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

12 - 30 MARCH 1990

MAGNETIC NUCLEAR RESONANCE

Part I

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Nuclear Magnetic Resonance in High- T_c Superconductors

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- absence of the Hebel-Slichter peak

- anomalous normal state behavior

4-2) Theoretical analysis ----- effect of the antiferromagnetic spin fluctuations

§ 1. INTRODUCTION TO THE NUCLEAR MAGNETIC RESONANCE PHENOMENA.

- 1-1) Motion of free nuclear spins in magnetic field.
- 1-2) Application of oscillatory magnetic field.
- 1-3) Effect of the surrounding "lattice".

§ 2. HYPERFINE INTERACTION IN SOLIDS

- 2-1) Derivation of the magnetic hyperfine interaction
- 2-2) Paramagnetic shift of resonance frequency.
- 2-3) Knight shift in metals and superconductors.
- 2-4) Nuclear spin-lattice relaxation (general formula).
- 2-5) Nuclear relaxation in metals and superconductors.

§ 3. NMR STUDIES OF $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ --- I (STATIC PROPERTIES)

- 3-1) General properties --- crystal structure, phase diagram
- 3-2) Study of electronic structure and static magnetic properties
 - Cu Knight shift
 - Cu anisotropic nuclear relaxation
 - study of hyperfine field
 - Oxygen Knight shift
 - Knight shift in the " $T_c \sim 60$ K" phase

§ 4. NMR STUDIES OF $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ --- II (DYNAMICAL PROPERTIES)

- 4-1) Cu, Oxygen and Yttrium nuclear spin relaxation

In this short lecture, I will try to give a brief survey of the present status of the nuclear magnetic resonance (NMR) study on high- T_c superconductors. I will start with the introduction to the fundamental concepts of NMR (§1 and §2). First I shall explain the basic principles of the magnetic resonance phenomena (§1), which itself is a beautiful realization of the coherence of the quantum spin system. I hope this will help the audience to become familiar with this experimental technique.

The resonance phenomena, although being interesting by itself, would have been useless in condensed matter physics if the nuclear spins were isolated from surrounding electrons. It is the hyperfine interaction -- the magnetic interaction between nuclear spins and the electronic spin or orbital magnetic moments -- which makes NMR such a useful probe for the electronic properties of solids. In §2, I shall review the basic aspects of the hyperfine interaction and show how the various quantities which characterize the resonance, such as the shift of resonance frequency, line shape, nuclear spin lattice relaxation rate etc., reflect the magnetic properties of the electronic system. The thorough knowledge of the hyperfine interaction is crucial for the interpretation of any NMR data. I will not discuss the electric hyperfine interaction which is important to analyze the quadrupole splitting of the NMR spectra and the NQR (nuclear quadrupole resonance) spectra. The typical behavior of the frequency shift (Knight shift) and the nuclear relaxation rate in conventional metals and superconductors will be also discussed.

The rest of the lecture will be devoted to the recent experimental progress in the NMR study of high- T_c superconductors. I shall focus on the results in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ since this system has been studied by far most extensively and has provided a wide variety of phenomena. There are two major issues to be discussed. The first issue is concerned with the electronic structure and the

static magnetic properties of this system. The second issue is the dynamical behavior of the electron spins and the nature of magnetic excitations.

It is by now widely recognized that the two dimensional CuO_2 planes are the most fundamental constituent of the high- T_c materials and the spin and charge excitations are associated with the Cu-3d and oxygen 2p states. However, the nature of these excitations in the normal state is not well understood. An important problem is whether the electron spins on the Cu-3d states and the oxygen 2p states have independent degrees of freedom or they are so strongly hybridized to form a single spin system. It is also important to know whether these electron spins have the character close to the localized moments such as the Cu^{2+} moments in the antiferromagnetic insulator $\text{YBa}_2\text{Cu}_3\text{O}_6$ or these are more like itinerant electron system which can be viewed as a Fermi liquid.

The static NMR properties i.e. the Knight shift, which I discuss in §3, give useful information about the first problem. The Knight shift measurement in the superconducting state also gives some insight about the nature of the pairing states (s or d-wave, magnitude of the superconducting gap). The measurement of the nuclear relaxation rate which will be discussed in §4 is related to the second problem. There has been substantial theoretical progress in the understanding of the spin dynamics in the normal states. I would like to emphasize the importance of antiferromagnetic short range correlations among Cu spins which is the key concept to understand the nuclear relaxation behavior in this system. Another important feature of the relaxation data is the absence of the so called Hebel-Slichter peak (coherence peak) in this system which is not fully understood yet.

REFERENCES

[NMR general]

- 1) C. P. Slichter, Principles of Magnetic Resonance, 3rd Ed. (Springer, New York, 1989).

- 2) A. Abragam, The Principles of Nuclear Magnetism, (Clarendon Press, Oxford, 1961).

[hyperfine interaction]

- 3) A. Abragam and B. Bleany, Electron Paramagnetic Resonance of Transition Ions, (Clarendon Press, Oxford, 1971).

- 4) J. Winter, Magnetic Resonance in Metals.

- 5) R. F. Watson and A. J. Freeman, Hyperfine Interaction, ed. A. J. Freeman and R. B. Frankel (Academic Press, New York, 1967) p. 53.

- 6) V. Jaccarino, Proc of Int. School of Physics, Enrico Fermi, Course XXXVII (Academic Press, New York, 1967).

