NQR Spin-Lattice Relaxation of Re in Perrhenates

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The temperature dependence of the spin-lattice relaxation time T_1 for the Re NQR in $KReO_4$, NH_4ReO_4 and ND_4ReO_4 has been measured between 77 K and 323 K. The relaxation is electric quadrupolar in all cases, and because of the large quadrupole moment of Re, T_1 is short. In $KReO_4$ T_1 follows a T^{-2} dependence. In NH_4ReO_4, T_1 decreases more rapidly than T^{-2} above about 100 K; between 170 K and 250 K T_1 is smaller than 100 μs and could not be measured, but above 250 K, T_1 increases to about 140 μs, and the measured data near room temperature lie close to the T^{-2} extrapolation from the T_1 values below 100 K. These results are interpreted as normal anharmonic Raman quadrupolar relaxation, with a T^{-2} dependence on temperature, combined with an additional relaxation process due to switching of the ammonium ion between two possible orientations.

Key words: NQR, Relaxation, Ammonium, Perrhenate, Disorder.

I. Introduction

The metal perrhenates $MReO_4$ (M = Na, K, Rb, Ag) crystallize in the tetragonal scheelite structure and show a normal temperature dependence of the NQR frequency and other properties. The ammonium salt, NH_4ReO_4, has the same structure but has a variety of anomalous properties which have been studied intensively by many methods [1, 2]. A theoretical model for the anomalous behaviour has been proposed by Taylor [3, 4], and the results of a recent neutron diffraction study of ND_4ReO_4 at closely spaced temperature between 20 K and 298 K give support to the theory [5]. By comparison, the structure and properties of $KReO_4$ show no anomalies over the same temperature range [2, 6].

It is clear that the anomalous properties of the ammonium salt are associated with the presence of the ammonium ion in the crystal, and that the dynamics of the ammonium ion reorientation are central to the problem. Armstrong et al. [7] measured proton relaxation times in NH_4ReO_4 and showed that ammonium ion reorientation is thermally activated with an activation energy of 9.3 kJ/mol above liquid nitrogen temperatures. The NMR spectrum at helium temperatures gives evidence of tunnelling [8]. A study of quasi-elastic neutron scattering in NH_4ReO_4 [9] gives support to the NMR results, for the Arrhenius parameters for ammonium ion rotation derived from this experiment are very close to those determined by Armstrong et al. [7]. All these experiments show that the ammonium ion is rotating rapidly except perhaps at the very lowest temperatures.

The present work on spin-lattice relaxation of the NQR of Re in NH_4ReO_4 and ND_4ReO_4 was carried out as a test of the theoretical model and a supplement to the proton relaxation time studies. Measurements on $KReO_4$ were also performed for comparison with the ammonium salts. Some preliminary results have been published previously [2].

II. Theory

The basis for the current theory [3, 4] of the anomalous behaviour of ammonium perrhenate is that there are two energetically inequivalent orientations for the ammonium ion in the scheelite structure [10]. Each cation is surrounded with eight oxygen atoms in two sets of four; in the two orientations of the cation, the N–H bonds point respectively to one or other of these sets of oxygen atoms. The energy difference between the two orientations is a function of the lattice geometry, and the anomalous thermal expansion and other properties are explained as the result of a cooperative coupling between the ammonium ion orientation and the lattice strain, i.e. the unit cell dimensions.

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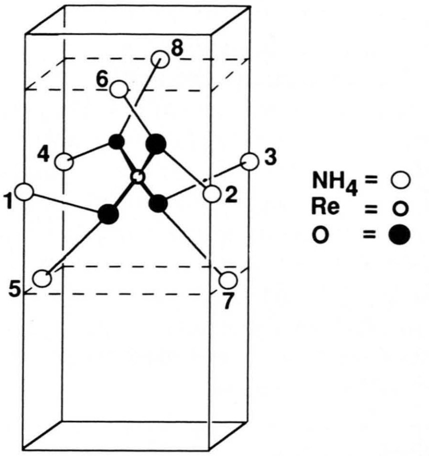

Fig. 1. The geometrical arrangement of ammonium ions around a particular ReO_4^- anion in the scheelite structure. The cations numbered 1 to 4 lie at the same level the *c*-axis as the Re atom; these positions are described as equatorial positions relative to the anion. The cations numbered 5 to 8 are displaced by $\pm c/4$ along the *c*-axis, and occupy axial positions relative to the anion. The four Re–O bonds point into the spaces defined by the following pairs of cations: (1, 5), (3, 7), (2, 6), and (4, 8); the two lighter lines from each oxygen atom indicate the two neighbouring cations.

