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NMR Studies of the Normal State of High Temperature Superconductors

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Abstract. — We review NMR and NQR studies in the normal state of high- T_c superconducting cuprates. Emphasis is given on the three major contributions brought by these techniques: the presence of antiferromagnetic fluctuations, the possible justification of a single spin fluid model, and the opening of a pseudogap in the spin excitations for underdoped compounds. Some recent developments are addressed and compared to theoretical models. In particular, quantitative analysis of the nuclear relaxation are detailed for ^{63}Cu , ^{89}Y and ^{17}O nuclei, enabling a comparison with inelastic neutron scattering data, and finally pointing out to a serious difficulty with the one-band approach.

1. Introduction

Besides the appealing perspectives opened by the discovery of a new class of superconductors [1] with values of T_c above the temperature of liquid nitrogen, one of the great merit of the discovery of the cuprate high T_c superconductors (HTSC) has been to highlight the peculiar role played by the dimensionality $D = 2$ in solid state physics. Can one explain the many unconventional properties of the cuprates, including the high value of T_c , as natural consequences of the presence of Van-Hove singularities in the density of states or antiferromagnetic (AF) fluctuations [3, 4], in a quasi two-dimensional (2-D) Fermi liquid, or do they require a more fundamental reexamination of low dimensional solid state physics, *i.e.*, the possible extension to 2-D systems of new concepts strictly derived for one dimensional physics [5], like spin-charge separation? Ten years after the discovery of HTSC, these questions are still open, in spite of a huge amount of experimental work involving all techniques available in solid state physics. A microscopic description of the quasi-particles present in the normal state ($T > T_c$) of these strange metallic compounds is still highly controversial, as is the mechanism responsible for the formation of the superconducting ground state [6]. However, it is generally agreed that the basic ingredient of the HTSC is CuO_2 planes with a square lattice arrangement for Cu

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Fig. 1. — Schematic phase diagram for hole doped cuprates. The presence of a pseudogap phase is supported by numerous experiments.

and O atoms, separated by functional blocks playing the role of a charge reservoir. In the absence of hole (or electron) doping, the CuO₂ planes form a good representation of a quasi-2D Heisenberg antiferromagnet (La₂CuO₄, YBa₂Cu₃O₆) with an insulating Néel ground state. By introducing holes in the CuO₂ planes the Néel temperature is rapidly decreased, before producing a new “metallic” phase with a superconducting ground state [7]. The value of the superconducting transition temperature first increases with the hole concentration n_h in the CuO₂ plane (underdoped regime), reaches a maximum value for an optimal doping, and then decreases with a further increase of n_h (overdoped regime) [8]. The full evolution according to this ideal phase diagram (Fig. 1) is not usually observed in a single system. For example, a variation in x going from 0 to 1 in YBa₂Cu₃O_{6+x} shows an AF phase for $x < 0.4$, covers the underdoped regime from 0.4 to 0.94 ($T_c = 93$ K), and has a small range of concentration in the overdoped regime. La_{2-x}Sr_xCuO₄ as a function of x exhibits first an AF phase, separated from the metallic one by a spin-glass regime. The optimal doping is around $x = n_h = 0.15$ and the

overdoped range is difficult to obtain in stable form [9]. On the contrary, $\text{Ti}_2\text{Ba}_2\text{CuO}_{6+\delta}$ only exists in the overdoped regime, with T_c values ranging between ≈ 85 to 0 K. Nowadays, there is more and more experimental evidence that the underdoped and the overdoped regimes have quite different electronic properties [10–12]. Indeed, this was inferred very early [13,14], from the experimental data obtained by Nuclear Magnetic Resonance (NMR) in various HTSC systems. This technique, which played a crucial role in the test of the Bardeen-Cooper-Shrieffer (BCS) theory for conventional superconductors [15,16], has been extensively applied to the study of the HTSC during the past decade and has proved to be a major tool for investigating the low energy excitations in these compounds.

The goal of this paper is to review the current knowledge of NMR experimental data in the cuprates and to discuss how they put constraints on the various theoretical models competing for the description of the quasi-particles which are responsible for the superconducting ground state. We shall limit ourselves to the normal state ($T > T_c$) of the metallic part of the phase diagram. For NMR studies of the antiferromagnetic phase, and that of the superconducting state, we refer the reader to other review papers [17–22]. The paper will be organized as follows: in Section 2, we review the NMR background necessary to appreciate the contribution of NMR to our better understanding of the physical properties of the cuprates. Section 3 will be devoted to the notion of single spin fluid, which has been supported by NMR, to the Mila-Rice Hamiltonian commonly used to describe the Hamiltonian of the various nuclei in the cuprates, and to the description of the magnetic hyperfine couplings. In Section 4, we review the experimental results obtained by nuclear spin lattice and spin-spin relaxation measurements, and discuss current interpretations in the literature, within the framework of the nearly antiferromagnetic Fermi liquid, and the quantum critical regime of disordered 2D Heisenberg antiferromagnets. Section 5 is devoted entirely to the question of the spin gap in underdoped systems, which was first revealed by NMR experiments, and has become a central issue in the understanding of electronic and magnetic properties of the normal state of HTSC. In Section 6, we discuss the comparison between NMR and inelastic neutron scattering data and how it affects the interpretation of the NMR data. Section 7 briefly mentions the NMR data concerning the problems of phase separation. In the concluding remarks, we try to summarize the contribution of NMR to the present understanding of the properties of the normal state of HTSC, and to stress upon the open questions which should be addressed in a near future.

2. NMR and NQR Background

Nuclear spins in solids are submitted to various couplings due to their environment, formed by localized and delocalized electrons in the structure. Their total Hamiltonian can be written as:

$$\mathcal{H}_{\text{total}} = \mathcal{H}_{\text{zeeman}} + \mathcal{H}_Q + \mathcal{H}_{\text{mhf}} + \mathcal{H}_{\text{nuclei-nuclei}} \quad (1)$$

where the various terms are respectively the Zeeman term, the quadrupolar term, the magnetic hyperfine interaction, and the nuclear spin-spin interaction.

NMR usually refers to the case where the main Hamiltonian is the Zeeman coupling of the nuclear spins $\mathbf{I}$ to the external magnetic field $\mathbf{H} = H_0 \mathbf{k}$, $\mathcal{H}_{\text{zeeman}} = -\gamma_i \hbar \sum_i I_z^i H_0$, where γ_i is the gyromagnetic ratio of the isotope i . In the absence of any other perturbation, the Zeeman Hamiltonian gives rise to a single line spectrum, at the Larmor frequency $\omega_n = 2\pi\gamma_i H_0$.

2.1. ELECTRIC FIELD GRADIENTS. — For spin $I > 1/2$, and non-cubic local symmetry, the largest perturbation to the Zeeman Hamiltonian is usually the quadrupole Hamiltonian $\mathcal{H}_Q$,

which couples the quadrupole moment Q of the nuclei to the electric field gradient (EFG) due to the surrounding electronic charge distribution. Note that Q is specific to each isotope. The EFG tensor is a second rank tensor which usually strongly reflects the local symmetry of the environment. If we call $V_{\alpha\alpha}$ the components of the EFG tensor along its principal axes ($\alpha = X, Y, Z$), $\mathcal{H}_Q$ can be expressed as:

$$\mathcal{H}_Q = \frac{h\nu_Q}{2} \left[I_Z^2 - \frac{I(I+1)}{3} + \frac{\eta}{6}(I_+^2 + I_-^2) \right] \quad (2)$$

where ν_Q is called the quadrupole frequency, $\eta = \frac{V_{XX} - V_{YY}}{V_{ZZ}}$ is the asymmetry parameter with the convention $|V_{ZZ}| \geq |V_{YY}| \geq |V_{XX}|$, and ν_Q is related to the largest component of the EFG tensor by $\nu_Q = \frac{3eQV_{ZZ}}{2I(2I-1)\hbar}$. In a high magnetic field, the quadrupole perturbation (for odd values of $2I$) leads to a splitting of the resonance into a central line ($m = -1/2 \leftrightarrow 1/2$ transition) and satellites on each side of it, the value of the splitting being related to both ν_Q and the orientation of the external magnetic field with respect to the principal axis of the EFG tensor. In the case where ν_Q is large, the spectrum for unoriented powder samples is a complicated pattern [23, 24], which usually inhibits useful studies. Fortunately, most of the cuprate powder samples can be oriented with the application of an external magnetic field, so that the c -axis (perpendicular to the CuO_2 plane) of each of the grains (which have to be single-crystals) is aligned along the field direction [25]. Working on such oriented powders with $H_0 \parallel c$ -axis is equivalent to work on single crystals. When H_0 is perpendicular to the c -axis, two different situations are encountered: if there is no detectable asymmetry of the tensor in the ab -plane (which is the case for the planar copper) the spectrum is again similar to that obtained in a single crystal. However, when the largest component of the tensor lies in the ab -plane (copper in the chains of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$, planar oxygen) one obtains a broad 2D powder spectrum.

In the absence of both external magnetic field and spontaneous spin polarization, $\mathcal{H}_Q$ becomes the main Hamiltonian and transitions can be induced between its eigenstates. This situation is called Nuclear Quadrupole Resonance (NQR), a technique which has been widely used in the study of cuprates, namely for Cu and La nuclei (the quadrupole coupling at the oxygen sites is too small to allow a direct detection in zero external magnetic field). One advantage of NQR is the possibility to follow the nuclear spin-lattice relaxation time T_1 in zero field, avoiding complications related to the presence of vortices in the mixed phase.

The knowledge of the quadrupole tensor for each particular nuclear site (when it exists) is a prerequisite to study the $\mathcal{H}_{\text{mhf}}$ Hamiltonian. Studies of the EFG tensor provide valuable information about the site symmetry and the degree of disorder in the local environment [26, 27]. A recent development is worth being noted: thanks to the increasing number of NMR studies in various systems, it seems that all compounds having a high (or potentially high) T_c show systematically relatively low ν_Q values for Cu in the CuO_2 planes. This behavior, first noted by Zheng *et al.* [28], has been tentatively ascribed to a higher in-plane Cu-O hybridization. Such a conclusion seems to be supported by recent NMR results in Hg-based cuprates where the buckling of the CuO_2 planes is negligible [29, 30]. However, the respective weights of the electronic on-site and lattice contributions to the EFG are not well understood, making this issue still controversial. We shall not discuss the EFG tensors in more detail here; the reader is referred to review [19] or specialized papers [31, 32], dealing with this matter.

