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A fictitious-spin calculation of the nuclear magnetic relaxation of nuclei of spin $I = 3/2$ in the presence of strong quadrupole coupling

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Abstract. The problem of the nuclear relaxation of nuclei of spin $I = 3/2$ in the presence of strong quadrupole coupling is treated by means of the fictitious-spin (FS) formalism. Considering the magnetic hyperfine field as the only source of spin–lattice relaxation, we employed the FS method to obtain both the multiexponential decay law of the spin–lattice relaxation (T_1) and the so-called T_1-contribution to the transverse relaxation (T_2). As an example we discuss the determination of the spin–spin relaxation rate of the planar copper in the $YBa_2Cu_3O_{6+x}$ high-temperature superconductor.

1. Introduction

Nuclei with spin larger than $I = 1/2$ have electric quadrupole moments which interact with the electric field gradient (EFG) at their position [1]. When the quadrupole coupling is present the data reduction of the NMR results is far more complicated than for the simple case of spin $I = 1/2$ or the case of zero EFG. The main effects of the quadrupole coupling are to shift the unperturbed Zeeman energy levels (m_Z), making them unequally spaced, and to mix these states when the EFG is asymmetric. The consequences are a complicated spectrum of several lines and also, in general, a multiexponential decay of the spin–lattice relaxation. As is well known, the spin–lattice relaxation is given by a single-exponential decay whenever a Boltzmann distribution of the level population is guaranteed [2, 3]. However, once the quadrupole coupling promotes the inequality of the level spacing, the mutual flips of the nuclear spins, which would maintain a Boltzmann distribution of the level populations, are strongly suppressed, giving rise to a multiexponential decay of the spin–lattice relaxation.

The problem of the spin–lattice relaxation of nuclei of spin $I = 3/2$ in the presence of strong quadrupole coupling has already been treated by other authors in the past few years, but using a theoretical approach different from the one that we propose here. Andrew and Tunstall [4] have derived the multiexponential decay laws by solving the population master equation. This same method was employed by Narath [5] and more recently by Horvatić [6], who has also focused on the problem of the admixture of the Zeeman states by the asymmetry of the quadrupole coupling. While in the simplest situation, that of negligibly

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mixed Zeeman states, the multiexponential decay of the longitudinal magnetization obeys a well defined standard function, in the case studied by Horvatić [6] this fails and the decay law must be found iteratively. Here we shall restrict ourselves to the simplest case of no admixture of the Zeeman states. The interest in this case arises from the NMR investigation of the copper nuclei (^{63,65}Cu, $I = 3/2$) belonging to the CuO_2 layers in the $YBa_2Cu_3O_{6+x}$ (YBCO) high-temperature superconductor (HTSC) [7] and related materials. Although the quadrupole frequency of the so-called planar copper is relatively large ($\nu_{NQR} = 31.45$ MHz) in the YBCO, the nearly tetragonal symmetry ensures the validity of the condition of small admixture of the Zeeman states ($\eta \ll 1$, so $h\nu_{NQR}\eta \ll \hbar\gamma H_0$ when H_0 is parallel to the c-axes).

Our motivation in this article is not just to provide another derivation of the decay laws of the spin–lattice relaxation, but mainly to show the usefulness of the fictitious-spin (FS) [8] formalism in treating both the longitudinal and the transverse relaxation. In particular, the transverse relaxation of the planar copper in the YBCO (and related) compounds has recently attracted great interest. This interest came about after the pioneering work of Pennington *et al* [9], who have shown that the gaussian spin–spin relaxation time (T_{2g}) of the planar copper provides key information for the investigation of the staggered spin susceptibility, $\chi'(\mathbf{Q}_{AF}, \omega = 0)$. This interesting information, however, must be extracted from the transverse relaxation, which also contains the spin–lattice contribution, T_{2R}, in addition to the spin–spin part. The spin–lattice contribution is also called the T_1-contribution to T_2 and we will be concerned with how to calculate it exactly using the FS formalism. Pennington *et al* [9] have employed the Redfield theory (see [2, 10]) to derive T_{2R}; thus the method presented here is an alternative.

Continuing this paper, in section 2, we briefly review the FS formalism, summarizing the development given by Petit and Korb [8]. In section 3 we apply the tools of section 2 to derive the decay laws of the nuclear spin–lattice relaxation and the T_1-contribution to T_2. In section 4, as an example, we discuss the determination of the gaussian component of the nuclear spin–spin relaxation of the planar copper in YBCO. Section 5 contains the concluding remarks.

