, I_+ and I_- for $I = 5/2$

Consequently, the allowed transitions are between levels, ADJACENT in energy

$$\hbar\omega = \Delta E = \gamma\hbar H_0$$

or $\boxed{\omega = \gamma H_0}$ ← Resonance condition.

Note that Planck's constant has disappeared from the resonance equation.
This fact suggests → result closely related to a classical picture

The essential elements in NMR, therefore, ARE:

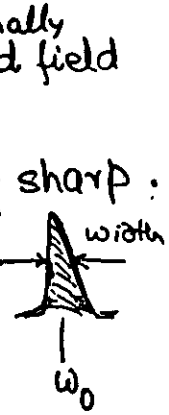
1. A nuclear system with nuclei having non-zero magnetic moment
2. A dc magnetic field to split the NUCLEAR levels
3. An alternating field to excite transitions among these levels.

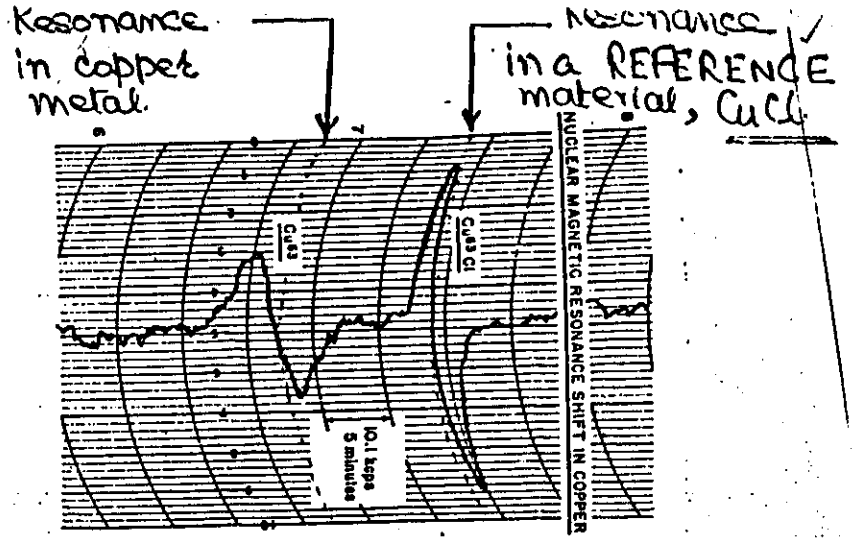
The resonance condition

$\boxed{\omega = \gamma H_0}$; H_0 = Externally Applied field

is for a 'bare' nucleus.

→ NO resonance line is perfectly sharp.
Factors governing the width will be of interest.
The width may arise due to the interaction of the nuclei with their surroundings as well as among themselves.





Knight-shift of ^{63}Cu nucleus in copper metal (From the original work of W.D. Knight)

$\frac{\Delta H}{H}$ (for copper nuclei in copper metal)

$= 0.23\%$

In metals, studies of Knight shift has led to a deeper understanding of various phenomena; SUPERCONDUCTIVITY is one of them.

Nuclear Magnetization in THERMAL EQ'LBM:

Consider an assembly of identical weakly interacting nuclei of spin I, in thermal equilibrium at a temp. T in a steady mag. field H_0.

1. $E_m = -\gamma\hbar H_0 m$

2. N(m) = number of nuclear moments /vol. in state m, the relative populations are determined by

3. $\frac{N(m)}{N(m')} = \exp\left(\frac{E_{m'} - E_m}{kT}\right)$

$\cong 1 + \frac{E_{m'} - E_m}{kT}$ → [$\because x = \frac{\gamma\hbar H_0}{kT} \ll 1$ for weak fields & T >> ...]

4. $N(m) = \frac{N_0}{2I+1}\left(1 + \frac{m.\gamma\hbar H_0}{kT}\right)$

where N_0 = Total no. of spins /vol.

$$\left\{ \sum_{m=-I}^{I} N(m) = N_0 \right\}$$

→ Mag./vol. M_0 is given by

$$M_0 = \sum_{-I}^{I} N(m).\, m\gamma\hbar = \sum_{-I}^{I} \frac{N_0}{(2I+1)}\left(m\hbar\gamma I - \frac{H_0}{kT}\right)$$

$$= \frac{N_0 H_0 \gamma^2\hbar^2}{kT(2I+1)} \sum_{-I}^{I} m^2 \rightarrow \left[= \tfrac{1}{3} I(I+1)(2I+1)\right]$$

$$= \frac{N_0 H_0 \gamma^2\hbar^2 I(I+1)}{3kT}$$

Thus

$$\chi_0 = \frac{M_0}{H_0} = \frac{N_0\gamma^2\hbar^2 I(I+1)}{3kT}$$

This is $\sim 10^{-10}$ or 10^{-11} emu/cc. at R.T.

This means that the nuclear paramagnetism is swamped by the electronic diamagnetism, or by the electronic paramagnetism if it is present.

Of course, detecting directly the nuclear paramagnetism in magnetic materials is certainly not possible.

It is in this sense that the measurements of Lasarew and Schubnikow (1937) of nuclear paramagnetism of protons in solid hydrogen are very important and instructive.

This is particularly important considering the fact that early calculations of the relaxation time T_1 in, for example ionic crystals, suggested impossibly long (T_1).

Relaxation Times T_1 and T_2 and Block's Equations :

The spin system cannot approach a thermal equilibrium without contact to a reservoir. In the present context it is called 'lattice'.

T_1 = characteristic time associated with the approach to thermal equibrium with the 'lattice'. It is called

SPIN-LATTICE RELAXATION TIME

For example, if we deal with a sample that is initially unmagnetized, the magnetization process is described by an exponential rise to the Eqbm:

$$M(t) = M_0 (1 - e^{-t/T_1})$$

The diff. equation $M_z(t)$ follows is (?)

$$\frac{dM_z}{dt} = \frac{M_0 - M_z}{T_1}$$

There is another relaxation time that is introduced in NMR-phenomenology:

SPIN-SPIN RELAXATION TIME

This relaxation process is required.

to ensure that in thermal equilibrium under a static field, the magnetization will vanish in the x- and y- directions; i.e. The thermal magnetization will be parallel to H_0

$$\frac{dM_x}{dt} = -\frac{M_x}{T_2} \; ; \; \frac{dM_y}{dt} = -\frac{M_y}{T_2}$$

This means, $M_x(t)$ and $M_y(t)$, once produced, will decay to ZERO exponentially.

Notice that: T_1 — involves exchange of energy between the spin system and the lattice

T_2 — involves the destruction of coherence of the phases of various magnetic

Bloch Equations :

In the eqn. of motion

$$\frac{d\vec{M}}{dt} = \gamma \vec{M} \times \vec{H}$$

we introduce the relaxation effects as well to describe the 'complete' time-evolution of the three components:

$$\frac{dM_z}{dt} = \gamma (\vec{M}\times\vec{H})_z + \frac{M_0 - M_z}{T_1}$$
$$\frac{dM_x}{dt} = \gamma (\vec{M}\times\vec{H})_x + \left(-\frac{M_x}{T_2}\right)$$
$$\frac{dM_y}{dt} = \gamma (\vec{M}\times\vec{H})_y + \left(-\frac{M_y}{T_2}\right)$$

Bloch Equations

$\vec{H}$ includes the rotating RF-field also.

