Spin-lattice relaxation measurements by improved signal decay method

1970 J. Phys. E: Sci. Instrum. 3 525

(http://iopscience.iop.org/0022-3735/3/7/312)

Spin-lattice relaxation measurements by improved signal decay method

J Stepišnik, J Porok and V Eržen
Institut 'Jožef Stefan', Ljubljana, Yugoslavia

MS *received 19 December 1969, in revised form 6 April 1970*

Abstract Spin-lattice relaxation time measurements in solids by decay of the absorption magnetic resonance signal are described. The signal decay method is improved by synchronization of the measurements to the trigger mechanism of a computer of average transients.

1 Introduction

It is possible to measure spin-lattice relaxation times T_1 by the decay of the absorption nmr signal under the influence of the rf field (Linder 1957). The method is suitable for time measurements from 10 ms to a few minutes or more. The signal decay, improved by the averaging technique is used to investigate the relaxation times of the spin systems with weak signal. The other important feature of the method is the possibility of measuring the relaxation time T_1 of the different lines of the spectra, which enables investigation of the nonequivalent nuclei. The method is easily incorporated into a standard continuous wave nmr spectrometer at relatively small expense, and its results are independent of the rf field strength or modulation.

2 Description of the method

We used the technique with uninterrupted rf field, but the magnetic field was rapidly changed by additional coils. The field sweep was stopped on one wing of the derivative curve, since the signal amplitude is the largest at these points. The rf field strength was sufficient to partially saturate the nmr signal.

The additional magnetic field, which is large in comparison with the linewidth, was switched on and the time, estimated to be about three times greater with respect to T_1, was allowed to elapse. Then the recorder (or computer of average transients) with the time sweep was started, and at the same time the additional magnetic field was turned off. The signal was observed to decay from an unsaturated value to a partially saturated signal.

3 Influence of the rf field to the signal

The theory of the signal decay, under the influence of the rf field, is developed in the frame of the Provotorov theory of saturation (Provotorov 1961, 1962). Its validity is restricted to the following cases: (i) where the temperature is high (i.e. the nuclear polarization is so low that it is permissible to develop the density matrix to the first order as a function of the inverse spin temperature; (ii) where the rf field H_1 is far smaller than the local field experienced by the nuclei, due to their coupling with neighbouring spins.

In the spin system, neglecting the cross-relaxations, the following kinetic equations are valid

$$\frac{d\alpha}{dt} = -f(\Delta)(\alpha - \Delta\beta) + \frac{\alpha_0 - \alpha}{T_1}$$

$$\frac{d\beta}{dt} = \hbar\Delta\epsilon f(\Delta)(\alpha - \Delta\beta) + \frac{\beta_0 - \beta}{T_1'}.$$

α and β are proportional to the inverse temperatures of the Zeeman and dipolar sub-system respectively, $f(\Delta)$ is proportional to the square of the rf field strength, and Δ is the frequency shift from the resonance. The above system gives the time dependence of the absorption signal, and contains different decay constants depending on T_1, T_1', and rf field strength. Under the condition of the properly high modulation frequency, the time dependence of the absorption signal has the following form

$$x'' = x_0'' + x_1''\{\exp(-At) - 1\} + x_2''\{\exp(-Bt) - 1\}.$$

After x_0'', x_1'', x_2'', A and B have been determined from the experimental data, T_1 can be evaluated from the equation

$$x_1''\Big/\left(1 - \frac{1}{AT_1}\right) + x_2''\Big/\left(1 - \frac{1}{BT_1}\right) = x_0''.$$

In the following two cases the decay is more simple and has the one exponential form. (i) The spin-lattice relaxation time of dipolar energy is much shorter than the spin-lattice relaxation of the Zeeman energy. (ii) If the decay is measured in the middle of the absorption curve ($\Delta = 0$). In this case the experimental technique has to be slightly modified. The lock-in detection is rearranged for measuring the second derivative of the absorption curve, because the first derivative is zero in the middle of the curve. In both cases the time dependence of the absorption signal has the form

$$x'' = x_0'' + x_1''\left\{\exp\left(-\frac{x_0''}{x_0'' - x_1''}\frac{t}{T_1}\right) - 1\right\}.$$

4 Averaging

In nuclear magnetic experiments, it is often necessary when working with a weak resonance signal to use a computer of average transients in order to obtain a reasonable signal-to-noise ratio. Such instrumentation increases signal-to-noise ratio by a factor of $n^{1/2}$, where n is the number of times the experiment is repeated. It is necessary to synchronize the transfer of the computer memory store with the variable being swept in the experiment. In our case the variable was time. Therefore, we used only internal or external pulse systems in advance of the address, but the triggering of the computer has to be synchronized by the circuit for switching the electric current through additional coils. The pulse is supplied to the trigger of the averaging computer before the extra magnetic field is turned off (figure 2). The circuit for the current switching through additional coils is shown schematically in figure 1.

