Direct measurement of the lattice and impurity components of nuclear spin-lattice relaxation under magnetic-saturation conditions

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The case of Na^{23} nuclei in a NaI crystal is used as an example to demonstrate a new method for directly separating and measuring the lattice and impurity components of the spin–lattice relaxation during steady-state magnetic saturation of the NMR line.

The nuclear spin-lattice relaxtion time T_1 in a real solid is known to be determined by two competing mechanisms: a lattice mechanism, which is reponsible for the relaxation in ideal samples, and an impurity mechanism. The resultant relaxation is thus characterized by a time[1] $T_1^{\Sigma} = \{(T_1^{\text{latt}})^{-1} + (T_1^{\text{imp}})^{-1}\}^{-1}$. Separating these components is an important problem in rf spectroscopy of solids. In this letter we demonstrate a new method for directly separating and measuring the times T_1^{latt}, T_1^{imp}, and T_1^{Σ} under conditions of a steady-state magnetic saturation of the nuclear spin system.

The impurity spin-lattice relaxation occurs because relaxation processes occur considerably more rapidly near the paramagnetic centers than elsewhere in the sample. As a result, the local reciprocal spin temperature in the vicinity of a defect, α_{loc}, which is proportional to the local nuclear magnetization, is closer than the average value over the volume ($\bar{\alpha}$) to the reciprocal of the lattice temperature, α_l:

$$|\alpha_{\text{loc}} - \alpha_l| < |\bar{\alpha} - \alpha_l|. \quad (1)$$

A local change in the spin temperature propagates over the entire volume of the sample because of spin diffusion. Relation (1) is a necessary condition for effectiveness of the impurity mechanism for spin-lattice relaxation.

Efitsenko *et al.*[2] have proposed a new method for suppressing the impurity relaxation of quadrupole nuclei. That method is based on the use of versions of double nuclear resonances: electric and acoustic saturation of the NMR line. The reason why the impurity mechanism for relaxation is suppressed is that, in the case of steady-state electric or acoustic excitation of quadrupole transitions between the NMR levels at twice the Larmor frequency, the probability for induced transitions near paramagnetic centers is considerably greater than the probability for transitions elsewhere in the volume of the sample.[3–6] As a result, there is local heating of the spin system near the defects, to a value $\alpha_{\text{loc}} \simeq 0$, and inequality (1) is violated. If the spin-lattice relaxation time is measured by the most common method—based on the time evolution of the restoration of the nuclear-magnetization signal after a pulsed magnetic saturation (i.e., if the time is determined from the value $\bar{\alpha} = 0$)—then the spin-lattice relaxation

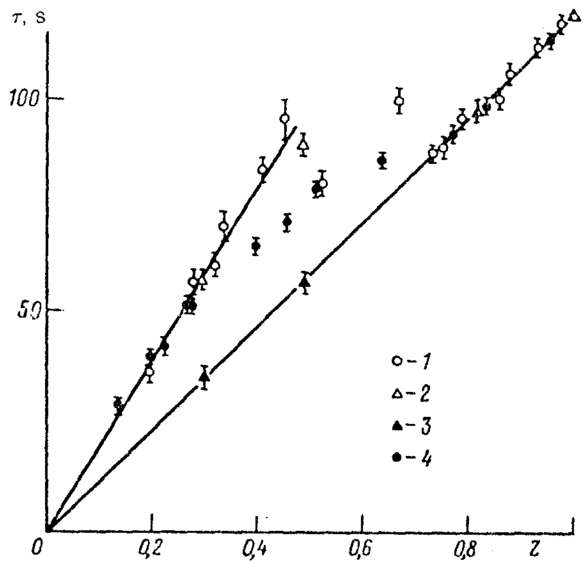

FIG. 1. $\tau(Z)$ during (*1*, *3*) steady-state magnetic saturation and (*4*) acoustic saturation. *1,4*—During restoration of the magnetization after complete pulsed saturation; *2,3*—during restoration after a 180° pulse under the condition $\bar{\alpha} > 0$ (*2*) and under the condition $\bar{\alpha} < 0$ (*3*).

should be determined by the lattice mechanism alone throughout the restoration process. The validity of this conclusion has been demonstrated in the examples of GaAs (Ref. 2) and NaI (Ref. 7) crystals.

In the present study we observe that a suppression of the impurity relaxation mechanism due to local heating near a defect also occurs in the case of magnetic saturation of the NMR line.

Figure 1 shows the measured restoration time (τ) of the MNR signal after complete pulsed saturation as a function of the factor Z, which represents the steady-state magnetic saturation of the NMR line of the Na^{23} nuclei in the nominally pure NaI crystal, which was studied in Ref. 7. The factor Z is defined as the ratio $\bar{\alpha}_{st}/\alpha_l$, where $\bar{\alpha}_{st}$ is the value of $\bar{\alpha}$ in the case of steady-state saturation. The time τ is related to the spin-lattice relaxation time T_1 by[2] $\tau = ZT_1$. This relation can be derived easily from the equation for the change caused in the spin temperature by external resonant excitation and relaxation. Measurements were carried out at 77 K in a static magnetic field $B = 0.42$ T, directed along a cubic axis of the crystal. Steady-state magnetic saturation was reached by inducing transitions at the Larmor frequency by means of an auxiliary coil wound around the sample.