$\Longrightarrow$ Solution of the Bloch Equations for H_1 (NO NONLINEAR EFFECTS, SATURATION IS AVOIDED)

It is instructive to write them in the rotating frame (to get rid of the time dependence of RF-field in the lab-frame)

$$\frac{d\vec{M}}{dt} = \vec{M}\times\gamma\left[\left(H_0 - \frac{\omega}{\gamma}\right)\hat{k} + H_1\hat{i}\right] + \frac{M_0 - M_z}{T_1}\hat{k} - \frac{M_x}{T_2}\hat{i} - \frac{M_y}{T_2}\hat{j}$$

$$\frac{dM_z}{dt} = -\gamma M_y H_1 + \frac{M_0 - M_z}{T_1}$$
$$\frac{dM_x}{dt} = \gamma M_y h_0 - \frac{M_x}{T_2}$$
$$\frac{dM_y}{dt} = \gamma\left[M_z H_1 - M_x h_0\right] - \frac{M_y}{T_2}$$

Here $h_0 = H_0 - \frac{\omega}{\gamma}$

Since M_x and M_y must vanish as $H_1 \to 0$ (we are considering linear effects in H_1), it follows from the $\dot{M}_z$ equation, that in the steady state ($\dot{M}_z = 0$), M_z differs from M_0 to order H_1^2. We, therefore, replace M_z by M_0 in the last eqn.

We also define

$$M_+ = M_x + iM_y$$

Adding 2nd Eqn. to i times the last eqn.,

$$\frac{dM_+}{dt} = -M_+\kappa + i\gamma M_0 H_1$$

where $\kappa = \frac{1}{T_2} + i\gamma h_0$

$$\Rightarrow M_+ = Ae^{-\alpha t} + \frac{i\gamma M_0 H_1}{\frac{1}{T_2} + i\gamma h_0}$$

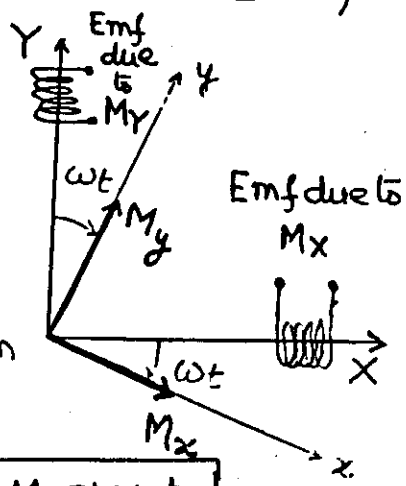
Transient

$$M_x = \chi_0 \omega_0 T_2 \frac{(\omega_0 - \omega)T_2}{1 + (\omega - \omega_0)^2 T_2^2} H_1$$
$$M_y = \chi_0 \omega_0 T_2 \frac{1}{1 + (\omega - \omega_0)^2 T_2^2} H_1$$

where $M_0 \to \chi_0 H_0$; $\omega_0 = \gamma H_0$

These equations show that the magnetization is a constant in the rotating frame, and therefore is rotating at frequency ω in the laboratory.

The coil, along the X-axis of the lab frame, will pick up the emf induced due to the variation in the X-component of the magnetization which is:



$$\rightarrow M_x(t) = M_x \cos\omega t + M_y \sin\omega t$$

Also

$$\rightarrow M_y(t) = -M_x \sin\omega t + M_y \cos\omega t$$

Now in actual practice, we apply a linearly polarized oscillating field

$$H_x(t) = H_{x_0} \cos\omega t \,, \quad H_{x_0} = 2H_1$$

$\therefore$ $H_x(t) \rightarrow$ induces magnetization in X- as well as Y- direction

Also $\rightarrow$ induces both 'in-phase' and 'out-of-phase' time dependent components.

One introduces susceptibilities χ' and χ'' as:

$$\rightarrow M_x(t) = [\chi'(\omega)\cos\omega t + \chi''(\omega)\sin\omega t] H_{x_0}$$

Then, we have

$$\chi'(\omega) = \frac{\chi_0}{2}(\omega_0 T_2)\frac{(\omega_0-\omega)T_2}{1+(\omega-\omega_0)^2 T_2^2}$$

$$\chi''(\omega) = \frac{\chi_0}{2}(\omega_0 T_2)\frac{1}{1+(\omega-\omega_0)^2 T_2^2}$$

It is convenient to regard both $M_x(t)$ and $H_x(t)$ as being the real parts of complex functions $M_x^c(t)$ & $H_x^c(t)$. Then defining the complex susceptibility χ as

$$\boxed{\chi(\omega) = \chi'(\omega) - i\chi''(\omega)}$$

and writing

$$H_x^c(t) = H_{x_0} e^{i\omega t}$$

$$\rightarrow M_x^c(t) = \chi H_x^c(t)$$

or $M_x(t) = \mathrm{Re}[\chi(\omega) H_x^c(t)]$

$$= \mathrm{Re}[\chi'(\omega) - i\chi''(\omega)] H_{x_0} e^{i\omega t}$$

Similarly, in terms of these susceptibilities:

$$\rightarrow M_y(t) = -M_x \sin\omega t + M_y \cos\omega t$$

$$= [-\chi'(\omega)\sin\omega t + \chi''(\omega)\cos\omega t] H_{x_0}$$

Electric Quadrupole Effects

So far we have considered interaction of the nuclear magnetic dipole moment with the magnetic field at the nuclear site. Energy of this interaction is orientation dependent

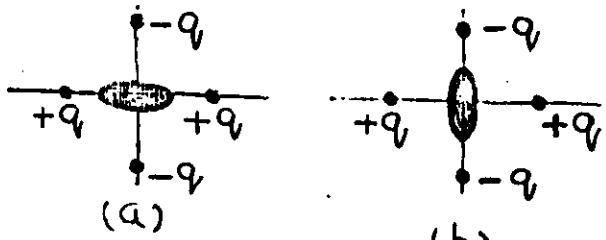
$$E(\theta) = -\vec{\mu}\cdot\vec{H}$$

$$= -\mu H\cos\theta \quad \text{(classical)}$$

which leads to the splitting of nuclear levels (for various m-values).

For nuclei with non-spherical charge distribution, electrostatic interaction between nucleus and its surroundings can also lead to orientation dependent energy which, in turn, gives rise to splitting of the nuclear levels.

For instance :



$$E_{(b)} < E_{(a)}$$

(+) From C.P.S Littler's book, 6th Chapter

Classically, the interaction energy E of a charge distribution of density ρ with a potential V due to external sources is

$$E = \int \rho(\vec{r})\, V(\vec{r})\, d\vec{r}$$

$$V(\vec{r}) = V(0) + \sum_{\alpha} x_\alpha \frac{\partial V}{\partial x_\alpha}\Big)_{\vec{r}=0} + \frac{1}{2!}\sum_{\alpha,\beta} x_\alpha x_\beta \frac{\partial^2 V}{\partial x_\alpha \partial x_\beta}\Big)_{\vec{r}=0} + \cdots\cdots$$

where x_α ($\alpha = 1, 2, 3$) stand for x, y, z.

Defining

$$V_\alpha \equiv \frac{\partial V}{\partial x_\alpha}\Big)_{\vec{r}=0}$$

$$V_{\alpha\beta} \equiv \frac{\partial^2 V}{\partial x_\alpha \partial x_\beta}\Big)_{\vec{r}=0}$$

we can write

$$E = \underset{1}{V(0)\int \rho\, d\vec{r}} + \underset{2}{\sum_\alpha V_\alpha \int x_\alpha \rho\, d\vec{r}} + \underset{3}{\sum_{\alpha,\beta} V_{\alpha\beta}\int x_\alpha x_\beta \rho\, d\vec{r}} + \cdots\cdots$$

Choosing the origin at the mass centre of the nucleus, we have :

1st Term – electrostatic energy of the nucleus taken as a point charge. Not of interest
E(0)

2nd Term – Interaction of the electric dipole moment of the nucleus
E(1)
Nuclei do have a definite parity. Also nucleus in Eqbm experiences ZERO average electric field.

⇓

This TERM VANISHES

3rd Term – Electric Quadrupole term
E(2)
with which we are now concerned.