2. The fictitious-spin formalism

Petit and Korb [8] (hereafter PK) have extensively developed the fictitious-spin formalism to describe the nuclear relaxation of spins with $I > 1/2$. Their purpose was to generalize the approach of Abragam [3], expressing the nuclear relaxation through a set of macroscopic kinetic equations. Indeed, PK were able to show that it is always possible to obtain these kinetic equations using a complete basis set of FS operators (in terms of which one can expand the observables and the density matrix). Now we recapitulate the basics of the FS method.

The FS operators $\mathbf{I}_r^{cd}$ are defined in table 1 of the original work of PK. Following their notation the indices r stand for the polarization x, y, z and $c < d \in \{1, \ldots, 2I+1\}$ stand for the eigenstates $m \in \{I, I-1, \ldots, -I\}$ of the Zeeman Hamiltonian. Therefore, there are more FS operators than the $4I(I+1)$ elements necessary to form a complete basis set (together with the $(2I+1)^2$ unit matrix) of the Hilbert space of a spin I. The problem is a redundancy in the z-subspace which makes it necessary to restrict the choice of the $\mathbf{I}_z^{cd}$ operators. PK solved this problem by imposing the orthogonality relation $\mathrm{Tr}\{\mathbf{I}_z^{cd}\mathbf{I}_z^{ef}\} = (1/2)\delta_{ce}\delta_{df}$. So,

given the FS basis set, any operator $\mathbf{Q}$ can be expressed in this basis as

$$\mathbf{Q} = a_0\mathbf{1} + \sum_r \sum_{c<d} q_r^{cd}\mathbf{I}_r^{cd} \tag{1}$$

where $\mathbf{1}$ is the $(2I+1)^2$ unit matrix and

$$a_0 = \frac{1}{2I+1}\mathrm{Tr}\{Q\} \qquad q_r^{cd} = 2\,\mathrm{Tr}\left\{Q\mathbf{I}_r^{cd}\right\}. \tag{2}$$

Consider now a nuclear spin system whose Hamiltonian is $\mathbf{H} = \mathbf{H}_0 + \mathbf{H}_1(t)$, where $\mathbf{H}_0$ is the static part (which includes the Zeeman and quadrupole interactions) and $\mathbf{H}_1(t)$ is the time-dependent perturbation. The master equation for the density matrix ($\boldsymbol{\sigma}$) [3] gives its time evolution:

$$\frac{\mathrm{d}}{\mathrm{d}t}\boldsymbol{\sigma}^*(t) = -\frac{1}{\hbar^2}\int_0^\infty \mathrm{d}\tau\ \overline{\left[\mathbf{H}_1^*(t), \left[\mathbf{H}_1^*(t-\tau), \boldsymbol{\sigma}^*(t) - \boldsymbol{\sigma}_0\right]\right]} \tag{3}$$

where $\mathbf{X}^* = \mathrm{e}^{\mathrm{i}\mathbf{H}_0 t/\hbar}\mathbf{X}\mathrm{e}^{-\mathrm{i}\mathbf{H}_0 t/\hbar}$ denotes the interaction representation, the overbar stands for the statistical average over the spin system, and $\boldsymbol{\sigma}_0$ is the equilibrium density matrix.

The expectation value of the observable $\mathbf{Q}$ can be computed from

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle\mathbf{Q}(t)\rangle^* \equiv \mathrm{Tr}\left\{\mathbf{Q}\frac{\mathrm{d}}{\mathrm{d}t}\boldsymbol{\sigma}^*(t)\right\}. \tag{4}$$

The main goal of PK was to demonstrate that using the FS formalism it is always possible to rewrite the equation above as a generalized kinetic equation

$$\frac{\mathrm{d}}{\mathrm{d}t}\left\langle\mathbf{Q}\right\rangle^* = -\left[\frac{1}{T_i}\right](\langle\mathbf{Q}\rangle^* - \langle\mathbf{Q}\rangle_0). \tag{5}$$

In fact, decomposing (4) in the FS basis one obtains for each one of the $4I(I+1)$ independent FS components the kinetic equation

$$\frac{\mathrm{d}}{\mathrm{d}t}\left\langle\mathbf{I}_r^{cd}\right\rangle^* = -\sum_s \sum_{\substack{e,f \\ e<f}} \frac{1}{T_i^{cd,ef}}\{\langle\mathbf{I}_s^{ef}\rangle^* - \langle\mathbf{I}_s^{ef}\rangle_0\} \tag{6}$$

with

$$\frac{1}{T_i^{cd,ef}} = \gamma^2 \sum_{p,p',q} J^{(q)}(\omega_p^q)\,\mathrm{Tr}\{[\mathbf{A}_{p'}^{-q}, [\mathbf{A}_p^q, \mathbf{I}_r^{cd}]]\mathbf{I}_s^{ef}\}\exp(\mathrm{i}[\omega_{p'}^{-q} - \omega_p^q]t).$$