At low temperatures, analysis of neutron diffraction data from the deuterated salt shows that the N–D bonds of the ammonium ion are oriented towards the four closest oxygen atoms, which are attached to anion displaced by $\pm c/4$ along the *c*-axis, the so-called "axial" orientation [5, 10]. At higher temperatures, it is assumed that some ammonium ions are oriented towards the four slightly more distant oygen atoms attached to anions at the same level along the *c*-axis as the ammonium ion. This is called the "equatorial" orientation. In the diffraction analysis based upon a single deuterium position [5], the room temperature results indicate that (i) the N–D bond points close to the direction of the midpoint between the positions of the axial and equatorial oxygen atoms, and (ii) the deuterium atom shows a highly anisotropic thermal ellipsoid with the long axis extending between the two likely deuterium sites, as a result of approximately equal populations of the two orientations of the ammonium ion.

In Taylor's theory, a pseudospin $\sigma_z(i)$ is assigned takes values of $+1$ and -1 corresponding respectively to the axial and equatorial orientation. The energy of the crystal is written in terms of an effective field related to the crystal strain, and the interactions between ammonium ions [4].

In the analysis of the rhenium NQR relaxation times, attention is focussed on the anions rather than the cations, but the geometrical considerations are similar. Each ReO_4^- anion is surrounded by eight ammonium ions, in two sets of four. The positions of ammonium ions around a particular anion (which may be thought of as being at the origin for present purposes) are shown in Figure 1. Four ammonium ions, numbered 1 to 4 in the diagram, lie at the same level along the *c*-axis, and the other four, numbered 5 to 8, are displaced by $\pm c/4$ along the *c*-axis. The first four ammonium ions are in equatorial *positions* relative to the chosen anion, while the second four ammonium ions are in axial *positions*. Each of these eight ammonium ions may be in either the axial or equatorial *orientation*.

In the neighbourhood of each of the four oxygen atoms in a particular anion there are two cations, one in the axial position and the other in the equatorial position. With the numbering defined in Fig. 1, each oxygen atom or Re–O bond can be identified by an index $b = 1, 2, 3, 4$, such that the Re–O bond with index b points into the space between cations numbered b and $b+4$. At 20 K the distance from an oygen atom to the neighbouring equatorial nitrogen atom, i.e. $O \cdots N(b)$, is 3.03 Å, and the distance to the axial nitrogen atom, i.e. $O \cdots N(b+4)$, is 2.87 Å. These distances hardly change with temperature in spite of the very large thermal expansion [5].

When a cation in an equatorial position relative to the anion at the origin is in its equatorial orientation, one of its N–H bonds points at an oxygen atom of the anion at the origin; if it is oriented axially, then none of its N–H bonds point at the anion at the origin. When a cation in an axial position is in its axial orientation, one of its N–H bonds points at an oxygen atom of the anion at the origin; if it is oriented equatorially, then none of its N–H bonds point at the anion at the origin. Consequently each oxygen atom in a given anion may have 0, 1 or 2 N–H bonds pointing towards it, depending upon the orientations of the two two nearby cations.

The eight neighbouring cations contribute to the electric field gradient (EFG) at the Re atom at the origin, and the contribution of each cation depends upon its orientation. The number of possible combinations of orientations of these eight cations is $2^8 = 256$. At low temperatures, all cations are in the axial orientation and the configuration can be described, using the pseudo-spins $\sigma_z(i)$ to indicate the orientations of these eight cations, as follows:

cation:	1	2	3	4	5	6	7	8
$\sigma_z(i)$:	+1	+1	+1	+1	+1	+1	+1	+1

At higher temperatures, some cations will be excited to the equatorial orientation ($\sigma_z(i) = -1$), singly at first:

$$\begin{array}{cccccccc} -1 & +1 & +1 & +1 & +1 & +1 & +1 & +1 \\ +1 & -1 & +1 & +1 & +1 & +1 & +1 & +1 \\ \text{etc.} \end{array}$$

Single excitations are expected to become important at about 90 K, the temperature at which anomalous thermal expansion begins [5]. At high enough temperatures, there are multiple excitations and all 256 possible combinations become occupied:

$$\begin{array}{cccccccc} -1 & -1 & +1 & +1 & +1 & +1 & +1 & +1 \\ -1 & +1 & -1 & +1 & +1 & +1 & +1 & +1 \\ \text{etc.} \\ \text{etc.} \\ -1 & -1 & -1 & -1 & -1 & -1 & -1 & -1\,. \end{array}$$

For each of these possible configurations there is a corresponding EFG at the Re site. A change in the orientations of the eight neighbouring cations causes (in general) a change in the EFG at the Re site, but if a cation rotates without change of orientation, then the EFG does not change. The fluctuations of the EFG caused by changes in the orientation of the cations cause quadrupolar relaxation of the Re nuclear spin, in addition to the phonon relaxation which is responsible for relaxation in the alkali metal perrhenates. The present experiments were undertaken to detect this additional relaxation.

