# PROTON RESONANCE STUDIES OF TWO FERROELECTRIC SULFATES

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By

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SCOPE AND CONTENTS:

The nuclear magnetic resonance spectrum of the protons in rubidium hydrogen sulfate, and the spin-lattice relaxation time for the protons in lithium hydrazinium sulfate have been examined as a function of temperature, in order to obtain information about the motions of the protons in the different states of these substances.

Rubidium hydrogen sulfate becomes ferroelectric below —15°C, and the possibility of a change in the proton resonance linewidth associated with this transition was investigated.

The free-precession (spin echo) NMR technique was used to obtain the proton spin-lattice relaxation time in lithium hydrazinium sulfate, over a wide temperature range. The observed changes in relaxation time gave further data on the hydrazinium ion motions that were inferred from proton NMR studies by Cuthbert and Petch in 1963.

# ACKNOWLEDGEMENTS

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# INTRODUCTION

Although the phenomenon of ferroelectricity has been studied intensively in recent years, much remains to be understood on an atomic scale about its nature. Nuclear Magnetic Resonance (N.M.R.) techniques provide an excellent method for the study of changes in atomic environments, such as take place at ferroelectric phase transitions. In hydrogen-bonded ferroelectrics, N.M.R. is particularly valuable in clarifying the role of the hydrogen atoms.

For atoms such as hydrogen having nuclei with spin I = 1/2, it is the shape and width of the resonance line that are studied. These quantities often are strongly affected by the motion of the nuclei, particularly if the frequency of this motion is in the range $10^3$ to $10^5$ c/s. This is because the resonance line is broadened predominantly by magnetic dipolar interactions with neighbouring nuclear spins, (ignoring the effects of field inhomogeneities), and this effect is dependent on the relative orientation of each pair of dipoles. Thus a change in the shape or width of an absorption line can be related to changes in the angular relationships between neighbouring dipoles, such as would be caused by fairly high frequency reorientation.

An important property of a nuclear spin system in the condensed state is the rate at which it decays back to thermal equilibrium after being excited. This rate is characterised by a time-constant $T_1$, the spin-lattice relaxation time.* Measurements of $T_1$ provide a remarkably sensitive indicator

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* The overall time which relates to processes in the lattice which shorten the phase memory of precession has been denoted by $T_2$, which includes the effect of $T_1$ as well. Since the "phase coherence" time $T_2$ shows the additional effects of spin-spin interactions, field inhomogeneities, etc., generally $T_2 \ll T_1$.

of the motion of the resonating nuclei relative to their immediate environment, since changes in $T_1$ of three or four orders of magnitude are commonly found. This is easily understood, since loss of energy from a nuclear spin system to its surroundings depends directly on the degree of coupling between the nuclei and the lattice. This is itself dependent on the types of coupling that are possible (e.g., dipole, quadrupole, etc.), and on the relationship between the motional frequency and the frequency of Larmor precession of the nuclear spins. For example, if an atomic group can rotate within a crystal, this rotation has its greatest effect on $T_1$ when the Larmor frequency equals the rotational frequency so that the spin system is strongly coupled to the lattice; in this case, $T_1$ may be reduced by a factor of more than 100.

The two ferroelectric sulfates, lithium hydrazinium sulfate, $Li(N_2H_5)SO_4$ (abbreviated LiHzS) and rubidium hydrogen sulfate, $RbHSO_4$, are materials in which one might expect proton motions to play an important role in the ferroelectric behaviour. Accordingly, the purpose of this work was to examine as a function of temperature the N.M.R. spectra of the protons in $RbHSO_4$, and the spin-lattice relaxation time for the protons in LiHzS, in order to obtain information about the motions of the protons in the different states of these substances.

This thesis includes a description of an attempt to determine whether there is a change detectable by N.M.R. methods, in the motion of the hydrogen nuclei (protons) in $RbHSO_4$ as the latter is taken through its ferroelectric transition at −15°C. That is, if the room-temperature (non-polar) phase of $RbHSO_4$ is characterized by a dynamic disorder of protons alternating between two structural sites which freezes out when the crystal transforms to the low-temperature polar phase, the linewidth of the proton resonance might broaden abruptly as the crystal is cooled through the transition temperature. A change in the proton linewidth does not always accompany such a phase transition because the proton reorientation frequencies may not be in the sensitive range, or the change produced in the proton configuration may be too small to be detected.

In 1963, Cuthbert and Petch inferred from proton N.M.R. studies of lithium hydrazinium sulfate that as the temperature was raised above —130°C, first the $-NH_3^+$ group and then the $-NH_2$ group began to rotate about the N-N axis of the hydrazinium ion, $H_2N-NH_3^+$. At still higher temperatures they found that the hydrazinium ions themselves began to rotate about additional axes and even to diffuse through the structure.

This thesis describes the use of the free-precession (spin echo) N.M.R. technique to obtain more data on these motions. The temperature dependence of the spin-lattice relaxation time $T_1$ was determined for the range —110°C to +150°. These results were used to obtain values for the activation energy for rotation of the $NH_3^+$ group, the correlation (i.e., rotational) frequency $\nu_c$, for this motion, and information on other types of motion, such as the activation energy for hindered rotation of the $NH_2$ group, at higher temperatures.

# THEORY

The structure of the polar phase of a ferroelectric crystal is non-centrosymmetric, thus allowing sub-atomic displacements of the charge distribution within each unit cell to be manifested as an overall polarization of the crystal, detectable on a macroscopic scale. LiHzS is a good example of this phenomenon, in that it contains hydrogen bonds, each of which may have the proton closer to one or the other of two neighbouring nitrogen atoms in a chain along the ferroelectric axis (see Fig. 3). The switch from one configuration to the other would need to be accompanied by a change of the surrounding $LiSO_4$ framework from a right to a left-handed form: these two changes together producing an overall change in polarization of the crystal, that is, ferroelectric switching.

## Analysis of an N.M.R. Absorption Line

The moments of an absorption line give a sensitive measure of its shape since, from the definition* of the $n^{th}$ moment $(\Delta H)^n$, it can be seen that they are directly related through a Fourier transformation to g(H), the lineshape. In our case of dipolar broadening, the resonance is symmetrical about $\nu_o$ and the odd moments are zero. Van Vleck's 1948 calculation of the second moment gives:

$$(\Delta H)^2 = \frac{3\,\mu_j^2}{2} \times \frac{\mu_o}{4\pi N_s} \sum_{j>k} \sum_{k} (3\cos^2\theta_{jk} - 1)^2 \;/\; r_{jk}^6$$

$$+ \;\mu_o/12\pi N_s \sum_{j} \sum_{f} \mu_f^2 \,(3\cos^2\theta_{jf} - 1)^2 \;/\; r_{jf}^6$$

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* $(\Delta H)^n = \int (H - H_o)^n \times g(H)\, dH$

where: $\theta_{jk}$, $\theta_{jf}$ are the angles between the applied field and the internuclear vectors;

j, k refer to resonating nuclei;

f refers to non-resonating nuclei having strong local fields; and

$N_s$ is the number of resonating nuclei.

It can be seen that relative motion of pairs of resonating nuclei will result in a space and time variation of $\theta_{jk}$, giving a certain value of $(\Delta H)^2$. A change in the degree of motion of these nuclei will alter the range of variation of the $\theta_{jk}$s, and thus result in a change in $(\Delta H)^2$.

## Physical Background to the Measurement of $T_1$

The spin-echo technique is more correctly described as a transient method, using two (or a sequence of) $\pi/2$ pulses to rotate the z component of the spin magnetization 90° away from the direction of $H_o$, into the x-y plane where its Larmor precession will induce a corresponding voltage in the receiver coil surrounding the sample. This "free induction" signal is shown in Fig. 1 as the tail following pulses AB, and EF, with the height at the beginning of the tail being proportional to the magnetization in the z-direction at the time each pulse is applied. This signal decays exponentially with the relatively short time-constant $T_2$, as the spin vectors lose phase coherence (see (b) to follow).

