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Separation of magnetic and quadrupolar relaxation rates from spin–lattice recovery laws at short times with illustration in a high-T_c superconductor

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Abstract. A method to separate the magnetic and quadrupolar rates in the spin–lattice relaxation process for the populations of the levels, without completely solving the master equations, is described. The method can be used, in particular, to evaluate separately the quadrupolar contributions due to the lattice vibrations and the magnetic contribution due to electronic spin dynamics in the ^{139}La and ^{63}Cu NQR relaxation in high-T_c superconductors of the La_2CuO_4 family. An experimental illustration for the ^{139}La NQR relaxation measurements in $La_{2-x}Sr_xCuO_4$ is given.

1. Introduction

In NMR experiments in solids, when the Zeeman energy levels are equally spaced, a common spin temperature is usually maintained by fast T_2-driven transitions. Therefore the spin–lattice relaxation process is described by an exponential law and T_1 is given by [1]

$$T_1^{-1} = \sum_{m,n} W_{mn}(E_m - E_n)\Big/ 2\sum_n E_n^2$$

where W_{mn} are the transition probabilities connecting the various pairs of eigenlevels of energy $E_{m,n}$. However, the levels are often not equally spaced. In NMR, this might be due to the static quadrupolar interaction perturbing the pure Zeeman eigenstates while, in NQR, for $I \geqslant \frac{5}{2}$ the resonance lines fall at different frequencies from the intrinsic structure of the eigenvalues of the pure quadrupole Hamiltonian. Therefore a common spin temperature cannot exist and the spin–lattice relaxation process, in general, is not described by a simple exponential law. In order to find the recovery law and to relate the experimental time constant to the relaxation transition probabilities $W_{mm'}$, one has to solve the master equations for the populations N_m by taking into account given initial conditions induced by the RF pulses disturbing the equilibrium and by considering in detail the nature (magnetic and/or quadrupolar) of the relaxation mechanisms reflected in $W_{mm'}$. For the relaxation process driven by the fluctuations of a local fictitious magnetic field at the nuclear site, one has $\Delta m = \pm 1$ relaxation probabilities defined by [2]

$$W^{(\mathrm{M})}_{m,m-1} = W_{\mathrm{M}}(I+m)(I-m+1) \tag{1}$$

while, for the relaxation driven by the electric quadrupolar interaction, one has the $\Delta m = \pm 1$ and $\Delta m = \pm 2$ relaxation transition probabilities

$$\begin{aligned} W_{m,m-1} &= W_1(2m-1)^2(I+m)(I-m+1)/2I(2I-1)^2 \\ W_{m,m-2} &= W_2(I+m)(I-m+1)(I+m-1)(I-m+2)/2I(2I-1)^2. \end{aligned} \tag{2}$$

The recovery laws and the relationships of the characteristic time constant T_1 to $W_{1,2}$ or W_{M} have been found in several cases [2–8].

For NQR experiments in nuclei at $I \geqslant \frac{5}{2}$, some difficulties arise, particularly when both the magnetic and the quadrupolar relaxation mechanisms are present. This is the case, for instance, for the La NQR relaxation in $La_{2-x}Sr_xCuO_4$ [9] where a recovery in the form of three exponentials has been experimentally observed. A suitable analysis of the recovery plots to extract W_{M} and $W_{1,2}$ on the basis of the theoretical laws requires data at long times, where the experimental errors are larger. Furthermore the theoretical recovery law cannot always be obtained from the master equations (this is, for example, so for $I = \frac{7}{2}$ in NQR, since in general one has a secular equation of high order when $W_1 \neq W_2$ and $W_{\mathrm{M}} \neq 0$, or for $I = \frac{9}{2}$ in NMR).

In this paper a simple method is suggested, allowing one to obtain direct relationships of the time constants for the recovery plots for $t \to 0$ with W_{M}, W_1, W_2 without completely solving the master equations, thus yielding separate evaluations of the magnetic and quadrupolar relaxation rates by using different sequences of RF pulses and/or by irradiating different lines.

2. Description of the method

A description of the experimental approach will be given in the following by labelling the levels involved in the transitions and in the RF irradiation in terms of the quantum number m. This is directly applicable to NMR as well as to NQR when the EFG tensor has cylindrical symmetry. However, one should stress that the formalism is more general and may also be applied to non-diagonal cases of the hyperfine interaction, e.g. with mixed magnetic and quadrupolar contributions or with $\eta \neq 0$.

Let us define, in NMR, N_1 as the statistical population of the level $+I$, N_2 at the level $+I-1$ and so on while, in NQR, N_1 corresponds to the level $\pm\frac{1}{2}$ for a half-integer spin and 0 for an integer spin, N_2 to the level $\pm\frac{3}{2}$ in a half-integer spin and ± 1 for an integer spin and so on.