When an ammonium ion rotates from one energy minimum to another, the hydrogen atoms move collectively to new positions, which may correspond to a permutation of the atoms among the original positions with no change in the orientation of the ion relative to the cage of oxygen atoms, or may be new positions corresponding to a change in orientation. The correlation time determined from dipole-dipole relaxation in NMR refers to rotational motion, without regard to changes in orientation. The correlation time for the additional relaxation process which is postulated here is related to changes in the orientations of the eight cations adjacent to each anion, and so may be quite different in magnitude, for two reasons. Firstly, all eight cations adjacent to each anion influence the EFG, and secondly not every rotation leads to a change of orientation.

The effect of the orientations of the adjacent ammonium ions on the EFG at the Re site is not easily calculated, but the possibilities can be explored using the pseudo-spin formalism and a point charge model. For each Re–O bond, there are two nearby cations, each of which is in one of two orientations. The four possible situations are given in the following table, in which b identifies the Re–O bond and takes the values 1, 2, 3, or 4, $\sigma_z(b)$ is the pseudo-spin variable for the cation in the equatorial position, and $\sigma_z(b+4)$ is the pseudo-spin variable for the cation in the axial position (see Figure 1); $n_{\text{eq}}(b)$ and $n_{\text{ax}}(b)$ are the number of hydrogen atoms which are coordinated to the oxygen atom $0(b)$ from the equatorial and axial cations respectively, and $n(b)$ is the sum of these.

$\sigma_z(b)$	$\sigma_z(b+4)$	$n_{\text{eq}}(b)$	$n_{\text{ax}}(b)$	$n(b)$
+1	+1	0	1	1
+1	−1	0	0	0
−1	+1	1	1	2
−1	−1	1	0	1

The situation at each of the four Re–O bonds can be catalogued in this way for all 256 possible configurations of the eight cations adjacent to a given anion. In the "ground state" in which all cations are oriented axially, every oxygen atom has one hydrogen atom from the cation in the axial position coordinated to it; other states may have either zero, one or two hydrogen atoms coordinated to a given oxygen atom, with a corresponding distortion of the electronic charge distribution in the cation which affects the EFG at the Re atom.

The contribution to the EFG induced at the Re site can be modelled by replacing each hydrogen atom by a point charge if the N–H bond is directed to the anion at the origin, and ignoring it otherwise. An alternative would be to represent the ammonium ion by an electric octupole centred at the nitrogen atom, but this is more complicated and not necessarily more accurate. The EFG at the Re site will be modified by Sternheimer effects due to the electronic charge distribution in the covalently bonded anion. For a single charge at coordinates (X, Y, Z) in a coordinate frame (x, y, z) in which the z axis coincides with the crystallographic c axis, the EFG at the origin is given by the following, apart from a constant factor:

$$V_{xx} = -(R^2 - 3X^2)/R^5\,, \quad V_{yy} = -(R^2 - 3Y^2)/R^5\,,$$
$$V_{zz} = -(R^2 - 3Z^2)/R^5, \quad V_{xy} = 3XY/R^5\,,$$
$$V_{yz} = 3YZ/R^5, \quad V_{zx} = 3ZX/R^5$$

where $R = (X^2 + Y^2 + Z^2)^{1/2}$.

We consider first the case in which the angle θ between the z-axis and the direction of the charge is equal to the tetrahedral angle, so that $Z = \pm R/\sqrt{3}$ and $V_{zz} = 0$. The (x, y) axes may be chosen arbitrarily in the (a, b) plane since $\eta = 0$ overall; if the axes are chosen so that the charge is equidistant from them, then $X = Y = \pm R/\sqrt{3}$, and so:

$$V_{xx} = V_{yy} = V_{zz} = 0, \quad V_{xy} = R^{-3}\,\mathrm{sgn}(X\,Y),$$
$$V_{yz} = R^{-3}\,\mathrm{sgn}(YZ), \quad V_{zx} = R^{-3}\,\mathrm{sgn}(Z\,X),$$

where sgn(.) takes the values ± 1 corresponding to the sign of the argument of the function. Thus a tetrahedrally placed charge makes no contribution to the diagonal elements of the EFG in the crystal axis frame, but does generate off-diagonal elements. Fluctuations in the off-diagonal elements of the EFG tensor due to due to addition or removal of the charge (which would mimic a change in orientation of a nearby cation) would cause quadrupolar relaxation of the Re nucleus. The V_{xy} component causes $\Delta m = \pm 2$ transitions, and the V_{yz} and V_{zx} components cause $\Delta m = \pm 1$ transitions, among the three doubly degenerate levels of the static $I = 5/2$ pure quadrupolar energy levels [11]. Thus measurements of the nuclear spin relaxation time for the Re nucleus should be sensitive to changes in cation orientation. The onset of additional spin relaxation should occur at the same temperature that anomalous thermal expansion becomes apparent, namely about 90 K, since the two effects are associated with the excitation of the cations to the equatorial orientation.

