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ON SPIN-SPIN RESERVOIR RELAXATION IN NQR

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ABSTRACT

An attempt is made to discuss in a preliminary manner the question of the possible influence of absence of the inner equilibrium in the quadrupole spin system on the nuclear quadrupole spin-lattice relaxation. A general approach is proposed and special situations considered: small percentage of the quadrupole nuclei on the one hand and the paramagnetic impurity relaxation mechanism on the other. In the case of spin 3/2 and zero asymmetry parameter the spin-lattice relaxation time of the "quadrupole spin-spin reservoir" is calculated and compared with the "usual" quadrupole spin-lattice relaxation time.

INTRODUCTION

It is well known that in magnetic relaxation studies it proved useful to characterize different non-equilibrium processes in the system considered by means of the time evolution of the temperatures of properly defined sub-systems. In the case of the nuclear quadrupole spin-lattice relaxation study the system in question is the system of quadrupole nuclei. Its Hamiltonian may be put down as follows:

$$\mathcal{H} = \mathcal{H}_Q + \mathcal{H}'_{II} + \mathcal{H}''_{II} + \mathcal{H}_{IL} + \mathcal{H}^* \quad (1)$$

where $\mathcal{H}_Q$ represents the interaction of the quadrupole nuclei with the electric field gradient, $\mathcal{H}'_{II}$ and $\mathcal{H}''_{II}$ secular and non-secular parts of the mutial interaction between the quadrupole nuclei, $\mathcal{H}_{IL}$ the spin-lattice interaction of the quadrupole nuclei, and $\mathcal{H}^*$ different interactions involving non-quadrupole nuclei and paramagnetic ions if any. One usually assumes the sub-systems $\mathcal{H}_Q$, $\mathcal{H}'_{II}$, and $\mathcal{H}''_{II}$ to be in equilibrium with one another and so to have the same temperature which, if not equal to the lattice temperature, tends to reach it exponentially, the relevent relaxation time being named the quadrupole spin-lattice relaxation time. On the other hand in the NMR (ref.1) and EPR (ref.2) investigations just the absence of the inner equilibrium in the spin system and its influence on the spin-lattice relaxation was taken into account successfully. In the paper presented an attempt is made to begin doing the same in the case of the quadrupole spin-lattice relaxation.

RESULTS

General approach

We'll accept the scheme used in the NMR and EPR cases: the lattice is all the time in the inner equilibrium (inverse temperature β_L = const), sub-systems $\mathcal{H}_Q$ and $\mathcal{H}'_{II}$ pass through equilibrium states (inverse temperatures $\beta_Q(t)$ and $\beta_R(t)$ respectively), but there is no equilibrium between $\mathcal{H}_Q$ and $\mathcal{H}'_{II}$ ($\beta_Q(t) \neq \beta_R(t)$), and $\mathcal{H}_Q$ and $\mathcal{H}'_{II}$ are not in equilibrium with the lattice ($\beta_Q(t)=\beta_L$, $\beta_R(t) \neq \beta_L$). In the framework of this scheme it seems natural to choose $\beta_Q(t)$ and $\beta_R(t)$ as the macroscopic coordinates and $\beta_Q(t)-\beta_L$ and $\beta_R(t)-\beta_L$ as the non-equilibrium parameters; the role played by the sub-systems $\mathcal{H}''_{II}$, $\mathcal{H}_{IL}$, and $\mathcal{H}^*$ is supposed to be taken into account by means of some perturbation theory techniqe.

In the conventional linear approximation the equations of motion for $\beta_Q(t)$ and $\beta_R(t)$ are:

$$\dot{\beta}_Q(t) = -\alpha_{QQ}\left[\beta_Q(t)-\beta_L\right] - \alpha_{QR}\left[\beta_R(t)-\beta_L\right] , \tag{2}$$

$$\dot{\beta}_R(t) = -\alpha_{RQ}\left[\beta_Q(t)-\beta_L\right] - \alpha_{RR}\left[\beta_R(t)-\beta_L\right] . \tag{3}$$

To calculate the kinetic coefficients entering the equations (2) and (3), one has to obtain these equations using some quantum-statistical method. The method proposed by Zubarev (ref.3) was used. In the case of the nuclear magnetic relaxation taking place in an applied magnetic field which is high enough the kinetic coefficients analogous to α_{QR} and α_{RQ} are much smaller than those analogous to α_{QQ} and α_{RR} (ref.1). It is easy to show that the same is valid with respect to the kinetic coefficients entering (2) and (3) if the electric field gradient is high enough. Let us confine ourselves to dicussion of such a case. So we are only in need of the coefficients α_{QQ} and α_{RR} the corresponding relaxation times being $\alpha_{QQ}^{-1} \equiv \tau_{QL}$ and $\alpha_{RR}^{-1} \equiv \tau_{RL}$