2.2. MAGNETIC HYPERFINE SHIFTS. — Here, we shall concentrate on the magnetic hyperfine interaction. The net result of the Hamiltonian $\mathcal{H}_{\text{mhf}}$ can be considered as the interaction of a

nuclear spin with a time dependent *local* magnetic hyperfine field h_L due to the electronic spins and orbital motion. The static (time-averaged) part h_L gives rise to a shift of the NMR line proportional to the applied external field, which is denoted as the Magnetic Hyperfine Shift (MHS) tensor $\mathbf{K}$. Its components can be decomposed into a spin, an orbital and a diamagnetic part:

$$K_{\alpha\alpha}(T) = K_{\alpha\alpha}^{\text{spin}} + K_{\alpha\alpha}^{\text{orb}} + K_{\alpha\alpha}^{\text{dia}} \quad (3)$$

where α denotes the x, y, z directions. In HTSC compounds, $\mathbf{K}^{\text{orb}}$ is temperature independent and $\mathbf{K}^{\text{dia}}$ is usually negligible. Well below T_c , $\mathbf{K}^{\text{spin}}$ vanishes, as the signature of singlet spin pairing and thus, the remaining MHS tensor is the orbital one. In the following, we shall only consider the MHS tensor of the copper and oxygen nuclei in the CuO_2 plane (usually referred to as Cu(2) and O(2,3) in the case of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$), and that of the yttrium when present in between the CuO_2 planes. (In all NMR studies, the apex oxygen nuclei have been found to be quite weakly coupled to the spin susceptibility, and therefore results concerning this site will not be discussed here.) For copper and yttrium, the MHS tensors have an axial symmetry and the components will be denoted K_c and K_{ab} for H_0 parallel or perpendicular to the CuO_2 plane [33]. For the planar oxygen sites, the main component of the MHS tensor lies along the Cu-O-Cu bond; thus the in-plane components are denoted as $K_{\parallel}$ along this bond and $K_{\perp}$ perpendicular to it, and the MHS tensor is usually expressed as $(K_c, K_{\perp}$ and $K_{\parallel})$.

The spin part of the MHS tensor can be formally related to the average susceptibility per site through the relationship:

$$K_{\alpha\alpha} = A_{\alpha\alpha} \chi_{\alpha\alpha} / g_{\alpha} \mu_B \quad (4)$$

where $A_{\alpha\alpha}$ is the hyperfine field per spin unit [34], g_{α} is the Lande factor for the electron, μ_B the Bohr magneton, and α is the direction of the magnetic field, which we always suppose to be along one of the principal axis of the MHS tensor. This simple formula hides actually a rather complex reality. One ambiguity in the cuprates is whether one should consider the electronic spins as localized as in magnetic insulators [35] or as itinerant as in transition metals for example [36]. In both cases, the coupling between the nucleus and the electronic spin density is rather local, and usually decomposed in several components corresponding to the spin polarization of the various atomic wave functions on which the whole many body electronic wavefunction is projected. For example, in the case of the planar Cu site, the spin part of the MHS is expected to be mainly due to the spin polarization of the on-site $d_{x^2-y^2}$ orbital. However, after an analysis of the experimental MHS tensor [37, 38], of the planar copper in $\text{YBa}_2\text{Cu}_3\text{O}_7$, it was concluded that an important contribution was due to a super-transferred hyperfine field proportional to the spin polarization carried by the nearest neighbors Cu(2), through the oxygen O(2p) and the Cu(4s) wave-functions [39]. As far as the MHS tensor of the planar oxygen is concerned, it has to be analyzed in terms of spin polarization of the oxygen O(2p) and O(2s) orbitals [40–42]. Consequently, after removal of the dipolar contribution due to the spin density on the Cu(2) sites, the MHS tensor of oxygen is written as:

$$^{17}\text{K}^{\text{spin}}(\theta) = ^{17}\text{K}_{\text{iso}}^{\text{spin}} + ^{17}\text{K}_{\text{ax}}^{\text{spin}} \frac{(3 \cos^2 \theta - 1)}{2} \quad (5)$$

where $^{17}\text{K}_{\text{iso}}$ and $^{17}\text{K}_{\text{ax}}$ are related to the spin polarization of the O(2s) and O(2p) orbitals, respectively, and θ is the angle between the magnetic field H_0 and the Cu-O-Cu bond in the ab -plane. In equation (5) we neglected the small deviation from the axial symmetry which is revealed by experimental data, so that experimentally, $^{17}\text{K}_{\text{iso}}$ and $^{17}\text{K}_{\text{ax}}$ are defined as:

$$^{17}\text{K}_{\text{iso}} = (^{17}\text{K}_c + ^{17}\text{K}_{\perp} + ^{17}\text{K}_{\parallel})/3, \quad ^{17}\text{K}_{\text{ax}} = 2[^{17}\text{K}_{\parallel} - (^{17}\text{K}_c + ^{17}\text{K}_{\perp})/2]/3 \quad (6)$$

Finally, the yttrium MHS tensor is dominated by the core-polarization of closed yttrium shells by the spin density at the Cu(2) site through the O(2p) orbitals [43]. Similar situation can be found for other nuclei like ^{43}Ca , ^{205}Tl , or ^{199}Hg in other systems, but we shall not comment on them here.

2.3. NUCLEAR SPIN LATTICE RELAXATION. — The nuclear spin-lattice relaxation rate (NSLRR), which is the rate at which the nuclear magnetization relaxes to its thermal equilibrium value along the external magnetic field, is due to the fluctuations of the magnetic hyperfine field h_L (the fluctuations of the EFG tensor have been shown to have a negligible contribution in the normal state, at least for the nuclei species which have been studied). According to Moriya [44], the NSLRR rate can be written as:

$$\imath(T_1 T)_\alpha^{-1} = \frac{k_B \gamma_i^2}{\mu_B^2} \sum_{q, \alpha' \neq \alpha} |A_{\alpha'\alpha'}^i(q)|^2 \frac{\chi''_{\alpha'\alpha'}(q, \omega_n)}{g_{\alpha'\alpha'}^2 \omega_n} \quad (7)$$

where $\imath$ stands for the nuclear species, α for the direction of H_0 (supposed to be parallel to one of the principal axes of $A_{\alpha'\alpha'}$ and $\chi''_{\alpha'\alpha'}$ tensors), $A_{\alpha'\alpha'}^i(q)$ is the Fourier transform of the hyperfine field defined above $[A_{\alpha'\alpha'}^i(\mathbf{q}) = \sum_{R_i} A_{\alpha'\alpha'}^i(\mathbf{R}_i) \exp(-i\mathbf{q} \cdot \mathbf{R}_i)]$, and $\chi''_{\alpha'\alpha'}(q, \omega_n)$ is the imaginary part of dynamic spin susceptibility for the wavevector $\mathbf{q}$ and nuclear Larmor frequency ω_n ($\hbar\omega_n \approx 0$) for the direction α' perpendicular to α . Again, the use of this formula in HTSC compounds hides some ambiguity, depending on whether one considers the electronic spins as localized or itinerant. For example, in the case of the oxygen relaxation, the use of the traditional formulae for $(T_1 T)^{-1}$ in metals [35,36] would lead to consider the fluctuations of the isotropic part of the hyperfine tensor and that of the axial one, as incoherent. On the contrary, in the picture of localized spins at the copper site, coupled to the oxygen nuclei through a transferred hyperfine field, A_{iso} and A_{ax} act coherently. Obviously, both descriptions lead to quite different values for the anisotropy of the oxygen NSLRR. Experimental data [45,46], favor the localized picture.

2.4. NUCLEAR SPIN-SPIN RELAXATION. — In most solids, the Hamiltonian $\mathcal{H}_{\text{nuclei-nuclei}}$ is restricted to the nuclear dipole-dipole interaction. It thus gives rise to a temperature independent spin-spin relaxation rate which often has the form $\exp(-t^2/2(T_{2G})^2)$ where $1/(T_{2G})^2$ is equal to the second-moment of the line-shape. By designating H'_{nn} as the part of $\mathcal{H}_{\text{nuclei-nuclei}}$ which connects states of the same energy, $1/(T_{2G})^2$ can be evaluated as a trace:

$$1/(T_{2G})^2 = -\frac{\text{Tr}[H'_{\text{nn}} \cdot I_x]^2}{\hbar^2 \text{Tr} I_x^2}$$

However, indirect nuclear spin-spin interactions can be mediated by the electronic spin susceptibility [36]. The group of Slichter [47] was the first to point out the importance of T_{2G} to obtain information about the antiferromagnetic exchange between the electronic spins. Formally, this type of indirect spin-spin interaction can be written as:

$$\sum_{\alpha, i, j} \frac{\gamma_i \gamma_j}{2(g_{\alpha\alpha} \mu_B)^2} I_\alpha^i I_\alpha^j \sum_{R, R'} A_{\alpha\alpha}(R_i - R) \chi(R - R') A_{\alpha\alpha}(R_j - R') \quad (8)$$

where $\chi(\mathbf{R} - \mathbf{R}')$ is the Fourier transform of the real part of the electronic spin susceptibility $\chi(\mathbf{q})$. Later, it has been shown that this quantity was temperature dependent [48,49], and that the nuclear dipole-dipole contribution was negligible compared to that of the indirect

interactions. The study of the temperature dependence of T_{2G} has become a major tool in NMR and NQR studies of HTSC, since due to the presence of a transferred hyperfine interaction in these materials (see Sect. 3.2.), T_{2G} is able to provide information about the static part of the staggered susceptibility $\chi'(\mathbf{q} \approx \mathbf{Q}_{AF}, \omega = 0)$.

3. Magnetic Hyperfine Couplings

3.1. A SINGLE SPIN-FLUID. — In the first few years after the discovery of the cuprates, there has been an intense effort to find the simplest model Hamiltonian which would describe the low energy properties of the CuO_2 planes. Very early, Anderson [5] proposed an effective Hamiltonian known as the t-J model, which corresponds to a single band 2D Hubbard model in the limit of infinite on-site Coulomb repulsion U . Whether such a simple model could keep the essential features of a more general Hamiltonian containing Cu and O bands and intra- and interatomic Coulomb interactions has been a long debate. To justify the t-J model, Zhang and Rice [50] have proposed that the holes introduced by doping the CuO_2 planes would delocalize onto the four oxygen sites around a Cu^{2+} ion and form a local singlet with it. This singlet would then move through the lattice of Cu^{2+} ions, in a similar way as a hole. *i.e.*, a missing spin, in a simple square Cu^{2+} ion lattice. The ability of the t-J model to cover the whole physics of the starting two-band Hamiltonian has been criticized by Emery and Reiter [51], who claimed that the two-band Hamiltonian implies the existence of a second spin degree of freedom related to the O(2p) band, which cannot be accounted within the framework of the t-J model. This question has polarized the interpretation of the temperature dependence of the magnetic hyperfine shifts in high T_c superconductors. Early measurements of the anisotropic part of the MHS at oxygen sites in $\text{YBa}_2\text{Cu}_3\text{O}_7$ [40–42], which is directly related to the spin polarization of the O(2p) orbitals, have shown that most of the total spin polarization ($> 85\%$) was carried by the copper sites in these compounds. As regards the temperature dependence of the MHS, it was first reported by Alloul *et al.* [52] that in the $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ system, the MHS of yttrium was scaling linearly the macroscopic susceptibility. Since the main coupling of the yttrium to the magnetic susceptibility in the CuO_2 plane occurs through the polarization of the oxygen orbitals this was interpreted as a proof of the existence of a single spin fluid [53] in agreement with the t-J model. Soon after, it was shown by Takigawa *et al.* [54] that $^{63}K_{ab}$, $^{17}K_{\text{iso}}$, and $^{17}K_{\text{ax}}$ had the same temperature dependence in $\text{YBa}_2\text{Cu}_3\text{O}_{6.63}$ (Fig. 2). Subsequently, this behavior, *i.e.*, the same T -dependence on all nuclear sites coupled to the Cu spin polarization, was observed in all the cuprates where it was studied ($\text{YBa}_2\text{Cu}_4\text{O}_8$ [55], $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ [56] for example). Strictly speaking, this behavior by itself does not exclude the existence of a temperature independent susceptibility due to an O(2p) band. For example, the T dependence of the Knight shift in Platinum metal varies linearly with the macroscopic susceptibility, regardless of the presence of an s-p band giving rise to a T independent contribution [57]. The validity of the single spin-fluid picture in HTSC thus relies on the precise knowledge of the orbital shifts of the oxygen, copper, and yttrium nuclei. Let us consider for example the axial part of the oxygen MHS. There are three possible contributions: one proportional to the polarization of the O(2p) orbitals by hybridization with the Cu(2) orbitals, one proportional to the susceptibility (supposed to be temperature independent) of some O(2p) band, and a (temperature independent) orbital contribution:

$$^{17}K_{\text{ax}}(T) - ^{17}K_{\text{const}} = 2f_p A^{2p} \chi^{\text{spin}} = \lambda(^{63}K_{ab}(T) - ^{63}K_{\text{orb}}) \quad T > T_c$$

with

$$^{17}K_{\text{const}} = A^{2p} \chi^{\text{holes}} + ^{17}K_{\text{ax}}^{\text{orb}}$$

Fig. 2. — Various components of the Cu and O magnetic hyperfine shift tensors in $\text{YBa}_2\text{Cu}_3\text{O}_{6.63}$. From Takigawa *et al.* [54].

$$^{17}\text{K}_{\text{ax}}(T=0) = ^{17}\text{K}_{\text{ax}}^{\text{orb}} \quad ^{63}\text{K}_{\text{ax}}(T=0) = ^{63}\text{K}_{\text{orb}} \quad T \ll T_c$$

It is clear that the single spin fluid hypothesis can only be validated if experimentally, $^{17}\text{K}_{\text{const}} = ^{17}\text{K}_{\text{ax}}^{\text{orb}}$. It can be seen in reference [54] that although some deviation from this equality seems to occur, it is well within the error bars, and leads to a negligible value of χ^{holes} . However, one must remember that the determination of the orbital shifts in the superconducting state is difficult, because of the corrections due to the finite magnetization in the mixed state and the change in the lineshape due to the presence of a vortex lattice [16].

3.2. THE MILA-RICE HAMILTONIAN, HYPERFINE COUPLING TENSORS AND FORM FACTORS. — The single spin fluid picture, and the fact that most of the spin density is borne by the copper sites, has led to the following hyperfine Hamiltonian, in which the only source of coupling are the electronic spins localized at the copper site:

$$\mathcal{H}_{\text{mhf}} = ^{63}\gamma\hbar \sum_i ^{63}\mathbf{I}_i(\mathbf{A}\mathbf{S}_i + \sum_{\delta=1-4} \mathbf{B}\mathbf{S}_{i+\delta}) + ^{17}\gamma\hbar \sum_{j,\delta'=1-2} ^{17}\mathbf{I}_j\mathbf{C}\mathbf{S}_{j+\delta'} + ^{89}\gamma\hbar \sum_{k,\delta''=1-8} ^{89}\mathbf{I}_k\mathbf{D}\mathbf{S}_{k+\delta''} \quad (9)$$

where the tensor $\mathbf{A}$ corresponds to the Cu on-site hyperfine field tensor, $\mathbf{B}$ is the (isotropic) supertransferred hyperfine field from the 4 nearest neighbors copper sites, $\mathbf{C}$ is the (anisotropic) transferred hyperfine coupling to the planar oxygen from its two nearest neighbors copper sites, and $\mathbf{D}$ the supertransferred hyperfine tensor to the yttrium from the eight nearest neighbors copper sites (in the case of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ and related compounds). This Hamiltonian, usually quoted as the Mila-Rice or the Shastry-Mila Rice Hamiltonian [58] is commonly used in the

literature to quantitatively analyze the NMR data. The first step in the analysis of NMR data usually concerns the determination of the hyperfine field. However, this is not obvious in the cuprates for several reasons. In the case of the planar copper, there are three quantities to determine: A_c , A_{ab} and B , although experimentally, only $A_c + 4B$ and $A_{ab} + 4B$ can be obtained from equation (4). The determination of $A_c + 4B$, $A_{ab} + 4B$, C_α , and D_α is more accurate in compounds where the susceptibility is strongly temperature dependent, that is, in underdoped compounds. Indeed, few experiments that include susceptibility and MHS measurements on the same samples can be found in the literature [42, 56, 59, 60]. In addition, it is not obvious what susceptibility to use in equation (4) in compounds like $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ where part of the susceptibility is carried by the copper atoms located on the chains. Usually, the Cu atomic susceptibility is obtained by dividing the total susceptibility by $2 + x$ and assuming that copper in the chains and in the planes bear the same spin susceptibility. This assumption has been used as well for the determination of $A_{ab} + 4B$ [59] and $C_{\alpha\alpha}$ [42]. The anisotropy of the static susceptibility is usually not taken into account. As far as $A_c + 4B$ is concerned, it turns out that experimentally for $H_0 \parallel c$ -axis, the MHS is found independent of temperature and have identical values in the metallic and superconducting state within the experimental uncertainties in the $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$, $\text{YBa}_2\text{Cu}_4\text{O}_8$, $\text{La}_{2-x}\text{Sr}_x\text{Cu}_2\text{O}_4$ compounds. Thus $A_c + 4B \approx 0$ is an usual assumption in all these compounds. The same is not true for compounds like $\text{Tl}_2\text{Ba}_2\text{CuO}_{6+\delta}$ [61], $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ [62], $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ [63, 64], and $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_8$ [29, 30]. By assuming that A_c and A_{ab} are intrinsic properties of the planar Cu ion and taking the current values for $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$, tentative values of B have been extracted from the ratio $(A_c + 4B)/(A_{ab} + 4B)$. They are systematically larger than in the YBCO and LASCO compounds, which may indicate a larger value of the exchange coupling in these materials [29, 30, 61, 62]. This behavior is usually accompanied by a smaller value of the planar copper quadrupole coupling, as already mentioned above, a feature which has been attributed to a larger hybridization between $d_{x^2-y^2}$ and $O(2p)$ orbitals [28, 29]. Both phenomena seem to be controlled by the buckling of the Cu-O-Cu bonding.

Finally, the ratio $2C_c/(A_{ab} + 4B)$ has been determined in some compounds $\text{YBa}_2\text{Cu}_3\text{O}_{6.63}$ (0.58) [54], $\text{YBa}_2\text{Cu}_4\text{O}_8$ (0.67) [55], $\text{La}_{2-x}\text{Sr}_x\text{Cu}_2\text{O}_4$ (0.68) [56], $\text{Tl}_2\text{Ba}_2\text{CuO}_{6+\delta}$ (0.30) [61], $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ (0.50) [62] as well as $(8D_c + D_{\text{dip},c})/C_c(-0.127)$ in $\text{YBa}_2\text{Cu}_3\text{O}_{6.63}$ [65]. Typical values of the hyperfine field constants can be found in references [22, 66, 67]. It must be emphasized that these values are approximate: in the most favorable cases they are not known with an accuracy better than 20%.

The knowledge of these coupling is of primary importance for a quantitative interpretation of the nuclear spin-lattice and spin-spin relaxation data. In the hypothesis of a single spin degree of freedom, the evaluation of $1/T_1$ and $1/T_{2G}$ involves a summation over the Brillouin zone of the product of the imaginary or the real part of the dynamic spin susceptibility located at the planar copper sites square with the form factors $F(\mathbf{q}) = |A(\mathbf{q})|^2$. These form factors $F(\mathbf{q})$ can be expressed as:

$$^{63}F_{ab}(\mathbf{q}) = [A_{ab} + 2B(\cos q_x a + \cos q_y b)]^2 \quad (10a)$$

$$^{63}F_c(\mathbf{q}) = [A_c + 2B(\cos q_x a + \cos q_y b)]^2 \quad (10b)$$

$$^{17}F_\alpha(\mathbf{q}) = 2C_{\alpha\alpha}^2[1 + (\cos q_x a + \cos q_y b)/2] \quad (10c)$$

$$^{89}F_\alpha(\mathbf{q}) = 8D_{\alpha\alpha}^2(1 + \cos q_x a)(1 + \cos q_y b)(1 + \cos q_z d) \quad (10d)$$

where d is the distance between the two CuO_2 planes in YBCO compounds.

Note that for $\mathbf{q} = \mathbf{Q}_{\text{AF}} = (\pi/a, \pi/a)$, which is the AF wavevector of the undoped parent compounds of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ and $\text{La}_{2-x}\text{Sr}_x\text{Cu}_2\text{O}_4$, $^{17}F_\alpha(\mathbf{Q}_{\text{AF}})$ and $^{89}F_\alpha(\mathbf{Q}_{\text{AF}})$ are zero, whereas $^{63}F_c(\mathbf{Q}_{\text{AF}})$ and $^{63}F_{ab}(\mathbf{Q}_{\text{AF}})$ present a maximum (Fig. 3). Let us suppose that AF fluctuations.

Fig. 3. — The q -dependence of the hyperfine form factors for planar ^{63}Cu , planar ^{17}O and ^{89}Y , derived from the Shastry-Mila-Rice Hamiltonian. From Slichter *et al.* in reference [18].

reminiscent of the long range order present in the parent compounds, are present in the metallic phase, producing a peak around $\mathbf{Q}_{\text{AF}}$ in the imaginary part of the dynamic spin susceptibility. Obviously, these AF fluctuations will strongly drive the copper NSLRR, but their contribution is heavily attenuated at the oxygen site, and still more so at the yttrium site. This purely geometrical effect, known for fifteen years in magnetic insulators [68], does not really depend on whether the copper spins are localized or not. On the contrary, the calculation of the anisotropy of the NSLRR using the form factors defined above in equation (10) fully assumes that the electronic spins can be considered as localized.