If the charge is not at the tetrahedral angle to the z axis, then there is a contribution to the principal component of the EFG tensor V_{zz}, which may be positive or negative depending on the angle. In the NH_4ReO_4 structure, the hydrogen atom positions with respect to the Re atom do not have perfect tetrahedral symmetry and as a result, there may be a significant contribution to the principal component V_{zz} of the EFG tensor. The contributions from axial and equatorial hydrogen atoms are probably of opposite sign, because the relevant angles are on opposite sides of the tetrahedral angle. At low temperature, all cations are oriented axially, and V_{zz} reflects the "all-axial" configuration. In the high temperature limit, there are equal numbers of equatorially- and axially-oriented cations, and the correlation time for switching between orientations is very short, so V_{zz} reflects the average of the "all-axial" and "all-equatorial" configurations. Cancellation of terms of opposite sign is likely to lead to a reduced contribution of the cations at high temperature.

Hence changes of orientation of neighbouring cations may contribute to the observed temperature dependence of the NQR frequency, because the hydrogen atoms on these ammonium ions are not situated tetrahedrally relative to the Re nucleus. This local effect would be in addition to the changes in the long-range lattice EFG due to the anisotropic thermal expansion. The effect of reorientation on the spin relaxation would be almost the same as if the angles were exactly tetrahedral. Taylor [4] has pointed out a linear relationship between NQR frequency and strain, although it is not clear whether this arises from the overall thermal distortion of the lattice, or from the specific local effect under consideration here.

III. Experimental

In the perrhenate salts, relaxation times are very short even though the NQR frequencies in perrhenates are not unusually high, because of the combination of a large quadrupole moment (for both rhenium isotopes) and the near tetrahedral symmetry of the perrhenate ion. Between about 150 K and 250 K, the large temperature dependence of ν_0 in the ammonium salt in combination with temperature gradients, makes in the resonance difficult to follow because of very short T_2^* values. These conditions generate some practical difficulties in measuring T_1.

The spectrometer used is based upon a Novex transceiver using quadrature detection, controlled by a pulse programmer supplied by Dr. L. Guibé of Université de Paris IX. The power amplifier is an Amplifier Research Model 200L, and the peak pulse power, measured with a Bird RF Power Analyst model 4391, was typically 150 W. A Nicolet 1270 signal averager was used to collect the free induction decay (FID) or echo. Temperature was controlled in a cryostat using either a flow of cold nitrogen gas or a liquid nitrogen splash [12]. Temperatures were read with two thermocouples attached to the block of the cryostat.

The $KReO_4$ sample was in the form of a powder, supplied by Strem Chemicals (Newburyport, MA). After some initial measurements on NH_4ReO_4 powder, it was decided to use a singe crystal. The use of a single crystal meant that the tip angle of the RF pulses was well defined, and the response to multiple pulses was simpler to interpret. The single crystal was coated with epoxy glue in order to avoid disintegration of the sample as a result of cracking due to temperature gradients. There was no evidence of distortion of the NQR signal or a shift in frequency due to stresses on the crystal caused by the epoxy coating. The single crystal was oriented with the *c*-axis perpendicular to the RF field by means of the Zeeman effect on the resonance in a small magnetic field. The sample of ND_4ReO_4 had been deuterated by repeated recrystallization from D_2O, and was in the form of a powder.

Measurements on the 1/2–3/2 resonance in $KReO_4$ powder were done with a $\pi/2-\tau-\pi/2-\tau_e-\pi/2$ sequence, with the echo delay τ_e held constant at 100 µs; the length of the $\pi/2$ pulses was adjusted to give maximum signal following the pulse, and was generally in the vicinity of 8 µs. The second half of the echo was collected in the signal averager and Fourier transformed in order to plot the recovery as a function of τ.

Measurements on the 3/2–5/2 resonance in NH_4ReO_4 powder near room temperature using this method were not successful because of the very short T_1 and the appearance of multiple echoes at short values of τ. This problem was avoided by using a single crystal and the simplest possible pulse sequence, namely the inversion-recovery sequence $\pi-\tau-\pi/2$ with the signal recovery monitored by the FID amplitude. The FID amplitude following a single pulse was measured as a function of pulse length over more than one cycle of tip angle to confirm that signal inversion was taking place; the $\pi/2$ pulse length was determined in this way after each major change of temperature, and was found to vary between 3 and 5 µs. This procedure gave satisfactory results from room temperature down to about 250 K.

