TITLE:

Temperature Dependence of Spin Lattice Relaxation Time of Cl^35 in Pure Quadrupole Resonance

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TEMPERATURE DEPENDENCE OF SPIN LATTICE RELAXATION TIME OF Cl^{35} IN PURE QUADRUPOLE RESONANCE*

BY ·

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ABSTRACT

The spin lattice relaxation time (T_1) of Cl^{35} nuclei between quadrupole resonance levels in para-dichlorobenzene and in sodium chlorate was measured at several temperatures by the use of the 90°–90° pulse method. To analyse the obtained data, two approaches were undertaken: the first was done by following Bayer's theory and the second by Van Kranendonk's and Yoshida-Moriya's theories. Although the approaches were bold and rough, and detailed interpretations were not possible, yet both gave fairly satisfactory explanation for the obtained data of temperature dependence of T_1. An experiment is proposed which would decide which approach is better.

1. Introduction

The quadrupolar relaxation is one of the most important relaxation mechanisms for nucleus whose spin number is greater than 1/2. A few systematic investigations have been carried out both theoretically (1, 2, 3, 4) and experimentally (5, 6) on quadrupolar relaxation in nuclear magnetic resonance (NMR). In pure quadrupole resonance (PQR), the relaxation mechanism is almost entirely quadrupolar. As to the quadrupolar relaxation in molecular crystal in PQR, Bayer's theory (7) is the only one as far as we know. Although some workers have measured T_1 in PQR (8, 9, 10), any systematic investigations, particularly on the temperature dependence of T_1 in PQR, which are the most convenient ways to study the mechanism, have not yet been made experimentally**. We have therefore measured the temperature dependence of T_1 of Cl^{35} in PQR on para-dichlorobenzene (p–Cl$_2\phi$) and on sodium chlorate (NaClO$_3$), which are standard samples in PQR, the former being a molecular crystal and the latter an ionic. To analyse

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** At the beginning of March, Dr. Tanttila kindly communicated that he and his co-workers made experiments of the same kind as ours, and that they analysed the obtained data following Chang's theory, of which any publication has not been accessible. The author expresses his thanks to Dr. Tanttila for sending a copy of the following article before publication.
P. A. Bender, D. A. Jennings and W. H. Tanttila: J. Chem. Phys. (in press).

the obtained data, two approaches were undertaken: the first was to follow directly Bayer's theory and the second was to apply Van Kranendonk's theory (1), Yoshida-Moriya's theory (2) and Kondo-Yamashita's theory (3) to our case, which were originally concerned with the quadrupolar relaxation in NMR in ionic crystals, particularly of NaCl and CsCl type. Though there is Khutsishvilli's theory (4) for the quadrupolar relaxation in NMR, which predicts $T_1 \propto T^{-4}$ at high temperatures, it does not fit some experiments in NMR (6) nor our results, so we shall not consider this theory. In the following sections, the experimental results and the analysis will be given.

2. Experimental method and results

In order to measure T_1 of Cl^{35} in PQR, a pulsed PQR apparatus operating near 30 Mc/sec was constructed. The 90°–90° pulse method was employed. The apparatus and the procedures were essentially the same as those we used for measuring T_1 in NMR (11). A few modifications were made as described below. (1) The pulsed oscillation was made to be initially at the low power level, and then amplified to the desired power level, for the purpose of increasing the stability of the apparatus. (2) The pulsed rf power was fed to the sample coil from a low impedance source, so that the sample coil was easily immersed in a refrigerant, while the input to the nuclear signal receiver was of high impedance type as before. (3) The straight nuclear signal receiver was replaced by the superheterodyne system, so that the apparatus was suitable for following the change of PQR resonance frequency (ν) by the change of sample and of temperature. The intermediate frequency was chosen to be 13.5 Mc/sec, and the frequency of local oscillator to be on the higher frequency side to avoid the direct power leakage of the local oscillation to the detector. Only the modified parts of the apparatus are shown schematically in Fig. 1.
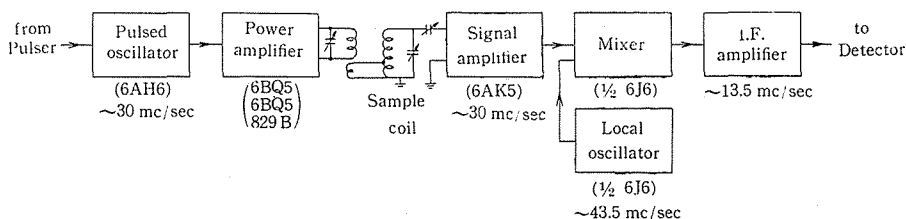