Another important consequence of the q -dependence of the Fourier transform of the hyperfine field is its effect on the nuclear spin-spin relaxation. By taking the Fourier transform of the expression given by equation (8), it turns out that the longitudinal component $A_c + 2B(\cos q_x a + \cos q_y b)$ is much larger than the transverse one for $\mathbf{q} = \mathbf{Q}_{\text{AF}}$. This, in addition to other arguments [49] justifies neglecting the transverse terms in the expression of $T_{2\text{G}}$ for $H_0 \parallel c$ -axis, which can then be written as [69, 70]:

$$\left[\frac{1}{T_{2\text{G}}} \right]^2 = \frac{c_i (\gamma_i \hbar)^4}{8\hbar^2 (g\mu_B)^4} \left[\sum_q |A_{cc}(q)|^4 \chi^2(q) - \left\{ \sum_q |A_{cc}(q)|^2 \chi(q) \right\}^2 \right], \quad (11)$$

where i stands for the copper isotope 63 or 65 and c_i for their natural abundance. Because of the q -dependence of A_{cc} , which is maximum for $\mathbf{q} = \mathbf{Q}_{\text{AF}}$ and close to zero for $q = 0$, it is clear that in the case where $\chi(\mathbf{q})$ is peaked around $\mathbf{Q}_{\text{AF}}$, $T_{2\text{G}}$ shows the temperature dependence of $\chi(\mathbf{Q}_{\text{AF}})$.

4. Nuclear Spin-Lattice and Spin-Spin Relaxation in HTSC

4.1. NUCLEAR SPIN-LATTICE RELAXATION. — One of the most striking results obtained by NMR in HTSC, is the completely different temperature dependence observed for the copper and oxygen nuclei in the same CuO_2 plane. This result is quite general. It is observed in all studied

Fig. 4. — ^{63}Cu T_1T in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ for various Sr contents. From Ohsugi *et al.* [71].

compounds, including overdoped compounds, although the more underdoped is the compound, the higher is the contrast. When starting from high temperature the Cu NSLRR divided by temperature, $^{63}(T_1T)^{-1}$, increases when T decreases. In the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ compounds, which can be studied on a larger temperature range than the other families, it has been clearly shown that $^{63}(T_1T)^{-1}$ follows a Curie-Weiss behavior, or alternatively $^{63}(T_1T)$ varies linearly with T at high temperature [71] (Fig. 4). Still more striking are the results obtained by Imai *et al.* who have shown that above ≈ 700 K, $1/^{63}T_1$ is constant and has the same value within 5%, for x ranging from 0 to 0.15, that is from the pure antiferromagnetic parent compound to the optimally doped superconductor. This result seems to indicate that in the high temperature limit, the motion of the holes is not felt by the localized Cu spins. However, a slightly different result has been recently reported by the ISSP group [73], which claims that there is a 20% difference between the high temperature limit of $x = 0$ and $x = 0.15$, which they attribute to the motion of holes. In all other HTSC compounds, but for $\text{YBa}_2\text{Cu}_4\text{O}_8$ [74], Cu NSLRR measurements have been performed at temperatures below 350 K and the Curie-Weiss behavior is not as well defined. For underdoped compounds, $^{63}(T_1T)^{-1}$ passes through a maximum at a temperature $T^* \approx 150$ K (for YBCO) or higher (for $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ [29]), that is well above T_c , and then decreases with T , sometimes without a noticeable anomaly at $T = T_c$. For overdoped compounds, $^{63}(T_1T)^{-1}$ increases continuously as T is decreased down to T_c (with some exceptions that we shall comment later), and then falls abruptly.

The situation is quite different for the NSLRR of the planar oxygen (Figs. 5 and 6). In the first approximation, $^{17}(T_1T)^{-1}$ follows the same temperature dependence as the MHS (*i.e.*, the spin-susceptibility). It decreases with T in the underdoped regime and is nearly constant at optimal doping. In the overdoped regime, the situation is not as clear, as in some cases it increases slightly with decreasing T [14, 75], whereas in others it decreases slightly [61].

Fig. 5. — Left panel: magnetic hyperfine shift of planar ^{17}O for different field orientations in (a) $\text{YBa}_{1-92}\text{Sr}_{0.08}\text{Cu}_3\text{O}_7$ and (b) $\text{YBa}_2\text{Cu}_3\text{O}_{6.52}$. Right panel: nuclear spin-lattice relaxation rate of planar ^{17}O , for different field orientations in (a) $\text{YBa}_{1-92}\text{Sr}_{0.08}\text{Cu}_3\text{O}_7$ and (b) $\text{YBa}_2\text{Cu}_3\text{O}_{6.52}$. From Horvatić *et al.* [46].

Fig. 6. — T -dependence of the planar ^{63}Cu and ^{17}O spin-lattice relaxation rates in $\text{YBa}_2\text{Cu}_4\text{O}_8$. From Mangelschots *et al.* [55].

Fig. 7. — Temperature dependence of the ratio $^{17}T_1/^{63}T_1$. From Tomeno *et al.* [60].

In all cases, however, the ratio $^{63}(T_1T)^{-1}/^{17}(T_1T)^{-1}$ increases with decreasing T , with some more or less evident flattening near T_c . Note that below T_c , where the AF fluctuations disappear at low energy, the ratio $^{63}(T_1T)^{-1}/^{17}(T_1T)^{-1}$ falls down [60,76] (Fig. 7). We shall see later that a similar temperature dependence is observed for $^{63}(T_{2G})^{-1}$, at least above T_c . This sounds like the signature of the presence of AF fluctuations, even in overdoped compounds [61]. The sites between the CuO_2 planes in bi-layers compounds, such as yttrium [52] in the YBCO family, or occasionally thallium as an impurity in $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$ [77], behave qualitatively and nearly quantitatively as the planar oxygen.

Because the Fermi liquid character of the normal state of HTSC cuprates has been strongly questioned, there has been an intense search for a Korringa relationship $K^2T_1T = \text{const.}$ for those nuclei which are less sensitive to AF fluctuations, like oxygen and yttrium. The quantitative comparison between the spin part of the MHS tensor and the NSLRR for oxygen or yttrium nuclei is not an easy task, since it requires precise knowledge of the orbital MHS tensor. For most of the oxygen results obtained in the underdoped regime, plots of $^{17}(T_1T)^{-1}$ or $^{17}(T_1T)^{-1/2}$ versus $^{17}K_{\alpha\alpha}$ exhibit a linear dependence within the error bars, simply leading to different values for $^{17}K_{\text{orb}}$. In the first case, this leads to the relation $KT_1T = \text{const.}$, which can be interpreted as $(T_1T)^{-1}$ proportional to $\chi(T)/\Gamma$, where $\hbar/\Gamma$ is a temperature independent averaged correlation time. The other case leads to the more familiar Korringa relationship, $K^2T_1T = \text{const.}$ A similar situation is found for the yttrium data [52]. However, in spite of some recent interpretations in terms of Korringa behavior in the case of $\text{YBa}_2\text{Cu}_4\text{O}_8$ [60,78], the validity of the relation $KT_1T = \text{const.}$ is commonly accepted, neglecting clear deviations at high temperature observed at the yttrium site [65,79]. Indeed, the ratio $^{17}(T_1T)/^{89}(T_1T)$ has been found to increase by 30% between 300 and 100 K with decreasing temperature, in spite of the fact that $^{17}K(T)/^{89}K(T)$ is constant [65]. This unexpected temperature dependence is difficult to explain using the Mila-Rice Hamiltonian. At the same time, the anisotropy of NSLRR of the planar oxygen has been found T -dependent in the normal state of the “60 K phase” of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ [45,46], which is also impossible to explain within the framework of the Mila-Rice Hamiltonian [80].

Quite surprisingly, a magnetic field dependence of T_1 has been reported by Kambe *et al.* [81] in the single layer system $\text{Ti}_2\text{Ba}_2\text{CuO}_{6+\delta}$, both below and above T_c . Soon after, part of their results has been confirmed by Vyaselev, Kolesnikov and Shegolev [82]. In fact, Kambe *et al.* have shown that $1/T_1 \propto 1/\ln(H_0)$, a relation predicted for spin-diffusion processes in 2D paramagnets. Both groups have found that the more overdoped is the sample the larger is the effect. However, the fact that this behaviour is observed for ^{63}Cu and ^{205}Tl relaxation, which probe excitations around $\mathbf{Q}_{\text{AF}}$, but not for ^{17}O , which probes those around $q = 0$, is particularly intriguing. Usual spin-diffusion processes are characterized by the low frequency divergence of $q \approx 0$ modes [83]. Here, something new seems to be combined, involving AF spin excitations, a fact by itself remarkable in such overdoped samples where the spin fluctuations are usually considered to be relatively weak and the system more three dimensional. It remains to be investigated whether such an effect can be produced by simple spin excitation diffusion or if it requires more sophisticated mechanisms, like for example, collective hole motion, including domain walls and antiphase spin domains [84]. In any case, we should learn quite a lot on the spin dynamics from this experiment, which has not yet received further experimental or theoretical clarification.

4.2. NUCLEAR SPIN-SPIN RELAXATION RATE. — As already mentioned, the quantity T_{2G} measures the strength of the indirect nuclear spin-spin interaction mediated by the non-local spin susceptibility. It has been measured on planar copper either by NQR or in high field experiments with $H_0 \parallel c$ -axis. It is a delicate measurement, particularly because to get reliable values of T_{2G} , it is necessary that the radiofrequency excitation covers the whole NMR or NQR line, which becomes technically difficult when the linewidth exceeds 200 kHz. Furthermore, the time dependence of the amplitude of the spin-echo is also strongly affected by an inelastic life-time contribution $1/T_1^*$ so that $S(\tau) = \exp[-\tau^2/(2T_{2G}^2)] \exp(-2\tau/T_1^*)$. The $1/T_1^*$, which is a linear combination of the NSLRR for $H_0 \parallel c$ -axis and for $H_0 \parallel ab$ -plane, has to be known accurately as a function of the temperature.

The temperature dependence of $1/T_{2G}$ has been measured for various values of x in $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ [48,49,70,85,86], in $\text{YBa}_2\text{Cu}_4\text{O}_8$ [48,87,88] and $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$ [87], in $\text{Ti}_2\text{Ba}_2\text{CuO}_{6+\delta}$ [89], $\text{Ti}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ [62], $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ [29,30] and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ [64]. It has also been measured in the paramagnetic phase of La_2CuO_4 [90], where it has been found proportional to $^{63}(T_1 T)^{-1}$ and quite recently in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ [91]. In all cases, it has been found to increase with decreasing temperature, with sometimes a flattening or a small decrease close to T_c . This can be safely considered as a proof for the existence of AF correlations in all these compounds. As we shall see later, the comparison of the temperature dependence of $1/T_{2G}$ and $^{63}(T_1 T)^{-1}$ is essential in the interpretation of the NMR data (Fig. 8).