It should be noted that the magnetization that has been rotated into the x-y plane by the first 90° pulse will gradually return to its thermal equilibrium direction along the magnetic field, with a time constant $T_1$ (which, in our samples, can vary from 0.03 seconds up to over 30 seconds). It is this latter magnetization, $M_z$ increasing according to:

$$1 - \exp(-\tau/T_1)$$

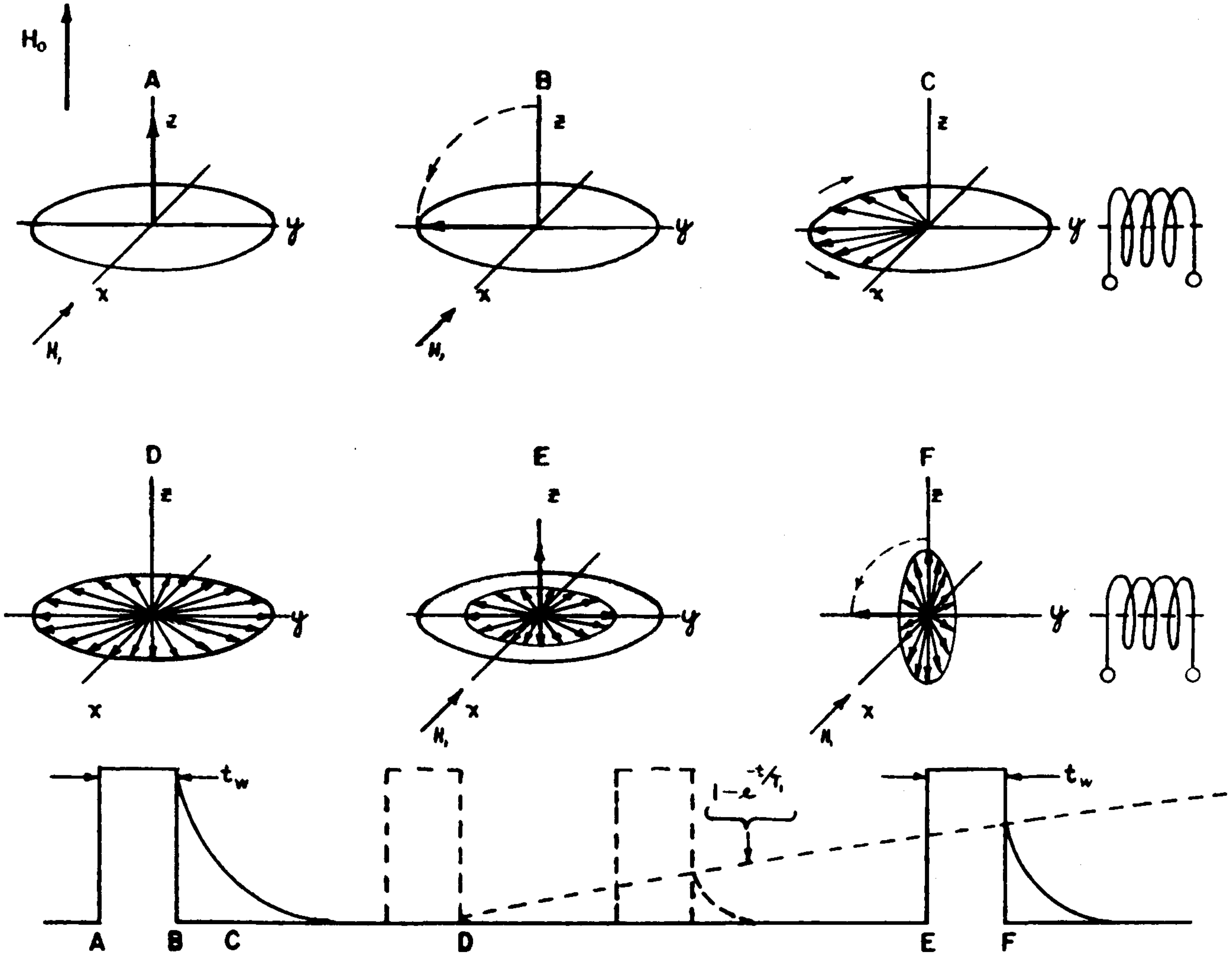


Fig. 1

. Scheme for measurement of $T_1$. The sequence from *A* through C is the same as in Fig. 2. At the time a pulse is applied at time *E* a fraction of the total nuclear magnetism has returned to thermal equilibrium along the *z* axis. Following this pulse at *F* a free induction signal results which is proportional to this magnetism.

that is flipped by the second $\pi/2$ pulse, detected by the receiving coil, and then measured. A set of these signals is recorded, with 5 or 6 suitable time spacings ($\tau$) between the first and second pulse, in order to plot the exponential curve from which $T_1$ is obtained.

A little further explanation of Fig. 1 may be warranted. Firstly, the x and y axes as drawn are, with reference to laboratory coordinates, rotating about the z-axis (the direction of $H_o$) at the Larmor frequency $\nu_o$. Thus, a magnetization vector that appears stationary in this x-y plane is able to induce a voltage, at frequency $\nu_o$, in the pick-up coil whose axis is in this plane. Secondly, there are two equally valid descriptions for the action of the alternating (R.F.) magnetic field $H_1$, whose direction is perpendicular to the z-axis:

(a) In the quantized or individual spin picture, the energy in the $\frac{\pi}{2}$ pulse (at the resonance frequency $\nu_o$) is sufficient to excite enough spins from the lower energy level ($M_z$ parallel to $H_o$) to the upper level ($M_z$ opposite to $H_o$) to produce equal populations in these two levels. When the magnetization is then averaged over all the spins in the sample, this leaves no macroscopic magnetization in the z-direction. However, it is clear that the magnetic moments of nuclei with spin 1/2 do not lie precisely along the direction of the magnetic field, but rather precess around it, and it is the z-component $\mu_z$ of the actual spin magnetic moment $\mu$ that has been referred to so far. Thus, at the time just after the R.F. pulse, when the populations of the upper and lower levels are equal, this still leaves the sum of the x and y components, now lying in the x-y plane, to precess around the z-axis and induce a signal in the pick-up coil.

(b) In the classical description, the sample is considered to be made up of microscopic volume elements, each of which has its own magnetic moment, and is subject to a single value of the static magnetic field $H_o$. (However, this may vary from place to place throughout the sample.) The action of the R.F. magnetic field on this system is described by E. L. Hahn (Physics Today, Nov. '53) along the following lines: at thermal equilibrium the net magnetic moment $M_o$ which is aligned with the field $H_o$ can be compared to a "sleeping" mechanical top that spins with its axis along the direction of the gravitational field. If the top is perturbed by applying a torque perpendicular to its spin axis, it will precess about the spin axis. When the nuclear magnetic top is tipped away from the $H_o$ or z axis by rotating R.F. magnetic fields in the xy plane, it consequently precesses about the z axis at the Larmor frequency given by $\nu_o = \gamma H_o$ after the xy perturbing field is removed. ($\gamma$ is the nuclear gyromagnetic ratio.) The time that the induction signal due to a classically precessing $M_o$ vector can persist is also the time for which constituent nuclear spins precess in phase before they begin to lose phase coherence, as a result of dipole interactions and field inhomogeneities.