In equation (6) $[T_1^{-1}]$ is the relaxation matrix, $J(\omega)$ is the spectral density, and the indices p and p' stand for the different transition frequencies. The subscript q stands for the qth irreducible spin tensor component of the perturbing Hamiltonian. As usual, if we restrict ourselves to the secular contribution, only the terms where $\omega_{p'}^{-q} - \omega_p^q = 0$ are to be taken into account [11].

The correlation time τ_c characterizes the correlation function of the random process brought about by the perturbing Hamiltonian, and the approach described here is valid as long as $\tau_\mathrm{c} \ll t, T_1$ and T_2 [3, 11]. This perturbing Hamiltonian is usually written as the scalar product of lattice ($\mathbf{F}^q$) and spin ($\mathbf{A}^q$) irreducible tensor components:

$$\mathbf{H}_1(t) = -\gamma\hbar\sum_q \mathbf{F}^q(t)\mathbf{A}^q \tag{7}$$

where

$$\mathbf{F}^q(t) = \exp(\mathrm{i}\mathbf{H}_\mathrm{e}t/\hbar)F^q\exp(-\mathrm{i}\mathbf{H}_\mathrm{e}t/\hbar)$$

is a lattice operator and $\mathbf{H}_e$ is the electronic Hamiltonian. The corresponding correlation function and spectral density are given, respectively, by

$$g^{(q,q')}(\tau) = \mathrm{Tr}_e\{e^{-\mathbf{H}_e/kT}\mathbf{F}^q(t)\mathbf{F}^{q'^+}(t+\tau)\}/Z_e = \mathrm{Tr}_e\{e^{-\mathbf{H}_e/kT}\mathbf{F}^q(t)\mathbf{F}^{-q'}(t+\tau)\}/Z_e \tag{8}$$

and

$$\frac{1}{2}J^{(q,q')}(\omega) = \int_0^\infty \mathrm{d}t\ g^{(q,q')}(t)e^{-i\omega t} + i\int_0^\infty \mathrm{d}t\ g^{(q,q')}(t)\sin\omega t$$

where $Z_e = \mathrm{Tr}\{\exp(-\mathbf{H}_e/kT)\}$ is the partition function and $e^{-\mathbf{H}_e/kT}/Z_e$ is the density matrix of the electronic spin system.

Regarding the correlation function and the spectral density, few assumptions were made in order to arrive to the kinetic equation (6). Firstly, it was assumed that the $\mathbf{F}^q(t)$ are statically independent, so that $g^{(q,-q')}(\tau) = \delta_{q,-q'}g^{(q)}$ (and the same holds for the spectral density). In addition, the contribution from the imaginary part of the spectral density, which gives rise to the small dynamical shift, was ignored [8].

The main advantage of the kinetic equations (5) and (6) over the spin-density method is that one does not need to explicitly solve the master equation (3) of the spin-density matrix. From the Redfield method a kinetic equation is also obtained, but the FS basis is more convenient for the description of the observables associated with spin subspaces in the case of nuclear spins with $I > 1/2$. Finally, to facilitate the calculation of the double commutators present in equation (6), we present in table 1 the commutation rules for the fictitious spin operators. A more general development of the kinetic equation (6), including a superposition of different relaxation mechanisms, may be found in [8]. In the application that follows we restricted consideration to one perturbing interaction of the first rank ($q = \{-1, 0, 1\}$), namely the magnetic hyperfine field.

Table 1. Commutation rules for the fictitious-spin operators.

$$[I_+^{ij}, I_+^{kl}] = \delta_{jk}I_+^{il} - \delta_{il}I_+^{kj} \qquad [I_z^{ij}, I_z^{kl}] = 0 \qquad [I_-^{ij}, I_-^{kl}] = \delta_{il}I_+^{kj} - \delta_{jk}I_+^{il}$$

$$[I_+^{ij}, I_z^{kl}] = \frac{1}{2}I_+^{ij}(\delta_{jk} - \delta_{jl} + \delta_{li} - \delta_{ik})$$

$$[I_-^{ij}, I_z^{kl}] = \frac{1}{2}I_-^{ij}(\delta_{ik} - \delta_{li} + \delta_{lj} - \delta_{jk})$$

$$[I_+^{ij}, I_-^{kl}] = \delta_{jl}(1-\delta_{ik})[\Theta(ik)I_+^{ik} + \Theta(ki)I_+^{ki}] - \delta_{ki}(1-\delta_{lj})[\Theta(lj)I_+^{lj} + \Theta(jl)I_+^{jl}] + \delta_{lj}\delta_{ik}(2I_z^{il})$$

$$\Theta(ij) = \begin{cases} 1 & \text{if } i < j \\ 0 & \text{if } i > j \end{cases}$$