Finally, we would like to mention a creative experiment performed in $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$, a compound which can be viewed as a natural superlattice consisting of alternating blocks of $\text{YBa}_2\text{Cu}_4\text{O}_8$ and $\text{YBa}_2\text{Cu}_3\text{O}_7$ [87,90]. This situation makes the two CuO_2 planes of a bi-layer structurally inequivalent. Thus, one obtains two different Cu NMR resonance lines, each corresponding to one plane of the bi-layer. It offers the unique opportunity to perform a spin-echo double resonance (SEDOR) experiment: while performing a classical spin-echo pulse sequence $(\pi/2, \pi)$ on one of the two Cu lines, one also applies a (π) pulse at the resonance frequency of the other line, *i.e.*, the nuclear spins are flipped in the second plane. By observing a reduction of the size of the spin-echo when applying the second pulse, Stern *et al.* [93] have shown that nuclear spins in one plane could be depolarized by electronic spins in the other plane [94]. In other words, there exists an electronic coupling $J_\perp$ between the two planes. From this experiment, Millis and Monien have deduced that $J_\perp = 14$ meV [95], in good agreement

Fig. 8. — Left panel: temperature dependence of $(T_1T)^{-1}/(A-4B)^2$ in various cuprates (courtesy of Kitaoka). Right panel: the T -dependence of $(T_{2G})^{-1}/(A-4B)^2$ in $\text{YBa}_2\text{Cu}_3\text{O}_{6.63}$ [70], $\text{YBa}_2\text{Cu}_4\text{O}_8$ [48], $\text{YBa}_2\text{Cu}_3\text{O}_{6.92}$ [85], $\text{YBa}_2\text{Cu}_3\text{O}_{6.94}$ [86], slightly underdoped $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ [62], and overdoped $\text{Tl}_2\text{Ba}_2\text{CuO}_{6+\delta}$ [89].

with the recent value of 10 meV inferred from the measurement of the optical magnon dispersion in $\text{YBa}_2\text{Cu}_3\text{O}_{6.2}$ [96].

4.3. QUANTITATIVE ANALYSIS OF THE NUCLEAR RELAXATION. — The striking difference in the temperature dependence of the NSLRR for the copper and oxygen sites in the CuO_2 planes of $\text{YBa}_2\text{Cu}_3\text{O}_7$ [40] was immediately identified as a proof for the existence of AF fluctuations in the whole metallic range of the $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ and a consequence of the form factor of the oxygen. However, to go further in the interpretation required a model for the dynamic spin susceptibility. There have been many theoretical works devoted to the NSLR in the cuprates [97]. In this section, we shall only consider two of them: i) the nearly antiferromagnetic Fermi liquid model (NAFL), proposed independently by Millis Monien and Pines (MMP) [98,99] and Moriya, Takahashi and Ueda [100]. ii) the model based on the scaling properties of a disordered 2D Heisenberg antiferromagnet [101,102]. These models allow a quantitative analysis of the NSLR and NSSR data, and thus a comparison between the various compounds. For other types of model, the reader is referred to references [84,97,103]; some of them will be discussed in Section 6.

MMP have proposed a phenomenological expression within the RPA approximation:

$$\chi''(Q_{\text{AF}} + q, \omega_n) = \frac{\pi\omega_n\chi_0(T)}{\Gamma_0} + \frac{\omega_n\beta\chi_0(Q_{\text{AF}})\xi^4}{\Gamma_0(Q_{\text{AF}})(1+\xi^2q^2)^2} = \chi''_{\text{QP}} + \chi''_{\text{AF}}, \quad (12)$$

where χ''_{AF} describes the contribution of the AF fluctuations, χ''_{QP} is a background contribution of the quasi-particles. $\chi_0(T)$ is the macroscopic susceptibility, $\hbar\Gamma_0$ and $\hbar\Gamma_0(Q_{\text{AF}})$ are characteristic energies of the unperturbed Fermi liquid, β represents the strength of the AF fluctuations, and ξ is the static correlation length. The susceptibility χ''_{AF} can be rewritten as:

$$\chi''_{\text{AF}}(Q_{\text{AF}} + q, \omega_n) = \frac{\omega_n\chi_{\text{AF}}(Q_{\text{AF}} + q)}{\Gamma(Q_{\text{AF}} + q)}$$

with

$$\chi_{\text{AF}}(Q_{\text{AF}} + q) = \frac{\beta^{1/2} \chi_0(Q_{\text{AF}}) \xi^2}{(1 + \xi^2 q^2)} = \frac{\alpha \xi^2}{(1 + \xi^2 q^2)} \quad (13)$$

and

$$\Gamma(Q_{\text{AF}}) = \Gamma_0(Q_{\text{AF}}(1 + \xi^2 q^2)/\beta^{1/2} \xi^2) \quad (14)$$

For large values of ξ/a ($\xi/a \geq 2$), $^{63}(T_1 T)^{-1}$ in this model varies as $(\xi/a)^2$, which is made to vary as $1/T$ in order to fit the NMR data. In addition, large values of ξ/a ensure an efficient filtering of the contribution of the AF fluctuations at the oxygen and yttrium sites, the relaxation of these nuclei being thus governed by χ''_{QP} . This model obviously fits the data [104] for a Γ_0 value approximately constant since for these nuclei, $(T_1 T)^{-1}$ is roughly proportional to $\chi_0(T)$.

By extending their self-consistent renormalization theory of spin-fluctuations to 2-D, Moriya, Takahashi and Ueda [100] have derived independently a rather similar model. Their calculations provides values of $(\xi/a)^2$ that vary as $1/T$. The correspondence between the parameters in these two theories of nearly antiferromagnetic Fermi liquid are:

$$\beta = \frac{q_B^4}{4\pi\alpha_S T_A T_0}, \quad \Gamma(Q_{\text{AF}}) = 2\pi T_0 \xi^{-2} q_B^{-2}, \quad \chi(Q_{\text{AF}}) = \frac{q_B^2 \xi^2}{2\alpha_S T_A}$$

where q_B is a cutoff wave vector of the order of π/a , α_S is related to the enhancement of the staggered susceptibility, and T_A and T_0 are two characteristic energies ($\hbar = k_B = 1$).

A quite different model, based upon scaling analysis of the phase diagram of a disordered 2D Heisenberg antiferromagnet has been proposed by Sokol and Pines [101]. Following Chubukov and Sachdev [102], Pines and collaborators [105] assume that below some temperature corresponding to a correlation length value $\xi/a \approx 2$, the cuprates in the underdoped regime belong to the quantum critical regime defined by Chakravarty, Halperin and Nelson [106]. Within this regime, both the static susceptibility and ξ/a vary as T^{-1} and the only characteristic energy is set by the temperature. Below a particular temperature, the system enters into the quantum disordered regime; that is, ξ/a becomes constant and a spin gap opens with a value $\Delta \approx c/\xi$, where c is related to the spin wave velocity. In this description, the parameter g , which is a measure of the strength of the disorder, is larger than the critical value g_c which separates the long range ordered from the quantum disordered ground states at $T = 0$. The parameter g is assumed to increase with the hole concentration n_h in the plane [107]. When n_h becomes too large, Sokol and Pines have suggested that magnon-type spin excitations present in the system become overdamped, and that the NAFL regime should be recovered.

By using scaling arguments, one may assume, following Sokol and Pines, that $\chi(Q_{\text{AF}} + q) = \chi(Q_{\text{AF}})f(\xi q)$ with $\chi(Q_{\text{AF}}) = \alpha \xi^{2-\eta}$ with $\eta \approx 0$ and α a constant [108]. This relation implies from equation (11) that $1/T_{2G}$ is proportional to $\xi^{1-\eta}$ in both descriptions. On the other hand,

$$\lim_{\omega \rightarrow 0} \text{Im} \chi(q, \omega)/\omega = \frac{\chi(Q_{\text{AF}} + q)}{\Gamma(Q_{\text{AF}} + q)} \propto \frac{\alpha \xi^{2-\eta} f(\xi q)}{\xi^{-z} \Gamma_{\text{AF}} g(\xi q)}, \quad (15)$$

where z is the dynamic critical exponent which describes the variation of the characteristic energy as a function of ξ , i.e., $\Gamma(Q_{\text{AF}} + q) = \Gamma_{\text{AF}} \xi^{-z} g(\xi q)$. After summation over the Brillouin zone, $^{63}(T_1 T)^{-1}$ is proportional to $\alpha \xi^{2-\eta}/\Gamma_{\text{AF}}$.

In the quantum critical regime $z = 1$, so that $\frac{T_1 T}{T_{2G}}$ must be independent of the temperature and proportional to Γ_{AF} [109]. In the case of the NAFL, we see easily from equations (13, 14) that $z = 2$ (and $\eta = 0$), so that it is now $\frac{T_1 T}{(T_{2G})^2}$ which must be temperature independent

Fig. 9. — Ratios T_1T/T_{2G} and $T_1T/(T_{2G})^2$ for ^{63}Cu in $\text{YBa}_2\text{Cu}_4\text{O}_8$. From Corey *et al.* [88].

and proportional to $\Gamma_{\text{AF}}\chi(Q_{\text{AF}})$, the prefactor depending only on the hyperfine couplings. Experimentally, in the metallic part of the phase diagram, $T_1T/T_{2G} = \text{const.}$ seems to be obeyed for all underdoped compounds, for temperatures above the spin gap regime, if one takes the raw experimental value of $^{63}\text{T}_1T$. A very good example is the case of $\text{YBa}_2\text{Cu}_4\text{O}_8$ [48,87,88] for which the results of reference [88] are shown in Figure 9. However, if one subtracts from the experimental value the contribution of $\chi_{\text{QP}} = \frac{\omega_n \pi \chi_0(T)}{\Gamma_0}$, (this can be done by multiplying the planar oxygen NSLRR $^{17}(T_1T)^{-1}$ by an appropriate coefficient k which can be directly derived from the hyperfine coupling constant so that $^{63}(T_1T)_{\text{AF}}^{-1} = ^{63}(T_1T)_{\text{exp}}^{-1} - k^{17}(T_1T)_{\text{exp}}^{-1}$, it seems that the relation $T_1T/(T_{2G})^2 = \text{const.}$ is well obeyed for temperatures above the spin-gap regime, as expected in the NAFL approach. This latter type of interpretation has been promoted and systematically adopted by the ISSP group [110]. This approach, however, depends on the validity of the single spin fluid model to explain the spin dynamics, a question which is far from being obvious.

The great majority of the nuclear relaxation data has been quantitatively analyzed within the framework of these two models, which permit to evaluate the values of $\chi(Q_{\text{AF}})$ and $\Gamma(Q_{\text{AF}})$. from those of T_1T and T_{2G} . Both models suppose that ξ is temperature dependent, which is not obvious as we shall see later. Whatever is the chosen procedure, there are strong indications that the value of the characteristic energy $\Gamma(Q_{\text{AF}})$ correlates with the optimal value of T_c in a given system [29,30,62].