Fig. 1.   Block diagram of only the modified parts of our experimental apparatus. For other parts, see reference 11.

The sample used (p-Cl$_2\phi$ and NaClO$_3$) were polycrystals. The value of T_1 in PQR, which is of course determined by the quadrupolar relaxation, is independent

of whether the sample is single crystal or polycrystal, at least in our temperature region (**5, 10**).

Because of the temperature dependence of PQR resonance frequency, we must use a cryostat which has the following characteristics: (1) The temperature inside the cryostat must be constant within about $\pm 0.1°K$ during one measurement, which takes about half an hour for a long T_1. (2) The temperature gradient through the sample must be smaller than about $\pm 0.1°K$. Up to the present, however, the author has not obtained such a cryostat, and therefore the sample was immersed in an appropriate refrigerant and T_1 was measured only at several temperatures.

The data thus obtained are tabulated in Table I below.

Table I. Measured values of T_1 of Cl^{35} at several temperatures.

T ($°K$)	T_1 (m sec) (on p-Cl$_2$ ϕ)	T ($°K$)	T_1 (m sec) (on NaClO$_3$)
77	560 ± 50	77	1900 ± 100
90	450 ± 40	90	1450 ± 70
195	60 ± 5	195	137 ± 7
271	27 ± 3	286	50 ± 4
292	22 ± 2		
300	19 ± 2		

3. First approach—Analysis by Bayer's theory

The obtained data of T_1 on p-Cl$_2\phi$ sample was first analysed by Bayer's theory. This theory is based on the model that the energy of spin system relaxes to the energy of the torsional vibration of a molecule, and that the torsional vibration itself is disturbed by other motions in the crystal. The results of analysis were already reported (**12**), so that they will not be reproduced here in detail. We could not apply Bayer's theory to NaClO$_3$ sample, however, because the information necessary for analysis about the torsional vibrational frequency of this sample was lacking. The comparison between the theoretical curve and the experimental points is shown in Fig. 2 (cf. reference **12**), where one adjustable parameter, i.e. the average life-time in the excited states of the torsional vibration, was assumed to be 1.23×10^{-11} sec.

To sum up, Bayer's theory has the following characteristic features: (1) It stands on a relatively simple model and has only one adjustable parameter. (2) It explains the general feature of the temperature dependence of T_1. (3) It gives a reasonable value for the average life-time in the excited states of the torsional vibration. (4) In addition, it predicts the temperature dependence of the PQR

resonance frequency, and this prediction was almost correct for many substances, as already examined by many workers (13).
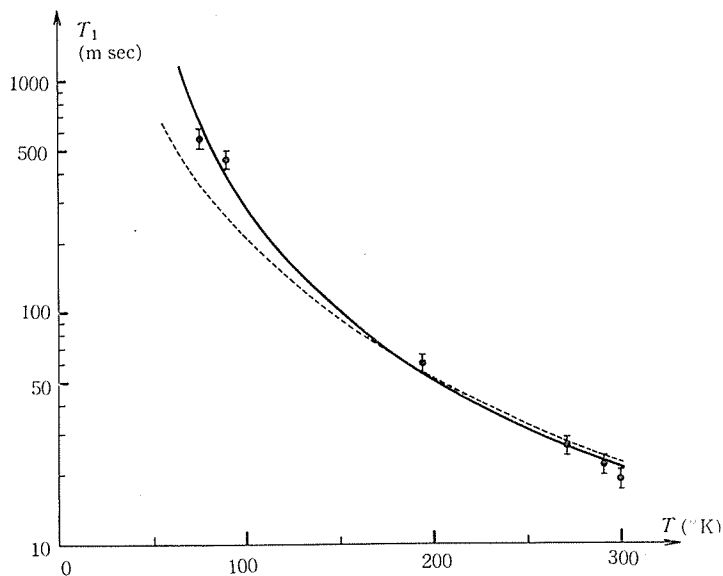