3. The nuclear relaxation of nuclei of spin $I = 3/2$

First, let us precisely state the case to be considered. A strong magnetic field is applied parallel to the Z-axis of the EFG tensor, which is assumed to be axially symmetric so that the asymmetry $\eta = 0$. Under these conditions the quadrupole coupling makes the Zeeman states unequally spaced in energy, but the eigenstates remain unmixed because the asymmetry is null. Note that in the case of pure NQR ($H_0 = 0$) the axis of quantization is Z and the eigenstates do not mix ($\eta = 0$), so the formalism below accounts for both the NMR and the NQR cases.

The nuclear relaxation process that we will analyse is dominated by the fluctuation of the (anisotropic) magnetic hyperfine field (whose principal axes coincide with those of the EFG tensor):

$$\mathbf{H}_1(t) = -\gamma\hbar\left[A_{\|}\mathbf{S}_z(t)\mathbf{I}_z + \frac{A_\perp}{2}(\mathbf{S}_+(t)\mathbf{I}_- + \mathbf{S}_-(t)\mathbf{I}_+)\right] \tag{9}$$

where $\mathbf{I}$ and $\mathbf{S}$ are nuclear and electronic spin operators, and A_i are the principal values of the magnetic hyperfine coupling tensor.

Decomposing the spin operators in the fictitious-spin basis according to the rules defined by PK one obtains

$$\mathbf{I}_z = 3\mathbf{I}_z^{14} + \mathbf{I}_z^{23} \qquad \mathbf{I}_{x,y} = \sqrt{3}(\mathbf{I}_{x,y}^{12} + \mathbf{I}_{x,y}^{34}) + 2\mathbf{I}_{x,y}^{23}.$$

Then, transforming the Hamiltonian (9) to the interaction representation:

$$\begin{aligned}\mathbf{H}_1^*(t) = -\gamma\hbar\Bigg(&A_{\|}\mathbf{S}_z(3\mathbf{I}_z^{14} + \mathbf{I}_z^{23}) + \frac{A_\perp\mathbf{S}_-}{2}[\sqrt{3}(\mathbf{I}_+^{12}\mathrm{e}^{\mathrm{i}\omega_{12}t} + \mathbf{I}_+^{34}\mathrm{e}^{\mathrm{i}\omega_{34}t}) + 2\mathbf{I}_+^{23}\mathrm{e}^{\mathrm{i}\omega_{23}t}] \\ &+ \frac{A_\perp\mathbf{S}_+}{2}[\sqrt{3}(\mathbf{I}_-^{12}\mathrm{e}^{-\mathrm{i}\omega_{12}t} + \mathbf{I}_-^{34}\mathrm{e}^{-\mathrm{i}\omega_{34}t}) + 2\mathbf{I}_-^{23}\mathrm{e}^{-\mathrm{i}\omega_{23}t}]\Bigg).\end{aligned} \tag{10}$$

The longitudinal relaxation can now be calculated from the kinetic equation (6) together with equation (10). It is worthwhile to note that the restriction to the secular contribution reduces the number of terms to be calculated. Moreover, the commutators containing exclusively operators $\mathbf{I}_z$, though they are not restricted, do not contribute because they are null. As a consequence, only those terms with double commutators such as $[\mathbf{I}_\pm^{if}, [\mathbf{I}_\mp^{if}, \mathbf{I}_z^{cd}]]$ have to be calculated. After some calculation one arrives at the kinetic equation

$$\frac{\mathrm{d}}{\mathrm{d}t}\begin{pmatrix}\langle\mathbf{I}_z^{12}\rangle^* \\ \langle\mathbf{I}_z^{23}\rangle^* \\ \langle\mathbf{I}_z^{34}\rangle^*\end{pmatrix} = W\begin{pmatrix}-6 & 4 & 0 \\ 3 & -8 & 3 \\ 0 & 4 & -6\end{pmatrix}\begin{pmatrix}\langle\mathbf{I}_z^{12}\rangle^* - \langle\mathbf{I}_z^{12}\rangle_0 \\ \langle\mathbf{I}_z^{23}\rangle^* - \langle\mathbf{I}_z^{23}\rangle_0 \\ \langle\mathbf{I}_z^{34}\rangle^* - \langle\mathbf{I}_z^{34}\rangle_0\end{pmatrix} \tag{11}$$

where $W = \gamma^2|A_\perp|^2 J(\omega)/4$ is the transition probability, which is a function of the electronic spin spectral density,

$$J(\omega) = \int_{-\infty}^{\infty} \overline{S_\pm(0)S_\mp(t)}\,\mathrm{e}^{-\mathrm{i}\omega t}$$