Let us introduce the time-dependent population difference vector

$$N(t) = \begin{pmatrix} N'_n(t) \\ N'_{n-1}(t) \\ \vdots \\ N'_1(t) \end{pmatrix} \tag{3}$$

where N'_i indicate the normalized population difference, namely, in NMR,

$$N_i' = (N_i - N_{i+1} - n_0)/n_0 \qquad (i = 1, \ldots, n) \tag{4a}$$

or, in NQR,

$$N_i' = (N_i - N_{i+1} - in_0)/in_0 \qquad (i = 1, \ldots, n) \tag{4b}$$

where

$$n_0 = \frac{N\Delta}{n+1}$$

with

$$N = \sum_{i=1}^{n+1} N_i \qquad \Delta = h\nu_{L,Q}/kT.$$

The master equations for the statistical populations have the form

$$\dot{N}(t) = \mathbf{M}N(t) \tag{5}$$

where the matrix $\mathbf{M}$, which has a structure similar to the Redfield [10] matrix, is given by

$$\mathbf{M} = \begin{pmatrix} M_{11} & M_{12} \ldots & M_{1n} \\ \vdots & \vdots & \vdots \\ M_{n1} & M_{n2} \ldots & M_{nn} \end{pmatrix} \tag{6}$$

M_{ij} being a proper linear combination of the relaxation transition probabilities W_M, W_1 and W_2.

Let us define the effective spin–lattice relaxation rate r_i as

$$r_i = \dot{N}_i'(t)\Big|_{t\to 0} \equiv \dot{N}_i'(0) \tag{7}$$

for the ith transition.

By defining a relaxation rate vector $\boldsymbol{R}$ having $\dot{N}_i'(0)$ as components, in the light of equations (5) and (7), one sees that $\boldsymbol{R}$ obeys the general equation

$$\boldsymbol{R} = \mathbf{M}N(0) \tag{8}$$

with

$$\boldsymbol{R} = \begin{pmatrix} r_n \\ r_{n-1} \\ \vdots \\ r_1 \end{pmatrix}$$

where $N(0)$ is the initial conditions vector (see equation (3)). By irradiating with different sequences and/or by saturating different transitions one can change the initial conditions vector $N(0)$. Equation (8) represent a system of linear equations where each equation corresponds to the rate of the saturated transition with a given sequence of pulses. One can observe from equations (5)–(8) that a separate estimate of W_M, W_1 and W_2 can be obtained if one has three different r_i. Two equations can be obtained by changing, on a given ith line, the irradiation sequence perturbing the thermal equilibrium:

(i) single effective $\pi/2$ pulse, so that $N_i'(0) = -1$ while for $j \neq i$ the initial conditions $N_j'(0)$ follow consequently;

(ii) sequence of $\pi/2$ pulses, the separation between pulses being greater than T_2, while the duration of the whole sequence is much greater than all the W, so that the initial conditions are $N_i'(0) = -1$ and $N_j'(0) = 0$ (see equation (4)).

The third equation, when required, must be obtained by irradiating and measuring the recovery of another line.

3. Illustration

An illustration of this method is presented here by referring to ^{139}La ($I = \frac{7}{2}$) NQR measurements in high-T_c superconducting $La_{2-x}Sr_xCuO_4$ samples, for $x = 0.01$. In this particular case we shall use only the $3\nu_Q$ ($\pm\frac{7}{2} \leftrightarrow \pm\frac{5}{2}$, the asymmetry parameter η being $\eta \cong 0$) transition where the effective rate is r_3. From equation (8), one has

$$r_3 = -N_3'(0)(14W_M + 2W_1 + W_2/3) + N_2'(0)(12W_M + 16W_1/21 + 8W_2/21) + N_1'(0)(5W_2/21). \quad (9)$$

Let us assume that the quadrupolar relaxation mechanism in these sample is such that $W_1 \cong W_2 \equiv W_Q$. This rather general condition is observed in most powdered samples. Then we can measure the rates for two different irradiation sequences: the 'short' sequence ($\tau \ll r_i^{-1}$; see (i) in the previous section) and the 'long' sequence ($\tau \gg r_i^{-1}$, see (ii)), where τ is the total length of a sequence of $\pi/2$ pulses separated by a time longer than T_2.

For the $3\nu_Q$ transition ($N_3'(0) = -1$) we define from equation (9) r_{3S} and r_{3L}, respectively, as the rates for a 'short' ($N_2'(0) = \frac{3}{4}$, $N_1'(0) = 0$) and a 'long' sequence ($N_2'(0) = N_1'(0) = 0$).

To simplify the rate equations, let us define a magnetic rate r_M and a quadrupolar rate r_Q as obtained from equation (9) in the case of the 'short' sequence, namely

$$r_M = 23W_M \qquad r_Q = 67W_Q/21.$$

Then one obtains

$$\begin{aligned} r_{3S} &= r_M + r_Q \\ r_{3L} &= 14r_M/23 + 49r_Q/67. \end{aligned} \quad (10)$$

The rates r_{3S} and r_{3L} have been evaluated by taking the tangent at the origin of the magnetization recovery (figure 1). In figure 1, one can observe that the values of the effective rates are sensitive enough when changing the sequence and allows one to separate the contributions.

