Investigation of the ¹H Spin-Lattice Relaxation in Polycrystalline NH₄ReO₄ Induced by Mechanical Sample Rotation

H. Rager

Fachbereich Geowissenschaften der Universität Marburg

Measurements of the proton spin-lattice relaxation time, T_1, in polycrystalline NH₄ReO₄ have shown that mechanical sample rotation in the static magnetic field reduces T_1 for proton magnetic resonance frequencies within the range 30−42 MHz. The rotation induced proton spin-lattice relaxation times, T_1', were measured at different Larmor frequencies, sample rotation frequencies, and temperatures. At room temperature T_1' increases with increasing proton Larmor frequency. The dependence of T_1' on sample rotation frequency and temperature is small. The "normal" proton T_1 times were determined as a function of temperature at 30 and 42 MHz. From these measurements an average activation energy of 2.4 kcal/mole was obtained for the NH₄⁺ reorientation. The "normal" spin-lattice relaxation behavior was observed to be non-exponential at 30 MHz above 200 K and at 42 MHz above 260 K and is nearly independent on temperature above 300 K.

1. Introduction

The ¹⁸⁷Re and ¹⁸⁵Re NQR frequencies of the transition $\pm 5/2 - \pm 3/2$ range from about 32.2 MHz at 240 K to about 35.14 MHz at 300 K. Using proton Larmor frequencies ranging from 30 to 40 MHz polycrystalline NH₄ReO₄ should be a good example for proton relaxation via interaction with the rhenium quadrupole levels. Upon rotation of the sample, the angular dependence of the Zeeman splitting of the rhenium quadrupole levels enables the ¹⁸⁵Re and ¹⁸⁷Re resonance frequencies to be brought into coincidence with that of the protons. The resulting energy transfer and spin exchange between rhenium isotopes and protons provide an indirect contact of the protons with the lattice, thereby reducing the proton T_1 time. Thus, the proton spin-lattice relaxation induced by mechanical sample rotation was studied and is expected to reflect the coupling of the proton spin system with that of the rheniums.

Further, the proton spin-lattice relaxation in NH₄ReO₄ was investigated in order to obtain information about the reorientational motions of the ammonium tetrahedra. These motions accompanied with an order-disorder phase-transition was assumed to be responsible for the gradual broadening and disappearance of the rhenium nuclear quadrupole resonance (NQR) frequencies between 160 K and

Reprint requests to Dr. H. Rager, FB Geowissenschaften der Universität Marburg, Kristallographie und Mineralogie, Lahnberge, *D-3550 Marburg (Lahn)*.

240 K as well as for the unusual temperature dependence between 160 K and 360 K [1−4].

2. Experimental Procedure and Results

Ammonium perrhenate was prepared by neutralizing an aqueous solution of Re₂O₇ (Degussa, Hanau, Germany) with aqueous ammonium hydroxide. Small crystals were grown by slow evaporation of this solution. The spin-lattice relaxation time measurements were carried out on a Bruker BKR 320 s pulse spectrometer. The proton spin-lattice relaxation times, T_1, were determined using a saturation method for T_1 times longer than 500 msec and a 90-τ-90 sequence for T_1 times shorter than 500 msec. They were measured i) at 142 K at different Larmor frequencies and ii) at Larmor frequencies of 30 and 42 MHz as a function of temperature.

Further, T_1 was measured rotating the sample mechanically in the static magnetic field H_0. The rotation-induced proton spin-lattice relaxation time, T_1', was determined using the same methods which were employed to determine the "normal" T_1 times. The sample rotation frequency, f, was varied roughly from 2 Hz to 20 Hz. A slight decrease of T_1' with increasing frequency f was found. But because of the simple apparatus used to rotate the sample no attempt was made to investigate the T_1' dependence on sample rotation frequency in detail.

At 30 MHz, T_1 was measured at temperatures ranging from 90 K to 400 K. The relaxation behavior was observed to be exponential below 200 K and non-exponential above. At 42 MHz, T_1 was measured between 142 K and 295 K. Here, the

relaxation behavior was observed to be exponential below 260 K and non-exponential above this temperature. These observations point to a frequency dependent non-exponential relaxation behavior. In the temperature ranges where the relaxation behavior is purely exponential, the equation

$$M(t) = M_0 (1 - \exp\{-t/T_1\}) \qquad (1)$$

was used to determine the spin-lattice relaxation times. They are accurate within an error of $\pm 5\%$. To describe the non-exponential relaxation behavior the experimental $[M_0 - M(t)]/M_0$ vs t curves were fitted to the equation

$$[M_0 - M(t)]/M_0 = \alpha \exp\{-t/T_{1,\mathrm{I}}\} + $$
$$+ \beta \exp\{-t/T_{1,\mathrm{II}}\} \qquad (2)$$