The action of the $\frac{\pi}{2}$ R.F. pulse may be understood with reference to Fig. 2. The alternating field $H_1$, along some direction in the x-y plane, is considered to be composed of two oppositely directed circularly polarized field components, rotating in the x-y plane at the average Larmor frequency of the sample. The component that is rotating in the same sense as the Larmor precession of $M_o$ exerts a continuous torque on it, for a time $t_w$, the duration of the $H_1$ pulse. This results in a rotation of $M_o$ away from the z axis through an angle $\theta = H_1 t_w$, and for suitable $H_1$ and $t_w$ values

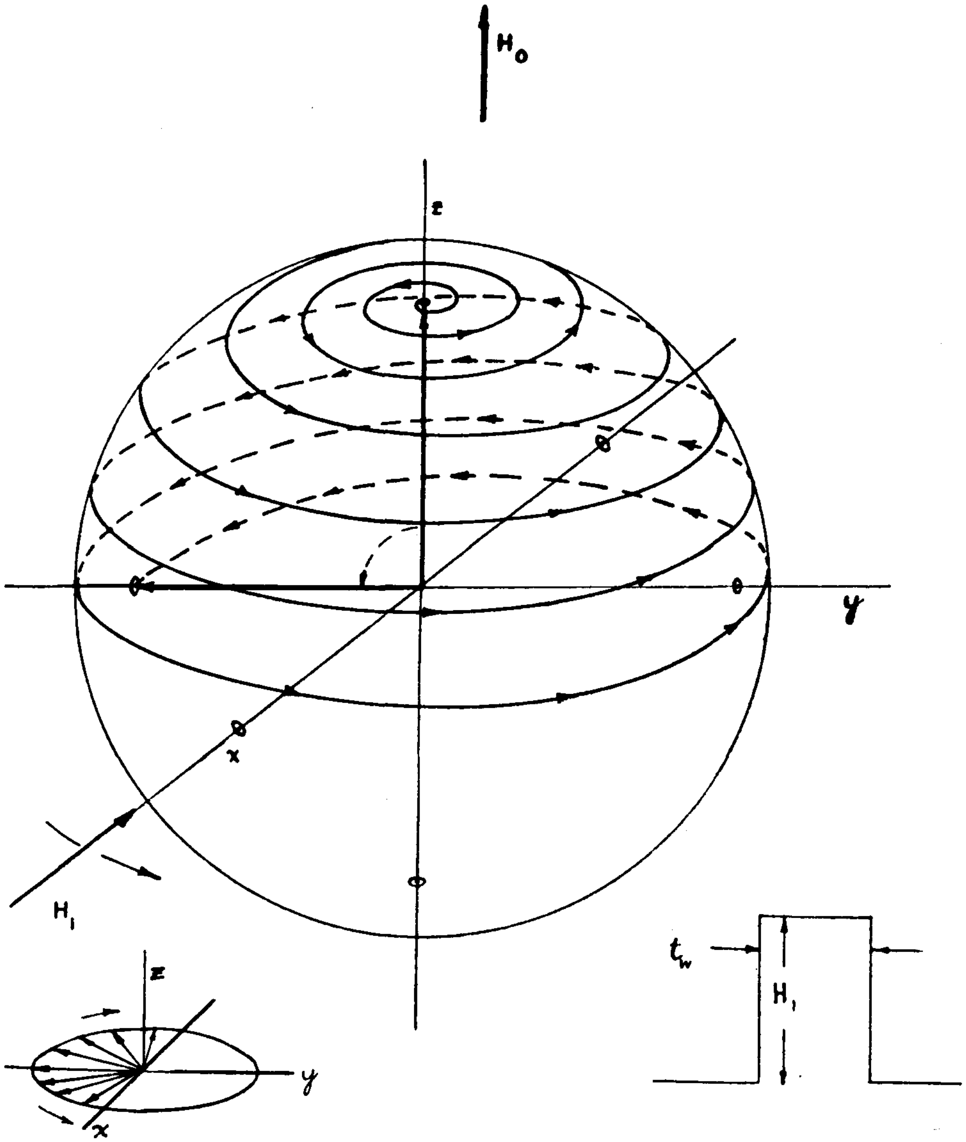


Fig. 2

As seen in the laboratory frame of reference the classical magnetic moment precesses toward the *xy* plane in a spiral motion due the torque effect of the rf field $H_1$ at nuclear resonance. In the frame of reference rotating with $H_1$ the magnetic moment appears to precess in a plane perpendicular to $H_1$.

$\theta = \frac{\pi}{2}$ radians. For example, in our experiment, the $H_1$ value of 23.5 gauss required a $t_w$ of 2.5 μ sec., during which time the $M_o$ vector spiralled around the z axis 70 times (at our Larmor frequency of 28 Mc/s), in rotating the 90° into the x-y plane. The other $H_1$ field component, rotating in the opposite direction to the precession of $M_o$, can be ignored because its effective torque is alternately positive and negative, and averages to zero over the 70 cycles during which it is applied.

## CRYSTAL INFORMATION

Pepinsky et al. (1958) reported that LiHzS is ferroelectric at room temperature, with a spontaneous polarization along the c axis. The structure was solved in 1963 by I. D. Brown, (Acta Cryst. 17, 654), and the crystal data are as follows:

System : Orthorhombic
Space Group : $Pbn2_1$ ($C_{2}^{9}$)
Cell Dimensions: a = 8.99, b = 9.94, c = 5.18 (all ± 0.01) Å
Cell Contents : 4 $\{Li(N_2H_5)SO_4\}$

In crystals of lithium hydrazinium sulfate, the sulfur and lithium atoms are both surrounded by tetrahedra of oxygen atoms. These tetrahedra share corner oxygen atoms to form a three-dimensional framework. Each oxygen atom is bonded to one lithium atom and to one sulfur atom, so that every $LiO_4$ tetrahedron is surrounded by four $SO_4$ tetrahedra, and vice versa. These alternating $LiO_4$ and $SO_4$ tetrahedra thus form chains running along the two glide directions and spiralling around the screw axis.

Around half of the screw axes are large channels which run through the crystal in the direction of the c-axis. The hydrazinium ions lie within these channels with their N-N bond axes perpendicular to c. The $NH_2$ groups of the hydrazinium ions are linked into infinite chains by hydrogen bonds along the screw axes, as shown by Fig. 3, thus leaving the positively charged $-NH_3^+$ groups out on the end of the N-N bond, in a hollow in the $LiO_4$ and $SO_4$ tetrahedra of the $(LiSO_4)^-$ framework.

From the structure, we could expect that there would be three kinds of motion capable of relaxing the proton spins to the lattice temperature:

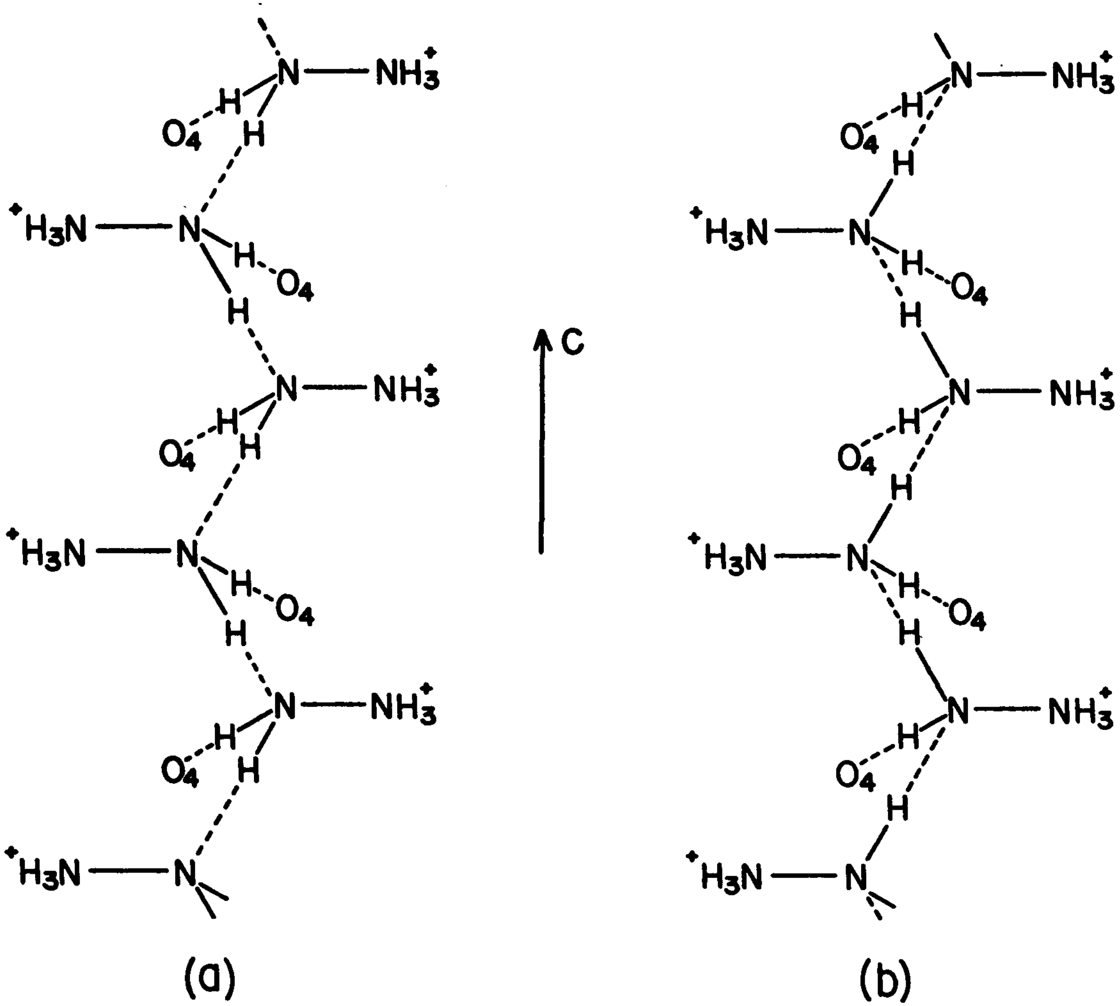


Fig. 3

The two alternative configurations of hydrogen bonds linking the hydrazinium ions: (*a*) N—H···N directed in the negative *c* direction; (*b*) N—H···N directed in the positive *c* direction.

(1) Rotation of the $NH_3^+$ group around the N-N axis

(2) Rotation of the $NH_2$ group around the N-N axis

(3) Proton migration from one hydrazinium ion to the next, perhaps together with a tumbling of the hydrazinium ions, and even a translational motion of these ions along the channels

As was mentioned in the Introduction, the N.M.R. results strongly indicated that these possibilities actually did occur. The second moment of the proton resonance curve showed this, in that it changed from about 40 $gauss^2$ at low temperature to 16.5 $gauss^2$ between −70°C and +50°C, whence it dropped to 8.8 $gauss^2$ at +150°C, followed immediately by a decrease to the very low value of 0.74 $gauss^2$ at +210°C. These four values correspond nicely to the expected second moment in the rigid lattice, followed by the three successive types of proton motion outlined above.

In 1941, E. Bengtsson obtained the following crystal data for $RbHSO_4$:

System : Orthorhombic
Space Group : Cmma
Cell Dimensions: a = 14.8, b = 24.6, c = 4.6Å
Cell Contents : 16 {$RbHSO_4$}

However, in 1960, Pepinsky and Vedam made a further (and probably more accurate; see below) x-ray determination of the space group and cell dimensions at room temperature, and described it as follows:

System : Pseudo-orthorhombic; β = 90° 3'
Space Group : $B2_1/a$

Cell Dimensions : a' = 24.61, b' = 4.62, c' = 14.81 Å
Cell Contents : 16 {$RbHSO_4$}

Alternative System : Monoclinic; β = 121.0°
Space Group : $P2_1/c$
Cell Dimensions: a = 14.35, b = 4.62, c = 14.81 Å
Cell Contents : 8 {$RbHSO_4$}

The material is ferroelectric below −15°C, with the polar direction along the c axis. X-ray observations at −170°C indicate the space group is Pc.

To decide which is the correct description of the structure, P. Ashmore (Department of Physics, McMaster University) in 1966 made precession-camera x-ray studies of a water-grown crystal of $RbHSO_4$, and found that the room-temperature structure was monoclinic. He also noted that, using 4-day exposures, he was able to detect reflections that Bengtsson had counted as absences, but found that they were two orders of magnitude lower in intensity than the weakest reflections that Bengtsson had observed.

## APPARATUS AND EXPERIMENTAL PROCEDURE

### Preparation of Crystal Samples

The polycrystalline cylinder of $RbHSO_4$ that was used in this experiment was prepared as follows:

The $RbHSO_4$ obtained from Alfa Inorganics was contaminated with a visible amount of brownish substance, which was eliminated by three successive recrystallizations from aqueous solution (at 40 - 45°C), by slow evaporation. Of the small crystals obtained in each of these stages, almost all had at least 1 mm as their smallest dimension.

At this stage, a number of attempts were made to grow good single crystals, using slow (3 - 4 weeks) cooling of a saturated aqueous solution of $RbHSO_4$. However, each of the small (5x5x10 mm) crystals tested showed an extremely narrow proton resonance line in the centre of the 2.6 gauss wide normal curve. The narrowness of the line (<30 milligauss) strongly indicated that it was from entrapped liquid water. However, the crystals grew so slowly that it is not easy to explain how this could occur.

The purified $RbHSO_4$ crystals were ground up and put in a thin-walled, 8 mm I.D. test tube which was then left in an oven and kept at +212 (±2)°C for more than 12 hours (M.P. +208°C) to drive off the water that is otherwise retained within the crystals. This sample was then rapidly recrystallized by plunging the tube into boiling water. This resulted in a polycrystalline lump, with crystallites of a size smaller than a 2 mm cube.

However, the unusually long proton spin-lattice relaxation time (of about 25 secs) restricted the useable R.F. field ($H_1$) of the absorption experiment to such a low value that a signal-to-noise ratio of only about 8:1 could be obtained, at best. Paramagnetic centres (e.g., broken hydrogen bonds and electron-hole pairs) were introduced by irradiation with greater than 100 Mrad from a $^{60}Co$ source. This, plus optimum use of the spectrometer's integrating circuits, allowed us to attain better than 50:1 signal-to-noise ratio.

The sample of $Li(N_2H_5)SO_4$ was chosen from crystals that had originally been prepared by J. Vanderkooy for a conductance experiment (Vanderkooy, Cuthbert and Petch, 1964). They had been grown from a stoichiometric mixture of reagent grade $Li_2CO_3$ and $(N_2H_6)SO_4$, and then purified with one cycle of recrystallization. The resulting crystals were carefully ground to a very fine powder, using a ceramic pestle and mortar.

### Experimental Arrangement for N.M.R. Measurements in $RbHSO_4$

A Varian V-4300A N.M.R. spectrometer and V-FR2503 Fieldial to control the magnetic field were used in this experiment. Since the N.M.R. sample head (containing transmitter-, receiver-, and modulation-coils) could not be cooled below 0°C, a thin-walled, unsilvered dewar tube was used to isolate the sample from the sample head, permitting temperatures down to −50°C to be reached.

The polycrystalline sample (in its glass sample tube) was cooled with a stream of nitrogen gas. The nitrogen, at a constant flow rate, passed through a cold-trap and then was cooled by passing it through several feet of copper tubing immersed in a bath of liquid nitrogen. The desired temperature was reached and maintained by re-heating this cold gas by passing it over electrically-heated resistance wire whose temperature was easily controlled by a Variac. From here, the gas went into the dewar tube and past the sample.

The sample temperature was measured by a thermocouple attached to the outside of the sample tube with epoxy resin, this being more than 1.5 cm below the (thin) receiver coil. A minimum of one hour was allowed for the sample to stabilize at each temperature.

The experimental conditions and spectrometer settings were as follows:

Modulation Amplitude: 0.47 gauss peak-to-peak, at 80 c/s

(N.B. - Linewidth was 2.6 ± 0.2 gauss)

Field sweep rate: 10 gauss in 25 minutes

Response time (i.e., RC of integrating circuit): 30 sec.

R.F. power level (i.e., $H_1$): This was set with reference to the onset of saturation, as determined by the first visible asymmetry of the absorption line ($1^{st}$ derivative). This latter occurred at an R.F. level of 18 - 20 μ amps into the transmitter coil, so the whole experiment was carried out with an R.F. level of 4 - 5 μ amps.

Magnetic field ($H_o$): 3754 gauss (corresponding to a Larmor precession frequency of 16 M c/s)

Several spectra, with alternately increasing and decreasing $H_o$, were taken at each temperature.