The behaviour of r_{3S} and r_{3L} are shown in figure 2. By using equation (10), one extracts the magnetic contribution r_M and quadrupolar contribution r_Q shown in figure 3. Thus we have been able to separate the quadrupolar relaxation mechanism due to the phonons from that related to Cu spin dynamics in $La_{2-x}Sr_xCuO_4$. The separation has shown that the time-dependent part of the quadrupolar Hamiltonian becomes the important mechanism for nuclear relaxation for $T \gtrsim 120$ K. In particular the temperature behaviour of the soft modes around the structural phase transitions in these compounds can be studied, in principle, through the quadrupolar part of the relaxation

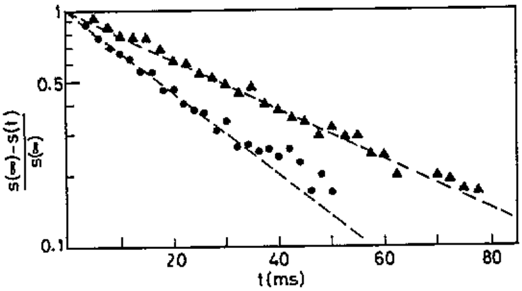

Figure 1. Recovery plots $y \equiv [s(\infty) - s(t)]/s(\infty)$ $(y \equiv -N'_3(t))$, $s(t)$ being the amplitude of the signal at time t after a saturating pulse or sequence, and estimate of the effective relaxation rates for different sequences at $T = 77$ K: for the 'short' (●) sequence and 'long' (▲) sequence for the $3\nu_Q$ (transition $\pm\frac{5}{2} \leftrightarrow \pm\frac{7}{2}$) NQR line in $La_{1.99}Sr_{0.01}CuO_4$.

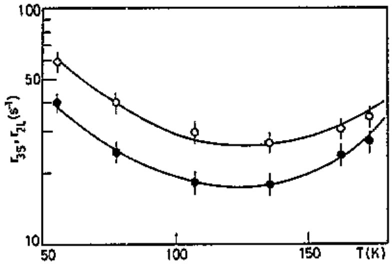

Figure 2. Effective relaxation rates r_{3S} (○) and r_{3L} (●) as a function of the temperature. The full curves are guides for the eye.

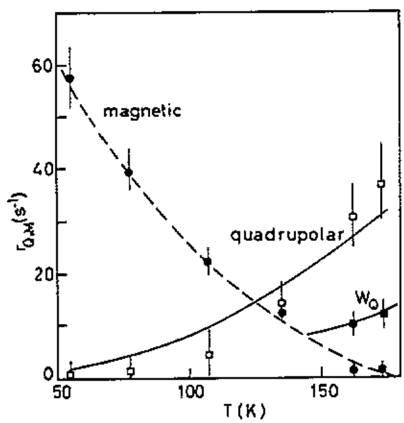

Figure 3. Magnetic (●) and quadrupolar (□) contributions to the relaxation rate versus temperature, as derived from the data in figure 2 and from equation (10) in the text. The broken curve is a function of the form $a\exp(b/T)$, while the full curve is proportional to T^2. The $\Delta m = \pm 1$ and $\Delta m = \pm 2$ relaxation transition probabilities W_1 and W_2 (■) turn out to be very close and one almost has $W_1 \cong W_2 \equiv W_Q \equiv 3r_Q/10$.

process, as shown for several structural transitions [11]. For $T \leqslant 120$ K in La_2CuO_4, and around the superconducting phase transition in Sr-doped samples, the relaxation mechanism is mostly due to the Cu^{2+} magnetic moments and thus it is possible to extract information on the correlated spin dynamics. In particular it has been shown [12, 13] that the Cu^{2+} spin dynamics in low-doped systems ($x \leqslant 0.05$) are not controlled by thermal fluctuations but rather by a kind of 'diffusion' of the charge defects introduced by the doping. For larger x, implying a transition to the superconducting state, a decrease in the effective Cu spin has also been demonstrated [14].

As can be seen, in the high-temperature range ($T > 160$ K) the magnetic contribution can be neglected. Therefore it becomes possible to extract W_1 and W_2 for the quadrupolar contribution without any assumption about their ratio. In figure 3 we show that W_1 is actually very close to W_2.

It should be emphasized that, when one of the transition probabilities is much smaller than the others, then the separation is affected by the unavoidable experimental errors.

However, I have shown in this paper that in general it is possible to separate the contributions easily; the magnetic and quadrupolar contributions to the relaxation process can be obtained without numerical solution of the master equations and by analysing only the short-time region of the recovery plots.

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