Non-exponential magnetic relaxation of I=3/2 nuclear spins in solids

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Abstract. A nuclear magnetic double-resonance experiment, performed on the ^{23}Na spin system in a single crystal of NaNO$_2$ at 130 K, has shown that the spin–lattice relaxation is magnetic, as opposed to quadrupolar, at that temperature. The approach to equilibrium of the high-frequency satellite of this spin system, after excitation by a selective 90° pulse, was found to be quite non-exponential at 130 K and roughly in agreement with a simple theory. The approaches to equilibrium of both the high-frequency satellite and the central resonance after excitation of the latter by a selective 90° pulse were found to be exponential, in marked contrast to the theory. The reason for the discrepancy is not known.

1. Introduction

Spin–lattice relaxation of a system of nuclei with spin number $I > 1/2$ occurs via a magnetic interaction between the nuclear magnetic moments and fluctuating local magnetic fields, and via a quadrupole interaction between the nuclear electric quadrupole moments and fluctuating local electric field gradients. It is well known that the quadrupole relaxation of such a spin system in a solid is in general non-exponential (Andrew and Tunstall 1961), provided the time average quadrupole interactions are large enough to suppress spin exchanges between different pairs of adjacent Zeeman levels. The magnetic relaxation of such a spin system is also expected to be non-exponential, although this does not seem to be so widely appreciated.

The purpose of this paper is to show that the spin–lattice relaxation of the ^{23}Na spin system (for which $I = 3/2$) in the ferroelectric material NaNO$_2$ is magnetic at 130 K, and to demonstrate that it can be quite non-exponential at that temperature, even though exact agreement between experiment and theory was not found.

We begin by summarizing the theory of the magnetic relaxation of $I = 3/2$ spin systems, firstly in terms of a very simple model using rate equations and secondly using the results of a density matrix calculation.

2. Theory

The probabilities of the magnetic spin–lattice transitions $m = 3/2 \leftrightarrow 1/2$, $m = 1/2 \leftrightarrow -1/2$, and $m = -1/2 \leftrightarrow -3/2$ for a system of $I = 3/2$ nuclei, situated at identical sites in a single crystal and experiencing identical fluctuating magnetic fields,

are in the ratio 3:4:3 as shown in figure 1(*a*), where Δ is $h\nu_0/kT$ and ν_0 is the unperturbed NMR frequency. (We assume that, in thermal equilibrium, the population differences between adjacent Zeeman levels are equal, a condition approximately satisfied if the quadrupole interaction is much smaller than the Zeeman interaction.) Corresponding quadrupole transition probabilities are shown in figure 1(*b*). If the population difference between the mth and $(m+1)$th levels is denoted by $N_{m+1/2}$, and the difference between $N_{m+1/2}$ and the equilibrium population difference is denoted by $N'_{m+1/2}$, the rate equations, in the absence of externally applied RF fields, can be written as

$$\mathrm{d}N'_{\pm 1}/\mathrm{d}t = 4W_3 N'_0 - 6W_3 N'_{\pm 1}$$
$$\mathrm{d}N'_0/\mathrm{d}t = 3W_3 N'_1 - 8W_3 N'_0 + 3W_3 N'_{-1}. \tag{1}$$
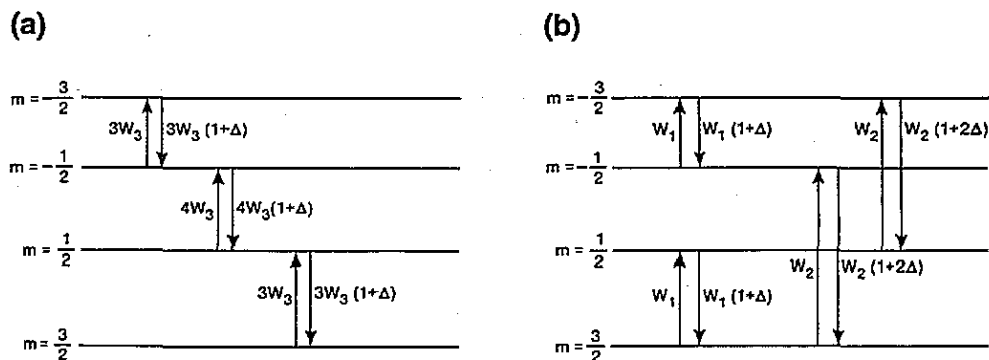
(a)   **(b)**