After some calculation, the expressions of τ_{QL} and τ_{RL} may be put down as follows:

$$\tau_{QL}^{-1} = \left[\sum_{ab}\left(E_a^{(0)} - E_b^{(0)}\right)^2 W_{ab}\right]\left(2\sum_a E_a^{(0)2}\right)^{-1} , \tag{4}$$

$$\tau_{RL}^{-1} = \left[\sum_{ab}\left(\Delta E_a - \Delta E_b\right)^2 W_{ab}\right]\left(2\sum_a \Delta E_a^2\right)^{-1} ; \tag{5}$$

here E_a are the $\mathcal{H}_Q$ levels, ΔE_a the shifts of these levels due to $\mathcal{H}'_{II}$, and W_{ab} the transition probabilities in the $\mathcal{H}_Q + \mathcal{H}'_{II}$ spectrum induced by $\mathcal{H}''_{II} + \mathcal{H}_{IL}$

Special cases

The expressions (4) and (5) are quite general but obviously they may be of practical interest only in special cases and on condition that some approximate methods are used.

Consider (4) and (5) in the case where the percentage of the quadrupole nuclei is small and their distribution random ("quadrupole impurity"). In this case the statistical method (ref.4) developed in the theory of the EPR line shape in magnetically diluted crystals may be used. Let us begin with τ_{RL} which is the spin-lattice relaxation time of the "quadrupole spin-spin reservoir" $\mathcal{H}'_{II}$ analogous to the "dipole spin-spin reservoir" widely used in the NMR and EPR theories. The statistical method mentioned is based on the assumption of validity of the pair interaction approximation. In this approximation (5) gives:

$$\tau_{RL}^{-1} = \sum_k P(r_{jk}) \sum_{cd} \left(\Delta E_c^{jk} - \Delta E_d^{jk}\right)^2 W_{cd}^{jk} \left[2 \sum_k P(r_{jk}) \sum_c \left(\Delta E_c^{jk}\right)^2\right]^{-1}, \tag{6}$$

the right hand side of (6) being not dependent on j; here j,k and c,d are numbers of the lattice knots occupied by the quadrupole nuclei and the pair spectrum states respectively, r_{jk} is the distance between the knots, $P(r_{jk})$ the probability of the knot k being occupied by a quadrupole nucleus on condition that the knot j is occupied, and ΔE and W have the same meaning as in (5) but for the pair spectra.

The transition probabilities W_{cd}^{jk} entering (6) are determined by the relaxation mechanism in question. It is known that in the nuclear magnetic relaxation case one of the most effective spin-lattice mechanisms is that realised through the paramagnetic impurities. Let us see what is the role of this mechanism in the quadrupole case. The probabilities W_{cd}^{jk} were calculated by means of the stochastic perturbation theory with respect to the dipole interaction of the dipole-coupled pairs of the quadrupole nuclei and the paramagnetic impurity ions. Assuming the space distributions of the quadrupole nuclei and the paramagnetic ions to be uniform, one gets from (6):

$$\tau_{RL}^{-1} = 3^{-1} \hbar^{-2} r^{-3} (g\beta)_I^2 (g\beta)_S^2 S(S+1) n \left\{ \left[A + \frac{B}{1+\omega_I^2 \tau_1^2}\right] \tau_1 + \left[\frac{C}{1+\omega_S^2 \tau_2^2} + \frac{D}{1+(\omega_I+\omega_S)^2 \tau_2^2} + \frac{E}{1+(\omega_I-\omega_S)^2 \tau_2^2}\right] \tau_2 \right\} \tag{7}$$

where r_o is the shortest distance between nuclei, n the paramagnetic ion concentration, S is the electronic spin, ω_I and ω_S the nucleus and electron resonance frequencies, and τ_1 and τ_2 are longitudinal and transverse correlation times of electronic spin components. The calculation of the coefficients A,...,E is rather complicated. It was performed for I=3/2 and zero asymmetry parameter; the result is this: A=4.6, B=5.2, C=9.4, D=10.0, E=17.0.

As to the calculation of the relaxation time τ_{QL}, the scheme for it is just the same as for the τ_{RL} calculation. The expression of τ_{QL} proved to be of the same type as that of τ_{RL} given by (7) but with different values of B, D, E and without terms with A and C. It is important to note that in the case of high electric field gradient we are considering here the relaxation time τ_{QL} is practically the "usual" quadrupole spin-lattice relaxation time τ_{IL}.

Conclusions

Two relaxation times τ_{IL} and τ_{RL} characterize the quadrupole spin-lattice relaxation in two physically different situations: in the presence and in one of the possible cases of absence of the inner equilibrium in the quadrupole spin system respectively. The ratio of the rates of the relevent relaxation processes to one another may be different; for example, $\tau_{RL} \sim \tau_{IL}$ if $\omega_I \tau_1 \ll 1$ and $\tau_{RL} \ll \tau_{IL}$ if $\omega_I \tau_1 \gg 1$.

There are two possible applications of the results presented. Firstly, after trying to interpret experimental data on the quadrupole spin-lattice relaxation on the basis of the theoretical approaches fitting in with two situations above mentioned, one may find reasons to accept some version of what relaxation mechanism actually is realized. And secondly, after having made probable, in such a manner, the validity of some theoretical scheme, one could use the experimental data to obtain information about concentration and space distribution of the paramagnetic ions.

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