At low temperatures (below 160 K) the inversion recovery sequence could not be used because of probe ringing and shorter T_2^* values. Instead a saturation recovery method was used, using the sequence $t_{sat}-\tau-\pi/2-\tau_e-\pi/2$ with a single long pulse t_{sat} of 100 µs to achieve saturation. The recovery of the echo amplitude was monitored; the echo amplitude approached zero for short τ, indicating that saturation had been achieved. A 500 ms delay was used between pulse sequences to avoid sample heating. This method was also used for measurements on powdered ND_4ReO_4 at all temperatures. Relaxation times measured this way showed better reproducibility than those obtained by other methods.

In each of these experiments, T_1 values were determined by fitting the data to the appropriate exponential recovery function using a Simplex procedure. No deviation from exponential recovery was detected. The accuracy of the T_1 values was estimated to be $\pm 10\%$, but the consistency is not as good for the shorter T_1 values.

IV. Results and Discussion

(1) $KReO_4$

The temperature dependence of T_1 for $K^{187}ReO_4$ powder plotted as $\ln(T_1/\mu s)$ *versus* $\ln(T/K)$ is shown in Fig. 2, some of the data having been published in [2]. The data are consistent with the expected T^{-2} dependence [13] over most of the range, but the slope of the graph suggests a slightly steeper dependence at low temperatures. At room temperature, T_1 is only about 340 µs, showing that relaxation is rapid even in the alkali metal salt in which there is no rotating polyatomic cation.

(2) NH_4ReO_4

The $^{187}Re/^{185}Re$ ratio of T_1 values in NH_4ReO_4 at 99 K was found to be 1.18 ± 0.17, which is consistent with quadrupolar relaxation. The best indication that the relaxation is quadrupolar rather than magnetic dipolar is that T_1 in ND_4ReO_4 is smaller than in NH_4ReO_4. The magnetic dipole moment of the deuteron is about 1/9 of that of the proton, and so deuteration should increase T_1 if magnetic interactions contributed significantly to spin relaxation.

The temperature dependence of T_1 in $NH_4{}^{187}ReO_4$ plotted as $\ln(T_1/\mu s)$ *versus* $\ln(T/K)$ is shown in Figure 3. The graph shows that in the middle of the temperature range the mechanism responsible for the relaxation is not lattice phonons alone. The strong deviation from the line of slope -2 starting at about 90 K shows that there is an additional relaxation mechanism operating, which can be attributed to quadrupolar relaxation due to changes in the orientation of the cations. The reduction in T_1 begins at the same temperature at which anomalous thermal expansion begins.

Between 170 K and 250 K T_1 is so short that it was not measurable, and the exact temperature dependence could not be determined; the form of the curve on either side of the gap suggests a fairly deep mini-