## Technical Details of the Apparatus for Measurement of $T_1$ in LiHzS

This nuclear resonance pulse apparatus (see block diagram in Fig. 4) is an improved version of the equipment originally described by Mansfield and Powles (1963), in J. Sci. Instrum. 40, 232. It is capable of giving medium power (25 gauss) pulses at up to 30 Mc/s, having pulse widths down to less than 2 μ sec. and very rapid rise and fall times.

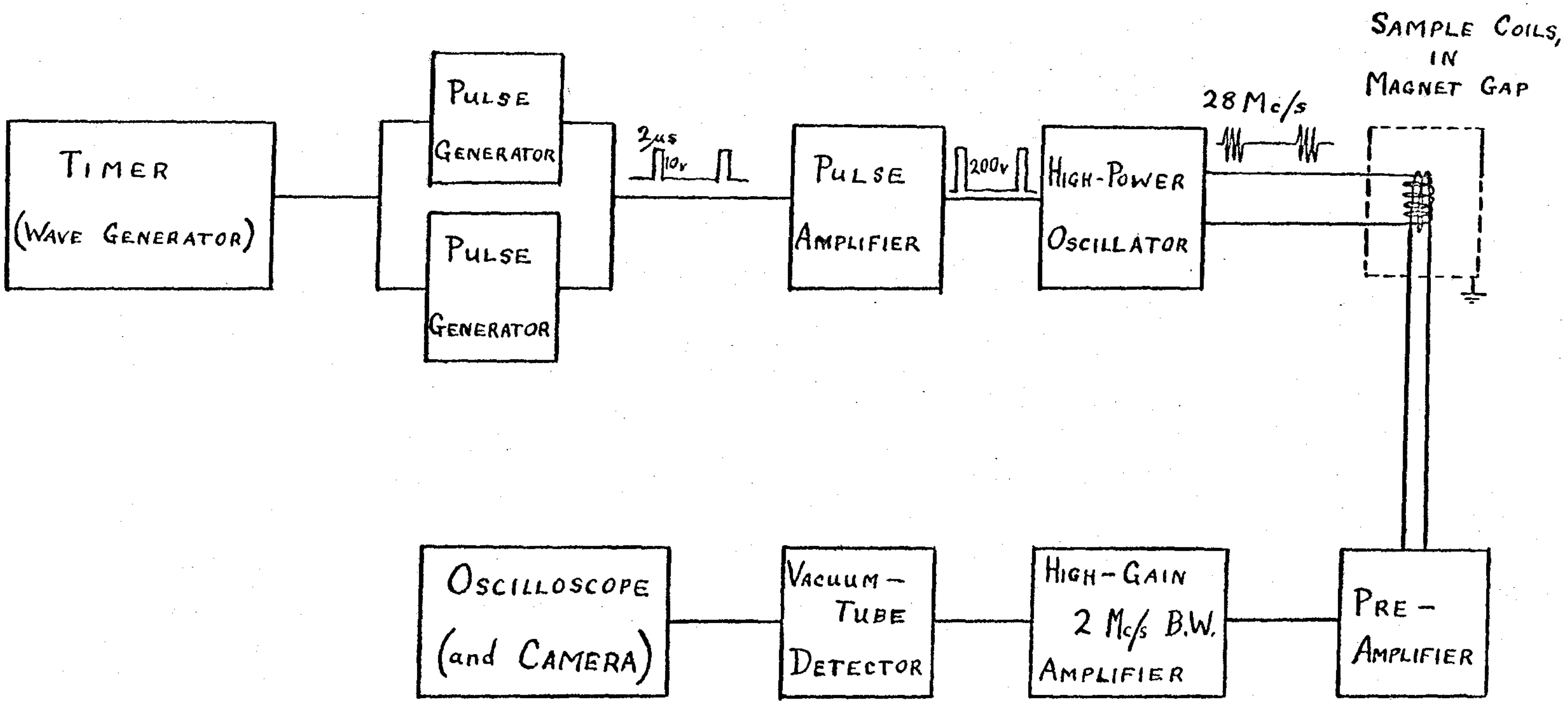


Fig. 4 Nuclear Resonance Pulse Apparatus

It also has a very fast recovery time, high gain receiver, which allows the nuclear signal to be read 1 μ sec. after the V/2 point on the trailing edge of the transmitted pulse. Finally, it produces any of the following pulse sequences: 90°, τ, 90°; 90°, τ, 180°; and 180°, τ, 90°; where τ is the pulse separation, from 0.1 millisecond upwards.

A schematic diagram is given in Fig. 5 for the pulse amplifier, high-power R.F. oscillator, sample coils, receiver pre-amplifier, and 2 Mc/s band-width amplifier (including diode detector). In general, it uses conventional circuit techniques, but some points are worth noting.

The first and third pentodes (type 15A6) in the pulse amplifier are connected as triodes, the first as a normal amplifier, with 240V across the tube plus its 5.5 KΩ of plate load and cathode resistors, but the third is used as a cathode follower with particularly high power output capability, since it has the full 420V across tube and 4.7 KΩ cathode resistor. In addition, it is direct-coupled to the plate of the second tube (used as a pentode), thus avoiding a potential source of distortion of the shape of the pulse. Another valuable point is that the screen grid of this pentode can be connected directly to ground, since a −240V cathode supply, and a +180V plate supply have been used. This makes for very effective isolation between plate and grid circuits. Also, a large pulse height (>200V) was obtained by making use of the phase reversal characteristics of the first amplifier tube to allow removal of the cathode resistor, so that as much voltage as possible is developed across the 20 KΩ load resistor. The grid of the pentode has been clamped at ground potential (through the 0.1 MΩ grid resistor) except during the few microseconds that the incoming pulse, now with a <u>negative</u> polarity, is