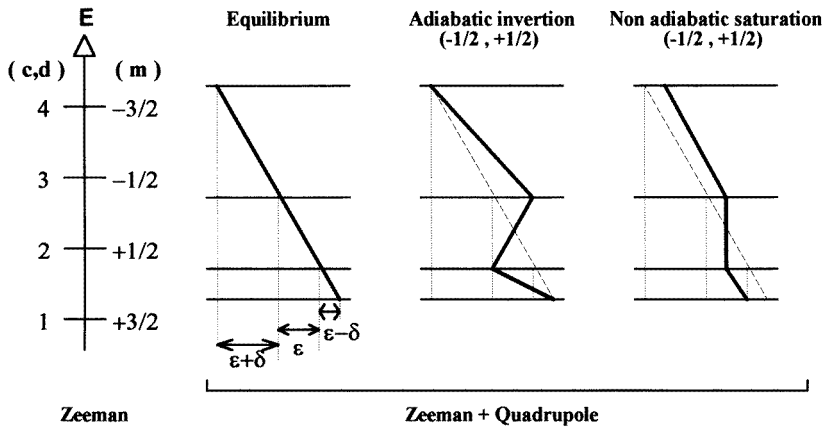
and

$$\overline{S_\pm(0)S_\mp(t)} = \mathrm{Tr_e}\{\mathrm{e}^{-\mathbf{H}_\mathrm{e}/kT}\mathbf{S}_\pm(0)\mathbf{S}_\mp(t)\}/Z_\mathrm{e}$$

is the correlation function of the electronic spin.

The system in equation (11) is easily solved and the solution is simply given by $\Delta^*\mathbf{I}(t) = \mathbf{A}(\exp\mathbf{D}t)\mathbf{A}^{-1}\,\Delta^*\mathbf{I}(t=0)$, where the matrices $\mathbf{A}, \mathbf{D}$ and $\mathbf{A}^{-1}$ are given in the appendix. However, as the solution is dependent both on how the nonequilibrium magnetization is prepared and on how its recovery is observed, it is useful to analyse a number of commonly encountered situations. A number of these experimental situations are summarized in figure 1, and the corresponding solutions for the recovery law are listed in table 2.

The recovery laws in table 2 are generally multiexponentials. Despite this, one observes that in these functions there is always just one time constant to be determined, which is defined as the spin–lattice relaxation rate $T_1^{-1} = 2W$. Actually, the possibility of defining a single relaxation rate is an important consequence of the fact that the spectral densities were considered constant in the range of frequency probed by the NMR and NQR (typically up to 150 MHz). This approximation, called the extreme-narrowing condition, allowed us



Preparation Sequence		$\Delta I^{*}_{34} \propto a_{-1/2}$	$\Delta I^{*}_{23} \propto a_{+1/2}$	$\Delta I^{*}_{12} \propto a_{3/2}$
	a.i. (+ 1/2 , –1/2)	+ε	–2ε	+ε
	a.i. (– 1/2 , –3/2)	–2ε	+ε	0
NMR	a.i. (+ 3/2 , + 1/2)	0	+ε–δ	–2 (ε–δ)
	n.a.s (+ 1/2 , – 1/2)	0	–ε	0
	sudden turn on of H_0	–ε	–ε	–ε
NQR	inversion (± 3/2 , ± 1/2)	–2δ	0	+2δ

Figure 1. A schematic diagram for the deviations (Δ) from the equilibrium population differences between levels 12, 23 and 34. The diagrams present the offset from the equilibrium (dotted line) populations, with $\varepsilon = (N/4)(h\nu_0/k_BT)$ and $\delta = (N/4)(h\nu_Q/k_BT)$. In the table there are the deviations $\Delta I^{*}_{cd} \propto a_m = [(N_m - N_{m-1})_{\text{prepared}} - (N_m - N_{m-1})_{\text{equilibrium}}]$ for different initial conditions. An adiabatic inversion, denoted by a.i.(m, m'), means a π-pulse on the corresponding transition line which does not change the other level populations. In contrast, a non-adiabatic saturation, denoted by n.a.s.(m, m'), means a saturation of this transition line that alters the population of the other levels, keeping their differences equal to the equilibrium values.