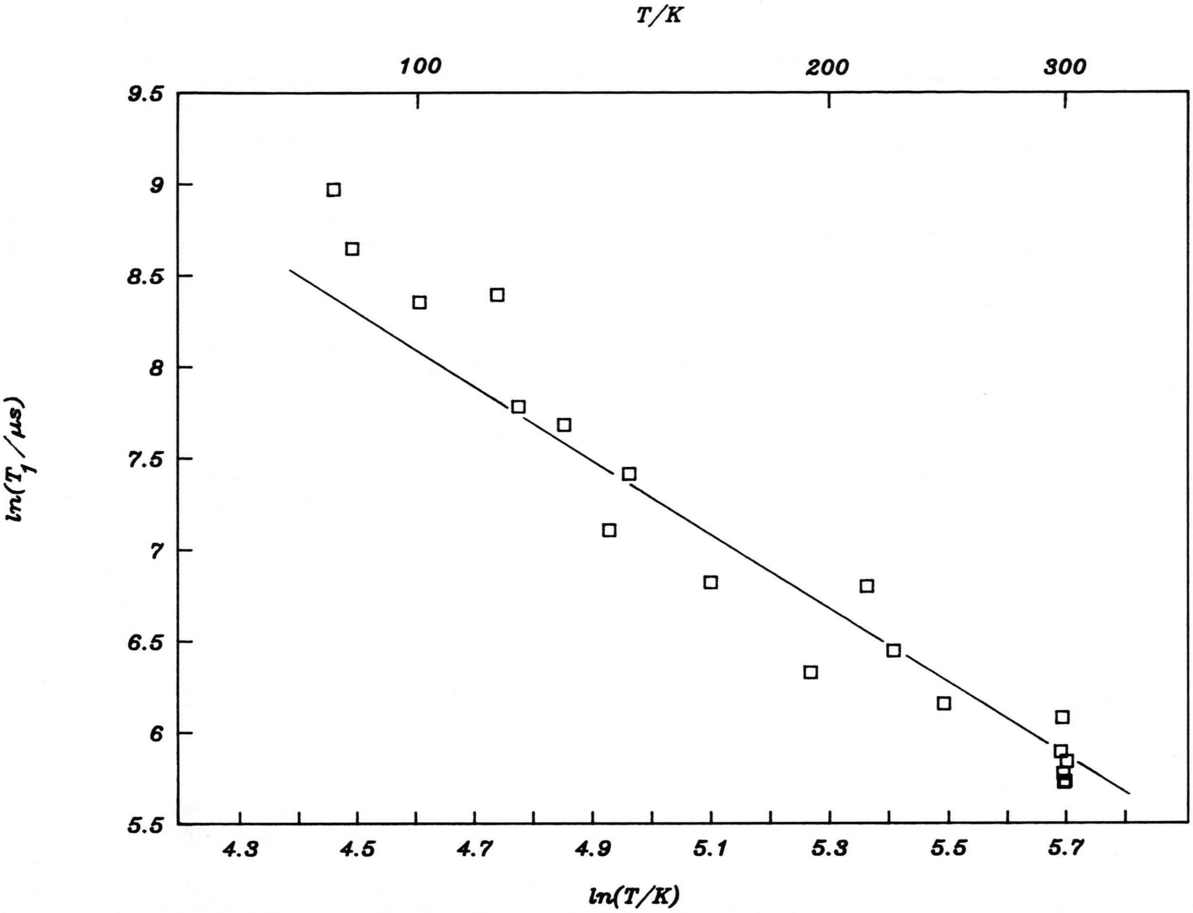

Fig. 2. Temperature dependence of T_1 for the 1/2–3/2 transition of ^{187}Re in $KReO_4$, plotted as $\ln(T_1/\mu s)$ *versus* $\ln(T/K)$. The line has a slope of -2 and is drawn for comparison with the data.

mum centred at about 200 K. This is also the region where the temperature dependence of the NQR frequency becomes very large, and observation of the resonance is difficult due to temperature gradients; the observed shortening of T_1 on either side of the gap is not due to any difficulties in observing the resonance.

Above 250 K, T_1 becomes measurable again with a value of approximately 140 μs; the data are consistent with a T^{-2} extrapolation of the low temperature data, although a T^{-2} dependence of T_1 above room temperature is not discernible in the measurements. Apparently as the correlation time for the fluctuation of the EFG at Re becomes shorter, phonon-induced relaxation again becomes the dominant relaxation mechanism.

The quadrupolar relaxation time for Re was estimated by Armstrong et al. as 265 μs at 167 K [7], for measurements of proton relaxation times $T_{1\varrho}$ and T_{1D}. This is larger than the value of 170 ± 15 μs at that temperature obtained from the present measurements. Their value was based upon a number of assumptions, and the agreement on the general order of magnitude can be regarded as satisfactory. At room temperature, Armstrong et al. determined a "rough" value of 75 μs, which is smaller than the present measured value of 140 ± 15 μs. The present results are not consistent with their deduction, based upon non-exponential decay of dipolar order, that T_1 follows at T^{-2} temperature dependence between 167 K and 298 K.

The apparent minimum in T_1 near 200 K suggests that at this temperature the correlation time for fluctuations in the EFG is of order $1/\omega_q$, i.e. 5×10^{-9} seconds. By comparison, the correlation time for rotation determined from both NMR [7] and quasi-elastic