Fig. 2. Experimental points and the results of the two approaches for p-Cl$_2\phi$ sample. The dotted curve is due to the first approach (the same figure as that in reference 12), and the solid-line curve to the second.

When we fix our attention on the form of the temperature dependence of T_1 but not on its absolute value, T_1 given by Bayer's theory can be expressed, to good accuracy, as $T_1 \propto T^{-2}$ in our temperature range. As we can easily see from Fig. 2, the experimental curve for the temperature dependence of T_1 is steeper than the theoretical one. It was impossible to explain this discrepancy by a simple modification of Bayer's theory, because the theory is too bold in its assumption to be modified easily. Thus, another approach will be considered in the next section.

4. Second approach—Analysis by Van Kranendonk's theory

As a second approach, we shall make use of Van Kranendonk's theory which was originally concerned with the quadrupolar relaxation in ionic crystals in NMR. Detailed calculation, particularly for the temperature dependence of T_1, was carried out for the NaCl type ionic crystal. Both Yoshida-Moriya's theory and Kondo-Yamashita's theory are modifications of this Van Kranendonk's theory.

In the detailed calculation, these three theories stand on the two fundamental assumptions: (1) The relaxation takes place as two-phonon Raman process,

namely, one phonon of the frequency ν_p is absorbed and another phonon of the frequency $\nu_p + \nu$ is emitted, when the energy of spin system relaxes to the energy of the lattice vibration. (2) The spectrum of phonon system (lattice vibration) is assumed to be of acoustical Debye type.

In Van Kranendonk's theory, it is assumed that the time-varying electric field gradient causing the relaxation in spin system is caused by the vibration of oppositely charged nearest neighbour ions. In Yoshida-Moriya's theory and in Kondo-Yamashita's theory, it is assumed to be caused respectively by the modulation of covalency and that of overlap by lattice vibration. But, the temperature dependence of T_1 is of the same form in all these theories, so far as they stand on the above two assumptions, and the concrete expression for the temperature dependence of T_1 is given by Van Kranendonk's paper.

There are many questions about the application of these theories to the relaxation phenomena in PQR, for it is natural to consider that in PQR the energy of spin system relaxes to the energy of the normal vibration modes of a molecule (p–$Cl_2\phi$) or of an ion (ClO_3^- ion) and then relaxes to the energy of lattice vibration. But, at present, such elegant theories as taking the above consideration into account are not available, so we try to analyse our data by Van Kranendonk's theory. In this case, however, we follow Yoshida-Moriya's or Kondo-Yamashita's theory for the interpretation of the time-varying electric field gradient. At any rate, if we accept the above two assumptions, we do not think it so unnatural to apply these theories to T_1 in PQR, *at least for the temperature dependence.* Of the above assumptions, the first assumption (1) would be plausible in our case. But there remain many questions about the second assumption (2). Plausible excuses to approve this second assumption are that though there would be many complicated vibration modes in samples used for PQR, these vibration modes are averaged to an acoustical Debye mode and that the value of T_1 is the quantity which is averaged over all the lattice vibration modes, and, in general, such averaged quantities are insensitive to the detail of the lattice vibration spectrum (14).