to put $J(\omega) = J(0) = J(\omega_{12}) = J(\omega_{23}) = J(\omega_{34})$ so that we could extract W from the relaxation matrix (11) as a common prefactor. Whether the extreme-narrowing condition is fulfilled or not may be tested by measuring T_1^{-1} as a function of the frequency. If $T_1^{-1} = 2W$ determined from the recovery laws of table 2 does not depend on frequency, then the extreme-narrowing condition holds. In the case of the YBCO, Borsa *et al* [12] have reported a frequency dependence of T_1^{-1} at the planar copper site above T_c. However, at Grenoble, we have recently investigated this problem [13] and our results disagree with those of Borsa *et al*: in the normal state, the values T_1^{-1} for the planar copper measured at different frequencies are coincident within the experimental error.

Now we turn to calculating the nuclear transverse relaxation using the same formalism and conditions as we have considered for the spin–lattice relaxation. Putting $r = x$ in equation (6) the calculation is straightforward. First one must note that $\omega_p^{q=0} = 0$, so the

Table 2. Recovery laws of the spin–lattice relaxation. $X = 2Wt$ and by definition $T_1^{-1} = 2W$.

a.i.$(+1/2, -1/2)$	$\Delta I^*_{23} \propto \frac{1}{10}\mathrm{e}^{-X} + \frac{9}{10}\mathrm{e}^{-6X}$
a.i.$(\pm 1/2, \pm 3/2)$	$\Delta I^*_{12,34} \propto \frac{1}{10}\mathrm{e}^{-X} + \frac{5}{10}\mathrm{e}^{-3X} + \frac{4}{10}\mathrm{e}^{-6X}$
n.a.s.$(+1/2, -1/2)$	$\Delta I^*_{23} \propto \frac{4}{10}\mathrm{e}^{-X} + \frac{6}{10}\mathrm{e}^{-6X}$
Sudden turn on of H_0	$\Delta I^*_{12,23,34} \propto \mathrm{e}^{-X}$
Inversion $(\pm 3/2, \pm 1/2)$ (NQR)	$\Delta I^*_{12,34} \propto \mathrm{e}^{-3X}$

restriction $\omega_{p'}^{-q} + \omega_p^q = 0$ has no effect for $q = 0$ and, therefore, all of the contributions involving $[\mathbf{I}_z^{cd}, [\mathbf{I}_z^{ef}, \mathbf{I}_x^{kl}]]$ must be computed. On the other hand, for $q = \pm 1$ the restriction $\omega_{p'}^{-q} + \omega_p^q = 0$ imposes $p = p'$ and just the terms like $[\mathbf{I}_\pm^{ef}, [\mathbf{I}_\mp^{ef}, I_x^{cd}]]$ have to be considered. The calculation yields a system of linearly independent equations

$$\frac{\mathrm{d}}{\mathrm{d}t}\begin{pmatrix} \langle \mathbf{I}_x^{12}\rangle^* \\ \langle \mathbf{I}_x^{23}\rangle^* \\ \langle \mathbf{I}_x^{34}\rangle^* \end{pmatrix} = -\begin{pmatrix} 1/T_2^{12} & 0 & 0 \\ 0 & 1/T_2^{23} & 0 \\ 0 & 0 & 1/T_2^{34} \end{pmatrix}\begin{pmatrix} \langle \mathbf{I}_x^{12}\rangle^* - \langle \mathbf{I}_x^{12}\rangle_0 \\ \langle \mathbf{I}_x^{23}\rangle^* - \langle \mathbf{I}_x^{23}\rangle_0 \\ \langle \mathbf{I}_x^{34}\rangle^* - \langle \mathbf{I}_x^{34}\rangle_0 \end{pmatrix} \tag{12}$$

where:

$$1/T_2^{12} = 1/T_2^{34} = \gamma^2 J(\omega)\left[\frac{|A_\parallel|^2}{4} + \frac{5|A_\perp|^2}{4}\right] = (T_1)_\perp^{-1} + 2(T_1)_\parallel^{-1} \tag{13}$$

and

$$1/T_2^{23} = \gamma^2 J(\omega)\left[\frac{|A_\parallel|^2}{4} + \frac{7|A_\perp|^2}{4}\right] = (T_1)_\perp^{-1} + 3(T_1)_\parallel^{-1}. \tag{14}$$