where α, β, $T_{1,\mathrm{I}}$, and $T_{1,\mathrm{II}}$ are adjustable parameters. From the time constants $T_{1,\mathrm{I}}$ and $T_{1,\mathrm{II}}$ only one $(T_{1,\mathrm{I}})$ exhibits a reasonable temperature dependence. The temperature was controlled to ± 1 K and monitored with copper constantan thermocouples. The results of the relaxation time measurements on polycrystalline NH₄ReO₄ are given in Figure 1.
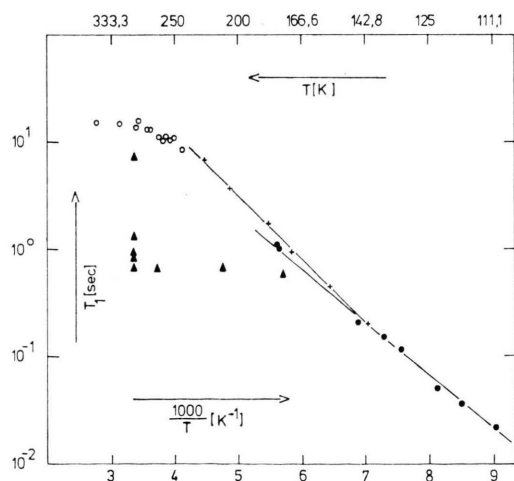

Fig. 1. Spin-lattice relaxation times T_1 and T_1' as a function of temperature for polycrystalline NH₄ReO₄. The T_1' values (see Table 1) are denoted by ▲. The T_1 values measured at 30 MHz and at 42 MHz are denoted by ● and +, respectively. The solid curves were calculated from Eqs. (3) and (4) using the parameters $V_a = 2.2$ kcal/mole, $\tau_c^0 = 7 \times 10^{-15}$ sec, $C = 5 \times 10^{10}$ sec⁻² at 30 MHz and $V_a = 2.6$ kcal/mole, $\tau_c^0 = 9 \times 10^{-15}$ sec, $C = 1 \times 10^{10}$ sec⁻² at 42 MHz. The $T_{1,\mathrm{I}}$ values obtained from Eq. (2) are denoted by ○.

3. Analysis and Discussion of the Results

Assuming the barrier to NH₄⁺ reorientation is sufficiently high and the proton dipolar interaction

within an NH₄⁺ ion is modulated by isotropic NH₄⁺ reorientations, T_1 is given by the BPP relation [5]

$$1/T_1 = \frac{C}{\omega_0}\left\{\frac{\omega_0\tau_c}{1+\omega_0^2\tau_c^2} + \frac{4\omega_0\tau_c}{1+4\omega_0^2\tau_c^2}\right\}. \qquad (3)$$

The experimental T_1 values deduced from Eq. (1) correspond to the limiting case $\omega_0^2\tau_c^2 \ll 1$ of Equation (3).

τ_c is the correlation time for the NH₄⁺ reorientation and C describes proton dipole-dipole interactions within an NH₄⁺ ion. Expressing τ_c in terms of the Arrhenius equation

$$\tau_c = \tau_c^0 \exp\{V_a/RT\}. \qquad (4)$$

Equation (3) was fitted to the experimental T_1 values obtained at 30 and 42 MHz by a least squares procedure. In this manner, for the NH₄⁺ reorientational motion, an average activation energy of $V_a = 2.4 \pm 0.3$ kcal/mole was computed. This value is in satisfactory agreement with activation energies obtained from spin-lattice relaxation time measurements for NH₄⁺ reorientation in similar compounds [6-8].

From the experimental T_1 data at 30 MHz and between 90 K and 200 K alone an activation energy of $V_1 = 2.2 \pm 0.2$ kcal/mole was calculated, which is in agreement with the activation energy of 2.2 ± 0.2 kcal/mole reported by Armstrong, Lourens, and Jeffrey [9]. The T_1 data at 42 MHz and between 142 K and 260 K gave an activation energy of $V_a = 2.6 \pm 0.2$ kcal/mole. Both V_a values agree with the limits of error with the average value of $V_a = 2.4$ kcal/mole so that difference in the values may not be significant. On the other hand Johnson, Rogers and Leroi [10] deduced from their infrared and laser excited Raman spectra that the ammonium ion motion undergoes a change between 77 K and 300 K. This would agree with the different activation energies found in different temperature ranges. Therefore, a differential thermal analysis of NH₄ReO₄ from 77 K to 273 K was made but no phase transition was observed. Armstrong et al. [9] presented a detailed study of molecular reorientation in NH₄ReO₄. From their proton magnetic relaxation measurements they concluded that there is no evidence for a previously postulated order-disorder phase transition involving the NH₄⁺ ions.