$V_{\alpha\beta}$ = Electric field gradient tensor; can always be diagonalized. In its principal frame of Reference,

$$V_{\alpha\beta} = 0 \quad \text{for } \alpha \neq \beta$$

Moreover, V satisfies LaPlace Eqn:

$$\nabla^2 V = 0$$

If the nuclear site has cubic symtry i.e. $V_{xx} = V_{yy} = V_{zz} = 0$
The quadrupole coupling term VANISHES

Instead of the integrals $\int x_\alpha x_\beta \rho\, d\vec{\tau}$, it is convenient to consider $Q_{\alpha\beta}$

$$Q_{\alpha\beta} = \int [3x_\alpha x_\beta - \delta_{\alpha\beta} r^2] \rho\, d\vec{\tau}$$

$$\int x_\alpha x_\beta \rho\, d\vec{\tau} = \tfrac{1}{3}\left[Q_{\alpha\beta} + \int \delta_{\alpha\beta} r^2 \rho\, d\vec{\tau}\right]$$

↓

This does not depend on the NUCLEAR ORIENTATION

Thus the quadrupole term E(2) may be written as:

$$E(2) = \frac{1}{2}\sum_{\alpha,\beta} V_{\alpha\beta} \int x_\alpha x_\beta\, d\vec{\tau}$$

$$= \frac{1}{6}\sum_{\alpha,\beta}\left[V_{\alpha\beta} Q_{\alpha\beta} + V_{\alpha\beta}\delta_{\alpha\beta}\int r^2 \rho\, d\vec{\tau}\right]$$

⇓ 0

$$= \frac{1}{6}\sum_{\alpha,\beta} V_{\alpha\beta} Q_{\alpha\beta}$$

If there is electronic charge at the nucleus, we must use Poisson's Eqn.

$$\sum_\alpha V_{\alpha\alpha} = -4\pi e\,|\psi(0)|^2$$

where $|\psi(0)|^2$ is the electronic prob. density at the nucleus.

The orientation independent term, ΔE, then is given by

$$\Delta E = \frac{1}{6}\sum_\alpha V_{\alpha\alpha}\int r^2 \rho\, d\vec{\tau} = -\frac{4\pi e}{6}|\psi(0)|^2 \times \int r^2 \rho\, d\vec{\tau}$$

This ΔE will be different for two nuclei of the same charge but diff. charge distribution (isotopes), or for two nuclei of the same mass & charge but diff. nuclear states

This effect is important in Mössbauer Spectroscopy

So far it is all classical. In order to obtain the corresponding quantum mechanical operator, we express $Q_{\alpha\beta}$ as a sum:

$$Q_{\alpha\beta} = e\sum_{\substack{k \\ (\text{protons})}} (3x_{\alpha_k}x_{\beta_k} - \delta_{\alpha\beta}r_k^2)$$

Quantum mechanical operator is then constructed by considering x_{α_k}'s (etc.) as operators.

Thus

$$\mathcal{H}_Q = \frac{1}{6}\sum_{\alpha,\beta} V_{\alpha\beta} Q_{\alpha\beta}^{(op)}$$

with $Q_{\alpha\beta}^{(op)}$ as the above operator, acting on the nuclear wave function.

We shall need only matrix elements of the kind,

$$\langle I m \eta | Q_{\alpha\beta}^{(op)} | I m' \eta \rangle$$

These matrix elements can be shown to obey the equation:

$$\rightarrow \langle I m \eta | Q_{\alpha\beta}^{(op)} | I m' \eta \rangle = C\langle I m | \tfrac{3}{2}(I_\alpha I_\beta + I_\beta I_\alpha) - \delta_{\alpha\beta} I^2 | I m' \rangle$$

This is discussed extensively in the book of C.P. Slichter

This equation expresses a linear relationship between the matrix elements of the operator $Q^{(op)}_{\alpha\beta}$ and a corresponding operator constructed out of the components of the angular momentum $\vec{I}$. The constant C can be expressed in terms of the matrix element for which $m = m' = I$, $\alpha = \beta = z$ as follows:

$$\langle II\eta | e\sum_{k\,(\text{Protons})} (3z_k^2 - r_k^2) | II\eta \rangle$$

$$= C \langle II\eta | 3I_z^2 - I^2 | II\eta \rangle$$

$$= C\, I(2I-1)$$

Also, let us define a symbol eQ

$$eQ = \langle II\eta | e\sum_k (3z_k^2 - r_k^2) | II\eta \rangle$$

eQ is called the quadrupole moment of the nucleus.

The quadrupole Hamiltonian, can, then be written as:

$$H_Q = \frac{eQ}{6I(2I-1)} \sum_{\alpha,\beta} V_{\alpha\beta} \left[\tfrac{3}{2} (I_\alpha I_\beta + I_\beta I_\alpha - \delta_{\alpha\beta} I^2 \right]$$

It is interesting to note that of the nine components of $Q^{(op)}_{\alpha\beta}$, only one nuclear constant, eQ, is needed.

The reason is as follows:
The fact that the nucleus is in a state of definite angular momentum is equivalent to the classical statement that the charge has cylindrical symmetry. Considering that the classical q.m. tensor is traceless, and given the cylindrical symmetry of the nucleus, it is clear that there is only one independent component of the q.m. tensor.

This Hamiltonian applies for an arbitrary orientation of the rectangular coordinates $\alpha, \beta = x, y, z$. However, in the principal frame of $V_{\alpha\beta}$,

$$V_{\alpha\beta} = 0 \quad \text{for } \alpha \neq \beta$$

$$\mathcal{H}_Q = \frac{eQ}{6I(2I-1)}\left[V_{xx}(3I_x^2 - I^2) + V_{yy}(3I_y^2 - I^2) + V_{zz}(3I_z^2 - I^2)\right]$$

Using $\sum_\alpha V_{\alpha\alpha} = 0$,

$$\mathcal{H}_Q = \frac{eQ}{4I(2I-1)}\left[V_{zz}(3I_z^2 - I^2) + (V_{xx} - V_{yy})(I_x^2 - I_y^2)\right]$$

It is customary to define two symbols,

$eq = V_{zz}$ & V_{zz} is taken to be the largest comp.

$\eta = \dfrac{V_{xx} - V_{yy}}{V_{zz}}$ & then V_{xx}, V_{yy}.

$$\mathcal{H}_Q = \frac{eQ.eq}{4I(2I-1)}\left[(3I_z^2 - I^2) + \eta(I_x^2 - I_y^2)\right]$$

For axially symmetric efg, $\eta = 0$ &

$$\boxed{\mathcal{H}_Q = \frac{e^2qQ}{4I(2I-1)}\left[3I_z^2 - I^2\right]}$$

& is useful in many situations where efg is axially symmetric.

Measurement of the two RELAXATION TIMES

The pulse-method is the most accurate technique to measure the relaxation times T_1 and T_2 of the nuclear species in materials of interest.

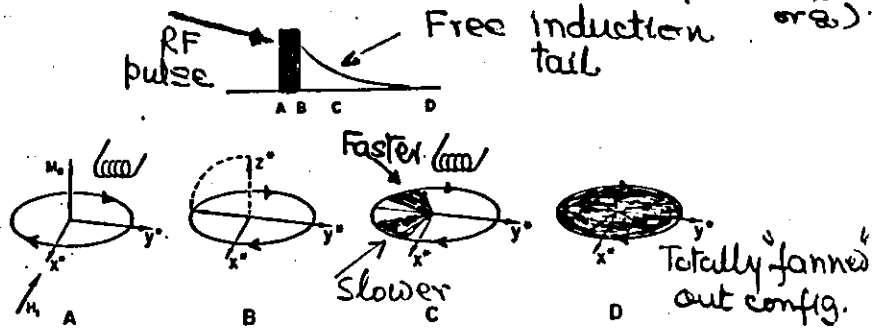
The technique has the inherent advantage that the spin system is left to itself, except for the brief duration of the pulse(s).