Figure 1. Spin–lattice transitions caused by (*a*) a magnetic mechanism and (*b*) a quadrupole mechanism, for a system of $I = 3/2$ nuclear spins, situated at identical sites in a single crystal and experiencing homogeneous relaxation.

If the orientation of the magnetic field is such that the central resonance, corresponding to N_0, and the two satellites, corresponding to N_1 and N_{-1}, overlap, or equivalently if the nuclei are in a cubic environment, spin exchanges will ensure the maintenance of a Boltzmann distribution among the Zeeman levels. The amplitude of the NMR signal will then be proportional to $(3N_1 + 4N_0 + 3N_{-1})$ and it follows from equations (1) that the relaxation will be exponential with a single relaxation time $(2W_3)^{-1}$. If, on the other hand, the resonances do not overlap, it is found by solving equations (1) that

$$N'_{\pm 1} = A\exp(-2W_3 t) \pm B\exp(-6W_3 t) + C\exp(-12W_3 t)$$
$$N'_0 = A\exp(-2W_3 t) - (3C/2)\exp(-12W_3 t) \tag{2}$$

where A, B and C depend upon the initial conditions. The fact that there are now three relaxation times, $(2W_3)^{-1}$, $(6W_3)^{-1}$ and $(12W_3)^{-1}$, is in accordance with the rule (Andrew and Tunstall 1961) which states that there are, in general, $2I$ magnetic relaxation times given by $[p(p+1)W_3]^{-1}$ where p is an integer running from unity to $2I$.

If the initial conditions are symmetric in N'_1 and N'_{-1}, the $\exp(-6W_3t)$ term vanishes and

$$
\begin{aligned}
N'_{\pm 1} &= A\exp(-2W_3t) + C\exp(-12W_3t) \\
N'_0 &= A\exp(-2W_3t) - (3C/2)\exp(-12W_3t).
\end{aligned}
\tag{3}
$$

Moreover, if the spin system is initially in thermal equilibrium and the central resonance only is perturbed by a selective RF pulse, the subsequent relaxation is given by

$$
N'_{\pm 1} = A[\exp(-2W_3t) - 6\exp(-12W_3t)]
\tag{4}
$$

$$
N'_0 = A[\exp(-2W_3t) + 9\exp(-12W_3t)].
\tag{5}
$$

If the spin system is initially in thermal equilibriuim and the $m = 3/2 \leftrightarrow 1/2$ satellite, say, is perturbed by a selective RF pulse (a situation requiring a single crystal), the relaxation in this asymmetric case is given by

$$
N'_{\pm 1} = A[\exp(-2W_3t) \pm 5\exp(-6W_3t) + 4\exp(-12W_3t)]
\tag{6}
$$

$$
N'_0 = A[\exp(-2W_3t) - 6\exp(-12W_3t)].
\tag{7}
$$

Petit and Korb (1988) have recently presented a general theory of the relaxation of spin systems with $I > 1/2$, using the density matrix formalism and fictitious spin 1/2 operators. For a system of $I = 3/2$ nuclei which experience identical but small first-order quadrupole splitting and which relax via a dipole–dipole interaction between like spins, their theory predicts multi-exponential decay of the longitudinal magnetization with four relaxation rates given by

$$
C[\tfrac{1}{10}J_0(0) + \tfrac{3}{4}J_1(\omega_I) + \tfrac{12}{5}J_2(2\omega_I)]
\tag{8}
$$