This agrees with our differential thermal analysis but the problem of slightly different reorientational motions of the NH₄⁺ ions is not decided definitely. The argumentation of Armstrong et al. [9] is based on

their proton magnetic relaxation study, especially on their T_{1D} study. The measurements are assumed to lead to an indirect determination of the rhenium spin-lattice relaxation time $T_1(Re)$. In the case of an order-disorder phase transition $T_1(Re)$ should show a strong temperature dependence near the phase transition point provided that a sufficiently strong dipole-dipole interaction exists between the protons and the rhenium spins. The validity of this condition is not proved. Therefore, we suggest T_{1D} measurements on a rotating NH₄ReO₄ sample. As shown in this paper this method improves the coupling between protons and rhenium nuclei remarkably. Also relaxation time measurements on NH₄ReO₄ single crystals in special orientations should be appropriate in contributing to the elucidation of the above problem.

The long spin-lattice relaxation time of about 13 sec found at room temperature indicates a weak magnetic coupling of the protons with the lattice. However, upon rotation of the sample T_1 is reduced to a value a short as 0.66 sec. Such a reduction of T_1 by means of sample rotation was first reported by Woessner and Gutowsky[11]. In the compound investigated here it reflects the coupling of the proton spin-system with that of the rheniums. The coupling depends on the Zeeman splitting of the rhenium electric quadrupole energy levels.

Dean[12] has discussed the Zeeman splittings of nuclear quadrupole levels. The applied static magnetic field H_0 removes the $\pm m$ degneracy, and the energy levels are then

$$E_m = E_m^0 + \gamma H_0 \hbar \cos \Theta\, m\, (m \mp 1/2) \qquad (5)$$

where Θ is the angle between the symmetry axis of the electric field gradient and the magnetic field H_0 and γ is the gyromagnetic ratio of the rhenium nucleus under investigation. From the two Re NQR transitions only the Zeeman splittings of the transition $\pm 5/2 - \pm 3/2$ were taken into account. The room temperature ¹⁸⁷Re and ¹⁸⁵Re NQR frequencies of the transition $\pm 3/2 - \pm 1/2$ are 16.64 and 17.58 MHz, respectively. The maximum Zeeman splittings of these frequencies due to the magnetic fields corresponding to proton Larmor frequencies of $30 - 42$ MHz result in a frequency range in which the $\pm 3/2 - \pm 1/2$ NQR transitions do not coincide with that of the protons. Thus, their Zeeman splittings are not effective in producing relaxation.

For the NQR transitions $\pm 5/2 - \pm 3/2$ two frequencies follow from Eq. (5):

$$\nu = \nu_0 \pm (\gamma H_0/2\pi) \cos \Theta \qquad (6)$$

ν_0 is the unperturbed rhenium quadrupole resonance frequency. The lowest and highest frequencies occur at $\Theta = 0$. By equating the frequencies in Eq. (6) to the Larmor frequency, the frequency range in which the various rhenium transitions coincide with that of the protons can be estimated. At 296 K the $\pm 5/2 - \pm 3/2$ NQR frequencies for the two rhenium isotopes are 35.14 MHz for ¹⁸⁵Re and 33.26 MHz for ¹⁸⁷Re. Then, the lowest and highest frequencies are roughly 28.4 and 42 MHz for ¹⁸⁵Re and 24.5 and 40 MHz for ¹⁸⁷Re.

To check this estimate experimentally at room temperature, the rotation induced spin-lattice relaxation time was measured at 42 MHz and 47 MHz. Table 1 shows that the rotation effect decreases clearly when the proton Larmor frequency is higher than 42 MHz in accordance with the estimation made above. At Larmor frequencies below 30 MHz the rotation effect was not investigated because the Zeeman splitting of the Re NQR transition $\pm 3/2 - \pm 1/2$ will overlap the splitting of the NQR transition $\pm 5/2 - \pm 3/2$ and no significant increase of T_1 is expected.

Table 1. Parameter dependent rotation induced spin-lattice relaxation times T_1' in NH₄ReO₄. Parameter: a) temperature, b) sample rotation frequency, and c) Larmor frequency.

T [K]	$\omega_0/2\pi$ [MHz]	T_1' [sec]	f * Hz	
175	30	0.58	5	
210	30	0.66	5	a)
266.4	30	0.67	5	
295	30	0.67	5	
295	30	0.62	2	
295	30	0.66	5	b)
295	30	0.93	20	
295	30	0.66	5	
295	32	0.66	5	
295	33	0.82	5	c)
295	42	1.30	5	
295	47	7.00	5	

* Only approximate values.

