Quadrupolar Relaxation – what would we do without it in High-T_c Superconductor Studies?

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This paper emphasizes the fact that valuable information on the dynamics of high-T_c superconductors is concealed in that part of the spin-lattice relaxation which arises from quadrupolar interactions. We briefly discuss the problem how to disentangle magnetic and quadrupolar time dependent interactions if both are present, thus leading to multiexponential magnetization recovery laws. We then discuss two examples from our studies of the high-T_c superconductor $YBa_2Cu_4O_8$ where the identification of a quadrupolar contribution to the spin-lattice relaxation has been essential to draw the relevant conclusions. One example is concerned with the charge fluctuations associated with an electronic crossover showing up in the oxygen relaxation. The second example is dealing with the separation of charge and spin excitations and the validity of the single-spin fluid model.

Key words: NQR; NMR; Quadrupolar Relaxation; High-Temperature Superconductors.

1. Introduction

NMR and NQR are still playing an important role in the understanding of high-temperature superconductors (HTSC) at the atomic level [1, 2]. As in "classical" superconductors, it turned out that relaxation time studies are an essential and, quite often, indispensable tool to decipher the complex information provided by other NMR/NQR parameters. Since many HTSC are derived from antiferromagnetic parent compounds, either by doping or increasing the oxygen content, short-range antiferromagnetic spin fluctuations are one of their characteristic features. Therefore, in most cases spin-lattice relaxation (in particular that of Cu nuclei in the CuO_2 planes) is dominated by the magnetic coupling between nuclei and the fluctuating electrons.

Quite often, however, in HTSC and other condensed matter NMR experiments, both magnetic and quadrupolar time dependent interactions are present, leading to multiexponential magnetization recovery laws. The question arises whether it is possible to deduce, directly from the experiment, the admixture of a weak contribution, either due to magnetic or quadrupolar interactions. In this paper, we will start with a brief review of the general problem and will then discuss two examples from our studies of the high-T_c superconductor $YBa_2Cu_4O_8$ where the identification of a quadrupolar contribution to the spin-lattice relaxation has been essential to draw the relevant conclusions.

2. Mixed Magnetic and Quadrupolar Relaxation

The literature contains mainly calculations of multiexponential magnetization recovery laws for the case of either *purely* magnetic or *purely* quadrupolar fluctuations, see *e. g.* [3]. Recently, we have discussed [3] the multiexponential recovery which appears in spin-lattice relaxation when NMR lines are split by quadrupole interaction. We have treated the case of a static quadrupolar perturbed Zeeman Hamiltonian in the presence of both magnetic and quadrupolar fluctuations under the assumption that the spin–exchange coupling can be omitted and the eigenfunctions of the static Hamiltonian can be approximated by Zeeman eigenfunctions.

The calculations were carried out for three cases differing by the initial conditions of the spin system. We have presented exact solutions for spin $I = 1$ and $I = 3/2$. For spin $I = 5/2$ we found an exact solution if the quadrupolar transition probabilities W_1 and W_2 are equal, and an approximated solution for the general case $W_1 \neq W_2$. The spin $I = 7/2$ was treated for magnetic fluctuations (with probability W) only. We analyzed the whole parameter space constructed by the (W, W_1, W_2) probabilities. This is a necessity when dealing with single crystals or partially oriented powders (the latter is standard practice in many NMR/NQR studies of HTSC), since in these cases the different contributions of the fluctuations depend on the angle they form with the external magnetic field, so that extended parts of the parameter space are sampled.

We found that, in a surprisingly large region of the (W, W_1, W_2) parameter space, it is almost impossible, within experimental errors, to separate magnetic and quadrupolar contributions to the relaxation. Instead, the "dominant" contribution determines the time evolution of the recovery law, *i. e.* the system can approximately be described by a single time constant, T_1^{eff}. In other words, even if the initial assumption of the experimentalist is wrong (lets say, the assumption of pure magnetic fluctuations), the extracted T_1 is of the right order of magnitude.

Thus, to test any hypothesis about the origin of the spin–lattice relaxation in the system under consideration, additional information is necessary, which may be provided, for instance, by the temperature dependence of the relaxation. If the nucleus studied has two magnetic isotopes, as in the case of copper (^{63}Cu and ^{65}Cu), the admixture can be estimated from the ratio of the relaxation times, T_1. If single crystals are available, the relaxation's angular dependence yields valuable information. If all this fails, a new approach is necessary, as will be discussed below.