[for NMR in superconductors, see 4) and]

- 7) D. E. McLaughlin, in Solid State Physics, ed. H. Ehrenreich, F. Seitz and D. Turnbull (Academic Press, New York, 1976).

for review of NMR studies in high- T_c superconductors

- 8) C. H. Pennington and C. P. Slichter, in Physical Properties of High-Temperature Superconductors, II ed. D. M. Ginsberg (World Scientific, NJ, 1990).

- 9) R. E. Walstedt and W. W. Warren, Jr. to be published in Science.

[papers referred to in the lecture (not related to high- T_c)]

- 10) M. Shaham, U. El-Hanany and D. Zamir, Phys. Rev. B17, 3513 (1978).

- 11) H. L. Fine et al., Phys. Lett. 29A, 366 (1969).

- 12) A. M. Clogston et al., Rev. Mod. Phys. 36, 170 (1964).

- 13) Y. Masuda and A. G. Redfield, Phys. Rev. 125, 159 (1962).

- 14) T. Moriya, J. Phys. Soc. Japan 18

[papers referred to in the lecture (related to high- T_c)]

- 15) M. Takigawa et al., Phys. Rev. Lett. 63, 1865 (1989).

- 16) H. Alloui, T. Ohno and D. Mendels, Phys. Rev. Lett. 63, 1700 (1989).

- 17) V. J. Emery and G. Reiter, Phys. Rev. B38, 11938 (1988).

- 18) F. C. Zhang and T. M. Rice, Phys. Rev. B37, 3759 (1988).

- 19) Y. Nakazawa and M. Ishikawa, Physica C158, 381 (1989).

- 20) R. E. Walstedt, W. W. Warren, Jr., R. F. Bell, R. J. Cava, G. P. Espinosa, L. F. Schneemeyer and J. V. Waszczak, Phys. Rev. B to be published.

- 21) T. Shimizu, H. Yasuoka, T. Tsuda, K. Koga and Y. Ueda, Proceedings of the 10th ISMAR Meeting, Morzine, France, 1989, to be published in Bulletin of Magnetic Resonance.

- 22) W. W. Warren, Jr. et al., Phys. Rev. Lett. 62, 1193 (1989).

- 23) H. Yasuoka, T. Imai and T. Shimizu, Strong Correlation and Superconductivity, eds. H. Fukuyama, S. Maekawa and A. P. Malozemoff (Springer-Verlag, 1989).

- 24) A. J. Millis, H. Monien and D. Pines, unpublished.

- 25) N. Bulut, D. Hone, D. Scalapino and N. E. Bickers, Phys. Rev. B41, 1797 (1990).

- 26) M. Takigawa, Proceedings of the NATO Workshop on Dynamics of Magnetic Fluctuations in High- T_c Superconductors, eds G. Reiter, P. Horsch and G. Psaltakis (Prenum Press, 1990).

- 27) M. Takigawa et al., Phys. Rev. B39, 300 (1989); M. Takigawa, P. C. Hammel, R. H. Hefner and Z. Fisk, Phys. Rev. B39, 7371 (1989).

- 3
- 1
- 28) W. W. Warren, Jr. et al., Phys. Rev. B₃₉, 831 (1989).
 29) S. E. Barrett et al., Phys. Rev. B₄₁ (April, 1990)
 30) F. Mila and T. M. Rice, Physica C₁₅₁, 561 (1989).
 31) M. Takigawa et al., Physica C₁₆₂₋₁₆₄, 831 (1989).
 32) M. Horvatic et al., Physica C₁₅₉, 689 (1989).
 33) J. Owen and J. H. M. Thormley, Rep. Prog. Phys. 29, 675 (1966).
 34) Y. Kitaoka et al., Strong Correlation and Superconductivity, eds. H. Fukuyama, S. Maekawa and A. P. Malozemoff (Springer-Verlag, 1989).
 35) P. C. Hammel et al., Phys. Rev. Lett. 63, 1992 (1989).
 36) B. S. Shstry, Phys. Rev. Lett., 63, 1288 (1989).
 37) R. E. Walstedt et al., Phys. Rev. B₃₈, 9229 (1988); R. E. Walstedt et al., Phys. Rev. B₄₀, 2572 (1989).
 38) T. Imai et al., J. Phys. Soc. Japan 57, 2280 (1988).

§1 Nuclear Magnetic Resonance Phenomena (ref. 1, 2)

1-1) motion of free nuclear spin in magnetic field

$$[\text{nuclear spin } \vec{I} \quad \vec{\mu} = \gamma_N \vec{I} \quad \gamma_N : \text{gyromagnetic ratio}$$

magnetic moment $\vec{\mu}$

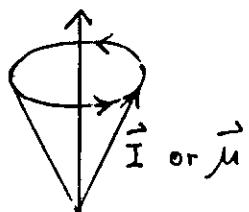
Energy (Hamiltonian) of nuclear spin in uniform magnetic field

$$\mathcal{H} = - \vec{H} \cdot \vec{\mu} = - \gamma_N \hbar \vec{H} \cdot \vec{I}$$

a) classical equation of motion

torque acting on a magnetic moment $\vec{\mu} \times \vec{H}$
= time derivative of angular momentum

$$\hbar \frac{d\vec{I}}{dt} = \vec{\mu} \times \vec{H} = \gamma_N \hbar (\vec{I} \times \vec{H})$$