In these theories, the transition probability from m state to $(m+\mu)$ state is given by

$$P(m, m+\mu) = C'|Q_{\mu,m}|^2 T^{*2} E(T^*) E_\mu(\infty),$$

where C' is considered to be an adjustable parameter (which includes the Sternheimer antishielding coefficient in Van Kranendonk's theory and the degree of covalency in Yoshida-Moriya's theory, $T^* = T/T_D$ (T_D being the Debye temperature), $Q_{\mu,m}$ is the matrix element for the quadrupole operator between states m and $m+\mu$, $E(T^*)$ is a numerical function given by Van Kranendonk, and $E_\mu(\infty)$

is a numerical constant of the order of 100 given by Van Kranendonk.

In our case, there are only two energy levels, where T_1 is given by

$$T_1 = \left[2\left\{P\left(\frac{1}{2}, \frac{3}{2}\right) + P\left(\frac{1}{2}, -\frac{3}{2}\right)\right\}\right]^{-1}.$$

So we assume roughly that, at least concerned with the temperature dependence, T_1 is given by

$$T_1 = \frac{C}{E(T^*)T^{*2}},$$

where both C and T_D are adjustable parameters.

Using the above formulas, we can determine T_D and then C from the observed data, obtaining

$$T_D = 280°\text{K}, \quad C = 0.024 \text{ sec for } p\text{-Cl}_2\phi,$$
$$T_D = 380°\text{K}, \quad C = 0.028 \text{ sec for NaClO}_3.$$

The curve thus obtained and the experimental points are shown in Figs. 2 and 3. In the determination of T_D and C, the values of T_D are not so critical and the deviation of about $\pm10\%$ from the above value does not change the general feature of the curve, when a suitable change of the value of C is made.
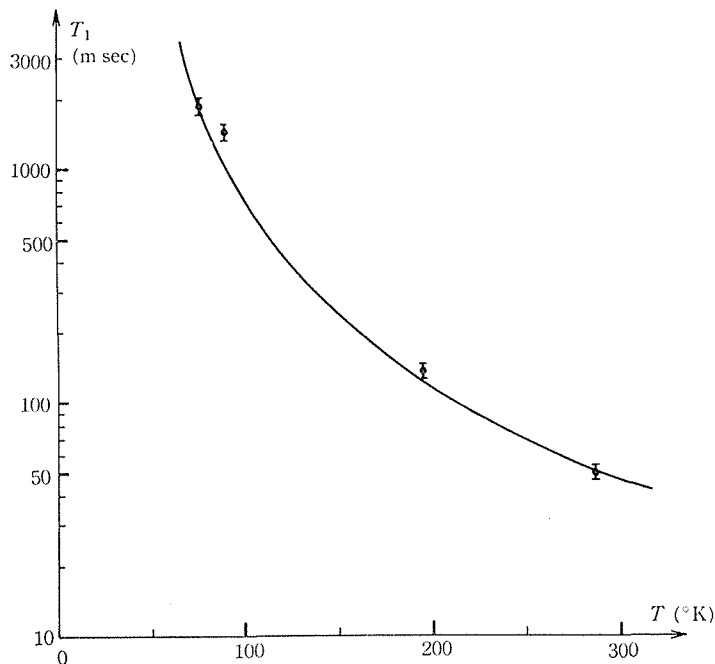

Fig. 3. Experimental points and the results of the second approach for NaClO₃ sample.

This approach, which has two adjustable parameters (T_D and C), gives more satisfactory agreement than the first approach, but the two deduced values of adjustable parameters could hardly be related to the other physical quantities. For T_D, we might consider that among many vibrational modes in the crystal, the modes with frequencies smaller than ν_D ($=k T_D/h$), which is equal to 194 cm^{-1} for p-Cl$_2\phi$ and to 264 cm^{-1} for NaClO$_3$, are effective in the quadrupolar relaxation. About C, we have nothing to say. Rather we should consider the above formulas semi-empirical.