In the passage from (12) to (13) and (14), two important assumptions were made. First, the fluctuations were assumed to be isotropic so that $J^{+-}(\omega) = 2J^z(\omega)$. Secondly, the extreme-narrowing condition was adopted, allowing us to put $J(0) = J(\omega)$. Thus, equations (12)–(14) give the T_1-contribution to T_2, which is a single exponential and whose time constant $T_{2\mathrm{R}}$ is a combination of the spin–lattice relaxation rates measured with $\boldsymbol{H}_0$ parallel and perpenicular to $\boldsymbol{Z}$ (the c-axis). Furthermore, the relaxation rate $T_{2\mathrm{R}}^{-1}$ when one excites the central line is different to that when one excites a satellite line. The physical origin of this contribution is the lifetime of the nuclear states, and it is important when T_1 is short.

4. The planar copper in $YBa_2Cu_3O_{6+x}$

The NMR and NQR techniques have been extensively used in the study of the low-energy excitations in the HTCS and related materials, mainly the $YBa_2Cu_3O_{6+x}$ compounds [7]. In particular, the planar copper site, denoted Cu(2), is of prime interest for these materials. The temperature dependences of both T_1 and T_2 at the Cu(2) site have been measured in the normal state ($T > T_\mathrm{c}$) in order to extract information on the generalized electronic spin dynamical susceptibility, $\chi(\boldsymbol{q}, \omega)$ [14, 15]. These measurements require as basic knowledge the recovery laws of the spin–lattice relaxation as well as the contribution of T_1 to T_2. The exactness of the recovery law of the longitudinal relaxation was discussed by Horvatić [6] and here we will focus on the validity of $T_{2\mathrm{R}}$ in the transverse relaxation measurements

The transverse relaxation may be divided into two parts: the spin–spin contribution and the T_1-contribution. The first part arises from the nuclear spin–spin interactions (direct

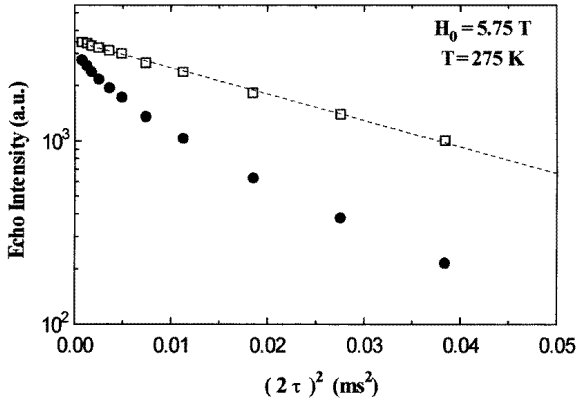


Figure 2. The echo envelope decay as function of $(2\tau)^2$ (τ is the time interval between $\pi/2$–π pulses) measured on the central line of the ^{63}Cu(2) in a single crystal of $YBa_{1.92}Sr_{0.07}Cu_3O_{6.92}$. The ● represent the raw data and □ the data after the correction for the expected T_1-contribution $e^{-t/T_{2R}}$, where $T_{2R}^{-1} = (T_1)_{\perp}^{-1} + 3(T_1)_{\parallel}^{-1} = (7.9 \pm 0.3) \times 10^3$ s^{-1}, with $(T_1)_{\parallel}^{-1} = (1.28 \pm 0.05) \times 10^3$ s^{-1} and $(T_1)_{\perp}^{-1} = (4.0 \pm 0.1) \times 10^3$ s^{-1} measured independently for the same sample. The dashed line is the result of a fitting with a gaussian decay, from which the spin–spin relaxation rate $T_{2g}^{-1} = (8.3 \pm 0.3)$ ms^{-1} is extracted. Details of the experiment and sample are given elsewhere [13].

dipolar and indirect) and gives rise to an undefined decay of the transverse magnetization, except in few special cases [3]. On the other hand the T_1-contribution is exponential, and its time constant T_{2R} may be calculated exactly through the FS method described above or using the Redfield theory (see [2, 10]). Usually the significant physical information is contained in the spin–spin relaxation, making it necessary to extract the T_1-contribution from the raw data. This is precisely the case for YBCO compounds, where the spin–spin relaxation is dominated by a temperature-dependent indirect coupling, in which one is interested because it is related to the static spin susceptibility, $\chi'(\boldsymbol{q}, \omega \sim 0)$. The aim of the T_2-measurements is then to extract the spin–spin relaxation time and relate it to $\chi'(\boldsymbol{q}, \omega \sim 0)$, which is the physical information of interest [16].