It follows from Fig. 1 that at low saturation levels, i.e., at values of Z close to one, the $\tau(Z)$ dependence is a straight line. The slope of this line gives us the resultant spin-lattice relaxation time T_1^{Σ}, which is evidently the same as the spin-lattice relaxation time measured in the absence of saturation: $T_1^{\Sigma} = 119 \pm 2$ s. Beginning at a value

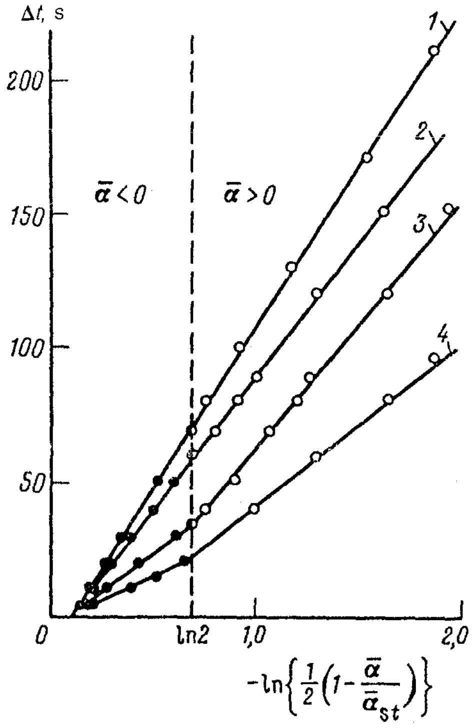

FIG. 2. Restoration of the steady-state magnetization after a 180° pulse. *1*—$Z = 1.0$; *2*—0.81; *3*—0.49; *4*—0.30.

$Z \simeq 0.7$, the $\tau(Z)$ dependence deviates from the straight line. It then straightens out again, and it has a large slope. Shown for comparison in Fig. 1 are measurements from Ref. 7 of $\tau(Z)$ in the case of acoustic saturation of the NMR line. We see that the overall shape of the $\tau(Z)$ curve remains the same, regardless of the nature of the saturation. On the basis of the results of Refs. 2 and 7, we can assume that the slope of the straight part of the plot at $\tau(Z)$ at small values of Z gives us the lattice spin-lattice relaxation time $T_1^{\text{latt}} = 197 \pm 10$ s. We then calculate $T_1^{\text{imp}} = 300 \pm 20$ s.

The results in Fig. 1 demonstrate quite convincingly the suppression of the impurity relaxation under conditions of steady-state magnetic saturation. However, this effect and its interpretation can be tested in another way, by measuring the time T_1 from the restoration of the NMR signal after a 180° pulse which reverses the magnetization. In the first step of the restoration of the magnetization, in which the average reciprocal spin temperature $\bar{\alpha}$ is negative, the inequality $\alpha_{\text{loc}} > \bar{\alpha}$ still holds, and relation (1) holds, regardless of the degree of steady-state saturation, i.e., regardless of the value of Z. The restoration of the reciprocal spin temperature of the magnetization from the negative value to $\bar{\alpha} = 0$ should therefore be determined by the resultant contribution of the lattice and impurity mechanisms for relaxation, at any value of Z. The restoration of $\bar{\alpha}$ from $\bar{\alpha} = 0$ to $\bar{\alpha} = \bar{\alpha}_{st}$, on the other hand, should be characterized by a time $\tau = ZT_1^{\Sigma}$, at large values of Z, and by a time $\tau = ZT_1^{\text{latt}}$ at small values of Z. The validity of these assertions is illustrated by Fig. 2, which shows the restoration of the steady-state spin relaxation of Na^{23} nuclei in the same NaI sample as a plot of $\ln\{\frac{1}{2}[1-(\alpha/\alpha_{st})]\}$ (along the abscissa) versus the time interval (Δt) between the 180° pulse and the 90° probing pulse. It is convenient to plot the results in this way because the scope of the straight lines gives us the value of τ. It follows from Fig. 2 that at large values of Z ($Z=1.0$ and 0.81), the restoration is exponential in the regions with $\bar{\alpha}>0$ and $\bar{\alpha}<0$, and the relaxation time τ is the same. At $Z=0.49$ and 0.30, the restoration in the region with $\bar{\alpha}<0$ is again exponential, but the time is shorter than in the region with $\bar{\alpha}>0$. The corresponding times τ are plotted in Fig. 1. We see that the values of τ for $Z=0.81$ and 1.0 and the values of τ for $Z=0.49$ and 0.30 in the region with $\bar{\alpha}<0$ conform to the $\tau(Z)$ dependence characterized by the resultant relaxation time T_1^{Σ}, while the values of τ for $Z=0.49$ and 0.30 in the region with $\bar{\alpha}>0$ conform to a straight line characterized by the lattice relaxation time T_1^{latt}.

In summary, it has been demonstrated experimentally in this study that the impurity relaxation mechanism is suppressed under conditions of steady-state magnetic saturation. This fact opens up some wide opportunities in NMR spectroscopy for directly measuring the impurity and lattice components of the spin-lattice relaxation and for controlling the quality of samples.

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