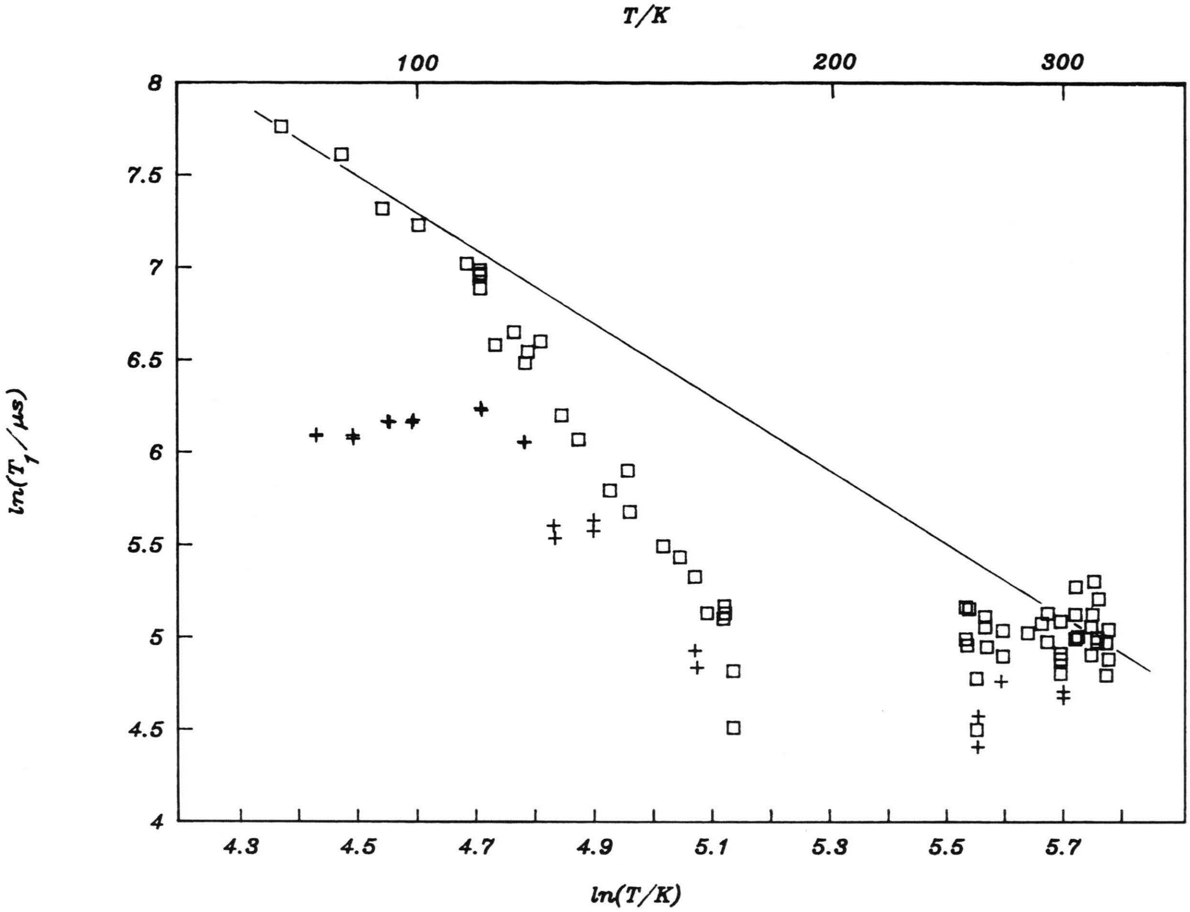

Fig. 3. Temperature dependence of T_1 for the 3/2–5/2 transition of ^{187}Re in NH_4ReO_4 (□) and ND_4ReO_4 (+), plotted as $\ln(T_1/\mu s)$ *versus* $\ln(T/K)$. The line has a slope of -2 and is drawn for comparison with the data.

neutron scattering [9] is about 6×10^{-12} seconds at this temperature. The much longer timescale for fluctuations of the EFG relative to the correlation time for rotation suggests that changes in the orientation of an individual ammonium ion are relatively rare. The ratio of populations of cations in the axial and equatorial orientations are determined by the temperature, as described in the pseudo-spin theory [3, 4], and the ratio of probabilities for equatorial → axial and axial → equatorial rotations must be consistent with the ratio of populations. However both these probabilities are apparently much smaller than the probabilities for rotations in which there is no change in orientation.

If the phonon-induced relaxation rate is assumed to the described by the straight line of slope -2 in Fig. 3, the relaxation rate due to changes in cation orientation, $1/T_c$, can be calculated as the difference between the measured relaxation rate $1/T_1$ and the phonon-induced relaxation rate; the Arrhenis plot for the cation-induced relaxation rate $1/T_c$ below 170 K is shown in Figure 4. The data covers two orders of magnitude, and gives an activation energy of 9.0 ± 0.5 kJ/mol. This is practically the same as the activation energies obtained from proton spin-lattice relaxation and neutron scattering.