5. Spin Gap

As already emphasized in the introduction, the evidence for a pseudogap in the spin excitations of underdoped compounds has been a major outcome of NMR investigations in the normal state of the cuprates. A large amount of data have been accumulated, and in the past years, evidence has been presented for a pseudo gap showing up in many physical properties, involving both spin and charge degrees of freedom. Consequently, the striking difference between the underdoped and overdoped regimes is increasingly debated, and is now considered as one of the very central questions in the physics of the cuprates [111]. Since the early days, the notion

of spin (pseudo) gap has considerably evolved and contradictory definitions can be found in the literature. Therefore, we first survey the experimental situation from the NMR point of view, and discuss some connections with other experimental techniques.

Originally, the term "spin-gap" referred to the peculiar T -dependence of the quantity $^{63}(T_1T)^{-1}$ which is proportional to the dynamic susceptibility $\chi''(\mathbf{Q}_{AF}, \omega_n)$. Indeed, it was early discovered in underdoped $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$, that $^{63}(T_1T)^{-1}$ passes through a maximum around 130–150 K that is well above T_c , and then decreases with temperature [112,113]. This feature was first identified as a loss in the spectral weight of the low energy antiferromagnetic excitations by Yasuoka *et al.* [114]. Later on, the opening of such a gap for the spin excitations at $\mathbf{Q}_{AF} = (\pi/a, \pi/a)$ was confirmed by inelastic neutron scattering [115], and finally recognized as a characteristic feature of underdoped compounds [14,116], although the situation was not clear in the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ system [71]. Here, we caution the reader that the expression "spin-gap" is sometimes used in the neutron scattering community to describe the low temperature behaviour of $\chi''(\mathbf{Q}_{AF}, \omega)$ far below T_c (4.2 K in general), where a true gap is indeed observed presumably related to the superconducting one. However, this definition cannot account for the features observed above T_c by NMR, which actually measures:

$$\frac{\chi''(\mathbf{Q}_{AF}, \omega_n)}{\omega_n} = \lim_{\omega \rightarrow 0} \left(\frac{\partial \chi''(\mathbf{Q}_{AF}, \omega)}{\partial \omega} \right),$$

i.e., the slope of $\chi''(\mathbf{Q}_{AF}, \omega)$ at $\omega = 0$. In fact, there is no discrepancy at all between Cu NMR and neutron results, since with decreasing T , a gradual decrease of this slope is indeed observed by inelastic neutron scattering (INS) in the normal state of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ [115]. This effect is then referred to as a "pseudogap" since what is really observed in INS experiments is a progressive transfer of the spectral weight from low to high energies. This spin pseudogap appears to be the only quantity one should compare to $^{63}(T_1T)^{-1}$. In NMR experiments, the above described removal of spectral weight has been later confirmed through measurements of the indirect spin-spin relaxation rate T_{2G} , which reflects the temperature dependence of the staggered susceptibility at $\mathbf{Q}_{AF}$ [48]. This result is easy to understand if one considers [48,85], that $^{63}(T_1T)^{-1}$ is proportional to $\chi''(\mathbf{Q}_{AF}, \omega)/\omega$ for $\omega \approx 0$ whereas $(T_{2G})^{-1}$ is proportional to $\chi'(\mathbf{Q}_{AF}, 0)$, i.e., to $\int_{-\infty}^{+\infty} \frac{\chi''(\mathbf{Q}_{AF}, \omega)}{\omega} d\omega$. As long as the frequency dependence of $\chi''(\mathbf{Q}_{AF}, \omega)/\omega$ is not modified, the two quantities are proportional. As soon as a pseudogap opens, however, the amplitude of $\chi''(\mathbf{Q}_{AF}, \omega)/\omega$ at the origin will decrease much faster than the integral, so the ratio $^{63}(T_1T)/^{63}(T_{2G})$ will increase (Fig. 10). It is important to realize that this ratio will always show a rapid variation at the opening of the gap, whatever is the actual form of $\chi''(\mathbf{Q}_{AF}, \omega)$. Experimentally, this modification of the ratio in $^{63}(T_1T)/^{63}(T_{2G})$ has been clearly observed in all underdoped compounds for which it has been measured: $\text{YBa}_2\text{Cu}_4\text{O}_8$ [48,87,88], $\text{YBa}_2\text{Cu}_3\text{O}_{6.63}$ [70], $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$ [87], $\text{YBa}_2\text{Cu}_3\text{O}_{6.92}$ [85], $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ [62], $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ [29]. In contrast, this ratio has been shown to be constant or smoothly varying, with a sharp modification occurring only at the superconducting transition, for the optimally doped $\text{YBa}_2\text{Cu}_3\text{O}_{6.94}$ ($T_c = 93$ K) [86], $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ and for the overdoped compounds $\text{YBa}_2\text{Cu}_3\text{O}_{6.98}$ [48,117], $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ [64] and $\text{Tl}_2\text{Ba}_2\text{CuO}_{6+\delta}$ [89]. The case of these two latter compound deserves to be emphasized, since $^{63}(T_1T)^{-1}$ exhibits a maximum above T_c , but the ratio $^{63}(T_1T)/^{63}(T_{2G})$ is constant. Consequently, the decrease of $^{63}(T_1T)^{-1}$ is currently believed to have another origin, that is not yet clarified (the uniform spin susceptibility also shows a maximum around 120 K). Experimentally it therefore appears, at least for bi-layer and tri-layer compounds, that the opening of a spin-gap at $\mathbf{q} = \mathbf{Q}_{AF}$ is only present in underdoped compounds and that the optimal composition is a singular point in the phase diagram as a function of the hole concentration. In order to draw more quantitative information

Fig. 10. — $(T_1 T)^{-1}$ and $(T_{2G})^{-1}$ from ^{63}Cu NQR in $\text{YBa}_2\text{Cu}_4\text{O}_8$. Data from Itoh *et al.* [48].

from the NMR data, such as the doping dependence of the cross-over temperature T^* corresponding to the opening of this spin-gap, one has to choose a criterion to define T^* . Several definitions have been proposed: one is the temperature at which $^{63}(T_1 T)^{-1}$ is maximum, the other is the deviation of $^{63}(T_1 T)$ from its linear T -dependence. The case of the optimally doped compound [85] shows that these two definitions may be hazardous close to the optimal concentration [118], a safer definition being to define T^* from the temperature dependence of the ratio $^{63}T_1 T / ^{63}T_{2G}$. From the maximum of $^{63}(T_1 T)^{-1}$, Machi *et al.* [119] in $\text{Y}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_4\text{O}_8$ and Matsumura *et al.* [120] in $\text{Y}(\text{Ba}_{1-x}\text{La}_x)_2\text{Cu}_3\text{O}_y$ found a negative linear dependence of T^* on the hole concentration, which roughly extrapolates to T_c for the optimal concentration. On the other hand, Berthier and collaborators have found that $T^* = T_c$ in optimally doped $\text{YBa}_2\text{Cu}_3\text{O}_{6.94}$ ($T_c = 93$ K) [121], and that $T^* = 150$ K in a slightly underdoped sample having T_c as high as 91 K [85] (Fig. 11). These observations suggest a rapid variation of T^* close to the optimal value of T_c . Altogether, one must recognize that rather little is known concerning the (presumably weak) dependence of T^* on the carrier concentration. Recently, a surprisingly high T^* ($\cong 230$ K) has been found in underdoped $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ with $T_c = 115$ K [29] (the optimal T_c value at ambient pressure is 135 K). This finding, along with the fact that high values for Γ_{AF} and the super-transferred hyperfine field B have also been reported in the same compound [29,30], strongly suggest that the AF spin fluctuations play an important role in the pairing mechanism.

Let us now turn to the static uniform spin susceptibility $\chi(q = 0, \omega = 0) = \chi_0$, as probed by the magnetic hyperfine shift of various nuclei. This information is basically the same as that obtained by measuring the macroscopic susceptibility, but it is often more accurate since NMR is not sensitive to additional macroscopic spurious phases. In many compounds the quantity χ_0 exhibits an anomalous decrease with T below some temperature T_0 , well above T_c (Fig. 12). Actually, the decrease at high temperature is not sharp, and looks rather like the opening of a pseudogap. However, the slope becomes steeper and steeper with decreasing T and there is only small change of the curvature in the vicinity of T_c . It is possible, but not proved, that the more rapid fall off starts at T^* [105,122]. These features are quite universal for underdoped compounds, whatever is the number of CuO_2 planes per unit cell, but they are also sometimes observed in slightly overdoped compounds, like $\text{Tl}_2\text{Ba}_2\text{CuO}_{6+\delta}$ ($T_c = 85$ K) [61] or $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ [62]. Also, great care must be taken for compounds close

Fig. 11. — $(T_1T)^{-1}$ and $(T_2G)^{-1}$ measured in the slightly underdoped $\text{YBa}_{1.93}\text{Sr}_{0.07}\text{Cu}_3\text{O}_{6.92}$ with $T_c = 91$ K (triangles) and in the optimally doped $\text{YBa}_2\text{Cu}_3\text{O}_{6.94}$ with $T_c = 93$ K (circles). Data from Gillet *et al.* [121].

Fig. 12. — ^{89}Y magnetic hyperfine shift in $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ for various oxygen contents. From Alloul *et al.* [52].

to or at the optimal doping, where a decrease above T_c might be related to a precursor effect of the superconducting transition (For example, in overdoped $\text{YBa}_2\text{Cu}_3\text{O}_7$ [65,79] a maximum is observed close to T_c in the yttrium MHS). The values of T_0 usually range from T_c for samples near optimal doping, to more than 400 K for the less doped ones. Thus, contrary to T^* , the doping dependence of T_0 is rather well-defined, with T_0 decreasing roughly linearly with n_h , *i.e.* in a way opposite to T_c . As far as we can see, two different crossover temperatures now emerge from NMR measurements, with $T_0 \geq T^* \geq T_c$. Whereas the upper concentration delimiting the

pseudogap phase at $\mathbf{Q}_{AF}$ seems to coincide *precisely* with the optimal doping, some ambiguity remains concerning the pseudogap at $q = 0$. It must be pointed out that if up to now, the opening of a pseudogap at $\mathbf{Q}_{AF}$ has not been clearly observed in compounds having a single CuO_2 plane per unit cell, the pseudogap behavior at $q = 0$ has to be considered as a property which takes place within a single CuO_2 plane. Not only it is observed in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, but in the case of $(\text{Bi-Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ [123] and $(\text{Tl-Pb})\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{9-\delta}$ [124] the oxygen MHS has been observed to decrease with the temperature for the inner plane, whereas it remains constant for the outer ones, thus showing a difference of doping for the inner and the outer planes.