At any rate, Bayer's theory gives $T_1 \propto T^{-2}$ in our temperature range, while Van Kranendonk's theory gives $T_1 \propto T^{-2}$ in the temperature range defined by $E(T^*) \approx 1$, and Van Kranendonk's function $E(T^*)$ describes the deviation from the T^{-2}-law for $T < T_D$. And this deviation is favourably compared with experiments.

5. Discussions

Since the mechanism of quadrupolar relaxation in PQR is very complicated, that is, since we must consider the electronic structure of the sample, while we have only to consider the magnetic moment in the nuclear magnetic relaxation, it is very difficult to construct an excellent theory to give a satisfactory agreement with the experimental data. In the preceding sections, the obtained data were analysed by two different theories, each of which corresponds respectively to Einstein's and Debye's model in the theory of specific heat. Of course, we think these analyses are only of rough approximations, because in the first approach the process of calculation was too simplified and in the second the model on which the theories stand was too simple for the relaxation phenomena in PQR. But, both explained the general feature of the experimental data, though detailed interpretations were not possible. This would be due to the fact that the value of T_1 is insensitive to the detail of the lattice vibration spectrum. In fact, the temperature dependences of T_1 by both Bayer's and Van Kranendonk's theories are nearly the same, that is, $T_1 \propto T^{-2}$ at high temperatures, and also it should be emphasized that the temperature dependences of T_1 for both samples (p-Cl$_2\phi$ and NaClO$_3$) were nearly the same.

However, it is interesting to clarify, by experiments, which approach is better. Though there might be many kinds of experiments to solve this question, the following is proposed as an example. In Bayer's theory, the $|\Delta m|=2$ transition is more effective by the order of one or two than the $|\Delta m|=1$ transition in relaxation mechanism, but in Van Kranendonk's theory, these are comparable in the order. We shall try to examine this point.
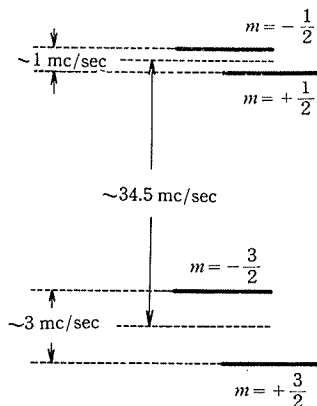
Fig. 4. Energy level diagram in the proposed experiment, where external magnetic field (about 2,500 gauss) is parallel to the symmetry axis of the electric field gradient at Cl^{35} nuclei in p-$Cl_2\phi$ sample.
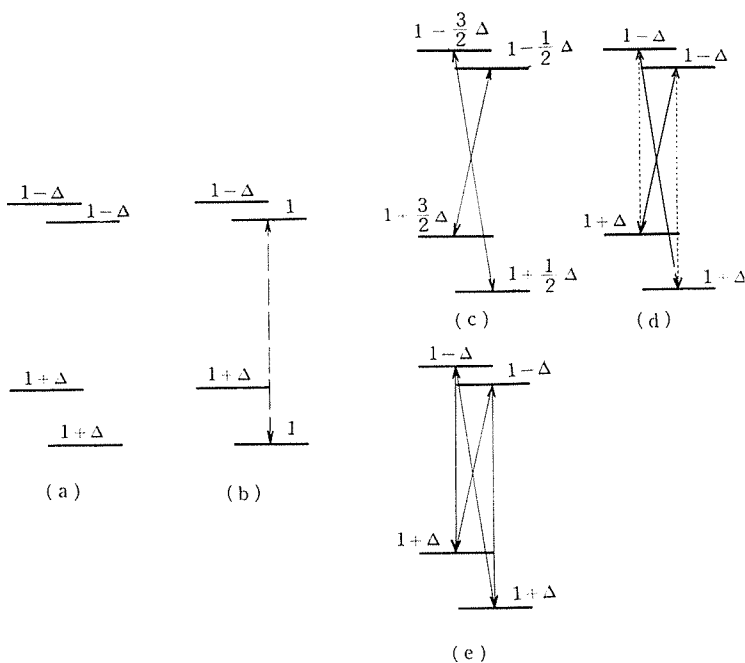
Fig. 5. Relative spin populations at each level, illustrating the proposed experiment $(\Delta = h\nu/2kT)$, (a) at thermal equilibrium; (b) just after the first 90° pulse applied between 1/2 and 3/2 levels; (c) after a time interval of the order of T_1, according to Bayer's theory; (d) after a time interval of the order of 100 T_1, according to Bayer's theory; (e) after a time interval of the order of T_1, according to Van Kranendonk's theory. The difference between (c) and (e) would be easily detected.