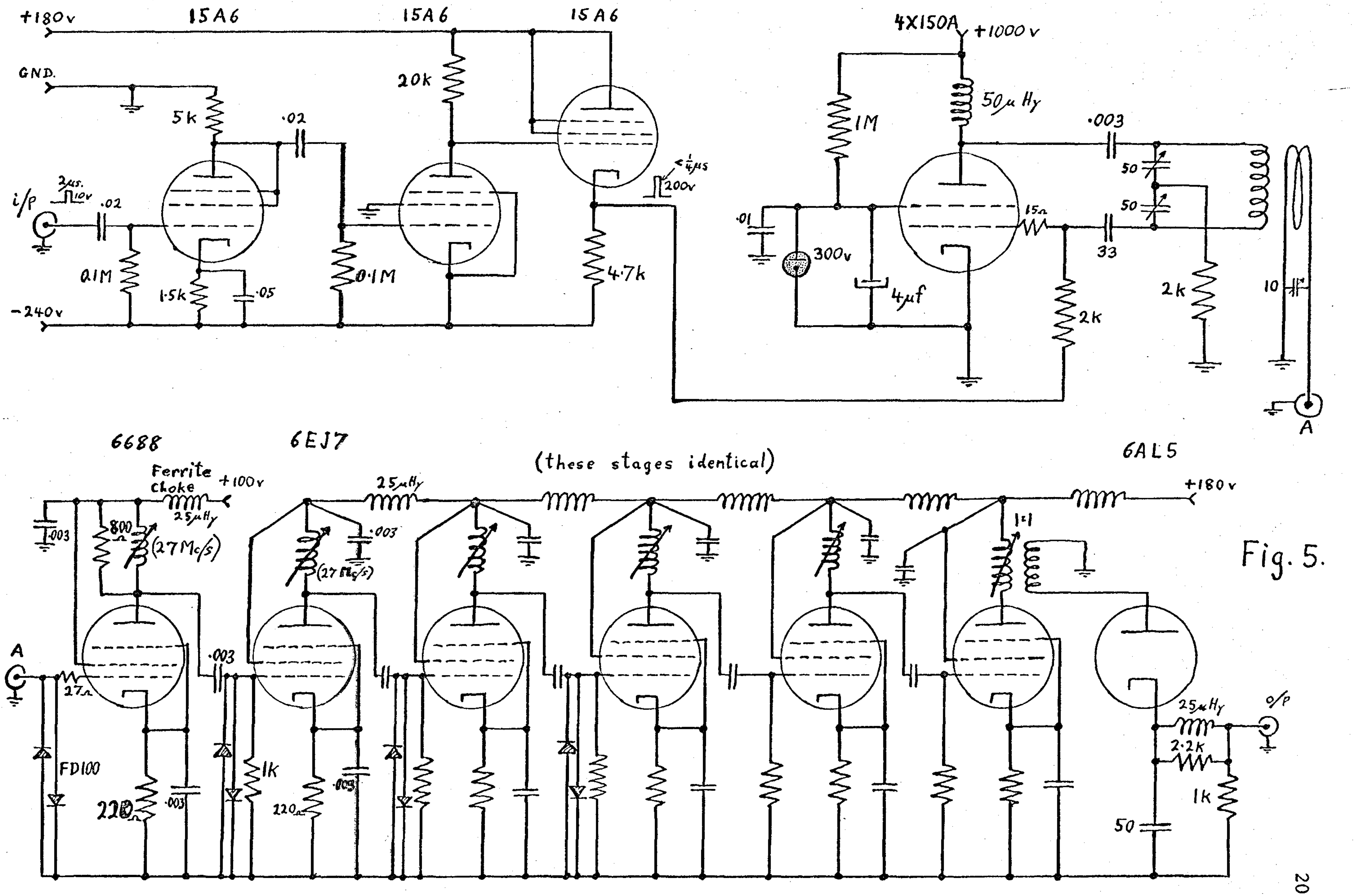

+180v
15A6
15A6
15A6
GND.
5k
20k
.02
i/p
2μs.
10v
.02
0.1M
1.5k
.05
0.1M
4.7k
1/4μs
200v
-240v
4X150A
+1000v
1M
50μ Hy
.003
50
50
.01
300v
4μf
15Ω
33
2k
2k
10
A
6688
6EJ7
(these stages identical)
6AL5
Ferrite choke
25μHy
+100v
25μHy
+180v
.003
800Ω
(27Mc/s)
.003
(27Mc/s)
1:1
A
27Ω
.003
FD100
220Ω
.003
1k
220Ω
.003
25μHy
o/p
2.2k
1k
50

Fig. 5.

applied to the grid. Finally, the heaters of this pulse amplifier section must be floating, and have as low a capacitance to ground as possible, in order that the large voltage excursions do not break down the heater-to-cathode insulation.

The amplifier is capable of producing a +200V, 2 to 8 μ sec. output pulse, having a fall time (trailing edge) of less than 1/4 μ sec.

The air-cooled power tetrode, 4X150A, in the power oscillator can be used with plate supply voltages of 750 to 1300 volts. The screen grid was kept steady at +300V by means of the series of five 60V neon tubes (NE-2), used as a voltage regulator, in conjunction with the 4 μf electrolytic and 0.01 μf ceramic capacitors. The Colpitts oscillator circuit used a small (2 x 50 pf) butterfly type tuning capacitor.

In the quiescent state, the oscillator tube is held off by the negative potential at the cathode of the cathode-follower, which is itself kept almost at cutoff by the previously described low anode voltage of the pentode pulse amplifier. When the incoming, positive-going pulse turns the tube on, the oscillations build up to maximum amplitude in only a few cycles (at about 28 Mc/s), because of the high R.F. feedback and gain characteristics of this circuit.

To reduce direct pick-up of the transmitted pulse, the sample coils were oriented at right angles to each other (and to $H_o$) with the transmitter coil's axis parallel to the axis of the cylindrical sample. The receiver coil was wound lengthwise over the transmitter coil, with the turns at one end split in half so that the sample could be inserted. The 10 pf fixed capacitor was mounted right alongside the receiver coil, within the grounded shielding tube which surrounded the coil system. Both coils and shield were firmly supported within a silvered glass dewar tube, which itself was contained in a rigid brass tube (soldered to the oscillator chassis) within the 3-inch magnet gap.

The pre-amplifier (using a type 6688 tube) is actually mounted on the same chassis as the oscillator, as close as possible to the receiver coil without entering the magnetic field. From there, it is connected with a short (less than five inches) length of coaxial cable to the main receiver amplifier. The only two points that may be worth mentioning about this very straightforward circuit are:

(1) the small grid resistors (27Ω in the pre-amplifier and 15Ω in the R.F. power oscillator) damp out V.H.F. parasitic oscillations that might otherwise occur in these pulsed circuits;

(2) the back-to-back silicon diodes (type FD100) in the grid circuits of the first four stages act as limiters on the incoming signal, keeping the peak amplitude below about 0.6V. This helps to prevent saturation of the amplifier during the time of the transmitted pulse.

The effective gain of this amplifier plus the type CA preamplifier on the type 533 Tektronix Oscilloscope is about $5 \times 10^4$, over a band-width of 2 Mc/s.

# RESULTS AND DISCUSSION

## Rubidium Hydrogen Sulfate

The second moment $(\Delta H)^2$ of the proton resonance line of $RbHSO_4$ was calculated for temperatures in the range −45°C to +20°C (see Fig. 6). For this calculation, the absorption curve was obtained from its first derivative by step-wise integration. The second moment was then obtained using the formula $(\Delta H)^2 = \int_{-\infty}^{\infty} g(H) \times (H_0 - H)^2 dH \Big/ \int_{-\infty}^{\infty} g(H) dH$, where g(H) is the (un-normalized) amplitude of the absorption curve at the field H, with $H_0$ being the centre of the curve. In practice, this procedure was approximated using finite intervals (about 62 to each curve), the calculation being carried out by computer. First moments and area differences were also calculated, to check for correct choice of the centre-point.

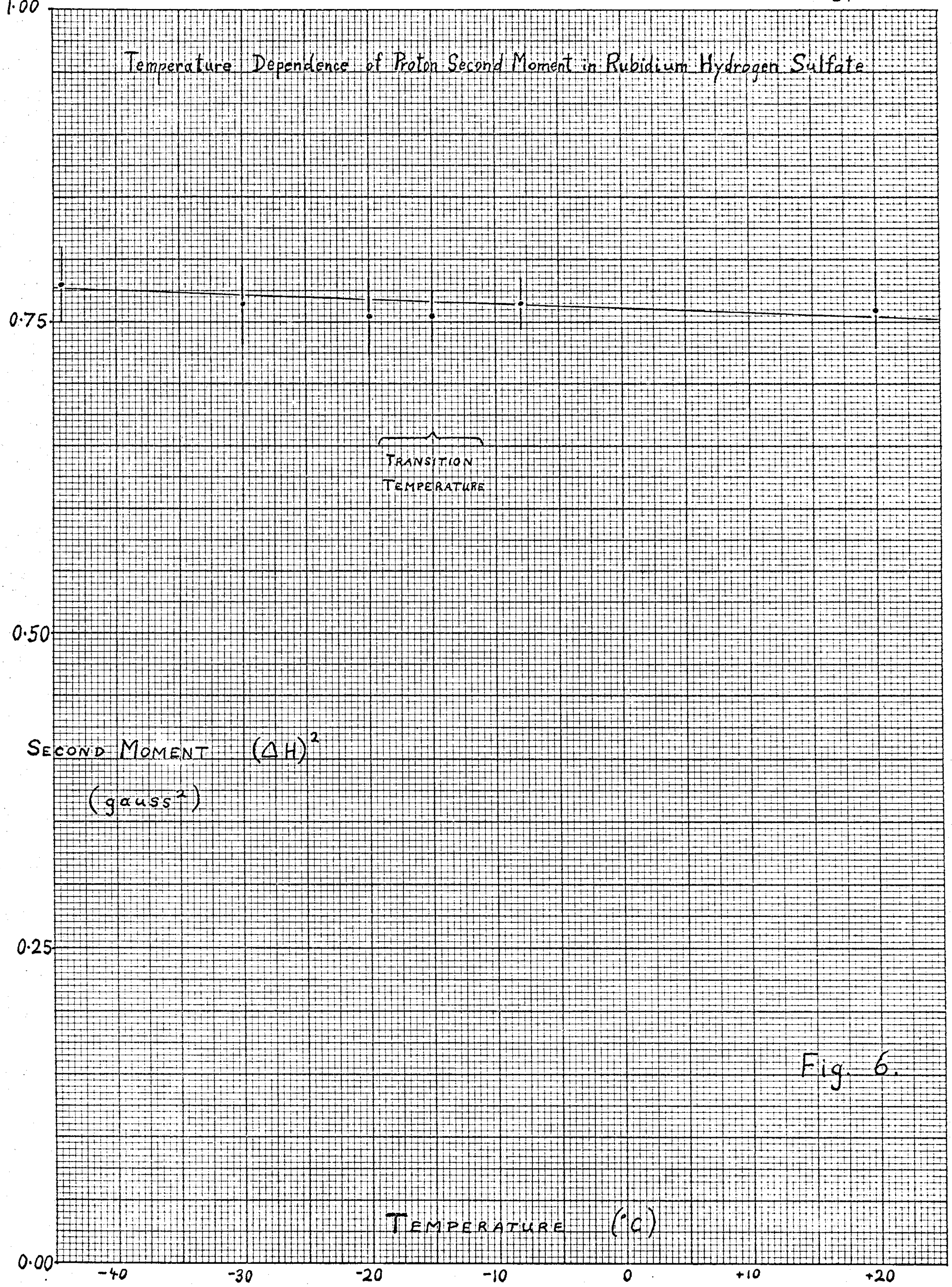
The results show a slight steady decrease with, in particular, no abrupt change at the Curie point, $T_c = -15°C$. A steady decrease in $(\Delta H)^2$ with increasing temperature may be expected because of expansion of the material, and if the expansion coefficients $\alpha_i$ are available, it is possible to obtain an estimate of the decrease to be expected from this mechanism. Since the $\alpha_i$ for $RbHSO_4$ are unknown, the observed decrease of 2.5% in $(\Delta H)^2$ (from 0.775 gauss$^2$ at −37°C to 0.755 gauss$^2$ at +120°C) was used to estimate a value for the average expansion coefficient, to find whether it is of the right order of magnitude:

$$(\Delta H)^2 \propto r^{-6}, \quad \therefore \quad (\Delta H)^2 = K r_0^{-6} (1-\alpha T)^{-6}$$

$$\therefore \quad (\Delta H)^2_{T_1} \Big/ (\Delta H)^2_{T_2} = (1-\alpha T_1)^{-6} \Big/ (1-\alpha T_2)^{-6}$$

$$\therefore \quad (0.775 / 0.755)^6 = (1-236\alpha) / (1-293\alpha)$$

$$\therefore \quad \alpha = 1.5\text{x}10^{-3} \text{ per degree}$$



Temperature Dependence of Proton Second Moment in Rubidium Hydrogen Sulfate

Fig. 6.

This figure seems quite reasonable, and may be compared with those for Rochelle salt and $KH_2PO_4$, of $8.1\times10^{-3}$ and $1.4\times10^{-3}$ respectively, which were calculated using information in Sec. 8-3 and the statement "--- the Curie constant is equal to the reciprocal of the linear coefficient of expansion," found in Dekker: Solid State Physics, pages 192 and 197.

Thus, the observed decrease in $(\Delta H)^2$ with increasing temperature is consistent with a gradual expansion of the $RbHSO_4$ crystal.

The non-appearance of an abrupt decrease in $(\Delta H)^2$ at $T_c$, within the $\pm4\%$ estimated experimental error, means that any change in the proton-proton distance $(r_{12})$ at the ferroelectric transition must have an upper limit of about 0.03 $\overset{o}{A}$. This figure was calculated using the relation $(\Delta H)^2$ is proportional to $(r_{12})^{-6}$.

Lithium Hydrazinium Sulfate

The spin-lattice relaxation time $T_1$ was measured as a function of temperature over the range –150°C to +180°C. A plot of ln $T_1$ vs. 1/T (where T is in °K) is given in Fig. 7. The very pronounced minimum which occurs at –82°C is characteristic of the effect of molecular reorientation on the relaxation time. The physical reason for the existence of a minimum is that, when $\nu_{Larmor} = 2\pi/\tau_c = \nu_{correlation}$, the coupling between the nuclear spin system and the atomic (or molecular) motion is at a maximum, so that the nuclear spin energy can be leaked away to the surrounding lattice at the greatest rate, which is equivalent to saying that the spin-lattice relaxation time is at its shortest.

This type of reorientation process affects $T_1$ according to the formula given by Bloembergen, Purcell and Pound (1948):

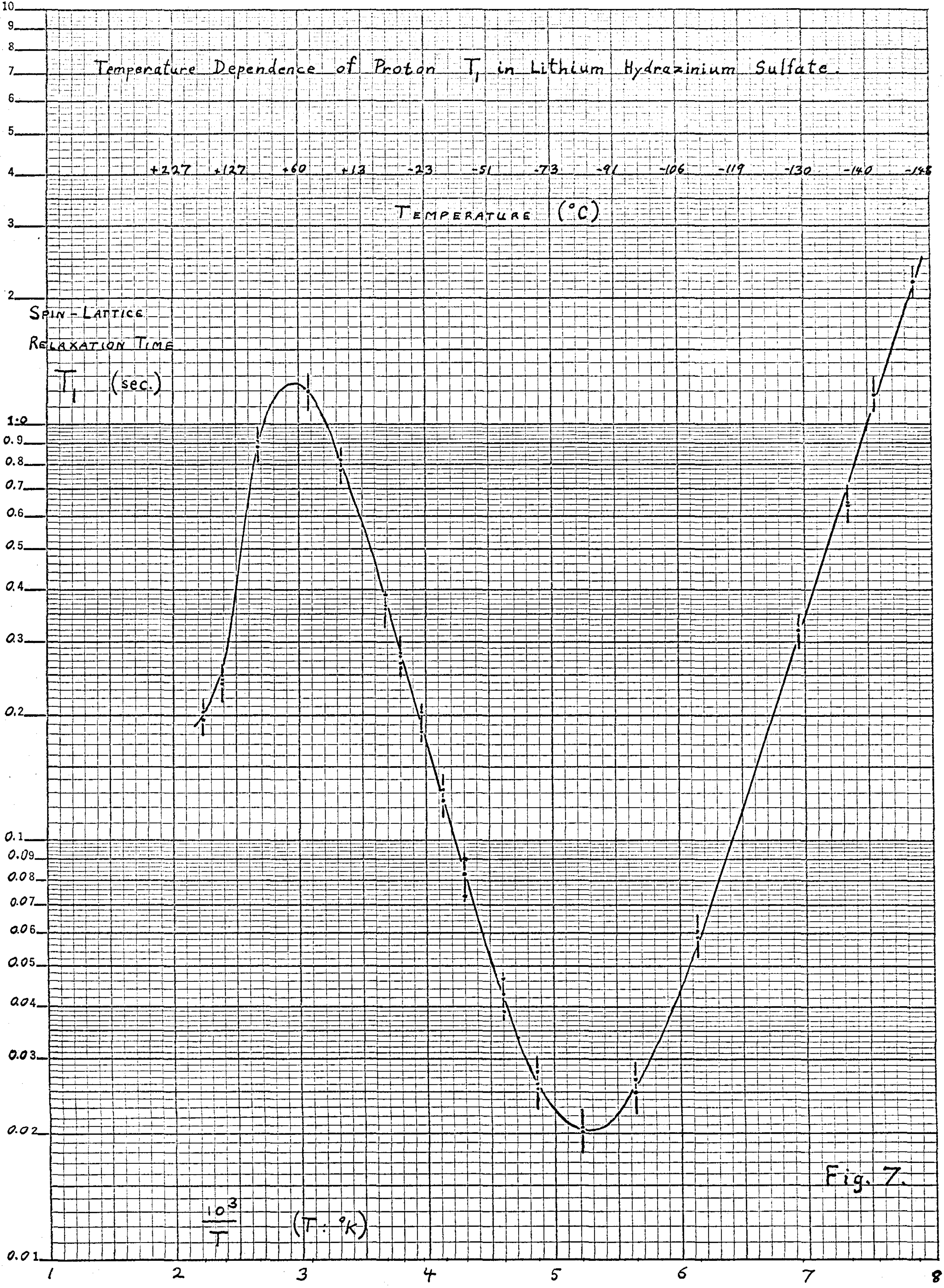

Temperature Dependence of Proton $T_1$ in Lithium Hydrazinium Sulfate.
+227
+127
+60
+13
-23
-51
-73
-91
-106
-119
-130
-140
-148
Temperature (°C)
Spin-Lattice
Relaxation Time
$T_1$ (sec.)
10
9
8
7
6
5
4
3
2
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
1
2
3
4
5
6
7
8
$\frac{10^3}{T}$ (T: °K)