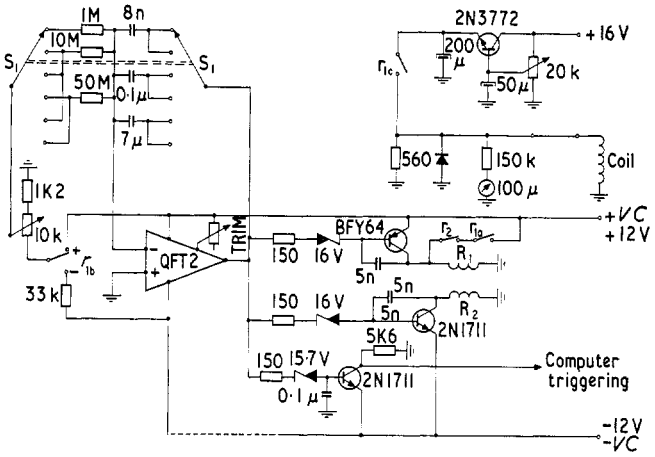

Figure 1 Switching circuit

The main part of the circuit is an integrator. By using switch S_1, it is possible to change the time constant of integration from 0·1 s to 1 h. The direction of the integration (decreasing or increasing of output voltage level) is defined by the polarity at the input of the integrator, i.e. by the position of the switch r_{1b}.

The output of the integrator is connected to the level switches, which at definite voltage levels trigger the computer of average transients, and turn on relays R_1 and R_2 (figure 1). The relays R_1 and R_2 have the switches r_{1a}, r_{1b}, r_{1c} and r_2. The decreasing voltage level action is obtained (figure 2)

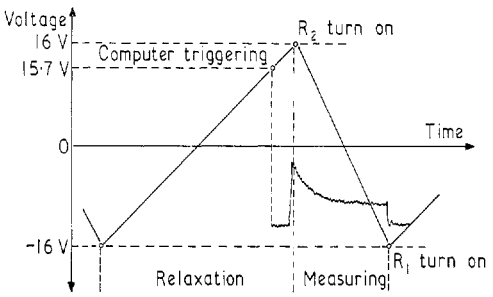

Figure 2 Integrator output voltage level as a function of time

with the switch r_{1b} in the '+' position. When the voltage level reaches the value −16 V, the first level switch turns on relay R_1. At the same time the switch r_{1c} joins the current through additional coils, the switch r_{1b} jumps into the '−' position, and switch r_{1a} connects the circuit of relay R_2 in order to keep R_2 in working condition. The voltage levels start to rise from −16 V. During this time the spins relax. When the voltage level achieves +15·7 V, the level switch triggers the averaging computer, and when the output voltage is +16 V relay R_2 through switch r_2 interrupts the circuit of relay R_1. The switches r_{1a} and r_{1c} are then turned off, and switch r_{1b} jumps into the '+' position. At the same time the signal decay measurement begins. The ratio of the measuring time and the time of the relaxation is 1:3, and it is defined by the resistors at the input of the integrator.

5 Results

We have applied this method to a variety of solids and spin systems, with T_1 ranging from 10 ms to a few minutes.

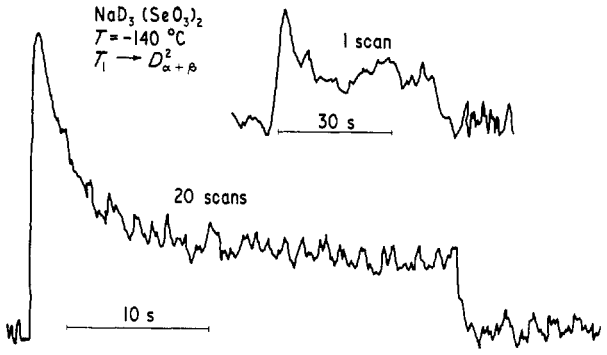

Figure 3 Recorder tracing of data for signal decay from the averaging computer

However, there is a time constant associated with the decay of additional magnetic field which practically limits the measurements of T_1 to a region greater than a few milliseconds. Figure 3 shows the measured decay of the deuterium signal of $NaD_3(SeO_3)_2$ monocrystal. The first decay shows the measurement without repetition and the second results after twelve scans on the computer. The relaxation time of the protons in KH_2PO_4 crystal measured by this method agrees within experimental error with the one obtained by pulsed nmr technique. Finally, it should be mentioned that the method described in this paper is not limited only to nuclear magnetic resonance, but is also applicable, with minor modification, to electron paramagnetic resonance.

Acknowledgments

During the course of this work, the authors had many useful discussions with Professor R Blinc.

References

Linder S 1957 *J. Chem. Phys.* **26** 900–5

Provotorov B N 1961 *Zh. Eksp. Teor. Fiz.* **41** 1582–91 (transl. *Soviet Phys. JETP* **14** 1126)

Provotorov B N 1962 *Zh. Eksp. Teor. fiz.* **42** 882–8 (transl. *Soviet Phys. JETP* **15** 611)

Journal of Physics E: Scientific Instruments 1970 Volume 3
Printed in Great Britain