Richardson and Howard [9] concluded that their neutron scattering results were fitted best if ammonium ion rotation takes place by C_3 rotations about the N–H bonds. Such rotations do not lead to a change in orientation, and so this conclusion is consistent with the present conclusion that the correlation time for change of orientation is long compared with that for rotation generally. The simplest means for changing orientation is through rotations of about 90°

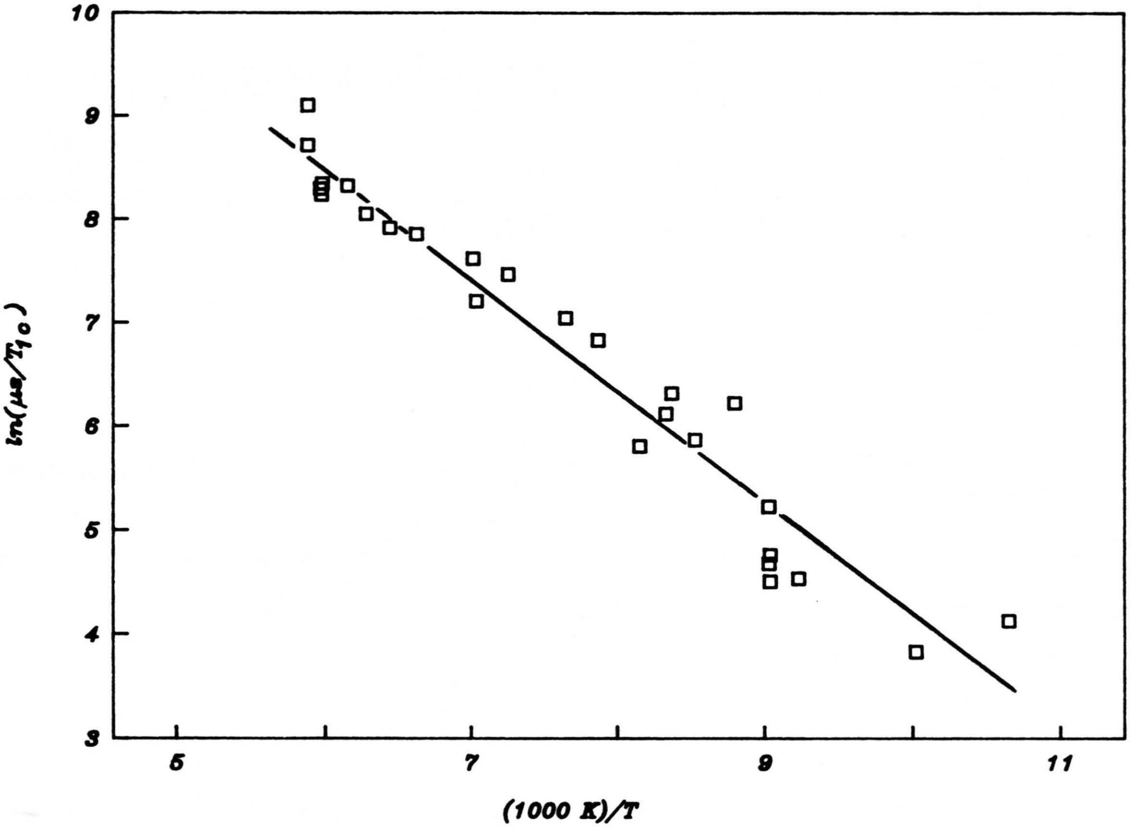

Fig. 4. Arrhenius plot for the cation-induced relaxation rate $1/T_{1c}$ in NH_4ReO_4 for temperatures below 170 K. The slope of the least-squares line corresponds to an activation energy of 9.0 ± 0.5 kJ/mol.

about the C_2 axes, which may follow a quite different energy profile from the C_3 rotation; if this is so, the agreement among the various activation energies is a little surprising.

It is interesting to compare the three activation energies of about 9 kJ/mol (determined by NMR, NQR and neutron scattering) with the energy difference between the axial and equatorial orientations of the cation. The latter was determined to be 1.7 kJ/mol (equivalent to 210 K) at low temperatures, falling to much smaller values at higher temperatures; this result was obtained by fitting the parameters of the pseudo-spin theory to thermal expansion data [4]. The comparison shows that the axial and equatorial orientations of the cation are associated with well-defined minima in the potential energy surface, and that the equatorial orientation is not the transition state between adjacent axial orientations.

(3) ND_4ReO_4

The measured NQR frequency agreed closely with published data for the deuterated salt [14], over the whole temperature investigated; this was taken as evidence of a high degree of deuteration.

The T_1 data for ND_4ReO_4 are plotted in Fig. 3, and show that T_1 is slightly smaller than in NH_4ReO_4 near room temperature, showing that quadrupolar relaxation is dominant. The temperature dependence generally follows that of NH_4ReO_4 above about 110 K, but below that temperature T_1 becomes approximately constant. The reason for this behaviour is not known. The timescale for ammonium ion rotation is expected to be longer by a factor in the range of $\sqrt{2}$ to 2, but this is not sufficient to explain the observation. The possibility of relaxation by paramagnetic impurities at low temperatures was considered. The

EPR spectrum of the sample was run in an X-band spectrometer between 500 gauss and 3500 gauss with a modulation amplitude up to 20 gauss. No signal was observed, suggesting the absence of paramagnetic impurities.

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