Fig. 7.

$$\frac{1}{T_1} = C_1 \left\{\frac{\tau_c}{1 + \omega^2 \tau_c^2} + \frac{4 \tau_c}{1 + 4 \omega^2 \tau_c^2}\right\}$$

where: $C_1$ includes the factors which are independent of temperature and frequency;

$\tau_c$ the correlation time, is a characteristic of the random atomic motion; and

$\omega$ is the angular Larmor frequency ($=2\pi \nu_L$).

The asymptotic behaviour of $T_1$ is simple:

for $\omega\tau_c \ll 1$: $T_1 \propto 1/\tau_c$;

for $\omega\tau_c \gg 1$: $T_1 \propto \tau_c$.

In the intermediate region, the above formula predicts a minimum in $T_1$ at $\omega\tau_c = 0.616$.

The type of motion expected to occur within a solid may be characterised by a model in which only a limited number of orientations are permitted, the transitions from one to another taking place in a "jump". The frequency of these jumps may be related to the barrier height (activation energy) $E_a$ and the temperature T by the methods of statistical mechanics, with the result that the jump frequency $\nu_c = \nu_{oc} \times \exp(-E_a / RT)$ (with $E_a$ in calories, and R, the gas constant, in calories/mole), where $\nu_c$ is the correlation frequency, and is related to $\tau_c$ by $\tau_c = 2\pi/\nu_c$. Therefore, rewriting the asymptotic behaviour to show the temperature dependence of $T_1$ gives:

for $\omega\tau_c \ll 1$: $T_1 \propto \left[\tau_{oc} \times \exp(E_a / RT)\right]^{-1}$;

for $\omega\tau_c \gg 1$: $T_1 \propto \tau_{oc} \times \exp(E_a / RT)$.

Thus, in these two regions, a straight line (slope = $E_a/R$) will result if $\ln T_1$ is plotted vs. $1/T$, the slope being positive for low temperature ($\omega\tau_c \gg 1$), and negative at high temperature, leaving a minimum in the intermediate region, at the point where $\omega\tau_c = 0.616$.

Applying this analysis to the $\ln T_1$ vs. $1/T$ curve given in Fig. 7 (in which the line was fitted to the points by eye), the slopes either side of the —82°C minimum give:

low temperature side: $E_a = (4.1 \pm 0.25) \times 10^3$ cal/mole.

high temperature side: $E_a = (4.85 \pm 0.3) \times 10^3$ cal/mole.

(The linear regions are —148°C to —113°C, and —50°C to —5°C respectively.) On the low side there is one main process governing the relaxation rate, whereas at higher temperatures (and therefore higher reorientational frequencies), a certain amount of cross-relaxation is supposed between the $NH_3^+$ and $NH_2$ groups. Thus the low temperature figure for the activation energy is expected to be more accurate.

It is instructive to compare the foregoing results with the work of Cuthbert and Petch on proton resonance linewidths, mentioned earlier. An approximate formula given by Waugh and Fedin (1963) is used to find the activation energy: $E_a \simeq 37\ T_{TR}$, where $T_{TR}$ is the temperature (°K) at which the NMR line begins to narrow. The linewidth transitions observed by Cuthbert and Petch are estimated (from their Fig. 3) to occur at approximately —170°C (103°K) and +20°C (293°K), which implies activation energies of $(3.7 \pm 1) \times 10^3$ cal/mole and $(11 \pm 1.5) \times 10^3$ cal/mole respectively.

Also, a calculation of $T_{TR}$ can be made using the values of $E_a$, the Larmor frequency $\nu_L$, and $T_{min}$ from the $T_1$ experiment, for comparison with the $T_{TR} \approx 103°K$ of the N.M.R. experiment.

This proceeds in two parts:

(a) Calculation of $\nu_{oc}$:

from: $\omega_L . \tau_c = 0.616$, $(\tau_c = \frac{2\pi}{\nu_c})$

$$\nu_c = \nu_L / 0.616$$

Therefore, from: $\nu_c = \nu_{oc} \times \exp(-E_a / RT_{min})$;

(using: $\nu_L = 27$ Mc/s, and
$E_a = 4.1 \times 10^3$ cal/mole)

$$\nu_{oc} = \nu_L / 0.616 \times \exp(E_a / RT_{min})$$
$$= 2.7 \times 10^7 / 0.616 \times \exp(4.1 \times 10^3 / 2.0 \times 191)$$
$$= 4.39 \times 10^7 \times \exp(2.05/191)$$
$$= 1.8 \times 10^{12} \text{ c/s}$$

(b) Calculation of $T_{TR}$:

linewidth at $T_{TR}$, $(\Delta\nu)_{T_{TR}} = \nu_{oc} \times \exp(-E_a / RT_{TR})$

i.e., $9 \times 10^4 = 1.8 \times 10^{12} \times \exp(-2.05 \times 10^3 / T_{TR})$

$$\ln (9 \times 10^4) = \ln(1.8 \times 10^{12}) - 2.05 \times 10^3 / T_{TR}$$

$$11.4 = 28.2 - 2.05 \times 10^3 / T_{TR}$$

$$T_{TR} = \frac{2050}{16.8}$$

$$= 120°K$$

There is sufficiently good agreement between this and the $T_{TR} \approx 103°K$ of the NMR experiment, together with the agreement between the activation energies determined by the two types of experiments, (3.7 $\pm$ 1) Kcal/mole and (4.1 $\pm$ 0.25) Kcal/mole, to prove that the motion in lithium hydrazinium sulfate that caused the linewidth transition in the region of 110°K is also responsible for the observed minimum in ln $T_1$ vs. 1/T.

To determine the nature of this motion, a useful comparison can be made with the linewidth transition in hydrazine sulfate ($N_2H_6SO_4$). Deeley, Lewis and Richards (1954) observed the proton resonance line to have a $T_{TR}$ of approximately 120°K. This would indicate that the $NH_3^+$ groups in the hydrazonium ion $(H_3N - NH_3)^{++}$ have an activation energy of $(4.5 \pm 0.5)\times 10^3$ cal/mole, using the Waugh, Fedin formula. The agreement of this figure with the $(4.1 \pm 0.25)\times 10^3$ cal/mole obtained from the ln $T_1$ vs. 1/T curve suggests strongly that the motion at this temperature in LiHzS is reorientation of the $NH_3^+$ group about the N-N axis of the hydrazinium ion.

However, as the temperature is raised into the region above room temperature, a motion sets in that is sufficiently effective at relaxing the spin system to the lattice that it reduces $T_1$ from about 1.25 sec. at +60°C down to about 0.18 sec., at +180°C. Unfortunately, limitations of the apparatus and decomposition of the sample did not allow temperatures higher than +180°C to be reached. However, the shape of the curve suggests the existence of a minimum, and on this assumption, an activation energy was calculated from the slope in the region +105°C to +135°C. There is reasonable agreement between this activation energy of (10 $\pm$ 2.5) Kcal/mole and the (11 $\pm$ 1.5) Kcal/mole calculated from the linewidth transition that starts at about room temperature.

This agreement fits in very well with the above-mentioned NMR results, in which rotation of the $NH_2$ group was followed (as the temperature was raised) by proton migration from one hydrazinium ion to the next, and above +200°C, by a probable translational motion of the hydrazinium ions along the channels in the ($LiSO_4$) framework.

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