Based on the discussion above we conclude that the frequency dependent non-exponential relaxation behavior of the "normal" spin-lattice relaxation is also due to the coupling of the proton spin-system with that of the rheniums. In the sample used the

orientations of the electric field gradient (EFG) are random. In order for proton-rhenium spin exchange to occur, the EFG at the rheniums must make a particular angle Θ with H_0. This condition is satisfied only by those vectors which form a cone with an apex angle of Θ. The probability that a given rhenium fulfils the spin exchange condition is angular dependent in a complex way. Qualitatively, it is zero at $\Theta = 0$ and increases with increasing Θ. It follows from Eq. (6) that at 30 MHz the probability of fulfilling the spin-exchange condition is greater than at 42 MHz. Taking the temperature dependence of the "normal" T_1 times and of the Re $\pm 5/2 - \pm 3/2$ NQR frequencies into account, it seems reasonable that at 30 MHz the proton rhenium coupling is more efficient in producing relaxation at lower temperatures than at 42 MHz, in agreement with the experiments. However, the spin-exchange between protons and rhenium nuclei occurs not only through direct spin interaction, but also through spin diffusion from distant to nearer protons. This has to be considered in a more detailed frequency dependent investigation of the non-exponential relaxation behavior of the "normal" spin-lattice relaxation.

As already mentioned, the dependence of T_1' on sample rotation frequency f was found to be small. Following the model of Gutowsky and Woessner [11] there are two effects governing the dependence of T_1' on f. If the number of passes through mutual resonance increases with increasing f the thermal contact of the protons with the lattice via Re nuclei becomes stronger and T_1' should decrease. This holds true providing the time between passes through mutual resonance is long compared with the rhenium spin-lattice relaxation time $T_1(\mathrm{Re})$. On the other hand hand, with increasing f the time τ spent at mutual resonance decreases and T_1'

should increase. The net effect observed as the rotation frequency is increased up to 20 Hz is that T_1' increases slightly. This points to the fact that at sample rotation frequency of about 20 Hz $T_1(\mathrm{Re})$ becomes comparable to τ.

The other borderline case is that the time τ spent at mutual resonance becomes very long ($\tau \rightarrow \infty$, $f \rightarrow 0$). Then, T_1' is expected to approach the "normal" T_1 of the ^{1}H spin-lattice relaxation. However, the dependence of T_1' on very slow sample rotation was not investigated because of the simple apparatus used to rotate the sample.

The temperature dependence of T_1' was measured at a fixed sample rotation frequency of about 5 Hz. It was observed that in the temperature range 300 K – 200 K T_1' is nearly independent on temperature. Below 200 K T_1' decreases and is expected to approach the "normal" T_1 time at still lower temperatures because the coupling of the protons with the lattice becomes stronger due to suitable reorientation frequencies of the ammonium tetrahedra.

In conclusion, the investigation shows a distinct coupling between the ^{1}H and $^{185/187}$Re spin system in NH_4ReO_4 when the sample is rotated in a static magnetic field. No clear evidence for a phase transition was observed in any of the measurements. However, this problem is believed to be still open. Therefore, frequency dependent measurements of T_1 and T_1' on both single crystals and powder of NH_4ReO_4 are suggested to obtain a more detailed picture of the proton rhenium coupling.

[1] A. A. Boguslavskii, R. Sh. Lotfullin, R. V. Magera, and V. V. Pechenov, Sov. Phys. Solid. State **16**, 1602 [1975].
[2] R. A. Johnson and Max T. Rogers, J. Magn. Resonance, **15**, 584 [1974].
[3] Max T. Rogers and K. V. S. Rama Rao, J. Chem. Phys. **58**, 3233 [1973].
[4] Paul K. Burkert and Max F. Eckol, Z. Naturforsch. **28 b**, 379 [1973].
[5] N. Bloembergen, E. E. Purcell, and R. V. Pound, Phys. Rev. **73**, 679 [1948].
[6] L. Niemelä and T. Lohinkainen, Physik der kondens. Materie **6**, 376 [1967].
[7] D. E. O'Reilly, E. M. Peterson, and Tung Tsang, Phys. Rev. **160**, 333 [1967].
[8] S. R. Miller, R. Blinc, M. Brenman, and J. S. Wanger, Phys. Rev. **126**, 528 [1962].
[9] R. L. Armstrong, J. A. J. Lourens, and K. R. Jeffrey, J. Magn. Resonance **23**, 115 [1976].
[10] R. A. Johnson, M. T. Rogers, and G. E. Leroy, J. Chem. Phys. **56**, 789 [1972].
[11] D. Woessner and H. S. Gutowsky, J. Chem. Phys. **29**, 804 [1958].
[12] C. Dean, Phys. Rev. **96**, 1053 [1954].