The technique affords direct measurements of the relaxation times

In this technique, the nuclear system is exposed to pulses of intense RF-field and the response of the system is observed in the absence of RF-radiation.

The technique was introduced by E.L. Hahn in 1950 and has not changed, in principle, over the last forty years or so. New and highly sophisticated electronics, however, has brought almost a revolution in practice.

FREE INDUCTION DECAY (See Hahn's original work, Phys. Rev. 1950 or so)



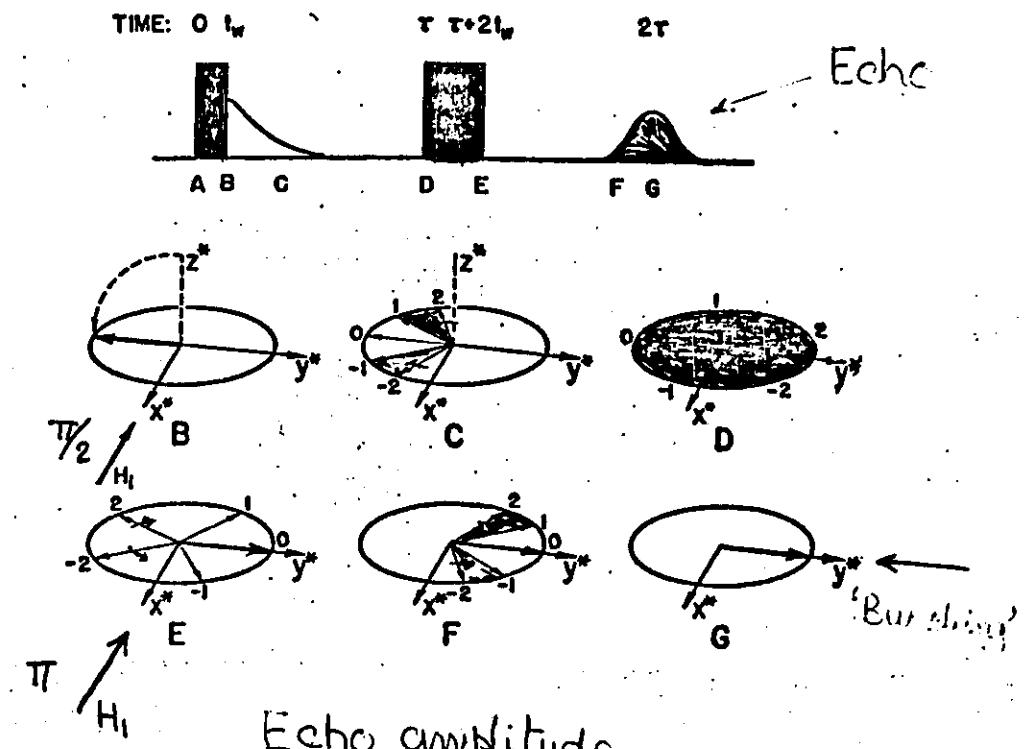
1. $H_1 \perp H_0$ and sufficiently large so that $H_1 > H_{Loc}$
   ↓
   Several gauss.

2. Before the pulse is applied, M_0 is the eqlbm. magnetization of the nuclear system.

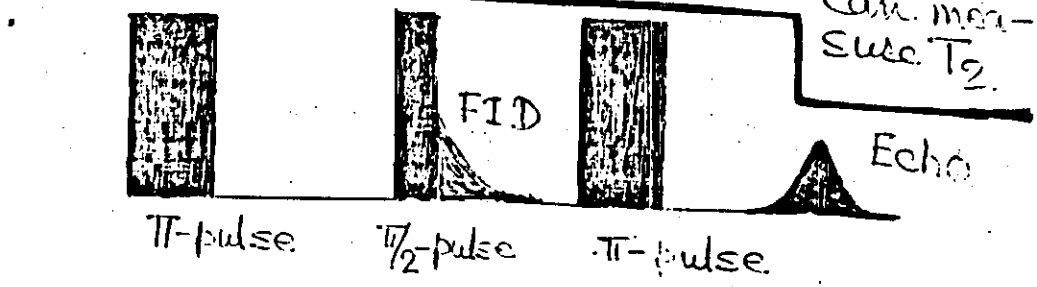
3. The pulse is of such a duration that
   $$\gamma H_1 t_\omega = \pi/2 \quad (90°\text{-pulse})$$
   ↑
   duration of the pulse (or the pulse width)

4. We suppose $t_\omega \ll T_2, T_1$.

5. $x^*-y^*-z^*$ is the rotating frame, rotating with angular frequency
   $$\omega_0 = \gamma H_0$$
   in the same direction as the nuclear moments.

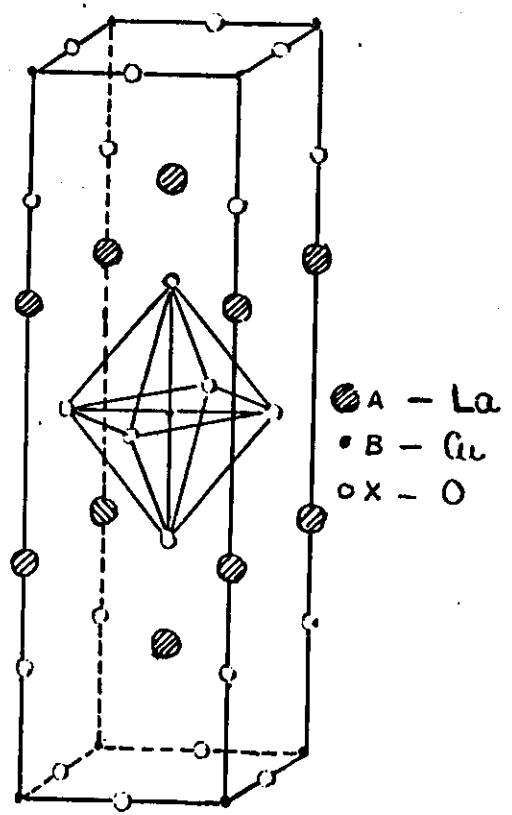


Echo amplitude $\propto e^{-2\tau/T_2}$ → This enables us to measure T_2.



A pulse scheme used to measure T_1

Tetragonal unit cell – K_2NiF_4-Type



Room temp. structure of superconducting $La_{2-x}M_xCuO_{4-y}$ materials

Cu-atoms do NOT have mag. moment ($\mu_{Cu} \leq 0.01 \mu_B$) in the normal AS WELL AS superconducting state.

La_2CuO_{4-y}

→ Parent compound for the doped High-T_c (40K) superconductors.

→ Undergoes a second order structural phase transition.