Larmor precession
frequency $\omega = \gamma_N H$

b) quantum theoretical treatment

Heisenberg equation $\frac{d\vec{I}}{dt} = \frac{i}{\hbar} [\mathcal{H}, \vec{I}]$

$$\begin{aligned} \frac{dI_x}{dt} &= -\gamma_N i H [I_z, I_x] = \gamma_N H I_y \\ \frac{dI_y}{dt} &= -\gamma_N H I_x \\ \frac{dI_z}{dt} &= 0 \end{aligned}$$

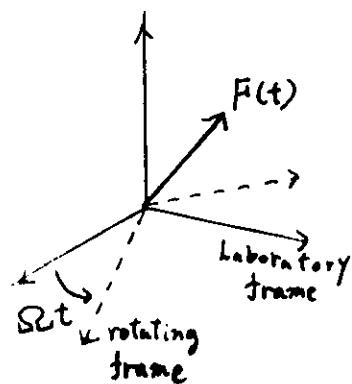
$$\Rightarrow \frac{d\vec{I}}{dt} = \gamma_N (\vec{I} \times \vec{H})$$

taking expectation value $\frac{d\langle \vec{I} \rangle}{dt} = \gamma_N (\langle \vec{I} \rangle \times \vec{H})$

identical to the classical expression

1-2) Application of oscillatory magnetic field

a) concept of the rotating frame

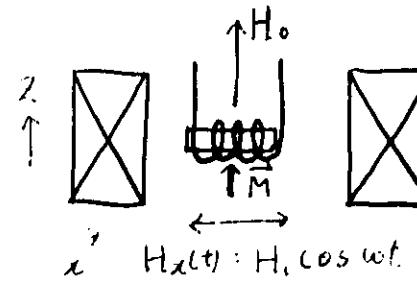


motion of $\vec{F}(t)$ with respect to the rotating frame

$$\frac{d\vec{F}}{dt} = \frac{S}{\delta t} \vec{F} + (\vec{S}_0 \times \vec{F})$$

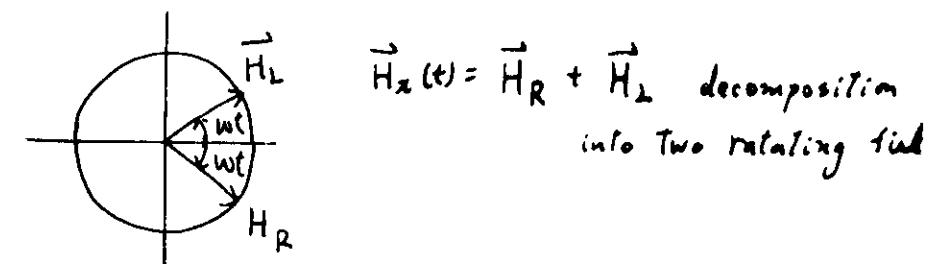
Lab. frame rotating frame

b) ensemble of free nuclear spins.



sample
 $\uparrow \downarrow \downarrow \uparrow \downarrow$
Boltzmann distribution.

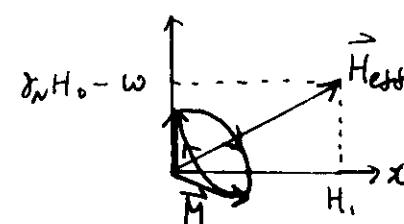
$$\vec{M} = \langle \vec{\mu} \rangle \propto \frac{\vec{H}_0}{k_B T}$$



In the rotating frame with $S_0 z = -\omega$, H_R becomes a static field along \vec{x}

$$\frac{d\vec{M}}{dt} = \vec{M} \times [\vec{z}(\gamma_N H_0 - \omega) + \vec{z} \cdot \vec{\sigma}_N \vec{H}_1]$$

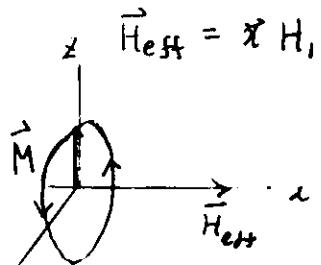
$$= \vec{H}_{\text{eff}}$$



Larmor precession around \vec{H}_{eff}

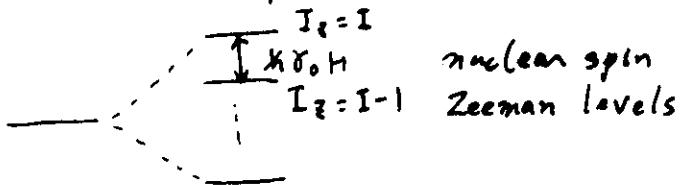
4

When $\omega = \gamma_N H_0$ (resonance)



\vec{M} is rotating in the \overline{XY} plane with frequency $\omega_r = \gamma_N H_i$

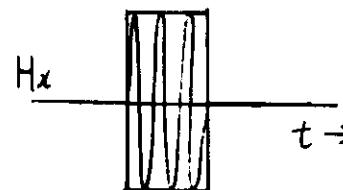
- alternative picture of resonance



Transition between $|I_z = I\rangle$ and $|I_z = I-1\rangle$ is caused by transverse field $H_x = H_i \cos \omega t$
 $(V_{ac} - H_x I_x = -H_x (I_+ - I_-)/2)$

when $\hbar \omega = \hbar \gamma_0 H_i$.