$$
C[\tfrac{9}{10}J_0(0) + \tfrac{11}{4}J_1(\omega_I) + \tfrac{28}{5}J_2(2\omega_I)]
\tag{9}
$$

$$
C[\tfrac{1}{2}J_0(0) + \tfrac{3}{2}J_1(\omega_I) + 3J_2(2\omega_I)]
\tag{10}
$$

$$
C[\tfrac{3}{10}J_0(0) + \tfrac{3}{4}J_1(\omega_I) + \tfrac{6}{5}J_2(2\omega_I)].
\tag{11}
$$

Here, C is $(4/3)I(I+1)\gamma_I^4\hbar^2$, ω_I is the unperturbed resonance frequency and $J_0(0)$, $J_1(\omega_I)$ and $J_2(2\omega_I)$ are the spectral density functions (Abragam 1961a). If the initial conditions of the spin system are symmetric in N_1 and N_{-1}, only three relaxation rates are expected, there being no contribution corresponding to relaxation rate (10).

The range spanned by these relaxation rates obviously depends upon the particular spin system involved. However, if the same very short correlation time is assumed for all the random quantities involved, a situation more often found in liquids than in solids, then $J_0(0)$, $J_1(\omega_I)$ and $J_2(2\omega_I)$ are in the ratio 6:1:4, respectively (Abragam 1961a), in which case the relaxation rates span a range of roughly a factor of three. Thus, there does not seem to be a dramatic difference between the results of a density matrix calculation and those obtained using simple rate equations.

3. Results and discussion

Our recent study of the spin–lattice relaxation of ^{23}Na in a single crystal of NaNO$_2$ (Towta and Hughes 1990) showed an anomalous increase in the relaxation rate below 150 K, which was tentatively attributed to a magnetic interaction. To confirm this assignment, a double-resonance experiment was performed on the same crystal at 130 K, in which the amplitude of the high-frequency satellite was measured by a selective 90° RF pulse after the central resonance was saturated by a long train of selective 90° pulses. If the relaxation is magnetic, saturating the central resonance for a time long compared to the relaxation times will have no effect on the amplitude of the satellites (Abragam 1961b). However, if the relaxation is quadrupolar, the high-frequency satellite will be enhanced by a factor $[W_1 + (2 - \delta)W_2]/(W_1 + W_2)$ (Hughes and Reed 1971), where δ is the ratio of the quadrupole splitting to the Larmor frequency.

The experiment was carried out in a 1.28 T magnetic field directed along the ferroelectric (*b*) axis of the crystal. The 90° pulses were 138 μs long and therefore sufficiently weak not to excite the satellite resonances located 573 kHz away from the central resonance. The interval between the 90° pulses was 13.7 ms, much longer than the spin–spin relaxation time but much shorter than the spin–lattice relaxation times.

To check the procedure, the experiment was first carried out at room temperature where the relaxation is known to be entirely quadrupolar (Hughes and Spencer 1982, Towta and Hughes 1990). The enhancement is shown in figure 2(*a*) as a function of the duration, τ, of the 90° pulse train. The curve shows a least-squares fit of the data to a single decaying exponential. The asymptote when $\tau \rightarrow \infty$ is (1.628 ± 0.008). Since δ is 0.0393 at room temperature, this implies that the ratio W_2/W_1 is 1.89 ± 0.07, in satisfactory agreement with the value 1.96 ± 0.03 found by Hughes and Spencer (1982) and the value 1.96 obtained using the M-tensor components determined by Towta and Hughes (1990). (The enhancement at $\tau = 0$, following an ideal 90° pulse, should be $(1.5 + \delta)/(1 + \delta) = 1.481$. The fitted enhancement at $\tau = 0$ is (1.457 ± 0.013), indicating that the 90° pulses were probably slightly shorter than the ideal duration.)