TETRAGONAL $\xrightarrow{T_t}$ ORTHORHOMBIC.
T_t ~ well above room temperature

→ T_t - Highly sensitive to y (450K–530K)

→ Undergoes antiferromagnetic transition

T_N — Highly sensitive to y; $T_N \sim 0$ $y \cong 0$ & $\sim 295K$ $y \cong 0.1$

This magnetic anomaly disappears [illegible]

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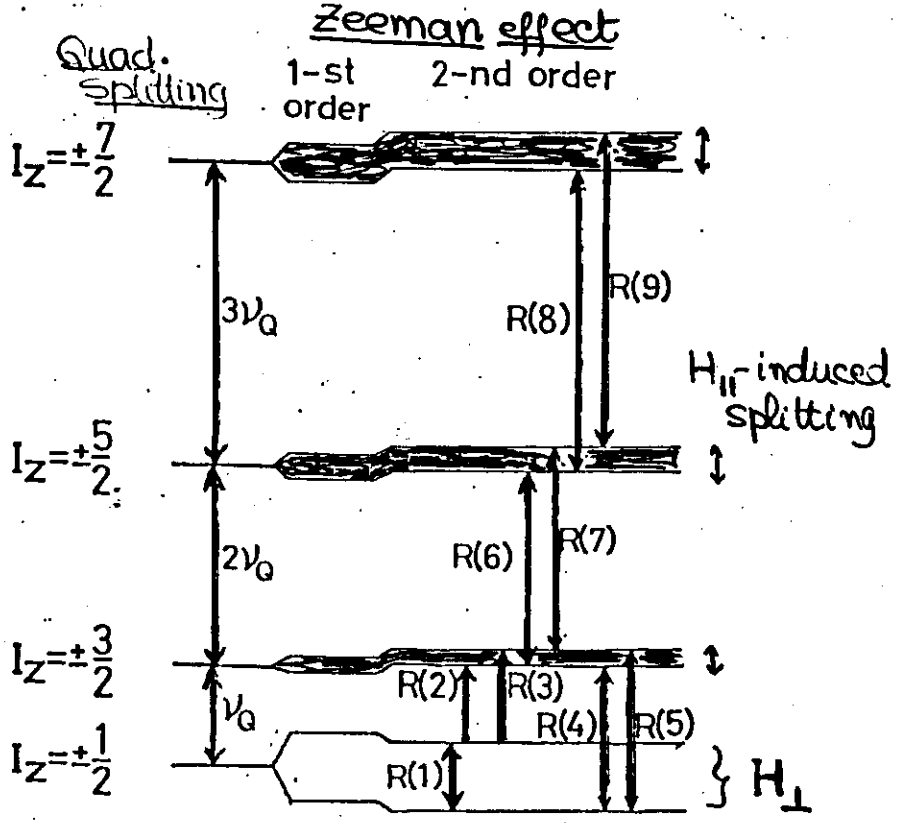
Quadrupole splitting of ^{139}La levels with Zeeman "perturbation"

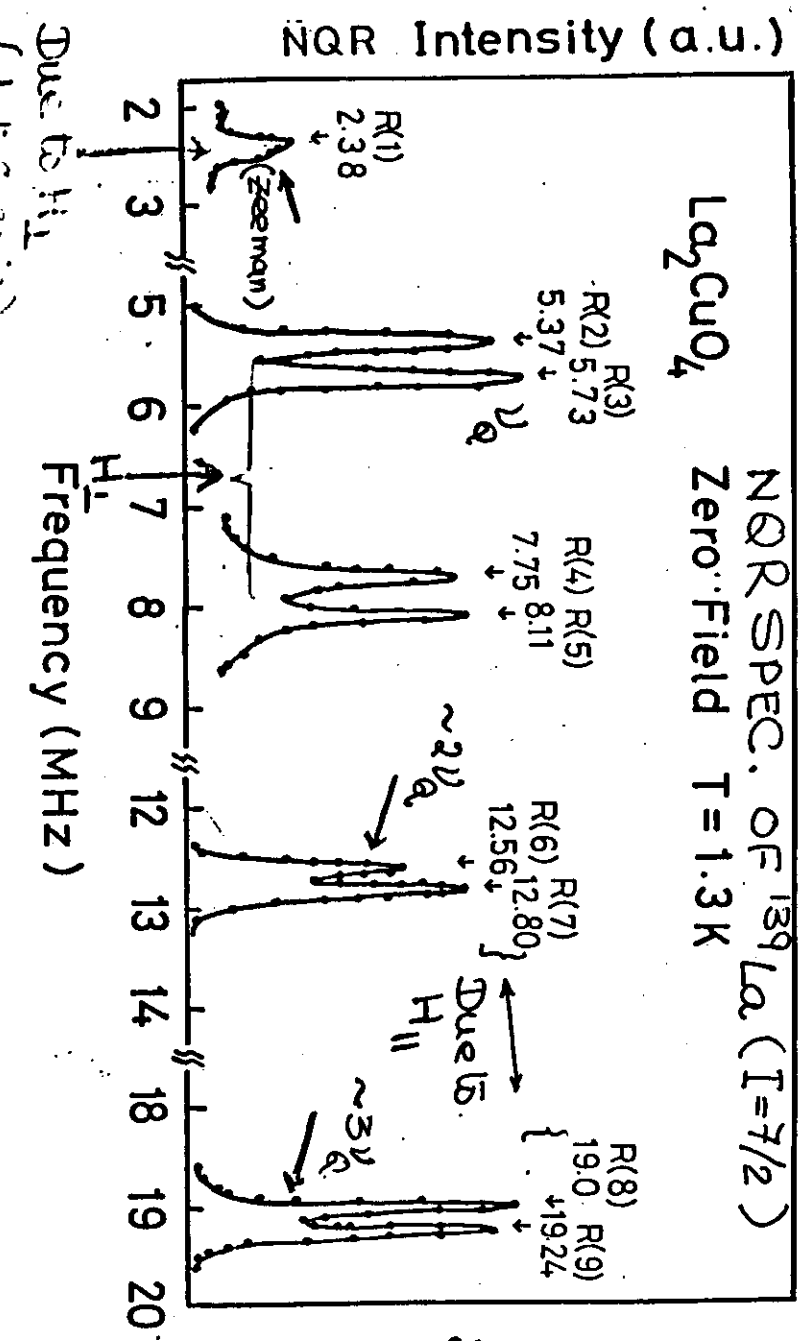


can split ± ½ levels.

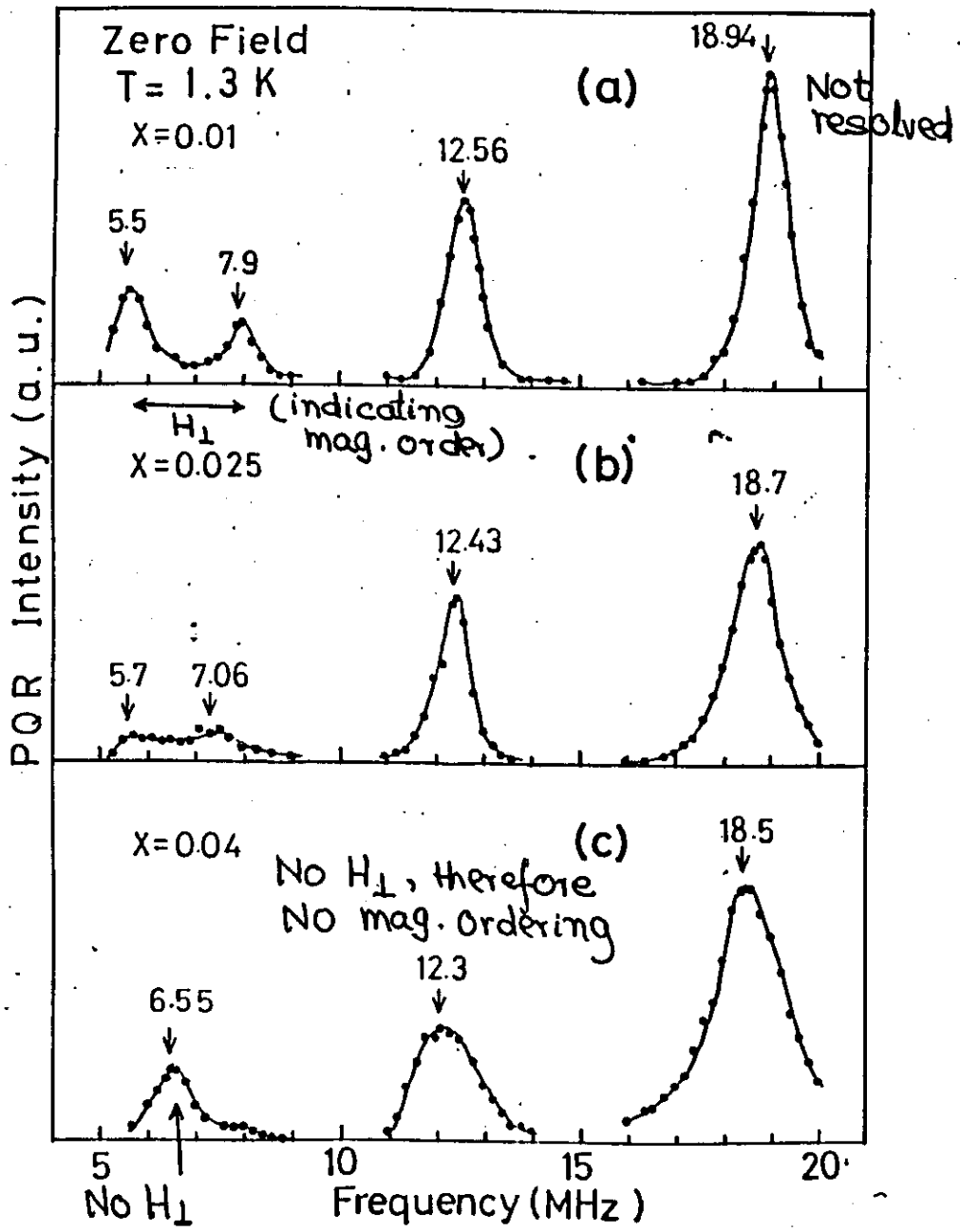
$\nu_{R(1)} \rightarrow H_\perp$; and also $\nu_{R(4)} + \nu_{R(5)} - \nu_{R(2)} - \nu_{R(3)}$