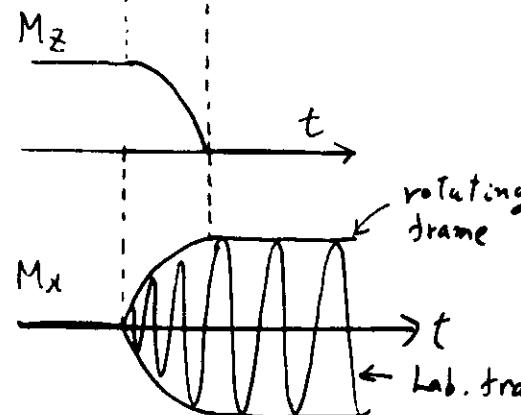
c) observation of resonance



90° pulse

$$t_w = \frac{\pi}{2} \frac{1}{\gamma_N H_i}$$

$(t_w \omega_r = \frac{\pi}{2})$ frame

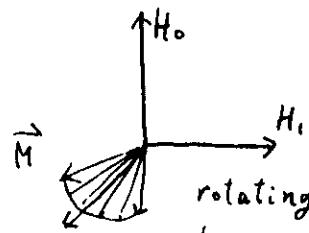


Voltage induced across the coil

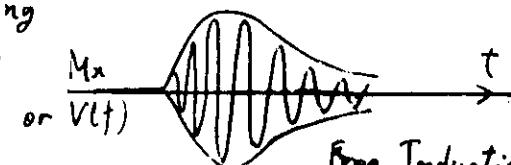
$$V(t) \propto \frac{dM_x}{dt} = \omega M$$

$$\propto \frac{H_0^2}{kT}$$

d) Inhomogeneous magnetic field.



dephasing: Some spins precess fast, some spins precess slow.



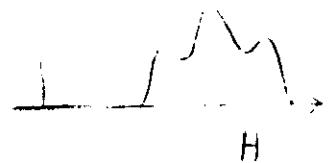
Free Induction Decay

5

distribution of local magnetic field

(inhomogeneity of magnet,
anisotropic chemical shift
quadrupole interaction)

$P(H)$



$P(H)$: distribution function

local Larmor frequency

$$\omega = \gamma_N H$$

after

$$90^\circ \text{ pulse} \quad M_x(t) = \int P(H) \cos(\gamma_N H t) dH$$

$$M_y(t) = \int P(H) \sin(\gamma_N H t) dH$$

principles of FT-NMR.

take data of $M_x(t), M_y(t)$ ($t > 0$)



Fourier transform of $M_x(t) + iM_y(t)$

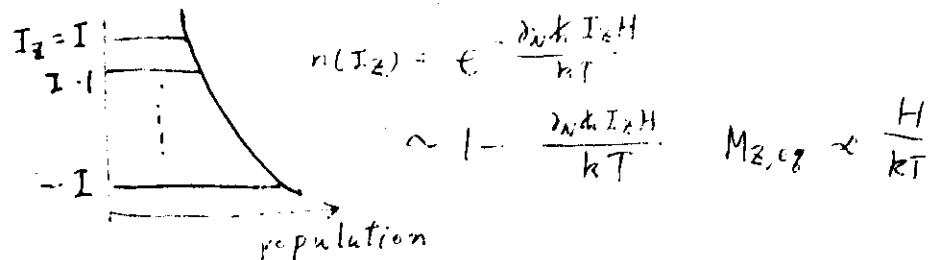
$$= \int P(H) e^{i\gamma_N H t} dH$$



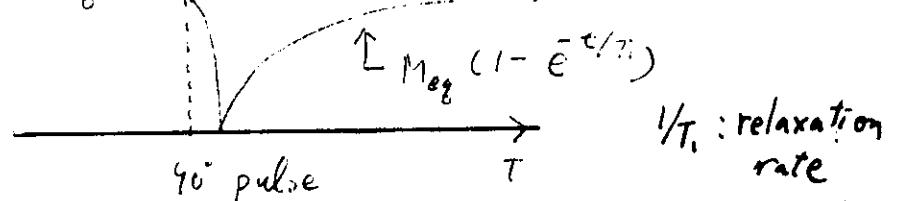
Obtain distribution function $P(H)$.

1-3) Effect of the interaction between nuclear spin system and external "lattice"
(electrons, phonons, etc.)

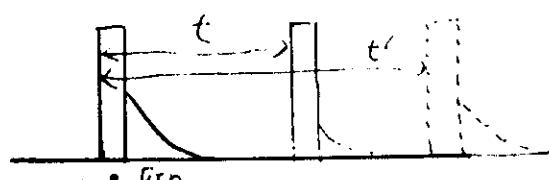
→ relaxation toward the Boltzmann distribution.



$M_{z,eq}$ nuclear spin-lattice relaxation



measurement of T_1



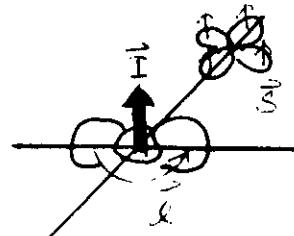
FID intensity $I(t)$ after 90° pulse
 $\propto (1 - e^{-t/T_1})$

$1/T_1$: relaxation rate

T_1 : relaxation time

§2. Hyperfine Interaction in Solids (ref. 1-6)

(Electron-Nucleus interaction)



Nuclear spins interact with surrounding electronic (spin or orbital) magnetic moments

\downarrow
magnetic hyperfine interaction

$$H = -\gamma_N \hbar \vec{I} \cdot \vec{H}_{hf} \quad \vec{H}_{hf}: \text{hyperfine field}$$

(electron operator.)