When the experiment was repeated at 130 K, the enhancement was found to approach, exponentially, an asymptote of 0.980 ± 0.008, as shown in figure 2(*b*). This is close to unity, showing that the spin–lattice relaxation mechanism is, without doubt, *magnetic* at 130 K. As described elsewhere (Pandey and Hughes 1992), the relaxation is believed to occur by spin diffusion, a magnetic interaction, to regions in the crystal where the local relaxation is very rapid and probably caused by reorienting NO$_2$ groups. The fact that this rapid local relaxation is, in all likelihood, quadrupolar rather than magnetic should not affect the enhancement, provided the overall relaxation is dominated by spin diffusion.

To try to demonstrate non-exponential magnetic relaxation, the following experiments were performed on the same spin system at 130 K, with the magnetic field again parallel to the *b* axis of the crystal.

(i) A selective 90° pulse was applied to the high-frequency satellite and its subsequent approach to equilibrium was monitored by applying a second selective 90° pulse at a variable time τ later.

(ii) A selective 90° pulse was applied to the central resonance and the subsequent approach to equilibrium of the high-frequency satellite was monitored by applying a selective 90° pulse to it at a variable time τ later.

(iii) An experiment analogous to (i) was carried out on the central resonance.

In these experiments, a repetition time of 350 s was used to ensure that proper thermal equilibrium was achieved before each pulse sequence.

The results of experiment (i) are shown in figure 3(a). To extract both the pre-exponential factors and the decay rates of three or four exponentially decaying components with rates ranging over a factor of order six would require a very large number of data points and a signal-to-noise ratio of several hundred to one (Fenrich and Allen 1992), which is beyond the capability of our equipment and sample. Instead, we fitted the data in figure 3(a) to both a single exponential decay and to equation (6). The χ^2 obtained with the single exponential was nearly three times larger than that obtained by fitting to equation (6). Since both fits invoked three fitting parameters (the third parameter being the signal amplitude as $\tau \to \infty$), it is safe to conclude that the relaxation of the high-frequency satellite in experiment (i) is almost certainly non-exponential. The distribution of residuals found by fitting to equation (6) indicates that the data are consistent with that equation, and the three relaxation times $(12W_3)^{-1}$, $(6W_3)^{-1}$ and $(2W_3)^{-1}$ are (9.7 ± 0.3) s, (19.4 ± 0.6) s and (58.1 ± 1.7) s, respectively.

Because of the limited signal-to-noise ratio alluded to earlier, an attempt to fit the data to equation (6) while allowing all the pre-exponential factors to vary independently, did not converge. However, a four-parameter fit, where the amplitude of the exp $(-2W_3t)$ component was allowed to vary relative to the amplitudes of the other two components, did converge giving an amplitude of (1.4 ± 0.6) for the exp $(-2W_3t)$ component, consistent with the theoretical value of unity. That confirms that equation (6) provides a reasonable approximation to the relaxation behaviour of the high-frequency satellite in experiment (i).

The results of the double-resonance experiment (ii) are shown in figure 3(b). The approach to equilibrium is evidently faster than in figure 3(a) and the data are well fitted by a single exponential with a decay time of (9.3 ± 0.4) s. This is in excellent agreement with the shortest relaxation time $(12W_3)^{-1} = (9.7 \pm 0.3)$ s found in experiment (i). When the data were fitted to equation (4), the fit was not nearly as good, giving a χ^2 three times larger than the exponential fit. This finding is in agreement with our earlier work (Towta and Hughes 1990), which showed no evidence of the exp $(-2W_3t)$ component at 135 K and 145 K.

The approach to equilibrium of the central resonance in experiment (iii) is not shown. However, the data are well fitted by a single exponential with a decay time of (7.9 ± 0.2) s. When the data were fitted to equation (5), the χ^2 was nearly twice as large as that given by the exponential fit. The decay time, (7.9 ± 0.2) s, is significantly shorter than the shortest decay time found in experiments (i) and (ii), possibly because the spin diffusion coefficient for the central resonance is larger than that of the satellites because of the different matrix elements involved.