3. The Electronic Crossover

The first example deals with an electronic crossover occuring at a temperature $T^\dagger$ in the normal state of the superconductor $YBa_2Cu_4O_8$ (T_c = 82 K) [4, 5]. Our conclusion about the occurence of this crossover was based on the fact that the temperature dependence of several NMR/NQR parameters exhibits an anomaly at $T^\dagger$ = 180 K. These results had an essential importance for our theoretical study [6] which investigated the

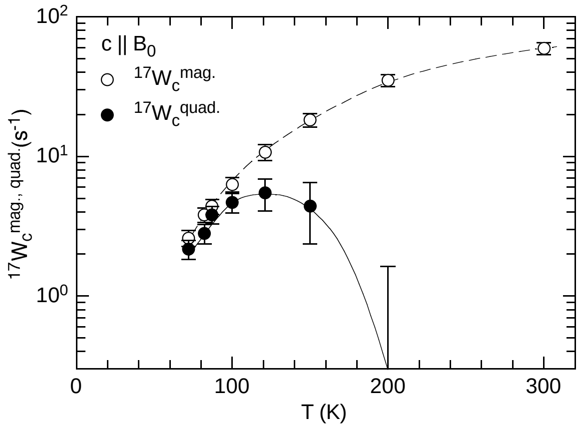

Fig. 1. ^{17}O magnetic and quadrupolar relaxation rates of O(2,3) vs. temperature. The lines serve as a guide to the eyes (from [4]).

possibility whether these anomalies support the idea that the so-called spin gap phenomenon is caused, at least partly, by a transition due to a charge density wave. The presence of a spin gap means that spectral weight in the electron spin fluctuations is transferred from lower to higher energy.

We concluded that, in the chains and planes of $YBa_2Cu_4O_8$, there are enhanced charge fluctuations at temperatures below $T^\star$. These fluctuations open, in addition to the strong magnetic relaxation, a quadrupolar relaxation channel thus explaining the unusual temperature dependence of the ratio of the relaxation rates of *in-plane* oxygen ^{17}O(2,3) and yttrium ^{89}Y. And this in turn supports the link between the crossover and a charge density wave instability.

The relative magnitude of the quadrupolar contribution $^{17}W_c$ to the total relaxation rate of O(2,3) can be calculated as follows [4]. [c indicates that the external magnetic field is parallel to the c axis.] We assume that the magnetic and quadrupolar contributions are almost independent of each other and that both yttrium and O(2,3) couple to the same spin-degree of freedom, described by the dynamic electronic susceptibility. Since the form factors for these two isotopes, within the Mila-Rice Hamiltonian [1, 2], are very similar, T_1 should exhibit almost the same temperature dependence for Y and O(2,3). This then allows one to separate the magnetic and the quadrupolar contribution to $^{17}W_c$. We obtain

$$^{17}W_c^{\text{quad.}} \simeq \left[\frac{^{17}W_c}{^{89}W_c} - \left(\frac{^{17}W_c}{^{89}W_c}\right)_{300\ \text{K}}\right] {}^{89}W_c \qquad (1)$$

and ${}^{17}W_c^{\text{mag.}} = {}^{17}W_c - {}^{17}W_c^{\text{quad.}}$. The result is given in Figure 1. Below 100 K, the two contributions are of the same order of magnitude. In view of the temperature dependence of ${}^{17}(W_{\|}/W_c)$, it follows that the quadrupolar fluctuations have to be the strongest along the Cu-O bond.

However, is there *direct* evidence for the quadrupolar contribution to the ^{17}O relaxation? We have solved this problem by employing a pulse double-irradiation method which allows one to separate magnetic from quadrupolar contributions in the spin–lattice relaxation [7]. The method involves a special initial condition of the spin system which we call dynamic saturation and which we had already mentioned previously [3].

The pulse sequence fully saturates one transition while another is observed. The clue is that the observed transition changes its intensity if and only if a $|\Delta m| = 2$ quadrupolar contribution is present; the change is monitored with respect to a standard spin-echo experiment. We calculated analytically this intensity change for spins $I = 1, 3/2, 5/2$, thus providing a quantitative analysis of the experimental results. Since the presented pulse sequence takes care of the absorbed radio-frequency power, no problems due to heating arise. The method is especially suited when only *one* NMR sensitive isotope is available as it is the case with ^{17}O. Different cross-checks were performed to prove the reliability of the obtained results.