Take a single crystal sample, in which the electric field gradient at Cl nuclei is, exactly or nearly, axially symmetric (e.g. p–Cl$_2\phi$), and place it in a magnetic field (e.g. of about a few thousand gauss), whose direction is parallel to the symmetry axis of the electric field gradient. In this case, $\pm 1/2$ levels are not mixed. The energy levels are shown schematically in Fig. 4. Here, for simplicity, the effect of the existence of symmetry axes of different directions in a single crystal (there being two in the case of p–Cl$_2\phi$ (**15**)) is neglected.

We pay attention only to the population difference between 1/2 and 3/2 levels. A 90° pulse (circularly polarized rf pulse inducing only $\varDelta m = -1$ transition being favourable) is applied between 3/2 and 1/2 levels. After a time interval τ, the population difference between 1/2 and 3/2 levels is searched for by a second 90° pulse. Then, (1) according to Bayer's theory, the population difference would approach to half of the original value with a time constant of the order of T_1, which is the spin lattice relaxation time measured in our experiments, and then it would approach to the original value with a time constant one hundred times as large as T_1 in the order, and (2) according to Van Kranendonk's theory, it would approach to the original value with a time constant of the order of T_1, though the approach would not be of a single exponential type in this case (cf. Fig. 5).

It is considered that this difference might be easily detected experimentally. Such an experiment may become complicated owing to the situations that there are some different directions of the symmetry axis of the electric field gradient in a single crystal, but it would not be difficult to pick up the desired resonance by using a suitable sample and an appropriate value of magnetic field.

Acknowledgments

REFERENCES

1. J. Van Kranendonk: Physica **20** (1954), 781.
2. K. Yoshida and T. Moriya: J. Phys. Soc. Japan **11** (1956), 33.
3. J. Kondo and J. Yamashita: J. Phys. Chem. Solids **10** (1959), 285.
4. G. R. Khutsishvilli: Sov. Phys. JETP **4** (1957), 382.
5. C. V. Briscoe and C. F. Squire: Phys. Rev. **112** (1958), 1540.
6. R. L. Mieher: Phys. Rev. Letters **4** (1960), 57.
7. H. Bayer: ZS f. Phys. **130** (1951), 227.
8. W. G. Proctor and W. H. Tanttila: Phys. Rev. **101** (1956), 1757.

9. D. E. WOESSNER and H. S. GUTOWSKY: J. Chem. Phys. **27** (1957), 1072.

10. T. HASHI: J. Phys. Soc. Japan **13** (1958), 911.

11. T. HASHI, A. HIRAI, M. SASAKI and T. KAWAI: Memoirs of the College of Science, Univ. of Kyoto, A **29** (1959), 205.

12. A. HIRAI: J. Phys. Soc. Japan **15** (1960), 201.

13. For example, see, T. P. DAS and E. L. HAHN: *Nuclear Quadrupole Resonance Spectroscopy* (Academic Press, New York, 1958), p. 39 ff.

14. M. BORN and K. HUANG: *Dynamical Theory of Crystal Lattice* (Clarendon Press, Oxford, 1954).

15. U. CROATTO, S. BEZZI and E. BUA: Acta Cryst. **5** (1952), 201 ; also, reference **13**, p. 114 ff.