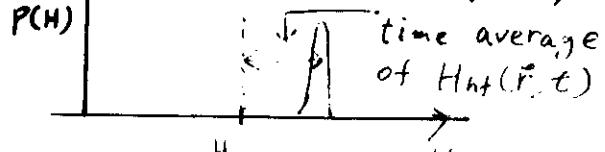
The effective field acting on the nuclear spin

$$H_{eff} = H_{ext} + H_{hf}(r, t)$$

$\overline{\cdot}$: statistical average
for electronic systems

two major effects

1) shift of the resonance frequency



2) nuclear spin-lattice relaxation

2-1) Derivation of the Magnetic Hyperfine Interaction

- magnetic field produced by a nuclear moment

$$\vec{H} = \vec{\nabla} \times \vec{A}, \quad \vec{A} = \frac{\vec{\mu}_n \times \vec{r}}{r^3} = \vec{\nabla} \times \left(\frac{\vec{\mu}_n}{r} \right), \quad \vec{\mu}_n = \hbar \sigma_n \vec{I}$$

- Hamiltonian for electrons

$$H_e = \frac{1}{2m} (\vec{p} + \frac{e}{c} \vec{A})^2 + g \mu_B \vec{s} \cdot \vec{\nabla} \times \vec{A} \quad \vec{s}: \text{electron spin}$$

1st order in \vec{I}

$$H_{el-hf} = 2\mu_B \frac{\vec{\mu}_n \cdot \vec{s}}{r^3} + 3\mu_B \vec{s} \cdot \vec{\nabla} \times \vec{\nabla} \times \left(\frac{\vec{\mu}_n}{r} \right)$$

$$\begin{aligned} \vec{\nabla} \times (\vec{\nabla} \times \vec{B}) &= \vec{\nabla} \cdot (\vec{\nabla} \cdot \vec{B}) - \nabla^2 \vec{B} \\ \nabla^2 \left(\frac{1}{r} \right) &= -4\pi \delta(\vec{r}) \end{aligned}$$

$$H_{el-hf} = \frac{8\pi}{3} g \mu_B \sigma_n \hbar \delta(\vec{r}) \vec{I} \cdot \vec{s} \quad \text{Fermi contact (s-states)}$$

$$- 3\mu_B \sigma_n \hbar \vec{I} \left[\frac{1}{r^3} - 3 \frac{\vec{r}(\vec{s} \cdot \vec{r})}{r^5} \right] \quad \text{Spin Dipole (non-s state)}$$

$$+ 3\mu_B \frac{\vec{\mu}_n \cdot \vec{I}}{r^3} \quad \text{Orbital (non-s state)}$$

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2-2) Shift of the resonance frequency

Effective field for nuclear spins

$$\langle \hat{H}_{hf} \rangle = g\mu_B \langle \vec{S} \cdot \vec{B} \rangle + \mu_B \left\langle \frac{s\vec{r}(\vec{S} \cdot \vec{P})}{r^3} - \frac{\vec{S}}{r^3} \right\rangle + 2\mu_B \left\langle \frac{\vec{I}}{r^3} \right\rangle$$

$\langle \quad \rangle$: expectation value
in particular states.

- 1st and 2nd term $\neq 0$
only for the unpaired electrons
- Last term $\neq 0$ only for the electron in the open shell.

Examples of finite $\langle H_{hf} \rangle_{av}$.

① Ferromagnetic materials (Fe, Co, Ni ...)

$$M = g\mu_B \langle \vec{S} \rangle \neq 0$$

$$\langle \hat{H}_{hf} \rangle_{av} = \frac{8\pi}{3} g\mu_B |4(0)|^2 \langle \vec{S} \rangle = H_{int}$$

Resonance is observed at zero external field at
 $\omega_n = \gamma_N H_{int}$

	ω_N (MHz)	H_{int} (kOe)
Co	23.0	227
Fe	46.5	332
Ni	28.5	75

② paramagnetic materials (linear response to external field)

$$\begin{aligned} M_{spin} &= g\mu_B \langle \vec{S} \rangle = X_{spin} H_{ext} \\ M_{orb} &= \mu_B \langle \vec{I} \rangle = X_{orb} H_{ext} \end{aligned} \quad X: \text{magnetic susceptibility}$$

$$\begin{aligned} \langle \hat{H}_{hf} \rangle &= \frac{8\pi}{3} \langle |4(0)|^2 \rangle X_{spin} H_{ext} + \dots \\ &\quad + \langle \frac{2}{r^3} \rangle X_{orb} H_{ext} \end{aligned}$$

(Knight) shift

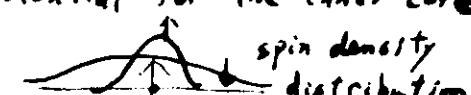
$$K = \frac{\langle H_{hf} \rangle}{H_{ext}} = \frac{8\pi}{3} \underbrace{\langle |4(0)|^2 \rangle}_{\text{hypersfine coupling constant}} X_{spin} + \dots + \underbrace{\langle \frac{2}{r^3} \rangle}_{\text{hypersfine coupling constant}} X_{orb}$$

in general,

$$\begin{aligned} K &= A_S X_{S, \text{spin}} + A_{P(d,f,\dots)} X_{P(d,f,\dots), \text{spin}} \\ &\quad + B_{P(d,f,\dots)} X_{P(d,f,\dots), \text{orb}} \end{aligned}$$

• core polarization effect.