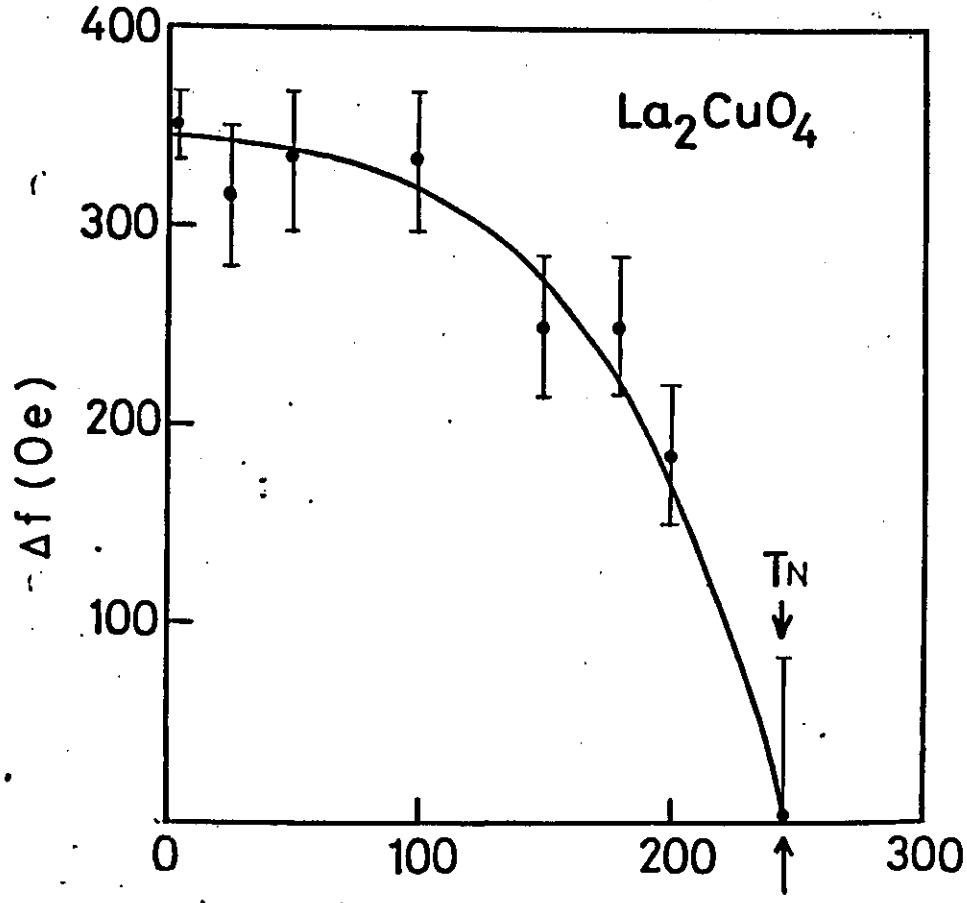
$\nu_{R(9)} - \nu_{R(8)} \rightarrow H_{II}$

Yoshio KITAOKA et.al J. Phys. Soc. Japan 56, 3024 (1987)



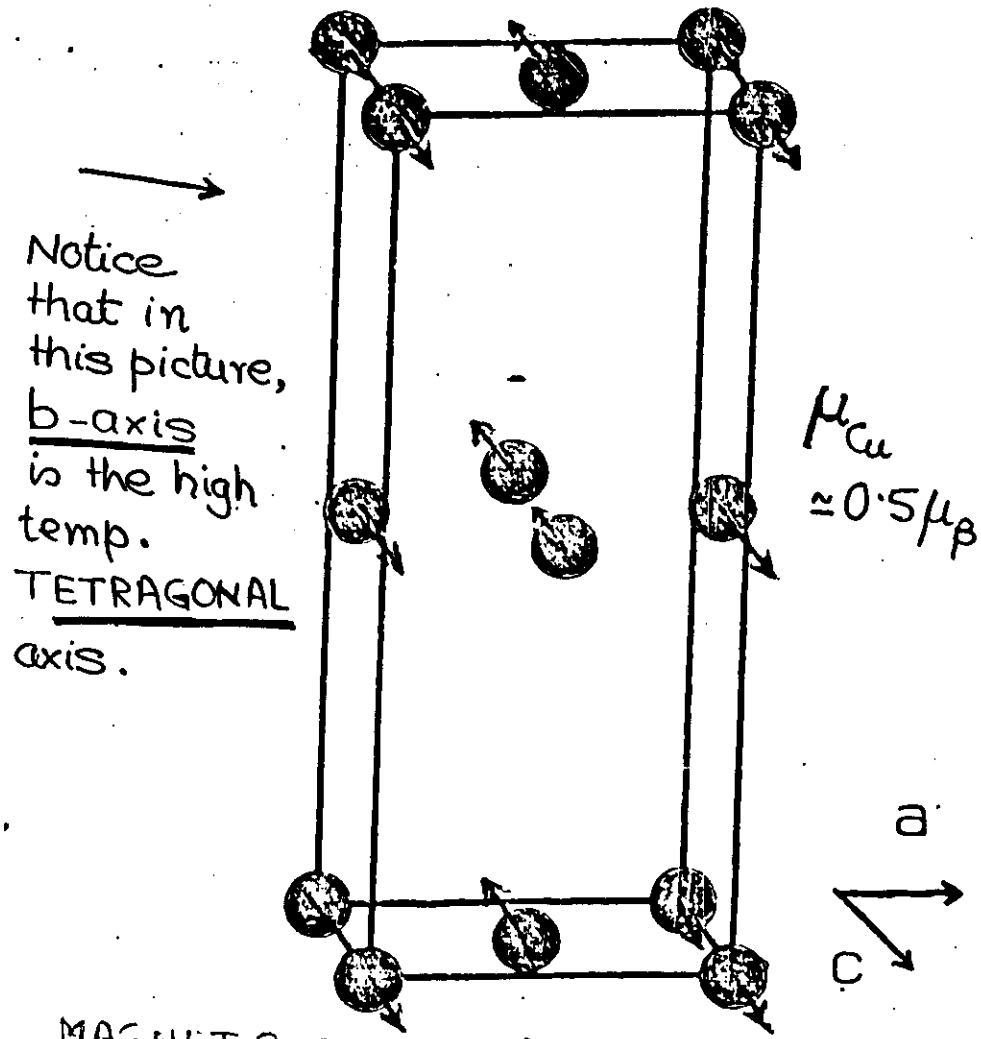
^{139}La - NQR in $(La_{1-x}Ba_x)_2CuO_{4-y}$





Magnetic Transition temp. inferred from the appearance of Zeeman effect in NQR

MAGNETIC UNIT CELL OF La_2CuO_4.