It was pointed quite early that the in-plane resistivity ρ_{ab} also showed related anomalies, namely in optimal compounds the resistivity decreases linearly with temperature down to T_c , whereas it deviates from this linearity in all underdoped compounds, below some characteristic temperature T_p (at the same time ρ_c tends to diverge exponentially). It turns out that a majority of data indicate that $T_p = T_0$ [125,126], within experimental accuracy, the notable exception being $\text{YBa}_2\text{Cu}_4\text{O}_8$ [127]. Furthermore, a striking resemblance between ρ_{ab}/T and χ_0 was evident. Recently, both quantities have been measured in very similar single crystals of $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ [29], and have been shown to scale for all temperatures almost down to T_c . For now, the Hall effect and specific heat anomalies seem to correlate quite well with this pseudogap features at $q = 0$ [126,128]. Finally, the most spectacular evidence for the occurring of a gap above T_c was recently given by photoemission experiments in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ [10]. These experiments have clearly shown that the Fermi surface is quite different in overdoped and underdoped compounds, with the existence of an anisotropic gap (which seems to have a d-like symmetry) already preformed above T_c . This is perfectly in agreement with the NMR experiments of Walstedt *et al.* in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ [63].

In strongly correlated systems, the study of impurity doping effects can usually provide essential information. Particularly, the substitution of Cu by Zn in the CuO_2 planes has attracted considerable attention by virtue of its dramatic effects on both the critical temperature and the AF fluctuations. The impact on the spin-gap behaviour may be summarized as follows: ^{63}Tl measurements at sites far from the Zn impurity have shown that T^* disappears for Zn concentrations as low as 1% [129], while T_0 appears to be practically insensitive to the Zn content from both the NMR shift [130] and resistivity measurements [131].

The pseudo spin-gap behaviour has given rise to a huge amount of theoretical work, of which we can only give a very limited and incomplete account. One of the early theoretical work explicitly trying to explain the NMR and INS findings at $\mathbf{Q}_{AF}$ was that of Bulut and Scalapino [132], based on a dynamical nesting in the framework of the Hubbard model. In this model, the value of the gap is closely related to the difference in chemical potential with respect to the case of the half filled band. However, it is now quite clear that a drastic change in the electronic properties occurs in the vicinity of the optimal doping, which cannot be accounted in that kind of models. The fact that the distinction between underdoped and overdoped compounds, which originally described the variation of T_c , extends to the metallic state of the cuprates is a strong indication that electronic correlations play a predominant role in the pairing mechanism. Furthermore, this suggests that the variation of T_c with doping arises from the interplay between two distinct parameters, and not from the continuous variation of a single one. In other words, there is no symmetry with respect to the optimal doping, which suggests that the two transition lines (T_c versus n_h) for underdoped and overdoped regime have a different origin (Fig. 1). This kind of behaviour is explicitly incorporated in some theoretical phase diagrams. One class is the *t-J model* treated in the framework of spin-charge separation, where the spin-gap corresponds to the formation of an RVB state [133]. In other scenarios, the spin-gap is rather the manifestation of a quantum disordered ground state, and

the crossover from underdoped to overdoped corresponds to overdamping of localized spin-excitations [101, 105, 134]. All these approaches promote the formation of a spin-liquid state at temperatures higher than T_c in the underdoped regime, instead of a Fermi liquid in the overdoped regime. There are also other models, such as a spin density wave gap of a metal near an AF instability [3, 135], the duality between itinerant and localized magnetism [134, 136], or peculiar dynamics related to frustrated phase separation [84, 137].

An intense subject of debate has concerned the proposition of Millis and Monien [122] that the spin-gap at $\mathbf{Q}_{AF}$ could be related to an interplane singlet [138] pairing since its existence had only been demonstrated in bi-layer compounds at that time. Especially, no clear sign of spin-gap could be found in the single-layer $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$. However, the objection has been raised [29] that the identical T -dependence of ^{63}Tl in the three CuO_2 planes of underdoped $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ was hard to explain within an interlayer pairing model, because in such a case the inner layer should be more sensitive to the pairing. Recent investigations of the bi-layer t - J model have also questioned the interplane singlet order [139]. Also, Wen and Lee [140] have recognized the possibility that the spin gap phase could be more stable with respect to in-plane gauge fluctuations with an $\text{SU}(2)$ symmetry than with $\text{U}(1)$, since this approach permits to start with a better mean field solution. One possibility to explain the apparent absence of pseudogap at $\mathbf{Q}_{AF}$ in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ would then be that T^* is very close to T_c because T_c is low. On the contrary, a pseudogap at $q = 0$ is unambiguously observed in this compound.

Aside the theories which explicitly include AF fluctuations, other classes of model have been proposed to explain the spin-gap as the formation of bi-polarons [141]. It has also been proposed that the underdoped regime corresponds to the existence of preformed pairs above T_c without phase coherence [142].

Although the general tendency in the NMR literature is to favour the models including AF fluctuations, the mechanism of the spin-gap formation is still a quite open question. The recent photoemission results which explicitly demonstrate that this gap is anisotropic, and that the “credo” in a large Fermi surface in all the cuprates has to be revised, is a strong stimulation to reconsider some aspects of the spin dynamics.

6. NMR *versus* Inelastic Neutron Scattering

Inelastic neutron scattering (INS) experiments can in principle directly measure the dynamical structure factor $S(\mathbf{q}, \omega) \propto \chi''(\mathbf{q}, \omega) / [1 - \exp(-\hbar\omega/k_B T)]$ as a function of $\mathbf{q}$ and ω . It is thus a tool of major importance in study of the dynamic magnetic susceptibility in the cuprates. In practice, the exploration range in energy is limited between 1 meV and 60 meV (300 meV using spallation sources). In q space, however, one cannot approach the $q = 0$ region of the Brillouin zone. Moreover, the sensitivity requires large single crystals, which up to now has limited the investigations to two systems, $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ and $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$. A crucial problem, when using unpolarized neutrons, is to separate the contribution of the phonons from that of the spin excitations. This difficulty can be avoided by using spin polarized neutrons, but in that case, one has to pay with a drastic reduction of the beam intensity. Obviously, any theory that claims to explain the NMR results should be consistent with the INS findings too, unless some new characteristic energy falls between a few meV and zero. To cover the whole literature on INS data and interpretation is beyond the scope of this paper; the reader is referred to recent reviews on the subject [143–145]. We shall only summarize the INS results which are available at the moment in the two systems mentioned above, before comparing them with NMR results. In both systems, evidence for antiferromagnetic fluctuations has been found in the whole metallic range. Although this point is still controversial in optimal and overdoped $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$, recent measurements in overdoped compounds have finally confirmed the observation of magnetic

scattering at Q_{AF} at low energy (≤ 10 meV) above T_c [146]. The situation is, however, quite different for the two systems as far as the shape and the temperature dependence of $\chi''(q, \omega)$ is concerned. In the case of $La_{2-x}Sr_xCuO_4$, in the low energy range 1 – 40 meV, the shape of $\chi''(q, \omega)$ consists of four peaks centered at $(\pi/a(1 \pm \delta), \pi/a)$ and $(\pi/a, \pi/a(1 \pm \delta))$ with $\delta = 0.245 \pm 0.004$ for $x = 0.14$ [147, 148]. The inverse length scale κ measuring the sharpness of the peaks was found experimentally to vary as: $\kappa^2(T, \omega) = \kappa_0^2 + a_0^{-2} (k_B T/E_T)^2 + (\hbar\omega/E_\omega)^2$ with $\kappa_0 = 0.034 \text{ \AA}^{-1}$, $a_0^{-1} = 0.26 \text{ \AA}^{-1}$, $E_T = E_\omega = 47$ meV [149]. These results suggest that a spin pseudogap does not open above T_c . In the case of $YBa_2Cu_3O_{6+x}$, $\chi''(q, \omega)$ is peaked at $(\pi/a, \pi/a)$ for all concentrations studied. In contrast with $La_{2-x}Sr_xCuO_4$, κ was found to be independent of T and ω (if one excludes the so-called “resonance” [143, 144], which appears only in the superconducting state) and equal to $0.12 \text{ \AA}^{-1}$ and $0.24 \text{ \AA}^{-1}$ for underdoped samples belonging to the “60 K” and “90 K” plateau, respectively. This result is in total disagreement with the NAFL model, as well as with the description within the quantum critical regime. A pseudo spin-gap, *i.e.*, a transfer from low energy to high energy in the spectral weight of the spin excitations, has been clearly observed in $YBa_2Cu_3O_{6.69}$ [143], $YBa_2Cu_3O_{6.6}$ [150] and with difficulty in $YBa_2Cu_3O_{6.92}$. In the latter case, the same sample was studied by NMR and INS. The comparison of the temperature dependence of $^{63}(T_1T)^{-1}$ with that of $\chi''(Q_{AF}, \hbar\omega = 10 \text{ meV})$ shows a good agreement [85, 86, 116], although the error bars for the INS data are rather large. As already mentioned, for doping level where the INS intensity becomes too weak, the comparison between $^{63}(T_1T)^{-1}$ and $^{63}(1/T_2G)$ becomes more efficient to detect the opening of a pseudogap around Q_{AF} .

Quantitative comparison between NMR and INS results can be carried out in the following way. In the case of $YBa_2Cu_3O_{6.92}$ where the absolute amplitude of $\chi''(Q_{AF}, \hbar\omega = 10 \text{ meV})$ is not known, the following analysis has been used [85, 121]. In equation (15), we make the assumption for the q -dependence of $\chi(Q_{AF} + q)$ and $\Gamma(Q_{AF} + q)$ that $g = f^{-1}$ (this relation occurs for the MMP susceptibility), with f being either a Lorentzian or a Gaussian. It is then possible through equations (7, 10, 11) to calculate Γ_{AF} and $\chi(Q_{AF})$ as a function of ξ for a given experimental set of $[^{63}(T_1T)^{-1}, ^{63}T_{2G}^{-1}]$ and for a given temperature (*e.g.* [121] 200 K) above T^* . Comparison of the Γ_{AF} value with the value of $\Gamma_N(Q_{AF}) = [2 \int_0^\infty \chi''(Q_{AF}, \omega)/\omega d\omega]/[\pi \chi''(Q_{AF}, \omega_n)/\omega_n]$ deduced from the neutron experimental data on the same single crystal and at the same temperature provides a good agreement between $\Gamma_N(Q_{AF})$ and the value of Γ_{AF} obtained from the NMR data corresponding to $\kappa = 0.24 \text{ \AA}^{-1}$, which is precisely the value obtained from the neutron data. Thus, the INS data and the Cu NMR data obtained on the same sample can be interpreted quantitatively with the same parameters. However, use of the same dynamic susceptibility to calculate NSLRR at the planar oxygen site leads to a striking disagreement [121]. The calculated contribution of the AF fluctuations for $\xi/a = 1$ is as large as 90% of the experimental value for a Gaussian, and 200% for a Lorentzian (see Fig. 13). In these conditions, the temperature dependence of the oxygen NSLRR should have the same behavior as the Cu NSLRR, a situation which is never observed. The conclusion is thus that either the q -dependence of $\chi''(q, \omega)$ at the NMR energy scale is different from that obtained at 10 meV, which is possible, but unlikely, or that the Mila-Rice Hamiltonian and the single spin fluid picture, including an arbitrary separation between χ''_{QP} and χ''_{AF} is inadequate to describe the dynamic part of the NMR data. The same conclusion has been reached by Walstedt *et al.* [151] using their NMR data and the INS data of Aeppli *et al.* in $La_{1.85}Sr_{0.15}CuO_4$ [149]. In that case, $\chi''(q, \omega)$ peaks around Q_{AF} are narrow and temperature dependent, as expected in the NAFL theories, but they are located at incommensurate positions. From INS determination of the absolute intensity of $\chi''(q, \omega)$, Walstedt and