Spin polarization of d, f (p) states produces an spin-dependent exchange potential for the inner core s-state $V_p(\vec{r}) + V_d(\vec{r})$



This produces spin polarization of inner s-state with opposite direction.

2-3) Knight shift in Metals and superconductors.

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a) simple metals (T -independent Pauli para)

	Li	Na	Al	Cu	Sn	Pb
$K(0)$	0.026	0.114	0.164	0.24	0.78	1.54

b) transition metals (red. 10)

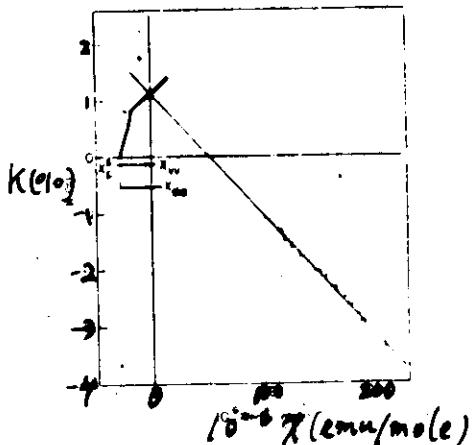
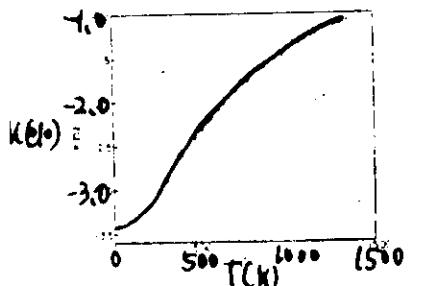
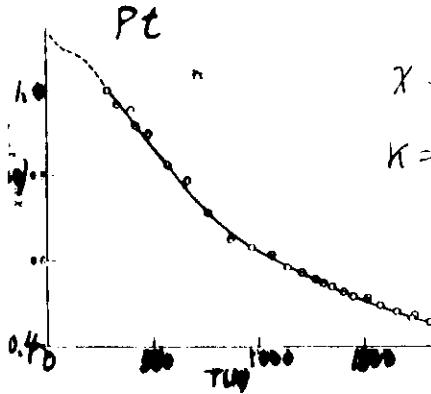
Pt

$$\chi = \chi_{\text{dia}} + \chi_{\text{sp}} + \chi_d(1) + \chi_{\text{orb}}$$

$$K = K_{\text{sp}} + K_d(T) + K_{\text{orb}}$$

$$K_d(T) = A_d \chi_d(T)$$

$A_d < 0$ core polarization



c) superconductors.

13

$$X_{\text{spin}} = -2\mu_B^2 \sum_k \frac{\partial f_k}{\partial E_k}$$

normal state

$$\sum_k \frac{\partial f_k}{\partial E_k} = \sum_k \delta(E_F - E_k) = g(E_F)$$

density of states

super.

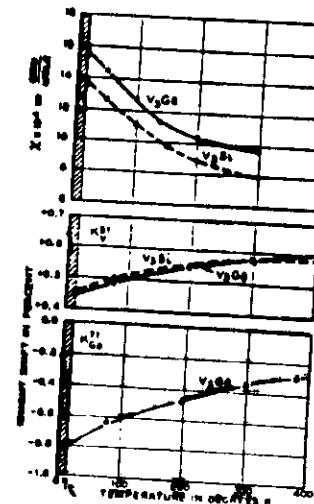
$$X_{\text{spin}} = -2\mu_B^2 \frac{\partial f}{\partial E_k}$$

$E_k = \sqrt{E_n^2 + \Delta^2}$: quasi-particle energy.

Δ : gap

$$X_{\text{spin}} \propto e^{-\Delta/kT} \quad (T \rightarrow 0)$$

AlS compounds (ref. 12)



T -dependent χ_s
(narrow d-band)

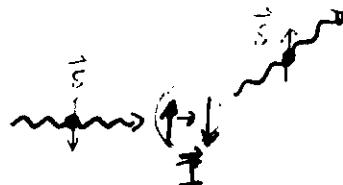
$K_{\text{spin}} < 0$: core polarization

large $K(0)$: orbital shift.

$$\propto \sum_{E_n > E_F} \frac{1}{E_n - E_m}$$

Van Vleck type

2-4) Nuclear spin-lattice Relaxation (general formula)
(Dynamical fluctuations of electronic magnetic moments)



typical process in metals

$$\begin{aligned} I &= \frac{1}{2} \\ I_x &= -\frac{1}{2} \\ I_y &= \omega_0 / \gamma_0 H_0 \\ I_z &= \frac{1}{2} \end{aligned}$$

$$H = -\partial_N \hbar \vec{I} \cdot \vec{H}_{ht}$$

$$= -\partial_N \hbar L I_z H_{ht}^2 + \frac{1}{2} (I_+ H_{ht}^- + I_- H_{ht}^+)$$

$$\begin{cases} I_+ = I_x + i I_y \\ I_- = I_x - i I_y \end{cases}$$

perturbation causing the transition $I_z = -\frac{1}{2} \leftrightarrow \frac{1}{2}$