MAGNETIC STRUCTURE AS DETERMINED BY NEUTRONS [D. Vaknin, S.K. Sinha---
P.R.L. 58, 2802 (1987)]

Antiferromagnetic ordering in O-deficient $YBa_2Cu_3O_{7-y}$

For $y \sim 1 \rightarrow$ Neutron & μ^+-SR

$\downarrow$

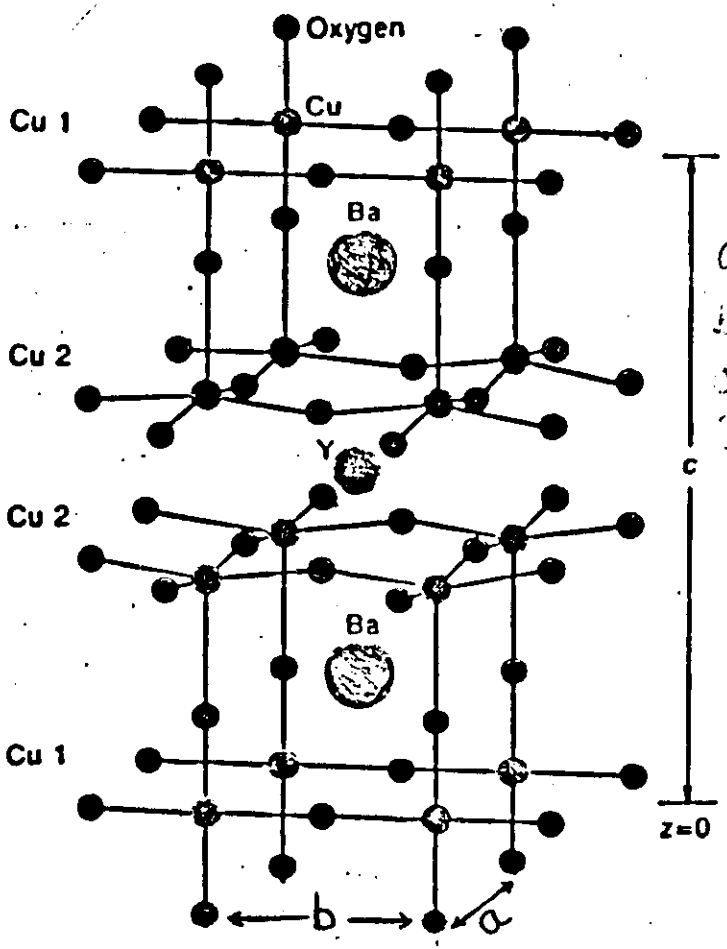
$T_N \sim 400 - 500K$

→ In-plane Cu spins along the c-axis coupled ↑↓ between both intra- and inter-plane Cu-spins.

NQR results on $YBa_2Cu_3O_{6.3}$

$T_N \sim 20K$

Thus antiferromagnetic ordering in O-deficient materials (essentially two-dimensional) of $YBa_2Cu_3O_{7-y}$-type and T_N being very sensitive to $y \leftrightarrow La_{2-x}M_xCuO_{4-y}$ type systems.



A unit cell of $YBa_2Cu_3O_{7-x}$.
Cu(2) atoms are more abundant;
and have nearly tetragonal environment

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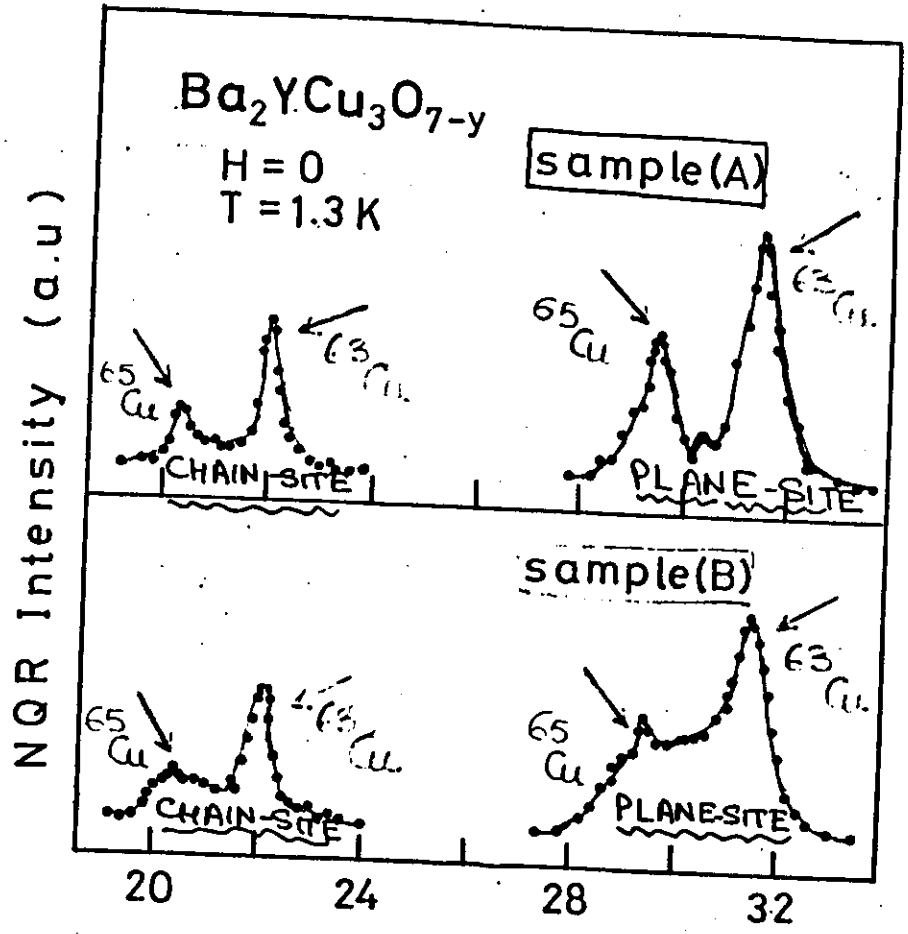
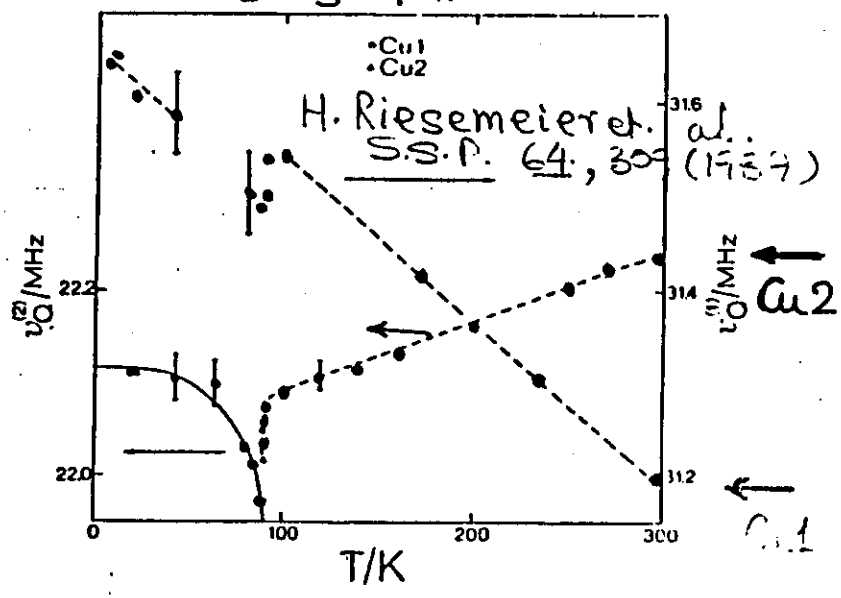
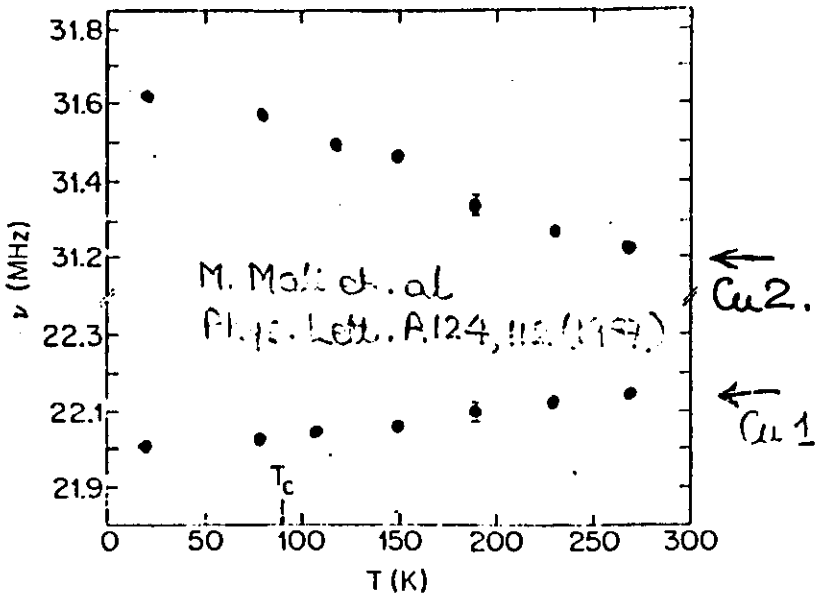
2 preprint.