Fig. 13. — Calculated contribution of AF fluctuations to $(T_1T)^{-1}$ for ^{89}Y relaxation (left panel) and planar ^{17}O relaxation (right panel), as a function of the AF correlation length ξ/a [121]. The dynamic susceptibility at $\mathbf{Q}_{\text{AF}}$ is supposed to be described by either a Lorentzian, a Gaussian or the sum of four Gaussians and adjusted to fit the Cu $(T_1T)^{-1}$ and $(T_{2G})^{-1}$ values in $\text{YBa}_{1.93}\text{Sr}_{0.07}\text{Cu}_3\text{O}_{6.92}$ at 200 K. The full span of the vertical axes covers 2 – 200 % of the experimental value of ^{89}Y and ^{17}O $(T_1T)^{-1}$ at 200 K, and the horizontal dotted line indicates 20% of it, a value indicating an approximate limit above which the AF contribution should be experimentally observable. From neutron data, $\xi/a \approx 1$.

Aeppli have concluded the NMR and the INS data could be reconciled as far as the Cu data were concerned, but again, they have shown that the calculated contribution at the oxygen site due to the AF fluctuations is too strong compared to the experimental value of $^{17}(T_1T)^{-1}$, and they have questioned the validity of the single band picture.

At this stage, it is useful to return to the problem of the planar oxygen NSLRR. As we have seen above, for underdoped compounds, $^{17}K(T)^{17}(T_1T)^{-1} = \text{const.}$ within a rather wide range of temperature. This can be well accounted by assuming a perfect cancellation of the AF fluctuations contributions to the NSLRR, and writing:

$$\begin{aligned} {}^{17}(T_1T)^{-1}_\alpha &= 2^{17}\gamma^2 \left[\frac{(C_{\beta\beta})^2}{(g_{\beta\beta})^2} + \frac{(C_{\gamma\gamma})^2}{(g_{\gamma\gamma})^2} \right] \frac{k_B\pi\chi_0(T)}{(\mu_B)^2\Gamma_0} \\ &= {}^{17}\gamma^2 \left[\frac{K_{\beta\beta}(T)C_{\beta\beta}}{g_{\beta\beta}} + \frac{K_{\gamma\gamma}(T)C_{\gamma\gamma}}{g_{\gamma\gamma}} \right] \frac{\pi k_B}{\mu_B\Gamma_0} \end{aligned}$$

The value of $\hbar\Gamma_0$ is 0.24 eV in $\text{YBa}_2\text{Cu}_3\text{O}_{6.52}$, $\text{YBa}_2\text{Cu}_3\text{O}_7$ [152] and 0.3 eV in $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$. These are strikingly similar results for the three compounds, in spite of quite different behavior of $\chi''(\mathbf{q},\omega)$ as evidenced by Cu NSLRR and INS results. These features seem to indicate that in all cases the AF fluctuations do not contribute to the NSLRR of the planar oxygen, suggesting a common origin for $^{17}T_1$ in all cuprates, nearly independent of the doping level. This is also supported by the absence of a field dependence of the NSLRR in the planar oxygen in $\text{Tl}_2\text{Ba}_2\text{CuO}_{6+\delta}$, whereas the Cu NSLRR exhibit a logarithmic dependence as a function of H , which is a signature of 2D diffusive motion of some type of excitation. As already mentioned, there is another puzzling feature concerning the NSLRR of planar oxygen, that is the temperature dependence of the anisotropy of the NSLRR in the normal state, which

cannot be explained simply with the usual single spin fluid picture, the Mila Rice Hamiltonian, and the separation of the susceptibility into χ_{QP} and χ_{AF} (both of them acting on the two sites).

To solve the contradiction between the NMR and INS data as far as the oxygen NSLRR is concerned, Varma [153] recently proposed a completely different approach of the NSLRR in the CuO_2 plane, based on orbital relaxation for Cu and oxygen sites. However, it seems difficult to completely forget the existence of the AF fluctuations. It has also been suggested that the incommensurate peaks measured by INS in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ could be due to discommensurations rather than to the band structure. This leads to a much better filtering of the AF fluctuations at the oxygen site, since in that case the fluctuations measured locally by NMR are commensurate [154]. The same argument may also apply to YBCO, although the existence of incommensurate peaks is not settled down [150]. In a more conservative approach, Zha *et al.* [66] have recently proposed that the oxygen nuclei would be coupled not only to their Cu nearest neighbors, but also to the next nearest Cu neighbors. In this way, they manage to reduce considerably the contribution of the AF fluctuations to the oxygen NSLRR. Although this possibility cannot be excluded, it seems to us that the inconsistency between INS and oxygen NMR indicates that something more fundamental has not been taken into account in the analysis currently applied to the NMR data. It is also clear that as long as the mechanism of oxygen NSLRR is not well understood, the analysis of $^{63}(T_1T)/^{63}(T_{2G})^z$, where z is the dynamical critical exponent, has to be considered with caution.

7. NMR and Phase Separation

So far, we have not mentioned the works dedicated to the possibility of phase separation between the AF background of localized spins and mobile holes. In spite of growing evidence that such a phenomenon may take place in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+\delta}$ [155–157] and that it may even be a key feature of the physics of the cuprates [158], a possible extension of these ideas to other systems and especially to their normal state remains unproved. There have been only a few NMR/NQR studies fully devoted to this problem in the metallic phase, among which we must cite the comprehensive contribution of Teplov and collaborators [159]. We shall not further develop this point, which we feel being rising. It is clear that any kind of frustrated (dynamic) phase separation [84] will lead to averaged properties at the NMR timescale (single line, single T_1), but it still remains tempting to interpret some peculiar aspects of the spin dynamics discussed in this paper as connected to these inhomogeneous phases.

8. Concluding Remarks

One of the major difficulties in the understanding of the properties of the cuprate HTSC, is to separate what is really generic for this class of compounds, from the numerous peculiarities due to the various types of blocks allowing the doping of the CuO_2 planes. At the same time, it seems necessary to understand the evolution of physical properties in the whole range of doping level. So, one of the strength of NMR has been its ability to investigate most of the HTSC cuprate families, at various doping levels, and to reveal very early some quite general features: 1) The existence of antiferromagnetic fluctuations in the whole range of doping of the HTSC has been revealed by numerous experiments. The ratio of the Cu nuclear spin-lattice relaxation rate to that of the planar oxygen is a monotonously increasing function with decreasing T . The indirect nuclear spin-spin interaction (T_{2G} measurements on copper) is also continuously increasing with decreasing T down to T_c , showing the temperature dependence of the staggered susceptibility $\chi(\mathbf{Q}_{AF})$. It is clear that these temperature dependences weaken

as the doping level is increased, however, they are still present even in the overdoped regime. Perhaps one of the most spectacular evidence for the unusual magnetic susceptibility in the normal state of the cuprates has been revealed by the observation of local magnetic moment induced by a *non-magnetic* impurity in the CuO_2 plane [130].

ii) The striking difference between the magnetic properties of the underdoped and the overdoped compounds was first revealed by NMR through two phenomena: One is the decrease of the static spin susceptibility below some temperature T_0 , which was finally recognized as due to the opening of a pseudogap, observed as well on spin and charge properties for all underdoped compounds. Another one is a maximum in $^{\text{Cu}}(T_1 T)^{-1}$ at some temperature T^* , ($T_c < T^* < T_0$), followed by a simultaneous decrease of $^{\text{Cu}}(T_1 T)^{-1}$ and an increase of $^{\text{Cu}}(T_{2G})^{-1}$ with decreasing temperature, which is the signature of a pseudogap for the spin-excitations at $\mathbf{Q}_{\text{AF}}$. This pseudogap is present in the whole underdoped regime, and disappears precisely at the optimal doping. However, it has not been convincingly observed the single-layer material $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, so the question whether its opening is due to the coupling between adjacent CuO_2 layers or is an intrinsic property of a single layer is still a controversial point.

The origin of these pseudogaps, the difference between most of the physical properties in the underdoped and overdoped regimes, like resistivity, Hall effect, specific heat or photoemission, are presently the subject of an intense debate.

Quantitative interpretation of NMR data requires a model for the dynamic spin susceptibility $\chi''(\mathbf{q}, \omega)$, and therefore is more subject to controversy. However, it comes out from analysis of T_1 and T_{2G} that the energy scale Γ_{AF} of the antiferromagnetic fluctuations, is larger in the systems where the optimal T_c is the highest. This is usually accompanied by a larger value of the supertransferred hyperfine field B between nearest neighbors copper, and a smaller value of the quadrupolar coupling constant ν_Q for the planar copper. A comparison between NMR and inelastic neutron scattering results is obviously of primary importance to test the various models of $\chi''(\mathbf{q}, \omega)$. Several models refer to commensurate AF fluctuations $\chi''(\mathbf{q}, \omega)$ peaked at $\mathbf{Q}_{\text{AF}}$ with a temperature dependent correlation length $\xi(T)$. Experimentally, INS data show a temperature dependence for ξ , but incommensurate peaks in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, and conversely, T -independent ξ and commensurate fluctuations in $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$. Using the neutron data on $\chi''(\mathbf{q}, \omega)$ to interpret the NMR relaxation in both systems leads to a quantitative agreement as far as the copper nuclear spin-lattice relaxation is concerned, but to a severe failure in the case of the planar oxygen, for which the contribution of the AF fluctuations is found experimentally much less than the computed one. Since it is unlikely that there exists another characteristic energy between the meV and the nuclear Zeeman energy ($\approx \mu\text{eV}$), it is clear that we have to revise, at least partially, our way of thinking the nuclear spin-lattice relaxation in the cuprates, perhaps including a better microscopic description of the hole dynamics in the CuO_2 planes.

Note Added in Proofs

In a recent preprint, Y. Itoh *et al.* show by ^{63}Cu NMR the existence of a spin pseudogap at $\mathbf{Q}_{\text{AF}}$ in the underdoped, single layered, $\text{HgBa}_2\text{CuO}_{4+\delta}$. In the heavily doped regime ($T_c = 50$ K), they found $T^* \sim 250$ K, which is comparable to the value found in underdoped $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ with $T_c = 115$ K.

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