Transition probability (Golden rule)

$$N_{1/2 \rightarrow -1/2} = \frac{2\pi}{\hbar} \sum_{n,m} | \langle I_z = -\frac{1}{2}, m | -\frac{1}{2} \partial_N \hbar I \cdot H_{ht}^+ | I_z = \frac{1}{2}, n \rangle |^2 e^{-E_n/kT} \delta(E_n - E_m + \hbar\omega_0)$$

$\langle m |, \langle m |$: electronic states

$$= \frac{2\pi}{\hbar} \sum_{n,m} | \langle m | \frac{\partial N \hbar}{4} H_{ht}^+ | n \rangle |^2 e^{-E_n/kT} \delta(E_n - E_m + \hbar\omega_0)$$

$$\delta(E_n - E_m + \hbar\omega_0) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt e^{i(\frac{E_n - E_m}{\hbar} + \omega_0)t}$$

$$\begin{aligned} N_{1/2 \rightarrow -1/2} &= \frac{\partial N}{4} \int_{-\infty}^{\infty} dt \sum_{nm} | \langle m | H_{ht}^+ | n \rangle |^2 C^{i(\frac{E_n - E_m}{\hbar} + \omega_0)t} e^{-E_n/kT} \\ &= \frac{\partial N^2}{4} \int_{-\infty}^{\infty} dt \sum_{nm} \langle n | H_{ht}^- | m \rangle \langle m | H_{ht}^+ | n \rangle C^{i\omega_0 t} \\ &\quad \left[\begin{array}{l} \langle m | H_{ht}^+ | n \rangle^* = \langle m | H_{ht}^- | m \rangle \\ H_{ht}^+(t) = e^{\frac{iHt}{\hbar}} H_{ht}^+ e^{-\frac{iHt}{\hbar}} \\ \text{(Heisenberg representation)} \\ \langle m | H_{ht}^+ | n \rangle e^{i(\frac{E_n - E_m}{\hbar})t} = \langle m | H_{ht}^+(t) | n \rangle \end{array} \right] \\ &= \frac{\partial N^2}{4} \int_{-\infty}^{\infty} dt \langle H_{ht}^- H_{ht}^+(t) \rangle e^{i\omega_0 t} \end{aligned}$$

$\langle \rangle$: statistical (thermal) average

$\langle H_{ht}^- H_{ht}^+(t) \rangle$: time correlation function of hyperfine field.

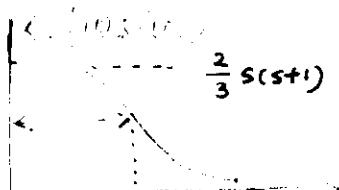
$$1/T_1 = 2 W_{1/2 \rightarrow -1/2}$$

$$\text{if } \vec{H}_{ht} = A \vec{S}_i \quad (\text{e.g. } {}^{55}\text{Mn in MnO etc})$$

$$1/T_1 = \frac{\partial N^2 A^2}{2} \int_{-\infty}^{\infty} \langle S_i^z(t) S_i^z(0) \rangle e^{i\omega_0 t} dt$$

relaxation rate is given by the auto spin correlation function.

- interacting localized moments.



$$\frac{2}{3} S(0) e^{-t/\tau_c}$$

τ_c : correlation time

$$k/\tau_c \sim J \gg \omega_0$$

$$V_{T_1} = \frac{n^2 A^2}{2} \frac{2S(0)}{3} \tau_c$$

$$\begin{matrix} \nearrow & \searrow \\ J & \end{matrix}$$

- relation to dynamical spin susceptibility
response to the space-time varying field

$$H(\vec{r}, t) = H_0 e^{i(\vec{k}\vec{r} - \omega t)}$$

$$\boxed{\text{spin system}} \xrightarrow{\text{linear response}} S(\vec{r}, t) = S_0 e^{i(\vec{k}\vec{r} - \omega t)}$$

$$\chi(\vec{r}, \omega) = \frac{S_0}{H_0} : \text{dynamical susceptibility}$$

$\text{Im } \chi(\vec{r}, \omega) \Rightarrow$ dissipation of the system

general correlation function (fluctuation)

$$\langle S_i(t) S_j(t') \rangle = \int_{-\infty}^{\infty} \langle S_i(t) S_j(t') \rangle e^{i\omega t'} dt'$$

$$\langle S_i(t) S_j(t') \rangle e^{i\omega t'} dt' = \sum_l \langle S_l(t) \rangle$$

fluctuation - dissipation theorem.

$$g(\theta, \omega) = \frac{kT}{\omega} \text{Im } \chi(\theta, \omega) \quad (kT \gg \omega)$$