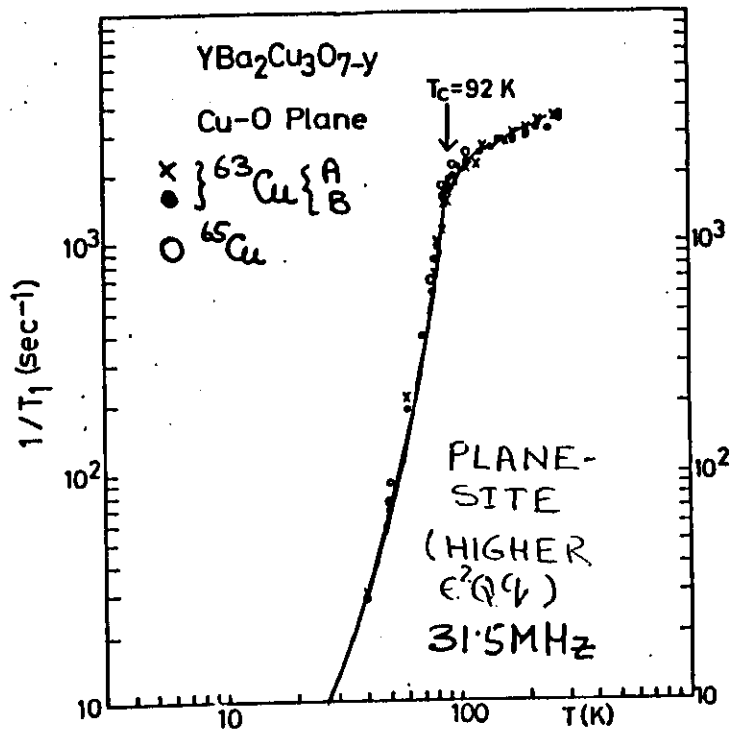
NQR of copper in 1-2-3 system
Sample A → $T_c = 92K$, $\Delta T_c = 1.7K$
Sample B → $T_c = 90K$, $\Delta T_c = 12.K$.

NQR of Cu-in $YBa_2Cu_3O_{7-x}$





Y. Kitaoka - Preprint



NOTE THAT : Below T_c, $\frac{1}{T_1}$ decreases rapidly WITH no ENHANCEMENT just BELOW T_c.

Al, for example, shows this.

$2\Delta_0 \sim 12\, k_B T_c$ from the fit $T_1^{-1} \sim e^{-2\Delta/kT}$

From L. C. Hebel and C. P. Slichter, Phy. Rev. 113 (1957) 1504.
See also D. E. Mac Laughlin,
Solid State Phys. 31 (1976) page 1.

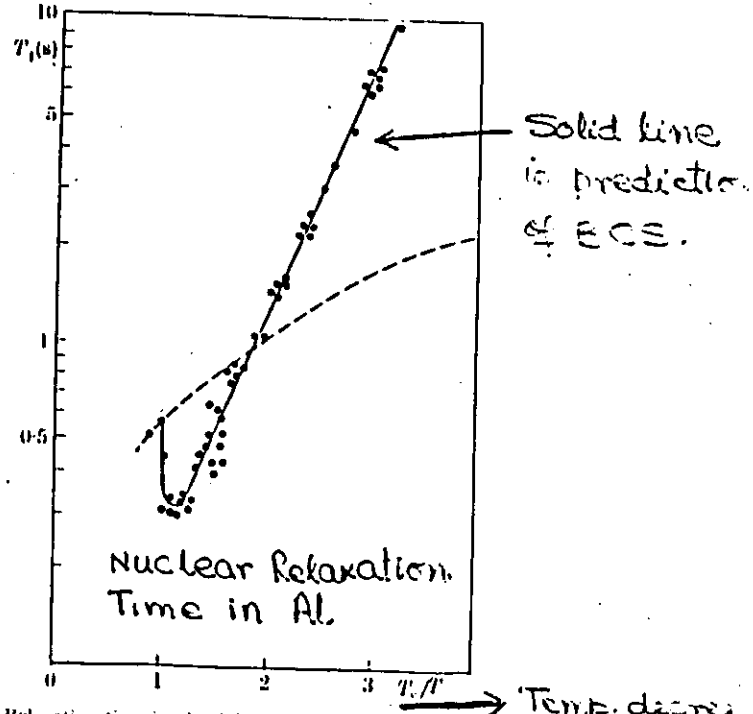


FIG. 3.5. Relaxation time in aluminium as a function of the temperature. The dotted line is the relaxation rate for a normal metal. The solid line is a calculated relaxation using a gap $2\Delta = 3.2kT_c$ and assuming $10\% < \Delta(T)$.[10]

The relaxation rate for T slightly less than T_c is greater than in the normal state. Much below T_c, relaxation rate falls rapidly with decrease of T.

The dominant relaxation mechanism in superconductors involves nuclear spin flips induced by unpaired excitations (quasi-particles) and is proportional to the density of these excitations.

Evidence For Two Pairing Energies From Nuclear Spin-Lattice Relaxation in Superconducting $Ba_2YCu_3O_{7-x}$

P.R.L. 59, 1860 (1987)

Warren, Walstedt, Brennert, Espinosa, Remeika.

→ $2\Delta_0/k_BT_c \sim 8.3$ [chain] ←
(Cu1) — (31.5 MHz)

~ 2.4 [plane]
(Cu2) (22.4 MHz)