It is not clear why the relaxation of the centre line and high-frequency satellite is exponential in experiments (ii) and (iii). To see whether the small quadrupole relaxation due to phonons could be responsible, the simple theory based on the rate equations was generalized to include the quadrupole transition probabilities shown in figure 1(b). The relaxation of the satellites in experiment (ii) was found to be of the form

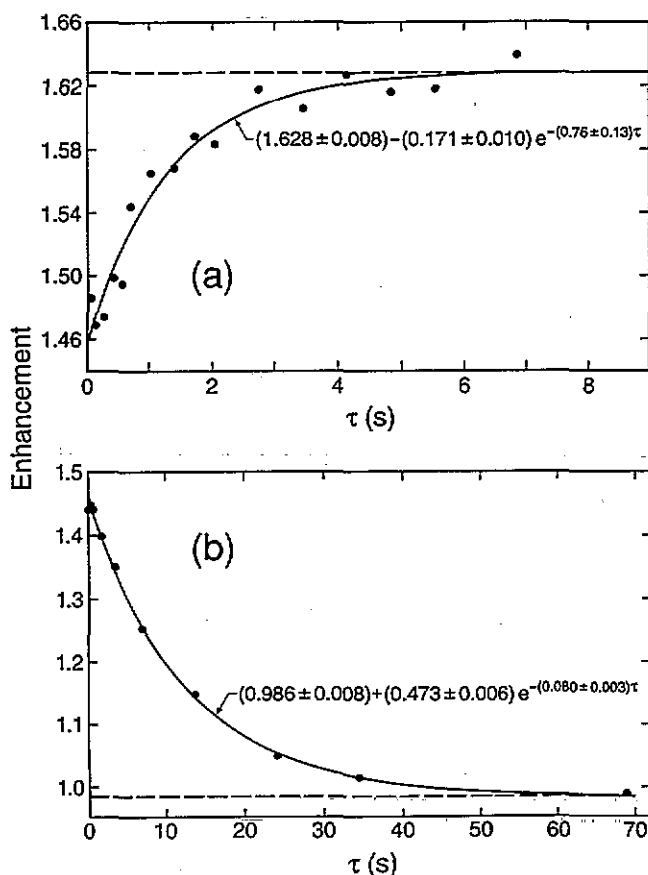$$N'_{\pm 1} = A[\exp(-\lambda_+ t) - B \exp(-\lambda_- t)] \tag{12}$$

where

Figure 2. Enhancement of the high-frequency satellite of the ^{23}Na spin system in NaNO$_2$ shown as a function of the time τ for which the central resonance was saturated by a train of selective 90° pulses at (a) room temperature and (b) 130 K. The curves are least-squares fits of the data to single decaying exponentials. The broken lines represent the asymptotes.

$$\lambda_{\pm} = -(W_1 + W_2 + 7W_3) \pm [(W_1 - W_2)^2 + 6W_3(W_1 - W_2) + 25W_3^2]^{1/2} \tag{13}$$