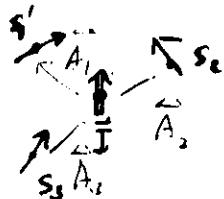
$$V_{T_1} = \frac{n^2 A^2}{2} k_B T \sum_g \frac{\text{Im } \chi(g, \omega)}{\omega}$$

general case (Anisotropic A or X, non-local A)

$$V_{T_1} = \frac{n^2 k_B T}{2} \sum_g \left[|A_g^{xx}|^2 \frac{\text{Im } \chi^{xx}(g, \omega)}{\omega_0} + |A_g^{yy}|^2 \frac{\text{Im } \chi^{yy}(g, \omega)}{\omega_0} \right]$$

$$H_0 \parallel z$$

$$A_g = \sum_i A_{gi} e^{i\vec{k}\vec{r}_i}$$



2-5) nuclear relaxation in metals and superconductors

a) Korringa relation (free electron)

$$\Delta E = -\delta \nu k A \vec{I} \cdot \vec{S}$$

$$1/T_1 = \frac{4\pi}{k} \sum_{k,k'} |(k\uparrow + k'\downarrow)|^2 \text{ with } A = \epsilon_F^2 / (2\pi^2 N) \quad \text{and} \quad f(E_F) = S(\epsilon_F - \epsilon_F + \hbar\omega)$$

$$= \pi \delta_{kk'} k A^2 \left\{ \int d\epsilon d\epsilon' f(\epsilon) (1-f(\epsilon')) \frac{\omega_0 - \epsilon}{kT + (E_F - \epsilon)} S(E_F) \right\}$$

$$= \pi \delta_{kk'} k A^2 \frac{\omega_0 - \epsilon}{kT} \int f(E_F) d\epsilon$$

right shift $k_s = A \chi_s \propto A S(E_F)$

$$T_1 T k^2 = \left(\frac{k}{4\pi k_B} \right) \frac{\partial^2 \mu}{\partial n^2} \quad \text{Korringa relation.}$$

Intuitive picture

assume Lorentzian spectrum $\frac{\text{Im} \chi(\omega)}{\omega} = C \frac{\Gamma}{\omega^2 + \Gamma^2}$

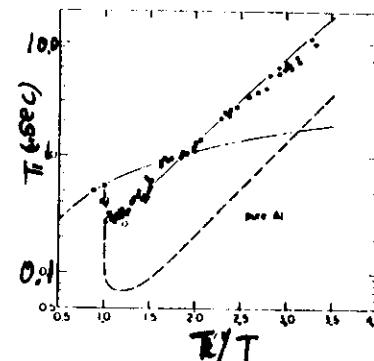
sum rule $\int \frac{\text{Im} \chi(\omega)}{\omega} d\omega = \pi \chi(\omega=0) = \pi \chi_g$

$$C = \chi_g \quad \left. \frac{\text{Im} \chi(\omega)}{\omega} \right|_{\omega \rightarrow 0} = \chi_g / \Gamma \quad \left[\sum \frac{\text{Im} \chi(\omega)}{\omega} \propto \rho(E_F) \right]$$

$$\chi_g \propto \rho(E_F), \quad \Gamma \propto 1/\rho(E_F)$$

b) nuclear relaxation rate in superconducting state.

- coherence effect.
- elementary excitation

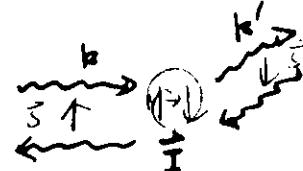


AL (ref. 13)

scattering processes

$(k\uparrow \rightarrow k'\downarrow), (-k\uparrow \rightarrow k\downarrow)$

not independent



transition probability $\propto Z_g = -1/2 \rightarrow 1/2$

$$| \langle \alpha (a_{k\uparrow}^\dagger a_{k\downarrow} + a_{-k\uparrow}^\dagger a_{-k\downarrow}) | m \rangle |^2$$

$$\Rightarrow (\underbrace{U_k U_{k'} + V_k V_{k'}}_{\frac{1}{2} (1 + \frac{\epsilon \epsilon'}{E E'} + \frac{\Delta^2}{E E'})}) (Y_{k\uparrow}^\dagger Y_{k\downarrow} + Y_{-k\uparrow}^\dagger Y_{-k\downarrow})$$

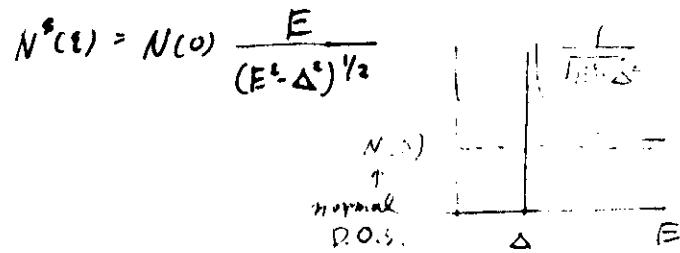
\Rightarrow average over k, k'

[see textbook
by J.R.Schrieffer] $\Rightarrow \frac{1}{2} (1 + \frac{\Delta^2}{E E'})$: coherence factor

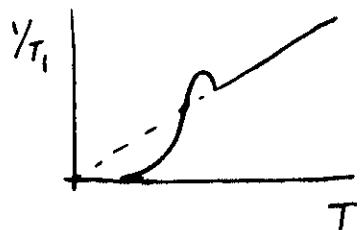
$$1/T_1 \propto \int_0^\infty N^>(E_i) N^<(E_F) \left(1 + \frac{\Delta^2}{E_i E_F} \right) f(E_i) (1-f(E_F)) S(E-E_F) dE$$

E: quasi particle energy $E = \sqrt{\Delta^2 + \epsilon^2}$

- quasiparticle density of states.



- γ_{T_1} shows a peak below T_c ($\approx 0.9 T_c$)



- at low T $\gamma_{T_1} \propto e^{-T/\Delta}$ $\Delta: gap$