An illustration of the procedure for extracting the T_1-contribution from the transverse relaxation is given in figure 2, where the echo envelope decay measured on the central line of the ^{63}Cu(2) is semilogarithmically plotted against $(2\tau)^2$ (where τ is the time interval between the $\pi/2$–π pulses of the spin-echo experiment). Two procedures may be used to analyse the data. In the first, we correct the raw data (closed circles) for the appropriate theoretical T_1-contribution, given by equation (14) as $T_{2R}^{-1} = (T_1)_{\perp}^{-1} + 3(T_1)_{\parallel}^{-1} = (7.9 \pm 0.3) \times 10^3$ s^{-1}, where $(T_1)_{\parallel}^{-1} = (1.28 \pm 0.05) \times 10^3$ s^{-1} and $(T_1)_{\perp}^{-1} = (4.0 \pm 0.1) \times 10^3$ s^{-1} were measured independently for the same sample. The resulting spin–spin relaxation (open squares) is very well fitted by a gaussian decay with $T_{2g}^{-1} = (8.3 \pm 0.3)$ ms^{-1}. Alternatively, if one fits the transverse relaxation decay with a gaussian times an exponential decay

$$f(t) = A \exp\{-t/T_{2R}\} \exp\{-(t^2/2T_{2g}^2)\}$$

one obtains $T_{2R}^{-1} = (8.2 \pm 0.3) \times 10^3$ s^{-1} and $T_{2g}^{-1} = (8.5 \pm 0.3)$ ms^{-1}, in fair agreement with the values obtained from the previous method. Therefore, the good agreement between the two procedures described above confirms that the origin of the exponential component of the transverse relaxation is due to the contribution of T_1 to T_2. Moreover, this enables

one to rely on the theoretical prediction for T_{2R}^{-1} to derive both $(T_1)_{\parallel}^{-1}$ and $(T_1)_{\perp}^{-1}$ from the transverse relaxation measurement, provided that the anisotropy of T_1 is known.

5. Conclusion

In this paper we have revised the fictitious spin formalism and applied it to solve the problem of the nuclear relaxation of nuclei of spin $I = 3/2$ in the presence of strong and axially symmetric quadrupole effects. We considered the fluctuations of the (anisotropic) magnetic hyperfine field as the only source of spin–lattice relaxation. Though we have developed the specific case of $I = 3/2$, the extension of this formalism to any value of I is straightforward. The great advantage of the FS approach developed here is that it provides not only the spin–lattice relaxation, as does the master population equation method, but also the transverse relaxation. Both the recovery law of the nuclear spin–lattice relaxation and the contribution of T_1 to T_2 were derived for a number of different conditions commonly encountered in experiments. The practical application to the study of the spin–spin relaxation of the planar copper site in the YBCO high-T_c compound was given as an example. In this example, T_{2R}^{-1} expected for the contribution of T_1 to T_2 agrees fairly well with the relaxation rate measured for the exponential component of the transverse relaxation.

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Appendix

$$\mathbf{A} = \begin{pmatrix} 2 & -1 & 1 \\ -3 & 0 & 1 \\ 2 & 1 & 1 \end{pmatrix} \qquad \mathbf{D} = \begin{pmatrix} -12W & 0 & 0 \\ 0 & -6W & 0 \\ 0 & 0 & -2W \end{pmatrix}$$

$$\mathbf{A}^{-1} = \frac{1}{10}\begin{pmatrix} 1 & -2 & 1 \\ -5 & 0 & 5 \\ 3 & 4 & 3 \end{pmatrix}. \tag{A1}$$

The recovery law of the spin–lattice relaxation is given by

$$\Delta^*\mathbf{I}(t) = \mathbf{A}(\exp \mathbf{D}t)\mathbf{A}^{-1}\,\Delta^*\mathbf{I}\ (t = 0).$$

As an example consider the case of an adiabatic inversion of the population of the central line $(1/2 \leftrightarrow -1/2)$ (see figure 1). The recovery of the magnetization of the central line will follow:

$$\Delta^*\mathbf{I}_z^{23}(t) \propto (0\ 1\ 0)\mathbf{A}(\exp \mathbf{D}t)\mathbf{A}^{-1}(1\ -2\ 1) \tag{A2}$$

$$\Delta^*\mathbf{I}_z^{23}(t) \propto \tfrac{1}{10}\{\mathrm{e}^{-2Wt} + 9\mathrm{e}^{-12Wt}\}. \tag{A3}$$

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