Applying this method to O(2,3) in $YBa_2Cu_4O_8$, we could show [8] that the spin–lattice relaxation rate, below approximately 180 K, consists of magnetic as well as quadrupolar contributions, *i. e.* low-frequency charge fluctuations. In the superconducting state, this newly established quadrupolar relaxation diminishes faster than the magnetic one, indicating that the underlying relaxation process is strongly influenced by the superconducting transition. There are two degrees of freedom involved in the low-energy excitations of the electronic system, one of them is the single-spin degree, implying that the single-spin fluid model is partially correct, whereas the other one is the *charge* degree of freedom with predominantly oxygen character, since it is not observed at the copper sites.

4. Separation of Charge and Spin Excitations

The second example is concerned with the relaxation of the *chain* Cu nuclei in $YBa_2Cu_4O_8$. Because

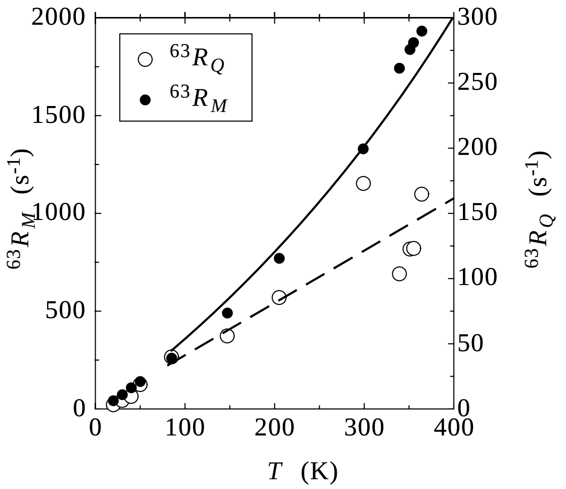

Fig. 2. Temperature dependence of the magnetic (R_M) and quadrupolar (R_Q) spin-lattice relaxation rate. The solid line is a fit of the 1D electron-gas model to the data. The dashed line is a guide to the eye (from [9]).

of the anisotropy of the electronic properties suggested by the crystalline structure and confirmed experimentally, the Cu-O chains present a good example of a quasi one-dimensional (1D) electronic conductor. In the past two decades, 1D systems have been a playground for theoretical and experimental investigations of non-Fermi liquid behavior. If probed by NMR or NQR, the chains of $YBa_2Cu_3O_7$ and $YBa_2Cu_4O_8$ do not exhibit simple metallic behavior. For instance, the Cu Knight shift varies linearly with temperature, and the spin-lattice relaxation rate, $1/T_1$, increases approximately with the temperature cubed, while, in a simple metal, the Knight shift is temperature independent and $1/T_1$ increases linearly with temperature.

Recently, we made an attempt [9] to explain the puzzling behavior of the spin susceptibility of the chains in $YBa_2Cu_3O_7$ and $YBa_2Cu_4O_8$ by invoking the results of a theory treating nuclear spin-lattice relaxation in 1D conductors [10]. This theory is based essentially on the results of the scaling theory for the quasi-1D correlated electron gas [11].

The Cu spin-lattice relaxation rate $1/T_1$ can be written as a sum of two contributions: $1/T_1 = R_M + R_Q$. The “magnetic relaxation rate” R_M is related to magnetic field fluctuations at the nuclear site induced by the valence electron spins, while the “quadrupolar relaxation rate” R_Q is associated with electric field gradient fluctuations which can arise from valence electron and/or ionic charges. We decompose the Cu $1/T_1$ raw data into the two contributions by utilizing the fact that R_M is proportional to the gyromagnetic ratio squared γ^2 and R_Q is proportional to the quadrupole moment squared $(eQ)^2$. The result is given in Fig. 2: R_M and R_Q have different temperature dependences and R_M is dominating.

R_M can be explained in the framework of the 1D electron gas model, where the anisotropy and the correlation of the chain electrons system are taken into account. To explain R_Q, various mechanisms are feasible. Relaxation by phonons can be excluded because of the temperature dependence of R_Q and its large value. In a metal with non-s conduction electrons, the quadrupolar relaxation due to the charge carriers is finite and can be comparable to their magnetic dipolar contribution. In the absence of other relaxation channels, we believe that this is the origin of the quadrupolar relaxation in the Cu chains. The different temperature dependence of R_M and R_Q, which is not expected for a simple metal, is an indication for the separation of spin and charge excitations expected in the framework of the 1D electron gas model. In such a case, R_Q would be related to the spectral density of holons.

The relaxation rate of the apex oxygen scales neither with that of chain Cu nor with plane Cu, but with the quadrupolar relaxation R_Q of the chain copper. This implies that the electric field gradient fluctuations, presumably induced by the holons in the chains, are also responsible for the apex oxygen relaxation.

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