$$B = (\lambda_+ + 2W_1 + 14W_3)/(\lambda_- + 2W_1 + 14W_3). \tag{14}$$

It has been estimated by Pandey and Hughes (1992) that W_1 of ^{23}Na in NaNO$_2$ due to phonons is roughly 4×10^{-7} T^2 when the magnetic field is parallel to the b axis, so that W_1 at 130 K $\simeq 6.8 \times 10^{-3}$ s^{-1}. Point charge calculations (Hughes and Spencer 1982) indicate that $W_2 \simeq 1.4W_1$ at that crystal orientation. By substituting numerical values of W_1, W_2 and W_3 in equations (13) and (14), it is found that λ_-/λ_+ is 3.4 and B is 6.2 at 130 K. For the relaxation of the central resonance, the ratio of the amplitudes of the two exponential terms is found to be 10.7 instead of 9 as in equation (5). Thus, the phonon quadrupole relaxation should have little effect on the relative contributions of the two exponential terms in experiments (ii) and (iii). However, the actual relaxation times differ by a factor of 3.4 instead of 6, so that the observed behaviour should be closer to a single exponential. As expected, when the data in figure 3(b) were fitted to equation (12) using the above values of B
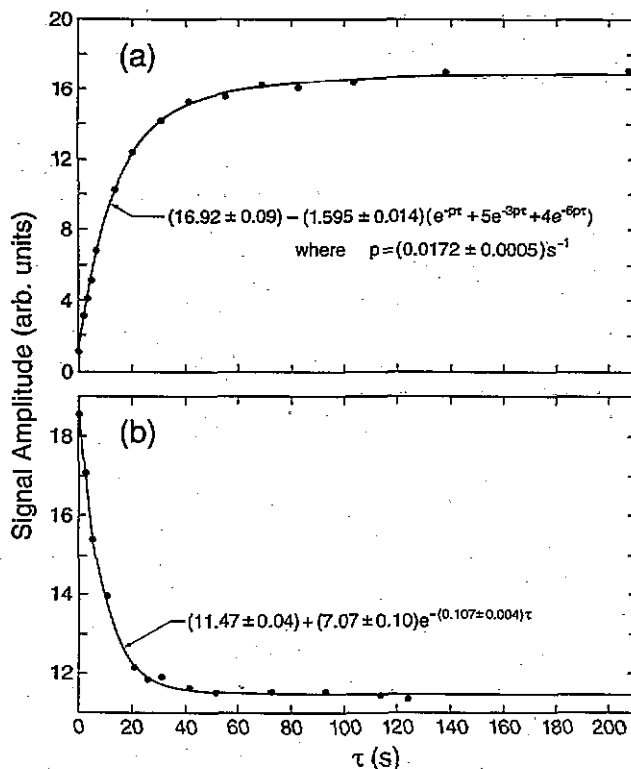
Figure 3. (*a*) Approach to equilibrium of the high-frequency satellite of the [23]Na spin system in NaNO$_2$ at 130 K, after it was subjected to a selective 90° pulse at $\tau = 0$. The curve is a least-squares fit of the data to equation (6). (*b*) Approach to equilibrium of the high-frequency satellite after the central resonance was subjected to a selective 90° pulse at $\tau = 0$. The curve is a least-squares fit of the data to a single decaying exponential.

and λ_-/λ_+, the fit was better than when using equation (4), but was still not nearly as good as the exponential fit. It could be argued that perhaps $W_2 \simeq W_1$ and that W_1 and W_2 are much larger than the estimated values, thereby causing λ_-/λ_+ to be much closer to unity. However, W_1 and W_2 are unlikely to be much larger than the estimated values, since the phonon quadrupole relaxation rates are expected to fall off faster than the assumed T^2 dependence at low temperatures (Van Kranendonk 1954, Van Kranendonk and Walker 1968).

We note that the relaxation at 130 K, if dominated by spin diffusion as previously deduced (Pandey and Hughes 1992), is inherently inhomogeneous and is therefore a superposition of exponentials with different relaxation times. Nevertheless, it is difficult to see how that could explain the good agreement between the data and equation (6) in experiment (i), and the poor agreement between the data in experiments (ii) and (iii) and equations (4) and (5), respectively.

In conclusion, experiment and theory indicate that the magnetic relaxation of $I = 3/2$ spin systems can be quite non-exponential. Care must therefore be taken in experiments involving such spin systems if the spins are required to reach proper thermal equilibrium between pulse sequences, since the presence of a small slowly

relaxing component may well be masked by the larger faster relaxing components.

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